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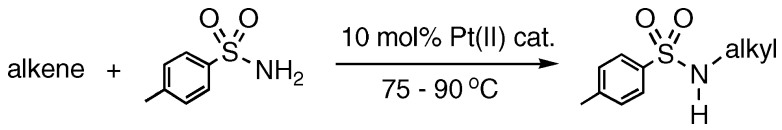

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Platinum-Based Catalysts for the Hydroamination of Olefins with Sulfonamides and Weakly Basic Anilines

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Abstract: Electrophilic Pt(II) complexes catalyze efficient hydroaminations of olefins by sulfonamides and weakly basic anilines. Catalysts include the structurally characterized complex (COD)Pt(OTf)$_2$ (**1**) and the known dimer [PtCl$_2$(C$_2$H$_4$)]$_2$, activated by AgBF$_4$. Experiments with substituted anilines establish an empirical pK_a cutoff (conjugate acid pK_a < 1) for the participation of nitrogen-containing substrates in this catalysis. Arylsulfonamides (conjugate acid p$K_a \approx -6$) with various para substituents hydroaminate olefins such as cyclohexene in yields greater than 95% at 90 °C. Hydroamination of propylene by *p*-toluenesulfonamide proceeds with Markovnikov selectivity, suggesting a mechanism that involves olefin activation at Pt. With norbornene and *p*-toluenesulfonamide as the substrates and **1** as the catalyst, intermediate [(COD)Pt(norbornene)$_2$][OTf]$_2$ (**3**) was identified and characterized by ^{19}F and ^{195}Pt NMR spectroscopies and mass spectrometry. Kinetic studies provide the empirical rate law, rate = k_{obs}[Pt][sulfonamide], and are consistent with a mechanism in which attack of a sulfonamide on the Pt-coordinated olefin is the rate-determining step.

Introduction

Hydroamination, the formal addition of an N−H bond across an unsaturated organic fragment, is a convenient and atom-economical method for the preparation of amine derivatives.[1] Although several efficient catalysts for the hydroamination of alkynes,[1b,2] vinylarenes,[3] dienes,[4] and electron-deficient alkenes[5] have recently been discovered, general systems for intermolecular hydroaminations of unactivated olefins remain elusive.[6] Lanthanide-based catalysts developed by Marks and co-workers constitute a notable exception, as broad substrate scopes in both the olefin and the amine have been realized.[1e,7] However, late transition metal complexes, which tend to exhibit greater stability and functional group tolerance, may represent more versatile alternatives as hydroamination catalysts.[8]

A number of studies have implicated electrophilic Pt complexes as efficient catalysts for transformations that involve olefin activation at the metal center.[9] For example, a recent study details the addition of carboxamides to ethylene and propylene catalyzed by a Pt−triphenylphosphine complex,[9c] while two other reports describe PtBr$_2$-catalyzed hydroamination of olefins by aniline in an ionic solvent.[9d,e] Both of these systems appear to feature attack of an amine on a coordinated olefin as a key mechanistic step. Furthermore, related Pd-based amination catalysts that participate in Wacker-type chemistry also proceed by olefin activation.[10] Many of the factors involved in the hydroamination of olefins by electrophilic transition metal ions

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Table 1. Summary of Crystallographic Data for (COD)Pt(OTf)$_2$·0.5C$_6$H$_6$ (**1**·0.5C$_6$H$_6$)

formula	$PtS_2F_6O_6C_{13}H_{15}$
MW	640.46
crystal color, habit	colorless, platelike
crystal dimensions	0.05 × 0.15 × 0.15 mm^3
crystal system	monoclinic
cell determination (2θ range)	3487 ($5.00 < 2\theta < 55.00°$)
lattice parameters	$a = 24.017(2)$ Å $b = 12.684(1)$ Å $c = 13.349(1)$ Å $\beta = 114.421(2)°$ $V = 3702.7(7)$ Å^3
space group	$C2/c$ (no. 15)
Z value	8
D_{calcd}	2.298 g/cm^3
μ (Mo Kα)	78.61 cm^{-1}
temperature	−127 °C
scan type	ω (0.3° per frame)
no. of reflections measured	total: 11 764 unique: 4713 ($R_{int} = 0.040$)
corrections	Lorentz-polarization absorption ($T_{max} = 1.00$, $T_{min} = 0.63$)
structure solution	direct methods (SIR97)
refinement	full-matrix least squares
no. reflections observed	3265 [$I > 3.0\sigma(I)$]
no. variables	263
R; R_w; R_{all}	0.026; 0.029; 0.040
GOF	1.02
max peak in final diff. map	1.76 e$^-$/Å^3
min peak in final diff. map	−0.73 e$^-$/Å^3

have been examined in recent theoretical studies.[11] Still, while hydroamination with late transition metal complexes is an actively growing area, mechanistic aspects of this transformation remain to be fully elucidated.

The current study was motivated by our recent finding that certain electrophilic Pt complexes catalyze olefin hydroarylation, which appears to involve nucleophilic attack of an arene onto a platinum-bound olefin.[12] This prompted an investigation of analogous reactions involving the addition of N−H bonds to olefins, since amines seemed to be potential candidates as analogous nucleophiles in a related process. In this report, we describe an efficient system for the hydroamination of olefins with sulfonamides and weakly basic anilines.

Results and Discussion

Catalytst Characterization. Previous investigations of the hydroarylation of olefins with electrophilic platinum complexes demonstrated that (COD)Pt(OTf)$_2$ (**1**) is a convenient catalyst precursor, presumably because the triflate ligands are labile enough to be readily displaced by the olefin substrate.[12] To obtain structural information on this complex, an X-ray diffraction study was completed (Table 1). The molecular structure of **1** (Figure 1) features η^1-coordination for both triflate anions. The Pt−O distances in this complex are fairly short, 2.085(3) and 2.087(3) Å, suggesting strong Pt−triflate interactions as compared to those in related phosphine complexes. For example, Pt−O distances in (dppe)Pt(OTf)$_2$ (dppe = 1,2-bis-diphenylphosphinoethane) are 2.120(4) and 2.138(4) Å.[13] It should be noted that **1** is highly water-sensitive, and attempted crystallization of **1** from methylene chloride containing trace amounts of water led instead to formation of the hydroxo-bridged dinuclear complex [(COD)Pt(OTf)-μ-OH−(OTf)Pt(COD)]OTf (**2**), whose structure was established by X-ray crystallography.[14] Thus, all manipulations involving **1** were performed under inert atmosphere and with rigorously dry solvents.

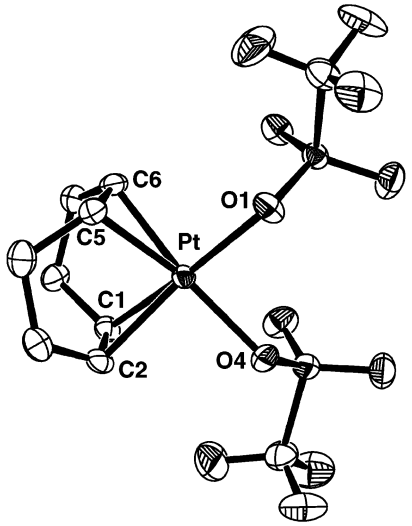

Figure 1. ORTEP diagram of the X-ray crystal structure of (COD)Pt(OTf)$_2$·0.5C$_6$H$_6$ (**1**·0.5C$_6$H$_6$). Hydrogen atoms and the C$_6$H$_6$ molecule are omitted for clarity. Bond lengths (Å): Pt−O1 = 2.085(3), Pt−O4 = 2.087(3), Pt−C1 = 2.155(5), Pt−C2 = 2.141(5), Pt−C5 = 2.144(5), Pt−C6 = 2.137(5), C1−C2 = 1.393(7), C5−C6 = 1.376(7).

Table 2. Catalytic Hydroamination of Norbornene by ArNH$_2$[a]

Ar	pK_a (conj. acid)	conditions	yield (%)
C_6F_5	0.3	80 °C, 2 h	100
p-NO_2−C_6H_4	1.0	90 °C, 16 h	35
3,5-$(CF_3)_2C_6H_3$	1.8	90 °C, 16 h	45
C_6H_5	4.6	130 °C, 16 h	0

[a] Catalyst: 10 mol % **1**, solvent: 1,2-dichloroethane.

Hydroamination with Weakly Basic Anilines. With 10 mol % of **1** as a potential catalyst, norbornene did not react with either aniline or morpholine at temperatures up to 130 °C in *o*-dichlorobenzene solvent. An examination of additional amine substrates, however, revealed that **1** catalyzes the quantitative hydroamination of norbornene with the weakly basic amine pentafluoroaniline (conjugate acid pK_a = 0.3) at 80 °C over the course of 2 h.[15] Since hydroamination appeared to correlate with amine basicity, the reactivity of anilines with conjugate acid pK_a values falling between those of pentafluoroaniline and aniline (conjugate acid pK_a = 4.6) was examined. Both 3,5-(bis-trifluoromethyl)aniline (conjugate acid pK_a = 1.8) and *p*-nitroaniline (conjugate acid pK_a = 1.0) participated in the catalyzed hydroamination of norbornene to form the corresponding *N*-norbornyl aniline derivatives, but these reactions required more forcing conditions and proceeded to lower yields (Table 2).[16] Still, these transformations are highly selective for hydroamination products, and unreacted olefin and aniline

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(14) See Supporting Information for crystallographic data for **2**.
(15) For this and all other products of norbornene hydroamination reported herein, *exo*-substituted isomers were exclusively formed.
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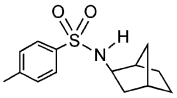
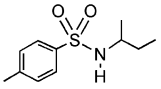
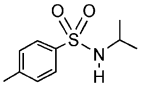
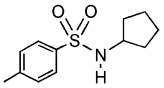
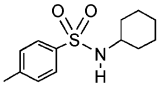
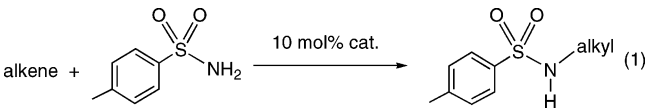
Table 3. Catalytic Hydroamination of Olefins by *p*-Toluenesulfonamide[a]

Alkene	Product	Conditions[(b)]	Yield (%)
		cat. 1, 75 °C, 2 h	> 95
		cat. 2, 85 °C, 3 h[(c)]	> 95
		cat. 2, 85 °C, 3 h[(c)]	> 95
		cat. 1, 90 °C, 12 h	> 95
		cat. 1, 90 °C, 12 h	> 95

[a] Solvent: *o*-dichlorobenzene. [b] Catalyst 1 = 10 mol % **1**; catalyst 2 = 5 mol % $[PtCl_2(C_2H_4)]_2$ and 10 mol % $AgBF_4$. [c] 1 atm pressure.

derivative account for the remaining components of the reaction mixtures. Similar observations were made by Brunet and co-workers, who reported that the number of turnovers for $PtBr_2$-catalyzed ethylene hydroamination increased with decreasing basicity of the substituted aniline substrate.[9d]

Hydroamination with Sulfonamides. With the above observations, an empirical pK_a cutoff for predicting the participation of amines in this catalytic system was established, leading us to examine the reactivity of additional weak nitrogen bases (conjugate acid pK_a < 1) in olefin hydroaminations catalyzed by **1**. Sulfonamides were chosen for a more in-depth study because of their appropriately low basicity (conjugate acid pK_a of benzenesulfonamide = −6.3)[17] and their extensive use in the pharmaceutical industry.[18] The synthesis of *N*-alkylsulfonamides is normally achieved by the reaction of deprotonated sulfonamides with alkyl halides[19a] or by the condensation of sulfonyl chlorides and amines,[19b] which generate stoichiometric amounts of salt or acid byproducts, respectively. With *p*-toluenesulfonamide as a test substrate and **1** as the catalyst, it was found that norbornene, cyclohexene, and cyclopentene were hydroaminated (eq 1) in yields in excess of 95% under the experimental conditions given in Table 3. The equimolar (per metal) combination of $[PtCl_2(C_2H_4)]_2$ (Zeise's dimer) and $AgBF_4$ catalyzed the hydroamination of cyclohexene by *p*-toluenesulfonamide under milder conditions than those for **1** (80 °C, 2 h), but the active species presumably formed by chloride abstraction from the Pt center could not be isolated.



Hydroamination of the inherently less reactive olefins *cis*-2-butene and propylene was not catalyzed by **1** and required the more active catalyst combination of Zeise's dimer and $AgBF_4$ (Table 3). A control experiment in which $AgBF_4$ by itself was used as a potential catalyst for a reaction between *cis*-2-butene and *p*-toluenesulfonamide yielded no hydroamination products. Notably, the reaction of *p*-toluenesulfonamide with propylene led to exclusive formation of the Markovnikov product *N*-isopropyl-*p*-toluenesulfonamide. The same selectivity was observed by Widenhoefer and co-workers for propylene hydroamination by an alkylcarboxamide using a neutral Pt(II)−triphenylphosphine catalyst, but under more forcing reaction conditions (120 °C, 80 h, 100 psi).[9c] In a significant contrast with the system described in this report, however, cyclohexene, cyclopentene, and norbornene did not undergo Pt-catalyzed hydroamination by carboxamides.[20] Nevertheless, the results of Widenhoefer's study are consistent with the prediction that the appropriate basicity of carboxamides (conjugate acid pK_a of benzamide = −2.1)[21] should enable their participation in the Pt-catalyzed hydroamination. Indeed, norbornene was hydroaminated by benzamide at 110 °C over the course of 40 h with **1** as the catalyst (1,2-dichloroethane solvent, >95% yield).[22]

Examination of additional olefin substrates revealed that 1-hexene was rapidly isomerized to a mixture of internal hexenes that reacted with *p*-toluenesulfonamide at 85 °C over the course of 12 h to give a mixture of two *N*-hexyl regioisomers, with an overall yield of 60% (complex **1** was used as the catalyst). Interestingly, although olefin isomerization is commonly promoted by Pt(II) complexes, a recent report described $PtBr_2$-catalyzed Markovnikov hydroamination of 1-hexene by aniline where no products derived from internal olefins were detected.[9e] Furthermore, ethylene was unreactive with Zeise's dimer and $AgBF_4$ as the catalyst combination at temperatures up to 120 °C, while styrene was only oligomerized with either catalyst system. In contrast, ethylene was reported to undergo Pt-catalyzed hydroamination by various carboxamides at 120 °C.[9c] This result further underscores the differences in substrate scope between the two catalyst systems and suggests that, despite the similarity of amide derivatives that were used, some mechanistic aspects of the two transformations may be quite distinct.

Operative electronic factors for this catalysis were probed by varying *para*-aryl ring substituents of the sulfonamides (eq 2). With cyclohexene as the olefin substrate, sulfonamides with various *para*-aryl groups (−OMe, −Cl, −H, and $-CF_3$) were subjected to the standard reaction conditions (Table 4). All of these derivatives participated in high-yielding hydroaminations to form the corresponding *N*-cyclohexyl products. Note that, in a related HOTf-catalyzed intramolecular hydroamination of alkenes by tethered sulfonamides, substrates containing the methoxybenzene functionality decomposed via acid-promoted ether cleavage.[23] Thus, observation of clean hydroamination of

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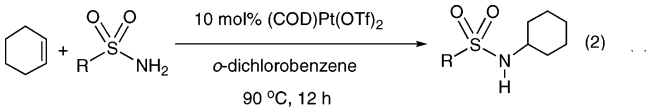
(21) Liler, M. *Spectrochim. Acta, Part A* **1967**, *23*, 139−147.
(22) For another example of norbornene hydroamination by benzamide, see: Aufdenblatten, R.; Diezi, S.; Togni, A. *Monatsh. Chem.* **2000**, *131*, 1345−1350.

Table 4. Catalytic Hydroamination of Cyclohexene by RSO_2NH_2[a]

R	product	yield (%)
phenyl	*N*-cyclohexylbenzenesulfonamide	>95
p-OMe-phenyl	*N*-cyclohexyl-*p*-OMe-benzenesulfonamide	>95
p-Cl-phenyl	*N*-cyclohexyl-*p*-Cl-benzenesulfonamide	>95
p-CF_3-phenyl	*N*-cyclohexyl-*p*-CF_3-benzenesulfonamide	>95
methyl[b]	*N*-cyclohexylmethanesulfonamide	>95

[a] Conditions as in eq 2. [b] 110 °C, 30 h reaction time.

p-methoxybenzenesulfonamide by the Pt-based catalyst **1** reflects a degree of functional group tolerance.

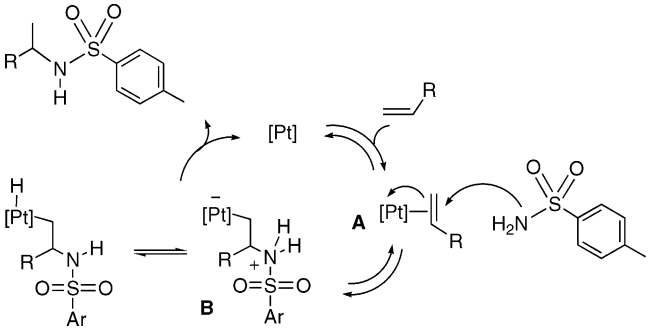


The electronic effects of aryl ring substituents in the sulfonamides were further accessed via competition experiments involving reactions of excess norbornene with equimolar mixtures of a para-substituted sulfonamide and the parent benzenesulfonamide, and the yields of hydroamination products were quantified by gas chromatography. No significant dependence on the electronic nature of the substituents was observed, as relative rates decreased in the order Me (2.0) > CF_3 (1.5) > OMe (1.4) > H (1.0) > Cl (0.9). This observation suggests that the substituted arylsulfonamides that were examined may have fairly similar basicities, and analogous results were reported by Widenhoefer and co-workers for Pt-catalyzed ethylene hydroamination with substituted arylcarboxamides.[9c] Interestingly, the substrate methanesulfonamide, which contains a relatively electron-donating methyl group, required rather forcing conditions for cyclohexene hydroamination (Table 4). This result is consistent with the general observation that higher nitrogen basicity leads to lower reactivity in this catalysis.

Identification of the Active Form of the Catalyst. Generally, two types of catalytic cycles are proposed for hydroaminations with late transition metal catalysts. The first is based on initial N−H bond activation, followed by olefin insertion and product-forming reductive C−H or C−N bond elimination,[8a] while the second involves nucleophilic attack of an amine onto a coordinated olefin and a product-forming proton-transfer step (Scheme 1).[9d] The Markovnikov regioselectivity of the hydroamination of propylene by *p*-toluenesulfonamide and the lack of precedent for stoichiometric N−H bond activations by Pt(II) seem to highly favor the latter mechanism for reactions catalyzed by **1**. Indeed, attack of nitrogen and oxygen nucleophiles on Pt-coordinated olefin species has been demonstrated in a number of cases for electrophilic Pt(II)−olefin complexes.[24]

To identify potential intermediates in the hydroamination catalysis, reaction mixtures involving norbornene as the substrate were examined by mass spectrometry and NMR spectroscopy. Excess (10 equiv) of norbornene was added to complex **1** dissolved in 1,2-dichloroethane, and the resulting mixture was analyzed by fast ion bombardment mass spectrometry (FAB-MS). A species at $m/z = 490$ $(M - 1)^+$, resulting from the loss of a proton from the dication $[(COD)Pt(norbornene)_2]^{2+}$, was observed exclusively, and the actual and simulated isotope patterns for this ion are virtually identical (see Supporting Information). Unfortunately, attempts to isolate the complex $[(COD)Pt(norbornene)_2][OTf]_2$ (**3**) by removing the solvent and excess olefin under vacuum led to the formation of intractable mixtures.

Scheme 1. Proposed Catalytic Cycle for the Hydroamination of Olefins by Pt(II) Complexes



In addition to its mass spectrometric identification, **3** was fully characterized in solution by ^1H, ^{19}F, and ^{195}Pt NMR spectroscopies and was shown to be a persistent intermediate in the catalytic hydroamination of nobornene by *p*-toluenesulfonamide. Upon addition of excess (10 equiv) of norbornene to a solution of **1** in 1,2-dichloroethane-d_4 at 50 °C, the ^{195}Pt NMR resonance for the starting Pt complex (−3084 ppm) was replaced after 20 min by a new resonance at −3771 ppm, presumably corresponding to complex **3**. This signal persists after *p*-toluenesulfonamide (10 equiv) is added to the reaction mixture, indicating that the initially formed olefin complex does not undergo ligand substitution with the added sulfonamide under these conditions. The signal at −3771 ppm persists as the reaction mixture is further heated to 75 °C, and a new signal at −3320 ppm, possibly due to a catalyst decomposition product, appears only when most of the olefin (>90%) has been consumed in the catalytic reaction. In addition, ^1H NMR spectra of the reaction mixture taken during the course of catalysis show that cyclooctadiene remains bound to Pt. In 1,2-dichloroethane-d_4, the olefinic resonance for the COD ligand of complex **3** appears at 5.72 ppm ($J_{Pt-H} = 80$ Hz), as compared to 5.98 ppm for **1** ($J_{Pt-H} = 77$ Hz).

Infrared and $^{19}F\{^1H\}$ NMR spectroscopies confirm the displacement of OTf^- from the Pt center upon addition of norbornene to **1**. A solution IR spectrum of **3** contains a characteristic band at 1242 cm^{-1} that is indicative of ionic triflate, while the IR spectrum of **1**, featuring a band at 1344 cm^{-1}, suggests the presence of covalently bound, monodentate triflate.[25] Furthermore, while the $^{19}F\{^1H\}$ NMR spectrum of complex **1** contains a resonance at −78.0 ppm, a new resonance at −79.1 ppm appears upon formation of **3** by the addition of 10 equiv of norbornene and heating to 50 °C in 1,2-dichloroethane-d_4. The $^{19}F\{^1H\}$ NMR chemical shift for **3** suggests the presence of outer-sphere triflate, since the resonance of PPN-[OTf],[26] a salt that contains a free ionic triflate, is at −79.2 ppm. As with the ^1H and ^{195}Pt resonances, the $^{19}F\{^1H\}$ signal for **3** persists after *p*-toluenesulfonamide is added and the catalytic reaction proceeds. Thus, complex **3**, which forms in solution from **1** and excess norbornene, remains as the dominant Pt-containing species during norbornene hydroamination with *p*-toluenesulfonamide.

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(26) PPN = bis(triphenylphosphoranylidene)ammonium.

Reaction of 3 with Morpholine. The origin of the differences in reactivity for various nitrogen bases in this system was further probed by examining the interactions of **3** with morpholine. While, as described above, **3** does not undergo a rapid reaction with *p*-toluenesulfonamide, the addition of 10 equiv of morpholine to **3** (generated from **1** and 10 equiv of norbornene in 1,2-dichloroethane-d_4) at room temperature is accompanied by the immediate replacement of the resonance for **3** with two new resonances (−3708 and −3710 ppm) in the ^{195}Pt NMR spectrum. While the components of this mixture could not be identified further, the observation of a rapid reaction of morpholine with the bis-norbornene complex **3** may provide a justification for its lack of participation in catalytic hydroaminations.

On the basis of known reactivity modes for Pt−olefin complexes with amines, there seem to be two reasonable explanations for the fact that morpholine (and other amines for which the pK_a of the conjugate acid > 4) does not engage in this hydroamination catalysis. First, the more basic amines may bind too strongly to the Pt center, thus preventing the olefin substrate from undergoing competitive activation via coordination. Second, it may be that these amines form intermediate ammonium adducts (with the olefin substrate or with the COD ligand) that are not acidic enough to undergo product-forming proton transfer. Both ligand substitution and C−N bond formation pathways have been observed in previous studies of the stoichiometric reactions of amines with Pt−olefin complexes. For example, a recent report indicates that various α-olefins are easily displaced from *cis*-(PPh_3)(olefin)$PtCl_2$ by excess diethylamine at room temperature.[27] In contrast, studies by Vitagliano and co-workers demonstrate that dicationic Pt(II)−olefin complexes react readily with aniline to form stable zwitterionic Pt−aminoalkyl species.[28] Given the spectroscopic results currently at hand, it is not possible to determine which factor may be important in preventing morpholine from participating in the catalysis. However, since poisoning of potential hydroamination catalysts via alkylamine binding was observed in a related system,[29] we believe that ligand substitution of Pt-bound norbornene by morpholine is the more likely pathway for inhibiting the catalytic reactivity for this substrate.

Further Mechanistic Studies of Norbornene Hydroamination. Weak nitrogen bases such as sulfonamides are not expected to compete with olefins as ligands for Pt, and this is confirmed by the persistence of **3** in the course of catalytic hydroamination of norbornene by *p*-toluenesulfonamide. Moreover, intermediate **B** (Scheme 1) is predicted to be much more acidic for sulfonamides than for alkylamines, allowing for a facile proton transfer to cleave the Pt−C bond. The intermediacy of a protonated sulfonamide species is consistent with the observation that 1 equiv (relative to the Pt catalyst) of 2,6-di-*tert*-butyl-4-methylpyridine, a sterically hindered base, completely shuts down the catalytic reactivity in this system. Consistent with this observation, base additives have been used in Pd-catalyzed oxidative amination chemistry to prevent the formation of undesired olefin hydroamination products,[10b] while acid additives have been used to promote the hydroamination of electron-deficient olefins by aniline, also with a Pd-based catalyst.[30]

Further support for the mechanism depicted in Scheme 1 was provided by a study of the kinetics of hydroamination of norbornene by 4-*n*-butylbenzenesulfonamide, which was used because of its high solubility in dichloromethane. Measurements of the kinetics were conducted at 37 °C in CD_2Cl_2, and reaction progress was monitored by quantifying the concentration of the *N*-norbornyl product by ^{1}H NMR spectroscopy. Reaction orders in the sulfonamide and catalyst **1** were determined by measuring reaction rates under conditions of excess norbornene (10 equiv of norbornene relative to the sulfonamide) and 5−20 equiv of the sulfonamide relative to **1**. The reaction order in norbornene was determined by varying the concentration of norbornene (1−10 equiv relative to the sulfonamide). These experiments provided the empirical rate law, rate $= k_{obs}$[Pt][sulfonamide], where $k_{obs} = 1.28 \times 10^{-2}$ M^{-1} s^{-1}. This rate expression is consistent with a pre-equilibrium involving the binding of norbornene to form intermediate **A**, followed by a rate-determining C−N bond-forming event that produces intermediate **B**, which transforms rapidly via proton transfer to form the hydroamination product (Scheme 1). Another mechanistic possibility that leads to the observed rate expression involves a rapid equilibrium between intermediates **A** and **B** (with $K \ll 1$), followed by a rate-determining cleavage of the Pt−C bond by the acidic proton. Thus, further studies are needed to differentiate between the two pathways.

Attempts to establish the stereochemical outcome of the hydroamination of norbornene by the reaction with N-deuterated *p*-toluenesulfonamide[31] were complicated by deuterium scrambling into various positions of the *N*-norbornyl product. This process, which may occur via a sequence of rapid C−H bond activation/C−D bond elimination steps,[32] also hindered efforts to establish the kinetic isotope effect by determining the rate of norbornene hydroamination by N-deuterated 4-*n*-butylbenzenesulfonamide.[31] The apparent propensity of hydroamination products to undergo C−H bond activation has been noted by Widenhoefer and co-workers, who established that the Pt-catalyzed coupling of styrene and benzamide is reversible.[33] Thus, deuterium labeling cannot serve as an accurate stereochemical probe in this system.

Concluding Remarks

Catalytic hydroamination that proceeds via olefin activation at the metal center appears to necessitate a nitrogen base that is a weak donor, such that it does not compete with the olefin for metal binding. However, the amine must be nucleophilic enough to attack a carbon atom of the metal−olefin complex. These conflicting requirements appear to limit the range of substrates that may currently be used in hydroamination, as catalyzed by electrophilic Pt complexes. Interestingly, many of the factors relevant for late transition metal-catalyzed hydroamination (e.g., proton transfer and ligand substitution of olefin by amine) were considered in a recently published theoretical article.[11a] That

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study concluded that group 10 transition metal ions represent promising potential catalysts for olefin hydroamination, and the results described here, and in related investigations reported elsewhere,[9c−e] appear to bear out this prediction.

The catalytic system described in this report represents a promising new approach for the hydroamination of olefins by sulfonamides and weakly basic amines. While further studies are needed to elucidate the details of this catalysis, the reaction appears to involve olefin activation by coordination to Pt and a subsequent attack on this species by an external nitrogen nucleophile. Thus, hydroamination may proceed by a mechanism similar to that for the Pt-catalyzed hydroarylation reported earlier.[12] This points to the potential generality of electrophilic Pt complexes in olefin activation catalysis.

Although $(COD)Pt(OTf)_2$ is a convenient and easily prepared catalyst precursor, efforts to expand the scope of olefin hydroamination to include basic anilines and alkylamines are likely to involve complexes with more elaborate ligands on Pt. In particular, electronic properties of the ligand may increase the tendency of the metal center to bind olefins rather than amines, while steric factors may be used to direct the hydroamination toward anti-Markovnikov selectivity. In addition, Pt complexes containing chiral ligands may catalyze an enantioselective variant of this transformation. Efforts directed toward these goals are currently underway in our laboratories.

Experimental Section

General. All experiments were conducted under a nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres drybox. Nondeuterated solvents were distilled under N_2 from appropriate drying agents and stored in PTFE-valved flasks. Deuterated solvents (Cambridge Isotopes) were vacuum-transferred from appropriate drying agents.

With the exception of 4-*n*-butylbenzenesulfonamide, which was purchased from Maybridge, all olefins, anilines, and sulfonamides were purchased from Aldrich. Norbornene was purified by sublimation. Cyclopentene, cylcohexene, and 1-hexene were dried over sodium metal and vacuum-transferred onto activated molecular sieves before use. Ethylene, propylene, and 2-butene were used as received. Liquid anilines were dried over molecular sieves, and solid anilines and sulfonamides were dried by heating under vacuum. Catalyst precursors **1**[12] and $[PtCl_2(C_2H_4)]_2$[34] (Zeise's dimer) were prepared as reported in the literature.

Analytical Methods. ^1H (400.1 MHz), $^{19}F\{^1H\}$ (376.5 MHz), and ^{195}Pt (86.0 MHz) NMR spectra were recorded using a Bruker AVB400 spectrometer equipped with a 5-mm BB probe or a Bruker AVQ400 spectrometer equipped with a 5-mm QNP probe. Spectra were recorded at room temperature and referenced to the residual nondeuterated solvent for ^1H, to external C_6F_6 for ^{19}F, and to external K_2PtCl_6 for ^{195}Pt. FT-infrared spectra were recorded in 1,2-dichloroethane solution using a Mattson FTIR 3000 spectrometer at a resolution of 4 cm^{-1}. Identities of organic products were confirmed by ^1H NMR spectroscopy[35,36] and by GC−MS, using an Agilent Technologies 6890N GC system with an HP-5MS column. FAB-MS spectra were recorded on a ZAB2-EQ spectrometer from Micromass.

General Procedure for Catalytic Runs. Reactions were conducted in 5-mm Wilmad NMR tubes equipped with a J. Young Teflon valve seal, which were heated in temperature-controlled oil baths. Samples were prepared in the drybox by dissolving the catalyst, amine, and solid or liquid olefin in the specified solvent. Gases were introduced on a Schlenk line into J. Young NMR tubes containing the catalyst and amine dissolved in the specified solvent. Reaction progress was monitored by ^1H NMR spectroscopy (a small amount of cyclohexane-d_{12} was added to all samples to obtain a lock signal). Product yields were quantified by GC, using a calculated response factor to account for the difference in ionization between the integration standard (naphthalene) and *N*-norbornyl-*p*-toluenesulfonamide.

Sample Procedure for the Isolation of Organic Products. In a drybox, a flask equipped with a Teflon-sealable valve was charged with $(COD)Pt(OTf)_2$ (0.050 g, 0.083 mmol), norbornene (0.078 g, 0.830 mmol), and *p*-toluenesulfonamide (0.142 g, 0.830 mmol). These reactants were dissolved in 5 mL of 1,2-dichloroethane, and the flask was sealed and heated with stirring to 75 °C in a temperature-controlled oil bath for 2 h. The reaction mixture was then cooled to room temperature, diluted with 5 mL of diethyl ether, and filtered through a plug of silica to remove metal-containing residues. The solvent was then removed, yielding *N*-norbornyl-*p*-toluenesulfonamide as a crystalline colorless solid (0.202 g, 92%). The ^1H NMR spectrum of the product ($CDCl_3$) agrees with the previously reported data.[36a]

Competition Experiments. Reactions were conducted in sealed NMR tubes containing 10 equiv of both benzenesulfonamide and a substituted arylsulfonamide relative to catalyst **1** and 100 equiv of norbornene relative to **1** in 1,2-dichloroethane solvent (a small amount of cyclohexane-d_{12} was added to all samples to obtain a lock signal). Product yields were quantified by GC.

Measurements of Reaction Kinetics. Reactions were monitored by ^1H NMR spectroscopy with a Bruker AVB400 spectrometer, using 5-mm Wilmad NMR tubes with a Teflon valve seal. Samples were prepared in a drybox by dissolving the appropriate quantities of **1**, norbornene, and 4-*n*-butylbenzenesulfonamide in 1 mL of CD_2Cl_2 containing a known amount of bis-(4-fluorophenyl)methane standard. The sample was then placed in an NMR probe preheated to 37 °C, which was calibrated using a neat ethylene glycol sample and monitored with a thermocouple. Single-scan spectra were acquired automatically at preset time intervals, and the peaks were integrated relative to the internal standard.

X-ray Structure Determination of 1. X-ray quality crystals of $(COD)Pt(OTf)_2 \cdot 0.5C_6H_6$ formed upon slow diffusion of pentane into a 1,2-dichloroethane solution containing a small amount of benzene to assist the crystal growth. The compound crystallizes with eight molecules of $(COD)Pt(OTf)_2$ and four molecules of benzene in the unit cell. The benzene is located on the crystallographic twofold axis and is additionally disordered between the two possible orientations of a twofold axis in the plane of a benzene molecule. The occupancy parameter was refined with the total occupancy constrained to be unity.

All non-hydrogen atoms in the structure were refined anisotropically. Positions of olefinic hydrogens were refined in the final least squares cycles, and hydrogen atoms were calculated for the disordered benzene of solvation. Other hydrogen atoms on the COD ligand were included in the idealized calculated positions but not refined.

The X-ray analysis of compound **1** was carried out at the UC Berkeley CHEXRAY crystallographic facility. Measurements were made on a Bruker SMART CCD area detector with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Data were integrated by the program SAINT and analyzed for agreement using XPREP. Empirical absorption corrections were made using SADABS. The structure was solved by direct methods and expanded using Fourier techniques. All calculations were performed using the teXsan crystallographic software package.

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Supporting Information Available: Actual and simulated isotope patterns for **3** (PDF), X-ray crystallographic data for **1** and **2** (PDF and CIF), and representative kinetic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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