

## Distinct Electronic Effects on Reductive Eliminations of Symmetrical and Unsymmetrical Bis-Aryl Platinum Complexes

Shashank Shekhar and John F. Hartwig\*

Contribution from the Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107

Received May 5, 2004; E-mail: John.Hartwig@yale.edu

**Abstract:** Symmetrical bis-aryl platinum complexes (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)<sub>2</sub> (R = NMe<sub>2</sub>, OMe, CH<sub>3</sub>, H, Cl, CF<sub>3</sub>) and electronically unsymmetrical bis-aryl platinum complexes (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)(C<sub>6</sub>H<sub>4</sub>-4-X) (R = CH<sub>3</sub>, X = NMe<sub>2</sub>, OMe, H, Cl, F, CF<sub>3</sub>; R = OMe, X = NMe<sub>2</sub>, H, Cl, F, CF<sub>3</sub>; R = CF<sub>3</sub>, X = H, Cl, NMe<sub>2</sub>; and R = NMe<sub>2</sub>, X = H, Cl) were prepared, and the rates of reductive elimination of these complexes in the presence of excess PPh<sub>3</sub> are reported. The platinum complexes reductively eliminated biaryl compounds in quantitative yields with first-order rate constants that were independent of the concentration of PPh<sub>3</sub>. Plots of Log(k<sub>obs</sub>/k<sub>obs(H)</sub>) vs Hammett substituent constants ( $\sigma$ ) of the para substituents R and X showed that the rates of reductive elimination reactions depended on two different electronic properties. The reductive elimination from symmetrical bis-aryl platinum complexes occurred faster from complexes with more electron-donating para substituents R. However, reductive elimination from a series of electronically unsymmetrical bis-aryl complexes was not faster from complexes with the more electron-donating substituents. Instead, reductive elimination was faster from complexes with a larger *difference* in the electronic properties of the substituents on the two platinum-bound aryl groups. The two electronic effects can complement or cancel each other. Thus, this combination of electronic effects gives rise to complex, but now more interpretable, free energy relationships for reductive elimination.

### Introduction

Electronic effects lie at the heart of all reactivity. In transition metal chemistry, the electronic properties of both the ligands ancillary to the reaction and ligands participating directly in the reaction affect rates and selectivity.<sup>1,2</sup> The electronic properties of ancillary ligands generally control the overall electron density of the transition metal center and can influence reactivity at a position *cis* or *trans* to one of the ligands.<sup>3–8</sup> The effect of the electronic properties of a ligand that participates directly in the reaction can be complex and is sometimes interpreted in terms of ground-state energy,<sup>9–15</sup> nucleophilicity

or electrophilicity,<sup>16–21</sup> or capacity to stabilize an accumulation of charge.<sup>13,15,22</sup> The potential for synergistic or cooperative effects from changes to the electronic properties of two ligands simultaneously participating in a reaction may increase the complexity of the effect of electronic perturbations. The properties of one ligand participating in a reaction could influence the magnitude or even direction of the effect of an electronic perturbation of the second ligand.<sup>16,17,22–24</sup> Such synergistic effects could be important in reductive elimination, migratory insertion, and nucleophilic attack on coordinated ligands. The work here focuses on assessing potential synergistic electronic effects on reductive elimination.

Theoretical studies have suggested that reductive elimination is faster from complexes with more electron-donating ligands

- (1) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; John Wiley & Sons: New York, 2001.
- (2) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.
- (3) Yamashita, M.; Vicario, J. V. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 16347–16360.
- (4) Rajanbabu, T. V.; Casalnuovo, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 6325–6326.
- (5) Faller, J. W.; Lambert, C.; Mazzieri, M. R. *J. Organomet. Chem.* **1990**, *383*, 161–177.
- (6) Faller, J. W.; Mazzieri, M. R.; Nguyen, J. T.; Parr, J.; Tokunaga, M. *Pure Appl. Chem.* **1994**, *66*, 1463–1469.
- (7) Deerenberg, S.; Kamer, P. C. J.; van Leeuwen, P. *Organometallics* **2000**, *19*, 2065–2072.
- (8) Casalnuovo, A. L.; Rajanbabu, T. V.; Ayers, T. A.; Warrens, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9869–9882.
- (9) Selmecky, A. D.; Jones, W. D.; Osman, R.; Perutz, R. N. *Organometallics* **1995**, *14*, 5677–5685.
- (10) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1986**, *108*, 6115–6128.
- (11) Tatsumi, K.; Hoffmann, R.; Yamaoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857–1867.

- (12) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 2436–2448.
- (13) Burger, B. J.; Sanatarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134–3146.
- (14) Halpern, J.; Okamoto, T. *Inorg. Chim. Acta* **1984**, *89*, L53.
- (15) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670–2682.
- (16) Baranano, D.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 2937–2938.
- (17) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 8232–8245.
- (18) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163–1188.
- (19) Hartwig, J. F.; Richards, S.; Baranano, D.; Paul, F. *J. Am. Chem. Soc.* **1996**, *118*, 3626–3633.
- (20) Huang, J.; Harr, C. M.; Nolan, S. P.; Marcone, J. E.; Moloy, K. G. *Organometallics* **1999**, *18*, 297–299.
- (21) Calhoda, M. J.; Brown, J. M.; Cooley, N. A. *Organometallics* **1991**, *10*.
- (22) Widenhofer, R. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 6504–6511.
- (23) Schmidtberg, G. S.; Stapp, B.; Brune, H. A. *J. Organomet. Chem.* **1986**, *307*, 129–137.
- (24) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1974**, *65*, 275–287.

participating in the bond-forming process.<sup>10,11</sup> The origin of this prediction can be traced to stronger bonds between a metal and a ligand with an electron-withdrawing substituent because of increased ionic character.<sup>25,26</sup> The theoretical studies, therefore, imply that the barriers for reductive elimination are affected more by changes in the energies of the reactants than by changes in the energies of the transition states.<sup>10</sup> From this information, one might predict that the rate of reductive elimination of unsymmetrical compounds would relate closely to the sum of the strengths of the two metal–ligand bonds broken in the reductive elimination process.

Some results are consistent with faster reductive elimination from complexes in which more electron-donating groups undergo reductive elimination.<sup>9,27–29</sup> For example, the reductive elimination of biaryl from  $(\text{PPh}_3)_2\text{Pt}(p\text{-tol})$  was faster than elimination from  $(\text{PPh}_3)_2\text{PtPh}_2$ , which contains a less electron-donating aryl group.<sup>30</sup> Similarly, reductive elimination of amine from  $(\text{DPPF})\text{Pd}(p\text{-tol})(\text{NAr})_2$ <sup>17</sup> was much faster than reductive elimination of ether from  $(\text{DPPF})\text{Pd}(p\text{-tol})(\text{OAr})$ .<sup>27,31</sup> However, changes in the rates for reductive elimination from electronic perturbations cannot be traced to the electron-donating or -withdrawing property of the ligand in other cases. For example, reductive eliminations of amines,<sup>17</sup> ethers,<sup>22,31</sup> and sulfides<sup>16</sup> from arylpalladium amide, alkoxide, and thiolate complexes are slower when the complexes contain more electron-donating groups on the palladium-bound aryl group, and *cis*- $(\text{PPh}_3)_2\text{Pt}(4\text{-CH}_3\text{C}_6\text{H}_4)(4\text{-NO}_2\text{C}_6\text{H}_4)$  was stated to be too unstable to isolate, while *cis*- $(\text{PPh}_3)_2\text{Pt}(4\text{-CH}_3\text{C}_6\text{H}_4)_2$  requires elevated temperature to undergo reductive elimination.<sup>23</sup>

The reductive elimination of biaryls from arylmetal complexes<sup>23,28,30,32–34</sup> could provide a context to reveal rigorously whether increased or decreased electron-donating properties of a covalent, reactive ligand accelerate the rate of reductive elimination and the extent to which the electronic properties of the two groups undergoing reductive elimination are synergistic. The electronic properties of an aryl group can be varied systematically within bis-aryl metal complexes without varying significantly the steric properties, and both ligands would be bound through similar types of metal–ligand interactions.<sup>35</sup> Moreover, reductive elimination of biaryls is the step in catalytic cross-coupling between main-group organometallic compounds and organic halides or triflates that forms the new carbon–carbon bond in the product.<sup>36–39</sup> Thus, an understanding of the

factors that influence the reductive elimination of biaryls will not only improve our understanding of electronic effects on organometallic reactivity, but could improve our ability to predict the scope of cross-coupling and to design improved systems.

We have used the reductive elimination from symmetrical and unsymmetrical platinum bis-aryl complexes as a case study to reveal the electronic effects in an organometallic reaction that is common and that involves simultaneous participation of two covalent ligands. Palladium and nickel complexes are often used as catalysts for coupling reactions that form biaryls, but the bis-aryl complexes of these metals have not been isolated. Platinum complexes are now known that catalyze such coupling reactions,<sup>40–42</sup> and platinum bis-aryl complexes<sup>43,44</sup> can be isolated that undergo reductive elimination.<sup>23,28,30,32,33</sup>

We show that reductive elimination from unsymmetrical bis-aryl platinum complexes is not simply slower from complexes with more electron-withdrawing substituents and stronger metal–ligand bonds. Instead, reductive elimination is faster from complexes with a larger difference between the electron-donating properties of the two aryl groups. The electronic properties of one group affect the magnitude and direction of the result of electronic perturbations to a second group. The electronic effects on reductive elimination are synergistic.

## Results

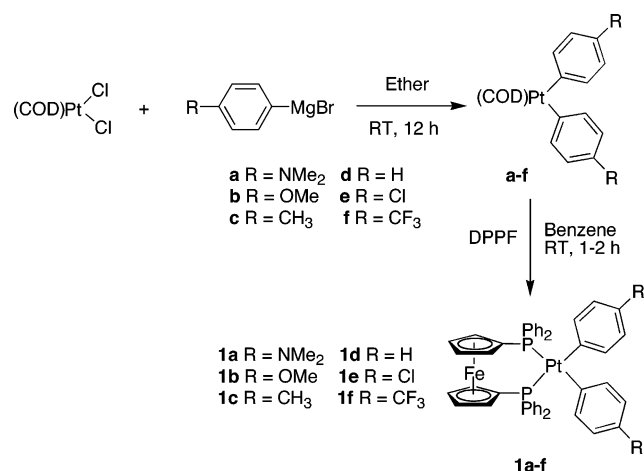
**1. Selection of Model Complexes for Analysis.** To find platinum bis-aryl complexes with a broad spectrum of electronic properties that are stable enough to isolate but reactive enough to undergo reductive elimination, we prepared platinum bis-aryl complexes with a series of ancillary ligands. Bis-aryl platinum complexes with 1,5-cyclooctadiene (COD), triphenylphosphine, 1,2-bis(diphenylphosphino)ethane (DPPE), and 1,1'-bis(diphenylphosphino)ferrocene (DPPF) as ancillary ligands were prepared. Complexes containing COD as ancillary ligand required a temperature of 150 °C to reductively eliminate biaryls at a rate convenient to be monitored by NMR spectroscopy. Moreover, several side products were observed, in addition to the biaryls. Some of the complexes containing  $\text{PPh}_3$  as ligands were unstable at room temperature and were difficult to isolate. For example, complexes of the type  $(\text{PPh}_3)_2\text{Pt}(\text{C}_6\text{H}_4\text{-4-NMe}_2)(\text{C}_6\text{H}_4\text{-4-X})$ , in which  $\text{X} = \text{NMe}_2, \text{OMe}, \text{CH}_3,$  and  $\text{Cl}$ , decomposed at room temperature. Elimination of biaryls from bis-aryl complexes ligated by DPPE required 2–3 days at 150 °C. However, bis-aryl complexes ligated by DPPF were simple to prepare and formed biaryl products in quantitative yields at 95 °C over 1–20 h. Thus, our detailed studies focused on the reductive elimination of biaryls from DPPF-ligated platinum complexes.

**2. Synthesis and Characterization of Symmetrical Bis-Aryl Platinum Complexes (1a–f).** The synthesis of symmetrical bis-aryl platinum complexes  $(\text{DPPF})\text{Pt}(\text{C}_6\text{H}_4\text{-4-R})_2$  is summarized in Scheme 1. Reaction of aryl Grignard reagents with (COD)- $\text{PtCl}_2$  in ether formed bis-aryl platinum complexes (COD)Pt-

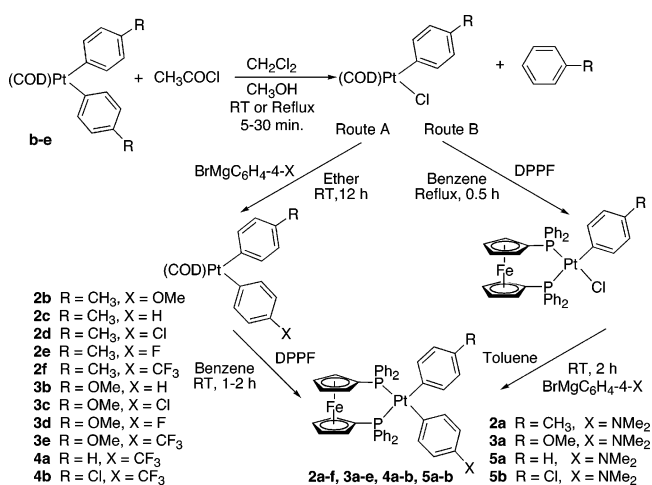
- (25) Holland, P. L.; Anderson, R. A.; Bergman, R. G.; Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1997**, *119*, 12800–12814.  
(26) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercau, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444–1456.  
(27) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852–860.  
(28) Braterman, P. J.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1306–1310.  
(29) Ozawa, F.; Mori, T. *Organometallics* **2003**, *22*, 3593–3599.  
(30) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1892–1897.  
(31) Mann, G.; Shelby, Q.; Roy, A. H. *Organometallics* **2003**, *22*, 2775–2789.  
(32) Merwin, R. K.; Schnabel, R. C.; Koola, J. D.; Roddick, D. M. *Organometallics* **1992**, *11*, 2972–2978.  
(33) Braterman, P. S.; Cross, R. J. *J. Chem. Soc., Perkin Trans.* **1973**, *2*, 271–294.  
(34) Brune, H.-A.; Hess, R.; Schmidtberg, G. Z. *Naturforsch* **1984**, *39b*, 1772–1780.  
(35) For mechanistic and theoretical studies on reductive elimination from metal alkyl complexes, see refs 10, 11, 36–48, and 51–52.  
(36) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147–168.  
(37) Hassan, J.; Sevingo, M.; Gozzi, C.; Emmanuelle, L.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359–1469.  
(38) Stanforth, S. P. *Tetrahedron* **1998**, *54*, 263–303.  
(39) Negishi, E. *Handbook of Organopalladium Chemistry for Organic Synthesis*; John Wiley & Sons: New York, 2002; Vol. 1.

- (40) Mateo, C.; Fernandez-Rivas, C.; Cardenas, D. J.; Echavarran, A. M. *Organometallics* **1998**, *17*, 3661.  
(41) Clarke, M. L. *Polyhedron* **2001**, *20*, 151–164.  
(42) Bedford, R. B.; Hazelwood, S. L.; Abisson, D. A. *Organometallics* **2002**, *21*, 2599–2600.  
(43) Brown, J. M.; Perez-Torrente, J. J.; Alcock, N. W. *Organometallics* **1995**, *14*, 1195–1203.  
(44) Alvarro-Rodriguez, J. G.; Toscano, R. A.; Boyko, W. J. *J. Organomet. Chem.* **1998**, *557*, 169–179.

Scheme 1



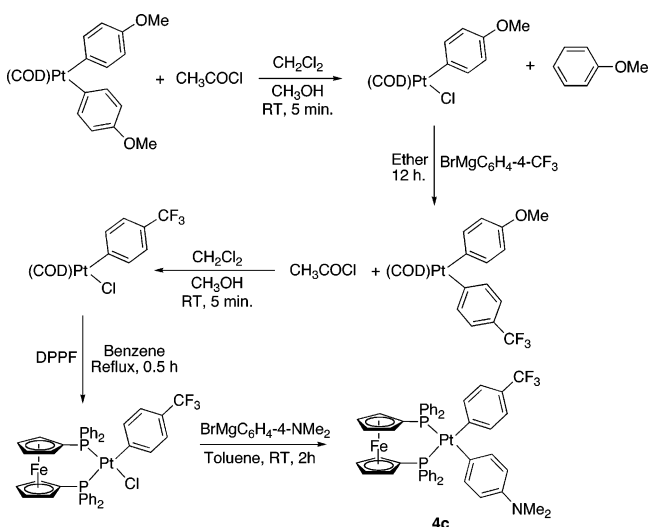
Scheme 2



(C<sub>6</sub>H<sub>4</sub>-4-R)<sub>2</sub> in 55–75% yield. Reaction of DPPF with (COD)-Pt(C<sub>6</sub>H<sub>4</sub>-4-R)<sub>2</sub> in benzene formed DPPF-ligated bis-aryl platinum complexes (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)<sub>2</sub> in 80–95% yield. The complexes were characterized by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy and elemental analysis, and complexes **1b** and **1e**, were sufficiently soluble to be characterized by <sup>13</sup>C NMR spectroscopy.

**3. Synthesis and Characterization of DPPF Ligated Unsymmetrical Bis-Aryl Platinum Complexes.** The synthesis of DPPF-ligated unsymmetrical bis-aryl platinum complexes **2a–f**, **3a–e**, **4a,b** and **5a,b** is summarized in Scheme 2. Complexes **2b–f**, **3b–e**, and **4a,b** were prepared by Route A. Reaction of CH<sub>3</sub>COCl with (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)<sub>2</sub> (**b–e**) in a mixture of CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>OH formed (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)Cl in 73–89% yield.<sup>45</sup> Protonolysis of the aryl group of **1b–d** proceeded in 5–30 min at room temperature, but protonolysis of the *p*-chlorophenyl group in **1e** required refluxing in CH<sub>2</sub>Cl<sub>2</sub> and MeOH. Reaction of the resulting aryl platinum complexes with BrMgC<sub>6</sub>H<sub>4</sub>-4-X (X = OMe, CH<sub>3</sub>, H, Cl, F, CF<sub>3</sub>) formed the unsymmetrical COD-ligated, bis-aryl complexes (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)(C<sub>6</sub>H<sub>4</sub>-4-X) in 55–75% yield. Reaction of DPPF with (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)(C<sub>6</sub>H<sub>4</sub>-4-X) in ether formed the DPPF-ligated, unsymmetrical, bis-aryl platinum complexes (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)(C<sub>6</sub>H<sub>4</sub>-4-X) (**2b–f**, **3b–e**, **4a,b**) in 70–

Scheme 3



95% yield. Complexes **2b–f**, **3b–e**, and **4a,b** were characterized by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy and elemental analysis, and complexes **3b** and **3c**, were sufficiently soluble to be characterized by <sup>13</sup>C NMR spectroscopy.

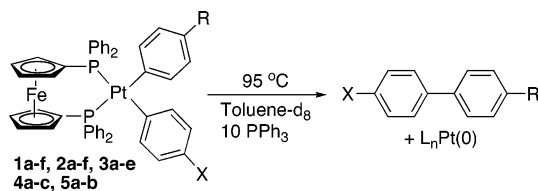
Unsymmetrical bis-aryl platinum complexes **2a**, **3a**, and **5a,b** were inaccessible by Route A because the COD-ligated biaryl species (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X) (X = OMe, CH<sub>3</sub>, H, Cl) decomposed at room temperature, and efforts to generate (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)Cl by protonolysis of the *p*-dimethylaminophenyl group in **1a** led to the decomposition of **1a** without generation of the aryl platinum chloride. Thus, complexes **2a**, **3a**, and **5a,b** were synthesized by Route B in Scheme 2. Reaction of DPPF with (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)Cl formed (DPPF)-Pt(C<sub>6</sub>H<sub>4</sub>-4-R)Cl, and this complex was converted to the unsymmetrical bis-aryl complex by reaction with the Grignard reagent BrMgC<sub>6</sub>H<sub>4</sub>-4-X. Complexes **2a**, **3a**, and **5a,b** were unstable to moisture and were characterized by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy.

The unsymmetrical bis-aryl complex (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>) (**4c**) was prepared by a circuitous route shown in Scheme 3 because of the inaccessibility of either (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)Cl or (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)Cl by protonolysis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)<sub>2</sub> or (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)<sub>2</sub>. Protonolysis of L<sub>2</sub>Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)<sub>2</sub> (L<sub>2</sub> = COD or DPPF) was fast, but not clean, while protonolysis of L<sub>2</sub>Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)<sub>2</sub> (L<sub>2</sub> = COD or DPPF), even with HCl in refluxing benzene, was slow.

Reaction of CH<sub>3</sub>COCl with (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)<sub>2</sub> in a mixture of CH<sub>2</sub>Cl<sub>2</sub> and MeOH formed (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)Cl in 92% yield. This complex was converted to (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>) in 72% yield by reaction with BrMgC<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>. Treatment of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>) with CH<sub>3</sub>COCl in a mixture of CH<sub>2</sub>Cl<sub>2</sub> and MeOH then formed (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)Cl in 94% yield. Reaction of DPPF with (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)Cl in refluxing benzene formed (DPPF)-Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)Cl in 87% yield, and conversion of this complex to (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>) occurred upon addition of BrMgC<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub> in 35% yield after recrystallization. This final complex was characterized by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy.

(45) Peters, B. T.; Zheng, Q.; Stahl, J.; Bohling, J. C.; Arif, A. M.; Hampel, F.; Gladysz, J. A. *J. Organomet. Chem.* **2002**, *641*, 53–61.

Scheme 4



**Table 1.** First-Order Rate Constants for Thermal Decomposition of Symmetrical Bis-Aryl Platinum Complexes ((DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)<sub>2</sub>)<sup>a</sup>

R	complex	$k_{\text{obs}}$ (s <sup>-1</sup> ) × 10 <sup>-5</sup>
NMe <sub>2</sub>	<b>1a</b>	32.3
OMe	<b>1b</b>	5.35
CH <sub>3</sub>	<b>1c</b>	15.5
H	<b>1d</b>	9.22
Cl	<b>1e</b>	3.77
CF <sub>3</sub>	<b>1f</b>	1.39

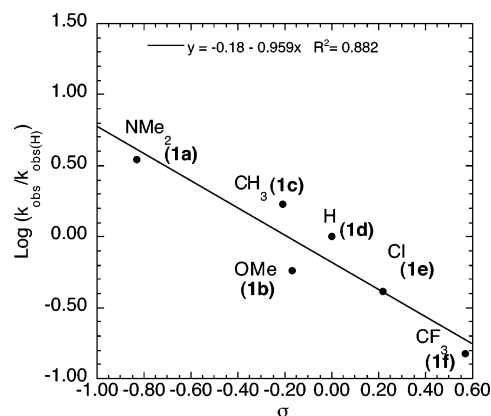
<sup>a</sup> Measured at 95 °C. [Pt] = 0.011 M, [PPh<sub>3</sub>] = 0.110 M.

**4. Reductive Elimination from Bis-Aryl Platinum Complexes.** Heating of bis-aryl platinum complexes in toluene at 95 °C in the presence of excess of PPh<sub>3</sub> formed the corresponding biaryl products in quantitative yields (Scheme 4). Pt(PPh<sub>3</sub>)<sub>3</sub>, which rapidly exchanges with free PPh<sub>3</sub>,<sup>46</sup> was the predominant metal product, as observed by <sup>31</sup>P NMR spectroscopy, along with small quantities of a material with a <sup>31</sup>P NMR resonance at  $\delta$  27.2 ( $J_{\text{Pt-P}} = 4103$  Hz) that we attributed to the previously reported (DPPF)<sub>2</sub>Pt.<sup>47</sup> Warming of the bis-aryl platinum complexes in the absence of a reagent that would trap the Pt(0) fragment formed the biaryl products in lower yields. In the absence of added phosphine, biaryl products derived from the phenyl groups of the phosphine were generated.<sup>16,48</sup>

**5. Rates of Reductive Elimination from Symmetrical Bis-Aryl Platinum Complexes (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-R)<sub>2</sub>.** Rate constants for reductive elimination of biaryls from bis-aryl platinum complexes were determined from plots of the decay of the platinum complexes vs time, generated from <sup>1</sup>H and <sup>19</sup>F NMR data obtained over greater than three half-lives. The reactions of bis-aryl complexes **1a–e**, **2a–f**, **3a–e**, and **5a–c** were monitored by <sup>1</sup>H NMR spectroscopy, and the reactions of **1f** and **4a,b** were monitored by <sup>19</sup>F NMR spectroscopy. Reactions of the bis-aryl platinum complexes were first order for greater than three half-lives. Values of  $k_{\text{obs}}$  for reductive elimination of complexes **1a–f** are listed in Table 1. The rates of reductive elimination of **1b** and **1c** were independent of the concentration of PPh<sub>3</sub>, and we presumed that the rate for reaction of the other derivatives was also independent of the concentration of added phosphine.

The rate constant for reductive elimination from bis-dimethylaminophenyl complex **1a** was approximately 20 times larger than that for elimination from bis-trifluoromethylphenyl complex **1f**. The overall order of reactivity was R = NMe<sub>2</sub> > CH<sub>3</sub> > H > OMe > Cl > CF<sub>3</sub>.

Correlations between the rate constants and the electronic parameters of the para substituents were explored by plotting  $\text{Log}(k_{\text{obs}}/k_{\text{obs(H)}})$  ( $k_{\text{obs(H)}} = k_{\text{obs}}$  for **1d**) vs various Hammett parameters based on ionization of benzoic acids ( $\sigma$ ), enhanced



**Figure 1.** Hammett plot of rates of reductive elimination of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)<sub>2</sub> (**1a–f**).

para substituent constants ( $\sigma^-$ ), and electrophilic substituent constants ( $\sigma^+$ ). The correlation coefficient of the plot of  $\text{Log}(k_{\text{obs}}/k_{\text{obs(H)}})$  vs  $\sigma$  shown in Figure 1 was higher than that vs  $\sigma^-$  or  $\sigma^+$ . This plot had a slope of  $-0.9$  and a correlation coefficient of  $0.88$ .

$\text{Log}(k_{\text{obs}}/k_{\text{obs(H)}})$  was also plotted using dual substituent parameters based on resonance and inductive effects.<sup>49,50</sup> The synthetic Hammett parameter ( $\bar{\sigma}$ ) was generated from a linear combination of the inductive and resonance substituent constants  $\sigma_I$  and  $\sigma_R$  with the formula  $\bar{\sigma} = (\sigma_I + \lambda\sigma_R)/(1 + \lambda)$ . In accord with established procedures, the value of  $\lambda$  was generated from the best fit to the equation  $\text{Log}(k_{\text{obs}}/k_{\text{obs(H)}}) = \rho\bar{\sigma}$ .<sup>49,50</sup> The correlation coefficient was somewhat higher for this plot of  $\text{Log}(k_{\text{obs}}/k_{\text{obs(H)}})$  vs  $\bar{\sigma}$ .

**6. Rates of Reductive Elimination from Unsymmetrical, Bis-Aryl Platinum Complexes (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)(C<sub>6</sub>H<sub>4</sub>-4-X).** To study potential synergistic effects of electron-donating and electron-withdrawing substituents on the platinum-bound aryl groups, we compared the rates of reductive elimination from several series of electronically unsymmetrical bis-aryl platinum complexes of the type (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)(C<sub>6</sub>H<sub>4</sub>-4-X). In each series, the para substituent R was maintained constant, and the para substituent X was varied. Reductive eliminations from all the unsymmetrical bis-aryl platinum complexes (**2a–f**, **3a–e**, **4a–c**, **5a,b**) followed first-order behavior over more than three half-lives. The values of  $k_{\text{obs}}$  for the reactions of complexes (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X) (**1f**, **2f**, **3e**, **4a–c**), (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X) (**1a**, **2a**, **3a**, **4c**, **5a,b**), (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X) (**1c**, **2a–f**), and (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-X) (**1b**, **3a–e**) are listed in Tables 2–5.

The values of  $\text{Log}(k_{\text{obs}}/k_{\text{obs(H)}})$  were plotted vs the Hammett substituent constants  $\sigma$ ,  $\sigma^-$ , and  $\sigma^+$  for the groups X in (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)(C<sub>6</sub>H<sub>4</sub>-4-X). Again, the correlation coefficients were higher for plots of  $\text{Log}(k_{\text{obs}}/k_{\text{obs(H)}})$  vs  $\sigma$  than vs  $\sigma^-$  or  $\sigma^+$ . Plots of  $\text{Log}(k_{\text{obs}}/k_{\text{obs(H)}})$  vs synthetic Hammett parameters  $\bar{\sigma}$  generated different values of  $\lambda$  for the different series of compounds with different groups R. Hence, we focused our interpretation of the rates of the reaction of the unsymmetrical compounds on the plots obtained by fitting  $\text{Log}(k_{\text{obs}}/k_{\text{obs(H)}})$  vs  $\sigma$ .

(46) Sen, A.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 1073–1075.

(47) Chaloner, P. A.; Broadwood-Strong, G. T. L. *J. Chem. Soc., Dalton Trans.* **1996**, 1049–1043.

(48) Kong, K. C.; Cheng, C. H. *J. Am. Chem. Soc.* **1991**, *113*, 6313–6315.

(49) Wells, P. R.; Ehemson, S.; Taft, R. W. *Prog. Phys. Org. Chem.* **1968**, *6*, 147–189.

(50) Mann, G.; Baranano, D.; Hartwig, J. F.; Rheingold, A. L.; Guzel, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 9205–9219.

**Table 2.** First-Order Rate Constants for Thermal Decomposition of Platinum Complexes of the Type (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X)<sup>a</sup>

X	complex	$k_{\text{obs}} (\text{s}^{-1}) \times 10^{-5}$
CF <sub>3</sub>	<b>1f</b>	1.39
CH <sub>3</sub>	<b>2f</b>	17.6
OMe	<b>3f</b>	23.3
H	<b>4a</b>	6.63
Cl	<b>4b</b>	3.89
NMe <sub>2</sub>	<b>4c</b>	159

<sup>a</sup> Measured at 95 °C. [Pt] = 0.011 M, [PPh<sub>3</sub>] = 0.110 M.**Table 3.** First-Order Rate Constants for Thermal Decomposition of Platinum Complexes of the Type (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X)<sup>a</sup>

X	complex	$k_{\text{obs}} (\text{s}^{-1}) \times 10^{-5}$
NMe <sub>2</sub>	<b>1a</b>	32.3
CH <sub>3</sub>	<b>2a</b>	33.2
OMe	<b>3a</b>	32.3
H	<b>5a</b>	30.8
Cl	<b>5b</b>	52.3
CF <sub>3</sub>	<b>4c</b>	159

<sup>a</sup> Measured at 95 °C. [Pt] = 0.011 M, [PPh<sub>3</sub>] = 0.110 M.**Table 4.** First-Order Rate Constants for Thermal Decomposition of Platinum Complexes of the Type (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X)<sup>a</sup>

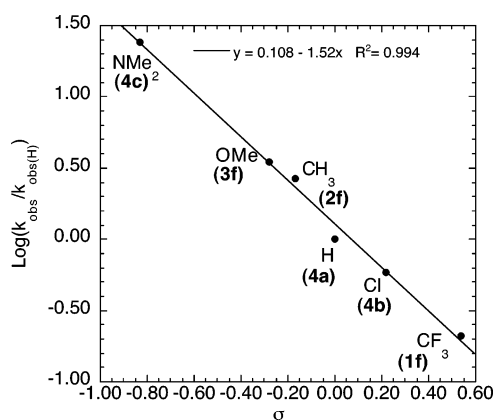
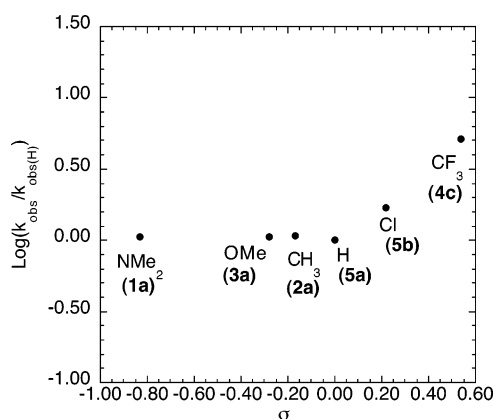
X	complex	$k_{\text{obs}} (\text{s}^{-1}) \times 10^{-5}$
CH <sub>3</sub>	<b>1c</b>	15.5
NMe <sub>2</sub>	<b>2a</b>	33.3
OMe	<b>2b</b>	27.1
H	<b>2c</b>	11.9
Cl	<b>2d</b>	7.19
F	<b>2e</b>	2.29
CF <sub>3</sub>	<b>2f</b>	17.6

<sup>a</sup> Measured at 95 °C. [Pt] = 0.011 M, [PPh<sub>3</sub>] = 0.110 M.**Table 5.** First-Order Rate Constants for Thermal Decomposition of Platinum Complexes of the Type (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-X)<sup>a</sup>

X	complex	$k_{\text{obs}} (\text{s}^{-1}) \times 10^{-5}$
OMe	<b>1b</b>	5.35
NMe <sub>2</sub>	<b>3a</b>	32.6
CH <sub>3</sub>	<b>3b</b>	27.1
H	<b>3c</b>	16.0
Cl	<b>3d</b>	7.16
F	<b>3e</b>	3.25
CF <sub>3</sub>	<b>3f</b>	23.3

<sup>a</sup> Measured at 95 °C. [Pt] = 0.011 M, [PPh<sub>3</sub>] = 0.110 M.

A plot of  $\text{Log}(k_{\text{obs}}/k_{\text{obs(H)}})$  ( $k_{\text{obs(H)}} = k_{\text{obs}}$  for **4a**) vs the Hammett substituent constant ( $\sigma$ ) of X in (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X) is presented in Figure 2. These data demonstrate a linear free energy relationship ( $R^2 = 0.99$ ), with a  $\rho$ -value of  $-1.5$ . The absolute value of this  $\rho$ -value is larger than that for reductive elimination from the symmetrical bis-aryl platinum complexes, even though a single aryl group is varied in this series of compounds, instead of two aryl groups as in the series of compounds of Figure 1. The rate constant for reductive elimination from trifluoromethylphenyl complex **1f** was 115 times smaller than that for elimination from dimethylaminophenyl complex **4c**. The overall order of reactivity was  $X = \text{NMe}_2 > \text{OMe} > \text{CH}_3 > \text{H} > \text{Cl} > \text{CF}_3$ .

**Figure 2.** Hammett plot of rates of reductive elimination from (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X) (**1f**, **2f**, **3f**, **4a-c**).**Figure 3.** Hammett plot for the rates of reductive elimination from (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X) (**1a**, **2a**, **3a**, **4c**, **5a,b**).

A plot of  $\text{Log}(k_{\text{obs}}/k_{\text{obs(H)}})$  ( $k_{\text{obs(H)}} = k_{\text{obs}}$  for **5a**) vs the Hammett substituent constant ( $\sigma$ ) of X in (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X) is presented in Figure 3. These data are distinct from those in Figure 2 and show that the rates of reductive elimination from complexes with X = NMe<sub>2</sub>, CH<sub>3</sub>, OMe, and H are similar and that complexes with electron-withdrawing groups X react faster than those with electron-donating groups. For example, the rate constant for reductive elimination from *p*-chlorophenyl complex **5b** was 1.5 times greater than that for reductive elimination from **1a**, **2a**, **3a**, and **5a**. The rate constant for reductive elimination from *p*-trifluoromethylphenyl complex **4c** was about 5 times greater than that for elimination from dimethylaminophenyl complex **1a**.

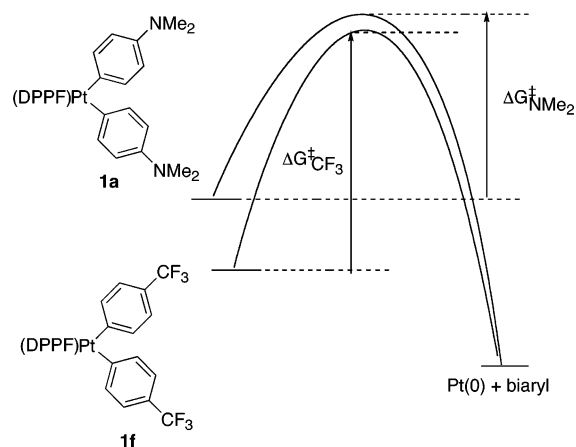
Plots of  $\text{Log}(k_{\text{obs}}/k_{\text{obs(H)}})$  vs the Hammett substituent constant ( $\sigma$ ) of the group X in the series of compounds (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X) and (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-X) with one constant substituent in the middle of the range of electronic parameters (Figure S1 and S2) lacked a simple linear free energy relationship for reductive elimination. However, several comparisons with this series of compounds will be shown in the Discussion section to follow from the proposed origin of the electronic effects on these reductive eliminations. Complex **2a**, which contains one *p*-dimethylaminophenyl group, and complex **2f**, which contains one *p*-trifluoromethylphenyl group, were the compounds with one *p*-tolyl group that underwent the fastest reductive elimination. These two compounds reacted with nearly the same rate constant, even though one aryl group possesses a

strongly electron-donating substituent and the other possesses a strongly electron-withdrawing substituent. Further, complex **3a** with a *p*-dimethylamino group and complex **3e** with a *p*-trifluoromethyl group were the compounds with one *p*-methoxyphenyl group that underwent the fastest reductive elimination. In contrast to the prediction that reductive elimination will be slower from complexes with less electron-donating groups undergoing reductive elimination, complex **3e**, with one trifluoromethyl group and one methoxy group, eliminated roughly 5 times faster than the compound **1b** with two methoxy groups.

## Discussion

**Reductive Elimination of Biaryls from Bis-Aryl Platinum Complexes.** Both symmetrical and unsymmetrical bis-aryl platinum complexes produced biaryls by C–C bond-forming reductive elimination. Two trends were found to affect the rates of the reductive elimination reactions. Complexes with aryl groups containing more electron-donating substituents underwent reductive elimination faster than complexes with aryl groups containing more electron-withdrawing substituents, and complexes with a greater difference in electron-donating capacities of the substituents on the two aryl groups underwent reductive elimination faster than those with a smaller difference in electron-donating capacities of the substituents on the two aryl groups. As a result of these two effects, the influence of the electronic properties of one aryl group on the rate of reductive elimination depended on the electronic properties the second aryl group.

**Reductive Elimination from Symmetrical Bis-Aryl Platinum Complexes (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-X)<sub>2</sub>.** The negative  $\rho$ -value for the Hammett plot of the reductive elimination from symmetrical complexes (Figure 1), which indicates faster reaction of complexes with more electron-rich aryl groups, is consistent with theoretical calculations<sup>10,11</sup> and the previous experimental observation that (PPh<sub>3</sub>)<sub>2</sub>Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)<sub>2</sub> underwent reductive elimination of biaryl faster than (PPh<sub>3</sub>)<sub>2</sub>Pt-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>.<sup>53</sup> A rationalization for the faster reaction of complexes with more electron-donating covalent ligands can be made by comparing the metal–carbon bond strengths of the symmetric bis-aryl platinum complexes. The strengths of M–X covalent bonds tend to be greater to groups that possess stronger H–X bonds.<sup>9,25,26,54–58</sup> Although data on C–H bond strengths of substituted arenes are limited, the C–H bond strengths in substituted toluenes increase with an increase in the electron-withdrawing capacity of the para substituent on toluene.<sup>59</sup> Further, the strengths of the M–X bonds tend to be more sensitive to inductive effects than the strengths of the H–X bond.<sup>25</sup> Thus, the strengths of the platinum–aryl bonds in



**Figure 4.** Qualitative energy diagram for the reductive elimination from symmetrical bis-aryl platinum complexes.

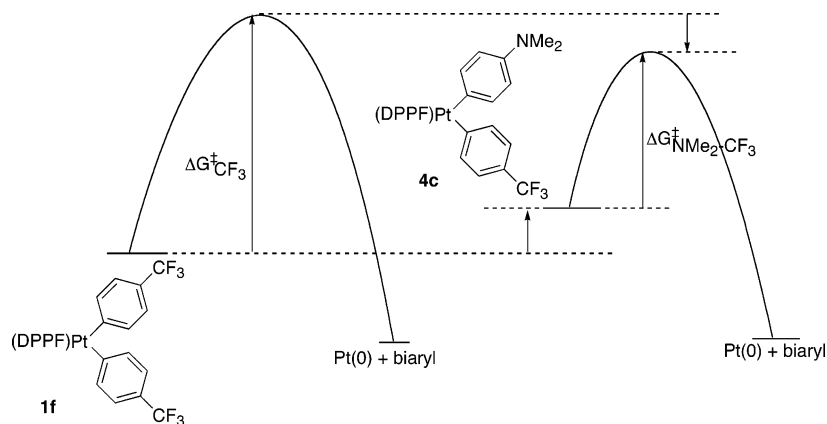
complexes with electron-withdrawing groups will be greater than those in complexes with electron-donating groups on the aryl ring.

A qualitative free energy diagram for reductive eliminations from complexes **1a** and **1f** that results from this analysis is shown in Figure 4. If the difference in Pt–C bond strengths in complexes **1f** and **1a** is larger than the difference in energies of the transition states as shown, then reductive elimination from complex **1f** will be slower than reductive elimination from complex **1a**. This argument has been used previously to rationalize the faster rate of reductive elimination of arene from (C<sub>5</sub>Me<sub>5</sub>)Rh(PMe<sub>3</sub>)(3,5-C<sub>6</sub>H<sub>3</sub>(*t*-Bu)<sub>2</sub>)(H) than from (C<sub>5</sub>Me<sub>5</sub>)Rh-(PMe<sub>3</sub>)(3,5-C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>)(H).<sup>9</sup>

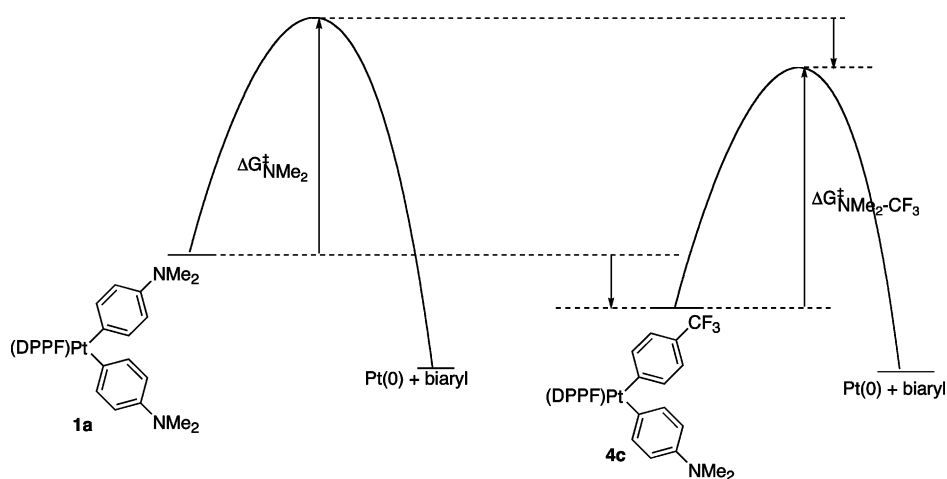
**Electronic Effects on the Reductive Elimination from (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X) Complexes.** The slope of the Hammett plot for reductive elimination from a series of bis-aryl platinum complexes (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X) containing one *p*-trifluoromethylphenyl group and one variable aryl group was also negative (Figure 2), but the absolute value (–1.5) was larger than that of the  $\rho$ -value of the Hammett plot derived from reactions of symmetric bis-aryl complexes. As noted in the Results section, the  $\rho$ -value of the plot in Figure 2 is larger than that in Figure 1, even though the differences in rate constants result from changes to a single aryl group, rather than to changes to both aryl groups. This larger  $\rho$ -value from the plot in Figure 2 provided the first evidence that the rates of reductive elimination result from factors other than the sum of the electronic parameters of the two aryl groups on platinum.

A qualitative energy diagram that depicts graphically our proposed origin of the difference in rates for reductive elimination from (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)<sub>2</sub> (**1f**) and (DPPF)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>) (**4c**) is shown in Figure 5. We propose that the large difference in rate between reductive elimination from the mixed trifluoromethylphenyl dimethylaminophenyl complex **4c** and from the symmetrical bis-trifluoromethylphenyl complex **1f** results from a combination of significant differences in energies of both the ground states and transition states. Just as the ground state of bis-dimethylaminophenyl complex **1a** surely lies at higher energy than the ground state of bis-trifluoromethylphenyl complex **1f**, the ground state of **4c** would lie at higher energy than the ground state of **1f** because of the presence of a more electron-donating substituent on one of the aryl groups. However, it does not seem reasonable to attribute the

- (51) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.  
 (52) Connors, K. A. *Chemical Kinetics. The Study of Reaction Rates in Solution*; John Wiley & Sons: New York, 1990.  
 (53) Komiya, S.; Abe, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1983**, *2*, 1466–1468.  
 (54) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; John Wiley & Sons: New York, 2001.  
 (55) Bulls, A. R.; Bercaw, J. E.; Manriquez, J. M.; Thompson, M. E. *Polyhedron* **1988**, *7*, 1409–1428.  
 (56) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701–7715.  
 (57) Clot, E.; Oelckers, B.; Klahn, A. H.; Eisenstein, O.; Perutz, R. N. *Dalton Trans.* **2003**, 4065–4074.  
 (58) Clot, E.; Besora, M.; Maseras, F.; Megret, C.; Eisenstein, O.; Oelckers, B.; Perutz, R. N. *Chem. Commun.* **2003**, 490–491.  
 (59) Luo, Y. *Handbook Of Bond Dissociation Energies In Organic Compounds*; CRC Press: Boca Raton, FL, 2003.



**Figure 5.** Qualitative energy diagram for the comparison of the rates of reductive elimination from (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)<sub>2</sub> and (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)-(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>).



**Figure 6.** Qualitative energy diagram for the comparison of the rates of reductive elimination from (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>) and (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)-(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>).

large difference between the rate constants for reaction of **1f** and **4c** to ground-state effects alone. The difference between the rates of reaction of mixed trifluoromethylphenyl dimethylaminophenyl complex **4c** and the symmetric bis-trifluoromethylphenyl complex **1f** is larger than the difference between the rates of reaction of the symmetric dimethylamino- and trifluoromethyl-substituted **1a** and **1f**, even though **4c** and **1f** differ by a single aryl group instead of two.

Thus, we propose that the difference in the substituents in **1f** and **4c** leads not only to a higher ground-state energy of **4c** but also to a substantially lower energy transition state for reaction of **4c**. In this case, the  $\rho$ -value for reaction of the unsymmetrical complexes with one trifluoromethylphenyl group would be larger than the  $\rho$ -value for reaction of the symmetrical complexes because of two reinforcing effects: the electron-donating group in **4c** would destabilize the ground state by making the metal–ligand bond weaker and would stabilize the transition state by creating a larger difference in electronic properties between the trifluoromethylphenyl group and the second aryl group.

**Reductive Elimination from (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)-(C<sub>6</sub>H<sub>4</sub>-4-X) Complexes.** Our proposed combination of electronic effects suggests that the influence of substituents in complexes with one constant dimethylaminophenyl group will be different from the influence of substituents in complexes with one constant trifluoromethylphenyl group. Among a series of

complexes with one dimethylaminophenyl group, increased electron-donating properties of an aryl group would give rise to two counteracting effects, depicted graphically in Figure 6. Increased electron-donating properties of the second aryl group would lead to higher ground-state energies of the reactants for reasons noted above, and this effect would accelerate the reaction. However, increased electron-donating properties of the second aryl group would also lead to higher energies of the transition states in this case because of decreased differences between the electronic properties of the dimethylaminophenyl group and the variable group. This effect would retard the reaction.

Therefore, the differences in rates that would result from changes in the electronic properties of the aryl group among this series of compounds would be small, and the Hammett plot for reductive elimination of a series of complexes with one dimethylaminophenyl group and one variable group would have a slope that is smaller in magnitude than that of the plots in Figures 1 and 2. The slope of the plot would be positive if the accelerating effect of two electronically distinct aryl groups is larger than the accelerating effect of an electron-donating group and would be negative if the accelerating effect of two electronically distinct aryl groups is smaller than the accelerating effect of an electron-donating group.

The Hammett plot generated from the rate constants for reductive elimination from the series of compounds with one

dimethylaminophenyl group and one variable group did display a small positive slope (Figure 3). Most striking, the compound with two electron-donating dimethylaminophenyl groups reacted *slower* than the compound with one electron-donating dimethylaminophenyl group and one electron-withdrawing trifluoromethylphenyl group. This decelerating effect of the increasing electron-donating property of substituents in this series of compounds is the opposite of the effect of electron-donating substituents in the series of compounds with a constant trifluoromethylphenyl group or in the series of symmetrical compounds.

The small differences in rate constants combined with subtle differences in the relative magnitudes of the two compensating effects on the rate of reductive elimination of individual compounds makes the relationship between the rate constants and the  $\sigma$ -values less linear for the series of compounds with a dimethylaminophenyl group than for the series of compounds with larger differences in rate constants for reductive elimination. Nevertheless, the difference in magnitude and direction of the electronic effects on the rate of reductive elimination from compounds with one constant dimethylaminophenyl group and on the rate of reductive elimination from compounds with one constant trifluoromethyl group or with two equivalent aryl groups is striking.

**Reductive Elimination from (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X) and (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-X) Complexes.** The proposal that both the overall electron-donating ability of an aryl group and the difference in electron-donating ability of two aryl groups affect the rate of reductive elimination also predicts that the electronic effects of substituents in a series of compounds with one aryl group containing a constant substituent, such as methyl or methoxy, that lies in the middle of the spectrum of donating and withdrawing groups should lead to a complex Hammett plot. The number of compounds that could be prepared with substituents that are more donating and less donating than a methyl or methoxy group were too small to examine in detail the rates of reductive elimination from such series of compounds.

Nevertheless, it was clear that the compounds in these series that eliminated the fastest did not possess the most negative  $\sigma$ -values. Instead, compounds **2a** with one trifluoromethylphenyl group and **2f** with one dimethylaminophenyl group reacted with nearly the same rate constants, and **3a** and **3f** that similarly contained one trifluoromethylphenyl or one dimethylaminophenyl group reacted with nearly the same rate constants. Moreover, the rate constants for reaction of compounds **2a** and **2f** and for reaction of **3a** and **3f** were among the largest of the series of compounds that contain one *p*-tolyl or one *p*-methoxyphenyl aryl group, and compounds **2a** and **2f** and **3a** and **3f** contained the largest difference in electronic properties between the variable group and the common *p*-tolyl or *p*-methoxyphenyl group.

Compounds **2a** and **2f** reacted with nearly the same rate constant, despite the disparate electronic properties of the two variable substituents, and compound **3f** with one trifluoromethylphenyl group reacted faster than compound **1b** with two *p*-methoxyphenyl groups. These results are, again, consistent with a large influence of the difference in electronic properties of the two aryl groups on the energy of the transition state for reductive elimination.

**Conclusions.** We have demonstrated two distinct electronic effects on reductive elimination of biaryls from bis-aryl platinum compounds. One effect was predicted by theoretical methods and causes reductive elimination to be faster from compounds with more electron-donating groups. A second effect had not been identified clearly and causes reductive elimination to be faster from compounds with two aryl groups possessing more dissimilar electronic properties. This second effect appears to be roughly equal in magnitude to the more commonly cited effect of faster elimination from compounds with more donating groups. These two effects lead to complex, though interpretable, linear free energy relationships.

Thus, the electronic effects on reductive elimination are synergistic; the properties of one group dictate the effect of electronic perturbations of a second group. A large increase in the rate of reductive elimination from (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X) was observed when X was more electron-donating, but small differences in the rates of reductive elimination were observed from (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X) when X was more electron-donating. Further, the versions of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X) with the most electron-donating groups X eliminated *slower* than those with the most electron-withdrawing groups X. In the first set of compounds, the more electron-donating X groups destabilized the ground state and stabilized the transition state, and this distinct effect on the ground- and transition-state energies led to large differences in the rate of reaction. In the second set of compounds, the electron-donating groups destabilized the ground state *and* the transition state, and this similar effect on both ground and transition states led to small differences in reaction rates.

The slower reductive elimination from compounds with more electron-withdrawing groups is most likely due to ground-state effects, such as stronger metal–ligand bonds in the reactants. Metal–ligand covalent bonds tend to be stronger to groups that are less electron-donating than to similar groups that are more electron-donating. In contrast, the increased rates for reductive elimination from compounds with larger differences in the properties of the two aryl groups most likely result from transition-state effects. To explain the difference in reaction rates with ground-state arguments, one must invoke unfavorable thermodynamics for a compound with one donating and one withdrawing group, and such a proposal seems unlikely. Instead, the favorable pairing of an electron-rich and electron-poor group lowers the energy of the transition state for reductive elimination, and this favorable pairing of two groups with discrete electronic properties may be considered to parallel the favorable pairing of a nucleophile and electrophile in many organic reactions or the favorable pairing of an electron-poor olefin with an electron-rich diene in a Diels–Alder reaction. Because many organometallic reactions involve bond formation between two ligands, these synergistic electronic effects may contribute to the trends in reactivity among many sets of organometallic compounds.

## Experimental Section

**General Methods.** Unless otherwise noted, all reactions and manipulations were performed in an inert atmosphere glovebox. All <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts are reported in parts per million relative to an 85% H<sub>3</sub>PO<sub>4</sub> external standard. Shifts downfield of the standard are reported as positive. Toluene, benzene, ether, and pentane were distilled from sodium/benzophenone prior to use. Dichloromethane was distilled from calcium hydride. Absolute methanol was used as obtained.



Phenylmagnesium bromide, 4-methylphenylmagnesium bromide, 4-methoxyphenylmagnesium bromide, 4-chlorophenylmagnesium bromide, 4-fluorophenylmagnesium bromide, *N,N*-dimethylaminophenylmagnesium bromide, and 1,5-cyclooctadiene were all purchased from Aldrich Chemicals. Potassium tetrachloroplatinate and DPPF were obtained from Strem Chemicals. 4-Trifluorophenylmagnesium bromide<sup>60</sup> and 1,5-cyclooctadieneplatinumdichloride<sup>61</sup> were synthesized by literature procedures.

**General Procedure for the Preparation of Symmetrical Bis-Aryl Platinum Complexes of the Type (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)<sub>2</sub>.** In a drybox, (COD)PtCl<sub>2</sub> was weighed into a 100 mL round-bottom flask. A stir bar was added, followed by 30 mL of ether. The Grignard reagent (2.2 equiv) was added, and the reaction mixture was allowed to stir at room temperature for 12 h. The reaction mixture was brought outside the glovebox, and saturated aqueous NH<sub>4</sub>Cl (20 mL) was added. The ether layer was separated, and the water layer was extracted with ether. The combined ether extracts were dried over anhydrous MgSO<sub>4</sub> and filtered through a 1 cm pad of Celite and a 2 cm pad of decolorizing carbon. Ether was evaporated from the filtrate under reduced pressure. The white solid obtained was recrystallized from a mixture of dichloromethane and pentane.

(COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)<sub>2</sub>, obtained in the above step, was weighed into a screw-capped vial. A stir bar was added, followed by 10 mL of benzene. DPPF (1 equiv) was added, and the mixture was allowed to stir for 1 h at room temperature. The solvent was evaporated under reduced pressure. The yellow solid obtained was recrystallized from a mixture of dichloromethane and pentane.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)<sub>2</sub> (1a).** (COD)PtCl<sub>2</sub> (0.418 g, 1.12 mmol) and 4-NMe<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>MgBr (4.50 mL, 2.25 mmol) in 30 mL of ether gave 0.347 g (59%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)<sub>2</sub>. DPPF (0.097 g, 0.175 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)<sub>2</sub> (0.089 g, 0.159 mmol) in 10 mL of benzene gave 0.165 g (95%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)<sub>2</sub>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.49–7.44 (m, 10H, DPPF), 7.29–7.25 (m, 4H, DPPF), 7.17–7.15 (m, 6H, DPPF), 6.74–6.55 (m, 4H, Pd-Ar), 6.03 (d, 4H, *J* = 7.6 Hz, Pd-Ar), 4.23–4.21 (b, 4H, Cp-H), 4.14–4.12 (b, 4H, Cp-H), 2.52 (s, 12H, NMe<sub>2</sub>-H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, benzene): δ 15.27 (s, *J*<sub>PtP</sub> = 1772 Hz). Anal. Calcd for C<sub>50</sub>H<sub>48</sub>N<sub>2</sub>FeP<sub>2</sub>Pt: C, 60.67; H, 4.89; N, 2.83. Found: C, 60.39; H, 4.81; N, 2.62.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)<sub>2</sub> (1b).** (COD)PtCl<sub>2</sub> (0.593 g, 1.59 mmol) and 4-OMe-C<sub>6</sub>H<sub>4</sub>MgBr (7.0 mL, 3.5 mmol) in 30 mL of ether gave 0.597 g (70%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)<sub>2</sub>. DPPF (0.110 g, 0.198 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)<sub>2</sub> (0.098 g, 0.181 mmol) in 10 mL of benzene gave 0.171 g (94%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)<sub>2</sub>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.44–7.38 (m, 8H, DPPF), 7.23–7.16 (m, 4H, DPPF), 6.72–6.65 (m, 12H, DPPF and Pd-Ar), 6.05 (d, 4H, *J* = 7.2 Hz, Pd-Ar), 4.32 (b, 4H, Cp-H), 4.24 (b, 4H, Cp-H), 3.51 (s, 6H, OMe-H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, benzene): δ 15.27 (s, *J*<sub>PtP</sub> = 1796 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 55.38 (s), 72.77 (app t, *J* = 2.76 Hz), 74.89 (app t, *J* = 4.78 Hz), 76.80 (m), 113.58 (b), 127.82 (app t, *J* = 4.78 Hz), 129.85 (s), 134.22 (m), 134.92 (app t, *J* = 4.78 Hz), 136.08 (b, *J*<sub>PtC</sub> = 36.35 Hz), 150.60 (dd, *J* = 102.63 Hz, 13.33 Hz), 154.74 (s). Anal. Calcd for C<sub>48</sub>H<sub>42</sub>O<sub>2</sub>FeP<sub>2</sub>Pt: C, 59.82; H, 4.39. Found: C, 59.96; H, 4.26.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)<sub>2</sub> (1c).** (COD)PtCl<sub>2</sub> (0.505 g, 1.35 mmol) and 4-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>MgBr (3.0 mL, 3.0 mmol) in 30 mL of ether gave 0.372 g (57%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)<sub>2</sub>. DPPF (0.059 g, 0.106 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)<sub>2</sub> (0.045 g, 0.096 mmol) in 10 mL of benzene gave 0.102 g (95%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)<sub>2</sub>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.73–7.72 (m, 8H, DPPF), 7.33–7.31 (m, 4H, DPPF), 7.02–7.01 (m, 12H, DPPF and Pd-Ar), 6.62 (d, 4H, *J* = 7.3 Hz, Pd-Ar), 4.40 (b, 4H, Cp-H), 3.87 (b, 4H, Cp-H), 2.04 (s, 6H,

Me-H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, benzene): δ 15.51 (s, *J*<sub>PtP</sub> = 1772 Hz). Anal. Calcd for C<sub>48</sub>H<sub>42</sub>FeP<sub>2</sub>Pt: C, 61.87; H, 4.54. Found: C, 62.12; H, 4.56.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (1d).**<sup>62</sup> (COD)PtCl<sub>2</sub> (0.205 g, 0.549 mmol) and C<sub>6</sub>H<sub>5</sub>MgBr (1.2 mL, 1.2 mmol) in 30 mL of ether gave 0.181 g (72%) of (COD)Pt(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>. DPPF (0.092 g, 0.166 mmol) and (COD)Pt(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (0.076 g, 0.150 mmol) in 10 mL of benzene gave 0.131 g (87%) of (DPPF)Pt(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.63–7.59 (m, 2H, DPPF), 7.54–7.45 (m, 8H, DPPF), 7.37–7.35 (m, 4H, DPPF), 7.29–7.25 (m, 8H, DPPF), 6.96–6.82 (m, 4H, Pd-Ar), 6.39–6.36 (m, 4H, Pd-Ar), 4.33 (b, 4H), 4.24 (b, 4H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>): δ 15.56 (s, *J*<sub>PtP</sub> = 1784 Hz). Anal. Calcd for C<sub>46</sub>H<sub>38</sub>FeP<sub>2</sub>Pt: C, 61.14; H, 4.24. Found: C, 61.01; H, 4.34.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-Cl)<sub>2</sub> (1e).** (COD)PtCl<sub>2</sub> (0.441 g, 1.18 mmol) and 4-Cl-C<sub>6</sub>H<sub>4</sub>MgBr (2.5 mL, 2.5 mmol) in 30 mL of ether gave 0.455 g (73%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-Cl)<sub>2</sub>. DPPF (0.136 g, 0.245 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-Cl)<sub>2</sub> (0.114 g, 0.222 mmol) in 10 mL of benzene gave 0.209 g (88%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-Cl)<sub>2</sub>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.43–7.40 (m, 8H, DPPF), 7.31–7.28 (m, 4H, DPPF), 7.22–7.17 (m, 8H, DPPF), 6.73–6.62 (m, 4H, Pd-Ar), 6.36 (d, 4H, *J* = 7.9 Hz, Pd-Ar), 4.23 (b, 4H, Cp-H), 4.15 (b, 4H, Cp-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, benzene): δ 15.17 (s, *J*<sub>PtP</sub> = 2566 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 73.06 (app t, 2.89 Hz), 74.95 (app t, 4.90 Hz), 75.95 (m), 126.89 (s), 127.13 (app t, 3.02 Hz), 128.07 (app t, 5.03 Hz, *J*<sub>PtC</sub> = 33.58 Hz), 130.24 (s), 133.66 (dd, 54.7 Hz, 3.77 Hz), 134.765 (app t, 5.28 Hz), 137.10 (b, *J*<sub>PtC</sub> = 33.96 Hz), 158.49 (dd, 115.95 Hz, 13.21 Hz). Anal. Calcd for C<sub>46</sub>H<sub>36</sub>Cl<sub>2</sub>FeP<sub>2</sub>Pt: C, 56.81; H, 3.73. Found: C, 56.90; H, 3.69.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)<sub>2</sub> (1f).** (COD)PtCl<sub>2</sub> (0.107 g, 0.286 mmol) and 4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>MgBr (3.5 mL, 0.64 mmol) in 30 mL of ether gave 0.118 g (69%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)<sub>2</sub>. DPPF (0.098 g, 0.177 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)<sub>2</sub> (0.099 g, 0.161 mmol) in 10 mL of benzene gave 0.153 g (83%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)<sub>2</sub>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.45–7.38 (m, 8H, DPPF), 7.32–7.29 (m, 4H, DPPF), 7.23–7.19 (m, 8H, DPPF), 6.97–6.83 (m, 4H, Pd-Ar), 6.58 (d, 4H, *J* = 7.6 Hz, Pd-Ar), 4.26 (b, 4H, Cp-H), 4.17 (b, 4H, Cp-H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, benzene): δ 15.44 (s, *J*<sub>PtP</sub> = 1856 Hz). Anal. Calcd for C<sub>48</sub>H<sub>36</sub>F<sub>6</sub>FeP<sub>2</sub>Pt: C, 55.44; H, 3.49. Found: C, 55.43; H, 3.26.

**General Procedure for the Synthesis of Unsymmetrical Bis-Aryl Platinum Complexes of the Type (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)(C<sub>6</sub>H<sub>4</sub>-4-X) (2b–f, 3b–e, 4a–b) via Route A (Scheme 2).** (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)<sub>2</sub> was taken in a screw-capped vial. A stir bar was added, followed by a mixture of 5 mL of CH<sub>2</sub>Cl<sub>2</sub> and 5 mL of anhydrous MeOH. CH<sub>3</sub>COCl (1 equiv) was added, and the reaction mixture was stirred for 10–30 min at room temperature or at 70 °C, depending upon the nature of R. The solvent was evaporated under reduced pressure. The white solid obtained was recrystallized from a mixture of dichloromethane and pentane. In a drybox, (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)Cl obtained above was taken in a 100 mL round-bottom flask. A stir bar was added, followed by 30 mL of ether. The Grignard reagent (2.2 equiv) was added, and the reaction mixture was allowed to stir for 12 h at room temperature. The reaction mixture was brought outside the glovebox, and saturated aqueous NH<sub>4</sub>Cl (20 mL) was added. The ether layer was separated, and the water layer was extracted with ether. The combined ether extracts were dried over anhydrous MgSO<sub>4</sub> and filtered through a 1 cm pad of Celite and a 2 cm pad of decolorizing carbon. Ether was removed from the filtrate under reduced pressure. The white solid obtained was recrystallized from a mixture of dichloromethane and pentane. (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)(C<sub>6</sub>H<sub>4</sub>-4-X) obtained above was weighed into a screw-capped vial. A stir bar was added, followed by 10 mL of benzene. DPPF (1 equiv) was added to the above reaction mixture and allowed to stir for 1 h at room temperature. The solvent was evaporated

(60) Sawamura, M.; Iikura, H.; Hirai, A.; Nakamura, E. *J. Am. Chem. Soc.* **1998**, *120*, 8285.

(61) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521–6528.

(62) Colacot, T. J.; Teichman, R. A.; Cea-Olivares, R.; Alvarado-Rodriguez, J. G.; Toscano, R. A.; Boyko, W. J. *J. Organomet. Chem.* **1998**, *557*, 169.

under reduced pressure. The yellow solid obtained was recrystallized from a mixture of dichloromethane and pentane.

**Synthesis of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)Cl.**<sup>45</sup> The above general procedure was followed using (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)<sub>2</sub> (0.204 g, 0.421 mmol) and CH<sub>3</sub>COCl (30 μL, 0.42 mmol) in a mixture of 5 mL of dichloromethane and 5 mL of methanol to give 0.132 g (73%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)Cl.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-OMe) (2b).** 4-OMe-C<sub>6</sub>H<sub>4</sub>MgBr (0.50 mL, 0.25 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)Cl (0.098 g, 0.228 mmol) in 30 mL of ether gave 0.062 g (54%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-OMe). DPPF (0.068 g, 0.123 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-OMe) (0.056 g, 0.118 mmol) in 10 mL of benzene gave 0.099 g (87%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-OMe). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.45–7.39 (m, 8H, DPPF), 7.29–7.25 (m, 4H, DPPF), 7.15–7.20 (m, 8H, DPPF), 6.73–6.56 (b, 4H, Pd-Ar), 6.22 (d, 2H, *J* = 7.2 Hz, Pd-Ar), 6.06 (d, 2H, *J* = 7.6 Hz, Pd-Ar), 4.22–4.21 (m, 4H, Cp-H), 4.14–4.13 (m, 4H, Cp-H), 3.44 (s, 3H, OMe-H), 1.87 (s, 3H, Me-H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, benzene): δ 15.19 (s, *J*<sub>PP</sub> = 1778 Hz). Anal. Calcd for C<sub>48</sub>H<sub>42</sub>OFeP<sub>2</sub>Pt: C, 60.83; H, 4.47. Found: C, 60.72; H, 4.26.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>) (2c).** C<sub>6</sub>H<sub>5</sub>MgBr (0.55 mL, 0.55 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)Cl (0.209 g, 0.486 mmol) in 30 mL of ether gave 0.175 g (74%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>). DPPF (0.218 g, 0.393 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>) (0.175 g, 0.371 mmol) in 10 mL of benzene gave 0.307 g (91%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.51–7.44 (m, 8H, DPPF), 7.35–7.16 (m, 12H, DPPF), 6.93–6.79 (m, 2H, Pd-Ar), 6.79–6.66 (m, 2H, Pd-Ar), 6.45–6.42 (m, 2H, Pd-Ar), 6.37–6.33 (m, 1H, Pd-Ar), 6.29–6.27 (m, 2H, Pd-Ar), 4.30–4.29 (m, 4H, Cp-H), 4.21 (s, 4H, Cp-H), 1.93 (s, 3H, Me-H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, benzene): δ 15.11 (d, *J*<sub>PP</sub> = 1772 Hz, *J*<sub>PP</sub> = 14 Hz), 16.76 (d, *J*<sub>PP</sub> = 1772 Hz, *J*<sub>PP</sub> = 14 Hz). Anal. Calcd for C<sub>48</sub>H<sub>42</sub>OFeP<sub>2</sub>Pt: C, 60.83; H, 4.47. Found: C, 60.72; H, 4.26.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-Cl) (2d).** 4-Cl-C<sub>6</sub>H<sub>4</sub>-MgBr (0.25 mL, 0.25 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)Cl (0.082 g, 0.191 mmol) in 30 mL of ether gave 0.045 g (46%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-Cl). DPPF (0.053 g, 0.096 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-Cl) (0.037 g, 0.087 mmol) in 10 mL of benzene gave 0.073 g (87%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-Cl). <sup>1</sup>H NMR (400 MHz, C<sub>7</sub>D<sub>8</sub>): δ 7.45–7.39 (m, 10H, DPPF), 7.31–7.26 (m, 5H, DPPF), 7.24–7.16 (m, 5H, DPPF), 6.77–6.68 (m, 2H, Pd-Ar), 6.68–6.57 (m, 2H, Pd-Ar), 6.34 (d, 2H, *J* = 7.5 Hz, Pd-Ar), 6.23 (d, 2H, *J* = 6.5 Hz, Pd-Ar), 4.24 (d, 2H, *J* = 1.5 Hz, Cp-H), 4.21 (d, 2H, *J* = 1.5 Hz, Cp-H), 4.14 (s, 4H, Cp-H), 1.88 (s, 3H, Me-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, toluene): δ 15.41 (d, *J*<sub>PP</sub> = 14 Hz, *J*<sub>PP</sub> = 1778 Hz), 15.02 (d, *J*<sub>PP</sub> = 14 Hz, *J*<sub>PP</sub> = 1884 Hz). Anal. Calcd for C<sub>47</sub>H<sub>39</sub>ClFeP<sub>2</sub>Pt: C, 59.29; H, 4.13. Found: C, 59.09; H, 3.87.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-F) (2e).** 4-F-C<sub>6</sub>H<sub>4</sub>-MgBr (0.30 mL, 0.60 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)Cl (0.231 g, 0.537 mmol) in 30 mL of ether gave 0.175 g (67%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-F). DPPF (0.218 g, 0.393 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-F) (0.175 g, 0.357 mmol) in 10 mL of benzene gave 0.299 g (89%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-F). <sup>1</sup>H NMR (400 MHz, C<sub>7</sub>D<sub>8</sub>): δ 7.53–7.46 (m, 8H, DPPF), 7.37–7.33 (m, 4H, DPPF), 7.29–7.16 (m, 8H, DPPF), 6.84–6.77 (m, 2H, Pd-Ar), 6.70–6.61 (m, 2H, Pd-Ar), 6.30 (d, 2H, *J* = 6.8 Hz, Pd-Ar), 6.24–6.19 (m, 2H, Pd-Ar), 4.31–4.28 (m, 4H, Cp-H), 4.19 (s, 4H, Cp-H), 1.92 (s, 3H, Me-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, toluene): δ 15.37 (d, *J*<sub>PP</sub> = 15 Hz, *J*<sub>PP</sub> = 1778 Hz), 14.86 (d, *J*<sub>PP</sub> = 15 Hz, *J*<sub>PP</sub> = 1906 Hz). Anal. Calcd for C<sub>47</sub>H<sub>39</sub>FFeP<sub>2</sub>Pt: C, 60.33; H, 4.20. Found: C, 60.08; H, 4.05.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>) (2f).** 4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>MgBr (0.40 mL, 0.20 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)Cl (0.083 g, 0.193 mmol) in 30 mL of ether gave 0.056 g (54%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>). DPPF (0.084 g, 0.151 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>) (0.074 g, 0.137 mmol) in 10 mL of benzene gave 0.130 g (87%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>).

<sup>1</sup>H NMR (400 MHz, C<sub>7</sub>D<sub>8</sub>): δ 7.70–7.64 (m, 8H, DPPF), 7.55–7.52 (m, 4H, DPPF), 7.47–7.42 (m, 8H, DPPF), 7.19–7.16 (m, 2H, Pd-Ar), 6.93–6.90 (m, 2H, Pd-Ar), 6.81 (d, 2H, *J* = 6.8 Hz, Pd-Ar), 6.49 (d, 2H, *J* = 6.8 Hz, Pd-Ar), 4.55–4.53 (m, 2H, Cp-H), 4.45–4.32 (m, 6H, Cp-H), 2.09 (s, 3H, Me-H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, toluene): δ 16.19 (d, *J*<sub>PP</sub> = 14 Hz, *J*<sub>PP</sub> = 1896 Hz), 14.65 (d, *J*<sub>PP</sub> = 14 Hz, *J*<sub>PP</sub> = 1930 Hz).

**Synthesis of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)Cl.** The above general procedure was followed with (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)<sub>2</sub> (0.294 g, 0.568 mmol) and CH<sub>3</sub>COCl (40 μL, 0.57 mmol) in a mixture of 5 mL of dichloromethane and 5 mL of methanol to give 0.202 g (80%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)Cl.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>5</sub>) (3b).** C<sub>6</sub>H<sub>5</sub>MgBr (0.60 mL, 0.60 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)Cl (0.228 g, 0.511 mmol) in 30 mL of ether gave 0.216 g (87%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>5</sub>). DPPF (0.271 g, 0.489 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>5</sub>) (0.216 g, 0.443 mmol) in 10 mL of benzene gave 0.373 g (90%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>5</sub>). <sup>1</sup>H NMR (400 MHz, C<sub>7</sub>D<sub>8</sub>): δ 7.55–7.54 (m, 10H, DPPF), 7.44–7.29 (m, 10H, DPPF), 6.96–6.73 (m, 4H, Pd-Ar), 6.49–6.41 (m, 3H, Pd-Ar), 6.18–6.17 (m, 2H, Pd-Ar), 4.35 (b, 4H, Cp-H), 4.25 (b, 4H, Cp-H), 3.55 (s, 3H, OMe-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, toluene): δ 15.37 (d, *J*<sub>PP</sub> = 15 Hz, *J*<sub>PP</sub> = 1820 Hz), 15.06 (d, *J*<sub>PP</sub> = 15 Hz, *J*<sub>PP</sub> = 1752 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 55.41 (s), 72.82 (d, *J* = 5.9 Hz), 74.14 (d, *J* = 15.72 Hz), 74.86 (s), 74.94 (s), 76.71 (dd, *J* = 50.56 Hz, 9.56 Hz), 76.86 (dd, *J* = 50.56 Hz, 7.42 Hz), 127.20 (dd, *J* = 5.9 Hz, 2.01 Hz), 127.86 (dd, *J* = 9.56 Hz, 2.65 Hz, *J*<sub>PtC</sub> = 35.59 Hz), 128.71 (dd, *J* = 47.54 Hz, 5.03 Hz), 128.87 (s), 128.94 (s), 129.87 (s), 130.64 (b), 133.76 (s), 133.91 (s), 134.29 (dd, *J* = 48.67 Hz, 7.54 Hz), 134.92 (m), 136.40 (dd, *J* = 34.84 Hz, 1.88 Hz), 139.30 (s), 139.38 (s), 150.26 (dd, *J* = 113.19 Hz, 11.44 Hz), 154.79 (s). Anal. Calcd for C<sub>47</sub>H<sub>40</sub>OFeP<sub>2</sub>Pt: C, 60.46; H, 4.32. Found: C, 60.20; H, 4.07.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-Cl) (3c).** 4-Cl-C<sub>6</sub>H<sub>4</sub>-MgBr (0.42 mL, 0.42 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)Cl (0.180 g, 0.404 mmol) in 30 mL of ether gave 0.113 g (54%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-Cl). DPPF (0.083 g, 0.150 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-Cl) (0.068 g, 0.130 mmol) in 10 mL of benzene gave 0.112 g (89%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-Cl). <sup>1</sup>H NMR (400 MHz, C<sub>7</sub>D<sub>8</sub>): δ 7.52–7.47 (m, 8H, DPPF), 7.39–7.34 (m, 5H, DPPF), 7.29–7.26 (m, 7H, DPPF), 6.79–6.76 (t, 2H, Pd-Ar), 6.71–6.67 (m, 2H, Pd-Ar), 6.43 (d, 2H, *J* = 7.8 Hz, Pd-Ar), 6.13 (d, 2H, *J* = 7.8 Hz, Pd-Ar), 4.33–4.30 (m, 2H, Cp-H), 4.29–4.27 (m, 2H, Cp-H), 4.24–4.22 (m, 4H, Cp-H), 3.52 (s, 3H, OMe-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, toluene): δ 15.94 (d, *J*<sub>PP</sub> = 14 Hz, *J*<sub>PP</sub> = 1774 Hz), 15.18 (d, *J*<sub>PP</sub> = 14 Hz, *J*<sub>PP</sub> = 1806 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 54.92 (s), 72.45 (d, *J* = 5.9 Hz), 72.50 (d, *J* = 5.9 Hz), 74.41 (s), 74.52 (s), 75.74 (dd, *J* = 45.28 Hz, 5.16 Hz), 76.10 (dd, *J* = 46.53 Hz, 11.44 Hz), 113.20 (d, *J* = 4.78 Hz, *J*<sub>PtC</sub> = 100.62 Hz), 126.55 (d, *J* = 6.54 Hz, *J*<sub>PtC</sub> = 88.04 Hz), 127.51 (app t, *J* = 10.56 Hz), 129.59 (d, *J* = 13.71 Hz), 133.36 (s), 133.73 (s), 134.39 (m), 135.64 (s, *J*<sub>PtC</sub> = 50.30 Hz), 136.68 (s, *J*<sub>PtC</sub> = 50.30 Hz), 148.66 (s), 149.46 (s), 149.53 (s), 154.47 (s), 158.55 (s), 159.44 (s), 159.51 (s). Anal. Calcd for C<sub>47</sub>H<sub>39</sub>-ClOFeP<sub>2</sub>Pt: C, 58.31; H, 4.06. Found: C, 58.28; H, 4.08.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-F) (3d).** 4-F-C<sub>6</sub>H<sub>4</sub>MgBr (0.30 mL, 0.60 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)Cl (0.237 g, 0.531 mmol) in 30 mL of ether gave 0.179 g (67%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-F). DPPF (0.202 g, 0.364 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-F) (0.141 g, 0.279 mmol) in 10 mL of benzene gave 0.264 g (99%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-F). <sup>1</sup>H NMR (400 MHz, C<sub>7</sub>D<sub>8</sub>): δ 7.01–6.92 (m, 8H, DPPF), 6.78–6.76 (m, 4H, DPPF), 6.70–6.68 (m, 8H, DPPF), 6.24–6.07 (m, 4H, Pd-Ar), 5.67–5.63 (m, 2H, Pd-Ar), 5.56 (d, 2H, *J* = 8.0 Hz, Pd-Ar), 3.74 (s, 2H, Cp-H), 3.71 (s, 2H, Cp-H), 3.67–3.61 (b, 4H, Cp-H), 2.94 (s, 3H, OMe-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, toluene): δ 15.31 (d, *J*<sub>PP</sub> = 48 Hz, *J*<sub>PP</sub> = 1950 Hz), 15.02 (d, *J*<sub>PP</sub> = 48 Hz, *J*<sub>PP</sub> = 1950 Hz). Anal. Calcd for C<sub>47</sub>H<sub>39</sub>-FOFeP<sub>2</sub>Pt: C, 59.32; H, 4.13. Found: C, 59.10; H, 3.95.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-CF<sub>3</sub>) (3f).** 4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-MgBr (0.40 mL, 0.24 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)Cl (0.102 g, 0.229 mmol) in 30 mL of ether gave 0.101 g (76%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>). DPPF (0.111 g, 0.200 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>) (0.101 g, 0.182 mmol) in 10 mL of benzene gave 0.166 g (91%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.45–7.38 (m, 8H, DPPF), 7.32–7.24 (m, 4H, DPPF), 7.21–7.17 (m, 8H, DPPF), 6.96 (m, 2H, Pd-*Ar*), 6.68 (m, 2H, Pd-*Ar*), 6.57 (d, 2H, *J* = 7.2 Hz, Pd-*Ar*), 6.08 (d, 2H, *J* = 7.6 Hz, Pd-*Ar*), 4.29–4.28 (m, 2H, Cp-H), 4.23–4.14 (m, 6H, Cp-H), 3.45 (s, 3H, OMe-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, benzene): δ 16.19 (d, *J*<sub>PP</sub> = 15 Hz, *J*<sub>PP'</sub> = 1928 Hz), 14.56 (d, *J*<sub>PP</sub> = 15 Hz, *J*<sub>PP'</sub> = 1912 Hz). Anal. Calcd for C<sub>48</sub>H<sub>39</sub>F<sub>3</sub>OFeP<sub>2</sub>: C, 60.95; H, 4.16. Found: C, 60.83; H, 4.21.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>) (4a).** (COD)Pt(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (0.311 g, 0.679 mmol) and CH<sub>3</sub>COCl (48 μL, 0.68 mmol) in a mixture of 5 mL of dichloromethane and 5 mL of methanol gave 0.228 g (81%) of (COD)Pt(C<sub>6</sub>H<sub>5</sub>)Cl. 4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>MgBr (0.40 mL, 0.32 mmol) and (COD)Pt(C<sub>6</sub>H<sub>5</sub>)Cl (0.115 g, 0.276 mmol) in 30 mL of ether gave 0.105 g (72%) of (1,5-(COD)Pt(C<sub>6</sub>H<sub>5</sub>)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)). DPPF (0.122 g, 0.220 mmol) and (COD)Pt(C<sub>6</sub>H<sub>5</sub>)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>) (0.105 g, 0.199 mmol) in 10 mL of benzene gave 0.1754 g (89%) of (DPPF)Pt(C<sub>6</sub>H<sub>5</sub>)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, C<sub>7</sub>D<sub>8</sub>): δ 7.42–7.33 (m, 9H, DPPF), 7.22–7.18 (b, 1H, DPPF), 7.15–7.11 (m, 10H, DPPF), 6.93–6.79 (m, 2H, Pd-*Ar*), 6.75–6.65 (m, 2H, Pd-*Ar*), 6.50 (d, 2H, *J* = 7.5 Hz, Pd-*Ar*), 6.34–6.25 (m, 3H, Pd-*Ar*), 4.23–4.22 (b, 2H, Cp-H), 4.13–4.07 (m, 6H, Cp-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, toluene): δ 15.98 (d, *J*<sub>PP</sub> = 15 Hz, *J*<sub>PP'</sub> = 1770 Hz), 15.07 (d, *J*<sub>PP</sub> = 17 Hz, *J*<sub>PP'</sub> = 1830 Hz). Anal. Calcd for C<sub>47</sub>H<sub>37</sub>F<sub>3</sub>FeP<sub>2</sub>: C, 58.10; H, 3.84. Found: C, 57.99; H, 3.85.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-Cl) (4b).** (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-Cl)<sub>2</sub> (0.107 g, 0.203 mmol) and CH<sub>3</sub>COCl (15 μL, 0.20 mmol) in a mixture of 5 mL of dichloromethane and 5 mL of methanol at 70 °C gave 0.082 g (89%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-Cl)Cl. 4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>MgBr (0.25 mL, 0.20 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-Cl)Cl (0.074 g, 0.164 mmol) in 30 mL of ether gave 0.059 g (64%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-Cl)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>). DPPF (0.064 g, 0.115 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-Cl)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>) (0.059 g, 0.105 mmol) in 10 mL of benzene gave 0.090 g (84%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-Cl)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, C<sub>7</sub>D<sub>8</sub>): δ 7.45–7.37 (m, 9H, DPPF), 7.32–7.27 (m, 8H, DPPF), 7.27–7.17 (m, 3H, DPPF), 6.94–6.82 (m, 2H, Pd-*Ar*), 6.76–6.65 (m, 2H, Pd-*Ar*), 6.57 (d, 2H, *J* = 7.0 Hz, Pd-*Ar*), 6.37 (d, 2H, *J* = 7.5 Hz, Pd-*Ar*), 4.27 (b, 2H, Cp-H), 4.17–4.15 (m, 6H, Cp-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, toluene): δ 15.98 (d, *J*<sub>PP</sub> = 15 Hz, *J*<sub>PP'</sub> = 1770 Hz), 15.07 (d, *J*<sub>PP</sub> = 17 Hz, *J*<sub>PP'</sub> = 1830 Hz). Anal. Calcd for C<sub>47</sub>H<sub>36</sub>ClF<sub>3</sub>FeP<sub>2</sub>: C, 56.11; H, 3.61. Found: C, 56.04; H, 3.35.

**General Procedure for the Synthesis of Unsymmetrical Bis-Aryl Platinum Complexes of the Type (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>) (2a, 3a, 5a,b) via Route B (Scheme 2).** (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)-Cl was taken in a screw-capped vial. A stir bar was added, followed by 5 mL of benzene. DPPF (1.1 equiv) was added, and the reaction mixture was refluxed for 30 min to afford (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)Cl. Yellow powder was washed with ether. In a drybox, (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-R)Cl was taken in a 100 mL round-bottom flask. A stir bar was added, followed by 20 mL of toluene. Grignard reagent (4-NMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>MgBr) (1.1 equiv) was added, and the reaction mixture was allowed to stir for 2 h at room temperature. The reaction mixture was concentrated to one-third of the initial volume and then filtered through a 1 cm pad of Celite and a 2 cm pad of decolorizing charcoal. The filtrate obtained was layered with pentane and stored overnight in a freezer (–35 °C). Yellow precipitate of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-X)(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>) was obtained. The solvent was decanted, and the product was dried under reduced pressure.

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>) (2a).** DPPF (0.201 g, 0.362 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)Cl (0.140 g, 0.326 mmol) in 5 mL of refluxing benzene gave 0.249 g (92%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)Cl. 4-NMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>MgBr (0.44 mL, 0.22 mmol) and

(DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)Cl (0.168 g, 0.195 mmol) in 20 mL of toluene gave 0.112 g (62%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, C<sub>7</sub>D<sub>8</sub>): δ 7.41–7.35 (m, 8H, DPPF), 7.29–7.25 (m, 4H, DPPF), 7.20–7.15 (m, 8H, DPPF), 6.73–6.56 (b, 4H, Pd-*Ar*), 6.23–6.21 (m, 2H, Pd-*Ar*), 6.07–6.05 (m, 2H, Pd-*Ar*), 4.22–4.21 (m, 4H, Cp-H), 4.14–4.13 (m, 4H, Cp-H), 3.44 (s, 3H, OMe-H), 1.87 (s, 3H, Me-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, toluene): δ 16.15 (d, *J*<sub>PP</sub> = 14 Hz, *J*<sub>PP'</sub> = 1782 Hz), 15.21 (d, *J*<sub>PP</sub> = 14 Hz, *J*<sub>PP'</sub> = 1750 Hz).

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>) (3a).** DPPF (0.299 g, 0.539 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)Cl (0.219 g, 0.491 mmol) in 5 mL of refluxing benzene gave 0.376 g (90%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)Cl. 4-NMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>MgBr (0.66 mL, 0.33 mmol) and (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)Cl (0.255 g, 0.290 mmol) in 20 mL of toluene gave 0.152 g (55%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, C<sub>7</sub>D<sub>8</sub>): δ 7.45–7.41 (m, 8H, DPPF), 7.27–7.24 (m, 5H, DPPF), 7.20–7.17 (m, 7H, DPPF), 6.75–6.52 (m, 4H, Pd-*Ar*), 6.07–6.00 (m, 4H, Pd-*Ar*), 4.22–4.21 (m, 4H, Cp-H), 4.13 (b, 4H, Cp-H), 3.45 (s, 3H, OMe-H), 2.52 (s, 6H, NMe<sub>2</sub>-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, toluene): δ 15.26 (s, *J*<sub>PP</sub> = 1786 Hz).

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>5</sub>)(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>) (5a).** (COD)(C<sub>6</sub>H<sub>5</sub>)-Cl (0.186 g, 0.447 mmol) and DPPF (0.248 g, 0.45 mmol) in 5 mL of refluxing benzene gave 0.359 g (93%) of (DPPF)Pt(C<sub>6</sub>H<sub>5</sub>)Cl. 4-NMe<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>MgBr (0.50 mL, 0.25 mmol) and (DPPF)Pt(C<sub>6</sub>H<sub>5</sub>)Cl (0.196 g, 0.231 mmol) in 20 mL of toluene gave 0.146 g (68%) of (DPPF)Pt(C<sub>6</sub>H<sub>5</sub>)(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, C<sub>7</sub>D<sub>8</sub>): δ 7.59–7.58 (m, 9H, DPPF), 7.32–7.29 (m, 1H, DPPF), 7.14–7.10 (m, 2H, DPPF), 6.94–6.88 (m, 13H, DPPF and Pd-*Ar*), 6.67–6.64 (m, 2H, Pd-*Ar*), 6.50–6.47 (m, 1H, Pd-*Ar*), 6.25 (d, 2H, *J* = 6.8 Hz, Pd-*Ar*), 4.25 (b, 4H, Cp-H), 3.71 (b, 4H, Cp-H), 2.24 (b, 6H, NMe<sub>2</sub>-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, toluene): δ 16.15 (d, *J*<sub>PP</sub> = 14 Hz, *J*<sub>PP'</sub> = 1782 Hz), 15.21 (d, *J*<sub>PP</sub> = 14 Hz, *J*<sub>PP'</sub> = 1782 Hz).

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-Cl)(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>) (5b).** (COD)-Pt(C<sub>6</sub>H<sub>4</sub>-4-Cl)Cl (0.232 g, 0.515 mmol) and DPPF (0.314 g, 0.566 mmol) in 5 mL of refluxing toluene gave 0.462 g (87%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-Cl)Cl. 4-NMe<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>MgBr (0.30 mL, 0.15 mmol) and (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-Cl)Cl (0.108 g, 0.122 mmol) in 20 mL of toluene gave 0.079 g (71%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-Cl)(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, C<sub>7</sub>D<sub>8</sub>): δ 7.62–7.59 (m, 9H, DPPF), 7.17–6.98 (m, 15H, DPPF and Pd-*Ar*), 6.66–6.64 (m, 2H, Pd-*Ar*), 6.32 (b, 2H, Pd-*Ar*), 4.32–4.30 (m, 4H, Cp-H), 3.85 (b, 4H, Cp-H), 2.31 (b, 6H, NMe<sub>2</sub>-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, toluene): δ 15.98 (d, *J*<sub>PP</sub> = 14 Hz, *J*<sub>PP'</sub> = 1764 Hz), 15.03 (d, *J*<sub>PP</sub> = 14 Hz, *J*<sub>PP'</sub> = 1820 Hz).

**Synthesis of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>) (4c) (Scheme 3).** In a drybox, (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)Cl (0.447 g, 0.100 mmol) was taken in a 100 mL round-bottom flask. A stir bar was added, followed by addition of 30 mL of ether and 4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>MgBr (0.40 mL, 0.12 mmol), and the mixture was stirred at room temperature for 12 h. The reaction mixture was brought outside the glovebox, and saturated aqueous NH<sub>4</sub>Cl (20 mL) was added. The ether layer was separated, and the water layer was extracted with ether. The combined ether extracts were dried over anhydrous MgSO<sub>4</sub> and filtered through a 1 cm pad of Celite and a 2 cm pad of decolorizing carbon. Ether was removed from the filtrate under reduced pressure. The white solid obtained was recrystallized from a mixture of dichloromethane and pentane to give 0.399 g (72%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>). (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>) (0.205 g, 0.369 mmol) was taken in a screw-capped vial, and a stir bar was added, followed by addition of a mixture of 5 mL of dichloromethane and 5 mL of methanol. CH<sub>3</sub>COCl (26 μL, 0.37 mmol) was added, and the reaction mixture was stirred for 5 min. The solvent was evaporated under reduced pressure, and the white solid obtained was recrystallized from a mixture of dichloromethane and pentane to give 0.167 g (94%) of (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)Cl. DPPF (0.150 g, 0.271 mmol) and (COD)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)Cl (0.119 g, 0.246 mmol) were taken in a screw-capped vial. A stir bar was added, followed by the addition of 10 mL of benzene. The reaction mixture was stirred for 30 min in refluxing benzene. The solvent was

removed under reduced pressure, and the yellow solid obtained was washed with ether to give 0.199 g (87%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)Cl. In a drybox, (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)Cl (0.101 g, 0.109 mmol) was taken in a screw-capped vial. A stir bar was added, followed by addition of 15 mL of toluene. The reaction mixture was stirred at room temperature for 2 h. The solvent was reduced to one-third of the initial volume under reduced pressure and layered with 5 mL of pentane. The reaction mixture was stored overnight at -35 °C to give yellow crystals. The solvent was decanted, and the crystals were dried under reduced pressure to give 0.038 g (35%) of (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CF<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, C<sub>7</sub>D<sub>8</sub>): δ 7.64–7.55 (m, 9H, DPPF), 7.32–7.29 (m, 15H, DPPF and Pd-*Ar*), 7.13–6.97 (m, 2H, *J* = 8.0 Hz, Pd-*Ar*), 6.26 (b, 2H, Pd-*Ar*), 4.37 (s, 2H, Cp-H), 4.27–4.26 (m, 2H, Cp-H), 3.86 (m, 2H, Cp-H), 3.83 (m, 2H, Cp-H), 2.39 (s, 6H, NMe<sub>2</sub>-H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, toluene): δ 16.71 (d, *J*<sub>PP</sub> = 12 Hz, *J*<sub>PtP</sub> = 1798 Hz), 14.48 (d, *J*<sub>PP</sub> = 12 Hz, *J*<sub>PtP</sub> = 1826 Hz).

**Determination of the Rate Constants (*k*<sub>obs</sub>) for the Reductive Elimination of Biaryls from Bis-Aryl Platinum Complexes.** Bis-aryl platinum complexes (**1a–f**, **2a–f**, **3a–e**, **4a–c**, **5a,b**) (9.23 × 10<sup>-6</sup> mol), PPh<sub>3</sub> (9.23 × 10<sup>-5</sup> mol), and 1,3,5-trimethoxybenzene (6.4 × 10<sup>-5</sup> mol, internal standard) were dissolved in toluene-*d*<sub>8</sub> (0.8 mL) in

a screw-capped NMR tube. The NMR tube was added to a preheated probe at 95 °C. The temperature in the probe cavity was measured by inserting a copper thermocouple into an NMR tube containing toluene in the probe.<sup>63</sup> Decay of the biaryl platinum complexes was monitored by <sup>1</sup>H NMR and spectroscopy and <sup>19</sup>F NMR spectroscopy (**1f**, **4a,b**) over at least three half-lives. Kinetic data were fit to the expression  $y = m_1 + m_2 \exp^{-kt}$ , in which *k* is the first-order rate constant *k*<sub>obs</sub>.

**Acknowledgment.** We thank Dr. Timothy Boller for useful discussions on the interpretation of the rates of reductive elimination.

**Supporting Information Available:** <sup>1</sup>H and <sup>31</sup>P NMR spectra of complexes of the type (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-NMe<sub>2</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X), and Hammett plots for the rates of reductive elimination from (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-OMe)(C<sub>6</sub>H<sub>4</sub>-4-X) and (DPPF)Pt(C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>-4-X). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0480365

(63) Bornais, J.; Brownstein, S. *J. Magn. Reson.* **1978**, *29*, 207–211.