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Pt−Ag Catalyst System for Hydroarylations with Unactivated Arenes and Olefins

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Summary: A series of Pt complexes activated by Ag(I) salts have been shown to catalyze Markovnikov hydroarylations of unactivated olefins under mild conditions.

The selective, catalytic functionalization of hydrocarbons represents an important challenge in chemistry.[1] One area of focus concerns the activation of arene C−H bonds and the use of such reactions in the functionalization of arenes by homogeneous catalysts.[2] This work has led to significant advances in the development of hydroarylations, which effect the formal addition of an Ar−H bond across a double or triple C−C bond.[2−5] Although a number of late-transition-metal complexes, including those containing Ru,[2b,4] Rh,[3c,d] Ir,[3e,f] Pd,[2a,3a,b,5a] and Au,[3g] have been shown to catalyze these transformations, many of the systems require activated substrates or forcing conditions. A Ru-based catalyst developed by Gunnoe and co-workers constitutes a notable exception, as hydroarylation of ethylene and propylene by benzene takes place under the relatively mild conditions of approximately 2 atm pressure of the olefin and 90 °C.[4a] Although Pt complexes have found widespread utility in promoting stoichiometric activations of Ar−H bonds,[1c] their use in catalytic hydroarylation chemistry has been limited to intramolecular cyclizations and to activated olefins and alkynes.[5] Here we report a novel Pt/Ag catalyst system for the hydroarylation of unfunctionalized olefins by benzene and other unactivated arenes under mild conditions.

Initial efforts to develop a hydroarylation catalyst focused on access to a 14-electron intermediate of the type $[(NN)PtL]^+$, where (NN) represents a bidentate, monoanionic, nitrogen-based ligand. This cationic fragment was expected to initiate a catalytic cycle via benzene C−H bond activation, resulting in a five-coordinate Pt(IV) hydride intermediate that might undergo further reactions. The nitrogen-donor ligand

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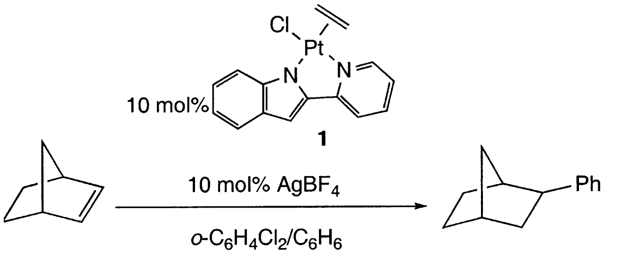
Table 1. Catalysts for the Hydrophenylation of Norbornene[a]

entry	catalyst[b]	conditions	yield (%)
1	**1** + AgOTf	115 °C, 20 h	79
2	**1** + $AgBF_4$	80 °C, 2 h	92
3	0.5 equiv Zeise's dimer + $AgBF_4$	80 °C, 2 h	89
4	$(COD)Pt(OTf)_2$	90 °C, 20 h	81
5	$(COD)Pt(OTf)_2$ + AgOTf	90 °C, 7 h	85
6	$(COD)PtCl_2$ + 3 equiv $AgBF_4$	65 °C, 2 h	78
7	$(COD)Pt(OTf)_2$ + 0.5 equiv tol−$(CuOTf)_2$	90 °C, 7 h	81

[a] Conditions: *o*-dichlorobenzene−benzene mixed solvent (2:1 by volume). [b] Catalyst concentration of 0.041 M (10 mol %).

chosen for this study is 2-(2-pyridyl)indole,[6] which was introduced via reaction of its potassium salt with $[(C_2H_4)PtCl(\mu\text{-}Cl)]_2$ (Zeise's dimer) to produce complex **1** (eq 1).[7]



(1)

Using benzene and norbornene as substrates in an *o*-dichlorobenzene−benzene (2:1 volume ratio) mixed solvent, we found that complex **1** was not an active catalyst for hydroarylation at temperatures of up to 130 °C.[8] In contrast, a combination of **1** and an equimolar amount of AgOTf (OTf^- = triflate) catalyzed the conversion of 10 equiv of norbornene to *exo*-phenylnorbornane (eq 1) at 115 °C over the course of 20 h (Table 1, entry 1). With 1 equiv of $AgBF_4$ as the additive, the reaction was significantly more rapid, as norbornene was hydrophenylated at 80 °C over 2 h (Table 1, entry 2).

To further probe the utility of electrophilic Pt complexes in this hydroarylation chemistry, we examined the equimolar (per metal) combination of Zeise's dimer and $AgBF_4$. It was found that this simple catalyst system was active for norbornene hydrophenylation under conditions similar to those for **1** and $AgBF_4$ (Table 1, entry 3). In addition, a control experiment in which $AgBF_4$ by itself was used as a potential catalyst yielded no hydroarylation products.

In an attempt to develop a single-component catalyst system, we examined the simple platinum triflate $(COD)Pt(OTf)_2$.[9] This complex catalyzed norbornene hydrophenylation over the course of 20 h at 90 °C (Table 1, entry 4). The addition of 1 equiv of AgOTf to $(COD)Pt(OTf)_2$, however, produced a catalyst that converted norbornene to *exo*-phenylnorbornane upon heating for only 7 h at 90 °C (Table 1, entry 5). The combination of equimolar amounts of $(COD)Pt(OTf)_2$ and [PPN]OTf[10] did not lead to an increase in the rate of norbornene hydrophenylation compared to only $(COD)Pt(OTf)_2$, showing that enhanced catalytic reactivity was not derived merely from the increased concentration of the triflate ion. While it is not clear that the same effect is operative for the catalyst systems in entries 1−3, this result suggests that the role of AgX salts in this transformation may extend beyond chloride abstraction and implies that Ag^+ increases the rate of conversion of the olefin to the hydroarylation product.

Table 2. Catalytic Hydroarylation of Olefins by Benzene[a]

entry	alkene	product	yield (%)
1	norbornene	*exo*-phenylnorbornane	92
2	2-butene[b]	*sec*-butylbenzene	84
3	propylene[c]	isopropylbenzene	79
4	cyclopentene	cyclopentylbenzene	62
5	cyclohexene	cyclohexylbenzene	65

[a] Conditions: *o*-dichlorobenzene−benzene mixed solvent (2:1 by volume), 5 mol % Zeise's dimer, 10 mol % $AgBF_4$, 80 °C, 2 h. [b] Reaction time 4 h. [c] Reaction time 20 h.

With $(COD)PtCl_2$ and 3 equiv of $AgBF_4$ as the catalyst, the reaction proceeded at 65 °C, a remarkably low temperature for an intermolecular hydroarylation (Table 1, entry 6). Furthermore, it was shown that Cu could be substituted for Ag without a significant loss of catalytic activity. Thus, an equimolar (per metal) combination of $(COD)Pt(OTf)_2$ and $\eta^2{:}\eta^2\text{-}\mu\text{-}(C_7H_8)(CuOTf)_2$ (2:1 copper(I) triflate−toluene complex) catalyzed the hydroarylation of norbornene at 90 °C over the course of 7 h (Table 1, entry 7), a result comparable to that achieved with $(COD)Pt(OTf)_2$ and AgOTf. Also, since the presence of Pt is the constant in all of the successful catalytic runs, a mercury test was performed to rule out the involvement of colloidal Pt.[11] It was determined that added Hg had no effect on the catalytic reactivity.

Once various catalysts had been examined using norbornene as a model substrate, inherently less reactive olefins were surveyed for hydroarylation reactivity (Table 2). It was found that 2-butene (as a cis/trans mixture), an unstrained olefin, was hydrophenylated to form *sec*-butylbenzene in 84% yield. Cyclopentene and cyclohexene were hydroarylated in lower yields (62% and 65%, respectively), with side products resulting from olefin dimerization and benzene overalkylation. Propylene reacted with benzene more slowly than the other olefins studied (20 h at 80 °C) and was converted to isopropylbenzene in 79% yield. Ethylene was unreactive, while isobutene gave only the products of olefin dimerization and trimerization.

To obtain additional information about the reaction mechanism, the hydroarylation of cyclohexene by toluene was examined (conditions as in Table 2, using toluene instead of benzene). The major products of this reaction were *p*-tolylcyclohexane and *o*-tolylcyclohexane, and only a small amount of *m*-tolylcyclohexane was formed (*o*:*m*:*p* ratio of 31:6:63). In addition, the overall yield of hydroarylation products in this case was significantly higher than in the comparable reaction with benzene (87% vs 65%). The distribution of isomers in

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(7) See the Supporting Information. For an example of a similar ligand on Pt, see: Iverson, C. N.; Carter, C. A. G.; Baker, R. T.; Scollard, J. D.; Labinger, J. A., Bercaw, J. E. *J. Am. Chem. Soc.* **2003**, *125*, 12674.

(8) *o*-Dichlorobenzene was inert under all of the reaction conditions examined.

(9) See the Supporting Information. COD = 1,5-cyclooctadiene.

(10) Obendorf, D.; Peringer, P. *Anorg. Chem. Org. Chem.* **1986**, *41*, 79. PPN = bis(triphenylphosphoranylidene)ammonium.

(11) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228.

the toluene experiment strongly suggests that mechanism involving benzene C−H bond activation at Pt is not operative and raises the possibility that an electrophilic, Friedel−Crafts-type pathway is in effect. In Friedel−Crafts reactions of monosubstituted arenes, the electronic effect of donating substituents increases arene nucleophilicity primarily in the ortho and para positions, leading to the preferential formation of the corresponding isomers.[12] In contrast, no straightforward dependence on the electronic nature of ring substituents is observed in Ar−H activations by Pt complexes.[1c]

Moreover, the C−H bond activation mechanism seems to be inconsistent with the result of propylene hydrophenylation. If a Pt hydride were involved, the *n*-propylbenzene product would be favored, due to the expected 1,2-insertion of the olefin into the M−H bond.[3e,4a] In fact, the branched product isopropylbenzene, presumably derived from the attack of benzene on the more stable secondary propyl species, was exclusively formed.

Strong Lewis and Brønsted acids, which activate the olefinic substrate toward nucleophilic attack, are typically used as catalysts for Friedel−Crafts reactions. In fact, 10 mol % triflic acid (HOTf) was found to catalyze norbornene hydroarylation under the same conditions as with the metal systems (80 °C, *o*-dichlorobenzene−benzene mixed solvent, catalyst concentration of 0.041 M). To rule out the possibility that HOTf, which could be formed by the hydrolysis of a metal triflate by adventitious water, acted as a catalyst in metal-mediated runs, a hydroarylation experiment using phenyltrimethylsilane ($PhSiMe_3$) as the arene substrate was conducted. The arylsilane $PhSiMe_3$ contains a reactive C−Si bond that can be cleaved by strong acids. While the combination of Zeise's dimer and $AgBF_4$ converted norbornene to (trimethylsilylphenyl)norbornane (as a mixture of regioisomers) in 88% yield (conditions as in Table 2, using $PhSiMe_3$ instead of benzene), HOTf did not catalyze this transformation. Instead, as expected, a reaction occurred between HOTf and the arene to provide benzene and Me_3SiOTf as the products. These experiments indicate that triflic acid is not involved in the catalysis by the Pt/Ag system.

The mechanism of this catalysis has not yet been established, but it is interesting to speculate on the roles that both metals might play in activating the substrates. One possibility involves coordination of the olefin to the Pt center. Dimerization and oligomerizaton of olefins are standard examples of transformations catalyzed by Lewis acidic, cationic Pt centers,[13] and this reactivity was observed for isobutene. The function of Ag^+ and Cu^+ salts in the enhancement of the catalytic activity is more difficult to explain, but it is possible that these additives play a role beyond simple halide abstraction and may participate in substrate activation.

The catalytic system described above provides a novel methodology for the hydroarylation of unactivated olefins. The reaction conditions are fairly mild and avoid the use of strong Lewis or Brønsted acids. This should allow extension of the scope of hydroarylation to functionalized organic substrates. Moreover, the reaction seems to proceed by an unusual mechanism, possibly involving the interaction of substrates activated at two different metal centers. Elucidation of the mechanism of this process may aid in the design of new catalytic transformations.

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Supporting Information Available: Text giving experimental procedures for the synthesis of new compounds and the procedure for catalytic runs. This material is available free of charge via the Internet at http://pubs.acs.org.

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