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Structural and Reactivity Properties of
Perfluoroalkylphosphine Complexes of Platinum(0)[†]

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Abstract

The synthesis and structural characterization of 2- and 3-coordinate Pt(0) complexes with π -acceptor perfluoroalkylphosphine ligands (PFAP's) is reported. (dfebp)₂Pt (dfebp = (C₂F₅)₂P^tBu) was prepared in moderate yield by either thermolysis of (cod)Pt(Ph)₂ in neat dfebp or, more efficiently, by the treatment of (nbe)₃Pt with 2 equiv. dfebp in the presence of H₂. Addition of 1 equiv. CF₃CO₂H to (dfebp)₂Pt generates the expected Pt(II) *trans*-(dfebp)₂Pt(O₂CCF₃)(H) product, while treatment with the mesitylenium acid (C₆Me₃H₄)⁺B(C₆F₅)₄⁻ leads to phosphine loss and formation of the arene complex [(η^6 -C₆Me₃H₃)Pt(dfmp)(CH₃)]⁺(B(C₆F₅)₄)⁻. Addition of ethylene to (dfebp)₂Pt results in facile and reversible equilibria with the ethylene adducts (dfebp)₂Pt(C₂H₄) and (dfebp)Pt(C₂H₄)₂, which have been quantified by VT NMR spectroscopy.

[†]*Submitted in honor of Malcolm L. H. Green, on the occasion of his 80th birthday*

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1. Introduction

Homo- and heteroleptic organophosphine complexes are ubiquitous in inorganic and organometallic chemistry.^{1,2} In the years following Tolman's pioneering work quantifying phosphine steric and electronic effects,³ the systematic manipulation of phosphine ligand steric and electronic properties in coordination complex chemistry has been widely studied and exploited in homogeneous metal catalyst design.^{4,5} More sophisticated analyses of phosphine ligand properties using experimental or computational data have appeared over the years.⁶ Orpen and coworkers as well as Cundari have employed computational methods to map out phosphine "ligand space".^{7,8} Cundari, in particular, has noted that sterically-demanding phosphines with electron-withdrawing perfluoroalkyl groups (which we refer to more specifically as perfluoroalkylphosphines, or "PFAPs") occupy a region of phosphine ligand space that is underrepresented.⁹

Group 10 metal homoleptic phosphine complexes have been studied extensively and often serve as illustrative models for phosphine steric influence over coordination number, ranging from classic 4-coordinate 18-electron $(\text{Et}_3\text{P})_4\text{M}^{10}$ ($\Theta(\text{Et}_3\text{P}) = 132^\circ$) and 3-coordinate 16-electron $(\text{Ph}_3\text{P})_3\text{M}$ ($\Theta(\text{Ph}_3\text{P}) = 145^\circ$)^{11,12,13} systems to two-coordinate 14-electron complexes $(\text{R}_3\text{P})_2\text{M}$ ($\text{R}_3\text{P} = \text{Cy}_3\text{P},^{14} \text{}^t\text{Bu}_3\text{P},^{15} (o\text{-tol})_3\text{P}^{16}$). A large range of palladium 2-coordinate phosphine complexes $(\text{R}_3\text{P})_2\text{Pd}$ have been prepared with varying steric and electronic phosphine properties and applied to Pd-mediated coupling reactions;¹⁶⁻¹⁷ only a limited number of structurally characterized $(\text{R}_3\text{P})_2\text{Pt}(0)$ systems have been reported.^{14a,18} In the context of fundamental coordination chemistry,

(R₃P)₂Pd(0) and (R₃P)₂Pt(0) complexes have been attractive systems for oxidation addition studies, since prior loss of phosphine is not required.^{10a,16,17g,18a,19}

The established range of homoleptic group 10 phosphine complexes is largely restricted to donor ligands with negligible or modest π -accepting ability. In our studies with strongly π -accepting perfluoroalkylphosphine ligands, we have reported the synthesis and reactivity properties of the coordinatively-saturated PFAP chelate (C₂F₅)₂PCH₂CH₂P(C₂F₅)₂ (dfepe) complexes (dfepe)₂M (M = Ni,²⁰ Pd,²¹ Pt²²) as well as the monodentate platinum four-coordinate complex (dfmp)₄Pt (dfmp = (C₂F₅)₂PMe; Θ = 140°).²³ In this paper we correct our earlier finding and show that the putative (dfmp)₄Pt product is actually the structurally characterized three-coordinate complex (dfmp)₃Pt. We also describe new PFAP Pt(0) coordination chemistry with the more sterically encumbering ligands (C₂F₅)₂P^{*i*}Bu (dfebp; Θ = 161°) and (C₂F₅)₂P^{*i*}Pr (dfeip; Θ = 154°)^{3,24} and present an initial survey of (dfebp)₂Pt reactivity.

2. Results and Discussion

2.1 Synthesis of (dfmp)₃Pt and (dfebp)₂Pt.

Donor phosphine (R₃P)₂Pd(0) phosphine complexes are readily accessed by the direct reaction of the appropriate phosphine with the labile Pd(0) precursor CpPd(allyl).^{18c,25} The corresponding (R₃P)₂Pt(0) complexes have been obtained by either donor phosphine displacement of cod from (cod)₂Pt or by reduction of (R₃P)₂PtCl₂ precursors.^{18c,26,18b} Our group has previously accessed the bis-chelates (dfppe)₂Pt and (dfepe)₂Pt by thermolysis of (cod)Pt(Ph)₂ in the presence of excess phosphine;²² the key to this synthetic route is activation of (PFAP)_nPt(Ar)₂ intermediates toward reductive

elimination by the poorly donating PFAP ligands. In 2004 we reported the formation of (dfmp)₄Pt via either thermolysis of *cis*-(dfmp)₂Pt(Me)₂ at 80 °C or by the reaction of (cod)Pt(Ph)₂ with excess dfmp at ambient temperatures.²³ However, upon reexamination of this dfmp system we have found that careful recrystallization of “(dfmp)₄Pt” from hexanes at 4 °C yields the 3-coordinate complex (dfmp)₃Pt (**1**) as an analytically pure crystalline yellow solid. ¹H and ³¹P NMR data for **1** are identical to what we previously reported for (dfmp)₄Pt, and moreover are invariant in the presence of excess added dfmp. Subsequent ¹⁹⁵Pt NMR spectra of **1** clearly establish the phosphine stoichiometry: a ¹J_{PtP} quartet is observed at -2947 ppm both in the presence or absence of added excess dfmp; the chemical shift for **1** falls within the range reported for Pt(0) complexes.²⁷ We conclude that our initial (dfmp)₄Pt formulation was in error and that (dfmp)₃Pt is the preferred stoichiometry. DFT analysis (see Experimental Section) supports this conclusion: ΔG_{rxn} for dfmp binding to (dfmp)₃Pt to form (dfmp)₄Pt is estimated to be unfavorable by 15.1 kcal mol⁻¹.

The crystal structure of **1** is shown in Figure 1. The asymmetric unit of **1** is trigonal planar and closely approximates a C_{3h} coordination symmetry with the C₂F₅ groups on each phosphorus mirror related about the P₃Pt plane and all the Me groups related by the perpendicular C₃ axis. The sum of the P-Pt-P angles is 359.9° and the angles are 120 ± 0.4°. The average Pt-P bond distance, 2.236(12) Å, is shorter than Pt-P distances reported for (Cy₃P)₃Pt (2.303(13) Å),²⁸ (Ph₃P)₃Pt (2.266(2) Å),¹³ and (tBu₂PH)₃Pt (2.281(2) Å).²⁹ Systematically shorter M-P bonds in PFAP complexes has been previously noted in our work.³⁰

Figure 1. Molecular view of (dfmp)₃Pt (**1**) with 30% thermal ellipsoids. Selected metrical data: Pt(1)-P(1): 2.2377(13) Å, Pt(1)-P(2): 2.2302(12) Å, Pt(1)-P(3): 2.2416(12) Å; P(1)-Pt(1)-P(2): 120.20(5)°, P(1)-Pt(1)-P(3): 120.35(5)°, P(2)-Pt(1)-P(3): 119.37(4)°.

Initial attempts to prepare (dfebp)₂Pt (**2**) using stoichiometric dfebp and (cod)PtPh₂ showed only limited product formation after warming to 80 °C for three days. Instead, **2** was obtained as a maroon solid in moderate yield by thermolysis of (cod)Pt(Ph)₂ in neat dfebp at 80 °C for 5 days and was separated from the nonfluorous byproducts by selective precipitation from cold methanol (Equation 1).

Efforts to obtain the analogous isopropyl derivative (dfeip)₂Pt using this synthetic approach were not successful: after 24 hrs at 80 °C, complete decomposition of (cod)Pt(Ph)₂ occurred. ³¹P NMR spectra for (dfebp)₂Pt exhibit a broadened (due to unresolved ¹⁹F coupling) resonance at 79.7 ppm with a distinct large ¹J_{Pt} of 5070 Hz. **2** undergoes only limited decomposition in benzene at ambient temperatures (approx.

10% after 4 weeks, as judged by released free dfebp), and complete decomposition was observed after 17 hrs at 120 °C. No changes in the ^{31}P NMR spectra of **2** in the presence of excess dfebp are observed at 25 °C, suggesting that associative exchange via 3-coordinate $(\text{dfebp})_3\text{Pt}$ does not occur to an appreciable extent on the NMR timescale. ΔG_{rxn} for dfmp binding to $(\text{dfebp})_2\text{Pt}$ to form $(\text{dfebp})_3\text{Pt}$ is calculated using DFT methods to be unfavorable by 37 kcal mol $^{-1}$.

$(^t\text{Bu}_3\text{P})_2\text{M}$ (M = Pd or Pt; $\Theta = 182^\circ$) complexes undergo slow decomposition in the presence of oxygen, but less bulky 2-coordinate phosphine complexes such as $(\text{Ph}(^t\text{Bu})_2\text{P})_2\text{Pt}$ and $(\text{Cy}_3\text{P})_2\text{Pt}$ ($\Theta = 170^\circ$) readily coordinate $\eta^2\text{-O}_2$.³¹ Monitoring the reaction of $(\text{dfebp})_2\text{Pt}$ with 800 torr O_2 by ^{31}P NMR spectroscopy in benzene showed no evidence for oxygen adduct formation, but rather the slow appearance of a new ^{31}P resonance at 49.6 ppm which we tentatively assign as the free phosphine oxide $^t\text{Bu}(\text{C}_2\text{F}_5)_2\text{Pt}(\text{O})$. Complete conversion to the oxide occurred at room temperature over the course of 24 hrs.

The crystal structure of **2** is shown in Figure 2. $(\text{dfebp})_2\text{Pt}$ resides on a crystallographic 2-fold axis which enforces a trans rotational conformation of the dfebp ligand groups and a 180° P-Pt-P angle. The Pt-P bond distance, 2.205(2) Å, is once again somewhat shorter than donor phosphine Pt-P distances found in the reported analogous structures $(\text{Cy}_3\text{P})_2\text{Pt}$ (2.231(4) Å),^{14a} $(\text{phosphabarrelene})_2\text{Pt}$ (2.241(4) Å),^{18b} $[(\text{CyCH}_2)_3\text{P}]_2\text{Pt}$ (2.226(1) Å),^{18a} and $[(^t\text{Bu})_2\text{PPh}]_2\text{Pt}$ (2.252(1) Å).^{18c}

Figure 2. Molecular view of (dfeb)₂Pt (**2**) with 30% thermal ellipsoids. Selected metrical data: Pt(1)-P(1): 2.205(2) Å, Pt(1)-C(1): 1.927(6) Å, Pt(1)-C(3): 1.914(6) Å, Pt(1)-C(5): 1.865(6) Å,

An improved synthesis of **2** starting from the Pt(0) precursor (nbe)₃Pt has been developed (Scheme 1): treatment of (nbe)₃Pt with one equivalent dfeb cleanly affords the monophosphine complex (dfeb)Pt(nbe)₂ (**3**). Further displacement of nbe to give (dfeb)₂Pt(nbe) or (dfeb)₂Pt in the presence of excess dfeb was not observed. Isolation from cold petroleum ether or methanol yielded **3** as a solidified oil, which melted upon warming to ambient temperatures. Stirring (nbe)₃Pt in the presence of 2.5 equiv. dfeb in toluene under ~ 3 atm H₂ for one day resulted in the complete hydrogenation of nbe to norbornane and afforded (dfeb)₂Pt in 62% yield.

Scheme 1

An extension of this methodology to the isopropyl ligand dfeip was attempted: Addition of 1.2 equiv. dfeip to (nbe)₃Pt in benzene-*d*₆ resulted in partial nbe displacement and the formation of a 3:1 mixture of (dfeip)Pt(nbe)₂ (**4**) and (dfeip)₂Pt(nbe) (**5**). Further addition of 2.4 equiv. dfeip (3.6 equiv. total) resulted in a 1:3 mixture of **4** and **5**, respectively. Treatment of this mixture with 3 atm H₂ for 4 days resulted in the complete hydrogenation of nbe and the formation of a single major species with a broad ³¹P resonance at 81.9 ppm (¹J_{PPt} = 4750 Hz) and a very broad (ν_{□□□□} = 450 Hz) hydride resonance at δ -6.9. Removal of excess dfeip and H₂ gave a complex mixture of (dfeip)_nPt(H)_x products; further characterization of these hydride products was not pursued.

2.2 (dfebp)₂Pt Reactivity Studies.

The synthesis of (dfebp)₂Pt via thermolysis of (cod)PtPh₂ in the presence of excess phosphine presumably involves initial formation of the thermally unstable 16-electron Pt(II) complex (dfebp)PtPh₂. Following our prior synthesis of the dimethyl complex *cis*-(dfmp)₂PtMe₂ from dfmp substitution with (nbd)PtMe₂,²³ we examined the reaction of (nbd)PtMe₂ with dfebp as well as the donor phosphine (^tBu)₃P as a potential route to (R₃P)_nPtMe₂ (n = 1 or 2) products. Treatment of (nbd)PtMe₂ with excess (> 2 equiv.) dfebp or (^tBu)₃P in benzene did not result in any significant displacement reaction up to 80 °C, as judged by ¹H and ³¹P NMR spectroscopy. The synthesis of (dfebp)₂Pt shown in Scheme 1 relies on the sacrificial hydrogenation of competing nbe ligands as well as the stability of (dfebp)₂Pt towards subsequent H₂ addition. This was confirmed directly: benzene-*d*₆ solutions of (dfebp)₂Pt under 800 torr H₂ showed no

evidence for (dfeb_p)₂PtH₂ formation or exchange broadening of the dissolved H₂ resonance.

2.3 (dfeb_p)₂Pt Protonation Chemistry.

In contrast to the lack of (dfeb_p)₂Pt OA reactivity with the nonpolar substrate H₂, reactions with protic acids do occur: addition of 1 equiv. CF₃CO₂H to **2** in benzene-*d*₆ results in a slow conversion over 2 days to *trans*-(dfeb_p)₂Pt(O₂CCF₃)(H) (**6**) (Equation 2). Unlike the previously reported dfmp analog *trans*-(dfmp)₂Pt(O₂CCF₃)(H), which upon removal of volatiles reverts back to (dfmp)₃Pt,³² **6** is stable to acid loss under vacuum.

We have recently reported that reaction of *cis*-(dfmp)₂PtMe₂ with the arenium acid (C₆Me₃H₄)⁺B(C₆F₅)₄⁻ in 1,2-difluorobenzene (ODFB) cleanly produces the unusually stable arene complex [(η⁶-C₆Me₃H₃)Pt(dfmp)(CH₃)]⁺(B(C₆F₅)₄)⁻.³³ The corresponding reaction of (dfeb_p)₂Pt with 1 equivalent (C₆Me₃H₄)⁺B(C₆F₅)₄⁻ was monitored by ¹H and ³¹P NMR spectroscopy. After 30 min at 20 °C ³¹P NMR spectra showed unreacted **2**, a new dfeb_p resonance at 58.3 ppm identified as the arene hydride complex (η⁶-C₆Me₃H₃)Pt(dfeb_p)(H)⁺ (**7**), and free dfeb_p in a 0.7:1:1 ratio (Scheme 2). Addition of excess (4 equiv) mesitylenium acid gave after an additional 30 min a 1:1 mixture of **7** and a new ³¹P resonance at -53.2 ppm which was later identified as protonated dfeb_p. (tBu)(C₂F₅)₂PH⁺ on the basis of a separate control experiment combining dfeb_p and

mesitylenium acid in ODFB. Complete decomposition of **7** and conversion of released dfebP to $(t\text{Bu})(\text{C}_2\text{F}_5)_2\text{PH}^+$ and unidentified Pt products in the presence of excess acid was observed after 1 hr. ^1H NMR spectra for **7** showed a Pt-coupled methyl singlet for bound mesitylene at δ 4.41 and a platinum hydride resonance at δ -24.66 (d, $^2J_{\text{PH}} = 28$ Hz, $^1J_{\text{PtH}} = 1623$ Hz). Interestingly, two *t*-butyl proton resonances are observed in a 40:60 ratio at δ 0.52 and 0.24 that, together with closely overlapping ^{31}P resonances at 58.5 and 58.3 ppm, are consistent with two distinct rotational conformers of the dfebP ligand with respect to the coordinated arene ligand. These observations are consistent with protonation of $(\text{dfebP})_2\text{Pt}$ by mesitylenium acid to initially form a transient $(\text{dfebP})_2\text{PtH}^+$ intermediate, followed by dfebP displacement to form $(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Pt}(\text{dfebP})\text{H}^+$ as the major product (Scheme 2). Acid trapping of released dfebP and the subsequent complete consumption of **7** to form $(\text{dfebP})\text{H}^+$ prevents the isolation of this product.

Scheme 2

2.4 Reaction of $(\text{dfebP})_2\text{Pt}$ with ethylene.

16-electron ethylene complexes $(\text{R}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4)$ have been indirectly prepared by displacement of H_2 from $(\text{R}_3\text{P})_2\text{PtH}_2$,³⁴ reductive trapping of $(\text{R}_3\text{P})_2\text{PtCl}_2$,³⁵ trapping of thermally³⁶ or photolytically generated $(\text{R}_3\text{P})_2\text{Pt}$,³⁷ and by thermolysis of bis-phosphine diethyl precursors.³⁸ The formation of $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4)$ products via phosphine

displacement from $(\text{Ph}_3\text{P})_3\text{Pt}$ by ethylene is mildly disfavored ($K = 0.122$).³⁹ Otsuka has reported the direct association of maleic anhydride with two-coordinate complexes $[\text{Ph}(\text{tBu})_2\text{P}]_2\text{M}$ ($\text{M} = \text{Pd}, \text{Pt}$), and the competitive association of dimethyl fumarate (DF); thermolysis in the presence of excess DF led to the isolation of stable mono phosphine adducts $[\text{Ph}(\text{tBu})_2\text{P}]\text{M}(\text{DF})_2$.^{31b}

We have examined the reaction of $(\text{dfebp})_2\text{Pt}$ with ethylene. The addition of 1 atm C_2H_4 to $(\text{dfebp})_2\text{Pt}$ in benzene results in the loss of one equivalent dfebp and the clean formation of $(\text{dfebp})\text{Pt}(\text{C}_2\text{H}_4)_2$ (**8**) within minutes at ambient temperatures (Scheme 3). ^1H NMR spectra under excess ethylene at 25 °C exhibit a sharp singlet for the coordinated C_2H_4 ligands of **8** at 2.96 ($^2J_{\text{PtH}} = 59$ Hz), confirming that ethylene exchange is slow on the NMR timescale. C_2H_4 substitution is readily reversed: removal of ethylene *in vacuo* at 25 °C leads to the loss of coordinated ethylene and clean reversion to $(\text{dfebp})_2\text{Pt}$. Incomplete removal of ethylene or the addition of sub-stoichiometric amounts of ethylene leads to the partial formation of the mono-ethylene complex, $(\text{dfebp})_2\text{Pt}(\text{C}_2\text{H}_4)$ (**9**).

Scheme 3

In contrast to **8**, the mono-ethylene complex **9** undergoes fast exchange with ambient C_2H_4 on the ^1H NMR timescale (Figure 3): ^1H NMR spectra for **8** - **9** mixtures in the presence of 0.5 equiv. C_2H_4 at 25 °C show a highly broadened ($\nu_{\text{C}_2\text{H}_4} = 40$ Hz) C_2H_4 resonance at $\delta_{\text{C}_2\text{H}_4}$ which, upon cooling, shifts upfield and reaches a slow exchange

limit at -30 °C. No $^3J_{\text{PH}}$ ethylene coupling is resolved for either **8** and **9**, and singlet resonances indicate that either ethylene coordination is perpendicular to the trigonal plane or rapid rotation about the Pt-ethylene axis is occurring on the NMR time scale.

Figure 3. ^1H (400.13 MHz) expanded VT NMR spectra for $(\text{dfebp})_2\text{Pt}$ with 0.5 equiv. added ethylene in $\text{toluene-}d_8$. (●) and (■) denote the ethylene resonances for $(\text{dfebp})_2\text{Pt}(\text{C}_2\text{H}_4)$ (**9**) and for $(\text{dfebp})\text{Pt}(\text{C}_2\text{H}_4)_2$ (**8**), respectively.

The equilibria between $(\text{dfebp})_2\text{Pt}$, $(\text{dfebp})_2\text{Pt}(\text{C}_2\text{H}_4)$, and $(\text{dfebp})\text{Pt}(\text{C}_2\text{H}_4)_2$ were assessed by monitoring ^1H and ^{31}P NMR spectra in the presence of 0.25 – 2.0 equivalents of added C_2H_4 . The equilibrium between $(\text{dfebp})_2\text{Pt}$ and $(\text{dfebp})_2\text{Pt}(\text{C}_2\text{H}_4)$ lies far toward adduct formation and K_1 could not be directly determined. However, at -40 °C in the presence of 0.75 equiv. added C_2H_4 , the relative amounts of free ethylene, $(\text{dfebp})_2\text{Pt}(\text{C}_2\text{H}_4)$ $(\text{dfebp})\text{Pt}(\text{C}_2\text{H}_4)_2$ were readily quantified and K_2 was determined to be 6.1(5) at this temperature. The initial association of ethylene with

(dfebp)₂Pt (fast, $K_1 \gg 1$) followed by phosphine loss to form (dfebp)Pt(C₂H₄)₂ (slow, $K_2 > 1$) mirrors the alkene exchange behavior previously reported for [(^tBu)₂PPh]₂Pt.^{31b}

In light of facile ethylene substitution chemistry, the binding affinity of the 14-electron (dfebp)₂Pt to nitriles was briefly examined. Dissolution of **2** in neat benzonitrile or CD₃CN at 25 °C showed no significant changes in ³¹P chemical shift or the ¹J_{PtP} value of **2**, indicating that the affinity of this 2-coordinate PFAP complex for nitriles is negligible.

3. Summary

We have presented the first examples of 2- and 3-coordinate π -acceptor phosphine complexes of Pt(0), (dfebp)₂Pt, and (dfmp)₃Pt. The estimated cone angle for dfebp, 161°, is somewhat less than structurally-characterized 2-coordinate donor phosphine systems with Cy₃P and Ph(^tBu)₂P ($\Theta \sim 170^\circ$ for both). Attempts to prepare an analogous 2-coordinate PFAP complex using the slightly smaller dfeip ligand were unsuccessful, and accessing (dfeip)₂Pt indirectly following the sacrificial nbe dehydrogenation procedure outlined in Scheme 1 failed due to the formation of (dfeip)_nPt(H)_x product mixtures; this is presumably due to more favorable H₂ addition to the less sterically protected (dfeip)₂Pt system. The successful synthesis of stable (PFAP)₂Pt products requires a subtle balance of ligand steric effects.

Addition of a conventional HX acid, CF₃CO₂H, with a coordinating acetate counteranion to (dfebp)₂Pt gives the expected *trans*-(dfebp)₂Pt(H)(X) product. In the case of the mesitylenium acid (C₆Me₃H₄)⁺B(C₆F₅)₄⁻, the (dfebp)₂PtH⁺ intermediate is unstable toward dfebp loss and the arene complex (η^6 -C₆Me₃H₃)Pt(dfebp)(H)⁺ is formed. (dfebp)₂Pt does not form adducts with nitriles, but does readily react with

ethylene to sequentially form $(\text{dfepb})_2\text{Pt}(\text{C}_2\text{H}_4)$ and $(\text{dfepb})\text{Pt}(\text{C}_2\text{H}_4)_2$. In light of the extensive use of low-coordinate donor phosphine palladium complexes in C-C bond coupling chemistry, the extension of $(\text{dfebp})_2\text{Pt}$ synthesis methodology to electron-poor $(\text{dfebp})_2\text{Pd}$ chemistry is worth pursuing.

4. Experimental

4.1 General Procedures.

All manipulations were conducted under an atmosphere of nitrogen by using Schlenk, high-vacuum line, and/or glovebox techniques. Dry, oxygen-free solvents were vacuum distilled prior to usage. Elemental analyses were performed by Desert Analytics, Inc. NMR spectra were recorded with a Bruker DRX-400 instrument using 5 mm NMR tubes fitted with Teflon valves (Chemglass, CG-512). ^{31}P spectra were referenced to a 85% H_3PO_4 external standard. *Ortho*-difluorobenzene was purchased from Synquest Laboratories, Inc. and was distilled and dried over activated 3Å molecular sieves before use. $(\text{C}_2\text{F}_5)_2\text{P}^t\text{Bu}$ (*dfebp*),⁴⁰ $(\text{C}_2\text{F}_5)_2\text{PMe}$ (*dfmp*),²³ $(\text{nbe})_3\text{Pt}$,⁴¹ and $(\text{C}_6\text{Me}_3\text{H}_4)^+\text{B}(\text{C}_6\text{F}_5)_4^{-42}$ were prepared following literature procedures.

4.2. Synthesis of *Bis(pentafluoroethyl)isopropylphosphine (dfeip)*.

To a 250 mL three-necked flask under an atmosphere of nitrogen was added 34.5 mL of BuLi (2.5 M in hexanes, 86 mmol). The hexanes were removed under vacuum, and the BuLi oily residue was taken up in 75 mL of diethyl ether. After cooling to -78 °C, 10 mL of $\text{C}_2\text{F}_5\text{Cl}$ (bp -34 °C, density 1.88 g/mL, 122 mmol) maintained at -78 °C was slowly transferred into the well-stirred BuLi/ether solution so as to maintain the reaction temperature below -75 °C. Upon completion of the transfer the solution

temperature was maintained at -78 °C and stirred for an additional 20 min. At this point a 4.3 mL aliquot of (*i*Pr)PCl₂ (5 g, density 1.18 g/mL, 35 mmol) was slowly added via syringe under a nitrogen counterflow to the solution while the bath temperature was maintained below -75 °C. The reaction mixture was stirred for an additional 15 min after complete addition and then allowed to slowly warm to room temperature. Ether and butyl chloride were removed by distillation at atmospheric pressure, the pressure was reduced to 265 Torr, and 6.65 g (4.38 mL, d = 1.52 g/mL, 62%) of > 95% pure product was collected between 81 - 86 °C. ¹H NMR (benzene-*d*₆, 400.13 MHz, 27 °C): δ 0.91 (dd, ³J_{PH} = 16 Hz, ³J_{HH} = 7 Hz, 6H; C(CH₃)₂H), 2.03 (heptet, ³J_{HH} = 7 Hz, 1H; C(CH₃)₂H). ¹⁹F NMR (benzene-*d*₆, 376.45 MHz, 27 °C): δ -81.72 (d, ³J_{PF} = 8 Hz, 6F; PCF₂C_F₃), -106.6 to -109.8 (AB portion of ABX system, ²J_{FF} = 310 Hz, ²J_{PFa} = 49 Hz, ²J_{PFb} unresolved, 4F; C_F₂CF₃). ³¹P NMR (benzene-*d*₆, 161.97 MHz, 27 °C): δ 22.3 (m).

4.3. Synthesis of (dfmp)₃Pt (**1**).

A mixture of (cod)Pt(Ph)₂ (313 mg, 0.684 mmol) and dfmp (620 μL, 3.42 mmol) were combined in 10 mL toluene at -78 °C. Warming to ambient temperature with stirring for 24 hrs produced a yellow homogeneous solution. Removal of ca. 5 mL toluene and addition of ca. 5 mL methanol followed by cooling to -78 °C produced a light yellow solid, which was collected by cold filtration and dried under vacuum (547 mg, 76.4%). Careful recrystallization from hexanes at 4 °C yielded analytically pure yellow crystalline **1**. Anal. calcd for C₁₅H₉F₃₀P₃Pt: C, 17.20; H, 0.87. Found: C, 17.20; H, 0.98. ¹H NMR (400.13 MHz, benzene-*d*₆, 27 °C): δ 1.53 (s, ²J_{PH} = 34 Hz; Pt[P(C₂F₅)₂(CH₃)]). ³¹P NMR (161.97 MHz, benzene-*d*₆, 27 °C): δ 59.8 (m, ¹J_{PtP} = 4805 Hz). ¹⁹⁵Pt NMR (85.59 MHz, *o*-difluorobenzene, 27 °C): δ -2947 (q, ¹J_{PtP} = 4805 Hz). ¹⁹F

NMR (benzene- d_6 , 376.46 MHz, 22 °C): δ -76.91 (s, 18F; $\text{PCF}_2\text{C}\underline{\text{F}}_3$), -111.80 (m, 12F; $\text{C}\underline{\text{F}}_2\text{CF}_3$).

4.4. (dfebpt)₂Pt (2), Method A.

(cod)Pt(Ph)₂ (411 mg, 0.899 mmol) and dfebpt (1.8 mL, 5.4 mmol) were combined and warmed to 80 °C for 5 days, during which time the solution became red-brown. The volatiles were removed (NOTE: the crude distillate was reserved for future recovery of dfebpt), the residue was taken up in 25 mL hot methanol and filtered. Concentration of the filtrate, cooling to -78 °C, filtration, and drying under vacuum afforded maroon solid 2 (476 mg, 63%). Careful recrystallization of the crude product from hot methanol yielded crystals suitable for X-ray diffraction and elemental analysis. Anal. calcd for C₁₆H₁₈F₂₀P₂Pt: C, 22.68; H, 2.13. Found: C, 22.61; H, 2.29. ¹H NMR (400 MHz, benzene-*d*₆, 23 °C): δ 1.28 (ps. t, J_{PH} = 9 Hz; P(C(CH₃)₃). ³¹P NMR (161.97 MHz, benzene-*d*₆, 23 °C): δ 79.7 (br. s, ²J_{PPt} = 5070 Hz). ¹⁹F NMR (376.05 MHz, benzene-*d*₆, 23 °C): δ -79.4 (s, 6F; PCF₂CF₃), δ -105 to -108 (overlapping ABX multiplets; PCF₂CF₃).

4.5. (dfebpt)₂Pt (2), Method B.

(nbe)₃Pt (190 mg, 0.398 mmol), dfebpt (0.225 mL, 1.00 mmol) and 8 mL toluene were added to a 100 mL Pyrex tube fitted with a Teflon valve and the mixture was stirred at ambient temperature for one hour to form (dfebpt)Pt(nbe)₂. 1 atm H₂ was admitted at 77 K (~ 3 atm at 20 °C) and the mixture was warmed to ambient temperature and stirred for one day. The volatiles were removed and the crude product was taken up in 10 mL warm methanol and filtered. Concentration and cooling to -78 °C afforded, after filtering, spectroscopically pure 2 (208 mg, 62%).

4.6. (dfebpt)Pt(nbe)₂ (**3**).

A mixture of (nbe)₃Pt (150 mg, 0.314 mmol), dfebpt (81 μ l (dfebpt density = 1.52 g/mL), .377 mmol) and 15 mL toluene were combined and stirred for one hour at ambient temperature, during which time the solution became dark brown. Removal of toluene and addition of 5 mL methanol followed by cooling to -78 °C gave 143 mg (65%) of dark brown solidified **3**, which melted upon warming to 20 °C. The purity, as judged by NMR spectroscopy, was > 95%. ¹H NMR (400 MHz, benzene-*d*₆, 23 °C): δ 3.19 (br. s, ²J_{PTH} = 66 Hz, 4H; Pt(nbe)₂ (C-2,3)H), δ 2.88, (br. s, 4H; Pt(nbe)₂ (bridgehead, C-1,4)H), δ 1.57 (dm, ²J_{HH} = 7 Hz, 4H; Pt(nbe)₂ (C-5,6)HH'), δ $\square\square\square$ 24 (d, ³J_{PH} = 6 Hz, 9H; (CH₃)₃CP), δ 1.20 (ddm, ²J_{HH} = 8 Hz, ³J_{HH} = 2 Hz, 4H; Pt(nbe)₂ (C-5,6)HH'), δ 0.39 (dm, ²J_{HH} = 9 Hz, 2H; Pt(nbe)₂ (C-7)HH'), δ 0.18 (dm, ²J_{HH} = 9 Hz, 2H; Pt(nbe)₂ (C-7)HH'). ³¹P NMR (161.97 MHz, acetone-*d*₆, 23 °C): δ 97.1 (tt, ²J_{PF} = 73, 54 Hz, ²J_{PPt} = 3990 Hz). ¹⁹F NMR (376.05 MHz, benzene-*d*₆, 23 °C): δ -77.5 (s, br. 6F; PCF₂CF₃), δ -102 to -105 (overlapping ABX multiplets; PCF₂CF₃).

4.7. (dfeipt)Pt(nbe)₂ (**4**) and (dfeip)₂Pt(nbe) (**5**).

A 5 mm NMR tube fitted with a Teflon valve was charged with 11 mg (0.023 mmol) (nbe)₃Pt and 0.5 mL benzene-*d*₆. After the addition of 5.7 μ L dfeip (1.2 equiv.) at ambient temperature, ¹H and ³¹P spectra confirmed partial nbe loss and a 4:1 mixture of (dfeip)Pt(nbe)₂ (**4**) and (dfeip)₂Pt(nbe) (**5**). Further addition of 2.4 equiv. dfeip resulted in further reaction to give a 1:3 mixture of **4** and **5**, respectively. Isolation of these nbe adducts was not attempted. **NMR data for 4:** ¹H NMR (400.13 MHz, benzene-*d*₆, 23 °C): δ 3.24 (m, 4H; Pt(nbe)₂ (C-2,3)H), δ 2.88, (br. s, 4H; Pt(nbe)₂ (bridgehead, C-1,4)H), δ 2.85 (heptet, ³J_{HH} = 7 Hz, 1H; P(CH(CH₃)₂), δ 1.56 (dd, ²J_{HH} = 7.5 Hz, ³J_{HH} =

1.6 Hz, 4H; Pt(nbe)₂ (C-5,6)HH'), δ 2.00 (dd, $^2J_{HH} = 7.5$ Hz, $^4J_{HH} = 2.5$ Hz, 4H; Pt(nbe)₂ (C-5,6)HH'), δ 1.03 (d, $^3J_{HH} = 7$ Hz, 6H; P(CH(CH₃)₂)), δ 0.43 (dm, $^2J_{HH} = 9$ Hz, 2H; Pt(nbe)₂ (C-7)HH'), δ 0.17 (dm, $^2J_{HH} = 9$ Hz, 2H; Pt(nbe)₂ (C-7)HH'). ³¹P NMR (benzene-*d*₆, 161.97 MHz, 23 °C): δ 81.7 (pseudo pentet, $^1J_{PPt} = 3930$ Hz, $^2J_{PFa} = ^2J_{PFb} = 72$ Hz). **NMR data for 5:** ¹H NMR (benzene-*d*₆, 400.13 MHz, 23 °C): δ 3.24 (m, $^2J_{PtH} = 75$ Hz, 2H; Pt(nbe) (C-2,3)H), δ 2.91, (m, 4H; Pt(nbe) (bridgehead, (C-1,4)H), δ 2.88 (heptet, $^3J_{HH} = 7$ Hz, 2H; P(CH(CH₃)₂)), δ 1.54 (m, 2H; Pt(nbe) (C-5,6)HH'), δ 1.09 (m, 12H; P(CH(CH₃)₂)), δ 0.65 (dm, $^2J_{HH} = 8$ Hz, 1H; Pt(nbe) (C-7)HH'), δ 0.35 (dm, $^2J_{HH} = 8$ Hz, 1H; Pt(nbe) (C-7)HH'). ³¹P NMR (benzene-*d*₆, 161.97 MHz, 23 °C): δ 83.2 (m, $^1J_{PPt} = 4000$ Hz)

4.8. *trans*-(dfeb₂Pt(H)(O₂CCF₃)) (6).

A 5 mm NMR tube fitted with a Teflon valve was charged with 15 mg (0.018 mmol) of (dfeb)₂Pt, 1.3 μ L CF₃CO₂H (1.49 g/mL, 0.019 mmol) and 0.5 mL benzene-*d*₆. After 2 days the complete conversion to *trans*-(dfeb)₂Pt(H)(O₂CCF₃) was observed, as judged by ¹H and ³¹P NMR spectroscopy. NMR spectra after solvent removal and addition of benzene-*d*₆ were unchanged. ¹H NMR (400 MHz, benzene-*d*₆, 27 °C): δ 1.22 (pseudo t, $^3J_{PH} = 9$ Hz, 9H; P(C(CH₃)₃); δ -21.40 (t, $^2J_{PH} = 15$ Hz; $^1J_{PtH} = 868$ Hz; 1H; PtH). ³¹P NMR (161.97 MHz, benzene-*d*₆, 27 °C): δ 71.9 (m, $^1J_{PPt} = 3540$ Hz).

4.9. (η^6 -C₆H₃Me₃)Pt(dfeb)H⁺ (7).

A 5 mL NMR tube fitted with a Teflon valve was charged with 10 mg (0.012 mmol) of (dfeb)₂Pt and 9 mg (0.011 mmol) of mesitylenium acid in 0.5 mL *ortho*-difluorobenzene (ODFB). After 30 min at ambient temperature a 0.7:1:1 mixture of

unreacted $(\text{dfeb})_2\text{Pt}$, $(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Pt}(\text{dfeb})\text{H}^+$, and free dfeb was established, as judged by ^1H and ^{31}P NMR spectroscopy. NMR data for **7** are consistent with a ~60:40 ratio of dfeb rotational conformational isomers. **NMR data for $(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Pt}(\text{dfeb})\text{H}^+$:** ^1H NMR (400 MHz, ODFB, 25 °C): δ 4.41 (s, br. $J_{\text{PtH}} = 14$ Hz, 9H; $(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Pt}$); δ 0.52 (m; 40% rotational conformer, $^t\text{BuP}(\text{C}_2\text{F}_5)_2$); δ 0.24 (d, $^3J_{\text{PH}} = 14$ Hz; 60% rotational conformer, $^t\text{BuP}(\text{C}_2\text{F}_5)_2$); δ -24.66 (d, $^2J_{\text{PH}} = 28$ Hz, $^1J_{\text{PtH}} = 1622$ Hz). ^{31}P NMR (161.97 MHz, ODFB, 25 °C): δ 58.5 ppm (pseudo pentet, $^2J_{\text{PF}} = 65$ Hz, $^1J_{\text{PtP}} = 5475$ Hz, 40% conformer); δ 58.3 (pseudo pentet, $^2J_{\text{PF}} = 65$ Hz, $^1J_{\text{PtP}} = 5665$ Hz, 60% conformer).

4.10. Reactions of $(\text{dfeb})_2\text{Pt}$ with ethylene.

A 5mm NMR tube fitted with a Teflon valve was charged with 15 mg (0.018 mmol) of $(\text{dfeb})_2\text{Pt}$ and 0.5 mL toluene- d_8 . Successive portions of 0.25 equiv. ethylene were added via syringe and the distribution of reactants and products was quantified by ^1H and ^{31}P NMR spectroscopy. Sufficient $(\text{dfepe})_2\text{Pt}(\text{C}_2\text{H}_4)$ (**9**) for spectral characterization was observed -40 °C after 0.25 equiv. added ethylene. **NMR data for $(\text{dfepe})_2\text{Pt}(\text{C}_2\text{H}_4)$ (**9**):** ^1H NMR (400 MHz, d_8 -toluene, -40 °C): δ 2.68 (s, br. $^2J_{\text{PtH}} = 64$ Hz, 4H; $\text{Pt}(\text{C}_2\text{H}_4)$); δ 1.08 (m, 18H; $\text{P}(\text{C}(\text{CH}_3)_3)_3$). ^{31}P NMR (161.97 MHz, d_8 -toluene, -40 °C): 96 ppm (m, $^1J_{\text{PPt}} = 4110$ Hz). Addition of 800 torr ethylene to $(\text{dfeb})_2\text{Pt}$ and 0.5 mL toluene- d_8 resulted in clean conversion to the bis-ethylene complex $(\text{dfepe})\text{Pt}(\text{C}_2\text{H}_4)_2$. **NMR data for $(\text{dfepe})\text{Pt}(\text{C}_2\text{H}_4)_2$ (**8**):** ^1H NMR (400 MHz, toluene- d_8 , 24 °C): δ 2.88 (s, $^2J_{\text{PtH}} = 60$ Hz, 8H; $\text{Pt}(\text{C}_2\text{H}_4)_2$); δ 0.98 (d, $^3J_{\text{PH}} = 15$ Hz, 9H; $\text{P}(\text{C}(\text{CH}_3)_3)_3$). ^{31}P NMR (161.97 MHz, toluene, 24 °C): 88.7 ppm (ps. t, $^1J_{\text{PPt}} = 3940$ Hz).

4.11. X-ray Crystallography.

X-ray diffraction data for (dfmp)₃Pt (**1**) and (dfebp)₂Pt (**2**) 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). 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 and were integrated with the Bruker SAINT Software package⁴³ using a narrow-frame integration algorithm. Structure data and refinement details are given in the supplemental section.

4.12. Computational Details.

T₀₀₀gas-phase χ calculations at 298.15 K for the reactions “(dfmp)₃Pt + dfmp $\rightarrow$ (dfmp)₄Pt” and “(dfebp)₂Pt + dfebp $\rightarrow$ (dfebp)₃Pt” were calculated with Gaussian 09 Rev. A.02,⁴⁴ using the M06-L functional for geometry optimization and frequencies.⁴⁵ Def2-TZVP basis sets were used for hydrogen, carbon, and fluorine, the diffuse basis set def2-TZVPD was used for phosphorus, and def2-QZVPD was used for platinum.⁴⁶ All reactants and products were optimized to geometries with non-imaginary vibrational frequencies. An approximate C_{3h} starting refinement geometry for (dfebp)₃Pt was utilized with no symmetry restriction, following the solid state structure found for (dfmp)₃Pt.

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Table of Contents

The first examples of structurally-characterized 2- and 3-coordinate Pt(0) complexes with π -acceptor perfluoroalkylphosphine ligands (PFAP's) is reported. Addition of ethylene to (dfebp)₂Pt (dfebp = (C₂F₅)₂P^tBu) results in facile and reversible equilibria with the ethylene adducts (dfebp)₂Pt(C₂H₄) and (dfebp)Pt(C₂H₄)₂.