

Group 7 Elements

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A Complete Triad of Zero-Valent 17-Electron Monoradicals of Group 7 Elements Stabilized by *m*-Terphenyl Isocyanides

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Abstract: The first consistent series of mononuclear 17-electron complexes of three Group 7 elements has been isolated in crystalline form and studied by X-ray diffraction and spectroscopic methods. The paramagnetic compounds have a composition of $[M^0(CO)(CNp-F-Ar^{D_{ArF2}})_4]$ ($M = Mn, Tc, Re$; $Ar^{D_{ArF2}} = 2,6-(3,5-(CF_3)_2C_6H_3)_2C_6H_2F$) and are stabilized by four sterically encumbering isocyanides, which prevent the metalloradicals from dimerization. They have a square pyramidal structure with the carbonyl ligands as apexes. The frozen-solution EPR spectra of the rhenium and technetium compounds are clearly anisotropic with large ^{99}Tc and $^{185,187}Re$ hyperfine interactions for one component. High-field EPR (Q band and W band) has been applied for the elucidation of the EPR parameters of the manganese(0) complex.

chemistry.^[9] Moreover, photolytic generation of $[Mn(CO)_5]$ and $[Re(CO)_5]$ in the presence of a co-initiator leads to efficient free-radical polymerization^[10] and $[Mn(CO)_5]$ has been extensively studied for its role in radical-mediated olefin hydrogenation and in electrocatalytic CO_2 reduction.^[11–14] These examples show that a further characterization of Group 7 metalloradicals is of great interest also for technological purposes.

Monomeric zero-valent ML_5 complexes of the Group 7 metals have 17 valence electrons and are, hence, paramagnetic. The most known and fairly accessible examples of this class of compounds are the pentacarbonyl complexes $[M(CO)_5]$ ($M = Mn, Re$) or derivatives thereof. Such molecules can be generated by photolysis of the corresponding dimers $[M_2(CO)_{10}]$, but only in very low concentrations, due to the rapid dimerization process.^[15–17] The transient species $[Mn(CO)_5]$ and $[Re(CO)_5]$ could, therefore, be characterized exclusively by IR, EPR and electronic spectroscopy. They appear to adopt a square pyramidal geometry with C_{4v} symmetry.^[18–21] In contrast to the relatively inert six-coordinate complex, $[V(CO)_6]$, these five-coordinate, 17-electron species exhibit behavior that closely resembles simple organic radicals; which justifies their definition as metal-centered radicals.^[22] While transient, $[Mn(CO)_5]$ and $[Re(CO)_5]$ have been studied under conditions where their behavior can be evaluated, the chemistry of corresponding technetium compound, $[Tc(CO)_5]$, is practically unknown. Some tracer studies with the short-lived nuclear isomer ^{99m}Tc (pure γ emitter, half-life 6 hours), which was produced by neutron bombardment of $[^{99}Mo(CO)_6]$, have suggested that the metalloradical species, $[^{99m}Tc(CO)_5]$, can be generated transiently and reacts with photochemically-produced $[Mn^0(CO)_5]$ radicals to form $[TcMn(CO)_{10}]$.^[23] Corresponding studies with the long-lived isotope ^{99}Tc (weak beta emitter, half-life: 2.1×10^5 years) are to the best of our knowledge not known, but should be of great interest with regard to the central position of technetium in the d-block of the periodic table.^[11,24] More generally, reports describing the chemistry of technetium in its lowest oxidation states (i.e. 0, –1) are almost completely absent from the literature.

The generation of metalloradicals that are more persistent in solution can be achieved by the use of sterically encumbering ligands such as large tertiary phosphines.^[25–27] In rare cases, such complexes could even be isolated as crystalline solids. This has been shown in 1989 by Crocker et al. in an early example describing the isolation of $[Re(CO)_5(PCy_3)_2]$.^[28] More recently, the isolation, structure, and spectroscopic features of the stable five-coordinate MnL_5

Introduction

Only a few compounds of Group 7 metals in their lowest oxidation states (0 and –I) are known. The stabilization of such highly reduced metal centers essentially requires strong π -acceptor ligands, such as CO, isocyanides or phosphines.^[1–8] This limitation and their intrinsic lability and air-sensitivity have hindered the development of their chemistry. This is regrettable since transient radicaloid metal centers play an important role, for instance, in atom-transfer and radical processes in organic and organometallic

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metalloradical, $[\text{Mn}(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2]$ ($\text{Ar}^{\text{Dipp}2} = 2,6\text{-}(\text{iPr})_2\text{C}_6\text{H}_3)_2\text{C}_6\text{H}_3$), Figure 1), featuring two *meta*-terphenyl isocyanide ligands has been reported. Also here, the reactivity of $[\text{Mn}(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2]$ exactly reflects its formulation as a manganese-centered monoradical. For example, $[\text{Mn}(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2]$ can be formed by homolytic bond cleavage and undergoes atom transfer reactions with various reagents.^[29]

During our continuous studies on sterically encumbering isocyanides we found that the fluorine-substituted ligand $\text{CN}p\text{-F-Ar}^{\text{DArF}2}$ (Figure 1) is particularly suitable for the stabilization of rhenium(I) and technetium(I) compounds.^[30–32] It is able to selectively replace carbonyl ligands, and the coordination of up to four of such bulky ligands encloses the metal centers in organic shells, protecting them from further reactions—for instance from dimerization processes. It was shown that prolonged treatment of the rhenium(I) compound, $[\text{ReBr}(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF}2})_4]$ (**4**), with Na/Hg gives a mixture of the diamagnetic salt $\text{Na}[\text{Re}(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF}2})_4]$ (**5**) and variable amounts of the paramagnetic, zero-valent complex, $[\text{Re}(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF}2})_4]$ (**6**). From such mixtures, however, the individual compounds could not be isolated in pure crystalline form.^[30]

Herein we describe for the first time the syntheses, isolation, structural and spectroscopic features of a trio of isostructural, zero-valent complexes of Group 7 metals—

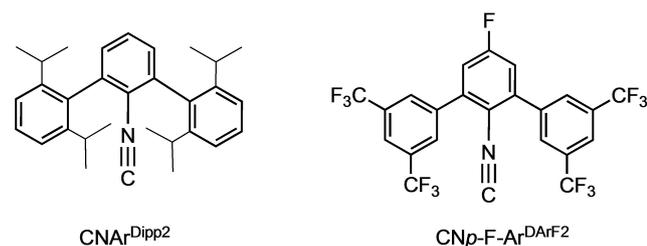
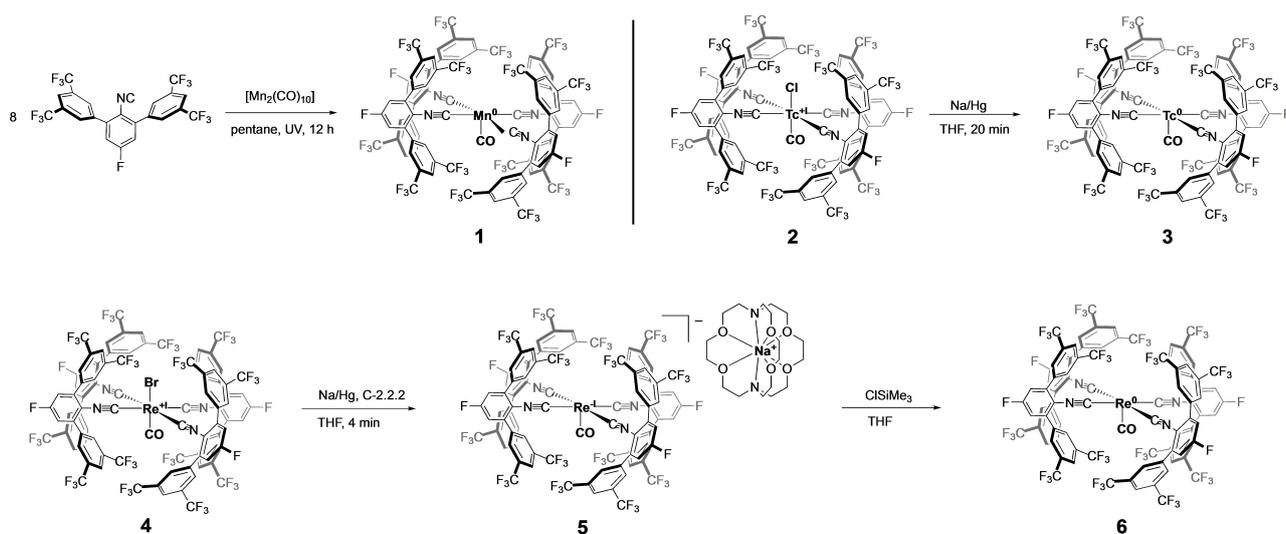


Figure 1. Sterically encumbering isocyanides.

manganese, technetium and rhenium—supported by *meta*-terphenyl isocyanide ligation (Scheme 1). The sterically encumbering and π -acidic nature of these ligands hinders dimerization processes and allows the stabilization and isolation of the three $[\text{M}(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF}2})_4]$ complexes ($\text{M} = \text{Mn, Tc, Re}$) in crystalline form.

Results and Discussion

There is no general route for the synthesis of these isostructural compounds, which is not completely surprising having in mind the differences in the redox potentials and reaction kinetics when crossing three transition metal rows. The synthesis of $[\text{Mn}(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF}2})_4]$ succeeds via a photolytic approach starting from $[\text{Mn}_2(\text{CO})_{10}]$ in THF solution as has previously been applied for the synthesis of $[\text{Mn}(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2]$.^[29] The product, $[\text{Mn}(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF}2})_4]$ (**1**), is a dark green solid, which is readily soluble in nonpolar solvents. Single crystals of the product for X-ray diffraction were grown from diethyl ether. The photolytic decomposition of $[\text{Tc}_2(\text{CO})_{10}]$ is not a suitable approach to $[\text{Tc}(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF}2})_4]$ (**3**), since the synthesis of deacarbonyltechnetium(0) is problematic and the work with the volatile compound causes a number of radiation protection problems. But instead, the reduction of the technetium(I) complex $[\text{TcCl}(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF}2})_4]$ (**2**) with an excess of Na/Hg gives a black-green solution which contains a mixture of $[\text{Tc}^0(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF}2})_4]$ (**3**) and $\text{Na}[\text{Tc}^{-1}(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF}2})_4]$ as a minor component. The formation of the technetium(−1) complex was already reported in our previous work and can be easily detected by its ⁹⁹Tc NMR spectrum and a high-field shift of the *para*-fluorine atom of the ligand to approximately −125 ppm in the ¹⁹F NMR spectrum.^[30] Such a shift is characteristic for the formation of highly reduced species and has already been observed for the rhenium analogue. The solution containing **3** turns deep blue, when THF is evaporated and



Scheme 1. Synthesis of the zerovalent mixed carbonyl/isocyanide complexes of the three Group 7 metals.

the oily residue is re-dissolved in toluene. Crystallization by layering of the toluene solution with pentane at -40°C led to black single crystals of $[\text{Tc}^0(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF2}})]$ in good yield.

Of the preparative chemistry leading to a homologous series of Group 7 metal ML_5 radicals, the search for a satisfactory synthesis of $[\text{Re}^0(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF2}})_4]$ (**6**) presented the greatest challenge. The photolytic cleavage of the decacarbonyl, which was successful for manganese, did not work for $[\text{Re}_2(\text{CO})_{10}]$. Thus, a reductive method was investigated. The treatment of $[\text{Re}^{\text{I}}\text{Br}(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF2}})_4]$ (**4**) with KC_8 or $\text{Na}(\text{naphthalene})$ in THF surprisingly lead only to the recovery of the starting material. Finally, the treatment of **4** with finely divided potassium, lead to the complete consumption of the starting material and the production of the desired reduced species. But even after 12 hours, this procedure generated the $\text{Re}(-1)$ salt $\text{K}[\text{Re}(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF2}})_4]$, along with a considerable amount of the paramagnetic complex $[\text{Re}(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF2}})_4]$, as concluded from the appearance of an intense EPR signal from the reaction mixture. Finally we found that the use of a large excess of Na/Hg and vigorous stirring for only four minutes gave the best yield of the $\text{Re}(-1)$ compound. Longer stirring over sodium amalgam leads to the formation of a dark insoluble material and lowers the yield without increasing the purity. Addition of Cryptand-2.2.2 affords the isolation of analytically pure $[\text{Na}(\text{Cryp-2.2.2})][\text{Re}(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF2}})_4]$ (**5**) as black crystals in good yield. The diamagnetic rhenium(-1) compound was characterized by elemental analysis, ^1H , ^{13}C and ^{19}F NMR spectroscopy. Particularly indicative is the ^{19}F NMR spectrum, which shows a marked change of the chemical shift of the fluorine atom of the central phenyl ring depending on the oxidation state of rhenium (**4**: -108.8 ppm, **5**: -121.1 ppm). An X-ray diffraction study on the black single crystals of **5** confirms the square pyramidal arrangement of the ligands with the CO in apical position. An ellipsoid representation of the structure and selected bond lengths and angles are shown in the Supporting Information.^[33]

For the preparation of the zero-valent manganese complex, $[\text{Mn}(\text{CO})_3(\text{CNAr}^{\text{Dipp2}})_2]$, comproportionation between the Mn^{I} triflate complex, $[\text{Mn}(\text{OTf})(\text{CO})_3(\text{CNAr}^{\text{Dipp2}})_2]$ and the $\text{Mn}(-1)$ salt, $\text{K}[\text{Mn}(\text{CO})_3(\text{CNAr}^{\text{Dipp2}})_2]$, had resulted in the best yield of the monoradical.^[29] Contrastingly, this approach was not successful for the rhenium analogue. Treatment of **5** with **4**, or with the corresponding triflate complex, $[\text{Re}(\text{CO})(\text{OTf})(\text{CN}p\text{-F-Ar}^{\text{DArF2}})]$, resulted in no observed reaction. Furthermore, attempts to oxidize **5** with $\text{Tl}(\text{OTf})$ led to intractable mixtures. However, pure samples of the neutral rhenium(0) complex $[\text{Re}(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF2}})_4]$ (**6**) could be prepared from **5** by a one-electron oxidation with $[\text{CoCp}_2]^+$ or by an unusual reaction with ClSiMe_3 . In the course of the latter reaction the product is formed in moderate yields, but with a high purity. The ^1H NMR spectrum of the reaction mixture shows a very broad signal around 1 ppm, which can be assigned to a polymerization product of ClSiMe_3 and provides an explanation for the oxidation of the $\text{Re}(-1)$ compound.

The ν_{CN} stretches in the Mn^0 and Re^0 complexes are found between the values found for the corresponding metal(-1) and metal(+1) complexes (e.g. $[\text{Re}^{-1}(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF2}})_4]^-$ (**5**): 1886 cm^{-1} , $[\text{Re}^0(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF2}})_4]$ (**6**): 1975 cm^{-1} , $[\text{Re}^{\text{I}}\text{Br}(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF2}})_4]$ (**4**): 2051 cm^{-1}). The observed values reflect the different degrees of π -backdonation into the isocyanide π^* orbitals. IR spectra of the highly sensitive, low-valent technetium compounds could not be measured for radiation protection reasons. However, we assume a similar trend will be observed.

Single crystals of the three zerovalent metal complexes could be measured by X-ray diffraction. The three structures are essentially identical. That of the technetium complex is shown in Figure 2, while the structures of compounds **1** and **6** are contained in the Supporting Information.^[33] Table 1 contains selected bond lengths and angles of all three complexes. They possess a square-pyramidal geometry (Addison-Reedijk $\tau_5 = 0.09$ for **1**, 0.15 for **3** and 0.23 for **6**),^[34] where the carbonyl ligands occupy the apical positions. Importantly, this geometry is consistent with that proposed for the ground-state geometry of d^7 $[\text{M}(\text{CO})_5]$ monoradicals

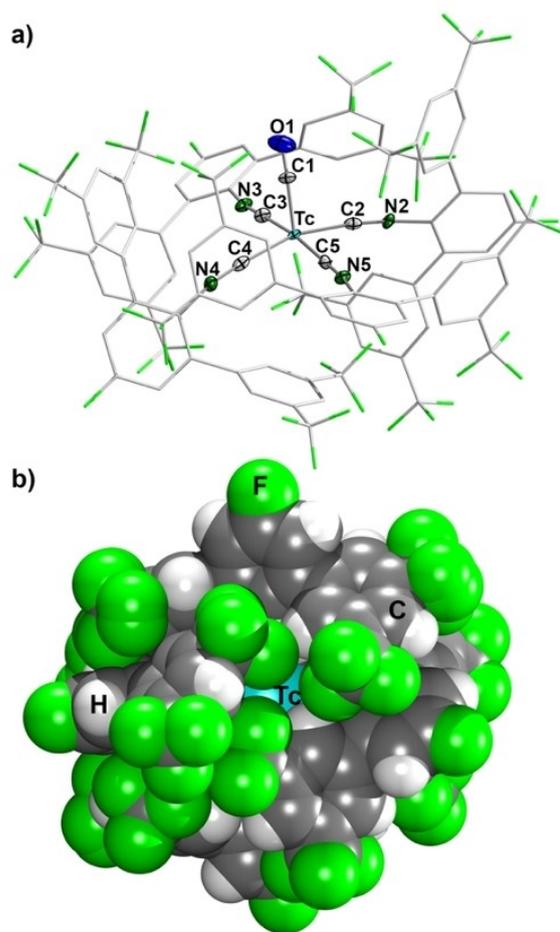


Figure 2. a) Ellipsoid representation and b) space-filling model of $[\text{Tc}^0(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF2}})_4]$ (**3**) illustrating the protective role of the bulky isocyanide ligands.^[33]

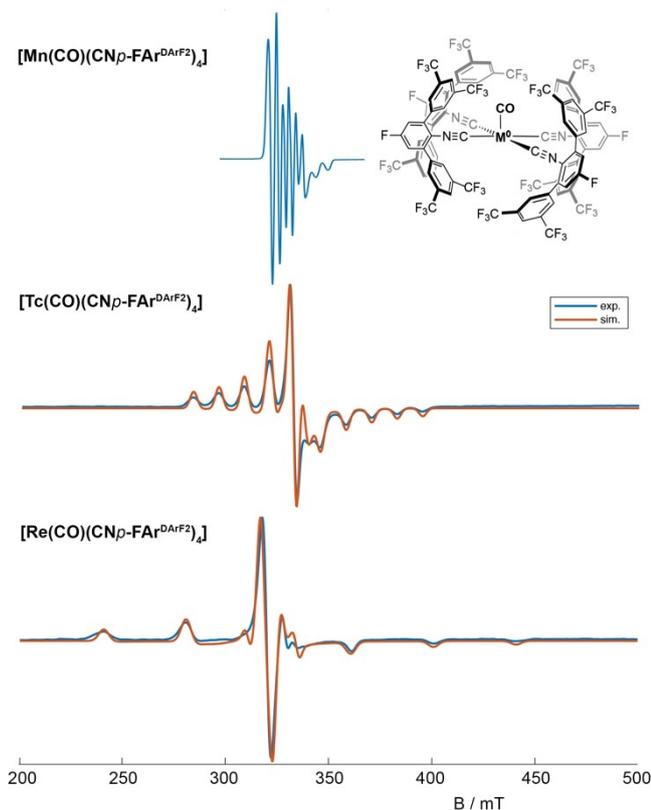
Table 1: Selected bond lengths [Å] and angles [°] in the $[M^0(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF2}})_4]$ complexes (1: M = Mn, 3: M = Tc, 6: M = Re).

	1	3	6
M–C1/C1–O1	1.807(2)/1.152(3)	1.945(7)/1.138(9)	1.970(4)/1.102(6)
M–C2/C2–N2	1.878(2)/1.180(3)	1.999(6)/1.162(8)	2.034(4)/1.155(5)
M–C3/C3–N3	1.877(2)/1.181(3)	2.021(6)/1.146(8)	2.005(4)/1.184(5)
M–C4/C4–N4	1.704(2)/1.186(3)	1.984(7)/1.181(8)	2.010(4)/1.173(5)
M–C5/C5–N5	1.874(2)/1.184(3)	1.998(6)/1.174(8)	2.006(4)/1.185(5)
C1–M–C2	93.8(1)	96.3(3)	98.7(2)
C1–M–C3	94.6(1)	91.7(3)	90.8(2)
C1–M–C4	103.2(1)	100.0(3)	97.5(2)
C1–M–C5	96.5(1)	96.4(3)	90.7(2)

on the basis of both theoretical and spectroscopic analyses.^[18–21]

The five-coordinate, paramagnetic $[M^0(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF2}})_4]$ complexes have a $S = 1/2$ electronic configuration (see also Supporting Information) and show frozen-solution EPR spectra with well-resolved ^{55}Mn , ^{99}Tc and $^{185,187}\text{Re}$ hyperfine structures (Figure 3).

The spectra of the technetium **3** and rhenium **6** compounds are characterized by 10 and 6 well-resolved lines, respectively, with constant spacing and additional intensities superimposed on lines 5, 6 for (**3**) and line 3 for (**6**) (from low field). The 10 and 6 line patterns are expected for strong hyperfine coupling to the central metal nucleus

**Figure 3.** Frozen-solution X-band EPR spectra ($T = 78$ K) of **1**, **3** and **6** (in toluene).

with spin $I = 9/2$ (^{99}Tc) and $I = 5/2$ ($^{185,187}\text{Re}$), i.e. multiplicities $2I+1$ of 10 and 6, respectively. Simulations of the spectra reveal the principal values of the g and A (hyperfine) matrices (Table 2) and show essentially “axial symmetry” of the magnetic parameters. The A matrices show pronounced axiality with ratios of about 10-fold larger coupling along the unique axis.

The X-band EPR spectrum of **1** in Figure 3 is narrower, lacks a constant spacing and is difficult to interpret on its own. Accordingly, multi-frequency EPR spectroscopy was employed to disentangle g and hyperfine anisotropy. Figure 4 depicts the EPR spectra of complex **1** at X-band ($B_0 \approx 0.33$ T), Q-band ($B_0 \approx 1.2$ T) and W-band ($B_0 \approx 3.3$ T). It is evident that the high-field measurements allow the deconvolution of the spectrum and the assignment of the individual g and hyperfine coupling components, which are given in Table 2.

The axial symmetry of the metal hyperfine coupling in all three complexes nicely reflects their square-pyramidal symmetry. It also indicates, that the largest hf tensor component, colinear with one of the axes of the g -matrix, is pointing out of the plane spanned by the four $\text{CN}p\text{-F-Ar}^{\text{DArF2}}$ ligands. This feature corroborates the d^7 configuration of the metal centers, in which the unpaired electrons occupy the dz^2 orbital along the M–CO axis. This interpretation is consistent with DFT calculations on the model complexes $[\text{M}(\text{CO})(\text{CNXyl}^{\text{F}})_4]$ ($\text{M} = \text{Mn}, \text{Tc}, \text{Re}$; $\text{Xyl}^{\text{F}} = 2,6\text{-Me}_2\text{-4-F-C}_6\text{H}_2$), which similarly revealed that the unpaired electron of each complex resides in a SOMO of predominantly d_{z^2} parentage (see Supporting Information, Figure S4.4). Importantly, this electronic structure motif is shared by the manganese monoradical $[\text{Mn}(\text{CO})_3(\text{CNAr}^{\text{Dipp2}})_2]$ and can be considered as a general feature for zero-valent ML_5 complexes of the Group 7 metals. Moreover, the dramatic increase of the largest hf tensor component when progressing from $\text{Mn} < \text{Tc} < \text{Re}$ is consistent with an increase in s/d_{z^2} orbital mixing. While this is expected due to increased relativistic stabilization of the d_{z^2} orbital in the heavier Group 7 metals,^[35] we are aware of only one previous study where such measurements have been made for a homologous triad of $S = 1/2$ metalloradicals.^[36]

Conclusion

While zero-valent Group 7 ML_5 complexes have traditionally been considered highly-reactive and transient species,

Table 2: EPR parameters derived from frozen toluene solutions of the $[M^0(\text{CO})(\text{CN}p\text{-F-Ar}^{\text{DArF2}})_4]$ complexes (1: M = Mn, 3: M = Tc, 6: M = Re). Hyperfine couplings are given in MHz.

	1	3	6
g_x	2.036	2.04	2.10
g_y	2.034	2.03	2.06
g_z	2.00	2.00	1.99
A_x^{M}	84	30	100
A_y^{M}	94	30	110
A_z^{M}	158	345	1117

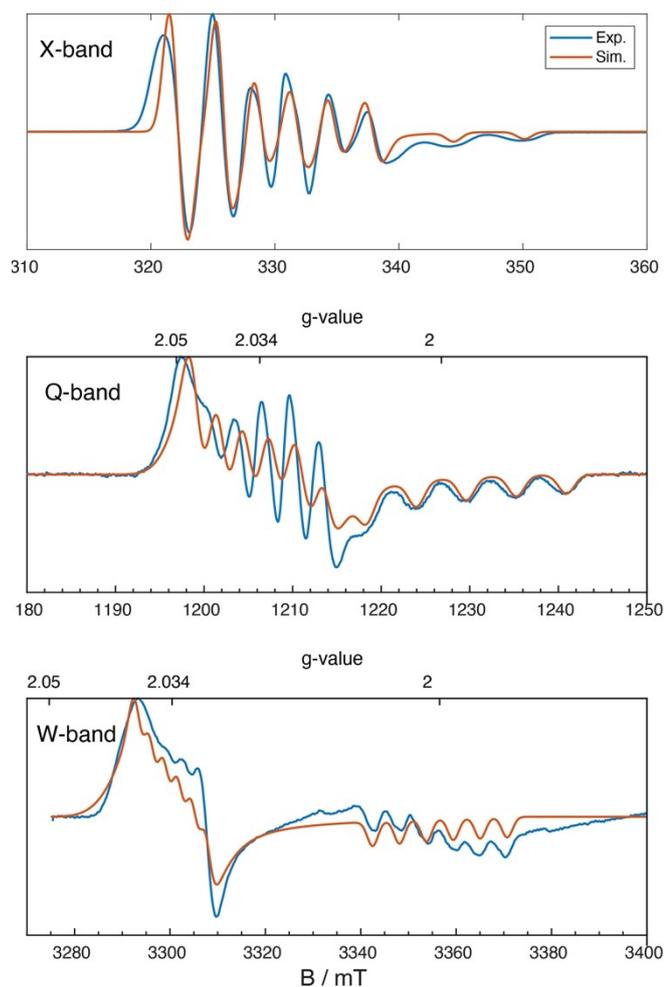


Figure 4. X-band, Q-band and W-band EPR spectra of a frozen solution of compound **1** in toluene.

there are now a growing number of isolated examples derived from sterically encumbering ligands.^[29,37–39] In the work presented here, we further exploit this strategy and outline synthetic routes leading to a complete triad of well-defined Group 7 ML_5 complexes supported by *m*-terphenyl isocyanides. Of the three, the monoradical $[Tc(CO)(CNp-F-Ar^{DArF2})_4]$ represents a unique and particularly elusive example of mononuclear technetium in the zero-valent state. As demonstrated by EPR spectroscopic studies, synthetic access to the complete triad of Group 7 metal $[M(CO)(CNp-F-Ar^{DArF2})_4]$ complexes—all possessing the same coordination environment—allowed for a rare determination of the effect of metal identity within a periodic group on the magnetic properties of a single unpaired electron. Accordingly, we are in the processes of elucidating the reactivity properties of this series of isolable Group 7 ML_5 monoradicals, with a specific focus on comparing and contrasting reaction outcomes as a function of metal identity.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Group 7 Elements · High-Field EPR · Metalloradicals · Monoradicals · *m*-Terphenyl Isocyanides

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