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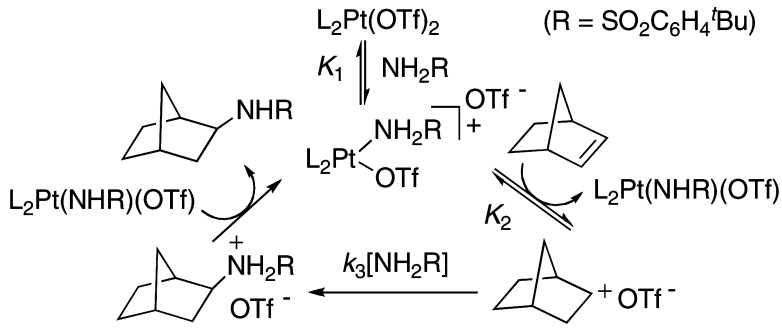

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Mechanistic Studies of the Hydroamination of Norbornene with Electrophilic Platinum Complexes: The Role of Proton Transfer

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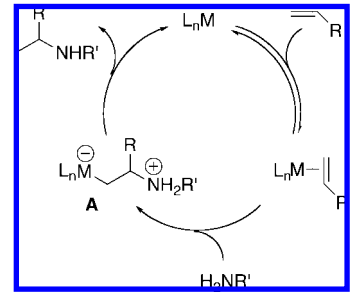
Abstract: Hydroaminations of norbornene with arylsulfonamides and weakly basic anilines were achieved using electrophilic Pt(II) bis(triflate) complexes of the type $L_2Pt(OTf)_2$ (L_2 = $^tBu_2$bpy, $^tBuC_6H_4N{=}C(CH_3)C(CH_3){=}NC_6H_4{}^tBu$, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$, *S*-BINAP). Pseudo-first-order kinetics reveal little to no dependence of the reaction rate on the ancillary ligand. Mechanistic studies do not favor an olefin coordination mechanism but are instead consistent with a mechanism involving sulfonamide coordination and generation of an acidic proton that is transferred to the norbornene. It is postulated that the resulting norbornyl cation is then attacked by free sulfonamide, and loss of proton from this adduct completes the hydroamination. The platinum−sulfonamide complex readily undergoes deprotonation to give a μ-amido platinum-bridged dimer that was isolated from the reaction solution. These studies also involve use of Me_3SiPh and Me_3SnPh as non-nucleophilic proton traps. Cleavage of the Ph−E bonds was used to detect the acidic, catalytically active species.

Introduction

A longstanding goal of research in catalysis is the development of general catalysts for the selective hydroamination of unactivated alkenes.[1,2] The search for such catalysts has generated a number of plausible mechanistic strategies, and notable progress has been made for certain substrates. Specifically, hydroaminations have been observed for vinylarenes,[3−5] dienes,[6] alkynes,[7,8] and electron-deficient alkenes.[5,9−11] In addition, several reports of hydroaminations with weakly basic amines (such as sulfonamides, carboxamides, and electron-deficient anilines) have appeared.[12−17] Despite these important advances, general catalysts that operate for unactivated alkenes and more basic amines, such as aniline and ammonia, have yet to be discovered. Only lanthanide catalysts exhibit a somewhat wide substrate scope covering a variety of alkene and amine substrates; however, these catalysts are highly moisture- and oxygen-sensitive.[18,19]

Scheme 1. Olefin Activation Mechanism for Hydroamination



Much of the effort directed toward development of general hydroamination catalysts has centered on late transition metals, since catalysts based on these metals are expected to be more moisture- and oxygen-tolerant. Also, these metals offer a number of potential mechanisms for activation of the amine and alkene substrates. In particular, mechanisms based on nucleophilic attack of amine onto a coordinated alkene (Scheme 1) and amine activation by N−H oxidative addition (Scheme 2) have received

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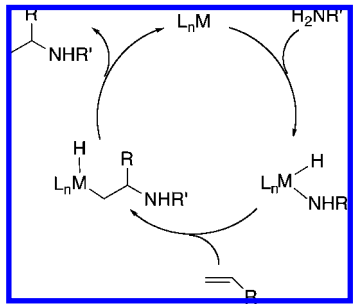
Scheme 2. Amine Activation Mechanism for Hydroamination

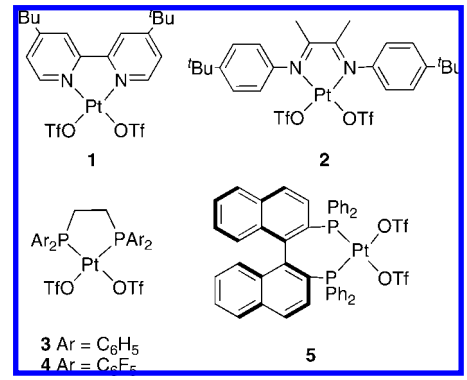


considerable attention.[7,20−24] Hydroaminations via the former mechanism would seem to require an electrophilic metal center in the catalyst, and for this reason research has focused on cationic complexes of the late transition metals. Several research groups have found that cationic late metal complexes with weakly coordinating anions catalyze a range of C−H or N−H additions across an alkene.[22,25] In our laboratories, electrophilic platinum catalysts such as (COD)Pt(OTf)$_2$, where COD = 1,5-cyclooctadiene, and [(η^2-C_2H_4)PtCl$_2$]$_2$/AgBF$_4$ have been found to mediate hydroarylations[26] and hydroaminations[15] of alkenes. The observed hydroaminations involved only weakly basic aniline and sulfonamide derivatives, and this reaction is associated with a substrate limitation in which amines with conjugate acid pK_a values above ca. 4 are unreactive. There are several possible mechanistic explanations for this limitation; however, the pK_a cutoff suggests the involvement of a proton transfer.

The possible role of Brønsted acidic species in observed, metal-catalyzed hydroarylations and hydroaminations is further suggested by the fact that strong acids are known to be catalysts for such reactions.[27−31] Thus, a detailed characterization of the role of electrophilic metal species in catalytic element-hydrogen additions to unsaturated substrates must include a thorough understanding of the potential participation of protons. In principle, this issue may be difficult to probe, since a standard mechanistic test for involvement of a Brønsted acid involves addition of a base (a proton trap). However, for reactions involving Lewis acidic metal centers and relatively acidic intermediates, an added base may inhibit the formation of products for a variety of reasons. Thus, it is important to develop mechanistic probes that reveal possible processes by which protonic species might result from the interaction of a Lewis acidic metal center with hydroamination substrates (an alkene and an amine). One possible reaction of this type was recently reported by Szuromi and Sharp, who described the interaction of (COD)Pt(OTf)$_2$ with norbornene, which results in alkene coupling at the metal center and the elimination of triflic acid.[32] Clearly, acidic species may also result from coordination of hydrogen-substituted amines to a metal center.

This contribution describes a mechanistic investigation of hydroaminations catalyzed by electrophilic bis(triflate) platinum complexes. This research involves kinetic and mechanistic studies, including the use of Me_3SiPh and Me_3SnPh as trapping reagents for protons. The results point to the platinum-mediated generation of an acidic species, which plays a crucial role in the catalysis.

Chart 1



Results and Discussion

The bis(triflate) platinum complex (COD)Pt(OTf)$_2$ has previously been reported to catalyze hydroarylations[26] and hydroaminations[15] of alkenes. For these reactions, experimental evidence suggests that the COD ligand remains coordinated to platinum and does not directly participate in the catalysis. Thus, to probe the role of the platinum center in hydroaminations, it was of interest to vary the nature of the chelating, ancillary L_2 ligand in catalysts of the type L_2Pt(OTf)$_2$.

Synthesis and Characterization of L_2Pt(OTf)$_2$ Complexes. These complexes were obtained in high yield by reaction of the corresponding L_2PtCl_2 compounds with 2 equiv of AgOTf in dichloromethane.[33−35] In this manner, a range of triflate derivatives containing both phosphine- and nitrogen-based ligands were prepared (Chart 1). Because these complexes are moisture-sensitive and readily form μ-OH bridged dimeric complexes upon exposure to water, the synthetic procedures involved the rigorous exclusion of air.[36,37] The L_2Pt(OTf)$_2$ complexes were completely characterized, and the nature of the L_2−Pt interactions was investigated by single crystal X-ray crystallography. For each complex investigated, both triflate ligands are coordinated to platinum through one oxygen atom. The Pt−O distances (Å) vary depending on the ligand sets, from 2.060(4) and 2.063(4) for **1** (Figure 1) to 2.115(3) and 2.119(3)

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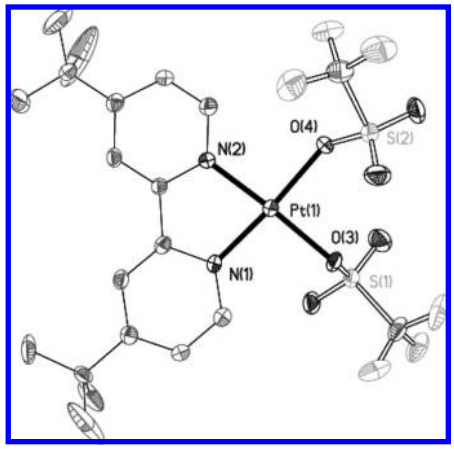


Figure 1. ORTEP diagram of the X-ray crystal structure of **1**. Hydrogen atoms are omitted for clarity. Bond lengths (Å): Pt−O4 = 2.060(4), Pt−O3 = 2.063(4), Pt−N1 = 1.967(5), Pt−N2 = 1.980(5).

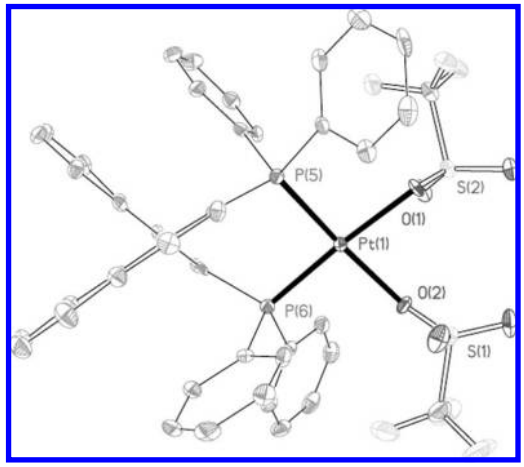
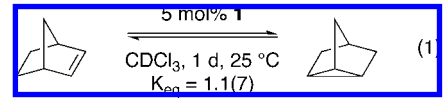


Figure 2. ORTEP diagram of the X-ray crystal structure of $\mathbf{5}\cdot C_4H_{10}O$. Hydrogen atoms and the $C_4H_{10}O$ molecule are omitted for clarity. Bond lengths (Å): Pt−O2 = 2.115(3), Pt−O1 = 2.119(3), Pt−P5 = 2.2258(14), Pt−P6 = 2.2165(14).

for **5** (Figure 2) and 2.120(4) and 2.138(4) for **3**,[38] illustrating only small variations in the Pt−triflate interactions.

Hydroamination with Weakly Basic Anilines and Sulfonamides. Previous studies found that the platinum bis(triflate) complex (COD)Pt(OTf)$_2$ is a catalyst for the hydroamination of norbornene with sulfonamides.[15] For catalysts **1**−**5**, hydroaminations occurred in near quantitative yields at 60 °C within 12 h. With catalyst **1**, the amine scope for the hydroamination was explored (Table 1). With 5 mol % of **1** relative to norbornene, no hydroamination products were observed for morpholine, aniline, or *p*-anisidine (conjugate acid pK_a > 4) at 100 °C over 3 days (Table 1, entries 1−3). However, if the conjugate acid pK_a value for the amine substrate is lowered to below 4, as for pentafluoroaniline, *p*-nitroaniline, and 3,5-(bistrifluoromethyl)aniline, hydroamination proceeds at 50−80 °C in >95% yields, with high selectivity for the *exo* product (Table 1, entries 4−6). With more acidic amines (sulfonamides and benzamide with pK_a < 0),[39−41] the hydroaminations occurred with both electron-deficient and electron-rich functional groups being tolerated (Table 1, entries 7−15). A similar dependence on the conjugate acid pK_a of the amine has been observed with other late transition metal catalysts.[15] Variation of the catalyst employed did not reveal a change in the observed pK_a limitation for the hydroamination. The exclusive formation of the *exo* products in these reactions indicates the intermediacy of a norbornyl cation, since insertions of norbornene into metal−ligand bonds result in *endo* products.[42,43] To further evaluate involvement of a norbornyl cation in the hydroamination catalysis, norbornene and 4-*tert*-butylbenzenesulfonamide-d_2 were subjected to catalytic conditions with 5 mol % **1** as the catalyst. By ^{2}H NMR spectroscopy, four C-D resonances were observed for the hydroamination product. The large number of C-D resonances strongly implies participation of a norbornyl cation (only one C-D product would be expected for an insertion mechanism). Lastly, when **5** was employed as the catalyst, a 50:50 mixture of enantiomers was observed as the product (by HPLC Chiracel OD). The complete lack of enantioselectivity with **5** as the catalyst suggests that the reaction does not involve the intermediacy of diastereomers and is consistent with the involvement of a norbornyl cation. Finally, compounds **1**−**5** were observed to catalyze the isomerization of norbornene to tricyclo(2.2.1.0(2,6))heptane, which is known to occur via an intermediate norbornyl cation.[42−44] For **1** as catalyst, an equilibrium of the two isomers was established after 1 day at 25 °C (K_{eq} = 1.1(7), eq 1).



Ancillary Ligand Effects on Reaction Rate. The influence of the ancillary ligand set on hydroamination reaction rates was investigated with kinetic studies. Under pseudo-first-order conditions with excess norbornene (20 equiv) and sulfonamide (20 equiv), k_{obs} values for each catalyst were determined at 37 °C. As shown in Table 2, there is only a small variation in rate constants among the catalysts employed, with nitrogen-based ancillary ligands (**1**, **2**) giving somewhat higher rate constants than phosphine ligands (**3**-**5**). As a reference, the k_{obs} value for triflic acid (5 mol %), a known catalyst for hydroaminations with sulfonamides, is two to 3 orders of magnitude greater than those for the platinum catalysts.

Kinetic Studies on Hydroamination. Mechanistic studies of the hydroamination of norbornene with sulfonamide included attempts to establish a rate law using kinetic measurements. For this purpose, catalyst **1** was employed, and reactions were monitored at 37 °C in chloroform-*d*. First-order dependence of the reaction rate on the concentration of **1** was established under pseudo-first-order conditions of excess norbornene and sulfonamide (10−100 equiv). The reaction order in sulfonamide was determined by varying its concentration (0.01−0.1 M) in the presence of a controlled amount of **1** (0.005 M) and excess norbornene (0.2 M). Under these pseudo-first-order conditions, plots of [sulfonamide] versus time were linear over 2−3 half-lives, and a plot of ln rate versus ln[sulfonamide] provided a reaction order of 1.1 for the sulfonamide. Variation of the

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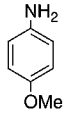
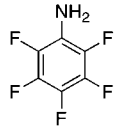
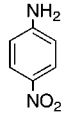
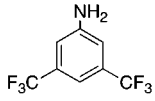
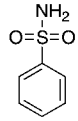
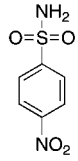
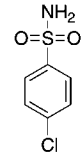
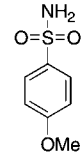
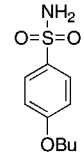
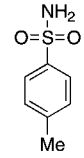
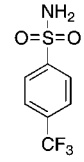
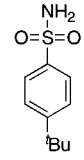
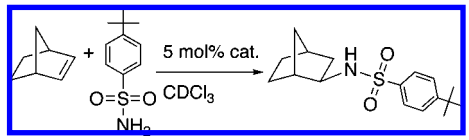
(44) Saunders, M.; Jarret, R. M.; Pramanik, P. *J. Am. Chem. Soc.* **1987**, *109*, 3735–3739.

Table 1. Intermolecular Hydroamination of Norbornene[a]

Entry	Amine	T(°C)	Time	Yield (%)[b]
1		100	3 d	0[c]
2		100	3 d	0[c]
3		100	3 d	0[c]
4		50	5 h	> 95
5		50	5 h	> 95
6		80	24 h	> 95
7[d]		100	3 d	> 95
8		50	5 h	> 95
9		80	12 h	> 95
10		50	12 h	> 95
11		50	5 h	> 95
12		50	5 h	> 95
13		50	5 h	> 95
14		50	5 h	> 95
15		50	5 h	> 95

[a] Reactions were conducted with 0.1 mmol of substrate and norbornene and 5 mol % of **1** in 1 mL of $ClCH_2CH_2Cl$. [b] Yields were determined by ^1H NMR spectroscopy using an internal standard and confirmed by GC−MS, and only the *exo* product was observed. [c] Norbornene and starting amine were isolated. [d] The long reaction time may be attributed to the low solubility of benzamide under the reaction conditions.

Table 2. Rate Constants for Catalytic Hydroamination of Norbornene



catalyst	k_{obs} (s^{-1})
(^{t}Bu$_2$bpy)Pt(OTf)$_2$ (**1**)	$1.4(9) \times 10^{-3}$
[^{t}BuC$_6$H$_4$N=C(CH$_3$)(CH$_3$)C=NC$_6$H$_4{}^t$Bu]Pt(OTf)$_2$ (**2**)	$3.2(8) \times 10^{-3}$
[[(C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$]Pt(OTf)$_2$ (**3**)	$5.3(9) \times 10^{-4}$
[[(C$_6$F$_5$)$_2$PCH$_2$CH$_2$P(C$_6$F$_5$)$_2$]Pt(OTf)$_2$ (**4**)	$5.3(9) \times 10^{-4}$
[*S*-(BINAP)]Pt(OTf)$_2$ (**5**)	$2.9(7) \times 10^{-4}$
triflic acid	$2.0(9) \times 10^{-1}$

norbornene concentration (0.03−0.08 M) in the presence of **1** (0.005 M) and excess sulfonamide (0.2 M) gave only small changes in the reaction rate, and an analogous kinetic analysis gave a reaction order of 0.2 for norbornene, over the concentration range examined (see Supporting Information, Figure S7). Under conditions employed for the kinetic studies, the rate of norbornene isomerization is much slower than the rate for hydroamination (<2% isomerization at complete conversion of norbornene in the catalysis). These experiments provide the approximate rate law: $d[product]/dt \approx k_{obs}[\mathbf{1}][sulfonamide]$, where $k_{obs} = 1.4(9) \times 10^{-3}\ s^{-1}\ M^{-1}$ at 37 °C (vide infra). The results also suggest that activation of the sulfonamide by the metal center is an important step in the catalysis and that norbornene activation by the metal center may not play an important role.

To investigate the kinetic influence of triflate anion on the catalysis, varied amounts of [NEt_4][OTf] were added to solutions of **1** (5 mol %), sulfonamide, and norbornene. As shown in Figure 3, increasing concentrations of triflate dramatically inhibit the catalysis. To examine the possibility of a salt effect[45] on this reactivity, hydroamination reactions with added [N^nBu_4][PF_6], involving a less coordinating anion, were monitored. As shown by the plot of Figure 3, such reactions are *faster*

(45) Loupy, A.; Tchoubar, B. *Salt Effects in Organic and Organometallic Chemistry*; VCH: Weinheim, 1992.

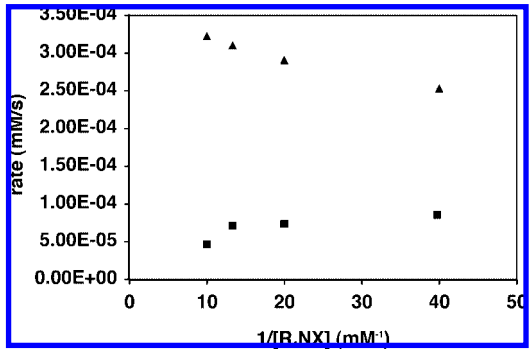


Figure 3. Plot of $1/[R_4NX]$ versus initial rate: $[Et_4N][OTf]$ (■) and $[^nBu_4N][PF_6]$ (▲).

in the presence of this salt, which is consistent with a typical salt effect for reactions involving ion pairs. The observed, opposite influence of $[NEt_4][OTf]$, in inhibiting the catalysis, is consistent with triflate dissociation playing an important role in activation of the sulfonamide via its coordination to platinum.

Mechanistic Investigations with Proton Trapping Reagents. The classic test for participation of a proton transfer involves monitoring a reaction in the presence of a sterically hindered amine. The addition of 2,6-di-*tert*-butyl-4-methylpyridine (1 equiv on the basis of **1**) to a catalytic mixture of **1**, norbornene, and the sulfonamide results in complete inhibition of the catalysis, and the formation of a diplatinum species with two μ-$NH(SO_2C_6H_4{}^tBu)$ ligands (vide infra). This trapping experiment suggests that an intermediate in the hydroamination catalysis is a coordination complex of the type $[(^tBu_2$-bpy)$Pt(NH_2SO_2C_6H_4{}^tBu)OTf]^+$, which may be deprotonated to give the observed μ-amido complex. However, it seemed possible that other deprotonations, having nothing to do with catalysis, might be responsible for deactivation of the catalyst. Thus, additional proton traps with different chemical properties were sought. In particular, it is of interest to develop non-nucleophilic proton traps that react rapidly and irreversibly with a Brønsted acid. In this regard, main group aryl compounds of the type R_nE-Ar are attractive candidates, since they may exhibit high rates of E-aryl bond cleavage via reaction with a Brønsted acid. For example, Sn-Ph and Si-Ph bonds undergo rapid E-Ph bond cleavage in the presence of an acidic proton such as TfOH, to give benzene and the corresponding E-OTf compound.[46−48]

Addition of a catalytic amount of **1** (5 mol %) to a 1:1:1 mixture of Me_3SiPh, sulfonamide, and norbornene in chloroform-*d* gave only a small amount of hydroamination product (10%) after 1 h at 25 °C. In addition, benzene (5%) and Me_3SiOTf (5%) were observed as products (by ^1H and ^{19}F NMR spectroscopy, eq 2). Thus, the transfer of protons to Me_3SiPh inhibits the hydroamination and stoichiometrically deactivates the catalyst. Furthermore, platinum complex **1** is required to facilitate this proton transfer, since a mixture of Me_3SiPh, sulfonamide, and norbornene in chloroform-*d* remained unchanged after 1 h. Under analogous conditions, the more reactive proton acceptor Me_3SnPh completely inhibited the hydroamination, while undergoing partial (5%) conversion to benzene and Me_3SnOTf with stoichiometric deactivation of the catalyst

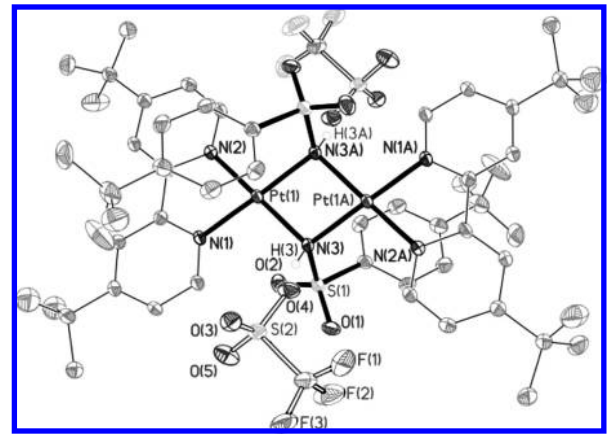
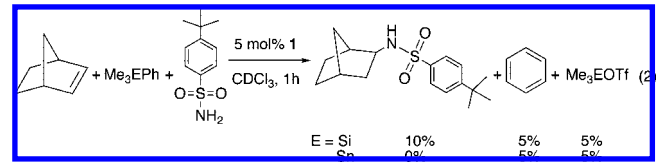


Figure 4. ORTEP diagram of the X-ray crystal structure of $\mathbf{6}\cdot CH_2Cl_2$. The hydrogen atoms (excluding those bound to nitrogen) and the CH_2Cl_2 molecules are omitted for clarity. Bond lengths (Å): Pt1−N1 = 2.013(5), Pt1−N2 = 2.009(5), Pt1−N3 = 2.058(5), Pt1−N3(A) = 2.082(5), O4···H3 = 1.944.

(eq 2). In the absence of norbornene, these reactions proceeded in a similar manner with cleavage of the Ph-E bond to give benzene (5%) and Me_3EOTf (5%) within 1 h. Thus, the proton being transferred in these reactions does not originate from the norbornene and most likely originates from the sulfonamide (in the absence of sulfonamide, no E-Ph cleavage is observed after 1 h). To quantify the rate of platinum-mediated proton transfer from p-$^tBuC_6H_4SO_2NH_2$, pseudo-first-order conditions were employed for **1** (5 mol %) with excess Me_3SiPh and sulfonamide. At 37 °C, the rate constant (k_{obs}) for this reaction is $1.7(9) \times 10^{-4}$ s^{-1}. This value is consistent with results from the competition reaction described below (eq 2), since it is similar to the value measured for hydroamination at this temperature ($1.4(9) \times 10^{-3}$ s^{-1}). Taken together, these trapping studies suggest that a key step for hydroamination may involve a platinum-mediated proton transfer.

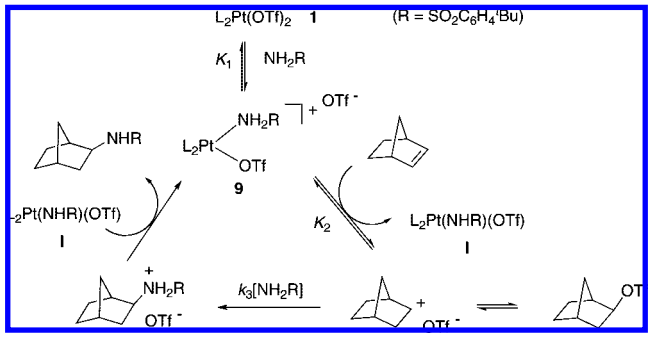


Investigation of the Active Form of the Catalyst: Observation of Sulfonamido (μ-$NHSO_2Ar$) and Sulfonamide (NH_2SO_2Ar) Complexes. Further experiments were designed to probe the active form of the catalyst and to define interactions of the substrates with the bis(triflate) platinum complexes. Particular attention focused on interaction of the sulfonamide with **1**, since the studies described above suggested that a key process might involve proton transfer from coordinated amine to the olefin substrate; therefore, the possible role of this process in the catalysis was examined.

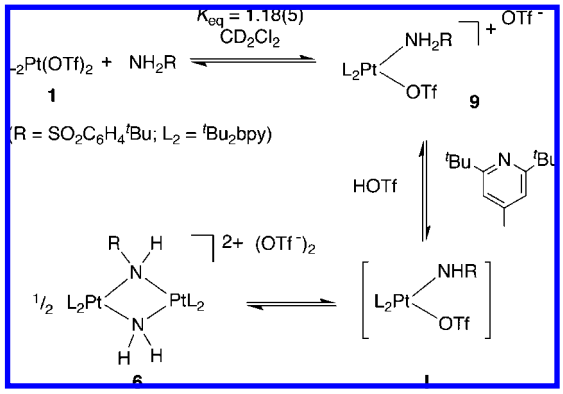
Addition of 5 mol % of the sterically hindered amine 2,6-di-*tert*-butyl-4-methylpyridine to 5 mol % of **1**, norbornene, and sulfonamide in dichloromethane-d_2 resulted in inhibition of hydroamination, such that no product was observed after 2 days at 65 °C. To isolate a metal complex from the reaction mixture, diethyl ether vapor was allowed to diffuse into the reaction solution. This resulted in formation of a small amount of a crystalline product, identified by X-ray crystallography as **6** (Figure 4). The formation of **6** upon addition of a base to the

(46) Bott, R. W.; Earborn, C.; Greasley, P. M. *J. Chem. Soc.* **1964**, 4804–4806.
(47) Alvanipour, A.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1980**, *201*, 233–247.
(48) Alizadeh, M. H.; Razavi, H.; Bamoharram, F. F.; Daneshvar, K. *J. Mol. Catal. A* **2003**, *206*, 89–93.

Scheme 3. Platinum-Generated Acid Catalysis Mechanism via Sulfonamide Coordination



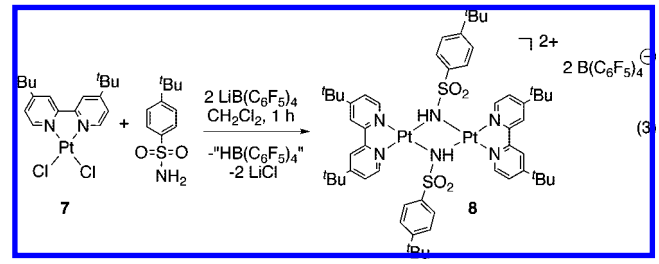
Scheme 4. Platinum Sulfonamide and Sulfonamido Equilibrium



reaction mixture suggests that the catalytic cycle for hydroamination involves a sulfonamide complex of platinum. This is described by the proposed mechanism of Scheme 3, which is consistent with the observed kinetics if proton transfer to norbornene is reversible (vide infra). Coordination of the sulfonamide to an electrophilic platinum center greatly increases the acidity of the N−H protons, and the resulting complex may be acidic enough to protonate the olefin and affect hydroamination.[27,28] In the presence of a base, deprotonation of an intermediate sulfonamide complex of this type could lead to an intermediate sulfonamido complex (**I**), which could then dimerize to give **6** (Scheme 4).

Dimeric **6** was also observed as the exclusive product in the stoichiometric reaction of **1** with the sulfonamide in the presence of 2,6-di-*tert*-butyl-4-methylpyridine at 25 °C (by NMR spectroscopy). However, it proved difficult to isolate **6** in large quantities from such reactions because of its tendency to cocrystallize with the byproduct pyridinium triflate. Fortunately, an analogous, bridging μ-amido complex (**8**) was synthesized in 86% yield from (^{t}Bu$_2$bpy)PtCl$_2$ (**7**), by addition of **7** to a mixture of 1 equiv of sulfonamide and 2 equiv of LiB(C$_6$F$_5$)$_4$ (eq 3). The isolated product was washed multiple times with diethyl ether, to ensure complete removal of any acidic impurities (via proton transfer from sulfonamide), and the purity of **8** was supported by elemental analysis, and by ^{1}H and ^{19}F NMR spectroscopy. The complete removal of Brønsted acids from samples of the dimeric μ-amido complex was essential for evaluation of the catalytic properties of this dimer, in the absence of any acid which could act as catalyst.[27,28]

Because μ-sulfonamido complexes may readily form under the conditions for catalytic hydroamination, it was important to establish whether such species are involved in the catalytic cycle. This was investigated by examination of the interactions



of **8** with norbornene. Addition of norbornene (1−20 equiv) to dichloromethane-d_2 solutions of **8** resulted in no reaction (by NMR spectroscopy), even after heating to 65 °C for 2 days. Under catalytic conditions with 5 mol % loading of **8**, no hydroamination of norbornene by sulfonamide was observed at 65 °C after 2 days. However, the addition of two equiv of triflic acid to **8** (in CD_2Cl_2) provides a mixture that is catalytically active, as determined by the further addition of norbornene (20 equiv) and sulfonamide (20 equiv). Complete conversion to product was observed after 1 h (37 °C).

The formation of μ-sulfonamido complexes **6** and **8** upon interaction of *p*-^{t}BuC$_6$H$_4$SO$_2$NH$_2$ with a platinum complex suggests that triflic acid might be produced simply by coordination of the sulfonamide to L$_2$Pt(OTf)$_2$. However, sulfonamides are known to be extremely weak nucleophiles and are rarely observed to function as ligands in metal complexes.[49,50] To investigate this possibility, the stoichiometric interaction of *p*-^{t}BuC$_6$H$_4$SO$_2$NH$_2$ with **1** in dichloromethane-d_2 was examined. At 25 °C, a 1:1 ratio of these compounds resulted in establishment of an equilibrium between **1** and a new complex, assigned as the adduct [(^{t}Bu$_2$bpy)Pt(NH$_2$SO$_2$C$_6$H$_4$^{t}Bu)(OTf)]OTf (**9**, Scheme 4). Note that this adduct is represented as possessing a Pt-NH$_2$SO$_2$Ar bond, but the coordination mode for the sulfonamide ligand has not been established. The formation of **9** is indicated by the appearance of a new set of ^{t}Bu$_2$bpy resonances, and new resonances for the coordinated sulfonamide. For this equilibrium mixture, only one very broad signal is observed for the NH$_2$ protons, at 4.92 ppm, indicating rapid exchange between the nitrogen-bound protons of free and coordinated NH$_2$SO$_2$C$_6$H$_4$^{t}Bu. The lack of an observable platinum hydride resonance for the reaction mixture excludes the presence of a direct product of N−H oxidative addition (as in Scheme 2). After 1 d, no further change in the ^{1}H NMR spectrum was observed, and a K_{eq} value of 1.18(5) was established. The addition of excess sulfonamide (2−20 equiv) did not produce another platinum-based species (e.g., a complex with two sulfonamide ligands); instead, a new equilibrium between **1** and **9** was reestablished. Perturbations of the equilibrium as a function of temperature were examined in chloroform-*d* to determine the enthalpy of reaction. A van't Hoff plot gave a $\Delta H°$ value of 4.2(7) kcal/mol and a $\Delta S°$ value of 13.9(2) eu. Finally, this equilibrium mixture was also produced upon addition of 2 equiv of triflic acid to the μ-NHSO$_2$Ar dimeric complex **6**. Attempts to isolate **9** from solutions obtained by adding sulfonamide (1 equiv or a large excess) to **1** have not been successful.

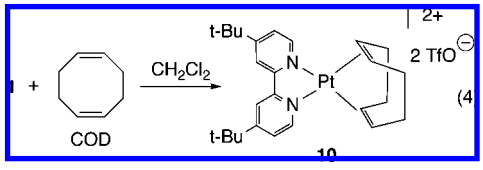
The platinum−sulfonamide interaction was further examined by ^{195}Pt NMR spectroscopy. For **1**, the ^{195}Pt NMR resonance was observed at −1530 ppm (in dichloromethane-d_2). Addition

(49) Beloso, I.; Castro, J.; Garcia-Vazquez, J. A.; Perez-Lourido, P.; Romero, J.; Sousa, A. *Polyhedron* **2006**, *25*, 2673–2682.
(50) Ishiwata, K.; Kuwata, S.; Ikariya, T. *Organometallics* **2006**, *25*, 5847–5849.

of 1 equiv of 4-*tert*-butylbenzenesulfonamide led to a new, additional resonance attributed to complex **9** (at −2010 ppm). This equilibrium mixture was cooled to −60 °C, and its interaction with norbornene (20 equiv) was monitored by ^{1}H NMR spectroscopy. No new platinum species were observed at this temperature, and hydroamination products were produced (after 10 min). Monitoring the catalysis (5 mol % **1**, dichloromethane-d_2, 25 °C) by ^{195}Pt NMR spectroscopy revealed the presence of a single platinum species (δ −1980) during the reaction. This new resonance is not attributed to the dimeric complex **6**, which exhibits a ^{195}Pt NMR resonance of −2024 ppm. It therefore seems possible that the resonance at −1980 ppm, associated with the resting state of the catalyst, is species **I** of Scheme 3. With little additional spectroscopic evidence for **I**, it is difficult to assign a specific structure to this species. However, on the basis of the observed chemistry, it appears that this is a Pt-NHSO$_2$C$_6$H$_4$^{t}Bu derivative, and we tentatively formulate it as the neutral sulfonamido complex L$_2$Pt(NHSO$_2$C$_6$H$_4$^{t}Bu)OTf. Attempts to independently generate **I** by addition of bases (2,6-di-*tert*-butyl-4-methylpyridine and 2,6-di-*tert*-butyl-4-methylphenol) to the equilibrium mixture involving **1** and **9** gave only **6** (by ^{1}H and ^{195}Pt NMR spectroscopy, Scheme 4). It is unclear why **I** is stable under catalytic conditions but is not cleanly generated from **6** or **9** under other, noncatalytic conditions. Clearly, this question would be easier to address with a full characterization of **I**.

Additional experiments were designed to investigate the possible role of platinum norbornene complexes in the hydroamination catalysis. As mentioned above, complex **1** catalyzes the isomerization of norbornene to tricyclo(2.2.1.0(2,6))-heptane (eq 1), and this result implies the existence of a transient norbornene complex that was not observed during this catalysis. However, addition of 20 equiv of norbornene to each of the bis(triflate) complexes **1**−**5**, in chloroform-*d* at 25 °C, did not lead to an observable Pt−norbornene complex (over 24 h). In each case, only resonances attributed to the bis(triflate) complex, free norbornene and tricyclo(2.2.1.0(2,6))heptane were observed (by ^{1}H and ^{19}F NMR spectroscopy). In addition, the ^{1}H NMR spectrum of a solution of **1** and 20 equiv norbornene in dichloromethane-d_2 at −60 °C contained no evidence for an olefin adduct. Interestingly, these studies also show that **1**−**5** do not mediate an olefin−olefin coupling process to generate triflic acid, as observed for (COD)Pt(OTf)$_2$ by Szuromi and Sharp.[32]

To further explore the potential role of bound alkene in hydroamination chemistry, a more stable, cationic alkene complex of platinum was investigated. This complex was obtained by addition of 10 equiv of COD to **1** in dichloromethane, which quantitatively produced **10** (eq 4). Excess COD was removed from the compound by multiple washings with pentane followed by extended drying under vacuum. Addition of 5 mol % of **10** to COD and the sulfonamide afforded no hydroamination products after 3 days at 100 °C. Similarly, **1** did not behave as a catalyst for the hydroamination of COD (for 2 days in chloroform-*d* at 100 °C). These conditions led to the rapid formation of **10** (by ^{1}H NMR spectroscopy).



Mechanism of Catalytic Hydroamination. The addition of L$_2$Pt(OTf)$_2$ catalysts to a mixture of substrates clearly initiates a proton-transfer process, as indicated by several lines of evidence including the observed pK_a cutoff for hydroamination, the lack of dramatic ancillary ligand effects on the hydroamination rate, and the observed chemistry for L$_2$Pt(OTf)$_2$ + sulfonamide mixtures. The kinetic behavior for this reaction (first-order dependence on L$_2$Pt(OTf)$_2$ and sulfonamide concentrations; little dependence on norbornene concentration) implies that the first step in the catalysis involves reversible coordination of sulfonamide to platinum, and this process has been observed as an equilibrium involving formation of the key intermediate [L$_2$Pt(NH$_2$SO$_2$C$_6$H$_4$^{t}Bu)(OTf)]$^+$. This intermediate appears to be a potent Brønsted acid, as indicated by its relatively rapid reactions with Me$_3$SiPh, Me$_3$SnPh and norbornene. A mechanism that is consistent with these facts is shown in Scheme 3, and a rate law derived from this mechanism is shown in eq 5 (where [Pt]$_0$ is the total concentration of Pt species).[51]

$$\frac{\mathrm{d[product]}}{\mathrm{d}t} = \frac{K_1K_2[\text{sulfonamide}]^2[\text{norbornene}][\text{Pt}]_0}{[\mathbf{I}] + K_1K_2[\text{sulfonamide}][\text{norbornene}]} \quad (5)$$

The observed kinetic behavior is consistent with reversible proton transfer to norbornene, followed by rate-determining attack of sulfonamide onto the norbornyl cation to produce an ammonium cation. The latter species then forms product by delivering a proton to a Pt-NH(SO$_2$C$_6$H$_4$^{t}Bu) sulfonamido intermediate (**I**), which appears to correspond to the resting state of the catalyst. Although it has not been possible to fully characterize **I**, its formulation as a Pt-NH(SO$_2$C$_6$H$_4$^{t}Bu) derivative seems chemically reasonable as the product of proton transfer from a cationic sulfonamide complex. The difficulty encountered with attempts to isolate **I** presumably relate to its ready conversion to **6** or **9** under appropriate conditions (see Scheme 4). The expression of eq 5 is consistent with the observed kinetics, if one assumes that the accessible concentration range for the experiments are near those that correspond to saturation in norbornene. Thus, the observed reaction order in norbornene is low (ca. 0.2), and the reaction order in sulfonamide is somewhat above 1 (1.1). Early in the reaction, it is likely that K_1K_2[sulfonamide][norbornene] ≫ [**I**] and the rate law simplifies to d[product]/d$t \approx k_3$[Pt]$_0$[sulfonamide]. To the extent that this is not true, the full rate law of eq 5 would apply, and some dependence on [norbornene] is to be expected.

Conclusions

The results presented here demonstrate that platinum complexes of the type L$_2$Pt(OTf)$_2$ catalyze hydroaminations of norbornene via a metal-mediated proton transfer to the olefin substrate. This work has important implications for interpretation of results from catalytic reactions involving bond activations mediated by electrophilic metal complexes and provides evidence for one type of mechanism for a metal-mediated proton-transfer catalytic reaction. Especially with further quantitative studies that help define this reactivity, it should be possible to design new processes that feature control of a metal center in delivery of a proton within a catalytic cycle. The use of main group aryl derivatives such as Me$_3$SiPh and Me$_3$SnPh as non-

(51) This analysis is based on the assumptions of conservation of charge and total platinum concentration (see Supporting Information).

nucleophilic proton traps, as reported here, is expected to provide key mechanistic probes in such studies.

Experimental Section

General. Unless otherwise noted, all experiments were conducted with dry, oxygen-free solvents using standard Schlenk techniques or in an inert atmosphere glovebox. Deuterated solvents were purchased from Cambridge Isotopes and dried with appropriate drying agents. The compounds AgOTf, COD, triflic acid, and $LiB(C_6F_5)_4$ were obtained from Aldrich and used without further purification. Norbornene was obtained from Aldrich and purified by sublimation. The compound 4-*n*-butoxybenzenesulfonamide was obtained from Ryan Scientific and used without further purification. The compound *p*-^{t}Bu$C_6H_4SO_2NH_2$ was synthesized according to literature procedure.[52] All other amines were purchased from Aldrich and liquid amines were dried over molecular sieves. The starting materials (*S*-BINAP)$PtCl_2$,[53] (^{t}Bu$_2$bpy)$PtCl_2$ (**7**),[54] [^{t}Bu-C_6H_4N=C(CH_3)C(CH_3)=N$C_6H_4{}^t$Bu]$PtCl_2$,[55] [$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$]Pt$(OTf)_2$ (**3**),[56] and [$(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$]$PtCl_2$[57] were synthesized according to literature procedures.

Analytical Methods. Solution NMR spectroscopy was performed using Bruker DRX-500 MHz, AV-500 MHz, AVQ-400 MHz, AVB-400 MHz, or AV-300 MHz spectrometers. ^{1}H NMR spectra were calibrated internally with the resonance for the residual proteo solvent relative to tetramethylsilane. $^{13}C\{^1H\}$ NMR spectra were calibrated internally with the resonance for the solvent relative to tetramethylsilane. ^{19}F NMR spectra were referenced relative to a hexafluorobenzene ($\delta = -163$) internal standard. $^{31}P\{^1H\}$ NMR spectra were referenced relative to an 85% H_3PO_4 external standard ($\delta = 0$). ^{195}Pt NMR spectra were referenced relative to a Na_2PtCl_6 external standard ($\delta = 0$). FT-IR spectra were recorded for samples as Nujol mulls on KBr plates using a Mattson FTIR 3000 spectrometer at a resolution of 4 cm^{-1}. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley. GC−MS was performed using an Agilent Technologies 6890N GC system with an HP-5MS column. Enantiomeric compositions were determined by HPLC using a Daicel CHIRACEL OD column (4.6 mm × 250 mm) with UV detection at 210 and 254 nm.

(^{t}Bu$_2$bpy)Pt$(OTf)_2$ (1). Compound **1** was synthesized using a previously reported procedure.[38,58] To 0.200 g of **7** (0.375 mmol) was added a solution of 0.200 g of AgOTf (0.781 mmol) in 10 mL of CH_2Cl_2. The reaction mixture was stirred for 1 h at room temperature. The reaction mixture was filtered, and the solvent was removed under reduced pressure. The resulting solid was washed three times with 5 mL of pentane. The yellow powder was dried under reduced pressure for 4 h (96% yield). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.66 (d, $J = 4.9$ Hz, 2H), 7.89 (s, 2H), 7.69 (d, $J = 4.9$ Hz, 2H), 1.45 (s, 18H). ^{13}C NMR (CD_2Cl_2, 125.8 MHz): δ 167.5, 157.0, 150.5, 124.8, 120.2, 119.6, 117.1, 29.8. ^{19}F NMR (CD_2Cl_2, 376.5 MHz): δ −77.5 (s, 6F). ^{195}Pt NMR (CD_2Cl_2, 85.9 MHz): δ −1530. Anal. Calcd for $C_{20}H_{24}N_2F_6O_6PtS_2$: C, 31.54; H, 3.18; N, 3.68 Found: C, 31.35; H, 2.97; N, 3.62.

[^{t}BuC_6H_4N=C(CH_3)C(CH_3)=N$C_6H_4{}^t$Bu]Pt$(OTf)_2$ (2). Compound **2** was synthesized using a procedure analogous to that used to prepare **1** (77.5% yield). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.46 (d, $J = 8$ Hz, 4H), 7.16 (d, $J = 8$ Hz, 4H), 2.05 (s, 2H), 1.28 (s, 18H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.8 MHz): δ 184.1, 165.0, 153.4, 143.0, 126.3, 122.3, 34.8, 31.0. ^{19}F NMR (CD_2Cl_2, 376.5 MHz): δ −77.6 (s, 6F). Anal. Calcd for $C_{26}H_{32}N_2F_6O_6PtS_2$: C, 37.10; H, 3.83; N, 3.33 Found: C, 36.79; H, 3.92; N, 3.35.

[$(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$]Pt$(OTf)_2$ (4). To 0.155 g of [$(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$]$PtCl_2$ (0.161 mmol) was added a solution of 0.073 g of Me_3SiOTf (0.322 mmol) in 10 mL CH_2Cl_2. The reaction mixture was stirred for 1 h. The solvent was removed under reduced pressure, and the resulting solid was washed three times with 5 mL of pentane. The white powder was dried under reduced pressure for 4 h. The powder was then recrystallized by vapor diffusion of ether into a methylene chloride solution (0.062 g, 31% yield). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.31 (m, 4H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 161.9 MHz): δ 15.7 ($^1J_{PtP} = 4552$ Hz). ^{19}F NMR (CD_2Cl_2, 376.5 MHz): δ −78.8 (s, 6F), −127.3 (s, 8F), −144.3 (s, 4F), −159.1 (s, 8F). Compound **4** has previously been generated in a solution of TfOH.[57]

(*S*-BINAP)Pt$(OTf)_2$ (5). Compound **5** was synthesized using a procedure analogous to that used to prepare **1** (77.5% yield). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.87 (br m, 4H), 7.71−7.63 (m, 12H), 7.45 (m, 6H), 7.12 (vt, $J = 7.6$ Hz, 2H), 6.90 (br m, 4H), 6.61 (d, $J = 8.8$ Hz, 4H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.8 MHz): δ 140.2(br), 135.5(br), 134.6, 134.4, 133.7, 133.5, 132.5, 132.0, 131.2(br), 130.6(br), 130.0(br), 129.5(br), 129.1, 128.7, 128.3, 128.2, 127.3, 127.1. $^{31}P\{^1H\}$ NMR: δ 0.0 ($^1J_{PtP} = 4219$ Hz). ^{19}F NMR (CD_2Cl_2, 376.5 MHz): δ −78.2 (s, 6F). Mp 230−240 °C (decomp). IR (cm^{-1}): 2727 (m), 2673 (m), 1584 (w), 1342 (s), 1192 (s), 984 (s), 742 (s), 694 (m), 631 (s), 525 (w). Anal. Calcd for $C_{46}H_{32}F_6O_6P_2PtS_2$: C, 49.51; H, 2.89; S, 5.75. Found: C, 49.19; H, 2.84; S, 6.05. Although **5** was previously synthesized,[38] its spectroscopic data was not reported.

[(^{t}Bu$_2$bpy)Pt(μ-N$HSO_2C_6H_4{}^t$Bu)]$_2(OTf)_2$ (6). To 0.100 g of **1** (0.133 mmol) was added a solution of 0.030 g of 4-*tert*-butylbenzenesulfonamide (0.141 mmol) and 0.035 g of 2,6-di-*tert*-butyl-4-methylpyridine (0.140 mmol) in 10 mL of CH_2Cl_2. The reaction mixture was stirred for 12 h. The solvent was removed under reduced pressure, and the resulting precipitate was washed three times with 10 mL of ether. The yellow powder was dried under reduced pressure for 4 h (80% yield). Complete removal of protonated pyridine was unsuccessful. ^{1}H NMR (CD_2Cl_2 with 2 equiv of 2,6-di-*tert*-butyl-4-methylpyridinium triflate, 400 MHz): δ 11.90 (br s, 2H), 8.96 (d, $J = 6.4$ Hz, 4H), 8.87 (d, $J = 8.8$ Hz, 4H), 7.75 (s, 4H), 7.58 (d, $J = 6.4$ Hz, 4H), 7.53 (s, 4H), 7.44 (d, $J = 8.8$ Hz, 4H), 2.64 (s, 6H), 1.57 (s, 36H), 1.44 (s, 36H), 1.40 (s, 18H). ^{19}F NMR (CD_2Cl_2, 376.5 MHz): δ −77.7 (s, 12F). ^{195}Pt NMR (CD_2Cl_2, 85.9 MHz): δ −2024.

[(^{t}Bu$_2$bpy)Pt(μ-N$HSO_2C_6H_4{}^t$Bu)]$_2$[$B(C_6F_5)_4$]$_2$ (8). To 0.100 g of **7** (0.187 mmol) was added a solution of 0.050 g of 4-*tert*-butylbenzenesulfonamide (0.235 mmol) and 0.256 g of $LiB(C_6F_5)_4$ (0.373 mmol) in 20 mL of CH_2Cl_2. The reaction mixture was stirred for 1 h and then filtered. The solvent was then removed under reduced pressure. The resulting solid was washed three times with 10 mL of ether. The yellow powder was dried under reduced pressure for 4 h (86% yield). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.32 (d, $J = 6.4$ Hz, 2H), 8.00 (s, 2H), 7.80 (d, $J = 8.4$ Hz, 2H), 7.65 (d, $J = 6.4$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 5.03 (s, 1H), 1.47 (s, 18H), 1.36 (s, 9H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.8 MHz): δ 169.0, 166.6, 159.9, 156.5, 155.8, 149.0(br), 148.5, 148.2, 147.1(br), 139.1, 137.2(br), 135.3(br), 134.3, 127.0, 125.8, 124.9, 121.1, 120.1, 35.9, 30.2, 29.4. ^{19}F NMR (CD_2Cl_2, 376.5 MHz): δ −132.26, −162.36, −166.23. Anal. Calcd for $C_{52}H_{38}N_3BF_{20}O_2PtS$: C, 46.10; H, 2.83; N, 3.10 Found: C, 45.34; H, 2.58; N, 2.42. ^{195}Pt NMR (CD_2Cl_2, 85.9 MHz): δ −2000.

Equilibrium mixture of 1, 9, and 4-*tert*-Butylbenzenesulfonamide. To 0.010 g of **1** (0.0133 mmol) was added a solution of 0.0034 g of 4-*tert*-butylbenzenesulfonamide (0.0133 mmol) in 1 mL of chloroform-*d*. The reaction mixture was left for 1 day to

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Table 3. Summary of Crystallographic Data for Compounds **1**, **5**, and **6**

	1	**5**	**6**
formula	$C_{20}H_{24}F_6N_2O_6PtS_2$	$C_{50}H_{42}F_6O_7P_2Pt_2S_2$	$C_{59}H_{78}Cl_2F_6N_6O_{10}Pt_2S_4$
MW	761.62	1190.00	1734.6
temperature (K)	150	153	141
crystal color, habit	colorless, block	colorless, block	yellow, block
crystal dimensions	0.04 × 0.04 × 0.03 mm^3	0.04 × 0.04 × 0.03 mm^3	0.05 × 0.04 × 0.03 mm^3
crystal system	monoclinic	orthorhombic	triclinic
2θ range	$3.56 < 2\theta < 52.74$	$3.08 < 2\theta < 49.42$	$2.58 < 2\theta < 49.54$
lattice parameters	a = 19.903(3) Å b = 14.063(2) Å c = 19.279(3) Å β = 100.987(2)° V = 5297.3(14) Å^3	a = 12.5853(8) Å b = 15.7440(10) Å c = 24.1309(17) Å V = 4781.4(5) Å^3	a = 11.779(3) Å b = 16.296(4) Å c = 20.316(8) Å α = 100.69(3)° β = 100.84(3)° γ = 96.14(2)° V = 3613.7(19) Å^3
space group	$I2/a$	$P2_12_12_1$	$P\bar{1}$
Z value	8	4	2
D_{calc}	1.910 g/cm^3	1.650 g/cm^3	1.594 g/cm^3
scan type	ω (0.3° per frame)	ω (0.3° per frame)	ω (0.3° per frame)
no. reflns measd	total 14794 unique 5339 (R_{int} = 0.0472)	total 24173 unique 8109 (R_{int} = 0.0486)	total 20696 unique 12158 (R_{int} = 0.0158)
corrections	Lorentz polarization Abs (T_{max} = 0.846, T_{min} = 0.801)	Lorentz polarization Abs (T_{max} = 0.913, T_{min} = 0.881)	Lorentz polarization Abs (T_{max} = 0.886, T_{min} = 0.820)
refinement	full-matrix least-squares	full-matrix least-squares	full-matrix least-squares
no. reflns obsd	5339 [$I > 2\sigma(I)$]	8109 [$I > 2\sigma(I)$]	12158 [$I > 2\sigma(I)$]
no. variables	334	613	811
R; R_w; R_{all}	0.037; 0.069; 0.072	0.031; 0.062; 0.063	0.039; 0.109; 0.114
GOF	0.788	1.018	1.035
max peak in final diff map	3.026	1.070	2.414
min peak in final diff map	−1.092	−0.429	−1.005

ensure no further changes in the concentrations. For **9**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.10 (d, J = 6.4 Hz, 2H, Ar*H*), 8.17 (d, J = 8.4 Hz, 2H, SO_2Ar*H* 9), 8.02 (s, 2H, Ar*H*), 7.86 (overlapping with resonance for SO_2Ar*H*, 4H, Ar*H*), 7.76 (d, J = 8.4 Hz, 2H, SO_2Ar*H*), 4.92 (br s, 2H), 1.51 (s, 36H, C*H*$_3$C overlapping with resonance for the C*H*$_3$C of **1**), 1.40 (s, 9H, C*H*$_3$C). For **1**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.53 (d, J = 6.4 Hz, 2H, Ar*H*), 7.98 (s, 2H, Ar*H*), 7.79 (d, J = 6.4 Hz, 2H, Ar*H*), 1.51 (s, 36H, C*H*$_3$C overlapping with resonance for the C*H*$_3$C of **9**). For 4-*tert*-butylbenzenesulfonamide: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.86 (overlapping m, 4H, SO_2Ar*H* and Ar*H,* **9**), 7.58 (d, J = 8.4 Hz, 2H, SO_2Ar*H*), 4.92 (br s, 2H), 1.35 (s, 9H, C*H*$_3$CArSO$_2$). ^{195}Pt NMR (CD_2Cl_2, 85.9 MHz): δ −2010, −1530. ^{19}F NMR (CD_2Cl_2, 376.5 MHz): δ −75.9, −78.0.

[(^{t}Bu$_2$bpy)Pt(COD)](OTf)$_2$ (10). To 0.050 g of **1** (0.066 mmol) was added a solution of 0.010 g of COD (0.092 mmol) in 5 mL of CH_2Cl_2. The reaction mixture was stirred for 2 h. The solvent was then removed under reduced pressure and the resulting solid was washed three times with 5 mL of pentane. The yellow powder was dried under reduced pressure for 24 h (95% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.25 (d, J = 4 Hz, 2H), 8.10 (s, 2H), 7.77 (d, J = 4 Hz, 2H), 6.33 (br t, 4H), 3.12 (d, J = 6.8 Hz, 4H), 2.62 (d, J = 6.8 Hz, 4H), 1.47 (s, 18H). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ −79.2. ^{13}C{^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 167.2, 157.0, 150.9, 128.3, 124.9, 119.9, 36.3, 30.1. Anal. Calcd for $C_{28}H_{36}N_2F_6O_6PtS_2$: C, 38.66; H, 4.17; N, 3.22 Found: C, 38.51; H, 4.11; N, 2.94.

4-*tert*-butylbenzenesulfonamide-d_2. To 1.00 g of 4-*tert*-butylbenzenesulfonamide in 5 mL of diethyl ether was added 3 mL of D_2O. The reaction mixture was left to stir for 24 h. The solvent was removed under reduced pressure, and the resulting product was treated three more times with the ether/D_2O mixture. After the last removal of solvent, the product was dissolved in diethyl ether and 1.00 g of $MgSO_4$. After 4 h, the solution was filtered, and the solvent was removed under reduced pressure (96% yield, 95% deuterium incorporation). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.87 (d, J = 6.8 Hz, 2H), 7.55 (d, J = 6.8 Hz, 2H), 1.35 (s, 9H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.8 MHz): δ 156.6, 139.0, 126.1, 126.0, 30.7. ^{2}H NMR ($CDCl_3$, 76.7 MHz): δ 4.61 (s).

General Procedure for Catalytic Runs. Reactions occurred in 5 mm NMR tubes equipped with J. Young Teflon screw caps. Temperature-controlled oil baths were utilized for heating. A solution of 0.106 mmol of olefin and 0.106 mmol of amine was prepared in 1 mL of 1,2-dichloroethane. To this solution was added 0.005 mmol of catalyst. The progress of the reaction was monitored by ^{1}H NMR spectroscopy (0.05 mL cyclohexane-d_{12} was added in order to obtain a lock signal). Once no further spectral change was observed by NMR, the solution was passed through silica to isolate the substrate or product. Identities of the organic products were confirmed by ^{1}H NMR spectroscopy[59,60] and GC−MS. All kinetic data was collected on a Bruker DRX-500 MHz spectrometer and an internal standard, 5.0 mg (0.0250 mmol) of bis(*p*-fluorophenyl)methane, was used. For kinetic runs, the sample was placed in an NMR probe preheated to 310.4 K and calibrated using an external methanol standard.[61] Single-scan spectra were obtained using an automated acquisition program that was started immediately after placing the sample in the probe, and the peaks were integrated relative to the internal standard.

General Considerations for X-ray Structure Determinations. The X-ray analyses of compounds **1**, **5**, and **6** were carried out at UC Berkeley CHEXRAY crystallographic facility. Measurements were made on Bruker SMART CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were integrated by the program SAINT and analyzed for agreement using XPREP. Empirical absorption corrections were made using SAD-

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ABS. Structures were solved by direct methods and expanded using Fourier techniques. All calculations were performed using the SHELXTL crystallographic package. Selected crystal structure and refinement data can be found in Table 3.

X-ray Structure Determination of 1. X-ray quality crystals of **1** formed upon slow vapor diffusion of ether into a methylene chloride solution of **1** at −35 °C. The compound crystallizes in the monoclinic space group *I*2/*a* with one molecule in the asymmetric unit.

X-ray Structure Determination of 5. X-ray quality crystals of **5** formed upon slow vapor diffusion of ether into a methylene chloride solution of **5** at −35 °C. The compound crystallizes in the orthorhombic chiral space group $P2_12_12_1$ with one molecule of ether and one molecule of **5** in the asymmetric unit. The enantiomorph of the space group and enantiomer of the molecule were determined by inspection of Friedel pairs of reflections followed by comparison of least-squares refinements. The results were unequivocally in favor of the enantiomorph reported.

X-ray Structure Determination of 6. X-ray quality crystals of **6** were isolated from a catalytic run by slow vapor diffusion of ether into the catalytic run solution of methylene chloride at −35 °C. The compound crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit and one molecule of methylene chloride.

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Supporting Information Available: Kinetic analysis, text describing complete X-ray experimental details and X-ray crystallographic data for **1**, **5**, and **6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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