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Biaryl Reductive Elimination Is Dramatically Accelerated by Remote Lewis Acid Binding to a 2,2′-Bipyrimidyl–Platinum Complex: Evidence for a Bidentate Ligand Dissociation Mechanism

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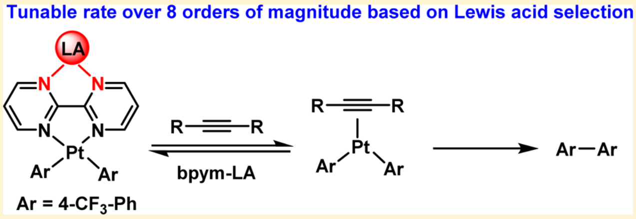
Supporting Information



ABSTRACT: The silicon and zinc Lewis acids $Si(cat)_2$ (cat = catecholato), $Si(cat^F)_2$ (cat^F = tetrafluorocatecholato), and $Zn(C_6F_5)_2$ bind to the remote ligand site of a 2,2′-bipyrimidyl–platinum diaryl complex. This platinum complex provides a platform to systematically evaluate electronic and reactivity differences triggered by Lewis acid binding. The electron density of the bipyrimidine ligand is substantially depleted upon Lewis acid binding, as evidenced by UV–vis spectroscopy and cyclic voltammetry. Biaryl reductive elimination studies allowed quantification of the effect of Lewis acid binding on reactivity, and Lewis acid binding accelerated reductive elimination rates by up to 8 orders of magnitude. Kinetics experiments in combination with DFT studies support an unusual mechanism featuring complete dissociation of the Lewis acid-coordinated bidentate bipyrimidine ligand prior to reductive elimination.

INTRODUCTION

Lewis acid activators can be used in combination with transition metal complexes to generate highly reactive intermediates. For example, boron and aluminum compounds are used to irreversibly abstract hydride and alkyl ligands from a wide range of transition metals.[1] In particular, $B(C_6F_5)_3$ is well known as an activator for metallocene alkene polymerization catalysts.[2] Recent research has extended the utility of Lewis acids as activators for chemical switches that operate by reversible abstraction of ligands. For example, alkali metal salts have been used to alter metal–oxygen interactions in iridium and rhodium complexes with ligands bearing aza-crown ether substituents.[3] In these cases, the Lewis acid activator operates by modifying the coordination environment of the metal center.

In contrast to the traditional Lewis acid-promoted ligand abstractions, binding of protons or neutral Lewis acids to the periphery of appropriately designed ligands allows for electronic tuning without steric modification.[4,5] The ligands in these systems feature pendant nitrogen- or oxygen-based functional groups that are in electronic communication with the primary metal center. These remote binding interactions offer a modular approach to rapidly assemble a series of complexes with different electronic properties from a common precursor, and comparisons of rates with and without the additive offer insight into the electronic preferences for a reaction.

Herein, we report remote Lewis acid binding to a 2,2′-bipyrimidyl–platinum (bpym–Pt) complex. Silicon- and zinc-based Lewis acids are demonstrated to have a strong affinity for coordination to the bidentate binding site of the bpym–Pt complex. A combination of methods, including ^1H, ^{13}C, and ^{195}Pt NMR and UV–vis spectroscopies and cyclic voltammetry, was used to probe electronic perturbations that occur upon Lewis acid binding. Biaryl reductive elimination reactions provide a benchmark for evaluation of reactivity, and tunable rate enhancements ranging from 10^3 to 10^8 were observed in the presence of Lewis acids. Mechanistic studies revealed an unexpected mechanism involving complete dissociation of the bidentate bipyrimidine ligand prior to C–C bond formation, demonstrating the ability of remote Lewis acid binding to profoundly alter ligand donor properties and reaction mechanisms.

RESULTS AND DISCUSSION

Synthesis of bpymPtAr$_2$ and Lewis Acid Adducts. Bis(4-trifluoromethylphenyl)platinum-2,2′-bipyrimidine (bpymPtAr$_2$, **1**) was prepared by treatment of $(4\text{-}CF_3\text{-}Ph)_2Pt(SEt_2)_2$ with 2 equiv of bpym in dichloromethane. Following purification by column chromatography on silica, yellow crystals of **1** were obtained by layering a toluene solution with pentane at −30 °C (for the ORTEP diagram of **1**, see Supporting Information, SI).

An initial attempt to bind tris(pentafluorophenyl)borane to the remote nitrogen site of **1** was unsuccessful, as no interaction was observed by ^1H or ^{19}F NMR spectroscopy. This is likely due to steric constraints enforced by the 2,2′-bipyrimidyl nitrogen placement. Instead, silicon and zinc compounds were sought as alternative Lewis acids that could simultaneously coordinate to both distal nitrogen sites of **1**.

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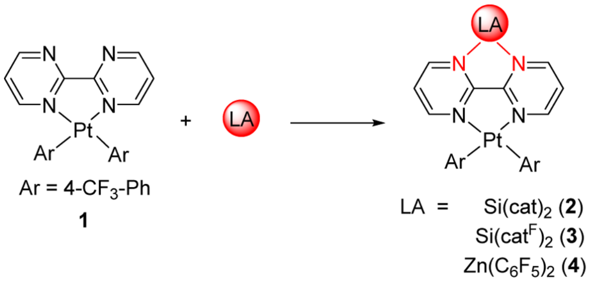


(1)

Treatment of **1** with bis(catecholato)silane, Si(cat)$_2$,[6] in toluene caused rapid formation of a red silicon−bpym−platinum complex (**2**, eq 1). We have previously reported that the bis(tetrafluorocatecholato)silane Si(cat^F)$_2$ is more Lewis acidic than the parent Si(cat)$_2$ compound.[7] For comparison with **2**, the dark brown Si(cat^F)$_2$ adduct **3** was prepared by treatment of **1** with Si(cat^F)$_2$(MeCN)$_2$. Lastly, treatment of **1** with bis(pentafluorophenyl)zinc(η^2-toluene)[8] allowed isolation of a platinum−zinc heterobimetallic complex **4** containing a bridging bpym ligand. Red single crystals of **2** and **4** were obtained by vapor diffusion of pentane into toluene solutions at −30 °C.

X-ray diffraction studies of **1**, **2**, and **4** provided solid-state structural comparisons (Figure 1). All complexes feature the expected square planar geometry at platinum. Compound **2** contains a hexacoordinate silicon center with approximately octahedral geometry. The zinc center of **4** is tetrahedral, as has been previously observed for pyridine adducts of diaryl zinc species.[9] There are negligible differences in the bond lengths of the bpym rings, platinum−bpym bonds, and platinum−aryl bonds of **1**, **2**, and **4**.

NMR Spectroscopy. The bpym ^{1}H NMR chemical shifts of **1**−**4** were compared to assess trends that result from Lewis acid binding. Signals due to the bpym protons *ortho* to platinum for adducts **2**−**4** are upfield-shifted by 0.10−0.37 ppm relative to those for **1** (see SI). Resonances due to the protons *ortho* to the remote nitrogen site of **2**−**4** appear downfield by 0.24−0.28 ppm compared to the corresponding signals in the parent complex. There is no trend in the ^{1}H NMR chemical shift of the bpym *meta* position. The ^{195}Pt NMR signals for **1**−**4** occur in a small region of the ~6000 ppm range typically observed for organoplatinum(II) complexes (see SI).[10] There is similarly no trend in the ^{13}C NMR chemical shifts of the bpym ligand. Taken together, these observations suggest that NMR chemical shifts are poorly correlated with the electronic properties of the complexes in this series. To provide additional information about electronic changes upon Lewis acid binding, UV−vis spectroscopy and cyclic voltammetry were employed as complementary diagnostic techniques.

UV−Vis Spectroscopy. UV−vis spectra of **1**−**4** are presented in Figure 2. An intense bipyrimidyl ligand π−π* transition is observed in the near-UV region for all complexes (not shown, λ_{max} ~300 nm). There are two diagnostic absorptions that have been assigned as MLCT transitions for similar platinum−bpym complexes.[11] The higher of the two in energy is not observed for the parent complex **1** (likely due to overlap with the intense π−π* transition), but occurs between 400 and 425 nm for adducts **2**−**4**. A lower energy absorption is observed at 450 nm for **1** and is shifted to 525−600 nm for the Lewis acid adducts. For both MLCT transitions, the shift in the absorption maxima to longer wavelengths is consistent with a significant lowering of the bpym π* orbital levels upon Lewis acid binding.

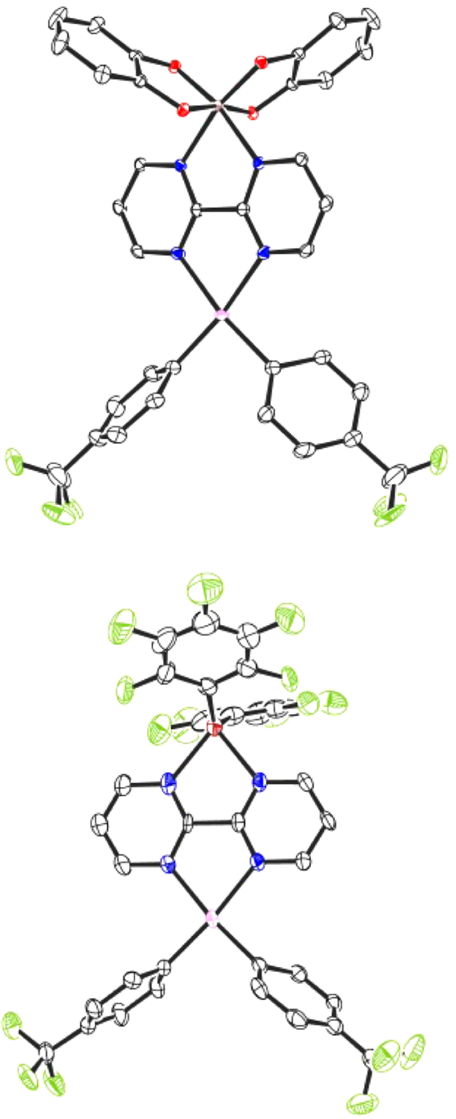


Figure 1. ORTEP diagrams of complexes **2** (top) and **4** (bottom), with all thermal ellipsoids shown at 50% probability.

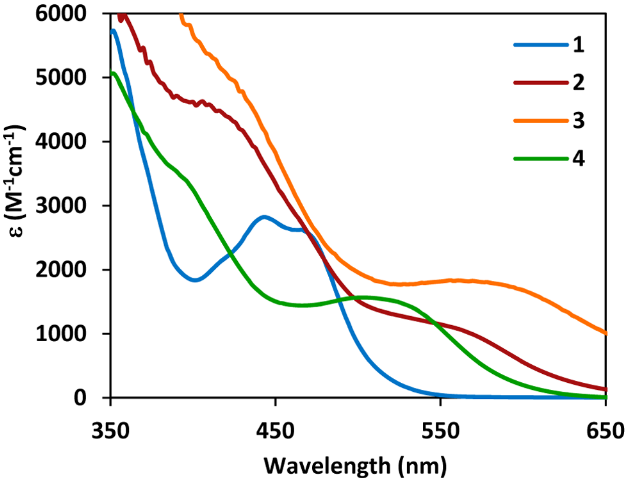


Figure 2. Absorption spectra of compounds **1**−**4**.

Electrochemical Experiments. Cyclic voltammetry was performed on complexes **1**−**4**. Silicon adducts **2** and **3** showed complicated, irreversible behavior upon reduction, likely due to the redox activity of the silicon-bound catecholate ligands.[12] In contrast, for the parent complex and $ZnAr^F_2$ adduct, **1** and **4**, two reversible bpym-based redox processes and one irreversible platinum-based oxidation event were observed (Figure 3). The first bpym reduction event ($bpym^0/bpym^{1-}$) for **4** is 600 mV less negative than that observed for complex **1**. Similarly, a shift of 400 mV was observed for the second bpym reduction event ($bpym^{1-}/bpym^{2-}$). In addition, the platinum-based oxidation requires a ~+100 mV greater potential upon remote zinc binding. These electrochemical data indicate that the electron density of the bpym ligand is substantially depleted upon zinc coordination, but the electronic perturbation at the platinum center is modest.

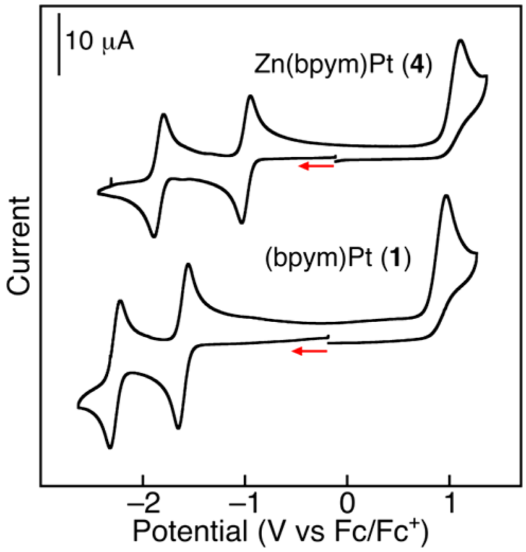
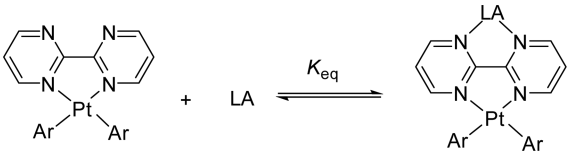


Figure 3. Cyclic voltammograms of **1** and **4** in *o*-difluorobenzene (1.0 mM with 0.1 M $[^nBu_4N][B(C_6F_5)_4]$).

Lewis Acid Binding Constants. Variable-temperature ^1H NMR experiments were performed to determine the relative strength of Lewis acid interactions in complexes **2**–**4** (eq 2). For complex **2**, partial, reversible dissociation of $Si(cat)_2$ occurs upon mild heating (40 °C), leading to a shift in the observed bipyrimidyl resonances due to averaging on the NMR time scale. Equilibrium constants were calculated based on the observed ^1H NMR chemical shift of the bpym resonances as a function of temperature. From van't Hoff analysis of the equilibrium constants between 30 and 80 °C, the enthalpy and entropy for binding of $Si(cat)_2$ to **1** were measured as $\Delta H = -18.2 \pm 1.5$ kcal/mol and $\Delta S = -47 \pm 4.7$ eu ($\Delta G = -4.2$ kcal/mol, $K_{eq} =$ ~1200 M^{-1} at 25 °C).

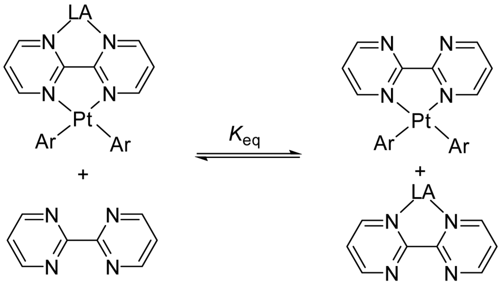


(2)

For $Si(cat)_2$, $\Delta G_{298} = -4.2$ kcal/mol
For $Si(cat^F)_2$, $\Delta G_{298} = -5.9$ kcal/mol
For $Zn(C_6F_5)_2$, $\Delta G_{298} \leq -8.6$ kcal/mol

In contrast to the behavior of $Si(cat)_2$, dissociation of $Si(cat^F)_2$ and $Zn(C_6F_5)_2$ from **3** and **4**, respectively, could not be observed at temperatures as high as 120 °C. Instead, competition experiments were performed to determine relative binding strengths. Mixing **3** with a 10-fold excess of $Si(cat)_2$ yielded a 1:1 mixture of **2** and **3**, allowing the free energy of $Si(cat^F)_2$ binding to **1** to be calculated as $\Delta G = -5.9$ kcal/mol at 25 °C. Treatment of **3** with $Zn(C_6F_5)_2$ led to the quantitative formation of **4** and free $Si(cat^F)_2$, suggesting that $\Delta G \leq -8.6$ kcal/mol for $Zn(C_5F_5)_2$ binding to **1** at 25 °C. Therefore, the relative strength of Lewis acid interactions with **1** increases in the order $Si(cat)_2 < Si(cat^F)_2 < Zn(C_6F_5)_2$.

Competition experiments were performed to establish the relative strength of Lewis acid interactions with bpym versus **1** (eq 3). For all Lewis acids, there is a preference for binding to free bpym rather than the platinum-bound bpym. Treatment of $Si(cat)_2$ with bpym and excess **1** led to a mixture of **1**, **2**, bpym, and bpym–$Si(cat)_2$ at 25 °C ($\Delta G = -3.4$ kcal/mol; see SI for details). In contrast, only **1** and bpym–$Si(cat^F)_2$ or bpym–$Zn(C_6F_5)_2$ could be observed in the analogous experiments with these Lewis acids. On the basis of the concentrations employed, and assuming 99% conversion to products based on the ^1H NMR detection limits, for both $Si(cat^F)_2$ and $Zn(C_6F_5)_2$, $\Delta G \leq -5.4$ kcal/mol at 25 °C.



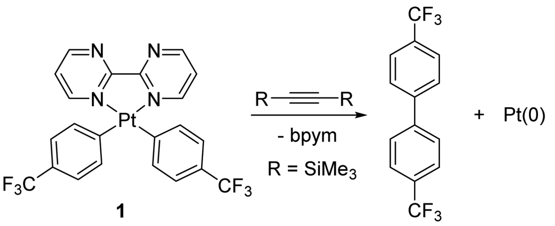
(3)

For $Si(cat)_2$, $\Delta G_{298} = -3.4$ kcal/mol
For $Si(cat^F)_2$, $\Delta G_{298} \leq -5.4$ kcal/mol
For $Zn(C_6F_5)_2$, $\Delta G_{298} \leq -5.4$ kcal/mol

Biaryl Reductive Elimination. Biaryl formation from complexes **1**–**4** was investigated, as this reaction represents a crucial step in carbon–carbon coupling reactions that often utilize group 10 catalysts.[13] We and others have shown that electron-deficient platinum complexes undergo facile reductive elimination compared to more electron-rich analogues.[5e,14] Therefore, this elementary step is a benchmark for the impact of remote Lewis acid binding on platinum-based reactivity.

Biaryl reductive elimination was exceptionally slow from **1**, requiring heating to 225 °C in nitrobenzene-d_5 to produce 4,4′-bis(trifluoromethyl)-1,1′-biphenyl, free bpym, and insoluble platinum(0) material. Coordination of $Zn(C_6F_5)_2$ promoted reductive elimination, with biaryl formation occurring at 140 °C with first-order kinetics and $k_{obs} = (1.5 \pm 0.1) \times 10^{-5}$ s^{-1}.[15]

The addition of bis(trimethylsilyl)acetylene (BTMSA) provided a lower energy pathway to reductive elimination (eq 4). Kinetics experiments in the initial rate regime indicated that



(4)

biaryl formation from **1** proceeded slowly in the presence of excess BTMSA at 150 °C (k_{obs} = (1.2 ± 0.1) × 10^{-6} s^{-1}), exhibiting first-order decay of **1** and concomitant appearance of the biaryl product. The reaction was determined to exhibit a first-order dependence on the concentration of BTMSA (Figure 4), consistent with an associative mechanism.[5e]

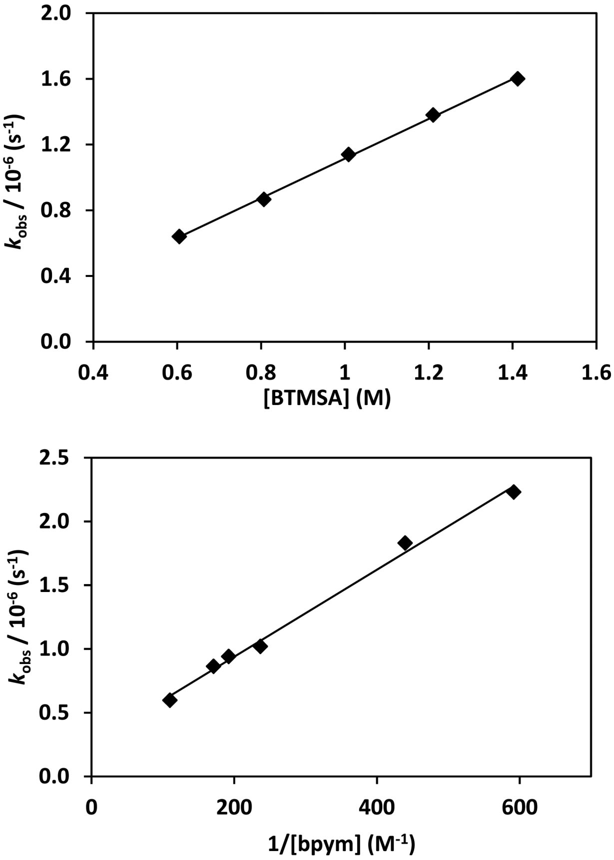


Figure 4. Effect of bis(trimethylsilyl)acetylene (top) and bpym (bottom) on the biaryl reductive elimination from **1** at 150 °C. A standard error of <5% is estimated from experiments performed in triplicate.

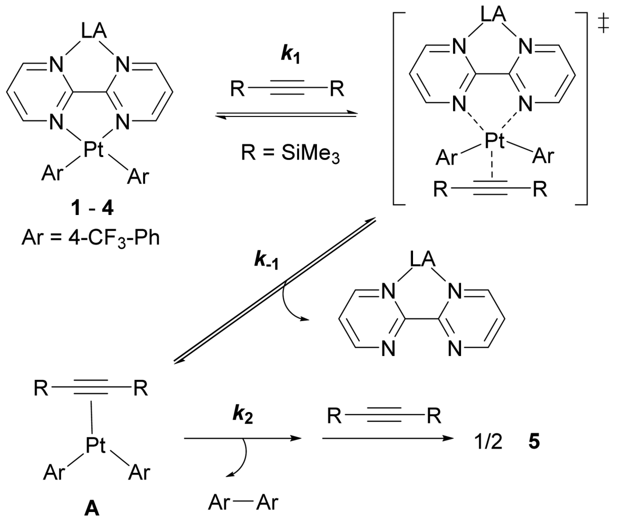
Next, experiments were performed to probe whether bpym dissociation occurs prior to reductive elimination. We have previously found that reductive elimination from a borane-activated bipyrazine (bpyz) platinum complex was not inhibited by addition of excess bpyz ligand.[5e] Surprisingly, the rate of reductive elimination from **1** slowed dramatically upon the addition of bpym. Quantitative kinetics experiments were performed, and a linear dependence was observed in a plot of k_{obs} versus 1/[bpym] (Figure 4), indicating that reductive elimination is inverse first-order in bpym. Therefore, different reaction profiles are observed in the alkyne-promoted biaryl reductive elimination reactions from the similar bipyrazine− and 2,2′-bipyrimidine−platinum complexes.

Complexes **2**−**4** also underwent reductive elimination in the presence of BTMSA, with widely varying temperatures required to induce C−C bond formation at rates convenient for monitoring by NMR spectroscopy. Biaryl elimination occurred at 120 °C for the $Si(cat)_2$ adduct **2**, 70 °C for the $Si(cat^F)_2$ adduct **3**, and 45 °C for the $Zn(C_6F_5)_2$ adduct **4** (see below for quantitative rate constant comparisons). For reactions at temperatures below 100 °C, the platinum(0) product was trapped as the soluble alkyne adduct $[Pt_2(\mu\text{-}Me_3SiCCSiMe_3)(Me_3SiCCSiMe_3)_2]$ (**5**).[16] At higher temperatures, this alkyne complex was unstable, and the platinum slowly precipitated as a black solid.

In all reactions, disappearance of **2**−**4** was first order in the initial rate regime, and no intermediates were observed. The reductive elimination exhibited a first-order dependence on the concentration of BTMSA and was inverse first order in bpym-$Si(cat)_2$ and bpym-$Si(cat^F)_2$ for complexes **2** and **3**, respectively. It is fortuitous that under the reaction conditions complexes **2** and **3** remain intact in the presence of added bpym-$Si(cat)_2$ and bpym-$Si(cat^F)_2$ (i.e., binding of a second equivalent of Lewis acid to bpym does not compete with binding to the bpym−platinum complex). In contrast, experiments with **4** in the presence of added bpym-$Zn(C_6F_5)_2$ were complicated by preferential dissociation of $Zn(C_6F_5)_2$ from **4** to generate **1** and the bis(zinc) adduct $(C_6F_5)_2Zn$-bpym-$Zn(C_6F_5)_2$. For **2**−**4**, addition of excess Lewis acid had no effect on reaction rate, suggesting that the Lewis acid does not dissociate from bpym during the reaction.

A proposed mechanism is shown in Scheme 1. First, there is associative ligand exchange of bpym for BTMSA to generate a three-coordinate platinum−alkyne complex (**A**). This must be reversible to account for the inhibition observed in experiments with added bpym. Biaryl reductive elimination occurs from the (BTMSA)$PtAr_2$ complex (**A**) in the rate-determining step to generate 4,4′-bis(trifluoromethyl)-1,1′-biphenyl, which is followed by trapping of platinum with additional alkyne to form **5**. Applying the steady-state approximation to the concentration of intermediate (BTMSA)$PtAr_2$, the rate expression for the mechanism shown in Scheme 1 is given in eq 5. If k_{-1}[bpym] ≫ k_2, this equation can be simplified to the form shown in eq 6. These expressions account for the observed first-order dependences for platinum and BTMSA as well as the inverse first-order behavior for bpym.

Scheme 1. Reductive Elimination Mechanism



$$\text{rate} = \frac{k_1k_2[\text{Pt}][\text{BTMSA}]}{k_{-1}[\text{bpym}] + k_2} \tag{5}$$

$$\text{rate} = \frac{k_1k_2[\text{Pt}][\text{BTMSA}]}{k_{-1}[\text{bpym}]} = \frac{K_{eq}k_2[\text{Pt}][\text{BTMSA}]}{[\text{bpym}]} \tag{6}$$

The complete dissociation of the bidentate bpym ligand in this reductive elimination reaction is unusual, although exchange of monodentate ligands is a well-precedented mechanism. For example, carbon−silicon reductive elimination from *cis*-PtMe($SiPh_3$)($PMePh_2$)$_2$ in the presence of diphenylacetylene proceeds by displacement of one phosphine ligand by alkyne.[17] Additionally, aryl−allyl reductive elimination from palladium(II) complexes was found to involve exchange of a triphenylarsine ligand for an alkene.[18] In contrast, with bidentate ancillary ligands, dissociation of one donor group is a more common pathway, as has been observed in studies of reductive elimination from octahedral platinum(IV) complexes.[19] Dissociation of bidentate ligands is often overlooked as a potential mechanism.

Biaryl formation from **1** was investigated by DFT calculations to determine the mechanism of ligand substitution (associative vs dissociative) and to calculate the expected barrier for biaryl reductive elimination (Figure 5). The barrier for direct bpym dissociation from (bpym)PtAr$_2$ (**1**) was determined to be 52.0 kcal/mol, while associative interchange, involving the concerted exchange of bpym for an incoming alkyne, was found to have a much lower barrier of 33.6 kcal/mol (favored mechanism shown in Scheme 1). This supports an associative ligand exchange process, as would be expected for a square planar d^8 platinum complex.[20]

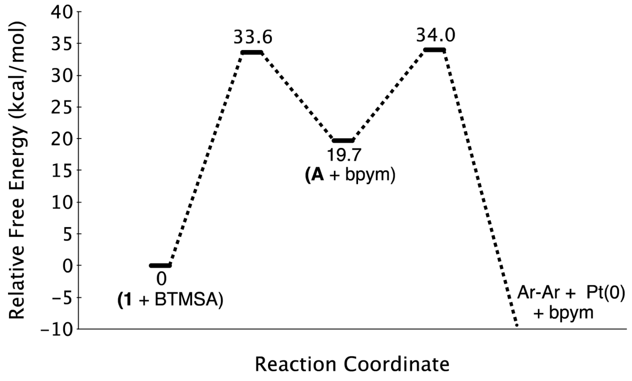


Figure 5. Reaction energy profile diagram (298 K, 1 atm).

It is fortuitous that complexes **1**−**4** display the same kinetics profiles, as the conserved mechanism allows for quantification of relative rates. Eyring analysis was performed for the reaction of **1** and excess BTMSA from 140 to 180 °C (Figure 6). The temperature dependence of the observed rate constant afforded activation parameters of $\Delta H^{\ddagger} = +31.6 \pm 0.96$ kcal/mol and $\Delta S^{\ddagger} = -11.4 \pm 2.2$ eu. The experimentally determined free energy of activation ($\Delta G^{\ddagger}_{298\text{ K}} = +35.0 \pm 1.6$ kcal/mol) matches the calculated value of 33.6 kcal/mol within error.

Initial rates of reductive elimination for complexes **2**−**4** were measured in triplicate in the presence of 0.35 M BTMSA (Table 1). To determine relative rates versus **1**, estimated rate constants for reductive elimination from **1** at 120 °C ($k = 5.8 \times 10^{-8}$ s^{-1}), 70 °C ($k = 1.6 \times 10^{-10}$ s^{-1}), and 45 °C ($k = 4.2 \times 10^{-12}$ s^{-1}) were calculated by extrapolation using the measured Eyring parameters. By comparing measured rate constants for **2**−**4** with extrapolated values for **1**, relative rates due to Lewis acid binding were calculated for **2** (1.5×10^3 at 120 °C), **3** (1.2×10^6 at 70 °C), and **4** (1.2×10^8 at 45 °C).

We sought to determine whether the Lewis acid binding leads to rate acceleration by shifting the bpym and alkyne exchange equilibrium, changing the rate at which the equilibrium is established, or both. The value of K_{eq} can be calculated based on a Boltzmann distribution with the energy difference between **1** and **A** from the DFT calculations and taking into account the effects of Lewis acid coordination from the binding constant measurements. For Si(cat)$_2$, the change in equilibrium constant accounts for an 80-fold rate acceleration for reductive elimination, while the remaining 20-fold rate acceleration is due to kinetic effects (see SI for details). Therefore, changes to both the location of the equilibrium position and the kinetics of the ligand exchange step due to Lewis acid binding give rise to the observed rate acceleration.

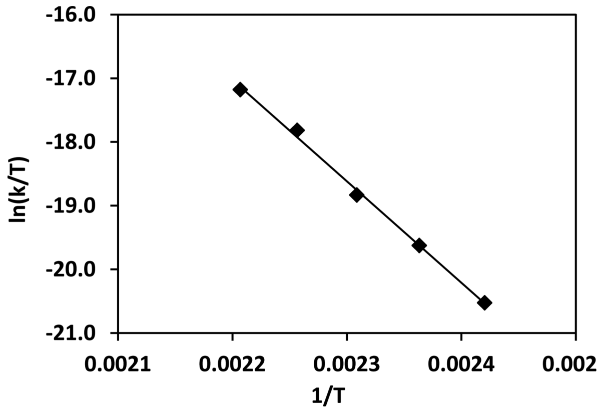


Figure 6. Eyring analysis of reductive elimination from **1** in the presence of BTMSA from 140 to 180 °C. A standard error of <5% is estimated based on triplicate experiments at one temperature.

Table 1. Comparison of Reductive Elimination Rates from 1−4

complex	Lewis acid	k_{obs} (s^{-1})	temp (°C)	relative rate
1	none	$(1.2 \pm 0.1) \times 10^{-6}$	150	1
2	Si(cat)$_2$	$(8.7 \pm 0.1) \times 10^{-5}$	120	1.5×10^3
3	Si(cat^F)$_2$	$(1.9 \pm 0.1) \times 10^{-4}$	70	1.2×10^6
4	Zn(C_6F_5)$_2$	$(4.8 \pm 0.1) \times 10^{-4}$	45	1.2×10^8

CONCLUSIONS

Coordination of silicon and zinc Lewis acids to the remote binding site of a platinum−bipyrimidine complex was investigated. Spectroscopic and electrochemical studies evidence substantial depletion of electron density from the bipyrimidine ligand upon Lewis acid binding. These electronic effects are also manifested in the rates of biaryl reductive elimination from these complexes, with tunable rates based on Lewis acid selection.

Mechanistic experiments and DFT calculations unexpectedly revealed complete dissociation of the Lewis acid-coordinated bpym ligand prior to reductive elimination. The combined experimental and theoretical results indicate that bidentate ligand dissociation is kinetically favored by Lewis acid coordination (i.e., bpym is more labile with Lewis acids bound). However, a *thermodynamic* driving force also favors ligand dissociation, due to stronger binding of the Lewis acids to free bpym than to the platinum-bound bpym ligand. Combined, these effects drastically modify the rate of biaryl elimination by factors of 10^3 to 10^8.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b01003.

DFT results and additional experimental details (PDF)
X-ray data (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345. (b) Chivers, T. *J. Fluorine Chem.* **2002**, *115*, 1. (c) Erker, G. *Dalton Trans.* **2005**, 1883.

(2) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

(3) (a) Kita, M. R.; Miller, A. J. M. *J. Am. Chem. Soc.* **2014**, *136*, 14519. (b) Ouyang, G.-H.; He, Y.-M.; Li, Y.; Xiang, J.-F.; Fan, Q.-H. *Angew. Chem., Int. Ed.* **2015**, *54*, 4334.

(4) (a) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560. (b) Hashiguchi, B. G.; Young, K. J. H.; Yousufuddin, M.; Goddard, W. A.; Periana, R. A. *J. Am. Chem. Soc.* **2010**, *132*, 12542. (c) Himeda, Y.; Onozawa-Komatsuzaki, N.; Sugihara, H.; Kasuga, K. *Organometallics* **2007**, *26*, 702. (d) Dixon, N. A.; McQuarters, A. B.; Kraus, J. S.; Soffer, J. B.; Lehnert, N.; Schweitzer-Stenner, R.; Papish, E. T. *Chem. Commun.* **2013**, *49*, 5571. (e) Hesp, K. D.; McDonald, R.; Ferguson, M. J.; Schatte, G.; Stradiotto, M. *Chem. Commun.* **2008**, 5645. (f) Hesp, K. D.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *J. Am. Chem. Soc.* **2008**, *130*, 16394.

(5) (a) Lee, B. Y.; Bazan, G. C.; Vela, J.; Komon, Z. J. A.; Bu, X. *J. Am. Chem. Soc.* **2001**, *123*, 5352. (b) Kim, Y. H.; Kim, T. H.; Lee, B. Y.; Woodmansee, D.; Bu, X.; Bazan, G. C. *Organometallics* **2002**, *21*, 3082. (c) Azoulay, J. D.; Rojas, R. S.; Serrano, A. V.; Ohtaki, H.; Galland, G. B.; Qu, G.; Bazan, G. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 1089. (d) Azoulay, J. D.; Koretz, Z. A.; Wu, G.; Bazan, G. C. *Angew. Chem., Int. Ed.* **2010**, *49*, 7890. (e) Liberman-Martin, A. L.; Bergman, R. G.; Tilley, T. D. *J. Am. Chem. Soc.* **2013**, *135*, 9612. (f) Trofymchuk, O. S.; Gutsulyak, D. V.; Quintero, C.; Parvez, M.; Daniliuc, C. G.; Piers, W. E.; Rojas, R. S. *Organometallics* **2013**, *32*, 7323. (g) Brennan, C.; Draksharapu, A.; Browne, W. R.; McGarvey, J. J.; Vos, J. G.; Pryce, M. T. *Dalton Trans.* **2013**, *42*, 2546. (h) Tseng, K.-N. T.; Kampf, J. W.; Szymczak, N. K. *ACS Catal.* **2015**, *5*, 411.

(6) Allcock, H. R.; Nugent, T. A.; Smeltz, L. A. *Synth. React. Inorg. Met.-Org. Chem.* **1972**, *2*, 97.

(7) Liberman-Martin, A. L.; Bergman, R. G.; Tilley, T. D. *J. Am. Chem. Soc.* **2015**, *137*, 5328.

(8) Walker, D. A.; Woodman, T. J.; Hughes, D. L.; Bochmann, M. *Organometallics* **2001**, *20*, 3772.

(9) Martin, E.; Spendley, C.; Mountford, A. J.; Coles, S. J.; Horton, P. N.; Hughes, D. L.; Hursthouse, M. B.; Lancaster, S. J. *Organometallics* **2008**, *27*, 1436.

(10) Priqueler, J. R. L.; Butler, I. S.; Rochon, F. D. *Appl. Spectrosc. Rev.* **2006**, *41*, 185.

(11) (a) Sutcliffe, V. F.; Young, G. B. *Polyhedron* **1984**, *3*, 87. (b) Thomson, S. K.; Young, G. B. *Polyhedron* **1988**, *7*, 1953. (c) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 1538. (d) Braterman, P. S.; Song, J.-I.; Vogler, C.; Kaim, W. *Inorg. Chem.* **1992**, *31*, 222. (e) Klein, A.; Kaim, W.; Hornung, F. M.; Fiedler, J.; Zalis, S. *Inorg. Chim. Acta* **1997**, *264*, 269.

(12) (a) Zanell, P.; Corsini, M. *Coord. Chem. Rev.* **2006**, *250*, 2000. (b) Broere, D. L. J.; Plessius, R.; van der Vlugt, J. I. *Chem. Soc. Rev.* **2015**, *44*, 6886.

(13) (a) Martin, R.; Buchwald, S. L. *Acc. Chem. Res.* **2008**, *41*, 1461. (b) Phapale, V. B.; Cardenas, D. J. *Chem. Soc. Rev.* **2009**, *38*, 1598. (c) Brown, J. M.; Cooley, N. A. *Chem. Rev.* **1988**, *88*, 1031.

(14) (a) Merwin, R. K.; Schnabel, R. C.; Koola, J. D.; Roddick, D. M. *Organometallics* **1992**, *11*, 2972. (b) Korenaga, T.; Abe, K.; Ko, A.; Maenishi, R.; Sakai, T. *Organometallics* **2010**, *29*, 4025. (c) Shiba, Y.; Inagaki, A.; Akita, M. *Organometallics* **2015**, *34*, 4844.

(15) Decomposition of the silane adducts **2** and **3** occurs at 140 °C, with no biaryl reductive elimination observed by ^{1}H or ^{19}F NMR spectroscopy.

(16) (a) Boag, N. M.; Green, M.; Grove, D. M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 2170. (b) Boag, N. M.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Wadepohl, H. *J. Chem. Soc., Dalton Trans.* **1981**, 862.

(17) Ozawa, F.; Hikida, T.; Hayashi, T. *J. Am. Chem. Soc.* **1994**, *116*, 2844.

(18) Kurosawa, H.; Emoto, M.; Urabe, A.; Miki, K.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 8253.

(19) (a) Crumpton-Bregel, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 9442. (b) Arthur, K. L.; Wang, Q. L.; Bregel, D. M.; Smythe, N. A.; O'Neill, B. A.; Goldberg, K. I.; Moloy, K. G. *Organometallics* **2005**, *24*, 4624.

(20) Hartwig, J. F. Ligand Substitution Reactions. In *Organotransition Metal Chemistry: From Bonding to Catalysis*; University Science Books: USA, 2010; pp 217–261.