

[(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)diphenylphosphine⁶ 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(NCCH₃)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(PPh₃)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(η⁵-Cp))₂][–] (M' = Mo, W) react with PPh₃, [CN][–], and 1,10-phenanthroline, resulting in [M'(CO)₃(η⁵-Cp)][–] via heterolytic M'–Cu cleavage.¹⁰ The lability of Cu(I)–Ge(II) bonds in L^{Me2}CuGe[(NMe₂)₂(CH)₂] and L^{Me2}CuGe[N(SiMe₃)₂]₂ (L^{Me2} = the β-diketiminato derived from 2-(2,6-dimethylphenyl)amino-4-(2,6-dimethylphenyl)imino-2-pentene) toward PPh₃-promoted heterolytic cleavage was exploited by Tolman to afford free germylenes and Cu(I)–PPh₃ adducts.¹¹ Substitution at a thiometalate-enforced Mo–Cu bond was recently reported; [O₂MoS₂CuCN]^{2–} reacts with KSAr (Ar = Ph, *o*-Tol, *p*-Tol) to afford [O₂MoS₂CuSAr]^{2–}.^{2a} The Cu(I) center of the thiolato-bridged [Cp₂Ti(μ-SMe)₂Cu(CH₃CN)₂]PF₆ reacts with phosphines (L = PMe₃, PCy₃) to afford [Cp₂Ti(μ-SMe)₂CuL]PF₆, 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}) ligand¹² seemed ideally suited to this task; $\eta^5\text{-Cp}$ 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 $[\text{M}(\text{CO})_3(\eta^5\text{-Cp}^{\text{PPh}})]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). Heterobimetallics with dative $\text{d}^6\text{--d}^{10}$ M–Cu bonds supported by only weak semibridging carbonyl interactions have been synthesized with $[\text{M}(\text{CO})_3(\eta^5\text{-Cp})]^-$.¹³ Due to the relatively robust nature of the M–Cu bonds in these complexes, we hypothesized that application of $[\text{M}(\text{CO})_3(\eta^5\text{-Cp}^{\text{PPh}})]^-$ 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 $[\text{K}(18\text{C}6)][\text{M}(\text{CO})_3(\eta^5\text{-Cp}^{\text{PPh}})]$. Bullock recently reported that LiCp^{PPh} and $\text{Mo}(\text{CO})_3(\text{diglyme})$ react to give $\text{Li}[\text{Mo}(\text{CO})_3(\eta^5\text{-Cp}^{\text{PPh}})]$, which was protonated to afford $\text{MoH}(\text{CO})_2(\eta^5\text{-}\eta^1\text{-Cp}^{\text{PPh}})$.¹⁴ This hydride was employed for catalytic hydrogenation of ketones. The importance of $[\text{Mo}(\text{CO})_3(\eta^5\text{-Cp}^{\text{PPh}})]^-$ as a catalyst precursor prompted us to isolate and crystallographically characterize $[\text{K}(18\text{C}6)][\text{M}(\text{CO})_3(\eta^5\text{-Cp}^{\text{PPh}})]$ ($\text{M} = \text{Cr}$ (**1**), Mo (**2**), W (**3**)).¹⁵ Reactions of $\text{M}(\text{CO})_3(\text{RCN})_3$ ($\text{M} = \text{Cr}, \text{R} = \text{Me}; \text{M} = \text{Mo}, \text{W}, \text{R} = \text{Et}$) 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 $\eta^5\text{-Cp}^{\text{PPh}}$ 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 $[\text{K}(18\text{C}6)]$ cations. Important average lengths and angles that define the geometries of the C_{3v} $\text{M}(\text{CO})_3$ fragments of **1–3** ($\text{M}=\text{C}(\text{O})$, $\text{C}=\text{O}$, $(\text{O})\text{C}=\text{M}=\text{C}(\text{O})$, $\text{O}=\text{C}=\text{M}$; averages given in the captions of Figure 1 and Figures S1 and S2) are statistically indistinguishable from those of $[\text{PPN}][\text{M}(\text{CO})_3(\eta^5\text{-Cp}^{\text{N}})]$,¹⁷ respectively. The average $\text{M}=\text{C}(\text{dienyl})$ lengths of **1–3** (given in the figure captions) are also statistically identical with the corresponding values of $[\text{PPN}][\text{M}(\text{CO})_3(\eta^5\text{-Cp}^{\text{N}})]$, respectively. The potassium of the $[\text{K}(18\text{C}6)]$ 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 $[\text{K}(18\text{C}6)]$ cations (**1**, 2.84(4) Å; **2** and **3**, 2.85(4) Å). The essentially linear O(1)–C(1)–M

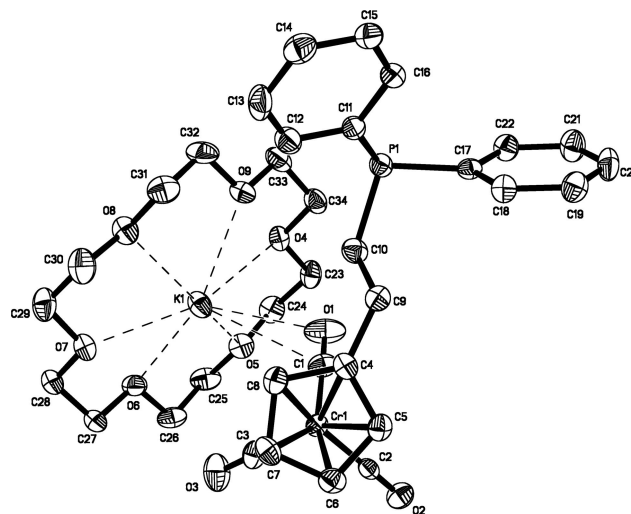


Figure 1. Molecular structure of **1** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cr–C(1) = 1.793(3), Cr–C(2) = 1.801(3), Cr–C(3) = 1.805(3), Cr–C(O) (av) = 1.80(1), Cr–C(4) = 2.257(3), Cr–C(5) = 2.224(3), Cr–C(6) = 2.210(3), Cr–C(7) = 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), $(\text{O})\text{C}=\text{Cr}=\text{C}(\text{O})$ (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).

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 $\nu(\text{CO})$ IR absorptions of **1–3**, which indicate unperturbed C_{3v} $\text{M}(\text{CO})_3$ units in solution.

Reactions at Group VI Metal–Copper(I) Bonds. While $[\text{M}(\text{CO})_3(\eta^5\text{-Cp})]^-$ instantaneously reduces CuCl to metallic copper in THF, $\text{Na}[\text{M}(\text{CO})_3(\eta^5\text{-Cp}^{\text{PPh}})]$ 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 $\nu(\text{CO})$ IR absorptions,^{18a} which are nearly indistinguishable from those of $\text{M}\{\text{CuPPh}_3\}(\text{CO})_3(\mu\text{-}\eta^5\text{-}\eta^1\text{-Cp}^{\text{PPh}})$ (vide infra). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of these $[\text{M}(\text{CO})_3(\eta^5\text{-Cp}^{\text{PPh}})]^-/\text{CuCl}$ reaction products exhibit two coupled doublets,^{18b} suggesting two $\eta^5\text{-Cp}^{\text{PPh}}$ 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 $[(\text{CO})_3\text{M}(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{M}'\text{M}']$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}, \text{M}' = \text{M}'' = \text{Ag}; \text{M} = \text{Cr}, \text{Mo}, \text{M}' = \text{M}'' = \text{Au}; \text{M} = \text{Mo}, \text{M}' = \text{Ag}, \text{M}'' = \text{Au}$) 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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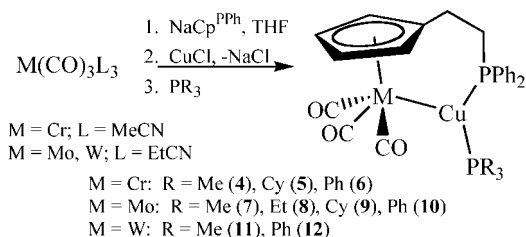
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(15) 18C6 = 1,4,7,10,13,16-hexaoxacyclooctadecane.

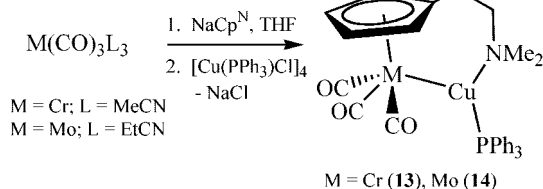
(16) Drawings illustrating the near eclipse of C(4) and C(1) in **1–3**, as well as angles between planes that quantify the orientation of the Cp rings relative to the $\text{M}(\text{CO})_3$ fragments, are provided in the Supporting Information.

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Scheme 1



Scheme 2



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 $\text{M}\{\text{CuL}\}(\text{CO})_3(\mu\text{-}\eta^5\text{-}\eta^1\text{-Cp}^{\text{PPh}})$ 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 $\eta^5\text{-Cp}^{\text{PPh}}$ ligand is apparently unable to support M–Cu bonds of cuprates; instantaneous heterolytic M–Cu bond cleavage occurs upon addition of *n*-butyllithium, $[\text{Bu}_4\text{N}][\text{CN}]$, and $[\text{PPN}]\text{Cl}$, affording $[\text{M}(\text{CO})_3(\eta^5\text{-Cp}^{\text{PPh}})]^-$. Heterolytic cleavage promoted by $[\text{PPN}]\text{Cl}$ underscores the importance of salt elimination to kinetically stabilize M–Cu bonds. However, these intermediates are inert toward triflates and tosylates. Although $\text{M}\{\text{Cu}(\text{tmeda})\}(\text{CO})_3(\eta^5\text{-Cp})$ is known,^{13b} analogous reactions of $[\text{M}(\text{CO})_3(\eta^5\text{-Cp}^{\text{N}})]^-$ and CuCl were not useful to obtain pure Cu(I) derivatives with a bridging $\eta^5\text{-Cp}^{\text{N}}$ ligand. However, $\text{M}'\{\text{CuPPh}_3\}(\text{CO})_3(\mu\text{-}\eta^5\text{-}\eta^1\text{-Cp}^{\text{N}})$ (M = Cr (**13**), Mo (**14**)) were obtained via $[\text{M}(\text{CO})_3(\eta^5\text{-Cp}^{\text{N}})]^-$ and $[\text{Cu}(\text{PPh}_3)\text{Cl}]_4$ (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 $[\text{M}(\text{CO})_3(\eta^5\text{-Cp}^{\text{N}})]^-$ 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 $\eta^5\text{-Cp}$ ligands and trigonal-planar Cu(I),

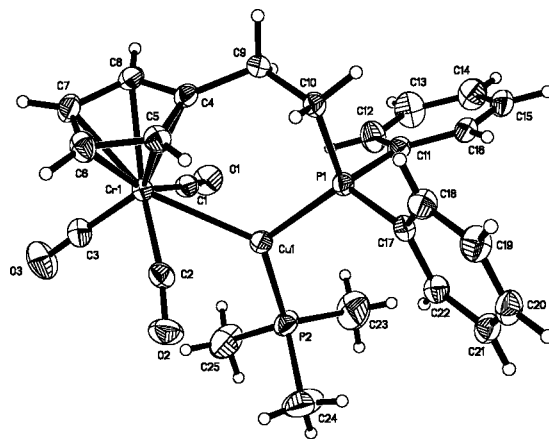


Figure 2. Molecular structure of **4** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Cr–Cu = 2.5943(4), Cr–C(1) = 1.8384(18), Cr–C(2) = 1.8285(19), Cr–C(3) = 1.8218(19), Cr–C(O) (av) = 1.830(8), Cr–C(4) = 2.2353(17), Cr–C(5) = 2.2166(18), Cr–C(6) = 2.2012(18), Cr–C(7) = 2.2012(18), 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).

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 $[\text{Cr}_2\text{Cu}_2(\text{DPhIP})_4](\text{CuCl}_2)_2$ (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 $\text{W}\{\text{Cu}(\text{PPh}_3)_2\}(\text{CO})_3(\eta^5\text{-Cp})$ (2.721(1), 2.771(1) Å),^{13a} $\text{Mo}\{\text{Cu}(\text{tmeda})\}(\text{CO})_3(\eta^5\text{-Cp})$ (2.592(1) Å)^{13b} and slightly longer than the Cu–Mo separation (2.6149(4) Å) in $[\text{Mo}_2\text{Cu}_2(\text{DPhIP})_4](\text{CuCl}_2)_2$.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 $\eta^5\text{-Cp}^{\text{PPh}}$ 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-

(18) (a) IR $\nu(\text{CO})$ spectral data for $[\text{M}(\text{CO})_3(\eta^5\text{-Cp}^{\text{PPh}})]^-/\text{CuCl}$ 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 $\nu(\text{CO})$ 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: $^3\text{P}\{^1\text{H}\}$ NMR (121 MHz) spectral data for the $[\text{Mo}(\text{CO})_3(\eta^5\text{-Cp}^{\text{PPh}})]^-/\text{CuCl}$ reaction product in $\text{C}_4\text{D}_8\text{O}$: δ –3.5 (d, $^2J_{\text{PP}} = 130$ Hz), –13.8 (d, $^2J_{\text{PP}} = 130$ 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 $[\text{M}(\text{CO})_3(\eta^5\text{-Cp}^{\text{PPh}})]^-$ and $[\text{Cu}(\text{PPh}_3)\text{Cl}]_4$.

(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 $\text{Mo}(\text{CO})_3(\eta^5\text{-Cp})$ fragment was very small.²³ This electronic insulation between Cu(I) and the $\text{Mo}(\text{CO})_3(\eta^5\text{-Cp})$ fragment is further supported on the basis of $\nu(\text{CO})$ IR spectral data, as the lowest energy $\nu(\text{CO})$ 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 $\eta^5\text{-Cp}^{\text{PPh}}$ 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 $\eta^5\text{-Cp}^{\text{PPh}}$ 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($\eta^5\text{-Cp}^{\text{PPh}}$)] (1). THF (125 mL) was added to $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ (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 $-10\text{ }^\circ\text{C}$ 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 $\sim 5\text{ mL}$ remained. Addition of Et_2O (70 mL) precipitated a pale yellow solid that was washed with Et_2O ($4 \times 30\text{ mL}$) and dried in vacuo. Recrystallization (THF/ Et_2O) provided pale yellow, air-sensitive microcrystals (1.04 g, 75%). Anal. Calcd for $\text{C}_{34}\text{H}_{42}\text{CrK}_2\text{O}_9\text{P}$: C, 56.97; H, 5.91. Found: C, 57.15; H, 5.96. Mp: $136\text{--}137\text{ }^\circ\text{C}$ dec. IR (THF): $\nu(\text{CO})$ 1890 (s), 1778 (s) cm^{-1} . IR (Nujol): $\nu(\text{CO})$ 1879 (s), 1772 (s, sh), 1759 (s) cm^{-1} . ^1H NMR (CD_3CN , 300 MHz): δ 7.51–7.33 (m, 10H, Ph), 4.39 (app t, $J = 2.1\text{ Hz}$, 2H, Cp), 4.29 (app t, $J = 2.1\text{ Hz}$, 2H, Cp), 3.57 (s, 24 H, 18C6), 2.35–2.20 (m, 4H, CH_2CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 75 MHz): δ 246.9 (s, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN , 121 MHz): δ -15.06 (s, PPh_2).

[K(18C6)][Mo(CO)₃($\eta^5\text{-Cp}^{\text{PPh}}$)] (2). Yield: 64%. Anal. Calcd for $\text{C}_{34}\text{H}_{42}\text{KM}_2\text{O}_9\text{P}$: C, 53.68; H, 5.57. Found: C, 53.92; H, 5.75. Mp: $149\text{--}152\text{ }^\circ\text{C}$ dec. IR (THF): $\nu(\text{CO})$ 1894 (s), 1781 (s) cm^{-1} . IR (Nujol): $\nu(\text{CO})$ 1886 (s), 1763 (s) cm^{-1} . ^1H NMR (CD_3CN , 300 MHz): δ 7.48–7.33 (m, 10H, Ph), 5.04 (app t, $J = 2.4\text{ Hz}$, 2H, Cp), 4.92 (app t, $J = 2.4\text{ Hz}$, 2H, Cp), 3.56 (s, 24 H, 18C6), 2.32–2.28 (m, 4H, CH_2CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 75 MHz): δ 236.6 (s, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN , 121 MHz): δ -15.06 (s, PPh_2).

[K(18C6)][W(CO)₃($\eta^5\text{-Cp}^{\text{PPh}}$)] (3). Yield: 67%. Anal. Calcd for $\text{C}_{34}\text{H}_{42}\text{KW}_2\text{O}_9\text{P}$: C, 48.12; H, 4.99. Found: C, 48.33; H, 5.29. Mp: $156\text{--}158\text{ }^\circ\text{C}$ dec. IR (THF): $\nu(\text{CO})$ 1888 (s), 1777 (s) cm^{-1} . IR (Nujol): $\nu(\text{CO})$ 1880 (s), 1766 (s, sh), 1759 (s) cm^{-1} . ^1H NMR (CD_3CN , 300 MHz): δ 7.50–7.33 (m, 10H, Ph), 5.07 (app t, $J = 2.1\text{ Hz}$, 2H, Cp), 4.96 (app t, $J = 2.1\text{ Hz}$, 2H, Cp), 3.57 (s, 24 H, 18C6), 2.43–2.26 (m, 4H, CH_2CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 75 MHz): δ 227.4 (s, CO), $^{183}\text{W}\text{--}^{13}\text{C}$ satellites 228.76, 226.13, $^1J_{\text{WC}} = 198\text{ Hz}$. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN , 121 MHz): δ -15.11 (s, PPh_2).

Cr{CuPMe₃}(CO)₃($\mu\text{-}\eta^5\text{-}\eta^1\text{-Cp}^{\text{PPh}}$) (4). THF (50 mL) was added to $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ (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 $[\text{Cr}(\text{CO})_3(\eta^5\text{-Cp}^{\text{PPh}})]^-$ 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 $\sim 2\text{ mL}$ remained. Addition of pentane (50 mL) resulted in the precipitation of a bright yellow solid that was isolated by filtration, washed with pentane ($4 \times 10\text{ mL}$), and dried in vacuo. Recrystallization from THF/pentane provided bright yellow, moderately air sensitive microcrystals (0.400 g, 61%). Anal. Calcd for $\text{C}_{25}\text{H}_{27}\text{O}_3\text{P}_2\text{CrCu}$: C, 54.30; H, 4.92. Found: C, 54.29; H, 5.19. Mp: $176\text{--}179\text{ }^\circ\text{C}$ dec. IR (THF): $\nu(\text{CO})$ 1905 (s), 1808 (s), 1771 (s) cm^{-1} . IR (Nujol): $\nu(\text{CO})$ 1902 (s), 1797 (s), 1759 (s), 1709 (s, sh) cm^{-1} . ^1H NMR ($\text{C}_4\text{D}_8\text{O}$, 300 MHz): δ 7.66–7.41 (m, 10H, Ph), 4.59 (app t, $J = 2.1\text{ Hz}$, 2H, Cp), 4.48 (app t, $J = 2.1\text{ Hz}$, 2H, Cp), 2.58–2.44 (m, 4H, CH_2CH_2), 1.20 (d, $^2J_{\text{PH}} = 6.0\text{ Hz}$, 9H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_4\text{D}_8\text{O}$, 75 MHz): δ 242.6 (s, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_4\text{D}_8\text{O}$, 121 MHz): δ -11.4 (s, br, PPh_2), -38.4 (s, br, PMe_3).

Cr{CuPCy₃}(CO)₃($\mu\text{-}\eta^5\text{-}\eta^1\text{-Cp}^{\text{PPh}}$) (5). Yield: 51%. Anal. Calcd for $\text{C}_{40}\text{H}_{51}\text{O}_3\text{P}_2\text{CrCu}$: C, 63.44; H, 6.79. Found: C, 63.60; H, 6.68. Mp: $171\text{--}172\text{ }^\circ\text{C}$ dec. IR (THF): $\nu(\text{CO})$ 1904 (s), 1806 (s), 1769 (s) cm^{-1} . IR (Nujol): $\nu(\text{CO})$ 1905 (s), 1793 (s), 1754 (s), 1730 (m, sh) cm^{-1} . ^1H NMR ($\text{C}_4\text{D}_8\text{O}$, 300 MHz): δ 7.64–7.42 (m, 10H, Ph), 4.55 (app t, $J = 2.1\text{ Hz}$, 2H, Cp), 4.45 (app t, $J = 2.1\text{ Hz}$, 2H, Cp), 2.46–2.29 (m, 4H, $\text{CH}_2\text{CH}_2\text{P}$), 1.79–1.08 (m, 33H, PCy_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_4\text{D}_8\text{O}$, 75 MHz): δ 243.8 (app t, $^3J_{\text{PC}} = 2.9\text{ Hz}$, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_4\text{D}_8\text{O}$, 121 MHz): δ 17.3 (d, $^2J_{\text{PP}} = 113\text{ Hz}$, PPh_2), -14.3 (d, $^2J_{\text{PP}} = 113\text{ Hz}$, PCy_3).

Cr{CuPPh₃}(CO)₃($\mu\text{-}\eta^5\text{-}\eta^1\text{-Cp}^{\text{PPh}}$) (6). Yield: 55%. Anal. Calcd for $\text{C}_{40}\text{H}_{33}\text{O}_3\text{P}_2\text{CrCu}$: C, 65.00; H, 4.50. Found: C, 65.46; H, 4.91. Mp: $183\text{--}184\text{ }^\circ\text{C}$ dec. IR (THF): $\nu(\text{CO})$ 1905 (s), 1811 (s), 1775 (s) cm^{-1} . IR (Nujol): $\nu(\text{CO})$ 1890 (s), 1797 (m, sh), 1765 (s), 1738 (s, sh), 1717 (s, sh) cm^{-1} . ^1H NMR (CD_2Cl_2 , 300 MHz): δ 7.40–7.16 (m, 25H, Ph), 4.70 (app t, $J = 2.1\text{ Hz}$, 2H, Cp), 4.62 (app t, $J = 2.1\text{ Hz}$, 2H, Cp), 2.62–2.40 (m, 4H, CH_2CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 75 MHz): δ 242.9 (s, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 121 MHz): δ 4.8 (d, $^2J_{\text{PP}} = 120\text{ Hz}$, PPh_3), -13.0 (d, $^2J_{\text{PP}} = 120\text{ Hz}$, PPh_2).

Mo{CuPMe₃}(CO)₃($\mu\text{-}\eta^5\text{-}\eta^1\text{-Cp}^{\text{PPh}}$) (7). Yield: 67%. Anal. Calcd for $\text{C}_{25}\text{H}_{27}\text{O}_3\text{P}_2\text{CuMo}$: C, 50.30; H, 4.56. Found: C, 50.71; H, 4.54. Mp: $163\text{--}164\text{ }^\circ\text{C}$ dec. IR (THF): $\nu(\text{CO})$ 1914 (s), 1813 (s), 1780 (s) cm^{-1} . IR (Nujol): $\nu(\text{CO})$ 1889 (m), 1790 (s), 1762 (s), 1737 (s), 1716 (s) cm^{-1} . ^1H NMR ($\text{C}_4\text{D}_8\text{O}$, 300 MHz): δ 7.64–7.40 (m, 10H, Ph), 5.24 (app t, $J = 2.4\text{ Hz}$, 2H, Cp), 5.04 (app t, $J = 2.4\text{ Hz}$, 2H, Cp), 2.66–2.46 (m, 4H, CH_2CH_2), 1.17 (d, $^2J_{\text{PH}} = 6.3\text{ Hz}$, 9H, PMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_4\text{D}_8\text{O}$, 75 MHz): δ 232.4 (s, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_4\text{D}_8\text{O}$, 121 MHz): δ -11.8 (d, $^2J_{\text{PP}} = 100\text{ Hz}$, PPh_2), -37.8 (d, $^2J_{\text{PP}} = 100\text{ Hz}$, PMe_3).

Mo{CuPEt₃}(CO)₃($\mu\text{-}\eta^5\text{-}\eta^1\text{-Cp}^{\text{PPh}}$) (8). Yield: 65%. Anal. Calcd for $\text{C}_{28}\text{H}_{33}\text{O}_3\text{P}_2\text{CuMo}$: C, 52.63; H, 5.21. Found: C, 52.97; H, 4.99. Mp: $169\text{--}170\text{ }^\circ\text{C}$ dec. IR (THF): $\nu(\text{CO})$ 1913 (s), 1812 (s), 1779 (s) cm^{-1} . IR (Nujol): $\nu(\text{CO})$ 1896 (s), 1792 (s), 1768 (s), 1733 (s), 1717 (s) cm^{-1} . ^1H NMR ($\text{C}_4\text{D}_8\text{O}$, 300 MHz): δ 7.64–7.38 (m, 10H, Ph), 5.23 (app t, $J = 2.1\text{ Hz}$, 2H, Cp), 5.04 (app t, $J = 2.1\text{ Hz}$, 2H, Cp), 2.58–2.42 (m, 4H, CH_2CH_2), 1.50 (dq, $J_{\text{PH}} = 14.1\text{ Hz}$, $J_{\text{HH}} = 7.2\text{ Hz}$, 6H, $\text{CH}_3\text{CH}_2\text{P}$), 0.89 (dt, $J_{\text{PH}} = 15.3\text{ Hz}$, $J_{\text{HH}} = 7.5\text{ Hz}$, 9H, $\text{CH}_3\text{CH}_2\text{P}$). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_4\text{D}_8\text{O}$, 75 MHz): δ 232.8 (dd, $^3J_{\text{PC}} = 12\text{ Hz}$, $^3J_{\text{PC}} = 2.4\text{ Hz}$, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_4\text{D}_8\text{O}$, 121 MHz): δ -5.3 (d, $^2J_{\text{PP}} = 130\text{ Hz}$, PPh_2), -13.3 (d, $^2J_{\text{PP}} = 130\text{ Hz}$, PEt_3).

Mo{CuPCy₃}(CO)₃($\mu\text{-}\eta^5\text{-}\eta^1\text{-Cp}^{\text{PPh}}$) (9). Yield: 63%. Anal. Calcd for $\text{C}_{40}\text{H}_{51}\text{O}_3\text{P}_2\text{CuMo}$: C, 59.96; H, 6.42. Found: C, 60.36; H, 6.23. Mp: $183\text{--}184\text{ }^\circ\text{C}$ dec. IR (THF): $\nu(\text{CO})$ 1912 (s), 1810 (s), 1778 (s) cm^{-1} . IR (Nujol): $\nu(\text{CO})$ 1914 (s), 1798 (s), 1763 (s)

cm^{-1} . ^1H NMR ($\text{C}_4\text{D}_8\text{O}$, 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, $\text{CH}_2\text{CH}_2\text{P}$), 1.90–1.05 (m, 33H, PCy_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_4\text{D}_8\text{O}$, 75 MHz): δ 233.7 (app t, $^3J_{\text{PC}} = 3.9$ Hz, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_4\text{D}_8\text{O}$, 121 MHz): δ 18.0 (d, $^2J_{\text{PP}} = 110$ Hz, PPh_2), –15.0 (d, $^2J_{\text{PP}} = 110$ Hz, PCy_3).

Mo{CuPPh₃}₃(CO)₃(μ - η^5 : η^1 -Cp^{PPh}) (10). Yield: 74%. Anal. Calcd for $\text{C}_{40}\text{H}_{33}\text{O}_3\text{P}_2\text{CuMo}$: C, 61.35; H, 4.25. Found: C, 61.56; H, 4.48. Mp: 191–192 °C dec. IR (THF): $\nu(\text{CO})$ 1916 (s), 1815 (s), 1783 (s) cm^{-1} . IR (Nujol): $\nu(\text{CO})$ 1897 (s), 1801 (s, sh), 1773 (s), 1717 (s, sh) cm^{-1} . ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 75 MHz): δ 233.1 (s, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 121 MHz): δ 5.1 (d, $^2J_{\text{PP}} = 119$ Hz, PPh_3), –13.5 (d, $^2J_{\text{PP}} = 119$ Hz, PPh_2).

W{CuPMe₃}₃(CO)₃(μ - η^5 : η^1 -Cp^{PPh}) (11). Yield: 46%. Anal. Calcd for $\text{C}_{25}\text{H}_{27}\text{O}_3\text{P}_2\text{CuW}$: C, 43.85; H, 3.97. Found: C, 44.27; H, 3.99. Mp: 188–189 °C dec. IR (THF): $\nu(\text{CO})$ 1909 (s), 1808 (s), 1774 (s) cm^{-1} . IR (Nujol): $\nu(\text{CO})$ 1892 (s), 1786 (s), 1757 (s) cm^{-1} . ^1H NMR ($\text{C}_4\text{D}_8\text{O}$, 300 MHz): δ 7.64–7.42 (m, 10H, Ph), 5.30 (app t, $J = 2.1$ Hz, 2H, Cp), 5.08 (app t, $J = 2.1$ Hz, 2H, Cp), 2.74–2.47 (m, 4H, CH_2CH_2), 1.18 (d, $^2J_{\text{PH}} = 6.0$ Hz, 9H, PMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_4\text{D}_8\text{O}$, 75 MHz): δ 222.6 (s, CO), ^{183}W – ^{13}C satellites 223.78, 221.41, $J_{\text{WC}} = 178$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_4\text{D}_8\text{O}$, 121 MHz): δ –8.8 (d, $^2J_{\text{PP}} = 108$ Hz, PPh_2), –35.3 (d, $^2J_{\text{PP}} = 104$ Hz, PMe_3).

W{CuPPh₃}₃(CO)₃(μ - η^5 : η^1 -Cp^{PPh}) (12). Yield: 71%. Anal. Calcd for $\text{C}_{40}\text{H}_{33}\text{O}_3\text{P}_2\text{CuW}$: C, 55.15; H, 3.82. Found: C, 55.30; H, 4.11. Mp: 198–199 °C dec. IR (THF): $\nu(\text{CO})$ 1910 (s), 1809 (s), 1777 (s) cm^{-1} . IR (Nujol): $\nu(\text{CO})$ 1900 (s), 1777 (s, sh), 1746 (s), 1715 (s, sh) cm^{-1} . ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 75 MHz): δ 223.6 (s, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 121 MHz): δ 6.2 (d, $^2J_{\text{PP}} = 121$ Hz, PPh_3), –10.4 (d, $^2J_{\text{PP}} = 121$ Hz, PPh_2).

Cr{CuPPh₃}₃(CO)₃(μ - η^5 : η^1 -Cp^N) (13). THF (70 mL) was added to $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ (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 $[\text{CuPPh}_3\text{Cl}]_4$ (0.648 g, 0.449 mmol) in THF (30 mL) was added; the $[\text{Cr}(\text{CO})_3(\eta^5\text{-Cp}^{\text{N}})]^-$ 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/Et₂O) provided pale

yellow, moderately air sensitive microcrystals (0.652 g, 61%). Anal. Calcd for $\text{C}_{30}\text{H}_{29}\text{O}_3\text{NPCuCr}$: 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): $\nu(\text{CO})$ 1906 (s), 1808 (s), 1773 (s) cm^{-1} . IR (Nujol): $\nu(\text{CO})$ 1885 (s), 1798 (m), 1791 (m), 1773 (s), 1760 (s) cm^{-1} . ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 75 MHz): δ 242.5 (s, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN , 121 MHz): δ –1.7 (s, br, PPh_3).

Mo{CuPPh₃}₃(CO)₃(μ - η^5 : η^1 -Cp^N) (14). Yield: 79%. Anal. Calcd for $\text{C}_{30}\text{H}_{29}\text{O}_3\text{NPCuMo}$: 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): $\nu(\text{CO})$ 1914 (s), 1813 (s), 1782 (s) cm^{-1} . IR (Nujol): $\nu(\text{CO})$ 1894 (s), 1794 (s), 1766 (s) cm^{-1} . ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 75 MHz): δ 232.6 (s, CO). $^{31}\text{P}\{^1\text{H}\}$ 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 Et₂O into a THF solution of the compound. Crystals of **9** were obtained by diffusion of pentane into a Et₂O/THF solution of the compound. These crystals were selected from the mother liquor in a N₂-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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