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Neutral and Cationic Palladium(II) Bis(pyrazolyl)methane Complexes

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The synthesis, structures, and reactivity of neutral and cationic Pd(II) complexes incorporating bis(pyrazolyl)methane ligands are described. The reaction of $(CH_3CN)_2PdCl_2$ with the appropriate bis(pyrazoyl)methane in CH_2Cl_2 yields $\{Ph_2C(3\text{-}^tBu\text{-}pz)_2\}PdCl_2$ (**1**) and $\{Ph_2C(pz)_2\}PdCl_2$ (**2**). Steric crowding associated with the ^{t}Bu groups of **1** increases the puckering of the chelate ring (boat conformation) and retards the chelate ring inversion relative to **2**. The reaction of $\{Me_2C(pz)_2\}PdMe_2$ (**3**) with $[HNMe_2Ph][B(C_6F_5)_4]$ yields $\{Me_2C(pz)_2\}PdMe(NMe_2Ph)^+$ (**4a**, $B(C_6F_5)_4^-$ salt), while treatment of **3** with $[H(OEt_2)_2][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ yields $\{Me_2C(pz)_2\}PdMe(OEt_2)^+$ (**4b**, $B\{3,5\text{-}(CF_3)_2C_6H_3\}_4^-$ salt). Complex **4a** reacts with ethylene at −60 °C (CD_2Cl_2) to yield $\{Me_2C(pz)_2\}PdMe(CH_2{=}CH_2)^+$ (**5**, $B(C_6F_5)_4^-$ salt) and free NMe_2Ph. Cation **5** undergoes ethylene insertion at −10 °C and oligomerizes ethylene (1 atm) to predominantly linear internal C_8 to C_{24} olefins (ca. 0.1 branches per 2 carbons) at 23 °C.

Introduction

Cationic Pd^{II} alkyl complexes $(L{-}L)PdR(L')^+$ containing a neutral bidentate nitrogen donor ligand (L−L) and a labile ligand or substrate (L′) cis to the alkyl group,[1] undergo a variety of important insertion reactions[2] and are active species for olefin polymerization,[3,4] olefin/CO copolymerization,[5] and olefin/alkyl−acrylate copolymerization.[6] The most intensively studied compounds of this type incorporate diimine or bipyridine ligands. A key advance in this area was the recognition that chain transfer in olefin polymerizations by these systems proceeds by associative olefin exchange and that the use of bulky L−L ligands which block the apical coordination sites disfavors this process.[3] We are interested in developing the chemistry of $(L{-}L)PdR(L')^+$ compounds containing other bidentate nitrogen donor ligands to probe how the electronic and steric properties of the ancillary ligands influence reactivity. Here we describe initial studies of several new $\{R_2C(pz')_2\}PdCl_2$ and $\{R_2C(pz')_2\}PdMe(L)^+$ complexes that incorporate bis(pyrazolyl)methane (pz′) ligands. Canty, Trofimenko, and others have prepared several types of Pd(II) bis(pyrazolyl)methane complexes, including $\{R_2C(pz')_2\}PdMe_2$ and $\{R_2C(pz')_2\}Pd(allyl)^+$.[7−9] The six-membered chelate rings in $\{R_2C(pz')_2\}PdX_2$ compounds adopt boat conformations and may undergo inversion, which results in exchange of the axial and equatorial CR_2 substituents.[10] Pyrazoles are weaker σ-donors than imine or pyridine ligands, and therefore $\{R_2C(pz')_2\}PdR^+$ cations may be more electrophilic than (diimine)PdR^+ or (bipy)PdR^+ species.[1,7,11]

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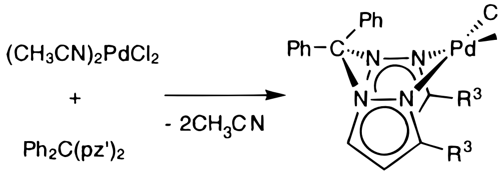
Table 1. Summary of Crystal Data for $\{Ph_2C(3\text{-}{}^tBu\text{-}pz)_2\}PdCl_2 \cdot 1.5CH_2Cl_2$ ($\mathbf{1} \cdot 1.5CH_2Cl_2$) and $\{Ph_2C(pz)_2\}PdCl_2 \cdot CH_2Cl_2$ ($\mathbf{2} \cdot CH_2Cl_2$)

	1·1.5CH$_2$Cl$_2$	**2**·CH$_2$Cl$_2$
formula	$C_{27}H_{32}Cl_2N_4Pd \cdot (1.5\ CH_2Cl_2)$	$C_{19}H_{16}Cl_2N_4Pd \cdot CH_2Cl_2$
fw	717.26	562.58
cryst size, mm	0.37 × 0.18 × 0.16	0.54 × 0.29 × 0.11
color/shape	orange/prism	orange-yellow/plate
d(calcd), Mg/m^3	1.520	1.699
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$	$Pbca$
a, Å	19.492(3)	14.426(2)
b, Å	15.283(2)	15.247(2)
c, Å	22.076(5)	20.004(3)
β, deg	107.56(1)	
V, Å^3	6270(2)	4400(1)
Z	8	8
T, K	210(2)	213(2)
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation, λ, Å	Mo Kα, 0.71073	Mo Kα, 0.71073
2θ range, deg	$4.0 < 2\theta < 50.0$	$4.0 < 2\theta < 50.0$
h; k; l collected	−23, 4; −1, 18; −25, 26	−17, 5; −1,18; −17, 23
no. of rflns measd	14001	6757
no. of unique rflns	10856	3824
R_{int}	0.0185	0.0162
no. of obsd rflns, criterion	9075, $I > 2\sigma(I)$	3303, $I > 2\sigma(I)$
μ, mm^{-1}	1.043	1.344
transmission range, %	95−100	95−100
structure solution[a]	direct methods	direct methods
GOF on F^2	1.109	1.069
R indices ($I > 2\sigma(I)$)[b,c]	R1 = 0.0272 wR2 = 0.0627	R1 = 0.0227 wR2 = 0.0597
R indices (all data)[b,c]	R1 = 0.0410 wR2 = 0.0701	R1 = 0.0302 wR2 = 0.0653
max resid density, e/Å^3	0.42, −0.33	0.62, −0.42

[a] XS, SHELXTL v 5.0, Siemens Anal. X-ray Inst, Madison, WI, 1996. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$.

Results and Discussion

Synthesis of $\{Ph_2C(pz')_2\}PdCl_2$ Complexes. The reaction of $(CH_3CN)_2PdCl_2$ with $Ph_2C(3\text{-}{}^tBu\text{-}pz)_2$ or $Ph_2C(pz)_2$ in CH_2Cl_2 yields the dichloride complexes $\{Ph_2C(3\text{-}{}^tBu\text{-}pz)_2\}PdCl_2$ (**1**) and $\{Ph_2C(pz)_2\}PdCl_2$ (**2**, eq 1). Recrystallization of the crude products from CH_2Cl_2 yields **1**·1.5CH$_2$Cl$_2$ and **2**·CH$_2$Cl$_2$ as orange crystalline solids.



(1)

1, R^3 = ^{t}Bu
2, R^3 = H

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $\{Ph_2C(3\text{-}{}^tBu\text{-}pz)_2\}PdCl_2$ (1)

Pd(2)−N(51)	2.034(2)	N(52)−C(53)	1.353(3)
Pd(2)−N(61)	2.051(2)	C(53)−C(54)	1.360(4)
Pd(2)−Cl(3)	2.2871(8)	C(54)−C(55)	1.397(4)
Pd(2)−Cl(4)	2.2909(8)	C(55)−C(56)	1.523(4)
C(50)−N(62)	1.488(3)	N(61)−C(65)	1.342(3)
C(50)−N(52)	1.492(3)	N(61)−N(62)	1.375(3)
C(50)−C(71)	1.535(4)	N(62)−C(63)	1.349(3)
C(50)−C(81)	1.539(3)	C(63)−C(64)	1.359(4)
N(51)−C(55)	1.348(3)	C(64)−C(65)	1.398(4)
N(51)−N(52)	1.374(3)	C(65)−C(66)	1.523(4)
N(51)−Pd(2)−N(61)	83.62(8)	C(53)−N(52)−N(51)	109.8(2)
N(51)−Pd(2)−Cl(3)	93.43(6)	C(53)−N(52)−C(50)	129.8(2)
N(61)−Pd(2)−Cl(3)	173.02(6)	N(51)−N(52)−C(50)	120.3(2)
N(51)−Pd(2)−Cl(4)	174.00(6)	C(65)−N(61)−N(62)	106.5(2)
N(61)−Pd(2)−Cl(4)	93.05(6)	C(65)−N(61)−Pd(2)	137.9(2)
Cl(3)−Pd(2)−Cl(4)	89.32(3)	N(62)−N(61)−Pd(2)	112.6(2)
C(55)−N(51)−N(52)	106.7(2)	C(63)−N(62)−N(61)	109.9(2)
C(55)−N(51)−Pd(2)	138.8(2)	C(63)−N(62)−C(50)	129.0(2)
N(52)−N(51)−Pd(2)	114.4(2)	N(61)−N(62)−C(50)	121.0(2)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $\{Ph_2C(pz)_2\}PdCl_2$ (2)

Pd(1)−N(1)	2.018(2)	N(5)−C(11)	1.492(3)
Pd(1)−N(6)	2.020(2)	N(6)−C(7)	1.328(3)
Pd(1)−Cl(2)	2.2787(7)	N(6)−N(10)	1.372(3)
Pd(1)−Cl(1)	2.2876(7)	C(7)−C(8)	1.394(4)
N(1)−C(2)	1.330(3)	C(8)−C(9)	1.370(4)
N(1)−N(5)	1.363(3)	C(9)−C(10)	1.351(3)
C(2)−C(3)	1.390(4)	N(10)−C(11)	1.485(3)
C(3)−C(4)	1.364(4)	C(11)−C(18)	1.530(3)
C(4)−N(5)	1.363(3)	C(11)−C(12)	1.537(3)
N(1)−Pd(1)−N(6)	89.51(8)	N(1)−N(5)−C(4)	109.4(2)
N(1)−Pd(1)−Cl(2)	89.99(6)	N(1)−N(5)−C(11)	119.6(2)
N(6)−Pd(1)−Cl(2)	179.32(6)	C(4)−N(5)−C(11)	128.1(2)
N(1)−Pd(1)−Cl(1)	177.23(6)	C(7)−N(6)−N(10)	106.1(2)
N(6)−Pd(1)−Cl(1)	90.14(6)	C(7)−N(6)−Pd(1)	130.0(2)
Cl(2)−Pd(1)−Cl(1)	90.38(3)	N(10)−N(6)−Pd(1)	123.91(15)
C(2)−N(1)−N(5)	106.5(2)	C(9)−N(10)−N(6)	109.9(2)
C(2)−N(1)−Pd1)	129.4(2)	C(9)−N(10)−C(11)	127.5(2)
N(5)−N(1)−Pd(1)	123.64(14)	N(6)−N(10)−C(11)	120.6(2)

Table 4. Dihedral Angles (deg) in $\{Ph_2C(3\text{-}{}^tBu\text{-}pz)_2\}PdCl_2$ (1), $\{Ph_2C(pz)_2\}PdCl_2$ (2), and $\{Me_2C(pz)_2\}PdCl_2$

dihedral angle	1	2	$\{Me_2C(pz)_2\}PdCl_2$[a]
N−Pd−N/N−N−N−N	130.2	162.7	157.6
N−C−N/N−N−N−N	135.3	130.2	129.7
pz/pz	126.0	146.8	
N−Pd−N/pz	51.8, 54.8	22.2, 23.2	
N−N−N−N/pz	31.1, 22.9	18.0, 15.3	

[a] Reference 12.

Molecular Structures of $\{Ph_2C(3\text{-}{}^tBu\text{-}pz)_2\}PdCl_2$ (1) and $\{Ph_2C(pz)_2\}PdCl_2$ (2). Compounds **1**·1.5CH$_2$Cl$_2$ and **2**·CH$_2$Cl$_2$ were characterized by X-ray crystallography (Tables1−4). The molecular structures of **1** and **2** are shown in Figures1 and 2. Both compounds adopt square-planar structures as expected. In **1**, the $Ph_2C(3\text{-}{}^tBu\text{-}pz)_2$ ligand bite angle is rather acute (N(51)−Pd−N(52) = 83.62(8)°), and the Pd atom is displaced from the square plane by 0.11 Å. As a result of these factors, the cis and trans N−Pd−Cl angles deviate slightly from the ideal square-planar values. In contrast, the bond angles around Pd in **2** are very close to ideal values. The Pd−N and Pd−Cl distances in **1** and **2** are similar and close to values for $\{Me_2C(pz)_2\}PdCl_2$.[12] The boat conformation of the chelate ring is significantly more pronounced in **1** than in **2** due to the steric crowding associated with the ^{t}Bu substituents in **1** (Table 4). The angle between the N−N−N−N and N−Pd−N planes in **2** (N(1)−N(5)−N(10)−N(6)/N(1)−Pd(1)−N(6) = 162.7°) is similar to that in $\{Me_2C(pz)_2\}PdCl_2$ (157.6°), while the corresponding angle in **1** is diminished by 32.5° (N(51)−N(52)−N(62)−N(61)/N(51)−Pd(2)−N(61)=130.2°) due to ^{t}Bu/Cl steric interactions.[13] However, the N−N−N−N/N−C−N dihedral angles of **1** and **2** are similar and are close to the value observed for $\{Me_2C(pz)_2\}PdCl_2$. The angle between the pyrazolyl ring planes is ca. 21° larger in **2** (146.8°) than in **1** (126.0°).

Dynamic Properties of 1 and 2. The variable-temperature ^{1}H NMR spectra (low-field region) for **1** are

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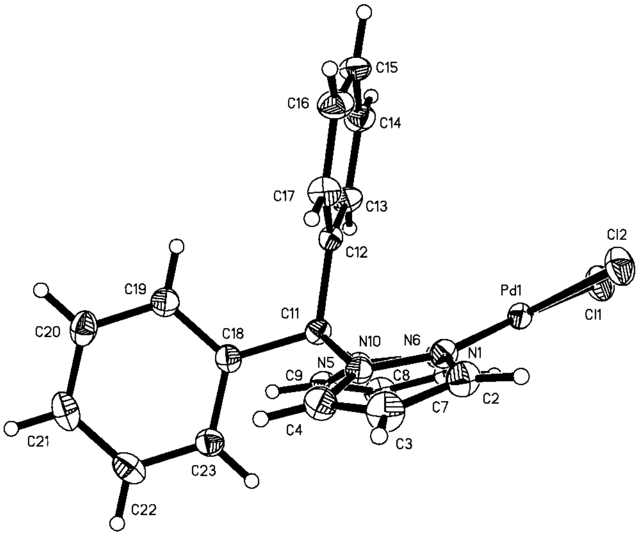


Figure 1. Molecular structure of {Ph$_2$C(3-^{t}Bu-pz)$_2$}PdCl$_2$ (**1**). The hydrogens have been removed from the ^{t}Bu groups for clarity.

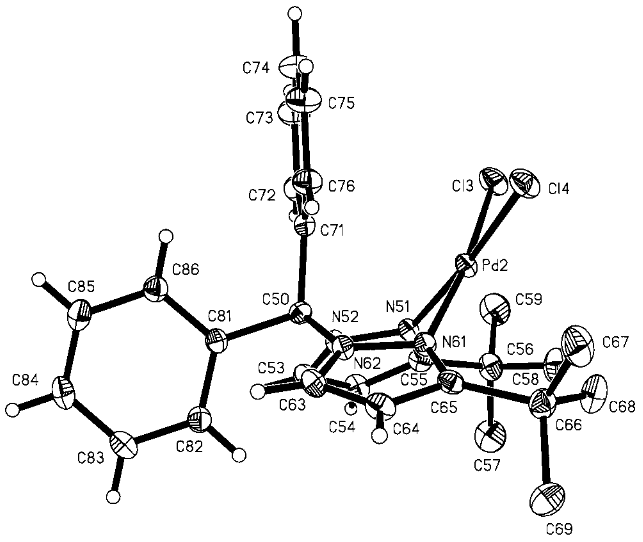


Figure 2. Molecular structure of {Ph$_2$C(pz)$_2$}PdCl$_2$ (**2**).

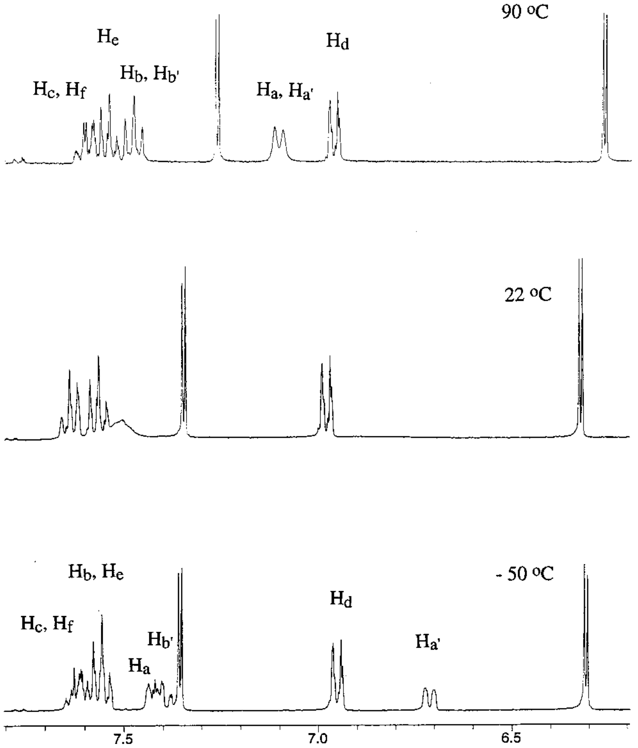
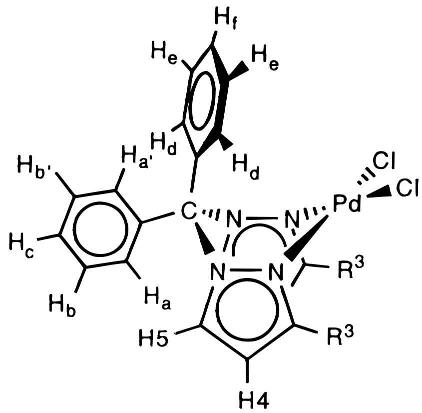


Figure 3. Variable-temperature ^{1}H NMR spectra of {Ph$_2$C(3-^{t}Bu-pz)$_2$}PdCl$_2$ (**1**). Only the low-field region is shown. The 90 °C spectrum was recorded in CDCl$_2$CDCl$_2$, and the 22 and −50 °C spectra were recorded in CD$_2$Cl$_2$. The phenyl resonances are identified using the lettering scheme in Chart 1. The doublets at δ 7.3 and 6.3 are due to the pyrazolyl H5 and H4 hydrogens, respectively.

Chart 1



shown in Figure 3. One set of pyrazolyl H4 (δ 6.3) and H5 (δ 7.3) resonances and one ^{t}Bu resonance (not shown) are observed, which is consistent with the C_s-symmetric structure observed in the solid state. The spectra contain two sets of phenyl resonances between −90 and 100 °C, which were assigned by 600 MHz COSY and NOESY spectra. The assignments are noted in Figure 3 using the lettering scheme in Chart 1. The axial phenyl resonances (H$_d$, H$_e$, H$_f$) remain unchanged over this temperature range. However, at −50 °C, two *o*-H resonances (H$_a$, H$_{a'}$), two *m*-H resonances (H$_b$, H$_{b'}$), and one *p*-H (H$_c$) resonance are observed for the equatorial phenyl ring, which indicates that rotation around the C−Ph$_{eq}$ bond is slow on the NMR time scale. The H$_a$ resonance was assigned on the basis of a NOESY correlation with H5, and the H$_{a'}$ resonance was assigned on the basis of a NOESY correlation with H$_d$. The high-field chemical shift (δ 6.7) for Ha′ results from anisotropic shielding by the axial phenyl group. As the temperature is raised, the H$_a$/H$_{a'}$ resonances collapse to one doublet and the H$_b$/H$_{b'}$ resonances collapse to one triplet, indicating that rotation around the C−Ph$_{eq}$ bond is rapid on the NMR time scale at higher temperatures. However, separate resonances for the axial and equatorial phenyl groups are still observed at 100 °C, indicating that inversion of the boat conformation of **1** is slow on the NMR time scale at this temperature.

The variable-temperature ^{1}H NMR spectra of **2** (low-field region) are shown in Figure 4. At −50 °C, the NMR spectrum of **2** is similar to that of **1**. One set of pyrazolyl ring resonances and two sets of phenyl resonances are observed, which is consistent with a C_s-symmetric structure and slow (NMR time scale) inversion of the

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(13) The closest ^{t}Bu−H/Cl contacts in **1** are 2.75 and 2.78 Å, which are shorter than the sum of the H and Cl van der Waals radii (2.9 Å). See: Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity,* 4th ed.; Harper Collins College Publishers: New York, 1993; p 292.

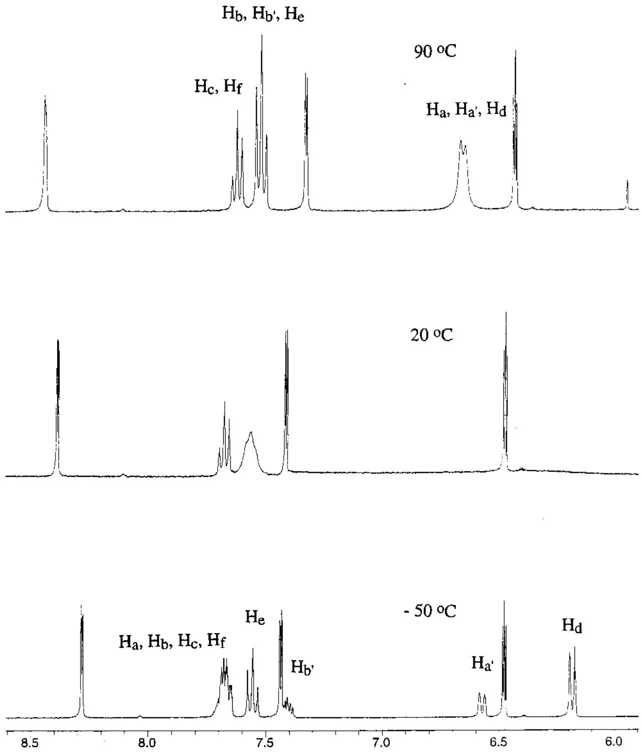
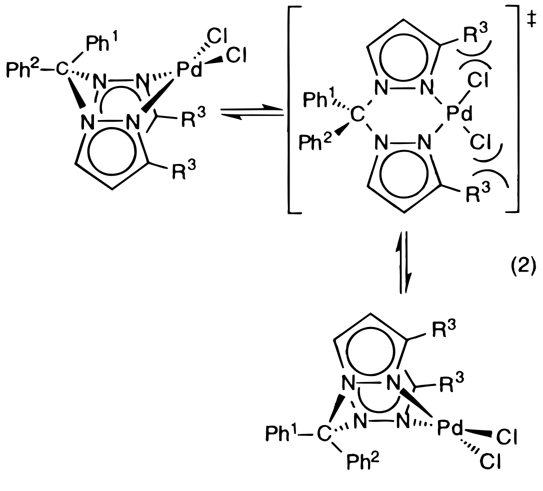


Figure 4. Variable-temperature ^{1}H NMR spectra of $\{Ph_2C(pz)_2\}PdCl_2$ (**2**). Only the low-field region is shown. The 90 °C spectrum was recorded in $CDCl_2CDCl_2$, and the 20 and −50 °C spectra were recorded in CD_2Cl_2. The phenyl resonances are identified using the lettering scheme in Chart 1. The doublets at δ 8.3 and 7.4 are due to the pyrazolyl H3 and H5 hydrogens, respectively, and the triplet at δ 6.5 is due to the pyrazolyl H4 hydrogens.

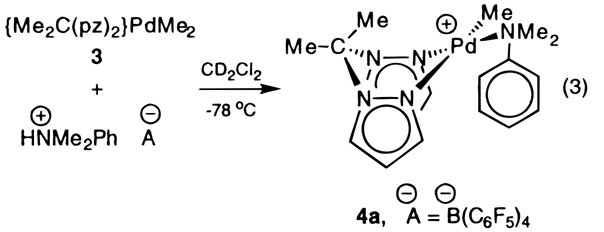
chelate ring. The ortho (H_a, $H_{a'}$) and meta (H_b, $H_{b'}$) resonances of the equatorial phenyl ring appear as two doublets and two triplets, respectively, indicating that rotation around the C−Ph_{eq} bond is slow on the NMR time scale. However, at higher temperatures only one set of phenyl ring resonances is observed, consistent with rapid inversion of the chelate ring. The ring inversion in **2** most likely occurs by a nondissociative process via a planar transition state (eq 2).[14] The steric repulsion between the 3-^{t}Bu groups and the chloride ligands destabilizes this transition state for **1** and retards ring inversion.



(2)

Attempted Synthesis of $\{Ph_2C(pz')_2\}PdMe_2$. Attempted alkylation of **1** and **2** with Me_2Mg or PhMgCl under a variety of conditions was unsuccessful. In most cases, the reaction mixtures turned dark, gas was evolved, and the $Ph_2C(pz')_2$ ligand was liberated upon warming to room temperature. The reaction of $(SMe_2)_2PdMe_2$ and $Ph_2C(3\text{-}^tBu\text{-}pz)_2$ was also unsuccessful. These results suggest that $\{Ph_2C(pz')_2\}PdMe_2$ complexes are thermally unstable. In contrast, the sterically less crowded analogue $\{Me_2C(pz)_2\}PdMe_2$ (**3**) was previously prepared and characterized by Canty and coworkers.[7] In our hands, **3** decomposes in CD_2Cl_2 solution in several hours at 23 °C, yielding a Pd mirror with formation of free $Me_2C(pz)_2$, CH_4, C_2H_6, and C_2H_4.[15]

Generation of $\{Me_2C(pz)_2\}Pd(Me)(L)^+$ Species. The reaction of **3** with $[HNMe_2Ph][B(C_6F_5)_4]$ in CH_2Cl_2 at −78 °C yields $[\{Me_2C(pz)_2\}PdMe(NMe_2Ph)][B(C_6F_5)_4]$ (**4a**, eq 3). **4a** decomposes slowly (ca. 40% after 3 days) in CD_2Cl_2 at 23 °C to afford a black solution and NMe_2Ph; the fate of the $\{Me_2C(pz)_2\}PdMe^+$ unit was not determined. The −60 °C ^{1}H NMR spectrum of **4a** contains NMe_2Ph resonances that are strongly deshielded from the resonances of free NMe_2Ph.[16] Six pyrazolyl resonances are observed as expected for a C_1-symmetric structure. Interestingly, one of the pyrazolyl H3 resonances appears at unusually high field (δ 5.30) compared to the other H3 resonance (δ 7.61) and the corresponding resonance in **3** (δ 7.70). This effect presumably results from shielding by the amine Ph ring. In the static structure of **4a** shown in eq 3, the NMe_2Ph methyl groups are diastereotopic, and accordingly, two methyl signals are observed in the ^{1}H NMR spectrum at −40 °C and in the ^{13}C NMR spectrum at −60 °C. However, below −40 °C, only one N*Me*$_2$Ph signal is observed in the ^{1}H NMR spectrum due to coincidental degeneracy.



The reaction of **3** with $[H(OEt_2)_2][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$[17] yields $[\{Me_2C(pz)_2\}PdMe(OEt_2)][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ (**4b**).[18] The ^{1}H NMR spectrum of **4b** at −60 °C establishes that 1 equiv of Et_2O is coordinated to the metal center (δ 3.68, 1.62) and that **4b** has C_1 symmetry. The six pyrazolyl resonances appear in the normal range, which supports the argument made above that the high-field pyrazolyl H3 chemical shift of **4a** is due to anisotropic shielding by the NMe_2Ph phenyl ring.

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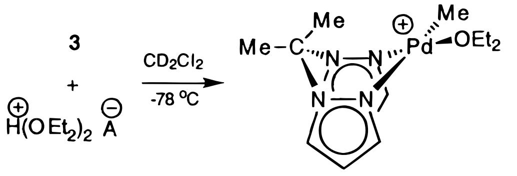
[14] For a discussion of a dissociative exchange mechanism in $\{R_2C(pz')_2\}Pd(2\text{-}Me\text{−}allyl)^+$ see ref 10a.

[15] (tmeda)$PdMe_2$ decomposes in a similar manner. See: de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907.

[16] ^{1}H NMR spectrum of NMe_2Ph (CD_2Cl_2 −60 °C): δ 7.27 (t, J = 8.1, 2H, *m*-Ph), 6.86 (t, J = 7.6, 1H, *p*-Ph), 6.83 (d, J = 9.0, 2H, *o*-Ph), 2.92 (s, 6H, Me).

[17] Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.

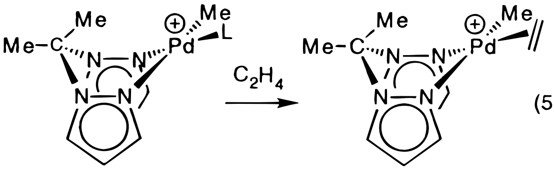
[18] The analogous compound (phen)$PdMe(OEt_2)^+$ has been characterized by X-ray crystallography. Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 2436.



(4)

4b, $A^- = B\{3,5-(CF_3)_2-C_6H_3\}_4^-$

Reaction of 4a with Ethylene. The reaction of **4a** with ethylene was initially investigated by NMR spectroscopy. At −60 °C, the ^{1}H NMR spectrum of a solution of **4a** containing ca. 8 equiv of ethylene exhibits resonances for free ethylene (δ 5.38), free NMe_2Ph, and the ethylene complex $[\{Me_2C(pz)_2\}PdMe(CH_2{=}CH_2)][B(C_6F_5)_4]$ (**5**, eq 5). The spectrum of **5** exhibits six pyrazolyl signals and a broad AA′BB′ pattern centered at δ 4.93 for the coordinated ethylene. The ^{13}C NMR spectrum (−60 °C) of **5** contains a triplet for the coordinated ethylene at δ 86.9 ($J_{CH} = 164$ Hz). These observations imply that **5** has C_1 symmetry, rotation around the Pd ethylene bond is fast on the NMR time scale, and the ethylene carbons retain predominant sp^2 character. The properties of **5** are similar to the properties of other cationic Pd^{II} and Pt^{II} olefin complexes.[3,19]



(5)

4a, L = NMe_2Ph **5**

At −10 °C, **5** undergoes ethylene insertion, leading to ethylene oligomerization.[20] ^{1}H NMR monitoring of this reaction reveals the gradual disappearance of **5** and the appearance of resonances that are assigned to higher $\{Me_2C(pz)_2\}Pd(CH_2R)(CH_2{=}CH_2)^+$ species.[21,22] The reaction of **5** (generated in situ) and ethylene was also performed on a larger scale (1 atm, 23 °C, CH_2Cl_2), and the organic products were analyzed by NMR and GC−MS. These results show that **5** reacts with ethylene to produce a mixture of predominantly linear, internal C_8−C_{24} olefins. Essentially no terminal olefins are observed, but some branched chains are present (ca. 0.1 branches per 2 carbons). These observations are consistent with the mechanism in Scheme 1, in which $\{Me_2C(pz)_2\}Pd(CH_2CH_2R)(L')^+$ species undergo chain walking (by β-H elimination/olefin rotation/insertion) and β-H elimination to form internal olefin complexes, which undergo olefin exchange with ethylene.[3]

Attempted Activation of $\{R_2C(pz')_2\}PdX_2$ Complexes with MAO. The activation of **1**−**3** by MAO for ethylene polymerization was briefly evaluated. **1**/MAO polymerizes ethylene with very low activity (1.8 kg-PE/(mol h) at 1 atm, 24 h). Very similar behavior is observed for $PdCl_2$/MAO. The similarity of the behavior of these two catalyst system suggests that $Ph_2C(3\text{-}^tBu\text{-}pz)_2$ is released upon reaction of **1** with MAO.[23] **2**/MAO and **3**/MAO are inactive for ethylene polymerization.

Conclusions

This work extends the range of known $\{R_2C(pz')_2\}PdCl_2$ compounds to the bulky bis(pyrazolyl)methane ligands $Ph_2C(3\text{-}^tBu\text{-}pz)_2$ and $Ph_2C(pz)_2$. Steric crowding associated with the ^{t}Bu groups in $\{Ph_2C(3\text{-}^tBu\text{-}pz)_2\}PdCl_2$ (**1**) enhances the puckering of the chelate ring (boat conformation) and retards the chelate ring inversion relative to $\{Ph_2C(pz)_2\}PdCl_2$ (**2**). Neither **1** nor **2** was successfully methylated, apparently because the donor ability of the $Ph_2C(pz')_2$ ligands is insufficient to stabilize $\{Ph_2C(pz')_2\}PdMe_2$ species toward reductive decomposition. The $Me_2C(pz)_2$ analogue, $\{Me_2C(pz)_2\}PdMe_2$ (**3**), which was prepared previously by Canty and co-workers, is comparatively more stable.[7] Compound **3** is converted to $\{Me_2C(pz)_2\}PdMe(L)^+$ cations (L = NMe_2Ph (**4a**), Et_2O (**4b**)) by protonolysis. Cation **4a** undergoes ligand substitution by ethylene to form $\{Me_2C(pz)_2\}PdMe(CH_2 = CH_2)^+$ (**5**), which oligomerizes ethylene to C_8−C_{24} internal olefins. The efficiency of ethylene oligomerization by **5** appears to be limited by catalyst stability. Bis(pyrazolyl)methanes support insertion chemistry at cationic Pd(II) alkyl centers, but modification to increase the binding constants of these ligands will be required to obtain more robust catalysts.

Experimental Section

General Procedures. All manipulations were performed using standard Schlenk or vacuum line techniques or in a Vacuum Atmospheres drybox unless noted otherwise. CD_2Cl_2 and CH_2Cl_2 were distilled from P_2O_5. $CDCl_2CDCl_2$ was dried over 4 Å molecular sieves. Hexanes and toluene were distilled from Na/benzophenone ketyl. Ethylene (research grade, Matheson) was used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-360 spectrometer at 25 °C unless noted otherwise. Chemical shifts are reported versus $SiMe_4$ and were determined by reference to the residual ^{1}H and ^{13}C solvent peaks. Coupling constants are reported in hertz (Hz). COSY and NOESY experiments were performed on a Bruker AMX-600 instrument at −50 °C. Elemental analyses were performed by Desert Analytics Laboratory.

$Ph_2C(3\text{-}^tBu\text{-}pz)_2$. A modification of the procedure reported by Trofimenko was used.[9] A mixture of $Ph_2C(OMe)_2$ (20.2 g, 88.5 mmol), $3\text{-}^tBu\text{-}pzH$ (22.0 g, 177 mmol),[24] and p-TsOH·H_2O (0.08 g, 0.4 mmol) was heated so that the evolved MeOH distilled slowly. When the MeOH evolution was about two-

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(19) The X-ray structure of $(daethyph)PtMe(C_2H_4)^+$ (daethyph = $(2,6\text{-}Et_2Ph)N{=}CMeCMe{=}N(2,6\text{-}Et_2Ph)$) has been reported. Fusto, M.; Giordano, F.; Orabona, I.; Ruffo, F.; Panunzi, A. *Organometallics* **1997**, *16*, 5981.

(20) (a) Skupinska, J. *Chem. Rev.* **1991**, *91*, 613. (b) Peuckert, M.; Keim, W. *Organometallics* **1983**, *2*, 594. (c) Peuckert, M.; Keim, W. *J. Mol. Catal.* **1984**, *22*, 289. (d) Keim, W.; Behr, A.; Limbacker, B.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 503. (e) Desjardins, S. Y.; Cavell, K. J.; Jin, H.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1996**, *515*, 233. (f) Abeywickrema, R.; Bennett, M. A.; Cavell, K. J.; Kony, M.; Masters, A. F.; Webb, A. G. *J. Chem. Soc., Dalton Trans.* **1993**, 59. (g) Killian, C. M.; Johnson, L. K.; Brookhart, M. *Organometallics* **1997**, *16*, 2005. (h) Desjardins, S. Y.; Way, A. A.; Murray, M. C.; Adirim, D.; Baird, M. C. *Organometallics* **1998**, *17*, 2382.

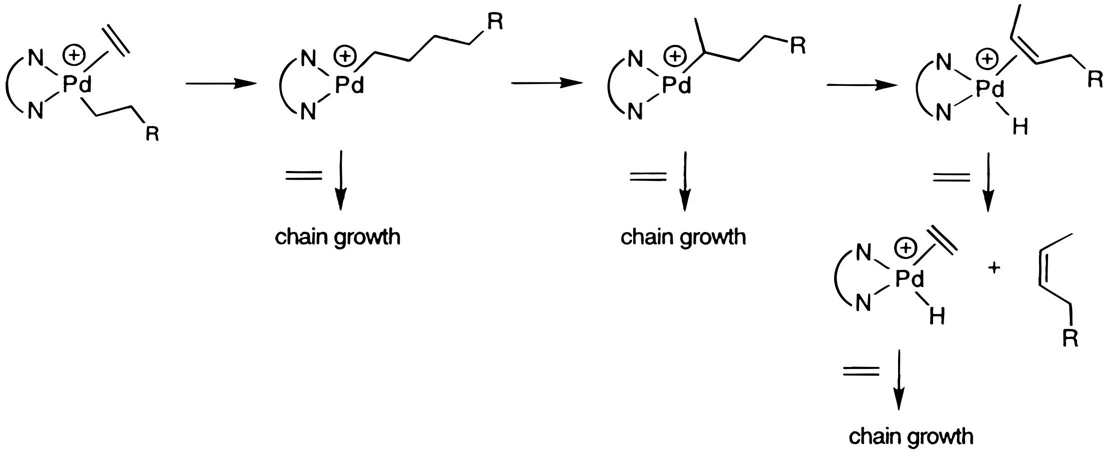
(21) ^{1}H NMR of $\{Me_2C(pz)_2\}Pd(CH_2R)(CH_2{=}CH_2)^+$ (CD_2Cl_2, −10 °C): δ 7.89 (br m, 1H, 3- or 5-pz), 7.85 (br m, 1H, 3- or 5-pz), 7.79 (br m, 1H, 3- or 5-pz), 7.39 (br m, 1H, 3- or 5-pz), 6.56, br m, 1H, 4-pz), 6.41 (br m, 1H, 4′−pz), 4.90 (br m, 4H, coordinated C_2H_4), 2.6 (br m, 6H, Me_2C), 0.95 (t, J = 7.2, PdCH_2R).

(22) The first-order rate constant for the disappearance of **5**, which corresponds to k_{insert}, is estimated to be $2.2(6) \times 10^{-4}$ s^{-1} at −10 °C. For comparison, k_{insert} for $\{ArN{=}C(H)C(H){=}NAr\}Pd(Me)(CH_2{=}CH_2)^+$ (Ar = $2,6\text{-}^iPr_2\text{-}C_6H_3$) is 1.9×10^{-3} s^{-1} at −30 °C. See ref 3a.

(23) The polyethylene produced by **1**/MAO and $PdCl_2$/MAO exhibited a T_m = 135 °C (DSC) but was insufficiently soluble for GPC analysis.

(24) Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507.

Scheme 1



thirds complete (4.00 g collected, 5.67 g expected), the volatiles were distilled off under reduced pressure. The resulting solid was purified by column chromatography on silica using ethyl acetate as an eluent and then recrystallized from hexanes (10 mL) to yield pale orange crystals (9.1 g, 25%). ^{1}H NMR (CD_2Cl_2): δ 7.39−7.29 (m, 6H, Ph), 7.12−7.09 (m, 6H, Ph and 5-pz), 6.12 (d, $J = 2.2$, 2H, 4-pz), 1.28 (s, 18H, ^{t}Bu). ^{13}C NMR (CD_2Cl_2): δ 162.9 (s, 3-pz), 141.9 (s, *ipso*-Ph), 132.9 (d, $J_{CH} = 189$, 5-pz), 129.7 (d, $J_{CH} = 156$, *m*-Ph), 129.0 (d, $J_{CH} = 162$, *p*-Ph), 128.0 (d, $J_{CH} = 156$, *o*-Ph), 101.7 (d, $J_{CH} = 174$, 4-pz), 87.3 (s, Ph_2C), 32.5 (s, Me_3C), 30.5 (q, $J_{CH} = 124$, Me_3C). Anal. Calcd for $C_{27}H_{32}N_4$: C, 78.59; H, 7.83; N, 13.58. Found: C, 78.35; H, 8.06; N, 13.41.

$Ph_2C(pz)_2$. A mixture of $Ph_2C(OMe)_2$ (9.7 g, 44 mmol), pyrazole (6.0 g, 88 mmol), and *p*-TsOH·H_2O (0.04 g, 0.2 mmol) was heated so that the evolved MeOH distilled slowly. When the MeOH evolution was half complete (1.4 g collected, 2.8 expected), the mixture was allowed to cool, affording a white solid and clear liquid. The solid was separated, washed with hexanes (10 mL), and recrystallized from toluene (10 mL), yielding white needles (2.5 g, 19%). ^{1}H NMR (CD_2Cl_2): δ 7.65 (d, $J = 1.7$, 2H, 3-pz), 7.52 (d, $J = 2.7$, 2H, 5-pz), 7.43−7.33 (m, 6H, Ph), 7.06−7.03 (m, 4H, Ph), 6.31 (dd, $J = 1.7$, 2.7, 2H, 4-pz). ^{13}C NMR (CD_2Cl_2): δ 140.9 (s, *ipso*-Ph), 140.4 (d, $J_{CH} = 187$, 3-pz), 132.9 (d, $J_{CH} = 190$, 5-pz), 129.6 (d, $J_{CH} = 160$, *m*-Ph), 129.4 (d, $J_{CH} = 161$, *p*-Ph), 128.2 (d, $J_{CH} = 161$, *o*-Ph), 105.6 (d, $J_{CH} = 175$, 4-pz), 87.9 (s, Ph_2C). Anal. Calcd for $C_{19}H_{16}N_4$: C, 75.96; H, 5.38; N, 18.66. Found: C, 75.69; H, 5.54; N, 18.40.

{$Ph_2C(3\text{-}^tBu\text{-}pz)_2$}$PdCl_2$ (1). A solution of $(CH_3CN)_2PdCl_2$ (2.08 g, 8.00 mmol) and $Ph_2C(3\text{-}^tBu\text{-}pz)_2$ (3.37 g, 8.16 mmol) in CH_2Cl_2 (160 mL) was stirred for 2 h at 23 °C in air. The mixture was filtered, and the solvent was removed from the filtrate under vacuum. The resulting orange solid was recrystallized from CH_2Cl_2 at −30 °C, yielding orange crystals (2.54 g, 54%). The presence of 1.5 equiv of CH_2Cl_2 of crystallization was established by ^{1}H NMR and X-ray crystallography. ^{1}H NMR (CD_2Cl_2): δ 7.64 (t, $J = 7$, 2H, *p*-Ph), 7.56 (t, $J = 7$, 2H, *m*-Ph), 7.5 (br, 2H, *m*-Ph), 7.34 (d, $J = 3$, 2H, 5-pz), 6.98 (m, 2H, *o*-Ph), 6.32 (d, $J = 3$, 2H, 4-pz), 1.71 (s, 18H, ^{t}Bu); the other *o*-Ph resonance is broadened into the baseline. ^{1}H NMR (CD_2Cl_2, −50 °C): δ 7.64−7.52 (m, 5H; H_b, H_c, H_e, H_f), 7.44−7.37 (m, 2H; H_a, $H_{b'}$), 7.35 (d, $J = 3.2$, 2H, 5-pz), 6.95 (m, 2H; H_d), 6.71 (br d, 1H, $H_{a'}$), 6.30 (d, $J = 3.2$, 2H, 4-pz), 1.64 (s, 18H, ^{t}Bu). ^{1}H NMR ($CDCl_2CDCl_2$, 90 °C): δ 7.61−7.53 (m, 4H, Ph), 7.48 (br t, 2H, *m*-Ph), 7.27 (d, $J = 3$, 2H, 5-pz), 7.11 (br d, 2H, *o*-Ph), 6.97 (m, 2H, *o*-Ph), 6.27 (d, $J = 3$, 2H, 4-pz), 1.73 (s, 18H, ^{t}Bu). ^{13}C NMR (CD_2Cl_2): δ 169.4 (s, 3-pz), 138.5 (s, *ipso*-Ph), 136.3 (d, $J_{CH} = 193$, 5-pz), 136.0 (s, *ipso*-Ph), 132.6 (d, overlapping, *m*- or *p*-Ph), 132.5 (d, $J_{CH} = 165$, *m*- or *p*-Ph), 130.9 (d, $J_{CH} = 163$, *m*- or *p*-Ph), 129.7 (d, $J_{CH} = 162$, *o*-Ph), 129.3 (d, $J_{CH} = 159$, *m*-Ph), 105.9 (d, $J_{CH} = 181$, 4-pz), 91.9 (s, Ph_2C), 34.0 (s, Me_3C), 31.2 (q, $J_{CH} = 127$, Me_3C).[25] Anal. Calcd for $C_{27}H_{32}N_4Cl_2Pd\cdot1.5CH_2Cl_2$: C, 47.71; H, 4.93; N, 7.81. Found: C, 47.77; H, 4.80; N, 7.82.

{$Ph_2C(pz)_2$}$PdCl_2$ (2). A solution of $(CH_3CN)_2PdCl_2$ (0.52 g, 2.0 mmol) and $Ph_2C(pz)_2$ (0.61 g, 2.0 mmol) in CH_2Cl_2 (40 mL) was stirred for 3 h at 23 °C in air. The mixture was filtered, and CH_2Cl_2 was removed from the filtrate under vacuum. The resulting orange solid was recrystallized from CH_2Cl_2/Et_2O at −50 °C yielding orange crystals (0.50 g, 52%). The presence of CH_2Cl_2 of crystallization was established by ^{1}H NMR and X-ray crystallography. ^{1}H NMR (CD_2Cl_2): δ 8.39 (dd, $J = 1.1$, 2.5, 2H, 3-pz), 7.68 (br t, 2H, *p*-Ph), 7.57 (br m, 4H, *m*-Ph), 7.42 (dd, 1.3, 3.2, 2H, 5-pz), 6.48 (t, $J = 2.9$, 2H, 4-pz).[26] ^{1}H NMR (−50 °C, CD_2Cl_2): δ 8.28 (dd, $J = 0.4$, 2.2, 2H, 3-pz), 7.71−7.63 (m, 4H; H_a, H_b, H_c, H_f), 7.55 (t, $J = 7$, 2H, H_e), 7.43 (dd, $J = 0.7$, 2.9, 2H, 5-pz), 7.4 (m, 1H, $H_{b'}$), 6.57 (d, 1H, $H_{a'}$), 6.48 (t, $J = 2.7$, 2H, 4-pz), 6.18 (m, 2H, H_d). ^{1}H NMR ($CDCl_2CDCl_2$, 90 °C): δ 8.45 (br, 2H, 3-pz), 7.63 (t, $J = 7$, 2H, *p*-Ph), 7.52 (t, $J = 8$, 4H, *m*-Ph), 7.34 (dd, $J = 0.7$, 2.9; 2H, 5-pz), 6.66 (br d, 4H, *o*-Ph), 6.44 (t, $J = 2.6$, 2H, 4-pz). ^{13}C NMR (CD_2Cl_2): δ 146.0 (d, $J_{CH} = 197$, 3-pz), 136.6 (d, $J_{CH} = 196$, 5-pz), 132 (v br, Ph), 129.9 (br d, $J_{CH} = 168$, *p*-Ph), 127 (v br, Ph), 106.9 (d, $J_{CH} = 183$, 4-pz).[27] Anal. Calcd for $C_{19}H_{16}N_4Cl_2Pd\cdot0.6CH_2Cl_2$: C, 44.53; H, 3.29; N, 10.60. Found: C, 44.71; H, 3.41; N, 10.61.

{$Me_2C(pz)_2$}$PdMe_2$ (3). $Me_2C(pz)_2PdMe_2$ was prepared using the procedure reported by Canty (white crystalline solid, 0.65 g, 65%).[7] ^{1}H NMR (CD_2Cl_2): δ 7.71 (dd, $J = 0.7$, 2.9, 2H, 5-pz), 7.70 (d, $J = 1.8$, 2H, 3-pz), 6.33 (dd, $J = 2.0$, 2.5, 2H, 4-pz), 2.64 (br s, 6H, Me_2C), 0.11 (s, 6H, $PdMe_2$). ^{13}C NMR (CD_2Cl_2, −60 °C): δ 140.5 (d, $J_{CH} = 190$, 3-pz), 127.7 (d, $J_{CH} = 190$, 5-pz), 105.5 (d, $J_{CH} = 180$, 4-pz), 75.3 (s, Me_2C), 29.7 (q, $J_{CH} = 132$, Me_2C), 25.4 (q, $J_{CH} = 130$, Me_2C), −10.5 (q, $J_{CH} = 126$, $PdMe_2$).

Generation of [{$Me_2C(pz)_2$}$PdMe(NMe_2Ph)$][$B(C_6F_5)_4$] (4a). An NMR tube was charged with {$Me_2C(pz)_2$}$PdMe_2$ (9.6 mg, 31 μmol) and [$HNMe_2Ph$][$B(C_6F_5)_4$] (24.7 mg, 30.8 μmol), and CD_2Cl_2 was added by vacuum transfer at −78 °C. The resulting solution was kept at −78 °C prior to NMR analysis. **4a** was the only organometallic product observed. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 7.81 (d, $J = 7.9$, 2H, *o*-Ph), 7.74 (d, $J = 2.9$, 1H, 5-pz), 7.63 (d, $J = 2.9$, 1H, 5′-pz), 7.61 (d, $J = 2.2$, 1H, 3-pz), 7.47 (t, $J = 8.0$, 2H, *m*-Ph), 7.35 (t, $J = 7.6$, 1H, *p*-Ph), 6.39 (t, $J = 2.7$, 1H, 4-pz), 6.01 (t, $J = 2.5$, 1H, 4′-pz), 5.30 (d, $J = 2.2$, 1H, 3′-pz), 3.23 (s, 6H, NMe_2), 2.85 (s, 3H, Me_{ax}), 2.41 (s, 3H, Me_{eq}), 1.10 (s, 3H, PdMe). ^{13}C NMR (CD_2Cl_2, −60 °C):

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[25] The other *o*-Ph signals are broadened into the baseline.

[26] The pyrazolyl H3 and H5 ^{1}H NMR resonances were assigned on the basis of a NOESY correlation between H5 and H_a. The *o*-Ph signal is broadened into the baseline at 20 °C.

[27] The ipso-Ph signals were not observed.

δ 152.0 (s, *ipso*-Ph), 147.5 (d, $J_{\mathrm{CF}} = 237$, $\mathrm{B(C_6F_5)_4^-}$), 143.5 (d, $J_{\mathrm{CH}} = 195$, 3-pz), 141.4 (d, $J_{\mathrm{CH}} = 191$, 3′-pz), 137.8 (d, $J_{\mathrm{CF}} = 259$, $\mathrm{B(C_6F_5)_4^-}$) 135.8 (d, $J_{\mathrm{CF}} = 244$, $\mathrm{B(C_6F_5)_4^-}$), 129.8 (d, $J_{\mathrm{CH}} = 192$, 5-pz), 129.4 (d, $J_{\mathrm{CH}} = 164$, *o*-Ph), 129.0 (d, $J_{\mathrm{CH}} = 191$, 5′-pz), 127.4 (d, $J_{\mathrm{CH}} = 164$, *p*-Ph), 123 (br, $\mathrm{B(C_6F_5)_4^-}$), 121.9 (d, $J_{\mathrm{CH}} = 158$, *m*-Ph), 106.9 (d, $J_{\mathrm{CH}} = 184$, 4-pz), 106.2 (d J_{CH} =181, 4′-pz), 75.5 (s, $\mathrm{Me_2}$*C*), 56.0 (q, J_{CH} =142, $\mathrm{NMe_2}$), 50.2 (q, J_{CH} =140, $\mathrm{NMe_2}$), 29.1 (q, J_{CH} =131, *Me₂*C), 25.6 (q, J_{CH} =130, *Me₂*C), 4.4 (q, J_{CH} =134, PdMe).

Generation of [{$\mathbf{Me_2C(pz)_2}$}$\mathbf{PdMe(OEt_2)}$][B{3,5-($\mathbf{CF_3)_2}$-$\mathbf{C_6H_3}$}$_4$] (4b). An NMR tube was charged with {$\mathrm{Me_2C(pz)_2}$}-$\mathrm{PdMe_2}$ (13 mg, 40 μmol) and [$\mathrm{H(Et_2O)_2}$][B{3,5-$\mathrm{(CF_3)_2C_6H_3}$}$_4$] (40 mg, 41 μmol), and $\mathrm{CD_2Cl_2}$ was added by vacuum transfer at −78 °C. The resulting solution was kept at −78 °C prior to NMR analysis. **4b** was formed in 100% NMR yield versus an internal standard. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, −60 °C): δ 7.78 (d, $J = 2.9$, 1H, 5-pz), 7.74 (br s, *o*-Ph, 8H), 7.69 (d, $J = 2.9$, 1H, 5′-pz), 7.55 (br s, 4H, *p*-Ph), 7.53 (d, $J = 1.8$, 1H, 3-pz), 7.46 (d, $J = 1.8$, 1H, 3′-pz), 6.39 (t, $J = 2.7$, 1H, 4-pz), 6.32 (t, $J = 2.4$, 1H, 4′-pz), 3.68 (q, $J = 7$, 4H, OCH_2), 2.75 (s, 3H, $\mathrm{Me_{ax}}$), 2.38 (s, 3H, $\mathrm{Me_{eq}}$), 1.62 (t, $J = 7$, 6H, $\mathrm{OCH_2}$$CH_3$), 0.84 (s, 3H, PdMe). ^{13}C NMR ($\mathrm{CD_2Cl_2}$, −60 °C): δ 161.5 (q, $J_{\mathrm{CB}} = 49$, *ipso*-Ph), 144.0 (d, $J_{\mathrm{CH}} = 194$, 3-pz), 140.9 (d, $J_{\mathrm{CH}} = 191$, 3′-pz), 134.4 (d, $J_{\mathrm{CH}} = 161$, *o*-Ph), 130.8 (d, $J_{\mathrm{CH}} = 194$, 5-pz), 128.9 (d, $J_{\mathrm{CH}} = 193$, 5′-pz), 128.4 (q, $J_{\mathrm{CF}} = 30$, *m*-Ph), 124.2 (q, J_{CF}= 273, $\mathrm{CF_3}$), 117.3 (d, $J_{\mathrm{CH}} = 163$, *p*-Ph), 106.9 (d, $J_{\mathrm{CH}} = 184$, 4-pz), 106.5 (d, $J_{\mathrm{CH}} = 185$, 4′-pz), 75.9 (s, $\mathrm{Me_2}$*C*), 72.3 (t, $J_{\mathrm{CH}} = 146$, O$CH_2$$\mathrm{CH_3}$), 30.1 (q, $J_{\mathrm{CH}} = 131$, *Me₂*C), 25.3 (q, $J_{\mathrm{CH}} = 132$, *Me₂*C), 15.9 (q, $J_{\mathrm{CH}} = 126$ $\mathrm{OCH_2}$$CH_3$), −0.8 (q, J_{CH} =134, PdMe).

Generation of [{$\mathbf{Me_2C(pz)_2}$}$\mathbf{PdMe(CH_2{=}CH_2)}$][$\mathbf{B(C_6F_5)_4}$] (5). An NMR tube was charged with {$\mathrm{Me_2C(pz)_2}$}$\mathrm{PdMe_2}$ (13 mg, 40 μmol) and [$\mathrm{HNMe_2Ph}$][$\mathrm{B(C_6F_5)_4}$] (32 mg, 40 μmol), and $\mathrm{CD_2Cl_2}$ was added by vacuum transfer at −196 °C. The tube was warmed to −78 °C prior to NMR analysis at −60 °C. The tube was then cooled to −196 °C, and 10 equiv of $\mathrm{C_2H_4}$ was added via a gas bulb. The tube was warmed to −78 °C prior to NMR analysis. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, −60 °C): δ 7.87 (d, $J = 3.2$, 1H, 5-pz), 7.79 (d, $J = 2.5$, 1H, 5′-pz), 7.69 (d, $J = 2.2$, 1H, 3-pz), 7.40 (d, $J = 2.2$, 3′-pz), 6.51 (t, $J = 2.6$, 1H, 4-pz), 6.40 (t, $J = 2.2$, 1H, 4′-pz), 4.93 (AA′BB′, 4H, $\mathrm{C_2H_4}$), 2.64 (s, 3H, $\mathrm{Me_{ax}}$), 2.47 (s, 3H, $\mathrm{Me_{eq}}$), 0.87 (s, 3H, PdMe). ^{13}C NMR ($\mathrm{CD_2Cl_2}$, −60 °C): δ 147.5 (d, $J_{\mathrm{CF}} = 243$, $\mathrm{B(C_6F_5)_4^-}$), 141.9 (d, $J_{\mathrm{CH}} = 193$, 3-pz), 140.2 (d, $J_{\mathrm{CH}} = 189$, 3′-pz), 137.7 (d, $J_{\mathrm{CF}} = 247$, $\mathrm{B(C_6F_5)_4^-}$), 135.8 (d, $J_{\mathrm{CF}} = 245$, $\mathrm{B(C_6F_5)_4^-}$), 130.5 (d, $J_{\mathrm{CH}} = 193$, 5-pz), 129.5 (d, $J_{\mathrm{CH}} = 193$, 5′-pz), 123 (br, $\mathrm{B(C_6F_5)_4^-}$), 106.9 (d, $J_{\mathrm{CH}} = 186$, 4, 4′-pz), 86.9 (t, $J_{\mathrm{CH}} = 164$, coordinated $\mathrm{C_2H_4}$), 75.9 (s, $\mathrm{Me_2}$*C*), 30.9 (q, $J_{\mathrm{CH}} = 130$, *Me₂*C), 25.2 (q, $J_{\mathrm{CH}} = 132$, *Me₂*C), 8.2 (q, $J_{\mathrm{CH}} = 138$, PdMe).

Ethylene Oligomerization Reactions. A 100 mL flask was charged with {$\mathrm{Me_2C(pz)_2}$}$\mathrm{PdMe_2}$ (9 mg, 30 μmol) and [$\mathrm{HNMe_2Ph}$][$\mathrm{B(C_6F_5)_4}$] (24 mg, 30 μmol). The flask was evacuated at −78 °C, and $\mathrm{CH_2Cl_2}$ (30 mL) was added by vacuum transfer at −78 °C. The solution was stirred and allowed to warm to room temperature, and during this period 1 atm of $\mathrm{C_2H_4}$ was introduced. The mixture was stirred at 23 °C for 22 h. The reaction was quenched with MeOH (5 mL). The volatiles were removed under vacuum, leaving a black solid and a small amount of clear liquid. The volatiles and the clear liquid were analyzed by ^{1}H and ^{13}C NMR and GC−MS.

Ethylene Polymerization Reactions. A 250 mL flask was charged with {$\mathrm{Ph_2C(3\text{-}^tBu\text{-}pz)_2}$}$\mathrm{PdCl_2}$ (**1**, 8.1 mg, 14 μmol) and toluene (90 mL). The solution was degassed by freeze/pump/thaw cycles, warmed to 23 °C, and exposed to 1 atm of $\mathrm{C_2H_4}$. MAO (toluene solution, 8.6 mL, 14 mmol Al) was added by cannula, and the mixture was stirred at room 23 °C for 24 h. The reaction was quenched with MeOH, and the polymer was collected by filtration, washed with HCl, water, and MeOH, and dried under vacuum (0.60 g).

X-ray Structure Determinations. Crystallographic details are summarized in Table 1. Specific comments for each structure follow. **1**·1.5 $\mathrm{CH_2Cl_2}$: Single crystals were grown from $\mathrm{CH_2Cl_2}$ at −30 °C. The asymmetric unit contains two independent molecules, which are structurally very similar. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included with the riding model (C−H = 0.93−0.97 Å, tetrahedral angles for sp^3 C atoms or bisecting angles for sp^2 C atoms, $U_{\mathrm{iso}} = 1.2U_{\mathrm{iso}}$(equiv)C for nonterminal C atoms or $U_{\mathrm{iso}} = 1.5U_{\mathrm{iso}}$(equiv)C for terminal C atoms). Three $\mathrm{CH_2Cl_2}$ solvent molecules are also included in the crystal structure. One (C(91), Cl(5), Cl(6)) is ordered, and two are disordered. The first disordered $\mathrm{CH_2Cl_2}$ molecule was modeled with two rigid groups (C(92), Cl(7), Cl(8) and C(93), Cl(8), Cl(9)). The occupancies were restrained to sum to 1.0 and refined to 0.74(2) and 0.26(2), respectively. The second disordered $\mathrm{CH_2Cl_2}$ was also modeled with two groups (C(94), Cl(11), Cl(12); occupancy 0.62(4) and C(95), Cl(13), Cl(14); occupancy 0.38(4)). The C and Cl atoms were refined with anisotropic thermal parameters. Thermal parameters of partial atoms within 0.75 Å were restrained to be similar. Hydrogen atoms were included with the riding model. The geometry of the ordered $\mathrm{CH_2Cl_2}$ molecule (taken near the end of the refinement) was used as the model for the rigid group fitting and refinement. **2**·$\mathrm{CH_2Cl_2}$: Single crystals for X-ray diffraction were grown from $\mathrm{CH_2Cl_2}$/hexanes at −30 °C. One $\mathrm{CH_2Cl_2}$ solvent molecule is present in the asymmetric unit. Non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included with the riding model.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic parameters, anisotropic displacement parameters, bond lengths and bond angles, and hydrogen atom coordinates and isotropic displacement factors for **1**·1.5 $\mathrm{CH_2Cl_2}$ and **2**·$\mathrm{CH_2Cl_2}$; COSY and NOESY spectra of **1** and **2** at low temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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