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TRIPHENYLPHOSPHANE COMPLEXES OF COPPER(I): STRUCTURAL AND ^{31}P NMR INVESTIGATIONS

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Abstract—The phosphane complexes $[(Ph_3P)_2CuCl_2Li(THF)_2]\cdot 1.5THF$, $[(Ph_3P)_2CuCl]\cdot 0.5THF$, $[(Ph_3P)_3CuCl]\cdot MeCN$, $[(Ph_3P)_3CuCl]\cdot THF$ and $[(Ph_3P)_2CuCl_2Cu(PPh_3)]$ (THF = tetrahydrofuran) have been prepared and characterized on the basis of analytical, IR, mass and NMR spectral techniques. The crystal structures of the complexes underline the ability of the copper(I) centre to exist in a distorted trigonal planar as well as in a distorted tetrahedral environment. Copyright © 1996 Elsevier Science Ltd

The importance of copper(I) in complex chemistry,[1] organometallic reagents,[2–7] mixed valence compounds[8,9] and biologically active sites[10,11] is based on the variable coordination ability and redox behaviour of the metal centre. The coordination chemistry of copper(I) has been studied intensively in the last three decades. Especially the combined fixation of phosphanes and halides at copper(I) has been of great interest.[12] Depending on the halide and the presence of the phosphane, a large variety of compositions can be realized.[13–19] During our research we obtained the title compound $[(Ph_3P)_2CuCl_2Li(THF)_2]\cdot 1.5THF$ (**1**·1.5THF; THF = tetrahydrofuran). In order to compare the spectroscopical and structural data, we synthesized the complexes $[(Ph_3P)_2CuCl]\cdot 0.5THF$ (**2**·0.5THF), $[(Ph_3P)_3CuCl]\cdot MeCN$ (**3**·MeCN), $[(Ph_3P)_3CuCl]\cdot THF$ (**3**·THF) and $[(Ph_3P)_2CuCl_2Cu(PPh_3)]$ (**4**). Moreover, the not always precise standard deviations of the already known complexes containing units like $(Ph_3P)_xCu$ initiated our research in this area. Compound **2** possesses the coordination number (CN) three at the copper atom, while **3** has a CN of four. Compound **4** contains two different copper(I) centres, one with CN three and one with CN four.

EXPERIMENTAL

Instruments and materials

The ^1H, ^{13}C and ^{31}P NMR spectra were recorded on the Bruker spectrometers AC-300 and AC-400 (^1H: 300.134 MHz; ^{13}C: 75.469 MHz; ^{31}P: 161.977 MHz). Standard was TMS (external; ^1H, ^{13}C) and 85% aqueous H_3PO_4 (external; ^{31}P) with $\delta = 0.0$. The IR spectra were measured on a Bruker instrument IFS-88 (Nujol mulls, CsI discs for the range 4000–500 cm^{-1}, polyethylene discs for the range 500–100 cm^{-1}). For the EI mass spectra, a Varian CH7a mass spectrometer (70 eV) was used. The melting points (m.p.) were measured with a Dr Tottoli (Büchi) melting point apparatus in sealed tubes under argon (values not corrected).

All preparative operations were performed under argon. Purification and drying of the solvents was done using standard methods.[20] CuCl was prepared following literature procedures.[21] LiCl and PPh_3 were purchased from Merck-Schuchardt and used without further purification.

Synthesis of the complexes

Preparation of $[(Ph_3P)_2CuCl_2Li(THF)_2]\cdot 1.5THF$ (**1**·1.5THF). PPh_3 (2.76 g, 10.52 mmol), CuCl (0.52 g, 5.26 mmol) and LiCl (0.22 g, 5.26 mmol) were dissolved in 50 cm^3 THF with constant stirring. The mixture was refluxed for 4 h. After

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cooling the solution to 5°C, large colourless crystals precipitated which were dried in a weak flow of argon. Yield: quantitative. Results of the elementary analysis, the melting points and the ^{31}P NMR signal are listed in Table 1. ^{1}H NMR (CD_3CN; ppm): 1.73 (m, 14H, THF), 3.59 (m, 14H, THF), 7.2–7.34 (m, 30H, phenyl H). ^{13}C NMR (CD_3CN; ppm): 25.2, 66.9 (THF), 129.3 [C(3/5)], 129.4 [C(4)], 130.5 [C(2/6)], 137.4 [C(1)]. Mass spectrum, *m/z* (%): 262 (100) $(PPh_3)^+$, 185 (9) $(PPh_2)^+$, 108 (27) $(PPh)^+$, 72 (6) $(C_4H_8O)^+$, 42 (18) $(LiCl)^+$. IR (cm^{-1}): 1966 w, 1898 w, 1832 w, 1659 w, 1632 w, 1584 w, 1435 m, 1308 m, 1290 m, 1183 m, 1156 m, 1093 s, 1071 s, 1051 s, 1027 s, 998 m, 912 m, 744 s, 696 s, 618 w, 526 m, 516 s, 433 m, 401 m (br), 342 w [$\nu(LiCl_2$, ring)], 306 [$\nu(CuO_2)$], 240 w [sh, $\nu(CuCl_2$, ring)], 214 m [br, $\nu(CuP_2)$], 163 w, 105 vw.

Preparation of $[(Ph_3P)_2CuCl]\cdot0.5THF$ (**2**·0.5THF). PPh_3 (3.72 g, 14.18 mmol) and CuCl (0.70 g, 7.09 mmol) were refluxed in 50 cm^3 THF for 5 h. The hot solution was filtered and cooled to 5°C. Colourless crystals were obtained which were dried in a weak flow of argon. Yield: 3.64 g (82%). ^{1}H NMR (CD_3CN; ppm): 1.73 (m, 2H, THF), 3.60 (m, 2H, THF), 7.21–7.33 (m, 30H, phenyl H). ^{13}C NMR (CD_3CN; ppm): 24.7, 66.6 (THF), 129.3 [C(3/5)], 129.7 [C(4)], 130.6 [C(2/6)], 134.8 [C(1)]. Mass spectrum, *m/z* (%): 262 (100) $(PPh_3)^+$, 183 (53) $(Ph_2P-2H)^+$, 108 (39) $(PPh)^+$. IR (cm^{-1}): 3049 s, 2249 w, 1909 vw, 1825 w, 1661 m, 1585 m, 1480 m, 1432 s, 1312 w, 1185 vw, 1155 vw, 1092 m, 1071 w, 1027 vw, 999 vw, 925 vw, 853 vw, 777 w, 764 w, 748 s, 696 vw, 619 vw, 518 s, 507 m, 486 w, 448 vw, 414 w, 251 vw [$\nu(CuCl)$], 223 m [$\nu(CuP_2)$], 105 m.

Preparation of $[(Ph_3P)_3CuCl]\cdot MeCN$ (**3**·MeCN). PPh_3 (3.94 g, 15.00 mmol) and CuCl (4.95 g, 5.00 mmol) were dissolved in 50 cm^3 MeCN and refluxed with constant stirring for 4 h. The hot mixture was filtered and the filtrate was cooled to 5°C. Colourless crystals were obtained which easily lose the acetonitrile. Yield: quantitative. ^{1}H NMR (CD_3CN; ppm): 7.20–7.57 (m, phenyl H). ^{13}C NMR (CD_3CN; ppm): 129.6 [C(3/5)], 130.8 [C(4)], 134.6 [C(2/6)], 134.8 [C(1)]. Mass spectrum, *m/z* (%): 262 (100) $(PPh_3)^+$, 183 (52) $(Ph_2P-2H)^+$, 108 (25) $(PPh)^+$. IR (cm^{-1}): 2725 w, 1669 w, 1584 w, 1436 s, 1310 m, 1184 m, 1157 m, 1120 m, 1094 m, 1071 w, 1027 w, 998 w, 923 vw, 855 vw, 743 m, 696 s, 619 vw, 540 m, 517 m, 504 m, 459 w, 445 m, 408 m, 397 m, 249 w [$\nu(CuCl)$], 228 w, 223 w [$\nu(CuP_3)$], 190 vw, 177 vw, 169 w, 149 vw, 134 vw.

Preparation of $[(Ph_3P)_3CuCl]\cdot THF$ (**3**·THF). The same reaction conditions as described for **3**·MeCN were applied with the exception of the use of THF as solvent. ^{1}H NMR (CD_3CN; ppm): 1.84 (m, 4H, THF), 3.74 (m, 4H, THF), 7.17–7.38 (m, 45H, phenyl H). ^{13}C NMR (CD_3CN): 26.5, 68.4 (THF), 129.1 [C(3/5)], 130.0 [C(4)], 130.8 [C(2/6)], 133.9 [C(1)]. Mass spectrum, *m/z* (%): 262 (100) $(PPh_3)^+$, 183 (44) $(Ph_2P-2H)^+$, 108 (32) $(PPh)^+$. IR (cm^{-1}): 2723 vw, 1961 w, 1583 w, 1434 s, 1308 m, 1263 m, 1182 m, 1156 m, 1090 m, 1067 m, 1026 m, 997 m, 914 w, 859 w, 768 w, 743 s, 694 s, 618 vw, 515 s, 490 m, 451 w, 442 w, 428 w, 416 w, 407 w, 340 vw, 307 vw, 280 vw, 245 m [$\nu(CuCl)$], 220 m [sh, $\nu(CuP_3)$], 182 vw, 147 vw.

Preparation of $[(Ph_3P)_2CuCl_2Cu(PPh_3)]$ (**4**). PPh_3 (4.32 g, 16.47 mmol) and CuCl (1.09 g, 11.01 mmol)

Table 1. Analytical data, melting points and ^{31}P NMR chemical shifts of the complexes

	Found (calc.) (%)							
Compound	C	H	N	Cu	Cl	P	m.p. (°C)[a]	$\delta(^{31}P)$ (ppm)
1·1.5THF	58.0 (58.4)	5.6 (5.4)	—	6.9 (6.9)	7.7 (7.7)	6.7 (6.7)	181	−4.5[b]
2·0.5THF	67.7 (67.8)	6.6 (6.6)	—	9.0 (9.1)	5.2 (5.1)	9.0 (8.9)	201	−3.6[c]
3·MeCN	72.2 (72.6)	5.3 (5.2)	1.5 (1.5)	6.9 (6.9)	4.0 (3.8)	9.9 (10.0)	204	−3.7[c]
3·THF	72.5 (72.7)	5.3 (5.6)	—	6.5 (6.6)	4.0 (3.7)	9.6 (9.7)	203	−4.7[c]
4	65.6 (65.9)	4.5 (4.6)	—	13.0 (12.9)	7.2 (7.2)	9.4 (9.4)	172	−3.4 (CuP_2)[b] −4.3 (CuP)

[a] Compounds without solvent (dried *in vacuo*).
[b] THF-d_8.
[c] CD_3CN.

were dissolved in 50 cm^3 THF and refluxed with constant stirring for 6 h. The hot reaction mixture was filtered and the filtrate was cooled to 5°C. Colourless crystals were obtained. Yield: 4.23 g (78%). ^1H (CD_3CN; ppm): 7.25–7.35 (m, phenyl H). ^{13}C NMR (CD_3CN; ppm): 129.0 [br, C(3/5)], 130.3 [br, C(4)], 131.2 [br, C(2/6)], 134.7 [br, C(1)]. Mass spectrum, *m*/*z* (%): 262 (100) $(PPh_3)^+$, 183 (50) $(Ph_2P-2H)^+$, 108 (36) $(PPh)^+$. IR (cm^{-1}): 3046 s, 2676 w, 1976 w, 1965 w, 1886 w, 1818 w, 1767 w, 1662 w, 1584 m, 1571 w, 1435 s, 1329 w, 1308 w, 1184 w, 1156 w, 1096 w, 1070 w, 998 w, 972 vw, 917 vw, 851 vw, 749 m, 743 s, 694 s, 619 vw, 527 m, 519 m, 502 m, 444 w, 437 w, 419 vw, 397 m, 304 w, 278 w, 240 vw [$\nu(CuCl_2$, ring)], 219 w [ν(CuP)], 174 w.

X-ray measurements and structure determination

The crystals were covered with a high boiling paraffin oil and mounted on the top of a glass capillary under a flow of cold gaseous nitrogen. The orientation matrix and preliminary unit cell dimensions were determined from 25 reflections on a four-circle diffractometer with graphite-monochromated (Mo-K_α) radiation ($\lambda = 71.073$ pm) (Siemens P4: **1**·1.5 THF, **3**·THF, **4**; Enraf–Nonius CAD4: **2**·0.5 THF, **3**·MeCN). The final cell parameters were determined from 25 high angle reflections.

The intensity data were corrected for Lorentz and polarization effects (collecting of the intensities and correction of the absorption effects; see Table 2). Refinement was by full-matrix least-squares, minimizing the function $\Sigma w(F_o^2 - F_c^2)^2$. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated for ideal positions and refined with a common thermal parameter. For the solution and refinement of the structures, the programs SHELXTL-PLUS[22] and SHELXL-93[23] were used. The calculations of the bond lengths, bond angles and U_{eq} were performed using the program PLATON.[24]

Three THF molecules in **1**·1.5THF are disordered at one carbon atom [occupation factors: C(821), C(822) 0.5; C(901) 0.7, C(902) 0.3; C(951), C(952) 0.5]. The THF molecule of **2**·0.5THF is disordered around a centre of symmetry [occupation factor: O(1)—C(82) 0.5, hydrogen atoms omitted]. The structure of **4** has already been determined in the space group $P2_1/c$ [$a = 1927(2)$, $b = 981(1)$, $c = 2702(3)$ pm, $\beta = 112.5(8)°$] with an isotropic refinement of the carbon atoms.[15]

RESULTS AND DISCUSSION

The heterometallic compound **1** can be synthesized according to the following equation:

$$2PPh_3 + CuCl + LiCl \xrightarrow{THF} \underset{\mathbf{1}}{[(Ph_3P)_2CuCl_2Li(THF)_2].}$$

Compound **1** and the analogous compounds **2**–**4** show all ^{31}P NMR resonances in the region of −3 to −5 ppm. A distinction whether the respective complex possesses CN four or CN three at the copper(I) centre is not possible using ^{31}P NMR spectroscopy in solution. In contrast, the solid state ^{31}P NMR analysis of copper(I) complexes allows to assign CN three because of the lower symmetry relative to CN four.[12,26] The values for **1**–**4** are in good agreement with the resonances of $[Cu(PPh_3)_2][NO_3]$ (0.3 ppm), $[Cu(PPh_3)_3][NO_3]$ (−2.9 ppm) and $[Cu(PPh_3)_4][ClO_4]$ (−5.0 ppm).[26] In general, the coordination of the triphenylphosphane to copper(I) causes no large shifts of the signal of the uncoordinated phosphane at −6.0 ppm.[27]

A better probe for the coordination sphere of the copper(I) ion is vibrational spectroscopy. A lower CN of the metal centre should shift the modes of vibration to higher wavenumbers. However, the IR bands ν(CuP), $\nu(CuP_2)$ and $\nu(CuP_3)$ in **1**·1.5THF–**4** give rise to only one absorption for each compound (see Table 3). All values are in the region 210–225 cm^{-1}. A small difference is detectable for the Cu—Cl vibrations. The ring vibrations [**1**·1.5THF: $\nu(CuCl_2Li)$; **4**: $\nu(Cu_2Cl_2)$] can be observed at 240 cm^{-1}, while the terminal Cu—Cl signals have somewhat higher modes at 251 (**2**·0.5THF), 249 (**3**·MeCN) and 245 cm^{-1} (**3**·THF). The EI mass spectra exhibit a series of low-mass, high-intensity peaks for all complexes caused by the fragmentation of PPh_3 [*m*/*z* = 262 $(PPh_3)^+$, 183 $(Ph_2P-2H)^+$, 108 $(PPh)^+$]. Only the decomposition of **1**·1.5THF produces a copper-containing fragment, $(CuClPPh)^+$, at *m*/*z* = 206.

Description of the structures

Selected bond lengths and angles are presented in Table 4. The coordination around the copper atom in **1**·1.5THF is distorted tetrahedral (Fig. 1). The Cu—P distances of 226.9(1) and 227.4(1) pm are surprisingly in good agreement with those of **2**·0.5THF [225.64(9), 226.79(9) pm] (Fig. 2), **4** [222.8(1), 224.3(1) pm], $[(Ph_3P)_2CuCl]\cdot0.5C_6H_6$ [226.0(2), 227.2(2) pm][12] and $[(Ph_3P)_2CuCl_2CuPPh_3]$ (mean value 224 pm).[15,16] The copper(I) centre with CN four in **3**·MeCN (Fig. 3), **3**·THF and structures which contain the complex unit

Table 2. Summary of crystal, intensity collection and refinement data

	1·1.5THF	**2**·0.5THF	**3**·MeCN	**3**·THF	**4**
Formula	$C_{50}H_{58}Cl_2LiO_{3.5}P_2$	$C_{38}H_{34}ClCuO_{0.5}P_2$	$C_{56}H_{48}ClCuNP_3$	$C_{58}H_{53}ClCuOP_3$	$C_{54}H_{45}Cl_2Cu_2P_3$
Formula weight	854.80	659.63	926.92	957.98	984.87
Crystal size (mm^3)	0.3 × 0.4 × 0.2	0.55 × 0.5 × 0.45	0.47 × 0.45 × 0.4	0.6 × 0.55 × 0.55	0.34 × 0.58 × 0.24
a (pm)	1301.5(2)	1012.4(2)	1137.1(1)	1326.0(2)	1913.7(3)
b (pm)	1302.0(2)	1281.8(2)	1319.5(1)	1005.5(2)	979.7(2)
c (pm)	1574.7(2)	1337.6(3)	1563.6(1)	3634.8(7)	2648.5(3)
α (°)	96.64(1)	76.88(1)	88.94(1)		
β (°)	99.43(1)	75.55(1)	84.18(1)	94.86(1)	109.67(1)
γ (°)	113.90(1)	74.33(1)	85.07(1)		
V (pm^3 · 10^6)	2357.1(6)	1594.5(6)	2325.2(3)	4829(1)	4676(1)
Space group	$P\bar{1}$ (No. 2^{25})	$P\bar{1}$	$P\bar{1}$	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
Z	2	2	2	4	4
D_{calc} (g cm^{-3})	1.204	1.374	1.324	1.318	1.399
Temp. (K)	213	223	193	223	223
2θ range (°)	4–50	4.8–52.6	4.6–50	4–50	4–50
Data for					
h	−14 to 14	−12 to 12	−13 to 0	−1 to 15	−1 to 22
k	−1 to 15	−15 to 0	−15 to 15	−1 to 11	−1 to 11
l	−18 to 18	−16 to 16	−18 to 18	−43 to 43	−31 to 30
Scan type	ω-scan				
Scan width (°)	1.2	0.81 + 0.47 tan θ	0.78 + 0.6 tan θ	1.6	1.2
Collection data	9416	6770	8608	11,440	9877
Unique data	8228	6467	8160	8481	7596
Data with $F_o > 4\sigma(F_o)$	4082	4825	5488	5534	4183
Refined parameter	564	382	561	578	551
Correction of absorption	no	no	empirical (8 psi-scans)	no	no
μ (cm^{-1})	6.8	9.0	6.7	6.5	11.6
$\Delta\rho_{max}/\Delta\rho_{min}$ (e pm^{-3} · 10^6)	0.51/−0.62	0.45/−0.45	0.62/−0.42	0.61/−0.45	0.28/−0.25
R_1	0.0458	0.0352	0.0419	0.0435	0.0396
R_{w2}[a]	0.0973[b]	0.0952[c]	0.1088[d]	0.1238[e]	0.0652[f]

[a] $P = [\max(F_o^2, 0) + 2F_c^2]/3$.
[b] $w = 1/[\sigma^2(F_o^2) + (0.0379P)^2]$.
[c] $w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 0.88P]$.
[d] $w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 2.74P]$.
[e] $w = 1/[\sigma^2(F_o^2) + (0.0646P)^2]$.
[f] $w = 1/[\sigma^2(F_o^2) + (0.0175P)^2]$.

Table 3. Major IR bands (cm^{-1}) of **1**·1.5THF, **2**·0.5THF, **3**·MeCN, **3**·THF and **4**

Compound	ν(CuP)	ν(CuCl)	ν(LiCl)	ν(LiO)
1·1.5THF	214[a]	240[b]	342[b]	306[a]
2·0.5THF	223[a]	251[a]		
3·MeCN	223[a]	249[a]		
3·THF	220[a]	245[a]		
4	219[a]	240[b]		

[a] Terminal.
[b] μ_2-Bridging.

$[(Ph_3P)_3CuCl]$[16,17,26] have a longer Cu—P bond of 233 pm (mean value). This is caused by the sterical demands of three PPh_3 groups. Interestingly, the Cu—P bonds in **3**·MeCN are significantly shorter [231.0(1), 231.2(1) pm] than the values in **3**·THF [233.5(1), 234.5(1) pm]. This is compensated by a longer Cu—Cl distance in **3**·MeCN [236.29(9) pm] compared to 233.6(1) ppm in **3**·THF. The bulk of the phosphane groups is also responsible for the long Cu—P bonds (226 pm average for **2**·0.5THF[12]) relative to 218.1(1) pm in **4** [copper(I) with CN three; Fig. 4].

Table 4. Selected bond lengths (pm) and angles (°) of **1**·1.5THF–**4**

	1·1.5THF[a]	**2**·0.5THF	**3**·MeCN	**3**·THF	**4**
Cu—P	226.9(1), 227.4(1)	225.64(9), 226.76(9)	230.6(1) -231.2(1)	233.5(1) -234.5(1)	218.1(1)[b] 222.8(1)[c] 224.3(1)
Cu—Cl	239.7(1) 240.7(1)	221.4(1)	236.29(9)	233.6(1)	225.0(1) 231.3(1)[b] 242.2(1) 245.5(1)[c]
P—Cu—P	122.70(5)	125.55(4)	112.29(4) -119.99(4)	111.77(3) -118.08(4)	131.63(5)
Cl—Cu—P	103.11(5) -114.00(5)	113.86(4), 120.58(4)	100.26(4) -105.39(4)	101.53(4) -104.40(4)	117.86(5) 134.27(5)[b,d] 102.30(4)[c] -113.61(5)

[a] Li(1)—Cl(1) 236.2(8), Li(1)—Cl(2) 232.5(9), Li(1)—O(1) 195.5(9), Li(1)—O(2) 195(1); Cl(1)—Cu(1)—Cl(2) 97.34(4), Cu(1)—Cl(1)—Li(1) 80.5(2), Cu(1)—Cl(2)—Li(1) 81.5(2), Cl(1)—Li(1)—Cl(2) 100.7(3), Cl(1)—Li(1)—O(1) 121.5(4), Cl(1)—Li(1)—O(2) 109.8(4), Cl(2)—Li(1)—O(1) 108.6(4), Cl(2)—Li(1)—O(2) 118.0(4), O(1)—Li(1)—O(2) 99.4(4).

[b] Cu^I: CN 3.

[c] Cu^I: CN 4.

[d] Cl(1)—Cu(1)—Cl(2) 107.25(5), Cl(1)—Cu(2)—Cl(2) 97.77(4), Cu(1)—Cl(1)—Cu(2) 76.08(4), Cu(1)—Cl(2)—Cu(2) 75.62(4).

The heterometallic four-membered $CuLiCl_2$ ring is nearly planar, typical of this geometry compared to other $MM'Cl_2$ rings.[28,29] This means small Cu—Cl—Li angles [80.5(2), 81.5(2)°], inner-ring angles above 90° for the metal centres [Cl(1)—Cu(1)—Cl(2) 97.34(4), Cl(1)—Li(1)—Cl(2) 100.7(3)°] and Li—O distances of 195 pm (average).

The coordination sphere of the metal atom in **2**·0.5THF and one of the copper(I) ions in **4** is distorted trigonal plane. In **2**·0.5THF there is no hint of an additional short Cu···C interaction. In contrast, a short contact of 325.1(6) pm between Cu(1) and C(30) can be observed, which is 75 pm less than the sum of the van der Waals radii (402 pm). However, this contact does not lead to pyramidalization of Cu(1) in **4**. The unsymmetrical coordination of the copper atoms is rather stable and can also be obtained with alkoxy groups and PPh_3, as in $[(Ph_3P)_2Cu(Otolyl)_2Cu(PPh_3)]$.[30] The geometry of the four-membered ring in **4** forces a Cu···Cu distance of 290.4(1) pm. Therefore, a

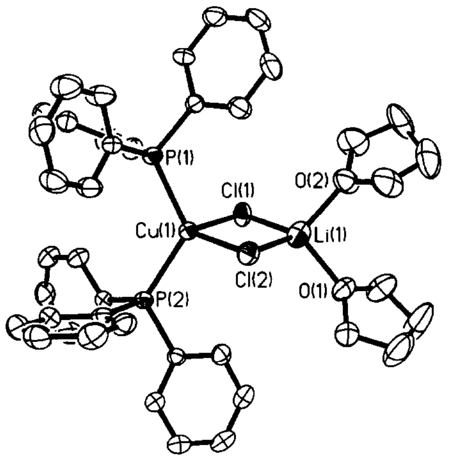

Fig. 1. Graphic representation of a molecule **1** in **1**·1.5THF (50% probability; SHELXTL-PLUS). The hydrogen atoms are omitted for clarity.

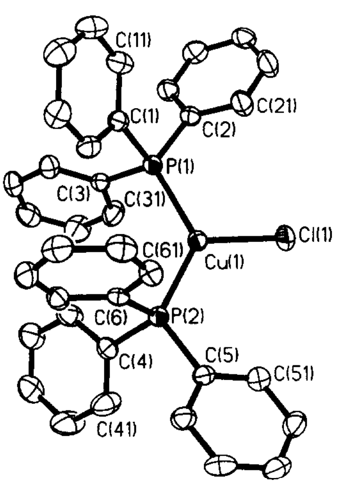

Fig. 2. View of the molecule **2** in **2**·0.5THF.

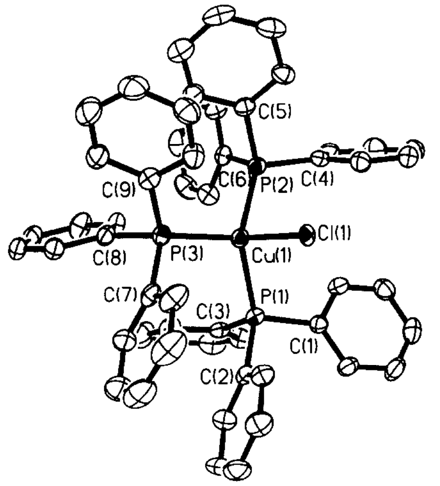

Fig. 3. View of the molecule **3** in **3** · MeCN.

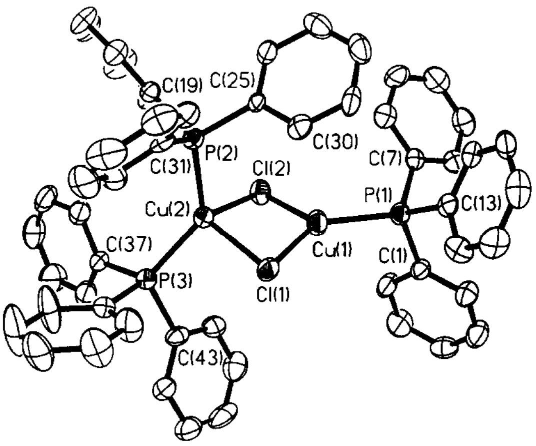

Fig. 4. Computer generated plot of the molecule **4**.

significant electronic interaction cannot be assumed.[31]

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