Phosphine and *N*-Heterocyclic Carbene Ligands on Pt(II) Shift Selectivity from Ethylene Hydrophenylation toward Benzene Vinylation

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Dedicated in memory of Prof. A. E. Shilov and his many seminal contributions to the fields of organometallic chemistry and catalysis

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ABSTRACT: A series of Pt(II) complexes of the type [(L~L)Pt(L')(Ph)][BAR'₄] (L~L = 1,2-bis(dimethylphosphino)ethane, 1,2-bis(diphenylphosphino)ethane, (*N*-pyrrolyl)₂P(CH₂)₂P(*N*-pyrrolyl)₂, 1,3-bis(diphenylphosphino)propane, 1,1'-bis(diphenylphosphino)ferrocene, (bis-(diphenylphosphino)methyl)methylamine, 8-(diisopropylphosphino)quinoline, 1,1'-methylene-3,3'-di-*tert*-butylimidazol-2,2'-diylidene); L' = THF or NCMe) has been synthesized and fully characterized. These complexes were screened as catalysts for ethylene hydrophenylation to yield ethylbenzene. All of the complexes exhibited selectivity for styrene production with low catalytic turnover. DFT calculations have been used to model reactivity of the [(dmpe)Pt(L)(Ph)][BAR'₄] (dmpe = 1,2-bis(dimethylphosphino)ethane). It is shown that selective styrene formation is a result of a calculated $\Delta\Delta G^\ddagger$ of 5 kcal/mol for the benzene C–H activation step in the catalytic cycles for styrene versus ethylbenzene formation.

Introduction

Alkyl arenes, such as ethylbenzene, are produced in large quantities from olefins and arenes using Friedel-Crafts (e.g., AlCl₃ and HF) or zeolite catalysts.^{1,2} These acid-mediated catalysts for olefin hydroarylation operate by activation of the olefin toward electrophilic aromatic substitution.³ Transition metal complexes have been demonstrated to catalyze olefin hydroarylation by a different mechanism that involves olefin insertion into a metal–aryl bond followed by aromatic C–H activation (Scheme

1).^{4–9} Such catalysts offer potential advantages over acid-mediated systems, such as reduced polyalkylation, control of linear:branched selectivity for the hydroarylation of α -olefins, control of the regioselectivity for the synthesis of dialkyl arenes, and direct oxidative olefin hydroarylation to produce vinyl arenes in one step.^{4,7,10} In some cases, the use of Pt(II) precursors has been demonstrated to initiate olefin hydroarylation by *in situ* generation of a Brønsted acid, which then catalyzed Friedel-Crafts aromatic alkylation.^{11,12}

Pt(II) complexes have been demonstrated to initiate C–H activation as well as mediate insertion reactions of olefins and alkynes.^{13–22} Our group has been studying Pt(II) complexes of the type [(N~N)Pt(THF)(Ph)][BAR'₄] (N~N = bis-chelating dipyriddy ligand, Ar' = 3,5-bis(trifluoromethyl)phenyl), which have been found to be active catalysts for ethylene hydrophenylation to yield ethylbenzene.^{4,23–28} In addition to ethylbenzene, the formation of styrene is typically observed when using these Pt(II) complexes as catalysts. For the [(N~N)Pt(THF)(Ph)][BAR'₄] catalysts, the formation of styrene is proposed to occur via β -hydride elimination from [(N~N)Pt(CH₂CH₂Ph)]⁺ intermediates followed by styrene dissociation. The formation of styrene appears to be linked with catalyst deactivation, which might occur through the decomposition of the Pt(II)–H intermediates (Scheme 1).^{23,29,30} We found that variation of the 4,4'-substituents of 2,2'-bipyridyl (bpy) ligands in a series of Pt(II) complexes of the type [(^obpy)Pt(L')(Ph)]⁺ (^obpy = 4,4'-X-2,2'-bipyridyl; L' = THF or NCMe) results in a systematic change in the ratio of ethylbenzene to styrene.²⁵ As the substituents in the 4,4'-position became more electron withdrawing, styrene formation becomes more competitive with ethylbenzene production.

Based on the trend in ethylbenzene/styrene ratio for the 4,4'-substituted bpy-supported catalysts, $[(^4\text{bpy})\text{Pt}(\text{THF})(\text{Ph})]^+$, we hypothesized that strongly donating phosphine and *N*-heterocyclic carbene (NHC) ligands on Pt(II) would favor ethylbenzene over styrene formation. Given the possible link between formation of styrene and catalyst decomposition,²³ it was anticipated that phosphine or NHC-ligated catalysts could show enhanced longevity compared to catalysts supported by 2,2'-bipyridyl ligands. Herein, we report the synthesis and characterization of a series of Pt(II) complexes of the type $[(\text{L}\sim\text{L})\text{Pt}(\text{L}')(\text{Ph})][\text{BAR}'_4]$ ($\text{L}' = \text{NCMe}$ or THF) in which $\text{L}\sim\text{L}$ is a bidentate phosphine or NHC ligand and an assessment of their activity as pre-catalysts for the vinylation of benzene.

Scheme 1. Simple mechanism for transition metal catalyzed hydrophenylation of ethylene and vinylation of benzene.

Results and Discussion

Scheme 2 shows the newly synthesized Pt(II) complexes with bidentate phosphine or NHC ligands that were screened for catalytic vinylation of benzene under 0.1 MPa of ethylene at 100 °C. The catalyst precursors were prepared by reaction of $[\text{Pt}(\text{Ph})_2(\mu\text{-Et}_2\text{S})]_2$ with the appropriate ligand to give $(\text{L}\sim\text{L})\text{Pt}(\text{Ph})_2$ complexes. Protonation of one of the phenyl ligands of $(\text{L}\sim\text{L})\text{Pt}(\text{Ph})_2$ gives the desired cationic Pt(II) complexes $[(\text{L}\sim\text{L})\text{Pt}(\text{L}')(\text{Ph})]^+$.²³

Scheme 2. Synthesis of Pt(II) complexes of type $[(\text{L}\sim\text{L})\text{Pt}(\text{L}')(\text{Ph})][\text{BAR}'_4]$.

The Pt(II) complexes **1-8** were tested for catalytic vinylation of benzene (Table 1). The catalyst precursors (0.01 mol % relative to benzene) were dissolved in benzene with hexamethylbenzene added as an internal standard, and the solutions were transferred to high-pressure reactors. The reactors were pressurized with 0.1 MPa ethylene and 0.8 MPa dinitrogen and heated to 100 °C. Catalytic activity was evaluated after 4 and 16 hours using GC/MS. Previous work has shown these conditions to be optimal for related Pt(II) catalysts.²³⁻²⁵ Under these conditions, catalyst precursors with bisphosphine ligands (complexes **1-6**) showed < 0.1 equivalents of ethylbenzene. Styrene was the dominant product for all of the catalyst precursors **1-6**. In all cases, ≤ 2 turnovers (TO) of styrene were observed after 4 hours at 100 °C. Styrene production was most efficient using **1**, which gave ~ 1.5 TO and ~ 3.3 TO of styrene after 4 and 16 h, respectively.

Table 1. Turnovers of styrene from vinylation of benzene.^a

Complex	TO (4 h)	TO (16 h)
1	1.5	3.3
2	1.9	2.0
3	0.9	0.9
4	1.5	1.8
5	1.2	1.4
6	1.2	1.3
7	n.d. ^b	n.d.
8	0.1	0.1

^a Using 0.01 mol% [Pt] in benzene with hexamethylbenzene as an internal standard at 100 °C under 0.1 MPa C_2H_4 . TOs determined by GC/MS. ^b n.d. = not detected.

A mixed phosphine-pyridyl chelate system was studied. The quinoline based complex $[(\text{diq})\text{Pt}(\text{THF})(\text{Ph})][\text{BAR}'_4]$ (**7**) ($\text{diq} = 8$ -diisopropylphosphino)quinoline) was synthesized. A crystal of the diphenyl precursor, $(\text{diq})\text{Pt}(\text{Ph})_2$ (**9**), was obtained by slow evaporation of a diethyl ether solution. The structure of **9** is presented in Figure 1. The P1-Pt-N1 bond angle is $83.01(7)^\circ$ which is consistent with other Pt(II) systems with a bidentate pyridine and phosphine ligand.³¹ The Pt-N1 bond is 0.12 Å shorter than the Pt-P1 bond, and the Pt-C1 bond is 0.04 Å shorter than the Pt-C7 bond, indicating a stronger trans influence of the phosphine group relative to the quinoline unit. Attempted hydrophenylation of ethylene using complex **7** did not yield ethylbenzene or styrene under a variety of conditions.

Figure 1. ORTEP of $(\text{diq})\text{Pt}(\text{Ph})_2$ ($\text{diq} = 8$ -diisopropylphosphino)quinoline (**9**) (50% probability; H atoms omitted for clarity). Selected bond lengths (Å): Pt-P1 2.2739(7), Pt-N1 2.152(2), Pt-C1 2.011(3), Pt-C7 2.051(3). Selected bond angles ($^\circ$): P1-Pt-N1 $83.01(7)$, C1-Pt-C7 $89.1(1)$.

Complex **8** was prepared to study the influence of a chelating NHC ligand. Similar to alkyl phosphines, NHC ligands are strongly donating.³² At 0.1 MPa ethylene and 100 °C, complex **8** produced only trace amounts of styrene (~0.1 TO) and ethylbenzene after 16 h. The number of TO observed for complex **8** was lower than any of the bisphosphine complexes (**1-6**).

Scheme 3. Catalytic cycle A energy landscape (kcal/mol).

As discussed above, for $[(N\sim N)Pt(L)(Ph)]^+$ catalysts, previous results indicate that decreasing the donor ability of 2,2'-dipyridyl ligands results in a decrease in the selectivity for ethylbenzene over styrene. Interestingly, all catalyst precursors **1-8** are selective for styrene. In fact, for most complexes **1-8** negligible or no ethylbenzene is observed. Computational modeling has been used to study and understand transition metal mediated C–H activation.³³ Thus, in order to better understand the source of this selectivity, we examined intermediates and transition states along the reaction pathway for styrene formation catalyzed by the cationic $(dmpe)Pt(NCMe)Ph$ complex using M06 density functional theory calculations.^{34,35} All calculations were performed using Gaussian 09.³⁶ All structures were optimized with the M06/LANL2DZ(6-31G(d,p)) (small) method in an SMD benzene solvent model.³⁷ Energies were further refined with the LANL2TZ(f)(6-311+G(2df,pd)) (large) basis set. Thermodynamic corrections were applied at 298 K and 1 atm. Solvated free

energies are the sum of $\Delta E_{large} + \Delta E_{(ZPE_{small})} + \Delta H_{small} - T\Delta S_{small} + \Delta G_{solv(small)}$.

The first mechanism we explored for styrene formation is the mechanism previously proposed for the $[(^t\text{bpy})Pt(L')(Ph)]^+$ (^tbpy = 4,4'-di-tert-butyl-2,2'-bipyridyl) catalyst,¹⁸ which gives predominately ethylbenzene and a small amount of styrene. The free-energy landscape for this mechanism (catalytic cycle A) is shown in Scheme 3. The reaction pathway begins with NCMe dissociation from $[(dmpe)Pt(NCMe)(Ph)]^+$ and ethylene coordination to give $[(dmpe)Pt(C_2H_4)(Ph)]^+$. This dissociative

pathway for NCMe loss requires $\Delta G = 20.5$ kcal/mol to access three-coordinate $[(dmpe)Pt(Ph)]^+$. Ethylene coordination is almost as favorable as NCMe coordination, and the formation of $[(dmpe)Pt(C_2H_4)(Ph)]^+$ from $[(dmpe)Pt(NCMe)(Ph)]^+$ intermediate is only slightly endergonic. Phenyl group migratory insertion into ethylene via **TS1** requires $\Delta G^\ddagger = 20.2$ kcal/mol relative to the starting $[(dmpe)Pt(NCMe)(Ph)]^+$ complex and 15.7 kcal/mol relative to $[(dmpe)Pt(C_2H_4)(Ph)]^+$. This reaction step is exergonic and the resulting $(dmpe)Pt(CH_2CH_2Ph)$ is $\Delta G = -4.5$ kcal/mol. This intermediate has several possible coordination modes with the formally vacant Pt coordination site. The lowest energy intermediate involves π -coordination of the phenyl group to the Pt metal center. Rearrangement of the CH_2CH_2Ph group allows a CH–Pt metal interaction in preparation for β -hydride elimination via **TS2** with $\Delta G^\ddagger = 8.8$ kcal/mol relative to $[(dmpe)Pt(CH_2CH_2Ph)]^+$ with π -coordination. This reaction step forms the product styrene and a Pt–H bond. Styrene liberation to give a three-coordinate Pt-hydride requires 21.6 kcal/mol of free energy.

Scheme 4. Possible catalytic cycles for styrene formation.

Catalytic turnover in this mechanism is accomplished by coordination of ethylene to give $[(\text{dmpe})\text{Pt}(\text{C}_2\text{H}_4)\text{H}]^+$, which has a calculated $\Delta G = -5.5$ kcal/mol relative to the starting complex $[(\text{dmpe})\text{Pt}(\text{NCMe})(\text{Ph})]^+$. The free-energy barrier for hydride migratory insertion into ethylene requires only 4.7 kcal/mol via **TS3**. The resulting $[(\text{dmpe})\text{Pt}(\text{Et})]^+$ intermediate with a weak CH-Pt interaction then coordinates benzene and undergoes C–H activation via a σ -bond metathesis transition state **TS4**. The resulting $[(\text{dmpe})\text{Pt}(\text{ethane})(\text{Ph})]^+$ intermediate can readily lose ethane to generate the three-coordinate $[(\text{dmpe})\text{Pt}(\text{Ph})]^+$ intermediate or reform the original $[(\text{dmpe})\text{Pt}(\text{NCMe})(\text{Ph})]^+$ complex. **TS4** has a calculated $\Delta G^\ddagger = 21.7$ kcal/mol relative to $[(\text{dmpe})\text{Pt}(\text{C}_6\text{H}_6)(\text{Et})]^+$. Inspection of the entire free-energy surface for catalytic cycle A suggests that **TS4** likely controls the rate of turnover for styrene production since formation of $[(\text{dmpe})\text{Pt}(\text{C}_2\text{H}_4)\text{H}]^+$ is exergonic and the relatively large barrier for benzene C–H activation. Overall, for the vinylation of benzene to form styrene the net reaction is: 2 ethylene + benzene $\rightarrow$ styrene + ethane where $\Delta G = -20.2$ kcal/mol and $\Delta G^\ddagger = 27.5$ kcal/mol.

Alternative to the σ -bond metathesis transition state **TS4**, there is the possibility of a two-step oxidative addition/reductive elimination reaction sequence for transformation of $[(\text{dmpe})\text{Pt}(\text{C}_6\text{H}_6)(\text{Et})]^+$ to $[(\text{dmpe})\text{Pt}(\text{C}_2\text{H}_6)(\text{Ph})]^+$. However, this oxidative addition transition state requires $\Delta G^\ddagger = 32.4$ kcal/mol relative to $[(\text{dmpe})\text{Pt}(\text{C}_6\text{H}_6)(\text{Et})]^+$. This significant preference for a σ -bond metathesis transition state versus an oxidative addition transition state is different from the $(^x\text{bpy})\text{Pt}$ catalysts where these two types of transition states are very similar in energy.¹⁸

Catalytic cycle B shown in Scheme 4 provides an alternative route for styrene formation. In this catalytic reaction mechanism there is also a migratory insertion step via **TS1**. However, instead of β -hydride elimination via **TS2**, ethylene coordinates to give $[(\text{dmpe})\text{Pt}(\text{C}_2\text{H}_4)(\text{CH}_2\text{CH}_2\text{Ph})]^+$. Note that the related complex, $[(^t\text{bpy})\text{Pt}(\text{C}_2\text{H}_4)(\text{CH}_2\text{CH}_2\text{Ph})]^+$, has been proposed as the resting state in catalytic ethylene hydrophenylation using $[(^t\text{bpy})\text{Pt}(\text{THF})(\text{Ph})]^+$ as the catalyst precursor.¹⁸ From this intermediate, β -hydride transfer via **TS5** results in the $[(\text{dmpe})\text{Pt}(\text{styrene})(\text{Et})]^+$ intermediate. Subsequent styrene dissociation and benzene C–H activation via **TS4** finalizes catalytic cycle B. The turnover controlling step in catalytic cycle B is the β -hydride transfer transition state **TS5** with a $\Delta G^\ddagger = 31.2$

kcal/mol relative to $[(\text{dmpe})\text{Pt}(\text{C}_2\text{H}_4)(\text{CH}_2\text{CH}_2\text{Ph})]^+$. This $\Delta G^\ddagger$ is 9.2 kcal/mol larger than the calculated $\Delta G^\ddagger$ for **TS4** in catalytic cycle A and therefore cycle B can be ruled out.

As an alternative to using a second equivalent of ethylene to react with the Pt-hydride complex $[(\text{dmpe})\text{Pt}(\text{H})]^+$ to regenerate the Pt-phenyl intermediate, we also examined the catalytic cycle where the Pt-hydride directly reacts with benzene. This mechanism (catalytic cycle C) is depicted in Scheme 5. In this mechanism $[(\text{dmpe})\text{PtH}]^+$ coordinates with benzene to form $[(\text{dmpe})\text{Pt}(\text{C}_6\text{H}_6)\text{H}]^+$, where $\Delta G = 7.3$ kcal/mol relative to $[(\text{dmpe})\text{Pt}(\text{NCMe})(\text{Ph})]^+$. The key transition state in catalytic cycle C is the σ -bond metathesis transition state **TS6** that converts $[(\text{dmpe})\text{Pt}(\text{C}_6\text{H}_6)\text{H}]^+$ into $[(\text{dmpe})\text{Pt}(\text{H}_2)(\text{Ph})]^+$. The $\Delta G^\ddagger$ for **TS6**, relative to $[(\text{dmpe})\text{Pt}(\text{NCMe})(\text{Ph})]^+$, is 30.2 kcal/mol. This free-energy barrier is ~ 8 kcal/mol larger than **TS4** and therefore catalytic cycle C is also ruled out.

To understand the preference for styrene formation versus ethylbenzene formation we also examined the free-energy landscape for the catalytic cycle shown in Scheme 6. This catalytic cycle is the same as that proposed for hydrophenylation of ethylene with the $[(^x\text{bpy})\text{Pt}(\text{L}')(\text{Ph})]^+$

Scheme 5. Catalytic cycle C for styrene formation.

catalysts.^{12,14} The first step in this catalytic cycle is identical to catalytic cycle A where $[(\text{dmpe})\text{Pt}(\text{Ph})]^+$ is transformed into $[(\text{dmpe})\text{Pt}(\text{CH}_2\text{CH}_2\text{Ph})]^+$. At this stage of the catalytic cycle benzene then coordinates to the Pt metal center and C–H activation occurs via **TS7** to generate ethylbenzene and reform $[(\text{dmpe})\text{Pt}(\text{Ph})]^+$. Similar to the benzene C–H activation in catalytic cycle A, the lowest energy C–H activation transition state, **TS7**, occurs via a σ -bond metathesis pathway rather than an oxidative addition transition state. Also similar to catalytic cycle A, analysis of the free-energy landscape indicates that the turnover-controlling step for ethylbenzene formation is likely **TS7**. Because of similar turnover-controlling steps, it is possible to directly compare the energetics of catalytic cycle A versus the hydrophenylation catalytic cycle. Scheme 7 shows abbreviated free-energy landscapes that compare the C–H activation steps for these catalytic cycles. Transition state **TS7** has a $\Delta G^\ddagger = 27.0$ kcal/mol. This is 5.3 kcal/mol higher in free energy than **TS4** and accounts for the preference for styrene formation versus ethylbenzene formation.

Scheme 6. Hydrophenylation catalytic cycle examined.

Scheme 7. Abbreviated free-energy surface that compares the C–H activation transition states for catalytic cycle A and the hydroarylation catalytic cycle.

Conclusions

Opposite to the trend observed for most $(^x\text{bpy})\text{Pt}(\text{II})$ complexes, catalysts supported by phosphine or NHC ligands are selective for the production of styrene over ethylbenzene. These new Pt(II) complexes are not long-lived, providing only a few TO of styrene in the best cases. A likely explanation is the instability of Pt-hydride intermediates that result from β -hydride elimination from $[(\text{L-L})\text{Pt}(\text{CH}_2\text{CH}_2\text{Ph})]^+$ intermediates. Computational modeling of possible catalytic cycles for styrene and ethylbenzene production using the $[(\text{dmpe})\text{Pt}(\text{NCMe})\text{Ph}]^+$ catalyst precursors provides an explanation for the selective formation of styrene in preference to ethylbenzene. The calculated rate limiting steps for the two catalytic cycles both involve benzene C–H activation. For ethylbenzene formation, the benzene C–H activation step is initiated by the $[(\text{dmpe})\text{Pt}(\text{C}_6\text{H}_6)(\text{CH}_2\text{CH}_2\text{Ph})]^+$ complex and involves proton transfer from benzene to the phenethyl ligand by σ -bond metathesis. For styrene production, the rate limiting step is benzene C–H activation by $[(\text{dmpe})\text{Pt}(\text{C}_6\text{H}_6)(\text{Et})]^+$, again by a σ -bond metathesis process. The calculated $\Delta\Delta G^\ddagger$ for these two C–H activations is 5.3 kcal/mol, indicating a substantial kinetic advantage for the activation by $[(\text{dmpe})\text{Pt}(\text{C}_6\text{H}_6)(\text{Et})]^+$, which is in the styrene catalytic cycle. Perhaps somewhat counterintuitive, these results indicate that the bias for ethylbenzene vs. styrene production, as a function of ancillary ligand, is not a result of the relative energetics for the various steps that lead to styrene formation, but rather the energetics for the benzene C–H activation step that reforms the active catalyst. Future work will seek to establish the generality of these circumstances that control the selectivity of vinyl arene versus alkyl arene formation.

Experimental Section

General Methods. Unless otherwise noted, all procedures were performed in a nitrogen-filled glovebox or by using standard Schlenk techniques. All glovebox reactions were performed where $\text{O}_2 < 15$ ppm as monitored by an oxygen analyzer. Tetrahydrofuran and diethyl ether were distilled over sodium/benzophenone and CaH_2 , respectively. *n*-Pentane was distilled over P_2O_5 . Methylene chloride and benzene were dried by passage through a column of activated alumina. Acetone- d_6 , dichloromethane- d_2 , and acetonitrile- d_3 were used as received and stored under a N_2 atmosphere over 4 Å molecular sieves. ^1H NMR spectra were recorded with a Varian Mercury 300 or 500 MHz spectrometer or a Bruker 800 MHz spectrometer. ^{13}C NMR spectra were recorded with a Bruker 800 MHz spectrometer (201 MHz operating frequency). All ^1H and ^{13}C NMR spectra are referenced against residual ^1H or ^{13}C resonances of the deuterated solvents. ^{31}P NMR spectra were obtained with a Varian Mercury 300 MHz spectrometer (121 MHz operating frequency) and referenced against the external standard H_3PO_4 ($\delta = 0$). GC/MS was performed using a Shimadzu GCMS-QP2010 Plus system with simulated electron impact or electron impact ionization. Ethylene (99.5%) was purchased from GTS-Welco and used as received. All other reagents were used as received from commercial sources. The synthesis of $(N\text{-pyrrolyl})_2\text{P}(\text{CH}_2)_2\text{P}(N\text{-pyrrolyl})_2$ (bppe),³⁸ bis-(diphenylphosphino)methylmethylamine (bma),³⁹ 8-(diisopropylphosphino)quinoline (diq),⁴⁰ 1,1'-methylene-3,3'-di-*tert*-butylimidazol-2,2'-diylidene (D'BuC),⁴¹ $(\text{dmpe})\text{Pt}(\text{Ph})_2$ ($\text{dmpe} = 1,2\text{-bis}(\text{dimethylphosphino})\text{ethane}$),⁴² $(\text{dppp})\text{Pt}(\text{Ph})_2$ ($\text{dppp} = 1,3\text{-bis}(\text{diphenylphosphino})\text{propane}$),⁴³ $(\text{dppe})\text{Pt}(\text{Ph})_2$ ($\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$),⁴⁴ and $(\text{dppf})\text{Pt}(\text{Ph})_2$ ($\text{dppf} = 1,1'\text{-bis}(\text{diphenylphosphino})\text{ferrocene}$)⁴⁵ were previously reported.

General procedure for the synthesis of $(\text{L}_2)\text{PtPh}_2$ complexes. Two equivalents of the appropriate ligand (L_2) were added to $[\text{Pt}(\text{Ph})_2(\mu\text{-Et}_2\text{S})_2]$ in Et_2O (30 mL). The solution was stirred at

room temperature for 12 h, after which it was reduced *in vacuo* and hexanes were added (~20 mL). The suspension was filtered and the solid was washed with Et₂O (5 mL) and hexanes (2 x 5 mL) and dried under vacuum.

(diq)Pt(Ph)₂ (9). L₂ = 8-(diisopropylphosphino)quinoline. Isolated 0.13 g (85%). ¹H NMR (600 MHz, CD₂Cl₂) δ 8.97 (dd, ³J_{HH} = 5 Hz, ⁴J_{HH} = 2 Hz, 1H, diq), 8.46 (d, ³J_{HH} = 8 Hz, 1H, diq), 8.06 (td, ³J_{HH} = 7 Hz, ³J_{HH} = 1 Hz, 1H, diq), 8.03 (d, ³J_{HH} = 8 Hz, 2H, H_o-Ph), 7.74 (t, ³J_{HH} = 8 Hz, 1H, diq), 7.54 (t, ³J_{HH} = 8 Hz, 1H, diq), 7.48 (d, ³J_{HH} = 8 Hz, 2H, H^o-Ph), 7.32 (dd, ³J_{HH} = 8 Hz, ³J_{HH} = 5 Hz, 1H, diq), 7.09 (m, 2H, H^m-Ph), 6.88 (m, 3H, H^m and H^p-Ph), 6.70 (m, 1H, H^p-Ph), 2.66 (m, 2H, CH-ⁱPr), 1.18 (d, ³J_{HH} = 7 Hz, 3H, Me-ⁱPr), 1.16 (d, ³J_{HH} = 7 Hz, 3H, Me-ⁱPr), 0.96 (d, ³J_{HH} = 7 Hz, 3H, Me-ⁱPr), 0.93 (d, ³J_{HH} = 7 Hz, 3H, Me-ⁱPr). ³¹P NMR (121 MHz, CD₂Cl₂) δ 41.58 (s, ¹J_{PP} = 1937 Hz, Pt satellites). ¹³C NMR (201 MHz, dichloromethane-*d*₂) δ 175.75, 175.54, 155.54, 153.84, 138.83, 138.14, 137.86, 137.25, 135.74, 131.56, 130.33, 127.90, 127.78, 127.05, 123.44, 122.36, 120.69, 23.53, 23.41, 17.86, 17.35. Anal. calcd. for PtNPC₂₇H₃₀ (%): C 54.53, H 5.09, N 2.36; found: C 54.38, H 5.26, N 2.30.

(bppe)Pt(Ph)₂. L₂ = 1,2-(bis-*N*-pyrrolylphosphino)ethane. Isolated 0.17 g (72%). ¹H NMR (800 MHz, acetone-*d*₆) δ 7.31 (m, 4H, H^o-Ph), 7.01 (m, 8H, β-*N*-pyrrolyl), 6.90 (t, ³J_{HH} = 8 Hz, 4H, H^m-Ph), 6.75 (tt, ³J_{HH} = 8 Hz, ⁴J_{HH} = 1 Hz, 2H, H^p-Ph), 6.30 (m, 8H, β-*N*-pyrrole), 2.80 (d, ²J_{PH} = 22 Hz, 4H, CH₂-bppe). ³¹P NMR (121 MHz, acetone-*d*₆) δ 108.37 (¹J_{PP} = 2123 Hz, Pt satellites). ¹³C NMR (201 MHz, acetone-*d*₆) δ 157.45 (dd, 142.01 MHz, 20.50 MHz), 137.45, 128.31, 124.48, 123.56, 113.85, 31.63 (CH₂CH₂). Anal. calcd. for PtN₄P₂C₃₀H₃₀ (%): C 51.20, H 4.31, N 7.96; found: C 51.35, H 4.58, N 7.57.

(bma)Pt(Ph)₂. L₂ = (Bis-(diphenylphosphino)methyl)methylamine. Isolated 0.62 g (91%). ¹H NMR (500 MHz, acetone-*d*₆) δ 7.57 (m, 8H, bma), 7.36 (m, 12H, bma), 6.97 (m, 4H, H^o-Ph), 6.44 (t, ³J_{HH} = 7 Hz, 4H, H^m-Ph), 6.31 (t, ³J_{HH} = 7 Hz, 2H, H^p-Ph), 3.59 (s, ³J_{PH} = 14 Hz Pt satellites, 4H, CH₂-bma), 2.32 (s, 3H, Me-N). ³¹P NMR (121 MHz, acetone-*d*₆) δ -4.94 (s, ¹J_{PP} = 1693 Hz, Pt satellites). ¹³C NMR (201 MHz, acetone-*d*₆) δ 162.11 (dd 113.38 MHz, 15.33 MHz), 137.57, 134.43, 132.95, 130.62, 128.66, 126.92, 121.13, 60.09, 51.59. Anal. calcd. for PtN₂C₃₉H₃₇ (%): C 60.30, H 4.81, N 1.80; found: C 60.45, H 4.73, N 1.92.

(D^tBuC)Pt(Ph)₂. L₂ = 1,1'-methylene-3,3'-di-*tert*-butylimidazol-2,2'-diylidene. The synthesis of this complex was taken from a reported preparation for the bis-methyl Pt(II) equivalent.⁴¹ Ag₂O (0.370 g, 1.60 mmol) and D^tBuC (0.169 g, 0.40 mmol) were mixed in DCM at room temperature. After 45 min, [Pt(Ph)₂(μ-SEt₂)₂] (0.176 g, 0.20 mmol) was added to the solution and allowed to stir for 2 h. The mixture was passed through celite and the volatiles were removed *in vacuo* to afford a white solid (0.139 g, 57%). ¹H NMR (300 MHz, acetone-*d*₆) δ 7.51 (d, ³J_{HH} = 7.90 Hz, ³J_{PH} = 28.83 Hz, 4 H, *o*-phenyl), 7.45 (m, 2 H, NCH=CHN), 7.17 (d, ³J_{HH} = 1.87 Hz, 2 H, NCH=CHN), 6.99 (d, ³J_{HH} = 12.46 Hz, 1 H, NCH₂N), 6.67 (t, ³J_{HH} = 7.49 Hz, 4 H, *m*-phenyl), 6.47 (t, ³J_{HH} = 7.09 Hz, 2 H, *p*-phenyl), 6.08 (d, ³J_{HH} = 12.48 Hz, 1 H, NCH₂N), 1.40 (s, 18 H, ^tBu). ¹³C NMR (150 MHz, acetone-*d*₆) δ 181.77 (s, carbene C), 140.37 (s, ²J_{PC} = 17.4 Hz, *m*-phenyl), 126.42 (s, ¹J_{PC} = 31.8 Hz, *o*-phenyl), 120.47 (s, *p*-phenyl), 119.65 (s, ²J_{PC} = 9.4 Hz, NCH=CHN), 118.38 (s, ²J_{PC} = 12.4 Hz, NCH=CHN), 65.09 (s, CH₂), 58.79 (s, C(CH₃)₃), 30.99 (s, C(CH₃)₃), *i*-phenyl not observed. Anal. Calcd. for PtN₄C₂₇H₃₄ (%): C 53.19, H 5.62, N 9.19; found: C 52.22, H 5.72, N 9.19.

General procedure for the synthesis of [(L~L)Pt(NCMe)(Ph)][Bar'₄] complexes. A suspension of (L~L)Pt(Ph)₂ in THF (30 mL) was cooled to -70 °C. One equivalent of [H(Et₂O)₂][Bar'₄] dissolved in THF (~10 mL, -70

°C) was added. The solution was allowed to stir for approximately 2 minutes before acetonitrile (~2 mL) was added. The solution was placed under vacuum, and the volatiles removed. The residue was treated with *n*-pentane (~2 mL), which was then removed under vacuum to afford a solid. The solid was dried *in vacuo*.

[(dmpe)Pt(NCMe)(Ph)][Bar'₄] (1). dmpe = (Bis-(diphenylphosphino)methyl)methylamine. Isolated 0.13 g (93%). ¹H NMR (300 MHz, CD₂Cl₂) δ 7.30 (m, 2H, H^o-Ph), 7.17 (t, ³J_{HH} = 7 Hz, 2H, H^m-Ph), 7.01 (t, ³J_{HH} = 7 Hz, 1H, H^p-Ph), 2.31 (s, 3H, NCMe), 1.86 (m, 4H, PCH₂CH₂P), 1.63 (d, ²J_{PH} = 10 Hz, 6H, Me-dmpe), 1.42 (d, ²J_{PH} = 2 Hz, ³J_{HH} = 52 Hz, 6H, Me-dmpe). ³¹P NMR (121 MHz, CD₂Cl₂) δ 29.99 (s, ¹J_{PH} = 1667 Hz, Pt satellites), 15.29 (s, ¹J_{PH} = 4076 Hz, Pt satellites). ¹³C NMR (201 MHz, dichloromethane-*d*₂) δ 162.23, 136.88, 135.21, 129.35, 127.03, 125.68, 125.13, 124.32, 122.97, 117.86, 29.68, 26.03, 12.78, 11.91, 3.86. Anal. calcd. for PtP₂NBF₂₄C₄₆H₃₆ (%): C 41.64, H 2.74, N 1.06; found: C 41.86, H 2.65, N 0.97.

[(dppe)Pt(NCMe)(Ph)][Bar'₄] (2). dppe = 1,2-bis(diphenylphosphino)ethane. Isolated 0.13 g (97%). ¹H NMR (300 MHz, CD₂Cl₂) δ 7.57 (m, 32H, Ar' and dppe), 6.90 (m, 5H, Ph), 2.42 (m, 4H, PCH₂CH₂P), 2.12 (s, 3H, NCMe). ³¹P NMR (121 MHz, CD₂Cl₂) δ 47.44 (s, ¹J_{PP} = 1671 Hz, Pt satellites), 33.92 (s, ¹J_{PP} = 4359 Hz, Pt satellites). ¹³C NMR (201 MHz, dichloromethane-*d*₂) δ 162.11, 151.79, 136.93, 135.11, 133.73, 133.24, 132.85, 130.07, 129.54, 129.18, 128.73, 126.96, 125.71, 125.60, 125.37, 124.76, 124.25, 117.86, 30.54, 24.87, 3.87. Anal. calcd. for PtP₂NBF₂₄C₆₆H₄₄ (%): C 50.33, H 2.82, N 0.89; found: C 50.37, H 2.99, N 1.02.

[(bppe)Pt(NCMe)(Ph)][Bar'₄] (3). bppe = 1,2-(bis-*N*-pyrrolylphosphino)ethane. Isolated 0.09 g (89%). ¹H NMR (300 MHz, CD₂Cl₂) δ 7.08 (m, 9H, α-*N*-pyrrole and Ph), 6.75 (m, 4H, α-*N*-pyrrole), 6.64 (m, 4H, β-*N*-pyrrole), 6.48 (m, 4H, β-*N*-pyrrole), 2.75 (m, 4H, CH₂CH₂-bppe), 2.44 (s, 3H, NCMe). ³¹P NMR (121 MHz, CD₂Cl₂) δ 109.56 (s, ¹J_{PP} = 2539 Hz, Pt satellites), 80.68 (s, ¹J_{PP} = 5599 Hz, Pt satellites). ¹³C NMR (201 MHz, acetonitrile-*d*₃) δ 161.61, 147.43, 135.64, 134.67, 128.90, 128.42, 125.47, 125.14, 124.00, 123.83, 117.71, 114.76, 114.53, 32.28, 25.27. Anal. calcd. for PtN₃P₂BF₂₄C₅₈H₄₀ (%): C 45.50, H 2.64, N 4.58; found: C 45.13, H 2.70, N 4.17.

[(dppp)Pt(NCMe)(Ph)][Bar'₄] (4). dppp = 1,3-bis(diphenylphosphino)propane. Isolated 0.09 g (91%). ¹H NMR (800 MHz, CD₂Cl₂) δ 7.58 (m, 8H, dppp), 7.34 (m, 8H, dppp), 7.23 (td, ³J_{HH} = 8 Hz, ⁴J_{HH} = 3 Hz, 4H, dppp), 6.93 (t, ³J_{HH} = 7 Hz, 2H, H^o-Ph), 6.69 (t, ³J_{HH} = 7 Hz, 2H, H^m-Ph), 6.64 (t, ³J_{HH} = 7 Hz, 1H, H^p-Ph), 2.74 (m, 2H), 2.66 (m, 2H), 1.99 (m, 2H), 1.70 (s, 3H, NCMe). ³¹P NMR (121 MHz, CD₂Cl₂) δ -0.06 (d, ²J_{PP} = 26 Hz), -4.20 (d, ²J_{PP} = 26 Hz). Pt coupling not resolved due to poor signal intensity. ¹³C NMR (201 MHz, dichloromethane-*d*₂) δ 162.17, 152.10, 136.29, 135.22, 133.45, 133.16, 132.15, 131.97, 129.82, 129.29, 128.98, 128.43, 127.35, 127.04, 125.67, 124.33, 124.25, 117.84, 24.84, 22.77, 18.79, 2.95. Anal. calcd. for PtP₂NBF₂₄C₆₇H₄₆ (%): C 50.64, H 2.92, N 0.88; found: C 50.84, H 2.92, N 0.81.

[(dppf)Pt(NCMe)(Ph)][Bar'₄] (5). dppf = 1,1'-bis(diphenylphosphino)ferrocene. Isolated 0.07 g (88%). ¹H NMR (300 MHz, CD₃CN) δ 7.90 (m, 4H, dppf), 7.57 (m, 17H, Ar' and dppf), 7.41 (m, 7H, H^o-Ph and dppf), 7.20 (m, 4H, dppf), 6.96 (m, 2H, H^m-Ph), 6.62 (m, 3H, H^p-Ph and dppf), 4.79 (m, 2H, Cp-dppf), 4.62 (s, 2H, Cp-dppf), 4.36 (s, 2H, Cp-dppf), 3.90 (m, 2H, Cp-dppf). Coordinated NCMe not observed due to rapid exchange with CD₃CN. ³¹P NMR 121 MHz, CD₃CN) δ 18.95 (d, ²J_{PP} = 17 Hz, ¹J_{PP} = 1717 Hz, Pt satellites), 11.00 (d, ²J_{PP} = 17 Hz, ¹J_{PP} = 4674 Hz, Pt satellites). ¹³C NMR (201 MHz, acetonitrile-*d*₃) δ 162.56, 150.38, 136.62, 135.60, 135.20, 135.03, 132.59, 132.25, 130.78, 130.18, 129.83, 129.07, 128.71, 126.07, 124.72, 124.45,

118.63, 77.18, 75.57, 75.40, 75.36, 74.71, 74.68. Anal. calcd. for $\text{PtFeP}_2\text{NBF}_{24}\text{C}_{74}\text{H}_{48}$ (%): C 51.35, H 2.80, N 0.81; found: C 51.27, H 2.92, N 0.82.

[(bma)Pt(NCMe)(Ph)][BAR'₄] (6). bma = (Bis-(diphenylphosphino)methyl) methylamine. Isolated 0.05 g (98%). ¹H NMR (300 MHz, CD₃CN) δ 7.54 (m, 32H, Ar', bma and Ph), 7.03 (t, ³J_{HH} = 7 Hz, 2H, H^m-Ph), 6.72 (m, 3H, bma and H^p-Ph), 3.80 (br s, 4H, CH₂-bma), 2.34 (s, 3H, Me-N). ³¹P NMR (121 MHz, CD₃CN) δ -4.82 (d, ²J_{PP} = 26 Hz, ¹J_{PtP} = 1530, Pt satellites), -7.03 (d, ²J_{PP} = 26 Hz, ¹J_{PtP} = 4243 Hz, Pt satellites). ¹³C NMR (201 MHz, acetonitrile-d₃) δ 162.55, 153.06, 137.26, 135.59, 134.38, 132.46, 130.12, 129.80, 129.70, 129.34, 128.44, 127.55, 127.21, 126.07, 124.72, 124.45, 118.70, 57.01, 56.69, 50.71. Anal. calcd. for $\text{PtN}_2\text{P}_2\text{BF}_{24}\text{C}_{67}\text{H}_{47}$ (%): C 50.17, H 2.96, N 1.75; found: C 49.83, H 2.94, N 1.16.

[(diq)Pt(Ph)(THF)][BAR'₄] (7). The synthesis for this complex was the same as that for the general [(L~L)Pt(NCMe)(Ph)][BAR'₄], except no acetonitrile was added to the reaction. L₂ = 8-(diisopropylphosphino)quinoline. Isolated 0.08 g (89%). ¹H NMR (500 MHz, CD₂Cl₂) δ 8.99 (s, 1H, diq), 8.63 (d, ³J_{HH} = 8 Hz, 1H, diq), 8.19 (d, ³J_{HH} = 8 Hz, 1H, diq), 8.08 (t, ³J_{HH} = 8 Hz, 1H, diq), 7.83 (t, ³J_{HH} = 8 Hz, 1H, diq), 7.42 (d, ³J_{HH} = 7 Hz, 2H, H^o-Ph), 7.13 (d, ³J_{HH} = 7 Hz, 2H, H^m-Ph), 7.08 (t, ³J_{HH} = 7 Hz, 1H, H^p-Ph), 4.11 (br s, 4H, α -THF), 2.68 (m, 2H, CH-ⁱPr), 1.88 (br s, 4H, β -THF), 1.20 (d, ³J_{HH} = 7 Hz, 3H, Me-ⁱPr), 1.17 (d, ³J_{HH} = 7 Hz, 3H, Me-ⁱPr), 0.96 (d, ³J_{HH} = 7 Hz, 3H, Me-ⁱPr), 0.92 (d, ³J_{HH} = 7 Hz, 3H, Me-ⁱPr). ³¹P NMR (121 MHz, CD₂Cl₂) δ 38.33 (s, ¹J_{PtP} = 4851 Hz, Pt satellites). ¹³C NMR (201 MHz, dichloromethane-d₂) δ 161.93, 149.77, 149.71, 140.51, 140.43, 137.99, 137.90, 135.78, 135.02, 133.04, 129.16, 128.72, 128.63, 126.85, 125.38, 124.14, 123.80, 117.70, 73.45, 25.50, 24.64, 24.39, 17.80, 17.05. Anal. calcd. for $\text{PtNPOBF}_{24}\text{C}_{57}\text{H}_{45}$ (%): C 47.12, H 3.13, N 0.96; found: C 47.32, H 3.10, N 1.08.

[(D'BuC)Pt(Ph)(NCMe)][BAR'₄] (8). D'BuC = 1,1'-methylene-3,3'-di-*tert*-butylimidazol-2,2'-diylidene. Isolated 0.05 g (97%). ¹H NMR (300 MHz, CD₂Cl₂) δ 7.72 (s, 8 H, *o*-Ar'), 7.56 (s, 4 H, *p*-Ar'), 7.21-7.17 (m, 4 H, NCH=CHN and *o*-phenyl), 7.04 (d, ³J_{HH} = 2.32 Hz, 2 H, NCH=CHN), 7.00 (t, ³J_{HH} = 7.27 Hz, 4 H, *m*-phenyl), 6.95 (t, ³J_{HH} = 7.27 Hz, 2 H, *p*-phenyl), 6.64 (d, ³J_{HH} = 12.85 Hz, 1 H, NCH₂N), 5.53 (d, ³J_{HH} = 12.95 Hz, 1 H, NCH₂N), 1.75 (s, 9 H, 'Bu), 1.31 (s, 9 H, 'Bu). ¹³C NMR (201 MHz, dichloromethane-d₂) δ 180.56, 173.93, 162.15, 139.13, 135.22, 129.22, 127.97, 127.03, 125.68, 124.47, 124.33, 123.02, 120.29, 120.01, 119.57, 117.89, 65.00, 60.36, 59.49, 32.48, 30.97, 4.13. Anal. Calc. for $\text{PtN}_4\text{BF}_{24}\text{C}_{55}\text{H}_{44}$ (%): C 45.98, H 3.09, N 4.87; found C 44.58, H 3.09, N 4.87.

General Catalysis Procedure. [(L~L)Pt(NCMe)(Ph)][BAR'₄] (13.5 mmol) was dissolved in 12.0 mL (135 mmol) of a benzene solution in a stainless steel pressure reactor (45 mL). An internal standard of hexamethylbenzene (13.5 mmol) was used. The reactor was pressurized with 0.1 MPa ethylene and 0.8 MPa N₂ and heated at 100 °C. After a given time period, the reaction mixture was allowed to cool to room temperature and was analyzed by GC/MS.

X-Ray Structure Determination for 9. Yellow crystals of compound **9** were obtained by slow evaporation of a diethyl ether solution. Crystal data: C₂₇H₃₀BNPPt, *M* = 594.58; crystal dimensions: 0.48 x 0.26 x 0.04 mm³; monoclinic, space group P2₁/n, *a* = 12.2305(6), *b* = 16.5915(9), *c* = 12.3537(9) Å, β = 110.304(1)°, *V* = 2351.1(2) Å³, *Z* = 4, *D*_c = 1.680 g/cm³, *T* = 153(2) K. X-ray data collection was carried out on a Bruker Kappa Duo CCD diffractometer using MoK α radiation. (λ = 0.71073 Å). The structure was solved applying direct methods

techniques in SHELXTL (Sheldrick, G. M. *SHELXTL Version 5.1 Reference Manual*, Bruker AXS, Inc: Madison, WI, 1997). Full-matrix least-squares refinement with anisotropic thermal displacement parameters for all non-hydrogen atoms yielded *R* = 0.047 (*R*_w = 0.078) for 9164 reflections with *I* > 2 σ (*I*). The final electron density map had the highest peak of 2.9 e/Å³. The data have been assigned the CCDC reference code 1033090.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data (CIF) for (diq)Pt(Ph)₂ (**9**), xyz coordinates and absolute energies of optimized structures. 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 interests.

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Graphical Abstract and Synopsis

Previously, Pt(II) complexes with chelating dipyridyl ligands have been shown to be active catalysts for ethylene hydrophenylation to form ethylbenzene. Herein, Pt(II) complexes with chelating bisphosphine and *N*-heterocyclic carbene ligands are shown to be selective catalysts for the conversion of benzene and ethylene to styrene formation with low turnover numbers.