# Structural, Computational, and Spectroscopic Investigation of $[Pd(\kappa^{3}-1,1'-bis(di-tert-butylphosphino)ferrocenediyl)X]^{+}$ (X = Cl, Br, I) Compounds

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**S** Supporting Information

**ABSTRACT:** The reaction of  $[Pd(dtbpf)Cl_2]$  (dtbpf = 1,1'-bis(di-*tert*butylphosphino)ferrocene) with sodium bromide yields [Pd(dtbpf)Br][Br], which displays an interaction between the iron and palladium atoms. The structure of this compound has been obtained and is compared to those of the previously reported  $[Pd(dtbpf)X]^+$  (X = Cl, I) analogues. Similar to  $[Pd(dtbpf)Cl]^+$ ,  $[Pd(dtbpf)Br]^+$  appears to undergo a solid-state isomerization at low temperature to a species in which the Fe–Pd interaction is disrupted. In addition to <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR and visible spectroscopy, the  $[Pd(dtbpf)X]^+$  (X = Cl, Br) compounds were also characterized by zero-field <sup>57</sup>Fe Mössbauer spectroscopy. DFT calculations on  $[Pd(dtbpf)-X]^+$  (X = Cl, Br, I) show that the Fe–Pd interaction is weak and noncovalent and that the strength of the interaction decreases as the halide



becomes larger. A related trend is noted in the potential at which oxidation of the iron center occurs; the larger the halide, the less positive the potential at which oxidation occurs. Finally, the catalytic activity of  $[Pd(dtbpf)X]^+$  (X = Cl, Br, I) in the arylation of an aromatic ketone was examined and compared to the activity of  $[Pd(dtbpf)Cl_2]$ .

# INTRODUCTION

1,1'-Bis(diphenylphosphino)ferrocene (dppf) is the bidentate phosphine with a metallocene backbone that has been studied the most, particularly as a ligand in catalytic systems.<sup>1</sup> There are many different types of ligands that are closely related to dppf, but the most common are ones in which the R groups on the phosphorus atoms are altered (Figure 1). Changing the R groups not only affects the potential at which oxidation of the iron center occurs,<sup>2</sup> it can also play a significant role in the reactivity of compounds containing these ligands. In particular, the steric bulk of the *tert*-butyl groups in dtbpf<sup>3</sup> has been proposed to be responsible for drastically different behavior



Figure 1. Common bis(phosphino)ferrocene ligands.

that has been observed in several studies of compounds containing this ligand.

The catalytic activity of compounds employing bis-(phosphino)ferrocene ligands can be significantly affected by the steric bulk of dtbpf. The coupling of diphenylphosphine and o-CF3C6H4Br was much more efficient with a dippf- $Pd(OAc)_2$  catalyst precursor than with dtbpf-Pd(OAc)<sub>2</sub>.<sup>4</sup> Of the  $[Pd(P^{\cap}P)Cl_2]$  (P^{\cap}P = dppf, dippf, dtbpf) catalysts, the dtbpf compound was found to be the least efficient in the crosscoupling of aryl Grignards with bromoanisoles.<sup>5</sup> For the allylic amination of a Morita-Baylis-Hillman acetate the catalystligand systems  $[Pd(C_3H_5)Cl]_2 - (P^{\cap}P)$  (P<sup>\circ</sup>P = dppf, dippf, dtbpf) were similar in terms of product formation, but the dtbpf catalyst gave much higher regioselectivity of the product.<sup>6</sup> Similarly, the reductive carbonylation of 4-bromoacetanilide using  $[Pd(dppf)Cl_2]$  as the catalyst gives predominantly the desired aryl aldehyde product, while using [Pd(dtbpf)Cl<sub>2</sub>] gives exclusively the arene.<sup>7</sup> For the  $[Ru(PPh_3)_3(CO)(H_2)] - (P^P)$  $(P^{\cap}P = dppf, dippf, dtbpf)$  catalyzed alkylation of *tert*-butyl

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ketonitrile with benzyl alcohol, the greater bulk of dtbpf significantly inhibits product formation.

In a noncatalytic system, the steric bulk of dtbpf can also play a significant role. Unlike the case for the related 1,1'bis(phosphine selenide)ferrocene compounds,9 oxidation of dtbpfSe2 results in the formation of an isolable Se-Se-bonded dication that has been structurally characterized.<sup>2d</sup> Reductive elimination of diaryl ethers from  $[Pd(P^{\cap}P)(Ar)(OAr')](P^{\cap}P =$ dppf, dtbpf) was found to be significantly faster for the bulkier dtbpf compound.<sup>10</sup> A study of the formation of palladium aryl enolates found that dppf bound as a bidentate ligand to palladium, whereas a similar reaction with dtbpf yielded a compound in which only one of the phosphorus atoms of dtbpf was bound to the palladium.<sup>11</sup> While 2 equiv of  $B(C_6F_5)_3$  will undergo nucleophilic aromatic substitution reactions with dippf to give  $[Fe(C_5H_4P(^iPr)_2C_6F_4BF(C_6F_5)_2)_2]$ , dtbpf only reacts with 1 equiv of  $B(C_6F_5)_3$  to give  $[Fe(C_5H_4P(^tBu)_2C_6F_4BF_5)_3]$  $(C_6F_5)_2(C_5H_4P(^tBu)_2)$ ; attempts to drive a reaction with a second equivalent of  $B(C_6F_5)_3$  lead to decomposition.<sup>1</sup>

Of greatest significance to this report are the studies in which dtbpf binds in a  $\kappa^3$  coordination mode to a palladium center (Figure 2). When [Pd(COD)ClCH<sub>3</sub>] is reacted with either



**Figure 2.** K<sup>3</sup> coordination mode of dtbpf.

dppf or dippf, the COD is replaced with the bidentate phosphine, yielding  $[Pd(P^{\cap}P)ClCH_3]$  ( $P^{\cap}P = dppf$ , dippf). However, when a similar reaction is performed with dtbpf, the greater steric bulk of the ligand does not allow formation of [Pd(dtbpf]ClCH<sub>3</sub>] but instead yields [Pd( $\kappa^3$ -dtbpf)CH<sub>3</sub>]- $[Cl]^{13}$  Similarly, the reaction of Na[BArF] with  $[Pd(P^{\cap}P)Cl_2]$  $(P^{\cap}P = dppf, dippf, dcpf)$  abstracts a chloride ligand from the palladium and results in the formation of a dimeric species,  $[Pd_2(P^{\cap}P)_2(\mu-Cl)_2][BArF]_2$ . The bulk of dtbpf prevents this dimerization following chloride abstraction, and thus  $[Pd(\kappa^3$ dtbpf)Cl][BArF] is formed in which the empty coordination site generated by removing a chloride ligand is occupied by a weak, noncovalent interaction between palladium and iron.<sup>14</sup> To further investigate these types of compounds,  $[Pd(\kappa^3$ dtbpf)Br]+ was synthesized and characterized by NMR spectroscopy and X-ray crystallography. The nature of the iron-palladium interaction was investigated computationally and compared to that of the analogous chloride and iodide compounds. In addition, the oxidative electrochemistry and visible spectra of these compounds are compared. Finally, the <sup>57</sup>Fe Mössbauer spectra of dtbpf and several compounds containing dtbpf are reported.

#### RESULTS AND DISCUSSION

Synthesis and Structural Characterization. Similar to the synthesis of  $[Pd(\kappa^3-dtbpf)Cl][BArF]$ ,<sup>14</sup> the reaction of  $[Pd(dtbpf)Cl_2]$  with K[TFAB] yields  $[Pd(\kappa^3-dtbpf)Cl]$ -[TFAB]. To begin to examine the reactivity of  $[Pd(\kappa^3$ dtbpf)Cl]<sup>+</sup>, an NMR tube reaction was performed in which [PPN]Cl reacted with  $[Pd(\kappa^3-dtbpf)Cl]^+$ . Unsurprisingly, the <sup>31</sup>P NMR spectrum indicated the presence of [Pd(dtbpf)Cl<sub>2</sub>]  $(68.7 \text{ ppm})^{\overline{15}}$  and  $[\text{PPN}]^+$  (21.7 ppm).<sup>16</sup> Similar reactions were performed by adding 1 equiv of either [NBu<sub>4</sub>]Br or [NBu<sub>4</sub>]I to  $[Pd(\kappa^3-dtbpf)Cl]^+$ . In these reactions the expected asymmetric dihalides [Pd(dtbpf)ClX] (X = Br, I) did not form. This was somewhat surprising, as the compound formulated [Pd(dtbpf)-Br<sub>2</sub>] has been reported and is commercially available.<sup>17</sup> The NMR-tube reaction of  $[Pd(\kappa^3-dtbpf)Cl]^+$  with  $[NBu_4]Br$ yielded an approximately 3:5 mixture of [Pd(dtbpf)Cl<sub>2</sub>] and  $[Pd(\kappa^3 - dtbpf)Br][TFAB]$ , while the reaction with  $[NBu_4]I$  gave  $[Pd(dtbpf)Cl_2]$  and  $[Pd(\kappa^3-dtbpf)I]^+$  in an approximately 1:10 ratio (Scheme 1). Formation of [Pd(dtbpf)ClX] (X = Br, I) is apparently unfavorable due to steric constraints. However, ligand substitution of the chloride ligand in  $[Pd(\kappa^3-dtbpf)Cl]^+$ occurs with the stronger field halides. The free chloride that is generated can then react with  $[Pd(\kappa^3-dtbpf)Cl]^+$  to yield [Pd(dtbpf)Cl<sub>2</sub>]. On the basis of the ratio of the products, it would appear that the iodide reacts significantly more quickly than the bromide.

Although [Pd(dtbpf)Br][TFAB] was isolated by scaling up the aforementioned reaction, it is not an efficient synthesis, as approximately half of the starting material is converted to  $[Pd(dtbpf)Cl_2]$ . On the basis of the synthesis of [Pd(dtbpf)-I][I],<sup>18</sup>  $[Pd(dtbpf)Cl_2]$  reacted with excess NaBr to yield [Pd(dtbpf)Br][Br]. In addition,  $[Pd(dtbpf)Cl]^+$  was found to react with either NaBr or NaI to give the corresponding  $[Pd(dtbpf)X]^+$  (X = Br, I). The <sup>31</sup>P NMR signal for  $[Pd(dtbpf)Br]^+$  is at 11.5 ppm, similar to that observed for the corresponding chloride and iodide cations.

The structure of [Pd(dtbpf)Br][TFAB] was determined (Figure 3) over a range of temperatures. Similar to the case for [Pd(dtbpf)Cl][SbCl<sub>6</sub>],<sup>14</sup> the structure of [Pd(dtbpf)Br]-[TFAB] undergoes a reversible isomerization in the solid state. At room temperature, the only form present is the  $\kappa^3$ dtbpf structure shown in Figure 3. This isomer displays an Fe-Pd distance similar to that found in the chloride<sup>14</sup> and iodide<sup>18</sup> analogues. A second isomer in which the dtbpf is coordinated in a  $\kappa^2$  coordination mode is observed at lower temperatures (see the Supporting Information). This second isomer was previously described as being three-coordinate;<sup>14</sup> however, further analysis suggests that this description is not appropriate. The low-temperature isomers of  $[Pd(dtbpf)X]^+$  (X = Cl, Br) display two significantly different P-Pd-X angles of approximately 105 and 150°. In addition, both structures display several short (approximately 2.7 Å) contacts between the palladium atom and the idealized positions for the hydrogen atoms of the tert-butyl groups. These observations suggest that the low-temperature isomer is also four-coordinate, with the fourth coordination site being occupied by an agostic interaction with the tert-butyl groups. However, even at temperatures approaching the freezing point of the CDCl<sub>3</sub>

Scheme 1. Reactions of  $[Pd(\kappa^3-dtbpf)C1]^+$  with  $[NBu_4]X$  (X = Br<sup>-</sup>, I<sup>-</sup>)

$$[Pd(\kappa^{3}-dtbpf)Br]^{+} + [Pd(dtbpf)Cl_{1}] \leftarrow [NBu_{4}]Br = [Pd(\kappa^{3}-dtbpf)Cl]^{+} \rightarrow [Pd(\kappa^{3}-dtbpf)l_{1}]^{+} + [Pd(dtbpf)Cl_{1}]$$



Figure 3. Perspective view of [Pd(dtbpf)Br][TFAB] with 30% probability ellipsoids at 100(2) K. Hydrogen atoms and  $[TFAB]^-$  are omitted for clarity.

solvent there were no indications of this interaction in the <sup>1</sup>H NMR spectrum of either compound.

The closely related structure of [Pd(dtbpf)I][I] has been reported at 150 K.<sup>18</sup> The structure was determined at several temperatures (see the Supporting Information), and while the space group changed from *Pbca* to  $P2_1/c$ , there was no evidence of isomerization. On comparison of the structures of [Pd-(dtbpf)X]<sup>+</sup> (X = Cl, Br, I) (Table 1), the Fe–Pd distances are

Table 1. Selected Distances (Å), Angles (deg), and Structural Parameters for [Pd(dtbpf)Cl][SbCl<sub>6</sub>], [Pd(dtbpf)Br][TFAB], and [Pd(dtbpf)I][I] at 100(2) K

	$ \begin{bmatrix} Pd(dtbpf)Cl \\ [SbCl_6]^{14} \end{bmatrix} $	[Pd(dtbpf)Br] [TFAB]	[Pd(dtbpf)I] [I]
Fe-Pd	2.977(7)	2.9395(18)	2.9390 <sup>a</sup>
Pd-P(1)	2.310(9)	2.3012(15)	2.2876 <sup>a</sup>
Pd-P(2)	2.280(9)	2.2904(15)	2.2892 <sup>a</sup>
Pd-X	2.336(7)	2.4494(14)	2.5970 <sup>a</sup>
P-Pd-P	162.5(4)	163.04(5)	161.88 <sup>a</sup>
P–Pd–Fe (av)	81.4	81.52	80.98 <sup>a</sup>
P-Pd-X (av)	98.6	98.42	99.08 <sup>a</sup>
$%V_{\rm bur}$	73.0	72.1	71.7 <sup>a</sup>
$\theta^{b}$	17.5(10)	19.27(14)	20.76 <sup>a</sup>
$\tau^{c}$	41.4(16)	41.7(2)	40.6 <sup>a</sup>
$\delta_{ ext{P}}^{d}$	0.09(4)	0.118(5)	0.141 <sup>a</sup>
	0.06(4)	0.125(5)	0.116 <sup>a</sup>
cent-Fe-cent <sup>e</sup>	162.5(6)	160.72(10)	161.28 <sup>a</sup>

"Average of two crystallographically independent molecules in the unit cell. <sup>b</sup>The tilt angle of the two C<sub>5</sub> rings. <sup>c</sup>The torsion angle formed between C<sub>a</sub>-cent<sub>a</sub>-cent<sub>b</sub>-C<sub>b</sub>, with C being the carbon atom bonded to phosphorus and cent the centroid of the C<sub>5</sub> ring. <sup>d</sup>The distance between the P atoms and the C<sub>5</sub> plane; a positive value means the P atom is closer to Fe. <sup>e</sup>The angle formed between the centroid of each C<sub>5</sub> ring and the Fe center.

all significantly longer than 2.71 Å, the sum of the covalent radii.<sup>19</sup> The C<sub>5</sub> rings are tipped from being parallel by approximately 20°, and the angle increases as the size of the halide increases. As seen in related compounds,<sup>14,18</sup> this tip causes a significant difference in the chemical shifts of the H<sub>a</sub> and H<sub>β</sub> protons of the C<sub>5</sub> rings in the <sup>1</sup>H NMR spectrum. The percent buried volume (%V<sub>bur</sub>) is a measurement of the space a

ligand occupies around a metal center.<sup>3a</sup> The calculated<sup>20</sup>  $%V_{bur}$  values for the dtbpf ligand in this series of compounds decreases slightly as the size of the coordinated halide increases.

Two other techniques were employed to further examine the Fe–Pd interaction in these compounds. The visible spectrum of these compounds displays a single absorbance that can be attributed to Fe d–d transitions (Table 2).<sup>21</sup> The  $\lambda_{max}$  values

Table 2. Visible Absorbance Data for  ${\sim}0.2$  mM Solutions in  $CH_2Cl_2$ 

compound	$\lambda_{\max}$ (nm)	$\varepsilon ~(\mathrm{M^{-1}~cm^{-1}})$
dtbpf	458	270
[Pd(dtbpf)Cl][TFAB]	450	3600
[Pd(dtbpf)Br][Br]	455	5200
[Pd(dtbpf)I][I]	478	5500

shift to higher wavelengths as the donor ability of the halide increases. This is opposite of the trend observed in [Pd- $(dtbpf)PR_3$ ]<sup>2+</sup> (PR<sub>3</sub> = PBu<sub>3</sub>, PPh<sub>2</sub>Me, PPh<sub>3</sub>),<sup>22</sup> [Pd- $((C_5H_5ER)_2Fe)PPh_3$ ]<sup>+2</sup> (E = S, Se; R = Me, Ph),<sup>23</sup> and [Ru(PR<sub>3</sub>)<sub>2</sub>(( $C_5H_4NH$ )<sub>2</sub>Fe)] (PR<sub>3</sub> = PMe<sub>2</sub>Ph, PPh<sub>3</sub>),<sup>24</sup> in which the weaker  $\sigma$ -donor ligands trans to iron display the higher wavelength absorbance. Similar to the case for [Pd(dtbpf)CH<sub>3</sub>]<sup>+,25</sup> there was no absorbance indicative of an Fe-Pd interaction at higher wavelengths. Such bands are noted in [Ru(PR<sub>3</sub>)<sub>2</sub>(( $C_5H_4NH$ )<sub>2</sub>Fe)] (PR<sub>3</sub> = PMe<sub>2</sub>Ph, PPh<sub>3</sub>),<sup>24</sup> which have been calculated to have Fe-Ru interactions stronger than the Fe-Pd interactions in these systems.

Mössbauer Spectroscopy. To further investigate the nature of the Fe-Pd interaction, zero-field 57Fe Mössbauer spectra were collected on dtbpf, [Pd(dtbpf)Cl<sub>2</sub>], and [Pd- $(dtbpf)X]^+$  (X = Cl, Br) (Figure 4 and Figures S8-10 in the Supporting Information). At 90 K, dtbpf has an isomer shift ( $\delta$ ) and quadrupole splitting  $(|\Delta E_O|)$  of 0.54 and 2.35 mm/s, respectively (Figure 4f and Figure S8). These are almost identical with the values for ferrocene<sup>26</sup> and are in line with those for other ferrocene compounds.<sup>26,27</sup> Complexation of PdCl<sub>2</sub> shifts  $\delta$  and  $|\Delta E_0|$  to 0.49 and 2.27 mm/s, respectively (Figure 4f and Figure S9). The geometry at the coordinated metal has been observed to play an important role in the resulting Mössbauer parameters; square-planar species tend to have smaller  $\delta$  and  $|\Delta E_0|$  values, followed by octahedral species with slightly perturbed values, and ultimately tetrahedral complexes with larger parameters relative to those of ferrocene.  $^{28}$  These findings correlate directly with the Fecent distance to the center of each Cp ring: the shortest values are found for square planar and the longest for tetrahedral complexes.<sup>28</sup> While the structure of dtbpf has not been reported, the Fe-cent distance in the closely related (S,S)-1,1',3-tris(di-tert-butylphosphino)-2'-(1-N,Ndimethylaminoethyl)ferrocene (1.670 Å)<sup>29</sup> is longer than that in  $[Pd(dtbpf)Cl_2]$  (1.634 Å)<sup>17a</sup> and thus one expects a lower isomer shift for the Pd adduct due to greater electron density withdrawal from the iron center.

As discussed previously, removal of a chloride from  $[Pd(dtbpf)Cl_2]$  produces the cationic  $[Pd(dtbpf)Cl]^+$  complex.<sup>14</sup> In  $[Pd(dtbpf)Cl]^+$ , the extent of the Fe–Pd interaction varies with temperature, as determined by the change in the Fe–Pd distance at 100 and 296 K (Table 3). There are very few examples of compounds containing  $\kappa^3$ -ferrocenyl moieties as ligands where structural and Mössbauer data have been reported. In fact, from an in-depth survey of the literature,



**Figure 4.** (a–e) Variable-temperature zero-field <sup>57</sup>Fe Mössbauer spectra for [Pd(dtbpf)Cl][SbCl<sub>6</sub>]: (a) 90 K; (b) 160 K; (c) 210 K; (d) 250 K; (e) 298 K. (f) Isomer shift ( $\delta$ ) and quadrupole splitting ( $|\Delta E_Q|$ ) parameters for dtbpf, [Pd(dtbpf)Cl<sub>2</sub>], and [Pd(dtbpf)Cl][SbCl<sub>6</sub>] at 90 K. (g)  $\delta$  and  $|\Delta E_Q|$  parameters extracted from (a–e).





<sup>*a*</sup>Reference 30. <sup>*b*</sup>room temp stands for room temperature. <sup>*c*</sup>Reference 31. <sup>*d*</sup>Reference 32. <sup>*e*</sup>R = <sup>*i*</sup>Bu; ref 33. <sup>*f*</sup>R = Me; ref 23. <sup>*g*</sup>Reference 17a. <sup>*h*</sup>Reference 14. <sup>*i*</sup>Distance observed in the minor component (<10%).

only two examples were found where Mössbauer spectra were reported at low (77 K) and high (~298 K) temperatures: namely, compounds A and B.<sup>31</sup> The variable-temperature spectral and structural behavior of the last two and of the square-planar  $\kappa^2$ -ferrocenyl compound C and [Pd(dtbpf)Cl<sub>2</sub>] are used as references for those reported here, displaying a small percentage of molecules isomerizing between long and short Fe–Pd distances (Table 3). To probe the temperaturedependent isomerization in [Pd(dtbpf)Cl]<sup>+</sup> and [Pd(dtbpf)-Br]<sup>+</sup>, Mössbauer spectra were collected at 90, 160, 210, 250, and 298 K (Figure 4a-e and Figure S3 in the Supporting Information). The resulting  $\delta$  and  $|\Delta E_Q|$  values obtained from fitting the data are shown in Figure 4g (for X = Br, see Figure S4 in the Supporting Information). The decrease in  $\delta$  as the temperature rises can be explained by the second-order Doppler effect<sup>34</sup> and, hypothetically, by full conversion to the shorter Fe-Pd interaction at room temperature. In related complexes with a proposed Fe–Pd interaction,  $\Delta\delta$  ranges from about 0.05 to 0.08 mm/s between low (77 K) and high (298 K) temperature (Table 3). The  $\Delta \delta_{90-298 \text{ K}}$  values in [Pd(dtbpf)-

Cl]<sup>+</sup> and  $[Pd(dtbpf)Br]^+$  are 0.08 and 0.07 mm/s, respectively; thus, the Fe–Pd interaction formed at high temperature seems to have little effect on the value of  $\delta$ .

In contrast to  $\delta$ , the quadrupole splitting  $(|\Delta E_0|)$  has been proposed to be more sensitive when equatorial interactions are proposed in ferrocene compounds.<sup>35</sup> It is well known that  $|\Delta E_0|$  has an almost negligible variation with temperature and thus any interaction with the iron atom in ferrocene compounds can be diagnosed via this parameter.<sup>36</sup> In Table 3, two examples are given with a short (A, B) and two with a long Fe-Pd distance (C, [Pd(dtbpf)Cl<sub>2</sub>]). Regardless of the presence of an Fe-Pd interaction, the temperature variation between 77 and 298 K of  $|\Delta E_0|$  on these four examples is approximately 0.04 mm/s on average. Thus, the observed  $\Delta |\Delta E_Q|_{90-298 \text{ K}}$  value of 0.09 mm/s in  $[Pd(dtbpf)Cl]^+$  is proposed to be the result of the sum of two effects: (1) the standard temperature dependence observed in related compounds (Table 3; A-C and [Pd(dtbpf)Cl<sub>2</sub>]) and (2) the formation of a weak Fe-Pd interaction. Further support for the Fe-Pd interaction in  $[Pd(dtbpf)Cl]^+$  is gained when comparing the Mössbauer data reported for  $[Pd(dppf)(PPh_3)]$ - $[BF_4]_2$  ( $d_{Fe-Pd} = 2.877(2)$  Å) and  $[Pd(dppf)(4-picoline)_2)]$ - $[BF_4]_2$  (<sup>1</sup>H NMR spectroscopic data suggest a long Fe–Pd distance).<sup>22</sup> The former compound, with a short Fe–Pd distance, displays Mössbauer parameters of  $[\delta, |\Delta E_Q| \text{ (mm/s)}: 0.51(1), 2.24(1)]$ , whereas the latter compound has  $[\delta, |\Delta E_Q| \text{ (mm/s)}: 0.57(1), 2.61(1)]$ .<sup>24</sup> In contrast, the Mössbauer data  $(\Delta \delta_{90-298 \text{ K}} \text{ and } \Delta |\Delta E_Q|_{90-298 \text{ K}})$  of  $[Pd(dtbpf)Br]^+$  suggest that there is a negligible change in the extent of the Fe–Pd interaction between low (90 K) and high (298 K) temperature (Figure S4 in the Supporting Information).

**Electrochemistry.** The electrochemistry of [Pd(dtbpf)Br]-[Br] was examined using cyclic voltammetry. Similar to the analogous chloride, the oxidative electrochemistry displays a single, chemically reversible wave (Table 4). This wave is due

Table 4. Electrochemical Data for  $[Pd(dtbpf)X]^+$  (X = Cl, Br, I) Compounds<sup>*a*</sup>

	$E^{\circ}$	$\Delta E$	$E_{\mathrm{p}}$	$E_{\rm p}$
[Pd(dtbpf)Cl] <sup>+</sup>	0.94 <sup>b</sup>	0.07 <sup>b</sup>	-1.01 <sup>c</sup>	-1.61 <sup>c</sup>
[Pd(dtbpf)Br]+	0.92	0.08	-0.90	-1.56
[Pd(dtbpf)I] <sup>+</sup>	0.88 <sup>b,d</sup>	0.11 <sup>b</sup>	-0.58 <sup>b</sup>	-0.85 <sup>b</sup>

<sup>*a*</sup>Potentials are in V vs  $FcH^{0/+}$ . <sup>*b*</sup>Reference 14. <sup>*c*</sup>In  $CH_2Cl_2$  with [NBu<sub>4</sub>][TFAB] as the supporting electrolyte. <sup>*d*</sup>Irreversible oxidative waves due to the iodide counterion are also observed.

to the oxidation of the iron center. The trend in the potentials follows what is predicted by the computational analysis (vide infra); as the strength of the Fe-Pd interaction increases, the potential at which the oxidation of iron occurs becomes more positive, although it is important to note the small changes between the three compounds. The reductive electrochemistry of [Pd(dtbpf)Br]<sup>+</sup> displays two irreversible waves attributed to reduction of the palladium. Previously, the reductive electrochemistry of [Pd(dtpbf)Cl]<sup>+</sup> was reported to display one irreversible wave, while  $[Pd(dtbpf)I]^+$  displayed two irreversible waves.<sup>14</sup> The reductive electrochemistry of [Pd(dtbpf)Cl]<sup>+</sup> was examined using [NBu<sub>4</sub>][TFAB] as the supporting electrolyte, and it was found to display two irreversible waves (Figure 5). The trend in the reduction potentials follows what was observed with oxidation; [Pd(dtbpf)Cl]<sup>+</sup> is the most difficult to reduce due to greater electron donation from the iron.

**Computational Studies.** The compounds [Pd(dtbpf)Cl]<sup>+</sup> and [Pd(dtbpf)I]<sup>+</sup> were previously examined by computational methods; however, because a different version of the software

was available, calculations were repeated for these compounds as well (Table 5). Geometry optimizations for [Pd(dtbpf)X]<sup>+</sup>

# Table 5. Computational Parameters for $[Pd(dtbpf)X]^+$ (X = Cl, I)

	$[Pd(dtbpf) \\ Cl]^+$	[Pd(dtbpf) Br] <sup>+</sup>	$\begin{bmatrix} Pd(dtbpf) \\ I \end{bmatrix}^+$
Fe-Pd (Å)	2.98	2.99	2.99
Mayer bond order	0.34	0.32	0.30
Mulliken charge			
Fe	-0.12	-0.12	-0.11
Pd	-0.46	-0.43	-0.67
Hirshfeld charge			
Fe	0.05	0.05	0.05
Pd	0.34	0.32	0.30
Wiberg bond index	0.13	0.12	0.11
NLMO bond order	0.13	0.14	0.14
natural charge			
Fe	0.20	0.20	0.20
Pd	0.33	0.29	0.21
Bader charge			
Fe	0.71	0.72	0.71
Pd	0.20	0.15	0.04
$\rho^{a}$	0.02	0.02	0.02
Laplacian $(\nabla^2_{\rho})$ at Fe–Pd BCP	0.03	0.03	0.03

<sup>a</sup>BCP is the bond critical point identified by Bader analysis.

(X = Cl, Br, I) were performed for the present study employing ADF2013.01,<sup>47</sup> using the PW91 functional and no frozen electron cores.<sup>48</sup> The optimized Fe–Pd distance (2.99 Å) for  $[Pd(dtbpf)Br]^+$  is close to that obtained experimentally (2.94 Å), as are other structural parameters (Table S1 in the Supporting Information). The calculated Mayer bond order<sup>49</sup> for  $[Pd(dtbpf)Br]^+$  is 0.32 and is similar to the values obtained for the chloride and iodide analogues (Table 5). These values are smaller than those reported for metal–metal single bonds in  $[Ru(CO)_4]_8$  (0.70) and  $Ru_3(CO)_{12}$  (0.62),<sup>50</sup> but they are similar to those reported for  $[((C_5H_4NH)_2Fe)Ru(PR_3)_2]$  (PR<sub>3</sub> = PPh<sub>3</sub>, 0.28; PR<sub>3</sub> = PMe<sub>2</sub>Ph, 0.26).<sup>24</sup>

Two significant bonding interactions were found between iron and palladium in  $[Pd(dtbpf)Br]^+$  (HOMO-4 and HOMO-5) (Figure 6). These orbitals have a relatively large contribution from the metal atomic orbitals (see the Supporting Information



Figure 5. Cyclic voltammogram for the reduction of 1.0 mM [Pd(dtbpf)Cl][TFAB] in  $CH_2Cl_2/0.05$  M  $[NBu_4]$ [TFAB] at a glassycarbon electrode and a scan rate of 100 mV/s.



Figure 6. Frontier molecular orbitals for [Pd(dtbpf)Br]<sup>+</sup>: HOMO-4 (left) and HOMO-5 (right); isosurface value 0.03.

## Scheme 2. Palladium-Catalyzed $\alpha$ -Arylation of Propiophenone with 4-Chlorotoluene



for details): HOMO-4 (39% Pd and 29% Fe) and HOMO-5 (14% Pd and 12% Fe).

In order to understand further the Fe–Pd interaction, natural bond orbital analysis was carried out using NBO 6.0,<sup>51</sup> and the natural localized molecular orbitals (NLMOs) were generated. For [Pd(dtbpf)Br]<sup>+</sup>, a  $\sigma$  bond is apparent in NLMO 87, which is centered on iron, similarly to what was found for [Pd(dtbpf)Cl]<sup>+</sup> (NLMO 79) and for [Pd(dtbpf)I]<sup>+</sup> (NLMO 96) (see the Supporting Information for details).

Topological analysis of the electron density was performed via Bader's atoms in molecule (AIM) theory.<sup>52</sup> AIM identifies bonds by calculating (3, -1) critical points, and it differentiates between covalent bonds and weak interactions, such as hydrogen bonds, van der Waals, and donor–acceptor interactions, by the value of the Laplacian  $(\nabla^2_{\rho})$ . If  $\nabla^2_{\rho} < 0$ , the interaction is considered covalent. If  $\nabla^2_{\rho} > 0$ , the interaction is a weak interaction. AIM has been used to calculate bond critical points between two metal centers<sup>53</sup> and in ferrocene complexes.<sup>54</sup> All three [Pd(dtbpf)X]<sup>+</sup> species show Fe–Pd bond critical points (Table 5) consistent with a weak, noncovalent interaction (see the Supporting Information for details).

Catalytic Studies. To further examine the effect of changing the halide, the catalytic activity of the  $[Pd(dtbpf)X]^+$ (X = Cl, Br, I) and [Pd(dtbpf)Cl<sub>2</sub>] was examined in the  $\alpha$ arylation of propiophenone with 4-chlorotoluene (Scheme 2). Previous reports have examined this same reaction using  $[Pd(dtbpf)Cl_2]$ ,  $[Pd(dtbpf)Br_2]$ , and  $[Pd(dtbpf)I_2]$  as the catalyst precursors.<sup>17</sup> Although those studies report the use of  $[Pd(dtbpf)Br_2]$  and  $[Pd(dtbpf)I_2]$ , it is likely that the compounds that were actually employed were [Pd(dtbpf)Br]<sup>+</sup> and  $[Pd(dtbpf)I]^+$ . At the writing of this paper, the only known reports of [Pd(dtbpf)Br2] do not include synthetic details or any characterization data.<sup>17</sup> While those same reports suggest the use of  $[Pd(dtbpf)I_2]$ , there is evidence that the compound used was actually [Pd(dtbpf)I][I].<sup>37</sup> Using conditions similar to those in the previous report, [Pd(dtbpf)Cl<sub>2</sub>] was found to be the most active catalyst (Table 6). For the  $[Pd(dtbpf)X]^+$  (X = Cl, Br, I) compounds, the catalytic activity decreased as the size of the halide increased, similar to the previously observed trend.<sup>17</sup> This suggests that the size of the halide plays an

Table 6. Catalytic Activity of Palladium Compounds for the  $\alpha$ -Arylation of Propiophenone with 4-Chlorotoluene

Pd catalyst	TON <sup>a</sup>
none	0
[Pd(dtbpf)Cl <sub>2</sub> ]	21.7(0.9)
[Pd(dtbpf)Cl] <sup>+</sup>	8.3(0.6)
[Pd(dtbpf)Br] <sup>+</sup>	5.5(0.9)
$[Pd(dtbpf)I]^+$	0.2(0.1)

"Turnover number is the average of three experiments reported with the average deviation from the mean. important role in this catalytic system and that the larger halides greatly decrease the activity of the catalyst. The lower activity of  $[Pd(dtbpf)Cl]^+$  in comparison to  $[Pd(dtbpf)Cl_2]$  suggests that the cationic species is not a likely resting state in this catalytic cycle, although the presence of the  $[BArF]^-$  counterion could have some impact on the catalytic activity.

As the catalytic study was performed in THF, the  ${}^{31}P{}^{1}H{}$ NMR spectra of the palladium compounds were obtained in THF and found to be similar to those obtained in CH<sub>2</sub>Cl<sub>2</sub> (differing only slightly in the chemical shifts), with the exception of  $[Pd(dtbpf)Br]^+$ . A sample of  $[Pd(dtbpf)Br]^+$ dissolved in  $CH_2Cl_2$  gave a single peak in the  ${}^{31}P{}^{1}H$ spectrum. When the solvent was removed in vacuo and the sample was dissolved in THF, five peaks were observed. The spectra were then recorded from 35 to -65 °C in 10 °C intervals. The spectra displayed five peaks from 35 to -5 °C and six peaks at lower temperatures (Table 7). While none of these species were isolated, it is possible to propose a reasonable formula on the basis of the available data. The peak at 12.4 ppm is [Pd(dtbpf)Br]<sup>+</sup>, and this remains the predominant species in solution at all temperatures. The four signals in the 60-70 ppm range are likely due to fourcoordinate species, in which there is no interaction between the iron and palladium centers. An approximately 50 ppm downfield shift is also observed on comparing [Pd(dtbpf)Cl]<sup>+</sup> to [Pd(dtbpf)Cl<sub>2</sub>].<sup>14</sup> The two doublets are likely due to an asymmetric compound, which is proposed to be [Pd(dtbpf)-Br(thf)]<sup>+</sup>. The remaining two peaks are likely due to symmetric species, which are proposed to be [Pd(dtbpf)Br2] and  $[Pd(dtbpf)(thf)_2]^{2+}$ . Presumably, the larger signal at 65.3 ppm is due to [Pd(dtbpf)Br<sub>2</sub>]. The species that appears at -15 °C is shifted downfield by approximately 20 ppm from the proposed signal for [Pd(dtbpf)Br<sub>2</sub>]. A similar difference in chemical shifts is noted in comparing [Pd(dppf)Cl<sub>2</sub>] and  $[Pd_2(dppf)_2(\mu-Cl)_2]^{2+,14}$  suggesting that the peak at 83.0 ppm could be due to the formation of  $[Pd_2(dtbpf)_2(\mu-Br)_2]^{2+}$ . When THF was removed in vacuo from this sample and the solid was dissolved in  $CH_2Cl_2$ , the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum displayed a single peak for [Pd(dtbpf)Br]<sup>+</sup>. Similar behavior was not observed for [Pd(dtbpf)Cl]<sup>+</sup>, likely due to the fact that the counteranion is not chloride; as reported above, the addition of chloride to [Pd(dtbpf)Cl]<sup>+</sup> cleanly results in the formation of  $[Pd(dtbpf)Cl_2]$ . For  $[Pd(dtbpf)I]^+$ , the larger iodide and/or the stronger donor ability of iodide may prevent the formation of species such as  $[Pd(dtbpf)I_2]$ . This could be additional evidence for why  $[Pd(dtbpf)I]^+$  is a significantly less effective catalyst for this  $\alpha$ -arylation reaction (Table 6).

# CONCLUSION

The synthesis of  $[Pd(dtbpf)Br]^+$  was carried out using different methods, but the most efficient synthesis was determined to be the reaction of  $[Pd(dtbpf)Cl_2]$  with sodium bromide. The <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of  $[Pd(dtbpf)Br]^+$  were consistent

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Table 7. Variable-Temperature <sup>31</sup>P{<sup>1</sup>H} NMR Spectroscopic Data for [Pd(dtbpf)Br]Br in THF

			rel integration										
peak (ppm)	mult	$^{2}J_{P-P}$ (Hz)	35 °C	25 °C	15 °C	5 °C	−5 °C	−15 °C	−25 °C	−35 °C	−45 °C	−55 °C	−65 °C
12.4	s		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
62.5	d	35	0.12	0.13	0.12	0.12	0.13	0.14	0.11	0.12	0.14	0.12	0.13
63.9	s		0.04	0.02	0.03	0.03	0.03	0.04	0.02	0.03	0.04	0.02	0.06
65.3	s		0.42	0.47	0.52	0.54	0.57	0.58	0.59	0.60	0.64	0.64	0.65
66.7	d	35	0.13	0.11	0.12	0.10	0.15	0.13	0.11	0.16	0.16	0.14	0.16
83.0	s							0.07	0.10	0.14	0.11	0.13	0.11

with the product having an interaction between the iron and palladium atoms. This Fe-Pd interaction was also evident in the X-ray crystal structure of [Pd(dtbpf)Br]<sup>+</sup>, which was similar to those of the analogous  $[Pd(dtbpf)X]^+$  (X = Cl, I) compounds. Similarly to [Pd(dtbpf)Cl]+, crystals of [Pd-(dtbpf)Br]<sup>+</sup> undergo an isomerization at low temperature, giving a species in which the Fe-Pd interaction is broken and presumably replaced with an agostic interaction with a C-H of a tert-butyl group of the dtbpf ligand. The 57Fe Mössbauer spectra of  $[Pd(dtbpf)X]^+$  (X = Cl, Br) were obtained at a variety of temperatures and are consistent with an Fe-Pd interaction. The oxidative electrochemistry of [Pd(dtbpf)Br]<sup>+</sup> was examined and compared to that of  $[Pd(dtbpf)X]^+$  (X = Cl, I). The potential at which the iron in these compounds is oxidized shifts to less positive potentials as the halide becomes more  $\pi$ -donating, suggesting that the Fe–Pd interaction weakens with the larger halides. DFT calculations support the electrochemical data and describe the Fe-Pd interaction as weak and noncovalent. Finally, the catalytic activity of the  $[Pd(dtbpf)X]^+$  (X = Cl, Br, I) was compared to the activity of [Pd(dtbpf)Cl<sub>2</sub>] for the arylation of an aromatic ketone. The catalytic reaction was found to be most efficient with  $[Pd(dtbpf)Cl_2]$ , and the activity of the  $[Pd(dtbpf)X]^+$ compounds decreased as the halide became larger.

# EXPERIMENTAL SECTION

General Considerations. All reagents were used as received unless otherwise indicated. [PdCl<sub>2</sub>(MeCN)<sub>2</sub>], sodium tetrafluoroborate, isopropylmagnesium chloride (2.0 M in THF), 1,3-bis-(trifluoromethyl)-5-bromobenzene, tetrabutylammonium bromide ([NBu<sub>4</sub>]Br), tetrabutylammonium iodide ([NBu<sub>4</sub>]I), phenanthrene, propiophenone, 4-chlorotoluene, and sodium tert-butoxide were purchased from Aldrich. Bis(triphenylphosphine)iminium chloride ([PPN]Cl) and 1,1'-bis(di-tert-butylphosphino)ferrocene (dtbpf) were purchased from Strem Chemicals, Inc. Sodium bromide, sodium iodide and THF-d<sub>8</sub> were purchased from Fisher Scientific. Lithium tetrakis(pentafluorophenyl)borate etherate and potassium tetrakis-(pentafluorophenyl)borate (K[TFAB]) were purchased from Boulder Scientific. Tetrabutylammonium hexafluorophosphate ([NBu<sub>4</sub>][PF<sub>6</sub>]) was purchased from Aldrich and dried under vacuum at 100 °C prior to use. Ferrocene (FcH) was purchased from Strem and sublimed prior to use. The compounds sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (Na[BArF]),<sup>38</sup> [Pd(dtbpf)Cl<sub>2</sub>],<sup>39</sup> tetrabutylammonium tetrakis(pentafluorophenyl)borate ([NBu<sub>4</sub>][TFAB]),<sup>40</sup> [Pd(dtbpf)-Cl][BArF],<sup>14</sup> and [Pd(dtbpf)I][I]<sup>18</sup> were prepared according to literature procedures. All reactions were carried out under argon using standard Schlenk techniques unless otherwise noted. Methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>), hexanes, and diethyl ether (Et<sub>2</sub>O) were purified using a Solv-Tek purification system similar to that previously described.<sup>41</sup> Acetone and benzene were degassed and purged with argon prior to use. THF was distilled from potassium benzophenone ketyl under argon prior to use. A JEOL Eclipse 400 FT-NMR spectrometer was used to acquire the <sup>31</sup>P{<sup>1</sup>H} NMR and <sup>1</sup>H NMR spectra. The <sup>1</sup>H NMR spectra were referenced to TMS ( $\delta$  0.00 ppm). Chemical shifts of the <sup>31</sup>P{<sup>1</sup>H} NMR spectra are referenced to an

external sample of 85% H<sub>3</sub>PO<sub>4</sub>. GC-MS data were obtained using a VG/FISONS Model MD800 gas chromatograph/mass spectrometer. All reported yields are isolated yields. Elemental analysis was performed by Quantitative Technologies, Inc.

**Synthesis of [Pd(dtbpf)Cl][TFAB].** K[TFAB] (0.0891 g, 0.124 mmol) was added to a brown-orange solution of [Pd(dtpbf)Cl<sub>2</sub>] (0.0778 g, 0.119 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. The reaction changed color to a darker brown-orange with stirring for 15 min. The solution was then filtered, and solvent was removed from the filtrate in vacuo. The residue was triturated with ether (3 × 5 mL) and dried under vacuum. The product was obtained as a black solid (0.0943 g, 61% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 5.19 (br s, 4H,  $H_{\beta}$ ), 3.96 (br s, 4H,  $H_{\alpha}$ ), 1.53 (br s, 36H,  $-CH_3$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$  9.8 (s). Anal. Calcd for C<sub>50</sub>H<sub>44</sub>BClF<sub>20</sub>FeP<sub>2</sub>Pd: C, 46.36; H, 3.42. Found: C, 46.12, H, 3.21.

**Reaction of [Pd(dtbpf)Cl][TFAB] with [PPN]Cl.** In an NMR tube reaction, [Pd(dtbpf)Cl][TFAB] (0.0089 g, 6.9  $\mu$ mol) and [PPN] Cl (0.0040 g, 7.0  $\mu$ mol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 mL). This resulted in a brown solution. <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>):  $\delta$  67.7 (s), 21.6 (s).

**Reaction of [Pd(dtbpf)Cl][TFAB] with [NBu<sub>4</sub>]Br.** [Pd(dtbpf)-Cl][TFAB] (0.0280 g, 22.6  $\mu$ mol) and [NBu<sub>4</sub>]Br (0.0073 g, 23  $\mu$ mol) were placed in an NMR tube and dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 mL). <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>):  $\delta$  67.7 (s), 15.1 (s).

**Reaction of [Pd(dtbpf)Cl][TFAB] with [NBu<sub>4</sub>]I.** [Pd(dtbpf)Cl]-[TFAB] (0.0221 g, 17.8  $\mu$ mol) and [NBu<sub>4</sub>]I (0.0066 g, 18  $\mu$ mol) were placed in an NMR tube and dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 mL). <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>):  $\delta$  67.7 (s), 10.9 (s).

**Synthesis of [Pd(dtbpf)Br][TFAB].** [NBu<sub>4</sub>]Br (0.0095 g, 30 μmol) was dissolved in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>. In a separate flask [Pd(dtbpf)Cl][TFAB] (0.0382 g, 29.5 μmol) was dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. The [Pd(dtbpf)Cl][TFAB] solution was slowly added over 10 min to the [NBu<sub>4</sub>]Br solution, and the resulting solution was stirred for 10 min. The solution was then layered with 20 mL of hexanes and placed in the freezer overnight. This yielded a black precipitate and an orange solution. The solution was filtered, and the solid was washed with 5 mL of ether and the dried in vacuo. The product was collected as a black solid (0.0170 g, 43% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 6.32 (br s, 4H,  $H_β$ ), 4.15 (br s, 4H,  $H_α$ ), 1.54 (br s, 36H,  $-CH_3$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 11.5 (s). Anal. Calcd for C<sub>50</sub>H<sub>44</sub>BBrF<sub>20</sub>FeP<sub>2</sub>Pd: C, 44.82; H, 3.31. Found: C, 44.90, H, 3.30.

Synthesis and Characterization of [Pd(dtbpf)Br][Br]. [Pd-(dtbpf)Cl<sub>2</sub>] (0.3798 g, 0.583 mmol) and sodium bromide (0.3025 g, 2.94 mmol) were placed in a flask and degassed. Acetone (15 mL) was added, giving a dark grayish red solution that was stirred for 22 h. The solvent was removed in vacuo, and the resulting residue was triturated with 2 × 5 mL of DI water. The resulting product was azeotropically dried with benzene (50 mL), which was then removed in vacuo. The remaining solid was dissolved in minimal CH<sub>2</sub>Cl<sub>2</sub> and layered with hexanes. The resulting solution was placed in the freezer overnight, yielding a dark red-black precipitate. The solution was filtered, washed with 2 × 5 mL of Et<sub>2</sub>O, and dried in vacuo, which yielded 0.2591 g (59%) of the product as a black solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 6.32 (br s, 4H,  $H_{\beta}$ ), 4.15 (br s, 4H,  $H_{\alpha}$ ), 1.54 (br s, 36H,  $-CH_3$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$  11.5 (s). Anal. Calcd for C<sub>26</sub>H<sub>44</sub>Br<sub>2</sub>FeP<sub>2</sub>Pd: C, 42.16; H, 5.99. Found: C, 42.22, H, 6.09.

X-ray Diffraction Studies. Crystals of [Pd(dtbpf)Br][TFAB] were obtained at room temperature by vapor diffusion of Et<sub>2</sub>O into a solution of each compound in CH2Cl2. A Bruker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo K $\alpha$  radiation was used for collecting X-ray diffraction data. A single red-orange crystal (0.33  $\times$  $0.19 \times 0.11 \text{ mm}^3$ ) was selected and mounted using Super Glue onto a glass fiber and cooled to 100 K with a stream of dry nitrogen gas. A second sample was used to record data at a variety of temperatures (see the Supporting Information). Cell parameters were retrieved using APEX II software<sup>42</sup> and refined using SAINT+<sup>43</sup> on all observed reflections. Unit cell parameters were obtained from 60 data frames,  $0.5^{\circ}$   $\Phi$ , from three different sections of the Ewald sphere. The data set was treated with SADABS<sup>44</sup> absorption corrections on the basis of redundant multiscan data. The structure was solved by direct methods and refined by least-squares methods on  $F^2$  using the SHELXTL program package.45 All hydrogen atoms were treated as idealized contributions. Except as noted, all non-hydrogen atoms were refined with anisotropic displacement parameters. The systematic absences were consistent with the centrosymmetric, monoclinic space group  $P2_1/n$ . The data set consisted of 69951 reflections (13516 unique,  $R_{int}$ = 0.0896) collected over  $\theta$  = 1.746–28.282°. The monoclinic crystal has an asymmetric unit that contains one molecule of the  $[Pd(dtbpf)Br]^+$  cation and one  $[TFAB]^-$  anion. After an anisotropic model of the molecule was completed, there remained large residual electron density peaks around the palladium, iron, and bromine atoms that suggested a second isomer was present as a minor component. Alternate sites for the Pd, Fe, Br, and P centers were located in the Fourier difference maps and were modeled as isotropic atoms whose relative occupancy was refined to keep unit cell contents constant. The minor component occupancy of the heavy atoms refined to 9%. The light atoms of the minor component were not modeled, and the occupancies of the corresponding major component were fixed at 1.0. This two-isomer model gave a goodness of fit on  $F^2$  of 1.032 with R1 = 4.28%  $(I > 2\sigma(I))$  and wR2 = 9.76% (all data) and with a largest difference peak and hole of 0.746 and -0.887 e/Å3. Reported measurements were taken using OLEX2.4

**Zero-Field** <sup>57</sup>**Fe** Mössbauer Spectroscopy. Spectra were collected at various temperatures by restraining the desired sample in Paratone-N oil. The data were measured with a constant acceleration spectrometer (SEE Co., Minneapolis, MN). Isomer shifts are given relative to  $\alpha$ -Fe metal at 298 K. Data were analyzed using an in-house package written by Evan R. King in Igor Pro (Wavemetrics).  $\gamma$  refers to the full width at half-maximum.

Electrochemical Procedure. Cyclic voltammetry was performed using a CH Instruments Model CHI260D potentiostat at room temperature (21  $\pm$  1 °C). Scans for [Pd(dtbpf)Br][Br] were conducted under an argon atmosphere. The analyte was 1.0 mM in CH<sub>2</sub>Cl<sub>2</sub> (10.0 mL), and the supporting electrolyte was 0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>]. Scans for [Pd(dtbpf)Cl][TFAB] were performed in an argon-filled glovebox. The analyte was 1.0 mM in CH<sub>2</sub>Cl<sub>2</sub> (10.0 mL), and the supporting electrolyte was 0.05 M [NBu<sub>4</sub>][TFAB]. All experiments were performed with a glassy-carbon working electrode (1.0 mm disk) that was polished with 1.0  $\mu$ m and then 0.25  $\mu$ m diamond paste and rinsed with CH2Cl2 prior to use. The experiments also employed a nonaqueous Ag/AgCl pseudoreference electrode, which was separated from the solution by a frit, and a platinum-wire counter electrode. FcH was added at the end of the experiments and used as an internal reference. Data were background-subtracted. Experiments were conducted at scan rates of 50 and 100-1000 mV/s in 100 mV/s increments. All data are reported at a scan rate of 100 mV/s.

**Computational Studies.** All structures were optimized using the ADF2013.01 software suite.<sup>47</sup> Full molecules were used for calculations. Optimizations were performed at the PW91<sup>48</sup> theory level, with full electron (no frozen cores) triple- $\zeta$ -potential (TZP) basis sets and using the relativistic scalar ZORA approximation. Mayer bond orders and atomic properties were calculated using the defaults implemented in the ADF2013.01 program suite. The optimized coordinates were used for further analysis with NBO 6.0 and Bader's atoms in molecules (AIM) methods, implemented in ADF.

**Catalytic Studies.** The reactions were performed under argon in THF (1.5 mL) with 1.5 mmol of 4-chlorotoluene, 1.65 mmol of propiophenone, 1.65 mmol of sodium *tert*-butoxide, and 0.03 mmol of the desired palladium complex ([Pd(dtbpf)Cl<sub>2</sub>], [Pd(dtbpf)Cl]-[BArF], [Pd(dtbpf)Br][Br], or [Pd(dtbpf)I][I]). The reaction mixtures were stirred and heated for 3 h at 60 °C before being cooled to room temperature. A 100  $\mu$ L sample of the reaction mixture was diluted in 1.00 mL of a THF solution of phenanthrene (~7 mg). The sample was then injected into a CG-MS, and the concentration of the desired product was determined. Reactions were performed three independent times with each catalyst.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.5b00889.

X-ray crystallographic data and experimental details, zero-field <sup>57</sup>Fe Mössbauer spectra and parameters, and computational results (PDF) Crystallographic data (CIF)

Cartesian coordinates for computational studies (XYZ)

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#### Notes

The authors declare no competing financial interest.

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