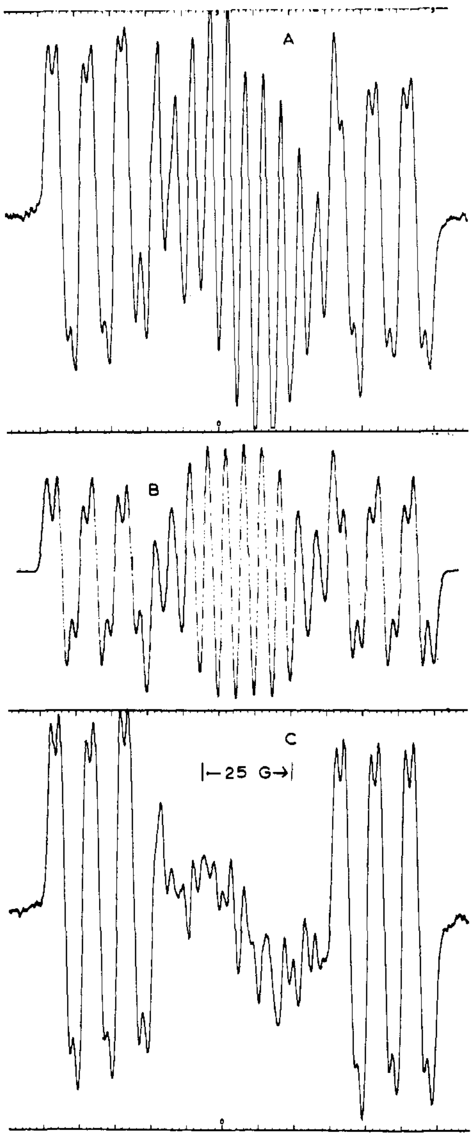

Figure 1. Esr spectra of uv-irradiated *n*-butylamine in an adamantane pellet: (A) mercury resonance lamp, 254 and 185 nm; (B) computer simulation of above; (C) same sample after exposure to high-pressure mercury arc radiation, λ >250 nm.

$a^{\beta H(8)}$, 9.9 G (H(1) is cis to the α H). The calculation confirms the large α-proton interaction and small β-proton interaction, as the β-proton coupling would be the same for all β protons in a freely rotating methyl group, and hence the calculation yields extremes.

Although fission of the α carbon–hydrogen bond has been postulated as a minor primary process in the uv photolysis of methylamine, the most important primary process in alkylamine photolysis has generally been considered to be fission of a bond to nitrogen.[6] Esr studies of the photolysis of primary, secondary, and tertiary methylamines frozen at 77°K have shown that alkylamino radicals are formed, and no evidence for fission of carbon–hydrogen bonds was obtained.[4c] Therefore, it is indeed surprising that in adamantane the radical found from uv irradiation of *n*-butylamine and *n*-propylamine is the same as that found from X-irradiation, the result of fission of the α C–H bond. The absence of alkylamino radicals does not necessarily mean that they are not formed in the primary process, as their lifetime at ambient temperature may be too short for observation. Also, although hydrogen-atom abstraction by free radicals from inclusion compounds in adamantane has not been reported and appears to be improbable, it cannot be absolutely ruled out as a mechanism for the formation of the alkylaminomethyl radical, I. This reservation precludes an unambiguous conclusion; however, it seems probable that radical I is formed in a primary photochemical process.

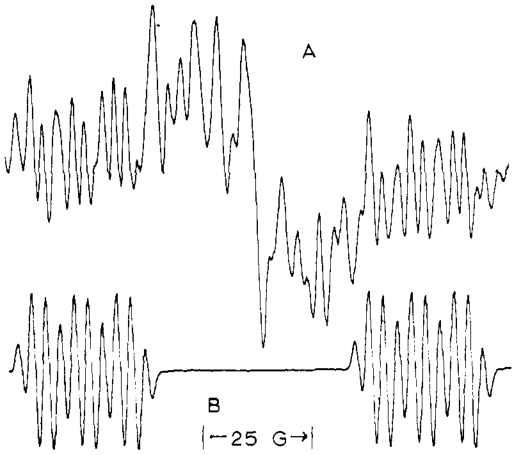

Figure 2. Esr spectra of uv-irradiated ethylamine in an adamantane pellet: (A) concurrent exposure to mercury resonance lamp and high-pressure mercury arc radiation; (B) computer simulation of ethylidenimino radical.

Acknowledgment. We thank Professor D. E. Wood for sending us helpful information prior to publication. This investigation was supported by a grant from the National Science Foundation.

T. Richerzhagen, D. H. Volman*
Department of Chemistry, University of California
Davis, California 95616

Received December 28, 1970

---

(6) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 455.

Preparation and Crystallographic Characterization of a Hexameric Triphenylphosphinecopper Hydride Cluster[1]

Sir:

Copper(I) hydrido species[2] have recently attracted attention as stereoselective reducing agents in certain organometallic reactions.[3] Such species have also been implicated as intermediates in the thermal decomposition of copper(I)–alkyl complexes.[4] However, although Würtz prepared a "copper(I) hydride" over a century ago,[5] no truly stoichiometric hydridocopper species have yet been isolated.[3]

We now report the preparation and crystallographic

---

(1) Work supported by the Petroleum Research Fund (J. A. O.), the National Science Foundation (Grant No. GP-26293 to M. R. C.), and the Advanced Research Projects Agency (M. R. C.).

(2) From the *in situ* reaction of copper(I) hydride with tri-*n*-butylphosphine in ether.

(3) G. M. Whitesides, J. San Filippo, Jr., E. R. Stredronsky, and C. P. Casey, *J. Amer. Chem. Soc.*, **91**, 6542 (1969).

(4) (a) G. M. Whitesides, E. R. Stredronsky, C. P. Casey, and J. San Filippo, Jr., *ibid.*, **92**, 1426 (1970); (b) K. Wada, M. Tamura, and J. Kochi, *ibid.*, **92**, 6656 (1970).

(5) A. Würtz, *Ann. Chim. Phys.*, [3] **11**, 250 (1844).

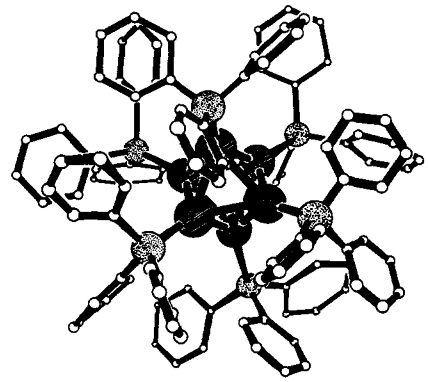

Figure 1. Stereochemistry of the $H_6Cu_6(PPh_3)_6$ cluster (hydrogen atoms omitted).

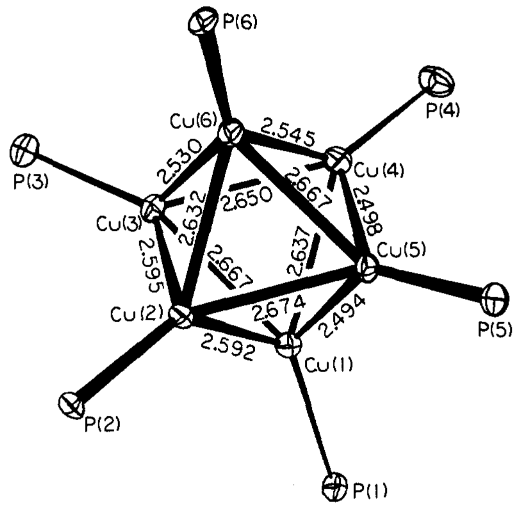

Figure 2. Copper–copper distances within the $H_6Cu_6(PPh_3)_6$ cluster. (Diagram also shows thermal ellipsoids for copper and phosphorus atoms.)

characterization of the hydridocopper cluster $H_6Cu_6(PPh_3)_6$.[6]

To a colorless solution of $[PPh_3CuCl]_4$[7] (0.40 g) in deoxygenated DMF[6] (30 ml) at room temperature is added solid sodium trimethoxyborohydride (0.43 g).[8] The solution immediately turns red, and, on cooling in an ice bath for 30 min, bright red crystals (later shown to be $H_6Cu_6(PPh_3)_6 \cdot DMF$, *vide infra*) are deposited. The crystals are filtered under argon, washed (in turn) with cold DMF, water, and acetonitrile, and dried *in vacuo* (yield 0.071 g). The complex is stable indefinitely under argon or *in vacuo* and, in the solid state, is oxidized only slowly by air (*cf.* the properties of copper(I) hydride). It is soluble in benzene, slightly soluble in DMF, and insoluble in acetonitrile and water, and appears to decompose in alcohols, ethers, and chlorinated hydrocarbons. Solutions of the complex are air sensitive. The solid material melts, with decomposition, at 111°. Chemical reactions of this species will be described separately.

The complex crystallizes as thin red hexagonal plates in the centrosymmetric orthorhombic space group *Pbca* ($D_{2h}{}^{15}$; no. 61) with a = 40.10 (4), b = 22.46 (2), c = 21.86 (2) Å, ρ_{obsd} = 1.367 (5) g cm^{-3} (by flotation in aqueous $CaBr_2$ solution), and ρ_{calcd} = 1.368 g cm^{-3} for M = 2028 and Z = 8.

X-Ray diffraction data to $\sin \theta = 0.65$ (Cu Kα radiation, λ 1.5418 Å) were collected for the levels $h0$-$14l$ and $hk0$-5 using a 0.01° incrementing Supper-Pace Buerger Automated Diffractometer and a stationary-background, ω-scan, stationary-background counting sequence. The 8905 reflections thus collected were corrected for Lorentz, polarization, and absorption (μ = 30.67 cm^{-1}) effects.

The positions of atoms of the Cu_6P_6 core were obtained by reiterative application of Sayre's equation to the 234 reflections having $E \geqslant 1.5$.[9] The 108 carbon atoms of the hexanuclear copper cluster were located from a series of difference-Fourier syntheses, the last of which showed a single DMF molecule of crystallization. The partial formula of our crystalline sample was then established as $H_xCu_6(PPh_3)_6 \cdot DMF$.

Subsequent refinement of positional parameters for the 125 nonhydrogen atoms, of anisotropic thermal parameters for Cu and P atoms, and of isotropic thermal parameters for C, N, and O atoms (with the 90 phenyl hydrogens in calculated positions) has led to convergence with R_F = 9.2% for the 3180 independent nonzero reflections.[10]

The geometry of the cluster is shown in Figure 1. The Cu_6 cluster is distorted from regular O_h symmetry, individual copper–copper distances ranging from 2.494 (5) to 2.674 (5), and averaging 2.599 ± 0.067 Å[11] (see Figure 2). The pattern of metal–metal bond lengths is such that two transoid triangular faces [Cu(1)–Cu(3)–Cu(4) and Cu(2)–Cu(5)–Cu(6)] are appreciably larger than the remaining six faces of the octahedron. Each copper atom is bonded to a single triphenylphosphine ligand, with individual copper–phosphorus distances ranging from 2.217 (7) to 2.262 (7), averaging 2.240 ± 0.017 Å. Other mean distances are: P–C = 1.825 ± 0.031 and C–C = 1.385 ± 0.043 Å.

As yet we have been unable to detect hydride ligands either by infrared or ^1H nmr spectroscopy (*cf.* ref 3). However, decomposition of the complex with a benzene solution of $C_6H_5CO_2D$ liberated hydrogen, the mass spectrum of which showed HD and H_2, but no D_2 (*cf.* ref 12). Three experiments performed with two independently prepared samples yielded the results shown in Table I (see ref 13). The mean H^-/Cu ratio

---

(6) Abbreviations used within the text are: Ph = phenyl, DMF = dimethylformamide.

(7) The complex may be prepared in a similar fashion using the analogous bromide, iodide, thiocyanate, or cyanide.

(8) All manipulations were performed under an inert (argon) atmosphere.

(9) Using a locally modified version of the IBM 7094 program, REL; see R. E. Long, Ph.D. Dissertation, University of California at Los Angeles, 1965.

(10) The low number of observable reflections is simply a result of the poor quality of the crystals which could be isolated. No reflections with $\sin \theta > 0.65$ were observed on long-exposure Weissenberg photographs.

(11) The large value of the deviation from the mean simply reflects the nonequivalence of these bonds.

(12) J. A. Dilts and D. F. Shriver, *J. Amer. Chem. Soc.*, **90**, 5769 (1968), especially Table II.

(13) (a) Assuming no isotope effect, these values have been corrected for the 97% deuteration of the benzoic acid (as determined by its nmr in $CDCl_3$). Experiments are now in progress to determine the magnitude of the isotope effect, if any. (b) The H^-/Cu ratio was calculated assuming that all of the generated H (in the H_2 and HD mixtures) originated as H^- in the cluster. To confirm the absence of H–D exchange with the benzoate ion or triphenylphosphine, these species were extracted from the reaction residue in the form of benzoic acid and $[PPh_3CuBr]_4$ by treatments with acetone solutions of HCl and LiBr, respectively. Comparison of the mass spectra of these products with those of authentic nondeuterated samples showed no detectable deuteration.

Table I

Acid:Cu	% H_2 in H_2–HD mixture[13a]	Mol of gas/ equiv of Cu	Active H^-/Cu[13b]
1.45:1	45.6	0.718	1.045
1.26:1	32.9	0.788	1.047
1.35:1	44.3	0.729	1.052

of 1.05 ± 0.05 indicates a molecular stoichiometry of $H_6Cu_6(PPh_3)_6$.[14]

Although the hydride ligands were not detected directly from the X-ray diffraction study, the following observations can be made. (i) The arrangement of phosphine ligands precludes the possibility of terminal hydride ligands; slight variations of phosphine ligands from truly apical positions $[\angle(P\text{—}Cu\cdots Cu_{trans}) = 168.3\text{–}177.3^{\circ}]$ appear to result from intramolecular phenyl···phenyl repulsions. (ii) There are three symmetric possibilities for hydride ligand locations: (a) bridging hydrides on each edge of the two large triangular faces, (b) bridging hydrides on the six shortest Cu–Cu vectors, or (c) triply bridging hydrides on the six small octahedral faces. Previously it was demonstrated that both bridging hydride ligands (in $[H_2Re_3(CO)_{12}^-]$)[15] and triply bridging hydride ligands (in $H_2Ru_6(CO)_{18}$)[16] cause *expansion* of the metal–metal bond, which would favor structural possibility a. However, there is insufficient evidence to determine positively the correct alternative.

Finally, if one assumes that each phosphine and hydride ligand contributes two electrons to the copper cluster, a noble gas configuration is achieved if each copper atom is linked by a bond of unit bond order to each of its nearest neighbors. It may be noted that the mean *bonding* Cu–Cu distance of ~2.60 Å in the present molecule and ~2.83 Å in $[Cu_8(i\text{-}MNT)_6^{4-}]$[17] are comparable to values of ~2.60 Å in $[AsEt_3CuI]_4$ and $Cu_4(S_2CNEt_2)_4$, where copper–copper interactions are claimed to be absent.[18]

Acknowledgments. We thank Dr. G. O. Dudek for assisting with the mass spectral studies and Professor R. H. Holm for the use of his Faraday balance for magnetic measurements.

(14) This formulation is also consistent with the apparent diamagnetism of the compound.

(15) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Amer. Chem. Soc.*, **90**, 7135 (1968).

(16) M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *Chem. Commun.*, 458 (1970).

(17) L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *J. Amer. Chem. Soc.*, **90**, 7357 (1968).

(18) M. C. Baird, *Progr. Inorg. Chem.*, **9**, 1 (1968), especially pp 114–118.

(19) National Science Foundation Predoctoral Fellow, 1968–1971.

(20) Alfred P. Sloan Fellow, 1968–1970.

(21) Graduate National Fellow of Harvard University, 1967–1970.

Susan A. Bezman,[19] Melvyn R. Churchill*[20]
John A. Osborn, John Wormald[21]
Department of Inorganic Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received December 12, 1970

Cation Radicals. III. Sterically Hindered Chlorinating Agents

Sir:

It is the ultimate goal of this effort to develop sterically hindered chlorinating agents that will selectively chlorinate (or oxidize) the terminal methyl of a long alkane chain. Such a reagent would mimic the enzymatic selectivity found in the conversion of stearic acid to 18-hydroxystearric acid[1] and in the terminal oxidation of linear alkanes.[2] Although this goal is still distant, results of sufficient significance have been obtained to warrant a preliminary report.

Table I summarizes the results of chlorination of isopentane and 2,2- and 2,3-dimethylbutanes with agents of increasing steric hindrance. The most unusual result is the chlorination of isopentane with *N*-chlorodi-*tert*-butylamine and *tert*-butyl-*tert*-amylamine (last two entries). In these two cases, the primary hydrogens are attacked 1.7 times faster than the tertiary hydrogen (after correcting for statistical effects). Other examples in the table show secondary hydrogens being attacked faster than tertiary.

Table I. Photochemical Chlorinations with R_2NCl in 30% H_2SO_4 at 15°

	Relative hydrogen reactivities						
	Isopentane[a]			2,2-Dimethylbutane[b]		2,3-Dimethylbutane[c]	
N-Chloro amine	p	s	t	p	s	p	t
Dimethyl	0.32	0.93	1	0.28	1	0.26	1
2,2,6,6-Tetramethylpiperidine	0.26	0.79	1	0.31	1		
Dicyclohexyl	0.40	1.12	1	0.36	1		
Diisopropyl	0.25	0.70	1	0.33	1	0.33	1
Dineopentyl	0.71	2.70	1	0.42	1	0.67	1
Di-*tert*-butyl	1.70	6.00	1	0.48	1		
tert-Butyl-*tert*-amyl	1.72	5.98	1				

[a] The products from primary attack were 1-chloro-2-methylbutane and 1-chloro-3-methylbutane in the statistical ratio 6:3. The products from secondary and tertiary attack were 2-chloro-3-methylbutane and 2-chloro-2-methylbutane, respectively. [b] The products from primary attack were 1-chloro-2,2-dimethylbutane and 1-chloro-3,3-dimethylbutane in the statistical ratio 9:3. The product from secondary attack was 2-chloro-3,3-dimethylbutane. [c] The products from primary and tertiary attack were 1-chloro-2,3-dimethylbutane and 2-chloro-2,3-dimethylbutane, respectively.

These are the first examples in which the normal order of tertiary > secondary > primary is reversed. This reversal is ascribed entirely to steric hindrance in the attacking radicals ($R_2NH\cdot^+$).

The products were analyzed by gas chromatography using a 6-ft 20% SE-30 column. Authentic samples were used for reference in every case.

The reactions were conducted at 15° using a 3% solution of R_2NCl in 30% H_2SO_4, a 5:1 ratio of alkane: R_2NCl, irradiation with a 300-W tungsten lamp, and vigorous stirring. The R_2NCl disappeared (KI test negative) after 1–4 hr. The conditions are similar to those used before with R_2NCl chlorinating agents.[3–5]

(1) B. Preiss and K. Bloch, *J. Biol. Chem.*, **239**, 85 (1964). For similar results since 1963 on other fatty acids, see M. Kusonose, E. Kusonose, and M. J. Coon, *ibid.*, **239**, 1374, 2135 (1964); A. S. Kester and J. W. Foster, *J. Bacteriol.*, **85**, 859 (1963); K. Wakabayashi and N. Shimazono, *Biochim. Biophys. Acta*, 70, 132 (1963).

(2) For references since 1964, see E. J. McKenna and R. E. Kallio, *Annu. Rev. Microbiol.*, **19**, 183 (1965); R. E. Kallio, Annual Report of the Petroleum Research Fund, American Chemical Society, 1967, p 20; R. D. McCarthy, *Biochim. Biophys. Acta*, **84**, 74 (1964); W. R. Finnerty and R. E. Kallio, *J. Bacteriol.*, **87**, 1261 (1964); J. A. Peterson, D. Basu, and M. J. Coon, *J. Biol. Chem.*, **241**, 5162 (1966); S. Ogino, K. Yano, G. Tamura, and K. Arima, *Agr. Biol. Chem.*, **29** (11), 1009 (1965); *Chem. Abstr.*, **64**, 7081 (1966).

(3) F. Minisci, G. P. Gardini, and G. Bertini, *Can. J. Chem.*, **48**, 544 (1970), and references cited therein.