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Probing Dynamic Equilibria between Platinum(II)– η^2 -Benzene Adducts and Unobserved Five-Coordinate Platinum(IV) C–H Oxidative Addition Intermediates

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Summary: Low-temperature addition of nitrile ligands to platinum(II) η^2 -benzene reagents, $[(\kappa^2\text{-HTp}')\text{Pt}(\eta^2\text{-C}_6\text{H}_6)(\text{R})][\text{BAr}'_4]$ (R = H, Ph), results in reversible trapping of the postulated five-coordinate C–H oxidative addition product to give cationic platinum(IV) nitrile adducts, $[(\kappa^2\text{-HTp}')\text{Pt}(\text{C}_6\text{H}_5)(\text{H})(\text{R})(\text{NCR}')][\text{BAr}'_4]$ (R = Ph, H, R' = Me, CMe₃, p-XC₆H₄). At higher temperatures, irreversible loss of benzene from the Pt(II) η^2 -benzene reagents occurs to form cationic Pt(II) nitrile products.

Selective activation of an alkane or arene C–H bond by a metal reagent followed by elimination of a functionalized hydrocarbon remains a major challenge.^{1–7} While many metal complexes cleave these C–H bonds, few perform alkane/arene functionalization.^{8–27} Func-

tionalization has proved to be elusive, due to the tendency of metal alkyl/aryl hydride complexes to reductively eliminate the hydrocarbon rather than the functionalized product. Research in this area has been fueled by the catalytic conversion of methane to methanol using Pt(II) salts reported more than 30 years ago.^{17,18} The mechanism of this Shilov oxidation has been extensively studied to provide guidance for the design of new catalysts capable of C–H activation and functionalization.^{28–35} The initial C–H activation step is believed to involve the intermediacy of a Pt(II) σ -alkane complex, which exists in equilibrium with a five-coordinate Pt(IV) hydridoalkyl species.^{36–43} Isolation of 16-electron platinum(IV) complexes resembling these proposed intermediates has been reported;^{44,45} however, no five-coordinate Pt(IV) alkyl/aryl hydride intermediates have been isolated. The five-coordinate intermediate is an attractive reagent for functionalization for two reasons: (1) the C–H bond has been successfully cleaved, and (2) there is a vacant coordina-

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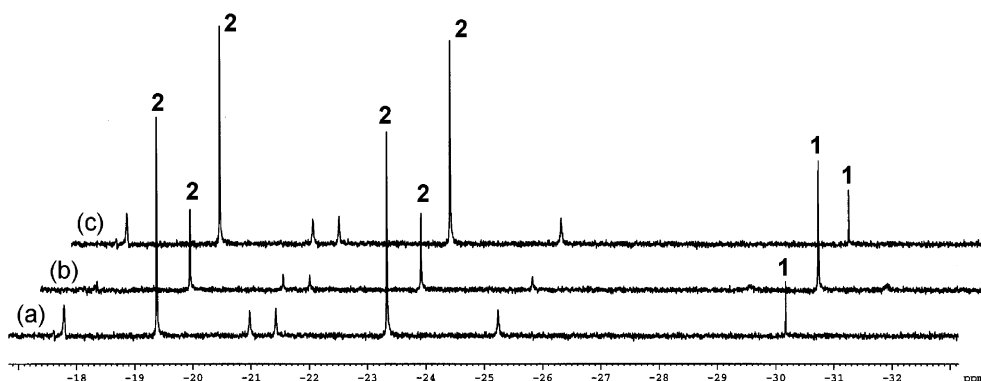


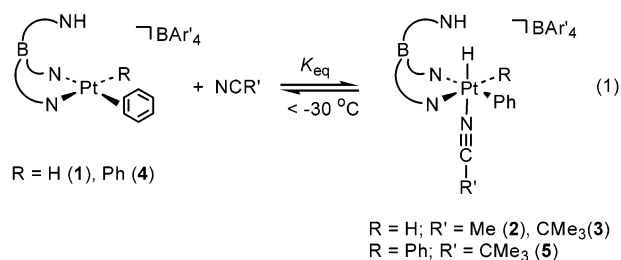
Figure 1. ^1H NMR spectra of the hydride region for complexes **1** and **2**: (a) at 193 K; (b) at 223 K; (c) after cooling back to 193 K.

tion site on the metal center available to promote additional reactions.

In the Tp'-stabilized platinum system, we have isolated the cationic platinum(II) η^2 -arene adducts $[(\kappa^2\text{-HTp}')\text{Pt}(\eta^2\text{-Ar-H})(\text{R})][\text{BAR}'_4]$ (Tp' = hydridotris(3,5-dimethylpyrazolyl)borate;⁴⁶ BAR'₄ = tetrakis(3,5-trifluoromethylphenyl)borate).⁴⁷ The energy barriers for exchange of the arene hydrogens with the platinum hydride, believed to reflect arene C–H activation in these complexes, range from 12.7 to 14.2 kcal/mol.^{48,49} If we can access reactions with this unobserved five-coordinate Pt(IV) phenyl hydride intermediate, where the C–H bond has been cleaved, the potential for functionalization of the phenyl group increases. We wish to report here a surprising reaction relevant to arene functionalization: addition of nitrile ligands to the η^2 -benzene platinum(II) reagent traps the previously postulated five-coordinate platinum(IV) benzene C–H cleavage intermediate.

Low-temperature protonation of either Tp'PtMe₂H or Tp'PtMeH₂ in the presence of nitrile resulted in rapid loss of methane to form a cationic Pt(II) nitrile complex.^{50,51} In contrast, low-temperature protonation of Tp'PtPhH₂ in the presence of R'CN formed the cationic platinum(II) η^2 -benzene hydride product $[(\kappa^2\text{-HTp}')\text{Pt}(\eta^2\text{-C}_6\text{H}_6)(\text{H})][\text{BAR}'_4]$ (**1**) but did not lead to simple displacement of coordinated benzene. Instead, addition of excess R'CN to the benzene hydride adduct **1** at 193 K yields a mixture of the platinum(IV) C–H oxidative addition product, $[(\kappa^2\text{-HTp}')\text{Pt}(\text{Ph})(\text{H})_2(\text{NCR}')][\text{BAR}'_4]$ (R' = Me (**2**), CMe₃ (**3**)), and the starting platinum(II) η^2 -benzene hydride reagent (**1**) (eq 1). The ^1H NMR spectrum at 193 K for **2** shows hydride resonances at -23.4 ($^1J_{\text{Pt-H}} = 1525$ Hz) and -19.4 ppm ($^1J_{\text{Pt-H}} = 1279$ Hz), integrating for one hydrogen each (Figure 1).⁵² The presence of two inequivalent hydride ligands in the product indicates that **2** is a Pt(IV) dihydride derivative. The data are incompatible with the product of simple platinum(II) benzene displacement, $[(\kappa^2\text{-HTp}')\text{Pt}(\text{NC-}$

Me)(H)][BAR'₄].⁵⁰ Irreversible trapping of Pt(II) σ -alkane and Pt(IV) five-coordinate intermediates with acetonitrile were observed by Tilset and co-workers in experiments which revealed that the metal is the kinetic site for protonation.⁵³



Not all of the platinum(II) η^2 -benzene hydride reagent was consumed, even when excess R'CN was added, indicative of a reversible reaction. Indeed, when the NMR sample was warmed from 193 to 223 K, the ratio of product to reagent decreased; when it was cooled back to 193 K, the system returned to the original 193 K equilibrium distribution (Figure 1). Low-temperature attempts to isolate the cationic platinum(IV) aryl hydride nitrile complexes under excess nitrile conditions were unsuccessful, and upon warming loss of benzene occurred.

Addition of trimethylacetonitrile to the η^2 -benzene phenyl adduct $[(\kappa^2\text{-HTp}')\text{Pt}(\eta^2\text{-C}_6\text{H}_6)(\text{Ph})][\text{BAR}'_4]$ (**4**) in CD₂Cl₂ at 210 K also resulted in an equilibrium mixture of the C–H oxidative addition product, now $[(\kappa^2\text{-HTp}')\text{Pt}(\text{Ph})_2(\text{H})(\text{NCCMe}_3)][\text{BAR}'_4]$ (**5**), and the starting platinum(II) η^2 -benzene phenyl reagent (**4**) (eq 1). Identification of complex **5** as the platinum(IV) aryl hydride nitrile complex was based on the observation of a hydride ligand in the ^1H NMR spectrum at 210 K at -22.9 ppm ($^1J_{\text{Pt-H}} = 1552$ Hz) integrating for one hydrogen.

Since addition of excess nitrile to the η^2 -benzene reagents results in a dynamic equilibrium with the

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(52) For **2**: ^1H NMR (CD₂Cl₂, 218 K, δ) 10.97 (s, 1H, pzNH), 6.89 (m, 5H, Pt-C₆H₅), 6.09, 6.08, 5.90 (s, 1H each, HTp'CH), 2.38, 2.34, 2.30, 2.25, 1.57, 1.50 (s, 3H, 3H, 3H, 6H, 3H, 3H, HTp'CH₃ and Pt-NCCCH₃), -19.40 (s, 1H, $^1J_{\text{Pt-H}} = 1279$ Hz, Pt-H), -23.37 (s, 1H, $^1J_{\text{Pt-H}} = 1525$ Hz, Pt-H); ^{13}C NMR (CD₂Cl₂, 193 K, δ) 152.8, 151.9, 148.4, 147.3, 147.2, 143.5 (HTp'CCH₃), 127.3, 123.6, 118.8 (Pt-C₆H₅), 115.3 (Pt-NCCCH₃), 109.1, 108.2, 107.4 (HTp'CH), 15.1, 13.3, 13.2, 13.0, 10.5, 10.4 (HTp'CCH₃), 3.2 (Pt-NCCCH₃).

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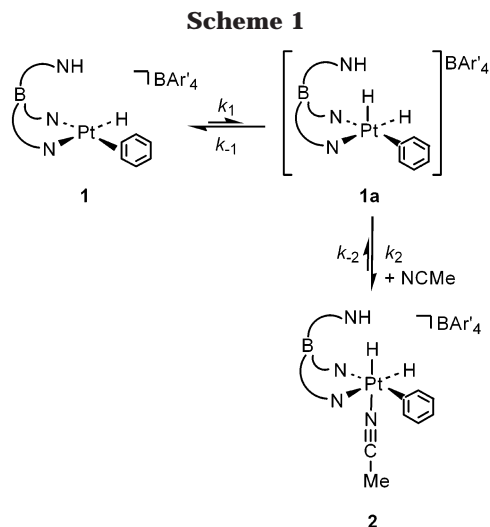


Table 1. Thermodynamic Parameters for Eq 1 at 230 K

R	R'	K_{eq}	ΔG° (kcal/mol)	ΔH° (kcal/mol)	ΔS° (cal/(mol K))
H	Me	1.9	-0.3	-5.9	-24
H	CMe ₃	5.0	-0.7	-5.5	-21
Ph	CMe ₃	3.0	-0.5	-6.0	-24

trapped platinum(IV) C–H oxidative addition product, determination of K_{eq} over a temperature range of 193–243 K provided thermodynamic parameters from a van't Hoff plot (Table 1). These data along with the energy barriers for arene C–H activation measured previously^{48,49} guided construction of a reaction coordinate diagram at 230 K for the equilibrium described in Scheme 1 (Figure 2). To probe the barrier between the unobserved intermediate **1a** and the nitrile adduct **2**, the Pt–C₆H₆ resonance in **1** was irradiated and the ¹H NMR spectrum was recorded at 230 K with [NCMe] = 0.4 M. The Pt–C₆H₆ resonance for **1** appears as a singlet in the ¹H NMR spectrum due to rapid platinum migration around the benzene ring. Exchange between the Pt–C₆H₆ protons of **1** and the Pt–H resonances of **2** was indicated by decreased intensities for both of the Pt–H signals of **2** upon saturation of the C₆H₆ signal of **1**. These results indicate that the barrier between complexes **1** and **2** under these conditions is 13.4 kcal/mol; the barrier between **1** and **1a** under these conditions is only slightly less, 12.8 kcal/mol. An increase of acetonitrile concentration to 0.8 M increases the ratio of **2**:**1** and only slightly alters the activation barriers. These experiments provide qualitative information indicating that the barrier heights relating **1** to **1a** and **1** to **2** are surprisingly similar under these conditions. We conclude that the rate of return from **1a** to **1** and the rate of trapping **1a** to form **2** are comparable at 230 K; increasing the nitrile concentration leads to more efficient trapping of **1a**.

To probe the electronic effects of nitrile substituents on this equilibrium, **1** was combined with a series of para-substituted benzonitriles, *p*-XC₆H₄CN, where X = OMe (**6**), Me (**7**), H (**8**), Cl (**9**), CF₃ (**10**), at low temperature (eq 2). Table 2 summarizes the equilibrium data obtained at 201 K, and the thermodynamic parameters were derived from van't Hoff plots over a range of temperatures. A plot of log K_{eq} vs σ_p shows a linear Hammett correlation with a ρ value of -1.8, indicating

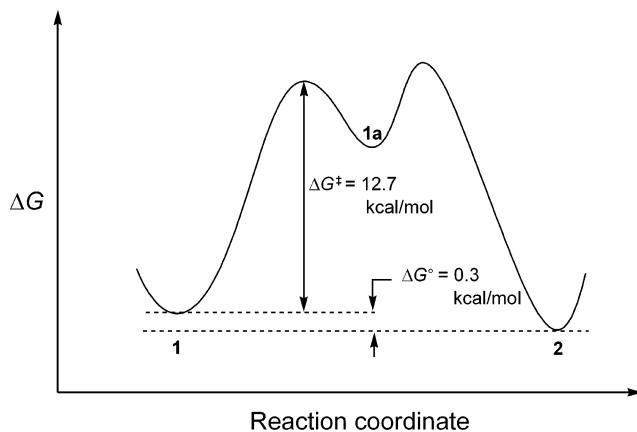


Figure 2. Reaction coordinate diagram at 230 K for the equilibrium in Scheme 1.

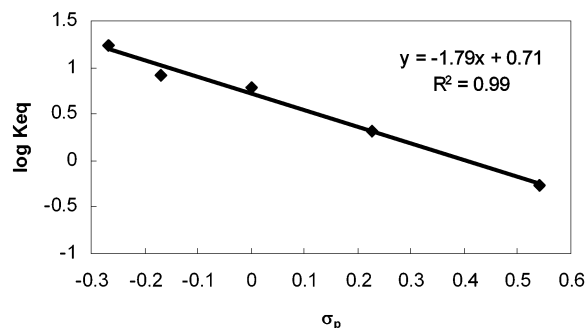
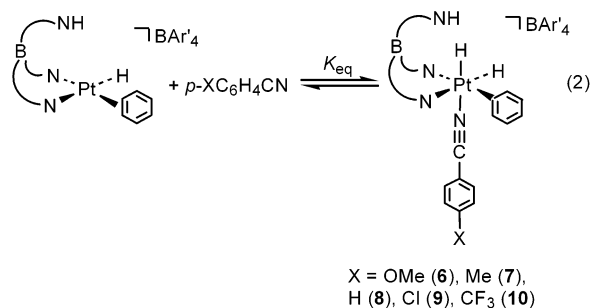


Figure 3. Hammett plot for eq 2 at 201 K.

Table 2. Substituent Effect on the Equilibrium in Eq 2 at 201 K

X	σ_p	K_{eq}	ΔH° (kcal/mol)	ΔS° (cal/(mol K))
OMe	-0.27	17.0	-5.0	-19
Me	-0.17	8.20	-4.8	-19
H	0	6.06	-4.7	-20
Cl	0.23	2.04	-4.2	-19
CF ₃	0.54	0.54	-4.0	-21

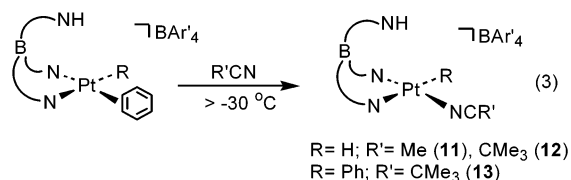
that the Pt(IV) aryl dihydride is stabilized by more electron rich nitriles (Figure 3). This is reflected in the small but systematic increase in exothermicity of the reaction as the electron-donating ability of the substituent is increased. The negative entropy associated with this equilibrium is consistent with coordination of free nitrile.



On the basis of the Hammett correlation, electron-rich alkyl nitriles should favor the Pt(IV) products more than the electron-poor para-substituted benzonitriles. Indeed, ΔH° is slightly more exothermic for reactions with alkyl nitriles. On the basis of this electronic trend, reaction of **1** with trimethylacetonitrile should be fa-

vored over that with acetonitrile, as indicated by the slightly more negative ΔG° value for the reaction with trimethylacetonitrile (Table 1).

At temperatures above -30°C , quantitative formation of the platinum(II) benzene replacement products $[\kappa^2\text{-(HTp')Pt(R)(NCR')}] [\text{BAR}'_4]$ ($\text{R} = \text{H}$, $\text{R}' = \text{Me}$ (**11**), CMe_3 (**12**); $\text{R} = \text{Ph}$, $\text{R}' = \text{CMe}_3$ (**13**)) is observed by ^1H NMR (eq 3). These reactions mimic the results of low-temperature protonations of $\text{Tp}'\text{PtMe}_2\text{H}$ and $\text{Tp}'\text{PtMeH}_2$.^{50,51}



In conclusion, addition of neutral nitrile ligands to Tp' platinum(II) η^2 -benzene adducts at temperatures below -30°C results in trapping of the postulated five-coordinate arene C–H activation intermediate as a six-coordinate Pt(IV) nitrile complex. A dynamic equilibrium between the Pt(II) arene reagent and the Pt(IV) aryl hydride nitrile adduct is established at low temperature ($T \leq -30^\circ\text{C}$), but benzene replacement by nitrile occurs at higher temperature.

Acknowledgment. We thank the reviewers for helpful suggestions and the National Science Foundation for support of this research.

Supporting Information Available: Complete synthetic and spectroscopic data for complexes **2**, **3**, **5–10**, **12**, and **13** and van't Hoff plots. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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