

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WESTERN ONTARIO,  
LONDON, ONTARIO, CANADA**Trifluoromethylplatinum Complexes and the Nature of the Pt-CF<sub>3</sub> Bond**

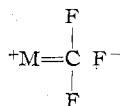
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Complexes of the types *trans*-Pt(CF<sub>3</sub>)<sub>2</sub>Q<sub>2</sub>L<sup>+</sup> and *trans*-Pt(CF<sub>3</sub>)ZQ<sub>2</sub> have been prepared, where Q = P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>), L is a neutral ligand, and Z is an anionic ligand. <sup>2</sup>J<sub>Pt-CF<sub>3</sub> for these complexes varies linearly with <sup>2</sup>J<sub>Pt-CH<sub>3</sub> for the corresponding methylplatinum complexes, except where L requires synergic σ-π bonding. The results suggest that the Pt-CF<sub>3</sub> bond does not depend very much on π back-bonding for its stability. The trans influence of the trifluoromethyl group is discussed, and some reactions of the trifluoromethylplatinum complexes are compared with those of corresponding methylplatinum compounds.</sub></sub>

**Introduction**

Perfluoroalkyl groups are of interest in organometallic chemistry because of the great stability of their complexes with transition metals compared with the corresponding alkyl-metal compounds. It has been suggested<sup>1-3</sup> that this stability is due at least in part to π back-bonding between filled d orbitals on the metal atom and σ\* orbitals of the perfluoroalkyl group or, in valence-bond terms, hyperconjugation of the type



Evidence from infrared spectra<sup>4</sup> and short metal-carbon bond lengths combined with large M-C-F angles in crystal structures of fluoroalkyl complexes<sup>5,6</sup> seem to support this postulate. However, an alternative explanation for the infrared data has been given,<sup>7</sup> and Graham's interpretation of carbonyl force constants<sup>8</sup> suggests that π back-bonding is not important. Consequently, this whole question must be considered an open one, especially in the current period of reaction against an earlier overindulgence in invoking π back-bonding in inorganic chemistry generally. It is worth noting that evidence has been mounting against the concept of fluorine hyperconjugation in organic compounds.<sup>9</sup>

It seemed to us that a study of <sup>2</sup>J<sub>Pt-CF<sub>3</sub> for a variety of trifluoromethylplatinum complexes might help to settle this question, as well as providing some information on factors affecting coupling constants involving <sup>195</sup>Pt. Although there have been several studies on the variation of <sup>2</sup>J<sub>Pt-CH<sub>3</sub> with trans ligands for methylplatinum(II)<sup>10,11</sup> and -platinum(IV)<sup>12,13</sup> compounds, there has been no comparable investigation for trifluoromethylplatinum complexes. Indeed, only a few of these compounds have been prepared.<sup>14-16</sup></sub></sub>

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In this paper, the preparation and nmr spectra of complexes *trans*-Pt(CF<sub>3</sub>)<sub>2</sub>Q<sub>2</sub>L<sup>+</sup> and Pt(CF<sub>3</sub>)ZQ<sub>2</sub> are discussed, where Q is dimethylphenylphosphine, L is a neutral ligand, and Z is an anionic ligand. A few platinum(IV) complexes are also included.

**Results**

A list of the trifluoromethylplatinum complexes prepared, together with analytical data, is given in Table I. Data for a few methylplatinum complexes not previously prepared are given in Table II.

All the Pt(II) complexes have the trans configuration about platinum, since the phosphine-methyl resonances appeared as triplets<sup>17,18</sup> (with triplet "satellites" from coupling to <sup>195</sup>Pt, *I* = 1/2, 34% abundant). Nmr spectroscopic data are tabulated in Table III. In a few cases the hexafluorophosphate salts were insufficiently soluble for nmr spectra to be obtained, so the more soluble tetrafluoroborate salts were used. For some complexes, as indicated in Table III, the dimethylphenylphosphine ligands exchanged rapidly at room temperature, so the solution was cooled until all coupling constants could be measured.

The <sup>19</sup>F spectra of the Pt(II) complexes are, in general, similar to the spectrum of *trans*-PtI(CF<sub>3</sub>)<sub>2</sub> previously reported,<sup>15</sup> consisting of a central triplet (from coupling to the two equivalent <sup>31</sup>P nuclei of the phosphine ligands), with triplet "satellites" from coupling with <sup>195</sup>Pt. When L is a phosphine in complexes *trans*-Pt(CF<sub>3</sub>)<sub>2</sub>Q<sub>2</sub>L<sup>+</sup>, each peak is further split into a doublet by coupling with the trans-<sup>31</sup>P nucleus.

Preparation and characterization of the Pt(IV) complexes not previously described<sup>15</sup> will be published later. Infrared C-F stretching frequencies are listed in Table III.

For complexes *trans*-Pt(R)ZQ<sub>2</sub> with Z = NCS, NCO, and NO<sub>2</sub>, linkage isomerism is possible. The very similar values of <sup>2</sup>J<sub>Pt-CH<sub>3</sub> for the complexes Pt(NCS)-(CH<sub>3</sub>)<sub>2</sub>Q<sub>2</sub> and Pt(NCO)(CH<sub>3</sub>)<sub>2</sub>Q<sub>2</sub> (and of <sup>2</sup>J<sub>Pt-CF<sub>3</sub> for the corresponding trifluoromethyl complexes) strongly suggest that these ligands are N bonded. The N-C stretching frequencies (Table V) are consistent with this assignment.<sup>19</sup> The relation between <sup>1</sup>J<sub>Pt-H</sub>, <sup>2</sup>J<sub>Pt-CH<sub>3</sub></sub>, and <sup>2</sup>J<sub>Pt-CF<sub>3</sub></sub> (Figures 1, 3) in the complexes *trans*-Pt(R)(NO<sub>2</sub>)(PR'<sub>3</sub>)<sub>2</sub> (R = H, CH<sub>3</sub>, CF<sub>3</sub>) indicates</sub></sub>

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TABLE I  
ANALYTICAL DATA FOR TRIFLUOROMETHYLPLATINUM COMPLEXES

Complex <sup>a</sup>	Analyses, %						Mp, <sup>b</sup> °C	Recrystn solv
	C		H		F			
	Calcd	Found	Calcd	Found	Calcd	Found		
[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> (NCCH=CH <sub>2</sub> )] [PF <sub>6</sub> ]	32.5	32.7	3.4	3.6			118-119	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O
[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> ( <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )] [PF <sub>6</sub> ]	36.7	36.7	3.6	3.3			133-136	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O
[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> {NH=C(OCH <sub>3</sub> )C <sub>6</sub> F <sub>5</sub> }] [PF <sub>6</sub> ]	33.0	32.8	2.9	2.5			134-135	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O
[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> { <i>p</i> -(NH=C(OCH <sub>3</sub> )) <sub>2</sub> C <sub>6</sub> F <sub>4</sub> }] [PF <sub>6</sub> ]	33.1	32.9	3.2	3.3			132-134	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O
[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> (NC <sub>6</sub> H <sub>5</sub> )] [PF <sub>6</sub> ]	34.6	34.8	3.6	3.8			171-173	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O
[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> (CO)] [PF <sub>6</sub> ]	30.3	30.7	3.1	3.3	24.0	23.2	137	CHCl <sub>3</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O
[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> (CNC <sub>2</sub> H <sub>5</sub> )] [PF <sub>6</sub> ]	32.4	32.6	3.7	3.6			118-120	CH <sub>3</sub> OH
[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> ( <i>p</i> -CNC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )] [PF <sub>6</sub> ]	36.7	36.6	3.6	3.4			155-156	CH <sub>2</sub> Cl <sub>2</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O
[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> {As(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> }] [PF <sub>6</sub> ]	42.7	42.6	3.8	3.6			100-102	C <sub>2</sub> H <sub>5</sub> OH
[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> {P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> }] [PF <sub>6</sub> ]	44.3	44.4	3.9	3.9			138-140	CH <sub>3</sub> OH
[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> ][PF <sub>6</sub> ]	36.5	36.9	4.0	4.2			100-102	(CH <sub>3</sub> ) <sub>2</sub> CO- <i>n</i> -C <sub>6</sub> H <sub>12</sub> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O
[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> {Sb(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> }] [PF <sub>6</sub> ] <sup>c</sup>	40.5	40.7	3.6	3.6			105-106	CH <sub>3</sub> OH
Pt(ONO <sub>2</sub> )(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	33.9	33.8	3.7	3.6	9.5	9.2	141	CH <sub>3</sub> OH
PtBr(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	32.9	32.8	3.6	3.5	9.2	9.1	134	CH <sub>3</sub> OH
PtCl(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	35.5	35.6	3.9	3.9	9.9	10.3	127-128	CH <sub>3</sub> OH
Pt(NCO)(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	37.1	37.2	3.8	3.6	9.8	9.6	118-120	CH <sub>3</sub> OH
Pt(NCS)(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	36.1	36.1	3.7	3.5	9.5	9.2	141-143	CH <sub>3</sub> OH
Pt(N <sub>3</sub> )(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	35.1	35.2	3.8	3.9	9.8	10.2	113	CH <sub>3</sub> OH
Pt(NO <sub>2</sub> )(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	34.8	35.0	3.8	4.0	9.7	10.0	126-127	CH <sub>3</sub> OH
Pt(CN)(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	38.2	38.3	3.9	3.9	10.1	10.3	127-129	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O-C <sub>6</sub> H <sub>14</sub>

<sup>a</sup> All complexes trans. Colorless unless otherwise stated. Q = P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>). <sup>b</sup> Uncorrected. <sup>c</sup> Pale yellow.

TABLE II  
METHYLPLATINUM COMPLEXES

Complex <sup>a</sup>	$\delta_{\text{Pt-CH}_3}^b$	Analyses, %						Mp (uncor), °C			
		<sup>2</sup> J <sub>Pt-CH<sub>3</sub></sub>		<sup>3</sup> J <sub>P-H</sub>		<sup>4</sup> J <sub>Pt-H</sub>					
		Hz	Hz	Hz	Hz	Hz	Hz				
Pt(ONO <sub>2</sub> )(CH <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	-0.18	86.0	7.1	-1.71	29.5	6.8	37.2	37.6	4.6	4.9	70-72
Pt(NCO)(CH <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	-0.11	78.0	7.0	-1.78	30.0	6.8	40.9	40.9	4.8	4.7	89-92
Pt(NCS)(CH <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	+0.02	78.5	7.2	-1.81	31.0	6.8	39.7	39.6	4.6	4.6	107-109
Pt(NO <sub>2</sub> )(CH <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	-0.04	71.3	7.7	-1.72	32.3	6.8	38.4	38.4	4.7	4.8	123-125
Pt(CN)(CH <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> <sup>c</sup>	+0.03	61.0	7.4	-2.06	32.6	8.0	42.1	42.3	4.9	4.8	98-99

<sup>a</sup> All complexes trans and colorless. Q = P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>). Spectra in CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> Ppm upfield from TMS. <sup>c</sup> Rapid phosphine exchange at room temperature. Spectrum run at low temperature.

that the bonding mode of the nitrite ligand is the same in these three complexes. Because the hydride resonance in the complex *trans*-Pt(H)(NO<sub>2</sub>)(PEt<sub>3</sub>)<sub>2</sub> showed no sign of coupling with the <sup>14</sup>N nucleus or broadening caused by its quadrupole (as observed for N-bound NCS and NCO) Powell and Shaw<sup>20</sup> suggested that in benzene solution the nitrile is O bonded. This reversed the earlier assignment<sup>21</sup> for the solid complex based on infrared spectra. Powell and Shaw also noted that  $\tau_{\text{H}}$  was rather high for an N-bound species. The lack of interaction between the hydride proton and the <sup>14</sup>N nucleus seems, however, to be very flimsy evidence on which to assign the configuration, since the quadrupole relaxation time is very dependent on the electric field gradient at the <sup>14</sup>N nucleus, which is related to molecular symmetry,<sup>22,23</sup> clearly different for N-bound nitrite from N-bound thiocyanate.

Arguments for N-bound nitrite are as follows. (i) *trans*-Pt(H)(NO<sub>2</sub>)(PEt<sub>3</sub>)<sub>2</sub> appears to be N bound in the solid state.<sup>21</sup> (ii) Platinum prefers nitrogen donors in general to oxygen donors. No O-bound platinum-nitrite complexes are known. (iii) As measured by coupling constants for *trans*-Pt(R)(NO<sub>2</sub>)(PR'<sub>3</sub>)<sub>2</sub> the trans influence of nitrite is greater than for the nitrogen donors N<sub>3</sub>, NCS, and NCO. If the nitrite were O

bound, its trans influence would be expected to be lower, perhaps comparable to that of nitrate.

Allen and Pidcock<sup>10</sup> and Atkins, et al.,<sup>24</sup> appear to consider nitrite as N bound in the complexes they studied, although they do not discuss this question.

In Figure 1, <sup>2</sup>J<sub>Pt-CF<sub>3</sub></sub> for the trifluoromethyl complexes is plotted against J<sub>Pt-CH<sub>3</sub></sub> for the corresponding methyl complexes. Except for the points representing L = Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> and CO, the cationic complexes Pt(R)Q<sub>2</sub>L<sup>+</sup> give a straight line. The points corresponding to the nonelectrolytes Pt(R)ZQ<sub>2</sub> lie on a slightly different line, while the Pt(IV) complexes give a line with a slope (<sup>2</sup>J<sub>Pt-CF<sub>3</sub></sub>/<sup>2</sup>J<sub>Pt-CH<sub>3</sub></sub>) much less than for Pt(II) complexes. All three lines may be extrapolated back to the origin.

In Figure 2, the chemical shifts of the trifluoromethyl groups are plotted against <sup>2</sup>J<sub>Pt-CF<sub>3</sub></sub>. For the nonelectrolyte complexes, there is clearly a general trend for the chemical shift to decrease as the coupling constant increases. For the cations, most points appear to follow a similar trend, but the chemical shifts for L = CO, RNC, and RCN appear to be "anomalously" high.

### Discussion

<sup>2</sup>J<sub>Pt-CF<sub>3</sub></sub> Compared with <sup>2</sup>J<sub>Pt-CH<sub>3</sub></sub>.—In most discussions of <sup>1</sup>J<sub>Pt-H</sub> in platinum hydride complexes it has been assumed that the coupling is dominated by the Fermi contact term<sup>24,25</sup>

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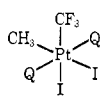
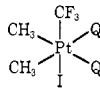
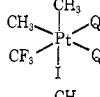
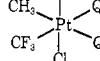
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TABLE III  
 SPECTROSCOPIC DATA FOR TRIFLUOROMETHYLPLATINUM COMPLEXES

No.	Complex <sup>a</sup>	$\delta_{CF_3}^b$ Hz	$^2J_{Pt-CF_3}$ Hz	$^3J_{P-F}$ Hz	$\delta_{P-CH_3}^c$ g	$^3J_{Pt-P-CH_3}$ Hz	$^4J_{Pt-H}$ Hz	$^2J_{Pt-CH_3}^d$ Hz	Ref <sup>e</sup>	Other peaks in spectra <sup>c</sup>	$\nu_{C-F}^f$ (sym), cm <sup>-1</sup>	$\nu_{C-F}^f$ (deg), cm <sup>-1</sup>
1	[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> (acetone)][PF <sub>6</sub> ]	11.20	858	g	g	g	g	88	16			
2	[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> (NCCH=CH <sub>2</sub> )] [PF <sub>6</sub> ]	15.22	780	20.0	2.01	30.8	7.6	80 <sup>k</sup>	11	g	1107 s	1000 sh 1011 1025 sh
3	[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> ( <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )] [PF <sub>6</sub> ]	14.71	778	20.0	2.06	30.0	8.4	80	40	$\delta_{OCH_3}$ 3.93	1105 s	1026 b
4	[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> {NH=C(OCH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> }] [PF <sub>6</sub> ]	13.88	724	19.0	1.93	29.2	7.2	76.4	40	$\delta_{OCH_3}$ 3.88	1104 s	1004 b 1027 sh
5	{[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> ]{ <i>p</i> -(NH=C(OCH <sub>3</sub> )) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> }} [PF <sub>6</sub> ] <sub>2</sub>	13.19	721	20.0	1.98	30.8	7.8	74.5	40	$\delta_{OCH_3}$ 3.63 $\delta_{NH}$ 8.67	1104 s	999 b 1017 b
6	[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> (NC <sub>2</sub> H <sub>5</sub> )] [PF <sub>6</sub> ]	13.81	702	18.2	1.78	30.4	7.2	74.0 <sup>h</sup>	11		1074 sh 1101 s	1001 b 1016 b
7	[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> (CO)] [PF <sub>6</sub> ] <sup>i</sup>	22.28	656	19.0	2.25	32.0	9.0	63.0 <sup>h</sup>	11		1117 s	1053 b
8	[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> (CNC <sub>2</sub> H <sub>5</sub> )] [PF <sub>6</sub> ] <sup>j</sup>	20.24	620	17.5	2.03	31.4	7.6	63.5	41	$\delta_{CH_2}$ 3.27 $\delta_{CH_3}$ 0.98 $J_{CH_2-CH_3} = 7.0$ Hz	1109 s	1008 b 1027 sh
9	[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> ( <i>p</i> -CNC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )] [PF <sub>6</sub> ] <sup>j</sup>	20.18	620	17.0	2.13	31.6	8.0	63.5	41	$\delta_{OCH_3}$ 3.84	1107 s	1017 b 1033 sh
10	[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> {As(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> }] [BF <sub>4</sub> ] <sup>i</sup>	14.36	662	19.8	1.64	27.2	7.2	67.0 <sup>h</sup>	11		1093 s <sup>m</sup>	1000 b <sup>m</sup> 1022 b
11	[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> {P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> }] [BF <sub>4</sub> ] <sup>i</sup>	15.40	566	57.0 <sup>h</sup>	1.53	30.4	7.2	60.0 <sup>i</sup>	11		1093 s <sup>m</sup>	
12	[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> ][PF <sub>6</sub> ] <sup>j</sup>	15.75	550	56.0 <sup>k</sup> 17.0 <sup>l</sup>	1.80 <sup>k</sup> 0.91 <sup>l</sup>	28.0 <sup>k</sup> 19.0 <sup>l</sup>	8.0 <sup>k</sup> 9.8 <sup>l</sup>	57.0 <sup>h</sup>	11		1097 s	995 sh 1010 b 1032 b
13	[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> {Sb(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> }] [BF <sub>4</sub> ] <sup>i</sup>	14.64	708	20.3	1.86	28.8	7.2	55.0 <sup>h</sup>	11		1072 sh <sup>m</sup> 1089 s	1000 b <sup>m</sup> 1018 b
14	[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> {CH <sub>2</sub> CH <sub>2</sub> OCCH <sub>3</sub> }] [PF <sub>6</sub> ]	19.97	482	g	g	g	g	51.0	39		1077 w 1107 s	972 b 1002 sh 1013 b 1041 w
15	[Pt(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub> {C(CH <sub>3</sub> )(OCH <sub>3</sub> )}] [PF <sub>6</sub> ]	19.85	468	g	g	g	g	51.0	39			
16	Pt(ONO <sub>2</sub> )(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	11.20	795	20.0	1.78	30.0	7.7	86.0			1101 s	992 b 1022 b
17	PtI(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	11.95	754	n	n	n	n	81.0	18		1084 s	982 b 1015 b
18	PtBr(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	10.79	763	20.1	1.90	29.4	7.5	83.0 <sup>h</sup>	18		1090 s	986 b 1015 b
19	PtCl(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	10.52	757	19.3	1.83	29.6	7.7	82.0	18		1091 s	981 b 1010 b
20	Pt(NCO)(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	11.81	714	18.8	1.81	30.5	7.7	78.0			1098 s	988 b 1008 b
21	Pt(NCS)(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	13.00	721	19.5	1.84	30.5	7.7	78.5			1100 s	997 b 1012 b
22	Pt(N <sub>3</sub> )(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	11.60	710	17.8	1.86	30.2	7.4	78.6 <sup>o</sup>	10		1097	1001 b
23	Pt(NO <sub>2</sub> )(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	15.04	644	18.5	1.77	32.4	7.8	71.3			1103	1001 b 1016 b
24	Pt(CN)(CF <sub>3</sub> ) <sub>2</sub> Q <sub>2</sub>	17.6	565	16.0	2.02	32.6	7.8	61.0			1102 s	982 b 1007 b
25		17.0	505	n	n	n	n	67.0 <sup>h</sup>	18			
26		19.3	517	n	n	n	n	70.0 <sup>h</sup>	18		1075 sh 1085 s 1105 sh	1007 b 1055 sh
27		22.62	419	<i>p</i>	<i>p</i>	<i>p</i>	<i>p</i>	56.0	18		1084	
28		29.45	411	<i>p</i>	<i>p</i>	<i>p</i>	<i>p</i>	56.0	18		1092 s 1110 sh	1017 b 1046 b

<sup>a</sup> Unless otherwise stated, nmr spectra in CH<sub>2</sub>Cl<sub>2</sub>; Q = P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>). <sup>b</sup> Ppm upfield from CFCl<sub>3</sub>. <sup>c</sup> Ppm downfield from TMS. <sup>d</sup> In corresponding methylplatinum complex. (In CH<sub>2</sub>Cl<sub>2</sub> unless otherwise stated.) <sup>e</sup> For preparation of methylplatinum complex, if not this work. <sup>f</sup> Nujol mulls. <sup>g</sup> Details in ref 16. <sup>h</sup> In CHCl<sub>3</sub>. <sup>i</sup> In (CD<sub>3</sub>)<sub>2</sub>CO. <sup>j</sup> Phosphine ligands exchange at room temperature. Spectrum run at low temperature. <sup>k</sup> Phosphine trans to CF<sub>3</sub>. <sup>l</sup> Phosphine cis to CF<sub>3</sub>. <sup>m</sup> PF<sub>6</sub><sup>-</sup> salt. <sup>n</sup> Details in ref 15. <sup>o</sup> Pt(N<sub>3</sub>)(CH<sub>3</sub>)(PET<sub>3</sub>)<sub>2</sub>. <sup>p</sup> Details in a later paper.

$$^1J_{Pt-H} \propto \gamma_{Pt} \gamma_H \alpha^2 P_t \alpha^2 H [\psi_{Pt(6s)}(0)]^2 [\psi_{H(1s)}(0)]^2 \Delta E^{-1} \quad (1)$$

where  $\gamma_i$  is the gyromagnetic ratio for the nucleus  $i$ ,  $\alpha^2_i$  is the  $s$  character of the hybrid orbital used by  $i$ ,  $[\psi_{i(ns)}(0)]^2$  is the  $ns$  electron density at the nucleus  $i$ , and  $\Delta E$  is the singlet-triplet excitation energy between the  $\sigma$ -bonding and antibonding orbitals for the Pt-H bond.

Since the equation applies to a covalent bond, any decrease in covalency will cause  $^1J_{Pt-H}$  to decrease. An analogous equation has been used in considering  $^1J_{195Pt-31P}$ .<sup>10,26</sup>

For  $^2J_{Pt-CH_3}$  in methylplatinum complexes, the situation (26) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1707 (1966).

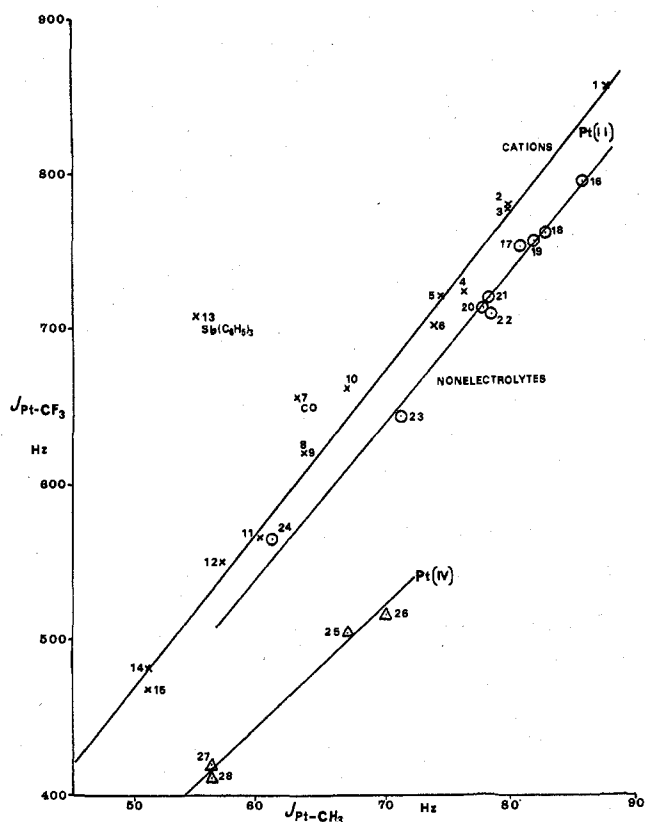


Figure 1.— $^2J_{\text{Pt}-\text{CF}_3}$  plotted against  $^2J_{\text{Pt}-\text{CH}_3}$  for  $\text{Pt}(\text{R})\text{ZQ}_2$ ,  $\text{Pt}(\text{R})\text{Q}_2\text{L}^+$ , and  $\text{Pt}(\text{IV})$  complexes ( $\text{R} = \text{CF}_3, \text{CH}_3$ ). Numbers from Table III.

where most of the symbols have the same significance as before, and  $f(C)$  is a function of the electronic factors that control transmission of the coupling through the carbon atom. At least to a first approximation,  $^2J_{\text{Pt}-\text{CH}_3}$  for the complexes  $\text{trans-Pt}(\text{CH}_3)\text{Z}(\text{PET}_3)_2$  varies linearly with  $^1J_{\text{Pt}-\text{H}}$  in the corresponding complexes  $\text{trans-Pt}(\text{H})\text{Z}(\text{PET}_3)_2$  as  $\text{Z}$  is changed (Figure 3). This indicates that  $^2J_{\text{Pt}-\text{CH}_3}$  is indeed governed by the same factors as  $^1J_{\text{Pt}-\text{H}}$ . Further, the ratio (1):(2) remains approximately constant as the ligand  $\text{Z}$  varies, so that changes in  $f(C)$  within the methylplatinum series cannot be very important. All other variable factors in (1) and (2) must also change proportionally in the two series. The recent observation<sup>28</sup> of a linear correlation between  $^1J_{\text{Pt}-\text{H}}$  and  $^2J_{\text{Pt}-\text{CH}_3}$  for a series of methylplatinum complexes also supports these conclusions.

In the treatments of  $^1J_{\text{Pt}-\text{H}}$ ,<sup>24,25</sup>  $^1J_{\text{Pt}-\text{P}}$ ,<sup>10,26</sup> and  $^2J_{\text{Pt}-\text{CH}_3}$ ,<sup>10</sup> it is usually considered that within a series of complexes the only factors likely to vary significantly are  $\alpha^2_{\text{Pt}}$ ,  $[\psi_{\text{Pt}(6s)}(0)]^2$ , and  $\Delta E$ . If changes in  $[\psi_{\text{Pt}(6s)}(0)]^2$  were dominant, the "cis influence" of a ligand would be comparable to its trans influence (measured by nmr coupling constants). That this is not so is quite clear, for example, from the large difference between the values of  $^1J_{\text{Pt}-\text{P}}$  for the phosphorus nuclei in  $\text{cis-PtCl}(\text{CH}_3)(\text{PET}_3)_2$ .<sup>10</sup>

Most authors<sup>10,26,28</sup> have assumed that the variation in  $\alpha^2_{\text{Pt}}$ , perhaps combined with a change in covalency, predominates. The presence of a very strong  $\sigma$  donor trans to the bond in question will cause rehybridization

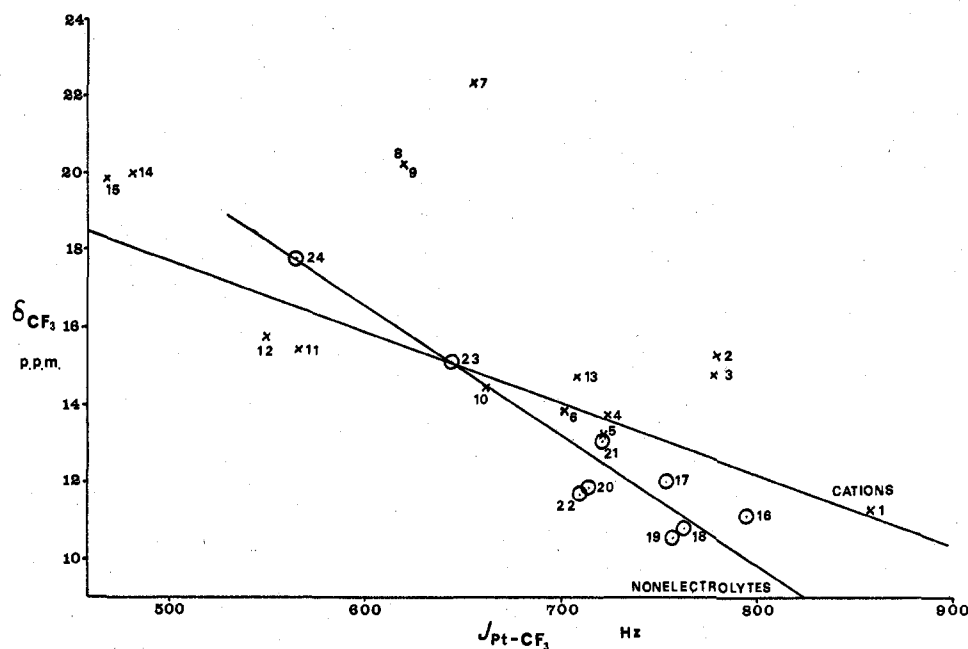


Figure 2.— $^{19}\text{F}$  chemical shift (ppm upfield from  $\text{CFCl}_2$ ) plotted against  $^2J_{\text{Pt}-\text{CF}_3}$  for the complexes  $\text{Pt}(\text{CF}_3)\text{ZQ}_2$  and  $\text{Pt}(\text{CF}_3)\text{Q}_2\text{L}^+$ . Numbers from Table III.

tion is theoretically more complex, but a treatment based on that of Smith,<sup>27</sup> assuming only Fermi contact contribution to coupling, would predict a relationship of the type

$$^2J_{\text{Pt}-\text{CH}_3} \propto \gamma_{\text{Pt}}\gamma_{\text{H}}\alpha^2_{\text{Pt}}\alpha^2_{\text{H}}f(C)[\psi_{\text{Pt}(6s)}(0)]^2[\psi_{\text{H}(1s)}(0)]^2 \times \Delta E^{-1} \quad (2)$$

(27) G. W. Smith, *J. Chem. Phys.*, **42**, 435 (1965).

of the Pt atom, and  $\alpha^2_{\text{Pt}}$  will decrease, or the bond could become less covalent (*i.e.*, more ionic) which would also decrease the coupling. It is difficult to separate these two effects within a series of Pt(II) complexes, but a comparison of coupling constants for analogous Pt(II) and Pt(IV) complexes suggests that  $\alpha^2_{\text{Pt}}$  is the domi-

(28) M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *Chem. Commun.*, 1627 (1971).

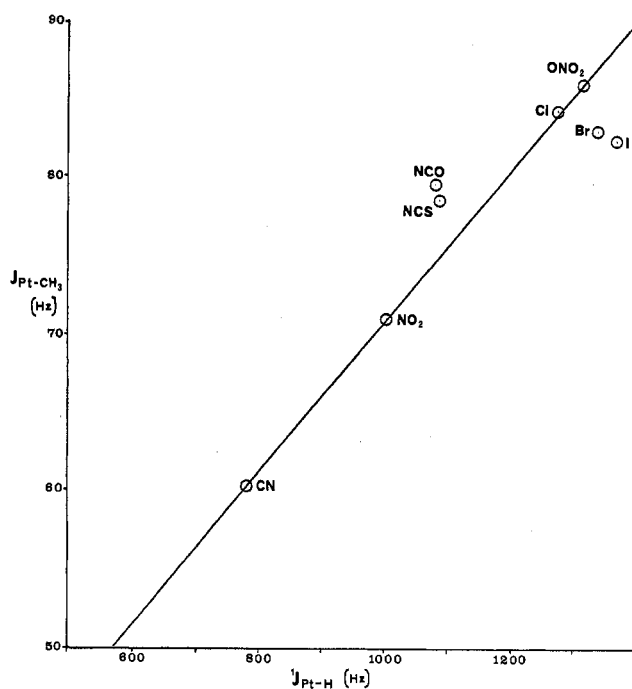


Figure 3.— ${}^2J_{\text{Pt}-\text{CH}_3}$  plotted against  ${}^1J_{\text{Pt}-\text{H}}$  for corresponding complexes  $\text{Pt}(\text{CH}_3)\text{Z}(\text{PEt}_3)_2$  and  $\text{Pt}(\text{H})\text{Z}(\text{PEt}_3)_2$ . Data from ref 10 and 20.

nant factor<sup>26</sup> (discussed later). Atkins, *et al.*,<sup>24</sup> have suggested on the basis of a relationship between  ${}^1J_{\text{Pt}-\text{H}}$  and the position of the trans ligand in the spectrochemical series that changes in  $\Delta E$  cannot be ignored when "gross changes" are made in the nature of this ligand. However, the position of a ligand in the spectrochemical series is not altogether unrelated to its position in the trans influence series if the latter is based mainly on a  $\sigma$ -donor bond strength. A ligand which is a good  $\sigma$  donor and forms strong covalent bonds will be high in both series. Except for the halogens, where changes in trans influence (measured by coupling constants) are relatively small, the two series are almost parallel.

Since coupling involving the  ${}^{19}\text{F}$  nucleus is rather more complicated in general than that involving  ${}^1\text{H}$  (*e.g.*, "through-space" contributions are often important), the dependence of  ${}^2J_{\text{Pt}-\text{CF}_3}$  on L or Z in the complexes *trans*- $\text{Pt}(\text{CF}_3)_2\text{Q}_2\text{L}^+$  and  $\text{Pt}(\text{CF}_3)\text{ZQ}_2$  could conceivably be much more complicated than that of  ${}^2J_{\text{Pt}-\text{CH}_3}$ . However, if the points representing L = CO and  $\text{Sb}(\text{C}_6\text{H}_5)_3$  are ignored, a good straight line may be drawn through the points representing cations in Figure 1 (*i.e.*,  $J_{\text{Pt}-\text{CF}_3}/J_{\text{Pt}-\text{CH}_3}$  is constant). This immediately indicates the following details.

(i) Factors influencing  ${}^2J_{\text{Pt}-\text{CF}_3}$  in trifluoromethyl complexes parallel those for  ${}^2J_{\text{Pt}-\text{CH}_3}$ , and an equation analogous to (2) determines the coupling. Further, since  $J_{\text{Pt}-\text{CF}_3}/J_{\text{Pt}-\text{CH}_3}$  is constant

$$\frac{\{\alpha^2_{\text{Pt}}\alpha^2_{\text{F}}f(\text{C})[\psi_{\text{Pt}(6s)}(0)]^2[\psi_{\text{F}(2s)}(0)]^2\Delta E^{-1}\}_{\text{CF}_3}}{\{\alpha^2_{\text{Pt}}\alpha^2_{\text{H}}f(\text{C})[\psi_{\text{Pt}(6s)}(0)]^2[\psi_{\text{H}(1s)}(0)]^2\Delta E^{-1}\}_{\text{CH}_3}} = \text{constant} \quad (3)$$

In particular, if variation in  $\alpha^2_{\text{Pt}}$  is the main factor

$$\frac{(\alpha^2_{\text{Pt}})_{\text{CF}_3}}{(\alpha^2_{\text{Pt}})_{\text{CH}_3}} = (\text{constant})' \quad (4)$$

(ii) The Pt-CF<sub>3</sub> bond is not very dependent on synergic  $\sigma$ - $\pi$  bonding for its strength. As L becomes a weaker  $\sigma$  donor (toward the upper right of Figure 1) the total electron density on the Pt atom will decrease significantly, the filled  $d_{z^2}$  and  $d_{y^2}$  orbitals will contract, and the availability of electrons for  $\pi$  back-bonding would decrease. A synergic bonding mechanism would depend on the availability of such electrons, and the line in Figure 1 would be expected to curve downward at the upper right of the graph or upward at the lower left (since the methyl group is incapable of  $\pi$  back-bonding). There is no sign of such curvature. Further, a similar argument would predict, if Pt-CF<sub>3</sub>  $\pi$  bonding were important, that  $J_{\text{Pt}-\text{CF}_3}/J_{\text{Pt}-\text{CH}_3}$  would be much larger for the complexes  $\text{Pt}(\text{R})\text{ZQ}_2$  than for the relatively electron-deficient cations  $\text{Pt}(\text{R})\text{Q}_2\text{L}^+$ . In fact, the slope of the line representing nonelectrolyte complexes is slightly less than that for the cations.

For L = CO and  $\text{Sb}(\text{C}_6\text{H}_5)_3$ ,  ${}^2J_{\text{Pt}-\text{CF}_3}$  is greater than would be expected from the value of  ${}^2J_{\text{Pt}-\text{CH}_3}$ . Unless the coupling mechanism for these compounds is different from that for other ligands, this implies that the Pt-L bond is considerably weaker in the trifluoromethyl complex than it is in the methyl complex. For L = CO, a rationalization can be given. It is well accepted that the carbonyl ligand bonds to transition metals by synergic  $\sigma$ - $\pi$  bonding.<sup>29</sup> When the Pt atom is bonded to the relatively electronegative trifluoromethyl group, its electron density will be considerably less than it is in the methylplatinum complex, reducing the availability of electrons for  $\pi$  back-bonding to the carbonyl group. Consequently, because of the  $\sigma$ - $\pi$  synergism, the Pt-CO  $\sigma$  bond becomes weaker. The C-O stretching frequencies (Table VI) are consistent with a considerable reduction in platinum-carbonyl  $\pi$  bonding for the trifluoromethyl complex. The deviation from the line in Figure 1 is much greater for the triphenylstibine complex. The explanation is presumably similar to that given above the carbonyl complex—*i.e.*,  $\text{Sb}(\text{C}_6\text{H}_5)_3$  forms a strong Pt-Sb  $\sigma$  bond only when electrons are available for  $\pi$  back-bonding. The apparently anomalous position of  $\text{Sb}(\text{C}_6\text{H}_5)_3$  in the trans influence series from  ${}^2J_{\text{Pt}-\text{CH}_3}$  has already been noted.<sup>11</sup> It has been suggested, on the basis of a variety of experimental data,<sup>30-32</sup> that  $\pi$  back-bonding is more important relative to the ligand-metal  $\sigma$  bond for stibines than for arsines or phosphines. Appreciable double-bond character in the Pt-Sb bond could also explain the high trans effect of stibines relative to arsines and phosphines in the complexes studied by Cheeseman, *et al.*<sup>33</sup>

Our results imply that the Pt-L  $\sigma$  bond for the other ligands under consideration is not appreciably affected by any Pt-L  $\pi$  bonding. That is, the ligands studied, other than CO and  $\text{Sb}(\text{C}_6\text{H}_5)_3$ , do not utilize synergic  $\sigma$ - $\pi$  bonding in these complexes. Olefinic and acetylenic ligands which must utilize a  $\sigma$ - $\pi$  synergic bonding mechanism do not form stable cationic trifluoromethylplatinum(II) cations. We would expect, however, that these compounds would also give values of  $(J_{\text{Pt}-\text{CF}_3}/$

(29) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 728.

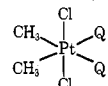
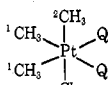
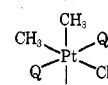
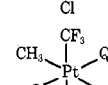
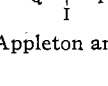
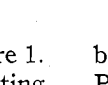
(30) C. R. Kistner, J. D. Blackman, and W. C. Harris, *Inorg. Chem.*, **8**, 2165 (1969).

(31) A. D. Westland, *Can. J. Chem.*, **47**, 4135 (1969).

(32) A. D. Westland, *J. Chem. Soc.*, 3060 (1965).

(33) T. P. Cheeseman, A. L. Odell, and H. A. Raethel, *Chem. Commun.*, 1496 (1968).

TABLE IV  
 COUPLING CONSTANTS INVOLVING  $^{95}\text{Pt}$ 

Pt(II) complex <sup>a</sup>	Pt(II) coupling, Hz	Ref	Pt(IV) complex <sup>a</sup>	Pt(IV) coupling, Hz	Ref	$J_{\text{Pt(IV)}}/J_{\text{Pt(II)}}$
$[\text{Pt}(\text{en})_2]\text{Cl}_2$	41.0 ( $^3J_{\text{Pt-N-CH}_2}$ )	b	<i>trans</i> - $[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Cl}_2$	26.0, 27.0 ( $^3J_{\text{Pt-N-CH}_2}$ )	b	0.64
			$[\text{Pt}(\text{en})_2]\text{Cl}_4$		c	0.66
<i>trans</i> - $\text{PtCl}[\text{P}(\text{n-Bu})_3]_2$	2380 ( $^1J_{\text{Pt-P}}$ )	26	<i>trans</i> - $\text{PtCl}_4[\text{P}(\text{n-Bu})_3]_2$	1462 ( $^1J_{\text{Pt-P}}$ )	26	0.615
<i>cis</i> - $\text{PtCl}_2[\text{P}(\text{n-Bu})_3]_2$	3508 ( $^1J_{\text{Pt-P}}$ )	26	<i>cis</i> - $\text{PtCl}_4[\text{P}(\text{n-Bu})_3]_2$	2070 ( $^1J_{\text{Pt-P}}$ )	26	0.590
<i>cis</i> - $\text{Pt}(\text{CH}_3)_2\text{Q}_2$	19 ( $^3J_{\text{Pt-P-CH}_3}$ )	18		10.5 ( $^3J_{\text{Pt-P-CH}_3}$ )	18	0.55
	67 ( $^2J_{\text{Pt-CH}_3}$ )			57 ( $^2J_{\text{Pt-CH}_3}$ )		0.85
				56 ( $^2J_{\text{Pt-}^2\text{CH}_3}$ )	18	0.84
<i>trans</i> - $\text{PtCl}(\text{CH}_3)_2\text{Q}_2$	85 ( $^2J_{\text{Pt-CH}_3}$ )	18		68 ( $^2J_{\text{Pt-CH}_3}$ )	18	0.80
	29.5 ( $^3J_{\text{Pt-P-CH}_3}$ )			17.6 ( $^3J_{\text{Pt-P-CH}_3}$ )		0.60
<i>trans</i> - $\text{PtI}(\text{CH}_3)_2\text{Q}_2$	80 ( $^2J_{\text{Pt-CH}_3}$ )	18		65 ( $^2J_{\text{Pt-CH}_3}$ )	15	0.81
<i>trans</i> - $\text{PtI}(\text{CF}_3)_2\text{Q}_2$	753 ( $^2J_{\text{Pt-CF}_3}$ )	15		505 ( $^2J_{\text{Pt-CF}_3}$ )	15	0.67

<sup>a</sup> Q = P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>); en = NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>. <sup>b</sup> T. G. Appleton and J. R. Hall, *Inorg. Chem.*, **10**, 1717 (1971). <sup>c</sup> T. G. Appleton, J. R. Hall, and C. J. Hawkins, *ibid.*, **9**, 1299 (1970).

$J_{\text{Pt-CH}_3}$ ) which would deviate from the line in Figure 1.

The slope ( $J_{\text{Pt-CF}_3}/J_{\text{Pt-CH}_3}$ ) of the line representing Pt(IV) complexes is significantly smaller than that for the Pt(II) complexes. From Table IV, it is clear that this is because the methylplatinum constants are "anomalously" high for Pt(IV) complexes. As pointed out by Pidcock, *et al.*,<sup>26</sup> on oxidation from square-planar Pt(II) to octahedral Pt(IV), the s orbital originally used in forming four hybrid orbitals must now be shared by six, so that  $\alpha^2_{\text{Pt(IV)}}/\alpha^2_{\text{Pt(II)}}$  would be 0.67, and if coupling depends mainly on  $\alpha^2_{\text{Pt}}$ , the ratio  $J_{\text{Pt(IV)}}/J_{\text{Pt(II)}}$  for a given nucleus coupled to Pt should approximate to this value. This argument is strictly applicable only when all the ligands attached to platinum are the same or similar in their demand for Pt(6s) orbital participation (*e.g.*, the ethylenediamine complexes in Table IV, for which nearly theoretical values are obtained). The situation is less clear-cut when ligands of different types are bound to Pt, but  $J_{\text{Pt(IV)}}/J_{\text{Pt(II)}}$  might be expected to approach 0.67 under the following conditions. (i) The coupling must be dominated by  $\alpha^2_{\text{Pt}}$ . All other factors in (2) and analogous equations must remain almost constant on oxidation. (ii) The trans ligand remains the same. (iii) The ligand in question is as demanding of Pt(6s) orbital contribution to its bond with Pt(IV) relative to the other ligands as it is for Pt(II).

Condition (ii) is fulfilled for all the complexes in Table IV. The rather low values of the ratios  $J_{\text{Pt(IV)}}/J_{\text{Pt(II)}}$  involving phosphines<sup>26</sup> may reflect the crudity of the arguments above. Alternatively, the bond from "soft" phosphines to relatively "hard" Pt(IV) may be appreciably weaker than that to "soft" Pt(II), so that condition (iii) is not quite fulfilled.

Almost certainly, the high values of  $J_{\text{Pt(IV)-CH}_3}/J_{\text{Pt(II)-CH}_3}$  ( $\sim 0.8$ ) reflect a greater demand by the methyl group for Pt(6s) participation in its bonding to Pt(IV) (relative to other ligands) than with Pt(II) (*i.e.*, condition (iii) is not fulfilled). This is probably associated with the comparative stability of the Pt(IV)-CH<sub>3</sub> bond, which, for example, is cleaved much less readily than the Pt(II)-CH<sub>3</sub> bond. The Pt-CH<sub>3</sub>

bonds in the complexes *cis*-Pt(CH<sub>3</sub>)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> and *trans*-PtCl(CH<sub>3</sub>)(PR<sub>3</sub>)<sub>2</sub> are readily cleaved by HCl and halogens,<sup>34</sup> while very severe conditions (*e.g.*, refluxing Br<sub>2</sub> in the presence of HBr<sup>35</sup>) are required to cleave the methyl-platinum bonds in the complexes [PtX(CH<sub>3</sub>)<sub>3</sub>]<sub>4</sub>, where no "stabilizing ligands"<sup>34</sup> are present. The ratios  $J_{\text{Pt(IV)-CF}_3}/J_{\text{Pt(II)-CF}_3}$  are almost "theoretical" (Table IV), indicating that condition (iii) holds for the trifluoromethyl group.

<sup>19</sup>F Chemical Shifts.—Pitcher, Buckingham, and Stone<sup>36</sup> explained the downfield chemical shifts of  $\alpha$ -fluorine atoms in perfluoroalkyl-transition metal complexes in terms of paramagnetic screening resulting from overlap between filled F p orbitals and metal d orbitals. If the ligand L or Z is a strong  $\sigma$  donor, (i) the electron density on Pt will increase, causing expansion of the d orbitals, resulting in a downfield chemical shift, (ii) the electronegativity of the group bound to CF<sub>3</sub> would decrease, causing an upfield chemical shift, (iii) the ligand probably has a high trans influence (low Pt-CF<sub>3</sub> coupling), tending to increase the Pt-C bond length, decreasing the orbital overlap, and causing an upfield chemical shift, and (iv) the ligand is probably high in the spectrochemical series, so that the excitation energy at the Pt atom will be high, and the fluorine resonance will shift upfield.

The trends displayed in Figure 2 (chemical shift upfield increasing with decreasing  $J_{\text{Pt-CF}_3}$ ) suggest that (ii), (iii), and (iv) outweigh (i) within a series.

The relatively high chemical shifts for the trifluoromethyl group in the complexes Pt(CF<sub>3</sub>)<sub>2</sub>Q<sub>2</sub>L<sup>+</sup> where L = CO, RNC, and RCN probably reflect the effect of anisotropic magnetic fields generated by the triple bonds in these ligands. For these same ligands the phosphine-methyl resonances are further downfield than for other L (Table III). Similar effects have been observed in some platinum hydride complexes.<sup>37</sup> Al-

(34) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959).

(35) J. R. Hall and G. A. Swile, *Aust. J. Chem.*, **24**, 423 (1971).

(36) E. Pitcher, A. D. Buckingham, and F. G. A. Stone, *J. Chem. Phys.*, **36**, 124 (1962).

(37) H. C. Clark and H. Kurosawa, *J. Organometal. Chem.*, **36**, 399 (1972).

though some of the anionic ligands, Z, in the nonelectrolyte complexes contain multiple bonds, there appears to be no pronounced anisotropic effect here (even for Z = CN, where the phosphine-methyl resonance does occur well downfield).

**Vibrational Spectra of the Trifluoromethyl Groups.**—Cotton and Wing<sup>4</sup> observed two bands in the region 1000–1100 cm<sup>-1</sup> in the infrared spectrum of the complex CF<sub>3</sub>Mn(CO)<sub>5</sub> attributable to C–F stretching. On the basis of band shapes in the spectrum of the gaseous complex, the higher frequency band (1063 cm<sup>-1</sup>) was assigned to symmetric C–F stretching and the lower frequency band (1045 cm<sup>-1</sup>) to the degenerate stretching modes. This order was the reverse of that found for the molecules CF<sub>3</sub>X (X = Cl, Br, I) and for non-transition-metal complexes, such as Hg(CF<sub>3</sub>)<sub>2</sub>.<sup>38</sup> Johnson,<sup>7</sup> in his discussion of the CF<sub>3</sub><sup>-</sup> stretching vibrations of a number of trifluoromethyl complexes, follows Cotton's assignment and notes that for some complexes the lower (degenerate) band is split, presumably as a result of low molecular symmetry.

With the trifluoromethylplatinum complexes discussed in this paper, a moderately sharp, strong band was always observed near 1100 cm<sup>-1</sup>, and at least one broad band (often split into two or three resolvable peaks) near 1000 cm<sup>-1</sup> (Table I). The splitting of this lower frequency band again supports its assignment as corresponding to the degenerate modes.

In the complexes *trans*-PtZ(CF<sub>3</sub>)<sub>2</sub>Q<sub>2</sub> and Pt(CF<sub>3</sub>)<sub>2</sub>Q<sub>2</sub>L<sup>+</sup>, both bands are sensitive to changes in Z or L. However, the splitting of the lower frequency band, with its components varying considerably in relative intensities, makes frequency comparisons between complexes difficult, and the following discussion will deal mainly with the higher frequency (symmetric stretching) band.

It is clear from Table I that the frequency of this band within the series of complexes Pt(CF<sub>3</sub>)<sub>2</sub>Q<sub>2</sub>L<sup>+</sup> is not very sensitive to changes in electron density on Pt caused by varying L. Thus, for the weak  $\sigma$  donor acrylonitrile the frequency is 1107 cm<sup>-1</sup>, while for the strong  $\sigma$  donors ethyl isocyanide and the cyclic carbene the frequencies are 1109 and 1107 cm<sup>-1</sup>, respectively. The band frequency, however, falls well below 1100 cm<sup>-1</sup> for the phosphine, arsine, and stibine complexes, the order being P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> > P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> ~ As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> > Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>. One would be tempted to correlate this order with  $\pi$ -acceptor capacity of L, except that when L = CO (certainly a  $\pi$  acceptor<sup>29</sup>) this frequency becomes very high (1117 cm<sup>-1</sup>, highest frequency for all the complexes examined; in this case the degenerate stretching frequency 1053 cm<sup>-1</sup> is also very high). A more valid correlation is with the mass of L. The ligands for which the frequency is lowest are the heaviest in the series, while carbonyl, for which it is highest, is the lightest ligand. Of course, more is involved than the mass of the ligand as a whole. The mass of the donor atom is probably most important, followed by the weights of directly bound groups. Technically, the complex [Pt(CF<sub>3</sub>)<sub>2</sub>Q<sub>2</sub>{*p*-(NH=C(OCH<sub>3</sub>))C<sub>6</sub>F<sub>4</sub>(C(OCH<sub>3</sub>)=NH)}Pt(CF<sub>3</sub>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> has the heaviest ligand (taken as a whole), since it can be considered to contain another Pt atom. However, the heavy part of the ligand is removed from the metal by several bonds, and

(38) A. J. Downs, *J. Chem. Soc.*, 5273 (1963).

the C–F stretching frequency is similar to that for other N donors.

Similar comments apply to the nonelectrolyte complexes PtZ(CF<sub>3</sub>)<sub>2</sub>Q<sub>2</sub>. Electron density on Pt, as affected by changes in Z, has little effect within the series, since the frequency differs by only 1 cm<sup>-1</sup> between Z = nitrate (a weak donor) and Z = cyanide (a strong donor). Once again, there appears to be a correlation between ligand mass and the frequency. Lowest frequencies are obtained when Z is a halogen and decrease in the order Cl > Br > I. For the other Z (donor atom N, C, or O) the frequency is within 3 cm<sup>-1</sup> of 1100 cm<sup>-1</sup>.

Cotton<sup>4</sup> considered  $\pi$  back-bonding from filled metal d orbitals to the trifluoromethyl group to be chiefly responsible for the low C–F stretching frequencies in trifluoromethyl-transition metal complexes. It would be predicted from this that, as electron density on Pt decreased, with consequent reduction of the availability of suitable d electrons, these frequencies would increase. Conclusions from coupling constants (discussed above) suggest, however, that Pt–CF<sub>3</sub>  $\pi$  back-bonding is not important for Pt(II) complexes. Johnson<sup>7</sup> predicted that as the electron-pair affinity of the metal increases (*i.e.*, electron density on Pt decreases),  $\nu_{C-F}$  should increase. There does seem to be a general trend for the frequencies in the cationic complexes to be slightly higher than in the nonelectrolytes (with similar masses of ligand donor atoms). This would be consistent with either theory, but the effect of ligand mass on the frequency is much greater than this "electronegativity" effect.

Both theories would predict higher frequencies for Pt(IV) complexes than for Pt(II). The frequencies are actually somewhat lower. Once again, it appears that this frequency shift is caused by a ligand mass effect. The total mass of ligands coordinated to Pt is greater in general for Pt(IV) than Pt(II), since Pt(IV) complexes contain two additional ligands. This hypothesis is supported by the frequencies observed in the complexes PtZ(CF<sub>3</sub>)(CH<sub>3</sub>)<sub>2</sub>Q<sub>2</sub>, Z = I, Cl (27, 28 in Table III). The frequency for the chloro complex (1092 cm<sup>-1</sup>) is considerably higher than for the iodo complex (1084 cm<sup>-1</sup>). For the other isomer of the iodo complex (26) the frequency is 1085 cm<sup>-1</sup>, so that the frequency is not very dependent on the particular ligand *trans*- to the trifluoromethyl group (iodide in the complex (26), phosphine in the complex (27)).

The dependence of  $\nu_{C-F}(\text{sym})$  on the mass of the ligands coordinated to Pt presumably occurs *via* coupling between the C–F stretching modes and  $\nu_{Pt-C}$ , which, in turn, must be sensitive to the mass of metal plus ligands. Such vibrational coupling may help to explain the absence, in both Raman and infrared spectra, of any reasonably intense band assignable to Pt–C stretching in these complexes, although corresponding methylplatinum complexes show moderately intense  $\nu_{Pt-C}$  bands in their Raman spectra.<sup>39–41</sup> The only band present in (some) trifluoromethylplatinum complexes not present in corresponding methylplatinum complexes in the region 200–600 cm<sup>-1</sup> was a very weak

(39) M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **10**, 1711 (1971).

(40) H. C. Clark and L. E. Manzer, *Chem. Commun.*, 387 (1971); *Inorg. Chem.*, **10**, 2699 (1971).

(41) H. C. Clark and L. E. Manzer, *J. Organometal. Chem.*, **30**, C89 (1971); *Inorg. Chem.*, **11**, 503 (1972).

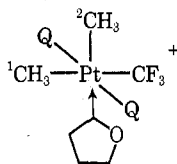
band in the vicinity of  $300\text{ cm}^{-1}$ , which may have some Pt-C stretching character. The C-F stretching bands were very weak in the Raman spectra.

**Trans Influence of the Trifluoromethyl Group.**—If  ${}^3J_{\text{Pt-P-CH}_3}$  depends mainly on  $\alpha^2_{\text{Pt}}$  in the Pt-P bond, the values of this coupling constant for the phosphine trans to Z or R in the complexes  $\text{PtZQ}_2^+$  and  $\text{PtRQ}_2^+$  (where R is a  $\sigma$ -bonded alkyl or aryl group) can be used to determine the trans influence of R, Z. A few such coupling constants are listed in Table V. The trans

TABLE V  
 ${}^3J_{\text{Pt-P-CH}_3}$  IN  $[\text{Pt}(\text{R})\text{Q}_2][\text{PF}_6]$  COMPLEXES

R	${}^3J_{\text{Pt-P-CH}_3}$ , Hz		Ref
	Cis to R	Trans to R	
Cl	23.5	40.0	11
$\text{CF}_3$	28.0	19.0	
$\text{CH}_3$	30.0	18.5	11

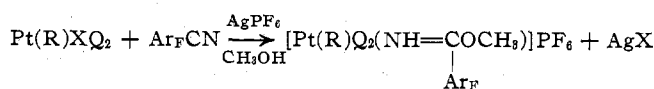
influence order deduced from these values is  $\text{CH}_3 > \text{CF}_3 > \text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5) \gg \text{Cl}$ . The trifluoromethyl group is almost as high in this series as the methyl group (*i.e.*, has almost the same effect on Pt hybridization) which would not be expected on the basis of a comparison between the electronegativities of the two groups. Despite the smaller degree of charge transfer to Pt, the trifluoromethyl group must form very strong covalent bonds with platinum, with much s character. This conclusion is consistent with the recent observation of a very low value of  ${}^2J_{\text{Pt-}^1\text{CH}_3}$  in the complex<sup>18</sup>



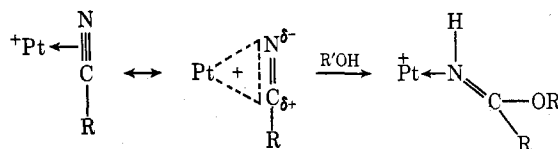
**Comparisons between Reactions and Properties of Trifluoromethyl- and Methylplatinum Complexes.**—Because the trifluoromethyl group is comparable both on steric grounds and in its effect on Pt hybridization to the methyl group, the chief difference between the moieties " $\text{CH}_3\text{PtQ}_2^+$ " and " $\text{CF}_3\text{PtQ}_2^+$ " will be the electron density on the Pt atom, since the more electronegative trifluoromethyl group will transfer less charge to the metal ion. The effect of this on the synergically bonding carbonyl and triphenylstibine ligands has already been discussed. Olefins and acetylenes also use synergic  $\sigma$ - $\pi$  bonding in their transition metal complexes and would be expected to form less stable complexes with the trifluoromethylplatinum group than with the methylplatinum group. Indeed, no simple complexes of the type  $\text{Pt}(\text{CF}_3)\text{Q}_2$  (unsaturated hydrocarbon)<sup>+</sup>, analogous to the known methylplatinum complexes,<sup>42</sup> have been sufficiently stable to be isolated. However, the complexes  $\text{trans-Pt}(\text{CF}_3)\text{Q}_2(\text{HC}\equiv\text{CH})^+$  and  $\text{trans-Pt}(\text{CF}_3)\text{Q}_2(\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{OH})^+$  must exist at least fleetingly in solution, since they are intermediates in the formation of the carbene complexes<sup>16,38</sup>  $\text{trans-Pt}(\text{CF}_3)\text{Q}_2\{\text{C}(\text{CH}_3)(\text{OCH}_3)\}^+$  and  $\text{trans-Pt}(\text{CF}_3)\text{Q}_2\{\text{C}(\text{CH}_2)_3\text{O}\}^+$ , respectively.

Some subtle effects of the relatively positive Pt atom in trifluoromethyl complexes can be seen in the re-

actions of alcohols with nitrile complexes. We have found that the reaction



(where X = Cl, I;  $\text{Ar}_F$  is a perfluoroaryl group) occurs more readily when R =  $\text{CF}_3$  than when R =  $\text{CH}_3$ . We have suggested<sup>40</sup> that these reactions proceed *via* a  $\pi$ -nitrile complex, which then undergoes nucleophilic attack



Since coupling constants suggest that  $\pi$ -nitrile is a better  $\sigma$  donor than  $\sigma$ -nitrile when R is a perfluoroaryl group,<sup>40</sup> the decreased electron density on the Pt atom in the trifluoromethyl complexes causes the preference for the  $\pi$ -bonded form to be greater than for the methyl complexes. Consequently, nucleophilic attack occurs more readily.

The low electron density on Pt in trifluoromethyl complexes is also reflected in the Raman spectra of coordinated nitriles and isocyanides. The frequencies of the  $\nu_{\text{C=N}}$  bands for various complexes are given in Table VI, together with the values of  $\Delta\nu_{\text{CN}}$  ( $\nu_{\text{CN}}(\text{complex}) - \nu_{\text{CN}}(\text{free ligand})$ ). For the isocyanides,  $\Delta\nu_{\text{CN}}$  decreases with increasing negative charge on the Pt atom.<sup>41</sup> As expected,  $\Delta\nu_{\text{CN}}$  is greater for the complexes  $\text{Pt}(\text{CF}_3)\text{Q}_2(\text{CN-R})^+$  than for  $\text{Pt}(\text{CH}_3)\text{Q}_2(\text{CN-R})^+$ .  $\Delta\nu_{\text{CN}}$  for  $\text{Pt}(\text{CF}_3)\text{Q}_2(\text{CN-C}_2\text{H}_5)^+$  is between the values for  $\text{PtClQ}_2(\text{CN-C}_2\text{H}_5)^+$  and  $\text{PtIQ}_2(\text{CN-C}_2\text{H}_5)^+$ , consistent with an electronegativity for the trifluoromethyl group between the values for the two halides.

The characteristic  $\nu_{\text{CN}}$  bands for coordinated nitriles and cyanide (where  $\nu_{\text{CN}}$  occurs as a doublet in the solid-state Raman spectrum) all occur at higher frequencies in trifluoromethyl complexes than in methylplatinum compounds, reflecting greater ligand-metal charge transfer and/or less  $\pi$  interaction between Pt and the ligand in the trifluoromethylplatinum complexes. Only with cyanate (NCO) and thiocyanate (NCS) is the  $\nu_{\text{N=C}}$  frequency lower in the trifluoromethyl complex. Here the C-O or C-S bond can acquire some double-bond character at the expense of N-C triple-bond character.<sup>19</sup> The high value of  $\nu_{\text{CO}}$  in the complex  $\text{Pt}(\text{CF}_3)\text{Q}_2(\text{CO})^+$  has already been mentioned.

### Experimental Section

**Preparation of Complexes.**—*trans*- $\text{PtI}(\text{CF}_3)\text{Q}_2$  was prepared as previously described<sup>15</sup> and served as the starting material for the preparation of all other trifluoromethylplatinum(II) complexes.

**Nonelectrolyte Complexes.**—The complexes *trans*- $\text{Pt}(\text{CF}_3)\text{ZQ}_2$  were prepared by a general method for Z = Br, Cl, NCS, NCO,  $\text{N}_3$ , and  $\text{NO}_2$ , which may be illustrated by the preparation of the nitrite complex.

$\text{PtI}(\text{CF}_3)\text{Q}_2$  (0.323 g, 0.48 mmol) dissolved in boiling methanol was treated with a solution of 0.104 g of  $\text{AgBF}_4$  (0.54 mmol) in methanol. Yellow silver iodide precipitated immediately. The colorless solution was filtered from this precipitate, and excess solid sodium nitrite was added. The solution was evaporated to dryness. The solid residue was extracted with dichloromethane, the solution was filtered, passed down a short Florisil column (to remove traces of silver salts), and evaporated to dryness. The



TABLE VI  
 SOME CHARACTERISTIC LIGAND VIBRATIONAL BANDS

Complex <sup>a</sup>	Band <sup>b</sup>	R = CH <sub>3</sub>		R = CF <sub>3</sub>	
		$\nu$ , cm <sup>-1</sup>	$\Delta\nu$ , <sup>c</sup> cm <sup>-1</sup>	$\nu$ , cm <sup>-1</sup>	$\Delta\nu$ , <sup>c</sup> cm <sup>-1</sup>
[Pt(R)Q <sub>2</sub> (NCC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )] [PF <sub>6</sub> ]	$\nu_{C=N}$ (R)	2270	57	2283	70
[Pt(R)Q <sub>2</sub> (CNC <sub>6</sub> H <sub>5</sub> )] [PF <sub>6</sub> ] <sup>e</sup>	$\nu_{N=C}$ (R)	2234	83	2256	105
[Pt(R)Q <sub>2</sub> ( <i>p</i> -CNC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )] [PF <sub>6</sub> ]	$\nu_{N=C}$ (R)	2193	68	2223	98
[Pt(R)Q <sub>2</sub> (CO)] [PF <sub>6</sub> ] <sup>d</sup>	$\nu_{C=O}$ (ir)	2095	-48	2140	-3
Pt(NCO)(R)Q <sub>2</sub>	$\nu_{N=C}$ (ir)	2240	75	2245	80
Pt(NCS)(R)Q <sub>2</sub>	$\nu_{N=C}$ (ir)	2120	79	2108	67
Pt(CN)(R)Q <sub>2</sub>	$\nu_{C=N}$ (R)	2111	30	2134	53
		2118	37	2143	62

<sup>a</sup> Q = P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>). <sup>b</sup> ir = infrared; R = Raman. <sup>c</sup>  $\Delta\nu = \nu(\text{complex}) - \nu(\text{free ligand})$ . <sup>d</sup> See ref 11 for preparation and spectrum of methyl complex. <sup>e</sup>  $\Delta\nu_{C=N}$ : R = Cl, 116 cm<sup>-1</sup>; R = I, 100 cm<sup>-1</sup>.

resultant solid was recrystallized from methanol to give colorless crystals (first crop 0.111 g).

Different procedures were used for Z = NO<sub>2</sub> and CN.

**Z = NO<sub>2</sub>.**—To a solution of 0.142 g of PtI(CF<sub>3</sub>)Q<sub>2</sub> in acetone was added excess ground silver nitrate. The suspension was warmed. Small quantities of silver nitrate were added until the particles no longer became coated with silver iodide (yellow). The suspended AgI and AgNO<sub>3</sub> were filtered off, and the solution was evaporated to dryness. The resultant solid was recrystallized from methanol to give colorless crystals (first crop 0.092 g).

**Z = CN.**—Great care was required in the preparation of *trans*-Pt(CN)(CF<sub>3</sub>)Q<sub>2</sub>, apparently because of the ability of cyanide to displace the phosphine ligands to yield complexes of the type Na[Pt(CN)<sub>2</sub>(CF<sub>3</sub>)Q]. The odor of phosphine was always noticed above the solution during the preparation. To a solution of 0.469 g of PtI(CF<sub>3</sub>)Q<sub>2</sub> (0.70 mmol) in boiling methanol was added a solution containing 0.2 g of AgPF<sub>6</sub> (0.79 mmol). Silver iodide was filtered off, and to the filtrate was added a solution of 0.04 g of sodium cyanide in methanol. The solution was evaporated to dryness to give an oil which was extracted with dichloromethane. When the filtered solution was evaporated, an oil was obtained which could not be crystallized. This oil was redissolved in dichloromethane and the solution was passed down a long Florisil column. Evaporation of the eluted solution gave a white solid which was recrystallized from ether-hexane (0.099 g).

The complexes *trans*-Pt(CH<sub>3</sub>)ZQ<sub>2</sub> which have not previously been prepared (Table II) were prepared by methods analogous to those used for the corresponding trifluoromethyl complexes, starting with *trans*-PtCl(CH<sub>3</sub>)Q<sub>2</sub>. For Z = NO<sub>2</sub>, NCS, and NCO the product was recrystallized from dichloromethane-hexane. For Z = NO<sub>2</sub>, crystallization occurred only with difficulty, and the complex could not be satisfactorily recrystallized from any solvent. Again, care was required for Z = CN. The oil obtained from evaporating a dichloromethane solution slowly crystallized under diethyl ether. For Z = N<sub>3</sub>, a pure complex could not be obtained.

**Cationic Complexes.**—The preparation of the complexes *trans*-[Pt(CF<sub>3</sub>)Q<sub>2</sub>L] [PF<sub>6</sub>] is illustrated by that of the *p*-NCC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub> complex. To a suspension of *trans*-PtI(CF<sub>3</sub>)Q<sub>2</sub> (0.171 g, 0.256 mmol) in 10 ml of methanol was added AgPF<sub>6</sub> (0.065 g,

0.258 mmol). Silver iodide was removed by centrifuge to give a colorless solution. *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CN (0.034 g, 0.255 mmol) in 2 ml of methanol was added. Solvent was removed on a rotary evaporator to give a pale yellow oil. This was dissolved in 2 ml of dichloromethane and diethyl ether was slowly added. White needles of *trans*-[Pt(CF<sub>3</sub>)Q<sub>2</sub>(*p*-NCC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)] [PF<sub>6</sub>] precipitated (0.140 g).

The imino ether complex [Pt(CF<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]Pt(CF<sub>3</sub>)Q<sub>2</sub>] [PF<sub>6</sub>]<sub>2</sub> was prepared by the following procedure. To a suspension of PtI(CF<sub>3</sub>)Q<sub>2</sub> (0.176 g, 0.264 mmol) in methanol was added AgPF<sub>6</sub> (0.067 g, 0.264 mmol) in 2 ml of methanol. Silver iodide was removed by centrifuge and *p*-NCC<sub>6</sub>F<sub>4</sub>CN was added (0.026 g, 0.013 mmol). The solution was stirred for 10 min. The volume of methanol was reduced to give a white precipitate which was filtered off and washed with ether and then pentane. The product was recrystallized from dichloromethane-ether (0.124 g). The preparation of [Pt(CF<sub>3</sub>)Q<sub>2</sub>{NH=C(OCH<sub>3</sub>)C<sub>6</sub>F<sub>3</sub>}] [PF<sub>6</sub>] was similar, except that the PtI-(CF<sub>3</sub>)Q<sub>2</sub>:nitrile molar ratio was halved.

Preparation of the complexes with L = acetone or a carbene has been previously described.<sup>16</sup>

**Spectra.**—<sup>1</sup>H and <sup>19</sup>F nmr spectra were run on a Varian HA-100 spectrometer, the former at 100 MHz with tetramethylsilane as internal reference-lock signal and the latter at 94.1 MHz with "Freon-11" (CFCl<sub>3</sub>) as the internal reference. Infrared spectra were run on a Beckman IR-7 spectrometer as Nujol mulls between CsI disks. Raman spectra were run on a Spex 1400 spectrometer (McMaster University, Hamilton, Ontario, Canada) using a He-Ne (6328 Å) or an argon (5145 Å) laser.

Analyses were obtained from Schwarzkopf Microanalytical Laboratory Inc., Woodside, N. Y., and Chemalytics Inc., Tempe, Ariz.

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