

## PROTONATION OF SOME FLUOROOLEFIN COMPLEXES OF PLATINUM(0)

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(Received May 2nd, 1972)

### SUMMARY

The zerovalent olefin complexes  $\text{Pt}(\text{C}_2\text{F}_4)\text{L}_2$ , ( $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{PEt}_2\text{Ph}, \text{PMePh}_2$ , or  $\text{PBu}_3$ ;  $\text{L}_2 = 2,2'$ -bipyridine) readily react with trifluoroacetic acid to give a convenient synthesis of the tetrafluoroethyl complexes,  $\text{Pt}(\text{OCOCF}_3)(\text{CF}_2\text{CF}_2\text{H})\text{L}_2$ . Similar reactions occur with hexafluoropropene, trifluoroethylene, chlorotrifluoroethylene, bromotrifluoroethylene and tetrachloroethylene complexes. Reactions of some of the complexes with hydrogen chloride, tertiary butyl chloride and mercury(II) chloride have also been examined. The nature of the ligand L appears to have a large effect on the reactivity of the tetrafluoroethylene complexes with hydrogen chloride.

### INTRODUCTION

In some previous studies<sup>1</sup> we have shown that electrophilic addition to fluoro-olefins is greatly enhanced by coordination of the fluoro-olefin to rhodium(I). As a continuation of these studies we have now examined the reactivity of a range of fluoro-olefin complexes of the type  $\text{Pt}(\text{Fluoro-olefin})\text{L}_2$  towards protonic acids which provides a very convenient synthesis of a variety of platinum(II) fluoroethyl complexes\*.

### RESULTS AND DISCUSSION

A variety of tetrafluoroethylene complexes of platinum(0),  $\text{Pt}(\text{C}_2\text{F}_4)\text{L}_2$ , ( $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{PEt}_2\text{Ph}, \text{PMePh}_2$ , or  $\text{PBu}_3$ ;  $\text{L}_2 = 2,2'$ -bipyridine) in methylene chloride solution readily react with trifluoroacetic acid to give tetrafluoroethyl complexes,  $\text{Pt}(\text{OCOCF}_3)(\text{CF}_2\text{CF}_2\text{H})\text{L}_2$ . The IR spectra of these crystalline air-stable complexes show bands characteristic of a unidentate trifluoroacetate ligand<sup>3</sup> and the <sup>19</sup>F NMR spectra of the more soluble complexes provide good evidence for the presence of a tetrafluoroethyl ligand. In addition the <sup>19</sup>F NMR spectra of the phenyl-diethylphosphine and tri-n-butylphosphine complexes, (Ia) and (Ib) respectively, suggest that these complexes have a *trans* configuration of ligands around the platinum. This isomerisation which therefore occurs during the preparation of these

\* For a preliminary account see ref. 2.



$\text{Pt}(\text{C}_2\text{Cl}_4)(\text{PPh}_3)_2$  also leads to a complex which on the basis of microanalytical and infrared data can be formulated as a tetrachloroalkyl complex,  $\text{Pt}(\text{OCOFCF}_3)-(\text{C}_2\text{Cl}_4\text{H})(\text{PPh}_3)_2$ . However, trifluoroacetic acid has no action on  $\text{Pt}(\text{hexafluorocyclobutene})(\text{PPh}_3)_2$  in refluxing chloroform.

Previous studies by Clark<sup>10</sup> have shown that a tetrafluoroethyl complex, *trans*- $\text{PtCl}(\text{CF}_2\text{CF}_2\text{H})(\text{PEt}_3)_2$  can be isolated from the action of tetrafluoroethylene on *trans*- $\text{PtClH}(\text{PEt}_3)_2$  in a stainless steel autoclave. However, in a glass vessel this type of reaction usually leads to fluorovinyl complexes, e.g. *trans*- $\text{PtCl}(\text{CF}=\text{CF}_2)(\text{PEt}_3)_2$ , and the intermediate tetrafluoroethyl complex is not isolated.

Since the reaction of mercury(II) chloride or bromide with the complexes  $\text{Pt}(\text{CF}_3\text{C}\equiv\text{CCF}_3)\text{L}_2$  ( $\text{L} = \text{PPh}_3$  or  $\text{PMePh}_2$ ) leads to mercurated products,  $\text{PtX}[\text{CCF}_3=\text{C}(\text{HgX})\text{CF}_3]\text{L}_2$ , ( $\text{X} = \text{Cl}$  or  $\text{Br}$ )<sup>4</sup> the reaction of mercury(II) chloride with  $\text{Pt}(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$  was therefore studied. However, no mercurated derivative could be prepared and only a mixture of *cis*- and *trans*- $\text{PtCl}_2(\text{PPh}_3)_2$  could be isolated. Similarly, attempts to alkylate the tetrafluoroethylene ligand in the complex  $\text{Pt}(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$  with tertiary butyl chloride also leads to a mixture of *cis*- and *trans*- $\text{PtCl}_2(\text{PPh}_3)_2$  and in this context it is noteworthy that Clark<sup>11</sup> has found that methyl iodide reacts with  $\text{Pt}(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$  to give  $\text{PtI}_2\text{Me}_2(\text{PPh}_3)_2$ .

In conclusion it is interesting to note that fluoro-olefin complexes of rhodium(I) appear to be more susceptible to protonation than platinum(0) complexes. Thus  $\text{RhCl}(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$  readily reacts with hydrogen chloride but  $\text{Pt}(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$  does not. This increased reactivity of the rhodium(I) complexes is probably related to the weaker metal-olefin bonding found with second row transition metals. The strength of the platinum-olefin bond in the zerovalent complexes clearly also has an effect on the course of the reaction. Thus the action of acid on the ethylene complex,  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ , does not lead to an alkyl complex<sup>12</sup> since the olefin complex is appreciably dissociated in solution. Similarly we find that the action of trifluoroacetic acid on  $\text{Pt}(\text{CF}_2=\text{CH}_2)(\text{PPh}_3)_2$ , in which the metal-olefin bond is also quite labile, leads to  $\text{Pt}(\text{OCOFCF}_3)_2(\text{PPh}_3)_2$ .

## EXPERIMENTAL

Analytical data, yields and melting points for all new complexes are given in Table 1. Infrared spectra were recorded in Nujol mulls on a Perkin-Elmer model 225 spectrophotometer. Proton and <sup>19</sup>F NMR spectra were obtained using Varian Associates T60 and DA60 spectrometers respectively. The <sup>19</sup>F NMR spectra were measured relative to benzotrifluoride as internal standard and were recorded at 56.4 MHz.

The complexes  $\text{Pt}(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$ <sup>13,14</sup>,  $\text{Pt}(\text{C}_2\text{F}_4)(\text{AsPh}_3)_2$ <sup>6</sup>,  $\text{Pt}(\text{C}_2\text{F}_4)(\text{PEt}_2\text{Ph})_2$ <sup>6</sup>,  $\text{Pt}(\text{C}_2\text{F}_4)(\text{PMePh}_2)_2$ <sup>6</sup>,  $\text{Pt}(\text{C}_2\text{F}_4)(\text{PMe}_2\text{Ph})_2$ <sup>6</sup>,  $\text{Pt}(\text{C}_2\text{F}_4)(\text{PBu}_3)_2$ <sup>6</sup>,  $\text{Pt}(\text{C}_2\text{F}_4)(\text{Bipy})_2$ <sup>6</sup>,  $\text{Pt}(\text{C}_2\text{F}_3\text{Br})(\text{PPh}_3)_2$ <sup>13</sup>,  $\text{Pt}(\text{C}_2\text{F}_3\text{Cl})(\text{PPh}_3)_2$ <sup>13</sup>,  $\text{Pt}(\text{C}_3\text{F}_6)(\text{PPh}_3)_2$ <sup>13</sup>,  $\text{Pt}(\text{cyclo-C}_4\text{F}_6)(\text{PPh}_3)_2$ <sup>13</sup>, and  $\text{Pt}(\text{C}_2\text{Cl}_4)(\text{PPh}_3)_2$ <sup>14</sup> were prepared as described in the literature. The chlorotrifluoroethylene and hexafluoropropene complexes,  $\text{Pt}(\text{C}_2\text{F}_3\text{Cl})(\text{PEt}_2\text{Ph})_2$  and  $\text{Pt}(\text{C}_3\text{F}_6)(\text{PEt}_2\text{Ph})_2$  were prepared by the reaction of phenyldiethylphosphine with the corresponding triphenylarsine complex using the method which we have described previously<sup>6</sup>.

TABLE 1

## ANALYTICAL DATA FOR COMPLEXES

Compound	Yield (%)	M.p. <sup>a</sup> (°C)	Analysis, found (calcd.) (%)		
			C	H	F
Pt(C <sub>2</sub> F <sub>3</sub> H)(PPh <sub>3</sub> ) <sub>2</sub>	89	170-172	57.1 (57.0)	4.0 (3.9)	
Pt(CF <sub>2</sub> CH <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	63	132-135	58.0 (58.2)	4.0 (4.1)	
Pt(C <sub>2</sub> F <sub>3</sub> Cl)(AsPh <sub>3</sub> ) <sub>2</sub>	50	162-165	49.0 (48.3)	3.3 (3.3)	6.1 (6.2)
Pt(C <sub>3</sub> F <sub>6</sub> )(AsPh <sub>3</sub> ) <sub>2</sub>	50	188-191	49.0 (48.9)	3.2 (3.2)	12.2 (12.2)
Pt(C <sub>2</sub> F <sub>3</sub> Cl)(PEt <sub>2</sub> Ph) <sub>2</sub>	50	106-110	41.2 (40.9)	4.8 (4.9)	9.1 (8.8)
Pt(C <sub>3</sub> F <sub>6</sub> )(PEt <sub>2</sub> Ph) <sub>2</sub>	89	108-112	41.2 (40.8)	4.3 (4.5)	16.9 (16.9)
Pt(OCOCF <sub>3</sub> )(CF <sub>2</sub> CF <sub>2</sub> H)(PPh <sub>3</sub> ) <sub>2</sub>	85	214-216	52.0 (51.8)	3.2 (3.3)	14.1 (14.2)
Pt(OCOCF <sub>3</sub> )(CF <sub>2</sub> CF <sub>2</sub> H)(AsPh <sub>3</sub> ) <sub>2</sub>	81	200-204	47.3 (47.3)	3.1 (3.1)	13.8 (13.8)
Pt(OCOCF <sub>3</sub> )(CF <sub>2</sub> CF <sub>2</sub> H)(PEt <sub>2</sub> Ph) <sub>2</sub>	74	201-203	39.3 (38.3)	4.0 (4.2)	17.9 (17.9)
Pt(OCOCF <sub>3</sub> )(CF <sub>2</sub> CF <sub>2</sub> H)(PMePh <sub>2</sub> ) <sub>2</sub>	92	128-130	44.2 (44.5)	3.4 (3.4)	17.0 (17.0)
Pt(OCOCF <sub>3</sub> )(CF <sub>2</sub> CF <sub>2</sub> H)(PBu <sub>3</sub> ) <sub>2</sub>	92	ca. 30	42.7 (41.3)	6.5 (6.8)	15.7 (16.4)
Pt(OCOCF <sub>3</sub> )(CF <sub>2</sub> CF <sub>2</sub> H)(Bipy) <sup>b</sup>	95	263-266	30.0 (29.8)	1.6 (1.6)	26.0 (25.5)
Pt(Cl)(CF <sub>2</sub> CF <sub>2</sub> H)(Bipy) <sup>c</sup>	70	270-276	29.7 (29.5)	1.8 (1.9)	13.8 (14.6)
Pt(OCOCF <sub>3</sub> )(C <sub>3</sub> F <sub>6</sub> H)(PPh <sub>3</sub> ) <sub>2</sub>	68	188-189	50.4 (50.1)	3.2 (3.2)	17.1 (17.3)
Pt(OCOCF <sub>3</sub> )(C <sub>3</sub> F <sub>6</sub> H)(AsPh <sub>3</sub> ) <sub>2</sub>	90	190-195	49.5 (49.9)	3.0 (2.9)	15.7 (15.9)
Pt(OCOCF <sub>3</sub> )(C <sub>2</sub> F <sub>3</sub> ClH)(PPh <sub>3</sub> ) <sub>2</sub>	73	225-227	50.8 (50.6)	3.4 (3.3)	11.9 (12.0)
Pt(OCOCF <sub>3</sub> )(C <sub>2</sub> F <sub>3</sub> ClH)(AsPh <sub>3</sub> ) <sub>2</sub>	87	175-177	46.6 (46.3)	3.1 (3.0)	11.4 (11.0)
Pt(OCOCF <sub>3</sub> )(C <sub>2</sub> F <sub>3</sub> BrH)(PPh <sub>3</sub> ) <sub>2</sub>	52	246-250	49.0 (48.3)	3.2 (3.1)	7.1 (7.4)
Pt(OCOCF <sub>3</sub> )(C <sub>2</sub> F <sub>3</sub> H <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	94	175-178	52.7 (52.5)	3.6 (3.5)	
Pt(OCOCF <sub>3</sub> )(C <sub>2</sub> Cl <sub>4</sub> H)(PPh <sub>3</sub> ) <sub>2</sub>	84	122-124	48.3 (48.1)	3.2 (3.7)	5.9 (5.7)

<sup>a</sup> With decomposition. <sup>b</sup> Found N 5.1, calcd. 5.0%. <sup>c</sup> Found Cl 6.9, calcd. 7.3%; N 5.9, calcd. 5.7%.

(Trifluoroethylene)bis(triphenylphosphine)platinum(0)

Excess trifluoroethylene was condensed onto a solution of Pt(*trans*-Stilbene)-(PPh<sub>3</sub>)<sub>2</sub> (0.8 g) in benzene (15 ml) contained in a thick-walled glass tube cooled in liquid nitrogen. The tube was sealed, allowed to warm to room temperature and heated at 60° for 48 h. The tube was then cooled and opened and the solution was

evaporated to dryness under reduced pressure. Recrystallisation of the residue from methylene chloride/methanol gave white crystals of the required product.

*(1,1-Difluoroethylene)bis(triphenylphosphine)platinum(0)*

As above excess 1,1-difluoroethylene and Pt(*trans*-Stilbene)(PPh<sub>3</sub>)<sub>2</sub> (0.9 g) in benzene (40 ml) gave on recrystallisation from a methylene chloride/ethanol/oxygen-free water mixture white crystals of the required product. The complex is stable in a methylene chloride solution at 0° under an atmosphere of 1,1-difluoroethylene but slowly decomposes at room temperature in methylene chloride to give a deep orange solution.

*(Hexafluoropropene)bis(triphenylarsine)platinum(0)*

Using a similar procedure to that described above, excess hexafluoropropene and Pt(AsPh<sub>3</sub>)<sub>4</sub> (2 g) in benzene (50 ml) at room temperature for 72 h gave on recrystallisation from methylene chloride/methanol white crystals of the required product.

*(Chlorotrifluoroethylene)bis(triphenylarsine)platinum(0)*

As above excess chlorotrifluoroethylene and Pt(AsPh<sub>3</sub>)<sub>4</sub> (2g) in benzene (40 ml) at room temperature for 48 h gave on recrystallisation from methylene chloride/methanol white crystals of the required product.

*Reaction of trifluoroacetic acid with Pt(C<sub>2</sub>F<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>*

Pt(C<sub>2</sub>F<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub> (0.5 g) in methylene chloride (20 ml) and trifluoroacetic acid (0.2 ml) were allowed to stand at room temperature for 1 h in a stoppered flask. Petroleum spirit (b.p. 100–120°) was added and the reaction mixture was evaporated to dryness under reduced pressure to remove excess trifluoroacetic acid. Recrystallisation of the residue from methylene chloride/ethanol afforded white crystals of the required complex which was collected and dried *in vacuo*.  $\nu(\text{CO}_2)$  asym, 1682 s, 1687 s;  $\nu(\text{CO}_2)$  sym, 1411 ms,  $\text{cm}^{-1}$ .

The other protonation reactions using trifluoroacetic acid were similarly performed except that the reactions involving Pt(C<sub>2</sub>F<sub>3</sub>Cl)(PPh<sub>3</sub>)<sub>2</sub>, Pt(C<sub>2</sub>F<sub>3</sub>Cl)-(PEt<sub>2</sub>Ph)<sub>2</sub>, Pt(C<sub>2</sub>F<sub>3</sub>Cl)(AsPh<sub>3</sub>)<sub>2</sub>, Pt(C<sub>2</sub>Cl<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>, Pt(cyclo-hexafluorobutene)-(PPh<sub>3</sub>)<sub>2</sub> were heated under reflux for 12 h. The products so formed were Pt(OCOCF<sub>3</sub>)-(CF<sub>2</sub>CF<sub>2</sub>H)(Bipy);  $\nu(\text{CO}_2)$  asym, 1718 s, 1700 s,  $\text{cm}^{-1}$ ;  $\nu(\text{CO}_2)$  sym, 1407 ms,  $\text{cm}^{-1}$ . <sup>19</sup>F NMR spectrum (DMF): +12.0 ppm (s, 3 F, OCOCF<sub>3</sub>) with platinum satellites, *J*(PtF) 19 Hz; +42.3 ppm (m, 2 F,  $\alpha$ -CF<sub>2</sub>), with platinum satellites, *J*(PtF) 270 Hz; +71.9 ppm (d of t, 2 F, CF<sub>2</sub>H), *J*(HF) 52 Hz, *J*(FF) 7 Hz, *J*(PtF) not discernible. Pt(OCOCF<sub>3</sub>)(CF<sub>2</sub>CF<sub>2</sub>H)(PBu<sub>3</sub>)<sub>2</sub>;  $\nu(\text{CO}_2)$  asym, 1714 s, 1698 s,  $\text{cm}^{-1}$ ;  $\nu(\text{CO}_2)$  sym, 1404 ms,  $\text{cm}^{-1}$ . <sup>19</sup>F NMR spectrum (CH<sub>2</sub>Cl<sub>2</sub>): +11.7 ppm (s, 3 F, OCOCF<sub>3</sub>), with platinum satellites, *J*(PtF) 17 Hz; +13.2 ppm (t, 2 F,  $\alpha$ -CF<sub>2</sub>), with platinum satellites, *J*(PF) 25 Hz, *J*(PtF) ca. 500 Hz; +65.0 ppm (d, 2 F, CF<sub>2</sub>H), with platinum satellites, *J*(HF) 55 Hz, *J*(PtF) 102 Hz. Pt(OCOCF<sub>3</sub>)(CF<sub>2</sub>CF<sub>2</sub>H)(PMePh<sub>2</sub>)<sub>2</sub>;  $\nu(\text{CO}_2)$  asym, 1690 s,  $\text{cm}^{-1}$ ,  $\nu(\text{CO}_2)$  sym, 1408 s,  $\text{cm}^{-1}$ . <sup>19</sup>F NMR spectrum (CH<sub>2</sub>Cl<sub>2</sub>): +11.9 ppm (s, 3 F, OCOCF<sub>3</sub>),  $\alpha$ -CF<sub>2</sub> resonance obscured by OCOCF<sub>3</sub> resonance; platinum satellite peaks suggest doublet, *J*(PF) 33 Hz, *J*(PtF) 469 Hz; +66 ppm (d, 2 F, CF<sub>2</sub>H), with platinum satellites, *J*(HF) 53 Hz, *J*(PtF) 99 Hz. <sup>1</sup>H NMR

spectrum ( $\text{CDCl}_3$ ): 8.56  $\tau$  (d, 3 H, PMe), with platinum satellites,  $J(\text{PH})$  10 Hz,  $J(\text{PtH})$  50 Hz; 7.17 (d, 3 H, PMe), with platinum satellites,  $J(\text{PH})$  9.8 Hz,  $J(\text{PtH})$  18 Hz; 3.98 (t, 1 H,  $\text{CF}_2\text{H}$ ),  $J(\text{HF}_{\text{vic}})$  6 Hz,  $J(\text{HF}_{\text{gem}})$  not discernible; 2.3-2.9 (m, 20 H,  $\text{C}_6\text{H}_5\text{P}$ ).  $\text{Pt}(\text{OCOCF}_3)(\text{CF}_2\text{CF}_2\text{H})(\text{AsPh}_3)_2$ ;  $\nu(\text{CO}_2)$  asym 1680 s,  $\text{cm}^{-1}$ ,  $\nu(\text{CO}_2)$  sym, 1410 m,  $\text{cm}^{-1}$ .  $^{19}\text{F}$  NMR spectrum ( $\text{CH}_2\text{Cl}_2$ ): +9.4 ppm (q, 2 F,  $\alpha\text{-CF}_2$ ),  $J(\text{HF})=J(\text{FF})$ , 5.8 Hz, platinum satellites not discernible; +11.1 ppm (s, 3 F,  $\text{OCOCF}_3$ ); +65.5 ppm (d of t, 2 F,  $\text{CF}_2\text{H}$ ),  $J(\text{HF})$  58 Hz,  $J(\text{FF})$  not measurable,  $J(\text{PtF})$  not discernible.  $\text{Pt}(\text{OCOCF}_3)(\text{CF}_2\text{CF}_2\text{H})(\text{PEt}_2\text{Ph})_2$ ;  $^{19}\text{F}$  NMR spectrum ( $\text{CH}_2\text{Cl}_2$ ): +11.4 ppm (s, 3 F,  $\text{OCOCF}_3$ ); +15.1 ppm (t of overlapping quartets, 2 F,  $\alpha\text{-CF}_2$ ), with platinum satellites,  $J(\text{PF})$  23 Hz,  $J(\text{HF})=J(\text{FF})$  5.7 Hz,  $J(\text{PtF})$  378 Hz; +64.7 ppm (d, 2 F,  $\text{CF}_2\text{H}$ ), with platinum satellites,  $J(\text{HF})$  49 Hz,  $J(\text{FF}) < 13$  Hz,  $J(\text{PtF})$  98 Hz.  $\text{Pt}(\text{OCOCF}_3)(\text{C}_3\text{F}_6\text{H})(\text{PPh}_3)_2$ ,  $\nu(\text{CO}_2)$  asym, 1714 s, 1694 m,  $\text{cm}^{-1}$ ,  $\nu(\text{CO}_2)$  sym, 1393 (sh) m,  $\text{cm}^{-1}$ .  $\text{Pt}(\text{OCOCF}_3)(\text{C}_3\text{F}_6\text{H})(\text{AsPh}_3)_2$ ,  $\nu(\text{CO}_2)$  asym, 1706 s, 1693 s,  $\text{cm}^{-1}$ ;  $\nu(\text{CO}_2)$  sym, 1409 ms, 1404 ms,  $\text{cm}^{-1}$ .  $\text{Pt}(\text{OCOCF}_3)(\text{C}_2\text{F}_3\text{ClH})(\text{AsPh}_3)_2$ ,  $\nu(\text{CO}_2)$  asym, 1679 s, 1652 s,  $\text{cm}^{-1}$ ;  $\nu(\text{CO}_2)$  sym, 1413 ms,  $\text{cm}^{-1}$ .  $\text{Pt}(\text{OCOCF}_3)(\text{C}_2\text{F}_3\text{BrH})(\text{PPh}_3)_2$ ,  $\nu(\text{CO}_2)$  asym, 1703 s,  $\text{cm}^{-1}$ ;  $\nu(\text{CO}_2)$  sym, 1400 s,  $\text{cm}^{-1}$ .  $\text{Pt}(\text{OCOCF}_3)(\text{C}_2\text{F}_3\text{ClH})(\text{PPh}_3)_2$ ,  $\nu(\text{CO}_2)$  asym, 1698 s,  $\text{cm}^{-1}$ ;  $\nu(\text{CO}_2)$  sym, 1400 m,  $\text{cm}^{-1}$ .  $\text{Pt}(\text{OCOCF}_3)(\text{C}_2\text{F}_3\text{H}_2)(\text{PPh}_3)_2$ ,  $\nu(\text{CO}_2)$  asym, 1685 s, 1655 s,  $\text{cm}^{-1}$ ;  $\nu(\text{CO}_2)$  sym, 1415 m,  $\text{cm}^{-1}$ .

#### Reaction of trifluoroacetic acid with $\text{Pt}(\text{CF}_2=\text{CH}_2)(\text{PPh}_3)_2$

$\text{Pt}(\text{CF}_2=\text{CH}_2)(\text{PPh}_3)_2$  (0.38 g) in methylene chloride (20 ml) and trifluoroacetic (0.05 g) were shaken for 12 h. Addition of ethanol to the orange solution and partial evaporation of the solvent afforded white crystals of  $\text{Pt}(\text{OCOCF}_3)_2(\text{PPh}_3)_2$  which was identical to an authentic sample<sup>15</sup>.

#### Reactions of hydrogen chloride

(a). With  $\text{Pt}(\text{C}_2\text{F}_4)(\text{Bipy})$ . Hydrogen chloride gas was bubbled through a suspension of the platinum complex (0.03 g) in methylene chloride (10 ml). The complex dissolved almost immediately and yellow crystals of  $\text{PtCl}(\text{CF}_2\text{CF}_2\text{H})(\text{Bipy})$  were deposited.  $\nu(\text{PtCl})$  346  $\text{cm}^{-1}$ . The  $^{19}\text{F}$  NMR spectrum showed peaks at +36.5 ppm (m, 2 F,  $\alpha\text{-CF}_2$ ), with platinum satellites,  $J(\text{PtF})$  260 Hz; +71.7 ppm (d, 2 F,  $\text{CF}_2\text{H}$ ),  $J(\text{HF})$  55 Hz,  $J(\text{PtF})$  not discernible.

(b). With  $\text{Pt}(\text{C}_2\text{F}_4)(\text{PMe}_2\text{Ph})_2$ . The platinum complex (0.13 g) in methylene chloride (5 ml) was treated with a 0.104 M solution (2.09 ml) of hydrogen chloride in methylene chloride. After 24 h the pale yellow solution was evaporated to a small volume and addition of hexane gave white crystals of *cis*- $\text{PtCl}_2(\text{PMe}_2\text{Ph})_2$  (0.04 g, 40%) which was identical to an authentic sample<sup>5</sup>. Evaporation of the hexane filtrate gave an intractable yellow oil which showed no signal in its  $^{19}\text{F}$  NMR spectrum in methylene chloride.

(c). With  $\text{Pt}(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$ . Hydrogen chloride gas was bubbled through a solution of  $\text{Pt}(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$  (0.5 g) in methylene chloride (10 ml) at room temperature for 1 h. Evaporation of the solvent under reduced pressure gave only unchanged  $\text{Pt}(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$ . Repeating the reaction in benzene (10 ml) in a sealed thick walled tube (180 ml) at 80° for 16 h gave a mixture of *cis*- and *trans*- $\text{PtCl}_2(\text{PPh}_3)_2$  which was identified by its IR spectrum<sup>14,16</sup>.

*Reactions of Pt(C<sub>2</sub>F<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>*

(a). *With tert-butyl chloride.* Pt(C<sub>2</sub>F<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub> (0.5 g) in benzene (20 ml) was introduced into a thick walled tube (180 ml). Freshly distilled tert-butyl chloride (2 ml) was added and the tube was evacuated and sealed at -196°. After heating at 80° for 16 h the tube was cooled and opened. The solution was filtered and on cooling white crystals formed in the filtrate which were identified as a mixture of *cis*- and *trans*-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> as above.

(b). *With mercury(II) chloride.* Pt(C<sub>2</sub>F<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub> (0.5 g) and mercury(II) chloride (0.3 g) in ethanol (30 ml) were heated under reflux for 18 h. The solution was evaporated to dryness and the residue was washed with water (20 ml). Recrystallisation of the product from methylene chloride/ethanol afforded crystals of a mixture of *cis*- and *trans*-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. (Found: C, 55.7; H, 3.9. C<sub>36</sub>H<sub>30</sub>Cl<sub>2</sub>P<sub>2</sub>Pt calcd.: C, 55.8; H, 3.8 %.)

## ACKNOWLEDGEMENTS

We thank Johnson, Matthey & Company Limited for a generous loan of platinum and the S.R.C. for financial support and grants (to G.W.L. and R.D.M.).

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