Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

Rhenium Nitrosyl Carbonyl Complexes

Jack R. Norton*[1a] and Giuliano Dolcetti[1b]

Received July 13, 1972

The recent report that the chloride-bridged dimer $[Re(NO)(CO)_2Cl_2]_2$ (**1**), first synthesized from $[Re(CO)_4Cl]_2$ (**2**) and NOCl,[2] could also be made by the prolonged action of NO and HCl on the same material[3] was surprising. It had previously been stated that $[Re(CO)_4Cl]_2$ was inert to the action of nitric oxide alone.[4] Our interest in the mechanism of this reaction (which we found to give erratic results) in particular, and in polynuclear nitrosyl carbonyls in general,[5] prompted an investigation of the preparation and properties of rhenium nitrosyl carbonyls.

Species containing the Re(NO)(CO) groups might be expected to show chemistry like that of the isoelectronic complexes containing $Os(CO)_2$. However, the results obtained here indicate that their chemistry much more resembles that of their rhenium carbonyl anion ($[Re(CO)_2]^-$) analogs.

Experimental Section

Microanalyses were performed by the Stanford Microanalytical Laboratory. Nmr spectra were taken on a Varian HA-100, infrared spectra on a Perkin-Elmer 457, and Raman spectra on a Spex Ramalog with 6328-Å laser excitation. Nitric oxide was passed through a trap containing silica gel at −78°. $[Re(CO)_4Cl]_2$ and $[Re(CO)_4Br]_2$ were prepared from rhenium carbonyl by standard methods.[6]

Tri-μ-chloro-pentacarbonylnitrosyldirhenium, $Re_2(NO)(CO)_5Cl_3$ (3). $[Re(CO)_4Cl]_2$ (500 mg) was dissolved in 700 ml of boiling carbon tetrachloride under nitrogen; nitric oxide was then passed slowly through the refluxing solution for 11 hr. The reaction mixture was cooled, purged with nitrogen, and filtered in air. Addition of heptane and removal of most of the solvent under vacuum gave 322 mg of impure green plates. Recrystallization from CH_2Cl_2-hexane gave 241 mg (50%) of light orange crystals of pure **3**. *Anal.* Calcd for $Re_2C_5NO_6Cl_3$: C, 9.26; N, 2.16; Cl, 16.39; mol wt 649. Found: C, 9.19; N, 2.26; Cl, 16.12; mol wt 649 (by mass spectroscopy). Infrared: $\nu_{CO}(CCl_4)$ 2113 (m), 2047 (vs), and 1946 (s) cm^{-1}; $\nu_{NO}(CCl_4)$ 1813 (m) cm^{-1}; ν_{Re-Cl}(KBr) 321 (m) and 276 (s, br) cm^{-1}. Raman: ν_{Re-Cl} 326, 282, and 272 cm^{-1}.

An analogous reaction with $[Re(CO)_4Br]_2$, CBr_4, and nitric oxide in benzene gave an inseparable mixture whose analysis and infrared spectra were consistent with a mixture of the bromine analogs of **3** and **1**.

Di-μ-chloro-dichlorotetracarbonyldinitrosyldirhenium, $[Re(NO)(CO)_2Cl_2]_2$ (1). $Re_2(NO)(CO)_5Cl_3$ (1.1 g) was dissolved in 600 ml of benzene, 50 ml of saturated ethanolic hydrogen chloride was added, and the resulting solution was deoxygenated with nitrogen. Nitric oxide was bubbled through the mixture at room temperature for 2.5 days and then purged with nitrogen. Removal of solvent gave an oil (ethanol solvate) which slowly solidified after being left overnight under high vacuum. Recrystallization from CCl_4-heptane gave 805 mg (69%) of product. The infrared spectrum was identical with that of an authentic sample of **1**.

Interaction of Rhenium Nitrosyl Carbonyl Complexes with Ethanol. The complexes **1** and **3** were more soluble in 1:1 C_6D_6-EtOH than in pure C_6D_6; addition of ethanol to a benzene solution of either complex changed its color from orange to a pale yellow-green. The solution of **1** in the mixed solvent showed ν_{CO} at 2095 and 2025 cm^{-1} and ν_{NO} at 1774 cm^{-1}. Solutions of **3** in the same mixture showed the same three peaks and in addition carbonyl bands at 2037 (s) and 1914 (vs) cm^{-1}. Both of these ethanol-solvation reactions were reversible: evaporation at reduced pressure yielded oils which slowly crystallized as the reformed dimers **1** and **3**.

Tetramethylammonium triiododicarbonylnitrosylrhenate(I), $[(CH_3)_4N][Re(NO)(CO)_2I_3]$ (6), was obtained by treatment of **1** in acetone with excess lithium iodide, removal of solvent, addition of water and saturated aqueous tetramethylammonium iodide, and slow concentration of the solution at room temperature. The resulting orange salt dissolved readily in acetone and ethanol to form remarkably air-stable solutions. Its conductance in acetone (measured at 0.001 *M*) was 140 mhos cm^2/mol, a reasonable value for a 1:1 electrolyte.[7] *Anal.* Calcd for $ReC_6H_{12}N_2O_3I_3$: C, 9.91; H, 1.66; N, 3.85; I, 52.36. Found: C, 9.96; H, 1.75; N, 3.82; I, 50.73. Infrared (KBr): ν_{CO} 2080 and 2014 cm^{-1} and ν_{NO} 1776 cm^{-1}.

Tri-μ-ethoxy-pentacarbonylnitrosyldirhenium, $Re_2(NO)(CO)_5(OC_2H_5)_3$ (7). $[Re(NO)(CO)_2Cl_2]_2$ (**1**) (200 mg), zinc dust (250 mg), and 70 ml of absolute ethanol were placed in a 300-ml autoclave. Carbon monoxide (1200 psi) was then added and the reaction was stirred at 125° for 6 hr. After cooling and venting, the unreacted zinc was removed by filtration and the filtrate was evaporated to dryness. The yellow residue was separated by tlc on silica gel with development by benzene. The first band (R_f 0.8) contained decacarbonyldirhenium; the second (R_f 0.6) yielded 72 mg (37%) of product, a fluffy yellow material subliming quantitatively at 100° under a pressure of 50 μ. *Anal.* Calcd for $Re_2C_{11}H_{15}NO_9$: C, 19.50; H, 2.23; N, 2.07; mol wt 678. Found: C, 19.82; H, 2.20; N, 2.36; mol wt 678 (by mass spectrometry). The formulation was further confirmed by exact mass measurement on the $[P - 2CO]^+$ fragment: calcd for $^{187}Re_2C_9H_{15}NO_7$, 622.9968; found, 622.9974. Infrared (cyclohexane): ν_{CO} 2076 (m), 2019 (s), 1999 (vs), and 1907 (vs) cm^{-1}; ν_{NO} 1771 (s) cm^{-1}. Nmr (C_6D_6, τ): 5.95 (m, 4 H trans from CO); 6.30 (q, 2 H trans from NO); 8.90 (t, 6 H); 9.05 (t, 3 H).

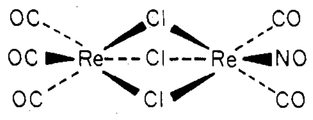
Results and Discussion

$[Re(CO)_4Cl]_2$ did prove to react slowly with pure nitric oxide in boiling benzene to give a polymeric product containing chlorine. This result suggested the use of carbon tetrachloride (which reacts with many metal carbonyls by free-radical mechanisms[8]) as solvent and halogen source. The following slow reaction occurred

$$[Re(CO)_4Cl]_2\ (2) \xrightarrow[CCl_4,\ 77^\circ]{NO} Re_2(NO)(CO)_5Cl_3\ (3)$$

No further reaction to form $[Re(NO)(CO)_2Cl_2]_2$ was detectable.

As all of its carbonyl and nitrosyl infrared bands were clearly terminal, **3** was assigned the structure



3

The existence of the triple-chloride bridge was substantiated by the lack of a $[P - Cl]^+$ fragment in the mass spectrum of **3**, in contrast to the observation of such a peak in that of **1** (see Table I); such a fragment appears to be characteristic of terminal halides.[9] Although the ν_{Re-Cl} values in **3** were

---

[1] (a) To whom correspondence should be addressed at Department of Chemistry, Princeton University, Princeton, N. J. 08540. (b) On leave from Centro Chimica Composti Organometallici, CNR, Bologna, Italy.

[2] F. Zingales, A. Trovati, and F. Cariati, "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier, New York, N. Y., 1968, p 248.

[3] F. Zingales, A. Trovati, F. Cariati, and P. Uguagliati, *Inorg. Chem.*, 10, 507 (1971).

[4] J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 7, 32 (1958).

[5] J. R. Norton, J. P. Collman, G. Dolcetti, and W. T. Robinson, *Inorg. Chem.*, 11, 382 (1972).

[6] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, 1, 933 (1962).

[7] W. J. Geary, *Coord. Chem. Rev.*, 7, 81 (1971).

[8] C. H. Bamford, G. C. Eastmond, and F. J. T. Fildes, *Chem. Commun.*, 144, 146 (1970).

Table I. Selected Fragments from Mass Spectra of Rhenium Nitrosyl Carbonyl Halides

$Re_2(NO)(CO)_5Cl_3$			$[Re(NO)(CO)_2Cl_2]_2$		
m/e[a]	Ion	Rel intens[b]	*m/e*[a]	Ion	Rel intens[b]
649	$Re_2(NO)(CO)_5Cl_3^+$	79	686	$Re_2(NO)_2(CO)_4Cl_4^+$	41
621	$Re_2(NO)(CO)_4Cl_3^+$	100	658	$Re_2(NO)_2(CO)_3Cl_4^+$	100
			651	$Re_2(NO)_2(CO)_4Cl_3^+$	8

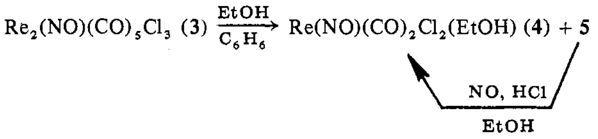
[a] For ^{187}Re and ^{35}Cl peaks. [b] Most intense peak = 100.

above the range suggested by Zingales[3] for bridging ν_{Re-Cl}, the pattern of infrared and Raman frequencies (see Experimental Section) agreed remarkably well with that observed in a detailed analysis of the tri-μ-chloro system in $Cs_3Tl_2Cl_9$.[10]

While the precise carbonyl anion analog of **3** has not been reported, the tri-μ-hydrido carbonyl anion $[Re_2(CO)_6H_3]^-$ is well known[11] and the tri-μ-azido manganese analog $[Mn_2(CO)_6(N_3)_3]^-$ has been the subject of a recent X-ray crystallographic study.[12] A similar reaction with $[Re(CO)_4Br]_2$ and CBr_4 in place of CCl_4 apparently yielded a mixture of the bromine analogs of **3** and **1**. The observation of some dinitrosylation with bromine but not with chlorine suggests that the tri-μ-bromo structure may be less stable than its chloro analog, as previously proposed in another system.[13]

Behavior of 1 and 3 in Ethanol Solution. Addition of ethanol to a deuteriobenzene solution of $[Re(NO)(CO)_2Cl_2]_2$ changed its infrared spectrum to one characteristic of monomeric complexes $Re(NO)(CO)_2Cl_2L$.[3] Removal of solvent and prolonged pumping regenerated **1**. Apparently an ethanol-solvated species $Re(NO)(CO)_2Cl_2(EtOH)$ (**4**) can be formed by reversible bridge cleavage of **1** just as the carbonyl anion analog of **1**, $[Re_2(CO)_6Cl_4]^{2-}$, undergoes solvolysis to monomeric units in acetonitrile.[14-17]

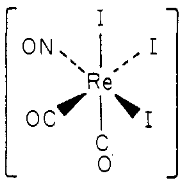
Similar treatment of $Re_2(NO)(CO)_5Cl_3$ also produced bridge cleavage by ethanol. The nitrosyl and carbonyl regions of the resulting infrared spectrum showed peaks due to **4** as well as others which must be due to a fragment **5** of formula "$Re(CO)_3Cl(EtOH)_n$" where the degree of solvation and extent of association are of course unknown. Removal of solvent regenerated **3**. However, treatment with nitric oxide in the presence of HCl readily nitrosylated the remaining rhenium and pure $[Re(NO)(CO)_2Cl_2]_2$ was obtained by evaporation of the solution of the solvate **4**.



$$Re_2(NO)(CO)_5Cl_3\ (\mathbf{3}) \xrightarrow[C_6H_6]{EtOH} Re(NO)(CO)_2Cl_2(EtOH)\ (\mathbf{4}) + \mathbf{5}$$

In view of these results it seems likely that the synthesis of $[Re(NO)(CO)_2Cl_2]_2$ reported[3] from **2** by the prolonged action of HCl and NO in boiling benzene proceeds through slow formation of $Re_2(NO)(CO)_5Cl_3$ and subsequent rapid reaction to give **1**.

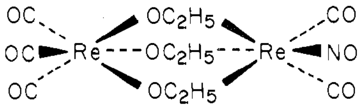
Bridge Cleavage by Iodide. The chloro complex **1**, which undergoes halide exchange in acetone to give $[Re(NO)(CO)_2I_2]_2$ in modest yield,[3] was readily extracted into water with lithium iodide to give which was isolated as the tetramethylammonium salt. The stereochemistry of **6** was assigned on the basis of the close resemblance of its infrared spectrum to that of $[Re(NO)(CO)_2I_2]_2$.[3] This reaction is analous to the formation of $[Re(CO)_3X_3]^{2-}$ from various starting materials with $[Re_2(CO)_6X_4]^{2-}$ as an apparent intermediate.[14]



6

Reduction. Dimers of the type $[M(CO)_3Cl_2]_2$ are known (in the case of ruthenium[18]) and probable (in the case of osmium) intermediates in the reductive carbonylation of ruthenium and osmium[5] trichlorides with zinc in alcohol to their respective carbonyls. Hence **1** under similar treatment might be expected to give a rhenium nitrosyl carbonyl. However, the reaction gives, along with some rhenium carbonyl, the novel nitrosyl carbonyl ethoxide $Re_2(NO)(CO)_5(OC_2H_5)_3$ (**7**). The carbonyl anion analog of **7**, $[Re_2(CO)_6(OC_2H_5)_3]^-$ (**8**), is well known as a product of the carbonylation of ReH_9^{2-} in ethanol.[11] Indeed, the infrared spectrum of **7** suggests a structure analogous to that of **8**.

$$[Re(NO)(CO)_2Cl_2]_2\ (1) \xrightarrow[EtOH,\ 125°]{CO,\ Zn} Re_2(CO)_{10} + Re_2(NO)(CO)_5(OC_2H_5)_3\ (7)$$



7

The nmr spectrum not only confirms the structure shown but also is of some intrinsic interest. The methylene protons in the ethoxide bridges trans to the carbonyl ligands display magnetic nonequivalence, with $J_{A-B} = -10.5$ cps and $\Delta\nu = 7.5$ cps at 100 MHz, similar to the nonequivalence observed in polymeric metal isopropoxides.[19-21] This observation substantiates the assignment of the *downfield* ethoxides as those trans to carbonyl groups and suggests that in this

---

(9) J. Lewis and B. F. G. Johnson, *Accounts Chem. Res.*, 1, 245 (1968).

(10) I. R. Beattie, T. R. Gilson, and G. A. Ozin, *J. Chem. Soc. A*, 2765 (1968).

(11) A. P. Ginsberg and M. J. Hawkes, *J. Amer. Chem. Soc.*, 90, 5930 (1968).

(12) R. Mason, G. A. Rusholme, W. Beck, H. Engelmann, K. Joos, B. Lindenberg, and H. S. Smedal, *Chem. Commun.*, 496 (1971).

(13) R. Saillant, R. B. Jackson, W. E. Streib, K. Polting, and R. A. D. Wentworth, *Inorg. Chem.*, 10, 1453 (1971).

(14) M. J. Hawkes and A. P. Ginsberg, *Inorg. Chem.*, 8, 2189 (1969).

(15) The same type of bridge cleavage in ethanol (and ethanol-containing chloroform) has just been demonstrated for the related compounds $[Ru(CO)_3X_2]_2$[16] and probably accounts for the reported[17] isomerization of $[Os(CO)_3Cl_2]_2$ in chloroform as well.

(16) E. Benedetti, G. Braca, G. Sbrana, F. Salvetti, and B. Grassi, *J. Organometal. Chem.*, 37, 361 (1972).

(17) M. I. Bruce, M. Cooke, M. Green, and D. J. Westlake, *J. Chem. Soc. A*, 987 (1969).

(18) M. I. Bruce and F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, 7, 427 (1968).

(19) A. Mehrotra and R. C. Mehrotra, *J. Chem. Soc., Chem. Commun.*, 189 (1972).

(20) The nonequivalence is clearly not due to stereoisomerism around the bridging oxygen, as no nonequivalence was observed for the ethoxide trans to the nitrosyl ligand and none was reported in the nmr spectrum of $[Re_2(CO)_6(OC_2H_5)_3]^-$.[11] The barrier to inversion at oxygen appears to be very small.[21]

(21) A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, *J. Amer. Chem. Soc.*, 93, 6507 (1971), and references therein.

particular complex the nitrosyl ligand (which has a rather high ν_{NO}, 1771 cm^{-1}) may be a poorer π acceptor than the carbonyl ligands.

Registry No. **1**, 25360-92-3; **3**, 37402-69-0; **6**, 37402-71-4; **7**, 37438-57-6.

Acknowledgments. The authors are grateful to Professor J. P. Collman for advice, encouragement, and financial support under National Science Foundation Grant No. GP20273X and Petroleum Research Fund Grant No. 3635, to Professor J. McLeod, Australian National University, Canberra, Australia, for mass spectroscopy, and to Professor F. Zingales, Padua, Italy, for an authentic sample of **1**.

Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506

Preparation of Ethylamine-Borane by Electrolysis of Sodium Tetrahydridoborate in Ethylamine

L. A. Melcher, I. A. Boenig, and K. Niedenzu*

Received July 28, 1972

Electrochemical studies in inorganic chemistry are primarily concerned with redox reactions of metal salts and/or polarographic investigations. However, boron compounds have received only scattered attention in this respect and experiments have been confined mainly to the preparation of perborates and of elemental boron[1] and the electrolysis of alkali metal tetrahydridoborates for the generation of diborane(6).[2] Also, it has been reported[3] that diborane(6) can be prepared by passing a mixture of boron trihalides and hydrogen into an electrolyzed melt of alkali metal halides and cursory reference[4] is made to some technical reports[5] describing the formation of amine-boranes by electrochemical methods. In the present work the preparation of ethylamine-borane, $C_2H_5NH_2 \cdot BH_3$, by electrolysis of sodium tetrahydridoborate in ethylamine is described.

Experimental Section

All reactions were carried out in a nitrogen or argon atmosphere and reagents were thoroughly dried by standard procedures before use.

Infrared spectra were obtained under standard operating conditions on a Perkin-Elmer Model 621 spectrometer on solutions of compounds in benzene, on the neat materials, and/or on KBr pellets. Proton magnetic resonance spectra were obtained on a Varian T60 instrument using internal TMS as reference. Boron-11 nuclear magnetic resonance data were obtained on a Varian HA60-IL spectrometer operated at 19.3 MHz and using external boron trifluoride etherate as reference. The Raman spectrum was recorded on the neat liquid on a Jarrell-Ash 25-300 Raman spectrometer. Mass spectra were provided by the University of Kentucky Mass Spectroscopy Center and were obtained with a Hitachi Perkin-Elmer double-focusing instrument, Model RMU-7.

Electrolysis with two-electrode circuitry was conducted on a series circuit consisting of a Kepco Model JQE 100-1M power supply, the cell, and a Decade resistance box (Muirhead & Co., D-825-N). An X-Y recorder (Hewlett-Packard Model 700/AM) was connected across the resistance box to measure the voltage drop across this known resistance (range from 0.1 to 10.0 ohms). The current, the voltage drop across the cell, and the cell resistance could be calculated. The glass cell was equipped with a thermometer and a Dry Ice condenser leading to a mercury bubbler. During electrolysis a platinum foil was used as the anode and a mercury pool as the cathode.

Table I. Vibrational Spectrum of Ethylamine-Borane, $C_2H_5NH_2 \cdot BH_3$[a]

Ir	Raman	Ir	Raman
3420 vw, b		1367 m	1363 w, b, dp?
3455 vs, b	3244 m, p	1344 vm	
3164 m	3164 w, p	1279 ms	1280 w, b
2988 m	2973 s, dp	1165 s, b	1172 m, dp
2949 m	2943 s, p	1113 ms	1116 m, p
2907 wm, sh	2931 ms, p	1059 m, sh	
2886 w	2885 m, p	1046 m	1051 wm, p
2555 vw, sh		967 w	
2370 vs, b	2383 vs, p	939 vw	942 wm, p
2320 vs, b	2362 s, p	877 w	880 m, p
2280 vs	2275 vs, p	796 w	800 vw, dp?
2134 vw			755 m, dp
1596 m	1596 w, dp		718 wm, p
1471 wm		692 vw	
1456 wm		417 vw	415 m, p
1405 w		319 vw	332 w, b, dp?
1390 m		270 vw?	

[a] Neat compound; frequencies in cm^{-1}. Key: w, weak; m, medium; s, strong; v, very; sh, shoulder, p, polarized; dp, depolarized.

Preparation of Ethylamine-Borane (Typical Experiment). A mixture of 1.29 g of $NaBH_4$ (0.0342 mol) and 100 ml of anhydrous ethylamine was electrolyzed at ice-bath temperature at +20 V and an initial current rate of 97 mA; electrolysis was continued until the current dropped to 2.8 mA for a total consumption of 3.79×10^3 C. Excess ethylamine was evaporated by removing the Dry Ice condenser and warming the reaction vessel to room temperature. The residue was extracted with dry benzene, and after removal of solvent from the filtrate at room temperature under vacuum a partly crystalline material remained, mp 26-27°, which was identified as ethylamine-borane (yield was *ca.* 60% based on the number of Faradays of electricity which were passed through the reaction mixture).

If the ethylamine is not completely removed before work-up of the reaction mixture, partial decomposition of the ethylamine-borane may occur to yield tris(ethylamino)borane, $B(NHC_2H_5)_3$.

Identification of Products. Neither ethylamine-borane nor ethylaminoborane, $C_2H_5NHBH_2$, is characterized completely in the literature. The former has been noted[6] to have a melting point of 19° and reportedly decomposes at a temperature of 30-40° under formation of hydrogen and ethylaminoborane. The latter is listed[7] to have a melting point of 76.5° but no further characterization is given.

Ethylamine-Borane. The boron-11 nuclear magnetic resonance spectrum of ethylamine-borane in benzene solution exhibited a quartet with a chemical shift (relative to boron trifluoride-etherate) of +19.6 ppm (J_{BH} = 92 Hz). The chemical shift value is indicative of four-coordinate boron as found in other amine-boranes, *e.g.*, $\delta(^{11}B)$ of dimethylamine-borane in benzene solution is +15.1 ppm.[8] The proton magnetic resonance spectrum of ethylamine-borane in carbon tetrachloride consists of three peaks with δ values of 1.20 (triplet, CH_3-CH_2), 2.80 (quartet, CH_3-CH_2), and 3.83 ppm (broad singlet, NH_2), respectively, with an area ratio of 3:2:1.8 ($J_{HCCH} = 7 \pm 0.5$ Hz). These data already seem to confirm the identification of ethylamine-borane which is further substantiated by the vibrational spectrum of the material as listed in Table I.

The BH valence vibrations of amine-boranes are normally[9] observed in the 2200-2300-cm^{-1} region whereas BH stretching of aminoboranes occurs at *ca.* 150 cm^{-1} higher frequencies. Also, the observed NH stretching modes near 3160 and 3250 cm^{-1} lend credence to the identification of the material as an amine-borane rather than an aminoborane.[10]

Mass spectral data do not unequivocally support the structure of the product since the observed parent peak corresponds to ethylaminoborane rather than ethylamine-borane. However, in view of

---

(1) R. M. Adams, "Boron, Metallo-boron Compounds and Boranes," Interscience, New York, N. Y., 1964.

(2) W. H. Schlechter, U. S. Patent 3,033,766 (May 8, 1962).

(3) W. Sundermeyer and O. Glemser, *Angew. Chem.*, **70**, 625 (1958).

(4) R. T. Holzmann, "Production of the Boranes and Related Materials," Academic Press, New York, N. Y., 1967.

(5) References 33, 231, and 255 cited in ref 6.

(6) H. Noth and H. Beyer, *Chem. Ber.*, **93**, 928 (1960).

(7) Army Report CCC-1024-TR-242.

(8) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

(9) A. Meller, *Organometal. Chem. Rev., Sect. A*, **2**, 1 (1967).

(10) K. Nagasawa, T. Yoshizaki, and H. Watanabe, *Inorg. Chem.*, **4**, 275 (1965).