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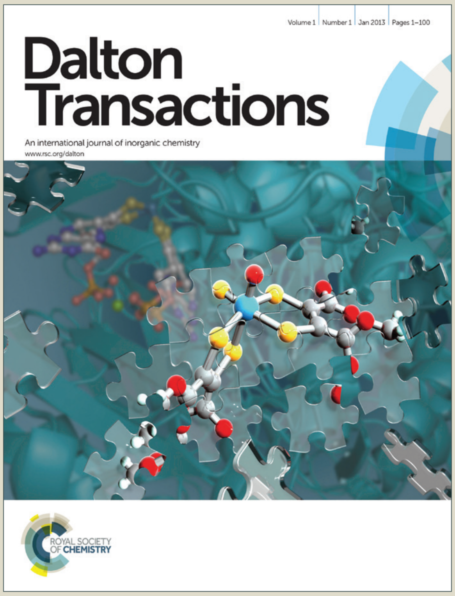

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Group VI Metal Complexes of Tris(diphenylphosphinomethyl)phenylborate: Modulation of Ligand Donation via Coordination of $M(CO)_3$ Units at the Borate Phenyl Substituent

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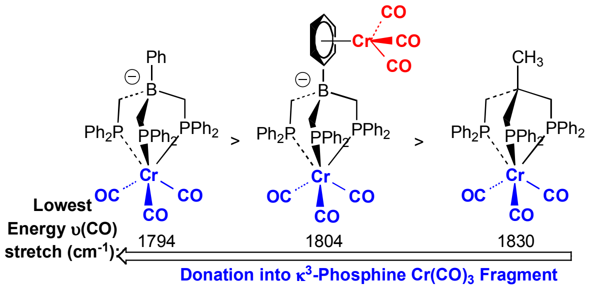
Table of Contents Textual Abstract

Modulation of tris(diphenylphosphinomethyl)phenylborate donation to κ^3-phosphine-bound fragments is inductively achieved by the coordination of 12-electron $M(CO)_3$ fragments at the borate phenyl substituent in the first application of tris(phosphino)borates as bi-functional ligands.

Table of Contents Graphical Abstract (within 8 cm * 4 cm maximum size)



Abstract

A series of d^6 metal complexes of tris(diphenylphosphinomethyl)phenylborate ($[PhB(CH_2PPh_2)_3]^{-}$, $PhBP_3$), including $[Et_4N][M(CO)_3(PhBP_3)]$ (M = Cr, Mo, W), inaugural group VI metal tris(phosphino)borate complexes, and zwitterionic $Mn(CO)_3(PhBP_3)$ have been synthesized and fully characterized. An analysis of IR ν(CO) data for $[Et_4N][M(CO)_3(PhBP_3)]$ indicates that $PhBP_3$ is significantly less strongly donating than Tp towards zerovalent $M(CO)_3$ fragments; $PhBP_3$ does not function as a *strongly donating scorpionate* in this system as its does towards cationic metal fragments suggesting that $PhBP_3$ may not function as an effective surrogate of hydrotris(1-pyrazolyl)borate towards zerovalent metals. While the metal centers of $[Et_4N][M(CO)_3(PhBP_3)]$ are very likely still more electron-rich than those of $M(CO)_3$(triphos), the anions of $[Et_4N][M(CO)_3(PhBP_3)]$ do not provide robust oxidative addition products analogous to those of $M(CO)_3$(triphos). A new bi-functional role for $PhBP_3$ was investigated via the synthesis of seven structurally characterized bimetallics in which zerovalent $M(CO)_3$ and monovalent $[Mn(CO)_3]^+$ fragments bind the three phosphine atoms and the borate phenyl substituent. IR ν(CO) data support modest attenuation of $PhBP_3$ donor ability at phosphorus upon η^6-phenyl substituent binding, representing a new inductive strategy for tuning tris(phosphino)phenylborate donation at the κ^3-phosphine-bound metal fragment.

Introduction

Tris(diphenylphosphinomethyl)phenylborate ($[PhB(CH_2PPh_2)_3]^{-}$, $PhBP_3$) is the most prolific member of a class of strong field ligands that are hybrids of tridentate phosphines and trispyrazolylborates.[1] The $PhBP_3$ ligand (and its $[R'B(CH_2PR_2)_3]^{-}$ analogues) have been dubbed *strongly donating scorpionates* as negatively charged, face-capping ligands that are better donors than hydrotris(1-pyrazolyl)borate.[2] For example, the linear nitrosyl ligands of L_3NiNO exhibit ν(NO) absorptions at 1786 cm^{-1} (L_3 = Tp*)[3] and 1737 cm^{-1} (L_3 = $PhBP_3$).[4] Due to the paucity of metal carbonyl anions containing κ^3-$PhBP_3$ (only two have been reported to date), available data is very limited for the important assessment of $PhBP_3$ donation relative to trispyrazolylborates towards zerovalent metal fragments. This information is necessary to predict the prospects of tris(phosphino)borates for applications with low valent metals in light of the interest in using $PhBP_3$ as a surrogate for Tp.[5] Substitution of tris(phosphino)borates for trispyrazolylborates is advantageous to avoid the purification challenges that arise during the preparation of Tp ligands.[5] Caballero and Pérez determined the activities afforded by catalyst precursor ($PhBP_3$)Cu(PPh_3) for a series of organic transformations as quite comparable to that of Tp*Cu(PPh_3).[5] Trispyrazolylborates are instrumental in zerovalent group VI metal dearomatization agents, where strong Tp donation results in extremely π-basic fragments (*e.g.*, {TpW(NO)(PMe_3)}) that bind aromatic substrates in an η^2-fashion.[6] An assessment of $PhBP_3$ donation towards zerovalent group VI metals is the first step to ascertain $PhBP_3$ compatibility as a Tp surrogate in analogous complexes.

Vigorous efforts have been made to modulate tris(phosphino)borate donor ability. Substitution of phenyl substituents at phosphorus has an obvious impact; $[PhB(CH_2PR_2)_3]^-$ (R=CH_2Cy,[7] ^{i}Pr,[4,8] *m*ter[9] (*m*ter = 3,5-*meta*-terphenyl), *p*-$CF_3C_6H_4$[10]) offer a range of profiles. Further tuning can be accomplished by changing the bridgehead boron substituent. Marks reported $[^nBuB(CH_2PR_2)_3]^-$ (R = Ph, ^{i}Pr) and Ag(PEt_3)(R'B($CH_2PR_2)_3$) (R' = ^{n}Bu, Ph) with $[^nBuB(CH_2PR_2)_3]^-$ providing stronger donation relative that assessed in $[PhB(CH_2PR_2)_3]^-$ analogues.[11] The enhanced donation of $[^nBuB(CH_2PR_2)_3]^-$ was attributed to a greater electrostatic interaction in Ag(PEt_3)(^{n}BuB($CH_2PR_2)_3$) between the Ag(I) and borate centers, relative that in Ag(PEt_3)(PhB($CH_2PR_2)_3$), where the phenyl substituent allows induction of negative charge away from the borate center. Despite the importance of the borate charge in rendering $[R'B(CH_2PR_2)_3]^{-}$ such strong donors, this study is the only attempt to date to directly modulate the extent of charge at the bridgehead boron, and subsequently the electrostatic contribution to metal-ligand binding. Since tris(phosphino)borates are used for spin-state tuning applications,[12] further investigation into this modulation strategy is warranted. As part of our examination of (phosphino)borate chemistry of low valent early transition metals,[13] we now report that $PhBP_3$ cannot be classified as a strongly donating scorpionate in the group VI metal salts $[Et_4N][M(CO)_3(PhBP_3)]$, and modulation of $PhBP_3$ donation via coordination of $M(CO)_3$ units at the borate phenyl substituent in the inaugural application of any tris(phosphino)borate as a bi-functional ligand.

Results and Discussion

$[Et_4N][M(CO)_3(PhBP_3)]$ and $Mn(CO)_3(PhBP_3)$. Nitrile substitution reactions of $Tl[PhBP_3]$ and $M(CO)_3(RCN)_3$ (M = Cr, R = Me; M= Mo, W, R = Et), followed by Et_4NBr metathesis, afforded $[Et_4N][M(CO)_3(PhBP_3)]$ (M = Cr (**1**), Mo (**2**), W (**3**)). Salts **1-3** join $[Li(THF)_3][Ni(CO)(PhBP_3)]$,[14] $[^{n}Bu_4N][Ni(CO)_2(\kappa^2\text{-}PhBP_3)]$[4] and $[Na(THF)_5][Fe(CO)_2(PhBP_3)]$[15] as containing the only anions of $PhBP_3$ and zerovalent metals; the aforementioned $Ni(NO)(PhBP_3)$ is also known.[4] Salts **1-3** are the first tris(phosphino)borate complexes that include each analogue within a triad. An assessment of $PhBP_3$ donor ability via comparative analyses of infrared ν(CO) spectral data of isoelectronic carbonyl complexes containing tridentate ligand benchmarks is a staple of $PhBP_3$ studies. These comparisons have been predominantly carried out with zwitterionic complexes. Such an IR ν(CO) analysis for d^8 $L_3Co(CO)_2$ suggests a ligand donor ranking of $PhBP_3$ ((C_6H_6): 2008, 1932 cm^{-1})[16] > hydrotris(3-isopropyl-5-methylpyrazolyl)borate (($C_6H_5CH_3$): 2016, 1939 cm^{-1})[17] > triphos ((CH_2Cl_2): 2025, 1965 cm^{-1} for $[Co(CO)_2(triphos)][BPh_4]$)[18] towards $[Co(CO)_2]^+$, supporting the strongly donating scorpionate $PhBP_3$ classification.[2] It should be noted that infrared ν(CO) arguments have been widely used to support tris(phosphino)borates as stronger donors than triphos[2] even though assessment of metal center electronics exclusively via this criteria can be problematic when the charge varies among the complexes being compared. An interrogation of metal electronics by electrochemical means would be useful to corroborate the working assumption that $PhBP_3$ complexes are inherently more electron-rich than their triphos analogues. It is interesting that the donor capability of $PhBP_3$ relative these face-capping ligands can be seemingly modulated with different metal fragments. For example, the IR ν(CO) spectral data for d^6 octahedral $L_3RuCl(CO)_2$ intimated Tp donation roughly equal to that of $PhBP_3$; the IR ν(CO) spectra in CH_2Cl_2 of $TpRuCl(CO)_2$ (2074, 2012 cm^{-1})[19] and $RuCl(CO)_2(PhBP_3)$ (2068, 2021 cm^{-1})[8a] exhibit absorptions that make an unambiguous ligand donor ranking challenging. A significant electrostatic contribution to the metal-$PhBP_3$ interaction is one property that allows the *strongly donating scorpionate* donor capability to be realized. The electrostatic contribution engendered by the cationic $[Co(CO)_2]^+$ fragment in its binding to $PhBP_3$, with two strong π-acceptor ligands is likely greater than that engendered by $[RuCl(CO)_2]^+$, in which chloride π-donation quenches some metal Lewis acidity. In addition, π-acceptance by the diphenylphosphinomethyl groups will decrease in importance as metal center Lewis acidity increases. IR ν(CO) data (Table 1) suggests that the donor ranking towards zerovalent d^6 $M(CO)_3$ fragments is Tp > $PhBP_3$ > triphos, with (1) $PhBP_3$ roughly intermediate that of Tp and triphos and (2) $PhBP_3$ donation discriminated significantly from Tp relative that observed in the zwitterionic six-coordinate d^6 $L_3RuCl(CO)_2$ model system. For example, the lower and higher energy ν(CO) absorptions of **3** are shifted 56 and

Table 1. ν(CO) IR Data for $M(CO)_3(\kappa^3\text{-}L)^a$

Complex	ν(CO) (cm^{-1})	Ref
$Cr(CO)_3$(triphos)	1905, 1830	20a
1	1889, 1794	
$[Et_4N][TpCr(CO)_3]$	1889, 1751	21
$Mo(CO)_3$(triphos)	1937, 1844	20b
2	1912, 1805	
$[Et_4N][TpMo(CO)_3]$	1888, 1752	21
$W(CO)_3$(triphos)	1930, 1835	20c
3	1906, 1800	
$[Et_4N][TpW(CO)_3]$	1878, 1744	21

[a] CH_2Cl_2 solutions of $M(CO)_3$(triphos); CH_3CN solutions of other complexes.

28 cm^{-1} higher, respectively, relative those of $[Et_4N][TpW(CO)_3]$. The lack of zwitterionic character in **1**-**3** apparently renders $PhBP_3$ a significantly weaker donor than Tp, but still a stronger one than triphos towards these neutral $M(CO)_3$ fragments. As noted earlier, electrochemical analyses of **1-3** would provide valuable data to further examine the relative impacts of these anionic and neutral face-capping ligands at $M(CO)_3$ units. Thermal ellipsoid drawings depicting the molecular structures of **1-3** are depicted in Figure 1 (**1**) and in the Supplementary Information (**2**, **3**); **1** contains the first structurally characterized $Cr(CO)_3(R''(MG)(CH_2PPh_2)_3)$ (R" = hydrocarbyl, MG = main group atom) fragment. No significant differences can be detected in the solid-state between neutral $M(CO)_3$(triphos) and anionic $M(CO)_3(PhBP_3)$ units.

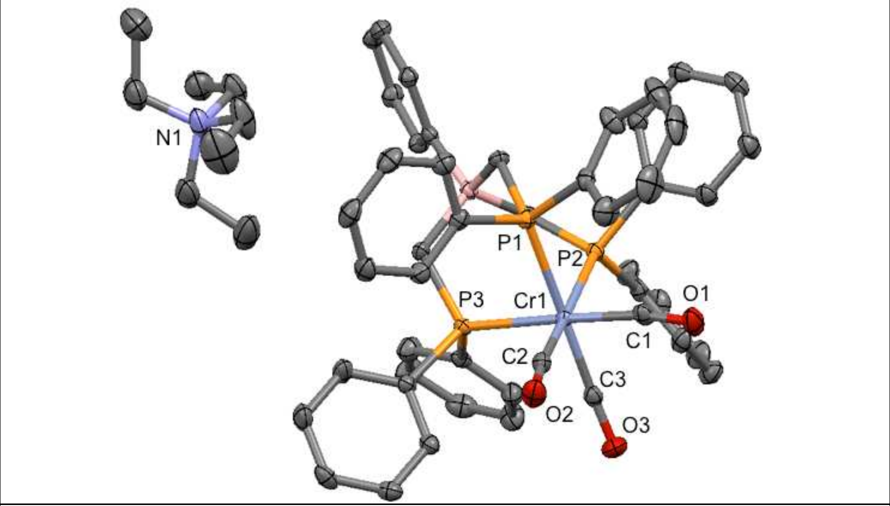


Fig. 1. Thermal ellipsoid plot depicting the molecular structure of **1**. Ellipsoids are drawn at 50% probability, and the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cr-P(1) = 2.3981(8), Cr-P(2) = 2.4139(8), Cr-P(3) = 2.4134(8), Cr-C(1) = 1.821(3), Cr-C(2) = 1.833(3), Cr-C(3) = 1.827(3), P(1)-Cr-P(3) = 87.30(3), P(1)-Cr-P(2) = 83.84(2), P(3)-Cr-P(2) = 85.48(3), C(1)-Cr-C(3) = 82.35(12), C(1)-Cr-C(2) = 85.18(11), C(3)-Cr-C(2) = 84.33(11), C(3)-Cr-P(2) = 99.99(8), C(1)-Cr-P(1) = 95.90(9), C(2)-Cr-P(1) = 91.77(8), C(3)-Cr-P(3) = 94.59(8), C(2)-Cr-P(3) = 96.66(9), C(1)-Cr-P(2) = 92.94(8).

Since the metal centers of **1-3** are predicted as more electron-rich relative those of their $M(CO)_3$(triphos) analogues, we anticipated **2** and **3** to react with halogens to afford zwitterionic products similar to those of $M'(CO)_3$(triphos) (M' = Mo (**12**), W (**13**)). However, while oxidative addition of I_2 and Br_2 to **12** and **13** provides $[MoI(CO)_3(triphos)]I_3$, $[WBr(CO)_3(triphos)]Br_3$, and $[WI(CO)_3(triphos)]I_3$ in high yield,[22] no spectroscopic evidence has been obtained to date for related $MoI(CO)_3(PhBP_3)$ and $WBr(CO)_3(PhBP_3)$. Reactions of I_2 and both **3** and $Tl[W(CO)_3(PhBP_3)]$ resulted in green solids that likely contain $WI(CO)_3(PhBP_3)$ (**14**). The IR ν(CO) spectrum of alleged **14** in the CH_2Cl_2 reaction mixture (2016 (s), 1951 (s), 1906 (m) cm^{-1}) is similar to that reported for $[WI(CO)_3(triphos)]I_3$ ((CH_2Cl_2): 2030 (s), 1973 (s), 1928 (m) cm^{-1}). Unfortunately, isolated crude samples containing hypothesized **14** (IR ν(CO) (nujol): 2006 (s), 1915 (s), 1897 (m) cm^{-1}) defied purification and further characterization by rapidly decomposing upon dissolution in a variety of solvents affording intractable products. Since the steric bulk of $PhBP_3$ and triphos rendered at $Mo(CO)_3$ and $W(CO)_3$ fragments is seemingly indistinguishable on the basis of X-ray crystallographic data, the seven-coordination of proposed $M'X(CO)_3(PhBP_3)$ should be accommodated. The formal intramolecular charge separation in these targeted divalent zwitterions may predispose these complexes towards weak M-X bonds. Reactions of **2** and **3** with one-electron oxidants are being investigated to directly probe whether zwitterionic metal-based radicals of formula $M(CO)_3(PhBP_3)$ are accessible, but our efforts thus far suggest that **1**-**3** do not react as would be expected of simply more electron-rich analogues of neutral $M(CO)_3(triphos)$.

Reaction of $Tl[PhBP_3]$ and $[Mn(CO)_3(C_{10}H_8)][BF_4]$ afforded zwitterionic **4**, noteworthy on the basis of previous difficulties in obtaining $Mn(CO)_3(PhB(CH_2P^iPr_2)_3)$. Lu and Peters[8b] obtained a Tl—Mn adduct, $[PhB(CH_2P^iPr_2)_3]Tl—MnBr(CO)_4$ from the reaction of $Tl[PhB(CH_2P^iPr_2)_3]$ and $MnBr(CO)_5$; heating afforded impure $Mn(CO)_3(PhB(CH_2P^iPr_2)_3)$ (IR ν(CO) (THF) (cm^{-1}): 1999, 1906). The IR ν(CO) spectra of **4** ((THF): 2009, 1931), $Mn(CO)_3Tp$ ((hexanes): 2042, 1941),[23] and $[Mn(CO)_3(triphos)][CF_3SO_3]$ (**14**) ((CH_2Cl_2): 2030, 1960)[24] intimates the usual donor ranking of $PhBP(CH_2P^iPr_2)_3$ > $PhBP_3$ > Tp > triphos observed in zwitterions. As with **2**, **3** and M'$(CO)_3$(triphos), the heightened donation of $PhBP_3$ (in **4**, Figure 2) relative triphos (in **14**) has no detectable structural impact at the Mn(I) center. The zwitterionic electronic ground state of **4** also has no apparent impact on the ligand framework-enforced Mn—B separations in **4** (3.631(3) Å) relative the Mn—bridgehead carbon separation in **14** (3.598(5) Å).

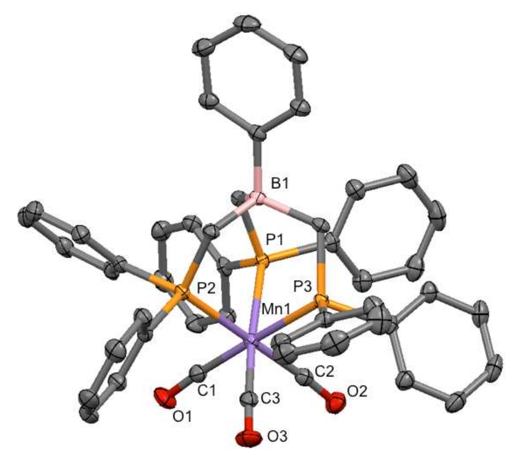
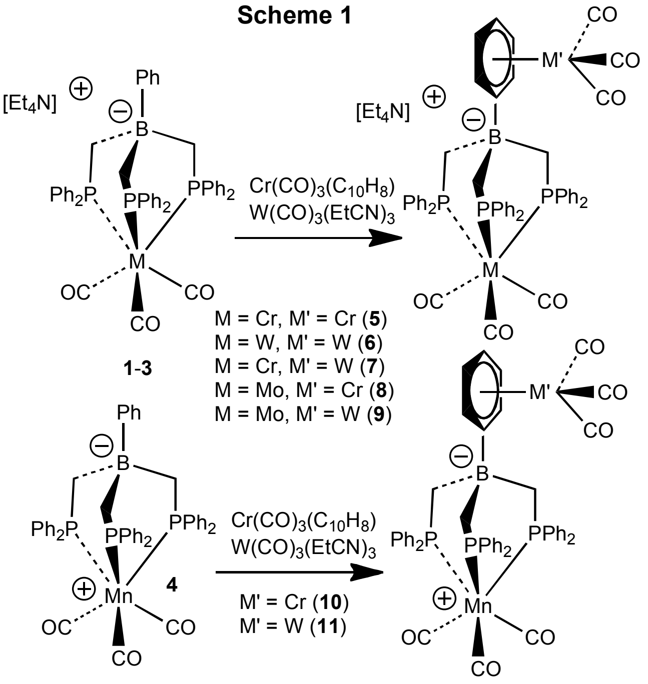


Fig. 2. Thermal ellipsoid plot depicting the molecular structure of **4**. Ellipsoids are drawn at 50% probability, and the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mn-P(1) = 2.3826(7), Mn-P(2) = 2.3667(7), Mn-P(3) = 2.3467(6), Mn-C(1) = 1.812(2), Mn-C(2) = 1.803(2), Mn-C(3) = 1.811(2), P(1)-Mn-P(3) = 85.618(19), P(1)-Mn-P(2) = 88.229(19), P(3)-Mn-P(2) = 90.04(2), C(1)-Mn-C(3) = 88.75(9), C(1)-Mn-C(2) = 89.36(9), C(3)-Mn-C(2) = 88.55(9), C(3)-Mn-P(2) = 92.42(7), C(1)-Mn-P(1) = 96.25(7), C(2)-Mn-P(1) = 90.84(6), C(3)-Mn-P(3) = 89.39(7), C(2)-Mn-P(3) = 90.31(6), C(1)-Mn-P(2) = 90.33(7).

Bimetallic Complexes. Early work established that tetraphenylborate can bind one or two d^6 $M(CO)_3$ units in an η^6-fashion.[25] An emerging ligand design strategy is η^6-coordination of organometallic fragments to ligand π systems to influence donation in bimetallics. Heterobimetallics $[M'Cl(NCN)Ru(C_5R_5)]^+$ (M' = Pt, Pd; R = H, Me), where the phenylene ring of an NCN-pincer ligand coordinates first to the M' center in a tridentate fashion via σ-bonds, and second to a ruthenium organometallic fragment via a π-interaction, feature significant electronic communication between the metal centers.[26] The η^6-coordinated ruthenium fragment has a strong electron-withdrawing effect on the pincer metal, impacting the reactivity of the latter metal towards electrophiles. The η^6 coordination of $[Cp^*Ru]^+$, $[CpRu]^+$, $[CpFe]^+$ and $Cr(CO)_3$ fragments to the aromatic ring of Ni(II), Pd(II) and Pt(II) naphthoresorcinate POCOP pincer compounds allows tuning of group 10 metal electronic properties.[27] These studies suggested the intriguing prospect of tuning $PhBP_3$ donation at phosphorus via coordination of 12-electron fragments at the boron phenyl substituent. Ragogna demonstrated that the phosphorus(I) proligand $(Ph_2B(CH_2PPh_2)_2)P$

reacts with $M(CO)_6$ to afford bimetallics consisting of a $M(CO)_5$ fragment on phosphorus and a $M(CO)_3$ fragment on a borate phenyl group.[28] Low yields prevented an examination of the electronic impact of $M(CO)_3$ binding at the $M(CO)_5$ fragment.[29] Reactions of **1**-**4** with $Cr(CO)_3(C_{10}H_8)$ and $W(CO)_3(EtCN)_3$ resulted in the installation of $Cr(CO)_3$ and $W(CO)_3$ fragments at the boron phenyl substituent (Scheme 1); **5**-**11** are the first bimetallic complexes of $PhBP_3$. Attempts to install $[Mn(CO)_3]^+$ at the phenyl substituents of **1**-**4** have been unsuccessful due to solvent incompatibility issues. The ideal solvent for arene exchange reactions of $[Mn(CO)_3(C_{10}H_8)][BF_4]$ is warm CH_2Cl_2,[30] conditions under which **4** decomposes and **1**-**3** are sparingly soluble; stoichiometric **1**-**4** cannot compete with donor solvents for $[Mn(CO)_3]^+$ binding.

Scheme 1



The IR ν(CO) spectra of **5**-**11** in solution exhibit well separated absorptions for each three-legged piano stool $M(CO)_3$ fragment; these vibrational modes are assumed to be decoupled. Comparison of the lower energy (*E* vibrational mode) stretching frequencies (Table 2) associated with the κ^3-phosphine $M(CO)_3$ units of **5** and **7** to that of **1**, **8** and **9** to that of **2**, **6** to that of **3**, and **10** and **11** to that of **4** are consistent with attenuation of $PhBP_3$ donation at the phosphine bound $M(CO)_3$ units as a result of $M'(CO)_3$ coordination. This modulation is likely a function of reduced electron density at the borate due to an increase in the group electronegativity of (η^6-phenyl)$M'(CO)_3$ relative to phenyl, representing a new strategy for attenuating tris(phosphino)phenylborate donation. This inductive effect is sufficiently subtle that different impacts at the phosphine-coordinated M(CO)$_3$ fragments due to Cr(CO)$_3$ versus W(CO)$_3$ binding at the phenyl substituent are not consistently observed. For example, the greater electron-withdrawing capability of Cr(CO)$_3$ relative to W(CO)$_3$ in M(CO)$_3$(η^6-arene) complexes is long known,[31] and the lower energy ν(CO) absorptions (cm^{-1}) associated with the κ^3-phosphine Cr(CO)$_3$ of **5** (1804), **7** (1797) and **1** (1794) (Table 2) could be interpreted on the basis of this increased inductive effect of Cr(CO)$_3$ (in **5**) relative to W(CO)$_3$ (in **7**) upon η^6-phenyl binding. However, the analogous data for the κ^3-phosphine Mo(CO)$_3$ complexes **8** (1816), **9** (1817) and **2** (1805) do not discriminate between the presence of Cr(CO)$_3$ (in **8**) versus W(CO)$_3$ (in **9**). The ~10 cm-1 blue-shift in this lower energy absorption is also observed between κ^3-phosphine W(CO)$_3$ complexes **6** (1810) and **3** (1800). An arguably negligible impact is observed at the [Mn(CO)$_3$]$^+$ fragments of **4**, **10**, and **11** with the pertinent lower energy absorptions (cm^{-1}) observed at 1935 (**10**), 1936 (**11**), and 1931 (**4**) with again no discrimination between Cr(CO)$_3$ versus W(CO)$_3$ coordinated to the phenyl substituent. The ^{13}CO resonances are shifted modestly upfield in these bimetallics relative those of **1-4**. For example, only 1.5 ppm separate the ^{13}CO resonances of the κ^3-phosphine Cr(CO)$_3$ units of **5** (δ 234.5),[32a] **7** (δ 234.8)[32a] and **1** (δ 236.0).[32b] The ^{11}B chemical shift is also insensitive in this regard, as indicated by the representative upfield shifts of the ^{11}B resonances (ppm) of **5** (δ -16.8)[32a] and **7** (δ -15.1)[32a] relative that of **1** (δ -14.7).[32b] An examination of the inductive

Table 2: Infrared ν(CO) Spectral Data (cm^{-1}) for κ^3-Phosphine M(CO)$_3$ Units of **1-11**

1 (M = Cr)	1899, 1794
5 (M = Cr, M’ = Cr)	1895, 1804
7 (M = Cr, M’ = W)	1897, 1797
2 (M = Mo)	1912, 1805
8 (M = Mo, M’ = Cr)	1912, 1816
9 (M = Mo, M’ = W)	1912, 1817
3 (M = W)	1902, 1800
6 (M = W, M’ = W)	1905, 1810
4 (M = Mn)	2009, 1931
10 (M = Mn, M’ = Cr)	2011, 1935
11 (M = Mn, M’ = W)	2010, 1936

1-3 in CH$_3$CN, **4-11** in THF

impact engendered by the coordination of cationic fragments at the borate phenyl substituent would provide further proof of concept for this strategy. Bimetallics **5-11** were characterized by X-ray crystallography. Thermal ellipsoid drawings of **6** and **10** are in Figures 3 and 4, respectively; the remaining complexes are displayed in the Supplementary Information. In each set of κ^3-phosphine M(CO)$_3$ complexes (M = Cr: **1**, **5**, **7**; M = Mo: **2**, **8**, **9**; M = W: **3**, **6**; M = Mn: **4**, **10**, **11**) the parameters that define the slightly elongated trigonal antiprismatic M(CO)$_3$P$_3$ coordination geometries are statistically identical.

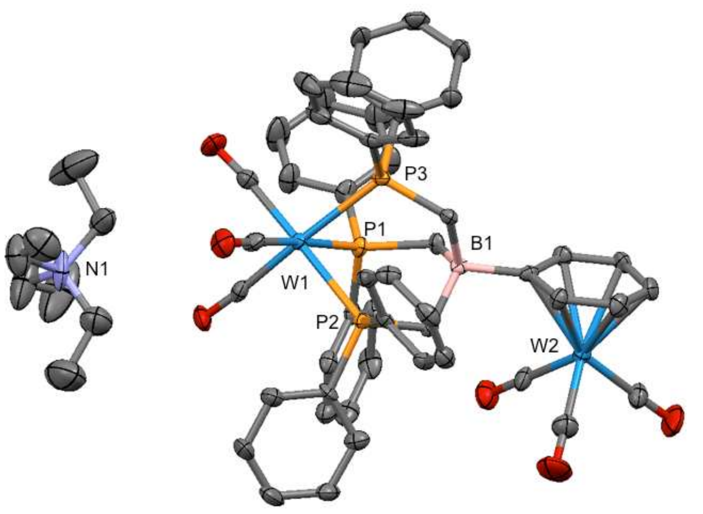


Fig. 3. Thermal ellipsoid plot depicting the molecular structure of **6**. Ellipsoids are drawn at 50% probability, and the hydrogen atoms are omitted for clarity. Selected average bond lengths (Å) and angles (deg): (a) Phosphine bound W(CO)$_3$: W-P = 2.547(3), W-C = 1.964(5), P-W-P = 83(3), *cis* P-W-C = 96(3), (O)C-W-C(O) = 85(1); (b) Arene bound W(CO)$_3$: W-C(arene) = 2.37(2), W-C(O) = 1.954(2); C(O)-W-C(O) = 86(2).

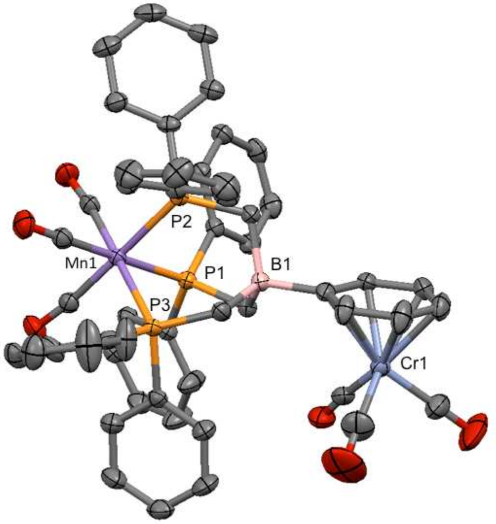


Fig. 4. Thermal ellipsoid plot depicting the molecular structure of **10**. Ellipsoids are drawn at 50% probability, and the hydrogen atoms are omitted for clarity. Selected average bond lengths (Å) and angles (deg): Mn-P = 2.37(2), Mn-C = 1.809(3), P-Mn-P = 88(2), *cis* P-Mn-C = 93(2), (O)C-Mn-C(O) = 86.3(9), Cr-C(arene) = 2.23(2), Cr-C(O) = 1.82(1); C(O)-Cr-C(O) = 87(2).

Summary and Conclusions

An analysis of IR ν(CO) data for the first group VI metal complexes of PhBP$_3$ and rare examples of anionic tris(phosphino)borate metal complexes, **1-3**, indicates that PhBP$_3$ donor ability is significantly weaker than that of Tp towards zerovalent M(CO)$_3$. PhBP$_3$ is not a "strongly donating scorpionate" in **1-3**, on the basis of a relatively low electrostatic contribution to the metal-PhBP$_3$ interactions compared to that present in the zwitterions in which PhBP$_3$ has been extensively employed. As a consequence, PhBP$_3$ may not be a good surrogate for Tp for applications with zerovalent group VI metals in contrast to that suggested with Cu(I) by the comparable catalytic activities of (PhBP$_3$)Cu and Tp*Cu.[5] For example, {(PhBP$_3$)M(PMe$_3$)(NO)} fragments may be handicapped as π-bases relative to analogous {TpM(PMe$_3$)(NO)} fragments[6] towards η^2-arene binding to affect substrate dearomatization. This finding is of interest on the basis of the ongoing development of alternate group VI metal π-basic fragments with modulated steric and electronic profiles.[33] Zwitterionic **4** is the first fully characterized Mn(CO)$_3$(R'B(CH$_2$PR$_2$)$_3$) complex; TlBF$_4$ elimination from [Mn(CO)$_3$(C$_{10}$H$_8$)][BF$_4$] and Tl[PhBP$_3$] precludes the Tl(I)-Mn(I) binding observed in [PhB(CH$_2$P^{i}Pr$_2$)$_3$]Tl—MnBr(CO)$_4$.[8b] A new bi-functional role for PhBP$_3$ was explored via the synthesis of bimetallics **5-11** in which M(CO)$_3$ fragments bind both the three phosphines and the borate phenyl substituent. IR ν(CO) data support attenuation of PhBP$_3$ donor ability at phosphorus upon η^6-phenyl substituent binding. This report enlightens a third general strategy, in addition to changing phosphine substituents and the introduction of alternate bridgehead boron substituents, for tuning tris(phosphino)borate donor ability at phosphorus. Modulation of PhBP$_3$ donation is of interest since this class of ligands is used for spin-state tuning applications.[12] The enhanced donor capability of PhBP$_3$ relative to triphos towards the M(CO)$_3$ fragments in **1-3**, in addition to the blue shifts in the IR ν(CO) absorptions observed for these κ^3-phosphine coordinated units upon coordination of M'(CO)$_3$ fragments at the borate phenyl substituents in **5-9**, provides further evidence that the borate charge plays a vital role in PhBP$_3$ donation even in complexes that are not zwitterionic.

Experimental

Similar procedures were conducted to synthesize **1-3** and **5-11**. Representative procedures for **1**, **5**, and **6** are provided below. All ^{1}H NMR data, and ^{13}C{^{1}H} NMR data, with the exception of ^{13}CO chemical shifts, are omitted below for **1-11**. General procedures, complete experimental details and characterization data (including annotated ^{31}P{^{1}H}, ^{11}B, ^{1}H, and ^{13}C{^{1}H} NMR spectra and summaries of these data for **1-11**) are in the Supplementary Information.

[Et_4N][$Cr(CO)_3(PhBP_3)$] (1)

THF (50 mL) was added to Tl[$PhBP_3$] (0.472 g, 0.531 mmol) and $Cr(CO)_3(CH_3CN)_3$ (0.131 g, 0.505 mmol). The yellow solution was refluxed (1.5 hr), transferred to Et_4NBr (0.117 g, 0.556 mmol) and stirred at ambient temperature (2 hr) before the solvent was removed in vacuo. The oily residue was dissolved in CH_3CN (50 mL) and the solution filtered through alumina. Most of the solvent from the yellow filtrate was removed in vacuo. Addition of Et_2O (40 mL) affected the precipitation of a yellow powder that was isolated by filtration, washed with Et_2O (3 * 10 mL) and dried in vacuo. Et_2O diffusion into a CH_3CN solution provided pale yellow microcrystals (0.343 g, 71%). Mp. 240 – 241 °C (dec). Found: C, 70.41; H, 6.33; N, 1.44. $C_{56}H_{61}BCrNO_3P_3$ requires C, 70.66; H, 6.46; N, 1.47. IR (CH_3CN) ν_{max}(CO)/cm^{-1} 1899 (s), 1794 (s); (Nujol) ν_{max}(CO)/cm^{-1} 1892 (s), 1787 (s). ^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ 44.5 (s). ^{11}B NMR (128 MHz, CD_3CN): δ□-14.7 (s). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN): δ(^{13}CO)□236.0 (m).

[Et_4N][$Mo(CO)_3(PhBP_3)$] (2)

Yield: 76%. Mp. 273 – 274 °C (dec). Found: C, 67.67; H, 6.51; N, 1.44. $C_{56}H_{61}BMoNO_3P_3$ requires C, 67.54; H, 6.17; N, 1.41. IR (CH_3CN) ν_{max}(CO)/cm^{-1} 1912 (s), 1805 (s); (Nujol) ν_{max}(CO)/cm^{-1} 1906 (s), 1801 (s). ^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ 26.2 (app. d, *J* = 6.0

Hz). ^{11}B NMR (128 MHz, CD_3CN): δ□-14.3 (s). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN): δ(^{13}CO)□225.3 (m).

[Et_4N][W(CO)$_3$(PhBP$_3$)] (3)

Yield: 72%. Mp. 300 – 304 °C (dec). Found: C, 61.93; H, 5.94; N, 1.47. $C_{56}H_{61}BNO_3P_3W$ requires: C, 62.07; H, 5.67; N, 1.29. IR (CH_3CN) ν_{max}(CO)/cm^{-1} 1906 (s), 1800 (s); (Nujol) ν_{max}(CO)/cm^{-1} 1902 (s), 1796 (s). ^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ 9.1 (app. d, J = 4.1 Hz, ^{31}P—^{183}W satellites: 9.8, 8.5, $^1J_{PW}$ = 210 Hz). ^{11}B NMR (128 MHz, CD_3CN): δ□-13.2 (s). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN): δ(^{13}CO)□ 217.5 (m).

Mn(CO)$_3$(PhBP$_3$) (4)

CH_2Cl_2 (80 mL) was added to Tl[PhBP$_3$] (0.948 g, 1.07 mmol) and [Mn(CO)$_3$($C_{10}H_8$)][BF_4] (0.358 g, 1.01 mmol). The orange solution was stirred at ambient temperature (16 hr) before the solvent was removed in vacuo. The oily residue was dissolved in THF (50 mL) and the solution filtered through alumina. Most of the solvent from the yellow filtrate was removed in vacuo. Addition of pentane (80 mL) affected the precipitation of a pale yellow powder that was isolated by filtration, washed with pentane (3 * 15 mL) and dried in vacuo (0.504 g, 60%). These samples of **4** contained varying amounts of THF (from ~0.5 to 1.5 equiv) on the basis of ^{1}H NMR spectroscopy even after extended drying under vacuum at ambient temperature. Pentane diffusion into a THF solution provided pale yellow blocks that analyze as **4** • 2THF. Mp. 264 – 265 °C (dec). Found: C, 69.78; H, 6.04. $C_{56}H_{57}BMnO_5P_3$ (**4** • 2THF) requires: C, 69.43; H, 5.93. IR (THF) ν_{max}(CO)/cm^{-1} 2009 (s), 1931 (s); (Nujol) ν_{max}(CO)/cm^{-1} 2009 (s), 1945 (m), 1923 (m). ^{31}P{^{1}H} NMR (162 MHz, C_4D_8O): δ 38.1 (m, br). ^{11}B NMR (128 MHz, C_4D_8O): δ -16.0 (s). ^{13}C{^{1}H} NMR (101 MHz, C_4D_8O): δ(^{13}CO) resonance not observed.

[Et_4N][Cr(CO)$_3${η^6-($PhBP_3$)Cr(CO)$_3$}] (5)

THF (40 mL) was added to Tl[$PhBP_3$] (0.474 g, 0.533 mmol) and Cr(CO)$_3$($C_{10}H_8$) (0.402 g, 1.52 mmol). The deep red solution gradually changed to pale red while stirring at ambient temperature (16 hr). ^{31}P{^{1}H} spectroscopy indicated only one phosphorus environment (δ 43.2), confirming that both [$PhBP_3$]$^-$ reactive sites had been metallated. The solvent was removed in vacuo; the red residue was extracted into Et_2O (50 mL). Filtration separated a grey solid from a red filtrate. The Et_2O was removed in vacuo; the residue was dissolved in THF (35 mL) and transferred to Et_4NBr (0.117 g, 0.556 mmol). After stirring at ambient temperature (2 hr), the orange solution was filtered through alumina. Most of the solvent from the resulting yellow filtrate was removed in vacuo. Addition of Et_2O (40 mL) affected the precipitation of a yellow powder that was isolated by filtration, washed with Et_2O (3 * 10 mL) and dried in vacuo. Et_2O diffusion into a THF solution provided bright yellow microcrystals (0.261 g, 45%). Mp. 294 – 296 °C (dec). Found: C, 64.79; H, 5.81; N, 1.13. $C_{59}H_{61}BCr_2NO_6P_3$ requires C, 65.14; H, 5.65; N, 1.29. IR (THF) ν_{max}(CO)/cm^{-1} 1948 (s), 1898 (m), 1863 (s), 1804 (m); (Nujol) ν_{max}(CO)/cm^{-1} 1944 (s), 1895 (s), 1865 (s, sh), 1842 (s), 1785 (s, sh), 1771 (s). ^{31}P{^{1}H} NMR (162 MHz, C_4D_8O): δ 43.1 (app d., *J* = 6.6 Hz). ^{11}B NMR (128 MHz, C_4D_8O): δ□-16.8 (s). ^{13}C{^{1}H} NMR (101 MHz, C_4D_8O): δ(^{13}CO)□237.2 (arene-bound Cr(CO)$_3$), 234.5 (m, P-bound Cr(CO)$_3$).

[Et_4N][W(CO)$_3${η^6-($PhBP_3$)W(CO)$_3$}] (6)

THF (40 mL) was added to Tl[$PhBP_3$] (0.486 g, 0.546 mmol) and W(CO)$_3$(CH_3CH_2CN)$_3$ (0.450 g, 1.04 mmol). The orange solution gradually changed to brown while under reflux (1.5 hr). This solution was added to Et_4NBr (0.120 g, 0.571 mmol) and stirred at ambient temperature (16 hr). Filtration through alumina resulted in a yellow filtrate. Most of the solvent from the filtrate was removed in vacuo. Addition of Et_2O (40 mL) affected the precipitation of a yellow powder that was isolated by filtration, washed with Et_2O (3 * 10 mL) and dried in vacuo. Et_2O diffusion into a THF solution provided pale yellow microcrystals (0.371 g, 53%). Mp. 280 °C (dec). Found: C, 52.63; H, 4.86; N, 1.15. $C_{59}H_{61}BNO_6P_3W_2$ requires C, 52.43; H, 4.55; N, 1.04. IR (THF) $v_{max}(CO)/cm^{-1}$ 1946 (s), 1905 (m), 1860 (s), 1810 (m); (Nujol) $v_{max}(CO)/cm^{-1}$ 1944 (s), 1901 (s), 1846 (s, br), 1793 (s, sh), 1774 (s). $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 9.6 (s, ^{31}P—^{183}W satellites: 10.3, 9.0, $^1J_{PW}$ = 210 Hz). ^{11}B NMR (128 MHz, C_4D_8O): δ□-13.6 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ(^{13}CO)□215.7 (m, P-bound $W(CO)_3$), 213.2 (s, ^{13}C—^{183}W satellites: 214.10, 212.23, $^1J_{CW}$ = 188 Hz, arene-bound $W(CO)_3$).

$[Et_4N][W(CO)_3\{\eta^6\text{-}(PhBP_3)Cr(CO)_3\}]$ (7)

Yield: 40%. Mp. 264 - 266 °C (dec). Found: C, 58.01; H, 5.34; N, 1.01. $C_{59}H_{61}BCrNO_6P_3W$ requires: C, 58.10; H, 5.04; N, 1.15. IR (THF) $v_{max}(CO)/cm^{-1}$ 1946 (s), 1905 (m, sh), 1897 (s), 1860 (s), 1797 (m); (Nujol): $v_{max}(CO)/cm^{-1}$ 1943 (s), 1894 (s), 1844 (s, br), 1787 (s, sh), 1770 (s). $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 45.4 (s). ^{11}B NMR (128 MHz, C_4D_8O): δ□-15.1 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ(^{13}CO)□234.8 (m, $Cr(CO)_3$), 214.2 (s, ^{13}C—^{183}W satellites: 215.15, 213.28, $^1J_{CW}$ = 188 Hz, $W(CO)_3$).

$[Et_4N][Cr(CO)_3\{\eta^6\text{-}(PhBP_3)Mo(CO)_3\}]$ (8)

Yield: 80%. Mp. 289 - 290 °C (dec). Found: C, 62.77; H, 5.52; N, 1.17. $C_{59}H_{61}BCrMoNO_6P_3$ requires: C, 62.61; H, 5.43; N, 1.24. IR (THF) $v_{max}(CO)/cm^{-1}$ 1948 (s), 1912 (s), 1863 (s), 1816 (m); (Nujol) $v_{max}(CO)/cm^{-1}$ 1944 (s), 1906 (s), 1850 (s, br), 1798 (s, sh), 1783 (s). $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 26.6 (s). ^{11}B NMR (128 MHz, C_4D_8O): δ□-14.5 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ(^{13}CO)□237.1 (s, $Cr(CO)_3$), 224.6 (m, $Mo(CO)_3$).

$[Et_4N][W(CO)_3\{\eta^6\text{-}(PhBP_3)Mo(CO)_3\}]$ (9)

Yield: 41%. Mp. 220 - 221 °C (dec). Found: C, 56.11; H, 5.33; N, 1.11. $C_{59}H_{61}BMoNO_6P_3W$ requires: C, 56.08; H, 4.87; N, 1.11. IR (THF) $v_{max}(CO)/cm^{-1}$ 1946 (s), 1912 (s), 1859 (s), 1817 (m); (Nujol): $v_{max}(CO)/cm^{-1}$ 1944 (s), 1906 (s), 1846 (s, br), 1804 (s, sh), 1783 (s). $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 25.0 (s). ^{11}B NMR (128 MHz, C_4D_8O): δ -16.5 (s). $^{13}C\{^1H\}$

NMR (101 MHz, C_4D_8O): $\delta(^{13}CO)$□221.7 (s, $Mo(CO)_3$), 211.4 (s, ^{13}C—^{183}W satellites: 212.32, 210.46, $^1J_{CW}$ = 188 Hz).

$Cr(CO)_3\{\eta^6$-$(PhBP_3)Mn(CO)_3\}$ (10)

Yield: 76%. Mp. 279 – 280 °C (dec). Found: C, 63.77; H, 4.30. $C_{51}H_{41}BCrMnO_6P_3$ requires C, 63.80; H, 4.54. IR (THF) ν_{max}(CO)/cm^{-1} 2011 (m), 1951 (s), 1935 (m), 1870 (s); (Nujol): ν_{max}(CO)/cm^{-1} 2006 (s), 1957 (m, sh), 1944 (s, sh), 1928 (s), 1852 (s). $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 35.6 (m, br). ^{11}B NMR (128 MHz, C_4D_8O): δ -16.5 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): $\delta(^{13}CO)$ resonance not observed for $Mn(CO)_3$, 233.8 (s, $Cr(CO)_3$).

$W(CO)_3\{\eta^6$-$(PhBP_3)Mn(CO)_3\}$ (11)

Yield: 59%. Found: C, 56.68; H, 4.50. $C_{55}H_{51}BMnO_7P_3W$ (**11** • Et_2O) requires: C, 56.63; H, 4.41. IR (THF) ν_{max}(CO)/cm^{-1} 2010 (m), 1949 (s), 1936 (m), 1865 (s); (Nujol): ν_{max}(CO)/cm^{-1} 2009 (s), 1951 (s), 1918 (m, sh), 1867 (m, sh), 1847 (s). $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 37.9 (m, br). ^{11}B NMR (128 MHz, C_4D_8O): δ -14.7 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): $\delta(^{13}CO)$ resonance not observed for $Mn(CO)_3$), 212.4 (s, ^{13}C—^{183}W satellites: 213.41, 211.55, $^1J_{CW}$ = 188 Hz, $W(CO)_3$).

X-ray Crystallography

X-ray quality crystals were obtained by diffusion of Et_2O into CH_3CN solutions (**1**—**3**), pentane into a THF solution (**4**), Et_2O into THF solutions (**5**—**9**), and pentane into THF:Et_2O (90:10 *v*:*v*) solutions (**10**, **11**). These crystals were selected from the mother liquor in a N_2-filled glove bag and placed onto the tip of 0.1 mm diameter glass capillary and mounted on a Bruker APEX-II CCD diffractometer with 0.71073 Å Mo-Kα radiation for data collection at 123(2) K. All structures were solved by direct methods using SHELXS-97 and refined with full-matrix least-squares procedures using SHELXL-2014.[34] All non-hydrogen atoms were refined with anisotropic displacement parameters; the hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Thermal ellipsoid drawings of **1-11**, and further details of crystallographic data collection, solution, and refinement can be found in the Supplementary Information. Crystallographic CIF files for these structures: CCDC 1039148-1039158

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