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Journal:	*Dalton Transactions*
Manuscript ID	DT-ART-09-2019-003562.R1
Article Type:	Paper
Date Submitted by the Author:	22-Oct-2019
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Seventeen-Electron Chromium(I)tricarbonyltris(phosphine) Complexes Supported by Tris(phosphinomethyl)phenylborates

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Abstract

The inaugural crystallographic characterization of chromium(I)tricarbonyltris(phosphine) radicals has been achieved. Oxidation of [PPN][$Cr(CO)_3(PhBP^{Ph}_3)$] ($PhBP^{Ph}_3$ = $PhB(CH_2PPh_2)_3]^-$) and analogous Cr(0) complexes featuring 3,5-dimethylphenyl and 3,5-bis(trifluoromethyl)phenyl borate substituents affords charge-neutral $Cr(CO)_3(PhBP^{Ph}_3)$ zwitterions, containing the first fully characterized $[Cr(CO)_3P_3]^+$ units. The stabilization affected by the intramolecular charge separation established by $PhBP^{Ph}_3$ ligands dramatically increases the robustness of these seventeen-electron Cr(I) complexes. Previous attempts to isolate salts of *mer*/*fac*-$[Cr(CO)_3P_3]^+$ were frustrated by the thermal instability of these cations. The EPR spectroscopic data of $Cr(CO)_3(PhBP^{Ph}_3)$ supports Rieger's hypothesized low temperature preparation of *fac*-$[Cr(CO)_3\{CH_3C(CH_2PPh_2)_3\}]^+$. The robust $[Cr(CO)_3P_3]^+$ unit of

$Cr(CO)_3(PhBP^{Ph}{}_3)$ motivated the preparation of structurally characterized Cr(0)/Cr(I) ($Cr(CO)_3\{\eta^6\text{-}(PhBP^{Ph}{}_3)Cr(CO)_3\}$, $Cr(CO)_3\{\eta^6\text{-}(((3,5\text{-}CH_3)C_6H_3)BP^{Ph}{}_3)Cr(CO)_3\}$) and W(0)/Cr(I) ($W(CO)_3\{\eta^6\text{-}(((3,5\text{-}CH_3)C_6H_3)BP^{Ph}{}_3)Cr(CO)_3\}$) complexes. While these bimetallics feature classical κ^3-phosphine and η^6-arene metal-binding, they are noteworthy since all other reported mixed-valent Cr(0)/Cr(I) complexes exhibit (a) significant thermal instability that has precluded their isolation and (b) greater uncertainty regarding the presence of distinct Cr(I) and Cr(0) centers. This work illustrates the utility of tris(phosphino)borates for the stabilization of cationic metal fragments within zwitterions that are inaccessible or difficult to characterize independently.

Introduction

The chemistry of chromium(I)tricarbonyltris(phosphine) and tris(phosphite) complexes has been of long interest, particularly in regards to *fac*/*mer* isomerization mechanisms and electronic structures.[1] Bond and Colton enlightened much of what is known about these d^5 chromium metalloradicals via electrochemical and EPR spectroscopic studies. It is well established that the Cr(0) species *fac*-$[Cr(CO)_3P_3]$ (P = phosphine, phosphite) are stable, but the corresponding *fac*-$[Cr(CO)_3P_3]^+$ complexes rapidly isomerize to *mer*-$[Cr(CO)_3P_3]^+$.[2] While these chromium(I) complexes have been interrogated in solution on time scales associated with cyclic voltammetry, X-ray crystallographic characterization of any $[Cr(CO)_3P_3]^+$ has proved elusive on the basis of their thermal instability. Bond and Colton isolated *mer*-$[Cr(CO)_3P_3]ClO_4$, (P = $P(OMe)_3$, $P(OMe)_2Ph$, PMe_2Ph) and *mer*-$[Cr(CO)_3(P(OPh)_3)_3]PF_6$ that afforded infrared ν(CO) and EPR spectroscopic data, but bulk purity was not indicated by elemental analyses.[3] Rieger reported frozen solution EPR spectra of *mer*-$[Cr(CO)_3(PMe_3)_3]^+$ and *fac*-$[Cr(CO)_3(PMe_2Ph)_3]^+$.[4] While attempts to generate *fac*-$[Cr(CO)_3\{CH_3C(CH_2PPh_2)_3\}]^+$ by electrochemical oxidation failed, this cation was prepared by low-temperature oxidation, and an EPR spectrum obtained by freezing the solution. This chromium(I) cation decomposes rapidly above 200 K.[4]

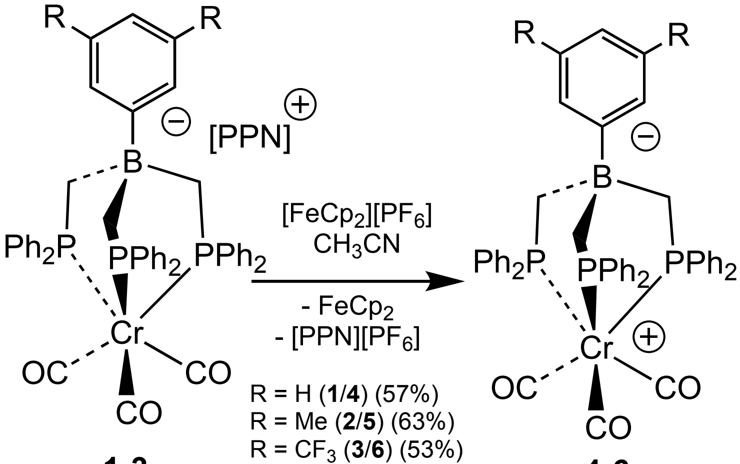
Recent years have seen a revival in d^5 chromium(I) metalloradical chemistry, with the characterization of long sought, archetypal species. The isolation and crystal structure of the seventeen-electron radical $[(\eta^6\text{-}C_6Me_6)Cr(CO)_3]^+$, stabilized by large polyfluoroaluminate anions, was reported by Wang in 2015.[5] Bohnenberger and Breher prepared and structurally characterized the homoleptic carbonyl radical cation $[Cr(CO)_6]^+$ also using $[Al(OR^F)_4]^-$ (R^F = $C(CF_3)_3$) as a counterion in 2019.[6] A theme of these studies is the kinetic stabilization of reactive cations by minimization of ion-pairing interactions.

An alternate strategy for stabilizing cationic metal fragments is the enforcement of an intramolecular charge separation via employment of ligands in which a partially insulated negative charge is fixed at a remote distance from the metal. Tris(phosphino)borates have been used extensively in this capacity. For example, the novel Co(II) electronic structure in $[PhBP^{Ph}_3]CoI$ ($[PhBP^{Ph}_3$ = $[PhB(CH_2PPh_2)_3]^-$) depends critically on this geometrically-enforced ligand design.[7] Specifically, independent cobalt(II) $[Co(PR_3)_3I]^+$ have not been prepared; five-coordinate $[Co(dppe)_2I][BPh_4]$[8] is known and an attempted synthesis of $[Co\{CH_3C(CH_2PPh_2)_3\}I]^+$ resulted in spontaneous Co(II) to Co(I) reduction.[9]

Our work with group VI metal tricarbonyl complexes of tris(phosphino)borates[10] included an examination of $[Et_4N][Cr(CO)_3(PhBP^{Ph}_3)]$ by cyclic voltammetry in CH_3CN. The reversible one-electron oxidation of $[Et_4N][Cr(CO)_3(PhBP^{Ph}_3)]$ and half wave potential (–0.37 V (vs. $[FeCp_2]^+/FeCp_2$)) suggested the electrochemical formation of d^5 chromium(I) $Cr(CO)_3(PhBP^{Ph}_3)$, a zwitterionic cousin of $[Cr(CO)_3P_3]^+$ species. The aforementioned paucity of structural data associated with chromium(I)tricarbonyltris(phosphine) complexes and the precedent of tris(phosphino)borates in stabilizing cationic metal fragments motivated a further examination of alleged $Cr(CO)_3(PhBP^{Ph}{}_3)$. Our findings are reported herein.

Results and Discussion

Early reactions of $[Cr(CO)_3(PhBP^{Ph}{}_3)]^-$ with I_2 in THF and CH_2Cl_2 resulted in rapid Cr(0) complex consumption and formation of uncharacterized products exhibiting no infrared ν(CO) absorptions, initially suggesting that $Cr(CO)_3(PhBP^{Ph}{}_3)$, like Rieger's putative *fac*-$[Cr(CO)_3\{CH_3C(CH_2PPh_2)_3\}][BF_4]$, exhibited high thermal instability. The subsequent cyclic voltammetry results suggested $[FeCp_2]^+$ as the oxidant and CH_3CN as the solvent. Dropwise addition of a suspension of $[FeCp_2][PF_6]$ in CH_3CN to solutions of $[PPN][Cr(CO)_3(PhBP^{Ph}{}_3)]$ (**1**), $[PPN][Cr(CO)_3(((3,5\text{-}Me)C_6H_3)BP^{Ph}{}_3)]$ (**2**)[11] and $[PPN][Cr(CO)_3(((3,5\text{-}CF_3)C_6H_3)BP^{Ph}{}_3)]$ (**3**)[10a] in CH_3CN results in precipitation of zwitterions **4-6** (Scheme 1). The fortuitous low solubility of **4-6** in these reaction mixtures allows $[PPN][PF_6]$ and $FeCp_2$ to be nearly completely removed from **4-6** by filtration, but crystallization from THF/pentane is necessary to obtain red microcystals with formulations confirmed by elemental microanalyses. The thermal stability of the d^5 cationic chromium(I) $[Cr(CO)_3P_3]$ units affected by the intramolecular charge separation in **4-6** is remarkable relative that observed for *fac*-$[Cr(CO)_3\{CH_3C(CH_2PPh_2)_3\}]^+$. While the latter decomposes at T > –73 °C in 1:1 CH_2Cl_2:1,2-$C_2H_4Cl_2$, the lowest decomposition temperature of solid **4-6** (that of **4**) is 192–193 °C. The IR



1-3 **4-6**

Scheme 1

spectrum and physical appearance of **4** was unchanged after heating a sample in an argon atmosphere at 180 °C for at least 4 hours.

The similar infrared ν(CO) spectra of **4**-**6** in nujol (**6**: 1999 (s), 1895 (m) cm^{-1}), the first of any *fac*-$[Cr(CO)_3P_3]^+$ units, exhibit absorption profiles very similar to that of $[Cr(CO)_3(\eta^6\text{-}C_6Me_6)]^+$ (2062 (s) , 1989 (m) cm^{-1}),[5] albeit at significantly lower energies. The d^5 Cr(I) centers of **4**-**6** participate in significantly attenuated π-backbonding on the basis of their ~100 cm^{-1} red-shifted ν(CO) absorptions relative the d^6 Cr(0) center of $[Et_4N][Cr(CO)_3(PhBP^{Ph}{}_3)]$ ((CH_3CN): 1899 (s), 1794 (s) cm^{-1}). The higher energy ν(CO) absorptions of **4** (2001 cm^{-1}), **5** (1999 cm^{-1}), and **6** (2002 cm^{-1}) in THF exhibit the trend expected on the basis of the 3,5-bridgehead boron phenyl substituents of **4** (H), **5** (CH_3) and **6** (CF_3), but any inductive modulation of tris(phosphino)borate donation affected by these remote groups[10a] is clearly very modest. These higher energy absorptions are blue-shifted by ~20 cm^{-1} relative that of $Cr(CO)_3Tp$ in THF (2024, 1865 cm^{-1}).[12] This trend is common in zwitterionic complexes, in which $PhBP^{Ph}{}_3$ ligands are classified as strongly donating scorpionates, and better donors than hydrotris(pyrazol-1-yl)borate.[13] Wolczanski's charge distribution via reporters method (CDVR)[14] allows an alternate assessment of the Scheme 1 species, with the prototypical $[Et_4N][Cr(CO)_3(PhBP^{Ph}{}_3)]$ and **4** discussed herein. The calculated charges[15] for CO (c_{CO}: $[Et_4N][Cr(CO)_3(PhBP^{Ph}{}_3)]$, –0.76; **4**, –0.55) and each phosphine function (c_{PR3}: $[Et_4N][Cr(CO)_3(PhBP^{Ph}{}_3)]$, –0.11; **4**, –0.32) are consistent with greater electron density accommodated by the CO ligands in the Cr(0) complex relative those in the Cr(I) complex **4**. The more negative c_{CO} of $[Et_4N][Cr(CO)_3(PhBP^{Ph}{}_3)]$ (–0.76), with three CH_2PPh_2 pendant donor arms, relative that of *fac*-$Cr(CO)_3(PMe_3)_3$ (–0.71) emphasizes the contribution of the borate negative charge in enhancing $PhBP^{Ph}{}_3$ donation. The less negative c_{PR3} of $[Et_4N][Cr(CO)_3(PhBP^{Ph}{}_3)]$ (–0.11) relative those of *fac*-$Cr(CO)_3(PMe_3)_3$ (–

0.16) and *fac*-$Cr(CO)_3(PMe_2Ph)_3$ (–0.16) complements the former by suggesting that the π-acceptor ability of $PhBP^{Ph}{}_3$ with respect to zerovalent $Cr(CO)_3$ units is handicapped by its negative charge, relative that offered by a set of neutral tertiary phosphines. However, upon $[Et_4N][Cr(CO)_3(PhBP^{Ph}{}_3)]$ oxidation to **4**, the borate charge inductively allows the $PhBP^{Ph}{}_3$ phosphines to accommodate more negative charge as the c_{PR3} of **4** (–0.32) increases by nearly a factor of three, concomitant with a ~30% decrease in c_{CO}. This is consistent with decreased π-backbonding into CO and an enhanced electrostatic contribution of $PhBP^{Ph}{}_3$ binding towards the $[Cr(CO)_3]^+$ unit of **4** relative these complementary features involving the $[Cr(CO)_3]^0$ unit of $[Et_4N][Cr(CO)_3(PhBP^{Ph}{}_3)]$.

Magnetic measurements using the method of Evans furnished magnetic moments of 1.8 μ_B (**4**), 1.6 μ_B (**5**), and 1.7 μ_B (**6**) indicative of the expected S = ½ ground state. These are similar to the magnetic moments reported for the low-spin d^5 chromium(I) salts *mer*-$[Cr(CO)_3(P(OMe)_2Ph)_3]ClO_4$ (1.84 μ_B) and *mer*-$[Cr(CO)_3(PMe_2Ph)_3]ClO_4$ (1.82 μ_B).[3a] To further probe the radical cation character of zwitterions **4**-**6**, frozen solutions of these substances in 1:1 THF:CH_2Cl_2 at 77 K were investigated by X-band EPR spectroscopy. The EPR data for **4**-**6** are virtually identical; the spectra cannot be distinguished from each other. A representative

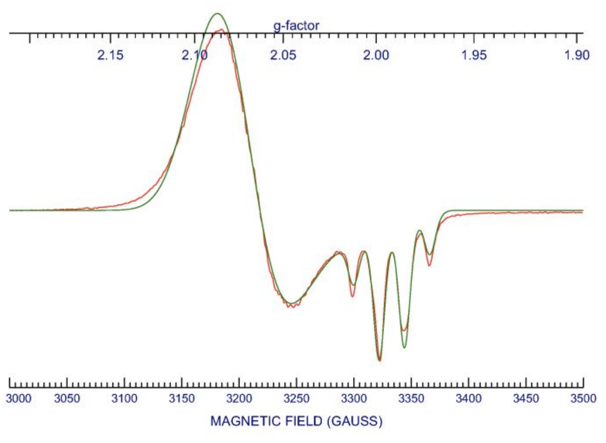


Fig. 1 Experimental (red) and C_3 Simulated (green)

EPR Spectrum of **4.**

EPR spectrum of **4** is in Fig. 1, along with a simulated spectrum assuming three symmetry-equivalent phosphorus atoms. The anisotropic *g*-values of **4** (g_x, 2.077; g_y, 2.077; g_z, 1.993) are very similar to those of *fac*-$[Cr(CO)_3(PPhMe_2)_3]^+$ (g_x, 2.054; g_y, 2.054; g_z, 1.988) and *fac*-$[Cr(CO)_3\{CH_3C(CH_2PPh_2)_3\}]^+$ (g_x, 2.080; g_y, 2.080; g_z, 1.994) obtained in 1:1 CH_2Cl_2:1,2-$C_2H_4Cl_2$ at 110 K.[4,16] These data strongly suggest the anticipated similar structures of **4-6** and *fac*-$[Cr(CO)_3\{CH_3C(CH_2PPh_2)_3\}]^+$ in solution. This observation, in combination with the thorough characterization of **4-6** described herein, supports Rieger's hypothesis of having trapped thermally unstable *fac*-$[Cr(CO)_3\{CH_3C(CH_2PPh_2)_3\}]^+$. The ranking $g_x \sim g_y > g_z \sim g_e$ (2.0023) for these *fac*-$[Cr(CO)_3P_3]^+$ units is consistent with nondegenerate electronic ground states and a SOMO of high d_{z^2} character. Fig. 1 shows hyperfine splitting along *z*, with an approximate 1:3:3:1 quartet indicating the coupling of the electron spin to three ^{31}P atoms. However, the anisotropic spectrum *x* and *y* features are very broad with no resolved hyperfine splitting. Two simulations were carried out, one assuming threefold symmetric phosphorus atoms and the other a rhombic geometry with just two phosphorus atoms related by a mirror plane. The C_3 simulation-derived hyperfine couplings associated with each P atom are 62 $\langle A_x \rangle$, 55 $\langle A_y \rangle$, and 62 $\langle A_z \rangle$ MHz, but large linewidths must be employed for the *x* and *y* features (*x*,*y*: 40 G; *z*: 9 G). Rieger reported a similar $\langle A_z \rangle$ for *fac*-$[Cr(CO)_3\{CH_3C(CH_2PPh_2)_3\}]^+$ (64 MHz) and noted an unresolved $g_\perp$ region.[4] A better resolved *fac*-$[Cr(CO)_3(PPhMe_2)_3]^+$ spectrum ($\langle A_x \rangle$, 66; $\langle A_y \rangle$, 66; $\langle A_z \rangle$, 78 MHz) was acquired.[4] While a slightly better fit for **4-6** arises with the consideration of rhombic symmetry, large linewidths are still required to model the *x* (48 G) and *y* (20 G) features. The origin of these broad EPR spectral attributes of **4-6** (and *fac*-$[Cr(CO)_3\{CH_3C(CH_2PPh_2)_3\}]^+$) is not clear, but relaxation broadening due to an Orbach process involving a low lying excited state is an intriguing possibility on the basis of calculations that predicted a very small $^2A/^2E$

energy gap in *fac*-$[Cr(CO)_3P_3]^+$ radical cations.[1] The failure to observe isotropic EPR spectra of these cations has been attributed to rapid spin-lattice relaxation in solution due to the relatively high accessibility of the ^2E excited state.

Thermal ellipsoid drawings depicting the molecular structures of **4** (Fig. 2) and **5** (Fig. 3) represent the inaugural X-ray crystallographic characterization of $[Cr(CO)_3P_3]^+$ units. These units of **4** and **5** are statistically identical, and exhibit mild tetragonal distortion, with the C–Cr–P angles more obtuse than the other angles that define the chromium(I) coordination environments. The average angles of **4** and **5** listed in the Fig. 2 and Fig. 3 captions are statistically indistinguishable to those of the Cr(0) anion of $[Et_4N][Cr(CO)_3(PhBP^{Ph}_3)]$ (Cr–C = 1.827(6), Cr–P = 2.41(1), C–Cr–C = 84(1), P–Cr–P = 86(2), C–Cr–P = 95(3)).[10b] The κ^3-chelation and tight tris(phosphino)borate binding enhanced by the intramolecular charge separation with respect to these d^5 $[Cr(CO)_3P_3]^+$ units results in no detectable geometric differences relative to their d^6 $Cr(CO)_3P_3$ precursors. The geometrically-enforced intramolecular Cr(I) to borate separations (Cr–B) of **4** (3.700(2) Å) and **5** (3.694(2) Å) are very modestly reduced relative the Cr(0) to borate separation in $[Et_4N][Cr(CO)_3(PhBP^{Ph}_3)]$ (3.725(2) Å).[10b] A similarly modest electronic impact of these cationic Cr(I) centers at boron is suggested via ^{11}B NMR spectroscopy, as the borate resonances of **4** (δ -10.4 (s)) and **5** (δ -10.2 (s)) in C_4D_8O are only slightly deshielded from that of $[Et_4N][Cr(CO)_3(PhBP^{Ph}_3)]$ (δ -14.7 (s)) in CD_3CN.

Mixed-Valent M(I)/M(0) Complexes

Despite the Cr–CO bond weakening expected upon Cr(0) to Cr(I) oxidation, the cationic Cr(CO)$_3$ units of **4** are robust with respect to CO substitution. No evidence of Cr(CO)$_2$L(PhBP$^{Ph}{}_3$) (L = PMe$_3$, C$_5$H$_5$N, 2,6-(CH$_3$)$_2$C$_6$H$_3$NC) could be obtained; substitution attempts in refluxing THF with an excess of these ligand candidates (50 equiv.) provided only IR spectroscopic evidence of **4** after 72 hours. Unchanged **4** was recovered nearly quantitatively from a suspension refluxed in CH$_3$CN for 3 days. Reduction of **4** with NaC$_{10}$H$_8$ does cleanly provide THF solutions containing d^6 [Cr(CO)$_3$(PhBP$^{Ph}{}_3$)]$^-$.

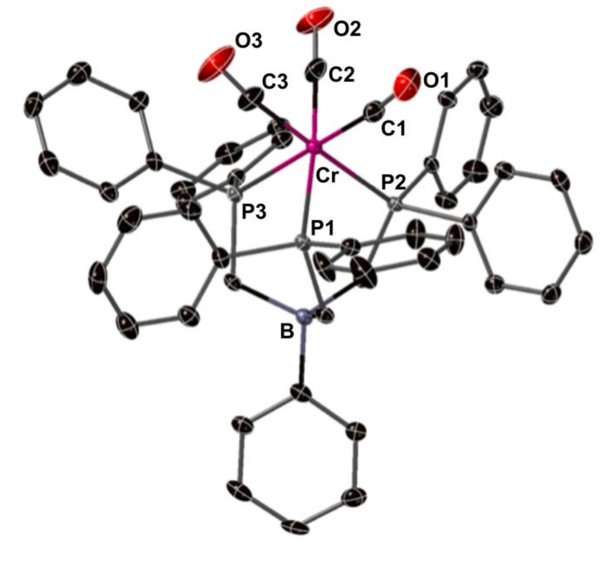


Fig. 2 Thermal ellipsoid (50%) drawing of **4**. Selected average bond lengths (Å) and angles (°) Cr–C = 1.88(1), Cr–P = 2.44(3), C–Cr–C = 85(4), P–Cr–P = 88(2), C–Cr–P = 94(2).

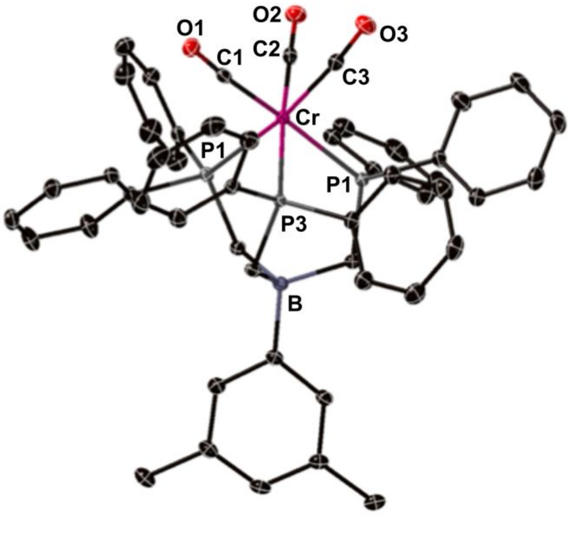


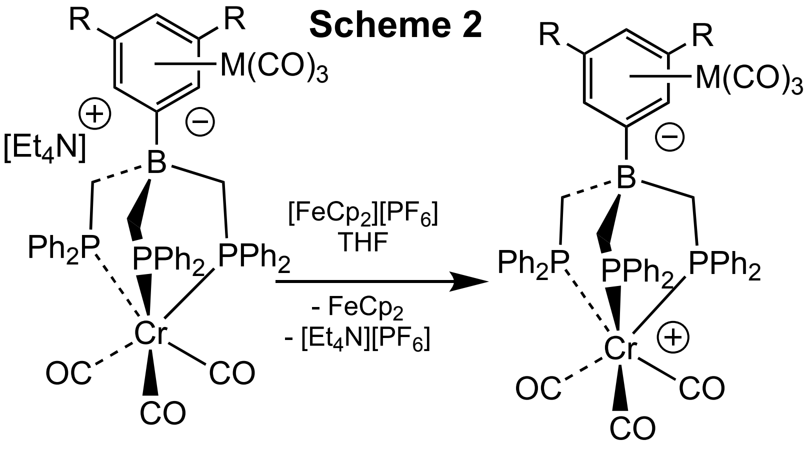
Fig. 3 Thermal ellipsoid (50%) drawing of **5**. Selected average bond lengths (Å) and angles (°) Cr–C = 1.89(1), Cr–P = 2.44(2), C–Cr–C = 85(9), P–Cr–P = 87(2), C–Cr–P = 94(4).

Previous work in our laboratory uncovered a PhBP$^{Ph}{}_3$ bi-functional role in which zerovalent M(CO)$_3$ fragments bind the three phosphine atoms and the borate phenyl substituent.[10b] The more positive half wave potential of Cr(CO)$_3$(η^6-C$_6$H$_6$) (+0.44 V vs. [FeCp$_2$]$^+$/FeCp$_2$)[17] relative that of [Et$_4$N][Cr(CO)$_3$(PhBP$^{Ph}{}_3$)] (–0.37 V (vs. [FeCp$_2$]$^+$/FeCp$_2$) suggested the ability of PhBP$^{Ph}{}_3$ to bridge d^5 [Cr(CO)$_3$]$^+$ and d^6 Cr(CO)$_3$ units. While the envisioned complexes are unremarkable in their employment of classical κ^3-phosphine and η^6-arene metal-binding, it is noteworthy that no mixed-valent Cr(0)/Cr(I) complex has been fully characterized. Geiger oxidized (η^6:η^6-biphenyl)[Cr(CO)$_2$(PPh$_3$)]$_2$ to afford [(η^6:η^6-biphenyl)[Cr(CO)$_2$(PPh$_3$)]$_2$][PF$_6$]; this salt was assessed as containing Cr$^{\mathrm{I}}$(CO)$_2$(PPh$_3$) and Cr^0(CO)$_2$(PPh$_3$) units by EPR and IR spectroscopies. The cation rapidly decomposes to the starting Cr(0)/Cr(0) bimetallic at 265 K.[18] Three related complexes in which two d^6 Cr(CO)$_2$(PPh$_3$) moieties are connected via substituted biphenyl linkages with the two η^6-arene rings disposed at varying dihedral angles were oxidized to afford Cr(0)/Cr(I) cations also classified as "trapped-valent".[19] The tetramethyldiphosphine-linked [(η^6:η^6-biphenyl)[Cr(CO)$_2$](μ-P$_2$Me$_4$)]$^+$ and [(η^6:η^6-diphenylmethane)[Cr(CO)$_2$](μ-P$_2$Me$_4$)]$^+$ also exhibit spectroscopic data consistent with distinct Cr(I) and Cr(0) centers.[20] The thermal instability of all these mixed-valent species has precluded their isolation. The robust d^5 [Cr(CO)$_3$]$^+$ units of **4-6** forecasted the accessibility of Cr(0)/Cr(I) complexes supported by PhBP$^{\mathrm{Ph}}_3$. Unlike the aforementioned μ-biphenyl complexes, in which the arene π-system offers an opportunity for intramolecular electronic communication between the chromium centers, the PhBP$^{\mathrm{Ph}}_3$ borate phenyl substituent π-system is significantly insulated from the phosphines; bimetallics with unambiguous Cr(I) and Cr(0) formal oxidation states were envisioned. The route targeted was one-electron oxidation of precursors with d^6 M(CO)$_3$ units already installed at both PhBP$^{\mathrm{Ph}}_3$ binding sites.

Our synthetic protocol for [Et$_4$N][Cr(CO)$_3${η^6-(PhBP$^{\mathrm{Ph}}_3$)Cr(CO)$_3$}] (**7**), which features Cr(CO)$_3$(C$_{10}$H$_8$) as a Cr(CO)$_3$ transfer agent for metalation of both the PhBP$^{\mathrm{Ph}}_3$ borate phenyl substituent and phosphines,[10b] was employed to prepare crystallographically characterized [Et$_4$N][Cr(CO)$_3${η^6-(((3,5-CH$_3$)C$_6$H$_3$)BP$^{\mathrm{Ph}}_3$)Cr(CO)$_3$}] (**8**). A thermal ellipsoid drawing of the anion of **8** is displayed in the ESI (Fig. S2). Similarly, W(CO)$_3$(CH$_3$CH$_2$CN)$_3$ was used to install d^6 W(CO)$_3$ at the borate phenyl substituent of [Et$_4$N[Cr(CO)$_3$(((3,5-Me)C$_6$H$_3$)BP$^{\mathrm{Ph}}_3$)]^{10a} to afford

$[Et_4N][W(CO)_3\{\eta^6\text{-}(((3,5\text{-}CH_3)C_6H_3)BP^{Ph}{}_3)Cr(CO)_3\}]$ (**9**). Reactions of **7-9** with $[FeCp_2][PF_6]$ in THF resulted in selective oxidation of the κ^3-phosphine $Cr(CO)_3$ units, affording the targeted zwitterionic bimetallics **10-12** as dark red microcrystals (Scheme 2).

The spectroscopic data for **10-12** include the diagnostic features of d^6 $M(CO)_3$ units and η^6-phenyl borate substituent binding, strongly supporting M(0) centers in these Cr(I)/M(0) species. The $\delta(^{13}CO)$ chemical shifts (ppm) of the arene-coordinated $M(CO)_3$ units of **7** (237.2 (s)), **8** (237.1 (s)) and **9** (215.0 (s)) in C_4D_8O are essentially identical to those of their one-electron oxidation products (**10**, 237.0 (s); **11**, 236.8 (s); **12**, 215.0 (s)). While the lower energy infrared ν(CO) absorptions associated with these d^6 $M(CO)_3$ units overlap the broad lower energy absorptions of the d^5 $[Cr(CO)_3]^+$ units of **10**-**12** in THF, the higher energy absorptions (cm^{-1}) of the d^6 $M(CO)_3$ units are well-separated (**10**, 1950; **11**, 1942; **12**, 1943) and extremely similar energetically to those of their d^6/d^6 precursors (**7**, 1948; **8**; 1945; **9**, 1943). Magnetic measurements using the method of Evans furnished magnetic moments of 1.8 μ_B (**10**), 1.7 μ_B (**11**), and 1.7 μ_B (**12**) diagnostic of d^5 Cr(I) centers in these first isolable bimetallics containing Cr(I) and M(0).



Scheme 2

R = H, M = Cr (**7**)
R = Me, M= Cr (**8**)
R = Me, M = W (**9**)

R = H, M = Cr (**10**); 58%
R = Me, M= Cr (**11**); 59%
R = Me, M = W (**12**); 62%

Zwitterions **10** (Fig. 4), **11** (Fig. S3) and **12** (Fig. 5) were characterized by X-ray crystallography. The parameters that define the $Cr(CO)_3P_3$ and η^6-arene-bound $M(CO)_3$ units are also consistent with Cr(**I**) and M(0) formal oxidation state assignments. The average $[Cr(CO)_3P_3]^+$ fragment lengths and angles listed in the Fig. 4 and Fig. 5 captions for **10**, **11** (Cr1–C = 1.888(5), Cr1–P = 2.44(2), C–Cr1–C = 84(9), P–Cr1–P = 86.5(7), C–Cr1–P = 95(5)), and **12** are statistically indistinguishable from those of **4** and **5**. The average Fig. 4 parameters associated with the zerovalent (η^6-arene)$Cr(CO)_3$ units of **10** are statistically identical to those of **7** (Cr2–C(O) = 1.831(8), Cr2–C(arene) = 2.22(2), (O)C–Cr2–C(O) = 89(2)), as are those of **11** (Cr2–C(O) = 1.84(1), Cr2–C(arene) = 2.24(3), (O)C–Cr2–C(O) = 88(1)) and **8** (Cr2–C(O) = 1.83(1), Cr2–C(arene) = 2.24(3), (O)C–Cr2–C(O) = 87(2)). Zerovalent (η^6-arene)$W(CO)_3$ units in **12** are supported by comparison of the Fig. 5 data with the analogous parameters of $[Et_4N][W(CO)_3\{\eta^6$-$(PhBP^{Ph}_3)W(CO)_3\}]$ (W–C(O) = 1.954(3), W–C(arene) = 2.38(2), (O)C–W–C(O) = 86(2)).[10b] The presence of distinct Cr(**I**) and M(0) centers in **10**-**12** seems unambiguous, in contrast to all previously prepared Cr(**I**)/Cr(0) bimetallics.

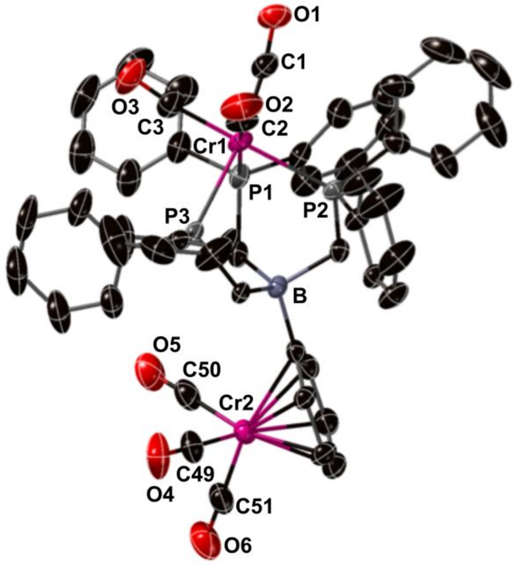


Fig. 4 Thermal ellipsoid (50%) drawing of **10.** Selected average bond lengths (Å) and angles (°) Cr1–C = 1.876(5), Cr1–P = 2.44(1), C–Cr1–C = 86(9), P–Cr1–P = 87(2), C–Cr1–P = 93(6), Cr2–C(O) = 1.82(1), Cr2–C(arene) = 2.23(2), (O)C–Cr2–C(O) = 87.6(3).

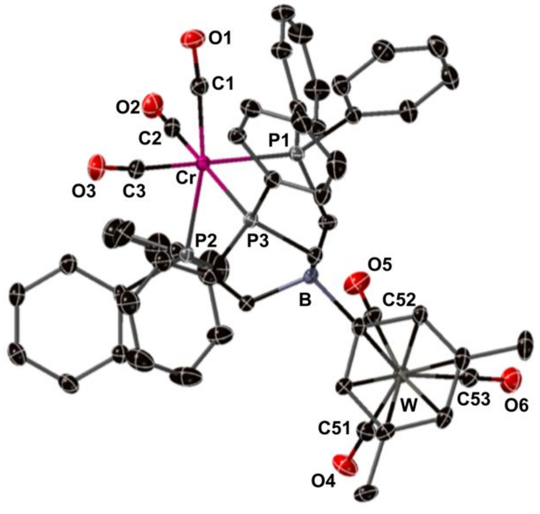


Fig. 5 Thermal ellipsoid (50%) drawing of **12.** Selected average bond lengths (Å) and angles (°) Cr–C = 1.88(1), Cr–P = 2.43(2), C–Cr–C = 88(11), P–Cr–P = 88(3), C–Cr–P = 93(8), W–C(O) = 1.96(1), W–C(arene) = 2.38(2), (O)C–W–C(O) = 86(1).

Closing Remarks

The stabilization affected by the intramolecular charge separation established by tris(diphenylphosphinomethyl)phenylborates permits isolation of remarkably thermally stable chromium(I)tricarbonyltris(phosphine) complexes; **4** and **5** are the first crystallographically characterized seventeen-electron $[Cr(CO)_3P_3]^+$ radicals. The complete characterization of these species supports Rieger's hypothesis of having trapped unstable *fac*-$[Cr(CO)_3\{CH_3C(CH_2PPh_2)_3\}]^+$. The robust d^5 $[Cr(CO)_3]^+$ units of **4**-**6** motivated the preparation of Cr(0)/Cr(I) (**10**, **11**) and W(0)/Cr(I) (**12**) complexes supported by bi-functional $PhBP^{Ph}{}_3$. While **10**-**12** are unremarkable in their employment of classical κ^3-phosphine and η^6-arene metal-binding, all previously studied mixed-valent Cr(0)/Cr(I) complexes exhibit (a) significant thermal instability that has precluded their isolation and (b) greater uncertainty regarding the presence of distinct Cr(I) and Cr(0) centers. This work further illustrates the utility of tris(phosphino)borates for the stabilization of formally cationic metal fragments within charge-neutral zwitterions that are inaccessible or very difficult to characterize as independent cations.

Experimental

Similar procedures were conducted to synthesize **4**-**6** and **10**-**12**. Representative procedures for **4** and **10** are provided below. General procedures, experimental details and spectra (NMR, IR, EPR) are in the ESI.

$Cr(CO)_3(PhBP^{Ph}{}_3)$ (4)

A deep blue suspension of $[FeCp_2][PF_6]$ (0.292 g, 0.882 mmol) in CH_3CN (100 mL) was added dropwise over 1 hr to a yellow solution of **1** (1.200 g, 0.882 mmol) in CH_3CN (50 mL). The reaction mixture became deep red and maroon microcrystals precipitated that were isolated by filtration, washed with CH_3CN (2 * 10 mL) and dried *in vacuo*. THF (30 mL) was added to the solid; the solution was filtered. The filtrate THF was removed *in vacuo* and pentane (30 mL) was added to the residue. The solid was isolated by filtration, washed with pentane (3 * 10 mL) and dried *in vacuo*. Diffusion of pentane into a nearly saturated THF/pentane solution resulted in dark red microcrystals (0.412 g, 57%). Mp. 219-220 °C (dec). Found: C, 70.08; H, 4.91. $C_{48}H_{41}BCrO_3P_3$ requires C, 70.17; H, 5.03. IR (nujol) ν_{max}(CO)/cm^{-1} 2000 (s), 1895 (m, br), 1864 (m, sh); (THF) ν_{max}(CO)/cm^{-1} 2000 (s), 1894 (m, br); (CH_2Cl_2) ν_{max}(CO)/cm^{-1} 2001 (s), 1896 (m, br). ^{11}B NMR (128 MHz, C_4D_8O): δ -10.4 (s). ^{1}H NMR (400 MHz, C_4D_8O): δ 8.02 (s, br), 7.62 (m), 7.49 (s, vb), 7.38 (m), 7.11 (m). ^{13}C{^{1}H} NMR (101 MHz, C_4D_8O): δ 134.0 (s), 132.1 (s), 131.0 (s), 127.3 (s), 126.4 (s), 120.1 (s). μ_{eff} (C_4D_8O, method of Evans, 20 °C): 1.8 μ_B (S = ½).

$Cr(CO)_3(((3,5\text{-}Me)C_6H_3)BP^{Ph}{}_3)$ (5)

Yield = 63%. Mp. 213-214 °C (dec). Found: C, 70.37; H, 5.06. $C_{50}H_{45}BCrO_3P_3$ requires C, 70.68; H, 5.34. IR (nujol) ν_{max}(CO)/cm^{-1} 1998 (s), 1893 (m, br), 1861 (m, sh); (THF) ν_{max}(CO)/cm^{-1} 1999 (s), 1894 (m, br). ^{11}B NMR (128 MHz, C_4D_8O): δ -10.2 (s). ^{1}H NMR (400 MHz, C_4D_8O): δ 7.68 (s, br), 7.62 (m), 7.48 (s, vb), 7.12 (s, br), 6.79 (s), 2.36 (s, CH_3). ^{13}C{^{1}H} NMR (101 MHz, C_4D_8O): δ 135.4 (s), 131.99 (s), 131.93 (s), 130.9 (s), 128.0 (s), 120.1 (s), 22.3 (s). μ_{eff} (C_4D_8O, method of Evans, 20 °C): 1.6 μ_B (S = ½).

$Cr(CO)_3(((3,5\text{-}CF_3)C_6H_3)BP^{Ph}{}_3)$ (6)

Yield = 53%. Mp. 192-193 °C (dec). Found: C, 62.90; H, 4.10. $C_{50}H_{39}BCrF_6O_3P_3$ requires C, 62.72; H, 4.11. IR (nujol) ν_{max}(CO)/cm^{-1} 1999 (s), 1895 (m, br); (THF) ν_{max}(CO)/cm^{-1} 2002 (s), 1895 (m, br); (CH_2Cl_2) ν_{max}(CO)/cm^{-1} 2003 (s), 1896 (m, br). ^{11}B NMR (128 MHz, C_4D_8O): δ -14.4 (s). ^{19}F{^{1}H} NMR (376 MHz, C_4D_8O) δ -62.9. ^{1}H NMR (400 MHz, C_4D_8O): δ 8.43 (s, br), 7.79 (s), 7.66 (m), 7.46 (s, vb), 7.13 (s, br). ^{13}C{^{1}H} NMR (101 MHz, C_4D_8O): δ 133.8 (s), 132.5

(s), 131.1 (s), 130.2 (s), 129.8 (s), 126.0 (q, ${}^1J_{CF}$ = 273 Hz, CF_3), 120.0 (s). μ_{eff} (C_4D_8O, method of Evans, 20 °C): 1.7 μ_B (S = ½).

$[Et_4N][Cr(CO)_3\{\eta^6$-$(((3,5\text{-}CH_3)C_6H_3)BP^{Ph}{}_3)Cr(CO)_3\}]$ (**8**)

THF (45 mL) was added to $[((3,5\text{-Me})C_6H_3)BP^{Ph}{}_3]Tl$ (0.489 g, 0.533 mmol) and $Cr(CO)_3(C_{10}H_8)$ (0.402 g, 1.52 mmol) affording a bright red solution. The solution was stirred at ambient temperature (18 hr); the resulting orange solution was transferred to $[Et_4N]Br$ (0.117 g, 0.556 mmol) and stirred (2 hr). Filtration through alumina separated a grey solid from a red filtrate. The filtrate solvent was removed *in vacuo* revealing an oily orange residue. Addition of Et_2O (60 mL) and trituration afforded a pale yellow solid that was isolated by filtration, washed with Et_2O until the rinses were no longer pale red indicating removal of excess $Cr(CO)_3(C_{10}H_8)$ (4 * 10 mL) and dried *in vacuo*. Diffusion of Et_2O into a THF solution resulted in bright yellow microcrystals (.409 g, 69%). Mp. 320 °C (dec). Found: C, 65.38; H, 5.74; N, 1.31. $C_{61}H_{65}BCr_2NO_6P_3$ requires C, 65.66; H, 5.87; N, 1.26. IR (nujol) ν_{max}(CO)/cm^{-1} 1941 (s), 1893 (s), 1863 (s), 1833 (s), 1789 (s, sh), 1773 (s); THF ν_{max}(CO)/cm^{-1} 1942 (s), 1899 (s), 1855 (s), 1803 (s). ${}^{31}P\{{}^1H\}$ (162 MHz, C_4D_8O): δ 45.1 (s). ${}^{11}B$ NMR (128 MHz, C_4D_8O): δ -14.9 (s). ${}^1H$ NMR (400 MHz, C_4D_8O): δ 7.52 (s, br, 12H, *o*-H, PPh_2), 6.94 (m, 18H, *m*/*p*-H, PPh_2), 5.10 (s, 2H, *o*-H, $(3,5\text{-}CH_3)C_6H_3$), 5.01 (s, 1H, *p*-H, $(3,5\text{-}CH_3)C_6H_3$), 3.24 (m, 8H, Et_4N), 2.08 (s, 6H, CH_3, $(3,5\text{-}CH_3)C_6H_3$), 1.26 (s, br, 12H, Et_4N), 1.11 (s, br, 6H, BCH_2). ${}^{13}C\{{}^1H\}$ NMR (101 MHz, C_4D_8O): δ 237.1 (s, arene-bound $Cr(CO)_3$), 234.6 (m, phosphine-bound $Cr(CO)_3$), 145.7 (m, *i*-C, PPh_2), 133.3 (m, *o*-C, PPh_2), 127.6 (m, *m*-C, PPh_2), 127.4 (s, *p*-C, PPh_2), 111.1 (s, $(3,5\text{-}CH_3)C_6H_3$), 97.8 (s, $(3,5\text{-}CH_3)C_6H_3$), 93.8 (s, $(3,5\text{-}CH_3)C_6H_3$), 53.0 (m, Et_4N), 21.3 (s, CH_3), 18.2 (m, BCH_2), 7.6 (s, Et_4N).

$[Et_4N][W(CO)_3\{\eta^6$-$(((3,5\text{-}CH_3)C_6H_3)BP^{Ph}{}_3)Cr(CO)_3\}]$ (**9**)

THF (60 mL) was added to $W(CO)_3(CH_3CH_2CN)_3$ (0.654 g, 1.51 mmol) and $[Et_4N][Cr(CO)_3(((3,5\text{-}CH_3)C_6H_3)BP^{Ph}{}_3)]$ (0.738 g, 0.755 mmol). The solution was refluxed (90 min). The resulting brown mixture was filtered through alumina affording a yellow filtrate; the solvent was removed *in vacuo* until ~2 mL remained. Addition of Et_2O (40 mL) resulted in precipitation of a yellow solid that was isolated by filtration, washed with Et_2O (2 * 10 mL) and dried *in vacuo*. Diffusion of Et_2O into a THF solution resulted in bright yellow microcrystals (0.345 g, 37%). Mp. 320 °C (dec). Found: C, 58.64; H, 5.17; N, 1.19. $C_{61}H_{65}BCrNO_6P_3W$ requires C, 58.72; H, 5.25; N, 1.12. IR (nujol) ν_{max}(CO)/cm^{-1} 1939 (s), 1894 (s), 1858 (s), 1831 (s), 1789 (s, sh), 1775 (s); THF ν_{max}(CO)/cm^{-1} 1941 (s), 1906 (m), 1900 (m, sh), 1852 (s), 1805 (m). $^{31}P\{^1H\}$ (162 MHz, C_4D_8O): δ 45.5 (s). ^{11}B NMR (128 MHz, C_4D_8O): δ -14.9 (s). ^1H NMR (400 MHz, C_4D_8O): δ 7.51 (s, br, 12H, *o*-H, PPh_2), 6.94 (m, 18H, *m*/*p*-H, PPh_2), 5.29 (s, 3H, $(3,5\text{-}CH_3)C_6H_3$), 3.25 (m, 8H, Et_4N), 2.31 (s, 6H, CH_3, $(3,5\text{-}CH_3)C_6H_3$), 1.27 (m, 12H, Et_4N), 1.08 (s, br, 6H, BCH_2). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ 234.3 (m, phosphine-bound $Cr(CO)_3$), 215.0 (s, ^{13}C-^{183}W satellites: 215.95, 214.06, $^1J_{CW}$ = 191 Hz, arene-bound $W(CO)_3$), 145.4 (m, *i*-C, PPh_2), 133.1 (m, *o*-C, PPh_2), 127.5 (m, *m*-C, PPh_2), 127.3 (s, *p*-C, PPh_2), 111.7 (s, $(3,5\text{-}CH_3)C_6H_3$), 96.3 (s, $(3,5\text{-}CH_3)C_6H_3$), 92.0 (s, $(3,5\text{-}CH_3)C_6H_3$), 52.8 (m, Et_4N), 20.9 (s, CH_3), 18.4 (m, BCH_2), 7.4 (s, Et_4N).

$Cr(CO)_3\{\eta^6\text{-}(PhBP^{Ph}{}_3)Cr(CO)_3\}$ (10)

A deep blue suspension of $[FeCp_2][PF_6]$ (0.229 g, 0.691 mmol) in THF (75 mL) was added dropwise over 45 min to a yellow solution of **7** (0.752 g, 0.691 mmol) in THF (30 mL). The resulting red solution was filtered through Celite; the filtrate solvent was removed *in vacuo* revealing a dark purple solid. CH_3CN (30 mL) was added, and the purple solid was separated from an orange solution via filtration; the solid was washed with CH_3CN (3 * 5 mL) and dried *in* *vacuo*. THF (30 mL) was added to this solid, and the resulting dark red solution was filtered. The filtrate solvent was removed *in vacuo*, and pentane (30 mL) was added to the solid residue. The pale red solid was isolated by filtration, washed with pentane (3 * 5 mL) and dried *in vacuo*. Diffusion of pentane in a nearly saturated THF/pentane solution resulted in dark red microcrystals (0.383 g, 58%). Mp. 206-208 °C (dec). Found: C, 63.91; H, 4.29. $C_{51}H_{41}BCr_2O_6P_3$ requires C, 63.97; H, 4.32. IR (nujol) ν_{max}(CO)/cm^{-1} 1994 (s), 1955 (s), 1944 (s), 1885 (s), 1865 (s), 1850 (s); THF ν_{max}(CO)/cm^{-1} 2001 (m), 1950 (s), 1870 (s). ^{11}B NMR (128 MHz, C_4D_8O): δ -16.0 (s). ^{1}H NMR (400 MHz, C_4D_8O): δ 7.64 (m), 7.50 (s, vb), 7.11 (m), 6.11 (s, br, *o*-H, C_6H_5 bound to zerovalent $Cr(CO)_3$), 5.72 (app. t, J = 6 Hz, *p*-H, C_6H_5 bound to zerovalent $Cr(CO)_3$), 5.54 (s, br, *m*-H, C_6H_5 bound to zerovalent $Cr(CO)_3$). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ 237.0 (s, arene-bound $Cr(CO)_3$), 132.3 (s), 131.2 (s), 120.1 (s), 103.3 (s), 96.7 (s), 93.4 (s). μ_{eff} (C_4D_8O, method of Evans, 20 °C): 1.8 μ_B (S = ½).

$Cr(CO)_3\{\eta^6$-$(((3,5\text{-}CH_3)C_6H_3)BP^{Ph}{}_3)Cr(CO)_3\}$ (**11**)

Yield = 59%. Mp. 263-265 °C (dec). Found: C, 64.92; H, 4.78. $C_{53}H_{45}BCr_2O_6P_3$ requires C, 64.58; H, 4.60. IR (nujol) ν_{max}(CO)/cm^{-1} 2005 (s), 1944 (s), 1877 (s), 1844 (s); THF ν_{max}(CO)/cm^{-1} 2001 (m), 1945 (s), 1863 (s). ^{11}B NMR (128 MHz, C_4D_8O): δ -16.1 (s). ^{1}H NMR (400 MHz, C_4D_8O): δ 7.64 (s, br), 7.48 (s, vb), 7.10 (s, br), 5.67 (s, br, *o*-H, $(3,5\text{-}CH_3)C_6H_3$), 5.42 (s, *p*-H, $(3,5\text{-}CH_3)C_6H_3$), 2.27 (s, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ 236.8 (s, arene-bound $Cr(CO)_3$), 132.2 (s), 130.9 (s), 120.0 (s), 111.1 (s), 99.5 (s), 95.6 (s), 21.3 (s). μ_{eff} (C_4D_8O, method of Evans, 20 °C): 1.7 μ_B (S = ½).

$W(CO)_3\{\eta^6$-$(((3,5\text{-}CH_3)C_6H_3)BP^{Ph}{}_3)Cr(CO)_3\}$ (**12**)

Yield = 62%. Mp. 240-241 °C (dec). Found: C, 57.53; H, 4.29. $C_{53}H_{45}BCrO_6P_3W$ requires C, 56.96; H, 4.06. IR (nujol) ν_{max}(CO)/cm^{-1} 2006 (s), 1944 (s), 1878 (s), 1841 (s); THF ν_{max}(CO)/cm^{-1} 2001 (m), 1943 (s), 1859 (s). ^{11}B NMR (128 MHz, C_4D_8O): δ -16.6 (s). ^{1}H NMR (400 MHz, C_4D_8O): δ 7.64 (s, br), 7.48 (s, vb), 7.10 (s, br), 5.82 (s, br, *o*-H, (3,5-CH_3)C_6H_3), 5.71 (s, *p*-H, (3,5-CH_3)C_6H_3), 2.50 (s, CH_3). ^{13}C{^{1}H} NMR (101 MHz, C_4D_8O): δ 215.0 (s, ^{13}C-^{183}W satellites: 215.92, 214.05, $^1J_{CW}$ = 189 Hz, arene-bound W(CO)$_3$), 132.2 (s), 130.9 (s), 120.0 (s), 111.7 (s), 98.1 (s), 93.6 (s), 21.1 (s). μ_{eff} (C_4D_8O, method of Evans, 20 °C): 1.7 μ_B (S = ½).

X-ray Crystallography

X-ray quality crystals were obtained by diffusion of liquid pentane into THF solutions (**2**, **4**, **5**, **10**-**12**) and liquid Et_2O into a THF solution (**8**). 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 a Bruker-AXS Venture Photon-II diffractometer with 0.71073 Å Mo-Kα radiation for data collection at 100(2) K. All structures were solved by direct methods using SHELXT-2014/5 and refined using SHELXT-2014/6[21a] or SHELXT-2018/3.[21b,22] 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 **2**, **8** and **11** and further details of crystallographic data collection, solution, and refinement can be found in the ESI. Crystallographic CIF files for these structures: CCDC 1824320, 1951033-1951038.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgments

The National Science Foundation (CHE-1464515) and the Henry Dreyfus Teacher-Scholar Awards Program supported this research. The Bruker-AXS D8 Venture Photon-II diffractometer was purchased from an NSF-MRI grant (#1229400) and the University of Minnesota. The authors are grateful to Dr. Mark Nilges and Michael Drummond (University of Illinois) for their EPR contributions, and Prof. Graham Sazama (Lawrence University) for a helpful discussion. P.J.F. dedicates this manuscript to Prof. Rebecca C. Hoye on her retirement from Macalester College, and in gratitude for her sharing of insight and experience of organic laboratory techniques.

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11. [PPN][Cr(CO)$_3$(((3,5-Me)C$_6$H$_3$)BP$^{Ph}{}_3$)] (**2**) was characterized by X-ray crystallography. A thermal ellipsoid drawing of **2** is displayed in the ESI (Fig. S1)

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15. These c_{CO} and c_{PR3} ($M^{2.6+}(CO)_3(PR_3)_3$) values were calculated using the average infrared ν(CO) stretching frequencies of the two absorptions of [Et$_4$N][Cr(CO)$_3$(PhBP$^{Ph}{}_3$)] in CH$_3$CN (ave: 1847 cm^{-1}) and **4** in THF (ave: 1947 cm^{-1}).

16. The *g*-values of all of these [Cr(CO)$_3$P$_3$]$^+$ species were derived with the assumption of threefold rotational symmetry of the phosphorus atoms.

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Table of Contents Textual Abstract

Tris(diphenylphosphinomethyl)phenylborates permit isolation of remarkably thermally stable chromium(I)tricarbonyltris(phosphine) complexes, the first crystallographically characterized $[Cr(CO)_3P_3]^+$ radicals.

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