Generation and Insertion Reactivity of Cationic Palladium Complexes That Contain Halogenated Alkyl Ligands

Stephen R. Foley, Han Shen, Umair A. Qadeer, and Richard F. Jordan*

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

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The generation of cationic palladium complexes that contain halogenated alkyl ligands (R^X) and their reactivity with vinyl chloride, ethylene, and CO are described. {(^{n}Hex)HC(mim)$_2$}Pd(CHCl$_2$)Cl (**1**; ^{n}Hex = *n*-hexyl, mim = *N*-methylimidazol-2-yl) reacts with 0.5 equiv of [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] to form [{{(^{n}Hex)HC(mim)$_2$}Pd(CHCl$_2$)}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] as a 1:1 mixture of diastereomers (**3a**,**b**). **3a,b** do not react with vinyl chloride. The reaction of **1** with 1 equiv of [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] in the presence of ethylene or CO yields [{(^{n}Hex)HC(mim)$_2$}Pd(CHCl$_2$)(L)][B(C$_6$F$_5$)$_4$] adducts (L = ethylene (**4**), CO (**5**)). The reaction of (dppp)Pd(^{n}C$_3$F$_7$)Me (**7**; dppp = 1,3-bis(diphenylphosphino)propane) with [HNMePh$_2$][B(C$_6$F$_5$)$_4$] yields [(dppp)Pd(^{n}C$_3$F$_7$)(NMePh$_2$)][B(C$_6$F$_5$)$_4$] (**8**). **8** does not react with vinyl chloride or ethylene but does react with CO to form [(dppp)Pd(^{n}C$_3$F$_7$)(CO)][B(C$_6$F$_5$)$_4$] (**9**). **4**, **5**, and **9** do not undergo insertion under mild conditions. The reaction of (^{t}Bu$_2$bipy)Pd(CH$_2$Cl)Cl (**10**; ^{t}Bu$_2$bipy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) with 0.5 equiv of [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] yields [{(^{t}Bu$_2$bipy)Pd(CH$_2$Cl)}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] (**11**). In the presence of one equiv of [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$], **11** reacts with vinyl chloride by net 1,2-insertion and β-Cl elimination to generate Pd−Cl$^+$ species and allyl chloride and with CO at −78 °C to form [(^{t}Bu$_2$bipy)Pd(CH$_2$Cl)(CO)][B(C$_6$F$_5$)$_4$] (**12**). At 20 °C, **12** undergoes slow CO insertion followed by β-Cl elimination to generate Pd−Cl$^+$ species and ketene. The reaction of (α-diimine)Pd(CH$_2$Cl)Cl (**13**; α-diimine = (2,6-^{i}Pr$_2$-C$_6$H$_3$)N═CMeCMe═N(2,6-^{i}Pr$_2$-C$_6$H$_3$)) with 1 equiv of [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] in the presence of vinyl chloride yields Pd−Cl$^+$ species and allyl chloride, most likely via net 1,2-insertion and β-Cl elimination of a (α-diimine)Pd(CH$_2$Cl)(CH$_2$═CHCl)$^+$ intermediate. In general, L$_2$Pd(R^X)(substrate)$^+$ species undergo slower insertion than non-halogen-substituted L$_2$Pd(R)(substrate)$^+$ analogues.

Introduction

The development of metal-catalyzed insertion polymerization reactions of vinyl halides is a challenging goal.[1] Previously we showed that single-site olefin polymerization catalysts based on early or late transition metals undergo net 1,2-insertion of vinyl chloride (VC), but the resulting L$_n$MCH$_2$CHRCl species undergo β-Cl elimination to form L$_n$MCl products and CH$_2$═CHR olefins, which precludes insertion polymerization.[1a−c] Similar 1,2-insertion/β-X elimination reactions of CH$_2$═CHX substrates (X = F, Cl, Br) have been reported by other groups.[2] In an effort to circumvent β-Cl elimination, we investigated the reaction of VC with cationic metal acyl complexes.[3] VC reacts with L$_2$Pd{C(═O)Me}$^+$ species (L$_2$ = 4,4′-dimethyl-2,2′-bipyridine, 4,4′-di-*tert*-butyl-2,2′-bipyridine (^{t}Bu$_2$bipy), 1,3-bis(diphenylphosphino)propane (dppp), 1,2-bis(dimethylphosphino)ethane) by 2,1-insertion to yield robust O-chelated L$_2$Pd{CHClCH$_2$C(═O)Me}$^+$ complexes. The VC 2,1-insertion regiochemistry is favored in part because the alternative L$_2$Pd{CH$_2$CHClC(═O)Me}$^+$ 1,2-insertion products would be destabilized by placement of the electron-withdrawing Cl and acyl substituents on the same carbon. However, L$_2$Pd{CHClCH$_2$C(═O)Me}$^+$ species do not undergo chelate ring opening or insertion reactions with VC, ethylene, or CO.

The observation of VC 2,1-insertion of L$_2$Pd{C(═O)Me}$^+$ species suggests that it may be possible to direct a 2,1-insertion polymerization of VC by using a headgroup (R^X) that contains an electron-withdrawing halogen substituent, which should be a weaker chelator than an acyl group (Scheme 1). In this strategy, it is envisioned that the L$_2$Pd(R^X)$^+$ initiator would undergo an electronically driven VC 2,1-insertion to yield L$_2$Pd(CHClCH$_2$R^X)$^+$, which is trapped by VC coordination rather than by chelation. The electron-withdrawing α-Cl substituent of the resulting L$_2$Pd(CHClCH$_2$R^X)(VC)$^+$ species would direct 2,1-insertion, leading to chain growth.

Metal alkyls containing α-halogen substituents are

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Scheme 1

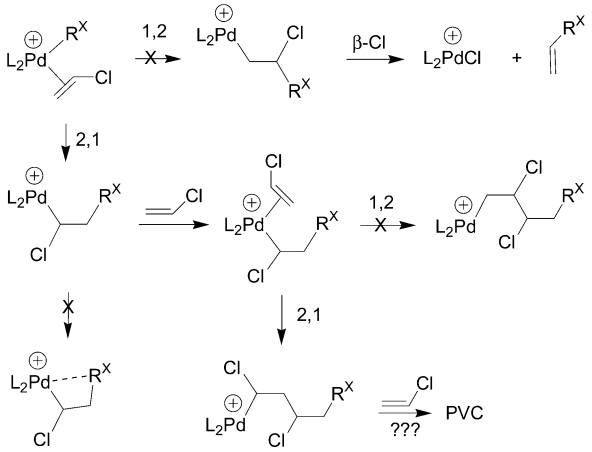
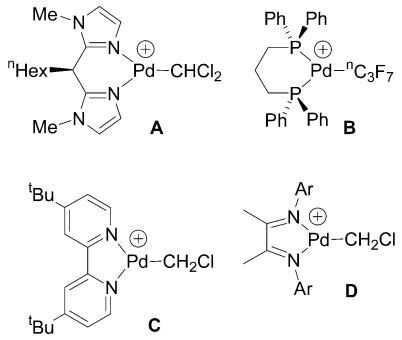


Chart 1[a]



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

quite common.[4−6] However, MCHClCH$_2$R species are susceptible to nucleophilic displacement of the α-chloride[7] and in some cases undergo α-Cl elimination to generate carbene complexes.[8] Additionally, the α-Cl substituent is expected to decrease the nucleophilic character and migratory aptitude of the MCHClCH$_2$R group, inhibiting subsequent insertions.[9] Nevertheless, reversible CO insertion of Co(CO)$_3$(L)CH$_2$Cl (L = CO, PPh$_3$) has been observed.[10]

To probe the feasibility of Scheme 1 and how halogen substituents on the alkyl ligand influence the reactivity of late-metal olefin polymerization catalysts, we have studied the generation and insertion chemistry of a set of cationic L$_n$Pd(R^X)$^+$ complexes that contain halogenated alkyl ligands (Chart 1). The complexes used for this study were chosen for synthetic accessibility and because the insertion reactivity of the corresponding L$_n$PdMe$^+$ cations has been studied previously. The (^{n}Hex)HC(mim)$_2$ (^{n}Hex = *n*-hexyl; mim = *N*-methylimidazol-2-yl) ligand (**A**) was chosen because {(^{n}Hex)HC(mim)$_2$}PdMe$^+$ is an ethylene dimerization catalyst and PdCHCl$_2$ species are easily accessible in this system.[11] The dppp ligand (**B**) was chosen because (dppp)PdMe$^+$ is among the most active catalysts known for CO/ethylene copolymerization.[12] The ^{t}Bu$_2$bipy and α-diimine (α-diimine = (2,6-^{i}Pr$_2$-C$_6$H$_3$)N=CMeCMe=N(2,6-^{i}Pr$_2$-C$_6$H$_3$)) ligands (**C**, **D**) were selected because (R$_2$bipy)PdMe$^+$ and (α-diimine)PdMe$^+$ are active for olefin dimerization and polymerization, respectively, and the reactivity of these species with VC has been studied in detail.[1,13]

Results

Activation of {(^{n}Hex)HC(mim)$_2$}Pd(CHCl$_2$)Cl. The dichloromethyl complex {(^{n}Hex)HC(mim)$_2$}Pd(CHCl$_2$)Cl (**1**) is prepared by exposure of {(^{n}Hex)HC(mim)$_2$}Pd(Me)Cl (**2**) to ambient room light in CH$_2$Cl$_2$.[11] The reaction of **1** with [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] at −40 °C yields the dinuclear complex [{{(^{n}Hex)HC(mim)$_2$}Pd(CHCl$_2$)}$_2$-(μ-Cl)][B(C$_6$F$_5$)$_4$] (**3a**,**b**) as a 1:1 mixture of diastereomers (Scheme 2). Complexes **3a**,**b** form by initial chloride abstraction from **1** to yield {(^{n}Hex)HC(mim)$_2$}Pd(CHCl$_2$)$^+$, which is trapped by **1**. The remaining 0.5 equiv of [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] does not react. Complexes **3a**,**b** decompose above 0 °C; the decomposition products were not identified.

The structures of **3a**,**b** were established by NMR, ESI-MS, stoichiometry, and derivatization experiments. The ^{1}H NMR spectra of **3a**,**b** contain two sets of resonances of equal intensity corresponding to the two diastereomers. The spectra show that, for each isomer, the two (^{n}Hex)HC(mim)$_2$ ligands are equivalent but the two mim

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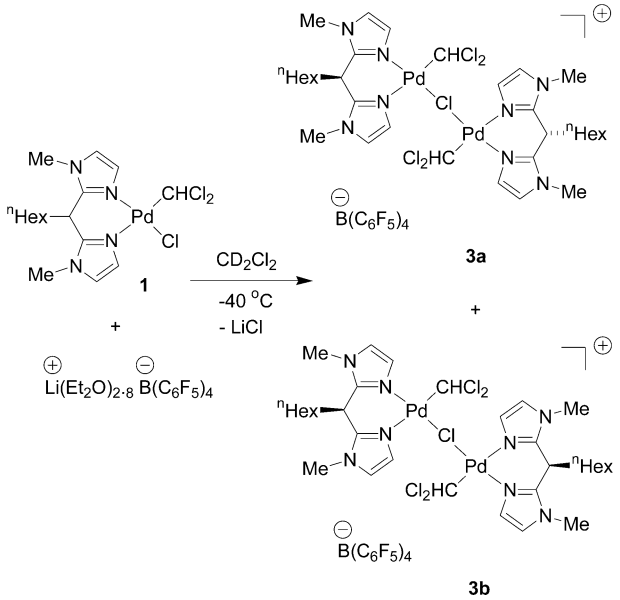
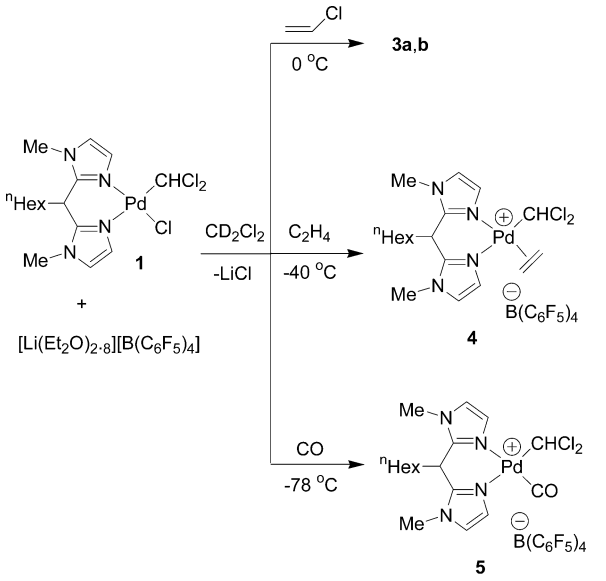
Scheme 2



Scheme 3



rings at a given Pd center are inequivalent, consistent with the C_i symmetry of **3a** and the C_2 symmetry of **3b**. The Pd−$CHCl_2$ units of **3a**,**b** are identified by ^{1}H (δ 6.34, 6.08) and ^{13}C (δ 61.6, 61.2) resonances which are similar to those of **1** (δ 6.34, δ 62.1). The positive ion ESI mass spectrum contains a parent ion pattern which matches the calculated isotope distribution. Additionally, the ^{1}H NMR spectra are the same for 2:1 and 1:1 mixtures of **1** and $[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$ in CD_2Cl_2, which confirms the stoichiometry in Scheme 2.

Reaction of 3a,b with CH_2=CHCl. The reaction of **1** and 1 equiv of $[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$ in the presence of VC in CD_2Cl_2 yields **3a**,**b** (Scheme 3). Above 0 °C, thermal decomposition of **3a**,**b** occurs in the same manner as in the absence of VC. These results show that VC does not displace **1** from **3**.

Reaction of 3a,b with CH_2=CH_2. As ethylene coordinates more strongly than VC to L_2PdR^+ species,[1b] the reaction of **3a**,**b** with ethylene was investigated. The reaction of **1** with $[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$ in the presence of excess ethylene at −40 °C quantitatively yields $\{(^nHex)HC(mim)_2\}Pd(CHCl_2)(CH_2{=}CH_2)^+$ (**4**; Scheme 3). The ^{1}H NMR spectrum of **4** contains two broad ethylene resonances (δ 5.34, 5.17 at 20 °C) that are shifted from the free ethylene position (δ 5.38). This result is consistent with the AA′BB′ pattern expected for a structure in which the C=C bond is perpendicular to the Pd square plane and olefin rotation is fast on the NMR time scale.[14] Complex **4** does not insert CH_2=CH_2 at 23 °C. For comparison, $\{(^nHex)HC(mim)_2\}Pd(Me)(C_2H_4)^+$ inserts ethylene rapidly above −10 °C, leading to catalytic ethylene dimerization.[11] Complex **4** slowly decomposes at 23 °C (ca. 31% after 19 h); the decomposition products are the same as those from the thermal decomposition of **3a**,**b** in the absence of ethylene.

Reaction of 3a,b with CO. As CO is potentially more reactive for insertion than ethylene, the reactivity of **3a**,**b** with CO was investigated. The reaction of **1** and $[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$ in the presence of excess CO (1 atm) at −78 °C yields $\{(^nHex)HC(mim)_2\}Pd(CHCl_2)(CO)^+$ (**5**) quantitatively (Scheme 3). The NMR spectra of **5** contain characteristic ^{1}H NMR (δ 5.85) and ^{13}C NMR (δ 61.0) resonances for the Pd−$CHCl_2$ unit. The Pd−*C*O ^{13}C resonance appears at δ 172.0, which is similar to the corresponding value for $\{H_2C(mim)_2\}Pd\{C(=O)Me\}(CO)^+$ (δ 173.8). The IR ν_{CO} value for **5** in CD_2Cl_2 solution is 2144 cm^{-1}, which is slightly higher than the free CO value (2139 cm^{-1} in CD_2Cl_2), indicating that **5** is a "nonclassical" CO complex, in which d−π* back-bonding is minimal.[15−17] For comparison, the ν_{CO} value of $\{H_2C(mim)_2\}Pd\{C(=O)Me\}(CO)^+$ is 2121 cm^{-1}.[11b]

Complex **5** does not undergo CO insertion up to 70 °C under 1 atm of CO. Above this temperature, **5** decomposes. In contrast, $\{H_2C(mim)_2\}Pd(Me)(CO)^+$ readily inserts CO at −78 °C and 1 atm.[11b]

Cationic Pd($^nC_3F_7$) Complexes. Hughes reported the synthesis of (tmeda)Pd($^nC_3F_7$)Me (**6**; tmeda = *N*,*N*,*N*′,*N*′-tetramethylenediamine),[18] which is a potential precursor to $L_2Pd(n\text{-}C_3F_7)^+$ species via ligand substitution and methide abstraction. The reaction of **6** with dppp yields (dppp)Pd($^nC_3F_7$)Me (**7**) quantitatively (Scheme 4).[19] The ^{31}P NMR spectrum of **7** contains two doublets of triplets at δ 13.9 and −0.4, due to the J_{PP} and J_{PF} coupling. The ^{19}F NMR spectrum contains resonances at δ −79.9, −92.6, and −117.6 for the *n*-C_3F_7 group.

(14) The ^{1}H NMR spectrum of **4** in the presence of excess free ethylene at −10 °C contains separate resonances for free and coordinated ethylene that are not significantly broadened, indicating that exchange of free and coordinated ethylene is slow on the NMR time scale. In contrast, $\{(^nHex)HC(mim)_2\}Pd(Me)(CH_2{=}CH_2)^+$ undergoes fast exchange with free ethylene under these conditions. As ethylene exchange occurs by an associative mechanism, the additional steric crowding due to the −$CHCl_2$ group of **4** apparently inhibits this process.

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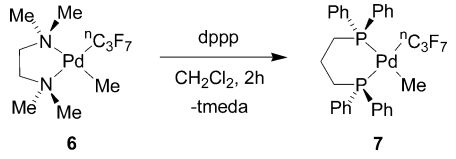
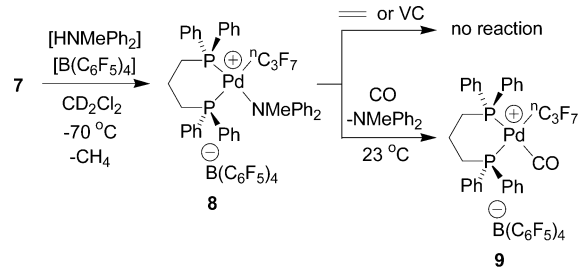
(19) Complex **6** does not react with ArN=CMeCMe=NAr (Ar = 2,6-^{i}Pr$_2$-C_6H_3) even after 10 days at 75 °C, under which conditions **6** gradually decomposes.

Scheme 4



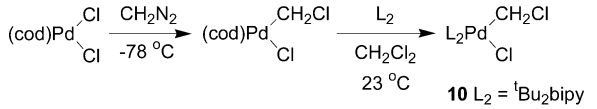
6 **7**

Scheme 5



8 **9**

Scheme 6



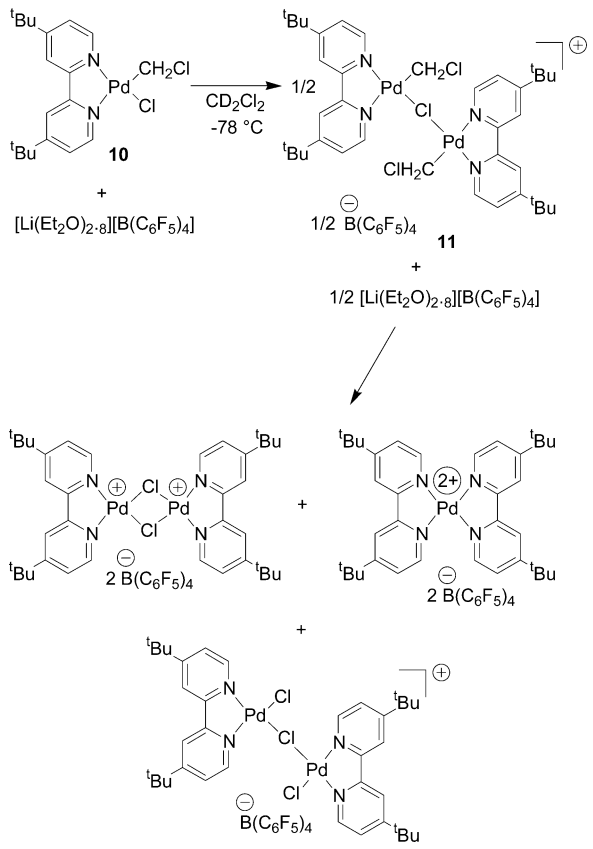
10 L_2 = ^{t}Bu$_2$bipy
13 L_2 = α-diimine

Complex **7** reacts with $[HNMePh_2][B(C_6F_5)_4]$ at −70 °C in CD_2Cl_2 to form $(dppp)Pd(^nC_3F_7)(NMePh_2)^+$ (**8**) quantitatively (Scheme 5). The *N*-Me ^{1}H and ^{13}C NMR resonances of **8** are slightly shifted from the free amine values, consistent with coordination of the $NMePh_2$ ligand.[20] Complex **8** does not react with VC or ethylene up to 23 °C, at which temperature it decomposes. However, **8** does react with CO (1 atm) at −78 °C to yield $(dppp)Pd(^nC_3F_7)(CO)^+$ (**9**) quantitatively. The ν_{CO} value for **9** is 2162 cm^{-1} (CD_2Cl_2), which indicates that this species is also a nonclassical carbonyl complex. Complex **9** is stable in CD_2Cl_2 at 23 °C for days in the presence of excess CO (1 atm). In contrast, $(dppp)Pd(Me)(CO)^+$ (ν_{CO} 2132 cm^{-1}) readily inserts CO under these conditions to yield $(dppp)Pd\{C(=O)Me\}(CO)^+$ (ν_{CO} 2130 cm^{-1}).[3,21]

Synthesis of PdCH$_2$Cl Complexes. The results described above show that $L_2Pd(CHCl_2)^+$ and $L_2Pd(^nC_3F_7)^+$ species are very resistant to insertion reactions. However, these species may be poor models for the $L_2Pd(CHClR)^+$ species in Scheme 1, due to the presence of multiple α-halogen substituents. Therefore, we investigated the chemistry of several $L_2Pd(CH_2Cl)^+$ species. McCrindle reported the synthesis of $L_2Pd(CH_2Cl)Cl$ complexes by the reaction of $(cod)PdCl_2$ (cod = cyclooctadiene) with CH_2N_2 followed by displacement of cod by bidentate dinitrogen and diphosphine ligands.[5a] We prepared (^{t}Bu$_2$bipy)Pd(CH$_2$Cl)Cl (**10**) and (α-diimine)Pd(CH$_2$Cl)Cl (**11**) by this route (Scheme 6).

Generation and Stability of (^{t}Bu$_2$bipy)Pd(CH$_2$Cl)$^+$ Species. The reaction of **10** with $[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$ at −78 °C in CD_2Cl_2 yields the dinuclear complex $[\{(^tBu_2bipy)Pd(CH_2Cl)\}_2(\mu\text{-}Cl)][B(C_6F_5)_4]$ (**11**; Scheme 7). The ^{1}H NMR spectrum of **11** contains a singlet at δ 4.00 for the PdCH_2Cl unit. The ^{1}H NMR spectrum also

Scheme 7



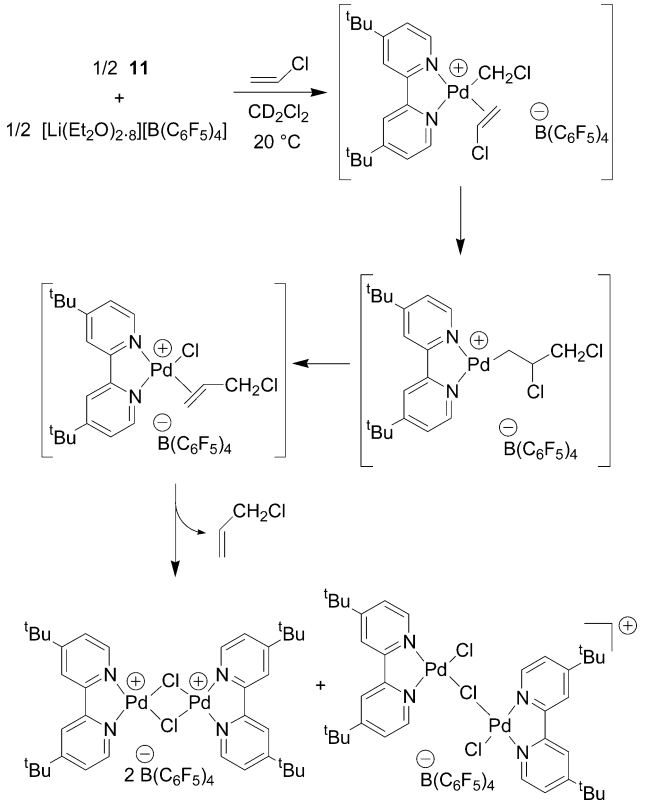
10 **11**

contains six bipy resonances and two ^{t}Bu resonances, which confirms that the two rings of a given ^{t}Bu$_2$bipy ligand are inequivalent. The positive ion ESI mass spectrum of **11** contains a parent ion peak envelope which matches the calculated isotope distribution. Additionally, the ^{1}H NMR spectra are the same for 2/1 and 1/1 mixtures of **10** and $[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$ in CD_2Cl_2, which confirms the stoichiometry in Scheme 7.

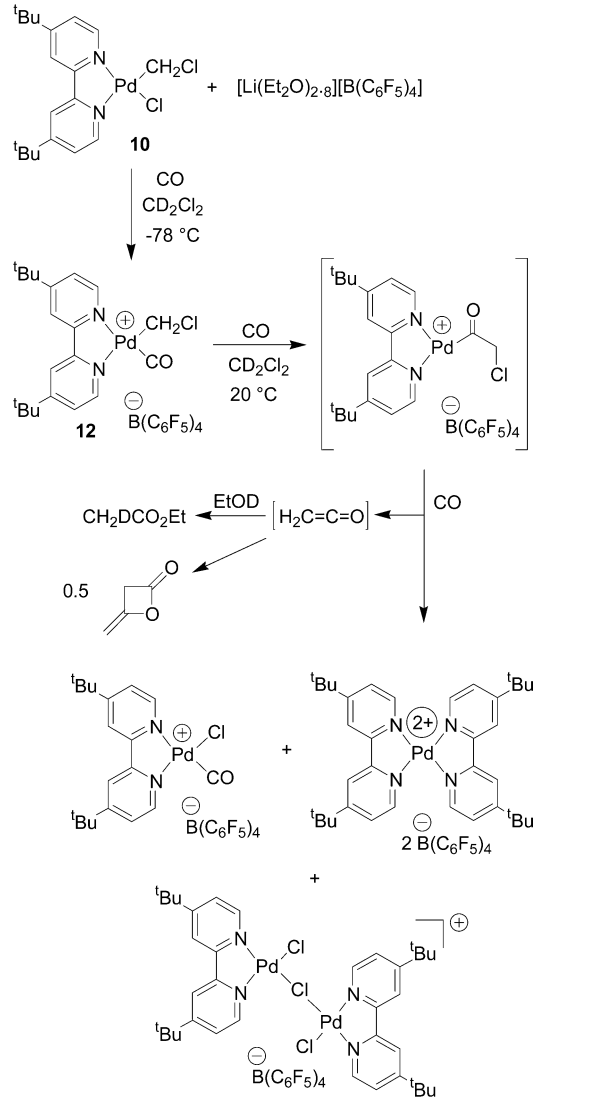
Complex **11** decomposes at 20 °C over 12 h in the presence of 1 equiv of $[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$ to a mixture of Pd^0 and three soluble (^{t}Bu$_2$bipy)Pd species (Scheme 7). The first two soluble species, $[(^tBu_2bipy)_2Pd][B(C_6F_5)_4]_2$ (11 mol % vs starting **10**) and $[\{(^tBu_2bipy)Pd(\mu\text{-}Cl)\}_2][B(C_6F_5)_4]_2$ (10 mol % vs **10**), were identified straightforwardly by NMR, ESI-MS, and independent synthesis. The third soluble Pd species is formed in 29 mol % yield versus **10**. The ^{1}H NMR spectrum of this species contains one set of bipy resonances at δ 8.83 (d, J = 6 Hz, 4H), 7.96 (d, J = 2 Hz, 4H) and 7.61 (dd, J = 6, 2 Hz, 4H), characteristic of effective C_2 (or higher) symmetry at Pd. The positive ion ESI mass spectrum of this species contains a prominent peak envelope at m/z 857.0 which matches the calculated isotope distribution for $\{(^tBu_2bipy)PdCl\}_2(\mu\text{-}Cl)^+$. A species with a very similar NMR spectrum and an identical ESI mass spectrum is generated by the reaction of (^{t}Bu$_2$bipy)PdCl$_2$ and $[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$ in CD_2Cl_2 or by mixture of $[\{(^tBu_2bipy)Pd(\mu\text{-}Cl)\}_2][B(C_6F_5)_4]_2$ and (^{t}Bu$_2$bipy)PdCl$_2$ in CD_2Cl_2. Therefore, the third species is assigned as $[\{(^tBu_2bipy)PdCl\}_2(\mu\text{-}Cl)][B(C_6F_5)_4]$.[22,23] The fate of the Pd−CH_2Cl group in Scheme 7 was not determined.[24]

(20) Casey, C. P.; Carpenetti, D. W., II; Sakurai, H. *Organometallics* **2001**, *20*, 4262.
(21) Shultz, C. S.; Ledford, J.; DeSimone, J. M.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6351.

Scheme 8



Scheme 9



Reaction of [{(^{t}Bu$_2$bipy)Pd(CH$_2$Cl)}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] and VC. The reaction of **10** and 1 equiv of [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] in the presence of VC (32 equiv) at −78 °C in CD_2Cl_2 yields **11**. No reaction with VC was observed up to 0 °C. However, **11** does react with VC slowly (10 h) at 20 °C to yield allyl chloride (45 mol % vs **10**), [{(^{t}Bu$_2$bipy)Pd(μ-Cl)}$_2$][B(C$_6$F$_5$)$_4$]$_2$ (16 mol % vs **10**), and [{(^{t}Bu$_2$bipy)PdCl}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] (34 mol % vs **10**).[23] No Pd^0 is observed. These observations are consistent with generation of (^{t}Bu$_2$bipy)Pd(CH$_2$Cl)(VC)$^+$, net 1,2-VC insertion into the Pd−CH$_2$Cl bond, and β-Cl elimination (Scheme 8). The yield of allyl chloride is lower than expected because the thermal decomposition of **11** (see Scheme 7) competes with VC insertion.

Reaction of [{(^{t}Bu$_2$bipy)Pd(CH$_2$Cl)}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] with CO. The presumed intermediate VC adduct in Scheme 8, (^{t}Bu$_2$bipy)Pd(CH$_2$Cl)(VC)$^+$, was not detected, and therefore it was not possible to compare the insertion rate of this species to that of (R$_2$bipy)Pd(Me)(VC)$^+$ species.[1b] To probe the migratory aptitude of the Pd−CH$_2$Cl group, the reaction of **11** with CO was studied. The reaction of **10** and [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] in the presence of excess CO at −78 °C yields [(^{t}Bu$_2$bipy)Pd(CH$_2$Cl)(CO)][B(C$_6$F$_5$)$_4$] (**12**, Scheme 9). Complex **12** is stable up to 20 °C, at which point it slowly reacts. In ^{1}H NMR monitoring experiments, after 20 min at 20 °C, 50% of **12** had reacted and resonances for diketene [−CH$_2$C(=CH$_2$)OC(=O)−] were observed. After 2 h at 20 °C, the consumption of **12** was complete. The ^{1}H NMR spectrum of the product mixture contains three sets of (^{t}Bu$_2$bipy)Pd resonances which correspond to [(^{t}Bu$_2$bipy)$_2$Pd][B(C$_6$F$_5$)$_4$]$_2$ (6 mol % vs **10**), [{(^{t}Bu$_2$bipy)PdCl}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] (28 mol % vs **10**), and a third species assigned as [(^{t}Bu$_2$bipy)Pd(Cl)(CO)][B(C$_6$F$_5$)$_4$] (31 mol % vs **10**). The formation of Pd(0) was also observed.[23] The carbonyl adduct [(^{t}Bu$_2$bipy)Pd(Cl)(CO)][B(C$_6$F$_5$)$_4$] was converted to [{(^{t}Bu$_2$bipy)Pd(μ-Cl)}$_2$][B(C$_6$F$_5$)$_4$]$_2$ by removing the volatiles under vacuum and dissolving the residue in CD_2Cl_2.

These observations are consistent with CO insertion of **12** followed by β-Cl elimination to yield PdCl$^+$ species and ketene, as illustrated in Scheme 9. It is well established that ketene readily dimerizes to diketene.[25] The diketene formed in Scheme 9 is consumed, although

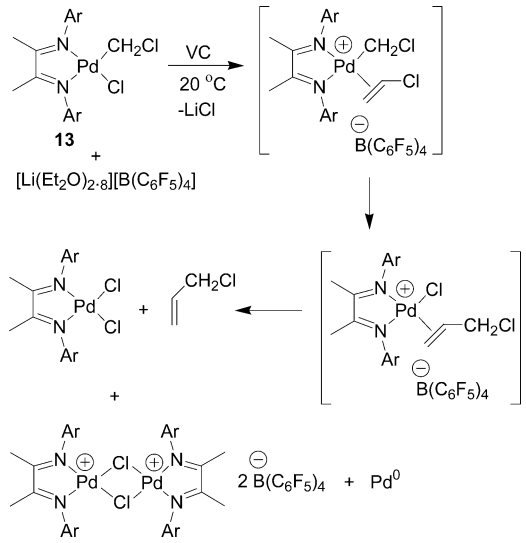
(22) The chemical shift and line width of the δ 8.83 ^{1}H NMR resonance of [{(^{t}Bu$_2$bipy)PdCl}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] varies slightly as the ratio of precursors is varied. The effective C_2 symmetry of [{(^{t}Bu$_2$bipy)PdCl}$_2$(μ-Cl)$^+$ and the broadening of the δ 8.83 resonance of this species likely arise from bridge/terminal Cl exchange or exchange of free (^{t}Bu$_2$bipy)PdCl$_2$ with [{(^{t}Bu$_2$bipy)PdCl}$_2$(μ-Cl)$^+$.

(23) The combined yields of [(^{t}Bu$_2$bipy)$_2$Pd][B(C$_6$F$_5$)$_4$]$_2$, [{(^{t}Bu$_2$bipy)Pd(μ-Cl)}$_2$][B(C$_6$F$_5$)$_4$]$_2$, and [{(^{t}Bu$_2$bipy)PdCl}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] total 100% based on the ^{t}Bu$_2$bipy ligand of starting **10** and 89% based on the Pd of starting **10**. The Pd^0 accounts for the remaining Pd from **10**. The combined chlorine content of [{(^{t}Bu$_2$bipy)Pd(μ-Cl)}$_2$][B(C$_6$F$_5$)$_4$]$_2$ and [{(^{t}Bu$_2$bipy)PdCl}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] corresponds to 1 equiv of Cl from **10**. Similarly, for Schemes 8−10, excellent mass balance of the ancillary ligand (^{t}Bu$_2$bipy or α-diimine) was observed. In some cases, the Cl content of the products exceeds the expected value, which is ascribed to reactions of the Pd byproducts with LiCl.

(24) No ethylene, allyl chloride, CH_2Cl_2, or CH_2ClCH_2Cl was observed in the decomposition of **11**.

(25) Clemens, R. J. *Chem. Rev.* **1986**, *86*, 241.

Scheme 10[a]



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

its fate is unknown. The formation of ketene was confirmed by a trapping experiment. Addition of excess EtOD (6 equiv) to a CD_2Cl_2 solution of [(^{t}Bu$_2$bipy)Pd(CH_2Cl)(^{13}CO)][$B(C_6F_5)_4$] (**12**-$^{13}C_1$) at −78 °C, followed by warming to room temperature for 3 h, produced the labeled ethyl acetate, $H_2DC(^{13}C{=}O)OCH_2CH_3$, derived from trapping of $H_2C{=}^{13}C{=}O$ by EtOD, in 65% yield.[26]

Several other examples of β-Cl elimination of chloroacetyl complexes have been reported previously. For example, (C_5H_5)M(CO)$_3${(C=O)CH_2Cl} species (M = Mo, W) undergo β-Cl elimination to generate (C_5H_5)M(CO)$_3$-Cl and ketene.[27] Additionally, CO insertion into a Rh−CH_2I bond followed by β-I elimination has been proposed.[28]

These results show that **12** inserts CO very slowly (hours) at 20 °C. For comparison, (^{t}Bu$_2$bipy)Pd(Me)-(CO)$^+$ inserts CO (1 atm) at −78 °C to yield (^{t}Bu$_2$bipy)-Pd{C(=O)Me}(CO)$^+$ within 5 min.[3]

Reaction of "(α-diimine)Pd(CH_2Cl)$^+$" and VC. The results described above show that "(^{t}Bu$_2$bipy)Pd-(CH_2Cl)$^+$" reacts with VC by net 1,2-insertion followed by β-Cl elimination. To determine if $L_2PdCH_2Cl^+$ species that are analogous to highly active L_2PdR^+ olefin polymerization catalysts exhibit similar chemistry, we briefly investigated the reactivity of (α-diimine)Pd(CH_2-Cl)Cl (**13**, Scheme 6). As shown in Scheme 10, the reaction of **13** and [Li(Et_2O)$_{2.8}$][$B(C_6F_5)_4$] in the presence of VC (78 equiv) for 10 h at 20 °C yields [{(α-diimine)-Pd(μ-Cl)}$_2$][$B(C_6F_5)_4$]$_2$ (14 mol % vs **13**), (α-diimine)$PdCl_2$ (72 mol % vs **13**),[1b] Pd^0, and free allyl chloride (80 mol % vs **13**).[23] These observations are consistent with generation of (α-diimine)Pd(CH_2Cl)(VC)$^+$ (not observed), net VC 1,2-insertion into the Pd−CH_2Cl bond, and β-Cl elimination.

Discussion

The studies described above probe how the reactivity of $L_2Pd(R^X)^+$ species is influenced by the presence of α-halogen substituents on the alkyl ligand. Several interesting points emerge from this work. First, while the electron-withdrawing power of a R^X group may enhance the electrophilic character of a $L_2Pd(R^X)^+$ species, it also decreases the back-bonding ability of the metal center and therefore inhibits coordination of π-acceptor substrates such as VC and ethylene. For example, VC does not displace {(^{n}Hex)HC(mim)$_2$}Pd-($CHCl_2$)Cl from the dinuclear cation **3a**,**b** and, perhaps more strikingly, neither VC nor ethylene displaces $NMePh_2$ from **8**. The weak back-bonding in $L_2Pd(R^X)^+$ species is manifested by the high ν_{CO} values of the carbonyl complexes {(^{n}Hex)HC(mim)$_2$}Pd($CHCl_2$)(CO)$^+$ (**5**, 2144 cm^{-1}) and (dppp)Pd($^{n}C_3F_7$)(CO)$^+$ (**9**, 2162 cm^{-1}). In fact, the ν_{CO} value for **9** is in the same range as the values for the "O-inside" isomers of the d^0 carbonyls (C_5R_5)$_2$Zr{C(=O)Me}(CO)$^+$ (R = Me, 2152 cm^{-1}; R = H, 2176 cm^{-1}), in which conventional back-bonding is absent.[17]

A second general observation is that $L_2Pd(R^X)$-(substrate)$^+$ species undergo much slower insertion than the corresponding L_2Pd(Me)(substrate)$^+$ complexes. Among the carbonyl adducts studied, neither **5** nor **9** undergo insertion, and **12** undergoes only very slow insertion, under conditions where the corresponding L_2-Pd(Me)(CO)$^+$ species insert rapidly. Similarly, ethylene complex **4** does not undergo insertion under conditions where related {RHC(mim)$_2$}Pd(Me)$^+$ derivatives insert rapidly. These results are in line with previous studies of CO insertion into M−R bonds, which have shown that, almost invariably, electron-releasing substituents on the migrating R group promote migration and stabilize the insertion product, while electron-withdrawing substituents have the opposite effects.[9] This trend has been ascribed to differences in bond strengths (M−R^X > M−R) and differences in the basicity/nucleophilicity of the migrating group (R > R^X). It is also possible that steric crowding associated with the −$CHCl_2$ inhibits insertion of **4** and **5**.[14]

A third key observation is that $L_2Pd(CH_2Cl)^+$ species (L_2 = ^{t}Bu$_2$bipy, α-diimine) react with VC to yield allyl chloride and products derived from $L_2Pd{-}Cl^+$ in high yield. The most direct route to these products is formation of a $L_2Pd(CH_2Cl)(VC)^+$ adduct, 1,2-VC insertion to produce a $L_2Pd(CH_2CHClCH_2Cl)^+$ intermediate, and β-Cl elimination. Alternatively, the initial insertion could occur with 2,1-regiochemistry to produce L_2Pd-($CHClCH_2CH_2Cl$)$^+$, which undergoes chain walking via a $L_2Pd(H)(CHCl{=}CHCH_2Cl)^+$ intermediate (**E**) to form $L_2Pd\{CH(CH_2Cl)CH_2Cl\}^+$, followed by β-Cl elimination. The available evidence is insufficient to distinguish these pathways. However, the sterically crowded, electron-poor CHCl=$CHCH_2Cl$ ligand of intermediate **E** should be easily displaced by VC (which is present in excess in Schemes 8 and 10) or allyl chloride. The absence of CHCl=$CHCH_2Cl$ in the products of Schemes 8 and 10 argues against the 2,1-insertion pathway. Further studies will be necessary to understand the regioselectivity of VC insertion into Pd−R^X and Pd−R bonds.[29]

(26) (a) Weston, W. S.; Cole-Hamilton, D. J. *Inorg. Chim. Acta* **1998**, *280*, 99. (b) Hommeltoft, S. I.; Baird, M. C. *J. Am. Chem. Soc.* **1985**, *107*, 2548.

(27) Dilgassa, M.; Curtis, M. D. *J. Organomet. Chem.* **1979**, *172*, 177.

(28) (a) Weston, W. S.; Lightfoot, P.; Cole-Hamilton, D. J. *J. Organomet. Chem.* **1998**, *553*, 473. (b) The reaction of (Cy_3P)$_2$Pd(CH_2-Cl)Cl with 30 atm of CO yields (Cy_3P)$_2PdCl_2$ and diketene, presumably by CO insertion and β-Cl elimination. Huser, M.; Francois, M.; Osborn, J. Fr. Patent 2637281, 1990.

Finally, it is interesting to note that (^{t}Bu$_2$bipy)Pd{C(=O)CH$_2$Cl}$^+$ undergoes fast β-Cl elimination to form products derived from (^{t}Bu$_2$bipy)PdCl$^+$ (Scheme 9), despite the fact that the high-energy species ketene is produced. As noted above, L$_2$Pd{C(=O)Me}$^+$ species undergo 2,1-insertion of VC to yield O-chelated L$_2$Pd{CHClCH$_2$C(=O)Me}$^+$ complexes.[3] However, L$_2$Pd{CHClCH$_2$C(=O)Me}$^+$ complexes do not undergo chelate ring opening or insertion with CO, which precludes VC/CO copolymerization. The present results suggest that even if these chelate complexes did insert CO, VC/CO copolymerization would be thwarted by β-Cl elimination of the resulting L$_2$Pd{C(=O)CHClCH$_2$C(=O)Me}$^+$ complexes.

Conclusions

This study shows that L$_2$Pd(CHCl$_2$)$^+$, L$_2$Pd(^{n}C$_3$F$_7$)$^+$, and L$_2$Pd(CH$_2$Cl)$^+$ complexes can be generated by methods used to generate analogous L$_2$Pd(Me)$^+$ species. In general, L$_2$Pd(R^X)$^+$ species are much less reactive for olefin or CO insertion compared to corresponding L$_2$Pd(R)$^+$ alkyl species. The chloromethyl complexes, L$_2$Pd(CH$_2$Cl)$^+$, do coordinate and insert vinyl chloride, but the insertion occurs with net 1,2-regiochemistry and is followed by fast β-Cl elimination to produce allyl chloride and products derived from L$_2$PdCl$^+$. Thus, while VC polymerization via repetitive 2,1-insertion (as in Scheme 1) may be feasible, the presence of the α-Cl substituent in the putative MCHClCH$_2$R$^+$ chain carrying active species will probably be insufficient by itself to direct a subsequent 2,1-insertion of VC. Other, presumably ligand-based strategies will be required to achieve a 2,1-insertion polymerization of VC.

Experimental Section

General Procedures. All manipulations were performed using drybox or Schlenk techniques under an N$_2$ atmosphere, or on a high-vacuum line, unless otherwise indicated. Nitrogen was purified by passage through columns containing activated molecular sieves and Q-5 oxygen scavenger. CH$_2$Cl$_2$ was distilled from CaH$_2$ and degassed prior to use. CD$_2$Cl$_2$ was distilled from P$_4$O$_{10}$ and degassed prior to use. Pentane was purified by passage through columns of activated alumina and BASF R3-11 oxygen removal catalyst. {(^{n}Hex)HC(mim)$_2$}Pd(CHCl$_2$)Cl was prepared as described elsewhere and contains ca. 5% {(^{n}Hex)HC(mim)$_2$}PdCl$_2$, which does not interfere in the reactions reported in this paper, as shown by NMR.[11] [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] was provided by Boulder Scientific and used as received. The Et$_2$O content was determined by ^{1}H NMR with C$_6$Me$_6$ as an internal standard. [HNMePh$_2$][B(C$_6$F$_5$)$_4$],[30] (tmeda)Pd(^{n}C$_3$F$_7$)Me,[18] ^{t}Bu$_2$bipy,[31] (cod)Pd(Me)Cl,[32] and CH$_2$N$_2$[33] were prepared by literature procedures. (cod)Pd(CH$_2$Cl) was prepared by the literature procedure, with the exception that CH$_2$N$_2$ was added at −78 °C.[5a] [Pd(MeCN)$_4$][BF$_4$]$_2$ was purchased from Strem and used as received. All other chemicals were purchased from Aldrich and used as received. Elemental analyses were performed by Midwest Microlab or Galbraith Laboratories, Inc.

NMR spectra were recorded on Bruker DMX-500 or DRX-400 spectrometers in Teflon-valved tubes at 23 °C unless otherwise indicated. ^{1}H and ^{13}C chemical shifts are reported versus SiMe$_4$ and were determined by reference to residual ^{1}H and ^{13}C solvent signals. Coupling constants are reported in Hz.

The NMR spectra of cationic complexes contained signals for the free B(C$_6$F$_5$)$_4^-$ anion, which are as follows: ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 148.5 (d, J = 242), 137.0 (d, J = 247), 135.6 (d, J = 244), 123.1 (br, C_{ipso}); ^{19}F NMR (CD$_2$Cl$_2$) δ −132.1 (d, J = 6, 8F, F_{ortho}), −161.3 (t, J = 20, 4F, F_{para}), −165.2 (t, J = 18, 8F, F_{meta}); ^{19}F NMR (CD$_2$Cl$_2$, −70 °C) δ −132.5 (d, J = 5, 8F, F_{ortho}), −161.7 (t, J = 20, 4F, F_{para}), −164.9 (t, J = 18, 8F, F_{meta}); ^{11}B NMR (CD$_2$Cl$_2$) δ −16.1 (br s); ^{11}B NMR (CD$_2$Cl$_2$, −70 °C) δ −15.8 (br s).

Unless otherwise noted, Et$_2$O does not coordinate to the Pd species described here. Data for free Et$_2$O are as follows: ^{1}H NMR (CD$_2$Cl$_2$, −70 °C) δ 3.35 (q, J = 7, 4H), 1.09 (t, J = 7, 6H); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −70 °C) δ 65.7, 15.2; ^{1}H NMR (CD$_2$Cl$_2$) δ 3.43 (q, J = 7, 4H), 1.15 (t, J = 7, 6H); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 66.0, 15.5.

Electrospray mass spectra (ESI-MS) were recorded on freshly prepared samples (ca. 1 mg/mL in CH$_2$Cl$_2$) using an Agilent 1100 LC-MSD spectrometer incorporating a quadrupole mass filter with an m/z range of 0−3000. A 5 μL sample was injected by flow injection using an autosampler. Purified nitrogen was used as the nebulizing and drying gas. Typical instrumental parameters: drying gas temperature 350 °C, nebulizer pressure 35 psi, drying gas flow 12.0 L/min, fragmentor voltage 0 or 70 V. In all cases where assignments are given, observed isotope patterns closely matched calculated isotope patterns. The listed m/z value corresponds to the most intense peak in the isotope pattern.

Generation of [{{(^{n}Hex)HC(mim)$_2$}Pd(CHCl$_2$)}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] (3a,b). A valved NMR tube was charged with {(^{n}Hex)HC(mim)$_2$}Pd(CHCl$_2$)Cl (10.0 mg, 0.0206 mmol) and [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] (18.4 mg, 0.0206 mmol), and CD$_2$Cl$_2$ (0.5 mL) was added by vacuum transfer at −196 °C. The tube was warmed to −40 °C and vigorously shaken. A slurry of a white solid in a pale yellow supernatant formed within ca. 3 h at −40 °C. The free Et$_2$O and LiCl coproducts were not removed. The tube was maintained at −78 °C until further characterization and reactions were carried out. The ^{1}H NMR spectrum established that **3a**,**b** had formed quantitatively. ^{1}H NMR (CD$_2$Cl$_2$, −40 °C): δ 7.65 (d, J = 1, 1H), 7.61 (d, J = 1, 1H), 7.17 (s, 2H), 7.01 (d, J = 1, 1H), 6.99 (d, J = 1, 1H), 6.93 (d, J = 1, 1H), 6.85 (d, J = 1, 1H), 6.34 (s, 1H, PdC*H*Cl$_2$), 6.08 (s, 1H, PdC*H*Cl$_2$), 4.20 (m, 2H, coincidental (^{n}Hex)C*H*), 3.75 (s, 3H), 3.74 (s, 3H), 3.71 (s, 3H), 3.69 (s, 3H), 3.56 (q, J = 7, 22.4H, free and Li$^+$-coordinated Et$_2$O), 2.65 (m, 2H, CHC*H*H), 2.35 (m, 2H, CHCH*H*), 1.29 (m, 16H, (C*H*$_2$)$_4$), 1.18 (t, J = 7, 33.6H, free and Li$^+$-coordinated Et$_2$O), 0.80 (m, 6H, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −40 °C): δ 144.8, 144.6, 144.2 (2 coincidental imidazole C), 126.9, 126.8, 126.5, 126.4, 121.8, 121.6, 121.3, 121.2, 66.0 (free and coordinated Et$_2$O), 61.6 (Pd*C*HCl$_2$), 61.2 (Pd*C*HCl$_2$), 38.4 (*C*H$_2$), 38.1 (*C*H$_2$), 34.4 (2 coincidental CH$_2$*C*H), 34.0 (*Me*), 33.9 (*Me*), 33.9 (*Me*), 33.8 (*Me*), 31.6 (*C*H$_2$), 31.5 (*C*H$_2$), 29.1(*C*H$_2$), 29.0 (*C*H$_2$), 27.6 (*C*H$_2$), 27.4 (*C*H$_2$), 22.6 (2 coincidental *C*H$_2$), 14.6 (free and coordinated Et$_2$O), 14.0 (CH$_2$*C*H$_3$), 13.9 (CH$_2$*C*H$_3$). Positive ion ESI-MS: m/z 936.8, {(^{n}Hex)HC(mim)$_2$}Pd(CHCl$_2$)}$_2$(μ-Cl)$^+$.

Generation of [{(^{n}Hex)HC(mim)$_2$}Pd(CHCl$_2$)(C$_2$H$_4$)][B(C$_6$F$_5$)$_4$] (4). A valved NMR tube containing a CD$_2$Cl$_2$ solution of 1:1 mixture of **3a**,**b** and [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$]

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generated as described above was frozen at −196 °C, and ethylene (5 equiv) was added by vacuum transfer from a calibrated gas bulb. The tube was warmed to −10 °C and maintained at −10 °C for 10 min, and the volatiles were removed under vacuum. CD_2Cl_2 was added by vacuum transfer at −196 °C. The tube was warmed to −78 °C, and a slurry of a fine white solid in a pale yellow supernatant was obtained. The tube was maintained at −78 °C until further characterization and reactions were carried out. The ^{1}H NMR spectrum established that **4** had formed quantitatively. ^{1}H NMR (CD_2Cl_2, −10 °C): δ 7.58 (d, J = 2, 1H), 7.07 (d, J = 2, 1H), 6.97 (d, J = 2, 1H), 6.71 (d, J = 2, 1H) 5.35 (s, 1H, C*H*Cl_2), 5.31 (m, coordinated ethylene and C*H*Cl_2), 5.13 (m, 2H, coordinated ethylene), 4.29 (dd, J = 8, 7, 1H, (^{n}Hex)C*H*), 3.78 (s, 3H, *Me*), 3.72 (s, 3H, *Me*), 2.47−2.36 (m, 1H, CHCH*H*), 2.32−2.23 (m, 1H, CHC*H*H), 1.38−1.17 (m, 8H, CH_2), 0.83 (t, J = 8, 3H, CH_2CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, −10 °C): δ 144.8, 144.7, 125.5, 124.4, 123.4, 122.2, 95.5 (coordinated ethylene), 64.0 (*C*HCl_2), 39.2 (*C*H_2), 34.7 (*Me*), 34.3 (*Me*), 34.1 (CH_2*C*H), 31.6 (*C*H_2), 29.0 (*C*H_2), 27.4 (*C*H_2), 22.6 (*C*H_2), 14.0 (CH_2*C*H_3).

Generation of [{(^{n}Hex)HC(mim)$_2$}Pd(CHCl$_2$)(CO)][B(C$_6$F$_5$)$_4$] (5). A valved NMR tube containing a CD_2Cl_2 solution of 1:1 mixture of **3a**,**b** and [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] generated as described above was exposed to CO (1 atm) for 5 min at −78 °C. The tube was warmed to 23 °C. A slurry of a fine white solid in a pale yellow supernatant was obtained. The tube was maintained at −78 °C until further characterization and reactions were carried out. The ^{1}H NMR spectrum established that **5** had formed quantitatively. ^{1}H NMR (CD_2Cl_2): δ 7.22 (d, J = 2, 1H), 7.10 (d, J = 2, 1H), 7.03 (d, J = 2, 1H), 6.96 (d, J = 2, 1H), 5.85 (s, 1H, Pd*C*HCl_2), 4.34 (t, J = 8, 1H, (^{n}Hex)-C*H*), 3.80 (s, 3H, *Me*), 3.77 (s, 3H, *Me*), 2.33−2.20 (m, 2H, CHCH_2), 1.35−1.21 (m, 8H, (CH_2)$_4$), 0.86 (t, J = 7, 3H, CH_2CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 172.0 (Pd-*C*O), 145.7, 144.8, 128.7, 125.8, 123.7, 123.4, 61.0 (Pd*C*HCl_2), 39.1 (*C*H_2), 35.0 (*Me*), 34.6 (*Me*), 34.5 (CH_2*C*H), 31.6 (*C*H_2), 29.0 (*C*H_2), 27.5 (*C*H_2), 22.8 (*C*H_2), 14.0 (CH_2*C*H_3). IR (CD_2Cl_2): ν_{CO} 2144 cm^{-1}.

(dppp)Pd(^{n}C$_3$F$_7$)Me (7). A flask was charged with (tmeda)Pd(^{n}C$_3$F$_7$)Me (200 mg, 0.492 mmol) and dppp (202 mg, 0.492 mmol), and CH_2Cl_2 (25 mL) was added by cannula. A clear yellow solution formed rapidly. The mixture was stirred at 23 °C for 2 h, and the volatiles were removed under vacuum. The solid was dissolved in CH_2Cl_2 (10 mL), and the volatiles were removed under vacuum. This procedure was repeated twice to yield (dppp)Pd(^{n}C$_3$F$_7$)Me as a pale yellow solid (290 mg, 84%). ^{1}H NMR (CD_2Cl_2): δ 7.58−7.31 (m, 20H), 2.39 (m, 4H), 1.74 (m 2H), 0.24 (t, J = 7, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 134.4 (d, J = 34), 133.7 (d, J = 4), 133.6 (d, J = 3), 131.7 (d, J = 42), 130.7, 130.2, 128.9 (d, J = 10), 128.5 (d, J = 10), 29.7 (dd, J = 20, 5, P*C*H_2), 27.8 (dd, J = 24, 6, P*C*H_2), 19.4 (PCH_2*C*H_2), 5.7 (d, J = 86, Pd*Me*); the C_3F_7 resonances were not observed. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 13.9 (dt, J = 41, 30), −0.4 (dt, J = 41, 38). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −79.9 (t, J = 9), −92.6 (br t), −117.6 (br). Anal. Calcd for $C_{31}H_{29}F_7P_2Pd$: C, 52.97; H, 4.16. Found: C, 52.59; H, 4.17.

Generation of [(dppp)Pd(^{n}C$_3$F$_7$)(NMePh$_2$)][B(C$_6$F$_5$)$_4$] (8). A valved NMR tube was charged with **7** (10.0 mg, 0.0142 mmol) and [HNMePh$_2$][B(C$_6$F$_5$)$_4$] (12.3 mg, 0.0142 mmol), and CD_2Cl_2 (0.5 mL) was added by vacuum transfer at −196 °C. The tube was warmed to −78 °C and vigorously shaken to yield a clear greenish yellow solution. The ^{1}H and ^{31}P NMR spectra established that **8** had formed quantitatively. Methane was also present. ^{1}H NMR (CD_2Cl_2, −70 °C): δ 7.75−7.15 (m, 20H, P*Ph*), 7.25 (t, J = 8, 4H, N*Ph*), 7.01 (d, J = 8, 4H, N*Ph*), 6.94 (t, J = 8, 2H, N*Ph*), 3.29 (s, 3H, N*Me*), 2.60 (br s, 2H), 2.48 (br s, 2H), 1.94 (br s, 2H). ^{13}C{^{1}H} NMR (CD_2Cl_2, −70 °C): δ 147.2 (N*Ph*), 132.9 (d, J = 11), 132.8, 132.6 (d, J = 10), 132.5, 129.7 (d, J = 11), 129.1 (d, J = 12), 129.0 (N*Ph*), 125.4 (d, J = 10), 125.0 (d, J = 24), 121.8 (N*Ph*), 119.8 (N*Ph*), 40.7 (N*Me*), 27.3 (d, J = 37, 14, P*C*H_2), 22.8 (dd, J = 34, 5, P*C*H_2), 17.2 (PCH_2*C*H_2); the C_3F_7 resonances were not observed. ^{31}P{^{1}H} NMR (CD_2Cl_2, −70 °C): δ 29.5 (dt, J = 53, 30), −3.2 (dt, J = 53, 42). ^{19}F{^{1}H} NMR (CD_2Cl_2, −70 °C): δ −80.4 (s), −89.9 (br s), −117.6 (s).

Generation of [(dppp)Pd(^{n}C$_3$F$_7$)(CO)][B(C$_6$F$_5$)$_4$] (9). A valved NMR tube containing a CD_2Cl_2 solution of **8** generated as described above was exposed to CO (1 atm) for 5 min at −78 °C. A clear pale yellow solution was obtained. The free $NMePh_2$ was not removed. The ^{1}H NMR spectrum established that **9** had formed quantitatively. Methane was also present. ^{1}H NMR (CD_2Cl_2): δ 7.70−7.44 (m, 20H), 7.28 (t, J = 8, 4H, N*Ph*), 7.03 (d, J = 8, 4H, N*Ph*), 6.98 (t, J = 8, 2H, N*Ph*), 2.61 (m, 4H), 2.15 (m, 2H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 149.5 (N*Ph*), 133.8, 133.6, 133.4 (d, J = 11), 132.5 (d, J = 11), 130.8 (d, J = 11), 130.1 (d, J = 11), 129.5 (N*Ph*), 127.4 (d, J = 50), 125.4 (d, J = 57), 121.5 (N*Ph*), 120.7 (N*Ph*), 26.0 (dd, J = 35, 12, P*C*H_2), 23.3 (dd, J = 28, 5, P*C*H_2), 18.3 (PCH_2*C*H_2); the assignment of the Pd−*C*O resonance was achieved using ^{13}CO, giving δ 174.3 (d, J = 104, Pd*C*O); the C_3F_7 resonances were not observed. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 11.3 (dt, J = 56, 44), −5.4 (dt, J = 56, 33). ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −79.8 (t, J = 13), −80.6 (t, J = 35), −133 (s). IR (CD_2Cl_2): ν_{CO} 2162 cm^{-1}.

(^{t}Bu$_2$bipy)Pd(CH$_2$Cl)Cl (10). A flask was charged with (cod)Pd(CH_2Cl)Cl (64 mg, 0.21 mmol), ^{t}Bu$_2$bipy (57 mg, 0.21 mmol), and CH_2Cl_2 (5 mL). The resulting clear yellow solution was stirred for 10 min and filtered, and the volatiles were removed under vacuum. The resulting brown powder was washed with hexanes (4 × 10 mL), dried under vacuum, and dissolved in CH_2Cl_2 (2 mL). Hexanes (10 mL) were added, resulting in the precipitation of (^{t}Bu$_2$bipy)Pd(CH_2Cl)Cl as a pale yellow powder (64 mg, 65%). ^{1}H NMR (CD_2Cl_2): δ 9.01 (d, J = 6, 1H), 8.76 (d, J = 6, 1H), 8.05 (d, J = 2, 1H), 7.99 (d, J = 2, 1H), 7.64 (dd, J = 6, 2, 1H), 7.55 (dd, J = 6, 2, 1H), 4.00 (s, 2H, Pd*C*H_2Cl), 1.45 (s, 9H), 1.41 (s, 9H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 164.4 (2C), 156.7 (2C), 149.6 (2C), 124.5, 124.0, 119.5, 118.5, 33.8 (Pd*C*H_2Cl), 35.9 (2C, *C*Me$_3$), 30.4 (C*Me*$_3$), 30.3 (C*Me*$_3$). Anal. Calcd for $C_{19}H_{26}N_2PdCl_2$: C, 49.64; H, 5.70; N, 6.09. Found: C, 49.87; H, 5.70; N 6.13.

Generation of [{(^{t}Bu$_2$bipy)Pd(CH$_2$Cl)}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] (11). A valved NMR tube was charged with (^{t}Bu$_2$bipy)Pd(CH_2Cl)Cl (9.7 mg, 0.022 mmol) and [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] (9.6 mg, 0.011 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. ^{1}H NMR (CD_2Cl_2, −70 °C): δ 8.82 (d, J = 6, 2H), 8.59 (d, J = 6, 2H), 8.07 (s, 2H), 8.03 (s, 2H), 7.66 (br d, J = 6, 2H), 7.58 (br d, J = 6, 2H), 4.00 (s, 4H, Pd*C*H_2Cl), 1.39 (s, 18H), 1.35 (s, 18H). Positive ion ESI-MS: m/z 885.0, {(^{t}Bu$_2$-bipy)Pd(CH_2Cl)}$_2$(μ-Cl)$^+$.

(^{t}Bu$_2$bipy)PdCl$_2$. A flask was charged with (cod)$PdCl_2$ (100 mg, 0.351 mmol) and ^{t}Bu$_2$bipy (94.1 mg, 0.351 mmol), and CH_2Cl_2 (25 mL) was added by cannula. The resulting clear yellow solution was stirred for 1 h at 23 °C, and the volatiles were removed under vacuum. (^{t}Bu$_2$bipy)$PdCl_2$ was obtained as a pale yellow solid (138 mg, 89%). ^{1}H NMR (CD_2Cl_2): δ 9.13 (d, J = 6, 2H), 7.93 (d, J = 2, 2H), 7.57 (dd, J = 6, 2, 2H), 1.43 (s, 18H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 165.6, 156.5, 150.5, 124.3, 119.7, 36.1 (*C*Me$_3$), 30.3 (C*Me*$_3$). Anal. Calcd for $C_{18}H_{24}N_2PdCl_2$: C, 48.51; H, 5.43; N, 6.29. Found: C, 48.31; H, 5.37; N, 6.29.

[{(^{t}Bu$_2$bipy)Pd(μ-Cl)}$_2$][B(C$_6$F$_5$)$_4$]$_2$. A flask was charged with (^{t}Bu$_2$bipy)$PdCl_2$ (150 mg, 0.34 mmol), $AgPF_6$ (85 mg, 0.34 mmol), and CH_2Cl_2 (10 mL). The mixture was stirred at room temperature for 15 min, yielding a yellow slurry. Solid [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] (307 mg, 0.34 mmol) was added, and the suspension was stirred for 30 min. The mixture was filtered to remove the white precipitate, yielding a clear yellow solution. The solution was condensed to 3 mL under vacuum and placed in a −30 °C freezer. [{(^{t}Bu$_2$bipy)Pd(μ-Cl)}$_2$][B(C$_6$F$_5$)$_4$]$_2$ precipitated overnight as a yellow powder, which was isolated by filtration and dried under vacuum (0.280 g,

75%). ^{1}H NMR (CD_2Cl_2): δ 8.16 (d, J = 6, 4H), 8.01 (d, J = 2, 4H), 7.61 (dd, J = 6, 2, 4H), 1.43 (s, ^{t}Bu, 36H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 169.6, 156.6, 149.9, 126.0, 121.7, 36.7 (*C*Me$_3$), 30.0 (C*Me*$_3$). Positive ion ESI-MS: *m*/*z* 411.0, [{(^{t}Bu$_2$bipy)Pd(μ-Cl)}$_2$]$^{2+}$. Anal. Calcd for $C_{84}H_{48}N_4Pd_2Cl_2B_2F_{40}$: C, 46.31; H, 2.22; N, 2.57. Found: C, 46.11; H, 2.37; N, 2.22.

Generation of [{(^{t}Bu$_2$bipy)PdCl}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$]. A valved NMR tube was charged with (^{t}Bu$_2$bipy)PdCl$_2$ (9.7 mg, 0.022 mmol), [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] (19.2 mg, 0.022 mmol), and CD_2Cl_2 (0.6 mL), yielding a slurry of a white precipitate in a pale yellow solution. NMR spectra showed that the reaction was complete after 15 min and no further reaction was observed after 3 days at room temperature. ^{1}H NMR (CD_2Cl_2): δ 8.83 (br d, J = 6, 4H), 7.96 (d, J = 2, 4H), 7.60 (dd, J = 6, 2, 4H), 1.44 (s, ^{t}Bu, 36H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 166.9, 156.6, 150.5, 124.9, 120.1, 36.2 (*C*Me$_3$), 30.2 (C*Me*$_3$). Positive ion ESI-MS: *m*/*z* 857.0, [{(^{t}Bu$_2$bipy)PdCl}$_2$(μ-Cl)}]$^+$.

[{(^{t}Bu$_2$bipy)PdCl}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] can also be generated by a mixture of [{(^{t}Bu$_2$bipy)Pd(μ-Cl)}$_2$][B(C$_6$F$_5$)$_4$]$_2$ (0.007 mmol) and (^{t}Bu$_2$bipy)PdCl$_2$ (0.014 mmol) in CD_2Cl_2 (0.6 mL), which results in a very similar NMR spectrum and an identical ESI mass spectrum.

[(^{t}Bu$_2$bipy)$_2$Pd][B(C$_6$F$_5$)$_4$]$_2$. An NMR tube was charged with ^{t}Bu$_2$bipy (11.4 mg, 0.042 mmol) and [Pd(MeCN)$_4$][BF$_4$]$_2$ (9.4 mg, 0.021 mmol), and CD_2Cl_2 (0.5 mL) was added by vacuum transfer at −196 °C. The tube was heated to 50 °C for 18 h, by which time the reactants had dissolved. The volatiles were removed under vacuum, and [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] (39.0 mg, 0.044 mmol) was added. The tube was opened under air, and CH_2Cl_2 was added. The tube was shaken vigorously, and a white precipitate formed immediately. The tube was allowed to stand at room temperature for 30 min. The mixture was filtered through a Celite plug, and the filtrate was placed in a −80 °C bath. Yellow block crystals formed overnight. The crystals were collected, washed with CH_2Cl_2, and dried under vacuum. ^{1}H NMR (CD_2Cl_2): δ 8.31 (d, J = 6, 4H, H6), 8.22 (d, J = 2, 4H, H3), 7.86 (dd, J = 6, 2, 4H, H5), 1.48 (s, 18H, ^{t}Bu). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 170.2, 156.9, 149.6, 126.8, 122.1, 36.8, 30.0. Positive ion ESI-MS: *m*/*z* 321.1, [(^{t}Bu$_2$bipy)$_2$Pd]$^{2+}$. Anal. Calcd for $C_{84}H_{48}B_2F_{40}N_4Pd$: C, 50.41; H, 2.42; N, 2.80. Found: C, 50.29; H, 2.60; N, 2.73.

Reaction of [{(^{t}Bu$_2$bipy)Pd(CH$_2$Cl)}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] and Vinyl Chloride. A valved NMR tube was charged with (^{t}Bu$_2$bipy)Pd(CH$_2$Cl)Cl (**10**, 5.0 mg, 0.011 mmol) and [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] (9.7 mg, 0.011 mmol), and CD_2Cl_2 (0.6 mL) and vinyl chloride (32 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. No reaction was observed until 20 °C. After 10 h at 20 °C, the ^{1}H NMR spectrum showed that [{(^{t}Bu$_2$bipy)PdCl}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] (34 mol % vs **10**), [{(^{t}Bu$_2$bipy)Pd(μ-Cl)}$_2$][B(C$_6$F$_5$)$_4$]$_2$ (16 mol % vs **10**), and free allyl chloride (45 mol % vs **10**) were present. No Pd(0) was observed.

Reaction of [{(^{t}Bu$_2$bipy)Pd(CH$_2$Cl)}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] and ^{13}CO. A valved NMR tube was charged with (^{t}Bu$_2$bipy)Pd(CH$_2$Cl)Cl (**10**, 5.0 mg, 0.011 mmol) and [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] (9.7 mg, 0.011 mmol), and CD_2Cl_2 (0.6 mL) and ^{13}CO (40 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. At −78 °C, the only product observed was [(^{t}Bu$_2$bipy)Pd(CH$_2$Cl)(^{13}CO)][B(C$_6$F$_5$)$_4$]. Data for [(^{t}Bu$_2$bipy)Pd(CH$_2$Cl)(^{13}CO)][B(C$_6$F$_5$)$_4$] are as follows: ^{1}H NMR (CD_2Cl_2, −70 °C) δ 8.60 (d, J = 6, 1H), 8.41 (d, J = 6, 1H), 8.12 (s, 1H), 8.10 (s, 1H), 7.78 (br d, J = 6, 1H), 7.63 (d, J = 6, 1H), 4.08 (s, 2H, Pd*C*H$_2$Cl), 1.37 (s, 9H), 1.33 (s, 9H); ^{13}C{^{1}H} NMR (CD_2Cl_2, −70 °C) δ 172.1 (Pd−^{13}*C*O), 165.0 (2C), 156.8 (2C), 150.3 (2C), 125.9, 125.1, 121.2, 120.3, 33.6 (Pd*C*H$_2$Cl), 36.1 (2C, *C*Me$_3$), 30.2 (C*Me*$_3$), 30.0 (C*Me*$_3$). No further reaction was observed until 20 °C. After 20 min at 20 °C, 50% of the Pd−CH$_2$Cl had reacted and resonances for ^{13}C-labeled diketene [−CH$_2$^{13}C(=CH$_2$)O^{13}C(=O)−] were observed by ^{1}H NMR. ^{1}H NMR of [−CH$_2$^{13}C(=CH$_2$)O^{13}C(=O)−] (CD_2Cl_2): δ 4.93 (ddtd, $^2J_{CH}$ = 7.1, $^2J_{HH}$ = 4.5, $^4J_{HH}$ = 1.9, $^4J_{CH}$ = 0.6, 1H, =C*H*$_2$), 4.59 (ddtd, $^2J_{CH}$ = 5.9, $^2J_{HH}$ = 4.5, $^4J_{HH}$ = 1.6, $^4J_{CH}$ = 0.8, 1H, =C*H*$_2$), 3.95 (dddd, $^2J_{CH}$ = 6.9, $^2J_{CH}$ = 5.4, $^4J_{HH}$ = 1.9, $^4J_{HH}$ = 1.6, 2H, C−C*H*$_2$). Coupling constant determinations were made by visually and iteratively fitting simulated spectra to experimental spectra. Simulations were performed using gNMR.[34] After 2 h, (^{t}Bu$_2$bipy)Pd(CH$_2$Cl)(^{13}CO)$^+$ had reacted completely to give [{(^{t}Bu$_2$bipy)PdCl}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] (28 mol % vs **10**), [(^{t}Bu$_2$bipy)Pd(Cl)(^{13}CO)][B(C$_6$F$_5$)$_4$] (31 mol % vs **10**), and [(^{t}Bu$_2$bipy)$_2$Pd][B(C$_6$F$_5$)$_4$]$_2$ (6 mol % vs **10**). Pd(0) was also observed. No further reaction was observed after 2 days. Data for [(^{t}Bu$_2$bipy)Pd(Cl)(^{13}CO)][B(C$_6$F$_5$)$_4$] are as follows: ^{1}H NMR (CD_2Cl_2) δ 9.11 (dd, J = 6, 2, 1H), 8.38 (dd, J = 6, 2, 1H), 8.12 (d, J = 2, 1H), 8.07 (d, J = 2, 1H), 7.79 (dd, J = 6, 2, 1H), 7.69 (d, J = 6, 2, 1H), 4.08 (s, 2H, Pd*C*H$_2$Cl), 1.50 (s, 9H), 1.48 (s, 9H); positive ion ESI-MS *m*/*z* 437.9, [(^{t}Bu$_2$bipy)Pd(Cl)(^{13}CO)]$^+$; ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 172.3 (Pd−^{13}*C*O). The solvent was removed under vacuum, and the residue was redissolved in CD_2Cl_2, resulting in the complete conversion of [(^{t}Bu$_2$bipy)Pd(Cl)(^{13}CO)][B(C$_6$F$_5$)$_4$] to [{(^{t}Bu$_2$bipy)Pd(μ-Cl)}$_2$][B(C$_6$F$_5$)$_4$]$_2$.

Trapping of Ketene from the Reaction of [{(^{t}Bu$_2$bipy)Pd(CH$_2$Cl)}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] and ^{13}CO. A CD_2Cl_2 solution of [(^{t}Bu$_2$bipy)Pd(CH$_2$Cl)(^{13}CO)][B(C$_6$F$_5$)$_4$] was generated in a valved NMR tube at −78 °C as described above. Excess CH$_3$CH$_2$OD (6 equiv) was added at −78 °C, and the tube was warmed to room temperature for 3 h. The ^{1}H NMR spectrum showed that H$_2$DC(^{13}C=O)OCH$_2$CH$_3$ had formed in 65% yield. Analysis of volatiles from the tube showed that this labeled ethyl acetate was the only major species present. ^{1}H NMR of H$_2$DC(^{13}C=O)OCH$_2$CH$_3$ (CD_2Cl_2): δ 4.08 (d of q, J = 7, 3, 2H), 1.99 (d of t, J = 7, 4, 2H), 1.26 (t, J = 7, 3H).

(α-diimine)Pd(CH$_2$Cl)Cl (13). A flask was charged with (cod)Pd(CH$_2$Cl)Cl (43.2 mg, 0.144 mmol), α-diimine (58.3 mg, 0.144 mmol), and CH_2Cl_2 (4 mL). The resulting clear orange solution was maintained at room temperature for 30 min. Pentane (20 mL) was added, resulting in precipitation of a deep yellow powder. The product was collected by filtration, washed with pentane (2 × 10 mL), and dried under vacuum, yielding a yellow powder (66 mg, 77%). This material was further purified by precipitation from a CH_2Cl_2 solution layered with pentane, which yielded **13**·0.25 CH_2Cl_2; the presence of solvent was confirmed by NMR and elemental analysis. Anal. Calcd for $C_{29}H_{42}N_2PdCl_2$·0.25 CH_2Cl_2: C, 56.92; H, 6.94; N, 4.54. Found: C, 56.53; H, 6.84; N, 4.79. ^{1}H NMR (CD_2Cl_2): δ 7.45−7.25 (m, 6H, Ar), 3.19 (s, 2H, Pd*C*H$_2$Cl), 3.09 (sept, J = 7, 2H, C*H*Me$_2$), 2.94 (sept, J = 7, 2H, C*H*Me$_2$), 2.11 (s, 3H, N=C*Me*), 2.08 (s, 3H, N=C*Me*), 1.41 (d, J = 7, 6H, CH*Me*$_2$), 1.36 (d, J = 7, 6H, CH*Me*$_2$), 1.17 (d, J = 7, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 175.6 (N=*C*), 174.5 (N=*C*), 139.3 (2C, Ar C$_{ipso}$), 138.4 (4C, Ar C$_{ortho}$), 128.5 (Ar C$_{para}$), 127.6 (Ar C$_{para}$), 124.7 (2C, Ar C$_{meta}$), 123.7 (2C, Ar C$_{meta}$), 36.8 (Pd−CH$_2$Cl), 29.4 (*C*HMe$_2$), 29.0 (*C*HMe$_2$), 24.1 (CH*Me*$_2$), 23.7 (CH*Me*$_2$), 23.5 (2 CH*Me*$_2$), 21.9 (N=C*Me*), 20.2 (N=C*Me*). Positive ion ESI-MS: *m*/*z* 561.2, [(α-diimine)Pd(CH$_2$Cl)]$^+$.

Reaction of (α-diimine)Pd(CH$_2$Cl)Cl/[Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] and VC. A valved NMR tube was charged with (α-diimine)Pd(CH$_2$Cl)Cl (7.0 mg, 0.012 mmol) and [Li(Et$_2$O)$_{2.8}$][B(C$_6$F$_5$)$_4$] (10.4 mg, 0.012 mmol), and CD_2Cl_2 (0.6 mL) and VC (78 equiv) were added by vacuum transfer at −196 °C. The tube was warmed to 20 °C, and NMR spectra were recorded periodically. After 10 h at 20 °C, [{(α-diimine)Pd(μ-Cl)}$_2$][B(C$_6$F$_5$)$_4$]$_2$ (14 mol % vs **13**) and (α-diimine)PdCl$_2$ (72 mol % vs **13**) were the only organometallic species observed by ^{1}H NMR.[1b] Allyl chloride (80 mol % vs **13**) was also present. Pd(0) was observed in the reaction tube. NMR and GC-MS analyses of volatiles showed that allyl chloride was the only major volatile species present.

(34) gNMR, version 4.1.2; Adept Scientific, Letchworth, U.K., 2000.

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