type of structure. As far as we are aware of, this question has not been addressed before. We can advance a simple interpretation on the basis of the formal ionic charge on the halide atoms. For the less electronegative early transition metals, the M–X bonds will have more ionic character and the halogen atoms will be more negatively charged. This will result in a decreased electrostatic repulsion in the meridional structure, where these ligands are further apart from each other. For the more electronegative middle and late transition metals, the M–X bonds will become more covalent and the electrostatic destabilization will not be as important, therefore allowing both *mer* and *fac* isomers to be obtained. The examples mentioned above illustrate this point.[18-22] Even in these cases, however, the meridional structure is expected to be thermodynamically more stable in the absence of additional electronic (e.g. π bonding) or steric factors. This has proven to be the case for $RhCl_3(MeCN)_3$, where the *fac* isomer has been shown to convert to the *mer* isomer under thermal conditions.[20]

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Registry No. $MoCl_3(THF)_3$, 39210-30-5; $MoI_3(THF)_3$, 107680-52-4; *mer*-$MoI_3(PMe_3)_3$, 107680-53-5; $MoBr_3(THF)_3$, 39210-32-7; $Mo_2Br_4(CO)_8$, 80594-72-5; Br_2, 7726-95-6; $MoCl_3(dppe)(THF)$, 119455-61-7; $MoBr_3(dppe)(THF)$, 119455-62-8; $MoI_3(dppe)(THF)$, 119455-63-9; *mer*-$MoI_3(dppe)(THF){\cdot}THF$, 119455-64-0; $MoI_3(dppe)(MeCN)$, 119455-65-1; $MoCl_3(dppe)(MeCN)$, 119455-66-2; $MoBr_3(dppe)(MeCN)$, 119455-67-3; *fac*-$MoI_3(dppe)(PMe_3)$, 119455-68-4; $MoBr_3(dppe)(PMe_3)$, 119455-69-5.

Supplementary Material Available: Listings of the Nujol mull FTIR absorptions for all new compounds and full tables of crystal data, bond distances and angles, and anisotropic displacement parameters for the compounds $MoI_3(dppe)(THF)$, $MoI_3(dppe)(PMe_3)$, and $MoI_3(PMe_3)_3$ (15 pages); listings of observed and calculated structure factors for $MoI_3(dppe)(THF)$, $MoI_3(dppe)(PMe_3)$, and $MoI_3(PMe_3)_3$ (57 pages). Ordering information is given on any current masthead page.

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Solid-State ^{31}P NMR, Far-IR, and Structural Studies on Two-Coordinate (Tris(2,4,6-trimethoxyphenyl)phosphine)copper(I) Chloride and Bromide

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The reactions of acetonitrile solutions of copper(I) chloride, CuCl, and copper(I) bromide, CuBr, with the sterically hindered, highly basic tertiary phosphine ligand tris(2,4,6-trimethoxyphenyl)phosphine [$\equiv P(2,4,6)_3$] have been shown to form 1:1 monomeric adducts, [$P(2,4,6)_3CuX$]. The two compounds are isomorphous, crystallizing in the tetragonal space group $P4_3$. For the chloride, a = 15.237 (4) Å, c = 12.373 (3) Å, Z = 4, and R = 0.029 for 2339 "observed" ($I \geq 3\sigma(I)$) reflections, while for the bromide, a = 15.312 (8) Å, c = 12.457 (6) Å, Z = 4, and R = 0.052 for 2148 "observed" reflections. Cu–P is 2.177 (1) Å and Cu–Cl is 2.118 (2) Å in the chloro compound; for the bromide, Cu–P is 2.197 (3) Å and Cu–Br is 2.259 (2) Å. In both complexes, the copper atom is displaced toward the nearest *o*-methoxy oxygen with Cu···O = 2.629 (4) (Cl) and 2.628 (7) Å (Br); P–Cu–X angles are 172.97 (6) (Cl) and 172.00 (9)° (Br). Far-infrared spectra show expected strong ν(Cu–Cl) and ν(Cu–Br) bands at 355 and 262 cm^{-1}, respectively. Strong bands in the range 90–100 cm^{-1} are assigned to δ(P–Cu–X) bending modes. No bands assignable to ν(Cu–P) modes were observable. The solid-state ^{31}P NMR spectrum of the ligand is characterized by a single line at −73 ppm (with respect to 85% H_3PO_4). The spectrum for each complex shows an asymmetric quartet centered at −65 ppm with highly asymmetric line spacings of 1.40, 2.21, and 2.50 kHz and 1.48, 2.17, and 2.43 kHz, respectively. These data have been used to estimate copper nuclear quadrupole coupling constants for the two compounds.

Introduction

The solid-state ^{31}P NMR spectra of $[(PR_3)_mCuX]_n$ complexes have shown that each crystallographically independent phosphorus atom gives rise to a quartet of lines with asymmetric spacings due to Cu–P quadrupole coupling effects. For example, in the four-coordinate tetrahedral complex $[(PPh_3)_3CuBr]$,[2] the line spacings are 0.93, 0.94, and 0.93 kHz, whereas for the three-coordinate, trigonal-planar complex $[(PPh_3)_2CuBr]$,[3] these are 0.88, 1.28, and 1.44 kHz. We were interested to extend our NMR studies on this class of compound to two-coordinate linear complexes $[(PR_3)CuX]$ where the quadrupole coupling effects might be expected to be considerably greater. The tertiary phosphine ligand, tris(2,4,6-trimethoxyphenyl)phosphine [$\equiv P(2,4,6)_3$] is a highly basic, bulky ligand that would be expected to form metal complexes with low coordination numbers.[4] We have now isolated reasonably air-stable crystalline material of the complexes [$P(2,4,6)_3CuCl$] and [$P(2,4,6)_3CuBr$] and characterized these as monomeric, two-coordinate species by X-ray diffraction and far-infrared spectroscopic techniques and have recorded the solid-state ^{31}P NMR spectra of each compound. From these NMR data, we have estimated values for the copper quadrupole coupling constants. We report this work here.

Experimental Section

Preparation of Compounds. The ligand $P(2,4,6)_3$ was prepared according to the procedures outlined in the literature[4] by the reaction of $P(OPh)_3$ and (2,4,6-trimethoxyphenyl)lithium in diethyl ether, followed by recrystallization from ethanol of the solid product formed. [P-

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Table I. Summary of Crystal Data for [P(2,4,6)$_3$CuCl] and [P(2,4,6)$_3$CuBr]

	[P(2,4,6)$_3$CuCl]	[P(2,4,6)$_3$CuBr]
formula	$C_{27}H_{33}ClCuO_9P$	$C_{27}H_{33}BrCuO_9P$
fw	631.5	676.0
cryst syst	tetragonal	tetragonal
space group	$P4_3$ (C_4^4 – No. 78)	$P4_3$
a/Å	15.237 (4)	15.312 (8)
c/Å	12.373 (3)	12.457 (6)
V/Å^3	2873	2921
Z	4	4
D_c/g cm^{-3}	1.46	1.54
μ_{Mo}/cm^{-1}	9.0	21.4
A_{min}; A_{max}	1.17; 1.28	not recorded
T/K	295	295
N_o, N	2339, 2644	2148, 2776
R	0.029	0.052
R'	0.030	0.039

(2,4,6)$_3$CuCl] and [P(2,4,6)$_3$CuBr] were prepared by the dissolution of equimolar quantities of CuX and P(2,4,6)$_3$ in warm, degassed acetonitrile under argon, followed by slow cooling and filtration of the resultant colorless crystals. The crystals decompose slowly in air and were stored under argon. Anal. Calcd for [P(2,4,6)$_3$CuCl] ($C_{27}H_{33}ClCuO_9P$): C, 51.1; H, 5.7. Found: C, 50.5; H, 5.2. Calcd for [P(2,4,6)$_3$CuBr] ($C_{27}H_{33}BrCuO_9P$): C, 47.8; H, 5.3. Found: C, 46.6; H, 4.8.

Structure Determinations. A summary of crystal data is presented in Table I. The structures were solved by direct methods. Analytical absorption corrections were made. A 9 × 9 block diagonal refinement was employed for each compound, minimizing $\sum w\Delta^2$ and refining extinction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; x, y, z, and U_{iso} were included for hydrogen atoms constrained at estimated values. Each structure refined smoothly in the chosen space group with no anomalies with respect to features such as thermal ellipsoids or disorder. Agreement factors were higher in the enantiomeric space group. Neutral atom complex scattering factors were used;[5] computation used the XTAL program system[6] implemented by S. R. Hall on a Perkin-Elmer 3240 computer.

Spectroscopy. Solid-state ^{31}P spectra of the compounds were obtained at room temperature on a Bruker CXP-300 spectrometer at 121.47 MHz by using ^1H–^{31}P cross-polarization with radio frequency fields of 8 and 20 G, respectively. Chemical shift data were referenced to 85% H_3PO_4 via solid triphenylphosphine (δ = –9.9 ppm). Far-infrared spectra were recorded at ca. 298 K as petroleum jelly mulls between polyethylene plates on a Digilab FTS-60 Fourier transform infrared spectrometer employing a FTS-60V vacuum optical bench and a 6.25-μm Mylar beam splitter.

Results and Discussion

Single-Crystal X-ray Diffraction. The structures determined by X-ray diffraction are consistent with the stoichiometric and connectivity properties expected for two-coordinate phosphine–copper(I) halide complexes (Figure 1; Tables II and III). The Cu–P distance of 2.177 (1) Å for the chloride is 0.02 Å shorter than the 2.197 (3) Å found for the bromide; the latter is comparable with the value of 2.193 (2) Å found for P(mes)$_3$CuBr [mes ≡ 2,4,6-trimethylphenyl].[7] The Cu–X distances are longer than their counterparts in other two-coordinate LCuX complexes. For example, the Cu–Cl distance of 2.118 (1) Å is 0.03 Å longer than that of 2.087 Å found in the two-coordinate nitrogen base complex (tmpip)CuCl (tmpip ≡ 2,2,6,6-tetramethylpiperidine).[8] The Cu–Br distance of 2.259 (2) Å is 0.05 Å longer than the 2.209 (2) Å reported for (tmpip)CuBr and 0.03 Å longer than the distance of 2.225 (1) Å found for P(mes)$_3$CuBr.[7]

The P–Cu–X fragment lies approximately in the plane of phenyl ring 3 with the copper atom approached by the methoxy oxygen O(32). Cu···O(32) distances are 2.629 (4) (Cl) and 2.628 (7) Å (Br); the interaction appears to be attractive in nature and responsible for diminution of the P–Cu–X angles to 172.97 (6)° for the chloride and 172.00 (9)° for the bromide. Phenyl rings 1 and 2 are disposed above and below this plane, twisted in opposite directions to accommodate the bulky substituent groups [Cu–P–C(11)–C(12) = –48°; Cu–P–C(21)–C(22) = –50°] with Cu···O distances ranging between 2.882 (3) and 3.116 (8) Å. This conformation contrasts with the quasi-C_3 conformation found in the P(mes)$_3$ ligand[9] and its CuBr complex.[7]

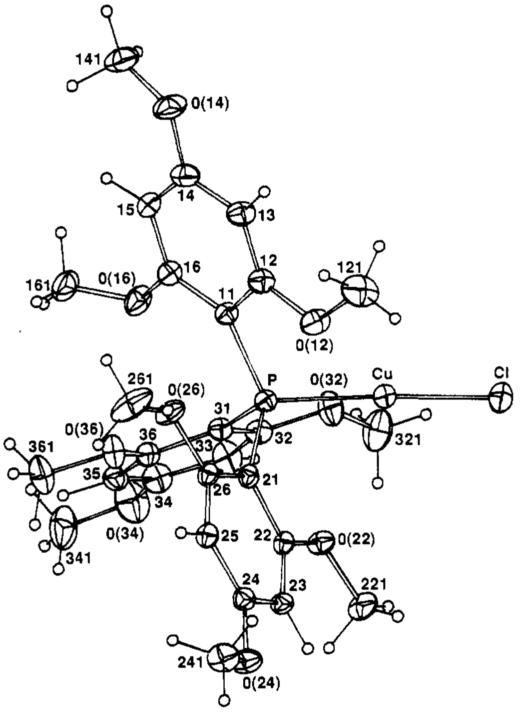

Figure 1. View of the molecule of [P(2,4,6)$_3$CuCl]. 20% thermal ellipsoids are shown. Hydrogen atoms have an arbitrary radius of 0.1 Å.

As a consequence of the steric influence of the methoxy substituents in the 2,6-positions of the phenyl rings, the C–P–C angles are opened out to average values of 108.5 (Cl) and 108.3° (Br) [cf. the following: PPh$_3$, 103.0°; P(*o*-tol)$_3$, 102.6 (3)°; P(mes)$_3$, 109.7°]. The P–C distances P–C(11) and P–C(21) lie in the normal range for aryl-substituted phosphines, ranging between 1.815 (5) and 1.828 (10) Å; the P–C(31) values of 1.798 (5) and 1.796 (9) Å are, however, marginally shorter, possibly as a result of the five-membered "chelate" ring structure formed by $\overline{\text{C(32)–O(32)···Cu–P–C(31)}}$.

It has been proposed that chelation of the acidic proton by methoxy groups may be one of the causes of the unusually high basicity of this ligand.[4] Certainly, the interaction between O(32) and copper in these complexes lends support to this possibility. Further speculation on this point, however, is premature in the absence of structural data on both the free ligand and its conjugate acid.

Far-Infrared Spectroscopy. The far-infrared spectra of the two complexes are shown in Figure 2. For complexes with a linear P–Cu–X arrangement, three new vibrational modes are expected in addition to those of the coordinated phosphine ligand. These are ν(Cu–P), ν(Cu–X), and δ(P–Cu–X). We have recently shown that ν(Cu–X) can be empirically correlated with the Cu–X bond length r.[10] For CuCl and CuBr complexes, this relationship may be represented by

$$\nu/\text{cm}^{-1} = b(r/\text{Å})^{-m} \qquad (1)$$

where b = 13 800 and 18 000 and m = 4.9 and 5.2 for X = Cl and Br, respectively. For the present complexes, this equation yields ν(Cu–Cl) = 350 cm^{-1} and ν(Cu–Br) = 260 cm^{-1}. Thus the

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Table II. Non-Hydrogen Atom Coordinates

	chloride			bromide		
atom	*x*	*y*	*z*	*x*	*y*	*z*
Cu[a]	0.65183 (3)	0.76853 (3)	1.0000 (-)	0.65013 (7)	0.77051 (7)	1.00000(−)
X	0.53277 (8)	0.78677 (9)	1.0854 (1)	0.52251 (6)	0.79116 (6)	1.0873 (1)
P	0.76443 (7)	0.74292 (8)	0.8964 (1)	0.7631 (1)	0.7447 (1)	0.8959 (2)
C(11)	0.7969 (3)	0.8373 (3)	0.8152 (4)	0.7959 (5)	0.8377 (5)	0.8150 (6)
C(12)	0.7286 (3)	0.8807 (3)	0.7592 (4)	0.7295 (5)	0.8822 (5)	0.7586 (8)
O(12)	0.6499 (2)	0.8406 (2)	0.7651 (3)	0.6497 (3)	0.8421 (4)	0.7659 (6)
C(121)	0.5753 (4)	0.8842 (4)	0.7246 (6)	0.5759 (6)	0.8843 (7)	0.721 (1)
C(13)	0.7432 (3)	0.9563 (3)	0.7033 (4)	0.7429 (5)	0.9570 (5)	0.7030 (8)
C(14)	0.8260 (4)	0.9925 (3)	0.7000 (4)	0.8254 (6)	0.9938 (5)	0.7017 (8)
O(14)	0.8341 (3)	1.0695 (2)	0.6427 (3)	0.8333 (4)	1.0707 (4)	0.6432 (6)
C(141)	0.9136 (4)	1.1163 (4)	0.6523 (7)	0.9136 (7)	1.1167 (6)	0.653 (1)
C(15)	0.8948 (3)	0.9527 (3)	0.7527 (5)	0.8941 (5)	0.9549 (5)	0.7527 (8)
C(16)	0.8800 (3)	0.8761 (3)	0.8093 (4)	0.8796 (5)	0.8772 (5)	0.8083 (7)
O(16)	0.9462 (2)	0.8397 (2)	0.8681 (3)	0.9447 (3)	0.8402 (4)	0.8679 (6)
C(161)	1.0316 (3)	0.8450 (4)	0.8311 (6)	1.0310 (6)	0.8472 (6)	0.833 (1)
C(21)	0.7334 (3)	0.6504 (3)	0.8123 (4)	0.7334 (5)	0.6516 (5)	0.8117 (6)
C(22)	0.6986 (3)	0.5783 (3)	0.8676 (3)	0.6971 (5)	0.5816 (5)	0.8678 (6)
O(22)	0.7002 (2)	0.5865 (2)	0.9781 (2)	0.6977 (4)	0.5890 (3)	0.9769 (4)
C(221)	0.6615 (4)	0.5194 (3)	1.0415 (4)	0.6598 (7)	0.5234 (6)	1.0414 (7)
C(23)	0.6653 (3)	0.5063 (3)	0.8162 (4)	0.6653 (5)	0.5078 (5)	0.8162 (7)
C(24)	0.6655 (3)	0.5039 (3)	0.7046 (4)	0.6674 (5)	0.5065 (5)	0.7055 (7)
O(24)	0.6296 (2)	0.4305 (2)	0.6609 (3)	0.6308 (4)	0.4321 (4)	0.6611 (5)
C(241)	0.6088 (4)	0.4293 (3)	0.5493 (4)	0.6121 (8)	0.4304 (6)	0.5513 (8)
C(25)	0.7000 (3)	0.5717 (3)	0.6460 (4)	0.7020 (5)	0.5725 (5)	0.6458 (7)
C(26)	0.7356 (3)	0.6436 (3)	0.6990 (4)	0.7352 (4)	0.6439 (5)	0.6998 (6)
O(26)	0.7742 (2)	0.7103 (2)	0.6456 (3)	0.7739 (4)	0.7123 (4)	0.6471 (5)
C(261)	0.7746 (5)	0.7112 (4)	0.5324 (4)	0.7739 (7)	0.7127 (7)	0.5366 (7)
C(31)	0.8571 (3)	0.7034 (3)	0.9721 (4)	0.8548 (5)	0.7062 (5)	0.9723 (6)
C(32)	0.8571 (3)	0.7082 (3)	1.0850 (4)	0.8544 (5)	0.7109 (5)	1.0832 (7)
O(32)	0.7857 (2)	0.7480 (2)	1.1317 (3)	0.7837 (4)	0.7509 (4)	1.1302 (5)
C(321)	0.7702 (4)	0.7314 (5)	1.2434 (5)	0.7689 (7)	0.7390 (8)	1.2394 (9)
C(33)	0.9243 (4)	0.6742 (4)	1.1450 (4)	0.9214 (6)	0.6779 (6)	1.1445 (7)
C(34)	0.9932 (3)	0.6374 (4)	1.0953 (5)	0.9905 (5)	0.6386 (5)	1.0961 (8)
O(34)	1.0574 (3)	0.6067 (3)	1.1665 (4)	1.0543 (4)	0.6086 (5)	1.1668 (7)
C(341)	1.1278 (4)	0.5654 (5)	1.1259 (6)	1.1235 (7)	0.5635 (8)	1.125 (1)
C(35)	0.9979 (3)	0.6285 (3)	0.9839 (5)	0.9956 (5)	0.6301 (5)	0.9852 (8)
C(36)	0.9289 (3)	0.6614 (3)	0.9233 (4)	0.9262 (5)	0.6638 (5)	0.9224 (8)
O(36)	0.9244 (2)	0.6575 (2)	0.8142 (3)	0.9227 (3)	0.6588 (4)	0.8157 (5)
C(361)	0.9927 (4)	0.6180 (4)	0.7561 (6)	0.9899 (6)	0.6202 (7)	0.756 (1)

[a] Defines origin.

Table III. Molecular Core Geometries for $[P(2,4,6)_3CuCl]$ and $[P(2,4,6)_3CuBr]$

	atoms	X = Cl	X = Br
distances/Å	Cu–X	2.118 (2)	2.259 (2)
	Cu–P	2.177 (1)	2.197 (3)
	P–C(11)	1.822 (4)	1.815 (9)
	P–C(21)	1.815 (5)	1.828 (10)
	P–C(31)	1.798 (5)	1.796 (9)
	Cu···O(12)	3.107 (4)	3.116 (8)
	Cu···O(22)	2.882 (3)	2.887 (6)
	Cu···O(32)	2.629 (4)	2.628 (7)
angles/deg	X–Cu–P	172.97 (6)	172.00 (9)
	Cu–P–C(11)	113.4 (1)	113.9 (3)
	Cu–P–C(21)	105.8 (1)	106.5 (3)
	Cu–P–C(31)	111.9 (2)	111.2 (3)
	C(11)–P–C(21)	111.6 (2)	111.2 (4)
	C(11)–P–C(31)	109.8 (2)	109.6 (4)
	C(21)–P–C(31)	104.1 (2)	104.0 (4)

strong bands at 355 and 262 cm^{-1} in the spectra of the chloride and bromide complexes respectively can be readily assigned as ν(Cu–X). Strong bands are also observed in the range 90–100 cm^{-1} in both complexes. These are close to the wavenumbers of the δ(X–Cu–X) modes in $[CuX_2]^-$, which occur at 110 and 81 cm^{-1} for X = Cl and Br, respectively.[11,12] Thus, the most likely assignment for these bands is to the δ(P–Cu–X) modes. It can be noted that similar bands are observed in the complexes (2,2,6,6-tetramethylpiperidine)CuX at 108 and 77 cm^{-1} for X = Cl and Br, respectively,[10] and would on this basis be assigned as δ(N–Cu–X). The assignment of ν(Cu–P) in the present complexes

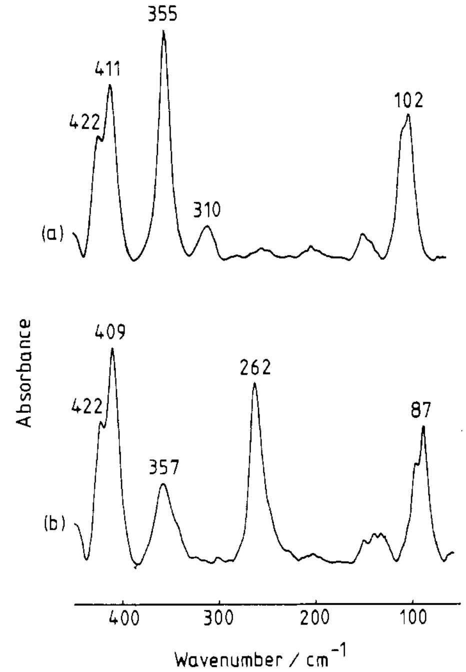

Figure 2. Far-infrared spectra of (a) $[P(2,4,6)_3CuCl]$ and (b) $[P(2,4,6)_3CuBr]$.

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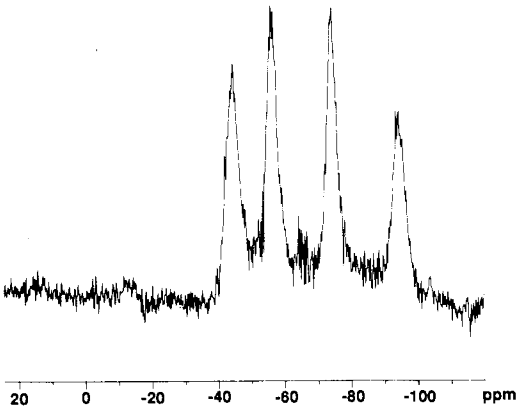

Figure 3. ^{31}P solid-state NMR spectrum of [P(2,4,6)$_3$CuCl].

is not as straightforward. In the closely related complexes PPh$_3$AuCl and PPh$_2$MeAuCl, bands at 182 and 359 cm^{-1}, respectively, have been assigned to ν(Au–P) modes by previous workers.[13,14] However, the difference between these frequencies seems to be too great, considering the similarity of the ligands involved, and this casts some doubt on the validity of the assignments. In the present complexes there are no bands in the far-IR spectra that can be readily assigned as ν(Cu–P).

Solid-State ^{31}P NMR. The solid-state ^{31}P NMR spectrum of the P(2,4,6)$_3$ ligand shows a single sharp line at $\delta = -73$ ppm (with respect to 85% H$_3$PO$_4$). The spectrum of each complex shows an asymmetric quartet centered at −65 ppm with line spacings of 1.40, 2.21, and 2.50 kHz and 1.48, 2.17, and 2.43 kHz for the chloride and bromide complexes, respectively (Figure 3). This asymmetric quartet splitting has been observed in a wide range of $[(PR_3)_mCuX]_n$ complexes and is due to the combined effects of scalar and dipolar spin–spin coupling between the phosphorus nucleus (^{31}P, nuclear spin $I = {}^1/_2$) and the copper nucleus (^{63}Cu, ^{65}Cu, nuclear spin $S = {}^3/_2$) and the copper nuclear quadrupole coupling. This has been discussed previously by Menger and Veeman,[15] who presented calculations of the line positions for the components of the quartet in terms of the various coupling constants involved. These are the copper nuclear Zeeman interaction $\gamma_S\hbar B$, the copper nuclear quadrupole coupling constant e^2qQ, and the phosphorus–copper scalar and dipolar coupling constants a and $\mu_0\gamma_I\gamma_S\hbar^2/4\pi r^3$ (r = the Cu–P bond length). Menger and Veeman carried out their calculations for the case in which the ratio R of the dipolar to the scalar coupling constant

$$R = \frac{\mu_0\gamma_I\gamma_S\hbar^2}{4\pi a r^3} \qquad (2)$$

is equal to 0.5 and calculated the quartet line positions as a function of the parameter

$$K = \frac{-3e^2qQ}{4S(2S-1)\gamma_S\hbar B} \qquad (3)$$

which is proportional to the ratio of copper quadrupole coupling constant to the copper nuclear Zeeman term. From these calculated line positions we can determine the spacings $\Delta\nu_i$ (i = 1–3) between adjacent lines in the quartet; these are given in Figure 4 in terms of the dimensionless quantity $h(\Delta\nu_i)/a$ as a function of K. For a fixed magnetic field strength B, K is proportional to the nuclear quadrupole coupling constant e^2qQ (eq 3). Previously, we have indicated the asymmetry of the line spacing in terms of the differences in absolute frequencies ($\Delta\nu_3 - \Delta\nu_1$). However, this parameter has the disadvantage that it depends on both a and e^2qQ, and it is clear that the ratio $\Delta\nu_3/\Delta\nu_1$ is a better indicator of the magnitude of the nuclear quadrupole coupling constant. This ratio is plotted as a function of K in Figure 5. The K values

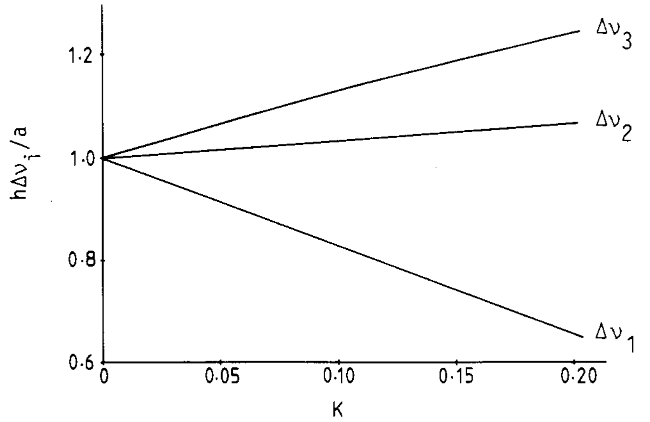

Figure 4. Plot of reduced quartet splittings $h(\Delta\nu_i)/a$ (a = phosphorus–copper scalar coupling constant) as a function of K (eq 3).

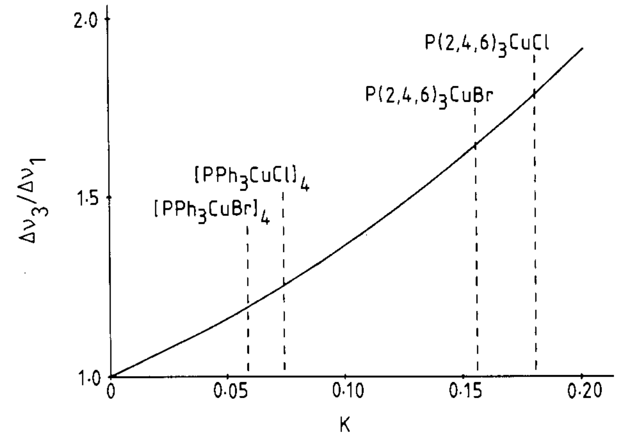

Figure 5. Plot of the quartet splitting ratio $\Delta\nu_3/\Delta\nu_1$ as a function of K.

obtained from the $\Delta\nu_3/\Delta\nu_1$ values for P(2,4,6)$_3$CuX (X = Cl, Br) are 0.182 and 0.156, respectively. From eq 3 the corresponding nuclear quadrupole coupling constants are 55 (Cl) and 47 MHz (Br). The data in Figure 4 can be used also to determine the scalar coupling constants from the observed line spacings $\Delta\nu_i$. This yields a/h = 2.06 (Cl) and 2.04 kHz (Br). With use of the Cu–P bond lengths determined from the X-ray crystal structures, the R values calculated from eq 2 are 0.61 and 0.59, respectively. These are somewhat larger than the value R = 0.50 that was used in the calculation of the line positions and upon which the present analysis is based. The value of R used is expected to significantly affect the value of e^2qQ/h.[15] For example, we have carried out a similar analysis of the results for the "cubane" [PPh$_3$CuX]$_4$ (X = Cl, Br) species. The ^{31}P solid-state NMR spectra[16] and structures[16,17] of these compounds have been reported previously. The results are, for X = Cl and Br respectively, as follows: e^2qQ/h = 22.2 and 17.4 MHz; a/h = 1.96 and 1.88 kHz; R = 0.62 and 0.63. The average e^2qQ/h value obtained for [PPh$_3$CuCl]$_4$ directly from a nuclear quadrupole resonance (NQR) study is 26.7 MHz,[18] which is about 20% higher than the value obtained in the above analysis of the ^{31}P solid-state NMR data.

Despite the uncertainties in determining absolute values by the above procedure, the splitting ratio $\Delta\nu_3/\Delta\nu_1$ does appear to give a good indication of the *relative* magnitudes of the copper quadrupole coupling constants for series of related compounds. Thus, the coupling constants for [P(2,4,6)$_3$CuX] are considerably greater in magnitude than those for [PPh$_3$CuX]$_4$ (Figure 5), consistent with the fact that the coordination environment in the

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Table IV. Scalar Phosphorus-Copper Coupling Constants, a/h, and Bond Lengths, r(Cu-P), for a Number of (Triarylphosphine)copper(I) Halide Complexes[a]

compound	Cu coord no.	(a/h)/kHz	r(Cu-P)/Å	R^b
[P(2,4,6)$_3$CuCl]	2	2.04	2.18	0.61
[P(2,4,6)$_3$CuBr]	2	2.03	2.20	0.59
[PPh$_3$CuCl]$_4$	4	1.95	2.19	0.63
[PPh$_3$CuBr]$_4$	4	1.88	2.21	0.63
[(PPh$_3$)$_2$CuCl]·0.5C$_6$H$_6$	3	1.21	2.27	0.91
[(PPh$_3$)$_2$CuBr]·0.5C$_6$H$_6$	3	1.20	2.27	0.92
[(PPh$_3$)$_3$CuCl]	4	0.93	2.35	1.07
[(PPh$_3$)$_3$CuBr]	4	0.93	2.35	1.07

[a] ^{31}P solid-state NMR and structural data from this work and ref 2, 3, 16, and 17. [b] R is the ratio of the Cu-P dipolar coupling constant to the Cu-P scalar coupling constant (eq 2).

latter case is closer to tetrahedral, where the copper quadrupole coupling constant would be zero. Also, for both sets of compounds, the coupling constant for the chloro compound is greater than that for the bromo compound. This is consistent with the previously observed trend for the CuX and [CuX$_2$]$^-$ species, which has been attributed to a greater contraction of the Cu 4p$_z$ orbital in the chloro complex relative to the bromo complex.[19,20] In the L$_n$CuX complexes there is the additional factor that CuCl is expected to be a stronger electron acceptor than CuBr, so the population of the Cu 4p$_z$ orbital is likely to be greater in the CuCl complexes, resulting in a greater copper quadrupole coupling constant.

The scalar phosphorus-copper coupling constants a/h determined by the above procedure are in all cases almost exactly equal to the mean of the three line spacings. From the data used to construct Figure 5, it can be shown that this is true to within an error of less than 1% for $0 < K < 0.2$. The scalar coupling constants obtained for [P(2,4,6)$_3$CuX] and for a number of related compounds with different copper coordination numbers are given in Table IV. It is clear that there is no direct correlation of these coupling constants with the copper coordination number. There is, however, a reasonable correlation with the Cu-P bondlengths, the coupling constant decreasing with increasing bond length. The dipolar coupling constant is proportional to the inverse cube of the bond length, so this also decreases with increasing bond length. However, the rates of decrease of the two coupling constants with increasing r(Cu-P) are not the same, so that the ratio R of the dipolar to the scalar coupling (eq 1) increases with increasing r(Cu-P) (Table IV). This suggests that further progress in the determination of copper quadrupole coupling constants from phosphorus-copper splitting patterns may require that calculations be carried out for a range of R values above 0.5, the value used in the only available published analysis.[15] We are currently carrying out such calculations.

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Registry No. [P(2,4,6)$_3$CuCl], 119638-24-3; [P(2,4,6)$_3$CuBr], 119176-00-0.

Supplementary Material Available: Tables Sup I-Sup IV, listing non-hydrogen thermal parameters, the derived hydrogen positions, ligand non-hydrogen geometries, and crystal data (6 pages); tables of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

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Band Electronic Structure Study of the Electronic Instability in the Magnéli Phase Mo$_4$O$_{11}$

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To probe the origin of the resistivity anomaly in the Magnéli phases γ- and η-Mo$_4$O$_{11}$, we carried out tight-binding band electronic structure calculations on their common building block, the Mo$_6$O$_{22}$ layer made up of MoO$_6$ octahedra. With two d electrons per formula unit Mo$_4$O$_{11}$, the bottom three bands of the Mo$_6$O$_{22}$ layer are partially filled. The Fermi surfaces of those partially filled bands are all closed, in agreement with the observation that Mo$_4$O$_{11}$ is a two-dimensional metal. Nevertheless, the Fermi surfaces have a partial nesting consistent with the superlattice spots at (0, 0.23b^*, 0) observed for η-Mo$_4$O$_{11}$. A charge density wave associated with this partial nesting is most likely to cause the resistivity anomaly in γ- and η-Mo$_4$O$_{11}$.

The Magnéli phase Mo$_4$O$_{11}$ has two modifications, γ- and η-Mo$_4$O$_{11}$.[2] Both are two-dimensional (2D) metals at room temperature and exhibit a resistivity anomaly at low temperature (the phase transition temperature T_p = 100 and 109 K for γ- and η-Mo$_4$O$_{11}$, respectively).[3,4] Diffuse X-ray and electron scattering studies on η-Mo$_4$O$_{11}$ show that the resistivity anomaly originates from a charge density wave (CDW),[4a] which leads to the satellite peaks centered at (0, 0.23b^*, 0). Although the CDW affects the resistivity anisotropically, Mo$_4$O$_{11}$ retains its 2D metallic character

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