The intermittent nmr spectra of these solutions show, in addition to the decreases in starting material signals (**2**: *t*-butyl singlet, δ 1.45; isopropyl doublet, δ 1.31) and increases in the signals associated with the products listed in Table I, a strong emission signal from chloroform, which becomes the most intense peak (negative) in the spectrum after about 200 sec. Such emission peaks are now expected from diamagnetic compounds formed from radical precursors.[3,4]

Table II summarizes the effects of additives on the emission. Cyclohexene increases the yield of chloroform while decreasing the emission intensity. *t*-Amylthiol completely destroys the emission, though chloroform is still a product in comparable yield. Thus, polarization resulting from a trichloromethyl–diamagnetic donor complex appears unlikely. When the starting material was deuterated in the methyl positions (96%), the emission intensity was reduced to 20%. These observations indicate that the emission signal is due to reaction between isopropyl–trichloromethyl radical pairs with a primary isotope effect of *ca.* 4.

Table II. Chloroform Emission Sensitivity to Additives[a]

Additive	$E_{\max}$[b]	A_{∞}[c]	V[3]
None	1.90	0.008	240
Cyclohexene (0.5 *M*)	1.75	0.040	44
Cyclohexene (1.9 *M*)	0.89	0.063	14
Cyclohexene (2.8 *M*)	0.46	0.050	9
t-Amylthiol (1.9)	0.	0.008	0

[a] Starting hyponitrite approximately 0.25 *M*. [b] Intensity of chloroform emission signal at its maximum in units of molar concentration of normal chloroform. [c] Intensity of final chloroform absorption signal in units of molar concentration.

The observed polarization could be explained by the simplified models originally put forth[3] if the chloroform arose from a hydrogen atom transfer from a radical in which the protons were previously polarized. However, the major isopropyl radical product (isopropyl chloride) shows only very weak enhanced absorption in both members of the methyl doublet. Addition of bromine or carbon tetrabromide diverts these radicals to the bromide, which still does not show emission. Fairly strong emission peaks were observed at the position corresponding to the methyl doublet of propylene. However, this product is consumed during the reaction so that the identification is complicated in this case.

The present reacting system may be treated as a simple two-step process

$$\mathbf{2} \xrightarrow{k_1} \mathrm{CHCl_3^*} \xrightarrow{k_2} \mathrm{CHCl_3}$$

in which k_1 is the rate constant for destruction of **2** and k_2 is the rate constant for relaxation of the chloroform.[5] The measured values of k_1 and k_2 are both *ca.* 7×10^{-3} sec^{-1}. These give an integrated enhancement factor of three times that measured at the maximum, or 600–700. This appears to exceed the theoretical limit for doublets,[6] using the original simplified models.

These observations are not consistent with the original dipolar relaxation models put forth.[3] They can be explained as being the result of a polarization mechanism similar to that recently proposed by Closs[7] if it is postulated that the positive nuclear spin subgroups of the triplet trichloromethyl–isopropyl pairs are transformed to disproportionation product more rapidly than the low nuclear spin subgroups, thus leading to emission from those products. The isopropyl radicals separating from such encounters would then be enriched in the low nuclear spin substates and would give enhanced absorption. The relatively short relaxation time and long time for formation of the isopropyl chloride would both lead to a weaker enhancement in absorption in the methyl doublet of this product.

It should also be noted that the products obtained from decomposition of **2** show different behavior than those obtained from decomposition of diacyl peroxides.[4] The methyl chloride produced from several hyponitrites, including **2**, shows emission, while that from acetyl peroxide shows enhanced absorption. Also, isopropyl chloride from diisobutyryl peroxide in hexachloroacetone[4] shows emission–absorption in the methyl doublet, while that from **2** shows only enhanced absorption. Further studies of products derived from the same formal radicals, obtained in different ways, should prove helpful in elucidating the mechanisms of these polarizations.

Acknowledgment. This work was supported by grants from the National Science Foundation.

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(3) R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5519 (1967); H. Fischer and J. Bargon, *Accounts Chem. Res.*, **2**, 110 (1969).

(4) R. Kaptein, *Chem. Phys. Lett.*, **2**, 261 (1968).

(5) The measured value for the relaxation time of chloroform at infinite dilution in carbon disulfide is *ca.* 300 sec: T. L. Pendred, A. M. Pritchard, and R. E. Richards, *J. Chem. Soc.*, 1009 (1966).

(6) Professor H. Ward has communicated to us privately that he has also observed an enhancement factor greater than 650 for chloroform formation.

(7) G. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969). This model has since been extended to cover energy polarization: G. L. Closs, private communication.

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Structure of Dichlorotris(triphenylphosphine)dicopper(I)–Benzene, a Chloride-Bridged Dimer Containing both Three- and Four-Coordinate Copper

Sir:

There has been extensive interest in the preparation and study of copper(I) complexes of the type $L_nCu_mX_m$, where L is a monodentate tertiary group Vb ligand and X is a halide ion.[1,2] Solid compounds of composition L_3CuX, $L_3Cu_2X_2$, L_2CuX, and LCuX are all known. At least two members of this series, chlorotris(diphenylmethylphosphine)copper(I)[3] and tetrameric iodotriethylarsinecopper(I),[4] have been studied by X-ray diffraction and shown to contain copper atoms in a distorted tetrahedral environment. Complexes of general

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(1) For references, *cf.* E. W. Abel, R. A. N. McLean, and I. H. Sabherwal, *J. Chem. Soc. A*, 133 (1969).

(2) W. T. Reichle, *Inorg. Nucl. Chem. Lett.*, **5**, 981 (1969).

(3) S. J. Lippard, D. Stowens, and D. A. Ucko, in preparation.

(4) A. F. Wells, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **94**, 447 (1936); F. G. Mann, D. Purdie, and A. F. Wells, *J. Chem. Soc.*, 1503 (1936).

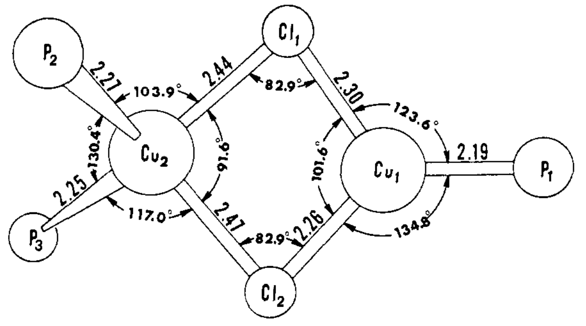

Figure 1. Perspective view of the basic structural unit in $(Ph_3P)_3$-Cu_2Cl_2. The P_2–Cu_2–Cl_2 and P_3–Cu_2–Cl_1 angles, 102.9 and 103.3°, respectively, have been omitted for clarity. Bond lengths, in ängstrøm units, have an estimated standard deviation of ±0.01 Å, and bond angles, ±0.3°.

formula $L_3Cu_2X_2$ are known for L = Ph_2PH, X = Cl[1] and for L = Ph_3P, X = Cl, Br, or I.[5] The compound $(Ph_3P)_3Cu_2Cl_2$ is one of the products of the hydrochloric acid decomposition[6] of $[(C_6H_5)_3P]_2Cu(BH_4)$, which has been the subject of recent studies in our laboratory.[7] The unusual stoichiometry of this complex, the possibility of three-coordination[1,2,8] for copper(I), and a general interest in the structural properties of $L_nCu_mX_m$ compounds as precursors of hydroborate complexes[3,7] provided incentive for the present X-ray structural investigation.

A sample of $(Ph_3P)_3Cu_2Cl_2$, prepared as described in the literature,[5c] was identical with material kindly supplied by Dr. W. T. Reichle which had been recrystallized from benzene solution. Analysis[9] was consistent with the presence of a benzene molecule of crystallization, which was found in the X-ray study. Preliminary precession photographs showed $(Ph_3P)_3$-$Cu_2Cl_2 \cdot C_6H_6$ to belong to the triclinic system. The choice of space group, $P\bar{1}$, was later confirmed by the successful refinement of the structure. The refined unit cell dimensions are $a = 12.307 \pm 0.005$, $b = 18.722 \pm 0.009$, $c = 13.574 \pm 0.005$ Å, $\alpha = 117.18 \pm 0.05$, $\beta = 73.80 \pm 0.05$, $\gamma = 107.55 \pm 0.05°$. The calculated density of 1.345 g cm^{-3} for two formula units ($M = 1062$) per cell is in good agreement with the observed density of 1.34 ± 0.02 g cm^{-3}. From the integrated intensities of 4900 independent reflections measured on a Picker four-circle automated diffractometer and corrected for absorption and Lp effects, the structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. The present value of the unweighted R factor, obtained by isotropic refinement of all nonhydrogen atoms, is 0.105 for 4180 nonzero reflections.

The molecular structure of the complex consists of chloride-bridged copper atoms, one of which is three-coordinate and the other four-coordinate (Figure 1). Such a structure is not entirely unexpected in view of the empirical formula, and was in fact suggested previously.[1] The benzene molecule of crystallization does not participate in this structural unit, although it undoubtedly has an influence on the packing of the dimeric units in the crystal lattice.[10] The closest nonbonded contacts involving the three-coordinate copper atom, apart from the Cu_1–Cu_2 interaction, are with phenyl ring carbon atoms, at a distance of 3.4–3.5 Å. The trigonal copper atom and its ligands are planar within experimental error.[11] The Cu_2Cl_2 rhombus is slightly folded about a line joining the chlorine atoms, with the dihedral angle between planes defined by Cl_1–Cu_1–Cl_2 and Cl_1–Cu_2–Cl_2 being 168.3 ± 0.2°. The dihedral angle between the latter plane and that defined by P_2–Cu_2–P_3 is 94.3 ± 0.1°, as compared to the idealized value of 90° expected for tetrahedral coordination about Cu_2. The long Cu_1–Cu_2 distance of 3.14 Å precludes metal-metal bonding. Three-coordinate copper has been observed before in various polymeric thiourea,[8a] olefin,[8b,c] and cyanide[8d] complexes. The present structure, together with that recently found for $Cu_2Cl_2(C_8H_{14})_3$,[8f] demonstrates the occurrence of trigonal cuprous atoms in discrete, dimeric molecules. The compound $[(Ph_3P)_3Cu](B_9H_{12}S)$ is isomorphous with its gold(I) analog, for which trigonal coordination has been established.[8e]

A comparison of the metal–ligand distances clearly reveals the shorter bond lengths about the trigonal copper atom (Figure 1). These observations are in accord with expectations based upon the difference in steric repulsions around the tetrahedral and trigonal copper atoms. Furthermore, since the trigonal copper atom may be considered as having essentially sp^2 hybrid orbitals, and the tetrahedral copper atom, sp^3 hybrid orbitals, the bond length differences may be revealing to some extent the tendency for orbitals with more s character to form shorter σ bonds.[12]

The angles at the copper and chlorine atoms within the Cu_2Cl_2 rhombus (Figure 1) reflect the differences in hybridization at the copper atoms as well as the normal constraints of the planar four-membered ring. The value of 130.4 ± 0.1° for the P_2–Cu_2–P_3 angle represents yet one more example in a growing list[7b,13] of such angular enlargements for "tetrahedral" $(Ph_3P)_2$-CuX complexes, where X is a bidentate, uninegative anion (in the case, $(Ph_3P)CuX_2^-$). Explanations for these large angles have been forwarded,[13a,b] but the difficulty of isolating steric and electronic effects makes a clear-cut rationale difficult. This as well as other

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(5) (a) F. Glockling and K. A. Hooton, *J. Chem. Soc.*, 2658 (1962); (b) G. Costa, G. Pellizer, and F. Rubessa, *J. Inorg. Nucl. Chem.*, **26**, 961 (1964); (c) G. Costa, E. Reisenhofer, and L. Stefani, *ibid.*, **27**, 2581 (1965).

(6) (a) J. M. Davidson, *Chem. Ind.* (London), 2021 (1964); (b) F. Cariati and L. Naldini, *Gazz. Chim. Ital.*, **95**, 3 (1965).

(7) (a) S. J. Lippard and K. M. Melmed, *J. Amer. Chem. Soc.*, **88**, 3929 (1967); (b) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **6**, 2223 (1967); (c) S. J. Lippard and D. A. Ucko, *ibid.*, **7**, 1051 (1968).

(8) W. A. Spofford and E. L. Amma, *Chem. Commun.*, 405 (1968); (b) N. C. Baenziger, G. F. Richards, and J. R. Doyle, *Inorg. Chem.*, **3**, 1529 (1964); (c) N. C. Baenziger, H. L. Haight, and J. R. Doyle, *ibid.*, **3**, 1535 (1964), and references cited therein; (d) D. T. Cromer, *J. Phys. Chem.*, **61**, 1388 (1957); (e) F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *Inorg. Chem.*, **7**, 2272 (1968); (f) P. Ganis, U. Lepore, and G. Paiaro, *Chem. Commun.*, 1064 (1969).

(9) *Anal.* Calcd for $[(C_6H_5)_3P]_3Cu_2Cl_2 \cdot C_6H_6$: C, 67.79; H, 4.80. Found: C, 68.45; H, 5.10.

(10) It is interesting in this regard that the bromide analog, $(Ph_3P)_3$-Cu_2Br_2, which was not recrystallized from benzene, crystallizes in the monoclinic system.[5b]

(11) A weighted best least squares plane was calculated through P_1, Cu_1, Cl_1, and Cl_2. The distances of these atoms from this plane are P_1, −0.002; Cu_1, 0.001; Cl_1, −0.001; Cl_2, −0.001 Å.

(12) See, for example, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 105. π bonding, involving the remaining p orbital on Cu_1, is also a possibility.

(13) (a) G. G. Messmer and G. J. Palenik, *Inorg. Chem.*, **8**, 2750 (1969); (b) S. J. Lippard and K. M. Melmed, *ibid.*, **8**, 2755 (1969); (c) M. Bartlett and G. J. Palenik, *Acta Crystallogr., Sect. A*, **25**, S173 (1969); (d) R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpont, and R. Eisenberg, *J. Amer. Chem. Soc.*, **92**, 738 (1970).

angular distortions (Figure 1) will be more fully discussed at a later date.

Although discrete $L_3Cu_2X_2$ units have now been shown to exist in the solid state, there is not yet any evidence for the existence of such a species in solution.[1] The correct identification of various $L_nCu_mX_m$ complexes in solution is not a simple task, since rapid exchange of L and X as well as multiple, concentration-dependent equilibria involving ligand dissociation and complex oligomerization reactions are taking place.[1,2,14] The fact that $L_3Cu_2X_2$ complexes have been isolated as solids under a variety of conditions and with various L and X groups,[1,5,6] however, requires that, in any interpretation of solution data, serious consideration be given to the possibility that dimers of this stoichiometry might be present.[15]

Acknowledgment. Support of this work by the National Science Foundation under Grant No. GP-10737 is gratefully acknowledged. We also thank Dr. W. T. Reichle of Union Carbide Corporation for providing a sample of $(Ph_3P)_3Cu_2Cl_2$ prepared in his laboratory.

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(14) (a) E. L. Muetterties, private communication; (b) S. J. Lippard and J. J. Mayerle, unpublished results.

(15) NOTE ADDED IN PROOF. Recent ^{31}P nmr studies by E. L. Muetterties and C. W. Alegranti (private communication, submitted for publication) have established the solution existence of $L_3Cu_2Cl_2$, for L = tri-*p*-tolylphosphine.

(16) Alfred P. Sloan Foundation Fellow, 1968–1970.

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Orbital Symmetry Forbiddenness in a Suprafacial 1,6 Cycloelimination of Sulfur Dioxide

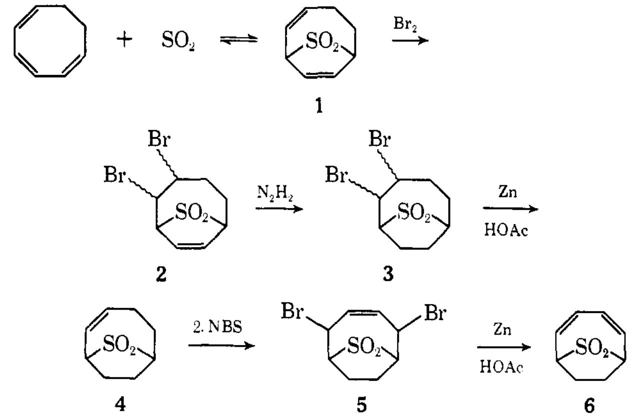
Sir:

In the absence of steric constraints, sulfur dioxide tends to interact with a 3-*cis*-hexatriene in an antarafacial manner (*trans*-1,6 addition or elimination).[1,2] We here report upon the thermal decomposition of a sulfone, **6** (9-thiabicyclo[4.2.1]nona-2,4-diene 9,9-dioxide), in which only suprafacial elimination of sulfur dioxide may take place in a concerted 1,6 fashion.[3]

The addition of sulfur dioxide to 1,3,5-cyclooctatriene produces only the 1,4 adduct, 9-thiabicyclo[4.2.1]-nona-2,7-diene 9,9-dioxide (**1**, Scheme I).[5] Bromine (1 equiv) was rapidly consumed by **1** to give **2**. Diimide reduction[6] of **2** gave **3**, which upon treatment with zinc and acetic acid produced **4**. Double allylic bromination of **4** gave the dibromide **5**, which upon treatment with zinc and acetic acid produced the diene **6**.

Direct, concerted fragmentation of **6** into cyclooctatriene and sulfur dioxide should be relatively[2] a disallowed process since it must proceed suprafacially (*cis* elimination) with respect to the triene component due to the constraints of the bicyclic system.[3] Molecular orbital symmetry considerations indicate that only the 1,4 process (*e.g.*, formation of **1**) should occur suprafacially with synchronous bond rupture through a symmetrical transition state (linear path).[4,7] Hence, comparison of the thermal stabilities of **1** and **6** should enable one to estimate the magnitude of symmetry factors in these electrocyclic transformations.[7]

Scheme I



Rates of decomposition of **1** and **6** were determined by measurement of sulfur dioxide liberated as a function of time.[8] Dissociation of **1** proceeded cleanly at conveniently measurable apparent first-order rates in the temperature range 100–120° ($k_{1,4} = 4.2 \times 10^{-4}$ sec^{-1} at 110°). From the temperature dependence of the rate the following activation parameters were obtained: $\Delta H^{\ddagger} = 31.2 \pm 0.9$ kcal/mol, $\Delta S^{\ddagger} = +7.0 \pm 3$ eu, $\Delta G^{\ddagger} = 28.5 \pm 0.9$ kcal/mol. These values are typical for sulfolene decompositions.[8] We therefore infer that the sulfone **1** is not appreciably strained and that there is no indication of greater nonsynchrony in the order of bond rupture in **1** relative to previously studied sulfolene decompositions.[8]

The sulfone **6** was completely stable at 110° and required temperatures over 100° higher for comparable rates of decomposition. Elimination proceeded less cleanly than in the case of **1**. In addition to sulfur dioxide (>80% of theory), the major volatile hydrocarbons were 1,3,5-cyclooctatriene and its valence tautomer bicyclo[4.2.0]octa-2,4-diene, which are inevitably in equilibrium at the decomposition temperature. Also detected by glpc were traces of other, unidentified products of similar volatility. Additionally, a residual tar was produced in small amount.

From the observed rate of sulfur dioxide production from **6** at 240–275° ($k_{1,6} = 4.2 \times 10^{-4}$ sec^{-1} at 250°) and the temperature dependence thereof, activation parameters may be derived: $\Delta H^{\ddagger} = 30.0 \pm 1.5$ kcal/mol, $\Delta S^{\ddagger} = -18 \pm 5$ eu, $\Delta G^{\ddagger} = 39.5 \pm 1.5$ kcal/mol. The difference in free energy of activation between **1** and **6** ($\Delta\Delta G^{\ddagger}$) is 10 kcal/mol at intermediate decomposition temperatures (*ca.* 180°), corresponding to a rate differential of 60,000 ($= k_{1,4}/k_{1,6}$). This difference, which we suggest may be taken as a measure (minimal) of the magnitude of orbital symmetry constraints in these cycloeliminations,[9] appears to reside in the entropy

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(1) W. L. Mock, *J. Amer. Chem. Soc.*, **89**, 1281 (1967).

(2) W. L. Mock, *ibid.*, **91**, 5682 (1969).

(3) More specifically, the realistic options are a [6s + 2s] path (linear cheletropic reaction, symmetry forbidden) and a [6s + 2a] path (nonlinear process, symmetry allowed).[4]

(4) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969). See especially under cheletropic reactions.

(5) The new compounds **1–6** analyze within 0.3% carbon and hydrogen; structures are supported by ir, uv, and, in particular, nmr spectroscopy.

(6) E. J. Corey, D. J. Pasto, and W. L. Mock, *J. Amer. Chem. Soc.*, **83**, 2957 (1961); E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, *ibid.*, **83**, 3725 (1961).

(7) W. L. Mock, *ibid.*, **88**, 2857 (1966).

(8) O. Grummitt, A. E. Ardis, and J. Fick, *ibid.*, **72**, 5167 (1950).