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Comparison of σ -Alkyl and σ -Perfluoroalkyl Groups as Ligands. 1. Crystal and Molecular Structures of the Methyl-, (Trifluoromethyl)-, and (Pentafluoroethyl)platinum(II) Complexes *trans*-PtClR(PMePh)₂ (R = CH₃, CF₃, C₂F₅)

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The crystal and molecular structures of the platinum(II) complexes *trans*-PtClR(PMePh)₂ (R = CH₃, **1**; R = CF₃, **2**; R = C₂F₅, **3**) have been determined by three-dimensional X-ray structural analysis using data collected by counter methods. The methyl complex **1** crystallizes in the space group *P2₁/c* with *a* = 11.5476 (4) Å, *b* = 11.3826 (4) Å, *c* = 21.2390 (5) Å, β = 113.40 (1)°, and *Z* = 4; the trifluoromethyl complex **2** crystallizes in the same space group with *a* = 9.3544 (8) Å, *b* = 15.7237 (14) Å, *c* = 10.6846 (11) Å, β = 121.62 (2)°, and *Z* = 2; the pentafluoroethyl complex **3** crystallizes in the space group *Pna2₁* with *a* = 15.4957 (4) Å, *b* = 9.9831 (3) Å, *c* = 38.7764 (11) Å, and *Z* = 8 (two formula units per equipoint). The structures were solved by conventional heavy-atom techniques and were refined by block-diagonal least-squares methods to final weighted and unweighted *R* factors of 0.033 and 0.044 (**1**), 0.045 and 0.098 (**2**), and 0.035 and 0.050 (**3**). **1** and **3** show small but significant distortions from planarity toward tetrahedral geometry, probably owing to steric crowding in the coordination sphere. Important bond lengths in **1** are Pt-C = 2.081 (6) Å, Pt-Cl = 2.412 (2) Å, and Pt-P = 2.292 (2) and 2.291 (2) Å and important bond lengths in **3** (averaged over two independent molecules) are Pt-C = 2.002 (9) Å, Pt-Cl = 2.363 (2) Å, Pt-P = 2.328 (2) and 2.341 (2) Å, C_(α)-F(av) = 1.39 (2) Å, C_(β)-F(av) = 1.33 (2) Å, and C_(α)-C_(β) = 1.546 (14) Å. Inversion disorder of the Cl and CF₃ groups about the platinum atom of **2** precludes accurate determination of the Pt-Cl, Pt-C, or C-F bond lengths, but IR ν (Pt-Cl) data indicate that CF₃ and C₂F₅ have similar structural trans influences. The Pt-P bond lengths of **2** [2.320 (2) Å, crystallographically equivalent] are intermediate between those of **1** and **3**. The Pt-P distances in **3** are not equivalent ($\Delta/\sigma \approx 4$), the longer bond of the pair in each molecule being adjacent to the CF₃ substituent of the pentafluoroethyl-group. The contraction of the Pt-C and Pt-Cl distances in **3** relative to **1** is attributed to the electrostatic effect of a positive charge induced on the ligating carbon atom by the electronegative fluorine atoms. C₂F₅ resembles CO in being higher in the trans-influence series based on NMR than in that based on Pt-Cl bond lengths or related parameters and also in tending to lengthen cis Pt-P bonds. Possible reasons for these similarities are discussed in the light of current views of transition-metal-fluoroalkyl bonding.

Introduction

Although it is well-known that transition-metal σ -perfluoroalkyl complexes are usually more thermally stable than their σ -alkyl counterparts¹⁻³ and that metal-carbon bond lengths in σ -perfluoroalkyl complexes are generally shorter than expected on the basis of covalent radii,⁴ the nature of the metal-carbon bond in perfluoroalkyls remains controversial. The electronegative fluorocarbon group may strengthen the metal-carbon bond by ionic-covalent resonance, e.g., M-CF₃ \leftrightarrow M⁺CF₃⁻, and the higher positive charge induced on the metal atom may contract the metal σ orbitals, thus improving overlap with the smaller carbon σ orbitals. In addition the presence of highly electronegative fluorine atoms may increase the *s* character of the carbon σ orbital, thus improving its overlap with the metal σ orbital.^{4,5} Finally, and most controversially, replacement of hydrogen by fluorine might lower the energy of the carbon-element σ^* orbital sufficiently to enable it to accept metal d_{π} -electron density, thus imparting some double-bond character to the metal-carbon bond. This last possibility was first advocated to account for the observed reduction of ca. 100 cm⁻¹ in ν (C-F) for various (trifluoromethyl)metal complexes relative to CF₃X (X = Cl, Br, I),⁶⁻⁹ but the interpretation has been disputed.^{5,10,11} Recent studies¹²⁻¹⁶ of planar platinum(II) and octahedral platinum(IV) complexes indicate that the NMR trans influences¹⁷ of CF₃⁻ and CH₃⁻ are not very different, which implies that the *s* characters of the orbitals used by platinum for bonding to these two groups are similar.

We thought it worthwhile to obtain an independent estimate of the structural trans influences of σ -alkyl and σ -perfluoroalkyl groups by X-ray diffraction analyses of comparable platinum(II) complexes. At the time we started our work, there were only two structure determinations of (perfluoroalkyl)platinum complexes in the literature, viz., *cis*-PtF-

[CH(CF₃)₂](PPh₃)₂¹⁸ and [Pt(CF₃)(η^4 -C₄Me₄)(PMe₂Ph)₂]-SbF₆¹⁹ and the only directly comparable σ -alkyl and σ -perfluoroalkyl complexes which had been studied by X-ray crystallography were η^5 -C₅H₅Mo(CO)₃C₂H₅²⁰ and η^5 -C₅H₅Mo(CO)₃-*n*-C₃F₇.²¹ Recently the structures of *cis*-Pt-(CF₃)₂[PMe₂(C₆F₅)₂] and [Pt(CH₃){PMe₂(C₆F₅)₂]₃PF₆ have been reported briefly.²² We describe here detailed structural analyses of the complexes *trans*-PtClR(PMePh)₂ (R = CH₃, **1**; R = CF₃, **2**; R = C₂F₅, **3**).

Experimental Section

Starting Materials. Ether was distilled from LiAlH₄ and stored over sodium. All other solvents were of AR grade and were dried over molecular sieves before use.

Measurements. ¹H NMR spectra were measured at 100 MHz on a Varian HA-100 instrument using either (CH₃)₄Si or CHDCl₂ as an internal reference. ³¹P NMR spectra were run on a Jeol C-60-HL CW spectrometer modified for ³¹P{¹H} heteronuclear decoupling and were accumulated using a PDP-8I computer. IR spectra in the range 4000-200 cm⁻¹ were taken on Nujol mulls on CsI windows or as CsI disks using Perkin-Elmer 457 and 225 spectrometers. Spectra below 250 cm⁻¹ were also measured on a Perkin-Elmer 180 instrument in the Research School of Physical Sciences of this University. Spectroscopic data are summarized in Table I. Microanalyses (Table II) were carried out in the Research School of Chemistry and the John Curtin School of Medical Research (Miss Brenda Stevenson and Dr. Joyce Fildes and their associates). Melting points were measured on a Gallenkamp hot-stage apparatus and are uncorrected.

Unless stated otherwise, all reactions were carried out in an atmosphere of dry nitrogen.

Preparations. *cis*-Bis(diphenylmethylphosphine)dichloroplatinum(II), *cis*-PtCl₂(PMePh)₂. A suspension of anhydrous platinum(II) chloride (4.0 g, 9.6 mmol) in ethanol (40 mL) was treated with a solution of diphenylmethylphosphine (4.4 g, 21.9 mmol) in ethanol (10 mL). After 5 h of stirring at 60 °C, the brown color due to PtCl₂ had almost disappeared and a colorless precipitate had formed. After the solution was cooled to room temperature, the solid was filtered off and

Table I. Selected IR and NMR Spectroscopic Data for Platinum(II) Complexes *trans*-PtClR(PMePh₂)₂^{a,b}

| | $\nu(\text{Pt-X})$ (X = Cl, Br) | $\nu(\text{C=O})$ | $\delta(\text{P-CH}_3)$ | $^2J_{\text{P-H}} +$ $^4J_{\text{P-H}}$ | $^3J_{\text{Pt-H}}$ | δ_{P} | $^3J_{\text{P-F}}$ | $^1J_{\text{Pt-P}}$ |
|---|------------------------------------|-------------------|-------------------------|--|---------------------|---------------------|--------------------|---------------------|
| PtCl(CH ₃)(PMePh ₂) ₂ , 1 | 272 | | 2.22 t ^c | 7.2 | 28.6 | 13.5 | | 3028 |
| PtCl(COCF ₃)(PMePh ₂) ₂ | 290 | 1670 | 2.16 t | 8.0 | 34.5 | nm | nm | nm |
| PtCl(CF ₃)(PMePh ₂) ₂ , 2 | 302 | | 2.13 t | 7.6 | 30.2 | 10.2 q | 19.6 | 2920 |
| PtBr(CF ₃)(PMePh ₂) ₂ | 198 | | 2.21 t | 7.8 | 31.2 | 7.9 q | 21.7 | 2886 |
| PtCl(COC ₂ F ₅)(PMePh ₂) ₂ | 280 | 1675 | 2.12 t | 7.6 | 34.4 | nm | nm | nm |
| PtCl(C ₂ F ₅)(PMePh ₂) ₂ , 3 | 315, 302 | | 2.17 t | 7.0 | 29.4 | 10.5 t | 26.2 | 2942 |
| PtBr(C ₂ F ₅)(PMePh ₂) ₂ | 201 | | 2.16 t | 7.6 | 30.0 | 8.2 t | 27.6 | 2896 |

^a IR bands (cm⁻¹) refer to Nujol mulls. ¹H chemical shifts (δ , CD₂Cl₂) are in ppm downfield (positive) of internal (CH₃)₄Si, coupling constants (J_{H}) are in Hz (± 0.5), ³¹P chemical shifts (δ_{P} , CH₂Cl₂) are in ppm downfield (positive) of external 85% H₃PO₄, coupling constants (J_{P}) are in Hz (± 0.5 for $J_{\text{P-F}}$, ± 1.0 for $J_{\text{Pt-P}}$). ^b Abbreviations: q, quartet; t, triplet; nm, not measured. ^c $\delta(\text{Pt-CH}_3) = 0.02$ (t with ¹⁹⁵Pt satellites, $^3J_{\text{P-H}} = 6.9$ Hz, $^2J_{\text{Pt-H}} = 80.8$ Hz).

Table II. Analytical Data for Platinum(II) Complexes *trans*-PtClR(PMePh₂)₂

| | % C | | % H | | % P | | % F | | % Cl or % Br | |
|---|-------|-------|-------|-------|-------|-------|-------|-------|--------------|-------|
| | calcd | found | calcd | found | calcd | found | calcd | found | calcd | found |
| PtCl(CH ₃)(PMePh ₂) ₂ , 1 | 50.2 | 50.4 | 4.5 | 4.9 | | | | | 5.5 | 5.2 |
| PtCl(COCF ₃)(PMePh ₂) ₂ | 46.2 | 46.2 | 3.6 | 3.9 | 8.5 | 8.2 | 7.8 | 7.8 | 4.9 | 4.85 |
| PtCl(CF ₃)(PMePh ₂) ₂ , 2 | 46.3 | 46.0 | 3.7 | 3.9 | 8.85 | 8.7 | 8.1 | 8.1 | 5.1 | 5.1 |
| PtBr(CF ₃)(PMePh ₂) ₂ | 43.6 | 43.8 | 3.5 | 3.9 | 8.3 | 7.9 | 7.7 | 7.3 | 10.7 | 10.65 |
| PtCl(COC ₂ F ₅)(PMePh ₂) ₂ | 44.8 | 44.9 | 3.4 | 3.6 | 8.0 | 7.7 | 12.2 | 11.9 | 4.6 | 4.8 |
| PtCl(C ₂ F ₅)(PMePh ₂) ₂ , 3^c | 44.8 | 45.0 | 3.5 | 3.6 | 8.3 | 8.0 | 12.7 | 11.2 | 4.7 | 5.65 |
| PtBr(C ₂ F ₅)(PMePh ₂) ₂ | 42.3 | 42.7 | 3.3 | 3.4 | 7.8 | 7.6 | 12.0 | 11.9 | 10.1 | 10.1 |

^a Calcd for PtCl(C₂F₅)(PMePh₂)₂·0.5CH₂Cl₂ (see text): C, 43.2; H, 3.4; P, 7.8; F, 12.0; Cl, 8.95.

washed with ethanol. Recrystallization from chloroform/ethanol gave colorless crystalline *cis*-PtCl₂(PMePh₂)₂, mp 248–250 °C [lit.²³ mp 253–268 °C] (5.7 g, 89%).

cis-Bis(diphenylmethylphosphine)dimethylplatinum(II), *cis*-Pt(CH₃)₂(PMePh₂)₂. The literature method²⁴ was slightly modified. A suspension of finely powdered *cis*-PtCl₂(PMePh₂)₂ (1.70 g, 2.5 mmol) in dry benzene (25 mL) was treated with methylmagnesium chloride (8.0 mmol) in ether and was stirred at 50 °C for 2 h. The mixture was hydrolyzed at 0 °C with 5% ammonium chloride solution. The product isolated from the organic layer was recrystallized from benzene/ethanol to give colorless crystals of *cis*-Pt(CH₃)₂(PMePh₂)₂, mp 157–160 °C (dec) [lit.²⁴ mp 145–150 °C] (0.81 g, 51%).

trans-Bis(diphenylmethylphosphine)chloro(methyl)platinum(II), *trans*-PtCl(CH₃)(PMePh₂)₂, **1**. A solution of *cis*-Pt(CH₃)₂(PMePh₂)₂ (0.5 g, 0.78 mmol) in ether (20 mL) was treated with hydrogen chloride in ether (1.4 mL, 0.553 M; 0.78 mmol). After 30 min of stirring, the product was filtered off and washed with ether. ¹H NMR examination showed it to be *trans*-PtCl(CH₃)(PMePh₂)₂; we could not detect the *cis* isomer isolated by Ruddick and Shaw.²⁴ Recrystallization from chloroform/ethanol gave colorless prisms of the *trans* isomer, mp 162–163 °C (dec) [lit.²⁴ mp 178–180 °C] (0.48 g, 95%).

Tetrakis(diphenylmethylphosphine)platinum(0), Pt(PMePh₂)₄. Two literature methods of preparation^{25,26} were modified as follows. A solution of diphenylmethylphosphine (1.1 g, 5.49 mmol) in 95% ethanol (10 mL) was added to a suspension of *cis*-PtCl₂(PMePh₂)₂ (1.5 g, 2.25 mmol) in ethanol (40 mL), and the mixture was stirred for 10 min. A solution of potassium hydroxide (0.3 g, 5.35 mmol) in 4:1 v/v aqueous ethanol (8 mL) was then added, and the mixture was kept at 60 °C for 1 h. The yellow solid was filtered off, washed with water and ethanol, and dried in vacuo. It was used in subsequent syntheses without further purification.

trans-Bis(diphenylmethylphosphine)chloro(trifluoroacetyl)platinum(II), *trans*-PtCl(COCF₃)(PMePh₂)₂. Trifluoroacetyl chloride was bubbled into a suspension of Pt(PMePh₂)₄ (2.0 g, 2.0 mmol) in *n*-hexane (40 mL). The yellow color of the platinum(0) complex was discharged almost immediately and a white precipitate was formed. After 30 min this was filtered off and washed successively with *n*-hexane and ethanol. Recrystallization from dichloromethane/ethanol gave colorless crystals of *trans*-PtCl(COCF₃)(PMePh₂)₂, mp 170–172 °C (1.02 g, 70%).

trans-Bis(diphenylmethylphosphine)chloro(trifluoromethyl)platinum(II), *trans*-PtCl(CF₃)(PMePh₂)₂, **2**. *trans*-PtCl(COCF₃)(PMePh₂)₂ (0.30 g, 0.04 mmol) was heated at 200–210 °C (10⁻³ mm) for 4 h, after which time the melt had almost stopped bubbling. After being cooled to room temperature, the white solid was dissolved in

dichloromethane (3 mL), the solution was filtered, and the product was crystallized by addition of ethanol to give colorless crystals of *trans*-PtCl(CF₃)(PMePh₂)₂, mp 168–170 °C (0.22 g, 78%).

trans-Bis(diphenylmethylphosphine)bromo(trifluoromethyl)platinum(II), *trans*-PtBr(CF₃)(PMePh₂)₂. A solution containing *trans*-PtCl(CF₃)(PMePh₂)₂ (0.1 g, 0.14 mmol) and lithium bromide (0.02 g, 0.23 mmol) in acetone (20 mL) was heated under reflux for 30 min. Acetone was distilled off and the residue was extracted with benzene. Addition of ethanol to the filtered solution gave colorless prisms of *trans*-PtBr(CF₃)(PMePh₂)₂, mp 200–202 °C (0.1 g, 96%).

trans-Bis(diphenylmethylphosphine)chloro(pentafluoropropionyl)platinum(II), *trans*-PtCl(COC₂F₅)(PMePh₂)₂. This was prepared similarly to PtCl(COCF₃)(PMePh₂)₂ by using pentafluoropropionyl chloride in place of trifluoroacetyl chloride. A 74% yield of colorless crystalline product, mp 155–157 °C, was obtained.

trans-Bis(diphenylmethylphosphine)chloro(pentafluoroethyl)platinum(II), *trans*-PtCl(C₂F₅)(PMePh₂)₂, **3**. Decarbonylation of PtCl(COC₂F₅)(PMePh₂)₂ as described above for PtCl(COCF₃)(PMePh₂)₂ gave the colorless crystalline product, mp 123–126 °C, in 65% yield.

Metathesis with lithium bromide in acetone gave colorless *trans*-PtBr(C₂F₅)(PMePh₂)₂, mp 150–151 °C, in 95% yield.

Collection and Reduction of X-ray Intensity Data. Crystals of PtCl(CH₃)(PMePh₂)₂, **1**, PtCl(CF₃)(PMePh₂)₂, **2**, and PtCl(C₂F₅)(PMePh₂)₂·0.5CH₂Cl₂, **3**, of size and quality suitable for single-crystal X-ray diffraction studies, were obtained as described in the previous section. Laue symmetry and approximate unit cell dimensions for crystals of each type were obtained in the usual way from preliminary Weissenberg and precession photographs. Photographs of **3** exhibit *mmm* (*D*_{2h}) Laue symmetry and systematic absences (*h*0*l*, *h* = 2*n* + 1; 0*kl*, *k* + *l* = 2*n* + 1) consistent with either of the orthorhombic space groups *Pnam* (*D*_{2h}¹⁶, No. 62) or *Pna*2₁ (*C*_{2h}⁹, No. 33). The choice of the noncentrosymmetric space group *Pna*2₁ (with two formula units per asymmetric scattering unit) was subsequently confirmed by the successful solution and refinement of the structure. Photographs of **1** and **2** each exhibit 2/*m* (*C*_{2h}) Laue symmetry and systematic absences (*h*0*l*, *l* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1) uniquely identifying the centrosymmetric monoclinic space group *P2*₁/*c* (*C*_{2h}⁵, No. 14). Crystal densities, measured by flotation in aqueous BaI₂, correspond to *Z* = 4 for **1**, *Z* = 2 for **2**, and *Z* = 8 for **3**. With *Z* = 2 in space group *P2*₁/*c*, the platinum atoms in the trifluoromethyl complex, **2**, are constrained to occupy crystallographic sites having $\bar{1}$ (*C*₂) symmetry. No such symmetry constraints are imposed by the packing arrangements in **1** or **3**.

X-ray diffraction data were recorded using a Picker FACS-1 fully automatic four-circle diffractometer and crystal-monochromated K α

radiation (Cu K α for **1** and **3**; Mo K α for **2**). For each complex, accurate unit cell dimensions and crystal orientation matrices were determined by least-squares analysis of the setting angles 2θ , ω , χ , and ϕ for 12 carefully centered high-angle reflections.²⁷ The estimated standard deviations in the tabulated cell dimensions derive directly from the least-squares analysis.

Crystal Data. **1**, PtCl(CH₃)[P(CH₃)(C₆H₅)₂]₂, M_r = 646.02 daltons, monoclinic, space group $P2_1/c$, a = 11.5476 (4) Å, b = 11.3826 (4) Å, c = 21.2390 (5) Å, β = 113.40 (1)°, V_{calcd} = 2562.1 Å³, ρ_{obsd} = 1.67 (2) g cm⁻³, ρ_{calcd} = 1.674 g cm⁻³, Z = 4, $F(000)$ = 1264, $\mu(\text{Cu K}\alpha)$ = 126.68 cm⁻¹, graphite monochromator, λ 1.5418 Å, t = 20 ± 2 °C.

2, PtCl(CF₃)[P(CH₃)(C₆H₅)₂]₂, M_r = 699.99 daltons, monoclinic, space group $P2_1/c$, a = 9.354 (1) Å, b = 15.724 (1) Å, c = 10.685 (1) Å, β = 121.62 (2)°, V_{calcd} = 1338.2 Å³, ρ_{obsd} = 1.73 (2) g cm⁻³, ρ_{calcd} = 1.737 g cm⁻³, Z = 2, $F(000)$ = 680, $\mu(\text{Mo K}\alpha)$ = 57.70 cm⁻¹, graphite monochromator, λ 0.7107 Å, t = 20 ± 2 °C.

3, PtCl(C₂F₅)[P(CH₃)(C₆H₅)₂]₂, M_r = 792.46 daltons, orthorhombic, space group $Pna2_1$, a = 15.4957 (4) Å, b = 9.9831 (3) Å, c = 38.7764 (11) Å, V_{calcd} = 5999.0 Å³, ρ_{obsd} = 1.75 (2) g cm⁻³, ρ_{calcd} = 1.754 g cm⁻³, Z = 8, $F(000)$ = 3080, $\mu(\text{Cu K}\alpha)$ = 120.13 cm⁻¹, graphite monochromator, λ 1.5418 Å, t = 20 ± 2 °C.

Reflection intensity measurement procedures closely followed those we have described elsewhere.²⁸ Reflection intensities were recorded throughout in the θ - 2θ scan mode with graphite-monochromated K α radiation ($2\theta_{\text{max}}$ = 127° for **1** and **3**, Cu K α radiation; $2\theta_{\text{max}}$ = 60° for **2**, Mo K α radiation). Including standards, 5413, 4255, and 5943 reflections were measured respectively for **1**, **2**, and **3**. Corresponding unique data sets contained, respectively, 3475, 2824, and 4392 reflections each with $I \geq 3\sigma(I)$. Additional details of the experimental parameters and of the data collection techniques employed have been tabulated and are available as supplementary material.

Intensities of three "standard" reflections were monitored repeatedly during collection of each data set. In each case, the "standards" exhibited a regular, time-dependent isotropic intensity loss, apparently due to crystal degradation.

In the case of **1**, the falloff would have been more than 10% in the time taken to collect a complete set of unique data (one full quadrant). Accordingly, we chose to collect about half of one unique data set from each of two crystals of **1** having similar (minimal) radiation exposure histories.²⁹ For **2** the falloff during data collection was 6.2% and for **3** the falloff was 2.4%. Prior to further calculation, time-only-dependent degradation corrections were applied to all reflection data from all crystals.

Reflection intensities were subsequently corrected for Lorentz and polarization effects, and the corrected structure amplitudes $|F_o|^{30}$ were assigned individual estimated standard deviations $\sigma(F_o)$.³¹ Instrumental uncertainty constants, ρ^{32} employed in calculation of the $\sigma(F_o)$ values were 0.0015, 0.040, and 0.0015 for **1**, **2**, and **3**, respectively. Reflection data for which individual background counts differed significantly [i.e., if $|B_1 - B_2|/(B_1 + B_2)^{1/2} > 3.0$] were discarded. Data sets were then sorted to orders convenient for subsequent calculations, equivalent reflection forms were averaged, and reflections for which $I < 3\sigma(I)$ were rejected as "unobserved". Statistical R factors (R_s)³³ for the terminal data sets were 0.018 (**1**, 3475 reflections), 0.018 (**2**, 2824 reflections), and 0.020 (**3**, 4392 reflections).

Solution and Refinement of the Structures. The structures of all three complexes were solved by conventional Patterson and Fourier syntheses and were refined by block-diagonal least-squares analyses. The course of refinement for each structure is summarized in Table III; the function minimized in each case was $\sum w||F_o| - k|F_c||^2$ with $w = 1/\sigma^2(F_o)$. During refinement, reflection data for all three complexes were corrected for the effects of specimen absorption by the numerical integration method.³⁴ For **3** an extinction correction was also applied; the value of the extinction parameter (C) in the correction factor $\{(1 + I\beta C)^{-1}\}^{35}$ applied to $|F_o|$ refined to 1.09×10^{-6} . For both **1** and **2** extinction effects were small and no corrections were applied.

Atomic scattering factors for all nonhydrogen atoms were taken from ref 36, and hydrogen atom scattering factors were taken from the compilation by Stewart et al.³⁷ Scattering factors for Pt, Cl, and P were corrected for both real and imaginary components of the anomalous scattering.³⁶

Contributions from phenyl hydrogen atoms, located by calculation (C-H = 0.95 Å assumed) and assigned fixed isotropic temperature factors $B_H = B_C + 1.0 \text{ \AA}^2$ (where B_C is the temperature factor for

Table III. Refinement Summary

| | 1 | 2 | 3 |
|--|---|---|---|
| no. of reflections assigned zero weight in terminal refinement cycle | 22 | | 26 |
| criterion for zero weighting | $\frac{ F_o - k F_c }{6\sigma(F_o)} >$ | | $\frac{ F_o - k F_c }{6\sigma(F_o)} >$ |
| max parameter shift in final cycle, esd | 0.08 | 0.12 | 0.12 |
| max excursion in final difference map, e/Å ⁻³ | 0.7 | 1.5 (in vicinity of disordered Cl and CF ₃ groups) | 1.7 (in vicinity of solvent Cl) |
| R at end of isotropic refinement | 0.086 | | 0.090 |
| R before inclusion of phenyl hydrogens | 0.037 | | 0.038 |
| R (final) | 0.033 | 0.045 | 0.035 |
| R_w value (final) | 0.044 | 0.098 | 0.050 |
| $\{\sum w F_o - k F_c - \sigma(F_o) \}^2 / (m - n)^{1/2}$ | 1.47 | 1.04 | 1.51 |
| m | 3453 | 2824 | 4366 |
| n | 280 | 147 | 679 |

the attached carbon), were included in the terminal scattering models for **1** and for **3**. Methyl hydrogen atom contributions (and the solvent hydrogen atoms in **3**) were not included at any stage. Hydrogen atom parameters were not refined but were recalculated prior to each new refinement cycle. For **2**, the scattering model does not include contributions from either methyl or phenyl hydrogen atoms, and the CF₃ and Cl groups have been constrained to isotropic thermal motion. A similar constraint was applied to C and Cl atoms of the solvent (CH₂Cl₂) molecule in **3**. Anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ were specified for all other nonhydrogen atoms.

The refinement analysis of the methyl complex, **1**, with one formula unit per asymmetric scattering unit, was entirely straightforward. Refinement of the pentafluoroethyl complex, **3**, for which each asymmetric scattering unit contains two crystallographically inequivalent molecules of the complex and approximately one molecule of solvent dichloromethane, was only marginally less straightforward. As defined by the diffraction data, occupancy factors for the two chlorine and carbon atoms of the solvent molecule average only about 0.75, and in the terminal refinement cycles occupancy factors for all three atoms were held at that value. The corresponding formulation would be PtCl(C₂F₅)(PMePh₂)₂·0.375CH₂Cl₂. However, since crystals of **3** appeared to lose solvent quite rapidly on standing in air, becoming increasingly opaque and powdery, those specimens used for single-crystal studies were coated with shellac. Crystals so treated remained transparent and continued to diffract sharply for long periods. Nevertheless it seems unlikely that this technique would completely inhibit solvent loss over the length of time required for data collection. Accordingly, the stoichiometry of freshly prepared crystals of **3** is considered to be best formulated as PtCl(C₂F₅)(PMePh₂)₂·0.5CH₂Cl₂, corresponding to unit occupancy factor for the solvent molecules. The ready loss of solvent from crystals of **3** is reflected in microanalytical data (Table I) which agree well with a solvent-free formulation. The possible additional complication, resulting from the fact that the space group of **3** ($Pna2_1$) is polar, is unambiguously resolved by the diffraction data. With hydrogen atom contributions not included (and nonhydrogen atoms anisotropic) the proposed model gave $R = 0.038$.³⁸ For the scattering model of opposite polarity, the best R value obtained was 0.048. The R -factor ratio is significant at better than 99.5%.³⁹

Crystal structure analysis of the trifluoromethyl complex **2** was only partially successful. The complex crystallizes with only two formula units per cell in space group $P2_1/c$; hence the platinum atoms are constrained to occupy (special) equipoints of rank 2 with crystallographic site symmetry $\bar{1}$ (C_i). Since molecules of **2** cannot possess an inversion center at the platinum atom, either the packing arrangement is disordered or, alternatively, the correct space group is Pc (C_s^2 , No. 7) and the apparent twofold screw absences are accidental rather than systematic. Refinement of the structure confirmed that

Table IV. Atom Coordinates for *trans*-PtCl(CH₃)(PMePh₂)₂, 1

| (a) Refined Nonhydrogen Atom Coordinates | | | |
|--|--------------|---------------|-------------|
| atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
| Pt | 0.25357 (2) | 0.09729 (2) | 0.20070 (1) |
| Cl | 0.37975 (17) | -0.07806 (14) | 0.21771 (9) |
| P(1) | 0.31240 (14) | 0.14639 (14) | 0.11294 (7) |
| P(2) | 0.22899 (13) | 0.06390 (13) | 0.30107 (7) |
| C(1) | 0.1432 (6) | 0.2477 (6) | 0.1854 (3) |
| C(101) | 0.4840 (6) | 0.1407 (7) | 0.1424 (3) |
| C(201) | 0.2399 (6) | -0.0882 (5) | 0.3293 (3) |
| C(111) | 0.2713 (5) | 0.2939 (5) | 0.0788 (3) |
| C(112) | 0.1680 (6) | 0.3159 (5) | 0.0191 (3) |
| C(113) | 0.1320 (7) | 0.4309 (6) | -0.0040 (4) |
| C(114) | 0.2009 (7) | 0.5235 (6) | 0.0339 (4) |
| C(115) | 0.3039 (7) | 0.5029 (6) | 0.0936 (4) |
| C(116) | 0.3383 (6) | 0.3893 (6) | 0.1165 (3) |
| C(121) | 0.2547 (5) | 0.0534 (5) | 0.0379 (3) |
| C(122) | 0.1664 (5) | -0.0337 (6) | 0.0308 (3) |
| C(123) | 0.1181 (7) | -0.1003 (6) | -0.0294 (4) |
| C(124) | 0.1563 (7) | -0.0827 (6) | -0.0811 (3) |
| C(125) | 0.2463 (7) | 0.0009 (6) | -0.0750 (3) |
| C(126) | 0.2952 (7) | 0.0687 (6) | -0.0156 (3) |
| C(211) | 0.0860 (5) | 0.1150 (5) | 0.3088 (3) |
| C(212) | -0.0222 (6) | 0.0460 (6) | 0.2850 (4) |
| C(213) | -0.1330 (7) | 0.0886 (7) | 0.2885 (5) |
| C(214) | -0.1360 (6) | 0.1962 (7) | 0.3158 (4) |
| C(215) | -0.0325 (6) | 0.2645 (6) | 0.3379 (3) |
| C(216) | 0.0794 (6) | 0.2260 (6) | 0.3345 (3) |
| C(221) | 0.3558 (5) | 0.1385 (5) | 0.3699 (3) |
| C(222) | 0.4274 (6) | 0.2226 (5) | 0.3548 (3) |
| C(223) | 0.5283 (6) | 0.2768 (6) | 0.4082 (3) |
| C(224) | 0.5561 (6) | 0.2452 (6) | 0.4754 (3) |
| C(225) | 0.4853 (6) | 0.1610 (5) | 0.4902 (3) |
| C(226) | 0.3849 (6) | 0.1091 (5) | 0.4384 (3) |

(b) Calculated Hydrogen Atom Coordinates and Fixed Isotropic Thermal Parameters^a

| atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>B</i> , Å ² |
|--------|------------|------------|------------|---------------------------|
| H(112) | 0.121 | 0.251 | -0.007 | 4.9 |
| H(113) | 0.061 | 0.445 | -0.046 | 6.3 |
| H(114) | 0.177 | 0.602 | 0.019 | 6.9 |
| H(115) | 0.351 | 0.568 | 0.120 | 6.8 |
| H(116) | 0.409 | 0.375 | 0.158 | 5.8 |
| H(122) | 0.139 | -0.046 | 0.067 | 4.9 |
| H(123) | 0.057 | -0.159 | -0.034 | 6.7 |
| H(124) | 0.123 | -0.129 | -0.122 | 6.2 |
| H(125) | 0.274 | 0.013 | -0.111 | 6.1 |
| H(126) | 0.357 | 0.127 | -0.011 | 5.6 |
| H(212) | -0.019 | -0.029 | 0.267 | 6.1 |
| H(213) | -0.207 | 0.041 | 0.273 | 7.7 |
| H(214) | -0.212 | 0.224 | 0.318 | 7.2 |
| H(215) | -0.036 | 0.340 | 0.356 | 6.0 |
| H(216) | 0.153 | 0.274 | 0.351 | 5.2 |
| H(222) | 0.408 | 0.244 | 0.308 | 4.9 |
| H(223) | 0.578 | 0.335 | 0.398 | 5.7 |
| H(224) | 0.625 | 0.282 | 0.511 | 5.5 |
| H(225) | 0.505 | 0.140 | 0.537 | 4.8 |
| H(226) | 0.335 | 0.051 | 0.449 | 4.5 |

^a Hydrogen atoms are numbered according to the carbon atoms to which they are bonded.

the correct space group was in fact *P2₁/c* and that the structure was disordered. Within experimental error, atom pairs in the two PMePh₂ groups on each platinum atom relate accurately via the crystallographic inversion center at the platinum. The disorder, which results from different enantiomers being distributed statistically in identical crystallographic sites, is manifest in the structure only as an apparently random interchange of the Cl and CF₃ moieties. Consequently, while the platinum and PMePh₂ groups, and to a lesser extent the fluorine atoms of the CF₃ group (with 50% occupancy), are well resolved by the diffraction data, the electron density distributions of the chlorine atom and of the CF₃ carbon atom are totally inseparable. Accordingly, in the scattering model, these two atoms could only be assigned approximate fixed coordinates, based loosely on the coordinates of the composite electron density peak in the difference map and the anticipated geometry about the platinum and CF₃ carbon atoms. Bond

Table V. Atom Coordinates for *trans*-PtCl(CF₃)(PMePh₂)₂, 2

| (a) Refined Nonhydrogen Atom Coordinates and Isotropic Thermal Parameters | | | | |
|---|--------------|-------------|-------------|---------------------------|
| atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>B</i> , Å ² |
| Pt | 0.00000 (0) | 0.00000 (0) | 0.00000 (0) | |
| P(1) | 0.0547 (2) | -0.0403 (1) | 0.2300 (2) | |
| C(101) | 0.1464 (12) | 0.0438 (6) | 0.3731 (9) | |
| C(111) | 0.1979 (8) | -0.1323 (4) | 0.3025 (7) | |
| C(112) | 0.3319 (10) | -0.1335 (5) | 0.4458 (9) | |
| C(113) | 0.4393 (14) | -0.1994 (7) | 0.5005 (8) | |
| C(114) | 0.4140 (12) | -0.2690 (6) | 0.4074 (10) | |
| C(115) | 0.2781 (12) | -0.2677 (5) | 0.2629 (9) | |
| C(116) | 0.1687 (11) | -0.1995 (5) | 0.2093 (9) | |
| C(121) | -0.1297 (9) | -0.0680 (4) | 0.2356 (7) | |
| C(122) | -0.2594 (17) | -0.0093 (4) | 0.1810 (14) | |
| C(123) | -0.3989 (12) | -0.0249 (7) | 0.1909 (11) | |
| C(124) | -0.4079 (10) | -0.0998 (6) | 0.2531 (8) | |
| C(125) | -0.2833 (10) | -0.1581 (5) | 0.3103 (9) | |
| C(126) | -0.1417 (10) | -0.1429 (4) | 0.2993 (8) | |
| F(11) | 0.3161 (10) | 0.0670 (5) | 0.2223 (9) | 4.88 (18) |
| F(12) | 0.1207 (11) | 0.1569 (5) | 0.1750 (9) | 4.84 (17) |
| F(13) | 0.2088 (12) | 0.1475 (6) | 0.0209 (9) | 5.57 (19) |

| (b) Calculated Chlorine and Trifluoromethyl Carbon Atom Coordinated and Isotropic Thermal Parameters | | | | |
|--|------------|------------|------------|---------------------------|
| atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>B</i> , Å ² |
| Cl | 0.2172 | 0.1073 | 0.0927 | 4.50 (7) |
| C(1) | 0.1759 | 0.0959 | 0.1132 | 1.13 (13) |

distances and bond angles not involving the chlorine or CF₃ carbon atoms appear quite unexceptional. Nevertheless, they are likely to be subject to systematic errors the magnitude of which may not be adequately reflected by the tabulated standard error estimates.

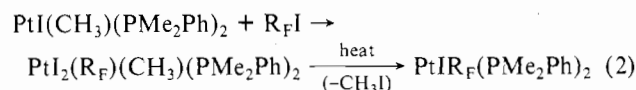
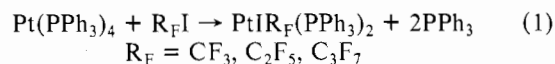
Maximum positive electron density excursions in the terminal difference maps, together with terminal values of *R*, *R_w*, and $\{\sum w||F_o| - |F_c||^2/(m-n)\}^{1/2}$ for each structure are listed in Table III. Weighting-scheme analyses confirmed that the distribution of $w\Delta^2$ [$\Delta = ||F_o| - |F_c||$] were essentially independent of both $|F_c|$ and $\sin \theta$ for all three structures.

Terminal atom coordinates, along with standard error estimates derived from inversion of the block-diagonal least-squares matrices, are listed in Tables IV (1), V (2), and VI (3). Tables of atom thermal parameters and tables of terminal $10|F_o|$ and $10|F_c|$ values (electrons) are available as supplementary material.

Computer Programs. Data reduction and analyses programs have been described elsewhere.²⁸ The molecular diagrams were produced using ORTEP.⁴⁰ Calculations were performed on the CDC3600 computer of the CSIRO Division of Computing Research, Canberra, Australia, and the IBM360/50 and Univac-1108 computers of The Australian National University Computer Centre.

Results

(Perfluoroalkyl)platinum(II)-iodo complexes have been prepared previously by oxidative additions of perfluoroalkyl iodides, either to Pt(PPh₃)₄⁴¹ (eq 1) or to PtI(CH₃)(PMe₂Ph)₂⁴² (eq 2). The chloro complex PtCl(CF₃)-



(PMe₂Ph)₂ has been made from its iodo analogue by treatment with AgBF₄ in methanol and reaction of the cationic species so generated with sodium chloride.¹² In an extension of earlier work on the reaction of acetyl or benzoyl chlorides with Pt(PPh₃)₄,^{43,44} we find that trifluoroacetyl chloride and pentafluoropropionyl chloride readily undergo oxidative addition to Pt(PMe₂Ph)₄ to give (perfluoroacyl)platinum(II) complexes PtCl(COR_F)(PMe₂Ph)₂, which can be thermally decarbonylated in vacuo to give good yields of the colorless, air-stable perfluoroalkyls PtClR_F(PMe₂Ph)₂ (R_F = CF₃, 2; R_F = C₂F₅,

Table VI. Atom Coordinates for *trans*-PtCl(C₂F₅)(PMePh₂)₂·0.5CH₂Cl₂, 3

(a) Refined Nonhydrogen Atom Coordinates

| molecule A | | | | molecule B | | | |
|------------|---------------|---------------|---------------|------------|--------------|---------------|--------------|
| atom | x/a | y/b | z/c | atom | x/a | y/b | z/c |
| Pt | 0.07363 (3) | -0.01334 (4) | 0.0 | Pt | 0.19190 (3) | 0.01435 (4) | 0.23770 (1) |
| Cl | -0.01928 (19) | -0.16074 (31) | -0.02979 (10) | Cl | 0.09620 (20) | 0.15664 (35) | 0.26795 (10) |
| P(1) | 0.19214 (18) | -0.13206 (29) | -0.02072 (8) | P(1) | 0.30831 (17) | 0.13360 (29) | 0.25988 (8) |
| P(2) | -0.05343 (18) | 0.10268 (27) | 0.01314 (7) | P(2) | 0.06707 (18) | -0.10516 (30) | 0.22329 (8) |
| F(11) | 0.2382 (4) | 0.1048 (7) | 0.0183 (2) | F(11) | 0.3577 (4) | -0.1019 (7) | 0.2210 (2) |
| F(12) | 0.1326 (5) | 0.2413 (7) | 0.0259 (2) | F(12) | 0.2530 (4) | -0.2372 (7) | 0.2097 (2) |
| F(21) | 0.1817 (7) | -0.0447 (10) | 0.0725 (2) | F(21) | 0.3057 (7) | 0.0589 (10) | 0.1666 (2) |
| F(22) | 0.2082 (6) | 0.1583 (11) | 0.0836 (2) | F(22) | 0.3336 (7) | -0.1453 (11) | 0.1540 (3) |
| F(23) | 0.0783 (5) | 0.0909 (11) | 0.0817 (2) | F(23) | 0.2024 (6) | -0.0790 (11) | 0.1560 (2) |
| C(1) | 0.1509 (7) | 0.1077 (13) | 0.0277 (4) | C(1) | 0.2726 (8) | -0.1002 (12) | 0.2108 (3) |
| C(2) | 0.1532 (8) | 0.0777 (15) | 0.0669 (4) | C(2) | 0.2805 (10) | -0.0690 (16) | 0.1719 (3) |
| C(101) | 0.2698 (7) | -0.1920 (12) | 0.0106 (3) | C(101) | 0.3899 (9) | 0.1932 (14) | 0.2299 (4) |
| C(201) | -0.1194 (9) | 0.1284 (16) | -0.0242 (4) | C(201) | 0.0053 (10) | -0.1404 (16) | 0.2634 (4) |
| C(111) | 0.1685 (7) | -0.2816 (11) | -0.0457 (3) | C(111) | 0.2828 (7) | 0.2825 (11) | 0.2846 (3) |
| C(112) | 0.1656 (11) | -0.4075 (15) | -0.0305 (4) | C(112) | 0.2808 (9) | 0.4060 (14) | 0.2677 (4) |
| C(113) | 0.1474 (11) | -0.5195 (13) | -0.0491 (6) | C(113) | 0.2624 (12) | 0.5181 (14) | 0.2874 (5) |
| C(114) | 0.1298 (11) | -0.5121 (15) | -0.0835 (4) | C(114) | 0.2408 (10) | 0.5137 (14) | 0.3219 (5) |
| C(115) | 0.1257 (11) | -0.3886 (18) | -0.0991 (4) | C(115) | 0.2444 (10) | 0.3934 (17) | 0.3388 (4) |
| C(116) | 0.1472 (9) | -0.2751 (15) | -0.0798 (3) | C(116) | 0.2623 (9) | 0.2785 (14) | 0.3195 (4) |
| C(121) | 0.2544 (7) | -0.0329 (11) | -0.0504 (3) | C(121) | 0.3692 (7) | 0.0305 (12) | 0.2907 (3) |
| C(122) | 0.3387 (8) | -0.0693 (17) | -0.0611 (4) | C(122) | 0.4502 (9) | 0.0686 (16) | 0.2997 (4) |
| C(123) | 0.3823 (9) | 0.0071 (17) | -0.0830 (4) | C(123) | 0.5000 (11) | -0.0156 (18) | 0.3222 (4) |
| C(124) | 0.3531 (10) | 0.1261 (17) | -0.0954 (4) | C(124) | 0.4625 (10) | -0.1285 (15) | 0.3344 (4) |
| C(125) | 0.2704 (12) | 0.1666 (15) | -0.0868 (4) | C(125) | 0.3822 (11) | -0.1634 (15) | 0.3260 (4) |
| C(126) | 0.2219 (8) | 0.0874 (13) | -0.0633 (4) | C(126) | 0.3356 (9) | -0.0841 (15) | 0.3030 (4) |
| C(211) | -0.0495 (8) | 0.2728 (11) | 0.0299 (3) | C(211) | 0.0737 (8) | -0.2688 (13) | 0.2037 (4) |
| C(212) | -0.0269 (8) | 0.3772 (13) | 0.0090 (4) | C(212) | 0.0897 (11) | -0.3819 (15) | 0.2226 (5) |
| C(213) | -0.0194 (10) | 0.5065 (12) | 0.0203 (5) | C(213) | 0.0945 (12) | -0.5082 (13) | 0.2068 (8) |
| C(214) | -0.0354 (11) | 0.5334 (13) | 0.0538 (6) | C(214) | 0.0924 (13) | -0.5161 (17) | 0.1702 (8) |
| C(215) | -0.0562 (11) | 0.4316 (16) | 0.0772 (4) | C(215) | 0.0722 (12) | -0.4037 (20) | 0.1517 (7) |
| C(216) | -0.0631 (8) | 0.3023 (12) | 0.0645 (4) | C(216) | 0.0647 (9) | -0.2858 (16) | 0.1678 (4) |
| C(221) | -0.1216 (7) | 0.0165 (10) | 0.0429 (3) | C(221) | -0.0068 (9) | -0.0124 (12) | 0.1955 (3) |
| C(222) | -0.2063 (8) | 0.0566 (14) | 0.0490 (4) | C(222) | -0.0914 (8) | -0.0553 (13) | 0.1925 (4) |
| C(223) | -0.2593 (9) | -0.0141 (14) | 0.0719 (5) | C(223) | -0.1476 (9) | 0.0089 (14) | 0.1706 (4) |
| C(224) | -0.2283 (9) | -0.1162 (14) | 0.0912 (4) | C(224) | -0.1194 (9) | 0.1135 (15) | 0.1509 (3) |
| C(225) | -0.1423 (9) | -0.1543 (14) | 0.0872 (4) | C(225) | -0.0354 (9) | 0.1571 (13) | 0.1537 (3) |
| C(226) | -0.0907 (8) | -0.0888 (12) | 0.0622 (3) | C(226) | 0.0214 (8) | 0.0937 (13) | 0.1756 (3) |

(b) Refined Solvate Chlorine and Carbon Atom Coordinates and Isotropic Thermal Parameters

| atom | x/a | y/b | z/c | B, Å ² |
|-------|------------|------------|-----------|-------------------|
| C | 0.061 (2) | 0.109 (3) | 0.367 (1) | 9.2 (8) |
| Cl(1) | -0.032 (1) | 0.009 (1) | 0.359 (1) | 15.4 (5) |
| Cl(2) | 0.145 (1) | -0.004 (1) | 0.373 (1) | 14.7 (5) |

(c) Calculated Hydrogen Atom Coordinates and Fixed Isotropic Thermal Parameters^a

| molecule A | | | | | molecule B | | | | |
|------------|--------|--------|--------|-------------------|------------|--------|--------|-------|-------------------|
| atom | x/a | y/b | z/c | B, Å ² | atom | x/a | y/b | z/c | B, Å ² |
| H(112) | 0.179 | -0.414 | -0.007 | 6.0 | H(112) | 0.293 | 0.410 | 0.244 | 4.9 |
| H(113) | 0.147 | -0.605 | -0.038 | 6.7 | H(113) | 0.262 | 0.602 | 0.276 | 6.4 |
| H(114) | 0.117 | -0.590 | -0.096 | 6.1 | H(114) | 0.227 | 0.592 | 0.335 | 5.6 |
| H(115) | 0.112 | -0.382 | -0.123 | 6.5 | H(115) | 0.232 | 0.389 | 0.363 | 5.9 |
| H(116) | 0.147 | -0.190 | -0.091 | 4.7 | H(116) | 0.262 | 0.194 | 0.331 | 4.9 |
| H(122) | 0.362 | -0.150 | -0.052 | 5.1 | H(122) | 0.474 | 0.149 | 0.291 | 5.3 |
| H(123) | 0.438 | -0.021 | -0.090 | 6.3 | H(123) | 0.557 | 0.008 | 0.329 | 6.4 |
| H(124) | 0.386 | 0.180 | -0.111 | 6.1 | H(124) | 0.495 | -0.184 | 0.350 | 5.9 |
| H(125) | 0.247 | 0.247 | -0.096 | 6.2 | H(125) | 0.359 | -0.244 | 0.335 | 5.9 |
| H(126) | 0.166 | 0.116 | -0.056 | 4.6 | H(126) | 0.279 | -0.108 | 0.296 | 5.0 |
| H(212) | -0.017 | 0.358 | -0.015 | 5.0 | H(212) | 0.096 | -0.374 | 0.247 | 7.3 |
| H(213) | -0.004 | 0.577 | 0.005 | 5.6 | H(213) | 0.105 | -0.586 | 0.220 | 10.0 |
| H(214) | -0.030 | 0.623 | 0.062 | 6.6 | H(214) | 0.098 | -0.600 | 0.159 | 10.8 |
| H(215) | -0.066 | 0.451 | 0.101 | 6.3 | H(215) | 0.066 | -0.411 | 0.127 | 9.7 |
| H(216) | -0.078 | 0.232 | 0.080 | 4.3 | H(216) | 0.054 | -0.208 | 0.154 | 5.7 |
| H(222) | -0.228 | 0.129 | 0.036 | 4.5 | H(222) | -0.111 | -0.129 | 0.206 | 4.3 |
| H(223) | -0.318 | 0.012 | 0.075 | 5.7 | H(223) | -0.206 | -0.020 | 0.169 | 5.0 |
| H(224) | -0.264 | -0.161 | 0.107 | 4.9 | H(224) | -0.158 | 0.157 | 0.136 | 4.5 |
| H(225) | -0.120 | -0.227 | 0.100 | 5.0 | H(225) | -0.016 | 0.231 | 0.140 | 4.4 |
| H(226) | -0.032 | -0.115 | 0.059 | 4.1 | H(226) | 0.080 | 0.123 | 0.177 | 3.9 |

^a Hydrogen atoms are numbered according to the carbon atom to which they are bonded.

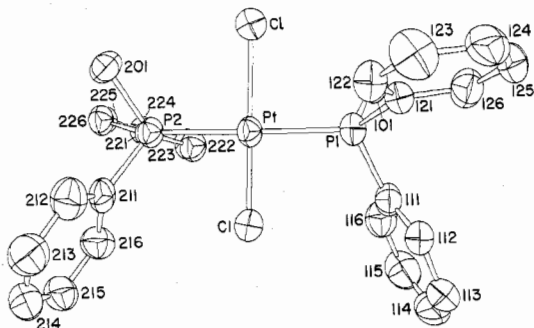


Figure 1. Atom nomenclature and stereochemistry of *trans*-PtCl(CH₃)(PMePh₂)₂, **1**.

3). Metathesis with lithium bromide gives the corresponding bromo derivatives. The ¹H NMR spectra of all these complexes contain 1:2:1 triplet methyl resonances, indicative of mutually trans diphenylmethylphosphine ligands. In their ³¹P NMR spectra the trifluoromethyl complexes show a quartet owing to P-F coupling (³J_{P-F} ≈ 20 Hz), and the pentafluoroethyl complexes show a triplet owing to coupling with the α-fluorine atoms (³J_{P-F} ≈ 26 Hz). Satellites due to coupling with ¹⁹⁵Pt (*I* = 1/2, 34% abundance) are also observed. The magnitudes of *J*_{P-P} are ca. 100 Hz lower than in PtCl(CH₃)(PMePh₂)₂, **1**, but are in the range expected for mutually trans phosphine ligands in this type of complex.⁴⁶ The far-IR spectra of **2** and **3** show a band (split in the case of **3**, presumably due to solid-state effects) at ca. 302 cm⁻¹ due to ν(Pt-Cl). This band is absent in PtBrR_F(PMePh₂)₂ and is replaced by a ν(Pt-Br) band at ca. 200 cm⁻¹. Since the value of ν(Pt-Cl) for **1** is only 272 cm⁻¹, the far-IR spectra clearly indicate a lower trans influence for perfluoroalkyl groups than for methyl.

Because of packing disorder in **2**, we could not directly compare salient metal-ligand bond distances in **2** and **1**. However, the close similarity in the spectroscopic properties of **2** and of **3** suggested that conclusions deriving from comparison of **3** and **1** would be equally valid for **2** and **1**. It was this rationale which led us to determine the structure of **3** and which is implicit in much of the subsequent discussion in this paper.

Description of the Structures. The crystal structures of all three complexes, **1**, **2**, and **3**, contain discrete molecular units separated by normal van der Waals distances. No symmetry constraints are imposed upon the unit cell contents in either **1** or **3**, whereas in **2** the platinum atoms are constrained to occupy crystallographic inversion centers. Occupancy factors for the dichloromethane solvent atoms in **3** suggest the formulation PtCl(C₂F₅)(PMePh₂)₂·0.375CH₂Cl₂. However, for reasons discussed in the Experimental Section, we consider that the appropriate formulation for freshly prepared crystals should be PtCl(C₂F₅)(PMePh₂)₂·0.5CH₂Cl₂. The two independent PtCl(C₂F₅)(PMePh₂)₂ moieties in each asymmetric scattering unit are quite closely related by a pseudo twofold rotor parallel to the crystallographic *a* axis. With very few exceptions, agreement between corresponding bond distances and bond angles in these two moieties is well within experimental error. The atom nomenclature and stereochemistry of the complexes are shown in Figures 1 (**1**), 2 (**2**), and 3 (**3**), respectively. Thermal ellipsoids have been drawn throughout to include 50% of the probability distribution and, for clarity, hydrogen atoms have been omitted from all figures. The hydrogen atom nomenclature accords with that of the carbon atoms to which they are attached. Principal interatomic distances and interbond angles, together with estimated standard errors, are listed in Table VII.

Intraphenyl ring distances and angles are listed variously in Tables VIII-X and the results of some least-squares-planes

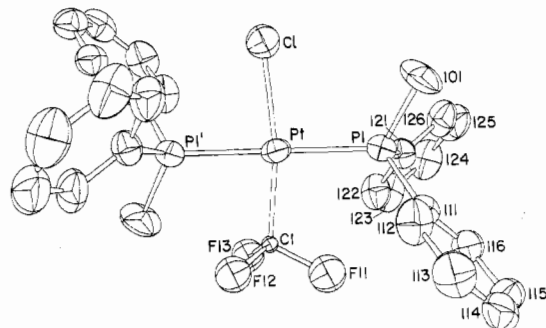


Figure 2. Atom nomenclature and stereochemistry of *trans*-PtCl(CF₃)(PMePh₂)₂, **2**.

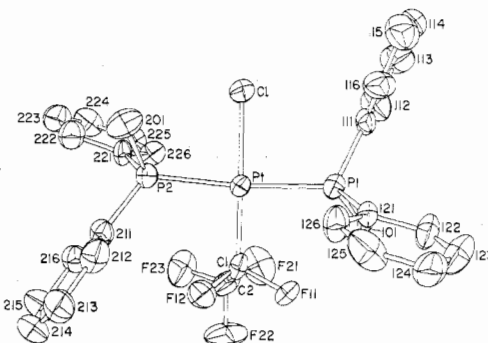


Figure 3. Atom nomenclature and stereochemistry of *trans*-PtCl(C₂F₅)(PMePh₂)₂, **3**.

calculations for selected molecular fragments are listed in Table XI.

As expected, all three complexes exhibit an essentially square-planar ligand arrangement about the central metal atom, with the tertiary phosphine ligands occupying mutually trans sites in agreement with the spectroscopic data. However, in both **1** and **3**, there are significant deviations from planarity. Although the angle Cl-Pt-C(1) of 179.45 (16)^o in **1** is close to the ideal value of 180^o, the angle P(1)-Pt-P(2) of 169.49 (5)^o departs significantly from this. The angles made by adjacent ligands at the platinum atom are close to 90^o, ranging from 88.12 (7) to 91.89 (21)^o. Alternate ligand atoms deviate from the mean coordination plane in opposite directions, the deviations being largest (ca. 0.2 Å) for the two phosphorus atoms. The distortions are greater than those observed in the closely related complex *trans*-PtCl{CH₂Si(CH₃)₃}(PMe₂Ph)₂,⁴⁷ but in other respects these two structures are very similar (see below). In **3**, the average angles P(1)-Pt-P(2) and Cl-Pt-C(1) of 172.0 (1) and 177.4 (3)^o are both less than 180^o, and there are appreciable deviations from the expected 90^o angles for P(2)-Pt-Cl [average 84.5 (1)^o] and P(2)-Pt-C(1) [average 95.4 (3)^o]. In contrast, the angles P(1)-Pt-Cl [average 89.7 (1)^o] and P(1)-Pt-C [average 90.6 (3)^o] are close to 90^o. The departure of those angles involving P(2) from 90^o may be caused by steric repulsion between the fluoroalkyl moiety and the tertiary phosphine ligand toward which the CF₃ substituent is directed. In both **1** and **3** the deviations make the coordination geometry about platinum tend toward a flattened tetrahedron. Because of the packing disorder, similar detail is not available for **2**, although it is noteworthy that in this complex the P-Pt-P moiety appears to be accurately linear.

The metal-ligand distances in **1** [Pt-Cl = 2.412 (2) Å, Pt-C(1) = 2.081 (6) Å, Pt-P = 2.292 (2), 2.291 (2) Å] each equal, within experimental error, the corresponding distances in the (trimethylsilyl)methyl complex *trans*-PtCl{CH₂Si(CH₃)₃}(PMe₂Ph)₂ [Pt-Cl = 2.415 (5) Å, Pt-C = 2.079 (14) Å, Pt-P = 2.294 (5), 2.292 (5) Å].⁴⁷ The Pt-C distance in

Table VII. Comparison of Important Bond Distances (Å) and Interbond Angles (deg) for PtCl(CH₃)(PMePh₂)₂, **1**, PtCl(CF₃)(PMePh₂)₂, **2**, and PtCl(C₂F₅)(PMePh₂)₂·0.5CH₂Cl₂, **3**

| (a) Bond Distances | | | | |
|--------------------|-----------|------------------|------------|------------|
| atoms | 1 | 2 ^{a,b} | 3 | |
| | | | molecule A | molecule B |
| Pt-Cl | 2.412 (2) | [2.42] | 2.361 (3) | 2.365 (4) |
| Pt-P(1) | 2.292 (2) | 2.320 (2) | 2.329 (3) | 2.326 (3) |
| Pt-P(2) | 2.291 (2) | | 2.341 (3) | 2.340 (3) |
| Pt-C(1) | 2.081 (6) | [2.09] | 2.013 (12) | 1.990 (12) |
| P(1)-C(101) | 1.827 (6) | 1.86 (1) | 1.813 (12) | 1.817 (15) |
| P(1)-C(111) | 1.816 (6) | 1.84 (1) | 1.817 (12) | 1.813 (12) |
| P(1)-C(121) | 1.807 (6) | 1.81 (1) | 1.797 (12) | 1.837 (13) |
| P(2)-C(201) | 1.820 (6) | | 1.792 (14) | 1.859 (16) |
| P(2)-C(211) | 1.818 (6) | | 1.820 (12) | 1.805 (14) |
| P(2)-C(221) | 1.818 (5) | | 1.785 (12) | 1.813 (12) |
| C(1)-C(2) | | | 1.546 (20) | 1.545 (18) |
| C(1)-F(11) | | [1.30] | 1.402 (13) | 1.377 (14) |
| C(1)-F(12) | | [1.41] | 1.366 (14) | 1.401 (14) |
| C(1)-F(13) | | [1.43] | | |
| C(2)-F(21) | | | 1.317 (18) | 1.350 (19) |
| C(2)-F(22) | | | 1.339 (17) | 1.320 (18) |
| C(2)-F(23) | | | 1.302 (15) | 1.363 (18) |

(b) Interbond Angles

| atom | 1 | 2 | 3 | |
|--------------------|-------------|-----------|------------|------------|
| | | | molecule A | molecule B |
| Cl-Pt-P(1) | 88.12 (7) | [85.1] | 89.7 (1) | 89.7 (1) |
| Cl-Pt-P(2) | 90.80 (7) | | 84.4 (1) | 84.6 (1) |
| Cl-Pt-C(1) | 179.45 (16) | [168.3] | 177.0 (4) | 177.8 (3) |
| P(1)-Pt-P(2) | 169.49 (5) | 180.0 (0) | 172.1 (1) | 171.9 (3) |
| P(1)-Pt-C(1) | 91.9 (2) | [85.1] | 91.2 (3) | 90.0 (4) |
| P(2)-Pt-C(1) | 88.3 (2) | | 95.0 (3) | 95.8 (4) |
| Pt-P(1)-C(101) | 110.1 (3) | 115.3 (4) | 117.4 (4) | 118.1 (5) |
| Pt-P(1)-C(111) | 115.8 (2) | 111.6 (4) | 116.3 (3) | 116.5 (4) |
| Pt-P(1)-C(121) | 116.8 (2) | 114.6 (3) | 111.3 (4) | 110.6 (4) |
| Pt-P(2)-C(201) | 116.5 (3) | | 112.0 (5) | 108.8 (5) |
| Pt-P(2)-C(211) | 118.9 (2) | | 120.8 (4) | 121.0 (4) |
| Pt-P(2)-C(221) | 108.3 (2) | | 113.6 (4) | 113.6 (4) |
| C(101)-P(1)-C(111) | 104.2 (3) | 107.0 (4) | 102.7 (6) | 102.8 (6) |
| C(101)-P(1)-C(121) | 104.5 (3) | 100.4 (6) | 104.7 (5) | 104.0 (6) |
| C(111)-P(1)-C(121) | 104.1 (3) | 107.0 (4) | 102.7 (6) | 103.1 (6) |
| C(201)-P(2)-C(211) | 102.8 (3) | | 100.0 (7) | 102.1 (7) |
| C(201)-P(2)-C(221) | 104.6 (3) | | 104.7 (6) | 105.5 (6) |
| C(211)-P(2)-C(221) | 104.4 (3) | | 103.9 (5) | 104.3 (6) |
| Pt-C(1)-C(2) | | | 114.9 (9) | 116.4 (9) |
| Pt-C(1)-F(11) | | [112.7] | 115.0 (8) | 117.3 (8) |
| Pt-C(1)-F(12) | | [113.1] | 115.8 (8) | 116.2 (8) |
| Pt-C(1)-F(13) | | [113.5] | | |
| C(2)-C(1)-F(11) | | | 103.3 (9) | 101.9 (10) |
| C(2)-C(1)-F(12) | | | 104.2 (11) | 100.6 (10) |
| F(11)-C(1)-F(12) | | [105.3] | 101.9 (9) | 101.8 (9) |
| F(11)-C(1)-F(13) | | [109.7] | | |
| F(12)-C(1)-F(13) | | [101.1] | | |
| C(1)-C(2)-F(21) | | | 110.4 (11) | 111.2 (11) |
| C(1)-C(2)-F(22) | | | 111.9 (11) | 116.6 (12) |
| C(1)-C(2)-F(23) | | | 113.2 (10) | 110.9 (12) |
| F(21)-C(2)-F(22) | | | 105.3 (11) | 106.6 (12) |
| F(21)-C(2)-F(23) | | | 108.7 (12) | 104.9 (12) |
| F(22)-C(2)-F(23) | | | 106.9 (12) | 105.8 (11) |

^a Values in square brackets derive from calculated, not refined, coordinates; see text. ^b Tabulated standard errors for **2** are probably underestimated due to uncertainties in the scattering model.

1 also equals that in the η^1 -allyl complex *trans*-PtCl-(C₃H₅)(PPh₃)₂ [Pt-C = 2.090 (4) Å],⁴⁸ within experimental error, but the Pt-Cl distance in the latter complex, 2.425 (2)

Table VIII. Bond Lengths (Å) and Interbond Angles (deg) in the Phenyl Rings of PtCl(CH₃)(PMePh₂)₂, **1**

| | <i>m</i> = 1, <i>n</i> = 1 | <i>m</i> = 1, <i>n</i> = 2 | <i>m</i> = 2, <i>n</i> = 1 | <i>m</i> = 2, <i>n</i> = 2 |
|---|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| P(<i>m</i>)-C(<i>mn</i> 1) | 1.816 (6) | 1.807 (6) | 1.818 (7) | 1.818 (5) |
| C(<i>mn</i> 1)-C(<i>mn</i> 2) | 1.376 (7) | 1.387 (9) | 1.391 (9) | 1.384 (9) |
| C(<i>mn</i> 2)-C(<i>mn</i> 3) | 1.401 (9) | 1.398 (10) | 1.398 (12) | 1.405 (8) |
| C(<i>mn</i> 3)-C(<i>mn</i> 4) | 1.372 (10) | 1.351 (13) | 1.362 (12) | 1.380 (10) |
| C(<i>mn</i> 4)-C(<i>mn</i> 5) | 1.372 (9) | 1.376 (11) | 1.344 (10) | 1.375 (10) |
| C(<i>mn</i> 5)-C(<i>mn</i> 6) | 1.383 (9) | 1.392 (9) | 1.394 (11) | 1.375 (7) |
| C(<i>mn</i> 6)-C(<i>mn</i> 1) | 1.388 (8) | 1.400 (11) | 1.391 (9) | 1.398 (8) |
| P(<i>m</i>)-C(<i>mn</i> 1)-C(<i>mn</i> 2) | 122.0 (4) | 120.8 (5) | 120.2 (5) | 120.1 (4) |
| P(<i>m</i>)-C(<i>mn</i> 1)-C(<i>mn</i> 6) | 119.7 (4) | 121.2 (5) | 121.3 (5) | 120.6 (5) |
| C(<i>mn</i> 2)-C(<i>mn</i> 1)-C(<i>mn</i> 6) | 118.0 (5) | 118.1 (5) | 118.3 (6) | 119.3 (5) |
| C(<i>mn</i> 1)-C(<i>mn</i> 2)-C(<i>mn</i> 3) | 121.4 (5) | 119.6 (7) | 119.6 (7) | 119.8 (6) |
| C(<i>mn</i> 2)-C(<i>mn</i> 3)-C(<i>mn</i> 4) | 119.4 (6) | 121.5 (7) | 120.9 (7) | 119.9 (7) |
| C(<i>mn</i> 3)-C(<i>mn</i> 4)-C(<i>mn</i> 5) | 119.9 (6) | 120.2 (6) | 120.0 (8) | 120.2 (5) |
| C(<i>mn</i> 4)-C(<i>mn</i> 5)-C(<i>mn</i> 6) | 120.4 (6) | 119.3 (8) | 121.0 (7) | 120.4 (6) |
| C(<i>mn</i> 5)-C(<i>mn</i> 6)-C(<i>mn</i> 1) | 120.9 (5) | 121.3 (7) | 120.2 (6) | 120.5 (6) |

Table IX. Bond Lengths (Å) and Interbond Angles (deg) in the Phenyl Rings of PtCl(CF₃)(PMePh₂)₂, **2**

| | <i>m</i> = 1, <i>n</i> = 1 | <i>m</i> = 1, <i>n</i> = 2 |
|---|----------------------------|----------------------------|
| P(<i>m</i>)-C(<i>mn</i> 1) | 1.84 (1) | 1.81 (1) |
| C(<i>mn</i> 1)-C(<i>mn</i> 2) | 1.38 (1) | 1.39 (2) |
| C(<i>mn</i> 2)-C(<i>mn</i> 3) | 1.35 (2) | 1.39 (3) |
| C(<i>mn</i> 3)-C(<i>mn</i> 4) | 1.41 (2) | 1.38 (2) |
| C(<i>mn</i> 4)-C(<i>mn</i> 5) | 1.39 (1) | 1.35 (1) |
| C(<i>mn</i> 5)-C(<i>mn</i> 6) | 1.38 (1) | 1.41 (2) |
| C(<i>mn</i> 6)-C(<i>mn</i> 1) | 1.38 (1) | 1.40 (1) |
| P(<i>m</i>)-C(<i>mn</i> 1)-C(<i>mn</i> 2) | 121.0 (6) | 117.8 (9) |
| P(<i>m</i>)-C(<i>mn</i> 1)-C(<i>mn</i> 6) | 118.2 (5) | 122.8 (6) |
| C(<i>mn</i> 2)-C(<i>mn</i> 1)-C(<i>mn</i> 6) | 120.8 (7) | 119.4 (11) |
| C(<i>mn</i> 1)-C(<i>mn</i> 2)-C(<i>mn</i> 3) | 122.0 (9) | 120.1 (12) |
| C(<i>mn</i> 2)-C(<i>mn</i> 3)-C(<i>mn</i> 4) | 118.7 (8) | 119.1 (11) |
| C(<i>mn</i> 3)-C(<i>mn</i> 4)-C(<i>mn</i> 5) | 119.2 (10) | 122.9 (11) |
| C(<i>mn</i> 4)-C(<i>mn</i> 5)-C(<i>mn</i> 6) | 121.1 (10) | 118.2 (9) |
| C(<i>mn</i> 5)-C(<i>mn</i> 6)-C(<i>mn</i> 1) | 118.2 (7) | 120.2 (8) |

Å, is significantly longer than that in **1**. The Pt-P distances in **1** are also equal, within experimental error, to that found in *trans*-PtCl(CH=CH₂)(PEt₂Ph)₂⁴⁹ but are marginally shorter than those observed in *trans*-PtCl(C₃H₅)(PPh₃)₂ [2.302 (2), 2.304 (2) Å],⁴⁸ *trans*-PtI(CH₃)(PPh₃)₂·SO₂ [2.300 (2), 2.310 (2) Å],⁵⁰ and *trans*-PtBr(*trans*-CH=CHPh)(PPh₃)₂ [2.310 (2), 2.304 (2) Å].⁵¹ The slightly greater Pt-P distances observed in the triphenylphosphine complexes are probably a consequence of increased steric crowding in the coordination sphere.

Because of the close correspondence of chemically equivalent bond distances and bond angles in the two independent PtCl(C₂F₅)(PMePh₂)₂ molecules in **3**, subsequent discussion of **3** will refer only to mean values. The Pt-Cl distance [2.363 (2) Å] is significantly shorter than that found in **1** [2.412 (2) Å]. The Pt-C distance in **3** [2.002 (8) Å] is also significantly shorter than that in **1** [2.081 (6) Å], but the relative contraction (ca. 0.08 Å) is less than that (0.11 Å) observed in passing from η^5 -C₅H₅Mo(CO)₃C₂H₅ [Mo-C(alkyl) = 2.397 (19) Å]²⁰ to the corresponding perfluoropropyl complex η^5 -C₅H₅Mo(CO)₃C₃F₇ [Mo-C(perfluoroalkyl) = 2.288 (9) Å].²¹ The Pt-C distance in **3** is also shorter than those found in *cis*-PtF[CH(CF₃)₂](PPh₃)₂¹⁸ and *cis*-Pt(CF₃)₂(PMe₂C₆F₅)₂²² [2.07 (2) and 2.058 (4) Å, respectively] which probably reflects the larger trans influence of tertiary phosphines relative to Cl⁻. The Pt-P distances in **3** are significantly different [Pt-P(1)

Table X. Bond Lengths (Å) and Interbond Angles (deg) in the Phenyl Rings of $\text{PtCl}(\text{C}_2\text{F}_5)(\text{PMePh}_2)_2$, **3**

| | $m = 1,$ $n = 1$ | $m = 1,$ $n = 2$ | $m = 2,$ $n = 1$ | $m = 2,$ $n = 2$ |
|---|---------------------|---------------------|---------------------|---------------------|
| Molecule A | | | | |
| P(<i>m</i>)-C(<i>mn</i> 1) | 1.82 (1) | 1.80 (1) | 1.82 (1) | 1.79 (1) |
| C(<i>mn</i> 1)-C(<i>mn</i> 2) | 1.39 (2) | 1.42 (2) | 1.37 (2) | 1.39 (2) |
| C(<i>mn</i> 2)-C(<i>mn</i> 3) | 1.36 (2) | 1.33 (2) | 1.37 (2) | 1.40 (2) |
| C(<i>mn</i> 3)-C(<i>mn</i> 4) | 1.37 (3) | 1.36 (2) | 1.35 (2) | 1.35 (2) |
| C(<i>mn</i> 4)-C(<i>mn</i> 5) | 1.38 (2) | 1.39 (2) | 1.40 (2) | 1.39 (2) |
| C(<i>mn</i> 5)-C(<i>mn</i> 6) | 1.40 (2) | 1.42 (2) | 1.39 (2) | 1.42 (2) |
| C(<i>mn</i> 6)-C(<i>mn</i> 1) | 1.36 (2) | 1.40 (2) | 1.39 (2) | 1.38 (2) |
| P(<i>m</i>)-C(<i>mn</i> 1)-C(<i>mn</i> 2) | 122 (1) | 123 (1) | 121 (1) | 122 (1) |
| P(<i>m</i>)-C(<i>mn</i> 1)-C(<i>mn</i> 6) | 122 (1) | 121 (1) | 123 (1) | 121 (1) |
| C(<i>mn</i> 2)-C(<i>mn</i> 1)-C(<i>mn</i> 6) | 117 (1) | 117 (1) | 117 (1) | 117 (1) |
| C(<i>mn</i> 1)-C(<i>mn</i> 2)-C(<i>mn</i> 3) | 122 (2) | 121 (1) | 124 (1) | 121 (1) |
| C(<i>mn</i> 2)-C(<i>mn</i> 3)-C(<i>mn</i> 4) | 121 (1) | 124 (1) | 119 (1) | 122 (1) |
| C(<i>mn</i> 3)-C(<i>mn</i> 4)-C(<i>mn</i> 5) | 119 (2) | 119 (1) | 122 (1) | 119 (1) |
| C(<i>mn</i> 4)-C(<i>mn</i> 5)-C(<i>mn</i> 6) | 119 (1) | 119 (1) | 118 (2) | 119 (1) |
| C(<i>mn</i> 5)-C(<i>mn</i> 6)-C(<i>mn</i> 1) | 123 (1) | 121 (1) | 122 (1) | 122 (1) |
| Molecule B | | | | |
| P(<i>m</i>)-C(<i>mn</i> 1) | 1.81 (1) | 1.84 (1) | 1.81 (1) | 1.81 (1) |
| C(<i>mn</i> 1)-C(<i>mn</i> 2) | 1.40 (2) | 1.36 (2) | 1.37 (2) | 1.38 (2) |
| C(<i>mn</i> 2)-C(<i>mn</i> 3) | 1.38 (2) | 1.44 (2) | 1.40 (3) | 1.38 (2) |
| C(<i>mn</i> 3)-C(<i>mn</i> 4) | 1.38 (3) | 1.35 (2) | 1.42 (5) | 1.37 (2) |
| C(<i>mn</i> 4)-C(<i>mn</i> 5) | 1.37 (2) | 1.33 (2) | 1.37 (3) | 1.38 (2) |
| C(<i>mn</i> 5)-C(<i>mn</i> 6) | 1.40 (2) | 1.39 (2) | 1.34 (3) | 1.38 (2) |
| C(<i>mn</i> 6)-C(<i>mn</i> 1) | 1.39 (2) | 1.35 (2) | 1.41 (2) | 1.38 (2) |
| P(<i>m</i>)-C(<i>mn</i> 1)-C(<i>mn</i> 2) | 119 (1) | 119 (1) | 122 (1) | 119 (1) |
| P(<i>m</i>)-C(<i>mn</i> 1)-C(<i>mn</i> 6) | 123 (1) | 121 (1) | 121 (1) | 121 (1) |
| C(<i>mn</i> 2)-C(<i>mn</i> 1)-C(<i>mn</i> 6) | 119 (1) | 120 (1) | 117 (1) | 119 (1) |
| C(<i>mn</i> 1)-C(<i>mn</i> 2)-C(<i>mn</i> 3) | 117 (1) | 119 (1) | 121 (2) | 121 (1) |
| C(<i>mn</i> 2)-C(<i>mn</i> 3)-C(<i>mn</i> 4) | 124 (1) | 118 (2) | 119 (2) | 120 (1) |
| C(<i>mn</i> 3)-C(<i>mn</i> 4)-C(<i>mn</i> 5) | 119 (1) | 122 (2) | 119 (2) | 120 (1) |
| C(<i>mn</i> 4)-C(<i>mn</i> 5)-C(<i>mn</i> 6) | 118 (1) | 120 (1) | 120 (2) | 121 (1) |
| C(<i>mn</i> 5)-C(<i>mn</i> 6)-C(<i>mn</i> 1) | 123 (1) | 121 (1) | 124 (2) | 120 (1) |
| Solvate Molecule | | | | |
| C-Cl(1) | 1.79 (4) | | | |
| C-Cl(2) | 1.74 (4) | | | |
| Cl(1)-C-Cl(2) | 105 (2) | | | |

= 2.328 (2) Å, Pt-P(2) = 2.341 (2) Å], reflecting the inequivalence of the nonbonding steric interactions between the tertiary phosphine ligands and the pentafluoroethyl group. A similar effect has also been observed in the phenylacetylide complex *trans*-PtCl(C≡CPh)(PEt₂Ph)₂, in which the angle at the ligating carbon atom is 162 (3)°. Both of the Pt-P bonds in **3** are significantly longer than those in **1** [2.291 (2), 2.292 (2) Å]. The Pt-P distance in **2** [2.320 (2) Å] is also significantly longer than that in **1**, indicating that this cis lengthening of the metal-phosphorus bonds is probably a feature of all platinum(II)-fluoroalkyl complexes.

The Pt(CF₂-CF₃) moiety adopts the expected staggered conformation, with a C-C distance of 1.546 (14) Å. The C(1)-F distances range from 1.366 (14) to 1.402 (14) Å [average 1.387 Å] and the C(2)-F distances range from 1.302

(15) to 1.363 (18) Å [average 1.332 Å]. Average values should be treated with some caution, since the ranges of individual values exceed those to be expected from probability statistics. Nevertheless, they are of similar magnitude to those found in other transition-metal-fluoroalkyl structures^{4,21} and the C(2)-F value (1.332 Å) is close to that observed in gaseous CF₃CF₂I [average 1.338 (4) Å] by electron diffraction. The C(1)-F distances are uniformly longer than the C(2)-F distances, perhaps due to libration effects. In this event, however, the agreement between the C(2)-F (shorter) distance and those in CF₃CF₂I must be purely fortuitous. Appreciable deviations from regular tetrahedral geometry are apparent in most of the interbond angles of the Pt(CF₂-CF₃) moiety. In particular, the F-C(1)-F angle [101.9 (6)°] is substantially decreased, while the Pt-C(1)-C(2) angle [115.7 (6)°] is substantially increased vis-à-vis 109°28'. The latter feature appears to be common to many alkyl- and (fluoroalkyl)metal complexes, e.g., 120.9° in η⁵-C₅H₅Mo(CO)₃C₂H₅,²⁰ 123.3° in η⁵-C₅H₅Mo(CO)₃C₃F₇,²¹ 121.2 (11)° in [Rh(C₂H₅)(N-H₃)₅]Br₂,⁵⁵ 119.5 (7)° in Co(C₂H₅)(salen)⁵⁶ [salen = *N,N'*-ethylenebis(salicylideneimino)], 116.4° in η⁵-C₅H₅RhI-(C₂F₃)(CO),⁵⁷ 121.2° (average) in *cis*-(HCF₂CF₂)₂Fe(CO)₄,⁵⁸ 119° in (HCF₂CF₂)Co(CO)₃(PPh₃),⁵⁹ and 119.7° in K₃[Co(CN)₅(CF₂CF₂H)].⁶⁰ Although repulsion of the α-carbon atom substituents by metal d-orbitals¹ and metal-carbon π bonding^{57,60} have variously been suggested as being responsible for the effect, it may be significant that the planar, relatively unhindered complex Ni(C₂H₅)(acac)(PPh₃) shows a Ni-C(α)-C(β) angle of 108°,⁶¹ close to the expected tetrahedral angle. Opening out of the M-C(α)-C(β) angle may therefore be dictated by ligand-ligand interaction in the coordination sphere and/or molecular packing.

Bond distances and angles in the diphenylmethylphosphine ligands of **1**, **2**, and **3** are all normal and the phenyl rings are planar within experimental error.

Discussion

Our structure determinations establish that the *trans* influence of the pentafluoroethyl ligand, as estimated by the Pt-Cl bond length *trans* to it, is less than that of methyl. This conclusion is supported by the ν(Pt-Cl) values (Table I) which also indicate that the *trans* influences of CF₃ and C₂F₅ are very similar. The structural *trans* influence of C₂F₅ is about the same as those of the carbene ligands and of triethylphosphine in *cis*-PtCl₂[C(OEt)NHPH](PEt₃)⁶² and *cis*-PtCl₂[C(NPhCH₂)₂](PEt₃).⁶³ The contraction in Pt-Cl bond length in **2** or **3** relative to **1** can be accounted for following arguments presented by Hall and Fenske⁵ for CH₃Mn(CO)₅ and CF₃Mn(CO)₅. Withdrawal of electron density by the fluorine atoms leaves the ligating carbon atom of CF₃⁻ more positively charged than that of CH₃⁻, and this positive charge stabilizes the metal orbitals to a greater extent in the fluoroalkyl than in the alkyl. In our complexes we can reasonably expect that the Pt-Cl bond will be affected to a greater extent by the

Table XI. Best Weighted Least-Squares Planes through Atoms Pt, Cl, P(1), P(2), and C(1)

| molecule | equation ^a | atom dist from plane, Å | | |
|--|--|-------------------------|--------------|------------------|
| | | atom | dist | σ |
| (a) PtCl(CH ₃)(PMePh ₂) ₂ , 1 | -0.6396X - 0.5147Y - 0.5709Z + 3.603 = 0 | Pt | 0.010 (0.2) | P(1) -0.210 (2) |
| | | Cl | 0.007 (2) | P(2) -0.189 (2) |
| | | | | C(1) 0.032 (8) |
| (b) PtCl(C ₂ F ₅)(PMePh ₂) ₂ , 3 molecule A | 0.0764X + 0.5757Y - 0.8141Z - 0.013 = 0 | Pt | -0.003 (0.5) | P(1) 0.110 (3) |
| | | Cl | -0.019 (4) | P(2) 0.099 (3) |
| | | | | C(1) -0.092 (13) |
| (c) PtCl(C ₂ F ₅)(PMePh ₂) ₂ , 3 molecule B | -0.0725X + 0.5953Y - 0.8002Z + 7.511 = 0 | Pt | -0.005 (0.5) | P(1) 0.118 (3) |
| | | Cl | -0.020 (4) | P(2) 0.105 (3) |
| | | | | C(1) -0.068 (12) |

^a The plane equations $LX + MY + NZ + D = 0$ refer to orthogonal coordinates: for **1** $X = 11.548x - 8.435z$, $Y = 11.383y$, $Z = 19.492z$; for **3** $X = 15.496x$, $Y = 9.983y$, $Z = 38.776z$.

positive charge than the more covalent Pt-P bonds. Thus the Pt-Cl bond is shortened, essentially as a consequence of an electrostatic dipolar effect induced by the electronegative fluorine atoms.

The present structures confirm the conclusion^{4,21} that transition-metal-carbon σ bonds are shorter in fluoroalkyls than in alkyls. Hall and Fenske⁵ note that this can be explained without invoking metal-carbon π back-bonding. Their calculations indicate that the $6a_1$ orbital of CH_3^- which is used for σ bonding to a metal has 13.5% carbon s character whereas the $3a_1$ orbital of CH_3^- which is used for σ bonding has only 6.4% carbon s character. Thus the electron density in the σ -bonding orbital is concentrated closer to the carbon atom in CF_3^- than in CH_3^- ; hence the metal-carbon distance will be shorter in the fluoroalkyl. However, it seems unlikely that an increase of only 7% s character can be the factor chiefly responsible for M-C bond length contractions of the order of 0.08 Å, since the estimated single-bond covalent radii of sp^3 -, sp^2 -, and sp -hybridized carbon atoms each differ by only 0.03–0.04 Å. As noted in the Introduction, the NMR trans influences of CH_3^- and CF_3^- are not very different; e.g., the $J_{\text{Pt-P}}$ values in $\text{Pt}(\text{CH}_3)_2(\text{dppe})$ and $\text{Pt}(\text{CF}_3)_2(\text{dppe})$ are 1794 \pm 100 and 1984 \pm 100 Hz, respectively,¹⁶ and the $J_{\text{Pt-C}}$ values for the olefinic carbon atoms in $\text{Pt}(\text{C}_2\text{H}_5)_2(\text{COD})$ and $\text{Pt}(\text{CF}_3)_2(\text{COD})$ are 47 \pm 2 and 56 \pm 2 Hz, respectively;¹⁵ in the latter pair of compounds, the $J_{\text{Pt-C}}$ values for the σ -bonded carbon atoms are almost identical, 55 \pm 3 and 56 \pm 3 Hz, respectively. The trends do suggest that CF_3^- makes slightly less demand on Pt 6s-electron density than does CH_3^- , in agreement with what one would predict on the basis of Hall and Fenske's calculation. However, the hybridizations of carbon (and platinum) in fluoroalkyl and alkyl complexes do not differ greatly and the main factor responsible for the shortening of the metal-carbon σ bond in fluoroalkyls is probably the electrostatic effect discussed above. Since Mössbauer quadrupole splittings are likely to be sensitive to both electrostatic and hybridization effects, it is not surprising that ¹²⁹I Mössbauer measurements on *trans*-PtIX(PMe₂Ph)₂ (X = I, CF₃, CH₃)⁶⁴ show the trans influence of CH_3^- to be considerably larger than that of CF_3^- , in agreement with the X-ray and far-IR results. It is worth noting for comparison that according to a recent X-ray photoelectron and theoretical study of trifluoromethyl-substituted benzenes⁶⁵ the CF_3 group, like CH_3 , donates electrons to the aromatic ring; the inductive effect of CF_3 is caused not by electron withdrawal but by the creation of a positive potential on the adjacent atoms owing to the positive dipole of CF_3 . We suggest that the same is true for (fluoroalkyl)metal complexes and note that the effect may not be limited to σ -carbon donor ligands: unexpectedly short Pt-Cl bond lengths have been observed trans to $\text{P}(\text{CF}_3)_2$ in $\text{PtCl}_2\{\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{CF}_3)_2\}$ ⁶⁶ and trans to PF_3 in *cis*- $\text{PtCl}_2(\text{PF}_3)\{\text{P}(\text{C}_2\text{H}_5)_3\}$.⁶⁷

An observation which may also be a consequence of the electrostatic effect of CF_3 is that element-carbon distances in main group trifluoromethyl derivatives may be shorter than, longer than, or about the same as the distances in the analogous methyls, depending on the electronegativity of the main-group element.⁶⁸ For example, carbon-halogen bonds are 0.02–0.07 Å shorter in trifluoromethyl halides than in methyl halides,⁶⁸ whereas in $(\text{CF}_3)_3\text{P}$, $(\text{CF}_3)_3\text{As}$,⁶⁸ and $(\text{CF}_3)_2\text{Hg}$ ⁶⁹ the element-carbon distances are significantly longer than in the corresponding methyl derivatives.

The positive charge on the ligating carbon atom of CF_3 or C_2F_5 might have been expected to contract all the platinum-ligand bonds to some extent, and it is therefore surprising that the shortening of the Pt-C and Pt-Cl bonds in **3** relative to **1** is accompanied by a significant lengthening of the Pt-P bonds cis to the σ -carbon ligand. This may account in part

for the somewhat smaller $J_{\text{Pt-P}}$ values in the fluoroalkyls relative to the methyl compound (Table I), though the reduction is less than one would have predicted on the basis of the correlation between Pt-P bond length and $J_{\text{Pt-P}}$ for a series of trialkylphosphine complexes.⁷⁰

There are two interesting similarities between CO and perfluoroalkyl groups in their platinum(II) complexes. First, the trans influence of CO based on Pt-Cl bond lengths or $\nu(\text{Pt-Cl})$ values is markedly smaller than that of triphenylphosphine and is even less than the trans influences of Cl or pyridine, whereas the NMR trans influence of CO is only slightly less than that of triphenylphosphine and is much higher than the trans influence of Cl⁻ or pyridine. Thus, irrespective of the criterion adopted, a perfluoroalkyl group has a higher trans influence than CO owing to its greater σ -donor ability, but the two ligands are similar to the extent that both are lower in the "Pt-Cl" based series than in the NMR-based series. The low structural trans influence of CO on Pt-Cl bonds has been attributed^{71,72} to an electrostatic effect caused by its π -back-bonding ability; the effect is thus similar to that induced by the electronegative fluoroalkyl group.

A second similarity is that CO, like C_2F_5 , appears to lengthen metal-phosphorus bonds cis to it. Muir et al.⁷⁰ have noted that in the structure of *cis*- $\text{PtCl}_2(\text{CO})(\text{PPh}_3)$ the Pt-P distance [2.282 (2) Å] and the Pt-Cl distance trans to PPh_3 [2.343 (2) Å] are significantly longer and shorter, respectively, than the mean Pt-P and Pt-Cl (trans to P) distances in the other complexes of the type *cis*- $\text{PtCl}_2\text{LL}'$ [L = L' = PMe_3 ; L = PEt_3 ; L' = $\text{C}(\text{NPhCH}_2)_2$, $\text{C}(\text{OEt})\text{NHPPh}$, or CNPh ; L = PEt_2Ph , L' = PEt_2Ph ; L = L' = CNPh]. These comparisons indicate that CO tends to weaken a *cis* Pt-P bond and to strengthen both *cis* and *trans* Pt-Cl bonds. It would have been useful to compare the Pt-P distances of $\text{PtCl}(\text{C}_2\text{F}_5)(\text{PMePh}_2)_2$ with those of *trans*- $[\text{PtCl}(\text{CO})(\text{PEt}_3)_2]\text{BF}_4$ [2.34, 2.35 Å],⁷³ but in the absence of quoted probable errors in the bond lengths of the latter structure an estimate of the relative *cis*-bond-weakening tendencies of CO and C_2F_5 cannot be made.

The lengthening of *cis* Pt^{II}-P bonds induced by σ -fluoroalkyl ligands has a close parallel in the effect of π -bonded tetrafluoroethylene in the rhodium(I) complex $\text{RhCl}(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$, the Rh-P bond lengths of which are about 0.05 Å longer than those in $\text{RhCl}(\text{PPh}_3)_3$.⁷⁴ Mason et al.⁷⁴ attributed this to competition by C_2F_4 with PPh_3 for Rh d_{π} -electron density, and *pace* Hall and Fenske,⁵ it may be that CF_3 or C_2F_5 can compete with PMePh_2 in our platinum(II) complexes. However, as noted elsewhere,⁶⁷ the π -bonding explanation in the case of the rhodium(I) complex seems unlikely, because the orientation of the C_2F_4 ligand will cause it to interact with a rhodium d_{π} orbital which is almost orthogonal to the π -acceptor orbitals of the PPh_3 ligands. Since the M-P bond lengthenings are associated with *cis* ligands having rather short metal-ligand distances, it may not be possible to neglect steric effects. Clearly much remains to be understood about *cis* effects in planar complexes; two theoretical treatments^{75,76} of platinum(II) complexes have predicted *cis* influences of similar trends and magnitudes to *trans* influences, and the most recent study⁷⁶ places CO near the bottom of the *cis*-influence series, which appears to be contrary to observation.

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Registry No. 1, 24833-61-2; 2, 68914-98-7; 3, 68908-21-4; *cis*- $\text{PtCl}_2(\text{PMePh}_2)_2$, 16633-72-0; *cis*- $\text{Pt}(\text{CH}_3)_2(\text{PMePh}_2)_2$, 24917-50-8; $\text{Pt}(\text{PMePh}_2)_4$, 27121-53-5; *trans*- $\text{PtCl}(\text{COCF}_3)(\text{PMePh}_2)_2$, 68908-22-5; *trans*- $\text{PtBr}(\text{CF}_3)(\text{PMePh}_2)_2$, 68908-23-6; *trans*- $\text{PtCl}(\text{COC}_2\text{F}_5)(\text{PMePh}_2)_2$, 68908-24-7; *trans*- $\text{PtBr}(\text{C}_2\text{F}_5)(\text{PMePh}_2)_2$, 68908-25-8.

Supplementary Material Available: Listings of anisotropic atomic thermal parameters, structure factor amplitudes, and data collection details (42 pages). Ordering information is given on any current masthead page.

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- (30) The structure amplitude ($|F_o|$) is calculated from $|F_o| = \{I(Lp)\}^{-1/2}$, where I (the net peak count) = $[CT - (t_p/t_b)(B_1 + B_2)]$, Lp (the Lorentz-polarization correction) = $(\cos^2 2\theta + \cos^2 2\theta_m)/\sin 2\theta (1 + \cos^2 2\theta_m)$, and the remaining symbols have the following significance: CT is the total reflection count uncorrected for background, t_p is the reflection counting time, t_b is the total background counting time, B_1 and B_2 are individual background counts (each for time $t_b/2$) at the scan extremities, and θ and θ_m are the specimen and monochromator Bragg angles, respectively.
- (31) $\sigma(F_o) = \{[\sigma(I)/(Lp)]^2 + \rho^2 |F_o|^{4/3}\}^{1/2}/2|F_o|$, where $\sigma(I) = [CT + (t_p/t_b)^2(B_1 + B_2)]^{1/2}$, ρ^2 is the instrumental uncertainty constant³² and the remaining symbols have the significance detailed above.
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