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Olefin Hydroarylation Catalyzed by (Pyridyl-Indolate)Pt(II) Complexes: Catalytic Efficiencies and Mechanistic Aspects

Benjamin A. Suslick, Allegra L. Liberman-Martin[‡], Truman C. Wambach, T. Don Tilley^{*}

Department of Chemistry, University of California, Berkeley, California 94720, United States

Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Supporting Information Placeholder

ABSTRACT: A series of Pt(II) complexes of the type (N–N)PtPh(SR₂) (N-N = 2,2'-pyridyl-indolate) were prepared, and their performance as catalysts for the hydroarylation of olefins was assessed. Evidence that the catalysis is homogeneous and Pt mediated is provided by control experiments with added hindered base (2,6-di-*tert*-butyl-4methylpyridine) and Hg(0). Two potential catalytic intermediates, ('BuPyInd)PtPh(C₂H₄) and ('BuPyInd)Pt(CH₂CH₂Ph)(C₂H₄), were synthesized and their catalytic efficacy was explored. Additionally, decomposition and deactivation pathways, including styrene formation *via* β -hydride elimination and ligand reductive demetallation, were identified.

INTRODUCTION

Catalytic C–C bond-forming processes are important for efficient utilization of abundant feedstock chemicals. These methods are critical to the industrial-scale syntheses of alkyl arene products, which are incorporated into many plastics and fine chemicals on an enormous scale. For example, polystyrene, which is manufactured from ethylbenzene, was consumed at an annual rate of 1.2×10^7 tons/year from 2000-2010.¹ While methods exist to couple alkyl and aryl fragments using molecular catalysis (*e.g.* cross coupling²), such systems often require the use of activated reagents such as ArSnR₃ or ArZnX, which generate additional synthetic steps. Moreover, these methods are atom inefficient and generate stoichiometric waste.

Given recent advances in C–H functionalization chemistry,³ reactions that can directly couple aryl C–H bonds and small molecules are feasible. In particular, the hydroarylation of carbon–carbon multiple bonds has garnered considerable attention over the last two decades.⁴ The initial developments of olefin hydroarylation catalyzed by RuH₂(CO)(PPh₃)₃ were described by Murai and coworkers⁵. Further mechanistic investigations with related Ru(II)⁶ and Ir(III)⁷ complexes illustrated that olefin insertion into a metal–aryl bond and arene C–H activation are key mechanistic steps.⁵⁻⁷ Several recent reports have indicated that the hydroarylation of olefins to generate alkyl arenes⁴ can also be achieved with transition metal catalysts with *d*⁸ electronic configurations (*e.g.*, Ir(I),⁸ Rh(I),^{9,10} and



 $Pd(II)^{11}$). It is worth noting that the mechanistic features of these systems have not been thoroughly elucidated.

Both cationic and neutral Pt(II) complexes supported by 4,4'di-tert-butyl-2,2'-bipyridine (tbpy)12 or 2,2'-pyridyl-pyrrole (PyPyr)¹³ ligands, respectively, have recently been reported as hydroarylation catalysts. Unlike other d⁸ metal catalysts, these systems operate with unactivated arene substrates that do not contain directing or coordinating functionalities, but the efficiencies of these catalysts are rather limited. $^{\rm 12,13}$ In the latter context, it has been suggested that modification of the ancillary ligand donating ability could potentially improve the activity of Pt-based catalysts.¹⁴ However, there has not been a thorough study of ligand electronic effects for neutral Pt catalysts, even though these systems appear to exhibit higher selectivities for mono- (vs. poly-) alkylation, relative to cationic catalysts.¹⁵ Moreover, detailed investigations into complex degredation pathways have not been performed for the neutral Pt(II) systems. Determining the primary decomposition routes is necessary to design robust catalysts and elucidate potential additives that suppress unproductive processes.

We have previously reported the use of Pt complexes bearing a parent 2,2'-pyridyl-indolate (PyInd) ligand for the hydroarylation of norbornene.¹⁶ Herein, the synthesis and olefin hydroarylation activity of Pt(II) complexes of the type (N– N)PtPh(SR₂) are described for a series of pyridyl-indolate complexes. The identification and isolation of several catalytic intermediates provide insight into the operative mechanism for

hydroarylation. Additionally, differences in catalytic performance as a function of substituents on the N–N ligand have been determined for a variety of olefin and arene substrates.

RESULTS AND DISCUSSION

Synthesis of Platinum Pyridyl-Indolate Complexes. A parent ligand bearing a 4'-'Bu group on the pyridyl moiety (**1a**) was chosen due to its solubility in hydrocarbons, as well as its diagnostic *tert*-butyl ¹H NMR resonance. Several highly-fluorinated derivatives were also synthesized (**1b** and **1c**). To thoroughly probe the electronic effects of this ligand type on catalysis, a series of (N–N) ligands with various electron withdrawing or donating substituents (**1d-1j**) was synthesized using a procedure adapted from Wang and coworkers.¹⁷ Condensation of ar-ylhydrazines with acetylpyridine afforded arylhydrazone intermediates. Treatment with neat polyphosphoric acid generated the desired substituted N–N ligands (see Supporting Information, SI, Scheme S1).

The pyridyl-indolate ligands were incorporated into platinum complexes by reactions with $(SMe_2)_2PtPh_2$, to afford complexes of the type $(N-N)PtPh(SMe_2)$ (**2a-j**, Scheme 1) which were purified by column chromatography. The analogous SEt₂ complex, $(PyInd)PtPh(SEt_2)$ (**2k**), was generated by treatment of $[(\mu-SEt_2)PtPh_2]_2$ with **1d** in benzene (Scheme 1).

Scheme 1. Synthesis of Catalysts 2a-k.



There are several diagnostic ¹H NMR resonances for complexes **2a-k**. The SMe₂ ligand of **2a-j** appears as a singlet with broad ¹⁹⁵Pt satellites ($\delta \sim 2.30$ ppm, $J_{PtH} \sim 60$ Hz in dichloromethane- d_2). The *o*-aryl protons on the phenyl ligand in complexes **2a-k** also exhibited ¹⁹⁵Pt coupling ($\delta \sim 7.60$, $J_{PtH} \sim 35$ Hz in dichloromethane- d_2). Single crystals of **2a** were obtained by slow diffusion of pentane into a toluene solution of the complex at -35 °C. Complex **2a** displays the expected square planar geometry, and the indolate donor is positioned *trans* to the phenyl ligand (Figure 1). The bond lengths and angles are consistent with related Pt(II) complexes.^{14,18} The crystal structures of complexes **2b** and **2c** are similar (see SI, Figures S1 and S2).



Figure 1. Crystal structure of **2a**, with hydrogen atoms omitted and thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (°) for **2a**: C(1)–Pt(1): 2.014(2), N(1)–Pt(1): 2.0529(18), N(2)–Pt(1): 2.1030(17), S(1)–Pt(1): 2.2580(5), C(1)–Pt(1)–N(1): 93.41(8), C(1)–Pt(1)–S(1): 90.57(6), N(1)–Pt(1)–N(2): 79.32(7), N(2)–Pt(1)–S(1): 96.70(5).

Catalytic Hydroarylation with (N–N)Pt(SMe₂)Ph Complexes. Olefin hydroarylation studies were performed to determine the catalytic efficacy of complexes **2a-k**. In the simplest hydroarylation reaction, neat benzene- d_6 and ethylene (1 atm) were heated to 100 °C in the presence of the catalyst (**2a**k; 3.7 mM). The formation of the product, ethylbenzene- d_6 (C₆D₅CH₂CH₂D),¹⁵ was monitored by ¹H NMR spectroscopy over the course of 46 h (see SI, Figure S3). With all catalysts tested, over-alkylation to form polyethylbenzenes was negligible (< 1 turnover for all examples) as determined by ¹H NMR spectroscopy and GC-MS (see SI, Figure S4). Moreover, H(D) scrambling occurs only to a minor extent (by ²H NMR spectroscopy).

Comparisons of total turnovers (after 24 h) and initial rates (as approximated by the number of turnovers after 1 h) for catalysts **2a-k** are presented in Table 1. In general, no catalyst decomposition was observed after 1 h, by ¹H NMR spectroscopy. However at longer reaction times (> 24 h), elemental Pt(0) was observed as a black precipitate as well as a thin film coating the walls of the reaction vessel. Moreover, minimal additional ethylbenzene production was observed beyond 24 h even upon exposure to additional ethylene, suggesting that this time point represents the catalysts' maximum lifespan.

Unfortunately, a clear trend of ethylbenzene formation as a function of the substitution pattern on the indolate fragment did not exist. In particular, substitution of the 5-position resulted in an inconclusive trend: both electron withdrawing (F,

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Cl) and electron donating (OMe) substituents resulted in an increase in initial rate and turnovers when compared to the parent catalyst **2d**; however, a few notable patterns are discernible. The inclusion of a 4'-^tBu moiety on the pyridyl fragment (**2a** vs. **2d**) appeared to have no effect on product formation. The position of indolate substitution with Cl appeared to have a slight effect; complex **2j** rapidly decomposed (resulting in reduced turnovers) whereas **2h** was still catalytically active after **24** h. Interestingly, replacing the ancillary SMe₂ ligand (**2d**) for the slightly bulkier SEt₂ donor (**2k**) resulted in a faster initial rate and higher turnover numbers. This superior performance may be attributed to the more labile SEt₂ ligand being easier to exchange for ethylene, which is a key step in the hydroarylation mechanism.

Table 1. Catalytic Ethylene Hydroarylation with 2a-k.

cat. 3.7 mM	$\overline{}$
100 °C, 24 h	þ

Catalyst ^a	Total Turnovers ^b	Initial Rate (TO / h) ^c
2a	7.4 ± 1.1	1.0 ± 0.02
2b	8.0 ± 0.7	0.7 ± 0.4
2c	6.2 ± 1.8	0.7 ± 0.2
2d	7.1 ± 0.7	1.4 ± 0.1
2e	25.2 ± 1.2	5.0 ± 0.2
2f	9.7 ± 0.6	1.8 ± 0.5
2g	18.7 ± 0.3	2.7 ± 0.2
2h	15.1 ± 0.8	2.6 ± 0.1
2i	8.6 ± 0.2	2.0 ± 0.2
2j	2.9 ± 0.6	1.3 ± 0.1
2k	20.0 ± 0.4	3.8 ± 0.3

^a Reaction conditions: Ethylene (1 atm), catalyst (0.0026 mmol, 3.7 mM), and Si(SiMe₃)₄ (internal standard) in benzene- d_6 (0.7 mL) at 100 °C. ^b Total turnovers at 24 h (average of triplicate experiments with standard deviations) determined by ¹H NMR spectroscopy. ^c Initial rate given as the turnover numbers after 1 h.

To elucidate the relative influence of catalyst decomposition on catalytic efficiency, the relationship between ethylbenzene d_6 production (total turnovers, at 24 h) and initial rate (turnovers at 1 h) was compared (Figure 2). The data were fit to a linear regression with a slope of ca. 5.4. Ethylene concentration in solution (as determined by ¹H NMR spectroscopy) was relatively constant since the reaction vessel's head-space contained a significant excess of ethylene relative to catalyst loading. The linearity of this relationship, and the low value of the slope (far less than 24), implies that the product yield is mainly influenced by the initial reaction rate, and that the decomposition rate is roughly the same for all catalysts.



Figure 2. Plot of total turnovers of ethylbenzene- d_6 for catalysts **2a-k** (measured at 24 h) *vs.* the initial rate of ethylbenzene- d_6 formation (approximated as the turnovers after 1 h). Error bars have been omitted for clarity. The dashed line is a linear fit of the data.

Table 2. Catalytic Propylene Hydroarylation with 2a-k.



Catalyst ^a	Total Turnovers ^b	Linear:Branched ^c
2a	5.6 ± 0.4	0.40 ± 0.03
2b	2.4 ± 0.1	0.36 ± 0.02
2c	2.5 ± 0.2	0.31 ± 0.02
2d	5.2 ± 0.4	0.43 ± 0.04
2e	19.8 ± 2.3	0.40 ± 0.03
2f	8.5 ± 0.7	0.44 ± 0.05
2g	6.4 ± 0.2	0.38 ± 0.03
2h	8.6 ± 0.2	0.36 ± 0.02
2i	7.5 ± 0.6	0.37 ± 0.02
2j	0.6 ± 0.03	0.70 ± 0.09
2k	8.0 ± 1.0	0.40 ± 0.02

^a Reaction conditions: Propylene (1 atm), catalyst (0.0026 mmol, 3.7 mM), and Si(SiMe₃)₄ (internal standard) in benzene- d_6 (0.7 mL) at 100 °C. ^b Total turnovers at 24 h (average of triplicate experiments with standard deviations) determined by ¹H NMR spectroscopy and refers to the sum of the turnovers of *n*-propylbenzene- d_6 and cumene- d_6 . ^c Determined as the ratio of TO_{Linear}:TO_{Branched}.

Propylene hydroarylation was surveyed using catalysts **2a-k** to determine the influence of ligand substitution on the ratio

of anti-Markovnikov (linear) vs. Markovnikov (branched) products (Table 2). Reactions were performed for 24 h at 100 °C, and product formation was monitored by ¹H NMR spectroscopy (see SI, Figure S5). Minimal variation in catalytic activity was observed for complexes **2a-k**, and the overall activity of propylene hydroarylation was reduced compared to ethylene. Interestingly, complex **2e** proved to be significantly more active than any of the other complexes tested, affording nearly 20 turnovers of propylene hydroarylation products after 24 h.

Only a minimal variation in regioselectivity was observed for complexes **2a-k**; the catalysts tended to form cumene- d_6 preferentially to *n*-propylbenzene- d_6 (*i.e.* Markovnikov selectivity), with a linear:branched ratio of ca. 0.40. This selectivity is similar to that observed previously for other platinum hydroarylation catalysts.^{14,15,19} The linear/branched ratio remained constant over the course of the reaction (see SI, Figure S6), which suggested that the product formation rates for the two regioisomers are similar. Lastly, a comparison of total turnovers *vs.* initial rate for the hydroarylation of propylene with benzene- d_6 suggested that the decomposition rates of catalysts **2a-k** are similar (see SI, Figure S7).

Attempted catalytic hydroarylations of other substituted olefins with complex **2a** were unsuccessful. While *tert*-butylethylene reacted with complex **2a** in benzene- d_6 , the rate of product formation was far slower than was observed for reactions with propylene or ethylene (ca. 1 turnover of the hydroarylation products after 24 h). Unfortunately, other olefins did not undergo hydroarylation: 1-octene rapidly isomerized to 2-octene, and cyclohexene did not undergo conversion over 24 h. This suggests that the rate of isomerization catalyzed by these complexes is faster than the rate of productive hydroarylation, and internal olefins (2-octene and cyclohexene) are inert under the catalytic conditions.

The regiochemistry of C–H bond cleavage during catalysis was probed with substituted arene substrates. Treatment of ethylene with catalyst **2a** in neat toluene yielded 8.4 ± 0.3 equivalents of ethyltoluenes after 24 h at 100 °C, with 98% selectivity for *meta*- and *para*-products (as analyzed by GC; *meta*- and *para*-ethyltoluene isomers could not be resolved). This suggests that the steric properties of the arene largely direct the C–H activations. Mesitylene was employed as a substrate to determine whether more highly substituted arenes could also be functionalized. Indeed, catalyst **2a** converted mesitylene into the corresponding hydroarylation product (8.8 ± 0.4 turnovers after 24 h at 100 °C), indicating that *ortho*-functionalization is viable.

Isotope Effects. To gain insight into the rate-determining step for catalysis, isotope effects on turnover numbers were examined. First, in separate experiments, the hydroarylation of ethylene using catalyst **2a** in either benzene or benzene- d_6 gave 18.1 ± 1.1 and 7.4 ± 1.1 turnovers, respectively, after 24 hours at 100 °C. The ratio of these two values (TO_H/TO_D = 2.4 ± 0.39) suggests that C–H(D) activation is important in the turnover-limiting step.^{2,20} However, note that this comparison does not reflect a kinetic isotope effect as it is not calculated using rate constants and a rate law for this catalytic system has not been determined.

In a separate experiment, equimolar amounts of benzene and benzene- d_6 were used as neat substrates for ethylene hydroarylation with **2a** as the catalyst (eq 1). In this experiment, hydroarylation could occur either through C–H or C–D activation to generate ethylbenzene or ethylbenzene- d_6 , respectively, assuming that intermolecular isotopic scrambling does not occur. The product ratio was determined by quantitative ¹³C{¹H} NMR spectroscopy after 24 hours at 100 °C (see SI, Figure S8). The terminal methyl carbons of the two products have different coupling patterns; for ethylbenzene, the CH₃ resonance appears as a singlet, whereas the CH₂D resonance appears as a triplet due to C–D coupling. The ratio of these resonances provided a product ratio of ethylbenzene:ethylbenzene- d_6 of 1.4:1.0, which is consistent with hydroarylation occurring faster with benzene than with benzene- d_6 .

The discrepancy in these values results from the fact that catalyst TON is a composite metric influenced by both reaction and decomposition rates and therefore is not a direct measure of $k_{\rm H}$ or $k_{\rm D}$. On the other hand, the isotopologue distribution as measured in the intermolecular competition experiment provides direct mechanistic information about the C–H activation step.²⁰



Synthesis and Isolation of Potential Catalytic Intermediates. It has been suggested that complexes of the type $[L_2Pt(CH_2CH_2Ph)(C_2H_4)]^+$ are either catalytic intermediates in hydroarylation or off-cycle species formed by the trapping of a 3-coordinate [L₂Pt(CH₂CH₂Ph)]⁺ intermediate with ethylene.^{14,19} To elucidate the role of such species during catalysis, several stoichiometric reactions with ethylene were performed to generate potential catalytic intermediates. Using a low-pressure J-Young NMR tube (3 mL volume) as a reaction vessel, complex 2a was treated with ethylene (1 atm) in benzene- d_6 at ambient temperatures over a 4 day period and the reaction was monitored by ¹H NMR spectroscopy. During the course of the ligand substitution reaction, a mixture of 2a, the ligand substitution product (${}^{t}BuPyInd$)PtPh(C₂H₄) (**3**), and the olefin insertion product (^tBuPyInd)Pt(CH₂CH₂Ph)(C₂H₄) (**4**) was observed by ¹H NMR spectroscopy after 3 days in a ratio of ca. 1.1:1.0:0.2, respectively (see SI, Figure S9).

Scheme 2. Synthesis of 3 from 2a or Zeise's Dimer.



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Compound **3** could be purified from the reaction mixture by column chromatography in low yield (isolated yield: 9 mg, 29%). An independent and scalable synthesis of **3** (Scheme 2) was accomplished by (i) metallation of Zeise's dimer, $[(C_2H_4)Pt(\mu-Cl)Cl]_2$, with 'BuPyInd in the presence of NaO'Bu, followed by (ii) treatment with AgOTf, and (iii) phenylation with PhLi (isolated yield: 25 mg, 20%). The X-ray structure of **3** (Figure 3) reveals a square planar geometry similar to that of complex **2a**, except that in **3** the phenyl ligand is *cis* to the indolate group. Overall, the Pt–N and Pt–C distances are similar in **2a** and **3**. The C–C bond of the bound ethylene ligand in **3** (1.386(6) Å) is slightly elongated compared to free ethylene (1.3305(10) Å).²¹ A broad ethylene resonance with ¹⁹⁵Pt satellites was observed in the ¹H NMR spectrum of **3** in dichloromethane- d_2 ($\delta = 3.84$ ppm, $J_{PtH} = 60$ Hz).



Figure 3. Crystal structure of 3, with thermal ellipsoids at 50% probability and hydrogen atoms omitted. Selected bond lengths (Å) and angles (°) for 3: C(1)-C(2): 1.386(6), C(1)-Pt(1): 2.115(4), C(2)-Pt(1): 2.130(4), C(3)-Pt(1): 2.013(4), N(1)-Pt(1): 2.121(3), N(2)-Pt(1): 2.023(3), C(3)-Pt(1)-N(2): 96.37(14), N(1)-Pt(1)-N(2): 79.52(12).

Exposure of **2a** to an excess of ethylene at 40 °C for 10 days cleanly afforded the insertion product **4** after purification *via* column chromatography in an overall yield of 22% (eq 2). In the ¹H NMR spectrum, diagnostic resonances were observed for the two sets of phenethyl methylene protons of **4** at 3.21 ppm (t, J = 8.1 Hz) and 2.10 ppm (t, $J_{HH} = 8.2$ Hz, $J_{PtH} = 67$ Hz). Additionally, the bound ethylene protons displayed a diagnostic, broadened singlet ¹H NMR resonance with ¹⁹⁵Pt coupling at 3.00 ppm (s, $J_{PtH} = 54$ Hz). The crystal structure of **4** (Figure 4) is similar to those of **2a** and **3**, with the phenethyl ligand positioned *cis* to the indolate donor.





Figure 4. Crystal structure of **4**, with thermal ellipsoids at 50% probability and hydrogen atoms omitted. Selected bond lengths (Å) and angles (°) for **4**: C(1)–C(2): 1.375(6), C(1)–Pt(1): 2.108(4), C(2)–Pt(1): 2.104(4), C(3)–Pt(1): 2.051(4), N(1)–Pt(1): 2.038(3), N(2)–Pt(1): 2.134(3), N(1)–Pt(1)–N(2): 76.69(12), N(1)–Pt(1)–C(3): 97.17(14).

Thermolysis and Hydroarylation Reactions with Complexes 2a, 3, and 4. The stability of complexes 2a, 3, and 4 in the absence of olefin was assessed by heating these complexes to 100 °C in benzene- d_6 and monitoring changes by ¹H NMR spectroscopy. Complex 2a was stable; after 4 h, no change in the ¹H NMR spectrum was observed. However, after 46 h isomerization to a mixture of 2a and *cis*-2a was observed by the formation of a second SMe₂ resonance as a singlet with ¹⁹⁵Pt–H coupling (see SI, Figure S10). Surprisingly, activation of benzene- d_6 to form (¹BuPyInd)Pt(C_6D_5)(SMe₂) did not occur. Decomposition to elemental Pt was not visually observed after 46 h.

At 100 °C in benzene- d_6 , complex **3** rapidly decomposed to elemental Pt, and free ethylbenzene- d_1 (1 equiv. vs. **3**) was observed by ¹H NMR spectroscopy after 1 h (see SI, Figure S11). In contrast, heating **4** at 100 °C for 2 h resulted in the formation of free ethylene and ethylbenzene- d_1 , 0.06 and 0.3 equiv relative to Pt, respectively (see SI, Figure S12). After 24 h, larger quantities of ethylbenzene- d_1 were observed, along with the disappearance of resonances corresponding to free ethylene and complex **4**. Additionally, elemental Pt was visually observed. This suggests that prior to hydroarylation, the ancillary ethylene ligand of **4** must dissociate to provide an open coordination site for C–H activation to occur. Complex **4**, therefore, is not the active species on the catalytic cycle and is instead an off-cycle intermediate.

The ethylene hydroarylation activities of complexes **3** and **4** were monitored over 46 h by ¹H NMR spectroscopy to determine the catalytic efficacy of these potential intermediates (Figure 5). Since these complexes lack a strongly coordinating SMe₂ ligand, an enhancement in turnovers in comparison to complex **2a** was expected. Under catalytic conditions, complexes **2a** and **4** displayed similar reaction profiles, with complex **2a** generating ethylbenzene- d_6 at a slightly faster initial rate. At 24 h, catalytic turnover for complexes **2a** and **4** were,

within error, identical $(7.4 \pm 1.1 \text{ and } 7.2 \pm 1.0 \text{ turnovers, respectively})$. In contrast, complex **3** exhibited significantly enhanced initial product formation rates and afforded 12.2 ± 0.7 turnovers at 24 h. Interestingly, both **3** and **4** appeared to be completely inactive after 24 h whereas **2a** was still minimally competent as a catalyst (albeit at a significantly slower rate). After 46 h, formation of elemental Pt was observed from all three complexes.

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Figure 5. Plot of turnovers of ethylbenzene- d_6 vs. time for catalysts **2a**, **3**, and **4**. Error bars are given as the standard deviation from triplicate experiments.

The effect of L-type ligand concentration on catalysis was explored. Ethylene hydroarylation with benzene- d_6 using complexes 2a or 4 with 10 equiv of added SMe₂ (relative to catalyst) was monitored over 46 h (see SI, Figure S13). While both 2a and **4** exhibited minimal turnovers of ethylbenzene- d_6 after 24 hours, the effect was greater for 2a than 4 (0.2 and 1.6 turnovers, respectively). A high ethylene pressure experiment illustrated the qualitative effect of ethylene concentration on catalytic activity. The turnover number of ethylbenzene- d_6 using 2a under a constant stream of ethylene at 3 atm was measured to be 4.1 and is the same, within error, to the turnovers measured with 1 atm of ethylene (3.6 ± 0.4) . The similar activity at higher ethylene pressure implies a complicated dependence on the concentration of ethylene; it likely both inhibits and promotes fundamental steps during the catalysis, as has been observed by Gunnoe and coworkers¹⁴ for cationic Pt hydroarylation catalysts.

Since catalysis with **2a**, **3**, and **4** likely proceeds through a common intermediate, variable temperature ¹H NMR spectroscopy experiments at 80 °C were performed in the presence of 1 atm of ethylene to elucidate the platinum complex speciation during catalysis (see SI, Figures S14–S16). At the initial time point (ca. 3 min of heating) using complex **2a** as the precatalyst, complexes **2a** and **3** were observed in a 0.83:1.00 ratio, implying that the exchange of SMe₂ for ethylene occurs

rapidly under catalytic conditions. Interestingly, the insertion product **4** was not observed to any appreciable extent over the course of 3 h at 80 °C. This suggests that C–H activation occurs more rapidly than trapping with ethylene, perhaps due to low concentrations of ethylene relative to benzene- d_6 . While the amount of ethylbenzene- d_6 increased over time, the amount of observed **3** remained relatively constant.

In an analogous experiment with **3** as the added precatalyst, rapid ethylbenzene- d_6 formation was observed, which was accompanied by a slow conversion of **3** to **4**. In a similar experiment using complex **4**, reduced activity towards the generation of ethylbenzene- d_6 was observed. Concurrent formation of complex **3** occurred at a slower rate compared to the analogous reaction using **2a** as the precatalyst. These results suggest that ethylene dissociation from complex **4** to form a catalytically active species is not rapid.

Testing the Active Catalyst Identity: Base and Hg(0) Poisoning Experiments. A recent report from this laboratory²² demonstrated that the hydroarylation of cyclohexene with mesitylene catalyzed by (COD)Pt(OTf)₂ proceeds by an acidcatalyzed mechanism, despite the lack of acid as an initial reagent. For this system, an initial metal-mediated olefin coupling²³ occurs to generate olefin dimers as well as an equivalent of HOTf, which can catalyze hydroarylation via a Friedel-Crafts mechanism. The addition of a bulky, non-coordinating base (2,6-di-*tert*-butyl-4-methylpyridine) reduced catalysis, with complete catalytic inhibition observed upon addition of only two equivalents of base relative to Pt.

To determine whether *in situ* acid generation caused the observed catalysis with complexes **2a-k**, hydroarylation of ethylene with benzene- d_6 was performed in the presence of 20 equiv of 2,6-di-*tert*-butyl-4-methylpyridine relative to catalyst **2a**. Catalytic activity was monitored by ¹H NMR spectroscopy over 46 h at 100 °C (see SI, Figure S17). No change in catalytic behavior was observed at any point during catalysis, which suggests that hydroarylation is not the result of adventitious acid-catalysis.

Hydroarylation experiments in the presence of added Hg(0) were used to elucidate whether the reaction was catalyzed by a soluble species or by a heterogeneous Pt(0) material formed by *in situ* decomposition of the molecular precatalysts.²⁴⁻²⁶ Mercury readily forms amalgams with Group 10 metals, which should trap any catalytically active heterogeneous species, assuming the rate of amalgamation is fast relative to catalysis.²⁴ To this end, addition of Hg(0) has been employed as a poison for adventitious nanoparticle catalyzed reactions.²⁵ As a result, if nanoparticles are indeed the catalytically active species then the inclusion of Hg(0) into the reaction mixture should inhibit product formation (assuming a fast rate of amalgamation).^{24,25}

Hydroarylation of ethylene with benzene- d_{6} , with **2a** or **3** as catalysts, was performed in the presence of Hg(0) and product formation was monitored over a 5 day period (see SI, Figure S18). Surprisingly, catalytic activity for both **2a** and **3** was improved with the addition of Hg (15.7 and 24.3 turnovers after 24 h at 100 °C in the presence of Hg(0) vs 7.8 and 12.2 turnovers in its absence, respectively). Moreover, decomposition rates were reduced in the presence of Hg. To elucidate the

cause for the improved performance, several further control experiments were performed.

To probe the existence of possible molecular Hg-Pt adducts which could be more catalytically active than the initial precatalysts, complex 2a was heated to 100 °C in benzene- d_6 with added mercury in the absence of ethylene. No change in the ¹H NMR spectrum was observed, which suggests that in the absence of olefin, Hg and 2a do not interact to form a detectable species. Additionally, catalysts 2a or 3 were prestirred in benzene- d_6 with Hg(0), carefully filtered, and then subjected to standard hydroarylation conditions (see SI, Figure S19). Catalyst 3 did not exhibit a change in activity compared to catalysis without prestirring with Hg(0). In contrast, complex 2a demonstrated a slight improvement in catalytic activity (albeit less so than in the presence of Hg). It has been reported that metallic nanoparticles can grow by an autocatalytic mechanism involving an acceleration of the conversion rate for molecular precursors after nucleation.²⁶ Therefore, we propose that sequestration of Pt(0) seed particles via amalgamation with Hg(0) results in reduced competitive decomposition rates and therefore an improvement to catalyst stability and longevity.

Proposed Hydroarylation Mechanism. Given the observations above, a mechanism for ethylene hydroarylation similar to those reported by Gunnoe¹⁴ and Goldberg¹⁵ is proposed (Figure 6). An equilibrium between the dimethylsulfide precatalyst **2a** and the active species **3** occurs via a rapid ligand exchange with ethylene. Olefin insertion into the Pt–Ph bond yields a coordinatively unsaturated (^tBuPyInd)Pt(CH₂CH₂Ph) species (**A**), likely stabilized by either an agostic interaction of the β -phenethyl C–H bond or a π -interaction of the phenethyl arene with the Pt center. Computations for analogous cationic Pt complexes suggest that a π -interaction is more stable than an agostic interaction, resulting in a larger kinetic barrier for C– H activation from the π -complex ($\Delta\Delta G^{\ddagger} = 5.0$ kcal/mol).¹⁴ Therefore, it is quite possible that the agostic complex is the catalytically relevant intermediate, **A**.

Intermediate **A** induces arene C–H activation of solvent by an oxidative addition reaction to form a five-coordinate, Pt^{IV}hydride intermediate (**B**). Subsequent reductive elimination from **C**, and exchange of the bound ethylbenzene ligand for ethylene, regenerates **3**. Alternatively, C–H activation can occur by a σ -bond metathesis mechanism to form ethylbenzene in a single step. Recent precedent for this type of mechanism has been published by the Gunnoe¹⁴ and Cundari¹⁹ groups. For cationic Pt species, DFT calculations suggest that a two-step oxidative addition/reductive elimination pathway is only slightly preferred over a σ -bond metathesis route ($\Delta\Delta$ G[‡] = 2.3 kcal/mol).^{14,19}

It has been suggested by Gunnoe and coworkers¹⁴ that complexes of the type $[(bpy)Pt(CH_2CH_2Ph)(C_2H_4)]^+$ are either catalytic intermediates or off-cycle species. Since complex **4** exhibits reduced hydroarylation activity compared to **2a** or **3**, and releases ethylene upon heating in benzene, it seems likely that this complex exists as an off-cycle intermediate in equilibrium with **A** *via* ethylene dissociation.



Figure 6. Proposed mechanism for productive catalytic ethylene hydroarylation with **2a**. Note that C–H bond activation can occur *via* either an oxidative addition/reductive elimination or σ -bond metathesis pathway.

Catalyst Decomposition Studies. While olefin hydroarylation is catalyzed by (N-N)-ligated Pt complexes, the stability of these catalytic species appears to be the major factor in defining catalytic efficiency (vide supra). In an effort to understand the decomposition pathways available during catalysis, a sample of 2a was exposed to benzene and ethylene (1 atm) at 100 °C for 20 h, and products were separated from elemental Pt by preparative thin-layer chromatography. Several species were identified by high resolution mass spectrometry (see Figure 7 and SI, Table S1). Organic species with m/z values consistent with free ligand (1a) and phenethyl substituted ^tBuPyInd (5) were identified. Complexes 2a and 3 were also observed. Surprisingly, m/z values that correspond to previously unobserved organometallic compounds were also detected: [(^tBu-PyInd)Pt(CH₂CH₂Ph)(SMe₂)] (6), [(^tBuPyInd)PtEt(SMe₂)] (7), and [(^tBuPyInd)PtPh(H₂C=CHPh)] (8). While relative amounts could not be quantified with high resolution mass spectrometry, the existence of these species suggests possible decomposition pathways.

Since styrene has been implied as a major decomposition product,^{14,15,18} a separate ethylene hydroarylation experiment was performed at 100 °C for 24 h and styrene content was determined by ¹H NMR spectroscopy. Unreacted ethylene was removed by a freeze/pump/thaw cycle, since ethylene and styrene vinylic resonances overlap. Multiple sets of vinylic resonances are consistent with styrene, \mathcal{B} -(\mathcal{E})-deuterostyrene, and \mathcal{B} -(\mathcal{Z})-deuterostyrene. The relative ratio of these three species (with respect to the initial catalyst loading) was ca. 10%:8%:12%, respectively.

Given these data, possible catalyst decomposition pathways are described in Figure 7. As in the productive hydroarylation mechanism (Figure 6), ligand exchange with ethylene from complex **2a** affords the ethylene complex **3** and subsequent insertion yields intermediate **A**. This intermediate is undoubtedly trapped by available L-type ligands (*i.e.* ethylene or SMe₂) to afford complexes **4** and **6**. These species can reenter

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Figure 7. Organometallic speciation and decomposition pathways in ethylene hydroarylation with benzene and catalyst **2a**. [i]: ligand substitution for ethylene; [ii]: olefin insertion; [iii]: coordination of either SMe₂ or ethylene; [iv]: reductive elimination of phenethyl and ^tBuPyInd; [v]: *β*-hydride elimination; [vi]: ligand substitution of styrene for ethylene, followed by olefin insertion and coordination of SMe₂; [vii]: reductive elimination of hydride and ^tBuPyInd; [viii]: ligand substitution of SMe₂ for styrene.

the catalytic cycle, but as shown above they are less effective than **3** and do not directly participate in the major catalytic cycle.

While A can undergo reaction to produce ethylbenzene (Figure 6), it may also be a key intermediate in catalyst decomposition. Intermediate A can undergo irreversible decomposition by reductive elimination of the phenethyl fragment with the ^tBuPyInd ligand, which results in the formation of Pt(0) and 5. Alternatively, β -hydride elimination from the phenethyl fragment can occur to generate a transient Pt-hydride complex D bearing a styrene ligand. Precedent for this decomposition route exists and has been supported by DFT calculations for cationic Pt systems.¹⁴ B-Agostic intermediates of the type [(^tbpy)Pt(CH₂CH₂Ph)]⁺ have been calculated to contain a shortened C_{sp^3} - C_{sp^3} bond distance, which is consistent with partial [(^tbpy)PtH(styrene)]⁺ character. Therefore, it is unsurprising that the Pt-hydride intermediate **A** likely undergoes a facile β hydride elimination to afford **D**. Reductive elimination can occur from D to generate free ligand (1a) as well as an equivalent of styrene and Pt(0). Goldberg and coworkers^{15,18} have observed styrene formation via β -hydride elimination as the primary decomposition pathway for a similar pyridyl-pyrrole ligated Pt(II) system. Given the existence of multiple styrene isotopomers and that the catalysis primarily affords ethylbenzene- d_6 , H(D) scrambling likely occurs from complex **D** and not a catalytically active species.

In a recent publication by Nozaki²⁷, complexes of the type [(P-O)PtPh(L)] supported by a 2-(di-*tert*-butylphosphanyl)benzenesulfonate ligand were employed as precursors in the generation of stable Pt–hydride species by treatment with ethylene. Olefin insertion from these PtPh complex was suggested to generate a Pt(CH₂CH₂Ph) fragment, although such species were not directly observed. Moreover, C–H activation to form ethylbenzene was not observed. Instead, a favorable β –hydride elimination event occurred to generate [(P–O)PtH(styrene)] as an isolable species capable of catalytic olefin polymerization. This suggests that the donating properties of the supporting ligand greatly affect the stabilities of intermediates during productive hydroarylation and catalyst decomposition processes; stabilization of Pt-hydride species prevents irreversible ligand reductive elimination while also favoring unproductive β -hydride elimination over C-H activation.

Complex **D** can also undergo ligand substitution of styrene for ethylene. Hydride migration to the bound ethylene can occur followed by coordination of an L-type ligand to generate the Pt(II)–ethyl complex **7**. Similar Pt–ethyl complexes have been identified as off-cycle organometallic products by the Gunnoe group,¹⁴ for cationic (^tbpy)Pt complexes. Finally, complex **2a** can also undergo ligand substitution with any styrene generated during the course of decomposition to afford the styrene-bound complex **8**. These data suggest that a series of common mechanistic steps occur to produce the observed organometallic side-products, organic decomposition species, and elemental Pt: θ -hydride elimination, olefin (or residual sulfide) binding at platinum, and reductive elimination involving the (N–N) ligand.

CONCLUSIONS

In summary, a series of Pt(II) catalysts featuring bidentate pyridyl-indolate ligands with varying substituents has been successfully synthesized. These complexes demonstrated the ability to catalyze olefin hydroarylation on a range of substrates. In general, complexes of the type $(N-N)PtPh(SR_2)$ exhibited reasonable activity compared to other reported Pt complexes.^{14,15} Additionally, reduced over-alkylation was observed using the current catalysts.

Two potential intermediates (**3** and **4**) were isolated and their activities were compared with that of precatalyst **2a**. Complex **3**, bearing Ph and C_2H_4 as ancillary ligands, rapidly catalyzed olefin hydroarylation. In contrast to complexes **2a** and **3**, the aforementioned complex (^fBuPyInd)Pt(CH₂CH₂Ph)(C₂H₄)

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exhibited reduced activity and therefore is not a direct catalytic intermediate in this system: ethylene dissociation is required for catalysis to occur. Interestingly, complex **2a** exhibited improved catalytic stability when compared to **3** or **4**, which suggests that the ancillary SMe₂ ligand retards decomposition at the expense of reduced activity.

Several studies were designed to probe the operative mechanism for catalysis. We have shown that efficiency in this platinum system is determined primarily by competing, irreversible catalyst decomposition. The competitive decomposition routes were studied to better understand how to combat poor catalytic stability. Many different organometallic and organic species were identified after completion of the catalysis; the organometallic complexes could likely reenter the catalytic cycle while the organic fragments arise from irreversible reductive eliminations. Unproductive β -hydride elimination is a major issue for catalytic stability due to the ease with which irreversible reductive elimination occurs from Pt-hydride species to form free ligand and elemental Pt. Moreover, the competing processes of catalyst turnover and decomposition involve ('Bu-PyInd)Pt(CH₂CH₂Ph) as a key, common intermediate. Therefore, further improvements in efficiencies of Pt-based hydroarylation catalysts should focus on improving the stabilities of catalytic intermediates, especially toward β -hydride eliminations.

External base and Hg(0) tests revealed that hydroarylation is metal mediated rather than adventitiously catalyzed either by acid generated *in situ* or elemental Pt nanoparticles. Interestingly, this study uncovered a potential additive in catalysis (elemental Hg) that seemingly suppresses catalyst decomposition and allows for longer catalyst lifetimes.²⁴⁻²⁶ This surprising inhibition of catalytic decomposition is an interesting feature of this system, which provides a potential solution to one of the major dilemmas in Pt catalyzed hydroarylation: competitive catalytic decomposition. While only Hg(0) has been employed in this study towards decomposition suppression, it may be possible that other additives can effectively sequester nucleating Pt nanoparticles and thereby prevent autocatalytic decay of hydroarylation catalysts.

ASSOCIATED CONTENT

Supporting Information

Experimental details, characterization data, X-ray crystallographic details, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

* E-mail: tdtilley@berkeley.edu

Present Address

[‡] A.L.L.-M.: Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Blvd, Pasadena, CA, 91125.

ORCID

 56
 Benjamin A. Suslick: 0000-0002-6499-3625

 57
 Allegra L. Liberman-Martin: 0000-0002-8447-905X

 58
 Truman C. Wambach: 0000-0001-7384-0412

 59
 T. Don Tilley: 0000-0002-6671-9099

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Notes

The authors declare no competing financial interests.

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