Dalton Transactions

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Journal:	*Dalton Transactions*
Manuscript ID	DT-ART-02-2018-000703.R1
Article Type:	Paper
Date Submitted by the Author:	30-Mar-2018
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Inductive Modulation of Tris(phosphinomethyl)phenylborate Donation at Group VI Metals via Borate Phenyl Substituent Modification

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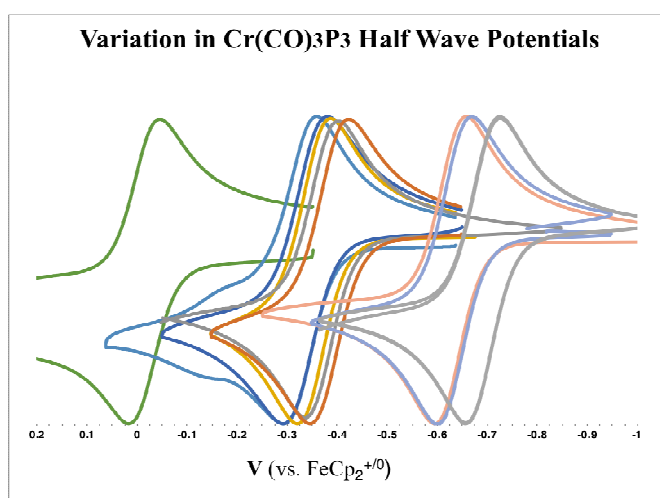[a]Department of Chemistry, Macalester College, 1600 Grand Avenue, Saint Paul, Minnesota 55105, USA

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Table of Contents Textual Abstract

IR spectral data and half wave potentials associated with the κ^3-phosphine bound $M(CO)_3$ units of anionic tris(phosphinomethyl)phenylborate complexes suggest a ligand donor ranking of Tp > PhBP$^{iPr}_3$ $\geq$ Cp > PhBP$^{Ph}_3$ > triphos. New PhBP$^{Ph}_3$ ligands were synthesized to explore possible tuning of PhBP$^{Ph}_3$ donation *via* inductive modulation of the borate negative charge. Cyclic voltammetry data suggests that rational tuning of this type occurs in complexes of zerovalent metals.
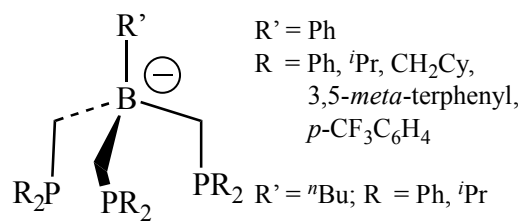
Table of Contents Graphical Abstract

Abstract

A series of zerovalent group VI metal complexes of tris(diisopropylphosphinomethyl)phenylborate ($PhB(CH_2P^{i}Pr_2)_3^-$, $PhBP^{iPr}_3$), including $[PPN][M(CO)_3(PhBP^{iPr}_3)]$ (M = Cr, Mo, W) and the first bimetallics in which $PhBP^{iPr}_3$ serves as a bridging ligand *via* binding $M(CO)_3$ units at the three phosphorus atoms and the borate phenyl substituent, have been synthesized and fully characterized. Two new tris(phosphinomethyl)borates featuring 3,5-dimethylphenyl and 3,5-bis(trifluoromethyl)phenyl borate substituents were prepared as crystallographically characterized thallium salts, and metallated giving their inaugural transition metal complexes $[PPN][M(CO)_3(((3,5-Me)C_6H_3)BP^{Ph}_3)]$ and $[PPN][M(CO)_3(((3,5-CF_3)C_6H_3)BP^{Ph}_3)]$. A comparative $\upsilon(CO)$ infrared spectroscopic analysis and examination of half wave potentials assessed by cyclic voltammetry supports a ligand donor ranking of $Tp > PhBP^{iPr}_3 \geq Cp > PhBP^{Ph}_3 > triphos$. For these anionic complexes, in which a lower electrostatic contribution to zerovalent metal-$PhBP^{R}_3$ binding is likely operative relative to that present in the zwitterionic complexes most commonly prepared with tris(phosphinomethyl)borates, $PhBP^{R}_3$ ligands do not function as *strongly donating scorpionates*. Nevertheless, $PhBP^{Ph}_3$ is a substantially stronger donor than triphos towards zerovalent $M(CO)_3$; the half wave potentials of $[Et_4N][M(CO)_3(PhBP^{Ph}_3)]$ are ~340 mV lower than those of $M(CO)_3(triphos)$. The potentials of the $((3,5-Me)C_6H_3)BP^{Ph}_3$ group VI metal tricarbonyl anions are more negative than those of the corresponding $((3,5-CF_3)C_6H_3)BP^{Ph}_3$ group VI metal tricarbonyl anions by ~50 mV, suggesting a modest, yet rational, tuning of $PhBP^{Ph}_3$ donation *via* inductive modulation of the borate anion charge.

Introduction

Negatively charged tris(diphenylphosphinomethyl)phenylborate ($[PhB(CH_2PPh_2)_3]^-$, $PhBP^{Ph}_3$)[1] and tris(diisopropylphosphinomethyl)phenylborate ($PhB(CH_2P^{i}Pr_2)_3^-$, $PhBP^{iPr}_3$)[2] are strong-field, face-capping ligands that offer a unique combination of steric hindrance and donation at metal fragments

relative to those engendered by triphos ($CH_3C(CH_2PPh_2)_3$) and hydrotris(1-pyrazolyl)borate (Tp). The utility of tris(phosphinomethyl)phenylborates (Figure 1) has been chronicled by Smith,[3] and more recently by Miller and Long.[4] The modular synthesis of this ligand class is an advantageous feature which permits convenient introduction of phosphine substituents with a range of steric and electronic profiles. Efforts to modulate $PhBP^R_3$ donation resulting in tuning of tris(phosphinomethyl)phenylborate metal complex chemical and physical properties from that provided by the aforementioned R = Ph, ^iPr prototypes (ligands with R = CH_2Cy,[5] 3,5-*meta*-terphenyl (*m*-ter)[6] and p-$CF_3C_6H_4$ (p-CF_3)[7] have been prepared) are ongoing. Pérez discovered that the more electrophilic Cu(I) center of ($PhBP^{p\text{-}CF3}_3$)Cu(PPh_3) facilitates catalytic styrene aziridination with electron-poor styrenes otherwise unreactive towards the parent ($PhBP^{Ph}_3$)Cu(PPh_3) pre-catalyst.[7] Peters studied the spin-crossover equilibria of [$PhBP^R_3$]Fe(NPR'_3) (R = Ph, CH_2Cy, *m*-ter, ^iPr; R' = Ph, Cy, Et) and elucidated trends correlated to phosphine substituent R in both Δ_rH^o and Δ_rS^o for the low spin to high spin d^6 conversion.[8]

The $PhBP^R_3$ charge plays a pivotal role in enabling the strong donor ability of this class of ligands. Comparison of the infrared carbonyl stretching frequencies of ($PhBP^{Ph}_3$)Co($CO)_2$ (2008, 1932 cm^{-1}) relative those of [(triphos)Co($CO)_2$][PF_6] (2030, 1972 cm^{-1}) provided early evidence[2a] that borate charge localization is important in establishing the extent of electron richness at the phosphine-bound metal centers of $PhBP^{Ph}_3$ complexes. The opportunity to tune $PhBP^R_3$ donation *via* inductively modulating this negative charge by varying the bridgehead boron substituent has been scarcely investigated. Marks reported $^nBuBP^R_3$ (R = Ph, ^iPr; Figure 1) and Ag(PEt_3)($R'BP^R_3$) (R' = ^nBu, Ph) with $^nBuBP^R_3$ providing greater donation relative that assessed in $PhBP^R_3$ analogues.[9] A relatively high ionic contribution to the anionic ligand–Ag(I) interaction was presumed in these zwitterions, with

Figure 1 (right side):

R'
|
B⊖
R_2P PR_2 PR_2

R' = Ph
R = Ph, ^iPr, CH_2Cy,
    3,5-*meta*-terphenyl,
    p-$CF_3C_6H_4$

R' = ^nBu; R = Ph, ^iPr

Figure 1: $R'BP^R_3$ Ligands

the greater electron releasing character of *n*-butyl relative phenyl at the bridgehead borate affecting stronger ^{n}BuBP$^{R}_3$ to Ag(I) than PhBP$^{R}_3$ to Ag(I) bonding. The efficacy of this ligand tuning strategy at zerovalent metals within *anionic* R'BP$^{R}_3$ complexes, in which the ionic contribution to the metal-borate interaction is reduced relative that in charge-neutral zwitterions, has not been systematically explored. Probing this fundamental question regarding R'BP$^{R}_3$ donation is important; these ligands are selected with a targeted π-basicity at the facially-capped phosphine-bound metal as the main criterion.

Our laboratory is interested in assessing low valent group VI metal R'BP$^{R}_3$ π-basic fragments as dearomatization agents in which tris(phosphinomethyl)phenylborates function as Tp surrogates. To guide these efforts, we synthesized [Et$_4$N][M(CO)$_3$(PhBP$^{Ph}_3$)] (M = Cr, Mo, W); an analysis of IR υ(CO) data indicated that PhBP$^{Ph}_3$ is significantly less strongly donating than Tp towards zerovalent M(CO)$_3$ fragments.[10] This observation suggested that the PhBP$^{Ph}_3$ *strongly donating scorpionate* classification, an assessment made by examination of zwitterionic tris(phosphinomethyl)phenylborate complexes, may not hold in anionic R'BP$^{R}_3$ complexes. A new bifunctional role for PhBP$^{Ph}_3$ was explored *via* the preparation of bimetallics in which zerovalent M(CO)$_3$ fragments bind the three phosphorus atoms and the borate phenyl substituent. IR υ(CO) data supported modest attenuation of PhBP$^{Ph}_3$ donor ability at phosphorus upon η^6-phenyl substituent binding, representing a new inductive strategy for tuning PhBP$^{Ph}_3$ donation at the κ^3-phosphine-bound metal fragment.[10]

An interrogation of metal electronics in [Et$_4$N][M(CO)$_3$(PhBP$^{Ph}_3$)] and related complexes by electrochemical means would help corroborate our working assumption regarding the rank of PhBP$^{Ph}_3$ as a donor relative Tp and other face-capping ligands towards zerovalent M(CO)$_3$. Furthermore, we were also interested if modulation of donation at the κ^3-phosphine-bound M(CO)$_3$ units observed upon introduction of M(CO)$_3$ fragments at the PhBP$^{Ph}_3$ borate phenyl substituent could be similarly affected in bimetallics of PhBP$^{iPr}_3$. Enhancing the inductive modulation of borate charge *via* the synthesis of

4

new R'BP$^R_3$ ligands with electron-donating and withdrawing substituents at the boron phenyl substituent was another intriguing prospect. Our findings are reported herein.

Results and Discussion

[PPN][M(CO)$_3$(PhBP$^{iPr}_3$)] and Bimetallics. Nitrile substitution reactions of [Li(THF)][PhBP$^{iPr}_3$] and M(CO)$_3$(RCN)$_3$ (M = Cr, R = Me; M = Mo, W, R = Et), followed by PPNCl metathesis in dichloromethane, afforded [PPN][M(CO)$_3$(PhBP$^{iPr}_3$)] (M = Cr (**1**), Mo (**2**), W (**3**)).   While [Li(THF)][PhBP$^{iPr}_3$][11] proved more convenient to synthesize relative Tl[PhBP$^{iPr}_3$],[2a] introduction of PhBP$^{iPr}_3$ as a lithium salt limits the solvents available for cation exchange driven by LiX elimination. A PPNCl solution in dichloromethane is ideal with respect to LiCl insolubility, but presents a risk of **1-3** oxidation.   Ambient temperature solutions of **1-3** in CH$_2$Cl$_2$ afford uncharacterized insoluble oxidation products after five hours but ~70% overall yields of **1-3** could be reproducibly obtained via a single hour metathesis period followed by prompt work-up.   Salts **1-3** join [ASN][Ni(CO)$_2$(κ^2-PhBP$^{iPr}_3$)][12] (ASN = 5-azoniaspiro[4.4]nonane) as the only well-characterized metal carbonyl anions of PhBP$^{iPr}_3$.   Thermal ellipsoid drawings of crystallographically characterized **1-3** are provided in the ESI (Section III, Figures S1-3).   No significant differences in the geometric parameters that define the M(CO)$_3$P$_3$ units of **1** and [Et$_4$N][M(CO)$_3$(PhBP$^{Ph}_3$)] (M = Cr (**4**))[10] and those of **2**, **3**, [Et$_4$N][M(CO)$_3$(PhBP$^{Ph}_3$)] (M = Mo (**5**), W (**6**)][10] and M'(CO)$_3$(triphos) (M' = Mo, W)[13] are evident in the solid-state; the differing steric bulk of PhBP$^{Ph}_3$ and PhBP$^{iPr}_3$ results in no detectable structural deviations at these metal centers, each exhibiting near octahedral coordination environments.
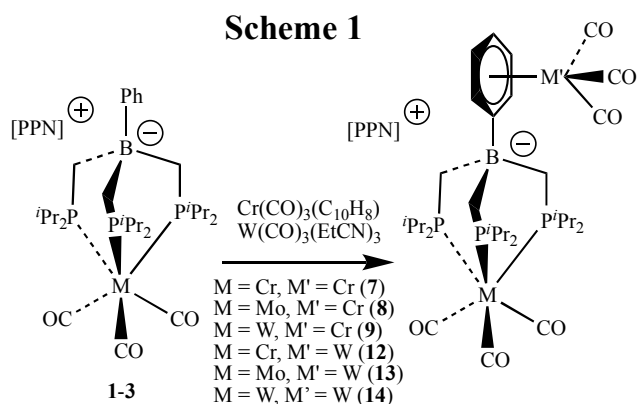
Scheme 1

Reactions of **1-3** with $Cr(CO)_3(C_{10}H_8)$ and $W(CO)_3(EtCN)_3$ resulted in installation of $Cr(CO)_3$ and $W(CO)_3$ fragments at the boron phenyl substituent (Scheme 1); **7-9** and **12-14** (see Table 1 for a compilation of the complexes discussed herein) are the first bimetallics in which $PhBP^{iPr}_3$ functions as a bridging ligand. The conditions required to prepare these complexes are analogous to those employed for $[Et_4N][Cr(CO)_3\{\eta^6\text{-}(PhBP^{Ph}_3)M'(CO)_3\}]$ (M' = Cr (**10**), Mo (**11**)) and $[Et_4N][W(CO)_3\{\eta^6\text{-}PhBP^{Ph}_3)M'(CO)_3\}]$ (M' = Cr (**15**), Mo (**16**), W (**17**)).[10] Bimetallics **7-9** and **12-14** were characterized by X-ray crystallography. A thermal ellipsoid drawing of the anion of **7** is in Fig. 2; those of the other five $PhBP^{iPr}_3$ bimetallics are in the ESI
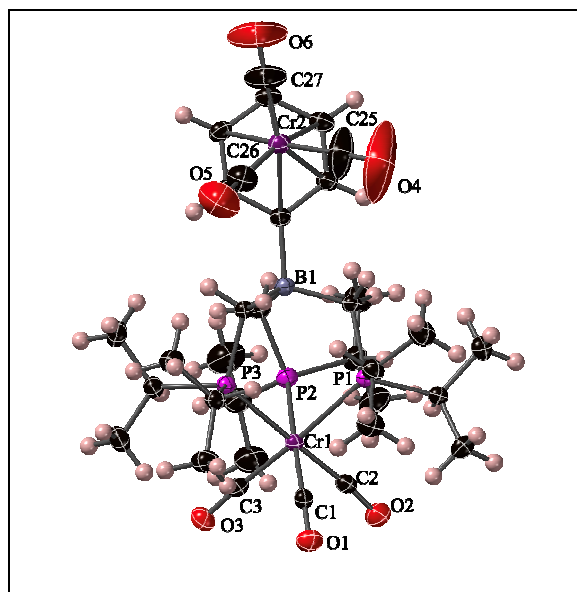
Figure 2 Thermal ellipsoid plot depicting the molecular structure of the anion of **7**. Ellipsoids are drawn at 50% probability. Selected average bond lengths (Å) and angles (°): (a) phosphine bound $Cr(CO)_3$: Cr-P = 2.431(7), Cr-C = 1.822(6), P-Cr-P = 87(2), *cis* P-Cr-C = 94(4), (O)C-Cr-C(O) = 86(4); (b) arene bound $Cr(CO)_3$: Cr-C(arene) = 2.23(3), Cr-C(O) = 1.81(2), (O)C-Cr-C(O) = 87(2).

(Figures S5-9). In each set of κ^3-phosphine $M(CO)_3$ complexes (M = Cr: **1**, **7**, **12**; M = Mo: **2**, **8**, **13**; M = W: **3**, **9**, **14**) the parameters that define the slightly elongated trigonal antiprismatic $M(CO)_3P_3$ coordination geometries are statistically identical.

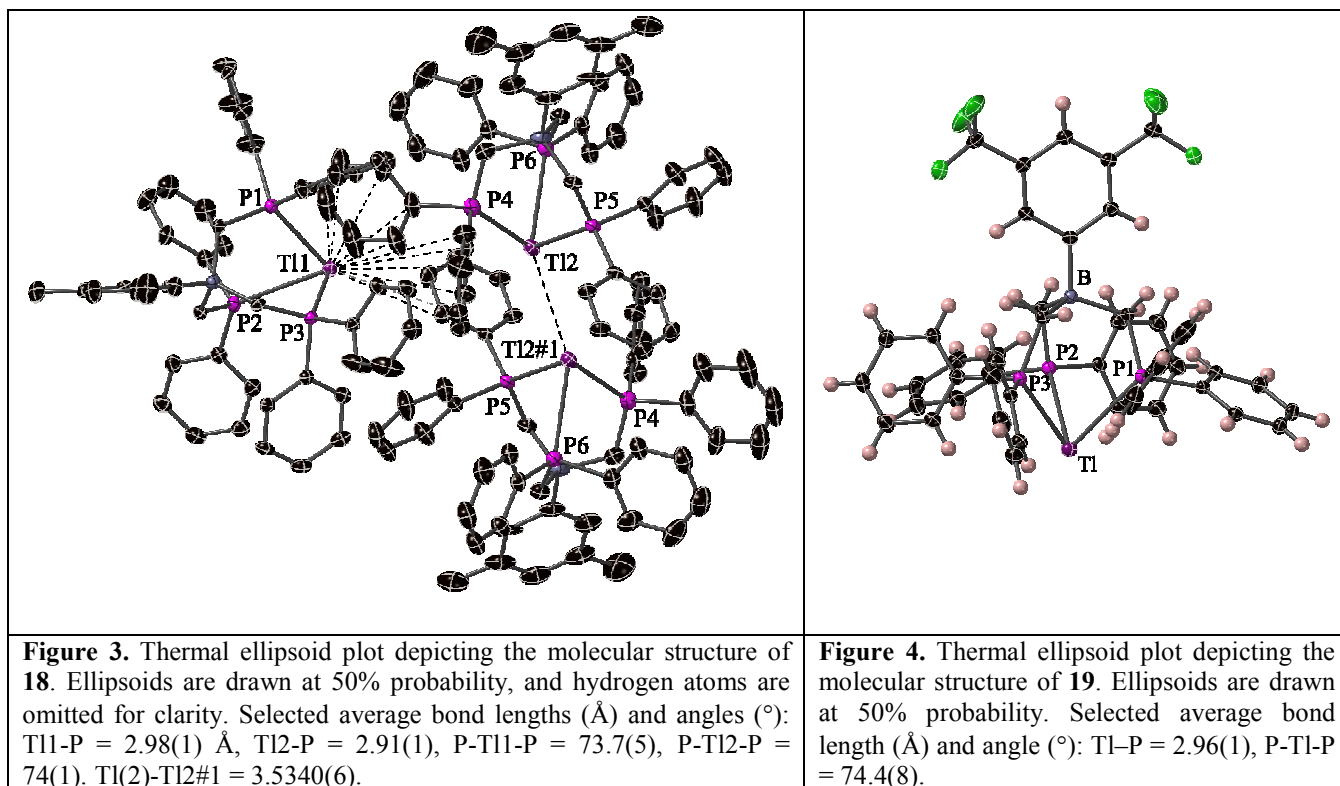**Tris(phosphinomethyl)phenylborates with Modified Bridgehead Boron Phenyl Groups.** While modest attenuation of donation into κ^3-phosphine bound $M(CO)_3$ units was suggested upon introduction of $W(CO)_3$ and $Cr(CO)_3$ fragments in $PhBP^{Ph}_3$ bimetallics **10-11** and **15-17**,[10] the relatively reactive

Table 1 Compilation of Complexes and Numbering Scheme	
$[PPN][M(CO)_3(PhBP^{iPr}_3)]$	M = Cr (**1**), Mo (**2**), W (**3**)
$[Et_4N][M(CO)_3(PhBP^{Ph}_3)]$	M = Cr (**4**), Mo (**5**), W (**6**)
$[PPN][Cr(CO)_3\{\eta^6\text{-}(PhBP^{iPr}_3)M(CO)_3\}]$	M = Cr (**7**), Mo (**8**), W (**9**)
$[Et_4N][Cr(CO)_3\{\eta^6\text{-}(PhBP^{Ph}_3)M(CO)_3\}]$	M = Cr (**10**), Mo (**11**)
$[PPN][W(CO)_3\{\eta^6\text{-}(PhBP^{iPr}_3)M(CO)_3\}]$	M = Cr (**12**), Mo (**13**), W (**14**)
$[Et_4N][W(CO)_3\{\eta^6\text{-}(PhBP^{Ph}_3)M(CO)_3\}]$	M = Cr (**15**), Mo (**16**), W (**17**)
$[((3,5\text{-Me})C_6H_3)BP^{Ph}_3]Tl$	**18**
$[((3,5\text{-CF}_3)C_6H_3)BP^{Ph}_3]Tl$	**19**
$[PPN][M(CO)_3(((3,5\text{-Me})C_6H_3)BP^{Ph}_3)]$	M = Cr (**20**), Mo (**21**), W (**22**)
$[PPN][M(CO)_3(((3,5\text{-CF}_3)C_6H_3)BP^{Ph}_3)]$	M = Cr (**23**), Mo (**24**), W (**25**)

(η^6-arene)M(CO)$_3$ units render this donor modulation strategy impractical to influence reactions targeted exclusively at phosphine-bound metal fragments. Practical application of this strategy requires tris(phosphinomethyl)phenylborates containing bridgehead boron phenyl substituents more resistant to chemical transformation (and displacement) than π-bound metal fragments. To this end we explored the syntheses of new PhBP$^{Ph}_3$ ligands with more tolerant electron-donating and withdrawing substituents at the *ortho*, *meta* and *para* positions of the boron phenyl substituent. The modular scheme pioneered by Peters, reaction of dichlorophenylboranes and [Li(TMEDA)][Ph$_2$PCH$_2$], was employed. Attempts with dichloro(2,4,6-trimethylphenyl)borane[14] and dichloro(pentafluorophenyl)borane[15] afforded complex product mixtures from which tris(phosphinomethyl)phenylborates could not be obtained. Application of dichloro(3,5-dimethylphenyl)borane[16] and dichloro(3,5-bis(trifluoromethyl)phenyl)borane[17] successfully resulted, following transmetalation with TlPF$_6$, in white [((3,5-Me)C$_6$H$_3$)BP$^{Ph}_3$]Tl (**18**) and brown [((3,5-CF$_3$)C$_6$H$_3$)BP$^{Ph}_3$]Tl (**19**) microcrystals. Salts **18** and **19** join Marks' [Li(TMEDA)][^{n}BuBP$^{Ph}_3$] as the only tris(diphenylphosphinomethyl)borates modified at the bridgehead boron relative the parent PhBP$^{Ph}_3$.[9] The ^{11}B NMR resonances of **18** (δ -11.2 ppm, C$_4$D$_8$O), **19** (δ -11.2 ppm, C$_4$D$_8$O) and [PhBP$^{Ph}_3$]Tl (δ -10.96 ppm, C$_6$D$_6$)[1c] are independent of the varying bridgehead boron phenyl substituents. The ^{31}P{^{1}H} spectra of these salts indicate strong thallium(I)-phosphine interactions in solution. However, the well-resolved ^{31}P-^{205}Tl and ^{31}P-^{203}Tl doublets observed in C$_6$D$_6$ solutions of [PhBP$^{Ph}_3$]Tl (δ, 21.6 (^{1}J$_{TlP}$ = 5214 Hz for ^{205}Tl, ^{1}J$_{TlP}$ = 5168 Hz for ^{203}Tl))[1c] are not resolved in C$_4$D$_8$O solutions of **18** and **19**, possibly due to enhanced solvation of Tl(I) by THF relative that in benzene. In the latter solutions, only doublets associated with the more abundant ^{205}Tl (70.5%) are observed (**18**: δ 20.6 (^{1}J$_{TlP}$ = 5124 Hz); **19**: δ 19.0 (^{1}J$_{TlP}$ = 4903 Hz)). Although the ^{205}Tl-^{31}P coupling constant of **19** is only ~4% less than that of **18**, a weaker ion-pairing interaction in **19** is consistent with more electron-withdrawing substituents at the bridgehead boron phenyl substituent in **19** than in **18**.

The tridentate binding of $((3,5\text{-Me})C_6H_3)BP^{Ph}_3$ and $((3,5\text{-CF}_3)C_6H_3)BP^{Ph}_3$ to thallium(I) in **18**

and **19** in solution was confirmed in the solid-state by X-ray crystallography. The solid-state structures

of zwitterions **18** (Fig. 3) and **19** (Fig. 4) are unique beyond the different 3,5-phenylborate substituents.

Salt **19** exhibits only one thallium(I) environment suggesting a homoleptic complex, while **18** features

two such environments: Tl1 participates in weak intermolecular π-interactions with a

diphenylphosphino unit of another ion-pair containing Tl2 in which Tl2 forms a weak contact with

Figure 3. Thermal ellipsoid plot depicting the molecular structure of **18**. Ellipsoids are drawn at 50% probability, and hydrogen atoms are omitted for clarity. Selected average bond lengths (Å) and angles (°): Tl1-P = 2.98(1) Å, Tl2-P = 2.91(1), P-Tl1-P = 73.7(5), P-Tl2-P = 74(1). Tl(2)-Tl2#1 = 3.5340(6).

Figure 4. Thermal ellipsoid plot depicting the molecular structure of **19**. Ellipsoids are drawn at 50% probability. Selected average bond length (Å) and angle (°): Tl–P = 2.96(1), P-Tl-P = 74.4(8).

a symmetry equivalent thallium(I) leading to a dimeric entity resembling that observed in crystals of

$[PhBP^{Ph}_3]Tl$ (Tl-Tl separation = 3.5652(2) Å);[1c] the sum of the covalent radii of Tl is 2.90(7) Å.[18] The

Tl(I) in **19** engages in weak intermolecular π-interactions with a diphenylphosphino unit of an adjacent

zwitterionic **19**, and does not point towards another Tl(I) center as does Tl2 of **18**. The average Tl-P

bond lengths in **18** and **19** feature smaller estimated standard deviations than does the corresponding

average in $[PhBP^{Ph}_3]Tl$ (2.92(4) Å), which does not feature symmetrically bound phosphine donors.

The intramolecular separations between the thallium and borate ions (Tl-B) of these zwitterions are

extremely similar in **18** (4.360(6) Å) and **19** (4.298(2) Å), suggesting negligible inductive impact of the

3,5-phenylborate substituents on this parameter.

      Nitrile substitution reactions of $M(CO)_3(RCN)_3$ (M = Cr, R = Me; M = Mo, W, R = Et) with **18**

and **19**, followed by metathesis with PPNCl, afforded inaugural metal complexes of these

tris(phosphinomethyl)phenylborates,

[PPN][$M(CO)_3(((3,5-Me)C_6H_3)BP^{Ph}_3)$] (M = Cr (**20**),

Mo (**21**), W (**22**)) and [PPN][$M(CO)_3(((3,5-$

$CF_3)C_6H_3)BP^{Ph}_3)$] (M = Cr (**23**), Mo (**24**), W (**25**)).

Indiscriminate $M(CO)_3$ binding at the 3,5-

dimethylphenyl substituent and the phosphines of **18**

was problematic when nitrile substitution was carried

out in THF. Exclusive κ^3-phosphine binding with **18** was

achieved in CH_3CN solvent; (η^6-arene)$M(CO)_3$

complexes are thermodynamically unstable with respect

to arene displacement by nitriles. The less electron-rich
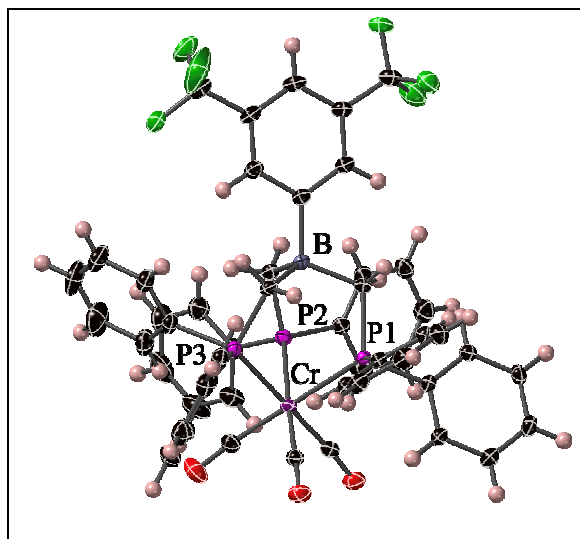
Figure 5. Thermal ellipsoid plot depicting the molecular structure of the anion of **23**. Ellipsoids are drawn at 50% probability. Selected average bond lengths (Å) and angles (°): Cr-P = 2.400(2), Cr-C = 1.833(4), P-Cr-P = 86.2(7), *cis* P-Cr-C = 93(1), (O)C-Cr-C(O) = 87(1).

3,5-bis(trifluoromethyl)phenyl substituent is noncompetitive towards $M(CO)_3$ binding, even when

THF is employed as the solvent for $M(CO)_3(RCN)_3$ reactions with **19**. Salts **20-25** were characterized

by single-crystal X-ray crystallography; thermal ellipsoid drawings of the anions are displayed in Fig.

5 (**23**) and in the ESI (**20-22**, **24**, **25** in Figures S12-14, S16-17). The average geometric parameters

that define the $Cr(CO)_3P_3$ geometries of **4**, **20** and **23** are statistically indistinguishable, as are those

that define the $M(CO)_3P_3$ geometries (M = Mo, W) of **5**, **6**, **21**, **22**, **24** and **25**. The methyl or

trifluoromethyl substituents in the 3,5 positions of the bridgehead borate phenyl group has no

detectable structural impact at the κ^3-phosphine bound $M(CO)_3$ units.

Electronic Impact of Tris(phosphinomethyl)phenylborates at κ^3-Phosphine Bound M(CO)$_3$: IR Spectroscopy. The relative donor abilities of PhBP$^{Ph}_3$, ((3,5-Me)C$_6$H$_3$)BP$^{Ph}_3$, ((3,5-CF$_3$)C$_6$H$_3$)BP$^{Ph}_3$ and PhBP$^{iPr}_3$, along with their rank as donors with respect to the triphos, Cp and Tp benchmarks was initially assessed *via* comparative analysis of infrared υ(CO) spectral data in CH$_3$CN solution (Table 2). The enhanced donation at phosphorus afforded by anionic PhBP$^{Ph}_3$ relative to neutral triphos is striking, with the lower energy carbonyl stretching frequency red-shifted by 35-39 cm^{-1} in **4-6** relative the corresponding M(CO)$_3$(triphos) absorptions. Donation of PhBP$^{iPr}_3$ into the zerovalent M(CO)$_3$ units of **1-3** is assessed as very similar to that provided by Cp in [Et$_4$N][CpM(CO)$_3$]; these data suggest PhBP$^{iPr}_3$ as a better donor than Cp towards Cr(CO)$_3$ fragments. Introduction of substituents at the 3,5-positions of the bridgehead boron phenyl substituent has seemingly minimal electronic impact at zerovalent M(CO)$_3$. The υ(CO) absorptions of the A_1 and E modes of **4-6**, **20-22**, and **23-25** with the same group VI metal vary by only 2-4 cm^{-1}, but are ordered as expected with ((3,5-CF$_3$)C$_6$H$_3$)BP$^{Ph}_3$ suggested as the weakest donor relative to ((3,5-Me)C$_6$H$_3$)BP$^{Ph}_3$ and PhBP$^{Ph}_3$. The ligand donor ranking of

Table 2 υ(CO) data for M(CO)$_3$ complexes with face-capping, six electron donor ligands	
Complex	υ(CO) (CH$_3$CN) (cm^{-1})
Cr(CO)$_3$(triphos)	1905, 1830
23	1901, 1798
4	1899, 1794
20	1899, 1794
[Et$_4$N][CpCr(CO)$_3$][19]	1888, 1768
1	1878, 1765
[Et$_4$N][TpCr(CO)$_3$][19]	1889, 1751
Mo(CO)$_3$(triphos)	1937, 1844
24	1914, 1809
5	1912, 1805
21	1911, 1805
2	1892, 1776
[Et$_4$N][CpMo(CO)$_3$][19]	1891, 1770
[Et$_4$N][TpMo(CO)$_3$][19]	1888, 1752
W(CO)$_3$(triphos)	1930, 1835
25	1908, 1803
6	1906, 1800
22	1906, 1801
3	1886, 1770
[Et$_4$N][CpW(CO)$_3$][18]	1886, 1765
[Et$_4$N][TpW(CO)$_3$][18]	1878, 1744

tris(phosphinomethyl)phenylborates, as assessed by IR υ(CO) data, has been reported as a function of the metal fragment, and these data provide another unique ranking. Towards zerovalent M(CO)$_3$ units, the Table 2 data indicate Tp > Cp $\approx$ PhBP$^{iPr}_3$ > PhBP$^{Ph}_3$ > triphos. Towards [Co(CO)$_2$]$^+$, PhBP$^{iPr}_3$ > PhBP$^{Ph}_3$ > Tp > Cp > triphos is suggested.[2a] Finally, υ(CO) IR spectral comparison of complexes of

[RuCl(CO)$_2$]$^+$ suggests Cp* > PhBP$^{iPr}_3$ > Cp > Tp > PhBP$^{Ph}_3$ > triphos.[2a] While assessment of metal center electronics using exclusively infrared υ(CO) arguments can be problematic, particularly when the charge varies among the complexes being compared, a significant electrostatic contribution to the metal-PhBP$^R_3$ interaction seems important to realize *strongly donating scorpionate* PhBP$^R_3$ capability, in which PhBP$^{iPr}_3$ and/or PhBP$^{Ph}_3$ are stronger donors than Tp.   The electrostatic contribution engendered by the cationic [Co(CO)$_2$]$^+$ fragment in its binding to PhBP$^R_3$, 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. The relative electrostatic contribution engendered by neutral M(CO)$_3$ in **1-6** is undoubtedly quite low, and likely not enhanced significantly *via* π-acceptance of the diphenylphosphinomethyl groups. From this perspective, the M(CO)$_3$ model system is not optimum to interrogate the electronic impact of ((3,5-CF$_3$)C$_6$H$_3$)BP$^{Ph}_3$ and ((3,5-Me)C$_6$H$_3$)BP$^{Ph}_3$ relative to PhBP$^{Ph}_3$.

The limitations of υ(CO) IR arguments to assess the electronic impact of Cr(CO)$_3$ and W(CO)$_3$ binding at the phenyl borate substituent on donation into κ^3-phosphine bound M(CO)$_3$ fragments in bimetallics **7-17** is made apparent in this study. The IR υ(CO) spectra of PhBP$^{iPr}_3$ bimetallics **7-9** and **12-14** in THF solution exhibit well-separated absorptions for each three-legged piano stool M(CO)$_3$ fragment; these vibrational modes are assumed to be decoupled. The lower energy (*E* vibrational mode) stretching frequencies associated with the κ^3-phosphine M(CO)$_3$ units of **7-9** and **12-14** are shifted only 3-4 cm^{-1} higher in energy than the corresponding absorptions of **1-3**, suggesting an insignificant impact of η^6-phenylborate M(CO)$_3$ binding on PhBP$^{iPr}_3$ donation into phosphine bound M(CO)$_3$ units. These data also do not discriminate between Cr(CO)$_3$ or W(CO)$_3$ binding at the borate phenyl substituent, even though these groups have different electron-withdrawing capabilities. Our previous spectral comparisons of **4-6** and PhBP$^{Ph}_3$ bimetallics **10**, **11** and **15-17** were handicapped; they employed IR data obtained in CH$_3$CN (**4-6**) and THF (**10**, **11** and **15-17**) solution, on the basis of

poor **4-6** THF solubility. Salts **20-22** exhibit high solubility in THF. Employment of IR $\upsilon(CO)$

spectral data for **20-22** obtained in THF permits a better comparison to the data obtained in THF

solution for **10**, **11** and **15-17**, since $PhBP^{Ph}_3$ and $((3,5-Me)C_6H_3)BP^{Ph}_3$ donation into $M(CO)_3$ units is

nearly indistinguishable as assessed by IR spectroscopy (Table 2). Such a comparison does not

indicate significant attenuation of donation into κ^3-phosphine bound $M(CO)_3$ units upon coordination

of $Cr(CO)_3$ or $W(CO)_3$ at the phenyl borate $PhBP^{Ph}_3$ substituent. For example, the $\upsilon(CO)$ IR spectrum

of **5** (1915, 1815 cm^{-1}) is nearly identical to the absorptions associated with the κ^3-phosphine bound

$Mo(CO)_3$ units in bimetallics **11** (1912, 1816 cm^{-1}) and **16** (1912, 1817 cm^{-1}).[10]

Electronic Impact of Tris(phosphinomethyl)phenylborates at κ^3-Phosphine Bound $M(CO)_3$:

Cyclic Voltammetry. For a complementary assessment of the electron-releasing character of

tris(phosphinomethyl)phenylborates, half wave potentials associated with the κ^3-phosphine bound

$M(CO)_3$ units were measured by cyclic

voltammetry. Similar to $[TpM(CO)_3]^-$ and

$[CpM(CO)_3]^-$,[19,20] each member of the series of

κ^3-phosphine bound $M(CO)_3$ features a

reversible M(0)/M(I) oxidation in acetonitrile

(0.4 M $[TBA][PF_6]$, 100 mv/s). The half wave

Figure 6. One Electron Waves of 1-3
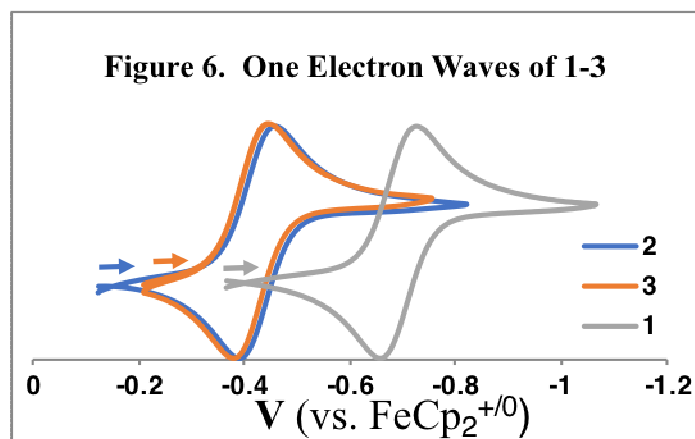
potentials associated with reversible one-electron oxidations of the κ^3-phosphine bound $M(CO)_3$ units

of **1-6** (as $[Et_4N]^+$ salts), **7**, **10**, **12**, **15**, **20-22**, **23-25**, $M(CO)_3$(triphos), $[Et_4N][TpM(CO)_3]$ and

$[Et_4N][CpM(CO)_3]$ are in Table 3 (referenced to $FeCp_2/[FeCp_2]^+$). The ease in oxidizing **4-6** relative

to $M(CO)_3$(triphos) is remarkable; the oxidation potentials of the $PhBP^{Ph}_3$-containing anions are shifted

more negative by 355 (**4**), 347 (**5**) and 333 (**6**) mV. The subsequent marked increase in $R'BP^R_3$

electron-releasing character leveraged *via* replacement of phenyl groups for isopropyl groups at the

phosphine donor positions leads to the half wave potentials of **1-3** (Figure 6) being more negative than

those of **4-6** by 321 (Cr), 290 (Mo) and 278 (W) mV. A similar shift (322 mV) was observed for the

Fe(II/I) couple of $[PhBP^{iPr}_3]FeCl$ relative that of $[PhBP^{Ph}_3]FeCl$.[2a] The half wave potentials of **20-22**

and **23-25** suggest a more differentiated electronic impact of the 3,5-phenylborate substituents

registered at κ^3-phosphine bound $M(CO)_3$ units than that indicated by $\upsilon(CO)$ IR spectroscopy.

Table 3 M(0)/M(I) half wave potentials (in CH_3CN) of κ^3-phosphine bound $M(CO)_3$ units and $M(CO)_3$ units of related zerovalent complexes

Complex	Phosphine Substituent	$PhBP^R_3$ Bridgehead Boron Substituent	$E_{1/2}$ (V) vs. $FeCp_2/[FeCp_2]^+$	Reference
Chromium Complexes				
$[Et_4N][TpCr(CO)_3]$	N/A	N/A	-0.821	20
1 ($[Et_4N]^+$ salt)	^iPr	Ph	-0.691	This work
$[Et_4N][CpCr(CO)_3]$	N/A	N/A	-0.688	20
7	^iPr	Ph{Cr(CO)$_3$}	-0.635	This work
12	^iPr	Ph{W(CO)$_3$}	-0.627	This work
20	Ph	Ph{3,5-Me}	-0.385	This work
4 ($[Et_4N]^+$ salt)	Ph	Ph	-0.370	This work
10	Ph	Ph{Cr(CO)$_3$}	-0.354	This work
15	Ph	Ph{W(CO)$_3$}	-0.341	This work
23	Ph	Ph{3,5-CF$_3$}	-0.336	This work
$Cr(CO)_3$(triphos)	Ph	N/A	-0.015	This work
Molybdenum Complexes				
$[Et_4N][TpMo(CO)_3]$	N/A	N/A	-0.521	20
2 ($[Et_4N]^+$ salt)	^iPr	Ph	-0.422	This work
$[Et_4N][CpMo(CO)_3]$	N/A	N/A	-0.403	20
21	Ph	Ph{3,5-Me}	-0.134	This work
5 ($[Et_4N]^+$ salt)	Ph	Ph	-0.132	This work
24	Ph	Ph{3,5-CF$_3$}	-0.088	This work
$Mo(CO)_3$(triphos)	Ph	N/A	+0.215	This work
Tungsten Complexes				
$[Et_4N][TpW(CO)_3]$	N/A	N/A	-0.582	20
3 ($[Et_4N]^+$ salt)	^iPr	Ph	-0.411	This work
$[Et_4N][CpW(CO)_3]$	N/A	N/A	-0.397	20
22	Ph	Ph{3,5-Me}	-0.151	This work
6 ($[Et_4N]^+$ salt)	Ph	Ph	-0.133	This work
25	Ph	Ph{3,5-CF$_3$}	-0.106	This work
$W(CO)_3$(triphos)	Ph	N/A	+0.200	This work

Specifically, the potentials of the $((3,5-Me)C_6H_3)BP^{Ph}_3$ complexes **20-22** are more negative than those

of the corresponding $((3,5-CF_3)C_6H_3)BP^{Ph}_3$ complexes **23-25** by 49 (Cr), 46 (Mo) and 45 (W) mV. The

potentials of the $PhBP^{Ph}_3$ complexes **4-6** are shifted modestly positive from their $((3,5-Me)C_6H_3)BP^{Ph}_3$

analogues **20-22** by 15 (Cr), 2 (Mo) and 18 (W) mV. The electronic impact of η^6-phenyl substituent

binding to $Cr(CO)_3$ and $W(CO)_3$ at κ^3-phosphine bound $Cr(CO)_3$ units in bimetallics **7**, **10**, **12** and **15** is also seemingly more significant when assessed by cyclic voltammetry than *via* IR spectroscopy. These half wave potentials of the $PhBP^{iPr}_3$ bimetallics are shifted higher by 56 (**7**) and 64 (**12**) mV relative that of **1**, suggesting a slightly greater inductive impact of $W(CO)_3$ relative $Cr(CO)_3$ binding at the bridgehead boron phenyl substituent. The half wave potentials of the κ^3-phosphine bound $Cr(CO)_3$ units in $PhBP^{Ph}_3$ bimetallic complexes **10** and **15** are shifted positive to a lesser extent (16 (**10**) and 29 (**15**) mV) relative that of **4**. While η^6-phenylborate substituent binding to $W(CO)_3$ again seemingly affects greater donor attenuation at facially-capped P-bound $Cr(CO)_3$ units than does η^6-phenylborate substituent binding to $Cr(CO)_3$, we had hypothesized that $PhBP^{Ph}_3$ donation at phosphorus would be more susceptible to inductive modulation than $PhBP^{iPr}_3$ donation. The donor ranking for these ligands towards zerovalent $M(CO)_3$ units as assessed *via* these potentials is $Tp > PhBP^{iPr}_3 \geq Cp > PhBP^{Ph}_3 >$ triphos, a rank consistent with that inferred by Table 2. Hydrotris(1-pyrazolyl)borate is unquestionably a much better donor than $PhBP^{iPr}_3$ within this system, with the half wave potentials of $[Et_4N][TpM(CO)_3]$ shifted lower than those of **1-3** by 130 (Cr), 99 (Mo) and 171 (W) mV. These data cast doubt on the utility of even $PhBP^{iPr}_3$ as a Tp surrogate in zerovalent group VI metal dearomatization agents in contrast to the viable Tp surrogacy suggested by the comparable catalytic activities of $(PhBP^{Ph}_3)Cu$ and $Tp*Cu$ towards catalytic carbene and nitrene transfer reactions reported by Pérez and Caballero.[21] This finding is of interest on the basis of the ongoing development of group VI metal π-basic fragments with modulated steric and electronic profiles[22] and the recent examination of the effects of borate group proximity on phosphine donation in anionic (phosphino)tetraphenylborate ligands.[23]

Summary

The important systematic assessment of tris(phosphinomethyl)phenylborate ligands as donors in complexes of zerovalent metals, in which the ionic component to metal-RBP^R_3 binding is expected to

be very low, has been conducted with group VI metal $M(CO)_3$ anions. A comparative analysis of

$\upsilon(CO)$ infrared spectral data and half wave potentials associated with the κ^3-phosphine bound $M(CO)_3$

units of **1-6** suggest that $PhBP^R_3$ are not *strongly donating scorpionates* within this model system, and

a ligand donor ranking of $Tp > PhBP^{iPr}_3 \geq Cp > PhBP^{Ph}_3 > triphos$. The first bimetallics of $PhBP^{iPr}_3$ (**7-**

12) were prepared in which $M(CO)_3$ units are facially-capped by both the phosphorus donor atoms and

the bridgehead phenylborate substituent. Two new $PhBP^{Ph}_3$ ligands as thallium(I) salts, **18** and **19**, with

3,5-dimethylphenyl and 3,5-bis(trifluoromethyl)phenyl boron substituents have been synthesized and

characterized to explore the tuning of $PhBP^{Ph}_3$ donation into P-bound metals *via* inductive modulation

of the borate negative charge. Cyclic voltammetry data suggests that modest but rational attenuation of

this type occurs at κ^3-phosphorus bound $M(CO)_3$ units in **7**, **10**, **12**, **15**, **20-22** and **23-25** relative the

parent complexes **1-6**. Exploration of possible manifestations of this apparent inductive effect on

metal-based reactivity is underway in this laboratory.

Experimental

Similar procedures were conducted to synthesize **1-3**, **7-9**, **12-14**, **20-22** and **23-25**. Representative

procedures for **1**, **7**, **12**, **20** and **23** are provided below. All ^1H NMR data, and $^{13}C\{^1H\}$ NMR data, with

the exception of ^{13}CO chemical shifts, are omitted below for all metal carbonyl complexes. General

procedures (Section I), experimental details (Section II) and characterization data (including $^{31}P\{^1H\}$,

^{11}B, ^1H, and $^{13}C\{^1H\}$ NMR spectra (Section VI) for **1-3**, **7-9**, **12-14**, **18-25**) are in the ESI.

[PPN][Cr(CO)$_3$(PhBP^{iPr}$_3$)] (1)

THF (40 mL) was added to [Li(THF)][PhBP^{iPr}$_3$] (0.300 g, 0.534 mmol) and Cr(CO)$_3$(CH$_3$CN)$_3$ (0.132

g, 0.509 mmol). The orange solution was refluxed (1.5 hr). An IR spectrum (IR (THF) υ(CO): 1887 (s),

1794 (m), 1778 (m, sh), 1711 (m) cm^{-1}) indicated complete consumption of Cr(CO)$_3$(CH$_3$CN)$_3$ and

formation of a contact ion-pair. The solvent was removed in vacuo leaving an oily yellow residue. A

solution of PPNCl (0.322 g, 0.560 mmol) in CH$_2$Cl$_2$ (40 mL) was added; the suspension was stirred (1

hr). The LiCl precipitate was separated by filtration through Celite, and the CH_2Cl_2 of the filtrate was removed in vacuo leaving a pale yellow solid. This solid was dissolved in CH_3CN (40 mL) and the solution filtered through alumina. Most of the filtrate solvent was removed in vacuo. Addition of pentane (50 mL) affected the precipitation of a pale yellow solid that was isolated by filtration, washed with pentane (3 * 10 mL) and dried in vacuo. Pentane diffusion into a THF solution provided pale yellow microcrystals (0.401 g, 68%). Mp. 205 – 207 °C (dec). Found C, 68.31; H, 7.21; N, 1.20. $C_{66}H_{83}BCrNO_3P_5$ requires C, 68.57; H, 7.24; N, 1.21. IR (CH_2Cl_2) $\upsilon_{max}(CO)/cm^{-1}$ 1876 (s), 1762 (m); (CH_3CN) $\upsilon_{max}(CO)/cm^{-1}$ 1878 (s), 1765 (m); (THF) $\upsilon_{max}(CO)/cm^{-1}$ 1886 (s), 1780 (m); (nujol) $\upsilon_{max}(CO)/cm^{-1}$ 1886 (s), 1769 (s). $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 52.8 (s, CrP), 21.1 (s, PPN). ^{11}B NMR (128 MHz, C_4D_8O): δ -15.2 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ(^{13}CO) 235.2 (m).

[PPN][Mo(CO)$_3$(PhBP$^{iPr}_3$)] (2)

Yield = 75%. Mp. 223 – 224 °C (dec). Found C, 66.00; H, 7.09; N, 1.09. $C_{66}H_{83}BMoNO_3P_5$ requires C, 66.06; H, 6.97; N, 1.17. IR (CH_2Cl_2) $\upsilon_{max}(CO)/cm^{-1}$ 1890 (s), 1772 (m); (CH_3CN) $\upsilon_{max}(CO)/cm^{-1}$ 1892 (s), 1776 (m); (THF) 1900 (s), 1791 (m); (nujol) $\upsilon_{max}(CO)/cm^{-1}$ 1900 (s), 1788 (s, sh) 1779 (s). $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 36.2 (s, MoP), 21.1 (s, PPN). ^{11}B NMR (128 MHz, C_4D_8O): δ -14.4 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ(^{13}CO) 225.9 (m).

[PPN][W(CO)$_3$(PhBP$^{iPr}_3$)] (3)

Yield: 69%. Mp. 215 – 217 °C (dec). Found C, 61.33; H, 6.74; N, 1.03. $C_{66}H_{83}BNO_3P_5W$ requires C, 61.55; H, 6.50; N, 1.09. IR (CH_2Cl_2) $\upsilon_{max}(CO)/cm^{-1}$ 1884 (s), 1767 (m); (CH_3CN) $\upsilon_{max}(CO)/cm^{-1}$ 1886 (s), 1770 (m); (THF) $\upsilon_{max}(CO)/cm^{-1}$ 1894 (s), 1785 (m); (nujol) $\upsilon_{max}(CO)/cm^{-1}$ 1893 (s), 1772 (s). $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 21.1 (s, PPN), 18.5 (s, br, ^{31}P-^{183}W satellites: 19.1 (br), 17.9 (br), $^1J_{PW}$ = 194 Hz, WP). ^{11}B NMR (128 MHz, C_4D_8O): δ -13.3 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ(^{13}CO) 218.0 (m).

[PPN][Cr(CO)$_3$\{η^6-(PhBP$^{iPr}_3$)Cr(CO)$_3$\}] (7)

THF (40 mL) was added to **1** (0.300 g, 0.259 mmol) and Cr(CO)$_3$(C$_{10}$H$_8$) (0.137 g, 0.519 mmol) affording a deep red solution. The intensity of this color decreased while the solution was stirred at ambient temperature (15 hr). The solution was filtered through alumina. Solvent removal from the filtrate in vacuo revealed orange oil. Addition of Et$_2$O (40 mL) resulted in the precipitation of a sticky bright yellow solid. Trituration freed the solid from the flask wall. The yellow solid was isolated by filtration, washed generously with Et$_2$O (4 * 15 mL) until the rinses were colorless (and free of excess Cr(CO)$_3$(C$_{10}$H$_8$)), and dried in vacuo. Pentane diffusion into a THF solution provided bright yellow microcrystals (0.193 g, 58%). Mp. 207 – 209 °C (dec). Found C, 64.03; H, 6.58; N, 0.99. C$_{69}$H$_{83}$BCr$_2$NO$_6$P$_5$ requires C, 64.14; H, 6.47; N, 1.08. IR (THF) υ_{max}(CO)/cm^{-1} 1946 (s) 1889 (s), 1863 (s), 1783 (s); (nujol) υ_{max}(CO)/cm^{-1} 1947 (s), 1883 (s, sh), 1868 (s, sh), 1857 (s), 1779 (s), 1751 (s). ^{31}P\{^{1}H\} NMR (162 MHz, C$_4$D$_8$O): δ 52.6 (s, br, CrP), 21.0 (s, PPN).[24] ^{11}B NMR (128 MHz, C$_4$D$_8$O): δ -15.5 (s). ^{13}C\{^{1}H\} NMR (101 MHz, C$_4$D$_8$O): δ(^{13}CO) 237.6 (s, arene-bound Cr(CO)$_3$), 235.0 (m, P-bound Cr(CO)$_3$).

[PPN][Cr(CO)$_3$\{η^6-(PhBP$^{iPr}_3$)Mo(CO)$_3$\}] (8)

Yield: 58%. Mp. 217 – 218 °C (dec). Found C, 62.01; H, 6.30; N, 0.99. C$_{69}$H$_{83}$BCrMoNO$_6$P$_5$ requires C, 62.03; H, 6.26; N, 1.05. IR (THF) υ_{max}(CO)/cm^{-1} 1946 (s) 1902 (s), 1863 (s), 1794 (s) cm^{-1}; (nujol) υ_{max}(CO)/cm^{-1} 1947 (s), 1897 (s, sh), 1869 (s, sh), 1857 (s), 1790 (s), 1764 (s) cm^{-1}. ^{31}P\{^{1}H\} NMR (162 MHz, C$_4$D$_8$O): δ 35.9 (s, MoP), 21.0 (s, PPN). ^{11}B NMR (128 MHz, C$_4$D$_8$O): δ -14.9 (s). ^{13}C\{^{1}H\} NMR (101 MHz, C$_4$D$_8$O): δ(^{13}CO) 237.5 (s, arene-bound Cr(CO)$_3$), 225.5 (m, P-bound Mo(CO)$_3$).

[PPN][Cr(CO)$_3$\{η^6-(PhBP$^{iPr}_3$)W(CO)$_3$\}] (9)

Yield: 73%. Mp. 207 – 209 °C (dec). Found C, 58.68; H, 6.01; N, 0.91. C$_{69}$H$_{83}$BCrNO$_6$P$_5$W requires C, 58.20; H, 5.88; N, 0.98. IR (THF) υ_{max}(CO)/cm^{-1} 1946 (s) 1896 (s), 1863 (s), 1789 (s) cm^{-1}; (nujol)

υ_{max}(CO)/cm^{-1} 1947 (s), 1891 (s), 1869 (s, sh), 1857 (s), 1785 (s), 1760 (s) cm^{-1}. ^{31}P{^{1}H} NMR (162 MHz, C$_4$D$_8$O): δ 21.0 (s, PPN), 18.2 (s, ^{31}P-^{183}W satellites: 18.8, 17.6, $^1J_{PW}$ = 197 Hz, WP)). ^{11}B NMR (128 MHz, C$_4$D$_8$O): δ -13.7 (s). ^{13}C{^{1}H} NMR (101 MHz, C$_4$D$_8$O): δ(^{13}CO) 237.5 (s, arene-bound Cr(CO)$_3$), 217.5 (m, P-bound W(CO)$_3$).

[PPN][W(CO)$_3${η^6-(PhBP$^{iPr}_3$)Cr(CO)$_3$}] (12)

THF (40 mL) was added to **1** (0.374 g, 0.324 mmol) and W(CO)$_3$(CH$_3$CH$_2$CN)$_3$ (0.280 g, 0.647 mmol) affording an orange solution. The solution turned dark brown while under reflux (1.5 hr). The solution was filtered through alumina. Solvent removal from the filtrate in vacuo revealed a sticky yellow residue that solidified upon addition of Et$_2$O (40 mL). The golden solid was isolated by filtration, washed with Et$_2$O (2 * 10 mL), and dried in vacuo. Pentane diffusion into a THF solution provided bright golden microcrystals (0.356 g, 77%). Mp. 207 – 209 °C (dec). Found C, 58.90; H, 6.10; N, 0.94. C$_{69}$H$_{83}$BCrNO$_6$P$_5$W requires C, 58.20; H, 5.88; N, 0.98. IR (THF) υ_{max}(CO)/cm^{-1} 1944 (s) 1889 (s), 1855 (s), 1784 (s); (nujol) υ_{max}(CO)/cm^{-1} 1946 (s), 1883 (s), 1867 (s, sh), 1853 (s), 1780 (s), 1752 (s). ^{31}P{^{1}H} NMR (162 MHz, C$_4$D$_8$O): δ 52.9 (s, CrP), 21.1 (s, PPN) ^{11}B NMR (128 MHz, C$_4$D$_8$O): δ -15.7 (s). ^{13}C{^{1}H} NMR (101 MHz, C$_4$D$_8$O): δ(^{13}CO) 235.0 (m, P-bound Cr(CO)$_3$), 214.4 (s, ^{13}C-^{183}W satellites: 215.38, 213.51, $^1J_{CW}$ = 189 Hz, arene-bound W(CO)$_3$).

[PPN][W(CO)$_3${η^6-(PhBP$^{iPr}_3$)Mo(CO)$_3$}] (13)

Yield: 63%. Mp. 176 – 178 °C (dec). Found C, 56.71; H, 5.81; N, 0.90. C$_{69}$H$_{83}$BMoNO$_6$P$_5$W requires C, 56.46; H, 5.70; N, 0.95. IR (THF) υ_{max}(CO)/cm^{-1} 1944 (s) 1902 (s), 1858 (s), 1794 (s); (nujol) υ_{max}(CO)/cm^{-1} 1947 (s), 1897 (s), 1867 (s, sh), 1853 (s), 1791 (s), 1765 (s). ^{31}P{^{1}H} NMR (162 MHz, C$_4$D$_8$O): δ 36.2 (s, MoP), 21.0 (s, PPN). ^{11}B NMR (128 MHz, C$_4$D$_8$O): δ -15.0 (s). ^{13}C{^{1}H} NMR (101 MHz, C$_4$D$_8$O): δ(^{13}CO) 225.4 (m, P-bound Mo(CO)$_3$), 214.4 (s, ^{13}C-^{183}W satellites: 215.34, 213.46, $^1J_{CW}$ = 190 Hz, arene-bound W(CO)$_3$).

[PPN][W(CO)$_3${η^6-(PhBP$^{iPr}_3$)W(CO)$_3$}] (14)

Yield: 67%. Mp. 216 – 217 °C (dec). Found C, 53.36; H, 5.48; N, 0.92. C$_{69}$H$_{83}$BNO$_6$P$_5$W$_2$ requires C, 53.27; H, 5.38; N, 0.90. IR (THF) υ_{max}(CO)/cm^{-1} 1945 (s) 1896 (s), 1857 (s), 1789 (s); (nujol) υ_{max}(CO)/cm^{-1} 1947 (s), 1892 (s), 1867 (s, sh), 1855 (s), 1786 (s), 1761 (s). ^{31}P{^{1}H} NMR (162 MHz, C$_4$D$_8$O): δ 21.1 (s, PPN), 18.4 (s, br, ^{31}P-^{183}W satellites: 19.1 (br), 17.8 (br), $^1J_{PW}$ = 198 Hz, WP)). ^{11}B NMR (128 MHz, C$_4$D$_8$O): δ -13.8 (s). ^{13}C{^{1}H} NMR (101 MHz, C$_4$D$_8$O): δ(^{13}CO) 217.4 (m, P-bound W(CO)$_3$), 214.4 (s, ^{13}C-^{183}W satellites: 215.32, 213.45, $^1J_{CW}$ = 189 Hz, arene-bound W(CO)$_3$).

[((3,5-Me)C$_6$H$_3$)BP$^{Ph}_3$]Tl (18)

Et$_2$O (350 mL) was added to [Li(TMEDA)][Ph$_2$PCH$_2$] (20.96 g, 65.02 mmol); the pale yellow suspension was cooled to -78 °C. A solution of freshly distilled C$_6$H$_3$(3,5-Me)BCl$_2$ (4.05 g, 21.67 mmol) in toluene (20 mL) was added dropwise to this cold suspension over 30 minutes. The reaction mixture was stirred while slowly warming to ambient temperature (20 hr). Pentane (320 mL) was added and the suspension was cooled to -78 °C with vigorous stirring. At this point, stirring was stopped, and the mixture was allowed to stand at -78 °C for ~30 minutes until nearly all the solid had deposited at the bottom of the round bottom flask. The filtrate was carefully decanted; the remaining solids were brought to ambient temperature and dried *in vacuo*. The remainder of the procedure was carried out efficiently in air. Hexanes (200 mL) were added to the solids; the suspension was filtered and the separated solids washed thoroughly with hexanes (2 * 100 mL). The solids were mixed with CH$_3$OH (150 mL); the suspension was filtered through Celite. The colorless filtrate was concentrated *in vacuo* revealing a white sticky solid. The mass of this crude [Li(TMEDA)][((3,5-Me)C$_6$H$_3$)BP$^{Ph}_3$] (14.77 grams) was determined by difference while being transferred as a solution in methanol (80 mL) into a 250 mL Erlenmeyer flask. An aqueous solution (50 mL) of TlPF$_6$ (7.57 g, 21.67 mmol) was added dropwise over 10 minutes to the stirring solution of crude [Li(TMEDA)][((3,5-Me)C$_6$H$_3$)BP$^{Ph}_3$] resulting in a white suspension that was stirred for an additional 10 minutes once the TlPF$_6$ addition

was complete. The product was extracted into CH_2Cl_2 (2 * 150 mL); the combined extracts were filtered through Celite, and the solvent removed *in vacuo* revealing a white solid. This solid was washed with hexanes (3 * 40 mL) and Et_2O (40 mL), and transferred to a 500 mL Erlenmeyer flask. Benzene (200 mL) and anhydrous $MgSO_4$ were added; the suspension was stirred (2 hr). The insolubles were removed via filtration; the filtrate was concentrated *in vacuo* revealing a white solid. Diffusion of pentane into a nearly saturated benzene solution resulted in white microcrystals (8.64 g, 43%). Mp. 214 °C (dec). Found: C, 62.03; H, 4.90. $C_{47}H_{45}BP_3Tl$ requires C, 61.50; H, 4.94. $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 20.6 (d, $^1J_{TlP}$ = 5124 Hz). ^{11}B NMR (128 MHz, C_4D_8O): δ -11.2 (s). ^1H NMR (400 MHz, C_4D_8O): δ 7.23 (m, 14H, *o*-H, (3,5-Me)C_6H_3 and PPh), 7.06 (m, 18H, *m/p*-H, PPh), 6.64 (s, br, *p*-H, (3,5-Me)C_6H_3), 2.29 (s, 6H, Me), 1.68 (m, 6H, BCH_2P). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ 140.1 (m, *i*-C, PPh), 135.6 (s, *o*-C, (3,5-Me)C_6H_3), 132.6 (s, br, *o*-C, PPh), 130.1 (s, *m*-C, (3,5-Me)C_6H_3), 129.2 (s, *p*-C, PPh), 128.9 (m, *m*-C, PPh), 125.5 (s, *p*-C, (3,5-Me)C_6H_3), 22.2 (s, Me), 16.9 (m, BCH_2P).

[((3,5-CF$_3$)C$_6$H$_3$)BP^{Ph}$_3$]Tl (19)

Et_2O (250 mL) was added to [Li(TMEDA)][Ph$_2$PCH$_2$] (13.00 g, 40.31 mmol); the pale yellow suspension was cooled to -78 °C. A solution of freshly distilled ((3,5-CF$_3$)C_6H_3)BCl_2 (3.96 g, 13.43 mmol) in toluene (50 mL) was added dropwise to this cold suspension over 45 minutes. The reaction mixture was stirred while slowly warming to ambient temperature (24 hr); the color of the mixture changed from pale yellow to dark brown. Pentane (250 mL) was added and the suspension was cooled to -78 °C with vigorous stirring. At this point, stirring was stopped, and the mixture was allowed to stand at -78 °C for ~30 minutes until nearly all the solid had deposited at the bottom of the round bottom flask. The filtrate was carefully decanted; the remaining solids were brought to ambient temperature and dried *in vacuo*. The remainder of the procedure was carried out efficiently in air. Hexanes (2 * 100 mL) were used to transfer the solid onto a filter funnel; the filtrate was discarded.

CH$_3$OH (250 mL) was added to the brown solid, and the solution was filtered through Celite. The light brown filtrate was concentrated *in vacuo* revealing a brown sticky solid. The mass of this crude [Li(TMEDA)][((3,5-CF$_3$)C$_6$H$_3$)BP$^{Ph}_3$] (9.52 grams) was determined by difference while being transferred as a solution in methanol (50 mL) into a 250 mL Erlenmeyer flask. An aqueous solution (25 mL) of TlPF$_6$ (3.52 g, 10.08 mmol) was added dropwise over 10 minutes to the stirring solution of crude [Li(TMEDA)][((3,5-CF$_3$)C$_6$H$_3$)BP$^{Ph}_3$] resulting in a brown suspension that was stirred for an additional 10 min once the TlPF$_6$ addition was complete. The product was extracted into CH$_2$Cl$_2$ (2 * 150 mL); the combined extracts were filtered through Celite, and the solvent was removed *in vacuo* revealing a brown solid. This solid was washed with hexanes (2 * 90 mL) and Et$_2$O (30 mL) and dried *in vacuo*. The solid was transferred to a 250 mL Erlenmeyer flask; benzene (150 mL) and anhydrous MgSO$_4$ were added. The suspension was stirred (2 hr). The suspension was filtered through Celite; the filtrate was concentrated in vacuo revealing a brown solid. Diffusion of pentane into a nearly saturated benzene solution resulted in light brown microcrystals (5.32 g, 39%). Mp. 245 °C (dec). Found: C, 55.45; H, 4.01. C$_{47}$H$_{39}$BF$_6$P$_3$Tl requires C, 55.02; H, 3.83. ^{31}P{^{1}H} NMR (162 MHz, C$_4$D$_8$O): δ 19.0 (d, $^1J_{TlP}$ = 4903 Hz). ^{11}B NMR (128 MHz, C$_4$D$_8$O): δ -11.2 (s). ^{19}F{^{1}H} NMR (376 MHz, C$_4$D$_8$O) δ -62.9 (s). ^{1}H NMR (400 MHz, C$_4$D$_8$O): δ 8.12 (s, br, 2H, *o*-H, (3,5-CF$_3$)C$_6$H$_3$), 7.62 (s, br, 1H, *p*-H, (3,5-CF$_3$)C$_6$H$_3$), 7.24 (m, 12H, *o*-H, PPh), 7.14 − 7.05 (m, 18H, *m/p*-H, PPh), 1.64 (m, 6H, BC*H$_2$*P). ^{13}C{^{1}H} NMR (101 MHz, C$_4$D$_8$O): δ 139.5 (m, *i*-C, PPh), 132.6 (s, br, *o*-C, PPh), 132.0 (s, br, *o*-C, (3,5-CF$_3$)C$_6$H$_3$), 129.2 (s, *p*-C, PPh), 129.1 (m, *m*-C, PPh), 125.9 (q, $^1J_{CF}$ = 274 Hz, *C*F$_3$), 117.8 (m, *m*-C, (3,5-CF$_3$)C$_6$H$_3$), 16.6 (m, BC*H$_2$*P).

[PPN][Cr(CO)$_3$(((3,5-Me)C$_6$H$_3$)BP$^{Ph}_3$)] (20)

CH$_3$CN (40 mL) was added to **18** (0.539 g, 0.587 mmol) and Cr(CO)$_3$(CH$_3$CN)$_3$ (0.145 g, 0.560 mmol). The yellow solution was refluxed (1.5 hr), and the solvent was removed *in vacuo*. THF (40 mL) was added to the yellow residue, and the resulting suspension was added to PPNCl (0.353 g, 0.615 mmol);

the mixture was stirred (1 hr). The suspension was filtered through alumina; most of the yellow filtrate

solvent was removed *in vacuo*. Addition of Et$_2$O (30 mL) affected the precipitation of a yellow solid

that was isolated by filtration, washed with Et$_2$O (3 * 10 mL) and dried *in vacuo*. Pentane diffusion

into a nearly saturated Et$_2$O:THF solution provided yellow microcrystals (0.462 g, 60%). Mp. 242 °C

(dec). Found: C, 74.06; H, 5.71; N, 0.91. C$_{86}$H$_{75}$BCrNO$_3$P$_5$ requires C, 74.41; H, 5.45; N, 1.01. IR

(THF) υ_{max}(CO)/cm^{-1} 1903 (s), 1805 (m); (CH$_3$CN) υ_{max}(CO)/cm^{-1} 1899 (s), 1794 (m); (nujol)

υ_{max}(CO)/cm^{-1} 1902 (s), 1793 (s, br). ^{31}P$\{^{1}$H$\}$ NMR (162 MHz, C$_4$D$_8$O): δ 46.5 (s, CrP), 21.0 (s, PPN).

^{11}B NMR (128 MHz, C$_4$D$_8$O): δ -14.6 (s). ^{13}C$\{^{1}$H$\}$ NMR (101 MHz, C$_4$D$_8$O): δ(^{13}CO) 234.3 (m).

[PPN][Mo(CO)$_3$(((3,5-Me)C$_6$H$_3$)BP$^{Ph}_3$)] (21)

Yield: 69%. Mp. 238 °C (dec). Found: C, 71.96; H, 5.35; N, 0.89. C$_{86}$H$_{75}$BMoNO$_3$P$_5$ requires C,

72.12; H, 5.28; N, 0.98. IR (THF) υ_{max}(CO)/cm^{-1} 1915 (s), 1815 (m); (CH$_3$CN) υ_{max}(CO)/cm^{-1} 1911 (s),

1805 (m); (nujol) υ_{max}(CO)/cm^{-1} 1914 (s), 1800 (s, br). ^{31}P$\{^{1}$H$\}$ NMR (162 MHz, C$_4$D$_8$O): δ 28.1 (s,

MoP), 21.0 (s, PPN). ^{11}B NMR (128 MHz, C$_4$D$_8$O): δ -14.1 (s). ^{13}C$\{^{1}$H$\}$ NMR (101 MHz, C$_4$D$_8$O):

δ(^{13}CO) 225.4 (m).

[PPN][W(CO)$_3$(((3,5-Me)C$_6$H$_3$)BP$^{Ph}_3$)] (22)

Yield: 65%. Mp. 231 °C (dec). Found: C, 67.78; H, 5.09; N, 0.87. C$_{86}$H$_{75}$BNO$_3$P$_5$W requires C, 67.95;

H, 4.97; N, 0.92. IR (THF) υ_{max}(CO)/cm^{-1} 1910 (s), 1810 (s) cm^{-1}; (CH$_3$CN) υ_{max}(CO)/cm^{-1} 1906 (s),

1801 (s) cm^{-1}; (nujol) υ_{max}(CO)/cm^{-1} 1908 (s), 1793 (s, br) cm^{-1}. ^{31}P$\{^{1}$H$\}$ NMR (162 MHz, C$_4$D$_8$O): δ

21.0 (s, PPN), 10.5 (s, br, ^{31}P-^{183}W satellites: 11.2 (br), 9.9 (br), $^{1}J_{PW}$ = 204 Hz, WP). ^{11}B NMR (128

MHz, C$_4$D$_8$O): δ -13.1 (s). ^{13}C$\{^{1}$H$\}$ NMR (101 MHz, C$_4$D$_8$O): δ(^{13}CO) 216.4 (m).

[PPN][Cr(CO)$_3$(((3,5-CF$_3$)C$_6$H$_3$)BP$^{Ph}_3$)] (23)

THF (40 mL) was added to **19** (0.360 g, 0.350 mmol) and Cr(CO)$_3$(CH$_3$CN)$_3$ (0.096 g, 0.334 mmol).

The pale yellow solution was refluxed (1.5 hr). The resulting yellow-brown solution was added to

PPNCl (0.211 g, 0.368 mmol); the mixture was stirred (2 hr). The suspension was filtered through

alumina; most of the yellow filtrate solvent was removed *in vacuo*. Addition of Et_2O (20 mL) affected the precipitation of a yellow solid that was isolated by filtration, washed with Et_2O (3 * 10 mL) and dried *in vacuo*. Pentane diffusion into a nearly saturated Et_2O:THF solution provided yellow microcrystals (0.276 g, 55%). Mp. 236 °C (dec). Found: C, 68.35; H, 4.73; N, 0.89. $C_{86}H_{69}BCrF_6NO_3P_5$ requires C, 69.04; H, 4.65; N, 0.94. IR (THF) $\upsilon_{max}(CO)/cm^{-1}$ 1906 (s), 1809 (m); (CH$_3$CN) $\upsilon_{max}(CO)/cm^{-1}$ 1901 (s), 1798 (m); (nujol) $\upsilon_{max}(CO)/cm^{-1}$ 1903 (s), 1798 (s, br). $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 45.6 (s, br, CrP), 21.0 (s, PPN). ^{11}B NMR (128 MHz, C_4D_8O): δ -14.4 (s). $^{19}F\{^1H\}$ NMR (376 MHz, C_4D_8O) δ -62.8 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ(^{13}CO) 234.1 (m).

[PPN][Mo(CO)$_3$(((3,5-CF$_3$)C$_6$H$_3$)BP$^{Ph}_3$)] (24)

Yield: 45%. Mp. 203 °C (dec). Found: C, 67.06; H, 4.56; N, 0.93. $C_{86}H_{69}BF_6MoNO_3P_5$ requires C, 67.07; H, 4.52; N, 0.91. IR (THF) $\upsilon_{max}(CO)/cm^{-1}$ 1919 (s), 1820 (m); (CH$_3$CN) $\upsilon_{max}(CO)/cm^{-1}$ 1914 (s), 1809 (m); (nujol) $\upsilon_{max}(CO)/cm^{-1}$ 1916 (s), 1810 (s, br). $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 27.0 (q, $^2J_{PC}$ = 6.0 Hz, MoP), 21.0 (s, PPN). ^{11}B NMR (128 MHz, C_4D_8O): δ -13.9 (s). $^{19}F\{^1H\}$ NMR (376 MHz, C_4D_8O) δ -62.8 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ(^{13}CO) 224.1 (m).

[PPN][W(CO)$_3$(((3,5-CF$_3$)C$_6$H$_3$)BP$^{Ph}_3$)] (25)

Yield: 55%. Mp. 205 °C (dec). Found: C, 63.51; H, 4.23; N, 0.83. $C_{86}H_{69}BF_6NO_3P_5W$ requires C, 63.45; H, 4.27; N, 0.86. IR (THF) $\upsilon_{max}(CO)/cm^{-1}$ 1914 (s), 1815 (s); (CH$_3$CN) $\upsilon_{max}(CO)/cm^{-1}$ 1908 (s), 1803 (s); (nujol) $\upsilon_{max}(CO)/cm^{-1}$ 1906 (s), 1792 (s, br). $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 21.0 (s, PPN), 9.37 (q, $^2J_{PC}$ = 5.0 Hz, ^{31}P-^{183}W satellites: 10.00 (m), 8.73 (m), $^1J_{PW}$ = 206 Hz, WP). ^{11}B NMR (128 MHz, C_4D_8O): δ -12.9 (s). $^{19}F\{^1H\}$ NMR (376 MHz, C_4D_8O) δ -62.8 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ(^{13}CO) 215.9 (m).

X-ray Crystallography

X-ray quality crystals were obtained by diffusion of pentane into THF solutions (**1-3**, **7-9**, **12-14**), pentane into benzene solutions (**18**, **19**) and pentane into Et_2O-THF (75:25 v:v) solutions (**20-23**); suitable crystals of **24** and **25** were obtained *via* slow evaporation of Et_2O-THF solutions. These crystals were selected from the mother liquor in a N_2-filled glove bag and placed onto the tip of a 0.1 mm diameter glass capillary and mounted on either a Bruker APEX-II CCD diffractometer with 0.71073 Å Mo-Kα radiation for data collection at 173(2) K (**1-3**, **7-9**, **12-14**) or a Bruker VENTURE PHOTON-II diffractometer with 0.71073 Å Mo-Kα radiation for data collection at 100(2) K (**18-25**). All structures were solved by direct methods using SHELXL-2014/5 and refined with full-matrix least-squares procedures using SHELXL-2014/6.[25] 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 **1-3**, **7-9**, **12-14** and **18-25** and further details of crystallographic data collection, solution, and refinement can be found in the ESI (Sections III and IV). Crystallographic CIF files for these structures: CCDC 1824309-1824325.

Cyclic Voltammetry

All manipulations were performed under argon inside of an MBraun glovebox maintained < 1 ppm O_2 and H_2O. Acetonitrile was deoxygenated *via* sparging with argon and dried *via* passage through an activated alumina column of an SG Water solvent purification system; the CH_3CN was stored over activated 4 Å molecular sieves until use. Cyclic voltammetry was conducted using a CH Instruments 600 electrochemical analyzer. The one-cell setup utilized a glassy carbon working electrode, platinum wire counter electrode and a $Ag/AgNO_3$ reference electrode in CH_3CN. Analyte solutions (each ~1.5 mM) were prepared in an 0.4 M CH_3CN solution of tetrabutylammonium hexafluorophosphate ([TBA][PF_6]) and referenced internally to the $FeCp_2/[FeCp_2]^+$ redox couple at the end of each

experiment. Cyclic voltammograms and additional information regarding these experiments can be found in the ESI (Section V).

Conflicts of Interest

There are no conflicts of interest to declare.

Acknowledgments

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24.   This broad Cr-^{31}P resonance is attributed to a paramagnetic impurity.   Reaction of **4** and [FeCp$_2$][PF$_6$] (1 equiv) results in zwitterionic and paramagnetic Cr(CO)$_3$(PhBP$^{Ph}_3$).   The examination of this and related metalloradicals of R'BP$^R_3$ will be reported in due course.   Our working hypothesis is that trace formation of a related one electron oxidation product of **7** leads to the broad resonance in the ^{31}P{^{1}H} spectrum of **7**.

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Inductive Modulation of Tris(phosphinomethyl)phenylborate Donation at Group VI Metals via Borate Phenyl Substituent Modification

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Table of Contents Textual Abstract

IR spectral data and half wave potentials associated with the κ^3-phosphine bound $M(CO)_3$ units of anionic tris(phosphinomethyl)phenylborate complexes suggest a ligand donor ranking of $Tp > PhBP^{iPr}_3 \geq Cp > PhBP^{Ph}_3 > triphos$. New $PhBP^{Ph}_3$ ligands were synthesized to explore possible tuning of $PhBP^{Ph}_3$ donation *via* inductive modulation of the borate negative charge. Cyclic voltammetry data suggests that rational tuning of this type occurs in complexes of zerovalent metals.

Table of Contents Graphical Abstract

Variation in Cr(CO)3P3 Half Wave Potentials

V (vs. FcCp$_2^{+/0}$)