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Measurement of the Barrier to *β*-Hydride Elimination in a *β*-Agostic Palladium−Ethyl Complex: A Model for the Energetics of Chain-Walking in (α-Diimine)PdR$^+$ Olefin Polymerization Catalysts

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The cationic Pd(II) ethyl complex $[[(2,6\text{-}(^iPr)_2C_6H_3)N{=}C(An)C(An){=}N(2,6\text{-}(^iPr)_2C_6H_3)]Pd(CH_2CH_2\text{-}\mu\text{-}H)]BAr'_4$ (**8**), which exhibits a *β*-agostic interaction, has been synthesized via protonation of the corresponding diethyl complex with $H(OiPr_2)_2BAr'_4$ ($Ar' = 3,5\text{-}(CF_3)_2C_6H_3$). The fluxional behavior of this ethyl cation has been studied quantitatively using ^1H and ^{13}C NMR spectroscopy. Two dynamic processes have been observed: (1) *β*-H elimination and reinsertion with opposite regiochemistry and (2) rotation about the C−C bond of the ethyl group. *β*-H elimination is the lower energy process, with $\Delta G^{\ddagger} = 7.1$ kcal/mol at −108 °C. Eyring analysis of the ^{13}C NMR data indicates $\Delta H^{\ddagger} = 6.1 \pm 0.2$ kcal/mol and $\Delta S^{\ddagger} = -5.2 \pm 0.9$ eu. Rotation of the agostic methyl group occurs with $\Delta G^{\ddagger}$ ca. 8.4 kcal/mol at −108 °C. These data provide insight into the energetics of chain walking, which is responsible for the unusual polyolefin microstructures produced using (α-diimine)PdR$^+$ catalysts.

Introduction

There has been considerable recent interest in the use of late transition metal complexes for olefin polymerization.[1−5] In 1995, we described a unique family of catalysts based on cationic Ni(II) and Pd(II) species bearing bulky aryl-substituted α-diimine ligands which are capable of polymerizing ethylene, α-olefins, and internal and cyclic olefins to high molecular weight polymers (Figure 1).[6]

The polyethylenes produced by these systems are distinguished from those made with early metal d^0 catalysts[7] by their structure, having branches along the main polymer backbone and possessing branches on these branches (a "hyperbranched" structure).[8−10]

Previous studies of the Pd and Ni catalysts have resulted in the mechanism for propagation and isomerization shown in Scheme 1.[11,12]

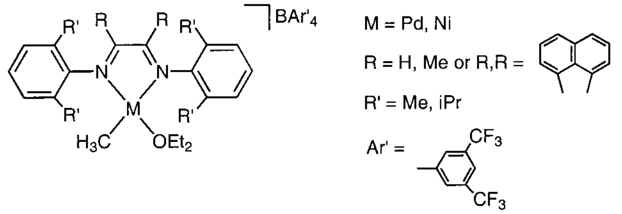

Figure 1. Cationic Ni and Pd α-diimine catalysts for olefin polymerization.

The catalyst resting state, observed by ^1H NMR spectroscopy, is an alkyl olefin complex (**1**). A key feature of this propagation mechanism which results in formation of branched polymer is rapid migration of the metal center along the chain in the *β*-agostic alkyl complexes (e.g., **2**, **4**) prior to insertion. Bulky, axially oriented substituents on the imine aryl rings retard chain transfer and chain termination reactions. This chain-walking process[13] occurs via a series of *β*-hydride elimination/readdition reactions (a common feature of d^8 metal alkyls[14]) coupled with rotation around the Pd−C$_\alpha$ bond, which interchanges *β*-agostic hydrogens on geminal C$_\beta$ carbons in secondary alkyl complexes.

We have previously reported the synthesis, characterization, and dynamic behavior of the isopropyl agostic cation $[[(2,6\text{-}(^iPr)_2C_6H_3)N{=}C(An)C(An){=}N(2,6\text{-}(^iPr)_2C_6H_3)]Pd(CH(CH_3)CH_2\text{-}\mu\text{-}H)]BAr'_4$ (**6**) ($Ar' = 3,5\text{-}(CF_3)_2C_6H_3$), shown in eq 1, which can be isolated from the insertion

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[13] For an early example of chain-walking in an α-olefin oligomerization process, see: (a) Möhring, V. M.; Fink, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1001−1003 (b) Schubbe, R.; Angermund, K.; Fink, G.; Goddard, R. *Makromol. Chem. Phys.* **1995**, *196*, 467−468.

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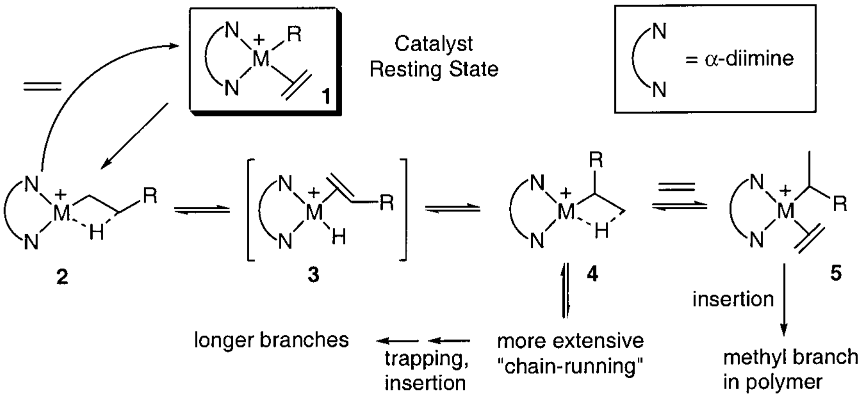
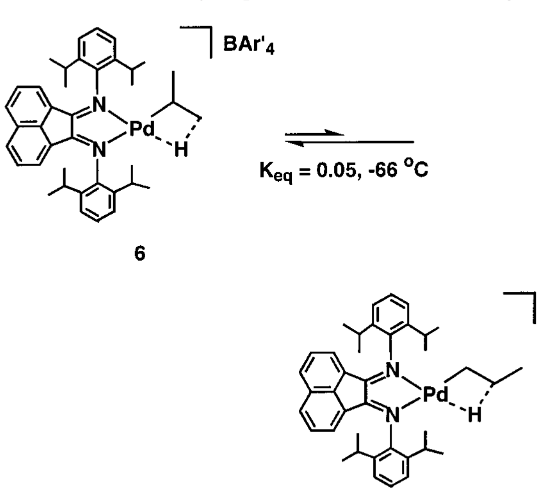
Scheme 1. Proposed Mechanism for Polymerization of Ethylene



of a single equivalent of ethylene into the Pd−methyl bond of the catalyst precursor shown in Figure 1.[15]



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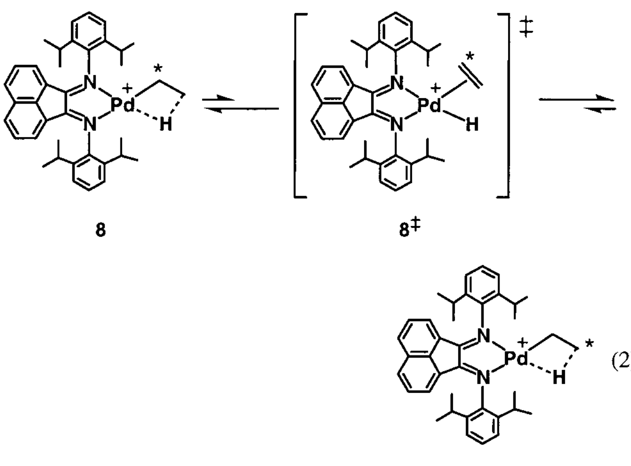
(1)

In the static ^{1}H NMR spectrum (−115 °C), the agostic proton resonance appears as a triplet ($^2J_{HH} = 17$ Hz) at −8.00 ppm. Above −10 °C, a broad resonance is observed at −0.84 ppm, accounting for the six methyl protons. In solution, the isopropyl agostic cation **6** exists in equilibrium with the *n*-propyl agostic isomer **7**, with the isopropyl species being favored by 20:1. Measurement of the barrier to interconversion between the two species, which presumably occurs through a propene hydride complex, is complicated not only by the lopsided equilibrium but also by bond rotations in the isopropyl cation: C_α−$C_{\beta(\mathrm{agostic})}$ bond rotation occurs with a barrier of 9.2 kcal/mol, while Pd−C_α bond rotation has a barrier of 9.6 kcal/mol. Because of these complications, we were only able to estimate an upper limit for the barrier to β-hydride elimination of 10.7 kcal/mol.[12] Significantly, no inversion at the Pd center is observed between −115 and 0 °C for these species.

The complications described above that prevent accurate measurement of the agostic alkyl isomerization process involving the olefin hydride can be circumvented by the synthesis of an agostic ethyl cation; β-H elimination in this species is a degenerate process occurring via a symmetrical ethylene hydride complex, and thus isotopic labeling could be used to quantify the energetics involved (eq 2).



8

Several cationic agostic ethyl species have been descibed in the literature for group 9 and 10 transition metals. Spencer[16,17] and Brookhart[18,19] have reported cations of the formula [(C_5R_5)Co(CH_2CH_2-μ-H)L]BF_4 (R = H, Me; L = C_2H_4, PMe_3, $P(OMe)_3$, P(o-tolyl)$_3$, PMe_2-Ph) (Figure 2).

These species undergo three dynamic processes: C_α−C_β bond rotation, β-H elimination, and inversion at the chiral Co center. The cation [(C_5Me_5)Co(CH_2CH_2-μ-H)(PMe_3)]BF_4 is the only species in the series for which the barrier to inversion at Co can be measured (13.4 kcal/mol).[20] The barrier to C−C bond rotation is lower, at 10.9 kcal/mol, while β-H elimination requires >15.6 kcal/mol. The other cations in the series have similar barriers, with C−C bond rotation always being a lower energy process than β-H elimination. Significantly, these species are active catalysts for the production of linear polyethylene, with the catalyst resting state being the agostic alkyl complex.[21]

Spencer has also published a series of agostic ethyl complexes of Ni, Pd, and Pt having chelating bisphos-

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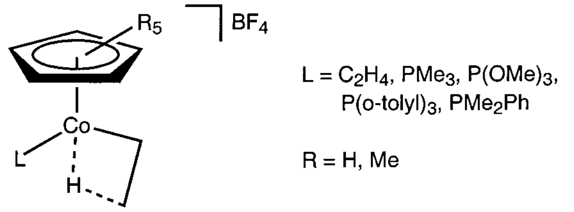


Figure 2. Cobalt(III) agostic ethyl cations reported by Spencer and Brookhart.

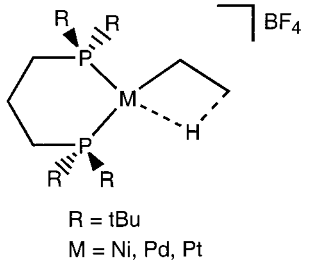


Figure 3. Bisphosphine group 10 ethyl agostic cations reported by Spencer.

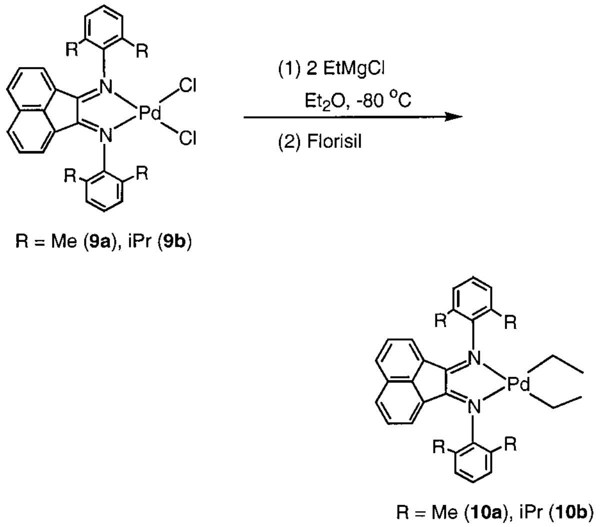
phine ligands; these species are synthesized by protonation of the corresponding M(II) diethyl species or M(0) ethylene complexes.[22–25] The complexes $[(^t\text{Bu}_2\text{P}(\text{CH}_2)_3\text{P}^t\text{Bu}_2)\text{M}(\text{CH}_2\text{CH}_2\text{-}\mu\text{-H})]\text{BF}_4$ (M = Ni, Pd, Pt) (Figure 3) have been characterized by ^{1}H and ^{13}C NMR spectroscopy; in the Pt case, the agostic proton resonates at −2.6 ppm (−110 °C) with a $^1J_{\text{CH}}$ of 60 Hz.[22,23]

All five hydrogens and both carbons in the Pt-ethyl group are equivalent above −30 °C; an overall upper limit for β-H elimination and C−C bond rotation processes of 8 ± 1.5 kcal/mol can be estimated from coalescence data at −77 °C. The Ni and Pd cations are reported, although the static ^{1}H NMR spectra are not resolved.

We report here the synthesis and characterization of the ethyl agostic cation $[[(2,6\text{-}(^i\text{Pr})_2\text{C}_6\text{H}_3)\text{N}{=}\text{C(An)C(An)}{=}\text{N}(2,6\text{-}(^i\text{Pr})_2\text{C}_6\text{H}_3)]\text{Pd}(\text{CH}_2\text{CH}_2\text{-}\mu\text{-H})]\text{BAr}'_4$ (**8**), which serves as a model for intermediates involved in the cationic (α-diimine)Pd(II)-catalyzed polymerization of ethylene. Observation of the dynamic processes exhibited by this complex yields the barrier to β-H elimination, one of the elementary steps involved in the migration of the Pd center along the polymer chain during the polymerization process.

Results and Discussion

Synthesis of Precursor Diethyl Complexes 10a and 10b. The α-diimine Pd diethyl complexes can be synthesized in a straightforward manner from the analogous dichloride complexes, which were known in the literature but had not been fully characterized.[26,27] Treatment of the dichloride complexes **9a**,**b** with 2 equiv of EtMgCl at −78 °C in diethyl ether affords the diethyl complexes (**10a**,**b**) in moderate yields (eq 3).



(3)

Removal of the magnesium salts is accomplished by filtration of the cold reaction mixture through Florisil, which also serves to remove any decomposition products from solution. The diethyl complexes are surprisingly stable for late transition metal alkyl complexes possessing β-hydrogens. They survive in the solid state for days at ambient temperature and give satisfactory combustion analyses. They are moderately stable (ca. 1 day) in solution in the absence of oxygen, but eventually decompose to ethylene, ethane, and unidentified palladium species.

The ^{1}H NMR spectrum of the diethyl complexes is straightforward; the presence of only one type of ligand methyl group (in the case of **10a**) or one kind of isopropyl methine hydrogen (in the case of **10b**) is indicative of a symmetric dialkyl complex. The methyl and methylene groups of the ethyl ligands appear as a multiplet at 0.92 ppm; the Pd center shields the methylene protons, causing them to be nearly coincident with the methyl groups. The observed C−H coupling constants for the ethyl group are 127 Hz (CH_2) and 129 Hz (CH_3), in the normal range for sp^3 carbon centers.[28]

Formation of the β-Agostic Ethyl Complex. When the diethyl complexes **10a** and **10b** are treated with $\text{H(OEt}_2)_2\text{BAr}'_4$ (Ar′ = 3,5-$(\text{CF}_3)_2\text{C}_6\text{H}_3$)[29] in CD_2Cl_2 at low temperature (−78 °C), ethane is formed, and the solution turns from deep brown to a light, clear orange color, indicative of protonolysis to form a cationic Pd(II) ethyl species. ^{1}H NMR spectra of the products at −78 °C show that they are cationic ethyl ether complexes (**11a**,**b**) rather than ethyl agostic species (eq 4).

Treatment of complexes **10a** and **10b** with $\text{H(OiPr}_2)_2\text{BAr}'_4$ at −78 °C in CD_2Cl_2 appears to give similar results; initially, both solutions become clear orange and a gas is evolved. However, species in solutions produced from **10a** begin to decompose immediately, precipitating Pd(0) and giving products that are unidentifiable by ^{1}H NMR spectroscopy. Protonation of **10b** with $\text{H(OiPr}_2)_2$-

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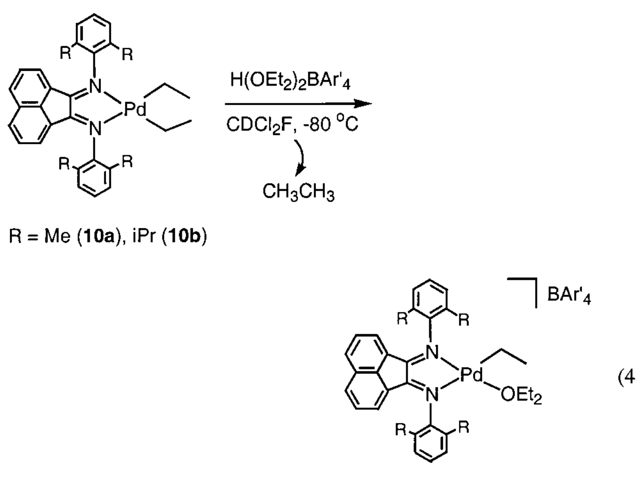
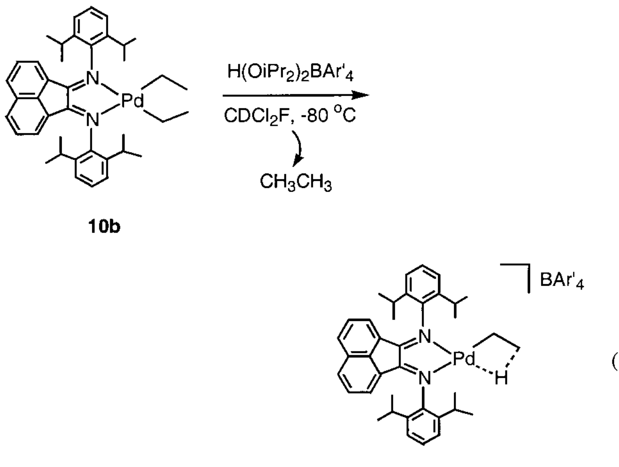


(4)

R = Me (**10a**), iPr (**10b**)

R = Me (**11a**), iPr (**11b**)

BAr'_4 gives the desired product, $[[(2,6\text{-}(^{i}Pr)_2C_6H_3)N{=}C(An)C(An){=}N(2,6\text{-}(^{i}Pr)_2C_6H_3)]Pd(CH_2CH_2\text{-}\mu\text{-}H)]BAr'_4$ (**8**) (eq 5).



(5)

10b

8

Static Spectrum of the Ethyl Agostic Complex 8. At −130 °C in $CDCl_2F$, the agostic hydrogen appears as a broad (ca. 60 Hz at half-height) triplet ($^2J_{HH} = 16$ Hz) at −8.9 ppm, due to coupling to the geminal protons on the β-carbon. The $^1J_{CH}$ for the agostic proton, indicative of donation of the C−H σ bond density to the metal center, was determined to be 67 Hz,[30] which is a clear indication of an agostic Pd- -H- -C three-center, two-electron interaction.[31] The geminal protons on C_β appear as a broad peak at 1.4 ppm, while the methylene protons on the α-carbon appear at 2.2 ppm. Because the complex possesses a plane of symmetry (corresponding to the square plane of the complex), only two methine resonances are observed for the diisopropyl ligand, at 3.24 and 3.14 ppm.

Dynamic Processes Observed in 8. Two distinct dynamic processes occur that serve to equilibrate the five ethyl protons of **8**. The first, β-hydride elimination and reinsertion with opposite regiochemistry (Scheme 2(i)), interchanges the two sets of methylene protons, keeping the agostic proton (H_a) distinct. The second, C−C bond rotation (Scheme 2(ii)), interchanges the agostic proton with the two geminal protons on the β-carbon while the α-methylene protons remain unaffected.

Observation of the ^1H NMR spectroscopic behavior of the ethyl moiety as the probe temperature is raised from −130 to 0 °C allows relative rate measurements for these processes. At −100 °C, the methylene resonance originally at 2.2 ppm has coalesced with the other methylene resonance (originally at 1.4 ppm) to a broad peak at 1.8 ppm; the resonance for the agostic proton remains distinct. This observation indicates that β-hydride elimination and reinsertion is the faster of the two fluxional processes. Using coalescence methods, a first-order rate constant $k = 1448\ s^{-1}$ is obtained for β-H elimination at $T_c = -108$ °C ($\Delta G^{\ddagger} = 7.1 \pm 0.4$ kcal/mol). From the line broadening of the agostic resonance at this temperature (−108 °C, $\Delta\omega = 12.5$ Hz), the C−C bond rotation barrier is estimated to be ca. 8.4 kcal/mol ($k = 40\ s^{-1}$). In the fast exchange limit at 0 °C, one broad resonance is observed at −0.4 ppm, accounting for all five ethyl hydrogens. This is consistent with the superposition of both dynamic processes illustrated in Scheme 2.

Both of the dynamic processes of the β-agostic ethyl cation result in ^1H site exchange and are therefore visible in the variable-temperature ^1H NMR spectra. However, the two processes can more easily be distinguished using ^{13}C NMR; β-hydride elimination and reinsertion with opposite regiochemistry equilibrate C_α and C_β, while C−C bond rotation results in no site exchange for C_α and C_β. Therefore, ^{13}C-labeling was used to quantify β-hydride elimination and reinsertion within a range of temperatures and without the complication of C−C bond rotation.

Synthesis of ^{13}C-Labeled β-Agostic Ethyl Complex 8-^{13}C. The ^{13}C-labeled diethyl complex (**10b-^{13}C**) was synthesized in the same manner as the unlabeled complex, using $CH_3{}^{13}CH_2MgBr$. Protonation of **10b-^{13}C** with $H(OiPr_2)_2BAr'_4$ in $CDCl_2F$ at −80 °C results in quantitative loss of ethane-^{13}C and formation of $[[(2,6\text{-}(^{i}Pr)_2C_6H_3)N{=}C(An)C(An){=}N(2,6\text{-}(^{i}Pr)_2C_6H_3)]Pd(^{13}CH_2\text{-}CH_2\text{-}\mu\text{-}H)]BAr'_4$ (**8-^{13}C**). Although only the α-methylene carbon is initially labeled with ^{13}C, very rapid β-hydride elimination and reinsertion at −80 °C results in equal distribution of the ^{13}C label between the α- and β-carbons by the time an NMR spectrum is acquired (Scheme 3).

The α-carbon appears at 38.5 ppm in the ^{13}C spectrum, having a $^1J_{CH}$ of 153 Hz; the β-carbon resonance at 19.3 ppm exhibits a $^1J_{CH}$ of 155 Hz with the nonagostic methylene protons and a $^1J_{CH}$ of 67 Hz with the agostic proton. The large C−H coupling constants between C_α and C_β and the methylene protons are in the range for sp^2 C−H coupling constants, indicating a significant amount of ethylene hydride character in this β-agostic ethyl species.[28]

Variable-Temperature ^{13}C NMR Spectra. As mentioned earlier, β-hydride elimination is the only one of the two dynamic processes that is observable by ^{13}C NMR; this process serves to interchange C_α and C_β. Thus, in the slow exchange limit (ca. −120 °C), two broad resonances are observed at 38.5 ppm (**8-^{13}C$_\alpha$**) and 19.3 ppm (**8-^{13}C$_\beta$**) in the proton-decoupled ^{13}C NMR spectrum, corresponding to the two labeled complexes

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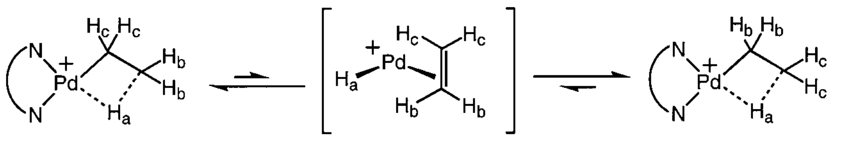
[30] This $^1J_{CH}$ was measured using the ^{13}C-labeled species **8-^{13}C**.

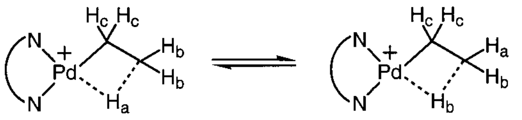
[31] Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1−124.

Scheme 2. Dynamic Processes of the β-Agostic Ethyl Cation 8

(i) β-Hydride elimination and reinsertion with opposite regiochemistry



(ii) C-C bond rotation



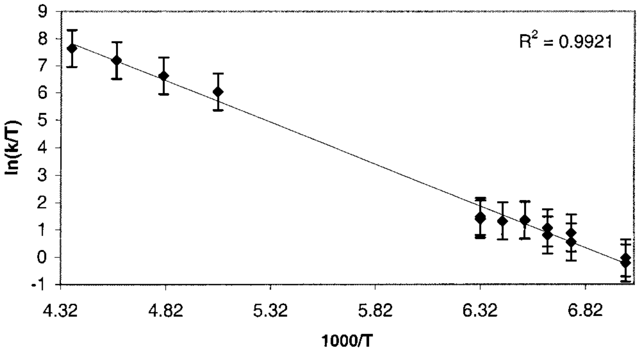
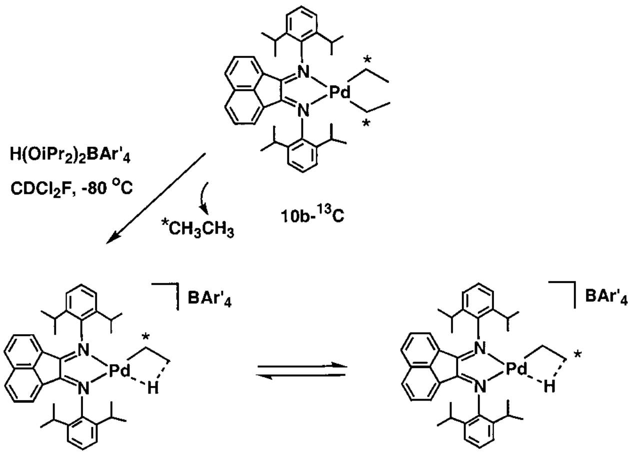


Figure 4. Eyring plot for β-hydride elimination in **8-^{13}C.**

Scheme 3. Protonation of 10b-^{13}C and Subsequent Equilibration of 8-^{13}C



8-^{13}C$_\alpha$ 8-^{13}C$_\beta$

in equilibrium ($K_{eq} = 1$ for degenerate species). As the probe temperature is raised, the two resonances broaden and disappear into the baseline, reappearing as a single, averaged peak (28.4 ppm) at warmer temperatures. Using the slow exchange approximation at −120 °C, a first-order rate constant of $k = 590$ s^{-1} for exchange was determined, corresponding to a barrier ($\Delta G^\ddagger$) to β-hydride elimination of 6.8 kcal/mol. In the fast exchange region (−55 °C), a first-order rate constant of $k = 2.9 \times 10^5$ s^{-1} can be estimated ($\Delta G^\ddagger = 7.2$ kcal/mol). An Eyring analysis of the first-order rate data between −40 and −125 °C (Figure 4) gives $\Delta H^\ddagger = 6.1 \pm 0.2$ kcal/mol and $\Delta S^\ddagger = -5.2 \pm 0.9$ eu.

The modest negative value of the entropy of activation is most likely due to the ordered, planar transition state

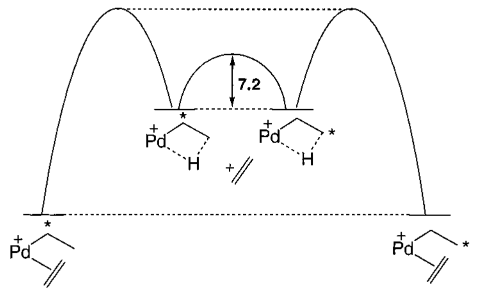


Figure 5. Free energy (ΔG) diagram (kcal/mol) for isomerization of ethyl ethylene complexes (−55 °C).

necessary for β-hydride elimination.[32] On the basis of these results and the observation from previous studies that the barrier to trapping with ethylene is higher than the barrier to β-H elimination, the free energy diagram shown in Figure 5 can be constructed for isomerization of ethyl ethylene complexes, which involves formation of the agostic ethyl cation. Using gradient-corrected DFT, Ziegler et al. have calculated the enthalpic barrier to β-hydride elimination in the analogous generic (diimine = −NHCHCHNH−) Pd system to be 5.84 kcal/mol for an agostic butyl system, in good agreement with our measured barrier ($\Delta H^\ddagger$) of 6.1 kcal/mol.[33] The agreement between DFT calculations using a generic diimine system (electronic effects only are considered) and the experimental barrier suggests that steric factors do not play a large role in determining the ground state or transition state energies for these cationic ethyl complexes.

Summary and Conclusions

A (diimine)Pd(II) β-agostic ethyl cation (**8**) has been synthesized via protonation of a (diimine)Pd(II) diethyl complex with H(OiPr$_2$)$_2$BAr'$_4$. The cation exhibits dynamic ^{1}H and ^{13}C NMR spectra which can be assigned to two dynamic processes: (1) β-H elimination ($\Delta G^\ddagger = 6.9$ kcal/mol, −108 °C) and (2) C$_\alpha$−C$_\beta$ bond rotation ($\Delta G^\ddagger$ ca. 8.4 kcal/mol, −108 °C). The energy ordering of these two processes distinguishes this agostic ethyl cation from those previously described in the literature, in which bond rotations were observed to be faster than β-H elimination.

The β-H elimination barrier determined by these experiments is one of two important barriers in the

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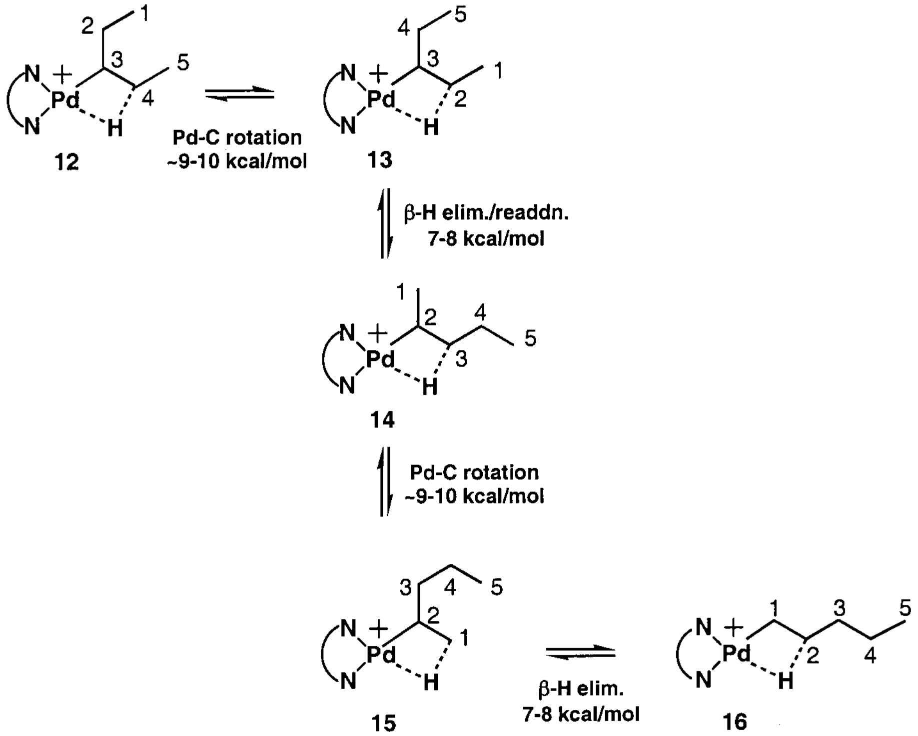
Scheme 4. Elementary Processes Involved in Chain-Walking



chain-walking process, the other being Pd−C bond rotation. Although Pd−C bond rotation does not produce site exchange in the ethyl cation, precluding measurement of its energetic cost, studies of the *β*-agostic isopropyl cation **6** (see eq 1) do allow measurement of this bond rotation barrier, $\Delta G^{\ddagger} = 9.6$ kcal/mol. The chain-walking process, involving both Pd−C rotation and *β*-H elimination, is illustrated in Scheme 4 for a Pd−C_5 alkyl moiety.

Migration of the Pd atom from C3 to C2 involves initial release of the agostic interaction in **12**, rotation about the Pd−C3 bond, and formation of an agostic bond with a C−H bond of C2 (**13**). Then *β*-H elimination/readdition can occur, placing the Pd atom on C2, with C3 in the *β*-agostic postion (**14**). Migration to C1 (**16**) again involves Pd−C2 bond rotation (**14** → **15**), followed by *β*-H elimination. Thus, the combination of these two processes, modeled with the ethyl cation (**8**) and the isopropyl cation (**6**), presents a detailed picture of the energetics of migration of Pd along the chain in the (α-diimine)Pd cations and suggests that the Pd−C_α bond rotation is the higher barrier, controlling the overall rate of chain migration.

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 MBraun drybox. NMR spectra were acquired with Bruker DRX400 or DRX500 spectrometers. NMR probe temperatures were measured using an Omega model HH21 thermocouple (type T) immersed in anhydrous methanol in a 5 mm NMR tube. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield of TMS and were referenced to residual ^{1}H NMR signals and to the ^{13}C NMR signals of the deuterated solvents, respectively. All coupling constants are reported in Hz. Elemental analyses were performed by Atlantic Microlab, Inc. of Norcross, GA.

Rate constants were determined by analysis of NMR line shapes using standard equations. At coalescence (where two resonances have merged to a single "flat-topped" peak), $k = \pi(\nu_a - \nu_x)/2^{1/2}$, where $\nu_a - \nu_x$ is the difference in resonance frequencies determined in the slow exchange limit. In the slow exchange region, $k = \pi\Delta\omega$, where $\Delta\omega$ is the line-width at half-height at a given temperature minus the line-width at half-height in the slow exchange limit. In the fast exchange region, $k = \pi(\nu_A - \nu_X)^2/2\Delta\omega$, where $\Delta\omega$ is the line-width at half-height at a given temperature minus the line-width at half-height in the fast exchange limit. Activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$) were calculated from measured rate constants and temperatures using the Eyring equation. Error analyses for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were based on Girolami's derivation of $\sigma\Delta H^{\ddagger}$ and $\sigma\Delta S^{\ddagger}$.[34] Error analysis of $\Delta G^{\ddagger}$ obtained for dynamic processes was based on Binsch's derivation of $\sigma\Delta G^{\ddagger}$ and incorporated an estimate of 10% error in *k* and ±1 °C error in temperature (±5 °C error for coalescence data).[35]

Materials. All solvents used for synthesis were deoxygenated and dried via passage over a column of activated alumina.[36] Dichlorofluoromethane-*d* ($CDCl_2F$) was prepared according to the literature,[37] dried over $CaCl_2$, vacuum-transferred, degassed by repeated freeze−pump−thaw cycles, and stored over 4 Å molecular sieves at −30 °C under argon. Methylene chloride-d_2 was dried over P_2O_5, vacuum-transferred, degassed by repeated freeze−pump−thaw cycles, and stored over 4 Å molecular sieves under argon. The α-diimine ligands,[38] $(PhCN)_2PdCl_2$,[39] and $H(OEt_2)_2BAr'_4$[29] were prepared

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according to the literature. $NaBAr'_4$ ($Ar' = 3,5\text{-}(CF_3)_2C_6H_3$) was purchased from Boulder Scientific and used as received. EtMgCl was purchased from Aldrich and stored at −30 °C. $CH_3{}^{13}CH_2Br$ was purchased from Aldrich, stored at −30 °C, and used as received. $CH_3{}^{13}CH_2MgBr$ was synthesized via standard procedures[40] and used as a solution in Et_2O; the molarity of this solution was determined using the method reported by Love et al.[41] The syntheses of the dichloride complexes (**9a** and **9b**) have been reported without spectral characterization.[42]

[(2,6-$(CH_3)_2C_6H_3$)N═C(An)C(An)═N(2,6-$(CH_3)_2C_6H_3$)]-$PdCl_2$ (9a). A clean, flame-dried Schlenk flask was charged with $(PhCN)_2PdCl_2$ (2.00 g, 5.21 mmol) and (2,6-$(CH_3)_2C_6H_3$)N═C(An)C(An)═N(2,6-$(CH_3)_2C_6H_3$) (2.23 g, 5.74 mmol) in an argon-filled drybox. The flask was placed under Ar, and 20 mL of CH_2Cl_2 were added via syringe. The homogeneous solution was stirred for 20 h. Pentane (30 mL) was added to cause precipitation of the product, which was isolated by cannula filtration and washed with pentane (3 × 10 mL). The orange-red solid was dried under reduced pressure at 25 °C for 19 h and stored under argon at room temperature. Yield: 2.50 g (85%). ^1H NMR (CD_2Cl_2, 400 MHz, 25 °C): δ 8.19 (d, J = 8.3, 2H, An pH), 7.53 (dd, J = 7.4, 8.2, 2H, An mH), 7.39 (dd, J = 7.0, 8.2, 2H, ArH), 7.30 (m, 4H, ArH), 6.64 (d, J = 7.3, 2H, An oH), 2.43 (s, 12H, Ar(CH_3)$_2$). ^{13}C NMR (CD_2Cl_2, 100 MHz, 25 °C): δ 176.2, 147.9, 143.7, 133.3, 131.8, 130.1, 129.9, 129.1, 128.9, 125.7, 124.8, 18.5. Anal. Calcd for $C_{28}H_{24}N_2PdCl_2$: C, 59.43; H, 4.28; N, 4.95. Found: C, 59.36, H, 4.69, N, 4.82.

[(2,6-$(^iPr)_2C_6H_3$)N═C(An)C(An)═N(2,6-$(^iPr)_2C_6H_3$)]-$PdCl_2$ (9b). A procedure similar to that for **9a** was followed, using $(PhCN)_2PdCl_2$ (0.66 g, 1.72 mmol) dissolved in 10 mL of CH_2Cl_2 and (2,6-$(^iPr)_2C_6H_3$)N═C(An)C(An)═N(2,6-$(^iPr)_2C_6H_3$) (0.95 g, 1.89 mmol) dissolved in 90 mL of CH_2Cl_2. The homogeneous ligand solution was added via cannula to the Pd solution. Reaction times, conditions, and workup were identical to that for **9a**. Yield: 0.93 g (80%). ^1H NMR (CD_2Cl_2, 400 MHz, 25 °C): δ 8.16 (d, J = 8.3, 2H, An pH), 7.53 (m, 4H, An mH, ArH), 7.40 (m, 4H, ArH), 6.53 (d, J = 7.3, 2H, An oH), 3.49 (sep, J = 6.8, 4H, CHMeMe′, C′HMeMe′), 1.51 (d, J = 6.8, 12H, CHMeMe′, C′HMeMe′), 0.99 (d, J = 6.8, 12H, CHMeMe′, C′HMeMe′). ^{13}C NMR (CD_2Cl_2, 100 MHz, 25 °C): δ 176.4, 147.4, 141.3, 140.5, 133.1, 131.8, 129.6, 126.4, 125.2, 124.7, 29.9, 23.9, 23.7 (one C missing). Anal. Calcd for $C_{36}H_{40}N_2PdCl_2$: C, 63.76; H, 5.95; N, 4.13. Found: C, 63.76, H, 6.01, N, 4.17.

[(2,6-$(CH_3)_2C_6H_3$)N═C(An)C(An)═N(2,6-$(CH_3)_2C_6H_3$)]Pd-$(C_2H_5)_2$ (10a). A flame-dried Schlenk flask was charged with ((2,6-$(CH_3)_2C_6H_3$)N═C(An)C(An)═N(2,6-$(CH_3)_2C_6H_3$))$PdCl_2$ (**9a**) (0.771 g, 1.36 mmol) in the drybox. The flask was then cooled to −78 °C in a dry ice/isopropyl alcohol bath. The orange solid was suspended in 20 mL of diethyl ether, and 2 equiv of C_2H_5MgCl (2.0 M, 1.36 mL, 2.73 mmol) was added via syringe. The mixture became brown within 5 min and was stirred at −78 °C for 2 h. Methanol (0.1 mL) was added via syringe to quench any unreacted Grignard reagent, and the cold reaction mixture was filtered through a 2−3 cm column of Florisil under argon into a receiving flask cooled to 0 °C. The Florisil was extracted with additional Et_2O (3 × 10 mL), and the volume of the red-brown filtrate was reduced in vacuo, producing a red-brown solid. The product was dried briefly in vacuo at 25 °C. Yield: 0.193 g (26%). ^1H NMR (CD_2Cl_2, 500 MHz, 25 °C): δ 8.05 (d, J = 8.0, 2H, An pH), 7.43 (dd, J = 7.0, 8.0, 2H, An mH), 7.28 (m, 6H, ArH), 6.70 (d, 7.0, 2H, An oH), 2.28 (s, 12H, Ar(CH_3)$_2$), 0.86 (m, 10H, PdCH_2CH_3). ^{13}C NMR (CD_2Cl_2, 125 MHz, 25 °C): δ 167.2, 145.7, 142.9, 130.2, 129.3, 128.7, 128.4, 128.2, 126.2, 123.3, 18.0 (Ar(CH$_3$)$_2$), 15.8 (PdCH$_2$$CH_3$), 11.5 (Pd$CH_2CH_3$). Anal. Calcd for $C_{32}H_{34}N_2Pd$: C, 69.50; H, 6.20; N, 5.07. Found: C, 69.65, H, 6.31, N, 5.00.

[(2,6-$(^iPr)_2C_6H_3$)N═C(An)C(An)═N(2,6-$(^iPr)_2C_6H_3$)]-$Pd(C_2H_5)_2$ (10b). A procedure identical to that for **2a** was followed, using ((2,6-$(^iPr)_2C_6H_3$)N═C(An)C(An)═N(2,6-$(^iPr)_2C_6H_3$)$PdCl_2$ (**9b**) (0.326 g, 0.48 mmol) and C_2H_5MgCl (2.0 M, 0.48 mL, 0.962 mmol). Yield: 0.078 g (24%). ^1H NMR (CD_2Cl_2, 400 MHz, 25 °C): δ 8.02 (d, J = 8.0, 2H, An pH), 7.39 (m, 8H, An mH, ArH), 6.58 (d, J = 7.0, 2H, An oH), 3.37 (sep, J = 6.8 Hz, 4H, CHMeMe′, C′HMeMe′), 1.38 (d, J = 6.8, 12H, CHMeMe′, C′HMeMe′), 0.92 (m, 10H, PdCH_2CH_3), 0.90 (d, J = 6.8, 12H, CHMeMe′, C′HMeMe′). ^{13}C NMR (CD_2Cl_2, 125 MHz, 25 °C): δ 167.8, 143.8, 142.8, 138.8, 131.8, 130.2, 128.9, 128.7, 126.9, 124.3, 124.2, 29.0 (CHMe$_2$), 24.0 (CHMeMe′), 23.4 (CHMeMe′), 16.4 (PdCH$_2$$CH_3$), 12.7 (Pd$CH_2CH_3$). Anal. Calcd for $C_{40}H_{50}N_2Pd$: C, 72.22; H, 7.58; N, 4.21. Found: C, 72.44, H, 7.61, N, 4.18.

[(2,6-$(^iPr)_2C_6H_3$)N═C(An)C(An)═N(2,6-$(^iPr)_2C_6H_3$)]Pd-$(^{13}CH_2CH_3)_2$ (10b-^{13}C). A procedure identical to that for **10b** was followed, using ((2,6-$(^iPr)_2C_6H_3$)N═C(An)C(An)═N(2,6-$(^iPr)_2C_6H_3$)$PdCl_2$ (**9b**) (0.60 g, 0.89 mmol) and $CH_3{}^{13}CH_2MgBr$ (0.45 M, 3.9 mL, 1.8 mmol). Yield: 0.253 g (43%). ^1H NMR (CD_2Cl_2, 400 MHz, 25 °C): δ 8.02 (d, J = 8.0, 2H, An pH), 7.39 (m, 8H, An mH, ArH), 6.58 (d, J = 7.0, 2H, An oH), 3.37 (sep, 4H, J = 6.8, CHMeMe′, C′HMeMe′), 1.38 (d, 12H, J = 6.8, CHMeMe′, C′HMeMe′), 0.93 (dq, 4H, J_{CH} = 127, $^3J_{HH}$ = 7.2, Pd^{13}CH_2CH$_3$),0.90 (d, 12H, J = 6.8, CHMeMe′, C′HMeMe′), 0.87 (t, 6H, J = 7.2, Pd^{13}CH$_2$CH_3).

$H(OiPr_2)_2BAr'_4$ ($Ar' = 3,5\text{-}(CF_3)_2C_6H_3$). $^iPr_2O$ was distilled from Na and stored in the absence of light under argon. A clean, flame-dried Schlenk flask containing activated 4 Å molecular sieves was charged with $NaBAr'_4$ (2.5 g, 2.8 mmol) in an argon-filled drybox. A 30 mL sample of dry $^iPr_2O$ was added, and the solution was allowed to stand overnight. It was then transferred to a clean, flame-dried Schlenk flask via cannula and was cooled to 0 °C. HCl(g), generated by the slow addition of concentrated H_2SO_4 to NaCl(s), was bubbled through the solution for 15 min. The mixture was then cooled to −78 °C, and argon was purged through the solution for 1 h to remove excess HCl(g). The solution was filtered through Celite in a jacketed frit kept at −78 °C into a flame-dried Schlenk flask. The solution volume was then reduced to 10−15 mL under reduced pressure, and 6 mL of pentane was added. The flask was sealed and placed in a −30 °C freezer for 20 h, causing crystallization. The supernatant was removed via cannula filtration, and the white crystals were washed with 3 mL of dry pentane. The solid was dried in vacuo at 25 °C for 15 min and stored at −30 °C in the drybox. Yield: 1.62 g (54%). ^1H NMR (CD_2Cl_2, 400 MHz, −80 °C): δ 16.39 (quintet, 1H, J = 2.4, H(O^{i}Pr$_2$)$_2$), 7.72 (s, 8H, BAr′$_4$ oH), 7.54 (s, 4H, BAr′$_4$ pH), 4.35 (doublet of septets, 4H, J = 6.4, 2.4, H(O(CHMe$_2$)$_2$)$_2$), 1.33 (d, 24H, J = 6.4, H(O(CHMe_2)$_2$)$_2$).

General Procedure for Variable-Temperature NMR Spectroscopic Experiments. A tared 5 mm NMR tube was charged with ca. 0.01 mmol of the desired diethyl complex (**10a** or **10b**) and 0.01 mmol of either $H(OEt_2)_2BAr'_4$ or $H(OiPr_2)_2BAr'_4$ in the drybox under Ar. The tube was capped with a septum and removed from the drybox; the septum was secured with Teflon tape and Parafilm. The tube was cooled to −78 °C (dry ice/acetone), and $CDCl_2F$ was added via a 22-gauge cannula (∼600−800 μL) or CD_2Cl_2 was added via a gastight syringe (700 μL). The tube was shaken and warmed slightly to dissolve the solids and facilitate the protonation reaction; gas evolution was observed, and the solution became clear orange. The tube was then transferred to a precooled (−78 °C) NMR probe for acquisition of spectra.

[[(2,6-$(Me)_2C_6H_3$)N═C(An)C(An)═N(2,6-$(Me)_2C_6H_3$)]Pd-$(CH_2CH_3)(OEt_2)$]BAr'_4 (11a). ^1H NMR (CD_2Cl_2, 400 MHz, −80 °C): δ 8.10 (d, 1H, J = 8.4, An pH), 8.06 (d, 1H, J = 8.4, An pH′), 7.72 (s, 8H, BAr′$_4$ oH), 7.49 (s, 4H, BAr′$_4$ pH), 7.45−

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7.25 (m, 8H, An *m*H, ArH), 6.66 (d, 1H, $J = 7.2$, An *o*H), 6.35 (d, 1H, $J = 7.2$, An *o*H′), 3.70 (q, 4H, $J = 6.8$, $\mathrm{Pd(O(C\mathit{H}_2CH_3)_2)}$), 2.22 and 2.18 (2 s, 6H each, $\mathrm{ArMe_2}$ and $\mathrm{Ar'Me_2}$), 1.46 (q, 2H, $J = 7.2$, $\mathrm{PdC\mathit{H}_2CH_3}$), 1.45 (t, 6H, $J = 6.8$, $\mathrm{Pd(O(CH_2C\mathit{H}_3)_2)}$), −0.05 (t, 3H, $J = 7.2$, $\mathrm{PdCH_2C\mathit{H}_3}$).

[[(2,6-(^{i}Pr)$_2$C$_6$H$_3$)N═C(An)C(An)═N(2,6-(^{i}Pr)$_2$C$_6$H$_3$)]Pd(CH$_2$CH$_3$)(OEt$_2$)]BAr′$_4$ (11b). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500 MHz, −80 °C): δ 8.05 (d, 1H, $J = 8.5$, An *p*H), 8.01 (d, 1H, $J = 8.5$, An *p*H′), 7.72 (s, 8H, BAr′$_4$ *o*H), 7.52 (s, 4H, BAr′$_4$ *p*H), 7.50−7.25 (m, 8H, An *m*H, ArH), 6.51 (d, 1H, $J = 7.0$, An *o*H), 6.26 (d, 1H, $J = 7.0$, An *o*H′), 3.51 (br, 4H, $\mathrm{Pd(O(C\mathit{H}_2CH_3)_2)}$), 3.16 and 3.13 (2 septets, 6H each, $J = 6.5$ and 6.5, ArC*H*MeMe and Ar′C*H*MeMe), 1.59 (br, 2H, $\mathrm{PdC\mathit{H}_2CH_3}$), 1.33 (br, 6H, $\mathrm{Pd(O(CH_2C\mathit{H}_3)_2)}$), 1.31, 1.28, and 0.82 (3 d, 6H, 6H, and 12H each, $J = 6.5$, 6.5, and 6.5, CH*Me*Me, CHMe*Me*, CH′*Me*Me, CH′Me*Me*), 0.19 (br, 3H, $\mathrm{PdCH_2C\mathit{H}_3}$).

[[(2,6-(^{i}Pr)$_2$C$_6$H$_3$)N═C(An)C(An)═N(2,6-(^{i}Pr)$_2$C$_6$H$_3$)]Pd(CH$_2$CH$_2$-μ-H)]BAr′$_4$ (8). ^{1}H NMR ($\mathrm{CDCl_2F}$, 500 MHz, −130 °C): δ 8.10 (d, 1H, $J = 8.5$, An *p*H), 8.08 (d, 1H, $J = 8.5$, An *p*H′), 7.77 (s, 8H, BAr′$_4$ *o*H), 7.54 (s, 4H, BAr′$_4$ *p*H), 7.55−7.40 (m, 8H, An *m*H, ArH), 6.81 (d, 1H, $J = 7.0$, An *o*H), 6.75 (d, 1H, $J = 6.5$, An *o*H′), 3.24 and 3.14 (m, 1H each, C*H*MeMe′, C′*H*MeMe′), 2.23 (m, 2H, $\mathrm{PdC\mathit{H}_2CH_2}$-$\mu$-H), 1.42 (m, 2H, $\mathrm{PdCH_2C\mathit{H}_2}$-$\mu$-H), 1.40−1.36 and 1.13−1.05 (br, 3H each, CH*Me*Me′, CHMe*Me*′, C′H*Me*Me′, C′HMe*Me*′), −8.90 (br t, 1H, $^2J_{\mathrm{HH}} = 16$, $\mathrm{PdCH_2CH_2}$-μ-*H*). ^{13}C NMR ($\mathrm{CDCl_2F}$, 100 MHz, −130 °C, static, selected peaks): δ 38.5 ($^1J_{\mathrm{CH}} = 153$, $\mathrm{Pd\mathit{C}H_2CH_2}$-$\mu$-H), 19.3 ($^1J_{\mathrm{CH}} = 155$, 67, $\mathrm{PdCH_2\mathit{C}H_2}$-$\mu$-H). ^{13}C NMR ($\mathrm{CDCl_2F}$, 100 MHz, 0 °C, dynamic, selected peaks): δ 28.4 ($\mathrm{PdC\mathit{H}_2C\mathit{H}_2}$-$\mu$-*H*).

Eyring Analysis via ^{13}C NMR Spectroscopy. The barrier to β-hydride elimination was determined using the ^{13}C-labeled ethyl agostic complex **8-^{13}C**. Samples were prepared as described above and transferred to a precooled (−78 °C) NMR probe for acquisition of spectra, which were acquired in the range between −135 and 0 °C. Line widths (ω) were measured in the ^{13}C{^{1}H} spectra in units of Hz for the two carbons in the ethyl moiety and were corrected for line widths (ω_o) in the absence of exchange ($\Delta\omega = \omega - \omega_o$). There is a 50% probability of β-hydride elimination being followed by reinsertion with the same regiochemistry (re-formation of starting materials rather than formation of products), so the actual rate of β-hydride elimination is twice the observed rate. To correct for this, all measured rate constants were doubled. These experiments were repeated twice with the same results; one of the data sets is shown in Figure 4.

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