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# (Hexaphenylcarbodiphosphorane)copper(I) chloride: A Mononuclear Organocopper Complex

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**Abstract.** $[Cu(C_{37}H_{30}P_2)]Cl$, $M_r = 635.59$, monoclinic, $P2_1/c$, $a = 9.540\,(2)$, $b = 18.741\,(3)$, $c = 17.935\,(1)$ Å, $\beta = 100.66\,(1)°$, $V = 3151.25$ Å$^3$, $Z = 4$, $D_x = 1.340$ g cm$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 9.03$ cm$^{-1}$, $F(000) = 1312$, $T = 294$ K, $R = 0.040$, $wR = 0.046$ for 490 refined parameters and 5394 unique, observed reflections with $I \geq 2.0\sigma(I)$. Hexaphenylcarbodiphosphorane forms a mononuclear organocopper(I) complex with CuCl. The Cu atom is digonally coordinated by the ylidic C atom, C(1), and the Cl atom [Cl—Cu—C(1) = 178.2 (1)°]. The distances Cu—Cl and Cu—C(1) are 2.113 (1) and 1.906 (2) Å, respectively. The latter distance is comparable to other Cu—C($sp^2$) two center–two electron bond lengths.

**Introduction.** With regard to their kinetic stability, Cu—C bonds are among the most elusive transition metal to carbon bonds (Jukes, 1974; Jardine, 1975; Van Koten & Noltes, 1982). Although this point is a decisive feature for the versatility of organocopper reagents in organic synthesis – especially for C—C bond formation – (Posner, 1980), recent interest also focused on the preparation and structural characterization of stable compounds containing Cu—C bonds. This is especially true for the structural chemistry of arylcopper compounds. As a recurrent structural theme, polynuclear Cu aggregates were observed to which the aryl moieties were bonded by either two center–two electron (2*c*–2*e*) or three center–two electron (3*c*–2*e*) bonds. Digonal and trigonal coordination of the Cu atoms was found to be a predominant feature (Edwards, Gellert, Marks & Bau, 1982; Van Koten & Noltes, 1982, and references cited therein). The structure of the anion $[CuAr_2]^-$ (Ar = mesitylide), a rare example of a mononuclear arylcopper compound, was described only recently (Leoni, Pasquali & Ghilardi, 1983). Far less is known about compounds with simple aliphatic ligands. Again a tendency to aggregation and formation of electron-deficient Cu—C bonds was observed as exemplified in the trimethylsilylmethylcopper(I) tetramer (Jarvis, Pearce & Lappert, 1977). The formation of clear-cut 2*c*–2*e* bonds at linearly coordinated Cu was found in $[Cu_2\{(CH_2)_2PMe_2\}_2]$ (Schmidbaur, Adlkofer & Buchner, 1973; Schmidbaur, Adlkofer & Heimann, 1974; Nardin, Randaccio & Zangrando, 1974) and $[Cu_3\{CH(PPh_2)_2\}_3]$ (Camus, Marsich, Nardin & Randaccio, 1973). We report here on the structure of the 1:1 complex formed from $Cu^ICl$ and the bis-ylidic species hexaphenylcarbodiphosphorane, $Ph_3P{=}C{=}PPh_3$ (Schmidbaur, Zybill, Müller & Krüger, 1983).

**Experimental.** Yellow cube-like crystals (0.29 × 0.54 × 0.50 mm) grown from tetrahydrofuran. Enraf–Nonius CAD-4 diffractometer equipped with a scintillation counter and a graphite monochromator. Cell dimensions and their e.s.d.'s by least squares from Bragg angles of 75 reflections from various parts of reciprocal space accurately centered on the diffractometer ($\theta = 7.2$–$25.9°$). 8805 measured reflections [$\theta$–$2\theta$ scan mode, $\omega$-scan width $(0.8 + 0.347\tan\theta)°$, scan speed 3.5–10° min$^{-1}$, scan range $1.1 < \theta < 28.9°$, *hkl* range ±13, +24, +24] merged to give 8289 unique data ($R_{\text{int}} = 0.013$) of which 2895 unobserved with $I < 2.0\sigma(I)$. Orientation (every 250 reflections) and intensity control (every 4000 s of X-ray exposure) by means of three standard reflections (0,10,0, $\bar{2}08$, 502); less than 3% decay during data collection. Lp but no absorption correction. Solution by Patterson methods and completion of the structure by difference Fourier syntheses; after anisotropic refinement of the

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non-H atoms (full matrix, $R = 0{\cdot}059$) all H-atom positions taken from difference map; final refinement of non-H atoms anisotropic, H atoms isotropic (490 parameters in three large blocks). Function minimized $\sum w(|F_o| - |F_c|)^2$, unobserved reflections not included in refinement; $R = 0{\cdot}040$, $wR = 0{\cdot}046$, $w = 1/\sigma^2(F_o)$, $S = 2{\cdot}24$, $R$(including unobserved reflections) = 0·049. Maximum ratio of shift to e.s.d. in last cycle < 0·01; final difference map qualitatively featureless, $(\Delta\rho)_{\max/\min} = +0{\cdot}56/-0{\cdot}70\ \text{e}\ \text{Å}^{-3}$. Further details of computing procedures and programs used as described elsewhere (Krüger, Müller, Erker, Dorf & Engel, 1985); scattering factors for neutral, isolated atoms (except for H) from Cromer & Waber (1965), those for H based on a bonded spherical atom model as given by Stewart, Davidson & Simpson (1965), correction for $f'$ and $f''$ (Mo $K\alpha$) applied for Cu, Cl and P atoms (*International Tables for X-ray Crystallography*, 1974).

**Discussion.** Table 1[*] contains the final fractional coordinates of the non-H atoms and their equivalent isotropic temperature factors, Table 2 summarizes important bond lengths and angles as well as torsion angles. Figs. 1 and 2 depict the molecular structure and the contents of the unit cell.

The compound is found to exist as discrete mononuclear species in the solid state (Fig. 1). The Cu atom is strictly linearly coordinated by the Cl atom and the ylidic carbon atom C(1) as shown by the valence angle of 178·2 (1)° at Cu. On coordination a trigonal planar array of substituents is formed at C(1) with the sum of the valence angles being 359·6°, equivalent to a deviation of C(1) from the plane through Cu, P(1), P(2) of only 0·06 Å. The collinearity of C(1), Cu, Cl implies that the Cl atom also lies in the same plane. The valence angles at C(1) show noticeable differences. While P(1)—C(1)—P(2) [123·8 (1)°] and P(1)—C(1)—Cu [122·1 (1)°] fall close to the $sp^2$ standard, P(2)—C(1)—Cu [113·7 (1)°] is significantly smaller. The reason for this becomes evident from an inspection of the conformations of the triphenylphosphine groups. As can be seen from the respective torsion angles (Table 2), the orientation of the phenyl *ipso* carbons at P(2) with respect to the C(1)—Cu bond is almost ideally staggered as expected for a tetrahedral geometry at P(2). In order to minimize the steric interaction of the phenyl ring C(20)—C(25) at P(2) with the aryl groups at P(1), the latter are expected to rotate into a staggered conformation with respect to the C(1)—P(2) bond. Because of the trigonal substituent geometry at C(1), this implies an eclipsed conformation of C(2) with the Cu—C(1) bond. This is what is actually observed, the small deviations from a fully eclipsed conformation probably originating from steric strain. It is immediately obvious that in this conformation the valence

Table 1. *Final fractional atomic coordinates and equivalent isotropic temperature factors for the non-*H *atoms*

$$U_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\text{eq}}$ |
|---|---|---|---|---|
| Cu | 0·4968 (1) | 0·1763 (1) | 0·1724 (1) | 0·047 |
| P(1) | 0·8331 (1) | 0·1765 (1) | 0·2030 (1) | 0·036 |
| P(2) | 0·6699 (1) | 0·2838 (1) | 0·2751 (1) | 0·038 |
| Cl | 0·2945 (1) | 0·1363 (1) | 0·1218 (1) | 0·067 |
| C(1) | 0·6785 (2) | 0·2111 (1) | 0·2210 (1) | 0·042 |
| C(2) | 0·7988 (2) | 0·1129 (1) | 0·1251 (1) | 0·038 |
| C(3) | 0·6891 (2) | 0·0636 (1) | 0·1233 (1) | 0·049 |
| C(4) | 0·6610 (3) | 0·0136 (1) | 0·0652 (1) | 0·058 |
| C(5) | 0·7420 (3) | 0·0125 (1) | 0·0097 (1) | 0·064 |
| C(6) | 0·8537 (3) | 0·0594 (1) | 0·0117 (1) | 0·062 |
| C(7) | 0·8838 (3) | 0·1098 (1) | 0·0699 (1) | 0·049 |
| C(8) | 0·9348 (2) | 0·1206 (1) | 0·2775 (1) | 0·043 |
| C(9) | 0·8736 (3) | 0·1008 (1) | 0·3388 (1) | 0·059 |
| C(10) | 0·9456 (5) | 0·0538 (2) | 0·3930 (2) | 0·086 |
| C(11) | 1·0759 (5) | 0·0267 (2) | 0·3859 (2) | 0·089 |
| C(12) | 1·1363 (4) | 0·0453 (1) | 0·3254 (2) | 0·074 |
| C(13) | 1·0666 (3) | 0·0914 (1) | 0·2701 (1) | 0·057 |
| C(14) | 0·9574 (2) | 0·2412 (1) | 0·1766 (1) | 0·049 |
| C(15) | 1·0893 (3) | 0·2564 (1) | 0·2211 (2) | 0·064 |
| C(16) | 1·1747 (4) | 0·3093 (2) | 0·1983 (3) | 0·098 |
| C(17) | 1·1321 (5) | 0·3452 (2) | 0·1317 (3) | 0·115 |
| C(18) | 1·0018 (6) | 0·3304 (2) | 0·0879 (3) | 0·100 |
| C(19) | 0·9127 (4) | 0·2787 (1) | 0·1097 (2) | 0·069 |
| C(20) | 0·8396 (2) | 0·3183 (1) | 0·3251 (1) | 0·042 |
| C(21) | 0·9114 (2) | 0·2810 (1) | 0·3876 (1) | 0·050 |
| C(22) | 1·0459 (3) | 0·3017 (1) | 0·4237 (1) | 0·060 |
| C(23) | 1·1094 (3) | 0·3610 (1) | 0·3980 (2) | 0·067 |
| C(24) | 1·0388 (3) | 0·3991 (1) | 0·3373 (2) | 0·070 |
| C(25) | 0·9026 (3) | 0·3781 (1) | 0·2997 (1) | 0·054 |
| C(26) | 0·5843 (2) | 0·3598 (1) | 0·2207 (1) | 0·045 |
| C(27) | 0·5607 (3) | 0·3571 (1) | 0·1424 (1) | 0·061 |
| C(28) | 0·5026 (4) | 0·4152 (2) | 0·0987 (2) | 0·075 |
| C(29) | 0·4681 (3) | 0·4761 (2) | 0·1336 (2) | 0·080 |
| C(30) | 0·4902 (4) | 0·4793 (2) | 0·2095 (2) | 0·094 |
| C(31) | 0·5473 (4) | 0·4223 (1) | 0·2542 (2) | 0·077 |
| C(32) | 0·5680 (2) | 0·2691 (1) | 0·3504 (1) | 0·041 |
| C(33) | 0·5824 (3) | 0·3143 (1) | 0·4128 (1) | 0·055 |
| C(34) | 0·5061 (3) | 0·3032 (1) | 0·4699 (1) | 0·060 |
| C(35) | 0·4147 (3) | 0·2469 (1) | 0·4666 (1) | 0·060 |
| C(36) | 0·3980 (3) | 0·2010 (2) | 0·4054 (1) | 0·068 |
| C(37) | 0·4743 (3) | 0·2119 (1) | 0·3477 (1) | 0·057 |

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *with their e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| Cu—Cl | 2·113 (1) | P(1)—C(8) | 1·829 (3) |
| Cu—C(1) | 1·906 (2) | P(1)—C(14) | 1·819 (3) |
| C(1)—P(1) | 1·696 (2) | P(2)—C(20) | 1·819 (3) |
| C(1)—P(2) | 1·684 (3) | P(2)—C(26) | 1·831 (3) |
| P(1)—C(2) | 1·819 (3) | P(2)—C(32) | 1·826 (3) |
| C(1)—Cu—Cl | 178·2 (1) | P(1)—C(1)—Cu | 122·1 (1) |
| P(1)—C(1)—P(2) | 123·8 (1) | P(2)—C(1)—Cu | 113·7 (1) |
| C(1)—P(1)—C(2) | 111·0 (1) | C(1)—P(2)—C(20) | 116·0 (1) |
| C(1)—P(1)—C(8) | 116·3 (1) | C(1)—P(2)—C(26) | 112·8 (1) |
| C(1)—P(1)—C(14) | 115·2 (1) | C(1)—P(2)—C(32) | 113·2 (1) |
| C(2)—P(1)—C(8) | 100·5 (1) | C(20)—P(2)—C(26) | 104·7 (1) |
| C(2)—P(1)—C(14) | 105·7 (1) | C(20)—P(2)—C(32) | 103·7 (1) |
| C(8)—P(1)—C(14) | 106·7 (1) | C(26)—P(2)—C(32) | 105·4 (1) |
| Cu—C(1)—P(1)—C(2) | 7·3 (3) | Cu—C(1)—P(2)—C(20) | 178·4 (3) |
| Cu—C(1)—P(1)—C(8) | −106·6 (3) | Cu—C(1)—P(2)—C(26) | −60·8 (3) |
| Cu—C(1)—P(1)—C(14) | 127·3 (3) | Cu—C(1)—P(2)—C(32) | 58·7 (3) |

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[*] Lists of additional crystal structure data, observed and calculated structure factors, $\sigma(F_o)$ values, anisotropic thermal parameters for the non-H atoms, and H-atom coordinates and temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42957 (64 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

angle Cu—C(1)—P(2) is affected by steric interaction between the linear C(1)—Cu—Cl moiety and two staggered phenyl rings and is amenable to reduction, as is observed. It should be kept in mind, however, that the observed staggered conformation of the phenyl rings at P(1) and P(2) is not mandatory in complexes of hexaphenylcarbodiphosphorane. Actually in the 1:1 complexes with selenium and iodonium approximately eclipsed and staggered conformations of the phenyl rings with respect to the line joining the two P atoms were observed (Schmidbaur, Zybill, Neugebauer & Müller, 1985). Even in the parent hexaphenylcarbodiphosphorane itself different conformations are observed in different modifications (Vincent & Wheatley, 1972; Hardy, Zink, Kaska & Baldwin, 1978). Apparently rotation of the phenyl rings around their P—C bonds can give rise to a variety of conformations which minimize steric interactions in these molecules.

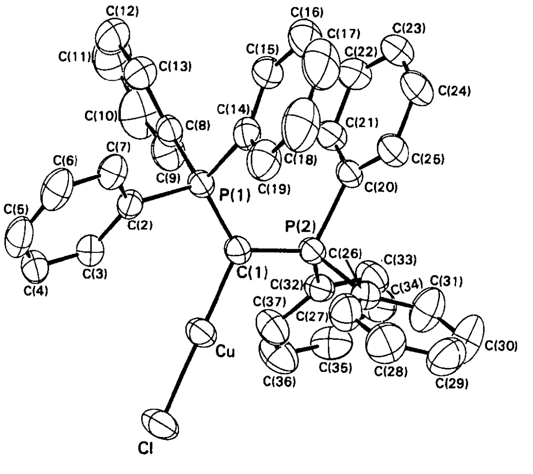

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the molecular geometry of the copper complex and atomic numbering scheme (thermal ellipsoids at 50% probability level, H atoms omitted for clarity).

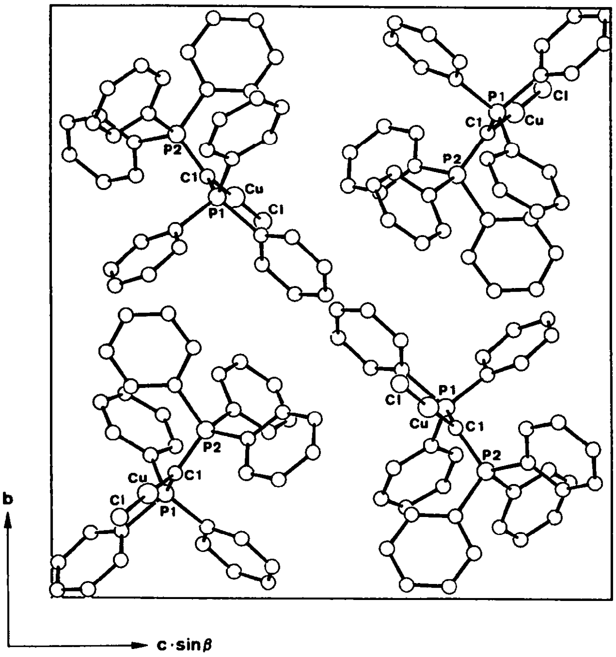

Fig. 2. A plot of the unit cell in the projection along **a** (atoms with arbitrary radii, H atoms omitted).

A similar flexibility is observed for the P(1)—C(1)—P(2) angle in hexaphenylcarbodiphosphorane and its Lewis-acid adducts. The observed angle of 123·8 (1)° in the title compound is much smaller than in the uncomplexed bis-ylide where different values were found depending on the modification (Vincent & Wheatley, 1972; Hardy *et al.*, 1978). Surprisingly, this angle is also smaller than in the Se and $I^+$ adducts mentioned above [135·9 (7) and 130·2 (4)°, respectively].

Regardless of this valence-angle flexibility, the trigonal planar substituent arrangement at C(1) points to $sp^2$ hybridization. The C(1)—Cu bond length of 1·906 (2) Å is in agreement with such a description. It is noticeably shorter than the electron-deficient three-center bonds formed between Cu and aromatic or aliphatic ligands where the bonds range between 1·95 and 2·15 Å, centering around 2·05 Å (Van Koten & Noltes, 1982, and references cited therein). It is also shorter than the 2*c*–2*e* Cu—C($sp^2$) bonds in $[Cu_2\{(CH_2)_2PMe_2\}_2]$ [1·95 (2) Å] (Nardin *et al.*, 1974) and $[Cu_3\{CH(PPh_2)_2\}_3]$, [1·96 (2), 2·00 (2) Å] (Camus *et al.*, 1973) but it is drastically longer than the Cu—C(*sp*) bonds encountered in the few structurally characterized $Cu^I$ carbonyls as, for example, 1·806 (6) Å in $[Cu(H_2NC_2H_4NH_2)(CO)BPh_4]$ (Pasquali, Floriani & Gaetani-Manfredotti, 1980) or 1·765 (14) Å in $[HB(C_3N_2H_3)_3]Cu(CO)$ (Churchill, DeBoer, Rotella, Abu Salah & Bruce, 1975). It is, however, directly comparable with the Cu—C bond lengths in the anion $[CuAr_2]^-$ (Ar = mesitylide), where 1·915 (9) Å was found (Leoni *et al.*, 1983). Thus the Cu—C bond in $[\{(C_6H_5)_3P\}_2C]CuCl$ may best be described as a 2*c*–2*e* bond involving an $sp^2$-hybridized C atom.

The P(1)—C(1) and P(2)—C(1) bond lengths are longer by about 0·05 Å than their counterparts in the parent bis-ylide, indicative of a reduction of bond order of the ylidic P—C bonds on coordination of C(1). Similar observations have been made in the other adducts mentioned above.

The mononuclearity of the adduct is particularly noteworthy as the terminal Cl atom would be ideally suited to form additional donor bonds. In the crystal, however, there are isolated monomers without any close contacts, as is also evident from a plot of a cell projection (Fig. 2). Apparently the steric bulk of the six phenyl rings effectively prevents the complex from oligomerization. However, concomitant electronic effects, especially the strong donor properties of the bis-ylidic ligand (Schmidbaur, 1983) resulting in an electronically more saturated Cu$^{I}$ center, may also be a contributing factor.

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# Structure of the Hexafluorophosphate Salts of $\mu$-($\eta^6$:$\eta^6$-Phenoxazine)-bis[$\eta^5$-cyclopentadienyliron(II)] (1) and ($\eta^5$-cyclopentadienyl)($\eta^6$-phenoxathiin)iron(II) (2)

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**Abstract.** (1): $[C_{22}H_{19}Fe_2NO](PF_6)_2$, $M_r = 715{\cdot}05$, monoclinic, $P2_1/n$, $a = 10{\cdot}635\,(2)$, $b = 9{\cdot}928\,(1)$, $c = 22{\cdot}562\,(7)$ Å, $\beta = 92{\cdot}41\,(1)°$, $V = 2380{\cdot}1\,(9)$ Å$^3$, $Z = 4$, $D_x = 2{\cdot}00$ g cm$^{-3}$ (163 K), Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 14{\cdot}63$ cm$^{-1}$, $F(000) = 1424$, T = 163 K, final $R = 0{\cdot}045$ for 4787 reflections. (2): $[C_{17}H_{13}FeOS]PF_6$, $M_r = 466{\cdot}18$, triclinic, $P\bar{1}$, $a = 8{\cdot}461\,(2)$, $b = 10{\cdot}273\,(2)$, $c = 10{\cdot}562\,(2)$ Å, $\alpha = 93{\cdot}75\,(2)$, $\beta = 110{\cdot}41\,(2)$, $\gamma = 102{\cdot}84\,(2)°$, $V = 828{\cdot}6\,(3)$ Å$^3$, $Z = 2$, $D_x = 1{\cdot}87$ g cm$^{-3}$ (163 K), Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 11{\cdot}95$ cm$^{-1}$, $F(000) = 468$, $T = 163$ K, final $R = 0{\cdot}046$ for 3031 reflections. The cyclopentadienyliron(II) moieties, ($\eta^5$-Cp)Fe$^{II}$, in (1) are *trans*. Coordination is to the terminal phenyl ring(s) in both complexes and results in a flattening of phenoxathiin in (2), while phenoxazine in (1) remains essentially unchanged. The heterocycles are nearly planar, with (1) having a dihedral angle between planes through the phenyl rings of 176·9 (1)° while (2) has a dihedral angle of 178·7 (1)°. Asymmetric C—O bond lengths are observed in (2) with the shorter bond being to the C atom of the coordinated ring,

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