

# Platinum(II)-Catalyzed Ethylene Hydrophenylation: Switching Selectivity between Alkyl- and Vinylbenzene Production

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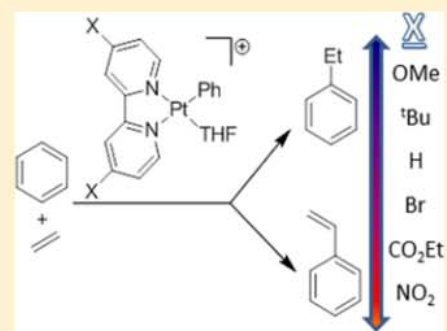
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## Supporting Information

**ABSTRACT:** The series of Pt<sup>II</sup> complexes [(<sup>x</sup>bpy)Pt(Ph)(THF)][BAR'<sub>4</sub>] (<sup>x</sup>bpy = 4,4'-X-2,2'-bipyridyl, X = OMe, <sup>t</sup>Bu, H, Br, CO<sub>2</sub>Et, NO<sub>2</sub>; Ar' = 3,5-bis(trifluoromethyl)phenyl) are catalyst precursors for ethylene hydrophenylation. The bipyridyl substituent provides a tunable switch for catalyst selectivity that also has significant influence on catalyst activity and longevity. Less electron donating 4,4'-substituents increase the propensity toward styrene formation over ethylbenzene.



## INTRODUCTION

The formation of C–C bonds with aromatic substrates has received considerable attention due to its importance in both fine and commodity chemical production.<sup>1</sup> While methods for the functionalization of aromatic C–X bonds (X = halide, triflate) have been successfully developed,<sup>1b,2</sup> atom-economical catalytic olefin hydroarylation (i.e., the addition of aromatic C–H bonds across olefin C=C bonds) offers potential advantages.<sup>1d,3</sup> For example, halogenation of aromatic substrates can generate substantial waste and reduce the overall yield of desired products. In addition, the conversion of aromatic C–X bonds to C–C bonds generally requires stoichiometric organometallic reagents (e.g., Grignard, tin, boron, etc.). Thus, the efficient direct functionalization of aromatic C–H bonds would reduce the generation of waste, especially that of halogenated and metal-containing byproducts. Given the substantial efforts to control the stereochemistry of olefin insertions (e.g., asymmetric olefin hydrogenation<sup>4</sup> or olefin polymerization<sup>5</sup>), extension of catalytic olefin hydroarylation to enantioselective variants is a reasonable proposal. Despite these potential advantages, examples of catalysts for the hydroarylation of olefins by a non-acid-catalyzed (i.e., non-Friedel–Crafts) pathway are relatively rare,<sup>3,6</sup> and catalysts for unactivated substrates, such as benzene with unfunctionalized olefins, are especially limited.<sup>3,6b,7</sup> In addition, the oxidative coupling of aromatic C–H bonds with alkenes to form vinyl arenes has typically been restricted to activated olefins.<sup>1d,6c,8</sup>

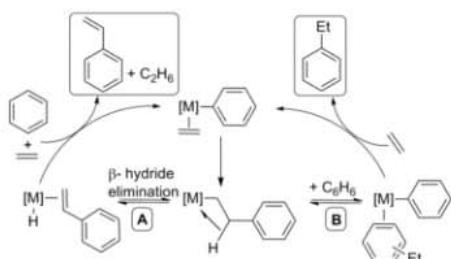
The development of selective catalysts for olefin hydroarylation presents several challenges, such as regioselective C–H activation of substituted aromatic substrates, selectivity for olefin insertion (e.g., 1,2- versus 2,1-insertion), selectivity for mono- versus polyalkylation (starting from unsaturated aromatic substrates), and selectivity for alkyl- versus vinyl arene production. Despite these obstacles, few detailed structure/activity studies that could guide new catalyst design exist.<sup>6b,7c,9</sup> In order to design improved catalysts, it is important to understand how modifications to the transition-metal complex influence the various facets of selectivity. In some cases, saturated alkyl arenes are desired while vinyl arenes are preferred for other applications. For transition-metal-catalyzed olefin hydroarylation, the selectivity for vinyl arene (pathway A) versus alkyl arene (pathway B) formation is presumably controlled by the relative kinetics of the steps shown in Scheme 1, and understanding how to use ligand modification to switch catalyst selectivity is a potentially important feature.

Recently, we reported a mechanistic study of ethylene hydrophenylation catalyzed by cationic Pt<sup>II</sup> supported by 4,4'-di-*tert*-butyl-2,2'-bipyridine.<sup>7c</sup> The bipyridyl ligand is easily modified to determine the impact of ligand donor ability on catalysis without altering the catalyst's steric profile. Herein, we report the influence of 4,4'-substituents on catalytic hydrophenylation of ethylene for the series of complexes [(<sup>x</sup>bpy)Pt-

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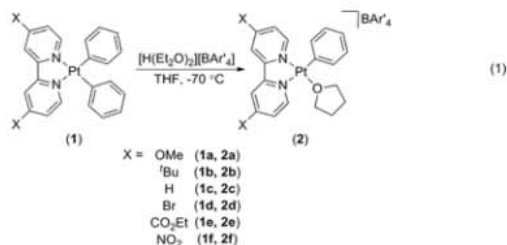
**Scheme 1. Likely Control of the Selectivity of Alkyl Arenes versus Vinyl Arenes (Ethylbenzene versus Styrene in this Scheme) during Catalytic Ethylene Hydrophenylation by the Relative Kinetics of Divergent Pathways that Follow Olefin Insertion**



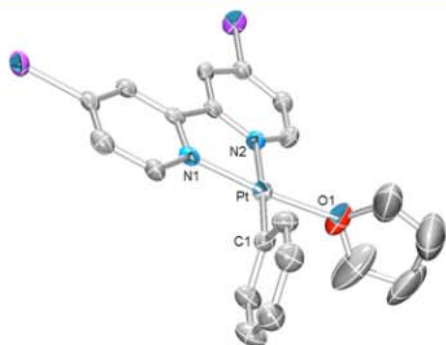
(Ph)(THF)[Pt(Ph)(THF)](BAR'<sub>4</sub>) (<sup>α</sup>bpy = 4,4'-X-2,2'-bipyridyl, X = OMe, <sup>t</sup>Bu, H, Br, CO<sub>2</sub>Et, NO<sub>2</sub>; Ar' = 3,5-bis(trifluoromethyl)phenyl). Of particular note is the ability to control alkyl- to vinyl arene ratios by adjusting the donor ability of the bipyridyl ligand. Controlling alkyl- versus vinyl arene production is important for achieving desired product selectivity. Moreover, the formation of vinyl arenes likely involves β-hydride elimination, which is a plausible decomposition route for some catalysts that mediate alkyl arene synthesis.

## RESULTS AND DISCUSSION

The complexes [(<sup>α</sup>bpy)Pt(Ph)(THF)](BAR'<sub>4</sub>) (2a–f) were prepared according to the procedure previously reported for [(<sup>β</sup>bpy)Pt(Ph)(THF)](BAR'<sub>4</sub>) (2b; <sup>β</sup>bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridyl) (eq 1).<sup>7c</sup> All complexes 2 have been isolated in



≥80% yield and characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy as well as elemental analysis. A crystal of complex 2d suitable for an X-ray diffraction study was grown (Figure 1).

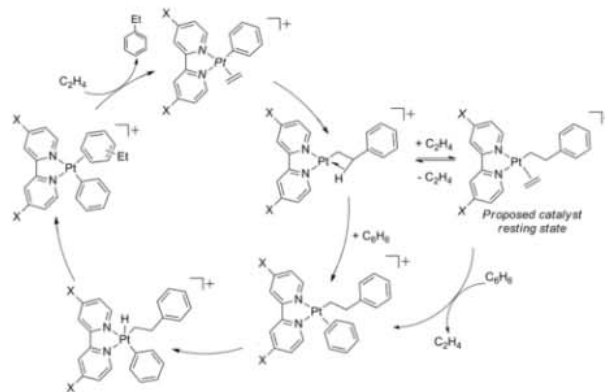


**Figure 1.** ORTEP drawing of [(<sup>β</sup>bpy)Pt(Ph)(THF)](BAR'<sub>4</sub>) (2d) (30% probability; H atoms and BAR'<sub>4</sub> anion omitted for clarity). Selected bond lengths (Å): Pt–N1 = 1.998(6), Pt–N2 = 2.075(6), Pt–O1 = 2.060(7), Pt–C1 = 2.014(8). Selected bond angles (deg): N1–Pt–N2 = 79.4(2), C1–Pt–O1 = 89.4(3).

The N1–Pt–N2 bond angle is compressed to 79.4(2)° relative to the ideal 90° bond angles for a square-planar complex, which is characteristic of Pt<sup>II</sup> bipyridyl and diimine complexes.<sup>10</sup> The Pt–N1 bond is 0.08 Å shorter than the Pt–N2 bond, indicative of a greater *trans* influence of the phenyl ligand relative to THF. Significant disorder exists for the THF ligand in the refined structure.

The proposed mechanism for Pt<sup>II</sup>-catalyzed ethylene hydrophenylation on the basis of previous experimental and computational studies<sup>7c</sup> is shown in Scheme 2. Catalytic

**Scheme 2. Proposed Mechanism for Ethylene Hydrophenylation Catalyzed by Cationic Pt<sup>II</sup> Complexes Supported by Bipyridyl Ligands**



ethylene hydrophenylation using complexes 2a–f was probed by heating benzene solutions of 2 (0.01 mol %) at 100 °C with 0.1 MPa of ethylene. The results are summarized in Table 1. Plots of turnovers (TO) versus time for 2a–c reveal no evidence of catalyst deactivation after 4 h (Figure 2). Thus, the

**Table 1.** Catalytic Ethylene Hydrophenylation using Complexes 2a–f with 0.1 MPa of Ethylene<sup>a</sup>

X	σ <sub>p</sub>	Et	Et	Et	<i>o</i> : <i>m</i> : <i>p</i> <sup>b</sup>	TOF <sup>c</sup> (10 <sup>4</sup> s <sup>-1</sup> )
OMe (2a)	-0.27	6.8 <sup>d</sup> (27.9) <sup>e</sup> [78.0] <sup>f</sup>	0.2 (0.3) [1.9]	1.5 (10.7) [23.7]	1:2.5:2.0	5.9
<sup>t</sup> Bu <sup>g</sup> (2b)	-0.2	15.7 (52.7) [63.9]	0.6 (1.0) [1.6]	3.6 (10.8) [18.8]	1:2.6:1.6	13.8
H (2c)	0.0	17.2 (47.1) [93.6]	0.8 (1.4) [3.6]	4.1 (10.9) [29.4]	1:2.6:1.5	15.3
Br (2d)	0.23	0.9 (2.7) [6.7]	1.4 (3.9) [7.5]	0 (0) [1.1]	–	1.6
CO <sub>2</sub> Et (2e)	0.45	5.3 (13.3) [46.2]	1.0 (3.5) [6.2]	1.3 (2.9) [11.3]	1:1.4:1.3	5.3
NO <sub>2</sub> (2f)	0.78	0.1 (0.2) [0.2]	1.0 (1.1) [1.1]	0 (0) [0]	–	–

<sup>a</sup>Conditions: 0.01 mol % catalyst dissolved in C<sub>6</sub>H<sub>6</sub> with hexamethylbenzene as an internal standard at 100 °C with 0.1 MPa of ethylene. <sup>b</sup>Ratio of 1,2-, 1,3-, and 1,4-diethylbenzene after 4 h. <sup>c</sup>Turnover frequency calculated on the basis of total turnovers after 4 h. <sup>d</sup>Turnovers after 4 h as determined by GC/MS. <sup>e</sup>Numbers in parentheses are turnovers after 16 h. <sup>f</sup>Numbers in brackets are TON values after catalyst deactivation. <sup>g</sup>Reference 7c

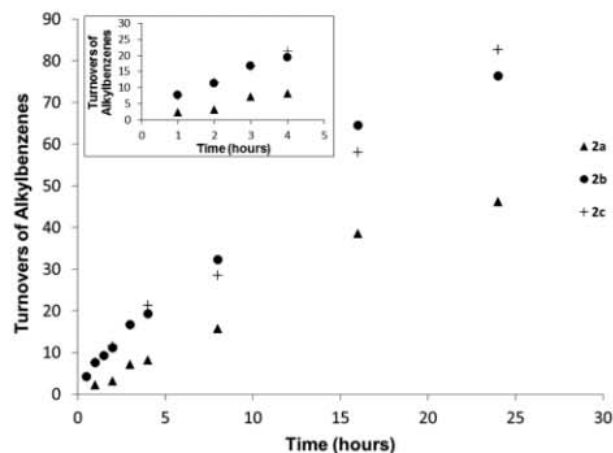


Figure 2. Plot of ethylbenzene and diethylbenzene TO values as a function of time for ethylene hydrophenylation catalyzed by complexes **2a–c** at 100 °C with 0.1 MPa of ethylene pressure.

TO after 4 h for these catalysts should reasonably reflect relative catalyst activities. For complexes **2a–c**, the relative rates of catalysis (based on total product formation after 4 h) are OMe (turnover frequency (TOF)  $5.9 \times 10^{-4} \text{ s}^{-1}$ ) < <sup>t</sup>Bu (TOF:  $13.8 \times 10^{-4} \text{ s}^{-1}$ ) < H (TOF  $15.3 \times 10^{-4} \text{ s}^{-1}$ ), which is consistent with less donating 4,4'-substituents providing a slight rate enhancement. Results with catalyst precursors **2d–f**, which possess less donating 4,4'-substituents than catalyst precursors **2a–c**, indicate less effective catalysis. Complex **2d** provides only 2.3 total TO, with more styrene than ethylbenzene, after 4 h, but a plot of TO versus time for **2d** reveals no signs of catalyst deactivation after 4 h (Figure 3). Although catalysis with **2e** is

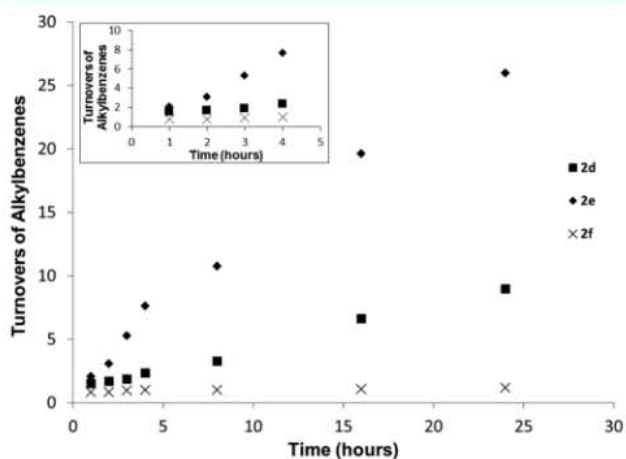


Figure 3. Plot of ethylbenzene and diethylbenzene TO values as a function of time for ethylene hydrophenylation catalyzed by complexes **2d–f** at 100 °C with 0.1 MPa of ethylene pressure.

more efficient than that with **2d**, it also performs less effectively than complexes **2a–c** with no evidence of substantial deactivation after 24 h. The nitro complex **2f** provides slightly more than 1 TO and undergoes relatively rapid deactivation to multiple intractable complexes within approximately 1 h.

The ratio of ethylbenzene to styrene is influenced by the donor ability of the 4,4'-bipyridyl functional groups. For example, catalysis using complex **2a** (OMe,  $\sigma_p = -0.27$ ) and 0.1 MPa of ethylene (100 °C) results in an ethylbenzene/styrene

ratio of 27.8 (after 4 h), in comparison to 0.1 for complex **2f** ( $\text{NO}_2$ ,  $\sigma_p = 0.78$ ). A Hammett plot was constructed using product ratios and the Hammett parameter  $\sigma_p$  (Figure 4).<sup>11</sup>

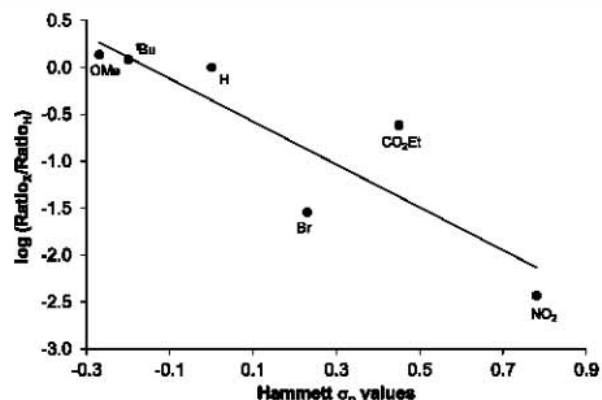


Figure 4. Hammett plot for the ratios of ethylbenzene to styrene from  $[(^*bpy)Pt(Ph)(THF)]^+$ -catalyzed ethylene hydrophenylation after 4 h at 100 °C with 0.1 MPa of ethylene (slope  $-2.3$ ,  $R^2 = 0.77$ ).

The effects of substituted pyridyl ligands are rarely amenable to Hammett correlations, since Hammett  $\sigma_p$  parameters do not accurately reflect substituent effects upon the basicity of pyridine, as the inductive and resonance interactions of the substituents differ from those found in benzoic acids.<sup>12</sup> In addition,  $\pi$  interactions with the metal center influence the correlation.<sup>12</sup> Thus, it is not surprising that the fit of the Hammett plot is not good ( $R^2 = 0.77$ ). However, the plot demonstrates that less donating 4,4'-substituents result in a decrease in the ratio of ethylbenzene to styrene. Using Hammett  $\sigma_p$  parameters as a relative gauge of substituted bipyridyl donation to  $Pt^{II}$ , plots of ethylbenzene to styrene ratio versus substituent Hammett parameters further demonstrate this trend (Figure 5). Complex **2d** (Br,  $\sigma_p = 0.23$ ) exhibits an ethylbenzene/styrene ratio similar to that of **2f** and falls outside of the observed linear trend shown in Figure 5. The deviation of **2d** from the remaining five catalysts is not currently understood.

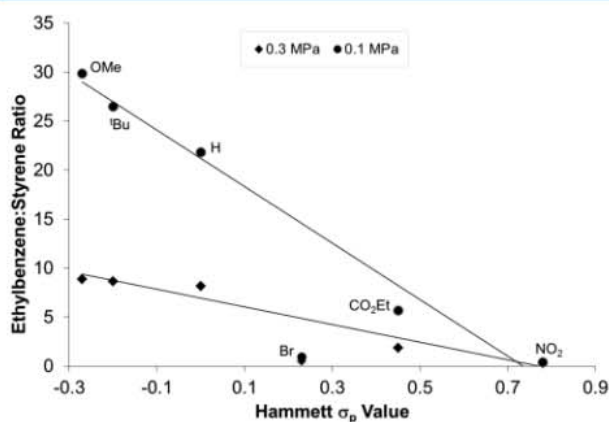


Figure 5. Ethylbenzene/styrene ratios from  $[(^*bpy)Pt(Ph)(THF)]^+$ -catalyzed ethylene hydrophenylation after 4 h at 100 °C with 0.1 and 0.3 MPa of ethylene versus Hammett parameters ( $\sigma_p$ ) for the 4,4'-substituent. Complex **2d** (X = Br) is not included in either linear fit (0.1 MPa,  $R^2 = 0.98$ ; 0.3 MPa,  $R^2 = 0.96$ ).

We sought to determine if ethylene concentration would influence ethylbenzene/styrene ratios. Catalysis performed under the conditions outlined above but with 0.3 MPa of ethylene results in decreased catalytic activity (Table 2), as

**Table 2. Catalytic Ethylene Hydrophenylation using Complexes 2a–f with 0.3 MPa of Ethylene<sup>a</sup>**

X	$\sigma_p$	$\sigma_p$	Et	Et	<i>o:m:p</i> <sup>b</sup>	TOF <sup>c</sup> (10 <sup>-4</sup> s <sup>-1</sup> )
OMe (2a)	-0.27	3.3 <sup>d</sup> (10.0) <sup>e</sup>	0.4 (0.6)	0.7 (2.7)	1:0.6:1.1	3.1
<sup>t</sup> Bu <sup>f</sup> (2b)	-0.2	4.0 (8.4)	0.5 (0.6)	0.9 (1.8)	1:1:1	3.8
H (2c)	0.0	5.5 (19.9)	0.7 (1.4)	1.4 (5.2)	1:1:1	5.3
Br (2d)	0.23	0.2 (0.4)	1.3 (2.1)	0 (0)	–	1.0
CO <sub>2</sub> Et (2e)	0.45	1.9 (3.5)	1.2 (3.2)	0.5 (0.7)	1:0.6:1.1	2.5
NO <sub>2</sub> (2f)	0.78	0 (0.1)	1.0 (1.1)	0 (0)	–	–

<sup>a</sup>Conditions: 0.01 mol % catalyst dissolved in C<sub>6</sub>H<sub>6</sub> with hexamethylbenzene as an internal standard at 100 °C with 0.3 MPa of ethylene. <sup>b</sup>Ratio of 1,2-, 1,3-, and 1,4-diethylbenzene after 4 h. <sup>c</sup>Turnover frequency calculated on the basis of total turnovers after 4 h. <sup>d</sup>Turnovers after 4 h as determined by GC/MS. <sup>e</sup>Numbers in parentheses are turnovers after 16 h. <sup>f</sup>Reference 7c.

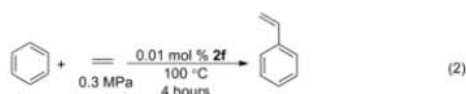
previously reported for 2b.<sup>7c</sup> Two observations relevant to styrene/ethylbenzene production are made. First, for all complexes, the ethylbenzene/styrene ratio decreases at higher ethylene pressure (Table 3). Second, similar to reactions at 0.1

**Table 3. Ratio of Ethylbenzene to Styrene as a Function of Ethylene Pressure**

X	$\sigma_p$	Ethylbenzene to Styrene Ratio	
		0.1 MPa	0.3 MPa
OMe (2a)	-0.27	29.6 <sup>a</sup>	8.6 <sup>b</sup>
<sup>t</sup> Bu <sup>c</sup> (2b)	-0.2	26.2	8.3
H (2c)	0.0	21.5	7.8
Br (2d)	0.23	0.6	0.2
CO <sub>2</sub> Et (2e)	0.45	5.3	1.6
NO <sub>2</sub> (2f)	0.78	0.1	0.0 <sup>d</sup>

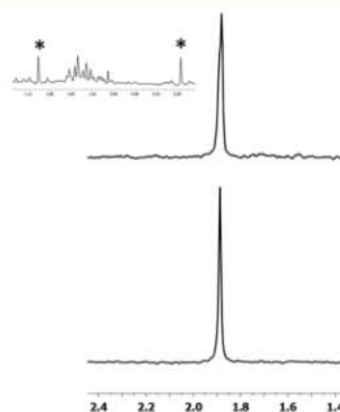
<sup>a</sup>Ethylbenzene/styrene ratio after 4 h at 100 °C. <sup>b</sup>Ratio after 4 h with 0.3 MPa of ethylene at 100 °C. <sup>c</sup>Reference 7c. <sup>d</sup>Only styrene observed.

MPa of ethylene, decreasing the donor ability of the 4,4'-substituents results in a decrease in the ethylbenzene/styrene ratio (Figure 3). Again, complex 2d deviates from the observed linear correlation of ethylbenzene/styrene ratio versus Hammett  $\sigma_p$  value. At 0.3 MPa, complex 2f gives exclusive formation of styrene after 4 h (eq 2). The dependence of

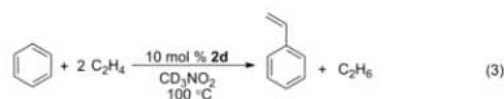


ethylbenzene/styrene ratios for all catalyst precursors on ethylene concentration is consistent with the possibility that the rate of styrene displacement by ethylene is a key factor in the ethylbenzene/styrene ratios (see below).

Complexes 2d,e produce >1.0 TO of styrene. For example, at 0.1 MPa of ethylene, complex 2d produces a TON of 7.5 for styrene after 4 days at 100 °C. The production of  $\geq 1$  equiv (relative to Pt) of styrene requires a hydrogen acceptor. Heating a CD<sub>3</sub>NO<sub>2</sub> solution of complex 2d and benzene under ethylene results in the formation of styrene and ethane, as observed by <sup>1</sup>H NMR spectroscopy. Confirmation of ethane formation was achieved using isotopically labeled <sup>13</sup>C<sub>2</sub>H<sub>4</sub>. In the <sup>1</sup>H and <sup>13</sup>C NMR spectra, ethane is clearly observed and identified using a comparison to an analytically pure standard (Figure 6). Therefore, the observed catalytic oxidative hydrophenylation of ethylene by 2d uses ethylene as the oxidant (eq 3).



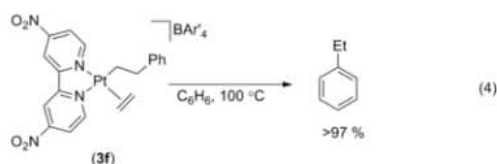
**Figure 6.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (top) and <sup>1</sup>H NMR spectrum (top inset, <sup>1</sup>J<sub>CH</sub> = 120 Hz) of <sup>13</sup>C<sub>2</sub>H<sub>6</sub> in CD<sub>3</sub>NO<sub>2</sub> resulting from the formation of styrene by complex 2d and benzene under <sup>13</sup>C<sub>2</sub>H<sub>4</sub> pressure and the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (bottom) of an analytically pure sample of C<sub>2</sub>H<sub>6</sub> in a CD<sub>3</sub>NO<sub>2</sub>/benzene solution.



The complex [(<sup>t</sup>bpy)Pt(CH<sub>2</sub>CH<sub>2</sub>Ph)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)]<sup>+</sup> (3b) has been shown to be the catalyst resting state using 2b as the catalyst precursor.<sup>7c</sup> Catalysis using 2a–f was monitored by <sup>1</sup>H NMR at 90 °C over 4 h to confirm that [(<sup>t</sup>bpy)Pt-(CH<sub>2</sub>CH<sub>2</sub>Ph)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)]<sup>+</sup> is the resting state for each <sup>t</sup>bpy ligand. This species is observed as the catalyst resting state using complexes 2a–e. Note that for complexes 2d,e the insertion product [(<sup>t</sup>bpy)Pt(CH<sub>2</sub>CH<sub>2</sub>Ph)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)]<sup>+</sup> is observed but is slowly consumed as the complexes [(<sup>t</sup>bpy)Pt-(Et)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)]<sup>+</sup> are formed, as a result of  $\beta$ -hydride elimination and styrene displacement. The Pt<sup>II</sup> ethyl complexes [(<sup>t</sup>bpy)Pt(Et)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)]<sup>+</sup> [X = Br (2d), CO<sub>2</sub>Et (2e)] eventually decompose. Consistent with the observation of  $\sim 1$  TO under catalytic conditions (see above), complex 3f is unstable and is consumed within minutes to yield stoichiometric equivalents of ethylbenzene and styrene as well as multiple Pt decomposition products.

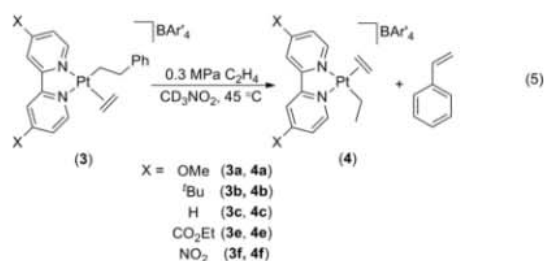
Previously, we reported that heating [(<sup>t</sup>bpy)Pt(CH<sub>2</sub>CH<sub>2</sub>Ph)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)]<sup>+</sup> under ethylene pressure in CD<sub>3</sub>NO<sub>2</sub> results in stoichiometric styrene production as well as the formation of [(<sup>t</sup>bpy)Pt(C<sub>2</sub>H<sub>5</sub>)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)]<sup>+</sup>.<sup>7c</sup> Styrene formation is not observed in the absence of excess ethylene. For example, the thermolysis (100 °C) of 3f in benzene results in the formation

of ethylbenzene in quantitative yield (eq 4). Thus, for complex **3f** the formation of styrene is dependent on the presence of



ethylene, which indicates that ethylene plays a role in the formation of free styrene and is consistent with the trends in ethylbenzene/styrene ratios as a function of ethylene pressure (see above). Therefore, it is likely that release of styrene occurs via an associative ligand exchange with ethylene.

The rates of stoichiometric styrene production from the thermolysis (45 °C) of  $[(^{\text{X}}\text{bpy})\text{Pt}(\text{CH}_2\text{CH}_2\text{Ph})(\eta^2\text{-C}_2\text{H}_4)]^+$  ( $\text{X} = \text{OMe}$  (**3a**),  $^t\text{Bu}$  (**3b**),  $\text{H}$  (**3c**),  $\text{CO}_2\text{Et}$  (**3e**),  $\text{NO}_2$  (**3f**); eq 5)

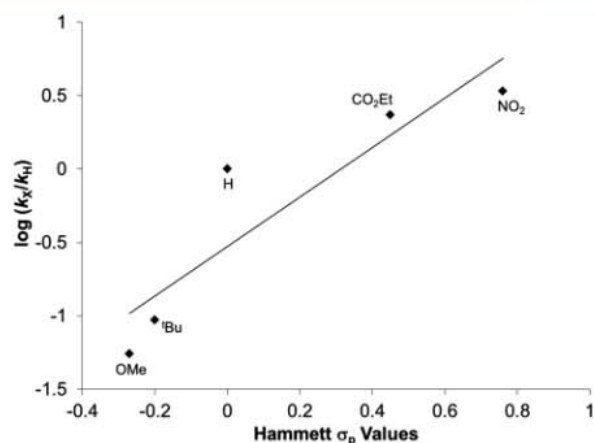


**Table 4.** Observed Rate Constants for Stoichiometric Styrene Production from Complexes **3a–3f**<sup>a</sup>

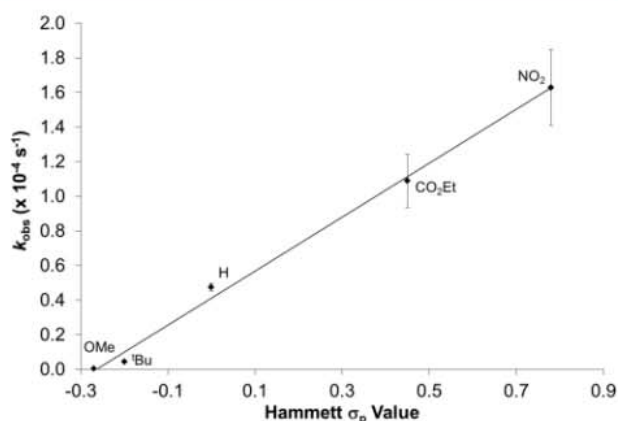
X	$\sigma_p$	$k_{\text{obs}}$ ( $\times 10^{-4} \text{ s}^{-1}$ )
OMe ( <b>3a</b> )	-0.27	0.026(2)
$^t\text{Bu}$ ( <b>3b</b> )	-0.2	0.044(3)
H ( <b>3c</b> )	0.0	0.47(2)
$\text{CO}_2\text{Et}$ ( <b>3e</b> )	0.45	1.1(2)
$\text{NO}_2$ ( <b>3f</b> )	0.78	1.6(2)

<sup>a</sup>Determined by  $^1\text{H}$  NMR spectroscopy at 45 °C using hexamethyldisilane as an internal standard.  $[\text{Pt}] = 0.03 \text{ M}$ .

were measured by  $^1\text{H}$  NMR spectroscopy (Table 4). Similar to the Hammett plot for ethylbenzene and styrene ratios, a Hammett plot using the rate constants for styrene formation from **3a–f** (without **3d**) reveals a poor linear correlation ( $R^2 = 0.83$ ; Figure 7). The curvature in the plot might indicate a change in mechanism or rate-determining step; however, given the precedent for poor Hammett correlations for substituted pyridyl groups,<sup>12</sup> it is difficult to interpret the plot definitively. Despite the poor linear correlation, the identity of the 4,4'-substituent has a clear effect on the rate of styrene evolution (Figure 8). Decreasing the electron donor ability of the 4,4'-substituent results in more rapid styrene production. For example, the formation of styrene from **3a** occurs with a pseudo-first-order rate constant of  $[2.6(2)] \times 10^{-6} \text{ s}^{-1}$  with 0.3



**Figure 7.** Hammett plot for styrene formation from  $[(^{\text{X}}\text{bpy})\text{Pt}(\text{CH}_2\text{CH}_2\text{Ph})(\eta^2\text{-C}_2\text{H}_4)]^+$  at 45 °C with 0.3 MPa of ethylene ( $R^2 = 0.83$ , slope 1.7).



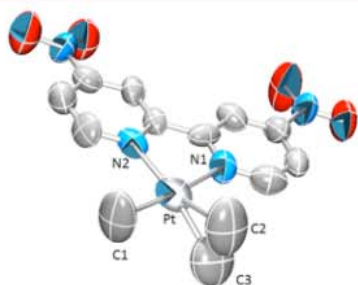
**Figure 8.** Plot of pseudo-first-order rate constants ( $k_{\text{obs}}$ ) for styrene formation from  $[(^{\text{X}}\text{bpy})\text{Pt}(\text{CH}_2\text{CH}_2\text{Ph})(\eta^2\text{-C}_2\text{H}_4)]^+$  at 45 °C with 0.3 MPa of ethylene versus Hammett  $\sigma_p$  parameter of the 4,4'-bipyridyl functionality ( $R^2 = 0.99$ ).

M ethylene at 45 °C. In contrast, complex **3f** produces styrene  $\sim 60$  times faster with an observed rate constant of  $[1.6(2)] \times 10^{-4} \text{ s}^{-1}$ . The relative rates of styrene formation cannot be directly compared to the results from catalysis, since the conditions used for catalysis and stoichiometric styrene production are different. Also, in addition to the relative rates of styrene formation, the relative rates of ethylbenzene formation play a role in ethylbenzene/styrene ratios. However, it can be stated definitively that the trend in the rates of stoichiometric styrene production from the five complexes  $[(^{\text{X}}\text{bpy})\text{Pt}(\text{CH}_2\text{CH}_2\text{Ph})(\eta^2\text{-C}_2\text{H}_4)]^+$  (**3a–c,e,f**) is identical with the trend in ethylbenzene/styrene ratios observed during catalysis. Interestingly, the rate of styrene formation from **3d**, which is the complex that deviates from the linear plots in Figure 3, is much faster than that of the other complexes. For example, at room temperature the reaction of **2d** with ethylene is complete within approximately 10 min.

The production of styrene by these  $\text{Pt}^{\text{II}}$  complexes is clearly facilitated by less donating bipyridyl ligands. The formation of styrene from complexes **3** is likely a multistep reaction involving ethylene dissociation,  $\beta$ -hydride elimination, and net dissociation of styrene. Possible explanations for the trends in styrene production include (i) the barrier to the reinsertion of

styrene after  $\beta$ -hydride elimination increases with less donating ligands, (ii) styrene is more readily displaced by ethylene for the Pt complexes with less donating ligands, or (iii) a combination of both effects.

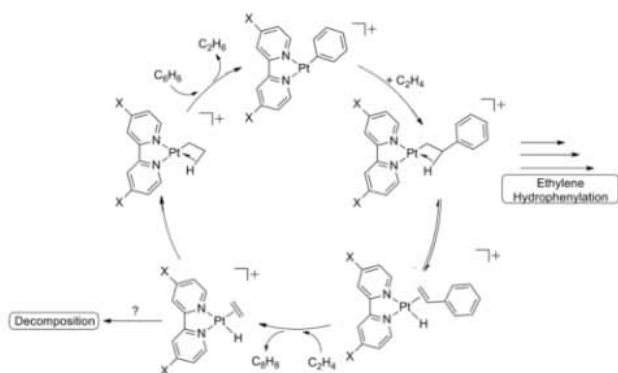
We sought to measure the rate of styrene displacement by ethylene as a function of the 4,4'-substituent using  $[(^x\text{bpy})\text{Pt}(\text{H})(\eta^2\text{-styrene})]^+$  ( $X = \text{}^t\text{Bu}, \text{NO}_2$ ). Attempts to synthesize the  $\text{Pt}^{\text{II}}$  hydride complexes were unsuccessful. Instead, the  $\text{Pt}^{\text{II}}$  methyl complexes  $[(^x\text{bpy})\text{Pt}(\text{Me})(\eta^2\text{-styrene})]^+$  ( $X = \text{}^t\text{Bu}$  (**5b**),  $\text{NO}_2$  (**5f**)) were used as models for the  $\text{Pt}-\text{H}$  variants. Unfortunately, the displacement of styrene by ethylene from both **5b** and **5f** was too rapid for measurement even at  $-120^\circ\text{C}$ . The Pt complexes were dissolved in a solvent mixture of  $\text{CD}_2\text{Cl}_2$ ,  $\text{CDCl}_3$ , and  $\text{CCl}_4$  (60/27/13, v/v/v) and then frozen. The tube was pressurized with 0.3 MPa of ethylene and allowed to thaw in the spectrometer. The first NMR spectrum showed complete conversion to  $[(^x\text{bpy})\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{Me})]^+$  and free styrene. The structure of  $[(^{\text{NO}_2}\text{bpy})\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{Me})]^+$  (**6f**) is shown in Figure 9.



**Figure 9.** ORTEP drawing of  $[(^{\text{NO}_2}\text{bpy})\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{Me})][\text{BAR}'_4]$  (**6f**) (50% probability; H atoms and  $\text{BAR}'_4$  anion omitted for clarity). Selected bond lengths (Å): Pt–N1 = 2.113(7), Pt–N2 = 2.063(6), Pt–C1 = 2.021(9), Pt–C2 = 2.073(13), Pt–C3 = 2.113(12), C2–C3 = 1.349(16). Selected bond angles (deg): N1–Pt–N2 = 77.5(2), N1–Pt–C1 = 173.1(3).

A plausible mechanism for styrene formation is shown in Scheme 3. Ethylene insertion into the  $\text{Pt}-\text{Ph}$  bond results in a  $\beta$ -agostic phenethyl intermediate, which coordinates ethylene to form the catalyst resting state, complex **3**. Complex **3** may either exchange ethylene with benzene and continue along the ethylene hydrophenylation catalytic cycle<sup>7c</sup> or dissociate ethylene and undergo  $\beta$ -hydride elimination to form  $[(^x\text{bpy})\text{Pt}(\text{H})(\eta^2\text{-styrene})]^+$ . Displacement of styrene with ethylene

### Scheme 3. Proposed Mechanism for Styrene Formation during $\text{Pt}^{\text{II}}$ -Catalyzed Ethylene Hydrophenylation



completes the process for styrene formation. For most  $^x\text{bpyPt}$  complexes (excluding **2d,e**), we presume that the  $\text{Pt}^{\text{II}}-\text{H}$  complexes are unstable and result in catalyst decomposition, since only  $\sim 1$  TO of styrene is observed. For  $X = \text{Br}$  (**2d**),  $\text{CO}_2\text{Et}$  (**2e**), ethylene insertion into the  $\text{Pt}-\text{H}$  bond and subsequent benzene  $\text{C}-\text{H}$  activation liberates ethane and regenerates the  $[(^x\text{bpy})\text{Pt}(\text{Ph})]^+$  fragment; however, catalytic production of styrene is not sustained over a long period, as evidenced by the low TON for styrene production (Table 1).

The  $\text{Pt}^{\text{II}}$  catalysts eventually decompose to multiple intractable complexes, and understanding the exact pathway for catalyst deactivation is challenging. However, inspection of the TON values for catalysts **2a-f** (Table 1) shows that complexes **2a-c**, which possess more donating bipyridyl ligands, give higher TON values than **2d-f**. Since complexes **2d-f**, which possess less donating bipyridyl ligands, exhibit a greater predilection for styrene production, one possible explanation for reduced TON for **2d-f** in comparison to **2a-c** is that the  $\text{Pt}^{\text{II}}-\text{H}$  complexes that result from  $\beta$ -hydride elimination (Scheme 3) are unstable and more prone to decomposition.

## SUMMARY AND CONCLUSIONS

Direct oxidative olefin hydroarylation to produce vinyl arenes is a desirable target, and the availability of a tunable "switch" that dictates alkyl- versus vinyl arene selectivity is potentially useful. For  $[(^x\text{bpy})\text{Pt}(\text{Ph})(\text{THF})]^+$  complexes, we have shown that catalyst selectivity for the production of vinyl arenes versus alkyl arenes can be controlled by the 4,4'-substituents on the bipyridyl ligand. Less donating 4,4'-substituents result in an increased propensity toward styrene production. Of course, for the  $\text{Pt}^{\text{II}}$  catalysts reported herein, application toward vinyl arene production will require conditions that permit catalytic turnover with oxidants other than ethylene. In addition, such structure/activity relationships are important, since the formation of vinyl arenes is a possible deactivation pathway for this series of  $\text{Pt}^{\text{II}}$  catalysts and possibly for other transition-metal catalysts.

## EXPERIMENTAL SECTION

**General Methods.** Unless otherwise noted, all synthetic procedures were performed under anaerobic conditions in a nitrogen-filled glovebox or by using standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer ( $\text{O}_2 < 15$  ppm for all reactions). Tetrahydrofuran and diethyl ether were dried by distillation over sodium/benzophenone and  $\text{CaH}_2$ , respectively. *n*-Pentane was distilled over  $\text{P}_2\text{O}_5$ . Methylene chloride and benzene were purified by passage through a column of activated alumina. Benzene- $d_6$ , acetone- $d_6$ , nitromethane- $d_3$  and dichloromethane- $d_2$  were used as received and stored under a  $\text{N}_2$  atmosphere over 4 Å molecular sieves.  $^1\text{H}$  NMR spectra were recorded using a Varian Mercury 300 or 500 MHz spectrometer or using a Bruker 800 MHz spectrometer.  $^{13}\text{C}$  NMR spectra were recorded using a Varian Mercury 300 or 500 MHz spectrometer (operating frequency 75 or 125 MHz, respectively) or using a Bruker 800 MHz spectrometer (operating frequency 201 MHz). All  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are referenced against residual proton signals ( $^1\text{H}$  NMR) or the  $^{13}\text{C}$  resonances ( $^{13}\text{C}$  NMR) of the deuterated solvents.  $^{19}\text{F}$  NMR (282 MHz operating frequency) spectra were obtained on a Varian 300 MHz spectrometer and referenced against an external standard of hexafluorobenzene ( $\delta = -164.9$  ppm). GC/MS was performed using a Shimadzu GCMS-QP2010 Plus system with a 30 m  $\times$  0.25 mm SHRXI-5MS column with 0.25 mm film thickness using electron impact ionization. Ethylene (99.5%) was purchased in a gas cylinder from GTS-Welco and used as received. All other reagents were used as purchased from commercial sources. The

preparation, isolation, and characterization of  $[\text{H}(\text{Et}_2\text{O})_2][\text{BAR}'_4]$  ( $\text{Ar}' = 3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3$ ),<sup>13</sup>  $[\text{Pt}(\text{Ph})_2(\text{Et}_2\text{S})_2]$ ,<sup>14</sup>  $(\text{bpy})\text{Pt}(\text{Ph})_2$  (**1c**; bpy = 2,2'-bipyridine),<sup>15</sup>  $(^t\text{bpy})\text{Pt}(\text{Ph})_2$  (**1b**;  $^t\text{bpy} = 4,4'$ -di-*tert*-butyl-2,2'-bipyridine),<sup>10a</sup>  $[(^t\text{bpy})\text{Pt}(\text{Ph})(\text{THF})][\text{BAR}'_4]$  (**2b**),<sup>7c</sup>  $[(^t\text{bpy})\text{Pt}(\text{CH}_2\text{CH}_2\text{Ph})(\eta^2\text{-C}_2\text{H}_4)][\text{BAR}'_4]$  (**3b**),<sup>7c</sup>  $[\text{Pt}(\text{Me})_2(\text{Et}_2\text{S})_2]$ ,<sup>16</sup> and  $^t\text{bpyPtMe}_2$ <sup>16</sup> have been previously reported.

**General Procedure for the Synthesis of  $(^t\text{bpy})\text{PtPh}_2$  Complexes 1a–f.** To a suspension of  $[\text{Pt}(\text{Ph})_2(\text{Et}_2\text{S})_2]$  in diethyl ether (30 mL) was added 2 equiv of the appropriate bipyridyl ligand. The solution was stirred at room temperature overnight. The solution was reduced in vacuo, and hexanes was added (~20 mL). The solution was filtered, and the precipitate was dried under vacuum.

**$^m\text{bpyPtPh}_2$  (**1a**).** The bipyridyl ligand was 4,4'-dimethoxy-2,2'-bipyridine ( $^m\text{bpy}$ ; 96% isolated yield, 0.288 g). <sup>1</sup>H NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.24 (d, 2H,  $\text{H}^6\text{-}^m\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz), 7.52 (d, 2H,  $\text{H}^3\text{-}^m\text{bpy}$ ,  $^4J_{\text{HH}} = 3$  Hz), 7.42 (d, 4H,  $\text{H}^{\text{Ph}}$ ,  $^3J_{\text{HH}} = 8$  Hz,  $^3J_{\text{PH}} = 69$  Hz, Pt satellites), 6.95 (t, 4H,  $\text{H}^{\text{m-Ph}}$ ,  $^3J_{\text{HH}} = 7$  Hz), 6.87 (dd, 2H,  $\text{H}^5\text{-}^m\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz,  $^4J_{\text{HH}} = 2$  Hz), 6.82 (m, 2H,  $\text{H}^{\text{P-Ph}}$ ), 3.94 (s, 6H,  $\text{OMe-}^m\text{bpy}$ ). <sup>13</sup>C NMR (201 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  167.0, 158.0, 151.5, 146.7, 138.7, 127.3, 121.8, 111.9, 109.8 ( $^m\text{bpy}$  and Ph), 56.6 ( $\text{OCH}_3$ ). Anal. Calcd for  $\text{PtN}_2\text{O}_2\text{C}_{24}\text{H}_{22}$ : C, 50.97; H, 3.93; N, 4.95. Found: C, 51.02; H, 3.99; N, 5.01.

**$^{\text{Br}}\text{bpyPtPh}_2$  (**1d**).** The bipyridyl ligand was 4,4'-dibromo-2,2'-bipyridine ( $^{\text{Br}}\text{bpy}$ ; 78% isolated yield, 0.176 g). <sup>1</sup>H NMR (300 MHz, acetone- $d_6$ ):  $\delta$  8.90 (d, 2H,  $\text{H}^3\text{-}^{\text{Br}}\text{bpy}$ ,  $^4J_{\text{HH}} = 2$  Hz), 8.29 (d, 2H,  $\text{H}^6\text{-}^{\text{Br}}\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz,  $^3J_{\text{PH}} = 21$  Hz, Pt satellites), 7.90 (dd, 2H,  $\text{H}^5\text{-}^{\text{Br}}\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz,  $^4J_{\text{HH}} = 2$  Hz), 7.40 (d, 4H,  $\text{H}^{\text{Ph}}$ ,  $^3J_{\text{HH}} = 8$  Hz,  $^3J_{\text{PH}} = 71$  Hz, Pt satellites), 6.89 (t, 4H,  $\text{H}^{\text{m-Ph}}$ ,  $^3J_{\text{HH}} = 8$  Hz), 6.75 (m, 2H,  $\text{H}^{\text{P-Ph}}$ ). <sup>13</sup>C NMR (75 MHz, acetone- $d_6$ ):  $\delta$  150.8, 146.6, 139.0, 134.7, 131.8, 128.2, 127.5, 127.0, 122.3 ( $^{\text{Br}}\text{bpy}$  and Ph). Anal. Calcd for  $\text{PtN}_2\text{Br}_2\text{C}_{22}\text{H}_{16}$ : C, 39.84; H, 2.44; N, 4.22. Found: C, 39.82; H, 2.30; N, 4.22.

**$^{\text{C}}\text{bpyPtPh}_2$  (**1e**).** The bipyridyl ligand was 4,4'-diethoxycarbonyl-2,2'-bipyridine ( $^{\text{C}}\text{bpy}$ ; 85% isolated yield, 0.171 g). <sup>1</sup>H NMR (300 MHz, acetone- $d_6$ ):  $\delta$  8.99 (d, 2H,  $\text{H}^3\text{-}^{\text{C}}\text{bpy}$ ,  $^4J_{\text{HH}} = 1$  Hz), 8.67 (d, 2H,  $\text{H}^6\text{-}^{\text{C}}\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz), 8.10 (dd, 2H,  $\text{H}^5\text{-}^{\text{C}}\text{bpy}$ ,  $^3J_{\text{HH}} = 6$ ,  $^4J_{\text{HH}} = 2$  Hz), 7.40 (d, 4H,  $\text{H}^{\text{Ph}}$ ,  $^3J_{\text{HH}} = 8$  Hz,  $^3J_{\text{PH}} = 70$  Hz, Pt satellites), 6.91 (t, 4H,  $\text{H}^{\text{m-Ph}}$ ,  $^3J_{\text{HH}} = 8$  Hz), 6.77 (m, 2H,  $\text{H}^{\text{P-Ph}}$ ), 4.48 (q, 4H,  $\text{OCH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7$  Hz), 1.43 (t, 6H,  $\text{OCH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7$  Hz). <sup>13</sup>C NMR (75 MHz, acetone- $d_6$ ):  $\delta$  164.7, 157.3, 151.1, 146.6, 140.1, 139.1, 127.8, 127.6, 123.8, 122.5 ( $^{\text{C}}\text{bpy}$  and Ph), 63.2 ( $\text{OCH}_2\text{CH}_3$ ), 14.4 ( $\text{OCH}_2\text{CH}_3$ ). Anal. Calcd for  $\text{PtN}_2\text{O}_4\text{C}_{28}\text{H}_{26}$ : C, 51.76; H, 4.04; N, 4.31. Found: C, 52.01; H, 3.94; N, 4.16.

**$^{\text{NO}_2}\text{bpyPtPh}_2$  (**1f**).** The bipyridyl ligand was 4,4'-dinitro-2,2'-bipyridine ( $^{\text{NO}_2}\text{bpy}$ ; 89% isolated yield, 0.779 g). <sup>1</sup>H NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.97 (d, 2H,  $\text{H}^6\text{-}^{\text{NO}_2}\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz), 8.92 (d, 2H,  $\text{H}^3\text{-}^{\text{NO}_2}\text{bpy}$ ,  $^4J_{\text{HH}} = 2$  Hz), 8.16 (dd, 2H,  $\text{H}^5\text{-}^{\text{NO}_2}\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz,  $^4J_{\text{HH}} = 2$  Hz), 7.39 (d, 4H,  $\text{H}^{\text{Ph}}$ ,  $^3J_{\text{HH}} = 8$  Hz), 7.06 (t, 4H,  $\text{H}^{\text{m-Ph}}$ ,  $^3J_{\text{HH}} = 8$  Hz), 6.91 (t, 2H,  $\text{H}^{\text{P-Ph}}$ ,  $^3J_{\text{HH}} = 8$  Hz). <sup>13</sup>C NMR (201 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  157.5, 153.6, 153.1, 144.0, 138.1, 127.8, 123.2, 122.2, 117.1 ( $^{\text{NO}_2}\text{bpy}$  and Ph). Anal. Calcd for  $\text{PtN}_4\text{O}_4\text{C}_{22}\text{H}_{16}$ : C, 44.37; H, 2.71; N, 9.41. Found: C, 44.63; H, 2.82; N, 9.37.

**General Procedure for the Synthesis of  $[(^t\text{bpy})\text{Pt}(\text{Ph})(\text{THF})][\text{BAR}'_4]$  Complexes 2a–f.** A solution/suspension of  $(^t\text{bpy})\text{Pt}(\text{Ph})_2$  in THF (30 mL) was cooled to approximately  $-70$  °C. One equivalent of  $[\text{H}(\text{Et}_2\text{O})_2][\text{BAR}'_4]$  dissolved in THF (~10 mL,  $-70$  °C) was added. The volatiles were removed in vacuo. The residue was treated with *n*-pentane (~2 mL), which was then removed under vacuum to afford a low-density solid. The solid was dried in vacuo.

**Spectroscopic Data for  $\text{BAR}'_4$  Anion.** The chemical shifts for the  $\text{BAR}'_4$  anion of various Pt complexes are virtually identical. The NMR spectroscopy data for the anion are as follows. <sup>1</sup>H NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.72 (s, 8H,  $\text{H}^{\text{P-}}\text{BAR}'_4$ ), 7.56 (s, 4H,  $\text{H}^{\text{m-}}\text{BAR}'_4$ ). <sup>13</sup>C NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  162.3 (q,  $\text{Ar}'$ ,  $^1J_{\text{B-C}} = 49$  Hz), 135.4 ( $\text{Ar}'$ ), 129.5 (q,  $m\text{-Ar}'$ ,  $^2J_{\text{C-F}} = 32$  Hz), 125.2 (q,  $\text{Ar}'$ ,  $^2J_{\text{C-F}} = 272$  Hz), 118.1 ( $\text{Ar}'$ ). <sup>19</sup>F NMR (282 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -63.1 (s,  $\text{CF}_3\text{-Ar}'$ ).

**$[(^m\text{bpy})\text{Pt}(\text{Ph})(\text{THF})][\text{BAR}'_4]$  (**2a**):** 80% isolated yield, 0.148 g. <sup>1</sup>H NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.24 (d, 1H,  $\text{H}^6\text{-}^m\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz), 8.01 (d, 1H,  $\text{H}^3\text{-}^m\text{bpy}$ ,  $^4J_{\text{HH}} = 7$  Hz), 7.55 (d, 1H,  $\text{H}^5\text{-}^m\text{bpy}$ ,  $^3J_{\text{HH}} = 2$  Hz), 7.45 (m, 3H,  $\text{H}^{\text{P-}}\text{bpy}$  and  $\text{H}^{\text{Ph}}$ ), 7.21 (dd, 1H,  $\text{H}^5\text{-}^m\text{bpy}$ ,  $^3J_{\text{HH}} =$

6 Hz,  $^4J_{\text{HH}} = 2$  Hz), 7.14 (t, 2H,  $\text{H}^{\text{m-Ph}}$ ,  $^3J_{\text{HH}} = 7$  Hz), 7.04 (m, 1H,  $\text{H}^{\text{P-Ph}}$ ), 6.74 (dd, 1H,  $\text{H}^5\text{-}^m\text{bpy}$ ,  $^3J_{\text{HH}} = 7$  Hz,  $^4J_{\text{HH}} = 3$  Hz), 4.12 (m, 4H,  $\alpha\text{-THF}$ ), 4.02 (s, 3H,  $\text{OCH}_3$ ), 3.95 (s, 3H,  $\text{OCH}_3$ ), 1.84 (m, 4H,  $\beta\text{-THF}$ ). <sup>13</sup>C NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  169.0, 168.5, 159.1, 155.5, 155.2, 148.1, 139.2, 136.5, 128.5, 125.3, 112.7, 112.1, 111.2, 110.5 ( $^m\text{bpy}$  and Ph), 77.8 ( $\alpha\text{-THF}$ ), 57.3 ( $\text{OCH}_3$ ), 57.1 ( $\text{OCH}_3$ ), 25.1 ( $\beta\text{-THF}$ ). Anal. Calcd for  $\text{PtN}_2\text{O}_3\text{BF}_4\text{C}_{24}\text{H}_{37}$ : C, 45.55; H, 2.62; N, 1.97. Found: C, 45.38; H, 2.81; N, 2.10.

**$[(^t\text{bpy})\text{Pt}(\text{Ph})(\text{THF})][\text{BAR}'_4]$  (**2c**):** 89% isolated yield, 0.201 g. <sup>1</sup>H NMR (800 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.49 (d, 1H,  $\text{H}^6\text{-}^t\text{bpy}$ ,  $^3J_{\text{HH}} = 5$  Hz), 8.31 (d, 1H,  $\text{H}^6\text{-}^t\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz), 8.24 (td, 1H,  $\text{H}^4\text{-}^t\text{bpy}$ ,  $^3J_{\text{HH}} = 8$  Hz,  $^4J_{\text{HH}} = 2$  Hz), 8.15 (d, 1H,  $\text{H}^3\text{-}^t\text{bpy}$ ,  $^3J_{\text{HH}} = 8$  Hz), 8.11 (td, 1H,  $\text{H}^4\text{-}^t\text{bpy}$ ,  $^3J_{\text{HH}} = 8$  Hz,  $^4J_{\text{HH}} = 1$  Hz), 8.03 (d, 1H,  $\text{H}^3\text{-}^t\text{bpy}$ ,  $^3J_{\text{HH}} = 8$  Hz), 7.78 (ddd,  $\text{H}^5\text{-}^t\text{bpy}$ ,  $^3J_{\text{HH}} = 8$  Hz,  $^3J_{\text{HH}} = 5$  Hz,  $^4J_{\text{HH}} = 1$  Hz), 7.47 (d, 2H,  $\text{H}^{\text{Ph}}$ ,  $^3J_{\text{HH}} = 8$  Hz), 7.30 (ddd, 1H,  $\text{H}^5\text{-}^t\text{bpy}$ ,  $^3J_{\text{HH}} = 8$  Hz,  $^3J_{\text{HH}} = 6$  Hz,  $^3J_{\text{HH}} = 2$  Hz), 7.17 (t, 2H,  $\text{H}^{\text{m-Ph}}$ ,  $^3J_{\text{HH}} = 8$  Hz), 7.09 (m, 1H,  $\text{H}^{\text{P-Ph}}$ ), 4.16 (m, 4H,  $\alpha\text{-THF}$ ), 1.88 (m, 4H,  $\beta\text{-THF}$ ). <sup>13</sup>C NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  158.0, 154.4, 154.0, 146.9, 141.0, 140.5, 138.8, 136.1, 128.7, 128.4, 128.2, 125.6, 123.7, 123.4 (bpy and Ph), 77.9 ( $\alpha\text{-THF}$ ), 25.1 ( $\beta\text{-THF}$ ). Anal. Calcd for  $\text{PtN}_2\text{O}_3\text{OBF}_4\text{C}_{24}\text{H}_{33}$ : C, 45.80; H, 2.44; N, 2.05. Found: C, 45.76; H, 2.34; N, 2.01.

**$[(^{\text{Br}}\text{bpy})\text{Pt}(\text{Ph})(\text{THF})][\text{BAR}'_4]$  (**2d**):** 94% isolated yield, 0.105 g. <sup>1</sup>H NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.32 (m, 2H,  $\text{H}^3\text{-}^{\text{Br}}\text{bpy}$  and  $\text{H}^6\text{-}^{\text{Br}}\text{bpy}$ ), 8.20 (d, 1H,  $\text{H}^3\text{-}^{\text{Br}}\text{bpy}$ ,  $^3J_{\text{HH}} = 2$  Hz), 8.12 (d, 1H,  $\text{H}^6\text{-}^{\text{Br}}\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz), 8.00 (dd, 1H,  $\text{H}^5\text{-}^{\text{Br}}\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz,  $^4J_{\text{HH}} = 2$  Hz), 7.50 (dd, 1H,  $\text{H}^5\text{-}^{\text{Br}}\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz,  $^4J_{\text{HH}} = 2$  Hz), 7.42 (d, 2H,  $\text{H}^{\text{Ph}}$ ,  $^3J_{\text{HH}} = 7$  Hz), 7.17 (t, 2H,  $\text{H}^{\text{m-Ph}}$ ,  $^3J_{\text{HH}} = 7$  Hz), 7.08 (m, 1H,  $\text{H}^{\text{P-Ph}}$ ), 4.14 (m, 4H,  $\alpha\text{-THF}$ ), 1.84 (m, 4H,  $\beta\text{-THF}$ ). <sup>13</sup>C NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  157.6, 154.5, 147.3, 138.1, 138.0, 135.8, 132.3, 132.1, 128.1, 127.9, 127.5, 126.8 ( $^{\text{Br}}\text{bpy}$  and Ph), 78.3 ( $\alpha\text{-THF}$ ), 25.0 ( $\beta\text{-THF}$ ), remaining two aromatic resonances obscured due to coincidental overlap. Anal. Calcd for  $\text{PtN}_2\text{Br}_2\text{BF}_4\text{C}_{22}\text{H}_{31}$ : C, 41.05; H, 2.06; N, 1.84. Found: C, 41.27; H, 2.05; N, 1.83.

**$[(^{\text{C}}\text{bpy})\text{Pt}(\text{Ph})(\text{THF})][\text{BAR}'_4]$  (**2e**):** 86% isolated yield, 0.099 g. <sup>1</sup>H NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.87 (s, 1H,  $\text{H}^3\text{-}^{\text{C}}\text{bpy}$ ), 8.73 (d, 1H,  $\text{H}^3\text{-}^{\text{C}}\text{bpy}$ ,  $^4J_{\text{HH}} = 2$  Hz), 8.68 (d, 1H,  $\text{H}^6\text{-}^{\text{C}}\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz), 8.51 (d, 1H,  $\text{H}^6\text{-}^{\text{C}}\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz), 8.39 (dd, 1H,  $\text{H}^5\text{-}^{\text{C}}\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz,  $^4J_{\text{HH}} = 2$  Hz), 7.85 (dd, 1H,  $\text{H}^5\text{-}^{\text{C}}\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz,  $^4J_{\text{HH}} = 2$  Hz), 7.45 (d, 2H,  $\text{H}^{\text{Ph}}$ ,  $^3J_{\text{HH}} = 8$  Hz), 7.20 (t, 2H,  $\text{H}^{\text{m-Ph}}$ ,  $^3J_{\text{HH}} = 8$  Hz), 7.11 (m, 1H,  $\text{H}^{\text{P-Ph}}$ ), 4.55 (q, 2H,  $\text{OCH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7$  Hz), 4.48 (q, 2H,  $\text{OCH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7$  Hz), 4.18 (m, 4H,  $\alpha\text{-THF}$ ), 1.88 (m, 4H,  $\beta\text{-THF}$ ), 1.47 (t, 3H,  $\text{OCH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7$  Hz), 1.42 (t, 3H,  $\text{OCH}_2\text{CH}_3$ ,  $^3J_{\text{HH}} = 7$  Hz). <sup>13</sup>C NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  163.0, 162.8, 158.3, 155.3, 154.4, 147.8, 142.6, 141.7, 135.8, 128.3, 128.0, 123.7, 123.5 ( $^{\text{C}}\text{bpy}$ , Ph and  $\text{CO}_2\text{Et}$ ), 78.3 ( $\alpha\text{-THF}$ ), 64.0 ( $\text{OCH}_2\text{CH}_3$ ), 25.1 ( $\beta\text{-THF}$ ), 14.3 ( $\text{OCH}_2\text{CH}_3$ ), remaining five resonances obscured due to coincidental overlap. Anal. Calcd for  $\text{PtN}_2\text{O}_5\text{BF}_4\text{C}_{28}\text{H}_{41}$ : C, 46.20; H, 2.75; N, 1.86. Found: C, 46.22; H, 2.79; N, 1.91.

**$[(^{\text{NO}_2}\text{bpy})\text{Pt}(\text{Ph})(\text{THF})][\text{BAR}'_4]$  (**2f**):** 92% isolated yield, 0.334 g. <sup>1</sup>H NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  9.13 (d, 1H,  $\text{H}^3\text{-}^{\text{NO}_2}\text{bpy}$ ,  $^4J_{\text{HH}} = 2$  Hz), 8.97 (d, 1H,  $\text{H}^3\text{-}^{\text{NO}_2}\text{bpy}$ ,  $^4J_{\text{HH}} = 2$  Hz), 8.95 (d, 1H,  $\text{H}^6\text{-}^{\text{NO}_2}\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz), 8.81 (d, 1H,  $\text{H}^6\text{-}^{\text{NO}_2}\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz), 8.68 (dd, 1H,  $\text{H}^5\text{-}^{\text{NO}_2}\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz,  $^4J_{\text{HH}} = 2$  Hz), 8.16 (dd, 1H,  $\text{H}^5\text{-}^{\text{NO}_2}\text{bpy}$ ,  $^3J_{\text{HH}} = 6$  Hz,  $^4J_{\text{HH}} = 2$  Hz), 7.43 (m, 2H,  $\text{H}^{\text{Ph}}$ ), 7.25 (m, 2H,  $\text{H}^{\text{m-Ph}}$ ), 7.17 (m, 1H,  $\text{H}^{\text{P-Ph}}$ ), 4.21 (m, 4H,  $\alpha\text{-THF}$ ), 1.91 (m, 4H,  $\beta\text{-THF}$ ). Note: complex **2f** decomposes over the course of hours at room temperature in  $\text{CD}_2\text{Cl}_2$ , which prevented the acquisition of <sup>13</sup>C NMR data. Anal. Calcd for  $\text{PtBN}_4\text{O}_5\text{F}_{24}\text{C}_{52}\text{H}_{31}$ : C, 44.08; H, 2.58; N, 3.67. Found: C, 43.71; H, 2.38; N, 3.93.

**General Procedure for the Synthesis of  $[(^t\text{bpy})\text{Pt}(\text{CH}_2\text{CH}_2\text{Ph})(\eta^2\text{-C}_2\text{H}_4)][\text{BAR}'_4]$  Complexes 3a–f.** Complex **2** was dissolved in dichloromethane (~5 mL). The solution was transferred to a stainless steel pressure reactor and pressurized with ethylene (0.3 MPa). After 12 h, the volatiles were removed in vacuo, and *n*-pentane (~2 mL) was added to the crude solid. The pentane was removed under vacuum to afford a low-density solid. The solid was collected and dried in vacuo.

**$[(^m\text{bpy})\text{Pt}(\text{CH}_2\text{CH}_2\text{Ph})(\eta^2\text{-C}_2\text{H}_4)][\text{BAR}'_4]$  (**3a**):** 92% isolated yield, 0.087 g. <sup>1</sup>H NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.61 (br d, 1H, bpy,  $^3J_{\text{HH}} = 7$  Hz), 7.81 (br d, 1H, bpy,  $^3J_{\text{HH}} = 7$  Hz), 7.64 (br s, 1H, bpy), 7.61

(br s, 1H, bpy), 7.30–7.10 (m, 6H, bpy and Ph), 4.17–3.88 (overlapping resonances, 10H, OMe and C<sub>2</sub>H<sub>4</sub>), 2.68 (t, 2H, Pt-CH<sub>2</sub>CH<sub>2</sub>Ph, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 1.39 (t, 2H, Pt-CH<sub>2</sub>CH<sub>2</sub>Ph, <sup>3</sup>J<sub>HH</sub> = 8 Hz). <sup>13</sup>C NMR (201 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 170.68, 169.4, 169.0, 159.5, 156.2, 150.3, 147.3, 144.0, 129.3, 128.9, 128.8, 126.8, 126.1 (<sup>m</sup>bpy and Ph), 69.0 (C<sub>2</sub>H<sub>4</sub>), 58.0 (OMe), 57.6 (OMe), 37.7 (CH<sub>2</sub>CH<sub>2</sub>Ph), 16.4 (CH<sub>2</sub>CH<sub>2</sub>Ph), remaining resonance obscured due to coincidental overlap. Anal. Calcd for PtBN<sub>2</sub>O<sub>2</sub>F<sub>24</sub>C<sub>54</sub>H<sub>37</sub>: C, 46.07; H, 2.65; N, 1.99. Found: C, 46.24; H, 2.61; N, 2.11.

[(<sup>bpy</sup>)Pt(CH<sub>2</sub>CH<sub>2</sub>Ph)(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>)](BAR'<sub>4</sub>) (3c): 81% isolated yield, 0.098 g. <sup>1</sup>H NMR (800 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 8.80 (br s, 1H, bpy), 8.34–8.22 (br m, 4H, bpy), 8.05 (br s, 1H, bpy), 7.84 (br s, 1H, bpy), 7.26 (m, 4H, H<sup>o</sup>-Ph), 7.17 (m, 1H, H<sup>p</sup>-Ph), 4.19 (br s, 4H, C<sub>2</sub>H<sub>4</sub>), 2.72 (t, 2H, Pt-CH<sub>2</sub>CH<sub>2</sub>Ph, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 1.54 (t, 2H, Pt-CH<sub>2</sub>CH<sub>2</sub>Ph, <sup>3</sup>J<sub>HH</sub> = 8 Hz). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 157.5, 154.1, 148.5, 145.8, 143.5, 141.4, 130.5, 129.4, 128.6, 126.6, 124.1 (bpy and Ph), 70.6 (C<sub>2</sub>H<sub>4</sub>), 37.4 (CH<sub>2</sub>CH<sub>2</sub>Ph), 17.0 (CH<sub>2</sub>CH<sub>2</sub>Ph), remaining three resonances obscured due to coincidental overlap. Anal. Calcd for PtBN<sub>2</sub>F<sub>24</sub>C<sub>52</sub>H<sub>31</sub>: C, 46.41; H, 2.33; N, 2.08. Found: C, 46.61; H, 2.41; N, 2.19.

[(<sup>bpy</sup>)Pt(CH<sub>2</sub>CH<sub>2</sub>Ph)(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>)](BAR'<sub>4</sub>) (3e): 88% isolated yield, 0.127 g. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 8.90 (m, 3H, <sup>bpy</sup>), 8.28 (m, 3H, <sup>bpy</sup>), 7.26 (m, 5H, Ph), 4.54 (overlapping m's, 4H, OCH<sub>2</sub>CH<sub>3</sub>), 4.30 (br s, 4H, C<sub>2</sub>H<sub>4</sub>, <sup>3</sup>J<sub>PH</sub> = 34 Hz, Pt satellites), 2.71 (t, 2H, Pt-CH<sub>2</sub>CH<sub>2</sub>Ph, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 1.60 (t, 2H, Pt-CH<sub>2</sub>CH<sub>2</sub>Ph, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 1.47 (overlapping m's, 6H, OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (201 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 157.8, 154.7, 149.8, 146.9, 144.3, 143.2, 142.9, 129.2, 128.6, 128.3, 126.8, 124.2 (<sup>bpy</sup> and Ph), 71.9 (C<sub>2</sub>H<sub>4</sub>), 64.4 (OCH<sub>2</sub>CH<sub>3</sub>), 64.2 (OCH<sub>2</sub>CH<sub>3</sub>), 37.5 (CH<sub>2</sub>CH<sub>2</sub>Ph), 17.5 (OCH<sub>2</sub>CH<sub>3</sub>), 14.3 (CH<sub>2</sub>CH<sub>2</sub>Ph), remaining five resonances obscured due to coincidental overlap. Anal. Calcd for PtBN<sub>2</sub>O<sub>4</sub>F<sub>24</sub>C<sub>58</sub>H<sub>41</sub>: C, 46.69; H, 2.78; N, 1.88. Found: C, 46.90; H, 2.78; N, 2.00.

[(<sup>NO<sub>2</sub>bpy</sup>)Pt(CH<sub>2</sub>CH<sub>2</sub>Ph)(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>)](BAR'<sub>4</sub>) (3f): 87% isolated yield, 0.108 g. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 9.14 (d, 1H, <sup>NO<sub>2</sub>bpy</sup>, <sup>3</sup>J<sub>HH</sub> = 2 Hz), 8.57 (br m, 2H, <sup>NO<sub>2</sub>bpy</sup>), 7.28 (br d, 2H, H<sup>o</sup>-Ph, <sup>3</sup>J<sub>HH</sub> = 7 Hz), 7.23–7.06 (m, 3H, H<sup>m</sup> and H<sup>p</sup>-Ph), 4.42 (br s, 4H, η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>), 2.70 (t, 2H, Pt-CH<sub>2</sub>CH<sub>2</sub>Ph, <sup>3</sup>J<sub>HH</sub> = 7 Hz), 1.71 (t, 2H, Pt-CH<sub>2</sub>CH<sub>2</sub>Ph, <sup>3</sup>J<sub>HH</sub> = 7 Hz), remaining <sup>NO<sub>2</sub>bpy</sup> signals obscured due to broadening or coincidental overlap. <sup>13</sup>C NMR (201 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 152.3, 149.1, 142.3, 128.9, 128.5, 126.8, 123.3, 118.2 (<sup>NO<sub>2</sub>bpy</sup> and Ph), 68.1 (C<sub>2</sub>H<sub>4</sub>), 37.0 (CH<sub>2</sub>CH<sub>2</sub>Ph), 18.0 (CH<sub>2</sub>CH<sub>2</sub>Ph), remaining five resonances obscured due to coincidental overlap. Anal. Calcd for PtBN<sub>4</sub>O<sub>4</sub>F<sub>24</sub>C<sub>52</sub>H<sub>31</sub>: C, 43.44; H, 2.18; N, 3.90. Found: C, 43.73; H, 2.15; N, 3.86.

**Synthesis of (<sup>NO<sub>2</sub>bpy</sup>)PtMe<sub>2</sub>.** A heterogeneous mixture of [(Me)<sub>2</sub>Pt(μ-SiEt<sub>2</sub>)<sub>2</sub>] (0.526 g, 0.834 mmol) and <sup>NO<sub>2</sub>bpy</sup> (0.4125 g, 1.68 mmol) in diethyl ether was stirred at room temperature for 16 h. The solvent volume was partially reduced under vacuum, and the resulting mixture was filtered. The filtrate was discarded, and the solid was dried in vacuo to afford a purple solid (0.737 g, 94%). <sup>1</sup>H NMR (300 MHz, acetone-*d*<sub>6</sub>): δ 9.78 (d, 2H, H<sup>6</sup>-<sup>NO<sub>2</sub>bpy</sup>, <sup>3</sup>J<sub>HH</sub> = 6 Hz, <sup>3</sup>J<sub>PH</sub> = 21 Hz, Pt satellites), 9.44 (d, 2H, H<sup>3</sup>-<sup>NO<sub>2</sub>bpy</sup>, <sup>4</sup>J<sub>HH</sub> = 2 Hz), 8.53 (dd, 2H, H<sup>5</sup>-<sup>NO<sub>2</sub>bpy</sup>, <sup>3</sup>J<sub>HH</sub> = 6 Hz, <sup>4</sup>J<sub>HH</sub> = 2 Hz), 1.38 (s, 6H, Pt-CH<sub>3</sub>, <sup>2</sup>J<sub>PH</sub> = 91 Hz, Pt satellites). The complex was too insoluble in organic solvents to obtain <sup>13</sup>C NMR data. Anal. Calcd for PtN<sub>4</sub>O<sub>4</sub>C<sub>12</sub>H<sub>12</sub>: C, 30.58; H, 2.57; N, 11.89. Found: C, 30.70; H, 2.56; N, 11.62.

**General Procedure for the Synthesis of [(<sup>bpy</sup>)Pt(Me)<sub>2</sub>(<sup>2</sup>-styrene)](BAR'<sub>4</sub>) (x = <sup>t</sup>Bu, NO<sub>2</sub>).** A solution of (<sup>bpy</sup>)Pt(Me)<sub>2</sub> and 1 equiv of styrene in dichloromethane (30 mL) was cooled to approximately -70 °C. One equivalent of [H(Et<sub>2</sub>O)<sub>2</sub>](BAR'<sub>4</sub>) dissolved in dichloromethane (~10 mL, -70 °C) was added to the Pt solution. The solution was reduced to approximately half volume in vacuo and filtered through Celite with dichloromethane as eluent. The volatiles were removed from the filtrate in vacuo. The residue was treated with *n*-pentane (~2 mL), which was then removed under vacuum to afford a low-density solid. The solid was dried in vacuo.

[(<sup>bpy</sup>)Pt(Me)(η<sup>2</sup>-styrene)](BAR'<sub>4</sub>) (5a): 87% isolated yield, 0.084 g. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 8.68 (d, 1H, H<sup>6</sup>-<sup>bpy</sup>, <sup>3</sup>J<sub>HH</sub> = 6 Hz, <sup>3</sup>J<sub>PH</sub> = 48 Hz, Pt satellites), 8.17 (s, 1H, H<sup>3</sup>-<sup>bpy</sup>), 8.09 (s, 1H, H<sup>3</sup>-<sup>tpy</sup>), 7.85 (m, 3H, <sup>bpy</sup>), 7.59 (m, 2H, H<sup>o</sup>-Ph), 7.33 (m, 3H, H<sup>m</sup>/H<sup>p</sup>-

Ph), 6.29 (dd, 1H, PhCH=CH<sub>2</sub>, <sup>3</sup>J<sub>HHTrans</sub> = 14 Hz, <sup>3</sup>J<sub>HHCis</sub> = 8 Hz) 4.49 (d, 1H, PhCH-CH<sub>2</sub>, <sup>3</sup>J<sub>HHTrans</sub> = 14 Hz), 4.19 (d, 1H, PhCH-CH<sub>2</sub>, <sup>3</sup>J<sub>HHCis</sub> = 8 Hz), 1.44 (s, 9H, <sup>bpy</sup>), 1.37 (s, 9H, <sup>bpy</sup>), 0.67 (br s, 3H, Me, <sup>2</sup>J<sub>PH</sub> = 71 Hz, Pt satellites). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 175.2, 168.6, 165.8, 157.3, 154.0, 147.6, 145.7, 136.0, 130.1, 129.1, 128.8, 125.2, 124.8, 120.3, 120.2, 90.9 (<sup>bpy</sup> and styrene), 36.2 (CCH<sub>3</sub>), 35.8 (CCH<sub>3</sub>), 29.7 (CCH<sub>3</sub>), 29.6 (CCH<sub>3</sub>), methyl resonance not observed due to broadening. Anal. Calcd for PtBN<sub>2</sub>F<sub>24</sub>C<sub>59</sub>H<sub>47</sub>: C, 49.01; H, 3.28; N, 1.94. Found: C, 49.31; H, 3.42; N, 2.10.

[(<sup>NO<sub>2</sub>bpy</sup>)Pt(Me)(η<sup>2</sup>-styrene)](BAR'<sub>4</sub>) (5f): 96% isolated yield, 0.582 g. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 9.25 (br d, 1H, H<sup>6</sup>-<sup>NO<sub>2</sub>bpy</sup>, <sup>3</sup>J<sub>HH</sub> = 5 Hz), 9.14 (br s, 1H, H<sup>3</sup>-<sup>NO<sub>2</sub>bpy</sup>), 9.04 (br s, 1H, H<sup>3</sup>-<sup>NO<sub>2</sub>bpy</sup>), 8.65 (br s, 1H, H<sup>6</sup>-<sup>NO<sub>2</sub>bpy</sup>), 8.30 (br s, 1H, H<sup>5</sup>-<sup>NO<sub>2</sub>bpy</sup>), 8.23 (br d, 1H, H<sup>5</sup>-<sup>NO<sub>2</sub>bpy</sup>, <sup>3</sup>J<sub>HH</sub> = 6 Hz), 7.60 (m, 2H, H<sup>o</sup>-styrene), 7.42 (m, 1H, H<sup>p</sup>-styrene), 7.33 (m, 2H, H<sup>m</sup>-styrene), 6.64 (dd, 1H, PhCH=CH<sub>2</sub>, <sup>3</sup>J<sub>HHTrans</sub> = 15 Hz, <sup>3</sup>J<sub>HHCis</sub> = 8 Hz), 4.78 (dd, 1H, PhCH-CH<sub>2</sub>, <sup>3</sup>J<sub>HHTrans</sub> = 15 Hz, <sup>2</sup>J<sub>HHgem</sub> = 1 Hz), 4.50 (dd, 1H, PhCH-CH<sub>2</sub>, <sup>3</sup>J<sub>HHCis</sub> = 8 Hz, <sup>2</sup>J<sub>HHgem</sub> = 1 Hz), 1.04 (s, 3H, Pt-CH<sub>3</sub>, <sup>2</sup>J<sub>PH</sub> = 74 Hz, Pt satellites). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 158.9, 156.5, 155.5, 155.2, 152.5, 150.7, 135.7, 131.5, 129.6, 129.4, 122.7, 118.7, 118.3, 100.5, 68.1 (<sup>NO<sub>2</sub>bpy</sup> and styrene), -0.8 (s, Pt-CH<sub>3</sub>, <sup>1</sup>J<sub>PC</sub> = 684 Hz, Pt satellites), remaining resonance obscured due to coincidental overlap. Anal. Calcd for PtBN<sub>4</sub>O<sub>4</sub>F<sub>24</sub>C<sub>51</sub>H<sub>29</sub>: C, 43.03; H, 2.05; N, 3.94. Found: C, 43.33; H, 1.92; N, 3.90.

**Catalytic Olefin Hydrophenylation.** A representative catalytic reaction is described. [(<sup>m</sup>bpy)Pt(Ph)(THF)](BAR'<sub>4</sub>) (2a; 0.019 g, 0.013 mmol) was dissolved in 12.0 mL of benzene containing 0.01 mol % (relative to benzene) of hexamethylbenzene (HMB) as an internal standard. The reaction mixture was placed in a stainless steel pressure reactor, charged with ethylene, pressurized to a total of 0.8 MPa with N<sub>2</sub>, and heated to 100 °C. After 4 and 16 h, the reaction mixture was cooled to room temperature and analyzed by GC/MS. Peak areas of the products and the internal standard were used to calculate product yields. Ethylbenzene, diethylbenzene, and styrene amounts were quantified using linear regression analysis of gas chromatograms of standard samples. For example, a set of five known standards were prepared consisting of 2/1, 4/1, 6/1, 8/1, and 10/1 molar ratios of ethylbenzene to HMB in benzene. A plot of the peak area ratios versus molar ratios gave a regression line. For the GC/MS system, the slope and correlation coefficient (*R*<sup>2</sup>) for ethylbenzene were 0.53 and 0.98, respectively. Identical procedures were used to quantify the production of styrene, 1,3-diethylbenzene, 1,4-diethylbenzene, and 1,2-diethylbenzene. The slope and correlation coefficients (*R*<sup>2</sup>) for these species are as follows, respectively: 0.55, 0.99; 0.56, 0.99; 0.56, 0.99; 0.52, 0.99.

**Kinetics of Styrene Formation.** A representative kinetic experiment is described. Complex 3e (0.044 g, 0.029 mmol) and hexamethyldisilane (HMDS, 1.5 μL), an internal standard, were dissolved in 1.0 mL of nitromethane-*d*<sub>3</sub>. The solution was then divided (0.3 mL for each sample) and added to three high-pressure NMR tubes. The tube was pressurized with 0.3 MPa of ethylene and placed into a temperature-equilibrated (45 °C) NMR probe. The temperature of the probe was determined using a solution of 80% ethylene glycol in DMSO-*d*<sub>6</sub>. Kinetic runs were performed in triplicate, and standard deviations are based on the average *k*<sub>obs</sub> values from the three experiments. The concentration of ethylene in solution was determined by integration against the internal standard. <sup>1</sup>H NMR spectra were collected every 10 min with eight scans and a 5.0 s pulse delay. Styrene resonances were integrated against that of HMDS, and from a plot of ln(1 - [styrene]<sub>t</sub>/[starting material]<sub>0</sub>) versus time (seconds) the rate constants were extracted. The rate of formation of styrene from complex 3e, in the presence of 0.34 M C<sub>2</sub>H<sub>4</sub>, was [1.1(2)] × 10<sup>-4</sup> s<sup>-1</sup> with a correlation coefficient (*R*<sup>2</sup>) of 0.99 for each plot.

**Thermolysis of [(<sup>NO<sub>2</sub>bpy</sup>)Pt(CH<sub>2</sub>CH<sub>2</sub>Ph)(<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>)](BAR'<sub>4</sub>) in C<sub>6</sub>H<sub>6</sub>.** In a glass pressure tube, complex 3f (0.024 g, 0.02 mmol) and benzene (4 mL) containing HMB as an internal standard were added. The reaction mixture was heated to 100 °C for 4 h, cooled to room temperature, and analyzed by GC/MS. Only ethylbenzene was detected (in quantitative yield).



## ■ ASSOCIATED CONTENT

## ● Supporting Information

CIF files giving crystallographic data for the crystal structure determinations in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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