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(η^5-Cyclopentadienyl)- and (η^5-Pentamethylcyclopentadienyl)copper Compounds Containing Phosphine, Carbonyl, and η^2-Acetylenic Ligands

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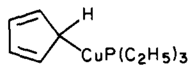
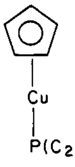
Abstract: The formation, spectra, and properties of a series of (η^5-pentamethylcyclopentadienyl)copper compounds have been investigated. Reactions between lithium pentamethylcyclopentadienide and $[ClCu(R_3P)]_4$ (R = C_6H_5, C_2H_5) produced $[\eta^5\text{-}C_5(CH_3)_5](PR_3)Cu$ in yields of 43% and 78%, respectively. A reaction between lithium pentamethylcyclopentadienide and copper(I) chloride in ethyl ether solution in the presence of carbon monoxide led to $[\eta^5\text{-}C_5(CH_3)_5](CO)Cu$. This carbonyl derivative was both air- and temperature-sensitive and decomposed in solution over 0 °C to afford copper metal, carbon monoxide, and decamethyl-1,1′-dihydrofulvalene. A reaction between copper(I) chloride and bis(trimethylsilyl)acetylene produced $[\eta^2\text{-}(CH_3)_3SiC{\equiv}CSi(CH_3)_3]_2Cu_2Cl_2$ in 76% yield. Treatment of the latter dimer with lithium pentamethylcyclopentadienide in ethyl ether solution afforded $[\eta^5\text{-}C_5(CH_3)_5][\eta^2\text{-}(CH_3)_3SiC{\equiv}CSi(CH_3)_3]Cu$. The parent compound $(\eta^5\text{-}C_5H_5)[\eta^2\text{-}(CH_3)_3SiC{\equiv}CSi(CH_3)_3]Cu$ was also obtained starting with lithium cyclopentadienide. Both products were air- and temperature-sensitive but could be readily converted into the respective triphenylphosphine derivatives. The complexes $[\eta^5\text{-}C_5(CH_3)_5][\eta^2\text{-}(CH_3)_3SiC{\equiv}CSi(CH_3)_3]Cu$ and $(\eta^2\text{-}C_5H_5)[\eta^2\text{-}(CH_3)_3SiC{\equiv}CSi(CH_3)_3]Cu$ represent the first "mixed-sandwich" compounds of copper, as predicted by the effective atomic number (EAN) rule.

The synthesis, molecular structures, bonding modes, and relative stabilities of cyclopentadienylcopper compounds have been the subject of considerable research in recent years. The first well-characterized cyclopentadienylcopper compound was described in 1956 by Wilkinson and Piper.[1] The reaction of Cu_2O with cyclopentadiene and triethylphosphine produced $(C_5H_5)[P(C_2H_5)_3]Cu$ (**1**), for which an η^1-cyclopentadienyl structure (**1a**) was proposed. Whitesides and Fleming supported this proposal of an η^1-cyclopentadienyl ring in **1** on the basis of a variable-temperature ^{1}H NMR study.[2] In 1970, detailed IR studies by Cotton and Marks[3] as well as X-ray diffraction investigations by Cotton and Takats[4] and by Dellacre et al.[5] demonstrated unequivocally that **1** possessed an η^5-cyclopentadienyl structure (**1b**), as did the related compound $(C_5H_5)[P(C_6H_5)_3]Cu$ (**2**).[6]



1a



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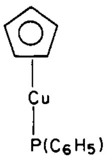

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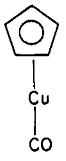

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Cotton and Marks[8] have also provided a much more useful route to phosphine compounds such as **1** and **2**, as well as to the related phosphite and isocyanide compounds $(\eta^5\text{-}C_5H_5)(L)Cu$ [L = $P(OCH_3)_3$ or CH_3NC] from reactions between $(LCuX)_4$ intermediates and cyclopentadienylthallium.

(η^5-Cyclopentadienyl)carbonylcopper (**3**) has proved more difficult to prepare and study compared to the phosphine analogues **1** and **2**, due to its intrinsic instability and the fact that stable precursors of the type $[Cu(CO)X]_n$ are unknown. However, the reaction of copper(I) chloride with C_5H_5Tl in the presence of carbon monoxide and a small amount of $(C_4H_9)_3P$ in pentane at 0 °C gave a pentane solution of **3**.[8] This compound was stable only under an atmosphere of carbon monoxide at low temperature and could not be entirely separated from the solvent. An alternate and useful method for the preparation of $(\eta^5\text{-}C_5H_5)(L)Cu$ compounds, including **1** and **3**, has been described by Saegusa et al.[9] from reactions of $(CH_3)_3CO\text{-}Cu(L)$ intermediates and cyclopentadiene.

Cotton and Marks[3] have suggested that it is possible to regard $(\eta^5\text{-}C_5H_5)(PR_3)Cu$ compounds as members of a rather long isoelectronic series in which the $(\eta^5\text{-}C_5H_5)M$ moieties interact with five-, four-, three-, and two-electron ligands. We have likewise pointed out that the effective atomic number (EAN) rule predicts a series of "mixed-sandwich" compounds which contain both an $(\eta^5\text{-}C_5H_5)$ ring as well as η-carbocyclic ring systems of varying size and hapticity.[10,11] Among the first period transition metals, the "mixed sandwich" compounds $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Cr$ (**4**),[12,13] $(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)Mn$ (**5**),[14,15] $(\eta^5\text{-}C_5H_5)_2Fe$ (**6**),[16,17] $(\eta^4\text{-}C_4H_4)(\eta^5\text{-}C_5H_5)Co$ (**7**),[18-20] and $(\eta^3\text{-}C_3R_3)(\eta^5\text{-}C_5H_5)Ni$ (**8**)[10,21]

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(2) Whitesides, G. M.; Fleming, J. S. *J. Am. Chem. Soc.* **1967**, *89*, 2855.

(3) Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 7281.

(4) Cotton, F. A.; Takats, J. *J. Am. Chem. Soc.* **1970**, *92*, 2353.

(5) Delbaere, L. T. J.; McBride, D. W.; Ferguson, R. B. *Acta Crystallogr. Sect. B* **1970**, *B26*, 515.

(6) The conclusion of Whitesides and Fleming of an η^1-cyclopentadienyl structure for **1** were based on low-temperature ^{1}H NMR spectra of **1** recorded in sulfur dioxide solution, and their interpretation is consistent with such a structural formulation.[2] Later studies by Marks[7] indicated that the closely related compound $(\eta^5\text{-}C_5H_5)[P(C_4H_9)_3]Cu$ readily formed an SO_2 adduct when prepared at low temperature in pentane solution. As pointed out by Marks,[7] it seems very likely that the species observed by Whitesides and Fleming in sulfur dioxide solution was some sort of adduct such as $(\eta^1\text{-}C_5H_5)(PR_3)(SO_2)_2Cu$, a result which would explain the ^{1}H NMR spectra and also satisfy the effective atomic number rule. The SO_2 in Marks' adduct appeared to dissociate readily, and rapidly reversible dissociation may be involved in the fluxional behavior of **1**.

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(14) Coffield, T. H.; Sandel, V.; Closson, R. D. *J. Am. Chem. Soc.* **1957**, *79*, 5826 (η^5-methylcyclopentadienyl analogue).

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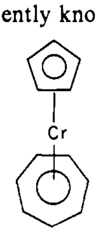
are presently known.



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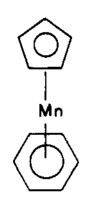

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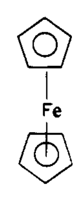

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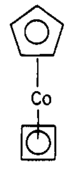

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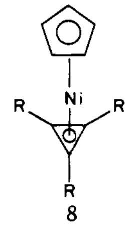
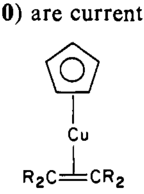


8

While $(\eta^5\text{-}C_5H_5)(L)Cu$ compounds in which L represents a phosphine, phosphite, carbonyl, or isocyanide ligand are therefore reasonably well established, the isoelectronic "mixed-sandwich" compounds $(\eta^5\text{-}C_5H_5)Cu(\eta^2\text{-olefin})$ (**9**) and $(\eta^2\text{-}C_5H_5)Cu(\eta^2\text{-acetylene})$ (**10**) are currently unknown. A logical extension of the above concepts would predict that copper compounds of these types might be isolable and characterizable.[23] In the present article, we describe the synthesis, spectral features, and chemical properties of the first "mixed-sandwich" compounds of copper, as well as the first series of organocopper compounds which contain the η^5-pentamethylcyclopentadienyl ligand.



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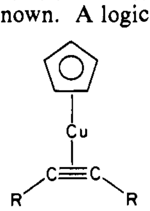
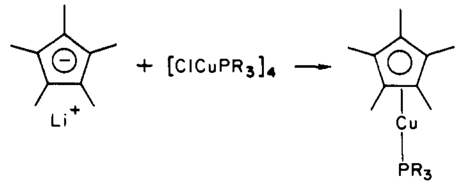


10

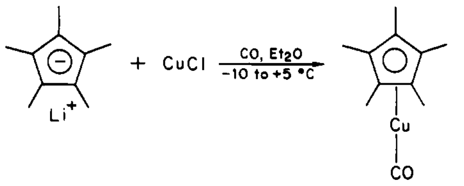
Results and Discussion

The relative stabilities of η^5-pentamethylcyclopentadienyl derivatives of the transition, lanthanide, and actinide metals vis-a-vis their η^5-cyclopentadienyl analogues are of considerable current interest.[29,30] η^5-Pentamethylcyclopentadienyl derivatives of copper are currently unknown, so it was of interest to attempt their synthesis and to compare their properties with the well-known $(\eta^5$-cyclopentadienyl)copper counterparts discussed above. $(\eta^5$-Pentamethylcyclopentadienyl)(triphenylphosphine)copper (**11**) was readily prepared in 43% yield from a reaction between lithium pentamethylcyclopentadienide and $[ClCuP(C_6H_5)_3]_4$. Similarly, $(\eta^5$-pentamethylcyclopentadienyl)(triethylphosphine)copper (**12**) was obtained in 78% yield from lithium pentamethylcyclopentadienide and $[ClCuP(C_2H_5)_3]_4$. Phosphine compounds **11** and **12** were extremely air-sensitive in solution; in solid form, **11** was more stable than **12**. Both **11** and **12** appear to be considerably more air-sensitive than the respective parent compounds **2** and **1**. In contrast, $[\eta^5\text{-}C_5H_4C(O)CH_3][P(C_2H_5)_3]Cu$, which contains an electron-withdrawing substituent on the η^5-cyclopentadienyl ring, is appreciably more air-stable than is **1**.[31] Both **11** and **12** exhibited single sharp resonances for the η^5-pentamethylcyclopentadienyl protons in C_6D_6 solution at δ 2.31 and 2.36, respectively.



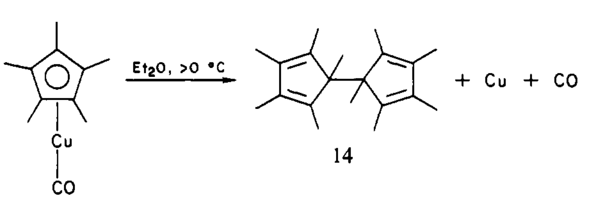
11, $R = C_6H_5$
12, $R = C_2H_5$

An etheral solution of lithium pentamethylcyclopentadienide reacted with copper(I) chloride in the presence of carbon monoxide between −10 and 5 °C to produce $(\eta^5$-pentamethylcyclopentadienyl)carbonylcopper (**13**). The parent compound **3** has previously been prepared in pentane solution by a related method involving cyclopentadienylthallium.[8] Like **3**, compound **13** could not be isolated in pure form, nor completely separated from the solvent, due to its very limited stability. Solutions of **13** were both air- and temperature-sensitive. Gradual decomposition of **13** occurred at 0 °C under carbon monoxide, and rapid decomposition occurred at 25 °C. Compound **13** was stable under a carbon monoxide atmosphere at −78 °C, however.



13

The decomposition of **13** in solution was found to produce carbon monoxide, copper metal, and the organic coupling product decamethyl-1,1′-dihydrofulvalene (**14**). In a separate experiment, **14** was prepared in 88% yield from a reaction between lithium pentamethylcyclopentadienide and copper(I) chloride in ethyl ether at 25 °C. Fulvalene derivative **14** obtained in these studies was shown to be identical with an authentic sample prepared by the method of Jutzi and Kohl.[32] The coupling of organic compounds with copper salts is a well-established process.[33-35]



14

13

Structural information concerning **13** was obtained, with some difficulty, by using spectroscopic techniques. The preparation of

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[21] The parent compound (R = H) has not yet been synthesized. The first authenticated example of an "η^5,η^3-mixed-sandwich" compound was the triphenyl derivative ($R = C_6H_5$), reported by one of us in 1970.[10] Subsequently, a tri-*tert*-butyl analogue ($R = t\text{-}C_4H_9$) has also been described.[22]

[22] Olander, W. K.; Brown, T. L. *J. Am. Chem. Soc.* **1972**, *94*, 2140.

[23] For the early transition metals Ti and V, diamagnetic "mixed-sandwich" compounds such as $(\eta^5\text{-}C_5H_5)Ti(\eta^9\text{-}C_9H_9)$ and $\eta^5\text{-}C_5H_5)V(\eta^8\text{-}C_8H_8)$ are likewise predictable. While organometallic compounds of this type are presently unknown and indeed may not be capable of synthesis due to steric or other factors, it is of interest that the isoelectronic compounds $(\eta^5\text{-}C_5H_5)Ti(\eta^8\text{-}C_8H_8)$ (paramagnetic, one unpaired electron)[24,25] and $(\eta^5\text{-}C_5H_5)V(\eta^7\text{-}C_7H_7)$ (paramagnetic, one unpaired electron)[26,27] are known and well-characterized. In this regard, a reaction between $(\eta^5\text{-}C_5H_5)TiCl_3$ and C_9H_9Li produced a green diamagnetic compound of composition $C_{14}H_{14}Ti$. Spectral data suggests that this mixed-sandwich compound is best formulated as $(\eta^5\text{-}C_5H_5)Ti(\eta^7\text{-}C_9H_9)$, however, in which seven of the nine π-electrons of the C_9H_9 ring are involved in bonding with Ti, resulting in a 16-electron configuration for the metal.[28]

[24] Van Oven, H. O.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1969**, *19*, 313.

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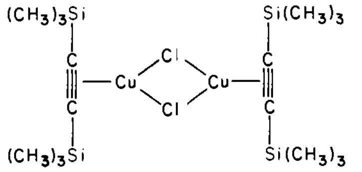
13 as described above produced a pale green etheral solution after filtration of the reaction mixture. When the ether was removed under vacuum at 0 °C, the solution turned orange and then red-brown. Treatment with carbon monoxide restored the green color. Upon continued removal of the ether under vacuum, a copper mirror appeared. A satisfactory, but tedious method of removing a small volume of ether was to prepare a solution of **13** under nitrogen and then pass a stream of carbon monoxide over it. This method gave concentrations of **13** in ether for which suitable ^{1}H NMR spectra could be obtained in toluene-d_8. The ^{1}H NMR spectrum of **13** at −5 °C exhibited a singlet at δ 2.03 for the pentamethylcyclopentadienyl protons. The spectrum also showed resonances for ethyl ether and for **14**.

The IR spectrum of **13** in ethyl ether solution exhibited a strong band at 2075 cm^{-1}, assignable to a terminal metal carbonyl stretching frequency. The corresponding frequency for the parent compound **3** in pentane has been reported as 2093 cm^{-1}. Such a shift to lower energy for **13** vs. **3** is approximately that predicted[36] for the introduction of five methyl substituents, and can be attributed to enhanced π-back-bonding to the carbonyl ligand as a result of increased electron density on the metal atom caused by the methyl groups. Analogous trends have also recently been demonstrated by us in the case of the decamethylmetallocene dicarbonyls (M = Ti, Zr, Hf) relative to their cyclopentadienyl counterparts.[30]

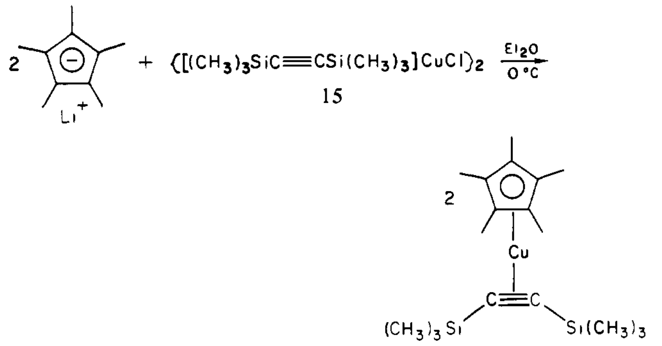
The conversion of **13** into a stable derivative provided additional evidence for its formation. Treatment of an etheral solution of **13** with an equimolar amount of triethylphosphine [based on the starting reagents $C_5(CH_3)_5Li$ and CuCl] produced **12** in 10% yield. The phosphine derivative obtained in this reaction had properties identical with those of **12** synthesized independently.

A reaction between copper(I) chloride and bis(trimethylsilyl)acetylene in ethyl ether at 25 °C produced a 76% yield of an adduct formulated as **15**. The structure of **15** was determined by its ^{1}H NMR, IR, and mass spectra as well as by elemental analysis. The latter indicated that a 1:1 adduct of bis(trimethylsilyl)acetylene and copper(I) chloride had been formed. The ^{1}H NMR spectrum of **15** exhibited a single resonance at δ 0.22 for the trimethylsilyl protons. The IR spectrum of **15** in hexane contained a very weak band at 1965 cm^{-1} which could be attributed to a coordinated acetylene. The mass spectrum of **15** showed peaks at *m/e* 170 for $[(CH_3)_3SiC{\equiv}CSi(CH_3)_3]^+$, *m/e* 155 for $[(CH_3)_2SiC{\equiv}CSi(CH_3)_3]^+$, *m/e* 97 for $[(CH_3)_2SiC_2]^+$, and *m/e* 73 for $[(CH_3)_3Si]^+$. Noteworthy peaks greater than *m/e* 170 were not observed. A subsequent X-ray diffraction study on **15** has demonstrated it to have a dimeric structure in the solid state, however.[37,38] When di-*tert*-butylacetylene was allowed to react with copper(I) chloride in a manner similar to the preparation of **16**, the corresponding complex $\{[(CH_3)_3CC{\equiv}CC(CH_3)_3]CuCl\}_n$ (δ 1.33 (s)) was obtained, but only in trace amounts. Moreover, reactions between copper(I) chloride and diphenylacetylene, 3-hexyne, dimethyl acetylenedicarboxylate, bis(pentafluorophenyl)acetylene, dimethyl fumarate, or 2,3-dimethyl-2-butene did not produce any detectable copper chloride adducts.



15

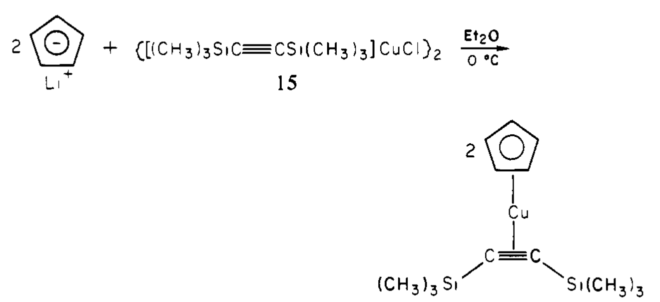
Complex **15** reacted with lithium pentamethylcyclopentadienide in ethyl ether at 0 °C to produce (η^5-pentamethylcyclopentadienyl)[η^2-bis(trimethylsilyl)acetylene]copper (**16**). Compound **16** was isolated as a red-brown oily solid, which was both air- and temperature-sensitive, and could not be obtained in analytically pure form. Carbon, hydrogen, and copper analyses of this product gave values within 3% of the theoretical percentages, however. Attempts to crystallize **16** from pentane at −78 °C were unsuccessful.



16

The ^{1}H NMR spectrum of **16** in C_6D_6 at −5 °C exhibited singlet resonances at δ 0.08 and 2.16 in the ratio of 18:15, assignable to the bis(trimethylsilyl)acetylene and η^5-pentamethylcyclopentadienyl ligands, respectively. As demonstrated by ^{1}H NMR, small amounts of **14** were invariably present in samples of **16**. The IR spectrum of **16** in hexane solution exhibited a strong coordinated acetylenic strretching band at 1915 cm^{-1}.

A similar reaction between lithium cyclopentadienide and **15** in ethyl ether at 0 °C produced (η^5-cyclopentadienyl)[η^5-bis(trimethylsilyl)acetylene]copper (**17**). Compound **17** was likewise air- and temperature-sensitive, but in contrast to the pentamethyl analogue **16**, could be crystallized from pentane at −78 °C as pale yellow crystals. Upon being warmed to 25 °C under vacuum, these crystals turned red-brown. Carbon, hydrogen, and copper analyses of this solid, however, were consistent with the proposed structure.



17

The ^{1}H NMR spectrum of **17** in C_6D_6 at −5 °C exhibited singlet resonances at δ 0.08 and 6.13 in the ratio of 20:5, assignable to the bis(trimethylsilyl)acetylene and η^5-cyclopentadienyl ligands, respectively. The IR spectrum of **17** contained a strong coordinated acetylenic stretching band at 1955 cm^{-1}, approximately 40 cm^{-1} higher than was observed for **16**.

The mixed-sandwich compounds **16** and **17** were both stable for several days under nitrogen at −30 °C but decomposed at 25 °C within 30 min. As shown by ^{1}H NMR, thermal decomposition of **16** resulted in the formation of the coupling product **14** as well as free bis(trimethylsilyl)acetylene. When **16** decomposed, a copper mirror was always observed in the NMR tube. The thermal decomposition of **17** as shown by ^{1}H NMR gave no apparent organic compounds other than free bis(trimethylsilyl)acetylene. Again, a copper mirror was invariably formed in the NMR tube.

When a hexane solution of **16** at 0 °C was treated with triphenylphosphine, the band at 1915 cm^{-1} disappeared in the IR spectrum. In a related experiment, treatment of **16** with an equimolar amount of triphenylphosphine (based on starting **15**) produced **11** in 15% yield. When a hexane solution of **17** was treated with triphenylphosphine, the band at 1955 cm^{-1} likewise disappeared. Further, a reaction of **17** with an equimolar amount

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of triphenylphosphine (based on starting **15**) produced **2** in 34% yield.

The mixed-sandwich compound **16** could also be formed when the carbonyl derivative **13** was treated with bis(trimethylsilyl)acetylene and when lithium pentamethylcyclopentadienide was allowed to react with copper(I) chloride in the presence of bis(trimethylsilyl)acetylene. Compound **16** could not be isolated from these reactions, although spectral evidence supported its formation in each case.

Experimental Section

All operations were carried out under dry, purified nitrogen by using standard Schlenk or vacuum line techniques. Ethyl ether was predried over sodium wire and distilled from sodium–benzophenone under argon. Tetrahydrofuran (THF) was predried over KOH, dried over sodium wire, and distilled from sodium–benzophenone under argon. Pentane was dried over calcium hydride and distilled under argon. Bis(trimethylsilyl)acetylene (99%) was obtained from Aldrich Chemical Co. Triphenylphosphine and triethylphosphine were obtained from Eastman Kodak Co. and Pressure Chemical Co., respectively. IR spectra were recorded on a Perkin-Elmer 237-B spectrometer. Low-temperature control was achieved with a V-6040 variable-temperature controller, and the temperature was calibrated with peak separations in a methanol sample. Mass spectra were obtained on a Perkin-Elmer Hitachi RMU-6L mass spectrometer. Copper(I) chloride was prepared according to the method of Keller and Wykoff[39] and was stored in the dark under nitrogen. 1,2,3,4,5-Pentamethylcyclopentadiene was prepared by the method of Threlkel and Bercaw.[40] Microanalyses were conducted by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. Tetrachlorotetrakis(triethylphosphine)copper and tetrachlorotetrakis(triphenylphosphine)copper were prepared according to literature procedures.[41]

Preparation of Lithium Cyclopentadienide. C_5H_5Li was prepared by modifying a published procedure.[42] To 30.0 mL (0.365 mol) of freshly cracked cyclopentadiene in 50 mL of ethyl ether at 0 °C under nitrogen was added dropwise 0.378 mol of methyllithium in ethyl ether solution. The reaction mixture became cloudy white, and gas was evolved. Following the addition, the ice bath was removed and the mixture was stirred for 1 h. The mixture was then filtered and the residue washed with ethyl ether. The solid was dried under reduced pressure, giving 24.23 g (92%) of lithium cyclopentadienide as white, air-sensitive powder.

Preparation of Lithium Pentamethylcyclopentadienide. In a 250-mL three-neck round-bottom flask equipped with nitrogen inlet and outlet valves were placed 1,2,3,4,5-pentamethylcyclopentadiene (10.90 g, 80.0 mmol) and 100 mL of ethyl ether. To this was added 1.6 M methyllithium (63.0 mL, 100.0 mmol). After the addition was complete, the mixture was heated to reflux overnight. The reaction mixture was then allowed to cool to room temperature and the resulting precipitate collected under nitrogen. The precipitate was washed with pentane/ether and dried under reduced pressure to afford 9.56 g (84%) of lithium pentamethylcyclopentadienide as a white air-sensitive solid.

Preparation of (η^5-Pentamethylcyclopentadienyl)(triphenylphosphine)copper (11). In a 250-mL single-neck round-bottom flask with a side arm were placed lithium pentamethylcyclopentadienide (0.86 g, 6.0 mmol) and tetrachlorotetrakis(triphenylphosphine)copper (2.19 g, 1.5 mmol). The flask was cooled to −10 °C and ca. 100 mL of THF was added. The reaction mixture was stirred for 6 h while warming slowly to 25 °C. The THF was removed under vacuum and the resulting residue extracted with ethyl ether. The combined extracts were filtered through decolorizing carbon and Celite. The filtrate was concentrated under vacuum and then cooled to −78 °C. After the filtrate was left standing overnight at this temperature, 1.21 g (43%) of (η^5-pentamethylcyclopentadienyl)(triphenylphosphine)copper was obtained. An analytical sample was prepared by several additional recrystallizations from ethyl ether at −78 °C to give off-white crystals: mp 145 °C dec (N_2); ^1H NMR (C_6D_6) δ 2.31 [s, 15 H, $C_5(CH_3)_5$], 6.88–7.20 [m, 15 H, $P(C_6H_5)_3$]. Anal. Calcd for $C_{28}H_{30}CuP$: C, 72.94; H, 6.56; P, 6.72. Found: C, 72.73; H, 6.58; P, 7.20.

Preparation of (η^5-Pentamethylcyclopentadienyl)(triethylphosphine)copper (12). In a 250-mL single-neck round-bottom flask were placed lithium pentamethylcyclopentadienide (0.45 g, 3.2 mmol) and tetrachlorotetrakis(triethylphosphine)copper (0.67 g, 0.78 mmol). The flask was cooled to −78 °C, and ca. 100 mL of ethyl ether was added. The reaction mixture was stirred for 6 h while being warmed slowly to 25 °C. The ether was then removed under vacuum and the resulting residue extracted with pentane. The combined extracts were filtered, and the filtrate was concentrated under vacuum. The concentrate was cooled to −78 °C overnight to give 0.76 g (78%) of (η^5-pentamethylcyclopentadienyl)(triethylphosphine)copper as white crystals. An analytical sample was obtained by several additional recyrstallizations from pentane at −78 °C: mp 152 °C dec (N_2); ^1H NMR (C_6D_6) δ 0.71–1.13 [m, 15 H, $P(C_2H_5)_3$], 2.36 [s, 15 H, $C_5(CH_3)_5$]. Anal. Calcd for $C_{16}H_{30}CuP$: C, 60.63; H, 9.54; P, 9.77. Found: C, 60.82; H, 9.40; P, 9.84.

Preparation of Decamethyl-1,1′-dihydrofulvalene (14). In a 100-mL single-neck round-bottom flask were placed lithium pentamethylcyclopentadienide (0.51 g, 3.4 mmol) and copper(I) chloride (0.36 g, 3.4 mmol). To this was added ca. 50 mL of ethyl ether, and the mixture was stirred at 25 °C for 4.5 h. After 2 h, a dark gray precipitate was present as well as a copper mirror. The solution was filtered and the solvent removed under vacuum to give 0.43 g (88%) of decamethyl-1,1′-dihydrofulvalene: ^1H NMR (C_6D_6) δ 1.15 (s, 6 H, 1,1′-CH_3), 1.69 and 1.77 (s, 24 H, 2,2′-, 3,3′-, 4,4′-, 5,5′-CH_3).

Preparation of (η^5-Pentamethylcyclopentadienyl)carbonylcopper (13). In a small Schlenk tube were placed lithium pentamethylcyclopentadienide (0.21 g, 1.5 mmol) and copper(I) chloride (0.15 g, 1.5 mmol). The tube was cooled to −10 °C, and ca. 25 mL of ethyl ether was added. A slow stream of carbon monoxide was then passed over the well-stirred solution. The reaction mixture was allowed to warm to 5 °C, and stirring was continued for 2 h. The mixture was subsequently filtered under an atmosphere of carbon monoxide through Celite into another Schlenk tube which had been cooled to −78 °C. The ether was concentrated under vacuum at 0 °C to ca. 10 mL and further via a stream of carbon monoxide to give a pale green solution of **13**: ^1H NMR (toluene-d_8 at −5 °C) δ 2.03 [s, $C_5(CH_3)_5$]; IR (ethyl ether) ν_{CO} 2075 (s) cm^{-1}.

Reaction of (η^5-Pentamethylcyclopentadienyl)carbonylcopper with Triethylphosphine. A solution of (η^5-pentamethylcyclopentadienyl)carbonylcopper was prepared as described above from lithium pentamethylcyclopentadienide (0.30 g, 2.1 mmol), copper(I) chloride (0.21 g, 2.1 mmol), ca. 30 mL of ethyl ether, and carbon monoxide. After filtration of the solution into a Schlenk tube which had been cooled to −78 °C, triethylphosphine (3.00 mL, 2.1 mmol) was added at this temperature. The mixture was allowed to warm to 25 °C, and the solvent was removed under vacuum. When the solution was cooled to −78 °C, 0.07 g (10%) of (η^5-pentamethylcyclopentadienyl)(triethylphosphine)copper was obtained as white crystals.

Preparation of [η^2-Bis(trimethylsilylacetylene)]chlorocopper(I) Dimer (15). In a 100-mL single-neck round-bottom flask with a side arm were placed copper(I) chloride (1.82 g, 19.4 mmol) and bis(trimethylsilyl)acetylene (3.14 g, 18.4 mmol). To this was added ca. 50 mL of ethyl ether, and the mixture was stirred at 25 °C for 20 h. The mixture was then poured into 300 mL of ether, and the solution was filtered. The filtrate was concentrated to ca. 50 mL and cooled to −20 °C. The resulting white crystals were collected and washed with a small amount of cold pentane to give 3.80 g (76%) of [η^2-bis(trimethylsilyl)acetylene]chlorocopper(I) dimer. An analytical sample was obtained by several recrystallizations from ethyl ether at −20 °C: mp 170 °C dec (N_2); ^1H NMR (C_6D_6) δ 0.22 [s, $Si(CH_3)_3$]; IR (hexane) $\nu_{C\equiv C}$ 1965 cm^{-1}; MS, *m/e* 170 [$(CH_3)_3SiC\equiv CSi(CH_3)_3{}^+$]. Anal. Calcd for $C_8H_{18}ClCuSi_2$: C, 35.67; H, 6.73. Found: C, 35.91; H, 6.82.

Preparation of (η^5-Cyclopentadienyl)[η^2-bis(trimethylsilyl)acetylene]copper (17). In a small Schlenk tube were placed lithium cyclopentadienide (0.80 g, 11.1 mmol) and [η^2-bis(trimethylsilyl)acetylene]chlorocopper(I) dimer (1.62 g, 3.0 mmol). The tube was cooled to −10 °C, and ca. 15 mL of THF was added. The reaction mixture was allowed to stir for 2 h at −10 °C to 0 °C. The THF was then removed under vacuum (0.01 mmHg) at 0 °C. The resulting residue was extracted with cold pentane and filtered into another Schlenk tube through decolorizing carbon and Celite which had been cooled to 0 °C. The filtrate was concentrated at 0 °C to a small volume and the Schlenk tube cooled to −78 °C. This process produced 0.54 g (30%) of faint yellow crystals. The pentane was decanted, and the crystals were washed with a small amount of cold pentane. The residual pentane was removed under vacuum (0.01 mmHg) to give a red-brown solid: ^1H NMR (C_6D_6 at −5 °C) δ 0.08 [s, 18 H, $Si(CH_3)_3$], 6.13 (s, 5 H, C_5H_5); IR (hexane) $\nu_{C\equiv C}$ 1955 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{23}CuSi_2$: C, 52.21; H, 7.75; Cu, 21.25. Found: C, 51.90; H, 7.72; Cu, 21.3.

Preparation of (η^5-Pentamethylcyclopentadienyl)[η^2-bis(trimethylsilyl)acetylene]copper (16). In a small Schlenk tube were placed lithium pentamethylcyclopentadienide (0.43 g, 3.0 mmol) and [η^2-bis(trimethylsilyl)acetylene]chlorocopper(I) dimer (0.78 g, 1.45 mmol). The tube was cooled to −10 °C, and 10 mL of THF was added. The reaction mixture was allowed to stir for 1.5 h at −10 to 0 °C. The THF was then removed under vacuum (0.01 mmHg) while the Schlenk tube was

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maintained at 0 °C. The resulting mixture was extracted with cold pentane and filtered through Celite into another Schlenk tube which had been cooled to 0 °C. The pentane was removed under vacuum at 0 °C to give initially a dark red oil which on prolonged standing under vacuum turned into 0.11 g (10%) of a red-brown oily solid. Attempts to crystallize this compound from a small amount of pentane at −78 °C were unsuccessful: ^{1}H NMR (C_6D_6 at −5 °C) δ 0.08 [s, 18 H, $Si(CH_3)_3$], 2.16 [s, 15 H, $C_5(CH_3)_5$]; IR (hexane) $\nu_{C\equiv C}$ 1915 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{33}CuSi$: C, 58.56; H, 9.01, Cu, 17.21. Found: C, 55.56; H, 8.93; Cu, 20.1.

Reaction of (η^5-Cyclopentadienyl)[η^2-bis(trimethylsilyl)acetylene]copper with Triphenylphosphine. In a small Schlenk tube were place lithium cyclopentadienide (0.24 g, 3.3 mmol) and [η^2-bis(trimethylsilyl)acetylene]chlorocopper(I) dimer (0.67 g, 1.25 mmol). The tube was cooled to −10 °C, and ca. 10 mL of THF was added. The mixture was stirred between −10 and 0 °C for 2 h. At 0 °C, triphenylphosphine (0.65 g, 2.5 mmol) was then added and the mixture stirred for 1 h while being warmed to 25 °C. The THF was removed under vacuum and the resulting residue extracted with ethyl ether. The combined ether extracts were filtered through Celite, and the filtrate was concentrated under vacuum. The Schlenk tube was cooled to −78 °C to produce white crystals. The crystals were washed with cold pentane and dried under vacuum to give 0.33 g (34%) of (η^5-cyclopentadienyl)(triphenylphosphine)copper, whose properties were identical with those of an authentic sample.

Reaction of (η^5-Pentamethylcyclopentadienyl)[η^2-bis(trimethylsilyl)acetylene]copper with Triphenylphosphine. In a small Schlenk tube were placed lithium pentamethylcyclopentadienide (0.28 g, 2.0 mmol) and [η^2-bis(trimethylsilyl)acetylene]chlorocopper(I) dimer (0.48 g, 0.9 mmol). The tube was cooled to −10 °C, and 10 mL of THF was added. The mixture was stirred for 2 h between −10 and 0 °C. At 0 °C, triphenylphosphine (0.45 g, 1.7 mmol) was then added and the mixture stirred for 30 min at 25 °C. The THF was removed under vacuum and the resulting residue extracted with ethyl ether. The combined ether extracts were filtered through Celite and decolorizing carbon, and the filtrate was concentrated under vacuum. The Schlenk tube was cooled to −78 °C to produce white crystals. The latter were dried under vacuum to give 0.12 g (15%) of (η^5-pentamethylcyclopentadienyl)(triphenylphosphine)copper, whose properties were identical with those of an authentic sample.

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Registry No. **11**, 86024-09-1; **12**, 86024-10-4; **13**, 86045-48-9; **14**, 69446-48-6; **15**, 77997-76-3; **16**, 86024-11-5; **17**, 86024-12-6; $[ClCuPPh_3]_4$, 50409-58-0; $[ClCuPEt_3]_4$, 55606-52-5; CuCl, 7758-89-6; lithium cyclopentadienide, 16733-97-4; lithium pentamethylcyclopentadienide, 51905-34-1; (η^5-cyclopentadienyl)(triphenylphosphine)copper, 31781-67-6.

Synthesis of Inequivalently Bridged Cyclopentadienyl Dimers of Molybdenum and a Comparison of Their Reactivities with Unsaturated Molecules and with Hydrogen

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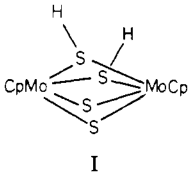
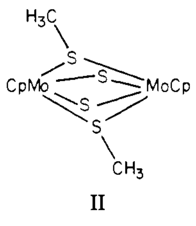
Abstract: A series of dimeric cyclopentadienyl complexes of molybdenum which are bridged by two inequivalent dithiolate ligands have been synthesized. The new complexes include $(CpMo)_2(S_2CH_2)(SC_2H_4S)$, IVa, $(CpMo)_2(S_2C(CH_3)_2)(SC_2H_4S)$, IVb, $(Cp'Mo)_2(S_2CS)(SC_2H_4S)$, V, and $(CpMo)_2(SCHCPhS)(SC_2H_4S)$, VI (Cp = C_5H_5, Cp′ = $CH_3C_5H_4$). The relative tendencies of the ethanedithiolate ligands to eliminate ethylene have been compared for the above series. The studies establish that the ligand lability is influenced by the nature of the other dithiolate bridge as well as by substituents on the cyclopentadienyl ligands. Alkynes and cumulenes react with the ethanedithiolate ligands in IV–VI to displace ethylene and form derivatives with unsaturated dithiolate bridges. Some of these unsaturated complexes can be hydrogenated under the mild conditions of 1–2 atm of H_2 at 60 °C. The reactions result in the stoichiometric reduction of alkynes to *cis*-alkenes, allenes to alkenes, and ketenes to aldehydes. The relationship between hydrocarbon lability in the dithiolate ligands and hydrogenation activity is discussed. Two X-ray diffraction studies of complexes which contain a η^2-μ-1,1-alkanedithiolate ligand have been completed. The acetylene adduct $(Cp'Mo)_2(S_2CH_2)(SC_2H_2S)$ crystallizes in space group $P2_1/c$ with a = 7.855 (2) Å, b = 8.433 (2) Å, c = 13.428 (3) Å, and β = 104.61 (2)°. The methylated derivative $(Cp'Mo)_2(S_2CH_2)(SCH_3)_2$ crystallizes in space group *Pbcn* with a = 17.143 (4) Å, b = 12.023 (2) Å, and c = 8.931 (2) Å. Structural parameters for these dimers are compared with those of other cyclopentadienylmolybdenum dimers with bridging thiolate ligands.

Cyclopentadienylmolybdenum complexes of the formula $[CpMo(\mu\text{-}S)(\mu\text{-}SR)]_2$ (R = H or alkyl) have been reported previously,[2] but the different stereochemistries which are possible for the bridging ligands in these complexes have made it difficult to compare reactivities. For example, in the hydrosulfido complex, the two bridging sulfido ligands form a reactive site which interacts with a variety of unsaturated molecules. This reactivity suggests that the complex contains a cis orientation of sulfido ligands (e.g., I) or can readily rearrange to this type of isomer. In contrast the sulfido ligands in the complex $[CpMo(\mu\text{-}S)(\mu\text{-}SCH_3)]_2$ do not react with ethylene or acetylene under similar mild conditions, suggesting that only trans isomers of this complex are formed (e.g., II).



I



II

We are interested in establishing how a range of structural and electronic effects influence the reactivity of two bridging sulfido ligands which are constrained in a cis configuration. Such an

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