Homoleptic Alkyl- and Aryl-Complexes of Transition Metals (Ti, Zr, Hf, Nb, and Cr) And Tetra-organyloxyvanadium-(V) and -(IV) Complexes

Inaugural-Dissertation

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by

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from Palestine

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"I humbly thank Allah Almighty, the Merciful and the Beneficent, who gave me health, thoughts and co-operative people to enable me achieve this goal."

Dedication

To the memory of my Father

To the memory of my Brother, Mohammed

To my mother, brothers and sisters

To my wife

To my children Areej, Mahmoud and Mohammed

This work was completed under the supervision of
Prof. Dr. K. Seppelt
at the Institute of Inorganic and Analytical Chemistry
of the Freie Universität Berlin.

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During this research work the following publication and poster were done

Publication:

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Poster:

Tungsten(VI) And Tungsten(V) Fluoride Complexes

Said El-Kurdi and Konrad Seppelt

16th European symposium on fluorine chemistry, Ljubljana, Slovania july 18-23, 2010

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I. Introduction

Homoleptic σ-organyl compounds (all the ligands are identical[1]) have the general formula $[ML_n]^{m-}$ (m = 0, ±1, ±2, …), and are of fundamental interest: their structure, stability, and chemical properties are affected only by a single type of group L, besides the electron configuration, charge and size of Metal M.

The structures of homoleptic $M(CH_3)_6$ (M = transition metal) gained a special interest since the methyl ligand is a pure σ-binding ligand of moderate electronegativity and is not subject to β-hydrogen elimination [2].

According to several theoretical predictions the neutral hexamethyl transition compounds, e.g. $W(CH_3)_6$ and $Re(CH_3)_6$ should not be octahedral[1,3-5]. In the meantime the structures of $[Zr(CH_3)_6]^{2-}$, $[W(CH_3)_6]$, $[Re(CH_3)_6]$, $[Mo(CH_3)_6]$, $[Nb(CH_3)_6]^-$, $[Ta(CH_3)_6]^-$, $[Ta(C_6H_5)_6]^-$ and $[Ta(4\text{-}CH_3C_6H_4)_6]^-$ have been determined experimentally, and all of these compounds have non-octahedral structures[6-11]. The structures of $[Mo(CH_3)_6]$, $[W(CH_3)_6]$, and $[Nb(CH_3)_6]^-$ are more or less distorted trigonal prismatic with retention of the C_{3v} symmetry, but $[Re(CH_3)_6]$, $[Ta(CH_3)_6]^-$ and $[Zr(CH_3)_6]^{2-}$ have a regular trigonal prismatic structure.

On the other hand little is known about similar compounds of the 1st transition metal series e.g. Cr, V and Ti. The number of complexes containing a near-trigonal prismatic coordinated metal center is still small, and more experimental data, particularly those containing metal atoms from the 1st transition metal series, would provide valuable insights for bond theories.

In 1989, Girolami [6] described the synthesis and characterization of the hexamethylzirconate salt $[Li(tmed)]_2[ZrMe_6]$, where the zirconium environment is close to regular trigonal prismatic. Later $[Ta(C_6H_5)_6]^-$ and $[Ta(4\text{-}CH_3C_6H_4)_6]^-$ were structurally characterized and found to have quite similar structures, where the Ta environment is slightly distorted trigonal

prismatic. On the other hand there exist no data of the hexa-aryl derivatives of niobium. For niobium only the $[Nb(CH_3)_6]^-$ have been prepared and shows a very small trigonal distortion.

In the area of σ-organotitanium(IV) chemistry, the five-coordinate $Ti(CH_3)_5^-$ species has been isolated and structurally characterized, however no related aryl analoges of d^0 -Ti, d^0 -Zr, and d^0-Hf have been described.

Therefore it was clear from the outcome of previous description that the σ-penta or –hexaaryl complexes of the d^0 transition metals, Ti, Zr, Hf and Nb still rare. The preparation of such complexes has been achieved in this work and crystal structures have been obtained, in order not only to establish the likely nonoctahedral coordination around the metal, but also to investigate the influence of aromatic ligands as compared to simple methyl groups. The attempts to prepare analogous Cr and V systems are also discussed.

The isolation of complexes $PhVOCl_2$[12], $MesVOCl_2$, $VOMes_3$[13], $VO(CH_2SiMe_3)_3$[14] and have been reported long time ago, but the data are very limited, especially no structural information available for any of them. The problem arises both from the extreme moistuire sensitivity of $VOCl_3$ and many of its complexes, and from the ease with which the vanadium is reduced to V(IV) and V(III). In this work the high unusual class of tetra-organyl complexes containing oxovanadium(V) and oxovanadium(IV) anions have been prepared and structurally characterized.

Several organochromium(III) compounds, for example $Cr(C_6H_5)_6^{3-}$, $Cr(C_6H_5)_5^{2-}$, $Cr(C_6H_5)_4^-$ have been isolated under different conditions[15-17]. Neutral trialkyl chromium are known only with very bulky R groups e.g. bis(trimethyl silylmethyl) $CH(TMS)_2$[18]. Homoleptic tetravalent chromium alkyls are less common, and only a few compounds with this oxidation state are known. These have been first isolated and characterized by Wilkinson in the 1970s [19], and

the only structuraly characterized complexes contain stericaly hindered group (C_6H_{11}[20], Me_3CCH_2, Me_3SiCH_2[21]) or a perhalophenyl group [22], which are thermally stable.

So chromium (IV) is not easily accessible, and homoleptic σ-organyl complexes, $[CrR_n]^{m-}$ (m= 0, ±1, ±2, …), are still rare. Since there is no evidence of molecules of that type attempts to synthesis such compounds starting from the reaction of $CrCl_3$ or Cr(O-*t*-Bu)$_4$ with different alkyling agent (RLi, Me_2Zn, $AlMe_3$, RMgX) were performed.

II. General Background, Results and Discussion

1. Homoleptic Penta- and Hexa-σ-Organyl d^0 Metal Complexes

1.1 Nonoctahedral Structures of Hexacoordinate Homoleptic Complexes

For many years after Werner's proof from stereochemical studies that many 6-coordinate complexes of chromium and cobalt had octahedral structures, it was believed that no other form of hexa-coordination occurred, and a vast amount of data from X-ray diffraction studies seemed to support this. [23]

In 1972 G. Wilkinson and A. Shortland announced the synthesis of the new remarkable complex hexamethyl tungsten $W(CH_3)_6$.[24] For many years it was thought to possess an octahedral structure. First theoretical calculations (1986) concerning the d^0 complexes predicted a non-octahedral structure as the most stable conformation.[4]

In 1989 G. Girolami found that the crystal structure of the anion $[Zr(CH_3)_6]^{2-}$ was an almost regular trigonal prism,[6] this finding led to increased interest in the structures of hexamethyl compounds, especially $W(CH_3)_6$ and $Re(CH_3)_6$. These compounds gained importance because they are classical example of neutral d^0 and d^1 complexes containing only σ-binding ligand.

In 1990 A. Haaland et al. proved from the gas-phase electron diffraction study on $W(CH_3)_6$ that it possess a trigonal prismatic coordination geometry. Furthermore many theoretical investigations concerning these findings were performed and it have been predicted that such complexes should be nonoctahedral.[11,5,25-28]

In 1996 K. Seppelt et al. have been published the crystal structures of the first two examples of a neutral, non-octahedral, hexa-coordinated homoleptic complexes $W(CH_3)_6$ and $Re(CH_3)_6$.[2]

In the meantime the structures of $[Zr(CH_3)_6]^{2-}$, $[W(CH_3)_6]$, $[Re(CH_3)_6]$, $[Mo(CH_3)_6]$, $[Nb(CH_3)_6]^-$, $[Ta(CH_3)_6]^-$, $[Ta(C_6H_5)_6]^-$ and $[Ta(4\text{-}CH_3C_6H_4)_6]^-$ have been determined experimentally and all of these compounds have non-octahedral structures.[6-11]

The complexes $[ReMe_6]$ (d^1), $[TaMe_6]^-$ (d^0) and $[ZrMe_6]^{2-}$ (d^0) contain regular trigonal prismatic (D_{3h}) metal centers, while in $[MoMe_6]$ (d^0), $[WMe_6]$ (d^0), $[NbMe_6]^-$ (d^0) and $[TaPh_6]^-$ (d^0) the coordination environment is distorted trigonal prismatic (C_{3v}). The common feature of the ligands in these complexes is that they are σ-donors, with no π-donating or π-accepting properties.

In $[Li(TMEDA)]_2[Zr(SC_6H_4\text{-}4\text{-}Me)_6]$ the $[Zr(SC_6H_4\text{-}4\text{-}Me)_6]_2^-$ ion also has a distorted trigonal prismatic structure. Although thiolate ligands are usually weak π-donor ligands, it has been suggested that the cation–anion interactions in crystalline $[Li(TMEDA)]_2$- $[Zr(SC_6H_4\text{-}4\text{-}Me)_6]$ result in the RS^- ligands behaving only as σ-donors [29].

The valence shell electron pair repulsion VSEPR model fails completely in describing these finding, since the octahedron is by far the most stable configuration in terms of ligand repulsion. On the other hand the MO model can explain the observed structures [3]. The methyl groups in these d^0 complexes form M–C σ-bonds, and 12 electrons are available for the bonding: one electron from each ligand and six electrons from the metal, including those from the negative charge where applicable.

The qualitative energy level diagram (See Figure 1) shows that, in a model ML_6 complex with an octahedral structure, these 12 electrons occupy the a_{1g}, e_g and t_{1u} MOs.

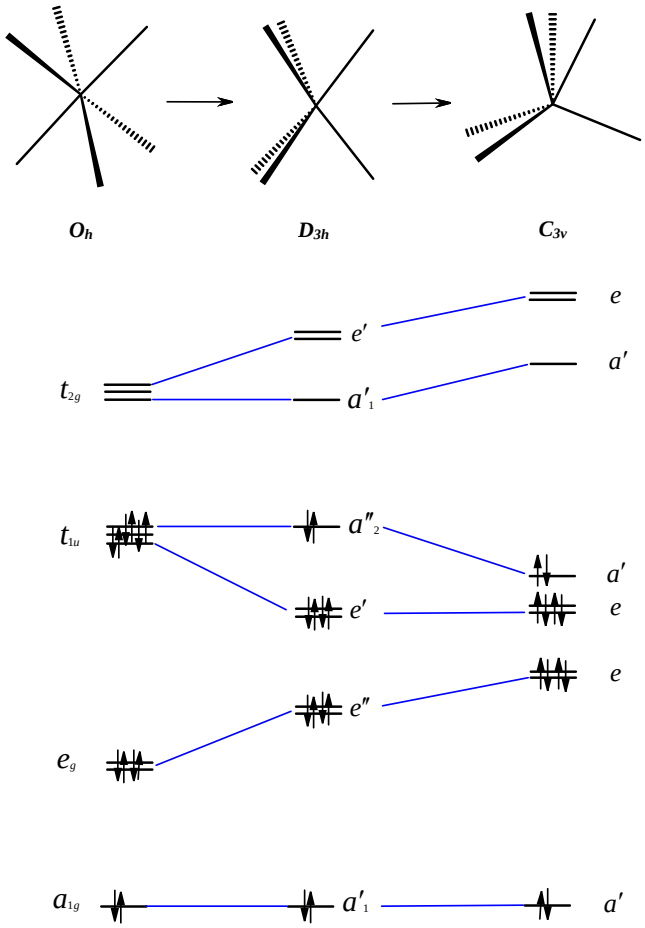


Figure 1. Qualitative molecular orbital diagram for d^0 ML_6 compounds.[27]

Distortion of the octahedron along one three-fold axis gives a trigonal prism, the point group changes from O_h to D_{3h}, and as a consequence, the properties of the MOs changes as shown in the figure. The number of electrons stays the same, but there is a qualitatively net gain in energy.

This stabilization explains why d^0 (and also d^1) complexes of the MMe_6 type show a preference for a trigonal prismatic structure. However, the situation is further complicated because of the observation that $[MoMe_6]$ and $[WMe_6]$, for example, exhibit structures with C_{3v} symmetry (i.e. distorted trigonal prismatic): three of the M–C bonds are normal but three are

elongated and have smaller angles between them. This distortion can also be explained in terms of MO theory, since further distortion into C_{3v} distorted trigonal prism results in another gain of energy.

If all orbitals are occupied in an 18 valence electron system, e.g., $W(CO)_6$ octahedron geometry is observed.

1.2 Homoleptic Pentacoordinate Complexes

Detailed discussion of a particular geometry usually involves bond lengths and angles determined in the solid state and these may be affected by crystal packing forces.

The VSEPR model predicts the trigonal-bipyramidal (*TBP*- 5) structure to be the most stable arrangement for pentacoordinate d^0 complexes and square pyramidal (*SP*-5) arrangement of the electron configuration d^1 and d^2. However, even for main group compounds, square-pyramidal (*SP*-5) structures are only very slightly higher in energy (usually by a few $kJmol^{-1}$).[30] As a result, many [ML_5] main group complexes are fluxional, often by the well-known Berry-pseudorotation pathway[31].

For ML_5 Muetterties and Guggenberger have defined an angle criterion for the description of the transition from trigonal bipyramidal to square pyramidal [32]. (**Figure 2**) In an ideal square pyramid (C_{4v}), the angle difference $\delta = 0°$, for the ideal trigonal bipyramid (D_{3h}) the $\delta = 60°$. In practice, many structures lie between these two extremes, and we can describe the distortion from ideal square pyramid (C_{4v}) or ideal trigonal bipyramid (D_{3h}) by specifying δ.

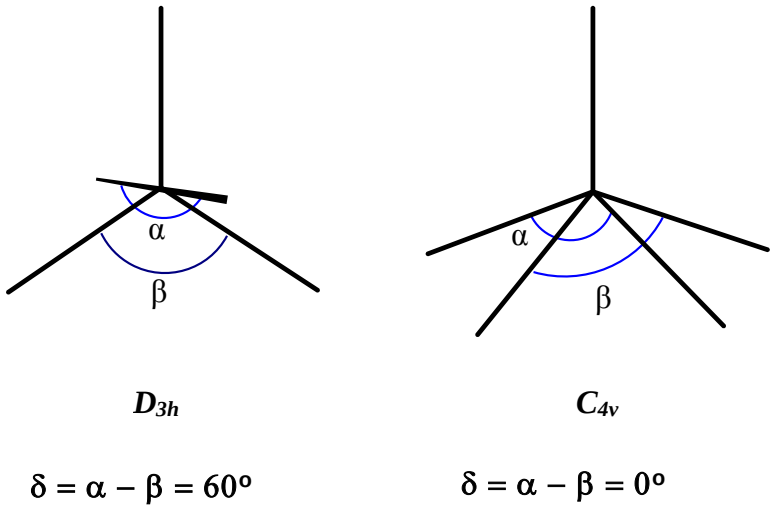


Figure 2. Description of the distortion of ML_5 (D_{3h} and C_{4v}) complexes, by using the angle δ.

2. Titanium Complexes

2.1 Pentaorganotitanium Complexes

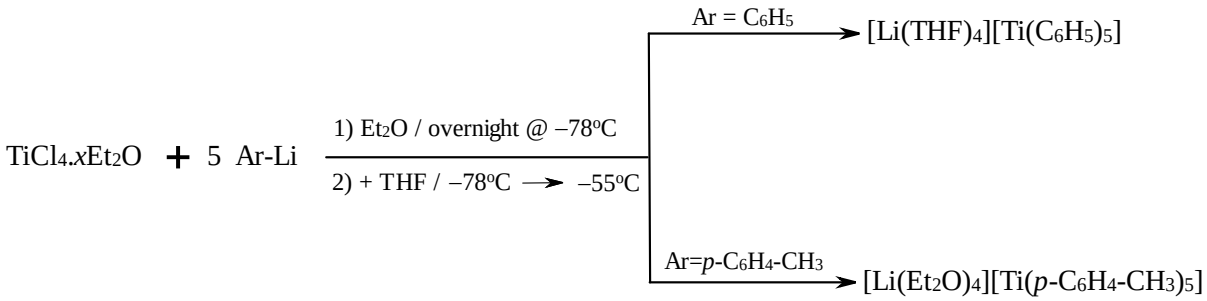
The number of homoleptic neutral 5-coordinate metal compounds is still very small. $Mo(CH_3)_5$ and $Ta(CH_3)_5$[33] have been crystalographically characterized and in both cases the metal was in a square pyramid environment.

The only one example to date of a $[TiL_5]^-$ stoichiometry is the methyl complex $[Ti(CH_3)_5]^-$, which has two different units in the lattice: one is closer to square pyramidal structure and the other closer to square pyramidal structure [34]. Recently Alonso et al. reported the preparation and characterization of the related $Ti(C_6F_5)_5^{2-}$ in which Ti(III) center is located in a strongly distorted trigonal-bipyramidal environment[35]. However, no related aryl derivatives of the species TiL_5^-, or even TiL_6^{2-} have yet been described.

Considering the lack of structural information currently available for homoleptic σ-aryl titanium(IV) compounds, it is would be interesting to obtain reliable data on the molecular geometry of this class of compounds and also to investigate the influence of aromatic ligands as compared to the simple methyl group. One aim of this work was the structure elucidation of hexaphenyl titanate IV.

2.1.1 Synthesis and Characterization of Pentaphenyl- and Pentatolyltitanate(IV)

The reaction between suspension of $TiCl_4 \cdot xEt_2O$ in Et_2O with Ar-Li (Ar = C_6H_5, *p*-C_6H_4-CH_3) was very sensitive towards the reaction conditions, especially the temperature and the equivalent amounts of Ar-Li. In case of C_6H_5Li, the reaction proceeds at −78°C and gives an orange-red solid companied with red solution. After the appropriate workup of the solid the $[Li(THF)_4][Ti(C_6H_5)_5]$ is obtained as yellow-brown solid in good yield (Scheme 1).



Scheme 1.

The resulted two complexes are extremely air and moisture sensitive and start to decompose above −50°C either in solution or in the solid state, and the color changed from orange to red above −40°C, and around −35°C the color changed to dark red, and finally a black suspension is formed when the temperature raises above −30°C. Both complexes are insoluble in Et_2O at low temperature but soluble in THF, hence these two combined solvents serves as a good

mixture for crystallization. Also these compounds are very soluble in CH_2Cl_2 even at very low temperature.

2.1.2 Crystal Structure of $[Li(THF)_4][Ti(C_6H_5)_5]$

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of a layer of Et_2O into a solution of the compound in THF with cooling from -50^oC to -80^oC.

The yellow-brown complex $[Li(THF)_4][Ti(C_6H_5)_5]$ crystallizes in space group C12/c1 of the monoclinic system, with 8 formula units in a cell of dimensions *a*=1388.35(20) pm, *b*=2004.62(33) pm, and *c*=1477.67(29) pm ; β = 94.833(14)°.

Table 1. Results of the X-ray structural determination of $[Li(THF)_4][Ti(C_6H_5)_5]$ and $[Li(Et_2O)_4][Ti(p\text{-}C_6H_4\text{-}CH_3)_5]$; selected bond lengths [pm] and angles [°].

$[Li(THF)_4][Ti(C_6H_5)_5]$		$[Li(Et_2O)_4][Ti(p\text{-}C_6H_4\text{-}CH_3)_5]$	
Ti–C13	215.35(4)	Ti–C1	216.49(5)
Ti–C7	216.46(4)	Ti–C29	216.15(4)
Ti–C1	215.89(3)	Ti–C8	216.37(5)
Ti–C7	216.46(4)	Ti–C15	2.16.02(7)
Ti–C1	215.89(3)	Ti–C22	216.95(6)
C1- Ti- C7	82.455(6)	C1–Ti–C29	109.039(21)
C1–Ti–C13	112.014(6)	C1–TI–C22	109.037(15)
C1–Ti–C7	83.842(5)	C1–Ti–C15	112.677(19)
C1–Ti–C13	112.014(6)	C1–Ti–C8	108.813(24)
C1–Ti–C7	82.455(6)	C15–Ti–C29	138.278(19)
C1–Ti–C7	83.842(5)	C15–Ti–C22	84.172(13)
C1–Ti–C1	135.971(7)	C22–Ti–C29	83.106(15)
C7–Ti–C13	108.556(6)	C8–Ti–C29	84.513(14)
C7–Ti–C7	142.888(6)	C8–Ti–C22	142.148(15)
C7–Ti–C13	108.556(6)	C8–Ti–C15	81.686(15)

The crystal structure of the anion $Ti(C_6H_5)_5^-$ as established by X-ray diffraction analysis on single crystals of $[Li(THF)_4][Ti(C_6H_5)_5]$ is presented in **Figure 3**. A selection of bond lengths and angles is given in **Table 1**.

The Ti center is located in almost square pyramidal (*SP*-5) environment formed by five terminal, σ-bonded C_6H_5 ligands (δ=7°, according to **Figure 2**), with the apical position occupied by the C(13) phenyl ring. The Ti−C bond lengths range from 215.35 pm to 216.46 pm with average 216.01 pm and have no significant difference between them.

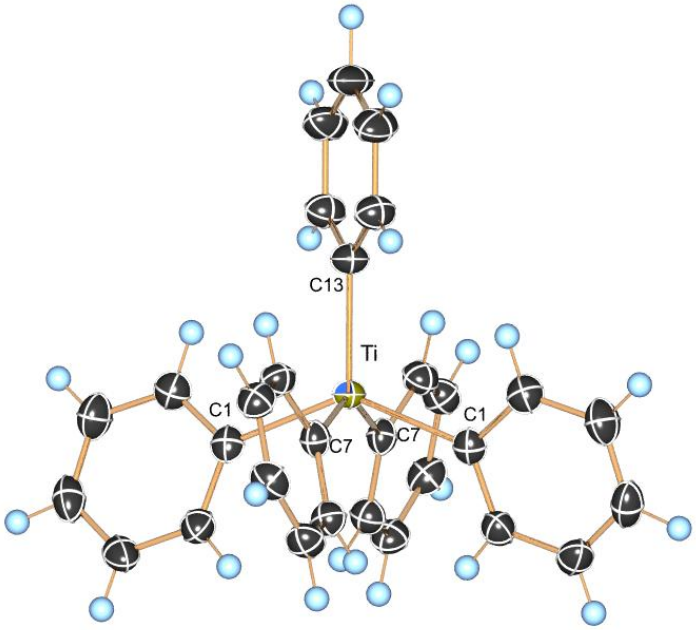


Figure 3. Crystal structure of the $Ti(C_6H_5)_5^-$ anion in $[Li(THF)_4][Ti(C_6H_5)_5]$ (thermal ellipsoid diagram; 50% probability).

In the crystal structure of $[Li(THF)_4][Ti(C_6H_5)_5]$: the $Li{\cdot}(THF)_4$ cation is separated (702.54 pm) from the formally anionic titanium atom, and shows the standard tetrahedral *T*-4 arrangement of THF molecules around Li^+ ion, as found in other cases.

2.1.3 Crystal Structure of $[Li(Et_2O)_4][Ti(p\text{-}C_6H_4\text{-}CH_3)_5]$

The yellow-brown complex $[Li(Et_2O)_4][Ti(p\text{-}C_6H_4\text{-}CH_3)_5]$ crystallizes in space group $P2_12_12_1$ of the orthorhombic system, with 4 formula units in a cell, a = 1224.3(4) pm, b = 1782.9(6) pm, and c = 2248.0(6) pm ; $\alpha = \beta = \gamma = 90°$.

The result of the single crystal determination is shown in **Figure 4**, and selected bond distances and angles are collected in **Table 1**.

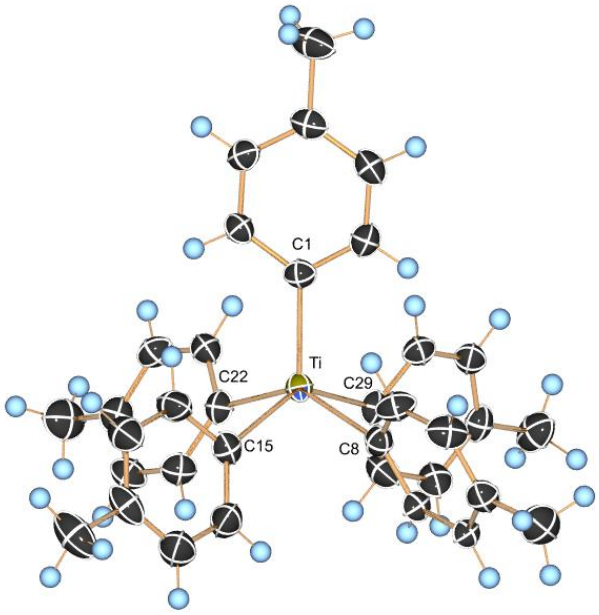


Figure 4. Crystal structure of the $Ti(p\text{-}C_6H_4\text{-}CH_3)_5^-$ anion in $[Li(Et_2O)_4][Ti(p\text{-}C_6H_4\text{-}CH_3)_5]$ (thermal ellipsoid diagram; 50% probability).

In all there is no significant difference between the $Ti(C_6H_5)_5^-$ and $Ti(p\text{-}C_6H_4\text{-}CH_3)_5^-$ anions regarding to their structure. Again the Ti center in $Ti(p\text{-}C_6H_4\text{-}CH_3)_5^-$ anion adopts a nearly square-pyramid structure (*SP*-5) in which $\delta = 4^o$, and average Ti−C bond length is 216.39 pm. The $Li\cdot(Et_2O)_4$ cation is separated (1392.37 pm) from the formally anionic titanium atom, and shows the standard tetrahedral *T*-4 arrangement around Li^+ ion as found in other cases.

For the homoleptic $[ML_5]^-$systems, in which L is purely σ-donor ligands e.g. H, Me, detailed theoretical calculations have been performed and predict the non-VSEPR *SP*-5 geometry as the most energetically favored. For $[TaH_5]$, the *TBP*-5 structure has been computed to be more than 80 $kJmol^{-1}$ above the *SP*-5 minimum[27].

In case of $[Ta(CH_3)_5]$, the *SP*-5 arrangement energetically was also favored over the trigonal bipyramidal (*TBP*-5).[27,36-37] (MP2 calculations give ca. 30 $kJmol^{-1}$,[27,36] other DFT calculations provide ca. 53 $kJmol^{-1}$ [33]).

Computational results are available for further hypothetical hydride complexes: such for the ion $[ZrH_5]^-$ an *SP*-5 minimum has been calculated to be more stable than the *TBP*-5 structure. Whereas the more ionic $[HfH_5]^-$ prefers *TBP*-5. [38]

In the single crystal structure determination, $[Ta(CH_3)_5]$ and $[Mo(CH_3)_5]$ have a square pyramidal arrangements. The d^1 complex $[Mo(CH_3)_5]$ has also been found to favor *SP*-5, and computations suggest that the stabilization relative to *TBP*-5 is large (97.5 $kJmol^{-1}$).[33]

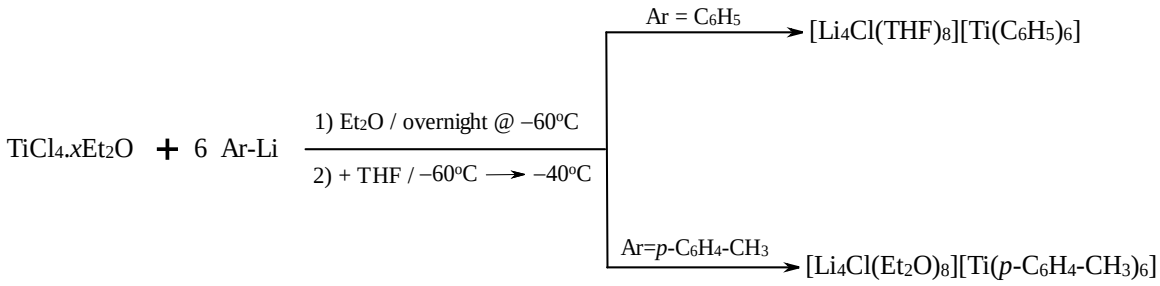
The $Ti(CH_3)_5^-$ ion in the solid state $[Li(Et_2O)_2].[Ti(CH_3)_5]$ is of special interest, it exhibits two crystallographically different ion pairs: one is closer to *SP*-5, the other closer to *TBP*-5. Calculations for the free anion indicate *SP*-5 to be lower than *TBP*-5 by only about 10 $kJmol^{-1}$.[34]

In this work $[Li(THF)_4][Ti(C_6H_5)_5]$, and $[Li(Et_2O)_4][Ti(p\text{-}C_6H_4\text{-}CH_3)_5]$ have been crystallographically characterized, and the Ti center in both cases is located in a *SP*-5 arrangement.

2.2 Hexa-aryltitanium(III) Complexes

2.2.1 Synthesis and Characterization of Hexaphenyl- and Hexatolyltitanium(III) Complexes

As described before, the reaction between a suspension of $TiCl_4 \cdot xEt_2O$ in Et_2O with Ar-Li (Ar = C_6H_5, *p*-C_6H_4-CH_3) is affected by two main factors: the temperature at which the reaction are performed, and the equivalent amounts of Ar-Li used. In case of using an excess C_6H_5Li (more than 6 equivalents), the reaction proceeds at -60^oC accompanied with metal reduction (scheme 2), to gives a dark red solution with small amount of red-brown solid.



Scheme 2.

Removing the solid, followed by THF extraction and subsequent treatment with Et_2O led to the formation of the new hexa-aryltitanium compound $[Li_4Cl(THF)_8][Ti(C_6H_5)_6]$, which was isolated as red solid in high yield (Scheme 2).

Also the *p*-tolyl derivative was prepared with the same procedure and the complex $[Li_4Cl(Et_2O)_8][Ti(p\text{-}C_6H_5\text{-}CH_3)_6]$ has been isolated as dark red solid.

These complexes are extremely air and moisture sensitive and start to decompose above -30^oC both in solution or in the solid state, similarly as the pentaphenyltitanium(IV) complex. The color changed from red to dark red and finally a black suspension appeared during thermal decomposition.

2.2.2 Crystal Structure of $[Li_4Cl(THF)_8][Ti(C_6H_5)_6]$

Crystals suitable for X-ray diffraction analysis were obtained by slow cooling of a solution of the compound in THF from −40°C to −80°C.

The dark red complex $[Li_4Cl(THF)_8][Ti(C_6H_5)_6]$ crystallizes in space group P-1 in the triclinic system, with 2 formula units in a cell, *a* = 1129.9(3) pm, *b* = 1157.5(3) pm, and *c* = 1288.8(3) pm ; α = 75.161(5)°, β = 85.903(6)°, γ = 84.115(5)°.

The crystal structure of the anion $Ti(C_6H_6)_5^{3-}$ as established by X-ray diffraction analysis on single crystals of $[Li_4Cl(THF)_4][Ti(C_6H_5)_6]$ is presented in **Figure 5**. A selection of bond lengths and angles is given in **Table 2**.

Table 2. Results of the X-ray structural determination of $[Li_4Cl(THF)_8][Ti(C_6H_5)_6]$; selected bond lengths [pm] and angles [°].

$[Li_4Cl(THF)_8][Ti(C_6H_5)_6]$			
Ti -C13 (2x)	230.9(5)	C13-Ti1-C13	180.000
Ti-C7 (2x)	231.3(5)	C13-Ti1-C7	88.64(18)
Ti-C1 (2x)	233.9(4)	C13-Ti1-C7	91.36(18)
C7-Ti1-C1	90.45(17)	C13-Ti1-C7	91.36(18)
C13-Ti1-C1	89.18(18)	C13-Ti1-C7	88.64(18)
C13-Ti1-C1	90.82(18)	C7-Ti1-C7	180.000(1)
C7-Ti1-C1	90.45(17)	C13-Ti1-C1	90.82(18)
C7-Ti1-C1	89.55(17)	C13-Ti1-C1	89.18(18)

The Ti center is located in almost octahedral (*OC*-6) environment formed by 6 terminal, σ-bonded C_6H_5 ligands. The anion $Ti(C_6H_5)_6^{3-}$ is involved in a direct interaction with two of the lithium cations (see Figure 5), both Li cations are capping two opposite trigonal faces, and the Ti···Li distance is 260.1(9) pm for both. Despite that the Ti center is affected by a sort of

interaction with two Li^+ cations, the titanium center is located in octahedral arrangement. It is obvious that the gemometry of the anion is not controlled by such interactions.

Ti−C bond lengths range from 230.9 pm to 233.9 pm with average 232.03, bond lengths are also slightly longer than those observed in the homoleptic $Ti(C_6H_5)_5^-$ (Ti─C = 216.01 pm), which obviously related to the different coordination numbers in the two anionic species and also to their different overall charges.

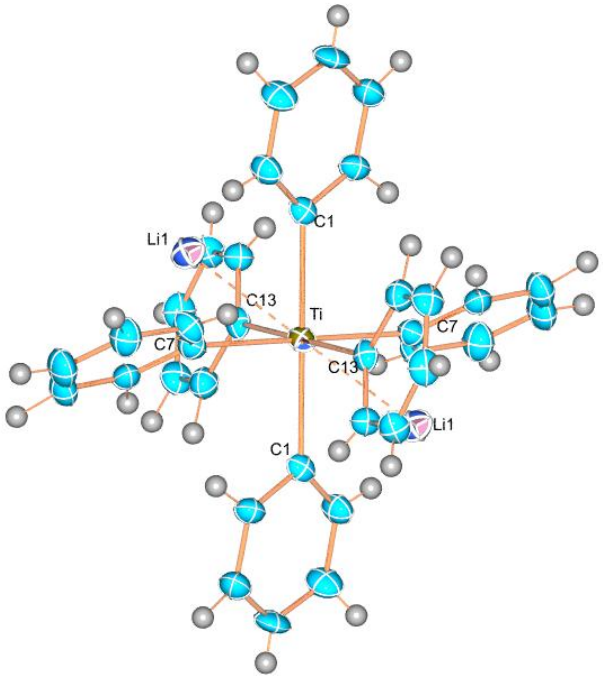


Figure 5. Crystal structure of the $Ti(C_6H_5)_6^{3-}$ anion in $Li_4ClTi(C_6H_5)_6 \cdot 8THF$ (thermal ellipsoid diagram; 50% probability).

2.2.3 Crystal Structure of $[Li_4Cl(Et_2O)_8][Ti(p\text{-}C_6H_4\text{-}CH_3)_6]$

Very poor-quality single crystals of the dark red complex $[Li_4Cl(Et_2O)_8][Ti(p\text{-}C_6H_4\text{-}CH_3)_6]$ were obtained, and the X-ray diffraction data collected were not of sufficient quality to carry a complete and precise structural determination of the complex. General information about the

geometry and connectivity of the $[Ti(p\text{-}C_6H_4\text{-}CH_3)_6]^-$ anion could be established[1] from X-ray diffraction data results, in order to compare its geometry with the analogues $[Ti(C_6H_5)_6]^-$ anion.

The geometry of $[Ti(p\text{-}C_6H_4\text{-}CH_3)_6]^-$ anion is very similar to the structure of $[Ti(C_6H_5)_6]^-$ ion, apart from the very large estimated standard deviation due to very poor crystal quality.

The geometry of the $[Ti(p\text{-}C_6H_4\text{-}CH_3)_6]^-$ anion, depicted in **Figure 6**, can be described as octahedral, with two Li^+ cations capping two parallel trigonal faces of the Octahedral, again with no effect on the overall geometry.

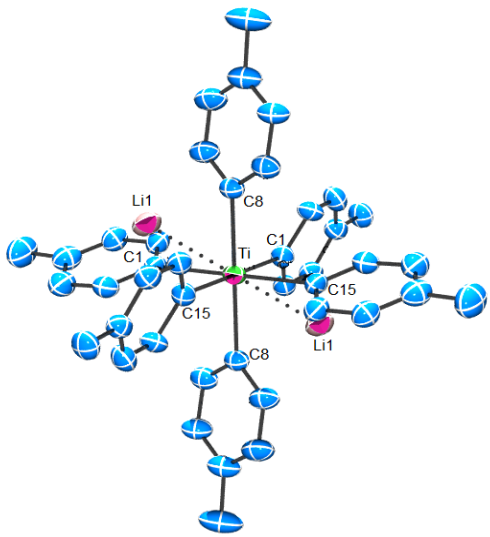


Figure 6. Crystal structure of the $Ti(p\text{-}C_6H_5\text{-}CH_3)_6^{3-}$ anion in $[Li_4Cl(Et_2O)_8][Ti(p\text{-}C_6H_4\text{-}CH_3)_6]$ (thermal ellipsoid diagram; 50% probability).

[1] Crystal data for $[Li_4Cl(Et_2O)_8][Ti(p\text{-}C_6H_4\text{-}CH_3)_6]$ Monoclinic, space group C12/c1, with 8 formula units in a cell, *a* = 2300.0(5) pm, *b* = 1415.8(3) pm, and *c* = 2600.8(6) pm ; $\alpha = \gamma = 90(6)°$, $\beta = 115.202(5)°$.

3. Zirconium and Hafnium Complexes

3.1 Zirconium Complexes

The organometallic chemistry of zirconium is dominated by zirconocene derivatives, which are usually derived from Cp_2ZrCl_2, first reported by Wilkinson in 1954[39]. Zirconoences are widely used as catalysts for olefin polymerization[40] and in organic synthesis[41]. Recently homoleptic σ-bound zirconohydrocarbons Zr(biphenl-2,2'-diyl)$_3^{2-}$ has been prepared and characterized[42], in which the 3 bidentate ligand are arranged arround Zr atom with a geometry closer to trigonal prismatic than octahedral. The first example of a nearly trigonal prismatic d^0 ML_6 complex with monodentate ligand has been the $[Li(tmeda)]_2[Zr(CH_3)_6]$ complex. After that the deviation from octahedral geometry has gained great attention. In spite of that there are no related homoleptic aryl derivatives of zirconium or hafnium that have been fully characterized. Girolami reported in 1999 that the arylation of $ZrCl_4$ with LiC_6F_5 proceed with partial arylation, and salts of ions $ZrCl_2(C_6H_5)_4^{2-}$ and $Zr(C_6F_5)_5F_2^{3-}$ were obtained depending on the reaction conditions[43]. Beside that the reaction between MCl_4 (M= Zr, Hf) with LiC_6Cl_5 proceeded with partial arylation forming the $M(C_6Cl_5)_3Cl_2^-$ ion [44].

A good number of homoleptic $[M(C_6X_5)_n]^{m-}$ (X = F, Cl) complexes were synthesized and structurally characterized[45]. It was realized that the stability of the corresponding homoleptic aryl transition metal derivatives was greatly enhanced by using perhalophenyl groups -C_6X_5 (X = F, Cl). There is no homoleptic-aryl zirconium or hafnium of the type ML_6^{2-} or ML_5^- that has yet been described and fully characterized.

3.1.1 Pentaphenyzirconium(IV) Complex

3.1.1.1 Synthesis and Characterization of $[NBu_4][Zr(C_6H_5)_5]\cdot 4CH_2Cl_2$

Treatment of $ZrCl_4$ with C_6H_5Li at −78°C, followed by addition of NBu_4Br at −35°C, resulted in formation of $[NBu_4][Zr(C_6H_5)_5]\cdot 4CH_2Cl_2$, which was isolated as an air- and moisture-sensitive, yellow solid (Scheme 3). All steps for the preparation were performed and kept at low temperature (−35°C) because the compound easily undergoes thermal decomposition.

$$ZrCl_4 + 5\ C_6H_5Li \xrightarrow[2)\ NBu_4Br/-35^oC]{1)\ Et_2O/-78^oC} [NBu_4][Zr(C_6H_5)_5].4CH_2Cl_2$$

Scheme 3

The crystal and molecular structure of the compound are established by X-ray diffraction.

In the process of decomposition an ethereal solution of the compound changes color from light brown to black.

3.1.1.2 Crystal Structure of $[NBu_4][Zr(C_6H_5)_5]\cdot 4CH_2Cl_2$

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of Et_2O layer to the CH_2Cl_2 solution of the compound at –80°C.

The yellow compound $[NBu_4][Zr(C_6H_5)_5]\cdot 4CH_2Cl_2$ crystallizes in space group C2/c in the monoclinic system with 8 formula units in a cell, a = 2361.8(13) pm, b = 2095.5(10) pm, and c = 2446(2) pm ; $\alpha = \gamma = 90^o$, $\beta = 117.89(7)^o$.

The crystal structure of the anion $Zr(C_6H_6)_5^-$ as established by X-ray diffraction analysis of single crystals of $[NBu_4][Zr(C_6H_5)_5]\cdot 4CH_2Cl_2$ is presented in **Figure 7**. A selection of bond lengths and angles is given in **Table 3**.

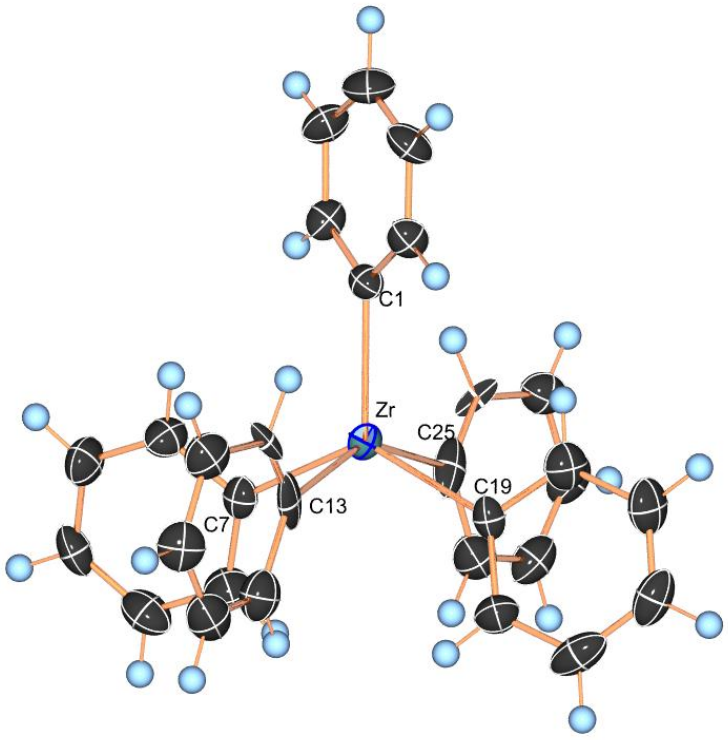


Figure 7. Crystal structure of the $Zr(C_6H_5)_5^-$ anion in $[NBu_4][Zr(C_6H_5)]\cdot 4CH_2Cl_2$ (thermal ellipsoid diagram; 50% probability).

Crystal of the compound $[NBu_4][Zr(C_6H_5)_5]\cdot 4CH_2Cl_2$ consist of discrete cations and anions, The NBu_4^+ cation has in general better behavior in organometallic and coordination chemistry than the $Li\cdot(THF)_4$ cation. As expected the salt $[NBu_4][Zr(C_6H_5)_5]\cdot 4CH_2Cl_2$ shows an enhanced thermal stability compared to the $[Li(THF)_4][Ti(C_6H_5)_5]$ compound.

In the anion the zirconium atom is surrounded by five phenyl groups in an arrangement very close to square pyramidal ($\delta=18^o$). Zr−C bond lengths range from 227.32 pm to 230.80 pm with average 229.12 pm, which is slightly longer than that observed for Ti─C bond in analogous complexes, $[Ti(C_6H_5)_5]^-$ (216.01 pm) $[Ti(p\text{-}C_6H_4\text{-}CH_3)_5]^-$ (216.39 pm).

Table 3. Selected interatomic distances [pm] and angles [°] and their estimated standerrd deviation for $Zr(C_6H_5)_5^-$ anion.

$Zr(C_6H_5)_5^-$			
Zr-C1	230.23(9)	C1-Zr-C7	114.327(37)
Zr-C25	230.80(14)	C7-Zr-C25	85.747(43)
Zr-C7	227.32(13)	C13-Zr-C25	147.997(55)
Zr-C19	227.51(21)	C19-Zr-C25	81.005(55)
Zr-C13	229.76(14)	C7-Zr-C13	83.953(47)
C1-Zr-C25	105.395(63)	C7-Zr-C19	130.648(51)
C1-Zr-C19	115.021(58)	C13-Zr-C19	82.980(44)
C1-Zr-C13	106.467(36)		

3.1.2 Hexaphenyl- and Hexatolylzirconium(IV) Complexes

Octahedral versus Trigonal Prismatic Geometry

The octahedron and trigonal prism are closely related, and can be described in terms of two triangles which are staggered or eclipsed. In another words an octahedral geometry can be changed into a trigonal prismatic one by rotating one triplet of ligands against the other triplet by 60°. For systems that are intermediate between octahedron and trigonal prism, a trigonal twist angles, χ, along the C_3 axis can be calculated to describe such system as distorted octahedral or distorted trigonal prismatic.

The twist angles were calculated by taking the average of the projection angles in the M-Cen direction, where Cen is the centroid of the top and bottom triangles on the $\boldsymbol{C_3}$ axis. The three twist angles were averaged. (See Figure 8)

In the ideal octahedron $\chi = 60°$, in the ideal trigonal prism (D_{3h}) $\chi = 0°$.

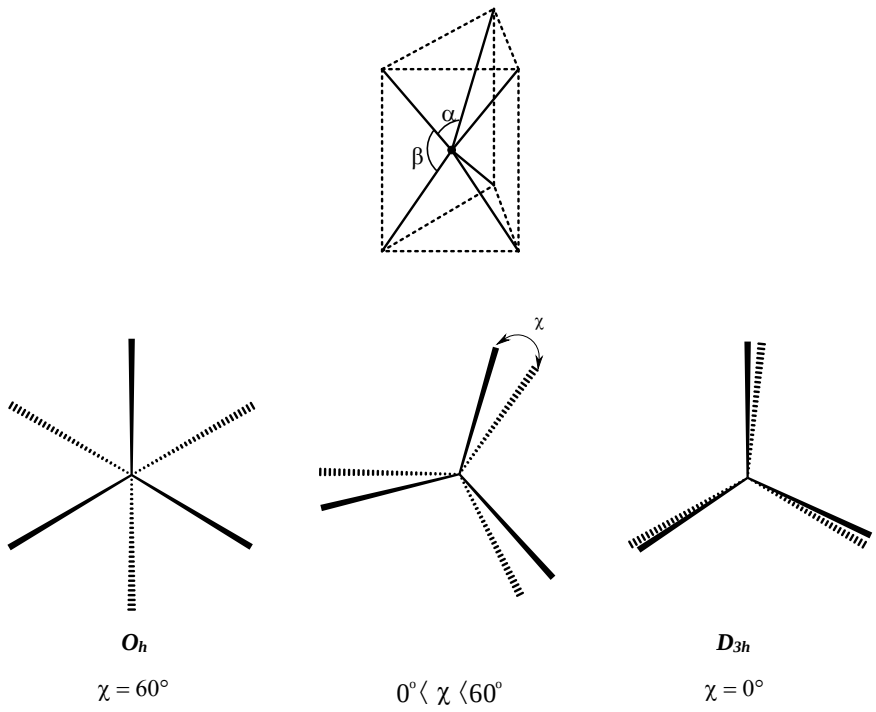
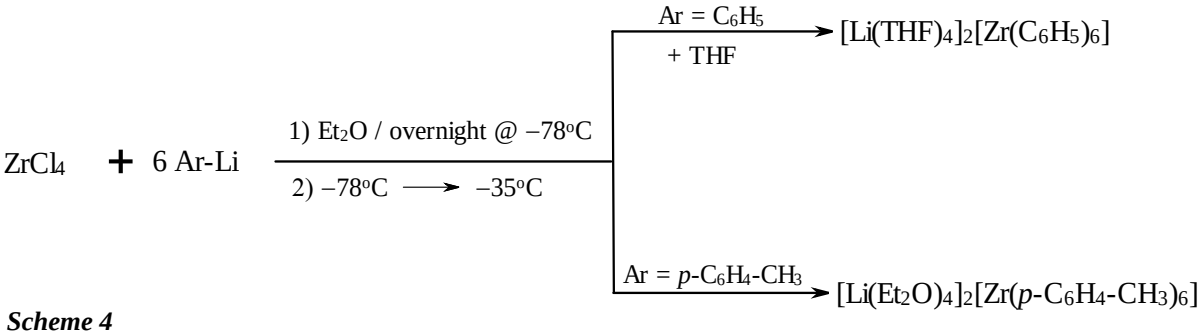


Figure 8. Definition of interligand angles, and the interchange of an octahedron to a trigonal prism.

If in an ideal trigonal prismatic coordination the bond angle α between ligands within one hemisphere is chosen to be 85^o, for example, then the angle β between close ligands between both hemispheres comes out at 77.54^o (see Figure 8)[45].

3.1.2.1 Synthesis and Characterization of $[Li(THF)_4]_2[Zr(C_6H_5)_6]$ and $[Li(Et_2O)_4]_2[Zr(p\text{-}C_6H_4\text{-}CH_3)_6]$

The arylation of $ZrCl_4$ with Ar-Li (Ar = C_6H_5, *p*-C_6H_4-CH_3) in Et_2O at −78°C, followed by the appropriate treatment, afforded $[Li(THF)_4]_2[Zr(C_6H_5)_6]$ as pink solid and $[Li(Et_2O)_4]_2[Zr(p\text{-}C_6H_4\text{-}CH_3)_6]$ as yellow solid, both in good yields (Scheme 4). The two complexes are extremely air- and moisture-sensitive and have a limited thermal stability, readily decomposing above −20°C both in solution and in the solid state.



Scheme 4

3.1.2.2 Crystal Structure of $[Li(THF)_4]_2[Zr(C_6H_5)_6]$

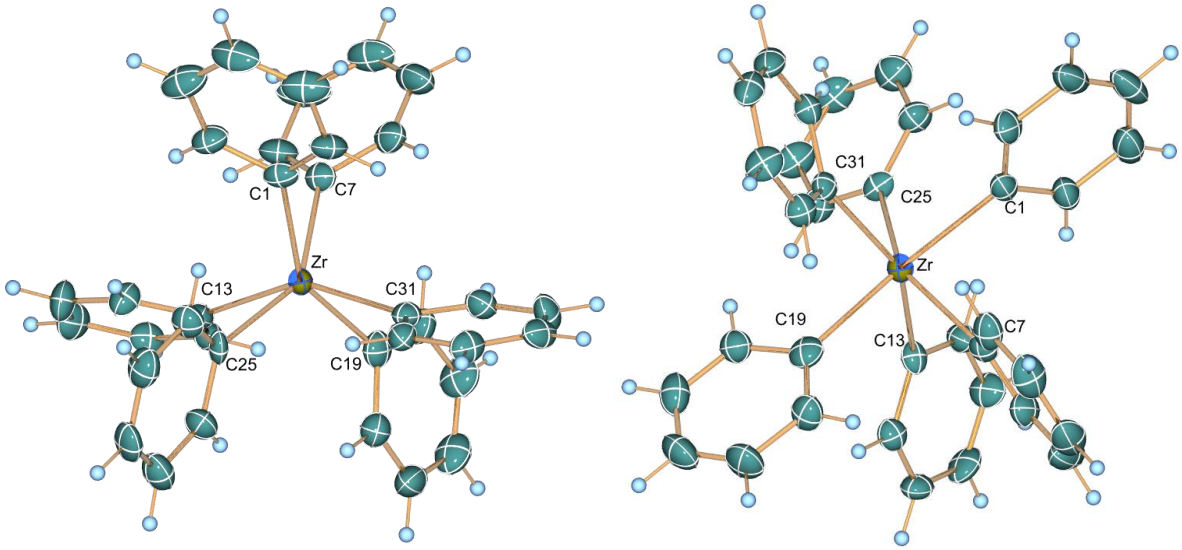
The pink colored compound $[Li(THF)_4]_2[Zr(C_6H_5)_6]$ crystallizes in space group P_{65} of the hexagonal system, with 6 formula units in a cell of dimensions a = 1317.3(3) pm, *b* = 1317.3(3) pm, and *c* = 6310(3) pm; $\alpha = \beta = 90^o$, $\gamma = 120^o$.

The crystal structure of the anion $Zr(C_6H_5)_6^{2-}$ as established by X-ray diffraction analysis on single crystals of $[Li(THF)_4]_2[Zr(C_6H_5)_6]$ is presented in **Figure 9**. A selection of bond lengths and angles is given in **Table 4**.

Table 4. Selected interatomic distances [pm] and angles [°] and their estimated standerrd deviation for $Zr(C_6H_5)_5^-$ and $Zr(p\text{-}C_6H_4\text{-}CH_3)_6^{2-}$anions.

$Zr(C_6H_5)_6^{2-}$		$Zr(p\text{-}C_6H_4\text{-}CH_3)_6^{2-}$	
Zr1-C31	237.04(6)	Zr1-C15	237.03(4)
Zr1-C1	236.53(5)	Zr1-C1	236.79(5)
Zr1-C25	237.77(5)	Zr1-C8	237.92(4)
Zr1-C19	234.45(5)	Zr1-C22	236.10(4)
Zr1-C7	234.95(4)	Zr1-C29	237.84(5)
Zr1-C13	236.99(4)	Zr1-C36	237.04(4)
C1-Zr1-C31	87.490(15)	C8-Zr1-C15	86.102(11)
C7-Zr1-C31	115.426(16)	C1-Zr1-C15	85.289(10)
C19-Zr1-C31	79.085(14)	C15-Zr1-C29	126.185(17)
C25-Zr1-C31	88.942(15)	C15-Zr1-C36	76.265(10)
C13-Zr1-C31	151.181(17)	C15-Zr1-C22	142.094(13)
C1-Zr1-C7	77.006(14)	C1-Zr1-C8	84.194(9)
C1-Zr1-C13	118.057(16)	C1-Zr1-C22	125.425(10)
C1-Zr1-C19	150.025(18)	C1-Zr1-C36	142.108(10)
C1-Zr1-C25	85.101(15)	C1-Zr1-C29	81.013(10)
C7-Zr1-C25	148.604(18)	C8-Zr1-C22	76.875(10)
C7-Zr1-C19	84.721(15)	C8-Zr1-C36	126.302(11)
C7-Zr1-C13	85.100(15)	C8-Zr1-C29	142.710(14)
C19-Zr1-C25	120.915(17)	C22-Zr1-C29	84.252(11)
C13-Zr1-C19	83.234(15)	C22-Zr1-C36	86.892(10)
C13-Zr1-C25	80.822(14)	C29-Zr1-C36	83.683(11)

The six phenyl ligands are disposed around the Zr atom with a geometry closer to trigonal prismatic than to octahedral (χ=18°). This is best seen if viewed along the approximate C_3 molecular axis of $Zr(C_6H_5)_6^{2-}$, as shown in **Figure 9a**, which shows a rotation of the triplets of ligands by about 18° against each other (**Figure 8)**. The corresponding angles α and β in $Zr(C_6H_5)_6^{2-}$ (see Table 4) are quite close to the values described before for trigonal prisms when α=85°, β=77.54°, see **Figure 8**.



(a) **(b)**

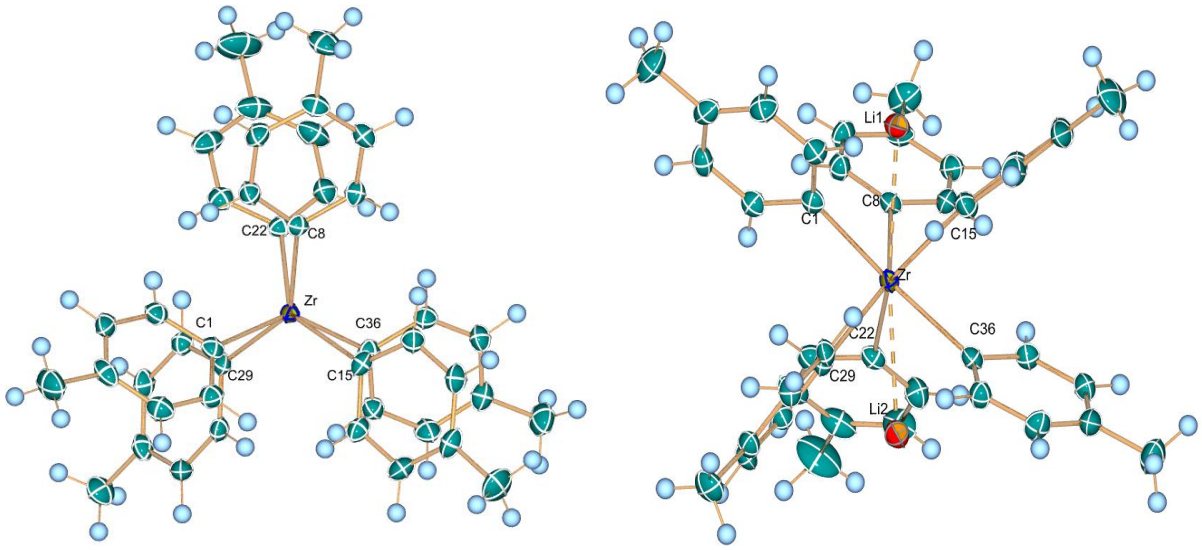
Figure 9. Crystal structure of the $Zr(C_6H_5)_6^{2-}$ anion in $[Li(THF)_4]_2[Zr(C_6H_5)_6]$ (thermal ellipsoid diagram; 50% probability); (a) view along the approximate threefold axis of the anion; (b) view perpendicular to the approximate threefold axis.

Zr−C bond lengths range from 234.45 pm to 237.77 pm with an average of 236.29 pm, which is slightly longer than that observed for Zr─C bond in pentaphenyl complexes, $[Zr(C_6H_5)_5]^-$ (229.12 pm). This lengthening in the bond is apparently caused by steric crowding and the addition of another new negative charge.

3.1.2.3 Crystal Structure of $[Li(Et_2O)_2]_2[Zr(p\text{-}C_6H_4\text{-}CH_3)_6]$

The yellow compound $[Li(Et_2O)_2]_2[Zr(p\text{-}C_6H_4\text{-}CH_3)_6]$ crystallizes in space group P $2_1/n$ in the monoclinic system with 4 formula units in a cell, a = 1093.3(3) pm, b = 1767.6(4) pm, and c = 2840.3(7) pm; $\alpha = \gamma = 90^o$, $\beta = 97.410(6)°$.

The crystal structure of the anion $Zr(p\text{-}C_6H_4\text{-}CH_3)_6^{2-}$ as established by X-ray diffraction analysis of single crystals of $[Li(Et_2O)_2]_2[Zr(p\text{-}C_6H_4\text{-}CH_3)_6]$ is presented in **Figure 10**. A selection of bond lengths and angles is given in **Table 4**.



(a) **(b)**

Figure 10. Crystal structure of the Zr(p-C_6H_4-CH_3)$_6^{2-}$ anion in Zr(p-C_6H_4-CH_3)$_6^{2-}$ (thermal ellipsoid diagram; 50% probability); (a) view along the approximate threefold axis of the anion; (b) view perpendicular to the approximate threefold axis with Zr···Li interaction.

As shown in **Figure 10**, the crystal structure of the Zr(p-C_6H_4-CH_3)$^{2-}$ anion is very similar to the structure of Zr(C_6H_5)$_6^{2-}$. Except that the anion Zr(p-C_6H_4-CH_3)$_6^{2-}$ is involved in a sort of interaction with the lithium cations (see Figure 10b), both Li cations are capping two parallel trigonal faces, and the average Ti···Li distance is 291.78(5) pm for both. (the same as in Ti(C_6H_5)$_6^{3-}$ and Ti(p-C_6H_4-CH_3)$_6^{3-}$).

Apart from that interaction, the Zr center is located in almost trigonal prismatic geometry formed by 6 terminal, σ-bonded p-C_6H_4-CH_3 ligands, with Zr─C distances comprised between 236.10(5) and 237.92(7) pm with average 237.12 pm.

The rotation of the triplets of the tolyl ligands against each other (χ) along the C_3 molecular axis is about **9°.**

Compared to the octahedral species $Te(C_6H_5)$ [46] and $Bi(C_6H_5)_6^-$ [47], in which the orientation of the phenyl ring planes is very regular (planes of adjacent phenyl groups are nearly perpendicular, and planes of opposite phenyl groups are nearly parallel) the orientation of the phenyl ring planes in both anions $[Zr(C_6H_5)_6]^{2-}$ and $[Zr(p\text{-}C_6H_4\text{-}CH_3)_6]^{2-}$ are quite irregular.

In the crystal structure of $[Li(THF)_4]_2[Zr(C_6H_5)_6]$ the two $Li\cdot(THF)_4$ cations are separated (883.16 pm, 747.87 pm) from the formally dianionic zirconium atom. The cation shows the usual tetrahedral arrangement of THF molecules around the Li^+ ion as found in other cases.

Their bulkiness, their almost spherical shape, and the long distance from Zr atom guarantees that little interaction between cations and anions is observed. Furthermore, the new analogues d^1 complex $[Li_4Cl(THF)_8][Ti(C_6H_5)_6]$ manage to adopt the expected octahedral structure despite having more stronger and direct interaction of two Li^+ (both Li cations are capping two parallel trigonal faces, and the Ti···Li distance is 260.1(9) pm for both).

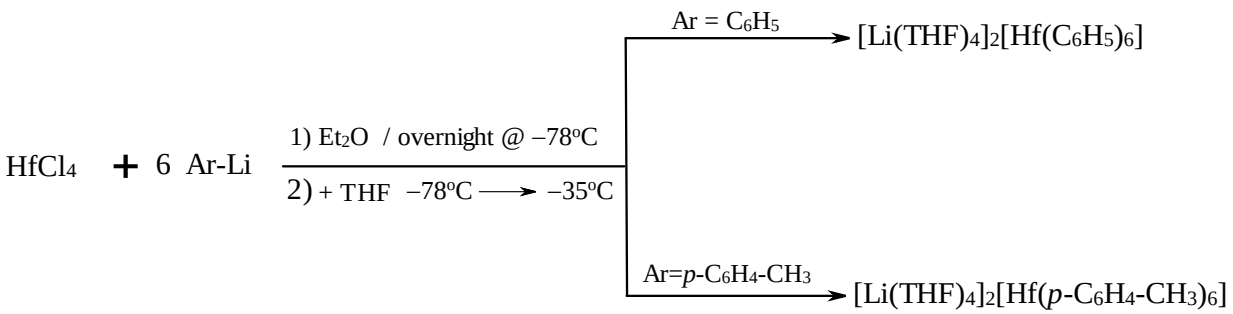
Related d^3 complexes such as $[Li(tmeda)]_2[Mn(CH_3)_6]$[48], $[Li(Et_2O)]_3[Cr(C_6H_5)_6]$[49] and $[Li(Et_2O)]_4[V(C_6H_5)_6]$[49] also, have an octahedral structure despite having similar Li···M interactions. One extreme case is $[Li(Et_2O)]_4[V(C_6H_5)_6]$. It has 4 Li^+ ions which cap four triangular faces of the octahedron in a tetrahedral manner. All these findings suggest that the Li···Zr interactions are not controlling the structure of $[Li(THF)_4]_2[Zr(C_6H_5)_6]$. Instead, the non-octahedral structure geometry obtained reflects an intrinsic electronic driving force to lower the symmetry. The situation is a little bit different for the complex $[Li(Et_2O)_2]_2[Zr(p\text{-}C_6H_4\text{-}CH_3)_6]$. The anion in this salt is involved in a sort of interaction with the lithium cations, and it is fair to ask: is whether the cation-anion interaction stabilizes the trigonal prismatic geometry?

3.2 Hafnium Complexes

3.2.1 Hexaphenyl- and Hexatolyl- Hafnium(IV) Complexes

3.2.1.1 Synthesis and Characterization of $[Li(THF)_4]_2[Hf(C_6H_5)_6]$ and $[Li(THF)_4]_2[Hf(p\text{-}C_6H_4\text{-}CH_3)_6]$.

The arylation of $HfCl_4$ with Ar-Li (Ar= C_6H_5, *p*-C_6H_4-CH_3) in THF at −78°C, followed by the appropriate treatment, afforded $[Li(THF)_4]_2[Hf(C_6H_5)_6]$ as pink solid and $[Li(THF)_4]_2[Zr(p\text{-}C_6H_4\text{-}CH_3)_6]$ as yellow solid, both in good yield (Scheme 4). The two complexes are extremely air- and moisture-sensitive and have a limited thermal stability, readily decomposing above −20°C both in solution and in the solid state.



Scheme 5

3.2.1.2 Crystal Structure of $[Li(THF)_4]_2[Hf(C_6H_5)_6]$

The pink colored compound $[Li(THF)_4]_2[Hf(C_6H_5)_6]$ crystallizes in space group P $2_1/c$ of the monoclinic system, with 4 formula units in a cell of dimensions a = 1178.94(16) pm, *b* = 1178.92(12) pm, and *c* = 2301.0(3) pm; $\alpha = \gamma = 90^o$, $\beta = 97.682(3)°$. The crystal structure of the anion $Hf(C_6H_6)_6^{2-}$ as established by X-ray diffraction analysis on single crystals of $[Li(THF)_4]_2[Hf(C_6H_5)_6]$ is presented in **Figure 11**. A selection of bond lengths and angles is given in **Table 5**.

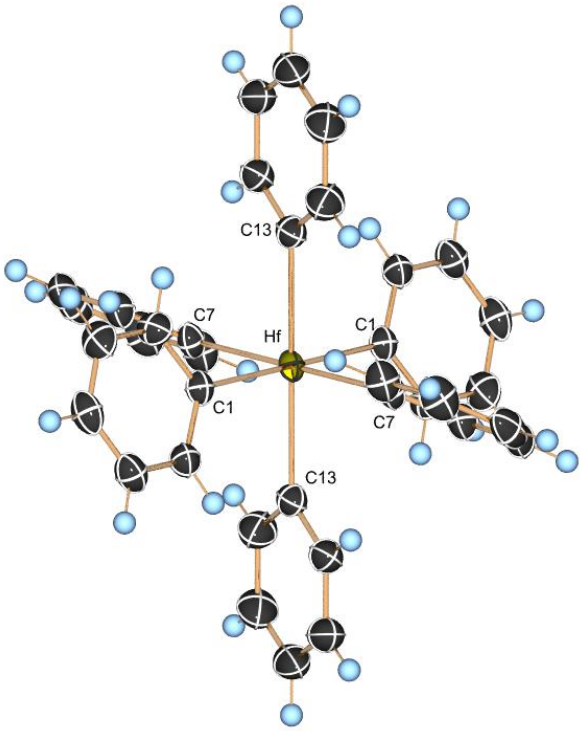


Figure 11. Crystal structure of the $Hf(C_6H_5)_6^{2-}$ anion in $Li_2(THF)_4Hf(C_6H_5)_6$ (thermal ellipsoid diagram; 50% probability).

In the anion the hafnium atom is surrounded by six phenyl groups in an octahedral arrangement. Hf−C bond lengths range from 238.60(2) pm to 239.71(2) pm with average 239.02 pm, which shows no pronounced difference compared to Zr─C bond in analogous complexes, $[Zr(C_6H_5)_5]^-$ (236.29 pm) $[Zr(p\text{-}C_6H_4\text{-}CH_3)_5]^-$ (237.12 pm).

As mentioned before, DFT calculations for Group 4 - 7 hexamethyl complexes, $[M(CH_3)_6]^n$ (n = −2, −1, 0, +1) show that the cationic and neutral complexes prefer distorted trigonal prisms, whereas the mono- and dianionic systems have regular trigonal prismatic structures, and the relative energy for the octahedron to the minimum structure is lowest for the dianions.[6]

That calculations show that the dianions $[M(CH_3)_6]^{2-}$ (M=Ti, Zr, Hf) and the monoanions $[M(CH_3)_6]^-$ (M=V, Ta) have regular prismatic D_3 structures, consistent with experimental X-ray results for $[Zr(CH_3)_6]^{2-}$ ion, $[TaR_6]^-$ (R= phenyl, tolyl), and $[Ta(CH_3)_6]^-$. Also within a

given group, the tendency of the complex to distort from octahedral structure increases from the 3d to the 4d complex but decreases to the 5d complex.

Table 5. Selected interatomic distances [pm] and angles [°] and their estimated standard deviation for $Hf(C_6H_5)_6^{2-}$ anion.

$Hf(C_6H_5)_6^{2-}$			
Hf1–C7	238.75(2)	C7–Hf1–C13	92.032(4)
Hf1–C13	239.71(2)	C7–Hf1–C7	180.000
Hf1–C1	238.60(2)	C1–Hf1- C13	89.508(6)
Hf1–C1	238.60(2)	C1–Hf1–C13	90.492(4)
Hf1–C13	239.71(2)	C1–Hf1–C1	180.000
Hf1–C7	238.75(2)	C1–Hf1–C7	89.440(4)
C1–Hf1–C7	90.560(5)	C7–Hf1–C13	92.032(4)
C7–Hf1–C13	87.967(5)	C1–Hf1–C13	90.492(4)
C1–Hf1–C7	89.440(4)	C13–Hf1– C13	180.000(6)
C1–Hf1–C13	89.508(6)	C1–Hf1–C7	90.560(5)
C7–Hf1–C13	87.967(5)		

From x-ray measurements, the structure of $Zr(C_6H_5)_6^{2-}$ anion can be described as an almost perfect trigonal prism agreeing with that calculation (if the phenyl group considered to behave as simple Me group), while the $Hf(C_6H_5)_6^{2-}$ anion has a perfectly octahedral arrangement. This difference may be attributed to larger ligand repulsion, because of the more polar M-C bonding in case of Hf. The bond polarity is larger for 5d than for 4d complexes, a result of the relativistic expansion of the 5d orbitals. Relativity reduces metal-ligand covalency and thereby increases ligand repulsion.[6]

4. Niobium Complexes

The number of characterized neutral homoleptic alkyls or aryls compounds of niobium and tantalum is limited to pentamethyltantalum, pentamethylniobium, pentabenzyltantalum and penta[(trimethylsilyl)methyl]tantalum.[50] π-Donating coligands remarkably stabilize the M─C σ-bond and many examples are known for the non-homoleptic mono- or bis(alkyl) or –aryl tantalum and niobium.[51]

Earlier work on the reaction of $NbBr_5$ and $TaBr_5$ with excess LiC_6H_5 had indicated that reduction products containing Nb(II) and Ta(II) were present in the reaction mixture[52].

Sarry et al. proved from NMR the presence of $Ta(4\text{-}C_6H_4\text{-}CH_3)_6^-$, and showed that $Ta(C_6H_5)_6^-$ undergoes ortho-lithiation with excess LiC_6H_5, resulting in benzyne complexes[53,54].

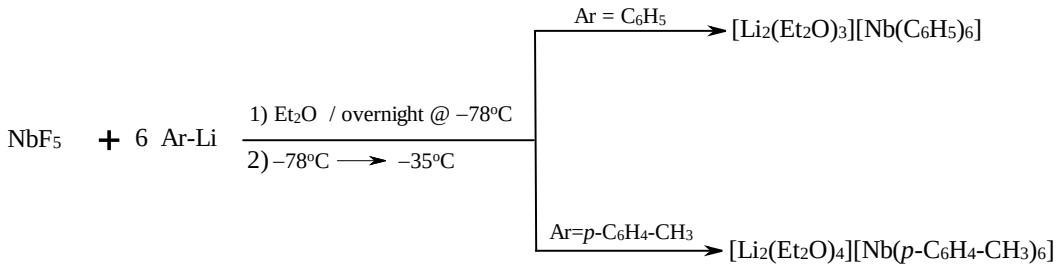
That finding were confirmed later when the crystal structures of both $[Ta(\eta^2\text{-}C_6H_4)_2(C_6H_5)_4Li(THF)_2$ and $[Nb(\eta^2\text{-}C_6H_4)_2(C_6H_5)_3]\cdot LiC_6H_5\cdot THF\cdot Li(THF)_4$ were established by Bartlett et al.[55].

In 1996 Seppelt et al. have described the preparation of the hexa-aryl homoleptic tantalum complexes $Ta(C_6H_5)_6^-$ and $Ta(p\text{-}C_6H_4\text{-}CH_3)_6^-$, by arylation of $TaCl_5$ with aryl lithium reagents[45]. Both complexes were structurally characterized and found to have quite similar structure which can be described as slightly distorted trigonal prismatic. On the other hand, the hexamethyl complex of tantalum and niobium have also been prepared and structurally characterized[9]. The structure of the ions $Ta(CH_3)_6^-$ and $Nb(CH_3)_6^-$ are both slightly distorted from ideal trigonal prismatic geometry.

4.1 Hexaphenyl- and Hexatolylniobium(IV) Complexes

4.1.1 Synthesis and Characterization of $[Li_2(Et_2O)_3][Nb(C_6H_5)_6]$ and $[Li_2(Et_2O)_4][Nb(p\text{-}C_6H_4\text{-}CH_3)_6]$

The low temperature reaction of NbF_5 in Et_2O with C_6H_5Li proceeds with metal reduction and formation of dark red solution and a small amount of black insoluble. (Scheme 6)



Scheme 6.

After appropriate workup, and upon cooling of the resulting dark red solution, brown-red crystals of $[Li_2(Et_2O)_3][Nb(C_6H_5)_6]$ were separated. By the same procedure a salt containing the $Nb(p\text{-}C_6H_4\text{-}CH_3)_6^-$ anion was obtained by reacting an NbF_5/Et_2O with a $Li(p\text{-}C_6H_4\text{-}CH_3)$/ether solution. After appropriate workup a red-orange crystals of $[Li_2(Et_2O)_4][Nb(p\text{-}C_6H_4\text{-}CH_3)_6]$ were formed.

The two complexes are extremely air- and moisture-sensitive, and readily decomposing above -35^oC both in solution and in the solid state.

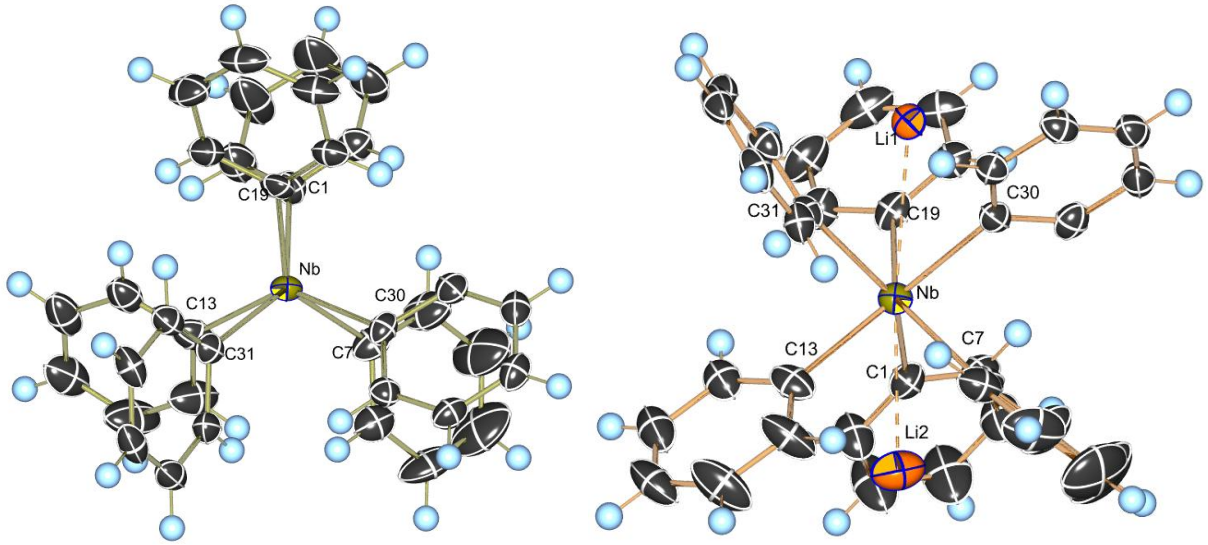
4.1.2 Crystal Structure of $[Li_2(Et_2O)_3][Nb(C_6H_5)_6]$.

The brown red colored compound $[Li_2(Et_2O)_3][Nb(C_6H_5)_6]$ crystallizes in space group $R\bar{3}$ of the trigonal system, with 18 formula units in a cell of dimensions a = 3006.5(5) pm, *b* = 3006.5(5) pm, and *c* = 2488.7(8) pm; $\alpha = \beta = 90^o$, $\gamma = 120°$.

The crystal structure of the anion $Nb(C_6H_5)_6^{2-}$ as established by X-ray diffraction analysis on single crystals of $[Li_2(Et_2O)_3][Nb(C_6H_5)_6]$ is presented in **Figure 11**. A selection of bond lengths and angles is given in **Table 5**.

Table 6. Selected interatomic distances [pm] and angles [°] and their estimated standard deviation for $Nb(C_6H_5)_6^{2-}$ and Nb(*p*-C_6H_4-$CH_3)_6^{2-}$anions.

$Nb(C_6H_5)^{2-}$		$Nb(p\text{-}C_6H_4\text{-}CH_3)_6^{2-}$	
Nb-C1	228.22(6)	Nb-C15	228.77(4)
Nb-C19	227.10(4)	Nb-C8	227.84(5)
Nb-C30	230.76(4)	Nb-C1	228.19(4)
Nb-C31	227.83(3)	Nb-C22	227.92(4)
Nb-C7	226.03(3)	Nb-C29	227.98(5)
Nb-C13	228.92(3)	Nb-C36	226.58(4)
C1-Nb-C31	141.764(9)	C1-Nb-C15	88.218(11)
C1-Nb-C19	76.169(7)	C8-Nb-C15	86.153(10)
C1-Nb-C30	126.501(10)	C15-Nb-C22	126.697(13)
C1-Nb-C7	86.818(9)	C15-Nb-C29	140.696(14)
C1-Nb-C13	85.911(7)	C15-Nb-C36	74.027(10)
C19-Nb C30	86.528(8)	C1-Nb-C8	87.470(11)
C19-Nb-C31	86.593(7)	C8-Nb-C22	140.235(11)
C7-Nb-C19	139.131(8)	C8-Nb-C29	77.751(10)
C13-Nb-C19	126.220(6)	C8-Nb-C36	125.448(11)
C30-Nb-C31	85.268(7)	C1-Nb-C22	73.66(1)
C7-Nb-C30	74.157(6)	C1-Nb-C29	125.988(15)
C13-Nb-C30	140.887(7)	C1-Nb-C36	140.090(13)
C7-Nb-C31	126.015(7)	C22-Nb-C29	85.495(11)
C13-Nb-C31	77.137(6)	C22-Nb-C36	88.585(11)
C7-Nb-C13	88.369(6)	C29-Nb-C36	86.519(11)



(a) **(b)**

Figure 12. Crystal structure of the $Nb(C_6H_5)_6^{2-}$ anion in $[Li_2(Et_2O)_3][Nb(C_6H_5)_6]$ (thermal ellipsoid diagram; 50% probability); (a) view along the approximate threefold axis of the anion; (b) view perpendicular to the approximate threefold axis and the Nb···Li interaction.

Surprisingly the six phenyl ligands are arranged around the Nb atom with a geometry closer to trigonal prismatic than to octahedral (χ=9^o). This is best seen if viewed along the approximate C_3 molecular axis of $Nb(C_6H_5)_6^{2-}$, as shown in Figure 12a, which shows a rotation of the triplets of ligands by about 9^o against each other.

In the crystal structure of d^1, $[Li_2(Et_2O)_3][Nb(C_6H_5)_6]$, the distance separated the two lithium cations from the formally dianionic niobium atom are 293.22 pm and 284.66 pm. Both cations are capping two parallel trigonal faces of the trigonal prism. It is obvious that the anion in this salt is involved in a sort of interaction with the lithium cations, and it is possible that the crystal-packing forces enforce the observed geometry over an octahedron. Nevertheless the analogous d^1 complex $Ti(C_6H_5)_6^{3-}$ has the expected octahedral structure despite having similar Li···M interactions, and the trigonal prismatic structure is probably

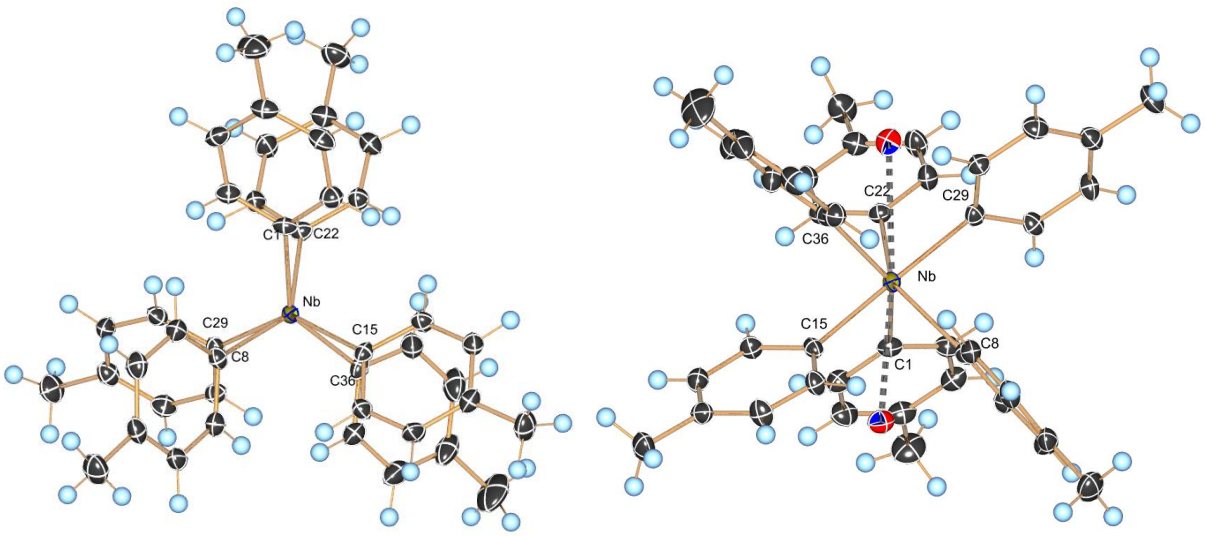
intrinsic to the $Nb(C_6H_5)_6^{2-}$ anion. As conclusion the two possibilities should be considered and at the meantime no one of each possibility can be denied.

4.1.3 Crystal Structure of $[Li_2(Et_2O)_4][Nb(p\text{-}C_6H_4\text{-}CH_3)_6]$.

The red-orange colored compound $[Li_2(Et_2O)_4][Nb(p\text{-}C_6H_4\text{-}CH_3)_6]$ crystallizes in space group P121/n1 of the monoclinic system, with 4 formula units in a cell of dimensions a = 1087.0(3) pm, *b* = 1762.1(4) pm, and *c* = 2828.4(7) pm; $\alpha = \gamma = 90^o$, $\beta = 97.642(6)°$.

The crystal structure of the anion $Nb(p\text{-}C_6H_4\text{-}CH_3)_6^{2-}$ as established by X-ray diffraction analysis on single crystals of $[Li_2(Et_2O)_4][Nb(p\text{-}C_6H_4\text{-}CH_3)_6]$ is presented in **Figure 11**. A selection of bond lengths and angles is given in **Table 5**.

The rotation of the triplets of the tolyl ligands against each other along the C_3 molecular axis is also about 9^o (χ)**.** In all, there is no noticeable difference between the $Nb(p\text{-}C_6H_4\text{-}CH_3)_6^{2-}$ and $Nb(C_6H_5)_6^{2-}$ anions with regard to their structure. Again the distance separated the two lithium cations from the formally dianionic niobium atom in the $Nb(p\text{-}C_6H_4\text{-}CH_3)_6^{2-}$ anion are 286.90 pm and 286.33 pm. Both cations are capping two parallel trigonal faces of the trigonal prism. That's mean the cation-anion interactions could be stabilize the trigonal prismatic geometry and controlling the structure of $Nb(p\text{-}C_6H_4\text{-}CH_3)_6^{2-}$. On the other hand we cannot rolled out the possibility of the intrinsic properties of the anion.



(a) **(b)**

Figure 13. Crystal structure of the Nb(p-C_6H_4-CH_3)$_6^{2-}$ anion in [$Li_2(Et_2O)_4$][Nb(p-C_6H_4-CH_3)$_6$] (thermal ellipsoid diagram; 50% probability); (a) view along the approximate threefold axis of the anion; (b) view perpendicular to the approximate threefold axis and the Nb···Li interaction.

From the first, the purpose from the reaction of NbF_5 with aryl lithium reagents was to prepare the hexa-arylniobium(V) comlexes in order to compare their structures with the analouges hexa-aryltantalum(V). However the reaction in this case proceeds with metal reduction and formation of the new Nb(IV) complexes which are here described for the first time.

For comparision purposes the reaction of TaF_5 with excess p-tolyl lithium in Et_2O (exactly under the same reaction conditions) was performed, and a light brown solution has been formed. From that solution a yellow crystals were seperated.

$$TaF_5 + 6\,(p\text{-}C_6H_4\text{-}CH_3)Li \xrightarrow[2)\ -78^oC \longrightarrow -35^oC]{1)\ Et_2O\ /\ \text{overnight @ } -78^oC} [Li_2Br(Et_2O)_7][Ta(p\text{-}C_6H_4\text{-}CH_3)_6]$$

From the result of X-ray measurments, the anion was identified sprisingly as the well-known Ta(p-C_6H_4-CH_3)$_6^-$.[45] It is obvious that the reaction in case of TaF_5 proceeds without metal

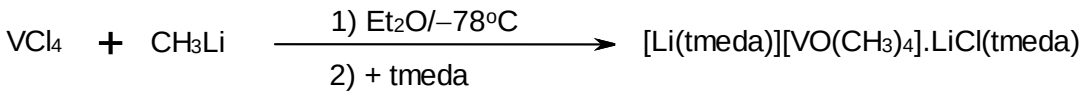
reduction. The structure of the anion in $[Ta(p\text{-}C_6H_4\text{-}CH_3)_6]^-$ in the compound has the same features, except that the cation here is $Li_2Br(Et_2O)_7^+$ and in the previously reported one[45] was $Li_4Br_3(Et_2O)_7^+$, also the procedure presented here gives a very good yield.

5. Tetra-σ-organyloxovanadium Complexes

The synthesis of σ-bonded alkyl and aryl complexes of vanadium, especially homoleptic tri- and tetravalent complexes, is generally difficult, most of these complexes are unstable and decomposed easily. Homoleptic alkyl or aryl vanadium-(III) complexes can be synthesized by reaction of VCl_3 with Grignard reagent or organolithium compounds. Derivatives of homoleptic σ-organovanadium(III) that have been isolated to date are $[VL_4]^-$ (L=2,4,6-trimethylphenyl (mes),[56] 2-methylphenyl[57] or 2,6-dimethoxyphenyl[58]) and $[VL_3]$ (L=mes[59] or $CH(SiMe_3)_2$ [60]), with no well-established structural information available for any of them. However products containing saterically hindered groups or pentahalophenyl group are thermally stable, and their structure and reactivity have been well studied e.g. $[Li(THF)_4][V(L_{Cl})_4]$, $[NBu_4][V(C_6Cl_5)_4]$ $[NBu_4]_2[V(C_6F_5)_5]$[61]. In a similar manner, some tetravalent homoleptic complexes VL_4; L= norbornyl,[62] CH_2TMS, [14] 2,4,6-$Me_3C_6H_2$[56b,63] have been synthesized and characterized.

Several trials to prepare homoleptic hexa-aryl or -alkyl derivatives of vanadium have been unsuccessful. All attempts using different vanadium starting materials (VCl_4, VF_5, and KVF_6) and different alkylating agents (MeLi, Me_2Zn, Me_3Al) with different reaction conditions have failed so far: either unidentified reaction products were obtained or strong reaction occurred with decomposition even at low temperature. Only in two cases a defined products were formed and identified. By the reaction of VCl_4 with 6 equivalents of C_6H_5Li in Et_2O at low temperature a dark blue solution was formed from which a black crystal separated and identified by X-ray measurement as the known complex $[Li(Et_2O)]_4[V(C_6H_5)_6]$[49]. It is obvious that the arylation of the metal center takes place together with a two-electron reduction process.

In the second case VCl_4 reacts at low temperature with excess amount of MeLi in presence of tmeda in Et_2O, afforded a dark blue crystal which identified as $Li(tmeda)VO(CH_3)_4$·-LiCl(tmeda). This compound results from a combined process entailing both alkylation and oxidation of the metal center. (Scheme 7)



Scheme 7.

This finding was the motivation for searching for safe and systematic procedures to prepare these unusual tetra-organyloxvanadium complexes and elucidate their structures. In the literature the reaction of vanadium oxidetrichloride ($VOCl_3$) with alkyl and aryl compounds of Zn, Hg, Sn are reported [12-14]. At low temperature limited number of complexes ($PhVOCl_2$ [12], $MesVOCl_2$, $VOMes_3$[13], $VO(CH_2SiMe_3)_3$[14]) have been reported and isolated long time ago, but there is no data regarding the crystal structural available for any of these complexes.

5.1 Reaction of $VOCl_3$ with alkyl- and aryl lithium in presence of tmeda

The reaction between $VOCl_3$ and MeLi in ether was very sensitive towards reaction conditions and the product formed depends on temperature, amount of both MeLi and tmeda, and especially the order of addition.

5.1.1 Synthesis of Tetra-methyloxyvanadium(V) Complex $[Li_2Cl(tmeda)_2][VO(CH_3)_4]$

Addition of CH_3Li/Et_2O to a suspension of $VOCl_3$ and tmeda 1:1 in Et_2O at low temperature (between -78^oC and -50^oC) led to the formation of dark blue solution from which a dark crystals of the compound $[Li_2Cl(tmeda)_2][VO(CH_3)_4]$ were isolated in 45% yield (Scheme 8)

$$VOCl_3 + \text{tmeda} \xrightarrow[2)\ -78^oC \text{ to } -50^oC]{1)\ Et_2O/+\ 5\ CH_3Li} [Li(tmeda)][VO(CH_3)_4].LiCl(tmeda)$$

Scheme 8.

The complex is extremely temperature sensitive, and readily decomposing above -50^oC both in solution and in the solid state.

5.1.2 Crystal Structure of $[Li_2Cl(tmeda)_2][VO(CH_3)_4]$

The black colored compound $[Li_2Cl(tmeda)_2][VO(CH_3)_4]$ crystallizes in space group C2/m in the monoclinic system, with 8 formula units in a cell. Cell dimensions: a = 1820.8(9) pm, b = 1624.1(8) pm, and c = 981.0(5) pm; $\alpha = \gamma = 90^o$, $\beta = 119.079(11)°$.

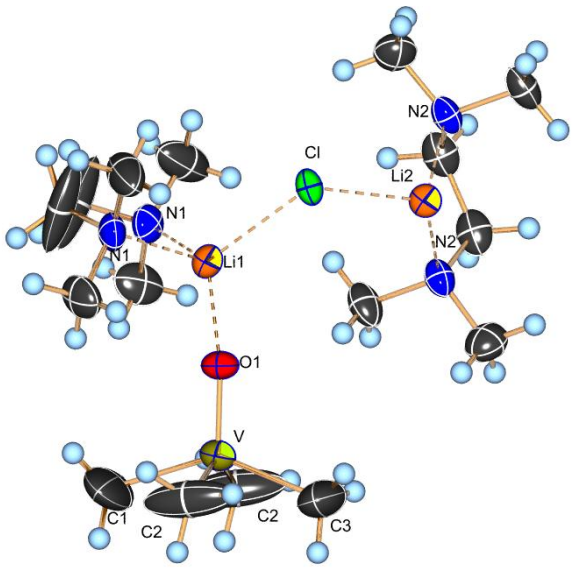


Figure 14. Thermal ellipsoid diagram (50% probability) of $[Li_2Cl(tmeda)_2][VO(CH_3)_4]$

The crystal structure of the $[Li_2Cl(tmeda)_2][VO(CH_3)_4]$ as established by X-ray diffraction is presented in **Figure 14**. A selection of bond lengths and angles is given in **Table 7**.

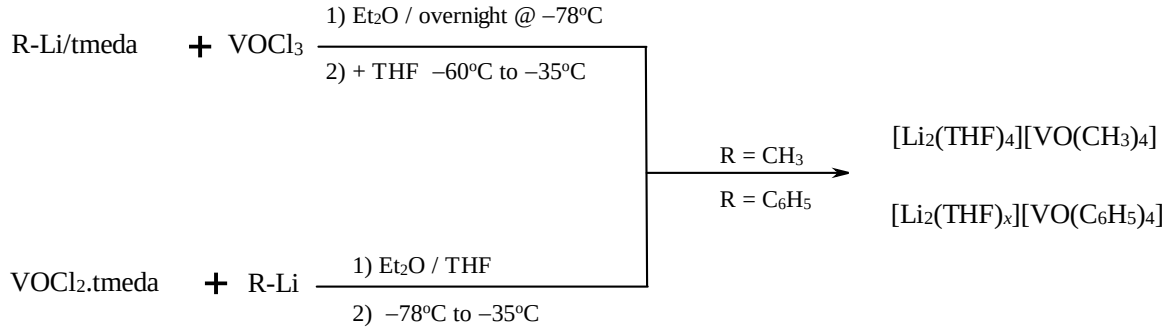
The tetramethyloxovanadium(V) anion is five coordinate and shows square-pyramidal geometry: the oxygen atom in the apical position, and the vanadium atom lies about 69.27 pm above the plane formed by the four C atoms of the methyl groups. The V─O bond length 161.66 pm, and V─C average bond lengths is 206.73 pm.

Table 7. Selected interatomic distances [pm] and angles [°] and their estimated standard deviation for $VO(CH_3)^{2-}$ anion and $VO(CH_3)^{2-}$.

$VO(CH_3)^-$		$VO(CH_3)^{2-}$	
V1-O1	161.66(9)	V1-O1	167.74(3)
V1-C1	209.8(1)	V1-C1	219.51(5)
V1-C2	205.80(9)	V1-C2	213.25(5)
V1-C2	205.80(9)	V1-C3	213.22(3)
V1-C3	205.53(10)	V1-C4	214.60(3)
O1-Li1	187.37(10)	Li2 -O1	187.03(3)
-	-	Li1- O1	189.84(3)
C1 -V1- O1	108.834(22)	C4 -V1- O1	107.936(10)
C2 -V1 -O1	109.593(16)	C2 -V1 -O1	113.836(9)
C3 -V1 -O1	110.260(26)	C3- V1- O1	114.379(10)
C2 -V1 -O1	109.593(16)	C1 -V1 -O1	100.386(10)
C2 -V1 -C3	85.000(15)	C2 -V1 -C4	84.156(8)
C1 -V1 -C3	140.906(26)	C1 -V1- C4	151.676(10)
C2 -V1 -C3	85.000(15)	C3 -V1- C4	84.765(8)
C1 -V1 -C2	82.098(14)	C1 -V1 -C2	84.230(8)
C2 -V1 -C2	140.642(12)	C2 -V1 -C3	131.639(8)
C1 -V1- C2	82.098(14)	C1 -V1 -C3	83.843(8)

5.2.1 Synthesis of Tetramethyl- and Tetraphenyl-oxyvanadium(IV) Complexes $[VOL_4]^{2-}$

Treatment of a suspension of CH_3Li-tmeda or C_6H_5Li-tmeda with $VOCl_3/Et_2O$ at low temperature (between −78°C and −35°C) proceeds with metal reduction, followed by extraction with THF led to the formation of tetraorganooxyvanadium(IV) compounds $[Li_2(THF)_4][VO(CH_3)_4]$ and $[Li_2(THF)_x][VO(C_6H_5)_4]$, which were isolated as blue and green crystals respectively in very good yields. Both compounds can alternatively be prepared directly from $VOCl_2$·tmeda (Scheme 9).



Scheme 9

The reduction of V(V) to V(IV) is probably due to the diamine. this behavior previously has been observed for vanadium[64-66]. The product of the amine oxidation has not been determined.

The two complexes are extremely air- and moisture-sensitive, and the phenyl complex is also light-sensitive and the color of the solid change from green to brown in attempt to remove the THF solvent or when exposed to light. The methyl complex is more stable in the solid state, in the crystalline form it is stable at −10°C for more than 1 hour, than in solution (decomposing at −35°C).

5.1.2 Crystal Structure of $[Li_2(THF)_4][VO(CH_3)_4]$

The blue colored compound $[Li_2(THF)_4][VO(CH_3)_4]$ crystallizes in space group $P2_1/n$ in the monoclinic system, with 8 formula units in a cell. Cell dimensions: a = 1820.8(9) pm, *b* = 1624.1(8) pm, and *c* = 981.0(5) pm; $\alpha = \gamma = 90^o$, $\beta = 119.079(11)°$.

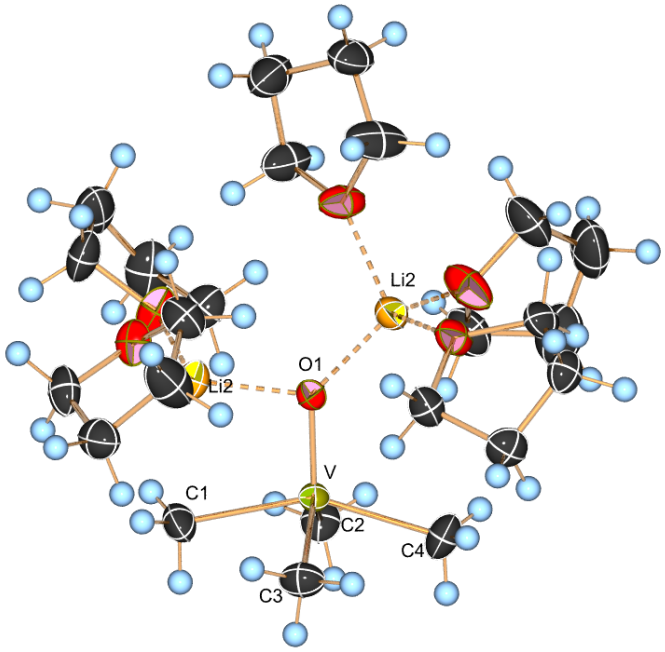


Figure 15. Displacement ellipsoid plot of $[Li_2(THF)_4][VO(CH_3)_4]$, drawn at 50% probability.

The crystal structure of the complex $[Li_2(THF)_4][VO(CH_3)_4]$ is depicted in Figure 15 and an interatomic distances and angles are collected in Table 5.

The local geometry around the V center in $VO(CH_3)_4^{2-}$ anion is similar to that found in the $VO(CH_3)_4^-$ species: both have a square pyramidal geometry with the oxygen atom in the apical position. The O-V-C angles in this species take values between 100.38^o and 114.38^o and the V-C distances are slightly longer (207.1(6)-209.5(7) pm) than those found in $VO(CH_3)_4^-$, as would be expected with a decrease in the oxidation state of the metal center.

5.1.3 Crystal Structure of $[Li_2(THF)_x][VO(C_6H_5)_4]$

Information about the geometry of the $[VO(C_6H_5)_4]^{2-}$ anion was obtained from the X-ray diffraction results. Poor-quality single crystals of $[Li_2(THF)_x][VO(C_6H_5)_4]$ were obtained, but the X-ray diffraction data collected were not of sufficient quality to carry out a complete structural determination of the complex. Nevertheless, its general shape and the connectivity could be established[2]. The geometry of the $[VO(C_6H_5)_4]^{2-}$ anion, depicted in Figure 16, can be described as square-pyramidal (*SP*-5) with the oxygen atom located in the apex of the pyramid. This coordination environment is similar to that found for the related $[VO(CH_3)_4]^{2-}$, apart from the very large estimated standard deviation due to poor crystal quality.

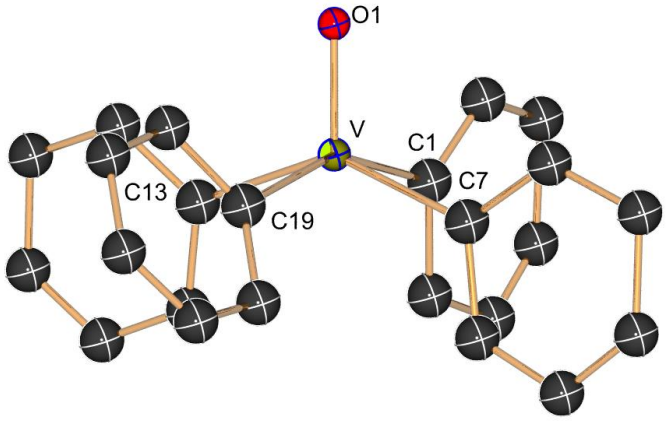


Figure 16. Schematic drawing of the anion $[VO(C_6H_5)_4]^{2-}$.

[2] Crystal data for $[Li_2(thf)_x][VO(C_6H_5)_4]$ Monoclinic, space group C2/c, with 8 formula units in a cell. Cell dimensions: *a* = 2020(2) pm, *b* = 1490.1(14) pm, and *c* = 3394(3) pm; $\alpha = \gamma = 90(6)°$, $\beta = 104.35(2)°$.

6. Chromium Complexes

Chromium (IV) is not easily accessible and homoleptic σ-organyl complexes, $[CrR_n]^{m-}$ (m=0, ±1, ±2, …), are still rare. Since there is no evidence of molecules of that type, attempts to synthesis such compounds starting from the reaction of $CrCl_3$ or $Cr(O\text{-}t\text{-}Bu)_4$ with different alkyling agent (RLi, Me_2Zn, $AlMe_3$, RMgX) were performed.

6.1 Preparation of Tetra-alkyl chromium(IV) compounds: CrR_4

CrR_4 (R= CH_3, C_2H_5, *t*-C_4H_9) were prepared from the reaction of $Cr(O\text{-}t\text{-}Bu)_4$ with corresponding alkyl lithium RLi in *n*-pentane at –78°C. The attempts to prepare a single crystal were not successful for methyl and ethyl compounds, and an oily product was separated in these cases.

In case of CrR_4 with R = *i*-C_3H_7, *t*-C_4H_9 there was no observable changes by the interaction of CrR_4 with RLi in ether at –78°C.

6.2 Attempts to prepare CrR_6^{2-} (R =CH_3, C_2H_5)

The addition of ≥ 6 mol RLi (R =CH_3, C_2H_5) to a solution of $Cr(O\text{-}t\text{-}Bu)_4$ in ether at –78°C in presence of $(CH_3)_2NCH_2CH_2N(CH_3)_2$ (tmeda) produced orange crystals in case of R=CH_3. According to the X-ray determination, the separated compound was the well-known anion[49] $Cr(CH_3)_6^{3-}$ rather than the ecpected anion $Cr(CH_3)_6^{2-}$.

With C_2H_5Li a red-brown solution was formed, and the attempts to separate suitable crystals for X-ray analysis failed.

6.3 Tetraisopropylchromium [Cr(*i*-prop)$_4$]

6.3.1 Synthesis and Characterization Cr(*i*-C_3H_7)$_4$

The preparation of the neutral homoleptic Cr(*i*-C_3H_7)$_4$ was carried out according to the original preparation described by Müller et al.[67] Reaction of chromium(III) chloride with isoprpylmagnesium bromide in diethyl ether at low temperature, followed by UV irradiation at room temperature, and after subsequent treatment by THF, *n*-pentane and ether led to the formation of Cr(*i*-C_3H_7)$_4$, which was isolated as dark brown solid in a good yield.

6.3.2 Crystal Structure of Cr(*i*-C_3H_7)$_4$

The dark brown colored compound Cr(*i*-C_3H_7)$_4$ crystallizes in space group C2/c in the monoclinic system, with 4 formula units in a cell. Cell dimensions: a = 1505.3(3) pm, b = 1148.0(2) pm, and c = 819.45(15) pm; $\alpha = \gamma = 90^o$, $\beta = 101.361(4)°$.

The crystal and molecular structure of the complex Cr(*i*-C_3H_7)$_4$ was determined by X-ray diffraction methods. The structure of the neutral complex Cr(*i*-C_3H_7)$_4$ is depicted in Figure 17 and a selection of interatomic distances and angles is given in Table 8.

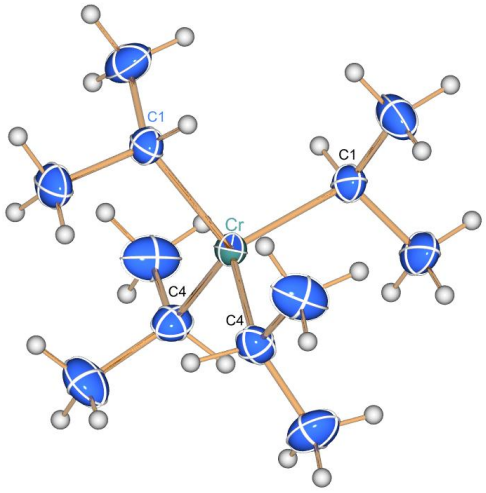


Figure 17. Crystal structure of the Cr(*i*-C_3H_7)$_4$ (thermal ellipsoid diagram; 50% probability).

Table 8. Selected interatomic distances [pm] and angles [°] and their estimated standerrd deviation for Cr(*i*-C_3H_7)$_4$.

Cr(i-C_3H_7)$_4$	
Cr- C1 (2x)	201.39(2)
Cr- C4 (2x)	201.83(2)
C1-Cr-C1	106.550(5)
C1-Cr-C4	115.055(4)
C1-Cr-C4	106.608(5)
C1-Cr-C4	106.608(5)
C1-Cr- C4	115.055(4)
C4-Cr- C4	107.247(4)

The chromium atom is located in an approximately tetrahedral (*T*-4) environment with almost identical Cr─C bond lengths (mean value: 201.16(4) pm), well in the range of the structurally characterized [CrR_4] related species (R= CH_2CMe_3 [21], CH_2CMe_3Ph [19], C_6H_{11} [20] , $CPh=CMe_2$ [68] and $C_6H_3Cl_2$-2,6[69])

The C─Cr─C angles ranging from 106.550(5)° to 115.055(4)°, two of these angles are larger than the ideal tetrahedral value (109.5°), while the remaining four are smaller.

III. Experimental Section

7. General Procedures

7.1 Abbreviations used

PFA	Perfluoroethene-perfluorovinylether-copolymer
n–BuLi	*n*-butyl lithium
Et_2O	Diethyl ether $(CH_3CH_2)_2O$
δ	NMR chemical Shift (given in ppm)
-o, -m, -p	Ortho, meta and para positions of an aromatic ring.
s, d, t, m, br.	Multiplicity of the NMR signals (singlet, doublet, triplet, multiplet and broad)
MeLi	Methyl lithium
PhLi	Phenyl lithium
p-TolLi	*p*-Tolyl lithium
THF	Tetrahydrofurane
tmeda	*N,N,N',N'*-tetramethylethylenediamine
NBu_4Br	Tetrabutylammoniumbromide

7.2 Instruments used

Water and Oxygen sensitive substances which stable at room temperature were handled in a glove box (Firma Braun GmbH, Type MB 150 B/G or Type MB 200) with automatic argon gas flow over a Cupper- catalyst which provides an H_2O and O_2 content level lower than 1 ppm.

For Raman spectra measurments samples were placed inside sealed glass ampule or PFA tubes (4 mm). Raman spectra were recorded at low temperature on a Bruker RFS 100 FT-Raman spectrometer which operates with a Nd-YAG-Laser (1064 nm, 10-550 mW).

Depending on the sample, NMR spectra were recorded with cooling or at room temperature using a JEOL JNM-LA 400 spectrometer. Chemical shift values are reported with respect to TMS (^{1}H, ^{13}C). Deuterated solvents where used as received.

Single crystals were handled in a special device, cut to an appropriate size, and mounted on a Bruker SMART CCD 1000 TU diffractometer, using Mo-Kα irradiation, a graphite monochromator, a scan width of 0.3° in w, and a measuring time of 20 s per frame. After semiempirical absorption corrections (SADABS) by equalizing symmetry-equivalent reflections, the SHELX programs were used for solution and refinement.[70] All atoms except hydrogen are refined anisotropically. Hydrogen atoms have been located by difference Fourier maps and refined independently from other atomic positions, however, with a single isotropic displacement parameter for all hydrogen atoms. To visualize the crystal structure, the program DIAMOND was used (Used Crystal Impact, Version 3.2e)[71].

7.3 Experimental

All reactions were carried out under dry argon atmosphere using Schlenk technique[72]. Solvents were dried by standard methods and distilled prior to use and kept over Molecular sieve (4 nm). Commercially available chemicals were used as received.

7.4 Reactants used

Mg	Available in stock
C_6H_5Br	Fa. Aldrich
p-CH_3-C_6H_4-Br	Fa. Merck
Li	Available in stock
i-C_3H_7Br	Fa. Merck
$CrCl_3$	Prepared according to ref. [73].

NbF_5	Available in stock
TaF_5	Available in stock
$ZrCl_4$	Available in stock
$HfCl_4$	Available in stock
$Cr(i\text{-}C_3H_7)_4$	Prepared according to ref. [64].
$TiCl_4$	Available in stock
PhLi	Prepared according to ref. [74].
p-TolLi	Prepared according to ref. [74].
MeLi	Fa. Aldrich
$VOCl_3$	Fa. Aldrich
$VOCl_2$·tmeda	Prepared according to ref. [75].
$Cr(O\text{-}t\text{-}Bu)_4$	Prepared according to ref. [76].
$CH_3(CH_2)_3NBr$	Fa. Acros

8. Synthesis and Crystal Structure Analysis

8.1 Titanium Complexes

8.1.1 $[Li(THF)_4][Ti(C_6H_5)_5]$

8.1.1.1 Preparation of $[Li(THF)_4][Ti(C_6H_5)_5]$

To a suspension of $TiCl_4 \cdot xEt_2O$ in diethyl ether (prepared by mixing $TiCl_4$ (0.56 g, 2.95 mmol) and Et_2O (30 mL), both precooled at –78°C) was added a solution of LiC_6H_5 (ca 17.7 mmol) in ether during 2 hr at –78°C and kept at that temperature overnight with stirring. The mixture was allowed to warm to –55°C, after 5 hr of stirring at this temperature the solution turned dark orange and an orange-red solid precipitated. The solid was collected by filtration, washed with Et_2O (2x5 mL), dried under vacuum, and redissolved in THF (40 mL) at –55°C. the solution was concentrated to about 20 mL and slow diffusion of Et_2O layer (40 mL) with cooling from –55°C to –80°C yielded the product as yellow-brown crystalline solid, the yield can be estimated to be more than 60% based on the titanium precursor).

8.1.1.2 Crystal Data and Crystal Structure Analysis $[Li(THF)_4][Ti(C_6H_5)_5]$

Table 1. Crystal data and structure refinement for $[Li(THF)_4][Ti(C_6H_5)_5]$.

Identification code	tiphe52	
Empirical formula	$C_{23}\ H_{28.50}\ Li_{0.50}\ O_4\ Ti_{0.50}$	
Formula weight	396.38	
Temperature	133(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	C12/c1	
Unit cell dimensions	a = 1388.4(2) pm	α= 90°.
	b = 2004.6(3) pm	β= 94.833(14)°.
	c = 1477.7(3) pm	γ = 90°.
Volume	4.0979(12) nm^3	
Z	8	
Density (calculated)	1.285 Mg/m^3	
Absorption coefficient	0.262 mm^{-1}	
F(000)	1688	
Crystal size	0.5 x 0.3 x 0.03 mm^3	
Theta range for data collection	1.79 to 30.57°.	
Index ranges	-15<=h<=19, -28<=k<=25, -21<=l<=21	
Reflections collected	32775	
Independent reflections	6269 [R(int) = 0.0427]	
Completeness to theta = 30.57°	99.5 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6269 / 0 / 351	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0541, wR2 = 0.1271	
R indices (all data)	R1 = 0.0934, wR2 = 0.1525	
Largest diff. peak and hole	0.457 and -0.374 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for $[Li(THF)_4][Ti(C_6H_5)_5]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3715(1)	6353(1)	6775(1)	28(1)
C(2)	3195(2)	6772(1)	6154(1)	35(1)
C(3)	2389(2)	6559(1)	5604(2)	44(1)
C(4)	2076(2)	5906(1)	5654(2)	42(1)
C(5)	2559(2)	5478(1)	6271(2)	39(1)
C(6)	3355(2)	5702(1)	6824(2)	34(1)
C(7)	5664(1)	6413(1)	6311(1)	28(1)
C(8)	5593(2)	5778(1)	5910(1)	32(1)
C(9)	6037(2)	5612(1)	5134(1)	35(1)
C(10)	6562(2)	6090(1)	4712(1)	36(1)
C(11)	6650(2)	6724(1)	5075(1)	35(1)
C(12)	6220(2)	6879(1)	5872(1)	33(1)
C(13)	5000	7831(1)	7500	31(1)
C(14)	5117(2)	8205(1)	8307(1)	36(1)
C(15)	5116(2)	8897(1)	8315(2)	46(1)
C(16)	5000	9246(2)	7500	51(1)
C(17)	9403(2)	6489(1)	5760(2)	41(1)
C(18)	9218(2)	5743(1)	5779(2)	54(1)
C(19)	8472(2)	5670(1)	6458(2)	48(1)
C(20)	8619(3)	6254(2)	7060(2)	63(1)
C(21)	9220(3)	8232(2)	8827(3)	76(1)
C(22)	8750(4)	8880(2)	8571(5)	102(2)
C(23)	7851(3)	8666(2)	7988(3)	82(1)
C(24)	8135(2)	8018(1)	7567(2)	48(1)
Li(1)	10000	7295(3)	7500	40(1)
O(1)	9263(1)	6716(1)	6655(1)	42(1)
O(2)	9038(1)	7818(1)	8044(1)	42(1)
Ti	5000	6757(1)	7500	24(1)

Table 3. Bond lengths [pm] and angles [°] for $[Li(THF)_4][Ti(C_6H_5)_5]$.

C(1)-C(2)	140.0(3)	C(16)-H(16)	100(4)
C(1)-C(6)	140.2(3)	C(17)-O(1)	142.7(3)
C(1)-Ti	215.90(19)	C(17)-C(18)	151.9(4)
C(2)-C(3)	139.4(3)	C(17)-H(171)	95(3)
C(2)-H(2)	98(2)	C(17)-H(172)	98(3)
C(3)-C(4)	138.3(4)	C(18)-C(19)	150.8(4)
C(3)-H(3)	97(3)	C(18)-H(181)	94(3)
C(4)-C(5)	138.4(3)	C(18)-H(182)	100(4)
C(4)-H(4)	98(3)	C(19)-C(20)	147.5(4)
C(5)-C(6)	139.0(3)	C(19)-H(191)	96(4)
C(5)-H(5)	96(3)	C(19)-H(192)	94(3)
C(6)-H(6)	94(2)	C(20)-O(1)	145.1(3)
C(7)-C(12)	140.5(3)	C(20)-H(201)	85(4)
C(7)-C(8)	140.4(3)	C(20)-H(202)	104(4)
C(7)-Ti	216.42(19)	C(21)-O(2)	142.9(3)
C(8)-C(9)	138.8(3)	C(21)-C(22)	148.9(6)
C(8)-H(8)	97(3)	C(21)-H(211)	91(5)
C(9)-C(10)	138.3(3)	C(21)-H(212)	104(5)
C(9)-H(9)	99(2)	C(22)-C(23)	151.7(7)
C(10)-C(11)	138.2(3)	C(22)-H(221)	88(5)
C(10)-H(10)	96(2)	C(22)-H(222)	90(6)
C(11)-C(12)	139.9(3)	C(23)-C(24)	150.7(5)
C(11)-H(11)	100(3)	C(23)-H(231)	89(6)
C(12)-H(12)	95(2)	C(23)-H(232)	108(4)
C(13)-C(14)	140.6(2)	C(24)-O(2)	144.3(3)
C(13)-C(14)#1	140.6(2)	C(24)-H(241)	104(3)
C(13)-Ti	215.3(3)	C(24)-H(242)	103(3)
C(14)-C(15)	138.7(3)	Li(1)-O(2)	192.7(3)
C(14)-H(14)	93(3)	Li(1)-O(2)#2	192.7(3)
C(15)-C(16)	139.0(3)	Li(1)-O(1)	193.3(4)
C(15)-H(15)	97(3)	Li(1)-O(1)#2	193.3(4)
C(16)-C(15)#1	139.0(3)	Ti-C(1)#1	215.90(19)
Ti-C(7)#1	216.42(19)	C(11)-C(12)-C(7)	122.13(19)

C(2)-C(1)-C(6)	115.21(18)	C(11)-C(12)-H(12)	117.8(13)
C(2)-C(1)-Ti	117.32(15)	C(7)-C(12)-H(12)	120.1(13)
C(6)-C(1)-Ti	127.40(15)	C(14)-C(13)-C(14)#1	115.6(3)
C(3)-C(2)-C(1)	122.9(2)	C(14)-C(13)-Ti	122.20(13)
C(3)-C(2)-H(2)	118.9(14)	C(14)#1-C(13)-Ti	122.20(13)
C(1)-C(2)-H(2)	118.2(14)	C(15)-C(14)-C(13)	122.7(2)
C(4)-C(3)-C(2)	119.9(2)	C(15)-C(14)-H(14)	118.3(16)
C(4)-C(3)-H(3)	119.1(17)	C(13)-C(14)-H(14)	119.1(16)
C(2)-C(3)-H(3)	121.0(17)	C(14)-C(15)-C(16)	119.8(2)
C(5)-C(4)-C(3)	119.0(2)	C(14)-C(15)-H(15)	120.8(17)
C(5)-C(4)-H(4)	118.6(16)	C(16)-C(15)-H(15)	119.4(17)
C(3)-C(4)-H(4)	122.2(16)	C(15)#1-C(16)-C(15)	119.5(3)
C(4)-C(5)-C(6)	120.3(2)	C(15)#1-C(16)-H(16)	120.25(15)
C(4)-C(5)-H(5)	118.9(16)	C(15)-C(16)-H(16)	120.25(15)
C(6)-C(5)-H(5)	120.8(16)	O(1)-C(17)-C(18)	105.12(19)
C(5)-C(6)-C(1)	122.6(2)	O(1)-C(17)-H(171)	106.0(15)
C(5)-C(6)-H(6)	115.4(15)	C(18)-C(17)-H(171)	116.4(15)
C(1)-C(6)-H(6)	122.0(15)	O(1)-C(17)-H(172)	109.0(16)
C(12)-C(7)-C(8)	115.42(18)	C(18)-C(17)-H(172)	110.9(16)
C(12)-C(7)-Ti	116.86(14)	H(171)-C(17)-H(172)	109(2)
C(8)-C(7)-Ti	127.71(15)	C(19)-C(18)-C(17)	103.6(2)
C(9)-C(8)-C(7)	123.1(2)	C(19)-C(18)-H(181)	117(2)
C(9)-C(8)-H(8)	118.1(15)	C(17)-C(18)-H(181)	107(2)
C(7)-C(8)-H(8)	118.8(14)	C(19)-C(18)-H(182)	117(2)
C(10)-C(9)-C(8)	119.58(19)	C(17)-C(18)-H(182)	108(2)
C(10)-C(9)-H(9)	120.7(14)	H(181)-C(18)-H(182)	103(3)
C(8)-C(9)-H(9)	119.7(14)	C(20)-C(19)-C(18)	104.8(2)
C(11)-C(10)-C(9)	119.73(19)	C(20)-C(19)-H(191)	110(2)
C(11)-C(10)-H(10)	119.8(15)	C(18)-C(19)-H(191)	111(2)
C(9)-C(10)-H(10)	120.5(15)	C(20)-C(19)-H(192)	113(2)
C(10)-C(11)-C(12)	120.0(2)	C(18)-C(19)-H(192)	113(2)
C(10)-C(11)-H(11)	121.8(15)	H(191)-C(19)-H(192)	105(3)
C(12)-C(11)-H(11)	118.2(15)	O(1)-C(20)-C(19)	108.5(2)
O(1)-C(20)-H(201)	106(3)	O(2)-C(24)-H(242)	105.2(18)
C(19)-C(20)-H(201)	120(3)	C(23)-C(24)-H(242)	112.3(17)

O(1)-C(20)-H(202)	109(2)	H(241)-C(24)-H(242)	112(2)
C(19)-C(20)-H(202)	108(2)	O(2)-Li(1)-O(2)#2	114.0(3)
H(201)-C(20)-H(202)	105(4)	O(2)-Li(1)-O(1)	104.38(7)
O(2)-C(21)-C(22)	104.9(4)	O(2)#2-Li(1)-O(1)	113.87(7)
O(2)-C(21)-H(211)	107(3)	O(2)-Li(1)-O(1)#2	113.87(7)
C(22)-C(21)-H(211)	115(3)	O(2)#2-Li(1)-O(1)#2	104.38(7)
O(2)-C(21)-H(212)	105(3)	O(1)-Li(1)-O(1)#2	106.3(3)
C(22)-C(21)-H(212)	111(3)	C(17)-O(1)-C(20)	108.36(19)
H(211)-C(21)-H(212)	114(4)	C(17)-O(1)-Li(1)	133.17(15)
C(21)-C(22)-C(23)	102.7(3)	C(20)-O(1)-Li(1)	115.30(17)
C(21)-C(22)-H(221)	122(4)	C(21)-O(2)-Li(1)	124.91(18)
C(23)-C(22)-H(221)	108(3)	C(24)-O(2)-Li(1)	123.52(14)
C(21)-C(22)-H(222)	106(4)	C(13)-Ti-C(1)	112.02(5)
C(23)-C(22)-H(222)	94(4)	C(13)-Ti-C(1)#1	112.02(5)
H(221)-C(22)-H(222)	119(5)	C(1)-Ti-C(1)#1	135.97(11)
C(24)-C(23)-C(22)	104.3(3)	C(13)-Ti-C(7)#1	108.56(5)
C(24)-C(23)-H(231)	114(4)	C(1)-Ti-C(7)#1	83.83(7)
C(22)-C(23)-H(231)	124(4)	C(1)#1-Ti-C(7)#1	82.46(7)
C(24)-C(23)-H(232)	111(2)	C(13)-Ti-C(7)	108.56(5)
C(22)-C(23)-H(232)	105(2)	C(1)-Ti-C(7)	82.46(7)
H(231)-C(23)-H(232)	98(4)	C(1)#1-Ti-C(7)	83.83(7)
O(2)-C(24)-C(23)	106.5(3)	C(7)#1-Ti-C(7)	142.88(11)
O(2)-C(24)-H(241)	108.6(18)	C(23)-C(24)-H(241)	112.2(18)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2 #2 -x+2,y,-z+3/2

Table 4. Anisotropic displacement parameters ($pm^2x\ 10^{-1}$) for $[Li(THF)_4][Ti(C_6H_5)_5]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	27(1)	34(1)	24(1)	-5(1)	4(1)	2(1)
C(2)	35(1)	38(1)	33(1)	2(1)	5(1)	1(1)
C(3)	37(1)	55(1)	37(1)	5(1)	-5(1)	5(1)
C(4)	29(1)	56(1)	39(1)	-14(1)	-1(1)	0(1)
C(5)	33(1)	34(1)	50(1)	-14(1)	6(1)	-1(1)
C(6)	32(1)	33(1)	38(1)	-4(1)	1(1)	4(1)

C(7)	25(1)	33(1)	25(1)	-1(1)	0(1)	1(1)
C(8)	33(1)	32(1)	32(1)	-1(1)	5(1)	-1(1)
C(9)	38(1)	32(1)	34(1)	-7(1)	4(1)	3(1)
C(10)	40(1)	39(1)	30(1)	-2(1)	8(1)	6(1)
C(11)	37(1)	35(1)	33(1)	4(1)	5(1)	-3(1)
C(12)	36(1)	29(1)	33(1)	-4(1)	1(1)	-2(1)
C(13)	37(2)	23(1)	32(1)	0	4(1)	0
C(14)	45(1)	31(1)	32(1)	0(1)	-1(1)	2(1)
C(15)	57(2)	32(1)	47(1)	-11(1)	-9(1)	3(1)
C(16)	64(2)	24(2)	60(2)	0	-16(2)	0
C(17)	45(1)	41(1)	37(1)	2(1)	10(1)	2(1)
C(18)	67(2)	41(1)	55(2)	-6(1)	18(1)	-2(1)
C(19)	41(1)	41(1)	61(2)	8(1)	4(1)	-2(1)
C(20)	61(2)	69(2)	62(2)	-16(2)	29(2)	-32(2)
C(21)	50(2)	91(3)	85(2)	-51(2)	-8(2)	5(2)
C(22)	101(3)	50(2)	163(5)	-37(3)	54(3)	-14(2)
C(23)	95(3)	78(2)	75(2)	7(2)	15(2)	51(2)
C(24)	44(1)	56(2)	43(1)	9(1)	2(1)	11(1)
Li(1)	36(3)	35(3)	49(3)	0	11(2)	0
O(1)	42(1)	43(1)	41(1)	-5(1)	15(1)	-11(1)
O(2)	34(1)	48(1)	42(1)	-9(1)	2(1)	6(1)
Ti	29(1)	21(1)	22(1)	0	1(1)	0

8.1.2 $[Li\{(CH_3CH_2)_2O\}_4][Ti(p\text{-}C_6H_4\text{-}CH_3)_5]$.

8.1.2.1 Preparation of $[Li\{(CH_3CH_2)_2O\}_4][Ti(p\text{-}C_6H_4\text{-}CH_3)_5]$.

To a suspension of $TiCl_4$ (0.52 g, 2.47 mmol) in ether (30 mL), *p*-tolyllithium (15 mmol, 0.84 M solution in Et_2O) was added dropwise at –78^oC over a period of 1 hr. The reaction mixture was kept with stirring at –78^oC overnight. The mixture was allowed to warm slowly to –50^oC. At this point the solution turned dark red and a yellow solid separated. After 3 hr of further stirring at –50^oC, the solid was filtered, washed with Et_2O (3x5 mL), and vacuum dried. (In all the preceding treatments, the reaction mixture has to be kept at –50^oC in order to avoid

thermal decomposition of the product.) The resulting solid was redissolved in THF (20 mL), and slow diffusion at –80°C of Et_2O layer (40 mL) into the preceding solution yielded the compund as a yellow-brown crystalline solid. ^{1}H NMR (400 MHz, CD_2Cl_2, −40°C): δ = 7.65 (tolyl-H, d), 6.86 (tolyl-H, d), 3.3 ($(CH_3CH_2)_2O$), 2.12 (tolyl-CH_3, s) 1.03 ppm ($(CH_3CH_2)_2O$); Raman (solid, 85 mW, λ= 1040): $\tilde{\nu}$ = 270 (12), 292 (48), 380 (39), 409 (8), 730 (100), 791 (6), 808 (7), 1041 (4), 1191 (6), 1286 (15), 1303 (7), 1381 (21), 1614 (14) cm^{-1}.

8.1.2.2 Crystal Data and Crystal Structure Analysis of $[Li\{(CH_3CH_2)_2O\}_4][Ti(p\text{-}C_6H_4\text{-}CH_3)_5]$.

Table 5. Crystal data and structure refinement for $[Li\{(CH_3CH_2)_2O\}_4][Ti(p\text{-}C_6H_4\text{-}CH_3)_5]$.

Identification code	titol	
Empirical formula	$C_{44}\ H_{60}\ Li\ O_4\ Ti$	
Formula weight	707.76	
Temperature	133(2) K	
Wavelength	71.073 pm	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 1224.3(4) pm	α= 90°.
	b = 1782.9(6) pm	β= 90°.
	c = 2248.0(6) pm	γ = 90°.
Volume	4.91(1) nm^3	
Z	4	
Density (calculated)	0.958 Mg/m^3	
Absorption coefficient	0.207 mm^{-1}	
F(000)	1524	
Crystal size	0.4 x 0.4 x 0.3 mm^3	
Theta range for data collection	1.46 to 25.99°.	
Index ranges	-15<=h<=14, -21<=k<=21, -16<=l<=27	
Reflections collected	50782	

Independent reflections	9585 [R(int) = 0.0401]
Completeness to theta = 25.99°	99.6 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9585 / 0 / 611
Goodness-of-fit on F^2	1.001
Final R indices [I>2sigma(I)]	R1 = 0.0438, wR2 = 0.1093
R indices (all data)	R1 = 0.0532, wR2 = 0.1156
Absolute structure parameter	0.00
Largest diff. peak and hole	0.543 and -0.277 e.Å^{-3}

Table 6. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (pm^{2}x10^{-1}) for [Li{$(CH_3CH_2)_2O$}$_4$][Ti(*p*-C_6H_4-CH_3)$_5$]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ti	5303(1)	7046(1)	2248(1)	28(1)
C(1)	6070(2)	6030(1)	1926(1)	31(1)
C(2)	6914(2)	6077(2)	1507(1)	34(1)
C(3)	7459(2)	5456(2)	1292(1)	36(1)
C(4)	7182(2)	4737(2)	1480(1)	35(1)
C(5)	6346(2)	4668(1)	1893(1)	35(1)
C(6)	5806(2)	5301(1)	2114(1)	32(1)
C(7)	7766(2)	4043(2)	1243(2)	54(1)
C(8)	5232(2)	7851(1)	1529(1)	31(1)
C(9)	5239(2)	7542(2)	955(1)	40(1)
C(10)	5222(2)	7974(2)	440(1)	43(1)
C(11)	5164(2)	8750(2)	469(1)	37(1)
C(12)	5164(3)	9230(2)	-92(1)	55(1)
C(13)	5125(2)	9079(1)	1029(1)	35(1)
C(14)	5169(2)	8641(1)	1542(1)	33(1)
C(15)	3555(2)	7049(2)	2115(1)	32(1)
C(16)	3111(2)	6339(2)	2032(1)	43(1)
C(17)	2018(2)	6223(2)	1892(2)	48(1)
C(18)	1298(2)	6808(2)	1841(1)	43(1)

C(19)	107(2)	6683(2)	1674(2)	62(1)
C(20)	1713(3)	7522(2)	1938(2)	51(1)
C(21)	2814(1)	7639(1)	2067(1)	46(1)
C(22)	4882(1)	6902(1)	3179(1)	31(1)
C(23)	4041(1)	7226(1)	3511(1)	37(1)
C(24)	3878(1)	7074(1)	4115(1)	40(1)
C(25)	4557(1)	6576(1)	4418(1)	38(1)
C(26)	4399(1)	6421(1)	5072(1)	57(1)
C(27)	5386(2)	6231(1)	4093(1)	38(1)
C(28)	5545(2)	6401(2)	3490(1)	35(1)
C(29)	6544(2)	7781(1)	2606(1)	29(1)
C(30)	7637(2)	7587(1)	2516(1)	33(1)
C(31)	8503(2)	8032(1)	2716(1)	36(1)
C(32)	8317(2)	8698(1)	3020(1)	34(1)
C(33)	9258(2)	9187(2)	3224(2)	51(1)
C(34)	7234(2)	8905(2)	3111(1)	39(1)
C(35)	6385(2)	8450(2)	2919(1)	42(1)
C(36)	8970(3)	1495(2)	-356(1)	53(1)
C(37)	9713(3)	883(2)	-561(1)	43(1)
C(38)	9549(2)	-459(2)	-395(1)	43(1)
C(39)	8366(3)	-586(2)	-535(1)	56(1)
C(40)	9051(3)	2148(2)	1454(2)	60(1)
C(41)	9780(3)	1487(2)	1586(1)	44(1)
C(42)	11405(2)	1675(2)	1019(1)	48(1)
C(43)	11888(3)	1562(2)	423(1)	51(1)
C(44)	11441(3)	-165(2)	1940(1)	55(1)
C(45)	12123(2)	-355(2)	1416(1)	46(1)
C(46)	12112(2)	-632(2)	374(1)	44(1)
C(47)	12161(3)	-1479(2)	355(2)	59(1)
C(48)	7295(3)	176(2)	1667(1)	62(1)
C(49)	7790(2)	73(2)	1058(1)	43(1)
C(50)	8885(3)	-1034(2)	1299(2)	56(1)
C(51)	8216(3)	-1601(2)	954(2)	57(1)
Li(1)	10130(3)	241(2)	727(2)	35(1)
O(1)	9743(2)	269(1)	-130(1)	41(1)

O(2)	10398(2)	1255(1)	1074(1)	39(1)
O(3)	11493(1)	-352(1)	875(1)	38(1)
O(4)	8857(1)	-292(1)	1062(1)	40(1)

Table 7. Bond lengths [pm] and angles [°] for $[Li\{(CH_3CH_2)_2O\}_4][Ti(p\text{-}C_6H_4\text{-}CH_3)_5]$.

Ti-C(15)	216.0(2)	C(15)-C(16)	139.0(4)
Ti-C(29)	216.2(2)	C(15)-C(21)	139.4(3)
Ti-C(8)	216.4(2)	C(16)-C(17)	139.0(4)
Ti-C(1)	216.6(3)	C(16)-H(16)	94(3)
Ti-C(22)	216.95(12)	C(17)-C(18)	137.0(4)
C(1)-C(2)	139.9(4)	C(17)-H(17)	84(4)
C(1)-C(6)	140.5(4)	C(18)-C(20)	138.8(5)
C(2)-C(3)	138.1(4)	C(18)-C(19)	152.2(4)
C(2)-H(2)	85(3)	C(19)-H(19A)	98.00
C(3)-C(4)	139.1(4)	C(19)-H(19B)	98.00
C(3)-H(3)	89(3)	C(19)-H(19C)	98.00
C(4)-C(5)	138.8(4)	C(20)-C(21)	139.4(3)
C(4)-C(7)	152.6(4)	C(20)-H(20)	84(4)
C(5)-C(6)	139.9(4)	C(21)-H(21)	95.00
C(5)-H(5)	100(3)	C(22)-C(28)	139.5(3)
C(6)-H(6)	97(3)	C(22)-C(23)	139.66
C(7)-H(7A)	98.00	C(23)-C(24)	139.92
C(7)-H(7B)	98.00	C(23)-H(23)	95.00
C(7)-H(7C)	98.00	C(24)-C(25)	139.44
C(8)-C(9)	140.3(3)	C(24)-H(24)	95.00
C(8)-C(14)	141.0(3)	C(25)-C(27)	139.3(3)
C(9)-C(10)	139.1(4)	C(25)-C(26)	151.00
C(9)-H(9)	90(3)	C(26)-H(26A)	98.00
C(10)-C(11)	138.7(4)	C(26)-H(26B)	98.00
C(10)-H(10)	110(3)	C(26)-H(26C)	98.00
C(11)-C(13)	139.0(4)	C(27)-C(28)	140.3(4)
C(11)-C(12)	152.4(4)	C(27)-H(27)	98(3)
C(12)-H(12A)	98.00	C(28)-H(28)	84(3)

C(12)-H(12B)	98.00	C(29)-C(35)	139.8(4)
C(12)-H(12C)	98.00	C(29)-C(30)	139.7(4)
C(13)-C(14)	139.4(4)	C(30)-C(31)	139.7(4)
C(13)-H(13)	102(3)	C(30)-H(30)	85(3)
C(14)-H(14)	92(3)	C(31)-C(32)	138.9(4)
C(31)-H(31)	99(3)	C(43)-H(43B)	98.00
C(32)-C(34)	139.2(4)	C(43)-H(43C)	98.00
C(32)-C(33)	151.6(4)	C(44)-C(45)	148.1(4)
C(33)-H(33A)	98.00	C(44)-H(44A)	98.00
C(33)-H(33B)	98.00	C(44)-H(44B)	98.00
C(33)-H(33C)	98.00	C(44)-H(44C)	98.00
C(34)-C(35)	138.8(4)	C(45)-O(3)	144.0(3)
C(34)-H(34)	99(3)	C(45)-H(45A)	94(4)
C(35)-H(35)	99(3)	C(45)-H(45B)	101(4)
C(36)-C(37)	149.3(4)	C(46)-O(3)	144.8(3)
C(36)-H(36A)	98.00	C(46)-C(47)	151.2(4)
C(36)-H(36B)	98.00	C(46)-H(46A)	108(3)
C(36)-H(36C)	98.00	C(46)-H(46B)	99(3)
C(37)-O(1)	146.3(3)	C(47)-H(47A)	98.00
C(37)-H(37A)	101(3)	C(47)-H(47B)	98.00
C(37)-H(37B)	96(3)	C(47)-H(47C)	98.00
C(38)-O(1)	144.8(3)	C(48)-C(49)	150.9(4)
C(38)-C(39)	150.0(4)	C(48)-H(48A)	98.00
C(38)-H(38A)	98(3)	C(48)-H(48B)	98.00
C(38)-H(38B)	94(3)	C(48)-H(48C)	98.00
C(39)-H(39A)	98.00	C(49)-O(4)	146.0(3)
C(39)-H(39B)	98.00	C(49)-H(49A)	103(3)
C(39)-H(39C)	98.00	C(49)-H(49B)	104(3)
C(40)-C(41)	150.7(4)	C(50)-O(4)	142.6(4)
C(40)-H(40A)	98.00	C(50)-C(51)	151.4(5)
C(40)-H(40B)	98.00	C(50)-H(50A)	101(4)
C(40)-H(40C)	98.00	C(50)-H(50B)	97(4)
C(41)-O(2)	143.8(3)	C(51)-H(51A)	98.00
C(41)-H(41A)	108(3)	C(51)-H(51B)	98.00
C(41)-H(41B)	94(3)	C(51)-H(51C)	98.00

C(42)-O(2)	144.9(4)	Li(1)-O(4)	197.5(5)
C(42)-C(43)	147.9(4)	Li(1)-O(1)	198.3(4)
C(42)-H(42A)	99(3)	Li(1)-O(2)	199.7(5)
C(42)-H(42B)	99(3)	Li(1)-O(3)	200.3(4)
C(43)-H(43A)	98.00	C(15)-Ti-C(29)	138.29(10)
C(15)-Ti-C(8)	81.68(9)	C(14)-C(8)-Ti	130.42(17)
C(29)-Ti-C(8)	84.51(9)	C(10)-C(9)-C(8)	123.2(2)
C(15)-Ti-C(1)	112.65(10)	C(10)-C(9)-H(9)	121.0(19)
C(29)-Ti-C(1)	109.05(9)	C(8)-C(9)-H(9)	115.9(19)
C(8)-Ti-C(1)	108.77(9)	C(11)-C(10)-C(9)	121.0(2)
C(15)-Ti-C(22)	84.19(7)	C(11)-C(10)-H(10)	115.8(16)
C(29)-Ti-C(22)	83.11(6)	C(9)-C(10)-H(10)	123.2(16)
C(8)-Ti-C(22)	142.15(7)	C(10)-C(11)-C(13)	117.6(2)
C(1)-Ti-C(22)	109.08(7)	C(10)-C(11)-C(12)	121.5(2)
C(2)-C(1)-C(6)	115.4(2)	C(13)-C(11)-C(12)	120.9(2)
C(2)-C(1)-Ti	119.67(18)	C(11)-C(12)-H(12A)	109.5
C(6)-C(1)-Ti	124.94(18)	C(11)-C(12)-H(12B)	109.5
C(3)-C(2)-C(1)	123.0(2)	H(12A)-C(12)-H(12B)	109.5
C(3)-C(2)-H(2)	114(2)	C(11)-C(12)-H(12C)	109.5
C(1)-C(2)-H(2)	123(2)	H(12A)-C(12)-H(12C)	109.5
C(2)-C(3)-C(4)	121.0(2)	H(12B)-C(12)-H(12C)	109.5
C(2)-C(3)-H(3)	117.2(19)	C(11)-C(13)-C(14)	120.9(2)
C(4)-C(3)-H(3)	121.8(19)	C(11)-C(13)-H(13)	115.0(16)
C(5)-C(4)-C(3)	117.7(2)	C(14)-C(13)-H(13)	124.1(16)
C(5)-C(4)-C(7)	120.5(3)	C(13)-C(14)-C(8)	122.9(2)
C(3)-C(4)-C(7)	121.8(2)	C(13)-C(14)-H(14)	116.6(17)
C(4)-C(5)-C(6)	121.0(2)	C(8)-C(14)-H(14)	120.3(17)
C(4)-C(5)-H(5)	118.9(17)	C(16)-C(15)-C(21)	114.9(2)
C(6)-C(5)-H(5)	120.0(17)	C(16)-C(15)-Ti	113.83(19)
C(5)-C(6)-C(1)	122.0(2)	C(21)-C(15)-Ti	131.13(17)
C(5)-C(6)-H(6)	115.7(16)	C(17)-C(16)-C(15)	122.8(3)
C(1)-C(6)-H(6)	122.3(16)	C(17)-C(16)-H(16)	119(2)
C(4)-C(7)-H(7A)	109.5	C(15)-C(16)-H(16)	118(2)
C(4)-C(7)-H(7B)	109.5	C(18)-C(17)-C(16)	121.7(3)
H(7A)-C(7)-H(7B)	109.5	C(18)-C(17)-H(17)	120(3)

C(4)-C(7)-H(7C)	109.5	C(16)-C(17)-H(17)	115(3)
H(7A)-C(7)-H(7C)	109.5	C(17)-C(18)-C(20)	116.7(3)
H(7B)-C(7)-H(7C)	109.5	C(17)-C(18)-C(19)	121.7(3)
C(9)-C(8)-C(14)	114.4(2)	C(20)-C(18)-C(19)	121.6(3)
C(9)-C(8)-Ti	115.19(17)	C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5	C(35)-C(29)-C(30)	114.7(2)
H(19A)-C(19)-H(19B)	109.5	C(35)-C(29)-Ti	127.30(18)
C(18)-C(19)-H(19C)	109.5	C(30)-C(29)-Ti	117.99(17)
H(19A)-C(19)-H(19C)	109.5	C(31)-C(30)-C(29)	122.6(2)
H(19B)-C(19)-H(19C)	109.5	C(31)-C(30)-H(30)	116.1(19)
C(21)-C(20)-C(18)	121.6(3)	C(29)-C(30)-H(30)	121.3(19)
C(21)-C(20)-H(20)	114(3)	C(32)-C(31)-C(30)	121.3(2)
C(18)-C(20)-H(20)	125(3)	C(32)-C(31)-H(31)	117.9(17)
C(15)-C(21)-C(20)	122.25(19)	C(30)-C(31)-H(31)	120.8(17)
C(15)-C(21)-H(21)	118.9	C(31)-C(32)-C(34)	117.1(2)
C(20)-C(21)-H(21)	118.9	C(31)-C(32)-C(33)	121.2(2)
C(28)-C(22)-C(23)	115.14(12)	C(34)-C(32)-C(33)	121.7(2)
C(28)-C(22)-Ti	114.93(13)	C(32)-C(33)-H(33A)	109.5
C(23)-C(22)-Ti	129.9	C(32)-C(33)-H(33B)	109.5
C(22)-C(23)-C(24)	123.0	H(33A)-C(33)-H(33B)	109.5
C(22)-C(23)-H(23)	118.5	C(32)-C(33)-H(33C)	109.5
C(24)-C(23)-H(23)	118.5	H(33A)-C(33)-H(33C)	109.5
C(25)-C(24)-C(23)	120.7	H(33B)-C(33)-H(33C)	109.5
C(25)-C(24)-H(24)	119.6	C(35)-C(34)-C(32)	120.8(2)
C(23)-C(24)-H(24)	119.6	C(35)-C(34)-H(34)	116.7(18)
C(27)-C(25)-C(24)	117.47(11)	C(32)-C(34)-H(34)	122.2(18)
C(27)-C(25)-C(26)	121.53(11)	C(34)-C(35)-C(29)	123.4(2)
C(24)-C(25)-C(26)	121.0	C(34)-C(35)-H(35)	120.2(18)
C(25)-C(26)-H(26A)	109.5	C(29)-C(35)-H(35)	116.4(18)
C(25)-C(26)-H(26B)	109.5	C(37)-C(36)-H(36A)	109.5
H(26A)-C(26)-H(26B)	109.5	C(37)-C(36)-H(36B)	109.5
C(25)-C(26)-H(26C)	109.5	H(36A)-C(36)-H(36B)	109.5
H(26A)-C(26)-H(26C)	109.5	C(37)-C(36)-H(36C)	109.5
H(26B)-C(26)-H(26C)	109.5	H(36A)-C(36)-H(36C)	109.5
C(25)-C(27)-C(28)	120.7(2)	H(36B)-C(36)-H(36C)	109.5

C(25)-C(27)-H(27)	120.2(17)	O(1)-C(37)-C(36)	111.0(2)
C(28)-C(27)-H(27)	118.8(17)	O(1)-C(37)-H(37A)	105.3(17)
C(22)-C(28)-C(27)	122.9(2)	C(36)-C(37)-H(37A)	113.2(18)
C(22)-C(28)-H(28)	118(2)	O(1)-C(37)-H(37B)	100.7(19)
C(27)-C(28)-H(28)	119(2)	C(36)-C(37)-H(37B)	115(2)
H(37A)-C(37)-H(37B)	110(3)	H(43A)-C(43)-H(43C)	109.5
O(1)-C(38)-C(39)	112.3(2)	H(43B)-C(43)-H(43C)	109.5
O(1)-C(38)-H(38A)	105.7(18)	C(45)-C(44)-H(44A)	109.5
C(39)-C(38)-H(38A)	108.8(19)	C(45)-C(44)-H(44B)	109.5
O(1)-C(38)-H(38B)	110.0(19)	H(44A)-C(44)-H(44B)	109.5
C(39)-C(38)-H(38B)	110.1(19)	C(45)-C(44)-H(44C)	109.5
H(38A)-C(38)-H(38B)	110(3)	H(44A)-C(44)-H(44C)	109.5
C(38)-C(39)-H(39A)	109.5	H(44B)-C(44)-H(44C)	109.5
C(38)-C(39)-H(39B)	109.5	O(3)-C(45)-C(44)	111.6(2)
H(39A)-C(39)-H(39B)	109.5	O(3)-C(45)-H(45A)	113(2)
C(38)-C(39)-H(39C)	109.5	C(44)-C(45)-H(45A)	111(2)
H(39A)-C(39)-H(39C)	109.5	O(3)-C(45)-H(45B)	107.7(18)
H(39B)-C(39)-H(39C)	109.5	C(44)-C(45)-H(45B)	114.2(18)
C(41)-C(40)-H(40A)	109.5	H(45A)-C(45)-H(45B)	99(3)
C(41)-C(40)-H(40B)	109.5	O(3)-C(46)-C(47)	112.8(3)
H(40A)-C(40)-H(40B)	109.5	O(3)-C(46)-H(46A)	111.5(16)
C(41)-C(40)-H(40C)	109.5	C(47)-C(46)-H(46A)	108.6(17)
H(40A)-C(40)-H(40C)	109.5	O(3)-C(46)-H(46B)	105.0(18)
H(40B)-C(40)-H(40C)	109.5	C(47)-C(46)-H(46B)	113(2)
O(2)-C(41)-C(40)	112.3(2)	H(46A)-C(46)-H(46B)	106(2)
O(2)-C(41)-H(41A)	108.5(18)	C(46)-C(47)-H(47A)	109.5
C(40)-C(41)-H(41A)	112.1(17)	C(46)-C(47)-H(47B)	109.5
O(2)-C(41)-H(41B)	107(2)	H(47A)-C(47)-H(47B)	109.5
C(40)-C(41)-H(41B)	114(2)	C(46)-C(47)-H(47C)	109.5
H(41A)-C(41)-H(41B)	101(3)	H(47A)-C(47)-H(47C)	109.5
O(2)-C(42)-C(43)	110.3(2)	H(47B)-C(47)-H(47C)	109.5
O(2)-C(42)-H(42A)	112.4(19)	C(49)-C(48)-H(48A)	109.5
C(43)-C(42)-H(42A)	102.5(19)	C(49)-C(48)-H(48B)	109.5
O(2)-C(42)-H(42B)	110(2)	H(48A)-C(48)-H(48B)	109.5
C(43)-C(42)-H(42B)	109(2)	C(49)-C(48)-H(48C)	109.5

H(42A)-C(42)-H(42B)	112(3)	H(48A)-C(48)-H(48C)	109.5
C(42)-C(43)-H(43A)	109.5	H(48B)-C(48)-H(48C)	109.5
C(42)-C(43)-H(43B)	109.5	O(4)-C(49)-C(48)	114.0(2)
H(43A)-C(43)-H(43B)	109.5	O(4)-C(49)-H(49A)	106.0(17)
C(42)-C(43)-H(43C)	109.5	C(48)-C(49)-H(49A)	113.0(17)
O(4)-C(49)-H(49B)	105.4(18)	O(1)-Li(1)-O(2)	113.3(2)
C(48)-C(49)-H(49B)	108.3(17)	O(4)-Li(1)-O(3)	109.9(2)
H(49A)-C(49)-H(49B)	110(2)	O(1)-Li(1)-O(3)	112.0(2)
O(4)-C(50)-C(51)	114.6(2)	O(2)-Li(1)-O(3)	106.0(2)
O(4)-C(50)-H(50A)	112(2)	C(38)-O(1)-C(37)	113.2(2)
C(51)-C(50)-H(50A)	106(2)	C(38)-O(1)-Li(1)	114.6(2)
O(4)-C(50)-H(50B)	109(2)	C(37)-O(1)-Li(1)	131.9(2)
C(51)-C(50)-H(50B)	105(2)	C(41)-O(2)-C(42)	111.6(2)
H(50A)-C(50)-H(50B)	110(3)	C(41)-O(2)-Li(1)	119.1(2)
C(50)-C(51)-H(51A)	109.5	C(42)-O(2)-Li(1)	125.1(2)
C(50)-C(51)-H(51B)	109.5	C(45)-O(3)-C(46)	112.1(2)
H(51A)-C(51)-H(51B)	109.5	C(45)-O(3)-Li(1)	126.1(2)
C(50)-C(51)-H(51C)	109.5	C(46)-O(3)-Li(1)	119.22(19)
H(51A)-C(51)-H(51C)	109.5	C(50)-O(4)-C(49)	116.0(2)
H(51B)-C(51)-H(51C)	109.5	C(50)-O(4)-Li(1)	124.7(2)
O(4)-Li(1)-O(1)	101.2(2)	C(49)-O(4)-Li(1)	119.3(2)
O(4)-Li(1)-O(2)	114.6(2)		

Symmetry transformations used to generate equivalent atoms:

Table 8. Anisotropic displacement parameters ($pm^2x\ 10^{-1}$) for $[Li\{(CH_3CH_2)_2O\}_4][Ti(p\text{-}C_6H_4\text{-}CH_3)_5]$.The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{1}
Ti	26(1)	28(1)	29(1)	0(1)	-1(1)	-1(1)
C(1)	30(1)	31(1)	32(1)	-1(1)	-3(1)	2(1)
C(2)	36(1)	33(1)	34(1)	3(1)	-2(1)	-6(1)
C(3)	28(1)	49(2)	31(1)	-5(1)	3(1)	-2(1)
C(4)	29(1)	39(1)	38(1)	-10(1)	-9(1)	3(1)
C(5)	30(1)	30(1)	45(1)	-1(1)	-7(1)	-2(1)

C(6)	27(1)	36(1)	34(1)	0(1)	0(1)	-1(1)
C(7)	37(2)	53(2)	72(2)	-22(2)	-6(1)	7(1)
C(8)	27(1)	32(1)	33(1)	2(1)	-1(1)	-3(1)
C(9)	47(2)	31(1)	40(1)	-6(1)	-11(1)	5(1)
C(10)	51(2)	48(1)	31(1)	-5(1)	-6(1)	11(2)
C(11)	32(1)	44(1)	35(1)	7(1)	-2(1)	5(1)
C(12)	58(2)	63(2)	44(2)	14(1)	-2(1)	9(2)
C(13)	30(1)	28(1)	47(1)	2(1)	0(1)	0(1)
C(14)	34(1)	31(1)	32(1)	-4(1)	3(1)	-4(1)
C(15)	29(1)	41(1)	27(1)	5(1)	-2(1)	0(1)
C(16)	32(1)	38(2)	60(2)	-7(1)	-1(1)	2(1)
C(17)	38(2)	44(2)	62(2)	-18(1)	4(1)	-8(1)
C(18)	28(1)	70(2)	31(1)	-8(1)	-1(1)	0(1)
C(19)	35(2)	97(3)	53(2)	-25(2)	-2(1)	-6(2)
C(20)	38(2)	51(2)	66(2)	11(2)	-3(1)	5(1)
C(21)	37(2)	40(1)	62(2)	13(1)	-2(1)	-2(1)
C(22)	31(1)	33(1)	28(1)	1(1)	-2(1)	-5(1)
C(23)	38(1)	40(1)	33(1)	0(1)	-5(1)	4(1)
C(24)	40(1)	44(1)	35(1)	-8(1)	2(1)	4(1)
C(25)	42(1)	40(1)	31(1)	-1(1)	-4(1)	-4(1)
C(26)	71(2)	66(2)	34(1)	3(1)	3(1)	9(2)
C(27)	39(1)	35(1)	39(1)	5(1)	-9(1)	4(1)
C(28)	29(1)	39(1)	36(1)	-1(1)	3(1)	0(1)
C(29)	33(1)	33(1)	22(1)	3(1)	-3(1)	-5(1)
C(30)	36(1)	30(1)	34(1)	3(1)	-2(1)	4(1)
C(31)	28(1)	36(1)	43(1)	8(1)	-3(1)	3(1)
C(32)	35(1)	36(1)	30(1)	7(1)	-6(1)	-7(1)
C(33)	45(2)	42(2)	65(2)	1(1)	-15(1)	-9(1)
C(34)	43(2)	42(2)	34(1)	-12(1)	3(1)	-6(1)
C(35)	31(1)	50(2)	46(2)	-13(1)	5(1)	0(1)
C(36)	56(2)	56(2)	47(2)	10(1)	6(1)	12(2)
C(37)	42(2)	54(2)	32(1)	6(1)	2(1)	3(1)
C(38)	48(2)	47(2)	33(1)	-6(1)	3(1)	4(1)
C(39)	62(2)	67(2)	40(2)	0(1)	-10(1)	-5(2)
C(40)	56(2)	70(2)	55(2)	-16(2)	-2(2)	20(2)

C(41)	48(2)	44(2)	40(1)	-10(1)	3(1)	-2(1)
C(42)	37(2)	53(2)	53(2)	-1(1)	-6(1)	-4(1)
C(43)	45(2)	52(2)	54(2)	2(1)	2(1)	-2(1)
C(44)	55(2)	74(2)	35(1)	1(1)	-13(1)	8(2)
C(45)	36(2)	52(2)	51(2)	3(1)	-17(1)	0(1)
C(46)	35(1)	52(2)	45(2)	-3(1)	4(1)	12(1)
C(47)	57(2)	51(2)	70(2)	-18(2)	-2(2)	6(2)
C(48)	48(2)	85(2)	54(2)	-20(2)	15(2)	-14(2)
C(49)	38(2)	53(2)	38(1)	-1(1)	2(1)	-4(1)
C(50)	55(2)	60(2)	54(2)	21(2)	-15(2)	-7(2)
C(51)	54(2)	52(2)	66(2)	15(2)	-6(2)	-10(2)
Li(1)	34(2)	41(2)	29(2)	-4(2)	-2(2)	6(2)
O(1)	50(1)	43(1)	29(1)	-1(1)	-2(1)	4(1)
O(2)	40(1)	40(1)	38(1)	-8(1)	0(1)	2(1)
O(3)	33(1)	47(1)	34(1)	-1(1)	-4(1)	7(1)
O(4)	35(1)	50(1)	36(1)	8(1)	-2(1)	-1(1)

8.1.3 $Li_4ClTi(C_6H_5)_6 \cdot 8(OC_4H_8)$

8.1.3.1 Preparation of $[Li_4Cl(THF)_8][Ti(C_6H_5)_6]$

To a suspension of $TiCl_4$ (0.35 g, 1.85 mmol) in diethyl ether (40 mL) was added a solution of LiC_6H_5 (ca 14.7 mmol) in diethyl ether (13.7 mL of 1.08 M phLi solution) at –60^{o}C over a period of 1hr. The mixture was allowed to warm slowly to –40^{o}C, after 5 hr of stirring at this temperature the solution turned red and small amount of orange-red solid precipitated. After removing the solid by filtration (still at –40^{o}C), the red solution was concentrated to dryness and the resulting residue was redissolved in THF (20 mL), and upon cooling from –40^{o}C to –80^{o}C dark red (black cube) crystals formed.

8.1.3.2 Crystal Data and Crystal Structure Analysis of $[Li_4Cl(THF)_8][Ti(C_6H_5)_6]$

Table 9. Crystal data and structure refinement for $Li_4ClTi(C_6H_5)_6 \cdot 8(OC_4H_8)$.

Identification code	tiphe6	
Empirical formula	$C_{40}\ H_{40}\ Cl_{0.50}\ Li\ O_4\ Ti_{0.50}$	
Formula weight	633.34	
Temperature	133(2) K	
Wavelength	71.073 pm	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 1129.9(3) pm	α= 75.161(5)°.
	b = 1157.5(3) pm	β= 85.903(6)°.
	c = 1288.8(3) pm	γ = 84.115(5)°.
Volume	1.6189(7) nm^3	
Z	2	
Density (calculated)	1.299 Mg/m^3	
Absorption coefficient	0.233 mm^{-1}	
F(000)	669	
Crystal size	0.4 x 0.4 x 0.3 mm^3	
Theta range for data collection	1.64 to 23.05°.	
Index ranges	-11<=h<=12, -12<=k<=12, -13<=l<=14	
Reflections collected	14187	
Independent reflections	4516 [R(int) = 0.0215]	
Completeness to theta = 23.05°	99.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4516 / 0 / 425	
Goodness-of-fit on F^2	1.790	
Final R indices [I>2sigma(I)]	R1 = 0.1048, wR2 = 0.3564	
R indices (all data)	R1 = 0.1167, wR2 = 0.3756	
Extinction coefficient	0.000(6)	
Largest diff. peak and hole	0.507 and -0.548 e.$Å^{-3}$	

Table 10. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($pm^2 x\ 10^{-1}$) for $Li_4ClTi(C_6H_5)_6 \cdot 8(OC_4H_8)$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ti(1)	0	10000	5000	22(1)
Li(1)	36(8)	7862(8)	4691(7)	33(2)
C(1)	-1208(4)	11674(4)	4113(4)	25(1)
C(2)	-1131(5)	12040(5)	2977(4)	29(1)
C(3)	-1938(5)	12889(5)	2367(5)	33(1)
C(4)	-2864(5)	13422(5)	2853(5)	37(2)
C(5)	-2988(5)	13123(5)	3961(5)	38(2)
C(6)	-2176(5)	12281(5)	4548(5)	31(1)
C(7)	548(5)	9530(4)	3383(4)	29(1)
C(8)	-247(5)	9337(4)	2683(4)	29(1)
C(9)	66(6)	9204(5)	1662(4)	36(1)
C(10)	1235(6)	9215(6)	1293(5)	43(2)
C(11)	2084(6)	9409(5)	1939(5)	41(2)
C(12)	1742(5)	9574(5)	2954(4)	31(1)
C(13)	1582(4)	11175(5)	4727(4)	26(1)
C(14)	2656(5)	10774(5)	5262(4)	32(1)
C(15)	3684(5)	11353(5)	4991(5)	34(1)
C(16)	3703(5)	12403(5)	4166(5)	34(1)
C(17)	2693(5)	12852(5)	3648(4)	32(1)
C(18)	1653(5)	12247(5)	3911(4)	28(1)
C(21)	-1183(6)	6241(6)	3836(6)	51(2)
C(22)	-852(12)	5635(15)	2986(9)	151(7)
C(23)	322(8)	5730(7)	2648(6)	64(2)
C(24)	868(6)	6141(6)	3493(5)	53(2)
C(25)	8072(7)	5827(6)	-166(7)	60(2)
C(26)	9000(9)	6500(7)	-836(8)	81(3)
C(27)	9144(7)	7506(8)	-395(7)	71(2)
C(28)	7933(7)	7721(7)	192(6)	60(2)
C(29)	5400(7)	8216(6)	-1727(4)	49(2)
C(30)	4601(8)	9259(8)	-2361(6)	72(2)

C(31)	3601(8)	9479(8)	-1540(6)	71(2)
C(32)	3981(12)	8748(19)	-530(7)	212(11)
C(33)	5689(9)	7096(8)	2579(6)	80(3)
C(34)	5245(12)	6458(14)	3628(7)	129(5)
C(35)	4266(7)	5826(7)	3446(6)	59(2)
C(36)	4003(8)	6262(15)	2344(6)	120(5)
Cl(1)	4909(6)	5115(5)	161(4)	24(1)
Li(2)	5624(10)	6679(11)	397(8)	56(3)
O(1)	-79(4)	6470(3)	4185(3)	37(1)
O(2)	7330(4)	6657(4)	313(3)	43(1)
O(3)	5111(4)	8165(4)	-604(3)	52(1)
O(4)	5010(5)	6858(6)	1794(4)	82(2)

Table 11. Bond lengths [pm] and angles [°] for $Li_4ClTi(C_6H_5)_6 \cdot 8(OC_4H_8)$.

Ti(1)-C(13)	230.9(5)	Ti(1)-C(13)#1	230.9(5)
Ti(1)-C(7)	231.3(5)	Ti(1)-C(7)#1	231.3(5)
Ti(1)-C(1)#1	233.9(5)	Ti(1)-C(1)	233.9(5)
Ti(1)-Li(1)	260.1(9)	Ti(1)-Li(1)#1	260.1(9)
Li(1)-O(1)	190.6(10)	Li(1)-C(13)#1	222.7(10)
Li(1)-C(1)#1	229.7(10)	Li(1)-C(7)	230.8(10)
Li(1)-C(18)#1	251.9(10)	Li(1)-C(6)#1	264.7(11)
Li(1)-C(8)	273.1(10)	C(1)-C(6)	140.0(8)
C(1)-C(2)	141.5(7)	C(1)-Li(1)#1	229.7(10)
C(2)-C(3)	139.2(8)	C(2)-H(2)	99(6)
C(3)-C(4)	135.6(9)	C(3)-H(3)	93(6)
C(4)-C(5)	138.2(9)	C(4)-H(4)	61(6)
C(5)-C(6)	137.8(8)	C(5)-H(5)	121(8)
C(6)-Li(1)#1	264.7(11)	C(6)-H(6)	81(6)
C(7)-C(8)	138.9(7)	C(7)-C(12)	142.2(8)
C(8)-C(9)	138.2(8)	C(8)-H(8)	107(6)
C(9)-C(10)	137.2(9)	C(9)-H(9)	114(6)
C(10)-C(11)	138.4(9)	C(10)-H(10)	96(8)
C(11)-C(12)	139.2(8)	C(11)-H(11)	117(6)

C(12)-H(12)	97(6)	C(13)-C(18)	141.2(7)
C(13)-C(14)	141.5(7)	C(13)-Li(1)#1	222.7(10)
C(14)-C(15)	137.9(8)	C(14)-H(14)	104(6)
C(15)-C(16)	139.5(8)	C(15)-H(15)	113(5)
C(16)-C(17)	135.2(8)	C(16)-H(16)	81(6)
C(17)-C(18)	140.6(8)	C(17)-H(17)	97(6)
C(18)-Li(1)#1	251.9(10)	C(18)-H(18)	93(6)
C(21)-O(1)	142.8(7)	C(21)-C(22)	145.3(13)
C(21)-H(21A)	99.00	C(21)-H(21B)	99.00
C(22)-C(23)	137.3(14)	C(22)-H(22A)	99.00
C(22)-H(22B)	99.00	C(23)-C(24)	148.8(10)
C(23)-H(23A)	99.00	C(23)-H(23B)	99.00
C(24)-O(1)	142.8(8)	C(24)-H(24A)	99.00
C(24)-H(24B)	99.00	C(25)-O(2)	143.9(8)
C(25)-C(26)	146.5(11)	C(25)-H(25A)	99.00
C(25)-H(25B)	99.00	C(26)-C(27)	144.8(12)
C(26)-H(26A)	99.00	C(26)-H(26B)	99.00
C(27)-C(28)	154.4(10)	C(27)-H(27A)	99.00
C(27)-H(27B)	99.00	C(28)-O(2)	143.7(8)
C(28)-H(28A)	99.00	C(28)-H(28B)	99.00
C(29)-O(3)	144.8(7)	C(29)-C(30)	152.3(9)
C(29)-H(29A)	99.00	C(29)-H(29B)	99.00
C(30)-C(31)	153.9(11)	C(30)-H(30A)	99.00
C(30)-H(30B)	99.00	C(31)-C(32)	142.7(12)
C(31)-H(31A)	99.00	C(31)-H(31B)	99.00
C(32)-O(3)	139.1(11)	C(32)-H(32A)	99.00
C(32)-H(32B)	99.00	C(33)-O(4)	140.8(10)
C(33)-C(34)	144.7(12)	C(33)-H(33A)	99.00
C(33)-H(33B)	99.00	C(34)-C(35)	145.2(12)
C(34)-H(34A)	99.00	C(34)-H(34B)	99.00
C(35)-C(36)	142.2(10)	C(35)-H(35A)	99.00
C(35)-H(35B)	99.00	C(36)-O(4)	143.9(11)
C(36)-H(36A)	99.00	C(36)-H(36B)	99.00
Cl(1)-Cl(1)#2	56.5(6)	Cl(1)-Li(2)	215.4(14)
Cl(1)-Li(2)#2	250.6(14)	Li(2)-O(2)	192.1(12)

Li(2)-O(3)	193.0(11)	Li(2)-O(4)	193.6(13)
Li(2)-Cl(1)#2	250.6(14)		
C(13)-Ti(1)-C(13)#1	180.0	C(13)-Ti(1)-C(7)	88.64(18)
C(13)#1-Ti(1)-C(7)	91.36(18)	C(13)-Ti(1)-C(7)#1	91.36(18)
C(13)#1-Ti(1)-C(7)#1	88.64(18)	C(7)-Ti(1)-C(7)#1	180.000(1)
C(13)-Ti(1)-C(1)#1	90.82(18)	C(13)#1-Ti(1)-C(1)#1	89.18(18)
C(7)-Ti(1)-C(1)#1	89.55(17)	C(7)#1-Ti(1)-C(1)#1	90.45(17)
C(13)-Ti(1)-C(1)	89.18(18)	C(13)#1-Ti(1)-C(1)	90.82(18)
C(7)-Ti(1)-C(1)	90.45(17)	C(7)#1-Ti(1)-C(1)	89.55(17)
C(1)#1-Ti(1)-C(1)	180.000(1)	C(13)-Ti(1)-Li(1)	126.5(2)
C(13)#1-Ti(1)-Li(1)	53.5(2)	C(7)-Ti(1)-Li(1)	55.6(2)
C(7)#1-Ti(1)-Li(1)	124.4(2)	C(1)#1-Ti(1)-Li(1)	55.1(2)
C(1)-Ti(1)-Li(1)	124.9(2)	C(13)-Ti(1)-Li(1)#1	53.5(2)
C(13)#1-Ti(1)-Li(1)#1	126.5(2)	C(7)-Ti(1)-Li(1)#1	124.4(2)
C(7)#1-Ti(1)-Li(1)#1	55.6(2)	C(1)#1-Ti(1)-Li(1)#1	124.9(2)
C(1)-Ti(1)-Li(1)#1	55.1(2)	Li(1)-Ti(1)-Li(1)#1	180.0(4)
O(1)-Li(1)-C(13)#1	120.9(5)	O(1)-Li(1)-C(1)#1	134.5(5)
C(13)#1-Li(1)-C(1)#1	92.3(4)	O(1)-Li(1)-C(7)	114.8(4)
C(13)#1-Li(1)-C(7)	93.6(4)	C(1)#1-Li(1)-C(7)	90.7(4)
O(1)-Li(1)-C(18)#1	102.7(4)	C(13)#1-Li(1)-C(18)#1	33.9(2)
C(1)#1-Li(1)-C(18)#1	87.8(3)	C(7)-Li(1)-C(18)#1	127.3(4)
O(1)-Li(1)-Ti(1)	167.9(5)	C(13)#1-Li(1)-Ti(1)	56.5(2)
C(1)#1-Li(1)-Ti(1)	56.6(2)	C(7)-Li(1)-Ti(1)	55.8(2)
C(18)#1-Li(1)-Ti(1)	80.6(3)	O(1)-Li(1)-C(6)#1	108.3(4)
C(13)#1-Li(1)-C(6)#1	124.2(4)	C(1)#1-Li(1)-C(6)#1	31.9(2)
C(7)-Li(1)-C(6)#1	88.1(4)	C(18)#1-Li(1)-C(6)#1	114.4(4)
Ti(1)-Li(1)-C(6)#1	80.2(3)	O(1)-Li(1)-C(8)	91.9(4)
C(13)#1-Li(1)-C(8)	89.0(3)	C(1)#1-Li(1)-C(8)	121.1(4)
C(7)-Li(1)-C(8)	30.6(2)	C(18)#1-Li(1)-C(8)	119.8(4)
Ti(1)-Li(1)-C(8)	76.5(3)	C(6)#1-Li(1)-C(8)	115.4(4)
C(6)-C(1)-C(2)	112.0(5)	C(6)-C(1)-Li(1)#1	88.0(4)
C(2)-C(1)-Li(1)#1	128.3(4)	C(6)-C(1)-Ti(1)	127.8(4)
C(2)-C(1)-Ti(1)	119.3(4)	Li(1)#1-C(1)-Ti(1)	68.3(3)
C(3)-C(2)-C(1)	123.7(5)	C(3)-C(2)-H(2)	115(3)
C(1)-C(2)-H(2)	121(3)	C(4)-C(3)-C(2)	120.5(5)

C(4)-C(3)-H(3)	119(3)	C(2)-C(3)-H(3)	120(3)
C(3)-C(4)-C(5)	119.1(5)	C(3)-C(4)-H(4)	117(6)
C(5)-C(4)-H(4)	124(6)	C(6)-C(5)-C(4)	119.3(5)
C(6)-C(5)-H(5)	116(4)	C(4)-C(5)-H(5)	123(4)
C(5)-C(6)-C(1)	125.3(5)	C(5)-C(6)-Li(1)#1	139.7(5)
C(1)-C(6)-Li(1)#1	60.1(3)	C(5)-C(6)-H(6)	119(4)
C(1)-C(6)-H(6)	116(4)	Li(1)#1-C(6)-H(6)	71(4)
C(8)-C(7)-C(12)	113.6(5)	C(8)-C(7)-Li(1)	91.8(4)
C(12)-C(7)-Li(1)	119.2(4)	C(8)-C(7)-Ti(1)	124.5(4)
C(12)-C(7)-Ti(1)	121.4(4)	Li(1)-C(7)-Ti(1)	68.5(3)
C(9)-C(8)-C(7)	124.4(5)	C(9)-C(8)-Li(1)	133.3(4)
C(7)-C(8)-Li(1)	57.6(3)	C(9)-C(8)-H(8)	117(3)
C(7)-C(8)-H(8)	118(3)	Li(1)-C(8)-H(8)	88(3)
C(8)-C(9)-C(10)	120.0(5)	C(8)-C(9)-H(9)	113(3)
C(10)-C(9)-H(9)	127(3)	C(9)-C(10)-C(11)	119.3(5)
C(9)-C(10)-H(10)	129(4)	C(11)-C(10)-H(10)	111(4)
C(10)-C(11)-C(12)	119.7(6)	C(10)-C(11)-H(11)	112(3)
C(12)-C(11)-H(11)	129(3)	C(11)-C(12)-C(7)	123.0(5)
C(11)-C(12)-H(12)	117(3)	C(7)-C(12)-H(12)	120(3)
C(18)-C(13)-C(14)	113.5(5)	C(18)-C(13)-Li(1)#1	84.4(4)
C(14)-C(13)-Li(1)#1	127.3(4)	C(18)-C(13)-Ti(1)	124.0(4)
C(14)-C(13)-Ti(1)	121.7(4)	Li(1)#1-C(13)-Ti(1)	69.9(3)
C(15)-C(14)-C(13)	123.3(5)	C(15)-C(14)-H(14)	115(3)
C(13)-C(14)-H(14)	121(3)	C(14)-C(15)-C(16)	120.5(5)
C(14)-C(15)-H(15)	129(3)	C(16)-C(15)-H(15)	110(3)
C(17)-C(16)-C(15)	119.0(6)	C(17)-C(16)-H(16)	128(4)
C(15)-C(16)-H(16)	113(4)	C(16)-C(17)-C(18)	120.4(5)
C(16)-C(17)-H(17)	115(3)	C(18)-C(17)-H(17)	124(3)
C(17)-C(18)-C(13)	123.2(5)	C(17)-C(18)-Li(1)#1	136.3(4)
C(13)-C(18)-Li(1)#1	61.6(3)	C(17)-C(18)-H(18)	130(3)
C(13)-C(18)-H(18)	105(3)	Li(1)#1-C(18)-H(18)	75(3)
O(1)-C(21)-C(22)	104.9(7)	O(1)-C(21)-H(21A)	110.8
C(22)-C(21)-H(21A)	110.8	O(1)-C(21)-H(21B)	110.8
C(22)-C(21)-H(21B)	110.8	H(21A)-C(21)-H(21B)	108.8
C(23)-C(22)-C(21)	111.6(7)	C(23)-C(22)-H(22A)	109.3

C(21)-C(22)-H(22A)	109.3	C(23)-C(22)-H(22B)	109.3
C(21)-C(22)-H(22B)	109.3	H(22A)-C(22)-H(22B)	108.0
C(22)-C(23)-C(24)	105.1(7)	C(22)-C(23)-H(23A)	110.7
C(24)-C(23)-H(23A)	110.7	C(22)-C(23)-H(23B)	110.7
C(24)-C(23)-H(23B)	110.7	H(23A)-C(23)-H(23B)	108.8
O(1)-C(24)-C(23)	107.4(6)	O(1)-C(24)-H(24A)	110.2
C(23)-C(24)-H(24A)	110.2	O(1)-C(24)-H(24B)	110.2
C(23)-C(24)-H(24B)	110.2	H(24A)-C(24)-H(24B)	108.5
O(2)-C(25)-C(26)	107.1(6)	O(2)-C(25)-H(25A)	110.3
C(26)-C(25)-H(25A)	110.3	O(2)-C(25)-H(25B)	110.3
C(26)-C(25)-H(25B)	110.3	H(25A)-C(25)-H(25B)	108.6
C(27)-C(26)-C(25)	106.8(7)	C(27)-C(26)-H(26A)	110.4
C(25)-C(26)-H(26A)	110.4	C(27)-C(26)-H(26B)	110.4
C(25)-C(26)-H(26B)	110.4	H(26A)-C(26)-H(26B)	108.6
C(26)-C(27)-C(28)	104.4(6)	C(26)-C(27)-H(27A)	110.9
C(28)-C(27)-H(27A)	110.9	C(26)-C(27)-H(27B)	110.9
C(28)-C(27)-H(27B)	110.9	H(27A)-C(27)-H(27B)	108.9
O(2)-C(28)-C(27)	106.2(5)	O(2)-C(28)-H(28A)	110.5
C(27)-C(28)-H(28A)	110.5	O(2)-C(28)-H(28B)	110.5
C(27)-C(28)-H(28B)	110.5	H(28A)-C(28)-H(28B)	108.7
O(3)-C(29)-C(30)	106.0(5)	O(3)-C(29)-H(29A)	110.5
C(30)-C(29)-H(29A)	110.5	O(3)-C(29)-H(29B)	110.5
C(30)-C(29)-H(29B)	110.5	H(29A)-C(29)-H(29B)	108.7
C(29)-C(30)-C(31)	104.1(5)	C(29)-C(30)-H(30A)	110.9
C(31)-C(30)-H(30A)	110.9	C(29)-C(30)-H(30B)	110.9
C(31)-C(30)-H(30B)	110.9	H(30A)-C(30)-H(30B)	109.0
C(32)-C(31)-C(30)	105.0(6)	C(32)-C(31)-H(31A)	110.7
C(30)-C(31)-H(31A)	110.7	C(32)-C(31)-H(31B)	110.7
C(30)-C(31)-H(31B)	110.7	H(31A)-C(31)-H(31B)	108.8
O(3)-C(32)-C(31)	112.7(8)	O(3)-C(32)-H(32A)	109.1
C(31)-C(32)-H(32A)	109.1	O(3)-C(32)-H(32B)	109.1
C(31)-C(32)-H(32B)	109.1	H(32A)-C(32)-H(32B)	107.8
O(4)-C(33)-C(34)	108.6(7)	O(4)-C(33)-H(33A)	110.0
C(34)-C(33)-H(33A)	110.0	O(4)-C(33)-H(33B)	110.0
C(34)-C(33)-H(33B)	110.0	H(33A)-C(33)-H(33B)	108.4

C(35)-C(34)-C(33)	106.4(7)	C(35)-C(34)-H(34A)	110.4
C(33)-C(34)-H(34A)	110.4	C(35)-C(34)-H(34B)	110.4
C(33)-C(34)-H(34B)	110.4	H(34A)-C(34)-H(34B)	108.6
C(36)-C(35)-C(34)	107.2(8)	C(36)-C(35)-H(35A)	110.3
C(34)-C(35)-H(35A)	110.3	C(36)-C(35)-H(35B)	110.3
C(34)-C(35)-H(35B)	110.3	H(35A)-C(35)-H(35B)	108.5
C(35)-C(36)-O(4)	107.4(7)	C(35)-C(36)-H(36A)	110.2
O(4)-C(36)-H(36A)	110.2	C(35)-C(36)-H(36B)	110.2
O(4)-C(36)-H(36B)	110.2	H(36A)-C(36)-H(36B)	108.5
Cl(1)#2-Cl(1)-Li(2)	122.8(15)	Cl(1)#2-Cl(1)-Li(2)#2	46.3(12)
Li(2)-Cl(1)-Li(2)#2	169.1(3)	O(2)-Li(2)-O(3)	103.9(5)
O(2)-Li(2)-O(4)	109.8(6)	O(3)-Li(2)-O(4)	105.3(6)
O(2)-Li(2)-Cl(1)	116.0(6)	O(3)-Li(2)-Cl(1)	114.7(6)
O(4)-Li(2)-Cl(1)	106.6(5)	O(2)-Li(2)-Cl(1)#2	107.8(6)
O(3)-Li(2)-Cl(1)#2	112.1(5)	O(4)-Li(2)-Cl(1)#2	117.1(5)
Cl(1)-Li(2)-Cl(1)#2	10.9(3)	C(21)-O(1)-C(24)	108.9(5)
C(21)-O(1)-Li(1)	120.6(4)	C(24)-O(1)-Li(1)	118.0(5)
C(28)-O(2)-C(25)	109.0(5)	C(28)-O(2)-Li(2)	122.5(6)
C(25)-O(2)-Li(2)	121.8(6)	C(32)-O(3)-C(29)	107.8(5)
C(32)-O(3)-Li(2)	122.5(8)	C(29)-O(3)-Li(2)	115.6(5)
C(33)-O(4)-C(36)	107.4(6)	C(33)-O(4)-Li(2)	125.2(6)
C(36)-O(4)-Li(2)	122.2(7)		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+2,-z+1 #2 -x+1,-y+1,-z

Table 12. Anisotropic displacement parameters ($pm^2 x\ 10^{-1}$) for $Li_4ClTi(C_6H_5)_6 \cdot 8(OC_4H_8)$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ti(1)	21(1)	25(1)	20(1)	-4(1)	-1(1)	-1(1)
Li(1)	35(5)	32(5)	31(5)	-5(4)	0(4)	-3(4)
C(1)	21(3)	28(3)	26(3)	-4(2)	-3(2)	-7(2)
C(2)	31(3)	27(3)	28(3)	-2(2)	-4(2)	-2(2)
C(3)	41(4)	32(3)	25(3)	-2(2)	-6(3)	-2(3)
C(4)	32(4)	36(3)	36(4)	2(3)	-17(3)	7(3)
C(5)	24(3)	46(3)	40(3)	-8(3)	-4(3)	6(3)

C(6)	32(3)	39(3)	21(3)	-6(2)	1(2)	0(2)
C(7)	29(3)	28(3)	27(3)	-5(2)	-2(2)	0(2)
C(8)	38(3)	22(3)	26(3)	-5(2)	-5(2)	0(2)
C(9)	44(4)	40(3)	25(3)	-7(2)	-3(3)	-7(3)
C(10)	55(4)	53(4)	22(3)	-14(3)	2(3)	-10(3)
C(11)	46(4)	46(3)	31(3)	-14(3)	7(3)	-9(3)
C(12)	30(3)	39(3)	24(3)	-5(2)	1(2)	-5(2)
C(13)	21(3)	34(3)	25(3)	-15(2)	4(2)	-3(2)
C(14)	31(3)	32(3)	34(3)	-10(3)	-4(2)	-3(2)
C(15)	23(3)	40(3)	41(3)	-12(3)	-4(2)	-4(2)
C(16)	26(3)	43(3)	36(3)	-11(3)	7(3)	-15(3)
C(17)	31(3)	35(3)	29(3)	-5(3)	2(2)	-12(2)
C(18)	26(3)	27(3)	29(3)	-5(2)	0(2)	-3(2)
C(21)	45(4)	57(4)	61(4)	-23(3)	-10(3)	-21(3)
C(22)	138(11)	274(19)	103(8)	-122(11)	25(8)	-132(13)
C(23)	89(6)	53(4)	54(4)	-28(3)	-9(4)	13(4)
C(24)	55(4)	52(4)	50(4)	-17(3)	3(3)	17(3)
C(25)	45(4)	46(4)	89(6)	-21(4)	11(4)	-5(3)
C(26)	89(6)	53(5)	101(6)	-31(4)	49(5)	-9(4)
C(27)	56(5)	87(6)	89(6)	-53(5)	30(4)	-34(4)
C(28)	60(5)	66(5)	69(5)	-42(4)	34(4)	-33(4)
C(29)	59(4)	58(4)	25(3)	-7(3)	4(3)	6(3)
C(30)	87(6)	76(5)	40(4)	-1(4)	-13(4)	20(5)
C(31)	64(5)	70(5)	71(5)	-16(4)	-17(4)	29(4)
C(32)	132(11)	410(30)	35(5)	-22(9)	-3(6)	181(15)
C(33)	109(7)	82(6)	60(5)	-28(4)	32(5)	-58(5)
C(34)	151(11)	204(13)	50(5)	-31(7)	20(6)	-124(11)
C(35)	59(5)	60(4)	53(4)	4(3)	-9(4)	-25(4)
C(36)	48(5)	263(15)	35(4)	1(6)	5(4)	-57(7)
Cl(1)	34(2)	13(2)	41(3)	-26(2)	-10(2)	-23(2)
Li(2)	48(7)	71(7)	32(5)	17(5)	4(5)	-6(6)
O(1)	41(2)	36(2)	36(2)	-14(2)	-2(2)	1(2)
O(2)	37(2)	47(2)	46(2)	-10(2)	2(2)	-11(2)
O(3)	51(3)	69(3)	28(2)	-9(2)	0(2)	17(2)
O(4)	44(3)	148(6)	34(3)	9(3)	14(2)	-14(3)

8.1.4 $Li_4ClTi(p\text{-}C_6H_4\text{-}CH_3)_6 \cdot 8(Et_2O)$

8.1.4.1 Preparation of $[Li_4Cl(Et_2O)_8][Ti(p\text{-}C_6H_4\text{-}CH_3)_6]$

p-Tolyllithium (18.9 mmol, 0.84 M solution in Et_2O) was added dropwise at –60°C over a period of 1 hr to a suspension of $TiCl_4$ (0.45 g, 2.37 mmol) in ether (20 mL). The mixture was allowed to warm slowly to –40°C, after 5 hr of further stirring at this temperature, the solution turned red and a small amount of yellow solid separated.

The red solution was separated from the yellow solid and reduced to about half of its volume by pumping at –40°C in vacuum. After several days at –78°C dark red (red brown) crystals were formed.

8.1.4.2 Crystal Data and Crystal Structure Analysis of $[Li_4Cl(Et_2O)_8][Ti(p\text{-}C_6H_4\text{-}CH_3)_6]$

Table 13. Crystal data and structure refinement for $Li_4ClTi(p\text{-}C_6H_4\text{-}CH_3)_6 \cdot 8(Et_2O)$.

Identification code	titol6	
Empirical formula	$C_{60}\ H_{80}\ Cl\ Li\ O_4\ Ti$	
Formula weight	955.53	
Temperature	293(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	C12/c1	
Unit cell dimensions	a = 2300.0(5) pm	α= 90°.
	b = 1415.8(3) pm	β= 115.202(5)°.
	c = 2600.8(6) pm	γ = 90°.
Volume	7.66(1) nm^3	
Z	8	
Density (calculated)	1.657 Mg/m^3	
Absorption coefficient	0.356 mm^{-1}	
F(000)	4112	
Crystal size	0.5 x 0.3 x 0.3 mm^3	
Theta range for data collection	1.74 to 25.12°.	

Index ranges	-27<=h<=27, -16<=k<=16, -30<=l<=30
Reflections collected	39411
Independent reflections	6785 [R(int) = 0.0473]
Completeness to theta = 25.12°	99.3 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6785 / 0 / 399
Goodness-of-fit on F^2	2.261
Final R indices [I>2sigma(I)]	R1 = 0.1680, wR2 = 0.4797
R indices (all data)	R1 = 0.2012, wR2 = 0.5122
Largest diff. peak and hole	6.852 and -1.087 e.Å^{-3}

Table 14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for $Li_4ClTi(p\text{-}C_6H_4\text{-}CH_3)_6 \cdot 8(Et_2O)$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	10678(3)	331(5)	4565(3)	37(2)
C(2)	11122(3)	-348(5)	4543(3)	41(2)
C(3)	11550(4)	-173(6)	4320(4)	47(2)
C(4)	11585(3)	696(5)	4084(3)	39(2)
C(5)	11155(3)	1383(5)	4085(3)	40(2)
C(6)	10724(3)	1190(5)	4331(3)	38(2)
C(7)	12076(4)	906(6)	3853(4)	49(2)
C(8)	9316(3)	1212(5)	4497(3)	38(2)
C(9)	9478(4)	2148(6)	4657(3)	44(2)
C(10)	9052(4)	2904(6)	4437(4)	49(2)
C(11)	8422(4)	2752(6)	4017(4)	52(2)
C(12)	8256(4)	1829(7)	3847(4)	56(2)
C(13)	8693(4)	1097(6)	4075(4)	47(2)
C(14)	7956(5)	3550(8)	3734(6)	80(3)
C(15)	9438(3)	-1030(5)	4260(3)	40(2)
C(16)	9653(4)	-1481(6)	3903(3)	47(2)
C(17)	9311(4)	-2164(6)	3494(4)	56(2)
C(18)	8685(4)	-2428(6)	3421(4)	53(2)

C(19)	8458(4)	-2019(6)	3783(3)	47(2)
C(20)	8825(4)	-1336(5)	4193(3)	42(2)
C(21)	8295(6)	-3092(7)	2964(4)	75(3)
C(22)	9441(10)	2450(20)	3225(11)	199(12)
C(23)	9115(7)	1682(7)	2898(6)	84(4)
C(24)	9064(5)	52(6)	2678(4)	59(2)
C(25)	8388(6)	-241(9)	2608(5)	82(3)
C(26)	4128(7)	2839(10)	1860(5)	95(4)
C(27)	3720(6)	1965(8)	1656(5)	79(3)
C(28)	3785(7)	1870(10)	710(6)	96(4)
C(29)	3180(9)	1850(20)	301(9)	209(14)
C(30)	3069(9)	-715(14)	2104(8)	150(8)
C(31)	3419(5)	-1173(7)	1812(4)	62(3)
C(32)	2850(5)	-576(9)	847(5)	89(4)
C(33)	2660(4)	-1458(9)	520(4)	70(3)
C(34)	3993(6)	-1023(10)	14(5)	91(4)
C(35)	4405(4)	-1129(7)	681(4)	63(3)
C(36)	5033(9)	304(11)	893(8)	124(7)
C(37)	5663(7)	34(17)	1320(11)	202(14)
Cl	5000	135(1)	2500	19(1)
Li(1)	9633(6)	359(11)	3899(6)	51(3)
Li(2)	4202(9)	178(11)	1494(8)	66(4)
O(1)	9334(3)	741(4)	3111(2)	55(2)
O(2)	3869(3)	1434(5)	1265(3)	70(2)
O(3)	3455(3)	-626(5)	1373(3)	61(2)
O(4)	4526(4)	-227(5)	955(4)	75(2)
Ti(1)	10000	0	5000	34(1)

Table 15. Bond lengths [pm] and angles [°] for $Li_4ClTi(p\text{-}C_6H_4\text{-}CH_3)_6 \cdot 8(Et_2O)$.

C(1)-C(6)	138.5(10)	C(1)-C(2)	142.2(10)
C(1)-Li(1)	228.7(14)	C(1)-Ti(1)	233.0(7)
C(2)-C(3)	136.2(12)	C(3)-C(4)	139.2(11)
C(4)-C(5)	138.6(10)	C(4)-C(7)	151.8(11)

C(5)-C(6)	141.7(10)	C(6)-Li(1)	255.7(16)
C(8)-C(9)	139.1(11)	C(8)-C(13)	139.4(11)
C(8)-Li(1)	231.8(17)	C(8)-Ti(1)	232.0(7)
C(9)-C(10)	139.9(10)	C(10)-C(11)	141.2(12)
C(11)-C(12)	137.9(13)	C(11)-C(14)	151.5(12)
C(12)-C(13)	138.8(11)	C(13)-Li(1)	261.1(16)
C(15)-C(16)	138.1(11)	C(15)-C(20)	141.5(11)
C(15)-Li(1)	230.3(17)	C(15)-Ti(1)	232.0(7)
C(16)-C(17)	140.4(12)	C(16)-Li(1)	260.6(17)
C(17)-C(18)	141.8(13)	C(18)-C(19)	138.3(12)
C(18)-C(21)	148.1(13)	C(19)-C(20)	142.0(11)
C(22)-C(23)	138(2)	C(23)-O(1)	144.8(12)
C(24)-O(1)	141.8(10)	C(24)-C(25)	154.3(16)
C(26)-C(27)	150.6(17)	C(27)-O(2)	141.7(13)
C(28)-C(29)	134(2)	C(28)-O(2)	150.4(14)
C(30)-C(31)	147.0(17)	C(31)-O(3)	141.2(11)
C(32)-C(33)	146.9(17)	C(32)-O(3)	148.0(11)
C(34)-C(35)	158.9(17)	C(35)-O(4)	143.0(10)
C(36)-C(37)	145(3)	C(36)-O(4)	145.3(14)
Cl-Li(2)#1	248(2)	Cl-Li(2)	248(2)
Li(1)-O(1)	194.1(15)	Li(1)-Ti(1)	266.6(14)
Li(2)-O(2)	192.7(19)	Li(2)-O(4)	193.5(18)
Li(2)-O(3)	197.0(18)	Ti(1)-C(8)#2	232.0(7)
Ti(1)-C(15)#2	232.0(7)	Ti(1)-C(1)#2	233.0(7)
Ti(1)-Li(1)#2	266.6(14)		
C(6)-C(1)-C(2)	112.7(6)	C(6)-C(1)-Li(1)	84.5(6)
C(2)-C(1)-Li(1)	121.4(6)	C(6)-C(1)-Ti(1)	125.6(5)
C(2)-C(1)-Ti(1)	121.6(5)	Li(1)-C(1)-Ti(1)	70.5(4)
C(3)-C(2)-C(1)	123.8(7)	C(2)-C(3)-C(4)	122.4(7)
C(5)-C(4)-C(3)	116.4(7)	C(5)-C(4)-C(7)	121.0(7)
C(3)-C(4)-C(7)	122.6(7)	C(4)-C(5)-C(6)	120.2(7)
C(1)-C(6)-C(5)	124.5(7)	C(1)-C(6)-Li(1)	62.9(5)
C(5)-C(6)-Li(1)	129.4(6)	C(9)-C(8)-C(13)	113.7(7)
C(9)-C(8)-Li(1)	125.1(7)	C(13)-C(8)-Li(1)	85.6(6)
C(9)-C(8)-Ti(1)	120.3(5)	C(13)-C(8)-Ti(1)	125.5(6)

Li(1)-C(8)-Ti(1)	70.2(4)	C(8)-C(9)-C(10)	123.7(7)
C(9)-C(10)-C(11)	120.6(8)	C(12)-C(11)-C(10)	116.4(7)
C(12)-C(11)-C(14)	120.6(9)	C(10)-C(11)-C(14)	122.8(8)
C(11)-C(12)-C(13)	121.3(8)	C(12)-C(13)-C(8)	124.2(8)
C(12)-C(13)-Li(1)	136.6(7)	C(8)-C(13)-Li(1)	62.3(5)
C(16)-C(15)-C(20)	113.6(7)	C(16)-C(15)-Li(1)	86.2(6)
C(20)-C(15)-Li(1)	124.6(6)	C(16)-C(15)-Ti(1)	128.1(6)
C(20)-C(15)-Ti(1)	117.9(5)	Li(1)-C(15)-Ti(1)	70.4(4)
C(15)-C(16)-C(17)	125.5(8)	C(15)-C(16)-Li(1)	61.9(5)
C(17)-C(16)-Li(1)	133.0(7)	C(16)-C(17)-C(18)	119.5(8)
C(19)-C(18)-C(17)	117.0(8)	C(19)-C(18)-C(21)	122.4(8)
C(17)-C(18)-C(21)	120.6(9)	C(18)-C(19)-C(20)	121.4(7)
C(15)-C(20)-C(19)	122.9(7)	C(22)-C(23)-O(1)	118.4(17)
O(1)-C(24)-C(25)	110.9(9)	O(2)-C(27)-C(26)	112.5(10)
C(29)-C(28)-O(2)	114.7(12)	O(3)-C(31)-C(30)	114.1(12)
C(33)-C(32)-O(3)	115.2(9)	O(4)-C(35)-C(34)	111.0(9)
C(37)-C(36)-O(4)	111.5(17)	Li(2)#1-Cl-Li(2)	177.1(7)
O(1)-Li(1)-C(1)	126.2(8)	O(1)-Li(1)-C(15)	128.7(8)
C(1)-Li(1)-C(15)	90.0(5)	O(1)-Li(1)-C(8)	119.4(7)
C(1)-Li(1)-C(8)	91.8(6)	C(15)-Li(1)-C(8)	90.0(6)
O(1)-Li(1)-C(6)	100.1(7)	C(1)-Li(1)-C(6)	32.6(3)
C(15)-Li(1)-C(6)	122.6(6)	C(8)-Li(1)-C(6)	89.8(6)
O(1)-Li(1)-C(16)	106.3(7)	C(1)-Li(1)-C(16)	88.2(5)
C(15)-Li(1)-C(16)	31.9(3)	C(8)-Li(1)-C(16)	122.0(7)
C(6)-Li(1)-C(16)	116.5(6)	O(1)-Li(1)-C(13)	97.2(6)
C(1)-Li(1)-C(13)	123.8(7)	C(15)-Li(1)-C(13)	87.2(5)
C(8)-Li(1)-C(13)	32.2(3)	C(6)-Li(1)-C(13)	118.0(6)
C(16)-Li(1)-C(13)	114.5(6)	O(1)-Li(1)-Ti(1)	174.2(8)
C(1)-Li(1)-Ti(1)	55.5(3)	C(15)-Li(1)-Ti(1)	55.1(4)
C(8)-Li(1)-Ti(1)	54.9(4)	C(6)-Li(1)-Ti(1)	79.3(4)
C(16)-Li(1)-Ti(1)	79.0(5)	C(13)-Li(1)-Ti(1)	78.2(5)
O(2)-Li(2)-O(4)	105.9(9)	O(2)-Li(2)-O(3)	106.3(10)
O(4)-Li(2)-O(3)	106.9(8)	O(2)-Li(2)-Cl	111.5(7)
O(4)-Li(2)-Cl	114.6(9)	O(3)-Li(2)-Cl	111.0(8)
C(24)-O(1)-C(23)	111.5(8)	C(24)-O(1)-Li(1)	119.0(7)

C(23)-O(1)-Li(1)	124.7(8)	C(27)-O(2)-C(28)	119.9(9)
C(27)-O(2)-Li(2)	117.0(8)	C(28)-O(2)-Li(2)	123.2(9)
C(31)-O(3)-C(32)	114.7(7)	C(31)-O(3)-Li(2)	122.3(8)
C(32)-O(3)-Li(2)	122.2(8)	C(35)-O(4)-C(36)	113.7(8)
C(35)-O(4)-Li(2)	125.0(8)	C(36)-O(4)-Li(2)	120.1(8)
C(8)-Ti(1)-C(8)#2	180.0(4)	C(8)-Ti(1)-C(15)#2	90.4(3)
C(8)#2-Ti(1)-C(15)#2	89.6(3)	C(8)-Ti(1)-C(15)	89.6(3)
C(8)#2-Ti(1)-C(15)	90.4(3)	C(15)#2-Ti(1)-C(15)	180.000(1)
C(8)-Ti(1)-C(1)#2	89.4(3)	C(8)#2-Ti(1)-C(1)#2	90.6(3)
C(15)#2-Ti(1)-C(1)#2	88.6(3)	C(15)-Ti(1)-C(1)#2	91.4(3)
C(8)-Ti(1)-C(1)	90.6(3)	C(8)#2-Ti(1)-C(1)	89.4(3)
C(15)#2-Ti(1)-C(1)	91.4(3)	C(15)-Ti(1)-C(1)	88.6(3)
C(1)#2-Ti(1)-C(1)	180.000(1)	C(8)-Ti(1)-Li(1)#2	125.1(4)
C(8)#2-Ti(1)-Li(1)#2	54.9(4)	C(15)#2-Ti(1)-Li(1)#2	54.5(4)
C(15)-Ti(1)-Li(1)#2	125.5(4)	C(1)#2-Ti(1)-Li(1)#2	54.0(3)
C(1)-Ti(1)-Li(1)#2	126.0(3)	C(8)-Ti(1)-Li(1)	54.9(4)
C(8)#2-Ti(1)-Li(1)	125.1(4)	C(15)#2-Ti(1)-Li(1)	125.5(4)
C(15)-Ti(1)-Li(1)	54.5(4)	C(1)#2-Ti(1)-Li(1)	126.0(3)
C(1)-Ti(1)-Li(1)	54.0(3)	Li(1)#2-Ti(1)-Li(1)	180.0(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+1/2 #2 -x+2,-y,-z+1

Table 16. Anisotropic displacement parameters ($pm^2 x\ 10^{-1}$)for $Li_4ClTi(p\text{-}C_6H_4\text{-}CH_3)_6 \cdot 8(Et_2O)$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	29(3)	45(4)	39(4)	-3(3)	17(3)	-3(3)
C(2)	33(4)	38(4)	51(5)	2(3)	17(3)	9(3)
C(3)	42(4)	49(5)	52(5)	-11(4)	23(4)	1(3)
C(4)	34(4)	39(4)	41(4)	-1(3)	14(3)	0(3)
C(5)	34(4)	44(4)	40(4)	1(3)	15(3)	-1(3)
C(6)	30(3)	44(4)	37(4)	-3(3)	11(3)	1(3)
C(7)	44(4)	57(5)	54(5)	-4(4)	30(4)	0(4)
C(8)	37(4)	40(4)	40(4)	7(3)	20(3)	6(3)
C(9)	41(4)	47(4)	52(5)	7(4)	26(4)	6(3)
C(10)	43(4)	43(4)	61(5)	15(4)	23(4)	9(3)

C(11)	44(4)	48(5)	70(6)	19(4)	30(4)	12(4)
C(12)	39(4)	67(6)	63(6)	14(4)	22(4)	15(4)
C(13)	35(4)	54(5)	54(5)	12(4)	21(4)	9(3)
C(14)	58(6)	61(6)	122(9)	31(6)	39(6)	23(5)
C(15)	39(4)	38(4)	33(4)	-4(3)	5(3)	5(3)
C(16)	45(4)	43(4)	48(5)	1(4)	15(4)	8(3)
C(17)	62(5)	43(4)	52(5)	-3(4)	14(4)	3(4)
C(18)	51(5)	45(4)	55(5)	5(4)	15(4)	-2(4)
C(19)	41(4)	49(4)	45(5)	-1(4)	13(4)	-5(3)
C(20)	43(4)	43(4)	36(4)	1(3)	12(3)	0(3)
C(21)	84(7)	59(6)	63(6)	-10(5)	14(5)	-9(5)
C(22)	137(15)	240(30)	240(20)	-170(20)	99(17)	-79(17)
C(23)	128(10)	46(5)	115(10)	19(6)	86(9)	10(6)
C(24)	54(5)	65(6)	44(5)	-15(4)	6(4)	-11(4)
C(25)	81(8)	82(7)	75(8)	7(6)	26(6)	-15(6)
C(26)	105(9)	95(9)	73(8)	-19(7)	27(7)	-2(7)
C(27)	84(7)	67(6)	97(9)	-8(6)	50(7)	5(6)
C(28)	118(11)	90(9)	77(8)	8(7)	40(8)	-17(8)
C(29)	116(13)	340(30)	143(16)	170(20)	25(12)	-8(17)
C(30)	165(16)	170(17)	183(17)	-103(15)	141(15)	-89(14)
C(31)	69(6)	79(6)	43(5)	0(5)	27(5)	-15(5)
C(32)	49(6)	79(7)	99(9)	30(7)	-9(5)	5(5)
C(33)	48(5)	107(8)	40(5)	2(5)	5(4)	7(5)
C(34)	103(9)	99(9)	96(9)	-40(7)	66(8)	-29(7)
C(35)	48(5)	56(5)	81(7)	-30(5)	23(5)	-4(4)
C(36)	150(15)	112(10)	179(16)	-69(11)	137(14)	-64(10)
C(37)	56(8)	320(30)	250(20)	-220(20)	84(12)	-90(12)
Cl	1(1)	33(1)	7(1)	0	-13(1)	0
Li(1)	36(7)	63(8)	44(8)	3(7)	8(6)	4(6)
Li(2)	88(12)	50(8)	78(12)	-17(8)	54(10)	-17(8)
O(1)	57(3)	53(3)	52(4)	-2(3)	21(3)	1(3)
O(2)	89(5)	67(4)	53(4)	9(3)	30(4)	-3(4)
O(3)	41(3)	68(4)	63(4)	20(3)	11(3)	-3(3)
O(4)	74(5)	66(4)	105(6)	-39(4)	59(5)	-29(3)
Ti(1)	30(1)	32(1)	38(1)	0(1)	12(1)	4(1)

8.2 Zirconium Complexes

8.2.1 $[NBu_4][Zr(C_6H_5)_5]\cdot 4CH_2Cl_2$

8.2.1.1 Preparation of $[NBu_4][Zr(C_6H_5)_5]\cdot 4CH_2Cl_2$

To a suspension of $ZrCl_4$ (0.520 g, 2.23 mmol) in 50 mL ether at –78^oC was added slowly a 14 mL solution of LiC_6H_5 (ca.13.38 mmol). The resulting suspension was allowed to warm up to –35^oC. At this stage the $ZrCl_4$-ether adduct, as well as any LiC_6H_5 that may have separated, dissolved and after that some white solid was separated and a yellow-brown solution formed. The reaction mixture was stirred for 6 h at –35^oC. The reaction mixture was filtered at –35^oC. $[NBu_4]Br$ (0.72 g, 2.23 mmol) was further added to the solution at –35^oC and the mixture was allowed to reach –15^oC. After the mixture had been stirred for 5 h at –15^oC, the white off solid in suspension was filtered off, washed with Et_2O and vacuum dried at –15^oC. The solid was dissolved in CH_2Cl_2 (30 mL) at –35^oC, yellow solution was formed with small amount of white solid. The resulting yellow solution was filtered off and concentrated to the half. Addition of Et_2O layer (30 mL) to the CH_2Cl_2 solution with slow diffusion at –80^oC gave a yellow solid, which was filtered off, washed with Et_2O at –35^oC and vacuum dried. ^1H NMR (400 MHz, CD_2Cl_2, −40^oC): δ = 7.93 (ph-H, d), 7.10 (ph-H, t), 6.97 (ph-H, t), 2.75 ($CH_3(CH_2)_3N$, s), 1.31($CH_3(CH_2)_3N$, br) 0.958 ppm ($CH_3(CH_2)_3N$, s); $[^1H]^{13}C$ NMR (100.4 MHz, CD_2Cl_2, −40^oC): δ = 132.7, 128.0, 126.2, 125.0, {58.4 ,23.9, 19.8, 13.8} ppm. ($CH_3(CH_2)_3N$).

8.2.1.2 Crystal Data and Crystal Structure Analysis of $[NBu_4][Zr(C_6H_5)_5]\cdot 4CH_2Cl_2$

Table 17. Crystal data and structure refinement for $[NBu_4][Zr(C_6H_5)_5]\cdot 4CH_2Cl_2$.

Identification code	zrphe	
Empirical formula	$C_{60}\ H_{60}\ Cl_8\ N_2\ Zr$	
Formula weight	1183.92	
Temperature	133(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 2361.8(13) pm	α= 90°.
	b = 2095.5(10) pm	β= 117.89(7)°.
	c = 2446(2) pm	γ = 90°.
Volume	10.70(1) nm^3	
Z	8	
Density (calculated)	1.470 Mg/m^3	
Absorption coefficient	0.648 mm^{-1}	
F(000)	4880	
Crystal size	0.4 x 0.3 x 0.3 mm^3	
Theta range for data collection	1.38 to 24.04°.	
Index ranges	-26<=h<=26, -24<=k<=19, -27<=l<=27	
Reflections collected	52005	
Independent reflections	8398 [R(int) = 0.0514]	
Completeness to theta = 24.04°	99.5 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8398 / 0 / 545	
Goodness-of-fit on F^2	1.010	
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.1046	
R indices (all data)	R1 = 0.0641, wR2 = 0.1168	
Largest diff. peak and hole	0.726 and -0.524 e.$Å^{-3}$	

Table 18. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for $[NBu_4][Zr(C_6H_5)_5]\cdot 4CH_2Cl_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	246(2)	1896(2)	951(2)	27(1)
C(2)	508(2)	1747(2)	1579(2)	31(1)
C(3)	259(2)	1280(2)	1807(2)	38(1)
C(4)	-268(2)	934(2)	1402(2)	41(1)
C(5)	-548(2)	1068(2)	777(2)	38(1)
C(6)	-294(2)	1538(2)	562(2)	32(1)
C(7)	1163(2)	3482(2)	1251(2)	29(1)
C(8)	1050(2)	3528(2)	1757(2)	36(1)
C(9)	1308(2)	4010(2)	2196(2)	44(1)
C(10)	1693(2)	4462(2)	2137(2)	40(1)
C(11)	1815(2)	4434(2)	1642(2)	44(1)
C(12)	1557(2)	3955(2)	1208(2)	39(1)
C(13)	-131(2)	3410(2)	85(2)	40(1)
C(14)	-109(2)	4018(2)	-174(2)	41(1)
C(15)	-640(2)	4414(2)	-419(2)	43(1)
C(16)	-1193(2)	4241(2)	-399(2)	40(1)
C(17)	-1218(2)	3660(2)	-143(2)	42(1)
C(18)	-638(2)	3254(2)	79(1)	30(1)
C(19)	528(2)	2494(2)	-395(2)	29(1)
C(20)	348(2)	1891(2)	-642(2)	38(1)
C(21)	279(2)	1721(2)	-1223(2)	46(1)
C(22)	387(2)	2158(2)	-1569(2)	46(1)
C(23)	552(2)	2769(2)	-1354(2)	48(1)
C(24)	626(2)	2935(2)	-771(2)	38(1)
C(25)	1686(2)	2323(2)	824(2)	40(1)
C(26)	1819(1)	1813(2)	1102(1)	24(1)
C(27)	2393(2)	1426(2)	1241(2)	41(1)
C(28)	2841(2)	1699(2)	1090(2)	39(1)
C(29)	2714(2)	2288(2)	807(2)	40(1)
C(30)	2145(2)	2598(2)	665(2)	41(1)
C(31)	6949(2)	2928(2)	2465(2)	29(1)

C(32)	6407(2)	3380(2)	2353(2)	34(1)
C(33)	6529(2)	3731(2)	2940(2)	41(1)
C(34)	6008(2)	4210(2)	2836(2)	47(1)
C(35)	6261(2)	2079(2)	1727(2)	29(1)
C(36)	6280(2)	1663(2)	2248(2)	37(1)
C(37)	5830(2)	1099(2)	2009(2)	37(1)
C(38)	5820(2)	718(2)	2535(2)	43(1)
C(39)	6713(2)	2906(2)	1348(2)	28(1)
C(40)	7231(2)	3375(2)	1421(2)	32(1)
C(41)	7053(2)	3724(2)	818(2)	38(1)
C(42)	7566(2)	4190(2)	865(2)	55(1)
C(43)	7453(2)	2114(2)	2123(2)	32(1)
C(44)	7446(2)	1637(2)	1658(2)	43(1)
C(45)	8072(2)	1268(2)	1911(2)	51(1)
C(46)	8091(2)	801(2)	1448(3)	62(1)
C(50)	982(2)	10240(2)	1055(2)	48(1)
C(51)	9004(2)	2556(2)	1278(2)	50(1)
C(52)	8208(2)	8961(2)	346(2)	47(1)
C(53)	5328(2)	344(2)	8835(2)	52(1)
Cl(1)	1676(1)	10083(1)	1752(1)	58(1)
Cl(2)	497(1)	9566(1)	786(1)	68(1)
Cl(3)	9051(1)	2719(1)	2001(1)	58(1)
Cl(4)	8217(1)	2444(1)	697(1)	58(1)
Cl(5)	8729(1)	9560(1)	351(1)	60(1)
Cl(6)	7502(1)	9293(1)	281(1)	73(1)
Cl(7)	5883(1)	-274(1)	9087(1)	80(1)
Cl(8)	5440(1)	841(1)	8321(1)	60(1)
N	6844(1)	2507(1)	1917(1)	27(1)
Zr	667(1)	2670(1)	579(1)	23(1)

Table 19. Bond lengths [pm] and angles [°] for $[NBu_4][Zr(C_6H_5)_5]\cdot 4CH_2Cl_2$.

C(1)-C(2)	139.6(5)	C(1)-C(6)	140.1(5)	C(1)-Zr	230.0(3)
C(2)-C(3)	138.7(5)	C(2)-H(2)	95.00	C(3)-C(4)	137.9(6)
C(3)-H(3)	95.00	C(4)-C(5)	138.2(6)	C(4)-H(4)	95.00

C(5)-C(6)	137.9(5)	C(5)-H(5)	95.00	C(6)-H(6)	95.00
C(7)-C(8)	138.4(5)	C(7)-C(12)	139.8(5)	C(7)-Zr	227.3(4)
C(8)-C(9)	139.0(5)	C(8)-H(8)	95.00	C(9)-C(10)	136.7(6)
C(9)-H(9)	95.00	C(10)-C(11)	137.1(6)	C(10)-H(10)	95.00
C(11)-C(12)	137.9(6)	C(11)-H(11)	95.00	C(12)-H(12)	95.00
C(13)-C(18)	123.4(5)	C(13)-C(14)	143.4(6)	C(13)-Zr	229.9(4)
C(14)-C(15)	138.5(6)	C(14)-H(14)	95.00	C(15)-C(16)	138.0(6)
C(15)-H(15)	95.00	C(16)-C(17)	138.2(6)	C(16)-H(16)	95.00
C(17)-C(18)	148.3(6)	C(17)-H(17)	95.00	C(18)-H(18)	95.00
C(19)-C(20)	138.0(5)	C(19)-C(24)	139.8(5)	C(19)-Zr	227.7(4)
C(20)-C(21)	139.8(5)	C(20)-H(20)	95.00	C(21)-C(22)	135.0(6)
C(21)-H(21)	95.00	C(22)-C(23)	137.0(6)	C(22)-H(22)	95.00
C(23)-C(24)	139.7(6)	C(23)-H(23)	95.00	C(24)-H(24)	95.00
C(25)-C(26)	122.8(5)	C(25)-C(30)	143.2(6)	C(25)-Zr	230.9(4)
C(26)-C(27)	147.8(5)	C(26)-H(26)	95.00	C(27)-C(28)	139.4(5)
C(27)-H(27)	95.00	C(28)-C(29)	137.7(6)	C(28)-H(28)	95.00
C(29)-C(30)	138.1(5)	C(29)-H(29)	95.00	C(30)-H(30)	95.00
C(31)-C(32)	151.1(5)	C(31)-N	152.6(4)	C(31)-H(31A)	99.00
C(31)-H(31B)	99.00	C(32)-C(33)	151.6(5)	C(32)-H(32A)	99.00
C(32)-H(32B)	99.00	C(33)-C(34)	151.4(6)	C(33)-H(33A)	99.00
C(33)-H(33B)	99.00	C(34)-H(34A)	98.00	C(34)-H(34B)	98.00
C(34)-H(34C)	98.00	C(35)-N	152.3(4)	C(35)-C(36)	152.7(5)
C(35)-H(35A)	99.00	C(35)-H(35B)	99.00	C(36)-C(37)	151.3(5)
C(36)-H(36A)	99.00	C(36)-H(36B)	99.00	C(37)-C(38)	152.4(5)
C(37)-H(37A)	99.00	C(37)-H(37B)	99.00	C(38)-H(38A)	98.00
C(38)-H(38B)	98.00	C(38)-H(38C)	98.00	C(39)-C(40)	151.4(5)
C(39)-N	152.4(4)	C(39)-H(39A)	99.00	C(39)-H(39B)	99.00
C(40)-C(41)	151.9(5)	C(40)-H(40A)	99.00	C(40)-H(40B)	99.00
C(41)-C(42)	151.8(6)	C(41)-H(41A)	99.00	C(41)-H(41B)	99.00
C(42)-H(42A)	98.00	C(42)-H(42B)	98.00	C(42)-H(42C)	98.00
C(43)-C(44)	150.8(5)	C(43)-N	152.3(4)	C(43)-H(43A)	99.00
C(43)-H(43B)	99.00	C(44)-C(45)	152.1(5)	C(44)-H(44A)	99.00
C(44)-H(44B)	99.00	C(45)-C(46)	151.3(6)	C(45)-H(45A)	99.00
C(45)-H(45B)	99.00	C(46)-H(46A)	98.00	C(46)-H(46B)	98.00
C(46)-H(46C)	98.00	C(50)-Cl(2)	174.2(4)	C(50)-Cl(1)	175.8(5)

C(50)-H(50A)	99.00	C(50)-H(50B)	99.00	C(51)-Cl(4)	174.8(5)
C(51)-Cl(3)	175.5(4)	C(51)-H(51A)	99.00	C(51)-H(51B)	99.00
C(52)-Cl(6)	174.2(5)	C(52)-Cl(5)	175.4(4)	C(52)-H(52A)	99.00
C(52)-H(52B)	99.00	C(53)-Cl(7)	173.8(5)	C(53)-Cl(8)	174.8(4)
C(53)-H(53A)	99.00	C(53)-H(53B)	99.00		
C(2)-C(1)-C(6)	114.9(3)	C(2)-C(1)-Zr	122.8(3)	C(6)-C(1)-Zr	122.2(3)
C(3)-C(2)-C(1)	123.2(3)	C(3)-C(2)-H(2)	118.4	C(1)-C(2)-H(2)	118.4
C(4)-C(3)-C(2)	119.6(3)	C(4)-C(3)-H(3)	120.2	C(2)-C(3)-H(3)	120.2
C(3)-C(4)-C(5)	119.4(4)	C(3)-C(4)-H(4)	120.3	C(5)-C(4)-H(4)	120.3
C(6)-C(5)-C(4)	120.0(4)	C(6)-C(5)-H(5)	120.0	C(4)-C(5)-H(5)	120.0
C(5)-C(6)-C(1)	123.0(3)	C(5)-C(6)-H(6)	118.5	C(1)-C(6)-H(6)	118.5
C(8)-C(7)-C(12)	115.5(3)	C(8)-C(7)-Zr	116.7(3)	C(12)-C(7)-Zr	127.8(3)
C(7)-C(8)-C(9)	123.0(4)	C(7)-C(8)-H(8)	118.5	C(9)-C(8)-H(8)	118.5
C(10)-C(9)-C(8)	119.6(4)	C(10)-C(9)-H(9)	120.2	C(8)-C(9)-H(9)	120.2
C(11)-C(10)-C(9)	119.3(4)	C(11)-C(10)-H(10)	120.4	C(9)-C(10)-H(10)	120.4
C(10)-C(11)-C(12)	120.7(4)	C(10)-C(11)-H(11)	119.6	C(12)-C(11)-H(11)	119.6
C(11)-C(12)-C(7)	121.9(4)	C(11)-C(12)-H(12)	119.0	C(7)-C(12)-H(12)	119.0
C(18)-C(13)-C(14)	117.7(4)	C(18)-C(13)-Zr	112.3(3)	C(14)-C(13)-Zr	129.9(3)
C(15)-C(14)-C(13)	120.7(4)	C(15)-C(14)-H(14)	119.6	C(13)-C(14)-H(14)	119.6
C(16)-C(15)-C(14)	120.5(4)	C(16)-C(15)-H(15)	119.7	C(14)-C(15)-H(15)	119.7
C(17)-C(16)-C(15)	119.3(4)	C(17)-C(16)-H(16)	120.4	C(15)-C(16)-H(16)	120.4
C(16)-C(17)-C(18)	116.3(4)	C(16)-C(17)-H(17)	121.8	C(18)-C(17)-H(17)	121.8
C(13)-C(18)-C(17)	125.3(4)	C(13)-C(18)-H(18)	117.4	C(17)-C(18)-H(18)	117.4
C(20)-C(19)-C(24)	115.4(3)	C(20)-C(19)-Zr	118.1(3)	C(24)-C(19)-Zr	126.5(3)
C(19)-C(20)-C(21)	123.0(4)	C(19)-C(20)-H(20)	118.5	C(21)-C(20)-H(20)	118.5
C(22)-C(21)-C(20)	119.9(4)	C(22)-C(21)-H(21)	120.1	C(20)-C(21)-H(21)	120.1
C(21)-C(22)-C(23)	119.7(4)	C(21)-C(22)-H(22)	120.1	C(23)-C(22)-H(22)	120.1
C(22)-C(23)-C(24)	120.2(4)	C(22)-C(23)-H(23)	119.9	C(24)-C(23)-H(23)	119.9
C(19)-C(24)-C(23)	121.8(4)	C(19)-C(24)-H(24)	119.1	C(23)-C(24)-H(24)	119.1
C(26)-C(25)-C(30)	118.2(4)	C(26)-C(25)-Zr	112.4(3)	C(30)-C(25)-Zr	129.3(3)
C(25)-C(26)-C(27)	125.0(3)	C(25)-C(26)-H(26)	117.5	C(27)-C(26)-H(26)	117.5
C(28)-C(27)-C(26)	116.2(4)	C(28)-C(27)-H(27)	121.9	C(26)-C(27)-H(27)	121.9
C(29)-C(28)-C(27)	119.2(4)	C(29)-C(28)-H(28)	120.4	C(27)-C(28)-H(28)	120.4
C(28)-C(29)-C(30)	120.4(4)	C(28)-C(29)-H(29)	119.8	C(30)-C(29)-H(29)	119.8
C(29)-C(30)-C(25)	120.8(4)	C(29)-C(30)-H(30)	119.6	C(25)-C(30)-H(30)	119.6

C(32)-C(31)-N	115.3(3)	C(32)-C(31)-H(31A)	108.5	N-C(31)-H(31A)	108.5
C(32)-C(31)-H(31B)	108.5	N-C(31)-H(31B)	108.5	H(31A)-C(31)-H(31B)	107.5
C(31)-C(32)-C(33)	111.2(3)	C(31)-C(32)-H(32A)	109.4	C(33)-C(32)-H(32A)	109.4
C(31)-C(32)-H(32B)	109.4	C(33)-C(32)-H(32B)	109.4	H(32A)-C(32)-H(32B)	108.0
C(32)-C(33)-C(34)	112.5(3)	C(32)-C(33)-H(33A)	109.1	C(34)-C(33)-H(33A)	109.1
C(32)-C(33)-H(33B)	109.1	C(34)-C(33)-H(33B)	109.1	H(33A)-C(33)-H(33B)	107.8
C(33)-C(34)-H(34A)	109.5	C(33)-C(34)-H(34B)	109.5	H(34A)-C(34)-H(34B)	109.5
C(33)-C(34)-H(34C)	109.5	H(34A)-C(34)-H(34C)	109.5	H(34B)-C(34)-H(34C)	109.5
N-C(35)-C(36)	114.4(3)	N-C(35)-H(35A)	108.7	C(36)-C(35)-H(35A)	108.7
N-C(35)-H(35B)	108.7	C(36)-C(35)-H(35B)	108.7	H(35A)-C(35)-H(35B)	107.6
C(37)-C(36)-C(35)	112.4(3)	C(37)-C(36)-H(36A)	109.1	C(35)-C(36)-H(36A)	109.1
C(37)-C(36)-H(36B)	109.1	C(35)-C(36)-H(36B)	109.1	H(36A)-C(36)-H(36B)	107.9
C(36)-C(37)-C(38)	111.6(3)	C(36)-C(37)-H(37A)	109.3	C(38)-C(37)-H(37A)	109.3
C(36)-C(37)-H(37B)	109.3	C(38)-C(37)-H(37B)	109.3	H(37A)-C(37)-H(37B)	108.0
C(37)-C(38)-H(38A)	109.5	C(37)-C(38)-H(38B)	109.5	H(38A)-C(38)-H(38B)	109.5
C(37)-C(38)-H(38C)	109.5	H(38A)-C(38)-H(38C)	109.5	H(38B)-C(38)-H(38C)	109.5
C(40)-C(39)-N	116.1(3)	C(40)-C(39)-H(39A)	108.3	N-C(39)-H(39A)	108.3
C(40)-C(39)-H(39B)	108.3	N-C(39)-H(39B)	108.3	H(39A)-C(39)-H(39B)	107.4
C(39)-C(40)-C(41)	111.0(3)	C(39)-C(40)-H(40A)	109.4	C(41)-C(40)-H(40A)	109.4
C(39)-C(40)-H(40B)	109.4	C(41)-C(40)-H(40B)	109.4	H(40A)-C(40)-H(40B)	108.0
C(40)-C(41)-C(42)	112.8(3)	C(40)-C(41)-H(41A)	109.0	C(42)-C(41)-H(41A)	109.0
C(40)-C(41)-H(41B)	109.0	C(42)-C(41)-H(41B)	109.0	H(41A)-C(41)-H(41B)	107.8
C(41)-C(42)-H(42A)	109.5	C(41)-C(42)-H(42B)	109.5	H(42A)-C(42)-H(42B)	109.5
C(41)-C(42)-H(42C)	109.5	H(42A)-C(42)-H(42C)	109.5	H(42B)-C(42)-H(42C)	109.5
C(44)-C(43)-N	115.6(3)	C(44)-C(43)-H(43A)	108.4	N-C(43)-H(43A)	108.4
C(44)-C(43)-H(43B)	108.4	N-C(43)-H(43B)	108.4	H(43A)-C(43)-H(43B)	107.4
C(43)-C(44)-C(45)	111.4(3)	C(43)-C(44)-H(44A)	109.3	C(45)-C(44)-H(44A)	109.3
C(43)-C(44)-H(44B)	109.3	C(45)-C(44)-H(44B)	109.3	H(44A)-C(44)-H(44B)	108.0
C(46)-C(45)-C(44)	112.9(4)	C(46)-C(45)-H(45A)	109.0	C(44)-C(45)-H(45A)	109.0
C(46)-C(45)-H(45B)	109.0	C(44)-C(45)-H(45B)	109.0	H(45A)-C(45)-H(45B)	107.8
C(45)-C(46)-H(46A)	109.5	C(45)-C(46)-H(46B)	109.5	H(46A)-C(46)-H(46B)	109.5
C(45)-C(46)-H(46C)	109.5	H(46A)-C(46)-H(46C)	109.5	H(46B)-C(46)-H(46C)	109.5
Cl(2)-C(50)-Cl(1)	111.4(2)	Cl(2)-C(50)-H(50A)	109.3	Cl(1)-C(50)-H(50A)	109.3
Cl(2)-C(50)-H(50B)	109.3	Cl(1)-C(50)-H(50B)	109.3	H(50A)-C(50)-H(50B)	108.0
Cl(4)-C(51)-Cl(3)	112.8(2)	Cl(4)-C(51)-H(51A)	109.0	Cl(3)-C(51)-H(51A)	109.0

Cl(4)-C(51)-H(51B)	109.0	Cl(3)-C(51)-H(51B)	109.0	H(51A)-C(51)-H(51B)	107.8
Cl(6)-C(52)-Cl(5)	110.8(2)	Cl(6)-C(52)-H(52A)	109.5	Cl(5)-C(52)-H(52A)	109.5
Cl(6)-C(52)-H(52B)	109.5	Cl(5)-C(52)-H(52B)	109.5	H(52A)-C(52)-H(52B)	108.1
Cl(7)-C(53)-Cl(8)	110.8(2)	Cl(7)-C(53)-H(53A)	109.5	Cl(8)-C(53)-H(53A)	109.5
Cl(7)-C(53)-H(53B)	109.5	Cl(8)-C(53)-H(53B)	109.5	H(53A)-C(53)-H(53B)	108.1
C(35)-N-C(31)	111.1(3)	C(35)-N-C(39)	106.0(3)	C(31)-N-C(39)	111.4(3)
C(35)-N-C(43)	111.1(3)	C(31)-N-C(43)	106.3(3)	C(39)-N-C(43)	110.9(3)
C(7)-Zr-C(19)	130.62(13)	C(7)-Zr-C(13)	83.90(15)	C(19)-Zr-C(13)	82.96(13)
C(7)-Zr-C(1)	114.39(13)	C(19)-Zr-C(1)	114.98(13)	C(13)-Zr-C(1)	106.52(15)
C(7)-Zr-C(25)	85.75(13)	C(19)-Zr-C(25)	80.96(15)	C(13)-Zr-C(25)	147.87(17)
C(1)-Zr-C(25)	105.47(15)				

Symmetry transformations used to generate equivalent atoms:

Table 20. Anisotropic displacement parameters ($pm^2 x\ 10^{-1}$)for $[NBu_4][Zr(C_6H_5)_5]\cdot 4CH_2Cl_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	28(2)	26(2)	29(2)	2(2)	13(2)	3(2)
C(2)	29(2)	37(2)	28(2)	-5(2)	13(2)	-5(2)
C(3)	38(2)	50(2)	26(2)	8(2)	15(2)	0(2)
C(4)	38(2)	38(2)	51(3)	9(2)	24(2)	-4(2)
C(5)	34(2)	32(2)	41(2)	-2(2)	13(2)	-7(2)
C(6)	32(2)	34(2)	26(2)	0(2)	10(2)	2(2)
C(7)	25(2)	31(2)	27(2)	0(2)	10(2)	5(2)
C(8)	36(2)	41(2)	32(2)	-4(2)	17(2)	-7(2)
C(9)	51(3)	49(3)	34(2)	-11(2)	21(2)	-2(2)
C(10)	37(2)	31(2)	38(2)	-11(2)	6(2)	2(2)
C(11)	37(2)	34(2)	57(3)	-1(2)	19(2)	-5(2)
C(12)	40(2)	43(2)	40(2)	-2(2)	23(2)	-3(2)
C(13)	64(3)	37(2)	13(2)	-4(2)	12(2)	16(2)
C(14)	48(3)	44(2)	36(2)	-2(2)	23(2)	2(2)
C(15)	56(3)	39(2)	31(2)	2(2)	18(2)	3(2)
C(16)	40(2)	42(2)	30(2)	-1(2)	9(2)	6(2)
C(17)	42(2)	51(3)	31(2)	-4(2)	15(2)	-1(2)

C(18)	54(3)	15(2)	3(2)	1(1)	-2(2)	-4(2)
C(19)	28(2)	32(2)	24(2)	1(2)	11(2)	8(2)
C(20)	43(2)	40(2)	29(2)	-2(2)	14(2)	2(2)
C(21)	49(3)	47(3)	32(2)	-11(2)	11(2)	6(2)
C(22)	40(2)	71(3)	24(2)	-3(2)	13(2)	16(2)
C(23)	41(2)	67(3)	41(2)	18(2)	24(2)	9(2)
C(24)	41(2)	40(2)	36(2)	2(2)	21(2)	1(2)
C(25)	25(2)	56(3)	37(2)	-30(2)	12(2)	-9(2)
C(26)	7(2)	63(3)	1(1)	3(2)	-1(1)	-6(2)
C(27)	43(2)	43(2)	30(2)	2(2)	13(2)	-2(2)
C(28)	30(2)	52(3)	32(2)	-5(2)	12(2)	3(2)
C(29)	33(2)	54(3)	34(2)	-4(2)	17(2)	-4(2)
C(30)	40(2)	44(2)	38(2)	1(2)	17(2)	4(2)
C(31)	31(2)	33(2)	16(2)	-1(2)	6(2)	-8(2)
C(32)	37(2)	36(2)	26(2)	-2(2)	12(2)	-4(2)
C(33)	43(2)	45(2)	37(2)	-13(2)	22(2)	-8(2)
C(34)	61(3)	42(2)	46(2)	-7(2)	32(2)	-7(2)
C(35)	27(2)	33(2)	24(2)	-3(2)	8(2)	-6(2)
C(36)	42(2)	42(2)	27(2)	-1(2)	14(2)	-12(2)
C(37)	42(2)	34(2)	38(2)	-2(2)	21(2)	-6(2)
C(38)	55(3)	37(2)	44(2)	-7(2)	30(2)	-13(2)
C(39)	30(2)	33(2)	19(2)	2(2)	10(2)	3(2)
C(40)	30(2)	35(2)	28(2)	4(2)	12(2)	0(2)
C(41)	40(2)	40(2)	34(2)	11(2)	19(2)	7(2)
C(42)	55(3)	58(3)	55(3)	23(2)	29(2)	1(2)
C(43)	24(2)	36(2)	29(2)	8(2)	7(2)	1(2)
C(44)	34(2)	44(2)	48(3)	-7(2)	17(2)	1(2)
C(45)	44(3)	41(3)	65(3)	10(2)	23(2)	12(2)
C(46)	50(3)	40(3)	107(4)	-5(3)	44(3)	6(2)
C(50)	53(3)	42(3)	54(3)	6(2)	29(2)	5(2)
C(51)	46(3)	60(3)	50(3)	-9(2)	29(2)	-2(2)
C(52)	56(3)	45(3)	36(2)	5(2)	17(2)	-12(2)
C(53)	65(3)	55(3)	42(3)	-12(2)	30(2)	-23(2)
Cl(1)	60(1)	54(1)	54(1)	1(1)	22(1)	-3(1)
Cl(2)	59(1)	47(1)	83(1)	-10(1)	19(1)	-3(1)

Cl(3)	65(1)	74(1)	39(1)	4(1)	28(1)	-3(1)
Cl(4)	51(1)	72(1)	46(1)	-3(1)	18(1)	1(1)
Cl(5)	59(1)	44(1)	73(1)	5(1)	29(1)	-12(1)
Cl(6)	83(1)	64(1)	100(1)	-8(1)	67(1)	-13(1)
Cl(7)	140(1)	45(1)	81(1)	4(1)	73(1)	7(1)
Cl(8)	65(1)	68(1)	55(1)	9(1)	36(1)	-5(1)
N	25(2)	30(2)	22(2)	-1(1)	7(1)	-4(1)
Zr	26(1)	25(1)	19(1)	0(1)	10(1)	-1(1)

8.2.2 $[Li(THF)_4]_2[Zr(C_6H_5)_6]$

8.2.2.1 Preparation of $[Li(THF)_4]_2[Zr(C_6H_5)_6]$

14.60 mL (18.25 mmol) of a 1.25 M solution of phenyl lithium in diethyl ether was added slowly to a slurry of $ZrCl_4$ (0.53 g, 2.27 mmol) in diethyl ether (50 mL) at –78°C. The resulting suspension was allowed to warm up to –35°C. At this point all insoluble materials dissolved forming a yellow-brown solution, after that some white precipitate formed. The reaction mixture was stirred overnight at –35°C. The reaction mixture was filtered at –35°C, and then the solvent was removed under vacuum. The resulting yellow-brown oily residue was dissolved in THF (25 mL) at –35°C, and slow diffusion of *n*-pentane layer (50 mL) at –45°C yielded **$[Li(THF)_4]_2[Zr(C_6H_5)_6]$** as a pink crystals. ^{1}H NMR (400 MHz, CD_2Cl_2, −40°C): δ = 7.89 (ph-H, d), 7.06 (ph-H, t), 6.92 (ph-H, t), 3.66 (C_4H_8O), 1.78 ppm (C_4H_8O); [^{1}H]^{13}C NMR (100.4 MHz, CD_2Cl_2, −40°C): δ = 132.4, 128.9, 126.1, 124.89, 67.9 (C_4H_8O), 25.7 ppm (C_4H_8O).

8.2.2.2 Crystal Data and Crystal Structure Analysis of $[Li(THF)_4]_2[Zr(C_6H_5)_6]$

Table 21. Crystal data and structure refinement for $[Li(THF)_4]_2[Zr(C_6H_5)_6]$.

Identification code	zrph6	
Empirical formula	$C_{68}\ H_{92}\ Li_2\ O_8\ Zr$	
Formula weight	1142.52	
Temperature	133(2) K	
Wavelength	71.073 pm	
Crystal system	Hexagonal	
Space group	P 65 (170)	
Unit cell dimensions	a = 1317.3(3) pm	α= 90°.
	b = 1317.3(3) pm	β= 90°.
	c = 6310(3) pm	γ = 120°.
Volume	9.48(1) nm^3	
Z	6	
Density (calculated)	1.200 Mg/m^3	
Absorption coefficient	0.226 mm^{-1}	
F(000)	3660	
Crystal size	0.4 x 0.4 x 0.3 mm^3	
Theta range for data collection	4.23 to 27.09°.	
Index ranges	-16<=h<=16, -16<=k<=16, -80<=l<=63	
Reflections collected	70963	
Independent reflections	11956 [R(int) = 0.0626]	
Completeness to theta = 27.09°	99.1 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11956 / 1 / 712	
Goodness-of-fit on F^2	1.111	
Final R indices [I>2sigma(I)]	R1 = 0.0652, wR2 = 0.1418	
R indices (all data)	R1 = 0.0749, wR2 = 0.1450	
Absolute structure parameter	-0.01(4)	
Largest diff. peak and hole	0.643 and -1.135 e.$Å^{-3}$	

Table 22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for $[Li(THF)_4]_2[Zr(C_6H_5)_6]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7694(4)	1748(4)	653(1)	29(1)
C(2)	8605(4)	2780(5)	741(1)	35(1)
C(3)	9687(5)	3443(5)	640(1)	46(2)
C(4)	9883(5)	3145(6)	449(1)	49(2)
C(5)	9001(6)	2129(6)	348(1)	50(2)
C(6)	7949(5)	1467(5)	457(1)	35(1)
C(7)	6592(4)	-577(4)	852(1)	28(1)
C(8)	7388(5)	-159(5)	1023(1)	37(1)
C(9)	7894(5)	-774(6)	1105(1)	48(2)
C(10)	7660(6)	-1820(6)	1016(1)	49(2)
C(11)	6912(5)	-2249(5)	850(1)	52(2)
C(12)	6389(4)	-1627(4)	768(1)	36(1)
C(13)	4428(4)	-1025(4)	559(1)	26(1)
C(14)	4609(5)	-928(4)	340(1)	32(1)
C(15)	4074(5)	-1877(5)	203(1)	39(1)
C(16)	3287(5)	-2980(5)	278(1)	41(1)
C(17)	3075(4)	-3119(4)	492(1)	32(1)
C(18)	3616(4)	-2173(4)	629(1)	30(1)
C(19)	4412(5)	-498(5)	1043(1)	35(1)
C(20)	4378(5)	-1301(5)	1190(1)	37(1)
C(21)	3443(6)	-1931(6)	1333(1)	48(2)
C(22)	2489(6)	-1802(5)	1325(1)	47(2)
C(23)	2448(5)	-1034(6)	1184(1)	43(2)
C(24)	3388(5)	-407(5)	1050(1)	34(1)
C(25)	5282(5)	1609(4)	516(1)	26(1)
C(26)	6051(5)	2575(5)	390(1)	34(1)
C(27)	5661(6)	3131(6)	255(1)	43(2)
C(28)	4492(6)	2777(5)	240(1)	40(1)
C(29)	3699(6)	1868(5)	364(1)	42(1)
C(30)	4093(5)	1289(5)	496(1)	35(1)
C(31)	6130(4)	2084(4)	1021(1)	26(1)

C(32)	6262(5)	1917(5)	1234(1)	33(1)
C(33)	6631(5)	2783(5)	1388(1)	38(1)
C(34)	6878(4)	3902(5)	1328(1)	36(1)
C(35)	6732(5)	4113(5)	1120(1)	35(1)
C(36)	6386(4)	3237(4)	968(1)	29(1)
C(40)	2974(6)	4492(6)	831(1)	51(2)
C(41)	3769(8)	4673(9)	646(2)	73(3)
C(42)	4608(5)	4333(6)	731(1)	50(2)
C(43)	3873(5)	3379(6)	884(1)	49(2)
C(44)	4598(8)	4945(7)	1619(2)	71(2)
C(45)	5296(11)	6143(8)	1678(2)	107(4)
C(46)	5640(8)	6865(7)	1489(1)	70(2)
C(47)	5013(6)	6024(5)	1307(1)	54(2)
C(48)	1583(8)	4613(9)	1494(2)	88(3)
C(49)	548(9)	4680(11)	1460(2)	110(4)
C(50)	-116(11)	3856(14)	1303(3)	143(6)
C(51)	399(7)	3098(8)	1268(2)	72(2)
C(52)	1843(5)	1235(5)	1497(1)	41(1)
C(53)	2379(5)	759(5)	1654(1)	42(1)
C(54)	3668(6)	1377(6)	1599(1)	57(2)
C(55)	3770(5)	2044(5)	1396(1)	49(2)
C(56)	10463(6)	6584(7)	576(1)	54(2)
C(57)	10610(5)	6530(5)	811(1)	44(2)
C(58)	9433(6)	6161(7)	906(1)	61(2)
C(59)	8678(6)	6066(7)	716(1)	62(2)
C(60)	11779(6)	8642(8)	160(2)	70(2)
C(61)	12430(7)	9448(7)	-23(1)	65(2)
C(62)	11455(7)	9254(7)	-168(1)	67(2)
C(63)	10468(6)	9022(7)	-20(1)	55(2)
C(64)	7079(6)	6413(6)	261(1)	61(2)
C(65)	6149(7)	6401(9)	123(2)	92(3)
C(66)	6642(8)	7607(9)	46(2)	105(4)
C(67)	7574(6)	8345(6)	199(1)	56(2)
C(68)	10832(7)	9584(7)	754(2)	75(3)
C(69)	10905(6)	10540(6)	887(1)	50(2)

C(70)	10501(6)	11144(6)	734(1)	56(2)
C(71)	9650(5)	10191(5)	592(1)	38(1)
Li(1)	2861(8)	3618(9)	1281(2)	41(2)
Li(2)	9514(7)	8033(8)	395(2)	35(2)
O(1)	3081(3)	3718(3)	976(1)	40(1)
O(2)	4239(4)	4913(3)	1404(1)	49(1)
O(3)	1517(4)	3701(4)	1362(1)	51(1)
O(4)	2794(3)	2248(3)	1401(1)	39(1)
O(5)	9482(3)	6768(3)	555(1)	38(1)
O(6)	10617(3)	8478(3)	161(1)	37(1)
O(7)	7989(3)	7598(4)	279(1)	43(1)
O(8)	10070(3)	9367(3)	587(1)	41(1)
Zr(1)	5742(1)	578(1)	773(1)	22(1)

Table 23. Bond lengths [pm] and angles [°] for $[Li(THF)_4]_2[Zr(C_6H_5)_6]$.

C(1)-C(6)	138.1(8)	C(1)-C(2)	140.2(8)
C(1)-Zr(1)	236.6(5)	C(2)-C(3)	139.8(8)
C(2)-H(2)	95.00	C(3)-C(4)	133.3(10)
C(3)-H(3)	95.00	C(4)-C(5)	141.1(10)
C(4)-H(4)	95.00	C(5)-C(6)	139.4(8)
C(5)-H(5)	95.00	C(6)-H(6)	95.00
C(7)-C(12)	137.6(7)	C(7)-C(8)	141.2(8)
C(7)-Zr(1)	234.9(5)	C(8)-C(9)	138.2(8)
C(8)-H(8)	95.00	C(9)-C(10)	137.0(10)
C(9)-H(9)	95.00	C(10)-C(11)	135.3(10)
C(10)-H(10)	95.00	C(11)-C(12)	140.7(8)
C(11)-H(11)	95.00	C(12)-H(12)	95.00
C(13)-C(14)	139.9(8)	C(13)-C(18)	141.6(7)
C(13)-Zr(1)	237.0(5)	C(14)-C(15)	139.0(8)
C(14)-H(14)	95.00	C(15)-C(16)	138.0(8)
C(15)-H(15)	95.00	C(16)-C(17)	137.8(9)
C(16)-H(16)	95.00	C(17)-C(18)	138.4(7)
C(17)-H(17)	95.00	C(18)-H(18)	95.00
C(19)-C(20)	139.0(8)	C(19)-C(24)	141.5(8)
C(19)-Zr(1)	234.5(6)	C(20)-C(21)	141.4(8)

C(20)-H(20)	95.00	C(21)-C(22)	135.0(9)
C(21)-H(21)	95.00	C(22)-C(23)	136.9(9)
C(22)-H(22)	95.00	C(23)-C(24)	138.0(8)
C(23)-H(23)	95.00	C(24)-H(24)	95.00
C(25)-C(30)	140.9(7)	C(25)-C(26)	141.0(7)
C(25)-Zr(1)	237.8(5)	C(26)-C(27)	138.2(8)
C(26)-H(26)	95.00	C(27)-C(28)	137.0(9)
C(27)-H(27)	95.00	C(28)-C(29)	137.2(9)
C(28)-H(28)	95.00	C(29)-C(30)	139.6(8)
C(29)-H(29)	95.00	C(30)-H(30)	95.00
C(31)-C(32)	138.7(8)	C(31)-C(36)	142.1(7)
C(31)-Zr(1)	237.1(5)	C(32)-C(33)	139.1(8)
C(32)-H(32)	95.00	C(33)-C(34)	139.4(8)
C(33)-H(33)	95.00	C(34)-C(35)	137.3(9)
C(34)-H(34)	95.00	C(35)-C(36)	139.1(7)
C(35)-H(35)	95.00	C(36)-H(36)	95.00
C(40)-O(1)	143.1(7)	C(40)-C(41)	150.2(10)
C(40)-H(40A)	99.00	C(40)-H(40B)	99.00
C(41)-C(42)	148.3(9)	C(41)-H(41A)	99.00
C(41)-H(41B)	99.00	C(42)-C(43)	149.4(9)
C(42)-H(42A)	99.00	C(42)-H(42B)	99.00
C(43)-O(1)	144.7(7)	C(43)-H(43A)	99.00
C(43)-H(43B)	99.00	C(44)-C(45)	142.3(12)
C(44)-O(2)	143.1(10)	C(44)-H(44A)	99.00
C(44)-H(44B)	99.00	C(45)-C(46)	145.1(13)
C(45)-H(45A)	99.00	C(45)-H(45B)	99.00
C(46)-C(47)	151.9(10)	C(46)-H(46A)	99.00
C(46)-H(46B)	99.00	C(47)-O(2)	143.5(7)
C(47)-H(47A)	99.00	C(47)-H(47B)	99.00
C(48)-C(49)	142.5(12)	C(48)-O(3)	143.0(8)
C(48)-H(48A)	99.00	C(48)-H(48B)	99.00
C(49)-C(50)	140.7(15)	C(49)-H(49A)	99.00
C(49)-H(49B)	99.00	C(50)-C(51)	147.8(12)
C(50)-H(50A)	99.00	C(50)-H(50B)	99.00
C(51)-O(3)	140.5(9)	C(51)-H(51A)	99.00

C(51)-H(51B)	99.00	C(52)-O(4)	143.1(6)
C(52)-C(53)	151.9(8)	C(52)-H(52A)	99.00
C(52)-H(52B)	99.00	C(53)-C(54)	151.0(9)
C(53)-H(53A)	99.00	C(53)-H(53B)	99.00
C(54)-C(55)	151.9(10)	C(54)-H(54A)	99.00
C(54)-H(54B)	99.00	C(55)-O(4)	143.9(6)
C(55)-H(55A)	99.00	C(55)-H(55B)	99.00
C(56)-O(5)	143.5(7)	C(56)-C(57)	150.3(10)
C(56)-H(56A)	99.00	C(56)-H(56B)	99.00
C(57)-C(58)	149.8(9)	C(57)-H(57A)	99.00
C(57)-H(57B)	99.00	C(58)-C(59)	152.5(10)
C(59)-O(5)	142.7(8)	C(59)-H(59A)	99.00
C(59)-H(59B)	99.00	C(60)-O(6)	143.5(8)
C(60)-C(61)	151.1(10)	C(60)-H(60A)	99.00
C(60)-H(60B)	99.00	C(61)-C(62)	149.0(11)
C(61)-H(61A)	99.00	C(61)-H(61B)	99.00
C(62)-C(63)	150.2(10)	C(62)-H(62A)	99.00
C(62)-H(62B)	99.00	C(63)-O(6)	141.3(8)
C(63)-H(63A)	99.00	C(63)-H(63B)	99.00
C(64)-O(7)	142.0(8)	C(64)-C(65)	149.5(11)
C(64)-H(64A)	99.00	C(64)-H(64B)	99.00
C(65)-C(66)	146.7(13)	C(65)-H(65A)	99.00
C(65)-H(65B)	99.00	C(66)-C(67)	148.3(12)
C(66)-H(66A)	99.00	C(66)-H(66B)	99.00
C(67)-O(7)	143.3(8)	C(67)-H(67A)	99.00
C(67)-H(67B)	99.00	C(68)-O(8)	138.3(9)
C(68)-C(69)	147.9(10)	C(68)-H(68A)	99.00
C(68)-H(68B)	99.00	C(69)-C(70)	151.0(10)
C(69)-H(69A)	99.00	C(69)-H(69B)	99.00
C(70)-C(71)	149.0(9)	C(70)-H(70A)	99.00
C(70)-H(70B)	99.00	C(71)-O(8)	144.4(6)
C(71)-H(71A)	99.00	C(71)-H(71B)	99.00
Li(1)-O(3)	189.6(11)	Li(1)-O(4)	191.9(10)
Li(1)-O(2)	192.5(11)	Li(1)-O(1)	193.8(12)
Li(2)-O(5)	192.8(11)	Li(2)-O(7)	193.7(10)

Li(2)-O(6)	194.5(10)	Li(2)-O(8)	195.0(10)
C(6)-C(1)-C(2)	114.2(5)		
C(6)-C(1)-Zr(1)	116.3(4)	C(2)-C(1)-Zr(1)	129.0(4)
C(3)-C(2)-C(1)	122.4(6)	C(3)-C(2)-H(2)	118.8
C(1)-C(2)-H(2)	118.8	C(4)-C(3)-C(2)	121.0(6)
C(4)-C(3)-H(3)	119.5	C(2)-C(3)-H(3)	119.5
C(3)-C(4)-C(5)	120.0(6)	C(3)-C(4)-H(4)	120.0
C(5)-C(4)-H(4)	120.0	C(6)-C(5)-C(4)	117.3(7)
C(6)-C(5)-H(5)	121.3	C(4)-C(5)-H(5)	121.3
C(1)-C(6)-C(5)	125.0(6)	C(1)-C(6)-H(6)	117.5
C(5)-C(6)-H(6)	117.5	C(12)-C(7)-C(8)	114.7(5)
C(12)-C(7)-Zr(1)	130.9(4)	C(8)-C(7)-Zr(1)	114.2(4)
C(9)-C(8)-C(7)	122.6(6)	C(9)-C(8)-H(8)	118.7
C(7)-C(8)-H(8)	118.7	C(10)-C(9)-C(8)	120.4(6)
C(10)-C(9)-H(9)	119.8	C(8)-C(9)-H(9)	119.8
C(11)-C(10)-C(9)	119.1(6)	C(11)-C(10)-H(10)	120.5
C(9)-C(10)-H(10)	120.5	C(10)-C(11)-C(12)	120.6(6)
C(10)-C(11)-H(11)	119.7	C(12)-C(11)-H(11)	119.7
C(7)-C(12)-C(11)	122.6(6)	C(7)-C(12)-H(12)	118.7
C(11)-C(12)-H(12)	118.7	C(14)-C(13)-C(18)	114.0(5)
C(14)-C(13)-Zr(1)	117.8(4)	C(18)-C(13)-Zr(1)	126.9(4)
C(15)-C(14)-C(13)	123.3(5)	C(15)-C(14)-H(14)	118.3
C(13)-C(14)-H(14)	118.3	C(16)-C(15)-C(14)	120.6(6)
C(16)-C(15)-H(15)	119.7	C(14)-C(15)-H(15)	119.7
C(17)-C(16)-C(15)	118.2(5)	C(17)-C(16)-H(16)	120.9
C(15)-C(16)-H(16)	120.9	C(16)-C(17)-C(18)	120.9(5)
C(16)-C(17)-H(17)	119.5	C(18)-C(17)-H(17)	119.5
C(17)-C(18)-C(13)	122.9(5)	C(17)-C(18)-H(18)	118.6
C(13)-C(18)-H(18)	118.6	C(20)-C(19)-C(24)	111.9(5)
C(20)-C(19)-Zr(1)	132.5(4)	C(24)-C(19)-Zr(1)	115.3(4)
C(19)-C(20)-C(21)	124.1(6)	C(19)-C(20)-H(20)	118.0
C(21)-C(20)-H(20)	118.0	C(22)-C(21)-C(20)	119.7(6)
C(22)-C(21)-H(21)	120.2	C(20)-C(21)-H(21)	120.2
C(21)-C(22)-C(23)	120.0(6)	C(21)-C(22)-H(22)	120.0
C(23)-C(22)-H(22)	120.0	C(22)-C(23)-C(24)	119.1(6)

C(22)-C(23)-H(23)	120.5	C(24)-C(23)-H(23)	120.5
C(23)-C(24)-C(19)	125.2(6)	C(23)-C(24)-H(24)	117.4
C(19)-C(24)-H(24)	117.4	C(30)-C(25)-C(26)	114.2(5)
C(30)-C(25)-Zr(1)	116.9(4)	C(26)-C(25)-Zr(1)	128.8(4)
C(27)-C(26)-C(25)	122.5(5)	C(27)-C(26)-H(26)	118.7
C(25)-C(26)-H(26)	118.7	C(28)-C(27)-C(26)	120.9(6)
C(28)-C(27)-H(27)	119.6	C(26)-C(27)-H(27)	119.6
C(27)-C(28)-C(29)	119.6(5)	C(27)-C(28)-H(28)	120.2
C(29)-C(28)-H(28)	120.2	C(28)-C(29)-C(30)	119.3(6)
C(28)-C(29)-H(29)	120.3	C(30)-C(29)-H(29)	120.3
C(29)-C(30)-C(25)	123.4(6)	C(29)-C(30)-H(30)	118.3
C(25)-C(30)-H(30)	118.3	C(32)-C(31)-C(36)	114.4(5)
C(32)-C(31)-Zr(1)	119.9(4)	C(36)-C(31)-Zr(1)	125.3(4)
C(31)-C(32)-C(33)	124.8(5)	C(31)-C(32)-H(32)	117.6
C(33)-C(32)-H(32)	117.6	C(32)-C(33)-C(34)	118.5(6)
C(32)-C(33)-H(33)	120.8	C(34)-C(33)-H(33)	120.8
C(35)-C(34)-C(33)	119.5(5)	C(35)-C(34)-H(34)	120.3
C(33)-C(34)-H(34)	120.3	C(34)-C(35)-C(36)	120.8(5)
C(34)-C(35)-H(35)	119.6	C(36)-C(35)-H(35)	119.6
C(35)-C(36)-C(31)	122.0(5)	C(35)-C(36)-H(36)	119.0
C(31)-C(36)-H(36)	119.0	O(1)-C(40)-C(41)	107.6(5)
O(1)-C(40)-H(40A)	110.2	C(41)-C(40)-H(40A)	110.2
O(1)-C(40)-H(40B)	110.2	C(41)-C(40)-H(40B)	110.2
H(40A)-C(40)-H(40B)	108.5	C(42)-C(41)-C(40)	103.8(6)
C(42)-C(41)-H(41A)	111.0	C(40)-C(41)-H(41A)	111.0
C(42)-C(41)-H(41B)	111.0	C(40)-C(41)-H(41B)	111.0
H(41A)-C(41)-H(41B)	109.0	C(41)-C(42)-C(43)	102.6(6)
C(41)-C(42)-H(42A)	111.2	C(43)-C(42)-H(42A)	111.2
C(41)-C(42)-H(42B)	111.2	C(43)-C(42)-H(42B)	111.2
H(42A)-C(42)-H(42B)	109.2	O(1)-C(43)-C(42)	105.4(5)
O(1)-C(43)-H(43A)	110.7	C(42)-C(43)-H(43A)	110.7
O(1)-C(43)-H(43B)	110.7	C(42)-C(43)-H(43B)	110.7
H(43A)-C(43)-H(43B)	108.8	C(45)-C(44)-O(2)	107.6(7)
C(45)-C(44)-H(44A)	110.2	O(2)-C(44)-H(44A)	110.2
C(45)-C(44)-H(44B)	110.2	O(2)-C(44)-H(44B)	110.2

H(44A)-C(44)-H(44B)	108.5	C(44)-C(45)-C(46)	109.1(9)
C(44)-C(45)-H(45A)	109.9	C(46)-C(45)-H(45A)	109.9
C(44)-C(45)-H(45B)	109.9	C(46)-C(45)-H(45B)	109.9
H(45A)-C(45)-H(45B)	108.3	C(45)-C(46)-C(47)	105.3(7)
C(45)-C(46)-H(46A)	110.7	C(47)-C(46)-H(46A)	110.7
C(45)-C(46)-H(46B)	110.7	C(47)-C(46)-H(46B)	110.7
H(46A)-C(46)-H(46B)	108.8	O(2)-C(47)-C(46)	105.9(6)
O(2)-C(47)-H(47A)	110.6	C(46)-C(47)-H(47A)	110.6
O(2)-C(47)-H(47B)	110.6	C(46)-C(47)-H(47B)	110.6
H(47A)-C(47)-H(47B)	108.7	C(49)-C(48)-O(3)	107.9(8)
C(49)-C(48)-H(48A)	110.1	O(3)-C(48)-H(48A)	110.1
C(49)-C(48)-H(48B)	110.1	O(3)-C(48)-H(48B)	110.1
H(48A)-C(48)-H(48B)	108.4	C(50)-C(49)-C(48)	107.7(8)
C(50)-C(49)-H(49A)	110.2	C(48)-C(49)-H(49A)	110.2
C(50)-C(49)-H(49B)	110.2	C(48)-C(49)-H(49B)	110.2
H(49A)-C(49)-H(49B)	108.5	C(49)-C(50)-C(51)	107.8(8)
C(49)-C(50)-H(50A)	110.1	C(51)-C(50)-H(50A)	110.1
C(49)-C(50)-H(50B)	110.1	C(51)-C(50)-H(50B)	110.1
H(50A)-C(50)-H(50B)	108.5	O(3)-C(51)-C(50)	105.2(8)
O(3)-C(51)-H(51A)	110.7	C(50)-C(51)-H(51A)	110.7
O(3)-C(51)-H(51B)	110.7	C(50)-C(51)-H(51B)	110.7
H(51A)-C(51)-H(51B)	108.8	O(4)-C(52)-C(53)	106.8(5)
O(4)-C(52)-H(52A)	110.4	C(53)-C(52)-H(52A)	110.4
O(4)-C(52)-H(52B)	110.4	C(53)-C(52)-H(52B)	110.4
H(52A)-C(52)-H(52B)	108.6	C(54)-C(53)-C(52)	105.0(5)
C(54)-C(53)-H(53A)	110.8	C(52)-C(53)-H(53A)	110.8
C(54)-C(53)-H(53B)	110.8	C(52)-C(53)-H(53B)	110.8
H(53A)-C(53)-H(53B)	108.8	C(53)-C(54)-C(55)	104.8(5)
C(53)-C(54)-H(54A)	110.8	C(55)-C(54)-H(54A)	110.8
C(53)-C(54)-H(54B)	110.8	C(55)-C(54)-H(54B)	110.8
H(54A)-C(54)-H(54B)	108.9	O(4)-C(55)-C(54)	105.1(5)
O(4)-C(55)-H(55A)	110.7	C(54)-C(55)-H(55A)	110.7
O(4)-C(55)-H(55B)	110.7	C(54)-C(55)-H(55B)	110.7
H(55A)-C(55)-H(55B)	108.8	O(5)-C(56)-C(57)	104.6(5)
O(5)-C(56)-H(56A)	110.8	C(57)-C(56)-H(56A)	110.8

O(5)-C(56)-H(56B)	110.8	C(57)-C(56)-H(56B)	110.8
H(56A)-C(56)-H(56B)	108.9	C(58)-C(57)-C(56)	105.8(5)
C(58)-C(57)-H(57A)	110.6	C(56)-C(57)-H(57A)	110.6
C(58)-C(57)-H(57B)	110.6	C(56)-C(57)-H(57B)	110.6
H(57A)-C(57)-H(57B)	108.7	C(57)-C(58)-C(59)	103.8(6)
O(5)-C(59)-C(58)	105.5(5)	O(5)-C(59)-H(59A)	110.6
C(58)-C(59)-H(59A)	110.6	O(5)-C(59)-H(59B)	110.6
C(58)-C(59)-H(59B)	110.6	H(59A)-C(59)-H(59B)	108.8
O(6)-C(60)-C(61)	107.4(6)	O(6)-C(60)-H(60A)	110.2
C(61)-C(60)-H(60A)	110.2	O(6)-C(60)-H(60B)	110.2
C(61)-C(60)-H(60B)	110.2	H(60A)-C(60)-H(60B)	108.5
C(62)-C(61)-C(60)	102.1(6)	C(62)-C(61)-H(61A)	111.4
C(60)-C(61)-H(61A)	111.4	C(62)-C(61)-H(61B)	111.4
C(60)-C(61)-H(61B)	111.4	H(61A)-C(61)-H(61B)	109.2
C(61)-C(62)-C(63)	103.9(7)	C(61)-C(62)-H(62A)	111.0
C(63)-C(62)-H(62A)	111.0	C(61)-C(62)-H(62B)	111.0
C(63)-C(62)-H(62B)	111.0	H(62A)-C(62)-H(62B)	109.0
O(6)-C(63)-C(62)	106.2(6)	O(6)-C(63)-H(63A)	110.5
C(62)-C(63)-H(63A)	110.5	O(6)-C(63)-H(63B)	110.5
C(62)-C(63)-H(63B)	110.5	H(63A)-C(63)-H(63B)	108.7
O(7)-C(64)-C(65)	107.2(6)	O(7)-C(64)-H(64A)	110.3
C(65)-C(64)-H(64A)	110.3	O(7)-C(64)-H(64B)	110.3
C(65)-C(64)-H(64B)	110.3	H(64A)-C(64)-H(64B)	108.5
C(66)-C(65)-C(64)	105.4(7)	C(66)-C(65)-H(65A)	110.7
C(64)-C(65)-H(65A)	110.7	C(66)-C(65)-H(65B)	110.7
C(64)-C(65)-H(65B)	110.7	H(65A)-C(65)-H(65B)	108.8
C(65)-C(66)-C(67)	105.3(8)	C(65)-C(66)-H(66A)	110.7
C(67)-C(66)-H(66A)	110.7	C(65)-C(66)-H(66B)	110.7
C(67)-C(66)-H(66B)	110.7	H(66A)-C(66)-H(66B)	108.8
O(7)-C(67)-C(66)	104.7(6)	O(7)-C(67)-H(67A)	110.8
C(66)-C(67)-H(67A)	110.8	O(7)-C(67)-H(67B)	110.8
C(66)-C(67)-H(67B)	110.8	H(67A)-C(67)-H(67B)	108.9
O(8)-C(68)-C(69)	110.0(5)	O(8)-C(68)-H(68A)	109.7
C(69)-C(68)-H(68A)	109.7	O(8)-C(68)-H(68B)	109.7
C(69)-C(68)-H(68B)	109.7	H(68A)-C(68)-H(68B)	108.2

C(68)-C(69)-C(70)	101.0(6)	C(68)-C(69)-H(69A)	111.6
C(70)-C(69)-H(69A)	111.6	C(68)-C(69)-H(69B)	111.6
C(70)-C(69)-H(69B)	111.6	H(69A)-C(69)-H(69B)	109.4
C(71)-C(70)-C(69)	104.8(5)	C(71)-C(70)-H(70A)	110.8
C(69)-C(70)-H(70A)	110.8	C(71)-C(70)-H(70B)	110.8
C(69)-C(70)-H(70B)	110.8	H(70A)-C(70)-H(70B)	108.9
O(8)-C(71)-C(70)	103.8(5)	O(8)-C(71)-H(71A)	111.0
C(70)-C(71)-H(71A)	111.0	O(8)-C(71)-H(71B)	111.0
C(70)-C(71)-H(71B)	111.0	H(71A)-C(71)-H(71B)	109.0
O(3)-Li(1)-O(4)	110.1(5)	O(3)-Li(1)-O(2)	109.6(6)
O(4)-Li(1)-O(2)	104.7(5)	O(3)-Li(1)-O(1)	112.0(6)
O(4)-Li(1)-O(1)	113.0(5)	O(2)-Li(1)-O(1)	107.2(5)
O(5)-Li(2)-O(7)	111.8(5)	O(5)-Li(2)-O(6)	110.3(4)
O(7)-Li(2)-O(6)	108.1(6)	O(5)-Li(2)-O(8)	106.9(6)
O(7)-Li(2)-O(8)	111.5(4)	O(6)-Li(2)-O(8)	108.2(5)
C(40)-O(1)-C(43)	107.6(5)	C(40)-O(1)-Li(1)	128.4(5)
C(43)-O(1)-Li(1)	119.1(5)	C(44)-O(2)-C(47)	108.4(5)
C(44)-O(2)-Li(1)	124.0(5)	C(47)-O(2)-Li(1)	127.4(5)
C(51)-O(3)-C(48)	109.0(6)	C(51)-O(3)-Li(1)	126.9(5)
C(48)-O(3)-Li(1)	122.6(6)	C(52)-O(4)-C(55)	106.4(4)
C(52)-O(4)-Li(1)	130.7(4)	C(55)-O(4)-Li(1)	122.8(4)
C(59)-O(5)-C(56)	105.1(5)	C(59)-O(5)-Li(2)	128.4(5)
C(56)-O(5)-Li(2)	124.3(4)	C(63)-O(6)-C(60)	109.1(5)
C(63)-O(6)-Li(2)	119.6(5)	C(60)-O(6)-Li(2)	129.0(5)
C(64)-O(7)-C(67)	108.9(5)	C(64)-O(7)-Li(2)	122.4(5)
C(67)-O(7)-Li(2)	128.7(5)	C(68)-O(8)-C(71)	109.7(5)
C(68)-O(8)-Li(2)	124.4(5)	C(71)-O(8)-Li(2)	125.5(4)
C(19)-Zr(1)-C(7)	84.75(18)	C(19)-Zr(1)-C(1)	150.1(2)
C(7)-Zr(1)-C(1)	77.00(16)	C(19)-Zr(1)-C(13)	83.23(18)
C(7)-Zr(1)-C(13)	85.12(18)	C(1)-Zr(1)-C(13)	118.05(19)
C(19)-Zr(1)-C(31)	79.07(18)	C(7)-Zr(1)-C(31)	115.42(18)
C(1)-Zr(1)-C(31)	87.51(18)	C(13)-Zr(1)-C(31)	151.17(16)
C(19)-Zr(1)-C(25)	120.90(18)	C(7)-Zr(1)-C(25)	148.60(18)
C(1)-Zr(1)-C(25)	85.09(18)	C(13)-Zr(1)-C(25)	80.81(18)
C(31)-Zr(1)-C(25)	88.95(17)		

Table 24. Anisotropic displacement parameters ($pm^2 x\ 10^{-1}$) for $[Li(THF)_4]_2[Zr(C_6H_5)_6]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	28(3)	29(3)	36(3)	10(2)	6(2)	18(2)
C(2)	23(2)	38(3)	47(4)	-1(3)	0(2)	17(2)
C(3)	34(3)	35(3)	69(5)	21(3)	11(3)	18(3)
C(4)	31(3)	50(4)	63(5)	33(3)	14(3)	18(3)
C(5)	52(4)	53(4)	55(5)	23(3)	23(3)	35(3)
C(6)	31(3)	38(3)	39(4)	7(3)	10(2)	19(2)
C(7)	29(2)	30(3)	26(3)	9(2)	5(2)	16(2)
C(8)	39(3)	51(3)	27(3)	9(3)	7(2)	28(3)
C(9)	40(3)	70(4)	42(4)	13(3)	0(3)	35(3)
C(10)	47(4)	52(4)	61(5)	29(3)	15(3)	35(3)
C(11)	36(3)	33(3)	92(6)	12(3)	7(3)	21(3)
C(12)	24(2)	38(3)	49(4)	3(3)	1(3)	17(2)
C(13)	18(2)	35(3)	24(3)	-4(2)	-3(2)	13(2)
C(14)	32(3)	26(3)	32(3)	-1(2)	6(2)	10(2)
C(15)	50(3)	38(3)	23(3)	-7(2)	-1(3)	19(3)
C(16)	45(3)	36(3)	44(4)	-21(3)	-7(3)	22(3)
C(17)	27(3)	20(2)	42(3)	-3(2)	-2(2)	7(2)
C(18)	27(2)	35(3)	30(3)	1(2)	-2(2)	16(2)
C(19)	42(3)	30(3)	31(3)	-10(2)	-4(2)	17(2)
C(20)	45(3)	44(3)	26(3)	5(2)	5(2)	26(3)
C(21)	53(4)	47(4)	41(4)	18(3)	15(3)	23(3)
C(22)	42(3)	44(3)	39(4)	6(3)	13(3)	10(3)
C(23)	37(3)	56(4)	38(4)	-11(3)	0(3)	26(3)
C(24)	37(3)	35(3)	30(3)	0(2)	1(2)	18(2)
C(25)	41(3)	29(2)	12(2)	-1(2)	-4(2)	21(2)
C(26)	40(3)	34(3)	32(3)	4(2)	-3(2)	22(2)
C(27)	58(4)	46(3)	29(3)	8(3)	4(3)	29(3)
C(28)	57(4)	48(3)	24(3)	4(3)	-9(3)	33(3)
C(29)	51(4)	46(3)	37(4)	-3(3)	-13(3)	30(3)
C(30)	37(3)	42(3)	34(3)	2(2)	-5(2)	25(3)
C(31)	20(2)	28(2)	29(3)	-2(2)	0(2)	12(2)

C(32)	31(3)	39(3)	33(3)	2(2)	-2(2)	20(2)
C(33)	44(3)	40(3)	29(3)	-9(2)	-14(3)	22(3)
C(34)	26(3)	34(3)	45(4)	-16(3)	-8(2)	14(2)
C(35)	31(3)	27(3)	43(4)	-8(2)	0(2)	12(2)
C(36)	27(2)	33(3)	26(3)	1(2)	2(2)	14(2)
C(40)	68(4)	54(4)	44(4)	4(3)	-7(3)	41(3)
C(41)	84(6)	103(7)	70(6)	27(5)	18(5)	75(5)
C(42)	41(3)	52(4)	56(5)	2(3)	3(3)	22(3)
C(43)	41(3)	58(4)	59(5)	13(3)	13(3)	33(3)
C(44)	79(5)	51(4)	52(5)	4(3)	-18(4)	9(4)
C(45)	143(10)	56(5)	89(8)	-6(5)	-54(7)	26(6)
C(46)	81(5)	50(4)	57(5)	-7(4)	-13(4)	15(4)
C(47)	62(4)	30(3)	49(4)	7(3)	10(3)	7(3)
C(48)	94(6)	103(7)	100(8)	-48(6)	-9(6)	74(6)
C(49)	97(7)	120(9)	151(12)	-42(8)	-1(7)	84(7)
C(50)	111(9)	226(15)	168(14)	-88(12)	-50(9)	141(11)
C(51)	52(4)	90(6)	75(6)	-22(5)	-3(4)	37(4)
C(52)	33(3)	35(3)	49(4)	16(3)	11(3)	13(2)
C(53)	46(3)	42(3)	39(4)	9(3)	4(3)	22(3)
C(54)	43(4)	54(4)	71(5)	17(4)	-6(3)	23(3)
C(55)	37(3)	40(3)	78(6)	20(3)	14(3)	25(3)
C(56)	59(4)	74(5)	48(4)	22(4)	9(3)	49(4)
C(57)	44(3)	37(3)	51(4)	1(3)	-2(3)	22(3)
C(58)	47(4)	90(5)	38(4)	24(4)	3(3)	29(4)
C(59)	40(3)	87(5)	55(5)	34(4)	12(3)	29(4)
C(60)	36(4)	90(6)	73(6)	37(5)	14(4)	24(4)
C(61)	55(4)	67(5)	54(5)	8(4)	13(4)	17(4)
C(62)	58(4)	71(5)	50(5)	15(4)	13(4)	16(4)
C(63)	52(4)	65(4)	52(5)	22(4)	4(3)	31(3)
C(64)	51(4)	51(4)	68(6)	-1(4)	-6(4)	17(3)
C(65)	54(5)	91(7)	105(9)	9(6)	-35(5)	15(5)
C(66)	72(6)	91(7)	139(11)	4(7)	-54(7)	32(5)
C(67)	46(4)	54(4)	73(6)	-3(4)	-13(3)	27(3)
C(68)	63(5)	71(5)	110(8)	-43(5)	-50(5)	48(4)
C(69)	45(4)	48(4)	54(4)	-20(3)	-14(3)	20(3)

C(70)	62(4)	42(3)	67(6)	-17(3)	-7(4)	29(3)
C(71)	48(3)	30(3)	44(4)	0(3)	-2(3)	27(3)
Li(1)	39(5)	39(5)	44(6)	6(4)	5(5)	20(4)
Li(2)	27(4)	35(5)	45(6)	-3(4)	9(4)	16(4)
O(1)	37(2)	45(2)	46(3)	5(2)	1(2)	27(2)
O(2)	46(2)	32(2)	39(3)	8(2)	-3(2)	-3(2)
O(3)	54(3)	68(3)	53(3)	-18(2)	-8(2)	46(2)
O(4)	34(2)	31(2)	55(3)	17(2)	9(2)	19(2)
O(5)	40(2)	42(2)	38(2)	16(2)	11(2)	26(2)
O(6)	34(2)	44(2)	34(2)	6(2)	4(2)	19(2)
O(7)	35(2)	49(2)	44(3)	-2(2)	-9(2)	20(2)
O(8)	40(2)	43(2)	50(3)	-4(2)	-9(2)	28(2)
Zr(1)	22(1)	25(1)	18(1)	0(1)	-1(1)	12(1)

8.2.3 $[Li_2(Et_2O)_4][Zr(4\text{-}C_6H_4\text{-}CH_3)_6]$

8.2.3.1 Preparation of $[Li_2(Et_2O)_4][Zr(4\text{-}C_6H_4\text{-}CH_3)_6]$

To a slurry of $ZrCl_4$ (0.32 g, 1.37 mmol) in diethyl ether (30 mL) was added slowly 10.96 mmol *p*-tolyl lithium (8.9 mL of a 1.23 M solution in diethyl ether) at –78^{o}C. The resulting suspension was allowed to warm to –30^{o}C, after stirring for 1 hr at –30^{o}C, all insoluble materials dissolved, and a yellow solution was formed followed by separation of white precipitate. Stirring at –30^{o}C overnight, filtration of the white precipitate, and concentrating to about 20 mL under vacuum gave a yellow solution. Yellow crystals formed from the solution when kept at –70^{o}C for several days. ^{1}H NMR (400 MHz, CD_2Cl_2, −40^{o}C): δ = 7.84 (tolyl-H, d), 6.91 (tolyl-H, d), 3.04 ($(CH_3CH_2)_2O$), 2.12 (tolyl-CH_3, s) 0.82 ppm ($(CH_3CH_2)_2O$); $[^1H]^{13}C$ NMR (100.4 MHz, CD_2Cl_2, −40^{o}C): δ = 136.9, 134.7, 129.1, 127.8, 64.9 ($(CH_3CH_2)_2O$), 21.4, 14.5 ppm ($(CH_3CH_2)_2O$).

8.2.3.2 Crystal Data and Crystal Structure Analysis of $[Li_2(Et_2O)_4][Zr(4\text{-}C_6H_4\text{-}CH_3)_6]$

Table 25. Crystal data and structure refinement for $[Li_2(Et_2O)_4][Zr(4\text{-}C_6H_4\text{-}CH_3)_6]$.

Identification code	zrtol	
Color	Colorless	
Empirical formula	$C_{58}\,H_{82}\,Li_2\,O_4\,Zr$	
Formula weight	948.34	
Temperature	133(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	P1 21/n 1	
Unit cell dimensions	a = 1093.3(3) pm	α= 90°.
	b = 1767.6(4) pm	β= 97.410(6)°.
	c = 2840.3(7) pm	γ = 90°.
Volume	5.44(1) nm^3	
Z	4	
Density (calculated)	1.157 Mg/m^3	
Absorption coefficient	0.244 mm^{-1}	
F(000)	2032	
Crystal size	0.4 x 0.2 x 0.2 mm^3	
Theta range for data collection	1.85 to 26.08°.	
Index ranges	-12<=h<=13, -21<=k<=21, -32<=l<=35	
Reflections collected	43114	
Independent reflections	10698 [R(int) = 0.0562]	
Completeness to theta = 26.08°	99.1 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10698 / 0 / 600	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0458, wR2 = 0.1089	
R indices (all data)	R1 = 0.0709, wR2 = 0.1218	
Largest diff. peak and hole	0.894 and -0.843 e.$Å^{-3}$	

Table 26. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($pm^2 x\ 10^{-1}$) for $[Li_2(Et_2O)_4][Zr(4\text{-}C_6H_4\text{-}CH_3)_6]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2550(2)	8500(2)	2136(1)	23(1)
C(2)	3185(3)	8868(2)	2530(1)	27(1)
C(3)	2832(3)	8836(2)	2984(1)	32(1)
C(4)	1798(3)	8434(2)	3072(1)	29(1)
C(5)	1155(3)	8056(2)	2693(1)	28(1)
C(6)	1520(3)	8085(2)	2246(1)	25(1)
C(7)	1382(3)	8408(2)	3558(1)	45(1)
C(8)	1091(2)	9220(1)	1200(1)	20(1)
C(9)	976(3)	9684(2)	795(1)	24(1)
C(10)	-89(3)	10082(2)	629(1)	26(1)
C(11)	-1134(3)	10023(2)	855(1)	28(1)
C(12)	-1068(3)	9563(2)	1250(1)	29(1)
C(13)	11(3)	9190(2)	1421(1)	25(1)
C(14)	-2297(3)	10452(2)	676(1)	41(1)
C(15)	4004(2)	9571(2)	1483(1)	24(1)
C(16)	3844(3)	10296(2)	1280(1)	27(1)
C(17)	4721(3)	10868(2)	1362(1)	31(1)
C(18)	5815(3)	10760(2)	1653(1)	31(1)
C(19)	6015(3)	10047(2)	1859(1)	29(1)
C(20)	5135(2)	9481(2)	1775(1)	26(1)
C(21)	6754(3)	11378(2)	1749(1)	48(1)
C(22)	1590(2)	7793(2)	723(1)	23(1)
C(23)	636(3)	7370(2)	887(1)	27(1)
C(24)	-335(3)	7055(2)	592(1)	36(1)
C(25)	-423(3)	7140(2)	103(1)	40(1)
C(26)	496(3)	7542(2)	-73(1)	42(1)
C(27)	1468(3)	7859(2)	230(1)	32(1)
C(28)	-1491(4)	6800(2)	-217(2)	67(1)
C(29)	3542(2)	7198(2)	1569(1)	21(1)
C(30)	3091(3)	6465(2)	1470(1)	24(1)
C(31)	3644(3)	5816(2)	1677(1)	27(1)

C(32)	4693(3)	5855(2)	2003(1)	27(1)
C(33)	5187(3)	6571(2)	2109(1)	26(1)
C(34)	4624(2)	7212(2)	1898(1)	23(1)
C(35)	5285(3)	5156(2)	2237(1)	38(1)
C(36)	4451(2)	8347(1)	832(1)	22(1)
C(37)	4307(3)	8815(2)	427(1)	25(1)
C(38)	5224(3)	8943(2)	143(1)	27(1)
C(39)	6380(3)	8613(2)	253(1)	29(1)
C(40)	6562(3)	8153(2)	649(1)	30(1)
C(41)	5624(3)	8022(2)	924(1)	25(1)
C(42)	7386(3)	8754(2)	-56(1)	42(1)
C(51)	6781(3)	2516(2)	3084(1)	41(1)
C(52)	7085(3)	3189(2)	2799(1)	38(1)
C(53)	7886(3)	3498(2)	2087(1)	45(1)
C(54)	8668(4)	3185(2)	1736(1)	58(1)
C(55)	1045(4)	1713(2)	1363(1)	46(1)
C(56)	764(3)	1166(2)	1742(1)	34(1)
C(57)	2648(3)	1331(2)	2264(1)	30(1)
C(58)	3645(3)	909(2)	2561(1)	35(1)
C(59)	4063(5)	7217(3)	-558(2)	77(1)
C(60)	4607(4)	6790(3)	-125(1)	66(1)
C(61)	2865(5)	5994(2)	27(2)	108(2)
C(62)	2941(11)	5368(5)	266(2)	245(7)
C(63)	6264(5)	5689(5)	958(2)	127(3)
C(64)	7471(5)	5590(3)	1246(2)	83(2)
C(65)	9515(5)	5207(3)	1203(2)	78(2)
C(66)	10285(5)	4868(4)	874(2)	107(2)
Li(1)	2246(5)	-202(3)	1836(2)	28(1)
Li(2)	3483(4)	7210(3)	719(2)	30(1)
O(1)	7706(2)	2932(1)	2421(1)	38(1)
O(2)	1832(2)	804(1)	1994(1)	28(1)
O(3)	3723(2)	6595(1)	187(1)	42(1)
O(4)	8282(3)	5224(2)	976(1)	68(1)
Zr(1)	2871(1)	8435(1)	1328(1)	17(1)

Table 27. Bond lengths [pm] and angles [°] for $[Li_2(Et_2O)_4][Zr(4\text{-}C_6H_4\text{-}CH_3)_6]$.

C(1)-C(2)	140.0(4)	C(1)-C(6)	141.3(4)
C(1)-Zr(1)	236.8(3)	C(1)-Li(1)#1	245.5(5)
C(2)-C(3)	139.4(4)	C(2)-Li(1)#1	266.7(6)
C(2)-H(2)	95.00	C(3)-C(4)	138.6(4)
C(3)-H(3)	95.00	C(4)-C(5)	138.0(4)
C(4)-C(7)	150.8(4)	C(5)-C(6)	137.8(4)
C(5)-H(5)	95.00	C(6)-H(6)	95.00
C(7)-H(7A)	98.00	C(7)-H(7B)	98.00
C(7)-H(7C)	98.00	C(8)-C(9)	140.6(4)
C(8)-C(13)	140.7(4)	C(8)-Li(1)#1	230.5(5)
C(8)-Zr(1)	237.9(3)	C(9)-C(10)	138.9(4)
C(9)-H(9)	95.00	C(10)-C(11)	138.4(4)
C(10)-H(10)	95.00	C(11)-C(12)	138.2(4)
C(11)-C(14)	151.0(4)	C(12)-C(13)	138.3(4)
C(12)-H(12)	95.00	C(13)-Li(1)#1	278.8(6)
C(13)-H(13)	95.00	C(14)-H(14A)	98.00
C(14)-H(14B)	98.00	C(14)-H(14C)	98.00
C(15)-C(20)	140.6(4)	C(15)-C(16)	140.7(4)
C(15)-Li(1)#1	231.4(6)	C(15)-Zr(1)	237.0(3)
C(16)-C(17)	139.3(4)	C(16)-Li(1)#1	265.2(6)
C(16)-H(16)	95.00	C(17)-C(18)	137.7(4)
C(17)-H(17)	95.00	C(18)-C(19)	139.6(4)
C(18)-C(21)	149.9(4)	C(19)-C(20)	138.7(4)
C(19)-H(19)	95.00	C(20)-H(20)	95.00
C(21)-H(21A)	98.00	C(21)-H(21B)	98.00
C(21)-H(21C)	98.00	C(22)-C(27)	139.6(4)
C(22)-C(23)	141.1(4)	C(22)-Li(2)	231.2(6)
C(22)-Zr(1)	236.1(3)	C(23)-C(24)	138.3(4)
C(23)-H(23)	95.00	C(24)-C(25)	138.6(5)
C(24)-H(24)	95.00	C(25)-C(26)	137.7(5)
C(25)-C(28)	150.9(5)	C(26)-C(27)	139.6(4)
C(26)-H(26)	95.00	C(27)-Li(2)	270.3(6)
C(27)-H(27)	95.00	C(28)-H(28A)	98.00

C(28)-H(28B)	98.00	C(28)-H(28C)	98.00
C(29)-C(30)	140.2(4)	C(29)-C(34)	141.0(4)
C(29)-Zr(1)	237.8(3)	C(29)-Li(2)	240.7(6)
C(30)-C(31)	139.2(4)	C(30)-Li(2)	258.8(6)
C(30)-H(30)	95.00	C(31)-C(32)	138.1(4)
C(31)-H(31)	95.00	C(32)-C(33)	139.3(4)
C(32)-C(35)	150.9(4)	C(33)-C(34)	138.8(4)
C(33)-H(33)	95.00	C(34)-H(34)	95.00
C(35)-H(35A)	98.00	C(35)-H(35B)	98.00
C(35)-H(35C)	98.00	C(36)-C(41)	139.9(4)
C(36)-C(37)	140.9(4)	C(36)-Li(2)	227.4(5)
C(36)-Zr(1)	237.0(3)	C(37)-C(38)	138.3(4)
C(37)-H(37)	95.00	C(38)-C(39)	139.0(4)
C(38)-H(38)	95.00	C(39)-C(40)	138.2(4)
C(39)-C(42)	151.2(4)	C(40)-C(41)	138.7(4)
C(40)-H(40)	95.00	C(41)-Li(2)	274.3(6)
C(41)-H(41)	95.00	C(42)-H(42A)	98.00
C(42)-H(42B)	98.00	C(42)-H(42C)	98.00
C(51)-C(52)	150.0(5)	C(51)-H(51A)	98.00
C(51)-H(51B)	98.00	C(51)-H(51C)	98.00
C(52)-O(1)	141.8(4)	C(52)-H(52A)	99.00
C(52)-H(52B)	99.00	C(53)-O(1)	141.0(4)
C(53)-C(54)	149.9(5)	C(53)-H(53A)	99.00
C(53)-H(53B)	99.00	C(54)-H(54A)	98.00
C(54)-H(54B)	98.00	C(54)-H(54C)	98.00
C(55)-C(56)	150.7(4)	C(55)-H(55A)	98.00
C(55)-H(55B)	98.00	C(55)-H(55C)	98.00
C(56)-O(2)	143.9(4)	C(56)-H(56A)	99.00
C(56)-H(56B)	99.00	C(57)-O(2)	144.1(3)
C(57)-C(58)	148.9(4)	C(57)-H(57A)	99.00
C(57)-H(57B)	99.00	C(58)-H(58A)	98.00
C(58)-H(58B)	98.00	C(58)-H(58C)	98.00
C(59)-C(60)	149.8(6)	C(59)-H(59A)	98.00
C(59)-H(59B)	98.00	C(59)-H(59C)	98.00
C(60)-O(3)	143.7(5)	C(60)-H(60A)	99.00

C(60)-H(60B)	99.00	C(61)-C(62)	129.5(9)
C(61)-O(3)	145.1(5)	C(61)-H(61A)	99.00
C(61)-H(61B)	99.00	C(62)-H(62A)	98.00
C(62)-H(62B)	98.00	C(62)-H(62C)	98.00
C(63)-C(64)	147.0(7)	C(63)-H(63A)	98.00
C(63)-H(63B)	98.00	C(63)-H(63C)	98.00
C(64)-O(4)	140.1(5)	C(64)-H(64A)	99.00
C(64)-H(64B)	99.00	C(65)-O(4)	141.7(5)
C(65)-C(66)	146.4(7)	C(65)-H(65A)	99.00
C(65)-H(65B)	99.00	C(66)-H(66A)	98.00
C(66)-H(66B)	98.00	C(66)-H(66C)	98.00
Li(1)-O(2)	190.2(5)	Li(1)-C(8)#2	230.5(5)
Li(1)-C(15)#2	231.4(5)	Li(1)-C(1)#2	245.5(5)
Li(1)-C(16)#2	265.2(6)	Li(1)-C(2)#2	266.7(6)
Li(1)-C(13)#2	278.8(6)	Li(1)-Zr(1)#2	293.4(5)
Li(2)-O(3)	190.8(5)	Li(2)-Zr(1)	290.2(5)
Zr(1)-Li(1)#1	293.4(5)		
C(2)-C(1)-C(6)	113.0(2)	C(2)-C(1)-Zr(1)	132.6(2)
C(6)-C(1)-Zr(1)	114.38(19)	C(2)-C(1)-Li(1)#1	82.7(2)
C(6)-C(1)-Li(1)#1	119.1(2)	Zr(1)-C(1)-Li(1)#1	74.92(13)
C(3)-C(2)-C(1)	123.6(3)	C(3)-C(2)-Li(1)#1	125.6(2)
C(1)-C(2)-Li(1)#1	65.90(18)	C(3)-C(2)-H(2)	118.2
C(1)-C(2)-H(2)	118.2	Li(1)#1-C(2)-H(2)	79.4
C(4)-C(3)-C(2)	121.2(3)	C(4)-C(3)-H(3)	119.4
C(2)-C(3)-H(3)	119.4	C(5)-C(4)-C(3)	116.9(3)
C(5)-C(4)-C(7)	121.1(3)	C(3)-C(4)-C(7)	122.0(3)
C(6)-C(5)-C(4)	121.5(3)	C(6)-C(5)-H(5)	119.3
C(4)-C(5)-H(5)	119.3	C(5)-C(6)-C(1)	123.9(3)
C(5)-C(6)-H(6)	118.1	C(1)-C(6)-H(6)	118.1
C(4)-C(7)-H(7A)	109.5	C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5	C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5	H(7B)-C(7)-H(7C)	109.5
C(9)-C(8)-C(13)	113.3(2)	C(9)-C(8)-Li(1)#1	111.4(2)
C(13)-C(8)-Li(1)#1	94.2(2)	C(9)-C(8)-Zr(1)	116.73(19)
C(13)-C(8)-Zr(1)	128.81(19)	Li(1)#1-C(8)-Zr(1)	77.55(14)

C(10)-C(9)-C(8)	123.7(3)	C(10)-C(9)-H(9)	118.1
C(8)-C(9)-H(9)	118.1	C(11)-C(10)-C(9)	120.8(3)
C(11)-C(10)-H(10)	119.6	C(9)-C(10)-H(10)	119.6
C(12)-C(11)-C(10)	117.4(3)	C(12)-C(11)-C(14)	121.5(3)
C(10)-C(11)-C(14)	121.1(3)	C(11)-C(12)-C(13)	121.2(3)
C(11)-C(12)-H(12)	119.4	C(13)-C(12)-H(12)	119.4
C(12)-C(13)-C(8)	123.5(3)	C(12)-C(13)-Li(1)#1	128.7(2)
C(8)-C(13)-Li(1)#1	55.53(17)	C(12)-C(13)-H(13)	118.2
C(8)-C(13)-H(13)	118.2	Li(1)#1-C(13)-H(13)	86.4
C(11)-C(14)-H(14A)	109.5	C(11)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5	C(11)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(14B)-C(14)-H(14C)	109.5
C(20)-C(15)-C(16)	113.5(2)	C(20)-C(15)-Li(1)#1	118.7(2)
C(16)-C(15)-Li(1)#1	87.3(2)	C(20)-C(15)-Zr(1)	114.39(19)
C(16)-C(15)-Zr(1)	131.3(2)	Li(1)#1-C(15)-Zr(1)	77.55(14)
C(17)-C(16)-C(15)	123.1(3)	C(17)-C(16)-Li(1)#1	129.3(2)
C(15)-C(16)-Li(1)#1	60.65(18)	C(17)-C(16)-H(16)	118.4
C(15)-C(16)-H(16)	118.4	Li(1)#1-C(16)-H(16)	81.3
C(18)-C(17)-C(16)	121.7(3)	C(18)-C(17)-H(17)	119.1
C(16)-C(17)-H(17)	119.1	C(17)-C(18)-C(19)	117.0(3)
C(17)-C(18)-C(21)	122.0(3)	C(19)-C(18)-C(21)	121.0(3)
C(20)-C(19)-C(18)	120.8(3)	C(20)-C(19)-H(19)	119.6
C(18)-C(19)-H(19)	119.6	C(19)-C(20)-C(15)	123.9(3)
C(19)-C(20)-H(20)	118.1	C(15)-C(20)-H(20)	118.1
C(18)-C(21)-H(21A)	109.5	C(18)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5	C(18)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5	H(21B)-C(21)-H(21C)	109.5
C(27)-C(22)-C(23)	113.4(3)	C(27)-C(22)-Li(2)	90.1(2)
C(23)-C(22)-Li(2)	117.7(2)	C(27)-C(22)-Zr(1)	131.4(2)
C(23)-C(22)-Zr(1)	114.16(19)	Li(2)-C(22)-Zr(1)	76.75(15)
C(24)-C(23)-C(22)	123.7(3)	C(24)-C(23)-H(23)	118.1
C(22)-C(23)-H(23)	118.1	C(23)-C(24)-C(25)	120.9(3)
C(23)-C(24)-H(24)	119.6	C(25)-C(24)-H(24)	119.6
C(26)-C(25)-C(24)	117.4(3)	C(26)-C(25)-C(28)	122.1(3)
C(24)-C(25)-C(28)	120.5(3)	C(25)-C(26)-C(27)	121.1(3)

C(25)-C(26)-H(26)	119.5	C(27)-C(26)-H(26)	119.5
C(26)-C(27)-C(22)	123.5(3)	C(26)-C(27)-Li(2)	130.7(2)
C(22)-C(27)-Li(2)	58.80(18)	C(26)-C(27)-H(27)	118.2
C(22)-C(27)-H(27)	118.2	Li(2)-C(27)-H(27)	81.9
C(25)-C(28)-H(28A)	109.5	C(25)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5	C(25)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5	H(28B)-C(28)-H(28C)	109.5
C(30)-C(29)-C(34)	113.1(2)	C(30)-C(29)-Zr(1)	134.7(2)
C(34)-C(29)-Zr(1)	112.13(18)	C(30)-C(29)-Li(2)	80.9(2)
C(34)-C(29)-Li(2)	125.2(2)	Zr(1)-C(29)-Li(2)	74.64(14)
C(31)-C(30)-C(29)	123.7(3)	C(31)-C(30)-Li(2)	131.2(2)
C(29)-C(30)-Li(2)	66.73(18)	C(31)-C(30)-H(30)	118.2
C(29)-C(30)-H(30)	118.2	Li(2)-C(30)-H(30)	73.8
C(32)-C(31)-C(30)	121.4(3)	C(32)-C(31)-H(31)	119.3
C(30)-C(31)-H(31)	119.3	C(31)-C(32)-C(33)	117.2(2)
C(31)-C(32)-C(35)	121.8(3)	C(33)-C(32)-C(35)	121.0(3)
C(34)-C(33)-C(32)	120.6(3)	C(34)-C(33)-H(33)	119.7
C(32)-C(33)-H(33)	119.7	C(33)-C(34)-C(29)	124.1(3)
C(33)-C(34)-H(34)	118.0	C(29)-C(34)-H(34)	118.0
C(32)-C(35)-H(35A)	109.5	C(32)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5	C(32)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5	H(35B)-C(35)-H(35C)	109.5
C(41)-C(36)-C(37)	113.4(2)	C(41)-C(36)-Li(2)	93.5(2)
C(37)-C(36)-Li(2)	113.7(2)	C(41)-C(36)-Zr(1)	129.5(2)
C(37)-C(36)-Zr(1)	115.71(19)	Li(2)-C(36)-Zr(1)	77.29(15)
C(38)-C(37)-C(36)	124.0(3)	C(38)-C(37)-H(37)	118.0
C(36)-C(37)-H(37)	118.0	C(37)-C(38)-C(39)	120.5(3)
C(37)-C(38)-H(38)	119.7	C(39)-C(38)-H(38)	119.7
C(40)-C(39)-C(38)	117.3(3)	C(40)-C(39)-C(42)	122.0(3)
C(38)-C(39)-C(42)	120.6(3)	C(39)-C(40)-C(41)	121.3(3)
C(39)-C(40)-H(40)	119.3	C(41)-C(40)-H(40)	119.3
C(40)-C(41)-C(36)	123.5(3)	C(40)-C(41)-Li(2)	129.8(2)
C(36)-C(41)-Li(2)	55.84(18)	C(40)-C(41)-H(41)	118.3
C(36)-C(41)-H(41)	118.3	Li(2)-C(41)-H(41)	85.2
C(39)-C(42)-H(42A)	109.5	C(39)-C(42)-H(42B)	109.5

H(42A)-C(42)-H(42B)	109.5	C(39)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5	H(42B)-C(42)-H(42C)	109.5
C(52)-C(51)-H(51A)	109.5	C(52)-C(51)-H(51B)	109.5
H(51A)-C(51)-H(51B)	109.5	C(52)-C(51)-H(51C)	109.5
H(51A)-C(51)-H(51C)	109.5	H(51B)-C(51)-H(51C)	109.5
O(1)-C(52)-C(51)	108.4(3)	O(1)-C(52)-H(52A)	110.0
C(51)-C(52)-H(52A)	110.0	O(1)-C(52)-H(52B)	110.0
C(51)-C(52)-H(52B)	110.0	H(52A)-C(52)-H(52B)	108.4
O(1)-C(53)-C(54)	109.1(3)	O(1)-C(53)-H(53A)	109.9
C(54)-C(53)-H(53A)	109.9	O(1)-C(53)-H(53B)	109.9
C(54)-C(53)-H(53B)	109.9	H(53A)-C(53)-H(53B)	108.3
C(53)-C(54)-H(54A)	109.5	C(53)-C(54)-H(54B)	109.5
H(54A)-C(54)-H(54B)	109.5	C(53)-C(54)-H(54C)	109.5
H(54A)-C(54)-H(54C)	109.5	H(54B)-C(54)-H(54C)	109.5
C(56)-C(55)-H(55A)	109.5	C(56)-C(55)-H(55B)	109.5
H(55A)-C(55)-H(55B)	109.5	C(56)-C(55)-H(55C)	109.5
H(55A)-C(55)-H(55C)	109.5	H(55B)-C(55)-H(55C)	109.5
O(2)-C(56)-C(55)	114.4(3)	O(2)-C(56)-H(56A)	108.7
C(55)-C(56)-H(56A)	108.7	O(2)-C(56)-H(56B)	108.7
C(55)-C(56)-H(56B)	108.7	H(56A)-C(56)-H(56B)	107.6
O(2)-C(57)-C(58)	109.7(2)	O(2)-C(57)-H(57A)	109.7
C(58)-C(57)-H(57A)	109.7	O(2)-C(57)-H(57B)	109.7
C(58)-C(57)-H(57B)	109.7	H(57A)-C(57)-H(57B)	108.2
C(57)-C(58)-H(58A)	109.5	C(57)-C(58)-H(58B)	109.5
H(58A)-C(58)-H(58B)	109.5	C(57)-C(58)-H(58C)	109.5
H(58A)-C(58)-H(58C)	109.5	H(58B)-C(58)-H(58C)	109.5
C(60)-C(59)-H(59A)	109.5	C(60)-C(59)-H(59B)	109.5
H(59A)-C(59)-H(59B)	109.5	C(60)-C(59)-H(59C)	109.5
H(59A)-C(59)-H(59C)	109.5	H(59B)-C(59)-H(59C)	109.5
O(3)-C(60)-C(59)	113.6(4)	O(3)-C(60)-H(60A)	108.8
C(59)-C(60)-H(60A)	108.8	O(3)-C(60)-H(60B)	108.8
C(59)-C(60)-H(60B)	108.8	H(60A)-C(60)-H(60B)	107.7
C(62)-C(61)-O(3)	117.8(5)	C(62)-C(61)-H(61A)	107.9
O(3)-C(61)-H(61A)	107.9	C(62)-C(61)-H(61B)	107.9
O(3)-C(61)-H(61B)	107.9	H(61A)-C(61)-H(61B)	107.2

C(61)-C(62)-H(62A)	109.5	C(61)-C(62)-H(62B)	109.5
H(62A)-C(62)-H(62B)	109.5	C(61)-C(62)-H(62C)	109.5
H(62A)-C(62)-H(62C)	109.5	H(62B)-C(62)-H(62C)	109.5
C(64)-C(63)-H(63A)	109.5	C(64)-C(63)-H(63B)	109.5
H(63A)-C(63)-H(63B)	109.5	C(64)-C(63)-H(63C)	109.5
H(63A)-C(63)-H(63C)	109.5	H(63B)-C(63)-H(63C)	109.5
O(4)-C(64)-C(63)	109.7(4)	O(4)-C(64)-H(64A)	109.7
C(63)-C(64)-H(64A)	109.7	O(4)-C(64)-H(64B)	109.7
C(63)-C(64)-H(64B)	109.7	H(64A)-C(64)-H(64B)	108.2
O(4)-C(65)-C(66)	108.1(4)	O(4)-C(65)-H(65A)	110.1
C(66)-C(65)-H(65A)	110.1	O(4)-C(65)-H(65B)	110.1
C(66)-C(65)-H(65B)	110.1	H(65A)-C(65)-H(65B)	108.4
C(65)-C(66)-H(66A)	109.5	C(65)-C(66)-H(66B)	109.5
H(66A)-C(66)-H(66B)	109.5	C(65)-C(66)-H(66C)	109.5
H(66A)-C(66)-H(66C)	109.5	H(66B)-C(66)-H(66C)	109.5
O(2)-Li(1)-C(8)#2	118.4(2)	O(2)-Li(1)-C(15)#2	120.0(2)
C(8)#2-Li(1)-C(15)#2	89.16(19)	O(2)-Li(1)-C(1)#2	144.9(3)
C(8)#2-Li(1)-C(1)#2	83.86(17)	C(15)#2-Li(1)-C(1)#2	84.55(18)
O(2)-Li(1)-C(16)#2	91.4(2)	C(8)#2-Li(1)-C(16)#2	90.94(18)
C(15)#2-Li(1)-C(16)#2	32.01(11)	C(1)#2-Li(1)-C(16)#2	116.5(2)
O(2)-Li(1)-C(2)#2	118.9(2)	C(8)#2-Li(1)-C(2)#2	115.2(2)
C(15)#2-Li(1)-C(2)#2	87.20(18)	C(1)#2-Li(1)-C(2)#2	31.38(10)
C(16)#2-Li(1)-C(2)#2	115.1(2)	O(2)-Li(1)-C(13)#2	103.7(2)
C(8)#2-Li(1)-C(13)#2	30.23(10)	C(15)#2-Li(1)-C(13)#2	118.8(2)
C(1)#2-Li(1)-C(13)#2	81.85(16)	C(16)#2-Li(1)-C(13)#2	118.98(19)
C(2)#2-Li(1)-C(13)#2	107.92(18)	O(2)-Li(1)-Zr(1)#2	163.9(2)
C(8)#2-Li(1)-Zr(1)#2	52.36(11)	C(15)#2-Li(1)-Zr(1)#2	52.08(11)
C(1)#2-Li(1)-Zr(1)#2	51.19(11)	C(16)#2-Li(1)-Zr(1)#2	76.48(14)
C(2)#2-Li(1)-Zr(1)#2	76.46(13)	C(13)#2-Li(1)-Zr(1)#2	73.88(12)
O(3)-Li(2)-C(36)	120.4(3)	O(3)-Li(2)-C(22)	118.2(3)
C(36)-Li(2)-C(22)	90.4(2)	O(3)-Li(2)-C(29)	143.2(3)
C(36)-Li(2)-C(29)	85.11(19)	C(22)-Li(2)-C(29)	84.66(19)
O(3)-Li(2)-C(30)	114.6(2)	C(36)-Li(2)-C(30)	117.2(2)
C(22)-Li(2)-C(30)	88.80(18)	C(29)-Li(2)-C(30)	32.34(11)
O(3)-Li(2)-C(27)	91.2(2)	C(36)-Li(2)-C(27)	91.80(19)

C(22)-Li(2)-C(27)	31.10(11)	C(29)-Li(2)-C(27)	115.7(2)
C(30)-Li(2)-C(27)	115.4(2)	O(3)-Li(2)-C(41)	105.4(2)
C(36)-Li(2)-C(41)	30.61(11)	C(22)-Li(2)-C(41)	120.4(2)
C(29)-Li(2)-C(41)	83.10(17)	C(30)-Li(2)-C(41)	108.56(19)
C(27)-Li(2)-C(41)	120.3(2)	O(3)-Li(2)-Zr(1)	164.5(3)
C(36)-Li(2)-Zr(1)	52.84(12)	C(22)-Li(2)-Zr(1)	52.38(12)
C(29)-Li(2)-Zr(1)	52.23(12)	C(30)-Li(2)-Zr(1)	79.25(15)
C(27)-Li(2)-Zr(1)	75.82(14)	C(41)-Li(2)-Zr(1)	74.90(13)
C(53)-O(1)-C(52)	113.9(2)	C(56)-O(2)-C(57)	112.6(2)
C(56)-O(2)-Li(1)	120.1(2)	C(57)-O(2)-Li(1)	125.5(2)
C(60)-O(3)-C(61)	116.3(4)	C(60)-O(3)-Li(2)	121.6(3)
C(61)-O(3)-Li(2)	121.1(4)	C(64)-O(4)-C(65)	113.3(4)
C(22)-Zr(1)-C(1)	125.43(10)	C(22)-Zr(1)-C(15)	142.09(10)
C(1)-Zr(1)-C(15)	85.29(9)	C(22)-Zr(1)-C(36)	86.89(9)
C(1)-Zr(1)-C(36)	142.11(9)	C(15)-Zr(1)-C(36)	76.27(9)
C(22)-Zr(1)-C(29)	84.25(9)	C(1)-Zr(1)-C(29)	81.01(9)
C(15)-Zr(1)-C(29)	126.19(10)	C(36)-Zr(1)-C(29)	83.68(9)
C(22)-Zr(1)-C(8)	76.88(9)	C(1)-Zr(1)-C(8)	84.19(9)
C(15)-Zr(1)-C(8)	86.10(9)	C(36)-Zr(1)-C(8)	126.30(9)
C(29)-Zr(1)-C(8)	142.71(9)	C(22)-Zr(1)-Li(2)	50.87(12)
C(1)-Zr(1)-Li(2)	133.45(12)	C(15)-Zr(1)-Li(2)	125.98(12)
C(36)-Zr(1)-Li(2)	49.88(11)	C(29)-Zr(1)-Li(2)	53.13(12)
C(8)-Zr(1)-Li(2)	126.24(12)	C(22)-Zr(1)-Li(1)#1	126.77(12)
C(1)-Zr(1)-Li(1)#1	53.88(11)	C(15)-Zr(1)-Li(1)#1	50.38(11)
C(36)-Zr(1)-Li(1)#1	125.43(11)	C(29)-Zr(1)-Li(1)#1	134.06(11)
C(8)-Zr(1)-Li(1)#1	50.09(11)	Li(2)-Zr(1)-Li(1)#1	172.67(13)

Symmetry transformations used to generate equivalent atoms: #1 x,y+1,z #2 x,y-1,z

Table 28. Anisotropic displacement parameters ($pm^2 x\ 10^{-1}$)for $[Li_2(Et_2O)_4][Zr(4\text{-}C_6H_4\text{-}CH_3)_6]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	23(1)	20(1)	26(1)	5(1)	3(1)	6(1)
C(2)	23(2)	27(2)	29(2)	0(1)	3(1)	1(1)
C(3)	33(2)	35(2)	27(2)	-2(1)	2(1)	3(1)

C(4)	36(2)	30(2)	23(1)	5(1)	7(1)	14(1)
C(5)	24(2)	25(1)	35(2)	10(1)	5(1)	2(1)
C(6)	25(2)	24(1)	26(2)	3(1)	0(1)	3(1)
C(7)	48(2)	62(2)	27(2)	6(2)	11(2)	6(2)
C(8)	21(1)	17(1)	22(1)	-1(1)	1(1)	-1(1)
C(9)	25(2)	25(1)	24(1)	0(1)	8(1)	-1(1)
C(10)	32(2)	24(1)	23(1)	3(1)	3(1)	4(1)
C(11)	28(2)	25(1)	29(2)	-2(1)	0(1)	8(1)
C(12)	21(2)	33(2)	34(2)	3(1)	9(1)	2(1)
C(13)	25(2)	24(1)	26(2)	5(1)	5(1)	2(1)
C(14)	36(2)	49(2)	39(2)	5(2)	0(2)	18(2)
C(15)	22(1)	22(1)	30(2)	-4(1)	9(1)	-3(1)
C(16)	28(2)	28(2)	26(2)	2(1)	5(1)	-2(1)
C(17)	36(2)	22(1)	34(2)	3(1)	9(1)	-4(1)
C(18)	32(2)	27(2)	36(2)	-5(1)	12(1)	-9(1)
C(19)	20(2)	32(2)	36(2)	-3(1)	4(1)	-3(1)
C(20)	23(2)	21(1)	34(2)	1(1)	7(1)	-1(1)
C(21)	48(2)	36(2)	59(2)	-4(2)	3(2)	-20(2)
C(22)	19(1)	19(1)	30(2)	-1(1)	0(1)	1(1)
C(23)	25(2)	26(2)	31(2)	0(1)	4(1)	4(1)
C(24)	24(2)	25(2)	57(2)	-1(1)	-2(2)	1(1)
C(25)	34(2)	30(2)	52(2)	-7(2)	-14(2)	2(1)
C(26)	49(2)	43(2)	29(2)	-1(1)	-12(2)	3(2)
C(27)	34(2)	29(2)	32(2)	6(1)	2(1)	-1(1)
C(28)	56(3)	55(2)	80(3)	-13(2)	-31(2)	-11(2)
C(29)	19(1)	24(1)	21(1)	4(1)	6(1)	0(1)
C(30)	24(1)	23(1)	26(1)	1(1)	4(1)	0(1)
C(31)	34(2)	17(1)	32(2)	2(1)	6(1)	-4(1)
C(32)	30(2)	22(1)	30(2)	7(1)	8(1)	5(1)
C(33)	21(1)	29(1)	27(1)	6(1)	1(1)	-1(1)
C(34)	24(1)	20(1)	27(1)	3(1)	6(1)	-5(1)
C(35)	40(2)	26(2)	46(2)	8(1)	1(2)	8(1)
C(36)	22(1)	17(1)	26(1)	0(1)	2(1)	-2(1)
C(37)	21(1)	25(1)	30(2)	3(1)	3(1)	2(1)
C(38)	32(2)	22(1)	28(2)	6(1)	6(1)	0(1)

C(39)	32(2)	26(2)	31(2)	-1(1)	11(1)	-3(1)
C(40)	24(2)	35(2)	32(2)	5(1)	6(1)	9(1)
C(41)	24(2)	25(1)	26(2)	4(1)	4(1)	2(1)
C(42)	38(2)	48(2)	44(2)	7(2)	20(2)	2(2)
C(51)	29(2)	46(2)	47(2)	-6(2)	2(2)	2(2)
C(52)	24(2)	31(2)	59(2)	-12(2)	6(2)	1(1)
C(53)	48(2)	32(2)	51(2)	1(2)	-2(2)	-4(2)
C(54)	69(3)	52(2)	56(2)	-7(2)	18(2)	-23(2)
C(55)	66(3)	34(2)	38(2)	6(1)	7(2)	9(2)
C(56)	37(2)	30(2)	34(2)	-5(1)	2(1)	5(1)
C(57)	34(2)	24(1)	32(2)	-7(1)	6(1)	-4(1)
C(58)	34(2)	35(2)	36(2)	-9(1)	8(1)	-2(1)
C(59)	93(4)	84(3)	60(3)	-12(3)	28(3)	-1(3)
C(60)	62(3)	89(3)	50(2)	-27(2)	17(2)	15(2)
C(61)	108(4)	37(2)	157(6)	-33(3)	-70(4)	0(3)
C(62)	450(17)	205(9)	77(4)	-16(5)	29(7)	-272(11)
C(63)	84(4)	218(8)	85(4)	-28(5)	37(3)	46(5)
C(64)	117(4)	77(3)	60(3)	2(2)	35(3)	12(3)
C(65)	96(4)	59(3)	72(3)	25(2)	-19(3)	-18(3)
C(66)	62(3)	158(6)	102(4)	29(4)	16(3)	20(4)
Li(1)	31(3)	23(2)	30(3)	-4(2)	5(2)	-1(2)
Li(2)	29(3)	26(2)	36(3)	2(2)	6(2)	0(2)
O(1)	39(1)	28(1)	48(1)	-4(1)	8(1)	4(1)
O(2)	32(1)	21(1)	31(1)	-5(1)	3(1)	0(1)
O(3)	41(1)	33(1)	52(1)	-15(1)	3(1)	-4(1)
O(4)	68(2)	75(2)	63(2)	-20(2)	11(2)	0(2)
Zr(1)	15(1)	16(1)	21(1)	2(1)	3(1)	0(1)

8.3 Hafnium Complexes

8.3.1 $[Li(THF)_4]_2[Hf(C_6H_5)_6]$

8.3.1.1 Preparation of $[Li(THF)_4]_2[Hf(C_6H_5)_6]$

0.53 g (1.65 mmol) of $HfCl_4$ and 50 ml of dry THF were heated at –78°C in a schlenk flask equipped with a magnetic stirring bar. 10.6 mL (13.2 mmol) of a 1.25 M solution of phenyl lithium in diethyl ether was added slowly. After stirring at –35°C overnight, a light brown solution and a white solid were formed. Filtration of the solid, and concentrating under vacuum to the half, and slow diffusion of *n*-pentane layer (1:1) at –35°C afforded a pink crystalline solid.

8.3.1.2 Crystal Data and Crystal Structure Analysis of $[Li(THF)_4]_2[Hf(C_6H_5)_6]$

Table 29. Crystal data and structure refinement for $[Li(THF)_4]_2[Hf(C_6H_5)_6]$.

Identification code	hfph64	
Empirical formula	$C_{15}\ H_{60}\ Hf_{0.50}\ Li\ O_4$	
Formula weight	400.82	
Temperature	133(2) K	
Wavelength	71.073 pm	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 1178.94(16) pm	α= 90°.
	b = 1178.92(12) pm	β= 97.682(3)°.
	c = 2301.0(3) pm	γ = 90°.
Volume	3.1694(7) nm^3	
Z	4	
Density (calculated)	0.840 Mg/m^3	
Absorption coefficient	1.671 mm^{-1}	
F(000)	884	
Crystal size	0.2 x 0.1 x 0.1 mm^3	
Theta range for data collection	1.74 to 30.28°.	
Index ranges	-15<=h<=16, -16<=k<=13, -32<=l<=32	

Reflections collected	46172
Independent reflections	8883 [R(int) = 0.0270]
Completeness to theta = 30.28°	93.6 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8883 / 0 / 358
Goodness-of-fit on F^2	1.075
Final R indices [I>2sigma(I)]	R1 = 0.0316, wR2 = 0.0773
R indices (all data)	R1 = 0.0516, wR2 = 0.0881
Largest diff. peak and hole	1.689 and -0.786 e.Å^{-3}

Table 30. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for $[Li(THF)_4]_2[Hf(C_6H_5)_6]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-1106(2)	9234(2)	702(1)	30(1)
C(2)	-604(3)	8701(3)	1217(1)	38(1)
C(3)	-1229(3)	8271(3)	1642(1)	44(1)
C(4)	-2409(3)	8338(3)	1563(1)	42(1)
C(5)	-2947(3)	8835(3)	1059(1)	40(1)
C(6)	-2306(2)	9281(3)	645(1)	35(1)
C(7)	711(2)	11458(2)	673(1)	31(1)
C(8)	841(3)	11334(3)	1283(1)	36(1)
C(9)	1314(3)	12170(3)	1672(1)	43(1)
C(10)	1670(3)	13190(3)	1467(2)	49(1)
C(11)	1554(3)	13360(3)	869(2)	50(1)
C(12)	1093(3)	12509(3)	484(2)	43(1)
C(13)	1589(3)	8853(3)	407(1)	34(1)
C(14)	1631(3)	7674(3)	328(2)	50(1)
C(15)	2566(4)	6997(3)	564(2)	55(1)
C(16)	3513(3)	7479(3)	893(2)	54(1)
C(17)	3507(3)	8637(3)	982(2)	49(1)
C(18)	2568(3)	9295(3)	748(1)	40(1)
C(19)	4515(4)	3017(4)	897(2)	74(1)
C(20)	4387(4)	2546(4)	279(2)	67(1)

C(21)	5046(3)	1451(3)	370(2)	51(1)
C(22)	6016(3)	1767(4)	812(2)	60(1)
C(23)	8071(3)	2506(3)	2805(1)	49(1)
C(24)	8574(4)	1414(3)	3066(2)	53(1)
C(25)	9065(3)	867(3)	2554(2)	49(1)
C(26)	8289(3)	1290(3)	2025(2)	55(1)
C(27)	7035(5)	5044(4)	882(3)	95(2)
C(28)	7905(5)	5705(4)	649(2)	76(1)
C(29)	8954(4)	5008(3)	714(2)	61(1)
C(30)	8769(4)	4126(5)	1185(2)	81(2)
C(31)	4894(4)	4478(5)	2358(2)	76(1)
C(32)	4778(5)	5635(6)	2586(4)	118(3)
C(33)	5852(5)	6159(5)	2649(4)	123(3)
C(34)	6687(4)	5292(4)	2531(2)	67(1)
Hf(1)	0	10000	0	24(1)
Li(1)	6732(5)	3334(5)	1738(2)	40(1)
O(1)	7663(2)	2249(2)	2202(1)	37(1)
O(2)	5598(2)	2633(2)	1177(1)	53(1)
O(3)	6030(2)	4383(2)	2234(1)	50(1)
O(4)	7633(2)	4260(2)	1304(1)	60(1)

Table 31. Bond lengths [pm] and angles [°] for $[Li(THF)_4]_2[Hf(C_6H_5)_6]$.

C(1)-C(2)	140.2(4)	C(1)-C(6)	140.4(4)	C(1)-Hf(1)	238.5(3)
C(2)-C(3)	139.5(4)	C(2)-H(2)	95.00	C(3)-C(4)	138.1(5)
C(3)-H(3)	95.00	C(4)-C(5)	137.6(5)	C(4)-H(4)	95.00
C(5)-C(6)	139.5(4)	C(5)-H(5)	95.00	C(6)-H(6)	95.00
C(7)-C(8)	140.0(4)	C(7)-C(12)	140.7(4)	C(7)-Hf(1)	238.8(3)
C(8)-C(9)	139.7(4)	C(8)-H(8)	95.00	C(9)-C(10)	137.7(5)
C(9)-H(9)	95.00	C(10)-C(11)	138.0(5)	C(10)-H(10)	95.00
C(11)-C(12)	139.8(4)	C(11)-H(11)	95.00	C(12)-H(12)	95.00
C(13)-C(14)	140.4(4)	C(13)-C(18)	140.6(4)	C(13)-Hf(1)	239.7(3)
C(14)-C(15)	140.9(5)	C(14)-H(14)	95.00	C(15)-C(16)	138.4(6)
C(15)-H(15)	95.00	C(16)-C(17)	138.0(5)	C(16)-H(16)	95.00
C(17)-C(18)	140.0(4)	C(17)-H(17)	95.00	C(18)-H(18)	95.00

C(19)-O(2)	142.4(4)	C(19)-C(20)	151.5(5)	C(19)-H(19A)	99.00
C(19)-H(19B)	99.00	C(20)-C(21)	150.6(5)	C(20)-H(20A)	99.00
C(20)-H(20B)	99.00	C(21)-C(22)	147.4(5)	C(21)-H(21A)	99.00
C(21)-H(21B)	99.00	C(22)-O(2)	144.9(4)	C(22)-H(22A)	99.00
C(22)-H(22B)	99.00	C(23)-O(1)	143.9(4)	C(23)-C(24)	150.9(5)
C(23)-H(23A)	99.00	C(23)-H(23B)	99.00	C(24)-C(25)	152.4(5)
C(24)-H(24A)	99.00	C(24)-H(24B)	99.00	C(25)-C(26)	150.5(5)
C(25)-H(25A)	99.00	C(25)-H(25B)	99.00	C(26)-O(1)	143.8(4)
C(26)-H(26A)	99.00	C(26)-H(26B)	99.00	C(27)-C(28)	144.7(7)
C(27)-O(4)	145.3(6)	C(27)-H(27A)	99.00	C(27)-H(27B)	99.00
C(28)-C(29)	147.5(6)	C(28)-H(28A)	99.00	C(28)-H(28B)	99.00
C(29)-C(30)	153.8(6)	C(29)-H(29A)	99.00	C(29)-H(29B)	99.00
C(30)-O(4)	141.2(5)	C(30)-H(30A)	99.00	C(30)-H(30B)	99.00
C(31)-O(3)	141.0(5)	C(31)-C(32)	147.4(8)	C(31)-H(31A)	99.00
C(31)-H(31B)	99.00	C(32)-C(33)	139.8(8)	C(32)-H(32A)	99.00
C(32)-H(32B)	99.00	C(33)-C(34)	147.0(6)	C(33)-H(33A)	99.00
C(33)-H(33B)	99.00	C(34)-O(3)	144.1(5)	C(34)-H(34A)	99.00
C(34)-H(34B)	99.00	Hf(1)-C(1)#1	238.5(3)	Hf(1)-C(7)#1	238.8(3)
Hf(1)-C(13)#1	239.7(3)	Li(1)-O(4)	189.6(6)	Li(1)-O(1)	191.5(6)
Li(1)-O(2)	191.8(6)	Li(1)-O(3)	194.3(6)		
C(2)-C(1)-C(6)	113.8(3)	C(2)-C(1)-Hf(1)	122.4(2)	C(6)-C(1)-Hf(1)	123.8(2)
C(3)-C(2)-C(1)	123.5(3)	C(3)-C(2)-H(2)	118.2	C(1)-C(2)-H(2)	118.2
C(4)-C(3)-C(2)	120.3(3)	C(4)-C(3)-H(3)	119.9	C(2)-C(3)-H(3)	119.9
C(5)-C(4)-C(3)	118.5(3)	C(5)-C(4)-H(4)	120.7	C(3)-C(4)-H(4)	120.7
C(4)-C(5)-C(6)	120.4(3)	C(4)-C(5)-H(5)	119.8	C(6)-C(5)-H(5)	119.8
C(5)-C(6)-C(1)	123.5(3)	C(5)-C(6)-H(6)	118.3	C(1)-C(6)-H(6)	118.3
C(8)-C(7)-C(12)	113.8(3)	C(8)-C(7)-Hf(1)	123.9(2)	C(12)-C(7)-Hf(1)	122.3(2)
C(9)-C(8)-C(7)	123.4(3)	C(9)-C(8)-H(8)	118.3	C(7)-C(8)-H(8)	118.3
C(10)-C(9)-C(8)	120.7(3)	C(10)-C(9)-H(9)	119.7	C(8)-C(9)-H(9)	119.7
C(9)-C(10)-C(11)	118.3(3)	C(9)-C(10)-H(10)	120.9	C(11)-C(10)-H(10)	120.9
C(10)-C(11)-C(12)	120.4(3)	C(10)-C(11)-H(11)	119.8	C(12)-C(11)-H(11)	119.8
C(11)-C(12)-C(7)	123.4(3)	C(11)-C(12)-H(12)	118.3	C(7)-C(12)-H(12)	118.3
C(14)-C(13)-C(18)	113.5(3)	C(14)-C(13)-Hf(1)	123.2(2)	C(18)-C(13)-Hf(1)	123.3(2)
C(13)-C(14)-C(15)	123.3(4)	C(13)-C(14)-H(14)	118.3	C(15)-C(14)-H(14)	118.3
C(16)-C(15)-C(14)	120.7(4)	C(16)-C(15)-H(15)	119.7	C(14)-C(15)-H(15)	119.7

C(17)-C(16)-C(15)	117.9(3)	C(17)-C(16)-H(16)	121.0	C(15)-C(16)-H(16)	121.0
C(16)-C(17)-C(18)	120.6(4)	C(16)-C(17)-H(17)	119.7	C(18)-C(17)-H(17)	119.7
C(17)-C(18)-C(13)	123.9(3)	C(17)-C(18)-H(18)	118.1	C(13)-C(18)-H(18)	118.1
O(2)-C(19)-C(20)	106.2(3)	O(2)-C(19)-H(19A)	110.5	C(20)-C(19)-H(19A)	110.5
O(2)-C(19)-H(19B)	110.5	C(20)-C(19)-H(19B)	110.5	H(19A)-C(19)-H(19B)	108.7
C(21)-C(20)-C(19)	101.5(3)	C(21)-C(20)-H(20A)	111.5	C(19)-C(20)-H(20A)	111.5
C(21)-C(20)-H(20B)	111.5	C(19)-C(20)-H(20B)	111.5	H(20A)-C(20)-H(20B)	109.3
C(22)-C(21)-C(20)	102.5(3)	C(22)-C(21)-H(21A)	111.3	C(20)-C(21)-H(21A)	111.3
C(22)-C(21)-H(21B)	111.3	C(20)-C(21)-H(21B)	111.3	H(21A)-C(21)-H(21B)	109.2
O(2)-C(22)-C(21)	106.6(3)	O(2)-C(22)-H(22A)	110.4	C(21)-C(22)-H(22A)	110.4
O(2)-C(22)-H(22B)	110.4	C(21)-C(22)-H(22B)	110.4	H(22A)-C(22)-H(22B)	108.6
O(1)-C(23)-C(24)	105.5(3)	O(1)-C(23)-H(23A)	110.6	C(24)-C(23)-H(23A)	110.6
O(1)-C(23)-H(23B)	110.6	C(24)-C(23)-H(23B)	110.6	H(23A)-C(23)-H(23B)	108.8
C(23)-C(24)-C(25)	102.8(3)	C(23)-C(24)-H(24A)	111.2	C(25)-C(24)-H(24A)	111.2
C(23)-C(24)-H(24B)	111.2	C(25)-C(24)-H(24B)	111.2	H(24A)-C(24)-H(24B)	109.1
C(26)-C(25)-C(24)	103.4(3)	C(26)-C(25)-H(25A)	111.1	C(24)-C(25)-H(25A)	111.1
C(26)-C(25)-H(25B)	111.1	C(24)-C(25)-H(25B)	111.1	H(25A)-C(25)-H(25B)	109.0
O(1)-C(26)-C(25)	108.2(3)	O(1)-C(26)-H(26A)	110.1	C(25)-C(26)-H(26A)	110.1
O(1)-C(26)-H(26B)	110.1	C(25)-C(26)-H(26B)	110.1	H(26A)-C(26)-H(26B)	108.4
C(28)-C(27)-O(4)	106.6(4)	C(28)-C(27)-H(27A)	110.4	O(4)-C(27)-H(27A)	110.4
C(28)-C(27)-H(27B)	110.4	O(4)-C(27)-H(27B)	110.4	H(27A)-C(27)-H(27B)	108.6
C(27)-C(28)-C(29)	106.8(4)	C(27)-C(28)-H(28A)	110.4	C(29)-C(28)-H(28A)	110.4
C(27)-C(28)-H(28B)	110.4	C(29)-C(28)-H(28B)	110.4	H(28A)-C(28)-H(28B)	108.6
C(28)-C(29)-C(30)	104.6(4)	C(28)-C(29)-H(29A)	110.8	C(30)-C(29)-H(29A)	110.8
C(28)-C(29)-H(29B)	110.8	C(30)-C(29)-H(29B)	110.8	H(29A)-C(29)-H(29B)	108.9
O(4)-C(30)-C(29)	106.8(4)	O(4)-C(30)-H(30A)	110.4	C(29)-C(30)-H(30A)	110.4
O(4)-C(30)-H(30B)	110.4	C(29)-C(30)-H(30B)	110.4	H(30A)-C(30)-H(30B)	108.6
O(3)-C(31)-C(32)	106.3(4)	O(3)-C(31)-H(31A)	110.5	C(32)-C(31)-H(31A)	110.5
O(3)-C(31)-H(31B)	110.5	C(32)-C(31)-H(31B)	110.5	H(31A)-C(31)-H(31B)	108.7
C(33)-C(32)-C(31)	108.7(4)	C(33)-C(32)-H(32A)	110.0	C(31)-C(32)-H(32A)	110.0
C(33)-C(32)-H(32B)	110.0	C(31)-C(32)-H(32B)	110.0	H(32A)-C(32)-H(32B)	108.3
C(32)-C(33)-C(34)	107.1(4)	C(32)-C(33)-H(33A)	110.3	C(34)-C(33)-H(33A)	110.3
C(32)-C(33)-H(33B)	110.3	C(34)-C(33)-H(33B)	110.3	H(33A)-C(33)-H(33B)	108.6
O(3)-C(34)-C(33)	105.8(4)	O(3)-C(34)-H(34A)	110.6	C(33)-C(34)-H(34A)	110.6
O(3)-C(34)-H(34B)	110.6	C(33)-C(34)-H(34B)	110.6	H(34A)-C(34)-H(34B)	108.7

C(1)#1-Hf(1)-C(1)	180.0	C(1)#1-Hf(1)-C(7)#1	90.56(9)	C(1)-Hf(1)-C(7)#1	89.44(9)
C(1)#1-Hf(1)-C(7)	89.44(9)	C(1)-Hf(1)-C(7)	90.56(9)	C(7)#1-Hf(1)-C(7)	180.00(11)
C(1)#1-Hf(1)-C(13)#1	89.52(10)	C(1)-Hf(1)-C(13)#1	90.48(10)	C(7)#1-Hf(1)-C(13)#1	87.98(10)
C(7)-Hf(1)-C(13)#1	92.02(10)	C(1)#1-Hf(1)-C(13)	90.48(10)	C(1)-Hf(1)-C(13)	89.52(10)
C(7)#1-Hf(1)-C(13)	92.02(10)	C(7)-Hf(1)-C(13)	87.98(10)	C(13)#1-Hf(1)-C(13)	180.0
O(4)-Li(1)-O(1)	111.0(3)	O(4)-Li(1)-O(2)	106.4(3)	O(1)-Li(1)-O(2)	112.5(3)
O(4)-Li(1)-O(3)	104.9(3)	O(1)-Li(1)-O(3)	110.8(3)	O(2)-Li(1)-O(3)	110.9(3)
C(26)-O(1)-C(23)	108.7(2)	C(26)-O(1)-Li(1)	130.2(2)	C(23)-O(1)-Li(1)	119.3(2)
C(19)-O(2)-C(22)	108.4(3)	C(19)-O(2)-Li(1)	132.1(3)	C(22)-O(2)-Li(1)	115.6(3)
C(31)-O(3)-C(34)	108.1(3)	C(31)-O(3)-Li(1)	131.4(3)	C(34)-O(3)-Li(1)	120.5(3)
C(30)-O(4)-C(27)	109.3(3)	C(30)-O(4)-Li(1)	130.6(3)	C(27)-O(4)-Li(1)	117.5(3)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+2,-z

Table 32. Anisotropic displacement parameters ($pm^2 x\ 10^{-1}$)for $[Li(THF)_4]_2[Hf(C_6H_5)_6]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	34(1)	28(1)	28(1)	-1(1)	8(1)	-2(1)
C(2)	36(2)	39(2)	39(2)	9(1)	8(1)	3(1)
C(3)	56(2)	42(2)	37(2)	14(1)	15(1)	7(2)
C(4)	51(2)	36(2)	42(2)	1(1)	23(1)	-4(1)
C(5)	37(2)	42(2)	44(2)	-5(1)	14(1)	-4(1)
C(6)	34(2)	42(2)	30(1)	-2(1)	7(1)	-1(1)
C(7)	32(1)	31(1)	31(1)	-8(1)	9(1)	-5(1)
C(8)	41(2)	34(2)	35(1)	-5(1)	9(1)	1(1)
C(9)	39(2)	51(2)	38(2)	-15(1)	6(1)	6(1)
C(10)	40(2)	47(2)	61(2)	-26(2)	9(2)	-4(2)
C(11)	52(2)	36(2)	64(2)	-12(2)	18(2)	-13(2)
C(12)	47(2)	38(2)	45(2)	-6(1)	14(1)	-9(1)
C(13)	37(2)	37(2)	30(1)	6(1)	9(1)	6(1)
C(14)	59(2)	41(2)	48(2)	-1(2)	0(2)	11(2)
C(15)	72(3)	42(2)	52(2)	5(2)	9(2)	21(2)
C(16)	58(2)	64(2)	40(2)	13(2)	10(2)	26(2)
C(17)	40(2)	67(2)	42(2)	6(2)	6(1)	10(2)
C(18)	37(2)	46(2)	39(2)	3(1)	7(1)	6(1)

C(19)	55(2)	99(4)	64(3)	-28(2)	-12(2)	28(2)
C(20)	62(2)	84(3)	51(2)	-21(2)	-10(2)	22(2)
C(21)	55(2)	54(2)	44(2)	-9(2)	5(2)	-2(2)
C(22)	53(2)	58(2)	65(2)	-20(2)	-1(2)	10(2)
C(23)	68(2)	42(2)	34(2)	-6(1)	-2(2)	8(2)
C(24)	75(3)	44(2)	39(2)	2(2)	2(2)	8(2)
C(25)	60(2)	42(2)	43(2)	3(1)	5(2)	10(2)
C(26)	57(2)	64(2)	43(2)	-8(2)	5(2)	23(2)
C(27)	73(3)	90(4)	129(5)	62(3)	38(3)	29(3)
C(28)	106(4)	43(2)	87(3)	11(2)	42(3)	10(2)
C(29)	60(2)	55(2)	71(3)	6(2)	21(2)	-13(2)
C(30)	49(2)	103(4)	93(3)	42(3)	17(2)	4(2)
C(31)	46(2)	98(4)	86(3)	-33(3)	22(2)	-7(2)
C(32)	71(4)	108(5)	177(7)	-48(5)	28(4)	38(4)
C(33)	88(4)	61(3)	230(8)	-64(4)	59(5)	-1(3)
C(34)	57(2)	55(2)	90(3)	-33(2)	14(2)	-6(2)
Hf(1)	28(1)	23(1)	23(1)	0(1)	7(1)	-1(1)
Li(1)	39(3)	37(3)	43(3)	-6(2)	2(2)	4(2)
O(1)	41(1)	39(1)	31(1)	-4(1)	3(1)	4(1)
O(2)	40(1)	67(2)	49(1)	-21(1)	-6(1)	12(1)
O(3)	37(1)	45(1)	69(2)	-22(1)	13(1)	0(1)
O(4)	56(2)	57(2)	70(2)	21(1)	23(1)	10(1)

8.3.2 $[Li(THF)_4]_2[Hf(p\text{-}C_6H_4\text{-}CH_3)_6]$

8.3.2.1 Preparation of $[Li(THF)_4]_2[Hf(p\text{-}C_6H_4\text{-}CH_3)_6]$

To a suspension of $HfCl_4$ (0.36 g, 1.12 mmol) in 50 mL diethyl ether was added slowly 6 mL solution of *p*-tolyl lithium (ca. 10 mmol). The resulting suspension was allowed to warm up to –20^{o}C, after stirring overnight at –20^{o}C, light yellow solution and some white solid formed. Filtration and then removing solvent at –20^{o}C produced a light yellow residue which redissolved in 50 mL THF at –20^{o}C. Slow cooling of the solution at –20^{o}C for about 3 days afforded a light brown crystalline solid.

8.4 Vanadium complexes

8.4.1 [Li(tmeda)][VO(CH$_3$)$_4$]·LiCl(tmeda)

8.4.1.1 Preparation of [Li(tmeda)][VO(CH$_3$)$_4$]·LiCl(tmeda)

A solution of $Me_2NCH_2CH_2NMe_2$ (0.235 g, 2.0 mmol) in Et_2O (10 mL) was frozen in liquid nitrogen and a solution of $VOCl_3$ (0.350 g, 2.0 mmol) in Et_2O (20 mL) syringed in. The mixture was allowed to thaw and then warm slowly to –78^{o}C to produce a dark brown suspension. The mixture was stirred for 1 hr at –78^{o}C. 10.0 mmol of MeLi (1.6 M solution in Et_2O) was added slowly to the preceding mixture at –78^{o}C with stirring for about 3 hr. The reaction mixture was allowed to warm to –50^{o}C and stirred for 1 hr, the solution turned dark blue and some colorless solid separated. Removing the insoluble materials by filtration and cooling the dark blue solution from –50^{o}C to –80^{o}C afforded black crystals. The yield can be estimated to be more than 45%.

8.4.1.2 Crystal Data and Crystal Structure Analysis of [Li(tmeda)][VO(CH$_3$)$_4$]-LiCl(tmeda)

Table 33. Crystal data and structure refinement for [Li(tmeda)][VO(CH$_3$)$_4$]·LiCl(tmeda).

Identification code	vome4	
Empirical formula	C_{12} H_{24} $Cl_{0.50}$ Li N_2 $O_{0.50}$ $V_{0.50}$	
Formula weight	254.47	
Temperature	143(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	C12/m1	
Unit cell dimensions	a = 1820.8(9) pm	α= 90°.
	b = 1624.1(8) pm	β= 119.079(11)°.
	c = 981.0(5) pm	γ = 90°.
Volume	2.54(1) nm^3	

Z	8
Density (calculated)	1.333 Mg/m^3
Absorption coefficient	0.521 mm^{-1}
F(000)	1096
Crystal size	0.1 x 0.1 x 0.03 mm^3
Theta range for data collection	1.79 to 25.02°.
Index ranges	-16<=h<=21, -19<=k<=19, -11<=l<=11
Reflections collected	6971
Independent reflections	2333 [R(int) = 0.0811]
Completeness to theta = 25.02°	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2333 / 0 / 131
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0663, wR2 = 0.1581
R indices (all data)	R1 = 0.1256, wR2 = 0.1900
Largest diff. peak and hole	0.578 and -0.590 $e.Å^{-3}$

Table 34. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for [Li(tmeda)][$VO(CH_3)_4$]·LiCl(tmeda). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1110(7)	0	2113(13)	158(8)
C(2)	2298(8)	1193(4)	2833(10)	140(5)
C(3)	3529(7)	0	3571(12)	107(4)
C(4)	1457(4)	1436(4)	6014(7)	64(2)
C(5)	1139(5)	402(4)	7380(14)	141(4)
C(6)	2162(4)	1443(5)	8750(7)	92(3)
C(7)	3918(3)	1825(4)	7265(6)	51(2)
C(8)	5281(4)	1649(4)	7515(7)	57(2)
C(9)	5128(4)	2510(3)	9368(6)	50(2)
Cl	3902(1)	0	9578(2)	31(1)
Li(1)	2615(7)	0	7334(13)	34(3)
Li(2)	5000	871(6)	10000	31(2)
N(1)	1787(2)	905(3)	7387(5)	43(1)

N(2)	4824(2)	1772(2)	8379(5)	37(1)
O(1)	2588(3)	0	5400(5)	39(1)
V(1)	2413(1)	0	3618(1)	37(1)

Table 35. Bond lengths [pm] and angles [°] for [Li(tmeda)][$VO(CH_3)_4$]·LiCl(tmeda).

C(1)-V(1)	209.8(11)	C(1)-H(1A)	98.00	C(1)-H(1B)	98.00
C(1)-H(1C)	98.00	C(2)-V(1)	205.8(7)	C(2)-H(2A)	98.00
C(2)-H(2B)	98.00	C(2)-H(2C)	98.00	C(3)-V(1)	205.5(10)
C(3)-H(3A)	98.00	C(3)-H(3B)	98.00	C(3)-H(3C)	98.00
C(4)-N(1)	146.1(7)	C(4)-H(4A)	98.00	C(4)-H(4B)	98.00
C(4)-H(4C)	98.00	C(5)-C(5)#1	130.7(14)	C(5)-N(1)	143.1(8)
C(5)-Li(1)	278.7(13)	C(5)-H(5A)	99.00	C(5)-H(5B)	99.00
C(6)-N(1)	146.0(8)	C(6)-H(6A)	98.00	C(6)-H(6B)	98.00
C(6)-H(6C)	98.00	C(7)-N(2)	147.3(6)	C(7)-H(7A)	98.00
C(7)-H(7B)	98.00	C(7)-H(7C)	98.00	C(8)-N(2)	146.1(7)
C(8)-H(8A)	98.00	C(8)-H(8B)	98.00	C(8)-H(8C)	98.00
C(9)-N(2)	147.0(6)	C(9)-C(9)#2	152.2(11)	C(9)-Li(2)	276.9(11)
C(9)-H(9A)	99.00	C(9)-H(9B)	99.00	Cl-Li(1)	230.7(12)
Cl-Li(2)#3	231.7(6)	Cl-Li(2)	231.7(6)	Li(1)-O(1)	187.4(12)
Li(1)-N(1)	212.4(9)	Li(1)-N(1)#1	212.4(9)	Li(1)-C(5)#1	278.7(13)
Li(2)-N(2)#2	206.9(8)	Li(2)-N(2)	206.9(8)	Li(2)-Cl#3	231.7(6)
Li(2)-C(9)#2	276.9(11)	Li(2)-Li(2)#3	283(2)	O(1)-V(1)	161.7(4)
V(1)-C(2)#1	205.8(7)			V(1)-C(1)-H(1A)	109.5
V(1)-C(1)-H(1B)	109.5	H(1A)-C(1)-H(1B)	109.5	V(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5	H(1B)-C(1)-H(1C)	109.5	V(1)-C(2)-H(2A)	109.5
V(1)-C(2)-H(2B)	109.5	H(2A)-C(2)-H(2B)	109.5	V(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5	H(2B)-C(2)-H(2C)	109.5	V(1)-C(3)-H(3A)	109.5
V(1)-C(3)-H(3B)	109.5	H(3A)-C(3)-H(3B)	109.5	V(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5	H(3B)-C(3)-H(3C)	109.5	N(1)-C(4)-H(4A)	109.5
N(1)-C(4)-H(4B)	109.5	H(4A)-C(4)-H(4B)	109.5	N(1)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5	H(4B)-C(4)-H(4C)	109.5	C(5)#1-C(5)-N(1)	124.8(3)
C(5)#1-C(5)-Li(1)	76.44(15)	N(1)-C(5)-Li(1)	48.3(3)	C(5)#1-C(5)-H(5A)	106.1
N(1)-C(5)-H(5A)	106.1	Li(1)-C(5)-H(5A)	126.7	C(5)#1-C(5)-H(5B)	106.1

N(1)-C(5)-H(5B)	106.1	Li(1)-C(5)-H(5B)	124.4	H(5A)-C(5)-H(5B)	106.3
N(1)-C(6)-H(6A)	109.5	N(1)-C(6)-H(6B)	109.5	H(6A)-C(6)-H(6B)	109.5
N(1)-C(6)-H(6C)	109.5	H(6A)-C(6)-H(6C)	109.5	H(6B)-C(6)-H(6C)	109.5
N(2)-C(7)-H(7A)	109.5	N(2)-C(7)-H(7B)	109.5	H(7A)-C(7)-H(7B)	109.5
N(2)-C(7)-H(7C)	109.5	H(7A)-C(7)-H(7C)	109.5	H(7B)-C(7)-H(7C)	109.5
N(2)-C(8)-H(8A)	109.5	N(2)-C(8)-H(8B)	109.5	H(8A)-C(8)-H(8B)	109.5
N(2)-C(8)-H(8C)	109.5	H(8A)-C(8)-H(8C)	109.5	H(8B)-C(8)-H(8C)	109.5
N(2)-C(9)-C(9)#2	111.8(4)	N(2)-C(9)-Li(2)	47.0(2)	C(9)#2-C(9)-Li(2)	74.05(12)
N(2)-C(9)-H(9A)	109.3	C(9)#2-C(9)-H(9A)	109.3	Li(2)-C(9)-H(9A)	150.9
N(2)-C(9)-H(9B)	109.3	C(9)#2-C(9)-H(9B)	109.3	Li(2)-C(9)-H(9B)	97.5
H(9A)-C(9)-H(9B)	107.9	Li(1)-Cl-Li(2)#3	124.0(2)	Li(1)-Cl-Li(2)	124.0(2)
Li(2)#3-Cl-Li(2)	75.2(4)	O(1)-Li(1)-N(1)	110.8(4)	O(1)-Li(1)-N(1)#1	110.8(4)
N(1)-Li(1)-N(1)#1	87.5(5)	O(1)-Li(1)-Cl	118.8(5)	N(1)-Li(1)-Cl	112.3(4)
N(1)#1-Li(1)-Cl	112.3(4)	O(1)-Li(1)-C(5)	117.7(6)	N(1)-Li(1)-C(5)	30.2(2)
N(1)#1-Li(1)-C(5)	57.3(3)	Cl-Li(1)-C(5)	121.6(5)	O(1)-Li(1)-C(5)#1	117.7(6)
N(1)-Li(1)-C(5)#1	57.3(3)	N(1)#1-Li(1)-C(5)#1	30.2(2)	Cl-Li(1)-C(5)#1	121.6(5)
C(5)-Li(1)-C(5)#1	27.1(3)	N(2)#2-Li(2)-N(2)	89.9(5)	N(2)#2-Li(2)-Cl	111.53(12)
N(2)-Li(2)-Cl	119.82(12)	N(2)#2-Li(2)-Cl#3	119.82(12)	N(2)-Li(2)-Cl#3	111.53(12)
Cl-Li(2)-Cl#3	104.8(4)	N(2)#2-Li(2)-C(9)	59.5(3)	N(2)-Li(2)-C(9)	31.3(2)
Cl-Li(2)-C(9)	134.9(2)	Cl#3-Li(2)-C(9)	117.88(19)	N(2)#2-Li(2)-C(9)#2	31.3(2)
N(2)-Li(2)-C(9)#2	59.5(3)	Cl-Li(2)-C(9)#2	117.88(19)	Cl#3-Li(2)-C(9)#2	134.9(2)
C(9)-Li(2)-C(9)#2	31.9(3)	N(2)#2-Li(2)-Li(2)#3	135.1(2)	N(2)-Li(2)-Li(2)#3	135.1(2)
Cl-Li(2)-Li(2)#3	52.4(2)	Cl#3-Li(2)-Li(2)#3	52.4(2)	C(9)-Li(2)-Li(2)#3	164.05(12)
C(9)#2-Li(2)-Li(2)#3	164.05(13)	C(5)-N(1)-C(6)	111.4(6)	C(5)-N(1)-C(4)	111.3(6)
C(6)-N(1)-C(4)	106.9(5)	C(5)-N(1)-Li(1)	101.5(4)	C(6)-N(1)-Li(1)	114.5(5)
C(4)-N(1)-Li(1)	111.3(4)	C(8)-N(2)-C(9)	110.9(4)	C(8)-N(2)-C(7)	109.0(4)
C(9)-N(2)-C(7)	111.6(4)	C(8)-N(2)-Li(2)	115.4(4)	C(9)-N(2)-Li(2)	101.7(3)
C(7)-N(2)-Li(2)	108.1(3)	V(1)-O(1)-Li(1)	171.4(5)	O(1)-V(1)-C(3)	110.3(3)
O(1)-V(1)-C(2)#1	109.6(2)	C(3)-V(1)-C(2)#1	85.0(3)	O(1)-V(1)-C(2)	109.6(2)
C(3)-V(1)-C(2)	85.0(3)	C(2)#1-V(1)-C(2)	140.6(4)	O(1)-V(1)-C(1)	108.8(4)
C(3)-V(1)-C(1)	140.9(5)	C(2)#1-V(1)-C(1)	82.1(4)	C(2)-V(1)-C(1)	82.1(4)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y,z #2 -x+1,y,-z+2 #3 -x+1,-y,-z+2

Table 36. Anisotropic displacement parameters ($pm^2 x\ 10^{-1}$) for [Li(tmeda)][$VO(CH_3)_4$]· LiCl(tmeda). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	63(8)	340(20)	43(6)	0	4(6)	0
C(2)	315(15)	59(5)	102(6)	28(5)	145(9)	51(7)
C(3)	80(8)	195(14)	58(7)	0	44(6)	0
C(4)	64(4)	61(4)	55(4)	11(3)	21(3)	33(3)
C(5)	93(6)	78(5)	321(14)	50(7)	154(8)	24(4)
C(6)	66(5)	141(7)	52(4)	-21(4)	16(4)	48(5)
C(7)	38(3)	47(3)	48(3)	13(3)	4(3)	-1(3)
C(8)	63(4)	61(4)	55(4)	13(3)	34(3)	4(3)
C(9)	46(3)	32(3)	61(4)	8(3)	17(3)	-2(3)
Cl	23(1)	29(1)	35(1)	0	8(1)	0
Li(1)	33(6)	34(6)	39(6)	0	20(6)	0
Li(2)	36(6)	21(5)	36(6)	0	18(5)	0
N(1)	29(2)	48(3)	47(3)	6(2)	16(2)	10(2)
N(2)	31(2)	31(2)	40(2)	7(2)	9(2)	-1(2)
O(1)	47(3)	45(3)	29(3)	0	20(2)	0
V(1)	42(1)	37(1)	30(1)	0	16(1)	0

8.4.2 $[Li_2(THF)_4][VO(CH_3)_4]$

8.4.2.1 Preparation of $[Li_2(THF)_4][VO(CH_3)_4]$

Method A: To 10.7 mmol MeLi (6.7 mL of 1.6 M solution in Et_2O) a 0.5 g tmeda in 10 mL Et_2O was added slowly at RT. The resulting suspension was stirred for 1 hr and cooled to –78°C. To this suspension a solution of $VOCl_3$ (2.14 mmol, 0.370 g) in Et_2O (30 mL) was added slowly over 1 hr and kept at –78°C overnight. A blue deposit and light black solution were formed. The reaction mixture was stirred at –35°C for 3-5 hr, and finally a blue precipitate was formed. The blue solid was collected by filtration washed with Et_2O (3*x*10 mL) dried under vacuum, and redissolved in THF (30 mL). Slow cooling of the resulting blue

solution from –35°C to –80°C afforded blue crystals of the product which were isolated by filtration, washed by small amount of THF (5 mL) and dried in vacuum at –35°C. Yield 50-60%.

Method B: To a suspension of $VOCl_2$·tmeda (4.1 mmol, 1.05 g) in THF (20 mL) 13 mL solution of 1.6 M MeLi in Et_2O was added at –78°C. The reaction mixture was warm to –35°C and stirred for 3 hr at this temperature. All insoluble reactants were dissolved and green-blue solution formed. The resulting blue solution was cooled from –35°C to –80°C to afford blue crystals of the product which were isolated by filtration, washed by small amount of THF (5 mL) and dried in vacuum at –35°C. High yield produced from this procedure, about 80%.

8.4.2.2 Crystal Data and Crystal Structure Analysis of $[Li_2(THF)_4][VO(CH_3)_4]$

Table 37. Crystal data and structure refinement for $[Li_2(THF)_4][VO(CH_3)_4]$.

Identification code	vome43	
Empirical formula	$C_{20}\ H_{44}\ Li_2O_5\ V$	
Formula weight	429.37	
Temperature	133(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	P121/n1	
Unit cell dimensions	a = 1102.4(3) pm	α= 90°.
	b = 1679.3(4) pm	β= 102.951(5)°.
	c = 1640.7(4) pm	γ = 90°.
Volume	2.9599(12) nm^3	
Z	4	
Density (calculated)	0.964 Mg/m^3	
Absorption coefficient	0.355 mm^{-1}	
F(000)	932	
Crystal size	0.4 x 0.4 x 0.4 mm^3	
Theta range for data collection	1.76 to 30.53°.	

Index ranges	-15<=h<=15, -24<=k<=17, -23<=l<=23
Reflections collected	46575
Independent reflections	9031 [R(int) = 0.0381]
Completeness to theta = 30.53°	99.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9031 / 0 / 347
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0507, wR2 = 0.1252
R indices (all data)	R1 = 0.0773, wR2 = 0.1395
Largest diff. peak and hole	0.432 and -0.486 e.Å^{-3}

Table 38. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for $[Li_2(THF)_4][VO(CH_3)_4]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2762(2)	2577(1)	1785(2)	40(1)
C(2)	4821(2)	3667(1)	1836(2)	40(1)
C(3)	3638(2)	1832(1)	435(1)	41(1)
C(4)	5977(2)	2675(2)	806(2)	44(1)
C(5)	6671(3)	964(2)	4419(1)	53(1)
C(6)	7015(3)	340(2)	5066(2)	61(1)
C(7)	8071(2)	-94(2)	4792(2)	53(1)
C(8)	7707(3)	-42(2)	3870(2)	68(1)
C(9)	6248(2)	359(1)	1131(1)	39(1)
C(10)	6895(2)	301(1)	414(1)	41(1)
C(11)	8165(2)	-21(1)	849(1)	39(1)
C(12)	8415(2)	418(1)	1672(1)	38(1)
C(13)	9450(2)	1926(2)	3433(2)	64(1)
C(14)	10184(3)	2671(2)	3295(2)	78(1)
C(15)	9234(3)	3207(2)	2760(2)	75(1)
C(16)	8031(2)	2921(2)	2954(2)	58(1)
C(17)	3640(2)	2081(2)	4632(2)	51(1)
C(18)	4294(2)	2616(2)	5322(2)	63(1)
C(19)	4662(3)	3321(2)	4862(2)	64(1)

C(20)	4956(2)	2956(1)	4111(1)	45(1)
C(21)	1904(2)	582(1)	2606(2)	44(1)
C(22)	1835(2)	149(1)	1793(1)	45(1)
C(23)	3058(2)	-295(2)	1942(2)	69(1)
C(24)	3855(2)	46(1)	2713(2)	45(1)
Li(1)	3908(3)	1779(2)	2841(2)	34(1)
Li(2)	6828(3)	1332(2)	2666(2)	33(1)
O(1)	5278(1)	1827(1)	2318(1)	26(1)
O(2)	6955(2)	657(1)	3671(1)	46(1)
O(3)	7212(1)	566(1)	1853(1)	40(1)
O(4)	8193(1)	2073(1)	3023(1)	58(1)
O(5)	4141(1)	2272(1)	3921(1)	40(1)
O(6)	3206(1)	725(1)	2940(1)	39(1)
V(1)	4621(1)	2433(1)	1530(1)	24(1)

Table 39. Bond lengths [pm] and angles [°] for $[Li_2(THF)_4][VO(CH_3)_4]$.

C(1)-V(1)	219.5(2)	C(1)-Li(1)	232.7(4)	C(1)-H(1)	98(2)
C(1)-H(2)	100(3)	C(1)-H(3)	96(3)	C(2)-V(1)	213.3(2)
C(2)-H(2A)	93(3)	C(2)-H(2B)	95(3)	C(2)-H(2C)	92(3)
C(3)-V(1)	213.2(2)	C(3)-H(3A)	99(3)	C(3)-H(3B)	95(3)
C(3)-H(3C)	96(3)	C(4)-V(1)	214.6(2)	C(4)-H(4A)	97(3)
C(4)-H(4B)	93(3)	C(4)-H(4C)	92(3)	C(5)-O(2)	142.9(3)
C(5)-C(6)	147.9(3)	C(5)-H(5A)	99.00	C(5)-H(5B)	99.00
C(6)-C(7)	152.4(3)	C(6)-H(6A)	99.00	C(6)-H(6B)	99.00
C(7)-C(8)	147.8(3)	C(7)-H(7A)	99.00	C(7)-H(7B)	99.00
C(8)-O(2)	143.2(3)	C(8)-H(8A)	99.00	C(8)-H(8B)	99.00
C(9)-O(3)	144.5(2)	C(9)-C(10)	150.9(3)	C(9)-H(9A)	99.00
C(9)-H(9B)	99.00	C(10)-C(11)	152.1(3)	C(10)-H(10A)	99.00
C(10)-H(10B)	99.00	C(11)-C(12)	150.9(3)	C(11)-H(11A)	99.00
C(11)-H(11B)	99.00	C(12)-O(3)	144.4(2)	C(12)-H(12A)	99.00
C(12)-H(12B)	99.00	C(13)-O(4)	142.0(3)	C(13)-C(14)	153.4(4)
C(13)-H(13A)	99.00	C(13)-H(13B)	99.00	C(14)-C(15)	150.4(5)
C(14)-H(14A)	99.00	C(14)-H(14B)	99.00	C(15)-C(16)	151.0(4)
C(15)-H(15A)	99.00	C(15)-H(15B)	99.00	C(16)-O(4)	143.6(3)

C(16)-H(16A)	99.00	C(16)-H(16B)	99.00	C(17)-O(5)	143.4(2)
C(17)-C(18)	149.8(3)	C(17)-H(17A)	99.00	C(17)-H(17B)	99.00
C(18)-C(19)	150.7(4)	C(18)-H(18A)	99.00	C(18)-H(18B)	99.00
C(19)-C(20)	147.6(3)	C(19)-H(19A)	99.00	C(19)-H(19B)	99.00
C(20)-O(5)	144.9(2)	C(20)-H(20A)	99.00	C(20)-H(20B)	99.00
C(21)-O(6)	143.7(2)	C(21)-C(22)	150.6(3)	C(21)-H(21A)	99.00
C(21)-H(21B)	99.00	C(22)-C(23)	151.2(3)	C(22)-H(22A)	99.00
C(22)-H(22B)	99.00	C(23)-C(24)	148.3(3)	C(23)-H(23A)	99.00
C(23)-H(23B)	99.00	C(24)-O(6)	143.9(3)	C(24)-H(24A)	99.00
C(24)-H(24B)	99.00	Li(1)-O(1)	189.9(3)	Li(1)-O(5)	191.9(3)
Li(1)-O(6)	195.4(3)	Li(1)-V(1)	268.5(3)	Li(1)-Li(2)	338.0(4)
Li(1)-H(3)	223(3)	Li(2)-O(1)	187.0(3)	Li(2)-O(4)	193.9(4)
Li(2)-O(3)	196.6(3)	Li(2)-O(2)	197.9(4)	Li(2)-V(1)	328.3(3)
O(1)-V(1)	167.74(12)			V(1)-C(1)-Li(1)	72.79(10)
V(1)-C(1)-H(1)	101.3(14)	Li(1)-C(1)-H(1)	172.6(14)	V(1)-C(1)-H(2)	118.9(15)
Li(1)-C(1)-H(2)	82.6(15)	H(1)-C(1)-H(2)	104(2)	V(1)-C(1)-H(3)	116.6(17)
Li(1)-C(1)-H(3)	72.3(17)	H(1)-C(1)-H(3)	107(2)	H(2)-C(1)-H(3)	107(2)
V(1)-C(2)-H(2A)	117.2(19)	V(1)-C(2)-H(2B)	109.4(19)	H(2A)-C(2)-H(2B)	111(3)
V(1)-C(2)-H(2C)	112.8(19)	H(2A)-C(2)-H(2C)	103(3)	H(2B)-C(2)-H(2C)	102(3)
V(1)-C(3)-H(3A)	116.3(14)	V(1)-C(3)-H(3B)	104.6(18)	H(3A)-C(3)-H(3B)	106(2)
V(1)-C(3)-H(3C)	111.9(17)	H(3A)-C(3)-H(3C)	111(2)	H(3B)-C(3)-H(3C)	106(2)
V(1)-C(4)-H(4A)	116.2(18)	V(1)-C(4)-H(4B)	109.5(17)	H(4A)-C(4)-H(4B)	104(2)
V(1)-C(4)-H(4C)	113.1(18)	H(4A)-C(4)-H(4C)	112(2)	H(4B)-C(4)-H(4C)	100(2)
O(2)-C(5)-C(6)	106.95(19)	O(2)-C(5)-H(5A)	110.3	C(6)-C(5)-H(5A)	110.3
O(2)-C(5)-H(5B)	110.3	C(6)-C(5)-H(5B)	110.3	H(5A)-C(5)-H(5B)	108.6
C(5)-C(6)-C(7)	102.5(2)	C(5)-C(6)-H(6A)	111.3	C(7)-C(6)-H(6A)	111.3
C(5)-C(6)-H(6B)	111.3	C(7)-C(6)-H(6B)	111.3	H(6A)-C(6)-H(6B)	109.2
C(8)-C(7)-C(6)	102.89(19)	C(8)-C(7)-H(7A)	111.2	C(6)-C(7)-H(7A)	111.2
C(8)-C(7)-H(7B)	111.2	C(6)-C(7)-H(7B)	111.2	H(7A)-C(7)-H(7B)	109.1
O(2)-C(8)-C(7)	107.02(19)	O(2)-C(8)-H(8A)	110.3	C(7)-C(8)-H(8A)	110.3
O(2)-C(8)-H(8B)	110.3	C(7)-C(8)-H(8B)	110.3	H(8A)-C(8)-H(8B)	108.6
O(3)-C(9)-C(10)	105.35(16)	O(3)-C(9)-H(9A)	110.7	C(10)-C(9)-H(9A)	110.7
O(3)-C(9)-H(9B)	110.7	C(10)-C(9)-H(9B)	110.7	H(9A)-C(9)-H(9B)	108.8
C(9)-C(10)-C(11)	101.77(17)	C(9)-C(10)-H(10A)	111.4	C(11)-C(10)-H(10A)	111.4
C(9)-C(10)-H(10B)	111.4	C(11)-C(10)-H(10B)	111.4	H(10A)-C(10)-H(10B)	109.3

C(12)-C(11)-C(10)	102.15(16)	C(12)-C(11)-H(11A)	111.3	C(10)-C(11)-H(11A)	111.3
C(12)-C(11)-H(11B)	111.3	C(10)-C(11)-H(11B)	111.3	H(11A)-C(11)-H(11B)	109.2
O(3)-C(12)-C(11)	106.01(16)	O(3)-C(12)-H(12A)	110.5	C(11)-C(12)-H(12A)	110.5
O(3)-C(12)-H(12B)	110.5	C(11)-C(12)-H(12B)	110.5	H(12A)-C(12)-H(12B)	108.7
O(4)-C(13)-C(14)	106.2(2)	O(4)-C(13)-H(13A)	110.5	C(14)-C(13)-H(13A)	110.5
O(4)-C(13)-H(13B)	110.5	C(14)-C(13)-H(13B)	110.5	H(13A)-C(13)-H(13B)	108.7
C(15)-C(14)-C(13)	104.6(2)	C(15)-C(14)-H(14A)	110.8	C(13)-C(14)-H(14A)	110.8
C(15)-C(14)-H(14B)	110.8	C(13)-C(14)-H(14B)	110.8	H(14A)-C(14)-H(14B)	108.9
C(14)-C(15)-C(16)	102.5(3)	C(14)-C(15)-H(15A)	111.3	C(16)-C(15)-H(15A)	111.3
C(14)-C(15)-H(15B)	111.3	C(16)-C(15)-H(15B)	111.3	H(15A)-C(15)-H(15B)	109.2
O(4)-C(16)-C(15)	103.4(2)	O(4)-C(16)-H(16A)	111.1	C(15)-C(16)-H(16A)	111.1
O(4)-C(16)-H(16B)	111.1	C(15)-C(16)-H(16B)	111.1	H(16A)-C(16)-H(16B)	109.0
O(5)-C(17)-C(18)	105.87(19)	O(5)-C(17)-H(17A)	110.6	C(18)-C(17)-H(17A)	110.6
O(5)-C(17)-H(17B)	110.6	C(18)-C(17)-H(17B)	110.6	H(17A)-C(17)-H(17B)	108.7
C(17)-C(18)-C(19)	103.3(2)	C(17)-C(18)-H(18A)	111.1	C(19)-C(18)-H(18A)	111.1
C(17)-C(18)-H(18B)	111.1	C(19)-C(18)-H(18B)	111.1	H(18A)-C(18)-H(18B)	109.1
C(20)-C(19)-C(18)	103.1(2)	C(20)-C(19)-H(19A)	111.1	C(18)-C(19)-H(19A)	111.1
C(20)-C(19)-H(19B)	111.1	C(18)-C(19)-H(19B)	111.1	H(19A)-C(19)-H(19B)	109.1
O(5)-C(20)-C(19)	105.47(19)	O(5)-C(20)-H(20A)	110.6	C(19)-C(20)-H(20A)	110.6
O(5)-C(20)-H(20B)	110.6	C(19)-C(20)-H(20B)	110.6	H(20A)-C(20)-H(20B)	108.8
O(6)-C(21)-C(22)	105.46(16)	O(6)-C(21)-H(21A)	110.6	C(22)-C(21)-H(21A)	110.6
O(6)-C(21)-H(21B)	110.6	C(22)-C(21)-H(21B)	110.6	H(21A)-C(21)-H(21B)	108.8
C(21)-C(22)-C(23)	103.19(18)	C(21)-C(22)-H(22A)	111.1	C(23)-C(22)-H(22A)	111.1
C(21)-C(22)-H(22B)	111.1	C(23)-C(22)-H(22B)	111.1	H(22A)-C(22)-H(22B)	109.1
C(24)-C(23)-C(22)	106.5(2)	C(24)-C(23)-H(23A)	110.4	C(22)-C(23)-H(23A)	110.4
C(24)-C(23)-H(23B)	110.4	C(22)-C(23)-H(23B)	110.4	H(23A)-C(23)-H(23B)	108.6
O(6)-C(24)-C(23)	107.02(18)	O(6)-C(24)-H(24A)	110.3	C(23)-C(24)-H(24A)	110.3
O(6)-C(24)-H(24B)	110.3	C(23)-C(24)-H(24B)	110.3	H(24A)-C(24)-H(24B)	108.6
O(1)-Li(1)-O(5)	116.35(17)	O(1)-Li(1)-O(6)	116.46(17)	O(5)-Li(1)-O(6)	106.70(16)
O(1)-Li(1)-C(1)	89.62(14)	O(5)-Li(1)-C(1)	112.16(17)	O(6)-Li(1)-C(1)	115.13(16)
O(1)-Li(1)-V(1)	38.31(7)	O(5)-Li(1)-V(1)	124.12(15)	O(6)-Li(1)-V(1)	129.01(15)
C(1)-Li(1)-V(1)	51.35(8)	O(1)-Li(1)-Li(2)	26.04(9)	O(5)-Li(1)-Li(2)	103.98(14)
O(6)-Li(1)-Li(2)	102.02(14)	C(1)-Li(1)-Li(2)	115.66(13)	V(1)-Li(1)-Li(2)	64.35(9)
O(1)-Li(1)-H(3)	104.3(8)	O(5)-Li(1)-H(3)	88.2(8)	O(6)-Li(1)-H(3)	122.1(8)
C(1)-Li(1)-H(3)	24.2(7)	V(1)-Li(1)-H(3)	67.7(8)	Li(2)-Li(1)-H(3)	128.7(8)

O(1)-Li(2)-O(4)	113.64(18)	O(1)-Li(2)-O(3)	113.86(16)	O(4)-Li(2)-O(3)	110.74(17)
O(1)-Li(2)-O(2)	113.41(17)	O(4)-Li(2)-O(2)	102.19(16)	O(3)-Li(2)-O(2)	101.81(16)
O(1)-Li(2)-V(1)	21.04(6)	O(4)-Li(2)-V(1)	103.66(14)	O(3)-Li(2)-V(1)	103.18(12)
O(2)-Li(2)-V(1)	134.44(14)	O(1)-Li(2)-Li(1)	26.47(9)	O(4)-Li(2)-Li(1)	121.39(15)
O(3)-Li(2)-Li(1)	123.86(14)	O(2)-Li(2)-Li(1)	86.97(13)	V(1)-Li(2)-Li(1)	47.50(7)
V(1)-O(1)-Li(2)	135.37(12)	V(1)-O(1)-Li(1)	97.13(12)	Li(2)-O(1)-Li(1)	127.49(15)
C(5)-O(2)-C(8)	109.01(17)	C(5)-O(2)-Li(2)	121.39(16)	C(8)-O(2)-Li(2)	126.10(18)
C(12)-O(3)-C(9)	109.33(14)	C(12)-O(3)-Li(2)	126.82(15)	C(9)-O(3)-Li(2)	118.86(14)
C(13)-O(4)-C(16)	107.50(19)	C(13)-O(4)-Li(2)	129.8(2)	C(16)-O(4)-Li(2)	122.57(16)
C(17)-O(5)-C(20)	109.61(16)	C(17)-O(5)-Li(1)	131.15(16)	C(20)-O(5)-Li(1)	119.24(15)
C(21)-O(6)-C(24)	106.32(15)	C(21)-O(6)-Li(1)	120.01(16)	C(24)-O(6)-Li(1)	117.82(16)
O(1)-V(1)-C(3)	114.38(8)	O(1)-V(1)-C(2)	113.84(8)	C(3)-V(1)-C(2)	131.64(9)
O(1)-V(1)-C(4)	107.94(9)	C(3)-V(1)-C(4)	84.77(10)	C(2)-V(1)-C(4)	84.16(10)
O(1)-V(1)-C(1)	100.38(7)	C(3)-V(1)-C(1)	83.85(10)	C(2)-V(1)-C(1)	84.23(9)
C(4)-V(1)-C(1)	151.68(10)	O(1)-V(1)-Li(1)	44.56(8)	C(3)-V(1)-Li(1)	107.27(10)
C(2)-V(1)-Li(1)	104.00(10)	C(4)-V(1)-Li(1)	152.41(10)	C(1)-V(1)-Li(1)	55.87(9)
O(1)-V(1)-Li(2)	23.59(7)	C(3)-V(1)-Li(2)	112.58(9)	C(2)-V(1)-Li(2)	112.90(9)
C(4)-V(1)-Li(2)	84.35(9)	C(1)-V(1)-Li(2)	123.97(8)	Li(1)-V(1)-Li(2)	68.15(9)

Symmetry transformations used to generate equivalent atoms:

Table 40. Anisotropic displacement parameters ($pm^2 x\ 10^{-1}$)for $[Li_2(THF)_4][VO(CH_3)_4]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	28(1)	40(1)	54(1)	10(1)	12(1)	5(1)
C(2)	46(1)	25(1)	53(1)	0(1)	17(1)	1(1)
C(3)	46(1)	39(1)	34(1)	0(1)	-1(1)	-3(1)
C(4)	50(1)	46(1)	42(1)	-2(1)	24(1)	-10(1)
C(5)	75(2)	49(1)	38(1)	2(1)	20(1)	25(1)
C(6)	71(2)	66(2)	53(1)	16(1)	28(1)	20(1)
C(7)	53(1)	58(2)	45(1)	11(1)	8(1)	20(1)
C(8)	96(2)	60(2)	44(1)	-3(1)	7(1)	48(2)
C(9)	32(1)	41(1)	43(1)	-7(1)	7(1)	0(1)
C(10)	47(1)	43(1)	34(1)	-9(1)	7(1)	0(1)

C(11)	42(1)	36(1)	44(1)	-3(1)	19(1)	3(1)
C(12)	34(1)	44(1)	38(1)	1(1)	9(1)	12(1)
C(13)	33(1)	79(2)	74(2)	-14(2)	-3(1)	3(1)
C(14)	39(1)	116(3)	80(2)	-11(2)	17(1)	-21(2)
C(15)	76(2)	72(2)	81(2)	-15(2)	27(2)	-23(2)
C(16)	45(1)	58(2)	65(2)	-10(1)	2(1)	-5(1)
C(17)	54(1)	60(2)	49(1)	-7(1)	31(1)	-12(1)
C(18)	48(1)	106(2)	37(1)	-12(1)	13(1)	-10(1)
C(19)	69(2)	66(2)	61(2)	-30(1)	23(1)	-18(1)
C(20)	55(1)	33(1)	47(1)	-6(1)	14(1)	-11(1)
C(21)	35(1)	34(1)	68(1)	-1(1)	23(1)	-5(1)
C(22)	41(1)	42(1)	50(1)	5(1)	4(1)	-7(1)
C(23)	52(1)	95(2)	55(2)	-31(2)	4(1)	17(1)
C(24)	43(1)	35(1)	55(1)	-6(1)	6(1)	3(1)
Li(1)	36(2)	31(2)	37(2)	-3(1)	15(1)	-5(1)
Li(2)	28(1)	42(2)	30(2)	-1(1)	6(1)	6(1)
O(1)	24(1)	27(1)	28(1)	2(1)	7(1)	4(1)
O(2)	61(1)	46(1)	33(1)	4(1)	11(1)	27(1)
O(3)	34(1)	53(1)	32(1)	-6(1)	7(1)	14(1)
O(4)	34(1)	56(1)	75(1)	-2(1)	-8(1)	-5(1)
O(5)	54(1)	34(1)	39(1)	-10(1)	23(1)	-14(1)
O(6)	40(1)	30(1)	51(1)	-6(1)	16(1)	-8(1)
V(1)	24(1)	22(1)	27(1)	3(1)	6(1)	2(1)

8.4.3 $[Li_2(THF)_x][VO(C_6H_5)_4]$

8.4.2.1 Preparation of $[Li_2(THF)_x][VO(C_6H_5)_4]$

Method A: A solution of $VOCl_3$ (3.75 mmol, 0.650g) in 30 mL Et_2O was added slowly to a mixture of 16.9 mmol PhLi (20 mL of 0.84 M solution in Et_2O) and 0.87g tmeda in Et_2O over 1 hr and kept at –78^oC overnight. A green deposit and light black solution were formed. The reaction mixture was stirred at –35^oC for 6 hr. The green solid was collected by filtration washed with Et_2O (3*x*10 mL) dried under vacuum, and redissolved in THF (30 mL). Slow

cooling of the resulting green solution from –35°C to –80°C afforded green needles of the product which were isolated by filtration, and dried in vacuum at –35°C.

Method B: A suspension of $VOCl_2$·tmeda (3.9 mmol, 1.0 g) in THF (20 mL) was treated dropwise with PhLi (21 mL solution of 0.84 M PhLi in Et_2O) at –78°C. The reaction mixture was warm to –35°C and stirred for 3 hr at this temperature. The resulting green solution was cooled from –35°C to –80°C to afford green crystals of the product which were isolated by filtration, and dried in vacuum at –35°C.

8.4.2.2 Crystal Data and Crystal Structure Analysis of $[Li_2(THF)_x][VO(C_6H_5)_4]$

Table 41. Crystal data and structure refinement for $[Li_2(THF)_x][VO(C_6H_5)_4]$.

Identification code	vphe	
Empirical formula	C_{50} H_{40} Cl Li_4 O V	
Formula weight	770.97	
Temperature	293(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	C12/c1	
Unit cell dimensions	a = 2020(2) pm	α= 90°.
	b = 1490.1(14) pm	β= 104.35(2)°.
	c = 3394(3) pm	γ = 90°.
Volume	9.90(2) nm^3	
Z	8	
Density (calculated)	1.035 Mg/m^3	
Absorption coefficient	0.285 mm^{-1}	
F(000)	3200	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	1.24 to 17.62°.	
Index ranges	-17<=h<=15, -12<=k<=12, -28<=l<=28	
Reflections collected	13877	
Independent reflections	3156 [R(int) = 0.2969]	

Completeness to theta = 17.62°	98.2 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3156 / 0 / 523
Goodness-of-fit on F^2	1.185
Final R indices [I>2sigma(I)]	R1 = 0.1694, wR2 = 0.3431
R indices (all data)	R1 = 0.2596, wR2 = 0.3962
Largest diff. peak and hole	0.543 and -0.458 e.Å^{-3}

Table 42. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for $[Li_2(THF)_x][VO(C_6H_5)_4]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8611(10)	5674(18)	1311(7)	94(8)
C(2)	8413(13)	6399(15)	1517(7)	100(9)
C(3)	7832(13)	6962(14)	1325(9)	122(10)
C(4)	7489(12)	6660(20)	868(7)	142(13)
C(5)	7700(20)	6010(20)	679(12)	250(20)
C(6)	8204(12)	5450(20)	873(11)	163(16)
C(7)	9910(11)	5537(15)	1236(5)	72(7)
C(8)	10390(12)	6266(17)	1383(8)	104(9)
C(9)	10724(11)	6745(19)	1119(9)	120(11)
C(10)	10531(14)	6420(20)	679(7)	136(12)
C(11)	10078(11)	5760(20)	531(10)	137(13)
C(12)	9774(11)	5308(15)	800(7)	91(8)
C(13)	8667(9)	3732(14)	1525(7)	72(7)
C(14)	8502(12)	3346(16)	1876(6)	85(7)
C(15)	7992(12)	2688(15)	1830(9)	117(10)
C(16)	7685(13)	2405(19)	1404(9)	137(13)
C(17)	7878(18)	2750(20)	1083(9)	131(13)
C(18)	8323(13)	3432(17)	1130(9)	109(10)
C(19)	10137(10)	3716(14)	1582(7)	75(7)
C(20)	10374(11)	3268(13)	1974(6)	76(7)
C(21)	10945(12)	2564(16)	1995(8)	110(9)
C(22)	11188(14)	2360(20)	1656(9)	146(13)

C(23)	10930(15)	2790(20)	1294(8)	123(10)
C(24)	10422(13)	3477(16)	1248(7)	101(8)
C(30)	-1526(14)	-740(20)	4175(7)	133(11)
C(31)	-1773(11)	-410(19)	3711(7)	112(9)
C(32)	-1136(15)	-10(20)	3626(7)	166(14)
C(34)	-900(11)	-416(19)	4351(6)	115(10)
C(35)	11673(10)	4919(17)	1976(7)	98(8)
C(36)	12311(19)	4650(40)	2083(10)	390(40)
C(37)	12102(10)	5275(18)	2703(7)	115(9)
C(38)	12652(14)	4860(40)	2545(9)	300(30)
C(29)	892(17)	490(30)	3028(9)	201(18)
C(40)	454(17)	1150(20)	3058(8)	149(12)
C(41)	603(15)	1368(18)	3511(7)	129(10)
C(42)	3166(15)	441(17)	9068(7)	132(10)
C(43)	3485(11)	818(14)	9506(6)	84(7)
C(44)	940(20)	-2090(40)	4255(10)	250(20)
C(45)	1270(30)	-2280(40)	4626(13)	260(30)
C(46)	1090(40)	-2120(30)	4896(15)	430(50)
C(47)	860(17)	-220(20)	3413(9)	177(14)
C(50)	2524(18)	-40(20)	9211(10)	230(20)
C(51)	2709(17)	-180(20)	9613(14)	190(17)
C(52)	3160(30)	450(30)	9733(11)	320(30)
C(56)	980(30)	-980(20)	4809(11)	320(30)
C(54)	940(30)	1950(60)	4674(10)	740(60)
C(55)	1330(20)	2459(14)	4836(8)	230(20)
Li(1)	10550(20)	5120(50)	2418(11)	180(30)
Li(2)	610(13)	1220(30)	4601(11)	55(11)
O(1)	9671(5)	5113(8)	2074(3)	57(4)
O(3)	11476(6)	5125(9)	2357(4)	82(4)
O(4)	-626(9)	-26(14)	4025(7)	173(8)
O(5)	788(9)	485(12)	3698(5)	116(6)
O(6)	983(10)	-948(9)	4423(6)	126(7)
O(7)	1400(30)	1267(18)	4673(8)	420(30)
V	9420(2)	4787(2)	1590(1)	65(1)
O(9)	10702(14)	6794(19)	2445(9)	101(10)

C(57)	10000	7350(30)	2500	200(20)
C(58)	200(30)	1720(30)	4619(13)	94(15)
C(59)	11310(20)	7420(30)	2303(13)	99(15)
C(60)	10800(40)	8380(50)	2220(20)	210(30)

Table 43. Bond lengths [pm] and angles [°] for $[Li_2(THF)_x][VO(C_6H_5)_4]$.

C(1)-C(2)	140(3)	C(1)-C(6)	154(4)	C(1)-V	213(2)
C(2)-C(3)	146(3)	C(3)-C(4)	160(4)	C(4)-C(5)	129(4)
C(5)-C(6)	135(5)	C(7)-C(8)	146(3)	C(7)-C(12)	148(3)
C(7)-V	207(2)	C(8)-C(9)	144(3)	C(9)-C(10)	153(3)
C(10)-C(11)	135(4)	C(11)-C(12)	139(3)	C(13)-C(14)	144(3)
C(13)-C(18)	142(3)	C(13)-V	216(2)	C(14)-C(15)	140(3)
C(15)-C(16)	149(3)	C(16)-C(17)	135(4)	C(17)-C(18)	135(4)
C(19)-C(24)	144(3)	C(19)-C(20)	146(2)	C(19)-V	216(2)
C(20)-C(21)	155(3)	C(21)-C(22)	139(3)	C(22)-C(23)	137(3)
C(23)-C(24)	143(3)	C(30)-C(34)	135(3)	C(30)-C(31)	161(3)
C(31)-C(32)	151(3)	C(32)-O(4)	149(3)	C(34)-O(4)	147(2)
C(35)-C(36)	131(4)	C(35)-O(3)	148(2)	C(36)-C(38)	158(4)
C(37)-C(38)	149(3)	C(37)-O(3)	151(2)	C(29)-C(40)	135(4)
C(29)-C(47)	169(4)	C(40)-C(41)	153(3)	C(41)-O(5)	147(3)
C(42)-C(43)	157(3)	C(42)-C(50)	165(4)	C(43)-C(52)	125(3)
C(44)-C(45)	130(6)	C(44)-O(6)	178(5)	C(45)-C(46)	109(8)
C(46)-C(56)	173(6)	C(47)-O(5)	146(3)	C(50)-C(51)	134(5)
C(51)-C(52)	130(4)	C(56)-O(6)	131(4)	C(54)-O(7)	138(10)
C(54)-Li(2)	127(6)	C(54)-C(55)	113(4)	C(54)-C(58)	150(6)
C(55)-Li(2)	236(4)	Li(1)-O(1)	186(4)	Li(1)-O(1)#1	188(4)
Li(1)-O(3)	194(5)	Li(1)-Li(1)#1	240(9)	Li(1)-O(9)	252(7)
Li(1)-V	318(4)	Li(2)-C(58)	112(5)	Li(2)-O(7)	156(6)
O(1)-V	166.9(10)	O(1)-Li(1)#1	188(4)	O(9)-C(57)	169(4)
O(9)-C(59)	171(5)	C(57)-O(9)#1	169(4)	C(59)-C(60)	175(8)
		C(2)-C(1)-C(6)	120(2)	C(2)-C(1)-V	122.6(18)
C(6)-C(1)-V	117.6(19)	C(1)-C(2)-C(3)	121(2)	C(2)-C(3)-C(4)	112(2)
C(5)-C(4)-C(3)	125(3)	C(4)-C(5)-C(6)	121(4)	C(5)-C(6)-C(1)	120(3)
C(8)-C(7)-C(12)	117.3(19)	C(8)-C(7)-V	125.3(16)	C(12)-C(7)-V	117.4(17)

C(9)-C(8)-C(7)	122(2)	C(8)-C(9)-C(10)	114(2)	C(11)-C(10)-C(9)	126(3)
C(10)-C(11)-C(12)	118(3)	C(11)-C(12)-C(7)	123(2)	C(14)-C(13)-C(18)	120(2)
C(14)-C(13)-V	120.6(17)	C(18)-C(13)-V	119.6(19)	C(15)-C(14)-C(13)	120(2)
C(14)-C(15)-C(16)	115(2)	C(17)-C(16)-C(15)	123(3)	C(18)-C(17)-C(16)	121(3)
C(17)-C(18)-C(13)	121(3)	C(24)-C(19)-C(20)	120.0(19)	C(24)-C(19)-V	126.4(17)
C(20)-C(19)-V	113.4(15)	C(19)-C(20)-C(21)	115.1(18)	C(22)-C(21)-C(20)	121(2)
C(23)-C(22)-C(21)	121(3)	C(22)-C(23)-C(24)	122(2)	C(19)-C(24)-C(23)	121(2)
C(34)-C(30)-C(31)	111(2)	C(32)-C(31)-C(30)	103.8(19)	O(4)-C(32)-C(31)	104(2)
C(30)-C(34)-O(4)	107.3(19)	C(36)-C(35)-O(3)	106(2)	C(35)-C(36)-C(38)	112(3)
C(38)-C(37)-O(3)	102.3(19)	C(37)-C(38)-C(36)	105(2)	C(40)-C(29)-C(47)	104(2)
C(29)-C(40)-C(41)	105(3)	O(5)-C(41)-C(40)	102(2)	C(43)-C(42)-C(50)	92.6(19)
C(52)-C(43)-C(42)	106(2)	C(45)-C(44)-O(6)	86(3)	C(46)-C(45)-C(44)	125(6)
C(45)-C(46)-C(56)	97(5)	O(5)-C(47)-C(29)	95(2)	C(51)-C(50)-C(42)	109(2)
C(52)-C(51)-C(50)	102(3)	C(43)-C(52)-C(51)	124(3)	O(6)-C(56)-C(46)	100(4)
O(7)-C(54)-Li(2)	72(5)	O(7)-C(54)-C(55)	96(6)	Li(2)-C(54)-C(55)	160(7)
O(7)-C(54)-C(58)	119(6)	Li(2)-C(54)-C(58)	47(2)	C(55)-C(54)-C(58)	140(8)
C(54)-C(55)-Li(2)	11(4)	O(1)-Li(1)-O(1)#1	100(2)	O(1)-Li(1)-O(3)	137(2)
O(1)#1-Li(1)-O(3)	123(2)	O(1)-Li(1)-Li(1)#1	50.4(15)	O(1)#1-Li(1)-Li(1)#1	49.6(15)
O(3)-Li(1)-Li(1)#1	173(3)	O(1)-Li(1)-O(9)	97(2)	O(1)#1-Li(1)-O(9)	91(2)
O(3)-Li(1)-O(9)	83(2)	Li(1)#1-Li(1)-O(9)	96.1(12)	O(1)-Li(1)-V	24.1(7)
O(1)#1-Li(1)-V	122(2)	O(3)-Li(1)-V	114.0(16)	Li(1)#1-Li(1)-V	73.2(17)
O(9)-Li(1)-V	103.9(16)	C(58)-Li(2)-O(7)	134(4)	C(58)-Li(2)-C(54)	77(5)
O(7)-Li(2)-C(54)	57(4)	C(58)-Li(2)-C(55)	82(3)	O(7)-Li(2)-C(55)	52.5(18)
C(54)-Li(2)-C(55)	10(3)	V-O(1)-Li(1)	128.8(15)	V-O(1)-Li(1)#1	145.2(15)
Li(1)-O(1)-Li(1)#1	80(2)	C(35)-O(3)-C(37)	110.8(14)	C(35)-O(3)-Li(1)	124.7(17)
C(37)-O(3)-Li(1)	124.3(17)	C(32)-O(4)-C(34)	112.7(18)	C(41)-O(5)-C(47)	114.6(17)
C(56)-O(6)-C(44)	106(2)	C(54)-O(7)-Li(2)	51(2)	O(1)-V-C(7)	110.1(7)
O(1)-V-C(1)	105.6(8)	C(7)-V-C(1)	80.2(8)	O(1)-V-C(19)	100.8(7)
C(7)-V-C(19)	88.5(8)	C(1)-V-C(19)	153.5(9)	O(1)-V-C(13)	110.3(7)
C(7)-V-C(13)	139.6(9)	C(1)-V-C(13)	87.9(8)	C(19)-V-C(13)	85.3(7)
O(1)-V-Li(1)	27.1(9)	C(7)-V-Li(1)	95.1(12)	C(1)-V-Li(1)	126.7(13)
C(19)-V-Li(1)	77.9(11)	C(13)-V-Li(1)	122.2(13)	C(57)-O(9)-C(59)	116(3)
C(57)-O(9)-Li(1)	113(2)	C(59)-O(9)-Li(1)	129(2)	O(9)#1-C(57)-O(9)	121(4)
Li(2)-C(58)-C(54)	56(5)	C(60)-C(59)-O(9)	93(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x+2,y,-z+1/2

Table 44. Anisotropic displacement parameters ($pm^2 x\ 10^{-1}$)for $[Li_2(THF)_x][VO(C_6H_5)_4]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	47(15)	160(20)	64(16)	63(17)	-18(13)	23(16)
C(2)	160(20)	47(15)	120(20)	2(14)	87(19)	38(17)
C(3)	150(20)	57(16)	210(30)	94(18)	130(20)	73(16)
C(4)	71(17)	290(40)	43(15)	120(20)	-26(14)	-50(20)
C(5)	310(40)	180(30)	360(50)	-180(30)	310(40)	-150(30)
C(6)	55(18)	220(40)	210(30)	110(30)	30(20)	90(20)
C(7)	95(17)	120(20)	0(11)	23(11)	12(11)	39(15)
C(8)	61(16)	100(20)	120(20)	-45(18)	-36(16)	22(15)
C(9)	62(16)	170(30)	150(30)	80(20)	69(18)	19(16)
C(10)	110(20)	260(40)	46(16)	70(20)	28(17)	90(20)
C(11)	19(15)	150(30)	210(40)	-50(30)	-37(18)	-2(16)
C(12)	86(17)	83(17)	130(20)	49(16)	78(16)	34(14)
C(13)	43(14)	80(17)	77(17)	-31(15)	-17(14)	9(12)
C(14)	110(20)	83(19)	66(16)	20(14)	19(15)	27(16)
C(15)	79(18)	51(17)	230(30)	-12(19)	50(20)	-20(15)
C(16)	80(20)	140(30)	130(30)	-110(20)	-90(20)	29(18)
C(17)	150(30)	130(30)	90(20)	-10(20)	-10(20)	40(20)
C(18)	84(19)	80(20)	140(30)	-67(19)	-18(19)	0(16)
C(19)	57(14)	103(18)	60(15)	-14(15)	6(13)	8(13)
C(20)	105(19)	65(15)	35(14)	-3(12)	-25(13)	-3(15)
C(21)	75(18)	80(19)	150(30)	33(18)	-23(18)	25(15)
C(22)	130(20)	220(40)	110(20)	-10(20)	80(20)	60(20)
C(23)	150(30)	140(30)	90(20)	8(19)	30(20)	30(20)
C(24)	120(20)	86(19)	110(20)	-28(16)	49(18)	36(17)
C(30)	110(20)	230(30)	80(20)	-9(19)	52(18)	-40(20)
C(31)	72(16)	200(30)	73(18)	-6(17)	29(14)	-31(18)
C(32)	120(20)	270(40)	69(18)	10(20)	-55(19)	-60(30)
C(34)	40(14)	240(30)	72(16)	60(18)	26(14)	-55(17)
C(35)	52(14)	170(20)	88(17)	-4(16)	51(14)	29(16)
C(36)	140(30)	920(130)	120(30)	-250(50)	50(30)	-40(50)
C(37)	37(14)	170(20)	100(19)	-10(18)	-47(15)	15(16)

C(38)	60(20)	720(100)	120(30)	-160(40)	0(20)	20(40)
C(29)	180(30)	330(50)	100(20)	-10(30)	40(20)	120(30)
C(40)	190(30)	190(30)	80(20)	10(20)	60(20)	10(30)
C(41)	230(30)	100(20)	59(18)	14(16)	37(19)	-50(20)
C(42)	190(30)	100(20)	80(20)	16(17)	-10(20)	10(20)
C(43)	121(19)	85(17)	61(15)	-26(13)	49(15)	-41(15)
C(44)	240(40)	440(70)	120(30)	-170(40)	110(30)	-140(40)
C(45)	350(50)	320(60)	180(40)	-40(40)	210(40)	120(50)
C(46)	670(110)	210(50)	210(50)	120(40)	-250(60)	-210(60)
C(47)	270(40)	200(30)	90(20)	60(20)	80(20)	100(30)
C(50)	250(40)	160(30)	180(30)	140(20)	-150(30)	-180(30)
C(51)	150(30)	120(30)	340(50)	90(30)	130(30)	-20(20)
C(52)	520(60)	360(60)	180(30)	-180(30)	260(40)	-330(50)
C(56)	630(90)	80(30)	120(30)	30(20)	-110(40)	-80(40)
C(54)	710(60)	1420(140)	40(20)	-90(50)	30(40)	-990(80)
C(55)	610(60)	41(15)	100(20)	-76(14)	220(30)	-100(30)
Li(1)	100(30)	380(90)	40(20)	20(40)	-20(20)	90(50)
Li(2)	0(15)	80(30)	90(30)	-10(20)	6(17)	42(18)
O(1)	65(8)	76(9)	27(7)	9(6)	6(6)	3(7)
O(3)	72(10)	98(11)	77(10)	4(9)	21(10)	6(9)
O(4)	99(13)	230(20)	190(20)	11(18)	22(16)	-39(15)
O(5)	158(15)	120(15)	79(12)	-16(12)	46(11)	-61(13)
O(6)	200(17)	30(10)	183(18)	-18(12)	113(16)	-15(11)
O(7)	990(80)	180(20)	180(20)	109(18)	320(40)	350(40)
V	69(2)	75(3)	47(2)	-1(2)	5(2)	15(2)

8.5 Niobium Complexes

8.5.1 $[Li_2(Et_2O)_3][Nb(C_6H_5)_6]$

8.5.1.1 Preparation of $[Li_2(Et_2O)_3][Nb(C_6H_5)_6]$

NbF_5 (0.25 g, 1.33 mmol) was suspended in Et_2O (20mL) at –78°C, and 8.65 mmol of phenyllithium (8 mL of 1.08 M phLi solution in Et_2O) was added slowly, the reaction mixture was kept at –78°C overnight. The resulting red suspension was allowed to warm to –30°C, and further stirred for about 6 hr at that temperature. The color of the solution changed to dark red and small amount of black and colorless solids separated. Removing the insoluble materials by filtration and cooling the dark red solution from –30°C to –80°C afforded brown-red crystals.

8.5.1.2 Crystal Data and Crystal Structure Analysis of $[Li_2(Et_2O)_3][Nb(C_6H_5)_6]$

Table 45. Crystal data and structure refinement for $[Li_2(Et_2O)_3][Nb(C_6H_5)_6]$.

Identification code	nbphe2	
Empirical formula	$C_{48}\ H_{60}\ Li_2\ Nb\ O_3$	
Formula weight	791.75	
Temperature	133(2) K	
Wavelength	71.073 pm	
Crystal system	Trigonal	
Space group	R-3	
Unit cell dimensions	a = 3006.5(5) pm	α= 90°.
	b = 3006.5(5) pm	β= 90°.
	c = 2488.7(8) pm	γ = 120°.
Volume	19.48(1) nm^3	
Z	18	
Density (calculated)	1.215 Mg/m^3	
Absorption coefficient	0.316 mm^{-1}	

F(000)	7542
Crystal size	? x ? x ? mm^3
Theta range for data collection	1.13 to 24.06°.
Index ranges	-34<=h<=34, -34<=k<=34, -28<=l<=25
Reflections collected	63151
Independent reflections	6835 [R(int) = 0.0650]
Completeness to theta = 24.06°	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6835 / 0 / 397
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0652, wR2 = 0.1885
R indices (all data)	R1 = 0.0793, wR2 = 0.1978
Largest diff. peak and hole	3.468 and -0.425 e.$Å^{-3}$

Table 46. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for $[Li_2(Et_2O)_3][Nb(C_6H_5)_6]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	993(2)	7192(2)	4325(2)	37(1)
C(2)	478(2)	6823(2)	4240(2)	39(1)
C(3)	200(2)	6820(3)	3798(2)	58(2)
C(4)	436(3)	7196(3)	3409(3)	84(3)
C(5)	940(3)	7556(3)	3469(3)	78(2)
C(6)	1216(2)	7553(3)	3915(2)	54(2)
C(7)	854(2)	7395(2)	5527(2)	40(1)
C(8)	385(3)	7354(3)	5377(3)	66(2)
C(9)	113(4)	7512(4)	5700(4)	100(3)
C(10)	307(4)	7729(4)	6188(4)	101(3)
C(11)	765(3)	7795(3)	6354(3)	69(2)
C(12)	1034(2)	7627(2)	6034(2)	45(1)
C(13)	1962(2)	7923(2)	4997(2)	41(1)
C(14)	2299(2)	8010(2)	4569(2)	43(1)
C(15)	2696(2)	8494(2)	4430(3)	55(2)
C(16)	2792(3)	8921(2)	4725(3)	61(2)

C(17)	2478(3)	8849(2)	5157(3)	76(2)
C(18)	2078(3)	8367(2)	5290(2)	60(2)
C(19)	1188(2)	6403(2)	4617(2)	34(1)
C(20)	1554(2)	6512(2)	4210(2)	41(1)
C(21)	1546(2)	6142(3)	3879(2)	53(2)
C(22)	1158(3)	5633(3)	3926(2)	55(2)
C(23)	780(2)	5508(2)	4307(2)	47(1)
C(24)	806(2)	5893(2)	4646(2)	37(1)
C(25)	330(2)	6201(2)	5707(2)	35(1)
C(26)	5(2)	5859(2)	6094(2)	36(1)
C(27)	198(2)	5809(2)	6584(2)	37(1)
C(28)	717(2)	6108(2)	6682(2)	36(1)
C(29)	1045(2)	6452(2)	6290(2)	30(1)
C(30)	865(2)	6510(2)	5788(2)	30(1)
C(31)	2017(2)	7087(2)	5464(2)	30(1)
C(32)	2259(2)	6807(2)	5303(2)	35(1)
C(33)	2648(2)	6797(2)	5605(2)	40(1)
C(34)	2814(2)	7072(2)	6073(2)	42(1)
C(35)	2602(2)	7366(2)	6244(2)	40(1)
C(36)	2218(2)	7373(2)	5937(2)	34(1)
C(37)	1834(2)	5360(3)	5139(2)	53(2)
C(38)	1706(2)	5443(2)	5710(2)	37(1)
C(39)	814(2)	5138(2)	5937(2)	42(1)
C(40)	581(2)	4642(2)	5611(3)	57(2)
Li(1)	1351(3)	6177(3)	5468(3)	33(2)
Li(2)	1192(5)	7932(5)	4802(4)	62(3)
Nb	1318(1)	7091(1)	5115(1)	28(1)
O(1)	1281(1)	5544(1)	5699(1)	34(1)

Table 47. Bond lengths [pm] and angles [°] for $[Li_2(Et_2O)_3][Nb(C_6H_5)_6]$.

C(1)-C(6)	139.3(8)	C(1)-C(2)	139.8(7)	C(1)-Nb	228.3(5)
C(1)-Li(2)	232.2(12)	C(2)-C(3)	137.9(8)	C(2)-H(2)	95.00
C(3)-C(4)	138.4(9)	C(3)-H(3)	95.00	C(4)-C(5)	136.2(10)
C(4)-H(4)	95.00	C(5)-C(6)	138.9(8)	C(5)-H(5)	95.00

C(6)-Li(2)	250.2(13)	C(6)-H(6)	95.00	C(7)-C(8)	140.4(9)
C(7)-C(12)	141.3(8)	C(7)-Nb	225.9(5)	C(7)-Li(2)	229.3(13)
C(8)-C(9)	139.1(9)	C(8)-Li(2)	259.5(15)	C(8)-H(8)	95.00
C(9)-C(10)	136.5(12)	C(9)-H(9)	95.00	C(10)-C(11)	135.3(12)
C(10)-H(10)	95.00	C(11)-C(12)	139.5(9)	C(11)-H(11)	95.00
C(12)-H(12)	95.00	C(13)-C(14)	140.2(8)	C(13)-C(18)	140.5(8)
C(13)-Nb	228.9(5)	C(13)-Li(2)	237.9(13)	C(14)-C(15)	138.7(8)
C(14)-H(14)	95.00	C(15)-C(16)	137.6(9)	C(15)-H(15)	95.00
C(16)-C(17)	137.7(10)	C(16)-H(16)	95.00	C(17)-C(18)	138.3(9)
C(17)-H(17)	95.00	C(18)-Li(2)	260.7(14)	C(18)-H(18)	95.00
C(19)-C(24)	138.4(7)	C(19)-C(20)	141.0(7)	C(19)-Nb	227.3(5)
C(19)-Li(1)	234.9(9)	C(20)-C(21)	137.5(8)	C(20)-H(20)	95.00
C(21)-C(22)	139.0(9)	C(21)-H(21)	95.00	C(22)-C(23)	138.0(9)
C(22)-H(22)	95.00	C(23)-C(24)	140.2(7)	C(23)-H(23)	95.00
C(24)-Li(1)	249.0(9)	C(24)-H(24)	95.00	C(25)-C(26)	139.0(7)
C(25)-C(30)	141.3(7)	C(26)-C(27)	139.2(8)	C(26)-H(26)	95.00
C(27)-C(28)	137.8(7)	C(27)-H(27)	95.00	C(28)-C(29)	140.4(7)
C(28)-H(28)	95.00	C(29)-C(30)	140.9(7)	C(29)-Li(1)	254.6(9)
C(29)-H(29)	95.00	C(30)-Li(1)	228.8(10)	C(30)-Nb	230.9(5)
C(30)-H(30)	95.00	C(31)-C(36)	140.5(7)	C(31)-C(32)	141.7(7)
C(31)-Nb	227.8(5)	C(31)-Li(1)	245.3(9)	C(32)-C(33)	140.6(7)
C(32)-Li(1)	245.6(9)	C(32)-H(32)	95.00	C(33)-C(34)	136.9(8)
C(33)-H(33)	95.00	C(34)-C(35)	138.9(8)	C(34)-H(34)	95.00
C(35)-C(36)	139.3(7)	C(35)-H(35)	95.00	C(36)-H(36)	95.00
C(37)-C(38)	152.6(8)	C(38)-O(1)	145.3(6)	C(39)-O(1)	144.9(6)
C(39)-C(40)	152.4(8)	Li(1)-O(1)	189.7(9)	Li(1)-Nb	293.4(8)
Li(2)-Nb	284.8(10)			C(6)-C(1)-C(2)	114.8(5)
C(6)-C(1)-Nb	131.4(4)	C(2)-C(1)-Nb	113.8(4)	C(6)-C(1)-Li(2)	80.5(5)
C(2)-C(1)-Li(2)	119.4(5)	Nb-C(1)-Li(2)	76.4(3)	C(3)-C(2)-C(1)	123.5(5)
C(3)-C(2)-H(2)	118.2	C(1)-C(2)-H(2)	118.2	C(2)-C(3)-C(4)	119.5(6)
C(2)-C(3)-H(3)	120.2	C(4)-C(3)-H(3)	120.2	C(5)-C(4)-C(3)	118.9(6)
C(5)-C(4)-H(4)	120.5	C(3)-C(4)-H(4)	120.5	C(4)-C(5)-C(6)	120.9(6)
C(4)-C(5)-H(5)	119.5	C(6)-C(5)-H(5)	119.5	C(5)-C(6)-C(1)	122.3(6)
C(5)-C(6)-Li(2)	123.3(6)	C(1)-C(6)-Li(2)	66.2(4)	C(5)-C(6)-H(6)	118.9
C(1)-C(6)-H(6)	118.9	Li(2)-C(6)-H(6)	81.3	C(8)-C(7)-C(12)	113.5(5)

C(8)-C(7)-Nb	129.9(4)	C(12)-C(7)-Nb	116.4(4)	C(8)-C(7)-Li(2)	85.6(5)
C(12)-C(7)-Li(2)	115.4(5)	Nb-C(7)-Li(2)	77.4(3)	C(9)-C(8)-C(7)	123.7(7)
C(9)-C(8)-Li(2)	127.1(7)	C(7)-C(8)-Li(2)	61.8(4)	C(9)-C(8)-H(8)	118.1
C(7)-C(8)-H(8)	118.1	Li(2)-C(8)-H(8)	82.0	C(10)-C(9)-C(8)	119.5(8)
C(10)-C(9)-H(9)	120.3	C(8)-C(9)-H(9)	120.3	C(11)-C(10)-C(9)	120.2(7)
C(11)-C(10)-H(10)	119.9	C(9)-C(10)-H(10)	119.9	C(10)-C(11)-C(12)	120.3(7)
C(10)-C(11)-H(11)	119.9	C(12)-C(11)-H(11)	119.9	C(11)-C(12)-C(7)	122.7(6)
C(11)-C(12)-H(12)	118.6	C(7)-C(12)-H(12)	118.6	C(14)-C(13)-C(18)	113.8(5)
C(14)-C(13)-Nb	116.1(4)	C(18)-C(13)-Nb	130.1(4)	C(14)-C(13)-Li(2)	117.3(4)
C(18)-C(13)-Li(2)	82.8(5)	Nb-C(13)-Li(2)	75.2(3)	C(15)-C(14)-C(13)	123.3(6)
C(15)-C(14)-H(14)	118.4	C(13)-C(14)-H(14)	118.4	C(16)-C(15)-C(14)	120.9(6)
C(16)-C(15)-H(15)	119.5	C(14)-C(15)-H(15)	119.5	C(17)-C(16)-C(15)	117.6(6)
C(17)-C(16)-H(16)	121.2	C(15)-C(16)-H(16)	121.2	C(16)-C(17)-C(18)	121.4(7)
C(16)-C(17)-H(17)	119.3	C(18)-C(17)-H(17)	119.3	C(17)-C(18)-C(13)	123.0(7)
C(17)-C(18)-Li(2)	123.3(5)	C(13)-C(18)-Li(2)	64.8(4)	C(17)-C(18)-H(18)	118.5
C(13)-C(18)-H(18)	118.5	Li(2)-C(18)-H(18)	82.5	C(24)-C(19)-C(20)	114.5(5)
C(24)-C(19)-Nb	130.5(4)	C(20)-C(19)-Nb	114.9(4)	C(24)-C(19)-Li(1)	79.1(4)
C(20)-C(19)-Li(1)	117.6(4)	Nb-C(19)-Li(1)	78.8(2)	C(21)-C(20)-C(19)	123.1(6)
C(21)-C(20)-H(20)	118.4	C(19)-C(20)-H(20)	118.4	C(20)-C(21)-C(22)	120.4(6)
C(20)-C(21)-H(21)	119.8	C(22)-C(21)-H(21)	119.8	C(23)-C(22)-C(21)	118.7(5)
C(23)-C(22)-H(22)	120.6	C(21)-C(22)-H(22)	120.6	C(22)-C(23)-C(24)	119.5(6)
C(22)-C(23)-H(23)	120.3	C(24)-C(23)-H(23)	120.3	C(19)-C(24)-C(23)	123.7(5)
C(19)-C(24)-Li(1)	67.9(3)	C(23)-C(24)-Li(1)	122.1(4)	C(19)-C(24)-H(24)	118.2
C(23)-C(24)-H(24)	118.2	Li(1)-C(24)-H(24)	80.5	C(26)-C(25)-C(30)	122.3(5)
C(25)-C(26)-C(27)	120.8(5)	C(25)-C(26)-H(26)	119.6	C(27)-C(26)-H(26)	119.6
C(28)-C(27)-C(26)	118.7(5)	C(28)-C(27)-H(27)	120.6	C(26)-C(27)-H(27)	120.6
C(27)-C(28)-C(29)	120.5(5)	C(27)-C(28)-H(28)	119.8	C(29)-C(28)-H(28)	119.8
C(28)-C(29)-C(30)	122.4(5)	C(28)-C(29)-Li(1)	123.7(4)	C(30)-C(29)-Li(1)	63.2(3)
C(28)-C(29)-H(29)	118.8	C(30)-C(29)-H(29)	118.8	Li(1)-C(29)-H(29)	83.8
C(29)-C(30)-C(25)	115.3(4)	C(29)-C(30)-Li(1)	83.4(3)	C(25)-C(30)-Li(1)	115.5(4)
C(29)-C(30)-Nb	128.3(3)	C(25)-C(30)-Nb	116.2(4)	Li(1)-C(30)-Nb	79.3(3)
C(29)-C(30)-H(30)	122.4	C(25)-C(30)-H(30)	122.4	Li(1)-C(30)-H(30)	72.9
Nb-C(30)-H(30)	7.6	C(36)-C(31)-C(32)	114.2(4)	C(36)-C(31)-Nb	115.5(4)
C(32)-C(31)-Nb	130.1(3)	C(36)-C(31)-Li(1)	122.8(4)	C(32)-C(31)-Li(1)	73.3(3)
Nb-C(31)-Li(1)	76.6(2)	C(33)-C(32)-C(31)	122.8(5)	C(33)-C(32)-Li(1)	120.7(4)

C(31)-C(32)-Li(1)	73.1(3)	C(33)-C(32)-H(32)	118.6	C(31)-C(32)-H(32)	118.6
Li(1)-C(32)-H(32)	76.7	C(34)-C(33)-C(32)	119.9(5)	C(34)-C(33)-H(33)	120.1
C(32)-C(33)-H(33)	120.1	C(33)-C(34)-C(35)	120.0(5)	C(33)-C(34)-H(34)	120.0
C(35)-C(34)-H(34)	120.0	C(34)-C(35)-C(36)	119.3(5)	C(34)-C(35)-H(35)	120.3
C(36)-C(35)-H(35)	120.3	C(35)-C(36)-C(31)	123.8(5)	C(35)-C(36)-H(36)	118.1
C(31)-C(36)-H(36)	118.1	O(1)-C(38)-C(37)	109.6(4)	O(1)-C(39)-C(40)	112.5(5)
O(1)-Li(1)-C(30)	124.0(4)	O(1)-Li(1)-C(19)	129.0(4)	C(30)-Li(1)-C(19)	85.2(3)
O(1)-Li(1)-C(31)	137.7(4)	C(30)-Li(1)-C(31)	81.8(3)	C(19)-Li(1)-C(31)	81.1(3)
O(1)-Li(1)-C(32)	110.3(4)	C(30)-Li(1)-C(32)	115.3(4)	C(19)-Li(1)-C(32)	86.5(3)
C(31)-Li(1)-C(32)	33.6(2)	O(1)-Li(1)-C(24)	100.5(4)	C(30)-Li(1)-C(24)	88.9(3)
C(19)-Li(1)-C(24)	33.1(2)	C(31)-Li(1)-C(24)	114.2(3)	C(32)-Li(1)-C(24)	114.5(4)
O(1)-Li(1)-C(29)	101.8(4)	C(30)-Li(1)-C(29)	33.3(2)	C(19)-Li(1)-C(29)	118.0(4)
C(31)-Li(1)-C(29)	82.4(3)	C(32)-Li(1)-C(29)	109.0(3)	C(24)-Li(1)-C(29)	119.3(4)
O(1)-Li(1)-Nb	172.8(4)	C(30)-Li(1)-Nb	50.6(2)	C(19)-Li(1)-Nb	49.5(2)
C(31)-Li(1)-Nb	49.04(19)	C(32)-Li(1)-Nb	76.8(2)	C(24)-Li(1)-Nb	75.6(2)
C(29)-Li(1)-Nb	75.5(2)	C(7)-Li(2)-C(1)	85.1(4)	C(7)-Li(2)-C(13)	85.5(4)
C(1)-Li(2)-C(13)	83.0(4)	C(7)-Li(2)-C(6)	118.4(5)	C(1)-Li(2)-C(6)	33.3(2)
C(13)-Li(2)-C(6)	85.6(4)	C(7)-Li(2)-C(8)	32.6(3)	C(1)-Li(2)-C(8)	86.2(4)
C(13)-Li(2)-C(8)	117.9(5)	C(6)-Li(2)-C(8)	114.3(5)	C(7)-Li(2)-C(18)	88.2(4)
C(1)-Li(2)-C(18)	115.4(5)	C(13)-Li(2)-C(18)	32.3(3)	C(6)-Li(2)-C(18)	112.6(5)
C(8)-Li(2)-C(18)	117.2(5)	C(7)-Li(2)-Nb	50.7(2)	C(1)-Li(2)-Nb	51.2(2)
C(13)-Li(2)-Nb	51.0(2)	C(6)-Li(2)-Nb	77.8(3)	C(8)-Li(2)-Nb	75.5(3)
C(18)-Li(2)-Nb	76.2(3)	C(7)-Nb-C(19)	139.03(19)	C(7)-Nb-C(31)	125.99(19)
C(19)-Nb-C(31)	86.66(17)	C(7)-Nb-C(1)	86.82(19)	C(19)-Nb-C(1)	76.15(18)
C(31)-Nb-C(1)	141.82(17)	C(7)-Nb-C(13)	88.4(2)	C(19)-Nb-C(13)	126.3(2)
C(31)-Nb-C(13)	77.15(18)	C(1)-Nb-C(13)	85.92(18)	C(7)-Nb-C(30)	74.17(17)
C(19)-Nb-C(30)	86.43(18)	C(31)-Nb-C(30)	85.24(16)	C(1)-Nb-C(30)	126.46(18)
C(13)-Nb-C(30)	140.96(17)	C(7)-Nb-Li(2)	51.8(3)	C(19)-Nb-Li(2)	128.4(3)
C(31)-Nb-Li(2)	130.0(3)	C(1)-Nb-Li(2)	52.4(3)	C(13)-Nb-Li(2)	53.8(3)
C(30)-Nb-Li(2)	125.5(3)	C(7)-Nb-Li(1)	124.0(2)	C(19)-Nb-Li(1)	51.7(2)
C(31)-Nb-Li(1)	54.40(19)	C(1)-Nb-Li(1)	126.8(2)	C(13)-Nb-Li(1)	131.0(2)
C(30)-Nb-Li(1)	50.0(2)	Li(2)-Nb-Li(1)	174.8(3)	C(39)-O(1)-C(38)	113.6(4)
C(39)-O(1)-Li(1)	122.9(4)	C(38)-O(1)-Li(1)	123.1(4)		

Table 48. Anisotropic displacement parameters ($pm^2 x\ 10^{-1}$)for $[Li_2(Et_2O)_3][Nb(C_6H_5)_6]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	33(3)	42(3)	38(3)	-3(2)	-4(2)	21(2)
C(2)	43(3)	46(3)	34(3)	2(2)	-3(2)	27(3)
C(3)	41(3)	75(4)	50(4)	10(3)	-12(3)	23(3)
C(4)	60(5)	113(6)	59(4)	33(4)	-24(4)	27(4)
C(5)	50(4)	96(6)	55(4)	32(4)	-18(3)	11(4)
C(6)	44(3)	63(4)	42(3)	14(3)	-5(3)	16(3)
C(7)	55(3)	38(3)	36(3)	1(2)	5(3)	30(3)
C(8)	75(5)	92(5)	56(4)	-22(4)	-6(3)	61(4)
C(9)	108(7)	151(9)	89(6)	-43(6)	-9(5)	101(7)
C(10)	136(8)	134(8)	88(6)	-13(6)	22(6)	108(8)
C(11)	122(7)	61(4)	42(4)	-14(3)	8(4)	59(5)
C(12)	59(4)	36(3)	41(3)	3(2)	3(3)	26(3)
C(13)	49(3)	36(3)	30(3)	5(2)	-12(2)	16(3)
C(14)	36(3)	45(3)	37(3)	7(2)	-9(2)	12(3)
C(15)	37(3)	60(4)	50(4)	20(3)	-9(3)	10(3)
C(16)	65(4)	38(3)	51(4)	15(3)	-10(3)	5(3)
C(17)	103(6)	35(3)	54(4)	-5(3)	-11(4)	7(4)
C(18)	89(5)	30(3)	40(3)	2(3)	-3(3)	14(3)
C(19)	29(3)	47(3)	27(3)	-10(2)	-13(2)	20(2)
C(20)	41(3)	48(3)	33(3)	-11(2)	-7(2)	21(3)
C(21)	56(4)	74(4)	44(3)	-22(3)	-7(3)	43(4)
C(22)	71(4)	72(4)	44(3)	-29(3)	-24(3)	53(4)
C(23)	63(4)	44(3)	41(3)	-16(3)	-20(3)	31(3)
C(24)	40(3)	41(3)	32(3)	-9(2)	-11(2)	22(3)
C(25)	35(3)	37(3)	38(3)	-9(2)	0(2)	22(2)
C(26)	32(3)	29(3)	46(3)	-1(2)	8(2)	13(2)
C(27)	41(3)	32(3)	40(3)	6(2)	13(2)	19(2)
C(28)	46(3)	34(3)	29(3)	3(2)	5(2)	21(2)
C(29)	30(3)	27(2)	33(3)	-4(2)	-1(2)	13(2)
C(30)	34(3)	27(2)	31(3)	2(2)	8(2)	17(2)
C(31)	30(3)	27(2)	27(2)	5(2)	0(2)	10(2)

C(32)	31(3)	30(3)	37(3)	-2(2)	-5(2)	9(2)
C(33)	25(3)	32(3)	60(4)	6(3)	-5(2)	12(2)
C(34)	25(3)	42(3)	45(3)	18(3)	-4(2)	8(2)
C(35)	33(3)	39(3)	28(3)	6(2)	-3(2)	4(2)
C(36)	27(3)	38(3)	30(3)	1(2)	2(2)	9(2)
C(37)	53(4)	72(4)	50(3)	-21(3)	-8(3)	44(3)
C(38)	33(3)	43(3)	45(3)	0(2)	0(2)	26(2)
C(39)	37(3)	34(3)	52(3)	-1(2)	2(3)	15(2)
C(40)	49(4)	42(3)	70(4)	-10(3)	-4(3)	16(3)
Li(1)	30(4)	34(4)	31(4)	0(3)	-5(3)	13(4)
Li(2)	83(8)	66(7)	57(6)	0(5)	-2(6)	53(7)
Nb	31(1)	29(1)	23(1)	-2(1)	-4(1)	15(1)
O(1)	29(2)	32(2)	45(2)	3(2)	1(2)	18(2)

8.5.2 $[Li_2(Et_2O)_4][Nb(p\text{-}C_6H_4\text{-}CH_3)_6]$

8.5.2.1 Preparation of $[Li_2(Et_2O)_4][Nb(p\text{-}C_6H_4\text{-}CH_3)_6]$

NbF_5 (0.4 g, 2.13 mmol) was suspended in Et_2O (50 mL) and treated with *p*-tolyllithium (13.8 mmol, 1.2 M solution in Et_2O) at –78°C and kept at that temperature overnight. The resulting dark-red suspension was allowed to warm to –30°C and stirred for about 6 hr. The solution turned to dark red and small amount of black and colorless solids separated. After filtration at –30°C, the dark red solutions was concentrated to the half of its volume, and slow cooling for several days from –30°C to –80°C yielded red-orange crystals.

8.5.2.2 Crystal Data and Crystal Structure Analysis of $[Li_2(Et_2O)_4][Nb(p\text{-}C_6H_4\text{-}CH_3)_6]$

Table 49. Crystal data and structure refinement for $[Li_2(Et_2O)_4][Nb(p\text{-}C_6H_4\text{-}CH_3)_6]$.

Identification code	nbtol6
Empirical formula	$C_{58}\ H_{82}\ Li_2\ Nb\ O_4$
Formula weight	950.03
Temperature	133(2) K

Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	P121/n 1	
Unit cell dimensions	a = 1087.0(3) pm	α= 90°.
	b = 1762.1(4) pm	β= 97.642(6)°.
	c = 2828.4(7) pm	γ = 90°.
Volume	5.37(1) nm^3	
Z	4	
Density (calculated)	1.175 Mg/m^3	
Absorption coefficient	0.267 mm^{-1}	
F(000)	2036	
Crystal size	0.3 x 0.05 x 0.04 mm^3	
Theta range for data collection	1.86 to 26.07°.	
Index ranges	-13<=h<=13, -21<=k<=19, -32<=l<=34	
Reflections collected	53563	
Independent reflections	10592 [R(int) = 0.0729]	
Completeness to theta = 26.07°	99.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10592 / 0 / 601	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0497, wR2 = 0.1139	
R indices (all data)	R1 = 0.0815, wR2 = 0.1277	
Extinction coefficient	0.00040(17)	
Largest diff. peak and hole	0.914 and -0.634 e.$Å^{-3}$	

Table 50. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for $[Li_2(Et_2O)_4][Nb(p\text{-}C_6H_4\text{-}CH_3)_6]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8993(3)	5403(2)	1453(1)	21(1)
C(2)	10142(3)	5475(2)	1745(1)	23(1)
C(3)	10981(3)	4885(2)	1835(1)	25(1)
C(4)	10729(3)	4173(2)	1629(1)	28(1)

C(5)	9622(3)	4086(2)	1335(1)	29(1)
C(6)	8773(3)	4682(2)	1252(1)	24(1)
C(7)	11647(4)	3529(2)	1726(2)	42(1)
C(8)	7596(3)	6456(2)	2109(1)	20(1)
C(9)	8235(3)	6065(2)	2493(1)	24(1)
C(10)	7893(3)	6080(2)	2952(1)	28(1)
C(11)	6872(3)	6486(2)	3051(1)	26(1)
C(12)	6222(3)	6895(2)	2678(1)	26(1)
C(13)	6587(3)	6887(2)	2227(1)	23(1)
C(14)	6464(4)	6498(2)	3540(1)	38(1)
C(15)	6123(3)	5778(2)	1184(1)	19(1)
C(16)	5060(3)	5809(2)	1419(1)	22(1)
C(17)	3970(3)	5428(2)	1255(1)	26(1)
C(18)	3866(3)	4969(2)	860(1)	23(1)
C(19)	4907(3)	4912(2)	622(1)	23(1)
C(20)	5979(3)	5316(2)	773(1)	22(1)
C(21)	2688(3)	4549(2)	688(1)	34(1)
C(22)	9441(3)	6571(2)	863(1)	19(1)
C(23)	10590(3)	6946(2)	957(1)	24(1)
C(24)	11538(3)	6859(2)	673(1)	28(1)
C(25)	11386(3)	6405(2)	274(1)	26(1)
C(26)	10260(3)	6032(2)	163(1)	25(1)
C(27)	9334(3)	6113(2)	456(1)	22(1)
C(28)	12408(3)	6306(2)	-34(1)	37(1)
C(29)	8519(3)	7677(2)	1590(1)	20(1)
C(30)	9605(3)	7679(2)	1927(1)	21(1)
C(31)	10170(3)	8334(2)	2122(1)	23(1)
C(32)	9672(3)	9044(2)	2004(1)	25(1)
C(33)	8613(3)	9072(2)	1675(1)	25(1)
C(34)	8057(3)	8407(2)	1476(1)	21(1)
C(35)	10253(3)	9762(2)	2227(1)	34(1)
C(36)	6627(3)	7104(2)	740(1)	22(1)
C(37)	5642(3)	7536(2)	883(1)	24(1)
C(38)	4745(3)	7883(2)	565(2)	34(1)
C(39)	4749(4)	7824(2)	78(2)	38(1)

C(40)	5697(4)	7406(2)	-77(1)	40(1)
C(41)	6605(3)	7056(2)	245(1)	29(1)
C(42)	3757(5)	8206(3)	-270(2)	63(1)
C(51)	8653(3)	4034(2)	2553(1)	33(1)
C(52)	7643(3)	3618(2)	2245(1)	28(1)
C(53)	5740(3)	3798(2)	1728(1)	32(1)
C(54)	6013(4)	3253(2)	1346(2)	45(1)
C(55)	3629(5)	1722(3)	1705(2)	59(1)
C(56)	2878(4)	1411(2)	2066(2)	46(1)
C(57)	2060(3)	1747(2)	2776(2)	42(1)
C(58)	1763(4)	2425(2)	3060(2)	42(1)
C(59)	5379(5)	9975(4)	908(2)	92(2)
C(60)	4549(5)	9666(3)	1233(2)	70(2)
C(61)	2457(6)	9367(4)	1253(2)	86(2)
C(62)	1238(6)	9387(7)	974(2)	169(5)
C(63)	8170(6)	9727(3)	272(2)	92(2)
C(64)	7803(5)	8974(3)	90(2)	67(2)
C(65)	9622(5)	8267(3)	-92(2)	58(1)
C(66)	9151(6)	7814(3)	-519(2)	73(2)
Li(1)	8519(5)	7727(3)	740(2)	29(1)
Li(2)	7238(5)	5163(3)	1817(2)	28(1)
Nb(1)	7882(1)	6500(1)	1326(1)	15(1)
O(1)	8739(2)	8390(2)	230(1)	38(1)
O(2)	2684(2)	1992(2)	2392(1)	38(1)
O(3)	6823(2)	4157(1)	1983(1)	27(1)
O(4)	3331(3)	9720(2)	998(1)	62(1)

Table 51. Bond lengths [pm] and angles [°] for $[Li_2(Et_2O)_4][Nb(p\text{-}C_6H_4\text{-}CH_3)_6]$.

C(1)-C(6)	139.8(5)	C(1)-C(2)	140.8(5)	C(1)-Nb(1)	228.2(3)
C(1)-Li(2)	232.4(6)	C(2)-C(3)	138.5(5)	C(2)-H(2)	95.00
C(3)-C(4)	139.5(5)	C(3)-H(3)	95.00	C(4)-C(5)	137.7(5)
C(4)-C(7)	151.1(5)	C(5)-C(6)	139.8(5)	C(5)-H(5)	95.00
C(6)-Li(2)	260.1(7)	C(6)-H(6)	95.00	C(7)-H(7A)	98.00

C(7)-H(7B)	98.00	C(7)-H(7C)	98.00	C(8)-C(9)	139.1(5)
C(8)-C(13)	141.0(4)	C(8)-Nb(1)	227.8(3)	C(8)-Li(2)	243.7(7)
C(9)-C(10)	139.7(5)	C(9)-Li(2)	260.8(7)	C(9)-H(9)	95.00
C(10)-C(11)	138.1(5)	C(10)-H(10)	95.00	C(11)-C(12)	139.0(5)
C(11)-C(14)	150.7(5)	C(12)-C(13)	138.6(5)	C(12)-H(12)	95.00
C(13)-H(13)	95.00	C(14)-H(14A)	98.00	C(14)-H(14B)	98.00
C(14)-H(14C)	98.00	C(15)-C(16)	140.9(4)	C(15)-C(20)	141.1(5)
C(15)-Nb(1)	228.8(3)	C(15)-Li(2)	229.7(7)	C(16)-C(17)	138.7(4)
C(16)-Li(2)	273.1(7)	C(16)-H(16)	95.00	C(17)-C(18)	137.3(5)
C(17)-H(17)	95.00	C(18)-C(19)	139.4(5)	C(18)-C(21)	150.3(4)
C(19)-C(20)	138.4(5)	C(19)-H(19)	95.00	C(20)-H(20)	95.00
C(21)-H(21A)	98.00	C(21)-H(21B)	98.00	C(21)-H(21C)	98.00
C(22)-C(27)	139.9(5)	C(22)-C(23)	140.6(4)	C(22)-Li(1)	227.5(7)
C(22)-Nb(1)	227.9(3)	C(23)-C(24)	139.6(4)	C(23)-Li(1)	263.9(7)
C(23)-H(23)	95.00	C(24)-C(25)	137.6(5)	C(24)-H(24)	95.00
C(25)-C(26)	138.9(5)	C(25)-C(28)	150.9(5)	C(26)-C(27)	139.3(4)
C(26)-H(26)	95.00	C(27)-H(27)	95.00	C(28)-H(28A)	98.00
C(28)-H(28B)	98.00	C(28)-H(28C)	98.00	C(29)-C(34)	140.2(5)
C(29)-C(30)	141.5(4)	C(29)-Nb(1)	228.0(3)	C(29)-Li(1)	240.4(7)
C(30)-C(31)	138.7(4)	C(30)-H(30)	95.00	C(31)-C(32)	138.7(5)
C(31)-H(31)	95.00	C(32)-C(33)	138.0(5)	C(32)-C(35)	151.5(5)
C(33)-C(34)	140.3(5)	C(33)-H(33)	95.00	C(34)-Li(1)	250.9(7)
C(34)-H(34)	95.00	C(35)-H(35A)	98.00	C(35)-H(35B)	98.00
C(35)-H(35C)	98.00	C(36)-C(41)	140.0(5)	C(36)-C(37)	141.6(5)
C(36)-Nb(1)	226.6(3)	C(36)-Li(1)	233.1(7)	C(37)-C(38)	137.7(5)
C(37)-H(37)	95.00	C(38)-C(39)	138.1(6)	C(38)-H(38)	95.00
C(39)-C(40)	138.5(6)	C(39)-C(42)	151.8(5)	C(40)-C(41)	139.5(5)
C(40)-H(40)	95.00	C(41)-Li(1)	262.8(7)	C(41)-H(41)	95.00
C(42)-H(42A)	98.00	C(42)-H(42B)	98.00	C(42)-H(42C)	98.00
C(51)-C(52)	149.9(5)	C(51)-H(51A)	98.00	C(51)-H(51B)	98.00
C(51)-H(51C)	98.00	C(52)-O(3)	143.9(4)	C(52)-H(52A)	99.00
C(52)-H(52B)	99.00	C(53)-O(3)	144.1(4)	C(53)-C(54)	150.4(5)
C(53)-H(53A)	99.00	C(53)-H(53B)	99.00	C(54)-H(54A)	98.00
C(54)-H(54B)	98.00	C(54)-H(54C)	98.00	C(55)-C(56)	149.4(6)
C(55)-H(55A)	98.00	C(55)-H(55B)	98.00	C(55)-H(55C)	98.00

C(56)-O(2)	141.3(5)	C(56)-H(56A)	99.00	C(56)-H(56B)	99.00
C(57)-O(2)	142.1(5)	C(57)-C(58)	149.9(6)	C(57)-H(57A)	99.00
C(57)-H(57B)	99.00	C(58)-H(58A)	98.00	C(58)-H(58B)	98.00
C(58)-H(58C)	98.00	C(59)-C(60)	147.7(8)	C(59)-H(59A)	98.00
C(59)-H(59B)	98.00	C(59)-H(59C)	98.00	C(60)-O(4)	140.3(6)
C(60)-H(60A)	99.00	C(60)-H(60B)	99.00	C(61)-O(4)	141.1(6)
C(61)-C(62)	145.0(9)	C(61)-H(61A)	99.00	C(61)-H(61B)	99.00
C(62)-H(62A)	98.00	C(62)-H(62B)	98.00	C(62)-H(62C)	98.00
C(63)-C(64)	145.9(7)	C(63)-H(63A)	98.00	C(63)-H(63B)	98.00
C(63)-H(63C)	98.00	C(64)-O(1)	146.3(5)	C(64)-H(64A)	99.00
C(64)-H(64B)	99.00	C(65)-O(1)	142.5(5)	C(65)-C(66)	147.9(7)
C(65)-H(65A)	99.00	C(65)-H(65B)	99.00	C(66)-H(66A)	98.00
C(66)-H(66B)	98.00	C(66)-H(66C)	98.00	Li(1)-O(1)	189.8(7)
Li(1)-Nb(1)	286.3(6)	Li(2)-O(3)	190.4(6)	Li(2)-Nb(1)	286.9(6)
		C(6)-C(1)-C(2)	114.2(3)	C(6)-C(1)-Nb(1)	130.3(2)
C(2)-C(1)-Nb(1)	115.2(2)	C(6)-C(1)-Li(2)	84.7(2)	C(2)-C(1)-Li(2)	118.2(3)
Nb(1)-C(1)-Li(2)	77.04(17)	C(3)-C(2)-C(1)	123.4(3)	C(3)-C(2)-H(2)	118.3
C(1)-C(2)-H(2)	118.3	C(2)-C(3)-C(4)	120.8(3)	C(2)-C(3)-H(3)	119.6
C(4)-C(3)-H(3)	119.6	C(5)-C(4)-C(3)	117.3(3)	C(5)-C(4)-C(7)	121.9(3)
C(3)-C(4)-C(7)	120.7(3)	C(4)-C(5)-C(6)	121.4(3)	C(4)-C(5)-H(5)	119.3
C(6)-C(5)-H(5)	119.3	C(5)-C(6)-C(1)	122.8(3)	C(5)-C(6)-Li(2)	127.2(3)
C(1)-C(6)-Li(2)	62.9(2)	C(5)-C(6)-H(6)	118.6	C(1)-C(6)-H(6)	118.6
Li(2)-C(6)-H(6)	81.1	C(4)-C(7)-H(7A)	109.5	C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5	C(4)-C(7)-H(7C)	109.5	H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5	C(9)-C(8)-C(13)	113.9(3)	C(9)-C(8)-Nb(1)	131.1(2)
C(13)-C(8)-Nb(1)	115.0(2)	C(9)-C(8)-Li(2)	80.9(2)	C(13)-C(8)-Li(2)	119.3(3)
Nb(1)-C(8)-Li(2)	74.88(16)	C(8)-C(9)-C(10)	123.3(3)	C(8)-C(9)-Li(2)	67.3(2)
C(10)-C(9)-Li(2)	123.8(3)	C(8)-C(9)-H(9)	118.4	C(10)-C(9)-H(9)	118.4
Li(2)-C(9)-H(9)	79.6	C(11)-C(10)-C(9)	121.3(3)	C(11)-C(10)-H(10)	119.3
C(9)-C(10)-H(10)	119.3	C(10)-C(11)-C(12)	117.0(3)	C(10)-C(11)-C(14)	122.5(3)
C(12)-C(11)-C(14)	120.5(3)	C(13)-C(12)-C(11)	121.0(3)	C(13)-C(12)-H(12)	119.5
C(11)-C(12)-H(12)	119.5	C(12)-C(13)-C(8)	123.4(3)	C(12)-C(13)-H(13)	118.3
C(8)-C(13)-H(13)	118.3	C(11)-C(14)-H(14A)	109.5	C(11)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5	C(11)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	C(16)-C(15)-C(20)	113.8(3)	C(16)-C(15)-Nb(1)	127.9(2)

C(20)-C(15)-Nb(1)	117.7(2)	C(16)-C(15)-Li(2)	91.7(3)	C(20)-C(15)-Li(2)	111.1(3)
Nb(1)-C(15)-Li(2)	77.49(18)	C(17)-C(16)-C(15)	122.8(3)	C(17)-C(16)-Li(2)	126.3(3)
C(15)-C(16)-Li(2)	57.2(2)	C(17)-C(16)-H(16)	118.6	C(15)-C(16)-H(16)	118.6
Li(2)-C(16)-H(16)	87.0	C(18)-C(17)-C(16)	122.1(3)	C(18)-C(17)-H(17)	119.0
C(16)-C(17)-H(17)	119.0	C(17)-C(18)-C(19)	116.8(3)	C(17)-C(18)-C(21)	121.9(3)
C(19)-C(18)-C(21)	121.3(3)	C(20)-C(19)-C(18)	121.2(3)	C(20)-C(19)-H(19)	119.4
C(18)-C(19)-H(19)	119.4	C(19)-C(20)-C(15)	123.2(3)	C(19)-C(20)-H(20)	118.4
C(15)-C(20)-H(20)	118.4	C(18)-C(21)-H(21A)	109.5	C(18)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5	C(18)-C(21)-H(21C)	109.5	H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5	C(27)-C(22)-C(23)	113.7(3)	C(27)-C(22)-Li(1)	113.9(3)
C(23)-C(22)-Li(1)	88.3(3)	C(27)-C(22)-Nb(1)	117.0(2)	C(23)-C(22)-Nb(1)	128.8(2)
Li(1)-C(22)-Nb(1)	77.91(17)	C(24)-C(23)-C(22)	123.0(3)	C(24)-C(23)-Li(1)	126.5(3)
C(22)-C(23)-Li(1)	59.5(2)	C(24)-C(23)-H(23)	118.5	C(22)-C(23)-H(23)	118.5
Li(1)-C(23)-H(23)	84.7	C(25)-C(24)-C(23)	121.2(3)	C(25)-C(24)-H(24)	119.4
C(23)-C(24)-H(24)	119.4	C(24)-C(25)-C(26)	117.8(3)	C(24)-C(25)-C(28)	121.6(3)
C(26)-C(25)-C(28)	120.6(3)	C(25)-C(26)-C(27)	120.1(3)	C(25)-C(26)-H(26)	119.9
C(27)-C(26)-H(26)	119.9	C(26)-C(27)-C(22)	124.1(3)	C(26)-C(27)-H(27)	117.9
C(22)-C(27)-H(27)	117.9	C(25)-C(28)-H(28A)	109.5	C(25)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5	C(25)-C(28)-H(28C)	109.5	H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5	C(34)-C(29)-C(30)	113.2(3)	C(34)-C(29)-Nb(1)	132.4(2)
C(30)-C(29)-Nb(1)	114.4(2)	C(34)-C(29)-Li(1)	77.6(2)	C(30)-C(29)-Li(1)	124.2(3)
Nb(1)-C(29)-Li(1)	75.31(18)	C(31)-C(30)-C(29)	123.8(3)	C(31)-C(30)-H(30)	118.1
C(29)-C(30)-H(30)	118.1	C(32)-C(31)-C(30)	121.1(3)	C(32)-C(31)-H(31)	119.5
C(30)-C(31)-H(31)	119.5	C(33)-C(32)-C(31)	117.4(3)	C(33)-C(32)-C(35)	120.9(3)
C(31)-C(32)-C(35)	121.7(3)	C(32)-C(33)-C(34)	121.0(3)	C(32)-C(33)-H(33)	119.5
C(34)-C(33)-H(33)	119.5	C(29)-C(34)-C(33)	123.5(3)	C(29)-C(34)-Li(1)	69.4(2)
C(33)-C(34)-Li(1)	127.5(3)	C(29)-C(34)-H(34)	118.2	C(33)-C(34)-H(34)	118.2
Li(1)-C(34)-H(34)	74.3	C(32)-C(35)-H(35A)	109.5	C(32)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5	C(32)-C(35)-H(35C)	109.5	H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5	C(41)-C(36)-C(37)	113.8(3)	C(41)-C(36)-Nb(1)	129.2(3)
C(37)-C(36)-Nb(1)	116.7(2)	C(41)-C(36)-Li(1)	85.8(3)	C(37)-C(36)-Li(1)	116.6(3)
Nb(1)-C(36)-Li(1)	77.03(18)	C(38)-C(37)-C(36)	123.3(3)	C(38)-C(37)-H(37)	118.3
C(36)-C(37)-H(37)	118.3	C(37)-C(38)-C(39)	121.4(4)	C(37)-C(38)-H(38)	119.3
C(39)-C(38)-H(38)	119.3	C(38)-C(39)-C(40)	117.2(3)	C(38)-C(39)-C(42)	121.2(4)
C(40)-C(39)-C(42)	121.6(4)	C(39)-C(40)-C(41)	121.3(4)	C(39)-C(40)-H(40)	119.4

C(41)-C(40)-H(40)	119.4	C(40)-C(41)-C(36)	122.9(3)	C(40)-C(41)-Li(1)	126.2(3)
C(36)-C(41)-Li(1)	62.2(2)	C(40)-C(41)-H(41)	118.5	C(36)-C(41)-H(41)	118.5
Li(1)-C(41)-H(41)	82.6	C(39)-C(42)-H(42A)	109.5	C(39)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5	C(39)-C(42)-H(42C)	109.5	H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5	C(52)-C(51)-H(51A)	109.5	C(52)-C(51)-H(51B)	109.5
H(51A)-C(51)-H(51B)	109.5	C(52)-C(51)-H(51C)	109.5	H(51A)-C(51)-H(51C)	109.5
H(51B)-C(51)-H(51C)	109.5	O(3)-C(52)-C(51)	109.5(3)	O(3)-C(52)-H(52A)	109.8
C(51)-C(52)-H(52A)	109.8	O(3)-C(52)-H(52B)	109.8	C(51)-C(52)-H(52B)	109.8
H(52A)-C(52)-H(52B)	108.2	O(3)-C(53)-C(54)	114.4(3)	O(3)-C(53)-H(53A)	108.7
C(54)-C(53)-H(53A)	108.7	O(3)-C(53)-H(53B)	108.7	C(54)-C(53)-H(53B)	108.7
H(53A)-C(53)-H(53B)	107.6	C(53)-C(54)-H(54A)	109.5	C(53)-C(54)-H(54B)	109.5
H(54A)-C(54)-H(54B)	109.5	C(53)-C(54)-H(54C)	109.5	H(54A)-C(54)-H(54C)	109.5
H(54B)-C(54)-H(54C)	109.5	C(56)-C(55)-H(55A)	109.5	C(56)-C(55)-H(55B)	109.5
H(55A)-C(55)-H(55B)	109.5	C(56)-C(55)-H(55C)	109.5	H(55A)-C(55)-H(55C)	109.5
H(55B)-C(55)-H(55C)	109.5	O(2)-C(56)-C(55)	108.8(4)	O(2)-C(56)-H(56A)	109.9
C(55)-C(56)-H(56A)	109.9	O(2)-C(56)-H(56B)	109.9	C(55)-C(56)-H(56B)	109.9
H(56A)-C(56)-H(56B)	108.3	O(2)-C(57)-C(58)	109.0(3)	O(2)-C(57)-H(57A)	109.9
C(58)-C(57)-H(57A)	109.9	O(2)-C(57)-H(57B)	109.9	C(58)-C(57)-H(57B)	109.9
H(57A)-C(57)-H(57B)	108.3	C(57)-C(58)-H(58A)	109.5	C(57)-C(58)-H(58B)	109.5
H(58A)-C(58)-H(58B)	109.5	C(57)-C(58)-H(58C)	109.5	H(58A)-C(58)-H(58C)	109.5
H(58B)-C(58)-H(58C)	109.5	C(60)-C(59)-H(59A)	109.5	C(60)-C(59)-H(59B)	109.5
H(59A)-C(59)-H(59B)	109.5	C(60)-C(59)-H(59C)	109.5	H(59A)-C(59)-H(59C)	109.5
H(59B)-C(59)-H(59C)	109.5	O(4)-C(60)-C(59)	107.2(5)	O(4)-C(60)-H(60A)	110.3
C(59)-C(60)-H(60A)	110.3	O(4)-C(60)-H(60B)	110.3	C(59)-C(60)-H(60B)	110.3
H(60A)-C(60)-H(60B)	108.5	O(4)-C(61)-C(62)	109.8(5)	O(4)-C(61)-H(61A)	109.7
C(62)-C(61)-H(61A)	109.7	O(4)-C(61)-H(61B)	109.7	C(62)-C(61)-H(61B)	109.7
H(61A)-C(61)-H(61B)	108.2	C(61)-C(62)-H(62A)	109.5	C(61)-C(62)-H(62B)	109.5
H(62A)-C(62)-H(62B)	109.5	C(61)-C(62)-H(62C)	109.5	H(62A)-C(62)-H(62C)	109.5
H(62B)-C(62)-H(62C)	109.5	C(64)-C(63)-H(63A)	109.5	C(64)-C(63)-H(63B)	109.5
H(63A)-C(63)-H(63B)	109.5	C(64)-C(63)-H(63C)	109.5	H(63A)-C(63)-H(63C)	109.5
H(63B)-C(63)-H(63C)	109.5	C(63)-C(64)-O(1)	113.4(4)	C(63)-C(64)-H(64A)	108.9
O(1)-C(64)-H(64A)	108.9	C(63)-C(64)-H(64B)	108.9	O(1)-C(64)-H(64B)	108.9
H(64A)-C(64)-H(64B)	107.7	O(1)-C(65)-C(66)	114.4(4)	O(1)-C(65)-H(65A)	108.7
C(66)-C(65)-H(65A)	108.7	O(1)-C(65)-H(65B)	108.7	C(66)-C(65)-H(65B)	108.7
H(65A)-C(65)-H(65B)	107.6	C(65)-C(66)-H(66A)	109.5	C(65)-C(66)-H(66B)	109.5

H(66A)-C(66)-H(66B)	109.5	C(65)-C(66)-H(66C)	109.5	H(66A)-C(66)-H(66C)	109.5
H(66B)-C(66)-H(66C)	109.5	O(1)-Li(1)-C(22)	124.7(3)	O(1)-Li(1)-C(36)	119.3(3)
C(22)-Li(1)-C(36)	87.1(2)	O(1)-Li(1)-C(29)	143.1(3)	C(22)-Li(1)-C(29)	82.8(2)
C(36)-Li(1)-C(29)	82.3(2)	O(1)-Li(1)-C(34)	113.3(3)	C(22)-Li(1)-C(34)	115.7(3)
C(36)-Li(1)-C(34)	87.2(2)	C(29)-Li(1)-C(34)	33.08(13)	O(1)-Li(1)-C(41)	92.4(3)
C(22)-Li(1)-C(41)	88.9(2)	C(36)-Li(1)-C(41)	32.07(14)	C(29)-Li(1)-C(41)	114.2(3)
C(34)-Li(1)-C(41)	115.1(2)	O(1)-Li(1)-C(23)	107.9(3)	C(22)-Li(1)-C(23)	32.18(13)
C(36)-Li(1)-C(23)	118.7(3)	C(29)-Li(1)-C(23)	82.1(2)	C(34)-Li(1)-C(23)	108.4(2)
C(41)-Li(1)-C(23)	118.7(3)	O(1)-Li(1)-Nb(1)	165.9(3)	C(22)-Li(1)-Nb(1)	51.12(14)
C(36)-Li(1)-Nb(1)	50.47(14)	C(29)-Li(1)-Nb(1)	50.37(14)	C(34)-Li(1)-Nb(1)	77.89(18)
C(41)-Li(1)-Nb(1)	74.56(17)	C(23)-Li(1)-Nb(1)	74.74(17)	O(3)-Li(2)-C(15)	120.9(3)
O(3)-Li(2)-C(1)	121.0(3)	C(15)-Li(2)-C(1)	87.0(2)	O(3)-Li(2)-C(8)	145.1(3)
C(15)-Li(2)-C(8)	82.4(2)	C(1)-Li(2)-C(8)	82.9(2)	O(3)-Li(2)-C(6)	92.3(2)
C(15)-Li(2)-C(6)	89.4(2)	C(1)-Li(2)-C(6)	32.38(14)	C(8)-Li(2)-C(6)	115.2(2)
O(3)-Li(2)-C(9)	118.4(3)	C(15)-Li(2)-C(9)	114.1(3)	C(1)-Li(2)-C(9)	85.9(2)
C(8)-Li(2)-C(9)	31.78(13)	C(6)-Li(2)-C(9)	114.2(2)	O(3)-Li(2)-C(16)	105.6(3)
C(15)-Li(2)-C(16)	31.04(13)	C(1)-Li(2)-C(16)	117.3(3)	C(8)-Li(2)-C(16)	80.8(2)
C(6)-Li(2)-C(16)	118.3(2)	C(9)-Li(2)-C(16)	107.5(2)	O(3)-Li(2)-Nb(1)	164.9(3)
C(15)-Li(2)-Nb(1)	51.11(14)	C(1)-Li(2)-Nb(1)	50.81(14)	C(8)-Li(2)-Nb(1)	50.05(13)
C(6)-Li(2)-Nb(1)	75.64(17)	C(9)-Li(2)-Nb(1)	75.52(17)	C(16)-Li(2)-Nb(1)	73.26(16)
C(36)-Nb(1)-C(8)	125.46(12)	C(36)-Nb(1)-C(22)	88.57(11)	C(8)-Nb(1)-C(22)	140.24(11)
C(36)-Nb(1)-C(29)	86.52(12)	C(8)-Nb(1)-C(29)	77.75(11)	C(22)-Nb(1)-C(29)	85.50(11)
C(36)-Nb(1)-C(1)	140.08(12)	C(8)-Nb(1)-C(1)	87.47(12)	C(22)-Nb(1)-C(1)	73.66(11)
C(29)-Nb(1)-C(1)	125.99(12)	C(36)-Nb(1)-C(15)	74.03(11)	C(8)-Nb(1)-C(15)	86.15(11)
C(22)-Nb(1)-C(15)	126.69(12)	C(29)-Nb(1)-C(15)	140.70(11)	C(1)-Nb(1)-C(15)	88.21(11)
C(36)-Nb(1)-Li(1)	52.49(14)	C(8)-Nb(1)-Li(1)	131.54(15)	C(22)-Nb(1)-Li(1)	50.97(14)
C(29)-Nb(1)-Li(1)	54.32(15)	C(1)-Nb(1)-Li(1)	124.51(14)	C(15)-Nb(1)-Li(1)	125.38(14)
C(36)-Nb(1)-Li(2)	125.29(15)	C(8)-Nb(1)-Li(2)	55.07(15)	C(22)-Nb(1)-Li(2)	124.86(14)
C(29)-Nb(1)-Li(2)	132.18(15)	C(1)-Nb(1)-Li(2)	52.14(14)	C(15)-Nb(1)-Li(2)	51.40(14)
Li(1)-Nb(1)-Li(2)	173.39(17)	C(65)-O(1)-C(64)	116.0(4)	C(65)-O(1)-Li(1)	123.8(3)
C(64)-O(1)-Li(1)	119.0(3)	C(56)-O(2)-C(57)	113.9(3)	C(52)-O(3)-C(53)	112.2(3)
C(52)-O(3)-Li(2)	126.2(3)	C(53)-O(3)-Li(2)	119.4(3)	C(60)-O(4)-C(61)	112.6(4)

Table 52. Anisotropic displacement parameters ($pm^2x\ 10^{-1}$)for $[Li_2(Et_2O)_4][Nb(p\text{-}C_6H_4\text{-}CH_3)_6]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	19(2)	22(2)	23(2)	2(2)	9(1)	3(1)
C(2)	23(2)	21(2)	26(2)	2(2)	6(1)	2(1)
C(3)	18(2)	34(2)	25(2)	5(2)	5(1)	5(1)
C(4)	29(2)	25(2)	31(2)	4(2)	10(2)	7(2)
C(5)	36(2)	20(2)	31(2)	-2(2)	8(2)	4(2)
C(6)	25(2)	25(2)	24(2)	0(2)	3(1)	3(1)
C(7)	42(2)	34(2)	48(3)	5(2)	5(2)	17(2)
C(8)	22(2)	19(2)	19(2)	-4(2)	2(1)	-3(1)
C(9)	22(2)	26(2)	23(2)	-2(2)	1(1)	-1(1)
C(10)	33(2)	30(2)	20(2)	2(2)	-1(2)	-1(2)
C(11)	30(2)	28(2)	21(2)	-7(2)	3(1)	-8(2)
C(12)	22(2)	28(2)	28(2)	-10(2)	3(1)	-2(2)
C(13)	23(2)	24(2)	22(2)	-2(2)	-1(1)	-3(1)
C(14)	43(2)	48(2)	25(2)	-5(2)	9(2)	-5(2)
C(15)	16(2)	15(2)	23(2)	1(1)	-2(1)	-1(1)
C(16)	22(2)	22(2)	23(2)	-6(1)	4(1)	-1(1)
C(17)	16(2)	32(2)	32(2)	-7(2)	7(1)	-3(1)
C(18)	19(2)	26(2)	23(2)	5(2)	-1(1)	-3(1)
C(19)	25(2)	24(2)	21(2)	-2(2)	0(1)	1(1)
C(20)	20(2)	25(2)	22(2)	-2(2)	7(1)	-2(1)
C(21)	28(2)	41(2)	31(2)	-5(2)	0(2)	-13(2)
C(22)	17(2)	20(2)	20(2)	2(1)	4(1)	1(1)
C(23)	22(2)	27(2)	23(2)	-6(2)	2(1)	-2(1)
C(24)	21(2)	35(2)	29(2)	-6(2)	6(2)	-8(2)
C(25)	26(2)	24(2)	30(2)	1(2)	8(2)	1(2)
C(26)	30(2)	23(2)	24(2)	-3(2)	6(2)	1(2)
C(27)	21(2)	23(2)	21(2)	-3(2)	3(1)	-2(1)
C(28)	34(2)	40(2)	39(2)	-9(2)	17(2)	-3(2)
C(29)	21(2)	23(2)	17(2)	-3(1)	4(1)	-3(1)
C(30)	22(2)	18(2)	23(2)	-5(1)	6(1)	0(1)
C(31)	18(2)	25(2)	27(2)	-7(2)	-2(1)	1(1)

C(32)	26(2)	23(2)	26(2)	-4(2)	7(2)	-5(2)
C(33)	29(2)	19(2)	29(2)	0(2)	6(2)	2(1)
C(34)	20(2)	21(2)	21(2)	1(1)	2(1)	2(1)
C(35)	36(2)	23(2)	42(2)	-8(2)	2(2)	-6(2)
C(36)	20(2)	20(2)	24(2)	1(1)	-4(1)	-4(1)
C(37)	21(2)	26(2)	27(2)	2(2)	0(1)	-1(1)
C(38)	24(2)	27(2)	48(3)	0(2)	-4(2)	1(2)
C(39)	37(2)	24(2)	46(3)	2(2)	-17(2)	3(2)
C(40)	52(2)	37(2)	25(2)	1(2)	-11(2)	2(2)
C(41)	31(2)	29(2)	26(2)	-4(2)	-2(2)	3(2)
C(42)	60(3)	52(3)	66(3)	11(3)	-29(3)	15(2)
C(51)	32(2)	33(2)	33(2)	9(2)	6(2)	2(2)
C(52)	33(2)	21(2)	31(2)	6(2)	6(2)	6(2)
C(53)	35(2)	32(2)	27(2)	6(2)	0(2)	-3(2)
C(54)	63(3)	34(2)	37(2)	-5(2)	3(2)	-7(2)
C(55)	69(3)	54(3)	54(3)	2(2)	7(3)	22(3)
C(56)	48(2)	33(2)	54(3)	1(2)	-5(2)	2(2)
C(57)	23(2)	41(2)	60(3)	19(2)	5(2)	1(2)
C(58)	28(2)	50(3)	48(3)	10(2)	4(2)	-2(2)
C(59)	50(3)	116(6)	110(5)	-36(4)	15(3)	-11(3)
C(60)	76(4)	56(3)	70(4)	-18(3)	-21(3)	18(3)
C(61)	97(5)	114(5)	54(4)	-6(3)	32(3)	-34(4)
C(62)	83(5)	363(16)	62(4)	8(7)	18(4)	-106(7)
C(63)	119(6)	57(4)	106(5)	11(4)	32(4)	32(4)
C(64)	69(3)	36(3)	86(4)	22(3)	-22(3)	-4(2)
C(65)	64(3)	73(4)	41(3)	19(3)	21(2)	-5(3)
C(66)	97(4)	68(4)	59(4)	5(3)	30(3)	2(3)
Li(1)	26(3)	30(3)	30(3)	0(3)	3(2)	4(3)
Li(2)	31(3)	26(3)	28(3)	4(3)	5(3)	1(3)
Nb(1)	14(1)	15(1)	17(1)	-1(1)	2(1)	0(1)
O(1)	44(2)	33(2)	38(2)	13(1)	8(1)	6(1)
O(2)	39(2)	29(2)	47(2)	5(1)	5(1)	-4(1)
O(3)	30(1)	23(1)	27(1)	5(1)	1(1)	-2(1)
O(4)	54(2)	77(3)	55(2)	9(2)	6(2)	-13(2)

8.6 Chromium Complexes

8.6.1 $Cr(i\text{-}C_3H_7)_4$

8.6.1.1 Preparation of $Cr(i\text{-}C_3H_7)_4$

$Cr(i\text{-}C_3H_7)_4$ was prepared according to ref. [67] with slight modification.

To a suspension of $CrCl_3$ (3 g, 18.9 mmol) in ether (150 mL) was added a Grignard solution prepared from 1.83g Mg (75 mmol) and 7.14 mL $i\text{-}C_3H_7Br$ in ether (70 mL). The reaction mixture was allowed slowly to warm up to –10°C. When the reaction starts, a red brown color formed, immediately the temperature lowered again to –30°C, and stirred at this temperature untill all $CrCl_3$ reacted. The reaction mixture was allowed to warm slowly to RT. The reaction mixture was irradiated for 8 hr with UV light. The solvent was evaporated off at –20°C and the residue extracted with *n*-pentane, the resulting solution filtered over Al_2O_3. The *n*-pentane is evaporated off at –20°C and the residue redissolved in Et_2O (20 mL). The resulting red brown solution was cooled to –78°C to afford brown crystals which were isolated by filtration.

8.6.1.2 Crystal Data and Crystal Structure Analysis

Table 53. Crystal data and structure refinement for $Cr(i\text{-}C_3H_7)_4$.

Identification code	criprop4	
Empirical formula	C_{12} H_{28} Cr	
Formula weight	224.34	
Temperature	153(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	C12/c 1	
Unit cell dimensions	a = 1505.3(3) pm	α= 90°.
	b = 1148.0(2) pm	β= 101.361(4)°.
	c = 819.45(15) pm	γ = 90°.

Volume	1.3884(4) nm^3
Z	4
Density (calculated)	1.073 Mg/m^3
Absorption coefficient	0.788 mm^{-1}
F(000)	496
Crystal size	o.3 x 0.3 x 0.3 mm^3
Theta range for data collection	2.25 to 30.54°.
Index ranges	-19<=h<=19, -15<=k<=16, -11<=l<=11
Reflections collected	8493
Independent reflections	2057 [R(int) = 0.0166]
Completeness to theta = 30.54°	96.1 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2057 / 0 / 117
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0260, wR2 = 0.0693
R indices (all data)	R1 = 0.0331, wR2 = 0.0750
Extinction coefficient	0.0000(8)
Largest diff. peak and hole	0.339 and -0.135 e.$Å^{-3}$

Table 54. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for Cr(*i*-$C_3H_7)_4$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cr	5000	2555(1)	2500	22(1)
C(1)	5822(1)	3605(1)	1498(1)	28(1)
C(2)	6289(1)	4526(1)	2698(2)	42(1)
C(3)	6487(1)	2925(1)	694(2)	38(1)
C(4)	4366(1)	1513(1)	649(1)	30(1)
C(5)	3868(1)	2206(1)	-826(2)	48(1)
C(6)	3768(1)	616(1)	1250(2)	46(1)

Table 55. Bond lengths [pm] and angles [°] for Cr(*i*-C_3H_7)$_4$.

Cr-C(1)#1	201.39(11)	Cr-C(1)	201.39(11)
Cr-C(4)	201.83(11)	Cr-C(4)#1	201.83(11)
C(1)-C(3)	151.84(16)	C(1)-C(2)	151.93(17)
C(1)-H(1)	94.1(16)	C(2)-H(2)	93(2)
C(2)-H(3)	95.5(18)	C(2)-H(4)	92(2)
C(3)-H(5)	92(2)	C(3)-H(6)	93(2)
C(3)-H(7)	94.2(18)	C(4)-C(6)	151.25(19)
C(4)-C(5)	151.64(18)	C(4)-H(8)	95.4(18)
C(5)-H(9)	91(2)	C(5)-H(10)	92(2)
C(5)-H(11)	96.3(18)	C(6)-H(12)	96.8(17)
C(6)-H(13)	90(2)	C(6)-H(14)	90.5(19)
		C(1)#1-Cr-C(1)	106.55(6)
C(1)#1-Cr-C(4)	115.05(5)	C(1)-Cr-C(4)	106.61(5)
C(1)#1-Cr-C(4)#1	106.61(5)	C(1)-Cr-C(4)#1	115.05(5)
C(4)-Cr-C(4)#1	107.25(6)	C(3)-C(1)-C(2)	112.18(11)
C(3)-C(1)-Cr	112.36(8)	C(2)-C(1)-Cr	113.30(8)
C(3)-C(1)-H(1)	110.5(9)	C(2)-C(1)-H(1)	108.9(9)
Cr-C(1)-H(1)	98.8(9)	C(1)-C(2)-H(2)	113.0(12)
H(3)-C(2)-H(4)	105.6(16)	C(1)-C(3)-H(5)	111.4(14)
C(1)-C(3)-H(6)	112.1(14)	H(5)-C(3)-H(6)	106.0(15)
C(1)-C(3)-H(7)	110.6(10)	H(5)-C(3)-H(7)	107.8(17)
H(6)-C(3)-H(7)	108.8(17)	C(6)-C(4)-C(5)	112.60(13)
C(6)-C(4)-Cr	112.51(8)	C(5)-C(4)-Cr	111.99(8)
C(6)-C(4)-H(8)	110.6(10)	C(5)-C(4)-H(8)	109.9(10)
Cr-C(4)-H(8)	98.4(10)	C(4)-C(5)-H(9)	114.0(13)
C(4)-C(5)-H(10)	110.9(15)	H(9)-C(5)-H(10)	104.0(18)
C(4)-C(5)-H(11)	112.4(10)	H(9)-C(5)-H(11)	107.4(17)
H(10)-C(5)-H(11)	107.8(18)	C(4)-C(6)-H(12)	111.7(10)
C(4)-C(6)-H(13)	112.0(13)	H(12)-C(6)-H(13)	104.4(16)
C(4)-C(6)-H(14)	112.5(12)	H(12)-C(6)-H(14)	111.3(15)
H(13)-C(6)-H(14)	104.4(17)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+1/2

Table 56. Anisotropic displacement parameters ($pm^2 x\ 10^{-1}$) for Cr(i-C_3H_7)$_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cr	23(1)	21(1)	22(1)	0	7(1)	0
C(1)	27(1)	28(1)	30(1)	3(1)	12(1)	2(1)
C(2)	46(1)	38(1)	48(1)	-7(1)	22(1)	-14(1)
C(3)	38(1)	38(1)	45(1)	3(1)	23(1)	5(1)
C(4)	32(1)	29(1)	30(1)	-4(1)	5(1)	1(1)
C(5)	60(1)	41(1)	37(1)	-4(1)	-8(1)	4(1)
C(6)	50(1)	42(1)	45(1)	-10(1)	9(1)	-17(1)

IV. Summary

In order to explore the geometry of six and five d^0 complexes of the transition metals, new aryl complexes $[Li(THF)_4][Ti(C_6H_5)_5]$, $[Li(Et_2O)_4][Ti(p\text{-}C_6H_4\text{-}CH_3)_5]$, $[Li_4Cl(THF)_8][Ti(C_6H_5)_6]$, $[Li_4Cl(Et_2O)_8][Ti(p\text{-}C_6H_4\text{-}CH_3)_6]$, $[Bu_4N][Zr(C_6H_5)_5]$ $[Li_2(THF)_4][Zr(C_6H_5)_6]$, $[Li_2(Et_2O)_4][Zr(p\text{-}C_6H_4\text{-}CH_3)_6]$, and $[Li_2(THF)_4][Hf(C_6H_5)_6]$, have been synthesized and their crystal structure determined by X-ray diffraction measurements.

The Arylation of $TiCl_4 \cdot xEt_2O$ with C_6H_5Li gives five-coordinate, homoleptic organotitanium(IV) derivatives with the formula $[Li(THF)_4][Ti(C_6H_5)_5]$. The anion $Ti(C_6H_5)_5^-$ has an almost square pyramidal *SP-5* geometry, as observed in the solid-state structure of $[Li(THF)_4][Ti(C_6H_5)_5]$, similarly the $[Li(Et_2O)_4][Ti(p\text{-}C_6H_4\text{-}CH_3)_5]$ was prepared and the titanium center is located in square pyramidal environment. When the same reaction performed at different conditions of temperature and mole ratio, the new complexes with hexa aryl derivative of titanium(III) were isolated and structurally determined. From the X-ray measurement, the titanium atom in the two anions $Ti(C_6H_5)_6^{3-}$ and $Ti(p\text{-}C_6H_4\text{-}CH3)_6^{3-}$ located in an octahedral arrangement with some additional interaction between two Li^+ cations and the metal center.

The preparation of the unusual five-coordionate zirconium aryl:$[Bu_4N][Zr(C_6H_5)_5]$ is achieved by the low temperature arylation of $ZrCl_4$ with C_6H_5Li in presence of $BrNBu_4$. The structure of the anion is best described as a square pyramidal arrangement.

The arylation of $ZrCl_4$ with C_6H_5Li and $Li(p\text{-}C_6H_4\text{-}CH_3)$ under different arylation conditions also give a homoleptic hexa-arylzirconium(IV) compounds, $[Li_2(THF)_4][Zr(C_6H_5)_6]$ and $[Li_2(Et_2O)_4][Zr(p\text{-}C_6H_4\text{-}CH_3)_6]$. From x-ray diffractions result, the six C_6H_5, or $p\text{-}C_6H_4\text{-}CH_3$

groups define an approximately trigonal prismatic environment for the zirconium atom in both anions. On the other hand the reaction of $HfCl_4$ with C_6H_5Li under the same conditions also affords the hexaphenylhafnmoium(IV) complex, and the structure of the anion is surprisingly octahedral.

Attempts to prepare related $[Nb(C_6H_5)_6]^-$ complexes lead instead to the isolation of the new heax-arylniobiate(IV) complexes, $[Nb(C_6H_5)_6]^{2-}$ and $[Nb(p\text{-}C_6H_4\text{-}CH3)_6]^{2-}$, which both adopt an approximate trigonal prismatic structures, and the anion is affected by interaction with two Li^+ cations.

Attempts to prepare a related vanadium complexes such as $V(C_6H_5)_6^{2-}$ lead instead to the isolation of the reduced, well-known product $V(C_6H_5)_6^{4-}$.

The high unusual class of tetra-organyl complexes containing oxovanadium(V) and oxovanadium(IV) anions have been prepared and structurally characterized: $VO(CH_3)_4^-$, $VO(CH_3)_4^{2-}$ and $VO(C_6H_5)_4^{2-}$ where the vanadium atom in these anions is located in square pyramidal environment with the oxygen atom in the apical position.

Several attempts to syntheses hexamethyl or hexaphenylchromium(IV) compounds starting from the reaction of $CrCl_3$ or $Cr(O\text{-}t\text{-}Bu)_4$ with different alkyling agent (RLi, Me_2Zn, $AlMe_3$, RMgX) were performed. Unfortunately these attempts were unsuccessful, and usually the reaction proceeds with metal reduction or without specific products. The synthesis and crystal structure determination of $Cr(i\text{-}C_3H_7)_4$ is described. All four isopropyl groups are σ-bonded to the Cr(IV) center, which is located in a tetrahedral environment.

V. Zusammenfassung

Um die Geometrie von fünf- und sechsfach-koordinierten d^0-Komplexen der Übergangsmetalle zu erforschen, wurden die neuen Aryl-Komplexe, $[Li(THF)_4][Ti(C_6H_5)_5]$, $[Li(Et_2O)_4][Ti(p\text{-}C_6H_4\text{-}CH_3)_5]$, $[Li_4Cl(THF)_8][Ti(C_6H_5)_6]$, $[Li_4Cl(Et_2O)_8][Ti(p\text{-}C_6H_4\text{-}CH_3)_6]$, $[Bu_4N][Zr(C_6H_5)_5]$ $[Li(THF)_4]_2[Zr(C_6H_5)_6]$, $[Li_2(Et_2O)_4][Zr(p\text{-}C_6H_4\text{-}CH_3)_6]$, und $[Li(THF)_4]_2[Hf(C_6H_5)_6]$ synthetisiert und ihre Kristallstruktur durch Röntgenbeugung bestimmt.

Durch Umsetzung von $TiCl_4 \cdot xEt_2O$ mit C_6H_5Li konnte die fünffach-koordinierte, homoleptische Organotitan(IV)-Verbindung mit der Formel $[Li(THF)_4][Ti(C_6H_5)_5]$ synthetisiert und röntgenographisch charakterisiert werden. Das Anion $Ti(C_6H_5)_5^-$ hat eine fast quadratisch-pyramidale *SP*-5 Geometrie. Auch $[Li(Et_2O)_4][Ti(p\text{-}C_6H_4\text{-}CH_3)_5]$ wurde hergestellt und das Titan-Zentrum ist auch quadratisch-pyramidal umgeben.

Die gleiche Reaktion bei unterschiedlichen Bedingungen von Temperatur und Molverhältnis ergab die neuen sechsfach-koordinerten Aryl-Derivate des Titan(III). Nach der röntgenographischen Messung, befinden sich die Titan-Atome in den beiden Anionen $[Ti(C_6H_5)_6]^{3-}$ und $[Ti(p\text{-}C_6H_4\text{-}CH_3)_5]^{3-}$ in oktaedrischer Anordnung mit einer zusätzlichen Interaktion zwischen zwei Li^+-Kationen und dem Metall.

Die Herstellung des ungewöhnlichen fünffach koordinierten Zirkoniumaryls $[Bu_4N][Zr(C_6H_5)_5]$ wurde durch Arylierung bei niedriger Temperatur von $ZrCl_4$ mit C_6H_5Li in Anwesenheit von $BrNBu_4$ erreicht. Die Struktur des Anions wird am besten als quadratisch-pyramidal beschrieben.

Die Arylierung von $ZrCl_4$ mit C_6H_5Li und Li(*p*-C_6H_4-CH_3) unter verschiedenen Bedingungen führte ebenfalls zu den neuen homoleptischen Hexaarylzirconium(IV)-Verbindungen, $[Li(THF)_4]_2[Zr(C_6H_5)_6]$ und $[Li_2(Et_2O)_4][Zr(p\text{-}C_6H_4\text{-}CH_3)_6]$.

Im Kristall definieren die sechs C_6H_5- oder *p*-C_6H_4-CH_3- Gruppen eine annähernd trigonal prismatische Umgebung für das Zirkon-Atom in beiden Anionen.

Andererseits ergab die Reaktion von $HfCl_4$ mit C_6H_5Li unter den gleichen Bedingungen den Hexaphenylhafnium(IV)-Komplex, und die Struktur des Anions ist überraschenderweise oktaedrisch.

Die Umsetzung von NbF_5 mit Phenyllithium oder *p*-Tolyllithium in Et_2O führte zu den neuen Hexaarylniobiat(IV)-Verbindungen, $[Nb(C_6H_5)_6]^{2-}$ und $[Nb(p\text{-}C_6H_4\text{-}CH3)_6]^{2-}$. Die Anionen der Hexaphenyl- und Hexatolyl-Niobate weisen eine trigonal-prismatische Geometrie auf und das Anion hat zusätzliche Kontakte zu zwei Li^+-Kationen.

Versuche, den verwandten Vanadium-Komplex $V(C_6H_5)_6^{2-}$ zu erhalten, ergaben stattdessen die bekannte, reduzierte Spezies $V(C_6H_5)_6^{4-}$.

Die ungewöhnliche Klasse von Tetra-Komplexen mit Organyl-σ-oxovanadium(V)- und -oxovanadium(IV)-Anionen wurden hergestellt und strukturell charakterisiert: $VO(CH_3)_4^-$, $VO(CH_3)_4^{2-}$ und $VO(C_6H_5)_4^{2-}$, wobei das Vanadium Atom in diesen Anionen eine quadratisch-pyramidale Umgebung mit dem Sauerstoffatom in der apikalen Position hat.

Mehrere Versuche der Synthese von Hexamethyl- oder Hexaphenylchrom(IV)-Verbindungen durch Reaktion von $CrCl_3$ oder Cr(O-*t*-Bu)$_4$ mit unterschiedlichen Methylierungs- und Arylierungsreagentien (RLi, Me_2Zn, $AlMe_3$, RMgX) waren erfolglos. In der Regel verläuft die Reaktion unter Metall-Reduktion oder ohne spezifische Produkte. Die Synthese und Kristallstruktur von Cr(*i*-C_3H_7)$_4$ wurde beschrieben.

VI. References

[1] P.J. Davidson, M. F. Lappert, R. Pearce, *Chem. Rev*. **1976**, 76, 219.

[2] V. Pfennig, K. Seppelt, *Science* **1996**, 271, 626-8.

[3] K. Seppelt, *Acc. Chem. Res*. **2003**, 36, 147-153.

[4] A. Desmolliens, Y. Jean, O. Eisenstein, *Organometallics* **1986**, 5,1457 -1464.

[5] M. Kaupp, *J. Am. Chem. Soc*. **1996**, 118, 3018 - 3024.

[6] M. Kaupp, *Chem. Eur. J*. **1998**, 4, 1678 -1686.

[7] B. Roessler, K. Seppelt, *Angew. Chem. Int. Ed*. **2000**, 39, 1259 - 1261.

[8] P. M. Morse, G. S. Girolami, *J. Am. Chem. Soc*. **1989**, 111, 4114-4116.

[9] S. Kleinhenz, V. Pfennig, K. Seppelt, *Chem. Eur. J*. **1998**, 4,1687 - 1691.

[10] S. Kleinhenz, V. Pfennig, K. Seppelt, *Chem. Eur. J*. **2001**, 7, 3652 - 3656.

[11] A. Haaland, A. Hammel, K. Rapdal, H. V. Volden, *J. Am. Chem. Soc*. **1990**, 112, 4547 -4549.

[12] Von K. Thiele, W. Schuman, S. Wagner, W. Brüser, *Z. Anorg. Allg. Chem.* **1972**. 390, 280-288.

[13] W. Seidel, G. Kreisel, *Z. Anorg. Allg. Chem.* **1988**. 559, 118-122.

[14] W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, G. Wilkinson, *J. Chem. Soci., Dalton Trans.*, **1972**, 4, 533-542.

[15] Hein, F.; Feiss, R., *Z. Anorg. Allg. Chem.*, (1958) **27**, 145.

[16] Hein, F.; Schmiedeknecht, K., *J. Organomet.Chem.*, (1966) **5**, 454.

[17] Hein, F.; Schmiedeknecht, K., *J. Organomet.Chem.*, (1967) **8**, 503.

[18] Barker, G. K.; Lappert, M. F.; Howard, J. A., *J. Chem.Soc., Dalton Trans.*, (1978) 734.

[19] (a) Mowat, W.; Shortland, A. J.; Hill, N. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 770. (b) M. Bochman, G. Wilkinson, G. B. Young, *J. Chem. Soc., Dalton Ttrans.* **1980**, 1879. (c) Gramlich, V.; Pfefferkorn, K. *J. Organomet. Chem.* **1973**, *61*, 247.

[20] P. Stavropoulos, P. D. Savage, R. P. Tooze, G. Wilkinson, B. Hussain, M. Motevalli, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, **1987**, 557-562.

[21] C. Schulzke, D. Enright, H. Sugiyama, G. LeBlanc, S. Gambarotta, G. P. A. Yap, L. K. Thompson, D. R. Wilson, R. Duchateau, *Organometallics* **2002,** 21, 3810-3816.

[22] P. J. Alonso, J. Fornies, M. A. Garcia-Monforte, A. Martin, B. Menjon, C. C. Rillo, *Chem. Eur. J.* **2002**, 8(17), 4056-4065.

[23] C. E. Housecroft and A. G. Sharpe, *Inorganic Chemistry*,2nd ed. Pearson Education Limited **2005**. England.

[24] **a)** A. Shortland, G. Wilkinson. *J.C.S. Chem. Comm.* **1972**, 6, 318. **b)** A. Shortlan, G. Wilkinson. *J.C.S. Dalton Trans.* **1973**, *8*, 872-876. **c)** L. Galyer, G. Wilkinson. *J.C.S. Chem. Comm.* **1975**, *13*, 497-499.

[25] S. K. Kang, T. A. Albright, O. Eisenstein. *Inorg. Chem.* **1989**, *28*, No.9, 1611-1613.

[26] M. S. Shen, H. F. Schaefer, H. Partridge. *J. Chem. Phys.* **1993**, *98, No.1*, 508-521.

[27] S. K. Kang, H. Tang, T. A. Albright. *J. Am. Chem. Soc.* **1993**, *115*, 1971-1981.

[28] T. A. Albright, H. Tang. *Angew. Chem*, **1992**, *104*, 1523-1534.

[29] J. C. Friese, A. Krol, C. Puke, K. Kirschbaum, D. M. Giolando, *Inorg. Chem.* **2000**, 39, 1496-1500.

[30] *Angew. Chem. Int. Ed.*, **2001**, 40, 3534-3565.

[31] R. S. Berry, *J. Chem. Phys.* 1960, 32, 933.

[32] E.L.Muetterties, L.J. Guggenberger, *J. Am. Chem. Soc.* **1974**, 96, 1748-1756.

[33] B. Roessler, S. Kleinhenz, K. Seppelt, *Chemical Communications*, **2000**, 12, 1039-1040.

[34] S. Kleinhenz, K. Seppelt, *Chem. Eur. J.* **1999**, 5, 3573-3580.

[35] P. J. Alonso, L. R. Falvello, J.Fornies, M. A. Garcia-Monforte, B. Menjon, *Angew. Chem., Inte. Ed.* **2004**, 43, 5225-5228.

[36] T. A. Albright, H. Tang, Chem. Int. Ed. Engl. 1992, 31, 1462.

[37] C. Pulham, A. Haaland, A. Hammel, K. Rypdal, H. P. Verne, H. V. Volden, Angew. Chem. 1992, 104, 1534; Angew. Chem. Int. Ed. Engl. 1992, 31, 1464.

[38] C. A. Bayse, M. B. Hall, J. Am. Chem. Soc. 1999, 121, 1348.

[39] G. Wilkinson, J. M. Birmingham, *J. Am. Chem. Soc.* **1954**, *76*, 4281.

[40] Negishi, E.; Huo, S. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim, Germany, 2002; pp 1-49.

[41] Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 9, 1413-1418.

[42] C. L. Hilton, B. T. King, *Organometallics* **2006**, 25(17), 4058-4061.

[43] M. J. Nelsen, G. S. Girolami, *J. Organomet. Chem*., **1999**, 585, 275–284.

[44] M. A. Garcia-Monforte P. J. Alonso, J.Fornies, B. Menjon, *J.Chem.Soc.Dalton Trans*., **2007**, ,3347-3359.

[45] S. Kleinhenz, M. Schubert, K. Seppelt, *Chem. Ber./Recueil* ,**1997**, 130(7), 903-906.

[46] M. Minoura. T. Sagani, K. Akiba. *C.* Modrakowski, **A.** Sudau, **K.** Seppelt, ***S.*** Wallenhauer, *Angw. Chem.* **1996,** *108*, 2827-2829; *Angew. Chem. Intr. Ed. Eingl.* **1996,** 35**,** 2660-2661.

[47] S. Wallenhauer. D. Leopold. K. Seppelt, *Inorg. Chem.* **1993,** 32, 3948-3951.

[48] R. J. Morris and G. **S.** Girolam *Organometallics* **1991,** 10**,** 792-799.

[49] M. M. Olmstead, P. P. Power, S. C. Shoner, *Organometallics* **1988**, 7(6), 1380-5.

[50] R. Schrock. *J.Organometallic. Chem.*, **1976**, 122, 209-225.

[51] L.R. Chamberlin, I.P. Rothwell, J.C. Huffman, *J. Amer. Chem. Soc*., **1986**, 108, 1502.

[52] B. Sarry, V. Dobrusskin, *J. Organomet. Chem.* **1968.** 13, 1-8.

[53] B. Sarry, P. Velling, *Z. Anorg, Allg. Chem.*, **1976,** 426, 107-112.

[54] B. Sarry, R. Schaffernicht, *Z. Naturforsch.*, **1981,** 86b,1238- 1243.

[55] R. Rartlett, **I?** P. Power, S. *C.* Shoncr, *J. Am. Chem. Soc*., **1988,** 110, 1966-1968.

[56] a) W. Seidel, G. Kreisel, *Z. Anorg. Allg. Chem.*, **1976**, 426, 150; b) W. Seidel, G. Kreisel, *Z. Chem.* **1976**, 16, 115.

[57] G. Kreisel, P. Scholz, W. Seidel, *Z. Anorg. Allg. Chem.*, **1980**, 460, 51.

[58] W. Seidel, P. Scholz, G. Kreisel, *Z. Anorg. Allg. Chem.*, **1979**, 458, 263.

[59] R. Ferguson, E. Solari, C. Floriani, D. Osella, M. Ravera, N. Re, A. Chiesi-Villa, C. Rizzoli, *J. Am. Chem. Soc*., **1997**, 119, 10 104.

[60] a) G. K. Barker, M. F. Lappert, J. A. K. Howard, *J. Chem. Soc. Dalton Trans.*, **1978**, 734; b) G. K. Barker, M. F. Lappert, *J. Organomet. Chem.* **1974**, 76, C45.

[61] P. J. Alonso, J. Fornies, M. A. Garcia-Monforte, A. Martin, B. Menjon, C. C. Rillo, *Chem. Eur. J.* **2005**, 11, 4713 – 4724**.**

[62] B. K. Bower, H.G. Tennent, *J. Am.Chem. Soc.*, **1972**, 94, 2512.

[63] Glowiak, T., Grobelny, G., Jezowska-Trzebiatowska, B., Kreisel G., Seidel, W., Uhlig, E., *J.organomet. Chem.*, **1978**, 155, 39.

[64] P.B. Hitchcock,T.H. Lee,G. J. Leigh, *Inorg. Chim. Acta* **2003**, 349, 159-164.

[65] W. R. McGregor, F. J. Swinbourne, *J. Inorg. Nucl. Chem.* **1966**, 28(4), 1027-30.

[66] M. Antler, A. W. Laubengayer, *J. Am. Chem. Soc.*, **1955**, 77, 5250-3.

[67] J. Müller, W. Holzinger *Angew. Chem. Inter. Edit* (1975), 14, 760.

[68] C. J. Cardin, J. David, J. M. Kelly,R. J. Norton, A. Roy,B. J. Hathaway, T.J. King, *J. Chem. Soc., Dalton Trans.*, **1983**, 4, 671-7.

[69] P. J. Alonso, J. Fornies, M. A. Garcia-Monforte, A. Martin, B. Menjon, C. C. Rillo, *J. Organomet. Chem.* **2007**, 692(15), 3236-3247.

[70] G. Sheldrick, Program for Crystal Structure Solution; University of Göttingen, Germany. 1986. G. Sheldrick, SHELXS-97; University of Göttingen, Germany 1997.

[71] K. Brandenburg, *DIAMOND 3.2e*, *Visual Crystal Structure Information System*, 1997 - 2010 Crystal Impact GbR.

[72] D.F.Shriver, M.A. Drezdzon, *The manipulation of air-sensitive compounds* 2nd edition, New York: Wiley-Intersience (1996).

[73] D.Grdenic, M. Dordevic, *Croat. Chem. Acta*, **1958**, 30, 105.

[74] M.J. Lusch, W.V. Phillips, R.F. Sieloff, *Org. Synth.*, **1984**, 62, 101-110; Wittig, G. *Angew. Chem.*, **1940**, 53, 241-264.

[75] Hitchcock, Peter B.; Lee, Ting Huei; Leigh, G. *J. Inorganica Chimica Acta*, **2003**, 349. 159-164.

[76] Krauss, Hans Ludwig; Muenster, Gerhard. *Zeitschrift für Anorganische und Allgemeine Chemie*,**1967**, 352(1-2), 24-6.