

have later recognized<sup>5</sup> that bond energies determined by iodination<sup>3</sup> may need to be reassessed. However, the difference between the earlier<sup>26</sup> and present experiments is not completely resolved: Walsh has noted<sup>20</sup> that application of the present approach to the iodination data yields  $D_{298}(\text{H-Si}(\text{CH}_3)_3) \approx 390 \text{ kJ mol}^{-1}$ .

**3. Implications of the Derived  $D_{298}(\text{H-Si}(\text{CH}_3)_3)$ .** Our estimate of  $D_{298}(\text{H-Si}(\text{CH}_3)_3) = 398 \pm 6 \text{ kJ mol}^{-1}$  may be combined with  $\Delta H_{f,298}(\text{H})^{12} = 218.0 \text{ kJ mol}^{-1}$  and  $\Delta H_f(\text{HSi}(\text{CH}_3)_3)^{29} = -163 \pm 4 \text{ kJ mol}^{-1}$  to yield a new value of  $\Delta H_{f,298}(\text{Si}(\text{CH}_3)_3) = 17 \pm 7 \text{ kJ mol}^{-1}$ . In turn, this  $\Delta H_f$  may be combined with the recently redetermined  $\Delta H_{f,298}(\text{Si}_2(\text{CH}_3)_6, \text{g})^5 = -304 \pm 6 \text{ kJ mol}^{-1}$  to derive a new value of  $D_{298}((\text{CH}_3)_3\text{Si-Si}(\text{CH}_3)_3) = 338 \pm 12 \text{ kJ mol}^{-1}$ . Interestingly, this is almost the same as the value of  $344 \pm 10 \text{ kJ mol}^{-1}$  discussed by Pilcher et al.,<sup>5</sup> even though that value is based instead on  $\Delta H_{f,298}(\text{Si}(\text{CH}_3)_3) = -3 \pm 7 \text{ kJ mol}^{-1}$ . This observation provides a resolution of the discrepancy noted by Pilcher et al. between their  $\Delta H_{f,298}(\text{Si}_2(\text{CH}_3)_6, \text{g}) = -304 \pm 6 \text{ kJ mol}^{-1}$  determined via reaction-solution calorimetry and the value of  $-349 \pm 15 \text{ kJ mol}^{-1}$  derived from kinetics: the kinetic analysis was based on an essentially correct Si-Si bond energy coupled with an erroneous  $\Delta H_{f,298}(\text{Si}(\text{CH}_3)_3)$ .

We can also compare the Si-Si bond energy in  $\text{Si}_2(\text{CH}_3)_6$  with that in  $\text{Si}_2\text{H}_6$ . The  $\Delta H_{f,298}(\text{Si}_2\text{H}_6)^{30}$  of  $80.3 \pm 1.5 \text{ kJ mol}^{-1}$  and the recently determined  $\Delta H_{f,298}(\text{SiH}_3)^{10}$  of  $200.8 \pm 3.4 \text{ kJ mol}^{-1}$  imply  $D_{298}(\text{H}_3\text{Si-SiH}_3) = 321 \pm 5 \text{ kJ mol}^{-1}$ . Methyl substitution therefore appears to increase both the Si-H and Si-Si bond strengths. Further experiments to test this idea, by examination

of the thermochemistry of  $\text{H}_2\text{Si}(\text{CH}_3)_2$  and  $\text{H}_3\text{SiCH}_3$ , are desirable. It is also important to make direct observations of the reverse of reaction 2, i.e.  $\text{Si}(\text{CH}_3)_3 + \text{HBr}$ , which is critical in the estimation of  $\Delta H_f(\text{Si}(\text{CH}_3)_3)$ . Clearly, the greater reactivity of  $\text{HSi}(\text{CH}_3)_3$  toward O atoms, by comparison with  $\text{SiH}_4$ , does not reflect a lower Si-H bond energy in the former molecule: work on this topic is continuing.

## 5. Conclusions

The kinetics of the reactions of Cl and Br with trimethylsilane have been measured. The results are used to derive a new Si-H bond dissociation enthalpy of  $398 \pm 6 \text{ kJ mol}^{-1}$ , which suggests that methyl substitution in  $\text{SiH}_4$  increases the Si-H bond strength. This observation is confirmed by the ab initio investigation of a homodesmotic reaction that links the bond strength of  $\text{SiH}_4$  and  $\text{HSi}(\text{CH}_3)_3$ . The bond strength is used to derive a new value for  $\Delta H_f(\text{Si}(\text{CH}_3)_3)$ , which rationalizes a previous discrepancy concerning  $\Delta H_f(\text{Si}_2(\text{CH}_3)_6)$ . The results also suggest that methyl substitution in  $\text{Si}_2\text{H}_6$  increases the Si-Si bond dissociation enthalpy.

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**Registry No.**  $\text{SiH}_3$ , 13765-44-1;  $\text{SiH}_4$ , 7803-62-5; atomic chlorine, 22537-15-1; atomic bromine, 10097-32-2; trimethylsilane, 993-07-7; trimethylsilyl, 16571-41-8.

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## Study of Quadrupole-Perturbed Quartets in the Solid-State Magic-Angle Spinning $^{31}\text{P}$ NMR Spectra of Phosphine-Cu(I) Complexes. $^{63}\text{Cu}$ Electric Field Gradients and Anisotropy in the $^{31}\text{P}$ , $^{63}\text{Cu}$ Scalar Coupling

Alejandro Olivieri

Contribution from the Departamento de Quimica Analitica, Facultad de Ciencias Bioquimicas y Farmaceuticas, Suipacha 531, Rosario 2000, Argentina. Received July 5, 1991

**Abstract:** High-resolution solid-state  $^{31}\text{P}$  NMR spectra of phosphine-containing Cu(I) complexes show field-dependent, distorted quartets in which the line separations are not constant. This phenomenon is due to the combination of scalar  $J(^{31}\text{P}, ^{63}\text{Cu})$  coupling with incompletely averaged dipolar and anisotropic  $J$  interactions. A simple analysis is presented on literature data involving a series of compounds of the  $\text{P}_n\text{CuX}_m$  type (P = triphenylphosphine and derivatives, X = halide) having different Cu coordination numbers and core geometries. It is concluded that the quartet distortion is related to structural data (P-Cu bond distances and ligand-Cu-ligand angles) and interesting molecular data ( $^{63}\text{Cu}$  quadrupole coupling constants and anisotropy ( $\Delta J$ ) in the  $^{31}\text{P}$ ,  $^{63}\text{Cu}$  scalar coupling constant). In cases in which most of these data are available,  $\Delta J$  can be obtained and shows a fairly constant value of ca. +0.6 kHz. Extension to other cases leads to the calculation of  $\chi(^{63}\text{Cu})$ , both magnitude and sign. This information is discussed in light of a simple EFG analysis for the copper atom based on s-p hybridization schemes involving vacant  $\text{Cu}^+$  4p orbitals.

## Introduction

Great attention has been focused on copper(I) complexes as they show a remarkably wide variety of structures and Cu coordination numbers.<sup>1-5</sup> Halides of Cu(I) are known to form both

mono- and multinuclear complexes with phosphine ligands with coordination numbers ranging from 2 to 4.<sup>6</sup> Likewise, halogenocuprate anions react with phosphines to give several mono- and multinuclear structures.<sup>6,7</sup> In an elegant series of papers, Healy,

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White, and co-workers have produced a wealth of information concerning X-ray structural determinations as well as spectroscopic data (mainly infrared and solid-state magic-angle spinning  $^{31}\text{P}$  NMR spectroscopy).<sup>6-19</sup> While diffraction data have found a straightforward interpretation, providing coordination numbers and interesting geometrical parameters, the results derived from the application of  $^{31}\text{P}$  NMR spectroscopy to the solid complexes are somewhat lacking a similar status. These latter data undoubtedly merit further investigation, since they show the combined effects of  $^{31}\text{P}$ ,  $^{63}\text{Cu}$  scalar and dipolar coupling, and  $^{63}\text{Cu}$  being quadrupolar, they connect structural and molecular properties, such as bond distances and angles,  $^{63}\text{Cu}$  quadrupole coupling constants, and location of the electric field gradients (EFG) at the copper atom with respect to the molecular frame.<sup>20,21</sup> Further, the dipolar coupling may be superimposed to anisotropic  $J$  coupling effects, and this may lead to the indirect measurement of  $\Delta J$  ( $^{31}\text{P}$ ,  $^{63}\text{Cu}$ ), contributed to the very few known values of this magnitude.<sup>20,21</sup>

In recent years, the effect of quadrupolar nuclei on the high-resolution solid-state NMR spectra of spin  $-1/2$  nuclei has received great attention.<sup>20-25</sup> A considerable amount of work has been devoted to the study of  $^{13}\text{C}$ ,  $^{14}\text{N}$  pairs, as nitrogen-containing organic and biological samples are routinely probed through solid-state  $^{13}\text{C}$  NMR spectroscopy.<sup>26-29</sup> The phenomenon has been used to study complex line shapes arising from  $^{13}\text{C}$  nuclei coupled to several  $^{14}\text{N}$ ,<sup>29</sup> assignment of  $^{13}\text{C}$  signals,<sup>30,31</sup> conform-

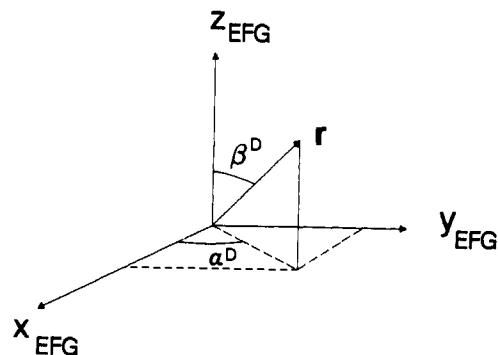


Figure 1. Orientation of the P,Cu internuclear vector  $r$  in the principal axis system of the electric field gradient tensor at the copper atom.

mation of macrocycles through nonbonded C,N interactions,<sup>32</sup> potential energy profiles in proton-exchanging solids,<sup>33</sup> etc. Data are also accumulating on other pairs of nuclei, such as ( $^{31}\text{P}$ ,  $^{14}\text{N}$ ) in phosphazenes;<sup>34</sup> ( $^{29}\text{Si}$ ,  $^{14}\text{N}$ ) in silicon ceramics;<sup>35,36</sup> ( $^{119}\text{Sn}$ ,  $^{35,37}\text{Cl}$ ) in organostannic compounds,<sup>20,37,38</sup> and ( $^{31}\text{P}$ ,  $^{27}\text{Al}$ ) in surface-immobilized substrates.<sup>39</sup> ( $^{31}\text{P}$ , high spin quadrupolar metals)<sup>40</sup> and ( $^{31}\text{P}$ ,  $^{63}\text{Cu}$ ) in phosphine-containing Cu(I) complexes.<sup>6-19,23</sup> In some of these cases, particularly when S has a spin greater than 1, the residual dipolar coupling has been found to be superimposed to both isotropic and anisotropic indirect coupling effects.<sup>20,21</sup> Although detailed theory is available,<sup>23</sup> it has been shown that the application of a simple first-order perturbation approach to this phenomenon is appropriate to study the qualitative aspect of line shapes, as well as to calculate the magnitude of the residual dipolar effects.<sup>20,21,25</sup> This method overcomes the use of full-Hamiltonian diagonalization and time-consuming space tiling procedures. The following equation has been previously derived and shown to apply to cases of coupling between spin  $-1/2$  and  $3/2$  nuclei:<sup>21</sup>

$$\nu_j = -jJ + (3\chi/20Z)[S(2S-1)]^{-1}[S(S+1) - 3j^2] \times \\ [(-\Delta J/3)(3 \cos^2 \beta^j - 1 + \eta \sin^2 \beta^j \cos 2\alpha^j) + \\ D(3 \cos^2 \beta^D - 1 + \eta \sin^2 \beta^D \cos 2\alpha^D)] \quad (1)$$

where  $\nu_j$  is the shift (relative to the unperturbed isotropic  $I$  frequency) produced by  $|j\rangle$  eigenstates of  $S$  ( $j = S, S-1, \dots, -S+1, -S$ ),  $J$  is the isotropic  $I,S$  scalar coupling constant ( $I = 1/2, S \geq 1$ ),  $D$  is the  $I,S$  dipolar coupling constant,  $\chi$  is the S quadrupole coupling constant,  $\eta$  is the asymmetry parameter of the electric field gradient (EFG) tensor at S,  $Z$  is the Zeeman frequency of S,  $\beta^D$  and  $\alpha^D$  are the polar and azimuthal angles which fix the location of the  $I,S$  internuclear vector in the principal axis system (PAS) of the quadrupolar tensor (Figure 1),  $\Delta J$  is the anisotropy in the J tensor ( $\Delta J = J_{\parallel} - J_{\perp}$ ; J is assumed axially symmetric), and  $\beta^j$  and  $\alpha^j$  define the orientation of the z axis of the J tensor in the principal axis system (PAS) of the EFG tensor. The first term ( $-jJ$ ) gives a quartet when  $S = 3/2$ , and the second one acts as a perturbation on the former, leading to field-dependent, distorted quartets in which the line separations are not constant.<sup>21</sup> This is the basis on which the experimental data for phosphine-containing Cu complexes will be explained. It is usual to assume that the principal axis of the J tensor lies along the internuclear

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line, so that  $\alpha^j = \alpha^D$  and  $\beta^j = \beta^D$ , and eq 1 becomes (upon introducing  $S = 3/2$ )

$$\nu_j = -jJ + (3\chi/80Z)(5 - 4j^2)(D - \Delta J/3) \times (3 \cos^2 \beta^D - 1 + \eta \sin^2 \beta^D \cos 2\alpha^D) \quad (2)$$

Equation 2 can be used in two ways. If enough information is available, i.e., experimentally determined quadrupole coupling constants and molecular location of EFG tensors (from nuclear quadrupole resonance measurements), P,Cu bond distances (from diffraction data), and  $^{31}\text{P}$  NMR line frequencies from high-resolution solid-state NMR studies, then it would be possible to establish the existence of anisotropic  $\Delta J$  effects, which will otherwise be difficult to distinguish from dipolar effects. On the other hand, eq 2 can be extended to cases where only diffraction and  $^{31}\text{P}$  NMR data are known, in order to determine the values and signs of  $^{63}\text{Cu}$  quadrupole coupling constants. The latter possibility is relevant in that signs of  $\chi$  are not normally obtained from NQR spectra (however see ref 41).

In the present paper, this approach is applied to several complexes of the type  $\text{P}_n\text{CuX}_m$  (P = triphenylphosphine and derivatives; X = halide) showing different Cu coordination numbers. After studying cases where all pertinent information is at hand, it is shown that the application of eq 2 leads to the determination of the anisotropic part of the P,Cu scalar  $J$  coupling. Extension of the above analysis to other, less characterized cases results in the calculation of  $^{63}\text{Cu}$  quadrupole coupling constants with their appropriate signs. The implications of the magnitudes and signs of the calculated  $\chi$  concerning the Cu coordination numbers and the electron population of Cu-ligand  $\sigma$  orbitals are also discussed. It should be noticed that the present approach is only applied to the study of the quartet appearance of the central band in MAS spectra. Additional information can be obtained by analyzing the spinning side band manifolds, which arise from the interplay of the dipolar coupling, the indirect scalar coupling, and the chemical shift tensors.<sup>40</sup> This latter analysis may directly yield the magnitude of the "effective" dipolar coupling constant ( $D - \Delta J/3$ ), although an ambiguity in its sign remains.<sup>40</sup>

### Theory

The application of first-order perturbation theory to the residual dipolar coupling effect in the case of a quadrupolar spin -1 nucleus is well-documented.<sup>25</sup> Coupling between spin  $-1/2$  and spin  $-3/2$  nuclei has also been previously discussed, but with less detail.<sup>21</sup> In particular, second-order effects were not given attention. In this section, the main results are briefly described, and emphasis is given on the appropriate interpretation of distorted quartets so as to highlight the first-order effects described by eq 2.

The failure of magic-angle spinning to remove the  $I,S$  dipolar interaction is due to the admixture of  $S$  Zeeman states induced by the quadrupole interaction. Perturbed Zeeman-quadrupole states  $|\psi_j\rangle$  are derived from unperturbed Zeeman  $S$  states  $|k\rangle$  through

$$|\psi_j\rangle = \sum_k a_{jk}|k\rangle \quad (j, k = 3/2, \dots, -3/2) \quad (3)$$

$$a_{jk} = {}^0a_{jk} + {}^1a_{jk} + {}^2a_{jk} + \dots \quad (4)$$

$${}^0a_{jk} = \delta_{jk} \quad (5)$$

$${}^1a_{jk} = -Q_{jk}/(E_j - E_k) \quad (j \neq k) \quad (6)$$

$${}^1a_{jj} = 0 \quad (7)$$

$${}^2a_{jk} = -Q_{jj} Q_{kj}/(E_k - E_j)^2 + \sum_{m \neq j} Q_{mj} Q_{km}/(E_m - E_j)(E_k - E_j) \quad (j \neq k) \quad (8)$$

$${}^2a_{jj} = -(1/2) \sum_{k \neq j} |Q_{kj}|^2/(E_k - E_j)^2 \quad (9)$$

where  $Q_{jk} = \langle j|H_Q|k\rangle$ .

**Table I.** Relative Values of the Integrals  $Q_{jk} = \langle j|H_Q|k\rangle$  and the First-Order ( ${}^1a_{jk}$ ) and Second-Order ( ${}^2a_{jk}$ ) Coefficients in the Expansion (Equation 3) of  $^{63}\text{Cu}$  Eigenstates<sup>a</sup>

	j	k			
		3/2	1/2	-1/2	-3/2
$Q_{jk}$	3/2	$Q_{11}$	$Q_{12}$	$Q_{13}$	0
	1/2	$Q_{12}^*$	$-Q_{11}$	0	$Q_{13}$
	-1/2	$Q_{13}^*$	0	$-Q_{11}$	$-Q_{12}$
	-3/2	0	$Q_{13}^*$	$-Q_{12}^*$	$Q_{11}$
${}^1a_{jk}$	3/2	0	${}^1a_{12}$	${}^1a_{13}$	0
	1/2	$-{}^1a_{12}^*$	0	0	${}^1a_{13}$
	-1/2	$-{}^1a_{13}^*$	0	0	$-{}^1a_{12}$
	-3/2	0	$-{}^1a_{13}^*$	${}^1a_{12}^*$	0
${}^2a_{jk}$	3/2	${}^2a_{11}$	${}^2a_{12}$	${}^2a_{13}$	${}^2a_{14}$
	1/2	$-{}^2a_{12}^*$	${}^2a_{11}$	${}^2a_{23}$	${}^2a_{13}$
	-1/2	$-{}^2a_{13}^*$	$-{}^2a_{23}^*$	${}^2a_{11}$	${}^2a_{12}$
	-3/2	$-{}^2a_{14}^*$	$-{}^2a_{13}^*$	$-{}^2a_{12}^*$	${}^2a_{11}$

<sup>a</sup>Only relative values are intended to be presented in this table. Subscripts refer to  $^{63}\text{Cu}$  eigenstates according to the following:  $|1\rangle = |3/2\rangle$ ;  $|2\rangle = |1/2\rangle$ ;  $|3\rangle = |-1/2\rangle$ ;  $|4\rangle = |-3/2\rangle$ .

If the orientation of the internuclear vector  $\mathbf{r}_{IS}$  in the Zeeman frame is defined by the angles  $\Omega$  and  $\phi$  and assuming, as before, that the  $J$  tensor is axially symmetric with  $J_{||}$  directed along  $\mathbf{r}$ , then the frequency shift  $\nu_j$  caused by the  $|\psi_j\rangle$  state on the  $I$  line is given by:<sup>21</sup>

$$\begin{aligned} \nu_j &= -\langle \psi_j | H_J + H_D | \psi_j \rangle \\ &= -jJ - (D - \Delta J/3) \langle \psi_j | S_z (1 - 3 \cos^2 \Omega) - \\ &\quad (3/2) \{ \sin \Omega \cos \Omega \} [S_+ \exp(-i\phi) + S_- \exp(i\phi)] | \psi_j \rangle \end{aligned} \quad (10)$$

Introducing eqs 4-9 the following zero-, first-, and second-order shifts result:

$${}^0\nu_j = -jJ - j(D - \Delta J/3)(1 - 3 \cos^2 \Omega) \quad (11)$$

$${}^1\nu_j = (3/2)(D - \Delta J/3) \{ \sin \Omega \cos \Omega \} [ \exp(-i\phi) \times (\sqrt{+} {}^1a_{j,j+1}^* + \sqrt{-} {}^1a_{j,j-1}) + \exp(i\phi) (\sqrt{+} {}^1a_{j,j+1} + \sqrt{-} {}^1a_{j,j-1}^*) ] \quad (12)$$

$$\begin{aligned} {}^2\nu_j &= -(D - \Delta J/3) \{ (1 - 3 \cos^2 \Omega) (\sum_k |k| a_{jk}|^2 + 2j^2 a_{jj}) - \\ &\quad (3/2) \{ \sin \Omega \cos \Omega \} [ \exp(-i\phi) (\sqrt{+} {}^2a_{j,j+1}^* + \\ &\quad \sqrt{-} {}^2a_{j,j-1} + \sum_k \sqrt{-} {}^1a_{jk}^* {}^1a_{j,k-1}) + \\ &\quad \exp(i\phi) (\sqrt{+} {}^2a_{j,j+1} + \sqrt{-} {}^2a_{j,j-1} + \sum_k \sqrt{+} {}^1a_{jk}^* {}^1a_{j,k+1}) ] \} \end{aligned} \quad (13)$$

where  $\sqrt{+} = [S(S+1) - j(j+1)]^{1/2}$  and  $\sqrt{-} = [S(S+1) - j(j-1)]^{1/2}$ .

Since the term  $(1 - 3 \cos^2 \Omega)$  averages to zero with MAS, the contribution due to eq 11 is reduced to the multiplet term  $(-jJ)$ . The first-order effect (eq 12) gives, using the information given in Table I,  ${}^1\nu_{\pm 3/2} = -{}^1\nu_{\pm 1/2} = \{(3^{3/2}/2)(D - \Delta J/3) \{ \sin \Omega \cos \Omega \} [ {}^1a_{12} \exp(-i\phi) + {}^1a_{12}^* \exp(i\phi) ] \}$  (see Table I for definitions of subscripts). This acts as a distortion on the  $^{31}\text{P}$  quartets, showing an angular dependence which is not averaged out by MAS, and constitutes the basis of the successful first-order perturbative approach.<sup>21,25</sup> As has been shown,<sup>21</sup> eq 12 leads to eq 2 once the proper values of the first-order coefficients are introduced, averaged over one cycle of magic angle rotation, and the centers of mass of the resulting powder patterns are calculated.<sup>21,25</sup> Assuming  $J(^{31}\text{P}, ^{63}\text{Cu})$  to be positive,<sup>23</sup> eq 2 predicts the following frequencies:  $(3/2)J + d$ ;  $(1/2)J - d$ ;  $(-1/2)J - d$ ; and  $(-3/2)J + d$ , where

$$d = -(3\chi/20Z)(D - \Delta J/3) \times (3 \cos^2 \beta^D - 1 + \eta \sin^2 \beta^D \cos 2\alpha^D) \quad (14)$$

so that the line separations are given by  $J + 2d$ ,  $J$ , and  $J - 2d$ .<sup>21</sup> Clearly,  $d$  is the distortion parameter affecting the quartet appearance. Figure 2 sketches the effect of the combined  $J$  multiplet structure and first-order quadrupole-perturbed coupling in this case.

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Table II. Different Types of  $P_nCuX_m$  Complexes Studied, Expected Values of  $\alpha^D$ ,  $\beta^D$ , and  $\eta$ , the Sign of  $\chi$ , and the Location of EFG Principal Axes

type	coord no.	core geom <sup>a</sup>	location of EFG	sign of $\chi^b$	$\beta^D$ , deg	$\eta$	$\alpha^D$ , deg
$P_3CuX$	4	T	$z$ along the CuX bond	-	100-109	0	NN <sup>c</sup>
$P_2CuX_2$	4	T	$z \perp$ to the XCuX plane $y \perp$ to the PCuP plane $x$ bisecting PCuP and XCuX angles	+	25-30	$\neq 0$	0
$PCuX_3$	4	T	$z$ along the CuP bond	+	0	0	NN
$P_2CuX$	3	P	$z \perp$ to the $P_2CuX$ plane $y \perp$ CuX bond $x$ along the CuX bond	-	90	$\neq 0$	$\approx 60$
$PCuX_2$	3	P	$z \perp$ to the PCuX <sub>2</sub> plane <sup>d</sup> $y$ along the CuP bond $x \perp$ to the CuP bond	-	90	$\neq 0$	90
$PCuX$	2	L	$z$ along the PCuX line	+	0	0	NN

<sup>a</sup>T = tetrahedral; P = planar trigonal; L = linear. <sup>b</sup>See also Table III. <sup>c</sup>NN = not needed (when  $\beta^D = 0$  and/or when  $\eta = 0$ ,  $d$  is independent of  $\alpha^D$ ). <sup>d</sup>The orientation of EFG axes in these cases coincides with that experimentally obtained from the study of the Zeeman effect on the NQR lines of the trigonal site in  $(Ph_3P)_3Cu_2Br_2$ .<sup>42</sup>

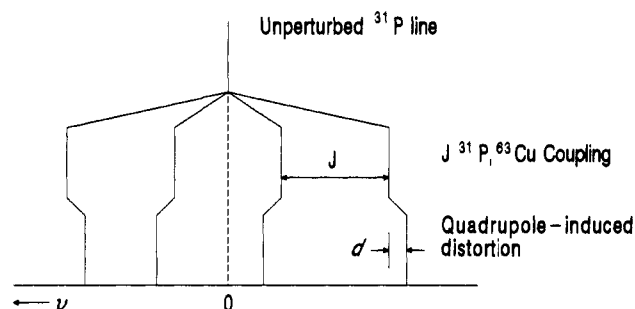


Figure 2. Scheme corresponding to a  $^{31}P$  solid-state NMR quartet showing the combined effects of the isotropic  $J(P,Cu)$  scalar coupling and the quadrupole-perturbed dipolar and anisotropic scalar couplings ( $d$ ). In the figure  $d$  is negative, as observed in phosphine-Cu(I) complexes.

The second-order effects (eq 13) are considered here in order to show how to interpret the  $^{31}P$  NMR spectra in cases where the quadrupole coupling constant is large enough so that deviations from the first-order conditions are observed. In these cases the line separations do not exactly conform to the above description. Only relative values of the coefficients  $^1a_{jk}$  and  $^2a_{jk}$  (Table I) are needed in order to study second-order effects. Substitution of the results presented in Table I in eq 13 leads to the conclusion that the second-order shifts  $^2\nu_{3/2}$  and  $^2\nu_{-3/2}$  are related by

$$^2\nu_{3/2} = -^2\nu_{-3/2} = f$$

$$= -(D - \Delta J/3)\{(1 - 3 \cos^2 \Omega)(|^1a_{12}|^2/2 - |^1a_{13}|^2/2 + 3^2a_{11}) - (3/2)\{\sin \Omega \cos \Omega\}[\exp(-i\phi)(3^{1/2}^2a_{12} + 2^1a_{13}^1a_{12}^*) + \exp(i\phi)(3^{1/2}^2a_{12}^* + 2^1a_{12}^1a_{13}^*)]\}$$
(15)

An analogous relationship is found for the shifts  $^2\nu_{1/2}$  and  $^2\nu_{-1/2}$ :

$$^2\nu_{1/2} = -^2\nu_{-1/2} = g$$

$$= -(D - \Delta J/3)\{(1 - 3 \cos^2 \Omega)(3|^1a_{12}|^2/2 - 3|^1a_{13}|^2/2 + ^2a_{11}) - (3/2)\{\sin \Omega \cos \Omega\}[\exp(-i\phi)(-3^{1/2}^2a_{12} + 2^2a_{23}) + \exp(i\phi)(-3^{1/2}^2a_{12}^* + 2^2a_{23}^*)]\}$$
(16)

From the above result it can be easily shown that, even when second-order effects are operating, one can still have access to the value of  $d$  by considering the difference between the two outer line separations. If  $d$ ,  $f$ , and  $g$  are all smaller than  $J$ , then the line separations are as follows (in the downfield direction):  $J - 2d - g + f$ ;  $J + 2g$ ;  $J + 2d + f - g$ ; and hence  $4d = \Delta\nu(\text{outer, downfield}) - \Delta\nu(\text{outer, upfield})$ . After comparison with the exact approach, this latter result seems to be accurate even when  $\chi \approx Z$ .<sup>23</sup> In the present work,  $|\chi|$  for  $^{63}Cu$  does not exceed  $Z$  (79.5 MHz) so that eq 14 can be confidently applied.

It should be noticed that the sign of  $d$  depends upon the relative values of the outer splittings (i.e.,  $d$  is positive if the line separations increase in going downfield and vice versa). The sign of  $d$  is, in turn, directly related to the sign of  $\chi$ .

Table III. Analysis of the Sign of  $\chi(^{63}Cu)$  According to Vega's Method for the Different Complex Types Shown in Table II<sup>a</sup>

type	$q$	$\eta$	sign of $\chi$ ( $=e^2qQ/h$ )
$P_3CuX$	$(3/4)(p_{CuX} - p_{CuP})q_0$	0	-
$P_2CuX_2$	$(3/4)(p_{CuP} - p_{CuX})q_0$	1	+
$PCuX_3$	$(3/4)(p_{CuP} - p_{CuX})q_0$	0	+
$P_2CuX$	$(-1/3)(2p_{CuP} + p_{CuX})q_0$	$0 < \eta < 1$	-
$PCuX_2$	$(-1/3)(2p_{CuP} + p_{CuX})q_0$	$0 < \eta < 1$	-
$PCuX^b$	$(1/2)(p_{CuX} + p_{CuP})q_0$	0	+

<sup>a</sup>In this table,  $q_0$  is the largest component of the EFG tensor due to a single electron in an atomic p orbital (for  $^{14}N$ , it has been estimated that  $e^2q_0Q/h = -10$  MHz),  $q$  is the resulting field gradient after taking into account the relative populations of Cu-ligand orbitals and the Cu hybridization.  $Q$  is the Cu nuclear quadrupole moment ( $-0.211$  b for  $^{63}Cu$ ), and  $p_{CuP}$  and  $p_{CuX}$  are the populations of Cu-P and Cu-X  $\sigma$  orbitals (in all cases  $p_{CuP} > p_{CuX}$ ). <sup>b</sup>Vega did only consider  $sp^2$  and  $sp^3$  hybridizations, but the result for PCuX follows straightforwardly from this method.

## Results and Discussion

Structural information on phosphine-containing Cu(I) complexes having halide and organic bases is described in detail in ref 6-19. Solid-state  $^{31}P$  NMR data can also be found in this series of papers, and they show the expected distorted quartets discussed above, with values of  $J(^{31}P, ^{63}Cu)$  ranging from 0.9 to 2 kHz.<sup>6-19</sup> For example, in  $(PPh_3)_2CuCl$ , the  $^{31}P$  quartet spacings are (in the downfield direction) 1.43, 1.27, and 0.94 kHz,<sup>11</sup> so that  $d = (0.94 - 1.43)/4 = -0.12$  kHz. The distortion parameter  $d$  has been found to be negative in all cases studied so far. The splittings are also affected by coupling to  $^{63}Cu$ , but the effect of this latter isotope is difficult to observe due to its lower natural abundance and similar nuclear properties as compared to  $^{63}Cu$ . Due to the broadness of the  $^{31}P$  lines, the expected effect from the reduction in nuclear quadrupole moment in going from  $^{63}Cu$  to  $^{65}Cu$  is not clear in the reported spectra.

Previous interpretations of these data have been rather qualitative, i.e. based on the assumption that larger distortions (measured either by the difference  $\Delta\nu_{\max} - \Delta\nu_{\min}$  or by the ratio  $\Delta\nu_{\max}/\Delta\nu_{\min}$ ) correspond to larger  $^{63}Cu$  quadrupole coupling constants, and this, in turn, implies a greater deviation from tetrahedral symmetry, allowing the distinguishing from coordination numbers 2 and 3 on one hand and 4 on the other.<sup>6-19</sup> However, as seen in eq 14, the distortion parameter  $d$  depends not only on the magnitude of  $\chi$  but also on several other molecular properties which may affect its value. Recently,<sup>17</sup> an attempt has been made to correlate these data by use of previously published accurate computer simulations of  $^{31}P$  NMR lines in a related P,Cu-containing complex.<sup>23</sup> However, the exact approach is difficult to implement, and the published results<sup>23</sup> are only applicable when  $D = J/2$ , when the  $^{63}Cu$  EFG is axially symmetric ( $\eta = 0$ ), and when  $\beta^D = 0$ .

In the present discussion attention is given to compounds of the  $P_nCuX_m$  type. Six different cases have been hitherto observed

**Table IV.** Comparison of Calculated and Observed Values of  $d$  in Cases Where Structural and Molecular Information Needed in Equation 14 is Available<sup>a</sup>

complex	type	$\chi$ , <sup>b</sup> MHz	$\eta$	$r$ , Å	$\beta^D$ , deg	$\alpha^D$ , deg	$d_{\text{calc}}$ , <sup>c</sup> Hz	$d_{\text{exp}}$ , Hz
(PPh <sub>3</sub> ) <sub>3</sub> Cu <sub>2</sub> Br <sub>2</sub> tetragonal site	P <sub>2</sub> CuX <sub>2</sub>	+28.6	1 <sup>d</sup>	2.25	25	0	-83	-75 -100
(PPh <sub>3</sub> CuCl) <sub>4</sub> "Cube"	PCuX <sub>3</sub>	+27.5 +26.0	0 0	2.19 2.19	0 0		-107 -101	-108 -100
(PPh <sub>3</sub> ) <sub>2</sub> CuCl	P <sub>2</sub> CuX	-66.3	0.3 <sup>d</sup>	2.26	90	63	-135	-123
(PPh <sub>3</sub> ) <sub>2</sub> CuBr	P <sub>2</sub> CuX	-64.3	0.3 <sup>d</sup>	2.27	90	63	-129	-140
(PPh <sub>3</sub> ) <sub>3</sub> Cu <sub>2</sub> Cl <sub>2</sub> trigonal site	PCuX <sub>2</sub>	-59.1	0.29	2.18	90	90	-150	-148
(PPh <sub>3</sub> ) <sub>3</sub> Cu <sub>2</sub> Br <sub>2</sub> trigonal site	PCuX <sub>2</sub>	-55.8	0.31	2.19	90	90	-142	-135
(PPh <sub>3</sub> ) <sub>3</sub> Cu <sub>2</sub> I <sub>2</sub> trigonal site	PCuX <sub>2</sub>	-53.7	0.33	2.22	90	90	-132	-130
(PPh <sub>3</sub> CuBr) <sub>4</sub> "step"; trigonal site	PCuX <sub>2</sub>	-56.2	0.3 <sup>d</sup>	2.21	90	90	-137	-158
(PPh <sub>3</sub> CuI) <sub>4</sub> "step"; trigonal site	PCuX <sub>2</sub>	-52.2	0.3 <sup>d</sup>	2.23	90	90	-123	-110

<sup>a</sup>P-Cu bond distances, bond angles needed to calculate  $\alpha^D$  and  $\beta^D$ , and <sup>31</sup>P NMR data (from which  $d$  is obtained, see text) were taken from refs 6-9, 11-13, 17, and 19; values of  $\chi$  and  $\eta$  (<sup>63</sup>Cu) are from refs 42-44 unless stated otherwise. <sup>b</sup>Signs of  $\chi$  are not available from NQR; those given in this table are from Table III. <sup>c</sup>Equation 14; in all cases  $\Delta J = +0.6$  kHz was assumed. <sup>d</sup>Assumed values.

according to the relative values of  $m$  and  $n$  (Table II).<sup>6-19</sup> They show different Cu coordination numbers and also different geometrical arrangements of ligands: approximately tetrahedral when  $(n + m) = 4$ , trigonal planar when  $(n + m) = 3$ , and linear when  $(n + m) = 2$ . In some of these cases, the location of EFG axes and asymmetry  $\eta$  are dictated by symmetry (Table II, types P<sub>3</sub>CuX, PCuX<sub>3</sub>, and PCuX). For PCuX<sub>2</sub>, the location of axes follows that experimentally observed from NQR measurements in a small magnetic field,<sup>42</sup> whereas for P<sub>2</sub>CuX<sub>2</sub> and P<sub>2</sub>CuX these are assumed orientations (though they also follow from the consideration of the relative electron populations of Cu-ligand  $\sigma$  orbitals, see below).

In several examples of Cu(I) complexes most of the necessary information to calculate the quartet distortion  $d$  is available: <sup>63</sup>Cu quadrupole coupling constant  $\chi$  and asymmetry parameter  $\eta$ .<sup>42-44</sup> Zeeman frequency of <sup>63</sup>Cu at the applied magnetic field (in all cases considered  $Z = 79.5$  MHz, corresponding to a <sup>1</sup>H frequency of 300 MHz),<sup>6-19</sup> dipolar coupling constant  $D = 12.9/r^3$  (in kHz, where  $r$  is the Cu-P bond distance in Å), and angles  $\alpha^D$  and  $\beta^D$  from diffraction data.<sup>6-19</sup> Two parameters remain undefined: the sign of  $\chi$  and the value of  $\Delta J$  (<sup>31</sup>P,<sup>63</sup>Cu). In the case under consideration, however, a reasonable estimation of signs can be made. The Cu<sup>+</sup> ion has filled 3d<sup>10</sup> orbitals whereas 4s and 4p are all vacant, so that both the magnitude and sign of  $\chi$  are in principle determined by the relative populations of the 4p orbitals, which depend upon the degree of donation of ligand electrons, and participate in different hybridizations depending on the coordination number. Although back-donation from 3d(Cu) orbitals has been found to play an additional role in determining  $\chi$  of <sup>63</sup>Cu in these complexes,<sup>42-44</sup> the main features are well-reproduced by the simpler approach based on Cu s-p intuitive hybridization schemes. An elegant method for connecting relative electron populations and magnitudes and signs of quadrupole coupling constants, as well as direction of EFG tensors in s-p hybrids of <sup>14</sup>N when molecules have a symmetry plane, has been described by Vega.<sup>45</sup> Table III summarizes the results obtained after applying Vega's approach, which was originally derived for <sup>14</sup>N, but gives a good qualitative picture of <sup>63</sup>Cu EFG, with due account to the change in magnitude and sign in the nuclear quadrupole moment in going from one nucleus to the other (<sup>14</sup>N,  $Q = +0.019$  b; <sup>63</sup>Cu,  $Q = -0.211$  b). In all cases it was assumed that electron populations of Cu-P bonds are higher than those of Cu-X bonds, as expected from both experiments and theory.<sup>7,43</sup> In fact, com-

parison of Tables II and III is a strong reminder of the useful correlations used in the case of <sup>14</sup>N, but with all signs reversed. For example, for PCuX<sub>3</sub> and PCuX (Table II) the EFG  $z$  axis definitely points along the direction of higher electron density, with  $\chi$  positive (one would immediately ascribe a negative sign if the nucleus were <sup>14</sup>N, as in tetrahedral amines or nitriles).<sup>46</sup> Furthermore, the locations of EFG axes according to Vega's method agree with that experimentally found in the study of the Zeeman effect on NQR signals of the trigonal sites in the binuclear compounds (PPh<sub>3</sub>)<sub>2</sub>CuX<sub>2</sub>Cu(PPh<sub>3</sub>) (all of them of the type PCuX<sub>2</sub>)<sup>42</sup> and also with those cases in which this location is dictated by symmetry considerations. In certain cases  $\chi$  is available but  $\eta$  is not known (for spin <sup>-3/2</sup> nuclei NQR does not provide  $\eta$  unless a Zeeman effect is introduced). Therefore,  $\eta$  had to be roughly assumed in some of the studied compounds.

When values of  $d$  are calculated in cases where all the necessary information is available but neglecting  $\Delta J$ , the results are consistently larger than the experimental values by ca. 20%. This is a strong indication that anisotropic  $\Delta J$  effects are operating. It is found that better agreement is obtained with observed values of  $d$  if a constant  $\Delta J = +0.6$  kHz is used throughout all studied cases. Table IV shows all the pertinent information used to calculate the values of  $d$ , the latter being compared with experimental values. It can be appreciated that the agreement is remarkable, in both magnitude and sign, for a variety of structural types, coordination numbers, and Cu s-p hybridizations, even in cases where  $\eta$  has been estimated. It should be noticed that experimental line splittings are affected by an error of  $\pm 20$ -30 Hz.<sup>6-19</sup>

The determination of  $\Delta J$  for these systems, albeit approximately, contributes to the very few experimental reports on this magnitude.<sup>47-49</sup> The effects due to the direct ( $D$ ) and anisotropic indirect ( $\Delta J$ ) couplings are difficult to separate, and  $\Delta J$  is usually small for nuclei of low atomic number; these two facts may prevent the experimental determination of the latter. Recently, values of  $\Delta J$  in the range +1.5 to +5 kHz have been reported for the <sup>31</sup>P,<sup>199</sup>Hg pair in Hg(II) complexes and phosphonates.<sup>50,51</sup> Since  $J$ -(<sup>31</sup>P,<sup>199</sup>Hg) are large (10-13 kHz), the anisotropic contribution to  $J$  lies in the range 15-50%, and has been shown to depend on the nature of groups bonded to either nucleus. It is therefore likely

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Table V. Calculated Values of  $\chi(^{63}\text{Cu})$  in Cases Where No NQR Data Are Available from the Literature<sup>a</sup>

complex	type	$d$ , Hz	$r$ , Å	$\beta^D$ , deg	$\alpha^D$ , deg	$\eta^b$	$\chi^d$ , MHz
(PPh <sub>3</sub> ) <sub>2</sub> CuI <sub>2</sub> <sup>-</sup>	P <sub>2</sub> CuX <sub>2</sub>	-38	2.29	29	0	1	+15.1
[(PPh <sub>3</sub> ) <sub>3</sub> CuBr] <sub>4</sub> "cube"	PCuX <sub>3</sub>	-80	2.21	0		0	+21.3
[(PPh <sub>3</sub> ) <sub>3</sub> CuI] <sub>4</sub> "cube"	PCuX <sub>3</sub>	-65	2.25	0		0	+18.5
[(PPh <sub>3</sub> ) <sub>3</sub> CuBr] <sub>4</sub> "step", tetragonal site	PCuX <sub>3</sub>	-85	2.21	0		0	+22.7
[(PPh <sub>3</sub> ) <sub>3</sub> CuI] <sub>4</sub> "step", tetragonal site	PCuX <sub>3</sub>	-110	2.24	0		0	+30.8
(PPh <sub>3</sub> ) <sub>2</sub> CuI	P <sub>2</sub> CuX	-138	2.27	90	63.5	0.3	-68.7
(PPh <sub>2</sub> Tol) <sub>2</sub> CuCl	P <sub>2</sub> CuX	-125	2.25	90	63.5	0.3	-60.3
		-163	2.25	90	63.5	0.3	-78.6
(PPh <sub>2</sub> Tol) <sub>2</sub> CuBr	P <sub>2</sub> CuX	-100	2.25	90	64	0.3	-48.0
		-120	2.25	90	64	0.3	-57.7
(PPh <sub>2</sub> Tol) <sub>2</sub> CuI	P <sub>2</sub> CuX	-75	2.26	90	63	0.3	-36.9
(PPh <sub>3</sub> ) <sub>3</sub> CuBr <sub>2</sub> <sup>-</sup>	PCuX <sub>2</sub>	-138	2.21	90	90	0.3	-56.6
[P(2,4,6) <sub>3</sub> ]CuCl <sup>c</sup>	PCuX	-275	2.18	0		0	+69.8
[P(2,4,6) <sub>3</sub> ]CuBr <sup>c</sup>	PCuX	-238	2.20	0		0	+62.4

<sup>a</sup> P-Cu bond distances, bond angles needed to calculate  $\alpha^D$  and  $\beta^D$ , and <sup>31</sup>P NMR data (from which  $d$  is obtained, see text) were taken from refs 6-9, 11-13, 17, and 19. <sup>b</sup> Assumed values, unless  $\eta = 0$  as required by symmetry. <sup>c</sup> (2,4,6) = 2,4,6-trimethoxyphenyl. <sup>d</sup> From eq 14; in all cases  $\Delta J = +0.6$  kHz.

that  $\Delta J(^{31}\text{P}, ^{63}\text{Cu})$  is also sensitive to the nature of ligands in the complexes studied in the present work. As has been previously shown,  $J(^{31}\text{P}, ^{63}\text{Cu})$  is positive,<sup>23</sup> i.e. in the range +1 to +2 kHz, so that a  $\Delta J = +0.6$  kHz for P,Cu would represent a  $\Delta J/J$  ratio on the same order as that found for the P,Hg case (although this comparison is not strictly valid because the metals belong to different groups of the periodic table). In both cases the implication is that mechanisms other than the isotropic Fermi contact one are operating.

Previous qualitative interpretations of <sup>31</sup>P,<sup>63</sup>Cu splittings were based on the assumption that trigonal Cu sites have larger quadrupole coupling constants (and induce correspondingly larger distortions) as compared with tetrahedral ones.<sup>6-19</sup> This is most noticeable when sites of coordination number 3 in Table IV are compared with complexes of the type P<sub>3</sub>CuX. For a variety of (PPh<sub>3</sub>)<sub>3</sub>CuX complexes in different polymorphic phases, the quartet distortion has been found to be very small.<sup>12</sup> However, the <sup>63</sup>Cu quadrupole coupling constant need not be zero in these cases. In fact, assuming a value similar to that for P<sub>2</sub>CuX<sub>2</sub> and PCuX<sub>3</sub>, the result is a very small  $d$  due to the fact that  $(3 \cos^2 \beta^D - 1) \approx 0$  for  $\beta^D$  in the range 103-109° (the average of the P-Cu-X bond angles).<sup>12</sup> Furthermore, the above trend is less satisfying for P<sub>2</sub>CuX<sub>2</sub> and PCuX<sub>3</sub> sites, which, being tetrahedral, give nevertheless a large  $d$  due to the favorable geometrical factor  $(3 \cos^2 \beta^D - 1)$ .

Table V collects cases in which the quadrupole information is absent. Using the reported <sup>31</sup>P line splittings, values of  $d$  are calculated, leading to the prediction of  $\chi(^{63}\text{Cu})$ . As expected, tetrahedral sites give lower quadrupole coupling constants as compared with trigonal ones. Further, two cases in which bulky triphenylphosphine derivatives lead to a copper coordination number of 2 are added.<sup>17</sup> They also give large Cu quadrupole coupling constants, as would be predicted by the large deviation from tetrahedral symmetry. These are the first reports on the value of  $\chi$  in such complexes.

In summary, it has been shown how to apply a simple approach to the quadrupole-perturbed dipolar and (anisotropic) scalar P,Cu interaction which acts upon the <sup>31</sup>P quartets obtained in magic-angle spinning NMR studies of copper(I) complexes. The results constitute an interesting link between relevant information obtained from several different techniques: X-ray diffraction, NQR, and solid-state NMR spectroscopy. It is hoped that this will stimulate

further investigation on less studied cases to confirm the gratifying trends communicated in this report.

### Conclusion

It has been shown how <sup>31</sup>P solid-state NMR spectra of Cu(I) complexes having triphenylphosphine and halide ligands can be analyzed so as to obtain the value and sign of a parameter  $d$  which characterizes the observed distortion in the P,Cu  $J$ -coupled <sup>31</sup>P quartets. The distortion is due to the incompletely averaged <sup>31</sup>P,<sup>63</sup>Cu coupling, which includes both dipolar and anisotropic scalar interactions. A simple equation has been discussed which correlates  $d$  with geometrical parameters (P,Cu distances and bond angles) and molecular data ( $\chi$  and  $\eta$  of <sup>63</sup>Cu EFG,  $\Delta J$  for <sup>31</sup>P,<sup>63</sup>Cu pairs). A series of literature data comprised of complexes showing different Cu coordination numbers, Cu-ligand  $\sigma$  bonding schemes, Cu hybridizations, and core geometries is analyzed. The outcome is the approximate calculation of  $\Delta J$ , contributing to the scarcely known values of this magnitude, as well as the determination of  $\chi$  (with appropriate sign) in cases where no NQR data are available for <sup>63</sup>Cu. Additionally, a discussion is presented concerning the values of  $\chi$  and the location of EFG principal axes in connection with the relative population of Cu-ligand  $\sigma$  orbitals.

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**Registry No.** (PPh<sub>3</sub>)<sub>3</sub>Cu<sub>2</sub>Br<sub>2</sub>, 47904-02-9; (PPh<sub>3</sub>CuCl)<sub>4</sub>, 50409-58-0; (PPh<sub>3</sub>)<sub>2</sub>CuCl, 25577-10-0; (PPh<sub>3</sub>)<sub>2</sub>CuBr, 47814-88-0; (PPh<sub>3</sub>)<sub>3</sub>Cu<sub>2</sub>Cl<sub>2</sub>, 34150-82-8; (PPh<sub>3</sub>)<sub>3</sub>Cu<sub>2</sub>I<sub>2</sub>, 60819-05-8; (PPh<sub>3</sub>CuBr)<sub>4</sub> (isomer 1), 50576-71-1; (PPh<sub>3</sub>CuI)<sub>4</sub> (isomer 1), 53432-64-7; (PPh<sub>3</sub>)<sub>2</sub>CuI<sub>2</sub>, 122700-06-5; (PPh<sub>3</sub>CuBr)<sub>4</sub> (isomer 2), 92011-27-3; (PPh<sub>3</sub>CuI)<sub>4</sub> (isomer 2), 19664-79-0; (PPh<sub>3</sub>)<sub>2</sub>CuI, 16109-82-3; (PPh<sub>2</sub>Tol)<sub>2</sub>CuCl, 110142-27-3; (PPh<sub>2</sub>Tol)<sub>2</sub>CuBr, 110142-28-4; (PPh<sub>3</sub>)<sub>3</sub>CuBr<sub>2</sub>, 118180-58-8; [P(2,4,6)<sub>3</sub>]CuCl, 119638-24-3; [P(2,4,6)<sub>3</sub>]CuBr, 119176-00-0; (PPh<sub>2</sub>Tol)<sub>2</sub>CuI, 110142-29-5.