Rhenium Complexes

Rhenium(V) Complexes with Selenolato- and Tellurolato-Substituted Schiff Bases – Released PPh3 as a Facile Reductant

Maximilian Roca Jungfer,[a] Adelheid Hagenbach,[a] Ernesto Schulz Lang,[b] and Ulrich Abram*[a]

Abstract: The salicylidene Schiff bases of bis(2-aminophenyl)disselenide and -ditelluride react with [ReOCl3(PPh3)2]o to give the arylimidorhenium(V) compounds [Re(NPhR)Cl3(PPh3)2] (R = H, F, CF3) with formation of rhenium(V) complexes with tridentate {O,N,Se/Te} chalcogenolato ligands. The ligands adopt a facial coordination mode with the oxygen donors trans to the multiply bonded O2– or NPhR2– ligands. The reduction of the dichalcogenides and the formation of the chalcogenolato ligands occurs in situ by released PPh3 ligands. The absence of additional reducing agents provides good yields of products with rhenium in the high formal oxidation state “+5”. A mechanism for the dichalcogenide reduction is proposed on the basis of the experimental results. In accordance with the proposed mechanism, best yields are obtained with a strict exclusion of oxygen, but in the presence of water.

Introduction

In contrast to the large number of alcoholato or thiolato complexes, organoselenolato and -tellurolato complexes of rhenium are rare. Only a few of such compounds have been characterized crystallographically.[1] The majority of them contains the metal in low oxidation states and tricarbonylrhenium(I) species dominate.[2–14] Organoselenolato and -tellurolato complexes with rhenium in higher oxidation states are even more scarce despite their proposed potentially beneficial catalytic properties.[15–17] They mainly contain simple, unsubstituted phenylselenolato ligands.[18–21] A few more rhenium(V) complexes with special ligands such as acylselenolates, a diselenolenate, and pyridine-2-selenolate have been reported.[22–24] The rarity of these reports may result from the more complicated syntheses of heavier organochalcogenolato ligands. For some organochalcogenolates, such as alkynylselenolates, exist some special synthetic routes.[25,26] But commonly, the corresponding selenols and tellurols are unstable and prepared by reduction of the corresponding diorganodichalcogenides directly before the complex formation. The reaction conditions of such procedures must be controlled carefully in order to avoid the parallel reduction of the transition metal ions. This problem has been described in detail for the synthesis of complexes of the composition (NBu4)[MVO(aryl)selenolate)4] (M = Tc, Re), where the use of Li(BH4) in THF proved to be a suitable and easy to control reductant.[27,28] Recently, an oxidorhenium(V) complex with pyridylselenolato ligands was prepared by the reaction of the corresponding diselenide with [ReOCl3(PPh3)2] without the addition of a reducing agent. Obviously, the released PPh3 acted as a selective reducing agent for dipyridyl diselenide, while the oxidation state of rhenium was retained.[24]

In the present work, we demonstrate that the assumed reaction pathway can be extended to other diorganodiselenides and -ditellurides. Thereto, we performed reactions of [ReOCl3(PPh3)2] and [Re(NPhR)Cl3(PPh3)2] (R = 4-H, 4-F or 4-CF3) with the Schiff bases prepared from salicylaldehyde and bis(2-aminophenyl)diselenide ({HLSe}2) and -ditelluride ({HLTe}2).

Results and Discussion

The salicylidene Schiff base of bis(2-aminophenyl)disselenide ([HLSe]2) was prepared by a reaction of di(2-aminophenyl)disselenide with two equivalents of salicylaldehyde in boiling ethanol. For the synthesis of ([HLTe]2), an excess of the aldehyde (about 3:1) was used to obtain good yields. The products precipitated as yellow-orange ([HLSe]2) or orange-red ([HLTe]2) solids and were recrystallized from CHCl3/EtOH. The synthetic route is simi-
lar to previous reports, but the optimized conditions described in the Experimental Part give better yields and pure products. The purity of the dichalcogenides can readily be checked by their $^{77}\text{Se}$ and $^{125}\text{Te}$ NMR spectra giving resonances at 363 ppm ($\{\text{HLSe}\}_2$) and 228 ppm ($\{\text{HLTe}\}_2$). The other spectral features match the previously reported data.

Single crystals of $\{\text{HLSe}\}_2$ and $\{\text{HLTe}\}_2$ suitable for X-ray diffraction were grown from CHCl$_3$/EtOH mixtures. Figure 1a shows an ellipsoid representation of the selenium compound with the atomic labelling scheme, which has also been applied for $\{\text{HLTe}\}_2$. A unit cell of the latter compound is shown in Figure 1b. It clearly illustrates that the ditelluride crystallizes in the present tetragonal polymorph with well-separated molecules. This is in contrast to the situation in the previously studied orthorhombic polymorph, in which each two molecules are connected by Te···Te interactions of 4.054 Å. In the compound under study, the shortest intermolecular Te···Te distances are larger than 6.5 Å.

![Figure 1. (a) Molecular structure of $\{\text{HLSe}\}_2$. Ellipsoids represent 50 % probability. Hydrogen atoms bonded to carbon atoms are omitted for clarity. (b) Unit cell plot of $\{\text{HLTe}\}_2$ illustrating the absence of intermolecular Te···Te interactions.](image)

Some fundamental bond lengths of the dichalcogenides are compared with those in the rhenium complexes in Table 1 and Table 2. Some more details are summarized in the Supporting Information.

Reactions of the two functionalized dichalcogenides with oxido- and arylimidorhenium(V) complexes show that they are reduced during such procedures and form tridentate selenolato and tellurolato ligands, which bind tridentate to the $\{\text{ReO}\}_3^{3+}$ or $\{\text{Re(NPhR)}\}_3^{3+}$ cores. A summary of the performed reactions and obtained products is shown in Scheme 1. Although all reactions worked at room temperature and without the addition of a supporting base, they are slow and the yields of the products are in many cases unsatisfactorily low. This comes, however, not completely unexpected with regard to the low solubility of most of the starting materials used. But surprisingly, also the use of the better soluble, fluorinated starting complex $\{\text{Re(NPhF)}\}_3\text{Cl}(\text{PPh}_3)$ does not necessarily improve the yields. This means that the conditions for the individual reactions had to be optimized in terms of solvent, temperature and reaction time. Generally, we found that the presence of traces of water and the absence of oxygen are mandatory for good yields.

Reactions of $\{\text{ReOCl}_3\text{PPh}_3\}_2$ with $\{\text{HLTe}\}_2$ give yields of $\{\text{ReO(LTe)Cl(PPh}_3)\}$ in the range of 70 %, when the reaction is performed at room temperature in moist CH$_2$Cl$_2$ under inert conditions. Interestingly, the yields are significantly lower (only about 20 %) when the reaction is done in dry solvent or on air. Since such a behavior suggests a sophisticated mechanism, we followed the course of the reaction by $^{31}\text{P}$ NMR spectroscopy. And indeed we found evidence for the formation of various phosphorus-containing species depending on the reaction time and the reaction conditions (presence of air and/or water). These experiments allow to propose a potential mechanism for the formation of $\{\text{ReO(LTe)Cl(PPh}_3)\}$, which is given in Scheme 2.

Initially, some phosphate (most probably together with one Cl$^-$ ligand) dissociates from $\{\text{ReOCl}_3\text{PPh}_3\}_2$ under replacement by a diselenide. The phosphate attacks the coordinated diselenide with formation of an intermediate, which may be assigned to $\{\text{Ph}_3\text{PSe(C}_6\text{H}_4\text{-}2\text{-N}=\text{CH(C}_6\text{H}_4\text{-}2\text{-O})\}^{+}\text{Cl}^-$, and the liberation of a (L$^{199}\dagger$) ligand. The recorded chemical shift of 30 ppm of this potential intermediate is in the range where also the $^{31}\text{P}$ resonances of the related organoseleno-phosphonium species $\{\text{Ph}_3\text{PSePh}\}_2\text{Br}$ (37 ppm), $\{\text{Bu}_3\text{PSeMe}\}_2\text{Cl}$ (50 ppm), $\{\text{Ph}_3\text{PSePh}\}_2\text{GaCl}_4$ (38 ppm) and $\{\text{Ph}_3\text{PSeMe}\}_2\text{BF}_4$ (36 ppm) are found. The reduction of disulfides and diselenides with phosphines with formation of phosphonium-chalcogenolate ion pairs or bis(organochalcogen)phosphoranes has been observed before. In the reactions of the present study, the phosphonium species seems to have a remarkably high formation probability and is also found as a fragment of high intensity in the ESI$^+$ mass spectra taken from CH$_2$Cl$_2$ solutions of $\{\text{ReO(LSe)Cl(PPh}_3)\}$. Therefore, we consider the formation of an intermediate phosphonium species as highly probable, although an reaction pathway via a coordinated phosphorane cannot completely be excluded.

The intermediate can either decompose slowly in the anhydrous pathway with formation of triphenylphosphine selenide or it can quickly hydrolyze and give triphenylphosphine oxide and the respective selenol. The highly air-sensitive selenol is quickly re-oxidized to the diselenide in air. Thus, for the formation of the rhenium chalcogenolate complex, the exclusion of air is required and the presence of water supports the formation of OPPh$_3$ instead of SePPh$_3$. Both reactions, which lead to OPPh$_3$ or SePPh$_3$ can be understood as nucleophilic attacks of H$_2$O or RSe$^-$ on the phosphorus atom of the $\{\text{Ph}_3\text{PSe(C}_6\text{H}_4\text{-}2\text{-N}=\text{CH(C}_6\text{H}_4\text{-}2\text{-O})\}^{+}\text{Cl}^-$ ion. In the case of water, the resulting pentacoordinate phosphorus species
Table 1. Selected bond lengths [Å] and angles (°) in [HLSe]₂, [ReO(LSe)Cl(PPh₃)], [Re(NPhF)(LSe)Cl(PPh₃)] and [Re(NPhCF₃)(LSe)Cl(PPh₃)]

<table>
<thead>
<tr>
<th>Bond</th>
<th>[HLSe]₂</th>
<th>[ReO(LSe)Cl(PPh₃)]</th>
<th>[Re(NPhF)(LSe)Cl(PPh₃)]</th>
<th>[Re(NPhCF₃)(LSe)Cl(PPh₃)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se1–C1</td>
<td>1.929(2)/1.933(2)</td>
<td>1.924(8)</td>
<td>1.923(2)</td>
<td>1.936(5)</td>
</tr>
<tr>
<td>O1–C11</td>
<td>1.356(2)/1.349(2)</td>
<td>1.332(9)</td>
<td>1.332(3)</td>
<td>1.345(6)</td>
</tr>
<tr>
<td>N1–C6</td>
<td>1.415(2)/1.415(2)</td>
<td>1.443(3)</td>
<td>1.443(6)</td>
<td>1.445(8)</td>
</tr>
<tr>
<td>N1–C17</td>
<td>1.287(2)/1.283(2)</td>
<td>1.305(5)</td>
<td>1.299(6)</td>
<td>1.306(9)</td>
</tr>
<tr>
<td>Re1–O10/N10</td>
<td>–</td>
<td>1.728(2)</td>
<td>1.723(4)</td>
<td>–</td>
</tr>
<tr>
<td>Re1–O1</td>
<td>–</td>
<td>2.020(2)</td>
<td>2.006(3)</td>
<td>–</td>
</tr>
<tr>
<td>Re1–P1</td>
<td>–</td>
<td>2.447(7)</td>
<td>2.430(1)</td>
<td>–</td>
</tr>
<tr>
<td>Re1–N1</td>
<td>–</td>
<td>2.967(7)</td>
<td>2.483(1)</td>
<td>–</td>
</tr>
<tr>
<td>Re1–Se1</td>
<td>–</td>
<td>2.117(2)</td>
<td>2.11(1)</td>
<td>–</td>
</tr>
<tr>
<td>O1–Re1–O10/N10</td>
<td>–</td>
<td>171.53(7)</td>
<td>172.3(2)</td>
<td>–</td>
</tr>
<tr>
<td>Re1–N10–C51</td>
<td>–</td>
<td>176.8(2)</td>
<td>174.1(4)</td>
<td>–</td>
</tr>
<tr>
<td>C1–Se1–Re1</td>
<td>–</td>
<td>92.9(3)</td>
<td>90.4(1)</td>
<td>–</td>
</tr>
</tbody>
</table>

(a) Values taken from [Re(NPhF)(LSe)Cl(PPh₃)]·CH₃CN.

Table 2. Selected bond lengths [Å] and angles (°) in [HLTe]₂, [ReO(LTe)Cl(PPh₃)], [Re(NPh)(LTe)Cl(PPh₃)] and [Re(NPhF)(LTe)Cl(PPh₃)]

<table>
<thead>
<tr>
<th>Bond lengths/Å</th>
<th>[HLTe]₂</th>
<th>[ReO(LTe)Cl(PPh₃)]</th>
<th>[Re(NPh)(LTe)Cl(PPh₃)]</th>
<th>[Re(NPhF)(LTe)Cl(PPh₃)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te1–C1</td>
<td>2.127(2)</td>
<td>2.119(8)/2.123(8)</td>
<td>2.126(6)</td>
<td>2.128(5)</td>
</tr>
<tr>
<td>O1–C11</td>
<td>1.356(3)</td>
<td>1.33(1)/1.325(9)</td>
<td>1.332(4)</td>
<td>1.328(4)</td>
</tr>
<tr>
<td>N1–C6</td>
<td>1.415(3)</td>
<td>1.45(1)/1.44(1)</td>
<td>1.447(4)</td>
<td>1.449(5)</td>
</tr>
<tr>
<td>N1–C17</td>
<td>1.287(3)</td>
<td>1.30(1)/1.30(1)</td>
<td>1.296(4)</td>
<td>1.299(5)</td>
</tr>
<tr>
<td>Re1–O10/N10</td>
<td>–</td>
<td>1.699(6)/1.695(6)</td>
<td>1.726(3)</td>
<td>1.720(3)</td>
</tr>
<tr>
<td>Re1–O1</td>
<td>–</td>
<td>1.962(6)/1.985(6)</td>
<td>1.994(2)</td>
<td>1.990(2)</td>
</tr>
<tr>
<td>Re1–P1</td>
<td>–</td>
<td>2.458(2)/2.458(2)</td>
<td>2.442(8)</td>
<td>2.443(7)</td>
</tr>
<tr>
<td>Re1–Cl1</td>
<td>–</td>
<td>2.539(2)/2.527(2)</td>
<td>2.504(9)</td>
<td>2.498(1)</td>
</tr>
<tr>
<td>Re1–N1</td>
<td>–</td>
<td>2.120(6)/2.105(7)</td>
<td>2.115(3)</td>
<td>2.107(3)</td>
</tr>
<tr>
<td>Re1–Te1</td>
<td>–</td>
<td>2.6146(6)/2.6469(6)</td>
<td>2.689(3)</td>
<td>2.6869(3)</td>
</tr>
<tr>
<td>O1–Re1–O10/N10</td>
<td>–</td>
<td>166.4(3)/164.1(3)</td>
<td>169.6(1)</td>
<td>172.2(1)</td>
</tr>
<tr>
<td>Re1–N10–C51</td>
<td>–</td>
<td>168.1(3)</td>
<td>172.3(3)</td>
<td>–</td>
</tr>
<tr>
<td>C1–Te1–Re1</td>
<td>–</td>
<td>86.1(2)/85.7(2)</td>
<td>86.2(1)</td>
<td>85.7(1)</td>
</tr>
</tbody>
</table>

(a) Values for two independent species.

Scheme 1. Synthesis of the rhenium(V) selenolato and tellurolato complexes (all reactions were performed under argon).
way with formation of Se{(C₆H₄)-2-N=CH(C₆H₄)-2-OH)}₂ and SePPh₃. The formation of such chalcogenoethers from organo-chalcogeno-phosphonium starting materials with formation of a formal phosphorus-chalcogen double bond is well-established.\[34–37\]

It should be noted that the relative rates of the described reactions are only valid in the presence of the rhenium complex. Reactions of [HLSe]₂ with pure PPh₃ are very slow and form under the same conditions considerable amounts of OPPPh₃ only within days or weeks.

The same general course of the reaction as outlined in Scheme 2 can also be assumed for the phenylimido starting complexes and also for reactions with [HL₉]₂. It should be mentioned that the reaction times may significantly differ and particularly the used solvent plays a crucial role. While [ReOCl₃(PPh₃)₂] and [Re(NPhCl)₃(PPh₃)]₃ are sparingly soluble in most solvents, it proved to be favorable to reduce the solubility of the fluorinated phenylimido complexes for the reactions under study. For example, [Re(NPhF)(L₅Cl)(PPh₃)] is formed only in low yields from reactions in CH₂Cl₂, in which the starting complex [Re(NPhF)Cl₃(PPh₃)]₃ is readily soluble. Higher yields are obtained in a CH₂Cl₂/CH₃CN (1:6) mixture, in which the starting material is less soluble.

The red to brown complexes are stable as solids. In solution, however, they show gradual decomposition, which is normally higher in non-degassed solvents and can be understood by the re-formation of the dichalcogenides on air. The instability of higher in non-degassed solvents and can be understood by the re-formation of the dichalcogenides on air. The instability of these complexes in solution is in situ monitored by NMR spectrometry. The ⁷⁷Se signals of the coordinated selenolato ligands appear between 360 and 395 ppm and the corresponding ¹²⁵Te resonances are found between 378 and 695 ppm. In the spectra of the well-soluble fluorinated complexes [Re(NPhF)(L₅Cl)(PPh₃)] and [Re(NPhCF₃)(L₅Cl)(PPh₃)], the ⁷⁷Se resonances are observed as doublets at 360 ppm (²Jₗₗ₉ = 22 Hz) and 395 ppm (²Jₗₗ₉ = 24 Hz). The coupling constants are within the magnitude of couplings, which have previously been observed for mixed selenolato/phosphine complexes of platinum.\[38,39\] The ¹²⁵Te NMR spectra show signals with a ²Jₗₜₚ coupling of 50–60 Hz, which is also in accord with the situation in similar Pt(II) compounds.\[18\] The ²⁷⁷Se and ¹²⁵Te couplings could not be observed in the respective ³¹P NMR spectra.

A key feature in the proton NMR spectra of Schiff base complexes is the resonance of their unique imine proton. It is well-separated from the remaining aromatic resonances. The imine protons in the selenolato complexes are more deshielded compared to those in the tellurolato complexes, which is similar to the situation in the corresponding dichalcogenides [HL₉]₂ and [HL₉]₂. Additionally, the imine protons are more deshielded in the oxido complexes compared to the phenylimido complexes. These observations can be attributed to the better donor abilities of the phenylimido ligands as compared to oxido ligands. In complexes with imine and phosphine ligands, the imine protons often couple to the ³¹P nuclei. This is also the case in the reported complexes with coupling constants of about 8 Hz and allows an in situ control of the complex formation. The ³¹P chemical shifts observed for the rhenium complexes are correlated to the donor strength of the rhenium multiple bonded cores. It is highest for the oxido complexes and decreases by 5 ppm to the phenylimido complexes. ESI+ mass spectra of the rhenium complexes under study show intense signals of their [M − Cl]⁺ ions. Typically, fragment peaks are observed, which correspond to ions with chalcogeno-phosphorus bonds, such as [Ph₃PSe(C₆H₄)-2-N=CH(C₆H₄)-2-OH]⁺ (m/z = 538.0818) or [Ph₃PSe(C₆H₄)-2-NH₂]⁺ (m/z = 343.0556). The number and the intensities of such fragments depend on the stability of the complexes in solution.

Crystallographic studies on single-crystals of [ReO(L₅Cl)(PPh₃)], [Re(NPhCl)(L₅Cl)(PPh₃)]·CH₂CN, [Re(NPhF)(L₅Cl)(PPh₃)]·0.5CH₂Cl₂, [Re(NPhCF₃)(L₅Cl)(PPh₃)]·CH₂Cl₂, [Re(NPhCl)(L₅Cl)(PPh₃)]·CH₂Cl₂, and [Re(NPhF)(L₅Cl)(PPh₃)]·CH₂Cl₂ and [Re(NPhCl)(L₅Cl)(PPh₃)]·CH₂Cl₂ have been undertaken. All complexes show the same general structure with facially bonded tridentate ligands. The hydroxyl group of the organic tridentate ligand is in trans position to the oxido or
phenylimido ligand in all compounds, PPh$_3$ and Cl$^-$ ligands complete the equatorial coordination spheres of rhenium with the latter ligand being arranged trans to the selenium or tellurium atoms of the Schiff base. The molecular structures of [ReO(L$_{Se}$)Cl(PPh$_3$)] and [Re(NPhCF$_3$)$_3$(L$_{Se}$)Cl(PPh$_3$)] are shown in Figure 2 and Figure 3 as representatives for the complexes with the selenium- and tellurium-containing ligands. Since the general features of the other oxido and phenylimido complexes with the tridentate ligands are similar, their structures are not shown here. They can be found in the Supplementary Information. Selected bond lengths and angles of all complexes and the corresponding dichalcogenides are summarized in Table 1 (selenium compounds) and Table 2 (tellurium compounds).

The rhenium atoms in the complexes have distorted octahedral coordination environments. Main distortions come from the restrictions caused by the facially coordinated tridentate ligands. The donor atoms of the tridentate ligands in the equatorial coordination sphere are all larger the 90°. This is a consequence of the steric demand of the double bonds, which are established between rhenium and the oxido and arylimido ligands.

Similar results have been found in a series of related complexes before.[40–43] The corresponding Re1–O10 (1.688(5)–1.699(5) Å) and Re1–N10 bonds (1.720(3)–1.728(3) Å) are in the usual ranges and the imido ligands are linear.[40] It is interesting to note that all Re1–O1 bonds are in the range or smaller than 2 Å. Such values are somewhat smaller than expected for Re–O single bonds, but not unusual for oxido or arylimido complexes of rhenium(V), since similar features are found with about 50 per cent of the crystallographically studied compounds of these types.[1] The effect is commonly explained by a partial transfer of electron density from the Re–O/N double bond to the trans Re–O bond.[40,44–46]

The Re–Se bonds between 2.439(1) and 2.5003(6) Å are relatively short and similar bond lengths have hitherto only been found in some rare examples of Re(V) complexes with terminal phenylselenolato complexes,[19,21,28] while in the majority of their rhenium complexes such ligands bridge two low-valent rhenium atoms and the related Re–Se bond are in the range of 2.6 Å or longer.[1] Short Re–Se bonds are also established in binuclear rhenium complexes with Re–Re bonds or diselenolene complexes.[18,23] Most of the few rhenium complexes with tellurolato ligands are carbonyl compounds of Re(I) and they have Re–Te bond lengths between 2.760 and 2.811 Å.[3,6,8,11–14]

Very recently, a series of [Re$^{IV}$O(aryltellurolate)$_4$$^-$ and [Re$^{II}$O(aryltellurolate)$_3$(PPh$_3$)(CH$_3$CN)] complexes was prepared and structurally characterized.[28] The Re–Te bond lengths in the Re(V) complexes are very similar to the values for the compounds of the present study.

An interesting feature is the bond length distribution in the six-membered chelate rings of the [ReO(L$_{Se}$)Cl(PPh$_3$)] and [Re(NPhR)(L$_{Se}$)Cl(PPh$_3$)] complexes (Y = Se, Te; R = H, F, CF$_3$). The N1–C17 bonds are only slightly lengthened compared to the related bonds in (HL$_{Se}$)$_2$ and (HL$_{Te}$)$_2$. This means that the imine double bonds remain mainly localized and no significant delocalization of π-electron density is observed in this chelate ring. A similar bonding situation is observed in analogous oxidorhenium(V) complexes with the salicylidene Schiff bases derived from 2-aminophenol ([L$_{Se}$]$^2$-) or 2-aminothiophenol ([L$_{Se}$]$^2$-).[47,48] Despite the fact that the tridentate O$_2$N$_2$O and O$_2$N$_2$S ligands are both coordinated in a meridional arrangement.

Since all hitherto structurally studied Re(V) complexes with the [L$_2$]$^2$- and [L$_2$]$^2$- show a mer-arrangement of these ligands,[47–55] and the complexes with their selenium and tellurium analogues of the present study contain the tridentate ligand exclusively in a facial coordination mode, we undertook a series of DFT calculations on the B3LYP level for both isomers of the [ReO(L$_2$)Cl(PPh$_3$)] (Y = O, Se, Te) complexes. Frequency calculations after the optimizations showed convergence of at least two out of four criteria in all cases and full convergence on the experimentally expected isomers. No negative frequencies were obtained. The calculated bonding parameters for the facial isomers with ([L$_{Se}$]$^2$-) and ([L$_{Te}$]$^2$-) match the determined crystal structures of fac-[ReO(L$_{Se}$)Cl(PPh$_3$)] and fac-[ReO(L$_{Te}$)-

Figure 2. Molecular structure of [ReO(L$_{Se}$)Cl(PPh$_3$)]. Ellipsoids are depicted at 50 % probability. Hydrogen atoms are omitted for clarity.

Figure 3. Molecular structure of [Re(NPhCF$_3$)$_3$(L$_{Se}$)Cl(PPh$_3$)]. Ellipsoids are depicted at 50 % probability. Hydrogen atoms are omitted for clarity.
Energetically favoured:

![Diagram of energetically favoured complexes](image)

Experimental:

![Diagram of experimental complexes](image)

Scheme 3. Calculated and experimentally isolated isomers for [ReO(L)X(PR3)] complexes (Y = O, S, Se, Te; X = Cl or OMe).

Table 3. Energies for the mer and fac isomers the [ReO(L)Cl(PPh3)] complexes (Y = O, S, Se, Te). The energies of the most stable geometries are in bold.

<table>
<thead>
<tr>
<th>Y</th>
<th>E_{mer}/Hartree</th>
<th>E_{fac}/Hartree</th>
<th>ΔE/kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>-1577.20576</td>
<td>-1577.19178</td>
<td>36.8</td>
</tr>
<tr>
<td>S</td>
<td>-1512.08892</td>
<td>-1512.08631</td>
<td>6.7</td>
</tr>
<tr>
<td>Se</td>
<td>-1511.20096</td>
<td>-1511.19872</td>
<td>5.9</td>
</tr>
<tr>
<td>Te</td>
<td>-1510.00999</td>
<td>-1510.01209</td>
<td>-5.4</td>
</tr>
</tbody>
</table>

A possible reason for this result might be given by the well-known labilization of the coordination sphere positions trans to the multiple-bonded oxido or arylimido ligands. It is generally accepted, that ligand exchange reactions at complexes with the (ReO/Na)³⁺ cores start with the substitution of the trans-ligand. Therefore, complexes with the fac-coordinated ligands should be the initial products in such reactions. As the reactions with the oxido complexes were performed under mild conditions, which means under kinetic control, a rationale for the observation of the fac complexes is given. Obviously, the formation of such intermediates at room temperature is faster than their subsequent isomerization. As the complexes tend to decompose at prolonged times of higher temperatures an isomerization to the mer-isomers could not be observed.

It would be interesting to study similar reactions with corresponding technetium compounds, where the kinetics of ligand exchange reactions is commonly faster. Unfortunately, there exists no oxidotechnetium(V) analogue to [ReOCl₂(PPh₃)₂] and the phenylimido complex [Tc(NPh)Cl₃(PPh₃)₂] is almost insoluble. But recently the synthesis of two fluorinated arylimidotechnetium(V) complexes, [Tc(NPh-4-F)Cl₃(PPh₃)₂] and [Tc(NPh-4-CF₃)Cl₃(PPh₃)₂], has been reported. Reactions between these novel precursors and dichalcogenides are planned for the future and their results may give a deeper insight into the mechanism of such reactions.

Conclusions

Rhenium(V) complexes with tridentate selenolato- and tellurolato-substituted Schiff base ligands are formed during reactions of the corresponding dichalcogenides {HLSe}²⁻ or {HLTe}²⁻ with phosphine-containing rhenium(V) complexes such as [ReOCl₃-PPh₃)] or [Re(NAr)Cl₃(PPh₃)] (Ar = Ph, PhF, PhCF₃). The resulting [ReO(L)Cl(PPh₃)] or [Re(NAr)LCl(PPh₃)] complexes (Y = Se, Te) contain the tridentate ligands in a facial arrangement.

A mechanism for such reactions has been deduced, in which released PPh₃ acts as reducing agent for the dichalcogenides. Optimal yields are obtained in the presence of water and under strict exclusion of dioxygen. The method is well-suited for the synthesis of high-valent rhenium complexes.
Single crystal X-ray diffraction data were collected on a Bruker D8 Venture or a STOE IPDS II T. Absorption corrections were carried out by the multiscan (Bruker D8 Venture) or integration methods (STOE IPDS II T).[62,63] Structure solutions and refinements were done with the SHELX-2008 program packages.[64,65] Hydrogen atom positions at heteroatoms or the imino carbon atoms were taken from the Fourier maps when possible or placed at calculated positions and refined by a riding model. All other hydrogen atoms were placed at calculated positions and refined by a riding model. The visualization of the molecular structures was done using the program DIAMOND 4.2.[66]

CCDC 1956176–1956184 (see Supporting Information for the reference number of each compound) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

DFT calculations were performed on the high-performance computing systems of the Freie Universität Berlin ZEDAT (Soroban, Curta) using the program packages GAUSSIAN 09 and GAUSSIAN 16.[67,68] The gas phase geometry optimizations were performed using coordinates derived from the X-ray crystal structures or have been modelled with the use of crystal structure fragments using GAUSSVIEW.[69] The calculations were performed with the hybrid density functional B3LYP.[70–72] The double-\(\zeta\) pseudopotential LANL2DZ basis set with the respective effective core potential (ECP) was applied to Re as well as to S, Se and Te.[73] The 6-311G**(basis set was applied for all other atoms.[74–76] The LANL2DZ and 6-311G** basis sets as well as the ECPs were obtained from the EMSL database.[77]

\((\text{HLTe})_2\), Salicylaldehyde (0.12 mL, 1.16 mmol) was added to a stirred suspension of bis(2-aminophenyl)dithiolenide (200 mg, 0.58 mmol) in 18 mL of EtOH. The mixture was heated under reflux for 4 h. A yellow solid precipitated over this period. After cooling to room temperature, the solid was filtered off and dried in vacuo. The product can be recrystallized from hot EtOH/CHCl₃, Orange-red crystals. Yield: 212 mg (0.44 mmol, 96 %).

Alternatively, if no precipitate is observed after one hour, the addition of dry MgSO₄ starts the reaction. The procedure is followed as described above. The precipitate is extracted with CH₂Cl₂ until the extract is colorless, the solvent is removed in vacuo and the residue recrystallized from EtOH/CHCl₃.

Elemental analysis: Calculated for C₄₈H₄₂N₂O₂Te₂: C 48.2, H 3.1, N 3.4 %; Found C 48.1, H 3.2, N 4.3 %. IR (cm⁻¹): ν = 1605 (s) C=N, 1578 (m), 1578 (m), 1492 (m), 1457 (m), 1345 (m), 1384 (m), 1283 (m), 1226 (m), 1183 (s), 1147 (s), 1110 (w), 1044 (w), 1029 (m), 970 (m), 936 (w), 907 (s), 862 (w), 843 (m), 781 (m), 746 (vs), 706 (s), 672 (s), 641 (m), 601 (w), 576 (w), 569 (w), 553 cm⁻¹ (s). 1H NMR (CDCl₃, ppm): 12.53 (2H, s, OH), 8.55 (2H, s, H-CRN=Te), 7.94–7.85 (2H, m, o-Te-m-NR=ArH), 7.47–7.38 (4H, m, o-CN=m-OH=ArH; p-CN=m-OH=ArH), 7.34–7.27 (2H, m, p-Te=m-NR=ArH). 13C NMR (CDCl₃, ppm): 126.7 (s, H-CRN=Te), 121.6 (s, p-Te=m-CRN=Te), 117.9 (s, o-CN=m-CRN=Te), 117.1 (s, o-Te=m-CRN=Te), 107.5 (s, R₂Te=Te). 125Te NMR (CDCl₃, ppm): 228 (s). [ReO(LTe)₂Cl(PPh₃)] (44 mg, 0.08 mmol) was dissolved in a degassed mixture of CH₂Cl₂ (6 mL) and water (1 drop). [ReOCl₃(PPh₃)]₂ (88 mg, 0.1 mmol) was added whilst stirring. The color changed from light yellow to dark brown and after 20 min of stirring at room temperature, the suspension became a clear brown solution. The mixture was overlayed with degassed diethyl ether (12 mL) and left in the freezer for slow diffusion. The formed crystals of [ReO(LTe)₂Cl(PPh₃)] were filtered off and washed with diethyl ether. Red-brown plates. Yield: 50 mg (68 %).

Elemental analysis: Calculated for C₄₈H₄₂Te₅O₂P₅Se₄: C 38.4, H 3.1, N 1.8 %; Found C 48.0, H 3.2, N 1.5 %. IR (cm⁻¹): ν = 3046 (w), 1601 (s) C=N, 1578 (vs), 1558 (w), 1492 (m), 1457 (m), 1345 (m), 1384 (m), 1274 (s), 1229 (w), 1225 (m), 1179 (m), 1154 (m), 1146 (m), 1108 (m), 1034 (m), 1018 (m), 975 (w), 937 (w), 905 (m), 853 (m), 841 (s), 779 (m), 747 (vs), 732 (sh), 708 (s), 666 (m), 638 (m), 575 (m), 551 (s) (ESI- MS (m/z): 648.9699 (calc. 648.9701) [M + H⁺], 670.9532 (calc. 670.9521) [M + Na⁺], 686.9269 (calc. 686.9259) [M + K⁺], 1318.9152 (calc. 1318.9147) [2M + Na⁺], 1334.8862 (calc. 1334.8885) [2M + K⁺].

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Elemental analysis: Calculated for C_{32}H_{26}Cl_{3}NO_{2}PReTe: C 44.7, H 3.1, N 1.6 %; Found C 45.1, H 3.1, N 1.6 %. IR (cm⁻¹): ð = 3054 (w), 1602 (s) C≡N, 1583 (s), 1566 (m), 1537 (s), 1481 (m), 1452 (m), 1432 (s), 1373 (m), 1341 (w), 1289 (s), 1263 (m), 1231 (w), 1189 (w), 1177 (w), 1160 (w), 1148 (m), 1121 (w), 1094 (s), 1072 (sh), 1028 (s), 988 (m), 961 (s) = O–O, 944 (s), 927 (m), 892 (w), 862 (m), 806 (m), 749 (vs), 732 (vs), 704 (sh), 690 (vs), 641 (w), 617 (s), 598 (m), 574 (sr), 559 (m), 544 (vs). ESI+ MS (m/z): 788.0143 (calc. 788.0147) [M – Cl]+. 1H NMR (CDCl₃, ppm): 8.00 (1H, d, ð = 7.1 Hz, CH≡N), 7.70–7.09 (1H, m, ArH), 7.05–7.03 (1H, m, ArH), 6.86–6.00 (1H, m, ArH). ¹³C NMR: CDCl₃ ppm: 169.8 (s, R₂P=C, ArH), 162.2 (s, RC=N-C, ArH), 137.7 (s, P-CN=m-O-C, ArH), 135.6 (R⁵C=C, ArH), 135.7 (s, C, ArH), 131.3 (d, ð = 7.0 Hz, C-Te, ArH), 127.8 (d, ð = 7.0 Hz, C-P, ArH), 120.3 (s, C, ArH), 119.5 (s, C, ArH), 119.3 (s, C, ArH). ¹³P NMR (CDCl₃ ppm): 63.9 (s). ¹²⁵Te NMR (CDCl₃ ppm): 695 (d, ð = 59 Hz).

[Re(NPPh)₃][Cl₂(PPh₃)₃]. A mixture of [Re(NPPh)Cl₃(PPh₃)₂] (88 mg, 0.1 mmol) was suspended in a degassed mixture of CH₂CN (6 mL) and water (1 drop). (HL⁵Cl)₂ (44 mg, 0.08 mmol) was added as a solid after heating this mixture to reflux. The color changed from dark green to red-violet immediately and a red solid precipitated together with unreacted (HL⁵Cl)₂. After 3 min, CH₂CN (1 mL) was added, which dissolved the remaining diselenide. The CH₂CN was removed in a stream of argon. The mixture was cooled to room temperature and the product was filtered off as a brown powder. After washing with diethyl ether (10 mL) to remove potentially remaining (HL⁵Cl)₂, a brown-violet powder was obtained. Yield: 44 mg (54 %).

Elemental analysis: Calculated for C₃₇H₃₉ClN₂OPReTe: C 50.7, H 3.4, N 3.2 %. IR (cm⁻¹): ð = 3051 (w), 1600 (m), C≡N, 1584 (m), 1567 (m), 1538 (m), 1483 (m), 1474 (m), 1451 (m), 1344 (s), 1372 (m), 1335 (m), 1312 (w), 1293 (s), 1262 (w), 1188 (m), 1177 (m), 1161 (m), 1148 (m), 1122 (m), 1095 (s), 1066 (m), 1024 (m), 990 (w), 968 (w), 936 (sh), 926 (s), 859 (m), 804 (s), 768 (s), 758 (s), 743 (s), 718 (w), 706 (m), 689 (vs), 625 (w), 615 (s), 603 (s), 572 (w), 560 (s), 545 (s). ESI+ MS (m/z): 863.0679 (calc. 863.0621) [M – Cl]+. ¹H NMR (CDCl₃ ppm): 8.28 (1H, d, ð = 59 Hz, HCR=πN), 7.91–7.83 (6H, m, m-P=Te), 7.72–7.64 (1H, m, m-P=Te), 7.52–7.45 (2H, m, 2 ¹H=Te, 7.4–5.71 (11H, m, integral corrected for CH₃CO, o-p-AH=πN=πTe, = 1H, 7.02–6.95 (1H, m, ¹H=Te), 6.79–6.70 (2H, m, νP=πTe), 6.51–6.44 (1H, m, H=Te), 6.44–6.33 (2H, m, νP=πTe). ¹¹C NMR (CDCl₃ ppm): 171.1 (s, νP=πTe), 166.8 (s, R₂C=O), 163.2 (s, =πTe), 162.2 (s, =πTe), 156.0 (s, R₂C=N=πTe), 136.4 (s, R₂C=Te), 136.2 (s, C, πTe), 135.3 (s, νP=πTe), 134.8 (s, νP=πTe), 134.4 (d, ð = 7.0 Hz, m-P=πTe), 134.6 (s, πTe), 130.6 (d, ð = 7.0 Hz, m-P=πTe), 128.2 (d, ð = 7.0 Hz, o-P=πTe), 127.7 (d, ð = 7.0 Hz, o-P=πTe), 126.5 (s, o-P=πTe), 124.8 (s, o-P=πTe), 124.0 (d, ð = 7.0 Hz, C=πTe), 122.0 (s, C=πTe), 119.9 (s, C=πTe), 118.6 (s, C=πTe). ¹³P NMR (CDCl₃ ppm): 1.5 (s). ¹²⁵Te NMR (CDCl₃ ppm): 378 (d, ð = 59 Hz).
off, washed with EtOH, diethyl ether and hexane and charged on a column of neutral alumina (d = 1 cm, h = 9.5 cm). Elution with CH₂Cl₂ containing 2.5 % MeOH gave a brown band of [Re(N(PF₆)₅Cl)(PPh₃)]. The solvent was evaporated in vacuo, the residue was re-dissolved in a minimum amount of CH₂Cl₂ and a large excess of diethyl ether was added. The precipitated [Re(N(PF₆)₅Cl)(PPh₃)] was filtered off, washed with diethyl ether and hexane and dried on air. Red-brown powder. Yield: 18.6 mg (20 %). Recrystallization can be done from CH₂Cl₂/hexane or CH₂Cl₂/diethyl ether mixtures.

Elemental analysis: Calculated for C₃₃H₃₃Cl₃F₃P₂Re: C 52.9, H 3.5, N 1.4 %. Found C 53.1, H 3.4, N 1.4 %. IR (cm⁻¹): ν = 3059 (w), 3025 (v), 2964 (m), 2920 (m), 2854 (s), 2820 (s), 2614 (w), 2569 (w), 1607 (s), 1583 (m), 1453 (m), 1434 (m), 1426 (w), 1382 (s), 1372 (s), 1315 (m), 1288 (s), 1170 (s), 1144 (s), 1123 (s), 1100 (s), 1090 (s), 1080 (s), 1008 (s), 998 (s), 988 (s), 945 (w), 937 (w), 895 (m), 860 (m), 839 (s), 803 (s), 761 (s), 742 (s), 718 (m), 706 (m), 690 (vs), 648 (m), 616 (s), 603 (s), 558 (s), 546 (s). ESI+ MS (m/z): 883.0565 (calc. 883.0572) [M – Cl]⁺.

H NMR (CDCl₃, ppm): 8.29 (1H, d, J₁P₂ = 8.84 Hz), 7.58–7.50 (2H, m, Ar-C₃), 7.45–7.34 (9H, m, o-P-Ar), 7.30–7.20 (2H, m, integral corrected for CHCl₃), 3.2H (2H, m, N-P-Ar), 2.5H (2H, m, N-P-Ar), 2.4H (2H, m, N-P-Ar), 2.0H (2H, m, N-P-Ar). ¹³C NMR (CDCl₃, ppm): 166.6 (s, R₂Car-C₂), 163.2 (s, Ar-CN), 162.2 (d, J₁C₃ = 156 Hz, H-P₃), 158.0 (m, R₂Car-C₃), 151.9 (d, J₁C₃ = 146 Hz, H-P₃), 147.5 (d, J₁C₃ = 140 Hz, H-P₃), 144.8 (d, J₁C₃ = 135 Hz, H-P₃), 142.0 (s, H-P₃), 134.9 (d, J₁C₃ = 102 Hz, H-P₃), 132.9 (d, J₁C₃ = 97 Hz, H-P₃), 131.0 (d, J₁C₃ = 106 Hz, H-P₃), 130.7 (s, H-P₃), 129.8 (s, H-P₃), 128.4 (d, J₁C₃ = 10 Hz, H-P₃), 128.2 (s, H-P₃), 127.8 (s, H-P₃), 125.7 (m, P-C₃), 124.9 (s, H-P₃), 124.5 (s, H-P₃), 120.4 (s, H-P₃), 118.6 (s, H-P₃), 118.4 (s, H-P₃), 116.0 (s, H-P₃), 115.8 (s, H-P₃). ¹⁹F NMR (CDCl₃ ppm): –60.8 ppm (pseudo-ddd). ¹⁹F NMR (CDCl₃, ppm): –60.8 ppm (pseudo-p, J₁F₂ = J₁F₁ = 37.1 Hz, 3F). ¹³C NMR (CDCl₃ ppm): 59 Hz.

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4982
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