basis of the available data, but the extra stability of the hydrogen bond would tend to favor I and one might expect that the phenolic –OH group in IV could be titrated in nonaqueous media. In fact, titration in anhydrous isopropyl alcohol with KOH in isopropyl alcohol failed to give any inflection. Also, the arsenic complex, II, which behaves very much like I, has been resolved into an optically active enantiomorph. This rules out a structure analogous to IV for the $[As(OH)(Hcat)(cat)_2]^-$ ion.

### Solvates of $(NH_4)_2[Si(cat)_3]\cdot H_2O$

Weiss, *et al.*,[2] reported isolating a complex containing 7 mol of catechol/2 g-atoms of silicon which they formulated as $(NH_4)_4[Si_2(cat)_5(Hcat)_2]\cdot 9H_2O$. They prepared the compound by adding ethanol to the filtrate obtained from the preparation of $(NH_4)_4[Si_2(cat)_6]\cdot 9H_2O$. Their synthesis was repeated in this work but it was found that the compound is really an ethanol solvate and should be formulated as $(NH_4)_2[Si(cat)_3]\cdot x H_2O\cdot C_2H_5OH$ where $x = 3$ or 4. The nmr spectrum in deuterated DMSO shows one ethyl group for every three catechol groups.

Besides the ethanol solvate, compounds were obtained containing catechol, dimethyl sulfoxide, and acetone: $(NH_4)_2[Si(cat)_3]\cdot H_2O\cdot H_2cat$, $(NH_4)_2[Si(cat)_3]\cdot H_2O\cdot 2CH_3SOCH_3$, and $(NH_4)_2[Si(cat)_3]\cdot H_2O\cdot CH_3COCH_3$. All have 1 mol of water, which supports the thesis that the water is an intimate part of the complex rather than simple water of crystallization.

**Acknowledgment.**—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. I also wish to acknowledge help with the experimental work from the following undergraduate students: Leslie Oga and Frank Eigner, conductivity studies; Ken Dunder, potentiometric titrations; Bill Dahl, examination of the X-ray diffraction patterns of compounds containing ammonia of crystallization.

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# Notes

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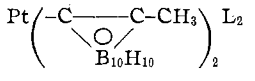
## The Preparation of σ-Bonded Platinum Complexes of Methylcarborane(12)

By R. ROGOWSKI AND K. COHN*

*Received December 4, 1970*

Reports of π-bonded transition metal complexes with $B_9C_2H_{11}^{2-}$, $B_7C_2H_9^{2-}$, and $B_6C_2H_8^{2-}$ ligands are numerous.[1] A few examples of neutral σ-bonded transition metal complexes involving single carbon–transition metal bonds have appeared in the literature. In this paper we report a number of σ-bonded phosphinoplatinum complexes of $1\text{-}CH_3\text{-}1,2\text{-}B_{10}C_2H_{11}$ of the type



$$Pt\left(-C\underset{B_{10}H_{10}}{\overset{\bigcirc}{——}}C-CH_3\right)_2 L_2$$

When L is $P(C_6H_5)_3$, $P(CH_3)(C_6H_5)_2$, $P(CH_3)_2(C_6H_5)$, or $P(CH_3)_3$, cis complexes were obtained. When the L is $P(n\text{-}C_4H_9)_3$, a trans complex is obtained. We suggest a reason that the cis complex of $P(n\text{-}C_4H_9)_3$ could not be obtained.

### Experimental Section

**General Techniques.**—A Perkin-Elmer 457 grating spectrophotometer was used to obtain the infrared spectra. Solid spectra were run either as Nujol or as Fluorolube mulls between CsI plates.

Proton nmr spectra were observed by means of a Varian Model 56/60 nuclear magnetic resonance spectrometer operating at the ambient temperature of the instrument. Tetramethylsilane was employed as internal standard. Phosphorus and boron nmr absorptions were obtained on an NMR Specialties MP1000 pulsed spectrometer with an operating frequency of 65 MHz and a field strength of 47.6 and 28.0 kG, respectively. Solutions of $P_4O_6$ and $B(OCH_3)_3$ were employed as internal references, by the capillary insertion technique.

Mass spectral data were obtained by means of a Hitachi-RMU-6 spectrometer operating with an ionizing voltage of 56 V.

The preparations were carried out under an atmosphere of dry nitrogen. Analyses were performed by Spang Laboratories, Ann Arbor, Mich., or by Chemalytics, Inc., Tempe, Ariz. Melting points were obtained by the use of a Thomas–Hoover capillary melting point apparatus.

**Methylcarborane [1-Methyl-1,2-dicarba-*closo*-dodecaborane-(12)].**—This was prepared from purified propargyl bromide (3-bromopropyne), acetonitrile, and decarborane (U. S. Air Force) by the use of a method previously described.[3] The identity of the product was established by its melting point (211 ± 2°, lit.[3] mp 211–213°) and by a comparison of the $^1H$ nmr with the reported values. The $^1H$ nmr spectrum ($CS_2$) exhibited absorptions at δ 3.50 (broad singlet, intensity 1, due to the C–H on methylcarborane(12)), and δ 2.00 (broad singlet, intensity 3, due to the *C*-methyl protons) (lit.[3] δ 3.48 and 1.48, respectively). The pure methylcarborane(12) was stored in an evacuated desiccator over $P_2O_5$ prior to use.

**Synthesis of the Cis Platinum–Phosphine Complexes.**—The following platinum compounds *cis*-dichlorobis(trimethylphosphine)platinum(II) [*cis*-$PtCl_2[P(CH_3)_3]_2$], *cis*-dichlorobis[di-

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[1] M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 879 (1968); M. F. Hawthorne and T. A. George, *ibid.*, **89**, 7114 (1967); T. A. George and M. F. Hawthorne, *ibid.*, **90**, 1661 (1968); G. Popp and M. F. Hawthorne, *ibid.*, **90**, 6553 (1968); M. F. Hawthorne and H. R. Ruhle, *Inorg. Chem.*, **8**, 176 (1969); T. A. George and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 5475 (1969); M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).

[2] S. Bresadola, P. Rigo, and A. Turco, *Chem. Commun.*, **20**, 1205 (1968); J. C. Smart, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 1031 (1969); C. M. Mitchell and F. G. A. Stone, *Chem. Commun.*, **22**, 1263 (1970); D. A. Owen and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **92**, 3194 (1970).

[3] M. F. Hawthorne, T. D. Andrews, P. M. Garrett, F. P. Olsen, M. Reintjes, F. N. Tebbe, L. F. Warren, P. A. Wegner, and D. C. Young, *Inorg. Syn.*, **10**, 91 (1967).

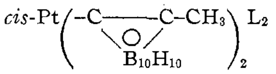
TABLE I

CHARACTERIZATION DATA OF THE *cis*-$PtCl_2L_2$ COMPLEXES

| L | % C |  | % H |  | Mp, °C |  |
|---|---|---|---|---|---|---|
|  | Theory | Found | Theory | Found | Lit. | Found |
| $P(CH_3)_3$ | 17.22 | 17.05 | 4.34 | 4.13 | 324–326[4c] | 323–325 |
| $P(CH_3)_2(C_6H_5)$ | 35.42 | 35.13 | 4.09 | 3.97 | . . . | 221–225 |
| $P(CH_3)(C_6H_5)_2$ | 46.84 | 46.76 | 3.93 | 3.47 | 253–258[4b] | 254–260 |
| $P(C_6H_5)_3$ | 54.68 | 54.60 | 3.80 | 3.75 | 310[4a] | 308–309 |

TABLE II

CHARACTERIZATION DATA FOR THE COMPLEXES

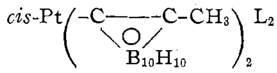

$cis\text{-}Pt\left(-\underset{B_{10}H_{10}}{C\text{——}C}\text{-}CH_3\right)_2L_2$

| L | % C |  | % H |  | Mol wt |  | Mp,[b] °C | % yield[a] |
|---|---|---|---|---|---|---|---|---|
|  | Theory | Found | Theory | Found | Theory | Found |  |  |
| $P(C_6H_5)_3$ | 48.74 | 47.34 | 5.41 | 5.04 | 1033 | 1002 | 216–218 | 65 |
| $P(CH_3)(C_6H_5)_2$ | 42.20 | 40.94 | 5.73 | 5.47 | 909 | 891 | 200–204 | 42 |
| $P(CH_3)_2(C_6H_5)$ | 33.63 | 32.84 | 6.12 | 5.47 | 785 | 739 | 188–192 | 30 |

[a] Approximate yield based on amount of methylcarborane(12) recovered. [b] All compounds decomposed on heating.

TABLE III

60-MHz $^1H$ NMR SECTRAL DATA OF THE COMPLEXES[a]

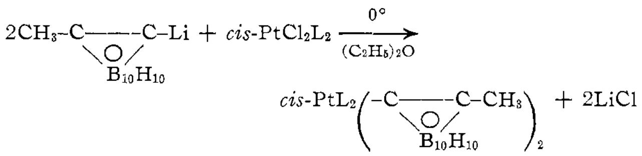

$cis\text{-}Pt\left(-\underset{B_{10}H_{10}}{C\text{——}C}\text{-}CH_3\right)_2L_2$

| L | δ,[b] ppm | Remarks |
|---|---|---|
| $P(C_6H_5)_3$ | 2.1 | Broad singlet; area 1.0; methyl protons of carborane |
|  | 7.5 | Broad multiplet; area 5.0; phenyl protons on phosphine |
| $P(CH_3)(C_6H_5)_2$ | 1.9 | Doublet; $J$ = 11 Hz; methyl protons attached to phosphorus |
|  | 2.05 | Singlet, overlaps with δ 1.9; methyl protons of carborane |
|  | 7.3 | Broad multiplet; phenyl protons on phosphine |
| $P(CH_3)_2(C_6H_5)$ | 2.0 | Doublet; $J$ = 11 Hz; methyl protons attached to phosphorus |
|  | 2.1 | Singlet, overlaps with δ 2.0; methyl protons of carborane |
|  | 7.4 | Broad multiplet; phenyl protons on phosphine |
| $P(CH_3)_3$ | 2.0 | Broad absorption; doublet and singlet methyl protons of the phosphine and methyl protons of the carborane |

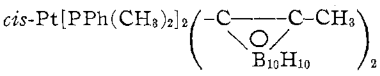
[a] The solvent used was $CS_2$. [b] Chemical shifts from tetramethylsilane.

methyl(phenyl)phosphine]platinum(II) [*cis*-$PtCl_2[P(CH_3)_2(C_6H_5)]_2$], *cis*-dichlorobis[methyl(diphenyl)phosphine]platinum(II) [*cis*-$PtCl_2[P(CH_3)(C_6H_5)_2]_2$], and *cis*-dichlorobis(triphenylphosphine)platinum(II) [*cis*-$PtCl_2[P(C_6H_5)_3]_2$] were prepared and characterized according to previously described methods.[4] Characterization data are found in Table I.

**General Reaction Procedures for the Methyl(phenyl)phosphine Complexes.**—The reaction at 0° of a 2-mmol sample of 1-($CH_3$)-1,2-$B_{10}C_2H_{11}$ with a 2-mmol sample of *n*-butyllithium (Alfa Inorganics Co.) in diethyl ether affords *n*-butane and the lithium salt[5] of the 1-($CH_3$)-1,2-$B_{10}C_2H_{10}^-$ ion. The subsequent treatment of this anion with a 1-mmol sample of a *cis*-dichlorobis[methyl(phenyl)phosphine]platinum(II) complex results in a σ-bonded phosphinoplatinum–methylcarborane(12) complex. The overall reaction is

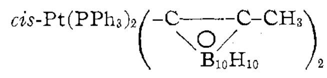

$$2CH_3\text{-}\underset{B_{10}H_{10}}{C\text{——}C}\text{-}Li + cis\text{-}PtCl_2L_2 \xrightarrow[(C_2H_5)_2O]{0°} cis\text{-}PtL_2\left(-\underset{B_{10}H_{10}}{C\text{——}C}\text{-}CH_3\right)_2 + 2LiCl$$

where L is $PPh_3$, $PPh_2CH_3$, $PPh(CH_3)_2$, or $P(CH_3)_3$. All preparations were carried out in an atmosphere of dry nitrogen. The addition of the platinum complex in diethyl ether was carried out in a 10-min period. The reaction mixture was maintained at 0° for 30 min and was then allowed to warm to 25° over a period of 1 hr. (For the $PPh(CH_3)_2$– and $P(CH_3)_3$–Pt complexes it was necessary to warm to 36°.) The diethyl ether was then removed by distillation *in vacuo*. The products were recrystallized from a 70:30 mixture of carbon disulfide and methyl chloride. A small amount of *n*-pentane was employed to initiate the precipitation of the product from solution. The solid was filtered and dried *in vacuo*. The characterization data for the *cis*-bis[methyl(phenyl)phosphine]bis[methylcarborane(12)]platinum(II) complexes are found in Table II. The 60-MHz $^1H$ nmr spectra of the *cis*-bis[methyl(phenyl)phosphine]bis[methylcarborane(12)]platinum(II) complexes obtained in carbon disulfide are presented in Table III. No $^{31}P$ or $^{11}B$ nmr spectra were obtained for the triphenylphosphine– or methyl(diphenyl)phosphine–platinum(II)–methylcarborane(12) complexes because the products were insoluble. The dimethyl(phenyl)phosphine–platinum(II)–methylcarborane(12) complex was more soluble but was less stable in air, presumably because of hydrolysis. The $^{31}P$ nmr data for


$cis\text{-}Pt[PPh(CH_3)_2]_2\left(-\underset{B_{10}H_{10}}{C\text{——}C}\text{-}CH_3\right)_2$

in $CH_2Cl_2$ consisted of a broad absorption, δ +120.4 from $P_4O_6$. The $^{11}B$ nmr spectrum ($CH_2Cl_2$) consisted of three broad absorptions of intensity 1 at δ 21.4, 22.6, and 23.8 from $B(OCH_3)_3$ and four additional broad absorptions at δ 27.7 (intensity 3), 29.4 (intensity 4), 31.0 (intensity 4), 33.4 (intensity 3).

The infrared spectra of these compounds were obtained as Nujol mulls between CsI plates. The infrared absorptions and relative intensities of


$cis\text{-}Pt(PPh_3)_2\left(-\underset{B_{10}H_{10}}{C\text{——}C}\text{-}CH_3\right)_2$

are 510 (s), 545 (ms), 670 (s), 740 (m), 993 (w), 1020 (mw), 1090 (ms), 1115 (w), 1180 (w), 1305 (w), 1570 (m), 2550 (s), 2720 (w), and 3410 (w) $cm^{-1}$. The bands tentatively assigned to Pt–Cl stretches present in the starting material were absent from the product. The peaks at 740 and 2550 $cm^{-1}$ are characteristic of the carborane cage and those at 1630 and 3410 $cm^{-1}$ are OH stretching modes which arise from hydrolysis of the compound.

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[4] (a) K. A. Jensen, *Z. Anorg. Allg. Chem.*, **229**, 225 (1936); (b) S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, **6**, 1133 (1967); (c) M. A. A. Beg and H. C. Clark, *Can. J. Chem.*, **38**, 119 (1960).

[5] T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *Inorg. Chem.*, **2**, 1097 (1963).

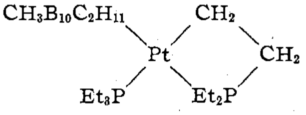
Similar infrared spectra were observed for the entire series of bis[phenyl(methyl)phosphine]bis[methylcarborane(12)]platinum(II) compounds. The peaks characteristic of the carborane cage were observed in each case while the characteristic hydrolysis bands (1630 and 3410 cm$^{-1}$) increased in intensity as the number of methyl groups on the phosphine was increased.

Magnetic susceptibility data obtained from all the phosphinomethylcarborane(12)–platinum complexes isolated (Guoy) indicate that in every case the complexes are diamagnetic.

**General Reaction Procedures for Tri-*n*-butylphosphine Complexes.**—The cis and trans isomers of dichlorobis(tri-*n*-butylphosphine)platinum(II) were prepared and characterized according to the method described by Kauffman and Teter.[6] The interaction of methylcarborane(12) with the cis and trans isomers of dichlorobis(tri-*n*-butylphosphine)platinum(II) was accomplished by means of the procedure previously described for the preparation of dichlorobis[methyl(phenyl)phosphine]platinum(II) reactions. Benzene rather than diethyl ether was employed as a solvent for solubility reasons. A small amount [about 5% yield based on the amount of *trans*-dichlorobis(tri-*n*-butylphosphine)platinum(II)] of the trans complex was isolated. This *trans*-bis(tri-*n*-butylphosphine)bis[methylcarborane(12)]platinum(II) complex was susceptible to hydrolysis. Both the OH stretching modes in the infrared and $^1$H nmr absorptions which are characteristic of the starting methylcarborane(12) [$\delta$ 3.5, broad singlet, due to C–H on the carborane(12) cage] grew in intensity when the complex was allowed to remain in air.

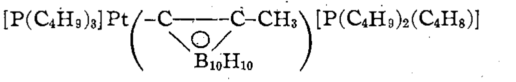
*Anal.* Calcd for $C_{30}H_{80}B_{20}P_2Pt$: C, 39.42; H, 8.76. Found: C, 39.75; H, 8.30. Molecular weight determined in benzene was 880 (theoretical 913). The melting point was 185 ± 5° dec.

Bresadola, Rigo, and Turco[2] reported that the interaction of methylcarborane(12) with the trans isomer of bis(triethylphosphine)platinum(II) resulted in a product which was formulated as



It is possible that the low yield of *trans*-bis(tri-*n*-butylphosphine)bis[methylcarborane(12)]platinum(II) may be a consequence of the formation of a complex analogous to that reported by Bresadola, Rigo, and Turco,[2] but we were unable to isolate a complex of this composition. The proton nmr spectrum of the complex we did obtain exhibited three resonances, two of which were broad multiplets at $\delta$ 1.0 and 1.6 (total intensity 3.1, due to the protons on the *n*-butyl groups). The remaining absorption ($\delta$ 2.1, singlet, intensity 1.0) is easily ascribed to the *C*-methyl protons of methylcarborane.

The interaction of *cis*-dichlorobis(tri-*n*-butylphosphine)platinum(II) with methylcarborane(12) was carried out as described for the *trans*-dichlorobis(tri-*n*-butylphosphine)platinum(II) reaction. A pale yellow solid which was very susceptible to hydrolysis was isolated. Attempts to obtain reproducible nmr data from this product were unsuccessful. All attempts to get precise analyses and melting points on this cis compound were unsuccessful. The molecular weight, which was low for the expected methylcarborane(12) complex of dichlorobis(tri-*n*-butylphosphine)platinum(II), is near the theoretical molecular weight for a product formulated as



$$[P(C_4H_9)_3]Pt\left(\underset{B_{10}H_{10}}{-C\text{———}C-CH_3}\right)[P(C_4H_9)_2(C_4H_8)]$$

(where $C_4H_8$ is a butyl group which is bonded to both phosphorus and platinum). This would be similar to the compound reported by Bresadola, Rigo, and Turco[2] and would account for the low molecular weight data. No such results were observed for the dichlorobis[methyl(phenyl)phosphine]platinum(II) reactions with methylcarborane(12).

Similar reactions involving the use of dichloro salts of palladium and nickel with methylcarborane(12) were attempted. No complexes could be isolated. Studies on these systems are still in progress.

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[6] G. B. Kauffman and L. A. Teter, *Inorg. Syn.*, **7**, 245 (1963).

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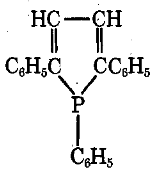
# The Chloramination of Some Heterocyclic Tertiary Phosphines

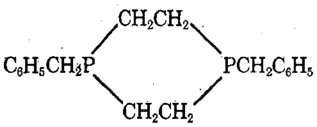
BY S. E. FRAZIER AND H. H. SISLER*

*Received July 13, 1971*

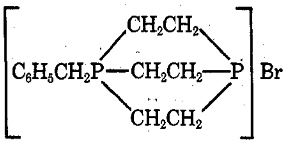
Chloramine has been shown to react with tertiary amines[1] and tertiary phosphines[2] to form the corresponding hydrazinium chlorides and aminophosphonium chlorides, respectively. Since a great number of novel heterocyclic phosphines are now available,[3] we have begun to extend the chloramine reaction to tertiary phosphines of various structural types. This communication reports the results of a study of the reactions of chloramine with 1,2,5-triphenylphosphole (I), with 1,4-dibenzyldiethylenediphosphine (II), and with 1-benzyltriethylenediphosphonium bromide (III).



I



II



III

These heterocyclic derivatives react with the chloramine in a manner similar to other tertiary phosphines and ditertiary phosphines.[4] With I, chloramination occurs at the phosphorus atom yielding 1-amino-1,2,5-triphenylphospholium chloride. Support for this structure is provided by the occurrence of a strong infrared band at 1120 cm$^{-1}$ in the infrared spectrum. Such a band is usually diagnostic of a phenyl group attached to a tetracoordinate phosphorus atom.

With II, chloramination occurs at both phosphorus atoms as demonstrated by elemental analysis and the nmr spectrum.

In attempting to synthesize triethylene diphosphine by a process which reportedly[5] gives extremely low yields of this product, we obtained the intermediate III. With chloramine, this compound undergoes quaternization and halogen exchange to yield $[C_6H_5CH_2P(C_2H_4)_3PNH_2]Cl_2$.

We were unable to carry out detailed nmr analyses of these products because of their low solubility in suitable solvents. 1-Amino-1,2,5-triphenylphospholium chloride is soluble in $CDCl_3$ and DMSO-$d_6$ but crystalline adducts precipitate on standing. 1,4-Diamino-1,4-dibenzyldiethylenediphosphonium dichloride and *P*-amino-*P'*-benzyltriethylenediphosphonium dichloride

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[1] G. Omietanski and H. H. Sisler, *J. Amer. Chem. Soc.*, **78**, 1211 (1956).

[2] H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *ibid.*, **81**, 2982 (1959).

[3] K. D. Berlin and D. M. Hellwege, *Top. Phosphorus Chem.*, **6**, 1 (1969).

[4] S. R. Jain and H. H. Sisler, *Inorg. Chem.*, **8**, 1243 (1969).

[5] R. C. Hinton and F. G. Mann, *J. Chem. Soc.*, 2835 (1959).