The Dynamics of the β-Agostic Isopropyl Complex (ArN=C(R)−C(R)=NAr)Pd(CH(CH$_2$-μ-H)(CH$_3$))$^+$BAr$_4'^-$ (Ar = 2,6-C$_6$H$_3$(*i*-Pr)$_2$): Evidence for In-Place Rotation versus Dissociation of the Agostic Methyl Group

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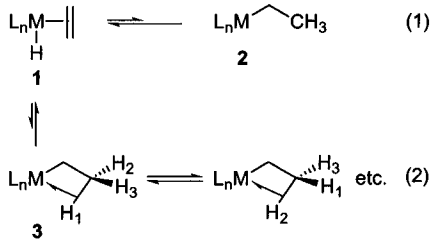
Variable-temperature ^{1}H and ^{13}C NMR spectroscopy has been used to study the dynamics of the β-agostic isopropyl complex (ArN=C(R)−C(R)=NAr)Pd(CH(CH$_2$-μ-H)(CH$_3$))$^+$BAr$_4'^-$ (Ar = 2,6-C$_6$H$_3$(*i*-Pr)$_2$). ^{1}H and ^{13}C line shape analysis suggests two independent processes occur: interchange of the agostic and nonagostic methyl groups and exchange of hydrogens within the agostic methyl group, which is best regarded as in-place methyl group rotation. Barriers for both of these processes are similar, with $\Delta G^{\ddagger}$ ca. 9 kcal/mol. The methyl groups undergo interchange without inversion at the Pd(II) center.

Introduction

The insertion of an olefin into a transition-metal hydride bond is a common step in a number of organometallic reactions, and thus, there have been several studies aimed at understanding this fundamental transformation.[1−11] The exchange of a metal hydride with hydrogens in an olefinic ligand has been detected by both H/D exchange reactions and dynamic NMR experiments. Examining the simplest case, an ethylene hydride complex, **1**, the exchange can be envisioned to occur through a classical mechanism involving a coordinatively unsaturated metal ethyl complex, **2**, (eq 1) or via a β-agostic intermediate, **3**, which undergoes facile "in-place" methyl rotation where the CH$_3$ group remains bound to the metal in the transition state for exchange (eq 2).



The in-place mechanism (eq 2) was first proposed by Green and Wong to account for the dynamic behavior of the bis-ethylene hydride complex Mo(*cis*-Ph$_2$PCH=CHPPh$_2$)$_2$(C$_2$H$_4$)$_2$H$^+$.[5,6] Green, Bercaw, et al. studied the dynamics of *exo*-Cp$_2$Nb(CH$_2$=CHCH$_3$)H and found that the niobium hydride exchanges with the methylene hydrogens ca. twice as fast as it exchanges with the methyl hydrogens.[7,8] This observation was interpreted in terms of an agostic isopropyl intermediate, **4**, in which in-place methyl rotation (k_1) is slightly faster than exchange of the methyl groups via rotation of the Nb−C$_\alpha$ bond (k_2). It is important to note that the dynamic results are also consistent with a classical mechanism involving nonagostic 16-electron alkyl intermediates.[1,7] However, circumstantial evidence was cited to favor in-place rotation in an agostic intermediate, **4**.

(1) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134−3146 and references therein.
(2) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Application of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; Chapters 10, 11, 13, 14, pp 383−391.
(3) (a) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1−124. (b) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395−408.
(4) (a) Brookhart, M.; Lincoln, D. M.; Volpe, A. F.; Schmidt, G. F. *Organometallics* **1989**, *8*, 1212−1218. (b) Brookhart, M.; Hauptman, E.; Lincoln, D. M. *J. Am. Chem. Soc.* **1992**, *114*, 10394−10401.
(5) (a) Green, M. L. H.; Wong, L.-L. *J. Chem. Soc., Chem. Commun.* **1988**, 677−679. (b) Derome, A. E.; Green, M. L. H.; Wong, L.-L. *New J. Chem.* **1989**, *10*, 747−753.
(6) For an earlier investigation of the dynamics of this system, see: (a) Byrne, J. W.; Kress, J. R. M.; Osborn, J.; Ricard, L.; Weiss, R. E. *J. Chem. Soc., Chem. Commun.* **1977**, 662−663. (b) Byrne, J. W.; Blaser, H. U.; Osborn, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3871−3873.
(7) Green, M. L. H.; Sella, A.; Wong, L.-L. *Organometallics* **1992**, *11*, 2650−2659.
(8) Bercaw, J. E.; Burger, B. J.; Green, M. L. H.; Santarsiero, B. D.; Sella, A.; Trimmer, M.; Wong, L.-L. *J. Chem. Soc., Chem. Commun.* **1989**, 734−736.
(9) McNally, J. P.; Cooper, N. J. *Organometallics* **1988**, *7*, 1704−1715.
(10) Casey, C. P.; Yi, C. S. *Organometallics* **1991**, *10*, 33−35.
(11) For investigations of similar nickel subgroup agostic alkyl complexes of the type (R$_2$P(CH$_2$)$_n$PR$_2$)M(CH$_2$C(R)H-μ-H)$^+$, see: (a) Spencer, J. L.; Mhinzi, G. S. *J. Chem. Soc., Dalton Trans.* **1995**, *23*, 3819−3824. (b) Carr, N.; Mole, L.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Dalton Trans.* **1992**, *18*, 2653−2662. (c) Mole, L.; Spencer, J. L.; Carr, N.; Orpen, A. G. *Organometallics* **1991**, *10*, 49−52. (d) Conroy-Lewis, F. M.; Mole, L.; Redhouse, A. D.; Litster, S. A.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1991**, *22*, 1601−1603.

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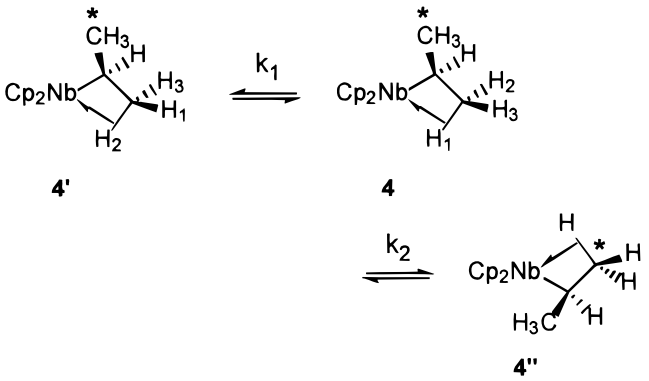
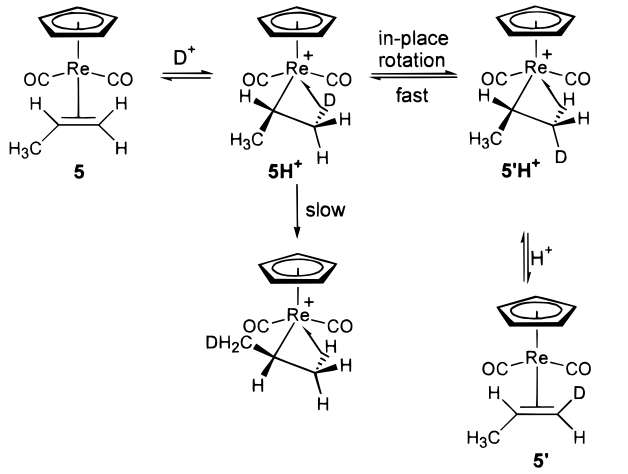
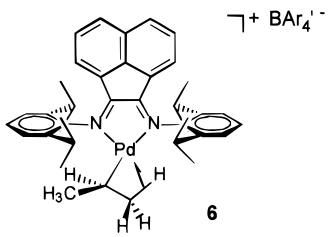


Similar to the above study, in-place methyl rotation in an agostic intermediate was invoked by Cooper to account for the fact that the tungsten hydride exchanges ca. 20 times faster with the methylene hydrogens than with the methyl hydrogens in $Cp_2W(CH_2{=}CHCH_3)H^+$.[9] The most dramatic difference in exchange rates was reported by Casey, who showed that the acid-catalyzed H/D exchange of the methylene hydrogens in **5** occurs several thousand times faster than deuterium incorporation into the methyl group.[10] Again, a β-agostic



isopropyl intermediate, $\mathbf{5H}^+$, was proposed in which in-place rotation and deprotonation occurs with a much lower barrier than methyl group exchange.

In the above cases, the agostic isopropyl complex was a *presumed* intermediate, not directly observable. Thus, the barrier to agostic methyl rotation and equilibration of the two methyl groups in the agostic species could not be directly measured. We report here the synthesis of a stable β-agostic isopropyl complex, **6**, which permits these barriers to be determined and the isomerization pathways to be quantitatively delineated for this system.[11]



Results and Discussion

Synthesis of β-Agostic Isopropyl Complex 6. The β-agostic isopropyl complex, **6,** can be formed in situ or isolated as a pure salt from the cationic methyl complex **7**. In a typical in situ experiment, 1 equiv of ethylene is introduced via gastight syringe to an NMR tube containing a solution of **7** in $CDCl_2F$ at −78 °C. Warming to −60 °C results in complete displacement of ether by ethylene. Migratory insertion of the methyl ethylene complex occurs at temperatures above −30 °C to give complex **6**, presumably via initial formation of the *n*-propyl agostic complex followed by isomerization (Scheme 1).[12] The ether-free salt of **6** can be prepared by purging ethylene through a CH_2Cl_2 solution of **7** at −78 °C, leading to displacement of ether by ethylene. Excess ethylene is removed by purging argon through the cooled solution for several minutes and then evacuating the cooled flask and back-filling with argon several times. Migratory insertion takes place upon stirring the solution at 0 °C for several minutes, and removal of the solvent under vacuum yields **6** as an orange-rust powder free of ether.

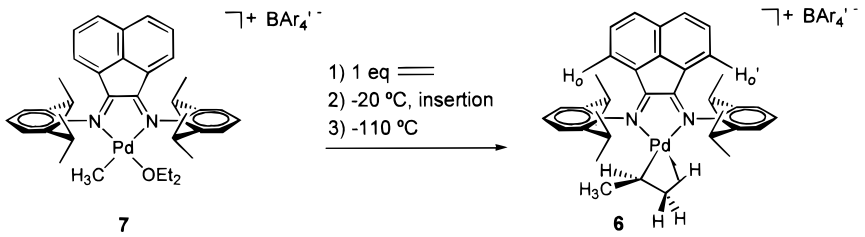
Static Spectrum of 6. The static ^{1}H NMR spectrum of **6**, recorded at −115 °C in $CDCl_2F$, exhibits a broad triplet at −8.00 ppm corresponding to the agostic hydrogen. This assignment is based on observed geminal H−H coupling constants of 17 Hz and a ^{13}C−H coupling constant of 65 Hz, all of which are characteristic of this type of hydrogen.[3,13] The nonagostic methyl group of the isopropyl substituent resonates at 0.08 ppm and appears as a broad doublet. Multiple signals arising from the diimine *ortho*-isopropyl methyl groups in the region from 0.75 to 1.30 ppm obscure the methylene hydrogens of the agostic methyl group. Similarly, the methine hydrogen of the Pd−isopropyl group overlaps with signals from the four methine hydrogens of the diimine ligand around 3 ppm. A ^{1}H NMR COSY experiment performed at −110 °C allowed these shifts to be determined. The methylene hydrogens, although chemically inequivalent, exhibit coincident cross-peaks at 1.17 ppm from coupling to the agostic hydrogen. The methine shift was located at 2.88 ppm from the cross-peak arising from coupling to the nonagostic methyl hydrogens. Significantly, the static structure lacks a plane of symmetry, and two well-resolved doublets are observed at 6.67 and 6.81 ppm arising from each of the two ortho hydrogens of the acenaphthyl ligand backbone (H_o and H_o', see Scheme 1).

General Description of the Dynamic NMR Behavior of 6. The dynamic NMR data are consistent with exchange occurring between the agostic hydrogen and both the methylene hydrogens on the agostic methyl group and the three hydrogens on the nonagostic methyl group (Scheme 2). This is exhibited in the high-temperature ^{1}H NMR spectrum (above ca. −10 °C, fast exchange region) by the presence of a broad signal centered at −0.84 ppm, which integrates for ca. six

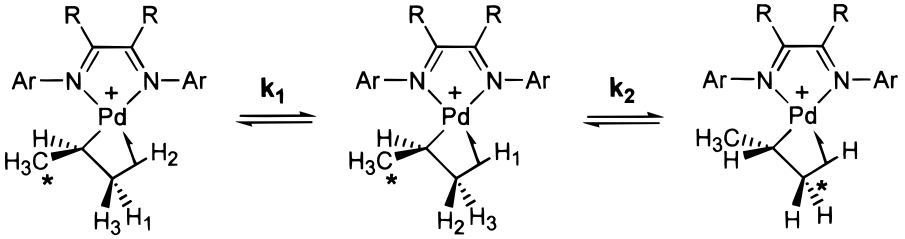
(12) Details of this isomerization will be discussed in a future publication. Theoretical studies predict the β-agostic isopropyl complex to be more stable than the *n*-propyl agostic complex, see: (a) Musaev, D. G.; Svensson, M.; Morokuma, K.; Strömberg, S.; Zetterberg, K.; Seigbahn, P. E. M. *Organometallics* **1997**, *16*, 1933−1945. (b) Musaev, D. G.; Froese, R. D. J.; Svensson, M.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 363−374. (c) Deng, L. Q.; Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 1094−1100. (d) Deng, L. Q.; Woo, T. K.; Cavallo, L.; Margl, P. M.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 6177−6186.

(13) ^{13}C−H coupling constant observed using ^{13}C-labeled material (**6***, see below).

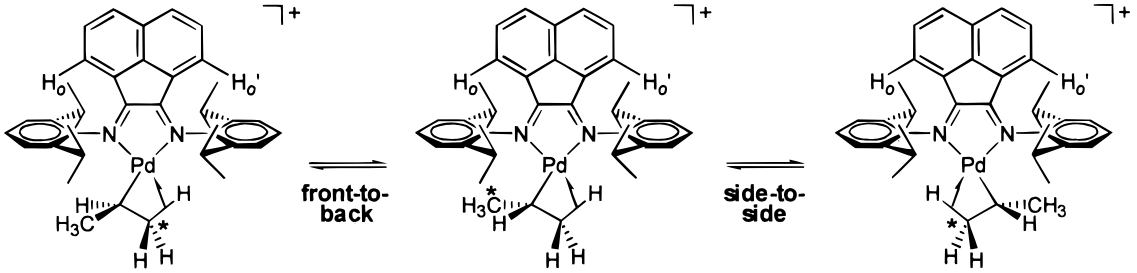
Scheme 1



Scheme 2



Scheme 3



hydrogens.[14] Furthermore, the initial broadening of both the $H_{agostic}$ resonance (−8.00 ppm) and the methyl resonance (0.08 ppm) suggests that exchange of the agostic hydrogen with the methylene hydrogens occurs at a rate roughly comparable to exchange with the methyl hydrogens.

Under fast-exchange conditions (above ca. −10 °C), the ^{1}H NMR spectrum of **6** also exhibits two sharp, distinct doublets at 0.95 and 1.04 ppm and two sharp doublets which overlap at 1.32 ppm in $CDCl_2F$ (these doublets are not coincident when a spectrum is acquired in CD_2Cl_2). These signals are attributed to pairwise averaging of the eight inequivalent methyl groups of the ligand *ortho*-isopropyl groups. This averaging can occur in one of two ways during exchange of the agostic hydrogen with the methyl hydrogens. The exchange must occur in either a side-to-side or front-to-back fashion relative to the square plane of the complex (Scheme 3). During fast exchange, the signals of the ortho hydrogens, H_o and H_o', of the acenaphthyl backbone *do not* broaden and coalesce, indicating that the observed signal averaging of the *ortho*-isopropyl groups must be due to front-to-back exchange rather than side-to-side exchange with concomitant inversion of Pd(II).[15]

A ^{13}C-labeled β-agostic isopropyl complex, **6***, was generated from precursor **7*** bearing a ^{13}C-labeled methyl group. The label is incorporated into one of the methyls of the isopropyl alkyl, and accordingly, the static proton-coupled ^{13}C NMR spectrum of **6*** exhibits a quartet at 19.91 ppm (J_{CH} = 128 Hz) corresponding to the labeled nonagostic methyl carbon and a triplet of doublets at 19.54 ppm (J_{CH} = 152 and 65 Hz) corresponding to the labeled agostic carbon.

Quantitative Rate Measurements. Simulations of the dynamic ^{1}H and ^{13}C NMR spectra were carried out[16] in order to determine the individual rates of methyl rotation (k_1) and methyl exchange (k_2) (see Scheme 2). Exchange of the labeled carbon in **6*** directly corresponds to methyl exchange and allows k_2 to be determined independently from k_1. The static ^{1}H-decoupled ^{13}C spectrum of **6*** at −115 °C was used to represent the slow-exchange limit for line shape analysis of the two-nuclei exchanging system. A series of spectra were acquired in the temperature range from 180.6 to 195.2 K (ca. −93 to −78 °C), and the line shape of the region containing the two ^{13}C-labeled resonances was simulated for each spectrum. This procedure yielded rate constants which were used to calculate values of $\Delta G_2^{\ddagger}$ for the methyl exchange process over the temperature range indicated (Table 1).

(14) Integration of this broad band is not sufficiently accurate to rule out a 7H band due to averaging of all seven hydrogens of the isopropyl group.

(15) A referee has suggested that the front-to-back averaging process which leads to a pairwise averaging of the isopropyl groups could be due to formation of a propene hydride complex, rotation of propene, and reinsertion. This process results in moving the nonagostic methyl group from front-to-back but does *not* result in averaging of the nonagostic and agostic methyl groups as observed by ^{13}C NMR spectroscopy. Since, qualitatively, analysis of the isopropyl ^{1}H line shapes suggests these processes occur at similar rates, we prefer the simplest explanation which ascribes the isopropyl group dynamics to the front-to-back process shown in Scheme 3. However, we cannot rule out some contribution to the isopropyl averaging process through an olefin hydride intermediate.

(16) Budzelaar, P. H. M. *gNMR for Macintosh, Version 3.6.5*; Cherwell Scientific Publishing Limited: Oxford, 1992−1996.

Table 1. Rates of Exchange of Methyl Groups in 6*

temp (K)	k_2 (s^{-1})	$\Delta G_2^{\ddagger}$ (kcal/mol)
180.6	11	9.6
183.0	14	9.6
185.5	21	9.6
187.9	27	9.6
190.3	36	9.6
192.8	56	9.6
195.2	79	9.6

Table 2. Rate Constants for Dynamic Processes in 6

temp (K)	$[k_2]^a$ (s^{-1})	$k_1{}^b$ (s^{-1})	$\Delta G_1^{\ddagger}$ (kcal/mol)	k_{exch} (s^{-1})
175.0	3.9	14	9.1	18
177.9	6.4	20	9.2	26
180.4	9.3	31	9.1	40
182.8	14	51	9.1	65
185.3	19	74	9.1	93
186.9	24	89	9.1	113
188.9	33	94	9.2	127
191.2	45	136	9.2	181

[a] Calculated from $\Delta G_2^{\ddagger} = 9.6$ kcal/mol. [b] $k_1 = k_{exch} - [k_2]$.

Analysis of the dynamic ^{1}H spectra is significantly more complicated than the above simple two-site ^{13}C exchange system. In the ^{1}H system, seven nuclei are directly involved, six of which exchange with one another. The methylene hydrogens are obscured, so their line shapes cannot be experimentally observed. The ^{1}H system was simplified by simulating only the *initial* broadening of the agostic signal at −8.00 ppm. This was satisfactory for temperatures up to ca. 191 K, but at higher temperatures, the signal became too broad for an accurate rate determination. Analysis in this fashion gives only the rate of a hydrogen *leaving* the agostic site and does not distinguish between k_1 and k_2, even when both methyl rotation and methyl exchange processes are included in the simulation analysis. In other words, for a given temperature, k_1 and k_2 can be varied without altering the calculated line shape of the $H_{agostic}$ resonance as long as the sum of the two rates remains equal, which corresponds to the rate of a hydrogen leaving the agostic site. We denote the rate constant for this total rate of exchange as k_{exch}. However, since k_2 was determined independently using **6***, k_1 could be determined by assigning a calculated value of k_2 for each temperature. The temperature range for both sets of spectra are approximately the same, so values of k_2 were calculated based on an average Gibb's free energy of activation of 9.6 kcal/mol (Table 2).

The fact that k_1 is ca. 3−4 times greater than k_2 shows that the rate of exchange of hydrogens within the agostic methyl group is somewhat greater than the rate of exchange of the agostic methyl group with the free methyl group. An interpretation of these differences is best advanced by considering the two most likely mechanisms of methyl group interchange. Consider a classical mechanism (Mechanism I, Scheme 4) where a true 14-electron isopropyl intermediate, **6i**, is formed, in which both methyl groups and all six hydrogens become equivalent. Upon collapse back to **6**, one-half the time the ^{13}C-labeled methyl group will exchange sites (path **a**) but $^5/_6$ of the time the agostic hydrogen, H_1, will exchange sites (paths **a** and **b**(**b**′)). Thus, exclusive operation of this mechanism to explain the dynamic behavior of **6** would predict $k_{exch} = {}^5/_6 k_i$ (k_i is the rate of formation of intermediate **6i** from **6**) and $k_2 = {}^3/_6 k_i$, which corresponds to $(k_1 + k_2)/k_2$ ca. 1.67, or k_1/k_2 ca. 0.67. While this mechanism does predict k_{exch} to be greater than k_2, the expected ratio of 1.67 is not in accord with the observed ratio of 4−5. Thus, presuming this to be the mechanism for methyl group exchange, there still must be a second, independent process for exchange of the agostic methyl hydrogens, best formulated as an in-place methyl rotation, which is 2.3−3.3 times faster than methyl group interchange (i.e. $k_{in-place\ rot} = k_1 - {}^2/_6 k_i = k_1 - 0.67k_2$).

A second mechanism can be considered in which methyl group exchange occurs via a concerted pathway (Mechanism II, Scheme 5). This mechanism involves a transition state in which two C−H bonds, one on each methyl group, are simultaneously coordinated to the Pd(II) center as shown by **6**‡. This type of process has been termed an "isopropyl rock" by Green, Bercaw, et al.[7,8] In this case, every trip over the barrier results in site exchange for a ^{13}C-labeled methyl group as well as movement of the agostic hydrogen to a new site. The exclusive operation of this mechanism would require $k_2 = k_{exch}$ and, therefore, $k_1 = 0$. As in the above case, this mechanism alone cannot account for the data. Were this the mechanism for methyl group exchange, the measured k_1 value would represent the rate constant for an independent in-place methyl rotation process.

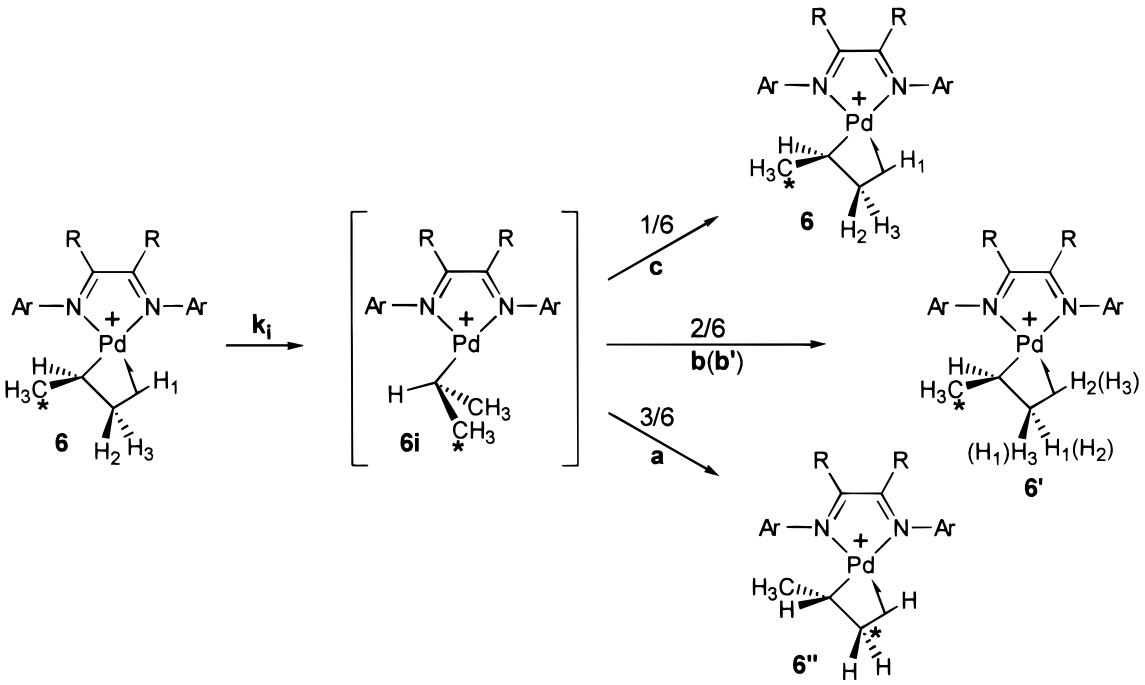
Conclusions

The above analysis establishes that neither Mechanism I nor Mechanism II for interchange of the agostic and nonagostic methyl groups can account for k_1/k_2 values as large as 3−4. This implies that there is a second, independent process for interchange of hydrogens on the agostic methyl group. The most reasonable proposal for this process is an in-place methyl rotation,[5] which has a barrier ca. 0.3−0.4 kcal/mol lower than methyl group exchange.

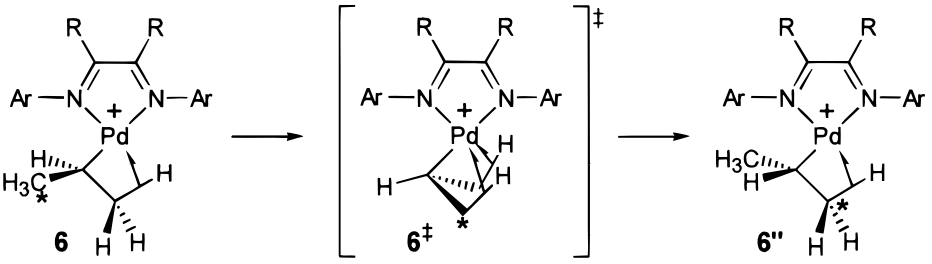
The rate difference between $H_{agostic}$ exchange with the methylene hydrogens and the hydrogens of the nonagostic methyl group (k_1 vs k_2) are small and comparable to those observed in the *exo*-Cp$_2$Nb(CH$_2$=CHCH$_3$)H system.[7,8] As noted in the Introduction, data concerning the Cp$_2$W(CH$_2$=CHCH$_3$)H$^+$ [9] and Cp(CO)$_2$Re(CH$_2$=CHCH$_3$)H$^+$ [10] systems establish much larger rate differences between in-place methyl rotation and methyl group interchange in the (presumed) agostic isopropyl intermediates. The structural and electronic features which account for these differences are not yet clear.

NMR analysis of β-agostic [(*t*-Bu)$_2$P(CH$_2$)$_3$P(*t*-Bu)$_2$]Pt(CH$_2$CH$_2$-μ-H)$^+$ led Spencer to propose a substantial barrier ($\Delta G^{\ddagger} > 12$ kcal/mol) to inversion at Pt(II) in this T-shaped alkyl cation.[11c] High inversion barriers in such species have been questioned.[7] The results reported here in which the *ortho*-acenaphthyl ^{1}H signals remain distinct at temperatures as high as 0 °C is in accord with Spencer's work and establishes a significant barrier to inversion in the cationic Pd(II) isopropyl complex **6**. From lack of line broadening at 0 °C (<2 Hz), a lower limit for the inversion barrier of ca. 15 kcal/mol can be estimated.

Scheme 4. Mechanism I



Scheme 5. Mechanism II



Experimental Section

General Considerations. All manipulations of compounds were performed using standard high-vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. Solid organometallic compounds were transferred in an argon-filled Vacuum Atmospheres drybox. NMR spectra were recorded with a Bruker AMX-300 spectrometer unless otherwise noted. NMR probe temperatures were measured using an external anhydrous methanol sample.[17] Simulations of the dynamic ^1H and ^{13}C NMR spectra were performed using the software package *gNMR for Macintosh*.[16] Elemental analyses were obtained from Atlantic Microlab Inc. of Norcross, GA.

Materials. All solvents used for synthesis were deoxygenated and dried via passage over a column of activated alumina.[18] Dichlorofluoromethane-*d* ($CDCl_2F$) was prepared according to the literature.[19] Dichlorofluoromethane-*d* and methylene chloride-d_2 were dried over CaH_2, vacuum transferred, degassed by repeated freeze−pump−thaw cycles, and stored over 4 Å molecular sieves. Additionally, $CDCl_2F$ was stored at 0 °C. Chloroform-*d* was stored over 4 Å molecular sieves. Polymer-grade ethylene was purchased from Matheson and used without further purification. $NaBAr_4'$ was prepared as reported in the literature.[20] The α-diimine ligand, ArN=C(An)−C(An)=NAr (Ar = 2,6-$C_6H_3(CHMe_2)_2$; An,An = acenaphthyl) was synthesized based on literature procedures.[21] This ligand[22] and its $PdMe_2$ complex[23] have been previously characterized.

(ArN=C(An)−C(An)=NAr)Pd(CH_3)$_2$. A Schlenk flask was charged with 0.2585 g (1.194 mmol) of [(pyridazine)Pd(CH_3)$_2$]$_n$[24] and cooled to −40 °C. ArN=C(An)−C(An)=NAr (0.6002 g, 1.199 mmol) was added as a slurry in 50 mL of diethyl ether, and the resulting suspension was stirred as the flask was warmed to room temperature. Stirring was continued for an additional 1 h at room temperature, and the ether solution was filtered into another Schlenk flask. The remaining

(17) Temperatures below −95 °C were extrapolated.
(18) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.
(19) Siegel, J. S.; Anet, F. A. L. *J. Org. Chem.* **1988**, *53*, 2629−2630.
(20) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920−3922. (Caution: preparation of the Grignard reagent from $(CF_3)_2C_6H_3Br$ can result in explosions. Extreme precautions are required.)
(21) (a) tom Dieck, H.; Svoboda, M.; Grieser, T. *Z. Naturforsch* **1981**, *36b*, 823−832. (b) Kliegman, J. M.; Barnes, R. K. *J. Org. Chem.* **1970**, *35*, 3140−3143. (c) van Asselt, R. Ph.D. Thesis, Universiteit van Amsterdam, 1993.
(22) van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L.; Benedix, R. *Recl. Trav. Chim. Pays-Bas* **1994**, *133*, 88−98.
(23) van Asselt, R.; Rijnberg, E.; Elsevier, C. J. *Organometallics* **1994**, *13*, 706−720.
(24) Byers, P. K.; Canty, A. J. *Organometallics* **1990**, *9*, 210−220.

product was extracted with CH_2Cl_2, the solvents were removed under vacuum, and the residue was washed with pentane until the washes were colorless (5 × 15 mL). The solid was dried overnight in vacuo to give 0.3660 g of a green powder (48% yield). Anal. Calcd for $C_{38}H_{46}N_2Pd$: C, 71.63; H, 7.28; N, 4.40. Found: C, 71.60; H, 7.24; N, 4.48.

(ArN=C(An)−C(An)=NAr)Pd(^{13}CH$_3$)$_2$. A Schlenk flask was charged with 0.3015 g (0.9997 mmol) of $(SMe_2)_2PdCl_2$[24] and 0.0620 g (1.10 mmol) of Mg(^{13}CH$_3$)$_2$[25] and cooled to −78 °C, and 50 mL of diethyl ether was added via syringe. The suspension was stirred as the flask was allowed to slowly warm to −40 °C and resulted in nearly complete consumption of the orange $(SMe_2)_2PdCl_2$ accompanying slight decomposition to Pd(0) black. To this solution of $(SMe_2)_2Pd(^{13}CH_3)_2$ was added 0.5010 g (1.001 mmol) of ArN=C(An)−C(An)=NAr as a slurry in 15 mL of diethyl ether. The reaction was warmed to room temperature and allowed to stir for 1 h. The ether was removed under vacuum, and the product was extracted with CH_2Cl_2. The ^{1}H NMR spectrum of the residual solid after removal of CH_2Cl_2 indicated a 55:45 mixture of dimethyl complex to methyl chloride complex. Enough Mg(^{13}CH$_3$)$_2$ was added to this residue to effect complete conversion to the desired dimethyl complex. Addition of ether at 0 °C to the resulting mixture of solids was followed by stirring at room temperature overnight. Removal of ether, extraction with CH_2Cl_2, evaporation of the CH_2Cl_2 under vacuum, washing with pentane (2 × 20 mL), and drying in vacuo gave 0.1028 g of product (16% yield). ^{1}H NMR ($CDCl_3$, 250 MHz): same as above except δ 0.05 (d, 6H, J_{CH} = 128 Hz, Pd*Me*$_2$).

[(ArN=C(An)−C(An)=NAr)Pd(CH$_3$)(OEt$_2$)]-BAr$_4'$ (7). A Schlenk flask was charged with 0.1948 g (0.3057 mmol) of (ArN=C(An)-C(An)=NAr)Pd$(CH_3)_2$ and 0.3090 g (0.3052 mmol) of H$(OEt_2)_2BAr_4'$. The flask was cooled to −78 °C, and 10 mL of ether was added via syringe. The stirring suspension was warmed to 0 °C in an ice bath, resulting in formation of a dark red solution. The solution was filtered, and the ether was removed under vacuum to give a dark orange glass, which was scraped into an orange powder and dried further in vacuo, yielding 0.4249 g of product (89% yield). ^{1}H NMR (CD_2Cl_2, −30 °C, 300 MHz): δ 8.08 (d, 1H, J = 8.4 Hz, An H$_p$), 8.04 (d, 1H, J = 8.4 Hz, An H$_{p'}$), 7.72 (s, 8H, BAr$_4'$ H$_o$), 7.51 (s, 4H, BAr$_4'$ H$_p$), 7.36−7.34 (m, 8H, An H$_m$, H$_{m'}$, H$_{aryl}$), 6.64 (d, 1H, J = 7.3 Hz, An H$_o$), 6.37 (d, 1H, J = 7.3 Hz, An H$_{o'}$), 3.36 (q, 4H, J = 7.0 Hz, O(C*H*$_2$CH$_3$)$_2$), 3.16 (2 septets, 2H each, J = 6.8 Hz, C*H*Me$_2$, C′*H*Me$_2$), 1.35 (d, 6H, J = 6.9 Hz, CH*Me*Me′), 1.32 (d, 6H, J = 6.9 Hz, CHMe*Me*′), 1.26 (t, 6H, J = 6.9 Hz, O(CH$_2$C*H*$_3$)$_2$), 0.86 (2d, 6H each, J = 6.5 Hz, C′H*MeMe*′), 0.67 (s, 3H, Pd*Me*). ^{13}C NMR (CD_2Cl_2, −30 °C, 300 MHz): δ 174.5 and 168.6 (N=*C*−*C*′=N), 161.6 (q, J_{CB} = 49.8 Hz, BAr$_4'$ C$_{ipso}$), 140.9 and 139.4 (Ar, Ar′ C$_{ipso}$), 138.2 and 137.1 (Ar, Ar′ C$_o$), 134.1 (BAr$_4'$ C$_o$), 128.0 (q, J_{CF} = 31.7 Hz, BAr$_4'$ C$_m$), 122.7 (q, J_{CF} = 274 Hz, BAr′$_4$ CF$_3$), 117.0 (BAr$_4'$ C$_p$), 144.7, 132.5, 131.8, 130.5, 129.2, 128.7, 128.2, 128.0, 127.8, 125.4, 125.2, 124.9, 124.6, and 124.4 (An 4 quaternary C; An C$_o$, C$_o'$, C$_p$, C$_p'$, C$_m$, C$_m'$; Ar, Ar′ C$_m$, C$_p$), 71.7 (O(*C*H$_2$-CH$_3$)$_2$), 28.7 and 28.4 (*C*HMe$_2$, *C*′HMe$_2$), 23.86, 23.56, 22.59, and 22.45 (CH*MeMe*′, C′H*MeMe*′), 14.7 (O(CH$_2$-*C*H$_3$)$_2$), 9.6 (Pd*Me*). Anal. Calcd for $C_{73}H_{65}N_2BF_{24}$OPd: C, 56.22; H, 4.20; N, 1.80. Found: C, 56.46; H, 4.14; N, 1.82.

[(ArN=C(An)−C(An)=NAr)Pd(^{13}CH$_3$)(OEt$_2$)]-BAr$_4'$ (7*). Following the above procedure (0.0502 g (0.0782 mmol) of (ArN=C(An)−C(An)=NAr)Pd(^{13}CH$_3$)$_2$; 0.0790 g (0.0780 mmol) of H$(OEt_2)_2BAr_4'$), **7*** was isolated as an orange powder in 90% yield (0.1215 g). ^{1}H NMR (CD_2Cl_2, −30 °C, 300 MHz): same as above except δ 0.67 (d, 3H, J_{CH} = 140 Hz, Pd*Me*).

[(ArN=C(An)−C(An)=NAr)Pd(CH(CH$_2$-μ-H)-(CH$_3$))]BAr$_4'$ (6). A Schlenk flask was charged with 0.2553 g (0.1637 mmol) of the cationic methyl complex, **7**. The flask was cooled to −78 °C, and 10 mL of CH_2Cl_2 was added via syringe. The flask was carefully warmed until the solid was completely dissolved. At −78 °C, the solution was purged with ethylene for ca. 5 min. The flask was then purged with argon for 20 min, evacuated and back-filled with argon several times, and warmed to 0 °C in an ice bath. The reaction was stirred at 0 °C for 5 min to allow migratory insertion to occur, and the solution was rapidly filtered into another flask cooled to 0 °C. Removal of CH_2Cl_2 and displaced ether under vacuum yielded 0.2312 g of an orange-rust solid (93% yield). ^{1}H NMR ($CDCl_2F$, −115 °C, 300 MHz): δ 7.96 (d, 1H, J = 8.4 Hz, An H$_p$), 7.93 (d, 1H, J = 8.9 Hz, An H$_{p'}$), 7.71 (s, 8H, BAr$_4'$ H$_o$), 7.44 (s, 4H, BAr$_4'$ H$_p$), 7.45−7.7.20 (m, 8H, An H$_m$, H$_{m'}$, H$_{aryl}$), 6.81 (d, 1H, J = 7.2 Hz, An H$_o$), 6.67 (d, 1H, J = 7.1 Hz, An H$_{o'}$), 3.28 and 3.13 (m, 1H each, C*H*Me$_2$, C′*H*Me$_2$), 2.88 (m, 1H, Pd(C*H*(CH$_2$-μ-H)(Me))), 2.88−2.79 (2m, 1H each, C″*H*-Me$_2$, C‴*H*Me$_2$), 1.28−1.22 and 0.96−0.89 (br, 3H each, CH*MeMe*′, C′H*MeMe*′, C″H*MeMe*′, C‴H*MeMe*′), 1.17 (obscured, 2H, Pd(CH(*CH$_2$*-μ-H)(Me))), 0.08 (br, 3H, Pd-(CH(CH$_2$-μ-H)(*Me*))), −8.00 (t, 1H, J = 16.8 Hz, Pd(CH-(CH$_2$-μ-*H*)(Me))). ^{13}C NMR ($CDCl_2F$, −115 °C, 300 MHz): δ 173.7 and 170.3 (N=*C*−*C*′=N), 162.2 (q, J_{CB} = 49.2 Hz, BAr$_4'$ C$_{ipso}$), 135.1 (BAr$_4'$ C$_o$), 129.2 (q, J_{CF} = 31.7 Hz, BAr$_4'$ C$_m$), 124.9 (q, J_{CF} = 271 Hz, BAr′$_4$ CF$_3$), 118.0 (BAr$_4'$ C$_p$) 146.1, 144.1, 142.1, 138.9, 137.9, 137.8, 137.3, 133.7, 133.2, 131.7, 129.7, 129.6, 129.4, 128.9, 128.6, 126.2, 125.8, 125.5, 125.4, 125.2, 125.0, and 124.5 (An 4 quaternary C, C$_o$, C$_o'$, C$_m$, C$_m'$, C$_p$, C$_p'$; Ar, Ar′ C$_{ipso}$, C$_{ipso}'$, C$_o$, C$_o'$, C$_o''$, C$_o'''$, C$_m$, C$_m'$, C$_m''$, C$_m'''$, C$_p$, C$_p'$), 30.2, 29.56, 29.54, 29.1, 23.83, 23.82, 23.79, 23.5, 23.2, 22.8, 22.6, and 22.3 (*C*HMe$_2$, *C*′HMe$_2$, *C*″HMe$_2$, *C*‴HMe$_2$, CH*MeMe*′, C′H*MeMe*′, C″H*MeMe*′, C‴H*MeMe*′), 25.9 (Pd(*C*H(CH$_2$-μ-H)(Me))), 19.9 (Pd(CH(CH$_2$-μ-H)(*C*H$_3$))), 19.5 (Pd(CH(*C*H$_2$-μ-H)(Me))). Anal. Calcd for $C_{71}H_{59}N_2BF_{24}Pd$: C, 56.35; H, 3.93; N, 1.85. Found: C, 55.75; H, 4.08; N, 1.84.

General Procedure for Variable-Temperature NMR Experiments. In a drybox under an argon atmosphere, an NMR tube was charged with ca. 15 mg of **7** (or **7***) (1 × 10^{-5} mol). The tube was capped with a rubber septum and removed from the drybox. After securing the septum with Teflon tape and Parafilm, the tube was cooled to −78 °C. $CDCl_2F$ was added to the NMR tube via a 22 gauge cannula (~600−800 μL), and the septum was sealed with silicon grease and re-wrapped with Parafilm. The tube was shaken and

(25) Prepared by Lynda K. Johnson according to literature procedure: Andersen, R. A.; Wilkinson, G. *Inorg. Synth.* **1979**, *19*, 262−265.

warmed slightly to facilitate dissolution of the complex. After acquiring a spectrum at −80 °C, 0.95 equiv of ethylene was added via gastight syringe to the solution cooled to −78 °C and the NMR tube was briefly shaken to completely dissolve the olefin. The tube was then transferred to the cooled NMR probe for acquisition of spectra. Migratory insertion of the methyl ethylene complex was followed at 0 °C and occurred within about 10 min. Formation of the desired β-agostic complex was confirmed by acquiring a spectrum at ca. −115 °C that exhibited a broad triplet at −8.00 ppm characteristic of the agostic hydrogen of **6** (or a 1:1 pattern of a triplet and a doublet of triplets for **6***).

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Supporting Information Available: Details of dynamic NMR spectroscopic analysis and simulation (7 pages). Ordering information is given on any current masthead page.

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