PROTONATION OF SOME FLUOROOLEFIN COMPLEXES OF PLATINUM(0)

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SUMMARY

The zerovalent olefin complexes $Pt(C_2F_4)L_2$, $(L=PPh_3, AsPh_3, PEt_2Ph, PMePh_2, or PBu_3; L_2=2,2'-bipyridine)$ readily react with trifluoroacetic acid to give a convenient synthesis of the tetrafluoroethyl complexes, $Pt(OCOCF_3)(CF_2CF_2H)L_2$. 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 studies¹ 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 $Pt(Fluoro-olefin)L_2$ 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), $Pt(C_2F_4)L_2$, $(L=PPh_3, AsPh_3, PEt_2Ph, PMePh_2, or PBu_3; L_2=2,2'-bipyridine)$ in methylene chloride solution readily react with trifluoroacetic acid to give tetrafluoroethyl complexes, $Pt(OCOCF_3)(CF_2CF_2H)L_2$. The IR spectra of these crystalline air-stable complexes show bands characteristic of a unidentate trifluoroacetate ligand³ and the ¹⁹F NMR spectra of the more soluble complexes provide good evidence for the presence of a tetrafluoroethyl ligand. In addition the ¹⁹F 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

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$$\begin{array}{c} L & CF_2CF_2H & (Ia; L = PEt_2Ph, \\ F_3COCO & L & Ib; L = PBu_3) \end{array} \xrightarrow{Ph_2MeP} Pt \xrightarrow{CF_2CF_2H} (II)$$

complexes should be contrasted with the action of trifluoroacetic acid⁴ on a series of hexafluoro-2-butyne complexes, $Pt(CF_3C=CCF_3)L_2$, which we have found leads initially to *cis*-alkenyl complexes. However, the appearance of the CH_3P proton signals of the methyldiphenylphosphine ligands of (II) in slightly different environments as doublets⁵ establishes a *cis* configuration for this product which is formed from $Pt(C_2F_4)(PMePh_2)_2$.

Although trifluoroacetic acid readily reacts with all the tetrafluoroethylene complexes studied the corresponding reactions with hydrogen chloride appear to be very sensitive to the nature of the donor ligand L. Thus while $Pt(C_2F_4)(Bipy)$ and hydrogen chloride react at room temperature to give $PtCl(CF_2CF_2H)(Bipy)$, hydrogen chloride and $Pt(C_2F_4)(PMe_2Ph)_2$ give only *cis*- $PtCl_2(PMePh_2)_2$ under these conditions whilst no reaction with $Pt(C_2F_4)(PPh_3)_2$ is observed to take place.

As in the related studies on hexafluoro-2-butyne platinum(0) complexes⁴ protonation of the tetrafluoroethylene complexes could initially occur either at the platinum or at the olefin ligand. Since the platinum-olefin bond will presumably be polarised in the sense $\delta^+ - \delta^-$ direct protonation of the coordinated fluoro-olefin could be favoured. Further since platinum to fluoro-olefin back-bonding will probably be greater in Pt(C₂F₄)(Bipy) than in Pt(C₂F₄)(PPh₃)₂ then the greater negative charge residing on the tetrafluoroethylene ligand in Pt(C₂F₄) (Bipy) could provide an explanation for the greater reactivity of this complex towards hydrogen chloride. Indeed some evidence for increased delocalisation of electron density in the platinumtetrafluoroethylene bond in the complex Pt(C₂F₄)(Bipy) over that in Pt(C₂F₄)(PPh₃)₂ is provided by the much greater value of J(Pt-F) which is found for the bipyridine complex⁶.

Protonation of the zerovalent platinum acetylene complexes has been considered to involve octahedral platinum hydride intermediates^{7,8} and similar octahedral intermediates, e.g. $Pt(OCOCF_3)(H)(C_2F_4)(PPh_3)_2$ could also be invoked in the present studies. This type of complex, $Pt(OCOCF_3)(H)[(CF_3)_2C=NMe](PPh_3)_2$, has indeed been isolated from the reaction of trifluoroacetic acid with $Pt-[(CF_3)_2C=NMe](PPh_3)_2^9$ but it is interesting to note that there appears to be no protonation of the C=N system in this complex.

In an attempt to determine the position of proton addition in some unsymmetrical fluoro-olefin complexes, the action of trifluoroacetic acid on the complexes $Pt(CF_2=CFCI)L_2$ and $Pt(CF_2=CFCF_3)L_2$, $(L=PPh_3, AsPh_3 \text{ or } PEt_2Ph)$ has also been investigated. All six complexes readily react with trifluoroacetic acid but solid products can only be isolated when L is either triphenylphosphine or triphenylarsine and these complexes are not sufficiently soluble for ¹⁹F NMR studies. Similarly no information concerning the structures of the fluoroethyl complexes isolated from the reactions of $Pt(CF_2=CFH)(PPh_3)_2$ and $Pt(CF_2=CFBr)(PPh_3)_2$ with trifluoroacetic acid could be obtained from their ¹⁹F NMR spectra. Protonation studies on unsymmetrical fluoro-olefin complexes of rhodium(I) have shown that hydrogen addition occurs at the carbon atom bonded to the most fluorine atoms¹, and similar products may be formed with the platinum complexes.

The action of trifluoroacetic acid upon the tetrachloroethylene complex,

 $Pt(C_2Cl_4)(PPh_3)_2$ also leads to a complex which on the basis of microanalytical and infrared data can be formulated as a tetrachloroalkyl complex, $Pt(OCOCF_3)-(C_2Cl_4H)(PPh_3)_2$. However, trifluoroacetic acid has no action on $Pt(hexafluoro-cyclobutene)(PPh_3)_2$ in refluxing chloroform.

Previous studies by $Clark^{10}$ have shown that a tetrafluoroethyl complex, trans-PtCl(CF_2CF_2H)(PEt₃)₂ can be isolated from the action of tetrafluoroethylene on trans-PtClH(PEt₃)₂ in a stainless steel autoclave. However, in a glass vessel this type of reaction usually leads to fluorovinyl complexes, *e.g.* trans-PtCl($CF=CF_2$) (PEt₃)₂, and the intermediate tetrafluoroethyl complex is not isolated.

Since the reaction of mercury(II) chloride or bromide with the complexes $Pt(CF_3C\equiv CCF_3)L_2$ (L=PPh₃ or PMePh₂) leads to mercurated products, PtX-[CCF₃=C(HgX)CF₃]L₂, (X=Cl or Br)⁴ the reaction of mercury(II) chloride with $Pt(C_2F_4)(PPh_3)_2$ was therefore studied. However, no mercurated derivative could be prepared and only a mixture of *cis*- and *trans*-PtCl₂(PPh₃)₂ could be isolated. Similarly, attempts to alkylate the tetrafluoroethylene ligand in the complex $Pt(C_2F_4)$ (PPh₃)₂ with tertiary butyl chloride also leads to a mixture of *cis*- and *trans*-PtCl₂-(PPh₃)₂ and in this context it is noteworthy that Clark¹¹ has found that methyl iodide reacts with $Pt(C_2F_4)(PPh_3)_2$ to give $PtI_2Me_2(PPh_3)_2$.

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 $RhCl(C_2F_4)(PPh_3)_2$ readily reacts with hydrogen chloride but $Pt(C_2F_4)(PPh_3)_2$ 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, $Pt(C_2H_4)(PPh_3)_2$, does not lead to an alkyl complex¹² since the olefin complex is appreciably dissociated in solution. Similarly we find that the action of trifluoro-acetic acid on $Pt(CF_2=CH_2)(PPh_3)_2$, in which the metal-olefin bond is also quite labile, leads to $Pt(OCOCF_3)_2(PPh_3)_2$.

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 ¹⁹F NMR spectra were obtained using Varian Associates T60 and DA60 spectrometers respectively. The ¹⁹F NMR spectra were measured relative to benzotrifluoride as internal standard and were recorded at 56.4 MHz.

The complexes $Pt(C_2F_4)(PPh_3)_2^{1^3,1^4}$, $Pt(C_2F_4)(AsPh_3)_2^6$, $Pt(C_2F_4)(PEt_2Ph)_2^6$, $Pt(C_2F_4)(PMePh_2)_2^6$, $Pt(C_2F_4)(PMePh_2)_2^6$, $Pt(C_2F_4)(PBu_3)_2^6$, $Pt(C_2F_4)(Bipy)^6$, $Pt(C_2F_3Br)(PPh_3)_2^{1^3}$, $Pt(C_2F_3Cl)(PPh_3)_2^{1^3}$, $Pt(C_3F_6)(PPh_3)_2^{1^3}$, $Pt(c_2C_4F_6)(PPh_3)_2^{1^3}$, and $Pt(C_2Cl_4)(PPh_3)_2^{1^4}$ were prepared as described in the literature. The chlorotrifluoroethylene and hexafluoropropene complexes, $Pt(C_2F_3Cl)(PEt_2Ph)_2$ and $Pt(C_3F_6)(PEt_2Ph)_2$ were prepared by the reaction of phenyldiethylphosphine with the corresponding triphenylarsine complex using the method which we have described previously⁶.

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TABLE 1

ANALYTICAL DATA FOR COMPLEXES

| Compound | Yield (%) | М.р." (°С) | Analysis, found (calcd.) (%) | | |
|---|--------------|----------------|------------------------------|--------------|----------------|
| | | | c | Н | F |
| $Pt(C_2F_3H)(PPh_3)_2$ | 89 | 170-172 | 57.1 | 4.0 | |
| | | | (57.0) | (3.9) | |
| $Pt(CF_{2}CH_{2})(PPh_{3})_{2}$ | 63 | 132–135 | 58.0 | 4.0 | |
| | 50 | 162 165 | (58.2) 49.0 | (4.1) 3.3 | 6 1 |
| $Pt(C_2F_3Cl)(AsPh_3)_2$ | 50 | 162–165 | (48.3) | 3.3 (3.3) | 6.1 (6.2) |
| $Pt(C_3F_6)(AsPh_3)_2$ | 50 | 188–191 | 49.0 | 3.2 | 12.2 |
| | 50 | 100-171 | (48.9) | (3.2) | (12.2) |
| $Pt(C_2F_3Cl)(PEt_2Ph)_2$ | 50 | 106-110 | 41.2 | 4.8 | 9.1 |
| | | | (40.9) | (4.9) | (8.8) |
| $Pt(C_3F_6)(PEt_2Ph)_2$ | 89 | 108-112 | 41.2 | 4.3 | 16.9 |
| | | | (40.8) | (4.5) | (16.9) |
| $Pt(OCOCF_3)(CF_2CF_2H)(PPh_3)_2$ | 85 | 214-216 | 52.0 | 3.2 | 14.1 |
| | | | (51.8) | (3.3) | (14.2) |
| $Pt(OCOCF_3)(CF_2CF_2H)(AsPh_3)_2$ | 81 | 200-204 | 47.3 | 3.1 | 13.8 |
| | | | (47.3) | (3.1) | (13.8) |
| $Pt(OCOCF_3)(CF_2CF_2H)(PEt_2Ph)_2$ | 74 | 201–203 | 39.3 | 4.0 | 17.9 |
| PHOCOCE VCE CE UNDADE) | 02 | 129 120 | (38.3) 44.2 | (4.2) 3.4 | (17.9) 17.0 |
| $Pt(OCOCF_3)(CF_2CF_2H)(PMePh_2)_2$ | 92 | 128-130 | 44.2 (44.5) | 3.4 (3.4) | (17.0) |
| Pt(OCOCF ₃)(CF ₂ CF ₂ H)(PBu ₃) ₂ | 92 | ca. 30 | 42.7 | 6.5 | 15.7 |
| | 14 | ca . 50 | (41.3) | (6.8) | (16.4) |
| Pt(OCOCF ₃)(CF ₂ CF ₂ H)(Bipy) ^b | 95 | 263-266 | 30.0 | 1.6 | 26.0 |
| | | | (29.8) | (1.6) | (25.5) |
| Pt(Cl)(CF ₂ CF ₂ H)(Bipy) ^c | 70 | 270–276 | 29.7 | 1.8 | Ì13.8 |
| | | | (29.5) | (1.9) | (14.6) |
| Pt(OCOCF ₃)(C_3F_6H)(PPh ₃) ₂ Pt(OCOCF ₃)(C_3F_6H)(AsPh ₃) ₂ | 68 | 188-189 | 50.4 | 3.2 | 17.1 |
| | | | (50.1) | (3.2) | (17.3) |
| | 90 | 190–195 | 49.5 | 3.0 | 15.7 |
| PHOCOCE VC E CHIVIDE) | 70 | 226 227 | (49.9) | (2.9) | (15.9) |
| $Pt(OCOCF_3)(C_2F_3ClH)(PPh_3)_2$ | 73 | 225–227 | 50.8 | 3.4 | 11.9 |
| $Pt(OCOCF_3)(C_2F_3CIH)(AsPh_3)_2$ | 87 | 175-177 | (50.6) 46.6 | (3.3) 3.1 | (12.0) 11.4 |
| | 07 | 175-177 | (46.3) | (3.0) | (11.4) |
| $Pt(OCOCF_3)(C_2F_3BrH)(PPh_3)_2$ | 52 | 246250 | 49.0 | 3.2 | 7.1 |
| | | | (48.3) | (3.1) | (7.4) |
| $Pt(OCOCF_3)(C_2F_3H_2)(PPh_3)_2$ | 94 | 175-178 | 52.7 | 3.6 | - |
| | | | (52.5) | (3.5) | |
| $Pt(OCOCF_3)(C_2Cl_4H)(PPh_3)_2$ | 84 | 122-124 | 48.3 | 3.2 | 5.9 |
| | | | (48.1) | (3.7) | (5.7) |

" With decomposition. " Found N 5.1, calcd. 5.0%. " 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)-(PPh₃)₂ (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 $Pt(trans-Stilbene)(PPh_3)_2$ (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 $Pt(AsPh_3)_4$ (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 $Pt(AsPh_3)_4$ (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 $Pt(C_2F_4)(PPh_3)_2$

 $Pt(C_2F_4)(PPh_3)_2$ (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*. $v(CO_2)$ asym, 1682 s, 1587 s; $v(CO_2)$ sym, 1411 ms, cm⁻¹.

The other protonation reactions using trifluoroacetic acid were similarly performed except that the reactions involving $Pt(C_2F_3Cl)(PPh_3)_2$, $Pt(C_2F_3Cl)$ - $(PEt_2Ph)_2$, $Pt(C_2F_3Cl)(AsPh_3)_2$, $Pt(C_2Cl_4)(PPh_3)_2$, Pt(cyclo-hexafluorobutene)- $(PPh_3)_2$ were heated under reflux for 12 h. The products so formed were Pt(OCOCF_3)- $(CF_2CF_2H)(Bipy); v(CO_2)$ asym, 1718 s, 1700 s, cm⁻¹; v(CO₂) sym, 1407 ms, cm⁻¹ ¹⁹F NMR spectrum (DMF): +12.0 ppm (s, 3 F, OCOCF₃) with platinum satellites, J(PtF) 19 Hz; +42.3 ppm (m, 2 F, α -CF₂), with platinum satellites, J(PtF) 270 Hz; +71.9 ppm (d of t, 2 F, CF₂H), J(HF) 52 Hz, J(FF) 7 Hz, J(PtF) not discernible. Pt(OCOCF₃)(CF₂CF₂H)(PBu₃)₂; ν (CO₂) asym, 1714 s, 1698 s, cm⁻¹; ν (CO₂) sym, 1404 ms, cm⁻¹. ¹⁹F NMR spectrum (CH₂Cl₂): +11.7 ppm (s, 3 F, OCOCF₃), with platinum satellites, J(PtF) 17 Hz; +13.2 ppm (t, 2 F, α -CF₂), with platinum satellites, J(PF) 25 Hz, J(PtF) ca. 500 Hz; +65.0 ppm (d, 2 F, CF₂H), with platinum satellites, J(HF) 55 Hz, J(PtF) 102 Hz. Pt(OCOCF₃)(CF₂CF₂H)(PMePh₂),; $v(CO_2)$ asym, 1690 s, cm⁻¹, $v(CO_2)$ sym, 1408 s, cm⁻¹. ¹⁹F NMR spectrum (CH₂Cl₂): +11.9 ppm (s, 3 F, OCOCF₃), α -CF₂ resonance obscured by OCOCF₃ resonance; platinum satellite peaks suggest doublet, J(PF) 33 Hz, J(PtF) 469 Hz; +66 ppm (d, 2 F, CF₂H), with platinum satellites, J(HF) 53 Hz, J(PtF) 99 Hz. ¹H NMR

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spectrum (CDCl₃): 8.56 τ (d, 3 H, PMe), with platinum satellites, J(PH) 10 Hz, J(PtH) 50 Hz; 7.17 (d, 3 H, PMe), with platinum satellites, J(PH) 9.8 Hz, J(PtH) 18 Hz; 3.98 (t, 1 H, CF₂H), J(HF_{vic}) 6 Hz, J(HF_{aem}) not discernible; 2.3-2.9 (m, 20 H, C_6H_5P). Pt(OCOCF₃)(CF₂CF₂H)(AsPh₃)₂; v(CO₂) asym 1680 s, cm⁻¹, $v(CO_2)$ sym, 1410 m, cm⁻¹. ¹⁹F NMR spectrum (CH₂Cl₂): +9.4 ppm (q, 2 F, α - CF_2 , J(HF) = J(FF), 5.8 Hz, platinum satellites not discernible; +11.1 ppm (s, 3 F, OCOCF₃): +65.5 ppm (d of t, 2 F, CF₂H), J(HF) 58 Hz, J(FF) not measurable, J(PtF) not discernible. Pt(OCOCF₃)(CF₂CF₂H) (PEt₂Ph)₂; ¹⁹F NMR spectrum (CH₂Cl₂): +11.4 ppm (s, 3 F, OCOCF₃); +15.1 ppm (t of overlapping quartets, 2 F, α -CF₂), with platinum satellites, J(PF) 23 Hz, J(HF) = J(FF) 5.7 Hz, J(PtF)378 Hz; +64.7 ppm (d, 2 F, CF₂H), with platinum satellites, J(HF) 49 Hz, J(FF) < 13Hz, J(PtF) 98 Hz. Pt(OCOCF₃)(C₃F₆H)(PPh₃)₂, v(CO₂) asym, 1714 s, 1694 m, cm^{-1} , $v(CO_2)$ sym, 1393 (sh) m, cm^{-1} . Pt(OCOCF₃)(C₃F₆H)(AsPh₃)₂, $v(CO_2)$ asym, 1706 s, 1693 s, cm⁻¹; v(CO₂) sym, 1409 ms. 1404 ms, cm⁻¹. Pt(OCOCF₃)- $(C_2F_3ClH)(AsPh_3)_2$, $v(CO_2)$ asym, 1679 s, 1652 s, cm⁻¹; $v(CO_2)$ sym, 1413 ms, cm⁻¹. $Pt(OCOCF_3)(C_2F_3BrH)(PPh_3)_2$, $v(CO_2)$ asym, 1703 s, cm⁻¹; $v(CO_2)$ sym, 1400 s, cm^{-1} . Pt(OCOCF₃)(C₂F₃ClH)(PPh₃)₂, v(CO₂) asym, 1698 s, cm⁻¹; v(CO₂) sym, 1400 m, cm⁻¹. Pt(OCOCF₃)(C₂F₃H₂)(PPh₃)₂, v(CO₂) asym, 1685 s, 1655 s, cm⁻¹; $v(CO_2)$ sym, 1415 m, cm⁻¹.

Reaction of trifluoroacetic acid with $Pt(CF_2=CH_2)(PPh_3)_2$

 $Pt(CF_2=CH_2)(PPh_3)_2$ (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 $Pt(OCOCF_3)_2(PPh_3)_2$ which was identical to an authentic sample¹⁵.

Reactions of hydrogen chloride

(a). With $Pt(C_2F_4)(Bipy)$. 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 $PtCl(CF_2CF_2H)$ -(Bipy) were deposited. v(PtCl) 346 cm⁻¹. The ¹⁹F NMR spectrum showed peaks at + 36.5 ppm (m, 2 F, α -CF₂), with platinum satellites, J(PtF) 260 Hz; +71.7 ppm (d, 2 F, CF₂H), J(HF) 55 Hz, J(PtF) not discernible.

(b). With $Pt(C_2F_4)(PMe_2Ph)_2$. 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*-PtCl₂(PMe₂Ph)₂ (0.04 g, 40%) which was identical to an authentic sample⁵. Evaporation of the hexane filtrate gave an intractable yellow oil which showed no signal in its ¹⁹F NMR spectrum in methylene chloride.

(c). With $Pt(C_2F_4)(PPh_3)_2$. Hydrogen chloride gas was bubbled through a solution of $Pt(C_2F_4)(PPh_3)_2$ (0.5 g) in methylene chloride (10 ml) at room temperature for 1 h. Evaporation of the solvent under reduced pressure gave only unchanged $Pt(C_2F_4)(PPh_3)_2$. 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*- $PtCl_2(PPh_3)_2$ which was identified by its IR spectrum^{14,16}.

Reactions of $Pt(C_2F_4)(PPh_3)_2$

(a). With tert-butyl chloride. $Pt(C_2F_4)(PPh_3)$ (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*-PtCl₂(PPh₃)₂ as above.

(b). With mercury(II) chloride. $Pt(C_2F_4)(PPh_3)_2$ (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*-PtCl₂(PPh₃)₂. (Found: C, 55.7; H, 3.9. $C_{36}H_{30}Cl_2P_2Pt$ calcd.: C, 55.8; H, 3.8%)

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