

Synthesis and Solution Multinuclear Nuclear Magnetic Resonance Studies of Homoleptic Copper(I) Complexes of Group 15 Donor Ligands*

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The homoleptic complexes $[\text{CuL}_4]\text{Y}$ ($\text{L} = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2, \text{PPh}_3, \text{PPh}_2\text{H}, \text{PPhH}_2, \text{AsMe}_3, \text{AsMe}_2\text{Ph}, \text{AsMePh}_2, \text{AsPh}_3, \text{SbMe}_3, \text{SbEt}_3$ or SbPh_3 ; $\text{Y} = \text{PF}_6$ or BF_4) and $[\text{Cu}(\text{L-L})_2]\text{Y}$ [$\text{L-L} = \text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2, o\text{-C}_6\text{H}_4(\text{PMe}_2)_2, \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1-4$), $cis\text{-Ph}_2\text{PCH}=\text{CHPPh}_2, o\text{-C}_6\text{H}_4(\text{PPh}_2)_2, o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2, cis\text{-Ph}_2\text{AsCH}=\text{CHAsPh}_2, o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2, \text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2$ or $\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2$] have been prepared from $[\text{Cu}(\text{MeCN})_4]\text{Y}$ and L or L-L . The ^{63}Cu and, where appropriate, $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR spectra, have been recorded from CH_2Cl_2 solutions of the complexes over the temperature range 300–175 K, including the first reported ^{63}Cu resonances from arsenic and antimony donor ligand compounds. The effects of ligand size and geometry upon the ^{63}Cu NMR spectra are discussed and typical copper chemical-shift ranges for Group 15 donor ligand compounds established. The structure of $[\text{Cu}(cis\text{-Ph}_2\text{AsCH}=\text{CHAsPh}_2)_2]\text{PF}_6$ has been established by X-ray crystallography: orthorhombic, space group $P2_12_12_1$, $a = 14.775(6)$, $b = 16.991(5)$, $c = 21.027(6)$ Å, $Z = 4$. The copper atom is in a distorted tetrahedral environment [$\text{Cu-As } 2.348(3)\text{-}2.358(3)$ Å].

There has been considerable recent interest in the study of copper(I) phosphine complexes of types CuL_3X , CuL_2X , $\{\text{CuL}_2\text{X}\}_2$ and $[\text{CuL}_4]\text{X}$ [$\text{L} = \text{PR}_3$ ($\text{R} = \text{alkyl}$ or aryl), $\text{X} = \text{monoanion}$ usually halide] in the solid state by NMR spectroscopy using cross-polarisation magic angle spinning (CPMAS) techniques.¹⁻⁴ Due to fast ligand exchange at the labile d^{10} copper(I) centre, solution NMR studies have usually provided very limited information, and have been relatively little used. Similarly although both isotopes of copper have good NMR sensitivities,[†] the substantial quadrupole moments would imply that only in high-symmetry environments would a copper resonance be observed, and indeed very few copper resonances have been observed in solution.⁵⁻⁸ During studies of copper(I) complexes of various Group 15 donor ligands, we observed ^{63}Cu signals from some homoleptic complexes $[\text{CuL}_4]^+$ [$\text{L} = \text{PR}_3, \text{AsR}_3$ or SbR_3 ($\text{R} = \text{alkyl}$ or aryl); $\text{L}_2 = \text{distibine}$] in solution. A preliminary report of some of this work has appeared,⁹ and here we report full details and further examples.

Results

Synthesis and Properties.—The complexes were made by reaction of the ligand with $[\text{Cu}(\text{MeCN})_4]\text{PF}_6^{10}$ in the appropriate ratio in MeCN or CH_2Cl_2 under a nitrogen atmosphere. In a few cases, the complexes were also isolated as BF_4^- salts,⁹ which were not significantly different. An unusual complex $[\text{Cu}_2\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}_2\{\mu\text{-Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}_2]\text{[BF}_4\text{]}_2$ was prepared by Mohr *et al.*⁶ from $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ and the diphosphine in methanol, and shown to have the dimeric structure by an X-ray diffraction study. We repeated the reaction of $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ with the diphosphine in either

MeCN or methanol solution, but obtained only $[\text{Cu}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}_2]\text{BF}_4$, which had (excluding the anion features) identical spectroscopic properties to the PF_6^- salt. From the fast atom bombardment (FAB) mass spectra, and the multinuclear NMR spectra discussed below, we believe our complexes contain the $[\text{Cu}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}_2]^+$ cation with chelated ligands, as established by an X-ray diffraction study on the $[\text{Cu}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}_2][\text{Cu}\{\text{Co}(\text{CO})_4\}_2]$ complex. The isolation of either dimeric or monomeric cations with this diphosphine is presumably a subtle function of the reaction conditions, but is nonetheless surprising for a labile metal centre like copper(I).

The complexes are white solids and their analytical data are given in Table 1. Those of alkyl-substituted ligands decompose slowly in air turning blue, but the complexes of aryl-substituted ligands appear indefinitely air-stable. The complexes of PPh_2H and especially PPhH_2 are also unstable in air. Like many other copper(I) phosphines, several of these complexes crystallised as solvates from a range of organic solvents, those of the phenyl-substituted bidentates being particularly prone to this. The structures of several of the cations have been established previously by single-crystal X-ray work (sometimes with other anions) *viz* $[\text{Cu}(\text{PMe}_3)_4]\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I},^{11} \text{CuMe}_2^{12}$ or CuCl_2^{13}), $[\text{Cu}(\text{PPh}_3)_4]\text{Y}$ ($\text{Y} = \text{PF}_6^{11}$ or ClO_4^{14}), $[\text{Cu}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}_2][\text{Cu}\{\text{Co}(\text{CO})_4\}_2]$,¹⁵ $[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2]\text{PF}_6$,¹⁶ $[\text{Cu}(cis\text{-Ph}_2\text{PCH}=\text{CHPPh}_2)_2]\text{PF}_6$,⁸ $[\text{Cu}\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}_2]\text{CF}_3\text{CO}_2$,¹⁷ $[\text{Cu}\{\text{Sb}(p\text{-C}_6\text{H}_4\text{F})_3\}_4]\text{BF}_4$,¹⁸ and the structure of $[\text{Cu}(cis\text{-Ph}_2\text{AsCH}=\text{CHAsPh}_2)_2]\text{PF}_6$ which is described below. The FAB mass spectra were recorded for the complexes in an attempt to confirm the formulations. However for the $[\text{CuL}_4]\text{PF}_6$ compounds, the major species were CuL_2^+ and CuL^+ , with only weak CuL_3^+ ions, and no evidence for CuL_4^+ was found. The data on the bidentate ligand complexes were more useful, and the $[\text{Cu}(\text{L-L})_2]\text{PF}_6$ [$\text{L-L} = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$, $n = 1-4$, $cis\text{-Ph}_2\text{PCH}=\text{CHPPh}_2$, $o\text{-C}_6\text{H}_4(\text{PPh}_2)_2$, $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$, $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$, $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$ or $cis\text{-Ph}_2\text{AsCH}=\text{CHAsPh}_2$] complexes all gave very simple spectra with $\text{Cu}(\text{L-L})_2^+$ and $\text{Cu}(\text{L-L})^+$ as the only significant ions. Unfortunately the distibine complexes decomposed.

* Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

† For ^{63}Cu $I = \frac{3}{2}$, 69%, $\Xi = 26.528$ MHz, $D_c = 365$, quadrupole moment = -0.211×10^{-28} m² and for ^{65}Cu $I = \frac{3}{2}$, 31%, $\Xi = 28.417$ MHz, $D_c = 201$, quadrupole moment = -0.195×10^{-28} m².

Table 1 Analytical data

Compound	Analysis* (%)			
	C	H	P	N
[Cu(PPh ₃) ₄]BF ₄	71.3 (72.1)	5.2 (5.0)	9.9 (10.3)	
[Cu(PMePh ₂) ₄]BF ₄	66.0 (65.7)	5.4 (5.5)	13.0 (13.0)	
[Cu(PMe ₂ Ph) ₄]PF ₆	50.4 (50.5)	6.0 (5.8)		
[Cu(PMe ₃) ₄]PF ₆	28.9 (28.1)	7.5 (7.1)	28.6 (30.1)	
[Cu(PMe ₃) ₄]BF ₄	32.3 (31.7)	8.1 (8.0)		
[Cu(PPh ₂ H) ₄]PF ₆	60.2 (60.5)	4.6 (4.7)	15.1 (16.2)	
[Cu(PPhH ₂) ₄]PF ₆	44.2 (44.4)	4.3 (4.4)		
[Cu(AsMe ₃) ₄]PF ₆	21.2 (20.9)	5.3 (5.3)		
[Cu(AsMePh ₂) ₄]PF ₆	52.2 (52.7)	4.4 (4.4)		
[Cu(AsMe ₂ Ph) ₄]PF ₆	41.1 (41.0)	4.9 (4.7)		
[Cu(AsPh ₃) ₄]PF ₆	60.1 (60.3)	4.6 (4.2)		
[Cu(SbMe ₃) ₄]BF ₄	17.4 (17.6)	4.5 (4.4)		
[Cu(SbPh ₃) ₄]BF ₄	55.5 (55.3)	3.9 (3.9)		
[Cu{o-C ₆ H ₄ (PMe ₂) ₂ }]PF ₆	39.5 (39.7)	5.5 (5.3)		
[Cu{Me ₂ P(CH ₂) ₂ PMe ₂ }]PF ₆ ·MeCN	29.9 (30.6)	6.0 (6.3)	28.0 (28.2)	2.0 (2.5)
[Cu{Me ₂ P(CH ₂) ₂ PMe ₂ }]BF ₄	31.7 (32.0)	7.2 (7.2)		
[Cu{o-C ₆ H ₄ (PPh ₂) ₂ }]PF ₆	65.5 (65.4)	4.6 (4.4)		
[Cu(Ph ₂ PCH ₂ PPh ₂) ₂]PF ₆	61.6 (61.5)	4.7 (4.5)		
[Cu{Ph ₂ P(CH ₂) ₃ PPh ₂ }]PF ₆ ·MeCN	61.6 (62.0)	4.9 (4.9)	14.7 (14.8)	1.2 (1.3)
[Cu{Ph ₂ P(CH ₂) ₃ PPh ₂ }]PF ₆	62.3 (62.8)	5.2 (5.1)	14.5 (15.0)	
[Cu{Ph ₂ P(CH ₂) ₃ PPh ₂ }]PF ₆	63.5 (63.4)	4.5 (5.3)		
[Cu(Ph ₂ PCH=CHPPh ₂) ₂]PF ₆ ·0.5MeCN	61.6 (62.3)	3.6 (4.5)	14.8 (15.2)	0.9 (0.7)
[Cu{o-C ₆ H ₄ (AsMe ₂) ₂ }]PF ₆	31.3 (30.8)	4.3 (4.1)		
[Cu(Ph ₂ AsCH=CHAsPh ₂) ₂]PF ₆	52.7 (53.0)	3.9 (3.8)		
[Cu{o-C ₆ H ₄ (SbMe ₂) ₂ }]PF ₆	24.4 (24.8)	3.5 (3.3)		
[Cu{Me ₂ Sb(CH ₂) ₃ SbMe ₂ }]BF ₄	19.9 (20.0)	4.4 (4.3)		
[Cu{Ph ₂ Sb(CH ₂) ₃ SbPh ₂ }]BF ₄	48.6 (48.5)	4.0 (3.9)		
[Cu{o-C ₆ H ₄ (PMe ₂)(AsMe ₂) ₂ }]BF ₄	37.9 (37.9)	5.1 (5.1)		
[Cu{o-C ₆ H ₄ (PMe ₂)(SbMe ₂) ₂ }]BF ₄	32.9 (33.0)	4.4 (4.4)		

* Calculated values in parentheses.

Table 2 Selected ¹H NMR data

Compound	δ(¹ H) ^a
[Cu(PMe ₃) ₄]PF ₆	1.27(s) ^b
[Cu(PMe ₃) ₄]BF ₄ ^c	1.30(s) ^b
[Cu(PMe ₂ Ph) ₄]PF ₆	1.39(s) ^b
[Cu(PMePh ₂) ₄]BF ₄	1.66(d) ² J(P-H) = 4 Hz
[Cu(AsMe ₃) ₄]PF ₆	1.23(s)
[Cu(AsMe ₂ Ph) ₄]PF ₆	1.37(s)
[Cu(AsMePh ₂) ₄]PF ₆	1.58(s)
[Cu(SbMe ₃) ₄]BF ₄	2.10(s)
[Cu(SbEt ₃) ₄]BF ₄	2.13(s, 2H), 2.19(s, 3H) ^d
[Cu(PPh ₂ H) ₄]PF ₆	6.05(d) ¹ J(P-H) = 321 Hz
[Cu(PPhH ₂) ₄]PF ₆	5.10(d) ¹ J(P-H) = 318 Hz
[Cu{Me ₂ P(CH ₂) ₂ PMe ₂ }]PF ₆	1.33(s, 12H), 1.73(t, 4H)
[Cu{Me ₂ P(CH ₂) ₂ PMe ₂ }]BF ₄ ^c	1.33(s, 12H), 1.73(t, 4H)
[Cu{o-C ₆ H ₄ (PMe ₂) ₂ }]PF ₆	1.60(s)
[Cu{o-C ₆ H ₄ (AsMe ₂) ₂ }]PF ₆	1.59(s)
[Cu{o-C ₆ H ₄ (SbMe ₂) ₂ }]PF ₆	1.18(s)
[Cu{Me ₂ Sb(CH ₂) ₃ SbMe ₂ }]BF ₄	1.06(s, 12H), 1.80(br, 6H)

^a In CD₂Cl₂ solutions unless indicated otherwise, alkyl group resonances only. ^b Broad singlet, see text. ^c In CDCl₃ solution. ^d No ³J(H-H) is resolved, the free SbEt₃ ligand also exhibits an A₂B₃ pattern (two singlets).

NMR Data.—The ¹H NMR data (Table 2) are unexceptional, apart from the absence of any resolved ²J(P-H) coupling in the [Cu(PMe₃)₄]⁺ and [Cu(PMe₂Ph)₄]⁺ complexes. It is probable that like [Ni(PMe₃)₄]¹⁹ these are strongly coupled {[A₉X]₄ and [A₆X]₄} spin systems. It is notable that the [Cu(PMePh₂)₄]⁺ cation which is undergoing fast exchange at room temperature exhibits a simple doublet methyl resonance. The ³¹P-¹H and ⁶³Cu NMR data are summarised in Tables 3 and 4. All spectra were recorded in CH₂Cl₂-CD₂Cl₂ (95:5) solution, and where observed the ¹J(³¹P-⁶³Cu) couplings were measured from the ⁶³Cu NMR spectra. Since the

magnetogyric moments of ⁶³Cu and ⁶⁵Cu are very similar [$\gamma(^{63}\text{Cu})/\gamma(^{65}\text{Cu}) = 0.934$], separate couplings in the ³¹P NMR spectra are rarely resolved, and hence the observed splittings in the phosphorus spectra contain superimposed couplings to both copper isotopes.

[Cu(PMe₃)₄]⁺ (Y = PF₆ or BF₄). The ³¹P-¹H NMR spectra at 300 K consisted of a 1:1:1:1 four-line pattern centred at δ -41, and under higher resolution the outer peaks showed clearly resolved shoulders due to coupling to ⁶⁵Cu. The spectra change little on cooling to 180 K, and the pattern was unaffected by the addition of free PMe₃. The ⁶³Cu resonance was a five-line quintet ¹J(³¹P-⁶³Cu) = 796 ± 6 Hz centred at δ +287. (The spectra are shown in ref. 9.) The copper resonance immediately disappeared on addition of [Cu(MeCN)₄]PF₆ due to rapid scrambling into low-symmetry [Cu(PMe₃)_{4-x}(MeCN)_x]⁺ species. Similar spectra have been observed from [Cu(PMe₃)₄]⁺ (Y = CuCl₂, hexafluoroacetylacetonate¹³ or CuMe₂¹²).

[Cu(PPh₃)₄]BF₄ and [Cu(PEt₃)₄]PF₆. No ⁶³Cu resonance was observed for either cation in the temperature range 300–180 K. The ³¹P-¹H NMR spectrum of the [Cu(PEt₃)₄]⁺ cation was a sharp singlet at δ -9, and addition of free PEt₃ to the solution resulted in a singlet whose chemical shift varied with the concentration of added ligand, consistent with fast exchange. On cooling to 200 K separate resonances were seen for the cation and free PEt₃, but no coupling to copper was evident. The ³¹P-¹H NMR spectrum of [Cu(PPh₃)₄]⁺ was a broad singlet at δ -1. The addition of free PPh₃ resulted in a singlet with a chemical shift varying with the amount of added PPh₃, and even at 175 K separate resonances for the cation and PPh₃ were not resolved, showing fast exchange occurred down to the freezing point of the solvent.

[Cu(PMe₂Ph)₄]PF₆ and [Cu(PMePh₂)₄]BF₄. The [Cu(PMePh₂)₄]⁺ cation exhibited fast exchange with free PMePh₂ at room temperature, but on cooling to 183 K separate resonances

Table 3 $^{31}\text{P}\{-^1\text{H}\}$ NMR data

Compound	$\delta(^{31}\text{P})^*$	Comments
$[\text{Cu}(\text{PMe}_3)_4]\text{PF}_6$	-41	Quartet with ^{65}Cu couplings evident on outer lines $^1J(^{31}\text{P}\text{-}^{65}\text{Cu}) = 830$ Hz
$[\text{Cu}(\text{PMe}_2\text{Ph})_4]\text{PF}_6$	-30	Broad $W_{\frac{1}{2}} = 2000$ Hz, quartet at <i>ca.</i> 250 K, collapses on further cooling
$[\text{Cu}(\text{PMePh}_2)_4]\text{BF}_4$	-18.3	Fast exchange with free PMePh_2 at room temperature
$[\text{Cu}(\text{PPh}_3)_4]\text{BF}_4$	-1	Singlet, fast exchange with PPh_3 at all temperatures
$[\text{Cu}(\text{PEt}_3)_4]\text{PF}_6$	-9	Singlet, fast exchange with PEt_3 at temperatures > 220 K
$[\text{Cu}(\text{PPh}_2\text{H})_4]\text{PF}_6$	-25	Very broad singlet at all temperatures
$[\text{Cu}(\text{PPhH}_2)_4]\text{PF}_6$	-94	At 250 K quartet, below 273 K see Fig. 2
$[\text{Cu}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}_2]\text{PF}_6$	-16	See Fig. 3
$[\text{Cu}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2]\text{PF}_6$	-6	Singlet, $\delta = -8$ at 175 K, no coupling to Cu at any temperature
$[\text{Cu}\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}_2]\text{PF}_6$	+8	Singlet, $W_{\frac{1}{2}} = 400$ Hz, broad singlet down to 175 K
$[\text{Cu}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}_2]\text{PF}_6$	-10	Broad singlet at 295 K, two lines (<i>ca.</i> 1:1) at $\delta = -6$ and -10 below 200 K
$[\text{Cu}\{\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}_2]\text{PF}_6$	-8	Singlet at 295 K, several lines at 180 K suggesting equilibria between complexes in solution
$[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]\text{PF}_6$	-18.2	See Fig. 4
$[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{PPh}_2)_2\}_2]\text{PF}_6$	+9.0	Singlet at all temperatures
$[\text{Cu}(\text{Ph}_2\text{PCH}=\text{CHPPh}_2)_2]\text{PF}_6$	+11	Singlet at all temperatures
$[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)(\text{AsMe}_2)_2\}_2]\text{BF}_4$	-11	Broad singlet
$[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)(\text{SbMe}_2)_2\}_2]\text{BF}_4$	-21	Broad singlet

* In $\text{CH}_2\text{Cl}_2\text{-CD}_2\text{Cl}_2$ (95:5) at 295 K relative to external 85% H_3PO_4 ; all PF_6^- salts showed sharp septet patterns at $\delta = -145$, $^1J(^{19}\text{F}\text{-}^{31}\text{P}) = 710$ Hz, which remained unchanged down to the freezing point of the solvent (*ca.* 175 K).

Table 4 Copper-63 NMR data

Cation ^a	$\delta(^{63}\text{Cu})^b$	$^1J(^{31}\text{P}\text{-}^{63}\text{Cu})/\text{Hz}$	Comments
$[\text{Cu}(\text{AsMe}_3)_4]^+$	+20 ^c	—	$W_{\frac{1}{2}} = 700$ Hz, $\delta = +29$ at 180 K
$[\text{Cu}(\text{AsMe}_2\text{Ph})_4]^+$	-17	—	$W_{\frac{1}{2}} = 1500$ Hz, $\delta = +3$ at 200 K
$[\text{Cu}(\text{AsMePh}_2)_4]^+$	-62	—	$W_{\frac{1}{2}} = 1200$ Hz, $\delta = -41$ at 180 K
$[\text{Cu}(\text{AsPh}_3)_4]^+$	-153	—	At 175 K, $W_{\frac{1}{2}} = 4000$ Hz, no resonance above <i>ca.</i> 180 K
$[\text{Cu}(\text{SbMe}_3)_4]^+ d$	-6	—	$W_{\frac{1}{2}} = 180$ Hz
$[\text{Cu}(\text{SbEt}_3)_4]^+ d$	+1	—	$W_{\frac{1}{2}} = 680$ Hz
$[\text{Cu}(\text{SbPh}_3)_4]^+$	-245	—	$W_{\frac{1}{2}} = 160$ Hz, $\delta = -232$ at 183 K
$[\text{Cu}(\text{PMe}_3)_4]^+$	+287	796	Quintet at all temperatures
$[\text{Cu}(\text{PMe}_2\text{Ph})_4]^+$	+265	785	At 250 K, quintet only over limited temperature range
$[\text{Cu}(\text{PMePh}_2)_4]^+ d$	+192	—	At 183 K, $W_{\frac{1}{2}} = 6300$ Hz. No resonance above <i>ca.</i> 200 K
$[\text{Cu}(\text{PPh}_3)_4]^+ d$	—	—	No resonance at any temperature
$[\text{Cu}(\text{PPh}_2\text{H})_4]^+$	+234	<i>ca.</i> 750	Ill defined coupling, see Fig. 1(a)
$[\text{Cu}(\text{PPhH}_2)_4]^+$	+250	800	At 273 K, see Fig. 2
$[\text{Cu}(\text{PEt}_3)_4]^+$	—	—	No resonance at any temperature
$[\text{Cu}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}_2]^+$	+194	805	Quintet remains above 200 K, see Fig. 3
$[\text{Cu}\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}_2]^+$	+150	—	$W_{\frac{1}{2}} = 3000$ Hz, line broadens on cooling, no resolved coupling
$[\text{Cu}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}_2]^+$	+231	—	At 273 K, $W_{\frac{1}{2}} = 4000$ Hz. No resonance at 300 K or below 250 K
$[\text{Cu}(\text{Ph}_2\text{PCH}=\text{CHPPh}_2)_2]^+$	+126	—	$W_{\frac{1}{2}} = 3000$ Hz, line broadens on cooling, no coupling
$[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]^+$	+210	800	Signal collapses to broad singlet on cooling, see Fig. 4
$[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2]^+$	-63	—	$W_{\frac{1}{2}} = 1600$ Hz, singlet; $\delta = -61$ at 180 K
$[\text{Cu}(\text{Ph}_2\text{AsCH}=\text{CHAsPh}_2)_2]^+$	-148	—	$\delta = -143$ at 250 K, no signal at 180 K
$[\text{Cu}\{\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2\}_2]^+ d$	-167	—	$W_{\frac{1}{2}} = 390$ Hz
$[\text{Cu}\{\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2\}_2]^+ d$	-197	—	$W_{\frac{1}{2}} = 1250$ Hz
$[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2\}_2]^+$	-179	—	Singlet, $W_{\frac{1}{2}} = 700$ Hz; $\delta = -166$ at 175 K

^a As PF_6^- salts in $\text{CH}_2\text{Cl}_2\text{-CD}_2\text{Cl}_2$ (95:5). Data at 295 K unless different temperature specified. ^b ± 1 ppm. ^c Erroneously reported in ref. 9 as $\delta = -42$. ^d As BF_4^- salts.

from the cation and free phosphine were observed, as exchange slowed. No ^{63}Cu resonance was observed > 200 K, but at 183 K a very broad singlet ($W_{\frac{1}{2}}$ *ca.* 6300 Hz) appeared; addition of PMePh_2 caused the loss of this resonance even at the lowest temperature (175 K). At 300 K the ^{63}Cu resonance of $[\text{Cu}(\text{PMe}_2\text{Ph})_4]^+$ was a broad singlet at $\delta + 251$ ($W_{\frac{1}{2}} = 2500$ Hz), as reported previously.²⁰ On cooling structure began to develop, and at 250 K a quintet due to coupling to four phosphorus nuclei was clearly resolved. Further cooling broadened the lines, and by 180 K only a singlet ($W_{\frac{1}{2}} = 2600$ Hz) at $\delta + 274$ was present. The effects were reversible with temperature, and were not affected by added PMe_2Ph . The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum at 300 K was a very broad feature at *ca.* $\delta = -30$ ($W_{\frac{1}{2}}$ *ca.* 2000 Hz) with no resolved coupling, but a sharp 1:1:1 quartet due to $^{63}/^{65}\text{Cu}$ coupling was clearly defined in the spectrum obtained on cooling the sample to *ca.* 250 K. Further cooling caused the quartet to collapse to a doublet, and by 180 K the feature had become a broad singlet.

$[\text{Cu}(\text{PPh}_2\text{H})_4]\text{PF}_6$ and $[\text{Cu}(\text{PPhH}_2)_4]\text{PF}_6$. At 295 K the ^{63}Cu NMR spectrum of $[\text{Cu}(\text{PPh}_2\text{H})_4]^+$ contained a broad

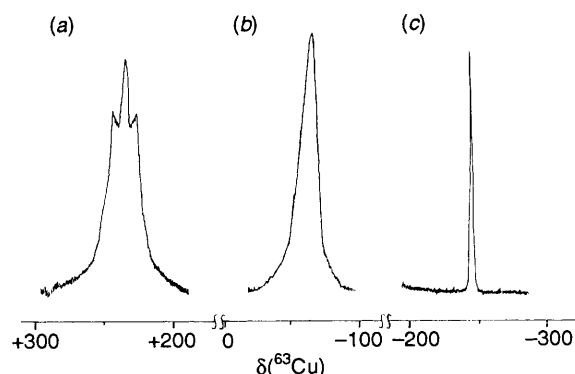


Fig. 1 Copper-63 NMR spectra of (a) $[\text{Cu}(\text{PPh}_2\text{H})_4]^+$, (b) $[\text{Cu}(\text{AsMePh}_2)_4]^+$ and (c) $[\text{Cu}(\text{SbPh}_3)_4]^+$ at 295 K

feature at δ *ca.* +234 which exhibited ill defined coupling, the centre three lines of the expected quintet being observed (Fig. 1).

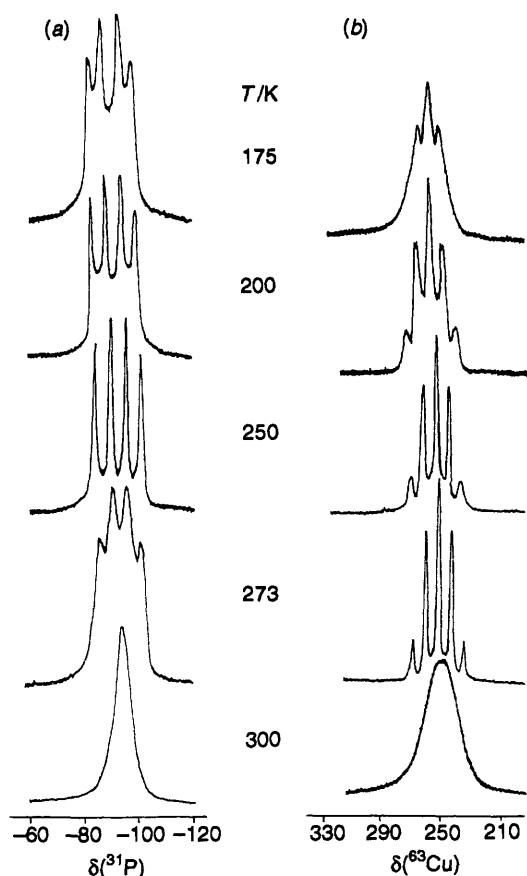


Fig. 2 Variable-temperature $^{31}\text{P}\{-^1\text{H}\}$ and ^{63}Cu NMR spectra of $[\text{Cu}(\text{PPhH}_2)_4]^+$

The coupling was lost on heating to 320 K, or on cooling below *ca.* 250 K to produce broad singlets. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum at 300 K was a very broad feature at δ *ca.* -25, which remained broad with no well defined structure down to 200 K. Addition of free PPh_2H showed that exchange was slow at low temperatures since separate resonances for the cation and free phosphine were resolved in the ^{31}P NMR spectrum. The proton-coupled ^{31}P NMR spectrum of this complex was little different.* The $[\text{Cu}(\text{PPhH}_2)_4]\text{PF}_6$ complex exhibited well resolved quartet and quintet resonances in the $^{31}\text{P}\{-^1\text{H}\}$ and ^{63}Cu NMR spectra respectively at temperatures < 280 K, and the coupling patterns remained visible down to low temperatures (Fig. 2).

$[\text{Cu}(\text{ER}_3)_4]\text{Y}$ ($\text{ER}_3 = \text{AsPh}_3, \text{AsMePh}_2, \text{AsMe}_2\text{Ph}, \text{AsMe}_3, \text{SbPh}_3, \text{SbMe}_3$ or SbEt_3 ; $\text{Y} = \text{PF}_6$ or BF_4). In contrast to the complex behaviour exhibited by many of the phosphine complexes, the spectra of the homoleptic stibine and arsine complexes are much less influenced by temperature. We previously reported⁹ that no ^{63}Cu resonance was observed for $[\text{Cu}(\text{AsPh}_3)_4]^+$ in CH_2Cl_2 down to 180 K. We confirm this, but at the lowest temperature obtainable before the solvent solidifies (175 K) a broad singlet ($W_{\frac{1}{2}} = 4000$ Hz) appeared at $\delta - 153$; confirmation that the signal was genuine was obtained both by cycling the temperature between 200 and 175 K, when the signal disappeared at 180 K and reappeared on cooling, and by addition of $[\text{Cu}(\text{MeCN})_4]^+$, which caused immediate and irreversible loss of the resonance due to ligand scrambling to form low-symmetry species. The spectra of the other arsine

* For this complex the proton-decoupler frequency was set on the frequency of the P-H resonance, since broad-band decoupling is often ineffective when large one-bond couplings are present.

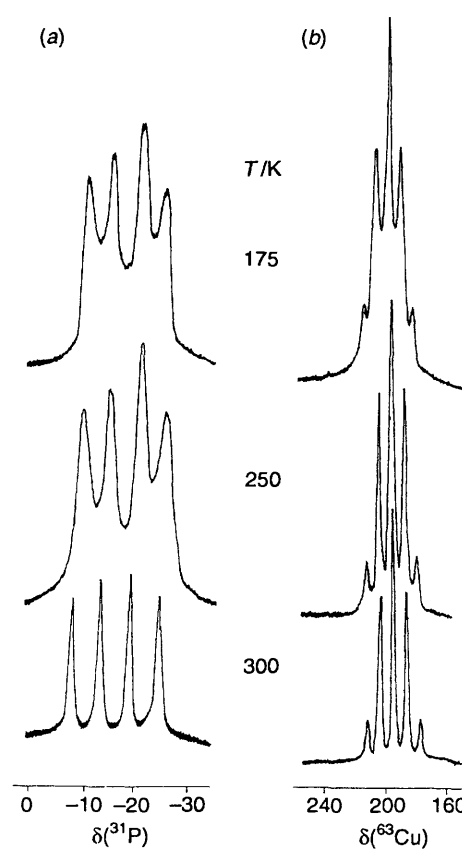


Fig. 3 Variable-temperature $^{31}\text{P}\{-^1\text{H}\}$ and ^{63}Cu NMR spectra of $[\text{Cu}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}_2]^+$

complexes and the stibines consisted of single lines at all temperatures between 300 and 175 K (Fig. 1, Table 4), the chemical shifts showing small positive drifts with decreasing temperatures; the resonances were unaffected by addition of the appropriate free ligand to the solutions.

$[\text{Cu}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}_2]\text{Y}$ ($\text{Y} = \text{PF}_6$ or BF_4) and $[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]\text{PF}_6$. The ^{63}Cu NMR spectrum of $[\text{Cu}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}_2]^+$ at 300 K was a well resolved quintet ($^1J(^{31}\text{P}\text{-}^{63}\text{Cu}) = 805 \pm 6$ Hz), and the structure was retained on cooling down to *ca.* 200 K. Below this temperature the lines broadened but even at 175 K, the coupling was still clearly evident. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum at 300 K was a sharp 1:1:1:1 quartet {in contrast to $[\text{Cu}(\text{PMe}_3)_4]^+$ where separate couplings to the two copper isotopes were resolved}, and at 175 K the quartet pattern was still present, although the lines had broadened (Fig. 3). This behaviour contrasts with that reported⁶ for the dinuclear complex $[\text{Cu}_2\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}_2][\text{BF}_4]_2$ which loses the resolved $^{31}\text{P}\text{-}^{63}\text{Cu}$ coupling on cooling below *ca.* 240 K.

The ^{63}Cu NMR spectrum of $[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]^+$ was a broad quintet at 300 K, but on cooling the pattern collapsed progressively, and by 190 K only a broad resonance ($W_{\frac{1}{2}} = 2000$ Hz) with no defined structure was present. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum also shows progressive loss of the quartet pattern on cooling (Fig. 4).

$[\text{Cu}\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}_2]\text{PF}_6$ ($n = 1-4$), $[\text{Cu}\{\text{cis-Ph}_2\text{PCH}=\text{CHPPh}_2\}_2]\text{PF}_6$ and $[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{PPh}_2)_2\}_2]\text{PF}_6$. The ^{63}Cu NMR spectrum of $[\text{Cu}\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}_2]\text{PF}_6$ was a very broad singlet at 300 K and remained broad and featureless down to 175 K. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum was also a single broad signal at 300 K, and although it sharpened on cooling, no coupling to copper was seen at any temperature. For the $[\text{Cu}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}_2]\text{PF}_6$, we did not observe a ^{63}Cu resonance at room temperature, but on cooling to 273 K a very

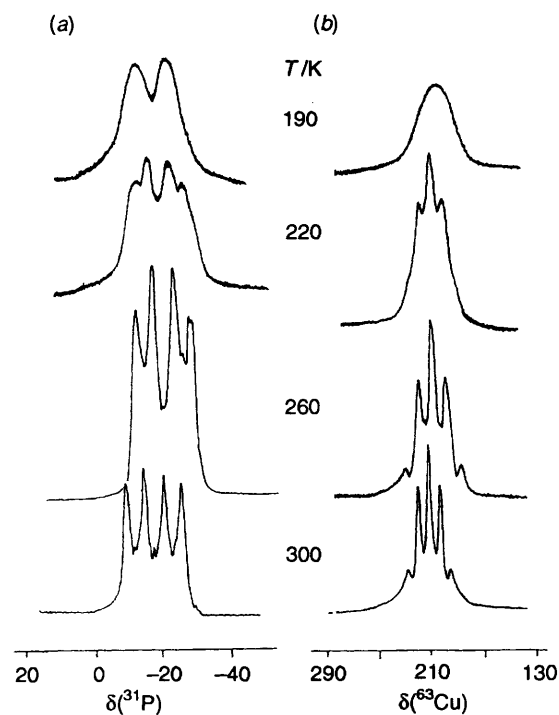


Fig. 4 Variable-temperature $^{31}\text{P}\{-^1\text{H}\}$ and ^{63}Cu NMR spectra of $[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]^+$

broad resonance appeared, which broadened further on cooling, and had disappeared by 250 K. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of this complex was a broad singlet at 295 K, which sharpened on cooling down to 220 K, and below this temperature split into two lines. We were unable to observe ^{63}Cu resonances from $[\text{Cu}\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}_2]\text{PF}_6$ ($n = 1$ or 4) at any temperature between 300 and 175 K, and the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra (Table 3) showed no coupling to copper. The variable-temperature $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of $[\text{Cu}(\text{cis-Ph}_2\text{PCH}=\text{CHPh}_2)_2]\text{PF}_6$ have been reported recently,⁸ and our data are identical (Table 3). However we did observe a ^{63}Cu resonance as a broad feature at $\delta + 126$ at *ca.* 273 K, but the resonance broadened rapidly on further cooling and was not visible below 250 K. For the complex of the rigid $o\text{-C}_6\text{H}_4(\text{PPh}_2)_2$, the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum was a sharp singlet at all temperatures, and a separate resonance was present even at 300 K when free ligand was added, showing slow exchange, but no ^{63}Cu signal was observed at any temperature in the usual range.

$[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2]\text{PF}_6$, $[\text{Cu}(\text{cis-Ph}_2\text{AsCH}=\text{CHAsPh}_2)_2]\text{PF}_6$, $[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2\}_2]\text{PF}_6$ and $[\text{Cu}\{\text{R}_2\text{Sb}(\text{CH}_2)_3\text{SbR}_2\}_2]\text{BF}_4$ ($\text{R} = \text{Me}$ or Ph). All of the above complexes showed broad singlet ^{63}Cu resonances in the range 300–200 K (Table 4), the resonance positions shifting slowly to more positive chemical shifts on cooling. The ^{63}Cu resonance of $[\text{Cu}(\text{cis-Ph}_2\text{AsCH}=\text{CHAsPh}_2)_2]\text{PF}_6$ was not observable at 180 K, but resonances for the other complexes remained visible down to 175 K.

Two hybrid ligand complexes, $[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)(\text{AsMe}_2)\}_2]\text{BF}_4$ and $[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)(\text{SbMe}_2)\}_2]\text{BF}_4$, were also examined. These showed broad singlet $^{31}\text{P}\{-^1\text{H}\}$ resonances, but no ^{63}Cu resonances were observed.

Structure of $[\text{Cu}(\text{cis-Ph}_2\text{AsCH}=\text{CHAsPh}_2)_2]\text{PF}_6$.—The structure consists of discrete cations with a four-co-ordinate copper atom (Fig. 5 and Table 5). The crystals are isomorphous with the corresponding phosphine compound.⁸ The CuAs_4 moiety has no crystallographic symmetry but closely approxi-

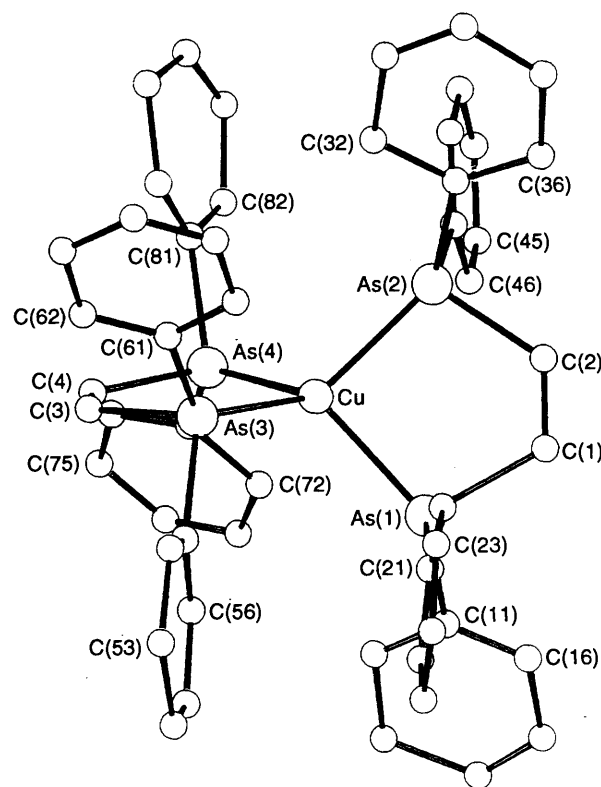


Fig. 5 View of the cation in $[\text{Cu}(\text{Ph}_2\text{AsCH}=\text{CHAsPh}_2)_2]\text{PF}_6$ showing the atom labelling scheme

Table 5 Selected bond lengths (Å) and angles (°) for $[\text{Cu}(\text{Ph}_2\text{AsCH}=\text{CHAsPh}_2)_2]\text{PF}_6$

Cu–As(1)	2.348(3)	Cu–As(3)	2.358(3)
Cu–As(2)	2.355(3)	Cu–As(4)	2.357(3)
C(1)–C(2)	1.29(3)	C(3)–C(4)	1.31(3)
As–C	1.89(2)–2.00(2)		
P–F	1.53(2)–1.57(2)		
C–C (phenyl)	1.24(3)–1.57(4)		
As(1)–Cu–As(2)	90.5(1)	As(2)–Cu–As(3)	129.9(1)
As(1)–Cu–As(3)	110.1(1)	As(2)–Cu–As(4)	110.1(1)
As(1)–Cu–As(4)	131.3(1)	As(3)–Cu–As(4)	90.2(1)
Cu–As(1)–C(1)	103.7(6)	Cu–As(3)–C(3)	104.0(6)
Cu–As(1)–C(11)	127.5(6)	Cu–As(3)–C(51)	116.9(6)
Cu–As(1)–C(21)	113.9(6)	Cu–As(3)–C(61)	127.0(6)
Cu–As(2)–C(2)	102.8(6)	Cu–As(4)–C(4)	101.7(6)
Cu–As(2)–C(31)	129.0(7)	Cu–As(4)–C(71)	130.9(6)
Cu–As(2)–C(41)	116.7(6)	Cu–As(4)–C(81)	114.5(6)
As(1)–C(1)–C(2)	118(2)	As(3)–C(3)–C(4)	121(2)
As(2)–C(2)–C(1)	124(2)	As(4)–C(4)–C(3)	122(2)
C–As–C	100.4(8)–104.2(8)		
C–C–C (phenyl)	112(3)–129(3)		

mates to the D_2 (222) point group and even with the inclusion of the carbon atoms this symmetry is still maintained. The planar phenyl rings (maximum deviation 0.05 Å) on each of the As atoms are approximately orthogonal (dihedral angles 92–106°) and presumably as a consequence of packing constraints, the phenyl rings on separate ligands are roughly parallel. The Cu–As distances [2.348(3)–2.358(3) Å] agree well with that found in $[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2]^+$ [2.360(1) Å] for which D_2 crystallographic symmetry was reported.¹⁶ The two ligands are essentially planar at the double bond [As–C=C–As –5°(average)] with the dihedral angle between the two chelate As_2Cu planes 72°. The origin of this twisting in the solid state which

was observed in the phosphine complex was ascribed⁸ to 'charge-transfer interactions between phenyl rings on each ligand . . .', but as essentially the same angle was observed¹⁶ in $[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2]^+$ where there are no phenyl rings the argument is not persuasive, and the origin of the twist is not obvious.

Discussion

Two main factors will determine the form of the observed ⁶³Cu and ³¹P NMR spectra resonances observed from these complexes, namely the rate of quadrupolar relaxation of the ^{63,65}Cu nuclei and the nature and rate of dynamic processes occurring in solution. These will in turn be influenced by the temperature, the distortions from regular symmetry and the steric and electronic properties of the ligands. It is also clear that there is considerable interrelation between these various factors and hence the observed behaviour is complex.

Extensive studies of copper(I) halide complexes of phosphine and arsine ligands have concluded²¹⁻²³ that the extent of dissociation in solution increased with ligand size (the Tolman cone angle), and was greater for arsenic than for phosphorus donor ligands. Ligand-exchange rates were usually too rapid for NMR spectroscopy to identify individual species, except at very low temperatures. Halide bridging is widespread in such systems, and thus the effects may not be comparable with the present complexes, where no bridging ligands are present.

The variations in NMR spectroscopic behaviour of the tertiary phosphine complexes $[\text{Cu}(\text{PR}_3)_4]\text{PF}_6$ detailed above are explained by the extent of ligand dissociation in solution and the corresponding fast quadrupolar relaxation of the copper nuclei in the low-symmetry environments produced. X-Ray diffraction studies of the solid $[\text{Cu}(\text{PMe}_3)_4]\text{Y}$ and $[\text{Cu}(\text{PPh}_3)_4]\text{Y}^{11-14}$ show both cations have close to tetrahedral symmetry, and thus distortion of the tetrahedron is not the cause of the fast relaxation. However the fast exchange with free ligand observed for the PPh_3 and PPh_2Me complexes in the ³¹P NMR spectra, produce low-symmetry species and result in rapid relaxation of the copper nuclei. The behaviour of the complex $[\text{Cu}(\text{PMe}_2\text{Ph})_4]\text{PF}_6$ confirms this. At room temperature some ligand dissociation produces broad singlets in the ⁶³Cu and ³¹P-¹H NMR spectra, but on cooling the exchange rate slows and the couplings are clearly resolved. The behaviour on further cooling is qualitatively in keeping with the predictions of Marker and Gunter²⁴ of the effects of the copper quadrupolar relaxation in ^{63,65}Cu-³¹P₄ bonded systems. The extent of phosphine dissociation increases with the Tolman cone angle²⁵ (PMe_3 θ 118, PMe_2Ph 122, PMePh_2 136, PPh_3 145°), and thus like the halide systems²¹⁻²³ the steric properties of the phosphines dominate the dissociation. Support for this comes from the complexes of the primary (PPhH_2) and secondary (PPh_2H) phosphines, their behaviour (Tables 3 and 4) fitting the pattern predicted by their cone angles (PPhH_2 θ 101, PPh_2H 128°). On this basis one would not expect to observe a ⁶³Cu resonance in a $[\text{CuL}_4]^+$ ion for ligands with $\theta \geq ca. 136^\circ$.

In the tertiary arsine series, only the $[\text{Cu}(\text{AsPh}_3)_4]\text{PF}_6$ complex is dramatically affected by varying the temperature, the ⁶³Cu resonance being observed only at or below 180 K. It seems that above this temperature dissociation is fast compared to the NMR time-scale and the resonance too broad to observe. For the other arsine and the stibine complexes (Table 4), ⁶³Cu resonances were observed at all temperatures in the range studied, although the linewidths decrease on lowering the temperature consistent with slower quadrupolar relaxation. The cone angles of tertiary arsines are estimated to be $\leq 5^\circ$ smaller than the corresponding phosphine with the corresponding stibine cone angle $\leq 5^\circ$ smaller still.^{25,26} The cone angles of SbPh_3 and AsMePh_2 are such that extensive dissociation of their $[\text{CuL}_4]^+$ complexes would be expected in solution if steric factors predominated, but the easy observation of ⁶³Cu NMR spectra at all temperatures examined, shows this is not the case.

We conclude that the tendency to ligand dissociation in the arsine and stibine complexes of type $[\text{CuL}_4]^+$ is much smaller than in the corresponding phosphines, and the persistence of the tetrahedral cations in solution accounts for the easy observation of the ⁶³Cu NMR spectra. The arsines and stibines are weaker σ donors, and it seems that this electronic effect reduces the tendency of the copper centre to lose ligands. Only for the largest ligand studied (AsPh_3) does the steric effect cause appreciable dissociation. The poorer donor power of stibines resulting in reduced dissociation (and sometimes higher coordination numbers), has been observed in a number of other systems.²⁶ The conclusion²¹ that in the halide systems the arsine complexes exhibit greater dissociation than the corresponding phosphines, suggests that replacement of a weak donor arsine by a bridging halide may be a contributing factor in those cases. In all the arsine and stibine complexes, the quadrupolar ⁷⁵As ($I = \frac{3}{2}$), ¹²¹Sb ($I = \frac{5}{2}$) and ¹²³Sb ($I = \frac{7}{2}$) are in low-symmetry environments, which would produce fast relaxation of these nuclei at all temperatures, and this provides a further mechanism for relaxation of the copper nuclei, *via* scalar relaxation of the second kind.

For the complexes of the bidentate ligands the same factors are expected to operate, with the added consequences from the steric constraints imposed by chelation. X-Ray diffraction studies^{8,15-17} of several complexes with five-membered chelate rings show L-Cu-L angles within the chelate ring of *ca.* 90°, and L-Cu-L between ligands ranging from *ca.* 110 to 130°, well removed from regular tetrahedral angles. In spite of this ⁶³Cu NMR resonances were observed in most cases, showing that quadrupolar relaxation of the copper does not become so fast that the lines are unobservably broad, simply due to distortions from cubic symmetry in these systems. The variable-temperature behaviour of the spectra of $[\text{Cu}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}_2]^+$ and $[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]^+$ (Figs. 3 and 4) are in good agreement with the calculations of Marker and Gunter,²⁴ for systems in which exchange is not significant, and the quadrupolar relaxation of the copper is the dominant mechanism.

For the phenyl diphosphine complexes $[\text{Cu}(\text{L-L})_2]^+$ [L-L = $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$, $n = 2$ or 3, or *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$] the ³¹P-¹H NMR spectra are broad singlets at room temperature which sharpen on cooling, but show no resolved coupling at any temperature. The ⁶³Cu spectra of the $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ compound is a broad singlet at all temperatures, but a ⁶³Cu resonance was only observed over a small temperature range for complexes of the vinylic and trimethylene backbone ligands. Reversible ring opening at high temperatures, and an increased correlation time for molecular reorientation (τ_c) of these bulky cations at low temperatures may be responsible for these effects.

The ⁶³Cu NMR spectra of $[\text{Cu}(\text{L-L})_2]^+$ [L-L = $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$, *cis*- $\text{Ph}_2\text{AsCH}=\text{CHAsPh}_2$, $o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2$ and $\text{R}_2\text{Sb}(\text{CH}_2)_3\text{SbR}_2$, R = Me or Ph] are broad singlets at room temperature, and apart from a high frequency drift in resonance position, the spectra change little on cooling.

The lack of observable ⁶³Cu resonances for complexes of $o\text{-C}_6\text{H}_4(\text{PMe}_2)(\text{AsMe}_2)$ or $o\text{-C}_6\text{H}_4(\text{PMe}_2)(\text{SbMe}_2)$, in contrast to those of the symmetrical analogues, is obviously due to the highly unsymmetrical *electronic* field about the copper produced by the different donor atoms.

Copper-63 Chemical Shifts and Coupling Constants.—From the data in the present work and in the previous literature,⁵ it is possible to identify typical ranges for ⁶³Cu chemical shifts as a function of ligand type. This is shown schematically in Fig. 6. Within each series of ligands, there are systematic trends with ligand substituents as seen in Table 4. For example, progressive replacement of Me by Ph in heavy Group 15 donor ligands results in a stepwise shift in the ⁶³Cu resonance to low frequency, and similar effects are seen with backbone type. Few one-bond coupling constants to copper have been observed,⁵

almost all involving phosphorus. The $^1J(^{31}\text{P}-^{63}\text{Cu})$ coupling constants in phosphite and phosphinite complexes lie in the range 1100–1320 Hz, whilst the values in phosphine complexes in the present work are smaller, *ca.* 800 Hz.

Experimental

Physical measurements were made as described previously.²⁷ The ^1H NMR spectra were recorded from solutions in CD_2Cl_2 or CDCl_3 on a JEOL FX90Q (90 MHz) spectrometer. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra were recorded from $\text{CD}_2\text{Cl}_2\text{-CH}_2\text{Cl}_2$ (5:95) solutions on a Bruker AM 360 spectrometer at 145.8 MHz, and ^{63}Cu NMR spectra similarly at 95.5 MHz. Phosphorus chemical shifts are reported relative to external 85% H_3PO_4 and copper shifts relative to a solution of $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ in MeCN at 300 K. Spectra were measured over the range 300–175 K (below this temperature the solvent begins to freeze). The FAB mass spectra were recorded on a VG Analytical 70–250–SE normal geometry double-focussing mass spectrometer, equipped with a FAB Ion Tech (Saddle Field Gun), and using 3-nitrobenzyl alcohol as the matrix.

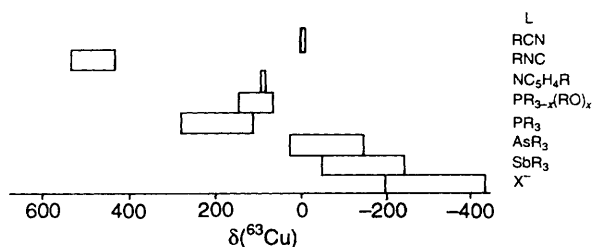


Fig. 6 Copper-63 NMR chemical-shift ranges (R = alkyl or aryl)

Syntheses.—The complexes $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ and $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ were made by literature methods.¹⁰ The complexes were prepared by the same general methods, examples of which are given below. All compounds had satisfactory analyses. All complexes of air-sensitive ligands were made under nitrogen.

$[\text{Cu}(\text{AsMe}_2\text{Ph})_4]\text{PF}_6$. The arsine AsMe_2Ph (0.87 g, 4.78 mmol) was added to a suspension of $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ (0.37 g, 0.97 mmol) in CH_2Cl_2 (10 cm^3), and the mixture refluxed for 1 h under nitrogen. The solvent was removed *in vacuo* and the resulting oil triturated with pentane. The white solid formed was washed with diethyl ether (10 cm^3) and dried *in vacuo*. Yield 0.76 g (81%).

$[\text{Cu}(\text{PMePh}_2)_4]\text{BF}_4$. The phosphine PMePh_2 (0.73 cm^3 , 3.92 mmol) was added to a solution of $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ (0.31 g, 0.97 mmol) in MeCN (10 cm^3). The mixture was stirred at 40 °C, when a white precipitate formed after *ca.* 15 min and then cooled in a freezer. The white solid was filtered off, and dried *in vacuo*. Yield 0.65 g (70%).

$[\text{Cu}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}_2]\text{PF}_6$. A solution of the diphosphine $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ (0.83 g, 2.0 mmol) and $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ (0.37 g, 0.97 mmol) in MeCN (30 cm^3) was stirred at 50 °C for 2 h. The solution was reduced in volume to *ca.* 5 cm^3 and cooled in a freezer. The resulting off-white microcrystalline product was filtered off, washed with diethyl ether and dried *in vacuo*. It was recrystallised from MeCN–pentane. Yield 0.88 g (87%).

$[\text{Cu}\{o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2\}_2]\text{PF}_6$. The stibine $o\text{-C}_6\text{H}_4(\text{SbMe}_2)_2$ (0.76 g, 2.0 mmol) was added to a solution of $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ (0.35 g, 0.95 mmol) in MeCN (20 cm^3). The mixture was stirred at 50 °C for 2 h, cooled and filtered. The filtrate was concentrated to an oil, triturated with pentane (10 cm^3) and

Table 6 Atomic coordinates for $[\text{Cu}(\text{Ph}_2\text{AsCH}=\text{CHAsPh}_2)_2]\text{PF}_6^a$

Atom	x	y	z	Atom	x	y	z
Cu	0.1898(1)	0.5079(1)	0.3573(1)	C(41)	0.3296(13)	0.6676(11)	0.2927(9)
As(1)	0.2961(1)	0.4053(1)	0.3543(1)	C(42)	0.3278(15)	0.7469(13)	0.2957(11)
As(2)	0.3073(1)	0.6009(1)	0.3665(1)	C(43)	0.3375(20)	0.7949(17)	0.2421(14)
As(3)	0.0721(1)	0.4768(1)	0.4287(1)	C(44)	0.3503(23)	0.7589(21)	0.1837(17)
As(4)	0.0828(1)	0.5506(1)	0.2818(1)	C(45)	0.3515(23)	0.6791(21)	0.1798(17)
P	0.1860(4)	0.0028(4)	0.5886(4)	C(46)	0.3435(18)	0.6321(15)	0.2378(12)
F(1)	0.2541(10)	-0.0567(10)	0.6175(11)	C(51)	0.0571(14)	0.3676(12)	0.4505(9)
F(2)	0.2511(12)	0.0692(11)	0.6112(14)	C(52)	0.0433(17)	0.3452(15)	0.5129(13)
F(3)	0.1321(14)	0.0096(17)	0.6504(8)	C(53)	0.0320(22)	0.2617(20)	0.5251(15)
F(4)	0.1127(15)	0.0614(16)	0.5622(11)	C(54)	0.0438(20)	0.2036(19)	0.4717(14)
F(5)	0.1226(11)	-0.0647(12)	0.5697(11)	C(55)	0.0555(21)	0.2335(19)	0.4157(16)
F(6)	0.2424(17)	0.0124(22)	0.5281(13)	C(56)	0.0621(16)	0.3166(14)	0.4035(11)
C(1)	0.4150(16)	0.4608(12)	0.3583(10)	C(61)	0.0448(14)	0.5285(12)	0.5074(9)
C(2)	0.4146(15)	0.5360(12)	0.3660(9)	C(62)	-0.0378(18)	0.5441(16)	0.5264(12)
C(3)	-0.0346(13)	0.4948(12)	0.3812(9)	C(63)	-0.0582(31)	0.5873(25)	0.5809(19)
C(4)	-0.0309(14)	0.5214(12)	0.3226(10)	C(64)	0.0117(28)	0.6079(22)	0.6121(17)
C(11)	0.3149(15)	0.3285(12)	0.2858(10)	C(65)	0.0918(29)	0.5903(22)	0.5963(18)
C(12)	0.2418(16)	0.3102(13)	0.2530(11)	C(66)	0.1116(21)	0.5484(17)	0.5466(13)
C(13)	0.2483(21)	0.2481(18)	0.2075(14)	C(71)	0.0642(13)	0.5203(12)	0.1957(9)
C(14)	0.3441(24)	0.2170(19)	0.1970(15)	C(72)	0.1317(15)	0.4750(13)	0.1642(10)
C(15)	0.4076(23)	0.2415(19)	0.2320(14)	C(73)	0.1098(16)	0.4477(14)	0.0989(11)
C(16)	0.3951(17)	0.3000(14)	0.2755(11)	C(74)	0.0383(15)	0.4670(13)	0.0725(11)
C(21)	0.3000(14)	0.3431(11)	0.4310(9)	C(75)	-0.0249(16)	0.5108(14)	0.0933(11)
C(22)	0.3129(17)	0.3829(15)	0.4872(12)	C(76)	-0.0112(17)	0.5382(14)	0.1607(11)
C(23)	0.3066(20)	0.3387(17)	0.5470(14)	C(81)	0.0682(13)	0.6639(10)	0.2770(9)
C(24)	0.3011(22)	0.2648(18)	0.5450(14)	C(82)	0.1017(14)	0.7046(12)	0.2248(10)
C(25)	0.2906(18)	0.2196(16)	0.4867(12)	C(83)	0.1040(16)	0.7898(14)	0.2202(12)
C(26)	0.2888(16)	0.2660(13)	0.4300(12)	C(84)	0.0684(21)	0.8240(19)	0.2693(14)
C(31)	0.3319(15)	0.6735(12)	0.4349(10)	C(85)	0.0286(24)	0.7848(21)	0.3301(17)
C(32)	0.2498(21)	0.7064(18)	0.4590(14)	C(86)	0.0379(19)	0.6991(18)	0.3290(14)
C(33)	0.2622(25)	0.7659(21)	0.5155(18)	C(1S) ^b	0.2510(26)	0.0166(24)	0.8063(19)
C(34)	0.3420(23)	0.7861(19)	0.5303(15)	C(2S) ^b	0.1212(35)	-0.0932(29)	0.8487(23)
C(35)	0.4195(23)	0.7498(20)	0.5067(15)	C(3S) ^b	0.0719(36)	-0.0821(29)	0.8223(23)
C(36)	0.4152(18)	0.6912(14)	0.4548(11)				

^a Carbon atoms are labelled C (*m*) where *m* (1–8) indicates the ring and *n* (1–6) identifies the atoms within one ring. ^b Solvate atoms (population 0.5).

then absolute alcohol (10 cm³). The white product was dried under a nitrogen stream. Yield 0.51 g (55%).

Crystal Structure Determination of [Cu(Ph₂AsCH=CHAsPh₂)₂]PF₆.—Air-stable colourless crystals of the compound were obtained by vapour diffusion of pentane into a CH₂Cl₂ solution of the complex. One crystal was successfully sealed in a thin-wall glass capillary.

Crystal data. C₅₂H₄₄As₄CuF₆P, *M* = 1177.13, orthorhombic, space group *P*2₁2₁2₁, *a* = 14.775(6), *b* = 16.991(5), *c* = 21.027(6) Å, *U* = 5278.7(4.9) Å³, *Z* = 4, *D*_c = 1.481 g cm⁻³, λ(Mo-Kα) = 0.710 69 Å, μ(Mo-Kα) = 29.5 cm⁻¹, *F*(000) = 2344, ambient temperature.

Data collection. Data were collected using a crystal 0.3 × 0.3 × 0.35 mm on an Enraf-Nonius CAD4 diffractometer equipped with Mo-Kα radiation and graphite monochromator. Cell dimensions were obtained from 25 reflections and intensity data for 5763 reflections were recorded (1 ≤ θ ≤ 26°; *h* 0–18, *k* 0–20, *l* 0–25). Lorentz-polarisation corrections were applied as well as allowance for a small amount of decay (ca. 3% on *F*) during the data processing. Systematic absences established the space group, and after averaging there remained 5732 unique reflections. No reflections suitable for a ψ -scan absorption correction were available.

Structure solution and refinement. The position of copper and arsenic atoms emerged from the application of SHELXS 86²⁸ and repeated structure-factor and electron-density calculations located the PF₆ anion and all the C atoms. At this point it was realised that the crystal was isomorphous with the corresponding phosphine and the coordinate origin was moved to conform to that used in the previous study. The later electron-density maps showed evidence for an extensively disordered solvate molecule and the three major peaks were introduced into the model; however the solvate was not satisfactorily modelled. This problem was also encountered in the phosphine derivative.⁸ The fully isotropic model (*R* = 0.09) was used prior to the application of the DIFABS absorption correction.²⁹ Subsequent full-matrix least-squares refinement³⁰ converged to *R* = 0.065 [2986 reflections, *F* > 4σ(*F*)], 331 parameters, anisotropic (Cu, As, P, F) and isotropic (C, H) atoms, *w*⁻¹ = σ²(*F*) + 0.002*F*², maximum shift/error = 0.05, *R*' = 0.087. The residual electron density was in the range 0.93 to -0.60 e Å⁻³ with the five largest peaks associated with the disordered solvate molecule. Although there was no evidence from the initial photographs and diffractometer peak widths, the crystal used does not seem to be of high quality possibly due to disorder and no attempt was made to determine the absolute configuration. Neutral-atom scattering factors and anomalous-dispersion corrections were taken from SHELX 76³⁰ and ref. 31 (Cu, As) and the calculations were carried out using SHELX 76, SHELXS 86 and PLUTO³² on an IBM 3090 computer. Atomic coordinates are listed in Table 6.

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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References

- G. W. Bowmaker, J. D. Cotton, P. C. Healy, J. D. Kildea, S. B. Silong, B. W. Skelton and A. H. White, *Inorg. Chem.*, 1989, **28**, 1462.
- G. A. Bowmaker, W. Jirong, R. D. Hart, A. H. White and P. C. Healy, *J. Chem. Soc., Dalton Trans.*, 1992, 787.
- S. Attar, G. A. Bowmaker, N. W. Alcock, J. S. Frye, W. H. Bearden and J. H. Nelson, *Inorg. Chem.*, 1991, **30**, 4743.
- L. F. Barron, J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Pakawatchai and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1987, 1089; L. F. Barron, J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Pakawatchai, V. A. Patrick and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1987, 1099.
- See, P. Granger, in *Transition Metal NMR*, ed. P. S. Pregosin, Elsevier, Amsterdam, 1991, p. 265.
- B. Mohr, E. E. Brooks, N. Rath and E. Deutsch, *Inorg. Chem.*, 1991, **30**, 4541.
- S. J. Berners-Price, C. Brevard, A. Pagelot and P. J. Sadler, *Inorg. Chem.*, 1986, **25**, 596.
- S. J. Berners-Price, L. A. Colquhoun, P. C. Healy, K. A. Byriel and J. V. Hanna, *J. Chem. Soc., Dalton Trans.*, 1992, 3357.
- A. Hetherington, W. Levason and M. D. Spicer, *Polyhedron*, 1990, **9**, 1609.
- G. J. Kubas, *Inorg. Synth.*, 1979, **19**, 90.
- G. A. Bowmaker, P. C. Healy, L. M. Engelhardt, J. C. Kildea, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1990, **43**, 1697.
- D. F. Dempsey and G. S. Girolami, *Organometallics*, 1988, **7**, 1208.
- K.-M. Chi, J. Farkas, M. J. Hampden-Smith, T. T. Kodas and E. N. Duesler, *J. Chem. Soc., Dalton Trans.*, 1992, 3111.
- L. M. Engelhardt, C. Pakawatchai, A. H. White and P. C. Healy, *J. Chem. Soc., Dalton Trans.*, 1985, 125.
- D. J. Darensbourg, C.-S. Chao, J. H. Reibenspies and C. J. Bischoff, *Inorg. Chem.*, 1990, **29**, 2153.
- O. M. Abu Salah, M. I. Bruce, P. J. Lohmeyer, C. L. Raston, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 962.
- A. Camus, N. Marsich, G. Nardin and L. Randaccio, *Transition Met. Chem.*, 1976, **1**, 205.
- A. Baiada, F. H. Jardine, R. D. Willett and K. Emerson, *Inorg. Chem.*, 1991, **30**, 1365.
- H. Schmidbauer, J. Adlkofer and K. Schwirten, *Chem. Ber.*, 1972, **105**, 3382; H. F. Klein and H. Schmidbauer, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 903.
- P. Kroneck, O. Lutz and H. Oehler, *Z. Naturforsch., Teil A*, 1980, **35**, 221.
- S. J. Lippard and J. J. Mayerle, *Inorg. Chem.*, 1972, **11**, 753.
- D. J. Fife, W. M. Moore and K. W. Morse, *Inorg. Chem.*, 1984, **23**, 1684.
- E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc.*, 1970, **92**, 4114.
- A. Marker and M. J. Gunter, *J. Magn. Reson.*, 1982, **47**, 118.
- C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
- N. R. Champness and W. Levason, *Coord. Chem. Rev.*, in the press.
- R. A. Cipriano, W. Levason, R. A. S. Mould, D. Pletcher and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1990, 2609.
- G. M. Sheldrick, SHELXS 86, Program for solution of crystal structures, University of Göttingen, 1986.
- N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
- G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.
- International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99, 149.
- W. D. S. Motherwell and W. Clegg, PLUTO, Program for plotting molecular and crystal structures, Universities of Cambridge and Göttingen, 1978.

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