Binuclear Copper(I) Complexes containing Bis(diphenylphosphino)methane Bridging Ligands: Crystal Structure of $[Cu_2(\mu\text{-dppm})_2(MeCN)_4][ClO_4]_2$†

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Novel binuclear copper(I) complexes of the types $[Cu_2(\mu\text{-dppm})_2(MeCN)_n]X_2$ (n = 2 or 4) and $[Cu_2(\mu\text{-dppm})_3]X_2$ (X = BF_4 or ClO_4, dppm = $Ph_2PCH_2PPh_2$) have been prepared. Proton and $^{31}P\text{-}\{^1H\}$ n.m.r. studies at room temperature show that they undergo ligand-dissociation processes in solution. The crystal structure of $[Cu_2(\mu\text{-dppm})_2(MeCN)_4][ClO_4]_2$ has been determined by *X*-ray methods. Crystals are monoclinic, space group *C*2/*c* with $Z = 4$ in a unit cell of dimensions $a = 22.407(9)$, $b = 13.052(6)$, $c = 21.522(8)$ Å, and $\beta = 108.69(3)°$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.079$ for 3 907 observed reflections $[I > 3\sigma(I)]$. The structure consists of $[Cu_2(\mu\text{-dppm})_2(MeCN)_4]^{2+}$ cations and of disordered perchlorate anions. In the cations the two copper atoms are bridged by dppm ligands to give eight-membered $Cu_2P_4C_2$ rings. The tetrahedral co-ordination around the copper is completed by two nitrogen atoms from acetonitrile ligands.

The diphosphine $Ph_2PCH_2PPh_2$ (dppm) is a particularly important bridging ligand. Many examples of binuclear complexes containing the eight-membered ring $M(\mu\text{-dppm})_2M'$ are known with a variety of metals and stereochemistries.[1] However, this is not the case with copper(I), which forms a number of tri- and tetra-nuclear complexes having related diphosphine-bridged structures with additional doubly or triply bridging anionic groups X^- such as Cl or I,[2] OH,[3] CS_3,[4] and RCS_2 (R = Ph, *o*-, *m*-, or *p*-MeC_6H_4).[5]

We now report the preparation of binuclear dppm copper(I) complexes $[Cu_2(\mu\text{-dppm})_2(MeCN)_n]X_2$ (n = 2 or 4) and $[Cu_2(\mu\text{-dppm})_3]X_2$ (X = BF_4 or ClO_4) in which the copper atoms are bridged only by dppm ligands. Proton and $^{31}P\text{-}\{^1H\}$ n.m.r. studies at room temperature show that the ligands undergo facile dissociation in solution. An *X*-ray single-crystal structural determination of $[Cu_2(\mu\text{-dppm})_2(MeCN)_4][ClO_4]_2$ shows that the dppm ligands are in a folded arrangement around the two copper atoms. Recently one further example, namely $[\{Cu(S_2CC_6H_4Me\text{-}o)(\mu\text{-dppm})\}_2]$ which contains a similar $Cu_2(\mu\text{-dppm})_2$ moiety, has been structurally characterized.[6]

Results and Discussion

The salt $[Cu(MeCN)_4]BF_4$ [7] reacts with an equimolar amount of dppm in CH_2Cl_2 at room temperature to give $[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2$ (**1**) which can be converted into $[Cu_2(\mu\text{-dppm})_2(MeCN)_4][BF_4]_2$ (**2**) by addition of an excess of MeCN. Alternatively, (**2**) can also be obtained by addition of an excess of dppm to a solution of $[Cu(MeCN)_4]BF_4$ in acetonitrile. Perchlorate salts can similarly be prepared.

Both complexes are obtained as colourless air-stable solids and their i.r. spectra (Nujol mulls) show $\nu(C{\equiv}N)$ absorptions characteristic of the acetonitrile ligands (see Experimental section). Similarly, when a solution of $[Cu(MeCN)_4]BF_4$ in acetone is heated under reflux with an excess of dppm and the solvent is evaporated an off-white air-stable solid, scarcely soluble in chlorinated solvents, is formed and was identified by elemental analyses and i.r. spectra as $[Cu_2(\mu\text{-dppm})_3][BF_4]_2$ (**3**). Recrystallization from acetonitrile–hexane or addition of MeCN to a dichloromethane solution leads to the dissociation of one dppm ligand to give (**2**) quantitatively [equation (1)].

$$[Cu_2(\mu\text{-dppm})_3][BF_4]_2 + 4MeCN \rightleftharpoons [Cu_2(\mu\text{-dppm})_2(MeCN)_4][BF_4]_2 + \text{dppm} \quad (1)$$

The i.r. spectra of compounds (**1**)—(**3**) exhibit absorptions characteristic of dppm (1 435s, 1 094m, 775m, 735s, and 689s cm^{-1}), and of the anionic groups (see Experimental section). Conductance data (acetone solutions) show that they are 1:2 electrolytes,[8] confirming their binuclear nature and the bridging character of dppm. The corresponding ^1H n.m.r. spectra in $CDCl_3$ at room temperature exhibit methylene and phenyl resonances at 3.3—3.5 (unresolved multiplets) and 7.0—7.2 p.p.m. respectively, along with a single methyl signal for (**1**) and (**2**) at approximately equal chemical shift (δ 2.2 p.p.m.). This resonance is gradually shifted to higher field when stoicheiometric amounts of acetonitrile are added to the n.m.r. tube, almost reaching the corresponding chemical shift for free MeCN (δ 1.95 p.p.m.) when a large excess (*ca.* 4:1) is used. It seems that a fast acetonitrile ligand exchange is taking place probably due to an equilibrium such as (2). Actually, the *X*-ray structural determination of $[Cu_2(\mu\text{-dppm})_2(MeCN)_4][ClO_4]_2$ (**4**) (see below) shows two structurally different acetonitrile ligands in the solid state, which in solution can become effectively equivalent by a rapid exchange process on the n.m.r. time-scale.

$$[Cu_2(\mu\text{-dppm})_2(MeCN)_4][BF_4]_2 \rightleftharpoons [Cu_2(\mu\text{-dppm})_2(MeCN)_{4-x}][BF_4]_2 + x\text{MeCN} \quad (2)$$

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† Bis[μ-bis(diphenylphosphino)methane-*PP'*]-bis[diacetonitrilecopper(I)] diperchlorate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

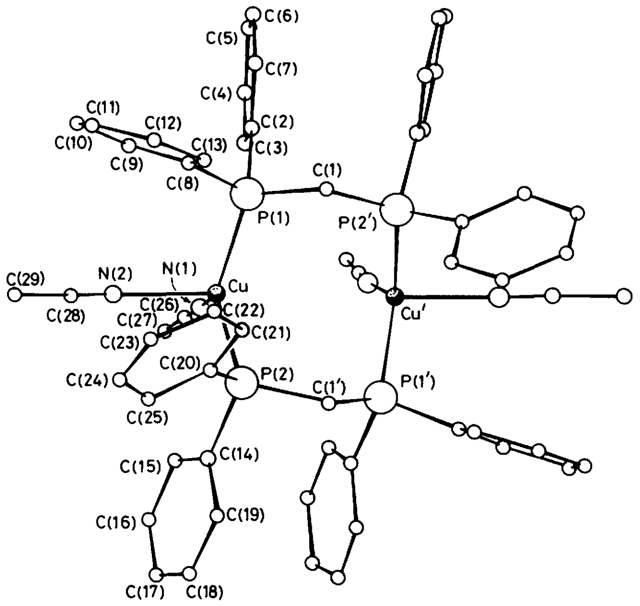

Figure 1. View of $[Cu_2(\mu\text{-dppm})_2(MeCN)_4]^{2+}$ with the atomic numbering scheme

Table 1. Selected bond distances (Å) and angles (°) for $[Cu_2(\mu\text{-dppm})_2(MeCN)_4][ClO_4]_2$ (**4**)*

Cu–P(1)	2.270(3)	P(2)–C(1′)	1.845(10)
Cu–P(2)	2.283(3)	P(2)–C(14)	1.815(10)
Cu–N(1)	1.999(9)	P(2)–C(20)	1.827(11)
Cu–N(2)	2.161(13)	N(1)–C(26)	1.16(2)
P(1)–C(1)	1.851(10)	C(26)–C(27)	1.49(2)
P(1)–C(2)	1.830(9)	N(2)–C(28)	1.14(2)
P(1)–C(8)	1.833(12)	C(28)–C(29)	1.49(2)

P(1)–Cu–P(2)	119.9(1)	Cu(8)–P(1)–Cu	109.9(3)
P(1)–Cu–N(1)	118.0(3)	Cu–P(2)–Cu(1′)	120.6(3)
P(1)–Cu–N(2)	101.7(3)	Cu–P(2)–C(14)	115.7(4)
P(2)–Cu–N(1)	117.0(3)	Cu–P(2)–C(20)	108.1(4)
P(2)–Cu–N(2)	94.8(3)	C(1′)–P(2)–C(14)	103.3(4)
N(1)–Cu–N(2)	96.1(4)	C(1′)–P(2)–C(20)	102.7(4)
Cu(1)–P(1)–Cu	116.4(3)	C(14)–P(2)–C(20)	104.7(4)
C(1)–P(1)–C(2)	104.8(4)	Cu–N(1)–C(26)	173.1(9)
C(1)–P(1)–C(8)	102.4(4)	N(1)–C(26)–C(27)	177.8(14)
C(2)–P(1)–Cu	119.3(3)	Cu–N(2)–C(28)	157.4(9)
C(2)–P(1)–C(8)	101.9(5)	N(2)–C(28)–C(29)	176.5(14)

* Primed atoms are related to the corresponding unprimed ones by the two-fold axis (symmetry equivalent position: $-x,y,\frac{1}{2}-z$).

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra in CH_2Cl_2 of complexes (**1**), (**2**), and (**3**) exhibit a single resonance at δ −8.5, −9.5, and −6.0 p.p.m. respectively, showing that all the phosphorus atoms in each molecule are chemically equivalent. Although no variable-temperature n.m.r. experiments have been made, a rapid fluxional process due to the Cu_2P_4 or Cu_2P_6 frameworks may be present. In order to obtain knowledge of these frameworks, which are relatively well known for other metals, an *X*-ray single-crystal structural determination of (**4**) was undertaken. However, we have not been able to obtain suitable crystals of (**3**). The $^{31}P\text{-}\{^1H\}$ n.m.r. studies on solutions of complex (**3**) at room temperature also show rapid dppm exchange. Thus, the spectrum corresponding to equilibrium (1) in CH_2Cl_2 shows a single signal at δ −12.4 p.p.m. which is shifted to values closer to that of free dppm (δ −23.5 p.p.m.) when additional ligand is added. In contrast, complex (**3**) in CH_2Cl_2 apparently does not dissociate dppm (δ −6.0 p.p.m.). However, the addition of further ligand to this solution leads to a shifting of the corresponding phosphorus resonance to higher field (molar ratio complex:dppm = 1:1, δ −13.8; 1:3, δ −17.8).

These data seem to indicate the co-ordination of one further dppm molecule to complex (**3**), which easily undergoes exchange with an excess of the ligand. Attempts to isolate this new complex with analytical purity were unsuccessful. In conclusion, these complexes show a special ability to undergo dissociation processes in solution, probably as a result of the known ability of copper to adopt three- and four-co-ordination.

Structure of $[Cu_2(\mu\text{-dppm})_2(MeCN)_4][ClO_4]_2$ (**4**).—The solid-state structure of complex (**4**) consists of dimeric $[Cu_2(\mu\text{-dppm})_2(MeCN)_4]^{2+}$ cations, having an imposed crystallographic C_2 symmetry, and of disordered perchlorate anions (see Experimental section). The structure of the cation is depicted in Figure 1 together with the atomic numbering scheme; selected bond distances and angles are given in Table 1. Two copper atoms are doubly bridged by two dppm ligands to form an eight-membered $Cu_2P_4C_2$ ring. The slightly distorted tetrahedral co-ordination around copper is completed by two nitrogen atoms from acetonitrile ligands. Noteworthy is the different behaviour of these ligands, one being linearly bound [Cu–N(1)–C(26) 173.1(9)°] and the other bent [Cu–N(2)–C(28) 157.4(9)°]. The corresponding Cu–N bond lengths are also different, Cu–N(1) [1.999(9) Å] being much shorter than Cu–N(2) [2.161(13) Å]. Copper atoms doubly bridged by two dppm ligands have been found also in $[\{Cu(S_2CC_6H_4Me\text{-}o)(\mu\text{-dppm})\}_2]$,[6] although the Cu ··· Cu separation of 3.426(3) Å is shorter than that found in complex (**4**) [3.757(3) Å]. Also the Cu–P bonds [2.240(6) and 2.249(6) Å] in the dithiotoluate derivative are shorter than those in (**4**) [2.270(3) and 2.283(3) Å].

The conformation of the $Cu_2P_4C_2$ ring is eclipsed (*i.e.* with P–Cu–P units eclipsed[9]), as shown in Figure 2, and is similar to that found in the dithiotoluate derivative[6] and in $[Ag_2(dppm)_2(NO_3)_2]$,[9] but differs from that (staggered) found in $[Au_2(dppm)_2Cl_2]$.[10] The Cu,P(1),P(2),C(1) atoms are displaced by −0.484(2), 0.316(3), 0.860(3), and 1.562(9) Å from the mean plane passing through them. The torsion angles in the ring are C(1)–P(1)–Cu–P(2) 32.3(4), P(1)–Cu–P(2)–C(1′) −60.4(4), Cu–P(2)–C(1′)–P(1′) −45.4(6), and P(2)–C(1′)–P(1′)–Cu′ 66.6(5)°.

Experimental

Measurements.—Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer (range 4 000—600 cm^{-1}) using Nujol mulls between NaCl plates. Conductivities were measured at room temperature, in *ca.* 10^{-3} mol dm^3 acetone solutions, with a Metrohm AG. E382 conductimeter. The C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. N.m.r. spectra were recorded on a Varian FT-80A spectrometer at 79.54 (^1H) or 32.20 MHz (^{31}P) using $SiMe_4$ and 85% H_3PO_4 as internal or external standards, respectively.

Synthesis.—The reactions were carried out with 2 mmol of $[Cu(MeCN)_4]X$[7] as starting material, using either the perchlorate or tetrafluoroborate salt. All reactions were performed under an argon atmosphere, and solvents were dried and distilled before use. Only the preparations of tetrafluoroborate complexes will be described.

$[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2$ (**1**). A mixture of $[Cu(MeCN)_4]BF_4$ and dppm (1:1 mol ratio) was stirred in

Table 2. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu	560(1)	1 413(1)	2 011(1)	C(9)	2 310(6)	2 168(9)	2 730(6)
P(1)	1 188(1)	2 026(2)	2 989(1)	C(10)	2 818(7)	2 701(11)	2 584(7)
P(2)	−193(1)	2 443(2)	1 331(1)	C(11)	2 821(8)	3 717(11)	2 575(8)
Cl	−1 244(2)	6 214(3)	1 282(2)	C(12)	2 359(8)	4 339(12)	2 746(8)
O(1)	−1 350(11)	5 235(16)	880(11)	C(13)	1 873(6)	3 825(9)	2 891(6)
O(2)	−765(10)	5 850(18)	1 865(11)	C(14)	−611(4)	1 912(7)	530(5)
O(3)	−1 317(15)	6 833(22)	807(14)	C(15)	−526(5)	888(9)	400(6)
O(4)	−1 856(15)	6 159(22)	1 258(15)	C(16)	−859(6)	457(10)	−202(7)
O(5)	−923(19)	6 742(29)	895(18)	C(17)	−1 273(6)	1 051(10)	−672(7)
O(6)	−1 705(50)	6 700(67)	1 558(49)	C(18)	−1 382(6)	2 092(10)	−564(6)
O(7)	−1 010(27)	6 920(41)	1 849(25)	C(19)	−1 059(5)	2 537(9)	32(5)
O(8)	−911(32)	5 325(51)	1 319(33)	C(20)	195(5)	3 589(7)	1 158(5)
N(1)	411(4)	−98(7)	1 925(4)	C(21)	383(5)	4 344(8)	1 630(5)
N(2)	1 182(5)	1 482(7)	1 425(5)	C(22)	769(6)	5 186(10)	1 563(7)
C(1)	830(4)	2 981(7)	3 398(4)	C(23)	944(7)	5 213(11)	977(7)
C(2)	1 593(4)	1 124(7)	3 638(5)	C(24)	761(7)	4 484(11)	515(7)
C(3)	1 430(5)	96(9)	3 558(5)	C(25)	366(6)	3 617(9)	575(6)
C(4)	1 750(6)	−624(10)	4 045(6)	C(26)	362(5)	−976(10)	1 834(6)
C(5)	2 260(6)	−305(10)	4 592(6)	C(27)	306(9)	−2 095(10)	1 694(11)
C(6)	2 418(6)	725(11)	4 658(7)	C(28)	1 482(6)	1 851(10)	1 148(6)
C(7)	2 092(5)	1 434(8)	4 185(6)	C(29)	1 862(8)	2 397(15)	795(8)
C(8)	1 849(5)	2 740(7)	2 873(5)				

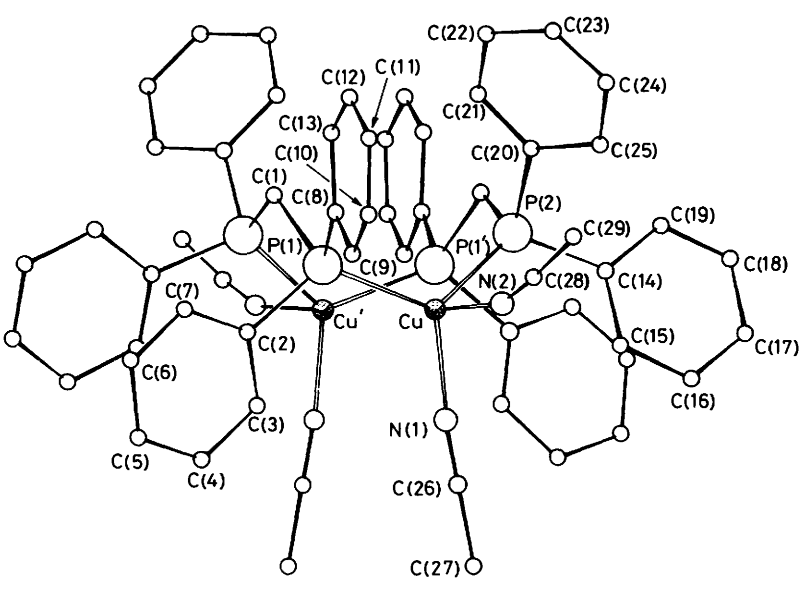

Figure 2. Perspective view of the $Cu_2P_4C_2$ ring

dichloromethane at room temperature for 6 h. Concentration of the resulting solution and addition of diethyl ether resulted in the precipitation of an off-white solid which was washed with diethyl ether and vacuum-dried. Yield: 96% (Found: C, 56.3; H, 4.4; N, 2.7. Calc. for $C_{54}H_{50}B_2Cu_2F_8N_2P_4$: C, 56.3; H, 4.3; N, 2.4%); Λ = 190 S cm^2 mol^{-1}. N.m.r.: ^{1}H ($CDCl_3$) δ 2.3 (6 H, s, MeCN), 3.5 (4 H, m, CH_2), 7.2 (40 H, s, br, Ph); ^{31}P-{^{1}H} (CH_2Cl_2), δ −8.5(s) p.p.m. I.r.: ν(C≡N) 2 290vw, 2 270w; ν(B–F) 1 100—1 000s,br cm^{-1}.

[Cu_2(μ-dppm)$_2$(MeCN)$_4$][BF_4]$_2$ (**2**). A mixture of [Cu(MeCN)$_4$]BF_4 and an excess of dppm was stirred in acetonitrile at room temperature for 6 h. Working up as above gave complex (**2**) as an off-white solid. Yield: 82% (Found: C, 56.4; H, 4.5; N, 4.4. Calc. for $C_{58}H_{56}B_2Cu_2F_8N_4P_4$: C, 56.5; H, 4.5; N, 4.5%). Λ = 192 S cm^2 mol^{-1}. N.m.r.: ^{1}H ($CDCl_3$) δ 2.2 (12 H, s, MeCN), 3.5 (4 H, m, CH_2), 7.2 (40 H, br s, Ph); ^{31}P-{^{1}H} (CH_2Cl_2), δ −9.5(s) p.p.m. I.r.: ν(C≡N) 2 300vw, 2 270w; ν(B–F) 1 100—1 000s,br cm^{-1}.

Compound (**2**) can similarly be obtained by addition of acetonitrile to either a dichloromethane solution of (**1**) (4:1 mol ratio) or (**3**) (in excess), after stirring at room temperature for 6 h and working up as above.

[Cu_2(μ-dppm)$_3$][BF_4]$_2$ (**3**). A mixture of [Cu(MeCN)$_4$]BF_4 and an excess of dppm was heated under reflux in acetone for 12 h and filtered while hot. The resulting solution was concentrated under reduced pressure and slow addition of diethyl ether gave a white microcrystalline solid which was washed with diethyl ether and vacuum dried. Yield: 88% (Found: C, 62.1; H, 4.8; P, 12.8. Calc. for $C_{75}H_{66}B_2Cu_2F_8P_6$: C, 62.0; H, 4.5; P, 12.8%). Λ = 197 S cm^2 mol^{-1}. N.m.r.: ^{1}H ($CDCl_3$), δ 3.35 (6 H, m, CH_2), 7.1 (60 H, m, Ph); ^{31}P-{^{1}H} (CH_2Cl_2), δ −6.0(s) p.p.m. I.r.: ν(B–F) 1 100—1 000s,br cm^{-1}.

Crystal Structure of Complex (**4**).—A white prismatic crystal, of approximate dimensions 0.20 × 0.25 × 0.30 mm, was used.

Crystal data. $C_{58}H_{56}Cl_2Cu_2N_4O_8P_4$, $M = 1\,258.99$, monoclinic, space group $C2/c$, $a = 22.407(9)$, $b = 13.052(6)$, $c = 21.522(8)$ Å, $\beta = 108.69(3)°$, $U = 5\,962(4)$ Å^3 (by least-squares refinement from the θ values of 25 accurately measured reflections, $\lambda = 0.710\,69$ Å), $Z = 4$, $D_c = 1.402$ g cm^{-3}, $F(000) = 2\,592$, $\mu(\text{Mo-}K_\alpha) = 9.64$ cm^{-1}.

Data collection and processing. A Philips PW-1100 diffractometer (θ—2θ mode, graphite-monochromated Mo-K_α radiation) was employed. All reflections in the range $3 \leqslant \theta \leqslant 27°$ were measured; of 6 970 independent reflections, 3 907 having $I \geqslant 3\sigma(I)$ were considered observed and used in the analysis. An absorption correction was applied by a semiempirical method[11] (maximum and minimum corrections: 1.075 and 1.000).

Structure solution and refinement. Patterson and Fourier methods, full-matrix least-squares refinement with anisotropic thermal parameters in the last cycles for atoms Cu,P,Cl,N, and C(1),C(26)—C(29). The perchlorate anion is disordered with the oxygen atoms distributed in three positions of equal occupancy. The three positions are occupied by O(1),O(2),O(3),O(4), O(1),O(2),O(5),O(6), and O(3),O(4),O(7),O(8) so that atoms O(1)—O(4) have twice the occupancy with respect to O(5)—O(7). The hydrogen atoms were placed at their geometrically calculated positions and introduced in the final calculations with isotropic thermal parameters. Weighting scheme used in the last cycles: $w = K/[\sigma^2(F_o) + gF_o^2]$ with $K = 0.9851$ and $g = 0.01$. Final R and R' values 0.079 and 0.089 respectively.

Programs and sources of scattering factors are given in refs. 12 and 13. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 2. All calculations were performed on the CYBER 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from The University of Parma.

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References

1 R. J. Puddephatt, *Chem. Soc. Rev.*, 1983, **12**, 99 and refs. therein; A. L. Balch, 'Homogeneous Catalysis with Metal Phosphine Complexes,' ed. L. H. Pignolet, Plenum, 1983, ch. 5, p. 167.
2 M. Marsich, G. Nardin, and L. Randaccio, *J. Am. Chem. Soc.*, 1973, **95**, 4053; G. Nardin and L. Randaccio, *Acta Crystallogr., Sect. B*, 1974, **30**, 1377; *Cryst. Struct. Commun.*, 1974, **3**, 607; N. Brescioni, N. Marsich, G. Nardin, and L. Nardaccio, *Inorg. Chim. Acta*, 1974, **10**, 15; A. Camus, G. Nardin, and L. Randaccio, *ibid.*, 1975, **12**, 23; G. Nardin, L. Randaccio, and E. Zangrando, *J. Chem. Soc., Dalton Trans.*, 1975, 2566.
3 D. M. Ho and R. Bau, *Inorg. Chem.*, 1983, **22**, 4079.
4 A. Manotti Lanfredi, A. Tiripicchio, A. Camus, and N. Marsich, *J. Chem. Soc., Chem. Commun.*, 1983, 1126.
5 A. Camus, N. Marsich, and G. Pellizer, *J. Organomet. Chem.*, 1983, **259**, 367.
6 A. M. Manotti Lanfredi, F. Ugozzoli, A. M. Camus, and N. Marsich, *Inorg. Chim. Acta*, 1985, **99**, 111.
7 G. J. Kubas, *Inorg. Synth.*, 1979, **19**, 90; B. J. Hathaway, D. G. Holah, and J. D. Postlethwaite, *J. Chem. Soc.*, 1961, 3215.
8 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
9 D. M. Ho and R. Bau, *Inorg. Chem.*, 1983, **22**, 4073.
10 H. Schmidbaur, A. Wohlleben, U. Schubert, A. Frank, and G. Huttner, *Chem. Ber.*, 1977, **110**, 2751.
11 A. C. T. North, D. C. Philips, and F. C. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
12 SHELX system of computing programs, G. M. Sheldrick, University of Cambridge, 1976.
13 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

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