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Hydroarylation of Unactivated Olefins Catalyzed by Platinum(II) Complexes

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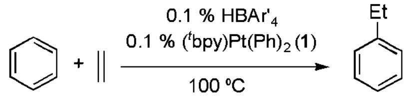
Summary: The Pt(II) complex [(^{t}bpy)Pt(Ph)(THF)][BAr′$_4$] catalyzes the hydroarylation of olefins utilizing unactivated substrates. Preliminary studies indicate that the reactions proceed via Pt-mediated C−H activation rather than a traditional Friedel−Crafts pathway.

Transition-metal-catalyzed additions of aromatic C−H bonds across C═C bonds of olefins to afford C−C bonds provide atom-economical alternatives to well-known Friedel−Crafts, Suzuki, Heck, Sonogashira, and related reactions.[1–3] Examples of C−H addition across olefins include ortho-selective conversion of aromatic ketones,[4] Pd-catalyzed reactions of activated substrates,[5] and variants with heteroaromatic substrates that are predominantly intramolecular transformations.[6–8] In contrast, the conversion of unactivated arenes (e.g., benzene) and olefins (e.g., ethylene, α-olefins) to alkylated arenes through mechanisms other than Friedel−Crafts pathways[9] are relatively rare.[10–12] Our group has reported that octahedral Ru(II) complexes supported by the tris(pyrazolyl)borate ligand can convert simple arenes and unactivated olefins to alkyl arene products.[11,13–15] Although catalyst development based on the six-coordinate d^6 motif for catalyst precursors continues to be of interest, we have also begun to extend such reactions toward different electronic and coordination environments.

Pt(II) complexes have been among the most widely studied systems for the activation of C−H bonds.[16,17] Most germane here are an interesting Pt−Ag co-catalyst system reported by Tilley et al. and C−H activation by Pt systems that possess N-donor ligands.[17–19] Given the robust nature of many Pt systems utilized for C−H activation and reports of insertion of olefins into Pt−C bonds,[20] we felt such complexes might prove amenable for catalytic olefin hydroarylation.

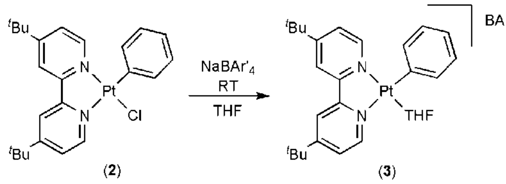
We chose as an entry point to olefin hydroarylation the (^{t}bpy)Pt(Ph)$_2$ (**1**; ^{t}bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) system.[21] It has been shown that protonolysis of a phenylplatinum(II) bond of **1** by strong acids induces the elimination of benzene to form (^{t}bpy)Pt(Ph)(X) (X = Cl, BF$_4$).[21] The protonation of complex **1** by HBAr′$_4$ {Ar′ = 3,5-(CF$_3$)$_2$C$_6$H$_3$} should result in the formation of free benzene and [(^{t}bpy)Pt(Ph)]$^+$, affording a site for substrate coordination and a potential entry into catalytic olefin hydroarylation. Heating a 0.1 mol % benzene solution of complex **1** with HBAr′$_4$ to 100 °C under 25 psi of ethylene results in 3.7 and 11.9 turnovers (TOs) of ethylbenzene after 4 and 16 h, respectively (eq 1).



(1)

Control experiments using HBAr′$_4$ in the absence of complex **1** as well as complex **1** in the absence of HBAr′$_4$ yielded minimal quantities of ethylbenzene. For example, heating a solution of benzene under ethylene pressure with 0.1 mol % of HBAr′$_4$ results in ~1 turnover of ethylbenzene after 16 h at 120 °C. Similarly, a benzene solution containing 0.1 mol % of **1** in the absence of HBAr′$_4$ under ethylene pressure at 120 °C produces only 0.4 turnover of ethylbenzene after the same duration. However, the poor solubility of HBAr′$_4$ in arene solvents may prevent the quantitative entry of Pt into the cycle. Therefore, isolable cationic Pt(II) precursors were targeted to increase catalyst efficiency.

Reacting (^{t}bpy)Pt(Cl)(Ph) (**2**) with NaBAr′$_4$ in THF yields [(^{t}bpy)Pt(Ph)(THF)][BAr′$_4$] (**3**) (eq 2).



(2)

Complex **3** has only been isolated in the presence of excess THF and has been characterized by ^{1}H and ^{19}F NMR spectroscopy, since the removal of excess THF results in decomposition of **3** to multiple products. Complex **3** was tested for catalytic hydrophenylation of ethylene over a range of temperatures (90−140 °C) and ethylene pressures (15−60 psi). Optimal catalysis is at 100 °C and 15 psi of ethylene pressure with 28

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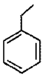
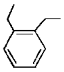
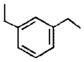
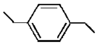
Table 1. Hydroarylation Products by 3 with Benzene and Ethylene

Conditions[a]		EtPh[c]	Diethyl benzenes[c]		
Temp (°C)	C_2H_4[b] (psi)				
90	15	7.2 (20.3)	0.33 (0.9)	1.5 (5.7)	0.9 (2.8)
100	15	27.9 (65.8)	0.8 (1.5)	7.8 (22.9)	4.0 (10.2)
100	30	7.9 (20.8)	0.6 (1.6)	1.8 (5.8)	1.0 (2.9)
100	45	5.0 (13.1)	0.5 (1.3)	1.1 (3.7)	0.6 (1.8)
100	60	0.6 (8.9)	0.4 (1.0)	0.8 (2.25)	0.4 (1.1)
120	15	38.6 (40.5)	0.4 (0.7)	9.0 (11.1)	4.3 (5.1)
140	15	35.8 (29.6)	0.3 (0.4)	7.3 (7.6)	3.3 (3.3)

[a] 0.1% catalyst in benzene with 0.1% hexamethylbenzene as internal standard. [b] Set up under a dinitrogen atmosphere purged and pressurized with ethylene to the desired amount and then brought to total pressure of 120 psi with N_2. [c] Turnovers relative to catalyst loading after 4 h (turnovers after 16 h).

TOs after 4 h (TOF ≈ 1.9×10^{-3} s^{-1}) and 66 TOs after 16 h (Table 1), giving a turnover frequency (TOF) of ~1.2×10^{-3} s^{-1} after 16 h. Including the production of diethylbenzenes, a total of ~100 catalytic turnovers were observed after 16 h, which corresponds to a turnover frequency of ~1.7×10^{-3} s^{-1}. Increasing the reaction temperature accelerates ethylbenzene production but also leads to more rapid catalyst decomposition. For example, catalytic reactions with 15 psi of ethylene pressure at 120 and 140 °C have higher TOs after 4 h in comparison to reactions performed at 100 °C with the calculated TOF at 120 °C of ~2.7×10^{-3} s^{-1}; however, only minimal TOs are observed with continued heating. Inspection of reaction mixtures after catalytic experiments at 120 and 140 °C reveal a black precipitate, suggestive of a competitive decomposition route at higher temperatures. Increasing the ethylene pressure suppresses catalysis. After 16 h at 100 °C, 0.1 mol % of complex **3** afforded 66, 21, 13, and 9 TOs of ethylbenzene at 15, 30, 45, and 60 psi of ethylene pressure, respectively. This suggests an inverse dependence of catalysis rate on olefin concentration, as has been observed with Ru(II)- and Ir(III)-catalyzed hydrophenylation of ethylene.[13,22]

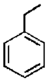
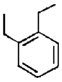
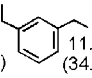
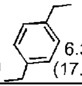
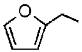
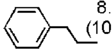
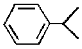
In addition to ethylbenzene, the hydrophenylation of ethylene catalyzed by **3** results in approximately 25−30% production of diethylbenzene and trace quantities of triethylbenzenes. At 100 °C under 15 psi of ethylene pressure, the selectivity for the alkylation of ethylbenzene (starting from benzene) is 1:13.6: 15.3 (ortho:para:meta) after statistical correction. The regioselectivity of **3** for meta C−H activation of monosubstituted benzenes is similar to the observations by Tilset et al. that the regioselectivity of stoichiometric toluene C−H activation by a cationic Pt(II) diimine complex is meta > para > ortho.[23] Interestingly, comparing the ratio of ethylbenzene to diethylbenzenes at 4 and 16 h time points suggests that the formation of these products is approximately invariant with reaction time (Table 1). For example, the ratio of ethylbenzene to diethylbenzenes at 90 °C and 15 psi of ethylene is 2.6 at 4 h and 2.2 at 16 h, while at 100 °C the ratios are 2.2 (4 h) and 1.9 (16 h). Table 2 shows the ratio of ethylbenzene to diethylbenzene at each time point for the various reaction conditions. With the exception of the reaction at 60 psi of ethylene (for which the 4 h time point has too little product for reliable integration), there is little variance in the ratio between 4 and 16 h. Also, the addition of the Lewis base THF appears to suppress the formation of diethylbenzene products. For example, for the catalytic reaction at 100 °C and 15 psi, the addition of 10% THF (relative to benzene) results in an ethylbenzene/diethylbenzene molar ratio of 4.6 after 4 h (versus a ratio of 2.2 in the absence of THF). The addition of THF also suppresses the rate of product formation. Both of these effects remain to be scrutinized in greater detail.

Table 2. Ratio of Ethylbenzene to Diethylbenzenes as a Function of Time under Various Reaction Conditions

temp (°C)	C_2H_4 (psi)	ratio[a] 4 h	16 h	4 h ratio/16 h ratio
90	15	2.6	2.2	1.2
100	15	2.2	1.9	1.2
100	30	2.3	2.0	1.1
100	45	2.3	1.9	1.2
100	60	0.4[b]	2.0[b]	0.2[b]
120	15	2.8	2.4	1.2
140	15	3.3	2.6	1.3

[a] Molar ratio of ethylbenzene to diethylbenzenes (determined by GC FID). [b] Integration at 4 h unreliable due to low concentration of products.

Table 3. Hydroarylation of Various Substrates at 100 °C[d]

Olefin	Aromatic	Products[c]
ethylene[a]		 0.1 (0.2)  11.3 (34.0)  6.3 (17.7)
ethylene[b]		 29.3(76.2)
propylene[a]		 8.5 (10.1)  25.0 (29.7)

[a] 0.1% catalyst. [b] 0.05% catalyst. [c] Turnovers relative to catalyst loading after 4 h (turnovers after 16 h). [d] All reactions run with 0.1% hexamethylbenzene internal standard, charged with 15 psi of olefin pressure, and then pressurized to a total pressure of 120 psi with N_2.

Table 3 shows a slightly expanded substrate scope for olefin hydroarylation. Complex **3** catalyzes ethylene hydroarylation using ethylbenzene at all three aromatic sites with 17.7 total turnovers after 4 h at 100 °C with ortho:para:meta ratio of 1:126: 113 (after statistical adjustment). Thus, similar to the formation of diethylbenzenes starting from benzene and ethylene, the hydroarylation of ethylene using ethylbenzene as the starting arene is selective for para/meta over ortho with an enhancement of the selectivity. Extension of ethylene hydroarylation to furan results in regioselective conversion to 2-ethylfuran with ~76 TOs after 16 h. In addition, the formation of 2,5-diethylfuran was observed in trace amounts. To investigate the reactivity for α-olefins, the hydrophenylation of propylene was tested. After 4 h at 100 °C, a total of 33.5 turnovers of propylbenzene were detected with a cumene to *n*-propylbenzene molar ratio of 3:1. *The production of linear alkylbenzene provides evidence against a Friedel−Crafts type pathway.*

Although we have insufficient data to propose a detailed mechanism, one viable possibility is shown in Scheme 1. THF/ethylene ligand exchange followed by olefin insertion would

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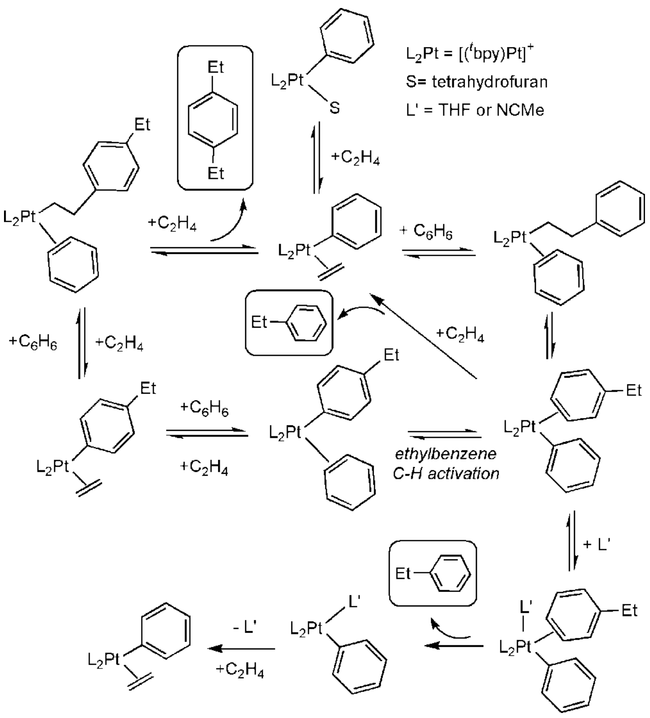
Scheme 1. Possible Catalytic Cycle To Produce Ethylbenzene and Diethylbenzene from Benzene and Ethylene Catalyzed by 3[a]



[a] Production of 1,4-diethylbenzene is shown as the potential representative pathway for formation of all diethylbenzene products.

form [(^{t}bpy)Pt(CH_2CH_2Ph)]$^+$ and produce ethylbenzene upon coordination and C−H activation of benzene. Benzene C−H activation could occur via oxidative addition, electrophilic substitution, or σ-bond metathesis. We cannot completely discount the possibility of intermolecular nucleophilic addition of benzene to coordinated olefin; however, to our knowledge such reactions with Pt cations have only been observed with electron-rich arenes.[24] In addition, the selectivity for meta and para positions over ortho for activation of ethylbenzene is inconsistent with a pathway that involves electrophilic addition to the arene. Interestingly, the TOF of hydroarylation of ethylene using ethylbenzene (Table 3) is ~1.2 × 10^{-3} s^{-1} (calculated after 4 h), which is quite similar to the rate of hydro*phenylation* of ethylene. Thus, the production of substantial quantities of diethylbenzenes for the conversion of benzene/ethylene cannot be accounted for by reaction of **3** with *free* ethylbenzene generated by catalysis. This suggests that a second C−H activation of ethylbenzene is competitive with the dissociation of ethylbenzene (Scheme 1). The approximate invariant ratio of ethylbenzene to diethylbenzene (by comparison of data at 4 and 16 h of catalysis; see above) during the course of catalysis is consistent with this proposal. Furthermore, the addition of excess THF decreases the extent of diethylbenzene production, which is *potentially* accounted for by associative displacement of ethylbenzene, as depicted in the bottom of Scheme 1.

In summary, our preliminary findings indicate that cationic Pt(II) systems can catalyze olefin hydroarylation. The inverse dependence of TOs on olefin concentration and the production of *n*-propylbenzene from benzene and propylene suggest that the mechanism is not a traditional Friedel−Crafts type pathway. To our knowledge, Tilley et al. were the first to report the use of Pt systems for catalytic olefin hydroarylation.[12,18] One of these systems appears to function via a Friedel−Crafts pathway (on the basis of the selectivity of reactions with toluene), while the other catalyst is reported to hydroarylate the activated olefin norbornene with relatively few turnovers. Thus, to our knowledge, the catalyst reported herein is the first example of Pt-catalyzed olefin hydroarylation with unactivated substrates and relatively high turnover numbers. These results provide a foundation on which to study other platinum systems in an effort to improve selectivity and reactivity.

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Supporting Information Available: Text and a figure giving details of experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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