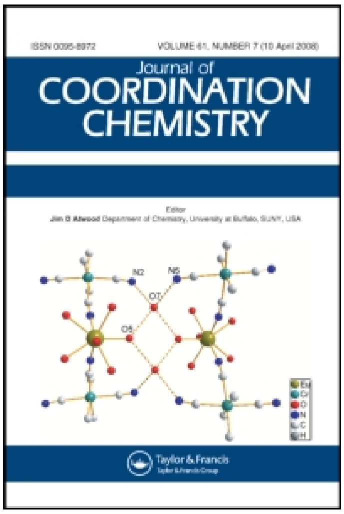

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Application of an electroneutral phosphine ligand to organo-platinum chemistry: Pentafluoroethyldiphenylphosphine (pfepp)

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Application of an electroneutral phosphine ligand to organo-platinum chemistry: Pentafluoroethyldiphenylphosphine (pfepp)

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The synthesis, characterization and molecular structures of two platinum complexes bearing the novel phosphine pentafluoroethyldiphenylphosphine (pfepp; **1**) is reported. pfepp is a sterically bulky, electronically neutral phosphine ligand. Treatment of (cod)$PtMe_2$ with two equivalents of pfepp yields *cis*-$(pfepp)_2PtMe_2$ **2**. Addition of one equivalent of acetyl chloride to a methanol/dichloromethane solution of **2** results in the formation of *trans*-$(pfepp)_2PtMeCl$ **3**. Complexes **2** and **3** were characterized by IR, multinuclear NMR and elemental analysis. The X-ray crystal structures of **2** and **3** are also reported and confirm the geometry assignments around the metal center.

Keywords: Platinum; Phosphine; Fluoroalkylphosphine; X-ray; Crystal structure; Electroneutral

1. Introduction

Tertiary phosphines, PR_3, are among the most utilized group of ligands in transition metal chemistry because of the ease with which the steric and electronic properties of phosphine ligands are controlled [1]. An a priori assessment of the stereoelectronic profile of known phosphine ligands indicated several large voids that include large, electron-poor phosphines and all phosphines that bridge the electronic gap between electron-rich and electron-poor phosphines [2]. With this consideration in mind, research in our group has focused on the development of a new class of phosphines of the type R_2PR_f (R = hydrocarbon substituent; $R_f = C_2F_3$ or C_2F_5). The combination of electron-donating groups and an electron-poor group (R_f) yields electroneutral phosphine ligands (neither electron rich nor electron poor in a Lewis base sense). We have recently reported the synthesis and characterization of a novel monodentate

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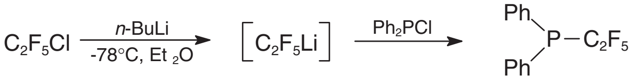
phosphine ligand bearing a perfluoroethyl pendant group [3], and its coordination chemistry with platinum.



(1)

Pentafluoroethyldiphenylphosphine ($Ph_2P–C_2F_5$ (**1**), abbreviated pfepp) [3] is conveniently prepared in high yield by the reaction of $Ph_2P–Cl$ with C_2F_5Li (equation 1). Treatment of (cod)$PtCl_2$ with pfepp in refluxing toluene readily afforded the *trans* dichloro product *trans*-(pfepp)$_2$$PtCl_2$. This reactivity was in contrast to the behavior of more electrophilic phosphines, such as $(C_2F_5)_2PPh$, which required a more labile starting material to produce the analogous platinum complex. Efforts to alkylate *trans*-(pfepp)$_2$$PtCl_2$ with Grignard reagents resulted in a mixture of intractable products. To extend our studies into the platinum coordination chemistry of the pfepp ligand, we report the synthesis, spectroscopic characterization and molecular structures of two new (pfepp)$_2$Pt(II) alkyl complexes.

2. Experimental

2.1. *General considerations*

All manipulations were conducted under an inert atmosphere using drybox (MBraun LabMaster 130), high-vacuum and/or Schlenck techniques. Aqueous and oxygen-free solvents were prepared from sodium/benzophenone ketal and vacuum distilled before use. Other reagents were obtained from Aldrich (Milwaukee, WI, USA) and used without further purification. NMR spectra were measured using a JEOL 270 MHz spectrometer operating at 270.17 and 109.37 MHz for the ^1H and ^{31}P nuclei, respectively. ^{31}P NMR spectra were referenced to phosphoric acid with downfield shifts taken to be positive. ^{19}F spectra were referenced to $CFCl_3$ with upfield shifts reported as negative. Elemental analyses were obtained from Desert Analytics. The syntheses of $Ph_2P(C_2F_5)$ [3], (cod)$PtCl_2$ [10] and (cod)Pt(Me)$_2$ [11] are reported elsewhere.

2.1.1. *cis*-(pfepp)$_2$Pt(Me)$_2$ (2). A solution of 0.506 g (1.50 mmol) of (cod)Pt(Me)$_2$ and 0.936 g (3.10 mmol) of pfepp in 20 mL of toluene was stirred at room temperature for 2 h. The toluene was removed under vacuum leaving a white powder. The reaction flask was transferred to a filtration assembly and the residue was slurried in 30 mL of petroleum ether and then filtered. Yield: 74%. Recrystallization was performed by dissolving 50 mg of crude product in 50 mL of diethyl ether, decanting this solution from the undissolved crude product for slow evaporation for 28 days at −23°C. Anal. Calcd. for *cis*-(pfepp)$_2$Pt(Me)$_2$, $C_{30}H_{26}F_{10}P_2Pt$(%): C, 43.22; H, 3.15. Found: C, 42.85; H, 3.06. ^1H NMR (δ): 7.70 (m), 6.85 (m), 1.46 (t, $^2J_{H–Pt} = 73$ Hz, $^3J_{H–P} = 8$ Hz, Pt–CH_3). ^{19}F NMR (δ): −76.2 (s, $^4J_{Pt–F} = 23$ Hz, P–CF_2–CF_3), −104.2 (d, $^2J_{P–F} = 47$ Hz, $^3J_{Pt–F} = 35$ Hz, Pt–P–CF_2). $^{31}P\{^1H\}$ NMR (δ): 43.8 (t, $^1J_{P–Pt} = 1799$ Hz, $^2J_{P–F} = 47$ Hz).

2.1.2. *trans*-(pfepp)$_2$Pt(Me)Cl (3). Acetyl chloride (43 µL, 0.60 mmol) was added dropwise to a solution of 0.507 g (0.61 mmol) of **2** in 30 mL of dichloromethane and

20 mL methanol in a swivel frit apparatus. This solution was allowed to stir for 1 h after the addition was complete. The methanol and dichloromethane were removed under vacuum and the residual white powder was slurried in 50 mL of petroleum ether and filtered. The solvent was removed under vacuum, and **3** was isolated as a white powder in moderate (56%) yield. Recrystallization was performed by dissolving 50 mg of crude product in 25 mL of diethyl ether, adding 25 mL of petroleum ether and evaporating the solvent slowly for 24 h at room temperature. Anal. Calcd. for **4**, $C_{29}H_{23}ClF_{10}P_2Pt$(%): C, 40.78; H, 2.72. Found: C, 41.23; H, 2.95. ^{1}H NMR (δ): 7.88 (m), 7.50 (m), 0.30 (t, $^{2}J_{H\text{–}Pt} = 76$ Hz, $^{3}J_{H\text{–}P} = 7$ Hz, Pt–CH_3). ^{19}F NMR (C_6D_6) δ −76.1 (s, CF_3); −103.4 (m, CF_2). $^{31}P\{^{1}H\}$ NMR (δ): 40.1 (m, $^{1}J_{P\text{–}Pt} = 3483$ Hz).

2.2. *X-ray diffraction studies*

The crystallographic data for compounds **2** and **3** are summarized in table 1. Crystals of **2** (CCDC No. 247228) were isolated from a low-temperature (−23°C), very slow evaporation (28 days) of a 1:1 mixture of diethyl ether and petroleum ether. Crystals of **3** (CCDC No. 247229) were obtained from an overnight evaporation of a 1:1 diethyl ether and petroleum ether mixture. Single-crystal X-ray data for **2** and **3** were collected on a Bruker P4 diffractometer equipped with a molybdenum tube ($\lambda = 0.71073$ Å) and a graphite monochromator. Absorption corrections based on face indexing integration were applied; the structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 using structure solution programs from the Bruker/SHELX97 system. All nonhydrogen atoms were refined anisotropically, while

Table 1. Crystal data and structure refinement details for *cis*-(pfepp)$_2$PtMe$_2$ (**2**) and *trans*-(pfepp)$_2$Pt(Me)Cl (**3**).

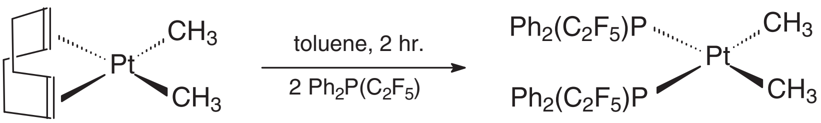
	cis-(pfepp)$_2$PtMe$_2$ **2**	*trans*-(pfepp)$_2$Pt(Me)Cl **3**
Empirical formula	$C_{30}H_{26}F_{10}P_2Pt$	$C_{29}H_{23}ClF_{10}P_2Pt$
Formula weight	833.54	853.98
Crystal system	Monoclinic	triclinic
Space group	$P2(1)/n$	$P\bar{1}$
Unit cell dimensions (Å)		
a (°)	10.0896(6)	8.3872(4)
b (°)	19.4340(9)	9.7065(5)
c (°)	15.7679(8)	10.9078(5)
α (°)		98.823(4)
β (°)	101.865(4)	106.630(4)
γ (°)		113.411(4)
Volume (Å^3)	3025.7(3)	743.93(6)
Z	4	1
Density (calculated) (Mg/m^3)	1.830	1.906
Absorption coefficient (mm^{-1})	4.825	4.995
F(000)	1616	412
Crystal size (mm^3)	0.59 × 0.44 × 0.25	0.48 × 0.43 × 0.25
θ range for data collection (°)	2.10 to 25.01	2.05 to 24.98
Reflections collected	6635	3149
Independent reflections	6635 [R(int) = 0.0337]	2568 [R(int) = 0.0182]
Max. and min. transmission	0.189 and 0.362	0.093 and 0.287
Temperature (K)	293(2)	293(2)
Data/restraints/parameters	5285/0/391	2568/0/228
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0641$, $wR2 = 0.0875$	$R1 = 0.0222$, $wR2 = 0.0599$
R indices (all data)	$R1 = 0.0325$, $wR2 = 0.0753$	$R1 = 0.0223$, $wR2 = 0.0599$

hydrogen atoms were placed in calculated positions and refined with fixed isotropic thermal parameters.

3. Results and discussion

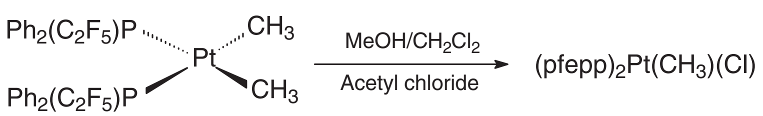
3.1. *Synthesis and spectroscopic characterization*

Alkylation of (pfepp)$_2$PtCl$_2$ with traditional alkylating reagents (Grignards, RLi) resulted in a mixture of products; therefore, we chose to examine the substitution chemistry of (cod)Pt(Me)$_2$ with the pfepp ligand as a potential method of preparing dialkyl complexes. Addition of two equivalents of pfepp to a toluene solution of (cod)Pt(Me)$_2$ resulted in the formation of (pfepp)$_2$Pt(Me)$_2$ (**2**) as a white powder in moderate yield (74%) (equation 2). (pfepp)$_2$Pt(Me)$_2$ was fully characterized by multinuclear NMR and elemental analysis. Proton NMR contained the typical aromatic resonances for the phenyl groups of the pfepp ligand at 7.70 and 6.85 ppm and a triplet at 1.46 ppm ($^3J_{\mathrm{PH}} = 8$ Hz) with characteristic satellites due to ^{195}Pt coupling ($^2J_{\mathrm{PtH}} = 73$ Hz). Phosphorus NMR contained only a single resonance, with coupling to both ^{19}F($^2J_{\mathrm{PF}} = 47$ Hz) and ^{195}P($^1J_{\mathrm{PtP}} = 1799$ Hz) observed. The low ($^1J_{\mathrm{PtP}} < 2000$ Hz) phosphorus–platinum coupling is diagnostic for coordination of a phosphine ligand *trans* to an alkyl ligand.



(2)

In the presence of excess HX, complexes with M–R bonds tend to completely substitute all M–R bonds through protonation of the R group, liberating R–H and generating M–X bonds. HCl may be carefully generated *in situ* when acetyl chloride is added to a methanol/CH$_2$Cl$_2$ solution. When one equivalent of acetyl chloride was added to a solution of **2** and methanol/CH$_2$Cl$_2$, (pfepp)$_2$Pt(Me)Cl complex **3** was cleanly afforded (equation 3). Proton NMR displayed aromatic resonances at 7.88 and 7.50 and a Pt–CH$_3$ resonance at 0.30 ppm (triplet; $^2J_{\mathrm{H\text{–}Pt}} = 76$ Hz, $^3J_{\mathrm{H\text{–}P}} = 7$ Hz). Phosphorus NMR indicated the presence of only one resonance at 40.1 ppm, and the $^1J_{\mathrm{P\text{–}Pt}}$ coupling constant of 3483 Hz clearly indicated that the phosphorus atoms were no longer *trans* to the methyl group. We therefore concluded the geometry of **3** to be *trans*.



(3)

3.2. *Molecular structure determination*

Single-crystal X-ray diffraction unambiguously determined the molecular structure of **2** and **3**. Crystals of **2** were difficult to obtain, but were finally grown from a very slow

(28 days), low-temperature (−23°C) evaporation of a 1:1 ether/petroleum ether solution. Single crystals of **3** were also grown from the evaporation of a 1:1 solution of ether/petroleum ether, although crystallization took place at room temperature over the course of 24 h.

The ORTEP representation of **2** is shown in figure 1 and confirms the *cis* geometry about the metal center. Crystal data collection, solution and refinement data for **2** and **3** are given in table 1 and relevant bond lengths and angles are summarized in tables 2 and 3. The Pt–P(1) and Pt–P(2) bond distances of 2.2987(14) and 2.3017(16) Å are essentially identical, and fall within the range of Pt–P bond distances in analogous *cis*–$(L)_2PtMe_2$ complexes [2.249(1) Å for L = $P(pyrl)_3$ and 2.344(1) for L = PCy_3] [6]. The Pt–C(29) and Pt–C(30) bond distances of 2.080(7) and 2.090(7) Å, respectively, are consistent with other *cis*-$PtL_2(CH_3)_2$ complexes (L = phosphine) [6–8].

Stereochemical preferences and metrical trends for *cis*–$(R_3P)_2Pt(X)(Y)$ complexes can be rationalized in terms of their steric and electronic parameters (θ and χ

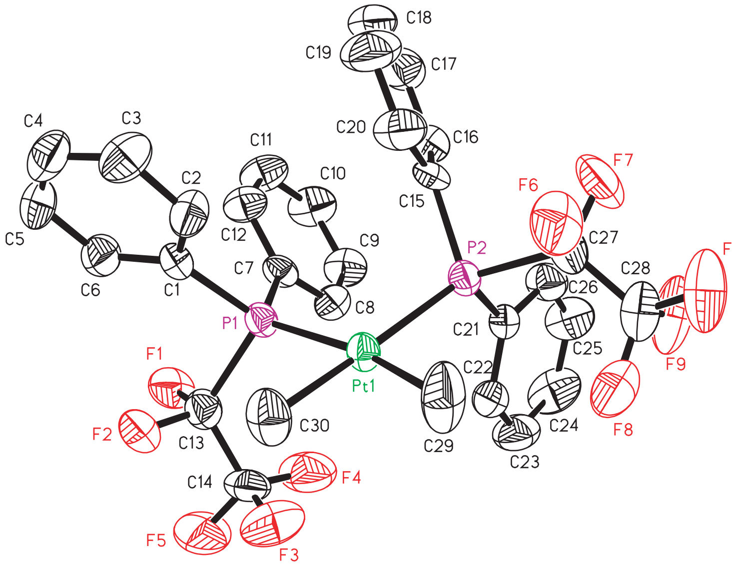


Figure 1. ORTEP representation of $(pfepp)_2PtMe_2$. Thermal ellipsoids are shown at the 50% probability level and hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for *cis*-$(pfepp)_2PtMe_2$ **2**.

Pt–C(29)	2.080(7)
Pt–C(30)	2.090(7)
Pt–P(1)	2.2987(14)
Pt–P(2)	2.3017(16)
C(29)–Pt–C(30)	80.8(3)
C(29)–Pt–P(1)	167.7(2)
C(29)–Pt–P(2)	94.9(2)
C(30)–Pt–P(1)	86.90(19)
C(30)–Pt–P(2)	173.8(6)
P(1)–Pt–P(2)	97.22(6)

Table 3. Selected bond lengths (Å) and angles (°) for *trans*-(pfepp)$_2$Pt(Me)Cl **3**.

Pt–P(1)	2.2828(9)
Pt–Cl	2.422(3)
Pt–C(15)	2.243(6)
P(1)–Pt–Cl(1)	97.24(7)
P(2)–Pt–Cl(1)	82.77(7)
C(15)–Pt–Cl(1)	171.2(3)
C(15)–Pt–P(1)	84.0(3)
C(15)–Pt–P(2)	96.0(3)
P(1)–Pt–P(2)	180.0

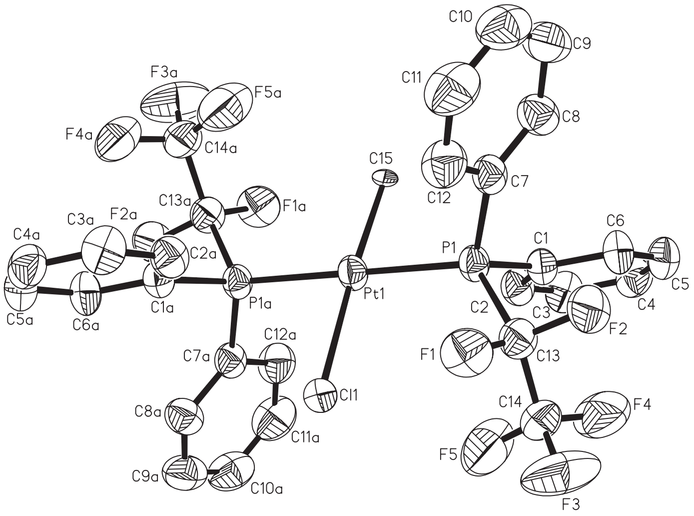


Figure 2. ORTEP representation of (pfepp)$_2$Pt(Me)Cl. Thermal ellipsoids are shown at the 30% probability level and hydrogen atoms are omitted for clarity.

respectively), introduced by Tolman [1]. Metal–phosphorus bond distances typically elongate with increasing θ and decrease with increasing χ. Our metrical data for **2** indicate that the bond distances in complexes of this type are fairly insensitive to the electronic nature of the phosphine ligand. However, with the introduction of the C_2F_5 group, the χ of the pfepp ligand increases, which suggests that the Pt–P bond length should be reduced. However, previous work in our laboratory has examined the effect of altering χ without significantly disturbing θ, and indicated that the nature of the Pt–P bond was similarly insensitive to the electronic nature of the phosphine ligand [3].

The P–Pt–P bond angle in **2** is 97.22(6)°, and is again consistent with analogous platinum dimethyl complexes. The departure from the expected square planar angle of 90° is rationalized in terms of the steric repulsion between the *cis*-phosphorus groups. Similarly, the C–Pt–C bond angle of 80.8(3)° is in accord with the notion that as the P–Pt–P bond angle (and thus θ) increases, the angle between the platinum and the methyls is compressed.

The ORTEP representation of **3** is shown in figure 2. The metrical data from **3** are also consistent with other *trans*-(L)$_2$Pt(Me)(Cl) complexes with one notable difference. The Pt–P and Pt–Cl distances of 2.2828(9) and 2.422(3) Å, respectively, are similar to those values reported for the triphenylphosphine analog *trans*-$(PPh_3)_2Pt(Me)Cl$ [9,10]. However, the Pt–C(15) bond distance of 2.243(6) Å is unusually long when compared to the triphenylphosphine analog (2.02(2) Å [10] and 2.08(1) Å [9]). This lengthening has also been noticed in other *trans*-$(L)_2Pt(Me)Cl$ complexes when the phosphine is extremely bulky [$L = P(Cy)_3$]. The Pt–C(15) bond length of 2.179(13) Å for *trans*–$[P(Cy)_3]_2Pt(Me)Cl$ is also significantly longer [11] than the Pt–methyl bond of the triphenylphosphine complex, although it is still much shorter than the Pt–methyl bond for **3**. This unusual bond length has been explained as an artifact of the disorder between the *trans* chloro and methyl ligands [11]. It should be noted that other metrical data in *trans*-$[P(Cy)_3]_2Pt(Me)Cl$ are essentially identical to **3**.

4. Summary

The synthesis, characterization and X-ray structures of two platinum alkyl complexes bearing the electroneutral phosphine ligand pfepp are reported. The Pt–C bond of 2.243 Å in *trans*-$(pfepp)_2Pt(Me)Cl$ is unusually long with respect to the Pt–C bond in other *trans*-$(L)_2Pt(Me)Cl$ species.

References

[1] C.A. Tolman, *Chem. Rev.* **77**, 313 (1977).
[2] K.D. Cooney, T.R. Cundari, N.W. Hoffman, K.A. Pittard, M.D. Temple, Y. Zhao, *J. Am. Chem. Soc.* **125**, 4318 (2003).
[3] J.D. Palcic, P.N. Kapoor, D.M. Roddick, R.G. Peters, *J. Chem. Soc., Dalton Trans.* 1644 (2004).
[4] J.X. McDermott, J.F. White, G.M. Whitesides, *J. Am. Chem. Soc.* **98**, 6521 (1976).
[5] H.C. Clark, L.E. Manzer, *J. Organomet. Chem.* **59**, 411 (1973).
[6] C.M. Haar, S.P. Nolan, W.J. Marshall, K.G. Moloy, A. Prock, W.P. Giering, *Organometallics* **18**, 474 (1999).
[7] J.M. Wisner, T.J. Bartczak, J.A. Ibers, *Organometallics* **5**, 2044 (1986).
[8] J.L. Butikofer, J.M. Hoerter, R.G. Peters, D.M. Roddick, *Organometallics* **23**, 400 (2004).
[9] R. Bardi, A.M. Piazzesi, L. Sindellari, *Inorg. Chim. Acta* **47**, 225 (1981).
[10] S. Otto, A. Roodt, J.G. Leipoldt, *S. Afr. J. Chem.* **48**, 114 (1995).
[11] S. Otto, *Acta Cryst. C* **57**, 793 (2001).