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A mixed isocyanide Mn(I) complex and its reduction to a metallate†

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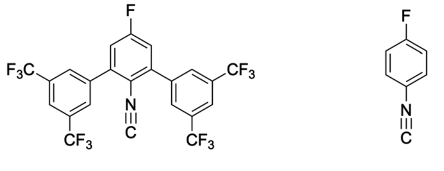
A stepwise ligand exchange starting from [Mn(CO)$_5$Br] allows the synthesis of the heteroleptic isocyanide manganese(I) complex *mer,trans*-[Mn(CN*p*-FAr^{DArF2})$_3$(CN^{t}Bu)$_2$Br] (DArF = 3,5-(CF$_3$)$_2$C$_6$H$_3$, ^{t}Bu = *tert*-butyl). Subsequent reduction gave the first heteroleptic isocyanide manganese(−1) complex, [K(18-crown-6)][Mn(CN*p*-FAr^{DArF2})$_3$(CN^{t}Bu)$_2$], exhibiting a five-coordinate, trigonal bipyramidal coordination sphere.

Isocyanides are versatile ligands due to their unique electronic properties, combining strong σ-donor and π-acceptor capabilities.[1,2] Their complexes have found consideration in various fields of application including nuclear medical procedures.[3–6] Several studies have demonstrated that, in analogy to the corresponding carbonyls, isocyanide complexes with metals in formally negative oxidation states can also be isolated.[7–14] Such complexes have been prepared with various metals in the d-block of the periodic table, including the full set of the group 7 metal triad.[12] Most of these metalate complexes contain carbonyl co-ligands,[10–13] but there is also one example of a manganese(−1) complex with five 2,6-dimethylphenyl isocyanide ligands.[14] Such isocyanide metalates are commonly homoleptic in terms of their CNR ligands. In general, heteroleptic transition metal isocyanide complexes are rare,[15–19] which is most probably related to the lack of suitable synthetic approaches. Nevertheless, the ready access to such compounds would be highly desirable, particularly for the synthesis of compounds with well-balanced properties for chemical (*e.g.* catalysis: manganese and rhenium) or medical applications (technetium). A good example is the use of [^{99m}Tc(CNR)$_6$]$^+$ cations for myocardial imaging in nuclear medicine. They contain six identical isocyanide ligands and it is evident that the optimization of their biological properties is difficult, requiring extensive tests with a huge number of different isocyanides before a hexakis complex with 2-methoxy-2-methylpropyl isocyanide was found to be suitable for the intended routine application.[6] The existence of only one or two molecular position(s) for ongoing coupling reactions is favourable for the development of conjugates with distinct chemical or biological properties.[19]

Recently, we described a stepwise ligand exchange of carbonyl ligands by different isocyanides, demonstrating that their reactivity can readily be influenced by steric and electronic factors.[20,21] Key compounds of such considerations are aromatic isocyanides. They are commonly more reactive than aliphatic ones, and their bonding capabilities can be controlled by the attachment of suitable substituents. Thus, reactions with fluorinated phenylisocyanides proved to be useful for the synthesis of heteroleptic isocyanide complexes, and compounds such as [Tc(CN*p*-FAr^{DArF2})$_3$(CN^{t}Bu)$_2$(CN^{n}Bu)](PF$_6$) (DArF = 3,5-(CF$_3$)$_2$C$_6$H$_3$, ^{t}Bu = *tert*-butyl, ^{n}Bu = *n*-butyl) could be isolated in crystalline form.[20] The terphenyl isocyanide CN*p*-FAr^{DArF2} (Fig. 1) provides sufficient reactivity to replace CO ligands, while the 3,5-(CF$_3$)$_2$C$_6$H$_3$ substituents at the *meta* position provide steric protection against the complete replacement of the central coordination sphere of the metal. In contrast, ligand exchange reactions with the 'unprotected' *p*-F-phenyl isocyanide readily give the corresponding hexakis(isocyanide) complexes.[20,21] Similar reactivity has been observed for rhenium, but marked differences in the observed reaction



CN*p*-FAr^{DArF2} CN*p*-FPh

Fig. 1 Fluorinated phenyl isocyanides.

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rates caused problems in the isolation of pure products in reasonable amounts.[11–13,19–21] This fact makes it interesting to extend the corresponding studies to compounds of the lightest 'group 7 element'.

The general route described for the synthesis of the heteroleptic isocyanide technetium(I) complexes also represents a suitable approach for the corresponding metalates. A reaction sequence, which gave access to the first example of such a compound, is shown in Scheme 1. It starts from $[Mn(CO)_5Br]$ (**1**) and its reaction with CN^tBu at room temperature. Such reactions with alkyl isocyanides typically end with the exchange of only two carbonyl ligands and the formation of neutral $[M(CO)_3(CNR)_2X]$ complexes (R = alkyl, X = Cl, Br) as has also been described for M = Tc or Re.[22–25] The progress of the reaction can readily be monitored by IR and NMR spectroscopy. The better donor capabilities of (particularly fluorinated) phenyl isocyanides can be used to replace the remaining three carbonyl ligands in $[Mn(CO)_3(CN^tBu)_2Br]$ (**2**). Thus, a subsequent reaction with three equivalents of CN*p*-FAr^{DArF2} in boiling toluene afforded the formation of the neutral manganese(I) complex *mer*,*trans*-$[Mn(CN$*p*-$FAr^{DArF2})_3(CN^tBu)_2Br]$ (**3**).

Bright orange-red crystals were obtained upon cooling with a yield of 40%. The IR spectrum of **3** displays characteristic ν_{CN} absorptions at 2113, 2024, and 1952 cm^{-1}, confirming the successful replacement of carbonyl ligands. ^{19}F and ^1H NMR spectra indicate magnetic equivalence of the CN^tBu ligands, but a 2 : 1 split of CN*p*-FAr^{DArF2} ligands, which can be best seen with the signals of the *p*-F atoms of the central ring. The spectra suggest an octahedral geometry for complex **3** with meridional coordination of CN*p*-FAr^{DArF2} ligands and a *trans* arrangement of the CN^tBu ligands. Such a bonding situation is analogous to that of the previously reported technetium complex,[20] and single-crystal X-ray diffraction confirms the spectroscopically derived arrangement of the ligands. The molecular structure of **3** is depicted in Fig. 2.

The M–C bond lengths in the manganese complex **3** are generally slightly shorter than those in the analogous technetium compound,[19,20] which is in accord with the corresponding ionic radii and electronegativities.[26,27] In both compounds, however, the same trends concerning the bonding to the different isocyanide ligands are observed. A complete listing of the bond lengths can be found in the ESI.† It is interesting to note that the bulkier CN*p*-FAr^{DArF2} ligands do not simply replace the carbonyl ligands in **2** but are shifted to meridional coordination positions. Such ligand rearrangements during CO/CNR or CNR^1/CNR^2 exchange reactions have previously been a matter of interest and are mainly attributed to electronic effects.[15,28–30] This might also play a role in the present case, but the observed direction of the bulkiest ligands at equatorial positions will also contribute to reducing steric strain in the coordination sphere. It should be noted that there is to date no example of the coordination of three CN*p*-FAr^{DArF2} ligands at *facial* positions.[29,30]

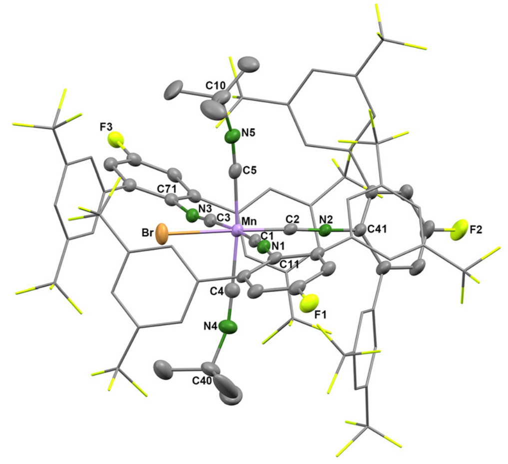
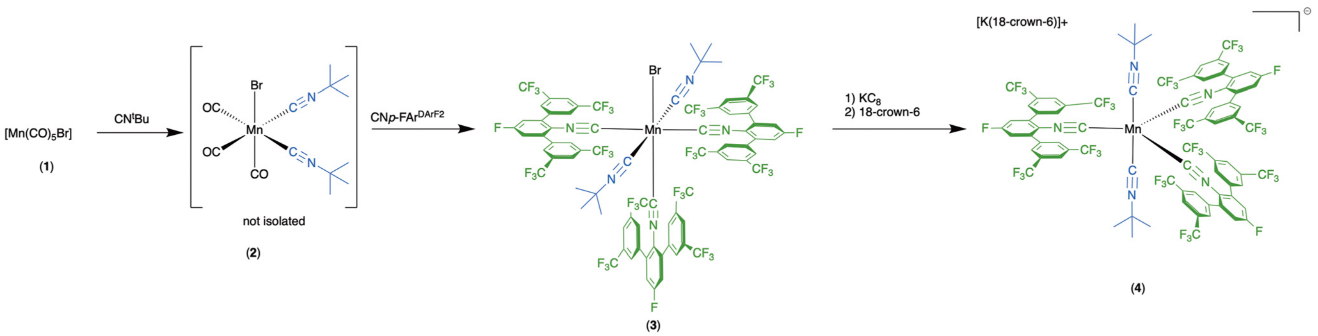


Fig. 2 Molecular structure of *mer*,*trans*-$[Mn(CN$*p*-$FAr^{DArF2})_3(CN^tBu)_2Br]$ (**3**). Thermal ellipsoids represent 30% probability.

Reduction of *mer*,*trans*-$[Mn(CN$*p*-$FAr^{DArF2})_3(CN^tBu)_2Br]$ with KC_8 in tetrahydrofuran (Scheme 1) yields the manganate complex $[K(18\text{-crown-}6)][Mn(CN$*p*-$FAr^{DArF2})_3(CN^tBu)_2]$ (**4**). The reaction proceeds by mixing the bromido complex **3** with two equivalents of freshly prepared KC_8 under an argon atmosphere, followed by the addition of 18-crown-6 to sequester the potassium ions. Dark red, moisture- and air-sensitive crystals were isolated in yields of approximately 40% after recrystallization from a cold toluene/benzene mixture. Slightly better yields are obtained using an excess of KC_8. The thus-formed



Scheme 1 Reaction pathway towards *mer*,*trans*-$[Mn(CN$*p*-$FAr^{DArF2})_3(CN^tBu)_2Br]$ (**3**) and its subsequent reduction with KC_8 to form $[K(18\text{-crown-}6)][Mn(CN$*p*-$FAr^{DArF2})_3(CN^tBu)_2]$ (**4**).

products, however, contain some impurities and hence, elaborate purification procedures are required.

The IR spectrum of product **4** exhibits strong ν_{CN} bands at 1896 and 1807 cm^{-1}. They are indicative of enhanced electron density on the manganese atom due to its reduction. The shifts to lower frequencies are consistent with an increased back-donation from the metal to the isocyanide ligands. ^{19}F and ^{1}H NMR spectra indicate magnetic equivalence of the three CN*p*-FAr^{DArF2} ligands as well as the two CN^{t}Bu ligands. The 3 : 2 integral ratio between the signals of both ligands suggests that the complex adopts a five-coordinate geometry with CN^{t}Bu ligands in a *trans* configuration. This is confirmed by X-ray diffraction (Fig. 3).

The manganese atom in the complex anion [Mn(CN*p*-FAr^{DArF2})$_3$(CN^{t}Bu)$_2$]$^-$ is expectedly five-coordinate with an almost perfect trigonal bipyramidal structure as can be concluded by means of the τ parameter of 0.8 introduced by Addison *et al.*[31,32] The same result is obtained following the continuous shape approach,[33–37] which gives a small continuous shape measure of 0.31353 for a trigonal bipyramid, which is in contrast to the significantly larger value of 3.50768 for a square pyramid. Some deviations from the ideal geometry are due to the steric bulk of the ligands and electronic factors. The sterically less demanding CN^{t}Bu ligands are in axial positions, while the bulky CN*p*-FAr^{DArF2} ligands occupy the equatorial coordination sphere.

The Mn–isocyanide bonds in the manganate ion are between 1.811(4) and 1.877(4) Å, with slightly larger values for the equatorial Mn–C1/C2/C3 bonds. An interesting structural feature in **4** is the widening of the C–N–C angles of the CN^{t}Bu ligand. Similar effects have been observed previously, particularly for highly reduced metal ions with bulky terphenyl isocyanides, including the corresponding compounds with the 'group 7 metals' technetium and rhenium.[9,12,13,17,18,30,38–43] Frequently, such bent bonds are accompanied by supporting η^6-bonded aromatic rings or by side-on coordination of alkali metal ions to the C≡N triple bond. This, however, is not the case in the mixed-ligand [Mn(CN*p*-FAr^{DArF2})$_3$(CN^{t}Bu)$_2$]$^-$ anion, and the observed effect is more evident for the axial aliphatic ligands than the equatorial terphenyl ones and shall here most probably be attributed to enhanced back-donation.

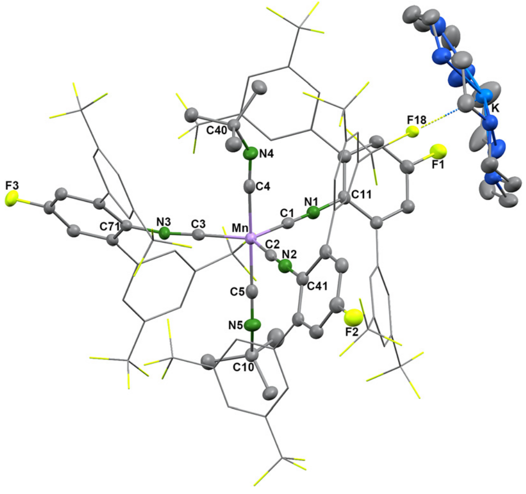


Fig. 3 Molecular structure of [K(18-crown-6)][Mn(CN*p*-FAr^{DArF2})$_3$(CN^{t}Bu)$_2$] (**4**). Thermal ellipsoids represent 30% probability.

The present study illustrates that technetium chemistry can be translated to manganese, enabling the synthesis of Mn(I) complexes with two different isocyanides. The subsequent reduction towards [K(18-crown-6)][Mn(CN*p*-FAr^{DArF2})$_3$(CN^{t}Bu)$_2$] represents a significant addition to the limited number of structurally characterized complexes known to contain Mn(−1).

Such highly reduced complexes can react with various electrophiles, thereby opening new pathways for synthetic chemistry. Related reactions have also been performed for technetium and rhenium.[11–13,41] Consequently, the metallate may prove to be a valuable intermediate, potentially allowing access to isocyanide chemistry comparable to the well-established carbonyl chemistry of manganese.[44] Reactions with electrophiles (including organic ones), which are outside the scope of the present communication, will be an interesting starting point for further studies.

Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data for compounds **2** and **3** have been deposited at the Cambridge Crystallographic Data Centre under accession numbers CCDC 2410581 (**2**) and 2410582 (**3**).†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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