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Synthesis and Platinum Coordination Chemistry of the Perfluoroalkyl Acceptor Pincer Ligand, 1,3-$(CH_2P(CF_3)_2)_2C_6H_4$

Jeramie J. Adams, Ade Lau, Navamoney Arulsamy, and Dean M. Roddick*

Department of Chemistry, Box 3838, University of Wyoming, Laramie, Wyoming 82071

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The synthesis of perfluoroalkyl-substituted "pincer"-type PCP ligands, 1,3-$C_6H_4(CH_2P(R_f)_2)_2$ (R_f = CF_3, C_2F_5), and platinum coordination studies (R_f = CF_3) are reported. 1,3-$C_6H_4(CH_2P(CF_3)_2)_2$ (^{CF_3}PCPH) reacts at ambient temperatures with (cod)Pt(Me)Cl (cod = 1,5-cyclooctadiene) and (cod)$PtMe_2$ to afford unmetalated PCPH-bridged products [(^{CF_3}PCPH)Pt(Me)Cl]$_x$ and *cis*-[(^{CF_3}PCPH)$PtMe_2$]$_2$, respectively. *cis*-[(^{CF_3}PCPH)$PtMe_2$]$_2$ is soluble and has been spectroscopically and crystallographically characterized. Thermolysis of these compounds results in the loss of methane and the formation of metalated complexes (^{CF_3}PCP)PtCl and (^{CF_3}PCP)PtMe. Treatment of (^{CF_3}PCP)PtCl with MeMgBr provides an alternative route to (^{CF_3}PCP)PtMe. The carbonyl cation (^{CF_3}PCP)Pt(CO)$^+SbF_6^-$ (ν(CO) = 2143 cm^{-1}) was readily prepared by chloride abstraction with $AgSbF_6$ under 1 atm CO. ν(CO) data indicates that ^{R_f}PCP ligands are electronically analogous to trans acceptor phosphine complexes such as *trans*-$((C_2F_5)_2PMe)_2$Pt(Me)(CO)$^+$ (ν(CO) = 2149 cm^{-1}).

Introduction

In recent years, there has been considerable growth in the coordination chemistry and applications of monoanionic terdentate PCP "pincer" (PCP = 2,6-$C_6H_3(EPR_2)_2$) and related ligands.[1] Of particular interest has been their use in the alkane dehydrogenation chemistry of iridium,[2] where PCP ligand stabilization of intermediates appears to be a key factor;[3] some of these systems exhibit surprisingly long-term catalytic activity at temperatures up to 250 °C.[4]

To date, most PCP ligands have incorporated donating phosphine groups such as EPR_2 = CH_2PR_2 (R = Ph, ^{i}Pr, ^{t}Bu). Recently, however, resorcinol-derived phosphinite derivatives, where EPR_2 = OPR_2 (R = ^{i}Pr, ^{t}Bu), have been effectively employed in a number of applications,[5] and aryl ring substitution on the PCP backbone has also been shown to tune reactivity characteristics.[6] Phosphinite pincer ligands introduce an increased degree of phosphine acceptor behavior but also a counteracting oxygen π-donation into the aryl backbone. In 2005, the syntheses of perfluoroaryl- and pyrrolyl-substituted PCP ligands which can be more accurately categorized as terdentate π-acceptor ligands were reported.[7,8] These ligands impart significant electronic and steric effects which set them apart from other PCP systems

* To whom correspondence should be addressed. E-mail: dmr@uwyo@edu.

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reported to date.[8,9] Beyond their interest as extensions to the PCP ligation motif, such ligands are unique in their ability to impose a rigid mutually trans π-acceptor geometry, an arrangement which is not favorable in conventional π-acceptor coordination chemistry.

Our research program has a longstanding interest in perfluoroalkylphosphine ("PFAPs") ligand coordination chemistry. Much of our work has focused on the bidentate ligand $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (dfepe). In contrast to the perfluoroaryl analogue $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$, dfepe systems exhibit enhanced reductive elimination chemistry and resistance to metal−carbon bond protonolysis, consistent with a substantially greater electron-withdrawing effect of perfluoroalkyl versus perfluoroaryl groups.[10] More recently, we have extended our studies to monodentate PFA ligands, $(C_2F_5)_2P(R)$, which are also strong π-acceptor phosphines and provide additional degrees of stereochemical flexibility and lability.[11]

In this paper, we report the synthesis of the strong π-acceptor PCPH diphosphine $1,3\text{-}C_6H_4(CH_2P(CF_3)_2)_2$ and its ligation behavior with platinum(II) centers. We observe that under mild conditions unmetalated PCPH-bridged products are cleanly produced, which react under more forcing condition to produce the expected metalated PCP substitution products.

Experimental Section

General Procedures. All manipulations were conducted under N_2 or vacuum using high-vacuum line and glovebox techniques unless otherwise noted. All ambient pressure chemistry was carried out under a pressure of approximately 590 Torr (elevation ~2195 m). All solvents were dried using standard procedures and stored under vacuum. Aprotic deuterated solvents used in NMR experiments were dried over activated 3 Å molecular sieves. Elemental analyses were performed by Desert Analytics. NMR spectra were obtained with a Bruker DRX-400 instrument. ^{31}P spectra were referenced to an 85% H_3PO_4 external standard. ^{19}F spectra were referenced to $CF_3CO_2CH_2CH_3$ (δ −75.32). The compounds 1,2-bis[(diethoxyphosphoryl)-methyl]benzene,[12] (cod)$PtCl_2$,[13] (cod)Pt$(CH_3)Cl$,[14] and (cod)Pt$(CH_3)_2$ were prepared following published procedures.[15] With the exception of phosgene gas (Linde), Me_3SiCF_3 (Synquest), and C_2F_5Cl (Synquest), all other reagents were purchased from Aldrich and were used without further purification.

Safety Note. *Phosgene is an extremely toxic low-boiling liquid, and care must be exercised in its use. All manipulations involving this compound were carried out in a well-ventilated fume hood.*

$1,3\text{-}C_6H_4(CH_2PH_2)_2$ (^{H}PCPH). To $LiAlH_4$ (16.52 g, 4353 mmol) in 300 mL of diethyl ether at −78 °C was added 55.2 mL of Me_3SiCl (47.25 g, 0.4349 mmol) dropwise over the course of ca. 30 min. The gray suspension was stirred at −78 °C for an additional 15 min, allowed to warm to 25 °C, and then stirred for an additional hour. The reaction mixture was cooled to 0 °C, and a solution of 1,3-bis[(diethoxyphosphoryl)methyl]benzene (33.03 g, 87.1 mmol) in 50 mL of Et_2O was added dropwise via cannula over 30 min. The light gray suspension was allowed to warm to room temperature and was stirred for an additional hour. After cooling to 0 °C, the reaction was quenched under nitrogen by the dropwise addition of deoxygenated water and stirred until hydrogen evolution ceased. A deoxygenated solution of aqueous 30% NaOH was then slowly added via syringe with vigorous stirring until the formation of a white precipitate was complete. The slurry was allowed to stand undisturbed, and the separated organic layer was transferred into a 500 mL round-bottom flask. The white precipitate was extracted twice with Et_2O (125 mL) and combined with the first organic layer. The combined extracts were washed with deoxygenated brine, the aqueous layer was removed via cannula, and the organic layer was dried over anhydrous $MgSO_4$. The diethyl ether was removed in vacuo, giving ^{H}PCPH as a colorless oil (12.62 g, 85% yield). Anal. Calcd for $C_8H_{12}P_2$: C, 56.48; H, 7.11. Found: C, 56.30; H, 7.34. ^{1}H NMR (C_6D_6, 400.13 MHz, 20 °C): δ 7.08 (t, J_{HH} = 8 Hz, 1H, ArH), 6.93 (s, 1H, ArH), 6.91 (d, J_{HH} = 6 Hz, 2H, ArH), 2.75 (m, 4H, CH_2P), 2.65 (td, J_{HH} = 8 Hz, J_{PH} = 192 Hz, 4H, PH_2). ^{31}P NMR (C_6D_6, 161.97 MHz, 20 °C): δ −121.9 (t, J = 192 Hz).

$1,3\text{-}C_6H_4(CH_2PCl_2)_2$ (^{Cl}PCPH). To ^{H}PCPH (12.62 g, 74.2 mmol) dissolved in 200 mL of CH_2Cl_2 cooled to −78 °C was added 26.58 mL (36.68 g, 371 mmol) of phosgene cooled to −78 °C via cannula over the course of 1.5 h. The reaction mixture was allowed to warm to room temperature and then stirred for an additional 2 h. Upon the addition of phosgene, the solution turned light yellow and a thick pale yellow suspension was formed, and as the solution warmed to room temperature the suspension dissolved and the solution turned colorless. Volatiles were removed in vacuo, and the resulting white solid residue was triturated with petroleum ether and isolated by filtration (20.89 g, 91%). Anal. Calcd for $C_8H_8P_2Cl_4$: C, 31.21; H, 2.62. Found: C, 30.90; H, 2.57. ^{1}H NMR (C_6D_6, 400.13 MHz, 20 °C): δ 6.91 (t, J_{HH} = 15.6 Hz, 1H, ArH), 6.71 (d, J_{HH} = 7.6 Hz, 2H, ArH), 6.60 (s, 1H, ArH), 3.06 (d, J_{PH} = 15.6 Hz, 4H, CH_2P). ^{31}P NMR (C_6D_6, 161.97 MHz, 20 °C): δ 179.5 (s).

$1,3\text{-}C_6H_4(CH_2P(C_2F_5)_2)_2$ (^{CF_3CF_2}PCPH). A volume of 56.0 mL of 2.5 M *n*-BuLi in hexane (140 mmol) was transferred into a 500 mL three-neck flask fitted with a vacuum adapter and a low-temperature thermocouple. Hexane was removed under vacuum and replaced with 250 mL of diethyl ether, and the solution was cooled to −80 °C. A 16 mL aliquot of C_2F_5Cl (bp −34 °C, density 1.88 g/mL, 195 mmol) was measured out in a calibrated volume at −80 °C and was slowly added to the *n*-BuLi solution by vacuum transfer

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so as to maintain the reaction temperature below −80 °C. After 30 min, the addition was complete and the solution was stirred for an additional 1 h, during which time the reaction mixture became slightly cloudy. A solution of ^{Cl}PCPH (8.64 g, 28.1 mmol) dissolved in 100 mL of diethyl ether and 50 mL of THF was added by syringe under nitrogen counterflow in 1 mL aliquots over a period of about 1 h to maintain the temperature below −80 °C. The solution turned brown upon addition, and after the addition was complete the mixture was maintained at −80 °C an additional 1 h and then allowed to warm slowly to room temperature. After 12 h at ambient temperature, the diethyl ether, THF, and *n*-butyl chloride were separated from the solids via cannula filtration. The resulting brown solution was evaporated to dryness via vacuum to afford the crude product (∼70%, with no major identifiable side products) and was not further purified. ^{1}H NMR (acetone-d_6, 400.13 MHz, 20 °C): δ 7.44−6.98 (m, 4H, ArH), 3.59 (m, 4H, CH_2P). ^{31}P NMR (acetone-d_6, 161.97 MHz, 20 °C): δ 7.08 (m). ^{19}F NMR (acetone-d_6, 376.50 MHz, 20 °C): δ −83.2 (s, 12F, CF_3), −113.2 (m, J_{PF} = 297 Hz, 8H, CF_2).

1,3-$C_6H_4(CH_2P(OPh)_2)_2$ (^{PhO}PCPH). To dry phenol (6.11 g, 64.9 mmol) dissolved in 50 mL of THF was added 9.04 mL of Et_3N (6.57 g, 64.9 mmol) via syringe, and the solution was cooled to 0 °C. ^{Cl}PCPH (5.00 g, 16.2 mmol) dissolved in 50 mL of THF was added to the phenol/Et_3N/THF solution via cannula, and the precipitation of Et_3NHCl occurred. The reaction mixture was warmed to room temperature and stirred for an additional hour, and the salt was removed by filtration and extracted several times with THF. The removal of volatiles from the filtrate in vacuo resulted in an oily white solid. The crude product was purified by dissolving in a 1:2 ratio of methylene chloride and hexanes, and the methylene chloride was removed slowly under vacuum to give the product as a pure white solid which was collected by filtration (7.45 g, 85% yield). Anal. Calcd for $C_{32}H_{28}P_2O_4$: C, 71.37; H, 5.24. Found: C, 71.15; H, 5.23. ^{1}H NMR (C_6D_6, 400.13 MHz, 20 °C): δ 7.24 (s, 1H, ArH), 7.08 (m, 3H, ArH), 7.00 (d, J_{HH} = 8.0 Hz, 8H, ArH), 6.93 (t, J_{HH} = 15.6 Hz, 8H, ArH), 6.77 (t, J_{HH} = 14.4 Hz, 4H, ArH), 3.22 (d, J_{PH} = 6.4 Hz, 4H, CH_2P). ^{31}P NMR (C_6D_6, 161.97 MHz, 20 °C): δ 176.2 ppm (s).

1,3-$C_6H_4(CH_2P(CF_3)_2)_2$ (^{CF_3}PCPH). To a mixture of ^{PhO}PCPH (6.00 g, 11.1 mmol) and dry CsF (6.73 g, 44.6 mmol) in 30 mL of diethyl ether was added 7.25 mL of CF_3SiMe_3 (6.97 g, 49.0 mmol) via syringe. The reaction mixture was allowed to stir at room temperature for 48 h, during which time the reaction slowly turned from clear to brown with a white CsF suspension. The diethyl ether was removed in vacuo, and vacuum distillation of the brown slurry gave the silyl ether side product $C_6H_5OSi(CH_3)_3$ (80−83 °C and 25 Torr) and the crude product at 68−71 °C under full vacuum (ca. 10^{-3} Torr). A small amount of residual silyl ether was removed by dissolving the crude product in petroleum ether and cooling to −78 °C, whereupon colorless crystals of ^{CF_3}PCPH were precipitated and the supernatant was removed via cannula. Repeating this procedure four times gave the pure product as a clear oil (3.35 g, 68% yield, density = 1.58 g/mL). Anal. Calcd for $C_{12}H_8P_2F_{12}$: C, 32.60; H, 1.82. Found: C, 32.54; H, 2.11. ^{1}H NMR (C_6D_6, 400.13 MHz, 20 °C): δ 6.81 (t, J_{HH} = 7.6 Hz, 1H, ArH), 6.64 (d, J_{HH} = 7.6 Hz, 2H, Ar), 6.58 (s, 1H, Ar), 2.82 (s, 4H, CH_2P). ^{31}P NMR (C_6D_6, 161.97 MHz, 20 °C): δ 1.0 (heptet, $^2J_{FP}$ = 64 Hz). ^{19}F NMR (C_6D_6, 376.50 MHz, 20 °C): δ 53.8 (d, $^2J_{PF}$ = 64 Hz).

{(^{CF_3}PCPH)Pt(Me)Cl}$_x$ (1). (cod)Pt(Me)Cl (0.300 g, 0.849 mmol) and ^{CF_3}PCPH (262 μL, 0.412 g, 0.933 mmol) were dissolved in 20 mL of CH_2Cl_2 and stirred at room temperature for 48 h, during which time a white precipitate formed. The insoluble precipitate was filtered in air, rinsed twice with dichloromethane, and then dried in vacuo (0.510 g, 87% yield). Anal. Calcd for $C_{26}H_{22}P_4F_{24}Pt_2Cl_2$: C, 22.71%; H, 1.61. Found: C, 23.06; H, 1.68.

(^{CF_3}PCP)PtCl (2). Complex **1** (1.020 g, 0.742 mmol) suspended in 10 mL of *m*-xylene was brought to reflux with stirring. After 4 h, the light yellow solution was cooled to room temperature, filtered, and ca. 40 mL hexanes were added, then the mixture was cooled to −78 °C to precipitate the white microcrystalline product. Filtration and drying in air afforded 0.942 g (94%) of **2**. Crystals suitable for X-ray diffraction were grown from a saturated benzene solution. Anal. Calcd for $C_{12}H_8P_2F_{12}PtCl$: C, 21.43; H, 1.20. Found: C, 21.40; H, 1.19. ^{1}H NMR (acetone-d_6, 400.13 MHz, 20 °C): δ 7.39 (m, 2H, ArH), 7.31 (m, 1H, ArH), 4.48 (m, 4H, CH_2P). ^{31}P NMR (acetone-d_6, 161.97 MHz, 20 °C): δ 64.8 ppm (m, $^1J_{PtP}$ = 3630 Hz). ^{19}F NMR (acetone-d_6, 376.50 MHz, 20 °C): δ −54.0 (m). Note: Small amounts of insoluble material are formed using *m*-xylene as the solvent, which can be removed by filtration. Using bromobenzene instead of *m*-xylene as a refluxing medium appears to minimize the formation of the insoluble material.

***cis*-[(^{CF_3}PCPH)PtMe$_2$]$_2$ (3).** A mixture of (cod)PtMe_2 (0.300 g, 0.901 mmol) and ^{CF_3}PCPH (303 μL, 0.451 g, 1.010 mmol) in 10 mL of benzene was stirred at room temperature for 48 h, during which time a white precipitate formed. A volume of 30 mL of hexanes was added to further precipitate the product, which was filtered in air and rinsed several times with hexanes and finally by a small portion (ca. 5 mL) of methylene chloride. The product was dried in vacuo (0.450 g, 75% yield). Crystals suitable for X-ray diffraction were grown from a solution of dichloromethane layered with methanol. Anal. Calcd for $C_{28}H_{28}P_4F_{24}Pt_2$: C, 25.19; H, 2.12. Found: C, 25.09; H,2.11. ^{1}H NMR (acetone-d_6, 400.13 MHz, 20 °C): δ 7.54 (s, 1H, ArH), 7.46 (m, 2H, ArH), 7.30 (m, 1H, ArH), 4.13 (d, $^2J_{PH}$ = 9.2 Hz, 4H, CH_2P), 1.19 (m, $^2J_{PtH}$ = 70.8 Hz, 6H, Pt(CH_3)). ^{31}P NMR (acetone-d_6, 161.97 MHz, 20 °C): δ 46.4 (m, $^1J_{PtP}$ = 1660 Hz). ^{19}F NMR (acetone-d_6, 376.50 MHz, 20 °C): δ 53.3 (d, $^2J_{FP}$ = 64 Hz).

(^{CF_3}PCP)PtMe (4). Complex **2** (0.920 g, 0.137 mmol) was dissolved in 50 mL of diethyl ether, and 0.50 mL (0.150 mmol) of 3.0 M CH_3MgBr was added via syringe. The solution turned yellow after 10 min and was stirred overnight. All volatiles were removed under vacuum, and the light yellow solid was extracted with petroleum ether in air. The solvent was removed, and the residue was dissolved in ca. 5 mL of hexanes and cooled to −78 °C. Cold filtration in air afforded 0.705 g (72%) of **4**. Crystals suitable for X-ray diffraction were grown from a saturated hexane solution. Anal. Calcd for $C_{13}H_{11}P_2F_{12}Pt$: C, 23.93; H, 1.70. Found: C, 23.93; H, 1.49. ^{1}H NMR (acetone-d_6, 400.13 MHz, 20 °C): δ 6.84 (m, 2H, ArH), 6.67 (m, 1H, ArH), 3.34 (m, 4H, CH_2P), 1.30 (t, $^2J_{PtH}$ = 27.6 Hz, $^3J_{PH}$ = 5.6 Hz, 3H, Pt(CH_3)). ^{31}P NMR (acetone-d_6, 161.97 MHz, 20 °C): δ 64.0 (m, $^1J_{PtP}$ = 3790 Hz). ^{19}F NMR (acetone-d_6, 376.50 MHz, 20 °C): δ −56.1 (m).

{(^{CF_3}PCP)Pt(CO)}SbF_6 (5). A mixture of **2** (0.150 g, 0.222 mmol) and $AgSbF_6$ (0.076 g, 0.22 mmol) was dissolved in 30 mL of methylene chloride at −78 °C, and 1 atm of CO was introduced. The reaction mixture was allowed to warm to room temperature and then stirred for an additional 20 h. AgCl was filtered off, the volume of the filtrate was reduced to ca. 10 mL, and ca. 40 mL of diethyl ether was added. Cooling to −78 °C and collection by cold filtration afforded 0.085 g (42%) of ***5***. Anal. Calcd for $C_{13}H_8P_2F_{18}OSbPt$: C, 17.34; H, 0.90. Found: C, 17.44; H, 0.83. ^{1}H NMR (CD_2Cl_2, 400.13 MHz, 20 °C): δ 7.58 (m, 3H, ArH), 4.55 (m, 4H, CH_2P). ^{31}P NMR (CD_2Cl_2, 161.97 MHz, 20 °C): δ 67.4 (m, $^1J_{PtP}$ = 3290 Hz). ^{19}F NMR: δ −52.7 (m, 12F). IR (Nujol, cm^{-1}): ν(CO) = 2143 cm^{-1}. Crystals suitable for X-ray diffraction

Table 1. Crystallographic Data for **2**, **5**, **4**, and **3**

	(^{CF_3}PCP)PtCl ·1.5C_6H_6 (**2**)	(^{CF_3}PCP)Pt(CO)$^+SbF_6^-$ (**5**)	(^{CF_3}PCP)PtMe (**4**)	*cis*−[(^{CF_3}PCPH)$PtMe_2$]$_2$ (**3**)
chemical formula	$C_{21}H_{16}ClF_{12}P_2Pt$	$C_{13}H_7F_{18}OP_2PtSb$	$C_{13}H_{10}F_{12}P_2Pt$	$C_{28}H_{28}F_{24}P_4Pt_2$
fw	788.82	899.97	651.24	1334.56
T, °C	−173	23	23	23
λ, Å	0.71073	0.71073	0.71073	0.71073
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a, Å	10.1108 (2)	11.7702(3)	14.7315(2)	10.625(2)
b, Å	19.2699 (3)	13.9500(4)	16.1886(2)	14.209(2)
c, Å	13.0819 (2)	14.5294(4)	17.7374(2)	14.545(2)
α, °	90	91.3090(10)	90	83.040(10)
β, °	102.8610 (10)	100.8130(10)	113.42	74.710(10)
γ, °	90	91.9000(10)	90	70.420(10)
V, Å^3	2484.86 (7)	2340.97(11)	3881.57(8)	1994.4(5)
Z	4	4	8	2
D_{calc}, Mg m^{-3}	2.109	2.554	2.229	2.222
μ, mm^{-1}	5.98	7.408	7.501	7.302
R1[$I > 2\sigma(I)$][a]	0.016	0.0369	0.0321	0.0592
wR2[$I > 2\sigma(I)$][b]	0.037	0.0899	0.0669	0.1211

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]\sum w(F_o^2)^2]\}^{1/2}$.

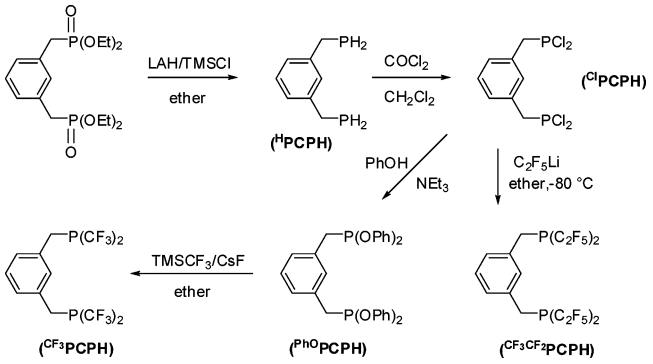
were grown by the slow evaporation of a methylene chloride solution.

X-ray Crystallography. X-ray diffraction data were collected for the unmetalated dimer **3** on a Bruker P4 diffractometer equipped with a molybdenum tube and a graphite monochromator. A colorless crystal glued to a glass fiber was used for data collection. A total of 6974 ($R_{int} = 0.0495$) reflections was gathered in the 2θ range of 4.14−50.00° with the data collected having $-12 \le h \le 1$, $-16 \le k \le 16$, $-17 \le l \le 16$ using the *XSCANS* program.[16] Three standard reflections measured after every 97 reflections exhibited no significant loss of intensity. The structure was solved by Patterson methods and refined by least-squares techniques adapting the full-matrix weighted least-squares scheme, $w^{-1} = \sigma^2F_o^2 + (0.0619P)^2$ where $P = (F_o^2 + 2F_c^2)/3$, on F^2 using the *SHELXTL* program.[17]

Crystallographic data for **2**, **4**, and **5** were collected on a Bruker AXS APEX2 diffractometer employing the graphite-monochromated Mo Kα radiation. Crystals were mounted on MiTeGen micromounts using Paratone-N oil. Several sets of narrow frames of data were collected (5 s exposure time per frame) at different values of θ with a scan width of 0.5° in ω or ϕ. The frames were integrated with the Bruker *SAINT* program using a narrow-frame integration algorithm. The unit cell parameters were obtained from a least-squares fit to the angular coordinates of all reflections. The data were corrected for Lorentz polarization effects and absorption using the *SADABS* program. The structures were solved by direct methods and refined by full-matrix least squares on all F^2 using the Bruker *SHELXT* program. All software programs employed are from the Bruker AXS *APEX2* software package.[18] Crystallographic data collection parameters and refinement data are collected in Table 1.

All nonhydrogen atoms were located in successive Fourier maps and were refined anisotropically. The hydrogen atoms were located and refined isotropically in the structures of **2** and **3**, and were placed in calculated positions in the structures of **4** and **5**. The asymmetric unit of ***2*** contains 1 $^1/_2$ benzene molecules. The molecules are well separated and well ordered. The asymmeric units of **4** and **5** contain two of the respective molecules, while the asymmetric unit of **3** consists of the dinuclear complex.

Scheme 1



Results and Discussion

Synthesis of 1,3-$C_6H_4(CH_2P(R_f)_2)_2$ (^{R_f}PCPH, $R_f = CF_3$, C_2F_5). The preparative scope of PCP ligands is limited compared with that of other organophosphine systems. Most benzylic PCP ligands have been prepared by the addition of secondary phosphines to 1,3-bis(halomethyl)benzene.[1,19,20] For cases in which the corresponding secondary phosphine is unavailable or insufficiently nucleophilic, the addition of XPR_2 (X = halide) to the di-Grignard 1,3-$C_6H_4(CH_2MgBr)_2$ is a complementary synthetic route which has been successfully employed.[7,8] Since the alkylation of halophosphine precursors is one of the most common synthetic strategies in organophosphine chemistry, we have prepared 1,3-$C_6H_4(CH_2PCl_2)_2$ (^{Cl}PCPH) and examined its potential as a precursor to other PCPH ligands.

The synthesis of ^{Cl}PCPH from 1,3-$C_6H_4(CH_2PH_2)_2$ is presented in Scheme 1. Reduction of the phosphonate ester by $LiAlH_4$ to form the primary phosphine 1,3-$C_6H_4(CH_2PH_2)_2$ (^{H}PCPH) in 50% yield has been recently reported.[21] With the use of a modified procedure using $LiAlH_4$/

(16) *XSCANS*, version 2.31; Bruker AXS, Inc.: Madison, WI, 1993.
(17) (a) *SHELXTL*, version 5.10; Bruker AXS, Inc.: Madison, WI, 1997. (b) Sheldrick, G. M. *SHELXS97* and *SHELXL97*; University of Göttingen: Göttingen, Germany, 1997.
(18) *APEX2 Software Suite*, version 2.1-0; Bruker AXS: Madison, WI, 2005.
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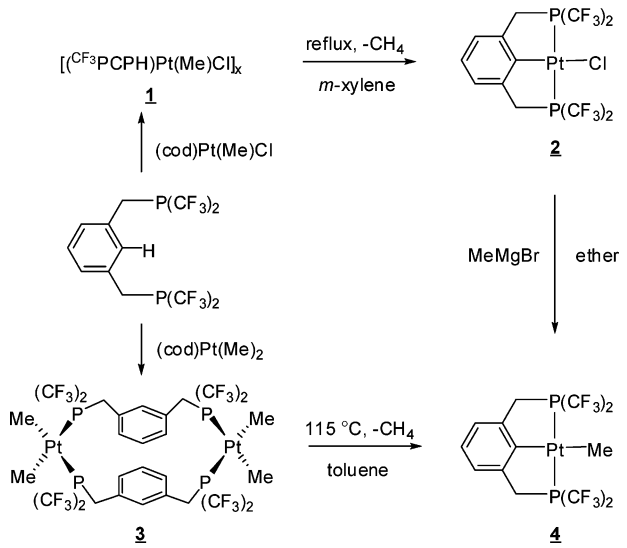
TMSCl as the reductant,[22] it was possible to prepare ^{H}PCP cleanly in 85% yield. Treatment of ^{H}PCPH with phosgene (***Safety Note:*** *Phosgene is extremely toxic, and care must be exercised in its use*) afforded the diphosphoryl tetrachloride 1,3-$C_6H_4(CH_2PCl_2)_2$ (^{Cl}PCPH) in high yield.[22a,b] The conversion of ^{Cl}PCPH to phosphinite derivatives was briefly surveyed: Treatment of ^{Cl}PCPH with methanol, biphenol, or trifluoroethanol resulted in clean conversion to products which were identified by ^{31}P NMR as 1,3-$C_6H_4(CH_2P(OMe)_2)_2$ (182.5 ppm), 1,3-$C_6H_4(CH_2P(O_2C_{12}H_8))_2$ (205.5 ppm), and 1,3-$C_6H_4(CH_2P(OCH_2CF_3)_2)_2$ (193.2 ppm), respectively.

The ligand ^{CF_3CF_2}PCPH was prepared from ^{Cl}PCPH in a fashion analogous to that of other perfluoroethyl-substituted phosphines in our laboratory.[23] The addition of ^{Cl}PCPH to CF_2CF_3Li at −80 °C gave 1,3-$C_6H_4(CH_2P(C_2F_5)_2)_2$ (^{CF_3CF_2}PCPH) as a viscous oil. ^{CF_3CF_2}PCPH was characterized by a broad phosphorus resonance at 7.08 ppm with unresolved $^2J_{PF}$ coupling. In addition to overlapping aromatic resonances, a characteristic benzylic resonance at 3.59 ppm is observed in the proton NMR spectrum.

Caffyn has reported a general and efficient synthesis of $(R_f)_nPR_{3-n}$ compounds by treatment of the corresponding arylphosphites $(ArO)_nPR_{3-n}$ with Ruppert's reagent (CF_3SiMe_3) as well as with higher perfluoroalkyl analogues $(R_f)SiMe_3$.[24] 1,3-$C_6H_4(CH_2P(OPh)_2)_2$ (^{PhO}PCPH) was readily prepared in good yield from ^{Cl}PCPH following literature procedures.[25] The addition of CF_3SiMe_3 to an ether suspension of ^{PhO}PCPH and excess CsF at ambient temperature produced a dark brown solution. Distillation under reduced pressure followed by recrystallization from petroleum ether at −78 °C afforded 1,3-$C_6H_4(CH_2P(CF_3)_2)_2$ (^{CF_3}PCPH) as a colorless oil. The ^{CF_3}PCPH ligand precursor is characterized by a distinctive phosphorus heptet multiplet pattern at 1.0 ppm ($^2J_{FP} = 66$ Hz) and a corresponding ^{19}F doublet at 53.8 ppm. Exposure of ^{CF_3}PCPH to air resulted in slow oxidation to produce what we believe are phosphine oxide derivatives of ^{CF_3}PCPH, based on the appearance of new downfield-shifted heptet ^{31}P resonances at 24.2 and 24.1 ppm.

Platinum ^{R_f}PCPH Metalation Studies. We have initially surveyed the applicability of ^{R_f}PCPH ligand precursors in metal coordination chemistry for platinum. Early studies employing (^{t}BuCN)$_2$PtCl$_2$ or PtX$_2$ afforded modest yields of (PCP)PtX product, plus significant amounts of poorly characterized and $[(PCPH)PtX_2]_x$ products which were presumed to be oligomeric due to their poor solubility.[26,27]

Scheme 2



Efficient PCPH metalation under mild conditions has been reported using [(2-methylallyl)Pt(μ-Cl)]$_2$ as a precursor.[28] Most metalated platinum PCP complexes have typically been prepared under more stringent thermolysis conditions using (cod)Pt(Me)Cl or (cod)PtCl$_2$.[29] Interestingly, no intermediates have been reported for the these latter syntheses.

We have found that ^{CF_3}PCPH initially produces unmetalated PCPH-bridged products: The addition of ^{CF_3}PCPH to (cod)Pt(Me)Cl in benzene at room temperature gave $[(^{CF_3}PCPH)Pt(Me)Cl]_x$ (**1**) in excellent yield (Scheme 2). Complex **1** is highly insoluble and not amenable to spectroscopic characterization; however, we tentatively assign its formulation as **1** based on the isolation and characterization of a more soluble analogue *cis*-$[(^{CF_3}PCPH)PtMe_2]_2$ (see later). Refluxing **1** in *m*-xylene for 4 h gave the expected metalated monomer (^{CF_3}PCP)PtCl (**2**). A separate sealed tube NMR experiment in toluene-d_8 confirmed the release of methane upon thermolysis. ^{1}H NMR shows 2:1 aromatic resonances, which are consistent with the loss of the aromatic hydrogen in the 1-position. A ca. 63 ppm downfield shift of the ^{31}P NMR resonance from the free ligand to 64.8 ppm is seen, and the observed $^1J_{PtP}$ coupling of 3630 Hz is consistent with trans phosphine coordination.

The unmetalated dimer *cis*-$[(^{CF_3}PCPH)PtMe_2]_2$ (**3**) was similarly formed by stirring a mixture of (cod)PtMe$_2$ and ^{CF_3}PCPH in benzene for 48 h at ambient temperature. Unlike the chloride derivative **1**, complex **3** is soluble in most organic solvents. ^{1}H NMR shows three aryl resonances in a 1:2:1 ratio, a methyl multiplet at 1.12 ppm, and a distinctive CH_2 benzylic doublet shifted 1.3 ppm downfield from the free ligand. ^{31}P and ^{19}F NMR data are similarly consistent with the coordination of the unmetalated PCPH ligand. The low $^1J_{PtP}$ value found for **3** (1660 Hz) indicates that the phosphorus groups are trans to methyl groups; X-ray

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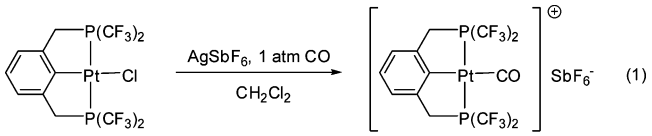
characterization for complex **3** confirmed the bimetallic structure and the metal cis coordination geometry (see later). Warming **3** to 115 °C for 24 h in toluene resulted in metalation to give primarily (~50−70%) methyl complex (^{CF_3}PCP)PtMe (**4**), with no other major identifiable products. The release of methane was confirmed by thermolysis in toluene-d_8 by ^{1}H NMR. Complex **4** was alternatively prepared by the reaction of **2** with a methyl Grignard reagent.

Synthesis of (^{CF_3}PCP)Pt(CO)$^+$SbF$_6^-$ (5). The electronic influence of ^{R_f}PCP ligands may be probed by comparing analogous carbonyl complexes. The carbonyl cation **5** was readily prepared by chloride abstraction with $AgSbF_6$ under 1 atm of CO (eq 1). The observed CO stretching frequency is 2143 cm^{-1}, 40 cm^{-1} higher than the value reported for the donor phosphine complex *trans*-$(Ph_2PMe)_2Pt(Ph)(CO)^+$,[30] and 63 cm^{-1} higher than ν(CO) for the only other PCP-substituted platinum carbonyl complex that we are aware of, the napthyl-backboned $(C_{10}H_5(CH_2PtBu_2)_2)Pt(CO)^+$.[31] The $\Delta(\nu(CO))$ value for these trans systems is slightly less than the difference between *trans*-$((C_2F_5)_2PMe)_2Pt(Me)(CO)^+$ (2149 cm^{-1}) and *trans*-$(Ph_3P)_2Pt(Me)(CO)^+$ (2100 cm^{-1}). The greater observed difference for cis chelate systems $((C_2F_5)_2PCH_2CH_2P\text{-}(C_2F_5)_2)Pt(Me)(CO)^+$ (2174 cm^{-1}) and $(Ph_2PCH_2CH_2PPh_2)\text{-}Pt(Me)(CO)^+$ (2117 cm^{-1}) ($\Delta\nu$(CO) = 57 cm^{-1}) reflects the larger electronic influence of trans phosphines on CO backbonding.



2 **5**

Crystallographic Studies. Previous structural studies for PFAP complexes have demonstrated significant structural difference relative to that of donor phosphine analogues. In particular, while PFAP systems for earlier transition metals exhibit significant shortening of M−P bonds, Pt−P bond lengths appear to be more sensitive to steric factors and relatively insensitive to phosphorus substituent electronic effects.[32] We have carried out diffraction studies on metalated complexes **2**, **4**, and **5** as well as the unmetalated precursor complex **3** to establish benchmark metrics for future acceptor PCP studies. Molecular views and selected metrical parameters are shown in Figures 1−4, respectively.

All reported donor PCP Pt(II) complexes possess distorted-square-planar ligation geometries, with essentially linear C(PCP)−Pt−X angles averaging 177.5° (range 174.7−180°) and a smaller P−Pt−P angle averaging 164° (range 161.0−167.5°) reflecting the PCP chelate constraints.[28,29,33,34] Complexes **2** and **4** are on the lower limit of the observed P−Pt−P range. This can be ascribed to a combination of shorter Pt−P and longer Pt−C(PCP) bonds to the ^{CF_3}PCP ligand. Compound **4** in particular has significantly shortened Pt−P bonds (2.201 and 2.205 Å) relative to the average Pt−P bond length of 2.276 Å, while having the longest Pt−C(PCP) bond yet reported of 2.089 Å. The only other complex with a comparable distortion of the PCP coordination sphere has a sterically encumbering η^1-C−$C_6H_3(CH_2NMe_2)_2$ aryl ligand

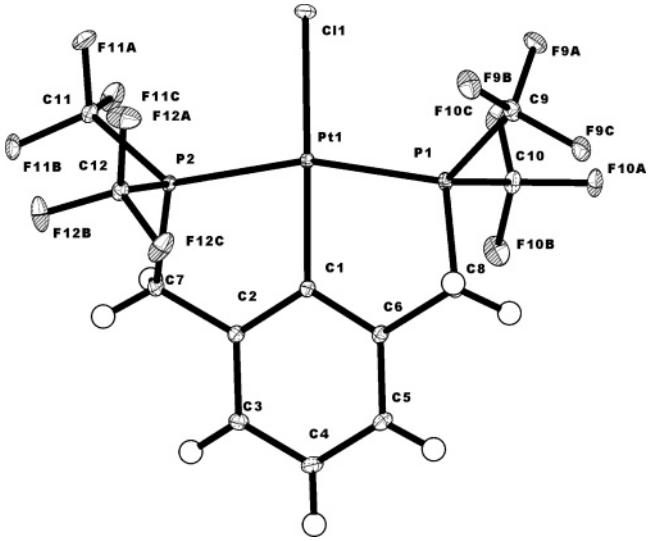


Figure 1. Molecular structure of **2** with atom labeling scheme (25% probability ellipsoids). Selected metrical data (bond lengths in Å and angles in deg): Pt(1)−P(1), 2.2383(3); Pt(1)−P(2), 2.2278(3); Pt(1)−Cl(1), 2.3699(3); Pt(1)−C(1), 2.0371(12); P(1)−Pt(1)−P(2), 161.06(1); C(1)−Pt(1)−Cl(1), 176.89(3).

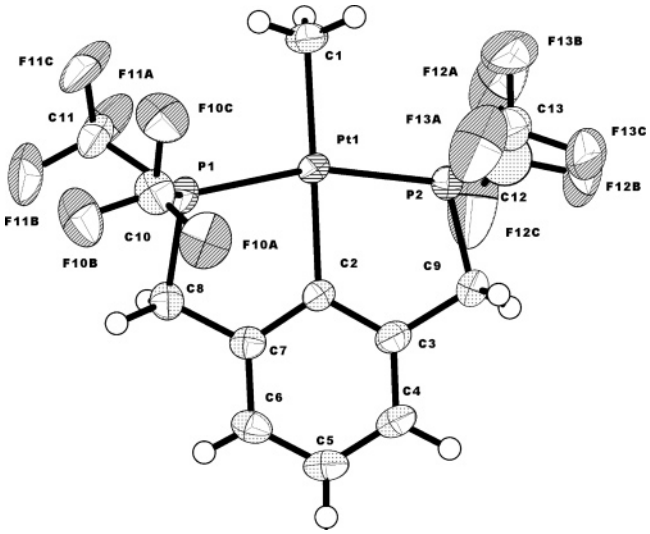


Figure 2. Molecular structure of **4** with atom labeling scheme (25% probability ellipsoids). Selected metrical data (bond lengths in Å and angles in deg): Pt(1)−P(1), 2.2049(13); Pt(1)−P(2), 2.2013(14); Pt(1)−C(1), 2.140(5); Pt(1)−C(2), 2.089(5); P(1)−Pt(1)−P(2), 160.99(5); C(1)−Pt(1)−C(2), 177.3(2).

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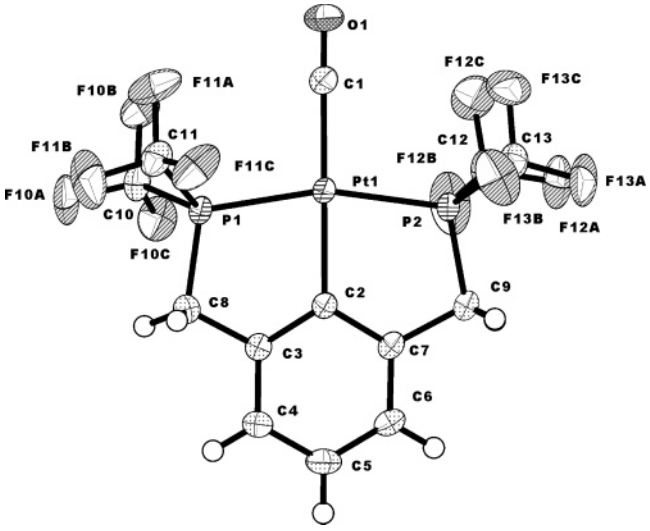

Figure 3. Molecular structure of **5** with atom labeling scheme (25% probability ellipsoids). Selected metrical data (bond lengths in Å and angles in deg): Pt(1)−P(1), 2.2562(10); Pt(1)−P(2), 2.2557(10); Pt(1)−C(1), 1.9650(5); Pt(1)−C(2), 2.053(4); C(1)−O(1), 1.114(6); P(1)−Pt(1)−P(2), 163.36(4); C(1)−Pt(1)−C(2), 179.0(2); Pt(1)−C(1)−O(1), 178.7(5).

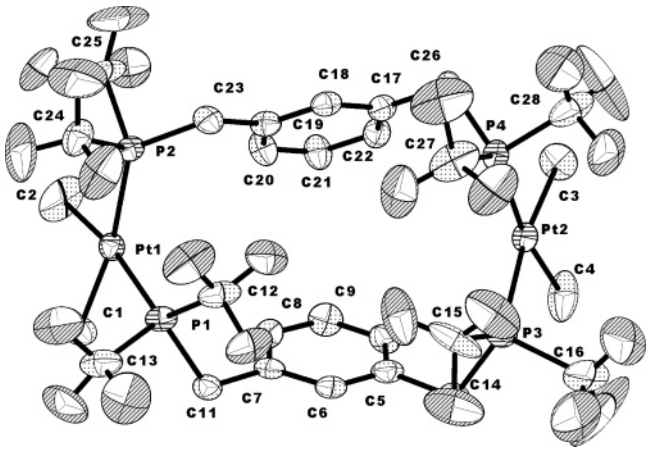

Figure 4. Molecular structure of **3** with atom labeling scheme (25% probability ellipsoids). Hydrogen atoms are omitted, and not all atoms are labeled for clarity. Selected metrical data (bond lengths in Å and angles in deg): Pt(1)−C(2), 2.095(15); Pt(1)−C(1), 2.113(14); Pt(1)−P(2), 2.266(4); Pt(1)−P(1), 2.270(4); Pt(2)−C(3), 2.100(15); Pt(2)−C(4), 2.092(17); Pt(2)−P(3), 2.270(4); Pt(2)−P(4), 2.252(4); C(2)−Pt(1)−C(1), 82.1(8); P(2)−Pt(1)−P(1), 103.43(13); C(4)−Pt(2)−C(3), 82.7(9); P(4)−Pt(2)−P(3), 109.15(17).

($\angle$(P−Pt−P) = 161.3° and Pt−C(PCP) = 2.084 Å).[34] While the Pt−Cl bond length in complex **2** (2.3699(3) Å) is comparable to that seen in (^{Ph}PCP)PtCl structures (2.367−2.386 Å), the Pt−C(PCP) bond length of 2.037 Å for **2** is significantly longer than that reported for other chloride complexes (2.000−2.015 Å) and the Pt−P bond lengths are ∼0.03−0.04 Å shorter.[28,33c] In contrast, complex **5** possesses a less distorted PCP coordination geometry due to a lengthening of the Pt−P bonds to 2.256 Å, which we attribute to reduced backbonding in this cationic carbonyl complex.

The bimetallic complex **3** adopts a "butterfly"-type configuration where the platinum coordination planes are slightly twisted with respect to each other and are spread out (interplanar angle = 79°). As expected, complex **3** has a cis methyl geometry due to antisymbiosis effects.[35] The P−Pt−P angles (103.43(12)° for Pt(1) and 109.15(17)° for Pt(2)) are slightly larger than those reported for the analogous *cis*-[(DPPMH)PtMe$_2$]$_2$ (DPPMH = 1,3-bis((diphenylphosphino)-methylene)mesitylene) dimeric complex (101.8(3)−99.2-(3)°).[36] The ^{CF_3}PCPH complex exhibits slightly shorter Pt−P bonds (2.252(4)−2.270(4) Å) relative to the DPPMH complex (2.286(9)−2.324(7) Å). The most distinctive structural difference between **3** and *cis*-[(DPPMH)PtMe$_2$]$_2$ is the folding of the PCP aryl backbone units: While in the latter structure the aryl backbones are directed away from the Pt−Me bonds, in **3** the aryl backbones are tucked down toward the Pt−Me bonds and are actually canted toward each other with an interplanar angle of 52.3°. This solid-state conformation leaves all the phosphine CF_3 groups directed roughly opposite to the Pt−Me bonds.

Summary

Dimeric PCPH-bridged species have been proposed as intermediates in the synthesis of metalated PCP complexes.[26,27] The actual mechanism of rearrangement and PCPH metalation may be quite complicated, as has been observed for transcyclometalation reactions between PtCl(NCN) and PCPH ligands.[34] To our knowledge, the only other well-defined example of an unmetalated PCP-bridged dimeric metal complex involves 1,3-(diphenylphosphino)-methylene)mesitylene ligand (DPPMH), where the 1-position is blocked by a methyl group.[36]

We expect that closer examination of PCPH metalation reactions with (cod)PtX$_2$ precursors prior to thermolysis would reveal similar dimeric or oligomeric unmetalated species. Despite the poorly donating nature of ^{R_f}PCPH ligands, metalation proceeds under thermolysis conditions similar to those of previously reported donor phosphine analogues to give (^{R_f}PCP)PtX products. This observation does not imply that the penultimate metalation steps are energetically comparable, since oligomer rearrangements and/or cis−trans isomerizations prior to metalation may be rate-determining. In any event, spectroscopic data confirms that these products are unique examples of stereochemically rigid complexes with an imposed mutually trans π-acceptor coordination geometry. Subsequent reports will detail the chemistry of these platinum compounds, as well as extensions to group 8 and 9 systems.

Supporting Information Available: Complete tables of atomic coordinates, thermal parameters, and bond distances and angles for complexes **2**−**5** in PDF format; four CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

IC701426U

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