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

Bradley A. McKeown,† H. Emanuel Gonzalez,§ Max R. Friedfeld,† Anna M. Brosnahan,† T. Brent Gunnoc,§,† Thomas R. Cundari,§,† and Michal Sabat§

†Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States
§Center for Advanced Scientific Computing and Modeling (CASCaM), Department of Chemistry, University of North Texas, Denton, Texas 76203, United States
§Nanoscale Materials Characterization Facility, Materials Science and Engineering Department, University of Virginia, Charlottesville, Virginia 22904, United States

5 Supporting Information

ABSTRACT: The series of PtII complexes [(bpy)Pt(Ph)(THF)][BAR′]2 (bpy = 2,2′-bipyridyl, X = OMe, Bu, H, Br, CO2Et, NO2; 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.1 While methods for the functionalization of aromatic C–X bonds (X = halide, triflate) have been successfully developed,2,3 atom-economical catalytic olefin hydroarylation (i.e., the addition of aromatic C–H bonds across olefin C=C bonds) offers potential advantages.4,5 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 hydrogenation6 or olefin polymerization7), 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,3,4 and catalysts for deactivated substrates, such as benzene with unfunctionalized olefins, are especially limited.3,4,8 In addition, the oxidative coupling of aromatic C–H bonds with alkynes to form vinyl arenes has typically been restricted to activated olefins.4,9,10

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.6b,7c,9 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 PtII supported by 4,4′-di-tert-butyl-2,2′-bipyridine.12 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 hydroarylation of ethylene for the series of complexes [(bpy)Pt-
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)[[BAR']4] [bpy = 4,4'-X-2,2'-bipyridyl, X = OMe, Bu, H, Br, CO2Et, NO2; 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 [(bpy)Pt(Ph)(THF)][BAR']4 (2a–f) were prepared according to the procedure previously reported for [(bpy)Pt(Ph)(THF)][BAR']4 (2b; bpy = 4,4'-di-tert-butyl-2,2'-bipyridyl) (eq 1).\textsuperscript{2c} All complexes 2 have been isolated in ≥80% yield and characterized by \textsuperscript{1}H and \textsuperscript{13}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 [(bpy)Pt(Ph)(THF)][BAR']4 (2d) (30% probability; H atoms and BAR' 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).](image)

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\textsuperscript{II} bipyridyl and diamine complexes.\textsuperscript{10} 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\textsuperscript{II} catalyzed ethylene hydrophenylation on the basis of previous experimental and computational studies\textsuperscript{2c} is shown in Scheme 2. Catalytic 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

<table>
<thead>
<tr>
<th>X</th>
<th>σ\textsubscript{C–X}</th>
<th>Ethene</th>
<th>Ethanol</th>
<th>Ethanol/σ\textsubscript{C–X}</th>
<th>TOP \textsuperscript{v} (10^4 s\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMe</td>
<td>-0.27</td>
<td>6.4\textsuperscript{h}</td>
<td>0.2</td>
<td>1.5</td>
<td>1.25\textsuperscript{h}</td>
</tr>
<tr>
<td>THF</td>
<td>-0.2</td>
<td>5.7\textsuperscript{h}</td>
<td>0.6</td>
<td>1.0</td>
<td>1.26\textsuperscript{h}</td>
</tr>
<tr>
<td>H</td>
<td>0.0</td>
<td>4.7\textsuperscript{h}</td>
<td>0.4</td>
<td>1.0</td>
<td>1.26\textsuperscript{h}</td>
</tr>
<tr>
<td>CO2Et</td>
<td>0.45</td>
<td>5.3</td>
<td>1.3</td>
<td>0.1</td>
<td>1.14\textsuperscript{h}</td>
</tr>
</tbody>
</table>

\textsuperscript{v}Conditions: 0.01 mol % catalyst dissolved in C\textsubscript{6}H\textsubscript{6} with hexamethylbenzene as an internal standard at 100 °C with 0.1 MPa of ethylene. \textsuperscript{h}Ratio of 1,2, 1,3, and 1,4-diethylbenzene after 4 h. \textsuperscript{h}Turnover frequency calculated on the basis of total turnovers after 4 h. \textsuperscript{h}Turnovers after 4 h as determined by GC/MS. Numbers in parentheses are turnovers after 16 h. Numbers in brackets are TON values after catalyst deactivation.  Reference 7c

2858 dx.doi.org/10.1002/omn1.2013.2858 2859
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 × 10^−4 s^−1) < Bu (TOF: 13.8 × 10^−4 s^−1) < H (TOF: 15.3 × 10^−4 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 ethylenebenzene, 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 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 ethylenebenzene to styrene is influenced by the donor ability of the 4,4′-bipyridyl functional groups. For example, catalysis using complex 2a (OMe, σ_p = −0.27) and 0.1 MPa of ethylene (100 °C) results in an ethylenebenzene/styrene ratio of 27.8 (after 4 h), in comparison to 0.1 for complex 2f (NO_2, σ_p = 0.78). A Hammett plot was constructed using product ratios and the Hammett parameter σ_p (Figure 4).^11

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

The effects of substituted pyridyl ligands are rarely amenable to Hammett correlations, since Hammett σ_p parameters do not accurately reflect substituent effects upon the basicity of pyridine, as the inductive and resonance interactions from the substituents differ from those found in benzoic acids. In addition, π interactions with the metal center influence the correlation. 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 ethylenebenzene to styrene. Using Hammett σ_p parameters as a relative gauge of substituted bipyridyl donation to Pt^III, plots of ethylenebenzene to styrene ratio versus substituent Hammett parameters further demonstrate this trend (Figure 5). Complex 2d (Br, σ_p = 0.23) exhibits an ethylenebenzene/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. Ethylenebenzene/styrene ratios from [(bpy)Pt(PPh)(THF)]^+. catalyzed ethylene hydrophenylation after 4 h at 100 °C with 0.1 and 0.3 MPa of ethylene versus Hammett parameters (σ_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).](image)
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 previously reported for 2b.7c 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 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 >1 equiv (relative to Pt) of styrene requires a hydrogen acceptor. Heating a CD$_2$NO$_2$ solution of complex 2d and benzene under ethylene results in the formation of styrene and ethene, as observed by $^1$H NMR spectroscopy. Confirmation of ethene formation was achieved using isotopically labeled $^{13}$C$_2$H$_4$. In the $^1$H and $^{13}$C NMR spectra, ethene 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. $^1$H NMR spectrum (top) and $^{13}$C NMR spectrum (top inset, $^{13}$C$_2$H$_4$ = 120 Hz) of 13C$_2$H$_4$ in CD$_2$NO$_2$ resulting from the formation of styrene by complex 2d and benzene under $^{13}$C$_2$H$_4$ pressure and the $^{13}$C($^1$H) NMR spectrum (bottom) of an analytically pure sample of C$_6$H$_6$ in a CD$_2$NO$_2$/benzene solution.](image)

The complex [[(bpy)Pt(CH$_2$CH$_2$Ph)(C$_2$H$_4$)]$^+$] (3b) has been shown to be the catalyst resting state using 2b as the catalyst precursor.7c Catalysis using 2a–f was monitored by $^1$H NMR at 90 °C over 4 h to confirm that [[(bpy)Pt(CH$_2$CH$_2$Ph)(C$_2$H$_4$)]]$^+$ is the resting state for each bpy ligand. This species is observed as the catalyst resting state using complexes 2a–e. Note that for complexes 2d,e the insertion product [[(bpy)Pt(CH$_2$CH$_2$Ph)C$_2$H$_4$]]$^+$ is observed but is slowly consumed as the complexes [[(bpy)Pt(4,4'-Et)](C$_2$H$_4$)]$^+$ are formed, as a result of $\beta$-hydride elimination and styrene displacement. The Pt$^4$ ethyl complexes [[(bpy)Pt(4,4'-Et)](C$_2$H$_4$)]$^+$ do not give the production of styrene, as shown by 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 [[(bpy)Pt(CH$_2$CH$_2$Ph)C$_2$H$_4$]] under ethylene pressure in CD$_2$NO$_2$ results in stoichiometric styrene production as well as the formation of [[(bpy)Pt(C$_2$H$_4$)C$_2$H$_4$]]$^+$ 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 [("bpy")Pt(CH₃CH₂Ph)(η²-C₅H₄)]⁺ (X = OMe (3a), "Bu (3b), H (3c), CO₂Et (3e), NO₂ (3f); eq 5)

Table 4. Observed Rate Constants for Stoichiometric Styrene Production from Complexes 3a–3f

<table>
<thead>
<tr>
<th>X</th>
<th>σₓ</th>
<th>kₓ (x 10⁶ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMe</td>
<td>-0.27</td>
<td>0.026(2)</td>
</tr>
<tr>
<td>&quot;Bu</td>
<td>-0.2</td>
<td>0.044(3)</td>
</tr>
<tr>
<td>H</td>
<td>0.0</td>
<td>0.047(2)</td>
</tr>
<tr>
<td>CO₂Et</td>
<td>0.45</td>
<td>1.1(2)</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.78</td>
<td>1.62(2)</td>
</tr>
</tbody>
</table>

* Determined by 'H NMR spectroscopy at 45 °C using hexamethyldisilane as an internal standard. [Pt] = 0.03 M.

were measured by '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 (R² = 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, 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)] x 10⁻⁶ s⁻¹ with 0.3 M ethylene at 45 °C. In contrast, complex 3f produces styrene ~60 times faster with an observed rate constant of [1.6(2)] x 10⁻⁵ 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 rate constants of ethylbenzene/styrene ratios. However, it can be stated definitively that the trend in the rates of stoichiometric styrene production from the five complexes [("bpy")Pt(CH₃CH₂Ph)(η²-C₅H₄)]⁺ (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 PtIII complexes is clearly facilitated by the N-donating pyridyl ligands. The formation of styrene from complexes 3 is likely a multistep reaction involving ethylene dissociation, β-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 β-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 (["bpy"]Pt−
(H)[(η²-styrene)]⁺ (X = 'Bu, NO₂). Attempts to synthesize the PtIII hydrade complexes were unsuccessful. Instead, the PtII methyl complexes (["bpy"]Pt(Me)(η²-styrene)]⁺ (X = 'Bu (5b), NO₂ (5f)) were used as models for the Pt−H variants. Unfortunately, the displacement of styrene by ethylene from both 5b and 5f was too fast for measurement even at −120 °C. The Pt complexes were dissolved in a solvent mixture of CD₂Cl₂, CDC₁₂, and CCl₄ (60/27/13, v/v/v) and then frozen. The tube was pressurized with 0.3 MPa of ethene and allowed to thaw in the spectrometer. The first NMR spectrum showed complete conversion to (["bpy"]Pt(η²-C₆H₆)(Me)]⁺ and free styrene. The structure of [([NC]₂"bpy")Pt(η²-C₆H₆)(Me)]⁺ (6f) is shown in Figure 9.

Figure 9. ORTEP drawing of [([NC]₂"bpy")Pt(η²-C₆H₆)(Me)]⁺ [BaF₂⁺] (50% probability; H atoms and BaF₂⁺ 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 = 77.8(2), N1−Pt−C1 = 173.1(3).

A plausible mechanism for styrene formation is shown in Scheme 3. Ethylene insertion into the Pt−Ph bond results in a β-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 or dissociate ethylene and undergo β-hydride elimination to form (["bpy"]Pt(H)(η²-styrene)]⁺. Displacement of styrene with ethylene completes the process for styrene formation. For most "bpy"Pt complexes (excluding 2aL), we presume that the PtII−H complexes are unstable and result in catalyst decomposition, since only 1 TO of styrene is observed. For X = Br (2d), CO₂Et (2e), ethylene insertion into the Pt−H bond and subsequent benzene C−H activation liberates ethane and regenerates the [(["bpy"]Pt(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 PtII 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 PtII−H complexes that result from β-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 allyl- versus vinyl arene selectivity is potentially useful. For [(["bpy"]Pt(Ph)(THF)]⁺ complexes, we have shown that catalyst selectivity for the production of vinyl arenes versus allyl 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 PtII 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 PtII 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. Gluowbox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer (O₂ <15 ppm for all reactions). Tetrahydrofuran and diethyl ether were dried by distillation over sodium/benzophenone and CaH₂, respectively. n-Pentane was distilled over P₂O₅. Methylene chloride and benzene were purified by passage through a column of activated alumina. Benzene-d₆, acetone-d₆, nitromethane-d₅, and dichloromethane-d₂ were used as received and stored under a N₂ atmosphere over 4 Å molecular sieves. ¹H NMR spectra were recorded using a Varian Mercury 300 or 500 MHz spectrometer or using a Bruker 800 MHz spectrometer. ¹³C 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 ¹H and ¹³C NMR spectra are referenced against residual proton signals (¹H NMR) or the ¹³C resonances (¹³C NMR) of the deuterated solvents. ¹⁹F NMR (282 MHz operating frequency) spectra were obtained on a Varian 300 MHz spectrometer and referenced against an external standard of hexafluoroisobutylene (δ = 164.9 ppm). 

GC/MS was performed using a Shimadzu GCMS-QP2010 Plus system with a 30 m × 0.25 mm SHIRI-SMS column with 0.25 µm film thickness using electron impact ionization. Ethylene (99.99%) was purchased in a gas cylinder from GTS-Wilco and used as received. All other reagents were used as purchased from commercial sources. The
preparation, isolation, and characterization of \([\text{HI})\text{Et}_2\text{CO}\] and \([\text{Ar}']\) (\(\text{Ar}' = 3,5-(\text{CF}_3)\text{C}_6\text{H}_{4}\)).\(^{2,3}\) \([\text{Pt}(\text{Ph})\text{Et}_2\text{Si}]\) \(^{2,4}\) \([\text{Pt}(\text{Ph})\text{H}_2\text{P}]\). (1H \(\text{bpy} = 2,2'\)-bipyridine) \(^{11}\) \([\text{Pt}(\text{Ph})\text{P}][\text{THF}]\) \(^{12}\) \([\text{Pt}][\text{CH}_3\text{C}_6\text{H}_4\text{N}(\text{py})\text{Cl}_2][\text{THF}]\) \(^{13}\) \([\text{NMe}_3]\) \(^{14}\) \([\text{Pt}(\text{Ph})\text{H}_2\text{P}]\). \(\text{bpy} = 2,2'\)-bipyridine; \(\text{bpy} = 4,4'\)-dipyridyl; 2,2'-bipyridine.\(^{10}\) \([\text{Pt}(\text{Ph})\text{P}][\text{THF}]\) \(^{12}\) \([\text{NMe}_3]\) \(^{14}\) \([\text{Pt}(\text{Ph})\text{H}_2\text{P}]\) \(^{13}\) \([\text{NMe}_3]\) \(^{14}\) \([\text{Pt}(\text{Ph})\text{P}][\text{THF}]\) \(^{12}\) \([\text{NMe}_3]\) \(^{14}\) \([\text{Pt}(\text{Ph})\text{H}_2\text{P}]\) \(^{13}\) \([\text{NMe}_3]\)

**General Procedure for the Synthesis of \([\text{bpy}][\text{Pt}][\text{Ph}][\text{THF}][\text{BzAr}']\) \(^{22}\):** 80% isolated yield, 0.148 g. \(\text{H} \) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.24 (d, 1H, \(\text{H}_2\text{bpy}, \gamma_{\text{H}} = 6 \text{ Hz}\)) 7.55 (s, 1H, \(\text{H}_2\text{bpy}, \gamma_{\text{H}} = 2 \text{ Hz}\)) 7.45 (m, 3H, \(\text{H}_2\text{bpy} \text{ and } \text{H}_2\text{P}\)) 7.21 (d, 1H, \(\text{H}_2\text{bpy}, \gamma_{\text{H}} = 6 \text{ Hz}\)) 7.14 (t, 2H, \(\text{H}_2\text{bpy}, \gamma_{\text{H}} = 7 \text{ Hz}\)) 7.04 (m, 1H, \(\text{H}_2\text{P}\)) 6.74 (d, 1H, \(\text{H}_2\text{bpy}, \gamma_{\text{H}} = 7 \text{ Hz}\)) 6.73 (d, 1H, \(\text{H}_2\text{bpy}, \gamma_{\text{H}} = 3 \text{ Hz}\)) 4.12 (m, 4H, \(\alpha\)-THF). \[^{14}\] \(\text{C} \) NMR (126 MHz, CDCl\(_3\)): \(\delta\) 169.0, 166.8, 159.1, 155.5, 155.2, 148.1, 139.2, 136.8, 125.8, 125.3, 112.7, 112.1, 111.2, 110.5 \(\text{bpy} \) and \(\text{Ph}\). 77.8 (\(\alpha\)-THF), 57.3 (\(\text{OCH}_3\)) 57.1 (\(\text{OCH}_2\)), 25.1 (\(\beta\)-THF). Anal. Calc. for \(\text{Pt}[\text{BzAr}']\text{Cl}_2\text{H}_4\text{P}: C\ 45.55, H 2.62, N 1.97.

**General Procedure for the Synthesis of \([\text{bpy}][\text{Pt}][\text{Ph}][\text{THF}][\text{BzAr}']\) \(^{23}\):** 80% isolated yield, 0.201 g. \(\text{H} \) NMR (800 MHz, CDCl\(_3\)): \(\delta\) 8.49 (d, 1H, \(\text{H}_2\text{bpy}, \gamma_{\text{H}} = 5 \text{ Hz}\)) 8.31 (d, 1H, \(\text{H}_2\text{bpy}, \gamma_{\text{H}} = 6 \text{ Hz}\)) 8.24 (d, 1H, \(\text{H}_2\text{bpy}, \gamma_{\text{H}} = 8 \text{ Hz}\)) 7.85 (s, 1H, \(\text{H}_2\text{bpy}, \gamma_{\text{H}} = 8 \text{ Hz}\)) 7.14 (d, 1H, \(\text{H}_2\text{bpy}, \gamma_{\text{H}} = 7 \text{ Hz}\)) 6.81 (m, 1H, \(\text{H}_2\text{P}\)) 4.16 (m, 4H, \(\alpha\)-THF). \[^{14}\] \(\text{C} \) NMR (126 MHz, CDCl\(_3\)): \(\delta\) 169.0, 154.3, 154.3, 145.9, 141.0, 140.5, 138.6, 136.1, 128.7, 128.1, 128.2, 128.1, 127.6, 127.5, 127.5, 122.3 (\(\text{bpy} \) and \(\text{Ph}\)) 58.6 (\(\text{OCH}_2\)). Anal. Calc. for \(\text{Pt}[\text{BzAr}']\text{Cl}_2\text{H}_4\text{P}: C\ 45.80, H 2.44.

**General Procedure for the Synthesis of \([\text{bpy}][\text{Pt}][\text{Ph}][\text{THF}][\text{BzAr}']\) \(^{24}\):** 94% isolated yield, 0.105 g. \(\text{H} \) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.32 (m, 2H, \(\text{H}_2\text{bpy} \text{ and } \text{H}_2\text{P}\)) 8.20 (d, 1H, \(\text{H}_2\text{bpy}, \gamma_{\text{H}} = 2 \text{ Hz}\)) 8.12 (d, 1H, \(\text{H}_2\text{bpy}, \gamma_{\text{H}} = 6 \text{ Hz}\)) 8.00 (s, 1H, \(\text{H}_2\text{bpy}, \gamma_{\text{H}} = 6 \text{ Hz}\)). 7.85 (dd, 1H, \(\text{H}_2\text{bpy}, \gamma_{\text{H}} = 8 \text{ Hz}\)) 7.10 (t, 2H, \(\text{H}_2\text{bpy}, \gamma_{\text{H}} = 6 \text{ Hz}\). 7.09 (m, 1H, \(\text{H}_2\text{P}\)) 4.16 (m, 4H, \(\alpha\)-THF). \[^{14}\] \(\text{C} \) NMR (126 MHz, CDCl\(_3\)): \(\delta\) 160.0, 154.3, 154.3, 145.9, 141.0, 140.5, 138.6, 136.1, 128.7, 128.1, 128.2, 128.1, 127.6, 127.5, 127.5, 122.3 (\(\text{bpy} \) and \(\text{Ph}\)) 58.6 (\(\text{OCH}_2\)). Anal. Calc. for \(\text{Pt}[\text{BzAr}']\text{Cl}_2\text{H}_4\text{P}: C\ 45.80, H 2.44.

**General Procedure for the Synthesis of \([\text{bpy}][\text{Pt}][\text{Ph}][\text{THF}][\text{BzAr}']\) \(^{25}\):** 80% isolated yield, 0.306 g. The solution was then cooled to a stainless steel pressure reactor and pressurized with ethylene (0.3 MPa). After 12 h, the solutions were removed in vacuum 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 dried in vacuum.
Organometallics

[br, s, 1H, bpy], 7.30–7.10 (m, 6H, bpy and Ph), 4.17–3.88
(overlapping resonances, 10H, OMe and C2H6), 2.68 (t, 2H, Pt-
CH2CH2Ph, JHH = 8 Hz), 1.39 (t, 2H, Pt–CH2CH2Ph, JHH = 8 Hz).

1: C NMR (201 MHz, CD2Cl2, δ): 170.69, 164.9, 160.9, 159.5, 156.2,
153.0, 147.5, 144.0, 129.3, 128.9, 128.6, 128.6, 126.1 (bpy and Ph),
69.0 (C5H5), 58.0 (OMe), 57.6 (OMe), 37.7 (CH2CH2Ph), 16.4
(CH3CH2Ph), remaining resonance observed due to coincidental
overlap. Anal. Calc. for Ph3Pb(C6H4)2C5H5: C, 46.07; H, 2.65; N, 1.99.
Found: C, 46.24; H, 2.61; N, 2.11.

{[bpy]PtCH2CH2Ph][{2-C4H4}]2[Cu][Ar] (3): 81% isolated yield, 0.058 g.
H NMR (800 MHz, CD2Cl2): δ 8.80 (br s, 1H, bpy), 8.34–8.22 (br
m, 4H, bpy), 7.84 (br s, 1H, bpy), 7.26 (m, 4H, H2N-Pt), 7.17 (m, 1H, H2P-
Pt), 4.19 (br s, 4H, C4H4), 2.72 (t, 2H, Pt–CH2CH2Ph, JHH = 8 Hz),
1.54 (t, 2H, Pt–CH2CH2Ph, JHH = 8 Hz). 13C NMR (126 MHz,
CD2Cl2, δ): 157.85, 154.1, 148.5, 143.5, 141.4, 130.5, 129.4, 128.6,
126.6, 124.1 (bpy and Ph), 70.6 (C5H5), 57.4 (CH2CH2Ph), 17.0 (CH3CH2Ph),
remaining three resonances observed due to coincidental overlap.
Anal. Calc. for Ph3Pb(C6H4)2C5H5: C, 56.21; H, 2.53; N, 2.08.
Found: C, 56.61; H, 2.41; N, 2.19.

{[bpy]PtCH2CH2Ph][{2-C4H4}]2[Cu][Ar] (3): 88% isolated yield, 0.127 g.
H NMR (300 MHz, CD2Cl2, δ): 8.90 (m, 3H, bpy), 8.28 (m,
3H, bpy), 7.26 (m, 3H, Ph), 4.54 (overlapping m, 4H, OCH2CH2),
4.30 (br s, 4H, C4H4), 3.48 (br s, 4H, C4H4), 1.71 (t, 2H, Pt–CH2CH2Ph,
JHH = 8 Hz), 1.60 (t, 2H, Pt–CH2CH2Ph, JHH = 8 Hz), 1.47 (overlapping
m, 4H, OCH2CH2), 1.41 (s, 3H, OMe). 13C NMR (201 MHz,
CD2Cl2, δ): 157.85, 154.75, 149.86, 146.39, 143.52, 142.89, 129.2,
128.6, 128.3, 128.6, 124.2 (bpy and Ph), 71.9 (C5H5), 64.2
(OCH2CH2), 52.2 (OCH2CH2), 11.2 (CH2CH2Ph), 14.3 (CH3CH2Ph),
remaining five resonances observed due to coincidental overlap.
Anal. Calc. for Ph3Pb(C6H4)2C5H5: C, 64.69; H, 2.78; N, 1.88.
Found: C, 64.90; H, 2.78; N, 2.00.

{[bpy]Pt([CH2CH2Ph][{2-C4H4}]2[Cu][Ar] (3): 87% isolated yield,
0.108 g. H NMR (300 MHz, CD2Cl2, δ): 9.14 (d, 1H, NO2
bpy, JHH = 2 Hz), 8.57 (br m, 2H, NO2bpy), 7.28 (br d, 2H, H2P-
Pt, JHH = 7 Hz), 7.23–7.06 (m, 3H, H2N-Pt, and Ph), 4.42 (br s, 4H, NO2bpy),
2.70 (t, 2H, Pt–CH2CH2Ph, JHH = 7 Hz), 1.71 (t, 2H, Pt–CH2CH2Ph,
JHH = 7 Hz), remaining NO2bpy signals obscured due to broadening
or coincidental overlap. 13C NMR (201 MHz, CD2Cl2, δ):
152.32, 149.11, 142.3, 128.9, 128.3, 126.8, 123.3, 118.2 (NO2bpy
and Ph), 68.1 (C4H4), 37.0 (CH2CH2Ph), 18.0 (CH3CH2Ph), remaining
five resonances observed due to coincidental overlap. Anal. Calc. for
Ph3Pb(C6H4)2C5H5: C, 64.43; H, 2.18, N, 3.30. Found: C, 43.73; H,
2.15; N, 3.86.

Synthesis of {[Me]Pt(bu-SEt)2} (1.052 g, 0.834 mmol) and NO2bpy (0.4125 g,
1.68 mmol) in dichloroethane 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 vacuum to afford a purple solid (0.737 g, 94%). 1H
NMR (300 MHz, acetone-d6, δ): 9.78 (d, 2H, H2N-Pt, JHH = 6 Hz, JHH =
21 Hz, Pt satellites), 9.44 (d, 2H, H2P-OEt, JHH = 7 Hz), 8.53 (dd, 2H,
H2NO2bpy, JHH = 6 Hz, JHH = 2 Hz), 1.38 (s, 6H, Pt–CH2PH2, JHH =
91 Hz, Pt satellites). The complex was too insoluble in organic
solvents to obtain 13C NMR data. Anal. Calc. for Ph3Pb(C6H4)2C5H5:
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 {[bpy]Pt(Me)(2-
styrene)[Ar] (x = 'Bu, NO2). A solution of [bpy]Pt(Me)(2-
ethylene) in dichloromethane (30 mL) was cooled to approximately
−70 °C. One equivalent of [(EtOH)][{Ar}2] 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.

{[bpy]Pt(Me)(2-styrene)[Ar] (x): 87% isolated yield, 0.064 g.
H NMR (300 MHz, CD2Cl2, δ): 8.66 (d, 1H, H2P-OEt, JHH = 6 Hz,
JHH = 48 Hz, Pt satellites), 8.17 (s, 1H, H2P-OEt), 8.09 (s, 1H,
H2P-OEt), 7.85 (m, 3H, bpy), 7.59 (m, 2H, H2P-OEt), 7.55 (m, 3H, H2P-

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.

AUTHOR INFORMATION

Corresponding Author
E-mail: tbg77@virginia.edu (T.B.G.); tjunt@leeds.ac.uk (T.R.C.).

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

T.B.G. and T.R.C. acknowledge The Office of Basic Energy Sciences, U.S. Department of Energy, for support of this work (DE-SC0000776 and DE-FG02-03ER15387). T.B.G. acknowledges the National Science Foundation for the purchase of X-ray diffraction instrumentation at the University of Virginia (CHE-1126602).

REFERENCES


