Two-Coordinate Tribenzylphosphine (PBz_3) Complexes of Copper(I): Solid State ^{31}P NMR Studies and the Crystal Structure of $[Cu(PBz_3)_2]PF_6$

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Introduction

Interest in two-coordinate copper(I) arises from its relative rarity, especially when compared with the extensive chemistry established for four-coordinate copper(I).[2] Solid-state ^{31}P NMR spectroscopy has proved to be a useful probe for the coordination environment of copper(I) phosphine complexes (e.g. refs 3−10), but there is a paucity of data for two-coordinate complexes, the only structural data available for homoleptic bis-tertiary phosphine $[CuP_2]^+$ complexes being a report of the Cu−P bond length for the trimesitylphosphine ($PMes_3$) complex, $[Cu(PMes_3)_2]BF_4$,[11] and the structure of the tribenzylphosphine (PBz_3) complex, $[Cu(PBz_3)_2][CuBr_2]$ (**1**).[12] The novel structural characteristics of **1** prompted us to examine further the coordination chemistry of copper(I) with PBz_3 in an attempt to obtain other examples of two-coordinate copper(I) for solid-state ^{31}P NMR spectroscopic studies. With hexafluorophosphate as the counterion, we were able to isolate another two-coordinate complex, viz., $[Cu(PBz_3)_2]PF_6$ (**2**). We report here the results of the X-ray structure determination of this complex and a comparison of the solid-state ^{31}P CPMAS NMR parameters of **1** and **2** with those obtained from a range of other two-, three-, and four-coordinate copper(I) phosphine complexes.

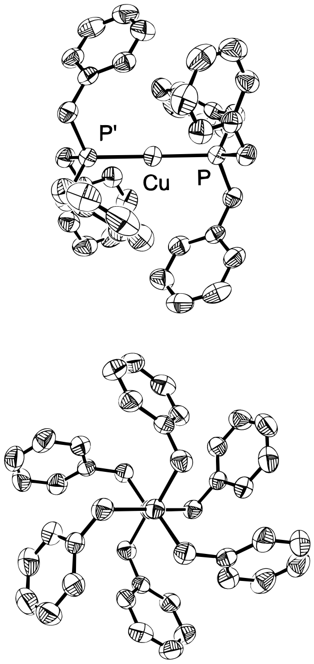

Figure 1. ORTEP diagrams showing two views of the cation in **2** with ellipsoids drawn at the 40% probability level.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[Cu(PBz_3)_2]PF_6$ (2)[a]

Cu−P(1)	2.191(1)	P(1)−C(3)	1.829(4)
Cu−P(1)#	2.191(1)	P(1)−C(1)	1.836(5)
P(1)−C(2)	1.826(5)		
P(1)−Cu−P(1)#	180.0	C(2)−P(1)−Cu	115.6(2)
C(2)−P(1)−C(3)	105.6(2)	C(3)−P(1)−Cu	114.0(1)
C(2)−P(1)−C(1)	105.4(2)	C(1)−P(1)−Cu	110.5(1)
C(3)−P(1)−C(1)	104.8(3)		

[a] Symmetry transformation used to generate equivalent atoms: (#) −*x*, −*y*, −*z*.

Results and Discussion

The reaction of PBz_3 with $[Cu(CH_3CN)_4]PF_6$ in a 2:1 molar ratio afforded air-stable, colorless crystals of $[Cu(PBz_3)_2]PF_6$ (**2**) in good yield. One tribenzylphosphine ligand is readily lost under the conditions used to record the positive ion liquid secondary ionization mass spectrum, the most prominent peak (based on ^{63}Cu) being assigned to the $[Cu(PBz_3)]^+$ ion at *m*/*z* 367 (100%), although the parent ion, $[Cu(PBz_3)_2]^+$, is seen as a moderately intense peak at *m*/*z* 671 (50%). Other strong peaks are $[Cu(PBz_2)]^+$ (276, 18%) and $[Cu(PBz)]^+$ (185, 19%); however, these latter two peaks form part of two clusters of peaks of similar intensity. Thus, peaks are also observed at *m*/*z* 275, 184, and 183 (assignable to $[Cu(PBz_2)\text{-}H]^+$, $[Cu(PBz) - H]^+$, and $[Cu(PBz) - 2H]^+$, respectively), indicating the possible formation of ortho-metalated species.

The single-crystal X-ray structure of **2** (Figure 1 and Table 1) confirms that the complex contains discrete $[Cu(PBz_3)_2]^+$ cations with a homoleptic "P_2" donor set, creating a linear two-coordinate environment for the copper(I) atom. In **2**, as in **1**,[12] the copper atom of the cation is located on a center of symmetry such that the P−Cu−P angle is exactly 180° and the two ligands are perfectly staggered and of opposite chirality; however, cation−anion interactions lead to subtle structural differences within the $[Cu(PBz_3)_2]^+$ cations. The exact 3-fold symmetry axis

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Table 2. Structural and Solid-State CPMAS ^{31}P NMR Chemical Shifts for Two-, Three- and Four-Coordinate Copper(I) Phosphine Complexes at $B_0 = 9.40$ T

	Cu−P, Å	δ, ppm	Δ_{21}, kHz	Δ_{32}, kHz	Δ_{43}, kHz	J, kHz	d, kHz	d_1, kHz	$d\nu_{Cu}$, 10^9Hz^2
$[Cu(PBz_3)_2]PF_6$	2.191(1)[a]	19[a]	0.98	1.66	1.93	1.56	0.24	0.05	25.4
$[Cu(PBz_3)_2][CuBr_2]$	2.195(1)[b]	20[a]	1.03	1.58	1.91	1.52	0.22	0.03	23.3
$[Cu(PTmp)_2]ClO_4$		−80[c]	1.35	2.02	2.19	1.90	0.21	0.06	23.3
[Cu(PTmp)Cl]	2.177(1)[d]	−63[d]	1.60	2.15	2.40	2.08	0.20	0.04	21.2
[Cu(PTmp)Br]	2.197(3)[d]	−63[d]	1.64	2.16	2.36	2.08	0.18	0.04	19.1
[Cu(PTmp)I]	2.188(4)[c]	−63[c]	1.62	2.10	2.30	2.03	0.17	0.04	18.0
$[Cu(PTol_3)Cl]_2$[l]	2.191(1)[e]	−20[f]	1.63	1.97	2.12	1.92	0.12	0.02	12.9
$[Cu(PPh_3)Cl]_4$	2.193(2)[g]	−9[f]	1.78	1.97	2.08	1.95	0.07	0.01	8.0
$[Cu(PPh_3)(cpy)]_2$[l]	2.192(2)[f]	−6[f]	1.58	1.67	1.71	1.65	0.03	0.01	3.5
$[Cu(PPh_3)_2(NO_3)]$	2.249(1)[h]	0[i]	1.20	1.45	1.58	1.42	0.09	0.01	10.0
$[Cu(PPh_3)_2(BH_4)]$	2.276(2)[j]	−1[i]	1.00	1.16	1.26	1.14	0.07	0.01	7.0
$[Cu(PPh_3)_2(AN)_2]BF_4$[l]	2.258(4)[k]	−3[k]	1.22	1.31	1.37	1.30	0.04	0.00	4.0
	2.276(4)	4	1.09	1.15	1.18	1.14	0.02	0.00	2.5

[a] This work, J values ±0.01 kHz. [b] Reference 12. [c] Reference 10. [d] Reference 8. [e] Reference 7. [f] Reference 6. [g] Reference 25. [h] Reference 26. [i] Reference 27. [j] Reference 28. [k] Reference 9. [l] cpy = 4-cyanopyridine, AN = acetonitrile, $PTol_3$ = tris(2-methylphenyl)phosphine.

along P−Cu−P, seen in **1**,[13] is lost as the F(3) and F(3′) of the PF_6^- anion interact (F···H 2.41(5) Å) with the ortho hydrogens on one of the phenyl groups on each of the PBz_3 ligands (H(15) and H(23′), respectively) such that the Cu−P−C angles, each 113.0(2)° in **1**, are distributed between 110.5(1) and 115.6(2)° in **2**. This results in a suprastructure of infinite one-dimensional chains of PF_6^- anions and $[Cu(PBz_3)_2]^+$ cations.

In both structures, the phenyl groups on the PBz_3 ligands sweep back over the copper atom to generate a novel intramolecular form of the "sextuple phenyl embrace" (SPE)[14] between the two phosphines in which hydrogen atoms from each phenyl are directed toward the plane of a phenyl group on the opposite ligand. Atom−atom potential energy calculations[14] show SPE interactions to be strongly attractive, with stabilization energies estimated to range between 60 and 85 kJ mol^{-1}, and provide a compelling reason for the preference shown for the formation of the two-coordinate bis(phosphine) cation rather than two-coordinate 1:1 $[Cu(PBz_3)X]$ or three-coordinate 1:2 $[Cu(PBz_3)_2X]$ complexes, both of which would cause significant disruption to the SPE interactions. The Cu−P bond lengths of 2.191(1) Å for **1** and 2.196(1) Å for **2** are short compared with the corresponding distance of 2.242(2) Å reported for $[Cu(PMes_3)_2]BF_4$.[11] The shortening of Cu−P in these complexes is likely to reflect not only the increased basicity and decreased steric crowding of the PBz_3 ligand compared to $PMes_3$ but also, potentially, the role played by the SPE interaction in pulling the two ligands closer together than would otherwise be the case.

The parameters for the ^{31}P CPMAS NMR spectra of **1** and **2** at a field strength of 9.40 T, together with structural and NMR data for a representative range of two-, three-, and four-coordinate copper(I) phosphine complexes, are reported in Table 2. The spectra of **1** and **2** correspond closely to those reported for other copper(I)−phosphine complexes studied at high fields (>7 T) and governed by slow ^{63,65}Cu relaxation conditions[3−10] in that they consist of a superposition of two similar ^{31}P−^{63}Cu and ^{31}P−^{65}Cu asymmetric quartets for each crystallographically independent phosphorus atom. The magnitude of this asymmetry is determined by the degree of the quadrupolar perturbation to the Zeeman states, and by how this perturbation impinges upon the overall MAS averaging when combined direct (dipolar) and indirect (scalar J) couplings between the ^{31}P ($I = {}^1/_2$, natural abundance 100%) and ^{63,65}Cu ($I = {}^3/_2$, natural abundances 69.09%, 30.91%) isotopes need to be considered.[15−20] The two quartets are not generally resolved, and observed spectra are dominated by the ^{63}Cu spectrum, with the ^{65}Cu spectrum identified (when the line width is sufficiently narrow) as a splitting of the outer peaks of the quartet.

Analysis of the quadrupolar effects as a first-order perturbation of the J spectrum[18] predicts the outer two lines (δ_1, δ_4) to shift to lower frequency and the inner two lines (δ_2, δ_3) to higher frequency by a field-dependent parameter d such that $(\Delta_{32} - \Delta_{21}) = (\Delta_{43} - \Delta_{32}) = 2d$, from which $d = (\Delta_{43} - \Delta_{21})/4$. Multiplication of d by the ^{63}Cu Zeeman frequency, ν_{Cu}, yields a field-independent parameter, $d\nu_{Cu}$, that enables direct comparison of the magnitude of these quadrupolar distortion effects from data recorded at different field strengths. In practice, higher order quadrupole effects result in the observed line spacings deviating from this first-order model with $(\Delta_{32} - \Delta_{21}) > 2d > (\Delta_{43} - \Delta_{32})$.[15,19] A complete calculation of the influence of these effects on the spectra of copper(I) complexes is beyond the scope of this present study, but a reasonable guide to the magnitude of these higher order interactions can be obtained as, under the experimental conditions, they cause a shift of peaks 1 and 3 to lower frequency and a shift of peaks 2 and 4 to higher frequency by a magnitude d_1 such that $\Delta_{21} = J - 2d - 2d_1$, $\Delta_{32} = J + 2d_1$, and $\Delta_{43} = J + 2d - 2d_1$; from which $d = (\Delta_{43} - \Delta_{21})/4$, as before, $J = (\Delta_{21} + 2\Delta_{32} + \Delta_{43})/4$, and $d_1 = (\Delta_{32} - J)/2$. For the present complexes and also for the other linear complexes listed in Table 2, the values of d_1 are relatively small by comparison with the first-order effects and will not be considered further here, except to note that they appear to be significantly greater than the values found for three- and four-coordinate complexes.

The values of 1.52 and 1.56 kHz for $^1J(^{31}P-^{63}Cu)$ (J) in **1** and **2**, respectively, are relatively small compared with the corresponding value of 1.90 found for $[Cu(PTmp)_2]ClO_4$ (PTmp

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(13) In $[Cu(PBz_3)_2][CuBr_2]$ (**1**)[12] the P−Cu−P axis lies on a 3-fold crystallographic symmetry axis generating C_3 symmetry for the ligands and S_6 symmetry for the cation. The $[CuBr_2]^-$ anion also lies along the 3-fold axis such that the bromide atoms interact symmetrically with the axial methylene hydrogens with the Br···H distances 3.4 Å.

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= tris(2,4,6-trimethoxyphenyl)phosphine) and are only 10% greater than the 1.4 kHz observed for the 1:2 four-coordinate triphenylphosphine complex [Cu(PPh_3)$_2$(NO_3)]. This 20% decrease in *J* appears unusual given the expected decrease in the Cu−P bond length in passing from the PTmp to the PBz_3 complexes and the general inverse correlation observed between *J* and the Cu−P distance (e.g. ref 21[21]), and it will be of interest to see if this develops as a trend after further structural and NMR studies on these and related complexes. SPE interactions in these complexes may also decrease the Cu−P bond lengths without a corresponding effect on the value the scalar coupling constant. In addition, the low values of *J* in these complexes may be caused by the interaction between the copper atom and the phenyl groups on the ligand, effectively increasing the coordination number of the copper. This can be discounted by the magnitude of the quadrupolar distortion parameters $d\nu_{Cu}$ (10^9 Hz^2) of 23.3 and 25.4 for **1** and **2**, which are similar to the values recorded for other linear copper(I) complexes (Table 2), and also the high ^{63}Cu nuclear quadrupolar coupling constants of 84.60(1) and 82.96(1) MHz[20] (cf. [Cu($PMes_3$)]Br, 70.9 MHz[22]), which clearly identifies the copper(I) environment in these complexes as purely two-coordinate. It is interesting to note that, even in the absence of available quadrupolar coupling constant data, the magnitudes of $d\nu_{Cu}$ clearly distinguish the family of two-coordinate complexes from three- and four-coordinate complexes.

Conclusions

This present study shows that bis(tribenzylphospine)copper(I) salts preferentially form two-coordinate linear "CuP_2" complexes as a result of the presence of a strongly attractive intramolecular sextuple phenyl embrace (SPE) between the two phosphine ligands. In the complexes formed, both the Cu−P bond lengths and the scalar spin−spin coupling constants $^1J(^{31}P-^{63}Cu)$ are smaller than might be expected on the basis of comparison with the available results for other copper(I) phosphine complexes. These effects may, in part, be a consequence of the SPE interactions, but further synthetic, structural, and spectroscopic studies are required to establish this.

Experimental Section

General Procedures. These have been reported previously.[23]

Synthesis of [Cu(PBz_3)$_2$][$CuBr_2$] (1). This was prepared following the method of Akrivos et al.[12]

Synthesis of [Cu(PBz_3)$_2$]PF_6 (2). To a stirred solution of [Cu(CH_3CN)$_4$][PF_6] (0.189 g, 0.508 mmol) in 30 mL of dichloromethane/ethanol (1:1) under dinitrogen was added solid PBz_3 (0.498 g, 1.637 mmol). The reaction mixture was heated under reflux for 5 min and then allowed to stand at room temperature for 1 h. The colorless crystals of **2** that were deposited were filtered, washed with ice-cold ethanol, and dried in vacuo. Yield = 0.465 g (81%). Anal. Calcd for $C_{42}H_{42}CuF_6P_3$: C, 61.8; H, 5.1. Found: C, 61.6; H, 4.7.

Table 3. Summary of Crystal, Intensity Collection, and Refinement Data for **2**

empirical formula	$C_{42}H_{42}CuF_6P_3$
fw	817.21
temp, °C	20(2)
wavelength, Å	0.710 73
cryst syst	monoclinic
space group	$C2/c$
a, Å	14.694(3)
b, Å	13.484(3)
c, Å	19.536(4)
β, (deg)	90.79(3)
V, Å^3	3870(1)
Z	4
ρ(calcd), g cm^{-3}	1.402
μ, cm^{-1}	7.47
final *R* indices [$F > 4\sigma(F)$]	$R(F_o) = 0.0406$, $Rw(F_o^2) = 0.1115^a$

[a] $wR^2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ where $w^{-1} = [\sigma^2(F_o2) + (aP)^2 + bP]$, ($a = 0.0658$; $b = 2.16$), and $P = [\max(F_o^2,0) + 2F_c^2]/3$. The structure was refined of F_o^2 using all data; $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

^{31}P CPMAS NMR Spectroscopy. Solid-state ^{31}P cross-polarization, magic-angle-spinning (CPMAS) NMR spectra were acquired at 9.40 T on a Bruker MSL-400 spectrometer operating at a ^{31}P frequency of 161.92 MHz. Spectra were acquired at ambient temperatures with ^{1}H $\pi/2$ pulse times of 3.5 μs, Hartmann−Hahn contact periods of 5 ms and recycle delays of 30 s common to all experiments, and an MAS rate of 10 kHz using a Bruker double-air-bearing probe system. Chemical shift data is referenced to 85% H_3PO_4 via an external setup reference sample of [NH_4][H_2PO_4] (δ = 1.0 ppm with respect to 85% H_3PO_4), and all spectra have been numerically processed (Fourier transformed) without the aid of line-broadening or weighting functions.

X-ray Structure Determination. A suitable crystal was obtained by diffusing diethyl ether vapor into a solution of **1** in acetonitrile. Data collection, reduction, solution, and refinement were performed as previously described,[24,] and a summary of the data is given in Table 3.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles (7 pages). Ordering information is given on any current masthead page.

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