

(Nujol) shows the expected bands due to the organosilicon function, but the characteristic silacyclobutane ring vibra-

ν (Fe-Si);⁷ there is no corresponding absorption in the spectrum of the 2,2-dimethoxy analogue of (II).

Complex (II) has considerable thermal stability: after 2.5 days at 80°, approximately half the initial sample condensed on cooling to room temperature. The compound is decomposed only slowly (hours) by pure oxygen, but is rapidly (<1 min) destroyed by moist air. A number of reactions is outlined in the Scheme.

Neither carbon monoxide nor hydrogen reacted with (II) at 1 atm. and 20–80°, while chlorine in carbon tetrachloride at 22° caused total decomposition to FeCl₃, no volatile silicon products being detected.

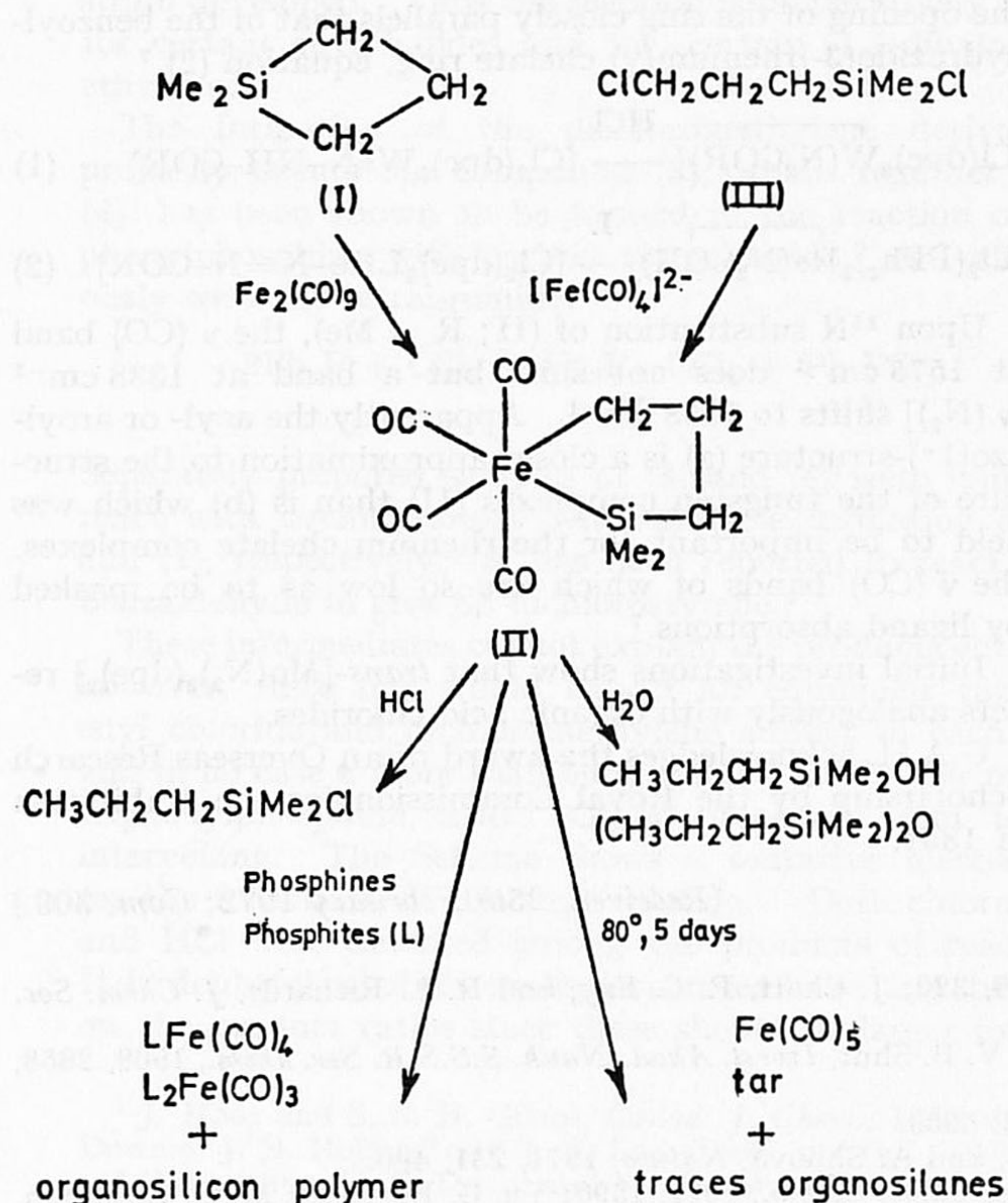
Reactions of (II) with HX (X = Cl, OH) parallel those⁸ of the parent silacyclobutane (which were run as controls) but that of (II) with deoxygenated water is very much faster. Complex changes occur upon addition of neutral ligands L, the latter being incorporated in the resulting polymer in some cases (*e.g.*, L = 4-picoline). The role of ring-insertion processes is under investigation. We have not to date observed any release of intact silacyclobutane from (II).

Preliminary experiments show that the insertion of Fe(CO)₄ is a general reaction for silacyclobutanes, 1,3-disilacyclobutanes, and 2,3-benzo-1-silacyclobutenes.

The present results are significant for the reasons outlined in the introductory paragraph and additionally because (a) reactions between suitable transition metal complexes and strained heterocycles could furnish a general synthesis for compounds having metal-metal bonds, (b) (II) may be the forerunner of a family of stable transition metal chelate alkyls [*cf.*, Li₃Cr₃(C₄H₈)₃·2.5C₄H₈O₂⁹], and (c) (II) represents a model for intermediates proposed¹⁰ in the transition metal complex catalysed polymerisation of silacyclobutanes and related compounds.

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tions⁶ (1188, 1122, 927 cm⁻¹) are absent. A medium band at 302 cm⁻¹ [absent from the i.r. spectrum of (I)] may be

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A Tetranuclear Cluster Complex of Copper(I) with Bridging Aryl Ligands: the Crystal Structure of (4-Methyl-2-cupriobenzyl)dimethylamine

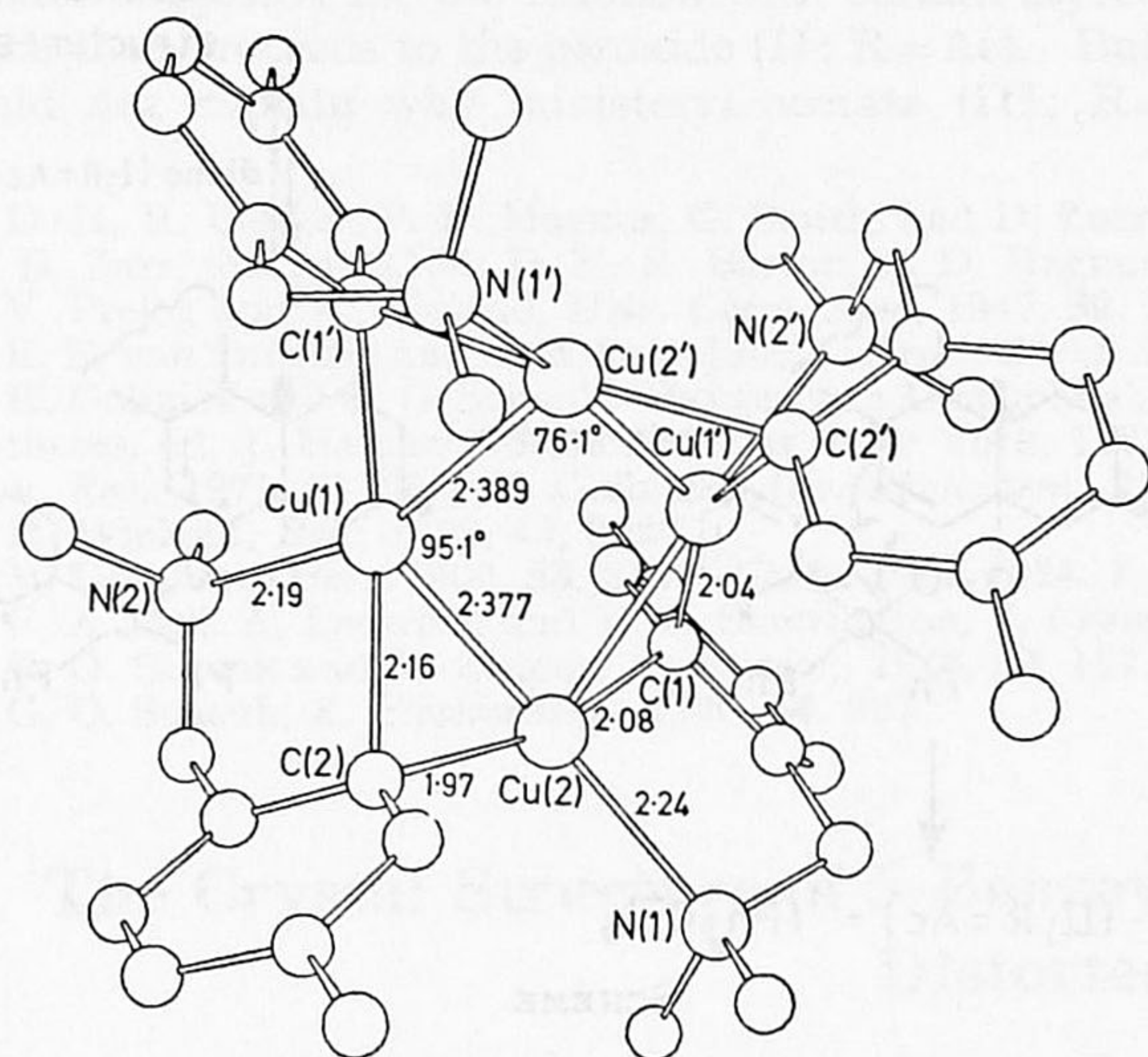
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Summary An X-ray diffraction analysis of (4-methyl-2-cupriobenzyl)dimethylamine establishes its tetranuclear

nature; the aryl ligands bridge copper atoms separated by 2.38 Å.

THE synthesis of stable aryl copper(I) complexes has been described¹ but their structures are not known with certainty; phenylcopper is supposed to be polymeric² while a cubic arrangement with mobile-bridging benzotrifluoride groups has been proposed for the octameric *m*-(trifluoromethyl)-phenylcopper(I).³ (4-Methyl-2-cupriobenzyl)dimethylamine exists in solution as discrete tetramers¹ which suggests that



FIGURE

its structure is based on a tetranuclear cluster similar to that of $[\text{CuI}(\text{AsEt}_3)]_4$.⁴ Our present crystallographic results define the arrangement.

Crystals (from benzene) are monoclinic with $a = 18.02$,

$b = 11.35$, $c = 19.58$ Å, $\beta = 97.6^\circ$; space group $C2/c$; $Z = 4$. Structural analysis was based on Fourier and least-squares analysis of 1424 reflexions observed on a PAILRED diffractometer ($\text{Mo-K}\alpha$) and having $F^2 \geq 2.0 \sigma(F^2)$. R has converged to 0.07. The complex has C_2 symmetry in the crystal, its stereochemistry being illustrated in the Figure; e.s.d.'s in the bond lengths average 0.003 Å (Cu-Cu), 0.015 Å (Cu-C and Cu-N), and 0.02 Å (C-C and C-N).

The observation of an aryl group bridging transition metals has a precedent only in an osmium trinuclear complex.⁵ As in Al_2Ph_6 and $\text{Al}_2\text{Me}_4\text{Ph}_2$,⁶ the aryl ligand has its plane oriented perpendicular to the metal-metal bond but it is only in the osmium complex that the M-C-M bond angle approaches 90° . The maximum overlap and alternative 'explanations' of acute M-C-M bond angles in alkyl- and aryl-bridged electron deficient molecules are discussed elsewhere.⁷ We prefer to describe the bonding in the present complex in terms of the metal using only s and p valence orbitals to any significant extent and to rule out direct metal-metal bonding in spite of the very short Cu-Cu distances; each copper atom then has a distorted trigonal planar stereochemistry. An alternative description would be to imagine that each metal ion obeys the rare-gas rule when it becomes necessary to regard the direct bond between the bridged copper atoms as of order two. Such extensive use of metal d orbitals seems to us to be unlikely on promotion energy considerations.

The copper atoms form a distorted 'butterfly' arrangement. The origin of this distortion from a more regular cluster arrangement is not clear at the present time.

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An Unusual Synthesis of Ergosterol Acetate Peroxide

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Summary Trityl tetrafluoroborate and tris-(*p*-bromophenyl)aminium cation-radical are exceptionally effective catalysts for oxygenation of ergosteryl acetate (I; R=Ac) to the peroxide (II; R=Ac); the trityl cation catalysed reaction is a photo-oxygenation, whilst the aminium cation-radical catalysed reaction is thermal.

DURING studies related to the use of trityl cation for the deprotection of masked steroidal alcohols¹ we treated ergosterol acetate with trityl tetrafluoroborate (0.3 equiv.) in dichloromethane without precautions to exclude oxygen. At -78°C the peroxide² (II; R=Ac) was formed in quanti-

tative yield. Ergosteryl benzoate (I; R=Bz) similarly gave the benzoate (II; R=Bz).

Further investigation showed that the acetate (I; R=Ac) (100 mg) in dry dichloromethane with a catalytic amount (10 mg) of trityl tetrafluoroborate at -78°C with exposure to air and laboratory lighting gave the peroxide (II; R=Ac) quantitatively in 2.75 h. Irradiation of the above system with a tungsten lamp (500 W) gave the peroxide (II; R=Ac) in 30 min. Under pure oxygen (1.03 mol uptake) peroxide (II; R=Ac) formation was complete in 10 min at -78°C , even on a preparative scale (>1 g). The trityl cation was isolated as tritylmethanol (86%) from aqueous