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Regioselective Carbon–Fluorine Bond Cleavage Reactions from the Interaction of Transition-Metal Fluorocarbon Complexes with Nucleophiles[1]

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The use of fluoro substituents has been tested as a means to stabilize the amide bond to divalent platinum. Products have been obtained which show that complexed fluoroalkyls and fluoroaryls have a high reactivity to nucleophiles. The complex *trans*-$PtCF_3Cl(PPh_3)_2$ reacts with $LiN(CH_3)_2$ to give products derived from $Pt(PPh_3)_2$. The complex *trans*-$[PtCH_3(THF)(PPh_2C_6F_5)_2]ClO_4$, prepared from *trans*-$PtCH_3Cl(PPh_2C_6F_5)_2$ and $AgClO_4$ in THF solvent, reacts with hydroxide ion to give the cyclometalated complex *trans*-$PtCH_3(2\text{-}OC_6F_4PPh_2)(PPh_2C_6F_5)$. The crystal structure of *trans*-$PtCH_3(2\text{-}OC_6F_4PPh_2)(PPh_2C_6F_5)$ has a monoclinic $P2_1/c$ cell with a = 12.437 (2) Å, b = 25.749 (8) Å, c = 10.788 (2) Å, β = 102.35 (1)°, Z = 4. Reaction of this complex with HCl results in ring opening to give *trans*-$PtCH_3Cl(2\text{-}HOC_6F_4PPh_2)(PPh_2C_6F_5)$. Reacting *trans*-$[PtCH_3(THF)(PPh_2C_6F_5)_2]ClO_4$ with methoxide ion gives *trans*-$PtCH_3(OCH_3)(PPh_2C_6F_3(OCH_3\text{-}2,6)_2)_2$, where all the fluorines in the 2-positions of the fluorophenyl rings have been replaced by methoxide. Treating this complex with water gives *trans*-$PtCH_3(2\text{-}OC_6F_3(OCH_3\text{-}6)PPh_2)(PPh_2C_6F_3(OCH_3\text{-}2,6)_2)$. Heating a mixture of triphenylphosphine, bromopentafluorobenzene and nickel bromide at 200 °C, followed by hydrolysis of the melt, gives the phosphonium salt $[Ph_3(C_6F_4H\text{-}4)P]Br$. The use of D_2O in the hydrolysis yields $[Ph_3(C_6F_4D\text{-}4)]Br$. Hydroxide ion reacts with the phosphonium salt to give P–C cleavage. 1,2,4,5-Tetrafluorobenzene is formed from $[Ph_3(C_6F_4H\text{-}4)]Br$ and OH^-, 1,2,4,5-tetrafluorodideuteriobenzene is formed from $[Ph_3(C_6F_4D\text{-}4)]Br$ and OD^-, and 1,2,4,5-tetrafluoro-3-deuteriobenzene is formed from either $[Ph_3(C_6F_4H\text{-}4)]Br$ and OD^- or $[Ph_3(C_6F_4D\text{-}4)]Br$ and OH^-.

Introduction

As part of an effort directed toward the development of new catalysts for the amination of alkenes, we are investigating the synthesis and reaction chemistry of amide complexes of the late transition metals. Such complexes are rather rare. This scarcity is partly due to the concept of "hard and soft acids and bases", where it has been theorized that the metal–amide bond to a late-transition-metal ion should be relatively weak. For the early-transition-metal ions, the metal–amide bonding is strengthened by π-donation from the lone pair of electrons on nitrogen into an empty d orbital on the metal, but for the late-transition-metal ions such empty low-lying orbitals are not always available. This situation pertains for platinum(II) where the LUMO is a high-energy $d_{x^2-y^2}$ orbital.

Because of our need to study the insertion reactions of coordinately unsaturated dimethylamide complexes, we have decided to attempt their synthesis at a 16-electron platinum(II) center. Previous efforts to synthesize coordinately unsaturated amide complexes have been unsuccessful because they undergo facile β-hydrogen transfer with the elimination of an imine.[2] Our strategy has therefore been to use electron-withdrawing substituents on platinum(II) in order to increase the stability of the $Pt\text{–}N(CH_3)_2$ bond by partial π-donation of the lone electron pair on nitrogen to the platinum(II) center. We have used two approaches to achieve this goal. One approach is to place a trifluoromethyl group trans to the proposed coordination site of the dimethylamide, and a second approach is to use fluorophenyl substituents on the supporting phosphine ligands.[3]

Both strategies have failed to yield dimethylamide complexes of platinum(II). This failure has been caused by a change in the expected regioselectivities of the reactions whereby nucleophilic attack occurs at an electron-poor carbon center rather than at the platinum center. As a result, we have uncovered several interesting reactions that involve the cleavage of C–F bonds. In particular, we have discovered several systems where the platinum(II) center is directly involved in the C–F cleavage. These reactions are particularly significant because they occur selectively. We have discovered reactions where this selectivity occurs at an aromatic C–F bond in competition with an aromatic C–H bond, and also at the ortho C–F bonds of a perfluorinated phenyl ring rather than at the para and meta positions.

Experimental Section

Potassium tetrachloroplatinate was supplied by either Matthey Bishop Inc. or by Engelhard Inc. and used without prior purification. All reactions were carried out on a Schlenk line using a high-purity nitrogen atmosphere. Solvents were dried by refluxing over either sodium/benzophenone or $LiAlH_4$. Precursor complexes were prepared by literature procedures, and references are included where necessary. Sodium amide and lithium dimethylamide were purchased from Aldrich. ^1H, ^2H, ^{31}P, ^{13}C, ^{19}F, and ^{195}Pt NMR spectra were measured on a Bruker AC200 spectrometer in $CDCl_3$ solvent unless otherwise noted. The ^{19}F NMR spectra were obtained at 188.31 MHz by using the high-resolution proton probe and a preamplifier tuned for this ^{19}F frequency. The following reference standards for δ 0.0 were used: TMS for ^1H, ^2H, and ^{13}C, 85% H_3PO_4 for ^{31}P, CCl_3F for ^{19}F, and H_2PtCl_6 for ^{195}Pt. Deuterated solvents were purchased from Aldrich Chemical Co. Infrared spectra were measured on a Perkin-Elmer Model 683 or a Mattson Cygnus 100 spectrometer. The complex *trans*-$PtCH_3Cl(1,5\text{-}COD)$ was prepared by the literature procedure.[4] The complex *trans*-$PtCF_3Cl(PPh_3)_2$ was synthesized by reacting $Pt(PPh_3)_3$ with trifluoromethyl bromide, followed by reaction with silver perchlorate and chloride ion.[5] The compounds $PPh_2C_6F_5$ and $P(C_6F_5)_3$ were synthesized according to the literature procedures.[3] Triphenylphosphine was purchased from Aldrich.

Reaction of *trans*-Chloro(trifluoromethyl)bis(triphenylphosphine)-platinum with Lithium Dimethylamide. To a solution of *trans*-$PtCF_3Cl(PPh_3)_2$ and excess lithium dimethylamide in a 5-mm NMR tube was added THF-d_8 under a nitrogen atmosphere. A black precipitate formed immediately. The solution was centrifuged and the NMR spectra of the solution species measured. $^{31}P\{^1H\}$ NMR: δ 50.8 s. $^{195}Pt\{^1H\}$ NMR: δ −4561 q ($^1J(PtP)$ = 4465 Hz). A solution of hydrogen chloride in D_2O was then added to the mixture of the NMR tube. The aqueous layer was transferred by syringe to a clean 5-mm NMR tube. The ^{19}F NMR spectrum of this solution was measured. ^{19}F NMR: δ −133 s. This spectrum was compared with that of an authentic sample of $[CF_3ND(CH_3)_2]Cl$. This solution was prepared by passage of excess trifluoromethyl bromide through a suspension of lithium dimethylamide in THF-d_8, in a 25-mL round-bottom flask followed by addition of a solution of hydrogen chloride in D_2O to the reaction mixture. The aqueous layer was transferred to a 5-mL NMR tube by means of a syringe, and the ^{19}F NMR spectrum showed a single broad resonance at δ −133.

***trans*-Chloromethylbis(diphenyl(pentafluorophenyl)phosphine)platinum, $PtCH_3Cl(PPh_2C_6F_5)_2$.** A mixture of $PtCH_3Cl(1,5\text{-}COD)$ (500 mg, 1.41 mmol) and $PPh_2C_6F_5$ (995 mg, 2.83 mmol) in $CHCl_3$ (20 mL) was stirred for 1 h under a N_2 atmosphere. Removal of the solvent on a rotary evaporator gave a colorless solid. This solid was dissolved in *n*-hexane (10 mL) to give a colorless solution, which upon being kept at

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−5 °C for 12 h gave colorless crystals of the complex. Yield: 1.19 g (89%). ^{1}H NMR: δ 7.1–7.9 m (20 H, *phenyl*), 0.11 t (3 H, CH_3, ^3J(PH) = 6.7 Hz, ^2J(PtH) = 71.3 Hz). ^{13}P{^{1}H} NMR: δ 22.3 s (^1J(PtP) = 3315 Hz). ^{19}F NMR: δ −125.0 d (2 F, ortho), −149.1 t (1 F, para), −160.7 t (2 F, meta). Anal. Calcd for $C_{37}H_{23}ClF_{10}P_2Pt$: C, 46.8; H, 2.44. Found: C, 47.3; H, 2.64.

***trans*-Methyl((2-hydroxytetrafluorophenyl)diphenylphosphinato)((pentafluorophenyl)diphenylphosphine)platinum, *trans*-PtCH$_3$(2-OC$_6$F$_4$PPh$_2$)(PPh$_2$C$_6$F$_5$). Safety Note.** *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution. A solution of *trans*-[PtCH$_3$(THF)(PPh$_2$C$_6$F$_5$)$_2$]ClO$_4$ was prepared from *trans*-PtCH$_3$Cl(PPh$_2$C$_6$F$_5$)$_2$ (200 mg, 0.21 mmol) and silver perchlorate (44 mg, 0.21 mmol) in tetrahydrofuran (30 mL). To this stirred solution was added aqueous KOH (25 mg in 3 mL of water) in a dropwise manner under a nitrogen atmosphere. After 30 min, the solvent was removed under high-vacuum conditions and the residue dried in vacuo for 12 h. Column chromatography of the residue on silica gel with benzene eluant gave a pale yellow solution. The solution volume was reduced to ca. 3 mL by evaporation under nitrogen. Addition of *n*-hexane (10 mL) to the solution gave pale yellow microcrystals. The complex was isolated by filtration and dried in vacuo for 12 h. Yield: 130 mg (68%). Anal. Calcd for $C_{37}H_{23}F_9OP_2Pt$: C, 48.8; H, 2.54. Found: C, 49.0; H, 2.67. ^{1}H NMR (C_6D_6): δ 6.9–8.0 m (20 H, *phenyl*), 0.88 t (3 H, CH_3, ^3J(PH) = 6.3 Hz, ^2J(PtH) = 79 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 20.7 d (^1J(PtP) = 3116 Hz, ^2J(PP) = 448 Hz), δ 31.9 d (^1J(PtP) = 3254 Hz). ^{19}F NMR (C_6D_6): δ −124 d (2 F, ortho), −132d (1F), −148t (1 F, para), −151 t (1 F), −159 t (2 F, meta) −163 d (1 F), −176 t (1 F) (^3J(FF)$_{all}$ = 19–23 Hz).

The compound was also obtained when a solution containing *trans*-PtCH$_3$Cl(PPh$_2$C$_6$F$_5$)$_2$ (200 mg, 0.21 mmol) and silver perchlorate (44 mg, 0.21 mmol) in tetrahydrofuran (20 mL) was transferred under nitrogen to a 50-mL Schlenk vessel containing lithium dimethylamide (11 mg, 0.22 mmol) via a stainless-steel needle and filter. The reaction mixture immediately gave a black suspension. The suspension was stirred for 30 min, after which the solvent was removed under vacuum. The resulting solid was extracted into benzene-d_6. A pure sample of the complex was obtained by column chromatography on silica gel and isolated by the addition of *n*-hexane to a benzene solution of the complex. Yield: 35 mg (18%).

***trans*-Chloromethyl((2-hydroxytetrafluorophenyl)diphenylphosphine)((pentafluorophenyl)diphenylphosphine)platinum, *trans*-PtCH$_3$Cl(2-HOC$_6$F$_4$PPh$_2$)(PPh$_2$C$_6$F$_5$).** A solution of this complex was prepared by bubbling hydrogen chloride through a benzene-d_6 solution of *trans*-PtCH$_3$(2-OC$_6$F$_4$PPh$_2$)(PPh$_2$C$_6$F$_5$) in a 5-mm NMR tube for 10 s. The complex was observed by NMR spectroscopy, and only small amounts of (<10%) of impurities were present. ^{1}H NMR: δ 9.07 br (1 H, O*H*), 7.3–7.9 m (20 H, *phenyl*), δ 0.09 t (3 H, CH_3, ^3J(PH) = 6.6 Hz, ^2J(PtH) = 78 Hz). ^{19}F NMR: δ −122.9 d (2 F, ortho), −123.3 d (1 F), −146.2 t (1 F, para), −147.4 t (1 F), −155.3 d (1 F), −158.5 t (2 F, meta), −163.7 t (1 F) (^3J(FF)$_{all}$ = 19–23 Hz).

***trans*-Methoxymethylbis((2,6-dimethoxytrifluorophenyl)diphenylphosphine)platinum, *trans*-PtCH$_3$(OCH$_3$)(PPh$_2$C$_6$F$_3$(OCH$_3$)$_2$-2,6)$_2$.** A solution of *trans*-[PtCH$_3$(THF)(PPh$_2$C$_6$F$_5$)$_2$]ClO$_4$ was prepared from *trans*-PtCH$_3$Cl(PPh$_2$C$_6$F$_5$)$_2$ (200 mg, 0.21 mmol) and silver perchlorate (44 mg, 0.21 mmol) in tetrahydrofuran (30 mL). To this stirred solution was added methanolic sodium methoxide (30 mg in 3 mL dry methanol) in a dropwise manner under a nitrogen atmosphere. After 30 min, the solvent was removed under high-vacuum conditions and the residue dried in vacuo for 12 h. The resulting solid was extracted into benzene-d_6. The yield in solution is >95% as measured by NMR spectroscopy. Analytically pure samples could not be obtained because of the high solubility of the complex in all organic solvents and because of its conversion to *trans*-PtCH$_3$(2-OC$_6$F$_3$(OCH$_3$)-6-PPh$_2$)(PPh$_2$C$_6$F$_3$(OCH$_3$)$_2$-2,6) in the presence of traces of water. ^{1}H NMR (C_6D_6): δ 7.0–8.3 m (20 H, *phenyl*), 3.32 d (12 H, OCH_3, ^5J(HF) = 2.4 Hz), 3.14 s (3 H, OCH_3, ^3J(PtH) = 23 Hz), 0.23 t (3 H, PtCH_3, ^3J(PH) = 6.4 Hz, ^2J(PtH) = 73.6 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 16.7 s (^1J(PtP) = 3527 Hz). ^{19}F NMR (C_6D_6): δ −151.6 t (2 F, para; ^3J(FF) = 20.3 Hz), −155.8 d (4 F, meta).

***trans*-Methyl((2-hydroxy-6-methoxytrifluorophenyl)diphenylphosphinato)((2,6-dimethoxytrifluorophenyl)diphenylphosphine)platinum–0.5-Dichloromethane *trans*-PtCH$_3$(2-OC$_6$F$_3$(OCH$_3$)-6-PPh$_2$)(PPh$_2$C$_6$F$_3$(OCH$_3$)$_2$-2,6)·0.5CH$_2$Cl$_2$.** To a stirred solution of the previous complex prepared on the same scale in benzene (20 mL) was added dropwise a solution of potassium hydroxide (20 mg) in methanol (5 mL). The mixture was stirred under nitrogen for 30 min, the solvent was removed under high vacuum, and the residue was dried in vacuo for 12 h. Column chromatography of the resulting solid on silica gel with dichloromethane eluant gave a pale yellow solution. The solution volume was reduced to ca. 1 mL by evaporation under a flow of nitrogen. Addition of *n*-hexane (5 mL) to the solution at −78 °C gave a pale yellow precipitate, which was isolated by low-temperature filtration. The complex was dried in vacuo for 12 h. Yield: 85 mg (41%). Anal. Calcd for $C_{40.5}H_{33}ClF_6O_4P_2Pt$: C, 49.1; H, 3.36. Found: C, 49.3; H, 3.36. ^{1}H NMR (C_6D_6): δ 6.8–8.1 m (20 H, *phenyl*), 3.23 d (6 H, OCH_3, ^5J(HF) = 2.5 Hz), 3.00 d (3 H, OCH_3, ^5J(HF) = 2.7 Hz), 0.83 dd (3 H, CH_3, ^3J(PH) = 7.0 Hz, ^3J(PH) = 5.5 Hz, ^2J(PtH) = 79.9 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 33.8 d (^2J(PP) = 442 Hz, ^1J(PtP) = 3187 Hz), 20.7 d (^1J(PtP) = 3090 Hz). ^{19}F NMR (C_6D_6): δ −150.7 t (1 F, para), δ −152.1 t (1 F, para), δ −155.6 d (2 F, meta), δ −163.7 d (1 F, meta), δ −169.6 d (1 F, meta) (^3J(FF)$_{all}$ = 20.5 Hz).

***trans*-Methyl((2-aminotetrafluorophenyl)diphenylphosphinato)((4-aminotetrafluorophenyl)diphenylphosphine)platinum, *trans*-PtCH$_3$(2-NHC$_6$F$_4$PPh$_2$)(PPh$_2$C$_6$F$_4$NH$_2$-4).** A THF solution (30 mL) containing *trans*-PtCH$_3$Cl(PPh$_2$C$_6$F$_5$)$_2$ (200 mg, 0.21 mmol) and silver perchlorate (44 mg, 0.21 mmol) was transferred under nitrogen to a 50-mL Schlenk vessel containing sodium amide (43 mg, 1.1 mmol) via a stainless-steel needle and filter. The stirred suspension changed from colorless to dark green over a period of 2 h. The solvent was removed under high vacuum and the resulting dark green solid dried for 12 h. Column chromatography of this solid on silica gel with dichloromethane eluant gave a dark green solution. The volume was reduced to ca. 3 mL under a flow of nitrogen, and addition of *n*-hexane (10 mL) gave a green percipitate. The complex was filtered and dried in vacuo. Yield: 124 mg (65%). Anal. Calcd for $C_{37}H_{26}F_8N_2P_2Pt$: C, 49.0; H, 2.89; N, 3.09. Found: C, 49.6; H, 3.12; N, 2.55. ^{1}H NMR (C_6D_6): δ 6.8–8.0 m (20 H, *phenyl*), δ 4.54 br (1 H, N*H*, ^2J(PtH) = 30 Hz), 3.08 s (2 H, *NH*$_2$), 0.73 t (3 H, CH_3, ^3J(PH) = 6.5 Hz, ^2J(PtH) = 69.1 Hz) ^{31}P{^{1}H}NMR(C_6D_6): δ 33.5 d (^2J(PP) = 450 Hz. ^1J(PtP) = 2683 Hz), 16.4 d (^1J(PtP) = 3204 Hz). ^{19}F NMR (C_6D_6): δ −126.5 d (2 F), −130.8 d (1 F), −153.1 t (1 F) −159.0 d (2 F), −165.6 d (1 F), −181.5 t (1 F).

(4-Aminotetrafluorophenyl)diphenylphosphine, 4-NH$_2$C$_6$F$_4$PPh$_2$. A mixture of (pentafluorophenyl)diphenylphosphine (250 mg, 0.71 mmol) and sodium amide (150 mg, 3.85 mmol) in tetrahydrofuran (20 mL) was stirred under nitrogen for 3 h, during which time the solution became dark brown. The solvent was removed under vacuum, and the resulting solid was extracted with benzene. After filtration of this solution through a short silica gel column, the solvent was removed under vacuum to give a dark brown solid, which was identified as the product by ^{19}F NMR spectroscopy. ^{19}F NMR (C_6D_6): δ −132.2 dd (2 F, ortho, ^3J(PF) = 39 Hz, ^3J(FF) = 17 Hz), −158.3 d (2 F, meta).

Triphenyl(2,3,5,6-tetrafluorophenyl)phosphonium Bromide, [Ph$_3$(2,3,5,6-C$_6$F$_4$H)P]Br. A mixture of triphenylphosphine (5 g, 19 mmol), bromopentafluorobenzene (4.71 g, 19 mmol), and nickel bromide (2.08 g, 9.5 mmol) in a 100-mL round-bottom flask was refluxed in an oil bath at 200 °C for 3 h under a nitrogen atmosphere. The resulting deep blue melt was cooled to ca. 90 °C. Boiling water (50 mL) was added, and the mixture was refluxed until the solution was homogeneous and the color had changed to pale brown. The resulting solution was allowed to cool to ambient temperature, followed by extraction with diethyl ether (3 × 10 mL) to remove unreacted reactants. Extraction of the aqueous layer with dichloromethane (3 × 20 mL) gave a pale yellow solution. The organic layer was dried over magnesium sulfate and filtered. The solution volume was reduced to ca. 10 mL on a rotary evaporator, and diethyl ether (30 mL) was added to give a pale yellow precipitate. The compound was filtered and dried in vacuo for 12 h. Yield: 2.7g (29%). Anal. Calcd for $C_{24}H_{16}BrF_4P$: C, 58.7; H, 3.28. Found: C, 58.8; H, 3.45. ^{31}P{^{1}H} NMR: δ 16.2 t (^3J(PF) = 6.0 Hz). ^{19}F NMR: δ −123.5 (F^a), −131.3 (F^b) (^3J(PF^b) = 6.05 Hz, ^3J(F^{a}F^b) = 9.00 Hz, ^3J(HF^a) = 10.30 Hz, ^4J(PF^a) = 0.05 Hz, ^5J(F^{a}F^b) = −13.50 Hz, ^4J(F^{b}F^a) = −1.75 Hz, ^4J(F^{b}F^b) = 9.00 Hz).

Structure Determination and Results. Crystals of $C_{33}H_{23}F_9OP_2Pt$ were grown from benzene at 25 °C over a period of 2 weeks. A tan prismatic crystal (0.43 mm × 0.43 mm × 0.31 mm) was cut from a larger crystal suitable for the experiment. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation (graphite monochromator). The data were collected at 25 °C using variable scan rates and ω–2θ scans (2θ = 2–50°), over the range of $-14 \le h \le +14$, $0 \le k \le +30$, $0 \le l \le -12$. A total of 6412 data were collected of which 5614 were unique; 3958 data were observed with $I_0 > 3\sigma I$. Empirical absorption corrections were based on six ψ scans of reflections near χ = 90°. The space group, $P2_1/c$, was unambiguously determined by systematic absences.

The structure solution and refinement were performed by using the Enraf-Nonius Structure Determination Package.[6] The raw data were

(6) *Structure Determination Package*; B. A. Frenz and Associates, Inc. College Station, TX; Enraf-Nonius: Delft, Holland, 1985.

Table I. Crystallographic Data for *trans*-PtMe(2-$OC_6F_4PPh_2$)($PPh_2C_6F_5$)

chem formula: $C_{37}H_{23}F_9OP_2Pt$	fw = 911.6
a = 12.437 (2) Å	space group: $P2_1/c$
b = 25.749 (8) Å	T = 23 °C
c = 10.788 (2) Å	λ = 0.71073 Å (Mo Kα)
β = 102.35 (1)°	ρ_{calc} = 1.794 g cm^{-3}
V = 3374.8 Å^3	μ = 43.7 cm^{-1}
Z = 4	transm coeff: 0.999–0.716
R = 3.7	
R_w = 5.5	

Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B,[a] Å^2
Pt	0.06932 (2)	0.09532 (1)	0.26679 (3)	3.250 (6)
P1	0.2439 (2)	0.0936 (1)	0.2378 (2)	3.58 (5)
P2	−0.1032 (2)	0.10294 (9)	0.3038 (2)	3.42 (5)
F1	0.2336 (4)	0.1854 (3)	0.6515 (4)	5.6 (1)
F2	0.4539 (5)	0.2032 (3)	0.7073 (5)	6.5 (2)
F3	0.5846 (4)	0.1680 (3)	0.5561 (5)	6.1 (2)
F4	0.4937 (4)	0.1163 (3)	0.3405 (5)	6.0 (1)
F5	−0.1411 (5)	0.0458 (3)	0.5493 (5)	6.8 (2)
F6	−0.1047 (6)	0.0815 (3)	0.7835 (5)	7.8 (2)
F7	−0.0373 (6)	0.1783 (3)	0.8358 (5)	8.2 (2)
F8	−0.0010 (6)	0.2427 (3)	0.6461 (6)	7.7 (2)
F9	−0.0407 (5)	0.2077 (3)	0.4087 (5)	6.0 (1)
O1	0.1401 (4)	0.1341 (3)	0.4383 (4)	3.9 (1)
C1	0.3156 (6)	0.1256 (4)	0.3836 (7)	3.9 (2)
C2	0.2464 (7)	0.1422 (4)	0.4622 (7)	3.9 (2)
C3	0.2976 (7)	0.1675 (4)	0.5729 (7)	4.4 (2)
C4	0.4070 (7)	0.1773 (4)	0.6016 (7)	4.5 (2)
C5	0.4728 (7)	0.1596 (4)	0.5231 (8)	4.7 (2)
C6	0.4265 (7)	0.1343 (4)	0.4161 (8)	4.2 (2)
C7	0.3055 (7)	0.0306 (4)	0.2259 (8)	4.1 (2)
C8	0.3440 (8)	0.0039 (5)	0.3386 (9)	5.3 (3)
C9	0.3821 (9)	−0.0479 (5)	0.332 (1)	6.3 (3)
C10	0.375 (1)	−0.0731 (5)	0.222 (1)	6.6 (3)
C11	0.3316 (9)	−0.0452 (5)	0.104 (1)	6.3 (3)
C12	0.2981 (8)	0.0068 (4)	0.1079 (9)	5.1 (2)
C13	0.2726 (7)	0.1327 (4)	0.1120 (7)	4.0 (2)
C14	0.3658 (7)	0.1290 (5)	0.0618 (8)	5.1 (2)
C15	0.3873 (9)	0.1644 (5)	−0.0242 (8)	6.4 (3)
C16	0.3129 (9)	0.2068 (5)	−0.0645 (8)	6.5 (3)
C17	0.2195 (9)	0.2087 (5)	−0.0208 (9)	6.2 (3)
C18	0.1977 (7)	0.1740 (4)	0.0660 (8)	4.5 (2)
C19	−0.0955 (6)	0.1269 (4)	0.4668 (7)	3.5 (2)
C20	−0.1092 (7)	0.0955 (4)	0.5685 (8)	4.4 (2)
C21	−0.0914 (8)	0.1117 (4)	0.6892 (8)	4.9 (2)
C22	−0.0570 (7)	0.1627 (5)	0.7161 (7)	5.2 (2)
C23	−0.0395 (8)	0.1943 (4)	0.6216 (9)	5.3 (3)
C24	−0.0578 (7)	0.1756 (4)	0.5007 (8)	4.5 (2)
C25	−0.1877 (7)	0.0446 (4)	0.2839 (7)	4.4 (2)
C26	−0.1320 (9)	−0.0044 (5)	0.294 (1)	6.2 (3)
C27	−0.197 (1)	−0.0493 (5)	0.277 (1)	7.5 (3)
C28	−0.3103 (9)	−0.0466 (5)	0.256 (1)	7.0 (3)
C29	−0.3620 (9)	0.001 (5)	0.248 (1)	6.3 (3)
C30	−0.2984 (7)	0.0471 (5)	0.2627 (9)	5.9 (3)
C31	−0.1889 (6)	0.1515 (4)	0.2056 (7)	3.7 (2)
C32	−0.1740 (8)	0.1597 (5)	0.0850 (9)	5.6 (3)
C33	−0.2404 (9)	0.1945 (5)	0.005 (1)	6.3 (3)
C34	−0.3221 (9)	0.2190 (5)	0.044 (1)	6.8 (3)
C35	−0.343 (1)	0.2105 (6)	0.163 (1)	8.4 (4)
C36	−0.2729 (8)	0.1768 (4)	0.244 (1)	5.5 (3)
C37	0.0142 (7)	0.0531 (4)	0.1014 (8)	4.7 (2)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3) \times [a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

corrected for Lorentz and polarization effects. Atomic scattering factors and corrections for anomalous dispersion were taken from ref 7. The structure was solved by the MULTAN 11/82 direct-methods program.[8] The position of the Pt atom was confirmed by Patterson methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques. The hydrogen atoms were placed in a combination of observed and calculated positions, and then held positionally and thermally invariant. No correction for secondary extinction was indicated. A final Δ Fourier map showed no unusual features. The maximum Δ/σ = 0.06, $\Delta(\rho)$ = 0.95 e Å^{-3} (1.01 Å from Pt), with R = 3.7 and R_w = 5.5. The crystallographic data are collected in Table I. Final atomic positional parameters are listed in Table II. Interatomic distances and angles are given in Tables III and IV, respectively.

Table III. Bond Distances (Å)[a]

Pt–P1	2.259 (2)	F7–C22	1.32 (1)
Pt–P2	2.273 (2)	F8–C23	1.34 (1)
Pt–O1	2.12 (1)	F9–C24	1.34 (1)
Pt–C37	2.08 (1)	O1–C2	1.31 (1)
P1–C1	1.83 (1)	C1–C2	1.40 (1)
P1–C7	1.81 (1)	C1–C6	1.37 (1)
P1–C13	1.787 (8)	C2–C3	1.39 (1)
P2–C19	1.846 (9)	C3–C4	1.35 (1)
P2–C25	1.820 (5)	C4–C5	1.37 (1)
P2–C31	1.827 (6)	C5–C6	1.34 (1)
F1–C3	1.361 (9)	C19–C20	1.40 (1)
F2–C4	1.34 (1)	C19–C24	1.36 (1)
F3–C5	1.38 (1)	C20–C21	1.340 (9)
F4–C6	1.37 (1)	C21–C22	1.39 (1)
F5–C20	1.34 (1)	C22–C23	1.36 (1)
F6–C21	1.32 (1)	C23–C24	1.36 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Bond Angles (deg)[a]

P1–Pt–P2	175.61 (7)	F3–C5–C6	121.4 (7)
P1–Pt–O1	84.1 (3)	C4–C5–C6	119.2 (8)
P1–Pt–C37	91.2 (3)	F4–C6–C1	120.2 (9)
P2–Pt–O1	92.1 (3)	F4–C6–C5	118.2 (9)
P2–Pt–C37	92.6 (3)	C1–C6–C5	121.6 (8)
O1–Pt–C37	174.4 (4)	P1–C7–C8	116.9 (6)
Pt–P1–C1	100.3 (3)	P1–C7–C12	120.8 (6)
Pt–P1–C7	117.5 (4)	P1–C13–C14	125.3 (6)
Pt–P1–C13	116.6 (3)	P1–C13–C18	117.5 (6)
C1–P1–C7	109.1 (4)	P2–C19–C20	124.2 (7)
C1–P1–C13	105.0 (4)	P2–C19–C24	120.6 (7)
C7–P1–C13	107.2 (4)	C20–C19–C24	114.4 (7)
Pt–P2–C19	109.7 (3)	F5–C20–C19	120.7 (7)
Pt–P2–C25	116.8 (2)	F5–C20–C21	115.3 (7)
Pt–P2–C31	114.4 (2)	C19–C20–C21	124.0 (8)
C19–P2–C25	107.4 (3)	F6–C21–C20	123.0 (8)
C19–P2–C31	103.2 (4)	F6–C21–C22	118.7 (7)
C25–P2–C31	104.2 (3)	C20–C21–C22	118.3 (8)
Pt–O1–C2	117.4 (7)	F7–C22–C21	118.3 (8)
P1–C1–C2	114.1 (6)	F7–C22–C23	121.6 (9)
P1–C1–C6	125.1 (7)	C21–C22–C23	121.6 (9)
C2–C1–C6	120.8 (8)	F8–C23–C22	121.1 (8)
O1–C2–C1	124.0 (9)	F8–C23–C24	119.8 (9)
O1–C2–C3	120.1 (8)	C22–C23–C24	119.1 (9)
C1–C2–C3	115.9 (7)	F9–C24–C19	117.9 (8)
F1–C3–C2	118.2 (6)	F9–C24–C23	118.0 (9)
F1–C3–C4	119.2 (6)	C19–C24–C23	124.0 (8)
C2–C3–C4	122.5 (6)	P2–C25–C26	117.4 (3)
F2–C4–C3	121.3 (7)	P2–C25–C30	121.7 (4)
F2–C4–C5	118.7 (7)	P2–C31–C32	118.4 (5)
C3–C4–C5	120.0 (7)	P2–C31–C36	122.5 (4)
F3–C5–C4	119.4 (8)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Results

Two strategies have been employed for coordinating a fluorinated ligand to platinum(II). The first of these uses a perfluoromethyl group directly complexed to the metal, and the second uses a pentafluorophenyl moiety attached to a ligating phosphine.

(7) Cromer, D. T. *International Tables for Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(8) Main, P.; Fiske, S. J.; S. E.; Lessinger, L.; Germaine, G.; Declercq, J. P.; Woolfson, M. M. MULTAN 11/82. Universities of York, England and Louvain, Belgium, 1982.

Both types of complex have been reacted with the dimethylamide anion.

Reaction of trans-$PtCF_3Cl(PPh_3)_2$ with Dimethylamide Ion. The complex *trans*-$PtCF_3Cl(PPh_3)_2$ has been synthesized by reacting $Pt(PPh_3)_3$ with trifluoromethyl bromide, followed by reaction with $AgClO_4$ and then chloride ion (eq 1).[5] A THF solution of this

$$Pt(PPh_3)_3 + CF_3Br \xrightarrow[(ii)Cl^-]{(i)\ AgClO_4} trans\text{-}PtCF_3Cl(PPh_3)_2 + PPh_3 + AgBr + ClO_4^- \quad (1)$$

complex reacts with lithium dimethylamide in a reaction that involves a 2-electron reduction at platinum. The final product solution contains $Pt(PPh_3)_3$ and $CF_3N(CH_3)_2$, along with a black precipitate of platinum (eq 2). The formation of $Pt(PPh_3)_3$ is

$$trans\text{-}PtCF_3Cl(PPh_3)_2 + LiN(CH_3)_2 \rightarrow \tfrac{2}{3}Pt(PPh_3)_3 + \tfrac{1}{3}Pt + CF_3N(CH_3)_2 + LiCl \quad (2)$$

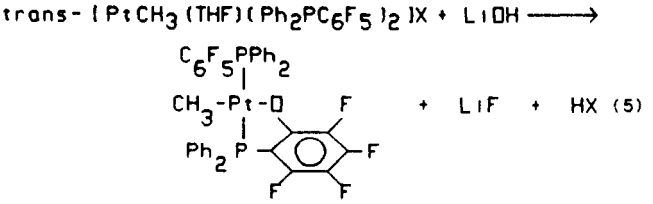
verified by NMR spectroscopy ($^{31}P\{^1H\}$ NMR: δ 50.8 s. ^{195}Pt NMR: δ −4561 q ($^1J(PtP)$ = 4465 Hz)).[9] The compound $[CF_3ND(CH_3)_2]Cl$, which was extracted from the reaction mixture with a solution of HCl in D_2O, shows a single ^{19}F NMR peak at δ −133. The identity of this compound has been confirmed by its independent synthesis in solution from trifluoromethyl bromide and lithium dimethylamide, followed by addition of HCl (eq 3).

$$CF_3Br + LiN(CH_3)_2 \rightarrow CF_3N(CH_3)_2 + LiBr \quad (3)$$

Reactions of the (Pentafluorophenyl)phosphine Complexes with Oxygen Nucleophiles. Because of the reactivity of the complexed trifluoromethyl carbon to nucleophiles, we have introduced the electron-withdrawing fluoro substituent at the phosphine ligand rather than at the methyl group. Our initial attempt to use tris(pentafluorophenyl)phosphine instead of triphenylphosphine failed because we were unable to prepare *trans*-$PtCH_3Cl(P(C_6F_5)_3)_2$ by the conventional route. We have therefore used the compound $Ph_2PC_6F_5$ instead, and have synthesized the complex *trans*-$PtCH_3Cl(PPh_2C_6F_5)_2$. The $^{31}P\{^1H\}$ resonance at δ 22.3 shows no coupling due to $J(PF)$. This complex in solution does not react with lithium dimethylamide. The electrophilicity of the platinum(II) center has been increased by replacing the anionic chloride ligand by tetrahydrofuran. This transformation has been accomplished by using silver perchlorate in THF solution (eq 4).

$$trans\text{-}PtCH_3Cl(PPh_2C_6F_5)_2 + AgClO_4 + THF \rightarrow trans\text{-}[PtCH_3(THF)(PPh_2C_6F_5)_2]X + AgCl \quad (4)$$

The complex *trans*-$[PtCH_3(THF)(PPh_2C_6F_5)_2]ClO_4$ reacts with $LiN(CH_3)_2$ in dry THF to give a product that has no complexed dimethylamide. The complex has the oxocarboplatinum structure *trans*-$PtCH_3(2\text{-}OC_6F_4PPh_2)(PPh_2C_6F_5)$. This complex results from the presence of trace amounts of water in the reaction, which react with $LiN(CH_3)_2$ to give LiOH (eq 5). Careful drying of



all reagents decreases the rate of formation of this product; nevertheless, we have been unable to obtain any dimethylamide or hydride product from any of these reactions, even under the most stringent drying conditions. The oxocarboplatinum complex is rapidly formed at ambient temperature when hydroxide ion is used in place of the dimethylamide ion. The complex has been characterized by X-ray crystallography, as well as by ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectroscopy.

(9) Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans* **1980**, 776–785.

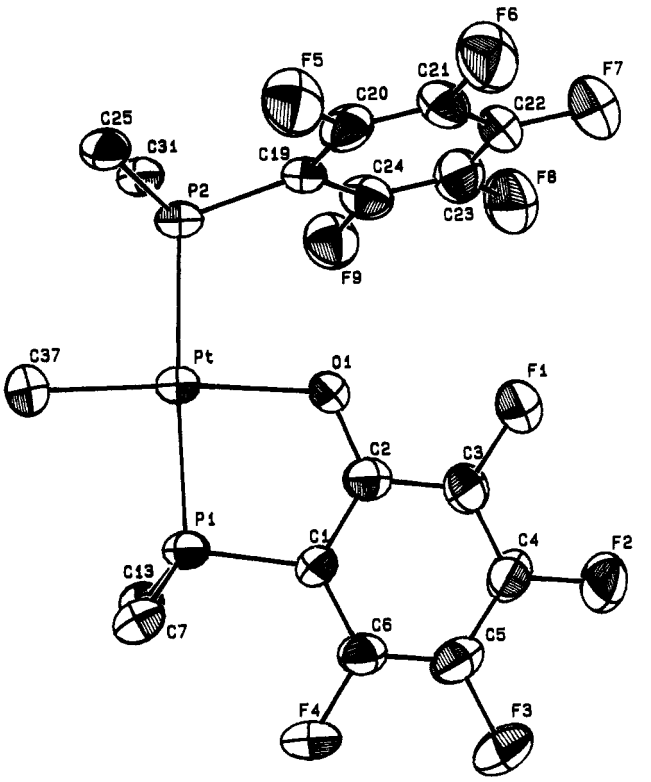
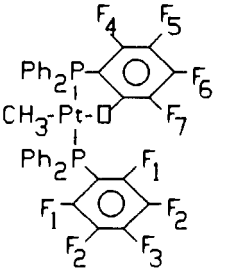


Figure 1. Molecular structure and atom-labeling scheme for $C_{37}F_9OP_2PtH_{23}$ shown with 50% thermal ellipsoids. The C7–C18 and C26–C36 series phenyl ring bonded to P1 and P2 are shown as the ipso atoms only.

The structure of *trans*-$PtCH_3(2\text{-}OC_6F_4PPh_2)(PPh_2C_6F_5)$ (Figure 1) shows Pt–O1 and Pt–C37 bond distances of 2.12 (1) and 2.08 (1) Å, respectively. These distances are normal and give no indication of any significant strain in the oxoplatinacyclic ring.[10] The slightly lengthened Pt–O1 distance is a consequence of the high trans influence of the methyl ligand. The absence of strain is also supported by the observation of an O1–Pt–C37 angle of 174.4 (4)°, which is only slightly distorted from linearity. The O1–C2–C1 angle of 124.0 (9)° is only slightly greater than the 120° expected for a substituent on an aromatic ring.

The ^{19}F NMR resonances are assigned for the complex $PtCH_3(2\text{-}OC_6F_4PPh_2)(PPh_2C_6F_5)$ by using a combination of spin multiplicities and chemical shift comparisons. The numbering system for the individual fluorines is shown in structure **1** and the

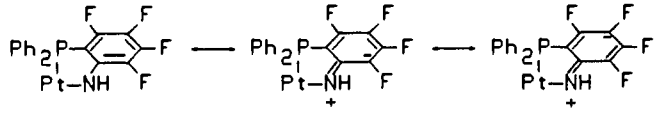


1

line intensities are shown in parentheses in the text after the shift values. The $^3J(PF)$ coupling in $PPh_2C_6F_5$ is absent in the complexes. The doublet resonance at δ −129.6 (2) is due to F_1 with coupling to F_2. The triplet resonance at δ −165.0 (2) is due to F_2 with numerically equal coupling to F_1 and F_3. The triplet at δ −153.2 (1) corresponds to F_3 coupling to F_1 and F_3. We assign the doublet at δ −137.5 (1) to F_4 because its chemical shift is close

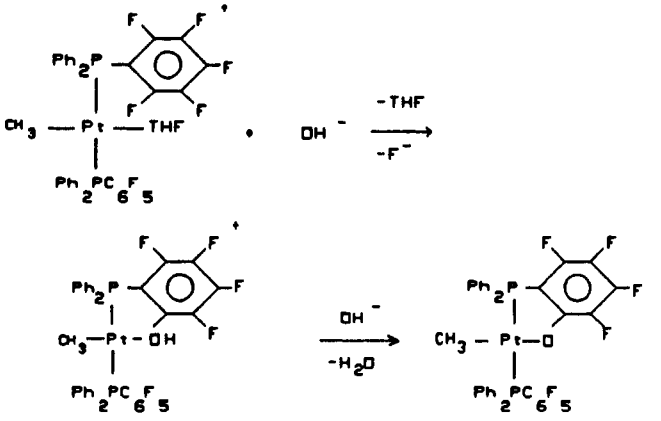
(10) Examples of Pt–O distances are the values of 1.97 (2) Å in *trans*-$Pt(2\text{-}OC_6H_4PBu_2)_2$ (O'Flynn, K. H. P.; McDonald, W. S. *Acta Crystallogr.* **1977**, *B33*, 194–195) and 1.99 (1) Å in *trans*-$PtPh(OOBu)(PPh_3)_2$ (Strukul, G.; Michelin, R. A.; Orbell, J. D.; Randaccio, L. *Inorg. Chem.* **1983**, *22*, 3706–3713).

Scheme I



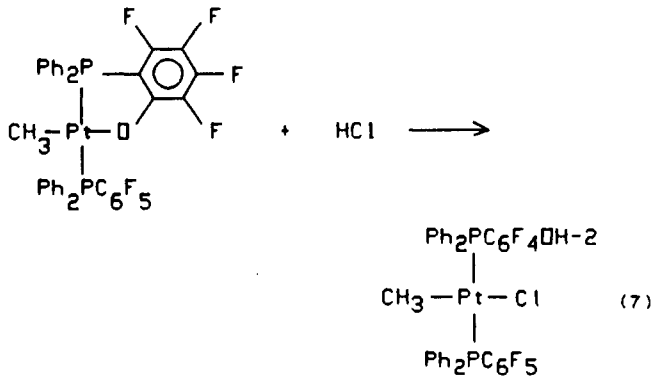
to that of F_1, and the triplet at δ −156.2 (1) is assigned to F_6 because of its closeness in chemical shift position to F_3. The triplet pattern is due to coupling with F_5 and F_7. We assign the triplet at δ −181 (1) to F_5, and the doublet at δ −168.5 (1) to F_7.

The formation of this oxoplatinacyclic complex is an unusual example of a C–F bond cleavage reaction under mild conditions.[11] No reaction is observed between the *free* ligand $Ph_2PC_6F_5$ and group I hydroxides in THF solution. No products resulting from the cleavage of any other C–F bonds in *trans*-$[PtCH_3(THF)(PPh_2C_6F_5)_2]ClO_4$ are detectable. The product complex has been formed by the replacement of the ortho fluorine by hydroxide ion, followed by deprotonation to yield the product oxoplatinacycle (eq 6). Formation of this stable five-membered ring product



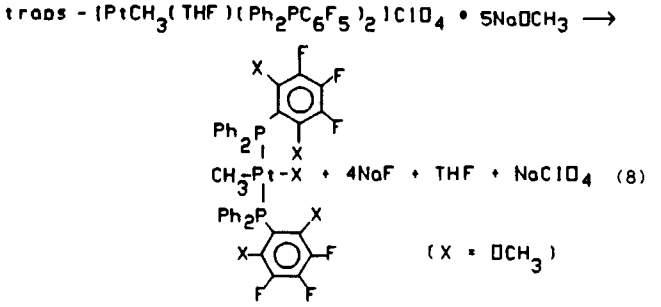
(6)

prevents further reaction with hydroxide ion. The platinacycle can be cleaved by the addition of protonic acids; hydrochloric acid yields the complex *trans*-$PtCH_3Cl(2\text{-}HOC_6F_4PPh_2)(PPh_2C_6F_5)$ where protonation has occurred at oxygen (eq 7).



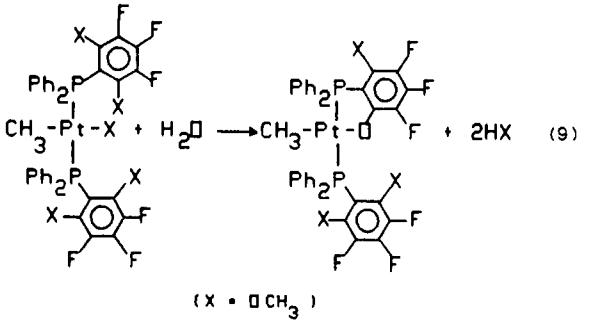
(7)

Methoxide ion can be expected to show reactivity similar to that of hydroxide ion, except that now it is unlikely that C–O cleavage will occur to give the oxoplatinacycle. Treating *trans*-$[PtCH_3(THF)(PPh_2C_6F_5)_2]ClO_4$ with excess sodium methoxide results in the formation of the complex *trans*-$PtCH_3(OCH_3)(PPh_2C_6F_3(OCH_3)_2\text{-}2,6)_2$ where all the ortho fluorines on the fluorinated ring have been replaced by methoxides (eq 8). Such a reaction occurs in a sequential fashion whereby



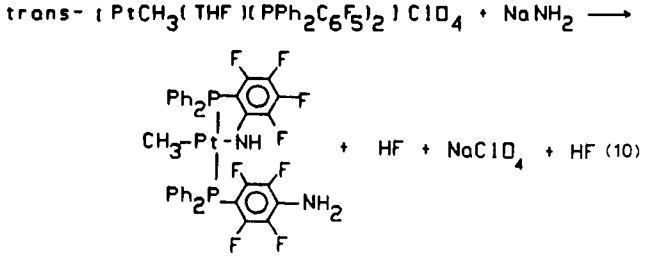
(8)

each ortho fluorine in the pentafluorophenyl ring can undergo reaction with methoxide ion. This sequence occurs with methoxide because a complexed oxygen of the formed methyl phenyl ether ligands binds sufficiently weakly that the intramolecular replacement of all the ortho fluorines occurs as free rotation brings each ortho fluorine into close proximity with the platinum center. The intramolecular nature of these substitution reactions is evidenced by the observation that only the ortho fluorines are replaced by the methoxy group. This complex, *trans*-$PtCH_3(OCH_3)(PPh_2C_6F_3(OCH_3)_2\text{-}2,6)_2$, is slowly converted by water or hydroxide ion into the cyclometalated complex *trans*-$PtCH_3(2\text{-}OC_6F_3(OCH_3)\text{-}6\text{-}PPh_2)(PPh_2C_6F_3(OCH_3)_2\text{-}2,6)$ (eq 9). This unexpected reaction involves cleavage of a C–O bond in the 2-position of the fluorinated ring.



(9)

Reaction of the (Pentafluorophenyl)phosphine Complexes with the Amide Ion. An interesting example of *both* ortho and para substitution of aromatic fluorines is observed in the reaction of *trans*-$[PtCH_3(THF)(PPh_2C_6F_5)_2]ClO_4$ with sodium amide. The product is the cyclometalated complex *trans*-$PtCH_3(2\text{-}NHC_6F_4PPh_2)(PPh_2C_6F_4NH_2\text{-}4)$ (eq 10). The structure has been



(10)

confirmed by a combination of ^1H, $^{31}P\{^1H\}$, and ^{19}F NMR spectroscopy. The NMR spectral peaks are observed with the following positions and intensities. ^1H NMR: δ 4.54 br (1 H, N*H*; $^2J(PtH)$ = 30 Hz), 3.08 s (2 H, NH_2). The control reaction between the free ligand $PPh_2C_6F_5$ and sodium amide results in the selective substitution of the fluorine in the 4-position by an amine moiety (eq 11).[12] It is likely therefore that the amine

$$Ph_2PC_6F_5 + NaNH_2 \rightarrow Ph_2PC_6F_4NH_2\text{-}4 + NaF \quad (11)$$

(11) Other examples of C–F cleavage reactions involving transition-metal complexes can be found in the following references: Richmond, T. G.; Osterberg, C. E.; Arif, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 8091–8092. Crabtree, R. H.; Faller, J. W.; Mellea, M. F.; Quirk, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 2913–2917. Gross, M. E.; Johnson, C. E.; Maroney, M. J.; Trogler, W. C. *Inorg. Chem.* **1984**, *23*, 2968–2973. Michelin, R. A.; Ros, R.; Guadalupi, G.; Bombieri, G.; Benetollo, F. *Inorg. Chem.* **1989**, *28*, 840–846. Bruce, M. I.; Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 747–753. Cooke, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 170–173. Bruce, M. I.; Harbourne, D. A.; Waugh, F.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 895–898. Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1966**, 1837–1842. King, R. B.; Bisnette, M. B. *J. Organometal. Chem.* **1964**, *2*, 38–43.

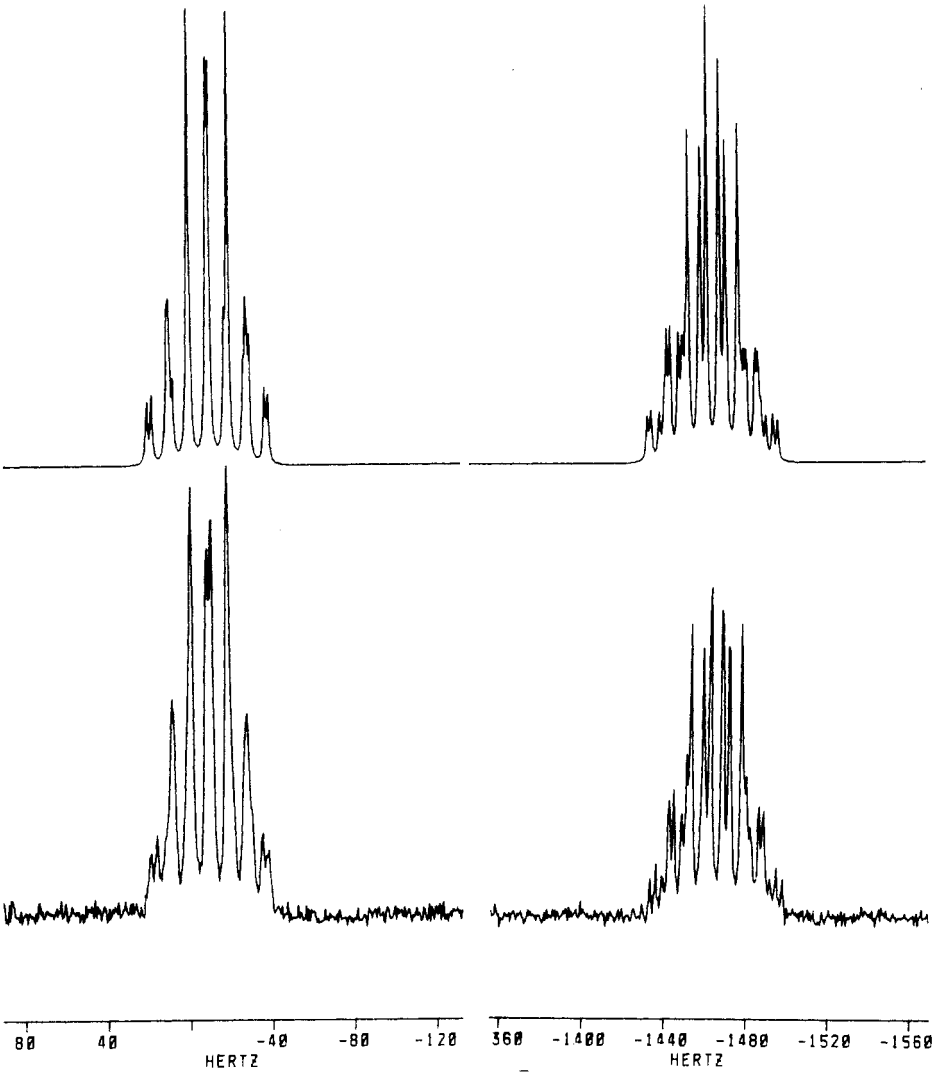


Figure 2. Experimental and calculated ^{19}F NMR spectra of $[Ph_3(C_6F_4H\text{-}4)P]Br$.

functionality in the complex, which is bonded to the 4-position of the noncyclometalated ring, results from a substitution reaction that is not induced by the platinum center. The formation of the cyclometalated ring with an NH functionality in the 2-position of the fluorinated ring shows that the intramolecular cyclometalation reaction is faster than the expected substitution reaction in the 4-position. Direct comparison of the rate with the free ligand itself is invalid, however, because the nucleophilic displacement of the fluorine in the 4-position of the fluorophenyl by NH_2 is itself likely to be accelerated by complexation of the phosphine to platinum(II). The failure to observe further substitution of fluorine by amine in the amidoplatinacyclic ring subsequent to its formation is due to the deactivation of the ring to nucleophilic substitution by the amino group in the 2-position. The resonance forms shown in Scheme I show that the lone-pair electron pair on the platinacyclic amino group can localize into the fluoroaryl ring.

Reaction of Triphenyl(pentafluorophenyl)phosphonium Bromide with Nickel(II) Complexes. Complexation of a tertiary phosphine to a cationic platinum center can be expected to induce a similar electron density at phosphorus as that of a phosphonium ion. In order to test whether such a parallel is conceptually reasonable, we have attempted the synthesis of the unknown compound $[Ph_3(C_6F_5)P]Br$ using an analogous method to that reported for $[Ph_4P]Br$. The published synthetic method for $[Ph_4P]Br$ involves heating a mixture of triphenylphosphine, bromobenzene, and nickel bromide to produce a melt, which is then subsequently hydrolyzed with water to give the phosphonium compound as its bromide salt.[13] The adaptation we have employed involves replacing bromobenzene with bromopentafluorobenzene. We have not, however, succeeded in synthesizing any of the desired product. Instead, we find that the reaction yields the compound $[Ph_3(C_6F_4H\text{-}4)P]Br$, which is formed after the final hydrolysis step. The $^{31}P\{^1H\}$ NMR spectrum of the salt shows a triplet centered at δ 16.2 ($^3J(PF)$ = 6.0 Hz). The ^{19}F NMR spectrum shows two multiplets of equal intensity at δ −123.5 and −131.3. Hydrolysis with D_2O instead of H_2O gives $[Ph_3(C_6F_4D\text{-}4)P]Br$. The experimental and simulated ^{19}F NMR spectra for $[Ph_3(C_6F_4H\text{-}4)P]Br$ and $[Ph_3(C_6F_4D\text{-}4)P]Br$ are shown in Figures 2 and 3, respectively.[14] The ^2D NMR spectrum of this salt shows a broad band at δ 7.81. The IR spectrum shows a band due to $\nu(CD)$ at 2196 cm^{-1}. The hydrolysis product from H_2O cannot arise from the direct attack of water on $[Ph_3(C_6F_5)P]Br$ in the melt; such a reaction is expected to yield $[Ph_3(C_6F_4OH\text{-}4)P]Br$ by regioselective nucleophilic attack by water at the 4-position of the pentafluorophenyl ring in $[Ph_3(C_6F_5)P]Br$.

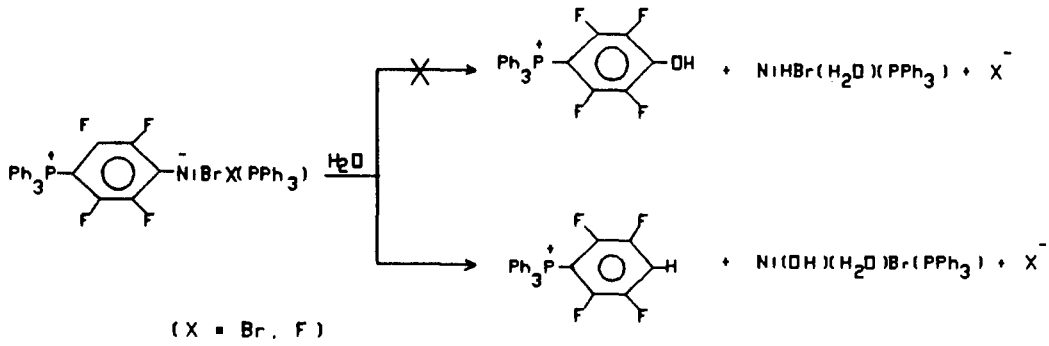
An explanation for these results is that the melt formed in the initial fusion process contains an organonickel phosphonium salt

(12) Fluoroaromatics are well-known to undergo nucleophilic attack; see: Tatlow, J. C. *Endeavour* **1963**, *22*, 89–95 and Banks, R. E. *Fluorocarbons and their Derivatives*, 2nd ed.; MacDonald: London, 1970; pp 218–221.

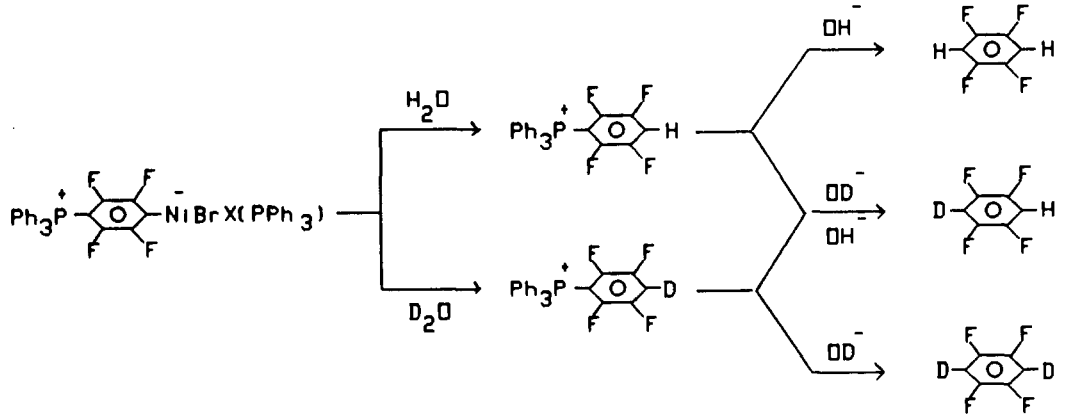
(13) Horner, L.; Mummenthey, G.; Moser, H.; Beck, P. *Chem. Ber.* **1966**, *99*, 2782–2788. Affandi, S.; Green, R. L.; Hsieh, B. T.; Holt, M. S.; Nelson, J. H.; Alyea, E. C. *Synth. React. Inorg. Met.-Org. Chem.* **1987**, *17*, 307–318.

(14) PANIC 83.3004. *Aspect 3000 NMR Software Manual*; Bruker Spectrospin: Karlsruhe, West Germany.

Scheme II

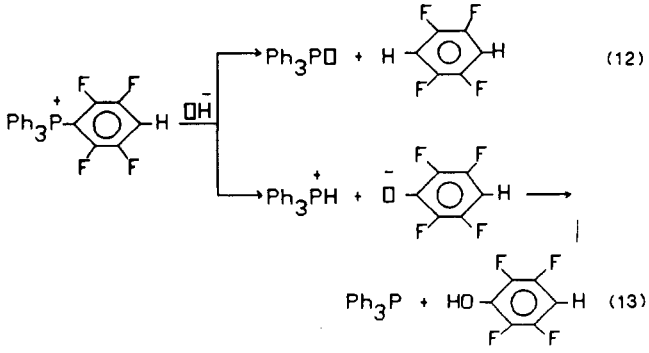


Scheme III



that has a nickel–carbon bond at the 4-position of the pentafluorophenyl ring. Subsequent hydrolysis of this solid material esults in selective cleavage of this Ni–C bond whereby the hydrogen transfers to carbon and the hydroxyl to nickel; the reverse regioselectivity is not detected (Scheme II). A plausible formulation for this organometallic complex is $Ph_3(C_6F_4(Ni^-BrX(PPh_3)\text{-}4)P^+$ (X = F or Br). If smaller amounts of triphenylphosphine are used in the reaction, the nitrogen purge stream oxidizes iodide ion to iodine. This observation supports a pathway involving the reductive elimination of halogen from a higher valent nickel intermediate.

The phosphonium salt $[Ph_3(C_6F_4H\text{-}4)P]Br$ formed in the hydrolysis reaction reacts with hydroxide ion with selective cleavage of the phosphorus–fluorocarbon bond. The phosphorus center is a stronger oxophile than the carbon center bonded to phosphorus. The final product is therefore 1,2,4,5-tetrafluorobenzene and not 1,2,4,5-tetrafluorophenol, which would result from the opposite selectivity (eqs 12 and 13). Reaction of $[Ph_3(C_6F_4H\text{-}4)P]Br$ with



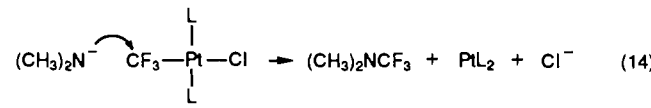
(12)

(13)

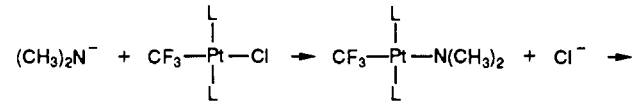
KOH in D_2O gives 1,2,4,5-tetrafluoro-3-deuteriobenzene. The ^1H NMR spectrum of this compound shows a triplet of triplets centered at δ 7.03 (^3J(HF), ^5J(HF) = 9.7, 7.5 Hz). The ^{19}F NMR spectrum shows a multiplet centered at δ −139.3 for chemically equivalent but magnetically inequivalent fluorine nuclei. This selectively monodeuterated compound can also be prepared by treating the melt with D_2O, followed by reacting the product phosphonium salt with OH^-. A sequence of reactions using D_2O and OD^- yields the dideuterated product 1,2,4,5-tetrafluorodideuterobenzene (Scheme III). The ^{19}F NMR spectrum of this compound in C_6D_6 shows a single resonance at δ −138.4.

Discussion

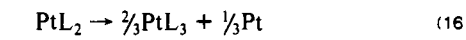
Reaction of *trans*-$PtCF_3Cl(PPh_3)_2$ with Dimethylamide Ion. The formation of $CF_3N(CH_3)_2$ in reaction 2 is unexpected. Two sites of attack by the dimethylamide anion at *trans*-$PtCF_3Cl(PPh_3)_2$ can lead to this product; these are the platinum center or the electrophilic carbon of the complexed trifluoromethyl group. The formation of $CF_3N(CH_3)_2$ is best explained by the proposition that the site of attack is the carbon center. This attack at carbon by the strongly reducing dimethylamide anion results in a complementary redox reaction to give the intermediate complex $Pt(PPh_3)_2$. Subsequent ligand disprportionation gives $Pt(PPh_3)_3$ and metallic platinum. Attack at platinum by the dimethylamide anion can result in several alternate products. One pathway is the substitution of chloride ion by dimethylamide, leading to the formation of *trans*-$PtCF_3(N(CH_3)_2)(PPh_3)_2$. We do not observe the formation of this complex, nor of the stable complex *trans*-$PtCF_3H(PPh_3)_2$ resulting from β-hydrogen transfer in *trans*-$PtCF_3(N(CH_3)_2)(PPh_3)_2$. Reductive elimination from *trans*-$PtCF_3H(PPh_3)_2$ will give CF_3H rather than the observed $CF_3N(CH_3)_2$. Our data do not differentiate between pathways involving either nucleophilic attack by the dimethylamide anion at the trifluoromethyl carbon, or reductive elimination from *trans*-$PtCF_3(N(CH_3)_2)(PPh_3)_2$. These routes are shown in eqs 14–16 where L = PPh_3. The pathway shown in eq 14 explains our



(14)



(15)



(16)

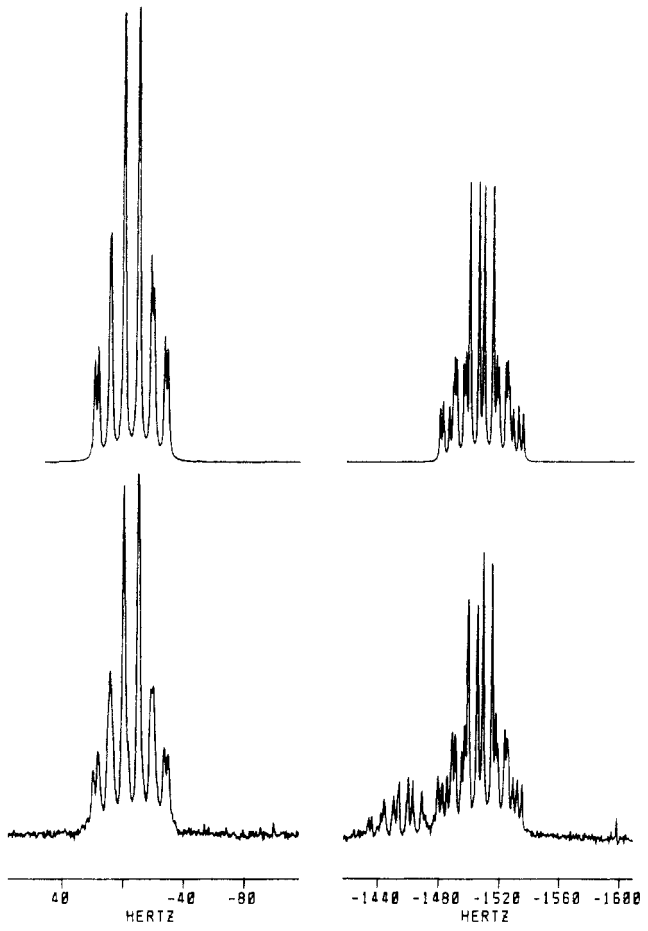
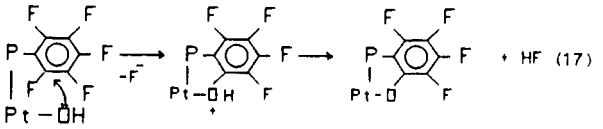


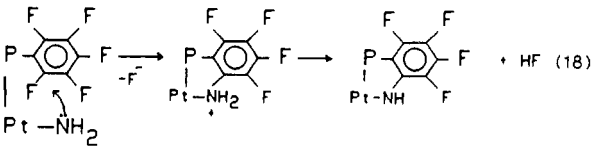
Figure 3. Experimental and calculated ^{19}F NMR spectra of $[Ph_3(C_6F_4D\text{-}4)P]Br$. The sample contains a small quantity of $[Ph_3(C_6F_4H\text{-}4)P]Br$.

observations. The pathway shown in eq 15 is feasible, but this route requires the assumption that the reductive-elimination step is fast compared to β-hydrogen transfer. Several arguments can be made against this premise. Since β-hydride transfer is the only observed pathway for the hydrocarbon analogue complex *trans*-$PtCH_3(N(CH_3)_2)(PPh_3)_2$, it is unlikely that reductive elimination is faster for the trifluoromethyl complex. If we use the approximate bond enthalpies (kcal mol^{-1}) of 50, 24, and 84 for Pt–C, Pt–N, and C–N, respectively, in *trans*-$PtCF_3(N(CH_3)_2)(PPh_3)_2$, reductive elimination is a favored process.[15] For *trans*-$PtCH_3(N(CH_3)_2)(PPh_3)_2$ we estimate the Pt–C, Pt–N, and C–N bond enthalpies to be 36, 24, and 75 kcal mol^{-1}, respectively. In this case the enthalpy change for reductive elimination is 15 kcal mol^{-1}, which is larger than the 10 kcal mol^{-1} for *trans*-$PtCF_3(N(CH_3)_2)(PPh_3)_2$. Unless the two complexes show distinctly different reductive elimination pathways, it is unlikely that such a mechanism is preferentially favored for the case where the enthalpy change is smaller. A second pathway resulting from attack at platinum(II) by the dimethylamide anion is replacement of the coordinated CF_3 by $N(CH_3)_2$. Such a pathway is expected to yield *trans*-$Pt(N(CH_3)_2)Cl(PPh_3)_2$, or the β-hydride-transfer product, *trans*-$PtHCl(PPh_3)_2$. Neither of these complexes are observed. In summary, therefore, our data are best explained by a complementary redox pathway involving nucleophilic attack by $(CH_3)_2N^-$ at the complexed trifluoromethyl carbon.

Reactions of the (Pentafluorophenyl)phosphine Complexes with Oxygen and Nitrogen Nucleophiles. The reaction between nucleophiles and fluoroaromatics is well-known, with substitution usually occurring at the 4-position. Substitution of fluorine at the 2-position has been observed with nitropentafluorobenzene, and this different regioselectivity has been explained on the basis of an intramolecular association between the nucleophile and the nitro group.[12] The substitution pattern observed between *trans*-$[PtCH_3(THF)(PPh_2C_6F_5)_2]ClO_4$ and either OH^-, OCH_3^-, or NH_2^- bears a strong resemblance to the nitro group induced intramolecular attack at the fluorine in the 2-position of nitropentafluorobenzene. Coordination of a hydroxy or methoxy group to platinum(II) places it in close proximity to the fluorine in the 2-position of the pentafluorophenyl group of the coordinated phosphine. Subsequent intramolecular attack by the uncoordinated lone pair on the hydroxy or methoxy ligand at the electrophilic carbon results in substitution (eq 17). The reaction with amide



ion can follow an analogous pathway as outlined in eq 18. The



formation of this amide complex verifies that substitution at the 2-position is induced by complexation to the metal ion and that it requires a vacant site in the coordination plane of platinum. If platinacycle formation blocks the fourth coordination position, the replacement of the ortho fluorine on the other fluorophenyl ring is suppressed.

A second mechanism for these substitution reactions is plausible, yet more speculative. This alternative explanation involves coordination of a fluorine atom in the 2-position of the pentafluoro ring into the fourth coordination position in an agostic manner.[16] Such an association can weaken the C–F bond, thereby increasing the electrophilicity of the carbon to which it is bonded. Furthermore, since only a fluorine atom in the 2-position of the pentafluorophenyl is geometrically arranged for such coordination, this theory explains the observed selectivity.

These results show that introducing fluoro substituents onto the aromatic ring is not a useful method to stabilize a metal amide bond because of the high reactivity of the ring fluorines to nucleophilic substitution reactions.

Reactions of Triphenyl(pentafluorophenyl)phosphonium Bromide with Nickel(II) Complexes. Our results with divalent nickel complexes lead us to conclude that the regioselectivity for attack at a fluoroaromatic ring by nickel halide is the same as that observed with other nucleophiles. The favored substitution is again at the 4-position. We conclude in our reactions with platinum(II) complexes, where we observe substitution at the 2-position, that this different regioselectivity is due to intramolecular effects via interaction with the platinum center.

We have not succeeded in isolating any nickel-containing compounds from the melt of triphenylphosphine, nickel bromide, and bromopentafluorobenzene. The only reagent that dissolves the nickel compounds is water, and the addition of this solvent results in rapid hydrolysis to give the phosphonium compound. A likely reaction sequence in the melt involves the initial formation of $[Ph_3(C_6F_5)P]Br$, which then undergoes insertion of nickel(II)

(15) These estimated enthalpies have been obtained from the following values. The Pt–CF_3 value is the sum of the Pt–CH_3 estimate of 36 kcal/mol plus 14 kcal/mol increase for CF_3 over CH_3. See: Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 6928–6937. Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71. The Pt–$N(CH_3)_2$ value of 24 kcal/mol is based on the estimate that this bond will be 12 kcal/mol weaker than the Pt–CH_3 bond enthalpy. See: Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444–1456. Bryndza, H. E.; Domaille, P. J.; Tam, W.; Fong, L. K.; Paciello, R. A.; Bercaw, J. E. *Polyhedron.* **1988**, *7*, 1441–1452. The CF_3–$N(CH_3)_2$ value of 84 kcal/mol is estimated from a value of 75 kcal/mol for CH_3–$N(CH_3)_2$ plus an increment of 9 kcal/mol for the CF_3 group as compared to the CH_3. See McMillen, D. P.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.

(16) For a review of this literature, see: Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395–408.

into the carbon–fluorine bond. This result is significant because it provides a useful example of a competition experiment whereby the insertion reaction occurs at the carbon–fluorine bond in the 4-position, rather than at the 4-position in the phenyl carbon–hydrogen bonds.

Acknowledgment. We thank the Louisiana Board of Regents for support through the Louisiana Education Quality Support Fund. We thank Professors F. G. A. Stone and J. E. Bercaw for useful suggestions. We thank the Office of Naval Research for funds to purchase the FTIR spectrometer.

Supplementary Material Available: Tables of positional parameters, bond distances, bond angles, general displacement parameters, and torsion angles (13 pages); a table giving values of F_o and F_c (40 pages). Ordering information is given on any current masthead page.

Notes

Contribution from the Institut für Anorganische Chemie der Universität, Callinstrasse 9, D-3000 Hannover 1, FRG, and FB Naturwissenschaftliche Technik, Fachhochschule Ostfriesland, Constantinplatz 4, D-2970 Emden, FRG

^{19}F NMR Chemical Shift of SF_2 in the Gas Phase

Willy Gombler,[‡] Jörg Schaebs,[†] and Helge Willner*,[†]

Received October 19, 1989

In the series of fluorides SiF_4, PF_3, SF_2, and ClF, sulfur difluoride can be considered as a laboratory curiosity. It is unstable with respect to disproportionation into SSF_2 and SF_4.[1] Due to this instability the existence of SF_2 could not be verified until 1969, when the compound was detected by mass and microwave spectroscopy in the gas phase at low pressures (≤0.1 mbar).[2,3] All efforts to enhance the partial pressure by condensation failed because SF_2 dimerizes spontaneously even at temperatures as low as −196 °C.[1] The well-characterized dimer SF_3SF[4,5] is not a suitable precursor for SF_2, because its dissociation is kinetically hindered.[1] However, by reaction of F_2 with COS under suitable conditions, partial pressures of more than 30 mbar of SF_2 could be obtained, and it became possible to record a high-resolution IR spectrum.[6] The new synthesis initiated extensive research into the macroscopic properties of SF_2.[1] Although SF_2 has already been characterized by mass,[2] microwave,[3,7] infrared,[6,8] and photoelectron[9] spectroscopy, its ^{19}F NMR spectrum has not been reported. Recently, ^{19}F and ^{33}S chemical shifts have been calculated with the IGLO method[10] and compared with experimental values for related compounds.[11] The $\delta(^{19}F)$ values in the series of compounds SiF_4, PF_3, SF_2, and ClF do not change monotonically, and it was questionable whether the shielding in SiF_4 or ClF is unusual. The chemical shifts of SF_2 are therefore of great interest.

Experimental Section

Sulfur difluoride was prepared from COS (Baker) and F_2 (Kali-Chemie) according to the published method.[6] The concentration of SF_2 was monitored by FTIR spectroscopy. Unreacted COS is observed, and CO, SF_4, and traces of SF_6 are formed as byproducts. The NMR tube, equipped with a rotational symmetrically valve[12] (type VNMR-10, Young, London), was treated with boiling hydrochloric acid, vacuum-dried, and finally passivated with the COS/F_2 reaction products. The molar ratio COS/F_2 of approximately 1/1 was adjusted to yield a maximum concentration of SF_2. Then the NMR tube was filled with about 100 mbar of the reaction products containing about 30 mbar of SF_2 and inserted into the probe of the NMR spectrometer, which was cooled to −30 °C. For a fast pulse sequence of 7 s^{-1}, the measurement of the ^{19}F NMR gas spectrum took about 20 min. According to the FTIR spectrum of the sample, the concentration of SF_2 had decreased by about 50% after that time, and the dimer of SF_2 as well as the decomposition products SF_4 and SSF_2 was formed. The ^{19}F chemical shift of SF_2 was referenced to the signals of SF_3SF. In a separate experiment, a mixture of CCl_3F and SF_3SF was measured under the same conditions.

The NMR spectrum was recorded on a Bruker MSL 200 spectrometer at 188.31 MHz using a 10-mm $^1H/^{19}F$ dual probe. The FTIR spectra were measured with a Nicolet MX 3600 instrument using a DTGS detector.

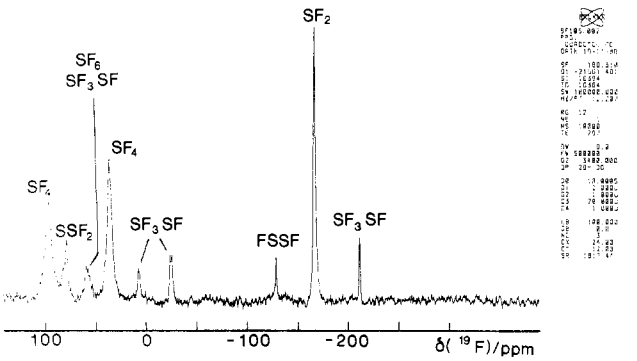


Figure 1. Gas-phase ^{19}F NMR spectrum of a sample containing SF_2 and other binary sulfur fluorides.

Table I. ^{19}F Chemical Shifts for Gaseous and Liquid Binary Sulfur Fluorides (Referenced to CCl_3F)

	$\delta(^{19}F)$/ppm	
	gas phase at −30 °C	liquid state
SF_2	−167.0	
SF_4 (ax)	93.0	88.4[a]
SF_4 (eq)	34.2	34.1[a]
SF_6	54.9	56.5[a]
SSF_2	77.8	79.0[a]
FSSF	−128.8	−123.2[b]
S_2F_4 (1)	54.9	53.2[c]
S_2F_4 (2)	7.0	5.7[c]
S_2F_4 (3)	−24.7	−26.3[c]
S_2F_4 (4)	−211.1	−204.1[c]

[a] Reference 13; −50 °C. [b] Reference 14; −50 °C. [c] Reference 4; −100 °C.

[†] Universität Hannover.
[‡] Fachhochschule Ostfriesland.

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