1148 *Organometallics* **2009,** *28,* 1148–1157

Acceptor Pincer Coordination Chemistry of Platinum: Reactivity Properties of $({}^{CF_3}PCP)Pt(L)^+$ ($L = NC_5F_5, C_2H_4$)

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Received September 11, 2008

Synthetic strategies toward the synthesis of electron-poor pincer complexes $({}^{CF_3}PCP)PtH$ and $({}^{CF_3}PCP)Pt(\eta^2\text{-}H_2)^+$ are described. Metathesis of $({}^{CF_3}PCP)PtCl$ with hydride reagents does not lead to $({}^{CF_3}PCP)PtH$; $({}^{CF_3}PCP)PtCl$ with KH in tetrahydrofuran (THF) afforded an unusual metallated bimetallic pincer product $({}^{CF_3}PCP)Pt[\kappa^1\text{-}C,\kappa^{3-}P,C,P\text{-}2,6\text{-}(CHP(CF_3)_2)(CH_2P(CF_3)_2)\text{-}C_6H_3]PtCl$, which has been structurally characterized. Chloride abstraction from $({}^{CF_3}PCP)PtCl$ or protonolysis of $({}^{CF_3}PCP)PtMe$ in the presence of H_2 gives the structurally characterized hydride-bridged dimer $\{({}^{CF_3}PCP)Pt\}_2(\mu\text{-}H)^+$. In the presence of trapping ligands H_2O, C_2H_4, or pentafluoropyridine, the corresponding complexes $({}^{CF_3}PCP)Pt(L)^+$ ($L = H_2O, C_2H_4, NC_5F_5$) are cleanly produced and have been structurally characterized. The C_2H_4 and NC_5F_5 adducts may be alternatively prepared by methide abstraction from $({}^{CF_3}PCP)PtMe$ with $Ph_3C^+B(C_6F_5)_4^-$ in the presence of trapping ligand. Evidence for the transient formation of $({}^{CF_3}PCP)PtH$ from treatment of $({}^{CF_3}PCP)PtCl$ or $({}^{CF_3}PCP)Pt(NC_5F_5)^+$ with $Et_3Si^+B(C_6F_5)_4^-$ is presented. $({}^{CF_3}PCP)Pt(C_2H_4)^+$ serves as a catalyst for ethylene hydrogenation (0.30 turnovers h^{-1}, 70 °C) and hydrosilation with Et_3SiH (460 turnovers h^{-1}, RT) and Cl_3SiH (5 turnovers h^{-1}, RT). At elevated temperatures, $({}^{CF_3}PCP)Pt(C_2H_4)^+$ also exhibits limited ethylene dimerization activity (0.07 turnovers h^{-1}, 155 °C) and 1-butene isomerization (0.9 turnovers h^{-1}, 80 °C).

Introduction

Research involving monoanionic terdentate PCP "pincer" ($PCP = 2,6\text{-}C_6H_3(EPR_2)_2$; $E = CH_2$ or O) ligands has expanded to include a diverse range of steric and electronic tuning effects.[1,2] Most PCP ligands incorporate donating phosphine groups such as $EPR_2 = CH_2PR_2$ ($R = Ph, {}^iPr, {}^tBu$), but more recently phosphinite, perfluoroaryl-, and pyrrolyl-substituted PCP ligands have been introduced which have significant π-acceptor abilities.[3−5] We have recently reported the synthesis and coordination properties of a new strong π-acceptor PCP ligand, $1,3\text{-}C_6H_4(CH_2P(CF_3)_2)_2$ (${}^{CF_3}PCPH$).[6] Initial work focused on the synthesis of platinum derivatives $({}^{CF_3}PCP)Pt(X)$ ($X =$ Cl, Me); of particular interest was the synthesis of the carbonyl cation $({}^{CF_3}PCP)Pt(CO)^+$ by halide abstraction by Ag^+, since this demonstrated access to the $({}^{CF_3}PCP)Pt^+$ moiety. We are interested in exploring the chemistry of $({}^{CF_3}PCP)Pt^+$ and its potential as a stable strongly electrophilic 14 e^- metal center for mediating substrate activation processes. Initial targets for this work included $({}^{CF_3}PCP)Pt(\eta^2\text{-}H_2)^+$ and $({}^{CF_3}PCP)Pt(\eta^2\text{-alkene})^+$.

We report here efforts to prepare the hydride or dihydrogen complexes $({}^{CF_3}PCP)PtH$ and $({}^{CF_3}PCP)Pt(\eta^2\text{-}H_2)^+$ and the synthesis of the adducts $({}^{CF_3}PCP)Pt(NC_5F_5)^+$ and $({}^{CF_3}PCP)Pt(\eta^2\text{-}C_2H_4)^+$. $({}^{CF_3}PCP)Pt(\eta^2\text{-}C_2H_4)^+$ serves as a catalyst for ethylene hydrogenation (0.30 turnovers h^{-1}, 70 °C) and also exhibits limited ethylene dimerization activity (0.07 turnovers h^{-1}, 155 °C). We find that $({}^{CF_3}PCP)Pt(NC_5F_5)^+$ reacts rapidly at subambient temperatures with Et_3SiH to give redistribution products. In the presence of excess ethylene or propylene, catalytic hydrosilation is observed with Et_3SiH and Cl_3SiH and $({}^{CF_3}PCP)Pt(\eta^2\text{-}C_2H_4)^+$ under ambient conditions. The underlying mechanism of these reactions is discussed.

Results and Discussion

Attempted Synthesis of $({}^{CF_3}PCP)Pt(H)$ and $({}^{CF_3}PCP)Pt(\eta^2\text{-}H_2)^+$. The synthesis of $({}^{tBu}PCP)PtH$ from $({}^{tBu}PCP)PtCl$ and $NaBH_4$ or $LiAlH_4$ is well known.[7] However, treatment of $({}^{CF_3}PCP)PtCl$ with hydride reagents $NaBH_4$, $LiAlH_4$, and $LiEt_3BH$ led to uncharacterized product mixtures with no associated ^1H NMR hydride resonances. Treatment of $({}^{CF_3}PCP)PtCl$ or $({}^{CF_3}PCP)PtMe$ with either stoichiometric or excess Et_3SiH similarly did not afford identifiable products. The reaction of $({}^{CF_3}PCP)PtCl$ with excess $PhSiH_3$ in benzene resulted in vigorous hydrogen evolution; after 5 h, the solution was a deep red color, and ^{31}P NMR showed only uncoordinated ${}^{CF_3}PCPH$. Some insight into these observations is given by the reaction of $({}^{CF_3}PCP)PtCl$ with KH in tetrahydrofuran (THF):

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(6) Adams, J. J.; Lau, A.; Arulsamy, N.; Roddick, D. M. *Inorg. Chem.* **2007**, *46*, 11328–11334.

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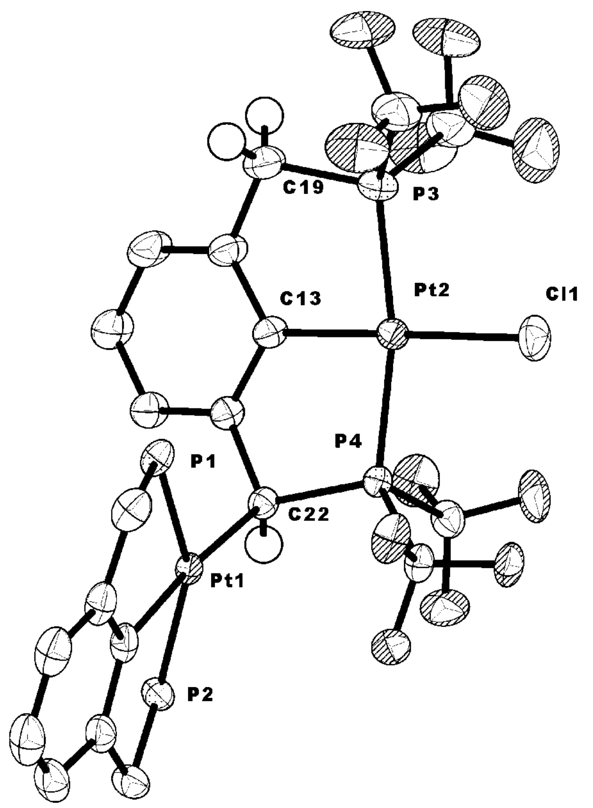
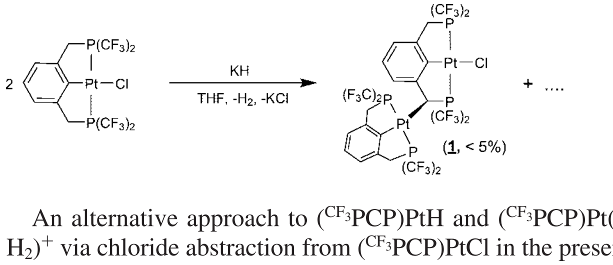


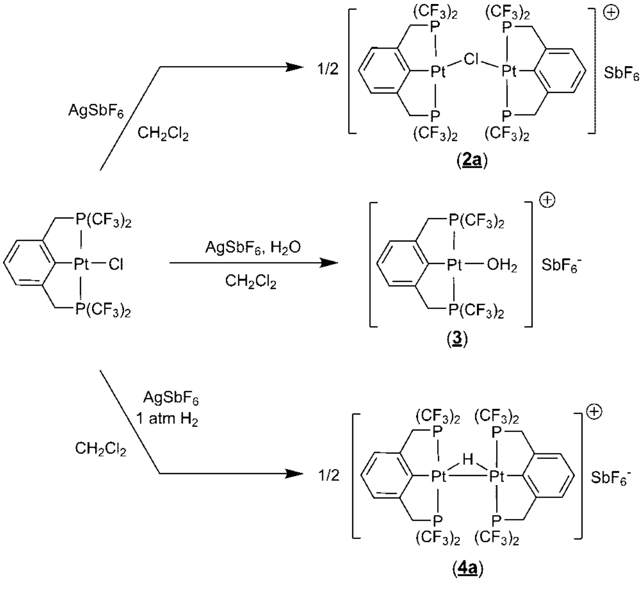
Figure 1. Molecular structure of (^{CF_3}PCP)Pt[κ^1-C,κ^3-P,C,P-2,6-(CHP(CF$_3$)$_2$)(CH$_2$P(CF$_3$)$_2$)-C$_6$H$_3$]PtCl (**1**) with partial atom labeling scheme (50% probability ellipsoids). Only one of the independent molecular units is shown. Aromatic hydrogen atoms and the CF$_3$ groups on P1 and P2 are omitted for clarity. Selected metrical data: Pt(1)−P(1), 2.2475(8); Pt(1)−P(2), 2.2206(8); Pt(1)−Cl(1), 2.100(3); Pt(1)−C(22), 2.182(3); Pt(2)−P(3), 2.2292(8); Pt(2)−P(4), 2.2356(7); Pt(2)−C(13), 2.033(3); Pt(2)−Cl(1), 2.2656(7). P(1)−Pt(1)−P(2), 153.59(3); C(1)−Pt(1)−C(22), 174.61(11); P(3)−Pt(2)−P(4), 163.08(3); C(13)−Pt(2)−Cl(1), 179.05(9).

slow evaporation of a dichloromethane filtrate extract of the initial complex product mixture afforded a small amount (<5%) of an unusual metallated bimetallic product (^{CF_3}PCP)Pt[κ^1-C,κ^3-P,C,P-2,6-(CHP(CF$_3$)$_2$)(CH$_2$P(CF$_3$)$_2$)C$_6$H$_3$]PtCl (**1**) which was characterized by X-ray crystallography (eq 1, Figure 1). The origin of this metallated product is likely due to deprotonation of a benzylic CH$_2$ group by KH, which is rendered acidic by the adjacent P(CF$_3$)$_2$ center, followed by alkylation of unreacted (^{CF_3}PCP)PtCl. This sensitivity of the ^{CF_3}PCP ligand to benzylic deprotonation may explain a lack of success with hydridic/basic reagents, though we note that (^{CF_3}PCP)PtCl is cleanly alkylated, not deprotonated, by MeMgBr to form (^{CF_3}PCP)PtMe.[6]



(1)

Scheme 1



An alternative approach to (^{CF_3}PCP)PtH and (^{CF_3}PCP)Pt(η^2-H$_2$)$^+$ via chloride abstraction from (^{CF_3}PCP)PtCl in the presence of dihydrogen was also examined. In the absence of added hydrogen, (^{CF_3}PCP)PtCl combined with AgSbF$_6$ in CH$_2$Cl$_2$ cleanly produced the chloride-bridged dimer, {(^{CF_3}PCP)Pt}$_2$(μ-Cl)$^+$SbF$_6^-$ (**2a**) (Scheme 1), which was structurally characterized (see later). In the presence of water, halide abstraction by AgSbF$_6$ yielded the aquo complex (^{CF_3}PCP)Pt(H$_2$O)$^+$SbF$_6^-$ (**3**). In the presence of 1 atm of H$_2$, the hydride-bridged cation {(^{CF_3}PCP)Pt}$_2$(μ-H)$^+$SbF$_6^-$ (**4a**) was cleanly produced. Monitoring the reaction between (^{CF_3}PCP)PtCl and AgSbF$_6$ by NMR in CD$_2$Cl$_2$, acetone-d_6, THF, and 1,2-difluorobenzene under 1−3 atm of H$_2$ showed only **4a** being formed, with no evidence for the intermediacy of (^{CF_3}PCP)Pt(η^2-H$_2$)$^+$ or (^{CF_3}PCP)PtH. There was no change in the course of the reaction in the presence of excess (~4 equiv) added Et$_3$N. The formulation of **4a** as a hydride-bridged cation is clearly indicated by ^{1}H NMR, which exhibits a pentet ($^2J_{PH}$ = 10 Hz) hydride resonance at δ −5.33 with a characteristic 1:8:18:8:1 splitting due to two equivalent platinum centers with natural abundance ^{195}Pt ($^1J_{PtH}$ = 254 Hz). The molecular structure of **4a** has been determined (see later).

Protonolysis of (^{CF_3}PCP)PtMe by the mesitylenium acid reagent (C$_6$Me$_3$H$_4$)$^+$B(C$_6$F$_5$)$_4^-$ was also examined. In methylene chloride, the chloride-bridged dimer {(^{CF_3}PCP)Pt}$_2$(μ-Cl)$^+$B(C$_6$F$_5$)$_4^-$ (**2b**) was cleanly produced in the absence of hydrogen gas (Scheme 1). We have recently reported the analogous production of {(dfepe)Pt(Me)}$_2$(μ-Cl)$^+$ from (dfepe)PtMe$_2$ and (C$_6$Me$_3$H$_4$)$^+$B(C$_6$F$_5$)$_4^-$ in CH$_2$Cl$_2$.[8] In the less reactive solvent 1,2-difluorobenzene under 1 atm of H$_2$, {(^{CF_3}PCP)Pt}$_2$(μ-H)$^+$B(C$_6$F$_5$)$_4^-$ (**4b**) was exclusively produced.

The protonolysis of (^{CF_3}PCP)PtMe by (C$_6$Me$_3$H$_4$)$^+$B(C$_6$F$_5$)$_4^-$ in 1,2-difluorobenzene was monitored by VT NMR. Upon thawing at −30 °C, evolution of methane was observed and a new major species (ca. 70−80%) was produced. This product had significant shifts in ^{1}H, ^{19}F, and ^{31}P NMR resonances relative to (^{CF_3}PCP)PtMe (see Experimental Section) and persisted in solution at ambient temperatures. Attempts to isolate the major product from this reaction, however, were unsuccessful. In the presence of 3 atm of H$_2$, −30 °C spectra again show the same major product with no associated hydride resonances. Upon warming to 10 °C, however, the hydride-bridged dimer **4b** was formed. At 25 °C, ~60% had converted to **4b**, and complete conversion occurred after 20 min at 25 °C.

Interestingly, the elusive hydride complex (^{CF_3}PCP)PtH has been observed as a transient species in the reaction of (^{CF_3}PCP)PtCl with Et$_3$Si$^+$B(C$_6$F$_5$)$_4^-$ in 1,2-difluorobenzene. After several minutes at ambient temperatures ^{1}H NMR spectra

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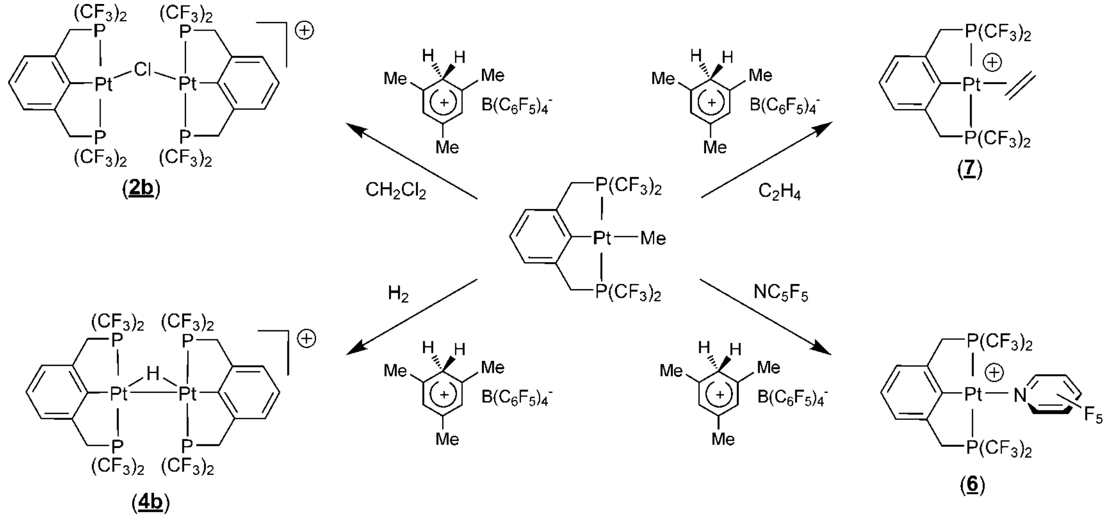
[8] Basu, S.; Arulsamy, N.; Roddick, D. M. *Organometallics* **2008**, *27*, 3659–3665.

Scheme 2



showed a 2:1 mixture of hydride-bridged dimer **4b** and a new species with a triplet hydride resonance at δ −5.73 ($^1J_{\mathrm{PtH}} = 7$ Hz, $^2J_{\mathrm{PH}} = 224$ Hz) which we assign to ($^{\mathrm{CF_3}}$PCP)PtH (**5**). After 3 h at ambient temperature, **5** quantitatively converted to the hydride-bridged dimer. VT NMR experiments confirmed the formation of the hydride complex **5**: at −30 °C, an ~80:20 mixture of ($^{\mathrm{CF_3}}$PCP)PtH and **4b** was observed, and at −20 °C a 50% conversion to the cationic dimer had occurred. The ultimate source of the hydride was not identified. Attempts to extract neutral complex **5** from the ($^{\mathrm{CF_3}}$PCP)PtCl and $\mathrm{Et_3Si^+B(C_6F_5)_4^-}$ reaction mixture into benzene or pentafluoropyridine resulted in the precipitation of **4b**.

Control experiments were carried out: treating ($^{\mathrm{CF_3}}$PCP)Pt$\mathrm{(NC_5F_5)^+B(C_6F_5)_4^-}$, a labile source of the ($^{\mathrm{CF_3}}$PCP)Pt$^+$ moiety (see below), with $\mathrm{Et_3SiCl}$ in 1,2-difluorobenzene resulted in no reaction after heating at 100 °C for 24 h. However, reaction of ($^{\mathrm{CF_3}}$PCP)Pt$\mathrm{(NC_5F_5)^+B(C_6F_5)_4^-}$ with $\mathrm{Et_3Si^+B(C_6F_5)_4^-}$ gave the hydride complex **5** in 70% yield after 10 min at RT, as judged by NMR spectroscopy. Interestingly, after 48 h, **5** had reverted back to primarily ($^{\mathrm{CF_3}}$PCP)Pt$\mathrm{(NC_5F_5)^+B(C_6F_5)_4^-}$ (90%) and only ~10% of the hydride-bridged dimer **4b** was observed. VT ^{1}H and ^{13}C NMR spectra showed a series of resonances in the ethylsilyl region which suggest that the silyl cation from $\mathrm{Et_3Si^+B(C_6F_5)_4^-}$ undergoes complex reactivity and is likely the source for the hydride ligand.

Synthesis of ($^{\mathrm{CF_3}}$PCP)Pt(L)$^+$ (L = $\mathrm{NC_5F_5}$, $\mathrm{C_2H_4}$). The transient ($^{\mathrm{CF_3}}$PCP)Pt$^+$ moiety can be efficiently trapped by added ligands. Thus, the reaction between ($^{\mathrm{CF_3}}$PCP)PtMe and $\mathrm{(C_6Me_3H_4)^+B(C_6F_5)_4^-}$ in the presence of pentafluoropyridine or ethylene cleanly afforded ($^{\mathrm{CF_3}}$PCP)Pt$\mathrm{(NC_5F_5)^+B(C_6F_5)_4^-}$ (**6**) and ($^{\mathrm{CF_3}}$PCP)Pt(η^2-$\mathrm{C_2H_4)^+B(C_6F_5)_4^-}$ (**7**), respectively (Scheme 2).

In our recently reported syntheses of (dfepe)Pt(Me)(L)$^+$ complexes, we noted that methide abstraction from (dfepe)$\mathrm{PtMe_2}$ by trityl cation did not readily occur. In contrast, ($^{\mathrm{CF_3}}$PCP)PtMe does react with $\mathrm{Ph_3C^+B(C_6F_5)_4^-}$ in the presence of $\mathrm{C_2H_4}$ or pentafluoropyridine to also give **6** and **7**, presumably due to the greater trans-labilizing ability of the PCP aryl unit. In the absence of trapping ligand, 80% conversion to a new species was observed by NMR; ^{31}P NMR spectra show a major resonance at 65.8 ppm ($^1J_{\mathrm{PtP}} = 3480$ Hz), ^{19}F NMR spectra show a corresponding new $\mathrm{PCF_3}$ multiplet at −55.8, and a new benzylic proton resonance was observed at 2.75 ppm. The methyl resonance of 1,1,1-triphenylethane was also observed at 0.89 ppm in ^{1}H NMR spectra. The spectroscopic data obtained for the reaction of ($^{\mathrm{CF_3}}$PCP)PtMe and trityl cation does *not* match data for the product from protonolysis in the absence of trapping ligands. We are not able to account for this difference. ^{13}C NMR spectra for **7** show an ethylene resonance at δ 87.3 with a $^1J_{\mathrm{CH}}$ coupling of 168 Hz, somewhat higher than the free ethylene value of 157 Hz. This is consistent with the very high ν(CO) value observed for the analogous carbonyl complex ($^{\mathrm{CF_3}}$PCP)Pt(CO)$^+$ (2143 cm^{-1})[8] and similarly reflects limited metal backbonding in this system. A VT ^{1}H NMR experiment with **7** and 1 equiv of $\mathrm{C_2H_4}$ was carried out: some broadening and shifting of the free and coordinated $\mathrm{C_2H_4}$ resonances were observed, but no coalescence occurred up to 100 °C in 1,2-difluorobenzene.

Crystallographic Studies. All structurally characterized complexes consist of square planar platinum units with minor deviations from planarity stemming from steric influences. The κ^1,κ^3 metallated bridging mode observed in **1** has not been previously observed in PCP ligand coordination chemistry, though α-carbon phosphine metalation and dimer formation is known for dppm,[9] dmpe,[10] and $\mathrm{Ph_2P}$(cyclopentadienyl) phosphine systems.[11] In **1**, the environment around the platinum attached to the benzylic position (Pt1) is distorted with the phosphorus atoms bent slightly (0.20, 0.21 Å from the least-squares Pt coordination plane) toward the less sterically crowded PCP arene ring and away from the $\mathrm{P(CF_3)_2}$ group adjacent to the point of metalation (Figure 1). The planar coordination environment about Pt(2), in contrast, has deviations less than 0.07 Å and reflects less sterically induced distortion. A metrical parameter that exhibits a good correlation with ($^{\mathrm{CF_3}}$PCP)Pt steric environment is the P−Pt−P bond angle. In relatively undistorted square planar complexes and in the Pt(2) unit of **1**, P−Pt−P angles range between 161° and 163°. For the Pt(1) center in **1** (153.6°) and the dimeric bridged complexes **2a** (158.7° ave) and **4a** (153.6° ave), this angle decreases due to bending the pendant phosphine pincer arms out of the platinum coordination plane.

For all complexes, the C(aryl)−Pt distances vary according to the *trans* influence of the remaining ligand. The longest C(aryl)−Pt distance is observed for Pt(1) in **1** (2.100(3) Å), where the *trans* group is the benzyl group of the pincer ligand

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[9] Brown, M. P.; Yavari, A. *J. Organomet. Chem.* **1983**, *256*, C19–C22.

[10] Cotton, F. A.; Hunter, D. L.; Frenz, B. A. *Inorg. Chim. Acta* **1975**, *15*, 155–160.

[11] Fallis, K. A.; Anderson, G. K.; Lin, M.; Rath, N. P. *Organometallics* **1994**, *13*, 478–488.

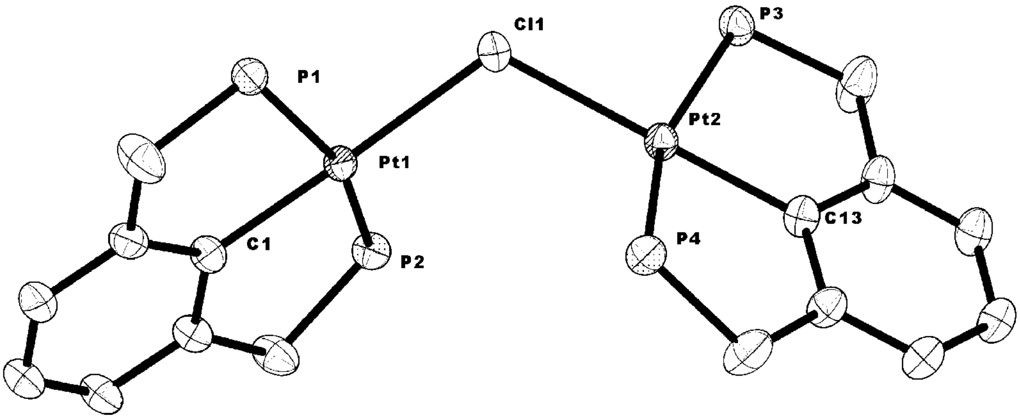

Figure 2. $[(^{CF_3}PCP)Pt]_2(\mu\text{-}Cl)^+SbF_6^-$ (**2a**) with partial atom labeling scheme (50% probability ellipsoids). Phosphine CF_3 groups have been omitted for clarity. Selected metrical data: Pt(1)−P(1), 2.2372(7); Pt(1)−P(2), 2.2483(6); Pt(1)−C(1), 2.035(2); Pt(1)-C1(1), 2.4196(6); Pt(2)−P(3), 2.2423(7); Pt(2)−P(4), 2.2421(7); Pt(2)−C(13), 2.029(3); Pt(2)−Cl(1), 2.4144(6); Pt(1)−Pt(2), 4.0872(2); P(1)−Pt(1)−P(2), 158.59(3); C(1)−Pt(1)−Cl(1), 175.91(7); P(3)−Pt(2)−P(4), 158.80(3); C(13)−Pt(2)−Cl(1), 176.75(7); Pt(1)−Cl(1)−Pt(2), 115.45(3).

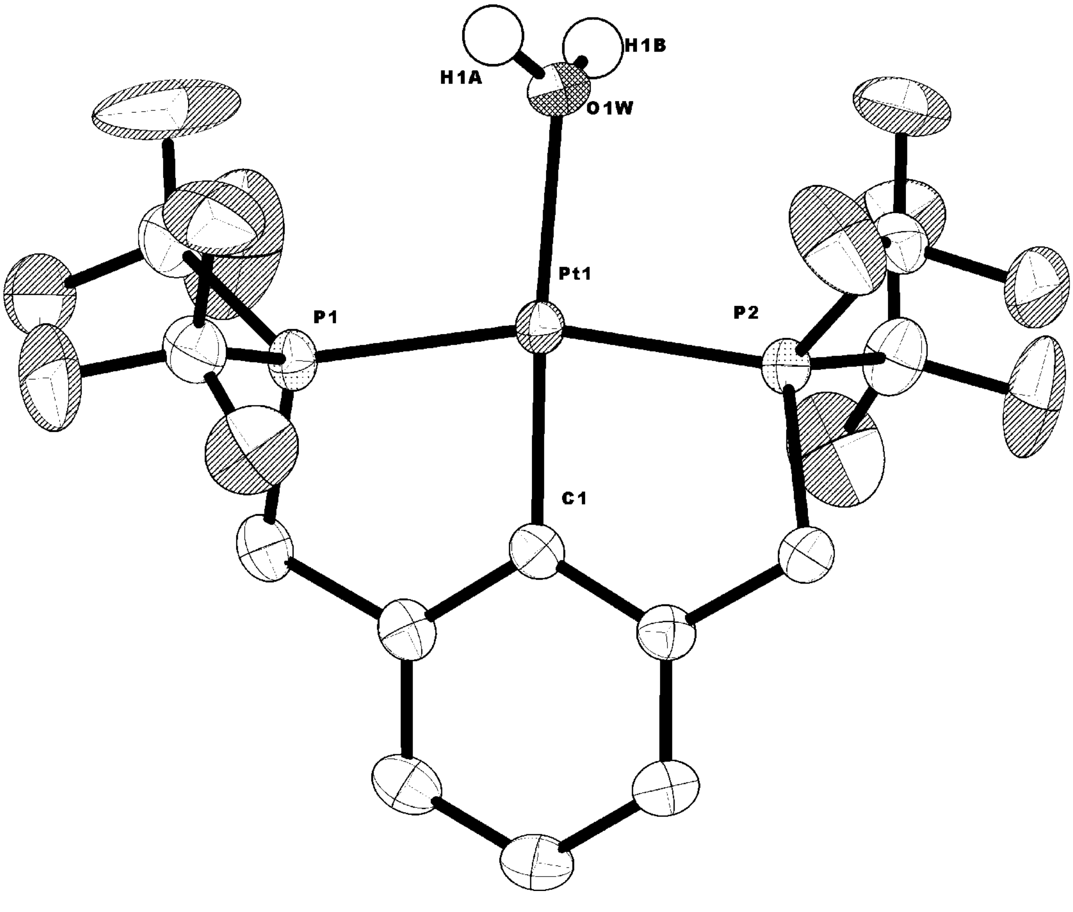

Figure 3. Molecular structure of $(^{CF_3}PCP)Pt(H_2O)^+SbF_6^-$ (**3**) with partial atom labeling scheme (50% probability ellipsoids). Only one of the independent molecular units is shown. Selected metrical data: Pt(1)−C(1), 2.016(2); Pt(1)-O(1W), 2.145(2); Pt(1)−P(2), 2.2446(7); Pt(1)−P(1), 2.2449(7). C(1)−Pt(1)−O(1W), 176.25(10); P(2)−Pt(1)−P(1), 163.29(2).

on Pt(2). Of intermediate length are C(aryl)−Pt in the hydride-bridged dimer **4a** (2.066(2), 2.067(2) Å) and in ethylene complex **7** (2.051(3) Å), and the shortest bond distances are observed for Pt(2) in **1** (2.033(3) Å), **2a** (2.029(3), 2.035(2) Å), **3** (2.016(2) Å), and **6** (2.0302(19) Å) for terminal chloride, bridging chloride, water, and pentafluoropyridine adducts, respectively.

Complexes **2a** and **4a** consist of two bridged square planar platinum centers bridged by a chlorine and a hydrogen atom, respectively (Figures 2 and 4). The C(aryl)−Pt-H angles in **4a** (170.1, 170.6°) and the C(aryl)−Pt−Cl angles in **2a** (175.9, 176.8°) reflect an essential linear coordination geometry, with the smaller angle in the hydride dimer ascribed to a greater steric interaction between the two metal units. Relief of steric crowding is achieved by canting the platinum centers by 85.4° for **2a** and 74.8° for **4a**. The interplatinum distance in **4a** is 2.832 Å, which is on the low end of the range reported for similar $\{(X)(R_3P)_2Pt\}_2(\mu\text{-}H)^+$ structures (2.710−3.237 Å).[12,13] Venanzi et al. has noted that hydride-bridged dimers in this class of compounds have shorter Pt−Pt distances for less electron-

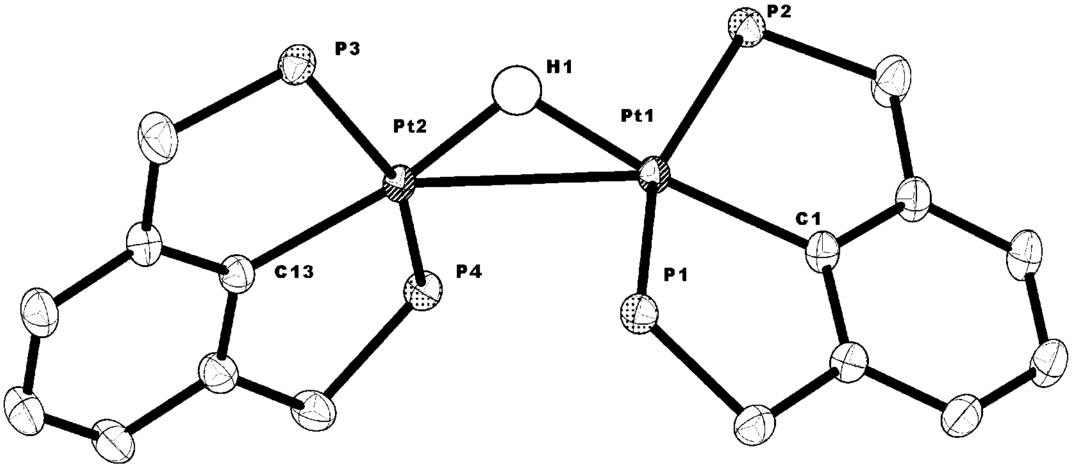

Figure 4. Molecular structure of $[(^{CF_3}PCP)Pt]_2(\mu\text{-}H)^+SbF_6^-$ (**4a**) with partial atom labeling scheme (50% probability ellipsoids). Phosphine CF_3 groups have been omitted for clarity. Selected metrical data: Pt(1)−Pt(2), 2.8324; Pt(1)−P(1), 2.2461(5); Pt(1)−P(2), 2.2244(5); Pt(1)−C(1), 2.066(2); Pt(1)−H(1), 1.79(4); Pt(2)−P(3), 2.2227(5); Pt(2)−P(4), 2.2486(5); Pt(2)−C(13), 2.067(2); Pt(2)−H(1), 1.67(4). P(1)−Pt(1)−P(2), 153.56(2); C(1)−Pt(1)−H(1), 170.1(13); P(3)−Pt(2)−P(4), 153.662(19); C(13)−Pt(2)−H(1), 170.6(16); Pt(1)−H(1)−Pt(2), 110.05.

rich metal centers.[12] While a significant metal−metal interaction can be inferred in **4a**, where the Pt(1)−H−Pt(2) bond angle is 110°, the Pt−Cl−Pt bond angle in **2a** of 115.45° combined with long Pt−Cl bond lengths results in a nonbonding Pt−Pt distance of 4.087 Å.

The asymmetric unit for **3** contains two independent $(^{CF_3}PCP)Pt(H_2O)^+$ cations (Figure 3). In the Pt(1) unit, a C_2 twist of 13.2° of the PCP aromatic backbone and benzyl carbons with respect to the plane defined by the platinum and attached atoms is observed, whereas in the Pt(2) unit the PCP dibenzyl plane is not twisted but canted 9.9° above the platinum square plane. These two distinct types of distortions serve to relieve chelate strain in the (PCP)Pt moiety. A number of *trans*-$(R_3P)_2Pt(X)(H_2O)^+$ complexes have been reported with X = H,[14] Cl,[15] aryl,[16] or vinyl group as the *trans* ligand.[17] The Pt−O bond lengths found for $(^{CF_3}PCP)Pt(H_2O)^+SbF_6^-$ of 2.145(2) and 2.133(2) Å are somewhat shorter than the 2.175−2.19 Å range reported for complexes with X = aryl and are consistent with a stronger water−platinum interaction in this more electrophilic acceptor phosphine system.

$(^{CF_3}PCP)Pt(NC_5F_5)^+B(C_6F_5)_4^-$ (**6**) is only the fourth structurally characterized pentafluoropyridine complex (Figure 5).[8,18,19] The observed Pt−N bond distance of 2.1727(16) Å is very similar to that found for $(dfepe)Pt(Me)(NC_5F_5)^+B(C_6F_5)_4^-$ (2.153(4) Å),[8] in keeping with the strong *trans* influence of both phosphorus and hydrocarbyl groups. The NC_5F_5 aryl plane is essentially perpendicular to the Pt coordination plane (interplanar angle = 89.6°) and is comparable to that found for (tmeda)Pt(Me)-$(NC_5F_5)^+B[m\text{-}(CF_3)_2C_6H_3]_4^-$ (88°) and $(dfepe)Pt(Me)(NC_5F_5)^+B(C_6F_5)_4^-$ (78°).

$(^{CF_3}PCP)Pt(\eta^2\text{-}C_2H_4)^+B(C_6F_5)_4^-$ (**7**) is the first structurally characterized ethylene complex in the PCP Pt motif (Figure 6). The ethylene adduct is symmetrically bonded to the Pt metal center with identical $Pt-C(C_2H_4)$ bonds of 2.305(5) and 2.306(4) Å, and the ethylene Pt plane is nearly perpendicular to the aryl plane with an interplanar angle of 88.26°. The ethylene C−C bond (1.305(7) Å) is significantly shorter than the complex $(^{Ph}PNP)Pt(C_2H_4)^{2+}$ (1.359(10) Å).[20] In contrast, the $Pt-C(C_2H_4)$ bonds are ~0.13 Å longer, consistent with the greater *trans* influence of the aryl backbone compared to the pyridine backbone.

Reactivity Studies

Reactivity of $(^{CF_3}PCP)Pt(NC_5F_5)^+B(C_6F_5)_4^-$ with H_2 and R_3SiH. The pentafluoropyridine adduct $(^{CF_3}PCP)Pt(NC_5F_5)^+B(C_6F_5)_4^-$ (**6**) serves as a convenient source of the electrophilic 16-electron $(^{CF_3}PCP)Pt^+$ moiety for study. Earlier, we noted that generation of $(^{CF_3}PCP)Pt^+$ in the presence of H_2 resulted in the formation of the hydride-bridged dimer, $\{(^{CF_3}PCP)Pt\}_2(\mu\text{-}H)^+$. VT NMR studies of $(^{CF_3}PCP)Pt(NC_5F_5)^+B(C_6F_5)_4^-$ in 1,2-difluorobenzene under 3 atm of H_2 at −20 °C did not show any displacement of pentafluoropyridine to form observable $\eta^2\text{-}H_2$ or classical hydride intermediates, but rather slow conversion to $\{(^{CF_3}PCP)Pt\}_2(\mu\text{-}H)^+$ at ambient temperature over the course of 3 days. In contrast, **6** reacts more rapidly with silanes: addition of 10 equiv of Et_3SiH in 1,2-difluorobenzene at 27 °C resulted in the rapid generation of $(^{CF_3}PCP)Pt\}_2(\mu\text{-}H)^+$. Initial spectra after 2 min showed a 1:1.4 mixture of $(^{CF_3}PCP)Pt(H)/\{(^{CF_3}PCP)Pt\}_2(\mu\text{-}H)^+$, which after 10 min had completely converted to the cationic hydride dimer. Over the course of 45 min, a slow redistribution reaction was

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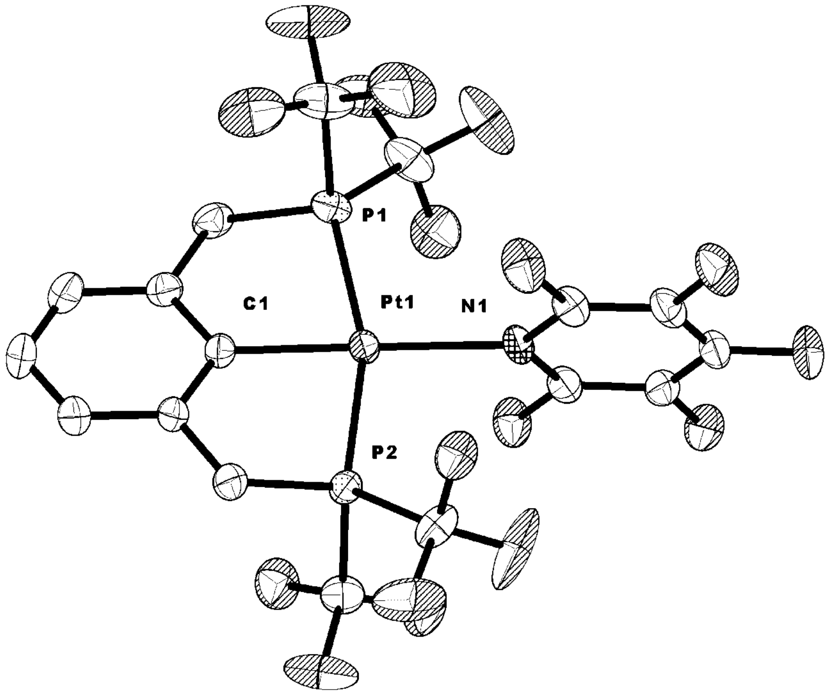
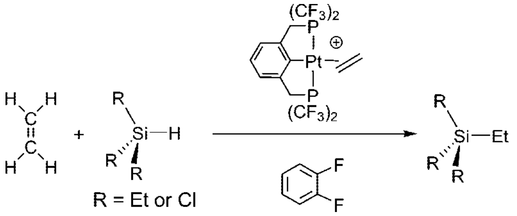


Figure 5. Molecular structure of $(^{CF_3}PCP)Pt(NC_5F_5)^+B(C_6F_5)_4^-$ (**6**) with partial atom labeling scheme (50% probability ellipsoids). Selected metrical data: Pt(1)−C(1), 2.030(2); Pt(1)−N(1), 2.173(2); Pt(1)−P(1), 2.2443(5); Pt(1)−P(2), 2.2424(5); P(1)−Pt(1)−P(2), 161.34(2); C(1)−Pt(1)−N(1), 179.19(7).

observed to generate a new ethylsilyl product, which was identified by ^1H and ^{13}C NMR as tetraethylsilane. After 22.5 h, the Et_3SiH/Et_4Si ratio was 1.67:1. Observation of a singlet at δ 3.43 confirmed the generation of free H_2 in this reaction.

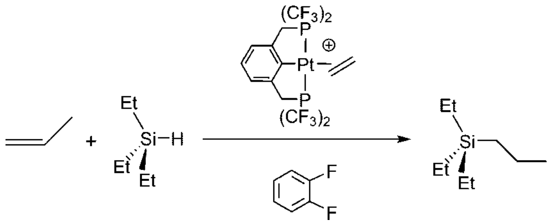
Hydrosilation and Hydrogenation Activity of $(^{CF_3}PCP)Pt(\eta^2\text{-alkene})^+B(C_6F_5)_4^-$ Complexes. 16-Electron $(PCP)Pt(L)^+$ complexes are formally coordinatively saturated Pt(II) systems, with no readily accessible site for coreactant A−B bond oxidative addition and subsequent reaction with substrate L. Nevertheless, $(^{CF_3}PCP)Pt(\eta^2\text{-}C_2H_4)^+B(C_6F_5)_4^-$ (**7**) has some limited alkene hydrogenation catalyst activity. At ambient temperature, 1.7 equiv of ethane were produced from 43 equiv of C_2H_4 and 3 atm of H_2 after 77 h. Heating this reaction mixture for 16 h at 70 °C generated 6.5 equiv of CH_3CH_3. Thus, the rate of hydrogenation is 0.02 turnovers h^{-1} at ambient temperature and 0.30 turnovers h^{-1} at 70 °C.

Many metal systems efficiently catalyze hydrosilation of olefins with tertiary silanes;[21] however, to our knowledge, no PCP-based catalysts are known. We report that $(^{CF_3}PCP)Pt(\eta^2\text{-}C_2H_4)^+$ is a modestly active hydrosilation catalyst (eq 2). Treatment of **7** with 70 equiv of C_2H_4 and 15 equiv of Et_3SiH as a limiting reagent in 1,2-difluorobenzene gave complete conversion to the hydrosilation product Et_4Si after 2 min at ambient temperature. The chlorosilane Cl_3SiH reacted much more slowly to give 91% conversion to $EtSiCl_3$ after 5 h (~5 turnovers h^{-1}). Monitoring the reaction of **7** with 8.9 equiv of ethylene with 14.8 equiv of Et_3SiH at −10 °C in 1,2-difluorobenzene by ^1H NMR showed a first order disappearance of ethylene with an apparent rate constant of 0.005 s^{-1} (~18 turnovers h^{-1}).



(2)

Hydrosilation of propene with Et_3SiH promoted by $(^{CF_3}PCP)Pt(\eta^2\text{-}C_2H_4)^+$ is regioselective: reaction of 6 equiv of Et_3SiH with 22 equiv of propene at room temperature for 40 min resulted in complete conversion to the *n*-propyl product, $Et_3Si(CH_2CH_2CH_3)$, with no isopropyl isomer $Et_3Si(CH(CH_3)_2)$, as judged by ^1H and ^{13}C NMR (eq 3). During the course of reaction, **7** underwent clean conversion to the propylene complex $(^{CF_3}PCP)Pt(\eta^2\text{-}H_2C{=}C(H)Me)^+B(C_6F_5)_4^-$ (**8**), which was spectroscopically characterized and independently prepared from the reaction of the pentafluoropyridine complex **6** and propene. The attempted hydrosilation of the more sterically hindered tertiary olefin 1-methyl-1-cyclohexene resulted in complicated mixtures.



(3)

Ethylene Dimerization and Isomerization of 1-Butene by $(^{CF_3}PCP)Pt(\eta^2\text{-}C_2H_4)^+B(C_6F_5)_4^-$. Ni(II) and Pd(II) systems exhibit high catalytic activities for ethylene dimerization, oligomerization, or polymerization.[22] Limited activity for dimerization has been reported for Pt(II) complexes $(dfepe)Pt(Me)(O_2CCF_3)$ at 80 °C and $(diimine)Pt(H)(\eta^2\text{-}$

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[21] For recent examples, see. (a) Hamze, A.; Provot, O.; Brion, J.-D.; Alami, M. *Tetrahedron Lett.* **2008**, *49*, 2429–2431. (b) Deglmann, P.; Ember, E.; Hofmann, P; Pitter, S.; Walter, O. *Chem.—Eur. J.* **2007**, *13*, 2864–2879. (c) Bruner, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 2749–2750. (d) Field., L. D.; Ward, A. J. *J. Organomet. Chem.* **2003**, *681*, 91–97. (e) Glaser, P. B.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 13640–13641.

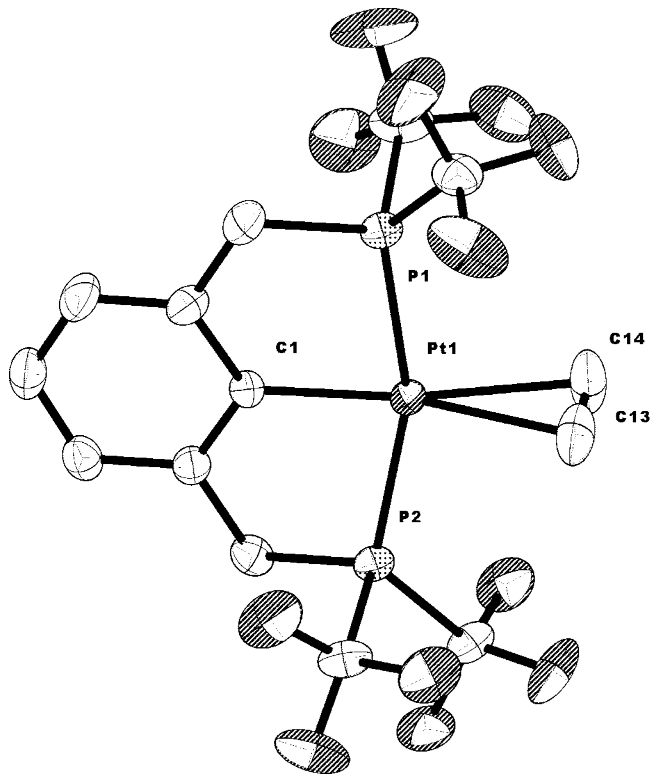
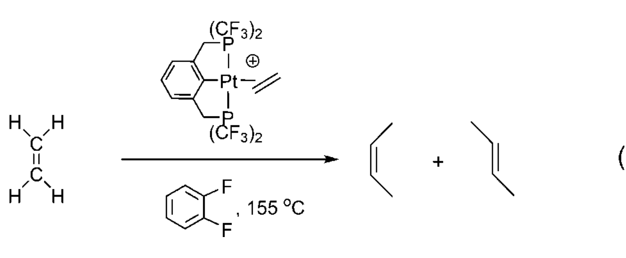


Figure 6. Molecular structure of $(^{CF_3}PCP)Pt(C_2H_4)^+B(C_6F_5)_4^-$ (**7**) with partial atom labeling scheme (50% probability ellipsoids). The anion and hydrogens are omitted for clarity. Selected metrical data: Pt(1)−C(1), 2.051(3); Pt(1)−P(1), 2.2510(10); Pt(1)−P(2), 2.2543(9); Pt(1)−C(14), 2.306(4); Pt(1)−C(13), 2.305(5); C(13)−C(14), 1.305(7). C(1)−Pt(1)−P(1), 80.78(11); C(1)−Pt(1)−P(2), 79.74(10); P(1)−Pt(1)−P(2), 160.36(4).

$C_2H_4)^+BAr_f^-$ at 100 °C.[23,24] More recently, our research group has shown the system $[(dfepe)Pt(Me)(NC_5F_5)]^+B(C_6F_5)_4^-$ to be orders of magnitude more reactive than these related systems.[8] Interestingly, despite the absence of an adjacent alkyl ligand to initiate and promote insertion, **7** exhibited limited catalytic activity for the dimerization of ethylene at high temperatures to a ~2:1 *trans*/*cis* mixture of 2-butenes (0.07 turnovers h^{-1}, 155 °C, 1:1 1,2-difluorobenzene/benzene (eq 4)). After 60 h at 155 °C, about 10% decomposition of complex **7** was noted.



(4)

Alkene isomerization catalysis generally proceeds via metal hydride or metal-allyl hydride intermediates[25] and involves the availability of an adjacent hydride ligand or an additional site of coordinative unsaturation to support an equilibrium between L_nM(alkene) and $L_{n-1}M$(allyl)(H). Nevertheless, **7** exhibits modest alkene isomerization activity: warming a mixture of **7** and 10 equiv of 1-butene to 80 °C in 1,2-difluorobenzene produced 3.6 equiv of a ~1:1 mixture of *cis*- and *trans*-2-butene. A single platinum species was observed during the course of reaction and was tentatively assigned as $(^{CF_3}PCP)Pt(\eta^2\text{-}H_2C{=}C(H)CH_2Me)^+B(C_6F_5)_4^-)$.

Summary

The initial goal of preparing a labile source of the $(^{CF_3}PCP)Pt^+$ moiety has been partially realized with the preparation of the pentafluoropyridine adduct $(^{CF_3}PCP)Pt(NC_5F_5)^+$. The reactions of $(^{CF_3}PCP)PtMe$ with $(C_6Me_3H_4)^+B(C_6F_5)_4^-$ or $Ph_3C^+B(C_6F_5)_4^-$ in 1,2-difluorobenzene afford major species which are similar yet not spectroscopically identical. A preliminary assignment of these products as either the ion pair $(^{CF_3}PCP)Pt^+B(C_6F_5)_4^-$ or solvate $(^{CF_3}PCP)Pt^+(solv)B(C_6F_5)_4^-$ is not supported by their lack of reactivity with H_2 at low temperature to form $(^{CF_3}PCP)Pt(\eta^2\text{-}H_2)^+$, and work is continuing to further characterize these products.

In contrast to $(^{tBu}PCP)Pt(\eta^2\text{-}H_2)^+$, which is moderately stable under a H_2 atmosphere,[7a] the unobserved dihydrogen adduct $(^{CF_3}PCP)Pt(\eta^2\text{-}H_2)^+$ is unstable with respect to proton loss and formation of the cationic hydride-bridged dimer $\{(^{CF_3}PCP)Pt\}_2(\mu\text{-}H)^+B(C_6F_5)_4^-$ (**4**). Thus far, all attempts to cleanly prepare and isolate the neutral hydride $(^{CF_3}PCP)PtH$ have been unsuccessful. We believe that any $(^{CF_3}PCP)PtH$ formed in the presence of a potential source of $(^{CF_3}PCP)Pt^+$ is efficiently trapped to give **4**. The result that $(^{CF_3}PCP)Pt^+$ (generated initially either by Cl^- abstraction from $(^{CF_3}PCP)PtCl$ or by pentafluoropyridine displacement from $(^{CF_3}PCP)Pt(NC_5F_5)^+$) reacts with the electrophilic reagent $Et_3Si^+B(C_6F_5)_4^-$ to form substantial amounts of $(^{CF_3}PCP)PtH$ is quite surprising and not readily explained.

Hydrosilation catalysis by late transition metal systems generally follows a classic or modified Chalk−Harrod mechanism involving oxidative addition of Si−H bonds to a coordinatively unsaturated metal center.[26] While hydrosilation by labile $(phen)Pd(Me)(L)^+$ systems proceed via alkene adducts, $(phen)Pd(SiR_3)(\eta^2\text{-alkene})^+$,[27] the 16-$e^-$ Pt(II) complex $(^{CF_3}PCP)Pt(\eta^2\text{-}C_2H_4)^+$ lacks a readily accessible site for silyl coordination. Nevertheless, hydrosilation (and olefin hydrogenation) is observed to occur. No silane addition intermediates have been observed at −30 °C which would support a tentative reaction mechanism. We speculate that either (a) direct addition of Si−H bonds to alkene activated by the electrophilic metal center is occurring, (b) Si−H bond addition to form tetravalent platinum intermediates takes place, or (c) dissociation of a pendant phosphine group and/or Si−H addition across the PCP aryl−Pt bond is occurring.[28] The release of $^{CF_3}PCPH$ from reaction of

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$({}^{CF_3}PCP)PtCl$ with excess $PhSiH_3$ may reflect the latter reaction pathway. The greater reactivity of $({}^{CF_3}PCP)Pt(\eta^2\text{-}C_2H_4)^+$ toward the more electron-rich silane Et_3SiH relative to Cl_3SiH is in qualitative support of a nucleophilic silane addition reaction path. In a similar fashion, conventional alkene hydrogenation, dimerization, and isomerization catalysis by **7** requires additional coordination sites by either expanding the coordination sphere of $({}^{CF_3}PCP)Pt(alkene)^+$ or partial dissociation of the PCP framework.

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. Pentafluoropyridine and 1,2-difluorobenzene (Synquest, Inc.) were dried over activated 4 Å molecular sieves. Et_3SiH, Cl_3SiH, Et_3SiCl, and KH were purchased from Aldrich and used as received. Aprotic deuterated solvents used in NMR experiments were dried over activated 3 Å molecular sieves. Ethylene (Airgas), H_2 (US Welding), and propene (Aldrich) were used as received. Elemental analyses were performed by Desert Analytics. NMR spectra were obtained with a Bruker DRX-400 instrument. ^1H NMR spectra in 1,2-difluorobenzene were locked and referenced to the residual protons of acetone-d_6 sealed in a capillary. ^{31}P NMR spectra were referenced to an 85% H_3PO_4 external standard. ^{19}F NMR spectra were referenced to $CF_3CO_2CH_2CH_3$ (δ −75.32). $Ph_3C^+B(C_6F_5)_4^-$,[29] $(C_6Me_3H_4)^+B(C_6F_5)_4^-$,[29] $({}^{CF_3}PCP)PtCl$, and $({}^{CF_3}PCP)PtMe$ were prepared following literature procedures.[6] $Et_3Si^+B(C_6F_5)_4^-$ was prepared from $Ph_3C^+B(C_6F_5)_4^-$ and Et_3SiH following a modified literature procedure, isolated by triturating with petroleum ether, and stored at −25 °C in an inert atmosphere dry box.[29] $Ph_3C^+B(C_6F_5)_4^-$ was prepared from $KB(C_6F_5)_4$ and Ph_3CCl following a modified procedure.[30]

Reaction of $({}^{CF_3}PCP)PtCl$ with KH. $({}^{CF_3}PCP)Pt(Cl)$ (0.100 g, 0.149 mmol) was dissolved in 30 mL of THF, and 6 mg of KH (0.149 mmol) was added at ambient temperature. Vigorous bubbling occurred, and the solution turned initially purple and then pale yellow with a white precipitate. The solvent was removed; ^1H NMR spectra of the residue in C_6D_6 revealed a complex product mixture with no characteristic high field hydride resonances. The residue was dissolved in ~3 mL methylene chloride, filtered, and hexane was layered on top and allowed to slowly diffuse at ambient temperature. Less than a 5% yield of colorless crystals was obtained which was subsequently identified as $({}^{CF_3}PCP)Pt[\kappa^1\text{-}C,\kappa^{3-}P,C,P\text{-}2,6\text{-}(CHP(CF_3)_2)(CH_2P(CF_3)_2)C_6H_3]PtCl$ (**1**) by X-ray analysis.

$\{({}^{CF_3}PCP)Pt\}_2(\mu\text{-}Cl)^+SbF_6^-$ (2a). $({}^{CF_3}PCP)PtCl$ (0.200 g, 0.298 mmol) and $AgSbF_6$ (0.101 g, 0.298 mmol) were dissolved in 30 mL of methylene chloride and stirred for 24 h in the absence of light. AgCl and was filtered off, and the filtrate was reduced to ~7 mL and cooled to −78 °C, producing a white precipitate which was collected and dried under vacuum (0.197 g, 86% yield). Slow evaporation from methylene chloride yielded crystals suitable for X-ray diffraction. Anal. Calcd for $C_{24}H_{14}P_4F_{30}ClSbPt_2$: C, 18.68%; H, 0.92%. Found: C, 18.68%; H, 0.82%. ^1H NMR (CD_2Cl_2, 400.13 MHz, 20 °C): δ 7.32 (m, 3H; Ar), 4.06 (m, 4H; $ArCH_2$). ^{31}P NMR (CD_2Cl_2, 161.97 MHz, 20 °C): δ 63.0 (m, $^1J_{,PtP}$ = 3640 Hz). ^{19}F NMR (CD_2Cl_2, 376.50 MHz, 20 °C): δ −54.8 (m, PCF_3).

$\{({}^{CF_3}PCP)Pt\}_2(\mu\text{-}Cl)^+B(C_6F_5)_4^-$ (2b). Methylene chloride (1.5 mL) was condensed onto a mixture of $({}^{CF_3}PCP)PtMe$ (0.030 g, 0.046 mmol) and $(C_6Me_3H_4)^+B(C_6F_5)_4^-$ (0.041 g, 0.0.51 mmol) at −195 °C. Upon thawing, vigorous bubbling was observed and the reaction was allowed to warm to ambient temperature. Colorless needles began to precipitate after ~4 h, and slow evaporation to ~0.3 mL and removal of the supernatant gave 0.029 g (63%) of **2b**. ^1H, ^{31}P, and CF_3 ^{19}F NMR data for **2b** were identical to **2a** data.

$({}^{CF_3}PCP)Pt(H_2O)^+SbF_6^-$ (3). $({}^{CF_3}PCP)PtCl$ (0.113 g, 0.168 mmol) was added to $AgSbF_6$ (0.200 g, 0.585 mmol) wetted with water (50 μL, 2.77 mmol). Methylene chloride (20 mL) was added, and the reaction mixture was stirred at ambient temperature for 5 h. The resulting AgCl precipitate was filtered off, and crystalline white product (0.127 g, 85%) was precipitated from the filtrate by addition of ~75 mL of hexanes. Crystals suitable for X-ray diffraction were grown by the slow diffusion of hexane into a methylene chloride solution of **3**. Anal. Calcd for $C_{12}H_9P_2F_{18}OSbPt$: C, 16.20%; H, 1.02%. Found: C, 17.44%; H, 0.83%. ^1H NMR (CD_2Cl_2, 400.13 MHz, 20 °C): δ 7.32 (m, 3H; Ar), 4.08 (m, 4H; $ArCH_2$), 2.19 (br.s, 2H; H_2O). ^{31}P NMR (CD_2Cl_2, 161.97 MHz, 20 °C): δ 64.4 (m, $^1J_{PtP}$ = 3660 Hz). ^{19}F NMR (acetone-d_6, 376.50 MHz, 20 °C): δ −53.5 (m, PCF_3). IR (Nujol, cm^{-1}): $\nu(H_2O)$ = 3453 cm^{-1}.

$\{({}^{CF_3}PCP)Pt\}_2(\mu\text{-}H)^+SbF_6^-$ (4a). $({}^{CF_3}PCP)PtCl$ (0.250 g, 0.373 mmol) and $AgSbF_6$ (0.127 g, 0.373 mmol) were dissolved in 30 mL of methylene chloride at −78 °C, and the mixture was stirred under 1 atm of H_2 in the dark. The reaction was allowed to warm to ambient temperature and then stirred for an additional 20 h. The solid mixture was filtered off and then redissolved in ~10 mL acetone. AgCl was removed by filtration, and the acetone was removed from the filtrate and replaced by ~10 mL methylene chloride. Trituration and filtration afforded a pale yellow crystalline solid (0.136 g, 48% yield). Crystals suitable for X-ray diffraction were grown by slow evaporation from methylene chloride. Anal. Calcd for $C_{24}H_{15}P_4F_{30}SbPt_2$: C, 19.10%; H, 1.00%. Found: C, 19.11%; H, 0.99%. ^1H NMR (acetone-d_6, 400.13 MHz, 20 °C): δ 7.69 (m, 4H; Ar), 7.60 (m, 2H; Ar), 4.89 (m, 8H; CH_2), −5.33 (pp, $^1J_{PtH}$ = 254 Hz, $^2J_{PH}$ = 10 Hz, 1H; $Pt_2(\mu\text{-}H)$). ^{31}P NMR (acetone-d_6, 161.97 MHz, 20 °C): δ 70.6 (m, $^1J_{PtP}$ = 3470 Hz). ^{19}F NMR (acetone-d_6, 376.50 MHz, 20 °C): δ −54.7 (m, PCF_3).

$\{({}^{CF_3}PCP)Pt\}_2(\mu\text{-}H)^+B(C_6F_5)_4^-$ (4b).

Method A. 1,2-Difluorobenzene (20 mL) was condensed onto a mixture of $({}^{CF_3}PCP)PtMe$ (0.250 g, 0.384 mmol) and $(C_6Me_3H_4)^+B(C_6F_5)_4^-$ (0.338 g, 0.422 mmol) at −78 °C and placed under 1 atm of H_2. Upon thawing, vigorous bubbling was observed and the reaction mixture was allowed to warm with stirring to ambient temperatures and stirred an additional 4 h. The solvent volume was reduced to ~5, and 25 mL of petroleum ether was slowly added to precipitate an off-white solid (0.221 g, 59% yield). ^1H, ^{31}P, and CF_3 ^{19}F NMR data for **4b** were identical to **4a** data.

Method B. A mixture of $({}^{CF_3}PCP)PtCl$ (0.150 g, 0.224 mmol) and $Et_3Si^+B(C_6F_5)_4^-$ (0.195 g, 0.246 mmol) were dissolved in 20 mL of benzene. The initially colorless solution turned yellow after 1 h, and a precipitate began to form. The reaction mixture was stirred for 24 h and filtered to give pale yellow crystalline solid **4b** (0.200 g, 92% crude yield, ~90% purity by NMR).

Reaction of $({}^{CF_3}PCP)PtMe$ with $(C_6Me_3H_4)^+B(C_6F_5)_4^-$. The reaction between $({}^{CF_3}PCP)PtMe$ and $(C_6Me_3H_4)^+B(C_6F_5)_4^-$ was monitored by VT NMR. A 5 mm NMR tube fitted with a Teflon valve was charged with $({}^{CF_3}PCP)PtMe$ (0.018 g, 0.028 mmol), $(C_6Me_3H_4)^+B(C_6F_5)_4^-$ (0.024 g, 0.030 mmol), and 0.5 mL of 1,2-difluorobenzene and then placed under 3 atm of H_2. Upon thawing at −30 °C, gas evolution was observed and the production of methane was confirmed by ^1H NMR (δ −1.07). A single major (~70−80%) product was characterized spectroscopically. ^1H NMR: δ 2.53 (m, 4H; CH_2). ^{31}P NMR: δ 62.2 (m, $^1J_{PtP}$ = 3760 Hz). ^{19}F NMR: δ −53.7 (m, 12F; PCF_3), −131.8 (br.s, 8F; *ortho*-$B(C_6F_5)_4$), −162.4 (t,$^3J_{FF}$ = 19 Hz, 4F; *para*-$B(C_6F_5)_4$), −166.4 (m, 8F; *meta*-$B(C_6F_5)_4$).

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Reaction of (^{CF_3}PCP)PtMe with $Ph_3C^+B(C_6F_5)_4^-$. The reaction between (^{CF_3}PCP)PtMe and $Ph_3C^+B(C_6F_5)_4^-$ was monitored at ambient temperature by NMR. A 5 mm NMR tube fitted with a Teflon valve (Chemglass, CG-512) was charged with (^{CF_3}PCP)PtMe (0.021 g, 0.032 mmol), $Ph_3C^+B(C_6F_5)_4^-$ (0.030 g, 0.032 mmol), and 0.5 mL of 1,2-difluorobenzene. Approximately half of (^{CF_3}PCP)PtMe was converted to a major species after 30 min, and after 5 h the reaction mixture showed 85+% conversion to a major species as judged by NMR. ^{1}H NMR: δ 2.75 (m, 4H; CH_2). ^{31}P NMR: δ 65.8 (m, $^1J_{PtP}$ = 3480 Hz). ^{19}F NMR: δ −55.8 (m, 12F; PCF_3), −131.5 (br.s, 8F; *ortho*-$B(C_6F_5)_4$), −162.7 (t,$^3J_{FF}$ = 19 Hz, 4F; *para*-$B(C_6F_5)_4$), −166.5 (m, 8F; *meta*-$B(C_6F_5)_4$). ^{1}H NMR for 1,1,1-triphenylethane: δ 0.90 (s, 3H; CH_3), 6.79 (m), 6.44 (m), 6.27 (m).

Reaction of (^{CF_3}PCP)PtCl with $Et_3Si^+B(C_6F_5)_4^-$. A NMR tube charged with (^{CF_3}PCP)PtCl (0.030 g, 0.044 mmol), $Et_3Si^+B(C_6F_5)_4^-$ (0.043 g, 0.054 mmol), and 0.5 mL of 1,2-difluorobenzene was monitored by NMR. After 15 min at ambient temperature, ^{31}P NMR spectra showed a ∼2:1 mixture of hydride-bridged dimer **4b** and a new species tentatively assigned as the neutral hydride, (^{CF_3}PCP)PtH (**5**). After 3 h, the hydride complex had quantitatively converted to **4b**. Data for **5**: ^{1}H NMR (400.13 MHz, 20 °C): δ 2.88 (m, 4H; CH_2), −5.73 (t, $^1J_{PtH}$ = 7 Hz, $^2J_{PH}$ = 224 Hz, 1H; PtH). ^{31}P NMR (161.97 MHz, 20 °C): δ 63.7 (m, $^1J_{PtP}$ = 3570 Hz). ^{19}F NMR (376.50 MHz, 20 °C): δ −55.7 (m, 12F; PCF_3).

(^{CF_3}PCP)Pt(NC_5F_5)$^+B(C_6F_5)_4^-$ (6).

Method A. Pentafluoropyridine (7 mL) was condensed onto a mixture of (^{CF_3}PCP)PtMe (0.300 g, 0.461 mmol) and $(C_6Me_3H_4)^+B(C_6F_5)_4^-$ (0.405 g, 0.506 mmol) at −195 °C. Upon thawing, vigorous bubbling was observed and the reaction mixture was allowed to warm to ambient temperature and then stirred for an additional 4 h. The white precipitate of **6** (0.571 g, 83%) was collected via filtration and dried under vacuum. Crystals suitable for X-ray diffraction were grown by slow evaporation from a 1:1.5 mixture of 1,2-difluorobenzene/pentafluoropyridine. Anal. Calcd for $BNC_{41}H_7P_2F_{37}Pt$: C, 33.16%; H, 0.48%; N, 0.94%. Found: C, 33.54%; H, 0.69%; N, 0.88%. ^{1}H NMR (1,2-difluorobenzene, 400.13 MHz, 20 °C): aromatic resonances obscured by 1,2-difluorobenzene; δ 2.90 (m, 4H, CH_2). ^{31}P NMR (1,2-difluorobenzene, 161.97 MHz, 20 °C): δ 63.2 ppm (m, $^1J_{PtP}$ = 3540 Hz). ^{19}F NMR (1,2-difluorobenzene, 376.50 MHz, 20 °C): δ −55.3 (m, 12F; PCF_3), −79.9 (m, 2F; *ortho*-NC_5F_5), −116.2 (p, J_{FF} = 19 Hz, 1F; *meta*-NC_5F_5), −131.4 (br.s, 8F; *ortho*-$B(C_6F_5)_4$), −154.4 (d,$^3J_{FF}$ = 19 Hz, 2F; *para*-NC_5F_5), −162.8 (t,$^3J_{FF}$ = 20 Hz, 4F; *para*-$B(C_6F_5)_4$), −166.6 (br.t, 8F; *meta*-$B(C_6F_5)_4$).

Method B. A mixture of (^{CF_3}PCP)PtMe (0.100 g, 0.153 mmol) and $Ph_3C^+B(C_6F_5)_4^-$ (0.141 g, 0.153 mmol) was dissolved in 7 mL pentafluoropyridine. The yellow solution was stirred at ambient temperature for 2 h, at which point a precipitate began to form. The reaction mixture was allowed to stand undisturbed for 16 h, giving a pale yellow crystalline solid **6**, which was then collected by filtration (0.140 g, 62%, ∼95+% purity by NMR).

(^{CF_3}PCP)Pt(η^2-C_2H_4)$^+B(C_6F_5)_4^-$ (7). 1,2-Difluorobenzene (20 mL) was condensed onto a mixture of (^{CF_3}PCP)PtMe (0.500 g, 0.768 mmol) and $(C_6Me_3H_4)^+B(C_6F_5)_4^-$ (0.613 g, 0.768 mmol), and 1 atm of C_2H_4 was admitted. Upon thawing, vigorous bubbling was observed and the reaction mixture was allowed to warm up to ambient temperature and stirred for an additional 6 h. The solvent was removed, 20 mL of hexanes was added, and the solid residue was triturated. The hexanes were removed, and the solid was dissolved in ∼40 mL of methylene chloride. The solution volume was reduced to ∼7 mL and cooled to afford a white precipitate (0.544 g, 53%), which was isolated and dried under vacuum. Crystals suitable for X-ray diffraction were grown by slow diffusion of 2-methyl-2-butene into a methylene chloride solution of **7**. 2-Methyl-2-butene, initially examined as a potential reactant, was found to promote crystal growth and also slowed decomposition of **7** to **2b**. Anal. Calcd for $BC_{38}H_{11}P_2F_{32}Pt$: C, 33.95%; H, 0.83%. Found: C, 33.38%; H, 0.54%. ^{1}H NMR (CD_2Cl_2, 400.13 MHz, 20 °C): δ 7.60 (br.s, 3H; Ar), 5.20 (t, $^2J_{PtH}$ = 33 Hz, 4H; C_2H_4), 4.36 (m, 4H, $ArCH_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.61 MHz, 20 °C): 87.2 (t, $^3J_{CP}$ = 13 Hz, $^2J_{CH}$ = 168 Hz; Pt(C_2H_4)), 34.3 (m; CH_2P). ^{31}P NMR (CD_2Cl_2, 161.97 MHz, 20 °C): δ 63.9 (m, $^1J_{PtP}$ = 3380 Hz). ^{19}F NMR (CD_2Cl_2, 376.50 MHz, 20 °C): δ −54.5 (m, 12F; PCF_3), −133.2 (br.s, 8F; *ortho*-$B(C_6F_5)_4$), −163.7 (t,$^3J_{FF}$ = 20 Hz, 4F; *para*-$B(C_6F_5)_4$), −167.6 (m, 8F; *meta*-$B(C_6F_5)_4$).

(^{CF_3}PCP)Pt(η^2-$H_2C{=}C(H)Me$)$^+B(C_6F_5)_4^-$ (8). One atm of propene was introduced into a flask containing **6** (0.150 g, 0.101 mmol) dissolved in 7 mL of 1,2-difluorobenzene. The reaction mixture was stirred at room temperature for 16 h, and the solution remained colorless. The volatiles were removed, and the remaining viscous oil was triturated in 15 mL to give a white solid, which was collected by filtration (0.086 g, 63% crude yield, 90% pure by NMR). ^{1}H NMR (1,2-difluorobenzene, 400.13 MHz, 20 °C): aromatic resonances obscured by 1,2-difluorobenzene; δ 4.45 (dt, $^3J_{HH}$ = 15.6 Hz, $^3J_{PH}$ = 4 Hz, $^2J_{PtH}$ = 34 Hz, 1H; $C\underline{H}_2CHCH_3$), 3.22 (d, $^3J_{HH}$ = 8.2, $^2J_{PtH}$ = 40 Hz, 1H; $C\underline{H}_2CHCH_3$), 2.90 (m, 5H; overlapping benzylic and $CH_2C\underline{H}CH_3$ resonances), 0.77 (d, $^3J_{HH}$= 6.1 Hz, $^3J_{PtH}$ = 17 Hz, 3H; $CH_2CHC\underline{H}_3$). ^{31}P NMR (1,2-difluorobenzene, 161.97 MHz, 20 °C): δ 65.3 ppm (m, $^1J_{PtP}$ = 3460 Hz). ^{19}F NMR (1,2-difluorobenzene, 376.50 MHz, 20 °C): δ −54.6 (m, 12F; PCF_3), −131.4 (br.s, 8F; *ortho*-$B(C_6F_5)_4$), −162.8 (t,$^3J_{FF}$ = 20 Hz, 4F; *para*-$B(C_6F_5)_4$), −166.5 (br.t, 8F; *meta*-$B(C_6F_5)_4$).

Catalysis NMR Studies. The following describe specific NMR experiments for hydrogenolysis, hydrosilation, dimerization, and isomerization. Liquid reagents were added via microliter syringe. All gaseous reagents (C_2H_4, C_3H_7, C_4H_8) were condensed into valved NMR tubes at −195 °C. The stated equivalents were determined by solution integration.

Hydrogenation of C_2H_4 by 7. A NMR tube was charged with **7** (0.025 g, 0.019 mmol), 0.5 mL of 1,2-difluorobenzene, C_2H_4 (43 equiv), and 3 atm of H_2. The only metal species present throughout the reaction was **7**, as judged by NMR. After 77 h, 1.7 equiv of CH_3CH_3 was observed by ^{1}H NMR spectroscopy. Warming to 70 °C for 16 h produced a total of 6.5 equiv of ethane.

Hydrosilation of C_2H_4 and Et_3SiH by 7 at 20 °C. A NMR tube was charged with **7** (0.019 g, 0.014 mmol), 0.5 mL of 1,2-difluorobenzene, C_2H_4 (70 equiv), and Et_3SiH (15 equiv) at 77 K and thawed immediately before taking spectra at 20 °C. Initial NMR spectra showed quantitative conversion of Et_3SiH to Et_4Si (∼2 min acquisition time). Complex **7** was the sole metal species observed.

Hydrosilation of C_2H_4 and Et_3SiH by 7 at −10 °C. A NMR tube was charged with **7** (0.019 g, 0.014 mmol), 0.5 mL of 1,2-difluorobenzene, C_2H_4 (8.9 equiv), and Et_3SiH (14.8 equiv) and warmed to −10 °C. After 44 min, ^{1}H NMR spectra showed the conversion of 7.0 equiv of ethylene to Et_4Si. A plot of $\ln\{[C_2H_4]/[C_2H_4]_0\}$ versus time over two half-lives gave a first order rate constant of 0.005 s^{-1} (R^2 = 0.998).

Hydrosilation of C_2H_4 and $HSiCl_3$ by 7. A NMR tube was charged with **7** (0.020 g, 0.015 mmol), 0.5 mL of 1,2-difluorobenzene, C_2H_4 (40 equiv), and $HSiCl_3$ (27 equiv) and warmed to 20 °C. Complex **7** remained the sole metal species during the course of the reaction, and after 5 h 91% conversion of $HSiCl_3$ to $CH_3CH_2SiCl_3$ was observed. Spectroscopic data for $EtSiCl_3$: ^{1}H NMR (1,2-difluorobenzene, 400.13 MHz, 20 °C): δ 0.17 (q, $^3J_{HH}$ = 8 Hz, 2H; CH_2,), −0.00 (t, $^3J_{HH}$ = 8 Hz, 3H; CH_3). ^{13}C NMR (1,2-difluorobenzene, 100.61 MHz, 20 °C): δ 16.64 (s; CH_2), 5.30 (s; CH_3).

Hydrosilation of Propene and Et_3SiH by 7. A NMR tube was charged with **7** (0.018 g, 0.013 mmol), 0.5 mL of ODF, propene (22 equiv), and Et_3SiH (6 equiv, 12.9 μL, 0.078 mmol). NMR spectra taken 15 min after warming the reaction mixture to 20 °C showed clean conversion of **7** to **8** and quantitative conversion of $SiEt_3H$ to $Et_3Si(CH_2CH_2CH_3)$. Spectroscopic data for

Table 1. Crystallographic Data for (1), $[(^{CF_3}PCP)Pt]_2(\mu\text{-}Cl)^+SbF_6^-$ (2a), $(^{CF_3}PCP)Pt(H_2O)^+B(C_6F_5)_4^-$ (3), $[(^{CF_3}PCP)Pt]_2(\mu\text{-}H)^+SbF_6^-$ (4a), $(^{CF_3}PCP)Pt(NC_5F_5)^+B(C_6F_5)_4^-$ (6), and $(^{CF_3}PCP)Pt(\eta^2\text{-}C_2H_4)^+B(C_6F_5)_4^- \cdot C_5H_{10}$ (7)

compound	**1**·$^1/_2C_6H_6$	$[(^{CF_3}PCP)Pt]_2(\mu\text{-}Cl)^+SbF_6^-$	$(^{CF_3}PCP)Pt(H_2O)^+SbF_6^-$	$[(^{CF_3}PCP)Pt]_2(\mu\text{-}H)^+SbF_6^-$	$(^{CF_3}PCP)Pt(NC_5F_5)^+B(C_6F_5)_4^-$	$(^{CF_3}PCP)Pt(\eta^2\text{-}C_2H_4)^+B(C_6F_5)_4^- \cdot C_5H_{10}$
chemical formula	$C_{27}H_{16}ClF_{24}P_4Pt_2$	$C_{24}H_{14}ClF_{30}P_4Pt_2Sb$	$C_{12}H_9F_{18}OP_2PtSb$	$C_{24}H_{15}F_{30}P_4Pt_2Sb$	$C_{41}H_7BF_{37}NP_2Pt$	$C_{43}H_{21}BF_{32}P_2Pt$
fw	1345.91	1543.61	889.97	1509.17	1484.32	1413.44
T, °C	−123	−123	−123	−123	−123	−123
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
space group	$P2_1/n$	$P2_1/n$	$C2/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a, Å	16.4459(2)	14.0640(5)	41.9243(8)	13.5979(3)	13.9317(2)	11.4117(5)
b, Å	20.6746(3)	16.9140(6)	10.4572(2)	17.6629(3)	17.1374(3)	22.9772(10)
c, Å	22.0032(3)	17.9834(6)	22.5118(4)	16.7502(3)	19.2130(3)	16.9942(8)
α, °	90	90	90	90	90	90
β, °	90.6980(10)	106.098(2)	110.5430(10)	103.5910(10)	98.2910(10)	98.609(3)
γ, °	90	90	90	90	90	90
V, Å^3	7480.81(17)	4110.1(2)	9241.8(3)	3910.38(13)	4539.22(12)	4405.8(3)
Z	8	4	16	4	4	4
D_{calc}, mg m^{-3}	2.390	2.495	2.559	2.563	2.172	2.131
μ, mm^{-1}	7.857	7.821	7.504	8.152	3.351	3.430
$R1$ $[I > 2\sigma(I)]^a$	0.0306	0.0350	0.0273	0.0236	0.0248	0.0429
$wR2$ $[I > 2\sigma(I)]^b$	0.0611	0.0698	0.0598	0.0476	0.0505	0.1020

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

$Et_3Si(CH_2CH_2CH_3)$: ^1H NMR (1,2-difluorobenzene, 400.13 MHz, 20 °C): δ 0.22 (m, 2H; CH_2), 0.16 (t, $^3J_{HH} = 8$ Hz, 12H; CH_3), −0.60 (q, $^3J_{HH} = 8$ Hz, 12H; CH_3). ^{13}C NMR (1,2-difluorobenzene, 100.61 MHz, 20 °C, DEPT 90 and 135): δ 18.24 (s; CH_3), 17.54 (s; CH_2), 14.14 (s; CH_2), 7.03 (s, 3C; CH_3), 3.33 (s, 3C; CH_2).

Ethylene Dimerization by 7. A NMR tube was charged with **7** (0.025 g, 0.019 mmol), 0.5 mL of ODF, 0.5 mL of benzene, and C_2H_4 (30 equiv). The reaction mixture was heated at 155 °C for 60 h. About 10% of **7** and the anion $B(C_6F_5)_4$ underwent decomposition as judged by ^{19}F NMR. Eight equivalents of were C_2H_4 consumed, producing 4 equiv of a 2:1 mixture of *trans* and *cis* butenes and a trace amount of 1-butene.

1-Butene Isomerization by 7. A NMR tube was charged with **7** (0.014 g, 0.009 mmol), 0.5 mL of 1,2-difluorobenzene, and 1-butene (10 equiv). After 4 h at 80 °C, 3.6 equiv of a ∼1:1 mixture of *cis*- and *trans*-2-butene was produced (36% conversion). A single metal species was observed during the reaction which has been tentatively assigned as $(^{CF_3}PCP)Pt(\eta^2\text{-}H_2C{=}C(H)CH_2Me)^+B(C_6F_5)_4^-)$. ^1H NMR (1,2-difluorobenzene, 400.13 MHz, 20 °C): aromatic resonances obscured by 1,2-difluorobenzene; δ 4.56 (dm, $^3J_{HH} = 14.8$ Hz, $^2J_{PtH} = 50$ Hz, 1H; $C\underline{H}_2CHCH_2CH_3$), 3.37 (d, $^3J_{HH} = 7.6$, $^2J_{PtH} = 41$ Hz, 1H; $C\underline{H}_2CHCH_2CH_3$), 3.00 (m, 5H; overlapping benzylic and $CH_2C\underline{H}CH_2CH_2CH_3$ resonances), 0.61 (m, 2H; $CH_2CHC\underline{H}_2CH_3$), 0.03 (t, $^3J_{HH} = 8.3$ Hz, 3H; $CH_2CHCH_2C\underline{H}_3$). ^{31}P NMR (1,2-difluorobenzene, 161.97 MHz, 20 °C): δ 64.8 (m, $^1J_{PtP} = 3420$ Hz). ^{19}F NMR (1,2-difluorobenzene, 376.50 MHz, 20 °C): δ −54.3 (m, 6F; PCF_3), −54.8 (m, 6F; PCF_3), −131.4 (br.s, 8F; *ortho*-$B(C_6F_5)_4$), −162.8 (t, $^3J_{FF} = 20$ Hz, 4F; *para*-$B(C_6F_5)_4$), −166.6 (br.t, 8F; *meta*-$B(C_6F_5)_4$).

X-ray Crystallography. X-ray diffraction data for **1**, **2a**, **3**, **4a**, **6**, and **7** were measured on a Bruker SMART APEX II CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube operated at 1.5 kW power (50 kV, 30 mA) with the detector placed at a distance of 5.9 cm from the crystal. Crystals were attached to a MiTeGen micromount using Paratone N oil.

A series of narrow frames of data were collected with a scan width of 0.5° in ω or ϕ and an exposure time of 10 s per frame. The frames were integrated with the Bruker SAINT software package[31] using a narrow-frame integration algorithm. The data were corrected for absorption effects by the numerical face-indexing technique (SADABS). A summary of crystallographic data collection parameters and refinement data are collected in Table 1. Structures were solved by direct methods using the Bruker SHELXTL (v. 6.10) software package.[31] All non-hydrogen atoms were located in successive Fourier maps and refined anisotropically. The hydrogen atoms were placed in calculated positions and refined isotropically employing a riding model. The asymmetric unit of **1** consists of two crystallographically distinct $[Pt_2(C_{12}H_7P_2F_{12})(C_{12}HP_2F_{12})Cl]$ molecules and a well-ordered benzene molecule. **2a** crystallizes as two independent $[Pt(pcp)(H_2O)]^+$ cations and two SbF_6^- anions. The asymmetric unit of **7** consists of well-ordered $[Pt(pcp)(C_2H_4)]^+$ and borate anions and a disordered 2-methyl-2-butene molecule. The hydrogen atoms of the 2-methyl-2-butene molecule were not located or placed in calculated positions. The carbon atoms of the 2-methyl-2-butene were refined isotropically.

Acknowledgment. We thank The National Science Foundation (CHE-0457435) and DOE/EPSCoR (DE-FG02-05ER46185) for financial support.

Supporting Information Available: Complete tables of atomic coordinates, thermal parameters, and bond distances and angles for complexes **1**, **2a**, **3**, **4a**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) *APEX2 Software Suite*, v. 2.1-0; Bruker AXS: Madison, WI, 2004.