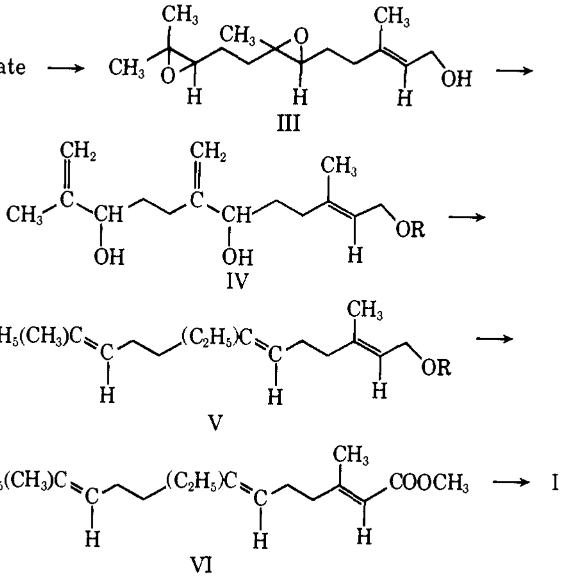
60 Mc) were observed at δ 7.20, 5.62–4.83, 3.35, 1.65, 1.58, 1.46, and 0.98. Geometrical isomers in hand at this point were not separated but carried through to the triene ester stage. To prepare for oxidation of the primary alcohol unit, the trityl group was removed from Vb by means of HCl–THF.

Manganese dioxide oxidation, first in hexane (of trienol Va to the corresponding trienal) and subsequently with cyanide[16] in methanol, generated the expected *trans* α,β-unsaturated ester system VI. Preparative glpc permitted separation of *t,c,c*:*t,c,t*:*t,t,c*:*t,t,t* geometrical isomers (1:2:1:1 ratio) and identification of the desired *trans,trans,cis* case was made by suitable glpc retention time and mass spectral comparison with authentic material. Formal completion of the synthesis depends on the well-established terpenoid terminal epoxidation process (N-bromosuccinimide–H_2O, followed by base),[2a] already utilized in the conversion of *trans,trans,cis*-triene ester VI to juvenile hormone I.[4]



a, R = H; b, R = $(C_6H_5)_3C$

In keeping with the general experience of others in the juvenile hormone area, we did not encounter crystalline materials in this synthesis. However, where possible and appropriate, assigned structures of intermediates were supported by ultimate analyses and by spectral means, including nmr, ir, and mass spectra. Yields of the various reactions were observed to be in general good, and in all cases (disregarding stereochemical aspects) above 50%.

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The Molecular Structure of μ-Diazido-tetrakis(triphenylphosphine)dicopper(I)

Sir:

To date, X-ray structure determinations of transition metal complexes containing the azide ion[1,2] have shown the N_3^- groups to coordinate solely through one of the terminal nitrogen atoms[3] with the two N–N bond distances exhibiting a significant difference. For example, in the complex $[Co(NH_3)_5N_3]^{2+}$,[2] the two N–N distances are found to be 1.145 (7) and 1.208 (7) Å, the longer distance occurring between the middle nitrogen atom and the nitrogen atom attached to the metal ion. The ability of the azide group to bridge two transition metal ions through the terminal nitrogen atoms was first suggested by Snellgrove and King[4] for the electron transfer reaction between Cr^{2+} ion and *cis*-$Cr(H_2O)_4(N_3)_2^+$ and by Haim[5] for the corresponding reaction between Cr^{2+} ion and *cis*-$Co(NH_3)_4(N_3)_2^+$. These authors suggested that the activated complex possesses a symmetric doubly bridged structure. As part of our structural and photochemical[6] studies of azido complexes of group Ib metals we have determined the crystal and molecular structure of the complex μ-diazido-tetrakis(triphenylphosphine)dicopper(I), which represent the first example of a complex containing a diazo bridged structure.[7]

The complex was synthesized as described previously[7] and crystals suitable for a single-crystal X-ray study were grown from chloroform–hexane solution. On the basis of Weissenberg and precession photographs, the complex was found to crystallize in space group $P2_1/c$ of the monoclinic system with a unit cell of refined dimensions $a = 23.524$ (15), $b = 13.690$ (8), $c = 20.035$ (15) Å, $\beta = 106.3 \pm 0.1°$, and $V = 6193$ Å^3. An experimental density of 1.35 (1) g/cm^3 is in agreement with a calculated value of 1.36 g/cm^3 for four dimeric molecules of formula $Cu_2P_4N_6C_{72}H_{60}$ per unit cell.

A complete set of independent intensity data was collected by the θ–2θ scan technique using a Picker four-circle automatic diffractometer. Zr-filtered Mo Kα radiation and pulse height analysis were employed for the data collection. The intensities of 3200 reflections were measured, of which 2637 reflections were observed to be greater than σ. The intensity data were corrected for Lorentz and polarization effects, but not for absorption owing to the smallness of μ (8.74 cm^{-1}) and the uniformity of the crystal dimensions (0.41 × 0.38 × 0.31 mm). The structure was solved by standard Patterson and Fourier techniques and was refined by least-squares methods. In the refinement, the phenyl rings were treated as rigid groups described by three positional and three angular parameters. Each carbon atom was assigned its own isotropic thermal parameter, as were the nitrogen atoms of the azide groups. The Cu and P atoms were assumed to vibrate according to an anisotropic thermal model. This refinement of

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(7) The complex is monomeric in solution: R. F. Ziolo and Z. Dori, *J. Amer. Chem. Soc.*, **90**, 6560 (1968).

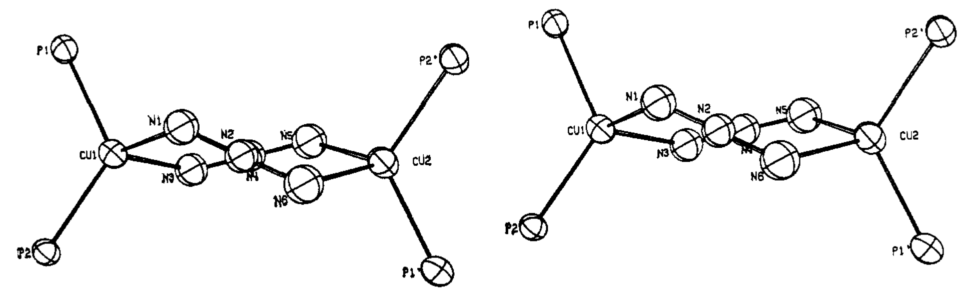


Figure 1. A stereoscopic view of the coordination geometry of the dimeric molecule $[((C_6H_5)_3P)_2CuN_3]_2$.

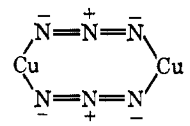
positional, thermal, and scale parameters converged to a final R factor of 6.5% and a weighted R factor of 7.2% for 2628 reflections above σ. The hydrogen atom contributions to the calculated structure factors were included as fixed contributions in the final cycles of refinement.

The structure consists of well-separated dimers, in which the two copper atoms are bridged by the two azide groups through the end nitrogen atoms to form an eight-membered ring. Each copper atom thus possesses a four-coordinate geometry. A stereoscopic view of the coordination geometry of the dimer is presented in Figure 1; selected bond distances and angles are in Table I. The tetrahedral geometry about the Cu atoms exhibits significant distortions as manifested in the large P–Cu–P bond angles.[8]

Table I. Selected Intramolecular Distances and Angles

Distances, Å		Angles, deg	
Cu_1–N_1	2.102 (10)	N_1–Cu_1–N_3	98.0 (4)
Cu_1–N_3	2.085 (10)	N–Cu_2–N	99.7 (4)
Cu_2–N_5	2.109 (11)	P_1–Cu_1–P_2	122.3 (1)
Cu_2–N_6	2.116 (10)	P_1'–Cu_2–P_2'	120.8 (1)
Cu_1–P_1	2.271 (4)	N_1–N_2–N_6	177.0 (1.0)
Cu_1–P_2	2.250 (3)	N_3–N_4–N_5	178.6 (1.1)
Cu_2–P_1'	2.269 (4)		
Cu_2–P_2'	2.266 (3)		
N_1–N_2	1.169 (11)		
N_2–N_6	1.193 (12)		
N_3–N_4	1.179 (13)		
N_4–N_5	1.194 (12)		

The inner coordination of the dimer possesses essentially D_2 symmetry although no crystallographic symmetry conditions are imposed on the structure. As can be seen from the table, all of the N–N distances in the bridging azide groups are equal within experimental error, averaging 1.178 (12) Å, and both N_3^- ions possess an essentially linear structure. The four independent Cu–N bond distances also exhibit structural equivalency and average 2.102 (10) Å. It should be noted that the N–N distances are approximately the same as the corresponding values observed in ionic azides.[2] Hence, we believe that the predominant canonical form describing the ground state structure of the dimer is



As illustrated in the structure, the eight-membered ring formed by the two copper atoms and the two azide groups is not planar. The two azide ions are tilted by 38° with respect to each other and each of the Cu–N_3–Cu bridges deviates quite significantly from planarity. Two factors which may contribute to this unusual geometry are first, packing effects which optimize the efficiency of the packing and minimize the nonbonded repulsions between the phenyl rings, and second, the allenic nature of the middle nitrogen atom which opposes the planarity of the Cu–N_3–Cu bridge.

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[8] For a compilation of the P–Cu–P angle in phosphine complexes of Cu(I) see S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **8**, 2755 (1969).

[9] Temple University Fellow, 1969–1970.

Chlorine Kinetic Isotope Effects in Nucleophilic Displacements at a Saturated Carbon

Sir:

We have studied the reactions of various aliphatic and aromatic chlorides with both aromatic and aliphatic oxides and thiooxides in methanol. Product analysis by nmr shows that these second-order nucleophilic displacement reactions result in near-quantitative production of ethers or thioethers along with chloride anion. These reactions have been thought to proceed by way of a concerted transition state[1] symbolized as

$$N{:} + RCl \longrightarrow [N\sim R\sim Cl] \longrightarrow NR + {:}Cl$$

We chose to make changes in electron density at N and R (when R = benzyl) in order to determine if the chlorine leaving group kinetic isotope effects offered a valid probe for studying subtle changes in transition-state geometry. We believe that these effects may provide a highly informative test of our concepts of transition-state structure and may also suggest the relative importance of the factors thought to be involved in determining the nucleophilic power of the attacking group.

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[1] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 310.