

Mechanism of Ethylene Oligomerization by a Cationic Palladium(II) Alkyl Complex that Contains a (3,5-Me₂-pyrazolyl)₂CHSi(*p*-tolyl)₃ Ligand

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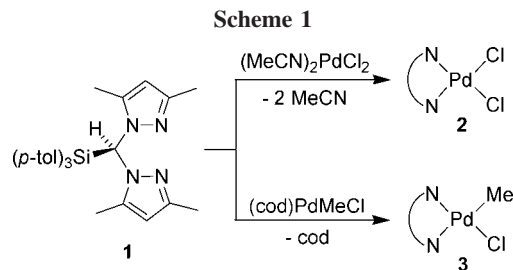
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The reactivity of the ethylene oligomerization catalyst (N[^]N)Pd(Me)(ethylene)⁺ (**5**), which contains a silyl-capped bis-pyrazolyl methane ligand (N[^]N = (3,5-Me₂-pyrazolyl)₂CHSi(*p*-tolyl)₃ (**1**)) was investigated. The reaction of (N[^]N)PdMeCl (**3**) with Li[B(C₆F₅)₄] and ethylene in CH₂Cl₂ generates **5**. Complex **5** undergoes ethylene insertion at –10 °C with a rate constant of $k_{\text{insert, Me}} = 3.3(3) \times 10^{-3} \text{ s}^{-1}$. Complex **5** catalytically oligomerizes ethylene to branched C₆–C₂₀ internal olefins (–10 to 20 °C; 2.7–30 atm ethylene). NMR studies show that an equilibrium mixture of base-free β-agostic secondary alkyl (N[^]N)PdR⁺ species (**8**) and ethylene adducts (N[^]N)Pd(R)(ethylene)⁺ (**9**) is present under oligomerization conditions. Complex **9** decomposes to Pd⁰ at 20 °C, resulting in catalyst decomposition. (N[^]N)Pd(R)(L)⁺ species containing R groups that can function as internal donors (either η²-acyl or agostic β-H) undergo a dynamic process that exchanges the two pz* rings and are thermally unstable. It is proposed that catalyst decomposition and pz* exchange both involve initial coordination of the internal donor to generate a configurationally labile five-coordinate intermediate, which isomerizes, resulting in pz* site exchange or displacement of one arm of the N[^]N ligand.

Introduction

The ethylene oligomerization and polymerization reactivity of (N[^]N)PdR(C₂H₄)⁺ species that contain bis(*N*-heterocycle)-methane (N[^]N) donor ligands was explored in previous work.¹ (N[^]N)PdR⁺ cations that contain sterically small N[^]N ligands catalytically dimerize ethylene by an insertion/β-H elimination mechanism. The catalyst resting state is the (N[^]N)Pd(Et)(ethylene)⁺ complex. Incorporation of bulky substituents in the bridging methylene position of the N[^]N ligand shifts the product distribution to higher molecular weight due to inhibition of chain transfer. Increasing the electrophilic character (*N*-heterocycle = imidazole < pyridine < pyrazole) and the steric bulk of the (N[^]N)Pd unit leads to moderate (up to ca. 10-fold) increases in ethylene insertion rates of (N[^]N)Pd(R)(ethylene)⁺ species. During this work, we discovered that the {(*p*-tolyl)₃SiCH(pz*)₂}PdMe⁺ cation (pz* = 3,5-Me₂-pyrazole), which contains a silyl-capped bis-pyrazolyl-methane ligand, displays unique reactivity. This species exhibits higher ethylene insertion and oligomerization rates but is much less thermally stable compared



to other (N[^]N)PdR⁺ cations. Here we describe a detailed study of the {(*p*-tolyl)₃SiCH(pz*)₂}PdMe⁺ catalyst aimed at understanding the oligomerization behavior and the low thermal stability of this system.

Results and Discussion

Synthesis and Structure of (N[^]N)PdCl₂ and (N[^]N)PdMeCl

The bis-pyrazolyl methane ligand (*p*-tolyl)₃SiCH(pz*)₂ (**1**) was prepared by deprotonation of (pz*)₂CH₂ with ⁿBuLi in THF at –78 °C, followed by reaction with (*p*-tolyl)₃SiOTf. The reaction of **1** with (MeCN)₂PdCl₂ affords {(*p*-tolyl)₃SiCH(pz*)₂}PdCl₂ (**2**, Scheme 1). The solid state structure of **2** was determined by X-ray diffraction (Figure 1) and is similar to those of other {bis(*N*-heterocycle)methane}Pd^{II} complexes.^{1b,c,2} The geometry at Pd is square planar, the (N[^]N)Pd chelate ring has a boat conformation, and the (*p*-tolyl)₃Si group occupies the axial position on the bridging carbon. The ¹H NMR spectrum of **2** contains one set of pz* resonances, consistent with C_s symmetry. The spectrum also contains one set of sharp *p*-tolyl resonances, indicating that rotation around the Si–CH and Si–tolyl bonds is fast on the NMR time scale.

The reaction of **1** with (COD)PdMeCl affords {(*p*-tolyl)₃SiCH(pz*)₂}PdMeCl (**3**, Scheme 1). The ¹H NMR spectrum of **3** at 25 °C in CD₂Cl₂ solution contains two sets of

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(1) (a) Burns, C. T.; Jordan, R. F. *Organometallics* **2007**, *26*, 6726. (b) Burns, C. T.; Jordan, R. F. *Organometallics* **2007**, *26*, 6737. (c) Tsuji, S.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1999**, *18*, 4758. For studies of related L₂PdR⁺ species see: (d) Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 1137. (e) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746. (f) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (g) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (h) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888. (i) Temple, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686. (j) Ikeda, S.; Ohhata, F.; Miyoshi, M.; Tanaka, R.; Minami, T.; Ozawa, F.; Yoshifuji, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4512. (k) Daugulis, O.; Brookhart, M. *Organometallics* **2002**, *21*, 5926. (l) Doherty, M. D.; Trudeau, S.; White, P. S.; Morken, J. P.; Brookhart, M. *Organometallics* **2007**, *26*, 1261. (m) Ledford, J.; Shultz, C. S.; Gates, D. P.; White, P. S.; DeSimone, J. M.; Brookhart, M. *Organometallics* **2001**, *20*, 5266. (n) Salo, E. V.; Guan, Z. *Organometallics* **2003**, *22*, 5033.

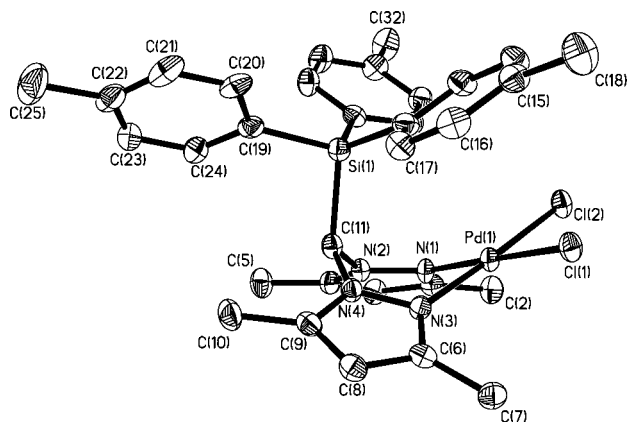
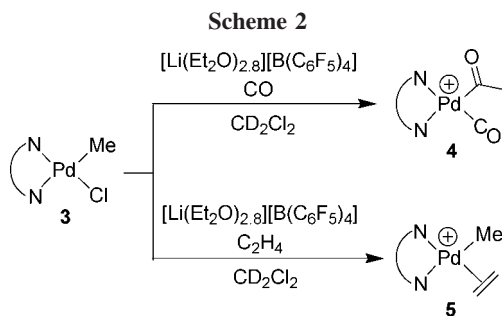
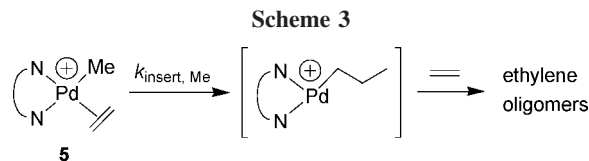


Figure 1. ORTEP view (50% probability ellipsoids) of $\{(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2\}\text{PdCl}_2$ (**2**). H atoms are omitted. Key bond distances (Å) and angles (deg): Pd(1)–Cl(1) 2.28(1); Pd(1)–Cl(2) 2.29(1); N(1)–Pd(1) 2.03(3); N(3)–Pd(1) 2.03(3); N(3)–N(4) 1.38(4); N(1)–N(2) 1.37(4); N(4)–C(11) 1.46(5); N(2)–C(11) 1.45(5); C(11)–Si(1) 1.95(1); N(3)–Pd(1)–N(1) 88.2(1); N(3)–Pd(1)–Cl(1) 91.7(9); N(1)–Pd(1)–Cl(1) 179.2(9); N(3)–Pd(1)–Cl(2) 177.1(9); N(1)–Pd(1)–Cl(2) 92.8(9); Cl(1)–Pd(1)–Cl(2) 87.4(4). Angles between intersecting planes N(1)–N(2)–N(3)–N(4) and N(1)–Pd(1)–N(3) 158.1; N(1)–N(2)–N(3)–N(4) and N(2)–C(11)–N(4) 133.2; two heterocycle planes 126.8.



pz^* resonances consistent with C_1 symmetry. As in **2**, fast rotation around the Si–CH and Si–tolyl bonds is observed.

Generation of a Pd Acyl Carbonyl Complex. The acyl carbonyl complex $\{(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2\}\text{Pd}\{\text{C(=O)Me}\}(\text{CO})^+$ (**4**) was generated quantitatively by the reaction of **3** and $[\text{Li}(\text{Et}_2\text{O})_{2.8}][\text{B}(\text{C}_6\text{F}_5)_4]$ in CD_2Cl_2 in the presence of CO (Scheme 2). The ^{13}C NMR spectrum of **4** at -60°C in the presence of excess CO contains sharp resonances for bound CO (δ 171.3) and free CO (δ 184), indicating that intermolecular CO exchange is slow on the NMR time scale under these conditions.³ The ν_{CO} value for the carbonyl ligand of **4** in CD_2Cl_2 solution is 2122 cm^{-1} (cf. free CO 2139 cm^{-1}), which indicates that **4** contains a moderately electrophilic Pd center. This value is lower than the values for $\{\text{H}_2\text{C}(\text{pz})_2\}\text{Pd}\{\text{C(=O)Me}\}\text{CO}^+$ (2133 cm^{-1}) and $\{\text{H}_2\text{C}(\text{pz}^*)_2\}\text{Pd}\{\text{C(=O)Me}\}\text{CO}^+$ (2132 cm^{-1}),^{1a} most likely due to the inductive and field



effects of the $-\text{Si}(p\text{-tolyl})_3$ group. For comparison, incorporation of a $-\text{C}(p\text{-tolyl})_3$ group at the bridge position in a closely related system caused a smaller reduction in ν_{CO} (i.e., $\{(p\text{-tolyl})_3\text{CCH}(\text{mim})_2\}\text{Pd}\{\text{C(=O)Me}\}\text{CO}^+$ (2118 cm^{-1}) vs $\{\text{H}_2\text{C}(\text{mim})_2\}\text{Pd}\{\text{C(=O)Me}\}\text{CO}^+$ (2122 cm^{-1})).^{1,4} Complex **4** decomposes to Pd^0 in a few hours at 25°C .

Generation of $\{(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2\}\text{PdMe}(\text{C}_2\text{H}_4)^+$. The methyl ethylene complex $[\{(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2\}\text{PdMe}(\text{C}_2\text{H}_4)]\text{-}[\text{B}(\text{C}_6\text{F}_5)_4]$ (**5**) was generated quantitatively by the reaction of **3** and $[\text{Li}(\text{Et}_2\text{O})_{2.8}][\text{B}(\text{C}_6\text{F}_5)_4]$ in CD_2Cl_2 in the presence of ethylene at -60°C (Scheme 2). Under these conditions insertion is not observed. The ^1H NMR spectrum of **5** at -60°C contains two sharp sets of $\text{pz}^*\text{-H}_4$ resonances (δ 6.06, 5.85), consistent with C_1 symmetry. The Pd–Me resonance appears at δ 0.38, ca. 0.63 ppm downfield from the Pd–Me resonance of **3**. The ^1H NMR spectrum contains separate signals for bound (δ 4.15, 4.38) and free (δ 5.38) ethylene at -60°C . Similarly, the ^{13}C spectrum contains separate resonances for bound (δ 87.5, br) and free (δ 130.0) ethylene. These data are consistent with slow exchange of bound and free ethylene and fast rotation around the Pd–(C_2H_4 centroid) axis in **5**.⁵

To probe the dynamics of Pd–(C_2H_4) rotation, **5** was generated in CDCl_2F solution and low-temperature NMR spectra were recorded. At -120°C , the ^1H NMR spectrum contains four broad signals (δ 5.21, 4.54, 4.26, 2.86) and the ^{13}C spectrum contains two broad signals (δ 83.6, 92.1) for the bound ethylene, indicating that ethylene rotation is slow on the chemical shift time scale at this temperature. The ^1H ethylene signals at δ 4.54 and 4.25 coalesce at -105°C , from which the barrier to ethylene rotation was determined to be $\Delta G_{\text{rot}}^\ddagger = 8.2\text{ kcal mol}^{-1}$.

Kinetics of Ethylene Insertion of **5.** In the presence of excess ethylene at -10°C , **5** undergoes ethylene insertion to yield higher Pd–alkyl complexes and eventually ethylene oligomers (Scheme 3). The rate of insertion of **5** is first-order in Pd and zero-order in ethylene. The insertion rate constant, $k_{\text{insert, Me}} = 3.3(3) \times 10^{-3}\text{ s}^{-1}$, was determined by monitoring the disappearance of the Pd–Me ^1H NMR resonance. The insertion barrier is $\Delta G^\ddagger = 18.3\text{ kcal mol}^{-1}$. The $k_{\text{insert, Me}}$ value for **5** is greater than that for $\{\text{Me}_2\text{C}(\text{pz})_2\}\text{PdMe}(\text{C}_2\text{H}_4)^+$ ($2.2 \times 10^{-4}\text{ s}^{-1}$), $\{\text{H}_2\text{C}(\text{pz})_2\}\text{PdMe}(\text{C}_2\text{H}_4)^+$ ($3.6 \times 10^{-4}\text{ s}^{-1}$), and $\{\text{H}_2\text{C}(\text{pz}^*)_2\}\text{PdMe}(\text{C}_2\text{H}_4)^+$ ($1.3 \times 10^{-3}\text{ s}^{-1}$) at the same temperature.^{1a,c} **5** undergoes ethylene insertion faster than any of the $\{\text{bis}(N\text{-heterocycle})\text{methane}\}\text{Pd}(\text{R})(\text{ethylene})^+$ species studied previously.¹

Ethylene Oligomerization Behavior of $\{(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2\}\text{PdMe}^+$. Preparative scale ethylene oligomerizations were performed using **5** generated in situ by the reaction of **3** and $[\text{Li}(\text{Et}_2\text{O})_{2.8}][\text{B}(\text{C}_6\text{F}_5)_4]$ in CH_2Cl_2 in the presence of ethylene. At -10°C under 2.7 atm of ethylene, **5** produces a distribution of branched $\text{C}_6\text{--C}_{20}$ internal olefins (Figure 2). Very little Pd^0 formation is observed under these conditions, indicating that

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(4) (a) Increasing the electron density at a remote position of a ligand lowered ν_{CO} in related complexes: Wu, F.; Jordan, R. F. *Organometallics* **2006**, 23, 5631. (b) Lu, C. C.; Peters, J. C. *J. Am. Chem. Soc.* **2002**, 124, 5272. (c) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2001**, 123, 5100.

(5) The four ethylene hydrogens comprise an ABCD system under slow rotation conditions, and an AA'BB' system under fast rotation conditions.

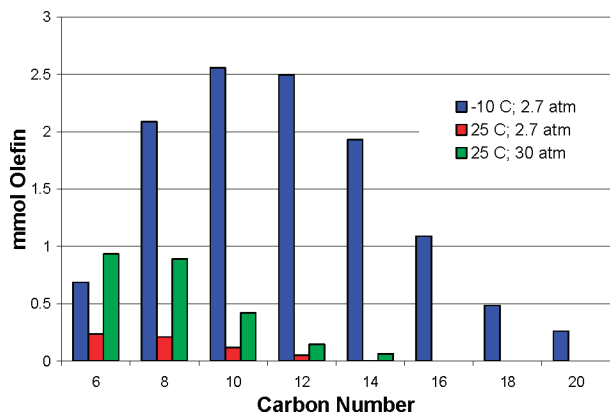
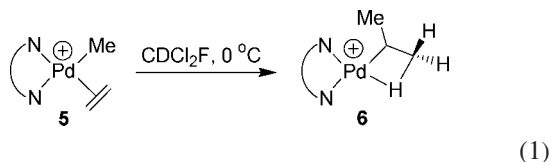


Figure 2. Distribution of olefins produced by **5**. Conditions: in situ generation of **5** from 30 μmol of **3** and 30 μmol of $[\text{Li}(\text{Et}_2\text{O})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ in 20 mL of CH_2Cl_2 . Blue bars: -10°C , 2.7 atm of ethylene; red bars: 25°C , 2.7 atm of ethylene; green bars: 25°C , 30 atm of ethylene.

catalyst decomposition is minimal. The turnover frequency ($13 \times 10^{-3} \text{ s}^{-1}$) is ca. 4 times higher than the ethylene insertion rate of **5**. At 25°C under 2.7 atm of ethylene, **5** produces a distribution of branched $\text{C}_6\text{--C}_{12}$ internal olefins (39 branches/ 10^3 C). The product distribution is very similar at 30 atm of ethylene pressure. Rapid formation of Pd^0 is observed during the 25°C reactions, indicating that the catalyst is not stable at this temperature.⁶

To probe the nature of the decomposition process, a CH_2Cl_2 solution of **5** was exposed to ethylene (650 mm on demand) at 25°C to model the oligomerization conditions. Pd^0 was recovered in 85% mass balance after 2 h. NMR and ESI-MS analysis of the product mixture showed that $[(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2]\text{H}^+$ was a major decomposition product, indicating that the ligand remains intact upon decomposition of the catalyst.⁷

Generation of $[(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2]\text{PdCHMeCH}_2\text{-}\mu\text{-H}$ [$\text{B}(\text{C}_6\text{F}_5)_4$] (6**).** The reaction of **5** in CDCl_2F at 0°C in the absence of ethylene generates the $\beta\text{-H}$ agostic isopropyl species $[(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2]\text{PdCHMeCH}_2\text{-}\mu\text{-H}$ [$\text{B}(\text{C}_6\text{F}_5)_4$] (**6**) in 95% yield along with ca. 5% of higher $\beta\text{-agostic}$ alkyl complexes (eq 1). Complex **6** is stable in CDCl_2F solution below 0°C .



The ^1H NMR spectrum of **6** in CDCl_2F at -115°C contains a $\text{PdCHMeCH}_2\text{-}\mu\text{-H}$ resonance at δ 3.31, a nonagostic methyl resonance at δ 0.77, and $\text{PdCHMeCH}_2\text{-}\mu\text{-H}$ resonances at δ -0.04 and 0.81 . The agostic $\beta\text{-H}$ appears as a triplet at δ -8.91 ($^2J_{\text{HH}} = 18 \text{ Hz}$), which is characteristic of $\beta\text{-H}$ agostic $\text{Pd}\text{-}i\text{Pr}$

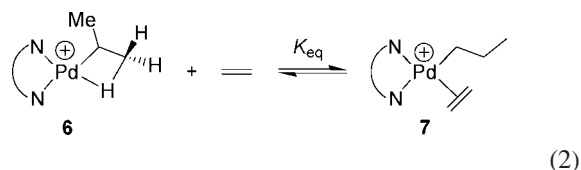
(6) The oligomerization distribution produced by **5** at 30 atm of ethylene fit a Shultz–Flory distribution ($\alpha = 0.35$ and $\beta = 1.8$). However, oligomerizations at 2.7 atm of ethylene pressure did not produce Shultz–Flory distributions.

(7) The compound $[\text{1H}][\text{B}(\text{C}_6\text{F}_5)_4]$ was generated quantitatively by the reaction of **1** (10 mg, 20 μmol) and $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (16 mg, 20 μmol) in CD_2Cl_2 (0.7 mL) for 10 min at 25°C . ^1H NMR (CD_2Cl_2 , 25°C): δ 12.63 (br s, 1H, H^+), 7.24 (m, 12 H, 4-Me- C_6H_4), 6.50 (s, 1H, CH), 6.06 (s, 2H, pz^*H_4), 2.39 (s, 9H, 4-Me- C_6H_4), 2.21 (s, 3H, pz^*Me), 2.05 (s, 3H, pz^*Me). ESI-MS: $[(\text{pz}^*)_2\text{CHSi}(p\text{-tolyl})_3]\text{H}^+$ calcd m/z 505.2, found 505.2. $[\text{1H}][\text{B}(\text{C}_6\text{F}_5)_4]$ decomposes in CD_2Cl_2 solution at 25°C (ca. 25% after 24 h).

species.⁸ These assignments were confirmed by a COSY spectrum. Sharp singlets are observed for the $(p\text{-tolyl})_3\text{SiCH}$ (δ 6.45) and $\text{pz}^*\text{-H}_4$ (δ 6.05, 5.92) resonances.

At 0°C , the ^1H NMR spectrum of **6** contains a broad signal at δ -2.10 for the isopropyl methyl hydrogens and a singlet at δ 3.09 for the $\text{PdCHMeCH}_2\text{-}\mu\text{-H}$ methine hydrogen. The spectrum also contains two sets of pz^* resonances, showing that the sides of the N^*N ligand remain inequivalent at this temperature. These results imply that in-place rotation around the $\text{Pd}\text{-C}$ bond and concomitant exchange of agostic and nonagostic Me units is fast at 0°C .⁹

Reaction of **6 with Ethylene.** The reaction of **6** with 1 equiv of ethylene in CD_2Cl_2 at -80°C results in partial reversible formation of the $n\text{-propyl}$ ethylene species $[(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2]\text{Pd}^i\text{Pr}(\text{C}_2\text{H}_4)[\text{B}(\text{C}_6\text{F}_5)_4]$ (**7**, (eq 2)). Complex **7** is stable in CD_2Cl_2 solution up to -35°C , at which temperature ethylene insertion occurs. The ^1H NMR spectrum of **7** in CD_2Cl_2 at -80°C contains a broad resonance for the bound ethylene (δ 4.26)¹⁰ and sharp singlets for the $(p\text{-tolyl})_3\text{SiCH}$ (δ 6.70) and $\text{pz}^*\text{-H}_4$ (δ 6.13, 5.90) hydrogens. The $n\text{-propyl}$ resonances were identified with the aid of a COSY spectrum (-80°C ; $\text{PdCH}_2\text{CH}_2\text{CH}_3$: δ 1.72, 0.77; $\text{PdCH}_2\text{CH}_2\text{CH}_3$: δ 1.94; $\text{PdCH}_2\text{CH}_2\text{CH}_3$: δ 0.77).



The dynamics of ethylene rotation of **7** were probed by low-temperature NMR in CDCl_2F solution. At -115°C , the ^1H NMR spectrum of **7** contains four resonances (δ 5.41, 4.54, 3.94, 2.83), and the ^{13}C NMR contains two resonances (δ 93.7, 86.1) for the bound ethylene, indicating slow rotation. The ^1H ethylene signals at δ 4.54 and 3.94 coalesce at -90°C , giving $\Delta G_{\text{rot}}^\ddagger = 8.1 \text{ kcal mol}^{-1}$, similar to the value for **5**.

The equilibrium constant for ethylene coordination to **6** (eq 2), $K_{\text{eq}} = [\text{7}][\text{6}]^{-1}[\text{C}_2\text{H}_4]^{-1}$, was determined over the temperature range -80 to -35°C by ^1H NMR using the characteristic $(p\text{-tolyl})_3\text{SiCH}$ resonances of **6** and **7**. At -80°C , $K_{\text{eq}} = 430 \text{ M}^{-1}$. Thermodynamic parameters for this equilibrium were determined by a van't Hoff analysis and are listed in Table 1. Extrapolation of the van't Hoff plot to -10°C , the optimum ethylene oligomerization temperature, gives $K_{\text{eq}} = 2.8 \text{ M}^{-1}$.

NMR Monitoring of the Reaction of **5 with Excess Ethylene.** The **5**-catalyzed ethylene oligomerization reaction at -10°C in CD_2Cl_2 was monitored by ^1H NMR by periodically cold-quenching the reaction and collecting ^1H NMR spectra at -80°C . These spectra showed that a mixture of $\beta\text{-H}$ agostic higher secondary alkyl complexes (**8**, R = distribution of alkyl groups) and alkyl ethylene complexes (**9**, R' = distribution of alkyls groups) was present, as shown in Scheme 4. After the ethylene is consumed, the only Pd species in solution is **8**.

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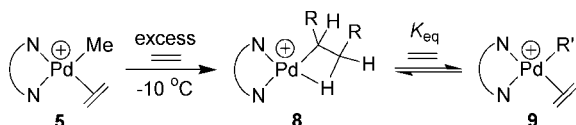
(9) Two diastereomers are possible for **6**, which differ in the relative configurations of the N^*N bridging carbon and the isopropyl methine carbon. Exchange of the agostic and nonagostic methyl groups by $\text{Pd}\text{-C}$ bond rotation interconverts the diastereomers of **6**. However, only one set of resonances is observed for **6** at all temperatures. It is likely that the NMR spectra of the two diastereomers are very similar due to the remoteness of the two stereocenters.

(10) The broad resonance at δ 4.26 integrates for 4H and results from the overlap of the two resonances expected for the bound ethylene, which, based on the low-temperature limit spectrum, have very similar chemical shifts ($\Delta\delta = 0.12$).

Table 1. Thermodynamic Parameters for Ethylene Coordination to $\{(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2\}\text{PdR}^+$ Species^a

	6 (R = ⁱ Pr) ^{b,c}	8 (R = alkyl) ^{d,e}
ΔH (kcal mol ⁻¹)	-7.4(5)	-5.8(3)
ΔS (cal mol ⁻¹ K ⁻¹)	-27(2)	-23(2)
ΔG_{293} (kcal mol ⁻¹) ^f	0.51	0.94
K_{eq} at -10 °C (M ⁻¹) ^g	2.8	0.72

^a Determined in CD₂Cl₂ solution. ^b Coordination of ethylene to **6** gives the *n*-propyl ethylene complex **7**. ^c Based on NMR data in the temperature range -80 to -35 °C. ^d R = distribution of oligoethylene chains. ^e Based on NMR data in the temperature range -80 to -40 °C. ^f ΔG evaluated at 293 K. ^g $K_{\text{eq}} = [(\text{N}^{\wedge}\text{N})\text{PdR}(\text{ethylene})^+]/[(\text{N}^{\wedge}\text{N})\text{PdR}^+][\text{ethylene}]$; determined by extrapolation of the van't Hoff plot.

Scheme 4

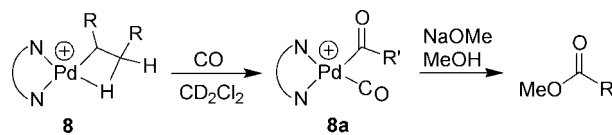
The ¹H NMR data for **8** are similar to those for isopropyl analogue **6**. The ¹H NMR chemical shifts (CD₂Cl₂, -80 °C) for the (*p*-tolyl)₃SiCH (δ 6.37), pz^{*}-H4 (6.04, 5.93) and agostic β -H (δ -9.50, m) units of **8** are very similar to those for **6**.¹¹ The alkyl region of the ¹H spectrum of **8** was challenging to assign because a distribution of alkyl chain lengths is present (vide infra). However, the -80 °C COSY spectrum contains correlations between the β -H agostic, terminal β -H (δ 0.42, m), and α -methine signals (δ 3.03, m), and these signals integrate in a 1/1/1 ratio, confirming the β -H agostic secondary alkyl structure.¹²

The NMR data for **9** are similar to those for the *n*-propyl analogue **7**. The ¹H NMR chemical shifts (CD₂Cl₂, -80 °C) for the (*p*-tolyl)₃SiCH (δ 6.69), pz^{*}-H4 (δ 6.08, 5.82), and bound ethylene (δ 4.15, br) units of **9** are very similar to those for **7**. The ¹H NMR spectrum of **9** in CDCl₃F solution at -120 °C contains four ethylene signals (δ 4.45, 3.91, 3.57, 2.75). The δ 3.91 and 3.57 resonances coalesce at -90 °C, giving $\Delta G_{\text{rot}}^\ddagger = 8.3$ kcal mol⁻¹, similar to the values for **5** and **7**.

The equilibrium constant for ethylene coordination to **8** (Scheme 4), $K_{\text{eq}} = [\mathbf{9}][\mathbf{8}]^{-1}[\text{C}_2\text{H}_4]^{-1}$, was determined by ¹H NMR from -80 to -40 °C, using the (*p*-tolyl)₃SiCH resonances for **8** and **9**. The thermodynamic parameters for this equilibrium are similar to the values for **6** and are listed in Table 1. K_{eq} is estimated to be 0.72 M⁻¹ at -10 °C, slightly lower than the value for **6**.

Characterization of Alkyl Chain Length Distribution in **8.** To determine alkyl chain length distribution in **8**, this species was reacted with CO and then NaOMe/MeOH to generate the corresponding distribution of methyl esters as shown in Scheme 5.¹³ GC-MS analysis showed that a distribution of C₅ to C₁₇ methyl esters formed. Multiple isomers were detected for each carbon number. These results are consistent with branching in the ethylene oligomers produced by **5** in Scheme 3.

Ethylene-*d*₄ Labeling Experiments. To confirm that **8** and **9** are involved in the catalytic ethylene oligomerization cycle,

Scheme 5

the reaction of **8** with ethylene-*d*₄ at -10 °C in CD₂Cl₂ was studied. The ¹H NMR spectrum (collected at -80 °C) showed that after 20 min at -10 °C the characteristic (*p*-tolyl)₃SiCH(pz^{*})₂ resonances for **8** and **9** were present, but the agostic β -H, terminal β -H, and methine C-H resonances of **8** and the ethylene resonance of **9** were absent. Upon subsequent reaction with unlabeled ethylene, the β -H agostic, terminal β -H, and methine C-H signals of **8** and the ethylene resonance of **9** appeared within 20 min. These results confirm that **8** and **9** are active growing species.

Catalyst Stability. The results above show that $\{(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2\}\text{Pd}^+$ species exist as an equilibrium mixture of **8** and **9** under catalytic ethylene oligomerization conditions. As noted above, fast catalyst decomposition to Pd⁰ occurs in ethylene oligomerization at 25 °C. However, CD₂Cl₂ solutions of **8** are very stable at 25 °C (<10% decomposition after 2 days). Therefore, the low catalyst stability must result from instability of **9**.

Dynamic Properties of (N[^]N)Pd Complexes. The ¹H NMR spectrum of $\{(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2\}\text{Pd}\{\text{C}(\text{=O})\text{Me}\}(\text{CO})^+$ (**4**) at -60 °C contains two sharp sets of pz^{*} signals, consistent with the expected inequivalence of the pz^{*} units. However, the pz^{*} resonances broaden and coalesce to one set as the temperature is raised; for example, the pz^{*}-H4 signals coalesce at -40 °C as shown in Figure 3. In contrast, the (*p*-tolyl)₃SiCH and Pd{C(=O)Me} resonances remain sharp under these conditions. Similarly, the ¹³C NMR spectrum of **4** exhibits broadening of the pz^{*} resonances but not the (*p*-tolyl)₃SiCH or Pd{C(=O)Me} signals at -40 °C. The bound and free CO signals remain sharp at -40 °C, indicating that exchange of free and coordinated CO is slow.¹⁴ These results show that **4** undergoes a dynamic process that exchanges the pz^{*} units but does not involve the Pd{C(=O)Me} unit and does not involve intermolecular CO exchange (eq 3).¹⁵

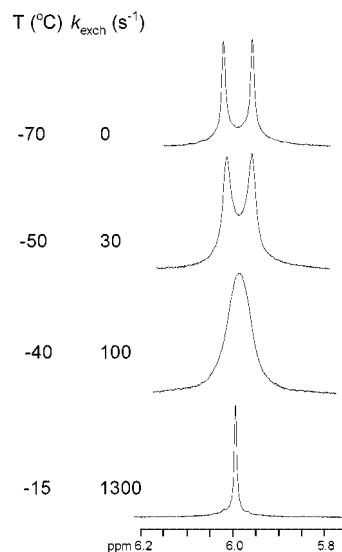


Figure 3. Variable-temperature ¹H NMR of **4** in CD₂Cl₂. The pz^{*}-H4 region is shown. The first-order rate constants for the pz^{*} exchange (k_{exch}) were determined by simulation of the observed spectra.

(11) Shultz, L. H.; Tempel, D. J.; Brookhart, M. *J. Am. Chem. Soc.* **2001**, *123*, 11539.

(12) The acetonitrile complex $[(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2]\text{Pd}(\text{R})(\text{MeCN})$ [**8b**] was generated to probe the alkyl chain distribution. However, reaction of MeCN with **8** in CD₂Cl₂ at -10 °C yields an equilibrium mixture of **8** and **8b** ($K_{\text{eq}} = [\mathbf{8b}][\mathbf{8}]^{-1}[\text{MeCN}]^{-1} = 240$ M⁻¹), from which little information about the alkyl chain distribution could be obtained.

(13) Liu, J.; Heaton, B. T.; Iggo, J. A.; Whyman, R. *Chem. Commun.* **2004**, 1326.

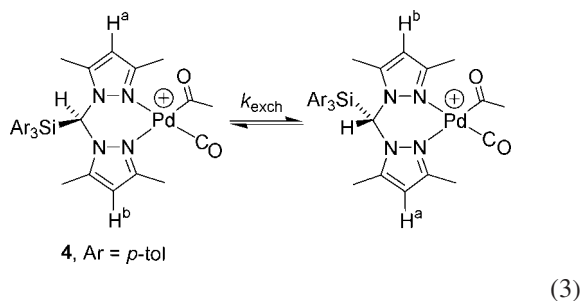
Table 2. Activation Parameters for pz^* Site Exchange in $\{(p\text{-tolyl})_3\text{SiCH}(pz^*)_2\}\text{Pd}$ Species Determined by Variable-Temperature NMR

complex	$\Delta G^\ddagger_{293}^a$ (kcal mol ⁻¹)	$\Delta H^\ddagger$ (kcal mol ⁻¹)	$\Delta S^\ddagger$ (cal mol ⁻¹ K ⁻¹)
3	17.8	21.7(6)	13(2)
4	11.0	9.2(3)	-6(2)
6	15.4		
7	11.4	7.2(4)	-14(2)
9	11.3	8.5(4)	-9(2)

^a $\Delta G^\ddagger$ evaluated at 293 K.

Activation parameters for the exchange were obtained from the variable-temperature ¹H NMR spectra and are listed in Table 2. Complex **8a** (Scheme 5), which contains a distribution of alkyl chains, also undergoes fast pz^* site exchange.¹⁶

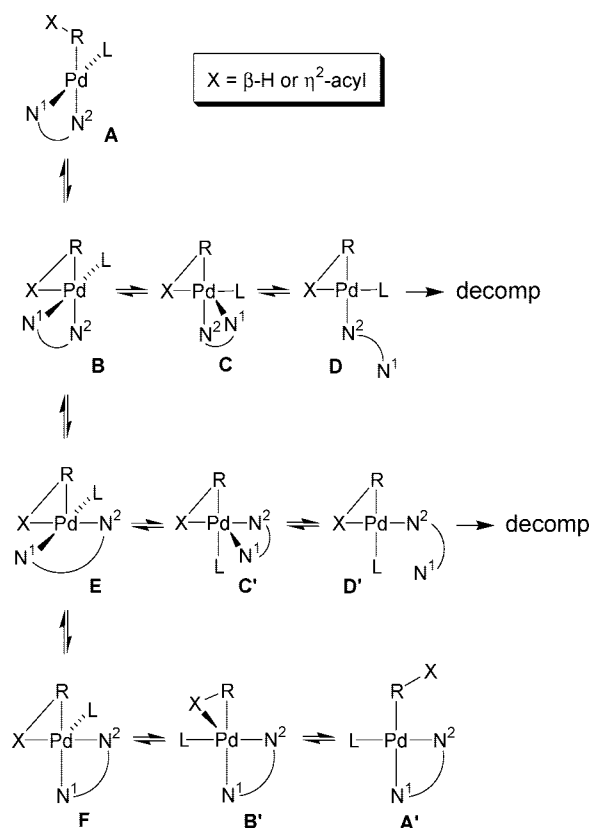
The alkyl ethylene complexes **7** and **9** also display selective



broadening of the pz^* signals, even at -80 °C, indicating that pz^* exchange is fast in these cases. The activation parameters for pz^* exchange for **7** and **9** are listed in Table 2 and are similar to those for **4**. The rate of pz^* exchange in **7** and **9** is independent of ethylene concentration over a wide range (**7**: 10–140 mM; **9**: 70–1340 mM). Therefore, pz^* exchange cannot be explained by intermolecular ethylene exchange.

In contrast, the other $\{(p\text{-tolyl})_3\text{SiCH}(pz^*)_2\}\text{Pd}$ species studied here undergo much slower (or no) pz^* exchange. The ¹H NMR spectrum of **3** (in 1,1,2,2-tetrachloroethane-*d*₂) contains two sharp sets of pz^* signals at 25 °C, but these resonances broaden as the temperature is raised, showing that slow pz^* exchange occurs. Activation parameters for pz^* exchange of **3** were determined from the coalescence of the $pz^*\text{-H4}$ resonances (δ 5.92, 5.58) and are listed in Table 2. The pz^* exchange barrier for **3**, $\Delta G^\ddagger_{298} = 17.8$ kcal mol⁻¹, is much higher than those for **4**, **7**, and **9**. EXSY spectra of **3** at 20 °C confirm that pz^* exchange occurs and show that the barrier is similar in CD₂Cl₂ ($\Delta G^\ddagger_{293} = 17.7$ kcal mol⁻¹) and THF-*d*₈ (17.9 kcal mol⁻¹). The absence of a significant solvent dependence of the barrier suggests that solvent coordination does not play a critical role in the pz^* exchange of **3**. Similarly, the ¹H NMR spectra of **8** (at 25 °C) and **5** (up to -40 °C; insertion occurs above this temperature) contain two sharp sets of pz^* signals characteristic of slow pz^* exchange.

Complex **6** undergoes pz^* exchange at an intermediate rate. The ¹H NMR spectra of **6** exhibit two sharp sets of pz^* signals

Scheme 6

up to 0 °C, but these resonances are selectively broadened at 20 °C. The barrier to pz^* exchange estimated from the excess line width is $\Delta G^\ddagger_{298} = 15.4$ kcal mol⁻¹ (Table 2).¹⁷

Mechanism of Pz^* Exchange and Relationship to Catalyst Stability. Interestingly, there is a qualitative correlation between the thermal stability and the barriers to pz^* site exchange of $\{(p\text{-tolyl})_3\text{SiCH}(pz^*)_2\}\text{Pd}$ species. Complexes **3** and **8** are very stable at 25 °C and exhibit very slow pz^* site exchange, while **4** and **9** are unstable at 25 °C and exhibit fast pz^* exchange rates. A common feature of the unstable, fast- pz^* -exchange species is that they contain a possible internal donor (either $\eta^2\text{-acyl}$ or agostic $\beta\text{-H}$),¹⁸ while the more stable, slow- pz^* -exchange species do not. These considerations suggest that catalyst decomposition and pz^* exchange both involve initial coordination of the internal donor. A reasonable mechanism that explains catalyst decomposition and pz^* exchange is shown in Scheme 6.

The key feature of Scheme 6 is the formation of a configurationally labile five-coordinate intermediate **B** by coordination of the internal donor *X* ($\beta\text{-H}$ agostic or $\eta^2\text{-acyl}$). **B** can isomerize (via trigonal bipyramidal intermediates that are not shown) to **C**, which contains a pz^* ligand in the axial site from which it can dissociate (**D**), ultimately leading to loss of the N²N¹ ligand and decomposition. **B** can also isomerize to **E** and then **C'**, leading to decomposition. Alternatively, **E** can isomerize to **F** and then **B'**, ultimately resulting in pz^* exchange (**A'**). A more complete mechanism showing the trigonal bipyramidal intermediates is given in the Supporting Information.

(14) Even if intermolecular CO exchange were fast on the NMR time scale, the pz^* site exchange would not be explained since associative CO exchange is expected to be stereospecific.

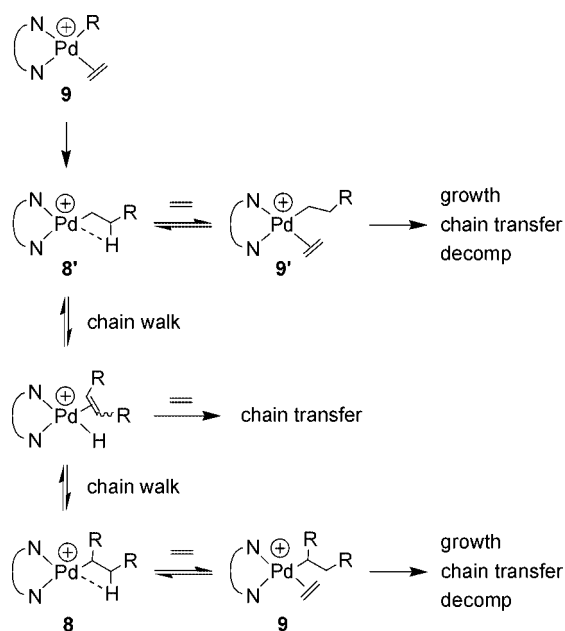
(15) A similar exchange process was noted for $\text{H}_2\text{C}(pz)_2\text{Pd}\{\text{C}(\text{=O})\text{Me}\}\text{CO}^+$ and $\text{H}_2\text{C}(3,5\text{-Me}_2\text{-pz})_2\text{Pd}\{\text{C}(\text{=O})\text{Me}\}\text{CO}^+$ but was not studied in detail. See ref 1a.

(16) The ¹H NMR spectrum of **8a** contains one broad resonance for the two $pz^*\text{-H4}$ hydrogens at -40 °C. The ¹³C NMR pz^* resonances are broadened into the baseline and the bound and free CO resonances are sharp at -40 °C. The results show that pz^* exchange is fast on the NMR time scale and does not involve intermolecular CO exchange at -40 °C.

(17) For **6** at 20 °C, the excess linewidth of the $pz^*\text{-H4/H4'}$ resonance is $\Delta\omega_{1/2} = 6$ Hz (relative to the $(p\text{-tolyl})_3\text{SiCH}$ resonance), and $k_{\text{exch}} = \pi\Delta\omega_{1/2} = 19$ s⁻¹.

(18) (a) Shultz, C. S.; DeSimone, J. M.; Brookhart, M. *J. Am. Chem. Soc.* **2001**, *123*, 9172. (b) Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *118*, 7337. (c) Svensson, M.; Matsubara, T.; Morokuma, K. *Organometallics* **1996**, *15*, 5568.

Scheme 7



Mechanism of Ethylene Oligomerization. The key observations pertaining to the mechanism of ethylene oligomerization by **5** are as follows: (i) **5** produces a distribution of branched internal olefins, (ii) the oligomer distribution is essentially independent of ethylene pressure, (iii) an equilibrium mixture of β -H agostic species **8** and ethylene adducts **9** is present under catalytic conditions, (iv) catalyst deactivation occurs rapidly at 25 °C with loss of the N[^]N ligand, and (v) **8** is stable at 25 °C, while **9** is unstable at 25 °C. A mechanism that is consistent with these results is shown in Scheme 7. The alkyl ethylene complex **9** undergoes insertion to generate the primary alkyl species **8'**. Species **8'** either is trapped by ethylene to yield a primary alkyl ethylene adduct **9'** or chain walks to generate a secondary alkyl species (**8**) and the corresponding ethylene adduct **9**. Species **9** and **9'** insert, resulting in chain growth, or decompose as described above. Chain transfer occurs by ethylene displacement of olefin from the (N[^]N)Pd(H)(olefin)⁺ chain-walk intermediates, or by β -H transfer to coordinated ethylene in **9** or **9'**.

Conclusion

The $\{(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2\}\text{Pd}(\text{Me})(\text{ethylene})^+$ cation (**5**) catalytically oligomerizes ethylene to branched C₆–C₂₀ internal olefins. NMR studies show that an equilibrium mixture of base-free β -agostic secondary alkyl (N[^]N)PdR⁺ species (**8**) and ethylene adducts (N[^]N)Pd(R)(ethylene)⁺ (**9**) is present under oligomerization conditions. At 20 °C, **9** undergoes fast site exchange of the pz^{*} rings and decomposes readily to Pd⁰, while **8** does not undergo pz^{*} site exchange and is stable. It is proposed that the decomposition and pz^{*} exchange of **9** both involve initial coordination of a β -H to generate a configurationally labile five-coordinate intermediate, which can isomerize, resulting in pz^{*} site exchange or displacement of one arm of the N[^]N ligand.

Experimental Section

General Considerations. All manipulations were performed using glovebox or Schlenk techniques under purified N₂. Nitrogen was purified by passage through columns containing activated molecular sieves and Q-5 oxygen scavenger. Pentane, hexanes, toluene, and benzene were purified by passage through

columns of activated alumina and BASF R3-11 oxygen scavenger. Diethyl ether and tetrahydrofuran were distilled from Na/benzophenone ketyl. Dichloromethane was distilled from P₂O₅. Cl₂DCCl₂, CDCl₃, and CD₂Cl₂ were distilled from CaH₂ or P₂O₅. CDCl₂F was prepared according to the literature and distilled from P₂O₅.¹⁹ CO was purchased from Aldrich and used as received. Ethylene (research grade) was obtained from Matheson and used as received. [Li(Et₂O)_{2.8}][B(C₆F₅)₄] was obtained from Boulder Scientific and used as received. The Et₂O content of the [Li(Et₂O)_{2.8}][B(C₆F₅)₄] salt was determined by ¹H NMR with C₆Me₆ as an internal standard. (MeCN)₂PdCl₂ was obtained from Strem and used as received. The compounds (pz^{*})₂CH₂ (pz^{*} = 3,5-Me₂-pyrazole),²⁰ (*p*-tolyl)₃SiCl,²¹ (*p*-tolyl)₃SiOSO₂CF₃,²² and (cod)Pd(Me)Cl²³ were prepared as described in the literature. All other chemicals were purchased from standard suppliers and used without further purification.

Elemental analyses were performed by Midwest Microlabs (Indianapolis, IN). Infrared spectra were obtained at 25 °C under an N₂ atmosphere using a Nicolet NEXUS 470 FT-IR spectrometer. GC-MS analyses were performed on a HP-6890 instrument equipped with a HP-5973 mass selective detector.

NMR spectra were recorded in Teflon-valved NMR tubes on Bruker DRX-400 or -500 spectrometers at ambient probe temperature unless otherwise indicated. ¹H and ¹³C chemical shifts are reported versus SiMe₄ and were determined by reference to the residual solvent peaks. ¹⁹F and ¹¹B chemical shifts were referenced to external neat CFCl₃ and BF₃·Et₂O, respectively. Coupling constants are reported in Hz. NMR probe temperatures were calibrated by a MeOH thermometer.²⁴ For variable-temperature NMR experiments, the probe was maintained at a given temperature for 20–30 min to allow the sample to reach thermal equilibrium.

The NMR spectra of cationic Pd compounds contain signals of the free B(C₆F₅)₄[−] anion. ¹³C{¹H} NMR (CD₂Cl₂, −60 °C): δ 147.5 (dm, *J* = 241, C2), 137.8 (dm, *J* = 238, C4), 135.8 (dm, *J* = 249, C3), 123.6 (br, C1). ¹¹B NMR (CD₂Cl₂, −60 °C): δ −16.9 (s). ¹⁹F NMR (CD₂Cl₂, −60 °C): δ −133.7 (br s, 2F, *o*-F), −163.0 (t, *J* = 23, 1F, *p*-F), −167.0 (t, *J* = 19, 2F, *m*-F). Solutions of cationic species generated in situ from the reaction of **2** and [Li(Et₂O)_{2.8}][B(C₆F₅)₄] contain LiCl and free Et₂O. In some experiments the Et₂O was used as an internal standard in NMR experiments.

(pz^{*})₂CHSi(*p*-tolyl)₃ (1). A solution of (3,5-Me₂-pz)₂CH₂ (0.727 g, 3.56 mmol) in THF (75 mL) was cooled to −78 °C, and ⁿBuLi (2.66 M in hexanes, 1.40 mL, 3.74 mmol) was added over 5 min while the mixture was stirred. A white precipitate formed. The mixture was stirred at −78 °C for 1 h. A solution of (*p*-tolyl)₃SiOTf (1.68 g, 3.74 mmol) in THF (30 mL) cooled to −78 °C was added by cannula. The resulting yellow solution was stirred at −78 °C for 2 h, allowed to warm to 25 °C, and stirred for 12 h. The yellow mixture was quenched with saturated aqueous NH₄Cl (150 mL) and extracted with CH₂Cl₂ (3 × 75 mL). The clear yellow CH₂Cl₂ extract was washed with aqueous 10% Na₂CO₃ (200 mL), saturated aqueous NaHCO₃ (200 mL), and H₂O (200 mL) and finally dried over MgSO₄. The solvent

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(22) Asadi, A.; Avent, A. G.; Eaborn, C.; Hill, M. S.; Hitchcock, P. B.; Meehan, M. M.; Smith, J. D. *Organometallics* **2002**, *21*, 2183.

(23) Rülke, R. E.; Ernsting, J. M.; Spek, A. L.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K. *Inorg. Chem.* **1993**, *32*, 5769.

(24) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679.

was removed under vacuum. The resulting white solid was purified by column chromatography using neutral alumina, eluting with pentane (150 mL) and then pentane/CH₂Cl₂ (1:1 v/v, 150 mL). The second fraction was dried over MgSO₄ and taken to dryness under vacuum to afford a white solid (1.38 g, 77%). ¹H NMR (CDCl₃): δ 7.38 (m, 6H, 4-Me-C₆H₄), 7.07 (m, 6H, 4-Me-C₆H₄), 6.64 (s, 1H, CH), 5.68 (s, 2H, pz* H4), 2.31 (s, 9H, 4-Me-C₆H₄), 2.08 (s, 6H, pz*-Me), 1.78 (s, 6H, pz*-Me). ¹³C{¹H} NMR (CDCl₃): δ 146.3, 140.1, 139.2, 136.8, 128.9, 128.2, 106.4, 67.8, 21.5, 13.4, 10.9. Anal. Calcd for C₃₂H₃₆N₄Si: C, 76.15; H, 7.19; N, 11.10. Found: C, 75.76; H, 7.27; N, 10.57.

{(p-tolyl)₃SiCH(pz*)₂}PdCl₂ (2). A solution of (MeCN)₂PdCl₂ (0.259 g, 1.00 mmol) and (3,5-Me₂-pz)₂CHSi(p-tolyl)₃ (0.530 g, 1.05 mmol) in CH₂Cl₂ (25 mL) was stirred for 2 h at 25 °C. The orange solution was taken to dryness under vacuum. The resulting orange solid was suspended in Et₂O (25 mL), stirred for 30 min, and collected by filtration. The solid was washed with pentane (20 mL) and dried under vacuum to yield **2** as an orange powder (0.587 g, 86%). ¹H NMR (CDCl₃): δ 7.45 (m, 6H, 4-Me-C₆H₄), 7.18 (m, 6H, 4-Me-C₆H₄), 6.58 (s, 1H, CH), 5.77 (s, 2H, pz* H4), 2.54 (s, 6H, pz* 5-Me), 2.35 (s, 9H, 4-Me-C₆H₄), 1.96 (s, 6H, pz* 3-Me). ¹³C{¹H} NMR (CDCl₃): δ 153.9, 141.3, 140.4, 137.0, 129.5, 125.0, 108.0, 65.4, 21.7, 15.6, 11.7. Anal. Calcd for C₃₂H₃₆Cl₂N₄PdSi: C, 56.35; H, 5.32; N, 8.21. Found: C, 56.40; H, 5.31; N, 8.10.

{(p-tolyl)₃SiCH(pz*)₂}PdMeCl (3). A flask was charged with (cod)PdMeCl (0.265 g, 1.00 mmol) and (3,5-Me₂-pz)₂CHSi(p-tolyl)₃ (0.510 g, 1.01 mmol), and Et₂O (15 mL) was added by syringe at 25 °C. A white precipitate formed rapidly. The mixture was stirred at 25 °C for 4 h, and the solid was collected by filtration. The solid was washed with Et₂O (2 × 10 mL), washed with pentane (10 mL), and dried under vacuum to yield a white solid (0.499 g, 75%). The isolated solid contained 0.12 equiv of Et₂O, which was quantified by ¹H NMR. ¹H NMR (CD₂Cl₂): δ 7.34 (m, 6H, 4-Me-C₆H₄), 7.14 (m, 6H, 4-Me-C₆H₄), 6.58 (s, 1H, CH), 5.92 (s, 1H, pz* H4/H4'), 5.63 (s, 1H, pz* H4/H4'), 2.38 (s, 3H, pz* Me), 2.30 (s, 9H, 4-Me-C₆H₄), 2.15 (s, 3H, pz* Me), 2.15 (s, 3H, pz* Me), 1.92 (s, 3H, pz* Me), -0.25 (s, 3H, PdMe). ¹³C{¹H} NMR (CD₂Cl₂): δ 151.0 (3/3'-pz*), 150.4 (3/3'-pz*), 140.5, 140.2 (5/5'-pz*), 138.6 (5/5'-pz*), 136.5, 128.7, 126.0, 107.0 (4/4'-pz*), 106.0 (4/4'-pz*), 63.3 (CH), 21.2 (4-Me-C₆H₄), 14.9 (pz* Me), 13.6, (pz* Me), 11.7 (pz* Me), 11.6 (pz* Me), -6.5 (PdMe). Anal. Calcd for C₃₃H₃₉ClN₄PdSi · 0.12Et₂O: C, 59.97; H, 5.99; N, 8.36. Found: C, 59.70; H, 6.05; N, 8.35.

Generation of {(p-tolyl)₃SiCH(pz*)₂}Pd{C(=O)Me}-(CO)][B(C₆F₅)₄] (4). A valved NMR tube containing a CD₂Cl₂ (0.7 mL) solution of **2** (0.020 g, 0.030 mmol) and [Li(Et₂O)_{2.8}][B(C₆F₅)₄] (0.027 g, 0.030 mmol) was cooled to -196 °C and exposed to CO (1 atm) for 5 min. The tube was sealed and warmed to -78 °C. The tube was briefly warmed to 23 °C and vigorously shaken. A slurry of a white solid in a colorless supernatant was obtained. The tube was kept at -78 °C and transferred to a precooled (-60 °C) NMR probe, and NMR spectra were recorded. The ¹H NMR spectrum established that **4** had formed (100% vs Et₂O). ¹H NMR (CD₂Cl₂, -60 °C): δ 7.22 (m, 6H, 4-Me-C₆H₄), 7.17 (m, 6H, 4-Me-C₆H₄), 6.50 (s, 1H, CH), 6.00 (s, 1H, pz* H4/H4'), 5.92 (s, 1H, pz* H4/H4'), 2.60 (s, 3H, COMe), 2.34 (s, 9H, 4-Me-C₆H₄), 2.18 (s, 3H, pz* Me), 2.12 (s, 3H, pz* Me), 2.09 (s, 3H, pz* Me), 1.77 (s, 3H, pz* Me). ¹³C{¹H} NMR (CD₂Cl₂, -60 °C): δ 210.7 (C(O)Me), 171.3 (PdCO), 151.8 (3/3'-pz*), 150.6 (3/3'-pz*), 142.9 (5/5'-pz*), 142.3, 141.9 (5/5'-pz*), 137.0, 129.3, 123.5,

108.2 (4/4'-pz*), 107.7 (4/4'-pz*), 63.1 (CH), 43.7 (COMe), 21.5 (4-Me-C₆H₄), 15.3, 14.4, 11.8, 11.2; the free CO resonance appears at δ 184.3. IR (CD₂Cl₂, cm⁻¹): 2122 (ν_{CO}), 1746 (ν_{acyl}).

Generation of {(p-tolyl)₃SiCH(pz*)₂}PdMe(H₂C=CH₂)-[B(C₆F₅)₄] (5). A valved NMR tube containing a CD₂Cl₂ (0.7 mL) solution of **2** (0.013 g, 0.020 mmol) and [Li(Et₂O)_{2.8}][B(C₆F₅)₄] (0.018 g, 0.020 mmol) was cooled to -196 °C, and ethylene (0.18 mmol) was added by vacuum transfer. The tube was sealed, warmed to -78 °C, and transferred to a precooled (-60 °C) NMR probe, and NMR spectra were recorded at -60 °C. The ¹H NMR spectrum established that **5** had formed (100% vs Et₂O after 20 min). Under these conditions (-60 °C), exchange of coordinated and free ethylene is slow, but rotation of the bound ethylene is fast on the NMR chemical shift time scale. ¹H NMR (CD₂Cl₂, -60 °C): δ 7.21 (m, 6H, 4-Me-C₆H₄), 7.06 (m, 6H, 4-Me-C₆H₄), 6.59 (s, 1H, CH), 6.06 (s, 1H, pz* H4/H4'), 5.85 (s, 1H, pz* H4/H4'), 4.38 (m, 2H, H₂C=CH₂), 4.15 (br m, 2H, H₂C=CH₂), 2.34 (s, 9H, 4-Me-C₆H₄), 2.32 (s, 3H, pz* Me), 2.07 (s, 3H, pz* Me), 2.04 (s, 3H, pz* Me), 1.82 (s, 3H, pz* Me), 0.38 (s, 3H, PdMe). ¹³C{¹H} NMR (CD₂Cl₂, -60 °C): δ 151.5 (3/3'-pz*), 150.6 (3/3'-pz*), 142.0 (5/5'-pz*), 141.9, 141.1 (5/5'-pz*), 136.2, 129.3, 124.1, 108.2 (4/4'-pz*), 108.1 (4/4'-pz*), 87.5 (br, H₂C=CH₂), 63.3 (CH), 21.3 (4-Me-C₆H₄), 14.9, 12.6, 11.7, 11.3, 7.0 (PdMe). A solution of **5** in CDCl₂F was generated as described above and analyzed by variable-temperature (-60 °C to -120 °C) NMR. ¹H NMR (CDCl₂F, -120 °C): δ 5.21 (br m, H₂C=CH₂), 4.54 (br m, H₂C=CH₂), 4.26 (br m, H₂C=CH₂), 2.86 (br m, H₂C=CH₂). ¹³C{¹H} NMR (CDCl₂F, -120 °C): δ 92.1 (br, H₂C=CH₂), 83.6 (br, H₂C=CH₂).²⁵ The rotational barrier Δ*G*_{rot} = 8.2 kcal mol⁻¹ was obtained from the coalescence of the δ 4.54 and 4.26 resonances, using the coalescence approximation ($k = \pi(\nu_a - \nu_b)/2^{1/2}$; $k_{\text{rot}} = 310 \text{ s}^{-1}$ at $T_{\text{coalescence}} = -105 \text{ }^{\circ}\text{C}$).²⁶

Kinetics of Insertion of {(p-tolyl)₃SiCH(pz*)₂}PdMe-(H₂C=CH₂)-[B(C₆F₅)₄] (5). A CD₂Cl₂ solution of **5** containing free ethylene (280 mM) was generated in a valved NMR tube as described above and maintained at -10 °C. Periodically the tube was cold-quenched in a -78 °C bath for 5 min and transferred to a precooled (-60 °C) NMR probe, where a ¹H NMR spectrum was recorded. Values of *I*_{0,PdMe}, *I*_{PdMe}, and *I*_{Et₂O} where *I*_{0,PdMe} = the integral of the Pd-Me resonance of **5** at the start of the experiment, *I*_{PdMe} = the integral of the Pd-Me resonance at time point, and *I*_{Et₂O} = the integral of the Et₂O internal standard, were obtained. A plot of ln(*A*_{PdMe}/*A*_{0,PdMe}), where *A*_{PdMe} = *I*_{PdMe}/*I*_{Et₂O} and *A*_{0,PdMe} = *I*_{0,PdMe}/*I*_{Et₂O}, versus time was linear (*r*² = 0.996). The slope of the line equals -*k*_{insert,Me}. For **5**, *k*_{insert,Me} = 3.3(3) × 10⁻³ s⁻¹ at -10 °C (~3 half-lives). An identical result was obtained for [free H₂C=CH₂] = 110 mM, which shows that the insertion rate is zero-order in ethylene.

Low-Pressure Oligomerization of Ethylene by {(p-tolyl)₃SiCH(pz*)₂}PdMe(H₂C=CH₂)-[B(C₆F₅)₄] (5). A 200 mL Fischer-Porter bottle equipped with a magnetic stir bar was charged with **2** (0.020 g, 0.030 mmol) and [Li(Et₂O)_{2.8}][B(C₆F₅)₄] (0.027 g, 0.030 mmol). The bottle was attached to a stainless steel double-manifold vacuum/ethylene line, placed under vacuum to remove the nitrogen atmosphere, and then charged with ethylene (3 atm). The bottle was cooled (-78 °C) and vented to decrease the ethylene pressure to 1 atm, and CH₂Cl₂ (20 mL) was added by syringe. The ethylene pressure was immediately

(25) The pz* and (p-tolyl)₃SiCH resonances do not shift or broaden significantly due to temperature or solvent.

(26) The other two ethylene ¹H NMR resonances (δ 5.42, 2.86) were broadened into the baseline at -105 °C.

increased 3 atm, and the solution was warmed to the desired temperature and stirred for 18 h, during which time the total pressure was kept constant (3 atm) by feeding ethylene on demand. The ethylene feed was turned off and the reactor was vented. In the $-10\text{ }^{\circ}\text{C}$ experiments, the product mixture was a slurry of a white solid in a pale yellow supernatant. In the room-temperature experiments, the product mixture was a slurry of a black solid in a yellow supernatant. Toluene (50 μL , for use as an internal standard) was added when the pressure reached 1 atm. An aliquot (ca. 200 μL) of the mixture was filtered through a small pad of silica with 2-methylbutane (3 mL) as the eluent. The filtrate was analyzed by quantitative GC-MS to determine the oligomer distribution. A solution of HCl in MeOH (1 M, 5 mL) was added to the remainder of the mixture, and the mixture was taken to dryness under vacuum. The residue was taken up in hexanes (20 mL) and filtered through a plug of silica gel. The solvent was removed under vacuum to afford a mixture of C_{12} – C_{20} oligomers, which was characterized by GC-MS. ^1H NMR (CDCl_3): δ 5.36 (m, $\text{RHC}=\text{CHR}'$), 5.08 (br s, $\text{RR}'\text{C}=\text{CHR}''$), 1.98 (m, allylic H), 1.60 ($\text{H}_3\text{CRC}=\text{CR}'\text{R}''$), 1.25 (CH_2 , CH), 0.83 (m, CH_3). The branch number (39 branches/ 10^3 C) carbons was determined by ^1H NMR.^{27,28}

High-Pressure Oligomerization of Ethylene by $[(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2]\text{PdMe}(\text{H}_2\text{C}=\text{CH}_2)[\text{B}(\text{C}_6\text{F}_5)_4]$ (5). An autoclave was charged with **2** (0.020 g, 0.030 mmol) and $[\text{Li}(\text{Et}_2\text{O})_{2.8}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.027 g, 0.030 mmol), CH_2Cl_2 (20 mL) was added by syringe, and the autoclave was pressurized with ethylene (30 atm) that was fed on demand. The mixture was stirred for 18 h at $25\text{ }^{\circ}\text{C}$. The autoclave was vented and toluene (50 μL , for use as an internal standard) was added when the pressure reached 1 atm. The product mixture was a slurry of a black solid in a yellow supernatant. An aliquot (ca. 200 μL) of the mixture was filtered through a small pad of silica with 2-methylbutane (3 mL) as the eluent. This solution was analyzed by quantitative GC-MS to determine the oligomer distribution. A solution of HCl in MeOH (1 M, 5 mL) was added to the remainder of the mixture, and the mixture was taken to dryness under vacuum. The residue was taken up in hexanes (20 mL) and filtered through a plug of silica gel. The solvent was removed under vacuum to afford a mixture of C_{12} – C_{20} oligomers (0.045 g), which was characterized by GC-MS.

Generation of $[(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2]\text{PdCHMeCH}_2\text{-}\mu\text{-H}[\text{B}(\text{C}_6\text{F}_5)_4]$ (6). A valved NMR tube containing a CDCl_2F (0.6 mL) solution of **2** (13 mg, 0.020 mmol) and $[\text{Li}(\text{Et}_2\text{O})_{2.8}][\text{B}(\text{C}_6\text{F}_5)_4]$ (18 mg, 0.020 mmol) was cooled to $-196\text{ }^{\circ}\text{C}$, and ethylene (0.020 mmol) was added by vacuum transfer. The solution was thawed at $-78\text{ }^{\circ}\text{C}$, warmed to $0\text{ }^{\circ}\text{C}$ for 30 min, cooled to $-78\text{ }^{\circ}\text{C}$, and transferred to a precooled ($-115\text{ }^{\circ}\text{C}$) NMR probe, and NMR spectra were recorded. The NMR spectra established that **6** had formed (100% vs Et_2O). ^1H NMR (CDCl_2F , $-115\text{ }^{\circ}\text{C}$): δ 7.27–7.15 (br m, 12H, 4-Me- C_6H_4), 6.45 (s, 1H, CH), 6.05 (s, 1H, $\text{pz}^*\text{H4/H4}'$), 5.92 (s, 1H, $\text{pz}^*\text{H4/H4}'$), 3.31 (m, 1H, $\text{PdCHMeCH}_2\text{-}\mu\text{-H}$), 2.35 (s, 9H, 4-Me- C_6H_4), 2.31 (s, 3H, pz^*Me), 2.19 (s, 3H, pz^*Me), 2.11 (s, 3H, pz^*Me), 1.71 (s, 3H, pz^*Me), 0.85 (m, 1H, $\text{PdCHMeCH}_2\text{-}\mu\text{-H}$), 0.77 (d, $J = 6\text{ Hz}$, 3H, $\text{PdCHMeCH}_2\text{-}\mu\text{-H}$), -0.04 (m, 1H, $\text{PdCHMeCH}_2\text{-}\mu\text{-H}$), -8.91 (t, $J = 18\text{ Hz}$, 1H, $\text{PdCHMeCH}_2\text{-}\mu\text{-H}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_2F , $-115\text{ }^{\circ}\text{C}$): δ 151.8 ($3/3'\text{-pz}^*$), 149.5 ($3/3'\text{-pz}^*$), 142.6 ($5/5'\text{-pz}^*$), 141.9 ($5/5'\text{-pz}^*$), 140.9, 136.9, 129.3, 124.3, 108.0

($4/4'\text{-pz}^*$), 106.7 ($4/4'\text{-pz}^*$), 63.3 (CH), 43.9 ($\text{PdCHMeCH}_2\text{-}\mu\text{-H}$), 21.3 (4-Me- C_6H_4), 20.7 ($\text{PdCHMeCH}_2\text{-}\mu\text{-H}$), 14.7, 14.3, 14.2 (br s, $\text{PdCHMeCH}_2\text{-}\mu\text{-H}$), 11.7, 10.8. Key ^1H – ^1H COSY correlations (CDCl_2F , $-115\text{ }^{\circ}\text{C}$): δ 3.31 ($\text{PdCHMeCH}_2\text{-}\mu\text{-H}$) coupled to δ 0.85 ($\text{PdCHMeCH}_2\text{-}\mu\text{-H}$), 0.77 ($\text{PdCHMeCH}_2\text{-}\mu\text{-H}$), and 0.04 ($\text{PdCHMeCH}_2\text{-}\mu\text{-H}$); δ 0.85 ($\text{PdCHMeCH}_2\text{-}\mu\text{-H}$) coupled to δ 0.04 ($\text{PdCHMeCH}_2\text{-}\mu\text{-H}$); δ 0.85 and 0.04 ($\text{PdCHMeCH}_2\text{-}\mu\text{-H}$) coupled to δ 0.77 ($\text{PdCHMeCH}_2\text{-}\mu\text{-H}$) and δ -8.90 ($\text{PdCHMeCH}_2\text{-}\mu\text{-H}$). The solution of **6** in CDCl_2F was warmed to $0\text{ }^{\circ}\text{C}$, and broadening of the $\text{PdCHMeCH}_2\text{-}\mu\text{-H}$ resonances was observed. ^1H NMR (CDCl_2F , $0\text{ }^{\circ}\text{C}$): δ 7.18 (m, 6H, 4-Me- C_6H_4), 7.07 (m, 6H, 4-Me- C_6H_4), 6.63 (s, 1H, CH), 6.03 (s, 1H, $\text{pz}^*\text{H4/H4}'$), 5.92 (s, 1H, $\text{pz}^*\text{H4/H4}'$), 3.09 (s, 1H, $\text{PdCHMeCH}_2\text{-}\mu\text{-H}$), 2.36 (s, 9H, 4-Me- C_6H_4), 2.32 (s, 3H, pz^*Me), 2.18 (s, 3H, pz^*Me), 2.09 (s, 3H, pz^*Me), 1.80 (s, 3H, pz^*Me), -2.10 (br, ca. 5H, $\text{PdCHMeCH}_2\text{-}\mu\text{-H}$). ^{13}C NMR (CDCl_2F , $0\text{ }^{\circ}\text{C}$): δ 152.3 ($3/3'\text{-pz}^*$), 142.7 ($3/3'\text{-pz}^*$), 141.8 ($5/5'\text{-pz}^*$), 141.5 ($5/5'\text{-pz}^*$), 136.5, 129.9, 124.3, 107.9 ($4/4'\text{-pz}^*$), 106.7 ($4/4'\text{-pz}^*$), 63.5 (CH), 43.7 ($\text{PdCHMeCH}_2\text{-}\mu\text{-H}$), 20.7 (4-Me- C_6H_4), 14.1, 13.9, 11.0, 10.1; the $\text{PdCHMeCH}_2\text{-}\mu\text{-H}$ and $\text{PdCHMeCH}_2\text{-}\mu\text{-H}$ were not observed.

Generation of $[(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2]\text{Pd}(\text{CH}_2\text{CH}_2\text{CH}_3)(\text{H}_2\text{C}=\text{CH}_2)[\text{B}(\text{C}_6\text{F}_5)_4]$ by Reversible Ethylene Coordination (7). A valved NMR tube containing a CD_2Cl_2 (0.6 mL) solution of **6** (0.020 mmol) was cooled to $-196\text{ }^{\circ}\text{C}$, and ethylene (0.020 mmol) was added by vacuum transfer. The sample was warmed to $-60\text{ }^{\circ}\text{C}$ for 1 h and placed in a precooled ($-80\text{ }^{\circ}\text{C}$) NMR probe, and NMR spectra were recorded. The spectra showed that an equilibrium mixture of **6**, **7**, and free ethylene had formed. The equilibrium constant, $K_{\text{eq}} = [\text{7}][\text{6}]^{-1}[\text{H}_2\text{C}=\text{CH}_2]^{-1}$, was determined by ^1H NMR from -80 to $-35\text{ }^{\circ}\text{C}$ using the integrals of the (*p*-tolyl) SiCH resonances for **6** and **7** and the free ethylene resonance, referenced to the Et_2O internal standard. $K_{\text{eq}} = 430\text{ M}^{-1}$ at $-80\text{ }^{\circ}\text{C}$; $\Delta H = -7.4(5)\text{ kcal mol}^{-1}$ and $\Delta S = -27(2)\text{ eu}$. The equilibrium expression was confirmed by two experiments in which $[\text{Pd}]$ and $[\text{H}_2\text{C}=\text{CH}_2]$ were varied. ^1H NMR (CD_2Cl_2 , $-80\text{ }^{\circ}\text{C}$): δ 7.26 (m, 6H, 4-Me- C_6H_4), 7.09 (m, 6H, 4-Me- C_6H_4), 6.70 (s, 1H, CH), 6.13 (s, 1H, $\text{pz}^*\text{H4/H4}'$), 5.90 (s, 1H, $\text{pz}^*\text{H4/H4}'$), 4.26 (br m, 4H, $\text{H}_2\text{C}=\text{CH}_2$), 2.39 (s, 12H, 4-Me- C_6H_4 and pz^*Me), 2.04 (pz^*Me), 1.94 (m, 2H, $\text{PdCH}_2\text{CH}_2\text{CH}_3$), 1.72 (s, 4H, pz^*Me and $\text{PdCH}_2\text{CH}_2\text{CH}_3$), 0.77 (m, 4H, $\text{PdCH}_2\text{CH}_2\text{CH}_3$ and $\text{PdCH}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , $-80\text{ }^{\circ}\text{C}$): δ 150.5 ($3/3'\text{-pz}^*$), 148.6 ($3/3'\text{-pz}^*$), 142.2 ($5/5'\text{-pz}^*$), 142.1, 140.9 ($5/5'\text{-pz}^*$), 136.7, 129.5, 124.8, 108.3 ($4/4'\text{-pz}^*$), 107.8 ($4/4'\text{-pz}^*$), 64.0 (CH), 28.9 ($\text{PdCH}_2\text{CH}_2\text{CH}_3$), 23.7 ($\text{PdCH}_2\text{CH}_2\text{CH}_3$), 21.6 (4-Me- C_6H_4), 15.1, 14.6, 12.7 ($\text{PdCH}_2\text{CH}_2\text{CH}_3$), 12.3, 11.2. Key ^1H – ^1H COSY interactions (CD_2Cl_2 , $-80\text{ }^{\circ}\text{C}$): δ 1.72 ($\text{PdCH}_2\text{CH}_2\text{CH}_3$) coupled to δ 0.77 ($\text{PdCH}_2\text{CH}_2\text{CH}_3$) and 1.94 ($\text{PdCH}_2\text{CH}_2\text{CH}_3$); δ 1.94 ($\text{PdCH}_2\text{CH}_2\text{CH}_3$) coupled to δ 0.77 ($\text{PdCH}_2\text{CH}_2\text{CH}_3$). A solution of **7** in CDCl_2F was generated as described above, and variable-temperature (-80 to $-115\text{ }^{\circ}\text{C}$) NMR experiments were conducted. ^1H NMR (CDCl_2F , $-115\text{ }^{\circ}\text{C}$): δ 5.41 (br m, $\text{H}_2\text{C}=\text{CH}_2$), 4.54 (br m, $\text{H}_2\text{C}=\text{CH}_2$), 3.94 (br m, $\text{H}_2\text{C}=\text{CH}_2$), 2.83 (br m, $\text{H}_2\text{C}=\text{CH}_2$). $^{13}\text{C}\{^1\text{H}\}$ (CDCl_2F , $-115\text{ }^{\circ}\text{C}$): δ 93.7 (br, $\text{H}_2\text{C}=\text{CH}_2$), 86.1 (br, $\text{H}_2\text{C}=\text{CH}_2$).⁸ The rotational barrier $\Delta G_{\text{rot}}^\ddagger = 8.1\text{ kcal mol}^{-1}$ was obtained from the coalescence of the δ 4.54 and 3.94 resonances, using the coalescence approximation ($k_{\text{rot}} = 670\text{ s}^{-1}$ at $T_{\text{coalescence}} = -90\text{ }^{\circ}\text{C}$).³⁰

(27) Daugulis, O.; Brookhart, M.; White, P. S. *Organometallics* **2002**, 21, 5935.

(28) The oligomer mixtures were hydrogenated (MeOH, 1 atm of H_2 , 10% Pd/C). GC-MS analysis of the product showed that a mixture of branched alkanes was formed.

(29) The integral is lower than expected due to peak broadness; $\Delta\nu_{1/2} = 250\text{ Hz}$.

(30) The other two bound ethylene ^1H NMR resonances (δ 5.41, 2.83) were broadened into the baseline at $-90\text{ }^{\circ}\text{C}$.

Generation of $[(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2]\text{PdCHRCHR-}\mu\text{-H}][\text{B}(\text{C}_6\text{F}_5)_4]$ (8b**, **R** = alkyl).** A valved NMR tube containing a CH_2Cl_2 (0.6 mL) solution of **2** (13 mg, 0.020 mmol) and $[\text{Li}(\text{Et}_2\text{O})_{2.8}][\text{B}(\text{C}_6\text{F}_5)_4]$ (18 mg, 0.020 mmol) was cooled to -196°C , and ethylene (1.1 mmol) was added by vacuum transfer. The solution was warmed to -10°C for 6 h. The volatiles were removed under vacuum to yield a brown oily residue, which was washed with pentane (3×2 mL). The tube was evacuated and CD_2Cl_2 (0.6 mL) was added by vacuum transfer at -78°C . The tube was transferred to a precooled (-80°C) probe and spectra were recorded. The spectra established that **8** had formed in essentially quantitative yield. ^1H and $^1\text{H}\text{-}^1\text{H}$ COSY NMR experiments established that **8** comprises a mixture of species with a distribution of $\beta\text{-H}$ agostic secondary alkyl complexes. The distribution of alkyl chains was established by methanolysis of the acyl complex **8a** described below. Key data for **8**: ^1H NMR (CD_2Cl_2 ; -80°C): δ 7.16 (m, 6H, 4-Me- C_6H_4), 6.97 (m, 6H, 4-Me- C_6H_4), 6.37 (s, 1H, CH), 6.04 (s, 1H, pz^* H4/H4'), 5.93 (s, 1H, pz^* H4/H4'), 3.03 (m, 1H, PdCHRCHR- $\mu\text{-H}$), 2.33 (s, 9H, 4-Me of 4-Me- C_6H_4), 2.29 (s, 3H, pz^* Me), 2.13 (s, 3H, pz^* Me), 2.06 (s, 3H, pz^* Me), 1.69 (s, 3H, pz^* Me), 0.42 (m, 1H, PdCHRCHR- $\mu\text{-H}$), -9.50 (m, 1H, PdCHRCHR- $\mu\text{-H}$). $^1\text{H}\text{-}^1\text{H}$ COSY correlations: Pd(CH-CH(R)- $\mu\text{-H}$)(R) to Pd(CHCH(R)- $\mu\text{-H}$)(R) and Pd(CHCH(R)- $\mu\text{-H}$)(R) to Pd(CHCH(R)- $\mu\text{-H}$)(R). $^{13}\text{C}\{^1\text{H}\}$ NMR CD_2Cl_2 ; -80°C): δ 151.9 (3/3'- pz^*), 149.5 (3/3'- pz^*), 142.8 (5/5'- pz^*), 141.9, 141.1 (5/5'- pz^*), 136.7, 129.2, 124.1, 108.0 (4/4'- pz^*), 106.7 (4/4'- pz^*), 63.5 (CH), 22.85 (4-Me- C_6H_4), 14.6 (pz^* Me), 14.4 (pz^* Me), 12.1 (pz^* Me), 11.1 (pz^* Me); the alkyl region is complex. The solution of **8** was warmed to 0°C , and broadening of the PdCHRCHR- $\mu\text{-H}$ signals was observed. ^1H NMR (CD_2Cl_2 , 0°C): δ 7.15 (m, 6H, 4-Me- C_6H_4), 7.02 (m, 6H, 4-Me- C_6H_4), 6.47 (CH), 5.98 (s, 1H, pz^* H4/H4'), 5.88 (s, 1H, pz^* H4/H4'), 3.09 (br, 0.5H, *trans*-PdCHRCHR- $\mu\text{-H}$), 2.72 (s, 0.5H *cis*-PdCHRCHR- $\mu\text{-H}$), 2.32 (s, 9H, 4-Me- C_6H_4), 2.28 (s, 3H, pz^* Me), 2.14 (s, 3H, pz^* Me), 2.05 (s, 3H, pz^* Me), 1.71 (s, 3H, pz^* Me), -8.75 (br, 0.1H, PdCHRCHR- $\mu\text{-H}$), -9.22 (br, 0.4H, PdCHRCHR- $\mu\text{-H}$).³¹

Identification of the Distribution of Alkyl Chain Lengths in **8 by Carbonylation to Generate $[(p\text{-tolyl})_3\text{SiCH}(\text{pz}^*)_2]\text{Pd}((\text{C}=\text{O})(\text{R}))\text{CO}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**8a**) and Methanolysis to Give a Mixture of Esters.** A valved NMR tube containing a CD_2Cl_2 (0.6 mL) solution of **8** (0.020 mmol) was cooled to -196°C and exposed to CO (1 atm) for 5 min. The tube was sealed, warmed to -78°C , and briefly warmed to 23°C with vigorous shaking. A slurry of white solid in a colorless supernatant formed. The tube was kept at -78°C and transferred to a precooled (-40°C) NMR probe, and NMR spectra were recorded. The NMR spectra showed that **8a** had formed. Key NMR data: ^1H NMR (CD_2Cl_2 , -40°C ; fast pz^* exchange): δ 7.23 (m, 6H, 4-Me- C_6H_4), 7.17 (m, 6H, 4-Me- C_6H_4), 6.54 (s, 1H, CH), 6.03 (br s, 2H, pz^* H4/H4'), 2.36 (s, 9H, 4-Me- C_6H_4), 2.16 (s, 6H, pz^* Me), 1.76 (s, 6H, pz^* Me); the alkyl region is complex. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -40°C , for **8a** generated using ^{13}CO): δ 217.9 (C(O)R), 216.3 (C(O)R), 215.6 (C(O)Me), 215.5 (C(O)R), 215.3 (C(O)R), 215.3 (C(O)R), 212.4 (C(O)R), 212.2 (C(O)R), 172.9 (PdCO), 172.8 (PdCO), 172.7 (PdCO), 171.8 (PdCO), 142.4, 136.9, 129.5, 124.6, 63.4 (CH), 63.3 (CH), 21.5 (4-Me- C_6H_4); free CO was observed at δ 184.3; the pz^* signals were broadened into the baseline due

Table 3. Summary of X-Ray Diffraction Data for **2** (3CHCl_3)

formula	$\text{C}_{64}\text{H}_{72}\text{Cl}_4\text{N}_8\text{Pd}_2\text{Si}_2 + 6(\text{CHCl}_3)$
fw	2080.29 (including solvent)
cryst size (mm)	$0.25 \times 0.25 \times 0.25$
D_{calc} (Mg/m^3)	1.543
cryst syst	triclinic
space group	$P\bar{1}$
a ($\text{\AA}$)	13.379(2)
b ($\text{\AA}$)	18.531(3)
c ($\text{\AA}$)	20.735(4)
α (deg)	114.939(3)
β (deg)	103.056(3)
γ (deg)	92.893(3)
V ($\text{\AA}^3$)	4478(1)
Z	2
temperature (K)	100
cryst color, habit	red-orange, fragment
goodness-of-fit on F^2	1.082
final R indices ($I > 2\sigma(I)$) ^a	$R1 = 0.0479$, $wR2 = 0.1148$
R indices (all data) ^a	$R1 = 0.0538$, $wR2 = 0.1186$

^a $R1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR2 = [\sum (w(F_o^2 - F_c^2))^2 / \sum (w(F_o^2))]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$.

to pyrazole ring exchange; the alkyl region is complex. A solution of NaOMe in MeOH (0.050 mL, 0.4 M) was added to the solution of **8a**, resulting in the immediate formation of Pd^0 . The mixture was exposed to air and diluted with hexanes (2 mL). The resulting black slurry was filtered through a pad of silica with hexanes/ CH_2Cl_2 (10/1 by volume). The filtrate was analyzed by GC/MS, which showed that a mixture of $\text{C}_5\text{-C}_{17}$ alkyl methyl esters had formed.

Generation of $[(p\text{-tolyl})_3\text{Si}(\text{HC}(\text{pz}^*)_2)]\text{PdR}(\text{H}_2\text{C}=\text{CH}_2)]\text{-}[\text{B}(\text{C}_6\text{F}_5)_4]$ (9**).** A valved NMR tube containing a solution of **8** (0.020 mmol) in CD_2Cl_2 (0.5 mL) containing Et_2O (0.060 mmol, as an internal standard) was cooled to -196°C , and ethylene (0.82 mmol) was added by vacuum transfer. The tube was thawed at -78°C and transferred to a precooled (-80°C) NMR probe. NMR spectra showed that an equilibrium mixture of **8**, **9**, and free ethylene had formed. The equilibrium constant, $K_{\text{eq}} = [\text{9}][\text{8}]^{-1}[\text{H}_2\text{C}=\text{CH}_2]^{-1}$, was determined by ^1H NMR from -80 to -55°C using the integrals of the $(p\text{-tolyl})_3\text{SiCH}$ resonances for **8** and **9** and the free ethylene resonance, referenced to the Et_2O internal standard. $K_{\text{eq}} = 35 \text{ M}^{-1}$ at -80°C . The resonances for the alkyl group (distribution of chain lengths) could not be assigned because they overlap with those of the N $^{\text{N}}$ ligand and **8**. Key data for **9**: ^1H NMR (CD_2Cl_2 , -80°C): δ 7.20 (m, 6H, 4-Me- C_6H_4), 7.02 (m, 6H, 4-Me- C_6H_4), 6.69 (CH), 6.08 (s, 1H, pz^* H4/H4'), 5.82 (s, 1H, pz^* H4/H4'), 4.15 (br m, 4H, Pd($\text{H}_2\text{C}=\text{CH}_2$)), 2.33 (s, 9H, 4-Me- C_6H_4), 2.28 (s, 3H, pz^* Me), 1.97 (br s, 3H, pz^* Me), 1.63 (s, 3H, pz^* Me); the alkyl region is complex. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_2F , -100°C): δ 151.2 (3/3'- pz^*), 150.3 (3/3'- pz^*), 142.6, 142.0 (5/5'- pz^*), 140.9 (5/5'- pz^*), 136.9, 129.4, 124.8, 108.5 (4/4'- pz^*), 108.3 (4/4'- pz^*), 93.1 (br, Pd($\text{H}_2\text{C}=\text{CH}_2$)), 85.3 (br, Pd($\text{H}_2\text{C}=\text{CH}_2$)), 63.8 (CH), 21.2 (4-Me- C_6H_4), 14.6 (pz^* Me), 12.2 (pz^* Me), 11.8 (pz^* Me), 10.7 (pz^* Me); the alkyl region is complex. A solution of **9** in CDCl_2F was generated as described above, and variable-temperature (-80 to -120°C) NMR spectra were measured. ^1H NMR (CDCl_2F , -120°C): δ 4.45 (br m, 1H, Pd($\text{H}_2\text{C}=\text{CH}_2$)), 3.91 (br m, 1H, Pd($\text{H}_2\text{C}=\text{CH}_2$)), 3.57 (br m, 1H, Pd($\text{H}_2\text{C}=\text{CH}_2$)), 2.75 (br m, 1H, Pd($\text{H}_2\text{C}=\text{CH}_2$)). The rotational barrier $\Delta G^\ddagger = 8.3 \text{ kcal mol}^{-1}$ was obtained from the

(31) The integrals for the agostic-H signals are low due to exchange between agostic and nonagostic $\beta\text{-H}$ hydrogens. For dynamics of cationic $\beta\text{-H}$ agostic Pd alkyl complexes see: Shultz, L. H.; Tempel, D. J.; Brookhart, M. *J. Am. Chem. Soc.* **2001**, *123*, 11539.

coalescence of the δ 3.91 and 3.57 resonances, using the coalescence approximation ($k_{\text{rot}} = 380 \text{ s}^{-1}$ at $T_{\text{coalescence}} = -90^\circ\text{C}$).³²

Measurement of pz* Exchange Rates. pz* exchange rates for **3**, **4**, **7**, and **9** were determined by variable-temperature ^1H NMR spectroscopy. Rate constants (k_{exch}) were determined by simulation of the pz* H4/H4' line shapes using gNMR.³³ The line width of the (*p*-tolyl)₃SiCH resonance was used as the line width in the absence of exchange. The measured k_{exch} values were independent of [Pd], and of the [free CO] for **4** and [free ethylene] for **7**. Activation parameters were determined from Eyring plots for each run.

X-Ray Crystallographic Analysis of {(p-tolyl)₃SiCH(3,5-Me₂-pz)₂}PdCl₂ (2**).** Single crystals of **2** were obtained by slow diffusion of pentane into a concentrated CHCl₃ solution at 23 °C. Crystallographic data are summarized in Table 3. Data were collected on a Bruker Smart Apex diffractometer using

(32) The other two ethylene ^1H NMR resonances (δ 4.45, 2.75) were broadened into the baseline at -90°C .

(33) *gNMR*, v. 4.1.2b; Adept Scientific: Letchworth, UK, 2000.

Mo K α radiation (0.71073 Å). The space group was determined as *P* $\bar{1}$ based on systematic absences and intensity statistics. Direct methods were used to locate the Pd, Cl, Si, and most C atoms from the E-map. Repeated difference Fourier maps allowed recognition of all expected C and N atoms. Following anisotropic refinement of all non-H atoms, ideal H atom positions were calculated. Final refinement was anisotropic for non-H atoms and isotropic-riding for H atoms. The asymmetric unit contains two molecules of **2**, which differ only in the orientation of the apical Si(*p*-tolyl)₃ group due to rotation around the (*p*-tolyl)₃Si-CH(3,5-Me₂-pz)₂ bond, and six CHCl₃.

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Supporting Information Available: NMR data, synthetic procedures, determination of ethylene binding constants and pz* site exchange rates, and complete mechanism of pz* exchange. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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