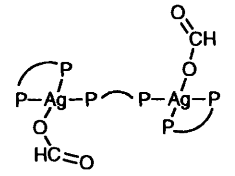
Promotion of Tetrahedral Copper(I) Dimers by Chelation of 1,1′-Bis(diphenylphosphino)ferrocene (dppf). Crystal Structures of $[\{Cu(\mu\text{-}X)(dppf\text{-}P,P')\}_2]$ ($X = O_2CH$, I or NO_3)†

Soh Ping Neo,[a] **Zhong-Yuan Zhou,**[b] **Thomas C. W. Mak**[*,b] **and T. S. Andy Hor**[*,a]
[a] *Department of Chemistry, Faculty of Science, National University of Singapore, 0511, Singapore*
[b] *Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong*

Treatment of $Cu(NO_3)_2$ with 1,1′-bis(diphenylphosphino)ferrocene (dppf) gave $[\{Cu(\mu\text{-}NO_3\text{-}O)(dppf\text{-}P,P')\}_2]$ which readily exchanged with NaO_2CH or KI to give $[\{Cu(\mu\text{-}O_2CH\text{-}O,O')(dppf\text{-}P,P')\}_2]$ or $[\{Cu(\mu\text{-}I)(dppf\text{-}P,P')\}_2]$. X-Ray structural analysis of the complexes revealed three tetrahedral copper(I) dimers with nitrate, iodide or formate preferentially in bridging and dppf consistently in chelating modes. The P–Cu–P chelate angle in the nitrate [117.8(1)°] is the largest of known dppf chelates in all geometries. These structures are different from their triphenylphosphine analogues which are all monomers. Exchanges of the nitrate complex with other carboxylates gave $[\{Cu(\mu\text{-}O_2CR)(dppf\text{-}P,P')\}_n]$ (R = Me, CF_3, Et, Pr^n or Ph). It also reacted with a stoichiometric amount of dppf to give $[Cu_2(NO_3\text{-}O)_2(\mu\text{-}dppf)(dppf\text{-}P,P')_2]$. The geometrical influence of PPh_3, $Ph_2PCH_2PPh_2$ and dppf, and their preferred bonding modes to Cu^I in relation to the complex nuclearity, are discussed.

Recent reports on 1,1′-bis(diphenylphosphino)ferrocene (dppf) have emphasized the variety of its co-ordination modes.[1] This variety is ascribed to its skeletal flexibility which, when compounded by variations in metal geometries, complex nuclearities and bonding modes of co-ligands, has led to the isolation of many intriguing structures.[2] These structures are often unpredictable as a result of a number of bonding contributions and an array of possible permutations in metal geometries and co-ordination modes. The complexity is best illustrated by the Group 11 d^{10} metals which generally do not show a clear preference for any particular geometry. Di-, oligo-, and poly-merization are hence common. A recent report also highlights the steric influence of phosphines on the structures of some carboxylato complexes of Cu^I and Cu^{II}.[3] Some representative examples of dppf complexes are summarized in Table 1. There are emerging examples of dppf co-ordinated to Ag^I and Au^I. On the other hand, the only structurally characterized examples for Cu^I are the binary complexes $[Cu_2(\mu\text{-}dppf)(dppf\text{-}P,P')_2]X_2$ ($X = BF_4$ or ClO_4).[4] These undergo partial dissociation in solution to give a mononuclear complex, with dppf in its unidentate mode. In order to understand the 'natural' co-ordination mode of dppf with Cu^I, we have examined the structures of three complexes $[\{CuX(dppf)\}_n]$ (X = I, HCO_2 or NO_3) in which both X and dppf can opt for any of the three common bonding modes, terminal (unidentate), chelating or bridging. The number of permutations which decide the resultant structures, especially when dimerization and oligomerization are also considered, are hence numerous. Iodide, formate and nitrate are ligands of choice because of their minimum steric demand and flexible modes of co-ordination. A related example for Ag^I is found in $[Ag_2(O_2CH\text{-}O)_2(dppf\text{-}P,P')_2(\mu\text{-}dppf)]$[5] **A** in which formate is unidentate and two co-ordination modes are adopted by dppf. The iodo complex was briefly reported but the structure is unclear.[12]



A

Results and Discussion

Treatment of $Cu(NO_3)_2$ with dppf gives a complex analysing as $[\{Cu(NO_3)(dppf)\}_2]$ **1**.[13] The facile reduction of Cu^{II} in the presence of phosphine in methanol has been reported in a similar reaction with PPh_3.[14] However, unlike the PPh_3 complex which is monomeric, **1** is presumed to be dimeric based on its similar IR absorptions bands with those of its silver(I) analogue.[5] X-Ray diffraction analysis confirmed that the complex consists of two Cu(dppf-*P*,*P*′) moieties linked by two single-oxygen-atom bridging nitrates (Fig. 1). Selected bond data are listed in Table 2, crystallographic details in Table 3, and atomic coordinates in Table 4. The structural framework contrasts that of its silver(I) analogue in which a $Ag_2(\mu\text{-}dppf)_2$ metallocycle is supported by two bridging dppf. The one-atom bridging mode of nitrate gives a Cu_2O_2 core in **1**. This is rare compared to the symmetrical *syn*/*syn* co-ordination through separate oxygens.[15] Similar bridges have been reported in $[\{Ag(\mu\text{-}NO_3)(PR_3)\}_2]$ (R = Ph[16] or OMe[17]). The Cu–O links in **1** are covalent and approximately equidistant [2.154(6) *vs.* 2.171(6) Å]. It readily exchanges with NaO_2CH to give $[\{Cu(\mu\text{-}O_2CH\text{-}O,O')(dppf\text{-}P,P')\}_2]$ **2**. Molecular-weight analysis in CH_2Cl_2 suggests it to be dimeric. The band separation between ν_{sym} and ν_{asym} (255 cm^{-1}) is considerably larger than those found for the typical formato-bridged complexes.[18] An X-ray crystallographic analysis was hence carried out to ascertain its structure. It confirms a centrosymmetric copper(I) dimer with formate in a bidentate end-to-end bridging mode and the bulkier dppf taking up a chelating position (Fig. 2). Several structural features are found in **2**. (*i*) As a result of this doubly bridged framework, the complex can be configured as an

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Some representative dppf complexes of Cu^I, Ag^I and Au^I

Metal	Complex	Metal geometry	Nuclearity	Bonding mode of dppf	Ref.
Au^I	$[Au_2Cl_2(dppf)]$	Linear	Dinuclear	Singly bridging	6
	$[\{AuCl(dppf)\}_n]$	Trigonal planar	Polymeric	Singly bridging	5, 7
	$[Au_2(dppf)_3]X_2$ (X = NO_3 or ClO_4)	Trigonal planar	Dinuclear	Singly bridging and chelating	8, 9
Ag^I	$[\{Ag(NO_3)(dppf)\}_2]$	Pseudo-planar	Dinuclear	Doubly bridging	5
	$[Ag_2(O_2CPh)_2(dppf)]$	Trigonal planar	Dinuclear	Co-bridging with two benzoates	5
	$[Ag_2(O_2CH)_2(dppf)_3]$	Tetrahedral	Dinuclear	Singly bridging and chelating	5
	$[\{Ag_2(O_2CMe)_2(dppf)\}_2]$	Tetrahedral	Tetranuclear	Co-bridging with two acetates	5
	$[Ag_2(dppf)_3]PF_6$	Trigonal planar	Dinuclear	Singly bridging and chelating	10
Cu^I	$[Cu_2(dppf)_3]X_2$ (X = ClO_4 or BF_4)	Trigonal planar	Dinuclear	Singly bridging and chelating	4
	$[Cu_2(dppf)_2(bipym)][BF_4]_2$*	Distorted tetrahedral	Dinuclear	Chelating	11

* bipym = 2,2′-Bipyrimidine.

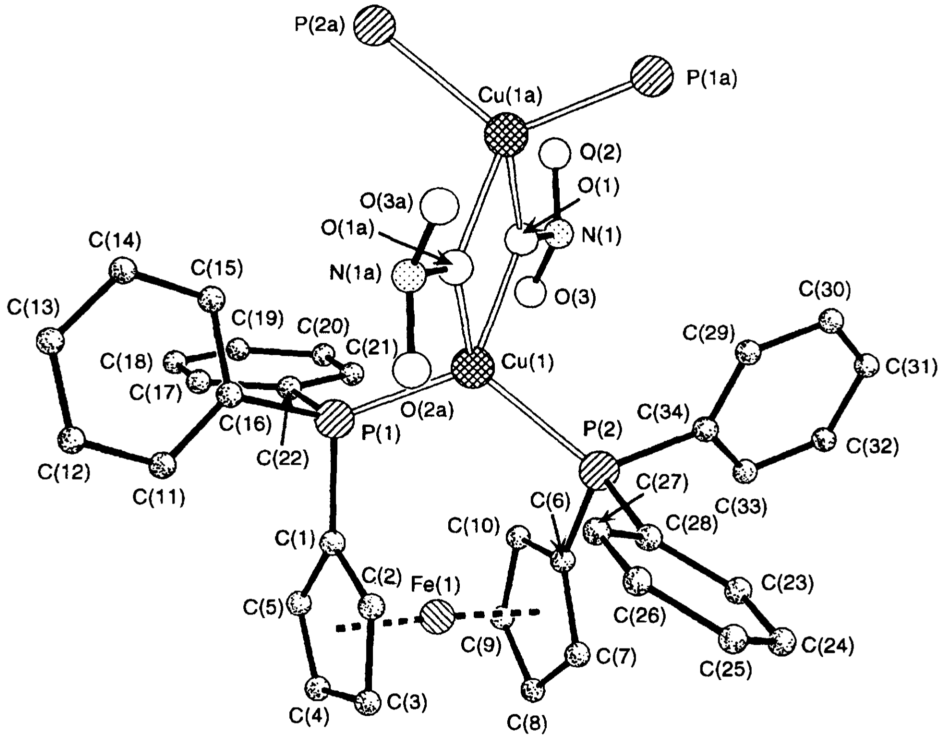


Fig. 1 Molecular structure of $[\{Cu(\mu\text{-}NO_3\text{-}O)(dppf\text{-}P,P')\}_2]$ **1** [ferrocenyl and phenyl groups on Cu(1a) removed for clarity]

eight-membered ring sandwiched between two ferrocenyl rings. (*ii*) The preference of formate for bridging and dppf for chelating at tetrahedral copper(I) avoids the formation of a unidentate mode for either ligand which bears a basic dangling site (**B** and **C**), or a strained four-membered ring for a chelating formate (**C** and **D**). Bidentate formato-bridged complexes are common in the literature,[18,19] but dinuclear or chain complexes containing solely formate as bridges are rare. A notable example of the latter is found in $[Ca_xCu(O_2CH)_y]$ ($x = 1, y = 4$; $x = 2$, $y = 6$),[20] a precursor for superconducting oxide materials. (*iii*) The formate ligands are bridging in an *anti-syn* conformation in order to accommodate the tetrahedral demand of the metals. The resultant configuration illustrates how a formate bridge with its small bite (O ··· O, 2.216 Å) can maximize the separation between two non-bonding metal centres (Cu ··· Cu 4.561 Å).

Similar replacement with other carboxylates can be carried out to give $[\{Cu(\mu\text{-}O_2CR)(dppf\text{-}P,P')\}_n]$ (R = Me **3**, CF_3 **4**, Et **5**, Pr^n **6** or Ph **7**). These metathesis reactions are summarized in Scheme 1. Infrared (KBr) analysis and a representative molecular-weight analysis (CH_2Cl_2) on **7** suggests an isostructural dimeric structure for all complexes except **6** which dissociates substantially in solution based on its molecular-weight data. Molecular-weight measurement of **7** suggests significant aggregation in benzene. With dppf in a chelating mode, the aggregates are held together by carboxylate bridges. The detailed solid-state structures of these complexes are uncertain without X-ray analysis. Some possible structures for the carboxylate phosphine complexes of Cu^I have been discussed.[21] The bis(diphenylphosphino)methane (dppm) analogue of **7**, for example, gives two linkage isomers, both with bridging dppm, but one with unidentate benzoate (**E**) and the other with benzoate bridging and unidentate (**F**).[22]

Nitrate displacement in complex **1** by iodide also gives a dinuclear complex $[\{Cu(\mu\text{-}I)(dppf\text{-}P,P')\}_2]$ **8** with bridging iodo and chelating dppf. This complex was first reported by Davison and co-workers,[12] being prepared by direct addition of CuI to dppf. The structure was not determined but the molecular formula appears to imply a mononuclear complex **G**. As the present X-ray analysis shows, **8** is in fact dimeric in the solid state. It is centrosymmetric with iodide in bridging and dppf in chelating modes (Fig. 3). The planarity of the central four-membered ring, which is crystallographically imposed, contrasts the folded structures found in other $Cu_2(\mu\text{-}I)_2$ dimers.[23]

The compound dppf is frequently compared with PPh_3 and dppm as a ligand. In many catalytic reactions the catalytic precursor bearing two monodentate PPh_3 or a bidentate

Table 2 Selected bond distances (Å) and angles (°) for complexes **1**, **2** and **8**

(*a*) Complex **1**[a]			
Cu(1)–P(1)	2.254(6)	Cu(1)–P(2)	2.263(6)
Cu(1)–O(1)	2.154(6)	Cu(1)–O(1a)	2.171(6)
Cu(1a)–O(1)	2.171(6)	N(1)–O(1)	1.284(13)
N(1)–O(2)	1.268(14)	N(1)–O(3)	1.227(11)
Fe(1)–C(1–5)	2.023(9)(mean)	Fe(1)–C(6–10)	2.052(10)
P(1)–Cu(1)–P(2)	117.8(1)	P(1)–Cu(1)–O(1)	112.3(4)
P(1)–Cu(1)–O(1a)	100.3(3)	P(2)–Cu(1)–O(1)	115.4(3)
P(2)–Cu(1)–O(1a)	130.3(4)	O(1)–Cu(1)–O(1a)	72.6(3)
Cu(1)–O(1)–Cu(1a)	104.9(3)	Cu(1)–O(1)–N(1)	120.8(7)
Cu(1a)–O(1)–N(1)	126.6(7)	O(1)–N(1)–O(2)	115.2(13)
O(1)–N(1)–O(3)	119.6(7)	O(2)–N(1)–O(3)	122.5(9)
(*b*) Complex **2**[b]			
Cu(1)–P(1)	2.276(1)	Cu(1)–P(2)	2.243(2)
Cu(1)–O(1)	2.055(4)	Cu(1)–O(2a)	2.111(4)
C(35)–O(1)	1.233(7)	C(35)–O(2)	1.210(6)
P(1)–C(1)	1.825(5)	P(2)–C(6)	1.820(5)
Fe(1)–C(1–5)	2.047(5)(mean)	Fe(1)–C(6–10)	2.042(5)(mean)
P(1)–Cu(1)–P(2)	110.8(1)	P(1)–Cu(1)–O(1)	108.1(1)
P(1)–Cu(1)–O(2a)	109.3(1)	P(2)–Cu(1)–O(1)	121.5(1)
P(2)–Cu(1)–O(2a)	108.0(1)	O(1)–Cu(1)–O(2a)	98.1(2)
O(1)–C(35)–O(2)	130.1(6)	Cu(1)–O(1)–C(35)	124.4(3)
C(35)–O(2)–Cu(1a)	131.4(4)	Cu(1)–P(1)–C(1)	116.0(2)
Cu(1)–P(2)–C(6)	109.1(2)		
(*c*) Complex **8**[b]			
Cu(1)–I(1)	2.649(6)	Cu(1)–I(1a)	2.736(7)
Cu(1a)–I(1)	2.736(7)	Cu(1)–P(1)	2.286(8)
Cu(1)–P(2)	2.28(1)	P(1)–C(5)	1.80(5)
P(2)–C(10)	1.81(4)	Fe(1)–C(1–5)	2.058(5)(mean)
Fe(1)–C(6–10)	2.046(4)(mean)		
P(1)–Cu(1)–P(2)	111.2(4)	I(1)–Cu(1)–I(1a)	98.2(2)
P(1)–Cu(1)–I(1)	117.7(4)	P(1)–Cu(1)–I(1a)	119.1(3)
P(2)–Cu(1)–I(1)	108.1(3)	Cu(1)–I(1)–Cu(1a)	81.8(2)
P(2)–Cu(1)–I(1a)	100.5(4)	Cu(1)–P(1)–C(5)	116(1)
Cu(1)–P(2)–C(10)	108(1)		

[a] Symmetry transformation: a $-x, y, \frac{1}{2} - z$. [b] Symmetry transformation: a $-x, -y, -z$.

diphosphine such as dppf is generally assumed to be isostructural.[1a] Identification of the three structures demonstrates unequivocally that this is a risky, and in these cases, invalid, assumption. Thus $[Cu(NO_3)(PPh_3)_2]$,[14] $[CuI(PPh_3)_2]$[24] and $[Cu(O_2CH\text{-}O,O')(PPh_3)_2]$[25] are all monomeric, but their dppf analogues, **1**, **2** and **8**, are dimeric. This difference can be traced to the steric differences between the two ligands. In general, $[Cu^{I}XL_2]$ complexes are monomeric unless X^- sterically or electronically favours bridge formation (*e.g.* SCN$^-$[26] or N_3^-[27]). Most are either trigonal planar (16 electron), when X^- is monodentate,[28] or tetrahedral (18 electron), when X^- is bidentate.[29] When L is a monophosphine, $[\{Cu(\mu\text{-}I)(PPhH_2)_2\}_2]$[30] and $[\{Cu(\mu\text{-}I)(PMePh_2)_2\}_2]\cdot SO_2$[31] are the only crystallographically proven dimers to date. Complex **8** is the sole example of dimeric halogeno complexes of copper(I) diphosphines. Similar dimers among silver(I) complexes are much more common.[32]

The compounds dppm[33] and dppf[34] share many similarities and stabilize similar A-frame and related structures. Complexes **1**, **2** and **8** however demonstrate a notable difference between dppm and dppf. The structures of both $[Cu(O_2CH)(dppm)]$ and $[Cu(NO_3)(dppm)]$ are unknown, but in the related complexes $[\{Ag(NO_3\text{-}O,O')(\mu\text{-dppm})\}_2]$,[35] $[\{Ag(O_2CMe\text{-}O,O')(\mu\text{-dppm})\}_2]$,[36] **H** and $[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-dppm})_3]Cl$,[37] the dppm is bridging. The dppf in all the present copper(I) complexes is however chelating. The bonding mode adopted by dppf depends on the metal geometry. Despite the wide distribution of dppf chelates, these complexes are the first crystallographically characterized $[\{CuX(L\text{–}L)\}_n]$ complexes in which the diphosphine (L–L) takes up the chelating mode. Similar behaviour has been reported for dppm and dppe $[Ph_2P(CH_2)_2PPh_2]$ in $[\{Cu(O_2CMe)(L\text{–}L)\}_2]$ but lacks crystallographic support.[21] Such a chelation tendency possibly precludes the formation of a linked structure such as $[\{Cu(\mu\text{-}I)_2Cu(\mu\text{-dppf})_2\}_n]$ **I**. Complexes of Cu^{I} on the contrary, containing bridging dppm are abundant.[38] The structures of **1**, **2** and **8** demonstrate for the first time the different co-ordination and structural preferences among dppf, dppm and PPh_3, and will be useful markers for our future design of copper(I) phosphine complexes.

The monomeric structure in $[CuI(PPh_3)_2]$ is stabilized by a large P–Cu–P angle [126.9(1)°], as expected for a bulky phosphine. This angle is significantly reduced in **8** [111.2(4)°] (Table 2) and the $PPhH_2$ analogue [117.0(1)°(mean)] (and complexes **1** and **2**), but is only slightly higher than that in $[\{Cu(\mu\text{-}I)(PMePh_2)_2\}_2]\cdot SO_2$ [125.4(1)°]. Chelates of dppf have been found in all commonly known geometries. Among these, chelate bites which match closely the geometry angles inherent to the hybrid orbitals are found only in tetrahedral complexes (*e.g.* mean chelate angles in known square-planar,[39] tetrahedral[5,40] and trigonal-planar[4,7,9,10] dppf complexes are ≈99, 108 and 109° respectively). The near-ideal chelate angles found in **2** [110.8(1)] and **8** [111.2(4)°] further support this phenomenon. Based on these data, we may conclude that chelating dppf is most comfortable in a tetrahedral environment. The large P–Cu–P chelate angle found in **1** [117.8(1)°] is exceptional and interesting. It is in fact the largest

Table 3 Crystallographic data and refinement details for $[\{Cu(\mu\text{-}NO_3\text{-}O)(dppf\text{-}P,P')\}_2]$ **1**, $[\{Cu(\mu\text{-}O_2CH\text{-}O,O')(dppf\text{-}P,P')\}_2]$ **2** and $[\{Cu(\mu\text{-}I)(dppf\text{-}P,P')\}_2]\cdot 2CH_2Cl_2$ **8***

	1	**2**	**8**
M	1359.8	1325.8	1659.6
Colour and habit	Golden-yellow prism	Yellow plate	Golden irregular-shaped crystal
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	20.173(4)	8.645(1)	12.684(3)
b/Å	12.767(3)	11.725(2)	12.807(3)
c/Å	24.355(5)	14.895(2)	13.876(3)
α/°	—	98.44(1)	97.00(2)
β/°	103.48(2)	103.90(1)	114.06(2)
γ/°	—	96.62(1)	111.78(2)
U/Å^3	6100(3)	1431.7(3)	1809.4(6)
Z	4	1	1
F(000)	2784	680	824
D_c/g cm^{-3}	1.481	1.538	1.52
Standard reflections	(2,0,−8), (2,2,6), (6,0,2)	(1,−2,1), (1,0,1)	(2,−2,−6), (3,−2,−6)
Intensity variation (%)	±1.1	±1.1	±1.0
R_{int} (from merging of equivalent reflections)	0.038	0.018	0.011
μ/cm^{-1}	13.14	1.394	20.9
Crystal size/mm	0.40 × 0.38 × 0.42	0.06 × 0.22 × 0.28	0.06 × 0.08 × 0.10
Mean μr	0.15	0.10	0.11
Transmission factors	0.64–0.86	0.741–0.981	0.056–0.214
Scan rate/° min^{-1}	3.00–60.00	2.00–29.30	3.0–14.6
Collection range	$-1 \leqslant h \leqslant 21$, $-1 \leqslant k \leqslant 15$, $-28 \leqslant l \leqslant 28$	$0 \leqslant h \leqslant 10$, $-13 \leqslant k \leqslant 13$, $-17 \leqslant l \leqslant 17$	h, $\pm k$, $\pm l$
$2\theta_{max}$/°	45	50	45
Unique data measured	5237	4483	2819
Observed data, n	1738 $[\lvert F_o\rvert > 3.0\sigma(\lvert F_o\rvert)]$	3099 $[\lvert F_o\rvert > 6.0\sigma(\lvert F_o\rvert)]$	1413 $[\lvert F_o\rvert > 3.0\sigma(\lvert F_o\rvert)]$
No. of variables, p	331	187	140
R	0.063	0.043	0.082
R'	0.060	0.056	0.078
S	1.73	1.44	1.72
Residual extrema in final difference map/e Å^{-3}	+0.53 to −0.47	+0.67 to −0.57	+0.62 to −0.43

* Details in common: T 294 K; scan range 0.80° below $K\alpha_1$ to 0.80° above $K\alpha_2$; stationary counts for one-fifth of scan time at each end of scan range; $R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$; $R' = [\Sigma w^2(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w^2\lvert F_o\rvert^2]^{\frac{1}{2}}$; $S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert^2)/(n - p)]^{\frac{1}{2}}$.

Table 4 Atomic coordinates for complexes **1** (× 10^5 for Cu, × 10^4 for others), **2** (× 10^5 for Cu and Fe, × 10^4 for others) and **8** (× 10^4)

Atom	x	y	z	Atom	x	y	z
(a) Complex **1**							
Cu(1)	−4 846(6)	873(4)	18 206(4)	C(4)	−1 555(3)	−1 564(5)	199(3)
N(1)	−1 101(4)	31(30)	2 838(3)	C(5)	−983(3)	−1 114(5)	578(3)
O(1)	−546(3)	−157(10)	2 682(2)	C(6)	−1 873(4)	1 582(6)	262(3)
O(2)	−1 093(3)	−214(8)	3 344(3)	C(7)	−2 457(4)	1 036(6)	−42(3)
O(3)	−1 632(3)	170(12)	2 480(3)	C(8)	−2 665(4)	330(6)	336(3)
Fe(1)	−1 693(1)	−8(8)	282(1)	C(9)	−2 210(4)	440(6)	873(3)
C(1)	−711(3)	−327(5)	282(3)	C(10)	−1 720(4)	1 214(6)	828(3)
C(2)	−1 114(3)	−290(5)	−280(3)	P(1)	−642(2)	−1 406(3)	1 313(1)
C(3)	−1 636(3)	−1 054(5)	−331(3)	P(2)	−998(2)	1 557(3)	1 408(1)
(b) Complex **2**							
Cu(1)	4 313(8)	561(6)	35 546(4)	C(6)	3 165(6)	2 069(4)	3 225(3)
Fe(1)	38 216(8)	10 051(6)	22 207(4)	C(7)	3 816(6)	2 739(4)	2 645(3)
P(1)	1 015(2)	−1 201(1)	2 410(1)	C(8)	5 409(6)	2 536(5)	2 702(3)
P(2)	1 170(2)	1 914(1)	3 436(1)	C(9)	5 768(6)	1 746(5)	3 323(3)
C(1)	2 305(6)	−557(4)	1 751(3)	C(10)	4 392(6)	1 445(4)	3 648(3)
C(2)	3 922(6)	−727(4)	1 802(3)	C(35)	−2 274(7)	−464(5)	4 376(4)
C(3)	4 511(7)	−41(4)	1 214(3)	O(1)	−1 853(4)	−535(3)	3 638(2)
C(4)	3 290(7)	535(4)	787(3)	O(2)	−1 721	206(4)	5 116(3)
C(5)	1 901(6)	232(4)	1 118(3)				
(c) Complex **8**							
I(1)	6 362(2)	4 586(3)	4 901(2)	C(4)	3 705(32)	5 375(42)	560(35)
Cu(1)	4 552(3)	5 139(4)	3 659(4)	C(5)	2 777(27)	4 654(34)	835(31)
Fe(1)	3 033(4)	6 389(5)	1 179(4)	C(6)	4 433(32)	8 112(41)	2 110(37)
P(1)	3 107(7)	3 918(8)	1 860(7)	C(7)	3 117(32)	8 028(41)	1 444(39)
P(2)	5 565(7)	7 058(8)	3 730(7)	C(8)	2 358(31)	7 376(41)	1 834(34)
C(1)	1 589(35)	4 683(47)	183(40)	C(9)	3 028(28)	6 890(37)	2 654(32)
C(2)	1 807(41)	5 392(51)	−469(49)	C(10)	4 335(28)	7.389(35)	2 786(32)
C(3)	3 110(36)	5 901(46)	−216(40)				

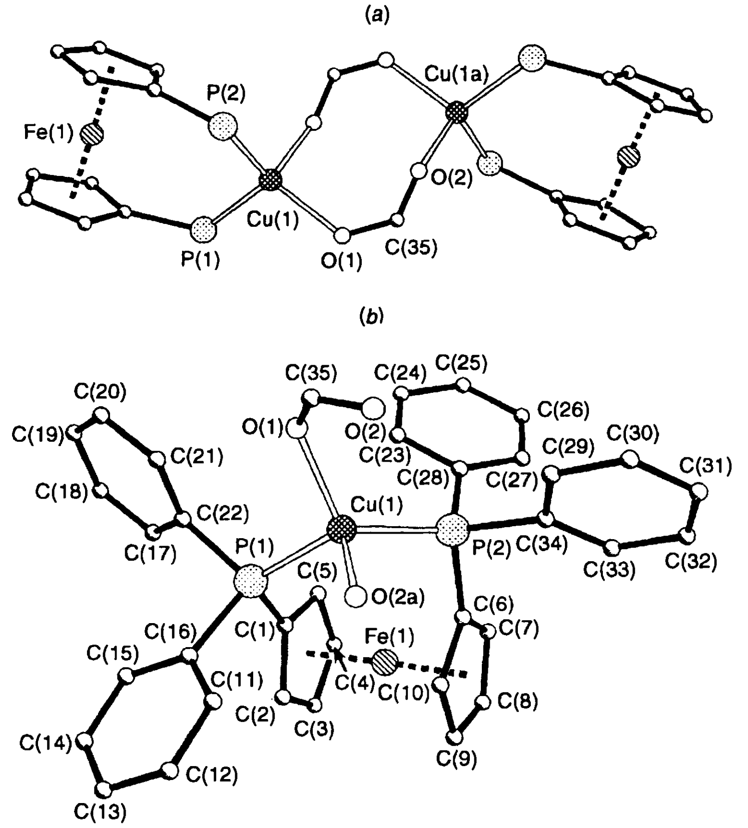
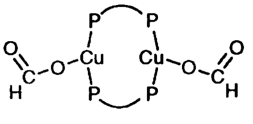


Fig. 2 (*a*) A perspective view of the molecular structure of [{Cu(μ-O_2CH-*O,O'*)(dppf-*P,P'*)}$_2$] **2**. (*b*) Half of the molecule of **2** showing the labelling scheme



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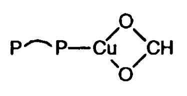
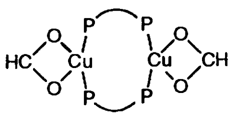


C



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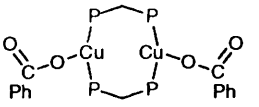

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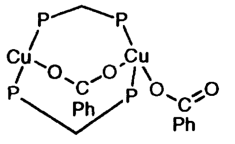

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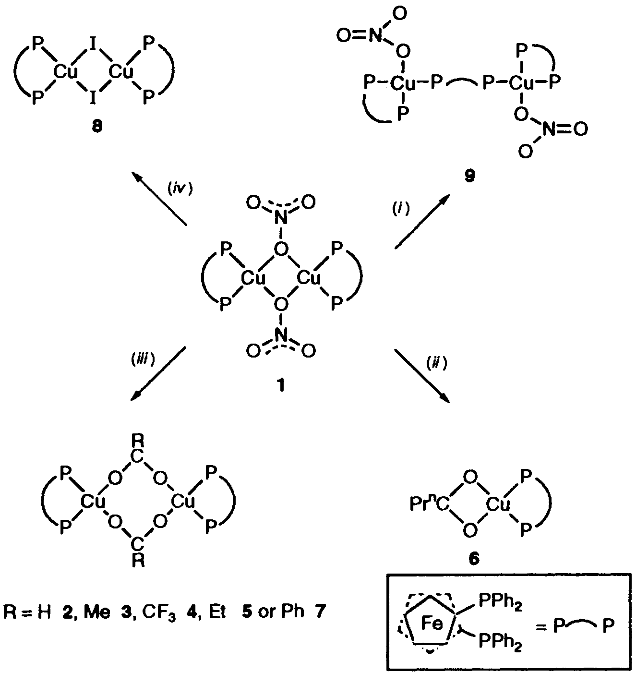


Scheme 1 (*i*) dppf; (*ii*) $Pr^nCO_2^-$; (*iii*) RCO_2^-; (*iv*) I^-

ever reported for dppf chelates for any metal in all geometries. Curiously perhaps, it is significantly larger than those found in trigonal-planar complexes, *e.g.* [Cu_2(μ-dppf)(dppf-*P,P'*)$_2$][ClO_4]$_2$,[4] which together with **8** has the second largest dppf bite (111.2°). This may not be surprising when one considers that even larger angles are found in other tetrahedral $CuX(PR_3)_2$ complexes. However, the phosphines in these complexes are invariably sterically demanding, and the P–Cu–P angles in monophosphine complexes are obviously not restricted by any conformational strain which is inherent to a chelate. The planarity of the Cu_2O_2 and NO_3 entities is probably a major contribution to this large bite angle.[17] The isolation and identification of complex **1** remove any lingering doubt that chelating dppf can support a geometry that requires a bite larger than ≈110° for stabilization. To conclude, although a tetrahedral environment is the 'natural' choice for chelating dppf, the chelate angle of dppf is very sensitive to the nature of the supporting ligands. The ability of this diphosphine ligand to adjust its chelating bite may be among the reasons why some catalytic reactions are supported better by dppf than by other di- and mono-phosphines.[41] For monodentate phos-

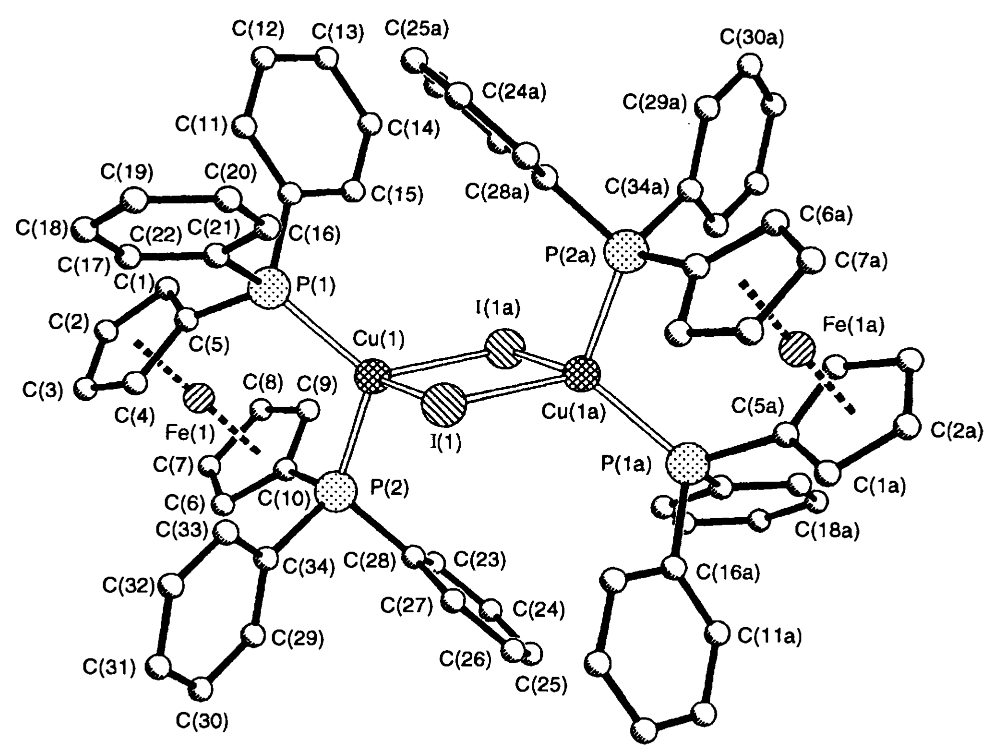
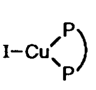
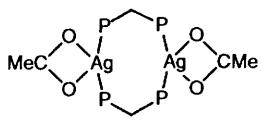


Fig. 3 Molecular structure of [{Cu(μ-I)(dppf-*P*,*P*′)}$_2$]·2CH$_2$Cl$_2$ **8** (solvent omitted)



G



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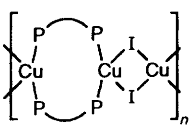
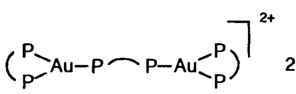


I



J

phines, the P–M–P angle is not subject to any chelating constraint. These ligands are however more susceptible to dissociation which could be detrimental to the stability of the catalyst, and hence product yield.

Addition of dppf to complex **1** readily gives [Cu$_2$(NO$_3$-*O*)$_2$(μ-dppf)(dppf-*P*,*P*′)$_2$] **9**. The analogous silver(I) structure was found to be dimeric with a singly bridging dppf between two Au(dppf) chelate rings and nitrate as an unco-ordinating anion (**J**). Infrared data for **9** conform to this bridged structure but ν(NO$_3$) is diagnostic of a unidentate nitrate. The difference between the two complexes is ascribed to the higher tendency for Cu^{I} compared to Au^{I} to adopt a higher co-ordination number. A similar conclusion has been drawn in a crystallographic study of [Au(PPh$_3$)$_2$]NO$_3$.[42] The silver(I) analogue of **9** and the structure of its PF$_6$$^-$ salt has been reported recently.[10]

Experimental

General.—All manipulations were routinely carried out under a dry argon atmosphere using freshly distilled solvents. The instruments used have been previously reported.[2a–c] Elemental analyses were performed by the Microanalytical Laboratory in the Chemistry Department in the National University of Singapore. Molecular-weight measurements were carried out by Galbraith Laboratories, Knoxville, TN, using vapour-pressure osmometry with a Knaüer–Dampfdruck osmometer. Infrared spectra were recorded on samples prepared in KBr discs. All NMR samples were in CDCl$_3$ solutions.

Syntheses.—[{Cu(μ-NO$_3$-*O*)(dppf-*P*,*P*′)}$_2$] **1**. The salt Cu(NO$_3$)$_2$·3H$_2$O (0.217 g, 0.90 mmol) in MeOH (20 cm^3) was transferred dropwise *via* a Teflon delivery tube to a tetrahydrofuran (thf) solution (20 cm^3) of dppf (0.500 g, 0.90 mmol). The reddish brown solution was stirred for 30 min, after which the mixture was reduced in volume to *ca.* 10 cm^3 in vacuum. The yellow precipitate obtained was filtered off and recrystallized from MeOH (0.33 g, 54%) (Found: C, 59.7; H, 4.0; Cu, 9.3; Fe, 8.6; N, 1.7. C$_{68}$H$_{56}$Cu$_2$Fe$_2$N$_2$O$_6$P$_4$ requires C, 61.0; H, 4.1; Cu, 9.3; Fe, 8.2; N, 2.1%); ν_{max}(NO$_3$) 1459s, 1384s and 1280s cm^{-1}; δ_H 4.21 (s, 8 H, C$_5$H$_4$), 4.36 (s, 8 H, C$_5$H$_4$) and 7.42–7.60 (m, 40 H, Ph); δ_P −14.5(s).

[{Cu(μ-O$_2$CH-*O*,*O*′)(dppf-*P*,*P*′)}$_2$] **2**. An aqueous solution (3 cm^3) of NaO$_2$CH (0.047 g, 0.69 mmol) was delivered by a Teflon tube to a methanolic solution (30 cm^3) of complex **1** (0.070 g, 0.05 mmol). The solution was stirred for 18 h and concentrated to give an orange precipitate. The solid obtained was recrystallized from CH$_2$Cl$_2$–hexane (0.049 g, 72%) (Found: C, 62.7; H, 4.5; Cu, 9.3; Fe, 8.7; P, 13.9. C$_{70}$H$_{58}$Cu$_2$Fe$_2$O$_4$P$_4$ requires C, 63.4; H, 4.4; Cu, 9.6; Fe, 8.4; P, 9.3%); *M* 1313 (CH$_2$Cl$_2$); ν_{max}(HCO$_2$) 1601s and 1346m cm^{-1}; δ_H 4.21 (s, br, 8 H, C$_5$H$_4$), 4.33 (m, 8 H, C$_5$H$_4$), 7.34–7.78 (m, 40 H, Ph) and 8.67 (s, 2 H, HCO$_2$); δ_P −17.4(s).

[{Cu(μ-O$_2$CR)(dppf-*P*,*P*′)}$_n$] (R = Me **3**, CF$_3$ **4**, Et **5**, Pr^n **6** or Ph **7**). A similar method to that for complex **2** was used using the corresponding sodium salt of the carboxylate.

Complex **3** (0.059 g, 85%) (Found: C, 63.7; H, 4.5; Cu, 8.9; Fe, 8.8; P, 13.4. C$_{76}$H$_{62}$Cu$_2$Fe$_2$O$_4$P$_4$ requires C, 63.9; H, 4.6; Cu, 9.4; Fe, 8.3; P, 9.2%): ν_{max}(MeCO$_2$) 1546s and 1400s cm^{-1}; δ_H 2.11 (s, 6 H, MeCO$_2$), 4.20 (m, 8 H, C$_5$H$_4$), 4.29 (m, 8 H, C$_5$H$_4$) and 7.32–7.78 (m, 40 H, Ph); δ_P −17.2(s).

Complex **4** (0.070 g, 62%) (Found: C, 58.8; H, 3.8; Cu, 8.1; F, 7.5; Fe, 7.4; P, 12.0. $C_{70}H_{56}Cu_2Fe_2O_4P_4$ requires C, 59.2; H, 3.9; Cu, 8.7; F, 7.8; Fe, 7.6; P, 8.5%): $\nu_{max}(CF_3CO_2)$ 1688s cm^{-1}; δ_H 4.23 (m, 8 H, C_5H_4), 4.35 (m, 8 H, C_5H_4) and 7.29–7.74 (m, 40 H, Ph); δ_P −16.0(s).

Complex **5** (0.084 g, 79%) (Found: C, 59.1; H, 4.4; Cu, 7.9; Fe, 7.1; P, 8.3. $C_{76}H_{70}Cu_2Cl_2Fe_2O_4P_4$ requires C, 58.8; H, 4.6; Cu, 8.2; Fe, 7.2; P, 8.0%): $\nu_{max}(EtCO_2)$ 1592s, 1567(sh) and 1409m cm^{-1}; δ_H 1.20 (t, 6 H, CH_3), 2.39 (q, 4 H, CH_2), 4.21 (m, 8 H, C_5H_4), 4.29 (m, 8 H, C_5H_4) and 7.32–7.78 (m, 40 H, Ph); δ_P −17.4(s).

Complex **6** (0.070 g, 89%) (Found: C, 64.6; H, 4.9; Cu, 8.0; Fe, 7.4; P, 8.9. $C_{76}H_{70}Cu_2Fe_2O_4P_4$ requires C, 64.7; H, 5.0; Cu, 9.0; Fe, 7.9; P, 8.8%): *M* 699 (CH_2Cl_2); $\nu_{max}(PrCO_2)$ 1540s and 1396m cm^{-1}; δ_H 0.96 (t, 6 H, CH_3), 1.68 (m, 4 H, CH_2), 2.37 (t, 4 H, CH_2), 4.21 (m, 8 H, C_5H_4), 4.28 (m, 8 H, C_5H_4) and 7.31–7.79 (m, 40 H, Ph); δ_P −17.4(s).

Complex **7** (0.091 g, 80%) (Found: C, 61.5; H, 4.2; Cu, 7.1; Fe, 7.0; P, 7.2. $C_{84}H_{70}Cu_2Fe_2O_4P_4$ requires C, 61.6; H, 4.4; Cu, 7.8; Fe, 6.8; P, 7.6%): $\nu_{max}(PhCO_2)$: 1542s and 1396s cm^{-1}; δ_H 4.26 (m, 8 H, C_5H_4), 4.31 (m, 8 H, C_5H_4) and 7.29–8.22 (m, 50 H, Ph); δ_P −17.4(s).

[{Cu(μ-I)(dppf-*P*,*P*′)}$_2$] **8**. This complex was prepared by a procedure similar to that for **2**, from **1** (0.233 g, 0.171 mmol) and KI (*ca.* 0.06 g, 0.362 mmol). Yield 0.135 g (53%) (Found: C, 54.8; H, 3.6; Cu, 9.0; Fe, 7.9; I, 17.2; P, 8.5. $C_{68}H_{56}Cu_2Fe_2I_2P_4$ requires C, 54.8; H, 3.8; Cu, 8.5; Fe, 7.5; I, 17.0; P, 8.3%); δ_H 4.20 (s, 8 H, C_5H_4), 4.34 (s, 8 H, C_5H_4) and 7.34–7.74 (m, 40 H, Ph); δ_P −19.36(s).

[Cu$_2$(NO$_3$-*O*)$_2$(μ-dppf)(dppf-*P*,*P*′)$_2$]·CH_2Cl_2·$2H_2O$ **9**. Solid dppf (0.030 g, 0.05 mmol) was added to a methanolic solution (25 cm^3) of complex **1** (0.073 g, 0.05 mmol). The mixture was stirred until it was practically free from dppf (TLC). The orange precipitate obtained on partial removal of the solvent was isolated and recrystallized from CH_2Cl_2–hexane (0.094 g, 91%). The solvent molecules present were identified by ^1H NMR spectroscopy (Found: C, 60.6; H, 4.2; Cu, 5.9; Fe, 8.7; N, 1.1; P, 9.9. $C_{103}H_{90}Cl_2Cu_2Fe_3N_2O_8P_6$ requires C, 60.8; H, 4.5; Cu, 6.2; Fe, 8.2; N, 1.4; P, 9.1%); $\nu_{max}(NO_3)$ 1418m and 1281s cm^{-1}; δ_H 4.07 (m, 12 H, C_5H_4); 4.25 (m, 12 H, C_5H_4) and 7.31–7.42 (m, 60 H, Ph); δ_P −13.1(s). Molar conductance Λ_m 34.0 Ω^{-1} cm^2 mol^{-1} (CH_2Cl_2).

X-Ray Crystallographic Analyses.—Single crystals of [{Cu(μ-O$_2$CH-*O*,*O*′)(dppf-*P*,*P*′)}$_2$], **2** and [{Cu(μ-I)(dppf-*P*,*P*′)}$_2$] **8** were grown from CH_2Cl_2–hexane and [{Cu(μ-NO$_3$-*O*)(dppf-*P*,*P*′)}$_2$] **1** from 1,2-dichloroethane–hexane. Those suitable for X-ray diffraction were mounted on thin-walled Lindemann glass capillaries under an atmosphere of nitrogen. Intensity data were measured on a Siemens P4 diffractometer with graphite-monochromatized Mo-Kα radiation (λ 0.710 73 Å) using the variable ω-scan technique. Two standard reflections were monitored after every 125 data measurements, showing only small random variations. The raw data were processed with the learnt-profile procedure,[43] and absorption corrections were applied by fitting a pseudo-ellipsoid to the ψ-scan data for selected strong reflections over a range of 2θ angles.[44] All the structures were solved with the Patterson superposition method and subsequent Fourier-difference syntheses. The structure analysis of complex **1** was more difficult than usual since direct phase determination tended to place the molecule on a centrosymmetric site whereas it actually lies on a crystallographic C_2 axis. Reflections *hkl* with *l* odd were generally weak since two molecules related by the *c* glide are also approximately related by the translation *c*/2. All the non-hydrogen atoms in **2** and **8** were refined anisotropically. Hydrogen atoms of the organic ligands were generated geometrically (C–H 0.95 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. The four phenyl groups in the asymmetric unit were treated as rigid groups. The other non-hydrogen atoms were refined anisotropically, and the hydrogen atoms of the cyclopentadienyl groups included in structure-factor calculations with assigned isotropic thermal parameters. All computations were performed with the SHELXTL PC program package.[45] Analytical expressions of neutral-atom scattering factors were employed, and anomalous-dispersion corrections were incorporated.[46] Crystal data, data-collection parameters, and results of the analyses are listed in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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