

Chapter 2

Experimental and Theoretical Studies of Olefin Insertion for *ansa*-Niobocene and *ansa*-Tantalocene Ethylene Hydride Complexes

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Abstract

Using dynamic NMR methods the rates of hydrogen exchange following intramolecular ethylene insertion into the metal–hydride bond have been measured for the following group 5 *ansa*-metallocene complexes: $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_3\text{-3-R})]\text{Nb}(\text{CH}_2\text{CH}_2)\text{H}$ ($\text{R} = \text{CHMe}_2$, CMe_3), *rac*- and *meso*- $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{H}_3\text{-3-CMe}_3)_2]\text{Nb}(\text{CH}_2\text{CH}_2)\text{H}$ and $[(1,2\text{-SiMe}_2)_2(\eta^5\text{-C}_5\text{H-3,5-(CHMe}_2)_2)(\eta^5\text{-C}_5\text{H}_2\text{-4-CMe}_3)]\text{Ta}(\text{CH}_2\text{CH}_2)\text{H}$. The singly bridged *ansa*-niobocenes exchange up to 3 orders of magnitude faster than unbridged complexes. However, the doubly bridged *ansa*-tantalocene complex exchanges at a rate comparable to that previously reported for $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ta}(\text{CH}_2\text{CH}_2)\text{H}$ and much slower than a singly bridged complex, $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)_2]\text{Ta}(\text{CH}_2\text{CH}_2)\text{H}$. These "*ansa*-effects" were investigated by DFT calculations on model complexes. The computed exchange pathway showed the presence of an agostic ethyl intermediate. The calculated barriers for hydrogen exchange of model unbridged, singly bridged, and doubly bridged niobocenes correlate with the experimental results.

Introduction

Olefin insertion into a metal–hydrogen bond and the microscopic reverse, β -hydrogen elimination, are elementary reactions in organometallic chemistry. These transformations are of considerable interest due to their fundamental importance, as well as for their widespread occurrence in synthetic and catalytic processes. Both reactions occur in transition-metal-catalyzed processes such as olefin polymerization, isomerization, and hydrogenation.¹ Mechanistic studies on the reversible insertion of alkenes into M–H bonds have been carried out for a series of group 5 olefin hydride complexes (Figure 1).² These complexes exist

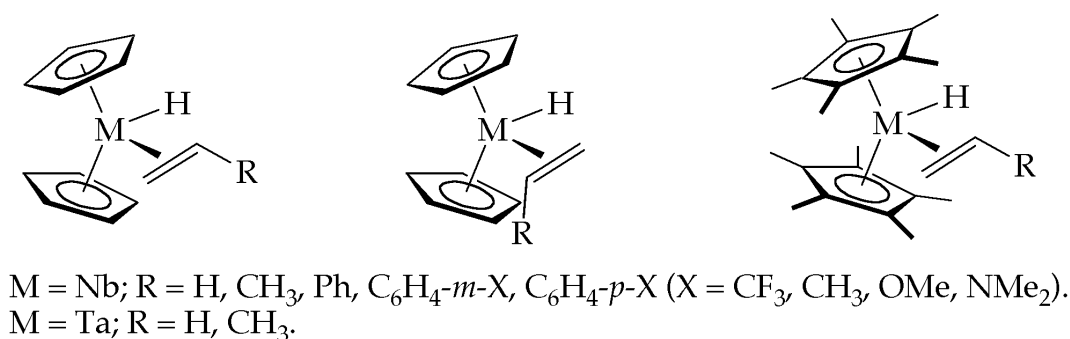
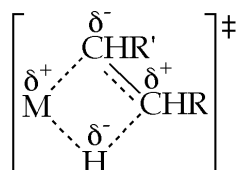


Figure 1. Group 5 olefin hydride complexes previously utilized to investigate olefin insertion into the M–H bond.

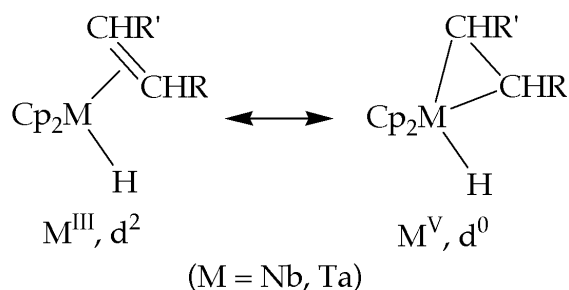
between two limiting resonance structures: d^2 , M^{III} olefin hydride or d^0 , M^V metallocyclopropane hydride (Scheme 1).

Rates of hydrogen exchange following olefin insertion were measured by either magnetization transfer or coalescence ¹H NMR techniques. The study revealed that the insertion step proceeds via a four-centered transition state with modest charge development:



Thus, the transition state is stabilized when R is electron donating and R' is electron withdrawing. On the other hand, the ground-state olefin hydride complex is stabilized when both R and R' are electron withdrawing, due to stronger π -back-bonding interactions. The ground state is also stabilized for tantalum relative to niobium. This can be understood if the insertion process is

Scheme 1



viewed as a reductive elimination of a C–H bond for the M^V , d^0 resonance structure, since higher oxidation states are generally preferred by the heavier congener of a periodic triad. Thus, the observed order of elimination rates is $k_{\text{ins}}(\text{Nb}) > k_{\text{ins}}(\text{Ta})$.

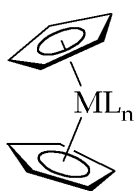
When comparing the effect of ancillary ligands on the rate of insertion, one would expect the more electron-donating pentamethylcyclopentadienyl ligands (Cp^*) to stabilize the M^V -like ground state relative to the M^{III} -like transition state. However, the Cp^* ligands would have the opposite effect sterically, as they would destabilize the congested ground state relative to the

less crowded transition state. The activation barriers for representative complexes are summarized in Table 1. For the ethylene hydride complexes, $\Delta G^\ddagger(\text{Cp}^*) > \Delta G^\ddagger(\text{Cp})$; thus, electronic effects dominate for the smallest olefin ligand. However, sterics dominate for larger olefins (propylene, styrene), since $\Delta G^\ddagger(\text{Cp}^*) < \Delta G^\ddagger(\text{Cp})$.

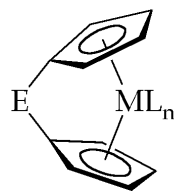
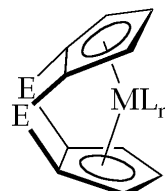
Table 1. Activation Barriers for Olefin Insertion of Selected Complexes.²

Complex	$\Delta G^\ddagger$ (50 °C, kcal mol ⁻¹)
$\text{Cp}^*_2\text{Nb}(\text{CH}_2\text{CH}_2)\text{H}$	18.3(1)
$\text{Cp}_2\text{Nb}(\text{CH}_2\text{CH}_2)\text{H}$	17.1(1)
$\text{Cp}^*_2\text{Nb}(\text{CH}_2\text{CHCH}_3)\text{H}$	14.6(1)
$\text{Cp}_2\text{Nb}(\text{CH}_2\text{CHCH}_3)\text{H}$	16.5(1)
$\text{Cp}^*_2\text{Nb}(\text{CH}_2\text{CHPh})\text{H}$	18.3(1)
$\text{Cp}_2\text{Nb}(\text{CH}_2\text{CHPh})\text{H}$	20.5(1)

ansa-Metallocenes (Chart 1) have attracted much interest in Ziegler-Natta catalysis due to recent success in the development of stereospecific polymerization catalysts by strategic placement of substituents on the rigid *ansa*-metallocene fragment.^{3,4,5} *ansa*-Metallocene complexes are also used as enantioselective catalysts for C–C and C–H bond formation.⁶ More recently, doubly bridged *ansa*-metallocenes have been prepared and are among the most active catalysts for the syndiospecific polymerization of propylene (Chart 1).⁷

Chart 1

metallocene

singly linked
ansa-metallocenedoubly linked
ansa-metallocene(E = CH₂, CMe₂, CPh₂, SiMe₂, C₂H₄)

Thus, the investigation of *ansa* complexes in comparison with their nonbridged counterparts has been an active area of research.

Studies have revealed that in some cases the reactivity of an *ansa* complex is substantially different than that of an unbridged analogue. For example, the thermal stability of [Me₂C(η⁵-C₅H₄)₂]W(CH₃)H is much greater than that of (η⁵-C₅H₅)₂W(CH₃)H.⁸ The *ansa* complex is stable to reductive elimination of methane under thermal and photochemical conditions (up to 120 °C), but the unbridged complex loses methane at ca. 50 °C. A theoretical study by Jardine and Green revealed that after reductive elimination from the singlet methane σ complex, {(η⁵-C₅H₅)₂W(CH₄)}, the proposed 16-electron intermediate, {(η⁵-C₅H₅)₂W}, is able to relax to a low-energy, parallel ring triplet state, facilitating methane loss.⁹ However, the *ansa* bridge constrains the rings, raising the triplet ground state of the intermediate such that little energy gain is possible upon methane loss. Other explanations have been proposed for the differing reactivity that the *ansa* bridge imparts in related metallocene systems. For example, Parkin has shown that the barrier to PMe₃ dissociation for

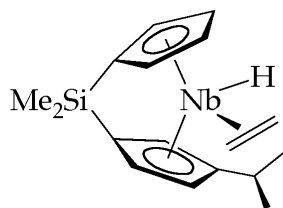
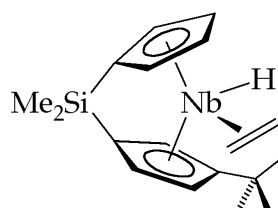
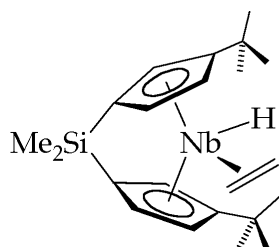
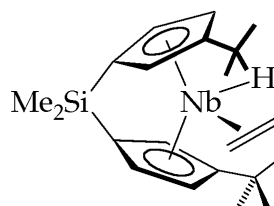
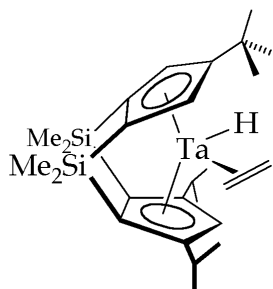
$[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)_2]\text{ZrH}_2(\text{PMe}_3)$ is much larger than that for $\text{Cp}^*_2\text{ZrH}_2(\text{PMe}_3)$, with $k_{\text{Cp}^*} > 500k_{\text{ansa}}$ at 25 °C.¹⁰ Shin and Parkin have also reported that the rate of olefin insertion for $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Ta}(\text{CH}_2\text{CH}_2)\text{H}$ is 3 orders of magnitude faster than that for the corresponding unbridged complex, $\text{Cp}^*_2\text{Ta}(\text{CH}_2\text{CH}_2)\text{H}$.¹¹ These authors argue that the singly bridged ansa ligand is less electron donating than the unconstrained cyclopentadienyl ligands, resulting in a more electrophilic metal center. Hence, the zirconium center binds PMe_3 more tightly in the ansa complex. Similarly, the tantalum center back-bonds to the olefin π^* orbital less efficiently for $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Ta}(\text{CH}_2\text{CH}_2)\text{H}$; the ground state is destabilized, and insertion is faster.

In this study, further investigations of ansa effects on olefin insertion have been undertaken by synthesizing and measuring hydrogen exchange rates for group 5 *ansa*-metallocene ethylene hydride compounds. Substitution patterns and the effects of introducing a second linking group for *ansa*-metallocene olefin hydride complexes have been investigated. DFT calculations have also been performed on model complexes.

Results and Discussion

Measurement of Hydrogen Exchange Rates. The *ansa*-niobocene and -tantalocene ethylene hydride complexes prepared for this study are shown in Chart 2. The synthesis and characterization (NMR, X-ray) of the complexes are reported elsewhere.¹² All complexes exhibit fluxional behavior observable by variable-temperature NMR due to olefin insertion into the M–H bond and

Chart 2

(1) *i*PrSpNb(CH₂CH₂)H(2) *t*BuSpNb(CH₂CH₂)H(3) *meso*-DpNb(CH₂CH₂)H(4) *rac*-DpNb(CH₂CH₂)H(5) *t*BuThpTa(CH₂CH₂)H

subsequent β -hydrogen elimination. Rates for this overall hydrogen exchange process upon ethylene insertion, C–C bond rotation for the ethyl product, and β -hydrogen elimination were determined by ^1H NMR line-shape analysis (all complexes) or magnetization transfer (complex 3). The temperature-dependent broadening of the hydride resonance was used to calculate exchange rates in the line-shape simulations, assuming that the hydrogens become equivalent after insertion to form the ethyl complex. Magnetization transfer analysis was most

suitable for **3**, since the complex is C_5 -symmetric, and the (equivalent) endo hydrogens undergoing exchange give rise to a well-defined triplet in the ^1H spectrum. On the other hand, analysis of magnetization transfer data for **1**, **2**, and **4** is complicated by the close proximity of the inequivalent endo hydrogens undergoing exchange and the complicated coupling patterns in these C_1 -symmetric niobocenes.^{13,14} Also, the endo and exo $\text{CH}_2=\text{CH}_2$ resonances are not well resolved for complex **5**. Nevertheless, the line-shape analysis data correlate well with magnetization transfer data for complex **3**, providing an independent check on the method (Figure 2).

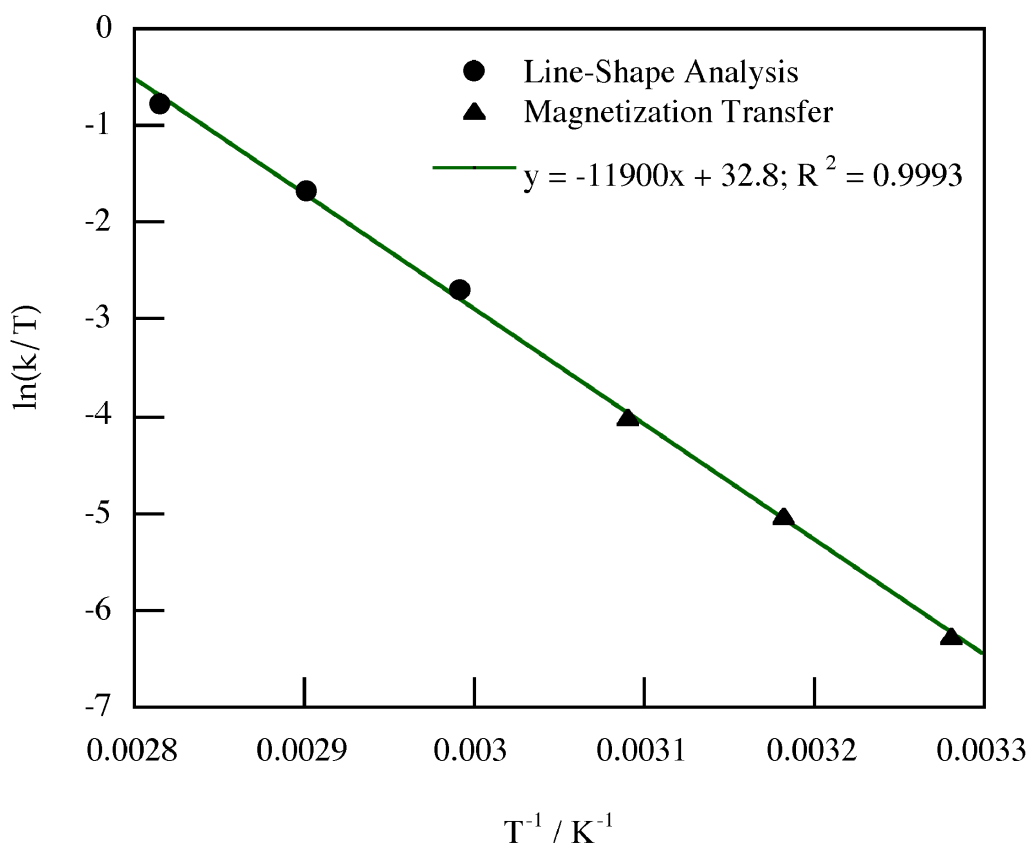


Figure 2. Eyring plot for endo methylene hydrogen/hydride exchange for complex **3** utilizing two different NMR methods: magnetization transfer and line-shape analysis.

Hydrogen exchange rate constants and free energies of activation at 318 K for *ansa*-niobocene complexes **1** - **4**, together with those for the previously studied complexes $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_2\text{CH}_2)\text{H}$ and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Nb}(\text{CH}_2\text{CH}_2)\text{H}$ for

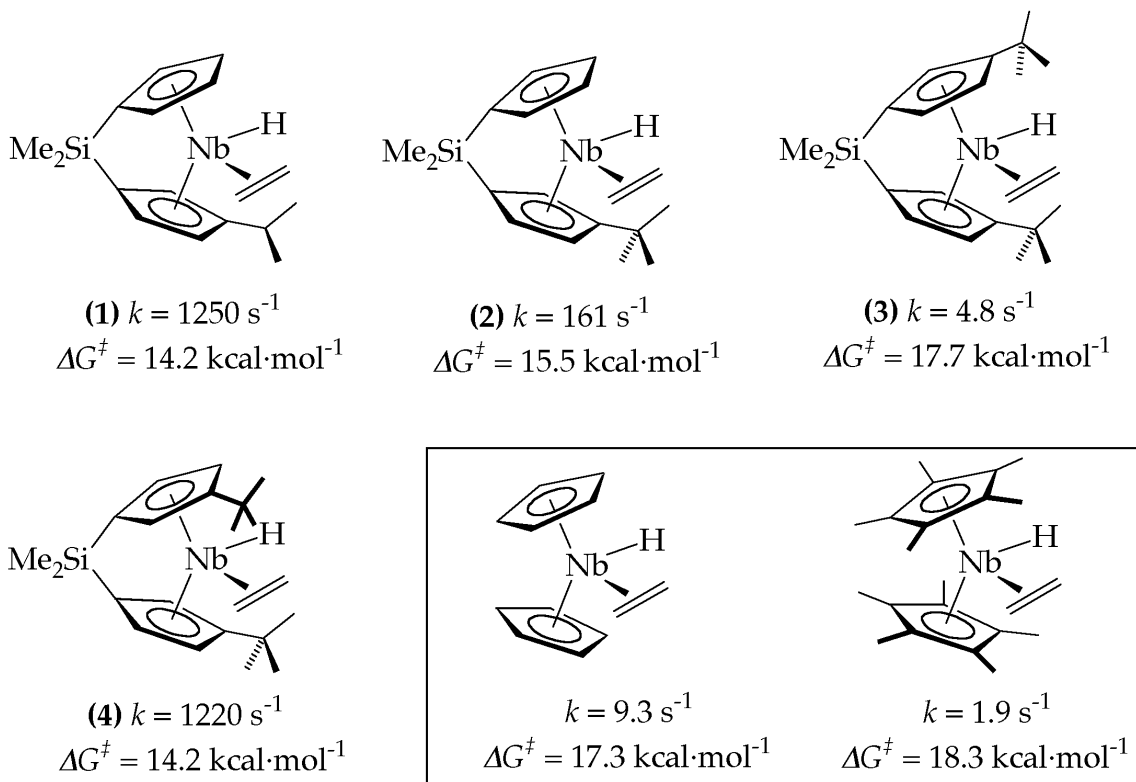


Figure 3. Olefin insertion rates and free energy barriers at 318 K for various niobocene ethylene hydride complexes. Rates for unbridged complexes (in box) have been reported in ref. 2.

comparison, are presented in Figure 3.² In agreement with Parkin's results for the *ansa*-tantalocene system (vide supra), the *ansa* ligand array appears to lower the activation barrier for hydrogen exchange compared to that for the unbridged complexes (complexes **1**, **2**, and **4**).¹¹ Although a direct comparison of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_2\text{CH}_2)\text{H}$ to $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2]\text{Nb}(\text{CH}_2\text{CH}_2)\text{H}$ is lacking, there appear to be large *ansa* effects on the rates of hydrogen exchange, as evidenced

by the greater than 2 order rate increase for **1** vs $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_2\text{CH}_2)\text{H}$. Less electron donation for a singly $[\text{SiMe}_2]$ -bridged ligand relative to an unlinked analogue has been attributed to pulling of the cyclopentadienyl rings back toward η^3, η^3 -hapticity.^{10,11} More recently, infrared, electrochemical and DFT studies for a large number of zirconocene complexes have been undertaken to probe the effect of introducing single and double ansa linkages to the parent unlinked system.¹⁵ These studies revealed lower electron density at the metal center for singly bridged metallocene fragments. By extension, the d^2 metal center of the $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2]\text{Nb}(\text{CH}_2\text{CH}_2)\text{H}$ is expected to be less electron rich, and the ground state is electronically destabilized relative to $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CH}_2\text{CH}_2)\text{H}$.

That there are specific steric interactions influencing hydrogen exchange is evident from the decrease in rates going from **1** to **2**, but, most strikingly, by the large difference in exchange rates for **3** and **4**. The racemic complex, **4**, is among the fastest to undergo exchange, whereas the meso complex **3** exchanges on the same time scale as the unbridged complexes. This difference in rates for **3** and **4** can be attributed solely to steric placement of the *tert*-butyl groups, since the complexes are essentially identical electronically. Increasing the steric bulk from isopropyl (**1**) to one or two *tert*-butyl groups (**2**, **3**) on one side of the metallocene wedge successively decreases the rate of exchange, culminating with the drastically slower exchange rate observed for **3**. We postulate that the preference for ethylene to reside on the side of the niobocene wedge away from the isopropyl or *tert*-butyl group(s) is steric in origin and that the insertion transition structures that necessarily move the ethylene toward the hydride ligand on the

other side are increasingly crowded on going from **1** with one isopropyl substituent to **2** with one *tert*-butyl substituent to **3** with two *tert*-butyl substituents. The ethylene hydride complex **4** has more steric crowding than **1**, **2**, or **3**, since the *rac* isomer necessarily possesses a close *tert*-butyl/ethylene interaction. Thus, the ground state is destabilized and the barrier for insertion is substantially reduced from that for **3**. Large steric effects have also been observed for the insertion of olefins into neutral group 4 zirconocene dihydrides.¹⁶ The doubly [SiMe₂]-bridged *ansa*-tantalocene complex, **5**, was

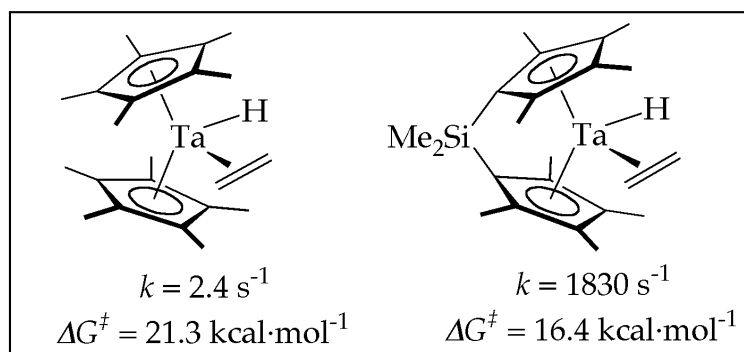
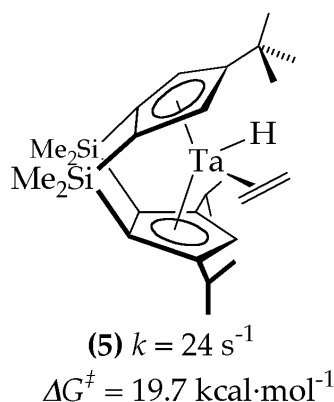
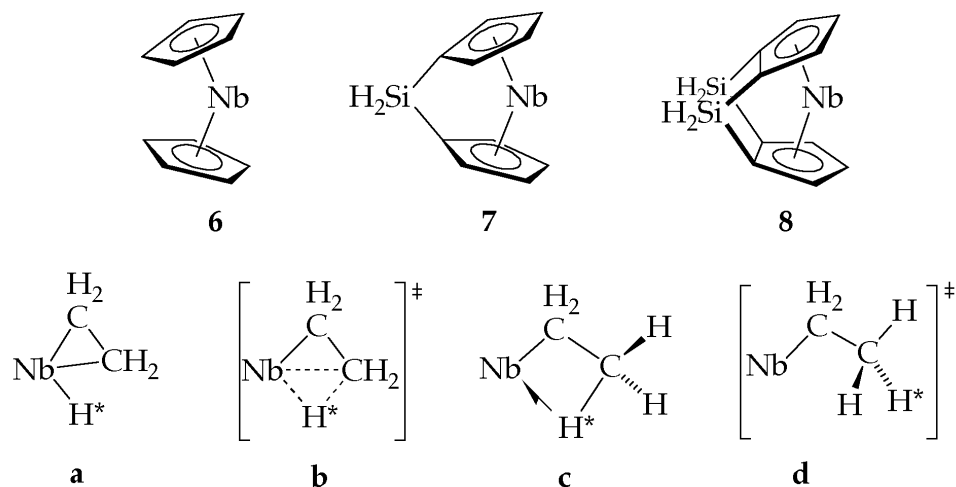


Figure 4. Olefin insertion rates and free energy barriers at 373 K for various tantalocene ethylene hydride complexes. Rates for complexes (in box) have been reported in refs 2b and 11, respectively.

found to exchange at a rate more comparable to unlinked $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ta}(\text{CH}_2\text{CH}_2)\text{H}$ than to the singly $[\text{SiMe}_2]$ -bridged *ansa*-tantalocene complex $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)_2]\text{Ta}(\text{CH}_2\text{CH}_2)\text{H}$ (Figure 4). At first sight it would appear puzzling that double linking of the cyclopentadienyl ligands has the net effect of unlinking them! Crystallographic data for $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$, $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2]\text{ZrCl}_2$, and $[(\text{Me}_2\text{Si})_2(\eta^5\text{-C}_5\text{H}_3)_2]\text{ZrCl}_2$ show that the $\text{Cp}_{\text{cent}}\text{-Zr-Cp}_{\text{cent}}$ angles decrease and the range of Zr-C bond lengths increases in a smooth progression as *ansa* linkages are introduced.^{15a} With regard to the electronic effects of doubly linking the cyclopentadienyl ligands, these recent investigations indicated that the electron-donating effect of two vicinal $[\text{Me}_2\text{Si}]$ *ansa* bridges in combination with a ligand conformation with an " η^2 -ene-allyl" type coordination mode reduces back-donation from the metal to the cyclopentadienyl ligands.^{15a} Hence, the d^2 metal center of $[(1,2\text{-SiMe}_2)_2(\eta^5\text{-C}_5\text{H-3,5-(CHMe}_2)_2)(\eta^5\text{-C}_5\text{H}_2\text{-4-CMe}_3)]\text{Ta}(\text{CH}_2\text{CH}_2)\text{H}$ is approximately as good a π donor, and the ground state is expected to be similar to $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ta}(\text{CH}_2\text{CH}_2)\text{H}$.

Density Functional Calculations. To increase understanding of the effect of single and double *ansa* bridges on the hydrogen exchange rate, density functional calculations were carried out on model systems, $[\text{Cp}^{\text{R}_2}\text{Nb}(\text{C}_2\text{H}_4)\text{H}]$, where $\text{Cp}^{\text{R}_2} = (\eta^5\text{-C}_5\text{H}_5)_2$ (**6**), $[\text{H}_2\text{Si}(\eta^5\text{-C}_5\text{H}_4)_2]$ (**7**), and $(\text{H}_2\text{Si})_2(\eta^5\text{-C}_5\text{H}_3)_2$ (**8**) (Chart 3). Four stationary points were identified on the hydrogen exchange surface for model complexes **6** - **8**: the ethylene hydride complex, $\text{Cp}^{\text{R}_2}\text{Nb}(\eta^2\text{-C}_2\text{H}_4)\text{H} = \mathbf{a}$, a β -agostic ethyl complex, $\text{Cp}^{\text{R}_2}\text{Nb}(\eta^2\text{-C}_2\text{H}_5) = \mathbf{c}$, an

Chart 3



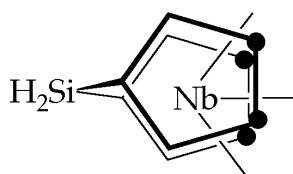
insertion transition state between these two minima, **b**, and the transition state for dissociation of the β -C-H bond, **d** (Chart 3).

Full geometry optimizations were carried out on all stationary points, and frequency calculations showed **a** and **c** to be local minima, having only positive frequencies, and **b** and **d** to be transition states, each having only one imaginary frequency. Energies relative to $\text{Cp}^{\text{R}}_2\text{Nb}(\eta^2\text{-C}_2\text{H}_4)\text{H}$ and key geometric parameters are given in Table 2.

Ground-State Structures. For all three ethylene hydride complexes, **6a** - **8a**, the Nb-H bond length is ca. 1.76 Å and the long C-C bond for the coordinated ethylene is around 1.43 Å. This latter value is in good agreement with the crystal structure of complex **2**, which has a C-C distance of 1.41 Å.¹² Such a bond length implies considerable back-donation to the olefin and an approach to a metallocyclopropane structure. The β -agostic ethyl structures, **c**, have very stretched agostic C-H bonds, ca. 1.2 Å, with the C-C bonds lengthened to around 1.50 Å. The Nb-H distances are consistent with agostic

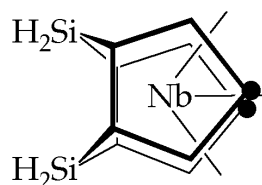
bonding at 1.98-2.01 Å. With a 60° rotation about the C–C bond, the exchanging hydrogens become equivalent at the transition states **d**, which have normal ethyl groups with C–H bond lengths of 1.105-1.110 Å and C–C bond lengths ranging between 1.534 and 1.543 Å. The Nb–H contacts for **d** are now long, being greater than 2.6 Å. The greatest differences between the systems are calculated for the insertion transition states **b**, which, on distance criteria, appear to be earliest for **7** and latest for **8**. The relative cyclopentadienyl ring orientations are fixed for **7** and **8**, constrained by their respective bridges, and the variation in inter-ring angle is small as one follows the reaction progression from **a** to **d**. However, for **6** the rings are closer to being eclipsed than staggered. The unlinked **6a** and **6b** have a two-carbon front face conformation, as in **8**, but for **6c** and **6d**, the rings reorient to give a four-carbon front face conformation, as in **7** (Chart 4).^{15a}

Chart 4



4-carbon front face

7



2-carbon front face

8

Mechanism for Hydrogen Exchange. Relative energies, given in Table 2 and represented diagrammatically in Scheme 2, concur well with the experimental values and trends, showing a significantly lower activation energy for the singly bridged system, **7**. The agostic ethyl, **c**, is lower in energy for **7** than for **6** or **8** (which fortuitously are calculated to have the same energy). As the insertion barrier and exchange barrier are also lower for **7**, this is consistent

with faster exchange rates measured for singly linked compounds. The energy differences between the agostic ethyl, **c**, and the transition state, **d**, are 2.0 kcal mol⁻¹ for **6**, 1.9 kcal mol⁻¹ for **7**, and 1.6 kcal mol⁻¹ for **8**. Complex **8d** shows

Scheme 2

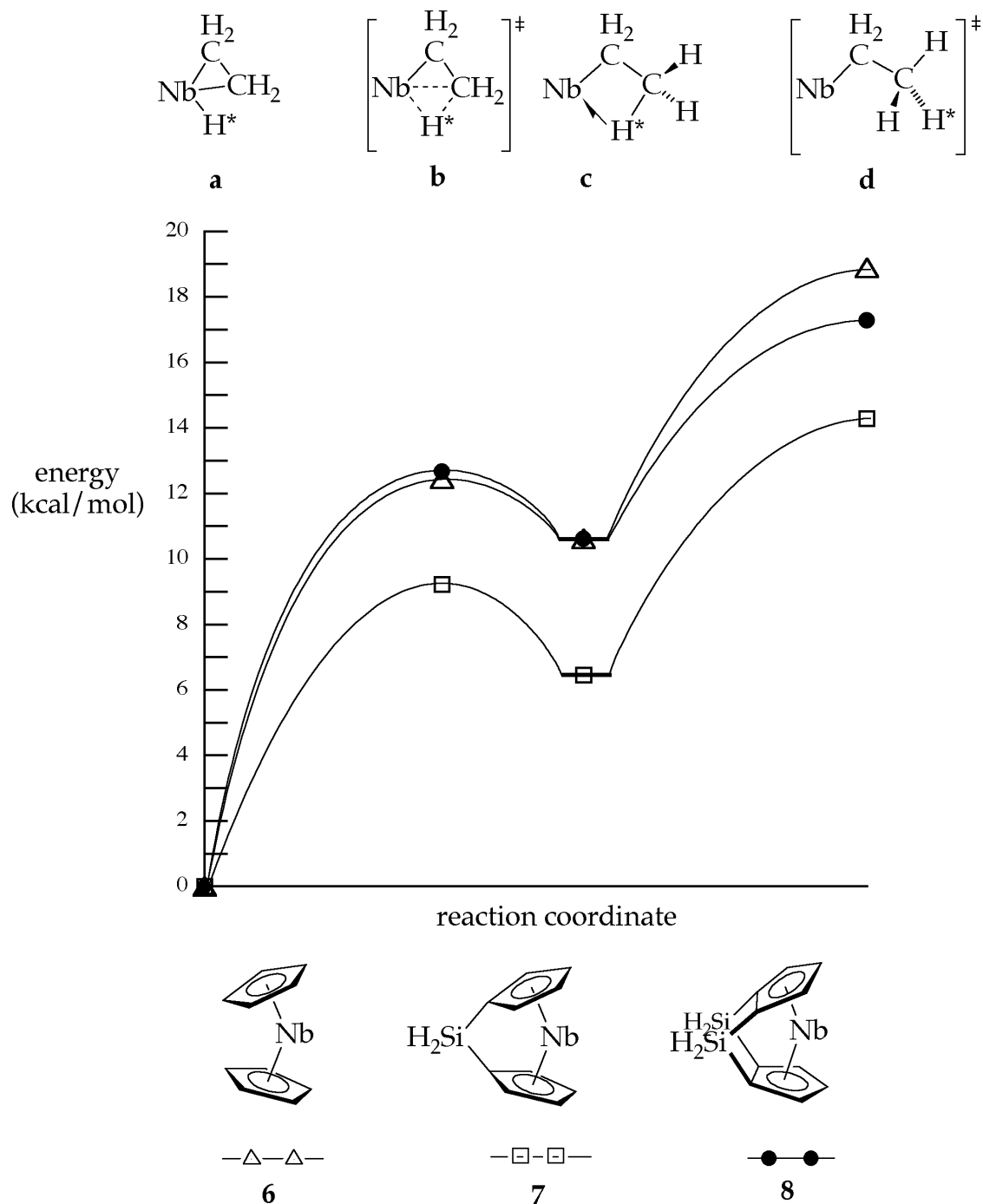


Table 2. Energies (kcal·mol⁻¹) and Selected Bond Lengths (Å) for **6 - 8**.

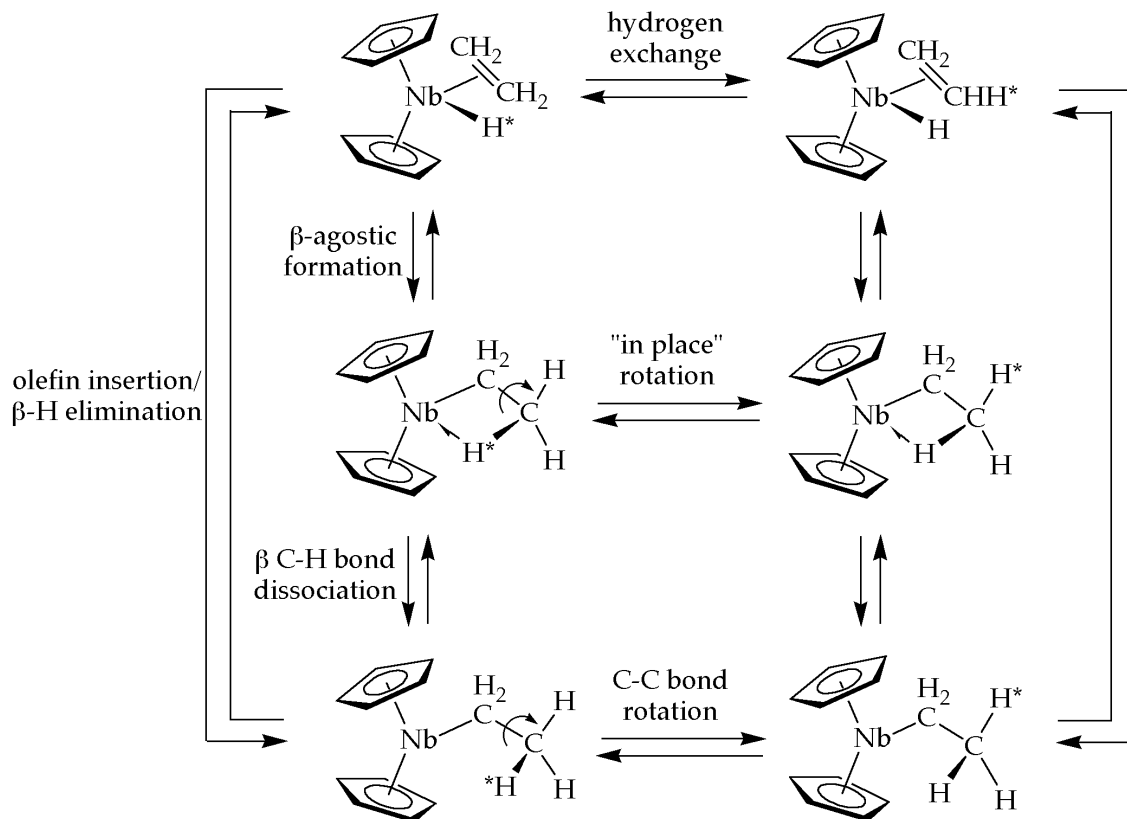
	Energy	Nb–H	C _{endo} –H	C–C	Nb–C _{exo}	Inter-ring Angle
6a	0	1.757	2.320	1.434	2.338	43
7a	0	1.765	2.332	1.427	2.344	54
8a	0	1.762	2.313	1.431	2.333	61
6b	12.45	1.814	1.430	1.466	2.299	38
7b	9.22	1.809	1.573	1.448	2.317	53
8b	12.68	1.881	1.385	1.478	2.281	58
6c	10.61	1.976	1.205	1.504	2.278	47
7c	6.46	1.988	1.200	1.503	2.268	53
8c	10.61	2.005	1.193	1.509	2.263	59
6d	18.91	2.856	1.105	1.543	2.265	48
7d	14.30	2.766	1.107	1.540	2.248	54
8d	17.30	2.681	1.110	1.534	2.249	60

marginally longer C–H bonds, and shorter Nb–H distances, suggesting that the transition state may maintain a very weak interaction between the exchanging hydrogens and the metal; however, for all three **d** is best described as a nonagostic ethyl. For all three systems a significant portion of the barrier to hydrogen exchange comes from the barrier to rotation of the methyl groups.

In previous studies of olefin insertion into group 5 metal–hydride bonds it has been assumed that, after the olefin inserts, there is a lower barrier to rotation about the C–C bond which exchanges the hydrogens, followed by fast

β -hydrogen elimination. An agostic interaction may or may not be cleaved following the insertion step to exchange the hydrogens (Scheme 3). The density functional calculations of this work support the formation and cleavage of a

Scheme 3



β -agostic structure to exchange the hydrogen atoms after the insertion event.

Our research groups had earlier suggested that an "in-place" rotation mechanism will exchange hydrogen atoms after propene or ethylene insertion into a metal-hydride bond.¹⁷ After insertion, the propyl or ethyl intermediate retains agostic bonding to the metal center while the hydrogens undergoing exchange rotate. Our calculations do not support this mechanism (except possibly for complex 8; *vide supra*), but suggest that upon C-C bond rotation the agostic interaction is

completely broken. Hydrogen atom exchange can then be observed in the ^1H NMR spectrum following β -hydrogen elimination.

When the relative barriers for insertion versus hydrogen atom exchange were compared, it was unexpected that the highest free energy barrier along the reaction profile for hydrogen exchange was methyl rotation (Scheme 2). This conclusion raises questions concerning the interpretations of the steric and electronic effects for olefin insertion for this system, since previously the rate-determining step was assumed to be the insertion step.² On the other hand, the calculations reveal that the largest differences for **6** - **8** are the barriers for olefin insertion (**b**) and the energies for **c**. The barriers for methyl rotation (**d**) are quite similar for the three systems (with the caveat that the doubly $[\text{SiH}_2]$ -bridged ansa complex has a slightly lower barrier, probably due to some weak agostic interactions as it rotates; vide supra). If this trend is general, i.e., the stereoelectronic influences on olefin insertion dominate, and the barriers for alkyl rotation are similar, then the principal conclusions reached from earlier studies are likely still valid.

Experimentally measuring these two separate barriers would be difficult for this group 5 metallocene system. Shultz and Brookhart have been able to measure independently the barriers to C–C bond rotation and β -H elimination for a cationic (diimine) Pd^{II} β -agostic ethyl complex by variable-temperature ^1H NMR.¹⁸ For their palladium system the most stable structure is the β -agostic ethyl complex that exhibits three distinct resonances for the α - and β -methylene protons and the agostic proton at low temperatures. Upon warming, coalescence of the α - and β -methylene resonances is observed before the resonance for the

agostic β -proton displays any line broadening. Thus, the β -H elimination/olefin rotation/reinsertion process is faster than the C–C bond rotation process for the β -agostic ethyl ground state. Line shape analysis of the resonance for the β -agostic hydrogen at higher temperatures revealed the barrier to C–C bond rotation. At high temperatures, all five resonances coalesce as a result of the combination of the two processes. Thus, the barrier for β -H elimination, $\Delta G^\ddagger(165\text{ K})$, was established as $7.1\text{ kcal}\cdot\text{mol}^{-1}$ and that for C–C bond rotation, $\Delta G^\ddagger(165\text{ K})$ as $8.4\text{ kcal}\cdot\text{mol}^{-1}$. For the group 5 metallocene ethylene hydride complexes the β -agostic ethyl is *not* the stable structure, and thus, a similar analysis is not possible.

Bonding Considerations. Formally, the formation of the ethyl transition state can be viewed as a reduction from Nb^{V} to Nb^{III} . Fragment analysis of the rotation transition states, **d**, confirm that these closely resemble a d^2 species where the two metal electrons occupy a $d(x^2)$ metallocene orbital lying in the metallocene bonding plane. The stability of the analogous orbital in zirconocene compounds has been shown to vary in the order $7 > 6 > 8$; ^{15a} thus, the relative ease of exchange found here is entirely consistent with our previous study.

Conclusions

Rates of hydrogen exchange comprising olefin insertion, C–C bond rotation, and β -hydrogen elimination have been measured for a series of group 5 *ansa*-niobocene or -tantalocene ethylene hydride complexes. The data indicate that both the steric bulk and the placement of cyclopentadienyl substituents have

large effects on the energy barrier for hydrogen exchange. Exchange rates decrease by 3 orders of magnitude as the steric bulk is increased for those metallocenes with unsymmetrical substitution: the transition-state structure becomes more crowded as ethylene moves toward the hydride on the more sterically hindered side of the metallocene wedge. However, the ground-state structure can be destabilized by placing steric bulk on both sides of the metallocene wedge, resulting in a large enhancement in exchange rate. The exchange rate is 3 orders of magnitude larger for niobocenes with a single [SiMe₂] ansa bridge; however, little rate enhancement is observed for a complex with two [SiMe₂] bridges. The density functional calculations agree with this trend and suggest that the electron population shifts from the ground state to the transition state is the most favorable for the singly linked complex; hence, the fastest observed exchange rate.

Experimental

General Considerations. All air- and moisture-sensitive compounds were manipulated using standard vacuum line and Schlenk techniques or in a drybox under a nitrogen atmosphere as described previously.¹⁹ Argon and dinitrogen gases were purified by passage over columns of MnO on vermiculite and activated molecular sieves. Toluene-*d*₈ was distilled from sodium benzophenone ketyl. NMR spectra were recorded on a Varian Inova or Unity⁺ 500 MHz spectrometer (¹H, 500.13 MHz, ¹³C, 125.77 MHz) or a Varian Mercury 300 MHz spectrometer (¹H, 300.07 MHz, ¹³C, 75.45 MHz).

Magnetization Transfer Experiments and Line Shape Analysis

Experiments. For both types of experiments, the niobocene ethylene hydride samples were dissolved in toluene-*d*₈ and flame-sealed in NMR tubes under 700 Torr of argon at -78 °C. Reaction temperatures were determined by measuring the peak separation of an ethylene glycol or methanol standard before and after the experiments. For the line shape analysis, spectra were recorded in 10 degree increments for 40-50 degrees when the hydride resonance began to broaden. This broadening was simulated using gNMR.²⁰ Magnetization transfer spectra were obtained by using a DANTE pulse sequence.²¹ Relaxation times (T₁) for the resonances of interest were measured at each temperature before the magnetization transfer experiment using the inversion recovery method. The magnetization transfer data were fitted using the program CIFIT to obtain rate constants.²² The reported rate constants for the elementary chemical processes of insertion followed by C–C bond rotation, *k*, were calculated by multiplying the exchange rate constant (obtained by line shape analysis or magnetization transfer), *k*_{ex}, by a statistical factor (1.5) according to the following relationship:

$$k_{ex} = (2/3)k.$$

This statistical factor is necessary, because, on average, after insertion and C–C bond rotation, the same hydrogen returns to niobium or tantalum one-third of the time.

Computational Methods. Calculations were performed using density functional methods of the Amsterdam Density Functional Package (Versions ADF99.02 and ADF2000.02). The generalized gradient approximation method was employed, using the local density approximation of Vosko, Wilk, and

Nusair²³ together with non-local exchange corrections by Becke,²⁴ and non-local correlation corrections by Perdew.²⁵ Type IV basis sets used triple- ξ accuracy sets of Slater type orbitals, with a single polarization function added to main group atoms. The cores of the atoms were frozen up to 1s for C, 2p for Si and 3d for Nb. First order relativistic corrections were made to the cores of all atoms. Relativistic corrections were made using the ZORA (Zero Order Relativistic Approximation) formalism.

Reaction pathways were modeled by stepping a reaction coordinate through a sequence of fixed values and allowing the other structural parameters to optimize to a minimal energy.

All local minima and transition states were characterized by frequency calculations.

Fragment calculations were carried out to elucidate the trends in the electronic structure on an orbital basis. The fragments used were the NbCp^R₂ unit and the C₂H₄, H or C₂H₅ units with the identical geometry to that which they have in the optimized structure of the molecule.

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- (14) Typically, the magnetization transfer experiment is utilized to measure exchange between uncoupled protons (singlets in the ^1H spectrum). However, if the coupling is small compared to the chemical shift separation of the exchanging resonances (which is the case for **3**, but not for **1**, **2** and **4**), the magnetization transfer experiment can provide meaningful rate data.² For more details on this

subject see: Doherty, N. M. Ph.D. Thesis, California Institute of Technology, Appendix I, 1984 and references cited therein.

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Chapter 3

Arene C–H Bond Activation and Arene Oxidative Coupling by Cationic Palladium(II) Complexes

The text of this chapter was taken in part from the following manuscript:

Ackerman, L. J.; Sadighi, J. P.; Kurtz, D. M.; Labinger, J. A.; Bercaw, J. E.
Organometallics, submitted **2003**.

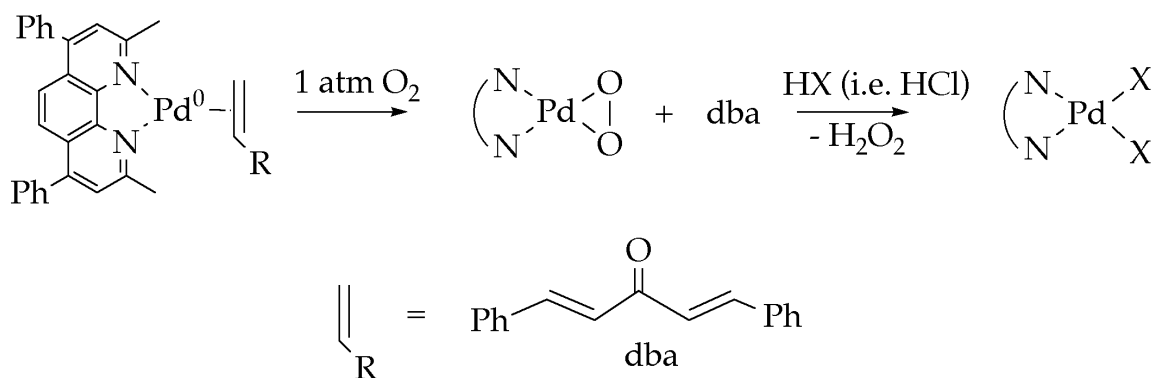
Abstract

N,N'-Diaryl- α -diimine-ligated Pd(II) dimethyl complexes, (tBu₂ArDAB^{Me})PdMe₂ and {(CF₃)₂ArDAB^{Me}}PdMe₂ {tBu₂ArDAB^{Me}: ArN=C(CH₃)–C(CH₃)=NAr, Ar = 3,5-di-*tert*-butylphenyl; (CF₃)₂ArDAB^{Me}: Ar = 3,5-bis-(trifluoromethyl)phenyl} undergo protonolysis with HBF₄ (aq) in trifluoroethanol (TFE) to form cationic complexes [(α -diimine)Pd(CH₃)(H₂O)][BF₄]. The cations activate benzene C–H bonds at room temperature. Kinetic analyses reveal trends similar to those observed for the analogous Pt complexes: the C–H activation step is rate determining (KIE = 4.1 $\pm$ 0.5), and is inhibited by H₂O. The kinetic data is consistent with a mechanism in which benzene substitution proceeds by a solvent- (TFE-) assisted associative pathway. Following benzene C–H activation under 1 atm O₂, the products of the reaction are biphenyl and a dimeric μ -hydroxide complex, [(α -diimine)Pd(OH)]₂[BF₄]₂. The Pd(0) formed in the reaction is reoxidized by O₂ to the same dimeric μ -hydroxide complex after the oxidative C–C bond formation. The regioselectivity of arene coupling was investigated with toluene and α,α,α -trifluorotoluene as substrates.

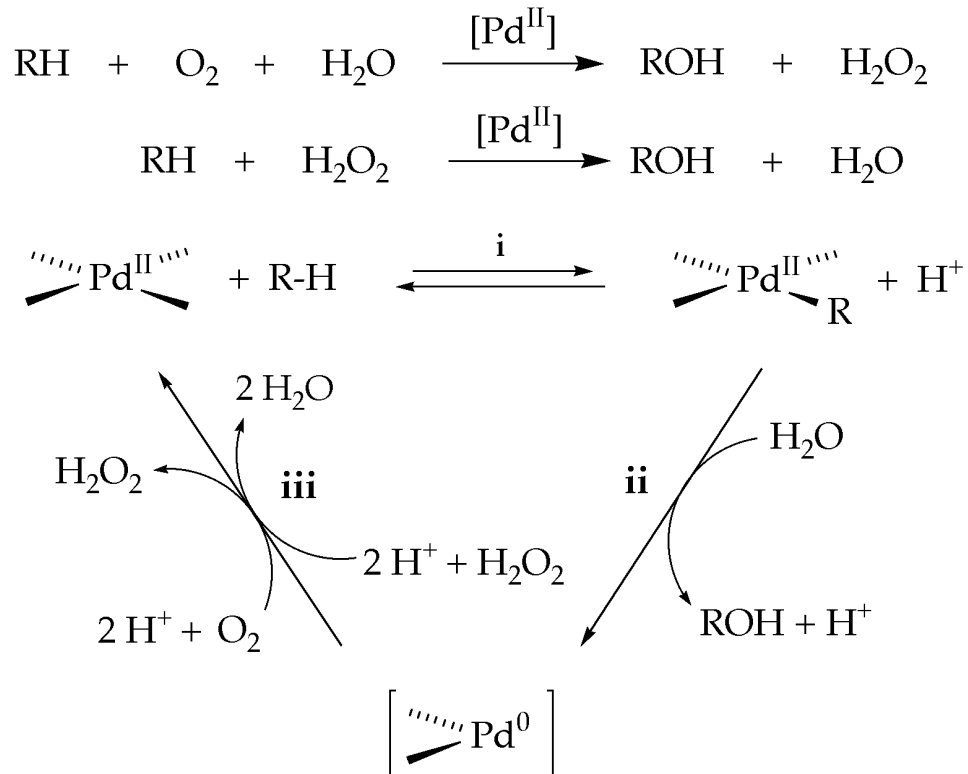
attack by water or chloride to liberate product and regenerate the Pt(II) catalyst.³ Recent efforts in our group have focused on exploiting oxidation of Pt(II) complexes by O₂ (or other oxidants) to circumvent the use of stoichiometric Pt(IV).⁴

An alternate strategy for O₂ would employ a Pd(0)/Pd(II) redox couple to achieve the desired chemistry. Recently, oxidations of arenes to phenols⁵ and of alcohols to aldehydes or ketones,⁶ using Pd(II) catalysts and O₂ as the stoichiometric oxidant, have been reported. In addition, Stahl and coworkers demonstrated the clean reaction of [(bathocuproine)Pd(0)(η²-dba)] (dba = dibenzylideneacetone) with O₂ to produce a Pd(II) peroxo complex, which liberates H₂O₂ upon treatment with acid (Scheme 2).⁷ If Pd(II) complexes can effect C–H activation as well, then the catalytic cycle shown in Scheme 3 could be feasible.

Scheme 2

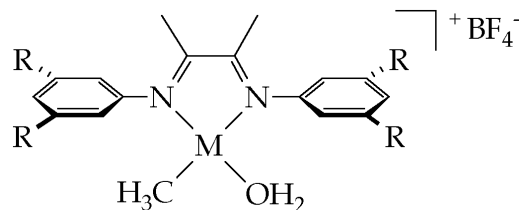


In Scheme 3, initial C–H bond activation, analogous to that observed in the Shilov system (i), is followed by a formal reductive elimination step (ii) to generate product and a Pd(0) fragment. Trapping and two-electron oxidation of

Scheme 3

the product Pd(0) complex by O₂ would then regenerate the Pd(II) catalyst (step **iii**). The H₂O₂ byproduct of the oxidation could serve as another oxidizing equivalent, or it could disproportionate to H₂O and O₂ in the presence of Pd(II) as observed in other catalytic oxidation chemistry.⁸ This proposed catalytic cycle is similar to that suggested by Periana and coworkers in the Hg(II)-catalyzed oxidation of methane to methyl bisulfate by H₂SO₄.⁹ Since neither Hg(II) nor Pd(II) can easily access the (IV) oxidation state (in contrast to Pt), the proposed product release involves a reductive step, followed by reoxidation to the active catalyst species.

Mechanistic studies of C–H activation by $[(\alpha\text{-diimine})\text{Pt}(\text{CH}_3)(\text{H}_2\text{O})][\text{BF}_4]$ complexes such as **1a/b** have been reported.¹⁰ Intramolecular C–H activation by similar cationic $[(\alpha\text{-diimine})\text{Pd}(\text{CH}_3)(\text{L})]^+$ complexes has been observed.^{11,12}



M = Pt

1a: R = CMe₃; **1b:** R = CF₃

M = Pd

2a: R = CMe₃; **2b:** R = CF₃

These results and the precedented reactivity of $[(\alpha\text{-diimine})\text{Pd}(0)]$ complexes with O₂ (vide supra) directed us to investigate the intermolecular C–H activation of Pd(II) **2a** and **2b**.

Results and Discussion

Synthesis of Pd Complexes. The α -diimine ligands have been prepared previously by the formic acid-catalyzed condensation of 2,3-butanedione with the corresponding aniline in methanol.^{10ab} Dimethyl Pd(II) complexes (α -diimine)PdMe₂, **3a** and **3b**, were prepared by treating $[(\text{pyridazine})\text{PdMe}_2]_n$ ¹³ and (COD)PdMe₂¹⁴ (COD = 1,5-cyclooctadiene), respectively with the corresponding ligand.¹¹ Protonolysis of **3a/b** by HBF₄ (aq) in trifluoroethanol (TFE) solvent generates the methyl aquo cations, **2a/b**. The analogous reaction of Pt(II) dimethyl complexes affords an equilibrium mixture of aquo and

trifluoroethanol adducts observable by NMR; the magnitude of the equilibrium constant for different α -diimine complexes depends on the electron density at the Pt center, as assayed by CO stretching frequencies.^{10a} Although we believe this aquo/solvento equilibrium is operative for **2a** or **2b** (vide infra), only one species is observed in the NMR spectra, even at low temperature or after addition of up to 50 μ L of D₂O. Small chemical shift differences between the aquo and trifluoroethanol adducts of **2a/b**, and/or a low kinetic barrier for their interconversion may account for this observation. Complexes **2a/b** are prepared *in situ* and have not been isolated as analytically pure solids.

Kinetics of Reactions with Benzene. Methyl cations **2a/b** react with benzene in TFE-*d*₃, with concomitant liberation of methane. ¹H NMR was used to monitor the disappearance of starting material from which rates were determined. When carried out under an atmosphere of dioxygen, these reactions proceed cleanly, affording biphenyl and palladium(II) products (vide infra). On the other hand, when **2a/b** react with benzene under an inert atmosphere (e.g., Ar), palladium metal deposition accompanies biphenyl and soluble palladium(II) product formation. The rates are not affected by ionic strength: several experiments were conducted at different D₂O concentrations with and without added NMe₄BF₄ with negligible change in rate constants (see Appendix). Hence, kinetic studies were carried out under 1 atm O₂ without controlling ionic strength. As previously found for the analogous platinum systems,¹⁰ the reaction is first-order in benzene, rates are decreased by added water, and $1/k_{\text{obs}}$ is linear with respect to $[\text{D}_2\text{O}]/[\text{C}_6\text{H}_6]$ (Figure 1).¹⁵ Reactivity falls off in the order **2a** > **2b** > **1a**.

The temperature dependence for the reaction between **2a** and C_6H_6 was studied over the range of 1 – 40 °C. The activation parameters calculated from the Eyring plot are ($\Delta H^\ddagger = 20 \pm 2 \text{ kcal}\cdot\text{mol}^{-1}$, $\Delta S^\ddagger = -2 \pm 6 \text{ e.u.}$) for C_6H_6 activation are similar to the values of $\Delta H^\ddagger = 20 \text{ kcal}\cdot\text{mol}^{-1}$, $\Delta S^\ddagger = -5 \text{ e.u.}$ for **1a**.^{10a,16}

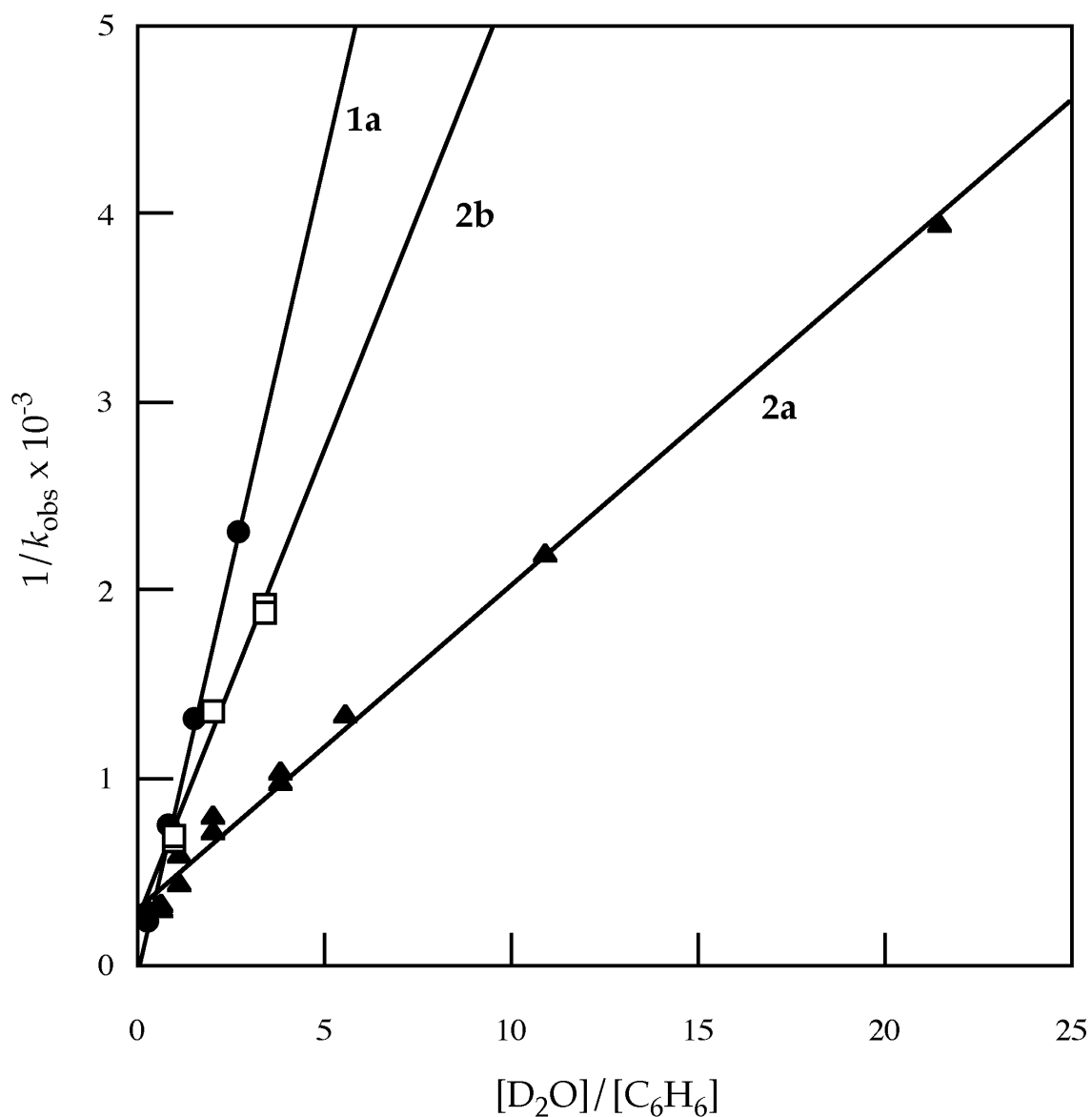


Figure 1. Plots of the reciprocal pseudo first order rate constants from the kinetics of reactions of $[(\alpha\text{-diimine})M(CH_3)(H_2O)](BF_4)$ with C_6H_6 (298 K) at varying D_2O concentrations ($M = Pd, Pt$).

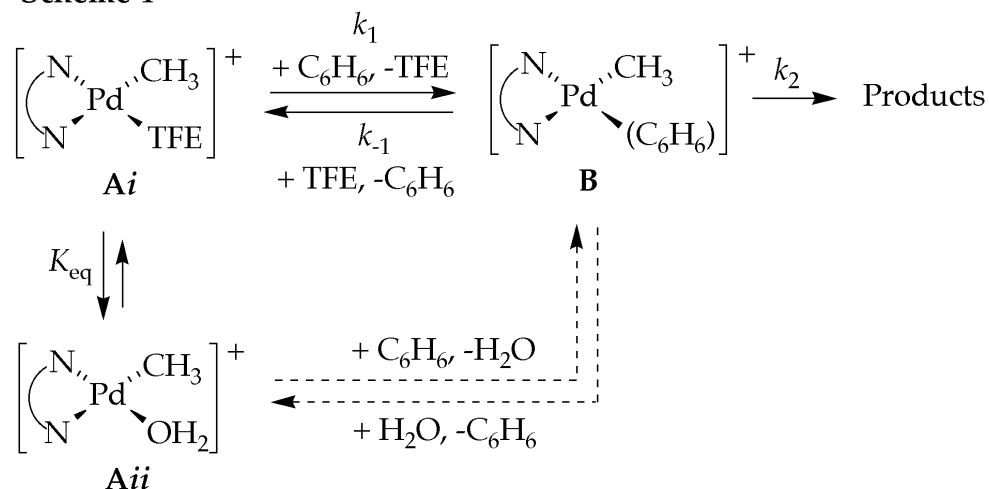
The kinetic isotope effect for the reaction was calculated by separately determining the rate constants for reactions of C_6H_6 and C_6D_6 under the same conditions. The measured isotope effect is 4.1 ± 0.5 . The observed primary kinetic isotope effect indicates that C–H bond cleavage (k_2 , Scheme 4) is rate-determining. Unlike **1a/b**, **2a/b** reacts with C_6D_6 to liberate only CH_3D without the observance of more highly deuterated methanes. Likewise, upon protonolysis of **3a/b** in $TFE-d_3$, only $[(CH_3)Pd(II)]$ cations are formed, whereas the analogous Pt dimethyl complexes are converted to both $[(CH_3)Pt(II)]$ and $[(CH_2D)Pt(II)]$ cations.^{10a} The exclusive formation of CH_3D in the deuterolysis of **3**, or in the reaction of **2** with deuterated benzene, indicates that the kinetic barrier to methane loss is small relative to that of the deuterium scrambling processes observed for **1a/b**. Deuterium scrambling for the Pt systems has been proposed to occur by formation of both methane and arene σ -complexes which undergo more than one oxidative addition/reductive elimination sequence before methane loss.^{10ac}

Mechanism of C–H Activation of Benzene by Palladium(II) Methyl Cations. All of the observed data are consistent with the mechanism and derived rate law previously proposed for the analogous Pt systems (Scheme 4).^{10ac}

In this scheme the aquo (**Aii**) and solvento (**Ai**) complexes are in rapid equilibrium, with benzene displacing the more weakly bound solvent ligand; direct attack of benzene on **Aii** to displace water is assumed to be negligible. Rate determining C–H activation (k_2) occurs after benzene coordination (complex **B**). The accelerated rates observed for **2a** vs **2b** (ligand effects) and also **2a/b** vs

1a/b (metal effects) can be accounted for by the magnitude of K_{eq} . Although K_{eq} cannot be measured directly for **2a/b** (vide supra), it is calculated from the slope and intercept of the $1/k_{obs}$ plot (see Appendix for rate law derivation). The

Scheme 4



$$-\frac{d[\text{Pd}]_T}{dt} = k_{obs}[\text{Pd}]_T = \frac{k_2}{k_{-1}[\text{TFE}] + k_2} \cdot \frac{k_1[\text{TFE}][\text{C}_6\text{H}_6][\text{Pd}]_T}{[\text{TFE}] + K_{eq}[\text{H}_2\text{O}]}$$

calculated K_{eq} values for the palladium complexes are 36 for **2a** and 122 for **2b** (298 K). The measured K_{eq} values for the platinum congeners are 430 for **1a** and 2800 for **1b** (293 K).^{10a} As reflected by the measured K_{eq} values, ground state differences between the aquo (**Aii**) and solvento (**Ai**) complexes for a series of $[(\alpha\text{-diimine})\text{Pt}(\text{CH}_3)(\text{H}_2\text{O})][\text{BF}_4]$ complexes (including **1a/b**) were proposed to account for differences in C–H activation rate.^{10a} The same behavior appears to be operative in the palladium cases. Thus, the more stable the aquo adduct (larger K_{eq}), the slower the C–H activation rate. The aquo adduct is more stable for the complexes with electron-withdrawing ligands (**1b** and **2b**) since the metal center is more electron-deficient, resulting in stronger bonding to the H_2O

molecule. In addition, the aquo adducts are more stable for the platinum complexes **1a/b** over the palladium analogs **2a/b** due to the stronger bonding of 5d transition metals to ligands compared to 4d transition metals.¹⁷

The kinetic data do not provide information about the exact nature of the C–H bond-breaking step for **2a/b** (e.g., oxidative addition vs σ -bond metathesis mechanisms). For platinum, a large body of evidence has been accumulated for a Pt(IV) hydride intermediate, supporting an oxidative addition mechanism for C–H activation by **1a/b**.^{10ac,18} Because the Pd(IV) oxidation state is less readily accessible, the analogous intermediate may be less likely, although it cannot be ruled out. Canty and coworkers have structurally characterized a variety of Pd(IV) complexes, such as [(bipy)Pd(CH₃)₃I], obtained from oxidative addition of CH₃I to [(bipy)Pd(CH₃)₂].¹⁹

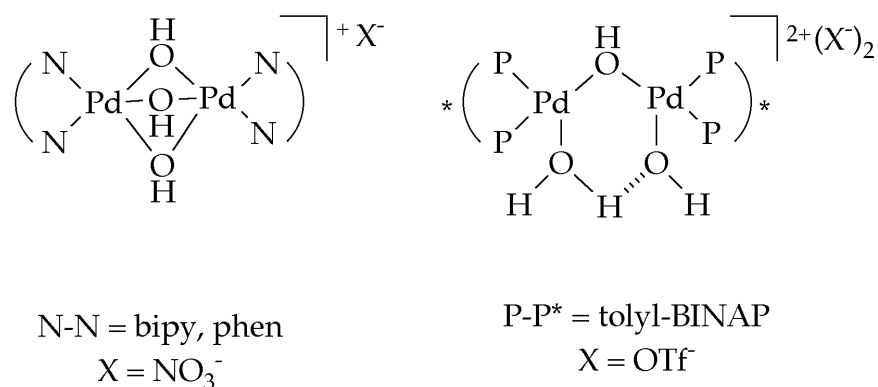
Reactivity of Palladium(II) Methyl Cations. Unlike their platinum congeners, **2a/b** do not form stable phenyl complexes upon reaction with benzene. As noted above, under an inert atmosphere reactions of **2a/b** with benzene deposit Pd(0) and produce unidentified palladium-containing byproducts and biphenyl. However, when the reaction is carried out under 1 atm of O₂, two identifiable Pd(II) species, [(α -diimine)Pd(H₂O)₂][BF₄]₂ (**4a/b**) and [(α -diimine)Pd(OH)]₂[BF₄]₂ (**5a/b**), as well as biphenyl form as the reaction proceeds. After complete reaction under O₂, the only products observed are **5a/b** and 0.5 equiv biphenyl, with no Pd(0) deposition.^{20,21}

Complexes **4a** and **5a** were identified by independent syntheses from the dichloride (^tBu₂ArDAB^{Me})PdCl₂ (**6a**)^{22,23} and isolation of the final product, **5a**, from the C–H activation reactions. **4a** and **5a** are synthesized by adding AgBF₄

to a solution of **6a** in wet $\text{CH}_2\text{Cl}_2/\text{THF}$ (10/1) as published previously.²³ Notably, **4a** could be isolated as the sole product after the reported 3 h reaction time, but at shorter reaction times (1-2 h) mixtures of both **4a**, **5a**, and other unidentified species were observed. Dissolving the mixture in $\text{TFE-}d_3$, followed by addition of HBF_4 (aq), results in the disappearance of the unidentified species, and only **4a** and **5a** are present in solution. Subsequent addition of HBF_4 converts all of **5a** to **4a**. **5a** is the sole product of the reaction of **2a** with benzene under O_2 ; the diagnostic protons on the bridging hydroxide groups were located in the ^1H NMR by evaporating the trifluoroethanol (protio solvent) and dissolving the residue in CD_2Cl_2 . These protons on the bridging hydroxide groups appear at - 3.5 ppm and disappear upon addition of D_2O . In other dinuclear (diimine) $\text{Pd}(\text{II})$ hydroxide complexes, these hydrogens resonate near -3 ppm (CD_2Cl_2).²³

The other species observed in the mixtures of **4a** and **5a** were not identified, but are most likely related complexes. Studies of the reaction of NaOH with N-ligated $[(\text{L}_2)\text{Pd}(\text{OH})_2][\text{NO}_3]_2$ complexes (L_2 = bipyridine or phenanthroline) in water have shown that several species form in solution which cannot be isolated in pure form.²⁴ The authors postulate that a trihydroxide bridged species may be a component of the mixture (Scheme 5).²⁴ Also, phosphine-ligated $[(\text{BINAP})\text{Pd}(\text{H}_2\text{O})_2][\text{X}]_2$ complexes have been isolated from the addition of AgX to the corresponding dichloride complexes ($\text{X} = \text{BF}_4^-$ or OTf). Unlike **4a**, the dimers $[(\text{BINAP})\text{Pd}(\text{OH})_2][\text{X}]_2$ are easily obtained from the bis(aquo) complexes by treating with 4 Å molecular sieves in acetone or treatment with 1 equiv NaOH . When an insufficient amount of sieves was used,

Scheme 5



a complex was isolated that was determined to be a binuclear mono- μ -hydroxo complex also having a (μ -HO $\cdots$ H $\cdots$ OH) as well (Scheme 5, ¹H NMR, ESI-MS).²⁵ These types of structures shown in Scheme 5 are likely related to the unidentified species observed for the α -diimine complexes in this study.

Although a hydroxide dimer complex could not be synthesized cleanly without some bis aquo complex, X-ray quality crystals of the hydroxide dimer complex **5b** were grown from an NMR tube reaction of **2b** and benzene (Figure 2). Details of the structure determination and labeled drawing are included in the Appendix.

Scheme 6 illustrates the proposed reaction sequence. The species, *i*, *ii*, and *iii* are unobserved, postulated intermediates. First, the phenyl product, *i*, disproportionates (possibly by phenyl group transfer), to produce *ii* and **4a/b**. Reductive elimination of biphenyl from *ii* produces a Pd(0) complex, which is reoxidized by O₂ to peroxo intermediate *iii* or possibly by hydrogen peroxide to *iii*.⁷ Alternatively, hydrogen peroxide may be disproportionated rapidly.⁸ Species similar to the postulated intermediates *i* and *ii* have been suggested for

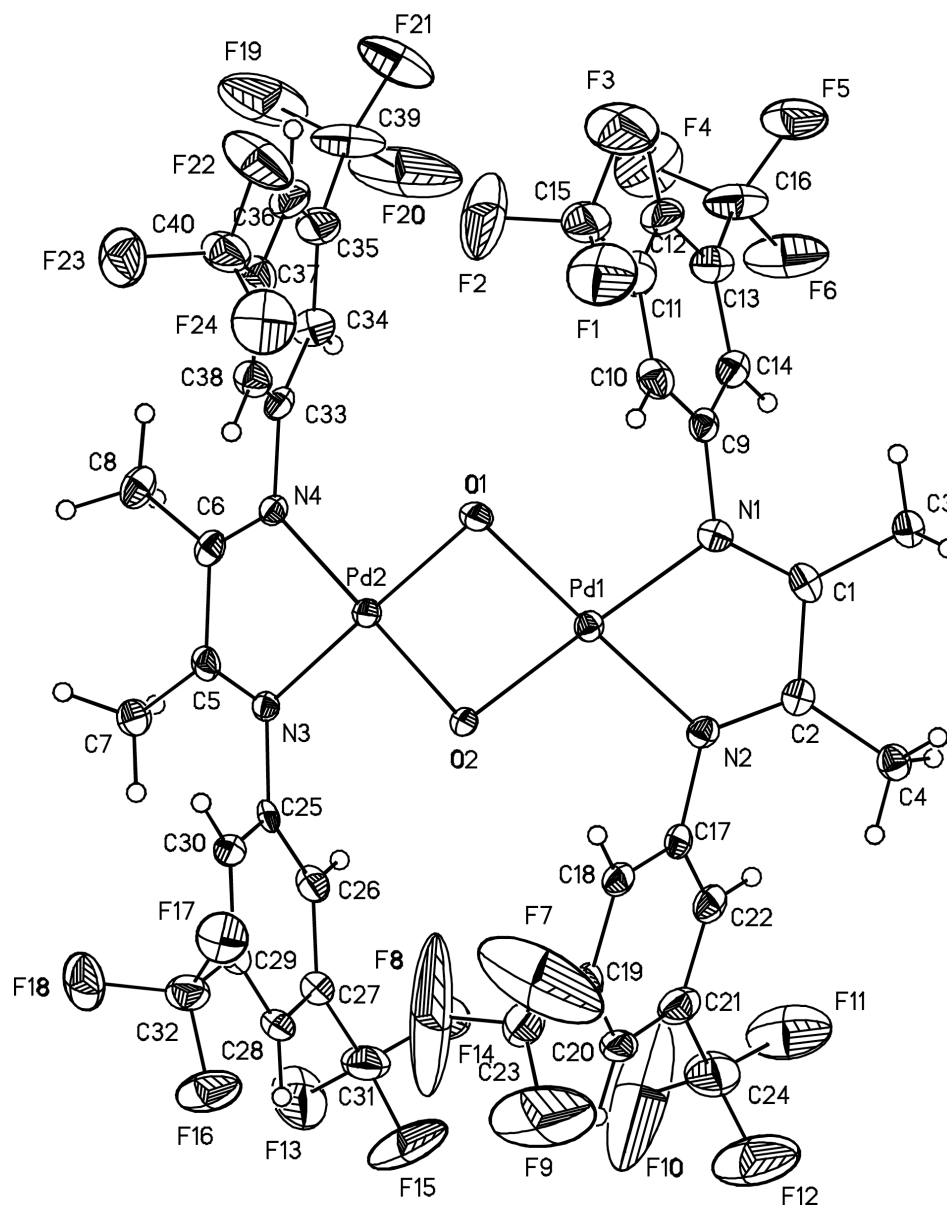
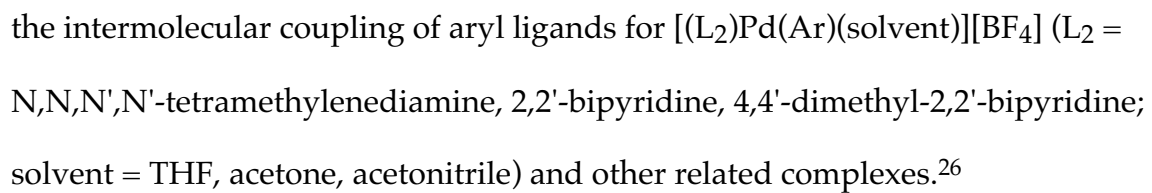
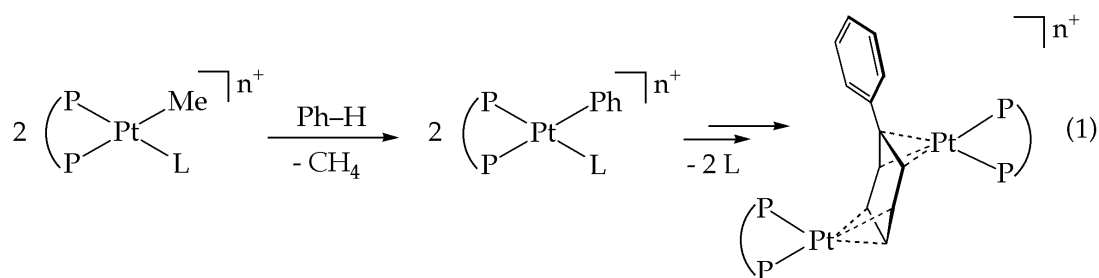


Figure 2. Molecular structure of **5b** with 50% probability ellipsoids. Hydrogen atoms and anions have been omitted. Selected bond distances (Å) and angles (deg) are as follows: Pd1–Pd2 = 2.9706, Pd1–N1 = 1.993(3), Pd1–N2 = 2.000(3), Pd1–O1 = 2.025(3), Pd1–O2 = 2.022(3), Pd2–N3 = 1.987(3), Pd2–N4 = 1.991(3), Pd2–O1 = 2.022(3), Pd2–O2 = 2.025(2), N1–Pd1–N2 = 79.03(13), N1–Pd1–O2 = 177.05(12), N1–Pd1–O1 = 99.60(12), Pd1–O1–Pd2 = 94.44(11), Pd1–O2–Pd2 = 94.45(11).

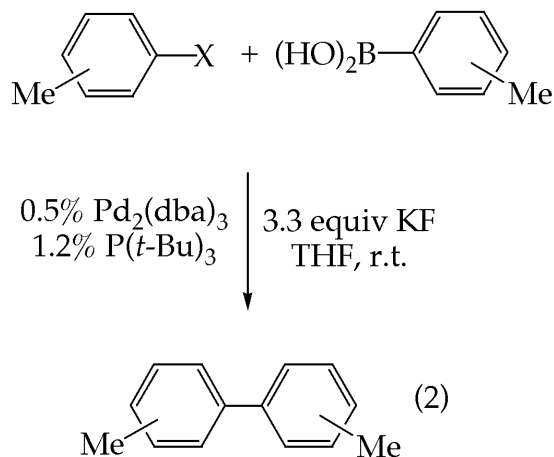


Other potential intermediates on the pathway to arene C–C coupling have been reported for similar Pt(II) systems. Recently, Kubas²⁷ and Peters²⁸ have isolated chelating bis(phosphine)Pt(II) dimer complexes which have a biphenyl unit sandwiched between the metal centers. One phenyl group of the biphenyl unit is bound as an η^3, η^3 -bis-allyl to the two Pt centers, while the other remains aromatic. These unusual dimers were isolated after cationic or neutral Pt(II) phosphine complexes reacted with either benzene or toluene via C–H activation and subsequent C–C bond formation (eq 1). In the Kubas system, the formally

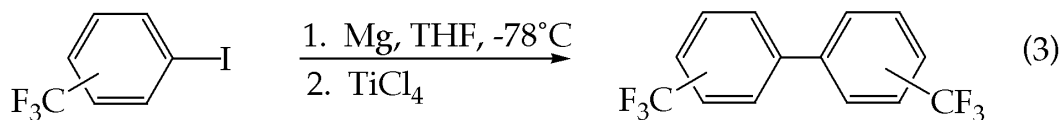


reduced biphenyl unit can be released upon oxidation with HCl to produce Pt(II) chloride dimers and H₂. These results led the authors to suggest that there is no formal redox reaction at Pt, and these dimers may resemble intermediates in Pd-mediated aryl coupling reactions. If such bis-allyl dimers are intermediates in this work, Pd acts as the oxidant for biphenyl release, since we observe Pd(0) deposition and the production of biphenyl (GC-MS) in the absence of oxidant.

Regioselectivity of Arene Coupling. Toluene and α, α, α -trifluorotoluene were investigated as substrates for arene coupling. Both substrates react with **2a** to produce mixtures of isomers as summarized in Scheme 7. Unfortunately, no substrate afforded a single coupled product which would be a synthetically useful feature of this reaction. Bitolyl products which are not commercially



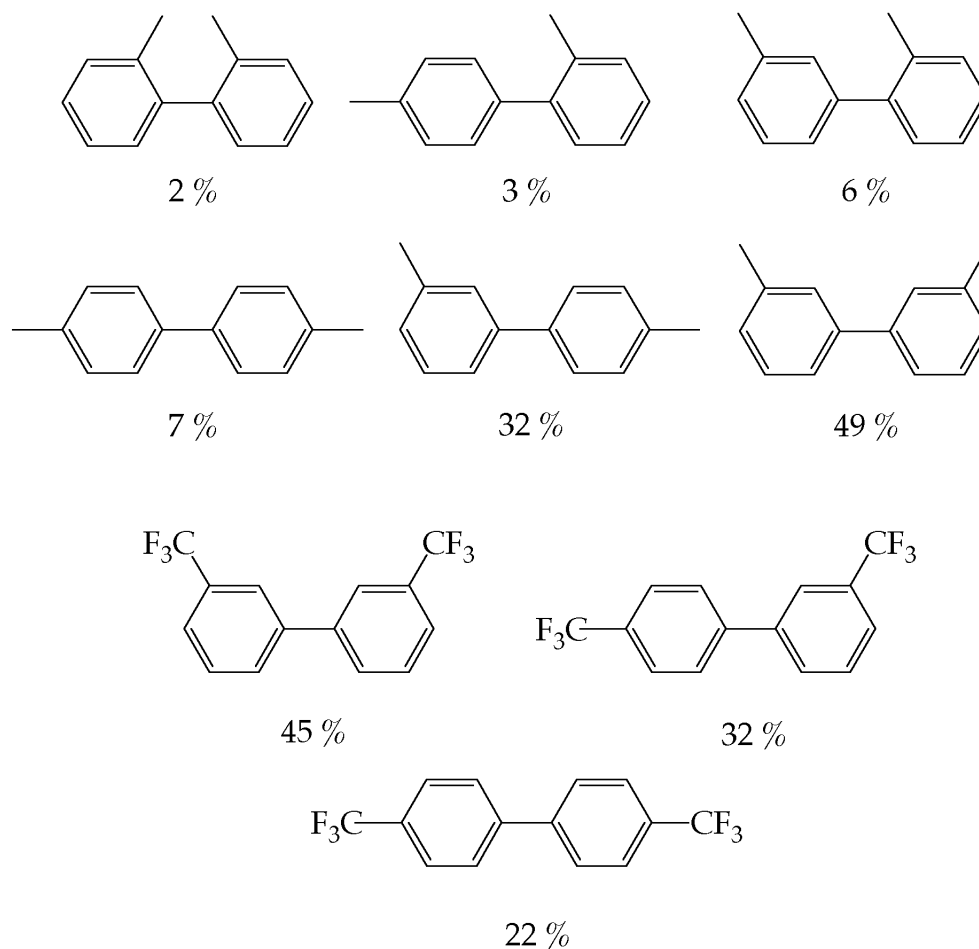
available were synthesized by the Suzuki coupling methodology developed by Fu (eq 2).²⁹ Bis(trifluoromethyl)biphenyl products were synthesized by oxidation of the aryl Grignard reagent by TiCl_4 (eq 3).³⁰ Toluene reacts with **2a**



faster and trifluorotoluene slower than benzene by a factor of two and ten, respectively. The *o:m:p* regioselectivity is approximately 1:10:7 for toluene and 0:4:5 for trifluorotoluene (after statistical correction for the number of C–H bonds).

It is possible that the regioselectivity is determined during the reductive coupling from the postulated diphenyl palladium(II) intermediate, during transmetallation (Scheme 6), or during formation of a binuclear intermediate such as Kubas' $[\text{L}_4\text{Pt}_2(\mu_2\text{-}\eta^3, \eta^3\text{-C}_6\text{H}_5\text{-Ph})]^2+$ (eq 1), if a different mechanism for C–C bond formation is occurring. On the other hand, if one assumes that the regioselectivity is determined by the C–H activation step, one may reconcile the observed regioselectivity as arising from a combination of steric and inductive

Scheme 7



effects of the [CH₃] and [CF₃] substituents. Thus, the palladium center more readily activates the *meta* C–H positions over the *para* C–H position, since it is the more electron-rich site inductively; the *ortho* C–H positions are sterically hindered. Similarly, for trifluorotoluene, the *para* C–H position is more reactive because it is farthest from the strongly electron withdrawing [CF₃] group and thus most electron-rich, whereas the *ortho* C–H positions are most sterically hindered and least electron-rich. In agreement with this proposal that inductive electronic effects operate during the C–H bond activation step of these oxidative

coupling reactions of arenes, the second order rate constant for reaction **2a** with toluene ($0.0124 \text{ M}^{-1} \text{ s}^{-1}$) is significantly greater than that with α,α,α -trifluorotoluene ($0.0005 \text{ M}^{-1} \text{ s}^{-1}$).

Conclusions

Stoichiometric C–H bond activation of benzene by cationic Pd(II)-methyl complexes has been observed under mild conditions. Kinetic studies of the C–H activation step for the palladium complexes reveal that the C–H activation step is rate-determining and inhibited by H_2O . The data suggest that coordinated H_2O must be displaced by solvent (trifluoroethanol) before benzene coordination and subsequent C–H activation. The rates of C–H activation are increased by destabilizing the ground state aquo complex with relatively electron-donating ancillary ligands. Also, the ground state aquo complexes are destabilized for Pd relative to Pt, resulting in faster C–H activation rates. Finally, the barrier to methane loss for Pd is small, and in contrast with the analogous Pt systems no deuterium scrambling occurs. The Pd-phenyl product formed upon C–H activation is unstable, and biphenyl is formed as the final organic product. Pd(0) produced in the reaction is reoxidized to Pd(II) by O_2 (1 atm). Using toluene and α,α,α -trifluorotoluene as substrates results in biaryl formation with enriched *meta* and *para* substitution, respectively. Although a catalytic process remains elusive, the tandem C–H activation/ O_2 activation sequence represents a promising step toward an aerobic oxidation of unactivated arenes to biaryls.

Experimental

General Considerations. All moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques or in a drybox under a nitrogen atmosphere. Argon and dinitrogen gases were purified by passage over columns of MnO on vermiculite and activated molecular sieves. Trifluoroethanol was purchased from either Aldrich or Lancaster, purified and dried over a mixture of $\text{CaSO}_4/\text{NaHCO}_3$ then either vacuum distilled or distilled under argon, and stored over activated molecular sieves under vacuum. Trifluoroethanol- d_3 was purchased from Aldrich or Cambridge Isotopes, stored over activated molecular sieves and a small amount of NaHCO_3 under vacuum, then vacuum distilled. The solvent was syringed into oven-dried screw-cap NMR tubes fitted with septa for kinetic studies. Benzene and benzene- d_6 were vacuum distilled from sodium benzophenone ketyl shortly before kinetic runs, and stored over activated molecular sieves. Diethyl ether, THF, and CH_2Cl_2 were purified over an activated alumina column. 1,4-Bis(3,5-di-*tert*-butylphenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene ($\text{tBu}_2\text{ArDABMe}$),^{10a} 1,4-bis(3,5-di-trifluoromethylphenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene $\{(\text{CF}_3)_2\text{ArDABMe}\}$,^{10b} $[(\text{COD})\text{PdMe}_2]$,¹⁴ $[(\text{pyridazine})\text{PdMe}_2]_n$,¹³ $(\text{tBu}_2\text{ArDABMe})\text{PdMe}_2$ (**3a**),¹¹ $\{(\text{CF}_3)_2\text{ArDABMe}\}\text{PdMe}_2$ (**3b**),¹¹ $[(\text{tBu}_2\text{ArDABMe})\text{Pd}(\text{H}_2\text{O})_2][\text{BF}_4]_2$ (**4a**),²³ $[(\text{tBu}_2\text{ArDABMe})\text{Pd}(\text{OH})_2][\text{BF}_4]_2$ (**5a**),²³ $[(\text{PhCN})_2\text{PdCl}_2]$,³¹ and $(\text{tBu}_2\text{ArDABMe})\text{PdCl}_2$ (**6a**),²² were synthesized according to literature procedures. All other solvents and reagents were used as received without further purification.

NMR spectra were recorded on a Varian CCE 600 (^1H , 599.662 MHz), a Varian INOVA 500 (^1H , 499.852 MHz) or a Varian Mercury 300 (^1H , 299.8 MHz, ^{19}F , 282.081 MHz, ^{13}C , 75.4626 MHz) spectrometer. Elemental analyses were performed at Midwest MicroLab LLC.

Synthesis and Characterization of Methyl Aquo Cations (2a/b). The aquo adducts of **3a/b** were prepared *in situ* by procedures described by Tilset and co-workers.^{10b} Complexes **2a/b** could not be isolated as pure solids, but are stable in TFE solution for > 12 hours. For the kinetic studies, cations **2a/b** are generated *in situ* (vide infra), and the chemical shifts reported below are for solutions in $\text{TFE-}d_3$ in the absence of substrate.

[($t\text{Bu}_2\text{ArDABMe}$)Pd(CH_3)(H_2O)] $[\text{BF}_4]$ (2a**).** ^1H NMR (300 MHz, $\text{TFE-}d_3$): δ = 0.492 (s, 3H, Pd- CH_3), 1.34, 1.36 (s, 18H, C(CH_3) $_3$), 2.12, 2.19 (s, 3H, N=C- CH_3), 6.77, 6.93 (d, $^4J_{\text{H-H}}$ = 1.6 Hz, 2H, *o*-Ar- H), 7.49, 7.55 (t, 1H, *p*-Ar- H).

[(CF_3) $_2\text{ArDABMe}$]Pd(CH_3)(H_2O)] $[\text{BF}_4]$ (2b**).** ^1H NMR (600 MHz, $\text{TFE-}d_3$): δ = 0.511 (s, 3H, Pd- CH_3), 2.20, 2.28 (s, 3H, N=C- CH_3), 7.50, 7.58 (br s, 2H, *o*-Ar- H), 7.94, 7.95 (br s, 1H, *p*-Ar- H).

($t\text{Bu}_2\text{ArDABMe}$)PdMe $_2$ (3a**).** A Schlenk flask was charged with [(pyridazine)PdMe $_2$] $_n$ (0.115 g, 0.530 mmol) and $t\text{Bu}_2\text{ArDABMe}$ (0.256 g, 0.556 mmol). The flask was cooled to 0 °C, and Et $_2\text{O}$ (15 mL) was transferred via cannula onto the solids. A dark red precipitate forms from the suspension of

starting materials almost immediately upon solvent addition. The mixture was stirred for 2 h at 0 °C, warmed to room temperature, and filtered. The crude product was dissolved in CH₂Cl₂ (3-4 mL); the resulting solution was filtered through Celite and concentrated in vacuo, affording **3a** as a red solid (0.199 g, 63%). ¹H NMR (300 MHz, CD₂Cl₂): δ = -0.269 (s, 6H, Pd-CH₃), 1.35 (s, 36H, C(CH₃)₃), 2.06 (s, 6H, N=C-CH₃), 6.73 (d, ⁴J_{H-H} = 1.8 Hz, 4H, *o*-Ar-H), 7.28 (t, ⁴J_{H-H} = 1.8 Hz, 2H, *p*-Ar-H). ¹³C {¹H} NMR (300 MHz, CD₂Cl₂): δ = -5.189 (Pd-CH₃), 20.16 (N=C-CH₃), 31.73 (C(CH₃)₃), 35.50 (C(CH₃)₃), 115.76 (*o*-Ar-C), 119.64 (*p*-Ar-C), 147.34, 151.92 (Ar-C), 169.84 (N=C-CH₃). Anal. Calcd for C₃₄H₅₄N₂Pd (Found): C, 68.38 (68.23/68.10); H, 9.11 (8.90/8.72); N, 4.69 (4.60/4.73).

{(CF₃)₂ArDABMe}PdMe₂ (3b). A Schlenk flask was charged with [(COD)PdMe₂ (0.122 g, 0.500 mmol) and (CF₃)₂ArDABMe (0.257 g, 0.500 mmol). The flask was cooled to 0 °C, and Et₂O (10 mL) was transferred via cannula onto the solids. A bright red precipitate formed from a clear solution, and the resulting red suspension was stirred for 1 h at 0 °C and warmed to room temperature. The red solid was filtered, washed with cold Et₂O and pentane, and dried in vacuo affording **3b** as a red powder (0.185 g, 58%). ¹H NMR (300 MHz, CD₂Cl₂): δ = -0.217 (s, 6H, Pd-CH₃), 2.11 (s, 6H, N=C-CH₃), 7.45 (br s, 4H, *o*-Ar-H), 7.84 (br s, 2H, *p*-Ar-H). ¹³C {¹H} NMR (300 MHz, acetone-*d*₆): δ = -4.72 (Pd-CH₃), 20.59 (N=C-CH₃), 119.50 (m, ³J_{C-F} = 3.8 Hz, *p*-Ar-C), 122.30 (m, ³J_{C-F} = 3.8 Hz, *o*-Ar-C), 124.10 (q, ¹J_{C-F} = 273 Hz, CF₃), 132.15 (q, ²J_{C-F} = 273 Hz, *m*-Ar-C-CF₃), 149.80 (Ar-C), 173.96 (N=C-CH₃). Anal. Calcd for C₂₂H₁₈F₁₂N₂Pd (Found): C, 40.98

(41.18/41.13); H, 2.81 (2.91/2.92); N, 4.34 (4.24/4.27).

[(*t*Bu₂ArDABMe)Pd(H₂O)₂][BF₄]₂ (4a**). (*t*Bu₂ArDABMe)PdCl₂ (**6a**, 0.250 g, 0.392 mmol) was slurried in 1:1 THF/CH₂Cl₂ solution (15 mL). AgBF₄ (0.156 g, 0.803 mmol) was dissolved in dry THF (1 mL) and added to the reaction flask dropwise. An off-white precipitated formed immediately in a yellow solution. After 3 h, the solution was filtered through Celite and the filtrate is removed in vacuo to afford **4a** as a yellow solid (0.225 g, 74%). ¹H NMR (300 MHz, TFE-*d*₃): δ = 1.37 (s, 36H, C(CH₃)₃), 2.27 (s, 6H, N=C-CH₃), 7.23 (d, ⁴J_{H-H} = 1.6 Hz, 4H, *o*-Ar-*H*), 7.77 (t, ⁴J_{H-H} = 1.6 Hz, 2H, *p*-Ar-*H*), O-*H* resonances not found due to exchange with CF₃CD₂OD. ¹³C {¹H} NMR (300 MHz, TFE-*d*₃): δ = 21.34 (N=C-CH₃), 31.99 (C(CH₃)₃), 37.01 (C(CH₃)₃), 118.42 (*o*-Ar-C), 127.17 (*p*-Ar-C), 143.91, 156.55 (Ar-C), 187.66 (N=C-CH₃). Anal. Calcd for C₃₂H₅₂N₂O₂F₈B₂Pd (Found): C, 49.48 (49.18/49.17); H, 6.75 (6.68/6.73); N, 3.61 (3.59/3.55).**

[(CF₃)₂ArDABMe]Pd(H₂O)₂][BF₄]₂ (4b**). ¹H NMR (600 MHz, TFE-*d*₃): δ = 2.19 (s, 6H, N=C-CH₃), 8.12 (br s, 4H, *o*-Ar-*H*), 8.18 (br s, 2H, *p*-Ar-*H*), O-*H* resonances not found due to exchange with CF₃CD₂OD.**

[(*t*Bu₂ArDABMe)Pd(OH)]₂[BF₄]₂ (5a**). This compound was synthesized in the same manner as **4a**, but is present in the solid isolated after a 1 h reaction time. This complex was not isolated cleanly from **4a** and other related products (see Results and Discussion Section), but can be isolated cleanly from the reaction of**

2a with C₆H₆ (under 1 atm O₂). ¹H NMR (300 MHz, TFE-*d*₃): δ = 1.24 (s, 72H, C(CH₃)₃), 2.09 (s, 12H, N=C-CH₃), 6.87 (d, ⁴J_{H-H} = 1.6 Hz, 8H, *o*-Ar-H), 7.52 (t, ⁴J_{H-H} = 1.6 Hz, 4H, *p*-Ar-H), O-H resonances not found due to exchange with CF₃CD₂OD. ¹H NMR (300 MHz, CD₂Cl₂): δ = -3.51 (s, 2H, OH), 1.19 (s, 72H, C(CH₃)₃), 2.06 (s, 12H, N=C-CH₃), 6.93 (d, ⁴J_{H-H} = 1.6 Hz, 8H, *o*-Ar-H), 7.34 (t, ⁴J_{H-H} = 1.6 Hz, 4H, *p*-Ar-H).

[(CF₃)₂ArDABMe]Pd(OH)₂[BF₄]₂ (**5b**). ¹H NMR (600 MHz, TFE-*d*₃): δ = 1.99 (s, 12H, N=C-CH₃), 7.61 (br s, 8H, *o*-Ar-H), 8.01 (br s, 4H, *p*-Ar-H), O-H resonances not found due to exchange with CF₃CD₂OD.

(^tBu₂ArDABMe)PdCl₂ (**6a**). ^tBu₂ArDABMe (0.520 g, 1.13 mmol) was dissolved in CH₂Cl₂ (10 mL) and added to a solution of [(PhCN)₂PdCl₂] (0.433 g, 1.13 mmol) in CH₂Cl₂ (10 mL). An orange precipitate formed immediately. The reaction was stirred for 1-2 h. The precipitate was filtered, washed with CH₃OH and Et₂O, and dried in vacuo to afford **6a** as an orange powder (0.529 g, 73%). Due to the very low solubility of this complex, NMR spectroscopic data could not be collected. Anal. Calcd for C₃₂H₄₈N₂Cl₂Pd (Found): C, 60.24 (60.17/60.21); H, 7.58 (7.41/7.48); N, 4.39 (4.41/4.36).

Measurement of Kinetics for C-H Bond Activation of Benzene. Dry TFE-*d*₃ (~700 μL) was added via syringe to an oven-dried 5 mm thin-walled NMR tube containing approximately 0.0075 mmol of (α-diimine)PdMe₂ (**3a/b**). Aqueous

HBF_4 (48 wt%, 1 μL , 0.00765 mmol) was added, and the mixture was shaken to form a clear, yellow solution. A predetermined amount of D_2O was then added to the tube. A screw-cap fitted with a septum was then affixed to the tube. The tube was frozen at $-78\text{ }^\circ\text{C}$, evacuated with a needle then backfilled with 1 atm O_2 (ultrahigh purity). After thawing, the mixture was analyzed by ^1H NMR to confirm clean conversion to aquo adducts **2a/b**. A predetermined amount of substrate was then added to the NMR tube, and after allowing the mixture to equilibrate to the preset temperature in the probe, disappearance of the starting material was monitored. (the same observed rate constants are obtained by monitoring the appearance of biphenyl). Probe temperatures were calibrated with a methanol standard and were maintained at $\pm 0.2\text{ }^\circ\text{C}$ throughout data acquisition. The observed rate constants are calculated by curve fitting to the expression $I_t = I_f + (I_0 - I_f) \times \exp(-k_{\text{obs}} \times t)$, where I_t is the integration of peak relative to the residual solvent peak, CF_3CHDOD . The water concentration is calculated as follows: $[\text{H}_2\text{O}] = [(1\text{ }\mu\text{L} \times 1.4\text{ g}\cdot\text{mL}^{-1} \times 52\% + y\text{ }\mu\text{L} \times 1\text{ g}\cdot\text{mL}^{-1}) / 18\text{ g}\cdot\text{mol}^{-1} / V\text{ (mL)}]$, where $1.4\text{ g}\cdot\text{mL}^{-1}$ is the density of the aqueous HBF_4 solution, 52% is the wt% of water in this aqueous solution, y is the amount of extra water added and $1\text{ g}\cdot\text{mL}^{-1}$ is the density of water. The volume of the reaction mixture is determined as $V\text{ (mL)} = 0.01384H - 0.006754$, where H is the solvent height in millimeters. Addition of a small amount of benzene (e.g., 15 μL) to $\text{TFE-}d_3$ shifts the resonances for the diimine backbone methyls by as much as 0.3 ppm, and can significantly affect shimming.

Appendix: Summary of C–H bond activation kinetic data and rate law

derivation for Scheme 4. Details of the structure determination for complex **5b**.³²

Summary of Benzene C–H Bond Activation Kinetic Data. In all cases, [Pd] is kept at 0.01 – 0.011 M; the observed rate constants have an uncertainty between 5 - 10% of the reported values and are the average of duplicate or triplicate experiments.

Table 1. Water Concentration Dependence.

Pd Complex	Substrate	T (°C)	[substrate](M)	[H ₂ O] (M)	<i>k</i> _{obs} (x 10 ⁴)
2a	C ₆ H ₆	25	0.218	0.056	32.8
2a	C ₆ H ₆	25	0.218	0.133	29.1
2a	C ₆ H ₆	25	0.218	0.249	22.9
2a	C ₆ H ₆	25	0.218	0.442	13.1
2a	C ₆ D ₆	25	0.220	0.442	3.2
2a	C ₆ H ₆	25	0.218	0.828	10.2
2a	C ₆ H ₆	25	0.218	1.21	7.3
2a	C ₆ H ₆	25	0.218	2.37	4.6
2a	C ₆ H ₆	25	0.218	4.68	2.7
2b	C ₆ H ₆	25	0.222	0.215	14.7
2b	C ₆ H ₆	25	0.233	0.451	7.4
2b	C ₆ H ₆	25	0.220	0.747	5.3

Table 2. Ionic Strength Experiments.

Pt Complex	Substrate	T (°C)	Substrate (M)	[H ₂ O] (M)	NMe ₄ BF ₄ (M)	<i>k</i> _{obs} (× 10 ⁴)
2a	C ₆ H ₆	25	0.218	0.442	--	13.1
2a	C ₆ H ₆	25	0.218	0.442	0.10	13.0
2a	C ₆ H ₆	25	0.218	0.828	--	10.2
2a	C ₆ H ₆	25	0.218	0.828	0.10	9.6

Table 3. Temperature Dependence.

Pt Complex	Substrate	T (°C)	[substrate](M)	[H ₂ O] (M)	<i>k</i> _{obs} (× 10 ⁴)
2a	C ₆ H ₆	1.1	0.218	0.442	0.43
2a	C ₆ H ₆	25	0.218	0.442	13.1
2a	C ₆ H ₆	41	0.218	0.442	53.9

Table 4. [C₆H₆] Dependence.

Pt Complex	Substrate	T (°C)	[substrate](M)	[H ₂ O] (M)	k_{obs} (× 10 ⁴)
2a	C ₆ H ₆	25	0.109	0.442	7.1
2a	C ₆ H ₆	25	0.218	0.442	13.1
2a	C ₆ H ₆	25	0.435	0.442	24.7
2b	C ₆ H ₆	25	0.111	0.451	2.5
2b	C ₆ H ₆	25	0.233	0.451	7.4
2b	C ₆ H ₆	25	0.435	0.451	13.3

Table 5. Substrate Dependence.

Pt Complex	Substrate	T (°C)	[substrate](M)	[H ₂ O] (M)	k_{obs} (× 10 ⁴)
2a	C ₆ H ₆	25	0.218	0.442	13.1
2a	C ₆ H ₅ CH ₃	25	0.217	0.442	26.8
2a	C ₆ H ₅ CF ₃	25	0.220	0.449	1.1

Rate Law Derivation

$$\text{Define } [\text{Pd}]_{\text{T}} = [\text{Ai}] + [\text{Aii}] \quad K_{eq} = \frac{[\text{Aii}][\text{TFE}]}{[\text{Ai}][\text{H}_2\text{O}]}$$

$$\text{Then } [\text{Pd}]_{\text{T}} = [\text{Ai}] \left[1 + \frac{K_{eq}[\text{H}_2\text{O}]}{[\text{TFE}]} \right]; \quad [\text{Ai}] = \frac{[\text{Pd}]_{\text{T}}}{1 + \frac{K_{eq}[\text{H}_2\text{O}]}{[\text{TFE}]}}$$

$$- \frac{d[\text{Pd}]_{\text{T}}}{dt} = k_2[\text{B}]$$

Applying the steady-state approximation on $[\text{B}]$

$$\frac{d[\text{B}]}{dt} = k_1[\text{Ai}][\text{C}_6\text{H}_6] - k_{-1}[\text{B}][\text{TFE}] - k_2[\text{B}] \approx 0$$

$$[\text{B}] = \frac{k_1[\text{Ai}][\text{C}_6\text{H}_6]}{k_{-1}[\text{TFE}] + k_2}$$

$$- \frac{d[\text{Pd}]_{\text{T}}}{dt} = k_2 \cdot \frac{k_1[\text{C}_6\text{H}_6]}{k_{-1}[\text{TFE}] + k_2} \cdot \frac{[\text{Pd}]_{\text{T}}}{1 + \frac{K_{eq}[\text{H}_2\text{O}]}{[\text{TFE}]}}$$

$$= k_{\text{obs}}[\text{Pd}]_{\text{T}} = \frac{k_2}{k_{-1}[\text{TFE}] + k_2} \cdot \frac{k_1[\text{TFE}][\text{C}_6\text{H}_6][\text{Pd}]_{\text{T}}}{[\text{TFE}] + K_{eq}[\text{H}_2\text{O}]}$$

Expression for $1/k_{obs}$ vs. $[H_2O]/[C_6H_6]$ plot:

$$\begin{aligned}\frac{1}{k_{obs}} &= \frac{k_{-1}[TFE] + k_2}{k_2} \cdot \frac{[TFE] + K_{eq}[H_2O]}{k_1[TFE][C_6H_6]} \\ &= \underbrace{\frac{k_{-1}[TFE] + k_2}{k_2} \cdot \frac{K_{eq}[H_2O]}{k_1[TFE][C_6H_6]}}_{\text{slope}} + \underbrace{\frac{k_{-1}[TFE] + k_2}{k_2} \cdot \frac{[TFE]}{k_1[TFE][C_6H_6]}}_{\text{intercept}} \\ \text{slope} &= \frac{k_{-1}[TFE] + k_2}{k_2} \cdot \frac{K_{eq}}{k_1[TFE]} \quad \text{intercept} = \frac{k_{-1}[TFE] + k_2}{k_2} \cdot \frac{1}{k_1[C_6H_6]}\end{aligned}$$

$$\frac{\text{intercept}}{\text{slope}} = \frac{1}{k_1[C_6H_6]} \cdot \frac{k_1[TFE]}{K_{eq}} = \frac{[TFE]}{K_{eq}[C_6H_6]}$$

K_{eq} calculated indirectly by this method

Crystallography: Crystal data, intensity collection, and refinement details are presented in Table 6 for compound **5b**.

Data Collection and Processing: Data for compound **5b** was collected on a Bruker SMART 1000 area detector running SMART.³³ The diffractometer was equipped with a Crystal Logic CL24 low temperature device and all datasets were collected at low temperature. The diffractometer used graphite-monochromated MoK α radiation with $\lambda = 0.71073$ Å.

The crystal was mounted on a glass fiber with Paratone-N oil. Data were collected as ω -scans at seven values of φ . The detector was 5 cm (nominal) distant at a θ of -28° . The data were processed with SAINT.³¹

Table 6. X-ray Experimental Data.

Compound	5b
formula	C ₄₀ H ₂₄ B ₂ F ₃₂ N ₄ O ₂ Pd ₂
formula weight	1435.05
crystal system	monoclinic
space group	P2 ₁
a, Å	15.7429(7)
b, Å	10.3772(5)
c, Å	15.8713(7)
α , °	90
β , °	108.1380(10)

γ , °	90
volume, Å ³	2464.01(19)
Z	2
ρ_{calc} , g/cm ³	1.934
μ , mm ⁻¹	0.89
F ₀₀₀	1396
crystal shape	plate
crystal color	yellow
crystal size, mm	0.26 x 0.14 x 0.09
T, K	98
type of diffractometer	SMART 1000 ccd
θ range, °	1.59, 28.44
h,k,l limits	-20, 20; -13, 13; -21, 20
data measured	50764
unique data	11439
data, $F_o > 4\sigma(F_o)$	11439
parameters / restraints	743 / 1
$R1^a, wR2^b$; all data	0.0403, 0.0686
$R1^a, wR2^b$; $F_o > 4\sigma(F_o)$	0.0352, 0.0679
GOF ^c on F ²	1.98
$\Delta\rho_{\text{max,min}}$, e·Å ⁻³	1.004, -0.683

All data were collected with graphite monochromated MoK α radiation ($\lambda=0.71073$ Å).

$$^a R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$^b wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

$$^c GOF = S = \{ \Sigma [w(F_o^2 - F_c^2)^2] / (n-p) \}^{1/2}$$

Structure analysis and refinement: SHELXTL v5.1 was used to solve, via direct methods, and to refine all structures using full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically.

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- (16) The reported $\Delta S^\ddagger = 5$ e.u. for **1a**^{10a} was miscalculated. The correct value is $\Delta S^\ddagger = -5$ e.u.

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- (17) Plots of $1/k_{\text{obs}}$ vs $[\text{C}_6\text{D}_6]/[\text{D}_2\text{O}]$ extrapolated to zero $[\text{D}_2\text{O}]$ indicate that the palladium complex **2a** reacts with benzene faster than the platinum complex **1a** by a factor of approximately two.
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