

analog,¹³ which was synthesized with known configuration by a route involving unambiguous stereochemistry.¹⁴

However, preliminary rate studies carried out on α -(triphenylsilyl)acetophenone have shown that the thermal rearrangement cleanly follows first-order kinetics for more than three half-lives (90% completion). Hence the isomerization must be intramolecular, involving a four-center transition state, and the rearrangement of (+)-I to (-)-II must lead to retention of configuration at silicon.^{15,16}

Thus, as shown in Figure 1, since (-)-siloxystyrene (II) may arise directly from (+)-benzoylsilane (IV) with retention of configuration, or indirectly *via* formation of (+)-silylacetophenone (I) and its subsequent thermal rearrangement, both the formation and rearrangement of I must also involve retention of configuration. Consequently all three compounds must have the same relative configuration at the asymmetric silicon center.

It might be asked whether the siloxyalkene which was isolated as one of the products from the reaction of diazomethane with benzoylsilane arose, not as a direct product of the reaction, but instead from the sequence of reactions acylsilane \rightarrow β -ketosilane \rightarrow siloxyalkene. That this is not possible follows from observation of the progress of the reaction of the acylsilane with diazomethane at 5° by both nmr and infrared spectroscopy which showed that the ratio of siloxyalkene to β -keto silane formed was independent of the reaction time, as would be required if both products arose from a common intermediate.

Attempts to effect this rearrangement by photochemical methods did not succeed because the reaction took alternative pathways leading to dimerization and photoreduction products. These will be described later, as will our further studies now in progress.

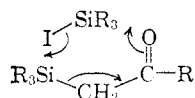
Acknowledgment. We acknowledge support of this research by a grant from the National Research Council of Canada and by a Fellowship to W. W. L. by Dow Corning Silicones of Canada.

(13) Both + enantiomers show virtually identical single positive Cotton curves down to about 320 μ , at which point absorption interferes.

(14) A. G. Brook and D. M. MacRae, unpublished results.

(15) There is ample precedent that four-center reactions involve retention of configuration—*e.g.*, the reduction of alkoxy silanes with lithium aluminum hydride¹⁰ and the Wittig reaction.¹⁷

(16) The catalyzed and therefore bimolecular reactions of Litvinova² undoubtedly involve six-center transition states such as



which would also be expected to involve retention of configuration.

(17) A. Bladé-Font, C. A. VanderWerf, and W. E. McEwen, *J. Am. Chem. Soc.*, **82**, 2396 (1960).

(18) Dow Corning Silicones of Canada Fellow, 1961–1962.

A. G. Brook, D. M. MacRae, W. W. Limburg¹⁸
Department of Chemistry, University of Toronto
Toronto 5, Canada

Received July 24, 1967

Phosphaboranes and Carbaphosphaboranes

Sir:

In the past few years there have been several reports concerning slightly distorted icosahedral boranes con-

taining one or two heteroatoms in the cage. The first series of these molecules to appear in the literature was 1,2-, 1,7-, and 1,12-dicarbaiclovododecaborane(12).¹⁻³ More recently brief communications concerning the $B_{11}H_{11}CH^-$ ion⁴ and the $B_{10}H_{10}SBC_6H_5$ molecule⁵ have appeared in the literature. All of these molecules are isoelectronic with the $B_{12}H_{12}^{2-}$ ion. In certain cases^{3,6,7} either X-ray or ¹¹B nmr studies have indicated that these molecules are best described as distorted icosahedra.

This communication concerns the formation, characterization, and preliminary chemistry of 1,2- $B_{10}H_{10}CHP$ (I), 1,7- $B_{10}H_{10}CHP$ (II), and $B_{11}H_{11}PC_6H_5$ (III). Slow addition of a 5% heptane solution of phosphorus trichloride to a slurry of $Na_3B_{10}H_{10}CH \cdot 2THF^8$ in heptane at reflux produced 1,2- $B_{10}H_{10}CHP$, mp 349–350°, in moderate yield. *Anal.* Calcd for $B_{10}H_{10}CHP$: C, 7.41, H, 6.4, P, 19.1, mol wt, 162. Found: C, 7.50, H, 6.84, P, 20.0; mol wt, 165 (cryoscopic in benzene). This compound is a white sublimable solid with an odor reminiscent of carborane ($B_{10}H_{10}C_2H_2$). The mass spectrum of I at low electron voltage (13 ev) cuts off at m/e 164 corresponding to the $^{12}C_1H_{11}^{11}B_{10}^{31}P_1^+$ ion. The ¹¹B nmr spectrum (32 Mc) of I is consistent with a 1:1:2:2:2:2 pattern expected for 1,2- or 1,7- $B_{10}H_{10}CHP$. Complete interpretation of the spectrum was not possible because of extensive overlap of the individual doublets. That the carbon and phosphorus atoms are *ortho* in I is suggested by the method of synthesis which formally involves insertion of a phosphorus atom into the open, carbon-containing pentagonal face of the $B_{10}H_{10}CH^{3+}$ ion to complete the distorted icosahedron. The proton nmr of I contains a broad doublet at τ 7.85 with a 14-cps splitting attributed to ³¹P–¹H coupling.

Heating I at 485° for 10 hr produced a new isomer (II), mp 325–327°, in 55% yield. Gas chromatographic analysis indicated that II was at least 98% pure. The ¹¹B nmr spectrum of II was too complex to be consistent with the two doublets expected for 1,12- $B_{10}H_{10}CHP$. The ¹H nmr spectrum of II contained a broad singlet (CH) at τ 7.52 with no observable ³¹P–¹H coupling. The nmr spectra suggest that II is best represented as 1,7- $B_{10}H_{10}CHP$ (Figure 1). This isomerization therefore appears to follow the rearrangement mechanism proposed by Lipscomb.⁹

The chemical properties of the carbaphosphaboranes are in some respects similar to the respective carborane analogs. Metalation of II with butyllithium and then reaction with methyl iodide produced 1,7- $B_{10}H_{10}C(CH_3)P$. An extensive derivative chemistry of the analogous 1-lithio-*m*-carborane has been reported.¹⁰ Reaction of I with excess bromine and aluminum chloride gave, as the ultimate product, 1,2- $B_{10}Br_3H_7CHP$.

(1) T. L. Heying, J. W. Ager, S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963).

(2) D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963).

(3) S. Papetti and T. L. Heying, *J. Am. Chem. Soc.*, **86**, 2295 (1964).

(4) W. H. Knoth, *ibid.*, **89**, 1274 (1967).

(5) E. L. Muetterties, "The Chemistry of Boron and Its Compounds," John Wiley and Sons, Inc., New York, N. Y., 1967, p 657.

(6) J. A. Potenza and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1917 (1966).

(7) J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1673 (1964).

(8) This solvated salt is obtained as a precipitate from the reaction of $B_{10}H_{12}CN(CH_3)_3$ with sodium metal in tetrahydrofuran.

(9) W. N. Lipscomb, *Science*, **153**, 373 (1966).

(10) T. P. Onak, *Advan. Organometal. Chem.*, **3**, 335 (1965).

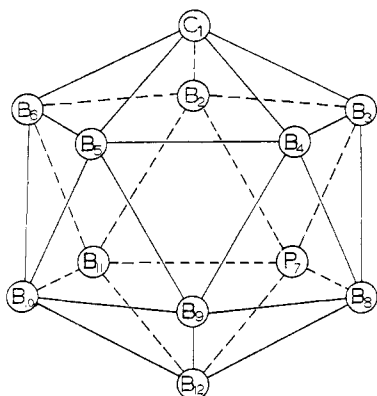


Figure 1. A proposed structure for 1,7-B₁₀H₁₀CHP.

The evolution of hydrogen bromide in this reaction and the broad doublet at τ 5.6 (CH) in the ¹H nmr spectrum indicate that halogen substitution occurs on the boron atoms. Bromination of *o*-carborane gave similar results.¹¹

Reaction of B₁₁H₁₃²⁻ with phenylphosphorus dichloride gave after repeated sublimation of the reaction products B₁₁H₁₁PC₆H₅ (III), mp 157–159°, in low yield. *Anal.* Calcd for B₁₁H₁₁PC₆H₅: C, 30.28; H, 6.78; P, 13.01. Found: C, 30.76; H, 6.62; P, 12.66. The mass spectrum of III at low electron voltage (13 ev) cuts off at *m/e* 241 corresponding to the ¹³C₁¹²C₅-¹H₁₆¹¹B₁₁³¹P₁⁺ ion. The ¹H nmr spectrum has a complex multiplet at τ 2.2 indicating the presence of a phenyl group. The ¹¹B nmr spectrum of III (32 Mc) contains three overlapping doublets with 1:5:5 relative areas at 3, 8.4, and 15 ppm, respectively [BF₃·(C₂H₅)₂O = 0 ppm]. This spectrum is consistent with an icosahedral cage structure for this phosphaborane. Relative to trivalent phosphines (*i.e.*, R₃P), I appears to be a weak Lewis base since it does not react with methyl iodide. The unknown B₁₁H₁₁P⁻ ion isoelectronic with III also contains a formally trivalent phosphorus atom. This ion should be more susceptible to attack by alkyl halides to form B₁₁H₁₁PR. This and other aspects of phosphaborane chemistry are under active investigation.

Acknowledgments. The authors wish to thank Dr. Donald F. Gaines, University of Wisconsin, for the 32-Mc ¹¹B nmr spectra and the National Science Foundation for support under Grant GP-4982.

(11) H. D. Smith, T. A. Knowles, and H. Schroeder, *Inorg. Chem.*, **4**, 107 (1965).

John L. Little, John T. Moran, Lee J. Todd
The W. A. Noyes Laboratory, University of Illinois
Urbana, Illinois 61801
Received July 5, 1967

Some Kinetic Evidence Pertaining to the Structure of the Cobalt(II)-Ethylenediaminetetraacetate (EDTA) Complex in Aqueous Solution

Sir:

The nature and number of bonding sites in multidentate ligands is one of the most interesting and important aspects of present-day coordination chemistry. In this context the investigations of the structures of metal-EDTA complexes in the solid state by Hoard and his colleagues¹ have produced some answers, but

the structures of the species in aqueous solution are less settled. The question has been carefully considered by Higginson,² who concluded that a substantial number of EDTA complexes of bivalent metals contained quinque-dentate ligand, *i.e.*, could be represented by M(EDTA)(H₂O)²⁻ with one uncoordinated carboxylate group. Support for this idea comes from the observation of a common *pK* ~ 3 for these complexes³ which is related to protonation of the free carboxylate group rather than involving any breakage of a metal-carboxylate bond. Offsetting this argument is the fact,⁴ which we have confirmed, that definite spectral changes in the visible accompany the protonation of the copper(II) and cobalt(II) complexes, and this is more easily rationalized in terms of at least some six-coordinated EDTA present.

Our approach to the problem has been to treat the cobalt(II)-EDTA complex at various acidities with a variety of rapidly reacting oxidants and to examine the spectra of the resultant cobalt(III) complex soon after it is formed. The various forms of the latter, Co(EDTA)⁻, Co(EDTAH)(H₂O), Co(EDTA)(H₂O)⁻, and Co(EDTA)(OH)²⁻ are well characterized.⁵ The three five-coordinate EDTA complexes revert to Co(EDTA)⁻, the hydroxo species particularly slowly⁵ so that solutions were adjusted to pH ~ 10 after reaction completion to prevent changes subsequent to the oxidation. As additional, necessary information the second-order rate constants have been determined. The results are shown in Table I.

With oxidants 1–4, outer-sphere oxidation occurs. The overwhelming product is Co(EDTA)⁻, and, were the rate constants for oxidation of five- and six-coordinated EDTA-cobalt(II) complexes identical, this would show that Co(EDTA)²⁻ is present to the extent of 97% or more. However, pH-dependence studies show that Co(EDTAH)(H₂O)⁻, which predominates at pH < 3 and in which EDTA must be acting as a five-coordinate ligand, reacts by a factor of some 5–12 slower than the unprotonated complex. This is not merely an electrostatic effect since this behavior persists even when the noncharged oxidant Fe(phen-5-SO₃)₃ is used. It appears reasonable therefore to assume that Co(EDTA)(H₂O)²⁻ will also react slightly slower than Co(EDTA)²⁻, and this must be allowed for in the analysis of the product distribution.⁶

For the oxidation by Fe(phen)₃³⁺, $k_{\text{Co(EDTA)}^{2-}}/k_{\text{Co(EDTA)(H}_2\text{O)}^{2-}}[\text{Co(EDTA)}^{2-}]/[\text{Co(EDTA)(H}_2\text{O)}^{2-}] \gtrsim 33$ and at pH 5.0, $k_1[\text{Co(EDTA)}^{2-} + \text{Co(EDTA)(H}_2\text{O)}^{2-}] = k_{\text{Co(EDTA)}^{2-}}[\text{Co(EDTA)}^{2-}] + k_{\text{Co(EDTA)(H}_2\text{O)}^{2-}}[\text{Co(EDTA)(H}_2\text{O)}^{2-}]$ so that with $k_1 = 9.1 \times 10^4$ (see Table I) and $k_{\text{Co(EDTA)(H}_2\text{O)}^{2-}} \sim k_{\text{Co(EDTAH)(H}_2\text{O)}^{2-}} \sim 1.6 \times 10^4$, this leads to a value of $\gtrsim 80\%$ of Co(EDTA)²⁻

(1) S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964), and previous references.

(2) W. C. E. Higginson, *J. Chem. Soc.*, 2761 (1962).

(3) G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, **34**, 567 (1951).

(4) T. R. Bhat and M. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **25**, 1147 (1963).

(5) I. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 260 (1958); R. Dyke and W. C. E. Higginson, *ibid.*, 1998 (1960).

(6) The reduced reactivity of Co(EDTAH)(H₂O)⁻ probably resides in its having a slightly more negative oxidation potential than Co(EDTA)²⁻, $E^\circ = -0.38$ v. That a five-coordinated EDTA species, however, would react inordinately slow and thus vitiate our reasoning is improbable when Co(A)(H₂O)⁻ (A = hydroxyethylethylenediaminetriacetate) reacts with Fe(bipy)₃³⁺ with a second-order rate constant (3.5×10^4 M⁻¹ sec⁻¹ at 25°) and gives CoA(H₂O)⁰, in which both Co(II) and Co(III) contain a five-coordinated ligand.