2370 *Inorg. Chem.* **1990**, *29*, 2370-2375

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Linear Oligophosphaalkanes. 23. Novel Copper(I) Complexes with Electron-Deficient Triply Bridging Secondary Phosphido Groups μ_3-PRR′ (R = iPr, tBu, R′ = CH_2–PR_2; R = R′ = Ph)

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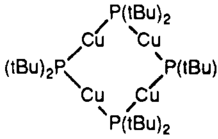
The copper complexes $Cu_4(R_2P–CH_2–PR)Cl_3(py)_2$ (**2a**, R = iPr; **2b**, R = tBu) have been prepared by reaction of the corresponding silylphosphines $R_2P–CH_2–PRSiMe_3$ with CuCl in the presence of pyridine (py). The structure of the hemietherate of **2a** has been determined by X-ray diffraction. The compound crystallizes in the monoclinic space group $C2/c$ with a = 18.197 (4) Å, b = 14.630 (3) Å, c = 24.926 (7) Å, β = 107.88 (2)°, and Z = 8. Refinement converged at $R(F_o)$ = 0.050 for the 2778 observed reflections. Two crystallographic independent $(Cu–Cl)_2$ bridges link **2a** into chains, the third chlorine bridging the other two Cu atoms in the formula unit. The phosphido atom P(1) is bonded to two C and three Cu atoms. The three electron-deficient coplanar P(1)–Cu bonds are roughly equidistant (2.223 (3)–2.251 (3) Å); furthermore, the PCu_3 fragment contains two Cu–Cu contacts (average 2.538 (4) Å) which are sufficiently short to be considered bonding. Treatment of polymeric $[Cu(PPh_2)]_n$ with CuCl and PMe_3 yields $Cu_4(PPh_2)_3Cl(PMe_3)_4$ (**4**). It crystallizes in the monoclinic space group $P2_1/c$ with a = 13.583 (2) Å, b = 19.586 (4) Å, c = 20.830 (4) Å, β = 100.32 (1)°, and Z = 4. Refinement converged at $R(F_o)$ = 0.042 for 6090 observed reflections. The core of **4** may be described as a six-membered $Cu_3(PPh_2)_3$ ring to which a CuCl is bound via two Ph_2P groups; thus **4** possesses one electron-precise PCu_2 bridge and two electron-deficient PCu_3 fragments. As in **2a**, the PCu_3 fragments possess short Cu–Cu contacts (average 2.51(2) Å). Reaction of $[Cu(PPh_2)]_n$ with PMe_3 affords a copper(I) phosphido complex of composition $[Cu(PPh_2)(PMe_3)]_n$ (**5**) for which a structure with μ_2-PPh_2 and μ_3-PPh_2 ligands is proposed.

Introduction

The coordination chemistry of coinage metals with tertiary phosphines is well established, and many complexes containing two-, three-, and four-coordinated metals M(I) (M = Cu, Ag, Au) have been characterized.[1] In contrast, there are very few reports on authenticated phosphido complexes of these metals in the literature.[2-6] Cowley and his coworkers[2] presented the first homoleptic copper(I) phosphide (A) very recently, and the gold(I) complex with a bridging diphenylphosphido ligand $[PPh_2(AuBr)_2]^-$ (B) has been obtained by treatment of $Bu_4N[AuBr_2]$ with diphenylphosphine.[3] Furthermore, the X-ray structure of the binuclear copper(I) phosphido complex $(PPh_2–C_2H_4–PPh_2)_2Cu_2(\mu_2\text{-}PPh_2)_2$ (C) has been reported independently by two groups.[5,6]

Phosphido anions $[PRR']^-$ with their two lone pairs are capable of bonding two transition metals, M–μ-PRR′–M units with electron-precise M–P bonds being formed. However, μ_2 bridging of transition metals may also be achieved by ligands X providing only one electron pair for bonding within the M—X—M units—the tetrameric copper(I) alkyls, e.g. $[Cu(CH_2SiMe_3)]_4$ (D)[7,8] with three-center–two-electron Cu–$CH_2(SiMe_3)$–Cu bonds (E) being well known examples. By analogy with the isoelectronic carbanions $CH_2SiMe_3^-$, the copper(I) phosphido species {PRR′Cu} may be expected to bind two additional Cu(I) ions in a similar way (F).

Thus by formation of one electron-deficient (three-center–two-electron) Cu–P–Cu unit and one electron-precise P–Cu bond, the phosphido anions $[PRR']^-$ should be able to coordinate three Cu(I) cations, forming electron-deficient PCu_3 units.



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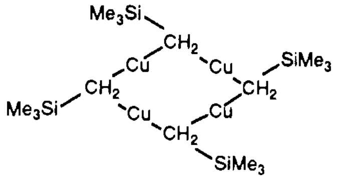

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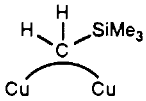

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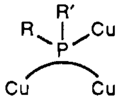

F

We recently announced in a preliminary publication[9] the first example of a transition-metal complex, $Cu_4[(iPr)_2P–CH_2–P(iPr)]Cl_3(py)_2$ (py = pyridine), containing such a triply bridging secondary phosphido group μ_2-PRR′ (R = iPr, R′ = CH_2–$P(iPr)_2$). Here we give a detailed report describing its synthesis and structure. Furthermore, we present further examples of μ_3-PR_2-bridged copper(I) complexes illustrating the potential significance of this new bonding mode of PR_2 ligands in coinage metal chemistry.

Experimental Section

All preparations were done under an atmosphere of dry nitrogen. The phosphines PMe_3,[10] Ph_2P-$SiMe_3$,[11] and $R_2P–CH_2–PR(SiMe_3)$ (R = iPr, tBu)[12] were prepared by literature methods. Solvents were reagent grade, distilled from the appropriate drying agents under N_2. Proton magnetic resonance spectra were measured on a Bruker AC 250 spectrometer at 250 MHz using Me_4Si as internal reference. Proton-decoupled Fourier transform phosphorus-31 NMR spectra were obtained from a Varian FT 80A spectrometer operating at 32.2 MHz. Phosphoric acid (85%) was used as external reference. Conductivity measurements were made by a Knick digital conductometer.

Preparation of $Cu_4(R_2P–CH_2–PR)Cl_3(py)_2$ (2a, 2b). The silylphosphines $R_2P–CH_2–PRSiMe_3$ (**1a**, 2.78 g, 10 mmol; **1b**, 0.84 g, 2.5 mmol) were added at 0 °C to a solution of 2.97 g (30 mmol) or 0.99 g (10 mmol) CuCl in tetrahydrofuran containing 4.75 g (60 mmol) or 1.58 g (20 mmol) pyridine, respectively. After 16 h the solvent was stripped off under reduced pressure (20 °C, 0.1 mbar). In the case of **2a**, methanol (10 mL) was added to the residue. After a period of 1 week,

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Table I. Crystallographic Data for the Ether Solvate of **2a** and **4**

	2a	**4**
chem formula	$C_{20}H_{33}Cl_3Cu_4N_2P_2{\cdot}0.5(C_4H_{10}O)$	$C_{48}H_{66}ClCu_4P_7$
fw	723.98 + 0.5(74.12)	1149.50
space group	*C*2/*c* (No. 15)	$P2_1/c$ (No. 14)
a, Å	18.197 (4)	13.583 (2)
b, Å	14.630 (3)	19.586 (4)
c, Å	24.926 (7)	20.830 (4)
β, deg	107.88 (2)	100.32 (1)
V, Å^3	6315 (3)	5452 (2)
Z	8	4
T, °C	23	23
λ, Å	0.71073	0.71073
ρ_{calc}, g cm^{-3}	1.601	1.400
μ, cm^{-1}	30.4	18.3
transm coeff	0.695–0.751	0.553–0.742
$R(F_o)$	0.050	0.042
$R_w(F_o)$	0.060	0.042

2a was precipitated as yellow crystals, which were recrystallized from a 1:2 mixture of CH_3CN/Et_2O. **2b** was obtained upon addition of diethyl ether (10 mL) to the evaporated reaction mixture. Yields: 3.4 g (63%) for **2a**; 1.5 g (78%) for **2b**. Anal. Calcd for $C_{22}H_{38}Cl_3Cu_4N_2O_{0.5}P_2$ (M_r = 761.1) (**2a**·$0.5Et_2O$): C, 34.72; H, 5.03; Cl, 13.98; N, 3.68; P, 8.14. Found: C, 34.91; H, 5.44; Cl, 14.48; N, 3.81; P, 8.44. Calcd for $C_{23}H_{39}Cl_3Cu_4N_2P_2$ (M_r = 766.0) (**2b**): C, 36.06; H, 5.13; Cl, 13.88; N, 3.65; P, 8.03. Found: C, 36.74; H, 5.08; Cl, 11.40; N, 4.11; P, 7.51.

Preparation of $[Cu(PPh_2)]_n$ (3).[13] The silylphosphine $Ph_2P{-}SiMe_3$ (1.29 g, 5.0 mmol) was added to a suspension of 0.49 g (5.0 mmol) CuCl in 10 mL of THF and 0.79 g (10 mmol) of pyridine. After the mixture was stirred for 16 h, the red precipitate formed was filtered off, washed with 10 mL of THF, and dried in vacuo (20 °C, 0.01 mbar). Yield: 1.16 g (93%). Anal. Calcd for $C_{12}H_{10}CuP$ (M_r = 248.7) (**3**): C, 57.59; H, 4.05; P, 12.45. Found: C, 57.82; H, 4.38; P, 12.27. Samples of **3** contained small quantities of chlorine: Cl, 0.41.

Preparation of $Cu_4(PPh_2)_3Cl(PMe_3)_4$ (4). To a suspension of 2.0 g (8.0 mmol) of **3** and 0.27 g (2.7 mmol) of CuCl in 10 mL of THF was added 0.82 g (10.7 mmol) of PMe_3 at ambient temperature, and the mixture was stirred for 16 h. The clear yellow reaction mixture was concentrated to 2.0 mL by stripping off the solvent in vacuo (20 °C, 0.01 mbar). Yellow crystals were precipitated after addition of 20 mL of petroleum ether 40/60. Yield: 1.9 g (61%). Anal. Calcd for $C_{48}H_{66}ClCu_4P_7$ (M_r = 1149.5) (**4**): C, 50.15; H, 5.79; Cl, 3.08; P, 18.86. Found: C, 50.79; H, 6.12; Cl, 2.79; P, 18.32.

Preparation of $Cu_4(PPh_2)_4(PMe_3)_4$ (5). Trimethylphosphine (0.3 g, 4.0 mmol) was added to a suspension of 1.0 g (4.0 mmol) of **3** (containing a small quantity of CuCl) in 10 mL of THF at ambient temperature. After **3** had been dissolved, the reaction mixture was stirred for 16 h and then concentrated to 5 mL in vacuo (20 °C, 0.01 mbar). Upon addition of 10 mL of petroleum ether 40/60, a small quantity (~30 mg) of yellow crystals of **4** was precipitated and collected by filtration. Further concentration of the filtrate gave **5** as a yellow precipitate. Yield: 0.98 g (75%). Anal. Calcd for $C_{60}H_{76}Cu_4P_8$ (M_r = 1299.2): C, 55.47; H, 5.90; Cl, 0.00; P, 19.07. Found: C, 55.47; H, 5.85; Cl, 0.02; P, 19.95.

X-ray Studies. Important crystallographic details are listed in Table I. Crystals of the ether solvate of **2a** and **4** were mounted in glass capillaries under argon. The space groups were suggested by the symmetry and systematic absences revealed by Weissenberg photographs and confirmed by the refinements. Further measurements were made at 23 °C with a Siemens AED-1 diffractometer employing Zr-filtered Mo Kα radiation (λ = 0.71073 Å). Cell constants were determined from the Bragg angles of 43 reflections for the ether solvate of **2a** and 47 reflections for **4**. Intensity data (*hkl*, $\bar{h}kl$) were collected by the ω–2θ step scan technique. The counting time was 0.62 s per step, and the number of steps ($\Delta\omega$ = 0.02°; $\Delta 2\theta$ = 0.04°) varied with the Bragg angle—the peak falling in the middle two-thirds of the scan range. If the initial pass yielded an $I/\sigma(I)$ ratio between 2 and 25, then the reflection was remeasured, and the results were accumulated. Remeasurement was made with an attenuated primary beam if the maximum intensity exceeded 10000 counts/s. System stability was checked by hourly monitoring of three standard reflections. Intensity data were corrected analytically for absorption and for the drift of the standards.

The structures were solved by a routine combination of direct methods and difference Fourier techniques. Since the ether solvate of **2a** is disordered about the 2-fold axis, the OC_2 fragment in the asymmetric unit was treated as a rigid group of isotropic atoms. Furthermore in this structure, disorder of the iPr group of the P(1) atom, which severely affects the C(3) atom, prohibited the inclusion of the H atoms of this group. All other H atoms were added in idealised positions (C–H = 0.95 Å) and assigned group isotropic thermal parameters. The other non-hydrogen atoms were refined anisotropically. Dispersion-corrected relativistic Hartee–Fock scattering factors were used for all atoms except H(SDS).[14] Coordinates of the ether solvate of **2a** and **4** are listed in Tables II and III, respectively. Programs used were SHELX-76[15] (absorption correction, structure determination), ORTEP-II[16] (drawings), and several local routines. Standard deviations of average values were taken as the larger of either the mean σ or that estimated from the spread.

Table II. Fractional Atomic Coordinates of **2a**

atom	*x*	*y*	*z*	U/U_{eq},[a] Å^2
Cu(1)	0.06686 (6)	0.05778 (8)	0.30040 (5)	0.0554 (5)
Cu(2)	0.20310 (6)	0.11057 (9)	0.35151 (5)	0.0575 (5)
Cu(3)	0.21105 (7)	0.19048 (8)	0.44365 (5)	0.0600 (5)
Cu(4)	0.25878 (6)	−0.00362 (9)	0.45453 (5)	0.0619 (5)
Cl(1)	0.3335 (1)	0.2211 (2)	0.4846 (1)	0.081 (1)
Cl(2)	0.0693 (1)	0.0130 (2)	0.2160 (1)	0.068 (1)
Cl(3)	0.2842 (1)	−0.0122 (2)	0.3685 (1)	0.073 (1)
P(1)	0.1024 (1)	0.1357 (2)	0.3822 (1)	0.0465 (9)
P(2)	0.1414 (1)	−0.0296 (2)	0.4575 (1)	0.054 (1)
N(1)	0.2428 (4)	0.1988 (6)	0.3051 (3)	0.066 (4)
N(2)	0.3643 (4)	−0.0337 (5)	0.5080 (3)	0.058 (3)
C(1)	0.0339 (8)	0.2355 (8)	0.3657 (6)	0.105 (7)
C(2)	0.0608 (9)	0.2998 (8)	0.3289 (6)	0.117 (7)
C(3)	−0.0226 (9)	0.245 (1)	0.3851 (9)	0.19 (1)
C(4)	0.0719 (4)	0.0624 (6)	0.4320 (4)	0.056 (4)
C(5)	0.0962 (6)	−0.1239 (7)	0.4085 (6)	0.084 (6)
C(6)	0.1517 (8)	−0.1993 (8)	0.4080 (6)	0.121 (8)
C(7)	0.0209 (7)	−0.1596 (9)	0.4178 (7)	0.127 (8)
C(8)	0.1321 (6)	−0.0568 (9)	0.5272 (5)	0.080 (5)
C(9)	0.1619 (8)	0.022 (1)	0.5672 (5)	0.116 (8)
C(10)	0.1756 (7)	−0.143 (1)	0.5509 (5)	0.122 (7)
C(11)	0.2960 (7)	0.2561 (9)	0.3290 (5)	0.095 (6)
C(12)	0.3235 (8)	0.320 (1)	0.2968 (6)	0.119 (7)
C(13)	0.2924 (7)	0.325 (1)	0.2412 (5)	0.104 (6)
C(14)	0.2391 (8)	0.265 (1)	0.2158 (5)	0.135 (8)
C(15)	0.2142 (7)	0.2035 (9)	0.2492 (6)	0.105 (7)
C(16)	0.4111 (6)	−0.0873 (7)	0.4904 (5)	0.071 (5)
C(17)	0.4833 (6)	−0.1120 (9)	0.5231 (6)	0.087 (6)
C(18)	0.5100 (7)	−0.0812 (9)	0.5757 (8)	0.106 (8)
C(19)	0.4642 (8)	−0.028 (1)	0.5949 (6)	0.120 (7)
C(20)	0.3896 (6)	−0.0051 (9)	0.5594 (5)	0.089 (6)
O	0.5000	0.055 (2)	0.2500	0.32 (1)
C(21)	0.4283	0.098 (2)	0.2425	0.26 (1)
C(22)	0.3678	0.024 (2)	0.2346	0.23 (1)

[a] $U_{eq} = {}^1/_3 \sum_i\sum_j U_{ij}\bar{a}_i{\cdot}\bar{a}_j a^*_i a^*_j$.

Results and Discussion

For the preparation of μ_3-PRR′-bridged copper(I) complexes, two related synthetic approaches may be used: (i) cleavage of the P–Si bond in silylphosphines $RR'P{-}SiMe_3$ with an excess of copper(I) halide in presence of Lewis bases (e.g. pyridine) and (ii) depolymerization of polymeric copper(I) phosphides $[Cu(PRR')]_n$ by Lewis bases (e.g. PMe_3) and copper(I) halides CuX (X = Cl, Br). In both cases the Lewis bases are playing the role of auxiliary ligands providing coordinative saturation at the Cu(I) centers of the intermediate μ_2-PRR′ phosphido complexes (G) and of the reaction products with μ_3-PRR′ bridges (H).

Cleavage of the P–Si Bond in $R_2P{-}CH_2{-}PR(SiMe_3)$ (R = iPr, tBu) with CuCl. The reaction of the silylphosphines $R_2P{-}CH_2{-}PR(SiMe_3)$[12] with 3 equiv of CuCl in the presence of pyridine was originally expected to yield $R_2P{-}CH_2{-}PR$-bridged clusters[17] of type I in which peripheral copper coordination sites would be occupied by both chloride and pyridine. However, instead of I,

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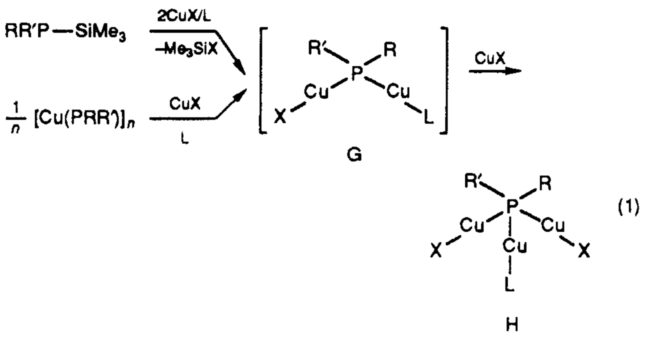
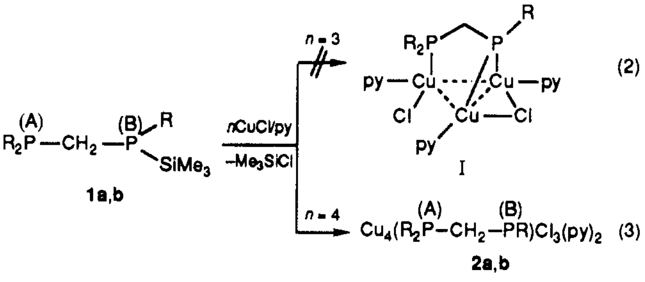
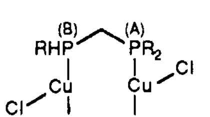


yellow crystalline compounds of composition $Cu_4(R_2P{-}CH_2{-}PR)Cl_3(py)_2$ (**2a,b**) were obtained after working up the reaction mixtures (eq 3).

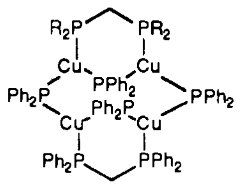


1a,2a: R = iPr
1b,2b: R = tBu

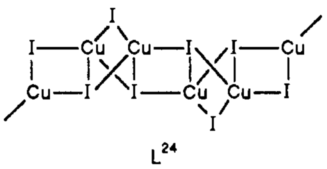
Complexes **2a** and **2b** are nonconductors in CH_2Cl_2 solution (10^{-3} M, 20 °C). The $^{31}P\{^1H\}$-NMR spectra of **2a** and **2b** (Table IV) are of AB-type with quadrupole line broadening by the $^{63}Cu/^{65}Cu$ nuclei.[18] By comparison of the ^{31}P chemical shift values with those for P(A) or P(B) in the ligands $R_2P{-}CH_2{-}PRH$ (R = iPr, tBu)[12] and their copper(I) halide complexes (e.g. J,[19] $\delta(P(A)) = +13$, $\delta(P(B)) = -34$ ppm) the signals at +18 and –54 ppm (**2a**) or +42 and –26 ppm (**2b**), respectively, may be assigned to the $P(A)R_2{-}CH_2$ groups coordinated to Cu(I) and the phosphido groups $[P(B)R{-}CH_2{-}]$ engaged in bridging to the remaining three copper ions. The formation of this new type of phosphido bridging (μ_3-PRR') results in a significant high-field shift of $\delta(P)$ (up to –70 ppm) by comparison with the corresponding μ_2-PRR' bridges bearing the same substituents R and R' (see ref 20a and compounds **4** and **5** below, containing μ_3-PPh_2 and μ_2-PPh_2 units).



J^{19} (R = iPr)



K^4



L^{24}

The $\delta(P)$ values of the secondary phosphido groups in **2a** and $Cu_8[(iPr)P{-}CH_2{-}P(iPr)]_2Cl_4(py)_5$ ($\delta(P) = -61.1$ ppm), for which X-ray structural analysis reveals μ_3-$P(iPr){-}CH_2$ bridging,[21] may well be compared, indicating similar bonding at P(B) in **2a**. In the case of **2b**, however, with the bulkier alkyl substituents at P(B), the chemical shift $\delta(P(B))$ is significantly lower than the expected value of ca. –50 ppm.[20b] This may be effected by a rapid exchange of the anionic $P(tBu){-}CH_2$ group between **2b** and species with μ_2-$P(tBu){-}CH_2$ bridging units, e.g. $Cu_3[(tBu)_2P{-}CH_2{-}P(tBu)]Cl_2(py)$ (eq 4).

$$\mathbf{2b} \rightleftharpoons CuCl(py) + Cu_3[(tBu)_2P{-}CH_2{-}P(tBu)]Cl_2(py) \quad (4)$$

Table III. Fractional Atomic Coordinates of **4**

atom	x	y	z	U_{eq},[a] Å^2
Cu(1)	0.21848 (4)	0.11977 (3)	0.19308 (3)	0.0406 (2)
Cu(2)	0.14692 (4)	0.23600 (3)	0.20313 (3)	0.0390 (2)
Cu(3)	0.06724 (4)	0.04875 (3)	0.19393 (3)	0.0412 (2)
Cu(4)	0.38343 (4)	0.09088 (3)	0.26591 (3)	0.0400 (2)
Cl	0.1861 (1)	0.11008 (7)	0.08433 (6)	0.0543 (5)
P(1)	0.02017 (9)	0.15990 (6)	0.20720 (6)	0.0365 (4)
P(2)	0.23137 (9)	0.01765 (6)	0.25000 (6)	0.0345 (4)
P(3)	0.31590 (9)	0.20589 (6)	0.24435 (5)	0.0338 (4)
P(4)	0.1187 (1)	0.33455 (7)	0.14917 (7)	0.0540 (5)
P(5)	–0.0283 (1)	–0.02780 (7)	0.13191 (7)	0.0521 (5)
P(6)	0.4758 (1)	0.08943 (7)	0.36907 (7)	0.0514 (5)
P(7)	0.4971 (1)	0.07178 (7)	0.19780 (7)	0.0547 (5)
C(1)	–0.0314 (3)	0.1628 (2)	0.2829 (2)	0.038 (2)
C(2)	0.0043 (4)	0.2086 (3)	0.3315 (2)	0.048 (2)
C(3)	–0.0286 (5)	0.2079 (3)	0.3903 (2)	0.063 (2)
C(4)	–0.0993 (5)	0.1626 (3)	0.4012 (3)	0.070 (3)
C(5)	–0.1366 (4)	0.1166 (3)	0.3532 (3)	0.068 (3)
C(6)	–0.1032 (4)	0.1166 (3)	0.2947 (2)	0.053 (2)
C(7)	–0.0859 (3)	0.1851 (2)	0.1441 (2)	0.038 (2)
C(8)	–0.1753 (4)	0.2108 (3)	0.1562 (2)	0.052 (2)
C(9)	–0.2509 (4)	0.2310 (3)	0.1059 (3)	0.069 (2)
C(10)	–0.2389 (4)	0.2256 (3)	0.0433 (3)	0.066 (2)
C(11)	–0.1508 (4)	0.2009 (3)	0.0293 (2)	0.063 (2)
C(12)	–0.0754 (4)	0.1803 (3)	0.0793 (2)	0.049 (2)
C(13)	0.2122 (3)	–0.0028 (2)	0.3327 (2)	0.032 (1)
C(14)	0.1500 (3)	0.0385 (2)	0.3619 (2)	0.044 (2)
C(15)	0.1396 (4)	0.0286 (3)	0.4255 (2)	0.055 (2)
C(16)	0.1864 (4)	–0.0244 (3)	0.4610 (2)	0.061 (2)
C(17)	0.2464 (4)	–0.0676 (3)	0.4330 (2)	0.056 (2)
C(18)	0.2603 (4)	–0.0559 (2)	0.3698 (2)	0.047 (2)
C(19)	0.2503 (3)	–0.0639 (2)	0.2106 (2)	0.036 (2)
C(20)	0.2162 (3)	–0.1262 (2)	0.2271 (2)	0.041 (2)
C(21)	0.2306 (4)	–0.1848 (3)	0.1922 (2)	0.052 (2)
C(22)	0.2779 (4)	–0.1813 (3)	0.1403 (2)	0.056 (2)
C(23)	0.3105 (4)	–0.1195 (3)	0.1223 (3)	0.065 (2)
C(24)	0.2958 (4)	–0.0616 (3)	0.1563 (2)	0.053 (2)
C(25)	0.3918 (3)	0.2574 (2)	0.1993 (2)	0.033 (2)
C(26)	0.4755 (3)	0.2944 (2)	0.2272 (2)	0.045 (2)
C(27)	0.5294 (4)	0.3309 (3)	0.1892 (3)	0.056 (2)
C(28)	0.5048 (4)	0.3295 (3)	0.1229 (3)	0.056 (2)
C(29)	0.4245 (4)	0.2916 (3)	0.0939 (2)	0.057 (2)
C(30)	0.3678 (3)	0.2566 (3)	0.1317 (2)	0.046 (2)
C(31)	0.3093 (3)	0.2488 (2)	0.3210 (2)	0.036 (2)
C(32)	0.3362 (4)	0.3155 (3)	0.3365 (2)	0.054 (2)
C(33)	0.3274 (5)	0.3428 (3)	0.3962 (3)	0.071 (3)
C(34)	0.2882 (4)	0.3062 (4)	0.4408 (3)	0.070 (3)
C(35)	0.2568 (4)	0.2414 (3)	0.4255 (3)	0.067 (2)
C(36)	0.2676 (4)	0.2123 (3)	0.3669 (2)	0.051 (2)
C(37)	–0.0022 (5)	0.3734 (4)	0.1495 (4)	0.106 (4)
C(38)	0.1132 (6)	0.3222 (4)	0.0628 (3)	0.108 (4)
C(39)	0.2061 (5)	0.4054 (3)	0.1660 (4)	0.098 (3)
C(40)	–0.0655 (5)	–0.1047 (3)	0.185 (4)	0.119 (4)
C(41)	–0.1472 (4)	0.0025 (3)	0.0874 (3)	0.084 (3)
C(42)	0.0323 (5)	–0.0646 (4)	0.0694 (3)	0.119 (4)
C(43)	0.4218 (5)	0.0779 (3)	0.4421 (2)	0.074 (3)
C(44)	0.5481 (5)	0.1670 (3)	0.3899 (3)	0.084 (3)
C(45)	0.5743 (5)	0.0249 (3)	0.3827 (3)	0.085 (3)
C(46)	0.4626 (5)	0.0849 (3)	0.1102 (3)	0.079 (3)
C(47)	0.5559 (4)	–0.0124 (3)	0.2007 (3)	0.081 (3)
C(48)	0.6070 (4)	0.1266 (3)	0.2156 (3)	0.093 (3)

[a] See Table II.

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(18) ^{63}Cu (69.09%), ^{65}Cu (30.91%), $I = {}^3/_2$, quadrupole moments -0.16×10^{-28} or -0.15×10^{-28} m^2, respectively.

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(20) (a) See for comparison the $\delta(P)$ values of $Cu_4(PhP{-}CH_2{-}PPh)_2(PEt_3)_4$ with μ_2-$PPh{-}CH_2$ bridges ($\delta(P) = -49.2$ ppm) and $Cu_8(PhP{-}CH_2{-}PPh)_2Cl_4(py)_8$ with μ_3-$PPh{-}CH_2Cu_3$ units ($\delta(P) = -91.7$ ppm). (b) For $Cu_8[(tBu)P{-}CH_2{-}P(tBu)]_2Cl_4(py)_5$ with μ_3-$P(tBu){-}CH_2Cu_3$ groups, a $\delta(P)$ value of –50 ppm was observed: Knüppel, P. C.; Stelzer, O. Unpublished results.

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Table IV. $^{31}P\{^1H\}$ NMR Data for **1a**, **1b**, **2a**, **2b**, **4**, and **5**

	$\delta(P(A))$[a]	$\delta(P(B))$[a]	$J(P(A)-P(B))$
1a[b]	−7.8	−86.8	97.2
1b[b]	13.4	−61.8	89.4
2a[b]	18 (55)[c]	−54 (55)[c]	85
2b[d]	42 (50)[c]	−26 (35)[c]	127
4[b]	−24 (100)[c] −47 (55)[c,e]	−96 (70)[c]	
5[f]	−24 (105)[c] −47 (75)[c,e]	−95 (80)[c]	

[a] Chemical shifts $\delta(P)$ relative to H_3PO_4 (85%); coupling constants in Hz. For indication of P atoms see formula. [b] Solvent CH_2Cl_2. [c] Line width $w_{1/2}$ in Hz in parentheses. [d] Solvent THF. [e] PMe_3 ligands. [f] Solvent CH_3CN.

Table V. Selected Distances (Å) in the Ether Solvate of **2a**

P(1)–Cu(1)	2.251 (3)	Cu(1)–Cl(2)	2.217 (3)
P(1)–Cu(2)	2.223 (3)	Cu(1)–Cl(2′)[a]	2.473 (3)
P(1)–Cu(3)	2.244 (2)	Cu(1)–Cu(2)	2.535 (1)
P(1)–C(1)	1.88 (1)	Cu(2)–Cl(3)	2.281 (3)
P(1)–C(4)	1.85 (1)	Cu(2)–Cu(3)	2.541 (2)
P(2)–Cu(4)	2.194 (3)	Cu(2)–N(1)	2.010 (9)
P(2)–C(4)	1.822 (9)	Cu(3)–Cl(1)	2.193 (3)
P(2)–C(5)	1.86 (1)	Cu(3)–Cl(1″)	2.534 (3)
P(2)–C(8)	1.84 (1)	Cu(4)–Cl(3)	2.332 (3)
		Cu(4)–N(2)	2.022 (7)

[a] Symmetry codes: $x', y', z' = -x, y, 0.5 - z$; $x'', y'', z'' = 0.5 - x, 0.5 - y, 1 - z$.

Upon addition of CuCl(py)[22] to CH_2Cl_2 solutions of **2b**, equilibrium 4 is shifted to the left as indicated by the concomitant high-field shift (ca. 10 ppm) of the $^{31}P\{^1H\}$ NMR signal of the phosphido group tBuP–CH$_2$. Determination of the molecular weight in CH_2Cl_2 by vapor phase osmometry gave for a sample of **2a** (without ether solvate) the expected value for a monomeric structure while for **2b** lower values (495 vs 766.0) were obtained. In order to get detailed information about the geometry of the new phosphido complexes of composition $Cu_4(R_2P-CH_2-PR)Cl_3(py)_2$ the X-ray structure of **2a** was obtained.

Structure of $Cu_4[(iPr)_2P-CH_2-P(iPr)]Cl_3(py)_2$ (2a). No interaction occurs between the ether solvate and the copper atoms of **2a**; instead, the monomers associate into chains by formation of sets of two crystallographically independent $(Cu-Cl)_2$ rings. The numbering scheme is given in Figure 1, and selected bond distances and angles are collected in Tables V and VI, respectively.

Three Cu atoms are bridged by the phosphido P(1) atom while the fourth, Cu(4), is bonded to the phosphino P(2) atom. The main difference in the bonding environment of the Cu(2) and Cu(4) atoms lies in the nature of their phosphorus ligands since both Cu atoms are coordinated by pyridine and bridged by the Cl(3) atom. Apparently the phosphino group is the better donor since the P(2)–Cu(4) distance is 0.029 (4) Å shorter than the P(1)–Cu(2) bond, while the Cl(3)–Cu(2) bond is 0.051 (4) Å shorter than the Cl(3)–Cu(4) linkage.

Because only two electron pairs are available for forming three P(1)–Cu bonds in **2a**, the PCu_3 bridging must be electron deficient. This may account for the above-mentioned differences in bond lengths of the Cu(2) and Cu(4) atoms since, unlike the P(1)–Cu(2) interaction, the P(2)–Cu(4) bond is electron precise. For electron-precise μ_2-phosphido bridges, the P–Cu bond lengths depend strongly on the coordination number (CN) of the Cu atom; that is, these bonds average 2.209 (5) Å in A (CN = 2),[2] 2.268 Å in $Cu_4(\mu_2-PPh_2)_4(Ph_2P-CH_2-PPh_2)_2$ (K) (CN = 3),[4] and 2.36(1) Å in C (CN = 4).[5,6] That the bond lengths in the PCu_3 fragments of **2a** fall between those of A and K may indicate that relative basicities of the phosphido and copper substituents also control the P–Cu bond distances.

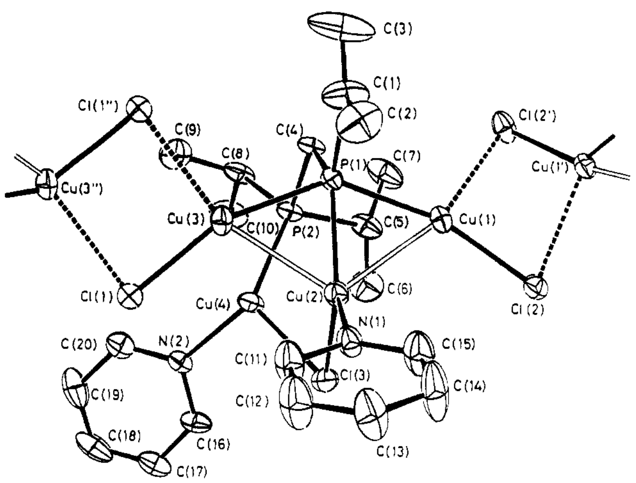

Figure 1. Segment of the infinite chains formed by **2a** with 20% probability thermal ellipsoids and hydrogens removed.

Table VI. Selected Bond Angles (deg) in the Ether Solvate of **2a**

Cu(1)–P(1)–Cu(3)	138.3 (1)	P(1)–Cu(1)–Cl(2)	157.8 (1)
Cu(1)–P(1)–Cu(2)	69.02 (8)	P(1)–Cu(1)–Cl(2′)[a]	106.2 (1)
Cu(2)–P(1)–Cu(3)	69.35 (9)	Cl(2)–Cu(1)–Cl(2′)	94.3 (1)
Cu(1)–P(1)–C(1)	102.0 (4)	P(1)–Cu(2)–Cl(3)	128.4 (1)
Cu(3)–P(1)–C(1)	104.9 (4)	P(1)–Cu(2)–N(1)	124.9 (3)
Cu(1)–P(1)–C(4)	104.6 (3)	Cl(3)–Cu(2)–N(1)	106.6 (3)
Cu(3)–P(1)–C(4)	97.6 (3)	P(1)–Cu(3)–Cl(1)	161.2 (1)
Cu(2)–P(1)–C(1)	127.9 (5)	P(1)–Cu(3)–Cl(1″)	105.0 (1)
Cu(2)–P(1)–C(4)	125.7 (3)	Cl(1)–Cu(3)–Cl(1″)	93.8 (1)
C(1)–P(1)–C(4)	106.4 (6)	P(2)–Cu(4)–Cl(3)	119.5 (1)
Cu(4)–P(2)–C(4)	116.0 (3)	P(2)–Cu(4)–N(2)	132.7 (3)
Cu(4)–P(2)–C(5)	110.2 (4)	Cl(3)–Cu(4)–N(2)	100.3 (3)
Cu(4)–P(2)–C(8)	116.3 (3)	Cu(3)–Cl(1)–Cu(3″)	86.2 (1)
C(4)–P(2)–C(5)	101.5 (4)	Cu(1)–Cl(2)–Cu(1′)	76.56 (9)
C(4)–P(2)–C(8)	103.6 (5)	Cu(2)–Cl(3)–Cu(4)	80.1 (1)
C(5)–P(2)–C(8)	108.1 (6)	P(1)–C(4)–P(2)	110.1 (5)

[a] See Table V.

The C(1), C(4), Cu(1), and Cu(3) positions define the vertices of a distorted tetrahedron about the P(1) atom with Cu(2) centered above the Cu(1)–Cu(3) edge. Thus the P(1), Cu(1), Cu(2), Cu(3) fragment is essentially planar (rms deviation 0.021 Å), and the Cu(1)–P(1)–Cu(3) angle is spread to 138.3 (1)°. The three P(1)–Cu bonds are essentially equidistant, the central P(1)–Cu(2) bond being only 0.025 (6) Å shorter than the average of the other two P(1)–Cu distances (2.248 (5) Å).

Symmetrical μ_3-phosphido bridging is new in transition-metal chemistry. The most closely related structures reported to date are those of the lithium phosphides $[Li_2(\mu_3-PR_2)(\mu_2-PR_2)THF]_2$ (R = tBu,[23a] SiMe$_3$[23b]), which possess planar PLi_3 fragments. Furthermore the planar ICu_3 units found in some iodocuprate anions[24-27] (e.g. $[Cu_2I_3]^-$ (L)) are formally related to the PCu_3 moiety of **2a** although the Cu–I bond lengths vary considerably (>0.2 Å).[24,25]

The Cu(1)–Cu(2) (2.535 (1) Å) and Cu(2)–Cu(3) distances (2.541 (1) Å) in **2a** are both shorter than Cu–Cu bonds in elemental copper (2.556 Å).[28] For shorter Cu–Cu distances, either electron-deficient aryl or alkyl bridging groups are required (e.g. D, 2.42 Å),[7] or the Cu–Cu contact has to be spanned by three bridging groups (e.g. L, 2.452 (3)–2.481 (2) Å).[24,25]

When pairs of Cu(I) ions are bridged, the nature of the resulting Cu---Cu interactions is controversial. Since all possible bonding and antibonding 3d(Cu)–3d(Cu) orbitals are filled, these inter-

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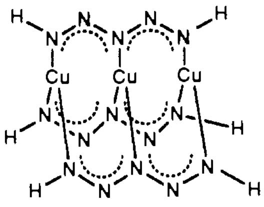
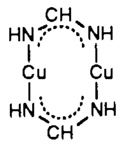
actions are clearly antibonding. Hoffmann and co-workers have shown that the 4s and 4p orbitals can be mixed into the 3d set so as to enhance the bonding and diminish the antibonding nature of the 3d(Cu)–3d(Cu) interactions.[29] However, it is not obvious that this mixing will in fact overcome the initial antibonding deficit and lead to significant Cu---Cu bonding. While extended Hückel calculations indicate the formation of "soft" Cu–Cu bonds in M (Cu–Cu = 2.35 Å),[29,30] Xα calculations on N (Cu–Cu = 2.49 Å) were interpreted as indicating no significant Cu–Cu bond formation.[31] Apparently the geometries of the latter compounds are determined mainly by the bonding requirements of the ligands.



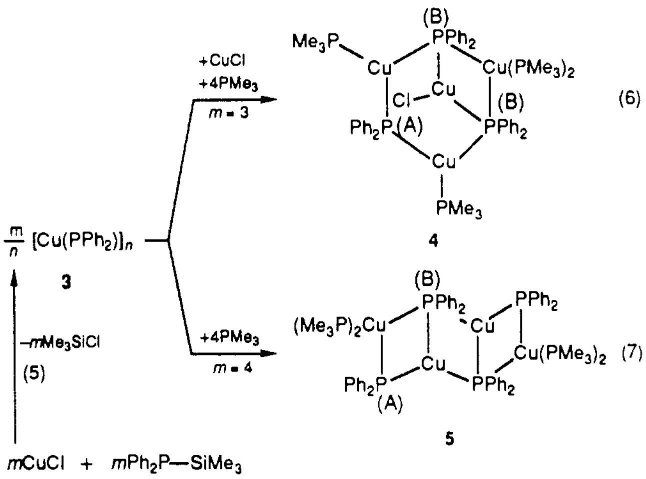
M



N

In **2a** and **4**, the μ_3-PRR′ or μ_3-PR$_2$ groups, respectively, use two tetrahedral orbitals to bind to three copper atoms—the covalency implied by this description being somewhat exaggerated. In order to form strong P–Cu bonds the copper atoms will be squeezed together. This bridging geometry might be stabilized by 3d, 4s, and 4p mixing, which will at least reduce the antibonding nature of the Cu–Cu interactions.

Reaction of [Cu(PPh$_2$)]$_n$ with CuCl and PMe$_3$. Cleavage of the polymeric structure of [Cu(PPh$_2$)]$_n$[13] by donor molecules L (e.g. PMe$_3$) was expected to give copper(I) phosphido complexes containing (CuPPh$_2$)$_n$ cores (n = 2–4) with the Cu(I) centers coordinatively saturated by the ligands L. Addition of copper(I) halide acceptors (e.g. CuCl) to the electron-precise Cu–P bonds of the Cu–μ_2-PPh$_2$–Cu bridges should lead to novel complexes with electron-deficient μ_3-PPh$_2$Cu$_3$ units.



Polymer [Cu(PPh$_2$)]$_n$ (**3**), which is insoluble in common organic solvents, was first prepared by Issleib and Fröhlich by reaction of KPPh$_2$·2 dioxane with Cu^{I}Br.[13a] Alternatively it may be synthesized by cleavage of the P–Si bond in Ph$_2$P–SiMe$_3$ with Cu^{I}Cl in good yields.[13b] Samples of [Cu(PPh$_2$)]$_n$ prepared by this method always contained small quantities of CuCl (eq 5).

If [Cu(PPh$_2$)]$_n$ (**3**)[13] is treated with a 1:4 mixture of CuCl and PMe$_3$ in THF, a clear yellow solution is obtained from which yellow crystals of composition Cu$_4$(PPh$_2$)$_3$Cl(PMe$_3$)$_4$ (**4**) may be isolated (eq 6). The ^{31}P{^{1}H} NMR spectrum of **4** (CH$_2$Cl$_2$ solution) showed three broad signals at −96, −47, and −24 ppm of relative intensity 2:4:1. The signal of the relative intensity 4 corresponds to the PMe$_3$ ligands coordinated to Cu(I).[32] Taking into account the high-field shift of δ(P) values on going from μ_2-PR$_2$ to μ_3-PR$_2$ groups,[20,21] the resonances at −96 ppm or −24 ppm may be assigned to μ_3-PPh$_2$ or μ_2-PPh$_2$ bridges, respectively (Table IV).

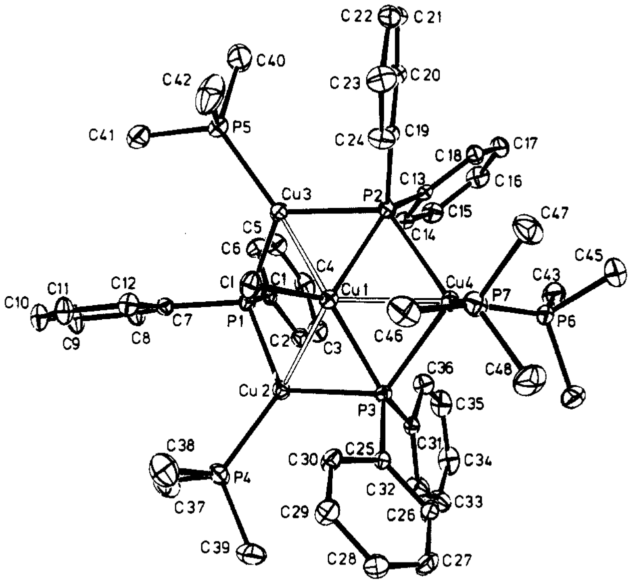


Figure 2. Perspective drawing of **4** without hydrogens and with 20% probability thermal ellipsoids.

On the basis of these NMR data and the results of the single-crystal X-ray diffraction study (see below), a structure in solution is suggested in which the CuCl unit coordinates to two Ph$_2$P groups of the Cu$_3$(PPh$_2$)$_3$ six-membered ring system, forming a cluster of composition Cu$_4$(PPh$_2$)$_3$Cl(PMe$_3$)$_4$ (**4**) with μ_3-PPh$_2$ and μ_2-PPh$_2$ bridges.

By reaction of [Cu(PPh$_2$)]$_n$ with PMe$_3$, however, a yellow copper(I) phosphido complex of composition Cu(PPh$_2$)PMe$_3$ (**5**) (eq 7) was obtained. Since the [Cu(PPh$_2$)]$_n$ employed contained a small quantity of Cl (0.41%; see Experimental Section) in form of CuCl, reaction 7 yielded small amounts of compound **4**.

The ^{31}P{^{1}H} NMR spectrum of **5** is similar to that of **4**. By analogy, the broad resonances at −95, −47, and −24 ppm with an 1:2:1 intensity ratio may be assigned to μ_3-PPh$_2$ (δ(P) = −95 ppm) or μ_2-PPh$_2$ bridges (δ(P) = −24 ppm), respectively, and to the PMe$_3$ ligands coordinated to Cu(I) (δ(P) = −47 ppm).

A tetranuclear planar structure containing μ_2-PPh$_2$ and μ_3-PPh$_2$ units in a 1:1 ratio linked by three- and four-coordinate Cu(I) ions is proposed for **5**. This structure is closely related to that of the lithium phosphide [Li$_2$(μ_3-tBu$_2$P)(μ_2-tBu$_2$P)(C$_4$H$_8$O)]$_2$[23a] in which two of the phosphido groups are triply bridging to three Li atoms, whereas the other two bridge only two. A Cu$_4$X$_4$ skeleton comparable to that in **5** is found in the nonplanar step structure, which copper(I) complexes of composition Cu$_4$X$_4$(PR$_3$)$_4$[33-35] show for large X as an alternative to the cubanoid structure for small X (e.g. Cu$_4$Cl$_4$(PPh$_3$)$_4$).[36]

In the ^{31}P{^{1}H} NMR spectra of THF solutions of **5** with added PMe$_3$ (equimolar amount), no separated signals for free and coordinated PMe$_3$[32,37] were observed, even at low temperature.

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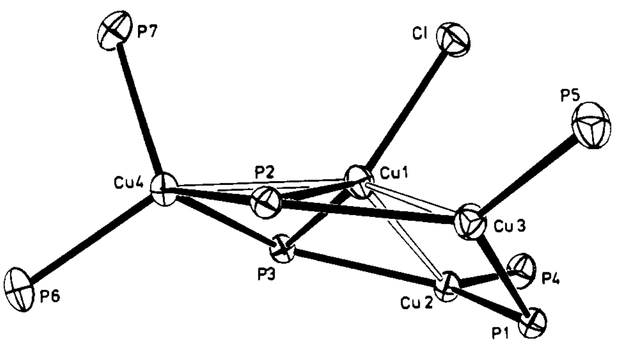

Figure 3. View of the $ClCu_4P_7$ core of **4** with 20% probability thermal ellipsoids.

Table VII. Selected Distances (Å) in **4**

Cu(1)–Cl	2.237 (1)	P(3)–C(25)	1.819 (5)
Cu(1)–P(2)	2.316 (1)	P(3)–C(31)	1.820 (5)
Cu(1)–P(3)	2.287 (1)	P(4)–C(37)	1.811 (7)
Cu(2)–P(3)	2.376 (1)	P(4)–C(38)	1.804 (6)
Cu(3)–P(2)	2.403 (1)	P(4)–C(39)	1.818 (6)
Cu(2)–P(1)	2.290 (1)	P(5)–C(40)	1.801 (8)
Cu(3)–P(1)	2.299 (1)	P(5)–C(41)	1.812 (6)
Cu(4)–P(2)	2.488 (1)	P(5)–C(42)	1.810 (8)
Cu(4)–P(3)	2.443 (1)	P(6)–C(43)	1.818 (6)
Cu(2)–P(4)	2.232 (2)	P(6)–C(44)	1.820 (6)
Cu(3)–P(5)	2.236 (1)	P(6)–C(45)	1.825 (6)
Cu(4)–P(6)	2.286 (1)	P(7)–C(46)	1.820 (6)
Cu(4)–P(7)	2.307 (2)	P(7)–C(47)	1.827 (6)
P(1)–C(1)	1.836 (5)	P(7)–C(48)	1.821 (6)
P(1)–C(7)	1.835 (4)	Cu(1)–Cu(2)	2.4988 (8)
P(2)–C(13)	1.832 (5)	Cu(1)–Cu(3)	2.4836 (8)
P(2)–C(19)	1.835 (5)	Cu(1)–Cu(4)	2.5345 (8)

This may be explained by a rapid exchange equilibrium according to eq 8.

$$\mathrm{Cu_4(PPh_2)_4(PMe_3)_4} \xrightleftharpoons{-\mathrm{PMe_3}} \mathrm{Cu_4(PPh_2)_4(PMe_3)_3} \xrightleftharpoons{-\mathrm{PMe_3}} \mathrm{Cu_4(PPh_2)_4(PMe_3)_2} \quad (8)$$

Solutions of **5** in CH_2Cl_2 are nonconductors, and molecular weight determinations in $CHCl_3$ gave values (~400) lower than those expected (1299.2) indicating an extensive dissociation of **5** in diluted $CHCl_3$ solution.

X-ray Study of $Cu_4(PPh_2)_3Cl(PMe_3)_4$ (4). The molecular structure is illustrated in Figure 2, and a view of the core of the molecule is given in Figure 3. The geometry of the latter deviates somewhat from C_s symmetry—the Cu(1), Cu(4), Cl, P(1), P(6), and P(7) atoms lying close to the approximate mirror plane. Examination of appropriate pairs of bond distances and angles (Tables VII and VIII, respectively) reveals numerous small but significant variations from C_s symmetry. This reduction in symmetry is probably provoked by steric interactions between the pendant Ph and PMe_3 groups. The orientations of the latter, which are undoubtedly determined by an interplay of intramolecular and packing forces, obviously violate the mirror plane (Figure 2).

As shown in Figure 3, **4** contains a chair-shaped Cu_3P_3 six-membered ring to which the Cu(1)–Cl entity is coordinated via the two μ_3-phosphorus atoms P(2) and P(3). While the Cu(1)–Cl distance is only 0.011 (2) Å shorter than that in $[CuCl(iPr)_2P\text{-}CH_2\text{-}P(iPr)H]_2$,[9] the Cu–P distances in the latter are 0.065 (25) Å shorter than those in **4**. Although the Cu(1) atom is displaced by 0.3837 (6) Å from its substituent plane toward P(1), the long Cu(1)–P(1) distance (2.871 (1) Å) indicates a very weak interaction; therefore, P(1) appears to bridge only the three-coordinate Cu(2) and Cu(3) atoms.

The Cu(1) atom caps the Cu(3)---Cu(4) and Cu(2)---Cu(4) edges of the coordination polyhedra of P(2) and P(3), respectively. Since Cu(2) and Cu(3) are three-coordinate while Cu(4) is four-coordinate, the P(2)–Cu(3) and P(3)–Cu(2) distances are on the average 0.08 (4) Å shorter than the P(2)–Cu(4) and P(3)–Cu(4) bond lengths. A similar average shortening (0.06 (2) Å) is shown by the Cu–PMe_3 bond distances upon reduction of the copper coordination number from four to three. The PCu_3 fragments of **4** exhibit more buckling than does that of **2a**; that is, the rms deviations for planarity of the P(2), Cu(1), Cu(3), and Cu(4) and P(3), Cu(1), Cu(2), and Cu(4) units are 0.078 and 0.156 Å, respectively.

Table VIII. Selected Bond Angles (deg) in **4**

Cl–Cu(1)–P(2)	115.36 (5)	Cu(1)–P(2)–C(13)	131.3 (1)
Cl–Cu(1)–P(3)	121.85 (5)	Cu(1)–P(3)–C(31)	129.4 (2)
P(2)–Cu(1)–P(3)	114.43 (5)	Cu(1)–P(2)–C(19)	121.7 (1)
P(1)–Cu(2)–P(3)	120.59 (5)	Cu(1)–P(3)–C(25)	120.1 (1)
P(1)–Cu(3)–P(2)	115.81 (5)	Cu(3)–P(2)–C(13)	103.7 (1)
P(1)–Cu(2)–P(4)	121.26 (6)	Cu(2)–P(3)–C(31)	90.3 (1)
P(1)–Cu(3)–P(5)	124.00 (5)	Cu(3)–P(2)–C(19)	101.3 (1)
P(3)–Cu(2)–P(4)	117.66 (5)	Cu(2)–P(3)–C(25)	106.0 (1)
P(2)–Cu(3)–P(5)	120.18 (5)	Cu(4)–P(2)–C(13)	104.8 (1)
P(2)–Cu(4)–P(3)	103.40 (4)	Cu(4)–P(3)–C(31)	109.9 (1)
P(2)–Cu(4)–P(6)	114.88 (5)	Cu(4)–P(2)–C(19)	112.4 (2)
P(3)–Cu(4)–P(6)	107.99 (5)	Cu(4)–P(3)–C(25)	112.2 (1)
P(2)–Cu(4)–P(7)	117.12 (5)	C(13)–P(2)–C(19)	106.6 (2)
P(3)–Cu(4)–P(7)	107.88 (5)	C(25)–P(3)–C(31)	108.5 (2)
P(6)–Cu(4)–P(7)	105.13 (6)	Cu(2)–P(4)–C(37)	115.8 (3)
Cu(2)–P(1)–Cu(3)	112.62 (6)	Cu(2)–P(4)–C(38)	111.0 (2)
Cu(2)–P(1)–C(1)	114.6 (1)	Cu(2)–P(4)–C(39)	121.0 (2)
Cu(3)–P(1)–C(1)	106.8 (2)	Cu(3)–P(5)–C(40)	119.6 (2)
Cu(2)–P(1)–C(7)	107.3 (2)	Cu(3)–P(5)–C(41)	116.6 (2)
Cu(3)–P(1)–C(7)	111.6 (2)	Cu(3)–P(5)–C(42)	113.0 (2)
C(1)–P(1)–C(7)	103.6 (2)	Cu(4)–P(6)–C(43)	123.6 (2)
Cu(3)–P(2)–Cu(4)	126.48 (5)	Cu(4)–P(6)–C(44)	113.3 (2)
Cu(2)–P(3)–Cu(4)	126.99 (5)	Cu(4)–P(6)–C(45)	114.7 (2)
Cu(1)–P(2)–Cu(3)	63.49 (4)	Cu(4)–P(7)–C(46)	120.9 (2)
Cu(1)–P(3)–Cu(2)	64.77 (4)	Cu(4)–P(7)–C(47)	117.5 (2)
Cu(1)–P(2)–Cu(4)	63.58 (4)	Cu(4)–P(7)–C(48)	113.2 (2)
Cu(1)–P(3)–Cu(4)	64.70 (4)	C(Me)–P–C(Me)	101.3 (13)[a]

[a] Average C–P–C angle of the PMe_3 groups.

All of the μ_3-bridging P–Cu distances in **4** are significantly longer than those of **2a**. On the average, the difference amounts to 0.08 (2) Å for the capping P–Cu bonds and is even greater (0.14 (2) Å) for the other P–Cu bonds involving three-coordinate Cu atoms. Part of this trend may be due to an inductive effect; that is, the μ-Cl and py ligands of **2a** are poorer donors than the μ-PPh_2 and PMe_3 ligands of **4**. Furthermore, bicyclic ring formation in **4** places additional restrictions on the PCu_3 fragments; that is, the capped Cu–P–Cu angles of **4**, which are found in the six-membered ring, are on the average 11.6 (4)° smaller than the corresponding angle in **2a**, which is not constrained by ring formation. With μ_3-bridging distances as in **2a**, the smaller capped Cu–P–Cu angles of **4** would require very short Cu–Cu distances (~2.37 Å). In fact, the three short Cu–Cu contacts (Figure 2) average 2.51 (2) Å, a value comparable to that in **2a**. Therefore, there should be a limit to which Cu–Cu distances may be compressed by μ_3-phosphorus bridges without affecting the accompanying P–Cu bonds.

In **4**, the mean of the capped Cu–P–Cu angles is 14.1 (4)° larger than the Cu(2)–P(1)–Cu(3) angle of the μ_2-bridge. The average of the P(1)–Cu(2) and P(1)–Cu(3) bond lengths (2.295 (6) Å) should be compared with that reported for K (2.268 Å),[4] which also contains three-coordinate copper atoms.

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Supplementary Material Available: Tables of full crystal data and refinement parameters, anisotropic temperature factors, idealized hydrogen parameters, nonessential bond distances and angles, and best planes of the μ_3 bridges (12 pages); tables of observed and calculated structure factor amplitudes (77 pages). Ordering information is given on any current masthead page.