

Centro Stabilita e Reattivita dei Composti di Coordinazione, CNR, and Istituto di Chimica Fisica, University of Padova, Padua, Italy

Carboranyl and *neo*-Carboranyl Complexes of Platinum(II) and Palladium(II) Formed through Metal-Carbon σ Bonds

S. BRESADOLA,* A. FRIGO, B. LONGATO, and G. RIGATTI

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Two types of stable phosphinoplatinum(II) complexes containing 2-R-1,2- and 7-R-1,7-B₁₀C₂H₁₀⁻ (R = CH₃, C₆H₅) ligands, (a) *cis*-(PR₃)₂PtCl(σ -carb), where R = C₂H₅, *n*-C₃H₇, or C₆H₅, and (b) *cis*-(PR₃)₂Pt(PR₂CH₂CHR')(σ -carb), where R = C₂H₅

or *n*-C₃H₇ and R' = H or CH₃, have been prepared by reaction of 1-lithiocarborane derivatives with *cis*-(PR₃)₂PtCl₂ and *trans*-(PR₃)₂PtCl₂, respectively. Both types of derivatives contain a B₁₀C₂H₁₀R⁻ (R = CH₃, C₆H₅) ligand bound to platinum through a metal-carbon σ bond. Type b derivatives achieve four-coordination by internal metalation of one alkyl group of a coordinated phosphine with formation of a second metal-carbon σ bond. The preparation, characterization, reactions, and proposed structures of these complexes are discussed. Analogous reactions with *trans*-[(C₂H₅)₃P]₂PdCl₂ give rise to internally metalated palladium(II) complexes similar to the type b platinum derivatives.

Introduction

The synthesis and the properties of π -bonded transition metal complexes containing B₆C₂H₈⁴⁻, B₇C₂H₉²⁻, B₈C₂H₁₀⁴⁻, and B₉C₂H₁₁²⁻ ligands have been described.¹⁻¹⁰ In a preliminary note¹¹ we have reported the preparation of platinum(II) complexes containing tertiary phosphines and 1,2- or 1,7-dicarba-*closo*-dodecaborane(12) derivatives which are the first examples of compounds in which the carbon atom of a carborane or *neo*-carborane nucleus is σ bonded to a transition metal. Subsequently we have also prepared similar σ -bonded carboranyl complexes of nickel,¹² cobalt,¹³ and rhodium.¹⁴ Recently, two series of complexes of iron(II) and manganese(I) containing the carborane σ bonded to the metal atom were reported by Owen, *et al.*¹⁵ We now report the details of the preparation and characterization of the neutral carborane and *neo*-carborane complexes of platinum(II) and in addition some derivatives of palladium(II).

Results

Table I lists the complexes of platinum and palladium which were prepared.

Complexes I-III were obtained by treating a suspension of *cis*-(PR₃)₂PtCl₂ in diethyl ether or tetrahydrofuran between

0 and 30° with an excess of 1-Li-2-R-1,2-B₁₀C₂H₁₀ (Li(carb)) (eq 1). These complexes show a unique stability in the solid

$$cis-(PR_3)_2PtCl_2 + Li(carb) \rightarrow cis-(PR_3)_2PtCl(\sigma-carb) + LiCl \quad (1)$$

state and in solution, and the chlorine atom bonded to the platinum does not react further with lithium carborane. In fact, no dicarboranyl derivatives were detected in the reaction mixture. The chlorine atom however is easily substituted by a CH₃ group. Thus the complex III reacts in solution, at room temperature, with methyllithium or methyl Grignard reagent to produce the corresponding methylated carboranyl-platinum(II) derivative (IV).

The reported formulations of the complexes I-III, which are diamagnetic and nonconductors at 25° in CH₂Cl₂ solution, are supported by elemental analyses and molecular weight data (Table I). The infrared spectra (Nujol mulls and CsI pellets) exhibited the bands due to the phosphine ligands, the Pt-Cl stretching absorption around 290 cm⁻¹, and the strong absorption bands of the B-H stretching in the region 2540-2620 cm⁻¹, typical of the dicarba-*closo*-dodecaborane(12) nucleus. The ν (C-H) absorption of the free carborane around 3060 cm⁻¹ was not observed, indicating that the compounds are C(1)-substituted carborane derivatives.

The ³¹P nmr spectrum of complex III, 1-[(P(*n*-Pr)₃)₂PtCl]-2-C₆H₅-1,2-(σ -B₁₀C₂H₁₀), in CH₂Cl₂ at 30°, shows two signals of the same intensity separated by 6.8 ppm. Each of the two main peaks show two signals due to the coupling of the ³¹P nuclei with the ¹⁹⁵Pt isotope with constants $J^{195Pt-31P} = 2320$ and 3850 Hz at low and high field, respectively. These data and the nonmeasurable value of J_{P-P} are in agreement with a structure of the complex III in which the phosphine ligands are mutually in *cis* position. On the basis of the well-known coupling constants of related *cis*- and *trans*-(PEt₃)₂PtClR (R = alkyl, aryl) complexes,¹⁶ we maintain that the constant $J^{195Pt-31P} = 2320$ Hz must be assigned to the phosphorus atom *trans* to the carboranyl group.

An unusual result was observed when reaction 1 was carried out using the *trans*-(PR₃)₂PtCl₂ isomers. Reaction of *trans*-(PR₃)₂PtCl₂ (R = C₂H₅, *n*-C₃H₇) with lithium derivatives of the carborane and the *neo*-carborane yielded complexes V-IX for which possible structures are suggested in Chart I. The reactions were usually performed with a large excess of the lithium carborane derivatives. However the same prod-

- (1) M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).
- (2) 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).
- (3) M. F. Hawthorne and T. A. George, *J. Amer. Chem. Soc.*, **89**, 7114 (1967).
- (4) M. F. Hawthorne and A. D. Pitts, *J. Amer. Chem. Soc.*, **89**, 7115 (1967).
- (5) T. A. George and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 1661 (1968).
- (6) J. N. Francis and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 1663 (1968).
- (7) T. A. George and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 5475 (1969).
- (8) M. F. Hawthorne and H. R. Ruhle, *Inorg. Chem.*, **8**, 176 (1969).
- (9) L. F. Warren, Jr., and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **92**, 1157 (1970).
- (10) G. B. Dunks and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **92**, 7213 (1970).
- (11) S. Bresadola, P. Rigo, and A. Turco, *Chem. Commun.*, 1205 (1968); S. Bresadola, A. Frigo, and A. Turco, "Progress in Organometallic Chemistry," Bristol, 1969, FZ.
- (12) S. Bresadola, G. Cecchin, and A. Turco, *Gazz. Chim. Ital.*, **100**, 628 (1970).
- (13) S. Bresadola, G. Cecchin, and A. Turco, *Proc. Int. Conf. Coord. Chem.*, **13th**, 1, 160 (1970).
- (14) S. Bresadola, B. Longato, and F. Morandini, *Proc. Int. Conf. Coord. Chem.*, **14th**, 448 (1972).
- (15) D. A. Owen, J. C. Smart, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **93**, 1362 (1971).

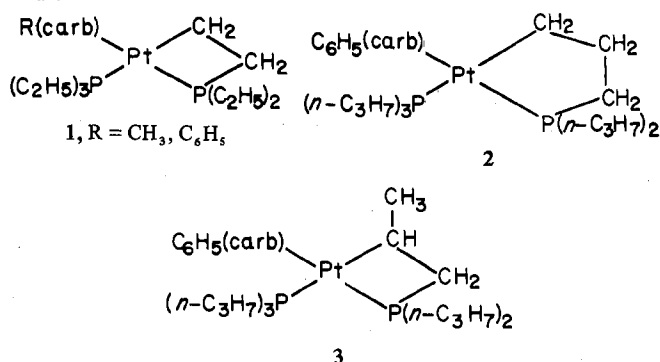
- (16) B. T. Heaton and A. Pidcock, *J. Organometal. Chem.*, **14**, 235 (1968); F. H. Allen and A. Pidcock, *J. Chem. Soc. A*, 2700 (1968).

Table I. Properties and Analytical Data of σ -Bonded Platinum(II)- and Palladium(II)-Carborane Complexes

No.	Compd	Color	Mp, ^a °C	Yield, %	Analysis, ^b %				Mol wt
					C	H	P	Cl	
I	1-[(PEt ₃) ₂ PtCl]-2-CH ₃ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	Pale yellow	147-149	45	28.81 (28.86)	6.84 (6.94)		5.61 (5.68)	620 ^f (624.2)
II	1-[(PPh ₃) ₂ PtCl]-2-CH ₃ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	Pale yellow	116-118	20	51.60 (51.33)	4.79 (4.75)		3.63 (3.88)	889 ^f (912.5)
III	1-[(P(<i>n</i> -Pr) ₃) ₂ PtCl]-2-C ₆ H ₅ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	Pale yellow	168-169	61	40.93 (40.53)	7.38 (7.45)	7.93 (8.04)	4.76 (4.60)	761 ^e (770.4)
IV	1-[(P(<i>n</i> -Pr) ₃) ₂ PtCH ₃]-2-C ₆ H ₅ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	White	174-175	80	43.01 (42.24)	7.71 (8.06)			745 ^f (750.0)
V	1-[(PEt ₃) ₂ Pt(PEt ₂ CH ₂ CH ₂)]-2-CH ₃ -1,2-(σ -B ₁₀ C ₂ H ₁₀) ^c	White	146-147	80	30.62 (30.65)	7.29 (7.20)	10.50 (10.54)		587 ^f (587.7)
VI	1-[(PEt ₃) ₂ Pt(PEt ₂ CH ₂ CH ₂)]-2-C ₆ H ₅ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	White	196-197	15	36.48 (36.96)	6.82 (6.82)	9.50 (9.53)		645 ^g (649.8)
VII	1-[(PEt ₃) ₂ Pt(PEt ₂ CH ₂ CH ₂)]-7-CH ₃ -1,7-(σ -B ₁₀ C ₂ H ₁₀)	White	100-101	46	30.51 (30.65)	7.16 (7.20)	10.50 (10.54)		580 ^e (587.7)
VIII	1-[(PEt ₃) ₂ Pt(PEt ₂ CH ₂ CH ₂)]-7-C ₆ H ₅ -1,7-(σ -B ₁₀ C ₂ H ₁₀)	White	121-122	10	37.51 (36.96)	6.86 (6.82)	9.60 (9.53)		656 ^f (649.8)
IX	1-[(P(<i>n</i> -Pr) ₃) ₂ Pt(P(<i>n</i> -Pr) ₂ CH ₂ CHCH ₃)]-2-C ₆ H ₅ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	White	151	50	43.52 (42.54)	7.94 (7.69)	8.50 (8.44)		713 ^e (733.1)
X	1-[(PEt ₃) ₂ Pd(PEt ₂ CH ₂ CH ₂)]-2-CH ₃ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	White	110-113	25	36.17 (36.10)	8.21 (8.48)	11.86 (12.41)		490 ^g (499.0)
XI	1-[(PEt ₃) ₂ Pd(PEt ₂ CH ₂ CH ₂)]-2-C ₆ H ₅ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	White	103-104 dec	5	42.27 (42.81)	8.31 (7.90)			555 ^g (561.1)
XII	1-[(PEt ₃) ₂ Pt(CN)]-2-CH ₃ -1,2-(σ -B ₁₀ C ₂ H ₁₀) ^d	White	99-100	75	31.39 (31.26)	6.75 (7.05)			613 ^f (614.7)
XIII	1-[(PEt ₃) ₂ Pt(PEt ₂ CH ₂ CH ₂)Cl ₂]-2-CH ₃ -1,2-(σ -B ₁₀ C ₂ H ₁₀)	Pale yellow	175-176	90	26.75 (27.35)	6.04 (6.42)	9.12 (9.40)	10.32 (10.72)	660 ^g (658.6)

^a Uncorrected. ^b Calculated values in parentheses. ^c Pt: 33.60 (33.19)%. ^d N: 2.48 (2.28)%. ^e Osmometric in CH₂Cl₂. ^f Osmometric in acetone. ^g Osmometric in THF.

Chart I



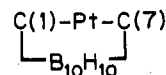
ucts were also obtained working with a 1:1 molar ratio of *trans*-(PR₃)₂PtCl₂ and lithium carborane and we were not able to isolate any intermediate complex containing chlorine and carborane of the type (PR₃)₂PtCl(σ -carb).

Good analytical data (Table I) have been obtained for complexes V-IX which are all monomeric nonelectrolytes in CH₂Cl₂ solution at 25° and diamagnetic (Gouy method). The infrared and ¹H nmr spectra ruled out the existence of metal-hydrogen bonds in these compounds. Carborane C-H stretching absorption around 3060 cm⁻¹ was not observed, which indicated that the products are C(1)-substituted carborane derivatives. Furthermore, the infrared spectrum of Nujol mulls exhibited the strong absorption bands of the B-H stretching in the region 2540-2620 cm⁻¹, indicating that no structural change of the dicarba-*closo*-dodecaborane-(12) nucleus has occurred on coordination.

The diamagnetic properties suggest either a d⁸ or a d¹⁰

configuration for the central metal atom. The existence of a spin coupling *via* metal-metal bonding of a d⁹ configuration is ruled out by the fact that these compounds are monomeric. The complex V, on titration with iodine in benzene-water, reacts with 1 mol of halogen, typical of platinum(II) complexes,¹⁷ and it suggests a d⁸ configuration. The conductivity measurements excluded the possibility that these complexes are three-coordinated species involving one metal-carbon bond and two platinum-phosphorus bonds, as this formulation would demand the existence of a positively charged species of the type [(PR₃)₂Pt(σ -carb)]⁺.

We suggest that these compounds are four-coordinated complexes and that this coordination is attained by internal metalation of one alkyl group of a coordinated phosphine followed by loss of HCl. The loss of hydrogen from the methyl or phenyl substituent on the carborane nucleus with concomitant internal formation of a metal-carbon σ bond is excluded as complexes with the same stoichiometry are formed by both 1,2-carborane and its 1,7 isomer. The distance between the carbon atom of the carborane nucleus and that of the methyl or phenyl substituent in the latter isomer is too large¹⁸ to allow the formation of an exocycle



The ³¹P nmr spectrum of complex V, 1-[(PEt₃)₂Pt(PEt₂CH₂CH₂)]-2-CH₃-1,2-(σ -B₁₀C₂H₁₀), is consistent with a

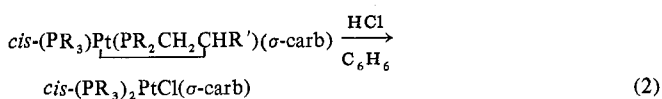
(17) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 4020 (1959).

(18) D. Grafstein and J. Dvorak, *Inorg. Chem.*, 2, 1128 (1963).

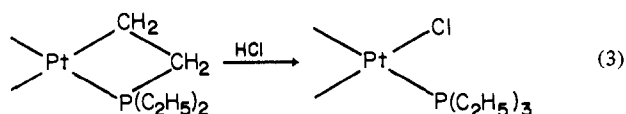
structure in which the two phosphine ligands are mutually in *cis* position. This spectrum consists of two signals separated from them by 36.4 ppm, and the P-P coupling is not detectable. The two different phosphorus signals are flanked by satellites due to coupling with the platinum-195 isotope separated by $J_{195\text{Pt}-31\text{P}}$ of 3060 Hz (low-field signal) and 1690 Hz (high-field signal). The high-field absorption can be assigned to the phosphorus nucleus *trans* to the carboranyl group.¹⁶

The ³¹P nmr spectrum of complex IX, 1-[(P(*n*-Pr)₃)Pt(P(*n*-Pr)₂CH₂CHCH₃)]-2-C₆H₅-(σ-B₁₀C₂H₁₀), is strictly like that of complex V and it is also in accordance with a *cis* configuration. The difference between the two main signals is 35.6 ppm, whereas $J_{195\text{Pt}-31\text{P}}$ is 3120 and 1700 Hz at low and high field, respectively. The close similarity of the two series of data indicates that in the propyl complex the internal metalation reaction gives a four-membered ring as pictured in structure 3 of Chart I, rather than a five-membered ring¹⁹ as in 2. The ¹H nmr spectra of both V and IX are very complex with broad signals and do not allow confirmation of the four-membered ring structures.

Complexes V-IX react with dry hydrogen chloride at room temperature in benzene solution by the general reaction

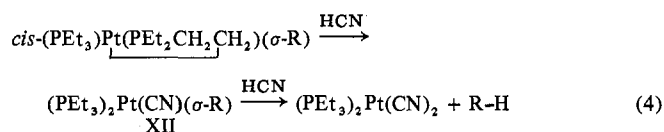


where R = C₂H₅, *n*-C₃H₇; R' = H, CH₃. The complexes obtained by this reaction have a *cis* configuration and are identical with those obtained by reaction of *cis*-(PR₃)₂PtCl₂ with lithium carborane derivatives (complexes I-III). Reaction 2 was carried out also with DCl. The ir spectrum of the deuterated product exhibited an absorption band at 290 cm⁻¹ assignable to ν(Pt-Cl). The analytical determination of deuterium, carried out *via* ir spectroscopy on the water obtained from the combustion of the sample, shows that each complex molecule contains one deuterium atom. In principle, the reaction with dry HCl appears to be similar to that of the platinum(II) dialkyl and diaryl derivatives which react with 1 mol of HCl to produce hydrocarbon R'-H and (PR₃)₂PtClR'.¹⁷ In our case the reaction leads to cleavage of the platinum-alkyl carbon bond and to opening of the carbon-platinum-phosphorus ring (eq 3). No cleavage



of the carboranyl or *neo*-carboranyl group bonded to Pt was observed when these complexes were treated with excess hydrogen chloride at temperatures up to 80°. This behavior is unique for platinum complexes containing metal-carbon σ bonds. In fact, cleavage of the both organic groups by an excess of dry hydrogen chloride occurs in both the *cis*- and *trans*-dialkyl- and diarylplatinum derivatives giving (PR₃)₂PtCl₂.¹⁷

In contrast to its behavior with HCl, the ring opening and the cleavage of the carboranyl group of complex V occurs sequentially when it is treated with dry hydrogen cyanide in benzene solution at room temperature



where R = 1,2-CB₁₀H₁₀CCH₃.

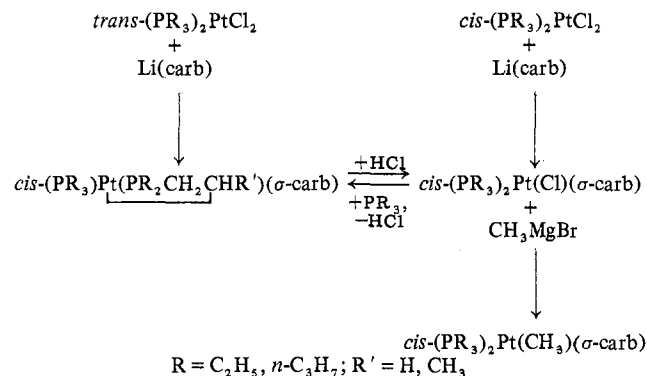
The infrared spectrum of complex XII (Nujol mull) exhibited, other than the absorption bands due to the carborane and phosphine ligands, a strong C≡N stretching absorption centered at 2130 cm⁻¹. The substitution of the carboranyl group bonded to the platinum(II) by CN⁻ is in accordance with the higher nucleophilic character of the latter.

By treating *trans*-(PEt₃)₂PdCl₂ with lithium-carboranyl derivatives we have also isolated carboranyl complexes of palladium(II). These complexes are diamagnetic and non-electrolytic in solution and have the same stoichiometry of the corresponding compounds obtained starting from *trans*-(PEt₃)₂PtCl₂. The reported formulas (X and XI) are supported by the analytical and spectroscopic data.

Discussion

The results obtained in this study are summarized in Scheme I. This behavior is different from the reactions of *cis*-

Scheme I



and *trans*-(PR₃)₂PtCl₂ with lithium alkyls or Grignard reagents. In these cases, a series of organoplatinum derivatives of the types *cis*- and *trans*-(PR₃)₂PtR'X and -(PR₃)₂PtR'₂ were successfully prepared.¹⁷ A recent paper²⁰ has claimed that bis(carboranyl)platinum(II) complexes of the type (PR₃)₂Pt(carb)₂ are obtained from *cis*-(PR₃)₂PtCl₂ (PR₃ = P(C₆H₅)₃, P(CH₃)(C₆H₅)₂, P(CH₃)₂(C₆H₅), P(CH₃)₃) and 1-Li-2-CH₃-1,2-B₁₀C₂H₁₀. We have tried unsuccessfully to prepare bis[triphenylphosphine] bis[methylcarborane(12)]-platinum(II) following the published procedure.²⁰ Instead, a sulfur-containing compound (*Anal. Found*: C, 49.86; H, 4.06; S, 6.21) is obtained after recrystallization from carbon disulfide, the recommended solvent for the recrystallization. Clearly carbon disulfide is involved in these reactions. It should be pointed out that only carbon and hydrogen analyses were presented in the previous work.²⁰ The failure to obtain dicarboranyl derivatives starting from *cis*-(PR₃)₂PtCl₂ (R = C₂H₅, *n*-C₃H₇, C₆H₅) in our opinion is due to the high steric requirements of the carborane moiety. Thus, the presence of one carboranyl group bonded to Pt makes the environment around the metal atom very crowded and prevents the substitution of the second chlorine atom by another bulky carboranyl group. In accordance with this suggestion, we have found that the chlorine atom in the (PR₃)₂PtCl(σ-carb) complexes could be easily substituted by small organic groups as exemplified by the preparation of IV.

(19) A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc. A*, 3833 (1971).

(20) R. Rogowsky and K. Cohn, *Inorg. Chem.*, **11**, 1429 (1972).

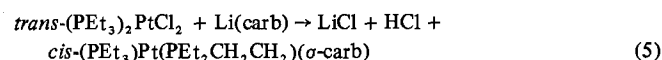
Steric factors also may be important in promoting the formation of the exocycle



via intramolecular elimination of HCl when the *trans*-(PR₃)₂-PtCl₂ isomers are allowed to react. The steric requirements of the carboranyl group bonded to the metal atom may induce the internal metalation by forcing the platinum or palladium atom and the alkyl group of the phosphine ligands closer together. If this assumption is correct, these complexes may be formed by fast elimination of HCl with concomitant formation of the exocycle



following the replacement by the carborane of the first chlorine (eq 5). The hydrogen chloride formed in the course



of the reaction reacts with the lithium carborane still present giving free carborane, which was found in the reaction mixture. Thus, by elimination of chlorine with formation of the exocycle and concomitant isomerization to a *cis* configuration, the environment of the metal atom in these complexes becomes less crowded.

Steric effects may also explain the behavior of the *trans*-(PPh₃)₂PtCl₂ complex which we have found to be unreactive toward the lithium or Grignard derivatives of 1,2-dicarba-*closo*-dodecaborane, whereas it reacts normally with butyllithium giving *cis*-(PPh₃)₂Pt(*n*-Bu)₂. Here, then, bulky coordinated triphenylphosphine molecules²¹ probably prevent the substitution of the chlorine by a group as large as carborane.

It is well-known that the triarylphosphine and triaryl phosphite complexes of many group VIII metals undergo intramolecular aromatic substitution,²² but only recently have the interactions of the aliphatic hydrogens of the phosphine ligands with transition metal atoms been investigated.^{19,23-25} In particular Cheney, *et al.*,^{19,25} noted the remarkable influence of bulky substituents on the phosphorus-donor atom in promoting internal metalation in platinum(II)-triphosphine complexes. Thus, *e.g.*, when *trans*-(P(*t*-Bu)(*n*-Pr)₂)₂PtCl₂ is heated in 2-methoxyethanol, a closed ring complex is formed and an *n*-propyl group is involved in the ring formation. The authors suggest *trans* structures for the two reported complexes (Chart II).

These results imply that the internal metalation reaction is possible only when the phosphine ligands are mutually *trans*. In agreement with this statement we have found that the complex I, 1-[(PEt₃)₂PtCl]-2-CH₃-1,2-(σ-B₁₀C₂H₁₀), having the *cis* configuration, is unaffected by heating under reflux in 1,2-dimethoxyethane or benzene solution. However, the addition of a catalytic amount of free triethylphosphine was effective to promote a very fast internal metalation reaction *via* HCl elimination with formation of complex V in quantitative yield. The presence of free triethylphosphine likely catalyzed the isomerization of complex I to the *trans* configuration and then the carboranyl group *trans* to the chlorine atom is able to promote the observed internal metalation reaction.

(21) C. A. Tolmann, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

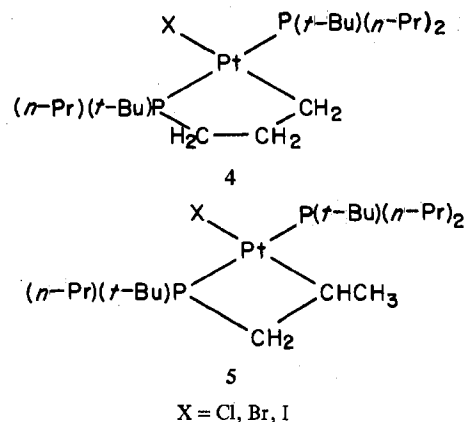
(22) G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).

(23) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).

(24) M. A. Bennett and P. A. Longstaff, *J. Amer. Chem. Soc.*, **91**, 6266 (1969).

(25) A. J. Cheney and B. L. Shaw, *J. Chem. Soc. A*, 754 (1972).

Chart II



Experimental Section

The solvents used were of reagent grade quality and were dried and degassed before use. The lithiocarboranes were prepared by treating the carboranes with lithium butyl as reported in the literature.²⁶ *cis*- and *trans*-(PR₃)₂PtCl₂ and *trans*-(PEt₃)₂PdCl₂ were prepared by literature methods.^{27,28} *trans*-(PPh₃)₂PtCl₂ was obtained by uv-activated isomerization of the *cis* isomer.²⁹ All reactions were carried out under dry nitrogen or argon atmospheres. ¹H 90-MHz and ³¹P 36.4-MHz nmr spectra were recorded in CH₂Cl₂ solutions with a Bruker HFX-90 spectrometer. Infrared spectra were obtained with Perkin-Elmer Model 457 and with Beckman IR-9 spectrometers. Osmometric molecular weights were determined on a Mechrolab Model 301 A osmometer. Conductivity measurements were made at 25° with a LKB bridge.

1-[(PEt₃)₂PtCl]-2-CH₃-1,2-(σ-B₁₀C₂H₁₀), I. A suspension of 0.91 g (1.8 mmol) of *cis*-(PEt₃)₂PtCl₂ in 25 ml of anhydrous tetrahydrofuran was added slowly under a nitrogen atmosphere to a stirred solution of 4.36 mmol of 1-Li-2-CH₃-1,2-B₁₀C₂H₁₀ in 15 ml of anhydrous THF at 0°. After being stirred at 0° for 3 hr, the reaction mixture was evaporated to a white solid. The solid was dissolved in 30 ml of CH₂Cl₂ and the resulting solution was washed three times with water. The organic layer was dried with Na₂SO₄, filtered, and rotary evaporated to a crude solid. This product was recrystallized from CH₂Cl₂-methanol (1:2). The yield of pale yellow crystals, mp 147-149°, was 0.48 g (45%); ν(Pt-Cl) 290 cm⁻¹.

Reaction of 1-[(PEt₃)₂PtCl]-2-CH₃-1,2-(σ-B₁₀C₂H₁₀), I, with 1-Li-2-CH₃-1,2-B₁₀C₂H₁₀. A solution of 0.86 g (1.38 mmol) of complex I in 15 ml of anhydrous tetrahydrofuran was treated under a nitrogen atmosphere with 2 mmol of 1-Li-2-CH₃-1,2-B₁₀C₂H₁₀ in 10 ml of tetrahydrofuran at room temperature. After being stirred for 3 hr, the reaction mixture was washed with water and the organic layer was separated, dried (Na₂SO₄), and rotary evaporated to dryness. The crude product was recrystallized from CH₂Cl₂-CH₃OH (1:2) and the starting platinum complex I was almost quantitatively recovered unchanged, mp 146-148°; ν(Pt-Cl) 290 cm⁻¹. The same reaction was carried out also at 50°, but decomposition of reagents was observed and uncrystallizable products were obtained.

1-[(PPh₃)₂PtCl]-2-CH₃-1,2-(σ-B₁₀C₂H₁₀), II. A suspension of 1.91 g (2.42 mmol) of *cis*-(PPh₃)₂PtCl₂ in 30 ml of anhydrous THF was added slowly under a nitrogen atmosphere to a stirred solution of 5.27 mmol of 1-Li-2-CH₃-1,2-B₁₀C₂H₁₀ in 20 ml of anhydrous THF at 35°. After being stirred at 35° for 2 hr, the reaction mixture was evaporated under reduced pressure. The obtained solid was dissolved in CH₂Cl₂ and washed with H₂O. The organic layer was dried with Na₂SO₄, filtered, and rotary evaporated to a yellow solid. The crude product was washed with hexane and crystallized from methanol. The fraction with mp 115-118° was further recrystallized by dissolving in acetone and adding pentane to give 0.44 g (yield 20%) of pale yellow crystals, mp 116-118°; ν(Pt-Cl) 296 cm⁻¹.

1-[(P(*n*-Pr)₃)₂PtCl]-2-C₆H₅-1,2-(σ-B₁₀C₂H₁₀), III. A solution of 2.0 g (3.41 mmol) of *cis*-(P(*n*-Pr)₃)₂PtCl₂ in 30 ml of anhydrous THF was added slowly under a nitrogen atmosphere to a stirred solution

(26) P. M. Garrett, J. C. Smart, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 4707 (1969).

(27) K. A. Jensen, *Z. Anorg. Allg. Chem.*, **229**, 238 (1936); J. C. Bailar, Jr., and H. Itatani, *Inorg. Chem.*, **11**, 1618 (1965); J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 2532 (1951).

(28) F. G. Mann and D. J. Purdie, *J. Chem. Soc.*, 1549 (1937).

(29) S. H. Mastin and P. Haake, *Chem. Commun.*, 202 (1970).

of 8.1 mmol of 1-Li-2-C₆H₅-1,2-B₁₀C₂H₁₀ in 20 ml of anhydrous THF. After being stirred at 35° for 3 hr, the reaction mixture was evaporated under reduced pressure to small volume. By addition of 50 ml of CH₃OH a crude solid was obtained, which was purified by dissolving it in CH₂Cl₂ and adding CH₃OH. The yield of pure pale yellow crystals, mp 168–169°, was 1.6 g (61%); ν (Pt-Cl) 290 cm⁻¹.

1-[(P(*n*-Pr)₃)₂PtCH₃]-2-C₆H₅-1,2-(σ -B₁₀C₂H₁₀), IV. A suspension of 0.729 g (0.946 mmol) of complex III in 20 ml of anhydrous diethyl ether was added slowly under a nitrogen atmosphere to a stirred solution of 1.5 mmol of CH₃MgBr in 10 ml of ether at room temperature. After being stirred for 2 hr, the reaction mixture was washed with H₂O. The organic layer was dried with Na₂SO₄, filtered, and rotary evaporated to a crude white solid. This product was purified by recrystallization from diethyl ether-ethanol to white crystals, mp 174–175° (0.56 g, 80% yield), of complex IV.

1-[(PEt₃)₂Pt(PEt₂CH₂CH₂)]-2-CH₃-1,2-(σ -B₁₀C₂H₁₀), V. A solution of 4.13 g (8.22 mmol) of *trans*-(PEt₃)₂PtCl₂ in 10 ml of anhydrous THF was added dropwise under a nitrogen atmosphere at 0° to a stirred solution of 19.6 mmol of 1-Li-2-CH₃-1,2-B₁₀C₂H₁₀ in 23 ml of anhydrous THF. After being stirred for 3 hr, the solvent was then removed by distillation *in vacuo* at 0°. The solid was dissolved in CH₂Cl₂ and washed with H₂O. The organic layer was separated, dried (Na₂SO₄), filtered, and rotary evaporated. The white crude product was purified by dissolving in dichloromethane and adding methanol. A total of 3.88 g (yield 80%) of pure white, crystalline product, mp 146–147°, was obtained.

1-[(PEt₃)₂Pt(PEt₂CH₂CH₂)]-2-C₆H₅-1,2-(σ -B₁₀C₂H₁₀), VI. A solution of 2.32 g (4.62 mmol) of *trans*-(PEt₃)₂PtCl₂ in 20 ml of anhydrous THF was added dropwise under a nitrogen atmosphere at 30° to a stirred solution of 11.1 mmol of 1-Li-2-C₆H₅-1,2-B₁₀C₂H₁₀ in 25 ml of anhydrous THF. After being stirred at 30° for 2 hr, the mixture was evaporated under reduced pressure. The crude product was separated and purified as above reported. A total of 0.48 g (yield 15%) of pure white, crystalline product, mp 196–197°, was obtained.

1-[(PEt₃)₂Pt(PEt₂CH₂CH₂)]-7-CH₃-1,7-(σ -B₁₀C₂H₁₀), VII. A solution of 1.25 g (2.49 mmol) of *trans*-(PEt₃)₂PtCl₂ in 10 ml of anhydrous THF was added under a nitrogen atmosphere at 30° to a stirred solution of 5.9 mmol of 1-Li-7-CH₃-1,7-B₁₀C₂H₁₀ in 15 ml of THF. After being stirred for 2 hr, the reaction mixture was evaporated under vacuum. The crude product was separated as reported above and purified by recrystallization from diethyl ether-pentane to give 0.51 g (yield 46%) of white crystals, mp 100–101°.

1-[(PEt₃)₂Pt(PEt₂CH₂CH₂)]-7-C₆H₅-1,7-(σ -B₁₀C₂H₁₀), VIII.

A solution of 1.02 g (2.03 mmol) of *trans*-(PEt₃)₂PtCl₂ in 10 ml of anhydrous benzene was added dropwise under a nitrogen atmosphere at 0° to a stirred solution of 4.81 mmol of 1-Li-7-C₆H₅-1,7-B₁₀C₂H₁₀ in 10 ml of benzene. After being stirred for 3 hr, the reaction mixture was washed with H₂O. The organic layer was separated, dried, filtered, and rotary evaporated. The crude product was purified by Al₂O₃ column chromatography with diethyl ether as eluent. The white fraction was collected and rotary evaporated. Recrystallization from diethyl ether gave 0.14 g (yield 10%) of white crystalline product, mp 121–122°.

1-[(P(*n*-Pr)₃)₂Pt(P(*n*-Pr)₂CH₂CHCH₃)]-2-C₆H₅-1,2-(σ -B₁₀C₂H₁₀), IX.

A solution of 3.4 g (5.8 mmol) of *trans*-(P(*n*-Pr)₃)₂PtCl₂ in 30 ml of anhydrous THF was added at 60° under a nitrogen atmosphere to a stirred solution of 17.3 mmol of 1-Li-2-C₆H₅-1,2-B₁₀C₂H₁₀ in 35 ml of THF. After stirring for 7 hr, the reaction mixture was evaporated *in vacuo*. The solid was dissolved in CH₂Cl₂ and the obtained solution was washed with H₂O. The organic layer was separated, dried, and rotary evaporated to a crude product. It was purified by recrystallization from CH₂Cl₂-methanol to give 2.12 g (yield 50%) of pure white crystals, mp 151°.

Reaction between *trans*-(PPh₃)₂PtCl₂ and 1-Li-2-R-1,2-B₁₀C₂H₁₀ (R = CH₃, C₆H₅). The complex *trans*-(PPh₃)₂PtCl₂ was quantitatively recovered unchanged after being heated under reflux for 2 days with lithium methyl- or phenylcarboranes in 1,2-dimethoxyethane or benzene solution.

Reaction between *trans*-(PPh₃)₂PtCl₂ and *n*-Butyllithium. To a stirred suspension of 0.5 g (0.63 mmol) of *trans*-(PPh₃)₂PtCl₂ in 30 ml of anhydrous benzene was added a solution of 2.0 mmol of *n*-butyllithium in 10 ml of hexane. After being stirred at room temperature for 40 min, the reaction mixture was washed with H₂O. The organic layer was separated, dried (Na₂SO₄), filtered, and rotary evaporated. The obtained crude product was purified by recrystal-

lization from acetone to white crystals, 0.2 g (yield 40%), mp 132–133°, of *cis*-(PPh₃)₂Pt(*n*-Bu)₂.³⁰

1-[(PEt₃)₂Pd(PEt₂CH₂CH₂)]-2-CH₃-1,2-(σ -B₁₀C₂H₁₀), X. A solu-

tion of 1.27 g (3.1 mmol) of *trans*-(PEt₃)₂PdCl₂ in 20 ml of anhydrous diethyl ether was added slowly at –63° under a nitrogen atmosphere to a stirred solution of 6.3 mmol of 1-Li-2-CH₃-1,2-B₁₀C₂H₁₀ in 25 ml of diethyl ether. After stirring for 1 hr at –63°, the reaction mixture was then allowed to warm at 0° and further stirred for 2 hr. It then was evaporated under vacuum and the crude product was separated as above and purified by double recrystallization from THF-pentane. The yield of pure product, white crystals, was 0.16 g (10%), mp 110–113°.

1-[(PEt₃)₂Pd(PEt₂CH₂CH₂)]-2-C₆H₅-1,2-(σ -B₁₀C₂H₁₀), XI. To a

stirred solution of 5.0 mmol of 1-Li-2-C₆H₅-1,2-B₁₀C₂H₁₀ in 20 ml of anhydrous diethyl ether at 0° was added dropwise a solution of 1.3 g (3.1 mmol) of *trans*-(PEt₃)₂PdCl₂ in 20 ml of diethyl ether. After being stirred for 4 hr at 0°, the reaction mixture was evaporated *in vacuo* to a solid. The purification was performed as above. Recrystallization from THF-pentane gave 0.090 g (yield 5%) of white crystals, mp 103–104° dec.

Reaction of 1-[(PEt₃)₂Pt(PEt₂CH₂CH₂)]-2-CH₃-1,2-(σ -B₁₀C₂H₁₀)

with HCl and DCl. Dry hydrogen chloride was passed into a solution of 0.20 g (0.34 mmol) of *cis*-1-[(PEt₃)₂Pt(PEt₂CH₂CH₂)]-2-CH₃-

1,2-(σ -B₁₀C₂H₁₀), V, in 10 ml of anhydrous benzene at room temperature for 40 min. The mixture was then stirred for 12 hr and a white solid was formed. This product was filtered and purified by recrystallization from CH₂Cl₂-CH₃OH to give 0.11 g (yield 52%) of pale yellow crystals of complex I, mp 147–149°. A deuterated complex was prepared by treating complex V with dry DCl in C₆D₆ solution. The deuterium content in the obtained deuterated product was determined by ir analysis on the water formed in the combustion of a sample at 600° in an O₂ atmosphere and in the presence of AgMnO₄. The results show that one deuterium atom is contained in one molecule of complex.

Reaction between 1-[(P(*n*-Pr)₃)₂Pt(P(*n*-Pr)₂CH₂CHCH₃)]-2-C₆H₅-

1,2-(σ -B₁₀C₂H₁₀) and HCl. Dry hydrogen chloride was passed into a solution of 0.21 g (0.29 mmol) of *cis*-1-[(P(*n*-Pr)₃)₂Pt(P(*n*-Pr)₂CH₂CHCH₃)]-

2-C₆H₅-1,2-(σ -B₁₀C₂H₁₀), V, in 15 ml of anhydrous benzene at room temperature for 2 hr. The yellow solid formed was filtered and recrystallized from CH₂Cl₂-CH₃OH to give 0.16 g (yield 74%) of pale yellow crystals of complex III, mp 168–169°.

Reaction between 1-[(PEt₃)₂Pt(PEt₂CH₂CH₂)]-2-CH₃-1,2-(σ -

B₁₀C₂H₁₀) and HCN. Dry hydrogen cyanide was passed into a solution of 0.59 g (1.0 mmol) of *cis*-1-[(PEt₃)₂Pt(PEt₂CH₂CH₂)]-2-CH₃-

1,2-(σ -B₁₀C₂H₁₀) in 10 ml of anhydrous benzene at 7° for 7.5 hr. The reaction mixture was evaporated under vacuum and the residue was washed with benzene and double recrystallized from acetone-pentane to give a white crystals, mp 99–100° (0.46 g, yield 75%), of *cis*-1-[(PEt₃)₂Pt(CN)]-2-CH₃-1,2-(σ -B₁₀C₂H₁₀), XII. Further, a white, crystalline product was separated from the benzene fraction by addition of pentane. This product was found to be (PEt₃)₂-Pt(CN)₂, mp 177–178°.³¹

1-[(PEt₃)₂Pt(PEt₂CH₂CH₂)Cl₂]-2-CH₃-1,2-(σ -B₁₀C₂H₁₀), XIII.

To a stirred solution of 0.59 g (1.0 mmol) of 1-[(PEt₃)₂Pt(PEt₂CH₂CH₂)]-2-CH₃-1,2-(σ -B₁₀C₂H₁₀) in 10 ml of anhydrous benzene was added at 5° a solution of chlorine in CCl₄ (2.0 mmol). After 1 hr the solution was evaporated to dryness and the residue was washed with diethyl ether and recrystallized from CH₂Cl₂-hexane to give 0.60 g (yield 90%) of pale yellow crystals, mp 175–176°; ν (Pt-Cl) 297 cm⁻¹.

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(30) B. A. Morrow, *Can. J. Chem.*, **48**, 2192 (1970).

(31) P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc. A*, 1462 (1966).

CH₃-1,2-B₁₀C₂H₁₀, 32630-05-0; *cis*-(PPh₃)₂PtCl₂, 15604-36-1; *cis*-(P(*n*-Pr)₃)₂PtCl₂, 15977-21-6; 1-Li-2-C₆H₅-1,2-B₁₀C₂H₁₀, 41655-52-1; *trans*-(PEt₃)₂PtCl₂, 15692-07-6; 1-Li-7-CH₃-1,7-B₁₀C₂H₁₀, 32630-07-

2; 1-Li-7-C₆H₅-1,7-B₁₀C₂H₁₀, 42012-25-9; *trans*-(P(*n*-Pr)₃)₂PtCl₂, 15977-22-7; *n*-butyllithium, 109-72-8; *trans*-(PEt₃)₂PdCl₂, 15642-19-0; HCl, 7647-01-0; HCN, 74-90-8; phosphorus-31, 7723-14-0.

Contribution from the William A. Noyes Laboratory, School of Sciences, Department of Chemistry, University of Illinois, Urbana, Illinois 61801 and Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544

Vibrational Spectra and Bonding in Pentacyanohaloplatinate(IV) Complexes¹

MELVIN N. MEMERING^{2a,b} LLEWELLYN H. JONES,^{2a} and JOHN C. BAILAR, Jr.^{*2b}

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The infrared and Raman spectra of solid complex species M₂Pt(CN)₅X (M = alkali metal; X = Cl, Br, I, CN) have been observed in the regions 2250–2000 and 540–35 cm⁻¹. Infrared intensities of C–N stretching vibrations and Raman polarization data have also been obtained for aqueous solutions of these complexes. The results have been combined to assign many of the fundamental frequencies. Replacement of a cyanide group by a halide results in a slight decrease of the M–C as well as the C–N stretching frequencies, iodide having the greatest effect and chloride, the least. Bonding implications are made on the basis of a mechanism in which the degree of σ interaction predominates over the extent of platinum–carbon π bonding.

Introduction

In contrast to the numerous vibrational studies concerning substituted metal carbonyls, relatively few studies have dealt with analogous metal cyanides. Because of the complexity of the spectra and the significant amount of mode mixing in the M–C stretching region, few detailed vibrational analyses have been made.³ Several approximate normal-coordinate analyses have been undertaken for a number of regular hexacyanometalates from which additional information on the bonding has been derived.⁴ Assignments made for these complexes are of great assistance in the interpretation of the spectra of substituted metal cyanides.

Platinum(IV) cyanide complexes are interesting in that the central metal is in a high oxidation state. The C–N and Pt–C stretching force constants of K₂Pt(CN)₆ have been found to be the largest yet determined for six-coordinate metal cyanide systems.⁵ These results indicate strong metal–carbon σ bonding and weak metal–carbon π bonding. Infrared intensity studies furnish additional information concerning the extent of electron delocalization during a particular vibration.⁶ For this reason we have measured the intensities of antisymmetric C–N stretching vibrations in order to compare the degree of π bonding with that found in other metal cyanides.

It is of interest to determine the changes in metal–ligand σ and π bonding which accompany partial replacement of cyanides with other ligands, such as the halides. For this purpose we have compared the fundamental M–C vibrations of the anions, Pt(CN)₅X²⁻ (X = Cl, Br, I), so that the effect

of the halide on the Pt–C bond strengths could be estimated. At the same time, we have investigated the effect on other vibrations and have also compared the magnitude of counterion interaction effects to the intramolecular electronic effects of the substituent halides. The results of this study should contribute to the current knowledge of bonding properties of substituted metal cyanides and related compounds.

Experimental Section

Preparations. In general, simple salts and other common reagents were of analytical grade. Platinum-containing starting materials such as Na₂PtCl₆ and PtCl₂ were purchased from Englehard Industries. The precursor complex, sodium tetracyanoplatinate(II), was obtained as the trihydrate from the reaction of platinum(II) chloride (PtCl₂) with an excess of sodium cyanide in aqueous solution. Potassium tetracyanonickelate(II) and -palladate(II) were available from previous studies.⁷

Preparation of K₂Pt(CN)₅I involved the method of Babkov in which K₂Pt(CN)₄ is oxidized by cyanogen iodide.⁸ The bromo and chloro species were prepared by *in situ* oxidations of the iodide by the respective halogen,⁹ the hexacyano complex, by cyanide substitution of the iodo complex.⁸ The sodium salts were obtained by analogous reactions with Na₂Pt(CN)₄ or by precipitating K₂SiF₆ from the appropriate potassium salt with fluosilicic acid and carefully neutralizing the filtrate with sodium bicarbonate. The cesium compounds were prepared by simple metathesis of the appropriate potassium salts using excess cesium sulfate, bromide, and chloride for the cesium–iodo, –bromo, and –chloro salts, respectively; the resulting salts were purified from potassium salts by recrystallizing from water. Analytical purity of the platinum(IV) complexes was verified by the Microanalytical Laboratory of the University of Illinois.

Instrumentation and Techniques. Infrared spectra of mineral oil mulls were recorded in the regions 2250–2000 and 540–250 cm⁻¹ on a Perkin-Elmer Model 521 spectrometer. The mulls were supported by NaCl, CsBr, and CsI plates, the latter two being used in the low-frequency region. The pressed-disk technique was not employed as we wished to avoid the possibility of solid-state reactions. Low-temperature spectra were measured using an evacuated liquid nitrogen cell having CsBr windows. Spectra were run at a dispersion of 5 cm⁻¹/cm at a scan speed of approximately 5 cm⁻¹/min. Mull spectra on polyethylene plates were measured in the far-infrared region (33–350 cm⁻¹) by a Beckman IR-11 spectrometer at a dispersion of 7.5–

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(2) (a) Los Alamos Scientific Laboratory. (b) Department of Chemistry, University of Illinois.

(3) D. M. Adams, "Metal-Ligand and Related Vibrations," Edward Arnold, London, 1967, p 117.

(4) (a) W. P. Griffith and G. T. Turner, *J. Chem. Soc. A*, 858 (1970); (b) J. P. Mathieu and H. Poulet, "Advances in Molecular Spectroscopy," Pergamon Press, Oxford, 1962, p 1016; (c) I. Nakagawa and T. Shiminouchi, *Spectrochim. Acta*, 18, 101 (1962); (d) L. H. Jones, *J. Chem. Phys.*, 36, 1209 (1962); 41, 856 (1964); (e) L. H. Jones, M. N. Memering, and B. I. Swanson, *ibid.*, 54, 4666 (1971).

(5) H. Siebert and A. Siebert, *Z. Naturforsch. B*, 22, 674 (1967).

(6) L. H. Jones, *Inorg. Chem.*, 2, 777 (1963).

(7) J. S. Coleman, H. Petersen, and R. A. Penneman, *Inorg. Chem.*, 4, 135 (1965).

(8) A. V. Babkov, *Dokl. Akad. Nauk SSSR*, 177, 337 (1967).

(9) I. B. Baranovskii and A. V. Babaeva, *Russ. J. Inorg. Chem.*, 11, 926 (1966).