Ethylene Dimerization by Cationic Palladium(II) Alkyl Complexes that Contain Bis(heterocycle)methane Ligands

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The catalytic ethylene dimerization reactions of (N^N)PdMe(L)$^+$ species that contain bidentate nitrogen donor ligands were studied (N^N = (1-Me-imidazol-2-yl)$_2$CH$_2$ (**a**); (1-Me-imidazol-2-yl)$_2$CH(C$_6$H$_{13}$) (**b**), 1,1′-di(triphenylmethyl)-4,4′-biimidazole (**c**), (5-Me-pyridin-2-yl)$_2$CH$_2$ (**d**), (pyrazol-1-yl)$_2$CH$_2$ (**e**), (3,5-Me$_2$-pyrazol-1-yl)$_2$CH$_2$ (**f**), (4-Me-C$_6$H$_4$)N=CMeCMe=N(4-Me-C$_6$H$_4$) (**g**), and (2,6-^{i}Pr$_2$-C$_6$H$_3$)N=CMeCMe=N(2,6-^{i}Pr$_2$-C$_6$H$_3$) (**h**)). (N^N)PdMe$_2$ (**2a**–**e**,**g**) and (N^N)Pd(Me)Cl (**3f**–**h**) complexes were converted to [(N^N)Pd{C(=O)Me}CO][B(C$_6$F$_5$)$_4$)] (**7a**,**c**–**h**), [(N^N)Pd(Me)(H$_2$C=CH$_2$)][B(C$_6$F$_5$)$_4$)] (**8a**−**g**), and [(N^N)Pd(Me)(H$_2$C=CH$_2$)][SbF$_6$] (**8f′**). The ν_{CO} values for **7a**,**c**−**f** show that there is weak back-bonding in these species, the donor ability of the N^N ligand varies in the order imidazole > pyridine > pyrazole, and variation of the chelate ring size does not strongly affect the electron density at Pd. **8a**,**c**−**g** and **8f′** dimerize ethylene by an insertion/β-H elimination mechanism. The catalyst resting state is (N^N)-Pd(Et)(H$_2$C=CH$_2$)$^+$ (**9a**,**c**−**g**). First-order rate constants for ethylene insertion of **8a**−**g** and **8f′** ($k_{insert,Me}$) and **9a**,**c**−**g** ($k_{insert,Et}$) were determined by NMR. The $k_{insert,Me}$ and $k_{insert,Et}$ values for analogous (N^N)Pd(R)(H$_2$C=CH$_2$)$^+$ species are similar. Increasing the electrophilic character and the steric bulk of the (N^N)Pd unit leads to moderate increases in ethylene insertion rates.

Introduction

A wide variety of (N^N)PdR$^+$ olefin oligomerization and polymerization catalysts that contain neutral bidentate nitrogen donor ligands (N^N) have been developed.[1–4] Brookhart and co-workers showed that the dimerization of ethylene by the (phen)PdR$^+$ system (phen = phenanthroline) proceeds by an insertion/β-H elimination mechanism and that the ethyl ethylene complex (phen)Pd(Et)(H$_2$C=CH$_2$)$^+$ is the catalyst resting state.[5] Brookhart and co-workers also developed the chemistry of (ArN=CRCR=NAr)PdR$^+$ α-diimine catalysts, which produce high molecular weight polymers from ethylene, α-olefins, internal olefins, and cyclic olefins when the N-aryl rings contain ortho substituents.[6] A key development in this area was understanding that chain transfer in these oligomerization/polymerization reactions proceeds by associative olefin exchange. The orthogonal orientation of the N-aryl rings with respect to the metal square plane in (α-diimine)Pd species positions the ortho substituents above and below the axial coordination sites, which inhibits associative ligand exchange processes and thus disfavors chain transfer.

In previous work, we studied {R$_2$C(pz)$_2$}Pd(R)(H$_2$C=CH$_2$)$^+$ complexes that contain bis(pyrazolyl)methane ligands (pz = pyrazolyl).[7] These species catalytically oligomerize ethylene to C$_8$−C$_{24}$ internal olefins. However, ethylene insertion of {Me$_2$(pz)$_2$}PdMe(H$_2$C=CH$_2$)$^+$ is much slower than for (phen)PdMe(H$_2$C=CH$_2$)$^+$ or (diimine)PdMe(H$_2$C=CH$_2$)$^+$ complexes. Canty, Trofimenko, and others prepared a variety of other {R$_2$C(pz)$_2$}Pd complexes, including {R$_2$C(pz)$_2$}PdMe$_2$ and {R$_2$C(pz)$_2$Pd(allyl)}$^+$.[8,9] The (N^N)Pd chelate rings in these compounds adopt boat conformations and may undergo inver-

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(1) (a) Keim, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466. (b) Peuckert, M.; Keim, W. *Organometallics* **1983**, *2*, 594. (c) Keim, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *19*, 235. (d) Skupinska, J. *Chem. Rev.* **1991**, *91*, 613.

(2) (a) Killian, C. M.; Johnson, L. K.; Brookhart, M. *Organometallics* **1997**, *16*, 2005. (b) Svejda, S. A.; Brookhart, M. *Organometallics* **1999**, *18*, 65. (c) Daugulis, O.; Brookhart, M.; White, P. S. *Organometallics* **2002**, *21*, 5935. (d) Salo, E. V.; Guan, Z. *Organometallics* **2003**, *22*, 5033. (e) Heinicke, J.; Köhler, M.; Peulecke, N.; Kindermann, M. K.; Keim, W.; Köckerling, M. *Organometallics* **2005**, *24*, 344. (f) Doherty, M. D.; Trudeau, S.; White, P. S.; Morken, J. P.; Brookhart, M. *Organometallics* **2007**, *26*, 1261. (g) Ledford, J.; Shultz, C. S.; Gates, D. P.; White, P. S.; DeSimone, J. P.; Brookhart, M. *Organometallics* **2001**, *20*, 5266.

(3) (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (b) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (c) Mecking, S. *Coord. Chem. Rev.* **2000**, *203*, 325. (d) Mecking, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 534. (e) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283.

(4) (a) Cherian, A. E.; Lobkovsky, E. B.; Coates, G. W. *Chem. Commun.* **2003**, 2566. (b) Camacho, D. H.; Salo, E. V.; Ziller, J. W.; Guan, Z. *Angew. Chem., Int. Ed.* **2004**, *43*, 1821. (c) Popeney, C.; Guan, Z. *Organometallics* **2005**, *24*, 1145. (d) Cherian, A. E.; Rose, J. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 13770. (e) Meinhard, D.; Rieger, B. *Chem. Asian J.* **2007**, *2*, 386. (f) Meinhard, D.; Wegner, M.; Kipiani, G.; Hearley, A.; Reuter, P.; Fischer, S.; Marti, O.; Rieger, M. *J. Am. Chem. Soc.* **2007**, *129*, 9182. (g) Desjardins, S. Y.; Way, A. A.; Murray, M. C.; Adirim, D.; Baird, M. C. *Organometallics* **1998**, *17*, 2382. (h) Liu, W.; Malinoski, J. M.; Brookhart, M. *Organometallics* **2002**, *21*, 2836. (i) Daugulis, O.; Brookhart, M. *Organometallics* **2002**, *21*, 5926. (j) Malinoski, J. M.; Brookhart, M. *Organometallics* **2003**, *22*, 5324.

(5) (a) Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 1137. (b) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746.

(6) (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888. (c) Mclain, S. J.; Feldman, J.; McCord, E. F.; Gardner, K. H.; Teasley, M. F.; Coughlin, E. B.; Sweetman, K. J.; Johnson, L. K.; Brookhart, M. *Macromolecules* **1998**, *31*, 6705. (d) Gates, D. P.; Svejda, S. A.; Oñate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320. (e) Temple, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686. (f) Gottfried, A. C.; Brookhart, M. *Macromolecules* **2001**, *34*, 1140. (g) Shultz, L. H.; Temple, D. J.; Brookhart, M. *J. Am. Chem. Soc.* **2001**, *123*, 11539.

(7) Tsuji, S.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1999**, *18*, 4758.

(8) Byers, P. K.; Canty, A. J. *Organometallics* **1990**, *9*, 210.

(9) (a) Byers, P. K.; Canty, A. J.; Honeyman, R. T. *Adv. Organomet. Chem.* **1992**, *34*, 1. (b) Trofimenko, S. *J. Am. Chem. Soc.* **1970**, *92*, 5118.

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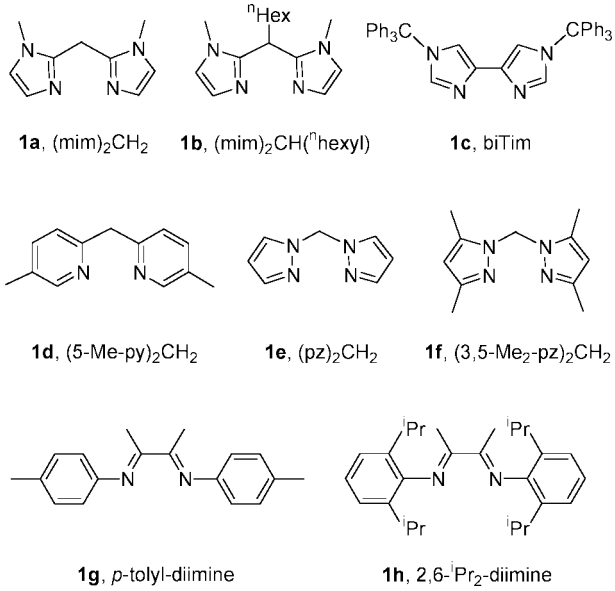
Chart 1



sion, which results in exchange of the axial and equatorial CR_2 substituents.[10,11]

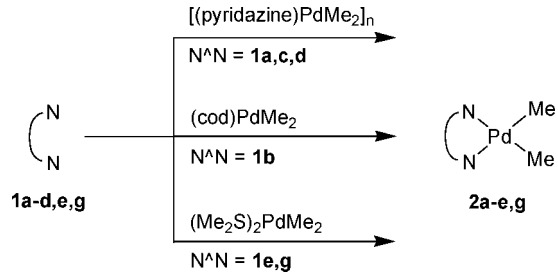
In the present work we have explored the chemistry of $(N^{\wedge}N)PdR(L)^+$ complexes that contain a wider range of bis(heterocyclic) N^N ligands, in order to probe how the electronic and steric properties of the heterocycle influence the ethylene insertion reactivity.

Results and Discussion

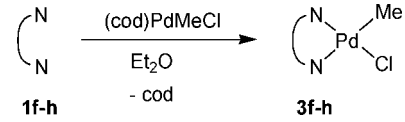
N^N Ligands. The N^N ligands **1a**−**h** in Chart 1 were prepared by literature routes.[12–20] Ligands **1a**−**h** were chosen for synthetic convenience and to enable investigation of how differences in donor properties, chelate ring size, and steric effects influence the rate of ethylene insertion in $(N^{\wedge}N)Pd(R)(H_2C{=}CH_2)^+$ species.

Synthesis of $(N^{\wedge}N)PdMe_2$ Complexes (2a–e,g). The $(N^{\wedge}N)PdMe_2$ compounds **2a**−**e**,**g** were synthesized by ligand substitution reactions of $[(pyridazine)PdMe_2]_n$, $(cod)PdMe_2$ (cod = cyclooctadiene), or $(Me_2S)_2PdMe_2$ as shown in Scheme 1.[8,21] In the solid state, **2e**,**g** decompose within minutes (**2e**) or hours (**2g**) at 25 °C. In CD_2Cl_2 solution, **2d**,**e**,**g** decompose to free N^N ligand, CH_4, C_2H_6, and Pd^0 within minutes (**2e**) or hours (**2d**,**g**) at 25 °C.[8] Complexes **2b**,**c** are more thermally stable, but decompose photochemically in CD_2Cl_2 to $(N^{\wedge}N)PdCl_2$.[15]

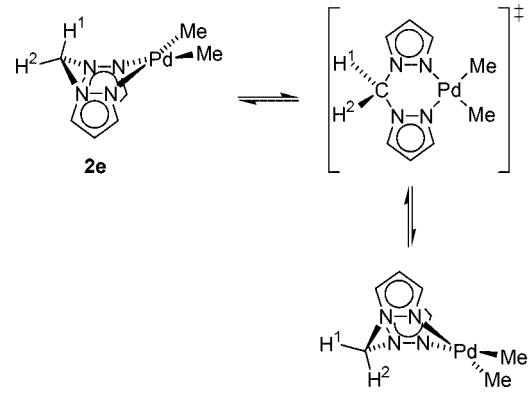
Scheme 1



Scheme 2



Scheme 3



Synthesis of $(N^{\wedge}N)Pd(Me)Cl$ Complexes (3f–h). The $(N^{\wedge}N)Pd(Me)Cl$ complexes **3f**–**h** were prepared by the reaction of (cod)Pd(Me)Cl with **1f**–**h** (Scheme 2).[6a,d,22] Compounds **3f**–**h** are more thermally stable than **2a**–**e**,**g**. However, **3g** decomposes slowly (days) in the solid state at 25 °C.

NMR and Dynamic Properties. Complexes **2a**,**b**,**d**,**e** and **3f** likely have boat conformations, as shown for **2e** in Scheme 3, similar to those observed for the analogous complexes {1,3-dioxolane)C(py)$_2$}$PdCl_2$, {$Me_2C(pz)_2$}$PdCl_2$, {$Ph_2C(pz)_2$}$PdCl_2$, and {(*n*-hexyl)HC(mim)$_2$}$PdCl_2$.[7,15,23–25] Previously, Canty observed a singlet for the methylene bridge hydrogens in the ^1H NMR spectrum of **2a** down to −70 °C, consistent with rapid inversion of the $(N^{\wedge}N)Pd$ chelate ring.[8] In contrast, slower ring inversion is observed for **2d**,**e**, and **3f**. The variable-temperature ^1H NMR spectra (δ 6.9–5.8 region) for **2e** are shown in Figure

(10) Jalón, F. A.; Manzano, B. R.; Otero, A.; Rodriguez-Perez, M. C. *J. Organomet. Chem.* **1995**, *494*, 179.
(11) (a) Brown, D. G.; Byers, P. K.; Canty, A. J. *Organometallics* **1990**, *9*, 1231. (b) Byers, P. K.; Canty, A. J.; Honeyman, R. T. *J. Organomet. Chem.* **1990**, *385*, 417.
(12) (N^N) = (1-Me-imidazol-2-yl)$_2$CH$_2$ (**1a**, (mim)$_2$CH$_2$), (1-Me-imidazol-2-yl)$_2$CH(C$_6$H$_{13}$) (**1b**, (mim)$_2$CH(*n*-hexyl)), 1,1′-di(triphenylmethyl)-4,4′-biimidazole (**1c**, biTim), (5-Me-pyridin-2-yl)$_2$CH$_2$ (**1d**, (5-Mepy)$_2$CH$_2$), (pyrazol-1-yl)$_2$CH$_2$ (**1e**, (pz)$_2$CH$_2$), (3,5-Me$_2$-pyrazol-1-yl)$_2$CH$_2$ (**1f**, (3,5-Me$_2$-pz)$_2$CH$_2$), (4-Me-C$_6$H$_4$)N=CMeCMe=N(4-Me-C$_6$H$_4$) (**1g**, *p*-tolyldiimine), and (2,6-^{i}Pr$_2$-C$_6$H$_3$)N=CMeCMe=N(2,6-^{i}Pr$_2$-C$_6$H$_3$) (**1h**, 2,6-^{i}Pr$_2$-diimine).
(13) Gorun, S. M.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 4244.
(14) Braussaud, N.; Ruther, T.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Synthesis* **2001**, 626.
(15) Burns, C. T,; Shen, H.; Jordan, R. F *J. Organomet. Chem.* **2003**, *683*, 240.
(16) Cliff, M. D.; Pyne, S. G. *Synthesis* **1994**, 681.
(17) Li, X.; Gibb, C. L. D.; Kuebel, M. E.; Gibb, B. C. *Tetrahedron* **2001**, *57*, 1175.
(18) Jameson, D. L.; Castellano, R. K.; Reger, D. L.; Collins, J. E.; Tolman, W. B.; Tokar, C. J. *Inorg. Synth.* **1998**, *32*, 51.
(19) Joshi, V. S.; Sarkar, A.; Rajamohanan, P. R. *J. Organomet. Chem.* **1991**, *409*, 240.
(20) Alcazar, J.; Begrup, M.; de la Hoz, A. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2467.
(21) Foley, S. R.; Stockland, R. A., Jr.; Shen, H.; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 4350.
(22) 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.
(23) Newkome, G. R.; Gupta, V. K.; Theriot, K. J.; Ewing, J. C.; Wicelinski, S. P.; Huie, W. R.; Fronczek, F. R.; Watkins, S. F. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 1352.
(24) Minghetti, G.; Cinellu, M. A.; Bandini, A. L.; Banditelli, G.; Demartin, F.; Manassero, M. *J. Organomet. Chem.* **1986**, *315*, 387.
(25) (a) Canty, A. J.; Minchin, N. J.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1992**, *45*, 423. (b) Newkome, G. R.; Gupta, V. K.; Taylor, H. C. R.; Fronczek, F. R. *Organometallics* **1984**, *3*, 1549.

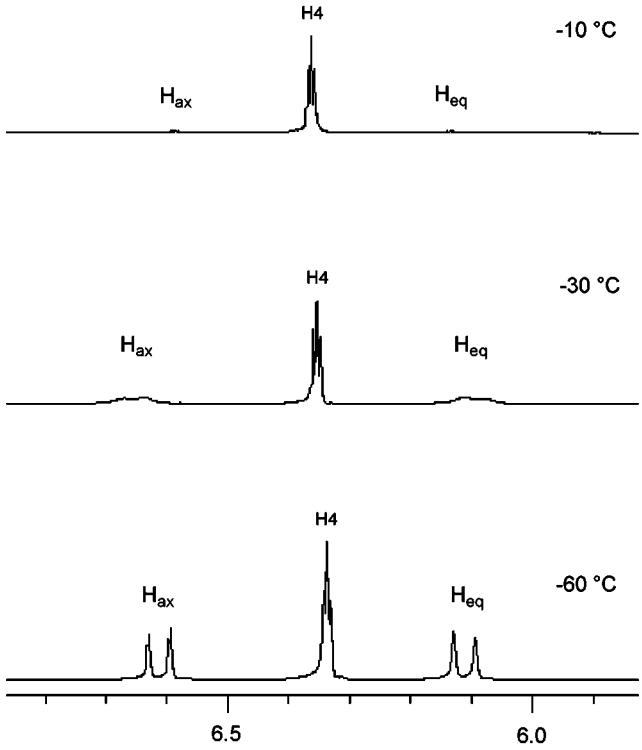


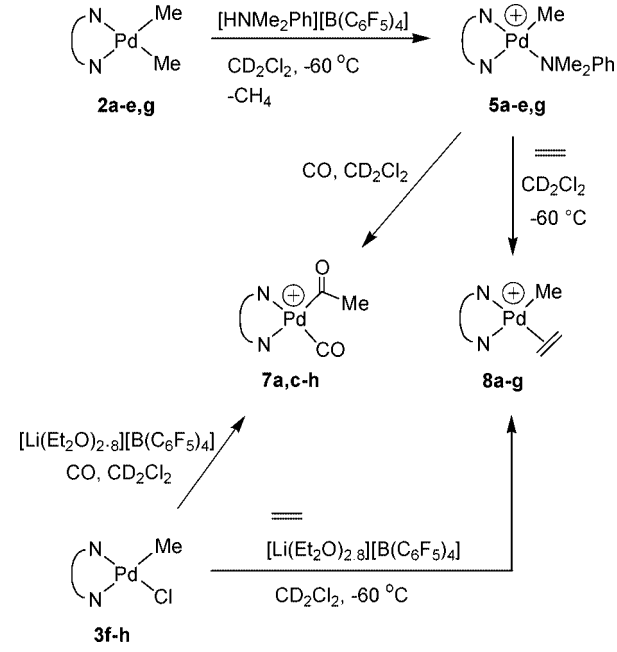
Figure 1. Variable-temperature ^{1}H NMR spectra (δ 6.9–5.8 region) of {H_2C(pz)$_2$}PdMe$_2$ (**2e**) in CD_2Cl_2 solution. The chemical shift scale is in δ units. NMR spectra were not obtained above −10 °C due to the thermal instability of **2e**. The broadening of the {H_2C(pz)$_2$}Pd resonances is due to chelate ring inversion.

1. At −60 °C, two doublets at δ 6.61 (H_{ax}) and 6.11 (H_{eq}) are observed for the methylene bridge hydrogens, which indicates that inversion of the chelate ring is slow on the NMR time scale at this temperature.[26] However, as the temperature is raised to −10 °C, the H_{ax} and H_{eq} resonances broaden selectively, indicating that inversion occurs. ^{1}H NMR spectra of **2e** could not be obtained above −10 °C due to the thermal instability of this species. The spectra of **2e** contain one set of pyrazole H3, H4, and H5 resonances and one PdMe resonance at all temperatures, consistent with the expected C_s-symmetric structure.

The ring inversion in **2e** most likely occurs by a nondissociative process via a planar transition state as shown in Scheme 3.[10] The free energy barrier for ring inversion in **2e**, estimated from the line broadening of the H_{ax} and H_{eq} resonances, is $\Delta G^{\ddagger}$ = 12.4(1) kcal/mol at −20 °C.[27] Similar results were observed for **2d** and **3f**. The inversion barrier for **2d** ($\Delta G^{\ddagger}$ = 13.1(1) kcal/mol at −20 °C) is similar to that for **2e**, while that for **3f** is ca. 3 kcal/mol higher ($\Delta G^{\ddagger}$ = 15.6(1) kcal/mol at 25 °C). Ring inversion in **3f** may be inhibited by the 3,5-Me$_2$ substituents on the pyrazole rings, which would crowd the Pd−Me and Pd−Cl groups in the planar transition state (cf. Scheme 3).

One conformer is observed for **2b** at both −60 and 25 °C. It is likely that the *n*-hexyl group occupies the axial position as observed for the analogous dichloride complex, {(*n*-hexyl)HC(mim)$_2$}PdCl$_2$.[15] Complexes **2c** and **3g** likely have planar conformations, similar to the analogous complexes {2,2′-bipyridine}PdCl$_2$, (2,6-^{i}Pr-BIAN)PdCl$_2$ (2,6-^{i}Pr-BIAN = bis{2,8-(2,6-di-isopropylphenylimino)}acenaphthene), and (*p*-MeO-BIAN)PdCl$_2$ (*p*-MeO-BIAN = bis{2,8-(4-methoxyphenylimino)}acenaphthene).[28]

Scheme 4



Generation of (N^N)PdMe(NMe$_2$Ph)$^+$ Species (5a–e,g). The (N^N)PdMe$_2$ complexes **2a**–**e**,**g** can be converted to (N^N)PdMe(L)$^+$ species in a variety of ways.[3b] The (N^N)-PdMe(L)$^+$ species described here are insufficiently thermally stable to isolate and therefore were characterized in situ by NMR. Complexes **2a**–**e**,**g** were reacted with [HNMe$_2$Ph]-[B(C$_6$F$_5$)$_4$] in CD_2Cl_2 at −60 °C to produce [(N^N)PdMe-(NMe$_2$Ph)][B(C$_6$F$_5$)$_4$] (**5a**–**e**,**g**; Scheme 4) in near quantitative yield. Complexes **5a**–**e**,**g** are quite stable at low temperature (−60 °C) but decompose slowly at 25 °C to yield black solutions and NMe$_2$Ph; the fate of the (N^N)PdMe$^+$ unit was not determined.

The −60 °C ^{1}H NMR spectra of **5a**–**e**,**g** show that in each case the sides of the N^N ligand are inequivalent and one NMe$_2$Ph ligand is present. The NMe$_2$Ph resonances are strongly deshielded compared to the resonances of free NMe$_2$Ph by coordination to the (N^N)PdMe$^+$ unit.[29] In **5a**–**e**, one heterocycle ring resonance (H4 in (mim)$_2$CH$_2$ and (mim)$_2$CH(*n*-hexyl); H2 in biTim; H6 in (5-Me-py)$_2$CH$_2$; H3 in (pz)$_2$CH$_2$) appears at a higher field ($\delta \leq$ 5.95) compared to the other ring resonances due to anisotropic shielding by the NMe$_2$*Ph* ring.

(26) (a) The assignment of the bridge methylene hydrogen resonances is based on Canty's results for {MeHC(py)$_2$}PdMe$_2$, which exists as a 1/1 mixture of conformers at −10 °C (see ref 8). In this case, two doublets were observed for the bridge C*H* in the ^{1}H NMR spectrum at −10 °C. The downfield C*H* resonance was assigned the conformer in which the C−*H* is in the axial position. The downfield shift was ascribed to the proximity of H_{ax} to Pd. (b) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; New, L. *J. Chem. Soc., Dalton Trans.* **1978**, 1490. (c) Polyakov, V. A.; Ryabov, A. D. *J. Chem. Soc., Dalton Trans.* **1986**, 589.

(27) *gNMR*, v. 4.1.2; Adept Scientific: Letchworth, 2000.

(28) (a) Canty, A. J.; Skelton, B. W.; Traill, P. R.; White, A. H. *Aust. J. Chem.* **1992**, *45*, 417. (b) Coventry, D. N.; Batsanov, A. S.; Goeta, A. E.; Howard, J. A. K.; Marder, T. B. *Polyhedron* **2004**, *23*, 2789.

(29) (a) NMR data for free NMe$_2$Ph: ^{1}H NMR (CD_2Cl_2): δ 7.20 (m, 2H, *o*-Ph), 6.72 (m, 2H, *m*-Ph), 6.67 (t, J = 7, 1H, *p*-Ph), 3.03 (s, 6H, Me). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 151.1 (C1), 129.3 (C2), 116.6 (C4), 112.8 (C3), 40.7 (Me). ^{1}H NMR (CD_2Cl_2, −60 °C): δ 7.18 (m, 2H, *o*-Ph), 6.67 (m, 2H, *m*-Ph), 6.63 (t, J = 7, 1H, *p*-Ph), 2.88 (s, 6H, Me). ^{13}C{^{1}H} NMR (CD_2Cl_2, −60 °C): δ 150.2 (C1), 128.7 (C2), 115.8 (C4), 111.9 (C3), 40.3 (Me). (b) If excess [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] is used in the generation of **5a**−**e** and **5g**, and the NMe$_2$Ph is then displaced from **5a**−**e** and **5g** by another ligand, the excess HNMe$_2$Ph$^+$ undergoes fast H$^+$ exchange with free NMe$_2$Ph and a single set of NMe$_2$Ph/HNMe$_2$Ph$^+$ resonances at the weighted average of the chemical shifts of these species is observed.

Table 1. Pd−*C*O ^{13}C NMR Chemical Shifts and ν_{CO} Values for (N^N)Pd{C(=O)Me}CO$^+$ Complexes in CD_2Cl_2 Solution

complex	N∧N ligand	δ^{13}C Pd−CO	ν_{CO} (cm^{-1})
7a	$(mim)_2CH_2$	173.8[a]	2122[a]
7c	biTim	173.5[b]	2123[a]
7d	$(5\text{-Me-py})_2CH_2$	173.1[b]	2128[a]
7e	$(pz)_2CH_2$	175.0 (br)[c]	2133[a]
7f	$(3,5\text{-Me}_2\text{-pz})_2CH_2$	171.7[d]	2132[a]
7g	*p*-tolyldiimine	172.4[d]	2130[a]
7h	2,6-^{i}Pr$_2$-diimine		2132[a]

[a] 23 °C. [b] −40 °C. [c] −20 °C. [d] −60 °C.

Similarly, in **5g**, one of the aryl resonances appears at high field (δ 6.24) due to anisotropic shielding by the NMe_2*Ph* ring.

The amine ligand of **5a**–**e**,**g** is easily displaced by olefins or other ligands.[7,30] The displaced NMe_2Ph has no effect on subsequent chemistry, but can be used as an internal standard for NMR integration.[29b]

(N^N)Pd{C(=O)Me}CO$^+$ Species (7a,c–h). The acyl carbonyl complexes [(N^N)Pd{C(=O)Me}CO][B(C$_6$F$_5$)$_4$] (**7a**,**c**–**h**) were prepared by two routes, as shown in Scheme 4. Exposure of frozen CD_2Cl_2 solutions of **5a**,**c**–**e** to CO followed by brief warming to 25 °C yields **7a**,**c**–**e** quantitatively. The reaction of **3f**–**h** with 1 equiv of [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] in CD_2Cl_2 in the presence of CO at 25 °C affords **7f**–**h** quantitatively. Complexes **7a**,**c**–**h** are stable at low temperatures (−78 to −40 °C) but decompose at 25 °C over the course of several hours.

Complexes **7a**,**c**–**h** were characterized by NMR at 23 °C (**7a**) or low temperature (**7c**–**h**) in the presence of excess CO. The Pd-*C*O ^{13}C NMR chemical shifts of **7a**,**c**–**g** are listed in Table 1. The Pd-*C*O signals fall within a small range (δ 171.4 to 175.0) and are shifted upfield from the free CO resonance (δ 184.0).[31] The acyl carbon signals appear in the range δ 209 to 217. These values are similar to those for (phen)Pd{C(=O)Me}CO$^+$ (δ 173.0 (Pd−CO), 216.5 (acyl)).[5] Separate Pd−*C*O and free CO resonances are observed for **7a** (25 °C) and **7c**–**h** (low temperature), indicating that CO exchange is slow on the NMR time scale.[32]

The ν_{CO} and ν_{acyl} values for **7a**,**c**–**h** were determined by solution IR spectroscopy and are listed in Table 1. Complexes **7a**,**c**–**h** exhibit high ν_{CO} values (2122–2133 cm^{-1}; cf. 2139 cm^{-1} for free CO in CD_2Cl_2) characteristic of minimal d−π* backbonding and electrophilic metal centers.[5,31,33] Comparison of the ν_{CO} values for **7a**,**c**–**f** shows that the donor ability of the heterocycles varies in the order imidazole > pyridine > pyrazole.[8,34] Comparison of the ν_{CO} values for **7e** and **7f**, and of **7g** and **7 h**, shows that the addition of alkyl groups does not strongly affect the donor property of the ligand. Comparison of the ν_{CO} values of **7a** and **7c**, and of **7d** and (phen)Pd(COMe)(CO)$^+$ (ν_{CO} = 2128 cm^{-1}), shows that chelate ring size does not dramatically affect the electron density at the Pd(II) center.[5] The high ν_{CO} values of **7g** and **7h** indicate that the α-diimines **1g** and **1h** are weak donor ligands.[35]

Generation of [(N^N)PdMe(H$_2$C=CH$_2$)][B(C$_6$F$_5$)$_4$] Species (8a–g). The methyl ethylene complexes [(N^N)PdMe(H$_2$C=CH$_2$)][B(C$_6$F$_5$)$_4$] (**8a**–**g**) were prepared by two routes, as shown in Scheme 4. Reaction of **5a**–**e**,**g** with ethylene at −60 °C yields **8a**–**e**,**g** by associative displacement of NMe_2Ph by ethylene. The reaction of **3f** with 1 equiv of [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] in the presence of ethylene yields **8f**. Complexes **8a**–**g** are stable in CD_2Cl_2 solution at −60 °C for long periods of time, but undergo insertion at higher temperatures (above ca. −40 °C for **8g** and ca. −20 °C for **8a**–**f**), as described below.

Complexes **8a**–**g** were characterized by NMR at −60 °C in CD_2Cl_2. Consistent with the displacement of NMe_2Ph by ethylene, the heterocycle ring and aryl resonances that were shifted upfield in **5a**–**e**,**g** by anisotropic shielding by the NMe_2*Ph* ring appear in their normal regions for **8a**–**g**.

Intermolecular exchange of free and coordinated ethylene is fast on the NMR chemical shift time scale for **8a**,**c**–**e**,**g** at −60 °C in the presence of excess ethylene (ca. 1–9 equiv). This exchange is stereospecific in the sense that the incoming ethylene occupies the same coordination site as the departing ethylene, so that the sides of the N^N ligand remain inequivalent under fast exchange conditions. It is presumed that ethylene exchange occurs by a standard associative mechanism.[5,6a,36] In contrast, the −60 °C ^{1}H NMR spectra of **8b**,**f** in the presence of excess ethylene contain separate resonances for bound (AA′BB′ pattern) and free ethylene (δ 5.37), indicating that intermolecular ethylene exchange is slow on the NMR chemical shift time scale in these cases.[37] For **8b**, the axial *n*-hexyl substituent may inhibit access to the axial coordination sites of the metal. For **8f**, the steric crowding and enhanced boating of the chelate ring due to methyl substituents of the 3,5-Me$_2$-pz rings inhibit associative ligand exchange processes.

Generation of [{H$_2$C(3,5-Me$_2$-pz)$_2$}PdMe(H$_2$C=CH$_2$)][SbF$_6$] (8f′). The reaction of **3f** with Ag[SbF$_6$] in Et$_2$O at 23 °C affords [{H$_2$C(3,5-Me$_2$-pz)$_2$}PdMe(OEt$_2$)][SbF$_6$] (**6f′**, Scheme 5) in near quantitative yield.[38,39] Complex **6f′** is quite stable at low temperature (−60 °C), and the labile Et$_2$O is easily displaced by olefins or other ligands. The reaction of **6f′** with ethylene at

(30) Wu, F.; Foley, S. R.; Burns, C. T.; Jordan, R. F. *J. Am. Chem. Soc.* **2005**, *127*, 1841.

(31) (a) Guo, Z.; Swenson, D. C.; Guram, A. S.; Jordan, R. F. *Organometallics* **1994**, *13*, 766. (b) Lupinetti, A. J.; Strauss, S. H.; Frenking, G. *Prog. Inorg. Chem.* **2001**, *49*, 1. (c) Willner, H.; Aubke, F. *Organometallics* **2003**, *22*, 3612.

(32) For **7e** at −10 °C, the Pd−*C*O and free CO ^{13}C resonances are broad, indicating that CO exchange is faster in this case. CO exchange by a normal associative mechanism should occur stereospecifically without permutation of the sides of the (pz)$_2$CH$_2$ ligand. However, the ^{1}H NMR (−20 °C) and ^{13}C NMR (−10 °C) spectra of **7e** in the presence of free CO contain one set of pz resonances, indicating that the sides of the (pz)$_2$CH$_2$ ligand are equivalent on the NMR time scale. Also, the ^{1}H NMR spectrum of **7f** (25 °C) contains one sharp set of 3,5-Me$_2$-pz signals, indicating that permutation of the sides of the (3,5-Me$_2$-pz)$_2$CH$_2$ ligand occurs. These results suggest that reversible decomplexation of the pz rings occurs.

(33) Foley, S. R.; Shen, H.; Qadeer, U. A.; Jordan, R. F. *Organometallics* **2004**, *23*, 600.

(34) Canty, A. J.; Lee, C. V. *Organometallics* **1982**, *1*, 1063.

(35) (a) Gasperini, M.; Ragaini, F.; Cenini, S. *Organometallics* **2002**, *21*, 2950. (b) Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378.

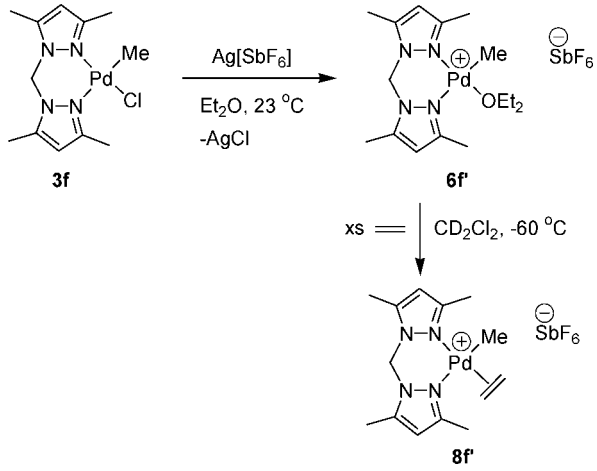
(36) (a) The −CPh$_3$ groups of **8c** are too remote from the Pd to strongly influence the associative ethylene exchange. For comparison, in [Cu(μ-η^1-NO$_3$)(NO$_3$)(biTim)]$_2$, the distance between the −*C*Ph$_3$ carbon and the Cu atom is 5.59 Å and the shortest H−Cu distance between the −C*Ph*$_3$ groups and the Cu atom is 5.28 Å. The Cu−N distances are similar to Pd−N distances in related Pd compounds. See: Aromi, G.; Gamez, P.; Kooijman, H.; Spek, A. L.; Driessen, W. L.; Reedijk, J. *Eur. J. Inorg. Chem.* **2003**, 1394. (b) Jiang, A.; Krüger, C.; Pfeil, B. Watkins, S. F. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *C43*, 2334.

(37) At 0 °C, the bound ethylene resonance of **8b** is broadened by exchange. The linewidth is greater at higher free ethylene concentrations, consistent with an associative exchange mechanism.

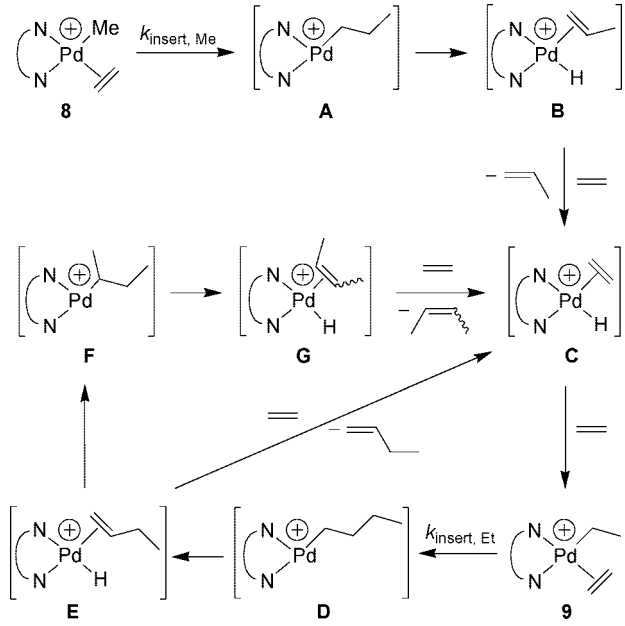
(38) Johnson, L. K.; Killian, C. M.; Arthur, S. D.; Feldman, J.; McCord, E. F.; McLain, S. J.; Kreutzer, K. A.; Bennett, M. A.; Coughlin, E. B.; Ittel, S. D.; Parthasarathy, A.; Tempel, D. J.; Brookhart, M. (E. I. Du Pont de Nemours & Co.). WO Patent 9623010, 1996 *Chem. Abstr.* **1996**, *125*, 222773. ^{1}H NMR (CD_2Cl_2): δ 7.29 (d, J = 8, 2H, Ar H3), 7.26 (d, J = 8, 2H, Ar H3′), 6.89 (d, J = 8, 2H, Ar H2), 6.82 (d, J = 8, 2H, Ar H2′), 2.39 (s, 6H, Ar*Me*), 2.15 (s, 3H, N=C*Me*), 2.04 (s, 3H, N=C*Me*), 0.44 (s, 3H, Pd*Me*).

(39) McCord, E. F.; McLain, S. J.; Nelson, L. T. J.; Arthur, S. D.; Coughlin, E. B.; Ittel, S. D.; Johnson, L. K.; Tempel, D.; Killian, C. M.; Brookhart, M. *Macromolecules* **2001**, *34*, 362.

Scheme 5



Scheme 6



−60 °C yields the ethylene complex **8f′**. The ^{1}H NMR spectrum of **8f′** is identical to that of the corresponding $B(C_6F_5)_4^-$ salt **8f**. As for **8f**, associative ethylene exchange is slow on the NMR time scale for **8f′**. This route to $(N^\wedge N)PdMe^+$ species avoids the use of thermally sensitive $(N^\wedge N)PdMe_2$ precursors.

Catalytic Ethylene Dimerization by $(N^\wedge N)PdMe(H_2C{=}CH_2)^+$ (8a–g,8f′). Complexes **8a–g** and **8f′** catalytically dimerize ethylene to a mixture of butenes. The mechanism for this reaction is shown in Scheme 6 and is directly analogous to that established by Brookhart for ethylene dimerization by $(phen)PdMe(H_2C{=}CH_2)^+$.[5] Ethylene insertion into the Pd−Me bond of **8** followed by β-H elimination forms intermediate Pd hydride propylene complex **B**. Subsequent exchange of the coordinated propylene by ethylene yields intermediate **C**. Ethylene insertion of **C** followed by ethylene coordination forms ethyl ethylene complex **9**, which is the catalyst resting state. Complex **9** inserts ethylene to form a Pd butyl cation (**D**), which undergoes β-H elimination to form Pd hydride 1-butene complex **E**. Intermediate **E** can undergo olefin exchange with ethylene to liberate 1-butene and re-form **C**, or undergo 2,1 insertion of 1-butene to form Pd *sec*-butyl complex **F**. β-H elimination of **F** followed by olefin exchange yields **C** and *cis*- or *trans*-2-butene.

Table 2. First-Order Rate Constants ($k_{insert,Me}$) for Ethylene Insertion of $(N^\wedge N)PdMe(H_2C{=}CH_2)^+$ Complexes in CD_2Cl_2 at −10 °C

compound	N^N ligand	$k_{insert,Me}$ (10^{-4} s^{-1})
8a	$(mim)_2CH_2$	1.2(1)
8b	$(mim)_2CH(n\text{-hexyl})$	1.6(1)
8c	biTim	1.0(1)
8d	$(5\text{-Me-py})_2CH_2$	9.0(9)
8e	$(pz)_2CH_2$	3.6(3)
8f	$(3,5\text{-Me}_2\text{-pz})_2CH_2$	13(1)
8f′	$(3,5\text{-Me}_2\text{-pz})_2CH_2$	12(1)
8g	*p*-tolyldiimine	39(4)
8g (−30 °C)	*p*-tolyldiimine	3.9(4)
8 h (−30 °C)	2,6-^{i}Pr$_2$-diimine	17[a]

[a] Data from ref 6a.

Consistent with Scheme 6, NMR monitoring of the reaction of **8a–g** with ethylene shows that as **8** is consumed, propylene and **9** form, and that **9** subsequently produces a mixture of 1-butene and *cis*- and *trans*-2-butene.[40] Complex **9** is the only major Pd species present in solution until all the ethylene is consumed, at which point Pd^0 formation is observed. Once the ethylene is consumed, the butenes are oligomerized by an unknown mechanism.

Characterization of $[(N^\wedge N)PdEt(H_2C{=}CH_2)][B(C_6F_5)_4]$ (9a,c–g). Complexes **9a**,**c–g** were characterized by ^{1}H NMR at low temperature. The ^{1}H NMR spectra of **9a**,**c**,**g** contain quartets for the $PdCH_2CH_3$ methylene hydrogens, which are coupled to triplets for the $PdCH_2CH_3$ hydrogens. The ^{1}H NMR spectra of **9d**,**e** contain two signals (pentets for **9d**, multiplets for **9e**) for the $PdCH_2CH_3$ hydrogens and a triplet for the $PdCH_2CH_3$ methyl group; in these cases the $PdCH_2$ hydrogens are inequivalent due to slow inversion of the $(N^\wedge N)Pd$ chelate ring. The ^{1}H NMR spectrum of **9f** at −60 °C contains a triplet at δ 0.67 for the $PdCH_2CH_3$ group, which is slightly upfield of the corresponding resonance for **9e**. The $PdCH_2CH_3$ signals of **9f** were not observed at −60 °C due to broadening and overlap with other resonances. However, the spectrum contains two doublets for the $(3,5\text{-Me}_2\text{-pz})_2CH_2$ hydrogens, which implies that chelate ring inversion is slow, as observed for **3f**, **6f′**, **7f**, and **8f**.

The ^{1}H NMR spectra of **9a**,**c–e** and **9g**, at −60 °C in the presence of excess ethylene, contain one resonance for free and coordinated ethylene, indicating ethylene exchange is fast on the NMR time scale under these conditions. In all cases the sides of the N^N donor ligands are inequivalent, consistent with the expected stereospecific exchange mechanism. In contrast, for **9f** separate resonances are observed for free and coordinated ethylene, indicating ethylene exchange is slow on the NMR time scale under these conditions for this case.

Kinetics of Ethylene Insertion into the Pd−Me Bond of 8a–g and 8f′ The rate of ethylene insertion of **8a–g** and **8f′** at −10 °C was measured by ^{1}H NMR by monitoring the disappearance of the Pd−Me resonance. These studies show that the rate of ethylene insertion is zero-order in ethylene and first-order in palladium. The first-order rate constants for insertion of the Pd−Me cations ($k_{insert,Me}$) are listed in Table 2. The $k_{insert,Me}$ values for **8f** and **8f′** are identical, which shows that the difference in noncoordinating anion ($B(C_6F_5)_4^-$ vs SbF_6^-) has no effect on the insertion rate.

Kinetics of Ethylene Insertion into the Pd−Et Bond of 9a,c–g. Since complex **9** is the resting state for the ethylene dimerization process in Scheme 6, the rate of ethylene insertion

(40) The 1-butene/2-butene ratios were as follows: **8a**: 1/7; **8c**: 1/9; **8d**: 1/4; **8e,f**: 1/7; **8g**: 1/6. The *cis*/*trans* 2-butene ratios were as follows: **8a-e**: ca. 1/1; **8f**: 1/1.5; **8g** 1/2.

Table 3. First-Order Rate Constants ($k_{insert,Et}$) for Ethylene Insertion of (N^N)PdEt($H_2C{=}CH_2$)$^+$ Complexes in CD_2Cl_2 at −10 °C

compound	N^N ligand	$k_{insert,Et}$ (10^{-4} s^{-1})
9a	$(mim)_2CH_2$	1.0(1)
9c	biTim	0.48(5)
9d	$(5\text{-Me-py})_2CH_2$	2.0(2)
9e	$(pz)_2CH_2$	2.0(2)
9f	$(3,5\text{-Me}_2\text{-pz})_2CH_2$	7.0(7)
9g	*p*-tolyldiimine	12(1)

into the Pd−Et bond is equal to the rate of butene formation. The rate of butene formation by **9a**,**c**–**g** at −10 °C was measured by ^{1}H NMR. These experiments show that the rate of butene formation and hence ethylene insertion into the Pd−Et bond is zero-order in ethylene and first-order in palladium. First-order rate constants for ethylene insertion, $k_{insert,Et}$, are listed in Table 3.

Reactivity Trends in (N^N)Pd(R)($H_2C{=}CH_2$)$^+$ species (R = Me, Et). The k_{insert} values in Tables 2 and 3 provide an initial picture of how N^N ligand properties influence the insertion reactivity of (N^N)Pd(R)($H_2C{=}CH_2$)$^+$ species. The $k_{insert,Me}$ values for **8a** and **8c** are essentially identical, which shows that the chelate ring size does not dramatically affect the rate of ethylene insertion. Ethylene insertion of **8e** is 3 times faster than for **8a**. Since **8e** and **8a** have very similar structures, this difference can be attributed to greater electrophilic character at Pd in **8e** versus **8a**, which results from the difference in donor ability of the pyrazole and imidazole ligands (cf. Table 1). Ethylene insertion of **8f** is ca. 3 times faster than for **8e**, which may reflect the steric crowding generated by the methyl substituents of the 3,5-Me_2-pz rings of **8f**. Ethylene insertion of **8d** is 8 times faster than for **8a**, due to the combination of the poorer donor ability and the larger ring size and concomitant greater steric crowding of the pyridine unit compared to the imidazole unit in the N^N ligands. Thus, increasing the electrophilic character and the steric bulk of the {bis(heterocycle)-methane}Pd unit leads to moderate (up to ca. 10-fold) increases in ethylene insertion rates. The $k_{insert,Et}$ values for **9a**,**c**−**g** are somewhat lower than $k_{insert,Me}$ values for the corresponding Pd−Me complexes **8a**,**c**−**g**.

Interestingly, the insertion rate of **8f**, which is the most reactive of the {bis(heterocycle)methane}Pd(R)(ethylene)$^+$ species studied here, is 3 to ca. 12 times slower than those of the (α-diimine)Pd(R)(ethylene)$^+$ species **8g** and **8h**. As the electronic properties of **8f**−**h** are quite similar (based on the ν_{CO} data in Table 1), this difference must result from differences in the steric properties and perhaps the degree of rigidity of the (N^N)Pd units in these systems.

Conclusions

Cationic {bis(heterocycle)methane}PdR$^+$ species catalyze the dimerization of ethylene by an insertion/β-H elimination mechanism. The catalyst resting state is the {bis(heterocycle)-methane}Pd(Et)(ethylene)$^+$ complex. Increasing the electrophilic character (heterocycle = pyrazole > pyridine > imidazole) and the steric bulk of the {bis(heterocycle)methane}Pd unit leads to moderate (up to ca. 10-fold) increases in ethylene insertion rates of {bis(heterocycle)methane}Pd(R)(ethylene)$^+$ species.

Experimental Section

General Procedures. All manipulations were performed under N_2 or vacuum using standard Schlenk or high-vacuum techniques or in a N_2-filled drybox. 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 refluxed for 24 h over CaH_2 and distilled. $CDCl_3$ and CD_2Cl_2 were dried over CaH_2 for 24 h, degassed by freeze–pump–thaw cycles, and vacuum transferred to a storage vessel. Acetone-d_6 was dried over 4 Å molecular sieves and then distilled onto 4 Å molecular sieves. CO and ^{13}CO were purchased from Aldrich and used as received. Ethylene (research grade) was obtained from Matheson and used as received. [$HNMe_2Ph$][$B(C_6F_5)_4$] and [$Li(Et_2O)_{2.8}$]-[$B(C_6F_5)_4$] were obtained from Boulder Scientific and used as received. The Et_2O content of the [$Li(Et_2O)_{2.8}$][$B(C_6F_5)_4$] salt was determined by ^{1}H NMR with C_6Me_6 as internal standard. (cod)$PdCl_2$ and Ag[SbF_6] were obtained from Strem and used as received. The compounds $(pz)_2CH_2$ (**1e**),[18] $(mim)_2CO$,[14] $(mim)_2CH_2$ (**1a**),[14] $(mim)_2CH$(*n*-hexyl) (**1b**),[15] $(5\text{-Me-py})_2CO$,[17] 1,1′-di(triphenylmethyl)-4,4′-biimidazole (**1c**),[16] $(5\text{-Me-py})_2CH_2$ (**1d**),[14] $(3,5\text{-Me}_2\text{-pz})_2CH_2$ (**1f**),[19] (4-Me-C_6H_4)N=CMeCMe=N(4-Me-C_6H_4) (**1g**),[20] (cod)Pd(Me)Cl,[22] (cod)$PdMe_2$,[21] (pyridazine)$PdMe_2$,[8] {$H_2C(mim)_2$}-$PdMe_2$ (**2a**),[8] {$H_2C(pz)_2$}$PdMe_2$ (**2e**),[8] {(2,6-^{i}Pr$_2$-C_6H_3)N=CMeCMe=N2,6-^{i}Pr$_2$-C_6H_3)}$PdMe_2$ (**2h**),[6] {(4-Me-C_6H_4)N=CMeCMe=N(4-Me-C_6H_4)}Pd(Me)Cl (**3g**),[38] {(2,6-^{i}Pr$_2$-C_6H_3)N=CMeCMe=N(2,6-^{i}Pr$_2$-C_6H_3)}Pd(Me)Cl (**3h**),[6d] [{$H_2C(mim)_2$}-$PdMe(NMe_2Ph)$][$B(C_6F_5)_4$] (**5a**),[30] and [{H_2C(5-Me-py)$_2$}$PdMe(NMe_2Ph)$][$B(C_6F_5)_4$] (**5d**)[30] were prepared by literature procedures. All other chemicals were purchased from Aldrich and used without further purification. Elemental analyses were performed by Midwest Microlabs (Indianapolis, IN). Infrared spectra were obtained at 25 °C under an N_2 atmosphere using a Nicolet NEXUS 470 FT-IR spectrometer. GC-MS analyses were performed on a HP-6890 instrument with a HP-5973 mass selective detector.

NMR spectra were recorded in flame-sealed or Teflon valve tubes on Bruker AMX-360, AMX-400, or AMX-500 spectrometers at ambient probe temperature unless otherwise indicated. ^{1}H and ^{13}C chemical shifts are reported versus $SiMe_4$ and were determined by reference to the residual ^{1}H and ^{13}C solvent peaks. ^{19}F and ^{11}B chemical shifts were referenced to external neat $CFCl_3$ and $BF_3\cdot Et_2O$ respectively. Coupling constants are reported in Hz. NMR probe temperatures were calibrated by a MeOH thermometer.[41]

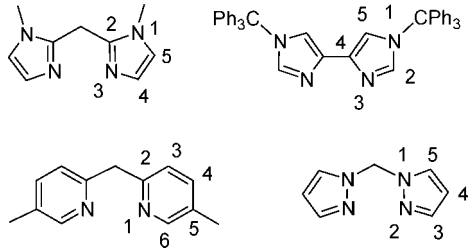
The NMR spectra of cationic Pd compounds contained signals of the free $B(C_6F_5)_4^-$ anion. ^{13}C{^{1}H} NMR (CD_2Cl_2, −60 °C): δ 147.5 (dm, J = 241, *C*2), 137.8 (dm, J = 238, C4), 135.8 (dm, J = 249, C3), 123.6 (br, C1). ^{11}B NMR (CD_2Cl_2, −60 °C): δ −16.9 (s). ^{19}F NMR (CD_2Cl_2, −60 °C): δ −133.7 (br s, 2F, *o*-F), −163.0 (t, J = 23, 1F, *p*-F), −167.0 (t, J = 19, 2F, *m*-F). NMR spectra of **7a**,**c**–**e**, **8a**–**e**,**g**, and **9a**,**c**–**e** and species derived from these species contain resonances for free NMe_2Ph.[29] Samples of CD_2Cl_2 solutions of cationic species generated in situ from the reaction of **3f**–**h** and [$Li(Et_2O)_{2.8}$][$B(C_6F_5)_4$] contain LiCl. Samples of CD_2Cl_2 solutions of cationic species generated in situ from the reaction of **3f** and Ag[SbF_6] contain AgCl.

Atom-labeling schemes for the ligands $(mim)_2CH_2$, biTim, $(5\text{-Me-py})_2CH_2$, and $(pz)_2CH_2$ and complexes derived from these ligands are given in Chart 2.

{(*n*-Hexyl)HC(mim)$_2$}$PdMe_2$ (2b). A slurry of (cod)$PdMe_2$ (0.218 g, 0.893 mmol) and $(mim)_2CH$(*n*-hexyl) (0.197 g, 0.759 mmol) in pentane (30 mL) was stirred for 30 min at −78 °C. The mixture was warmed to 0 °C and stirred for 1 h. The white solid was isolated by cannula filtration at 0 °C, washed with pentane (30 mL) at 0 °C, and dried under vacuum at 0 °C (0.100 g, 33%). **2b** was stored at −35 °C. ^{1}H NMR (CD_2Cl_2): δ 7.05 (s, 2H, mim H4/H5), 6.83 (s, 2H, mim H4/H5), 4.08 (t, J = 8, 1H, C*H*), 3.66 (s, 6H, mim N*Me*), 2.31 (q, J = 8, 2H, CH_2), 1.24 (m, 8H,

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

Chart 2



$CHCH_2(CH_2)_4CH_3$), 0.84 (t, $J = 4$, 3H, CH_2CH_3), −0.03 (s, 6H, Pd*Me*). ^{1}H NMR (CD_3COCD_3): δ 6.99 (s, 2H, mim H4/H5), 6.94 (s, 2H, mim H4/H5), 4.50 (t, $J = 8$, 1H, C*H*), 3.83 (s, 6H, mim N*Me*), 2.33 (m, 2H, CH_2), 1.24 (m, 8H, $CHCH_2(CH_2)_4CH_3$), 0.83 (t, $J = 7$, 3H, CH_2CH_3), −0.40 (s. 6H, Pd*Me*). ^{13}C{^{1}H} NMR (CD_3COCD_3): δ 145.6 (mim C2), 125.8 (mim C4/C5), 120.3 (mim C4/C5), 37.0, 32.9, 32.6, 31.3, 26.6, 22.1, 13.3, −10.3 (Pd*Me*). One signal unobserved due to overlap with acetone-d_6. Anal. Calcd for $C_{17}H_{30}N_4Pd$: C, 51.44; H, 7.61; N, 14.11. Found: C, 51.15; H, 7.43; N, 13.90.

{1,1′-Di(triphenylmethyl)-4,4′-biimidazole}PdMe$_2$ (2c). In the dark, a flask was charged with (pyridazine)$PdMe_2$ (0.108 g, 0.498 mmol) and 1,1′-di(triphenylmethyl)-4,4′-biimidazole (0.309 g, 0.499 mmol), and CH_2Cl_2 (20 mL) was added by syringe. The solution was stirred for 5 min in the dark at 23 °C, and the color changed from orange to yellow. The solution was poured into pentane (180 mL), and a white solid precipitated. The solid was collected by filtration, rinsed with acetone (5 mL), Et_2O (10 mL), and pentane (30 mL), and dried under vacuum to yield {1,1′-di(triphenylmethyl)-4,4′-biimidazole}$PdMe_2$ as a white solid (0.258 g, 68%). ^{1}H NMR (CD_2Cl_2, −60 °C): δ 7.50 (s, 2H, imidazole H2), 7.34 (m, 18H, trityl H3 and H4), 7.16 (m, 12H, trityl H2), 6.83 (s, 2H, imidazole H5), −0.18 (s, 6H, Pd*Me*). ^{13}C NMR (CD_2Cl_2, −60 °C): δ 141.0 (imidazole C2 and trityl C4), 136.2 (imidazole C4), 135.0 (trityl *ipso* C), 129.4 (trityl C2/C3), 128.2 (trityl C2/C3), 115.7 (imidazole C5), 75.7 ($C(C_6H_5)_3$), −13.5 (Pd*Me*). **2c** was stored at −35 °C due to its thermal instability and is insufficiently stable for elemental analysis.

{H$_2$C(5-Me-py)$_2$}PdMe$_2$ (2d). A flask was charged with (pyridazine)$PdMe_2$ (0.217 g, 1.00 mmol) and (5-Mepy)$_2CH_2$ (0.218 g, 1.10 mmol), and Et_2O (30 mL) was added by syringe. An off-white precipitate formed within 15 min. The mixture was stirred at 23 °C for a total of 30 min The solid was collected by filtration, rinsed with Et_2O (2 × 20 mL), and dried under vacuum to yield {H_2C(5-Me-py)$_2$}$PdMe_2$ as a white solid (0.185 g, 55%). ^{1}H NMR (CD_2Cl_2, −60 °C): δ 8.33 (s, 2H, py H6), 7.50 (d, $J = 8$, 2H, py H4), 7.25 (d, $J = 8$, 2H, py H3), 4.65 (d, $J = 14$, 1H, CH_2 H_{ax}), 4.03 (d, $J = 14$, 1H, CH_2 H_{eq}), 2.24 (s, 6H, py 5-*Me*), 0.00 (s, 6H, Pd*Me*). ^{1}H NMR (CD_2Cl_2, −40 °C): δ 8.36 (s, 2H, py H6), 7.50 (d, $J = 8$, 2H, py H4), 7.25 (d, $J = 8$, 2H, py H3), 4.69 (d, $J = 13$, 1H, CH_2 H_{ax}), 4.03 (d, $J = 13$, 1H, CH_2 H_{eq}), 2.26 (s, 6H, py 5-*Me*), 0.02 (s, 6H, Pd*Me*). ^{1}H NMR (CD_2Cl_2, −20 °C): δ 8.38 (s, 2H, py H6), 7.50 (d, $J = 8$, 2H, py H4), 7.25 (d, $J = 8$, 2H, py H3), 4.61 (br d, 1H, CH_2 H_{ax}), 4.03 (br d, 1H, CH_2 H_{eq}), 2.27 (s, 6H, py 5-*Me*), 0.05 (s, 6H, Pd*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2, −60 °C): δ 152.4 (py C2), 150.1 (py C6), 137.8 (py C4), 132.8 (py C5), 123.3 (py C3), 45.4 (CH_2), 17.8 (py 5-*Me*), −7.4 (Pd*Me*). **2d** was stored at −35 °C due to its thermal instability and is insufficiently stable for elemental analysis.

{(4-Me-C$_6$H$_4$)N═CMeCMe═N(4-Me-C$_6$H$_4$)}PdMe$_2$ (2g). A suspension of *trans*-$PdCl_2(SMe_2)_2$ (0.75 g, 2.5 mmol) in Et_2O (140 mL) was cooled to −78 °C, and MeLi (1.5 M in Et_2O, 3.6 mL, 5.5 mmol) was added via syringe. The mixture was stirred for 1 h, during which time most of the orange solid disappeared. The solution was warmed to −50 °C and stirred for 3 h, to afford a clear, colorless solution. A solution of (4-Me-C_6H_4)N═CMeCMe═N(4-Me-C_6H_4) (0.66 g, 2.5 mmol) in Et_2O (80 mL) was added via cannula, and a red solid immediately precipitated. The red suspension was warmed to −10 °C, and H_2O (1.5 mL) was added by syringe to quench any remaining MeLi. The mixture was filtered immediately to afford a red solid. The solid was rinsed with Et_2O (3 × 10 mL) and dried under vacuum. The solid was transferred to a 100 mL Schlenk flask, cooled to −20 °C, and dissolved in CH_2Cl_2 (50 mL). The red solution was filtered through a plug of Celite (LiCl removal) into a Schlenk flask kept at −78 °C. The clear red filtrate was warmed to 0 °C, and the solvent was removed under vacuum. The resulting red solid was suspended in Et_2O (20 mL), stirred for 5 min, filtered, rinsed with Et_2O (2 × 5 mL), and dried under vacuum (0.64 g, 64%). ^{1}H NMR (CD_2Cl_2, −60 °C): δ 0.7.22 (d, $J = 8$, 4H, Ar), 6.74 (d, $J = 8$, 4H, Ar), 2.33 (s, 6H, 4-Me), 2.01 (s, 6H, N═C*Me*), −0.40 (s, 6H, PdMe_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, −60 °C): δ 170.3 (N═Me), 144.3, 135.1, 129.0, 120.4, 20.7, 19.7, −5.9 (PdMe_2). **2g** is insufficiently stable for elemental analysis.

{H$_2$C(3,5-Me$_2$-pz)$_2$}Pd(Me)Cl (3f). A flask was charged with (cod)Pd(Me)Cl (0.530 g, 2.00 mmol) and (3,5-Me_2-pz)$_2CH_2$ (0.413 g, 2.02 mmol), and Et_2O (30 mL) was added by syringe. A white precipitate formed rapidly. The mixture was stirred at 23 °C for 4 h. The white solid was collected by filtration, rinsed with Et_2O (4 × 10 mL) and pentane (3 × 10 mL), and dried under vacuum for 1 h to yield {H_2C(3,5-Me_2-pz)$_2$}Pd(Me)Cl as a white solid (0.706 g, 97%). ^{1}H NMR (CD_2Cl_2): δ 7.14 (br d, $J = 14$, 1H, CH_{eq}), 6.00 (br d, $J = 14$, 1H, CH_{ax}), 5.95 (s, 1H, pz H4/H4′), 5.82 (s, 1H, pz H4/H4′), 2.37 (s, 6H, pz Me), 2.33 (s, 3H, pz Me), 2.32 (s, 3H, pz Me), 0.82 (s, 3H, Pd*Me*). ^{1}H NMR (CD_2Cl_2, −20 °C): δ 7.08 (d, $J = 15$, 1H, CH_{eq}), 5.97 (d, $J = 15$, 1H, CH_{ax}), 5.95 (s, 1H, pz H4/H4′), 5.82 (s, 1H, pz H4/H4′), 2.36 (s, 3H, pz Me), 2.35 (s, 3H, pz Me), 2.30 (s, 6H, pz Me), 0.77 (s, 3H, Pd*Me*). ^{1}H NMR (CD_2Cl_2, −60 °C): δ 7.03 (d, $J = 15$, 1H, CH_{eq}), 5.95 (d, $J = 15$, 1H, CH_{ax}), 5.94 (s, 1H, pz H4/H4′), 5.81 (s, 1H, pz H4/H4′), 2.33 (s, 3H, pz Me), 2.30 (s, 3H, pz Me), 2.27 (s, 3H, pz Me), 2.25 (s, 3H, pz Me), 0.71 (s, 3H, Pd*Me*). ^{1}H NMR (CD_2Cl_2, −80 °C): δ 7.01 (d, $J = 15$, 1H, CH_{eq}), 5.94 (d, $J = 15$, 1H, CH_{ax}), 5.95 (s, 1H, pz H4/H4′), 5.81 (s, 1H, pz H4/H4′), 2.34 (s, 3H, pz Me), 2.32 (s, 3H, pz Me), 2.28 (s, 3H, pz Me), 2.27 (s, 3H, pz Me) 0.67 (s, 3H, Pd*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 153.0 (3/3′-pz), 152.2 (3/3′-pz), 141.0, (5/5′-pz), 140.0 (5/5′-pz), 108.4 (4/4′-pz), 107.5 (4/4′-pz), 58.0 (*C*H), 14.6 (pz Me), 13.6, (pz Me), 11.6 (pz Me), 11.0 (pz Me), −7.5 (Pd*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2, −80 °C): δ 151.4 (3/3′-pz), 150.6 (3/3′-pz), 140.5, (5/5′-pz), 139.3 (5/5′-pz), 107.2 (4/4′-pz), 106.4 (4/4′-pz), 57.0 (*C*H), 14.1 (pz Me), 12.9, (pz Me), 11.2 (pz Me), 10.6 (pz Me), −7.7 (Pd*Me*). **3f** was stored at −35 °C due to its thermal instability and is insufficiently stable for elemental analysis.

Generation of [{(*n*-Hexyl)HC(mim)$_2$}PdMe(NMe$_2$Ph)][B(C$_6$F$_5$)$_4$] (5b). A valved NMR tube was charged with {(*n*-hexyl)HC(mim)$_2$}$PdMe_2$ (0.0123 g, 0.0310 mmol) and [$HNMe_2Ph$][$B(C_6F_5)_4$] (0.0247 g, 0.0310 mmol), and CD_2Cl_2 (0.7 mL) was added by vacuum transfer at −78 °C. The tube was shaken at −78 °C until both solids had dissolved to produce a clear yellow solution. The tube was kept at −78 °C and transferred to an NMR probe that had been precooled to −60 °C, and NMR spectra were recorded. Complete conversion to **5b** was observed. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 7.81 (d, $J = 8.0$, 2H, *o*-Ph), 7.42 (t, $J = 8$, 2H, *m*-Ph), 7.28 (t, $J = 8$, 1H, *p*-Ph), 6.87 (s, 1H, mim H4/H5), 6.86 (s, 1H, mim H4/H5), 6.53 (s, 1H, mim H4/H5), 4.85 (s, 1H, mim H4), 4.08 (t, $J = 8$, 1H, C*H*), 3.63 (s, 3H, mim N*Me*), 3.54 (s, 3H, mim N*Me*), 3.03 (s, 3H, N*Me*), 2.82 (s, 3H, N*Me*), 2.67 (m, 1H, CH_2), 1.29 (m, 1H, CH_2), 1.18 (br s, 8H, $CHCH_2(CH_2)_4CH_3$), 0.79 (br s, 6H, CH_2CH_3 and Pd*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2, −60 °C): δ 153.1 (*ipso*-Ph), 145.6 (mim C2/C2′), 144.9 (mim C2/C2′), 129.4 (*o*-Ph), 127.6 (*p*-Ph), 127.2, 125.6, 122.2

(*m*-Ph), 121.5, 121.4, 56.2 (N*Me*), 50.2 (N*Me*), 38.2, 34.3, 33.9, 33.6, 31.7, 29.3, 27.5, 22.8, 14.2, 2.2 (Pd*Me*).

Generation of [{1,1′-Di(triphenylmethyl)-4,4′-biimidazole}-PdMe(NMe$_2$Ph)][B(C$_6$F$_5$)$_4$] (5c). This compound was generated quantitatively from **2c** and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] using the procedure for **5b**. ^{1}H NMR (CD$_2$Cl$_2$, −60 °C): δ 7.61 (s, 1H, imidazole H5/H5′), 7.52 (d, J = 8, *o*-Ph), 7.33 (m, 18H, trityl H3 and H4), 7.08 (d, J = 8, 6H, trityl H2), 6.90 (d, J = 8, 6H, trityl H2), 6.80 (s, 1H, imidazole H2), 6.73 (t, J = 8, 1H, *p*-Ph), 5.30 (s, 1H, imidazole H2′), 3.01 (s, 3H, N*Me*), 2.98 (s, 3H, N*Me*), 0.82 (s, 3H, Pd*Me*). ^{13}C NMR (CD$_2$Cl$_2$, −60 °C): 153.4, 140.4, 140.2, 136.8 (imidazole C4/C4′), 136.6 (imidazole C4/C4′), 135.0 (imidazole C2/C2′), 132.4 (imidazole C2/C2′), 129.3, 129.0, 128.5, 128.4, 128.2, 128.1, 126.5, 116.4 (imidazole C5/C5′), 116.1 (imidazole C5/C5′), 76.8 (*C*(C$_6$H$_5$)$_3$), 75.8 (*C*(C$_6$H$_5$)$_3$), 52.1 (N*Me*$_2$Ph), 0.04 (Pd*Me*).

Generation of [{H$_2$C(pz)$_2$}PdMe(NMe$_2$Ph)][B(C$_6$F$_5$)$_4$] (5e). This compound was generated quantitatively from **2e** and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] using the procedure for **5b**. ^{1}H NMR (CD$_2$Cl$_2$, −60 °C): δ 7.79 (d, J = 8, 2H, *o*-Ph), 7.71 (d, J = 3, 1H, 5-pz), 7.59 (d, J = 2, 1H, 5′-pz), 7.56 (d, J = 2, 1H, 3-pz), 7.47 (t, J = 8, 2H, *m*-Ph), 7.34 (t, J = 8, 1H, *p*-Ph), 6.87 (d, J = 14, 1H, CH_{ax}), 6.41 (t, J = 2, 1H, 4-pz), 6.15 (d, J = 14, 1H, CH_{eq}), 6.05 (t, J = 2, 1H, 4′-pz), 5.27 (d, J = 2, 1H, 3′-pz), 3.19 (s, 3H, N*Me*), 2.83 (s, 3H, N*Me*), 1.09 (s, 3H, Pd*Me*). ^{13}C NMR (CD$_2$Cl$_2$, −60 °C): δ 152.0, 143.5, 141.9, 132.4, 132.0, 129.3, 127.3, 121.7, 108.2, 107.5, 63.3 (*C*H$_2$), 55.5 (N*Me*), 49.6 (N*Me*), 4.9 (Pd*Me*).

Generation of [(*p*-Tolyldiimine)PdMe(NMe$_2$Ph)][B(C$_6$F$_5$)$_4$] (*p*-tolyldiimine = (4-Me-C$_6$H$_4$)N=CMeCMe=N(4-Me-C$_6$H$_4$)) (5g). This compound was generated quantitatively from **2g** and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] using the procedure for **5b**. ^{1}H NMR (CD$_2$Cl$_2$, −60 °C): δ 7.27 (d, J = 8, 2H, Ar), 7.21 (m, 2H, NMe$_2$*Ph*), 7.16 (m, 3H, NMe$_2$*Ph*), 6.97 (d, J = 8, 2H, Ar), 6.79 (d, J = 8, 2H, Ar), 6.24 (d, J = 8, 2H, Ar), 2.61 (s, 6H, N*Me*$_2$Ph), 2.35 (s, 3H, 4-*Me*-C$_6$H$_4$), 2.29 (s, 3H, 4-*Me*-C$_6$H$_4$), 2.05 (s, 3H, N=C*Me*), 1.93 (s, 3H, N=C*Me*), 0.43 (s, 3H, Pd*Me*). ^{13}C NMR (CD$_2$Cl$_2$, −60 °C): δ 178.5 (N=*C*Me), 173.5 (N=*C*Me), 151.9, 143.9, 143.8, 137.3, 136.1, 130.2, 129.8, 129.0, 126.5, 120.7, 120.6, 118.5, 52.2 (N*Me*$_2$), 21.7, 20.7, 20.6, 20.1, 13.2 (Pd*Me*).

Generation of [{H$_2$C(3,5-Me$_2$-pz)$_2$}PdMe(OEt$_2$)][SbF$_6$] (6f′). A valved NMR tube was charged with **3f** (0.0072 g, 0.020 mmol) and Ag[SbF$_6$] (0.0069 g, 0.020 mmol), and Et$_2$O (1.0 mL) was added by vacuum transfer at −78 °C. The tube was sealed, briefly warmed to 23 °C, and vigorously shaken for 10 min. A slurry of a fine white solid in a colorless supernatant was obtained. The volatiles were removed under vacuum. The tube was cooled to −78 °C, and CD$_2$Cl$_2$ (0.7 mL) was added by vacuum transfer. The tube was kept at −78 °C and transferred to a precooled (−60 °C) NMR probe, and NMR spectra were recorded. The ^{1}H NMR spectrum established that **6f′** had formed quantitatively. ^{1}H NMR (CD$_2$Cl$_2$, −60 °C): δ 6.78 (d, J = 15, 1H, CH$_2$ H_{ax}), 6.21 (d, J = 15, 1H, CH$_2$ H_{eq}), 6.07 (s, 1H, pz H4/H4′), 5.86 (s, 1H, pz H4/H4′), 3.70 (m, 4H, coord. Et$_2$O CH_2), 2.37 (s, 3H, pz Me), 2.33 (s, 3H. pz Me), 2.27 (s, 3H, pz Me), 2.14 (s, 3H, pz Me), 1.63 (t, J = 7, 6H, coord. Et$_2$O CH_3), 0.79 (s, 3H, Pd*Me*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −60 °C): δ 152.7 (3/3′-pz), 150.6 (3/3′-pz), 142.3 (5/5′-pz), 140.7 (5/5′-pz), 108.1 (4/4′-pz), 106.9 (4/4′-pz), 71.8 (Et$_2$O *C*H$_2$), 57.2 (*C*H$_2$), 15.6 (Et$_2$O *C*H$_3$), 14.5, 12.9, 11.2, 10.6, −4.5 (Pd*Me*). Resonances for free Et$_2$O were also present.

Generation of [{H$_2$C(mim)$_2$}Pd{C(=O)Me}(CO)][B(C$_6$F$_5$)$_4$] (7a). A solution of **5a** in CD$_2$Cl$_2$ (0.7 mL) was generated in a valved NMR tube from **2a** (0.0096 g, 0.031 mmol) and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (0.025 g, 0.031 mmol) and cooled to −196 °C. The tube was exposed to CO (5 atm), sealed, and warmed to −78 °C. The tube was briefly warmed to 23 °C and vigorously shaken. The tube was kept at −78 °C prior to NMR and IR analysis at ambient temperature. The ^{1}H NMR spectrum established that **7a** had formed quantitatively. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.03 (br s, 2H, mim H4/H5), 6.86 (s, 1H, mim H4/H5), 6.83 (s, 1H, mim H4/H5), 4.14 (s, 2H, CH_2), 3.74 (s, 3H, mim N*Me*), 3.72 (s, 3H, mim N*Me*), 2.66 (s, 3H, CO*Me*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 217.4 (*C*(O)Me), 173.7 (Pd*C*O), 141.8, 140.4, 128.5, 127.5, 123.5, 123.2, 40.8 (CO*Me*), 34.8 (mim N*Me*), 34.2, (mim N*Me*), 23.1 (*C*H$_2$). The ^{13}C NMR assignments were confirmed by ^{13}CO experiments. IR (CD$_2$Cl$_2$, cm^{-1}): 2121 (ν_{CO}), 1734 (ν_{acyl}).

Generation of [{1,1′-Di(triphenylmethyl)-4,4′-biimidazole}-Pd{C(=O)Me}(CO)][B(C$_6$F$_5$)$_4$] (7c). This compound was generated quantitatively from **2c**, [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$], and CO (5 atm) using the procedure for **7a**. ^{1}H NMR (CD$_2$Cl$_2$, −40 °C): δ 7.57 (s, 1H, imidazole H), 7.38 (m, 19 H, trityl and imidazole H), 7.25 (d, J = 8, 12 H, trityl H2), 7.11 (s, 1H, imidazole H), 7.09 (s, 1H, imidazole H), 2.61 (s, 3H, CO*Me*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −40 °C): δ 213.0 (*C*(O)Me), 173.5 (Pd*C*O), 140.5, 140.1, 139.2 (imidazole C4/C4′), 138.5 (imidazole C4/C4′), 134.3 (imidazole C2/C2′), 132.4 (imidazole C2/C2′), 129.4 (2 C), 128.8, 128.7, 128.5, 128.4, 77.5, 77.1, 41.8 (CO*Me*). IR (CD$_2$Cl$_2$, cm^{-1}): 2123 (ν_{CO}). The ν_{acyl} stretch was not observed due to overlap with a solvent stretch.

Generation of [{H$_2$C(5-Me-py)$_2$}Pd{C(=O)Me}(CO)][B(C$_6$F$_5$)$_4$] (7d). This compound was generated quantitatively from **2d**, [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$], and CO (5 atm) using the procedure for **7a**. ^{1}H NMR (CD$_2$Cl$_2$, −40 °C): δ 8.23 (s, 1H, py H6/H6′), 8.12 (s, 1H, py H6/H6′), 7.74 (d, J = 8, 1H, py H4/H4′), 7.68 (d, J = 8, 1H, py H4/H4′), 7.47 (d, J = 8, 1H, py H3/H3′), 7.44 (d, J = 8, 1H, py H3/H3′), 4.71 (d, J = 15, 1H, CH$_2$ H_{ax}), 4.30 (d, J = 15, 1H, CH$_2$ H_{eq}), 2.64 (s, 3H, CO*Me*) 2.33 (s, 3H, py 5-Me), 2.30 (s, 3H, py 5-Me). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −40 °C): δ 218.0 (*C*(O)Me), 173.0 (Pd*C*O), 151.9 (py *C*2/*C*2′), 151.1 (py C6/C6′), 150.8 (py *C*2/*C*2′), 148.7 (py C6/C6′), 142.3 (py C4/C4′), 141.5 (py C4/C4′), 135.3 (py C5/C5′), 135.1 (py C5/C5′), 125.7 (py C3/C3′), 125.4 (py C3/C3′), 45.7 (CO*Me*), 40.9 (*C*H$_2$) 18.1 (py 5-Me), 17.8 (py 5-Me). IR (CD$_2$Cl$_2$, cm^{-1}): 2128 (ν_{CO}), 1741 (ν_{acyl}).

Generation of [{H$_2$C(pz)$_2$}Pd{^{13}C(=O)Me}(^{13}CO)][B(C$_6$F$_5$)$_4$] (7e). This compound was generated quantitatively from **2e**, [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$], and ^{13}CO (1 atm) using the procedure for **7a**. ^{1}H NMR (CD$_2$Cl$_2$, −20 °C): δ 7.81 (br s, 2H, pz H5/H5′), 7.64 (br s, 2H, pz H3/H3′), 6.39 (br s, 2H, pz H4/H4′), 6.39 (br s, 2H, CH_2), 2.76 (d, $J_{C\text{-}H}$ = 6, 3H, CO*Me*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −10 °C): δ 209.8 (*C*(O)Me), 175.0 (br s, Pd*C*O),144.5 (br s, pz C5/C5′), 129.2 (pz C3/C3′), 109.1 (pz C4/C4′), 63.7 (*C*H$_2$), 40.0 (d, $J_{C\text{-}C}$ = 32, CO*Me*). IR (CD$_2$Cl$_2$, cm^{-1}): 2133 (ν_{CO}), 1756 (ν_{acyl}).

Generation of [{H$_2$C(3,5-Me$_2$-pz)$_2$}Pd{C(=O)Me}(CO)][B(C$_6$F$_5$)$_4$] (7f). A valved NMR tube containing a CD$_2$Cl$_2$ (0.7 mL) solution of **3f** (0.0056 g, 0.016 mmol) and [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] (0.014 g, 0.016 mmol) was cooled to −196 °C and exposed to CO (5 atm). The tube was sealed and warmed to −78 °C. The tube was briefly warmed to 23 °C and vigorously shaken. A slurry of a fine 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 ^{1}H NMR spectrum established that **7f** had formed quantitatively. ^{1}H NMR (CD$_2$Cl$_2$, −60 °C): δ 6.43 (d, J = 15, 1H, CH$_2$ H_{ax}), 6.05 (d, J = 15, 1H, CH$_2$ H_{eq}), 6.03 (s, 1H, pz H4/H4′), 5.97 (s, 1H, pz H4/H4′), 2.62 (s, 3H, (CO*Me*)), 2.36 (s, 3H, pz Me), 2.34 (s, 3H. pz Me), 2.22 (s, 3H, pz Me), 2.11 (s, 3H, pz Me). ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ 6.45 (br s, 1H, H_{ax}), 6.22 (br s, 1H, H_{eq}), 6.04 (s, 2H, pz H), 2.65 (s, 3H, CO*Me*), 2.39 (s, 6H, pz Me), 2.22 (s, 6H, pz Me). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −60 °C): δ 211.3 (*C*(O)Me), 171.7 (Pd*C*O), 153.1 (3/3′-pz), 152.2 (3/3′-pz), 142.8 (5/5′-pz), 141.1 (5/5′-pz), 108.7 (4/4′-pz), 107.6 (4/4′-pz), 56.9 (*C*H$_2$), 40.4 (CO*Me*), 13.9, 13.6, 11.0, 10.6. IR (CD$_2$Cl$_2$, cm^{-1}): 2132 (ν_{CO}). The ν_{acyl} band was not observed due to overlap with a solvent band.

Generation of [(*p*-Tolyldiimine)Pd{C(=O)Me}(CO)][B(C$_6$F$_5$)$_4$] (7g). This compound was generated quantitatively from **3g**, [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$], and CO (5 atm) using the procedure for

7f. ^{1}H NMR (CD_2Cl_2, −40 °C): δ 7.29 (br d, 2H, Ar), 7.25 (br d, 2H, Ar), 6.89 (br d, 2H, Ar), 6.78 (br d, 2H, Ar), 2.35 (s, 6H, 4-*Me*-C_6H_4), 2.32 (s, 3H, *N* = C*Me*), 2.31 (s, 3H, N=C*Me*), 2.09 (s, 3H, CO*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2, −40 °C): δ 212.3 (*C*(O)Me), 180.4 (N= *C*Me), 172.4 (Pd*C*O and N=*C*Me), 143.7, 142.6, 131.3, 130.6, 130.5, 122.1, 120.2, 119.9, 36.4 (CO*Me*), 21.2, 20.9, 20.0. IR (CD_2Cl_2, cm^{-1}): 2130 (ν_{CO}), 1752 (ν_{acyl}).

Generation of [{(2,6-^{i}Pr$_2$-C$_6$H$_3$)N=CMeCMe=N(2,6-^{i}Pr$_2$-C$_6$H$_3$)}Pd{C(=O)Me}(CO)][B(C$_6$F$_5$)$_4$] (7h). [42] This compound was generated quantitatively from **3h**, $[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$, and CO (5 atm) using the procedure for **7f**. ^{1}H NMR (CD_2Cl_2, −40 °C): δ 7.41–7.27 (m, 6H, 2,6-^{i}Pr$_2$-C_6H_3 Ar), 2.74 (m, *J* = 7, 4H, C*H*Me$_2$), 2.39 (s, 3H, N=C*Me*), 2.27 (s, 3H, N=C*Me*), 2.01 (s, 3H, CO*Me*) 1.37 (d, *J* = 7, 12H, CH*Me*$_2$), 1.19 (d, *J* = 7, 6H, CH*Me*$_2$), 1.10 (d, *J* = 7, 6H, CH*Me*$_2$). IR (CD_2Cl_2, cm^{-1}): 2132 (ν_{CO}), 1757 (ν_{acyl}).

Generation of [{H$_2$C(mim)$_2$}PdMe(H$_2$C=CH$_2$)][B(C$_6$F$_5$)$_4$] (8a). A solution of **5a** (0.016 mmol) in CD_2Cl_2 (0.7 mL) was generated in a valved NMR tube from **2a** (0.0048 g, 0.016 mmol) and $[HNMe_2Ph][B(C_6F_5)_4]$ (0.012 g, 0.016 mmol), as described above, and cooled to −196 °C. The tube was exposed to ethylene (ca. 5 equiv) and sealed. The tube was warmed to −78 °C. The tube was kept at −78 °C and transferred to a precooled (−60 °C) NMR probe, and a ^{1}H NMR spectrum was recorded. The ^{1}H NMR spectrum established that **8a** had formed (100% versus NMe_2Ph). Under these conditions (−60 °C), exchange of coordinated and free ethylene is fast on the NMR chemical shift time scale. Fast exchange was also observed when 2.5 equiv of ethylene was used. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 7.04 (s, 1H, mim H4/H5), 7.00 (s, 2H, mim H4/H5), 6.65 (s, 1H, mim H4/H5), 5.22 (br s, free and coordinated $H_2C=CH_2$), 4.09 (s, 2H, CH_2), 3.73 (s, 3H, mim N*Me*), 3.67 (s, 3H, mim N*Me*), 0.55 (s, 3H, Pd*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2, −60 °C): δ 140.3 (mim C2/C2′), 138.9 (mim C2/C2′), 124.8, 122.8, 122.7, 121.9, 114.0 (br s, free and coord $H_2C=CH_2$), 34.3 (mim N*Me*), 33.8 (mim N*Me*), 22.5 (*C*H_2), 7.0 (Pd*Me*).

Generation of [{(*n*-Hexyl)HC(mim)$_2$}PdMe(H$_2$C=CH$_2$)][B(C$_6$F$_5$)$_4$] (8b). This compound was generated quantitatively from **2b**, $[HNMe_2Ph][B(C_6F_5)_4]$, and ethylene (ca. 4 equiv) using the procedure for **8a**. Under these conditions (−60 °C), exchange of coordinated and free ethylene (δ 5.37) is slow on the NMR chemical shift time scale. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 6.99 (s, 1H, mim H4/H5), 6.96 (s, 1H, mim H4/H5), 6.92 (s, 1H, mim H4/H5), 6.68 (s, 1H, mim H4/H5), 4.86 (br s, 2H, $H_2C=CH_2$), 4.72 (br s, 2H, $H_2C=CH_2$), 4.21 (t, *J* = 7, 1H, C*H*), 3.73 (s, 3H, mim N*Me*), 3.67 (s, 3H, mim N*Me*), 2.09 (m, 2H, CH_2), 1.15 (br s, 8H, $CHCH_2(CH_2)_4CH_3$), 0.77 (br s, 3H, CH_2CH_3), 0.57 (s, 3H, Pd*Me*).

Generation of [{1,1′-Di(triphenylmethyl)-4,4′-biimidazole}PdMe(H$_2$C=CH$_2$)][B(C$_6$F$_5$)$_4$] (8c). This compound was generated quantitatively from **2c**, $[HNMe_2Ph][B(C_6F_5)_4]$, and ethylene (ca. 10 equiv) using the procedure for **8a**. Under these conditions (−60 °C), exchange of coordinated and free ethylene is fast on the NMR chemical shift time scale. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 7.62 (s, 1H, imidazole H2/H2′), 7.32 (m, 18H, trityl H3 and H4), 7.29 (s, 1H, imidazole H2/H2′), 7.11 (d, *J* = 8, 6H, trityl H2/ H2′), 7.07 (d, *J* = 8, 6H, trityl H2/ H2′), 7.00 (s, 1H, imidazole H5/H5′), 6.99 (s, 1H, imidazole H5/H5′), 5.31 (s, free and coordinated $H_2C=CH_2$), 0.57 (s, 3H, Pd*Me*). ^{13}C NMR (CD_2Cl_2, −60 °C): 140.4, 140.1, 136.1 (imidazole C4/C4′), 135.9 (imidazole C4/C4′), 135.0 (imidazole C2/C2′), 132.8 (imidazole C2/C2′), 129.3, 129.2, 128.6, 128.4, 128.3, 128.2, 119.9 (br s, free and coordinated $H_2C=CH_2$), 117.2 (imidazole C5/C5′), 116.8 (imidazole C5/C5′), 76.9 (*C*$(C_6H_5)_3$), 76.6 (*C*$(C_6H_5)_3$), 3.6 (Pd*Me*).

Generation of [{H$_2$C(5-Me-py)$_2$}PdMe(H$_2$C=CH$_2$)][B(C$_6$F$_5$)$_4$] (8d). This compound was generated quantitatively from **2d**, $[HNMe_2Ph][B(C_6F_5)_4]$, and ethylene (ca. 8 equiv) using the procedure for **8a**. Under these conditions (−60 °C), exchange of coordinated and free ethylene is fast on the NMR chemical shift time scale. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 8.16 (s, 1H, py H6/H6′), 7.95 (s, 1H, py H6/H6′), 7.72 (d, *J* = 8, 1H, py H4/H4′), 7.63 (d, *J* = 8, 1H, py H4/H4′), 7.44 (d, *J* = 8, 1H, py H3/H3′), 7.39 (d, *J* = 8, 1H, py H3/H3′), 5.35 (br s, free and coordinated $H_2C=CH_2$), 4.71 (d, *J* = 14, 1H, CH_2 H_{ax}), 4.25 (d, *J* = 14, 1H, CH_2 H_{eq}), 2.33 (s, 3H, py 5-Me), 2.29 (s, 3H, py 5-Me), 0.71 (s, 3H, Pd*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2, −60 °C): δ 151.8 (py C2/C2′), 150.6 (py C2/C2′), 149.8 (py C6/C6′), 147.4 (py C6/C6′), 141.1 (py C4/C4′), 140.5 (py C4/C4′), 134.9 (py C5/C5′), 134.8 (py C5/C5′), 122.9 (br s, exchanging $H_2C=CH_2$), 45.3 (*C*H_2), 17.8 (py 5-Me), 17.7 (py 5-Me), 9.0 (Pd*Me*).

Generation of [{H$_2$C(pz)$_2$}PdMe(H$_2$C=CH$_2$)][B(C$_6$F$_5$)$_4$] (8e). This compound was generated quantitatively from **2e**, $[HNMe_2Ph][B(C_6F_5)_4]$, and ethylene (ca. 5 equiv) using the procedure for **8a**. Under these conditions (−60 °C), exchange of coordinated and free ethylene is fast on the NMR chemical shift time scale. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 7.81 (br s, 1H, pz H), 7.71 (br s, 2H, pz H), 7.47 (br s, 1H, pz H), 6.54 (m, 1H, pz H4/H4′), 6.50 (d, *J* = 15, CH_2 H_{ax}), 6.43 (m, 1H, pz H4/H4′), 6.21 (d, *J* = 15, CH_2 H_{eq}), 5.28 (s, free and coordinated $H_2C=CH_2$), 0.88 (s, 3H, Pd*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2, −60 °C): δ 142.1 (pz C5/C5′), 140.8 (pz C5/C5′), 133.5 (pz C3/C3′), 132.5 (pz C3/C3′), 115.2 (br s, exchanging $H_2C=CH_2$), 108.0 (pz C4/C4′), 107.9 (pz C4/C4′), 40.3 (*C*H_2), 8.9 (Pd*Me*).

Generation of [{H$_2$C(3,5-Me$_2$-pz)$_2$}PdMe(H$_2$C=CH$_2$)][B(C$_6$F$_5$)$_4$] (8f). A valved NMR tube containing a CD_2Cl_2 (0.7 mL) solution of **3f** (7.2 mg, 20.0 μmol) and $[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$ (17.8 mg, 20.0 μmol) was cooled to −196 °C and exposed to ethylene (ca. 3 equiv). The tube was sealed and warmed to −78 °C. The solution was kept at −78 °C and transferred to a precooled (−60 °C) NMR probe, and a ^{1}H NMR spectrum was recorded at −60 °C. The ^{1}H NMR spectrum established that **8f** had formed (100% versus Et_2O). Under these conditions (−60 °C), exchange of coordinated and free ethylene (δ 5.37) is slow on the NMR chemical shift time scale. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 6.60 (d, *J* = 15, 1H, CH_2 H_{ax}), 6.05 (s, 1H, pz H4/H4′), 6.02 (d, *J* = 15, 1H, CH_2 H_{eq}), 5.88 (s, 1H, pz H4/H4′), 5.15 (br s, 2H, $H_2C=CH_2$), 4.89 (br s, 2H, $H_2C=CH_2$), 2.37 (s, 3H, pz Me), 2.30 (s, 3H, pz Me), 2.28 (s, 3H, pz Me), 2.17 (s, 3H, pz Me), 0.80 (s, 3H, Pd*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2, −60 °C): δ 151.8 (3/3′-pz), 150.9 (3/3′-pz), 141.6 (5/5′-pz), 140.9 (5/5′-pz), 108.2 (4/4′-pz), 107.9 (4/4′-pz), 89.4 ($H_2C=CH_2$), 57.2 (*C*H_2), 13.9, 13.1, 10.9, 10.6, 5.9 (Pd*Me*).

Generation of [{H$_2$C(3,5-Me$_2$-pz)$_2$}PdMe(H$_2$C=CH$_2$)][SbF$_6$] (8f′). A solution of **6f′** (0.020 mmol) in CD_2Cl_2 in a valved NMR tube was generated as described above and cooled to −196 °C, and ethylene (ca. 8 equiv) was added by vacuum transfer. The tube was sealed and warmed to −78 °C. The tube was maintained at −78 °C and transferred to a precooled (−60 °C) NMR probe and NMR spectra were recorded. A ^{1}H NMR spectrum was recorded at −60 °C and showed that **8f′** had formed. Under these conditions (−60 °C), exchange of coordinated and free ethylene (δ 5.37) is slow on the NMR chemical shift time scale. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 6.66 (d, *J* = 15, 1H, CH_2 H_{ax}), 6.14 (d, *J* = 15, 1H, CH_2 H_{eq}), 6.03 (s, 1H, pz H4/H4′), 5.88 (s, 1H, pz H4/H4′), 5.15 (br s, 2H, $H_2C=CH_2$), 4.90 (br s, 2H, $H_2C=CH_2$), 2.39 (s, 3H, pz Me), 2.34 (s, 3H, pz Me), 2.29 (s, 3H, pz Me), 2.18 (s, 3H, pz Me), 0.79 (s, 3H, Pd*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2, −60 °C): δ 151.5 (3/3′-pz), 150.6 (3/3′-pz), 141.8 (5/5′-pz), 141.3 (5/5′-pz), 108.0 (4/4′-pz), 107.7 (4/4′-pz), 89.3 ($H_2C=CH_2$), 57.3 (*C*H_2), 13.9, 13.2, 10.9, 10.6, 5.8 (Pd*Me*).

Generation of [(*p*-Tolyldiimine)PdMe(H$_2$C=CH$_2$)][B(C$_6$F$_5$)$_4$] (8g). This compound was generated quantitatively from **2g**, $[HNMe_2Ph][B(C_6F_5)_4]$, and ethylene (ca. 6 equiv) and handled using the procedure for **8a**. Under these conditions (−60 °C), exchange of coordinated and free ethylene is fast on the NMR chemical shift

(42) van Asselt, R.; Gielens, E. E. C. G.; Rulke, R. E.; Vrieze, K.; Elsevier, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 977.

time scale. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 7.30 (d, J = 8, 4H, Ar), 6.79 (d, J = 8, 2H, Ar), 6.70 (d, J = 8, 2H, Ar), 5.20 (s, free and coordinated $H_2C{=}CH_2$), 2.35 (s, 6H, 4-*Me*-C_6H_4), 2.28 (s, 3H, N=C*Me*), 2.15 (s, 3H, N=C*Me*), 0.16 (s, Pd*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2, −60 °C): δ 180.4 (N=*C*Me), 174.5 (N=*C*Me), 141.6, 140.6, 137.8, 137.7, 130.4, 129.9, 120.2, 118.8, 117.1 (br s, exchanging $H_2C{=}CH_2$), 21.2, 20.7, 20.6, 20.2, 13.7 (Pd*Me*).

Generation of [{H_2C(mim)$_2$}PdEt($H_2C{=}CH_2$)][$B(C_6F_5)_4$] (9a). A valved NMR tube containing a CD_2Cl_2 solution of **8a** and 5 equiv of ethylene was kept at −10 °C for 90 min. A ^{1}H NMR spectrum was recorded at −10 °C and showed the following species were present in solution (% relative to free NMe_2Ph): unreacted **8a** (27%), propylene (61%), *cis*- and *trans*-2-butenes (24%), and {H_2C(mim)$_2$}PdEt($H_2C{=}CH_2$)$^+$ (**9a**, 73%). Under these conditions (−10 °C), exchange of coordinated and free ethylene is fast on the NMR time scale. ^{1}H NMR of {H_2C(mim)$_2$}PdEt($H_2C{=}CH_2$)$^+$ (CD_2Cl_2, −10 °C): δ 5.20 (br s, free and coordinated $H_2C{=}CH_2$ of **8a** and **9a**), 1.50 (q, J = 8, 2H, PdCH_2Me), 0.85 (t, J = 8, 3H, PdCH_2*Me*). The mim, bridge-CH_2, and NMe methyl resonances of **9a** could not be distinguished from those of **8a**.

Generation of [{1,1′-Di(triphenylmethyl)-4,4′-biimidazole}-PdEt($H_2C{=}CH_2$)][$B(C_6F_5)_4$] (9c). A valved NMR tube containing a CD_2Cl_2 solution of **8c** and 14 equiv of ethylene was kept at −10 °C for 7 h. A ^{1}H NMR spectrum was recorded at −10 °C and showed that **7c** had completely disappeared, and the following species were present (% relative to free NMe_2Ph): propylene (100%), *cis*- and *trans*-2-butenes (100%), 1-butene (23%), and {1,1′-di(triphenylmethyl)-4,4′-biimidazole}PdEt($H_2C{=}CH_2$)$^+$ (**9c**, 100%). Under these conditions (−10 °C), exchange of coordinated and free ethylene is fast on the NMR chemical shift time scale. ^{1}H NMR of {1,1′-di(triphenylmethyl)-4,4′-biimidazole}PdEt($H_2C{=}CH_2$)$^+$ (CD_2Cl_2, −10 °C): δ 7.65 (s, 1H, imidazole H2/H2′), 7.38 (br s, 18H, trityl H3 and H4), 7.31 (s, 1H, imidazole H2/H2′), 7.12 (br s, 12H, trityl H2/ H2′), 7.03 (br s, 2H, imidazole H5/H5′), 5.34 (br s, free and coordinated $H_2C{=}CH_2$),1.50 (br q, J = 8, 2H, PdCH_2Me), 0.85 (br t, J = 8, 3H, PdCH_2*Me*).

Generation of [{H_2C(5-Me-py)$_2$}PdEt($H_2C{=}CH_2$)][$B(C_6F_5)_4$] (9d). A valved NMR tube containing a CD_2Cl_2 solution of **8d** and 9 equiv of ethylene was kept at −10 °C for 125 min. A ^{1}H NMR spectrum was recorded at −60 °C and showed that **8d** had completely disappeared, and the following products were present (% relative to free NMe_2Ph): propylene (42%), *cis*- and *trans*-2-butenes (100%), 1-butene (32%), and {H_2C(5-Me-py)$_2$}PdEt($H_2C{=}CH_2$)$^+$ (**9d**, 80%). Under these conditions (−60 °C), exchange of coordinated and free ethylene is fast on the NMR time scale. ^{1}H NMR of {H_2C(5-Me-py)$_2$}PdEt($H_2C{=}CH_2$)$^+$ (CD_2Cl_2, −60 °C): δ 8.35 (s, 1H, py H6/H6′), 7.92 (s, 1H, py H6/H6′), 7.73 (d, J = 8, 1H, py H4/H4′), 7.61 (d, J = 8.0, 1H, py H4/H4′), 7.45 (d, J = 8, 1H, py H3/H3′), 7.38 (d, J = 8, 1H, py H3/H3′), 4.65 (d, J = 14, 1H, CH_2 H_{ax}), 4.25 (d, J = 14, 1H, CH_2 H_{eq}), 5.32 (br s, free and coordinated $H_2C{=}CH_2$), 2.35 (s, 3H, py 5-Me), 2.26 (s, 3H, py 5-Me), 1.72 (pentet, J = 8, 1H, PdCH_2Me), 1.44 (pentet, J = 8, 1H, PdCH_2Me), 0.65 (t, J = 8, 3H, PdCH_2*Me*).

Generation of [{H_2C(pz)$_2$}PdEt($H_2C{=}CH_2$)][$B(C_6F_5)_4$] (9e). A valved NMR tube containing a CD_2Cl_2 solution of **8e** and 4 equiv of ethylene was kept at −22 °C for 2 h. A ^{1}H NMR spectrum was recorded at −65 °C and showed the following species were present (% relative to free NMe_2Ph): **8e** (15%), propylene (85%), *cis*- and *trans*-2-butenes (36%), and {H_2C(pz)$_2$}PdEt($H_2C{=}CH_2$)$^+$ (**9e**, 85%). Under these conditions (−65 °C), exchange of coordinated and free ethylene is fast on the NMR chemical shift time scale. ^{1}H NMR of {H_2C(pz)$_2$}PdEt($H_2C{=}CH_2$)$^+$ (CD_2Cl_2, −65 °C): δ 5.20 (br s, free and coordinated $H_2C{=}CH_2$ of **8e** and **9e**), 1.95 (m, 1H, PdCH_2Me), 1.57 (m, 1H, PdCH_2Me), 0.85 (t, J = 7, 3H, PdCH_2*Me*). The pz, and bridge CH_2 resonances of **9e** could not be distinguished from those of **8e**. The ^{1}H NMR assignments for the PdEt group of **9e** were confirmed by a COSY experiment due to overlap of one of the methylene resonances with the *cis*- and *trans*-2-butene methyl resonance.

Generation of [{H_2C(3,5-Me_2-pz)$_2$}PdEt($H_2C{=}CH_2$)]-[$B(C_6F_5)_4$] (9f). A valved NMR tube containing a CD_2Cl_2 solution of **8f** and 13 equiv of ethylene was kept at −10 °C for 26 min. A ^{1}H NMR spectrum was recorded at −60 °C and showed that the following species were present (% relative to free NMe_2Ph): **8f** (14%), propylene (66%), *cis*- and *trans*-2-butenes (66%), and {H_2C(3,5-Me_2-pz)$_2$}PdEt($H_2C{=}CH_2$)$^+$ (**9f**, 85%). Under these conditions (−60 °C), exchange of coordinated and free ethylene is slow on the NMR chemical shift time scale. ^{1}H NMR of {H_2C(3,5-Me_2-pz)$_2$}PdEt($H_2C{=}CH_2$)$^+$ (CD_2Cl_2, −60 °C): δ 6.54 (d, J = 15, 1H, CH_2 H_{ax}), 6.99 (d, J = 15, 1H, CH_2 H_{eq}), 4.97 (br d, J = 15, 2H, $H_2C{=}CH_2$), 4.87 (br d, J = 10, 2H, $H_2C{=}CH_2$), 0.63 (t, J = 7, 3H, PdCH_2*Me*). The pz H4 and pz Me resonances of **9f** could not be distinguished from those of **8f**. The PdCH_2CH$_3$ resonances of **9f** were not observed at −60 °C due to broadening and overlap with other resonances.

Generation of [(*p*-Tolyldiimine)PdEt($H_2C{=}CH_2$)][$B(C_6F_5)_4$] (9g). A valved NMR tube containing a CD_2Cl_2 solution of **8g** and 4.5 equiv of ethylene was kept at −10 °C for 13 min. A ^{1}H NMR spectrum was recorded at −60 °C and showed the following species were present (% relative to free NMe_2Ph): propylene (43%), *cis*- and *trans*-2-butenes (44%), 1-butene (32%), and (*p*-tolyldiimine)PdEt($H_2C{=}CH_2$)$^+$ (**9g**, 86%). Under these conditions (−60 °C), exchange of coordinated and free ethylene is fast on the NMR chemical shift time scale. ^{1}H NMR of (*p*-tolyldiimine)PdEt($H_2C{=}CH_2$)$^+$ (CD_2Cl_2, −60 °C): δ 7.30 (br m, 4H, Ar), 6.86 (br d, J = 7, 2H, Ar), 6.69 (br d, J = 7, 2H, Ar), 5.23 (br s, free and coordinated $H_2C{=}CH_2$ and **9g**), 2.36 (br s, 3H, 4-*Me*-C_6H_4), 2.35 (br s, 3H, 4-*Me*-C_6H_4), 2.28 (br s, 3H, N=C*Me*), 2.14 (br s, 3H, N=C*Me*), 1.05 (q, 2H, J = 7, PdCH_2Me), 0.28 (t, J = 7, 3H, PdCH_2*Me*).

Kinetics of Insertion of (N^N)PdMe($H_2C{=}CH_2$)$^+$ Species. The first-order rate constants ($k_{insert,Me}$) for the insertion of ethylene into the Pd−Me bond of (N^N)PdMe($H_2C{=}CH_2$)$^+$ species **8a**−**g** and **8f′** were determined by ^{1}H NMR. The procedure for **8a** is described here. Analogous procedures were used for **8b**−**g** and **8f′**. Details and kinetic plots are provided in the Supporting Information. Procedure for **8a**: A CD_2Cl_2 solution of **8a** containing 4 equiv of excess free ethylene was generated in a valved NMR tube. The tube was placed in a −10 °C constant temperature bath for 20 min, placed in a −78 °C bath for 3 min, and transferred to a precooled (−60 °C) NMR probe where a ^{1}H NMR spectrum was recorded at −60 °C. This procedure was repeated at 20 min intervals. Values of $I_{0,PdMe}$, I_{PdMe}, and I_{NMe2Ph}, where $I_{0,PdMe}$ = the integral of the Pd−Me resonance of **8a** (δ = 0.61) at the start of the experiment, I_{PdMe} = the integral of the Pd−Me resonance of **8a** at the end of each 20 min interval, and I_{NMe2Ph} = the integral of the NMe_2Ph resonance (δ = 2.92), were determined by integration. A plot of $\ln(A_{PdMe}/A_{0,PdMe})$ versus time (at −10 °C), where $A_{PdMe} = I_{PdMe}/I_{NMe2Ph}$ and $A_{0,PdMe} = I_{0,PdMe}/I_{NMe2Ph}$, was linear. The slope of this plot equals $-k_{insert,Me}$. For **8a**, $k_{insert,Me} = (1.2 \pm 0.1) \times 10^{-4}$ s^{-1} at −10 °C (ca. 3 half-lives).

Kinetics of Insertion of (N^N)PdEt($H_2C{=}CH_2$)$^+$ Species 9a,c–g. The first-order rate constants ($k_{insert,Et}$) for the insertion of ethylene into the Pd−Et bond of (N^N)PdEt($H_2C{=}CH_2$)$^+$ species **9a**,**c**−**g** were determined by ^{1}H NMR. The procedure for **9a** is described here. Analogous procedures were used for **9c**−**g**, and details and kinetic plots are provided in the Supporting Information. *Procedure for* **9a**: A CD_2Cl_2 solution (0.7 mL) of **8a** was generated in a valved NMR tube as described above. The tube was transferred to a precooled (−40 °C) NMR probe. A ^{1}H NMR spectrum was recorded at −40 °C and showed that **8a** had formed (100% versus NMe_2Ph). Under these conditions (−40 °C), exchange of coordinated and free ethylene is fast on the NMR time scale. The NMR probe was warmed to −10

°C, thermally equilibrated, and maintained at this temperature, and ^{1}H NMR spectra were recorded periodically. Values of $I_{butenes}$ and I_{NMe2Ph}, where $I_{butenes}$ = the integral of the methyl resonances of *trans*-2-, *cis*-2- ($\delta = 1.59$) and 1-butene ($\delta = 0.98$) and I_{NMe2Ph} = the integral of the NMe_2Ph resonance ($\delta = 2.94$), were determined by careful integration of each spectrum and used to determine the moles butenes produced/moles of catalyst. A plot of turnovers (moles butenes produced/moles of catalyst) versus time was linear ($r^2 = 0.991$). The slope of this plot equals $k_{insert,Et}$. For **9a**, $k_{insert,Et} = (1.0 \pm 0.1) \times 10^{-4}$ s^{-1} at -10 °C.

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Supporting Information Available: Variable-temperature NMR spectra of **2d** and **3f**, details of kinetics studies, additional synthetic procedures, and representative NMR spectra of **2d**, **2g**, **3f**, **5d**, **7d**, **8d**, and **9d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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