

# {M<sup>I</sup>(CO)X(CNAr<sup>DArF2</sup>)<sub>4</sub>} (DArF = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; M = Re and Tc; X = Br and Cl) Complexes: Convenient Platforms for the Synthesis of Low-Valent Rhenium and Technetium Compounds

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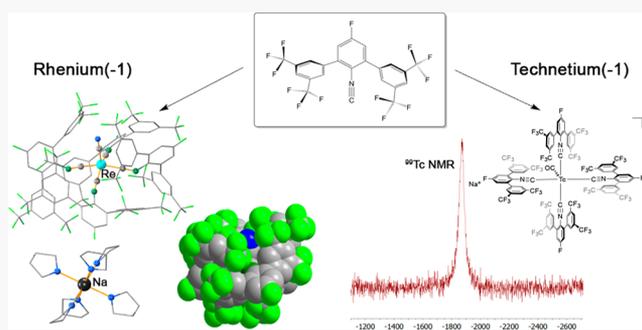
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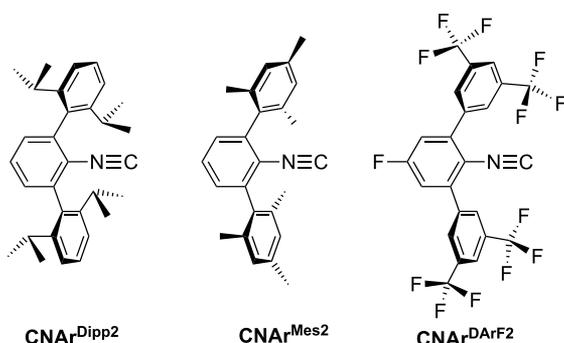
**ABSTRACT:** [Re(CO)Br(CNAr<sup>DArF2</sup>)<sub>4</sub>] and [Tc(CO)Cl(CNAr<sup>DArF2</sup>)<sub>4</sub>] (Ar<sup>DArF</sup> = 2,6-(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>-4-F-C<sub>6</sub>H<sub>2</sub>) were prepared by reactions of [Re(CO)<sub>5</sub>Br] or (NBu<sub>4</sub>)[Tc<sub>2</sub>(CO)<sub>6</sub>(μ-Cl)<sub>3</sub>] with the sterically encumbered isocyanide CNAr<sup>DArF2</sup>. These two compounds proved to be excellent starting materials for the synthesis of unprecedented low-valent rhenium and technetium complexes. The reduction of [Re(CO)Br(CNAr<sup>DArF2</sup>)<sub>4</sub>] with Na/Hg produces an equimolar mixture of [Re(CO)(CNAr<sup>DArF2</sup>)<sub>4</sub>] and Na[Re(CO)(CNAr<sup>DArF2</sup>)<sub>4</sub>] containing the transition metal in the formal oxidation states “0” and “-1”, respectively. The reduction of [Tc(CO)Cl(CNAr<sup>DArF2</sup>)<sub>4</sub>] with Na/Hg produces Na[Tc(CO)(CNAr<sup>DArF2</sup>)<sub>4</sub>], which was characterized by <sup>19</sup>F and <sup>99</sup>Tc NMR spectroscopy. The reactivity of Na[Re(CO)(CNAr<sup>DArF2</sup>)<sub>4</sub>] resembles that of [Re(CO)<sub>5</sub>]<sup>-</sup>, proved by reactions with a number of electrophiles such as MeI, HCl, or F<sub>6</sub>C<sub>5</sub>C(O)Cl.



## INTRODUCTION

Sterically encumbered isocyanides, in particular *meta*-terphenyl isocyanides, are able to form stable complexes with a wide variety of transition metals. They efficiently mimic low-valent and highly reactive carbonyl species, which otherwise would be inaccessible for preparative chemistry.<sup>1–4</sup> Very recently, we described the isolation and structural characterization of the rhenium monoanion [Re(CO)<sub>3</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub>]<sup>-</sup> (Dipp2 = 2,6-diisopropylphenyl, see Chart 1), which is an analog of the well-known [Re(CO)<sub>5</sub>]<sup>-</sup> anion, as a contact ion pair with a K<sup>+</sup> counterion.<sup>5</sup> Moreover, the extensive  $\pi$ -delocalization and the

Chart 1. Sterically Encumbering Isocyanides Used or Discussed in This Paper



efficient steric protection of the *meta*-terphenyl groups enabled us to isolate a rare example of a monomeric rhenium(0) complex, [Re(CO)<sub>3</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub>], which was characterized through EPR and IR spectroscopy.

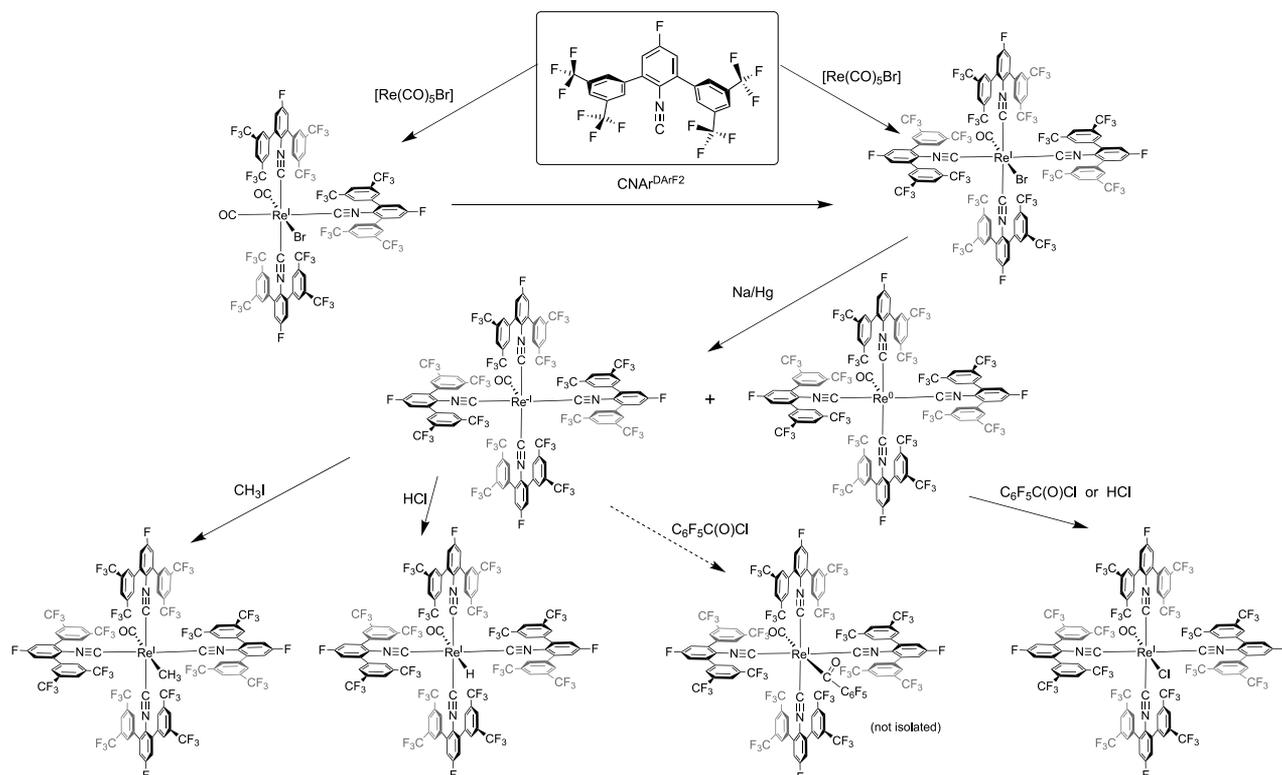
These promising results and previous studies on manganese<sup>1,6</sup> encouraged us to consider that a similar chemistry might also be extended to the homologous element technetium. Technetium is the lightest element of the periodic table that only possesses radioactive isotopes. The short-lived  $\gamma$ -emitting nuclear isomer <sup>99m</sup>Tc is used in nuclear medicine as an imaging agent for a wide variety of diagnostic tests.<sup>7</sup> The ground state of this nuclide, <sup>99</sup>Tc, is a low-energy  $\beta^-$ -emitter ( $E_{\text{max}} = 0.292$  MeV). Its long half-life ( $2.1 \times 10^5$  years) and availability in macroscopic amounts make it the ideal candidate for chemical studies.<sup>8</sup>

In contrast to its rhenium analog, the pentacarbonyltechnetate [Tc(CO)<sub>5</sub>]<sup>-</sup> is in practice hardly accessible, because of the absence of a facile synthesis procedure that is in compliance with radiation protection regulations.<sup>9</sup> For this reason, a

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Scheme 1. Rhenium Complexes with  $\text{CNAr}^{\text{DArF2}}$ 

possible use of isocyanides as CO surrogates would be of particular value, since it opens the door to a completely unexplored field of technetium chemistry.

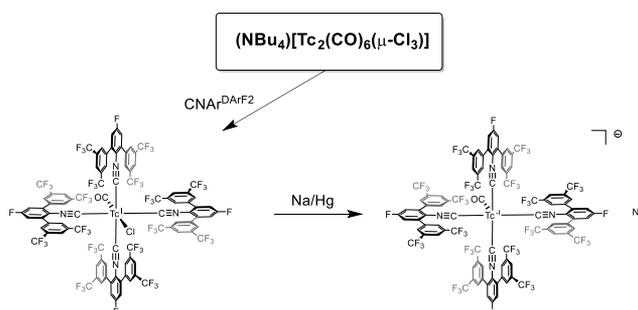
As reported by Lentz,<sup>10</sup> perfluorination of the organic residue of an isocyanide can increase its  $\pi$ -acceptor properties, offering a strategy to more finely mimic the electronic properties of CO. This is true, in general, for electron-withdrawing substituents on aryl isocyanides, and particularly for such in the *para*-position of the aromatic ring.<sup>11</sup> A detailed comparative study can be found in ref 12.

Recently, the fluorinated *meta*-terphenyl isocyanide  $\text{CNAr}^{\text{DArF2}}$  ( $\text{Ar}^{\text{DArF2}} = 2,6-(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_2-4\text{-F-C}_6\text{H}_2$ , see Chart 1) has been introduced. It can be synthesized by palladium-catalyzed cross-coupling of 2,6-dibromoaniline with 3,5-( $\text{CF}_3$ )<sub>2</sub>-4-F- $\text{C}_6\text{H}_2\text{B}(\text{OH})_2$  and subsequent formylation/dehydration steps.<sup>13</sup> Although  $\sigma$ -donor/ $\pi$ -acid ratios matching or exceeding that of CO may only be achieved by perfluorinated alkyl isocyanides, which are unstable and very difficult to handle,  $\text{CNAr}^{\text{DArF2}}$  might be a suitable candidate to mimic the bonding situation of CO ligands. Distant polyfluorination can effectively lower the  $\sigma$ -donor/ $\pi$ -acid ratio of the isocyano group, in a synthetically and operationally convenient manner.<sup>12</sup> At the same time,  $\text{CNAr}^{\text{DArF2}}$  offers a large degree of steric encumbrance, which combined with enhanced  $\pi$ -acceptor properties makes it very promising for the generation of low-coordinate isocyanide complexes.

In the present paper, we report an initial survey of the coordination capabilities of  $\text{CNAr}^{\text{DArF2}}$  to low-valent rhenium and technetium species. These studies are intended (i) to serve as the framework for uncovering the hitherto less explored (Re) or unknown (Tc) chemistry of these two elements in the formal oxidation states “0” and “−1” and (ii) to develop a new generation of organometallic Tc(I) cores with the required stability for nuclear-medicine labeling experiments.

## RESULTS AND DISCUSSION

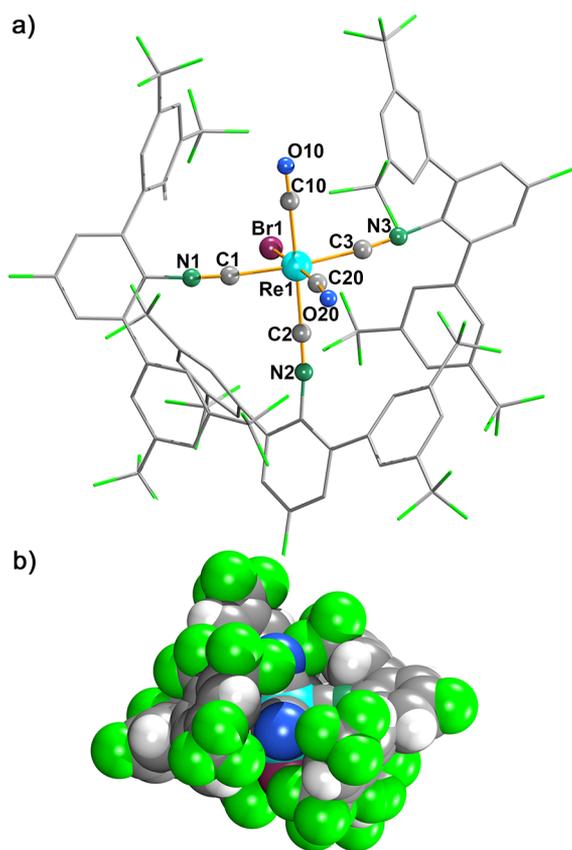
The interesting results of a previous report, which describes the formation of the tris-isocyanide complex  $[\text{Mn}(\text{CO})_2\text{Br}(\text{CNAr}^{\text{Mes2}})]_3$  by a facile reaction of  $[\text{Mn}(\text{CO})_5\text{Br}]$  and 3 equiv of the sterically encumbered isocyanide  $\text{CNAr}^{\text{Mes2}}$  ( $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ , see Chart 1) in THF,<sup>6</sup> encouraged us to undertake similar reactions with suitable tricarbonylrhenium(I) and -technetium(I) complexes. A summary of the reactions between  $\text{CNAr}^{\text{DArF2}}$  and  $[\text{Re}(\text{CO})_5\text{Br}]$  and subsequent reactions of the formed products is given in Scheme 1. Scheme 2 shows similar reactions done with technetium compounds.

Scheme 2. Technetium Complexes with  $\text{CNAr}^{\text{DArF2}}$ 

Unexpectedly, the reaction of  $[\text{Re}(\text{CO})_5\text{Br}]$  with 3 equiv of  $\text{CNAr}^{\text{DArF2}}$  in boiling THF led only to an intractable mixture from which no crystalline compounds could be isolated. Defined products, however, were obtained at higher temperature. Prolonged heating of such a reaction mixture in toluene afforded the complete consumption of the reactants, and an orange-red solid was isolated. The  $^{19}\text{F}$  NMR spectrum of the

crude product surprisingly shows three triplets around  $-109$  ppm (each one belonging to the *para*-fluorine substituent of the aryl group of a  $\text{CNAr}^{\text{DArF}_2}$  molecule). They can be assigned to two different species: (i) Two of the signals exhibit an approximate 1:2 integral ratio, which is consistent with a triligated  $\text{mer-}[\text{Re}(\text{CO})_2\text{Br}(\text{CNAr}^{\text{DArF}_2})_3]$  complex. (ii) One additional triplet suggests the formation of a complex with magnetically identical  $\text{CNAr}^{\text{DArF}_2}$  ligands. The presence of two new species is also confirmed by the IR spectrum of the product mixture, which shows two different carbonyl patterns. Interestingly, some unreacted starting material  $[\text{Re}(\text{CO})_5\text{Br}]$  also seems to be left, while the bulky isocyanide was completely consumed. These findings suggest the formation of at least one complex with four  $\text{CNAr}^{\text{DArF}_2}$  ligands, which was confirmed by X-ray structural analyses.

A few orange-red single crystals were hand-picked and identified as  $\text{cis,mer-}[\text{Re}(\text{CO})_2\text{Br}(\text{CNAr}^{\text{DArF}_2})_3]$ . The molecular structure of the compound is shown in Figure 1. Three



**Figure 1.** (a) Molecular structure of  $\text{cis,mer-}[\text{Re}(\text{CO})_2\text{Br}(\text{CNAr}^{\text{DArF}_2})_3]$  and (b) space-filling model of the molecule.

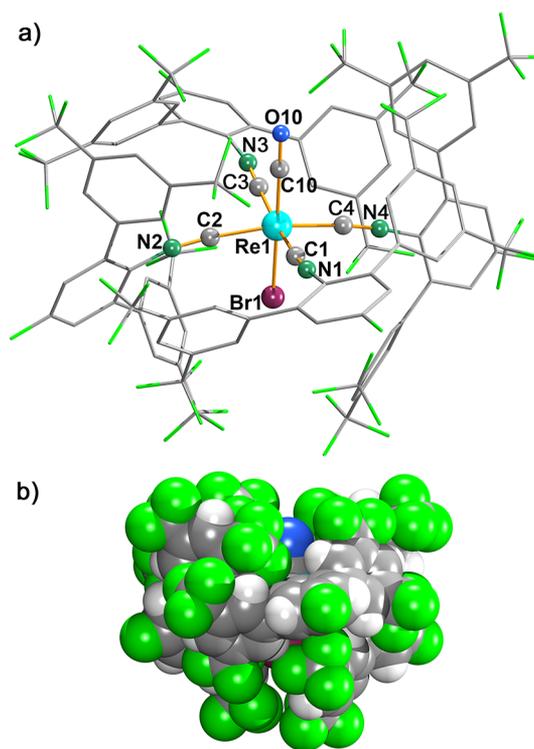
isocyanide ligands are coordinated in a meridional arrangement by the rhenium atom, the coordination sphere of which is completed by two *cis*-coordinated carbonyls and a  $\text{Br}^-$  ligand.

The third  $^{19}\text{F}$  NMR signal observed in the crude product mixture can be assigned to a complex with higher symmetry. It represents the “thermodynamic product” of the performed reaction,  $[\text{Re}(\text{CO})\text{Br}(\text{CNAr}^{\text{DArF}_2})_4]$ , which can be isolated in high yields and pure form, when at least 4 equiv of  $\text{CNAr}^{\text{DArF}_2}$  is used and the reaction is performed in boiling toluene.

The  $^{19}\text{F}$  NMR of  $[\text{Re}(\text{CO})\text{Br}(\text{CNAr}^{\text{DArF}_2})_4]$  reveals a perfect axial symmetry in solution through the magnetic equivalence of the four isocyanide ligands, which produces

only one triplet for the *para*-fluorine atoms at  $-109$  ppm and one singlet for the  $\text{CF}_3$  groups at  $-63$  ppm. The solid-state IR spectrum displays a broad band at  $2051\text{ cm}^{-1}$  for the isocyanides and a split band at  $1920\text{ cm}^{-1}$  for the CO ligand. The significant redshift of the isocyno stretch in comparison to that of the noncoordinated isocyanide ( $\nu_{\text{CN}} = 2118\text{ cm}^{-1}$ ) denotes an efficient  $\pi$ -back-donation, which was not observed in rhenium and technetium complexes with the nonfluorinated *m*-terphenyl isocyanide  $\text{CNAr}^{\text{Dipp}^2}$  or  $\text{CNAr}^{\text{Mes}^2}_{5,14,15}$ .

Single-crystal X-ray diffraction confirms the equivalence of the four  $\text{CNAr}^{\text{DArF}_2}$  ligands, which are coordinated in one plane (Figure 2). Selected bond lengths and angles as well as an ellipsoid representation of  $[\text{Re}(\text{CO})_2\text{Br}(\text{CNAr}^{\text{DArF}_2})_3]$  and  $[\text{Re}(\text{CO})\text{Br}(\text{CNAr}^{\text{DArF}_2})_4]$  are given in the Supporting Information.



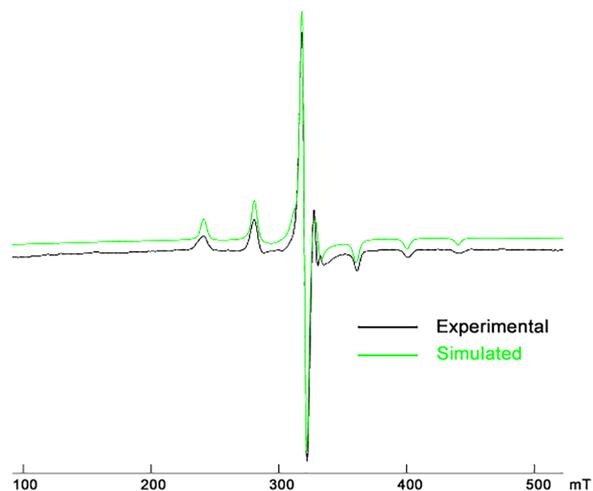
**Figure 2.** (a) Molecular structure of  $[\text{Re}(\text{CO})\text{Br}(\text{CNAr}^{\text{DArF}_2})_4]$  and (b) space-filling model of the molecule.

The space-filling model of  $[\text{Re}(\text{CO})\text{Br}(\text{CNAr}^{\text{DArF}_2})_4]$  (Figure 2b) illustrates that the rhenium atom is perfectly shielded in this compound by the interdigitation observed for the fluorinated flanking rings. This creates a qualitatively high degree of shielding for the central transition metal ion, which is clearly higher than that in the dicarbonyl compound  $[\text{Re}(\text{CO})_2\text{Br}(\text{CNAr}^{\text{DArF}_2})_3]$  (Figure 1b).

The efficient steric protection of the metal atom in  $[\text{Re}(\text{CO})\text{Br}(\text{CNAr}^{\text{DArF}_2})_4]$  provided by four encumbering *meta*-terphenyl isocyanides and the enhanced  $\pi$ -back-donation through fluorination makes this compound a convenient candidate for the preparation of highly reduced rhenium complexes. Indeed, treatment of  $[\text{Re}(\text{CO})\text{Br}(\text{CNAr}^{\text{DArF}_2})_4]$  with 0.1% sodium amalgam in THF led to a very dark solution, from which black crystals precipitated at  $-35\text{ }^\circ\text{C}$  after the addition of pentane. The obtained single crystals are unstable and rapidly decompose at room temperature. Solid-state IR analysis of the product confirms the complete consumption of

the reactants and the formation of (a) new compound(s) with broad CN absorption(s) around  $1906\text{ cm}^{-1}$ . Such a drastic redshift of almost  $150\text{ cm}^{-1}$  is indicative for the formation of a highly reduced rhenium compound as has been reported recently for similar  $\text{CNAr}^{\text{Dipp}2}$  complexes.<sup>5</sup>  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra confirm that the coordinated isocyanide ligands maintain their magnetic equivalence: Only one singlet at  $-62\text{ ppm}$  is found for the  $\text{CF}_3$  substituents of the four ligands, and only one triplet at  $-116\text{ ppm}$  is found for the *para*-fluorine atoms. The  $^{19}\text{F}$  NMR signals are slightly shifted in comparison to those of the starting material ( $-63$  and  $-109\text{ ppm}$ ).

Remarkably, a benzene/THF solution of the same black crystals also gives an intense EPR spectrum (Figure 3). It



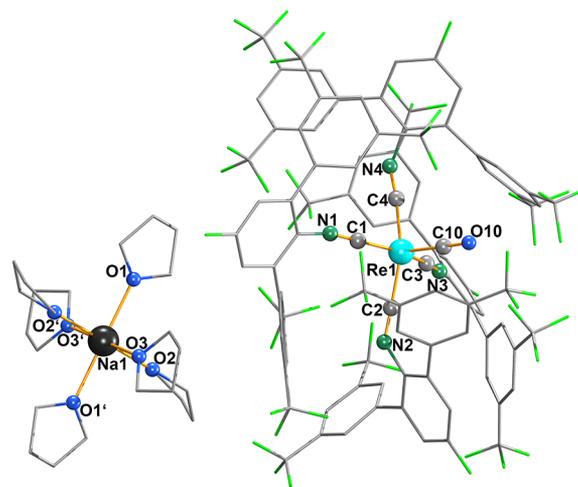
**Figure 3.** Frozen-solution X-band EPR spectrum of  $[\text{Re}(\text{CO})(\text{CNAr}^{\text{DArF}2})_4]$  in benzene/THF ( $g_x = 2.864$ ,  $g_y = 2.068$ ,  $g_z = 1.978$ ,  $A_x^{\text{Re}} = 22 \times 10^{-4}\text{ cm}^{-1}$ ,  $A_y^{\text{Re}} = 35 \times 10^{-4}\text{ cm}^{-1}$ ,  $A_z^{\text{Re}} = 368 \times 10^{-4}\text{ cm}^{-1}$ ).

shows well-resolved  $^{185,187}\text{Re}$  hyperfine couplings, which clearly prove the presence of a paramagnetic rhenium complex with the unpaired electron being mainly located at the transition metal. With respect to the experimental conditions (the treatment of a rhenium(I) compound with a strong reductant), it can be assigned to a monomeric rhenium(0) compound, most probably  $[\text{Re}(\text{CO})(\text{CNAr}^{\text{DArF}2})_4]$ . Persistent monomeric complexes of rhenium(0) are rare, and only two of them were stable enough to allow structural and/or spectroscopic studies:  $[\text{Re}(\text{CO})_3(\text{tricyclohexylphosphine})_2]$  and the recently published isocyanide complex  $[\text{Re}(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2]$ .<sup>5,16,17</sup> The EPR spectrum of  $[\text{Re}(\text{CO})(\text{CNAr}^{\text{DArF}2})_4]$  is essentially axially symmetric with only a marginal rhombic component. Interactions of the unpaired electron with the nuclear spin of  $I = 5/2$  of  $^{185,187}\text{Re}$  result in the observed six-line pattern with a hyperfine coupling of  $368 \times 10^{-4}\text{ cm}^{-1}$  in the parallel part of the spectrum, while that in the perpendicular part is significantly smaller. Generally, the spectrum is very similar to that of  $[\text{Re}^0(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2]$  with a less pronounced rhombic component, which is in agreement with the proposed higher symmetry of the axial coordination sphere of rhenium.

Surprisingly,  $[\text{Re}(\text{CO})(\text{CNAr}^{\text{DArF}2})_4]$  is relatively robust in solution and does not suffer from degradation after standing at room temperature in THF for at least 1 day. Even the addition of an equimolar quantity of water does not induce decomposition as long as the access of atmospheric oxygen is precluded. Thus, the detected instability of the single crystals

of the cocrystallized low-valent rhenium complexes might be assigned to the  $\text{Re}(-1)$  complex (or even only to the  $[\text{Na}(\text{THF})_6]^+$  cation).

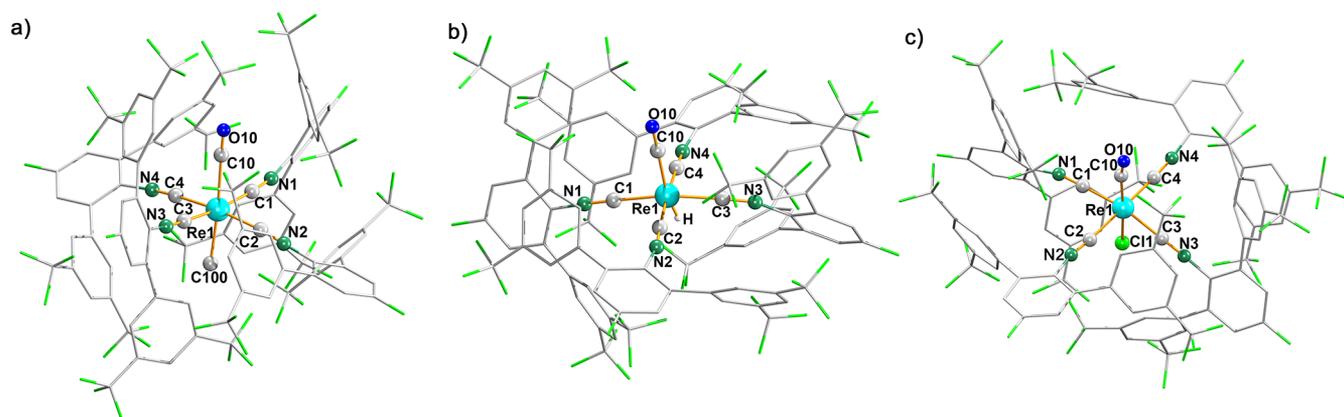
The results of an X-ray structure determination explain the unusual spectroscopic behavior of the dark solid, which gives high-quality NMR and EPR spectra at the same time: The black crystals represent a cocrystallization of two species:  $[\text{Na}(\text{THF})_6][\text{Re}^{1-}(\text{CO})(\text{CNAr}^{\text{DArF}2})_4]$  and  $[\text{Re}^0(\text{CO})(\text{CNAr}^{\text{DArF}2})_4]$ . Figure 4 shows the crystallographic results.



**Figure 4.** Molecular structures of the cocrystallized compounds  $[\text{Na}(\text{THF})_6][\text{Re}^{1-}(\text{CO})(\text{CNAr}^{\text{DArF}2})_4]$  and  $[\text{Re}^0(\text{CO})(\text{CNAr}^{\text{DArF}2})_4]$  (symmetry operation: (')  $-x, 2 - y, 2 - z$ ). Note that the  $[\text{Na}(\text{THF})_6]^+$  cation has only 50% occupancy.

The structure has been solved and refined in the triclinic space group  $P\bar{1}$ . The rhenium part of the structure has an occupancy of 1, while that of the  $[\text{Na}(\text{THF})_6]^+$  is 0.5. This is in agreement with the above-mentioned cocrystallization of two species. Such an interpretation is only sound when an almost uniform structure of the  $\text{Re}^0$  and the  $\text{Re}^{1-}$  complex species is assumed. Indeed, there is no crystallographic evidence for significant differences between these two species. Both contain rhenium in a square-pyramidal coordination sphere with the carbonyl ligand in the apical position. The structural similarity between both compounds also includes the fact that each two of the isocyanide ligands are coordinated “regularly” with  $\text{Re}-\text{C}-\text{N}$  angles of  $172$  and  $167^\circ$ , while the other two clearly show a bent arrangement with  $\text{Re}-\text{C}-\text{N}$  angles of  $130$  and  $134^\circ$ . Such a bent coordination of isocyanides to rhenium has recently also been found for the rhenium(-1) complex  $\text{K}[\text{Re}(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2]$ .<sup>5</sup> For a more detailed discussion of the bonding situation, however, structural data of the pure  $\text{Re}^0$  and  $\text{Re}(-1)$  species would be highly appreciated. We are currently working on the isolation of suitable single crystals of the two compounds.

The presence of two species with different reactivity in the black, crystalline material is also reflected by their reactions. The highly reduced rhenium(-1) species is expected to show a pronounced reactivity toward electrophilic agents as has been demonstrated before for similar manganese or molybdenum species,<sup>4,6</sup> while the  $\text{Re}^0$  complex may behave like a radical. Therefore, we tested the reactivity of the equimolar  $[\text{Na}(\text{THF})_6][\text{Re}^{1-}(\text{CO})(\text{CNAr}^{\text{DArF}2})_4]/[\text{Re}^0(\text{CO})(\text{CNAr}^{\text{DArF}2})_4]$  mixture in THF with reagents such as  $\text{MeI}$ ,  $\text{HCl}$ , and  $\text{C}_6\text{F}_5\text{C}(\text{O})\text{Cl}$  and isolated products from both reaction



**Figure 5.** Molecular structures of  $[\text{Re}(\text{CO})\text{Me}(\text{CNAr}^{\text{DArF2}})_4]$ ,  $[\text{Re}(\text{CO})\text{H}(\text{CNAr}^{\text{DArF2}})_4]$ , and  $[\text{Re}(\text{CO})\text{Cl}(\text{CNAr}^{\text{DArF2}})_4]$  as products of reactions of  $[\text{Na}(\text{THF})_6][\text{Re}^{1-}(\text{CO})(\text{CNAr}^{\text{DArF2}})_4]/[\text{Re}^0(\text{CO})(\text{CNAr}^{\text{DArF2}})_4]$  with MeI, HCl, and  $\text{C}_6\text{F}_5\text{C}(\text{O})\text{Cl}$ , respectively.

pathways. In some cases, the parallel formation of both possible products could be confirmed.

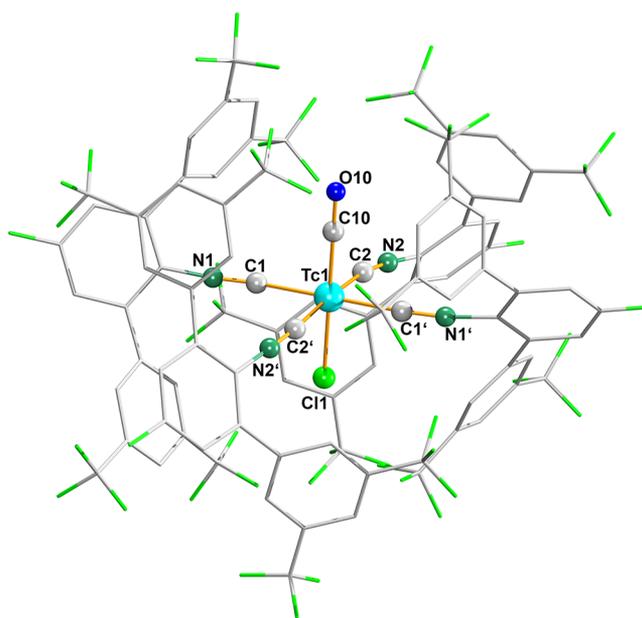
Addition of methyl iodide to a THF solution of the black crystals afforded the formation of  $[\text{Re}(\text{CO})\text{Me}(\text{CNAr}^{\text{DArF2}})_4]$  as the sole product, as is indicated by the detection of a  $\text{CH}_3$  signal at  $-1.8$  ppm in the  $^1\text{H}$  NMR spectrum of the compound and a single-crystal structure determination (see Figure 5a).

Treatment of  $[\text{Na}(\text{THF})_6][\text{Re}^{1-}(\text{CO})(\text{CNAr}^{\text{DArF2}})_4]/[\text{Re}^0(\text{CO})(\text{CNAr}^{\text{DArF2}})_4]$  with HCl, however, led to the formation of two products: (i) the hydrido complex  $[\text{Re}(\text{CO})\text{H}(\text{CNAr}^{\text{DArF2}})_4]$  and (ii)  $[\text{Re}(\text{CO})\text{Cl}(\text{CNAr}^{\text{DArF2}})_4]$ . The hydride could be isolated in the form of yellow crystals and characterized by X-ray diffraction (Figure 5b). The  $^1\text{H}$  NMR spectrum of the compound displays a characteristic hydride signal at  $-5$  ppm. The IR spectrum of  $[\text{Re}(\text{CO})\text{H}(\text{CNAr}^{\text{DArF2}})_4]$  shows bands at  $2021$ ,  $1979$ , and  $1938$   $\text{cm}^{-1}$ , which can be assigned to the  $\nu_{\text{C}\equiv\text{N}}$ ,  $\nu_{\text{Re}-\text{H}}$ , and  $\nu_{\text{C}\equiv\text{O}}$  vibrations. The parallel formation of some amount of  $[\text{Re}(\text{CO})\text{Cl}(\text{CNAr}^{\text{DArF2}})_4]$  is proven by the isolation of a yellow, crystalline material, which was characterized by NMR spectroscopy and X-ray diffraction. The compound is isostructural to the corresponding bromido complex. Its molecular structure is shown in Figure 5c.  $[\text{Re}(\text{CO})\text{Cl}(\text{CNAr}^{\text{DArF2}})_4]$  is also the main product of a reaction of  $[\text{Na}(\text{THF})_6][\text{Re}^{1-}(\text{CO})(\text{CNAr}^{\text{DArF2}})_4]/[\text{Re}^0(\text{CO})(\text{CNAr}^{\text{DArF2}})_4]$  with  $\text{C}_6\text{F}_5\text{C}(\text{O})\text{Cl}$ , which was performed for an attempted synthesis of a complex with a perfluorinated acyl ligand. We were hitherto not able to isolate the acyl complex in crystalline form, but there is evidence for its formation in the NMR spectra of the reaction mixture.

The obtained results demonstrate that the  $\{\text{Re}(\text{CO})(\text{CNAr}^{\text{DArF2}})_4\}$  core is suitable for the stabilization of species with highly reduced metal centers, in which the metal ion has a pronounced nucleophilic character and its reactivity resembles in some cases that of  $[\text{Re}(\text{CO})_5]^-$ .

The possibility of extending these results to technetium is particularly intriguing, since it would provide a synthetically accessible analogue of the practically unknown species  $[\text{Tc}(\text{CO})_5]^-$ . Reactions of  $(\text{NBu}_4)[\text{Tc}_2(\mu\text{-Cl})_3(\text{CO})_6]$  with 3 equiv of  $\text{CNAr}^{\text{DArF2}}$  in boiling toluene gave an intractable oil, but the use of 4 equiv of the ligand and prolonged heating in boiling toluene gave pure orange crystals of  $[\text{Tc}(\text{CO})\text{Cl}(\text{CNAr}^{\text{DArF2}})_4]$  in good yield. X-ray structural determination demonstrates that the complex is isostructural to the rhenium analog with four equatorially arranged  $\text{CNAr}^{\text{DArF2}}$  ligands and

the CO and  $\text{Cl}^-$  ligands in *trans* position to each other (Figure 6). Two well-separated bands (for the  $\nu_{\text{C}\equiv\text{N}}$  stretch at  $2064$

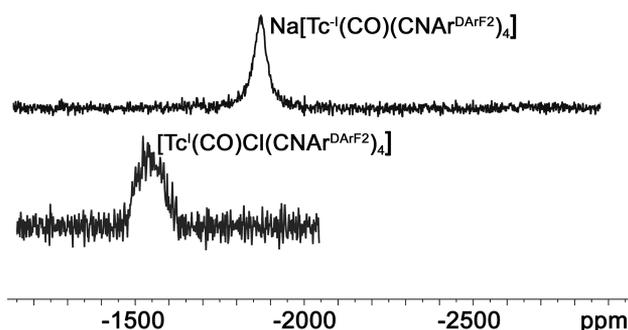


**Figure 6.** Molecular structure of  $[\text{Tc}(\text{CO})\text{Cl}(\text{CNAr}^{\text{DArF2}})_4]$  (symmetry operation:  $(\cdot) 1 - x, y, 1.5 - z$ ).

$\text{cm}^{-1}$  and for the  $\nu_{\text{C}\equiv\text{O}}$  stretch at  $1935$   $\text{cm}^{-1}$ ) are resolved in the IR spectrum of the compound. The redshift of the isocyanide band is less pronounced than that in the isostructural rhenium complex.  $^{99}\text{Tc}$  NMR spectroscopy exhibits a broad signal at  $-1542$  ppm, which is in the range typical of  $\text{Tc}(\text{I})$  tricarbonyl complexes. The  $^{19}\text{F}$  NMR spectrum of  $[\text{Tc}(\text{CO})\text{Cl}(\text{CNAr}^{\text{DArF2}})_4]$  shows the signal of the magnetically equivalent  $\text{CF}_3$  groups as a singlet at  $-66$  ppm, while a triplet at  $-124$  ppm can be assigned to the fluorine atom of the aromatic rings. These signals are slightly shifted with respect to the corresponding values for  $[\text{Re}(\text{CO})\text{Br}(\text{CNAr}^{\text{DArF2}})_4]$  ( $-63$  and  $-109$  ppm).

The reduction of  $[\text{Tc}(\text{CO})\text{Cl}(\text{CNAr}^{\text{DArF2}})_4]$  with 0.1% Na/Hg in THF led to a unique red diamagnetic compound of the composition  $\text{Na}[\text{Tc}(\text{CO})(\text{CNAr}^{\text{DArF2}})_4]$ , as can be concluded by its NMR spectra, which are very close to the values obtained for the analogous rhenium complex. The  $^{19}\text{F}$  NMR spectrum confirms the purity of the obtained product, showing

only one singlet at  $-65$  ppm and one triplet at  $-112$  ppm. The  $^{99}\text{Tc}$  NMR spectrum of  $\text{Na}[\text{Tc}(\text{CO})(\text{CNAr}^{\text{DArF}_2})_4]$  shows the complete consumption of  $[\text{Tc}(\text{CO})\text{Cl}(\text{CNAr}^{\text{DArF}_2})_4]$  and the formation of a new signal at  $-1865$  ppm, which is one of the first detections of a technetium complex with the formal oxidation state  $-1$  by  $^{99}\text{Tc}$  NMR spectroscopy (Figure 7). It should be mentioned that a well-resolved EPR spectrum belonging to a monomeric  $\text{Tc}(0)$  complex could also be registered during the course of the reaction.



**Figure 7.**  $^{99}\text{Tc}$  NMR spectra of  $\text{Na}[\text{Tc}(\text{CO})(\text{CNAr}^{\text{DArF}_2})_4]$  and  $[\text{Tc}(\text{CO})\text{Cl}(\text{CNAr}^{\text{DArF}_2})_4]$  in THF (chemicals shifts relative to  $\text{TcO}_4^-$ ).

Similar to  $[\text{Na}(\text{THF})_6][\text{Re}(\text{CO})(\text{CNAr}^{\text{DArF}_2})_4]$ , the highly reduced technetium complex reacts with electrophiles such as  $(\text{CF}_3\text{CO})_2\text{O}$ ,  $\text{SnCl}_2$ ,  $\text{P}_4$ , or  $\text{HCl}$ . Unfortunately, up to now no crystalline products could be isolated from such reactions, and the obtained  $^{99}\text{Tc}$  NMR spectra indicate the parallel formation of more than one product in most of the cases. However, there is clear evidence that the  $\text{Tc}(-1)$  compound is consumed and that  $\text{Tc}(\text{I})$  products are formed.

## CONCLUSIONS

Compounds with a central  $\{\text{M}^{\text{I}}(\text{CO})(\text{CNAr}^{\text{DArF}_2})_4\}^+$  unit ( $\text{M} = \text{Re}$  and  $\text{Tc}$ ) contain highly shielded metal ions. The four encumbering isocyanide ligands provide adequate steric protection in the proximity of the metal center, avoiding dimerization reactions and other degradation pathways. In addition, the fluorination in the periphery of the ligands increases the  $\pi$ -accepting properties of the isocyanides, which is fundamental for the stabilization of very low oxidation states. The reduction of  $[\text{Re}(\text{CO})\text{Br}(\text{CNAr}^{\text{DArF}_2})_4]$  and  $[\text{Tc}(\text{CO})\text{Cl}(\text{CNAr}^{\text{DArF}_2})_4]$  with  $\text{Na}/\text{Hg}$  produces low-valent complexes such as  $[\text{Re}^0(\text{CO})(\text{CNAr}^{\text{DArF}_2})_4]$ ,  $[\text{Na}(\text{THF})_6][\text{Re}^{-1}(\text{CO})(\text{CNAr}^{\text{DArF}_2})_4]$ , or  $\text{Na}[\text{Tc}^{-1}(\text{CO})(\text{CNAr}^{\text{DArF}_2})_4]$ . The encumbering fluorinated substituents donate a surprisingly high robustness to the reduced compounds, which readily undergo reactions with electrophiles.

## EXPERIMENTAL SECTION

**General Considerations.** All manipulations were carried out under an argon atmosphere using standard Schlenk and glovebox techniques. Unless otherwise stated, reagent-grade starting materials were purchased from commercial sources and either used as received or purified by standard procedures. Solvents were dried and deoxygenated according to standard procedures. Benzene- $d_6$  was distilled from  $\text{NaK}$  alloy and stored under  $\text{Ar}$  prior to use. Celite 405 (Fisher Scientific) was dried at a temperature above  $250$  °C and stored in the glovebox prior to use.  $\text{CNAr}^{\text{DArF}_2}$  and  $(\text{NBu}_4)[\text{Tc}_2(\text{CO})_6(\mu\text{-Cl})_3]$  were prepared as previously described.<sup>13,18</sup>

**Physical Measurements.** NMR spectra were recorded at  $20$  °C with a JEOL 400 MHz multinuclear spectrometer. The values given for the  $^{99}\text{Tc}$  and  $^{19}\text{F}$  chemical shifts are referenced to pertechnetate and  $\text{CFCl}_3$ , respectively. Positive- and negative-mode ESI mass spectra were measured for the rhenium compounds with an Agilent 6210 ESI-TOF (Agilent Technology) mass spectrometer. EPR spectra were recorded in the X-band at  $78$  K in THF with a Magnetech Miniscope spectrometer. Simulations were done with Easyspin.<sup>19</sup> For the IR spectra, a Nicolet iS10 FT-IR or a Shimadzu FTIR Affinity-1 spectrometer were used. The following abbreviations were used for the intensities and characteristics of IR absorption bands: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder.

The technetium content of  $[\text{Tc}(\text{CO})\text{Cl}(\text{CNAr}^{\text{DArF}_2})_4]$  was measured by a HIDEEX 300 SL liquid scintillation counter. An aliquot of three probes per sample with different concentrations was added to  $10$  mL of a scintillation cocktail (Rotiszint ecoplus, Carl Roth), and the net count rates were measured over 1024 channels with a counting time of  $60$  s. An average value was calculated for each sample.

**Radiation Precautions. Caution:**  $^{99}\text{Tc}$  is a long-lived weak  $\beta^-$ -emitter ( $E_{\text{max}} = 0.292$  MeV). Normal glassware provides adequate protection against the weak beta radiation when milligram amounts are used. Secondary X-rays (Bremsstrahlung) play a significant role only when larger amounts of  $^{99}\text{Tc}$  are handled. All manipulations were done in a laboratory approved for the handling of radioactive materials.

**X-ray Crystallography.** The intensities for the X-ray determinations were collected on a Bruker D8 Venture instrument with  $\text{Mo K}\alpha$  radiation. The space groups were determined by the detection of systematic absences. Absorption corrections were carried out by SADABS.<sup>20</sup> Structure solution and refinement were performed with the SHELX program package.<sup>21,22</sup> Hydrogen atoms were placed at calculated positions and treated with the "riding model" option of SHELXL. The representation of molecular structures was done using the program Diamond 4.2.2.<sup>23</sup>

Additional information on the structure determinations is contained in the Supporting Information and has been deposited with the Cambridge Crystallographic Data Centre.

**Synthesis of the Complexes.**  $[\text{Re}(\text{CO})\text{Br}(\text{CNAr}^{\text{DArF}_2})_4]$ . To a suspension of  $[\text{Re}(\text{CO})_3\text{Br}]$  ( $266$  mg,  $0.655$  mmol) in  $100$  mL of toluene was added  $\text{CNAr}^{\text{DArF}_2}$  ( $1.5$  g,  $2.75$  mmol,  $4.2$  equiv). The mixture was heated under reflux with stirring under argon for  $24$  h. The resulting yellow solution was concentrated to a volume of  $8$  mL, and hexane ( $20$  mL) was added. Storage at  $4$  °C for  $12$  h resulted in the precipitation of orange-red crystals of  $[\text{Re}(\text{CO})\text{Br}(\text{CNAr}^{\text{DArF}_2})_4]$ , which were collected and dried *in vacuo*. Crystals suitable for X-ray structure determination were obtained from  $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ . Yield:  $1.284$  g,  $0.517$  mmol,  $79\%$ . FTIR (in  $\text{KBr}$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{CN})$   $2051$  (s, broad),  $\nu(\text{CO})$   $1926$  (m),  $\nu(\text{CO})$   $1916$  (m),  $3054$  (w),  $2915$  (w),  $1622$  (w),  $1595$  (w),  $1479$  (m),  $1461$  (m),  $1433$  (m),  $1398$  (m),  $1362$  (s),  $1312$  (w),  $1276$  (vs),  $1220$  (w),  $1170$  (s),  $1127$  (vs),  $1105$  (vs),  $1056$  (vs),  $1000$  (m),  $971$  (w),  $952$  (w),  $912$  (m),  $902$  (s),  $879$  (m),  $861$  (w),  $847$  (m),  $798$  (w),  $750$  (s),  $735$  (w).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$   $7.58$  (two overlapped s,  $24\text{H}$ , Ph),  $7.08$  (d,  $J = 8$  Hz,  $8\text{H}$ , Ar-F).  $^{19}\text{F}$ -NMR ( $\text{CDCl}_3$ , ppm):  $\delta$   $-62.8$  (s,  $48\text{F}$ , Ph- $\text{CF}_3$ ),  $-108.8$  (t,  $J = 8$  Hz,  $4\text{F}$ , Ar-F). MS ESI+ ( $m/z$ ):  $[\text{M} + \text{Na}]^+$   $2497.1320$ . Calcd for  $\text{C}_{93}\text{H}_{32}\text{BrF}_{52}\text{N}_4\text{NaORe}$ :  $2497.0384$ .

$[\text{Re}(\text{CO})_2\text{Br}(\text{CNAr}^{\text{DArF}_2})_3]$ . To a suspension of  $[\text{Re}(\text{CO})_3\text{Br}]$  ( $122$  mg,  $0.3$  mmol,  $30$  mL) in toluene was added  $\text{CNAr}^{\text{DArF}_2}$  ( $491$  mg,  $0.9$  mmol,  $3.0$  equiv). The mixture was heated under reflux with stirring under argon for  $24$  h. The resulting yellow solution was concentrated to a volume of  $2$  mL, and hexane ( $15$  mL) was added. Storage at  $4$  °C for  $12$  h resulted in the formation of an orange-red solid consisting of a mixture of  $[\text{Re}(\text{CO})_2\text{Br}(\text{CNAr}^{\text{DArF}_2})_3]$  and  $[\text{Re}(\text{CO})\text{Br}(\text{CNAr}^{\text{DArF}_2})_4]$ . The product was dried *in vacuo*, and a few single crystals of pure  $[\text{Re}(\text{CO})_2\text{Br}(\text{CNAr}^{\text{DArF}_2})_3]$  could be separated after slow evaporation of a  $\text{Et}_2\text{O}/\text{hexane}$  solution of the mixture.  $^{19}\text{F}$  NMR (THF, ppm):  $\delta$   $-64.7$  (s, Ph- $\text{CF}_3$ ),  $-108.3$  (t,  $J = 8$  Hz, Ar-F),  $-109.5$  (t,  $J = 8$  Hz, Ar-F),  $-110.1$  (t,  $J = 8$  Hz, Ar-F).

$[\text{Na}(\text{THF})_6][\text{Re}(\text{CO})(\text{CNAr}^{\text{DArF}_2})_4]/[\text{Re}(\text{CO})(\text{CNAr}^{\text{DArF}_2})_4]$ .  $[\text{Re}(\text{CO})\text{Br}(\text{CNAr}^{\text{DArF}_2})_4]$  ( $60$  mg,  $0.024$  mmol) was dissolved in THF ( $3$

mL), and 0.1% Na/Hg (Na: 0.003 g; Hg: 3 g; 5 equiv of Na/Re) was added. The mixture was vigorously stirred for 3 h giving a very dark solution, which was concentrated under reduced pressure. Addition of pentane and storage at  $-35\text{ }^{\circ}\text{C}$  for 12 h yielded black crystals, which were collected and dried *in vacuo*. Yield: 38 mg, 60%. FTIR-ATR ( $\text{cm}^{-1}$ ):  $\nu(\text{CN})$  2010 (w),  $\nu(\text{CN})$  1906 (s, broad),  $\nu(\text{CO})$  1789 (s, broad), 1619 (w), 1461 (m), 1409 (m), 1362 (s), 1306 (w), 1276 (vs), 1168 (s), 1130 (vs), 1094 (w), 967 (w), 910 (w), 875 (w), 846 (w), 705 (m), 682 (m), 636 (w), 546 (w).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm):  $\delta$  7.60 (s, 16H, Ph), 7.53 (s, 8H, Ph), 6.52 (d,  $J = 8\text{ Hz}$ , 8H, Ar-F).  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ , ppm):  $\delta$  -62.5 (s, 48F, Ph-CF<sub>3</sub>), -115.7 (broad t, 4F, Ar-F). EPR (THF/benzene, 78 K): ( $g_x = 2.0638$ ,  $g_y = 2.0676$ ,  $g_z = 1.9783$ ,  $A_x^{\text{Re}} = 22 \times 10^{-4}\text{ cm}^{-1}$ ,  $A_y^{\text{Re}} = 35 \times 10^{-4}\text{ cm}^{-1}$ ,  $A_z^{\text{Re}} = 368 \times 10^{-4}\text{ cm}^{-1}$ ). MS ESI+ ( $m/z$ ):  $[\text{M}]^+$  2395.1699 (10%). Calcd for  $\text{C}_{93}\text{H}_{32}\text{F}_{52}\text{N}_4\text{ORe}$ : 1395.1303.

$[\text{Re}(\text{CO})\text{Me}(\text{CNAr}^{\text{DArF}_2})_4]$ .  $[\text{Re}(\text{CO})\text{Br}(\text{CNAr}^{\text{DArF}_2})_4]$  (60 mg, 0.024 mmol) was dissolved in THF (3 mL), and 0.1% Na/Hg (Na: 0.003 g; Hg: 3 g; 5 equiv of Na/Re) was added. The mixture was vigorously stirred for 3 h and filtered over Celite. The resulting solution was cooled to  $-95\text{ }^{\circ}\text{C}$ , and 350  $\mu\text{L}$  of MeI solution (0.08 M in THF) was slowly added to the reaction mixture, whereupon its color turned yellow. Yellow crystals suitable for X-ray diffraction were obtained from THF/toluene/benzene. Yield: 9 mg, 15%. FTIR-ATR ( $\text{cm}^{-1}$ ):  $\nu(\text{CN}/\text{CO})$  2015 (s, broad),  $\nu(\text{CO})$  1917 (m), 1622 (w), 1596 (w), 1461 (w), 1422 (w), 1398 (w), 1362 (s), 1311 (w), 1274 (vs), 1171 (s), 1126 (vs), 971 (w), 900 (s), 879 (m), 847 (m), 778 (s), 751 (w), 735 (w), 705 (w), 681 (s), 637 (s), 620 (w), 550 (m), 498 (w), 471 (s), 431 (w), 420 (w).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm):  $\delta$  7.68 (s, 8H, Ph), 7.56 (s, 16H, Ph), 6.41 (d,  $J = 8\text{ Hz}$ , 8H, Ar-F), -1.85 (s, 1H, Re-Me).  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ , ppm):  $\delta$  -62.6 (s, 48F, Ph-CF<sub>3</sub>), -109.7 (broad t, 4F, Ar-F). MS ESI+ ( $m/z$ ):  $[\text{M}]^+$  2410.170 (1.5%). Calcd for  $\text{C}_{94}\text{H}_{35}\text{F}_{52}\text{N}_4\text{ORe}$ : 2410.154.

$[\text{Re}(\text{CO})\text{H}(\text{CNAr}^{\text{DArF}_2})_4]$ .  $[\text{Re}(\text{CO})\text{Br}(\text{CNAr}^{\text{DArF}_2})_4]$  (60 mg, 0.024 mmol) was dissolved in THF (3 mL), and 0.1% Na/Hg (Na: 0.003 g; Hg: 3 g; 5 equiv of Na/Re) was added. The mixture was vigorously stirred for 3 h and filtered over Celite. The resulting solution was cooled to  $-95\text{ }^{\circ}\text{C}$ , and 350  $\mu\text{L}$  of a HCl solution (0.08 M in THF) was slowly added to the reaction mixture, whereupon its color turned yellow. Crystals suitable for X-ray structure determination were obtained from benzene. Yield: 6 mg, 10%. FTIR-ATR ( $\text{cm}^{-1}$ ):  $\nu(\text{CN})$  2021 (s),  $\nu(\text{presumably Re-H})$  1979 (s),  $\nu(\text{CO})$  1938 (s), 2963 (w), 1597 (w), 1462 (w), 1420 (w), 1399 (w), 1363 (s), 1312 (w), 1276 (s), 1260 (s), 1171 (s), 1126 (vs), 1098 (vs), 1015 (vs), 913 (m), 901 (s), 877 (s), 847 (s), 796 (vs), 752 (w), 734 (w), 705 (m), 694 (m), 666 (s), 637 (s), 620 (w), 569 (w), 564 (w), 434 (w).  $^1\text{H}$  NMR (THF- $d_6$ , ppm):  $\delta$  7.76 (s, 16H, Ph), 7.72 (s, 8H, Ph), 7.42 (d,  $J = 8\text{ Hz}$ , 8H, Ar-F), -4.96 (s, 1H, Re-H). MS ESI+ ( $m/z$ ):  $[\text{M}]^+$  2396.164 (2.7%). Calcd for  $\text{C}_{93}\text{H}_{33}\text{F}_{52}\text{N}_4\text{ORe}$ : 2396.138.

$[\text{Re}(\text{CO})\text{Cl}(\text{CNAr}^{\text{DArF}_2})_4]$ .  $[\text{Re}(\text{CO})\text{Br}(\text{CNAr}^{\text{DArF}_2})_4]$  (60 mg, 0.024 mmol) was dissolved in THF (3 mL), and 0.1% Na/Hg (Na: 0.003 g; Hg: 3 g; 5 equiv of Na/Re) was added. The mixture was vigorously stirred for 3 h and filtered over Celite. The resulting solution was cooled to  $-95\text{ }^{\circ}\text{C}$ , and 350  $\mu\text{L}$  of a  $\text{C}_6\text{F}_5\text{C}(\text{O})\text{Cl}$  solution (0.08 M in THF) was slowly added to the reaction mixture, whereupon its color turned yellow. Crystals suitable for an X-ray structure determination were obtained from  $\text{Et}_2\text{O}/\text{hexane}$ . Yield: 23 mg, 35%. FTIR-ATR ( $\text{cm}^{-1}$ ):  $\nu(\text{CN})$  2101 (sh),  $\nu(\text{CN})$  2052 (s),  $\nu(\text{CN})$  2033 (s),  $\nu(\text{CN})$  2026 (sh),  $\nu(\text{CO})$  1923 (w),  $\nu(\text{CO})$  1913 (w), 2963 (w), 1739 (br), 1652 (w), 1596 (w), 1524 (w), 1499 (m), 1475 (w), 1462 (w), 1422 (w), 1399 (m), 1363 (s), 1328 (w), 1314 (w), 1276 (vs), 1261 (s), 1222 (w), 1172 (s), 1127 (vs), 1099 (vs), 1006 (vs), 913 (w), 901 (s), 878 (m), 847 (m), 751 (vs), 735 (w), 705 (s), 694 (w), 681 (vs), 638 (m), 621 (w), 589 (w), 547 (w).  $^{19}\text{F}$  NMR (THF, ppm):  $\delta$  -64.6 (s, 48F, Ph-CF<sub>3</sub>), -111.9 (t,  $J = 8\text{ Hz}$ , 4F, Ar-F). MS ESI+ ( $m/z$ ):  $[\text{M} + \text{Na}]^+$  2452.5222. Calcd for  $\text{C}_{93}\text{H}_{32}\text{ClF}_{52}\text{N}_4\text{NaORe}$ : 2452.8895.

$[\text{Tc}(\text{CO})\text{Cl}(\text{CNAr}^{\text{DArF}_2})_4]$ .  $\text{CNAr}^{\text{DArF}_2}$  (436 mg, 0.80 mmol, 4.5 equiv) was added to a suspension of  $(\text{NBu}_4)[\text{Tc}_2(\mu\text{-Cl})_3(\text{CO})_6]$  (63 mg, 0.088 mmol) in 9 mL of toluene. The resulting mixture was stirred for 20 h in boiling toluene. The resulting orange-red solution was concentrated to a minimum volume, and hexane was added. Storage

at  $4\text{ }^{\circ}\text{C}$  for 12 h resulted in the formation of orange-red crystals of  $[\text{Tc}(\text{CO})\text{Cl}(\text{CNAr}^{\text{DArF}_2})_4]$ , which were collected and dried *in vacuo*. Crystals suitable for X-ray diffraction were obtained from THF/toluene. Yield: 0.304 g, 0.130 mmol, 74%. FTIR (in KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{CN})$  2064 (s),  $\nu(\text{CN})$  1982 (w),  $\nu(\text{CO})$  1935 (s), 3095 (w), 2961 (w), 2936 (w), 2874 (w), 1597 (m), 1460 (m), 1421 (w), 1398 (m), 1364 (s), 1312 (w), 1279 (s), 1175 (s), 1134 (s), 1109 (m), 972 (w), 903 (m), 879 (m), 847 (m), 752 (w), 735 (w), 706 (s), 683 (s), 638 (w), 594 (w), 523 (w), 463 (w). Elemental analysis: Tc, 4.6; calcd for  $\text{C}_{93}\text{H}_{32}\text{ClF}_{52}\text{N}_4\text{OTc}$ , 4.2%.  $^1\text{H}$  NMR (THF- $d_8$ , ppm):  $\delta$  7.74 (s, 16H, Ph), 7.73 (s, 8H, Ph), 7.42 (d,  $J = 8\text{ Hz}$ , 8H, Ar-F).  $^{19}\text{F}$  NMR (THF- $d_8$ , ppm):  $\delta$  -65.6 (s, 48F, Ph-CF<sub>3</sub>), -123.9 (broad t, 4F, Ar-F).  $^{99}\text{Tc}$  NMR (THF, ppm):  $\delta$  -1542.

$\text{Na}[\text{Tc}(\text{CO})\text{Cl}(\text{CNAr}^{\text{DArF}_2})_4]$ .  $[\text{Tc}(\text{CO})\text{Cl}(\text{CNAr}^{\text{DArF}_2})_4]$  (40 mg, 0.017 mmol) was dissolved in THF (3 mL), and 0.1% Na/Hg (Na: 0.003 g; Hg: 3 g; 8 equiv of Na/Tc) was added. The mixture was vigorously stirred for 3 h giving a deep red solution. This solution was decanted from Na/Hg for the measurement of the NMR (and EPR) spectra.  $^{19}\text{F}$  NMR (THF, ppm):  $\delta$  -65.1 (s, 48F, Ph-CF<sub>3</sub>), -112.2 (t,  $J = 8\text{ Hz}$ , 4F, Ar-F).  $^{99}\text{Tc}$  NMR (THF, ppm):  $\delta$  -1865.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.1c00124>.

Crystallographic tables, bond lengths, angles and ellipsoid plots. Spectroscopic data (PDF)

### Accession Codes

CCDC 2056019–2056025 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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