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Coordination Stabilised Copper(I) Fluoride. Crystal and Molecular Structure of Fluorotris(triphenylphosphine)copper(I)·Ethanol (1/2), $Cu(PPh_3)_3F \cdot 2EtOH$

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The structure of the title compound has been determined by single crystal X-ray diffraction. The crystals are orthorhombic a = *13.435(2),* b = *19.812(3),* c = *18.739(2)* Å, Z = *4, space group* $Pc2_1n$ *(No 33). A total of 3291 observed reflections were measured and refined to* R = *0.087. The copper is in a distorted tetrahedral environment* (P_3F) *with Cu–P = 2.325(3), 2.310(3) and 2.316(2), and Cu–F = 2.062(6)* Å. *The solvent and temperature dependent solution behaviour of this complex has been examined by a combination of* ^1H, ^{19}F *and* ^{31}P *NMR spectroscopy and conductivity measurements. The synthesis and properties of the unsolvated complex are briefly described.*

Introduction

The synthesis of copper(I) fluoride has been claimed and subsequently denied several times in the last hundred years. Poulenc's preparation [1] from copper(I) chloride and gaseous HF could not be repeated by Ruff [2]. Ebert and Woitinek [3] passed a mixture of fluorine and chlorine over copper and considered the red layer next to the metal to be CuF, which was assigned a zincblende structure from its X-ray powder pattern. However Haendler *et al.* [4] showed this product to be Cu_2O. Thermal decomposition of copper(II) fluoride was suggested to yield CuF which however disproportionated to CuF_2 and metallic copper on cooling [5]. More recent studies [4, 6, 7] however suggest that CuF_2 vaporises without decomposition, and X-ray powder patterns from cooled melts show lines only due to the difluoride, and it is now clear that solid CuF has never been prepared [8, 9].

There is good evidence for CuF and related oligomers $(CuF)_n$ n = 2–5 in the gas phase over CuF_2/Cu melts [7, 10, 11], and the microwave spectrum of ^{63}Cu–F and ^{65}Cu–F has been reported and the Cu–F bond length determined (1.745 Å) [12].

Only one complex of copper(I) fluoride is mentioned in the literature. Jardine *et al.* [13] briefly reported that $Cu(PPh_3)_3F$ is formed from copper(II) fluoride and PPh_3 in methanol, but the only characterisation was by analytical data and a melting point. We have undertaken a detailed study of this unique complex and report our results below.

Experimental

Preparation of $Cu(PPh_3)_3F \cdot 2EtOH$

The preparation is similar to the published route [13] with minor modifications. Triphenylphosphine (9.2 g, 0.035 mol) was refluxed with a suspension of hydrated copper(II) fluoride (ALFA Inorganics) (1.38 g, 0.01 mol) in methanol (100 cm^3) for 2 hours. The hot methanol solution was filtered to remove unreacted solid, and the volume of the solution reduced to 40 cm^3. On standing at 0 °C a white solid was precipitated, and on reducing the volume further, more solid precipitated. (Analysis and ^1H NMR spectra show that the crude product retains methanol). The crude material was recrystallised twice from absolute ethanol by cooling a saturated solution in a refrigerator, to give clear crystals of $Cu(PPh_3)_3F \cdot 2EtOH$ (3.7 g, 39%). *Anal.* Found: C = 73.0, H = 6.0, F = 1.6, Cu = 5.9%. Calcd. for $C_{58}H_{57}CuFO_2P_3$: C = 72.5, H = 6.0, F = 2.0, Cu = 6.6%. ^1H NMR ($CDCl_3$)(δ) 7.2–7.5(m, Ph), 3.65(q, $-\underline{CH_2}-CH_3$), 1.3(t, $-CH_2-\underline{CH_3}$), (the OH resonance was not observed). ^{13}C NMR ($CDCl_3$) 134.3, 133.7, 133.2, 129.4, 128.6, 128.3 (Ph), 57.8 (CH_2), 18.4 (CH_3). *Physical measurements:* ^1H and ^{13}C NMR spectra were recorded on a Varian XL-100 spectrometer in $CDCl_3$ solution relative to internal TMS. ^{19}F NMR spectra were obtained similarly in CD_2Cl_2 or CD_2Cl_2/*sec*-BuCl and CD_3OD referenced to internal C_6F_6. (ϕ scale C_6F_6 = $CFCl_3$ + 162.9). ^{31}P NMR spectra were recorded on solutions in CH_2Cl_2 and CH_3OH on a Bruker CXP 200 referenced to external PPh_3 in CH_2Cl_2. This can be converted to the 85% H_3PO_4 scale by adding +6.0 ppm. Other physical measurements were made as described previously [14].

Crystallographic Examination

Crystals for X-ray examination were prepared by cooling ethanolic solutions of $CuF(Ph_3P)_3$ in a refrigerator. Crystals formed over a few days and tended to grow as a few large crystals often aggregates. Difficulty was experienced in obtaining suitable small crystals. The crystals are initially transparent but on removal from the liquor become opaque.

Preliminary photographic examination with Weissenberg and precession techniques established an orthorhombic system and the systematic absences (hkl none; hk0, h + k = 2n; h0l; none; 0kl, l = 2n; h00, h = 2n; 0k0, k = 2n; 00l, l = 2n) indicated a primitive lattice and space group $Pc2_1n$ (No 33) or *Pcmn* (No 62). Precise cell dimensions were obtained from the setting angles for 25 accurately centred reflections on an Enraf Nonius CAD-4 diffractometer.

Crystal Data

$C_{58}H_{57}CuFO_2P_3$, M = 961.55, orthorhomic, a = 13.435(2), b = 19.812(3), c = 18.739(2) Å. U = 4987.8 $Å^3$, space group $Pc2_1n$ (No 33), $Z = 4$, Dc = 1.27, Do (flotation) = 1.27 kg dm^{-3}, $F(000) = 2016$, $\mu(Cu\text{-}K_\alpha)$ = 17.97 cm^{-1}, $\lambda(Cu\text{-}K_\alpha)$ = 1.5418 Å.

The intensities of 4869 unique reflections were recorded from one octant of reciprocal space with graphite monochromated Cu-K_α radiation using a Enraf Nonius CAD-4 diffractometer. Check reflections showed no significant crystal deterioration during the experiment. The data which were recorded from a room temperature crystal were corrected for Lorentz and polarisation factors in the usual way. The crystal size was 1.0 × 0.65 × 0.25 mm and no absorption correction was applied due to difficulties in adequately defining the crystal faces. This crystal opacity is ascribed to the partial loss of ethanol of crystallisation. The quality of the data is not expected to be high due to large crystal size, particularly in one dimension, and the lack of an absorption correction. 3291 reflections were used in the structure refinement omitting those where $I \leqslant 3 \times \sigma(I)$ (1260 reflections) and imposing a sinθ limit of 0.90 ($2\theta > 128.3°$) removed 318 weak reflections.

Structure Analysis and Refinement

The structure was solved by conventional heavy atom methods in the non-centrosymmetric space group $Pc2_1n$. A Patterson map gave a plausible copper atom position and repeated structure factor and electron density calculations gradually located the phosphorus atoms, fluorine and carbon atoms of the benzene rings, and the carbon and oxygen atoms of the ethanol molecules. Least squares refinement (isotropic atoms, unit weights, rigid body phenyl rings) gave R = 0.17. The temperature factors for all the carbon and oxygen atoms of the ethanol molecules were large unlike the carbon atoms associated with phenyl groups. This was attributed to the partial loss of ethanol. Removing the geometrical constraints on the phenyl groups and introducing anisotropic temperature factors for all atoms excluding the ethanol gave on least squares refinement a converged R = 0.087 and Rw = 0.083 ($R = \Sigma\Delta F/\Sigma F_o$, $Rw = \Sigma w\Delta F/\Sigma wF_o$). The total of refined variables was 556 giving a ratio of reflection/parameters of 5.9. A weighting scheme $w = 1/[\sigma^2(F_o) + 0.005\ F_o^2]$ was applied and gave a satisfactory value of $<w\Delta F^2>$ as a function of sinθ and $\overline{F_o}$. The ethanol was given a population parameter of 1. The scattering factor and anomalous dispersion for neutral copper was taken from Reference [15] and for neutral P, F, O and C from the SHELX program [16]. No hydrogen atoms were included in the calculation. A difference electron density map showed as expected no major peaks but a number of peaks were found with heights ~0.5 e$Å^{-3}$ which in some cases were in the correct position to be hydrogen atoms. The largest peak (1.1 e$Å^{-3}$) occurred close to the copper atom. Oxygen and carbon atoms in the ethanol were assigned assuming hydrogen bonding between O and F and by inspection of the bond lengths, though the latter were subject to large standard deviations. It was felt that the quality of the data did not warrant the inclusion of hydrogen atoms. No attempt was made to investigate which enantiomorph was present in the crystal. The final positional parameters together with the standard deviations from the least squares refinement are given in Table I. Table II contains selected bond lengths while Table III contains chemically significant angles and the equations of the best planes through the carbon atoms. Figure 1 shows a discrete molecule, and Fig. 2 a unit cell excluding the phenyl rings for clarity but showing the H-bonding. The final F_O and F_C values and the anisotropic temperature factors are available from the Editor/authors. All calculations

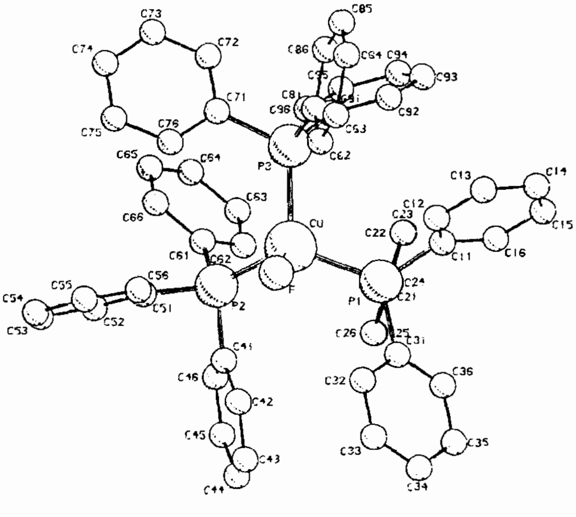

Fig. 1. View of a discrete molecule of $CuF(Ph_3P)_3$.

TABLE I. Final Positional Parameters (× 10^4) with estimated Standard Deviation in Parentheses.

Atom	X/A	Y/B	Z/C	Atom	X/A	Y/B	Z/C
Cu	615(1)	2500(0)	2288(1)	C(45)	−2747(10)	4055(8)	1216(8)
P(1)	−13(2)	1787(1)	1411(1)	C(46)	−1772(10)	4046(8)	1398(7)
P(2)	−108(2)	3556(1)	2225(1)	C(51)	−233(7)	4062(5)	3051(6)
P(3)	2338(2)	2527(1)	2258(1)	C(52)	−491(9)	4758(6)	3021(7)
F	237(5)	2120(3)	3276(3)	C(53)	−621(10)	5110(6)	3658(7)
O(1)	338(11)	940(9)	3919(7)	C(54)	−525(13)	4799(8)	4299(8)
C(1)	−302(24)	495(20)	3568(17)	C(55)	−252(13)	4104(9)	4341(7)
C(2)	−549(17)	−94(16)	4000(13)	C(56)	−103(9)	3751(6)	3693(6)
O(2)	−1465(15)	2241(14)	3927(12)	C(61)	571(7)	4118(5)	1595(5)
C(3)	−1627(20)	1988(16)	4555(15)	C(62)	484(9)	3983(5)	899(6)
C(4)	−1241(18)	2446(16)	5009(13)	C(63)	1026(10)	4365(7)	385(7)
C(11)	702(7)	1029(4)	1269(5)	C(64)	1702(11)	4833(8)	614(8)
C(12)	1166(8)	759(5)	1860(5)	C(65)	1816(11)	4950(8)	1359(8)
C(13)	1676(9)	113(6)	1811(7)	C(66)	1241(9)	4601(5)	1831(6)
C(14)	1675(10)	−192(7)	1173(9)	C(71)	2917(7)	3298(5)	2623(4)
C(15)	1264(11)	72(7)	586(7)	C(72)	3842(10)	3546(7)	2411(7)
C(16)	733(10)	693(6)	611(6)	C(73)	4246(11)	4126(8)	2751(7)
C(21)	−119(8)	2216(5)	537(5)	C(74)	3779(9)	4429(7)	3285(7)
C(22)	719(9)	2262(6)	97(5)	C(75)	2859(11)	4184(5)	3498(6)
C(23)	674(10)	2622(7)	−545(6)	C(76)	2442(9)	3607(5)	3182(5)
C(24)	−222(13)	2931(8)	−744(6)	C(81)	3034(7)	1893(5)	2751(4)
C(25)	−1068(11)	2886(9)	−310(7)	C(82)	2521(8)	1524(5)	3259(5)
C(26)	−979(10)	2497(7)	330(9)	C(83)	3041(10)	1050(5)	3682(5)
C(31)	−1259(8)	1467(5)	1564(6)	C(84)	4076(9)	957(6)	3603(5)
C(32)	−1674(10)	1552(7)	2252(6)	C(85)	4556(9)	1318(6)	3098(6)
C(33)	−2616(11)	1311(9)	2389(7)	C(86)	4038(9)	1785(6)	2662(5)
C(34)	−3199(9)	1004(7)	1862(7)	C(91)	2855(6)	2496(5)	1354(4)
C(35)	−2788(10)	929(6)	1166(8)	C(92)	3110(8)	1860(5)	1065(5)
C(36)	−1805(9)	1179(6)	1013(7)	C(93)	3433(9)	1841(7)	344(6)
C(41)	−1435(7)	3622(5)	1951(6)	C(94)	3449(8)	2434(7)	−77(5)
C(42)	−2120(12)	3202(8)	2292(8)	C(95)	3169(10)	3028(7)	218(5)
C(43)	−3072(11)	3226(9)	2133(9)	C(96)	2849(8)	3063(5)	930(5)
C(44)	−3436(10)	3635(11)	1577(10)				

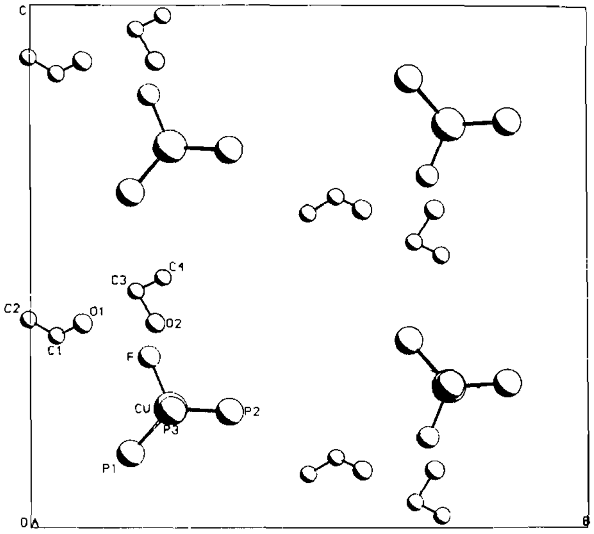

Fig. 2. View of unit cell excluding the phenyl groups looking from the positive *a* direction.

TABLE II. Selected Interatomic Distances (Å) with estimated Standard Deviation in Parentheses.

Cu–F	2.062(6)	P(1)–C(11)	1.802(9)
Cu–P(1)	2.325(3)	P(1)–C(21)	1.851(10)
Cu–P(2)	2.310(3)	P(1)–C(31)	1.813(11)
Cu–P(3)	2.316(2)		
P(2)–C(41)	1.860(10)	P(3)–C(71)	1.845(10)
P(2)–C(51)	1.851(10)	P(3)–C(81)	1.817(9)
P(2)–C(61)	1.861(9)	P(3)–C(91)	1.833(8)
O(1)–C(1)	1.40(4)	O(2)–C(3)	1.30(4)
C(1)–C(2)	1.46(5)	C(3)–C(4)	1.35(4)
F····O(1)	2.63(2)	F····O(2)	2.60(2)

were carried out on either a ICL2970 at Southampton University or (UMRCC) CDC7600 computer using the program SHELX [16], PLUTO [17] and XANADU [18] as well as some local programs.

TABLE III. Chemically Significant Angles (deg) and the Equations of the Best Planes passing through the Phenyl Groups.

(a) *Angles*

F–Cu–P(1)	108.9(1)	P(1)–Cu–P(2)	111.2(1)
F–Cu–P(2)	105.9(2)	P(2)–Cu–P(3)	113.5(1)
F–Cu–P(3)	106.0(2)	P(3)–Cu–P(1)	111.1(1)
Cu–P(1)–C(11)	114.7(3)	C(11)–P(1)–C(21)	107.0(4)
Cu–P(1)–C(21)	112.0(3)	C(21)–P(1)–C(31)	103.2(5)
Cu–P(1)–C(31)	115.8(3)	C(31)–P(1)–C(11)	103.0(4)
Cu–P(2)–C(41)	118.7(3)	C(41)–P(2)–C(51)	96.1(5)
Cu–P(2)–C(51)	119.1(3)	C(51)–P(2)–C(61)	104.5(4)
Cu–P(2)–C(61)	111.6(3)	C(61)–P(2)–C(41)	104.6(4)
Cu–P(3)–C(71)	115.6(3)	C(71)–P(3)–C(81)	99.6(4)
Cu–P(3)–C(81)	119.1(3)	C(81)–P(3)–C(91)	104.6(4)
Cu–P(3)–C(91)	113.6(3)	C(91)–P(3)–C(71)	102.1(4)
Cu–F····O(1)	136.3(5)	Cu–F····O(2)	127.1(7)

(b) *Planes*

The equation of the best plane through each phenyl group is AXo + BYo + CZo = D referred to orthogonal (Å) coordinates aligned along the crystallographic axes.

Atoms of ring	A	B	C	D	Distance of bonded P atom from plane (Å)
C(11)–C(16)	0.848	0.479	−0.230	1.24	0.16
C(21)–C(26)	0.270	0.833	0.482	4.09	0.13
C(31)–C(36)	−0.376	0.891	−0.255	2.49	0.01
C(41)–C(46)	−0.161	0.727	0.668	7.96	0.03
C(51)–C(56)	0.968	0.251	0.006	1.76	0.11
C(61)–C(66)	0.716	−0.697	0.048	−4.98	0.17
C(71)–C(76)	0.463	−0.594	0.658	1.18	0.08
C(81)–C(86)	0.182	0.717	0.673	6.89	0.12
C(91)–C(96)	0.945	0.169	0.281	5.15	0.14

Results and Discussion

Jardine *et al.* [13] reported the formation of unsolvated $Cu(PPh_3)_3F$ from copper(II) fluoride and PPh_3 in methanol under reflux, but did not describe the product in detail. In our hands this reaction using hydrated copper(II) fluoride $CuF_2 \cdot 2H_2O$:PPh_3 ratio of 1:3, 1:3.5 or 1:6 mol ratios in methanol gave the same complex $Cu(PPh_3)_3F \cdot xMeOH$ ($1 < x < 2$) from which the methanol was not removed by prolonged pumping at room temperature. Similar solvates were obtained from other solvents including ethanol, dichloromethane and chloroform, the value of x in $Cu(PPh_3)_3F \cdot x$solvent varying somewhat from preparation to preparation as estimated by a combination of analysis and ^1H and/or ^{13}C NMR spectroscopy. The complex $Cu(PPh_3)_3F \cdot xMeOH$ was also obtained by melting PPh_3 and $CuF_2 \cdot 2H_2O$ together under nitrogen and recrystallising from methanol. Anhydrous copper(II) fluoride reacted very slowly and incompletely with either PPh_3 in methanol or molten PPh_3 to form the same complex. As obtained above $Cu(PPh_3)_3F \cdot xMeOH$ is a white powder indefinitely stable in air, and readily soluble in organic solvents. Alcohol solutions are air-stable, but solutions in chlorinated solvents turn blue in air, although they are stable under nitrogen.

Neither triphenylarsine nor triphenylstibine reduce $CuF_2 \cdot 2H_2O$ on refluxing in methanol. Reduction occurs readily with other phosphines including $PhMe_2P$, $MePh_2P$, $Ph_2PCH_2CH_2PPh_2$ and $^nBu_3P$, but the products are very soluble in organic solvents and have not been separated in a pure state from the oxidation products.

X-Ray Structures

Single crystal X-ray data has been reported for numerous copper(I) phosphine complexes [19] including the following triphenylphosphine compounds: $[Cu(PPh_3)X]_4$ (X = Cl [20], Br [21], I [22]), [$Cu(PPh_3)_2Br$] [23], [$Cu(PPh_3)_2O_2CCH_3$] [24], [$Cu_2Cl_2(PPh_3)_3$] [25, 26], and of particular relevance to the present study [$Cu(PPh_3)_3BF_4$] [27] and [$Cu(PPh_3)_3Cl$] [19].

The structure of $Cu(PPh_3)_3F \cdot 2EtOH$ (Fig. 1) consists of a distorted tetrahedron about the copper comprised of three phosphorus and one fluorine atom. The Cu–P distances (Table II) have an average value of 2.317 Å and the P–Cu–P angle (av) is 111.9°. The comparable values in [$Cu(PPh_3)_3BF_4$] and [$Cu(PPh_3)_3Cl$] are 2.298 Å and 115.6°, and 2.351 Å and 109.8° respectively. The decrease in the P–Cu–P angle and the increase in Cu–P bond length along the series [$Cu(PPh_3)_3BF_4$]-[$Cu(PPh_3)_3F$]-[$Cu(PPh_3)_3Cl$] is a consequence of the increasing steric demands of the anions. It is generally accepted that the Cu^I–L bonds have little or no π-component, and that the bond lengths and angles are a consequence of minimising steric repulsions firstly between the strongly bound phosphines, and secondly those involving the anion–phosphine interactions [19].

The main reason for the present study was to establish the presence (or absence) of a Cu^I–F bond.† The Cu–F bond length (2.062 Å) shows the fluorine is strongly bound to the copper. Since this is the only known example of a solid copper(I) fluoride derivative direct comparisons are not possible, but it is clearly a much stronger interaction than in the case of the weakly bound fluoroborate ion in [$Cu(PPh_3)_3$-FBF_3] [27] (2.31 Å). In anhydrous CuF_2, which is tetragonal [28] the Cu–F bond lengths are 1.93 and 2.27 Å. It has been estimated [29] that in the hypothetical CuF with a rock salt structure the (predominantly ionic) Cu–F distance would be *ca* 2.16 Å based upon rCu^+ *ca* 0.91 Å.

Covalent radii are more appropriate to $Cu(PPh_3)_3F \cdot 2EtOH$. Taking the covalent radius of fluorine to be 0.72 Å [30], and estimating rCu^I from d(Cu–P) in the present compound and rP (1.10 Å) [30], we arrive at a bond length for Cu^I–F of *ca* 1.94 Å compared with the measured value of 2.06 Å. A similar calculation on $Cu(PPh_3)_3Cl$ using rCl of 0.99 Å [30] predicts a Cu–Cl distance of 2.24 Å which also underestimates the value slightly. Calculations of this type cannot be expected to lead to accurate predictions of bond length, but nonetheless they do suggest that the Cu–F bond in $Cu(PPh_3)_3F \cdot 2EtOH$ approximates to a normal single covalent bond.

The temperature factors of the C and O atoms of the ethanol molecules were large which we attribute to partial occupancy of the positions. Problems in accurately locating solvate molecules in similar complexes have been noted by others [21, 27]. The ethanol is hydrogen bonded to the fluorine with F---HO = 2.61(5) Å (av). The length of hydrogen bonds is very dependent upon the system concerned, but is comparable with other F---HO interactions in compounds such as $CuF_2 \cdot 2H_2O$ or [$M^{II}(H_2O)_6SiF_6$] which range from 2.65–2.71 Å [30].

The far IR spectrum of $Cu(PPh_3)_3F \cdot 2EtOH$ exhibits a medium intensity band at 292 cm^{-1} which we assign as ν(Cu–F). Although the hydrogen bonding will have some effect on this value, it is reasonable in comparison with those of $Cu(PPh_3)_3X$ [31] (X = Cl 220, X = Br 166, X = I 145 cm^{-1}).

Solution Properties

In methanol solution $Cu(PPh_3)_3F$ has $\Lambda(10^{-3}\ M)$= 67 $ohm^{-1}\ cm^2\ mol^{-1}$ which approaches the range 80–110 $ohm^{-1}\ cm^2\ mol^{-1}$ quoted for 1:1 electrolytes [32]. The ^{19}F NMR spectrum at room temperature in CD_3OD consists of a single sharp line at +9.6 ppm relative to internal C_6F_6. Solutions of NaF and NMe_4F in the same solvent have resonances at +14.6 and +15.4 ppm which may be taken as confirmation of ionic fluoride in methanol solutions of $Cu(PPh_3)_3F$. The ^{31}P NMR spectrum of the complex in CH_3OH is a single line at +7 ppm relative to PPh_3, with a peak width at half-height of ca 70 Hz. No significant change occurred on cooling before the solvent began to solidify. Since we did not appear to reach the low temperature limit in this system we can infer nothing about the nature of $Cu(PPh_3)_n^+$ in solution.

In CH_2Cl_2 the conductivity of the complex was 4 $ohm^{-1}\ cm^2\ mol^{-1}$ ($10^{-3}\ M$) compared with values of ca 20–60 $ohm^{-1}\ cm^2\ mol^{-1}$ reported [33] for 1:1 electrolytes indicating that only a small amount of free fluoride is present. The ^{19}F and ^{31}P NMR spectra were recorded over the range +20 to −105 °C using CD_2Cl_2 or CD_2Cl_2/*sec*-BuCl as solvent, and some examples are shown in Fig. 3. The ^{19}F NMR resonance of NMe_4F in this solvent is +65.8 ppm. It is clear that more than one exchange process is operating and that even at the lowest temperature attainable exchange was still occurring. Further complications arise from the line broadening due to the quadrupolar copper nucleus, and from the very similar ^{31}P chemical shifts of PPh_3 and the species we believe are $Cu(PPh_3)_3F$ and $Cu(PPh_3)_2F$. Muetterties and Alegranti [33, 34] studied a range of silver(I) complexes with tri(*p*-tolyl)phosphine(L) and depending upon the anion present and the temperature, found evidence for AgL_4^+, AgL_3^+, AgL_3X and AgL_2X. This system had the added advantage that both ^{107}Ag and ^{109}Ag have I = $\frac{1}{2}$, and ^{107}Ag–^{31}P and ^{109}Ag–^{31}P coupling could be resolved. In the present case a detailed explanation of the exchange processes is not possible, but the following brief account is consistent with the spectral data. Considering first the ^{31}P NMR spectra, we propose that the resonances in the −120 °C spectrum can be assigned to $Cu(PPh_3)_3F$ (+2.6 ppm) and $Cu(PPh_3)_2F$

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†The data on 'CuF' in reference 27 is based upon the work of Ebert [3] which is now known [4] to be in error.

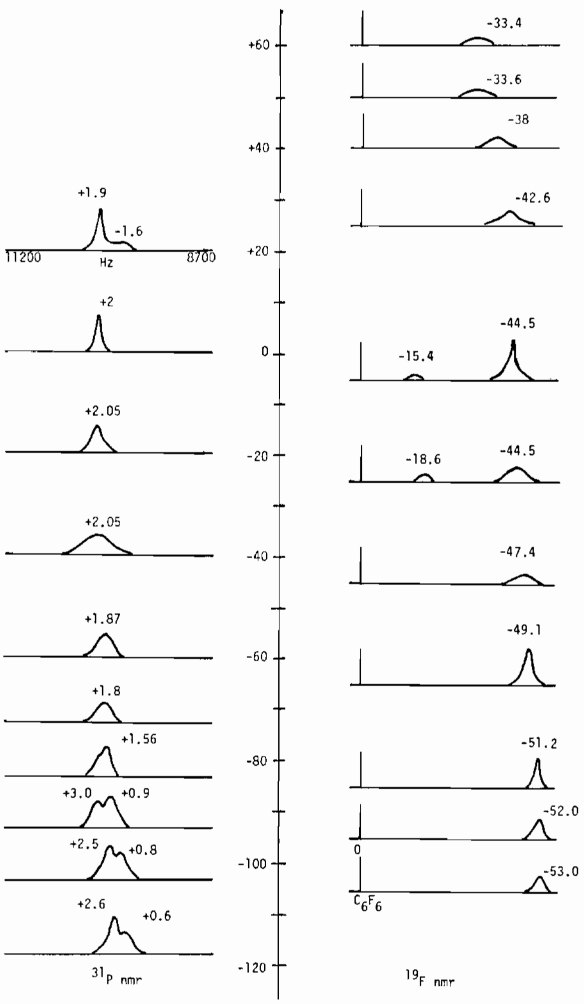

Fig. 3. Variable temperature ^{31}P and ^{19}F NMR spectra of Cu(PPh$_3$)$_3$F in halocarbon solvents.

(+0.6 ppm), the latter peak not being resolved from the free PPh$_3$ resonance. As the temperature increases, the amount of Cu(PPh$_3$)$_3$F present decreases, due to increased dissociation (Cu(PPh$_3$)$_3$F $\rightleftharpoons$ Cu(PPh$_3$)$_2$F + PPh$_3$). Further rise in temperature causes the resonances to broaden and coalesce, and then sharpen as the rate of phosphine exchange increases. The ^{19}F NMR data is more complicated. At low temperatures, it is suggested that all the fluorine is coordinated and the spectral changes are due to the rapid phosphine exchange. At ca –30 °C a new weak broad signal appears at –18.6 ppm, and disappears at ca +10 °C, the origin of this peak is unclear. As the temperature rises further the main signal due to Cu(PPh$_3$)$_n$F broadens, in this case due to exchange with the small amount of F$^-$ present. Over the temperature range –100 °C–0 °C the ^{19}F resonance attributable to Cu(PPh$_3$)$_n$F shifts downfield progressively. Addition of an excess of PPh$_3$ at 0 °C causes an upfield shift which suggests that Cu(PPh$_3$)$_3$F resonates at higher field than Cu(PPh$_3$)$_2$F, addition of free ligand shifting the equilibrium in favour of the former. Hence the downfield shift can be explained as due to the presence of increasing amounts of Cu(PPh$_3$)$_2$F.

Cu(PPh$_3$)$_3$F

Solvated products were obtained from all the common solvents examined, and complete removal of the solvent molecules was not possible at room temperature. However, on heating Cu(PPh$_3$)$_3$F$\cdot$2EtOH at 70 °C/0.01 torr for 4 hours a white powder was produced which had an analysis consistent with Cu(PPh$_3$)$_3$F. The ^{1}H and ^{13}C NMR spectra of this material confirmed the absence of the ethanol, but the resonances due to the complex were identical with those in spectra of the starting material. The IR spectrum of Cu(PPh$_3$)$_3$F in the region 1600–200 cm^{-1} differed from that of Cu(PPh$_3$)$_3$F$\cdot$2EtOH in that the IR absorptions due to EtOH were absent and some changes occurred in the pattern of benzene ring breathing modes. A new medium intensity broad band at *ca* 1940 cm^{-1} was present in the spectrum of Cu(PPh$_3$)$_3$F. The possibility that this was due to a carbonyl group was eliminated by a careful examination of the ^{13}C NMR spectrum. Moreover copper(I) carbonyls have [35] ν(CO) > *ca* 2050 cm^{-1} reflecting the weak π-backbonding from a d^{10} ion. Quantitative recovery of this material from ethanol reformed Cu(PPh$_3$)$_3$F$\cdot$2EtOH and the 1940 cm^{-1} IR band disappeared. We tentatively suggest that this absorption is due to a hydrogen bonding between the fluorine and *o*-protons on the phenyl rings.

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