Notes

Synthesis and Molecular Structure of a Perfluoroalkyl Complex of Platinum Containing a PCP Pincer Ligand

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Summary: Treatment of (TMEDA)Pt(C_3F_7)Me (TMEDA = tetramethylethylenediamine) with 1,3-bis[(diphenylphosphino)methyl]benzene (PCPH) in mesitylene under reflux affords the first known pincer complex of a group 10 metal with a fluoroalkyl ligand.

Introduction

Since the first reported example in 1976,[1] there have been many reports of complexes involving anionic mer-tridentate "pincer" ligands.[2] Ligands of the general type $[2,6\text{-}(CH_2PR_2)_2C_6H_3]^-$ (PCP) are generally synthesized by ligand displacement reactions at elevated temperatures and require not only binding by the two phosphorus atoms but also the activation of a bond from a carbon atom of the core arene to H, O, or C.[3−16]

We have been interested recently in developing synthetic routes to transition metal fluoroalkyl complexes, in view of renewed interest in their structures and chemistry.[17−24] To the best of our knowledge there are only two examples of transition metal pincer complexes that contain a metal−fluoroalkyl linkage, both of which involve rhodium.[5,9] Complex **1a** was made by heating the ligand $2,6\text{-}(CH_2P^tBu_2)_2C_6H_3CF_3$ in the presence of $[RhCl(L_2)]_2$, a reaction in which a remarkable insertion of rhodium into the strong aryl−CF_3 bond was observed. Alternatively, the iodide analogue **1b** was synthesized by an oxidative addition reaction of $Rh\{2,6\text{-}(CH_2P^tBu_2)_2C_6H_3\}(\eta^1\text{-}N_2)$ with CF_3I.

Results and Discussion

We have recently reported the synthesis of square planar palladium(II)[19] and platinum(II)[25] complexes **2** by oxidative addition of fluoroalkyl iodides to the dimethyl precursors **3**, followed by reductive elimination of CH_3I. The TMEDA ligand can be displaced by 1,2-bis(diphenylphosphino)ethane to give a diphosphine analogue **4**.[25] In an attempt to approach the synthesis of bis[(diphenylphosphino)methyl]phenyl (PCP) pincer[26−29] analogues by a similar route, we prepared the

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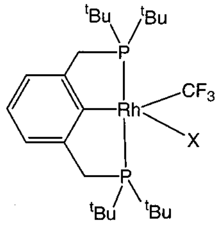
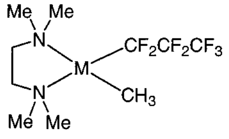


1a X = Cl
1b X = I



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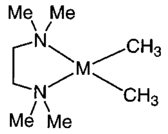
2b M = Pt



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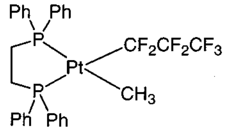

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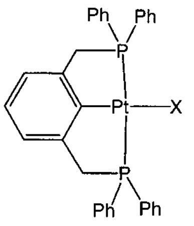
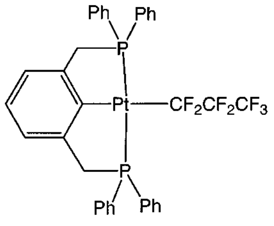


5a X = CH_3
5b X = Cl
5c X = CO_2H



6

previously reported methyl complex **5a**.[30] Attempts at preparation of Pt(IV) or Pt(II) fluoroalkyl complexes by treatment of **5a** with n-C_3F_7I afforded a mixture of products, the dominant component of which appeared to be (PCP)PtI, which could be converted back to **5a** by treatment with MeLi. As we have remarked previously,[19,25] the oxidative addition reactions of fluoroalkyl iodides with Pd(II) and Pt(II) precursors are often capricious in avoiding reproducibility from one system to another.

We next turned to a ligand displacement route, which proved to be successful. Treatment of the previously reported complex **2b**[25] with the pincer ligand precursor in refluxing mesitylene afforded the Pt(II) complex **6**. The probable mechanistic sequence of this reaction is shown in Scheme 1 and involves initial displacement of the TMEDA ligand by the relatively soft chelating diphosphine PCPH, followed by metalation of the aryl C−H bond to form the Pt(IV) intermediate **7**, which undergoes facile reductive elimination of methane to form the Pt(II) complex **6**. The solution structure of **6** is defined spectroscopically; the ^{19}F NMR spectrum exhibits the expected three resonances for the perfluoropropyl group, with the α-CF_2 resonance at δ −84.4 ppm showing strong coupling to ^{195}Pt ($^2J_{FPt} = 248$ Hz), and the $^{31}P\{^1H\}$ NMR spectrum a single resonance at δ 40.0 ppm, which appears as a triplet of triplets with coupling to the α- and β-CF_2 groups ($^3J_{PF} = 21$ Hz, $^4J_{PF} = 6$ Hz), with additional ^{195}Pt satellites ($^1J_{PPt} = 3041$ Hz).

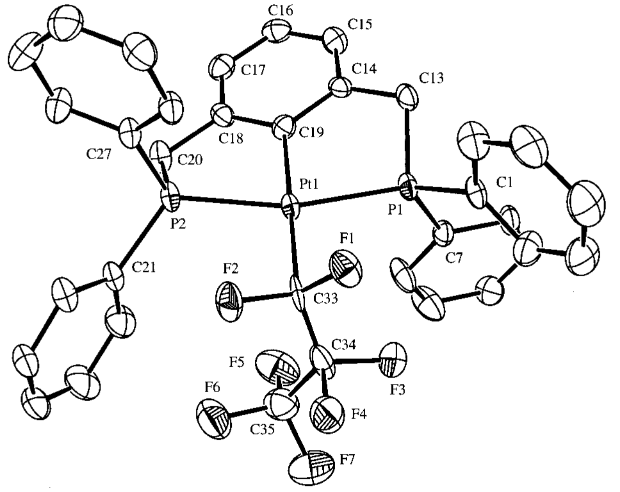
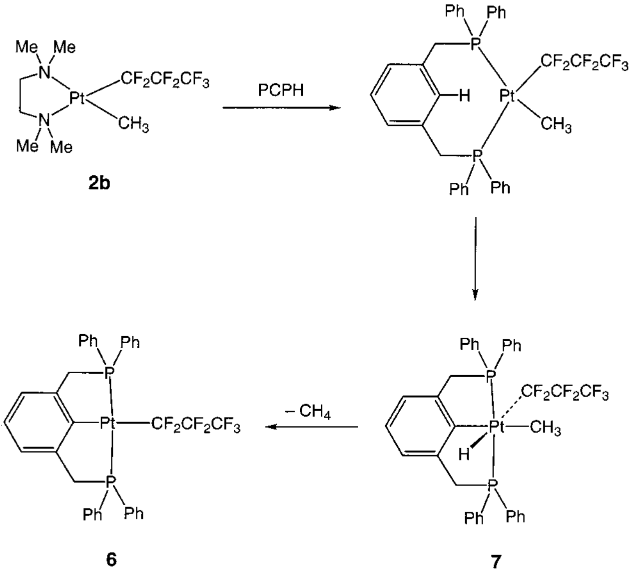


Figure 1. ORTEP diagram of the non-hydrogen atoms of **6**, showing atom-labeling scheme. Thermal ellipsoids are shown at the 30% level.

Scheme 1



X-ray quality crystals of **6** were grown from CH_2Cl_2/heptane. An ORTEP diagram of the structure is shown in Figure 1, with a different view of the coordination sphere around platinum in Figure 2. Details of the crystallographic determination are provided in Table 1, and representative bond lengths and angles appear in Table 2. The pincer ligand adopts an overall arrangement similar to that reported for the corresponding chloride complex **5b**,[30] with the arene portion of the pincer ligand canted with respect to the coordination plane by approximately 15°, as shown in Figure 2. The distance from Pt to the arene carbon, Pt(1)−C(19), is 2.072(7) Å, significantly longer than the 1.998(8) Å observed for **5b**,[30] and indistinguishable from the 2.066(3) Å reported for **5c**,[27] illustrating the expected order of structural *trans*-influences; perfluoropropyl $\approx$ CO_2H > Cl.[31] The P(1)−Pt(1)−P(2) angle of 162.89(8)° is identical to that found in **5b** [162.0(1)°],[30] and only very slightly larger than the 161.87(4)° found in **5c**,[27] illustrating that a significant change in the Pt-aryl

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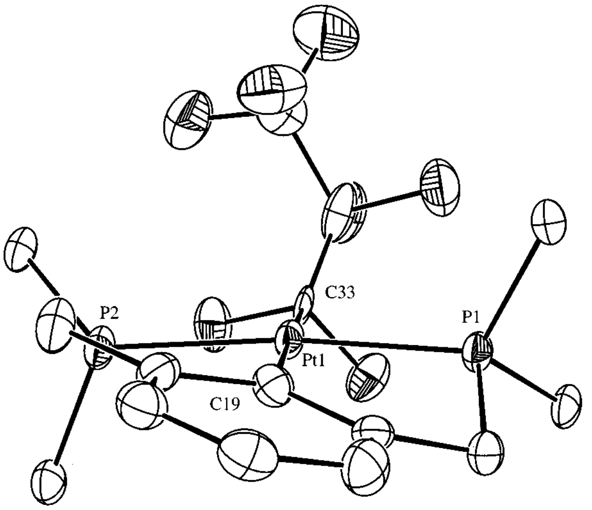


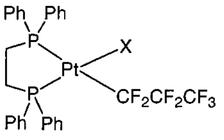
Figure 2. ORTEP diagram of the coordination sphere of **6**, with thermal ellipsoids shown at the 30% level. Only the ipso-carbon atoms of phenyl rings bound to phosphorus are shown for clarity.

Table 1. Crystal Data and Summary of X-ray Data Collection for 6

formula	$C_{35}H_{27}F_7P_2Pt$
fw	837.60
space group	$P2_1/c$
a, Å	10.192(3)
b, Å	18.106(8)
c, Å	17.018(3)
α, deg	90
β, deg	91.008(17)
γ, deg	90
V, Å^3	3140.0(17)
Z	4
D(calcd), g/cm^3	1.772
abs coeff, mm^{-1}	4.637
temp, K	293(2)
diffractometer	Siemens P4
radiation	Mo Kα 0.71073 Å
$R(F)$, %^{a}	3.95
$R(wF^2)$, %^{a}	10.03

[a] Quantity minimized = $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$.

distance does not result in a significant change in the diphosphine bite angle at the metal. The distance from Pt to the fluorinated carbon, Pt(1)−C(33), of 2.186(8) Å is longer than that observed in the square planar complexes **8a** [2.067(7) Å] and **8b** [2.087(6) Å].[25] It is difficult to distinguish whether this longer distance is a result of the stronger *trans*-influence of the aryl ligand in **6** compared to the *trans*-phosphorus ligand in complexes **8** or the combined steric effects of two *cis*-PPh_2 groups in **6**. The perfluoropropyl ligand itself exhibits the same pattern of acute F−C−F angles and obtuse Pt−C−C and C−C−C angles previously observed in a variety of transition metal complexes containing this ligand.[19,20,25,32]



8a X = CH_3
8b X = CF_3SO_3

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 6

Bond Lengths (Å)		Bond Angles (deg)	
Pt(1)−C(19)	2.072(7)	C(19)−Pt(1)−C(33)	177.1(3)
Pt(1)−C(33)	2.186(8)	C(19)−Pt(1)−P(2)	81.67(19)
Pt(1)−P(2)	2.2770(18)	C(33)−Pt(1)−P(2)	97.96(16)
Pt(1)−P(1)	2.2818(18)	C(19)−Pt(1)−P(1)	81.35(19)
C(33)−C(34)	1.376(12)	C(33)−Pt(1)−P(1)	98.89(16)
C(34)−C(35)	1.547(13)	P(2)−Pt(1)−P(1)	162.89(8)
F(1)−C(33)	1.374(8)	C(34)−C(33)−Pt(1)	120.2(5)
F(2)−C(33)	1.370(7)	F(2)−C(33)−F(1)	104.2(6)
F(3)−C(34)	1.412(9)	F(4)−C(34)−F(3)	104.8(6)
F(4)−C(34)	1.388(9)	C(33)−C(34)−C(35)	120.7(7)
F(5)−C(35)	1.274(11)	F(5)−C(35)−F(7)	110.5(10)
F(6)−C(35)	1.351(11)	F(5)−C(35)−F(6)	108.9(9)
F(7)−C(35)	1.340(11)	F(7)−C(35)−F(6)	106.3(8)

Attempts to further functionalize complex **6** by treatment with n-C_3F_7I or MeI failed to give oxidative addition products, and the starting complex was recovered unchanged.

Experimental Section

General Considerations. Unless otherwise noted, all reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen, which had been deoxygenated over BASF catalyst and dried using Aquasorb, or using drybox techniques. THF, diethyl ether, hexanes, and CH_2Cl_2 were dried and degassed over alumina columns under N_2.[33] ^1H NMR (300 MHz) and ^{19}F (282 MHz) were recorded on a Varian UNITY plus 300 System in the solvent indicated. ^1H NMR chemical shifts were referenced to TMS using the protio impurity in the solvent peak, and ^{19}F chemical shifts were referenced to $CFCl_3$. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory (Woodside, NY). Perfluoropropyl iodide was purchased from Aldrich, treated with $Na_2S_2O_3$ to remove residual I_2, and vacuum distilled before use. (TMEDA)Pt(CH_3)(C_3F_7) was prepared as previously reported.[25]

Preparation of {1,3-($CH_2PPh_2)_2C_6H_4$}. Bis[(diphenylphosphino)methyl]benzene is commonly prepared by treatment of 1,3-bis(bromomethyl)benzene with Ph_2PNa in liquid ammonia.[26−29] However, we found it more convenient to prepare by the following method.

Dropwise addition of 0.5 equiv of 1,3-bis(chloromethyl)benzene in THF to a solution of PPh_2Li in THF/hexane (prepared by dropwise addition of PPh_2H in THF to a solution of BuLi in hexanes at −40 °C) afforded a pale yellow solution, which was stirred overnight. The volatiles were removed, and the oily white solid was washed with hot EtOH. The residue was purified by extraction into Et_2O, filtration, and removal of solvent from the filtrate.

Preparation of {2,6-($CH_2PPh_2)_2C_6H_3$}Pt(Me). To a solution of (PCP)PtCl (100 mg, 0.148 mmol) in THF (15 mL) at −40 °C was added a solution of MeLi (0.15 mL, 1.4 M, 0.21 mmol) in Et_2O. The mixture was allowed to warm to room temperature and then stirred for 30 min. Addition of EtOH and removal of the THF in vacuo gave a yellow precipitate, which was collected on a glass frit and washed with EtOH and hexanes.

^1H NMR ($CDCl_3$, 300 MHz, 21 °C): δ 0.51 (t, $^3J_{HP} = 5.0$ Hz, $^2J_{HPt} = 54.6$ Hz, 3H, PtMe), 4.00−4.20 (m, 4H, CH_2), 7.00−7.21 (m, 3H, C_6H_3), 7.37−7.41 (m, 12H, Ph), 7.68−7.75 (m, 8H, Ph). ^{31}P NMR ($CDCl_3$, 121.4 MHz, 21 °C): δ 37.1 (s, $^1J_{PPt} =$ 3035 Hz).

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Preparation of {2,6-(CH_2PPh_2)$_2$$C_6H_3$}Pt($C_3F_7$). A mixture of 2,6-($CH_2PPh_2$)$_2$$C_6H_4$ (0.179 g, 0.401 mmol) and (TMEDA)-Pt(C_3F_7)Me (0.100 g, 0.202 mmol) was stirred in mesitylene under reflux for 16 h to give a pale yellow solution. Removal of solvent in vacuo gave a yellow-white tar, which was treated with a 3:1 mixture of hexanes and EtOH to afford a white precipitate, which was collected on a glass frit and washed with hexanes. Yield: 0.078 g, 46%. Anal. Calcd for $C_{31}H_{23}F_7P_2$-Pt: C, 50.19; H, 3.25. Found: C, 50.59; H, 3.32.

^{1}H NMR ($CDCl_3$, 300 MHz, 21 °C): δ 4.00−4.09 (m, 4H, CH_2), 6.99−7.11 (m, 3H, C_6H_3), 7.41−7.43 (m, 12H, Ph), 7.72−7.75 (m, 8H, Ph). ^{19}F NMR ($CDCl_3$, 282.3 MHz, 21 °C): δ −117.4 (m, β-CF_2, $^3J_{FPt} = 53$ Hz), −84.4 (brs, α-CF_2, $^2J_{FPt} = 248$ Hz), −79.5 (t, $^4J_{FF} = 10.5$ Hz, CF_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.4 MHz, 21 °C): δ 40.0 (tt, $^3J_{PF} = 20.5$ Hz, $^4J_{PF} = 5.8$ Hz, $^1J_{PPt} = 3041$ Hz).

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 groups. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. A DIFABS absorption correction was 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.

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Supporting Information Available: Atomic fractional coordinates, bond distances and angles, and anisotropic thermal parameters for complex **6** are available free of charge via the Internet at http://pubs.acs.org.

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