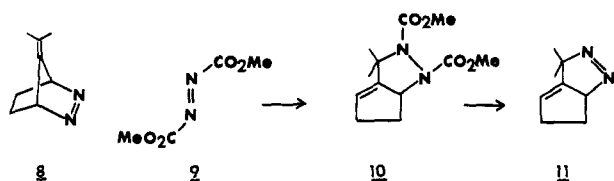


istic $C_{16}H_{24}$ dimers of **6**, which are formed in high yield in the absence of a trapping agent.⁴

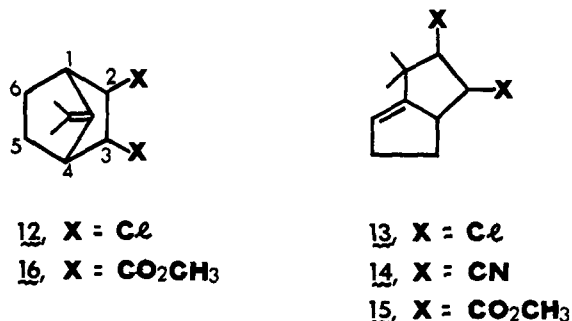
The efficiency of the cycloaddition, as measured by the competition between adduct formation and dimerization of **6**, is greater with conjugated olefins than with simple ones. 1,3-Cyclohexadiene, 2,4-hexadiene, methyl acrylate, acrylonitrile, fumaronitrile, and crotonitrile all form adducts in high yield, whereas cyclohexene, dihydropyran, and 1,2-diethoxyethylene do not.

Conjugated acetylenes do not seem to be good trapping agents. Decomposition of **8** in the presence of dimethyl acetylenedicarboxylate gives no adduct and a substantial amount of a polymeric product; in the presence of diphenylacetylene, **8** gives only the four $C_{16}H_{24}$ dimers of **6**.

The reaction of azo compound **8** with dimethyl azodicarboxylate **9** provides an example of an "azo transfer" reaction. The resulting cycloadduct **10** can be converted by a hydrolysis-decarboxylation-oxidation sequence to the fused azo compound **11**, isomeric with bridged azo compound **8**. Thermal decomposition of **11** gives the same four $C_{16}H_{24}$ dimers⁴ formed from **8**. The dimers are formed in proportions identical with those observed⁴ in other reactions leading to the diyl **6**.



Either *cis*- or *trans*-1,2-dichloroethylene gives about a 10% yield of an approximately 1:1 mixture of bridged (**12**) and fused (**13**) cycloadducts, whereas fumaronitrile gives a high yield (83% isolated) of the fused adducts **14**.⁶ The stereochemistry of these adducts is not yet known. Cycloadditions of dimethyl maleate and dimethyl fumarate give 95–100% yields of mixtures of fused⁶ and bridged cycloadducts. A typical product composition from maleate consists of the two fused adducts (**15** with *cis* carbomethoxy groups (27 and 36%), the corresponding fused adducts **15** with *trans* carbomethoxy groups (11 and 8%), and the bridged adducts (**16**, *endo-cis* (1%) and *trans* (17%)). Fumarate gives almost exclusively the *trans* adducts, fused (**15**, 57 and 33%) and bridged (**16**, 10%).⁷



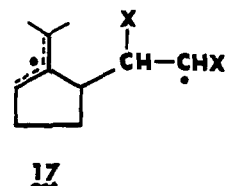
The stereochemical assignments in the bridged series **16** rest upon independent syntheses from or direct

(6) Elemental analysis and spectroscopic properties establish the molecular formula and structure.

(7) Analyses of product compositions by vapor chromatography.

comparisons with known⁸ compounds, obtained from Diels–Alder reactions of 6,6-dimethylfulvene. The *cis* compounds in the fused series (**15**) are identified by their preparation from the corresponding anhydrides, which are formed by the decomposition of azo compound **8** in molten maleic anhydride, and by their epimerization to mixtures of the two *trans* isomers with methanolic sodium methoxide.

Although some *cis* → *trans* crossover does occur in the maleate cycloaddition, it is clear that any intermediates in this and the corresponding fumarate reaction cannot be formulated as a single long-lived diradical (e.g., **17**), since that would produce identical adduct mixtures from each.



We hope to complete soon a quantitative ranking of the diylphilic reactivities of various olefins. In an accompanying paper,⁹ we report evidence on the mechanism of these cycloadditions.

(8) K. Alder and R. Rühmann, *Justus Liebigs Ann. Chem.*, **566**, 1 (1950).
(9) J. A. Berson, D. M. McDaniel, and L. R. Corwin, *J. Amer. Chem. Soc.*, **94**, 5509 (1972).

(10) Postdoctoral Fellow of the National Institute of General Medical Sciences, No. 1 FO2 GM37,585.

(11) Predoctoral Fellow of the National Institute of General Medical Sciences, No. 5 FO1 GM46,047.

Jerome A. Berson,* Dale M. McDaniel¹⁰
Leonard R. Corwin,¹¹ James H. Davis

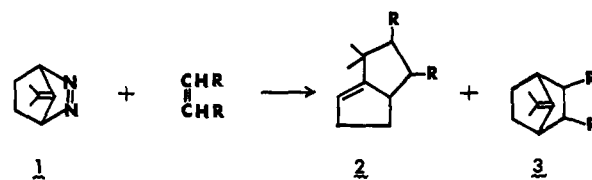
Department of Chemistry, Yale University
New Haven, Connecticut 06520

Received April 25, 1972

On the Mechanism of the Reaction of 7-Isopropylidene-2,3-diazanorborn-2-ene with Olefins. Evidence for a Symmetrical, Nitrogen-Free Intermediate¹

Sir:

When a mixture of 7-isopropylidene-2,3-diazanorborn-2-ene (**1**) and an appropriate olefin is kept at 40–60°, high yields of nitrogen and the cycloadducts **2** and **3** are formed.²



We record here experiments that establish the following features of the mechanism of these reactions.

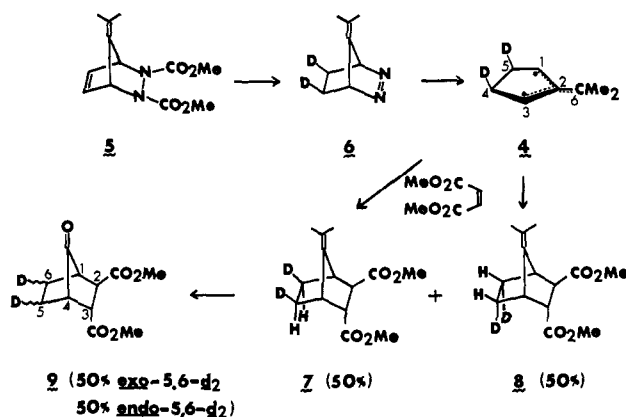
(1) The rate-determining step involves the conversion of the azo compound **1** to an intermediate which then

(1) This work was supported in part by the National Science Foundation (GP 11017X), the National Institute of General Medical Sciences (GM 16962), and the Hoffmann-LaRoche Foundation.

(2) J. A. Berson, D. M. McDaniel, L. R. Corwin, and J. H. Davis, *J. Amer. Chem. Soc.*, **94**, 5508 (1972).

reacts, either to give the four previously observed $^3\text{C}_{16}\text{H}_{24}$ dimers of 2-isopropylidenecyclopentane-1,3-diyl, or with the olefinic trapping agent to give **2** and/or **3**. The rate of disappearance of azo compound **1**, initial concentration 0.194 *M* in *o*-dichlorobenzene solution, is first order in **1** and zero order in the trapping agent ($k = 2 \times 10^{-4} \text{ sec}^{-1}$ at 52°, nmr analysis). The product composition, however, does depend on the olefin concentration. Increasing the initial concentration of fumaronitrile from zero up to 0.4 *M* changes the product from pure $\text{C}_{16}\text{H}_{24}$ dimer to largely the previously reported² cycloadduct **2**, R = CN. Similarly, in cyclohexane, in the presence of 2,4-hexadiene concentrations between 0 and 0.103 *M*, the decomposition of $4.6 \times 10^{-3} \text{ M}$ **1** has essentially the same rate constant as before ($3 \times 10^{-4} \text{ sec}^{-1}$ at 58°, uv) and is first order in **1**, although the product composition again changes from dimer to cycloadduct, depending on the initial concentration of the diene.

(2) In the reactive intermediate **4**, the ring and proximal side-chain carbons (C_1 - C_5 and C_6) are coplanar, either actually or on the time average. Catalytic semideuteration (10% Pd/C, EtOAc) of the diester **5**⁴ and then successive steps of hydrolysis-decarboxylation-oxidation give stereospecifically exo deuterated azo compound **6**. Decomposition of **6** in the presence of dimethyl maleate gives a mixture of products,² from which the labeled trans diester (**7**, **8**) can be isolated by vapor chromatography. Although the stereochemistry of the protons at C_5 and C_6 is difficult to determine by nmr in the adduct itself, ozonolysis smoothly converts this substance to the ketone **9**, in which the chemical shifts are different enough to show that the intensities of the 5,6 endo (δ 1.6) and 5,6 exo (δ 1.8) proton absorptions are equal. Hence the adduct consists of 50 \pm 5% each of **7** and **8**.



This result shows that any asymmetric species that may occur in the first stages of the decomposition of **6** (including but not limited to those produced by "double inversion" processes^{5,6}) become effectively symmetrical before being trapped by the olefinic diylophile. It is specifically difficult to ascribe this behavior to a product-forming intermediate in which only one of the C-N bonds is broken.⁷

(3) J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, *J. Amer. Chem. Soc.*, **93**, 1544 (1971).

(4) J. J. Tufariello and J. J. Spadaro, *Tetrahedron Lett.*, 3935 (1969).

(5) W. R. Roth and M. Martin, *Justus Liebigs Ann. Chem.*, **702**, 1 (1967); *Tetrahedron Lett.*, 3865, 4695 (1967).

(6) E. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, **91**, 6766 (1969).

(3) The partial loss of stereochemical integrity (cis olefin \rightarrow some trans cycloadduct) observed² in the addition of the diyl **4** to dimethyl maleate suggests that at least some of the cycloadduct results from sequential rather than simultaneous formation of the two new C-C bonds. Also formally compatible with the data is a mechanism in which there are two competing cycloadditions, one cis and one trans, both with simultaneous two-bond-forming transition states. In that case, however, to account for the greater crossover from cis than from trans, it must be assumed that the competition ratio for trans vs. cis addition is much greater with cis olefin than with trans. If the reaction occurs in two steps, the first is not detectably reversible, since *cis,cis*-2,4-hexadiene, *trans,trans*-2,4-hexadiene, dimethyl maleate, and dimethyl fumarate all can be recovered without loss of stereochemical integrity from reaction mixtures in which enough azo compound **1** has been decomposed to convert a substantial fraction of the olefinic diylophile to cycloadduct. In the case of *cis,cis*-2,4-hexadiene, for example, ring closure of the intermediate is at least 50 times as fast as reversal of the first step of the addition.

(4) The spin state of the reactive species in cycloaddition is uncertain. The observed³ strong nmr emission signals due to chemically induced dynamic nuclear polarization (CIDNP) of the $\text{C}_{16}\text{H}_{24}$ dimers in decompositions of azo compound **1** require⁸ that at least one of the reacting partners be a triplet in the process leading to polarized product. Theory⁸ suggests that a two-step addition of a triplet diradical to an olefin (singlet) might also form a polarized product. In a search for such an effect, we find that decompositions at 83° of azo compound **1** in acetonitrile or *o*-dichlorobenzene solutions of fumaronitrile in the magnetic field of an nmr spectrometer give either no CIDNP signals at all or only the previously observed³ emissions of the $\text{C}_{16}\text{H}_{24}$ dimers. Neither emission nor enhanced absorption is observed⁹ at the unobstructed chemical-shift positions corresponding to the absorption lines of the α -cyano protons of the cycloadduct (**2**, R = CN), which occur at δ 3.3. Although these observations do not exclude the triplet, it is conceivable that the reason for the formation of nonpolarized cycloadduct is that the main reactive intermediate under these conditions may be the singlet diradical.

We have observed that dilution of the initial olefin concentration causes a marked increase in the proportion of crossover product (trans cycloadduct from cis olefin) in the reaction of **1** with dimethyl maleate. This suggests the possibility that there may be two reactive intermediates, one formed directly from azo compound **1** and reacting rather stereospecifically, another formed after a time lag and reacting rather nonstereospecifically. These properties are consistent with those to be expected of a singlet and its derived triplet, although the completion of further experiments now in progress is a prerequisite for the advancement

(7) Note that the experiment described here is noncommittal with respect to the coplanarity of the methyl carbons of **4** with the ring and C_6 carbons.

(8) G. L. Closs, *J. Amer. Chem. Soc.*, **93**, 1546 (1971).

(9) Measurements began within 20 sec of insertion in the preheated probe and were done both by conventional scanning and by automatic repetitive scan, computerized data collection (PDP-8), and Fourier transform analysis with scan cycles of 4 sec. We thank Professor Martin Saunders for the latter experiment.

of this suggestion from the status of a working hypothesis to that of a mechanistic proposal.

(10) Postdoctoral Fellow of the National Institute of General Medical Sciences, No. 1 FO2 GM37,585.

(11) Predoctoral Fellow of the National Institute of General Medical Sciences, No. 5 FO1 GM46,047.

Jerome A. Berson,* Dale M. McDaniel,¹⁰ Leonard R. Corwin¹¹

Department of Chemistry, Yale University
New Haven, Connecticut 06520

Received April 25, 1972

Synthesis and Structural Characterization of Three New Platinum(IV) Halide Anions as Triphenylcarbenium¹ Salts. Isolation from Reaction of Platinum Tetrachloride with Trityl Chloride in Benzene of a Novel $[\text{Pt}(\text{C}_6\text{H}_5)_2\text{Cl}_{14}]^{2-}$ Anion Containing *o*-Phenylene Ligands²

Sir:

We wish to report the preparation and characterization of $[(\text{C}_6\text{H}_5)_3\text{C}]^+[\text{PtCl}_5 \cdot \text{CH}_2\text{Cl}_2]^-$ (**1**), $[(\text{C}_6\text{H}_5)_3\text{C}]^{+2}[\text{Pt}_2\text{Cl}_{10}]^{2-}$ (**2**), $[(\text{C}_6\text{H}_5)_3\text{C}]^{+2}[\text{Pt}_3\text{Cl}_{12}]^{2-}$ (**3**), $[(\text{C}_6\text{H}_5)_3\text{C}]^{+2}[\text{Pt}_3\text{Cl}_{12}]^{2-} \cdot 2\text{C}_2\text{H}_2\text{Cl}_4$ (**4**), and $[(\text{C}_6\text{H}_5)_3\text{C}]^{+2}[\text{Pt}_4(\text{C}_6\text{H}_4)_2\text{Cl}_{14}]^{2-} \cdot 2\text{CH}_2\text{Cl}_2$ (**5**) by the previously unreported reaction of $[\text{PtCl}_4]_4^3$ with $(\text{C}_6\text{H}_5)_3\text{CCl}$ in various solvents

(1) The term "carbenium" (rather than the inveterate "carbonium" ion, which will be used in this paper, has been suggested by G. A. Olah [*J. Amer. Chem. Soc.*, **94**, 808 (1972)] for "classical" trivalent carbocations to differentiate them from "nonclassical" penta- or tetracoordinated carbocations.

(2) (a) This research resulted from an initial investigation included in the dissertation submitted by P. M. Cook to the Graduate School at Colorado School of Mines in partial fulfillment of the requirements for the M.S. degree, 1968; (b) presented in part at the 61st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, Abstracts, INORG 95.

(3) Although platinum tetrachloride has been reported from a powder X-ray diffraction study to possess the solid-state SnI_4 structure comprised of tetrahedral molecules,⁴ we feel (in the absence to date of suitable single crystals for an X-ray crystallographic investigation) that our spectral data (presented below) provide conclusive evidence that this widely accepted possibility of such a simple monomeric species in the solid state can be definitely excluded. In addition (inasmuch as we cannot find such a suggestion in the literature), we propose that platinum tetrachloride has a cubane-like tetrameric structure both in the solid and vapor states and offer the following arguments to support our proposal. (a) No Pt(IV) complexes are known to possess tetrahedral coordination as proposed for platinum tetrachloride; furthermore, a crystalline arrangement of discrete PtCl_4 molecules would presumably give rise to a relatively volatile, paramagnetic complex which is not the case. Octahedral coordination can be achieved in $[\text{PtCl}_4]_z$ by chlorine bridge bonding either as in the known Pt(IV) cubane structures $[\text{Pt}(\text{CH}_3)_3\text{Cl}]_4$,⁵ $[\text{Pt}(\text{C}_2\text{H}_5)_3\text{Cl}]_4$,⁶ and $[\text{PtCl}(\text{C}_6\text{H}_5)\text{Cl}]_4$,⁷ or as in $[\text{PtI}_4]_z$,⁸ which contains an infinite zigzag chain of edge-linked PtCl_6 octahedra. The structure of PtX_3 ($\text{X} = \text{Cl}, \text{Br}$)⁹ contains Pt(II) in $[\text{Pt}_6\text{X}_{12}]$ units and Pt(IV) in $[\text{PtX}_4]_\infty$ chains as in $[\text{PtI}_4]_\infty$. Our spectral data indicate that the cubane structure is more likely. (b) The far-infrared spectrum¹⁰ of $[\text{PtCl}_4]_z$ shows absorption bands characteristic of both terminal and bridging chlorine atoms;¹¹ this spectrum is comparable to the spectra of $[\text{Pt}(\text{CH}_3)_3\text{Cl}]_4$ and $[\text{PtCl}(\text{C}_6\text{H}_5)\text{Cl}]_4$.⁷

	$\nu(\text{Pt}-\text{Cl})_t$	$\delta(\text{Pt}-\text{Cl})_t$	$\nu(\text{Pt}-\text{Cl})_b$	$\delta(\text{Pt}-\text{Cl})_b$
$[\text{Pt}(\text{CH}_3)_3\text{Cl}]_4$			220	140
$[\text{PtCl}(\text{C}_6\text{H}_5)\text{Cl}]_4$	330 d	180, 200	230	125
$[\text{PtCl}_4]_z$	337, 366, 376	182	275, 292	128

t = terminal chlorine, b = bridging chlorine, d = doublet

The large difference in the assigned platinum-bridging chlorine stretching frequencies can be readily rationalized by the strong trans influence of the terminal alkyl ligands in the two known cubane-like Pt(IV) compounds. The ability of a *trans*-methyl ligand to lower the Pt(IV)-Cl stretching frequency is illustrated in $\text{PtCl}_2(\text{CH}_3)_2\{\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)_2\}_2$ for which $\nu(\text{Pt}-\text{Cl})$ is 332 cm^{-1} when the methyl groups are *cis* to the chlorine atoms and $242, 265 \text{ cm}^{-1}$ when the methyl groups are *trans* to the chlorine atoms.¹² The same trans influence can be exerted on platinum-bridging chlorine stretching frequencies as in $\text{Pt}_2\text{Cl}_4\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ which has $\nu(\text{Pt}-\text{Cl})$ equal to 320 cm^{-1} when the chlorine atoms are *trans* to each

(including methylene chloride and benzene). The three polymeric platinum halide anions of 2-5 are hitherto unknown for platinum and its congeners (palladium and nickel); furthermore, the anion of 3 and 4 represents a rare example of a compound possessing metal atoms with mixed valency (*viz.*, Pt(II) and Pt(IV) within the same discrete unit), while the novel anion of 5 provides the first case determined by X-ray diffraction of a substituted benzene ring σ bonded to more than one transition metal atom. This communication thereby illustrates the possible diversity and scope of the general reaction of anhydrous transition metal chlorides with triphenylmethyl chloride under varying conditions to give new anions of unusual stoichiometry.

Our study of the reactions of $[\text{PtCl}_4]_4$ with $(\text{C}_6\text{H}_5)_3\text{CCl}$ was predicated on the basis that the well-known $[\text{PtCl}_4]^{2-}$ anion may not be produced due to the inability of a $[\text{PtCl}_5]^-$ species to ionize $(\text{C}_6\text{H}_5)_3\text{CCl}$ further. Since Pt(IV) invariably possesses an octahedral-like coordination, one may expect dimerization of $[\text{PtCl}_5]^-$ to give the previously unknown $[\text{Pt}_2\text{Cl}_{10}]^{2-}$ anion.

The coordinating ability of the solvent used for the reaction of $[\text{PtCl}_4]_4$ with $(\text{C}_6\text{H}_5)_3\text{CCl}$ appears to determine the nature and extent of the products isolated. A finely powdered slurry of $[\text{PtCl}_4]_4$ in CH_2Cl_2 reacts completely under nitrogen with $(\text{C}_6\text{H}_5)_3\text{CCl}$ in slight excess of 1:1 mole ratio to give an orange solution which yields yellow-orange crystals of **1** upon evaporation of solvent. A few deep red crystals of **2** and orange-red crystals of **3** invariably crystallize out with **1**. Slow evaporation of solvent from the red solution, which results from the above orange solution standing for 48 hr or more, gives some crystals of **1** with increased amounts of **2** and **3**. Although the yields of **2** and **3** vary from 5 to 20 and 10 to 40%, respectively, excess

other but 260 cm^{-1} when the chlorine atom is *trans* to triphenylphosphine.¹³ (c) The mass spectrum of $[\text{PtCl}_4]_z$ consists of a parent *m/e* peak centered at 1348 due to $[\text{Pt}_4\text{Cl}_{16}]^+$ and contains a rich fragmentation pattern completely consistent with a cubane structure. The only peaks found above the parent-ion peak are attributed to $[\text{Pt}_5\text{Cl}_{19}]^+$, $[\text{Pt}_6\text{Cl}_{22}]^+$, and $[\text{Pt}_7\text{Cl}_{25}]^+$ with only $[\text{Pt}_5\text{Cl}_{19}]^+$ having a high relative abundance; these three species are ascribed to a thermal rearrangement which is common for metal cluster systems. (d) Our X-ray powder film and powder diffractometry measurements of $[\text{PtCl}_4]_z$ samples prepared by the method of Keller¹⁴ and also purchased from Alfa Inorganics, Inc., do not correspond to the powder patterns reported by Falqui.⁴ Our patterns, which are all the same, cannot be indexed in the cubic crystal system. If $[\text{PtCl}_4]_z$ crystallizes into more than one crystal system, the cubic crystal form reported by Falqui⁴ should have the cubane structure since her determined lattice length of $a = 10.45 \text{ \AA}$ is nearly identical with that of $a = 10.55 \text{ \AA}$ given⁶ for $[\text{Pt}(\text{CH}_3)_3\text{Cl}]_4$, which also belongs to the cubic crystal system. Although the spatial requirement of a terminal methyl group about a platinum(IV) atom is almost exactly that of a terminal chlorine atom, a structure factor analysis of Falqui's powder diffraction data shows that crystalline $[\text{PtCl}_4]_z$ is not isomorphous with $[\text{Pt}(\text{CH}_3)_3\text{Cl}]_4$. A $[\text{PtI}_4]_\infty$ type of structure is impossible in her cubic unit cell.

(4) M. T. Falqui, *Ann. Chim. (Rome)*, **48**, 1160 (1958).

(5) R. E. Rundle and J. H. Sturdivant, *J. Amer. Chem. Soc.*, **69**, 1561 (1947).

(6) R. N. Hargreaves and M. R. Truter, *J. Chem. Soc. A*, 90 (1971).

(7) S. E. Binns, R. H. Cragg, R. D. Gillard, B. T. Heaton, and M. F. Pilbrow, *ibid.*, 1227 (1969).

(8) V. K. Brodersen, G. Thiele, and B. Holle, *Z. Anorg. Allg. Chem.*, **369**, 154 (1969).

(9) U. Wiese, H. Schäfer, H. G. Schnering, C. Brendel, and K. Rinke, *Angew. Chem., Int. Ed. Engl.*, **9** (2), 158 (1970).

(10) The far-infrared spectrum of a Nujol mull of $[\text{PtCl}_4]_z$ was measured on a Digilab FTS-14 spectrometer through the courtesy of Dr. Peter Griffiths of Sadtler Research Labs, Philadelphia, Pa.

(11) D. M. Adams and P. J. Chandler, *Chem. Commun.*, 3, 69 (1966).

(12) J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 2801 (1969).

(13) R. J. Goodfellow, P. L. Goggin, and L. M. Venanzi, *ibid.*, 1897 (1967).

(14) R. N. Keller in "Inorganic Syntheses," Vol. II, W. C. Fernelius, Ed., McGraw-Hill, New York, N. Y., 1946, p 253.