TABLE I

X-RAY DATA FOR $Ni(C_5H_5N)_4(ClO_4)_2$[a]

$Ni(C_5H_5N)_4(ClO_4)_2$ d_{hkl}		Blue compound recovered from $Ni(C_5H_5N)_4(ClO_4)_2 \cdot CHCl_3$ d_{hkl}	
8.28		8.33	
7.41	doublet very intense	7.47	doublet very intense
7.11		7.04	
5.81		5.74	
5.39		5.32	
4.56		4.52	
4.32		4.36	
4.12	very intense	4.10	very intense
3.69		3.71	
3.19		3.18	
2.91		2.92	

[a] Cu $K\alpha_1$ radiation (λ 1.54050 A); 2.5-hr exposure time.

$Ni(C_5H_5N)_4(anion)_2 \cdot 2H_2O$ and their infrared spectra indicate coordinated water and Td anions. A broad absorption from 1040 to 1140 cm^{-1} is observed in the case of the perchlorate, and a broad absorption from 960 to 1160 cm^{-1} is found in the case of the tetrafluoroborate. Analyses of the compounds indicate the presence of one chloroform molecule, and infrared spectra of the compounds indicate that water is not present, that chloroform (or dichloromethane in the case of this solvate) is present, and that the anions are not coordinated.

It is postulated that the acidic solvent interacts forming a weak hydrogen bond with an oxygen of ClO_4^- or fluorine of BF_4^-, removing the anion from the coordination sphere of the nickel(II) ion. This phenomenon occurs, it should be noted, without actual dissolution of the complex in the solvent. The yellow form obtained is the square-planar complex containing solvent and ionic anions.

Square-planar complexes of Ni(II) with several substituted pyridines have been reported and they are yellow in color.[4] The square-planar yellow complex, $Ni(C_5H_5N)_4^{2+}$, is highly susceptible to attack from water molecules, producing $Ni(C_5H_5N)_4(H_2O)_2^{2+}$.

A magnetic moment determined for $Ni(C_5H_5N)_4(BF_4)_2 \cdot CHCl_3$ indicates a marked reduction in its magnetic moment ($\mu_{eff} \sim 1$), relative to the fully paramagnetic blue compound (μ_{eff} 3.04). The low observed magnetism may be due to incomplete conversion of the solid to the diamagnetic form.

This appears to be the first reported case of a compound which undergoes stereochemical change due to "solvent" interaction in the solid state, resulting in a decrease in coordination number. The ability of these compounds to undergo such behavior is undoubtedly due to their highly tetragonal nature.[2]

Acknowledgment.—The authors wish to thank the Chemistry Branch of the Atomic Energy Commission for its generous support of this research through Contract No. AT (11-1) 758.

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(4) L. E. Moore, R. B. Gayhart, and W. E. Bull, *J. Inorg. Nucl. Chem.*, **26**, 896 (1964); S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, **3**, 671 (1964).

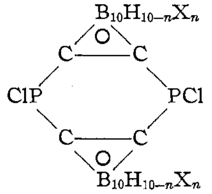
CONTRIBUTION FROM THE OLIN RESEARCH CENTER,
CHEMICALS DIVISION, NEW HAVEN, CONNECTICUT

Chemistry of Decaborane–Phosphorus Compounds. VI. Phosphino-*m*-carboranes[1,2]

BY ROY P. ALEXANDER AND HANSJUERGEN SCHROEDER

Received October 21, 1965

It was demonstrated in previous studies[1,3] that the dilithio salts of o-$B_{10}H_{10}C_2H_2$ and polyhalo-o-carboranes such as o-$B_{10}H_7Br_3C_2H_2$[1] and o-$B_{10}H_6Cl_4C_2H_2$[4] easily react with PCl_3 to form cyclic compounds containing a diphosphacyclohexane skeleton as illustrated below.

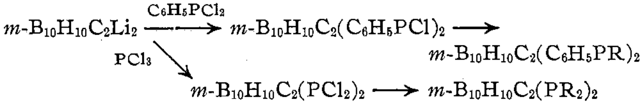


X = Br, Cl

n = 0–4

The formation of noncyclic compounds such as o-$B_{10}H_{10}C_2(PCl_2)_2$, which was actually expected, could not be observed. In contrast to such behavior it was established in these laboratories that the reaction of o-$B_{10}H_{10}C_2Li_2$ with $SiCl_4$[5] and with substituted chlorophosphines[3] and chlorosilanes[5] affords exclusively noncyclic derivatives. The fact that these compounds could be converted into the respective six-membered diphospha- and disilacyclohexane ring compounds by reaction with o-$B_{10}H_{10}C_2Li_2$[1,5,6] is irrelevant to the unique type of reaction obtained with PCl_3.

In the m-carborane series, Papetti and Heying[7] recently showed that m-$B_{10}H_{10}C_2Li_2$ and $SiCl_4$ gave as expected noncyclic products. From the results in the o-carborane series mentioned above, the possibility that m-$B_{10}H_{10}C_2Li_2$ and PCl_3 could react to form a cyclic or macrocyclic ring arose. To explore this idea, some reactions between m-$B_{10}H_{10}C_2Li_2$ and chlorophosphines were conducted and the chemistry of the products obtained was further investigated. The details of this study are summarized in the reactions below.



$$\begin{tikzcd}
 & m\text{-}B_{10}H_{10}C_2[P(C_6H_5)_2]_2 & \\
m\text{-}B_{10}H_{10}C_2Li_2 \arrow[ur, "(C_6H_5)_2PCl"] \arrow[r, "C_6H_5PCl_2"] \arrow[dr, "PCl_3"'] & m\text{-}B_{10}H_{10}C_2(C_6H_5PCl)_2 \arrow[r] & m\text{-}B_{10}H_{10}C_2(C_6H_5PR)_2 \\
 & m\text{-}B_{10}H_{10}C_2(PCl_2)_2 \arrow[r] & m\text{-}B_{10}H_{10}C_2(PR_2)_2
\end{tikzcd}$$

R = OCH_3, $N(CH_3)_2$

No indication of a cyclic monomeric product was observed. However, in allowing two molar equivalents of PCl_3 and one molar equivalent of m-$B_{10}H_{10}C_2Li_2$ to react, m-$B_{10}H_{10}C_2(PCl_2)_2$ was obtained in 40% yield

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(1) Preceding communication: H. D. Smith, T. A. Knowles, and H. Schroeder, *Inorg. Chem.*, **4**, 107 (1965).

(2) Nomenclature of the clovo boron–carbon hydrides is discussed by R. Adams, *ibid.*, **2**, 1087 (1963); the term m-carborane is used to designate 1,7-dicarbaclovododecaborane.

(3) R. P. Alexander and H. Schroeder, *ibid.*, **2**, 1107 (1963).

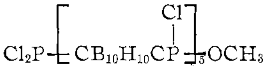
(4) H. Schroeder, T. L. Heying, and J. R. Reiner, *ibid.*, **2**, 1092 (1963).

(5) S. Papetti and T. L. Heying, *ibid.*, **2**, 1105 (1963).

(6) S. Papetti, B. B. Schaeffer, H. J. Troscianiec, and T. L. Heying, *ibid.*, **3**, 1444 (1964).

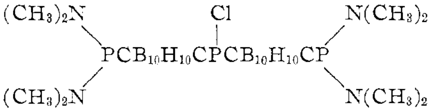
(7) S. Papetti and T. L. Heying, *ibid.*, **3**, 1448 (1964).

only, together with a product the consistency of which varied between highly viscous and brittle from run to run. Treatment of this by-product with methanol produced a solid which slowly hydrolyzed upon exposure to air. Elemental analysis and molecular weight determination indicated it to be an oligomer of the formula



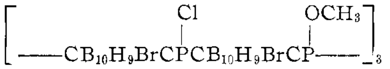
$$\mathrm{Cl_2P{-}\Big[CB_{10}H_{10}C\overset{\displaystyle Cl}{\overset{|}{P}}\Big]_5OCH_3}$$

Treatment of this polymeric compound with dimethylamine in benzene solution resulted in insoluble $(CH_3)_2NH{\cdot}HCl$ and the soluble amination product, the main part of which gave elemental analyses and molecular weight determination in accord with the structure



When the same reactants were combined in a 1:1 molar ratio, still some *m*-$B_{10}H_{10}C_2(PCl_2)_2$ was obtained. Although the yield of polymeric product, as expected, increased, the chain length remained unchanged.

Reaction of the analogous *m*-$B_{10}H_9BrC_2Li_2$ with PCl_3 did not afford the noncyclic monomer but a pasty product from which an oligomer was obtained by treatment with methanol.



$$\mathrm{\Big[{-\!-\!-}CB_{10}H_9BrC\overset{\displaystyle Cl}{\overset{|}{P}}CB_{10}H_9BrC\overset{\displaystyle OCH_3}{\overset{|}{P}}{-\!-\!-}\Big]_3}$$

From these results it appears that this type of reaction leads only to polymeric products of limited molecular weight. These polymers consisting of a number of phosphorus-linked *m*-carborane nuclei are believed to be linear since they resemble metal-linked poly-*m*-carboranes of established chain structure which are the subject of a current investigation.

Experimental Section[8]

1,7-Bis(diphenylphosphino)-*m*-carborane.—A dilithio-*m*-carborane solution[9] in ether (150 ml) was prepared from 4.3 g (0.03 mole) of *m*-carborane and 0.066 mole of butyllithium and added to a solution of diphenylchlorophosphine (14.6 g, 0.066 mole) in ether (15 ml), maintaining the temperature at 10–15°. The mixture was then refluxed for 1 hr and, after cooling to 20°, hydrolyzed with 20 ml of water. The ether layer was separated, dried, and evaporated to dryness. The solid residue was recrystallized from petroleum ether (bp 65–110°) to give 9.5 g (62%) of *m*-$B_{10}H_{10}C_2[P(C_6H_5)_2]_2$; mp 101°.

Anal. Calcd for $C_{26}H_{30}B_{10}P_2$ (512.7): C, 60.91; H, 5.90; B, 21.12; P, 12.09. Found: C, 61.34; H, 6.27; B, 21.02; P, 12.12.

1,7-Bis(chlorophenylphosphino)-*m*-carborane.—A Dilithio-*m*-carborane (0.1 mole) solution in ether (400 ml) and phenyldichlorophosphine (35.8 g, 0.2 mole) in ether (500 ml) were allowed to react in a manner identical with the preceding experiment. The crude product was distilled *in vacuo* to give 25 g (58.3%) of *m*-$B_{10}H_{10}C_2(C_6H_5PCl)_2$; bp 229° (0.35 mm); $n^{26}D$ 1.652.2.

Anal. Calcd for $C_{14}H_{20}B_{10}Cl_2P_2$ (429.4): C, 39.16; H, 4.70; B, 25.20; Cl, 16.51; P, 14.43. Found: C, 38.70; H, 4.80; B, 25.23; Cl, 16.50; P, 14.25.

1,7-Bis(dimethylaminophenylphosphino)-*m*-carborane.—Gaseous dimethylamine was passed for 2 hr through a solution of 5.0 g of *m*-$B_{10}H_{10}C_2(C_6H_5PCl)_2$ in 100 ml of benzene. The resulting slurry was filtered and the filtrate evaporated to dryness. Recrystallization of the crude residue from acetonitrile and ethanol gave 4.2 g (81%) of pure product, mp 100–102°.

Anal. Calcd for $C_{18}H_{32}B_{10}N_2P_2$ (446.6): C, 48.41; H, 7.22; B, 24.23; N, 6.27; P, 13.87. Found: C, 48.60; H, 7.45; B, 24.47; N, 6.76; P, 13.14.

1,7-Bis(methoxyphenylphosphino)-*m*-carborane.—*m*-$B_{10}H_{10}C_2(C_6H_5PCl)_2$ (30 g) was dissolved in 300 ml of methanol. After stirring at ambient temperature for 2 hr, the reaction product had precipitated and was recovered by filtration. Recrystallization from methanol afforded 22.1 g (75%) of pure *m*-$B_{10}H_{10}C_2(C_6H_5POCH_3)_2$, mp 112–114°.

Anal. Calcd for $C_{16}H_{26}B_{10}O_2P_2$ (420.5): C, 45.70; H, 6.23; B, 25.73; P, 14.73. Found: C, 45.82; H, 5.95; B, 25.56; P, 14.17.

Reaction of Dilithio-*m*-carborane with Phosphorus Trichloride in a 1:3 Ratio.—A dilithio-*m*-carborane (0.42 mole) slurry in ether (1000 ml) was added, with stirring and ice cooling, to a solution of PCl_3 (173 g, 1.26 moles) in ether (2000 ml) over a 20-min period. After stirring for 12 hr at ambient temperature, the solvent was removed *in vacuo*. The residual oil was extracted with 300 ml of benzene to give, after evaporation of the benzene, a viscous liquid which was subjected to vacuum distillation; yield of *m*-$B_{10}H_{10}C_2(PCl_2)_2$: 58 g (40%); bp 119° (0.3 mm); $n^{22}D$ 1.618.3.

Anal. Calcd for $C_2H_{10}B_{10}Cl_4P_2$ (346.1): C, 6.94; H, 2.91; B, 31.27; Cl, 40.98; P, 17.90. Found: C, 6.66; H, 2.90; B, 31.27; Cl, 40.20; P, 17.50.

The distillation residue was triturated with cold methanol to give 30 g (~35% based on *m*-carborane) of solid product, mp 120–135°.

Anal. Calcd for $C_{11}H_{53}B_{50}ClOP_6$ (1176.6): C, 11.23; H, 4.54; B, 45.98; Cl, 21.09; P, 15.80. Found: C, 11.25; H, 4.58; B, 45.81; Cl, 22.20; P, 15.47; mol wt (in toluene at 39°), 1117.

Reaction of Dilithio-*m*-carborane with Phosphorus Trichloride in a 1:1 Ratio.—The procedure as described above was repeated except for using 58 g (0.42 mole) of PCl_3 in 1000 ml of ether. The yield of *m*-$B_{10}H_{10}C_2(PCl_2)_2$ was 19 g (13% based on *m*-carborane); 52 g (~57%) of polymeric product (mol wt 1088) was obtained.

***m*-$B_{10}H_{10}C_2[(CH_3)_2P(CH_3)_2N]_2$.**—The reaction between *m*-$B_{10}H_{10}C_2(PCl_2)_2$ and $HN(CH_3)_2$ was carried out in a manner essentially identical with that described for the preparation of *m*-$B_{10}H_{10}C_2[C_6H_5PN(CH_3)_2]_2$. The yield of product after recrystallization from petroleum ether (bp 30–60°) was 74%; mp 73–75°.

Anal. Calcd for $C_{10}H_{34}B_{10}N_4P_2$ (380.6): C, 31.56; H, 9.01; B, 28.43; N, 14.72; P, 16.28. Found: C, 31.70; H, 9.15; B, 28.35; N, 14.44; P, 15.88.

***m*-$B_{10}H_{10}C_2[P(OCH_3)_2]_2$.**—An total of 5 g of *m*-$B_{10}H_{10}C_2(PCl_2)_2$ was dissolved in 50 ml of methanol. After removal of the solvent, a colorless liquid free of chlorine remained; $n^{26}D$ 1.542.0. Upon attempting to distil part of it *in vacuo*, sudden violent decomposition occurred.

Anal. Calcd for $C_6H_{22}B_{10}O_4P_2$ (328.4): C, 21.95; H, 6.75; B, 32.95; P, 18.18. Found: C, 20.55; H, 6.51; B, 33.44; P, 18.08.

Reaction of $Cl_2P[CB_{10}H_{10}CP(Cl)]_5OCH_3$ with Dimethylamine.—Gaseous dimethylamine was bubbled through a solution of 4.0 g of the polymer in 100 ml of benzene for 1 hr at 25°, then for another hour at 40°. After filtration to remove the $HN(CH_3)_2{\cdot}HCl$ formed in the reaction, the filtrate was evaporated to dryness and the residue triturated with 100 ml of petroleum ether (bp 30–60°) to give 1.8 g of solid, mp 90–94°.

Anal. Calcd for $C_{12}H_{44}B_{20}ClN_4P_3$ (589.3): C, 24.46; H,

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[8] Melting points are uncorrected (Mel-Temp apparatus); elemental analyses were by the Olin Microchemical Section; the molecular weights were determined by the differential vapor pressure method (Mechrolab osmometer, Model 301).

[9] For a detailed preparation of such a solution see ref 7.

7.53; B, 36.72; Cl, 6.02; N, 9.51; P, 15.77. Found: C, 23.83; H, 7.95; B, 36.76; Cl, 7.43; N, 8.88; P, 14.16; mol wt (in chloroform), 598.

Reaction of m-$B_{10}H_9BrLi$ with PCl_3.—A solution of m-$B_{10}H_9$-BrC_2H_2[1] (22.3 g, 0.1 mole) in ether (100 ml) was added, with stirring and ice cooling, to a solution of butyllithium (0.25 mole) in hexane (170 ml) and ether (100 ml). The reaction mixture was stirred at 0° for 1 hr, then filtered. The insoluble dilithium salt was washed with ether, then slurried with 250 ml of ether, and added with ice cooling to a solution of PCl_3 (41.1 g, 0.3 mole) in 500 ml of ether. After stirring for 12 hr at ambient temperature, the resulting mixture was filtered, and then the filtrate was evaporated to dryness. Trituration of the residue with methanol afforded 25 g of polymer, mp 115–120° (starts to shrink at 105°).

Anal. Calcd for $C_{15}H_{63}B_{60}Br_6Cl_2O_3P_6$ (1712.1): C, 10.52; H, 3.71; B, 37.91; Cl, 6.21; Br, 28.00; P, 10.85. Found: C, 9.67; H, 3.68; B, 36.34; Cl, 6.21; Br, 28.00; P, 11.08; mol wt (in toluene at 39°), 1784.

Acknowledgment.—The authors wish to thank Dr. T. L. Heying for helpful discussions. This work was supported by the Office of Naval Research.

CONTRIBUTION FROM THE GEORGE HERBERT JONES
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Tracer Experiments on the Oxidation of Methyl Esters of Oxalic Acid by Cerium(IV)

BY C. ANDRADE AND H. TAUBE

Received November 15, 1965

The oxygen tracer experiments which we describe in this note were undertaken in trying to develop convenient methods for determining in solution the isotopic composition of the oxygen contained in CH_3-C_2O_4H and $CH_3C_2O_4CH_3$. The reactions proved not quite clean enough to meet our analytical requirements, but the results we obtained are sufficiently clear-cut to provide insight into the mechanism of oxidation of these species.

Experimental Section

Earlier work has shown that CO_2 generated in aqueous solution can be removed rapidly enough by a stream of inert gas so that little exchange with solvent takes place.[1] The oxidation was done by adding the ester solution to the solution containing Ce(IV) and $HClO_4$. Each of the solutions was enriched in O^{18} to the same extent. The stream of N_2 used to carry off the CO_2 served also to stir the solution. Carbon dioxide was trapped out of the N_2 stream using liquid N_2 as coolant, and CO_2 was collected for isotopic analysis after it was sublimed from a Dry Ice–methanol trap. The isotopic composition of the solvent was determined by equilibration with CO_2.

The reaction of Ce(IV) with the oxalate esters is rapid, the half-time being less than 1 min under our conditions. The time of reaction was chosen as 5 min. A matter of some concern is the extent of oxygen exchange between the esters and the solvent in the highly acidic reaction medium. The rate of exchange of the esters has been determined, and an upper limit can be set on the incorporation of solvent oxygen by exchange. The extent of exchange is small and is dealt with in the next section.

Results

The results of the tracer experiments are shown in Table I. The values of n (see footnotes to Table I) are calculated from the equation

$$n = \frac{2E_{CO_2} - 1}{E_{solv} - 1}$$

TABLE I

OXYGEN TRACER RESULTS ON THE OXIDATION OF $(CH_3)_2C_2O_4$ AND $KCH_3C_2O_4$ BY Ce(IV)[a]

~2.5 M $HClO_4$, ~0.20 M Ce(IV)

	E[b] for		
Substrate,[a] M	Solvent	CO_2	n[c]
	$(CH_3)_2C_2O_4$		
0.0423	5.378	3.266	1.03
0.0508	5.328	3.238	1.03
	$CH_3C_2O_4H$		
0.0352	5.183	2.192	0.57
0.0422	5.125	2.166	0.57

[a] Room temperature. [b] E = enrichment ratio, that is the isotopic composition in the sample in question compared to that of normal CO_2. [c] n = number of atoms of oxygen for each CO_2 formed which are derived from the solvent. Note that 2 moles of CO_2 results from the oxidation of each mole of ester.

Discussion

The values of n, slightly in excess of 1.00 for $(CH_3)_2$-C_2O_4 and slightly in excess of 0.50 for $CH_3C_2O_4$, are upper limits on the incorporation of solvent oxygen into CO_2 by the reaction itself. Exchange of oxygen between solvent and unreacted complex must be allowed for, as must ester hydrolysis and exchange between the CO_2 formed and the solvent. Using as the half-life for reaction the upper limit of 1 min, and results[2,3] on the rates of oxygen exchange, the rate of oxidation for the diester compared to exchange is 200 or greater and the incorporation of solvent oxygen per CO_2 by exchange is less than 0.005. Making a similar estimate for $CH_3C_2O_4H$, assuming that the rate of exchange of the three exchangeable oxygens is one-half that observed for $H_2C_2O_4$, the upper limit to the number of atoms incorporated is ~0.1. Ester hydrolysis competing with oxidation can at most account for 0.015 solvent atom per CO_2 in the case of $(CH_3)_2C_2O_4$ and even less in the case of $CH_3C_2O_4H$. Incorporation by exchange between CO_2 and solvent is less than 2%. This analysis indicates that the actual incorporation of solvent oxygen by oxidation is exactly 1.00 in the case of $(CH_3)_2C_2O_4$ and very nearly 0.50 in the case of CH_3-C_2O_4H.

Oxidation in the three cases studied thus far results in bond breaking as indicated below.

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[1] R. M. Milburn and H. Taube, *J. Am. Chem. Soc.*, **81**, 3515 (1959).

[2] C. Andrade, Ph.D. Dissertation, University of Chicago, 1964.

[3] A. Skrabal, *Monatsh. Chem.*, **38**, 29 (1917).