Organometallics **2005,** *24,* 4845−4848 4845

Unexpected Formation of an Organoplatinum(IV) Fluoride Complex in the Reaction of Pt(TMEDA)(CH_3)$_2$ with Perfluoro-*sec*-butyl Iodide

Russell P. Hughes,[*,†] Roman B. Laritchev,[†] Lev N. Zakharov,[‡] and
Arnold L. Rheingold[‡]

*Departments of Chemistry, 6128 Burke Laboratory, Dartmouth College, Hanover,
New Hampshire 03755, and University of California, San Diego, California 92093-0358*

Received June 8, 2005

*Summary: Instead of undergoing a conventional oxidative addition reaction, Pt(TMEDA)Me_2 (**1**) reacts with perfluoro-sec-butyl iodide to afford a rare example of a terminal Pt(IV) fluoride complex, trans-Pt(TMEDA)(I)(F)Me_2 (**2**), along with a mixture of the trans- and cis-isomers of perfluoro-2-butene. Trapping experiments with CH_3OD result in significant quantities of $CF_3CF_2CFDCF_3$, indicating the intermediacy of a perfluorocarbanion. Complex **2** has been characterized by X-ray diffraction, and a mechanism for its formation is proposed.*

Introduction

Oxidative addition of perfluoroalkyl iodides to transition metals is one of the most frequently used approaches to making metal−fluoroalkyl bonds.[1] Recent work in our group has focused on the successful use of such chemistry for the synthesis of late transition metal−fluoroalkyl complexes, particularly those of metals from groups 9[2−10] and 10.[11−13] In some cases, however, the expected oxidative addition product is not observed and the reaction results in fluoroalkylation at ligand sites rather than, or in addition to, the metal center.[14−17]

We have previously pointed out[12,17] that oxidative addition reactions of iodofluoroalkanes to transition metals is unlikely to proceed via polar S_N2 attack by the metal at carbon due to the unfavorable polarity of the $C^{\delta-}-I^{\delta+}$ bond.[18,19] Indeed, nucleophilic attack at iodine is predicted from such considerations. In a previous report of reactions of $WCp_2(C_2H_4)$ with perfluoro-isopropyl iodide, in which the secondary perfluorocarbanion is favored as a leaving group by σ-stabilization of the negative charge by adjacent CF_3 groups,[20−23] we provided evidence that the reactions proceeded via initial nucleophilic attack on iodine by the metal to give the ion pair $[WCp_2(C_2H_4)I]^+(CF_3)_2CF^-$, with subsequent products formed by nucleophilic attack of the perfluorocarbanion on ligands. Formation of small amounts of $CF_3CF{=}CF_2$ by loss of fluoride ion provided an initial signature of the $(CF_3)_2CF^-$ intermediate;[23] fluorinated radical intermediates do not form fluoroalkenes.[24] Compelling evidence for a perfluoroalkyl carbanion intermediate was provided by use of CH_3OD as a trap[25] to afford $(CF_3)_2CFD$ by abstraction of the more acidic D; in a control experiment the corresponding perfluoroalkyl radical was shown to abstract the weaker[26] CH bond to give $(CF_3)_2CFH$ as the organic product.[17]

Here we report another reaction that proceeds via a perfluorocarbanion intermediate, but with a different result, affording unexpected formation of a Pt(IV) monofluoride complex. Terminal monofluoride[27,28] and

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[*] To whom correspondence should be addressed. E-mail: rph@dartmouth.edu.

[†] Dartmouth College.

[‡] University of California, San Diego.

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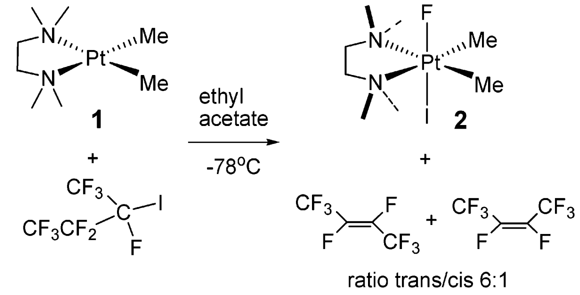
10.1021/om0504654 CCC: $30.25

Scheme 1



difluoride[29−31] complexes of organoplatinum(IV) systems are rare, and this reaction provides an unusual entry to this type of compound.

Results and Discussion

We have previously shown that reactions of Pt(TMEDA)Me$_2$ (**1**) (TMEDA = $(CH_3)_2NCH_2CH_2N(CH_3)_2$) with a variety of *n*-fluoroalkyl iodides (R_F-I) afford the expected octahedral oxidative addition products *trans*-Pt(TMEDA)(R_F)(I)Me$_2$.[12,32] In dramatic contrast, reaction of **1** with perfluoro-*sec*-butyl iodide in ethyl acetate at −78 °C resulted in no observable formation of a Pt-fluoroalkyl complex, but gave a single yellow crystalline Pt(IV) fluoride product in 91% yield. The fate of the fluoroalkyl group was revealed by closer examination of the volatile organic products of this reaction; ^{19}F NMR spectroscopy revealed complete conversion of the *sec*-C_4F_9 group into a 6:1 mixture of the *trans*- and *cis*-isomers of perfluoro-2-butene,[33] as shown in Scheme 1.

The platinum-containing product was unambiguously identified by a single-crystal X-ray diffraction study as **2**, resulting from apparent addition of IF to the Pt(II) precursor. An ORTEP diagram is provided in Figure 1, with details of the X-ray diffraction analysis presented in Table 1. The fluoride and iodide ligands are *trans* to each other, with an F1−Pt1−I1 angle of 175.85(14)°. The Pt−F bond distance is 2.001(4) Å, which is significantly shorter than for other organoplatinum(IV) monofluorides in which substituted phenyl groups are located *trans* to the fluoride ligand (2.07−2.08 Å),[27,28] consistent with an expected stronger *trans* influence[34] of phenyl compared to iodide. In the few examples of difluoride compounds of Pt(IV),[29−31] the two fluoride ligands are always *trans* to each other, with Pt−F bonds ranging between 1.93 and 1.96 Å, consistent with a weaker *trans* influence of fluoride compared to the iodide in **2**.

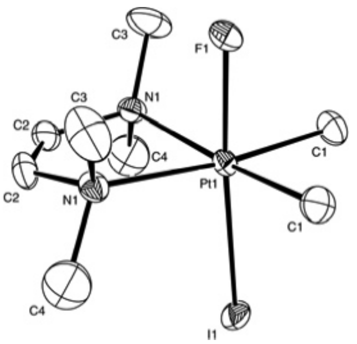


Figure 1. ORTEP diagram for **2** with ellipsoids drawn at the 30% probability level. Hydrogen atoms are excluded. Selected bond lengths (Å) and angles (deg): Pt(1)−F(1), 2.001(4); Pt(1)−C(1), 2.057(6); Pt(1)−N(1), 2.250(4); Pt(1)−I(1), 2.6015(7); F(1)−Pt(13)−C(1), 88.0(2).

Table 1. Crystallographic Summary for 2

formula	$C_8H_{22}FIN_2Pt$
fw	487.27
space group	*Pnma*
a, Å	12.364(2)
b, Å	13.339(2)
c, Å	7.8955(14)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	1302.2(4)
Z	4
cryst color, habit	yellow, block
D(calcd), g/cm^3	2.485
μ(Mo Kα(λ = 0.71073)), mm^{-1}	13.124
temp, K	213(2)
diffractometer	Bruker Smart Apex
no. of indep reflns	1629 [R_{int} = 0.0233]
R(*F*) [$I > 2\sigma(I)$], %[a]	2.76
R(*wF*^{2}) [$I > 2\sigma(I)$], %[a]	6.88

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R(wF^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

In agreement with the solid-state structure, the ^{1}H NMR spectrum of **2** in C_6D_6 showed the presence of two equivalent Pt-Me groups and two inequivalent pairs of TMEDA methyl groups. The ^{19}F NMR spectrum contained only a single septet resonance at δ −225.2 ppm with J_{FH} = 8.1 Hz and J_{PtF} = 562 Hz. The high-field chemical shift and large coupling constant to platinum are indicative of a Pt−F bond.

Essentially quantitative formation of **2** and perfluoro-2-butene in this reaction is strongly suggestive of a perfluorocarbanion intermediate $(CF_3)(C_2F_5)CF^-$, from which fluoride abstraction by platinum occurs to give the Pt−F complex and the alkene. Confirmation was provided by reaction of **1** with *sec*-C_4F_9I in the presence of 5 molar equiv of CH_3OD, in which the yield of **2** and perfluoro-2-butene was dramatically reduced and approximately 60% of the fluorine-containing product was $CF_3CFDCF_2CF_3$. This is only consistent with the formation of $(CF_3)(C_2F_5)CF^-$ followed by abstraction of D^+ from the trapping agent. Samples of $CF_3CFDCF_2CF_3$ (or $CF_3CFHCF_2CF_3$) for spectroscopic comparison were conveniently synthesized by photolysis of *sec*-C_4F_9I in *d*$_8$-toluene (or toluene) to give $CF_3CF^{\bullet}CF_2CF_3$ followed by radical abstraction of $D^{\bullet}$ (or $H^{\bullet}$). The tertiary CF fluorine resonances of $CF_3CFDCF_2CF_3$ and $CF_3CFHCF_2CF_3$ are clearly separated by 0.55 ppm and have clearly distinguishable coupling patterns ($^2J_{FH}$ is 43 Hz, while $^2J_{FD}$ is only 6.3 Hz).

Accordingly, we favor the reaction mechanism outlined in Scheme 2. Initial nucleophilic attack on iodine by the Pt(II) center affords the ion pair [Pt(TMEDA)-

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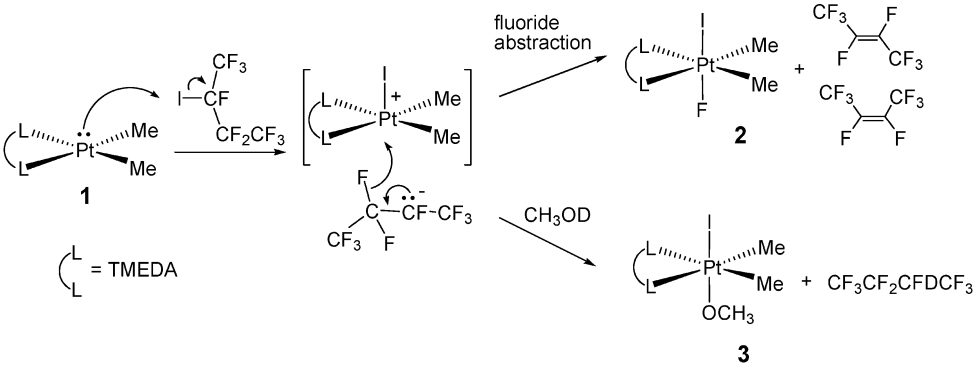
Scheme 2



$Me_2I]^+R_F^-$. Pt−C bond formation from this intermediate may be hindered by the bulkiness of the perfluoroalkyl anion, and fluoride abstraction by the platinum cation occurs to give **2** and a mixture of *trans*- and *cis*-perfluoro-2-butenes. When CH_3OD is present in the reaction mixture, reaction of R_F^- with D^+ now competes with fluoride abstraction to give $CF_3CFDCF_2CF_3$. The fate of the cationic platinum(IV) intermediate in reactions involving CH_3OD interception of the fluorocarbanion before fluoride abstraction can occur appears to be reaction with the methoxide side product to give **3** in about 60% yield as estimated by NMR integration. This compound could not be isolated pure from product **2**, but was identified by characteristic features in its ^1H NMR spectrum; the protons of the Pt−OMe group appear at 2.94 ppm with $^3J_{PtH} = 63$ Hz, which is very similar to previously reported data for the closely related analogue $Pt(TMEDA)(CH_3)_2(OCH_3)(OH)$.[35,36]

These results indicate that the formation of metal−fluoroalkyl bonds by oxidative addition reactions of fluoroalkyl iodides to low-valent metal centers may be limited in scope for particularly bulky fluoroalkyl groups, but that the potential exists for synthesis of other high-valent metal fluorides by fluoride abstraction reactions.

Experimental Section

General Procedures. Reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen that was deoxygenated over BASF catalyst and dried over Aquasorb, or in an MBraun drybox. Ethyl acetate (Pharmco) and CH_3OD (Aldrich) were used as received. *sec*-C_4F_9I (Lancaster) was purified over solid sodium thiosulfate to remove iodine. NMR spectra were recorded on a Varian Unity Plus 500 FT spectrometer. ^1H NMR spectra were referenced to the protio impurity in the solvent: C_6D_6 (7.15 ppm), CD_2Cl_2 (5.32 ppm), d_8-toluene (2.09 ppm, methyl group). ^{19}F NMR spectra were referenced to external $CFCl_3$ (0.00 ppm). Coupling constants are reported in hertz. Elemental analyses were performed by Schwartzkopf (Woodside, NY). $Pt(TMEDA)Me_2$ (**1**) was prepared according to the literature procedure.[37]

$Pt(TMEDA)Me_2FI$ (2). $Pt(TMEDA)Me_2$ (100 mg, 0.293 mmol) was dissolved in ethyl acetate (15 mL), and the solution was cooled to −78 °C. *sec*-C_4F_9I (115 mg, 55 μL, 0.33 mmol) was added dropwise. The color immediately changed from colorless to yellow. The mixture was warmed and stirred at room temperature for 10 min. The ^{19}F NMR spectrum of the reaction mixture showed the presence of only four species: complex **2**, *trans*- and *cis*-perfluoro-2-butene[33] in a ratio of 6:1, and a small amount of unreacted *sec*-C_4F_9I. The volatiles were removed under vacuum. Pure product was obtained by precipitation on reducing the volume of a toluene solution, yielding 131 mg (91%). Crystals of X-ray quality were obtained by recrystallization from CH_2Cl_2/hexane. Anal. Calcd for $C_8H_{22}FIN_2Pt$: C, 19.72; H, 4.55. Found: C, 19.79; H, 4.36. ^1H NMR (C_6D_6, 500 MHz, 21 °C): δ 1.83 (m, 2H, CH_2), 1.99 (m, 2H, CH_2), 2.07 (d, $^2J_{PtH} = 67$ Hz, $^3J_{HF} = 8.1$ Hz, 6H, $PtMe_2$), 2.10 (d, $^3J_{PtH} = 7.6$ Hz, $^4J_{HF} = 1.2$ Hz, 6H, NMe), 2.38 (s, $^3J_{PtH} = 16.4$ Hz, 6H, NMe); (CD_2Cl_2, 500 MHz, 21 °C) δ 1.64 (d, 6H, $PtMe_2$), 2.49 (d, $^3J_{PtH} = 7.6$ Hz, 6H, NMe), 2.71 (m, 2H, CH_2), 2.82 (m, 2H, CH_2), 2.85 (s, $^3J_{PtH} = 16.4$ Hz, 6H, NMe). ^{19}F NMR (C_6D_6, 470.3 MHz, 21 °C): δ −225.22 (septet, $^1J_{PtF} = 562$ Hz, $^3J_{HF} = 8.1$ Hz, 1F, PtF); (CD_2Cl_2, 470.3 MHz, 21 °C) δ −227.82 (septet, 1F, PtF).

Reaction of 1 with *sec*-C_4F_9I in the Presence of CH_3OD. $Pt(TMEDA)Me_2$ (50 mg, 0.146 mmol) was dissolved in ethyl acetate (15 mL), and CH_3OD (30 μL, 23 mg, 0.73 mmol, 5 equiv) was added. The resultant solution was cooled to −78 °C, and *sec*-C_4F_9I (52 mg, 25 μL, 0.15 mmol) was added dropwise as a solution in ethyl acetate (2 mL). The reaction mixture was allowed to warm to room temperature, and a ^{19}F NMR spectrum of the reaction mixture showed that $CF_3CF_2CFDCF_3$ made up approximately 60% of the fluorine-containing products, along with a 6:1 mixture of *trans*- and *cis*-perfluoro-2-butene, some unreacted *sec*-C_4F_9I, and complex **2**. The volatiles were removed, affording a solid mixture (68 mg) of **2** and **3** in a ratio of 60:40 along with about 10% of unidentified impurities (estimated by ^1H NMR integration), which could not be separated. Based on ^1H NMR integration data and the weight of the solid product mixture, approximate yields are **3** (37 mg, 51%) and **2** (24 mg, 34%). Compound **3** was characterized by ^1H NMR analysis. ^1H NMR (C_6D_6, 500 MHz, 21 °C): δ 1.81 (m, 2H, CH_2), 1.83 (d, $^2J_{PtH} = 74$ Hz, 6H, $PtMe_2$), 1.94 (m, 2H, CH_2), 1.98 (s, $^3J_{PtH} = 9$ Hz, 6H, NCH_3), 2.52 (s, $^3J_{PtH} = 14.5$ Hz, 6H, NCH_3), 2.94 (s, $^3J_{PtH} = 63$ Hz, 3H, OCH_3).

Similarly, use of CH_3OH as the trapping agent afforded $CF_3CF_2CFHCF_3$ instead of $CF_3CF_2CFDCF_3$ in the product mixture.

$CF_3CF_2CFDCF_3$ and $CF_3CF_2CFHCF_3$. These were prepared in situ by irradiation of d_8-toluene or toluene solutions of $CF_3CF_2CFICF_3$ with UV light in a Young's NMR tube. Without further separation the compounds were characterized by ^{19}F and ^1H NMR spectroscopy. **$CF_3CF_2CFHCF_3$** (more detailed NMR data than those previously reported[38] are included here): ^1H NMR (d_8-toluene, 500 MHz, 21 °C): δ 3.90 (ddqd, $^2J_{FH} = 43.0$ Hz, $^3J_{FH} = 17.5$ Hz, $^3J_{FH} = 5.8$ Hz, $^3J_{FH} = 3.1$ Hz, 1H). ^{19}F NMR (d_8-toluene, 470.3 MHz, 21 °C): δ −74.73 (ddddq, $^3J_{FF} = 11.5$ Hz, $^4J_{FF} = 11.0$ Hz, $^4J_{FF} = 9.6$ Hz, $^3J_{FH} =$

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5.8 Hz, $^5J_{FF}$ = 1.4 Hz, 3F, CF_3), −83.67 (dq, $^4J_{FF}$ = 10.3 Hz, $^5J_{FF}$ = 1.4 Hz, 3F, CF_3), −124.67 (dqdd, $^2J_{F(AB)}$ = 289 Hz, $^4J_{FF}$ = 11.0 Hz,$^3J_{FF}$ = 8.9 Hz, $^3J_{FH}$ = 3.1 Hz, 1F, CF_2), −130.83 (dddq, $^2J_{F(AB)}$ = 289 Hz, $^3J_{FH}$ = 17.5 Hz, $^3J_{FF}$ = 12.6 Hz, $^4J_{FF}$ = 9.6 Hz, 1F, CF_2), −214.33 (ddqqd, $^2J_{FH}$ = 43.0 Hz, $^3J_{FF}$ = 12.6 Hz, $^3J_{FF}$ = 11.5 Hz, $^4J_{FF}$ = 10.3 Hz,$^3J_{FF}$ = 8.9 Hz, 1F, CF). **$CF_3CF_2CFDCF_3$**: ^{19}F NMR (d_8-toluene, 470.3 MHz, 21 °C): δ −74.80 (ddddq, $^3J_{FF}$ = 9.0 Hz, $^4J_{FF}$ = 11.0 Hz, $^4J_{FF}$ = 9.6 Hz, $^3J_{FH}$ = 5.8 Hz, $^5J_{FF}$ = 1.4 Hz, 3F, CF_3), −83.69 (dq, $^4J_{FF}$ = 10.5 Hz, $^5J_{FF}$ = 1.4 Hz, 3F, CF_3), −124.75 (dqdd, $^2J_{F(AB)}$ = 289 Hz, $^4J_{FF}$ = 11.0 Hz,$^3J_{FF}$ = 8.7 Hz, $^3J_{FH}$ = 3.1 Hz, 1F, CF_2), −130.96 (dddq, $^2J_{F(AB)}$ = 289 Hz, $^3J_{FH}$ = 17.5 Hz, $^3J_{FF}$ = 12.5 Hz, $^4J_{FF}$ = 9.6 Hz, 1F, CF_2), −214.90 (dqdqd, $^3J_{FF}$ = 12.5 Hz,$^4J_{FF}$ = 10.5 Hz,$^3J_{FF}$ = 9.0 Hz, $^3J_{FF}$ = 8.7 Hz, $^2J_{FD}$ = 6.3 Hz, 1F, CF).

Crystallographic Structural Determination. Crystal, data collection, and refinement parameters are collected in Table 1. The systematic absences in the diffraction data are uniquely consistent for the reported space group. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. DIFABS absorption corrections were applied. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (5.10) program library.

Acknowledgment. R.P.H. is grateful to the National Science Foundation for generous financial support.

Supporting Information Available: Full crystallographic data for **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0504654