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Reaction of Vinyl Chloride with Cationic Palladium Acyl Complexes

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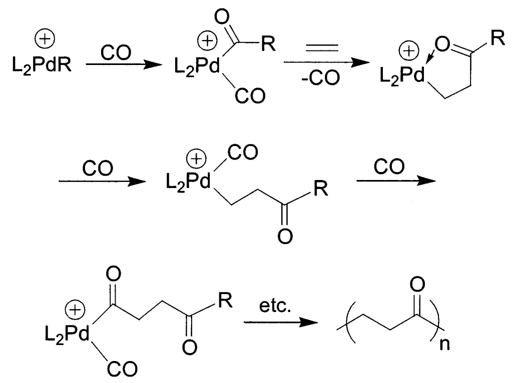
Vinyl chloride (VC) reacts with the cationic Pd complexes $[L_2Pd(Me)(CO)][B(C_6F_5)_4]$ (**3a**−**d**; L_2 = Me_2bipy, $^tBu_2$bipy, dppp, dmpe) and $[L_2Pd\{C({=}O)Me\}(CO)][B(C_6F_5)_4]$ (**4a**−**d**) by 2,1-insertion of $L_2Pd\{C({=}O)Me\}(VC)^+$ intermediates to yield the O-chelated products $[L_2Pd\{CHClCH_2C({=}O)Me\}][B(C_6F_5)_4]$ (**5a**−**d**). **5a**−**d** were characterized by NMR spectroscopy, and the molecular structures of **5a** and **5b**·CH_2Cl_2 were determined by X-ray crystallography. The VC 2,1-insertion regiochemistry is favored in part because the alternative $L_2Pd\{CH_2CHClC({=}O)Me\}^+$ 1,2-insertion products would be destabilized by placement of the electron-withdrawing Cl and acyl substituents on the same carbon. In contrast to analogous nonhalogenated $L_2Pd\{CHRCHR'C({=}O)Me\}^+$ species, **5a**,**c** do not further react with CO, due to the stability of the chelate ring and the low migratory aptitude of the $-CHClCH_2C({=}O)Me$ group.

Introduction

The alternating copolymerization of carbon monoxide and olefins catalyzed by late-transition-metal catalysts has been studied extensively.[1] In these reactions, cationic L_2PdR^+ species which are stabilized by neutral bidentate N-donor or P-donor ligands undergo alternating CO and olefin insertions to produce polyketones (Scheme 1). X-ray crystallographic determinations and NMR and IR studies have shown that the $L_2PdCH_2CH_2C({=}O)R^+$ intermediates adopt O-chelated structures.[1,2]

To date, studies of olefin/CO copolymerization have focused on nonfunctionalized olefins, including ethylene, propylene, styrene,[1] strained cyclic olefins such as norbornene,[3] and allene.[4] Studies of the copolymerization of CO with functionalized olefins may lead to functionalized polyketones and may also provide useful insights to the problem of designing catalysts for the homo- or copolymerization of polar monomers by insertion mechanisms.[5] Copolymerizations of CO with remotely functionalized $CH_2{=}CH(CH_2)_nX$ monomers (X = OAc, fluorophenyl, OH, CO_2H, epoxide, phenol, etc.) have been reported by several groups,[6] and insertion reactions of acrylates, vinyl acetate, and methyl vinyl ketone with cationic Pd acyl species have also been studied.[2d,e,g,h,7,8] Here we describe studies of the reaction of $L_2Pd\{C({=}O)Me\}^+$ complexes with vinyl chloride (VC), which are directed toward the long-term goal of prepar-

Scheme 1



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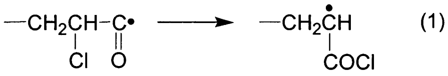
ing new materials by insertion polymerization or copolymerization of $CH_2{=}CHX$ monomers using metal catalysts. Free radical copolymerization of VC and CO yields a random copolymer composed of VC and acrylyl chloride units (i.e., $-CH_2CH(COCl)-$ instead of $-CH_2CHClC({=}O)-$). The pendant acyl chloride groups are formed by the rearrangement shown in eq 1.[9]



$$-CH_2CH(Cl)-\dot{C}({=}O) \longrightarrow -CH_2\dot{C}H(COCl) \qquad (1)$$

We showed previously that VC reacts with $(C_5R_5)_2ZrR^+$, $(C_5Me_4SiMe_2N^tBu)TiR^+$, $(Me_2bipy)PdR^+$, (salicylaldiminato)Ni(Ph)(PPh_3), and other early- and late-metal alkyl species by net 1,2-insertion and β-Cl elimination to produce M−Cl products and the corresponding $CH_2{=}CHR$ olefin.[10] Similarly, Wolczanski reported that $(^tBu_3SiO)_3TaH_2$ reacts with VC by 1,2-insertion/β-Cl elimination to afford $(^tBu_3SiO)_3TaHCl$ and ethylene, and Caulton showed that Cp_2ZrHCl reacts with vinyl fluoride in an analogous manner. More recently, Boone found that VC terminates {2,6-(*o*-tol-N=CMe)$_2$-pyridine}$FeCl_2$/MAO-catalyzed ethylene polymerization by 1,2 insertion/β-Cl elimination, and Sen observed that vinyl bromide reacts with {ArN=C(Me)C(Me)=NAr}$PdMe^+$ (Ar = 2,6-$^iPr_2$-C_6H_3) by 1,2-insertion/β-Br elimination.[11] The fast β-Cl elimination of L_nMCH_2CHClR species precludes VC homopolymerization by conventional olefin polymerization catalysts. We envisioned that $MCH_2CHClC({=}O)R^+$ intermediates formed by 1,2-insertion of VC into a metal−acyl bond would be stabilized against β-Cl elimination by O-chelation. In fact, we have found that $L_2Pd\{C({=}O)Me\}^+$ species react with VC by 2,1-insertion.

Results and Discussion

Generation of [{L_2PdMe}$_2$(μ-Cl)][B(C_6F_5)$_4$] (2a−d). Neutral $L_2Pd(Me)Cl$ complexes (**1a**−**d**; L_2 = 4,4′-Me_2-2,2′-bipyridine (Me_2bipy), 4,4′-$^tBu_2$-2,2′-bipyridine ($^tBu_2$bipy), 1,3-bis(diphenylphosphino)propane (dppp), 1,2-bis(dimethylphosphino)ethane (dmpe)), which are precursors to $L_2Pd\{C({=}O)Me\}^+$ acyl cations, are prepared in high yield by displacing cod (cod = cyclooctadiene) from (cod)Pd(Me)Cl with the L_2 ligand (eq 2).[12]

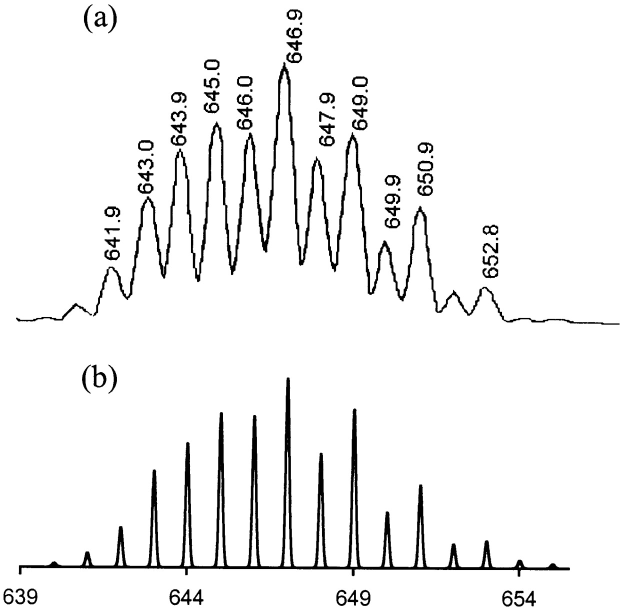
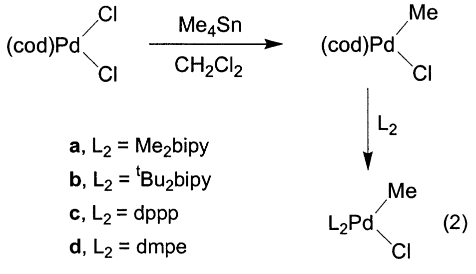


Figure 1. (a) Observed and (b) calculated molecular ion envelopes from ESI-MS spectra of the {(Me_2bipy)PdMe}$_2$(μ-Cl)$^+$ cation of **2a**.



1a-d

The R_2bipy ligands were chosen to enable comparison of Pd−acyl reactivity with (R_2bipy)Pd−Me^+.[10] The dppp ligand was chosen because (dppp)Pd^{II} systems are among the most active olefin/CO copolymerization catalysts known.[1,13] In contrast, (dmpe)Pd{C(=O)Me}$^+$ species exhibit relatively high barriers for olefin insertion and therefore may allow observation of intermediates in reactions with VC.[14]

The reaction of **1a**−**d** with 0.5 equiv of [Li(Et_2O)$_{2.4}$][B(C_6F_5)$_4$] in CD_2Cl_2 (23 °C, 1 min) quantitatively yields the dinuclear monocationic complexes [{L_2PdMe}$_2$(μ-Cl)][B(C_6F_5)$_4$] (**2a**−**d**; Scheme 2). Complexes **2a**−**d** form by initial Cl^- abstraction from **1a**−**d** to yield L_2PdMe^+, which is trapped by the remaining 0.5 equiv of **1a**−**d** by Cl bridging. The ^1H NMR spectra of 2:1 and 1:1 mixtures of **1a**−**d** and [Li(Et_2O)$_{2.4}$][B(C_6F_5)$_4$] in CD_2Cl_2 are very similar and are consistent with C_s symmetry at each Pd unit. The positive ion electrospray mass

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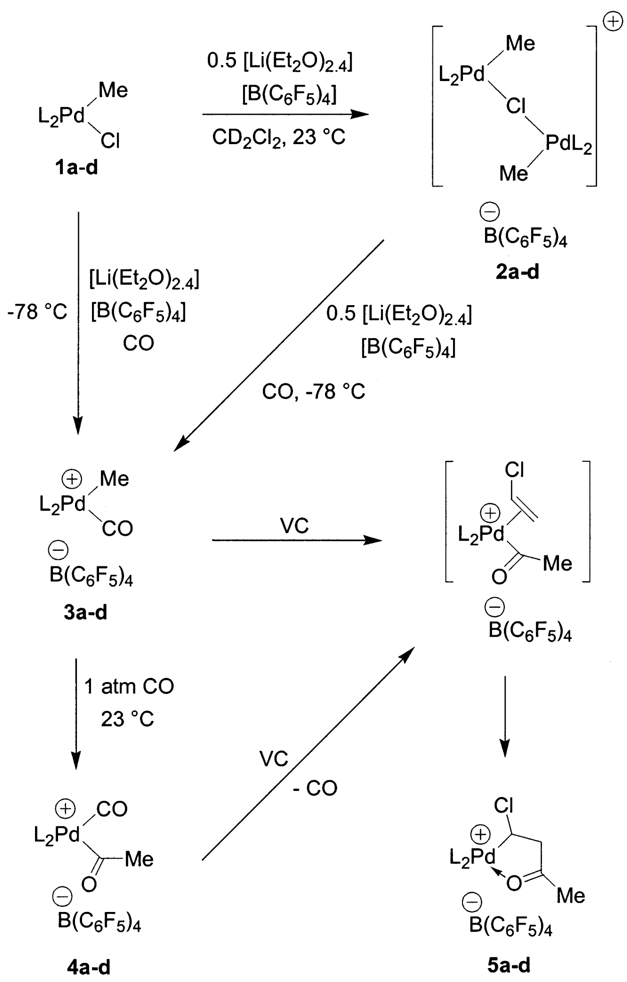
Scheme 2



spectra (ESI-MS) of **2a**−**d** exhibit parent ion peaks with isotope distributions that match calculated patterns; representative examples are shown in Figures 1 and 2.[15] Analogous incomplete halide abstraction and dinuclear cation formation were observed in the reaction of {ArN=C(R)C(R)=NAr}Pd(Me)Cl (R = Me, H; Ar = 2,6-$^{i}Pr_2$-C_6H_3) with Na[B{3,5-$(CF_3)_2$-C_6H_3}$_4$].[16]

Complexes **2a**−**c** are stable in CD_2Cl_2 for several hours at 23 °C, while **2d** decomposes within 5 min under these conditions and therefore was stored at −78 °C. The Et_2O released from $[Li(Et_2O)_{2.4}][B(C_6F_5)_4]$ does not compete with **1a**−**d** for the vacant site on the "L_2PdMe^+" cation generated by Cl^- abstraction from **1a**−**d**.[17] However, stronger Lewis bases displace **1a**−**d** from **2a**−**d**, leading, in the presence of 0.5 equiv of $[Li(Et_2O)_{2.4}][B(C_6F_5)_4]$, to clean formation of $L_2Pd(Me)(base)^+$ species.[18]

Generation of $[L_2Pd(Me)(CO)][B(C_6F_5)_4]$ (3a−d) and $[L_2Pd\{C(=O)Me\}(CO)]$ $[B(C_6F_5)_4]$ (4a−d). The reactions of **2a**−**d** with CO and VC are summarized in Scheme 2. Exposure of **2a**,**b**/$[Li(Et_2O)_{2.4}][B(C_6F_5)_4]$ mixtures to low CO pressure (60 mm) at −78 °C for 5 min yields the CO adducts $[(R_2bipy)Pd(Me)(CO)][B(C_6F_5)_4]$ (**3a**,**b**). If higher CO pressure is used, the CO insertion products **4a**,**b** start to form. Similarly, the reaction of **2c**,**d**/$[Li(Et_2O)_{2.4}][B(C_6F_5)_4]$ mixtures with CO (1 atm) at −78 °C yields CO adducts **3c**,**d**. Complexes **3a**−**d** are also formed directly by the reaction of **1a**−**d** and $[Li(Et_2O)_{2.4}][B(C_6F_5)_4]$ in the presence of CO at −78 °C. The reaction of **2a**−**d**/$[Li(Et_2O)_{2.4}][B(C_6F_5)_4]$ mixtures with 1 atm of CO at 23 °C rapidly yields the acyl cations $[L_2Pd\{C(=O)Me\}(CO)][B(C_6F_5)_4]$ (**4a**−**d**). **4a**−**c** are stable at 23 °C for hours, but **4d** decomposes rapidly under these conditions.

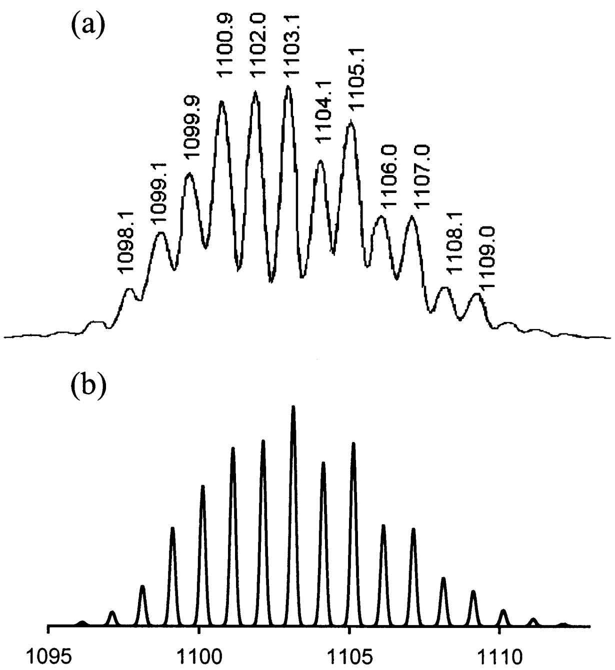


Figure 2. (a) Observed and (b) calculated molecular ion envelopes from ESI-MS spectra of the $\{(dppp)PdMe\}_2(\mu$-$Cl)^+$ cation of **2c**.

The NMR spectra of the cations of **3c**,**d** and **4c**,**d** are nearly identical to those of the corresponding B{3,5-$(CF_3)_2$-$C_6H_3\}_4^-$ salts.[14,19] For **3a**,**b**, the Pd−*Me* ^1H NMR resonances appear at δ 1.30 and 0.98, respectively, and the Pd−*C*O ^{13}C NMR resonances both appear at δ 176.0. These data are very similar to those reported for (bipy)Pd(Me)(CO)$^+$ (^1H, δ 1.49; ^{13}C, δ 176.0)[7] and (phen)Pd(Me)(CO)$^+$ (^1H, δ 1.66; ^{13}C, δ 176.3).[7,20] Key NMR data for **4a**,**b** include PdC(=O)*Me* ^1H NMR resonances at δ 2.81 and 2.82, respectively, and Pd*C*(=O)Me ^{13}C NMR resonances at δ 218.9 and 218.6. The Pd−*C*O ^{13}C NMR resonances for **4a**,**b** appear at δ 172.5. These data are similar to results for (phen)Pd{C(=O)Me}(CO)$^+$ (^1H, δ 2.92; ^{13}C, δ 216.5, 173.0).[7,20]

Reaction of 3a−d and 4a−d with VC. NMR studies show that **3a**−**d** react with VC above −40 °C to yield the O-chelated insertion products $[L_2Pd\{CHClCH_2C(=O)Me\}][B(C_6F_5)_4]$ (**5a**−**d**; Scheme 2). This reaction proceeds by VC-induced CO insertion to yield the interme-

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[17] The ^1H and ^{13}C NMR spectra of in situ generated **2a**−**d** at −70 °C contain only one set of Et_2O signals which are slightly different from those of free Et_2O under the same conditions, probably due to fast exchange of Li^+−OEt_2 and free Et_2O.

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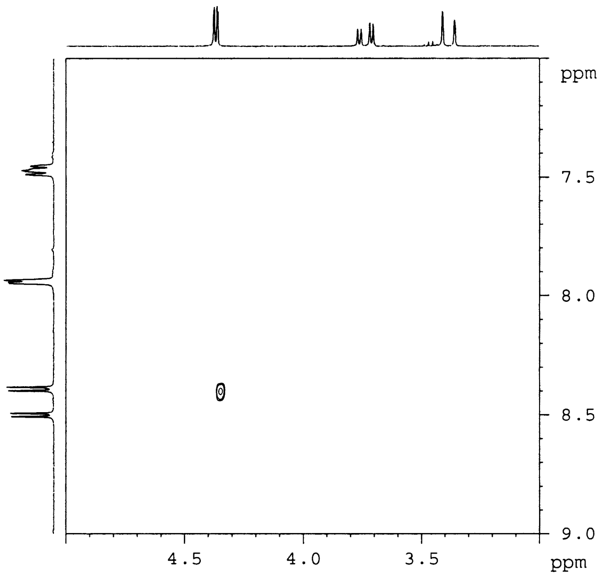
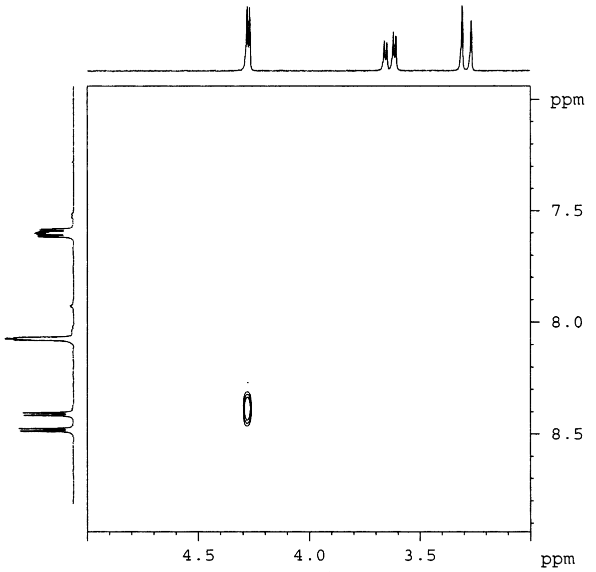
diate acyl VC complex $L_2Pd\{C(=O)Me\}(VC)^+$ (not observed), which in turn undergoes VC 2,1-insertion. Similarly, **4a**−**d** react with VC above −40 °C to yield **5a**−**d**. These reactions occur in the presence of LiCl and free Et_2O; therefore, **5a**−**d** can be synthesized on a preparative scale in a one-pot procedure by sequential treatment of **1a**−**d** with $[Li(Et_2O)_{2.4}][B(C_6F_5)_4]$, CO, and VC. Complexes **5a**−**d** are isolated as analytically pure solids by filtration to remove LiCl and vacuum drying to remove Et_2O.

Spectroscopic Studies of $[L_2Pd\{CHClCH_2C(=O)Me\}][B(C_6F_5)_4]$ (5a−d). NMR studies establish that **5a**−**d** adopt chelated structures with α-Cl substituents. For **5a**, the $-CH_2-$ ^1H NMR resonances are easily identified at δ 3.71 and 3.35 because they exhibit large $^1H-^1H$ geminal coupling constants (J = 20 Hz) characteristic of a CH_2 unit in a five-membered ring.[21] The δ 3.71 resonance exhibits vicinal coupling with a resonance at δ 4.34, which enables assignment of the latter as the −CHCl− resonance. This assignment of the −CHCl− resonance was confirmed by DEPT and HMQC experiments. The NOESY spectrum of **5a** (Figure 3a) exhibits a cross-peak between the −CHCl− resonance and a Me_2bipy ortho-H resonance (δ 8.39), which establishes that the −C*H*Cl− unit is α to Pd. Similarly, for **5b**, the $-CH_2-$ (δ 3.71, 3.37) and −CHCl− (δ 4.35) ^1H NMR resonances are identified by multiplicity analysis and DEPT and HMQC experiments. The NOESY spectrum of **5b** (Figure 3b) exhibits a cross-peak between the −CHCl− resonance and a $^tBu_2$bipy ortho-H resonance (δ 8.46), which, following the same argument for **5a**, establishes that the −C*H*Cl− unit is α to Pd.

The ^1H NMR spectra of **5c** and **5d** are complicated by $^1H-^{31}P$ coupling, and assignments of the $-CHClCH_2-$ resonances were made with the aid of ^{13}C NMR data. For **5c**, the −*C*HCl− ^{13}C resonance, which is the only aliphatic *C*H resonance in the spectrum, is identified at δ 69.2 by a DEPT-135 experiment (Figure 4a,b). This resonance appears as a doublet of doublets due to coupling to ^{31}P. The J_{PC} values (113 and 8 Hz) are in the range for $^2J_{PC}$(trans) and $^2J_{PC}$(cis) values for square-planar $(R_3P)_2Pd(R)(L)^+$ species and thus establish that the −CHCl− unit is α to Pd. If the −CHCl− unit were β to Pd, much smaller J_{PC} values would be expected.[22] The Pd*C*HCl− resonance is correlated with a ^1H NMR resonance at δ 3.16 in the HMQC spectrum, which is thus assigned to PdC*H*Cl−. The ^1H PdC*H*Cl− resonance exhibits a cross-peak with a P*Ph* resonance in the NOESY spectrum, which confirms the $PdCHClCH_2-$ connectivity (Figure 5a). For **5d**, the −*C*HCl− ^{13}C resonance is identified at δ 59.8 (J_{PC} = 120, 2 Hz) by the DEPT-135 spectrum (Figure 4c,d). This resonance is correlated with a ^1H NMR resonance at δ 3.98 in the HMQC spectrum, and the latter is correlated with P*Me* resonances at δ 1.69 and 1.66 in the NOESY spectrum (Figure 5b), which establishes that the −C*H*Cl− unit is α to Pd.



(a) **5a**; L_2 = Me_2bipy



(b) **5b**; L_2 = $^tBu_2$bipy

Figure 3. Partial NOESY spectra of $[L_2Pd\{CHClCH_2C(=O)Me\}][B(C_6F_5)_4]$ complexes: (a) complex **5a**; (b) complex **5b**. In each case the correlation between the −C*H*Cl and ortho R_2bipy resonances establishes that the Cl is α to Pd.

The coordination of the acyl oxygen in **5a**−**d** is established by the presence of low-field carbonyl ^{13}C NMR resonances (δ 234−238), which are shifted downfield from the free ketone region (δ 206−218),[23] as observed previously for analogous non-halogen-substituted Pd chelate complexes (δ 232−245).[2,7,20,24]

Reactivity of $[L_2Pd\{CHClCH_2C(=O)Me\}][B(C_6F_5)_4]$ (5a−d). Complexes **5a**−**d** are remarkably stable. These compounds are stable in C_6D_5Cl solvent up to 85

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[21] For example, geminal J_{HH} values are −21.5 Hz for 4-cyclopentene-1,3-dione and −22.3 Hz for fluorene: Lambert, J. B.; Shurvell, H. F.; Lightner, D. A.; Cooks, R. G. *Organic Structural Spectroscopy*; Prentice-Hall: Englewood Cliffs, NJ, 1998; pp 70−74.

[22] (a) Mann, B. E.; Taylor; B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981; p 23. (b) For example, for $(dppp)Pd\{CH_2CH_2C(=O)Me\}^+$, $^2J_{PC}$(trans) = 89 Hz for C_α ($^2J_{PC}$(cis) not observed) and $^3J_{PC}$(trans) = 6 Hz for C_β ($^2J_{PC}$(cis) not observed).[14,19]

[23] Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy: High-Resolution Methods and Applications in Organic Chemistry and Biochemistry*, 3rd ed.; VCH: Weinheim, Germany, 1987.

[24] Markies, B. A.; Verkerk, K. A. N.; Rietveld, M. H. P.; Boersma, J.; Kooijman, H.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1993**, 1317.

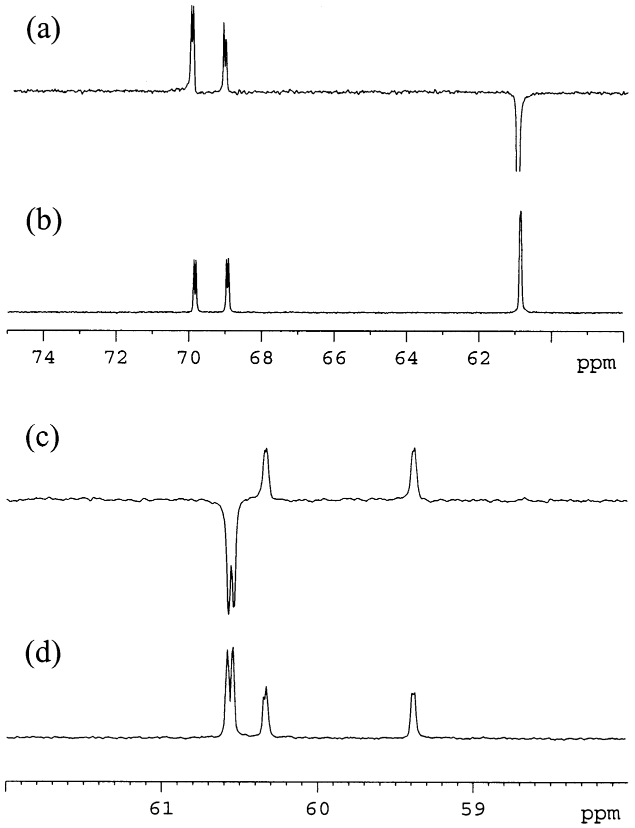
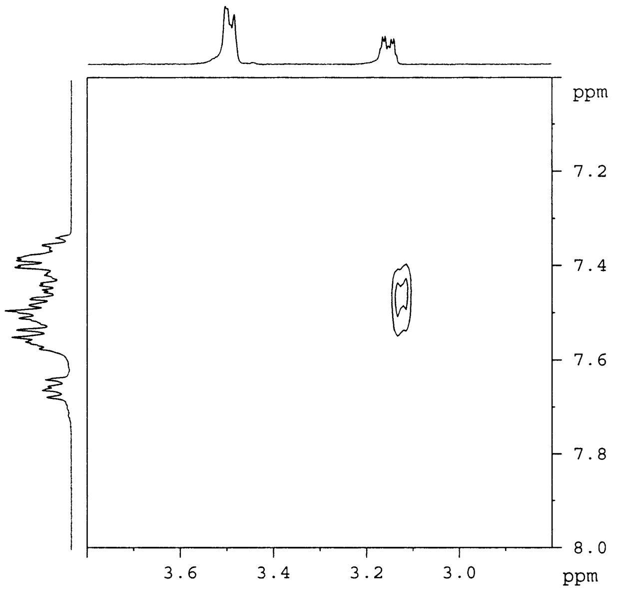


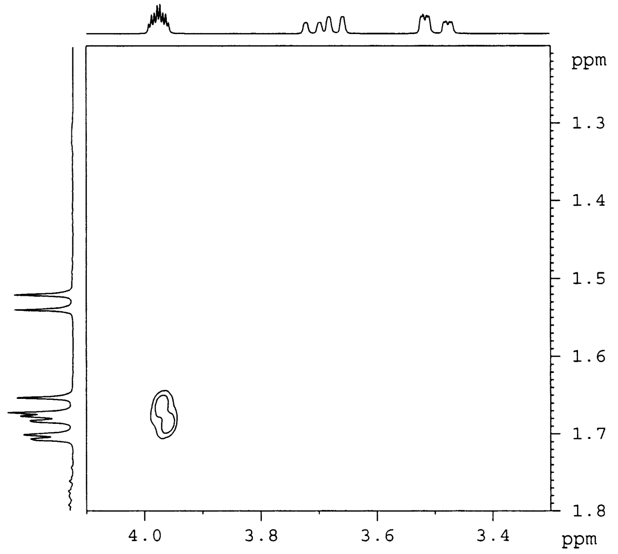
Figure 4. Partial ^{13}C NMR spectra of VC insertion products: (a) DEPT-135 and (b) ^{13}C{^{1}H} spectra of [(dppp)Pd{CHClCH$_2$C(=O)Me}][B(C$_6$F$_5$)$_4$] (**5c**); (c) DEPT-135 and (d) ^{13}C NMR spectra of [(dmpe)Pd{CHClCH$_2$C(=O)Me}][B(C$_6$F$_5$)$_4$] (**5d**).

°C but decompose to unidentified products above this temperature. Compounds **5a**,**c** do not react with CO, VC, VC/CO mixtures, C$_2$H$_4$, or C$_2$H$_4$/CO mixtures up to 85 °C. Additionally, the thermal decomposition of **5a**,**c** above 85 °C is unaffected by these substrates. The reactions of **5a** with VC/CO in the presence of AlCl$_3$, B(C$_6$F$_5$)$_3$, or PPh$_3$ were also investigated in an attempt to open the O-chelate ring. However, no insertion of VC or CO was observed and **5a** decomposes to unidentified products under these conditions.

Molecular Structure and Reactivity of 5b. The molecular structures of **5a** and **5b**·CH$_2$Cl$_2$ were determined by X-ray diffraction. ORTEP views of the (^{t}Bu$_2$-bipy)Pd{CHClCH$_2$C(=O)Me}$^+$ cation of **5b** are shown in Figure 6, and selected metrical parameters are listed in Table 1. The structure of **5a** is very similar to that of **5b** and is described in the Supporting Information. The cation of **5b** exhibits square-planar geometry with only a slight deviation (0.0266 Å) of Pd from the plane defined by N(1), N(2), C(19), and O(1). The ^{t}Bu$_2$bipy ligand is slightly twisted around the C(5)−C(6) bond such that the dihedral angle N(1)−C(5)−C(6)−N(2) is 7.9° and C(5) and C(6) deviate from the Pd(1)−N(1)−N(2) plane by −0.025 and 0.071 Å, respectively. The β-keto-alkyl chelate ring adopts an envelope conformation with C(20) and C(21) deviating from the Pd(1)−O(1)−C(19) plane by 0.642 and 0.321 Å, respectively.



(a) L$_2$ = dppp



(b) L$_2$ = dmpe

Figure 5. Partial NOESY spectra of [L$_2$Pd{CHClCH$_2$C(=O)Me}][B(C$_6$F$_5$)$_4$] complexes: (a) complex **5c**; (b) complex **5d**. In each case the correlation between the −C*H*Cl and P−R resonances establishes that the Cl is α to Pd.

The Pd−O (2.045 Å) and Pd−C (2.001 Å) bond distances of **5b** are at the short end of the ranges observed for Pd−O distances (2.028−2.155 Å) and Pd−C distances (2.001−2.068 Å) in analogous *nonhalogenated* O-chelated complexes which insert CO (Figures 7−9). This comparison indicates that the chelate ring of **5b** is unusually tight and suggests that the resistance of **5b** to insertion reactions may reflect a low tendency of this species to form chelate-opened (^{t}Bu$_2$bipy)Pd{CHClCH$_2$C(=O)Me}(substrate)$^+$ intermediates.[25,26] It should be

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[25] The insertion of imines into L$_n$Pd{C(=O)R}$^+$ species (M = Pd, Ni) produces O-chelated L$_n$MCH$_2$N(R′)C(=O)R$^+$ species, which are resistant to further CO or imine insertion. This lack of reactivity was ascribed to strong O chelation, which inhibits coordination of substrates. (a) Sen, A. *Pure Appl. Chem.* **2001**, *73*, 251. (b) Davis, J. L.; Arndtsen, B. A. *Organometallics* **2000**, *19*, 4657. (c) Cavallo, L. *J. Am. Chem. Soc.* **1999**, *121*, 4238. (d) Kacker, S.; Kim, J. S.; Sen, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 1251. (e) Dghaym, R. D.; Yaccato, K. J.; Arndtsen, B. A. *Organometallics* **1998**, *17*, 4. (f) Davis, J. L.; Arndtsen, B. A. *Organometallics* **2000**, *19*, 4657.

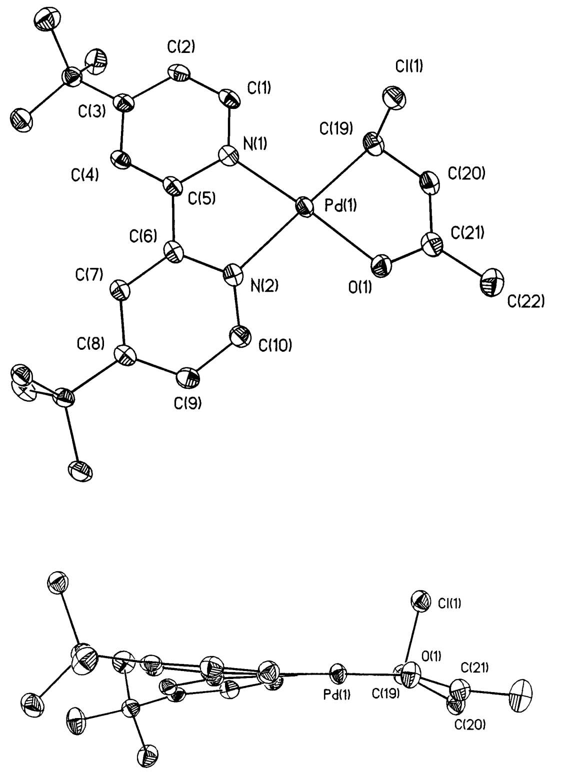

Figure 6. ORTEP views of the (^{t}Bu$_2$bipy)Pd{CHClCH$_2$C(=O)Me}$^+$ cation of **5b**. H atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 5b·CH$_2$Cl$_2$

Pd(1)−N(1)	2.013(3)	Pd(1)−N(2)	2.076(3)
Pd(1)−O(1)	2.045(3)	Pd(1)−C(19)	2.001(3)
C(19)−C(20)	1.521(4)	C(19)−Cl(1)	1.819(3)
C(20)−C(21)	1.472(4)	C(21)−C(22)	1.473(5)
C(21)−O(1)	1.241(4)		
N(1)−Pd(1)−N(2)	80.2(1)	C(15)−O(1)−Pd(1)	115.4(2)
C(13)−Pd(1)−N(1)	99.4(1)	C(13)−Pd(1)−O(1)	82.6(1)
N(1)−Pd(1)−O(1)	177.9(1)	C(13)−Pd(1)−N(2)	179.6(2)
O(1)−Pd(1)−N(2)	97.8(1)	O(1)−C(15)−C(16)	120.6(3)
O(1)−C(15)−C(14)	118.1(3)	C(16)−C(15)−C(14)	121.3(3)
C(15)−C(14)−C(13)	110.8(3)	C(14)−C(13)−Cl(2)	109.4(3)
C(14)−C(13)−Pd(1)	107.6(2)	Cl(2)−C(13)−Pd(1)	108.0(2)

noted, however, that neither the short Pd−O nor the short Pd−C bond *alone* can explain the low reactivity of **5b**. For example, (bipy)Pd{C$_7$H$_{10}$C(=O)Me}$^+$ (entry 2, Figure 7) has a slightly shorter Pd−O bond than **5b** but readily inserts CO (1 atm) at −30 °C. Similarly, {Ph$_2$PNHC(O)Me}Pd{CH$_2$CH$_2$C(=O)Me}$^+$ (entry 3) and {*o*-(diphenylphosphino)-*N*-benzaldimine}Pd{CH$_2$CH$_2$C(=O)CH$_2$CH$_2$C(=O)Me}$^+$ (entry 8) exhibit essentially the same Pd−C bond distances as **5b**, but both are active ethylene/CO copolymerization catalysts. A second factor that likely influences the reactivity of **5a**−**d** is the α-Cl substituent, which is expected to strengthen the Pd−C bond and reduce the nucleophilic character and migratory aptitude of the Pd−CHClCH$_2$C(=O)Me group. It is well established that electron-withdrawing substituents inhibit CO insertion into M−alkyl and M−aryl bonds.[27] For example, **3c** readily inserts CO but (dppp)Pd(n-C$_3$F$_7$)(CO)$^+$ does not.[28] Similarly {H(hexyl)C(mim)$_2$}Pd(CHCl$_2$)(CO)$^+$ (mim = *N*-methylimidazol-2-yl) does not insert CO but analogous nonhalogenated {HRC(mim)}Pd(Me)(CO)$^+$ species readily react to form {HRC(mim)}Pd{C(=O)Me}(CO)$^+$.[29] Therefore, we propose that both the tight chelation and low migratory aptitude of the −CHClCH$_2$C(=O)Me group contribute to the low reactivity of **5a**−**d**.

Regiochemistry of Olefin Insertions of Pd−Acyl Complexes. Olefin insertions of L$_2$Pd(R)(olefin)$^+$ and related group 10 metal *alkyl* species have been investigated by DFT methods by several groups, and several factors that influence the regioselectivity of these reactions have been identified.[30] Olefin "distortion energies", i.e., the energy required to distort the coordinated olefin from its structure in the olefin complex to that in the insertion transition state, and steric interactions between the olefin substituents and the migrating R group in the transition state both favor 2,1-insertion. On the other hand, asymmetry in the Pd−olefin bonding in the olefin complex (i.e., $d(\mathrm{Pd{-}C_{substituted}}) > d(\mathrm{Pd{-}C_{unsubstituted}})$) and steric interactions between the coordinated olefin and the ancillary ligand (L$_2$) favor 1,2-insertion. These same factors are also expected to be important in olefin insertion of L$_2$Pd{C(=O)R}(olefin)$^+$ species.[31]

Previous studies show that propylene reacts with (dppp)Pd{C(=O)R}$^+$ by competitive 2,1- and 1,2-insertions (relative frequency 1:3), which lead to regioirregular CO/propylene copolymer.[1a] However, when bulkier ancillary ligands are used, 1,2-insertion predominates and more highly regioregular CO/propylene copolymer is formed; e.g., >99% selectivity for 1,2-insertion is observed for L$_2$ = 1,3-bis(diisopropylphosphino)propane).[32,33] Our results show that (dppp)Pd{C(=O)Me}(VC)$^+$ and the sterically less crowded R$_2$bipy and dmpe analogues undergo exclusive VC 2,1-insertion, yielding L$_2$Pd{CHClCH$_2$C(=O)Me)}$^+$ products. VC is similar in size to propylene.[34] However, the presence of the

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[26] Pd(II)-catalyzed copolymerization of ethylene and acrylates is inhibited by O chelation of the ester group of the acrylate: Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888.

[27] (a) Axe, F. U.; Marynick, D. S. *J. Am. Chem. Soc.* **1988**, *110*, 3728. (b) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1986**, *108*, 6136. (c) Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115. (d) Blake, D. M.; Winkelman, A.; Chung, Y. L. *Inorg. Chem.* **1975**, *14*, 1326. (e) Calderazzo, F.; Noack, K. *Coord. Chem. Rev.* **1966**, *1*, 118.

[28] Shen, H.; Jordan, R. F. Unpublished results.

[29] Shen, H.; Burns, C. T.; Jordan, R. F. Unpublished results.

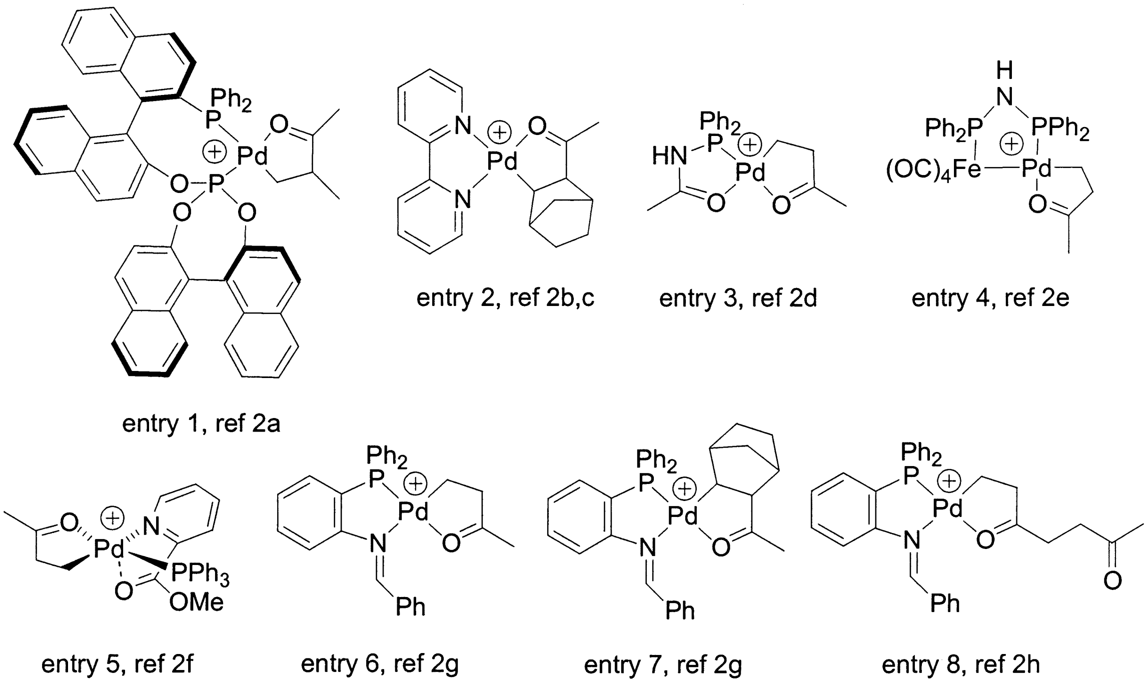
[30] (a) Michalak, A.; Ziegler, T. *J. Am. Chem. Soc.* **2001**, *123*, 12266. (b) Michalak, A.; Ziegler, T. *Organometallics* **1999**, *18*, 3998. (c) Michalak, A.; Ziegler, T. *Organometallics* **2000**, *19*, 1850. (d) Deubel, D. V.; Ziegler, T. *Organometallics* **2002**, *21*, 4432. (e) Deubel, D. V.; Ziegler, T. *Organometallics* **2002**, *21*, 1603. (f) Philipp, D. M.; Muller, R. P.; Goddard, W. A., III; Storer, J.; McAdon, M.; Mullins, M. *J. Am. Chem. Soc.* **2002**, *124*, 10198. (g) von Schenck, H.; Strömberg, S.; Zetterberg, K.; Ludwig, M.; Åkermark, B.; Svensson, M. *Organometallics* **2001**, *20*, 2813.

[31] See ref 25c and: (a) Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *118*, 7337. (b) Margl, P.; Zielger, T. *Organometallics* **1996**, *15*, 5519.

[32] Batistini, A.; Consiglio. G.; Suter, U. W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 303.

[33] Similarly, sterically open L$_2$Pd{C(=O)Me}$^+$ (L$_2$ = phen, bipy, bisoxazoline, etc.) species react with styrene by 2,1-insertion, whereas the bulky acyl complex {(*R,S*)-BINAPHOS}Pd{C(=O)Me}$^+$ ((*R,S*)-BINAPHOS = (*R,S*)-2-(diphenylphosphino)-1,1′-binaphthalen-2′-yl 1,1′-binaphthalene-2,2′-diyl phosphite) undergoes exclusive styrene 1,2-insertion in CO/styrene copolymerization: Nozaki, K.; Komaki, H.; Kawashima, Y.; Hiyama, T.; Matsubara, T. *J. Am. Chem. Soc.* **2001**, *123*, 534 and references therein.

[34] The C$_{sp^2}$−C distance (1.50 Å) is shorter than the C$_{sp^2}$−Cl distance (1.73 Å), but the van der Waals radius of CH$_3$ (2.0 Å) is larger than that of Cl (1.8 Å). (a) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 3rd ed.; Wiley: New York, 1985. (b) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins: New York, 1993. (c) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.



entry 1, ref 2a

entry 2, ref 2b,c

entry 3, ref 2d

entry 4, ref 2e

entry 5, ref 2f

entry 6, ref 2g

entry 7, ref 2g

entry 8, ref 2h

Figure 7. Crystallographically characterized O-chelated $L_2PdCHRCHR'C(=O)R''^+$ complexes which insert CO. Pd−O and Pd−C distances are compared in Figures 8 and 9.

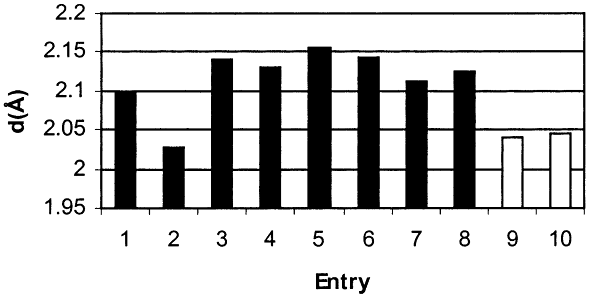


Figure 8. Pd−O bond distances of O-chelated $L_2PdCHR\text{-}CHR'C(=O)R''^+$ complexes. Entry assignments are given in Figure 7: entry 9, **5a**; entry 10, **5b**.

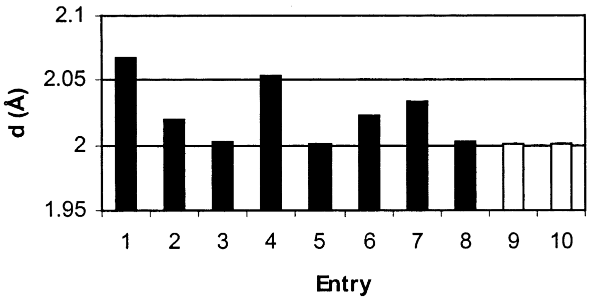


Figure 9. Pd−C bond distances of O-chelated $L_2PdCHR\text{-}CHR'C(=O)R''^+$ complexes. Entry assignments are given in Figure 7: entry 9, **5a**; entry 10, **5b**.

electron-withdrawing Cl substituent in VC provides an additional electronic driving force for 2,1-insertion, because the alternative 1,2-insertion product $L_2Pd\{CH_2\text{-}CHClC(=O)R)\}^+$ would be destabilized by placement of the electron-withdrawing Cl and acyl substituents on the same (β) carbon. Similar electronic effects may be important in the reactions of $L_2Pd\{C(=O)R\}^+$ species with methyl acrylate, methyl vinyl ketone, and vinyl acetate, for which exclusive 2,1-insertion has been observed.[2d,e,g,h,7,8]

Conclusions

Cationic $L_2Pd\{C(=O)Me\}^+$ acyl species (L = R_2bipy, dppp, dmpe) undergo VC 2,1-insertion to yield the O-chelated $L_2Pd\{CHClCH_2C(=O)Me\}^+$ complexes **5a**−**d**. The 2,1-regiochemistry is favored in part because the alternative 1,2-insertion products would be destabilized by placement of the electron-withdrawing Cl and acyl substituents on the same carbon. In contrast to analogous nonhalogenated $L_2Pd\{CH_2CH_2C(=O)R\}^+$ species, **5a**−**d** do not react with CO, due to the stability of the chelate ring and the low migratory aptitude of the $-CHClCH_2C(=O)Me$ group.

Experimental Section

General Procedures. All manipulations were performed using drybox or Schlenk techniques under a nitrogen atmosphere or on a high-vacuum line, unless otherwise indicated. Solvents were distilled from appropriate drying/deoxygenating agents (Et_2O, sodium benzophenone ketyl; CH_2Cl_2 and C_6H_5Cl, CaH_2; CD_2Cl_2 and C_6D_5Cl, P_4O_{10}). Pentane and benzene were purified by passage through columns of activated alumina and BASF R3-11 oxygen removal catalyst. Nitrogen was purified by passage through columns containing activated molecular sieves and Q-5 oxygen scavenger. $[Li(Et_2O)_n][B(C_6F_5)_4]$ was provided by Boulder Scientific, and both were used as received. The Et_2O content of the $[Li(Et_2O)_n][B(C_6F_5)_4]$ salt was determined by ^1H NMR with C_6Me_6 as internal standard (n = 2.4 or 2.8, depending on the batch from the supplier). (cod)Pd(Me)Cl,[12a] $^tBu_2$bipy,[35] (dppp)Pd(Me)Cl (**1c**),[12b] and (dmpe)Pd(Me)Cl (**1d**)[12c] were prepared by literature procedures. All other chemicals were purchased from Aldrich and used without further purification. Elemental analyses were performed by Midwest Microlab or Galbraith Laboratories, Inc.

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[35] Belser, P.; Zelewsky, A. *Helv. Chim. Acta* **1980**, *63*, 1675.

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 vs $SiMe_4$ and were determined by reference to residual ^{1}H and ^{13}C solvent signals. ^{11}B chemical shifts are referenced to external $Et_2O{\cdot}BF_3$. ^{19}F chemical shifts are reported relative to $CFCl_3$. ^{31}P chemical shifts are reported vs H_3PO_4 (85%). Coupling constants are reported in Hz.

The NMR spectra of cationic complexes contain signals for the free $B(C_6F_5)_4^-$ anion. $^{13}C\{^1H\}$ NMR (CD_2Cl_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_2Cl_2): δ −132.1 (br s, 8F, F_{ortho}), −161.3 (t, $J = 21$, 4F, F_{para}), −165.2 (t, $J = 17$, 8F, F_{meta}). ^{19}F NMR (CD_2Cl_2, −70 °C): δ −132.5 (br s, 8F, F_{ortho}), −161.7 (t, $J = 21$, 4F, F_{para}), −164.9 (t, $J = 17$, 8F, F_{meta}). ^{11}B NMR (CD_2Cl_2): δ −16.1 (br s). ^{11}B NMR (CD_2Cl_2, −70 °C): δ −15.8 (br s).

Unless otherwise noted, Et_2O does not coordinate to the Pd species described herein and exhibits NMR spectra characteristic of free Et_2O. ^{1}H NMR (CD_2Cl_2): δ 3.43 (q, $J = 7$, 4H), 1.15 (t, $J = 7$, 6H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 66.0 (s), 15.5 (s). ^{1}H NMR (CD_2Cl_2, −70 °C): δ 3.35 (q, $J = 7$, 4H), 1.09 (t, $J = 7$, 6H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −70 °C): δ 65.7 (s), 15.2 (s).

Electrospray mass spectra were recorded on freshly prepared samples (ca. 1 mg/mL in CH_2Cl_2) using an Agilent 1100 LC-MSD spectrometer incorporating a quadrupole mass filter with a m/z range of 0−3000. A 5 μL sample was injected by flow injection using an autosampler. Purified nitrogen was used as both 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 70 V.

$(Me_2bipy)Pd(Me)Cl$ (1a). A Schlenk flask was charged with (cod)Pd(Me)Cl (268 mg, 1.01 mmol) and Me_2bipy (186 mg, 1.01 mmol), and CH_2Cl_2 (15 mL) was added by cannula. A yellow precipitate formed rapidly. The reaction mixture was stirred at 23 °C for 2 h, and the volatiles were removed under vacuum. The solid was washed with ether (3 × 10 mL) to yield $(Me_2bipy)Pd(Me)Cl$ as a pale yellow solid (307 mg, 89%). ^{1}H NMR (CD_2Cl_2): δ 8.91 (d, $J = 5$, 1H), 8.44 (d, $J = 6$, 1H), 7.91 (s, 1H), 7.85 (s, 1H), 7.35 (d, $J = 6$, 1H), 7.32 (d, $J = 5$, 1H), 2.51 (s, 3H, bipy−*Me*), 2.50 (s, 3H, bipy−*Me*), 0.83 (s, 3H, Pd*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 157.0, 153.1, 151.2, 151.0, 148.6, 148.4, 127.5, 127.3, 123.6, 122.3, 21.7 (bipy−*Me*), 21.6 (bipy−*Me*), −2.0 (Pd*Me*). Anal. Calcd for $C_{13}H_{15}ClN_2Pd$: C, 45.77; H, 4.43; N, 8.21. Found: C, 45.70; H, 4.63; N, 8.12.

$(^tBu_2bipy)Pd(Me)Cl$ (1b). This compound was prepared from ^{t}Bu$_2$bipy and (cod)Pd(Me)Cl using the procedure for **1a**. Yield: 1.41 g, 89%, pale yellow solid. ^{1}H NMR (CD_2Cl_2): δ 9.00 (d, $J = 6$, 1H), 8.54 (d, $J = 6$, 1H), 8.04 (d, $J = 2$, 1H), 7.99 (d, $J = 2$, 1H), 7.56 (dd, $J = 6, 2$, 1H), 7.52 (dd, $J = 6, 2$, 1H), 1.43 (s, 9H), 1.41 (s, 9H), 0.85 (s, 3H, Pd*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 163.7, 163.6, 157.3, 153.4, 148.8, 148.6, 124.0, 123.9, 119.6, 118.3, 35.8 (CMe$_3$), 35.7 (CMe$_3$), 30.5 (CMe_3), 30.4 (CMe_3), −2.0. Anal. Calcd for $C_{19}H_{27}ClN_2Pd$: C, 53.65; H, 6.40; N, 6.59. Found: C, 53.56; H, 6.58; N, 6.20.

Generation of $[\{(Me_2bipy)PdMe\}_2(\mu\text{-}Cl)][B(C_6F_5)_4]$ (2a). A valved NMR tube was charged with **1a** (5 mg, 0.015 mmol) and $[Li(Et_2O)_{2.4}][B(C_6F_5)_4]$ (13 mg, 0.015 mmol), and CD_2Cl_2 (0.5 mL) was added by vacuum transfer. The NMR tube was briefly warmed to 23 °C and vigorously shaken. A slurry of a white solid in a pale yellow supernatant formed within 1 min. The unreacted $[Li(Et_2O)_{2.4}][B(C_6F_5)_4]$, free Et_2O, and LiCl coproducts were not removed. The ^{1}H NMR spectrum established that **2a** had formed quantitatively. Although the product is stable at 23 °C for several hours, the NMR tube was maintained at −78 °C until further reactions were carried out. ^{1}H NMR (CD_2Cl_2, −70 °C): δ 8.76 (d, $J = 5$, 1H), 8.33 (d, $J = 5$, 1H), 7.94 (s, 1H), 7.91 (s, 1H), 7.39 (d, $J = 5$, 2H), 7.36 (d, $J = 5$, 2H), 2.50 (s, 3H, bipy−*Me*), 2.49 (s, 3H, bipy−*Me*), 0.99 (s, 3H, Pd*Me*).[36] $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −70 °C): δ 156.0, 152.1, 151.9, 151.6, 147.8, 147.3, 127.4, 127.2, 123.5, 122.4, 21.4 (bipy−*Me*), 21.3 (bipy−*Me*), 3.1 (Pd*Me*). Positive ion ESI-MS: m/z 645.0, $\{(Me_2bipy)PdMe\}_2(\mu\text{-}Cl)^+$.

Generation of $[\{(^tBu_2bipy)PdMe\}_2(\mu\text{-}Cl)][B(C_6F_5)_4]$ (2b). This compound was generated quantitatively from **1b** (10 mg, 0.024 mmol) and $[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$ (21 mg, 0.024 mmol) using the procedure for **2a**. ^{1}H NMR (CD_2Cl_2, −70 °C): δ 8.78 (d, $J = 5$, 1H), 8.35 (d, $J = 5$, 1H), 8.08 (s, 1H), 8.05 (s, 1H), 7.54 (d, $J = 5$, 1H), 7.50 (d, $J = 5$, 1H), 1.36 (s, 9H, CMe_3), 1.35 (s, 9H, CMe_3), 0.92 (s, 3H, Pd*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −70 °C): δ 163.9, 163.6, 156.3, 152.3, 148.0, 147.4, 123.9, 123.8, 119.8, 118.7, 35.3 (CMe$_3$), 35.2(CMe$_3$), 29.6 (CMe_3), 29.5 (CMe_3), 3.1 (Pd*Me*). Positive ion ESI-MS: m/z 813.2, $\{(^tBu_2bipy)PdMe\}_2(\mu\text{-}Cl)^+$.

Generation of $[\{(dppp)PdMe\}_2(\mu\text{-}Cl)][B(C_6F_5)_4]$ (2c). This compound was generated quantitatively from **1c** (10 mg, 0.018 mmol) and $[Li(Et_2O)_{2.4}][B(C_6F_5)_4]$ (15 mg, 0.018 mmol) using the procedure for **2a**. ^{1}H NMR (CD_2Cl_2, −70 °C): δ 7.54−7.21 (m, 20H, Ph), 2.48 (m, 2H, PCH_2), 2.33 (m, 2H, PCH_2), 1.67 (m, 2H, CH_2), 0.47 (dd, $J = 7, 3$, 3H, Pd*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −70 °C): δ 133.2 (d, $J = 11$), 133.0 (d, $J = 11$), 131.1 (s), 130.9 (d, $J = 36$), 130.2 (s), 129.0 (d, $J = 55$), 128.5 (d, $J = 11$), 128.2 (d, $J = 9$), 28.3 (dd, $J = 32, 9$, PCH$_2$), 26.9 (d, $J = 21$, PCH$_2$), 18.0 (s, CH$_2$), 16.8 (d, $J = 94$, Pd*Me*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −70 °C): δ 28.8 (d, $J = 49$), −4.1 (d, $J = 49$). Positive ion ESI-MS: m/z 1101.1, $\{(dppp)PdMe\}_2(\mu\text{-}Cl)^+$.

Generation of $[\{(dmpe)PdMe\}_2(\mu\text{-}Cl)][B(C_6F_5)_4]$ (2d). This compound was generated quantitatively from **1d** (10 mg, 0.033 mmol) and $[Li(Et_2O)_{2.4}][B(C_6F_5)_4]$ (28 mg, 0.033 mmol) using the procedure for **2a**. **2d** decomposes within 5 min at 23 °C, and the NMR tube was maintained at −78 °C until further reactions were carried out. ^{1}H NMR (CD_2Cl_2, −70 °C): δ 1.92 (m, 2H, CH_2), 1.62 (m, 2H, CH_2), 1.51 (d, $J = 12$, 6H, P*Me*), 1.40 (d, $J = 9$, 6H, P*Me*), 0.29 (d, $J = 7$, 3H, Pd*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −70 °C): δ 29.8 (dd, $J = 36, 23$, CH$_2$), 23.7 (dd, $J = 28, 8$, CH$_2$), 12.8 (d, $J = 35$, P*Me*), 11.5 (d, $J = 18$, P*Me*), 5.9 (d, $J = 104$, Pd*Me*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −70 °C): δ 42.4 (d, $J = 23$), 25.8 (d, $J = 23$). Positive ion ESI-MS: m/z 577.0, $\{(dmpe)PdMe\}_2(\mu\text{-}Cl)^+$.

Generation of $[(Me_2bipy)Pd(Me)(CO)][B(C_6F_5)_4]$ (3a). A valved NMR tube containing a CD_2Cl_2 solution of **2a** and 1 equiv of $[Li(Et_2O)_{2.4}][B(C_6F_5)_4]$, generated as described above, was exposed to CO (60 mm Hg) for 5 min at −78 °C. The NMR tube was vigorously shaken at −78 °C. A slurry of a fine white solid in a pale yellow supernatant was obtained. The NMR tube was maintained at −78 °C until further characterization and reactions were carried out. The ^{1}H NMR spectrum established that **3a** had formed quantitatively. ^{1}H NMR (CD_2Cl_2, −70 °C): δ 8.41 (d, $J = 5$, 1H), 8.37 (d, $J = 6$, 1H), 8.23 (s, 1H), 8.22 (s, 1H), 7.52 (d, $J = 6$, 1H), 7.46 (d, $J = 5$, 1H), 2.55 (s, 3H, bipy−*Me*), 2.51 (s, 3H, bipy−*Me*), 1.30 (s, 3H, Pd*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −70 °C): δ 176.0 (Pd−CO), 156.1, 155.2, 154.0, 152.1, 150.6, 146.0, 128.7, 127.8, 124.0, 123.5, 21.5 (two bipy Me), 4.5 (Pd*Me*); the assignment of the Pd−CO resonance was confirmed using ^{13}CO.

Generation of $[(^tBu_2bipy)Pd(Me)(CO)][B(C_6F_5)_4]$ (3b). This compound was quantitatively generated from **2b**, $[Li(Et_2O)_{2.4}][B(C_6F_5)_4]$, and CO and handled using the procedures for **3a**. ^{1}H NMR (CD_2Cl_2, −70 °C): δ 8.82 (d, $J = 6$, 1H), 8.39 (d, $J = 6$, 1H), 8.06 (s, 1H), 8.03 (s, 1H), 7.56 (d, $J = 6$, 1H), 7.52 (d, $J = 6$, 1H), 1.37 (s, 9H), 1.36 (s, 9H), 0.98 (s, 3H, Pd*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −70 °C): δ 176.0, 163.9, 163.3, 156.3, 152.3, 148.0, 147.5, 123.9, 123.8, 119.7, 118.6, 35.3 (CMe$_3$), 35.2 (CMe$_3$), 29.6 (CMe_3), 29.5 (CMe_3), 3.1 (Pd*Me*).

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[36] The ^{1}H NMR spectrum of **2a** generated from a 2/1 mixture of **1a** and $[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$ is nearly identical, except that the Me_2bipy ortho-H resonances are shifted slightly downfield to δ 8.83 and 8.42. For **2b**−**d**, the ^{1}H NMR spectra are the same for samples generated using 1/1 and 2/1 ratios of **1b**−**d** to $[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$.

Generation of $\mathrm{[(dppp)Pd(Me)(CO)][B(C_6F_5)_4]}$ (3c) and $\mathrm{[(dmpe)Pd(Me)(CO)][B(C_6F_5)_4]}$ (3d). These species were quantitatively generated from **2c** or **2d**, $\mathrm{[Li(Et_2O)_{2.4}][B(C_6F_5)_4]}$, and CO and handled using the procedures for **3a**, except that CO (1 atm) was applied for 5 min at −78 °C. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR data agree with literature data.[14,19]

Generation of $\mathrm{[(Me_2bipy)Pd\{C({=}O)Me\}(CO)][B(C_6F_5)_4]}$ (4a). A valved NMR tube containing a $\mathrm{CD_2Cl_2}$ solution of **2a** and 1 equiv of $\mathrm{[Li(Et_2O)_{2.4}][B(C_6F_5)_4]}$ generated as described above was exposed to CO (1 atm) for 5 min at −78 °C. The NMR tube was briefly warmed to 23 °C and vigorously shaken. A slurry of a fine white solid in a yellow supernatant was obtained. The ^{1}H NMR spectrum established that **4a** had formed quantitatively. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, −70 °C): δ 8.23 (d, J = 5, 2H), 7.98 (m, 3H), 7.44 (m, 2H), 2.81 (s, 3H, C(=O)*Me*), 2.51 (s, 3H, bipy−*Me*), 2.50 (s, 3H, bipy−*Me*). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, −70 °C): δ 218.9 (*C*(O)Me), 172.5 (Pd*C*O), 154.8, 154.0, 153.8, 151.3, 150.0, 149.4, 128.2 (2 *C*), 123.7, 123.4, 40.9 (C(O)*Me*), 21.3 (two bipy Me).

Generation of $\mathrm{[(^tBu_2bipy)Pd\{C({=}O)Me\}(CO)][B(C_6F_5)_4]}$ (4b). This compound was quantitatively generated from **2b**, $\mathrm{[Li(Et_2O)_{2.4}][B(C_6F_5)_4]}$, and CO and handled using the procedure for **4a**. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, −70 °C): δ 8.26 (d, J = 6, 1H), 8.10 (s, 1H), 8.09 (s, 1H), 8.04 (d, J = 6, 1H), 7.60 (m, 2H), 2.82 (s, 3H, C(O)*Me*), 1.35 (s, 9H, ^{t}*Bu*), 1.33 (s, 9H, ^{t}*Bu*). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, −70 °C): δ 218.6 (*C*(O)Me), 172.5 (Pd*C*O), 166.6, 165.9, 154.5, 151.7, 150.4, 149.8, 125.0, 124.9, 120.0, 119.8, 40.8 (C(=O)*Me*), 35.6 (*C*Me$_3$), 35.5 (*C*Me$_3$), 29.4 (C*Me*$_3$), 29.3 (C*Me*$_3$).

Generation of $\mathrm{[(dppp)Pd\{C({=}O)Me\}(CO)][B(C_6F_5)_4]}$ (4c) and $\mathrm{[(dmpe)Pd\{C({=}O)Me\}(CO)][B(C_6F_5)_4]}$ (4d). These species were quantitatively generated from **2c** or **2d**, $\mathrm{[Li(Et_2O)_{2.4}][B(C_6F_5)_4]}$, and CO and handled using the procedure for **4a**. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR data agree with literature data.[14,19]

$\mathrm{[(Me_2bipy)Pd\{CHClCH_2C({=}O)Me\}][B(C_6F_5)_4]}$ (5a). A Schlenk flask was charged with (Me$_2$bipy)Pd(Me)Cl (500 mg, 1.47 mmol) and $\mathrm{[Li(Et_2O)_{2.8}][B(C_6F_5)_4]}$ (1.31 g, 1.47 mmol), and $\mathrm{CH_2Cl_2}$ (40 mL) was added at −78 °C by vacuum transfer. The pale yellow slurry was vigorously stirred for 10 min and then exposed to CO (1 atm) at −78 °C for 30 min to yield a white slurry in pale yellow solution. The mixture was frozen at −196 °C and evacuated, and VC (1.47 mmol) was added by vacuum transfer from a calibrated gas bulb. The reaction mixture was thawed, stirred, and warmed to 23 °C to yield a slurry of a white solid in a yellow supernatant. The mixture was filtered, and the filtrate was dried under vacuum to afford a yellow solid (1.43 g, 91%). IR (Nujol): ν_{CO} 1623 cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 8.49 (d, J = 6, 1H), 8.39 (d, J = 6, 1H), 7.94 (s, 1H), 7.93 (s, 1H), 7.48 (d, J = 6, 2H), 7.45 (d, J = 6, 2H), 4.34 (d, J = 6, 1H, C*H*Cl), 3.71 (dd, J = 20, 6, 1H, CH*H*), 3.35 (d, J = 20, 1H, C*H*H), 2.59 (s, 3H), 2.58 (s, 3H), 2.57 (s, 3H). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 237.7 (*C*OMe), 156.4, 154.3, 154.1, 152.7, 151.1, 148.9, 128.8, 128.5, 124.3, 123.5, 61.7 (*C*H$_2$), 56.0 (*C*HCl), 28.7 (CO*Me*), 21.9 (bipy−*Me*), 21.8 (bipy−*Me*). Anal. Calcd for $\mathrm{C_{40}H_{18}BClF_{20}N_2OPd}$: C, 44.68; H, 1.69; N, 2.60. Found: C, 44.72; H, 1.68; N, 2.71.

$\mathrm{[(^tBu_2bipy)Pd\{CHClCH_2C({=}O)Me\}][B(C_6F_5)_4]}$ (5b). This compound was prepared from **1b** using the procedure for **5a**. Yield: 1.31 g, 96%, yellow solid. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 8.55 (d, J = 6, 1H), 8.46 (d, J = 6, 1H), 8.08 (m, 2H), 7.66 (dd, J = 6, 2, 1H), 7.64 (dd, J = 6, 2, 1H), 4.35 (d, J = 6, 1H, C*H*Cl), 3.71 (dd, J = 20, 6, 1H, CH*H*), 3.37 (d, J = 20, 1H, C*H*H), 2.59 (s, 3H), 1.44 (s, 18H). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 237.8 (*C*OMe), 166.7, 166.6, 156.9, 153.1, 151.4, 149.1, 125.3, 125.0, 120.5, 119.7, 61.6 (*C*H$_2$), 56.2 (*C*HCl), 36.2 (two *C*Me$_3$), 30.2 (C*Me*$_3$), 30.1 (C*Me*$_3$), 28.5 (CO*Me*). Anal. Calcd for $\mathrm{C_{46}H_{30}BClF_{20}N_2OPd}$: C, 47.65; H, 2.61; N, 2.42. Found: C, 47.76; H, 2.86; N, 2.31.

$\mathrm{[(dppp)Pd\{CHClCH_2C({=}O)Me\}][B(C_6F_5)_4]}$ (5c). This compound was prepared from **1c** using the procedure described for **5a**. Yield: 1.01 g, 88%, pink solid. The color may be due to a trace impurity; however, further purification by crystallization was unsuccessful. IR (toluene): ν_{CO} 1641 cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 7.7−7.3 (m, 20H, Ph), 3.53 (m, 2H, CHClC*H*$_2$), 3.16 (m, 1H, C*H*Cl), 2.67 (m, 2H, PC*H*$_2$), 2.46 (m, 2H, PC*H*$_2$), 2.41 (s, 3H, COMe), 2.05 (br m, 2H, PCH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 234.7 (d, J = 8, *C*OMe), 133.7 (d, J = 25), 133.5 (s), 132.7 (d, J = 11), 132.6 (d, J = 12), 132.2 (d, J = 2), 131.6 (d, J = 2), 130.1 (s), 129.9 (d, J = 18), 129.8 (d, J = 2), 129.5 (s), 129.4 (d, J = 4), 129.0 (s), 128.9 (s), 128.6(s), 127.1 (s), 126.9 (s), 69.2 (dd, J = 113, 8, *C*HCl), 60.9 (d, J = 5, CHCl*C*H$_2$), 29.2 (s, CO*Me*), 27.4 (dd, J = 34, 8, P*C*H$_2$), 25.7 (dd, J = 25, 2, P*C*H$_2$), 18.8 (s, PCH$_2$*C*H$_2$). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 21.7 (d, J = 60), −3.3 (d, J = 60). Anal. Calcd for $\mathrm{C_{55}H_{32}BClF_{20}OP_2Pd}$: C, 50.68; H, 2.47. Found: C, 50.81; H, 2.78.

Table 2. Summary of Crystallographic Data for 5b·$\mathrm{CH_2Cl_2}$

formula	$\mathrm{C_{72}H_{32}BCl_3F_{20}N_2OPd}$
fw	1244.60
cryst size (mm)	0.24 × 0.16 × 0.12
d(calcd), Mg/m^3	1.746
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	14.438(3)
b, Å	21.234(4)
c, Å	16.274(3)
β, deg	109.035(3)
V, Å^3	4716(2)
Z	4
T (K)	100
diffractometer	Bruker SMART APEX
radiation, λ (Å)	Mo Kα, 0.710 73
2θ range (deg)	1.90−25.03
data collected: h; k; l	−17 to +17; −25 to +24; −19 to +19
no. of rflns collected	40 990
no. of unique rflns	8336
no. of obsd rflns	$I > 2\sigma(I)$, 6932
R_{int}	0.0469
μ, mm^{-1}	0.684
max/min transmissn	1.0/0.658
structure soln	Patterson methods[a]
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	8336/0/683
abs cor	SADABS based onredundant diffractions
GOF on F^2	1.070
R indices ($I > 2\sigma(I)$)[b]	R1 = 0.0374, wR2 = 0.1021
R indices (all data)[b]	R1 = 0.0448, wR2 = 0.1053
max diff peak/hole (e/Å^3)	2.615/−0.745

[a] SHELXTL-Version 5.1; Bruker Analytical X-ray Systems, Madison, WI. [b] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$ and wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = q/[\sigma^2(F_o^2) + (aP)^2 + bP]$.

$\mathrm{[(dmpe)Pd\{CHClCH_2C({=}O)Me\}][B(C_6F_5)_4]}$ (5d). This compound was prepared from **1d** using the procedure described for **5a**. Yield: 282 mg, 83%, yellow solid. IR ($\mathrm{CH_2Cl_2}$) ν_{CO} 1642 cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 3.98 (m, 1H, C*H*Cl), 3.69 (m, 1H, CHClCH*H*), 3.50 (m, 1H, CHClC*H*H), 2.53 (s, 3H, C(O)*Me*), 2.08 (m, 2H, PC*H*$_2$), 1.81 (m, 2H, PCH$_2$C*H*$_2$), 1.70 (d, J = 12, 3H, P*Me*), 1.69 (d, J = 12, 3H, P*Me*), 1.66 (d, J = 10, 3H, P*Me*), 1.53 (d, J = 10, 3H, P*Me*). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 234.9 (d, J = 10, (*C*(O)Me), 60.6 (d, J = 4, CHCl*C*H$_2$), 59.8 (dd, J = 120, 2, *C*HCl), 30.4 (dd, J = 38, 19, P*C*H$_2$), 28.9 (s, C(O)*Me*), 24.6 (dd, J = 31, 7, PCH$_2$*C*H$_2$), 13.9 (d, J = 35, P*Me*), 12.6 (d, J = 34, P*Me*), 12.5 (d, J = 21, P*Me*), 12.0 (d, J = 22, P*Me*). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 34.6 (d, J = 30), 22.3 (d, J = 30). Anal. Calcd for $\mathrm{C_{34}H_{22}BClF_{20}OP_2Pd}$: C, 39.22; H, 2.13. Found: C, 38.92; H, 2.19.

X-ray Crystallographic Analysis of 5b·$\mathrm{CH_2Cl_2}$. Single crystals of **5b**·$\mathrm{CH_2Cl_2}$ were grown from $\mathrm{CH_2Cl_2}$ at −80 °C. Crystal, data collection and refinement parameters are collected in Table 2. Integration of intensities and refinement of cell parameters were done using SAINT.[37] The space group was determined on the basis of systematic absences and intensity statistics. Patterson methods were used to locate all Pd atoms as well as most Cl atoms. Repeated difference Fourier maps allowed recognition of all C, O, N, F, and B atoms. Final refinement was anisotropic for non-hydrogen atoms and isotropic for H atoms. The CH_2Cl_2 solvent molecule is slightly disordered; the anisotropic displacement parameters for one Cl atom (Cl(3)) and the C atom (C(47)) are slightly larger than normal (see Supporting Information). No treatment was applied.

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Supporting Information Available: Text, figures, and tables which give ESI-MS spectroscopic data for **2b**,**d** and crystallographic data for **5a** and **5b**·CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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(37) All software and sources of scattering factors are contained in the SHELXTL (5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).