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## Cationic Organometallic Complexes with Unsaturated Systems.

## I. Methylplatinum(II)-Nitrile and -Imino Ether Complexes

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Cationic methylplatinum(II)-nitrile complexes of the type  $trans\text{-PtCH}_3\text{L}_2(\text{NCR})^+\text{X}^-$  have been prepared by the reaction of  $trans\text{-PtCH}_3\text{ClL}_2$ , where L = dimethylphenylphosphine or trimethylarsine, with an aryl nitrile and AgX, where  $\text{X}^- = \text{BF}_4^-, \text{PF}_6^-$ . Use of pentafluorobenzonitrile and 2,3,5,6-tetrafluoroterephthalonitrile in alcohol has led to the preparation of a series of imino ether complexes. A mechanism for imino ether formation, involving nucleophilic attack by an alcohol at a coordinated nitrile, is proposed and the course of the reaction is shown to be dependent not only on the alcohol but also on the size of the anion used.

## Introduction

There has recently been much interest in the isolation and chemical reactivity of complexes containing coordinated unsaturated systems.

We have previously<sup>1,2</sup> examined the reactions of tetrafluoroethylene and perfluorobut-2-yne with complexes of the type  $trans\text{-PtCH}_3\text{XL}_2$  (I) and  $cis\text{-Pt}(\text{CH}_3)_2\text{L}_2$  (X = halogen, L = tertiary phosphine or arsine) and found that insertion into the methylplatinum bond can occur, by rearrangement of intermediate  $\pi$  complexes.

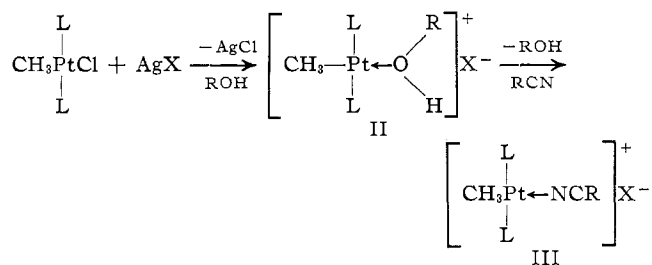
Nucleophilic attack by alcohols and amines at coordinated isocyanide complexes<sup>3-7</sup> has also led to a variety of neutral palladium(II)- and platinum(II)-carbene complexes. Reactions involving monoalkyl- and monoaryl-substituted acetylenes,  $\text{RC}\equiv\text{CH}$ , in methanol and ethanol with I and silver hexafluorophosphate led<sup>8,9</sup> to the formation of methoxy- and ethoxycarbene complexes  $[\text{PtCH}_3\text{L}_2\{\text{ROC}(\text{CH}_2\text{R}')\}]^+\text{PF}_6^-$ . Similar reactions involving some types of disubstituted acetylenes led<sup>10</sup> to the preparation of cationic methylplatinum(II)-acetylene complexes.

We have extended these investigations to other unsaturated systems such as isocyanides<sup>11</sup> and nitriles<sup>12</sup> and in this paper discuss the preparation of cationic methylplatinum(II)-nitrile complexes and subsequent nucleophilic attack by alcohols leading to the formation of imino ether complexes.

## Results and Discussion

**Preparation and Spectroscopic Data for Mononitrile Complexes.**—The chloride in  $trans\text{-PtCH}_3\text{ClL}_2$  (L =  $\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)$  or  $\text{As}(\text{CH}_3)_3$ ) is labile due to the strong trans influence of the methyl group, and the addition of a silver salt AgX ( $\text{X}^- = \text{BF}_4^-, \text{PF}_6^-, \text{SbF}_6^-, \text{NO}_3^-$ ) is known<sup>13</sup> to give an immediate precipitate of silver chlo-

ride with the formation of an intermediate alcohol complex (II). The silver chloride can be removed by centrifugation and the alcohol displaced by a nitrile (III) to give  $trans\text{-}[\text{PtCH}_3\text{L}_2(\text{N}\equiv\text{CR})]^+\text{X}^-$ . The compounds so obtained are described in Table I.



In general the complexes were difficult to crystallize, possibly due to their fairly high solubility in polar solvents and the weak coordinating power of the nitrile. However, the solubility could be decreased by changing the anion in the order  $\text{BF}_4^- > \text{NO}_3^- > \text{SbF}_6^- > \text{PF}_6^- \gg \text{B}(\text{C}_6\text{H}_5)_4^-$ . Care must be taken, however, when using sodium tetraphenylborate since it acts as a good phenylating agent when a weakly coordinating ligand is present.<sup>13</sup> In several instances, when sodium tetraphenylborate was added to a solution of  $trans\text{-}[\text{PtCH}_3\text{L}_2(\text{NCR})]^+\text{X}^-$  ( $\text{X}^- = \text{BF}_4^-, \text{PF}_6^-$ ) in methanol, white crystalline  $cis\text{-Pt}(\text{C}_6\text{H}_5)_2\text{L}_2$  was obtained. The reaction probably proceeds by way of nucleophilic attack by a phenyl ring to give an intermediate  $\pi$ -bonded complex<sup>14</sup> which then gives directly the insoluble diphenyl complex.

The CN triple bond possesses two sites for coordination, namely, the nitrogen lone pair and the  $\pi$  electrons. Nitriles are usually  $\sigma$  bonded through nitrogen,<sup>15</sup> this being accompanied by an increase of *ca.* 70–110  $\text{cm}^{-1}$  in  $\nu(\text{C}\equiv\text{N})$ . However, examples of  $\pi$  bonding are known. In the series  $\text{M}(\text{CO})_3(\text{NC}(\text{CH}_2)_n\text{CN})\text{X}$ <sup>16,17</sup> (M = Re, Mn;  $n = 1-3$ ) the dinitrile acts as a chelating ligand and because of the short carbon chain the nitrile groups are forced to  $\pi$  bond, this being shown spectroscopically by a decrease in  $\nu(\text{C}\equiv\text{N})$  of about 150–200  $\text{cm}^{-1}$ . Thus it was of interest to examine a variety of aromatic nitrile complexes to determine how the aryl group would affect the bonding. On coordination the

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TABLE I  
 ANALYTICAL AND PHYSICAL DATA FOR CATIONIC METHYLPLATINUM(II)-NITRILE AND -IMINO ETHER COMPLEXES

Compound <sup>a</sup>	Analyses, %				Decomp temp, <sup>b</sup> °C	Recrystn solvents	Color
	Carbon		Hydrogen				
	Calcd	Found	Calcd	Found			
[PtCH <sub>3</sub> A <sub>2</sub> (NCC <sub>6</sub> F <sub>6</sub> )](PF <sub>6</sub> )	21.37	21.47	2.72	2.60	156-176	CHCl <sub>3</sub> - <i>n</i> -C <sub>6</sub> H <sub>12</sub>	White
[PtCH <sub>3</sub> Q <sub>2</sub> (NCC <sub>6</sub> F <sub>6</sub> )](BF <sub>4</sub> )	37.62	37.54	3.28	3.43	>115	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	White
[PtCH <sub>3</sub> A <sub>2</sub> ( <i>o</i> -NCC <sub>6</sub> F <sub>2</sub> H <sub>3</sub> )](PF <sub>6</sub> )	22.59	22.73	3.25	3.16	140-148	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	White
[PtCH <sub>3</sub> A <sub>2</sub> ( <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )] [B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ]	52.83	52.53	5.47	5.32	90-93	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	White
[PtCH <sub>3</sub> Q <sub>2</sub> ( <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )] [B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ]	63.78	63.31	5.69	5.57	118-120	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	White
[PtCH <sub>3</sub> Q <sub>2</sub> ( <i>m</i> -NCC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )] [B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ]	63.78	63.10	5.69	5.49	95-110	CH <sub>3</sub> COCH <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	White
[PtCH <sub>3</sub> Q <sub>2</sub> ( <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )] (PF <sub>6</sub> )	39.27	39.36	4.23	4.13	107-112	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	White
[PtCH <sub>3</sub> Q <sub>2</sub> ( <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> )] (PF <sub>6</sub> )	36.98	36.43	3.75	3.48	121-125	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	Pale yellow
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>5</sub> )] (BF <sub>4</sub> )	37.59	37.93	3.66	3.67	129-132	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	White
[PtCH <sub>3</sub> Q <sub>2</sub> (NCC <sub>6</sub> H <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	36.29	36.36	3.91	3.65	226-228	Hot CH <sub>3</sub> OH	White
[PtCH <sub>3</sub> Q <sub>2</sub> (NCC <sub>6</sub> H <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	39.58	39.73	4.27	4.32	205-207	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	White
[PtCH <sub>3</sub> A <sub>2</sub> (NCC <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> A <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	19.00	19.19	3.05	3.12	178-194	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	Yellow
[PtCH <sub>3</sub> Q <sub>2</sub> (NCC <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	34.50	34.42	3.45	3.45	178-186	CH <sub>2</sub> Cl <sub>2</sub> - <i>n</i> -C <sub>6</sub> H <sub>12</sub>	Yellow
[PtCH <sub>3</sub> Q <sub>2</sub> (NCC <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ](SbF <sub>6</sub> ) <sub>2</sub>	30.68	30.72	3.06	2.97	206-207	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	Yellow
[PtCH <sub>3</sub> Q <sub>2</sub> (NCC <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	37.46	37.22	3.74	3.68	>184	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	Yellow
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	34.52	34.35	3.64	3.00	100-102	CH <sub>2</sub> Cl <sub>2</sub> - <i>n</i> -C <sub>6</sub> H <sub>12</sub>	Yellow
[PtCH <sub>3</sub> A <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> A <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	19.40	19.08	3.27	3.27	181-185	CH <sub>2</sub> Cl <sub>2</sub> -C <sub>2</sub> H <sub>5</sub> OH	Yellow
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	37.95	37.80	4.05	4.03	196-199	Hot C <sub>2</sub> H <sub>5</sub> OH	White
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	38.42	38.46	4.15	4.07	129-133	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	Pale yellow
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(O <sub>2</sub> C <sub>6</sub> H <sub>7</sub> )C <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	37.99	38.03	4.11	4.02	>155	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	Pale yellow
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> C(OCH <sub>3</sub> )=NH)PtCH <sub>3</sub> Q <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	37.46	37.22	3.74	3.68	207-208	Hot CH <sub>3</sub> OH	White
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> C(OCH <sub>3</sub> )=NH)PtCH <sub>3</sub> Q <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	39.80	39.64	4.40	4.37	134-136	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	White

<sup>a</sup> Q = P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>); A = As(CH<sub>3</sub>)<sub>3</sub>. <sup>b</sup> Melting points are corrected.

 TABLE II  
 RAMAN DATA<sup>a</sup> (CM<sup>-1</sup>) FOR CATIONIC METHYLPLATINUM(II)-NITRILE AND -IMINO ETHER COMPLEXES

Compound	$\nu(\text{C}\equiv\text{N})$	$\Delta\nu(\text{C}\equiv\text{N})^b$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{H})$	$\nu(\text{PtC}-\text{H})$
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>5</sub> )] (BF <sub>4</sub> )	...	...	1667	3251	551
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> C(OCH <sub>3</sub> )=NH)PtCH <sub>3</sub> Q <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	...	...	1671	3350, 3250	576
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> C(OCH <sub>3</sub> )=NH)PtCH <sub>3</sub> Q <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	...	...	1675	3263	558
[PtCH <sub>3</sub> Q <sub>2</sub> ( $\pi$ -NCC <sub>6</sub> F <sub>4</sub> C(OCH <sub>3</sub> )=NH)PtCH <sub>3</sub> Q <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	2141	-113	1667	3271	554
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	2282	28	1663	3340	551
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	2283	29	1668	3260	563
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	2281	27	1663	3315	552
[PtCH <sub>3</sub> A <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> A <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	2274	20	1662	3311	554
[PtCH <sub>3</sub> Q <sub>2</sub> (NCC <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	2292	38	...	...	556
[PtCH <sub>3</sub> A <sub>2</sub> (NCC <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> A <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	2272	18	...	...	554
[PtCH <sub>3</sub> Q <sub>2</sub> (NCC <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	2283	29	...	...	551
[PtCH <sub>3</sub> Q <sub>2</sub> (NCC <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ](SbF <sub>6</sub> ) <sub>2</sub>	2291	37	...	...	554
[PtCH <sub>3</sub> Q <sub>2</sub> (NCC <sub>6</sub> H <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	2264	28	...	...	567
[PtCH <sub>3</sub> Q <sub>2</sub> (NCC <sub>6</sub> H <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	2265	29	...	...	566
[PtCH <sub>3</sub> Q <sub>2</sub> (NCC <sub>6</sub> F <sub>5</sub> )] (BF <sub>4</sub> )	2276	27	...	...	549
[PtCH <sub>3</sub> A <sub>2</sub> (NCC <sub>6</sub> F <sub>5</sub> )] (PF <sub>6</sub> )	2274	29	...	...	556
[PtCH <sub>3</sub> Q <sub>2</sub> ( <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )] (PF <sub>6</sub> )	2270	57	...	...	572
[PtCH <sub>3</sub> A <sub>2</sub> ( <i>o</i> -NCC <sub>6</sub> F <sub>2</sub> H <sub>3</sub> )] (PF <sub>6</sub> )	2275	26	...	...	567
[PtCH <sub>3</sub> Q <sub>2</sub> ( <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )] [B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ]	2256	24	...	...	570
[PtCH <sub>3</sub> A <sub>2</sub> ( <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )] [B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ]	2254	22	...	...	570
[PtCH <sub>3</sub> Q <sub>2</sub> ( <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> )] (PF <sub>6</sub> )	2230	2	...	...	570
[PtCH <sub>3</sub> Q <sub>2</sub> ( <i>m</i> -NCC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )] (PF <sub>6</sub> )	2258	22	...	...	569

<sup>a</sup> Values are accurate to  $\pm 2$  cm<sup>-1</sup>. <sup>b</sup>  $\nu(\text{C}\equiv\text{N})(\text{complex}) - \nu(\text{C}\equiv\text{N})(\text{free ligand})$ .

intensity of the absorption due to  $\nu(\text{C}\equiv\text{N})$  is very weak and in some cases completely absent in the infrared, yet the band is very strong and sharp in the Raman spectra.

The Raman data are listed in Table II. Positive values for  $\Delta\nu(\text{C}\equiv\text{N})$  indicate that the nitrile is  $\sigma$  bonded through nitrogen, the increase in  $\nu(\text{C}\equiv\text{N})$  being primarily due to an increase in the CN force constant upon coordination.<sup>18</sup> The platinum-methyl stretching vibration appears as a strong and polarizable<sup>10</sup> (0.75*P*) band in the Raman spectrum in the region 575-545 cm<sup>-1</sup> yet is weak in the infrared.

The methyl groups in *trans*-[PtCH<sub>3</sub>L<sub>2</sub>(NCR)]<sup>+</sup>X<sup>-</sup> show the expected patterns in the proton nmr spectra (data given in Table III). The methyl groups in L, where L = P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>), give a 1:2:1 triplet due to strong phosphorus-phosphorus coupling<sup>19</sup> between the two *trans* <sup>31</sup>P nuclei, with triplet satellites of one-fourth intensity due to coupling with <sup>195</sup>Pt (*I* = 1/2, natural

abundance 33%). The platinum-methyl group gives a triplet due to coupling with two equivalent <sup>31</sup>P nuclei and platinum satellites of one-fourth intensity. When L = As(CH<sub>3</sub>)<sub>3</sub>, the methyl absorptions appear as singlets with platinum satellites.

The coupling constant *J*(Pt-C-H) (Table III) has been used as a measure of the relative  $\sigma$ -donor properties for a ligand *trans* to the methyl group, to establish a *trans*-influence series; *i.e.*, the larger the coupling constant, the weaker the  $\sigma$ -donor property of the ligand. The relatively large coupling constant of  $\sim 80$  Hz for nitrile *trans* to methyl indicates that the nitrile is in fact a fairly weak  $\sigma$  donor. This is also reflected by the *high* frequency of the platinum-methyl stretching vibration at  $\sim 560$  cm<sup>-1</sup>. These values may be compared with those of a strong  $\sigma$  donor, *e.g.*, carbene complexes,<sup>9</sup> with *J*(Pt-C-H)  $\approx 48$  Hz and  $\nu(\text{Pt}-\text{CH}_3) \approx 518$  cm<sup>-1</sup> (although this absorption is almost certainly not due to a pure Pt-CH<sub>3</sub> mode).

There is a marked decrease in  $\Delta\nu(\text{C}\equiv\text{N})$  as the Ham-

(18) K. F. Purcell and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 919 (1966).

(19) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

TABLE III  
<sup>1</sup>H NMR<sup>a</sup> DATA FOR CATIONIC METHYLPLATINUM(II)-NITRILE AND -IMINO ETHER COMPLEXES

Compound <sup>c</sup>	Phosphine or arsine methyls			—Platinum methyls—			Other resonances
	$\delta(\text{CH}_3)$	$J(\text{P-H})^b$	$J(\text{Pt-H})$	$\delta(\text{CH}_3)$	$J(\text{P-H})$	$J(\text{Pt-H})$	
[PtCH <sub>3</sub> Q <sub>2</sub> ( <i>m</i> -NCC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )] [B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ]	-1.86	7.4	32.8	-0.61	7.8	80.4	$\delta(\text{CH}_3)$ -2.63
[PtCH <sub>3</sub> As <sub>2</sub> (NCC <sub>6</sub> F <sub>5</sub> )] (PF <sub>6</sub> )	-1.58	...	23.4	-0.61	...	79.7	
[PtCH <sub>3</sub> Q <sub>2</sub> (NCC <sub>6</sub> F <sub>5</sub> )] (BF <sub>4</sub> )	-1.92	7.1	30.0	-0.51	8.0	80.4	
[PtCH <sub>3</sub> As <sub>2</sub> ( <i>o</i> -NCC <sub>6</sub> F <sub>5</sub> H <sub>3</sub> )] (PF <sub>6</sub> )	-1.60	...	23.6	-0.53	...	77.6	
[PtCH <sub>3</sub> As <sub>2</sub> ( <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )] [B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ]	-1.28	...	23.6	-0.52	...	76.0	$\delta(\text{CH}_3)$ -2.28
[PtCH <sub>3</sub> Q <sub>2</sub> ( <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )] [B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ]	-1.86	7.0	32.2	-0.61	7.8	80.2	$\delta(\text{CH}_3)$ -2.46
[PtCH <sub>3</sub> Q <sub>2</sub> ( <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )] (PF <sub>6</sub> )	-1.89	7.0	32.0	-0.46	7.7	80.0	$\delta(\text{OCH}_3)$ -3.86
[PtCH <sub>3</sub> Q <sub>2</sub> ( <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> )] (PF <sub>6</sub> )	-1.92	7.2	32.6	-0.55	7.8	80.4	
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>5</sub> )] (BF <sub>4</sub> )	-1.75	6.8	30.6	-0.31	7.6	76.4	$\delta(\text{NH})$ -9.18, $\delta(\text{OCH}_3)$ -3.94
[PtCH <sub>3</sub> Q <sub>2</sub> ( <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ] (PF <sub>6</sub> ) <sub>2</sub> <sup>d</sup>							
[PtCH <sub>3</sub> Q <sub>2</sub> ( <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ] (BF <sub>4</sub> ) <sub>2</sub>	-1.89	7.2	32.4	-0.55	7.8	80.4	
[PtCH <sub>3</sub> As <sub>2</sub> (NCC <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> As <sub>2</sub> ] (PF <sub>6</sub> ) <sub>2</sub>	-1.57	...	23.8	-0.61	...	80.8	
[PtCH <sub>3</sub> Q <sub>2</sub> (NCC <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ] (PF <sub>6</sub> ) <sub>2</sub>	-1.89	7.2	33.4	-0.48	7.9	80.4	
[PtCH <sub>3</sub> Q <sub>2</sub> (NCC <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ] (SbF <sub>6</sub> ) <sub>2</sub>	-1.92	7.0	31.5	-0.26	8.1	81.6	
[PtCH <sub>3</sub> Q <sub>2</sub> (NCC <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ] (BF <sub>4</sub> ) <sub>2</sub>	-1.94	7.3	31.2	-0.66	8.0	80.6	
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ] (PF <sub>6</sub> ) <sub>2</sub>	-1.91	7.2	31.2	-0.48	7.6	80.4	
	-1.76	7.2	31.2	-0.31	7.6	77.6	$\delta(\text{NH})$ -8.81, $\delta(\text{OCH}_3)$ -3.84
[PtCH <sub>3</sub> As <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ] (PF <sub>6</sub> ) <sub>2</sub>	-1.53	...	23.2	-0.56	...	80.0	$\delta(\text{NH})$ -9.05, $\delta(\text{OCH}_3)$ -4.14
	-1.38	...	20.0	-0.40	...	78.0	
[PtCH <sub>3</sub> Q <sub>2</sub> ( $\pi$ -NCC <sub>6</sub> F <sub>4</sub> C(OC <sub>2</sub> H <sub>5</sub> )=NH)PtCH <sub>3</sub> Q <sub>2</sub> ] (BF <sub>4</sub> ) <sub>2</sub>	-1.76	6.6	30.0	-0.27	7.6	75.4	$\delta(\text{NH})$ -9.04, $\delta(\text{OCH}_2)$ -4.13 $\delta(\text{CH}_3)$ -1.27, $J(\text{H-H})$ 7.2
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(OC <sub>2</sub> H <sub>5</sub> )C <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ] (BF <sub>4</sub> ) <sub>2</sub>	-1.92	7.0	30.4	-0.49	7.7	80.4	$\delta(\text{NH})$ -9.25, $\delta(\text{OCH}_2)$ -4.15 t $\delta(\text{CH}_3'')$ -0.94 t, $J(\text{H-H}')$ 7.0, $J(\text{H}''-\text{H}'')$ 7.1
	-1.77	7.0	30.8	-0.31	7.6	76.8	$\delta(\text{NH})$ -9.07
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(O <sub>2</sub> C <sub>2</sub> H <sub>5</sub> )C <sub>6</sub> F <sub>4</sub> CN)PtCH <sub>3</sub> Q <sub>2</sub> ] (BF <sub>4</sub> ) <sub>2</sub>	-1.78	6.8	30.4	-0.50	7.7	80.4	
	-1.78	6.8	30.4	-0.21	7.6	75.6	
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> C(OCH <sub>3</sub> )=NH)PtCH <sub>3</sub> Q <sub>2</sub> ] (BF <sub>4</sub> ) <sub>2</sub>	-1.77	7.0	30.8	-0.28	7.6	75.8	$\delta(\text{NH})$ -9.18, $\delta(\text{OCH}_3)$ -3.94
[PtCH <sub>3</sub> Q <sub>2</sub> (NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>4</sub> C(OCH <sub>3</sub> )=NH)PtCH <sub>3</sub> Q <sub>2</sub> ] (NO <sub>3</sub> ) <sub>2</sub>	-1.79	6.8	31.0	-0.25	7.7	76.8	$\delta(\text{NH})$ -9.13, $\delta(\text{OCH}_3)$ -3.84

<sup>a</sup> Chemical shifts ( $\delta$ ) in ppm relative to TMS using dichloromethane as internal standard. <sup>b</sup>  $^2J(\text{P-H}) + ^4J(\text{P-H})$  is quoted: R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964). <sup>c</sup> A = As(CH<sub>3</sub>)<sub>3</sub>, Q = P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>). <sup>d</sup> Insoluble.

met substituent constant ( $\rho$ ),<sup>20</sup> which may be used as a measure of the inductive effect of an aromatic substituent, increases (see Table IV) for cations of the type

TABLE IV

Substituent	$\Delta\nu(\text{C}\equiv\text{N})$ , cm <sup>-1</sup>	$\rho$	Substituent	$\Delta\nu(\text{C}\equiv\text{N})$ , cm <sup>-1</sup>	$\rho$
<i>p</i> -OCH <sub>3</sub>	57	-0.268	<i>m</i> -CH <sub>3</sub>	22	-0.069
<i>p</i> -CH <sub>3</sub>	24	-0.170	<i>p</i> -NO <sub>2</sub>	2	+0.778

PtCH<sub>3</sub>L<sub>2</sub>(NCC<sub>6</sub>H<sub>4</sub>X)<sup>+</sup>, where X is an aromatic substituent.

Thus, as the electron-withdrawing ability of the para substituent increases, so does the Hammett constant, yet the value for  $\Delta\nu(\text{C}\equiv\text{N})$  decreases. Consequently, drainage of electron density from the CN triple bond back into the aromatic  $\pi$  system as a result of an electronegative para substituent lowers the C $\equiv$ N  $\pi^*$ -antibonding orbitals and facilitates back-donation of platinum d electrons into these  $\pi^*$  orbitals. As a result, the C $\equiv$ N bond order is decreased and the Raman absorption occurs at a lower frequency, although  $\Delta\nu(\text{C}\equiv\text{N})$  is still positive. In contrast, in a series of complexes<sup>21,22</sup> of the type Ru(NH<sub>3</sub>)<sub>5</sub>(NCR)<sup>2+</sup>,  $\Delta\nu(\text{C}\equiv\text{N})$  is negative as a result of unusually strong back-donation into nitrile  $\pi^*$  orbitals. In the present case, also, there is essentially no change in  $J(\text{Pt}-\text{C}-\text{H})$  on varying the para substituent, indicating little effect on the  $\sigma$ -donor ability of the nitrile. On the other hand, a very strong electron-withdrawing group such as a perfluoronitrile might well change the relative energies of all the orbitals sufficiently to allow  $\pi$  bonding through the CN triple bond, although one cannot predict *a priori* whether end bonding or sideways bonding of the nitrile would be preferred.

(20) J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1962.

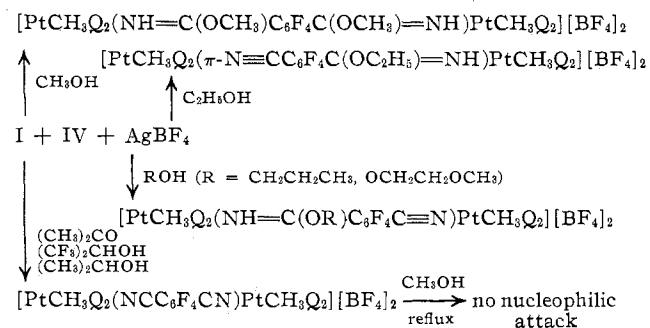
(21) R. E. Clarke and P. C. Ford, *Chem. Commun.*, 1109 (1968).

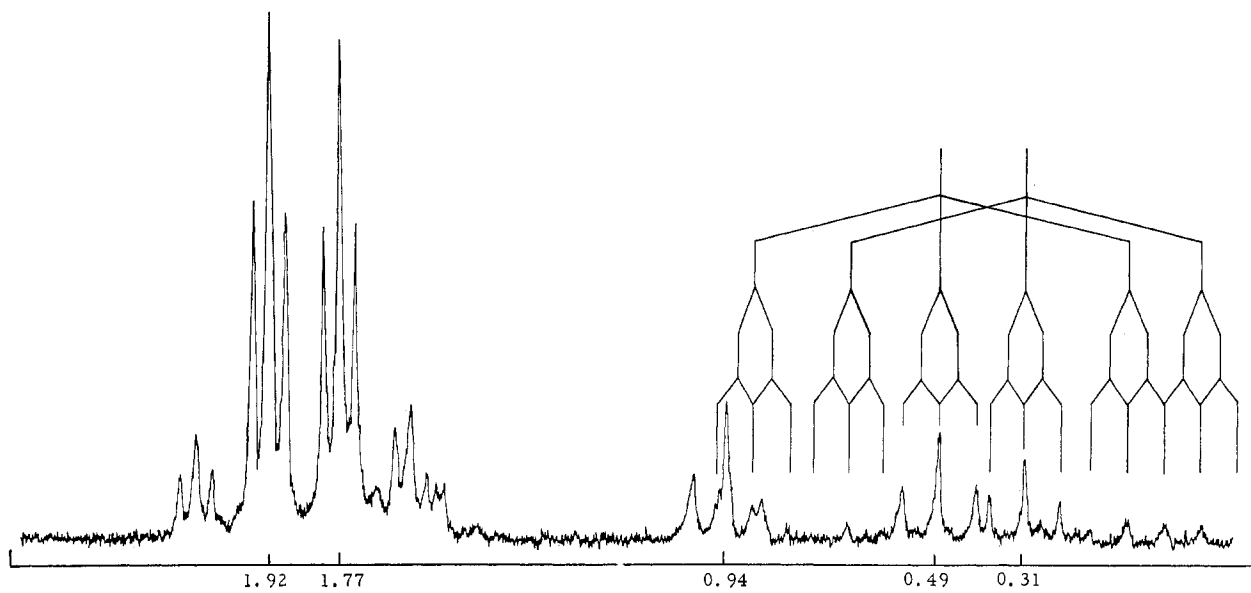
(22) R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 227 (1970).

Attempts to prepare cationic methylplatinum(II)-nitrile complexes with perfluoroalkyl nitriles, such as CF<sub>3</sub>CN, C<sub>2</sub>F<sub>5</sub>CN, and C<sub>3</sub>F<sub>7</sub>CN, led to viscous oils that could not be crystallized. However, examination of the <sup>1</sup>H nmr indicated that the phosphines had a cis configuration and the <sup>19</sup>F nmr showed that complete dealkylation had occurred with loss of the perfluoroalkyl group. The infrared spectra revealed the presence of C=N and N-H stretching vibrations; however a structure could not be assigned on the basis of the spectroscopic and analytical results.

**Preparation of Dinitrile and Imino Ether Complexes.**—*trans*-PtCH<sub>3</sub>ClQ<sub>2</sub> (where Q = P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)) with pentafluorobenzonitrile and silver hexafluorophosphate in methanol at 25° gave *trans*-[PtCH<sub>3</sub>Q<sub>2</sub>(NCC<sub>6</sub>F<sub>5</sub>)]<sup>+</sup>PF<sub>6</sub><sup>-</sup> in which the nitrile is acting as a  $\sigma$  donor as shown by an increase in  $\nu(\text{C}\equiv\text{N})$  to 2276 cm<sup>-1</sup>. However reaction in methanol using silver tetrafluoroborate gave the imino ether complex *trans*-[PtCH<sub>3</sub>Q<sub>2</sub>(NH=C(OCH<sub>3</sub>)C<sub>6</sub>F<sub>5</sub>)]<sup>+</sup>BF<sub>4</sub><sup>-</sup>, showing no  $\nu(\text{C}\equiv\text{N})$ , but  $\nu(\text{C}=\text{N})$  at 1667 cm<sup>-1</sup> and  $\nu(\text{N}-\text{H})$  at 3251 cm<sup>-1</sup>.

Using 2,3,5,6-tetrafluoroterephthalonitrile (IV) and silver tetrafluoroborate in methanol, a variety of products was obtained as shown in the following reaction scheme, depending on the alcohol





P. F. M.

Figure 1.—The  $^1\text{H}$  nmr spectra of the phosphine-methyl and platinum-methyl resonances of  $\text{trans-}[\text{PtCH}_3\{\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)\}_2(\text{NH}=\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{F}_4\text{C}\equiv\text{N})\text{PtCH}_3\{\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)\}_2](\text{BF}_4)_2$  at 100 MHz on a 250-Hz sweep width. Spectra recorded on a  $\text{CH}_2\text{Cl}_2$  solution at  $31^\circ$ .

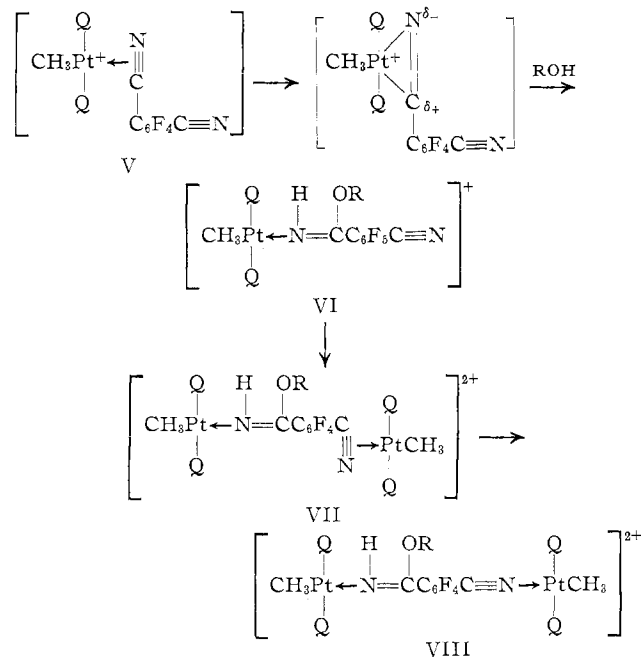
All the imino ether complexes show strong sharp  $\nu(\text{C}=\text{N})$  Raman and infrared absorptions in the region  $1675\text{--}1660\text{ cm}^{-1}$ . Absorption in the infrared spectra due to  $\nu(\text{N}-\text{H})$  appears as a weak peak at  $3400\text{--}3200\text{ cm}^{-1}$ . The proton nmr spectra of the coordinated imino ether complexes show  $\text{N}-\text{H}$  absorptions as broadened singlets at  $\delta(\text{N}-\text{H})$  ca.  $-9.20$  ppm. Platinum-methyl resonances, where  $\delta(\text{CH}_3)$  is in the region  $-0.70$  to  $-0.20$  ppm, show  $J(\text{Pt}-\text{C}-\text{H})$  of about 80 Hz, when methyl is trans to  $\sigma$ -bonded nitrile, and about 75 Hz, when methyl is trans to imino ether, indicating a stronger trans influence<sup>18</sup> for the coordinated imino ether.

In the reaction with ethanol, the product contains an imino ether group, as shown by  $\nu(\text{C}=\text{N})$  at  $1667\text{ cm}^{-1}$  in the Raman spectrum, as well as a  $\pi$ -bonded nitrile. This is revealed spectroscopically by a shift to lower frequency of the  $\nu(\text{C}\equiv\text{N})$  Raman absorption by  $113\text{ cm}^{-1}$  to  $2141\text{ cm}^{-1}$ . Products from reactions in 1-propanol and  $\beta$ -methoxyethanol contain one  $\sigma$ -bonded nitrile, in which  $\nu(\text{C}\equiv\text{N})$  is shifted to slightly higher frequency, and one imino ether. As a result the two  $\text{PtCH}_3[\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)]_2$  groups are not equivalent, as can be seen from Figure 1. The nonequivalence can easily be seen from the chemical shifts and coupling constants (Table III). The protons of the  $\text{OCH}_2\text{CH}_2\text{CH}_3$  group give the expected pattern: a triplet centered at  $\delta -4.15$  for the  $\alpha$  protons, a multiplet at ca.  $\delta -1.65$  for the  $\beta$  protons, and a triplet at  $\delta -0.94$  for the  $\gamma$  protons.

Reactions in acetone, 2-propanol, and hexafluoro-2-propanol give only the  $\sigma$ -bonded dinitrile complexes.

A plausible mechanism for imino ether formation can be based on the concept of a transition metal stabilized carbonium ion,<sup>23</sup> which clearly illustrates the accumulation of positive charge at the nitrile carbon.

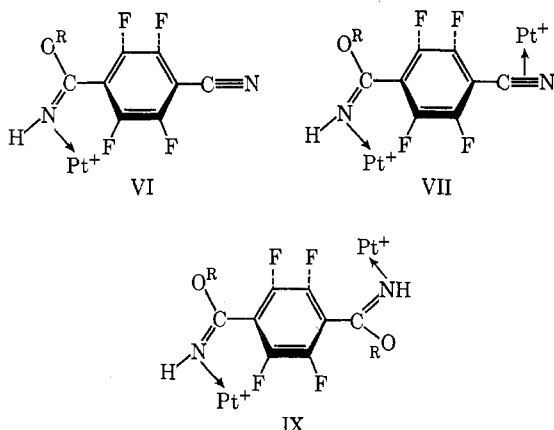
Initial  $\pi$ -bond formation (V) is apparently essential for nucleophilic attack, since refluxing the coordinated



$\sigma$ -bonded dinitrile complex in methanol for 6 hr did not lead to imino ether formation. This mechanism is also consistent with characterization of the  $\pi$ -bonded function in the ethanol product (VII). The apparent decrease in the reactivity of the second nitrile group of the ligand for different alcohols in the order  $\text{CH}_3\text{OH} > \text{C}_2\text{H}_5\text{OH} > n\text{-C}_3\text{H}_7\text{OH} > (\text{CF}_3)_2\text{CHOH}$ ,  $i\text{-C}_3\text{H}_7\text{OH}$  may be due largely to steric requirements of the  $-\text{OR}$  and  $-\text{C}_6\text{F}_4-$  groups assuming cis addition of the alcohol to the coordinated nitrile. Once nucleophilic attack has occurred at the first nitrile group (VI), the carbon-nitrogen orbitals are rehybridized from  $sp$  to  $sp^2$ . Steric interaction between the  $-\text{OR}$  group and the ortho fluorines twist the  $\text{C}=\text{N}$  bond out of the plane of the ring so that the  $-\text{NH}$  and  $-\text{OR}$  groups are now perpendicular

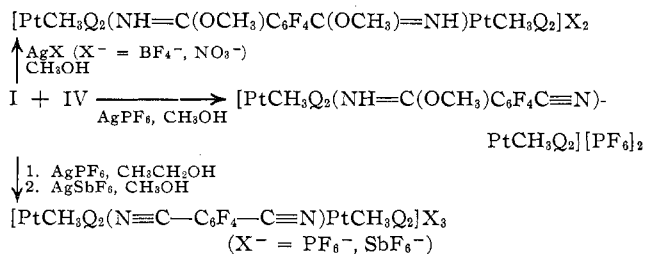
(23) M. H. Chisholm, H. C. Clark, and D. H. Hunter, *Chem. Commun.*, 809 (1971).

to the phenyl ring. As a result the nitrogen lone pair is directed below the ring with the platinum coordinated in this position (VI). Subsequent  $\pi$  bonding of the CN



triple bond (VII) is governed by the size of R. For R = CH<sub>3</sub>, attack can occur but this leads to a rather crowded molecule (IX). For R = CH<sub>2</sub>CH<sub>3</sub>, IX would be very crowded so the reaction stops at VII, and for R = CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> or OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>, there appears to be even greater crowding in VII. Hence  $\sigma$  bonding to platinum is preferred (VIII) where there is little steric interaction.

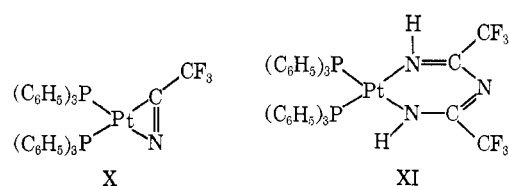
The course of the reaction is also anion dependent; the reactions with pentafluorobenzonitrile described above illustrate this. Similar dependence with 2,3,5,6-tetrafluoroterephthalonitrile was also found, *i.e.*



Silver nitrate with I and IV in methanol gave attack at both nitriles as was found in the reactions using silver tetrafluoroborate. However, silver hexafluorophosphate with I and IV in methanol gave attack at only one nitrile, the second being  $\sigma$  bonded to platinum. Reactions using silver hexafluorophosphate in ethanol or a higher alcohol and silver hexafluoroantimonate in methanol gave only the  $\sigma$ -bonded dinitriles. Since the same products were obtained using trimethylarsine, the course of the reaction appears to depend on the size of the anion used.

**Attempted Polymerization and Insertion Reactions.**—Various transition metals<sup>24,25</sup> have been found to catalyze the trimerization of benzonitrile to triphenyltriazine. Kemmett, *et al.*,<sup>26</sup> found that reactions of excess trifluoroacetonitrile with tetrakis(triphenylphosphine)platinum(0) in benzene led to oxidative addition reactions and isolated products in varying degrees of polymerization (X, XI).

Unlike the reactions of acetylenes<sup>1,2</sup> with I, which do lead to polymerization and insertion products, we have



found that perfluoroalkyl- and -aryl nitriles do *not* react with I even under vigorous conditions.

### Experimental Section

The following chemicals were obtained commercially and were sufficiently pure to be used without further purification: *p*-toluonitrile, *m*-toluonitrile, *p*-terephthalonitrile, *p*-methoxybenzonitrile, and *p*-nitrobenzonitrile from Eastman Kodak Co. (Toronto, Canada); pentafluorobenzonitrile and 2,5-difluorobenzonitrile from Peninsular Chemresearch Inc.; 2,3,5,6-tetrafluoroterephthalonitrile from Pierce Chemicals; silver hexafluorophosphate, silver tetrafluoroborate, and silver hexafluoroantimonate from Alfa Inorganics Inc.

Infrared spectra were recorded on Beckman IR-10 and IR-7 spectrophotometers as 2.0% by weight KBr disks and were unchanged as Nujol mulls.

Raman spectra were obtained from crystalline samples in capillary tubes using a Spex Model 1400 spectrometer with the 6328-Å line of the helium-neon laser. Proton nmr spectra were recorded on Varian T-60 and HA-100 spectrometers using dichloromethane as solvent as well as internal standard.

Microanalyses were performed by Chemalytics Inc., Tempe, Ariz.

All reactions were carried out under nitrogen and Spectro-grade solvents were used without further purification.

Since all of the complexes were prepared by similar methods, only a few representative examples will be outlined below. Physical and analytical data are listed in Table III.

*trans*-PtCH<sub>3</sub>ClL<sub>2</sub>, where L = dimethylphenylphosphine or trimethylarsine, was prepared by the method of Ruddick and Shaw.<sup>27,28</sup>

(a) **Preparation of Mononitrile Complexes.**—To a suspension of *trans*-PtCH<sub>3</sub>Cl[As(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub> (0.125 g) in 10 ml of methanol was added AgPF<sub>6</sub> (0.065 g) in 2 ml of methanol. A flocculent precipitate of silver chloride formed immediately. The solution was stirred for 10 min and the silver chloride was removed by centrifugation to give a clear solution. A solution of *p*-NC-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> (0.030 g) in 2 ml of methanol was added and the mixture was stirred for 10 min. The methanol was then removed on a rotary evaporator to give a clear colorless oil which did not crystallize from dichloromethane-ether. Consequently the oil was taken up in 10 ml of methanol, and the solution of sodium tetraphenylborate (0.089 g) in 2 ml of methanol was added slowly to give a white precipitate which was filtered off, washed with methanol and ether, and then recrystallized from dichloromethane-ether to give white crystals of *trans*-[PtCH<sub>3</sub>(As(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>(NCC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)]<sub>2</sub>[B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]<sub>2</sub> (0.089 g).

(b) **Preparation of Dinitrile Complexes.**—To a solution of *trans*-PtCH<sub>3</sub>Cl[P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub> (0.230 g) in 10 ml of acetone was added AgBF<sub>4</sub> (0.086 g) in 2 ml of acetone. After 10 min the silver chloride was removed and 2,3,5,6-tetrafluoroterephthalonitrile (0.0441 g) in 2 ml of acetone was added to give a bright yellow solution. Subsequent removal of the acetone yielded a clear, yellow oil which was taken up in the minimum amount of dichloromethane. The slow addition of ether yielded yellow needles which were filtered off, washed with ether, and dried under high vacuum for 15 min to give [PtCH<sub>3</sub>{P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}]<sub>2</sub>(N≡CC<sub>6</sub>F<sub>4</sub>C≡N)PtCH<sub>3</sub>{P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}]<sub>2</sub>[BF<sub>4</sub>]<sub>2</sub> (0.205 g).

(c) **Preparation of Imino Ether Complexes.**—To a suspension of *trans*-PtCH<sub>3</sub>[P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub> (0.205 g) in 1-propanol was added AgBF<sub>4</sub> (0.077 g). Silver chloride slowly precipitated and the solution was stirred for 15 min to allow complete removal of the chloride and coagulation of the silver chloride which was then removed by centrifugation to give a clear solution. 2,3,5,6-Tetrafluoroterephthalonitrile (0.039 g) was added and the solution was stirred for 2 hr to give a dirty brown precipitate which was filtered off and washed with ether. The precipitate was then dissolved in about 2 ml of dichloromethane and filtered

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through a small 1-in. Florisil column to remove any organic tars, colloidal silver, or platinum. A clear, pale yellow solution was eluted with dichloromethane and subsequent addition of diethyl ether yielded pale yellow needles of  $[\text{PtCH}_3\{\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)\}_2\text{-(NH=C(O-}n\text{-C}_3\text{H}_7)\text{C}_6\text{F}_4\text{C}\equiv\text{N})PtCH}_3\{\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)\}_2][\text{BF}_4]_2$  (0.190 g).

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## Polarized Crystal Spectra of Tris(diethyldithiophosphato)vanadium(III), -chromium(III), and -cobalt(III)<sup>1a</sup>

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The electronic structures of tris(diethyldithiophosphato)vanadium(III), -chromium(III), and -cobalt(III) have been investigated using the polarized ligand field spectra of the chromophores doped into the lattice of the colorless crystal of tris(diethyldithiophosphato)indium(III). Spectra were measured at 300, 80, and 5°K. Molecular polarizations (perpendicular and parallel to the  $C_3$  axes) have been calculated from the crystal spectra observed with light polarized along extinction directions in the monoclinic crystal. The selection rules allow an independent check of these calculations which confirms the validity of the method. Polarizations indicate close adherence to trigonal ( $D_3$ ) selection rules (with the exception of  $\text{V}(\text{dtp})_3$  at low temperatures) despite the  $C_1$  site symmetry of the metal ions. Trigonal splittings, as indicated by band maxima in the lower energy manifold of each spectrum, are 0.6 kK for  $\text{Cr}(\text{dtp})_3$  and  $\text{Co}(\text{dtp})_3$  and considerably less than this for  $\text{V}(\text{dtp})_3$ , with the E component at higher energy in each case. The  $\text{Cr}(\text{dtp})_3$  spectrum has been fitted to a crystal field model which indicates by its unusually large ratio of  $C/B$  the predominance of the  $\sigma$ -delocalization mechanism in this complex.

### Introduction

Metal complexes of diethyldithiophosphate ( $\text{dtp}^-$ ) have been of considerable practical and theoretical interest during the past decade. Their applications, as diverse as carcinostatic agents<sup>2</sup> and corrosion-inhibiting oil additives<sup>3</sup> have been explored. Studies of their spectral,<sup>2,4-16</sup> magnetic,<sup>17-21</sup> and structural proper-

ties<sup>3,11,22-26</sup> have engaged the interest of numerous investigators in both academic and industrial laboratories. In this paper we describe the results of our polarized single-crystal spectra of three complexes of the formula  $\text{M}(\text{dtp})_3$ ,  $\text{M} = \text{V}(\text{III})$ ,  $\text{Cr}(\text{III})$ , and  $\text{Co}(\text{III})$ , doped into the colorless host lattice  $\text{In}(\text{dtp})_3$ . The general trigonal symmetry predicted for these bidentate ligand complexes has been confirmed in the structure of the host.<sup>22</sup> Although some additional distortion of the coordination sphere is evident in this lattice, as well as in the isomorphous structure of  $\text{V}(\text{dtp})_3$ ,<sup>11</sup> the trigonal distortion is predominant and provides the framework for the analysis of the spectral results.

The solution spectra of the chromium and cobalt compounds and of other  $\text{dtp}^-$  complexes were first reported by Schäffer<sup>5</sup> and by Jørgensen,<sup>4,6</sup> who commented on the pronounced dichroism exhibited by the  $\text{Cr}(\text{dtp})_3$  crystals and speculated on the source of the unusually high molar absorptivities of both the  $\text{Cr}(\text{dtp})_3$  and  $\text{Co}(\text{dtp})_3$ . A preliminary report of the  $\text{V}(\text{dtp})_3$  crystal and solution spectra has recently appeared,<sup>11</sup> though the temperature dependence, detailed polarization results, and trigonal splitting parameters have not been previously reported.

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