4060 *Organometallics* **2000,** *19,* 4060−4065

Synthesis and Characterization of Functionally Substituted Cyclopentadienyl Derivatives of Silver and Copper

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Received July 17, 2000

A series of functionally substituted cyclopentadienyl derivatives of silver and copper have been synthesized and characterized. Reactions between sodium acetyl- or carbomethoxycyclopentadienylide, triphenylphosphine, and silver triflate ($AgSO_3CF_3$) in DME produced $Ag[C_5H_4C(O)CH_3](PPh_3)$ and $Ag[C_5H_4CO_2CH_3](PPh_3)$ in yields of 57−58%. Corresponding copper analogues were prepared using $[BrCu(PPh_3)]_4$. Similar reactions between sodium acetyl- or carbomethoxycyclopentadienylide and $AgSO_3CF_3$ in the presence of the bidentate ligand 1,2-bis(diphenylphosphino)ethane afforded the chelated compounds $Ag[C_5H_4C(O)CH_3][Ph_2P(CH_2)_2PPh_2]$ and $Ag[C_5H_4CO_2CH_3][Ph_2P(CH_2)_2PPh_2]$ in 55−72% yields. Dinuclear compounds of the type $[Ag(C_5H_4PPh_2)(PR_3)]_2$ (R = Ph, Et) resulted in 36−49% yield from reactions of silver chloride with the appropriate phosphine in refluxing toluene, followed by cooling to −78 °C and subsequent reactions with lithium diphenylphosphinocyclopentadienide. The compounds $M(C_5Ph_5)(PEt_3)$ (M = Ag, Cu) containing five bulky phenyl substituents were obtained in 44−56% yield from reactions of sodium pentaphenylcyclopentadienide and $[ClM(PEt_3)]_4$ in THF. In general, the new organosilver compounds containing functional substituents on the cyclopentadienyl ring as well as binuclear phosphine derivatives exhibited enhanced thermal and oxidative stabilities compared with the parent compound $Ag(C_5H_5)(PPh_3)$. ^{31}P NMR studies of the compounds have been undertaken and are in agreement with the proposed structures.

Introduction

The synthesis, structure, and reactivity of cyclopentadienyl compounds that contain functional substituents has become an important area of research in organometallic chemistry.[1−6] Of special importance is the application of functionally substituted metallocenes of group 4 metals as homogeneous catalysts for the polymerization of α-olefins to stereoregular polyolefins.[7,8]

In contrast with the rapidly developing chemistry of functionally substituted cyclopentadienyl derivatives of the early transition metals, corresponding derivatives of the group 11 metals copper and silver have been much less studied. A series of pentamethylcyclopentadienylcopper compounds that also contain phosphine,[9] carbonyl,[9] acetylene,[9] hexaphenylcarbodiphosphorane,[10] and bridging carbene and carbyne metal ligands[11] have been described. The vinyl and isopropenyl analogues $Cu[C_5H_4C(R){=}CH_2](PEt_3)$ (R = H, Me) are also known,[3] and the molecular structures of (η^5-methylcyclopentadienyl)(triphenylphosphine)copper(I)[12] and (η^5-pentaphenylcyclopentadienyl)(triphenylphosphine)copper(I)[13] have been reported.

The chemistry of functionally substituted cyclopentadienylsilver compounds is even more limited. The first cyclopentadienylsilver compound was described in 1976 by Van der Kerk and co-workers.[14] (η^5-Cyclopentadienyl)(triphenylphosphine)silver(I) (**1**) was produced by treatment of a solution of sodium cyclopentadienide and triphenylphosphine in THF with a solution of silver trifluoromethanesulfonate (triflate) in THF at −80 °C. Compound **1** was reported to be moisture, air, and temperature sensitive in the solid state and in solution. It could be stored at −80 °C without change, but decomposed within seconds at 75 °C. Subsequent studies confirmed the extreme air, moisture, and thermal instability of **1**, but demonstrated that it was a useful intermediate in the synthesis of phosphine-stabilized

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10.1021/om000618h CCC: $19.00

silver acetylide complexes.[15] Bruce and co-workers[16] have described the formation and structure of several silver complexes that contain $C_5(CO_2Me)_5$ ligands, and (η^5-pentamethylcyclopentadienyl)(hexaphenylcarbodiphosphorane)silver(I), analogous to the related organocopper compound mentioned above, has been reported.[10]

The central objective of the present study was to prepare cyclopentadienylsilver compounds that contain various functional substituents on the cyclopentadienyl ring, to compare the properties of these compounds with the parent compound **1**, and to examine structural features of the new organosilver compounds by means of ^{1}H and ^{31}P NMR techniques. During the course of this investigation, several analogous new cyclopentadienylcopper compounds have likewise been prepared and are discussed.

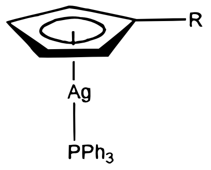
Results and Discussion

To expand the area of cyclopentadienylsilver chemistry, several approaches have been undertaken which should lead to analogues of **1** that possess enhanced overall stability. First, derivatives of **1** that contain electron-withdrawing substituents have been synthesized. Groups that can withdraw electron density away from the five-membered ring and in effect away from the metal center often tend to increase the stability of cyclopentadienylmetal compounds.[2] For example, Cu[η^5-$C_5H_4C(O)CH_3$](PEt_3), which contains an electron-withdrawing acetyl substituent on the cyclopentadienyl ring, is appreciably more air stable than either Cu(η^5-C_5H_5)(PEt_3) or Cu(η^5-C_5Me_5)(PEt_3).[9]

A second approach, which has been used in conjunction with the first approach, has been to study the effect of a bidentate phosphine ligand. Monodentate phosphine ligands are clearly important in forming cyclopentadienylsilver compounds such as **1**,[14,15] and increased stability might result from the use of a chelating bidentate phosphine ligand such as 1,2-bis(diphenylphosphino)ethane.

A third approach has been to utilize highly substituted cyclopentadienyl ligands that contain five phenyl substituents. These bulky ligands are known to impart kinetic stabilization by means of shielding the reactive metal center and making the compound less susceptible to decomposition as a result of steric hindrance.[4]

The synthesis of monodentate phosphine derivatives of silver and copper compounds was accomplished by utilizing electron-withdrawing groups on the cyclopentadienyl ring. The most effective groups for this study were acetyl and carbomethoxy. The phosphine chosen was triphenylphosphine due to its favorable solubility, ease of handling, and crystallization properties. In the case of silver, the acetyl (**2**) and carbomethoxy (**3**) derivatives could be obtained in good yields by addition of silver triflate to a solution of equimolar amounts of sodium acetyl- or carbomethoxycyclopentadienide and triphenylphosphine in DME at −10 °C. After filtration, washing with cold DME, and drying, **2** and **3** were obtained as off-white moderately air-stable solids.

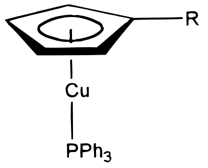


1 R = H
2 R = $C(O)CH_3$
3 R = CO_2CH_3

Compounds **2** and **3** could also be synthesized by a more direct route. By reacting equimolar amounts of sodium acetyl- or carbomethoxycyclopentadienide with mono(triphenylphosphine)silver triflate under the same conditions as described above, **2** and **3** were obtained in comparable yields. The organosilver compounds **2** and **3** were characterized by their ^{1}H NMR, ^{31}P NMR (vide infra), and IR spectra, as well as by elemental analysis.

Compared with **1**, compounds **2** and **3** were much more stable in air. On heating, **2** and **3** began to decompose at 50 °C, but were air stable for days at room temperature. In contrast, **1** is reported to be thermally unstable, decomposing in a matter of minutes to a black solid if left under an inert atmosphere at room temperature.[14,15] Compounds **2** and **3** were also appreciably less moisture sensitive than **1**.

The analogous copper compounds **4** and **5** were also prepared and characterized from reactions of either sodium acetyl- or carbomethoxycyclopentadienide with tetrakis[bromotriphenylphosphinecopper] in THF solution. The organocopper compounds **4** and **5** were much more thermally and oxidatively stable than the silver analogues **2** and **3**. Compared with the latter, **4** and **5** decomposed on heating at temperatures of 90 and 120 °C, respectively. Both **4** and **5**, like **2** and **3**, were also moderately air stable, but were much more stable in solution at ambient temperatures than were **2** or **3**.



4 R = $C(O)CH_3$
5 R = CO_2CH_3

Synthetic studies related to the formation of **2** and **3** but utilizing the potentially chelating bidentate ligand 1,2-bis(diphenylphosphino)ethane instead of triphenylphosphine were subsequently undertaken. Compounds **6** and **7** were prepared in DME at 0 °C from reactions of 1,2-bis(diphenylphosphino)ethane, sodium acetyl- or carbomethoxycyclopentadienide, and silver triflate, or from reactions of [1,2-bis(diphenylphosphino)]silver(I) triflate and sodium acetyl- or carbomethoxycyclopentadienide under the same conditions. After workup, **6** and **7** were obtained in yields of 72% and 55%, respectively. Both **6** and **7** were moderately air stable, decomposing on heating to 70 °C, and were more stable in solution than the triphenylphosphine analogues **2** and **3**.

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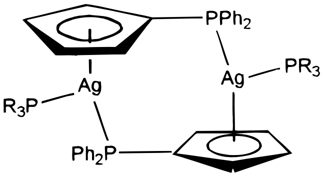
In view of the successful formation of **6** and **7**, several attempts were made to synthesize related bis(triphenylphosphine) complexes (**8**). However, reactions of either sodium acetyl- or carbomethoxycyclopentadienide with bis(triphenylphosphine)silver(I) triflate produced only the monophosphine analogues **2** or **3** as well as the free ligand triphenylphosphine. Similar results were obtained starting with bis(triphenylphosphine)copper triflate. The monophosphine complexes **4** and **5** were obtained, and no bis(triphenylphosphine) derivatives (**8**) could be isolated.

Cyclopentadienylsilver compounds have also been synthesized that contain the diphenylphosphinocyclopentadienyl ligand. This ligand is unique in that it leads to stabilized dinuclear complexes where the phosphorus atom attached to the ring bridges a second metal center. Two complexes (**9**, **10**) were obtained from reactions of equimolar amounts of silver chloride with the appropriate phosphine in refluxing toluene. After cooling the solution to −78 °C, lithium diphenylphosphinocyclopentadienide was added, and the reaction mixture was allowed to stir for several hours before crystallization at −20 °C. Compounds **9** and **10** were obtained in yields of 49% and 36%, respectively.

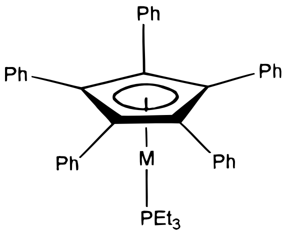


9 R = C_6H_5
10 R = C_2H_5

Organosilver complexes **9** and **10** were very stable thermally as well as air stable for extended periods of time. On heating, **9** decomposed at 180 °C, while **10** decomposed at 125 °C.

Complex **9** was also synthesized from a reaction of lithium diphenylphosphinocyclopentadienide, triphenylphosphine, and silver triflate in CH_2Cl_2 as the solvent. Under these conditions, the product crystallized as a solvate with 0.5 equiv of CH_2Cl_2, as determined by both ^1H NMR and elemental analysis. As in the case of complexes **6** and **7**, definitive conclusions concerning the bonding in these new organosilver compounds must await the results of X-ray diffraction studies.

Several highly substituted cyclopentadienyl derivatives of silver and copper have also been synthesized and characterized. Compounds **11** and **12** were prepared at −78 and −10 °C, respectively, from reactions of sodium pentaphenylcyclopentadienide and $[Cl(PEt_3)M]_4$ (where M = Ag or Cu) in THF. After allowing the reaction mixture to warm to room temperature, removal of the solvent and subsequent extraction and crystallization from diethyl ether produced **11**and **12** in yields of 56% and 44%, respectively. Compounds **11** and **12** had decomposition points of ca. 40 and 116 °C, respectively, and **11** was both thermally and air sensitive. The related compound $Cu(\eta^5\text{-}C_5Ph_5)(PPh_3)$ was found to be stable in air for at least several days.[13] In contrast, attempts to prepare $(\eta^5\text{-}C_5Me_5)Ag(PR_3)$ (R = Ph, Et) in our laboratory have been unsuccessful. $(\eta^5\text{-}C_5Me_5)Cu(PR_3)$ analogues are known to be considerably more air sensitive than the parent compounds $(\eta^5\text{-}C_5H_5)Cu(PR_3)$.[9]



11 M = Ag
12 M = Cu

The cyclopentadienylsilver compounds synthesized in this study have also been characterized by ^{31}P NMR techniques, including variable-temperature solution NMR and solid-state NMR. ^{31}P NMR is a valuable tool in this regard, since silver has two NMR active isotopes. ^{107}Ag and ^{109}Ag are both spin one-half nuclei with high natural abundances of 52% and 48%, respectively. At ambient temperatures in solution, Ag−P coupling is generally very broad in silver−phosphine compounds, due to rapid ligand exchange on the NMR time scale. However, the coupling can be observed in the solid state or at low temperatures in solution.[17−19]

For the organosilver compounds **2** and **3**, broad singlets were observed in the ^{31}P NMR spectra at 20 °C and broad doublets at −70 °C. The broadening is consistent with ligand exchange between the phosphine and the cyclopentadienylsilver moiety, and the low temperature doublet is consistent with bonding between phosphorus and silver. For **2**, the doublet was centered at 10.82 ppm with $^1J(Ag{-}P)$ coupling = 470 Hz. For **3**, the doublet was centered at 9.70 ppm with $^1J(Ag{-}P) =$ 361 Hz. Both of these coupling values are much larger than the value for the parent compound **1** ($^1J(Ag{-}P) \cong$ 200 Hz).[14] These results suggest that the silver−phosphorus bonding in **2** and **3** is stronger compared with **1**.

For compounds **6** and **7**, which both contain the potentially chelating ligand 1,2-bis(diphenylphosphino)ethane instead of triphenylphosphine, only one phosphorus resonance was observed in each case. For **7**, this resonance appeared as a broad singlet at 20 °C, and at −70 °C as a doublet centered at 4.21 ppm with $^1J(Ag{-}P) = 244$ Hz. The ^{31}P NMR solution spectrum of **6** appeared as a broad doublet at 20 °C and as a pair of sharp doublets at −40 °C, due to individual $^1J(^{109}Ag{-}P)$ and $^1J(^{107}Ag{-}P)$ couplings being observed. The pattern was centered at 4.46 ppm, with $^1J(^{109}Ag{-}P)$ and $^1J(^{107}Ag{-}P) = 266$ and 231 Hz, respectively. This represents the first example where the individual isotope splittings have been resolved for a cyclopentadienylsilver−phosphine derivative. The ratio of the coupling values is 1.15, which exactly equals the theoretical value.[20]

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For compounds **9** and **10**, binuclear complexes are formed in which two nonequivalent phosphorus nuclei are present. A silver atom is bonded to a cyclopentadienyl ring, a phosphorus atom of a phosphine, and a phosphorus atom of a second diphenylphosphinocyclopentadienyl ring. The low-temperature solution ^{31}P NMR spectra and the ^{31}P solid-state NMR spectra exhibited similar patterns for each complex.

The splitting patterns for **9** and **10** are explained by two types of couplings. Each nonequivalent ^{31}P nuclei is split by a silver nuclei (^1J) and by the other ^{31}P nuclei (^2J). For **9**, the pattern for the ^{31}P solution spectrum at −70 °C was centered at −6.62 ppm and exhibited ^1J(Ag−P) = 366 Hz, ^1J(Ag−P) = 422 Hz, and ^2J(P−P) = 130 Hz. The solution spectrum for **10** at −70 °C was centered at −4.50 ppm and exhibited ^1J(Ag−P) = 439 Hz, ^1J(Ag−P) = 408 Hz, and ^2J(P−P) = 149 Hz. The solid-state spectra for **9** and **10** also support the proposed structures. For **9**, ^1J(Ag−P) = 354 Hz, ^1J(Ag−P) 402 Hz, and ^2J(P−P) = 134 Hz, and the pattern was centered at −4.99 ppm. For **10**, ^1J(Ag−P) = 413 Hz, ^1J(Ag−P) = 386 Hz, and ^2J(P−P) = 155 Hz, and the pattern was centered at −10.50 ppm. The dimeric complexes **9** and **10** exhibited enhanced air and thermal stabilities, due to the presence of an additional phosphorus atom for back-bonding to silver and especially by having chelated dimeric structures.

Experimental Section

All operations were performed under an argon atmosphere using Schlenk and glovebox techniques. Argon was deoxygenated by BASF catalyst and dried with P_2O_5 and molecular sieves. Diethyl ether, 1,2-dimethoxyethane (DME), and tetrahydrofuran (THF) were predried over sodium wire and distilled from sodium−potassium alloy under argon. Methylene chloride was distilled under argon from calcium hydride. Pentane and hexane were distilled from sodium−potassium alloy under argon. All other solvents were used as commercially obtained. CAMAG alumina was heated under vacuum on a rotary evaporator to remove water and oxygen. The alumina was then deactivated with 5% (by weight) argon-satuarated water and stored under argon prior to use. Celite was obtained from Fisher Scientific Co. and was used with no prior treatment.

Ethyl acetate, methyl acetate, dimethyl carbonate, triethylphosphine, and chlorodiphenylphosphine were obtained from Aldrich Chemical Co. Silver trifluoromethanesulfonate (triflate), silver chloride, copper(I) chloride, copper(I) bromide, triphenylphosphine, and 1,2-bis(diphenylphosphino)ethane were also purchased from Aldrich. Cyclopentadiene dimer was purchased from Aldrich and cracked in refluxing decalin to give cyclopentadiene monomer, which was used immediately after distillation. Sodium acetylcyclopentadienide,[1,21] mono(triphenylphosphine)silver(I) trifluoromethanesulfonate,[22] sodium carbomethoxycyclopentadienide,[1,23] tetrakis[bromotriphenylphosphinecopper(I)],[24] bis(triphenylphosphine)silver(I) trifluoromethanesulfonate,[22] bis(triphenylphosphine)copper(I) trifluoromethanesulfonate,[25] [1,2-bis(diphenylphosphino)ethane]silver(I) trifluoromethanesulfonate,[22] lithium diphenylphosphinocyclopentadienide,[26] tetrakis[chloro(triethylphosphine)silver(I)],[27] sodium pentaphenylcyclopentadienide,[28] and tetrakis[chloro(triethylphosphine)copper(I)][29] were prepared by literature procedures.

^{1}H NMR spectra were obtained on either IBM 80 or 200 MHz spectrometers, or on Varian XL-200 or XL-300 spectrometers, and are referenced to tetramethylsilane as an internal standard. Solution ^{31}P (taken at room temperature unless otherwise noted) were obtained on either IBM 80 MHz, Varian XL-300, or MSL-300 spectrometers and are referenced to 85% H_3PO_4 in D_2O as an external standard. Solid-state ^{31}P NMR spectra were obtained on an IBM 200 MHz spectrometer and are referenced to $CaHPO_4$. IR spectra were recorded on a Perkin-Elmer 1310 spectrometer. Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

(η-Acetylcyclopentadienyl)(triphenylphosphine)silver (2). In a Schlenk flask were placed sodium acetylcyclopentadienide (0.39 g, 3.0 mmol) and triphenylphosphine (0.79 g, 3.0 mmol). The flask was cooled to −10 °C, and then ca. 50 mL of DME was added. Silver triflate (0.79 g, 3.0 mmol) was taken up in ca. 15 mL of DME and was slowly added to the cooled reaction mixture. After stirring at −10 °C for 3 h, a light-colored precipitate appeared. The reaction mixture was filtered cold, and the off-white solid was washed several times with cold DME. The solid was dried under vacuum for 24 h to yield 0.83 g (58%) of (η-acetylcyclopentadienyl)(triphenylphosphine)silver(I) (**2**).

Compound **2** can also be synthesized under the same reaction conditions using stoichiometric amounts of mono(triphenylphosphine)silver(I) triflate and sodium acetylcyclopentadienide. The yield of **2** was comparable to that of the above procedure. ^{1}H NMR ($CDCl_3$): δ 2.20 (3 H, s, CH_3), 6.06 (2 H, m, $CpH_{3,4}$), 6.56 (2 H, m, $CpH_{2,5}$), 7.10−7.48 (15 H, m, C_6H_5). ^{31}P NMR (75% CH_2Cl_2/25% $CDCl_3$, −70 °C): δ 10.82 (br d, ^1J(Ag−P) = 470 Hz). IR (νCO, CH_2Cl_2): 1643 cm^{-1}. Anal. Calcd for $C_{25}H_{22}AgOP$: C, 62.91; H, 4.65; Ag, 22.60. Found: C, 62.94; H, 4.63; Ag, 21.90.

(η-Carbomethoxycyclopentadienyl)(triphenylphosphine)silver(I) (3). In a Schlenk flask were placed sodium carbomethoxycyclopentadienide (0.58 g, 4.0 mmol) and triphenylphosphine (1.0 g, 4.0 mmol). The flask was cooled to −10 °C, and ca. 50 mL of DME was added. Silver triflate (1.0 g, 4.0 mmol) was taken up in ca. 15 mL of DME and was then slowly added to the reaction mixture. After stirring at −10 °C for 2−3 h, the DME was removed under reduced pressure. The residue was extracted with 25 mL of cold CH_2Cl_2 and then filtered through a 1 cm alumina plug. The golden-yellow solution was concentrated, and a small amount of diethyl ether was added. The solution was crystallized at −20 °C to yield 1.12 g (57%) of (η-carbomethoxycyclopentadienyl)(triphenylphosphine)silver(I) as an off-white solid. Compound **3** can also be synthesized under the same reaction conditions using stoichiometric amounts of mono(triphenylphosphine)silver(I) triflate and sodium carbomethoxycyclopentadienide. The yield was comparable to that of the above procedure. ^{1}H NMR ($CDCl_3$): δ 3.72 (3 H, s, CH_3), 6.24 (2 H, m, $CpH_{3,4}$), 6.97 (2 H, m, $CpH_{2,5}$), 7.15−7.75 (15 H, m, C_6H_5). ^{31}P NMR (75% CH_2Cl_2/25%$CDCl_3$, −70 °C): δ 9.70 (br d, ^1J(Ag−P) = 361 Hz). IR (ν_{CO}, CH_2Cl_2): 1639 cm^{-1}. Anal. Calcd for $C_{25}H_{22}AgO_2P$: C. 60.87; H, 4.50. Found: C, 60.55; H, 4.55.

(η-Acetylcyclopentadienyl)(triphenylphosphine)copper(I) (4). In a Schlenk flask were placed sodium acetylcy-

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clopentadienide (0.49 g, 3.8 mmol) and tetrakis[bromotriphenylphosphinecopper] (1.0 g, 0.62 mmol). The flask was cooled to −78 °C, and 35 mL of THF was added via a syringe. The reaction mixture was stirred at −78 °C for 2 h before warming to 25 °C and then stirred for an additional 2 h. The THF was removed under reduced pressure, and the residue was extracted with ca. 45 mL of hexane. After filtration through Celite, the light yellow solution was kept at −20 °C to form 0.42 g (39%) of (η-acetylcyclopentadienyl)(triphenylphosphine)copper(I). An analytically pure sample was obtained by an additional crystallization from hexane at −20 °C to give small off-white crystals. ^{1}H NMR ($CDCl_3$): δ 2.34 (3 H, s, CH_3), 6.09 (2 H, m, $CpH_{3,4}$), 6.67 (2 H, m, $CpH_{2,5}$), 7.25−7.46 (15 H, m, C_6H_5). ^{31}P NMR (75% CH_2Cl_2/25% $CDCl_3$, −70 °C): δ 7.78 (br s). IR (ν_{CO}, CH_2Cl_2): 1622 cm^{-1}. Anal. Calcd for $C_{25}H_{22}CuOP$: C, 69.35; H, 5.12. Found: C, 68,79; H, 5.28.

(η-Carbomethoxycyclopentadienyl)(triphenylphosphine)copper(I) (5). In a Schlenk flask were placed sodium carbomethoxycyclopentadienide (0.70 g, 4.8 mmol) and tetrakis[bromotriphenylphosphinecopper] (1.0 g, 6.2 mmol). The flask was cooled to −78 °C, and ca. 40 mL of THF was added via a syringe. The reaction mixture was stirred at −78 °C for 2 h before warming slowly to 25 °C and then stirred for an additional 2 h. The THF was removed under reduced pressure, and the residue was extracted with ca. 40 mL of diethyl ether. After filtration through Celite, the light orange solution was kept at −20 °C to form 0.72 g (64%) of (η-carbomethoxycyclopentadienyl)(triphenylphosphine)copper(I). An analytically pure sample was obtained by several crystallizations from diethyl ether at −20 °C to give small white crystals. ^{1}H NMR ($CDCl_3$): δ 3.72 (3 H, s, CH_3), 6.02 (2 H, m, $CpH_{3,4}$), 6.67 (2 H, m, $CpH_{2,5}$), 7.20−7.54 (15 H, m, C_6H_5). ^{31}P NMR (75% CH_2Cl_2/25% $CDCl_3$, −70 °C): δ 23.83 (br s). IR (ν_{CO}, CH_2Cl_2): 1678 cm^{-1}. Anal. Calcd for $C_{25}H_{22}CuO_2P$: C, 66.88; H, 4.94. Found: C, 66.92; H, 5.04.

(η-Acetylcyclopentadienyl)[1,2-bis(diphenylphosphino)ethane]silver(I) (6). In a Schlenk flask were placed sodium acetylcyclopentadienide (0.59 g, 4.5 mmol) and 1,2-bis(diphenylphosphino)ethane (1.8 g, 4.5 mmol). The flask was cooled to 0 °C, and ca. 90 mL of DME was added. Silver triflate (1.16 g, 4.5 mmol) was taken up in ca. 25 mL of DME and was then slowly added to the cold reaction mixture. The reaction was stirred at 0 °C for 2 h, and the DME was removed under reduced pressure. The residue was extracted with ca. 45 mL of cold CH_2Cl_2. The CH_2Cl_2 solution was filtered through a 2 cm alumina plug and concentrated, and then a small amount of diethyl ether was added. The solution was allowed to crystallize at −78 °C to yield 2.0 g (72%) of (η-acetylcyclopentadienyl)[1,2-bis(diphenylphosphino)ethane]silver(I) as an off-white solid. Compound **6** can also be synthesized under the same reaction conditions, using stoichiometric amounts of [1,2-bis(diphenylphosphino)ethane]silver(I) triflate and sodium acetylcyclopentadienide. The yield was comparable with that of the above procedure. ^{1}H NMR ($CDCl_3$): δ 2.17−2.40 (7 H, m, CH_3 and CH_2CH_2), 6.23 (2 H, m, $CpH_{3,4}$), 6.86 (2 H, m, $CpH_{2,5}$), 7.20−7.51 (20 H, m, C_6H_5). ^{31}P NMR (75% CH_2Cl_2/25% $CDCl_3$, −70 °C): δ 4.46 (dd, $^1J(^{109}Ag-P)$ = 266 Hz, $^1J(^{107}Ag-P)$ = 231 Hz. IR (ν_{CO}, CH_2Cl_2): 1642 cm^{-1}. Anal. Calcd for $C_{33}H_{31}AgOP_2$: C, 64.61; H, 5.09. Found: C, 64.13; H, 5.01.

(η-Carbomethoxycyclopentadienyl)[1,2-bis(diphenylphosphino)ethanesilver(I) (7). In a Schlenk flask were placed sodium carbomethoxycyclopentadienide (0.32 g, 2.2 mmol) and 1,2-bis(diphenylphosphino)ethane (0.88 g, 2.2 mmol). The flask was cooled to 0 °C, and ca. 50 mL of DME was added. Silver triflate (0.57 g, 2.2 mmol) was taken up in ca. 15 mL of DME and was then slowly added to the cold reaction mixture. The reaction was stirred at 0 °C for 2 h, and then the DME was removed under reduced pressure. The residue was extracted with ca. 20 mL of cold CH_2Cl_2. The CH_2Cl_2 solution was filtered through a 1 cm alumina plug and concentrated, and a small amount of diethyl ether was added. The solution was allowed to crystallize at −78 °C to yield 0.76 g (55%) of (η-carbomethoxycyclopentadienyl)[(1,2-bis(diphenylphosphino)ethane]silver(I) as an off-white solid. Compound **7** can also be synthesized under the same reaction conditions, using stoichiometric amounts of [1,2-bis(diphenylphospino)ethane]silver(I) triflate and sodium carbomethoxycyclopentadienide. The yield was comparable to that of the above procedure. ^{1}H NMR ($CDCl_3$): δ 2.14−2.49 (4 H, br m, CH_2-CH_2), 3.65 (3 H, s, CH_3), 6.25 (2 H, m, $CpH_{3,4}$), 6.94 (2 H, m, $CpH_{2,5}$), 7.10−7.92 (20 H, m, C_6H_5). ^{31}P NMR (75% CH_2Cl_2/25% $CDCl_3$, −70 °C): δ 4.21 (d, ^1J(Ag−P) = 2.44 Hz). IR (ν_{CO}, CH_2Cl_2): 1643 cm^{-1}. Anal. Calcd for $C_{33}H_{31}AgO_2P_2$: C, 62.97; H, 4.96, Ag, 17.14. Found: C, 63.16; H, 5.16; Ag, 16.96.

[(η-Diphenylphosphinocyclopentadienyl)(triphenylphosphine)silver(I)]$_2$ (9). In a Schlenk flask were placed silver chloride (0.72 g, 5.0 mmol) and triphenylphosphine (1.31 g, 5.0 mmol). Approximately 100 mL of toluene was added, and the combined solids were heated at reflux for 18 h. The opaque solution was then cooled to −78 °C, and a suspension of lithium diphenylphosphinocyclopentadienide (1.30 g, 5.0 mmol) in 25 mL of toluene was slowly added. The reaction was stirred at −78 °C for 4 h and was then gradually warmed to 25 °C and stirred for an additional hour. The reaction mixture was filtered through Celite to yield a light yellow solution. The solution was cooled to −20 °C to give 1.52 g (49%) of [(η-diphenylphosphinocyclopentadienyl)(triphenylphosphine)silver(I)]$_2$ as light yellow crystals.

Compound **9** can be synthesized under the same reaction conditions using separate stoichiometric amounts of mono(triphenylphosphine)silver(I) triflate and lithium diphenylphosphinocyclopentadienide. The yield was comparable to that of the above procedure. ^{1}H NMR ($CDCl_3$): δ 6.l9−6.39 (4 H, br m, C_5H_4), 6.91−7.45 (25 H, m, C_6H_5). ^{31}P NMR (75% CH_2Cl_2/25% $CDCl_3$, −70 °C): δ −6.62 (m, ^1J(Ag−P) = 366 Hz, ^1J(Ag−P) = 422 Hz, ^2J(P−P) = 130 Hz). Solid-state ^{31}P NMR: δ −4.99 (m, ^1J(Ag−P) = 354 Hz, ^1J(Ag−P) = 402 Hz, ^2J(P−P) = 134 Hz. Anal. Calcd for $C_{70}H_{58}Ag_2P_4$: C, 67.86; H, 4.72. Found: C, 68.16; H, 4.85.

[(η-Diphenylphosphinocyclopentadienyl)(triphenylphosphine)silver(I)]$_2$·0.5CH_2Cl_2. In a Schlenk flask were placed lithium diphenylphosphinocyclopentadienide (0.79 g, 3.0 mmol) and triphenylphosphine (0.79 g, 3.0 mmol). The flask was cooled to −78 °C, and ca. 65 mL of CH_2Cl_2 was added. Silver triflate (0.78 g, 3.0 mmol) suspended in ca. 15 mL of CH_2Cl_2 was then slowly added to the cold reaction mixture. The reaction was stirred at −78 °C for 3 h and then gradually warmed to 0 °C. The reaction mixture was filtered over Celite to yield a yellow solution. The solution was cooled to −20 °C to yield 0.85 g (43%) of [(η-diphenylphosphinocyclopentadienyl)(triphenylphosphine)silver(I)]$_2$·0.5CH_2Cl_2 as light yellow crystals. ^{1}H NMR ($CDCl_3$): δ 5.30 (1 H, s, 0.5 CH_2Cl_2), 6.33−6.45 (4 H, br m, C_5H_4), 7.09−7.43 (25 H, m, C_6H_5). Anal. Calcd for $C_{71}H_{60}Ag_2Cl_2P_4$: C, 64.42; H; 4.56. Found: C, 64.87; H, 4.54.

[(η-Diphenylphosphinocyclopentadienyl)(triethylphosphine)silver(I)]$_2$ (10). In a Schlenk flask were placed silver chloride (0.72 g, 5.0 mmol) and triethylphosphine (0.74 mL, 5.0 mmol). Approximately 80 mL of toluene was added, and the reaction mixture was heated at reflux for 2 h. The opaque solution was cooled to −78 °C, and a suspension of lithium diphenylphosphinocyclopentadienide (1.30 g, 5.0 mmol) in ca. 20 mL of toluene was slowly added. The opaque solution was stirred at −78 °C for 4 h before gradually being warmed to 25 °C. As the reaction mixture warmed, it turned yellow. The mixture was stirred at 25 °C for an additional 30 min and was then filtered over Celite. The light yellow solution was cooled at −20 °C to yield 0.86 g (36%) of [(η-diphenylphosphinocyclopentadienyl)(triethylphosphine)silver(I)]$_2$ as colorless crystals. ^{1}H NMR ($CDCl_3$): δ 0.64−1.59 (15 H, m, C_2H_5), 6.35−6.48 (4 H, br m, C_5H_4), 7.10−7.61 (15 H, m, C_6H_5). ^{31}P NMR

(75% CH_2Cl_2/25% $CDCl_3$, −70 °C): δ −4.50 (m, ^1J(Ag−P) = 439 Hz, ^1J(Ag−P) = 408 Hz, ^2J(P−P) = 149 Hz). Solid-state ^{31}P NMR: δ −10.50 (m, ^1J(Ag−P) = 413 Hz, ^1J(Ag−P) = 386 Hz, ^2J(P−P) = 155 Hz. Anal. Calcd for $C_{46}H_{58}Ag_2P_4$: C, 58.12; H, 6.15. Found: 58.02; H, 6.03.

(η-Pentaphenylcyclopentadienyl)(triethylphosphine)silver(I) (11). In an argon-flushed 100 mL Schlenk flask were placed sodium pentaphenylcyclopentadienide (1.0 g, 2.1 mmol) and tetrakis[chloro(triethylphosphine)silver] (0.55 g, 0.52 mmol). The flask was cooled to −78 °C, and ca.75 mL of THF was added. The golden-brown reaction mixture was stirred at −78 °C for 3 h before gradual warming to 0 °C. The THF was removed under reduced pressure, and the residue was extracted with ca. 50 mL of diethyl ether. The purple solution was cooled to −20 °C, yielding 0.79 g (56%) of (η-pentaphenylcyclopentadienyl)(triethylphosphine)silver(I) as crystalline purple solid.[30] ^{1}H NMR ($CDCl_3$): δ 0.92−1.80 (15 H, m, CH_2CH_3), 6.49−7.55 (25 H, m, C_6H_5). ^{31}P NMR ($CDCl_3$): δ 0.53 (br s). Anal. Calcd for $C_{41}H_{40}AgP$: C, 73.32; H, 6.00. Found: C, 74.02; H, 6.85.

(η-Pentaphenylcyclopentadienyl)(triethylphosphine)copper(I) (12). In a Schlenk flask were placed sodium pentaphenylcyclopentadienide (0.95 g, 2.0 mmol) and tetrakis[chloro(triethylphosphine)copper] (0.43 g, 0.5 mmol). The flask was cooled to −10 °C, and ca. 40 mL of THF was added. The reaction mixture was initially pink, but within 15 min it turned yellow. After stirring at −10 °C for 2 h, the reaction mixture was allowed to gradually warm to 25 °C and was stirred for an additional 2 h. The THF was removed under reduced pressure and the residue was extracted with ca. 25 mL of diethyl ether. After filtration through Celite, the yellow solution was cooled to −20 °C, yielding 0.55 g (44%) of (η^5-pentaphenylcyclopentadienyl)(triethylphosphine)copper(I) as small white crystals, mp 116 °C dec. ^{1}H NMR ($CDCl_3$): δ 0.87−1.83 (15 H, m, CH_2CH_3), 6.88−7.08 (25 H, m, C_6H_5). ^{31}P NMR (CH_2Cl_2/D_2O): δ 11.68 (br s). Anal. Calcd for $C_{41}H_{40}CuP$: C, 78.50; H, 6.43. Found: C, 77.98; H, 6.45.

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[30] Compound **11** was both thermally and air sensitive, and attempts to further purify **11** to obtain an analytically pure sample were unsuccessful.