ORGANOMETALLICS

Synthesis and Structural Characterization of an Unusual Platinum π -Arene Complex: (η^{6} -C₆H₃Me₃)Pt[(C₂F₅)₂PMe]Me⁺

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S Supporting Information

ABSTRACT: Treatment of *cis*-(dfmp)₂PtMe₂ (dfmp = $(C_2F_5)_2$ PMe) with the mesitylenium acid $(C_6Me_3H_4)^+B-(C_6F_5)_4^-$ in 1,2-difluorobenzene cleanly produces an unusually stable arene complex, $[(\eta^6-C_6Me_3H_3)Pt(dfmp)(CH_3)]^+(B-(C_6F_5)_4)^-$ (1). Facile arene exchange and competitive binding equilibria have been quantified for mesitylene relative to



toluene (K = 0.0030(3)) and durene (K = 20(2)). Reaction of 1 with H₂ at 80 °C results in hydrogenolysis to form the arene hydride (η^6 -C₆Me₃H₃)Pt(dfmp)(H)⁺ (2), while treatment of 1 with CO gives *trans*-(dfmp)₂Pt(CO)Me⁺ as the major phosphine product. Addition of excess Me₃P to 1 results in both arene and dfmp displacement to form (Me₃P)₃PtMe⁺. (η^6 -C₆Me₃H₃)Pt(dfmp)(CH₃)⁺ is a moderately active ethylene dimerization catalyst to form 2-butenes (~7 TO h⁻¹, 20 °C).

INTRODUCTION

Since Fischer's initial report of $(\eta^6$ -benzene)₂Cr¹, metal-arene complexes have played an important role in organometallic coordination chemistry as both supporting ancillary ligands and key intermediates in metal-mediated arene functionalization chemistry.² π -Arene complex chemistry across the d-block is extensive for the middle transition metals (groups 6-9). Literature reports of η^6 -arene complexes for the group 10 triad, in contrast, are much less common. η^6 -Arene complexes of Ni(0) of the general form (η^{6} -arene)Ni(L) (L = $\kappa^{1-t}Bu_{2}PCH_{2}P^{t}Bu_{2}^{-3}$ NO^{+,4} NHC,⁵ SiR₂⁶) and the Ni(II) complexes (η^{6} -arene)Ni(allyl)⁺ and (η^{6} -arene)Ni(X)₂ (X = C₆F₅, SiX₃) are known.^{7,8} In contrast, there is only a single clear example of a Pd(II) analogue, $(\eta^{6}$ -arene)M(allyl)^{+,9} For platinum only a single Pt(II) arene complex has been isolated and structurally characterized, $(\eta^6 - C_6 Me_6) Pt(\eta^4 - C_4 Me_4)^{2+,10}$ and $(\eta^6 - C_6 Me_6) Pt(\eta^3 - 2 - methylallyl)^+$ has been characterized as a thermally unstable solution species by NMR.¹¹ We have more recently reported the formation of the complex $(dfepe)Pt(\eta^{6}-C_{6}H_{6})^{2+}$ $(dfepe = (C_{2}F_{5})_{2}PCH_{2}CH_{2}P(C_{2}F_{5})_{2})$ with limited solution stability under superacidic conditions.

In 2008 we reported a highly active chelating perfluoroalkylphosphine (PFAP) platinum ethylene dimerization catalyst, $[(dfepe)Pt(Me)(NC_5F_5)]^+(B(C_6F_5)_4)^{-.13}$ This complex was shown to be *orders of magnitude* more reactive than the corresponding diimine platinum analogue;¹⁴ considering the extensive use of diimine ancillary ligands in group 10 alkene oligomerization chemistry,¹⁵ and the recognized importance of group 10 alkene oligomerization catalysts,¹⁶ the expansion of group 10 alkyl cation chemistry to a broader range of ligand sets such as phosphines, and more specifically PFAPs, is clearly warranted.¹⁷

The key to accessing the labile cationic platinum alkyl complex $[(dfepe)Pt(Me)(NC_5F_5)]^+(B(C_6F_5)_4)^-$ was the use of Reed's mesitylenium acid reagent, $[C_6Me_3H_4]^+(B(C_6F_5)_4)^{-,18}$

to effect a clean Pt–Me protonolysis. In an extension on this work we have examined routes to monodentate phosphine analogues of the general form (PFAP)_nPt(R)⁺. Here we report that treatment of *cis*-(dfmp)₂PtMe₂¹⁹ (dfmp = (C₂F₅)₂PMe) with $[C_6Me_3H_4]^+(B(C_6F_5)_4)^-$ does not afford anticipated (dfmp)₂PtMe⁺(L) products, but rather incorporates the released mesitylene group to form an unusual stable 18electron arene complex, (η^6 -C₆Me₃H₃)Pt(dfmp)(CH₃)⁺. This product is interesting in several respects: it is not only a very rare example of a stable platinum η^6 -arene complex, but it also possesses Pt–CH₃ functionality that affords the possibility of metal–alkyl bond chemistry. In this paper we detail the structural and spectroscopic properties of (η^6 -C₆Me₃H₃)Pt-(dfmp)(CH₃)⁺ and present a preliminary survey of its thermal stability, ligand exchange chemistry, and reactions with dihydrogen, CO, and ethylene.

RESULTS AND DISCUSSION

Synthesis and Characterization of (η^6 -C₆H₃Me₃)Pt-(dfmp)Me⁺. The reaction of *cis*-(dfmp)₂PtMe₂ with 1 equiv of mesitylenium acid in 1,2-difluorobenzene (abbreviated as ODFB) was monitored by ¹H and ³¹P NMR spectroscopy. As noted previously,¹³ ODFB is an exceptional solvent (liquid range: -34 to +92 °C) for studying highly electrophilic metal complex chemistry due to its high dielectric constant ($D_s =$ 13.8, 28 °C) and ability to solubilize complex ions,²⁰ its large electrochemical window (+2.0 V to -2.2 V vs SSCE),²¹ its relative inertness to halide extraction side reactions,^{22,23} and its weakly coordinating nature (see later). After 15 min at ambient temperature ³¹P NMR spectra indicate a clean conversion to a 1:1 mixture of free dfmp and a Pt-dfmp resonance at 18.6 ppm with an unusually large (¹J_{PtP} = 6380 Hz) platinum coupling

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constant. Proton spectra confirmed the formation of methane and free dfmp and the appearance of new Pt-coupled methyl resonances at δ 0.73 (${}^{3}J_{PtH} = 64$ Hz, ${}^{2}J_{PH} = 11$ Hz) and δ 0.08 (${}^{2}J_{PtH} = 81$ Hz, ${}^{3}J_{PH} = 3$ Hz), which are assigned to the dfmp and Pt-bound methyl groups, respectively. A new mesitylene methyl resonance was observed at δ 1.29 displaying 195 Pt coupling (${}^{3}J_{PtH} = 15$ Hz), which confirmed platinum–arene coordination. For comparison, ${}^{3}J_{PtH}$ couplings to the methyl protons in (η^{6} -C₆Me₆)Pt(η^{4} -C₄Me₄)²⁺ and (η^{6} -C₆Me₆)Pt(η^{3} -2methylallyl)⁺ are 17 and 16 Hz, respectively.^{10,11} No ${}^{2}J_{PtH}$ coupling is observed for the coordinated mesitylene aromatic C–H resonance at δ 5.61. Together these data are consistent with the quantitative conversion of *cis*-(dfmp)₂PtMe₂ to the novel cationic arene methyl complex (η^{6} -C₆H₃Me₃)Pt(dfmp)-Me⁺ (1) (eq 1). Complex 1 is readily isolated as a pale yellow

$$\overset{(C_2F_5)_2P}{\underset{Me}{\overset{(C_2F_5)_2P}{\overset{(C_2F_5)}}{\overset{(C_2F_5)}{\overset{(C_2F_$$

crystalline solid and is stable in solution in the absence of added mesitylene. The stability of **1** is exceptional: only 10% decomposition with release of mesitylene is observed after warming to 80 °C in ODFB for 6 h. The observation of a single mesitylene methyl resonance for this C_s symmetric complex down to -30 °C is consistent with rapid arene ring rotation/ equilibration on the NMR time scale.

The structure of 1 was confirmed by X-ray crystallography (Figure 1). The Pt-C(arene) bond distance average, 2.448 Å,



Figure 1. Crystal structure of $(\eta^6 - C_6 H_3 Me_3) Pt(dfmp) Me^+$ (1) with thermal ellipsoids at the 35% probability level. Selected metrical data: Pt(1)-C(1): 2.072(3) Å, Pt(1)-P(1): 2.1620(7) Å, Pt(1)-C(2): 2.470(3) Å, Pt(1)-C(3): 2.439(3) Å, Pt(1)-C(4): 2.520(3) Å, Pt(1)-C(5): 2.475(3) Å, Pt(1)-C(6): 2.390(3) Å, C(2)-C(3): 1.404(4) Å, C(3)-C(4): 1.421(4) Å, C(4)-C(5): 1.394(4) Å, C(5)-C(6): 1.410(4) Å, C(6)-C(7): 1.417(4) Å, C(7)-C(2): 1.413(4) Å; Pt(1)-C(7): 2.395(3) Å; P(1)-Pt(1)-C(1): 87.38(10)°.

is significantly longer and also has a wider Pt–C(aryl) bond length range (2.395(3)–2.520(3) Å) than that reported for (η^6 - C_6 Me₆)Pt(η^4 - C_4 Me₄)⁺ (2.319(5)–2.380(6) Å, 2.351 Å av).¹⁰ This bonding asymmetry is not correlated with any significant C(aryl)–C(aryl) bond alternation (1.394(4)–1.421(4) Å) or with trans influence effects of the dfmp and methyl ligands, but may be indicative of facile ring slippage and arene exchange/ dissociation, as has been noted for similar palladium and nickel systems.^{9,24} The short Pt–P bond distance of 2.1620(7) Å is in keeping with the generally observed trend for PFAP complexes.²⁵ Relative to other structurally characterized Pt(II)–PFAP systems, this bond distance falls within the range 2.135–2.186 Å found for Pt(II)–PFAP with weak trans influence groups such as trifluoroacetate,^{13,19} triflate,²⁶ pentafluoropyridine,¹³ and fluoroarsenate as well as antimonate anions,²⁷ suggesting that the effective trans influence of the π -arene ligand in complex **1** is low.

π-Arene Exchange Study. The relative labilities of the mesitylene and dfmp ligands in complex 1 are of interest, since this addresses the question of whether 1 can serve as an effective source of 16-electron (η^6 -C₆H₃Me₃)PtMe⁺ and/or 12-electron Pt(dfmp)Me⁺ fragments. Accordingly, a brief survey of phosphine and π-arene exchange chemistry for (η^6 -C₆H₃Me₃)-Pt(dfmp)Me⁺ has been carried out (Scheme 1). No degenerate

Scheme 1



phosphine exchange with excess added dfmp (14 equiv) in ODFB solutions of 1 at 20 °C was observed on the NMR time scale. Similarly, NMR monitoring of 1 in the presence of 1.5 equiv of the more sterically demanding monodentate PFAP ligand $(C_2F_5)_2P(^tBu)^{35}$ at 20 °C showed no evidence of arene or dfmp substitution after several hours. Addition of the strong donor phosphine Me_3P does, however, result in rapid displacement of both the dfmp and mesitylene ligands (see later, Scheme 3).



Scheme 3



Arene lability trends for $(\eta^6$ -arene)ML_n systems have been the subject of numerous studies.^{28,29} In general, the arene lability dramatically increases going from group 6 to group 10 metals ranging from thermally robust (arene) $M(CO)_3$ (M = Cr, Mo) complexes, which require elevated temperatures and/ or added donor solvents as catalysts to effect arene displacement, to $(arene)Ni(C_6F_5)_2$ compounds, which undergo uncatalyzed exchange at ambient temperatures,³⁰ and $(\eta^6$ - $C_6H_3Me_3)Pd(allyl)^+$, which undergoes exchange with free mesitylene on the NMR time scale down to -77 °C.^{7b} In all cases the order of arene binding affinity has followed increased donor ability: $C_6Me_6 > C_6H_2Me_4 > C_6H_3Me_3 > C_6H_4Me_2 >$ toluene > benzene > fluorobenzenes.²⁹ Facile arene exchange between the mesitylene ligand of 1 and free arenes occurs within minutes at ambient temperatures and has allowed us to readily measure competitive equilibrium constants for mesitylene relative to toluene and 1,2,4,5-tetramethylbenzene (durene). The ¹H NMR chemical shifts for the free arene methyl groups and the Pt-CH₃ resonances for each (η^6 arene)Pt(dfmp)Me⁺ complex are well separated and allow for quantification of all solution species by integration (representative examples are given in Figures S3 and S4). In accord with previous studies a clear preference for binding to electron-rich arenes also exists for $(\eta^{6}$ -arene)Pt(dfmp)Me⁺: at 20 °C the equilibria for exchange of 1 with toluene (K = 0.0030(3)) and durene (K = 20(2)) are fully established within 30 min. No evidence of mesitylene displacement by the ODFB aromatic solvent is observed, consistent with its electron-poor nature. Comparison of these values to corresponding ones reported by Muetterties for the exchange of $(\eta^6-C_6H_3Me_3)Mo(CO)_3$ with toluene (K = 0.034) and durene (K = 1.2) indicates a much more significant (~10-fold) preference of $(\eta^6$ -arene)Pt(dfmp)-Me⁺ systems for more electron-rich arenes.

Reactions of 1 with H₂ and CO. Facile arene exchange suggests that the formally coordinatively saturated 18-electron complex 1 may react under mild conditions with other potential substrates such as H₂ and CO and serve as a source of the 12-electron moiety "(dfmp)PtMe+". The reaction between $(\eta^6-C_6H_3Me_3)Pt(dfmp)Me^{+}$ and hydrogen (~3 atm) in ODFB was monitored by ¹H and ³¹P NMR. After 12 h at ambient temperature, methane loss and 10% conversion to a new species having $(\eta^6 - C_6 H_3 M e_3)$ Pt resonances at δ 5.57 and 1.41, a dfmp methyl doublet at δ 0.73, and an associated platinum-coupled doublet at δ –23.21 (¹ J_{HPt} = 1640 Hz, ² J_{HP} = 37 Hz) confirmed the formation of the arene hydride, (η^6 - $C_6H_3Me_3$)Pt(dfmp)H⁺ (2) (Scheme 2). Warming the reaction mixture to 80 °C for 3 h resulted in 55% conversion to 2, while further warming for 12 h resulted in a 3:1 mixture of hydride complex to starting complex with an accompanying 50% decomposition with the release of free mesitylene.

The reaction of $(\eta^6 \cdot C_6 H_3 Me_3) Pt(dfmp) Me^+$ with CO in ODFB has also been examined. After 10 min exposure to 1 atm of CO at ambient temperature, free mesitylene was observed as well as ill-defined broad resonances in ¹H NMR spectrum at δ 1.21 and 0.26. A single major resonance (~40% of the integrated total of all ³¹P resonances) appeared in the ³¹P NMR spectra at 34.5 ppm (m, ¹J_{PtP} = 3130 Hz), and no free dfmp was observed. A separate NMR experiment with 0.5 equiv of added CO revealed a distinctive Pt-Me proton resonance at δ 0.15 (²J_{PtH} = 58 Hz, ³J_{PH} = 9 Hz) and a ~1:1 mixture of the 34.5 ppm phosphorus species and unreacted 1: NMR data for this new dfmp product closely match data for the previously reported bis-phosphine complex *trans*-(dfmp)₂Pt(CO)Me⁺.¹⁸ These observations are consistent with either disproportionation or efficient scavenging of dfmp by an initially formed arene displacement product such as $(dfmp)Pt(CO)_2Me^+$ to form *trans*- $(dfmp)_2Pt(CO)Me^+$. ¹H NMR spectral broadening under excess CO is likely due to dfmp/CO exchange. Solution IR spectra of 1 treated with excess CO in dichloromethane show a sharp band at 2150 cm⁻¹ assignable to *trans*- $(dfmp)_2Pt(CO)$ -Me⁺, as well as a broad $\nu(CO)$ band at 2099 cm⁻¹; since no significant PFAP product other than *trans*- $(dfmp)_2Pt(CO)Me^+$ is observed, we tentatively attributed this additional band to an as yet unidentified dfmp-free platinum carbonyl species (see Figure S11).

Reaction of 1 with Me₃P. The clean formation of $(\eta^6$ - $C_6H_3Me_3$)Pt(dfmp)Me⁺ in eq 1 is facilitated by the lability and the electron-poor nature of the perfluorinated dfmp ligand. Reaction of the analogous donor phosphine complex cis-(Me₃P)₂PtMe₂ with mesitylenic acid in ODFB produced a 1:1 mixture of $(\eta^6 - C_6 H_3 M e_3) Pt(PM e_3) Me^+$ and $[(M e_3 P)_3 PtM e^+]^{31}$ due to efficient trapping of initially formed protonolysis product $(Me_3P)_2PtMe(solv)^+$ by released Me_3P (Scheme 3). $(Me_3P)_3PtMe^+$ may be cleanly generated by treatment of $(\eta^6$ - $C_6H_3Me_3$)Pt(dfmp)Me⁺ with excess Me₃P. The absence of detectable Me₃PH⁺ suggests that protonation of Me₃P by unreacted mesitylenium acid is not competitive with the kinetics of platinum cation trapping. For the poorly donating dfmp ligand, neither competitive trapping of platinum nor ³² It is likely that protonation to form dfmpH⁺ takes place.³² other, less donating and more sterically demanding phosphine systems $(Ar_3P, (RO)_3P, (pyr)_3P, (C_6F_5)_3P, etc.)$ may also favor arene product formation over protonolysis trapping and also lead to exclusive arene product formation.

Complex 1 has been surveyed for ethylene dimerization activity. Addition of ethylene (~ 27 equiv) to 1 in ODFB at 20 °C resulted in the complete displacement of mesitylene as well as a significant amount (\sim 50%) of dfmp and the appearance of very broad resonances at 0.7 and -1.0 ppm ($\nu_{1/2} \approx 100$ Hz). Monitoring the progress of reaction showed the appearance of stoichiometric propene and formation of a 2:1 thermodynamic mixture of *trans*- and *cis*-2-butene at a rate of \sim 7 TO h⁻¹. The absence of significant amounts of 1-butene in ethylene dimerization by 1 was also noted in dimerization catalysis by $[(dfepe)Pt(Me)(NC_5F_5)]^{+13}$ and contrasts with the competitive production of 1-butene by Brookhart and Templeton's $[(diimine)Pt(Et)(C_2H_4)]^+$ system.¹⁴ ¹H NMR spectra of a mixture of 1 and excess ethylene in ODFB cooled to -30 °C after reacting for 5 min at 25 °C revealed a distinctive Pt-CH₃ resonance at $\delta - 1.42 ({}^{3}J_{HP} = 20 \text{ Hz}, {}^{2}J_{HPt} = 59 \text{ Hz})$, and ${}^{31}P$ NMR displayed free dfmp and two Pt-bound resonances at 26.2 $({}^{1}J_{PPt} = 3400)$ and 4.4 ppm $({}^{1}J_{PPt} = 990)$ assignable to dfmp ligands trans to Pt-ethylene and Pt-CH₃ groups, respectively (Figures S9 and S10). On the basis of these data we tentatively assign the initial major (dfmp)Pt species formed under catalytic conditions as cis-(dfmp)₂Pt(C₂H₄)Me⁺. It is notable that, even though the major identified platinum-bound species is a bisdfmp adduct, which requires scavenging of an additional equivalent of dfmp from the catalyst precursor 1, 50% of the total dfmp under catalytic conditions is dissociated. As a result, we cannot discriminate between $cis-(dfmp)_2Pt(C_2H_4)Me^+$ and some phosphine-free compound as the catalyst resting state.

Summary. The ligand substitution and reaction chemistry of $(\eta^6-C_6H_3Me_3)Pt(dfmp)Me^+$ is dependent on the nature of the incoming substrate: for reactions with arene, clean exchange is observed, which maintains an intact $Pt(dfmp)Me^+$ moiety.

Degenerate phosphine exchange with added dfmp on the NMR time scale is not observed; quantification of a potential slower degenerate phosphine exchange rate utilizing deuterated dfmp or another appropriate competitive added ligand merits further study. The reaction of 1 with the strongly donating Me₃P ligand results in rapid loss of both arene and dfmp to form $(Me_3P)_3PtMe^+$. The reaction of 1 with CO is less well defined, but surprisingly forms a bis-dfmp product trans-(dfmp)₂Pt-(CO)Me⁺. The reaction of $(\eta^6-C_6H_3Me_3)Pt(dfmp)Me^+$ with H₂ is moderately selective toward Pt-Me bond hydrogenolysis, but requires heating and is accompanied by significant decomposition. The most probable mechanism of hydrogenolysis requires either dfmp loss or partial arene displacement (i.e., formation of a 16-electron $(\eta^4-C_6H_3Me_3)Pt(dfmp)$ -Me⁺ intermediate). The modest catalytic activity observed for $(\eta^6 - C_6 H_3 Me_3) Pt(dfmp) Me^+$ is lower than reported for $[(dfepe)Pt(Me)(NC_5F_5)]^+(B(C_6F_5)_4)^-$ (150 TO h⁻¹) but is still much higher than the only two other reported platinum ethylene dimerization catalysts.^{14,33} Future research is directed toward extending this new class of group 10 arene complexes and exploring the utility of $(\pi$ -arene)M(PFAP)R⁺ systems as effective synthons for electrophilic 12-electron (PFAP)MR⁺ moieties. In a broader context, the strategy of employing Reed's arenium or halocarborane acids to generate unsaturated metal cations through protonolysis, combined with the unique combination of polarity and ion solvation of weakly coordinating 1,2-difluorobenzene, may serve as a convenient general synthetic route to very labile cationic metal complexes with very weakly coordinating L' trapping ligands, $L_n M(L')^+$.

EXPERIMENTAL DETAILS

General Procedures. All manipulations were conducted under N2 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 ALS Environmental. IR spectra were recorded on a Varian FTS-800 FTIR. NMR spectra were obtained with a Bruker Avance-III-400 instrument using 5 mm NMR tubes fitted with Teflon valves (New Era Enterprises, Inc., NE-CAV5). Spectra taken in 1,2difluorobenzene were externally locked and referenced to acetone- d_6 capillaries (acetone- d_5 set to 2.07 ppm). ³¹P NMR spectra were referenced to an 85% H₃PO₄ external standard. ¹⁹F NMR spectra were referenced to a CF3CO2CH2CH3 (-75.32 ppm) external standard. 1,2-Difluorobenzene was purchased from Synquest Laboratories, Inc. All reagents, unless otherwise noted, were purchased from Aldrich and were used without further purification. (nbd)PtMe₂,³⁴ $(C_2F_5)_2$ PMe (dfmp) and *cis*-(dfmp)₂Pt(Me)₂,¹⁹ $(C_2F_5)_2$ P(^tBu),³⁵ and $[C_6Me_3H_4]^+(B(C_6F_5)_4)^-$ were prepared following literature procedures.

{(η⁶-C₆H₃Me₃)Pt[(C₂F₅)₂MeP]Me}⁺(B(C₆F₅)₄)⁻ (1). (dfmp)₂Pt-(Me)₂ (330 mg, 0.416 mmol) and [C₆Me₃H₄]⁺(B(C₆F₅)₄)⁻ (333 mg, 0.416 mmol) were dissolved in 10 mL of 1,2-difluorobenzene and stirred for 1 h at ambient temperature. All volatiles were removed, and the solid residue was dissolved in 10 mL of petroleum ether (35–60 °C); precipitation at -78 °C and cold filtration afforded 1 as an analytically pure pale yellow crystalline solid (375 mg, 70%). Anal. Calcd for C₃₉H₁₈F₃₀BPPt: C, 36.22; H, 1.40. Found: C, 36.10; H, 1.81. ¹H NMR (400.13 MHz, 1,2-difluorobenzene, 25 °C): δ 5.61 (s, 3H; (η⁶-C₆H₃Me₃)Pt), 1.29 (s, ³J_{PtH} = 15 Hz, 9H; (η⁶-C₆H₃Me₃)Pt), 0.73 (d, ³J_{HP} = 64 Hz, ²J_{HP} = 11 Hz, 3H; <u>Me</u>(C₂F₅)₂P), 0.08 (d, ²J_{HPt} = 81 Hz, ³J_{HP} = 3 Hz, 3H; Pt(C<u>H</u>₃)). ³¹P NMR (161.97 MHz, 1,2difluorobenzene, 25 °C): δ 18.6 (pseudopentet, ¹J_{PPt} = 6380 Hz, ³J_{PFa} ≈ ³J_{PEb} = 60 Hz). ¹⁹F NMR (CD₂Cl₂, 376.50 MHz, 25 °C): δ -77.8 (s, 6F; PCF₂C<u>F₃</u>), -112 to -115 (overlapping ABX multiplets, 4F; PC<u>F₂CF₃</u>), -133.1 (s, br, 8F; ortho-(C₆F₅)₄B), -163.7 (t, ³J_{FF} = 19 Hz, 4F; para-(C₆F₅)₄B), -167.6 (t, br, ³J_{FF} = 19 Hz, 8F; meta-(C₆F₅)₄B). NMR data in dichloromethane (10% CD₂Cl₂ in CH₂Cl₂; δ 5.32 CH₂Cl₂ used as internal reference): ¹H NMR (400.13 MHz, 25 °C): δ 6.86 (s, 3H; (η^6 -C₆H₃Me₃)Pt), 2.48 (s, ³J_{PH} = 15 Hz, 9H; (η^6 -C₆H₃Me₃)Pt), 1.92 (d, ³J_{HPt} = 64 Hz, ²J_{HP} = 11 Hz, 3H; <u>Me</u>(C₂F₅)₂P), 1.21 (d, ²J_{HPt} = 81 Hz, ³J_{HP} = 3 Hz, 3H; Pt(C<u>H₃</u>)). ³¹P NMR (161.97 MHz, 25 °C): δ 19.9 (ps. p, ¹J_{PPt} = 6360 Hz, ³J_{PFa} \approx ³J_{PFb} = 62 Hz). {(η^6 -C₆H₃Me₃)Pt[(C₂F₅)₂MeP]H}+(B(C₆F₅)₄)⁻ (2). The reaction

 $\{(\eta^{0}-C_{6}H_{3}Me_{3})Pt[(C_{2}F_{5})_{2}MeP]H\}^{*}(B(C_{6}F_{5})_{4})^{-}$ (2). The reaction between complex 1 and H₂ was monitored by ¹H and ³¹P NMR: A 5 mm Teflon-valved NMR tube containing 10 mg of 1 and 0.5 mL of 1,2-difluorobenzene was cooled to -195 °C, and 1 atm H₂ was admitted. After warming to ambient temperature (~3 atm H₂ pressure), ¹H NMR indicated ~10% reaction after 12 h. Warming to 80 °C for 3 h resulted in 55% conversion to $\{(\eta^{6}-C_{6}H_{3}Me_{3})Pt-[(C_{2}F_{5})_{2}MeP]H\}^{+}(B(C_{6}F_{5})_{4})^{-}$ (2). Further warming for 12 h resulted in a 3:1 mixture of 2 to 1 with an accompanying 50% decomposition with the release of free mesitylene. NMR data for 2: ¹H NMR (400.13 MHz, 1,2-difluorobenzene, 25 °C): δ 5.57 (s, 3H; (η⁶-C_{6}H_{3}Me_{3})Pt), 1.41 (s, ³J_{PtH} = 15 Hz, 9H; (η⁶-C₆H₃Me_{3})Pt), 0.73 (d, ³J_{HPt} = 82 Hz, ²J_{HP} = 11 Hz, 3H), -23.21 (d, ¹J_{HPt} = 1640 Hz, ²J_{HP} = 37 Hz, 1H; Pt(H)). ³¹P NMR (161.97 MHz, 1,2-difluorobenzene, 25 °C): δ 14.1 (m, ¹J_{PPt} = 5780 Hz).

Reaction of cis-(Me₃P)₂PtMe₂ with $[C_6Me_3H_4]^+(B(C_6F_5)_4)^-$. In a typical experiment, (nbd)PtMe₂ (10 mg) and excess (~20 equiv) Me₃P were combined in 0.5 mL of benzene- d_6 . Complete conversion to cis-(Me₃P)₂PtMe₂ was confirmed by ³¹P NMR (δ -23.9, ¹J_{PP+} = 1785 Hz). Removal of volatiles and addition of 0.5 mL of 1,2difluorobenzene with an acetone- d_6 locking capillary gave spectroscopically pure cis-(Me₃P)₂PtMe₂: ¹H NMR (400.13 MHz, 1,2difluorobenzene, 25 °C): δ 0.23 (ps. d, ${}^{3}J_{HPt} = 20$ Hz, $J_{HP} = 8$ Hz, 18H; ($\underline{Me_{3}P}$)₂Pt), -0.37 (m, ${}^{3}J_{HPt} = 66$ Hz, 6H; Pt $\underline{Me_{2}}$). ${}^{31}P$ NMR (161.97 MHz, 1,2-difluorobenzene, 25 °C): δ –25.6 (s, ¹J_{PPt} = 1792 Hz). After removal of volatiles, 1.2 equiv of $[C_6Me_3H_4]^+(B(C_6F_5)_4)^-$ was added, and 0.5 mL of 1,2-difluorobenzene was added while maintaining the temperature at -30 °C. Upon warming to 20 °C for 30 min, a clean conversion to a 1:1 mixture of $(\eta^6 - C_6 H_3 M e_3) Pt(M e_3 P) M e^+$ and $(Me_3P)_3PMe^+$ was indicated by ¹H and ³¹P NMR. NMR data for $(\eta^6-$ C₆H₃Me₃)Pt(Me₃P)Me⁺: ¹H NMR (400.13 MHz, 1,2-difluorobenzene, 25 °C): δ 5.31 (s, 3H; (η^6 -C₆<u>H</u>₃Me₃)Pt), 1.15 (s, $^3J_{PtH}$ = 11 Hz, 9H; $(\eta^6-C_6H_3Me_3)$ Pt), 0.4 to 0.2 (m, 9H; <u>Me_3P</u> overlapping with $(Me_3P)_3PMe^+$ trimethylphosphine resonances), -0.31 $(d, {}^2J_{HPt} = 87$ Hz, ${}^{3}J_{HP} = 2.4$ Hz, 3H; $Pt(CH_{3})$). ${}^{31}P$ NMR (161.97 MHz, 1,2difluorobenzene, 25 °C): δ –28.7 (s, ${}^{1}J_{PPt}$ = 5260 Hz). NMR data for (Me₃P)₃PtMe⁺ (comparable to literature values): ¹H NMR (400.13 MHz, 1,2-difluorobenzene, 25 °C): δ 0.4 to 0.2 (m, 27H; (Me₃P)₃PMe⁺ trimethylphosphine resonances overlapped with the Me₃P resonance of $(\eta^{6} \cdot C_{6}H_{3}Me_{3})Pt(Me_{3}P)Me^{+})$, -0.74 (dt, ${}^{2}J_{HPt} = 58$ Hz, ${}^{3}J_{HP}(cis) = 8.2$ Hz, ${}^{3}J_{HP}(trans) = 6.5$ Hz, 3H; $Pt(C\underline{H}_{3})$). ${}^{31}P$ NMR (161.97 MHz, 1,2-difluorobenzene, 25 °C): δ –20.3 (d, ¹J_{PPt} = 2570 Hz, ${}^{2}J_{PP} = 23.5$ Hz, 2P; Me₃P's cis to Pt-Me), -26.4 (t, ${}^{1}J_{PPt} =$ 1790 Hz, ${}^{2}J_{PP} = 23.5$ Hz, 1P; Me₃P trans to Pt-Me).

Catalytic Ethylene Dimerization Using 1. In a typical experiment, a Teflon-valved 5 mm NMR tube containing a sealed acetone- d_6 capillary was charged with 10 mg of 1 and 0.5 mL of 1,2-difluorobenzene, and excess ethylene was condensed in at 77 K. Integration of initial ¹H NMR spectra quantified the initial amount of added ethylene, which was typically ~25 equiv. NMR spectra at 25 °C were taken at 5 min intervals using both the residual acetone- d_5 and the 1,2-difluorobenzene as reference standards. Integration of *cis*- and *trans*-2-butene product methyl resonances was used to determine TONs. The catalytic activity was taken from the time period subsequent to complete propene formation.

X-ray Crystallography. X-ray diffraction data for $\{(\eta^6-C_6H_3Me_3)-Pt[(C_2F_5)_2MeP]Me\}^+(B(C_6F_5)_4)^-$ (1) were measured at 150 K on a Bruker SMART APEX II CCD area detector system equipped with a graphite monochromator and a Mo K α fine-focus sealed tube operated at 1.5 kW power (50 kV, 30 mA). Crystals were attached to glass fibers

using Paratone N oil. Collection and refinement details are included in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.5b00410.

Representative NMR spectra and tables giving X-ray diffraction data collection and refinement details for 1 (PDF)

CIF data for complex 1 (CIF)

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Notes

The authors declare no competing financial interest.

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