Supporting Information for the Paper Entitled:

"Electrophilic Functionalization of Well-Behaved Manganese Monoanions Supported by *m*-Terphenyl Isocyanides"

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Contents

S1 - Synthetic Procedures

S1.1. General Considerations. All manipulations were carried out under an atmosphere of dry dinitrogen or argon using standard Schlenk and glovebox techniques. Solvents were dried and deoxygenated according to standard procedures. Unless otherwise stated, reagent grade starting materials were purchased from commercial sources and were used as received or purified by standard procedures. The isocyanide ligands $CNAr^{Mes2}$ and $CNAr^{Dipp2}$ were prepared as previously reported.[1,2] Benzene-d_6 (Cambridge Isotope Laboratories) was degassed and stored over 4 Å molecular sieves for 2 d prior to use. Celite 405 (Fisher Scientific) was dried under vacuum (24 h) at a temperature above 250 ˚C and stored in the glovebox prior to use. KBr (FTIR grade from Aldrich) was stirred overnight in anhydrous THF, filtered and dried under vacuum (24 h) at a temperature above 250 ˚C prior to use.

Solution ^1H and $^{13}C\{^1H\}$ spectra were recorded on Varian Mercury 300 and 400 spectrometers, a Varian X-Sens500 spectrometer or a JEOL ECA-500 spectrometer. ^1H and $^{13}C\{^1H\}$ chemical shifts are reported in ppm relative to $SiMe_4$ (^1H and ^{13}C $\delta = 0.0$ ppm) with reference to residual solvent resonances of 7.16 ppm (^1H) and 128.06 ppm (^{13}C) for benzene-d_6 (^1H).[3] FTIR spectra were recorded on a Thermo-Nicolet iS10 FTIR spectrometer. Samples were prepared as either KBr pellets or as C_6D_6, THF or DME solutions injected into a ThermoFisher solution cell equipped with KBr windows. For solution FTIR spectra, solvent peaks were digitally subtracted from all spectra by comparison with an authentic spectrum obtained immediately prior to that of the sample. The following abbreviations were used for the intensities and characteristics of important IR absorption bands: vs = very strong, s = strong, m = medium, w = weak, vw = very weak; b = broad, vb = very broad, sh = shoulder. UV-vis spectra were collected in air-free quartz cuvets on a PerkinElmer Lamda 35 spectrophotometer. Combustion analyses were performed by Robertson Microlit Laboratories of Madison, NJ (USA).

S1.2. Synthesis of $BrMn(CO)_2(CNAr^{Mes2})_3$ (*trans,mer*- and *cis,mer*-isomers)

To a THF solution of $MnBr(CO)_5$ (0.270 g, 0.982 mmol, 20 mL), was added a THF solution of $CNAr^{Mes2}$ (1.000 g, 2.950 mmol, 30 mL, 3 equiv). The resulting solution was refluxed with stirring under N_2 for 16 h. All volatile materials were then removed under reduced pressure resulting in a yellow residue. ^1H NMR and solution FTIR spectra (C_6D_6) taken at this stage indicate that $BrMn(CO)_2(CNAr^{Mes2})_3$ is formed in a 95:5 ratio of *trans,mer* to *cis,mer* isomers. Dissolution of this mixutre in THF followed by filtration and storage at -35 ˚C for 12 h resulted in orange crystals of $BrMn(CO)_2(CNAr^{Mes2})_3$ as a 9:1 *trans,mer* : *cis,mer* mixture (^1H NMR, C_6D_6). These crytstals were collected, dried *in vacuo* and used immediately in subsequent steps. Yield: 0.831 g, 0.687 mmol, 70%. A single crystal obtained after storage of $BrMn(CO)_2(CNAr^{Mes2})_3$ for 36 h at -35 ˚C contained an 85:15 ratio of *trans,mer* to *cis,mer* isomers as determined by X-ray diffraction. Heating of $BrMn(CO)_2(CNAr^{Mes2})_3$ for up to 24 h at 100 ˚C (C_6D_6) does not appreciably accelerate the *trans,mer* to *cis,mer* conversion. However, solid or solution samples that are directly or intermittently exposed to ambient light will become enriched in the *cis,mer*-isomer over time (*ca* 50% after 1.5 weeks in direct ambient light (solid state)). ***trans,mer*-$BrMn(CO)_2(CNAr^{Mes2})_3$:** ^1H NMR (400.1 MHz, C_6D_6, 20 ˚C): δ = 6.96 (s, 8H, *m*-Mes), 6.92 (s, 4H, *m*-Mes), 6.87 (t, 1H, *J* = 8 Hz, *p*-Ar), 6.83 (d, 2H, *J* = 8 Hz, *m*-Ar), 6.81, (t, 2H, *J* = 8 Hz, *p*-Ar), 6.76 (d, 4H, *J* = 8 Hz, *m*-Ar), 2.50 (s, 6H, *p*-CH_3-Mes), 2.45 (s, 12H, *p*-CH_3-Mes), 2.15 (s, 24H, *o*-CH_3-Mes), 1.97 (s, 12H, *o*- CH_3-Mes) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6, 20 ˚C) δ = 210.91 ($C{\equiv}O$), 186.96 ($C{\equiv}N$), 178.87 ($C{\equiv}N$), 139.47, 138.23, 137.15, 137.06, 135.99, 135.36, 134.92, 134.74, 129.61, 128.90, 128.85, 128.13, 127.94, 126.29, 21.95 (*o*-*C*H$_3$-Mes), 21.75 (*o*-*C*H$_3$-Mes), 20.81 (*p*-*C*H$_3$-Mes), 20.27 (*p*-*C*H$_3$-Mes) ppm (two aromatic resonances obscured by C_6D_6 solvent). FTIR (C_6D_6, KBr windows): (ν_{CN}) 2086 (vs), 2063 (s) and 2033 (w) cm^{-1}, (ν_{CO}) 1990 (vs) cm^{-1}, also 2972, 2948, 2919, 2860, 1576, 1464, 1417, 1378, 1272, 1069, 850, 804, 756, 642 cm^{-1}. ***cis,mer*-BrMn(CO)$_2$(CNAr^{Mes2})$_3$:** ^{1}H NMR (400.1 MHz, C_6D_6, 20 ˚C): δ = 2.35 (s, 6H, *p*-C*H*$_3$-Mes), 2.30 (s, 12H, *p*-C*H*$_3$-Mes), 2.06 (s, 24H, *o*-C*H*$_3$-Mes), 1.99 (s, 12H, *o*-C*H*$_3$-Mes); aromatic resonances obscured by presence of *trans,mer* isomer. FTIR (C_6D_6, KBr windows, Isocyanide and CO stretching region): (ν_{CN}) 2123 (s), 2086 (vs) and 2063 (s) (latter two bands overlap with *trans,mer* isomer), (ν_{CO}) 2012 (s) and 1942 (w) cm^{-1}. Anal. Calcd. for $C_{77}H_{75}N_3O_2BrMn$ (9:1 mixture *trans,mer* to *cis,mer* isomers): C, 76.48; H, 6.25; N, 3.47. Found: C, 76.00; H, 6.31; N, 3.28.

S1.3. Synthesis of [K(DME)(18-c-6)][Mn(CO)$_2$(CNAr^{Mes2})$_3$]

To a thawing solution of BrMn(CO)$_2$(CNAr^{Mes2})$_3$ isomers (0.100 g, 0.083 mmol) in THF (10 mL), a freshly prepared ~0.01 M solution of K(anthracene) (0.165 mmol, 17 mL, 2.0 equiv) was added dropwise in two portions over 1 h with intermittent stirring. During this time, the solutions were periodically refrozen by placement into a glovebox cold well. After the addition was complete, the reaction mixture was allowed to warm to room temperature. Solid 18-crown-6 (0.023 g, 0.087 mmol, 1.05 equiv) was then added in one portion and the reaction mixture was allowed to stir for an additional 20 min. All volatile materials were then removed *in vacuo*. The resulting residue was then slurried in *n*-pentane and filtered. The solid obtained was then dissolved in DME and stored at -35 ˚C for 12 h, resulting in the formation of purple crystals of [K(DME)(18-c-6)][Mn(CO)$_2$(CNAr^{Mes2})$_3$], which were collected and dried *in vacuo*. Yield: 0.026 g, 0.017 mmol, 20%. ^{1}H NMR (400.1 MHz, C_6D_6, 20 ˚C): δ =7.4-6.2 (bm, aromatic), 3.33, (s, 4H, DME, non-coordinated[3]) 3.24 (s, 24H, K(18-crown-6)), 3.12 (s, 6H, DME, non-coordinated[3]), 2.50 (bs, 18H, *p*-C*H*$_3$-Mes), 2.00 (bs, 36H, *o*-C*H*$_3$-Mes). FTIR (DME, KBr windows, 25 ˚C): (ν_{CN}) 1891 (vs) cm^{-1} (ν_{CN} + ν_{CO}) 1841 (s, vb) cm^{-1}, also 1574, 1455, 1360, 1247, 1035, 1018, 855, 658 cm^{-1}. Due to the thermal instability of this complex, ^{13}C{^{1}H} NMR and combustion analysis data were not obtained.

S1.4. Synthesis of *mer,trans*-BrMn(CO)$_3$(CNAr^{Dipp2})$_2$

To a THF solution of MnBr(CO)$_5$ (0.324 g, 1.18 mmol, 20 mL), was added a THF solution of CNAr^{Dipp2} (1.00 g, 2.36 mmol, 30 mL, 2.0 equiv). The resulting solution was refluxed with stirring under N_2 for 16 h. The solution was then filtered and concentrated to a volume of 10 mL under reduced pressure. Storage of this solution at -35 ˚C for 12 h resulted in yellow crystals of BrMn(CO)$_3$(CNAr^{Dipp2})$_2$ which were collected and dried *in vacuo*. Yield: 0.811 g, 0.761 mmol, 65 %. ^{1}H NMR (400.1 MHz, C_6D_6, 20 ˚C): δ = 7.40 (t, 2H, *J* = 8 Hz, *p*-Ar), 7.19 (d, 4H, *J* = 8 Hz, *m*-Ar), 6.89 (d, 8H, *J* = 8 Hz, *m*-Dipp), 6.82 (t, 4H, *J* = 8 Hz, *p*-Dipp), 2.64 (sept, 8H, *J* = 7 Hz, C*H*(CH$_3$)$_2$), 1.38 (d, 24H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.02 (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 = 218.8 (*C*≡O), 210.0 (*C*≡O), 171.2 (*C*≡N), 146.6, 139.8, 134.4, 129.8, 129.7 123.4, 31.5 (*C*H(CH$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 24.4(CH(*C*H$_3$)$_2$) ppm (two aromatic resonances obscured by C_6D_6 solvent). FTIR (C_6D_6, KBr windows): (ν_{CN}) 2118 (vs) cm^{-1} (ν_{CO}) 2015 (s) and 1943 (s) cm^{-1}, also 2962, 2869, 1458, 1330, 812, 757, 646, 633 cm^{-1}. Anal. Calcd. for $C_{65}H_{74}N_2O_3BrMn$: C, 73.23; H, 7.00; N, 2.63. Found: C, 73.21; H, 7.27; N, 2.66.

S1.5. Synthesis of Na[Mn(CO)$_3$(CNAr^{Dipp2})$_2$]

To a stirred mixture of 0.18% Na/Hg (Na: 0.063 g, 2.74 mmol; Hg: 34.5 g; 10 equiv Na/Mn) and Et$_2$O (180 mL), was added an Et$_2$O suspension of BrMn(CO)$_3$(CNAr^{Dipp2})$_2$ (0.300 g, 0.281 mmol, 20 mL). The resulting solution was allowed to stir for 24 h, concentrated to a volume of 20 mL and then filtered to remove NaBr. All volatile materials were then removed under reduced pressure. The resulting residue was then dissolved in Et$_2$O (10 mL) and filtered. Storage of this solution at -35 ˚C for 12 h resulted in the formation of Na[Mn(CO)$_3$(CNAr^{Dipp2})$_2$] as red a microcrystalline material, which was collected and dried *in vacuo*. Yield: 0.131 g, 0.130 mmol, 47 %. Single crystals of [Na(NCMe)$_2$][Mn(CO)$_3$(CNAr^{Dipp2})$_2$] were obtained by allowing a 10:1 toluene/MeCN solution of Na[Mn(CO)$_3$(CNAr^{Dipp2})$_2$] to stand at -35 ˚C for 4 days. ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 20 ˚C): δ = 7.33 (m, 2H, *p*-Ar), 7.23 (d, 4H, *J* = 8 Hz, *m*-Ar), 6.99 (d, 8H, *J* = 8 Hz, *m*-Dipp), 6.89 (t, 4H, *J* = 8 Hz, *p*-Dipp), 2.83 (sept, 8H, *J* = 8 Hz, C*H*(CH$_3$)$_2$), 1.38 (d, 24H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.12 (d, 24H, J = 7 Hz, CH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, C$_6$D$_6$, 20 °C): δ = 275.7 (*C*≡O), 237.4 (*C*≡N), 147.4, 137.1, 136.6, 131.7, 129.6, 128.5, 124.6, 123.3, 31.4 (*C*H(CH$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$) ppm (one aromatic resonance obscured by C$_6$D$_6$ solvent). FTIR (THF, KBr windows): (ν_{CN}) 1910 (vs) cm^{-1} (ν_{CO}) 1896 (vs) and 1773 (s) cm^{-1}, also 1570, 1461, 1412, 1365, 1183, 1076, 914, 661 cm^{-1}. Anal. Calcd. for C$_{65}$H$_{74}$N$_2$O$_3$MnNa: C, 77.36; H, 7.39; N, 2.78. Found: C, 77.12; H, 7.48; N, 2.62.

S1.6. Synthesis of *mer,trans*-H$_3$CMn(CO)$_3$(CNAr^{Dipp2})$_2$

To an Et$_2$O solution of Na[Mn(CO)$_3$(CNAr^{Dipp2})$_2$] (0.100 g, 0.099 mmol, 30 mL) was added an Et$_2$O solution of CH$_3$I (0.014 g, 0.099 mmol, 10 mL, 1.0 equiv) dropwise over 5 min. The resulting solution was stirred for 30 min, concentrated to a volume of 3 mL and then filtered to remove liberated NaI. Storage of the filtrate at -35 ˚C for 12 h resulted in the formation of yellow crystals, which were collected and dried *in vacuo*. Yield: 0.071 g, 0.071 mmol, 72%. ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 20 ˚C): δ = 7.67 (t, 4H, *J* = 8 Hz, *m*-Ar), 7.17 (d, 2H, *J* = 8 Hz, *p*-Ar), 6.90 (d, 8H, *J* = 8 Hz, *m*-Dipp), 6.82 (t, 4H, *J* = 8 Hz, *p*-Dipp), 2.66 (sept, 8H, *J* = 7 Hz, C*H*(CH$_3$)$_2$), 1.34 (d, 24H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.03 (d, 24H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), -0.87 (s, 3H, Mn-C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, C$_6$D$_6$, 20 ˚C): δ = 219.3 (*C*≡O), 182.3 (*C*≡N), 146.4, 139.0, 134.9, 129.7, 129.6, 129.0, 127.2, 123.5, 31.3 (*C*H(CH$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$), -15.8 (Mn-*C*H$_3$) ppm (prolonged scanning failed to uncover the resonance for the carbonyl group *trans* to the Me unit). FTIR (C$_6$D$_6$, KBr windows): (ν_{CN}) 2076 (vs) cm^{-1}, (ν_{CO}) 1972 (m) 1964 (s) and 1935 (m) cm^{-1} also 2962, 2928, 2868, 1455, 1417, 1384, 1363, 1330, 1179, 1163, 1057, 866, 757, 604 cm^{-1}. Anal. Calcd. for C$_{66}$H$_{77}$N$_2$O$_3$Mn: C, 79.17; H, 7.75; N, 2.80. Found: C, 78.81; H, 7.70; N, 2.69.

S1.7. Synthesis of *mer,trans*-HMn(CO)$_3$(CNAr^{Dipp2})$_2$

To an Et$_2$O solution of Na[Mn(CO)$_3$(CNAr^{Dipp2})$_2$] (0.100 g, 0.099 mmol, 30 mL), was added a 0.1 M Et$_2$O solution of HCl (0.10 mmol, 1.0 mL, 1.0 equiv) dropwise over 5 min. The resulting solution was stirred for 30 min, concentrated to a volume of 3 mL and then filtered to remove liberated NaCl. Storage of the filtrate at -35 ˚C for 12 h resulted in the formation of yellow crystals, which were collected and dried *in vacuo*. Yield: 0.068 g, 0.069 mmol, 70%. ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 20 ˚C): δ = 7.36 (t, 2H, *J* = 8 Hz, *p*-Ar), 7.20 (d, 4H, *J* = 8 Hz, *m*-Ar), 6.90 (m, 12H, *m*-Dipp + *p*-Dipp), 2.66 (sept, 8H, *J* = 7 Hz, C*H*(CH$_3$)$_2$), 1.32 (d, 24H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.07 (d, 24H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), -7.82 (s, 1H, Mn-*H*) ppm. ^{13}C{^{1}H} NMR (100.3 MHz, C$_6$D$_6$, 20 ˚C): δ = 216.4 (*C*≡O), 180.2 (*C*≡N), 146.5, 138.8, 134.8, 129.6, 129.5, 129.2, 127.2, 123.4, 31.3 (*C*H(CH$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 24.0 (CH(*C*H$_3$)$_2$) ppm (prolonged scanning failed to uncover the resonance for the carbonyl group *trans* to the hydride unit). FTIR (C$_6$D$_6$, KBr windows): (ν_{CN}) 2080 (vs) cm^{-1}, (ν_{CO} or ν_{MnH} (vibronic mixing prevents definitive assingments)[4]) 2016 (w), 1968 (s) and 1947 (s) also, 2962, 2928, 2868, 1472, 1458, 1418, 1384, 1363, 1261, 1057, 1014, 812, 804, 791, 757, 739, 725 703, 668, 639 cm^{-1}. Anal. Calcd. for C$_{65}$H$_{75}$N$_2$O$_3$Mn: C, 79.08; H, 7.66; N, 2.84. Found: C, 78.83; H, 7.59; N, 2.95.

S1.8. Synthesis of *mer,trans*-(Me(Cl)$_2$Si)Mn(CO)$_3$(CNAr^{Dipp2})$_2$

To a thawing Et$_2$O solution of Na[Mn(CO)$_3$(CNAr^{Dipp2})$_2$] (0.100 g, 0.099 mmol, 30 mL) was added an equally cold Et$_2$O solution of MeSiCl$_3$ (0.015 g, 0.099 mmol, 1.00 equiv, 10 mL) over the course of 10 min. The reaction mixture was stirred for 30 min while warming to room temperature and then concentrated to a volume of 3 mL. Filtration of this solution to remove liberated NaCl, followed by storage at -35 ˚C for 24 h resulted in the formation of yellow crystals, which were collected and dried *in vacuo*. Yield: 0.070 g, 0.063 mmol, 64%. ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 20 ˚C): δ = 7.35 (t, 2H, *J* = 8 Hz, *p*-Ar), 7.22 (d, 4H, *J* = 8 Hz, *m*-Ar), 6.98 (d, 8H, *J* = 8 Hz, *m*-Dipp), 6.87 (t, 4H, *J* = 8 Hz, *p*-Dipp), 2.70 (sept, 8H, *J* = 7 Hz, C*H*(CH$_3$)$_2$), 1.41 (d, 24H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.00 (d, 24H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 0.60 (s, 3H, Mn-Si-C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, C$_6$D$_6$, 20 ˚C): δ = 215.0 (*C*≡O), 213.7 (*C*≡O), 175.5 (*C*≡N), 146.5, 138.9, 134.9, 130.8, 129.6, 128.6, 127.3, 123.7, 31.2 (*C*H(CH$_3$)$_2$), 25.4 (CH(*C*H$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$), 17.8 ($J_{C\text{-}Si}$ = 20 Hz, Si-*C*H$_3$) ppm. FTIR (C$_6$D$_6$, KBr windows): (ν_{CN}) 2084 (vs) cm^{-1} (ν_{CO}) 1983 (vs) and 1972 (vs) cm^{-1}, also 2963, 2936, 2906, 2868, 1578, 1459, 1414, 1385, 1363,1330, 1248, 1180, 813, 804, 793, 758, 653 cm^{-1}. Anal. Calcd. for C$_{66}$H$_{77}$N$_2$O$_3$SiCl$_3$Mn: C, 72.05; H, 7.05; N, 2.55. Found: C, 71.88; H, 7.19; N, 2.38.

S1.9. Synthesis of *mer,trans*-ClSnMn(CO)$_3$(CNAr^{Dipp2})$_2$.

To a thawing Et$_2$O solution of Na[Mn(CO)$_3$(CNAr^{Dipp2})$_2$] (0.040 g, 0.039 mmol, 40 mL) was added a thawing Et$_2$O slurry of SnCl$_2$ (0.008 g, 0.039 mmol, 20 mL, 1.0 equiv) dropwise in 5 portions over the course of two hours. During the additions, the solutions were periodically refrozen in a glovebox cold well. After the final addition, the mixture was allowed to stir for 1 h, concentrated to a volume of 3 mL and then filtered to remove liberated NaCl. Concentration of the filtrate to a volume of 2 mL followed by storage at -35 ˚C for 12 h resulted in the formation of dark green crystals, which were collected and dried *in vacuo*. Yield: 0.027 g, 0.024 mmol, 60%. ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 20 ˚C): δ = 7.39 (t, 2H, *J* = 8 Hz, *p*-Ar), 7.19 (d, 4H, *J* = 8 Hz, *m*-Ar), 6.85 (m, 12H, *m*-Dipp + *p*-Dipp), 2.59 (sept, 8H, *J* = 8 Hz, C*H*(CH$_3$)$_2$), 1.37 (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$_6$D$_6$, 20 ˚C): δ = 217.0 (*C*≡O), 172.3 (*C*≡N), 146.5, 139.1, 135.0, 129.9, 129.5, 127.3, 128.4, 123.7, 31.3 (*C*H(CH$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$) ppm (prolonged scanning failed to uncover the resonance for the carbonyl group *trans* to the hydride unit). FTIR (C$_6$D$_6$, KBr windows): (ν_{CN}) 2058 (vs) cm^{-1}, (ν_{CO}) 2000 (w), 1966 (s), 1938 (s) cm^{-1}, also 2963, 2868, 1499, 1437, 1363, 1118, 1056, 866, 815, 757, 648 cm^{-1}. UV-vis (Et$_2$O): λ_{max} = 490 nm. Anal. Calcd. for C$_{65}$H$_{74}$N$_2$O$_3$ClMnSn: C, 68.46; H, 6.54; N, 2.46. Found: C, 68.25; H, 6.80; N, 2.36.

S2. Crystallographic Structure Determinations

S2.1. General. Single crystal X-ray structure determinations were carried out at low temperature on a Bruker P4, Platform or Kappa Diffractometer equipped with a Bruker APEX II detector. All structures were solved by direct methods with SIR 2004[5] and refined by full-matrix least-squares procedures utilizing SHELXL-97.[6] Molecular structures of all complexes are depicted in Figures S2.1-S2.8. Crystallographic data collection and refinement information is listed in Table S2.1.

S2.2. Disorder and Refinement Specifics. The solid-state structures of the bromide complexes, $BrMn(CO)_2(CNAr^{Mes2})_3$ and $BrMn(CO)_3(CNAr^{Dipp2})_2$, suffered from positional disorder between the bromide and carbonyl ligands. For $BrMn(CO)_3(CNAr^{Dipp2})_2$, the disorder did not affect the stereochemistry of the complex and it was adequately modeled and refined with each site composed of $(CO)_{0.75}/Br_{0.25}$. For $BrMn(CO)_2(CNAr^{Mes2})_3$, the most stable model and refinement indicated that the isomers *trans,mer*-$BrMn(CO)_2(CNAr^{Mes2})_3$ and *cis,mer*-$BrMn(CO)_2(CNAr^{Mes2})_3$ are present within the crystal in a 85:15 ratio, respectively.

The solid-state structure of $HMn(CO)_3(CNAr^{Dipp2})_2$ also suffered from a positional disorder of the three carbonyl ligands over all four equatorial sites. This disorder was adequately modeled with a 75% carbonyl group occupancy at each site. Accordingly, definitive location of the hydride ligand was not possible.

Thermal ellipsoid restraints were used to treat a disordered toluene molecule of co-crystallization in the structure of $[Na(NCMe)_2][Mn(CO)_3(CNAr^{Dipp2})_2]$.

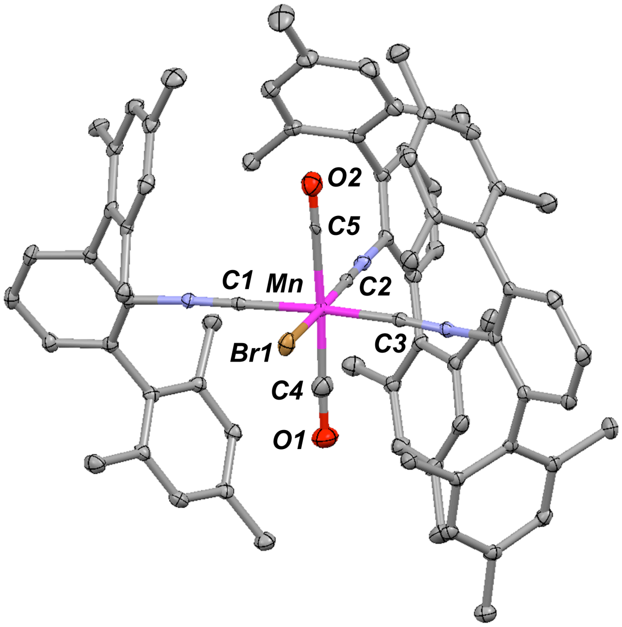

Figure S2.1. One disorder component (*trans,mer*; 85%) of the molecular structure of $BrMn(CO)_2(CNAr^{Mes2})_3$.

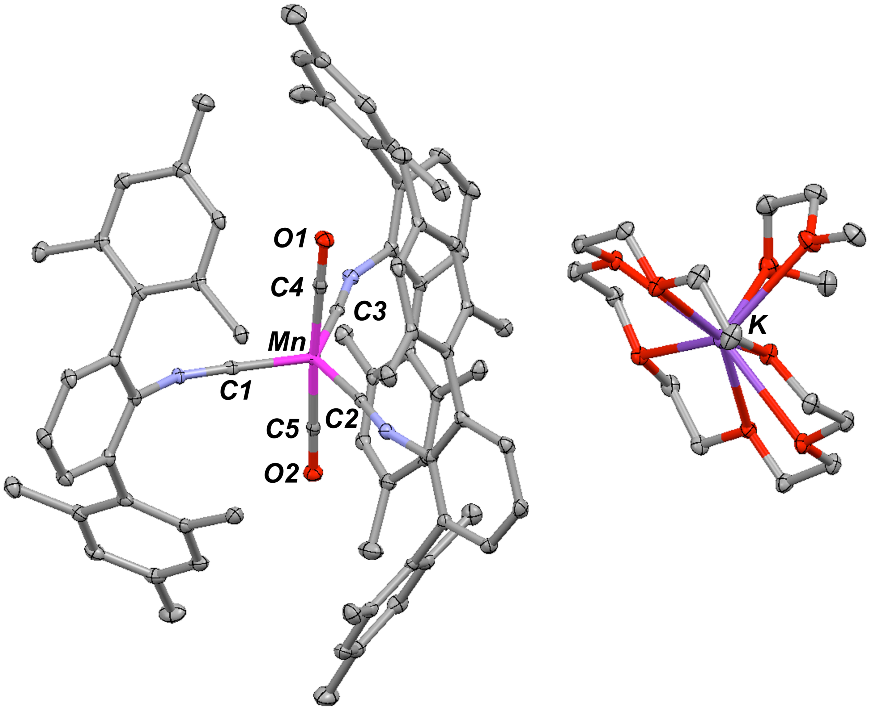

Figure S2.2. Molecular Structure of [K(DME)(18-c-6)][$Mn(CO)_2(CNAr^{Mes2})_3$].

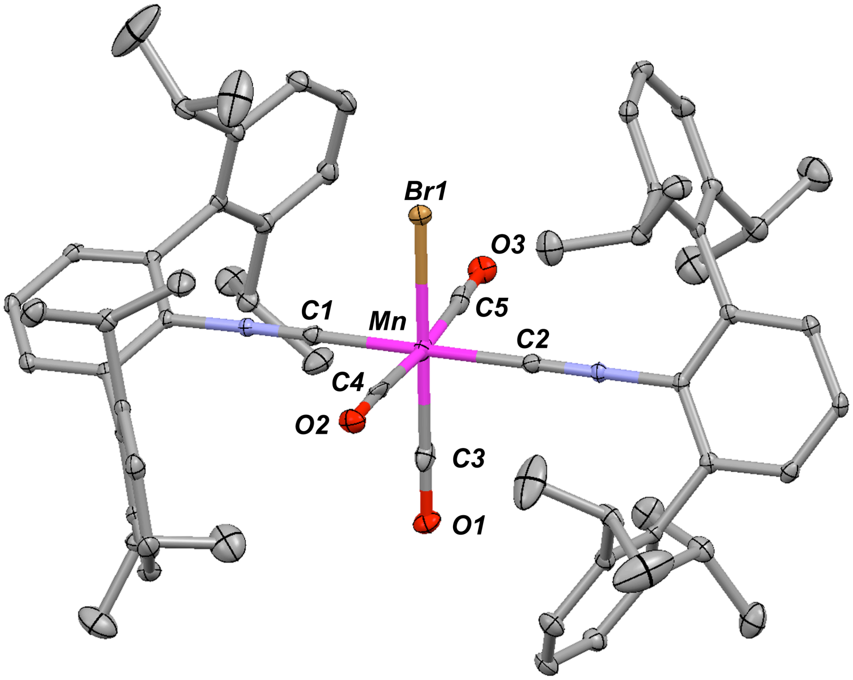

Figure S2.3. One disorder component of the molecular structure of $BrMn(CO)_3(CNAr^{Dipp2})_2$.

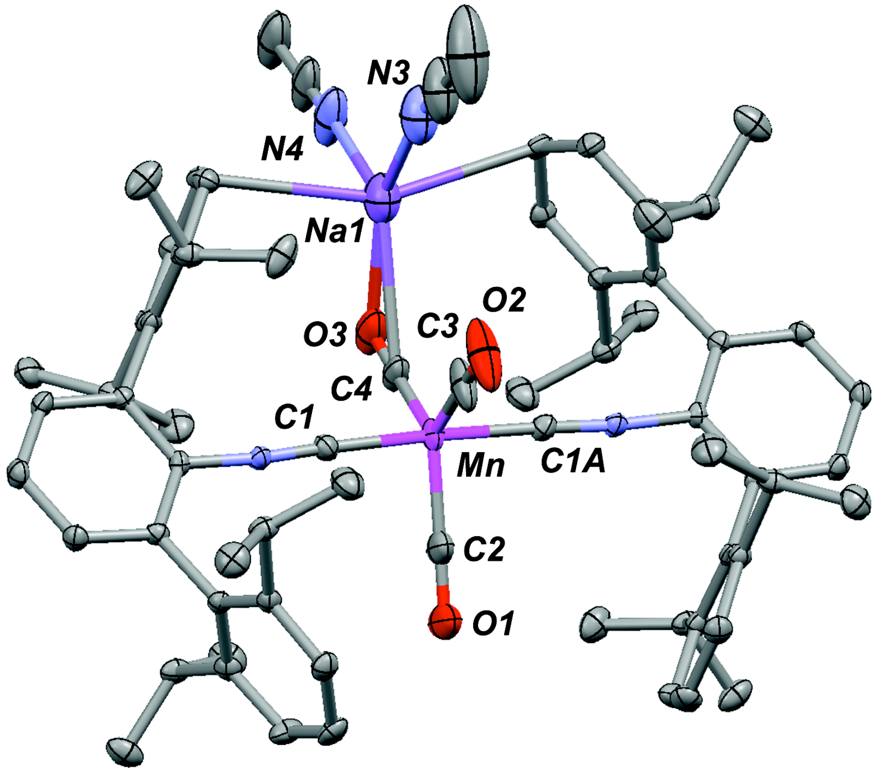

Figure S2.4. Molecular Structure of $[Na(NCMe)_2][Mn(CO)_3(CNAr^{Dipp2})_2]$.

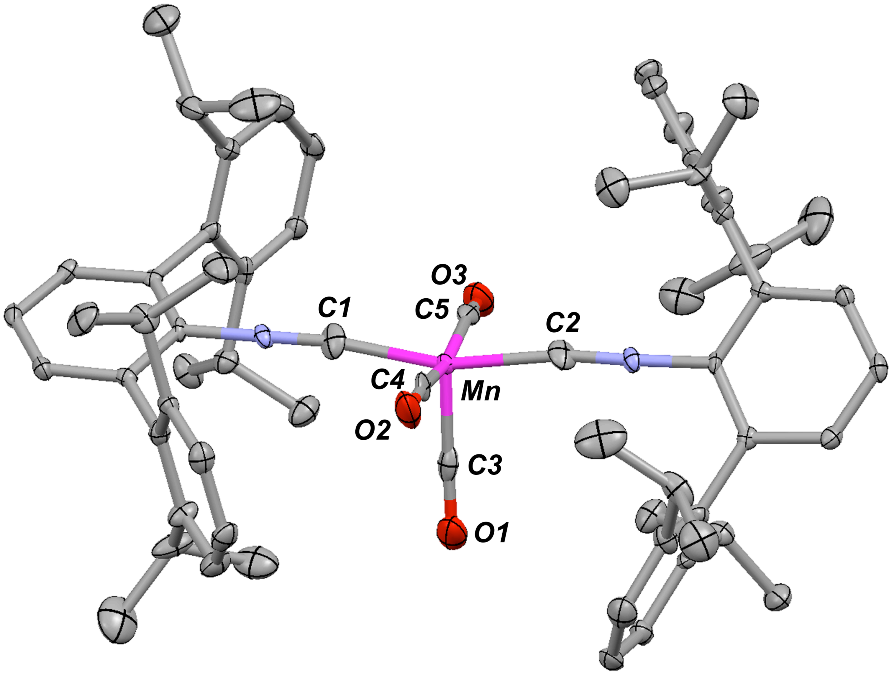

Figure S2.5. One disorder component of the molecular structure of $HMn(CO)_3(CNAr^{Dipp2})_2$.

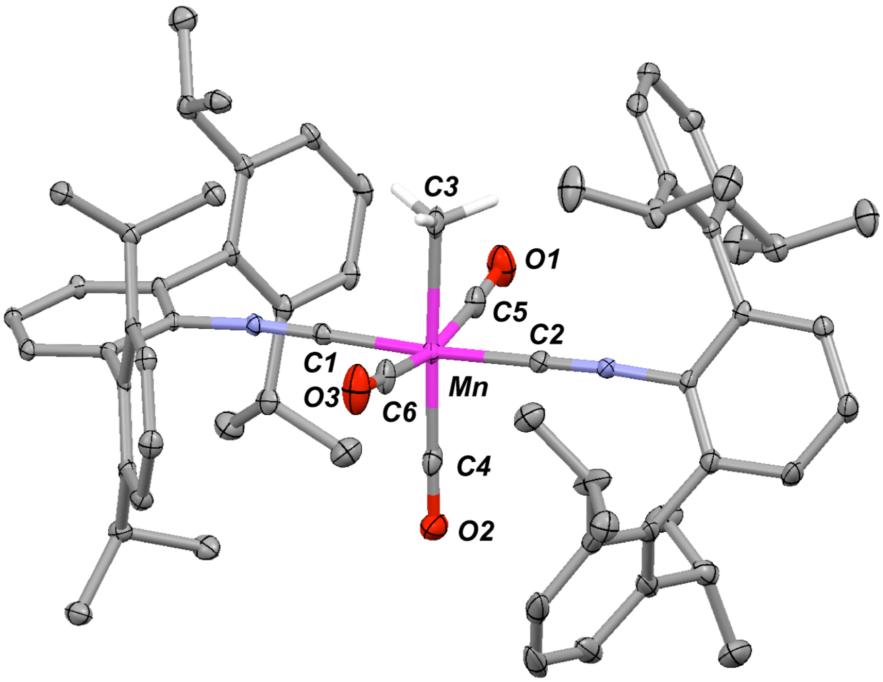

Figure S2.6. Molecular Structure of $MeMn(CO)_3(CNAr^{Dipp2})_2$.

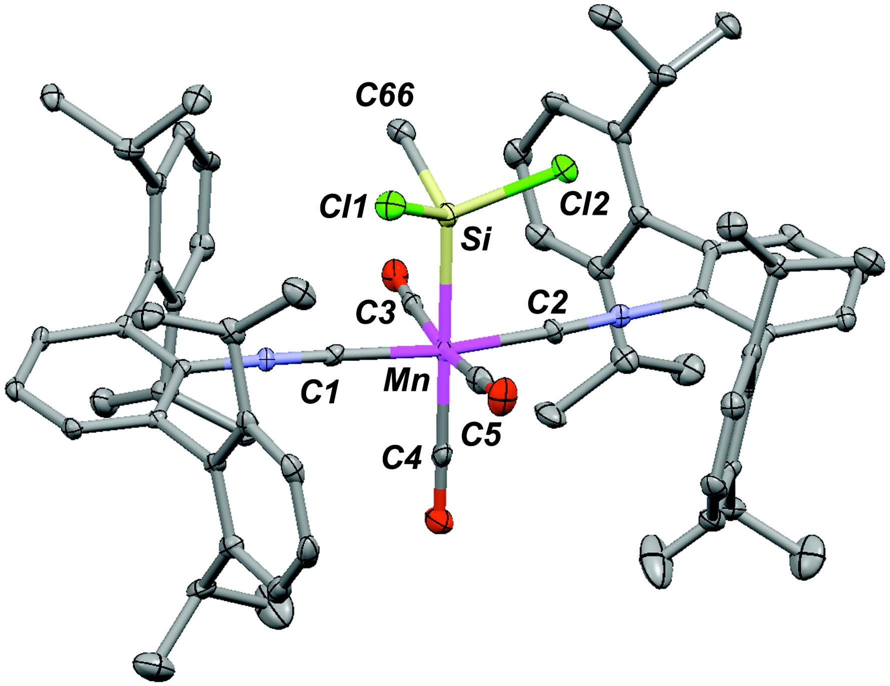

Figure S2.7. Molecular Structure of $Cl_2(Me)SiMn(CO)_3(CNAr^{Dipp2})_2$.

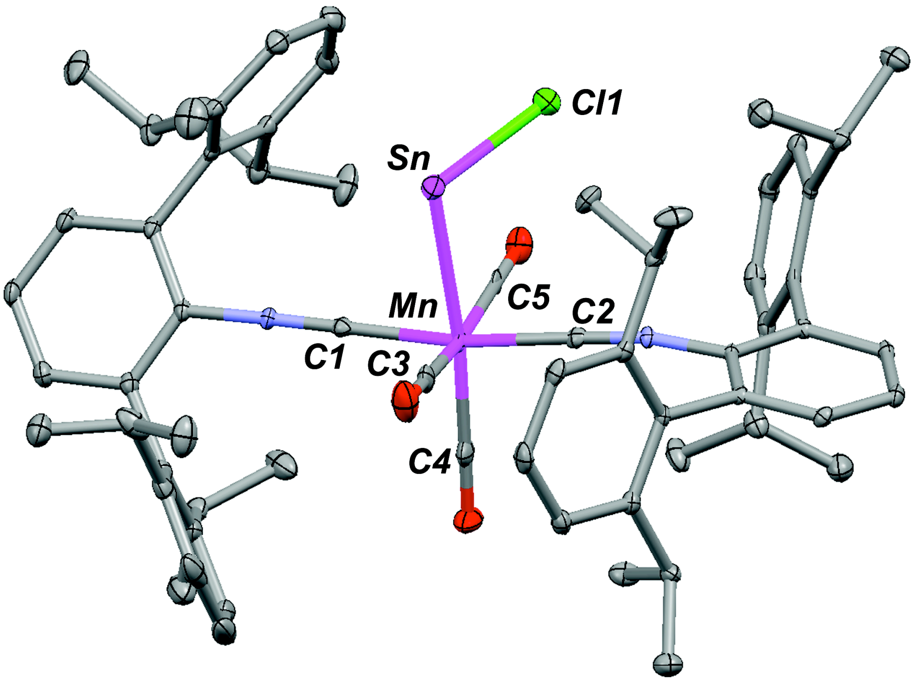

Figure S2.8. Molecular Structure of $ClSnMn(CO)_3(CNAr^{Dipp2})_2$.

Table S2.1. Crystallographic Data and Refinement Information.

	$BrMn(CO)_2(CNAr^{Mes2})_3\bullet 0.5Et_2O$	$[K(DME)(18\text{-}c\text{-}6)][Mn(CO)_2(CNAr^{Mes2})_3]\bullet 3DME$	$BrMn(CO)_3(CNAr^{Dipp2})_2$
Formula	$C_{79}H_{80}N_3O_{2.50}BrMn$	$C_{105}H_{139}N_3O_{16}KMn$	$C_{65}H_{74}N_2O_3BrMn$
Crystal System	Monoclinic	Triclinic	Monoclinic
Space Group	*P*2$_1$/*n*	*P*-1	*C*2/*c*
a, Å	17.8362(9)	12.881(5)	23.9872(18)
b, Å	15.7440(8)	15.819(5)	23.8244(18)
c, Å	24.2053(11)	24.700(5)	21.3103(16)
α, deg	90	96.168(5)	90
β, deg	103.907(3)	96.275(5)	108.9770(10)
γ, deg	90	98.166(5)	90
V, Å^3	6597.9(6)	4913(3)	11516.5(15)
Z	4	2	8
Radiation (λ, Å)	Cu-Kα, 1.54178	Mo-Kα, 0.71073	Mo-Kα, 0.71073
ρ (calcd.), g/cm^3	1.255	1.212	1.230

μ (Mo Kα), mm^{-1}	2.718	0.242	0.969
Temp, K	100(2)	100(2)	100(2)
θ max, deg	64.28	25.34	25.37
data/restraints/ parameters	10551 / 4 / 823	17902 / 0 / 1204	10536 / 0 / 699
R_1	0.0418	0.0436	0.0471
wR_2	0.1061	0.0976	0.1077
GOF	0.0902	1.050	1.032

Table S2.1. Con't.

	$[\mathrm{Na(NCMe)_2}][\mathrm{Mn(CO)_3(CNAr^{Dipp2})_2}]\bullet\mathrm{C_7H_8}$	$\mathrm{HMn(CO)_3(CNAr^{Dipp2})_2}$	$\mathrm{MeMn(CO)_3(CNAr^{Dipp2})_2}$
Formula	$\mathrm{C_{76}H_{88}N_4O_3MnNa}$	$\mathrm{C_{65}H_{75}N_2O_3Mn}$	$\mathrm{C_{66}H_{77}N_2O_3Mn}$
Crystal System	Monoclinic	Monoclinic	Triclinic
Space Group	*Cm*	*C*2/*c*	*P*-1
a, Å	16.0055(11)	23.733(6)	16.737(6)
b, Å	24.3120(17)	23.631(6)	18.896(8)
c, Å	11.5994(8)	21.360(5)	20.570(8)
α, deg	90	90	114.849(5)
β, deg	128.7135(7)	108.669(4)	90.031(5)
γ, deg	90	90	90.131(5)
V, $Å^3$	3521.9(4)	11349(5)	5903(4)
Z	2	8	2
Radiation (λ, Å)	Mo-Kα, 0.71073	Mo-Kα, 0.71073	Mo-Kα, 0.71073
ρ (calcd.), $\mathrm{g/cm^3}$	1.116	1.156	1.127
μ (Mo Kα), mm^{-1}	0.241	0.279	0.269
Temp, K	100(2)	100(2)	100(2)
θ max, deg	28.23	25.00	25.77
data/restraints/ parameters	8014 / 44 / 425	10318 / 0 / 689	21907 / 0 / 1373
R_1	0.0492	0.0953	0.0488
wR_2	0.1216	0.2181	0.1200
GOF	1.031	1.022	1.038

Table S2.1. Con't.

	$Cl_2(Me)SiMn(CO)_3(CNAr^{Dipp2})_2$	$ClSnMn(CO)_3(CNAr^{Dipp2})_2 \bullet 0.5Et_2O$
Formula	$C_{66}H_{77}N_2O_3Cl_2MnSi$	$C_{67}H_{79}N_2O_{3.50}ClMnSn$
Crystal System	Triclinic	Monoclinic
Space Group	*P*-1	$P2_1/c$
a, Å	10.625(3)	19.479(5)
b, Å	23.786(7)	16.599(5)
c, Å	25.576(8)	20.104(5)
α, deg	78.096(4)	90
β, deg	78.251(4)	113.546(5)
γ, deg	84.842(4)	90
V, $Å^3$	6185(3)	5959(3)
Z	4	4
Radiation (λ, Å)	Mo-Kα, 0.71073	Mo-Kα, 0.71073
ρ (calcd.), g/cm^3	1.182	1.312
μ (Mo Kα), mm^{-1}	0.364	0.724
Temp, K	100(2)	100(2)
θ max, deg	25.41	25.80
data/restraints/ parameters	22216 / 0 / 1386	11292 / 0 / 763
R_1	0.0818	0.0487
wR_2	0.1627	0.1363
GOF	1.013	1.033

S3. Input and Results of Computational Studies

S3.1. Computational Details.

Density Functional Theory calculations were performed with the Amsterdam Density Functional (ADF) program suite,[7,8] version 2007.01.[9] For all atoms, the triple-ζ Slater-type orbital TZ2P ADF basis set was utilized without frozen cores. Relativistic effects were included by use of the zeroth-order regular approximation (ZORA).[10,11] The local density approximation (LDA) of Vosko, Wilk and Nusair,[12] (VWN) was coupled with the generalized gradient approximation (GGA) corrections described by Becke[13] and Perdew[14,15] for electron exchange and correlation, respectively. Crystallographic atomic coordinates were used as input where appropriate. Optimized geometries and molecular orbitals were visualized with the ADFView graphical routine of the ADF-GUI.[16]

S3.2. Hardware Specifics. DFT calculations were performed on a home-built 72-CPU (1 x 8 master, 8 x 8 slave) Rocks 4.3 Linux cluster featuring Intel Xeon E5335 Quad-Core 2.00GHz processors. Job control was implemented with the Sun Grid Engine v. 5.3.

S3.3. Input for ClSnMn(CO)$_3$(CNAr^{Ph2})$_2$ (Optimization).

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 <<< "
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MAXMEMORYUSAGE 23000

RELATIVISTIC ZORA

RESTRICTED

CHARGE 0 0

SCF
DIIS
END

XC
 LDA VWN
 GGA Becke Perdew
END

SYMMETRY NOSYM
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 C     4.189001     0.956999    -2.827999
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 H    -4.709094    -0.471008    -3.891102
 H    -3.956118    -2.827397    -4.166022
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 C     4.770041    -2.410240     2.045408
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 C     5.233665    -0.185329     2.890881
 C     5.323639     0.294529     1.578768
 H     4.714691    -2.609083    -0.105851
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GEOMETRY
 GO
END

BASIS
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  core none
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 END INPUT
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S3.4. RESULTS

S3.4.1. **Optimized Cartesian Coordinates for** ClSnMn(CO)$_3$(CNAr^{Ph2})$_2$.

1.C	5.176582	-0.131797	-0.880224
2.C	4.044358	0.371331	-1.562416
3.C	4.151265	0.918967	-2.863310
4.C	5.405482	0.919711	-3.479230
5.C	6.527814	0.405745	-2.829736
6.C	6.408912	-0.108374	-1.538707
7.N	2.814331	0.326360	-0.954219
8.C	1.700454	0.165300	-0.581388
9.C	2.968190	1.507034	-3.558161
10.C	5.072979	-0.652778	0.514261
11.Mn	-0.058982	-0.146298	-0.036018
12.C	-0.698169	0.817654	-1.452169
13.O	-1.106657	1.444239	-2.338441
14.C	0.554249	-0.791115	1.570311
15.O	0.919629	-1.259191	2.562964
16.C	-1.809876	-0.231800	0.598691
17.N	-2.941492	-0.306197	0.943949
18.C	-4.226899	-0.389741	1.414815
19.C	-5.213709	-1.022288	0.628083
20.C	-6.507148	-1.120908	1.148215
21.C	-6.817109	-0.604975	2.406826
22.C	-5.835273	0.037099	3.162830
23.C	-4.530492	0.162756	2.682599
24.C	-4.878474	-1.553943	-0.725934
25.C	-3.476014	0.882881	3.452019
26.C	-0.156700	-1.757628	-0.839304
27.O	-0.216456	-2.794748	-1.355757
28.Sn	0.085259	2.318591	1.156446
29.Cl	1.966314	2.208070	2.706831
30.H	5.492821	1.335686	-4.481648
31.H	7.496227	0.414042	-3.325979
32.H	7.282787	-0.496964	-1.018707
33.H	-7.274373	-1.609663	0.550128
34.H	-7.828895	-0.695747	2.796717
35.H	-6.077592	0.456774	4.137375
36.C	-4.971114	-0.723782	-1.852028
37.C	-4.655061	-1.213168	-3.121185
38.C	-4.240989	-2.536784	-3.279235
39.C	-4.144722	-3.369979	-2.162492
40.C	-4.461485	-2.881691	-0.893533
41.H	-5.288537	0.312090	-1.730145
42.H	-4.725884	-0.554086	-3.985786
43.H	-3.986933	-2.916925	-4.268217
44.H	-3.811335	-4.400626	-2.276505
45.H	-4.375753	-3.530694	-0.022166
46.C	-2.667259	0.210178	4.378367
47.C	-1.654544	0.888578	5.060092
48.C	-1.437736	2.247985	4.826448

49.C	-2.245058	2.929509	3.910900
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53.H	-0.636142	2.772655	5.343536
54.H	-2.088678	3.991806	3.727786
55.H	-3.884200	2.782130	2.510879
56.C	4.811874	-2.007060	0.764114
57.C	4.742291	-2.483005	2.075205
58.C	4.933369	-1.611853	3.149543
59.C	5.190294	-0.261384	2.908267
60.C	5.258677	0.215384	1.598796
61.H	4.659990	-2.688674	-0.072732
62.H	4.532586	-3.536495	2.255952
63.H	4.872592	-1.982264	4.172448
64.H	5.326607	0.428823	3.739650
65.H	5.448508	1.272060	1.412635
66.C	2.678949	2.872078	-3.414525
67.C	1.593842	3.442916	-4.082415
68.C	0.782808	2.656017	-4.902239
69.C	1.061691	1.296510	-5.049358
70.C	2.146618	0.724350	-4.381274
71.H	3.313255	3.487509	-2.776034
72.H	1.381690	4.504297	-3.958484
73.H	-0.069415	3.099127	-5.416020
74.H	0.427534	0.674057	-5.679390
75.H	2.359058	-0.338763	-4.495429

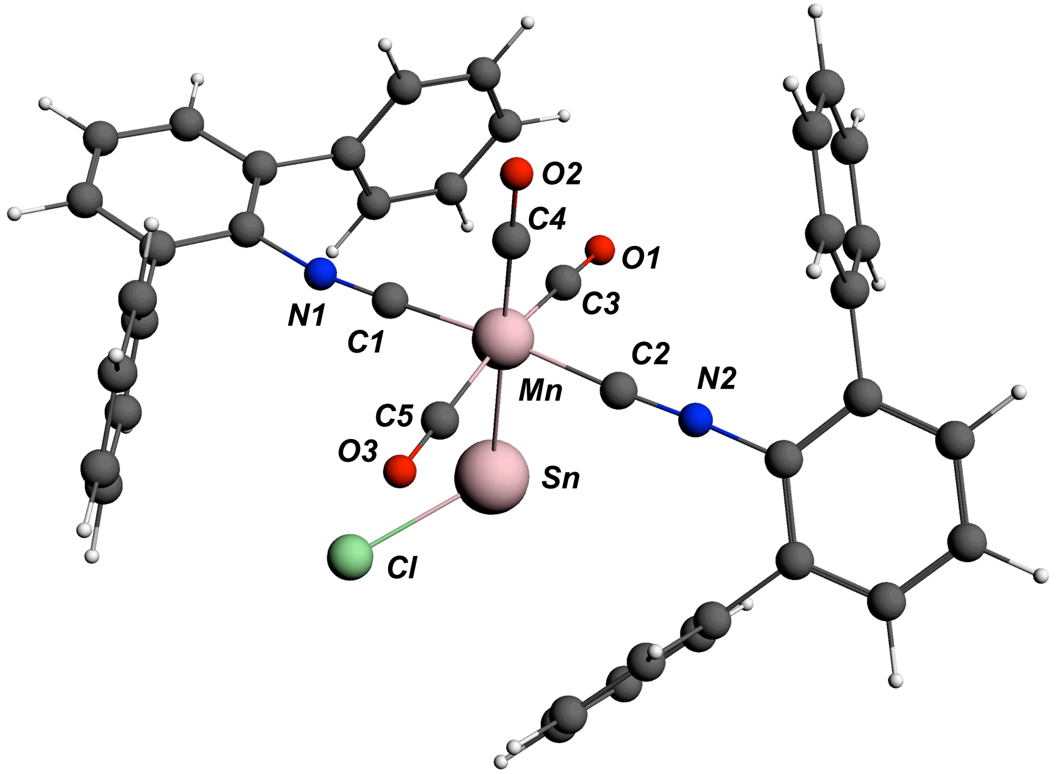

Figure S3.1. Optimized molecular structure of $ClSnMn(CO)_3(CNAr^{Ph2})_2$.

Table S3.1. Comparison of Calculated vs. Experimental Structures for $ClSnMn(CO)_3(CNAr^{Ph2})_2$ and $ClSnMn(CO)_3(CNAr^{Dipp2})_2$ (X-ray).

Parameter/ Complex	$ClSnMn(CO)_3(CNAr^{Ph2})_2$ (Calc)	$ClSnMn(CO)_3(CNAr^{Dipp2})_2$ (Exp)	% Difference
Mn-Sn	2.742 Å	2.6359(8) Å	4.0
Sn-Cl	2.440 Å	2.4048(12) Å	1.4
Mn-C1	1.868 Å	1.879(4) Å	0.5
Mn-C2	1.864 Å	1.902(4) Å	2.0
Mn-C3	1.828 Å	1.834(5) Å	0.3
Mn-C4	1.803 Å	1.845(4) Å	2.2
Mn-C5	1.836 Å	1.879(4) Å	2.2
Mn-Sn-Cl	106.0°	101.53(4)°	4.2
C1-Mn-C2	179.3°	170.97(15)°	4.6
Sn-Mn-C4	172.5°	173.73(13)°	0.7

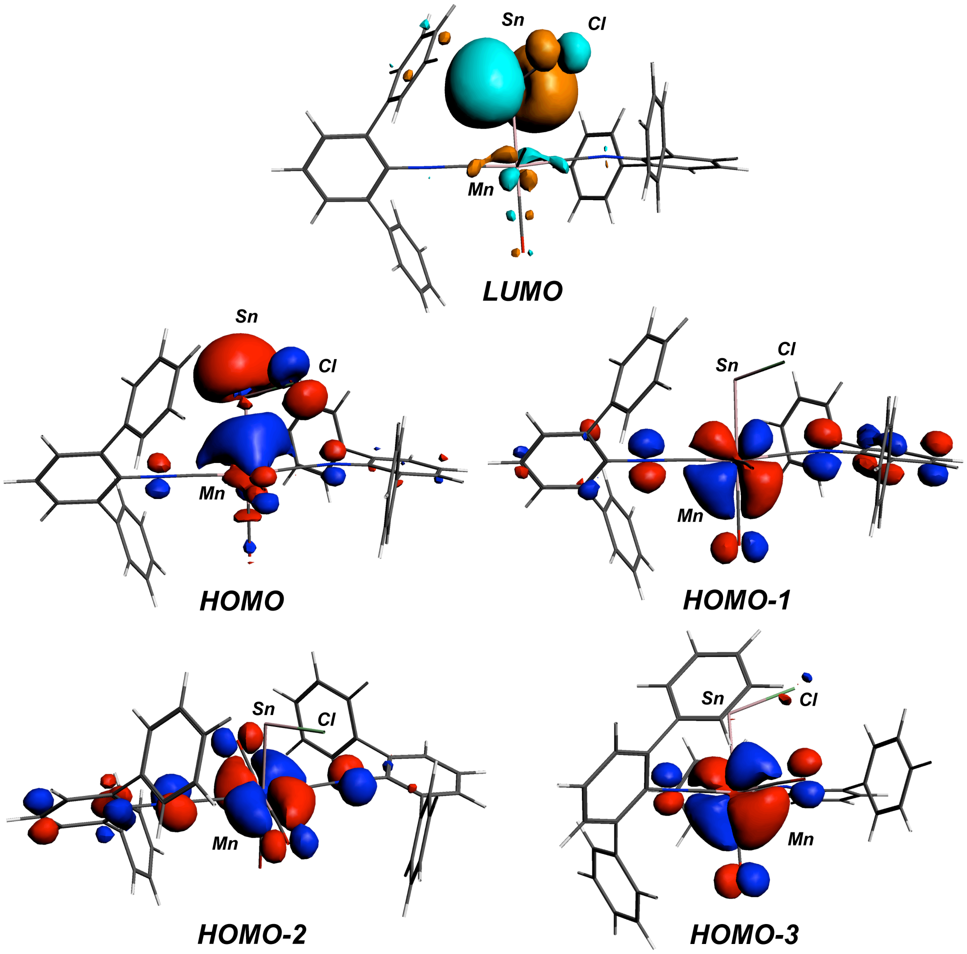

Figure S3.2. Frontier orbitals calculated for $ClSnMn(CO)_3(CNAr^{Ph2})_2$, including Mn π-backbonding interactions.

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