[(2-(Diphenylphosphino)ethyl)cyclopentadienyl]tricarbonylmetalates: Supporting Ligands for Reactions at Group VI Metal−Copper Bonds

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Salts of [(2-(diphenylphosphino)ethyl)cyclopentadienyl]tricarbonylmetalates react with CuCl to afford useful intermediates that permit installation of phosphines at copper(I), in a rare instance of nucleophilic attack at heterobimetallic M−Cu bonds without concomitant heterolytic cleavage.

Introduction

Heterobimetallic complexes containing transition-metal−copper(I) bonds are of fundamental organometallic and bioinorganic interest. The promise of novel reactivity afforded by synergistic and cooperative properties of early/late transition-metal bonds has motivated these studies for catalyst development.[1] The importance of bimetallic active sites containing copper in metalloenzymes has stimulated the synthesis of heterobimetallic model complexes.[2] The application of bridging ligands is a common strategy to stabilize transition-metal−copper(I) bonds, and these bonds are often imposed by molecular architecture that places the copper(I) center in close proximity to the transition metal. Dative metal−copper(I) bonds have been stabilized by bridging bidentate phosphines,[3] 2-(*N*-diphenylphosphinomethyl-*N*-cyclohexyl)aminopyridine,[4] 2-(diphenylphosphino)pyridine,[5] and (2-oxazoline-2-ylmethyl)diphenylphosphine[6] and thiolates.[7] Cotton showed that pendant imino groups of the deprotonated 2,6-(diphenylimino)piperidine ligand (DPhIP) create a pocket for copper(I) ion capture with concomitant coordination to quadruply bonded dichromium and dimolybdenum units.[8] Thiometalates of molybdenum and tungsten, $[M'O_{4-n}S_n]^{2-}$ (M′ = Mo, W; n = 1–4), have been used extensively for the construction of Mo−Cu and W−Cu units due to the high affinity of copper(I) for sulfur, by stepwise incorporation of neutral and cationic copper(I) fragments into the edges of these tetrahedral anions.[2a,9]

Two general synthetic strategies have been employed to establish copper ligand environments in these heterobimetallics. Either a labile source of Cu(I) (e.g., $[Cu(NCCH_3)_4]^+$) introduces the ion to a pre-established tethered coordination environment in close proximity to a metal or a donor-stabilized copper(I) halide derivative (e.g., $[Cu(PPh_3)Cl]_4$) is used where the donor ligand remains bound to copper(I) in the resulting heterobimetallic. Few examples of ligand substitution at copper that leave transition-metal−copper bonds intact have been reported in heterobimetallics. Salts of $[Cu(M'(CO)_3(\eta^5\text{-}Cp))_2]^-$ (M′ = Mo, W) react with PPh_3, $[CN]^-$, and 1,10-phenanthroline, resulting in $[M'(CO)_3(\eta^5\text{-}Cp)]^-$ via heterolytic M′−Cu cleavage.[10] The lability of Cu(I)−Ge(II) bonds in $L^{Me2}CuGe[(NMes)_2(CH)_2]$ and $L^{Me2}CuGe[N(SiMe_3)_2]_2$ (L^{Me2} = the β-diketiminate derived from 2-(2,6-dimethylphenyl)amino-4-(2,6-dimethylphenyl)imino-2-pentene) toward PPh_3-promoted heterolytic cleavage was exploited by Tolman to afford free germylenes and Cu(I)−PPh_3 adducts.[11] Substitution at a thiometalate-enforced Mo−Cu bond was recently reported; $[O_2MoS_2CuCN]^{2-}$ reacts with KSAr (Ar = Ph, *o*-Tol, *p*-Tol) to afford $[O_2MoS_2CuSAr]^{2-}$.[2a] The Cu(I) center of the thiolato-bridged $[Cp_2Ti(\mu\text{-}SMe)_2Cu(CH_3CN)_2]PF_6$ reacts with phosphines (L = PMe_3, PCy_3) to afford $[Cp_2Ti(\mu\text{-}SMe)_2CuL]PF_6$, but the suggested dative Cu→Ti interaction is also strictly enforced by the thiolate ligands.[7a]

The discovery of a ligand platform that could accommodate general substitution at M−Cu bonds of heterobimetallics would permit facile variation of the steric and electronic environment at the Cu(I) center, a necessary requirement to rationally

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modulate complex reactivity. Since the most promising heterobimetallic catalyst candidates containing copper(I) feature early transition metals, the optimum heterodifunctional ligand for stabilizing M−Cu bonds should combine substituents that form robust bonds to metals of contrasting hardness. The (2-(diphenylphosphino)ethyl)cyclopentadienyl (Cp^{PPh}) ligand[12] seemed ideally suited to this task; η^5-Cp forms strong bonds to early transition metals in a variety of oxidation states, and phosphines form robust interactions with soft Cu(I) ions. As a proof of concept for the general viability of this ligand application, we chose to investigate reactions of CuCl with salts of $[M(CO)_3(\eta^5\text{-}Cp^{PPh})]^-$ (M = Cr, Mo, W). Heterobimetallics with dative d^6-d^{10} M−Cu bonds supported by only weak semibridging carbonyl interactions have been synthesized with $[M(CO)_3(\eta^5\text{-}Cp)]^-$.[13] Due to the relatively robust nature of the M−Cu bonds in these complexes, we hypothesized that application of $[M(CO)_3(\eta^5\text{-}Cp^{PPh})]^-$ offered an excellent inaugural system to explore the possibility of reactions at related dative M−Cu bonds supported by the Cp^{PPh} ligand.

Results and Discussion

Synthesis and Characterization of $[K(18C6)][M(CO)_3(\eta^5\text{-}Cp^{PPh})]$. Bullock recently reported that $LiCp^{PPh}$ and $Mo(CO)_3$(diglyme) react to give $Li[Mo(CO)_3(\eta^5\text{-}Cp^{PPh})]$, which was protonated to afford $MoH(CO)_2(\eta^5{:}\eta^1\text{-}Cp^{PPh})$.[14] This hydride was employed for catalytic hydrogenation of ketones. The importance of $[Mo(CO)_3(\eta^5\text{-}Cp^{PPh})]^-$ as a catalyst precursor prompted us to isolate and crystallographically characterize $[K(18C6)][M(CO)_3(\eta^5\text{-}Cp^{PPh})]$ (M = Cr (**1**), Mo (**2**), W(**3**)).[15] Reactions of $M(CO)_3(RCN)_3$ (M = Cr, R = Me; M = Mo, W, R = Et) and KCp^{PPh}, followed by 18C6 complexation, provided the analytically pure salts **1**–**3**. The three-legged piano-stool structures of **1**–**3** are displayed in Figure 1 and Figures S1 and S2 (Supporting Information), respectively. The η^5-Cp^{PPh} ring is oriented such that C(4) nearly eclipses the carbonyl defined by C(1),[16] and the pendant phosphines engage in no significant interaction with the [K(18C6)] cations. Important average lengths and angles that define the geometries of the C_{3v} $M(CO)_3$ fragments of **1**–**3** (M−C(O), C−O, (O)C−M−C(O), O−C−M; averages given in the captions of Figure 1 and Figures S1 and S2) are statistically indistinguishable from those of $[PPN][M(CO)_3(\eta^5\text{-}Cp^N)]$,[17] respectively. The average M−C(dienyl) lengths of **1**−**3** (given in the figure captions) are also statistically identical with the corresponding values of $[PPN][M(CO)_3(\eta^5\text{-}Cp^N)]$, respectively. The potassium of the [K(18C6)] cation engages in an ion-pairing interaction via the carbonyl ligand defined by C(1) of **1**–**3** in the solid state. The K−O(1) distances in **1**–**3** (**1**, 2.910(3) Å; **2**, 2.958(3) Å; **3**, 2.944(6) Å) are statistically insignificant from, although slightly longer than, the average K−O lengths within the [K(18C6)] cations (**1**, 2.84(4) Å; **2** and **3**, 2.85(4) Å). The essentially linear O(1)−C(1)−M angles in **1**–**3** underscore the nearly imperceptible impact of this interaction on these anions. This interaction is insignificant in THF and CH_3CN on the basis of the ν(CO) IR absorptions of **1**–**3**, which indicate unperturbed C_{3v} $M(CO)_3$ units in solution.

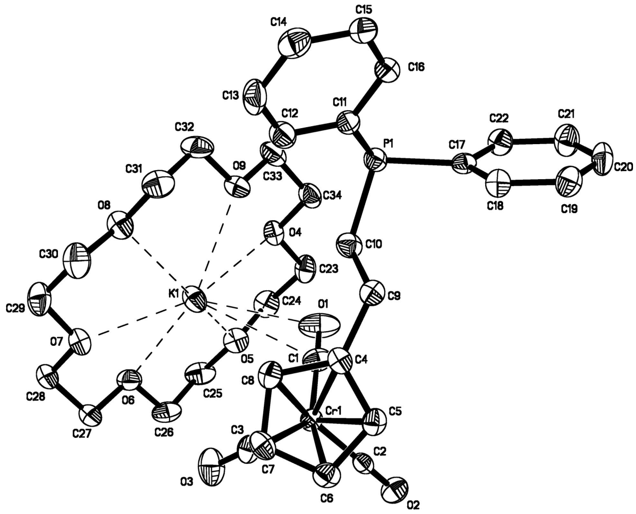

Figure 1. Molecular structure of **1** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cr−C(1) = 1.793(3), Cr−C(2) = 1.801(3), Cr−C(3) = 1.805(3), Cr−C(O) (av) = 1.80(1), Cr−C(4) = 2.257(3), Cr−C(5) = 2.224(3), Cr−C(6) = 2.210(3), Cr−C(7) = 2.209(3), Cr−C(8) = 2.235(3), Cr−C(dienyl) (av) = 2.23(2), C(1)−C(O) = 1.184(4), C(2)−O(2) = 1.177(4), C(3)−O(3) = 1.176(4), C−O (av) = 1.179(4); C(1)−Cr(1)−C(2) = 86.46(14), C(1)−Cr(1)−Cr(3) = 85.80(15), C(2)−Cr(1)−C(3) = 87.65(14), (O)C−Cr−C(O) (av) = 87(1), O(1)−C(1)−Cr = 175.3(3), O(2)−C(2)−Cr = 178.2(3), O(3)−C(3)−Cr = 176.8(3), O−C−Cr (av) = 177(1).

Reactions at Group VI Metal−Copper(I) Bonds. While $[M(CO)_3(\eta^5\text{-}Cp)]^-$ instantaneously reduces CuCl to metallic copper in THF, $Na[M(CO)_3(\eta^5\text{-}Cp^{PPh})]$ reacts with CuCl in this solvent, resulting in salt elimination and metal–carbonyl products. Although these isolable bright yellow solids have proved difficult to characterize, M−Cu bonding is strongly suggested on the basis of their ν(CO) IR absorptions,[18a] which are nearly indistinguishable from those of $M\{CuPPh_3\}(CO)_3(\mu\text{-}\eta^5{:}\eta^1\text{-}Cp^{PPh})$ (vide infra). The $^{31}P\{^1H\}$ NMR spectra of these $[M(CO)_3(\eta^5\text{-}Cp^{PPh}]^-$/CuCl reaction products exhibit two coupled doublets,[18b] suggesting two η^5-Cp^{PPh} phosphines coordinated to each Cu(I) center, possibly resulting in an oligomeric structure.[18c] Single crystals of these apparently amorphous substances[18d] could not be obtained, and ^1H NMR spectra suggest fluxional behavior in solution that has been not been unambiguously characterized. Heterobimetallic oligomers and polymers containing Cu(I) have been proposed;[7d,10] the propensity of Cu(I) to form aggregates through bridging interactions has long been known.[19] The series of related tetranuclear cyclic complexes $[\{(CO)_3M(\mu,\eta^5\text{-}C_5H_4PPh_2)\}_2M'M'']$ (M = Cr, Mo, W, M′ = M″ = Ag; M = Cr, Mo, M′ = M″ = Au; M = Mo, M′ = Ag, M″ = Au) have been thoroughly characterized.[20]

These intermediates readily react with phosphines to afford analytically pure heterobimetallic monomers (Scheme 1); nucleophilic attack occurs at Cu(I) without concomitant M−Cu cleavage. While this method is seemingly general for tertiary

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[12] Synthesis of KCp^{PPh}: Graham, T. W.; Llamazares, A.; McDonald, R.; Cowie, M. *Organometallics* **1999**, *18*, 3490.

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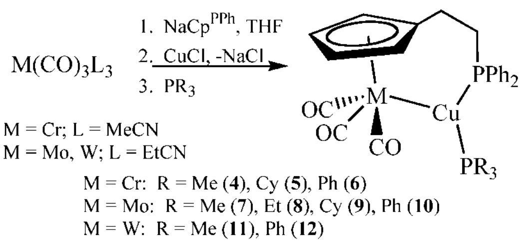
[15] 18C6 = 1,4,7,10,13,16-hexaoxacyclooctadecane.

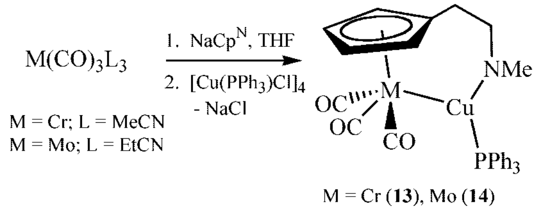
[16] Drawings illustrating the near eclipse of C(4) and C(1) in **1**–**3**, as well as angles between planes that quantify the orientation of the Cp rings relative to the $M(CO)_3$ fragments, are provided in the Supporting Information.

[17] Fischer, P. J.; Krohn, K. M.; Mwenda, E. T.; Young, V. G., Jr. *Organometallics* **2005**, *24*, 1776. Cp^N = (2-(dimethylamino)ethyl)cyclopentadienyl. $[PPN]^+ = [N(PPh_3)_2]^+$.

Scheme 1



Scheme 2



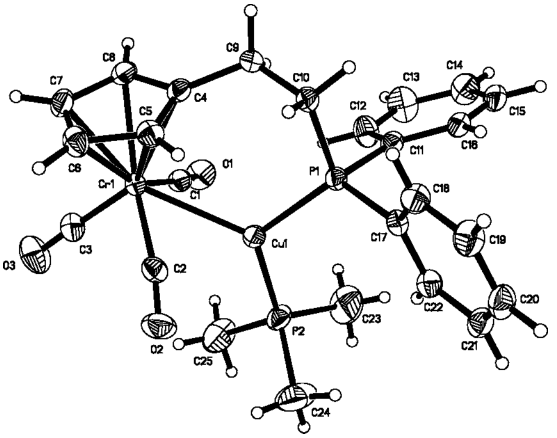


Figure 2. Molecular structure of **4** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Cr−Cu = 2.5943(4), Cr−C(1) = 1.8384(18), Cr−C(2) = 1.8285(19), Cr−C(3) = 1.8218(19), Cr−C(O) (av) = 1.830(8), Cr−C(4) = 2.2353(17), Cr−C(5) = 2.2166(18), Cr−C(6) = 2.2012(18), Cr−C(7) = 2.2012(18), Cr−C(8) = 2.2090(18), Cr−C(dienyl) (av) = 2.21(1), O(1)−C(1) = 1.171(2), O(2)−C(2) = 1.171(2), O(3)−C(3) = 1.161(2), C−O (av) = 1.168(6), Cu−C(1) = 2.3156(17), Cu−C(2) = 2.2585(18), Cu−P(1) = 2.2427(5), Cu−P(2) = 2.2533(5); O(1)−C(1)−Cr = 172.67(16), O(2)−C(2)−Cr = 171.38(17), O(3)−C(3)−Cr = 178.45(19), C(3)−Cr−C(1) = 85.19(8), C(3)−Cr−C(2) = 84.12(8), C(1)−Cr−C(2) = 104.65(8), C(3)−Cr−Cu = 114.48(6), C(1)−Cr−Cu = 60.15(5), C(2)−Cr−Cu = 58.39(6), P(1)−Cu−P(2) = 121.07(2), P(1)−Cu−Cr = 112.057(16), P(2)−Cu−Cr = 126.657(17).

phosphines, attempts to introduce other nucleophiles have been unsuccessful. Excess pyridine (10 equiv) and $AsPh_3$ (5 equiv) (L) were required to obtain analogous M−Cu derivatives in solution on the basis of IR spectroscopy, but attempts to isolate these apparent M{CuL}$(CO)_3(\mu\text{-}\eta^5{:}\eta^1\text{-}Cp^{PPh})$ complexes, with ether extraction of excess L, resulted in quantitative formation of species spectroscopically identical with those present before pyridine and $AsPh_3$ addition, respectively. The bridging η^5-Cp^{PPh} ligand is apparently unable to support M−Cu bonds of cuprates; instantaneous heterolytic M−Cu bond cleavage occurs upon addition of *n*-butyllithium, $[Bu_4N][CN]$, and [PPN]Cl, affording $[M(CO)_3(\eta^5\text{-}Cp^{PPh})]^-$. Heterolytic cleavage promoted by [PPN]Cl underscores the importance of salt elimination to kinetically stabilize M−Cu bonds. However, these intermediates are inert toward triflates and tosylates. Although M{Cu(tmeda)}$(CO)_3(\eta^5\text{-}Cp)$ is known,[13b] analogous reactions of $[M(CO)_3(\eta^5\text{-}Cp^N)]^-$ and CuCl were not useful to obtain pure Cu(I) derivatives with a bridging η^5-Cp^N ligand. However, M′{$CuPPh_3$}$(CO)_3(\mu\text{-}\eta^5{:}\eta^1\text{-}Cp^N)$ (M = Cr (**13**), Mo (**14**)) were obtained via $[M(CO)_3(\eta^5\text{-}Cp^N)]^-$ and $[Cu(PPh_3)Cl]_4$ (Scheme 2).[21] Complexes **13** and **14** are kinetic products whose solutions deposit metallic copper. The kinetic stability of these complexes decreases down the triad with increasing $[M(CO)_3(\eta^5\text{-}Cp^N)]^-$ reducing ability; the analogous W−Cu derivative could not be isolated without significant precipitation of copper metal. Solutions of **4**–**12** are stable indefinitely toward this decomposition pathway.

Characterization of Supported M−Cu Complexes. The four-legged piano-stool structures of **4**, **6**, **7**, **9**–**11**, and **14** containing substituted η^5-Cp ligands and trigonal-planar Cu(I), are displayed in Figure 2 and Figures S3–S8 (Supporting Information), respectively. Complexes **4** and **6** are the first structurally characterized heterobimetallics with only one Cr−Cu bond (Cr−Cu: **4**, 2.5943(4) Å; **6**, 2.6092(5) Å).[22] These distances are only slightly shorter than the separation between Cu(I) and the chromium of the quadruply bonded dichromium unit in $[Cr_2Cu_2(DPhIP)_4](CuCl_2)_2$ (2.628(2) Å).[8] The M′−Cu bonds (M′ = Mo, W) of **7**, **9**–**11**, and **14** range from 2.6423(7) to 2.7428(5) Å, similar to the corresponding lengths in the isomers of W{$Cu(PPh_3)_2$}$(CO)_3(\eta^5\text{-}Cp)$ (2.721(1), 2.771(1) Å),[13a] Mo{Cu(tmeda)}$(CO)_3(\eta^5\text{-}Cp)$ (2.592(1) Å)[13b] and slightly *longer* than the Cu−Mo separation (2.6149(4) Å) in $[Mo_2Cu_2(DPhIP)_4](CuCl_2)_2$.[8] The P(2)−Cu−M and P(1)−Cu−M angles are statistically more flexible relative to P(1)−Cu−P(2) to accommodate phosphines of varying steric bulk in **4**, **6**, **7**, and **9**–**11**. The P(2)−Cu−M angles in these complexes range from 125.04(3)° (**11**) to 135.13(3)° (**9**) (average 129(4)°), while the P(1)−Cu−M angles range from 103.19(3)° (**9**) to 112.057(16) (**4**) (average 109(3)°). The average P(1)−Cu−P(2) angle in these η^5-Cp^{PPh} complexes is 121(2)°. These complexes permit the extent of semibridging carbonyl−copper interactions to be examined with analogues featuring modulated electronic environments at Cu(I). The closest such separations (Cu−C(2)) in **7** (2.310(2) Å), **9** (2.338(3) Å), and **10** (2.277(3) Å) only vary by ~0.06 Å, despite the varying σ-donor abilities of PMe_3, PCy_3, and PPh_3, respectively. The corresponding O(2)−C(2)−Mo angles (**7**, 172.4(2)°; **9**, 171.7(3)°; **10**, 172.7(2)°) exhibit only very small deviations from linearity. These observations are consistent with molecular orbital calculations by Hall which indicated that back-donation from Cu(I) to semibridging car-

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[18] (a) IR ν(CO) spectral data for $[M(CO)_3(\eta^5\text{-}Cp^{PPh})]^-$/CuCl reaction products in THF: M = Cr, 1910 (s), 1813 (s), 1779 (s) cm^{-1}; M = Mo, 1917 (s), 1816 (s), 1786 (s) cm^{-1}; M = W, 1912 (s), 1810 (s), 1779 cm^{-1}. These complexes exhibit nearly indistinguishable IR ν(CO) spectra in CH_3CN. Ambient-temperature THF and CH_3CN solutions of these complexes are stable indefinitely under a purified Ar atmosphere. (b) For example: $^{31}P\ \{^1H\}$ NMR (121 MHz) spectral data for the $[Mo(CO)_3(\eta^5\text{-}Cp^{PPh})]^-$/CuCl reaction product in C_4D_8O: δ −3.5 (d, $^2J_{PP}$ = 130 Hz), −13.8 (d, $^2J_{PP}$ = 130 Hz). (c) A postulated structure of these products is provided in the Supporting Information. (d) These bright yellow solids invariably exhibited a glassy appearance; microcrystalline samples could not be obtained.

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[21] Complexes **6**, **10**, and **12** can be synthesized via analogous reactions of $[M(CO)_3(\eta^5\text{-}Cp^{PPh})]^-$ and $[Cu(PPh_3)Cl]_4$.

[22] Clusters with more than one Cr−Cu bond have been structurally characterized. For example, see: Klüfers, P.; Wilhelm, U. *J. Organomet. Chem.* **1991**, *421*, 39.

bonyls of the Mo(CO)$_3$(η^5-Cp) fragment was very small.[23] This electronic insulation between Cu(I) and the Mo(CO)$_3$(η^5-Cp) fragment is further supported on the basis of ν(CO) IR spectral data, as the lowest energy ν(CO) absorptions of **7**, **9**, and **10** only vary by 5 cm^{-1}.

Concluding Remarks. The discovery of new ligand platforms that support transition-metal−copper bonds has provided opportunities for new synthetic and catalytic investigations. The η^5-Cp^{PPh} ligand simultaneously offers binding sites appropriate for essentially all transition metals (Cp) and soft Cu(I) ions (tethered 2-(diphenylphosphino)ethyl group). This ligand sufficiently stabilizes group VI metal−copper bonds to permit rare nucleophilic attack at Cu(I) in heterobimetallics without concomitant heterolytic M−Cu bond cleavage. Since ligand substitution is a key step in most stoichiometric and catalytic organometallic reactions, application of η^5-Cp^{PPh} may offer reaction pathways previously inaccessible with M−Cu heterobimetallics. Further studies of transition-metal complexes containing Cp^{PPh}, Cp^{N}, and related ligands are underway in this laboratory.

Experimental Section

Similar procedures were conducted to synthesize **1**–**3**, **4**–**12**, and **13** and **14**, respectively. Representative procedures for **1**, **4**, and **13** are provided below. General procedures, complete experimental details for **1**, **2**, and **5**–**14**, and all ^{13}C NMR spectral data for **1**–**14** are given in the Supporting Information.

[K(18C6)][Cr(CO)$_3$(η^5-Cp^{PPh})] (1). THF (125 mL) was added to Cr(CO)$_3$(CH$_3$CN)$_3$ (0.500 g, 1.93 mmol) and KCp^{PPh} (0.732 g, 2.31 mmol). The yellow solution was refluxed for 1.5 h. The solution was filtered at −10 °C through Celite. The yellow filtrate was stirred with 18C6 (0.561 g, 2.12 mmol) for 2 h at ambient temperature prior to filtration through Celite. The THF was removed in vacuo until ~5 mL remained. Addition of Et$_2$O (70 mL) precipitated a pale yellow solid that was washed with Et$_2$O (4 × 30 mL) and dried in vacuo. Recrystallization (THF/Et$_2$O) provided pale yellow, air-sensitive microcrystals (1.04 g, 75%). Anal. Calcd for C$_{34}$H$_{42}$CrKO$_9$P: C, 56.97; H, 5.91. Found: C, 57.15; H, 5.96. Mp: 136–137 °C dec. IR (THF): ν(CO) 1890 (s), 1778 (s) cm^{-1}. IR (Nujol): ν(CO) 1879 (s), 1772 (s, sh), 1759 (s) cm^{-1}. ^{1}H NMR (CD$_3$CN, 300 MHz): δ 7.51–7.33 (m, 10H, Ph), 4.39 (app t, J = 2.1 Hz, 2H, Cp), 4.29 (app t, J = 2.1 Hz, 2H, Cp), 3.57 (s, 24 H, 18C6), 2.35–2.20 (m, 4H, CH_2CH_2). ^{13}C{^{1}H} NMR (CD$_3$CN, 75 MHz): δ 246.9 (s, CO). ^{31}P{^{1}H} NMR (CD$_3$CN, 121 MHz): δ −15.06 (s, PPh$_2$).

[K(18C6)][Mo(CO)$_3$(η^5-Cp^{PPh})] (2). Yield: 64%. Anal. Calcd for C$_{34}$H$_{42}$KMoO$_9$P: C, 53.68; H, 5.57. Found: C, 53.92; H, 5.75. Mp: 149–152 °C dec. IR (THF): ν(CO) 1894 (s), 1781 (s) cm^{-1}. IR (Nujol): ν(CO) 1886 (s), 1763 (s) cm^{-1}. ^{1}H NMR (CD$_3$CN, 300 MHz): δ 7.48–7.33 (m, 10H, Ph), 5.04 (app t, J = 2.4 Hz, 2H, Cp), 4.92 (app t, J = 2.4 Hz, 2H, Cp), 3.56 (s, 24 H, 18C6), 2.32–2.28 (m, 4H, CH_2CH_2). ^{13}C{^{1}H} NMR (CD$_3$CN, 75 MHz): δ 236.6 (s, CO). ^{31}P{^{1}H} NMR (CD$_3$CN, 121 MHz): δ −15.06 (s, PPh$_2$).

[K(18C6)][W(CO)$_3$(η^5-Cp^{PPh})] (3). Yield: 67%. Anal. Calcd for C$_{34}$H$_{42}$KO$_9$PW: C, 48.12; H, 4.99. Found: C, 48.33; H, 5.29. Mp: 156–158 °C dec. IR (THF): ν(CO) 1888 (s), 1777 (s) cm^{-1}. IR (Nujol): ν(CO) 1880 (s), 1766 (s, sh) 1759 (s) cm^{-1}. ^{1}H NMR (CD$_3$CN, 300 MHz): δ 7.50–7.33 (m, 10H, Ph), 5.07 (app t, J = 2.1 Hz, 2H, Cp), 4.96 (app t, J = 2.1 Hz, 2H, Cp), 3.57 (s, 24 H, 18C6), 2.43–2.26 (m, 4H, CH_2CH_2). ^{13}C{^{1}H} NMR (CD$_3$CN, 75 MHz): δ 227.4 (s, CO, ^{183}W−^{13}C satellites 228.76, 226.13, $^1J_{WC}$ = 198 Hz). ^{31}P{^{1}H} NMR (CD$_3$CN, 121 MHz): δ −15.11 (s, PPh$_2$).

Cr{CuPMe$_3$}(CO)$_3$(μ-η^5:η^1-Cp^{PPh}) (4). THF (50 mL) was added to Cr(CO)$_3$(CH$_3$CN)$_3$ (0.345 g, 1.33 mmol) and NaCp^{PPh} (0.400 g, 1.33 mmol); the yellow solution was refluxed for 1 h. This solution was added to solid CuCl (0.132 g, 1.33 mmol); the [Cr(CO)$_3$(η^5-Cp^{PPh})]$^-$ was consumed within 30 min. A 1.0 M solution of PMe$_3$ in THF (1.4 mL, containing 0.11 g, 1.4 mmol of PMe$_3$) was added; the resulting yellow solution was stirred for 30 min prior to filtration through alumina. The filtrate was concentrated in vacuo until ~2 mL remained. Addition of pentane (50 mL) resulted in the precipitation of a bright yellow solid that was isolated by filtration, washed with pentane (4 × 10 mL), and dried in vacuo. Recrystallization from THF/pentane provided bright yellow, moderately air sensitive microcrystals (0.400 g, 61%). Anal. Calcd for C$_{25}$H$_{27}$O$_3$P$_2$CrCu: C, 54.30; H, 4.92. Found: C, 54.29; H, 5.19. Mp: 176–179 °C dec. IR (THF): ν(CO) 1905 (s), 1808 (s), 1771 (s) cm^{-1}. IR (Nujol): ν(CO) 1902 (s), 1797 (s), 1759 (s), 1709 (s, sh) cm^{-1}. ^{1}H NMR (C$_4$D$_8$O, 300 MHz) δ 7.66–7.41 (m, 10H, Ph), 4.59 (app t, J = 2.1 Hz, 2H, Cp), 4.48 (app t, J = 2.1 Hz, 2H, Cp), 2.58–2.44 (m, 4H, CH_2CH_2), 1.20 (d, $^2J_{PH}$ = 6.0 Hz, 9H, CH_3). ^{13}C{^{1}H} NMR (C$_4$D$_8$O, 75 MHz): δ 242.6 (s, CO). ^{31}P{^{1}H} NMR (C$_4$D$_8$O, 121 MHz): δ −11.4 (s, br, PPh$_2$), −38.4 (s, br, PMe$_3$).

Cr{CuPCy$_3$}(CO)$_3$(μ-η^5:η^1-Cp^{PPh}) (5). Yield: 51%. Anal. Calcd for C$_{40}$H$_{51}$O$_3$P$_2$CrCu: C, 63.44; H, 6.79. Found: C, 63.60; H, 6.68. Mp: 171–172 °C dec. IR (THF): ν(CO) 1904 (s), 1806 (s), 1769 (s) cm^{-1}. IR (Nujol): ν(CO) 1905 (s), 1793 (s), 1754 (s), 1730 (m, sh) cm^{-1}. ^{1}H NMR (C$_4$D$_8$O, 300 MHz): δ 7.64–7.42 (m, 10H, Ph), 4.55 (app t, J = 2.1 Hz, 2H, Cp), 4.45 (app t, J = 2.1 Hz, 2H, Cp), 2.46−2.29 (m, 4H, CH_2CH_2P), 1.79–1.08 (m, 33H, PCy$_3$). ^{13}C{^{1}H} NMR (C$_4$D$_8$O, 75 MHz): δ 243.8 (app t, $^3J_{PC}$ = 2.9 Hz, CO). ^{31}P{^{1}H} NMR (C$_4$D$_8$O, 121 MHz): δ 17.3 (d, $^2J_{PP}$ = 113 Hz, PPh$_2$), −14.3 (d, $^2J_{PP}$ = 113 Hz, PCy$_3$).

Cr{CuPPh$_3$}(CO)$_3$(μ-η^5:η^1-Cp^{PPh}) (6). Yield: 55%. Anal. Calcd for C$_{40}$H$_{33}$O$_3$P$_2$CrCu: C, 65.00; H, 4.50. Found: C, 65.46; H, 4.91. Mp: 183–184 °C dec. IR (THF): ν(CO) 1905 (s), 1811 (s), 1775 (s) cm^{-1}. IR (Nujol): ν(CO) 1890 (s), 1797 (m, sh), 1765 (s), 1738 (s, sh), 1717 (s, sh) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 7.40–7.16 (m, 25H, Ph), 4.70 (app t, J = 2.1 Hz, 2H, Cp), 4.62 (app t, J = 2.1 Hz, 2H, Cp), 2.62–2.40 (m, 4H, CH_2CH_2). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75 MHz): δ 242.9 (s, CO). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121 MHz): δ 4.8 (d, $^2J_{PP}$ = 120 Hz, PPh$_3$), −13.0 (d, $^2J_{PP}$ = 120 Hz, PPh$_2$).

Mo{CuPMe$_3$}(CO)$_3$(μ-η^5:η^1-Cp^{PPh}) (7). Yield: 67%. Anal. Calcd for C$_{25}$H$_{27}$O$_3$P$_2$CuMo: C, 50.30; H, 4.56. Found: C, 50.71; H, 4.54. Mp: 163–164 °C dec. IR (THF): ν(CO) 1914 (s), 1813 (s), 1780 (s) cm^{-1}. IR (Nujol): ν(CO) 1889 (m), 1790 (s), 1762 (s), 1737 (s), 1716 (s) cm^{-1}. ^{1}H NMR (C$_4$D$_8$O, 300 MHz): δ 7.64–7.40 (m, 10H, Ph), 5.24 (app t, J = 2.4 Hz, 2H, Cp), 5.04 (app t, J = 2.4 Hz, 2H, Cp), 2.66–2.46 (m, 4H, CH_2CH_2), 1.17 (d, $^2J_{PH}$ = 6.3 Hz, 9H, PMe$_3$). ^{13}C{^{1}H} NMR (C$_4$D$_8$O, 75 MHz): δ 232.4 (s, CO). ^{31}P{^{1}H} NMR (C$_4$D$_8$O, 121 MHz): δ −11.8 (d, $^2J_{PP}$ = 100 Hz, PPh$_2$), −37.8 (d, $^2J_{PP}$ = 100 Hz, PMe$_3$).

Mo{CuPEt$_3$}(CO)$_3$(μ-η^5:η^1-Cp^{PPh}) (8). Yield: 65%. Anal. Calcd for C$_{28}$H$_{33}$O$_3$P$_2$CuMo: C, 52.63; H, 5.21. Found: C, 52.97; H, 4.99. Mp: 169–170 °C dec. IR (THF): ν(CO) 1913 (s), 1812 (s), 1779 (s) cm^{-1}. IR (Nujol): ν(CO) 1896 (s), 1792 (s), 1768 (s), 1733 (s), 1717 (s) cm^{-1}. ^{1}H NMR (C$_4$D$_8$O, 300 MHz): δ 7.64–7.38 (m, 10H, Ph), 5.23 (app t, J = 2.1 Hz, 2H, Cp), 5.04 (app t, J = 2.1 Hz, 2H, Cp), 2.58–2.42 (m, 4H, CH_2CH_2), 1.50 (dq, J_{PH} = 14.1 Hz, J_{HH} = 7.2 Hz, 6H, CH$_3$CH_2P), 0.89 (dt, J_{PH} = 15.3 Hz, J_{HH} = 7.5 Hz, 9H, CH_3CH$_2$P). ^{13}C{^{1}H} NMR (C$_4$D$_8$O, 75 MHz): δ 232.8 (dd, $^3J_{PC}$ = 12 Hz, $^3J_{PC}$ = 2.4 Hz, CO). ^{31}P{^{1}H} NMR (C$_4$D$_8$O, 121 MHz): δ −5.3 (d, $^2J_{PP}$ = 130 Hz, PPh$_2$), −13.3 (d, $^2J_{PP}$ = 130 Hz, PEt$_3$).

Mo{CuPCy$_3$}CO)$_3$(μ-η^5:η^1-Cp^{PPh}) (9). Yield: 63%. Anal. Calcd for C$_{40}$H$_{51}$O$_3$P$_2$CuMo: C, 59.96; H, 6.42. Found: C, 60.36; H, 6.23. Mp: 183–184 °C dec. IR (THF): ν(CO) 1912 (s), 1810 (s), 1778 (s) cm^{-1}. IR (Nujol): ν(CO) 1914 (s), 1798 (s), 1763 (s)

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cm^{-1}. ^{1}H NMR (C_4D_8O, 300 MHz): δ 7.65–7.40 (m, 10H, Ph), 5.20 (app t, $J = 2.1$ Hz, 2H, Cp), 5.03 (app t, $J = 2.1$ Hz, 2H, Cp), 2.52–2.35 (m, 4H, CH_2CH_2P), 1.90–1.05 (m, 33H, PCy_3). $^{13}C\{^1H\}$ NMR (C_4D_8O, 75 MHz): δ 233.7 (app t, $^3J_{PC} = 3.9$ Hz, CO). $^{31}P\{^1H\}$ NMR (C_4D_8O, 121 MHz): δ 18.0 (d, $^2J_{PP} = 110$ Hz, PPh_2), −15.0 (d, $^2J_{PP} = 110$ Hz, PCy_3).

Mo{CuPPh$_3$}(CO)$_3$(μ-η^5:η^1-Cp^{PPh}) (10). Yield: 74%. Anal. Calcd for $C_{40}H_{33}O_3P_2CuMo$: C, 61.35; H, 4.25. Found: C, 61.56; H, 4.48. Mp: 191–192 °C dec. IR (THF): ν(CO) 1916 (s), 1815 (s), 1783 (s) cm^{-1}. IR (Nujol): ν(CO) 1897 (s), 1801 (s, sh), 1773 (s), 1717 (s, sh) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.37–7.17 (m, 25H, Ph), 5.32 (app t, $J = 2.1$ Hz, 2H, Cp), 5.16 (app t, $J = 2.1$ Hz, 2H, Cp), 2.64–2.42 (m, 4H, CH_2CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz): δ 233.1 (s, CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz): δ 5.1 (d, $^2J_{PP} = 119$ Hz, PPh_3), −13.5 (d, $^2J_{PP} = 119$ Hz, PPh_2).

W{CuPMe$_3$}(CO)$_3$(μ-η^5:η^1-Cp^{PPh}) (11). Yield: 46%. Anal. Calcd for $C_{25}H_{27}O_3P_2CuW$: C, 43.85; H, 3.97. Found: C, 44.27; H, 3.99. Mp: 188–189 °C dec. IR (THF): ν(CO) 1909 (s), 1808 (s), 1774 (s) cm^{-1}. IR (Nujol): ν(CO) 1892 (s), 1786 (s), 1757 (s) cm^{-1}. ^{1}H NMR (C_4D_8O, 300 MHz): δ 7.64–7.42 (m, 10H, Ph), 5.30 (app t, $J = 2.1$ Hz, 2H, Cp), 5.08 (app t, $J = 2.1$, 2H, Cp), 2.74–2.47 (m, 4H, CH_2CH_2), 1.18 (d, $^2J_{PH} = 6.0$ Hz, 9H, PMe_3). $^{13}C\{^1H\}$ NMR (C_4D_8O, 75 MHz): δ 222.6 (s, CO, $^{183}W-^{13}C$ satellites 223.78, 221.41, $J_{WC} = 178$ Hz). $^{31}P\{^1H\}$ NMR (C_4D_8O, 121 MHz): δ −8.8 (d, $^2J_{PP} = 108$ Hz, PPh_2), −35.3 (d, $^2J_{PP} = 104$ Hz, PMe_3).

W{CuPPh$_3$}(CO)$_3$(μ-η^5:η^1-Cp^{PPh}) (12). Yield: 71%. Anal. Calcd for $C_{40}H_{33}O_3P_2CuW$: C, 55.15; H, 3.82. Found: C, 55.30; H, 4.11. Mp: 198–199 °C dec. IR (THF): ν(CO) 1910 (s), 1809 (s), 1777 (s) cm^{-1}. IR (Nujol): ν(CO) 1900 (s), 1777 (s, sh), 1746 (s), 1715 (s, sh) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.40–7.16 (m, 25H, Ph), 5.36 (app t, $J = 2.4$ Hz, 2H, Cp), 5.19 (app t, $J = 2.4$ Hz, 2H, Cp), 2.73–2.41 (m, 4H, CH_2CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz): δ 223.6 (s, CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz): δ 6.2 (d, $^2J_{PP} = 121$ Hz, PPh_3), −10.4 (d, $^2J_{PP} = 121$ Hz, PPh_2).

Cr{CuPPh$_3$}(CO)$_3$(μ-η^5:η^1-Cp^N) (13). THF (70 mL) was added to $Cr(CO)_3(CH_3CN)_3$ (0.465 g, 1.79 mmol) and NaCp^N (0.300 g, 1.88 mmol); the yellow solution was refluxed for 1.5 h. A suspension of $[CuPPh_3Cl]_4$ (0.648 g, 0.449 mmol) in THF (30 mL) was added; the $[Cr(CO)_3(\eta^5\text{-}Cp^N)]^-$ was consumed within 20 min. The resulting yellow solution was filtered through Celite. The filtrate was concentrated in vacuo until ~2 mL remained. Addition of pentane (40 mL) resulted in the precipitation of a pale yellow solid that was isolated by filtration, washed with pentane (3 × 30 mL), and dried in vacuo. Recrystallization (THF/Et_2O) provided pale yellow, moderately air sensitive microcrystals (0.652 g, 61%). Anal. Calcd for $C_{30}H_{29}O_3NPCuCr$: C, 60.25; H, 4.88; N, 2.34. Found: C, 60.29; H, 4.82; N, 2.40. Mp: 163–164 °C dec. IR (THF): ν(CO) 1906 (s), 1808 (s), 1773 (s) cm^{-1}. IR (Nujol): ν(CO) 1885 (s), 1798 (m), 1791 (m), 1773 (s), 1760 (s) cm^{-1}. ^{1}H NMR (CD_3CN, 300 MHz): δ 7.50–7.27 (m, 15H, Ph), 4.64 (app t, $J = 2.1$ Hz, 2H, Cp), 4.52 (app t, $J = 2.1$ Hz, 2H, Cp), 2.44–2.39 (m, 4H, CH_2CH_2), 2.19 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (CD_3CN, 75 MHz): δ 242.5 (s, CO). $^{31}P\{^1H\}$ NMR (CD_3CN, 121 MHz): δ −1.7 (s, br, PPh_3).

Mo{CuPPh$_3$}(CO)$_3$(μ-η^5:η^1-Cp^N) (14). Yield: 79%. Anal. Calcd for $C_{30}H_{29}O_3NPCuMo$: C, 56.12; H, 4.55; N, 2.18. Found: C, 55.79; H, 4.55; N, 2.06. Mp: 130–131 °C dec. IR (THF): ν(CO) 1914 (s), 1813 (s), 1782 (s) cm^{-1}. IR (Nujol): ν(CO) 1894 (s), 1794 (s), 1766 (s) cm^{-1}. ^{1}H NMR (CD_3CN, 300 MHz): δ 7.48–7.24 (m, 15H, Ph), 5.23 (app t, $J = 2.1$ Hz, 2H, Cp), 5.07 (app t, $J = 2.1$ Hz, 2H, Cp), 2.50 – 2.35 (m, 4H, CH_2CH_2), 2.17 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (CD_3CN, 75 MHz): d 232.6 (s, CO). $^{31}P\{^1H\}$ NMR (CD_3CN, 121 MHz): δ 4.3 (s, br, PPh_3).

X-ray Crystallographic Characterization of 1–4, 6, 7, 9–11, and 14. X-ray-quality crystals of **1**, **3**, **4**, **6**, **7**, **10**, **11**, and **14** were obtained by diffusion of pentane into a THF solution of each compound. Crystals of **2** were obtained by diffusion of Et_2O into a THF solution of the compound. Crystals of **9** were obtained by diffusion of pentane into a Et_2O/THF solution of the compound. These crystals were selected from the mother liquor in a N_2-filled glovebag.

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Supporting Information Available: Text, figures, and tables giving additional experimental details, ^{13}C NMR spectral data, and crystallographic data as well as data collection, solution, and refinement information for **1–4** , **6**, **7**, **9–11**, and **14**; crystallographic data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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