Reactions between Arylcopper Compounds and Dinitrophenylmethane. Synthesis and Crystal Structure of α-Nitro-α-*aci*-nitrotolueneatobis-(triphenylphosphine)copper(I)

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The synthesis and structure of the title compound have been determined. Copper is bonded to the dinitro(phenyl)-methane conjugate base by a nitro-group, acting as bidentate ligand. Cu–P and Cu–X bonding are discussed, in comparison with the structures of $[M(I)(PPh_3)_nX]$ compounds. The Cu–P bond lengths appear to be significantly influenced by the number of bonded phosphine ligands. The crystal structure has been determined by the heavy-atom method from three-dimensional *X*-ray diffraction data obtained by counter techniques. The structure was refined to R 0.077 for 4 107 independent reflections. Crystals are monoclinic, space group $P2_1/c$, with Z = 4 in a unit cell with parameters: a = 9.209(8), b = 14.210(9), c = 30.122(12) Å, β = 104.37(9)°.

RECENTLY the reactivity of arylcopper compounds with several hydrogen-containing compounds was investigated.[1] This type of reaction has been extended now to nitro-(dpmH) and dinitro-phenylmethane (dnpmH). The hydrogen–copper exchange with these molecules is slow and incomplete, but the products can be obtained in high yield as complexes, by addition of suitable uni- or bi-dentate ligands. In both cases series of Cu^I complexes of stoicheiometries $Cu(B)L_2$ and $(CuB)_2(L,L)_3$ were isolated [B = conjugate basis of npmH and dnpmH; L = triphenylphosphine, pyridine, γ-picoline, or quinoline; L,L = 1,2-bis(diphenylphosphino)ethane (dpe), bipyridine]. With bis(diphenylphosphino)methane (dpm) the stoicheiometry is of the first type.

These compounds will be described in detail elsewhere. Here we report the synthesis and structural study of the dnpm complex with triphenylphosphine as a typical example for the $Cu(B)L_2$ series. This product is obtained by the reaction of an arylcopper compound with dnpmH in the presence of triphenylphosphine, according to reaction (1). The compound is diamagnetic, stable at

$$\mathrm{ArCu} + \mathrm{dnpmH} + 2\mathrm{PPh_3} \longrightarrow [\mathrm{Cu(PPh_3)_2(dnmp)}] + \mathrm{ArH} \qquad (1)$$

room temperature, and not very sensitive to atmospheric agents. From a structural point of view it could be either an organo-copper complex or a derivative of a copper salt of dnpmH in its *aci*-form The latter alternative is supported by the high thermal stability of the compound and by its i.r. spectrum, similar to those of salts of the nitro-[2] or dinitro-carbanion.[3] The Cu–O bonds could,

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[1] N. Marsich and A. Camus, *J. Organometallic Chem.*, 1974, **81**, 87.

[2] M. J. Brookes and N. Jonathan, *J. Chem. Soc.* (*A*), 1968, 1529.

[3] M. J. Kamlet, R. E. Oesterling, and H. G. Adolph, *J. Chem. Soc.*, 1965, 5838; E. R. Lippincott, T. E. Kenney, T. R. Nanney, and C. K. Weiffenbach, *J. Chem. Soc.* (*B*), 1967, 32.

however, involve only one or both the nitro-groups, as mono- or bi-dentate ligands. The complete absence of bands in the region in which the $^{-}NO_2$ stretching modes occur in the free dnpmH, suggests that both nitro-groups are involved in the bond to copper. *X*-Ray analysis showed that, on the contrary, only one of them reacts in the *aci*-form, both the oxygen atoms being involved in the bonding.

EXPERIMENTAL

Preparation.—The dnpmH (0.2 mmol) and triphenylphosphine (0.4 mmol) were added in that order under nitrogen to a stirred ethereal suspension of ArCu (0.2 mmol) at 0 °C. In a short time a lemon-yellow solid was formed, which did not apparently change during the course of the reaction, even when the suspension was allowed to attain room temperature. It was washed with ether and dried *in vacuo*. It is soluble in common organic solvents. Crystals employed in the present study were obtained from hot methanol. M.p.: explosive decomp. at *ca*. 148 °C, exact temperature depending on heating conditions (Found: C, 66.9; H, 4.40; Cu, 8.25; N, 3.50. Calc. for $C_{43}H_{35}CuN_2O_4P_2$: C, 67.14; H, 4.59; Cu, 8.26; N, 3.64%). Conductivity at 20 °C: 0.2 (dichloroethane); 7.4 (acetone); 94.0 (methanol) Ω^{-1} cm^2 mol^{-1}.

Crystal Data.—$C_{43}H_{35}CuN_2O_4P_2$, $M = 769.3$, Monoclinic, $a = 9.209(8)$, $b = 14.210(9)$, $c = 30.112(12)$ Å, $\beta = 104.37(9)°$, $U = 3\,817.1$ Å^3, D_m (by flotation) $= 1.37$, $Z = 4$, $D_c = 1.34$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) $= 7.25$ cm^{-1}. Space group $P2_1/c$ (C^5_{2h}).

Cell parameters were determined from Weissenberg and precession photographs taken with Co-K_α radiation; accurate unit-cell parameters were obtained by use of 30 reflections carefully centered on automated Siemens diffractometer.

Intensity Measurements.—Three-dimensional intensity data were collected on a Siemens diffractometer by the θ—2θ scan mode with Mo-K_α radiation to 2θ max. 54°. A crystal of mean dimensions 0.35 mm was used. All reflections having $I < 3\sigma(I)$ were rejected, the remainder being corrected for Lorentz and polarization effects. A total of 4 107 independent reflections was used in the subsequent calculations. No correction for absorption (μR *ca*. 0.13) or anomalous dispersion by the copper atom was applied.

Structure Determination and Refinement.—The structure was determined by the conventional heavy-atom technique. After a least-squares isotropic refinement R was 0.095. Three cycles of anisotropic block-diagonal refinement gave R 0.077. Only Cu, P, O, and N atoms were treated anisotropically. The hydrogen atoms were neglected. The final weighting scheme was $w = 1/(A + B|F_o| + C|F_o|^2)$, where $A = 10.0$, $B = 1.0$, and $C = 0.005$, chosen to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $(\sin\theta/\lambda)$. Final atomic parameters are listed in Table 1, together with their estimated standard deviations. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21438 (12 pp., 1 microfiche)*

TABLE 1

Fractional co-ordinates ($\times 10^4$) and temperature factors,* with estimated standard deviations in parentheses

	x	y	z	B/Å^2
Cu	3 913(1)	2 212(1)	1 445(0)	*
P(1)	4 341(2)	1 389(1)	845(1)	*
P(2)	4 432(2)	1 924(1)	2 204(1)	*
O(1)	3 956(6)	3 778(4)	1 262(2)	*
O(2)	1 834(6)	3 029(4)	1 200(2)	*
O(3)	3 728(8)	5 561(5)	1 115(3)	*
O(4)	1 478(8)	6 100(4)	810(3)	*
N(1)	2 523(7)	3 797(4)	1 152(2)	*
N(2)	2 371(9)	5 441(5)	976(3)	*
C(1)	6 318(8)	1 080(5)	883(2)	3.3(1)
C(2)	6 792(9)	165(6)	817(3)	3.8(2)
C(3)	8 331(11)	−43(7)	853(3)	5.3(2)
C(4)	9 333(12)	696(8)	943(4)	6.2(2)
C(5)	8 911(12)	1 590(8)	1 005(4)	5.9(2)
C(6)	7 387(10)	1 798(7)	977(3)	4.8(2)
C(7)	3 768(8)	1 977(5)	290(2)	3.4(1)
C(8)	4 692(10)	1 986(6)	−21(3)	4.7(2)
C(9)	4 240(12)	2 480(8)	−438(4)	5.7(2)
C(10)	2 815(13)	2 952(8)	−531(4)	6.5(2)
C(11)	1 837(13)	2 906(8)	−245(4)	6.5(2)
C(12)	2 365(10)	2 427(7)	174(3)	4.7(2)
C(13)	3 370(8)	256(5)	774(2)	3.2(1)
C(14)	3 579(9)	−312(6)	1 158(3)	4.0(2)
C(15)	2 870(11)	−1 207(7)	1 128(3)	5.5(2)
C(16)	1 946(12)	−1 497(8)	713(4)	5.9(2)
C(17)	1 748(11)	−917(8)	324(3)	5.6(2)
C(18)	2 464(10)	−42(6)	355(3)	4.4(2)
C(19)	6 456(8)	1 844(5)	2 466(2)	3.4(1)
C(20)	7 400(9)	1 763(6)	2 154(3)	3.9(1)
C(21)	8 975(11)	1 715(7)	2 320(3)	5.1(2)
C(22)	9 619(12)	1 694(8)	2 783(3)	5.7(2)
C(23)	8 702(11)	1 771(7)	3 096(3)	5.3(2)
C(24)	7 147(10)	1 861(6)	2 937(3)	4.5(2)
C(25)	3 698(8)	2 767(5)	2 560(2)	3.1(1)
C(26)	3 656(10)	2 599(6)	3 009(3)	4.4(2)
C(27)	3 058(10)	3 283(7)	3 251(3)	4.8(2)
C(28)	2 545(10)	4 119(7)	3 058(3)	4.8(2)
C(29)	2 554(11)	4 293(7)	2 601(3)	5.5(2)
C(30)	3 115(10)	3 604(6)	2 349(3)	4.4(2)
C(31)	3 582(8)	819(5)	2 334(2)	3.1(1)
C(32)	4 182(10)	257(6)	2 713(3)	4.5(2)
C(33)	3 373(11)	−546(7)	2 792(3)	5.4(2)
C(34)	1 969(11)	−770(7)	2 482(3)	5.5(2)
C(35)	1 425(11)	−217(7)	2 101(3)	5.1(2)
C(36)	2 224(9)	583(6)	2 028(3)	4.1(2)
C(37)	1 655(9)	4 567(6)	1 005(3)	4.1(2)
C(38)	−25(10)	4 501(7)	863(3)	4.7(2)
C(39)	−719(12)	4 263(8)	425(4)	5.9(2)
C(40)	−2 337(13)	4 182(9)	289(4)	7.0(3)
C(41)	−3 172(14)	4 351(9)	604(4)	7.4(3)
C(42)	−2 493(13)	4 610(9)	1 034(4)	6.8(3)
C(43)	−908(11)	4 651(7)	1 180(3)	5.6(2)

*Anisotropic temperature factors ($\times 10^4$) are in the form: $[\exp - (\beta_{11}h^2 + \beta_{12}hk + \beta_{13}hl + \beta_{22}k^2 + \beta_{23}kl + \beta_{33}l^2)]$.

	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Cu	118(1)	25(1)	12(1)	36(0)	1(0)	9(0)
P(1)	96(2)	13(2)	10(1)	34(1)	2(1)	8(0)
P(2)	103(2)	11(2)	11(1)	35(1)	−1(1)	9(0)
O(1)	108(7)	7(8)	7(4)	52(3)	8(3)	15(1)
O(2)	130(7)	17(7)	20(4)	34(3)	6(2)	15(1)
O(3)	166(11)	−42(12)	−9(7)	63(4)	12(5)	35(2)
O(4)	198(11)	44(10)	11(6)	43(3)	17(3)	26(1)
N(1)	122(8)	12(9)	5(4)	37(3)	1(3)	10(1)
N(2)	180(11)	21(12)	6(6)	45(4)	8(3)	16(1)

Atomic scattering factors were calculated according to ref. 4.

Calculations.—All calculations were carried out on a CDC 6200 computer with programs described in ref. 5. A local

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[4] F. H. Moore, *Acta Cryst.*, 1963, **11**, 1169.

[5] V. Albano, A. Domenicano, and A. Vaciago, *Gazzetta*, 1966, **96**, 922.

program was used to obtain best molecular planes, whose equations were calculated according to ref. 6.

DISCUSSION AND DESCRIPTION OF THE STRUCTURE

The crystal consists of discrete molecules of [$Cu^I(PPh_3)_2$(dnpm)], separated by van der Waals distances. Figure 1 shows a view of the molecule, together with the numbering scheme for the non-hydrogen atoms, and bond lengths and angles are listed in Table 2. The geometry around the copper atom is similar to that found in the [$Cu^I(PPh_3)_2(NO_3)$] compound,[7] where the metal atom was assumed to be four-co-ordinate, the nitrate anion being bidentate. In both structures the steric hindrance of the nitro-group is minimized by the fact that its plane is nearly perpendicular to that of the P–Cu–P plane. However the nitrate derivative has exact C_2 symmetry with both Cu–O distances of 2.22(1) Å whereas the co-ordination of the dnpm anion to the copper atom causes small but significant deviations from that symmetry. In fact Cu–O bond lengths are 2.295(6) and 2.204(5) Å, and P–Cu–N angles 109.9(2) and 117.3(2)°. The value of the Cu–N(1)–C(37) angle [173.4(6)°] gives a more complete idea of the distortion.

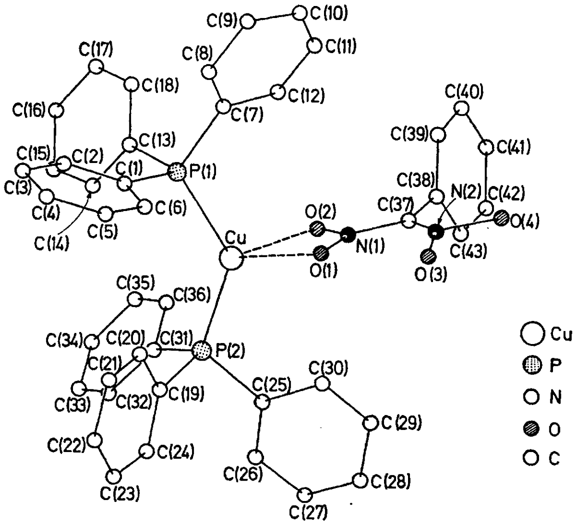


FIGURE 1 A view of the molecule, showing the atom numbering scheme

TABLE 2

Bond lengths (Å) and angles (°), with their standard deviations in parentheses

(a) Individual values

Cu–P(1)	2.267(3)	O(1)–Cu–O(2)	58.3(2)
Cu–P(2)	2.253(3)	Cu–P(1)–C(1)	115.9(2)
Cu–O(1)	2.295(6)	Cu–P(1)–C(7)	115.2(2)
Cu–O(2)	2.204(5)	Cu–P(1)–C(13)	111.8(3)
P(1)–C(1)	1.849(8)	C(1)–P(1)–C(7)	102.8(3)
P(1)–C(7)	1.825(7)	C(1)–P(1)–C(13)	104.1(3)
P(1)–C(13)	1.828(7)	C(7)–P(1)–C(13)	105.9(3)
P(2)–C(19)	1.838(7)	Cu–P(2)–C(19)	112.6(3)
P(2)–C(25)	1.844(8)	Cu–P(2)–C(25)	117.1(2)
P(2)–C(31)	1.839(7)	Cu–P(2)–C(31)	112.1(2)
O(1)–N(1)	1.279(8)	C(19)–P(2)–C(25)	105.6(3)
O(2)–N(1)	1.288(8)	C(19)–P(2)–C(31)	107.2(3)
O(3)–N(2)	1.23(1)	C(25)–P(2)–C(31)	101.2(4)
O(4)–N(2)	1.26(1)	O(1)–N(1)–O(2)	117.3(6)
N(1)–C(37)	1.36(1)	O(1)–N(1)–C(37)	125.9(6)
N(2)–C(37)	1.42(1)	O(2)–N(1)–C(37)	116.8(6)
C(37)–C(38)	1.50(1)	O(3)–N(2)–O(4)	122.6(8)
P(1)–Cu–P(2)	132.8(1)	O(3)–N(2)–C(37)	123.4(7)
P(1)–Cu–O(2)	107.0(2)	O(4)–N(2)–C(37)	114.0(7)
P(1)–Cu–O(1)	107.0(2)	N(1)–C(37)–N(2)	118.6(7)
P(1)–Cu–O(2)	108.3(2)	N(1)–C(37)–C(38)	121.5(8)
P(2)–Cu–O(1)	114.1(1)	N(2)–C(37)–C(38)	119.9(7)
P(2)–Cu–O(2)	112.5(2)		

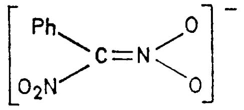
(b) Mean C–C bonds (Å) in phenyl ring containing atom:

C(1)	1.40(1)	C(25)	1.39(1)
C(7)	1.41(1)	C(31)	1.40(1)
C(13)	1.40(1)	C(37)	1.40(2)
C(19)	1.40(1)		

Mean C–C–C angles in Ph rings all 120(1)°.

The bond lengths and angles as well as the relative orientation of the triphenylphosphine groups are consistent with those already reported for similar compounds.[8]

The dnpm anion is nearly planar, with displacements of its atoms (excluding the carbon atoms of the phenyl group) of 0.09 Å from their mean plane. A small torsion of the N(2), O(3), O(4) group with respect to the remaining atoms is indicated by the angle of 5.9° between their respective mean planes. The plane of the phenyl group is normal to that of the dnpm anion, the angle between them being 91.8°. The complete geometry is in agreement with a carbanion stabilized in its *aci*-nitro-form (I).



$$\left[\begin{array}{l} Ph \\ \quad C{=}N\genfrac{}{}{0pt}{}{O}{O} \\ O_2N \end{array}\right]^-$$

(I)

It may be noted that only one NO_2 group of the dnpm anion is involved in co-ordination with copper. The geometries of the two nitro-groups show small but significant variations: the bond length and angle in the co-ordinated group are 1.284(8) Å (mean) and 117.3(6)°, and 1.245(10) Å (mean) and 122.6(8)° in the unco-ordinated group. However the difference observed in the present structure may be due to the higher thermal motion of atoms N(2), O(3), O(4) with respect to that of N(1), O(1), and O(2).

Copper–Phosphine Bonding.—Many questions arise concerning the geometry of the $(PPh_3)_nCu$ grouping. Table 3 lists Cu–P bonds in other compounds so far investigated by *X*-ray structure analysis. They are grouped according to the presence of one, two, or three copper–phosphorus bonds on the same metal atom. A comparison of these Cu–P bond lengths shows that: (*a*) those in compounds involving the same kind of phosphines (PPh_3, dpm, dpe) are dramatically influenced by the number of phosphine ligands bonded to the copper atom, whereas they are only slightly influenced by the co-ordination number of the metal; (*b*) other secondary effects may act to determine the trend in Cu–P bond-

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[6] V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600.

[7] G. G. Messmer and G. J. Palenik, *Inorg. Chem.*, 1969, **8**, 2750; *Canad. J. Chem.*, 1969, **47**, 1440.

[8] P. H. Davis, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, 1973, **12**, 213.

length variation in each group of compounds; and (*c*) the $(P)_2Cu$–X grouping often shows different Cu–P bond lengths and different P–Cu–X bond angles.

Point (*a*) is well illustrated in Figure 2, where, for each group of compounds in Table 3, mean values of the Cu–P distances are reported, together with their estimated standard deviations and the range of known values. The increase of *ca.* 0.05 Å in the Cu–P distance for each additional phosphine bonded to copper could be due to electronic and steric factors. Taking into account the quite different steric situation of the compounds examined, we suggest that the main effect is that due to electronic factors. Furthermore, in contrast with the conclusion of Lippard and Palenik,[9] we consider Cu–P π bonding essential in determining the trend in Cu–P distances. In fact, the increased number of phosphorus atoms about the metal must result in a decrease in Cu–P back donation and consequently in an increase in bond length, because of a reduced π bonding contribution.[10]

This hypothesis may also be valid for analogous series of copper derivatives with rather different phosphines, *e.g.* PMe_3. However, the values of Cu–P bond lengths in such series may not be comparable with those of the PPh_3 derivatives. The low values (2.238 and 2.222 Å) of these distances found in $[(PhC{\vdots}C)Cu(PMe_3)]$ could be indicative of the significant influence of the nature and hindrance of the organic group of the ligand.

TABLE 3

Comparison of copper(I) compounds, grouped according to the number of copper–phosphorus bonds in which the same copper atom is involved

(*a*) One Cu–P bond

	Cu–P(Å)	$\Delta_{4,3}$ [j]	Donor atoms	C.N.
$[(Ph_3P)_4Cu_4Cl_4]$ [a]	2.192(4)		$CuCl_3P$	4
	2.186(3)			
$[(Ph_3P)Cu_4Cl_4]$ [b]	2.193(2)		$CuCl_3P$	4
	2.192(2)			
$[(Ph_3P)_4Cu_4Br_4]$ [c]	2.207(3)	0.013	$CuBr_3P$	4
	2.194(4)		$CuBr_2P$	3
$[(Ph_3P)_6Cu_6H_6]$ [d]	2.240(17)	Mean	Cu_4CuP (formal)	
$[(Ph_3P)_3(CuCl)_2]$ [e]	2.183(4)		$PCuCl_2$	3
$[(dpe)_2Cu_4Cl_4]$ [f]	2.197(5)	0.002	$CuCl_3P$	4
	2.195(4)		$CuCl_2P$	3
$[(dpm)_2Cu_4Cl_4]$ [g]	2.203(3)	0.018	$CuCl_3P$	4
	2.185(3)		$CuCl_2P$	3
$[(dpm)_2Cu_4Br_4]$ [h]	2.19(1)	0.010	$CuBr_3P$	4
	2.18(1)		$CuBr_2P$	3
$[(dpm)_2CuI_4]$ [h,i]	2.230(8)	0.012	CuI_3P	4
	2.218(8)		CuI_2P	3
$[(Ph_3P)Cu(C_5H_5)]$ [l]	2.135(1)			

(*b*) Two Cu–P bonds

	Cu–P (Å)	$\Delta_{1,2}$ [k]	P–Cu–P(°)	Donor atoms	C.N.
$[(Ph_3P)_2Cu(tfa)]$ [m,w]	2.258(1)		126.45(5)	CuO_2P_2	4
	2.256(1)	0.002			
$[(Ph_3P)_2Cu(tta)]$ [m,w]	2.242(2)		127.53(6)	CuO_2P_2	4
	2.252(1)	0.010			
$[(Ph_3P)_2Cu(hfa)]$ [m,w]	2.239(2)		127.10(6)	CuO_2P_2	4
	2.236(2)	0.003			
$[(Ph_3P)_2Cu(BH_4)]$ [n]	2.276(1)		123.26(6)	$CuP_2(BH_4)$	3
$[(Ph_3P)_2Cu(B_3H_8)]$ [o]	2.274(1)	0.041	119.97(7)	$CuP_2(BH)_2$	4
	2.288(2)				
$[(Ph_3P)_2CuNO_3]$ *	2.256(3)		131.2(1)	$CuP_2(O_2N)$	4
$[(Ph_3P)_3(CuCl)_2]$ [e]	2.236(5)	0.009	131.8(2)	$CuCl_2P_2$	4
	2.245(5)				
$[(Ph_3P)_2Cu(dnpm)]$ †	2.253(3)	0.014	132.8(1)	$CuP_2(O_2N)$	4
	2.267(3)				
$[(Ph_3P)_2CuBr]$ ‡	2.282(2)	0.019	126.0(1)	CuP_2Br	3
	2.263(2)				
$[(Ph_3P)_4(CuN_3)_2]$ [p]	2.271(4)	0.019	122.3(1)	CuP_2N_2	4
	2.250(3)				
	2.269(4)	0.003	120.8(1)		
	2.266(3)				
$[(Ph_3P)_4(CuH_3BCN)_2]$ §	2.262(3)	0.020	124.8(1)	$CuP_2(N–BH_3)$	4
	2.242(3)				
	2.280(3)				
	2.272(3)	0.088	122.1(1)		
$[\{(dpm)CuCl\}_3]^+$ [q]	2.257(5)		128.6(2)	$Cu_2Cl_2P_2$	4
	2.268(4)				
	2.247(3)		124.4(2)		
$[(PhC{\vdots}C)Cu(PMe_3)]$ [r,x]	2.238(5)		123.8(2)	$CuP_2(C_2)$	4
	2.222(5)	0.016			
$[(MePh_2P)_4(CuNCS)_2]$ [s]	2.27(1)		123.0(1)	CuP_2NS	4
	2.24(1)				

Table 3 (*Continued*)

(*c*) Three Cu–P bonds

	Cu–P(Å)	Donor atoms	C.N.
$[(Ph_2MeP)_3CuCl]$	2.28 2.30 2.28	P_3Cl	4
$[(dpe)_3(CuN_3)_2]$ ¶	2.277(5) 2.298(5) 2.338(5)	P_3N	4
$[(dpe)_3Cu_2Cl_2]$ [y]	2.284(6) 2.311(4) 2.312(5)	P_3Cl	4
$[(dpe)_3Cu_2(CN_4)_2]$ [u]	2.317(6) 2.298(6) 2.318(6)	P_3N	4
$[(Ph_3P)_3CuBF_4]$ [v]	2.296(2) 2.296(2) 2.303(2)	P_3N	4

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* Ref. 7. † Present work. ‡ Ref. 8. ¶ Ref. 10. § Ref. 12. C.N. = Co-ordination no.

Only small, if significant, differences of *ca.* 0.01 Å are observed when the copper bonded to one phosphorus atom has trigonal or tetrahedral geometry.

As far as point (*b*) is concerned, the increase in the size and number of other atoms co-ordinated to the metal atom seem to affect the Cu–P distances. The values of 2.240 Å in $[(PPh_3)_6Cu_6H_6]$ and of 2.230 and 2.218 Å in $[(dpm)_2Cu_4I_4]$, which are above the averages, would be in agreement with this hypothesis.

As far as the 'two-phosphorus' group is concerned with regard to (*c*) a relationship between Cu–P bond length and P–Cu–P bond angle has been already observed [9] and attributed to the different *s*-electron character of the hybrid orbitals of the copper involved in the Cu–P bonds. The comparative data of Table 3 are illustrated in Figure 3, where, for each bond angle, values of each individual Cu–P bond length are shown. A general trend of decreasing bond length with increasing bond angle may be discerned, although less apparent than that reported.[9]

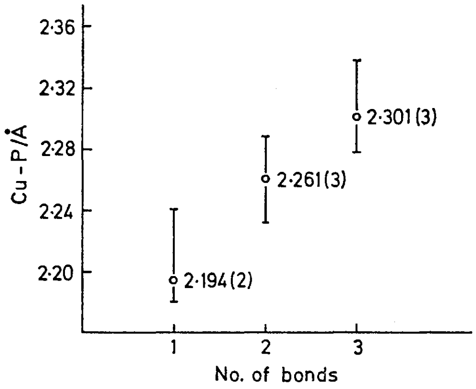

Figure 2 Mean Cu–P distances for each group of compounds listed in Table 3, together with their relative range. The estimated standard deviations of the means are given in parentheses

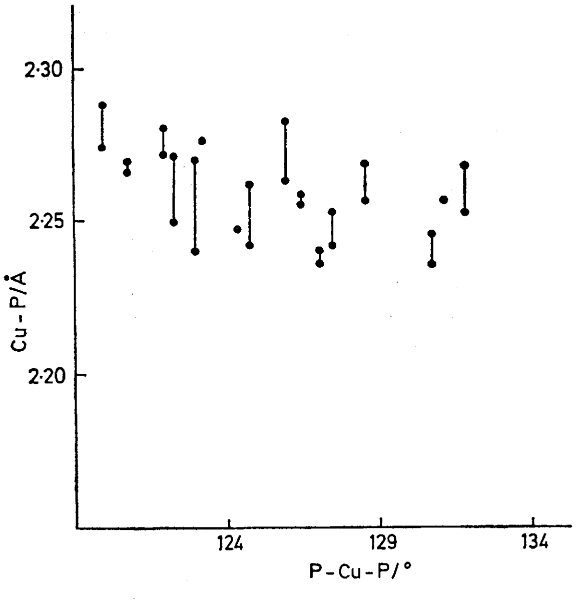

Figure 3 The trend of Cu–P bond length as a function of P–Cu–P bond angle. For each angle the two independent bond lengths are reported

Unless the crystallographic symmetry imposes equivalence on the P–Cu–X angle in [Cu(PPh$_3$)$_2$X] molecules, a significant difference between chemically equivalent angles is observed; for example in [Cu(PPh$_3$)$_2$Br] the P–Cu–Br angles are 112.8(1) and 121.0(1),[8] and in the gold analogue 109.2(1) and 118.7(1)°.[11]

The angular distortion is accompanied by an analogous asymmetry in the Cu–P bond lengths: the difference is 0.014(3) Å in the present complex and 0.019(2) Å for the bromine derivative. Differences of *ca.* 0.02 Å between the two chemically equivalent distances have been observed [12,13] in a series of dinuclear-bridged copper complexes [(P$_2$)CuXCu(P$_2$)] [P = (PPh$_3$)$_2$ or dpe]. We are unable to decide if such an effect has a chemical interpretation, although it would be easy to attribute these distortions to intra- and inter-molecular non-bonded interactions.

Copper-dnpm *Bonding*.—Another interesting feature in [(PPh$_3$)$_n$M^{I}X] compounds is the nature of the bonding between (PPh$_3$)$_n$M and X groups. Davis *et al.*[8] claim essentially ionic interaction between [(PPh$_3$)$_n$M$^+$] and X$^-$ ions, but it has been observed [11] that the d^{10} species are spherically symmetrical and hence a strongly ionic interaction would result in a linear unit [(PPh$_3$)$_2$M]$^+$, as for the [(PPh$_3$)$_2$Au(tcnq)] compound (tncq = 7,7,8,8-tetracyanoquindimethanido-anion).[14] Table 4 summarizes the known structures of [(PPh$_3$)$_n$M^I] complexes and the values of their P–M–P angles.

We believe that there is a gradual change from an essentially covalent interaction, *i.e.* [(PPh$_3$)$_2$CuCl], to an essential ionic bonding, *i.e.* [(PPh$_3$)$_2$Au(tcnq)] between the metal(I) and X species, as shown by data of Table 4. The present complex can be considered as mainly covalent, in agreement with the low values of its conductivity in dichloroethane and acetone solutions.

The bond lengths of the dnpm anion have not been determined sufficiently accurately to give the fraction of double-bond character in the C–N bonds, although C(37)–N(1) is shorter than C(37)–N(2). However, the planarity of the whole anion, except for the side phenyl group, may be indicative of some π delocalization on the molecular plane, a residue of the full delocalization in the hypothetical non-co-ordinated *aci*-form of the anion.

TABLE 4

Comparison of the [(PPh$_3$)$_n$M^{I}X] known structures

[(PPh$_3$)$_n$MX]	P–M–P(°)
[(PPh$_3$)$_3$CuBF$_4$] [a]	115.89(5) 115.22(6) 115.80(5)
[(PPh$_3$)[CuBr] [b]	126.0(1)
[(PPh$_3$)[CuNO$_3$] [c]	131.2(1)
[(PPh$_3$)[CuB$_3$H$_8$] [d]	119.97(7)
[(PPh$_3$)[CuBH$_4$] [e]	123.26(6)
[(PPh$_3$)[Cu(dnpm)] [f]	132.8(1)
[(PPh$_3$)[AuCl] [g]	132.1(1)
[(PPh$_3$)[AuCl] [h]	179.63 (P–Au–Cl)
[(PPh$_3$)[AuCN] [i]	169(2) (P–Au–C)
[(PPh$_3$)$_2$[Au(tcnq)] [j]	180

[a] Ref. *w* of Table 3. [b] Ref. 8. [c] Ref. 7. [d] Ref. *o* of Table 3. [e] Ref. *n* of Table 3. [f] Present work. [g] Ref. 11. [h] Ref. 14. [i] P. L. Bellon, M. Manassero, and M. Sansoni, *Ricerca Sci.*, 1969, **39**, 173. [j] Ref. 14.

The structure of the [Cu(PPh$_3$)$_2$(dnpm)] complex and the type of co-ordination of the dnpm anion can give useful indications for the structures of the related compounds of the [Cu(B)L$_2$] series. It is reasonable to assume a similar structure also for derivatives of the same stoicheiometry with unidentate N-containing ligands.

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