Organometallics 1987, *6*, 2489–2494

Mononuclear Complexes of Copper(I) and Silver(I) Featuring the Metals Exclusively Bound to Carbon. Synthesis and Structure of (η^5-Pentamethylcyclopentadienyl)[(triphenylphosphonio)-(triphenylphosphoranylidene)methyl]copper(I)

Chr. Zybill* and G. Müller

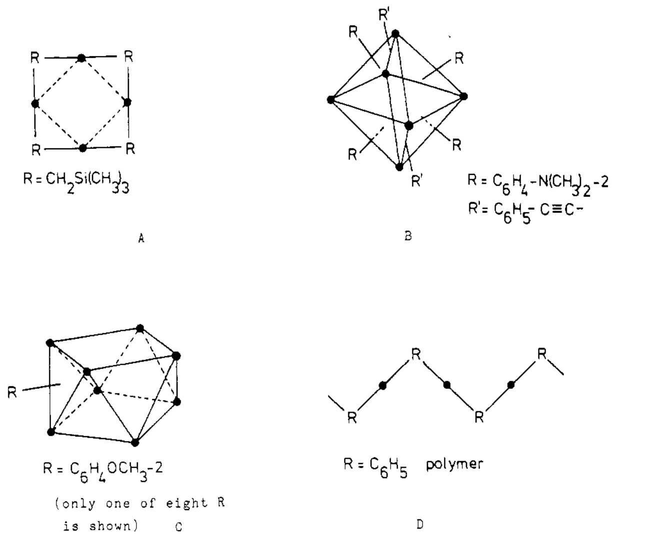
Anorganisch-chemisches Institut der Technischen Universität München, D-8046 Garching, West Germany

Received February 13, 1987

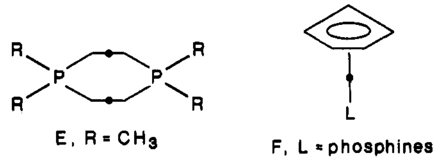
Hexaphenylcarbodiphosphorane, $(C_6H_5)_3P{=}C{=}P(C_6H_5)_3$, forms monomeric 1:1 adducts $[(C_6H_5)_3P{=}C{=}P(C_6H_5)_3]MCl$ with CuCl and AgCl. Chloride displacement by the cyclopentadienides $M'C_5R_5$ (M' = Li, Na; R = H, CH_3) affords the compounds $(\eta^5\text{-}C_5R_5)M[(C_6H_5)_3P{=}C{=}P(C_6H_5)_3]$. Alternatively, $(\eta^5\text{-}C_5R_5)Cu[(C_6H_5)_3P{=}C{=}P(C_6H_5)_3]$ (R = CH_3) is accessible by a stepwise reaction of $M'C_5R_5$ with CuCl and $(C_6H_5)_3P{=}C{=}P(C_6H_5)_3$. The intermediate cationic copper(I) half-sandwich complex $[C_5R_5Cu^+]$ has been trapped with triphenylphosphine. The structure of $(\eta^5\text{-}C_5(CH_3)_5)Cu[(C_5H_5)_3P{=}C{=}P(C_6H_5)_3]$ shows the Cu(I) center to be linearly coordinated by the Cp* ligand and the ylidic C atom of hexaphenylcarbodiphosphorane. The Cu–C(ylide) bond (1.922 (6) Å) is comparable to other 2c–2e bonds. (Crystals of $(\eta^5\text{-}C_5(CH_3)_5)Cu[(C_6H_5)_3P{=}C{=}P(C_6H_5)_3]$ are monoclinic of space group $P2_1/n$ with a = 11.495 (1) Å, b = 17.147 (2) Å, c = 20.181 (2) Å, β = 101.11 (1)°, V = 3903.2 Å^3, and Z = 4. Refinement of 286 parameters on 3499 observables produced R_w = 0.054, $w = 1/\sigma^2(F_o)$.)

Introduction

Organometallic compounds of copper(I) are the subject of continued interest because they are an important alternative to Grignard reagents.[1] Early work about "phenylcopper" and related Cu(I) compounds focused on the complex structures of $(R\text{–}Cu)_n$, which are now known to form aggregates of various size.[2] Depending on either the electronic or the stereochemical requirements of the substituents, several basic structures can be distinguished (A–D). A common principle of these aggregates is the



formation of multicenter bonds between copper and carbon.[3] The [(trimethylsilyl)methyl]copper(I) tetramer A,[4] e.g., forms an almost square-planar array of copper atoms with linearly coordinated Cu(I). With less bulky substituents higher aggregates like B,[5] C,[6] and D[7] are preferred. Mononuclear species with 2c–2e bonds of the type $[R\text{–}Cu\text{–}R]^-$, R = CH_3, C_6H_5, or 2,6-$(CH_3)_2C_6H_4$,[8] are still rare, and only few examples are known like the Cu ylide complex E[9] or the monomeric CuCp complexes F.[10] Most of the monomeric Cu(I) compounds F, however, have been restricted to examples with phosphines as stabilizing ligands.[11]



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Double ylides of phosphorus are versatile donor ligands in transition-metal and main-group chemistry.[12] Particularly the extremely bulky hexaphenylcarbodiphosphorane, 1, is of considerable interest because it is expected to stabilize low coordination numbers. Pertinent examples are already known with Cu, Ag, Au,[14] and Pt[15] but also with S, Se, Te, and I.[16]

In recent work, hexaphenylcarbodiphosphorane was probed as a stabilizing ligand for mononuclear complexes of Cu(I), in which the Cu atom forms only Cu–C bonds,[14] and this paper describes preparation, characterization, and structure of compounds of type F with L representing a bis-ylidic phosphorane.

Experimental Section

All experiments were performed with standard Schlenk tube techniques under an atmosphere of dry argon. The silver compounds were handled under exclusion of light. THF and pentane were distilled from NaK alloy prior to use; benzene, toluene, and diethyl ether were distilled from sodium–benzophenone in an atmosphere of dry nitrogen. Methanol and ethyl acetate were dried over molecular sieve. Cyclopentadienyllithium was used as a 1.6 M solution in THF; (pentamethylcyclopentadienyl)lithium and -sodium were prepared according to Jutzi.[17] All other chemicals were commercially available. Chromatography was carried out under argon with a column of 1-m length and 2-cm diameter equipped with a cooling jacket. The packing material (silica gel 200 mesh, sodium sulfate) was dried in vacuo and handled in an atmosphere of argon.

Infrared spectra were recorded on a Perkin-Elmer 577 instrument. The spectra were taken either as Nujol or Hostaflon mulls between KBr plates, as KBr pellets, or in solution in KBr cells. The ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL FX 60 and JEOL FX 270 spectrometers and ^{31}P NMR spectra on a Bruker XL 90. For the ^{1}H and ^{13}C NMR spectra the signals of the deuteriated solvents were taken as a reference; for ^{31}P NMR spectroscopy a H_3PO_4 capillary was used as the standard. UV spectra were taken on a Cary 17D. The mass spectra were recorded on a Varian MAT 311 A by EI or FD techniques. The elemental analyses were performed in the Mikroanalytisches Laboratorium der Technischen Universität München by M. Barth, U. Graf, and G. Schuller.

Bis(triphenylphosphoranylidene)methane, 1. 1 was synthesized by a procedure originally published by Birum and Matthews and later improved in our laboratories.[13] The phosphonium salt precursors are obtained by stepwise reaction of dibromomethane with triphenylphosphine. Triphenylphosphine (262.3 g, 1 mol) and 174.8 g (1 mol) of dibromomethane are heated to 100 °C in toluene for 24 h. The mixture is allowed to cool to room temperature and filtered. The (bromomethyl)triphenylphosphonium bromide is dissolved in 50 mL of dry methanol, reprecipitated by slow addition of 500 mL of ethyl acetate, filtered, and dried in vacuo; yield 148.3 g (34.4%) of white microcrystalline material.

A mixture of 43.6 g (0.1 mol) (bromomethyl)triphenylphosphonium bromide, 52.4 g (0.2 mol) of triphenylphosphine, and 50 g of triphenyl phosphate is heated for 6 h to 110 °C with stirring by a mechanical stirrer. After the solution is cooled to room temperature, 500 mL of benzene is added to the waxy solid and the mixture is stirred for further 30 min. The undissolved methylene[bis(triphenylphosphonium)] dibromide is now filtered off and reprecipitated twice from methanol with ethyl acetate as described previously: yield 32.8 g (47%) of white powder; mp 312.5 °C.

For the synthesis of 1, a given quantity of methylene[bis(triphenylphosphonium)] dibromide—typically 34.9 g (50 mmol)—is suspended in 500 mL of THF. At 50 °C 2.5 equiv of $NaNH_2$ are added portionwise to the reaction mixture. Depending on the activity of the $NaNH_2$, the mixture is refluxed for 1–24 h further until the evolution of NH_3 has stopped. The yellow bis(triphenylphosphoranylidene)methane, 1, is filtered, and the volatile substances are stripped off in a vacuum. The compound can be crystallized from toluene as yellow needles with a yield of 24.7 g (92.2%): mp 207 °C; ^{31}P NMR (C_6D_6) δ −2.5.

[(Triphenylphosphonio)(triphenylphosphoranylidene)methyl]copper(I) Chloride, 2. 2 is prepared by addition of a saturated solution of 1 (444.0 mg, 0.83 mmol) in about 50 mL of THF to a suspension of 82 mg (0.83 mmol) of CuCl in 10 mL of THF. After 5 min of vigorous stirring the almost clear yellow mixture is filtered and the filtrate concentrated in vacuo to 20 mL. At −15 °C 2 crystallizes as yellow cubes; fast cooling affords a solvate, 2·THF. 2: yield 486 mg (92%); mp 241 °C dec; ^{1}H NMR (CD_2Cl_2) δ 7.2–7.9 (m); ^{31}P NMR (C_6D_6) δ + 16.5; MS (30 eV), m/e 635 (M^+), 536 (M^+ − CuCl). Anal. Calcd for $C_{37}H_{30}ClCuP_2$ (635.59): C, 69.92; H, 4.76; P, 9.75; Cl, 5.58; Cu, 10.00. Found: C, 68.95; H, 4.59; P, 9.54; Cl, 5.43; Cu, 9.9.

(η^5-Cyclopentadienyl)[(triphenylphosphonio)(triphenylphosphoranylidene)methyl]copper(I), 3a. To a solution of 635 mg (1 mmol) of 2 in 100 mL of THF is added 0.69 mL (1.1 mmol) of a 1.6 M solution of cyclopentadienyllithium in THF dropwise at −40 °C. The mixture is stirred for 2 h at −20 °C. The brown solution is filtered through a short column (10 cm) packed with silica gel. **3a** crystallizes at −15 °C from THF as yellowish needles in a yield of 345.9 mg (52.0%): mp 30 °C dec; ^{1}H NMR (THF-d_8) δ 6.1 (m, 5 H), 6.9 (m, 18 H), 7.3–7.9 (m, 12 H); ^{13}C NMR (THF-d_8) δ 99.3 (virt quin, ^1J(HC) = 160.9 Hz, ^2J(HC) = 6.9 Hz), 128.4 (AM_2X, ^1J(HC) = 160.4 Hz), 131.1 (AM_2X, ^1J(HC) = 160.9 Hz), 133.7 (AM_2X, ^1J(HC) = 167.2 Hz), 127.3 (AM_2); ^{31}P NMR (C_6D_6) δ +8.5; IR (Nujol mull) 1012 cm^{-1}. Anal. Calcd for $C_{42}H_{35}CuP_2$ (665.23): C, 75.83; H, 5.30. Found: C, 75.91; H, 5.29.

(η^5-Pentamethylcyclopentadienyl)[(triphenylphosphonio)(triphenylphosphoranylidene)methyl]copper(I), 3b. To a solution of 635.6 mg (1.0 mmol) of 2 in 100 mL of THF is added 153.2 mg (1.1 mmol) of (pentamethylcyclopentadienylpotassium] portionwise. The mixture is stirred at 0 °C for 2 h and then purified by careful filtration through a layer of 10 cm of Na_2SO_4 in a water-cooled chromatography column.

The red solution is concentrated in vacuo to 10 mL. The concentrate is covered with a layer of 10 mL of pentane and stored at −15 °C. **3b** crystallizes as bright orange needles with a yield of 478.0 mg (65.0%): mp 120 °C dec; ^{1}H NMR (C_6D_6) δ 1.7 (s, 15 H), 6.8 (br, 18 H), 7.3–7.7 (m, 12 H); ^{13}C NMR (C_6D_6) δ 11.9, 102.5, 129.1 (AX_2), 131.6 (AX_2), 134.2 (AX_2), 137.0 (AX_2); ^{31}P NMR (C_6D_6) δ +7.5; IR (KBr) 1020 cm^{-1}; MS (30 eV), m/e 537 (M^+ − Cp*); UV-vis (THF) λ_{max} 365 nm (ϵ 1400). Anal. Calcd for $C_{47}H_{45}CuP_2$ (735.37): C, 76.77; H, 6.17. Found: C, 76.86; H, 6.00.

Reaction of CuCl with (Pentamethylcyclopentadienyl)lithium. A suspension of 99.0 mg (1 mmol) of CuCl is mixed with 139.2 mg (1 mmol) of (pentamethylcyclopentadienyl)lithium at −78 °C. The solution turns yellow. After the mixture was warmed to room temperature, the copper precipitate is filtered off and the solvent is removed in vacuo. A pale yellow liquid remains which is identified as $(Cp^*)_2$: yield 205 mg (76%); ^{1}H NMR ($CDCl_3$) δ 1.2 (s, 6 H), 1.5 (s, 12 H); MS, m/e 270 ($M^+/2$).

Trapping of (Pentamethylcyclopentadienyl)copper, 4, with Hexaphenylcarbodiphosphorane, 1. The yellow solution of 4 (1 mmol) is quenched at −78 °C with a solution of 536 mg (1 mmol) of 1 in 50 mL of THF. The red mixture is worked up as described for **3b**.

Reaction of 4 with *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA). Addition of 1 equiv of TMEDA to a solution of 4 at −78 °C prolongs the lifetime of this intermediate by a factor of 2. After workup at room temperature, 5 is obtained in quantitative yield along with a precipitate of copper.

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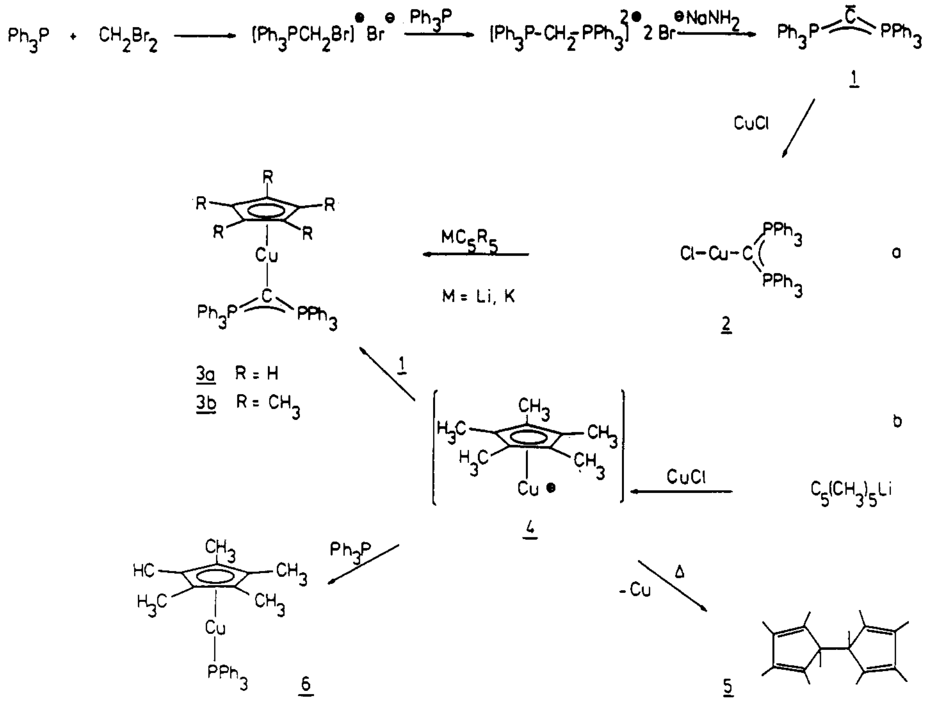
Scheme I



Reaction of 4 with Triphenylphosphine. 4 is quenched by addition of 1 equiv of triphenylphosphine in 50 mL of THF. The brown solution is stirred at 0 °C for 2 h and filtrated over Na_2SO_4. **6c** is crystallized from THF as colorless needles in a yield of 65%: mp 120 °C; ^{1}H NMR (C_6D_6) δ 1.8 (s, 15 H), 7.3–7.8 (m, 15 H); ^{31}P NMR (C_6D_6) δ +3.7. Anal. Calcd for $C_{28}H_{30}CuP$ (461.06): C, 72.94; H, 6.56. Found: C, 73.01; H, 6.56.

[(Triphenylphosphonio)(triphenylphosphoranylidene)-methyl]silver(I) Chloride, 7. The preparation is carried out as described for compound 2. 7 crystallizes from THF as colorless needles with 1 equiv of THF in a yield of 86.3%: mp 234 °C dec; ^{1}H NMR (CD_2Cl_2) δ 7.2–7.9 (m); ^{31}P NMR (CD_2Cl_2) δ +16.5. Anal. Calcd for $C_{37}H_{30}AgClP_2 \cdot C_4H_8O$ (752.03): C, 65.48; H, 5.09; Ag, 14.34. Found: C, 65.88; H, 4.74; Ag, 14.35.

(η^5-Pentamethylcyclopentadienyl)[(triphenylphosphonio)(triphenylphosphoranylidene)methyl]silver(I), 8. To a solution of 752 mg (1 mmol) of 7 in 200 mL of THF is added 1.1 mmol LiCp*. The solution is stirred for 30 min and filtered through a layer of 10 cm of silica gel. The product crystallizes from THF at −15 °C with a yield of 413 mg (53%): ^{1}H NMR (acetone-d_6) δ 1.6 (s, 15 H); 7.5–7.9 (m, 30 H); ^{31}P NMR (acetone-d_6) δ +6.5 (dd, ^2J(AgP) = 12.2/12.1 Hz); IR (KBr) 1025 cm^{-1}. Anal. Calcd for $C_{47}H_{45}AgP_2$ (779.69): C, 72.40; H, 5.82; Ag, 13.83. Found: C, 72.42; H, 5.82; Ag, 13.91.

X-ray Structure Determination of 3b. A suitable single crystal of **3b** (grown from THF/pentane) was sealed at dry ice temperature under an atmosphere of argon into a glass capillary. Diffractometer measurements (Syntex $P2_1$) indicated a primitive monoclinic cell which was confirmed by axial photographs and reduced cell calculations (TRACER). Exact cell constants were obtained by a least-squares fit of the parameters of the orientation matrix to the setting angles of 15 centered high-order reflections from various parts of reciprocal space. Crystal data and other numbers pertinent to intensity data collection and structure refinement are collected in Table I. Data collection and reduction closely followed previously described procedures.[18]

The structure was solved by direct methods (MULTAN 80) and completed by Fourier techniques. Eight hydrogen atoms could be located in difference maps, and the remainder was calculated at idealized geometrical positions. Thereby found hydrogens served to determine the conformation of all methyl groups. Refinement was done with anisotropic thermal parameters with the exception of the C(phenyl) atoms which were treated isotropically. The methyl groups were treated as rigid groups; all other H atoms were held constant (SHELX-76). Reference 18 contains the sources of the scattering factors and the programs used. Table II contains the atomic coordinates, Table III summarizes important distances and angles, and Figure 2 depicts the molecular structure.

Table I. Crystal Structure Data for 3b

formula	$C_{47}H_{45}CuP_2$
M_r	735.38
cryst system	monoclinic
space group	$P2_1/n$
a, Å	11.495 (1)
b, Å	17.147 (2)
c, Å	20.181 (2)
β, deg	101.11 (1)
V, Å^3	3903.2
Z	4
d_{calcd}, g cm^{-3}	1.251
μ(Mo Kα), cm^{-1}	6.7
F(000), e	1544
T, °C	−35
radiatn	Mo Kα
λ, Å	0.71069
scan	ω
scan width, deg	0.9
scan speed, deg min^{-1}	0.9–29.3
$[(\sin\theta)/\lambda]_{max}$, Å^{-1}	0.538
hkl range	+10,+18,±21[a]
reflctns measd.	7067
reflctns unique	4783
R_{int}	0.027
reflctns obsd [$I \geq 2.0\sigma(I)$]	3499
param ref	286
R[b]	0.069
R_w[c]	0.054
(shift/error)$_{max}$	0.09
$\Delta\rho_{fin}$(max/min), e Å^{-3}	0.89/−0.46

[a] In addition a partial set of equivalent reflections ($+h, -k, \pm l$) was measured. [b] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$.

Results and Discussion

Synthesis of (η^5-C_5R_5)Cu[(C_6H_5)$_3$P=C=P(C_6H_5)$_3$] (3a,b). The synthesis of hexaphenylcarbodiphosphorane,

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Table II. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors for 3b[a]

atom	x/a	y/b	z/c	U(eq/iso)
Cu	0.9825 (1)	0.2428 (1)	0.2051 (1)	0.038
P1	0.7430 (2)	0.2179 (1)	0.2345 (1)	0.026
P2	0.9605 (1)	0.2322 (1)	0.3503 (1)	0.024
C1	0.8846 (5)	0.2300 (3)	0.2715 (3)	0.026
C2	0.7265 (6)	0.1368 (3)	0.1740 (3)	0.032
C21	0.7924 (6)	0.0706 (4)	0.1956 (3)	0.052
C22	0.7844 (6)	0.0047 (4)	0.1508 (4)	0.071
C23	0.7144 (6)	0.0106 (4)	0.0894 (4)	0.067
C24	0.6504 (6)	0.0738 (4)	0.0678 (4)	0.069
C25	0.6551 (6)	0.1389 (4)	0.1111 (3)	0.048
C3	0.6777 (5)	0.3029 (3)	0.1862 (3)	0.026
C31	0.7477 (6)	0.3670 (3)	0.1805 (3)	0.029
C32	0.6991 (6)	0.4338 (3)	0.1471 (3)	0.037
C33	0.5789 (6)	0.4363 (3)	0.1194 (3)	0.041
C34	0.5086 (6)	0.3726 (4)	0.1244 (3)	0.047
C35	0.5555 (6)	0.3060 (3)	0.1588 (3)	0.040
C4	0.6338 (6)	0.1995 (3)	0.2872 (3)	0.027
C41	0.6014 (6)	0.2611 (3)	0.3253 (3)	0.036
C42	0.5180 (6)	0.2493 (4)	0.3663 (3)	0.044
C43	0.4692 (6)	0.1771 (4)	0.3697 (3)	0.048
C44	0.4999 (6)	0.1162 (4)	0.3338 (3)	0.044
C45	0.5828 (6)	0.1263 (3)	0.2925 (3)	0.035
C5	0.8777 (5)	0.2300 (3)	0.4181 (3)	0.025
C51	0.8684 (6)	0.2937 (3)	0.4590 (3)	0.039
C52	0.7996 (6)	0.2878 (4)	0.5091 (3)	0.046
C53	0.7383 (6)	0.2211 (4)	0.5164 (3)	0.046
C54	0.7479 (6)	0.1569 (3)	0.4772 (3)	0.041
C55	0.8165 (6)	0.1611 (3)	0.4274 (3)	0.030
C6	1.0518 (6)	0.3196 (3)	0.3652 (3)	0.027
C61	0.9992 (6)	0.3909 (3)	0.3418 (3)	0.041
C62	1.0654 (6)	0.4598 (4)	0.3528 (3)	0.049
C63	1.1802 (6)	0.4575 (4)	0.3843 (3)	0.052
C64	1.2345 (6)	0.3890 (4)	0.4076 (3)	0.052
C65	1.1693 (6)	0.3199 (3)	0.3977 (3)	0.041
C7	1.0649 (5)	0.1517 (3)	0.3726 (3)	0.024
C71	1.1090 (6)	0.1322 (3)	0.4395 (3)	0.034
C72	1.1886 (6)	0.0694 (3)	0.4553 (3)	0.044
C73	1.2186 (6)	0.0267 (4)	0.4042 (3)	0.046
C74	1.1738 (6)	0.0440 (3)	0.3381 (3)	0.044
C75	1.0956 (6)	0.1070 (3)	0.3213 (3)	0.033
C8	1.0456 (6)	0.3193 (4)	0.1311 (3)	0.036
C9	0.9883 (6)	0.2542 (5)	0.0952 (3)	0.033
C10	1.0554 (6)	0.1870 (4)	0.1162 (3)	0.035
C11	1.1546 (6)	0.2098 (4)	0.1653 (3)	0.034
C12	1.1491 (6)	0.2912 (4)	0.1754 (3)	0.033
C81	1.0107 (8)	0.4028 (4)	0.1193 (5)	0.049
C91	0.8790 (6)	0.2576 (5)	0.0405 (3)	0.058
C101	1.0316 (8)	0.1064 (4)	0.0874 (4)	0.061
C111	1.2566 (6)	0.1574 (4)	0.1973 (3)	0.043
C121	1.2397 (6)	0.3398 (4)	0.2208 (4)	0.053

[a] $U_{eq} = (U_1U_2U_3)^{1/3}$, where U_i are the eigenvalues of the $\mathbf{U}_{ij}$ matrix.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for 3b with Esd's in Units of the Last Significant Figure in Parentheses

	Bond Distances		
Cu–C1	1.922 (6)	C1–P1	1.668 (6)
Cu–C8	2.213 (6)	C1–P2	1.660 (5)
Cu–C9	2.240 (5)	P1–C2	1.836 (6)
Cu–C10	2.328 (6)	P1–C3	1.831 (6)
Cu–C11	2.344 (7)	P1–C4	1.823 (6)
Cu–C12	2.271 (6)	P2–C5	1.812 (6)
Cu–D[a]	1.94	P2–C6	1.821 (6)
		P2–C7	1.827 (6)
	Bond Angles		
C1–Cu–D[a]	177.9	C2–P1–C4	105.1 (3)
Cu–C1–P1	110.7 (3)	C3–P1–C4	101.0 (3)
Cu–C1–P2	113.3 (3)	C1–P2–C5	117.9 (3)
P1–C1–P2	136.0 (4)	C1–P2–C6	110.9 (3)
C1–P1–C2	111.1 (3)	C1–P2–C7	114.7 (3)
C1–P1–C3	113.8 (3)	C5–P2–C6	105.3 (3)
C1–P1–C4	118.8 (3)	C5–P2–C7	102.3 (2)
C2–P1–C3	105.6 (3)	C6–P2–C7	104.5 (3)

[a] Midpoint of the C_5Me_5 ring.

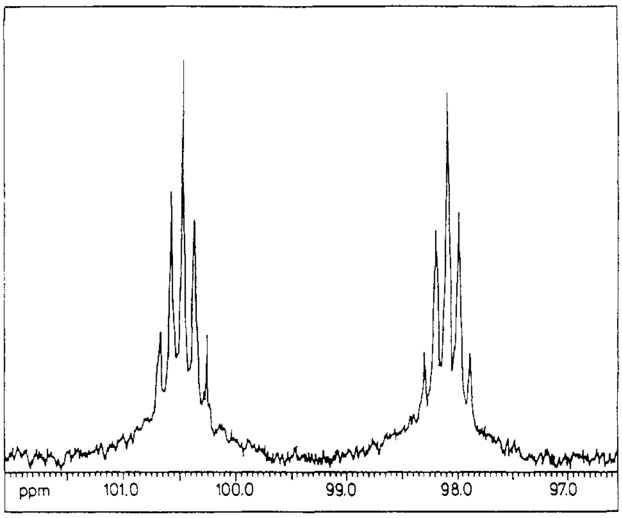

Figure 1. ^{1}H-coupled ^{13}C NMR spectrum (270 MHz) of **3a** (THF-d_8). Only the range of the C_5H_5 signals is displayed.

1, as outlined in Scheme I, was improved from the original procedure[13] by stepwise coupling of dibromomethane with triphenylphosphine and subsequent deprotonation of the phosphonium salt with $NaNH_2$. **1** readily depolymerizes CuCl to form **2** in almost quantitative yield. **2** is monomeric both in the solid state[14] and—according to cryoscopic data—in solution and therefore is an ideal starting material for other mononuclear organocopper compounds.

Yellow solutions of **2** in THF react instantaneously upon addition of equimolar amounts of alkali cyclopentadienides to give the products **3a** and **3b**. Alternatively, **3b** is also accessible from LiCp*, CuCl, and subsequent addition of **1** (Scheme I, path b), but pathway b is less convenient than path a because the intermediate **4** decomposes in a side reaction to give decamethylfulvalene (**5**) and copper. At room temperature this decomposition becomes the main reaction.

The spectroscopic data for **3a,b** clearly show an η^5-coordination of the cyclopentadienyl substituents to copper; the IR data in solution and in the solid state are in agreement with a local C_{5v} symmetry at the cyclopentadienyl ring (1020 cm^{-1} for C–C stretching vibration, symmetry type a_1).[10a] The ^{1}H NMR spectra show a singlet for the C_5R_5 protons in the temperature range between 28 and −85 °C (δ 6.2, **3a**; δ 1.8, **3b**). The ^{13}C NMR data for the C_5R_5 ring signals exhibit an exceptional large high-field shift (δ 99.3, **3a**; δ 102.5, **3b**). These values are comparable to those of the alkali cyclopentadienides [δ 102.8 (^1J(HC) = 159.1 Hz, CpLi), 69.2 (^1J(HC) = 174.8 Hz, Cp_2Fe)]. We therefore assume a high ionicity in the bonding between C_5R_5 and Cu. The gated decoupled ^{13}C NMR spectrum of **3a** shows a $^1J(^1H^{13}C)$ = 160.9 Hz for the C_5H_5 signal (Figure 1). A partially ionic Cp–Cu bond has also been inferred from spectroscopic data for Cp–CuPEt$_3$ by Cotton and Marks and rationalized considering the heavy-atom effect of copper.[19] However, the degree of ionicity in **3a,b** should even be higher than in CpCuPEt$_3$ as judged from ^{13}C NMR, and **3a** can indeed be compared with LiCp.

Direct combination of LiCp* and CuCl at low temperatures affords an unstable compound, **4**, which decomposes

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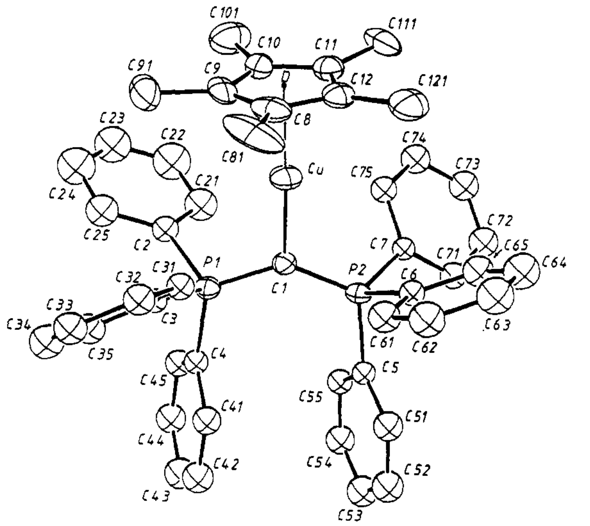
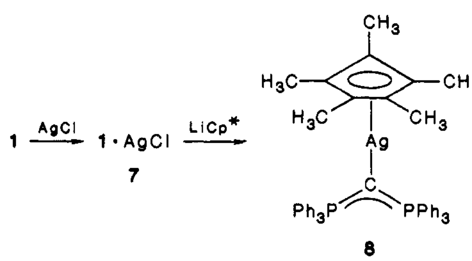


Figure 2. Perspective view of the molecular structure of **3b** and atomic numbering scheme (ORTEP, thermal ellipsoids at the 50% probability level, isotropic atoms with root-mean-square deviation as radius, H atoms omitted for clarity).

($t_{1/2}$ = 5 min at −78 °C) to give elemental copper and decamethylfulvalene, **5**. We propose a half-sandwich structure **4** for the intermediate of reaction b.[20] This assumption has been confirmed by several trapping experiments. Treatment of **4** with triphenylphosphine leads to **6**, the addition of TMEDA prolongs the lifetime of **4** by a factor of 2, and trapping of **4** with **1** leads to **3b**. A 16e species **4** has also been formulated as an intermediate of the reaction between LiCp* and CuCl by Stone and Rausch.[11,20] It can be assumed, however, that the open coordination site at the copper atom is occupied by a solvent molecule (THF). The experimental data strongly support the assumption of **4** as a reaction intermediate of path b. An ionic reaction can also be proposed for path a. Significantly, the use of a polar solvent appeared to be essential for this reaction.

Silver Complexes. For the heavier coinage metals an η^5-coordination of cyclopentadienyl ligands is less common.[22] η^5-Coordinated gold complexes for instance are still unknown, and for silver only one example has been reported.[23] An η^5-coordinated silver(I) compound has now become accessible through a procedure according to reaction 1. The preparation of **8** follows closely the synthesis



of **3a,b** by combination of AgCl with **1** and subsequent reaction with LiCp*. **8** can be purified by either column chromatography or crystallization. All the spectroscopic data of **8** are in agreement with an η^5-bonded half-sandwich structure. Particularly an IR absorption band at 1025 cm^{-1} is typical for an η^5-bonded Cp* ring. Also diagnostic for **8** are the coupling constants $^2J(^{109}Ag^{31}P)$ = 12.2 and $^2J(^{107}Ag^{31}P)$ = 12.1 Hz.

Molecular Structure of 3b. In the solid state, **3b** forms discrete monomers, and no unusually short intermolecular distances are observed. As is clearly seen from Figure 2, the central Cu atom is almost completely shielded by phenyl rings and methyl groups, which accounts for the absence of aggregation both in solution and in the solid state. It should be pointed out, however, that CpCu^I phosphine complexes F (L = PPh_3, PEt_3)[10] and the hexaphenylcarbodiphosphorane CuCl complex **2** also show a reduced tendency for aggregation. This indicates that already less bulky substituents are sufficient to prevent aggregation. Furthermore, the ligands in all these complexes are electron donors and stabilize the Cu(I) center by electronic saturation. This is certainly another contributing factor to the observed mononuclearity.

In **3b** the Cu(I) center is coordinated by the ylidic C atom C1 of the bent hexaphenylcarbodiphosphorane, **1**, and by the η^5-bound pentamethylcyclopentadienyl ligand (Cp*). The angle formed at Cu by C1 and the Cp* (D) midpoint is practically linear (177.9°, Table III). The η^5-coordination of the Cp* ligand can be judged from a comparison of the Cu–C distances (Table III) and by the angle of 4.1° formed between the normal to the Cp* ring plane and the line Cu–D. Obviously, the deviation from ideal η^5-coordination is caused by intramolecular steric interaction between C81 and C111 and the phenyl ring carbon atoms, respectively. This results in a slippage and tilt of the Cp* ring leading to a shorter Cu–C8 distance but a longer Cu–C11 distance. Particularly indicative for this effect are the positions of the methyl groups with respect to the Cp* ring plane. While all methyl C atoms are tilted out of the Cp* plane *away* from the Cu atom, the tilt of C81 and C111 is more pronounced (5.2° and 4.7° for C81 and C111 vs 2.9°, 3.7°, and 2.5° for C91, C101, C121, respectively).

The coordinated hexaphenylcarbodiphosphorane molecule **1** in **3b** features a perfectly planar donor center C1 (sum of the valence angles is 360.0°). The angles Cu–C1–P1/P2 do not differ much but are in contrast to a much larger angle P1–C1–P2 of 136.0 (4)°. The distance CuC1 (1.922 (6) Å) is noticeably shorter than the electron-deficient three-center bonds between Cu and aromatic or aliphatic ligands[14b] but is directly comparable to 2c–2e Cu–C bonds as, e.g., in E[9] or in organocuprates of the type $[R-Cu-R]^-$.[8] That the C1–P1/P2 bonds are slightly longer in **3b** than in the parent bis-ylide **1**—an indication of a reduction of the bond order on coordination of C1—is generally observed in the coordination chemistry of P ylides and has been discussed elsewhere.[12,14b]

A comparison between the structure of **3b** and the CuCl adduct **2** as well as with the phosphine complexes F (L = PPh_3,[10c] PEt_3[10d]) reveals some interesting differences. In **3b** the Cu–C1 bond is slightly longer than in **2**, whereas the C1–P bonds are shorter; this is clearly a consequence of the better electron donor properties of the Cp* ligand as compared to those of the electron-withdrawing chlorine. The much larger steric requirements of Cp* follow from noticeably different bond angles at C1 in **3b** and **2** and from a different conformation of the PPh_3 groups with respect to an assumed P1–P2 axis. The conformational and valence angle flexibility of hexaphenylcarbodiphosphorane, **1**, and its C1 complexes as induced by steric requirements is a well-known phenomenon and has been discussed previously.[14b] In F (L = PPh_3,[10c], PEt_3[10d]) the

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Cu–C(Cp) bonds are noticeably shorter than in **3b**. This certainly reflects the larger bulk of Cp* as well as the superior donor properties of **1** as compared to those of phosphines.

Acknowledgment. We are indepted to Professor H. Schmidbaur for support and to Dr. H. Fischer for help with the UV spectra. The mass spectra were recorded by Dr. F. Kreissl and Ms. S. Kreibich.

Registry No. **1**, 7533-52-0; **2**, 86847-08-7; **3a**, 110354-19-3; **3b**, 110354-18-2; **4**, 110354-17-1; **5**, 69446-48-6; **6**, 86024-09-1; **7**, 86847-09-8; **8**, 110354-20-6; CH_2Br_2, 74-95-3; Ph_3P, 603-35-0; $[Ph_3PCH_2Br]^+Br^-$, 1034-49-7; $[Ph_3PCH_2PPh_3]^{2+}2Br^-$, 14529-09-0; CuCl, 7758-89-6; AgCl, 7783-90-6.

Supplementary Material Available: Complete tables of atomic and thermal parameters (7 pages); observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

Synthetic Routes to Alumina-Supported Molybdenum Subcarbonyls. The Effect of the Supported Complex on Olefin Metathesis

George W. Wagner and Brian E. Hanson*

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Received February 17, 1987

Low-temperature synthetic routes to $Mo(CO)_3$(ads) and its derivatives on aluminum oxide are described. The arene complex (η^6-C_6H_6)$Mo(CO)_3$ loses benzene upon adsorption on partially dehydroxylated Al_2O_3 (CATAPAL SB) to yield $Mo(CO)_3$(ads). This is indistinguishable by infrared spectroscopy and catalytic activity from $Mo(CO)_3$(ads) generated directly from $Mo(CO)_6$. The tris(acetonitrile) complex $Mo(CO)_3$-$(CH_3CN)_3$ reacts in a more complicated fashion with the surface of partially dehydroxylated alumina. One of the products appears to be consistent with the formulation $Mo(CO)_3(CH_3CN)$(ads). All supported carbonyls generated from $Mo(CO)_3(CH_3CN)_3$ are inactive for olefin metathesis.

Introduction

It is well-documented that molybdenum hexacarbonyl reacts with aluminum oxide surfaces to yield supported molybdenum subcarbonyls.[1-3] The reaction of $Mo(CO)_6$ with Al_2O_3 may be accomplished either from the gas phase or from hydrocarbon solution of the carbonyl. The most stable of the subcarbonyls generated fgrom $Mo(CO)_6$ is $Mo(CO)_3$(ads); this is prepared at 100 °C in a flow of ultrapure helium.[1] It is postulated that $Mo(CO)_3$(ads) is stabilized by coordination to surface oxide and/or hydroxide groups depending upon the degree of dehydroxylation of the alumina.[1-4] Infrared spectroscopy has been used to further elucidate the structure of the adsorbed molybdenum tricarbonyl.[3,5,6] The presence of bands below 1600 cm^{-1} in the infrared spectrum has led to some controversy regarding the details of the coordination to the tricarbonyl group by the surface. The following structural features have all been proposed: (i) the presence of a bridging carbonyl interacting with a Lewis acid site on the surface,[7] (ii) a terminal carbonyl interacting with a Lewis acid site on the surface through the carbonyl oxygen,[4] and (iii) a surface hydroxyl group interacting with a carbonyl atom.[3] The materials generated from the adsorption of $Mo(CO)_6$ on aluminum oxide show catalytic activity for a number of reactions including olefin methathesis,[1,8] methanation,[9] and hydrogenation.[10] The olefin metathesis reaction was first recognized over molybdenum catalysts prepared from $Mo(CO)_6$.[11]

The solution chemistry of metal tricarbonyl moieties is well established in the organometallic literature;[12] molybdenum tricarbonyl may be added to a complex synthetically/ either directly from $Mo(CO)_6$ or from $Mo(CO)_3L_3$. The latter compound is typically synthesized thermally from $Mo(CO)_6$ and excess L. Subsequent reactions may then be performed under mild conditions.

In this paper we report the use of $Mo(CO)_3(CH_3CN)_3$ and (η^6-C_6H_6)$Mo(CO)_3$ as precursors to $Mo(CO)_3$(ads) on aluminum oxide. The resulting materials have been investigated via catalytic activity, reaction stoichiometry, and FTIR spectroscopy.

Experimental Section

The complex $Mo(CO)_3(CH_3CN)_3$ was synthesized by refluxing $Mo(CO)_6$ in acetonitrile according to a literature preparation.[13] It was characterized by infrared bands at 1915 and 1783 cm^{-1} (Nujol mull)[13] and satisfactory elemental analysis. The complex (η^6-C_6H_6)$Mo(CO)_3$ was prepared from (η^6-$C_6H_5CH_3$)$Mo(CO)_3$ by refluxing the toluene complex in benzene. The toluene complex was prepared directly from $Mo(CO)_6$ by refluxing in toluene. Removal of the solvent yielded a yellow solid that gave carbonyl bands at 1984 and 1916 cm^{-1} (pentane solvent) corresponding well with literature values.[14]

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