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Reaction of Vinyl Chloride with Late Transition Metal Olefin Polymerization Catalysts

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Abstract: The reactions of vinyl chloride (VC) with representative late metal, single-site olefin dimerization and polymerization catalysts have been investigated. VC coordinates more weakly than ethylene or propylene to the simple catalyst (Me_2bipy)$PdMe^+$ (Me_2bipy = 4,4′-Me_2-2,2′-bipyridine). Insertion rates of (Me_2bipy)Pd(Me)(olefin)$^+$ species vary in the order VC > ethylene > propylene. The VC complexes (Me_2-bipy)Pd(Me)(VC)$^+$ and (α-diimine)Pd(Me)(VC)$^+$ (α-diimine = (2,6-^{i}Pr$_2$−C_6H_3)N═CMeCMe═N(2,6-^{i}Pr$_2$−C_6H_3)) undergo *net* 1,2 VC insertion and β-Cl elimination to yield Pd−Cl species and propylene. Analogous chemistry occurs for (pyridine-bisimine)MCl_2/MAO catalysts (M = Fe, Co; pyridine-bisimine = 2,6-{(2,6-^{i}Pr$_2$−C_6H_3)N═CMe}$_2$-pyridine) and for neutral (sal)Ni(Ph)PPh_3 and (P−O)Ni(Ph)PPh_3 catalysts (sal = 2-{C(H)═N(2,6-^{i}Pr$_2$−C_6H_3)}-6-Ph-phenoxide; P−O = {$Ph_2PC(SO_3Na)$═C(*p*-tol)O}), although the initial metal alkyl VC adducts were not detected in these cases. These results show that the L_nMCH_2CHClR species formed by VC insertion into the active species of late metal olefin polymerization catalysts undergo rapid β-Cl elimination which precludes VC polymerization. Termination of chain growth by β-Cl elimination is the most significant obstacle to metal-catalyzed insertion polymerization of VC.

Introduction

The design or discovery of metal catalysts which are capable of polymerizing or copolymerizing functionalized olefins by insertion mechanisms, particularly CH_2═CHX monomers with functional groups directly bonded to the olefin unit, is a challenging goal.[1] While some success has been achieved in the copolymerization of acrylates and vinyl ketones with ethylene and propylene using palladium and nickel catalysts,[2] general strategies for designing catalysts with high functional group tolerance are lacking.

Vinyl chloride (VC) is a particularly attractive monomer for insertion polymerization/copolymerization because PVC and VC copolymers are important commercial materials,[3] and because many of the problems that complicate insertion polymerization of polar monomers, such as coordination of the monomer to the active species through the X group rather than the C═C bond, and reaction of the catalyst with the C−X bond or X group of the monomer, are anticipated to be unimportant for VC due to the weak tendency of halocarbons to coordinate to metals and the low reactivity of the vinyl C−Cl bond.[4,5] However, insertion polymerization of VC has never been convincingly demonstrated.

In previous work, we found that group 4 metal catalysts react with VC by two pathways: (i) radical polymerization initiated by radicals derived from the catalyst, and (ii) net 1,2 insertion followed by β-Cl elimination to yield metal chloride species and olefins (eq 1).[6] For example, radical VC polymerization is initiated by $(C_5R_5)_2ZrMe_2$/MAO catalysts in the presence of trace O_2 and by $(C_5Me_5)TiX_3$/MAO catalysts (X = Cl or OMe; low Al/Ti ratios, CH_2Cl_2 solvent) under anaerobic conditions. In principle, radical polymerization can be avoided by the use of redox inactive metals, anaerobic conditions, and radical scavengers. The insertion/β-Cl elimination pathway is observed for zirconocene catalysts under anaerobic conditions, (C_5Me_5)-TiX_3/MAO catalysts at high Al/Ti ratios, and ($C_5Me_4SiMe_2$-N^{t}Bu)MR^+ "constrained geometry" catalysts (M = Ti, Zr).

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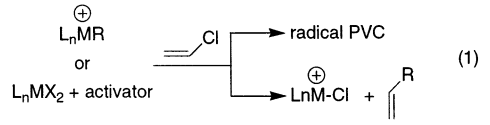
Catalysts which undergo monomer insertion faster than β-Cl elimination, or catalysts which undergo 2,1 VC insertion, will be required to avoid this termination pathway.

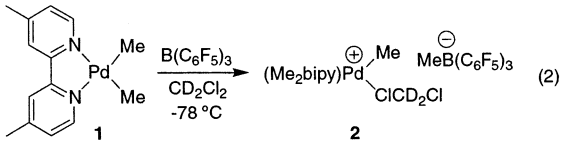


(1)

The facility of β-Cl elimination for group 4 metal catalysts is not surprising given the strong driving force for this process for early metals. For example, β-Cl elimination of a $ZrCH_2CHClR^+$ species is predicted to be exothermic by ca. 42 kcal/mol, primarily due to the large difference between the Zr−Cl (116 kcal/mol) and the Zr−Me (67 kcal/mol) bond strengths.[7,8] In contrast, the driving force for β-elimination of heteroatom groups from late transition metal species is anticipated to be less than that for early metal catalysts due to the smaller difference between M−X and M−C bond strengths.[9] For example, the Pt−Cl bond is estimated to be ca. 10 kcal/mol stronger than the Pt−Me bond in $(PEt_3)_2PtClX$ (X = Cl, Me), based on a calorimetric study.[10] Indeed, several late metal alkyl complexes which contain β-halogen substituents have been characterized, including $PtCl_5(CH_2CH_2Cl)^{2-}$,[11] (2,9-Me_2phen)-$PtCl_3(CH_2CH_2Cl)$,[12] and $Ir(CO)Br_2(PMe_2Ph)_2(CH_2CH_2Br)$.[13] The high oxidation states and absence of vacant coordination sites presumably help to disfavor β-Cl elimination in these cases. In this paper, we describe studies of the reaction of VC with representative late metal, single-site olefin dimerization and polymerization catalysts.[6c−f]

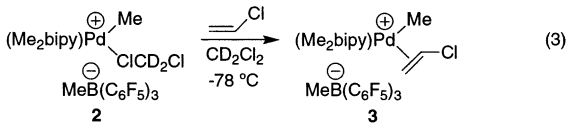
Results and Discussion

Generation of [(Me_2bipy)PdMe(ClCD_2Cl)][MeB(C_6F_5)$_3$] (2). To investigate the coordination and insertion chemistry of VC with a simple late metal alkyl complex, we first studied the reaction of VC with "(Me_2bipy)PdMe$^+$" (Me_2bipy = 4,4′-Me_2-2,2′-bipyridine). The precursor (Me_2bipy)$PdMe_2$ (**1**) is prepared by displacement of cyclooctadiene (cod) from (cod)-$PdMe_2$ by Me_2bipy (97%). Treatment of **1** with 1 equiv of $B(C_6F_5)_3$ (CD_2Cl_2, −78 °C) cleanly produces a new species which is assigned as the methylene chloride adduct [(Me_2bipy)-PdMe(ClCD_2Cl)][MeB(C_6F_5)$_3$] (**2**, eq 2). The ^{1}H and ^{13}C NMR spectra of **2** show that the two halves of the Me_2bipy ligand are inequivalent and contain *Me*B resonances at the free anion positions (δ 0.31 and δ 8.9, respectively; CD_2Cl_2, −88 °C). Resonances for coordinated CD_2Cl_2 are not observed in the low-temperature ^{13}C NMR spectrum of **2**, so it is likely that fast stereospecific solvent exchange occurs under these conditions. Similarly, Baird prepared (tmeda)PdMe(ClCD_2Cl)$^+$ (tmeda = $Me_2NCH_2CH_2NMe_2$) by methyl abstraction from (tmeda)$PdMe_2$ with $B(C_6F_5)_3$ in CD_2Cl_2.[14] Complex **2** decomposes above −50 °C.[15]



(2)

Generation, Structure, and Dynamics of (Me_2bipy)PdMe-(CH_2=CHCl)$^+$ (3). Treatment of a CD_2Cl_2 solution of **2** with VC at −78 °C generates the VC complex [(Me_2bipy)PdMe-(CH_2=CHCl)][MeB(C_6F_5)$_3$] (**3**, eq 3). For NMR characterization experiments, **3** was generated using 0.9 equiv of VC to avoid complications from associative intermolecular VC exchange (vide infra). The low-temperature NMR spectra of **3** show that the two halves of the Me_2bipy ligand are inequivalent and contain resonances for coordinated VC. The VC H_{int} ^{1}H NMR resonance is shifted 0.3 ppm downfield, and the H_{cis} and H_{trans} resonances are shifted by an average of 0.6 ppm upfield from the corresponding resonances of free VC.[16] The ^{13}C NMR resonances for the coordinated VC (δ 102.7 (d, J = 202, CHCl), 78.7 (t, J = 168, CH_2)) are shifted upfield by an average of Δ = 31 ppm. The shifts of the VC resonances establish that the VC is coordinated through the C=C bond and not the chlorine. Several other VC complexes have been characterized previously, including the square-planar complexes (acac)PtCl-(CH_2=CHCl) and (acac)Rh(CH_2=CHCl)$_2$. The ^{13}C NMR resonances for the coordinated VC in these cases appear at much higher field (Δ = ca. 50 ppm) than for **3**, reflecting the decreased d-π* back-bonding in cationic **3**.[17]



(3)

The low-temperature ^{1}H NMR spectrum of **3** contains a single set of sharp resonances consistent with the presence of one dominant isomer. The NOESY spectrum of **3** contains cross-peaks between the Pd−Me and the VC H_{cis} and H_{int} resonances (see eq 4 for assignments), which establishes that the C=C bond is oriented perpendicular to the N−N−Pd−Me square plane, as expected for a d^8 square-planar olefin complex, and that the Cl points away from the Pd−Me group, as illustrated in eq 4.[18] This conformation is supported by the presence of a cross-peak

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(15) (a) The decomposition products of **2** have not been fully characterized. However, resonances for $MeB(C_6F_5)_2$ are observed in the ^{1}H and ^{19}F NMR spectra after decomposition, suggesting that $C_6F_5^-$ transfer from $MeB(C_6F_5)_3^-$ to Pd occurs. (b) For examples of $C_6F_5^-$ abstraction from $MeB(C_6F_5)_3^-$ by electrophilic cations, see: Dagorne, S.; Guzei, I. A.; Coles, M.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 274 and references therein. (c) Data for $MeB(C_6F_5)_2$: ^{1}H NMR (CD_2Cl_2) δ 1.69 (s); ^{19}F NMR (CD_2Cl_2) δ −128.4 (m), −146.7 (t, J = 20, 2F), 160.7 (m, 4F). See: Qian, B.; Ward, D. L.; Smith, M. R. *Organometallics* **1998**, *17*, 3070.
(16) Data for free VC: ^{1}H NMR (CD_2Cl_2, −73 °C) δ 6.30 (dd, J = 14.5, 7.0, 1H, H_{int}), 5.51 (dd, J = 14.5, 1.5, 1H, H_{trans}), 5.45 (dd, J = 7.0, 1.5, 1H, H_{cis}); ^{13}C NMR (CD_2Cl_2, −73 °C) δ 125.4 (d, J = 197, =CHCl), 117.8 (t, J = 162, =CH_2).
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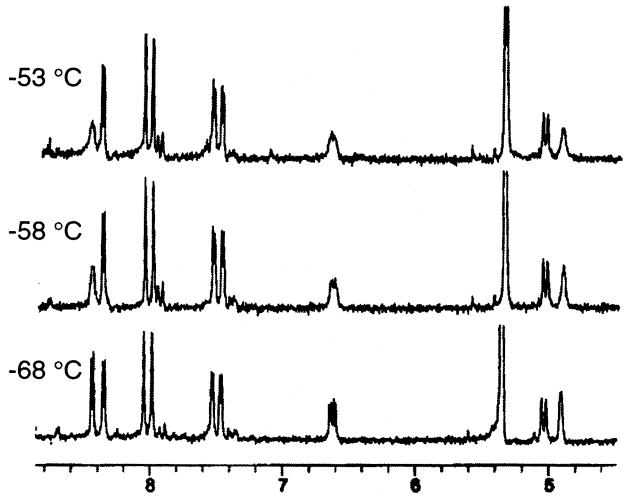
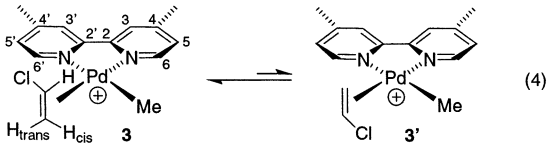


Figure 1. Variable temperature ^{1}H NMR spectra of in situ generated (Me_2-bipy)PdMe(CH_2═$CHCl$)$^+$ (**3**; CD_2Cl_2 solvent). The bipy and vinyl regions are shown. Assignments are based on the labeling scheme in eq 4 and were determined by 2D NMR experiments: δ 8.42, H6′; 8.33, H6; 8.02, H3′; 7.96, H3; 7.50, H5; 7.43, H5′; 6.59, ═C*H*Cl; 5.01, ═CH*H*$_{trans}$; 4.88, ═CH*H*$_{cis}$. A deficiency of VC was used to avoid intermolecular VC exchange. The chemical shift scale is in units of ppm.

between H6′ and H_{trans} and the absence of cross-peaks between H6′ and H_{cis} or H_{int}. Warming a CD_2Cl_2 solution of **3** from −68 to −53 °C results in broadening of the VC, PdMe, and Me_2-bipy-H6′ resonances (Figure 1). These NMR line shape changes are reversible, and the remaining Me_2bipy resonances are unaffected. The simplest explanation for these observations is that an isomer of **3** in which the chloride points toward the Pd−Me unit (**3′**) is present at low concentration (below the NMR detection limit), and as the temperature is raised, rotation around the Pd−VC bond occurs on the NMR time scale, resulting in exchange of **3** and **3′**. Because the structures of **3** and **3′** are very similar, only the resonances for the hydrogens close to the Pd−VC unit are sensitive to the VC conformation and are affected by the fluxional process. Support for this explanation is provided by the dynamic behavior of the analogous propylene complex (vide infra).



(4)

Complex **3** undergoes fast intermolecular exchange of VC by an associative mechanism, even at low temperature. The NMR spectra of **3** in the presence of even a slight excess of VC (CD_2Cl_2, −88 °C) display a single set of VC resonances at the weighted average of the free and coordinated VC chemical shifts (Figure 2). The Pd−Me and H6′ resonances broaden upon addition of excess VC, which shows that intermolecular exchange is accompanied by **3**/**3′** isomer exchange. However, the remaining Me_2bipy resonances remain sharp under fast exchange conditions, showing that the entering VC takes the same coordination site as the departing VC, as expected for a square-planar d^8 complex.[19]

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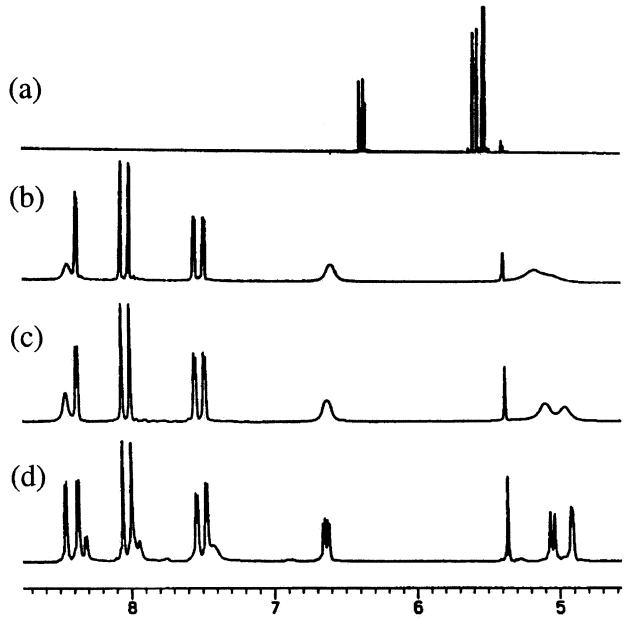


Figure 2. ^{1}H NMR spectra of (Me_2bipy)PdMe($ClCD_2Cl$)$^+$ (**2**) with added VC (CD_2Cl_2, −80 °C). The bipy and vinyl regions are shown. (a) Free VC, (b) **2** with 1.10 equiv of VC added, (c) **2** with 1.05 equiv of VC added, (d) **2** with 0.90 equiv of VC added. Peak assignments: δ 8.41, H6′; 8.33, H6; 8.02, H3′; 7.96, H3; 7.50, H5; 7.43, H5′; 6.59, ═CHCl; 5.01, ═CH*H*$_{trans}$; 4.88, ═CH*H*$_{cis}$. The broadening of the VC and H6′ resonances is due to associative VC exchange. The resonances at δ 8.33, 7.96, and 7.43 are due to **2**. The chemical shift scale is in units of ppm.

Generation and Properties of (Me_2bipy)PdMe(CH_2═CHR)$^+$ (R = Me, H). To better understand the properties of VC complex **3**, the analogous propylene and ethylene adducts were investigated. The reaction of **2** with propylene at −78 °C yields (Me_2bipy)PdMe(CH_2═$CHMe$)$^+$, which exists as a mixture of two isomers (**4**/**4′**, 1.5/1 isomer ratio, eq 5). As illustrated in Figure 3, the ^{1}H NMR spectrum of **4**/**4′** at −73 °C contains two sets of propylene, Pd−Me, and *Me*$_2$bipy resonances corresponding to the two isomers. Five of the Me$_2$*bipy* aromatic resonances are coincident for the two isomers, while the remaining Me$_2$*bipy* aromatic resonance, which is assigned to the ortho-H adjacent to the propylene ligand (H6′), appears at δ 7.80 for the major isomer and δ 8.30 for the minor isomer. Warming the solution to −15 °C (above this temperature insertion occurs) results in coalescence of the two sets of resonances due to fast isomer exchange; this process is reversible. The barrier for propylene rotation is ca. 11 kcal/mol.[20] Thus, the solution behavior of **4** is similar to that of **3** with the exception that both **4** and **4′** are directly observable. Addition of excess propylene to **4**/**4′** at −88 °C in CD_2Cl_2 results in coalescence of the **4** and **4′** resonances and of the free and coordinated propylene resonances, due to fast associative exchange of free and coordinated propylene.

(20) (a) Activation parameters for **4**/**4′** exchange were determined by simulation of the ^{1}H NMR spectra (H_{int} resonances) over the temperature range from −92 to −26 °C. Values for $\Delta G^{\ddagger}$ evaluated at −33 °C are as follows. Major to minor isomer, 11.1 kcal/mol; minor to major isomer, 10.7 kcal/mol. (b) It is also possible that a small amount of free propylene formed by dissociation from **4** (perhaps accompanying trace decomposition) could produce the line shape changes in Figure 3. However, the VT NMR spectra of a mixture of **3** + 0.75 equiv propene, which generates 0.75 equiv of **4** in the presence of excess **3** and ensures the complete absence of free propylene, are identical to those of pure **4** between −80 and −23 °C. This result confirms that the line shape changes are due to propylene rotation, not intermolecular propylene exchange.

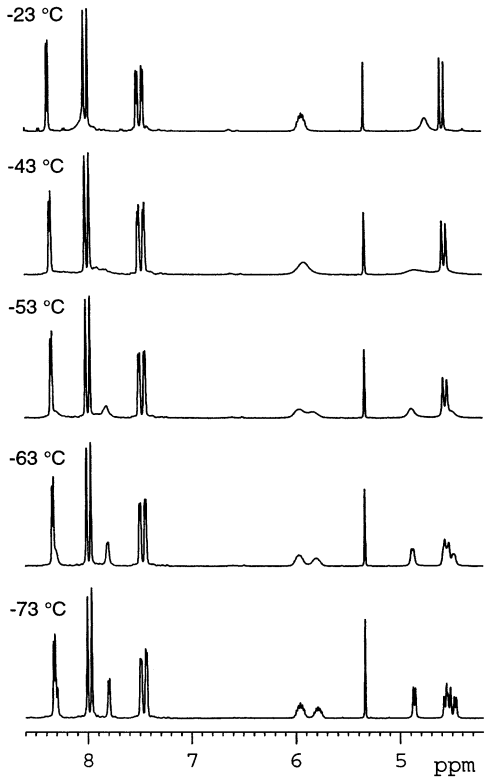
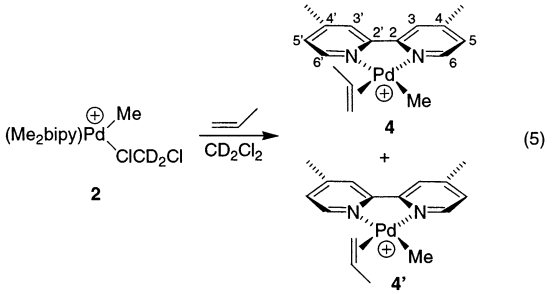
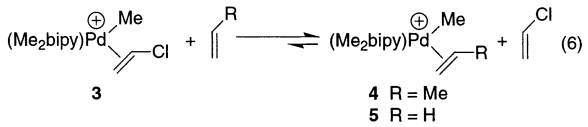


Figure 3. Variable temperature ^{1}H NMR spectra of in situ generated $(Me_2bipy)PdMe(CH_2{=}CHMe)^+$ (**4**/**4′**; CD_2Cl_2 solvent). The bipy and vinyl regions are shown. Assignments are based on the labeling scheme in eq 5. Major isomer: δ 8.32, H6; 8.00, H3 or H3′; 7.96, H3 or H3′; 7.80, H6′; 7.49, H5 or H5′; 7.44, H5 or H5′; 5.95, =C*H*Me; 4.87, =CH_2; 4.54, =CH_2. Minor isomer: δ 8.32, H6; 8.30, H6′; 8.00, H3 or H3′; 7.96, H3 or H3′; 7.49, H5 or H5′; 7.44, H5 or H5′; 5.79, =C*H*Me; 4.56, =CH_2; 4.47, =CH_2. The line shape changes are due to **4**/**4′** exchange.



The ethylene complex $(Me_2bipy)PdMe(CH_2{=}CH_2)^+$ (**5**) is generated by addition of ethylene to a CD_2Cl_2 solution of **2** at −78 °C. The ^{1}H NMR spectrum of **5** at −83 °C contains a broad AA′XX′ pattern centered at δ 4.9 for the coordinated ethylene. Complex **5** undergoes fast exchange with free ethylene at −83 °C. The analogous Pt complex, $[(^tBu_2bipy)PtMe(CH_2{=}CH_2)][MeB(C_6F_5)_3]$, was prepared previously by the reaction of $(^tBu_2bipy)PtMe_2$ and $B(C_6F_5)_3$ in the presence of ethylene.[21]

Relative Olefin Binding Strengths in $(Me_2bipy)PdMe(olefin)^+$. Competition experiments establish that VC coordinates more weakly to $(Me_2bipy)PdMe^+$ as compared to propylene or ethylene (eq 6). For example, addition of 1.04 equiv of propylene to **3** at −73 °C results in complete displacement of VC and formation of **4**/**4′**. Only one set of resonances are observed for the two isomers **4**/**4′** due to fast associative exchange between free and coordinated propylene, but the resonances for VC are sharp and appear at the free VC positions. Similarly, treatment of a CD_2Cl_2 solution of **3** with 0.4 equiv of ethylene at −88 °C results in the formation of 0.4 equiv of **5**, leaving 0.6 equiv of **3** unreacted. The ^{1}H NMR spectrum of the mixture contains a normal spectrum of **5**. However, only a single set of VC resonances is observed, and the Pd−Me and H6′ resonances of **3** are broadened. These results indicate the 0.4 equiv of free VC displaced by the ethylene exchanges rapidly with the coordinated VC of **3** (as expected from above). Addition of an additional 0.7 equiv of ethylene to this mixture results in quantitative formation of **5**. Only one ethylene resonance is observed (δ 4.98, s), indicating that the 0.1 equiv of free ethylene exchanges rapidly with the coordinated ethylene of **5** (as expected from above). However, the VC resonances are sharp and appear at the free VC positions.



The weaker coordination of the electron-poor olefin VC as compared to the sterically similar propylene in the $(Me_2bipy)PdMe(olefin)^+$ system reflects the poor back-bonding properties of the cationic Pd(II) center.[22] For comparison, the same trend in VC versus propylene binding strength was observed for solid $Ag(olefin)_2^+$, while the opposite trend was observed for $Ni\{P(O\text{-}o\text{-}tolyl)_3\}_2(olefin)$ and $(acac)Rh(olefin)_2$, in which d-π^* back-bonding plays a more significant role.[23]

VC Insertion of $(Me_2bipy)PdMe(CH_2{=}CHCl)^+$ (3). The reaction of **2** with VC was investigated in NMR experiments using internal standards (eq 7). The reaction of **2** with a large excess of VC (103 equiv) in CD_2Cl_2 at −78 °C, followed by warming to room temperature for 30 min, results in complete consumption of **2**, consumption of 1.9 equiv of VC, and formation of 1.8 equiv of propylene and 0.1 equiv of butenes (cis and trans 2-butene and isobutylene). The ^{1}H NMR spectrum of the product mixture contains a predominant set of (Me_2bipy)-Pd resonances which integrate for 0.95 equiv versus starting **2** and are nearly identical to those of $(Me_2bipy)PdCl_2$, with the exception that the Me_2bipy ortho-H resonance is shifted slightly upfield. In addition, resonances for the bis-ligand complex $(Me_2bipy)_2Pd^{2+}$ (0.03 equiv vs **2**) are observed; the identity of this species was confirmed by independent synthesis of the $B(C_6F_5)_4^-$ salt.[24] The ^{19}F NMR spectrum contains predominant resonances for free $B(C_6F_5)_3$ (ca. 86% of total C_6F_5 species), which are significantly broadened. These results show that the main organometallic products of the reaction are $(Me_2bipy)PdCl_2$ and

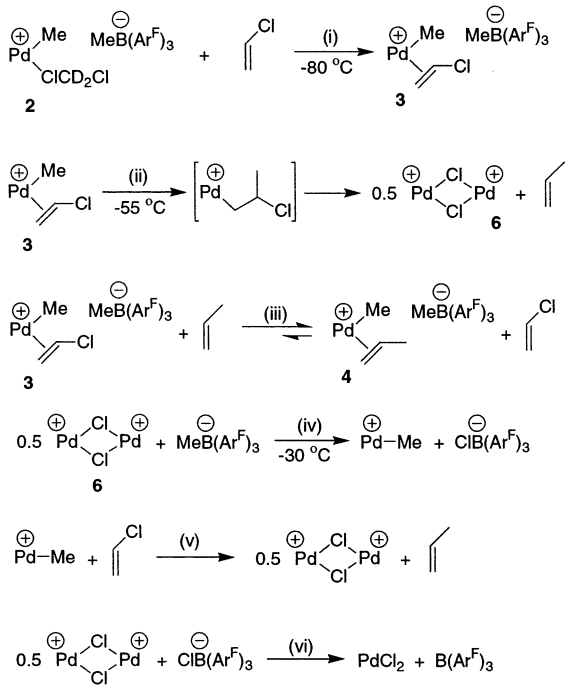
(21) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1996**, 1809.

(22) The poor back-bonding properties of L_2PdR^+ species are illustrated by the high ν_{CO} values for the carbonyl ligands in (1,10-phenanthroline)Pd{C(=O)Me}(CO)$^+$ (ν_{CO} = 2128 cm^{-1}) and (α-diimine)Pd{C(=O)Me}(CO)$^+$ (ν_{CO} = 2132 cm^{-1}). Similar values are expected for $(Me_2bipy)Pd\{C(=O)Me\}(CO)^+$. (a) Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 1137. (b) Burns, C. T.; Jordan, R. F. *Abstr. Pap. Am. Chem. Soc.* **2002**, *224*, 322-INOR. (c) Burns, C. T.; Jordan, R. F., unpublished results.

(23) (a) Quinn, H. W.; VanGilder, R. L. *Can. J. Chem.* **1971**, *49*, 1323. (b) Cramer, R. *J. Am. Chem. Soc.* **1967**, *89*, 4621. (c) Tolman, C. A. *J. Am. Chem. Soc.* **1974**, *96*, 2780.

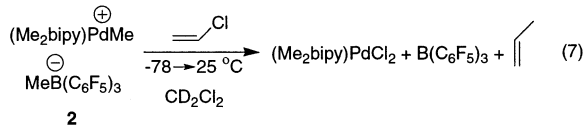
(24) For other $(Me_2bipy)_2Pd^{2+}$salts, see: (a) PF_6^- salt: Milani, B.; Anzilutti, A.; Vicentini, L.; Santi, A.; Zangrando, E.; Geremia, S.; Mestroni, G. *Organometallics* **1997**, *16*, 5064. (b) TfO^- salt: Wehman, P.; Dol, G. C.; Moorman, E. R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Fraanje, J.; Goubitz, K. *Organometallics* **1994**, *13*, 4856. (c) CF_3COO^- salt: Milani, B.; Corso, G.; Zangrando, E.; Randaccio, L.; Mestroni, G. *Eur. J. Inorg. Chem.* **1999**, *11*, 2085.

Scheme 1[a]



[a] Pd = $(Me_2bipy)Pd$, $Ar^F = C_6F_5$.

$B(C_6F_5)_3$. Control experiments establish that the minor shifting of the $(Me_2bipy)PdCl_2$ ^1H resonances and the broadening of the $B(C_6F_5)_3$ ^{19}F resonances result from interaction between these species. The ^1H and ^{19}F NMR spectra of a pyridine-d_5 solution (50 °C) of the solid remaining after removal of the volatiles from the product mixture of eq 7 confirm that $(Me_2bipy)PdCl_2$ and $B(C_6F_5)_3$ are present.



NMR studies were conducted to probe the mechanism of eq 7, and the results are summarized in Scheme 1. Low-temperature NMR monitoring of the reaction of **3** with 34 equiv of VC shows that **3** reacts slowly at −55 °C to produce the dinuclear dicationic species $\{(Me_2bipy)Pd(\mu\text{-}Cl)\}_2^{2+}$ (**6**, $MeB(C_6F_5)_3^-$ salt) and propylene. Gradual warming of the reaction mixture from −55 to −30 °C over 2.5 h results in 80% conversion of **3** to **6**. The identity of **6** was confirmed by independent synthesis of the $B(C_6F_5)_4^-$ salt.[25] Because propylene coordinates more strongly than VC to $(Me_2bipy)PdMe^+$ (as confirmed above), the propylene which is generated displaces VC from **3**. Thus, the NMR spectra show that a mixture of **3**, **4**, and **6** is present until one-half of the Pd−Me groups are consumed, after which point only **4** and **6** are present.[26] These observations are consistent with the *net* 1,2 VC insertion/β-Cl elimination and ligand exchange reactions in eqs ii and iii in Scheme 1, which are the only significant reactions occurring below −30 °C. It is also possible that **3** undergoes initial 2,1 insertion to give $(Me_2bipy)Pd(CHClCH_2Me)^+$, which isomerizes by β-H elimination and reinsertion to $(Me_2bipy)Pd(CHMeCH_2Cl)^+$, which in turn undergoes β-Cl elimination to yield the products of eq ii. However, no evidence for the intermediates or possible chloropropylene byproducts from this indirect process was observed. Above −30 °C, **6** consumes a second equiv of VC, and the final products of eq 7 are formed. This stage is complete within a few minutes at room temperature. These results are consistent with eqs iv−vi in Scheme 1, in which Me/Cl exchange between $\{(Me_2bipy)Pd(\mu\text{-}Cl)\}_2^{2+}$ and $MeB(C_6F_5)_3^-$ regenerates $(Me_2bipy)PdMe^+$, which in turn undergoes VC insertion and β-Cl elimination. The chloro species $(Me_2bipy)PdCl^+$ and $ClB(C_6F_5)_3^-$ collapse to $(Me_2bipy)PdCl_2$ and $B(C_6F_5)_3$.[27]

A key feature of Scheme 1 is that, although the equilibrium in eq iii lies far to the right, the barrier for VC insertion of **3** is much lower than that for propylene insertion of **4** (vide infra), so that $(Me_2bipy)PdMe^+$ consumes VC faster than propylene.

The minor butene products are derived from propylene insertion of **4**, chain walking of the resulting $(Me_2bipy)Pd(butyl)^+$ species, and eventual butene loss. The bis-ligand complex $(Me_2bipy)_2Pd^{2+}$ is likely formed by decomposition of the $(Me_2bipy)PdH^+$ species resulting from butene loss.[28] The yields of butenes and $(Me_2bipy)_2Pd^{2+}$ increase at the expense of the propylene and $(Me_2bipy)PdCl_2$ yields when the reaction is conducted in the presence of lower VC charges. For example, the reaction of **2** with 34 equiv of VC yields 1.3 equiv of propylene, 0.36 equiv of butenes, 0.9 equiv of $(Me_2bipy)PdCl_2$, and 0.05 equiv of $(Me_2bipy)_2Pd^{2+}$.

Propylene and Ethylene Insertion of $(Me_2bipy)PdMe(olefin)^+$ Species. To confirm that VC insertion of **3** is faster than propylene insertion of **4**, the latter reaction was investigated independently. The reaction of **4** with excess propylene was monitored by low-temperature NMR. These experiments show that no insertion occurs below −10 °C and that above this temperature the propylene is catalytically dimerized.[29] Similar experiments establish that ethylene complex **5** inserts ethylene only at ca. −23 °C; above this temperature, catalytic dimerization to internal butenes occurs.[22a,30] Thus, the insertion rate of $(Me_2bipy)_2Pd(Me)(olefin)^+$ species varies in the order: VC ≫ ethylene > propylene. These results are consistent with the observations of Brookhart and Sen which demonstrate that the rates of insertion of $(\alpha\text{-diimine})PdMe(olefin)^+$ (α-diimine = $(2,6\text{-}^iPr_2\text{-}C_6H_3)N{=}CMeCMe{=}N(2,6\text{-}^iPr_2\text{-}C_6H_3)$) vary in the order vinyl bromide > ethylene > propylene.[2a,31,32] The higher ground-state energies of the VC and vinyl bromide adducts, as

(25) For representative examples of other halide-bridged dinuclear dicationic Pd complexes, see: (a) Clater, M.; Hollis, T. K.; Overman, L. E.; Ziller, J.; Zipp, G. G. *J. Org. Chem.* **1997**, *62*, 1449. (b) Pignat, K.; Vallotto, J.; Pinna, F.; Strukul, G. *Organometallics* **2000**, *19*, 5160. (c) Neve, F.; Ghedini, M.; Tiripicchio, A.; Ugozzoli, F. *Organometallics* **1992**, *11*, 795.

(26) The ^1H NMR spectra of **3** and **4** are nearly identical except that Pd−Me resonances occur at δ 0.91 (−63 °C) and 0.84 (−43 °C), respectively. Thus, the Pd−Me resonance for the exchanging mixture of **3** and **4** gradually shifts from δ 0.90 to δ 0.84 as the first 50% of Pd−Me groups are consumed and thereafter remains constant at δ 0.84.

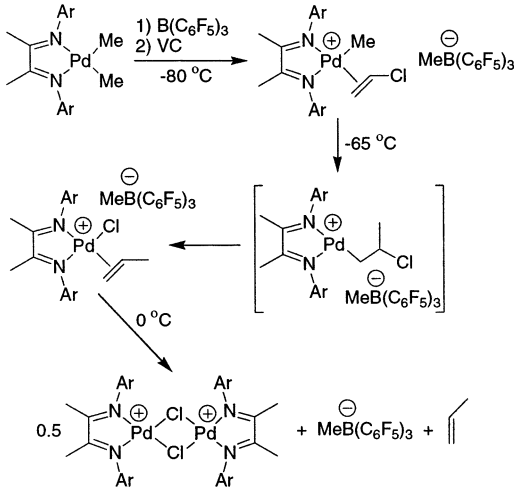
(27) The minor unidentified $B{-}C_6F_5$ products observed by ^{19}F NMR may result from competing redistribution reactions of $ClB(C_6F_5)_3^-$, which is known to be labile. For characterization and lability of $ClB(C_6F_5)_3^-$, see: (a) Zhou, J.; Lancaster, S. J.; Walker, D. A.; Beck, S.; Thornton-Pett, M.; Bochmann, M. *J. Am. Chem. Soc.* **2001**, *123*, 223. (b) Courtenay, S.; Stephan, D. W. *Organometallics* **2001**, *20*, 1442. (c) Bosch, B. E.; Erker, G.; Frölich, R.; Meyer, O. *Organometallics* **1997**, *16*, 5449.

(28) In several experiments, traces of ethylene were also observed. The ethylene is probably formed by VC insertion and β-Cl elimination of $(Me_2bipy)PdH^+$ species.

(29) A distribution of internal hexenes is produced which is similar to that produced by $\{PhN{=}C(R)C(R){=}NPh\}NiBr_2$/MAO (R, R = 1,8-naphth-diyl). See: Svejda, S. A.; Brookhart, M. *Organometallics* **1999**, *18*, 65.

(30) These results are similar to the behavior of $[(1,10\text{-phenanthroline})Pd(Me)(CH_2{=}CH_2)][B\{3,5\text{-}(CF_3)_2\text{-}C_6H_3\}_4]$. Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746.

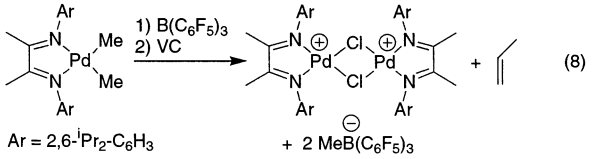
Scheme 2[a]



[a] Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$.

compared to the ethylene or propylene adducts, contribute to the lower insertion barriers for vinyl halides.[33]

Reaction of (α-Diimine)PdMe$^+$ with VC. The studies above show that the simple (Me$_2$bipy)PdMe$^+$ model system readily coordinates and inserts VC but that the resulting (Me$_2$bipy)Pd(CH$_2$CHMeCl)$^+$ intermediate undergoes rapid β-Cl elimination which precludes VC polymerization. One potential strategy for circumventing β-Cl elimination is to use sterically bulky catalysts. Accordingly, the reaction of Brookhart's sterically bulky (α-diimine)PdMe$^+$ catalyst with VC was investigated (eq 8).[31] The reaction of (α-diimine)PdMe$_2$ with B(C$_6$F$_5$)$_3$ and excess VC (20 equiv) at −78 °C followed by warming to room temperature for 24 h results in complete consumption of (α-diimine)PdMe$_2$ and formation of the dinuclear dicationic Cl-bridged complex [{(α-diimine)Pd(μ−Cl)}$_2$][MeB(C$_6$F$_5$)$_3$]$_2$ (0.35 equiv, 70%), (α-diimine)PdCl$_2$ (0.15 equiv, 15%), and propylene (0.8 equiv). The {(α-diimine)Pd(μ−Cl)}$_2^{2+}$ dication was generated independently as the B(C$_6$F$_5$)$_4^-$ salt and characterized by NMR and ESI-MS. These observations are consistent with net 1,2 VC insertion and β-Cl elimination of the initially generated (α-diimine)PdMe$^+$ species and dimerization of the resulting (α-diimine)PdCl$^+$ product as shown in Scheme 2, analogous to the reactivity observed for (Me$_2$bipy)PdMe$^+$. Evidently, realkylation of the (α-diimine)PdCl$^+$ product by MeB(C$_6$F$_5$)$_3^-$ is disfavored in this system by steric crowding.



(8)

Monitoring the reaction of (α-diimine)PdMe$_2$, B(C$_6$F$_5$)$_3$, and VC by low-temperature NMR enabled observation of the intermediates in Scheme 2. At −80 °C, the VC adduct [(α-diimine)PdMe(CH$_2$=CHCl)][MeB(C$_6$F$_5$)$_3$] was observed (60%).[34] At −65 °C, this species reacts to produce [(α-diimine)PdCl(CH$_2$=CHMe)][MeB(C$_6$F$_5$)$_3$]; this conversion is complete upon warming of the solution to −40 °C over 30 min. At 0 °C, [(α-diimine)PdCl(CH$_2$=CHMe)][MeB(C$_6$F$_5$)$_3$] converts to [{(α-diimine)Pd(μ-Cl)}$_2$][MeB(C$_6$F$_5$)$_3$]$_2$, releasing free propylene. Sen has reported analogous chemistry with vinyl bromide.[32]

Reaction of (Pyridine-bisimine)MCl$_2$/MAO Catalysts (M = Fe, Co) with VC. The active species in the catalysts studied above are square-planar L$_2$Pd(R)(olefin)$^+$ cations. An alternative possible approach to disfavoring β-Cl elimination is to use metal catalysts with higher coordination numbers. To probe this strategy, the reactions of VC with (pyridine-bisimine)MCl$_2$/MAO catalysts (M = Fe, Co; pyridine-bisimine = 2,6-{(2,6-^{i}Pr$_2$−C$_6$H$_3$)N=CMe}$_2$-pyridine) were examined.[35] The reaction of VC with (pyridine-bisimine)FeCl$_2$/MAO (Al/Fe = 1000) in C$_6$D$_6$ at 25 °C results in the immediate production of propylene. After 96 h at 25 °C, 42 equiv of VC per Fe is consumed and converted to propylene.[36] The reaction of (pyridine-bisimine)CoCl$_2$/MAO (Al/Co = 1000) with VC under similar conditions results in greater consumption of VC (220 equiv per Co after 96 h at 25 °C) and conversion to propylene. No PVC was observed in these reactions. The mechanism of these reactions was not examined in detail but is almost certainly analogous to that observed earlier for zirconocene catalysts.[6] The active L$_n$M−Me species generated from the reaction of the (pyridine-bisimine)MCl$_2$ complex and MAO undergoes net 1,2 VC insertion and β-Cl elimination, generating a L$_n$MCl species which is re-alkylated by MAO (Scheme 3).[37] VC insertion into the L$_n$MCH$_2$CHClR$^+$ intermediate does not compete with β-Cl elimination. These results are consistent with the recent report of Boone et al. that VC terminates {2,6-(*o*-tol-N=CMe)$_2$-pyridine}FeCl$_2$/MAO-catalyzed ethylene polymerization by 1,2 insertion/β-Cl elimination.[38]

Reaction of Neutral Ni Catalysts with VC. Another possible approach to circumventing β-Cl elimination is to use a neutral catalyst in which the driving force for M−Cl bond formation may be attenuated due to the reduced metal electrophilicity. To probe this possibility, we investigated the reaction of VC and ethylene/VC mixtures with several neutral nickel catalysts.

(31) (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S. Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686. (c) Gottfried, A. C.; Brookhart, M. *Macromolecules* **2001**, *34*, 1140. (d) Schultz, L. H.; Tempel, D. J.; Brookhart, M. *J. Am. Chem. Soc.* **2001**, *123*, 11539.

(32) Kang, M.; Sen, A.; Zakharov, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 12080.

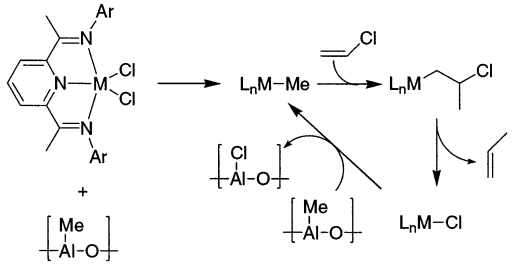
(33) (a) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 2436. (b) von Schenck, H.; Strömberg, S.; Zetterberg, K.; Ludwig, M.; Åkermark, B.; Svensson, M. *Organometallics* **2001**, *20*, 2813.

(34) The reaction of (α-diimine)PdMe$_2$ with B(C$_6$F$_5$)$_3$ in the presence of VC also produces a second species in 40% yield which was identified as the dinuclear μ-CH$_2$ complex [(α-diimine)Pd(μ-CH$_2$)(μ-Me)Pd(α-diimine)][MeB(C$_6$F$_5$)$_3$]. This species was recently reported by Baird and is the exclusive product of the reaction of (α-diimine)PdMe$_2$ with 0.5 or 1 equiv of B(C$_6$F$_5$)$_3$ in the absence of olefin at room temperature. Key ^{1}H NMR features of this species at −80 °C include a distinctive singlet at δ 5.43 for the μ-CH$_2$ group and a singlet at δ −0.14 for the μ-CH$_3$ group. We have also generated [(α-diimine)Pd(μ-CH$_2$)(μ-Me)Pd(α-diimine)][MeB(C$_6$F$_5$)$_3$] by the reaction of (α-diimine)PdMe$_2$ with B(C$_6$F$_5$)$_3$ at −80 °C and confirmed the NMR and ESI-MS results reported by Baird. Baird reported that this complex reacts with ethylene to partially form "(α-diimine)PdMe$^+$" which polymerizes the ethylene. We observed that [(α-diimine)Pd(μ-CH$_2$)(μ-Me)Pd(α-diimine)][MeB(C$_6$F$_5$)$_3$] reacts with VC at ca. 20 °C to yield the same final products as (α-diimine)Pd(Me)(VC)$^+$. See: Brownie, J. H.; Baird, M. C.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2003**, *22*, 33.

(35) (a) Small, B. L.; Bennett, A. M. A.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 4049. (b) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mctavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849. (c) Britovsek, G. J. P.; Bruce, V.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; Mctavish, S. J.; Redshaw, C.; Solan, G. A.; Stromberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728. (d) Small, B. L.; Brookhart, M. *Macromolecules* **1999**, *32*, 2120. (e) Bennett, A. M. A. WO 98/27124 (DuPont); *Chem. Abs.* **1998**, *129*, 122973x.

(36) (Pyridine-bisimine)FeCl$_2$/MAO is moderately active for the polymerization of propylene at −20 °C, but the activity is decreased at 0 °C. Small, B. L.; Brookhart, M. *Macromolecules* **1999**, *32*, 2120.

Scheme 3[a]



[a] M = Fe, Co; Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$.

The neutral Ni-phenyl complex (sal)Ni(Ph)PPh$_3$ (**7**) (sal = 2-{C(H)=N(2,6-^{i}Pr$_2$−C$_6$H$_3$)}-6-Ph-phenoxide) is an active catalyst for polymerization of ethylene, norbornene, and substituted norbornenes and exhibits some tolerance of Lewis bases.[39] The reaction of **7** with excess VC in C_6D_6 at 50 °C was monitored by ^{1}H NMR using toluene as an internal standard. The results are summarized in Scheme 4, and representative spectra are shown in Figure 4. After 4 days, 1 equiv (vs **7**) of VC is consumed, and 1 equiv of styrene is produced. No further consumption of VC is observed, and no PVC is produced. Over the course of the reaction, the two ^{i}Pr methyl ^{1}H NMR signals of **7** (δ 1.21, 1.12) disappear, and two broad ^{i}Pr methyl signals (δ 3.32, 2.19) corresponding to the paramagnetic complex (sal)Ni(Cl)(PPh$_3$) (**8**) appear. Broad ^{i}Pr methyl signals (δ 1.37, 1.15) corresponding to the bis-ligand complex (sal)$_2$Ni (**9**) grow in at later times. The total intensity of the ^{i}Pr methyl signals for **7**, **8**, and **9** is constant over the course of the reaction, which confirms good mass balance for the sal ligand. These observations are consistent with displacement of PPh$_3$ by VC, net 1,2 VC insertion, and subsequent β-Cl elimination. The slow overall reaction rate reflects the unfavorable displacement of PPh$_3$ by VC.[40] The initial Ni product **8** disproportionates to **9** and (Ph$_3$P)$_2$-NiCl$_2$, which precipitates from solution.

To confirm the identity of the Ni products, the reaction scale was increased, and **8**, **9**, and (Ph$_3$P)$_2$NiCl$_2$ were isolated as described in the Experimental Section. Compounds **8** and **9** were characterized by single-crystal X-ray diffraction, and the identity of **9** was confirmed by alternate synthesis from (Ph$_3$P)$_2$NiCl$_2$ and 2 equiv of Na[sal]. The identity of (Ph$_3$P)$_2$NiCl$_2$ was confirmed by powder X-ray diffraction. Attempts to synthesize **8** by the reaction of (Ph$_3$P)$_2$NiCl$_2$ with 1 equiv of Na[sal] produced mixtures of **8** and **9**, consistent with the facile disproportionation of **8**.

The molecular structure of **8** is shown in Figure 5, and key bond distances and angles are listed in Table 1. Compound **8** is a distorted tetrahedral complex. The O−Ni−N bond angle is constrained to 93.66(8)° by the chelation, while the O−Ni−Cl (124.06(6)°) and N−Ni−Cl (119.36(6)°) angles are correspondingly larger. The distances and angles associated with the (sal)Ni unit are similar to those for reported tetrahedral bis-salicylaldiminato nickel complexes.[41]

Complex **9** crystallizes with two independent molecules in the asymmetric unit, which have similar structures. The structure of one molecule of **9** is shown in Figures 6 and 7, and key

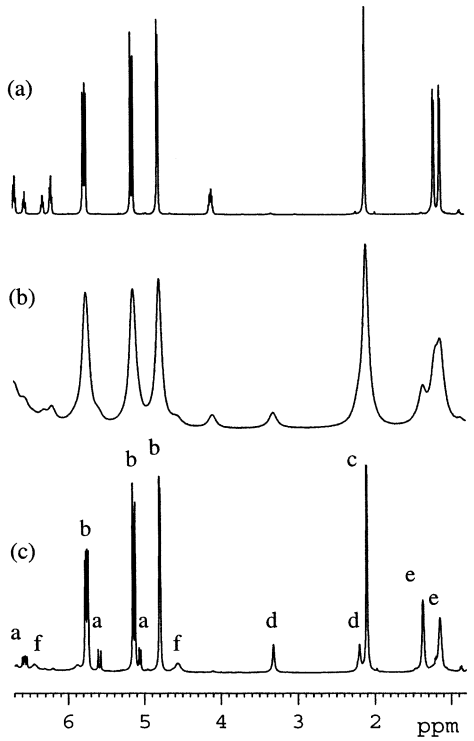
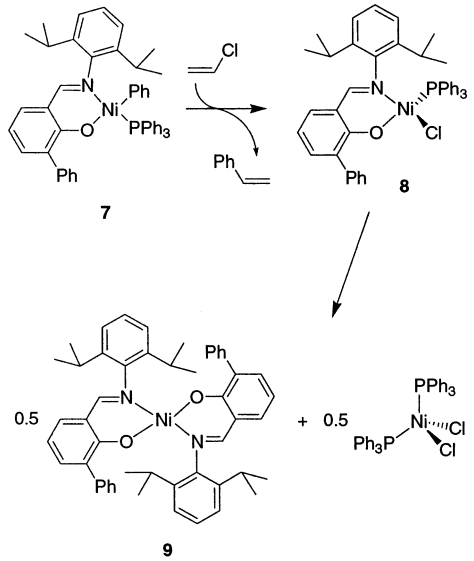


Figure 4. ^{1}H NMR spectra (500 MHz, C_6D_6) of the reaction of (sal)Ni(Ph)PPh$_3$ and VC in the presence of toluene (internal standard). (a) Before any reaction takes place (t = 0). (b) After 18 h at 50 °C. (c) After 4 d at 50 °C. Assignments: a, styrene; b, VC; c, toluene; d, resonances of **8**; e, ^{i}Pr methyl resonances of **9**; f, other resonances of **9**.

Scheme 4



(37) The active species for (pyridine-bisimine)FeCl$_2$/MAO is proposed to be (pyridine-bisimine)Fe(R)(olefin)$^+$. See: (a) Britovsek, G. J. P.; Gibson, V. C.; Spitzmesser, S. K.; Tellmann, K. P.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2002**, *1159*. (b) Deng, L.; Margyl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1999**, *121*, 6479. Activation of (pyridine-bisimine)CoCl$_2$/MAO has been proposed to involve alkylation/reduction to (pyridine-bisimine)CoMe followed by conversion to either a Co(I) or a Co(III) active species. See: (c) Gibson, V. C.; Humphries, M. J.; Tellmann, K. P.; Wass, D. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2001**, 2252. (d) Kooistra, T. M.; Knijnenburg, Q.; Smots, J. M. M.; Horton, A. D.; Budzelaar, P. H. M.; Gal, A. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 4719.

(38) Boone, H.; Athey, P. S.; Mullins, M. J.; Philipp, D.; Muller, R.; Goddard, W. A. *J. Am. Chem. Soc.* **2002**, *124*, 8790.

(39) (a) Younkin, T. R.; Conner, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460. (b) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149.

(40) Attempts to use a phosphine sponge (Ni(cod)$_2$ or B(C$_6$F$_5$)$_3$) to increase reaction rates resulted in catalyst decomposition as evidenced by Ni(0) plating on the reaction tubes.

(41) Fox, M. R.; Orioli, P. L.; Lingafelter, E. C.; Sacconi, L. *Acta Crystallogr.* **1964**, *17*, 1159.

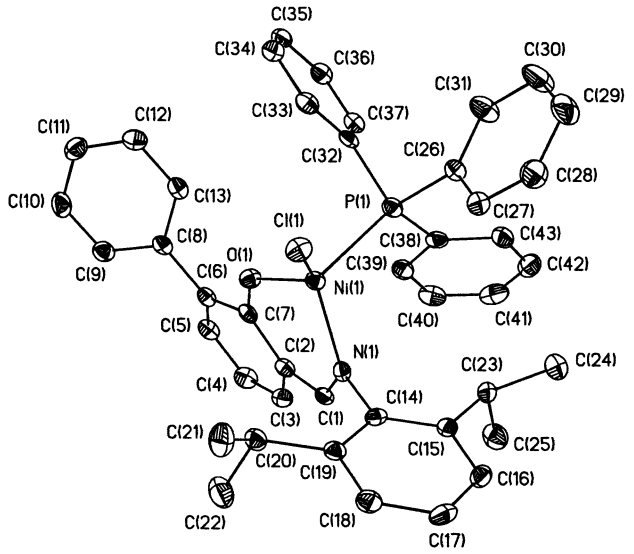


Figure 5. Molecular structure of (sal)Ni(Cl)PPh_3 (**8**). Hydrogen atoms are omitted.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for (sal)Ni(Cl)(PPh_3) (**8**)

Ni(1)−O(1)	1.881(2)	Ni(1)−P(1)	2.3257(8)
Ni(1)−N(1)	1.953(2)	N(1)−C(1)	1.298(3)
Ni(1)−Cl(1)	2.2059(8)	O(1)−C(7)	1.302(3)
O(1)−Ni(1)−N(1)	93.66(8)	O(1)−Ni(1)−P(1)	102.92(5)
O(1)−Ni(1)−Cl(1)	124.06(6)	N(1)−Ni(1)−P(1)	109.98(6)
N(1)−Ni(1)−Cl(1)	119.36(6)	Cl(1)−Ni(1)−P(1)	105.46(3)

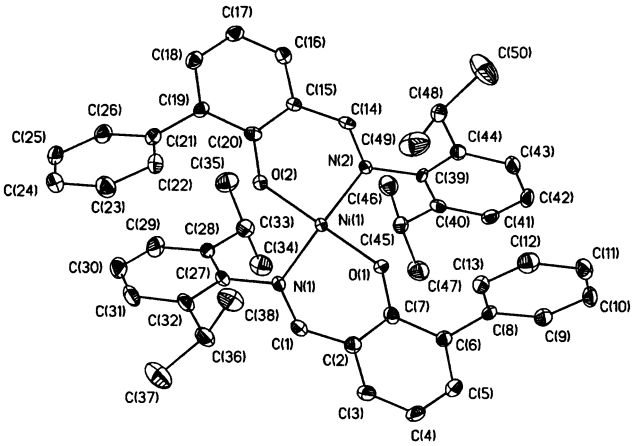


Figure 6. Molecular structure of $(sal)_2Ni$ (**9**). Hydrogen atoms are omitted.

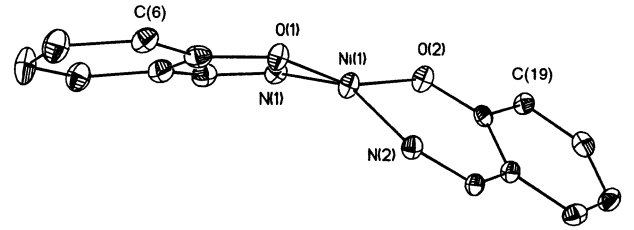


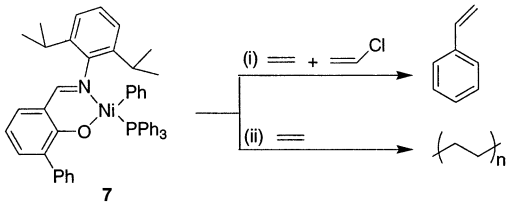
Figure 7. View of the core structure of **9** showing the distorted tetrahedral geometry at Ni. The Ph substituents at C(6) and C(19), the 2,6-^{i}Pr$_2$-phenyl substituents at N(1) and N(2), and all H atoms are omitted.

bond distances and angles are listed in Table 2. Compound **9** is a distorted square-planar complex. The angle between the N−Ni−O planes defined by the two ligands (θ) is 28°. The average Ni−O (1.846 Å) and average Ni−N (1.899 Å) distances

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(sal)_2Ni$ (**9**)

Ni(1)−O(1)	1.841(2)	N(1)−C(1)	1.299(4)
Ni(1)−O(2)	1.843(2)	N(2)−C(14)	1.299(4)
Ni(1)−N(2)	1.895(3)	O(1)−C(7)	1.308(4)
Ni(1)−N(1)	1.894(3)	O(2)−C(20)	1.300(4)
O(1)−Ni(1)−O(2)	160.4(1)	O(1)−Ni(1)−N(1)	93.5(1)
O(1)−Ni(1)−N(2)	90.7(1)	O(2)−Ni(1)−N(1)	90.9(1)
O(2)−Ni(1)−N(2)	93.7(1)	N(2)−Ni(1)−N(1)	153.9(1)

Scheme 5



are similar to those in the tetrahedrally distorted bis-salicylaldiminato complex (^{t}BuMesal-Et)$_2$Ni (1.856, 1.899 Å; θ = 22°).[42]

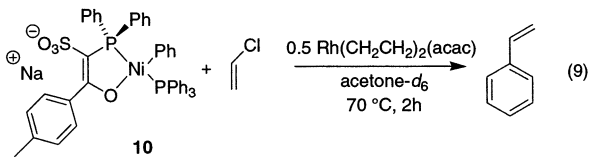
It is possible that the β-Ph group in the presumed (sal)Ni(CH_2CHPhCl) intermediate in Scheme 4 accelerates β-Cl elimination. Grubbs proposed that initiation of ethylene polymerization by **7** involves ethylene insertion into the Ni−Ph bond of **7** followed by β-H elimination to generate a Ni−H species and styrene.[39a] To explore the influence of the phenyl substituent, we investigated the reaction of ethylene/VC mixtures with **7** (eq i, Scheme 5). The reaction of **7** with 250 equiv of VC under 100 psi of ethylene at 20 °C in toluene yields styrene (not quantified). No polymer is formed. The reaction of **7** with ethylene in the absence of VC under otherwise identical conditions results in a high yield of solid polyethylene (TOF = 900/h, eq ii, Scheme 5). As independent experiments show that VC does not insert into the Ni−Ph bond of **7** at 20 °C, a likely mechanism for eq i in Scheme 5 is insertion of ethylene followed by β-H elimination to generate styrene and the corresponding Ni−H complex, which then undergoes net 1,2 VC insertion and rapid β-Cl elimination. Thus, (sal)Ni(CH_2CH_2Cl) undergoes fast β-Cl elimination even without the β-Ph substituent.

The sulfonated SHOP-type catalyst (P−O)Ni(Ph)PPh_3 (**10**, P−O = {$Ph_2PC(SO_3Na)$═C(*p*-tol)O}) catalyzes ethylene polymerization in a variety of media, including H_2O/toluene, in the presence of Rh(CH_2═CH_2)$_2$(acac) as a phosphine sponge.[43] The reaction of this catalyst system was briefly investigated by ^{1}H NMR. The reaction of **10**/0.5 Rh(CH_2═CH_2)$_2$(acac) with excess VC in acetone-d_6 yields styrene (0.8 equiv) after 2.5 h at 70 °C (eq 9). VC uptake could not be quantified due to broadening of the ^{1}H NMR signals. GC-MS analysis of the volatiles confirmed that styrene is the major volatile component. No PVC was detected. These results are consistent with net 1,2 VC insertion and subsequent fast β-Cl elimination. The reaction was repeated in the absence of VC, and no styrene was generated. This control experiment shows that the styrene

(42) ^{t}BuMesal-Et = 2-{C(H)═N(Et)}-4-Me-6-^{t}Bu-phenoxide; (a) Shkol'nikova, L. M.; Knyazeva, A. N.; Voblikova, V. A. *J. Struct. Chem.* **1967**, *8*, 77. (b) Knoch, R.; Elias, H.; Paulus, H. *Inorg. Chem.* **1995**, *34*, 4032.

(43) (a) Held, A.; Mecking, S. *Chem.-Eur. J.* **2000**, *6*, 4623. (b) Soula, R.; Broyer, J. P.; Llauro, M. F.; Tomov, A.; Spitz, R.; Claverie, J.; Drujon, X.; Malinge, J.; Saudemont, T. *Macromolecules* **2001**, *34*, 2438. (c) Soula, R.; Novat, C.; Tomov, A.; Spitz, R.; Claverie, J.; Drujon, X.; Malinge, J.; Saudemont, T. *Macromolecules* **2001**, *34*, 2022. (d) Held, A.; Bauers, F. M.; Mecking, S. *Chem. Commun.* **2000**, 301. (e) Bauers, F. M.; Mecking, S. *Macromolecules* **2001**, *34*, 1165.

in eq 9 does not arise by release of ethylene from $Rh(CH_2{=}CH_2)_2(acac)$, followed by ethylene insertion and β-H elimination of **10**. In both cases, the formation of $Rh(PPh_3)_2(acac)$ was observed by ^{31}P NMR.



10

Conclusions

The studies described here enable several conclusions to be made concerning the fundamental reactions of VC with late metal catalysts and the prospects for polymerizing this and other $CH_2{=}CHX$ monomers by insertion mechanisms.

(i) VC coordinates more weakly than ethylene or propylene to the simple catalyst $(Me_2bipy)PdMe^+$, which parallels the trend for monomer binding to the d^0 model system $(C_5H_4Me)_2Zr(O^tBu)^+$.[44] The weak coordination of the electron-poor VC reflects the predominance of the olefin-to-metal σ-donation and the absence of significant d-π* back-bonding in these metal olefin species. This trend is expected to be general for both early and late metal catalysts.

(ii) Insertion rates of $(Me_2bipy)Pd(Me)(olefin)^+$ species vary in the order VC > ethylene > propylene. This trend is consistent with previous observations by Brookhart and Sen that insertion rates of (α-diimine)Pd(Me)(olefin)$^+$ species vary in the order vinyl bromide > ethylene > propylene. The higher ground-state energies of the VC and vinyl bromide adducts, as compared to the ethylene or propylene adducts, contribute to the lower insertion barriers for vinyl halides.

(iii) The sterically open VC complex $(Me_2bipy)Pd(Me)(VC)^+$ and the crowded complex (α-diimine)Pd(Me)(VC)$^+$ undergo *net* 1,2 VC insertion and β-Cl elimination to yield Pd−Cl species and propylene. Analogous chemistry occurs for (pyridine-bisimine)MCl_2/MAO (M = Fe, Co) catalysts and for neutral (sal)Ni(Ph)PPh_3 and (P−O)Ni(Ph)PPh_3 catalysts, although the initial $L_nM(R)(VC)^+$ adducts were not detected in these cases. Recent DFT calculations predict that 2,1 insertion is favored over 1,2 insertion for the model systems {HN=CHCH=NH}-Pd(R)(VC)$^+$ (R = Me, Et).[33b,45] However, these calculations also predict that the 2,1 insertion product, {HN=CHCH=NH}-$PdCHClCH_2Et^+$, undergoes facile isomerization to {HN=CHCH=NH}$Pd(CH(Et)CH_2Cl)^+$ via β-H elimination/reinsertion and that the latter species undergoes facile β-Cl elimination. Our low-temperature NMR studies of the $(Me_2bipy)Pd(Me)(VC)^+$ and (α-diimine)Pd(Me)(VC)$^+$ systems did not provide evidence for $L_nPd(CHClCH_2CH_3)^+$ intermediates or chloropropylene byproducts. Thus, if 2,1 insertion is the kinetic pathway, isomerization of the initial insertion product to the 1,2 insertion product must be rapid and must occur without loss of olefin from the presumed $L_nPd(H)(ClHC{=}CHMe)^+$ intermediate.

(iv) The L_nMCH_2CHClR species formed by VC insertion into the L_nMR active species of late metal olefin polymerization catalysts, including sterically open and sterically crowded square-planar cationic Pd catalysts, five-coordinate (pyridine-bisimine)MCl_2/MAO (M = Fe, Co) catalysts, and neutral Ni catalysts, undergo fast β-Cl elimination. Due to the facility of β-Cl elimination for both early and late metal catalysts, insertion polymerization of VC and related monomers will likely require novel catalyst designs to favor 2,1 insertion or disfavor β-Cl elimination. Our work on these themes will be reported in due course.

Experimental Section

General Procedures. All reactions were performed under N_2 or vacuum using standard Schlenk techniques or in a N_2-filled drybox. Pentane, hexanes, toluene, and benzene were distilled from sodium/benzophenone or purified by passage through columns of activated alumina and BASF R3-11 oxygen removal catalyst. Toluene-d_8 and benzene-d_6 were distilled from sodium/benzophenone. Dichloromethane, chlorobenzene, dichloromethane-d_2, and chlorobenzene-d_5 were dried over CaH_2 and distilled. Nitrogen was purified by passage through columns containing activated molecular sieves and Q-5 oxygen scavenger. MAO (30% solution in toluene; MAO = methylalumoxane) was obtained from Albemarle. Dried MAO was prepared by drying a sample of MAO (30% toluene solution) under vacuum for 12 h at 25 °C. $B(C_6F_5)_3$ was obtained from Boulder Scientific and purified by sublimation. Vinyl chloride (VC) was obtained from Aldrich and used without further purification or received from Oxy Vinyl and dried over molecular sieves. $(cod)PdCl_2$ was purchased from Pressure Chemical and used as received. The ligands α-diimine ($(2,6\text{-}^iPr_2\text{-}C_6H_3)N{=}CMeCMe{=}N(2,6\text{-}^iPr_2\text{-}C_6H_3)$) and pyridine-bisimine (2,6-{(2,6-$^iPr_2$−C_6H_3)N=CMe}$_2$-pyridine) were obtained from Strem and used as received. The complexes (α-diimine)$PdMe_2$, (pyridine-bisimine)$FeCl_2$, and (pyridine-bisimine)$CoCl_2$ were prepared by literature procedures.[31,35]

Elemental analyses were performed by Midwest Microlabs. ESI-MS experiments were performed with a Hewlett-Packard Series 1100MSD instrument using direct injection via a syringe pump (ca. 10^{-6} M solutions). Good agreement between observed and calculated isotope patterns was observed in all cases.

NMR spectra were recorded at ambient temperature unless specified otherwise. ^1H and ^{13}C chemical shifts are reported relative to $SiMe_4$ and were determined by reference to the residual ^1H and ^{13}C solvent resonances. ^{11}B chemical shifts are reported relative to $BF_3(Et_2O)$, and ^{19}F chemical shifts are reported relative to $CFCl_3$. Coupling constants are given in Hz. NMR spectra for $(Me_2bipy)Pd$ salts containing the $MeB(C_6F_5)_3^-$ anion contain anion resonances which are nearly identical to those of $[NBu_3CH_2Ph)][MeB(C_6F_5)_3]$ and are thus characteristic of the free anion. Data for free $MeB(C_6F_5)_3^-$, ^1H NMR (CD_2Cl_2, −83 °C): δ 0.33 (s). ^{13}C NMR (CD_2Cl_2, −83 °C): 147.2 (d, J = 242), 136.7 (d, J = 237), 135.5 (d, J = 247), 127.1 (br s, *ipso*-C_6F_5), 9.0 (q, J = 127, MeB). ^{11}B NMR (CD_2Cl_2, −83 °C): δ −14.0 (br s). ^{19}F NMR (CD_2Cl_2, −83 °C): δ −132.2 (d, 6F, J = 22, *o*-F), −162.5 (t, 3F, J = 22, *p*-F), −165.3 (t, 6F, J = 22, *m*-F). NMR spectra for $B(C_6F_5)_4^-$ salts contain resonances characteristic of the free anion.[46]

(cod)PdMe$_2$.[47,48] A Schlenk flask was charged with $(cod)PdCl_2$ (997 mg, 3.50 mmol), and Et_2O (40 mL) was added by cannula to form a yellow suspension. The flask was cooled to −78 °C, and MeMgCl (2.35 mL, 3.0 M in THF, 7 mmol) was added dropwise. The reaction mixture was stirred at −35 °C for 1 h, and the volatiles were removed under vacuum at 0 °C. The resulting solid was extracted with pentane (40 mL) at 0 °C to yield a clear colorless extract. The volatiles were removed from the extract at 0 °C under vacuum to yield $(cod)PdMe_2$ as a white solid (480 mg, 56%). The product was used immediately

(44) Jordan, R. F.; Stoebenau, E. J., III. *Abstr. Pap. Am. Chem. Soc.* **2002**, *224*, 284-INOR.
(45) (a) Philipp, D. M.; Muller, R. P.; Goddard, W. A., III; Storer, J.; McAdon, M.; Mullins, M. *J. Am. Chem. Soc.* **2002**, *124*, 10198. See also: (b) Michalak, A.; Ziegler, T. *J. Am. Chem. Soc.* **2001**, *123*, 12266.
(46) Korolev, A. V.; Ihara, E.; Guzei, I. A.; Young, V. G., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 8291.
(47) Calvin, G.; Coates, G. E. *J. Chem. Soc.* **1960**, 2008.
(48) Rudler-Chauvin, M.; Rudler, H. *J. Organomet. Chem.* **1977**, *134*, 115.

for subsequent reactions. (cod)$PdMe_2$ decomposes at 25 °C in the solid state or in solution and should be stored below −30 °C. ^{1}H NMR (CD_2Cl_2): δ 5.40 (m, 4H, =CH), 2.60−2.34 (m, 8H, $-CH_2$), 0.26 (s, 6H, PdMe).

(Me_2bipy)$PdMe_2$ (1). A Schlenk flask was charged with (cod)$PdMe_2$ (245 mg, 1.00 mmol) and Me_2bipy (162 mg, 1.00 mmol), and pentane (20 mL) was added by cannula. The resulting yellow suspension was stirred at 0 °C for 1 h and filtered to yield a yellow solid. The solid was washed with pentane (3 × 10 mL) and dried under vacuum at 0 °C to yield (Me_2bipy)$PdMe_2$ as a bright yellow solid (276 mg, 88%). ^{1}H NMR (CD_2Cl_2): δ 8.58 (d, J = 5.5, 2H, H6), 7.87 (s, 2H, H3), 7.30 (d, J = 5.5, 2H, H5), 2.47 (s, 6H, *Me*$_2$bipy), 0.21 (s, 6H, PdMe). ^{13}C NMR (CD_2Cl_2, −53 °C): δ 154.3 (s, C2), 149.3 (s, C4), 147.0 (d, J = 183, C6), 126.5 (d, J = 161, C5), 122.2 (d, J = 162, C3), 21.3 (q, J = 127, *Me*$_2$bipy), −7.6 (q, J = 125, PdMe). Anal. Calcd for $C_{14}H_{18}N_2Pd$: C, 52.43; H, 5.62; N, 8.74. Found: C, 52.43; H, 5.60; N, 8.59.

Generation of [(Me_2bipy)PdMe($ClCD_2Cl$)][$MeB(C_6F_5)_3$] (2). An NMR tube was charged with (Me_2bipy)$PdMe_2$ (0.021 g, 0.065 mmol) and $B(C_6F_5)_3$ (0.033 g, 0.065 mmol), and CD_2Cl_2 (0.5 mL) was added by vacuum transfer at −196 °C. The tube was warmed to −78 °C and transferred to a precooled NMR probe, and NMR spectra were recorded. Complete conversion to **2** was observed. ^{1}H NMR (CD_2Cl_2, −88 °C): δ 8.23 (m, 2H, H6 & H6′), 7.94 (s, 1H, H3 or H3′), 7.89 (s, 1H, H3 or H3′), 7.40 (m, 2H, H5 & H5′), 2.49 (s, 3H, *Me*$_2$bipy), 2.45 (s, 3H, *Me*$_2$bipy), 0.98 (s, 3H, PdMe), 0.31 (br s, 3H, MeB). ^{13}C NMR (CD_2Cl_2, −88 °C): δ 155.4 (d, $^3J_{CH}$ = 9, C2 or C2′), 153.2 (m, C4 or C4′), 152.3 (m, C4 or C4′), 151.0 (d, $^3J_{CH}$ = 10, C2 or C2′), 147.3 (d, J = 185, C6′), 146.5 (d, J = 182, C6), 127.6 (d, J = 166, C5′), 127.2 (d, J = 166, C5), 123.7 (d, J = 163, C3′), 122.6 (d, J = 163, C3), 21.1 (q, J = 129, *Me*$_2$bipy), 21.0 (q, J = 129, *Me*$_2$bipy), 8.9 (br q, J ca. 126, MeB), 5.2 (q, J = 135, PdMe).

Generation of [(Me_2bipy)PdMe(CH_2=CHCl)][$MeB(C_6F_5)_3$] (3). An NMR tube was charged with (Me_2bipy)$PdMe_2$ (0.011 g, 0.034 mmol) and $B(C_6F_5)_3$ (0.018 g, 0.034 mmol), and CD_2Cl_2 (0.5 mL) and VC (0.9 equiv) were added by vacuum transfer at −196 °C. The tube was warmed to −78 °C and transferred to a precooled NMR probe, and NMR spectra were recorded. ^{1}H NMR (CD_2Cl_2, −73 °C): δ 8.41 (d, J = 5.5, 1H, H6′), 8.33 (d, J = 5.8, 1H, H6), 8.02 (s, 1H, H3′), 7.96 (s, 1H, H3), 7.50 (d, J = 5.5, 1H, H5), 7.43 (d, J = 5.4, 1H, H5′), 6.59 (dd, J = 12.5, 5.4, 1H, =CHCl), 5.01 (dd, J = 12.5, 1.8, 1H, $=CH_2$), 4.88 (dd, J = 5.2, 2.2, 1H, $=CH_2$), 2.54 (s, 3H, *Me*$_2$bipy), 2.48 (s, 3H, *Me*$_2$bipy), 0.89 (s, 3H, PdMe). ^{13}C NMR (CD_2Cl_2, −88 °C): δ 155.0 (d, $^2J_{CH}$ = 9, C2 or C2′), 154.5 (t, $^2J_{CH}$ = 6, C4 or C4′), 152.8 (t, $^2J_{CH}$ = 6, C4 or C4′), 152.1 (d, $^2J_{CH}$ = 10, C2 or C2′), 147.4 (d, $^1J_{CH}$ = 182, C6′), 146.3 (d, $^1J_{CH}$ = 183, C6), 127.5 (d, $^1J_{CH}$ = 162, C5′), 127.4 (d, $^1J_{CH}$ = 168, C5), 123.6 (d, $^1J_{CH}$ = 158, C3′), 123.2 (d, $^1J_{CH}$ = 163, C3), 102.7 (d, $^1J_{CH}$ = 202, =CHCl), 78.7 (t, $^1J_{CH}$ = 168, $=CH_2$), 21.3 (q, $^1J_{CH}$ = 129, *Me*$_2$bipy), 21.1 (q, $^1J_{CH}$ = 129, *Me*$_2$bipy), 14.7 (q, $^1J_{CH}$ = 137, PdMe).

Generation of [(Me_2bipy)PdMe(CH_2=CHMe)][$MeB(C_6F_5)_3$] (4). The procedure for **3** was followed with the substitution of propylene for VC. Isomer ratio at −73 °C: 1.5/1. ^{1}H NMR (CD_2Cl_2, −73 °C, major isomer): δ 8.32 (d, J = 6, 1H, H6), 8.00 (s, 1H, H3 or H3′), 7.96 (s, 1H, H3 or H3′), 7.80 (d, J = 5, 1H, H6′), 7.49 (d, J = 5, 1H, H5 or H5′), 7.44 (d, J = 5, 1H, H5 or H5′), 5.95 (m, 1H, =C*H*Me), 4.87 (d, J = 8.4, 1H, $=CH_2$), 4.54 (d, J = 15.5, 1H, $=CH_2$), 2.54 (s, 3H, *Me*$_2$bipy), 2.49 (s, 3H, *Me*$_2$bipy), 1.92 (d, J = 6.5, 3H, =CH*Me*), 0.79 (s, 3H, PdMe). ^{1}H NMR (CD_2Cl_2, −73 °C, minor isomer): δ 8.32 (d, J = 5.6, 1H, H6), 8.30 (d, J = 6, 1H, H6′), 8.00 (s, 1H, H3 or H3′), 7.96 (s, 1H, H3 or H3′), 7.49 (d, J = 5, 1H, H5 or H5′), 7.44 (d, J = 5, 1H, H5 or H5′), 5.79 (m, 1H, =C*H*Me), 4.56 (d, J = 14.4, 1H, $=CH_2$), 4.47 (d, J = 8.0, 1H, $=CH_2$), 2.54 (s, 3H, *Me*$_2$bipy), 2.49 (s, 3H, *Me*$_2$bipy), 1.94 (d, J = 7.6, 3H, =CH*Me*), 0.78 (s, 3H, PdMe). ^{1}H NMR (CD_2Cl_2, −23 °C, fast isomer exchange): δ 8.37 (d, J = 6, 1H, H6), 8.05 (br s, 2H, H6′), 8.03 (s, 1H, H3 or H3′), 7.96 (s, 1H, H3 or H3′), 7.51 (d, J = 5.5, 1H, H5 or H5′), 7.46 (d, J = 5.3, 1H, H5 or H5′), 5.93 (m, 1H, =C*H*Me), 4.74 (br s, 1H, $=CH_2$), 4.58 (d, J = 15.4, 1H, $=CH_2$), 2.58 (s, 3H, *Me*$_2$bipy), 2.53 (s, 3H, *Me*$_2$bipy), 1.97 (d, J = 6.3, 3H, =CH*Me*), 0.86 (s, 3H, PdMe). ^{13}C{^{1}H} NMR (CD_2Cl_2, −88 °C; both isomers; selected J_{CH} values taken from gated-{^{1}H} spectrum): δ 154.8 (C2 or C2′), 154.7 (C2 or C2′), 153.8 (C4 or C4′), 153.7 (C4 or C4′), 152.6 (C4 or C4′), 152.4 (C4 or C4′), 152.4 (C2 or C2′), 152.2 (C2 or C2′), 146.9 (C6 or C6′), 146.1 (C6 or C6′), 145.9 (C6 or C6′), 144.5 (C6 or C6′), 127.8 (C5 or C5′), 127.4 (C5 or C5′), 127.2 (C5 or C5′), 127.1 (C5 or C5′), 123.4, (C3 or C3′), 123.3 (C3 or C3′), 123.2 (C3 or C3′), 123.1 (C3 or C3′), 110.5 (d, J_{CH} = 155, =C*H*Me), 109.8 (d, J_{CH} = 160, =C*H*Me), 79.8 (t, J_{CH} = 160, $=CH_2$), 79.6 (t, J_{CH} = 161, $=CH_2$), 21.3 (two peaks overlapped, *Me*$_2$bipy), 21.2 (*Me*$_2$bipy), 21.1 (*Me*$_2$bipy), 20.7 (=CH*Me*), 20.6 (=CH*Me*), 13.3 (q, J_{CH} = 135, PdMe), 12.2 (q, J = 136, PdMe), 9.3 (MeB).

Generation of [(Me_2bipy)PdMe(CH_2=CH_2)][$MeB(C_6F_5)_3$] (5). The procedure for **3** was followed with the substitution of ethylene for VC. ^{1}H NMR (CD_2Cl_2, −83 °C): δ 8.31 (d, J = 6, 1H, H6), 8.00 (s, 1H, H3 or H3′), 7.94 (s, 1H, H3 or H3′), 7.80 (d, J = 6, 1H, H6′), 7.49 (d, J = 5.4, 1H, H5 or H5′), 7.43 (d, J = 5.4, 1H, H5 or H5′), 4.9 (m, 4H, CH_2=CH_2; broad AA′XX′), 2.54 (s, 3H, *Me*$_2$bipy), 2.47 (s, 3H, *Me*$_2$bipy), 0.70 (s, 3H, PdMe), 0.32 (br s, MeB). ^{13}C NMR (CD_2Cl_2, −83 °C): 154.9 (d, $^2J_{CH}$ = 9, C2 or C2′), 154.3 (t, $^2J_{CH}$ = 6, C4 or C4′), 152.9 (t, $^2J_{CH}$ = 6, C4 or C4′), 152.2 (d, $^2J_{CH}$ = 10, C2 or C2′), 146.3 (dd, J = 180, 4; C6 or C6′), 145.2 (dd, J = 180, 4; C6 or C6′), 128.1 (d, J = 168, C5 or C5′), 127.5 (d, J = 168, C5 or C5′), 123.6 (d, J = 164, C3 or C3′), 123.2 (d, J = 163, C3 or C3′), 87.5 (br, CH_2=CH_2), 21.5 (qt, J = 124, 5; *Me*$_2$bipy), 21.4 (qt, J = 124, 4; *Me*$_2$bipy), 11.5 (q, J = 136, PdMe).

Analysis of Organometallic Products from the Reaction of (Me_2bipy)PdMe($ClCD_2Cl$)$^+$ (2) and VC. An NMR tube containing (Me_2bipy)$PdMe_2$ (10.0 mg, 0.0312 mmol), $B(C_6F_5)_3$ (16.0 mg, 0.0312 mmol), C_6Me_6 (internal standard), and VC (115 equiv) in CD_2Cl_2 (0.5 mL) was warmed from −78 °C to room temperature over ∼1 min and then maintained at room temperature for 3 days. The volatiles were removed under vacuum, and the remaining solid was dissolved in pyridine-d_5 at 50 °C. C_6F_5H was added as a ^{19}F internal standard to quantify the $B(C_6F_5)_3$ in the final solution. Yields versus **1**: (Me_2bipy)$PdCl_2$, 70%; $B(C_6F_5)_3$, 66%. ^{1}H NMR (pyridine-d_5, 50 °C): δ 8.63 (d, J = 5 Hz, 2H), 8.52 (s, 2H), 7.06 (d, J = 5 Hz, 2H), 2.27 (s, Me, 6H). ^{19}F NMR (CD_2Cl_2): δ −130.4, −156.1, −162.6. These ^{1}H and ^{19}F NMR data are identical to data for authentic (Me_2bipy)$PdCl_2$ and $B(C_6F_5)_3$ in pyridine-d_5 at 50 °C.

(Me_2bipy)$PdCl_2$. A flask was charged with (cod)$PdCl_2$ (1.1 g, 3.9 mmol), Me_2bipy (0.71 g, 3.9 mmol), and CH_2Cl_2 (50 mL). The mixture was stirred for 1 h at 25 °C, and a pale yellow precipitate formed. The solid was collected by filtration and dried under vacuum to afford **4** as a yellow solid (1.3 g, 94%). ^{1}H NMR (CD_2Cl_2): δ 9.08 (d, J = 6, 2H, H6), 7.85 (s, 2H, H3), 7.35 (d, J = 6, 2H, H5), 2.56 (s, 6H, *Me*$_2$bipy). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 153.4, 150.3, 127.7, 123.6, 21.9; one quaternary C was not detected.

Generation of [(Me_2bipy)$_2$Pd][$B(C_6F_5)_4$]$_2$. An NMR tube was charged with (Me_2bipy)$PdCl_2$ (8.5 mg, 0.024 mmol), Me_2bipy (4.3 mg, 0.024 mmol), AgOTf (12.1 mg, 0.047 mmol), and CD_2Cl_2 (0.5 mL) and maintained at room temperature for 1 h. Solid [$Li(Et_2O)_{2.8}$]-[$B(C_6F_5)_4$] (40.6 mg, 0.047 mmol) was added, and the tube was maintained at room temperature for 1 day. The mixture was filtered to yield a clear yellow solution of [(Me_2bipy)$_2$Pd][$B(C_6F_5)_4$]$_2$. ^{1}H NMR (CD_2Cl_2): δ 8.26 (d, J = 6, 2H), 8.06 (s, 2H), 7.67 (m, 2H), 2.63 (s, 6H, Me). ^{19}F NMR (CD_2Cl_2): δ −133.3, −163.5, −167.4. ESI-MS: [(Me_2bipy)$_2$Pd]$^{2+}$ calcd. m/z 237.1, found 237.1. $B(C_6F_5)_4^-$ calcd. m/z 679.0, found 679.0.

[{(Me_2bipy)Pd(μ-Cl)}$_2$][$B(C_6F_5)_4$]$_2$. A flask was charged with (Me_2-bipy)$PdCl_2$ (0.120 g, 0.332 mmol), $AgPF_6$ (0.084 g, 0.33 mmol), and CH_2Cl_2 (10 mL). Immediate precipitation of [{(Me_2bipy)Pd(μ-Cl)}$_2$]-[PF_6]$_2$ and AgCl occurred. The mixture was stirred for 1 h, [$Li(Et_2O)_{2.8}$]-[$B(C_6F_5)_4$] (0.287 mg, 0.332 mmol) was added, and the mixture was

stirred for an additional hour. The mixture was filtered, yielding a white precipitate and a deep yellow filtrate. The filtrate was concentrated to 3 mL and cooled to −30 °C for 2 days, yielding a yellow microcrystalline solid which was collected by filtration (0.236 g, 73%). ^{1}H NMR (CD_2Cl_2): δ 8.12 (d, J = 6, 2H), 7.86 (s, 2H), 7.46 (d, J = 6, 2H), 2.63 (s, Me, 6H). ^{13}C NMR (CD_2Cl_2): δ 157.4, 156.2, 149.5, 129.3, 125.2, 22.0. ESI-MS [{(Me_2bipy)Pd(μ-Cl)}$_2$]$^{2+}$ calcd. m/z 326.0, found 325.8. $B(C_6F_5)_4^-$ calcd. m/z 679.0, found 678.7.

Ethylene Insertion of [(Me_2bipy)PdMe(CH_2═CH_2)][MeB(C_6F_5)$_3$] (5). An NMR tube was charged with (Me_2bipy)$PdMe_2$ (10.0 mg, 0.031 mmol) and $B(C_6F_5)_3$ (16.0 mg, 0.031 mmol), and CD_2Cl_2 (0.6 mL) and excess ethylene (ca. 30 equiv) were added by vacuum transfer at −196 °C. The tube was warmed to −78 °C and placed in an NMR probe precooled to −75 °C. The reaction was monitored from −75 to 20 °C. At −75 °C, [(Me_2bipy)PdMe(CH_2═CH_2)][MeB(C_6F_5)$_3$] (**5**) in fast exchange with free ethylene was the only significant species in solution. Ethylene insertion was observed at ca. −23 °C, resulting in the disappearance of **5**, the formation of propylene, and the formation of a new species presumed to be [(Me_2bipy)Pd(CH_2CH_3)(CH_2═CH_2)][MeB(C_6F_5)$_3$]. This species could not be definitively characterized at this temperature due to the presence of propylene, excess ethylene, and remaining **5**. Warming to 10 °C resulted in complete conversion of the ethylene to *cis*- and *trans*-2-butenes exclusively. Further warming to 20 °C resulted in conversion of the internal butenes to higher olefins.

Reaction of (α-Diimine)$PdMe_2$/B(C_6F_5)$_3$ and VC. An NMR tube was charged with (α-diimine)$PdMe_2$ (7.9 mg, 0.015 mmol) and $B(C_6F_5)_3$ (7.5 mg, 0.015 mmol), and CD_2Cl_2 (0.6 mL) and excess VC (20 equiv) were added by vacuum transfer at −196 °C. The tube was warmed to −78 °C, resulting in a red solution. The tube was placed in an NMR probe precooled to −80 °C, and the reaction was monitored from −80 to 20 °C. At −80 °C, the VC adduct, [(α-diimine)PdMe(CH_2═$CHCl$)][MeB(C_6F_5)$_3$], was observed (60%). ^{1}H NMR of [(α-diimine)PdMe(CH_2═$CHCl$)][MeB(C_6F_5)$_3$] (CD_2Cl_2, −80 °C): δ 7.34 (m, 4H, *meta*-H), 7.06 (m, 2H, *para*-H), 5.62 (br, 1H, VC H_{int}), 4.65 (br d, J = 12, 1H, VC H_{trans}), 4.58 (br d, J = 6, 1H, VC H_{cis}), 2.77 (m, 2H, C*H*Me_2), 2.65 (m, 2H, C*H*Me_2), 2.38 (s, 3H, N═C*Me*), 2.27 (s, 3H, N═C*Me*), 1.40 (d, J = 7, 3H, ^{i}Pr Me), 1.28 (d, J = 7, 3H, ^{i}Pr Me), 1.25 (m, 6H, ^{i}Pr Me), 1.14 (m, 12H, ^{i}Pr Me), 0.55 (s, 3H, Pd*Me*), 0.35 (*Me*B(C_6F_5)$_3$). ^{19}F NMR (CD_2Cl_2): δ −133.8, −164.3, −167.0. At −65 °C, this species was converted to [(α-diimine)PdCl(CH_2═$CHMe$)][MeB(C_6F_5)$_3$]. The conversion was 28% complete after 30 min at −65 °C and was 100% complete after the tube was warmed to −40 °C over 30 min. ^{1}H NMR of [(α-diimine)PdCl(CH_2═$CHMe$)][MeB(C_6F_5)$_3$] (CD_2Cl_2, −30 °C): δ 7.35 (m, 4H, *meta*-H), 7.10 (m, 2H, *para*-H), 5.40 (m, 1H, H_2C═C*H*Me), 5.30 (d, J = 16, 1H, propene H_{trans}), 4.32 (d, J = 8, 1H, propene H_{cis}), 3.00 (sept, J = 7, 2H, C*H*Me_2), 2.78 (sept, J = 7, 2H, C*H*Me_2), 2.35 (s, 3H, N═C*Me*), 2.31 (s, 3H, N═C*Me*), 1.90 (d, J = 6, H_2C═CH*Me*), 1.47 (d, J = 7, 3H, ^{i}Pr Me), 1.45 (d, J = 7, 3H, ^{i}Pr Me), 1.35 (d, J = 7, 6H, ^{i}Pr Me), 1.20 (d, J = 7, 6H, ^{i}Pr Me), 1.16 (d, J = 7, 6H, ^{i}Pr Me), 0.40 (*Me*B(C_6F_5)$_3$). ^{19}F NMR (CD_2Cl_2): δ −133.6, −164.8, −167.5. The tube was warmed to 0 °C for 15 min, and 20% conversion of [(α-diimine)PdCl(CH_2═$CHMe$)][MeB(C_6F_5)$_3$] to [{(α-diimine)Pd(μ-Cl)}$_2$][MeB(C_6F_5)$_3$]$_2$ and free propylene was observed. This species was generated independently as described below. After 24 h at 20 °C, [{(α-diimine)Pd(μ-Cl)}$_2$][MeB(C_6F_5)$_3$]$_2$ (0.35 equiv, 70%), (α-diimine)PCl_2 (0.15 equiv, 15%), and free propene (0.8 equiv) were present.

The reaction was repeated with 0.9 equiv of VC to facilitate characterization of the intermediate VC and propene adducts at low temperature with similar results. After 12 h at 20 °C, [{(α-diimine)-Pd(μ-Cl)}$_2$][MeB(C_6F_5)$_3$]$_2$ was the major species present (87%). VC was completely consumed, and the propylene had been converted to polypropylene by the remaining [(α-diimine)PdMe]$^+$.

(α-Diimine)$PdCl_2$.[49] A mixture of $PdCl_2$ (342 mg, 1.93 mmol) and CH_3CN (100 mL) was refluxed for 2 h to yield an orange solution. The solution was cooled to 25 °C, and (2,6-^{i}Pr_2-C_6H_3)N═CMeCMe═N(2,6-^{i}Pr_2-C_6H_3) (0.780 g, 1.93 mmol) was added. The mixture was refluxed for 12 h to yield a clear orange-yellow solution. The volatiles were removed under vacuum to yield an orange solid (1.12 g, 98%). ^{1}H NMR (CD_2Cl_2): δ 7.40−7.25 (m, 6H), 3.07 (sept, J = 7, 4H), 2.10 (s, 6H), 1.45 (d, J = 7, 12H), 1.20 (d, J = 7, 12H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 178.8, 141.1, 139.7, 129.1, 124.1, 29.7, 23.8, 23.7, 21.3. Anal. Calcd for $C_{28}H_{40}Cl_2N_2Pd$: C, 57.79; H, 6.93; N, 4.81. Found: C, 57.80; H, 7.18; N, 4.73.

Generation of [{(α-Diimine)Pd(μ-Cl)}$_2$][B(C_6F_5)$_4$]$_2$. An NMR tube was charged with (α-diimine)$PdCl_2$ (15.0 mg, 0.026 mmol), $AgPF_6$ (6.5 mg, 0.026 mmol), and CD_2Cl_2 (0.6 mL). The tube was maintained at room temperature for 15 min, yielding an orange slurry. Solid [$Li(Et_2O)_{2.8}$][B(C_6F_5)$_4$] (22.3 mg, 0.026 mmol) was added, and the tube was agitated for 15 min. The mixture was filtered to remove the white precipitate, resulting in a clear orange solution of [{(α-diimine)Pd(μ-Cl)}$_2$][B(C_6F_5)$_4$]$_2$. ^{1}H NMR (CD_2Cl_2): δ 7.40 (t, J = 7.8, 4H, H_{para}), 7.17 (d, J = 7.8, 8H, H_{meta}), 2.74 (sept, J = 6.8, 8H, C*H*Me_2), 2.24 (s, 12H, N═C(Me)), 1.28 (d, J = 6.8, 24H, CH*Me*), 1.16 (d, J = 6.8, 24H, CH*Me*). ESI-MS: [{(α-diimine)Pd(μ-Cl)}$_2$]$^{2+}$ calcd. m/z 546.2, found 546.3.

Reaction of VC with (Pyridine-bisimine)$FeCl_2$/MAO. An NMR tube was charged with (pyridine-bisimine)$FeCl_2$ (0.0011 g, 0.0018 mmol), dried MAO (0.105 g, 1.8 mmol), and toluene (internal standard), and C_6D_6 (0.5 mL) and VC (20.3 mL at 419 mm and 25 °C, 0.46 mmol) were added by vacuum transfer at −196 °C. The tube was warmed to room temperature, and a ^{1}H NMR spectrum was recorded within 5 min, which revealed the presence of propylene. The tube was maintained at 25 °C for 96 h. A comparison of the integrals before and after the 96 h revealed that 16% of the VC was consumed and converted into propylene (42 turnovers/Fe).

Reaction of VC with (Pyridine-bisimine)$CoCl_2$/MAO. An NMR tube was charged with (pyridine-bisimine)$CoCl_2$ (0.0011 g, 0.0018 mmol), dried MAO (0.11 g, 1.9 mmol), and toluene (internal standard), and C_6D_6 (0.5 mL) and VC (0.46 mmol) were added by vacuum transfer at −196 °C. The tube was warmed to 25 °C, and a ^{1}H NMR spectrum was recorded within 5 min, which revealed the presence of propylene. The tube was maintained at 25 °C for 96 h. A comparison of the integrals before and after the 96 h revealed that 85% of the VC was consumed and converted into propylene (220 turnovers/Co).

Reaction of (sal)Ni(Ph)(PPh_3) (7) and VC. An NMR tube was charged with (sal)Ni(Ph)(PPh_3) (**7**, 11.1 mg, 0.0147 mmol) and toluene (0.118 mmol; internal standard), and C_6D_6 (0.6 mL) was condensed into the tube at −196 °C under vacuum. VC (0.118 mmol) was condensed into the tube at −196 °C under vacuum. The tube was sealed, allowed to warm to room temperature, and NMR spectra were recorded periodically. No reaction between **7** and VC was observed at 25 °C. The tube was heated to 50 °C in an oil bath. The orange solution turned deep red over several hours. Over the course of 4 days, the NMR resonances for VC and **7** decreased in intensity. Resonances corresponding to styrene emerged, but no PVC resonances were observed. By integrating against toluene as the internal standard, it was determined that 1 equiv of VC (vs **7**) was consumed and 1 equiv of styrene was produced after 4 days at 50 °C. During the course of 4 days, as the resonances for **7** disappeared, resonances for (sal)Ni(Cl)(PPh_3) (**8**) and then (sal)$_2$Ni (**9**) appeared. The sum of the integrals of the ^{i}Pr methyl resonances for **7**, **8**, and **9** was constant during the reaction. The tube was maintained at 50 °C for an additional 4 days. The resonances for **7** slowly decreased in intensity, while those for **8** increased in intensity, and a green powder precipitated. The powder was analyzed by X-ray fluorescence, which confirmed the presence of Cl, P, and Ni. The powder was identified as $(Ph_3P)_2NiCl_2$ by powder X-ray diffraction by comparison of the pattern with that of an authentic sample. ^{1}H NMR

(49) (a) Ishii, H.; Goyal, M.; Ueda, M.; Takeuchi, K.; Asai, M. *Catal. Lett.* **2000**, *65*, 57. (b) Schmid, M.; Eberhardt, R.; Klinga, M.; Leskelä, M.; Rieger, B. *Organometallics* **2001**, *20*, 2321.

of VC (C_6D_6): δ 5.75 (dd, J = 7.0, 14.5, 1H, H_{int}), 5.13 (d, J = 14.5, 1H, H_{trans}), 4.80 (d, J = 7.0, 1H, H_{cis}). ^{1}H NMR of styrene (C_6D_6): δ 6.56 (dd, J = 10.8, 17.6, 1H, H_{int}), 5.58 (d, J = 17.6, 1H, H_{trans}), 5.10 (d, J = 10.8, 1H, H_{cis}). Spectral data for **7**−**9** are given below.

Isolation of Organometallic Products from the Reaction of (sal)Ni(Ph)PPh$_3$ (7) and VC. A flask was charged with a solution of (sal)Ni(Ph)PPh$_3$ (**7**, 0.273 g, 0.362 mmol) in benzene (20 mL), and VC (200 mL at 760 mm and 25 °C, 8.2 mmol) was condensed in at −78 °C under vacuum. The solution was stirred for 4 days at 50 °C, cooled to room temperature, and the volatiles were removed under vacuum. The resulting dark brown powder was taken up in hexanes (20 mL), and the mixture was filtered to remove the $(Ph_3P)_2NiCl_2$ precipitate. The filtrate was left to stand at 25 °C for 24 h, and red-brown crystals of (sal)Ni(Cl)(PPh$_3$) (**8**) precipitated and were separated by filtration (44 mg, 17% vs **7**). The filtrate was heated to 50 °C for an additional 4 days and filtered to remove the $(Ph_3P)_2NiCl_2$ precipitate (total yield of $(Ph_3P)_2NiCl_2$ = 34 mg, 0.052 mmol, 14% vs **7**). The filtrate was condensed to 4 mL under vacuum and cooled to −36 °C. Dark red crystals of (sal)$_2$Ni (**9**) were obtained after 4 days (66 mg, 24% vs **7**). Total isolated yield of **8**, **9**, and $(Ph_3P)_2NiCl_2$ = 55% versus **7**. Compounds **8** and **9** were characterized by X-ray diffraction and ^{1}H NMR. ^{1}H NMR of **7** (C_6D_6): δ 8.01 (d, 1H), 6.20−7.75 (m, 31H), 4.12 (sept, J = 6.8, C*H*Me$_2$, 2H), 1.21 (d, J = 6.8, CH*Me*$_2$, 6H), 1.13 (d, J = 6.8, CH*Me*$_2$, 6H). ^{1}H NMR of **8** (C_6D_6): δ 3.32 (br, CH*Me*$_2$, 6H), 2.19 (br, CH*Me*$_2$, 6H). ^{1}H NMR of **9** (C_6D_6): δ 7.18 (br, 14H), 6.83 (br, 6H), 6.43 (br, 2H), 5.88 (br, 2H), 4.56 (br, C*H*Me$_2$, 4H), 1.37 (br, CH*Me*$_2$, 12H), 1.15 (br, CH*Me*$_2$, 12H).

Generation of (sal)$_2$Ni (9). An NMR tube was charged with Na[sal] (11.7 mg, 0.0308 mmol) and $(Ph_3P)_2NiCl_2$ (10.0 mg, 0.0152 mmol), and C_6D_6 (0.6 mL) was condensed into the tube at −196 °C under vacuum. The tube was sealed and allowed to warm to room temperature. After 30 min, the ^{1}H NMR showed that **9** and free PPh$_3$ had formed.

Reaction of (sal)Ni(Ph)(PPh$_3$) (7) with VC and Ethylene. A 150 mL Fisher-Porter bottle was charged with (sal)Ni(Ph)(PPh$_3$) (**7**, 0.010 g, 0.013 mmol) and toluene (20 mL) under nitrogen. The solution was degassed, VC (250 equiv) was added, and the bottle was pressurized with ethylene (100 psi). The ethylene pressure was maintained, and the solution was stirred for 3 h at 20 °C. No physical change in the solution was observed. The bottle was vented, and the contents were poured into acidified MeOH (100 mL of a 1 M HCl solution), resulting in a clear, colorless solution. GC-MS revealed that styrene was present, but no α-olefins were detected. No polymer was formed.

Reaction of (sal)Ni(Ph)(PPh$_3$) (7) and Ethylene. A 150 mL Fisher-Porter bottle was charged with (sal)Ni(Ph)(PPh$_3$) (**7**, 0.010 g, 0.013 mmol) and toluene (20 mL) under nitrogen. The solution was degassed, and the bottle was pressurized with ethylene (100 psi). Ethylene pressure was maintained, and the solution was stirred for 3 h at 20 °C, resulting in the formation of a white precipitate. The bottle was vented, and the reaction mixture was poured into acidified MeOH (100 mL of a 1 M HCl solution). The solid precipitate was separated by filtration, washed with MeOH, and dried under vacuum, yielding 0.85 g of white polyethylene, which was identified by ^{1}H and ^{13}C NMR.

Reaction of {Ph$_2$PC(SO$_3$Na)═C(*p*-tol)O}Ni(Ph)PPh$_3$/Rh(CH$_2$CH$_2$)$_2$(acac) and VC. An NMR tube was charged with {Ph$_2$PC(SO$_3$Na)═C(*p*-tol)O}Ni(Ph)PPh$_3$ (0.019 g, 0.023 mmol), Rh(CH$_2$CH$_2$)$_2$(acac) (3.0 mg, 0.012 mmol), and toluene (0.023 mmol; internal standard). Acetone-d_6 (0.5 mL) and then VC (0.92 mmol) were condensed in at −196 °C. The tube was warmed to 23 °C, and the solution became pale orange. The tube was heated to 70 °C for 2.5 h to yield a slurry of a green precipitate in a red supernatant. A ^{1}H NMR spectrum showed that 0.18 mmol of styrene (0.8 equiv) was present. GC-MS confirmed the presence of styrene. No PVC was observed.

Table 3. Crystallographic Data for (sal)Ni(Cl)(PPh$_3$) (**8**) and (sal)$_2$Ni (**9**)

	8	**9** (hexane)
formula	$C_{43}H_{41}ClNNiOP$	$C_{106.7}H_{104}Ni_2N_4O_4$
cryst size (mm)	0.2 × 0.2 × 0.08	0.17 × 0.15 × 0.12
color/shape	red-brown/fragment	red/fragment
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	10.322(2)	14.477(4)
b (Å)	11.327(2)	14.703(4)
c (Å)	16.646(3)	42.60(1)
α (deg)	81.853(3)	
β (deg)	80.372(3)	99.574(5)
γ (deg)	69.761(3)	
V (Å^3)	1792.9(5)	8941(4)
Z	2	4
μ (mm^{-1})	0.695	0.473
diffractometer	Bruker SMART APEX	Bruker SMART APEX
radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
temp (K)	100	100
θ range (deg)	2.12−25.02	1.69−25.03
data collected: h; k; l	±12; −137; ±19	−15,17; ±17; ±50
no. of reflns	9288	44 655
no. of unique reflns	4717 (R_{int} = 0.0212)	15 762 (R_{int} = 0.0498)
structure solution	Patterson	direct methods
refinement	FMLS on F^2	FMLS on F^2
abs corr	SADABS	SADABS
transmn range (%)	89−100	90−100
data/restraints/params	5924/0/437	15 762/0/1062
goodness-of-fit on F^2	0.979	1.233
R indices ($I > 2\sigma(I)$)[a,b]	R1 = 0.0393, wR2 = 0.0812	R1 = 0.0714, wR2 = 0.1325
R indices (all data)[a,b]	R1 = 0.0479, wR2 = 0.0849	R1 = 0.0877, wR2 = 0.1389

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

X-ray Crystallography. X-ray data for **8** and **9** are summarized in Table 3, and full details of the crystallographic analyses are given in the Supporting Information. A disordered hexane molecule is present in the lattice of **9**; the disordered solvent atoms were modeled as carbon atoms. Thermal ellipsoids are drawn at the 50% probability level.

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Supporting Information Available: Tables of X-ray crystallographic data, atomic coordinates, bond lengths and bond angles, and anisotropic thermal parameters for (sal)Ni(Cl)PPh$_3$ (**8**) and (sal)$_2$Ni (**9**) (TXT). This material is available free of charge via the Internet at http://pubs.acs.org.

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