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Comparison of nucleophilic- and radical-based routes to the formation of manganese-main group element single bonds†

Douglas W. Agnew, Curtis E. Moore, Arnold L. Rheingold and Joshua S. Figueroa *

Using the stable metalloradical $Mn(CO)_3(CNAr^{Dipp2})_2$, we report the formation of manganese-main group complexes *via* the single-electron functionalization of main group halides. The reactions occur in a simple 1 : 1 stoichiometry, and demonstrate the utility of using stable open-shelled organometallics as precursors for metal-main group compounds. This has enabled the preparation of manganese complexes bearing terminal $-EX_n$ substituents, as shown through the isolation of $Mn(SnCl)(CO)_3(CNAr^{Dipp2})_2$ and $Mn(BiCl_2)(CO)_3(CNAr^{Dipp2})_2$ from $SnCl_2$ and $BiCl_3$, respectively. Through this approach, we have also isolated $Mn(SbF_2)(CO)_3(CNAr^{Dipp2})_2$ from SbF_3, which serves as a unique example of a terminal $-SbF_2$ complex. Although the metalloradical functionalization of binary main group halides provides the desired main group adduct in yields comparable to nucleophilic activation using the manganate $Na[Mn(CO)_3(CNAr^{Dipp2})_2]$, the former approach is shown to be far more atom-economical with respect to Mn. Additionally, we have found that $Mn(CO)_3(CNAr^{Dipp2})_2$ also serves as a convenient precursor to $MnF(CO)_3(CNAr^{Dipp2})$. The latter is an analogue to the elusive monofluoride $FMn(CO)_5$.

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Introduction

Bifunctional catalysis mediated by transition metal-main group compounds is becoming an increasingly effective means towards facilitating difficult bond cleavage steps in catalytic cycles.[1] While this concept has found wide applicability with ancillary boryl ligands,[2–5] it has recently been shown that other Group 13 element fragments,[6,7] as well as fragments featuring heavier pnictogen atoms,[8,9] can fill the role as an effective Lewis acid. However, the generation of these complexes remains a particular challenge due to the difficulty in preparing stable main-group nucleophiles to functionalize various metal species.[10,11] Additionally, the development of synthetic routes using binary main group halides remains largely limited to either oxidative addition with late-row transition metals[4,5,12,13] or nucleophilic reactions with classical carbonyl metallates.[14]

For nucleophilic derivatization reactions, complications can arise as a result of multiple additions in sterically uncongested systems,[15,16] as well as the tendency of main-group halides to function as oxidants[17] towards reduced metal species. This often results in irreversible dimerization of the transition metal complex as a consequence of metalloradical formation. However, in limited cases some dinuclear metal complexes are capable of homo-fragmentation to produce short-lived metalloradicals, which can subsequently react with a main group fragment.[18–20] This strategy has proven to be particularly powerful in generating unique transition metal-main group species.[20] To examine this pathway in more detail, we have investigated the activation of binary main group halides with the stable manganese metalloradical $Mn(CO)_3(CNAr^{Dipp2})_2$,[21] with comparison to nucleophilic reaction pathways accomplished by the corresponding manganate $Na[Mn(CO)_3(CNAr^{Dipp2})_2]$ (Ar^{Dipp2} = 2,6-(2,6-(i-Pr)$_2C_6H_3)_2C_6H_3$).[22] Importantly, we have found that the use of sterically encumbering *m*-terphenyl isocyanides[23–41] facilitates the formation of unique, terminal main group substituents without the occurrence of dimerization.

We recently reported the preparation of $Mn(CO)_3(CNAr^{Dipp2})_2$, a zerovalent, square-pyramidal complex that serves as an analogue to the unstable metalloradical $Mn(CO)_5$.[21] Consistent with its low-spin, d^7 ground state, $Mn(CO)_3(CNAr^{Dipp2})_2$ acts as a potent atom abstraction reagent and competent radical scavenger in solution. For example, addition of 1 equiv. $CHCl_3$ to $Mn(CO)_3(CNAr^{Dipp2})_2$ resulted in the generation of $MnCl(CO)_3(CNAr^{Dipp2})_2$ and $Mn(CHCl_2)(CO)_3(CNAr^{Dipp2})_2$ in a

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Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, Mail Code 0358, La Jolla, CA 92093, USA. E-mail: jsfig@ucsd.edu

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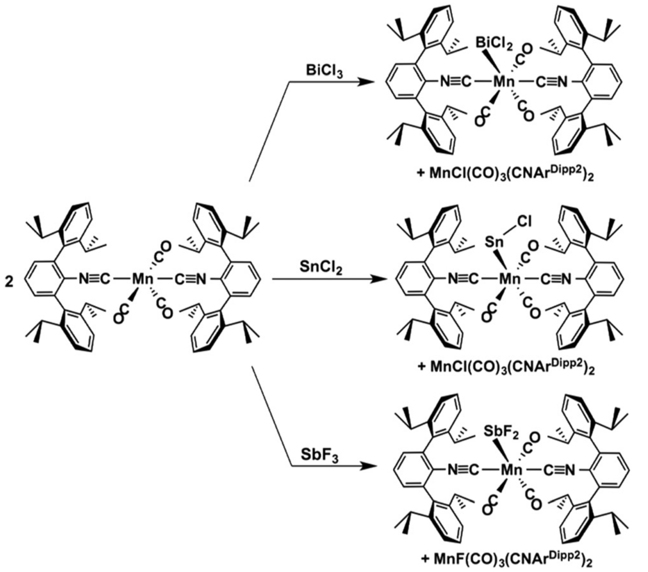
1 : 1 ratio. Interestingly, this reactivity was found to carry over to Sn(IV) species as well. For example, reaction of 1 equiv. of $HSn(n\text{-}Bu)_3$ with $Mn(CO)_3(CNAr^{Dipp2})_2$ was found to produce an equimolar mixture of $MnH(CO)_3(CNAr^{Dipp2})_2$ as well as the stannyl complex $Mn(Sn(n\text{-}Bu)_3)(CO)_3(CNAr^{Dipp2})_2$. This suggested that the intrinsic reactivity of $Mn(CO)_3(CNAr^{Dipp2})_2$ could be used to facilitate the formation of unique, low-valent manganese adducts with substrates containing homolytically cleavable E–X bonds. This mode of reactivity should thus be complementary to the manganate complex $Na[Mn(CO)_3(CNAr^{Dipp2})_2]$, which has been established to react with tin(II) dichloride to form the unique chloro-substituted metallostannylene, $Mn(SnCl)(CO)_3(CNAr^{Dipp2})_2$. Accordingly, herein we show that complexes possessing manganese/main group element bonds can be readily accessed by a radical-type approach using the neutral metalloradical $Mn(CO)_3(CNAr^{Dipp2})_2$. These reactions proceed with high atom-economy and can succeed in some cases where nucleophilic-derivitization/salt elimination routes fail to easily provide the desired product. In addition, in the course of this study we have prepared the monofluoro complex $MnF(CO)_3(CNAr^{Dipp2})_2$, which serves as an analogue to the unknown organometallic fluoride $FMn(CO)_5$.[42]

Results and discussion

Based upon the observed reactivity of $Mn(CO)_3(CNAr^{Dipp2})_2$ with $CHCl_3$ and $HSn(n\text{-}Bu)_3$, we anticipated that a simple 1 : 1 stoichiometry between $Mn(CO)_3(CNAr^{Dipp2})_2$ and a main group halide should result in a product mixture containing the Mn-main group adduct and the corresponding halide complex $MnX(CO)_3(CNAr^{Dipp2})_2$. Indeed, addition of $SnCl_2$ to a stirring diethyl ether solution of $Mn(CO)_3(CNAr^{Dipp2})_2$ provides $MnCl(CO)_3(CNAr^{Dipp2})_2$[21] and the previously reported metallostannylene complex, $Mn(SnCl)(CO)_3(CNAr^{Dipp2})_2$,[22] in approximately a 1.3 : 1 ratio, as assayed by ^1H NMR spectroscopy. Isolation of $Mn(SnCl)(CO)_3(CNAr^{Dipp2})_2$ is readily accomplished *via* *n*-pentane extraction of the product mixture, as $MnCl(CO)_3(CNAr^{Dipp2})_2$ is insoluble in *n*-pentane, providing green microcrystals in 32% yield upon removal of volatiles. While this yield falls below that previously reported for the corresponding salt metathesis route using $Na[Mn(CO)_3(CNAr^{Dipp2})_2]$, it is notable that the metalloradical pathway allows for nearly quantitative recovery of Mn metal centers (as $Mn(SnCl)(CO)_3(CNAr^{Dipp2})_2$ and $MnCl(CO)_3(CNAr^{Dipp2})_2$) by mass balance. As shown previously, the chloride complex can be easily reduced by one or two electrons to regenerate $Mn(CO)_3(CNAr^{Dipp2})_2$ or $[Mn(CO)_3(CNAr^{Dipp2})_2]^-$, respectively, which can then be reused in further reactions.[39] Importantly, this result supports a metalloradical approach towards Sn(II) derivatization, similar to that previously observed for the related reactivity with Sn(IV) substrates.

To further explore the generality of this metalloradical approach and its comparison to salt elimination using $Na[Mn(CO)_3(CNAr^{Dipp2})_2]$, we examined the reactivity with several readily available main group halides (Scheme 1). It was discovered that the character of the halide played an important role in facilitating a favorable transformation. Indeed, while $SbCl_3$ and SbI_3 led solely to $MnCl(CO)_3(CNAr^{Dipp2})_2$ and $MnI(CO)_3(CNAr^{Dipp2})_2$,[39] respectively, it was found that SbF_3 reacts with $Mn(CO)_3(CNAr^{Dipp2})_2$ over several days in DME solution to form $Mn(SbF_2)(CO)_3(CNAr^{Dipp2})_2$ and $MnF(CO)_3(CNAr^{Dipp2})_2$ in approximately a 1 : 1 ratio. Analysis of the product mixture by ^{19}F NMR spectroscopy reveals two singlets at −59.7 ppm and −166.0 ppm, and solution infrared spectroscopy supports the presence of two C_{2v}-symmetric complexes with isocyanide stretches at 2118 cm^{-1} and 2086 cm^{-1}. Indeed, crystallization of the product mixture in THF produces a combination of bright yellow and orange crystals. Extraction of this mixture with *n*-pentane followed by recrystallization in pyridine was found to provide $Mn(SbF_2)(CO)_3(CNAr^{Dipp2})_2$ in 43% yield, which gives rise to the ^{19}F NMR signal at −166.0 ppm. Crystallographic analysis of $Mn(SbF_2)(CO)_3(CNAr^{Dipp2})_2$ revealed an octahedral geometry about manganese in the solid state with a Mn–Sb distance of 2.6111(6) Å (Fig. 1). The three-coordinate Sb center adopts a distorted pyramidal geometry (average of two positionally disordered $-SbF_2$ fragments: $\angle(Mn\text{–}Sb\text{–}F) = 100.3(4)^\circ$; $\angle(F\text{–}Sb\text{–}F) = 92.0(5)^\circ$. While three-coordinate, terminal transition metal stibyl halides (*e.g.* L_nMSbX_2) are known for chloro-derivatives,[13,15,43] $Mn(SbF_2)(CO)_3(CNAr^{Dipp2})_2$ represents a unique example of a monomeric difluorostibyl complex without intermolecular catenation between $-SbF_2$ centers.[44] Notably, it was found that $Mn(SbF_2)(CO)_3(CNAr^{Dipp2})_2$ could also be synthesized *via* a salt elimination route from $Na[Mn(CO)_3(CNAr^{Dipp2})_2]$ and SbF_3 in 54% yield, thus revealing a complementarity between the nucleophilic displacement and atom abstraction approaches. However, as observed for the reactivity with $SnCl_2$, the atom



Scheme 1 Reactivity of $Mn(CO)_3(CNAr^{Dipp2})_2$ with $BiCl_3$, $SnCl_2$ and SbF_3.

abstraction route allows nearly quantitative recovery of Mn centers (as $Mn(SbF_2)(CO)_3(CNAr^{Dipp2})_2$ and $MnF(CO)_3(CNAr^{Dipp2})_2$), whereas 46% of the molar equivalents of Mn are lost to intractable products in the salt elimination route.

Radical-type formation of Mn-bound heavier pnictogen dihalides is not limited to antimony. While attempts to generate the corresponding $-BiF_2$ adduct using BiF_3 under similar conditions did not lead to a productive reaction, addition of 1 equiv. of solid $BiCl_3$ to a stirring diethyl ether solution of $Mn(CO)_3(CNAr^{Dipp2})_2$ provided $MnCl(CO)_3(CNAr^{Dipp2})_2$ and $Mn(BiCl_2)(CO)_3(CNAr^{Dipp2})_2$ in a 2.5 : 1 ratio, as assayed by ^1H NMR spectroscopy. We contend this low ratio is the result of the thermal- and photo-sensitivity of $Mn(BiCl_2)(CO)_3(CNAr^{Dipp2})_2$ (*vide infra*). Recrystallization of the product mixture affords red and yellow crystals of $Mn(BiCl_2)(CO)_3(CNAr^{Dipp2})_2$ and $MnCl(CO)_3(CNAr^{Dipp2})_2$, respectively, which can be manually separated. Following separation, ^1H NMR spectroscopic analysis of the red crystals indicated the isocyanide ligands are in identical chemical environments, supporting a *trans*-stereochemical orientation. Indeed, $Mn(BiCl_2)(CO)_3(CNAr^{Dipp2})_2$ adopts an octahedral coordination geometry about Mn in the solid state, with a Mn–Bi distance of 2.6809(10) Å, which is similar to other isolated transition metal halobismuth complexes.[12,15,45] While most transition metal halobismuth complexes form bridging interactions in the solid state,[46–48] $Mn(BiCl_2)(CO)_3(CNAr^{Dipp2})_2$ does not exhibit intermolecular contacts due to the encumbering nature of the $CNAr^{Dipp2}$ ligands. However, despite the increased kinetic stabilization afforded by $CNAr^{Dipp2}$, $Mn(BiCl_2)(CO)_3(CNAr^{Dipp2})_2$ is thermally unstable above −40 °C and shows significant sensitivity to light. Indeed, allowing $Mn(BiCl_2)(CO)_3(CNAr^{Dipp2})_2$ to stir in the dark at room temperature for 3 h, or exposing −40 °C solutions to ambient light for 20 minutes, resulted in the formation of $MnCl(CO)_3(CNAr^{Dipp2})_2$ and a black precipitate, which we presume to be solid Bi^0.

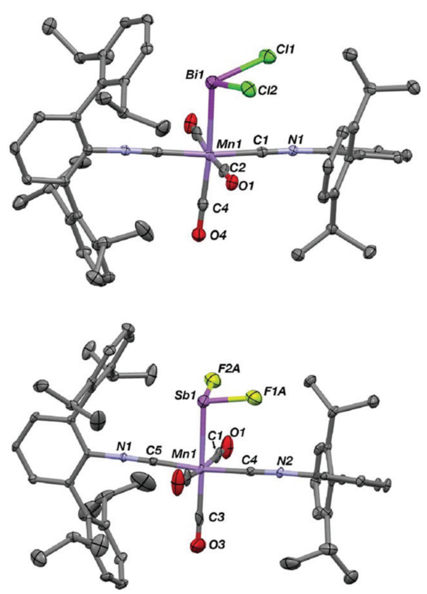


Fig. 1 Solid state structures of $Mn(BiCl_2)(CO)_3(CNAr^{Dipp2})_2$ (top) and $Mn(SbF_2)(CO)_3(CNAr^{Dipp2})_2$ (bottom), with selected Dipp rings and H atoms omitted for clarity.

As mentioned above, $MnF(CO)_3(CNAr^{Dipp2})_2$ is among the two-component mixture resulting from reaction of $Mn(CO)_3(CNAr^{Dipp2})_2$ and SbF_3. An alternate synthesis, involving the addition of solid XeF_2 to a stirring fluorobenzene solution of $Mn(CO)_3(CNAr^{Dipp2})_2$, was found to provide $MnF(CO)_3(CNAr^{Dipp2})_2$ in 41% yield. Notably, we have not identified conditions where the use of $Na[Mn(CO)_3(CNAr^{Dipp2})_2]$ as a starting material has been found to provide $MnF(CO)_3(CNAr^{Dipp2})_2$, which highlights the utility of an open-shell starting material for the formation of this transition metal monofluoride. The infrared spectrum of $MnF(CO)_3(CNAr^{Dipp2})_2$ in C_6D_6 possesses an isocyanide band at 2118 cm^{-1} that is identical to those of the C_{2v}-symmetric halide complexes $MnCl(CO)_3(CNAr^{Dipp2})_2$, $MnBr(CO)_3(CNAr^{Dipp2})_2$, and $MnI(CO)_3(CNAr^{Dipp2})_2$.[39] This observation strongly suggests that the identity of the halide ligand does not effect the degree of π-backbonding by Mn to the isocyanide ligands. The ^{19}F NMR spectrum of $MnF(CO)_3(CNAr^{Dipp2})_2$ in C_6D_6 displays a singlet at −59.7 ppm, with no other signals observed between 200 to −500 ppm. However, the three downfield peaks in the $^{13}C\{^1H\}$ NMR spectrum corresponding to $CNAr^{Dipp2}$, CO_{trans}, and CO_{cis} at 172.5 ppm, 210.0 ppm, and 218.0 ppm, respectively, display carbon–fluorine coupling (J_{CF} = 11 Hz (CO_{trans}), 150 Hz ($CNAr^{Dipp2}$), 172 Hz (CO_{cis})) with J_{CF} constants consistent with a *mer*,*trans*-stereochemical arrangement. Notably, this complex serves as a mixed isocyanide/carbonyl analogue of $MnF(CO)_5$, which to date has not been observed.[42,49–52]

In an attempt to gain further insight into the structure of $MnF(CO)_3(CNAr^{Dipp2})_2$, single crystals were grown from a concentrated diethyl ether solution at −35 °C and subjected to X-ray crystallographic analysis. The resultant structure solution indicated the expected *mer*,*trans*-stereochemical arrangement of the CO and $CNAr^{Dipp2}$ ligands, respectively, and the fluoride ligand was located in the apical position from the electron density map. However, additional electron density corresponding to another HF unit was observed in close proximity to the Mn-bound fluoride atom, such that the structure from these crystals is more appropriately assigned as the bifluoride adduct $Mn(FHF)(CO)_3(CNAr^{Dipp2})_2$ (Fig. 2), with a F⋯F distance of 2.276(2) Å. This is, to our knowledge, the first structurally characterized low-valent manganese biflouride complex.[53] Indeed, ^1H NMR analysis of these crystals revealed the presence of a new product (Fig. S1.8 and S1.9†), which displayed a doublet (J_{HF} = 411 Hz) at 10.91 ppm (C_6D_6, 20 °C). Additionally, a doublet (J_{HF} = 400 Hz) at −187.85 ppm as well as a broadened singlet at −482.20 ppm was observed in the ^{19}F NMR spectrum. These data are consistent with previously reported transition metal fluorides in which an HF molecule is strongly H-bonded to the terminal fluoride ligand.[53,54] We contend this HF molecule likely originates from the reaction of XeF_2 with adventitious water in the system.[55,56] Despite

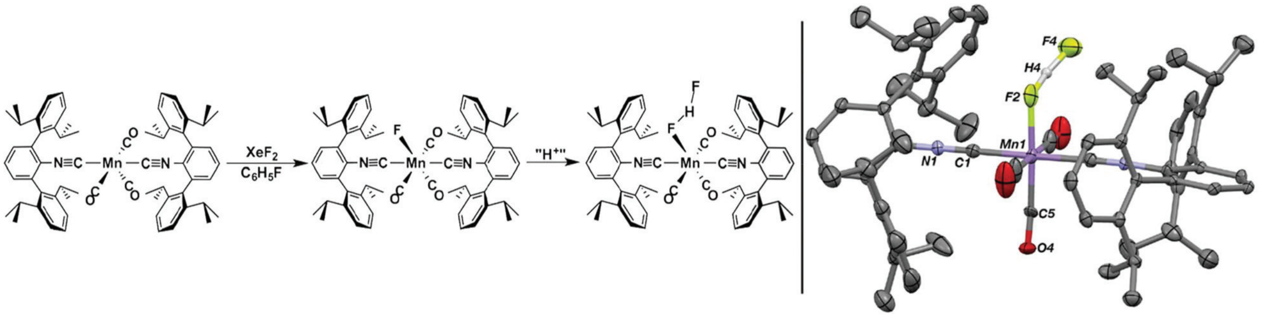


Fig. 2 (Left) Addition of XeF_2 in C_6H_5F results in the formation of $MnF(CO)_3(CNAr^{Dipp2})_2$. Decomposition *via* an adventitious proton source results in the formation of the bifluoride complex. (Right) Solid state structure of $Mn(FHF)(CO)_3(CNAr^{Dipp2})_2$ with H atoms omitted for clarity.

multiple attempts, we have thus far been unable to structurally characterize $MnF(CO)_3(CNAr^{Dipp2})_2$ in isolation; we nonetheless note that the formation of $MnF(CO)_3(CNAr^{Dipp2})_2$ in solution completes the halide series for mixed carbonyl/$CNAr^{Dipp2}$ manganese complexes, and provides a stable analogue to the unobserved metal carbonyl fluoride $FMn(CO)_5$.

While metalloradical $Mn(CO)_3(CNAr^{Dipp2})_2$ can be employed to generate metal bound main-group fragments, limitations were observed in several cases when attempting to more broadly extend this chemistry. For example, it was found that PCl_3, PCl_5, S_2Cl_2, and $AlCl_3$ generate $MnCl(CO)_3(CNAr^{Dipp2})_2$ as the exclusive product, and is invariant of the reaction stoichiometry. These reagents similarly produce $MnCl(CO)_3(CNAr^{Dipp2})_2$ when combined with $Na[Mn(CO)_3(CNAr^{Dipp2})_2]$, with the lone exception of $AlCl_3$, which generates $Mn(AlCl_2{\cdot}THF)(CO)_3(CNAr^{Dipp2})_2$ (Fig. 3) in 74% yield with loss of NaCl. The molecular structure determined from X-ray crystallography reveals an octahedral complex in which the Mn-bound $AlCl_2$ group also binds a THF molecule. Importantly, both the diamagnetic NMR spectrum as well as the isocyanide IR band (ν_{CN} = 2057 cm^{-1}) are consistent with a Mn(I) oxidation state, indicating the $-AlCl_2(THF)$ group to be behaving as an X-type ligand.[57] Attempts at thermal desolvation under vacuum led to intractable mixtures and, notably, preparations involving the use of non-coordinating solvents, such as benzene or toluene, led directly to the formation of $MnCl(CO)_3(CNAr^{Dipp2})_2$, potentially suggesting the necessity of an Al-solvento adduct in facilitating salt elimination. Interestingly, examples of transition metal-bound AlX_2 (X = halide) species are quite rare,[58,59] with only one reported metal-AlX_2 complex occurring with diamino substituents.[60] The pendant $Al(NR_2)_2$ groups in these latter complexes have been shown in some instances to behave as Lewis acidic sites and participate in cooperative reactivity with the transition metal center. Accordingly, we are currently developing an understanding of the pendant Lewis acidity in $Mn(AlCl_2{\cdot}THF)(CO)_3(CNAr^{Dipp2})_2$ towards Lewis-basic substrates.

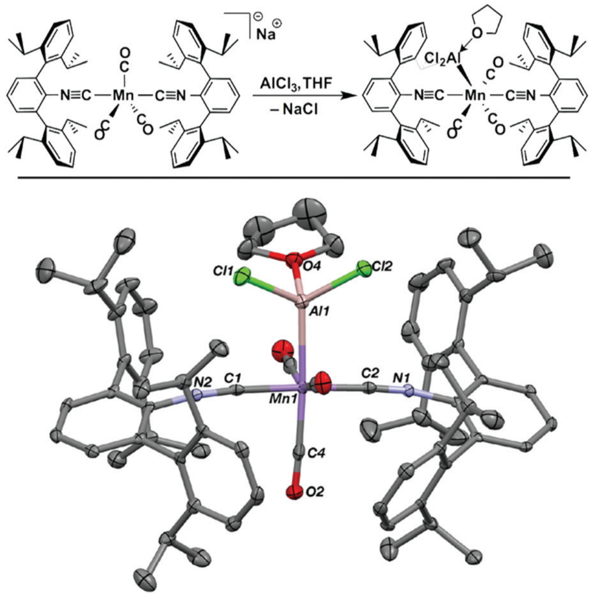


Fig. 3 (Top) Formation of $Mn(AlCl_2{\cdot}THF)(CO)_3(CNAr^{Dipp2})_2$ *via* addition of $AlCl_3$ to $Na[Mn(CO)_3(CNAr^{Dipp2})_2]$. (Bottom) Solid state structure of $Mn(AlCl_2{\cdot}THF)(CO)_3(CNAr^{Dipp2})_2$, with H atoms omitted for clarity.

The above results demonstrate that, under appropriate conditions, a diverse series of manganese-main group complexes are available by both metalloradical and traditional salt elimination routes. Notably, the product distribution in the cases of $BiCl_3$ and SbF_3 are significantly dependent on the starting metal complex, indicating different reaction pathways are being accessed. While this breadth of reactivity was not observed in all cases – $AlCl_3$ being the notable example – this indicates that bimodal, complementary reactivity available to the starting metal complex should allow for facile exploration of routes towards functionalized transition metal-main group adducts. We are currently working to expand the reaction chemistry surveyed here to understand more fully its advantages and limitations.

Experimental section

General considerations

All manipulations were performed under an atmosphere of dry dinitrogen using standard Schlenk and glovebox techniques, unless otherwise stated. Solvents were dried and degassed according to standard procedures. Reagent grade starting materials were purchased from commercial sources and used without further purification, unless otherwise stated. $SnCl_2$ was recrystallized from THF twice and thoroughly desolvated prior to use. The isocyanide ligand $CNAr^{Dipp2}$ was prepared according to literature procedures.[25] The compounds $Na[Mn(CO)_3(CNAr^{Dipp2})_2]$ and $Mn(CO)_3(CNAr^{Dipp2})_2$ have been previously reported.[21,22] Benzene-d_6 (Cambridge Isotope Laboratories) was stirred over NaK for two days, distilled, degassed, and stored over 4 Å molecular sieves.

Solution ^1H and ^{13}C NMR were recorded on a Bruker 300 spectrometer, a Varian 400 spectrometer, a Varian X-Sens 500 spectrometer, or a JEOL ECA-500 spectrometer. ^1H and ^{13}C NMR chemical shifts are reported in ppm relative to $SiMe_4$ (^1H and ^{13}C $\delta = 0.0$ ppm) with reference to residual proton resonances of 7.16 ppm (^1H) and 128.06 ppm (^{13}C) for benzene-d_6.[61] ^{19}F NMR spectra are reported relative to the external standard $BF_3{\cdot}(Et_2O)$ ($\delta = 0.0$ ppm). Room temperature FTIR spectra were recorded on a Thermo-Nicolet iS10 FTIR spectrometer. Samples were prepared as benzene-d_6 solutions injected into a ThermoFisher solution cell equipped with KBr windows. Solvent peaks were digitally subtracted from all solution FTIR spectra using a previously recorded spectrum of the solvent. Combustion analyses were performed by Robertson Microlit Laboratories of Madison, New Jersey (USA) and Midwest Microlabs of Indianapolis, Indiana. HR-MS was recorded at the UCSD Molecular Mass Spectrometry Facility using an Agilent 6230 Accurate-Mass TOFMS with acetonitrile as the eluent.

Synthesis of $Mn(SnCl)(CO)_3(CNAr^{Dipp2})_2$ and $MnCl(CO)_3(CNAr^{Dipp2})_2$

To a stirring diethyl ether solution of $Mn(CO)_3(CNAr^{Dipp2})_2$ (0.046 g, 0.046 mmol, 5 ml) was added solid $SnCl_2$ (0.009 g, 0.046 mmol, 1 eq.). The color of the solution turned from orange to light yellow over the course of 5 minutes, and the mixture was stirred a further 15 minutes before all volatiles were removed *in vacuo*. A ^1H NMR of the product mixture indicated a 1 : 1.3 distribution between $Mn(SnCl)(CO)_3(CNAr^{Dipp2})_2$ and $MnCl(CO)_3(CNAr^{Dipp2})_2$ based upon integration of the respective ($CH(CH_3)$) protons. Extraction of the product mixture with pentane (2 × 5 ml) provides $Mn(SnCl)(CO)_3(CNAr^{Dipp2})_2$ as a green solid. Yield: 0.032 g, 32%. Characterization data has been previously published.[22]

Synthesis of $Mn(SbF_2)(CO)_3(CNAr^{Dipp2})_2$ and $MnF(CO)_3(CNAr^{Dipp2})_2$

A DME solution of $Mn(CO)_3(CNAr^{Dipp2})_2$ (0.016 g, 0.016 mmol, 4 mL) was treated with SbF_3 (0.029 g, 10 eq.) in one portion at room temperature. The mixture was stirred for 12 hours, after which the DME was removed *en vacuo*. The solid was taken up in C_6H_6 and filtered, and all volatiles were removed under reduced pressure to provide a dull yellow solid. Integration from a ^1H NMR spectrum reveals formation of $Mn(SbF_2)(CO)_3(CNAr^{Dipp2})_2$ and $MnF(CO)_3(CNAr^{Dipp2})_2$ in a 1 : 1.1 ratio, respectively, based upon integration of the respective (p-Ar) protons. Extraction of this mixture with n-pentane (5 × 10 ml), followed by cooling of the extracts to −40 °C caused $Mn(SbF_2)(CO)_3(CNAr^{Dipp2})_2$ to precipitate as an orange solid. Yield: 0.008 g, 43%.

Synthesis of $Mn(SbF_2)(CO)_3(CNAr^{Dipp2})_2$ using $Na[Mn(CO)_3(CNAr^{Dipp2})_2$

To a stirring THF solution of $Na[Mn(CO)_3(CNAr^{Dipp2})_2]$ (0.108 g, 0.108 mmol, 8 ml) was added SbF_3 (0.029 g, 0.162 mmol, 1.5 eq.) as a solid, which turned the solution from deep purple to orange, with concurrent formation of a black precipitate. The mixture was filtered through a Celite plug and the volatiles removed under reduced pressure. The resulting orange solid was washed with pentane (4 × 5 ml) and then dissolved in benzene and filtered though a fiberglass plug. All volatiles were removed under reduced pressure, providing a light yellow solid. Yield: 0.067 g, 0.058 mmol, 54%. Diffraction quality crystals can be grown from a pyridine solution at −40 °C. ^1H NMR (500.2 MHz, C_6D_6, 20 °C) $\delta = 7.32$ (t, 2H, $J = 8$ Hz, p-Ar), 7.18 (d, 4H, $J = 8$ Hz, m-Ar), 6.93 (m, 8H, m-Dipp), 6.83 (dd, 4H, $J = 8.5$, 6.5 Hz, p-Dipp), 2.68 (sept, 8H, $J = 7$ Hz, $CH(CH_3)_2$), 1.38 (d, 24H, $J = 7$ Hz, $CH(CH_3)_2$), 1.01 (d, 24H, $J = 7$ Hz, $CH(CH_3)_2$) ppm. ^{13}C NMR (125 MHz, C_6D_6, 20 °C) = 211.6 (CO), 172.5 (CNR), 146.5, 139.2, 134.7, 130.1, 129.7, 123.6, 31.3 ($C(CH_3)_2$), 24.9 ($C(CH_3)_2$), 24.0 ($C(CH_3)_2$) ppm. Prolonged scanning did not uncover the second carbonyl resonance. ^{19}F NMR (470.6 Hz, C_6D_6, 20 °C) $\delta = -166.0$ ppm. FTIR (C_6D_6, KBr windows): $\nu_{CN} = 2087$ cm^{-1} (vs), $\nu_{CO} = 1979$ cm^{-1} (s), $\nu_{CO} = 1964$ cm^{-1} (s), also 2854, 1593, 1457, 1385, 1363, 1058, 758, 645 cm^{-1}. HR-MS (ESI-TOFMS): predicted for $[M + H_3O]^+ = C_{65}H_{77}F_2MnN_2SbO_4$, 1163.4270; found $m/z = 1163.4068$. Repeated samples failed to provide a satisfactory elemental analysis.

Synthesis of $MnF(CO)_3(CNAr^{Dipp2})_2$

Caution: XeF_2 is a highly reactive compound. Care must be taken to ensure limited contact with borosilicate glass containers for prolonged periods. In a darkened glovebox, a fluorobenzene solution of $Mn(CO)_3(CNAr^{Dipp2})_2$ (0.037 g, 0.0375 mmol, 5 ml) was set stirring at room temperature in a glass scintillation vial. In a separate plastic vial, a weighed sample of XeF_2 (0.010 g, 0.056 mmol, 1.5 eq.) was added in one portion to the stirring solution. The color of the solution gradually changed from orange to yellow over 5 minutes. With continued stirring, all volatiles were removed under reduced pressure to yield a yellow solid. The solid was washed with pentane (3 × 5 ml) and extracted with diethyl ether to provide a light yellow powder. The powder was dissolved into a minimal amount of THF, filtered through a fiberglass plug, and stored at −40 °C for 2 days. The resulting crystals were washed with n-pentane to providing a crystalline material. Yield: 0.015 g, 41%. ^1H NMR (500.1 MHz, C_6D_6, 20 °C) δ 7.41 (t, 4H, $J = 8$ Hz, p-Dipp), 7.19 (d, 8H, $J = 8$ Hz, m-Dipp), 6.89 (d, 4H, $J = 8$ Hz, m-Ar), 6.82 (dd, 2H, $J = 8$, 7 Hz, p-Ar), 2.64 (sept, 8H, $J = 7$ Hz, $CH(CH_3)_2$), 1.38 (d, 24H, $J = 7$ Hz, $CH(CH_3)_2$), 1.02 (d, 24H, $J = 7$ Hz, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6, 20 °C) $\delta = 218.0$ (cis-CO, d, *J* = 172 Hz), 210.0 (*trans*-*C*O, d, *J* = 11 Hz), 172.5 (*C*N, d, *J* = 150 Hz), 146.4, 139.7, 134.3, 139.7, 128.6, 123.6, 31.5 (*C*H(CH$_3$)), 24.6 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$), ppm (two CNAr^{Dipp2} aromatic resonances are obscured by the C_6D_6 signal). ^{19}F NMR (470.6 MHz, C_6D_6, 20 °C, TFA standard) δ = −59.7 ppm. FTIR (C_6D_6, KBr windows): ν_{CN} = 2117 cm^{-1} (vs), ν_{CO} = 2014 cm^{-1} (vs), 2008 cm^{-1} (sh), 1942 (s), also 2961, 2926, 2868, 1568, 1480, 1437, 1133, 758, 677, 647 cm^{-1}. Repeated combustion analyses routinely provided C and H values that indicated some incorporation of HF.

Synthesis of Mn(BiCl$_2$)(CO)$_3$(CNAr^{Dipp2})$_2$ and MnCl(CO)$_3$(CNAr^{Dipp2})$_2$

To a stirring diethyl ether solution of Mn(CO)$_3$(CNAr^{Dipp2})$_2$ (28 mg, 0.0284 mmol, 5 mL) was added a solution of BiCl$_3$ in diethyl ether (9 mg, 1 mL, 1 eq.). The orange solution became dark orange with concomitant precipitation of a black powder, and stirring was discontinued after 5 minutes. The solution was filtered and the solvent was removed under reduced pressure. Integration from ^{1}H NMR spectra reveals a conversion of Mn(CO)$_3$(CNAr^{Dipp2})$_2$ to Mn(BiCl$_2$)(CO)$_3$(CNAr^{Dipp2})$_2$ and MnCl(CO)$_3$(CNAr^{Dipp2})$_2$ in a 0.4 : 1 ratio, respectively, based upon integration of the respective (*p*-Ar) protons. Light red single crystals of Mn(BiCl$_2$)(CO)$_3$(CNAr^{Dipp2})$_2$ are obtained from a concentrated THF solution at −40 °C overnight. The compound is light sensitive and slowly decomposes above −40 °C; decomposition provides Bi^0 (as a black solid) and MnCl(CO)$_3$(CNAr^{Dipp2})$_2$. Spectroscopic data for Mn(BiCl$_2$)(CO)$_3$(CNAr^{Dipp2})$_2$: ^{1}H NMR (300.1 MHz, C_6D_6, 20 °C) δ = 7.34 (t, 2H, *J* = 8 Hz, *p*-Ar), 7.19 (d, 4H, *J* = 8 Hz, *m*-Ar), 6.92 (m, 8H, *m*-Dipp), 6.80 (dd, 4H, *J* = 8.5, 6.5 Hz, *p*-Dipp), 2.67 (sept, 8H, *J* = 7 Hz, C*H*(CH$_3$)$_2$), 1.35 (d, 24H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 0.99 (d, 24H, *J* = 7 Hz, CH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6, 20 °C) δ = 209.4 (*trans*-*C*O), 203.8 (*cis*-*C*O), 164.7 (*C*N), 146.7, 139.8, 134.7, 130.4, 130.0, 123.9, 31.3 (*C*H(CH$_3$)), 25.0 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$), ppm (two CNAr^{Dipp2} aromatic resonances are obscured by the *protio*-benzene impurity peak). FTIR (C_6D_6, KBr windows): ν_{CN} = 2093 cm^{-1} (vs), ν_{CO} = 1981 cm^{-1} (s), also 2964, 2926, 2869, 1458, 1030, 759, 645, 633 cm^{-1}. Attempts to collect combustion analysis of the purified material prepared in this synthesis or in the salt elimination reaction failed to provide satisfactory results. We believe this is due to the observed thermal instability which routinely provides MnCl(CO)$_3$(CNAr^{Dipp2})$_2$ as the sole identifiable compound.

Synthesis of Mn(BiCl$_2$)(CO)$_3$(CNAr^{Dipp2})$_2$ using Na[Mn(CO)$_3$(CNAr^{Dipp2})$_2$

To a thawing THF solution of Na[Mn(CO)$_3$(CNAr^{Dipp2})$_2$] (0.092 g, 0.091 mmol, 10 mL) was added a solution of BiCl$_3$ (0.029 g, 1.01 eq., 10 mL) over 15 minutes, slowly turning the solution deep orange. The solution was stirred for an additional 5 minutes, after which it was filtered through a Celite plug and the solvent removed under reduced pressure to provide a red solid. Yield: 0.037 g, 32%. Light red single crystals of Mn(BiCl$_2$)(CO)$_3$(CNAr^{Dipp2})$_2$ are obtained from a concentrated THF solution at −40 °C overnight.

Synthesis of Mn(AlCl$_2$·THF)(CO)$_3$(CNAr^{Dipp2})$_2$

A stirring THF solution of Na[Mn(CO)$_3$(CNAr^{Dipp2})$_2$] (0.063 g, 0.063 mmol, 5 ml) is slowly treated with a THF solution of AlCl$_3$ (0.009 g, 0.065 mmol, 1.05 eq., 2 ml) at room temperature over 5 minutes. After approximately 30 minutes stirring, the deep purple color lightens to yellow. Thereafter, the solvent is removed *en vacuo* to provide a yellow solid. This solid is then subject to two cycles of *n*-pentane addition and removal under vacuum to desolvate remaining salts. Extraction of the yellow solid with Et$_2$O (3 × 2 ml), followed by evaporation of the combined extracts under vacuum, provides analytically pure Mn(AlCl$_2$·THF)(CO)$_3$(CNAr^{Dipp2})$_2$ as a yellow solid. Yield: 0.053 g, 74%. ^{1}H NMR (500.1 MHz, C_6D_6, 20 °C) δ 7.32 (t, 4H, *J* = 8 Hz, *p*-Dipp), 7.23 (d, 8H, *J* = 8 Hz, *m*-Dipp), 7.06 (d, 4H, *J* = 8 Hz, *m*-Ar), 6.91 (dd, 2H, *J* = 8, 7 Hz, *p*-Ar), 3.44 (m, THF), 2.82 (sept, 8H, *J* = 7 Hz, C*H*(CH$_3$)$_2$), 1.48 (d, 24H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.27 (m, THF), 1.05 (d, 24H, *J* = 7 Hz, CH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6, 20 °C) δ = 219.1 (*trans*-*C*O), 210.0 (*cis*-*C*O), 182.4 (*C*N), 146.8, 137.8, 135.7, 130.9, 129.0, 126.1, 123.4, 72.5 (THF), 31.2 (*C*H(CH$_3$)$_2$), 25.7 (CH(*C*H$_3$)$_2$), 25.0 (THF), 23.5 (CH(*C*H$_3$)$_2$), ppm. FTIR (C_6D_6, KBr windows): ν_{CN} = 2057 cm^{-1} (vs), ν_{CO} = 1951 cm^{-1} (s), 1918 cm^{-1} (vs), also 3065, 2961, 2925, 2865, 1578, 1458, 1411, 1385, 1363, 1331, 1056, 1004, 757, 657 cm^{-1}. Anal. calcd for $C_{69}H_{82}AlCl_2MnN_2O_4$: C, 71.66; H, 7.15; N, 2.42. Found: C, 71.93; H, 6.75; N, 1.99.

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