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Oxidation of the Tris(carbene)borate Complex $PhB(MeIm)_3Mn^I(CO)_3$ to $Mn^{IV}[PhB(MeIm)_3]_2(OTf)_2$

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Reaction of the tris(carbene)borate ligand $PhB(MeIm)_3^-$ with $[Mn(CO)_3(^tBuCN)Br]_2$ leads to the manganese(I) tricarbonyl complex $PhB(MeIm)_3Mn(CO)_3$. In contrast to related complexes that are air-stable, $PhB(MeIm)_3Mn(CO)_3$ is O_2-sensitive and is converted to a homoleptic Mn^{IV} complex. IR and cyclic voltammetry measurements of these complexes establish the exceptionally strong donating nature of the tris(carbene)borate ligand.

Ligands that incorporate multiple N-heterocyclic carbene (NHC) donors are anticipated to be strongly electron-releasing because of the strong donor properties of NHCs.[1] Tripodal tris(carbene)borates (Figure 1),[2,3] which bind to metal centers in a facial manner, are one such ligand system. Initial investigations of some octahedral iron and cobalt tris(carbene)borate complexes provided electrochemical evidence for their strong donating properties. In particular, a stable species, proposed to be an Fe^{IV} complex, could be electrochemically generated, although the complex was not isolated.[4]

To obtain more information on the donor properties of these ligands, as well as spectroscopic data that would allow for comparison of these properties with related ligands, we decided to prepare tris(carbene)borate complexes of the $Mn(CO)_3^+$ fragment. Manganese(I) tricarbonyls are known for a wide variety of facially coordinating ligands,[5] and the ν_{CO} stretching frequencies of these complexes provide a quantitative measure of the supporting ligands' donor abilities.

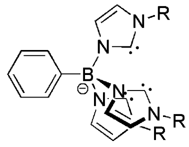

Figure 1. Phenyltris(carbene)borate ligands (R = Me, ^{t}Bu, Mes).

The tris(carbene)borate ligand $PhB(MeIm)_3^-$ is prepared in a procedure analogous to that reported for its bulkier congeners.[3] Thus, a 1:2:3 mixture of $PhBCl_2$, TMSOTf, and *N*-methylimidazole was heated at 100 °C in toluene to yield the boron dication $PhB(MeImH)_3OTf_2$ in 80% yield. Threefold deprotonation of this compound is effected by lithium diisopropylamide (LDA) and the resulting ligand transferred to metal centers in situ.

While the reaction of $PhB(MeIm)_3^-$ with $Mn(CO)_5Br$ results in the formation of an insoluble material, a clean reaction occurs with the new manganese tricarbonyl transfer reagent $[Mn(CO)_3(^tBuCN)Br]_2$,[6] leading to orange $PhB(MeIm)_3Mn(CO)_3$ in 76% yield. Although we have been unable to obtain X-ray-quality crystals of this complex, the structure can be assigned on the basis of its spectral data. Six resonances are observed in the diamagnetic ^1H NMR spectrum. Two signals, at 6.95 and 6.65 ppm, each integrating for three protons, are assigned to the imidazol-2-ylidine protons, while a single peak at 3.87 ppm, integrating for nine protons, is assigned to the methyl group. The protons from the phenyl group resonate as overlapping multiplets at 7.96 and 7.58 ppm. As expected for a complex of pseudo-C_{3v}

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(6) Orange-yellow $[Mn(CO)_3(^tBuCN)Br]_2$ is prepared by heating $Mn(CO)_5Br$ with excess ^{t}BuCN. Crystallographic data for $C_8H_9BrMnNO_3$: $M = 1721.37$, $P2_1/c$, $a = 9.5832(5)$ Å, $b = 11.4151(5)$ Å, $c = 10.5034(5)$ Å, $\beta = 95.603(2)°$, $V = 1143.51(10)$ Å^3, $T = 293(2)$ K, $Z = 4$, $F(000) = 592$, μ(Mo Kα) = 4.630 mm^{-1}, 15 422 reflections, 4086 unique ($R_{int} = 0.0418$), R1 = 0.0310, and wR2 = 0.0616. See the Supporting Information for full synthetic and characterization details.

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Table 1. ν_{CO} Data for Selected $L_3Mn(CO)_3$ Complexes

ligand	A_1/cm^{-1}	E/cm^{-1}	ref
$PhB(MeIm)_3^-$	1990	1889	this work
Cp*	2017	1929	7a
Tp*	2032	1927	7a
$PhB(C_3H_2N_2SMe)_3^-$	1995	1894	7b

symmetry, two CO stretching bands are observed in the solution IR spectrum. The frequencies of these bands, as well as comparative data for related ligands, are shown in Table 1. The low frequency of the bands in $PhB(MeIm)_3Mn(CO)_3$ is noteworthy. By this metric, the tris(carbene)borate ligand is the most strongly donating tripodal ligand known.

Unexpectedly, and in contrast to related complexes, $PhB(MeIm)_3Mn(CO)_3$ is air-sensitive. In the presence of O_2,[8] the orange complex is oxidized in solution over a number of days to dark-red-purple $[PhB(MeIm)_3]Mn^{2+}$ (isolated as the triflate salt following metathesis with KOTf).[9] This complex can also be prepared by reaction of $PhB(MeIm)_3^-$ with 0.5 equiv of $MnBr_2$, followed by oxidation with 2 equiv of AgOTf.

The X-ray crystal structure of $[PhB(MeIm)_3]Mn(OTf)_2$ (Figure 2a)[10] reveals it to be a rare example of a homoleptic organometallic Mn^{IV} complex[11,12] and, to our knowledge, the first Mn^{IV} NHC complex. The coordination environment around the Mn atom, which is located on a crystallographic inversion center, is slightly distorted from octahedral, with cis C−Mn−C bond angles of 87°. The Mn−C bond lengths are shorter than those of other structurally characterized Mn NHC complexes, all of which are of Mn^I and Mn^{II}.[13] The Mn−C bond lengths are comparable to those of other structurally characterized organometallic Mn^{IV} complexes.[11c,d,14] The metrical parameters of the NHC donors in $[PhB(MeIm)_3]Mn(OTf)_2$ do not show any significant differences from other structurally characterized NHC donors, suggesting that the tris(carbene)borate ligand is not oxidized.[15]

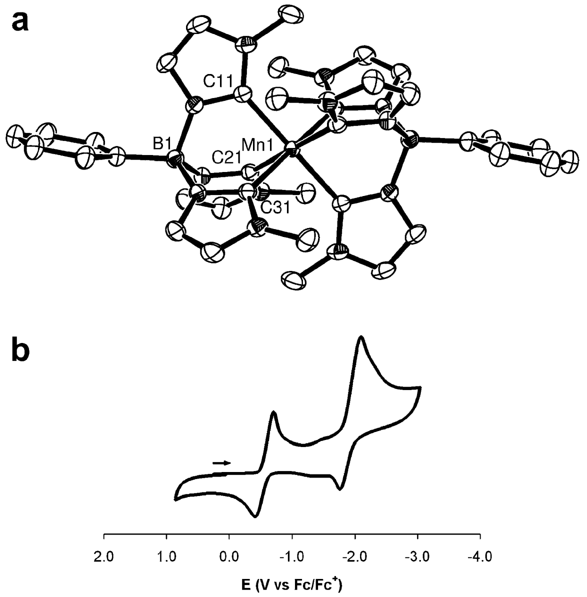

Figure 2. (a) ORTEP diagram of $[PhB(MeIm)_3]_2Mn(OTf)_2$. Thermal ellipsoids are shown at 50% probability. H atoms and counterions have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Mn1−C11, 2.025(3); Mn1−C21, 2.052(3); Mn1−C31, 2.053(3); C11−Mn1−C21, 86.83(11); C11−Mn1−C31, 86.95(11); C21−Mn1−C31, 86.98(11). (b) Cyclic voltammogram of 2 mM $[PhB(MeIm)_3]_2Mn(OTf)_2$ in MeCN/0.01 M NBu_4PF_6, glassy carbon electrode, scan rate = 500 mV/s.

Table 2. $E_{1/2}$ Values for Homoleptic Mn Complexes, Measured in MeCN, with 0.1 M NBu_4PF_6 as the Electrolyte (All Potentials Referenced to the Fc/Fc^+ Couple)

ligand	II/III	III/IV	ref
$PhB(MeIm)_3^-$	-2.09^a	−0.77	this work
Tp^{*b}	−0.13	0.99	17a
Cp*	−0.94		17b
Tp^{Me2}	−0.36	0.97	17c

[a] Quasi-reversible. [b] $C_2H_4Cl_2$ solvent.

The magnetic moment of $[PhB(MeIm)_3]_2Mn(OTf)_2$, determined by the Evans method [$\mu_{eff} = 3.1(3)\ \mu_B$], is consistent with the expected $S = {}^3/_2$ spin state. The complex is NMR-silent, and no EPR spectrum is observed at 77 K.

The electrochemical properties of $[PhB(MeIm)_3]Mn(OTf)_2$ are notable. Cyclic voltammetry (CV) measurements reveal two redox waves (Figure 2b). A reversible wave at −0.71 V is attributed to the $Mn^{III/IV}$ couple, and a quasi-reversible wave at −2.09 V is attributed to the $Mn^{II/III}$ couple. These electrochemical measurements show that the tris(carbene)borate ligand is significantly more stabilizing of higher oxidation states than other facially coordinating ligands (Table 2). Remarkably, the $Mn^{III/IV}$ potential is comparable to hexacoordinate Mn complexes of *dianionic* Schiff-base ligands such as l-hydroxy-3-(salicylideneamino)propane.[16]

To obtain insight into the unusual O_2 sensitivity of $PhB(MeIm)_3Mn(CO)_3$, we have recorded its cyclic voltam-

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(8) Control experiments have established that $PhB(MeIm)_3Mn(CO)_3$ is insensitive to light, water, or heat.

(9) The UV−vis and electrospray ionization mass spectrometry (ESI-MS) of the product obtained prior to anion metathesis are identical with those of $[PhB(MeIm)_3]Mn(OTf)_2$. There is no evidence in the IR spectrum of this material for CO ligands or a carbonate anion.

(10) Crystallographic data for $C_{38}H_{40}B_2F_6MnN_{12}O_6S_2$: $M = 1003.55$, $P2_1/c$, $a = 12.8947(5)$ Å, $b = 13.9914(5)$ Å, $c = 13.5128(5)$ Å, $\beta = 64.280(2)°$, $V = 2196.38(14)$ A^3, $T = 293(2)$ K, $Z = 4$, $F(000) = 1042$, $\mu(Mo\ K\alpha) = 0.482\ mm^{-1}$, 27 746 reflections, 3247 unique ($R_{int} = 0.0211$), R1 = 0.0404, and wR2 = 0.1132.

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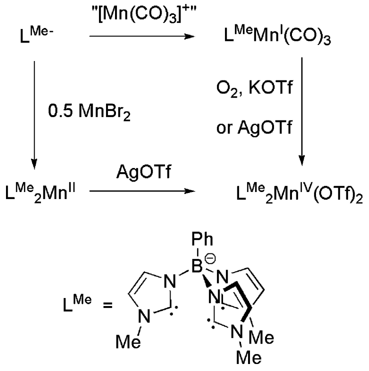
Scheme 1



mogram. In contrast to Cp*Mn(CO)$_3$, which can be reversibly oxidized at 0.64 V,[18] only irreversible oxidation is observed for PhB(MeIm)$_3$Mn(CO)$_3$. Chemical oxidation of PhB(MeIm)$_3$Mn(CO)$_3$, achieved by the addition of excess AgOTf, also results in the formation of the Mn^{IV} complex [PhB(MeIm)$_3$]$_2$Mn(OTf)$_2$.

These results suggest that PhB(MeIm)$_3$Mn(CO)$_3$ is initially oxidized by O$_2$. Although the oxidation state of Mn that is formed is unknown, it is likely that this species is unstable with respect to ligand redistribution, leading to the formation of the homoleptic Mn^{IV} complex. At present, the fate of the remaining Mn is unknown. A summary of the chemistry is shown in Scheme 1.

In conclusion, we have prepared and characterized the manganese(I) tricarbonyl complex PhB(MeIm)$_3$Mn(CO)$_3$. In contrast to the air stability of most complexes of this type, it is aerobically oxidized to a homoleptic Mn^{IV} complex. The stability of this high-valent complex contrasts with that of other homoleptic Mn^{IV} organometallic complexes that are typically air-sensitive.[12] Both IR and CV measurements of these complexes attest to the remarkable donor properties of tris(carbene)borates and, in particular, their ability to stabilize higher oxidation states.

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Supporting Information Available: Synthesis, characterization, and X-ray structural details, including UV−vis, CV, and ESI-MS of [PhB(MeIm)$_3$]Mn(OTf)$_2$ and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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