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## Cationic Platinum(II) Acetylenic Complexes and Their Derivatives. VI.<sup>1</sup>

### Aminolysis and Other Reactions of Cationic Platinum(II) Alkoxy-carbene Complexes

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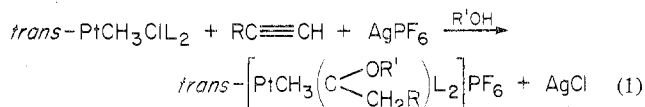
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The aminolysis of a series of cationic methylplatinum(II) alkoxy-carbene complexes is described; aminocarbene formation appears to occur by a mechanism involving a highly amine-crowded transition state so that steric effects of the amino group are important. Reactions of the corresponding cationic chloroalkoxy-carbene complexes yielded ethionyl derivatives. Reactions of the alkoxy-carbene complexes with halide ions, iodomethane, hydrogen chloride, and some neutral ligands are also described.

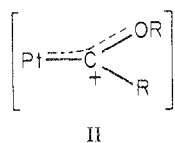
#### Introduction

Since Fischer's<sup>2</sup> original discovery of transition metal carbene complexes, several reaction pathways to complexes containing carbene ligands have been reported, and a number of reactions of the carbene complexes have been described.<sup>3</sup> However, most of the known reactions are those of carbene complexes of group VI metal carbonyls.<sup>3c</sup> Also, relatively few examples<sup>4,5</sup> are known of reactions in which a stable metal carbene complex can be used as a source of free carbene.

Previously we have reported the preparation of cationic platinum(II)<sup>6,7</sup> and platinum(IV)<sup>8</sup> alkoxy-carbene complexes, from reactions of type 1, which involve nucleophilic attack by



alcohol on  $\pi$ -acetylenic cations.<sup>7</sup> The alkoxy-carbene cation as in I can also be considered as a stabilized carbonium ion, II; we<sup>9</sup> and others<sup>10,11</sup> have expressed this view in light of the



<sup>13</sup>C shieldings of carbene carbons in these and related metal carbene complexes.

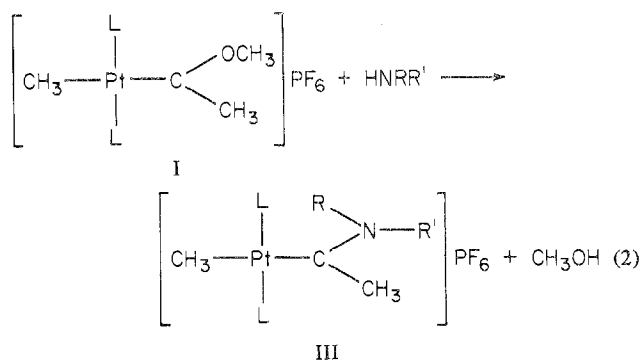
The reactivity of these cationic platinum(II) complexes is of interest, since four-coordinate d<sup>8</sup> metal complexes are well recognized to be kinetically labile toward associative reactions. They lead ultimately to oxidative addition, ligand displacement, or intramolecular ligand migration (insertion) products.

We now describe aminolysis and some other reactions of the cationic platinum carbene complexes.

#### Results and Discussion

**Reactions with Amines.** Aminolysis of alkoxy-carbene complexes has been used widely for the preparation of neutral aminocarbene complexes of group VI metal carbonyls.<sup>3</sup> The mechanism for the aminolysis of (CO)<sub>5</sub>CrC(OCH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>,<sup>12</sup> as well as substituent and steric effects in the formation of (CO)<sub>5</sub>CrC(NRR')CH<sub>3</sub>, has been studied.<sup>13</sup> The aminolytic reactions of the cationic platinum carbene complexes *trans*-[PtXL<sub>2</sub>C(OCH<sub>3</sub>)CH<sub>3</sub>]PF<sub>6</sub> (X = CH<sub>3</sub> or Cl) have now been investigated for comparison.

(a) **Methylplatinum Carbene Complexes.** By the aminolysis reaction 2, new cationic platinum aminocarbene complexes,



III, have been obtained from I in very good yields, when R, R' = H, H; H, CH<sub>3</sub>; CH<sub>3</sub>, CH<sub>3</sub> for L = both PPhMe<sub>2</sub> and AsMe<sub>3</sub>; R, R' = H, allyl for L = PPhMe<sub>2</sub>; and H, Et for L = AsMe<sub>3</sub>. When R, R' = H, CH(CH<sub>3</sub>)<sub>2</sub>, the yield was lower for L = AsMe<sub>3</sub> and no corresponding monoisopropylaminocarbene complex was isolated for L = PPhMe<sub>2</sub>. The analyses of the products are shown in Table I, as well as their numerical identification used later in this discussion. (For convenience, the identification number assigned to each compound is that used in the preceding paper.) Reactions of I with HNRR' (R, R' = Et<sub>2</sub>; (*i*-Pr)<sub>2</sub>; H, *t*-Bu) were also carried out but no aminocarbene complexes were isolated. Thus, the behavior of amines in reaction 2 is different from that in the aminolysis of (CO)<sub>5</sub>CrC(OCH<sub>3</sub>)CH<sub>3</sub>,<sup>13</sup> where all of the corresponding aminocarbene complexes could be formed from a series of primary alkylamines RNH<sub>2</sub> and also for HNEt<sub>2</sub>, although the rate of reaction decreased in the order R = H, Me, Et > *i*-Pr > *t*-Bu. The monoalkylaminocarbene ligands in the complexes (CO)<sub>5</sub>CrC(NHCH<sub>3</sub>)CH<sub>3</sub> have been shown to prefer the *cis* (syn) configuration,<sup>14</sup> while in the present cationic platinum carbene system, III, the monoalkylaminocarbene ligands prefer the *trans* (anti) configuration. This has been confirmed by means of the <sup>1</sup>H and <sup>13</sup>C nmr spectra which were discussed in the preceding paper.



The difference in reactivity of amines toward the alkoxy-carbene complexes may arise from steric effects which may influence either (i) the product stability or (ii) the ease of formation of the transition state. Thus the preference of III for the *trans* isomer may explain why no complexes with the mono-*tert*-butylaminocarbene ligand could be isolated. The fact that H<sub>2</sub>N-*i*-Pr gave the corresponding aminocarbene complex for L = AsMe<sub>3</sub> but not for L = PPhMe<sub>2</sub> may also

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Table I. Characterization Data for Carbene Complexes,  $trans-[PtX(L')L_2]^+PF_6^-$ 

No.	L'	X	L	Mp, °C	Analysis, %							
					C		H		N		Halogen	
					Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
1	CH <sub>3</sub> CNH <sub>2</sub>	CH <sub>3</sub>	As(CH <sub>3</sub> ) <sub>3</sub>	153-155	16.93	16.84	4.11	4.01	2.19	1.75		
2	Trans CH <sub>3</sub> CNHCH <sub>3</sub>	CH <sub>3</sub>	As(CH <sub>3</sub> ) <sub>3</sub>	173-175	18.40	18.51	4.33	4.34	2.15	2.13		
3	CH <sub>3</sub> CN(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	As(CH <sub>3</sub> ) <sub>3</sub>	146	19.82	19.62	4.54	4.27	2.10	1.98		
4	CH <sub>3</sub> CNHCH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	As(CH <sub>3</sub> ) <sub>3</sub>	176-177	19.83	19.92	4.53	4.08	2.10	1.84		
12	CH <sub>3</sub> CNHCH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	As(CH <sub>3</sub> ) <sub>3</sub>	154-156	21.22	21.62	4.60	4.73	2.06	1.95		
13	CH <sub>2</sub> =CHCH <sub>2</sub> NHCCH <sub>3</sub>	CH <sub>3</sub>	As(CH <sub>3</sub> ) <sub>3</sub>	172	21.24	21.48	4.46	4.39	2.06	1.80		
16	CH <sub>3</sub> CNH <sub>2</sub>	CH <sub>3</sub>	PPh(CH <sub>3</sub> ) <sub>2</sub>	155	33.83	33.96	4.49	4.37	2.08	1.96		
17	CH <sub>3</sub> CNHCH <sub>3</sub>	CH <sub>3</sub>	PPh(CH <sub>3</sub> ) <sub>2</sub>	134-135	34.89	35.10	4.69	4.70	2.08	1.87		
18	CH <sub>3</sub> CN(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	PPh(CH <sub>3</sub> ) <sub>2</sub>	160	35.90	35.99	4.88	5.04	1.99	1.88		
19	HO(CH <sub>2</sub> ) <sub>3</sub> CNH <sub>2</sub>	CH <sub>3</sub>	PPh(CH <sub>3</sub> ) <sub>2</sub>	132-135	35.10	34.94	4.49	4.44	1.95	1.89		
20	HO(CH <sub>2</sub> ) <sub>3</sub> CN(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	PPh(CH <sub>3</sub> ) <sub>2</sub>	170-175	37.00	36.54	5.13	4.87	1.88	1.65		
9	CH <sub>3</sub> CNHCH <sub>3</sub>	Cl	As(CH <sub>3</sub> ) <sub>3</sub>	210-212	16.07	16.25	3.75	3.12	2.08	2.20		
10	CH <sub>3</sub> CN(CH <sub>3</sub> ) <sub>2</sub>	Cl	As(CH <sub>3</sub> ) <sub>3</sub>	199-202	17.47	17.62	3.96	4.14	2.04	1.82	Cl 5.17	5.27
14	CH <sub>3</sub> CN(CH <sub>3</sub> ) <sub>2</sub>	I	As(CH <sub>3</sub> ) <sub>3</sub>	195-198	15.42	15.76	4.00	3.85	1.80	1.75	I 16.6	16.3
22	CH <sub>3</sub> CN(CH <sub>3</sub> ) <sub>2</sub>	Cl	PPh(CH <sub>3</sub> ) <sub>2</sub>	179	33.24	33.02	4.33	4.26	1.94	1.96	Cl 4.91	4.89
23	CH <sub>3</sub> CN(CH <sub>3</sub> ) <sub>2</sub>	I	PPh(CH <sub>3</sub> ) <sub>2</sub>	198-200	29.49	29.62	3.70	3.70	1.92	1.73	I 15.60	15.75
24	CH <sub>2</sub> CH <sub>2</sub> OCCCH <sub>2</sub>	Cl	PPh(CH <sub>3</sub> ) <sub>2</sub>	155-157	33.38	33.12	3.93	4.07			Cl 4.92	4.50
11	CH <sub>3</sub> COCH <sub>3</sub>	Cl	As(CH <sub>3</sub> ) <sub>3</sub>	185-190	16.02	16.22	3.59	3.57			Cl 5.27	5.59
15	CH <sub>3</sub> COCH <sub>3</sub>	I	As(CH <sub>3</sub> ) <sub>3</sub>	175-177	14.08	13.82	3.15	3.00			I 16.56	16.43
21	CH <sub>3</sub> CNHCH <sub>3</sub>	Cl	PPh(CH <sub>3</sub> ) <sub>2</sub>	169-171	32.19	32.52	4.12	3.98	1.97	1.95		

result from the enhanced steric interaction in the *trans* isomer between L and the amino substituent R = *i*-Pr.

However, such steric effects on product stability cannot be the controlling feature of reaction 2, since if this were the case, the isolation of *trans*-monoethyl- and -monoisopropylaminocarbene complexes (the latter for L = AsMe<sub>3</sub> only) would suggest that the corresponding diethylaminocarbene complexes should also be formed readily. There appears to be no reason to suppose that the presence of the second ethyl group could cause a sufficiently large additional steric effect in the expected diethylaminocarbene complex so as to prevent its isolation, as we observe. We therefore suggest that the nonformation of III with the diethylaminocarbene ligand is probably due to steric effects in the formation of the activated complex.

The mechanism of aminolysis of (CO)<sub>5</sub>CrC(OCH<sub>3</sub>)Ph has been studied in detail spectrophotometrically, and, in nonpolar solvents, the rather complex rate expression  $d[\text{aminocarbene complex}]/dt = k[\text{alkoxycarbene complexes}][\text{RNH}_2]^3$  has been established. On this basis, Werner, *et al.*,<sup>12</sup> proposed a highly amine-crowded transition state, in which the steric effects of the amine substituents and of the other ligands on the metals are more important than in the product. The observed behavior of amines toward I can best be explained by assuming a similar mechanism for reaction 2, despite the fact that the initial complexes, I, are only four-coordinate. Although this difference in geometry for I and (CO)<sub>5</sub>CrC(OCH<sub>3</sub>)Ph makes comparison difficult, steric hindrance in such an amine-crowded transition state due to the ligands AsMe<sub>3</sub> or PPhMe<sub>2</sub> in I may well be larger than for CO in the chromium complex.

In order to ascertain the generality of such a mechanism, we attempted a kinetic study of the reaction of I (L = PPhMe<sub>2</sub>) with HNMe<sub>2</sub> in methylene chloride, by monitoring aminocarbene formation by means of the methyl proton nmr signal of the liberated methanol.

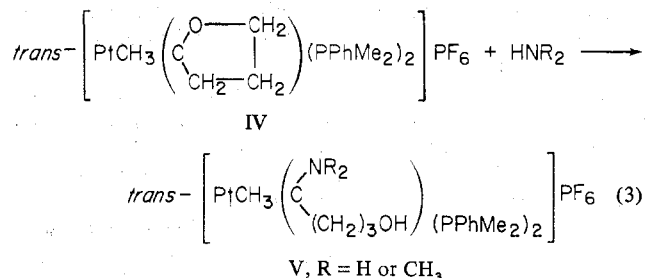
Our attempts were, unfortunately, thwarted because of competing side reactions at low amine concentrations. At 0°, for ratios of I (L = PPhMe<sub>2</sub>) to HNMe<sub>2</sub> of 1:0.5 and 1:1, only partial aminocarbene formation occurred and crystals of amine hexafluorophosphate salts were formed in the nmr tube, along with some PtCl<sub>2</sub>L<sub>2</sub> presumably as a result of a reaction involving the chlorinated solvent.<sup>15</sup> Even in acetone-*d*<sub>6</sub> a complex reaction occurred at low amine concentration, leading to some reduction to zerovalent platinum. These side reactions also

occurred in reaction 2 when amines with bulky substituents were used.

At concentration ratios of I (L = PPhMe<sub>2</sub>) to HNMe<sub>2</sub> of 1:4 and 1:10, formation of compound 18 was very rapid (too fast to be followed by nmr) and apparently quantitative in platinum.

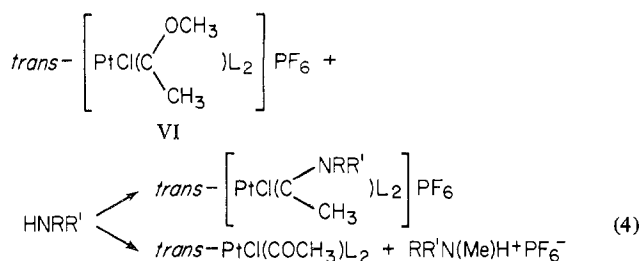
Although our present study lacks any quantitative interpretation, it does show clearly that aminocarbene formation is favored only at high amine:I ratios. This is consistent with Werner's mechanism.

The lack of reaction of I (L = AsMe<sub>3</sub>) with HN(*i*-Pr)<sub>2</sub> is also consistent with a steric effect influencing the transition state. In the reaction of HN(*i*-Pr)<sub>2</sub> with (CO)<sub>5</sub>CrC(OC-CH<sub>3</sub>)CH<sub>3</sub>, (CO)<sub>5</sub>CrC(NH-*i*-Pr)CH<sub>3</sub> was obtained which was formed from the initial formation of (CO)<sub>5</sub>CrC(N(*i*-Pr)<sub>2</sub>)CH<sub>3</sub> followed by elimination of propene from the quasi-ammonium nitrogen atom.<sup>13</sup> Hence, it seems reasonable to assume in the present case that there is no formation, as an unstable intermediate, of a diisopropylaminocarbene, particularly since 12 was readily isolated from the reaction of I (L = AsMe<sub>3</sub>) with H<sub>2</sub>N-*i*-Pr. The cyclic oxycarbene complex IV also reacts readily with NH<sub>3</sub> and HNMe<sub>2</sub> according to eq 3. These

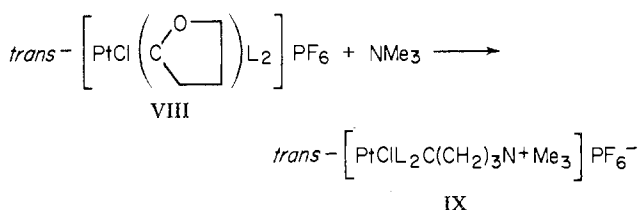


aminocarbene complexes were isolated as white air-stable crystalline solids which are soluble in dichloromethane, chloroform, acetone, and nitrobenzene but insoluble in nonpolar organic solvents; they showed greater thermal stability and decomposed less readily in chlorinated solvents than the alkoxycarbene complexes.

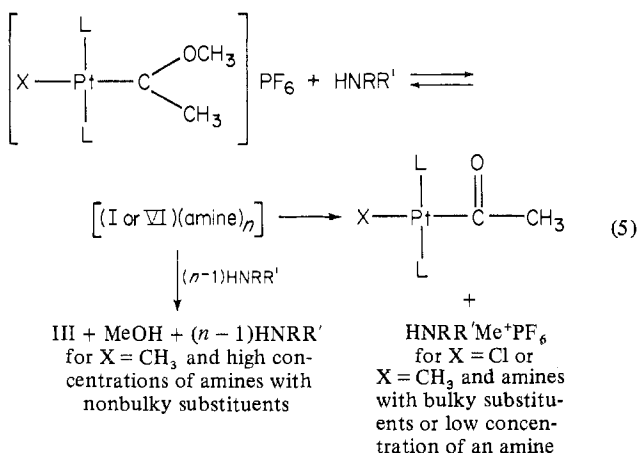
(b) **Chloroplatinum Carbene Complexes.** The reaction of VI with amines (in excess and under comparable conditions for reaction 2) did not yield aminocarbene complexes, VII, but led to ethionyl formation as shown in (4). Similarly, VI reacted with Et<sub>3</sub>N and pyridine according to (4). Conse-



quently, VII can only be formed by the reaction of III with HCl (see later). The trans-chloro platinum cyclooxycarbene complex VIII also reacts with amines but not to give the aminocarbene complex. Instead N-alkylation occurs yielding the acylplatinum complex IX having quaternary ammonium at the end which could be isolated as white crystals in the reaction with N(CH<sub>3</sub>)<sub>3</sub>.



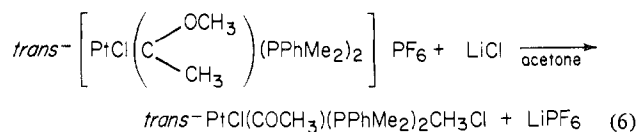
We suggest the general scheme 5 for reactions of cationic platinum alkoxycarbene complexes with amines.



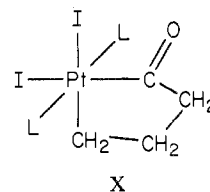
Although we have no direct evidence for the formation of *trans*-PtCH<sub>3</sub>(COCH<sub>3</sub>)L<sub>2</sub> where the amine is in low concentration or has bulky substituents, the observed formation of amine hexafluorophosphate salts, and PtCl<sub>2</sub>L<sub>2</sub> in dichloromethane, and Pt(0) in acetone-*d*<sub>6</sub> may be accounted for by this hypothesis.<sup>16</sup>

The facile methyl transfer in reaction 4 contrasts with the chemistry of other metal alkoxycarbene complexes, e.g., (CO)<sub>5</sub>CrC(OCH<sub>3</sub>)Ph. This difference may reflect the greater electron deficiency of the alkoxycarbene ligand in cationic platinum complexes, as described by II.

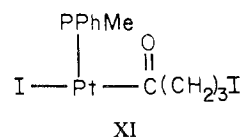
**Reactions with Halide Ions.** Compound I does not react with LiCl or NaI in acetone solution, but for VI, halide substitution and ethionyl formation are competing reactions. Thus when NaI (1 molar equiv) is added to VI (L = PPhMe<sub>2</sub>) in acetone, a precipitate of NaCl forms rapidly. The acetone-soluble species is *trans*-[PtI(PPhMe<sub>2</sub>)<sub>2</sub>C(OCH<sub>3</sub>)CH<sub>3</sub>]PF<sub>6</sub> (ca. 80%) together with a mixture of *trans*-PtI(COCH<sub>3</sub>)(PPhMe<sub>2</sub>)<sub>2</sub>, *trans*-PtCl(COCH<sub>3</sub>)(PPhMe<sub>2</sub>)<sub>2</sub>, and a little starting material. Addition of LiCl to VI (L = PPh<sub>2</sub>Me) in acetone leads, apparently quantitatively, to the reaction described by (6). VII reacts with NaI (1 molar equiv) to give an almost quantitative substitution of halide; i.e., the corresponding trans-iodo platinum-cyclic carbene cation is formed. The addition of 1 further molar equiv of NaI, or treatment of VIII with 2 molar



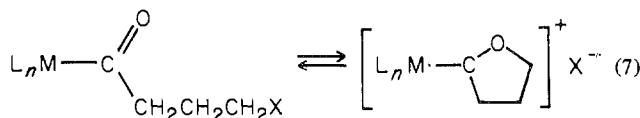
equiv of NaI, gives the neutral platinum(IV) acyl complex, X. Presumably this reaction proceeds *via* initial nucleophilic



attack on the alkoxymethylene carbon to give through ring opening the ω-iodoacyl complex XI, which then undergoes an internal oxidative addition reaction.



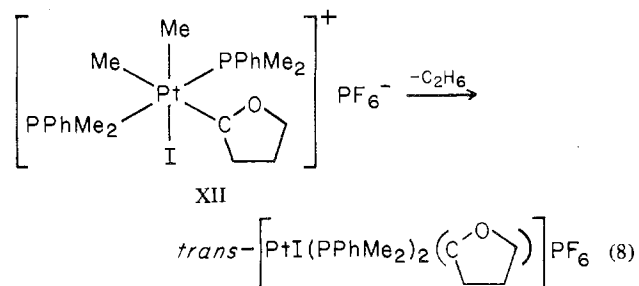
Cotton and Lukehart<sup>17,18</sup> have demonstrated the formation of 2-oxacyclopentylidene ligands from ω-haloacyl ligands, and their results together with ours support the generality of equilibrium 7. Compound 22 (see Table I) reacts with NaI



(≥1 molar equiv) to give only the halide substitution product, *trans*-[PtI{C[N(CH<sub>3</sub>)<sub>3</sub>]CH<sub>3</sub>}(PPhMe<sub>2</sub>)<sub>2</sub>]PF<sub>6</sub>. Thus we see a clear difference in the reactions of alkoxycarbene ligands in I and VI according to the nature of trans ligand X as shown in (7) and a difference between the reactions of alkoxy- and aminocarbene ligands for a given trans ligand.

**Reactions with Iodomethane.** A characteristic of square-planar platinum(II) complexes is their ability to undergo oxidative addition reactions.<sup>19</sup> For a reagent such as iodomethane, oxidative addition is markedly dependent on the nature of the ligands on platinum, and to a first approximation the ease of oxidation correlates with electron density at the metal. For example, the ease of oxidative addition of iodomethane decreases down the series PtMe<sub>2</sub>(PPhMe<sub>2</sub>)<sub>2</sub> > PtMeCl(PPhMe<sub>2</sub>)<sub>2</sub> > PtCl<sub>2</sub>(PPhMe<sub>2</sub>)<sub>2</sub>—the last complex being unreactive. It was therefore of interest to examine the reactions of iodomethane with cationic platinum carbene complexes.

The reaction of CH<sub>3</sub>I with IV gave the dimethyliodo-platinum(IV) carbene complex XII, which lost ethane by reductive elimination to give the iodo analog of VI.

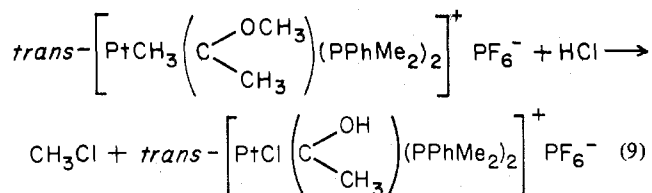


Compound I (L = AsMe<sub>3</sub>) also reacts with CH<sub>3</sub>I giving *trans*-[PtI(AsMe<sub>3</sub>)<sub>2</sub>C(OCH<sub>3</sub>)CH<sub>3</sub>]PF<sub>6</sub>, which similarly may be formed *via* an initial oxidative addition product, [Pt(CH<sub>3</sub>)<sub>2</sub>I(AsMe<sub>3</sub>)<sub>2</sub>C(OCH<sub>3</sub>)CH<sub>3</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup> followed by reductive

elimination of ethane. In other cases, although the products have not been isolated, the reactions could be followed by monitoring, in the nmr spectra, the formation of ethane. Thus I, 1-4, 12, 13, and 16 reacted with CH<sub>3</sub>I, but 18, VI, and VII did not. These observations suggest that substitution of methyl by chloride significantly reduces the electron density at platinum. Steric factors are also important since (a) trimethylarsine complexes reacted more readily than dimethylphenylphosphine complexes and (b) the diphenylmethylphosphine complex of I did not react at all. Similarly, while 16 reacted with CH<sub>3</sub>I, 18 did not.

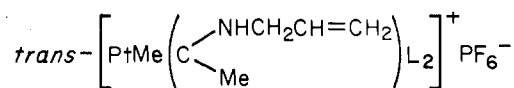
Cationic dimethylplatinum(IV) carbene complexes were unstable in solution slowly eliminating ethane. In this regard complexes of AsMe<sub>3</sub> were much more labile than those of PPhMe<sub>2</sub>. Reductive elimination trends in methylplatinum(IV) cations have been described previously.<sup>20</sup>

**Reactions with HCl.** Compounds I and III react with HCl (1 molar equiv) in dichloromethane, methanol, or THF to give VI and VII, respectively, with liberation of methane. The mechanism of this reaction is uncertain although an oxidative addition, reductive elimination sequence seems plausible. VI reacts only very slowly (over a period of several days) with excess anhydrous HCl in dichloromethane. Methyl chloride is produced quantitatively but the reaction is complex with respect to platinum, and PtCl(COCH<sub>3</sub>)L<sub>2</sub> was the only platinum-containing compound identified. Although all attempts to isolate other platinum-containing products failed, we suggest that the basic reaction may be represented by (9)

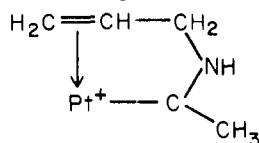


and that the hydroxycarbene cation is not stable but readily eliminates HPF<sub>6</sub> thereby allowing the isolation of *trans*-PtCl(COCH<sub>3</sub>)(PPhMe<sub>2</sub>)<sub>2</sub>. Under comparable conditions, 18 appeared indefinitely stable toward anhydrous HCl (1 molar equiv).

**Reactions with Neutral Ligands.** The carbene ligand in I is inert to displacement by reaction with any of the neutral ligands RNC, PR<sub>3</sub>, CO, and pyridine, although with RNC and PR<sub>3</sub>, displacement of L occurs rather than displacement of the carbene. This type of displacement reaction has previously been discussed.<sup>21</sup> VI does not react with EtO<sub>2</sub>CCH=CHCO<sub>2</sub>Et, MeO<sub>2</sub>CC≡CCO<sub>2</sub>Me, or MeC≡CMe upon ultraviolet irradiation either in methylene chloride at 0° or at 100° in nitrobenzene. This lack of reactivity with olefins and acetylenes probably reflects an unfavorable equilibrium for the formation of cationic, five coordinate π complexes. Even the allylaminocarbene complex



for which π complexation is possible, as shown in XIII, does

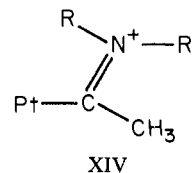


XIII

not show any evidence for Pt<sup>+</sup>-(CH=CH<sub>2</sub>) interaction in either the infrared, Raman, or nmr spectrum.

**Ir Spectra.** All these cationic platinum carbene complexes show characteristic absorption<sup>7</sup> bands of the ligands (PPhMe<sub>2</sub>

or AsMe<sub>3</sub>) and the anion PF<sub>6</sub><sup>-</sup>. For I and III, a strong, polarizable Raman band at *ca.* 520 cm<sup>-1</sup> is assigned to ν<sub>str</sub>(Pt-C) for the methylplatinum group. This low value of ν<sub>str</sub>(Pt-C) is indicative of the high trans influence<sup>22</sup> of the alkoxy- and aminocarbene ligands. We assign an ir band at *ca.* 1300 cm<sup>-1</sup> to ν<sub>str</sub>(C-O) of the alkoxy-carbene ligand in I and VI and a band at *ca.* 1590 cm<sup>-1</sup> to ν<sub>str</sub>(C-N) for the aminocarbene ligand in III and V. The high value of ν<sub>str</sub>(C-N) is consistent with the double-bond character of the carbene carbon-nitrogen bond and the extensive delocalization of positive charge from platinum to nitrogen as in XIV. Neither



ν<sub>str</sub>(C-O) nor ν<sub>str</sub>(C-N) appears to be sensitive to the nature of the trans ligand X, where X = CH<sub>3</sub>, Cl, and I. No band assignable to ν<sub>str</sub>(Pt-C) for the carbene moiety was observed, presumably because there is extensive coupling with other vibrational modes of the carbene ligand.

### Conclusions

I and III do not act as carbene precursors under mild conditions. Reactions of I and III occur at platinum or at the α-alkoxy carbon; in all cases the platinum-carbene bond is retained. Several differences in the reactions of methylplatinum and chloroplatinum complexes I and III are noted; these differences reflect the electron-releasing ability CH<sub>3</sub> > Cl<sup>-</sup>. The electron deficiency of the carbene carbon is extensively delocalized over the adjacent oxygen and nitrogen atoms in I and III, respectively.

### Experimental Section

General methods and the preparation of I have been described previously.<sup>7</sup>

**Reactions with Amines.** In a typical preparation, I (L = PPhMe<sub>2</sub>) (0.15 g, 0.22 mmol) was dissolved in dichloromethane (5 ml), and dimethylamine was bubbled through the solution for 1 min at room temperature. Solvent was removed *in vacuo* to give a pale yellow oil, which was dissolved in 2 ml of dichloromethane and chromatographed through a Florisil column (0.5 cm × 1 cm) with dichloromethane. Concentration of the eluted solution and addition of ether gave 18 as white crystals; yield 0.13 g, 0.18 mmol, 82%. Similarly, the reactions of I (L = PPhMe<sub>2</sub> or AsMe<sub>3</sub>) with NH<sub>3</sub>, H<sub>2</sub>NMe, H<sub>2</sub>NEt, H<sub>2</sub>N-*i*-Pr, and allylamine were carried out. Characterization data for all products are given in Table I.

**Reaction with *t*-BuNH<sub>2</sub>.** I (L = PPhMe<sub>2</sub>) (0.07 g, 0.1 mmol) was dissolved in dichloromethane (0.25 ml) in an nmr tube. *t*-BuNH<sub>2</sub> (10 μl, >1 mmolar equiv) was added. The nmr spectrum showed the methoxy protons of the methylmethoxy carbene ligand. The solution darkened with time, but even after 48 hr, the presence of the methoxycarbene ligand was clearly evident in the nmr spectrum. Slow decomposition occurred by elimination of the methylplatinum group as methane, while I (L = AsMe<sub>3</sub>) showed rapid elimination of the methylplatinum group. No platinum-containing product was isolated from these mixtures. Similar results were obtained using Et<sub>2</sub>NH, PhNHNH<sub>2</sub>, or (CH<sub>3</sub>)<sub>2</sub>NNH<sub>2</sub>.

**Reaction of VI (L = PPhMe<sub>2</sub>) with HNMe<sub>2</sub>.** VI (L = PPhMe<sub>2</sub>) (0.15 g, 0.21 mmol) was dissolved in dichloromethane (5 ml), and HNMe<sub>2</sub> was bubbled into the solution. Initially a fine white precipitate formed which redissolved with the addition of more amine. The solution was evaporated to dryness *in vacuo* to give a sticky solid. Ether (3 ml) was added, and the ether-soluble portion collected and crystallized by slow evaporation in the air. This gave white crystalline *trans*-PtCl(COCH<sub>3</sub>)(PPhMe<sub>2</sub>)<sub>2</sub> (0.1 g, 0.18 mmol, 86%).

Similar reactions occurred with NH<sub>3</sub> and NEt<sub>3</sub>. In the reaction with pyridine, the C<sub>5</sub>H<sub>5</sub>N<sup>+</sup>CH<sub>3</sub>PF<sub>6</sub><sup>-</sup> salt which formed was isolated and analyzed.

**Reaction of VIII with N(CH<sub>3</sub>)<sub>3</sub>.** VIII (0.18 g, 0.25 mmol) was dissolved in dichloromethane (3 ml), and N(CH<sub>3</sub>)<sub>3</sub> gas was bubbled

for 5 min at room temperature. A small amount of white precipitate immediately appeared, and after the mixture had stood overnight, large amounts of white crystals had deposited. These were extracted with acetone; the acetone-insoluble residue was dissolved in methanol-water and was not examined further. The pale pink acetone extract on evaporation gave pale pink solids which were insoluble in methanol and showed characteristic infrared absorption bands due to C=O and PF<sub>6</sub><sup>-</sup>. The solids were dissolved in the minimum amount of acetone, treated with active carbon, and then chromatographed through a short Florisil column. Evaporation of the eluted solution gave very pale pink crystals, IX: yield 0.13 g, 0.16 mmol, 64%; mp 125–127° dec. *Anal.* Calcd for C<sub>23</sub>H<sub>37</sub>ONClF<sub>6</sub>P<sub>2</sub>Pt: C, 35.37; H, 4.78, N, 1.79. Found: C, 34.35; H, 4.85; N, 1.86. The nmr spectrum showed the phosphine methyl resonances at  $\delta$  1.81,  $J(\text{PtH}) = 35.0$  Hz, and  $2^+J(\text{PH}) = 8.0$  Hz, and the ammonium methyl resonances at  $\delta$  3.09. The infrared spectrum showed  $\nu_{\text{C=O}}$  at 1630 cm<sup>-1</sup> (vs) and the characteristic bands of PF<sub>6</sub><sup>-</sup>.

**Reaction of I (L = PPnMe<sub>2</sub>) and VI (L = PPhMe<sub>2</sub>) with Halide Ions.** (i) I (L = PPhMe<sub>2</sub>) (0.2 g, 0.29 mmol) was dissolved in acetone (15 ml); LiCl (1 molar equiv) was added and the solution stirred magnetically for 1 hr. Solvent was then removed under reduced pressure to give an off-white solid, which contained no benzene-soluble portion. Starting material was recovered in 90% yield on extraction with dichloromethane. Similarly, no reaction occurred with NaI.

(ii) VI (L = PPhMe<sub>2</sub>) (0.2, 0.29 mmol) was dissolved in acetone (15 ml) and LiCl was added. The solution turned pale yellow, and removal of solvent under vacuum gave a cream-colored solid, from which 0.13 g (0.23 mmol, 79%) of *trans*-PtCl(COCH<sub>3</sub>)(PPhMe<sub>2</sub>)<sub>2</sub> was obtained by extraction with benzene. CH<sub>3</sub>Cl which was contained in the solvent distillate was identified spectroscopically.

(iii) VIII (0.25 g, 0.35 mmol) was treated similarly with NaI (2 molar equiv) to give a yellow solution and a fine white precipitate (NaCl). The solution was evaporated to dryness and extracted with dichloromethane (10 ml). The dichloromethane solution was reduced in volume to ca. 5 ml and ether was added. The yellow crystalline precipitate was collected by filtration, washed with ether, and dried *in vacuo*, mp 215–218°. PtI<sub>2</sub>(COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)(PPhMe<sub>2</sub>)<sub>2</sub>, X, was characterized as follows. *Anal.* Calcd for C<sub>20</sub>H<sub>28</sub>OI<sub>2</sub>P<sub>2</sub>Pt: C, 30.17; H, 3.52; I, 31.94. Found: C, 30.13; H, 3.48; I, 31.58. A sharp infrared absorption at 1725 cm<sup>-1</sup> was indicative of PtC(=O)R group. The nmr spectrum showed overlapping sets of triplets for the phosphine methyl resonances with coupling to <sup>195</sup>Pt of ~20 Hz. This is characteristic of a Pt(IV) species with trans phosphines and without a plane of symmetry containing the P<sub>2</sub>Pt axis:  $\delta$  (PMe) 2.55,  $J(\text{PtH}) = 20.0$  Hz,  $2^+J(\text{PH}) = 8.0$  Hz;  $\delta$  (PMe') 2.30,  $J(\text{PtH}) = 24.0$  Hz,  $2^+J(\text{PH}) = 8.0$  Hz. The low solubility of this compound precluded any definite assignment for the methylene protons in the ring; <sup>195</sup>Pt, <sup>31</sup>P, and H couplings further complicate these resonances.

In the mass spectrum, the molecular ion of X was not observed although the species formed by loss of COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> was readily apparent in the spectrum.

**Reactions with Iodomethane. Formation of XII.** V (0.15 g, 0.22 mmol) was dissolved in dichloromethane (1 ml) in a 5-ml flask. CH<sub>3</sub>I (1 ml) was added and the solution set aside. After 24 hr white crystals formed. Ether (1 ml) was then added to induce further crystallization. The stoppered flask was placed in a refrigerator for 12 hr; then the crystals were filtered, washed with ether, and dried *in vacuo*, mp 158–160°. *Anal.* Calcd for C<sub>22</sub>H<sub>34</sub>O<sub>2</sub>F<sub>6</sub>I<sub>2</sub>P<sub>2</sub>Pt: C, 31.32; H, 4.06; I, 15.06. Found: C, 31.41; H, 4.04; I, 14.93. The following nmr parameters confirm the geometry of the platinum cation XII: phosphine methyls (P(Me)(Me')Ph):  $\delta$  (PMe) 2.34,  $J(\text{PtH}) = 20.2$  Hz,  $2^+J(\text{PH}) = 8.0$  Hz;  $\delta$  (PMe') 1.88,  $J(\text{PtH}) = 21.2$  Hz,  $2^+J(\text{PH}) = 7.8$  Hz; platinum methyls, *Pt*-CH<sub>3</sub> trans to I:  $\delta$  (*Pt*-CH<sub>3</sub>) 1.34,  $J(\text{PtH}) = 64.3$  Hz,  $J(\text{PH}) = 5.5$  Hz; *Pt*-CH<sub>3</sub> trans to carbene:  $\delta$  (*Pt*-CH<sub>3</sub>) = 0.70,  $J(\text{PtH}) = 47.2$  Hz,  $J(\text{PH}) = 7.4$  Hz; 2-oxacyclopentylidene



$\delta(\text{CH}_2^\alpha)$  4.86,  $J(\text{H}^\alpha\text{H}^\beta) = 8.0$  Hz,  $J(\text{PtH}) = 6.0$  Hz;  $\delta(\text{CH}_2^\beta)$  0.90,  $J(\text{H}^\alpha\text{H}^\beta\text{H}^\gamma) = 8.0$ ;  $\delta(\text{CH}_2^\gamma)$  2.24,  $J(\text{H}^\beta\text{H}^\gamma) = 8.0$  Hz,  $J(\text{PtH}) \approx 6$  Hz.

**Reaction of I with CH<sub>3</sub>I.** I (L = AsMe<sub>3</sub>) (0.1 g, 0.14 mmol) was treated with CH<sub>3</sub>I (1 ml) similarly; after 6 hr white crystals started

to form. Ether (1 ml) was added and the flask was placed in a refrigerator for 12 hr. The crystals were identified as *trans*-[PtI{C(OCH<sub>3</sub>)CH<sub>3</sub>}(AsMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup> by analysis and by nmr and ir spectroscopy.

**Reactions with HCl.** (i) I (L = AsMe<sub>3</sub>) (0.1 mmol) was dissolved in dichloromethane (0.25 ml) in an nmr tube. Anhydrous HCl (0.1 mmol) was condensed into the tube, which was then sealed. As soon as the sample had warmed to probe temperature, the nmr spectrum was recorded. This showed complete loss of the platinum methyl resonance and the formation of methane. The tube was opened and the sample crystallized by the addition of ether to the condensed dichloromethane eluate obtained after passage through a Florisil column. This gave VI (L = AsMe<sub>3</sub>) as a white crystalline solid.

(ii) Compound 18 (see Table I) (0.28 g) was dissolved in dichloromethane (3 ml), and 2 ml of CH<sub>3</sub>OH was added. To this magnetically stirred solution acetyl chloride (30  $\mu$ l, 1 molar equiv) was added. The solution was stirred for 5 min and then the solvent was evaporated *in vacuo*. The white residue dissolved in dichloromethane was chromatographed on a Florisil column with dichloromethane. Condensation of the eluted solution and addition of ether gave white crystals of 22.

The above procedures are applicable to all methylplatinum carbene complexes I and III.

(iii) As in (i) above, VI (L = PPhMe<sub>2</sub>) was allowed to react with anhydrous HCl (1 molar equiv) in dichloromethane. The methoxy resonance was slowly eliminated and a new resonance corresponding to CH<sub>3</sub>Cl appeared. The PPhMe<sub>2</sub> methyl resonance of the new product consisted of 1:2:1 triplets with satellites due to coupling to <sup>195</sup>Pt. When the methoxy resonance had completely disappeared (4 days), the tube was opened and the solvent and other volatile products were distilled into another nmr tube under vacuum. The nmr spectrum of the mixture showed CH<sub>3</sub>Cl as the only organic product. The platinum-containing residue was extracted with dichloromethane causing considerable decomposition with etching of the walls of the nmr tube. All attempts to isolate the platinum-containing product failed. Finally the orange tar residue was extracted with benzene and passed through a short Florisil column. Evaporation of the benzene extract to dryness gave a sticky yellow solid. The ir spectrum of the product showed a sharp band at 1630 cm<sup>-1</sup> and the absence of PF<sub>6</sub><sup>-</sup>. The nmr showed *trans* PMePh ligands and features identical with those for *trans*-PtCl(COCH<sub>3</sub>)(PPhMe<sub>2</sub>)<sub>2</sub>.

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## Electronic Structure and Spectra of Square-Planar Cyano and Cyanoamine Complexes of Platinum(II)<sup>1</sup>

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Solution electronic absorption and magnetic circular dichroism (MCD) spectral measurements are reported for  $\text{Pt}(\text{CN})_4^{2-}$ , *cis*- and *trans*- $\text{Pt}(\text{NH}_3)_2(\text{CN})_2$ ,  $\text{Pt}(\text{en})(\text{CN})_2$ , and  $\text{Pt}(l\text{-pn})(\text{CN})_2$ , together with some absorption spectral data for the  $\text{Pt}(\text{dien})(\text{CN})^+$  ion. In addition, some low-temperature (26°K) absorption data are given for  $\text{Pt}(\text{CN})_4^{2-}$ , *trans*- $\text{Pt}(\text{NH}_3)_2(\text{CN})_2$ , and  $\text{Pt}(\text{en})(\text{CN})_2$  in poly(vinyl alcohol) (PVA) solid films prepared from aqueous PVA solutions. The cyanoamine complexes exhibit intense absorptions between 35 and 54 kK, similar to those observed for  $\text{Pt}(\text{CN})_4^{2-}$ . These transitions are ascribed to metal  $\rightarrow$  ligand ( $M \rightarrow L$ ) charge transfer from occupied metal d orbitals to the lowest energy  $\pi^* \text{CN}^-$  orbital. In addition, the *trans*- $\text{Pt}(\text{NH}_3)_2(\text{CN})_2$  and  $\text{Pt}(\text{dien})(\text{CN})^+$  complexes show an allowed  $d \rightarrow p$  transition above 50 kK. The  $M \rightarrow L$  spectra are interpreted by means of a model which involves a single  $\pi^* \text{CN}^-$  acceptor orbital and which includes metal spin-orbit coupling in the  $M \rightarrow L$  excited states. Some spin-orbit calculations are presented for  $\text{Pt}(\text{CN})_4^{2-}$ , *trans*- $\text{Pt}(\text{NH}_3)_2(\text{CN})_2$ , and  $\text{Pt}(\text{en})(\text{CN})_2$ . Spectral assignments are given for each complex and the results are discussed in terms of d-orbital participation in bonding and in terms of the donor-acceptor character of the  $\text{CN}^-$  ligand.

### Introduction

During the last 1.5 decades, there have been a number of investigations aimed at characterizing the electronic structure of the  $\text{Pt}(\text{CN})_4^{2-}$  ion and interpreting its electronic absorption and magnetic circular dichroism (MCD) spectra.<sup>2-9</sup> In spite of this effort, a model free of disagreement has failed to emerge, and the ordering of excited states accessible to optical transitions remains controversial. This is unfortunate because  $\text{Pt}(\text{CN})_4^{2-}$  is a prototypical planar cyano complex and might easily serve as a model for other planar complexes which contain  $\pi$ -acid ligands and which exhibit metal-ligand ( $M \rightarrow L$ ) bonding and charge-transfer spectra.

There have been two main points of disagreement in describing the electronic structure of the  $\text{Pt}(\text{CN})_4^{2-}$  ion: (1) the ordering of the occupied metal d molecular orbitals and their participation in bonding and (2) the extent to which the several empty, low-lying  $\pi^* \text{CN}^-$  molecular orbitals are involved in electronic transitions. For example, the three lowest energy absorption bands at 35.7, 39.1, and 41.3 kK in the solution electronic spectra were interpreted by Gray and Ballhausen<sup>3</sup> as  $M \rightarrow L$  transitions from the occupied d orbitals to a single  $\pi^* \text{CN}^-$  orbital,  $a_{2u}(\pi^*)$ . Their ordering of excited states implied the ordering of the occupied d levels as  $d_{xy} > d_{xz}d_{yz} > d_{z^2}$ , assuming negligible electronic repulsion differences. Moncuit<sup>4</sup> interpreted the electronic spectra, including an intense band at 46.3 kK in terms of  $M \rightarrow L$  transitions to three  $\pi^* \text{CN}^-$  orbitals,  $a_{2u}(\pi^*)$ ,  $e_u(\pi^*)$ , and  $b_{2u}(\pi^*)$ , and proposed the ordering  $d_{xy} > d_{z^2} > d_{xz}d_{yz}$ . Mason and Gray<sup>5</sup> assigned the low-temperature (77°K) EPA solution spectra using two  $\pi^*$  cyanide orbitals,  $a_{2u}(\pi^*)$  and  $e_u(\pi^*)$ , and the original ordering of the d levels of Gray and Ballhausen. Piepho, Schatz, and McCaffery<sup>6</sup> analyzed the MCD spectra of the

$\text{Pt}(\text{CN})_4^{2-}$  ion and offered an interpretation involving  $M \rightarrow L$  transitions to the  $a_{2u}(\pi^*)$  level but included spin-orbit coupling in excited states. As a consequence of spin-orbit coupling, formally spin-forbidden transitions were assumed to gain considerable intensity. The implied ordering of the d levels was  $d_{z^2} \sim d_{xz}d_{yz} > d_{xy}$ . Still other spectral interpretations and d-level orderings have been proposed<sup>8</sup> from studies on solid salts of  $\text{Pt}(\text{CN})_4^{2-}$ , but it seems clear that strong, specific solid-state perturbations are present in these cases because of features of the crystals which allow close platinum-platinum contact.<sup>9,10</sup>

In order to learn more about the bonding in planar cyano complexes and to provide an experimental basis for further discussion of the  $\text{Pt}(\text{CN})_4^{2-}$  problem, we have investigated a number of related cyanoamine complexes of platinum(II) and have compared them with  $\text{Pt}(\text{CN})_4^{2-}$ . Solution electronic absorption and MCD spectra were obtained for *cis*- and *trans*- $\text{Pt}(\text{NH}_3)_2(\text{CN})_2$ ,  $\text{Pt}(\text{en})(\text{CN})_2$ , and  $\text{Pt}(l\text{-pn})(\text{CN})_2$ ; some absorption spectra were also obtained for the  $\text{Pt}(\text{dien})(\text{CN})^+$  ion. In addition, some low-temperature (26°K) measurements were also made for  $\text{Pt}(\text{CN})_4^{2-}$ , *trans*- $\text{Pt}(\text{NH}_3)_2(\text{CN})_2$ , and  $\text{Pt}(\text{en})(\text{CN})_2$  in solid poly(vinyl alcohol) (PVA) films prepared from aqueous PVA solutions. These spectra were interpreted using the model developed by Piepho, *et al.*,<sup>6</sup> for  $\text{Pt}(\text{CN})_4^{2-}$ , which includes spin-orbit coupling in excited states and involves only a single  $\pi^* \text{CN}^-$  level for excited configurations.

### Experimental Section

**Preparation of Compounds.** The starting material for the platinum complexes was  $\text{H}_2\text{PtCl}_4$ , a solution of which was prepared from platinum sponge.<sup>11</sup> Potassium tetracyanoplatinate(II),  $\text{K}_2[\text{Pt}(\text{CN})_4]$ , and the tetra-*n*-butylammonium salt were prepared according to the