Kinetic Studies of Migratory Insertion Reactions at the (1,3-Bis(diphenylphosphino)propane)Pd(II) Center and Their Relationship to the Alternating Copolymerization of Ethylene and Carbon Monoxide

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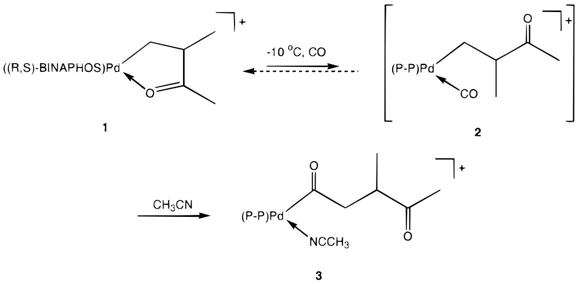
Abstract: The quantitative details of three migratory insertion processes relevant to the copolymerization of ethylene and CO by the highly active (dppp)Pd(II)-based catalyst have been examined. Cationic Pd(II) intermediates generated at low temperatures and characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy include (dppp)Pd(C_2H_4)(R)$^+$ (R = $-CH_3$, $-CH_2CH_3$), **6** and **7**; (dppp)Pd(CO)(R)$^+$ (R = $-CH_3$, $-CH_2CH_3$), **8** and **11**; and (dppp)Pd(C_2H_4)($COCH_3$)$^+$, **13**. Kinetic studies of the migratory insertion reactions of these species established the following activation parameters: **6**($\Delta G^\ddagger$ = 16.6(1) kcal/mol (−45.6 °C), $\Delta H^\ddagger$= 15.2(7) kcal/mol, $\Delta S^\ddagger$ = −6.2(2.9) eu), **7**($\Delta G^\ddagger$ = 16.3(1) kcal/mol (−33.7 °C), $\Delta H^\ddagger$ = 15.9(8) kcal/mol, $\Delta S^\ddagger$ = −1.6(3.7) eu), **8**($\Delta G^\ddagger$ = 14.8(1) kcal/mol (−81.7 °C), $\Delta H^\ddagger$ = 14.8(7) kcal/mol, $\Delta S^\ddagger$ = 0.1(3.0) eu), **11**($\Delta G^\ddagger$ = 13.4(1) kcal/mol (−94.2 °C)), **13**($\Delta G^\ddagger$ = 12.3(1) kcal/mol (−103.1 °C)). On the basis of the relative binding affinities of CO and C_2H_4 to the Pd(II) center and the relative rates of alkyl to CO and alkyl to ethylene migratory insertion reactions, it can be estimated that sequential ethylene insertions occur only once in ~10^5 turnovers, thus corroborating the exceptionally high fidelity of the alternating copolymerization.

Introduction

Migratory insertion reactions of transition metal alkyl carbonyl, alkyl olefin, and acyl olefin complexes are key transformations in a number of catalytic processes. We have previously investigated quantitative details of these transformations in connection with olefin/CO copolymerizations catalyzed by Pd(II) complexes bearing bidentate nitrogen ligands (1,10-phenanthroline, 2,2-bipyridine).[1,2] Of much more industrial relevance are Pd(II) systems employing bidentate phosphine ligands, in particular 1,3-bis(diphenylphosphino)propane, $(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2$ (dppp), whose Pd(II) complex is the most productive catalyst for ethylene/CO copolymerization reported by Drent and co-workers.[3,4]

There have been several reports of reactions resulting in CO insertion into Pd(II)−carbon bonds in bidentate phosphine complexes,[5−7] but few quantitative studies of the direct migratory insertion reactions of (P−P)Pd(II)(alkyl)(CO)$^+$ complexes (P−P = bidentate phosphine) have been performed. Tóth and Elsevier have reported half-lives for the conversion of [(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane]Pd(CH_3)(CO)$^+$ to the acyl carbonyl derivative (8 h at −90 °C and 100 min at −80 °C) that suggest a $\Delta G^\ddagger$ in the range of 14−15 kcal/mol. Nozaki[7] et al. has measured the rate of conversion of the chelate, **1**, to the acyl acetonitrile complex, **3**, (−10 °C, 20 atm CO, $CDCl_3$/CD_3CN) (eq 1). The alkyl carbonyl species, **2**, was not spectroscopically observed, and the measured free energy of activation (19.0 kcal/mol) likely reflects a pre-equilibrium followed by the migratory insertion reaction. Theoretical calculations of insertion barriers for alkyl carbonyl and alkyl olefin complexes have been reported by the Ziegler and Morokuma groups.[8−11] These studies will be discussed below.



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We report in this contribution the generation and quantitative measurement of migratory insertion barriers for (dppp)Pd(R)(CO)$^+$, (dppp)Pd($COCH_3$)(C_2H_4)$^+$, and (dppp)Pd(R)(C_2H_4)$^+$ (R = $-CH_3$, $-CH_2CH_3$). The first two processes constitute the key propagation steps in the alternating copolymerization of CO and ethylene, while the third process is responsible for errors (consecutive olefin insertions) in the alternating copolymer.

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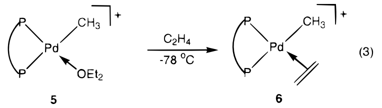
Results and Discussion

Synthesis of (dppp)PdMe(OEt$_2$)$^+$(BAr$'_4$)$^-$ (Ar$'$ = 3,5-(CF$_3$)$_2$C$_6$H$_3$$^-$), 5. A useful precursor for low-temperature generation of the methyl ethylene and methyl carbonyl complexes is the methyl diethyl ether complex (dppp)Pd(CH$_3$)(OEt$_2$)$^+$(BAr$'_4$)$^-$, **5**, in which the ether ligand is weakly coordinating and is easily displaced at very low temperatures. The ether complex was prepared by protonation of the dimethyl complex (dppp)Pd(CH$_3$)$_2$, **4**, with H(OEt$_2$)$_2$BAr$'_4$ in CH$_2$Cl$_2$/Et$_2$O (eq 2). Crystallization from the reaction mixture at −78 °C results in isolation of **5** in 76% yield as analytically pure material.

$$\underset{\mathbf{4}}{(dppp)Pd(CH_3)_2} \xrightarrow[Et_2O/CH_2Cl_2]{H(OEt_2)_2{}^+BAr'_4{}^-} \underset{\mathbf{5}}{(dppp)Pd(CH_3)(OEt_2)_2{}^+BAr'_4{}^-} + CH_4 \quad (2)$$

Generation and Migratory Insertion Barriers of (dppp)Pd(R)(C$_2$H$_4$)$^+$(BAr$'_4$)$^-$, (R = −CH$_3$ (6), −CH$_2$CH$_3$(7)). The reaction of the diethyl ether complex **5** with C$_2$H$_4$ in CD$_2$Cl$_2$ at −78 °C generates quantitatively the (dppp)PdMe(η^2-C$_2$H$_4$)$^+$BAr$'_4$$^-$ complex **6** (eq 3), which is too unstable to be isolated, but was characterized by NMR spectroscopy at low temperatures. In the −80 °C ^{1}H NMR spectrum of **6**, the η^2-bound ethylene signal appears as a singlet at δ 5.19, slightly upfield of free ethylene (δ 5.36). Rapid rotation of the bound ethylene ligand is responsible for the observation of only one resonance for these four protons. At −50 °C the signals for the bound and free ethylene are quite broad due to rapid associative interchange (see Supporting Information for spectra). The resonance for the CH$_3$ group at δ 0.32 is a doublet of doublets, (J^3_{HP} = 7 and 4 Hz) exhibiting both *cis* and *trans* coupling to phosphorus. ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR data are reported in the Experimental Section. Upon warming **6** to ∼−40 °C in the presence of excess ethylene, clean conversion to propylene and a complex assigned as the ethyl ethylene complex, **7**, can be monitored (eq 4). The rate of migratory insertion of the methyl ethylene complex, **6**, was followed by monitoring the decrease in the ^{1}H{^{31}P} NMR resonance of the Pd−CH_3 to yield k_{obs} = 4.9 × 10^{-5} s^{-1} at −45.6 °C and $\Delta G^\ddagger$ = 16.6(1) kcal/mol. Clean first-order kinetics were observed, and the rate was independent of the concentration of free ethylene.[12] Thirteen kinetic runs over a temperature range of −58 to −35 °C were carried out, and Eyring analysis (see Supporting Information) yielded $\Delta H^\ddagger$ = 15.2(7) kcal/mol and $\Delta S^\ddagger$ = −6.2(2.9) eu.



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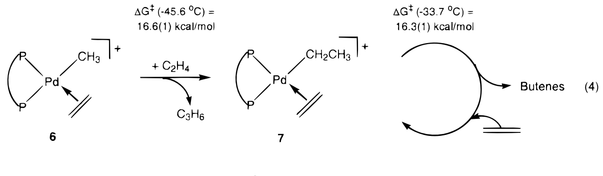
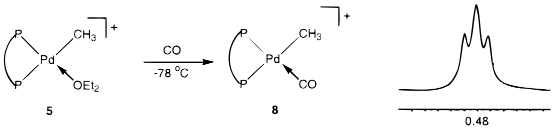


6 7 (4)

Following formation of propylene, ethylene is dimerized to butenes (eq 4). A single species (the catalyst resting state) is present in solution, which we assign as the ethyl ethylene complex **7**. The resonances for the CH$_2$CH$_3$ group were broadened due to the complex splitting patterns and appear at δ 1.41 (CH$_2$) and δ 0.40 (CH$_3$). ^{31}P decoupling reveals the expected quartet and triplet characteristic of an ethyl group. As expected, **6** and **7** have nearly identical ^{31}P{^{1}H} NMR spectra with respect to both chemical shift and $^2J_{PP}$ (see Experimental Section). The bound ethylene resonance in **7** is averaged with the free ethylene due to rapid associative interchange.[13] The turnover frequency of the catalytic cycle corresponds to the rate of migratory insertion in **7**. The formation of butenes follows zero order kinetics and directly provides the turnover frequency which is the slope of the least-squares line of equivalents of butene formed per second and yields k_{obs} = 5.5 × 10^{-3} s^{-1} at −33.7 °C and $\Delta G^\ddagger$ = 16.3(1) kcal/mol. This rate was measured at 13 temperatures between −54 and −35 °C, and Eyring analysis (see Supporting Information) yielded $\Delta H^\ddagger$ = 15.9(8) kcal/mol and $\Delta S^\ddagger$ = −1.6(3.7) eu. The $\Delta S^\ddagger$ and $\Delta H^\ddagger$ values for the migratory insertion reactions of **6** and **7** are within experimental error of each other for the two systems.

Generation and Migratory Insertion Barriers of (dppp)Pd(R)(CO)$^+$(BAr$'_4$)$^-$, (R = −CH$_3$ (8), −CH$_2$CH$_3$(11)). The methyl carbonyl complex (dppp)Pd(CH$_3$)(CO)$^+$, **8**, was rapidly and quantitatively generated in situ by purging a CH$_2$Cl$_2$ solution of ether complex, **5**, with CO at −90 °C (eq 5). To avoid further reaction to the acyl carbonyl complex, **10**, excess CO was removed from solution by purging with argon at −90 °C. Precipitation with hexane resulted in analytically pure **8** characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The CH$_3$ group exhibited a ^{1}H NMR resonance at δ 0.48 (eq 5) that appeared as a broad triplet (J ∼6 Hz) indicating similar coupling to the *cis* and *trans* phosphorus nuclei. In addition, the bound CO could be observed at δ 180.1 in the ^{13}C{^{1}H}NMR spectrum as a doublet of doublets with a large $^2J_{CP(trans)}$ of 118 Hz and a smaller $^2J_{CP(cis)}$ of 14 Hz.



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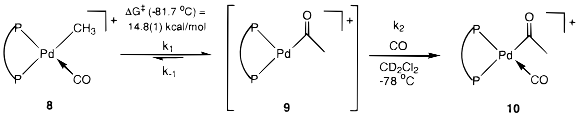
When treated with excess CO, the methyl carbonyl complex, **8**, undergoes migratory insertion to form the acyl carbonyl complex (dppp)Pd(COCH$_3$)(CO)$^+$(BAr$'_4$)$^-$, **10** (eq 6). Complex **10** could be isolated in moderate yields (35%) as a crystalline solid by recrystallization from CH$_2$Cl$_2$ at −30 °C under an atmosphere of CO and was characterized via ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy. The ^{1}H NMR resonance of the CH$_3$ group is now observed downfield as a singlet at δ 1.85. In the ^{13}C{^{1}H} NMR spectrum the acyl carbon could be observed at δ 232.0 as a doublet of doublets with a $^2J_{CP(trans)}$ of 85 Hz and a $^2J_{CP(cis)}$ of 8 Hz and the bound carbonyl at δ 175.7 as a doublet of doublets with a $^2J_{CP(trans)}$ of 83 Hz and a $^2J_{CP(cis)}$ of 20 Hz.



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[12] Kinetic runs repeated at 227.6 K with 4, 9, and 19 equiv of ethylene give k_{obs} = 5.1, 4.8, and 4.9 × 10 $^{-4}$ s^{-1}. [Pd] = 9.7 mM in each case. [C$_2$H$_4$] = 39, 87, and 184 mM, respectively. [C$_2$H$_4$] determined by integration.

[13] We cannot rule out the presence of small amounts of ethyl propylene or ethyl butene complexes in equilibrium with the ethyl ethylene complex. However, the large excess of ethylene and the stronger binding affinity of ethylene relative to α-olefins and internal olefins suggests these species would be present in insignificant amounts.

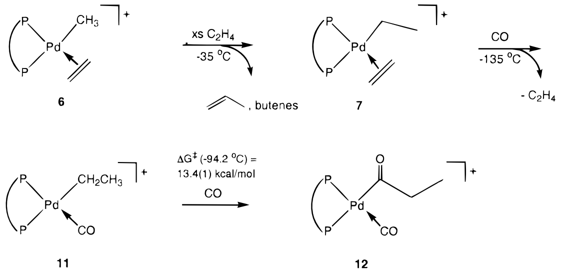
Table 1. Comparison of Calculated and Experimental Activation Barriers for Insertions

entry	complex[a]	$\Delta H^\ddagger$(calc)[b]	$\Delta H^\ddagger$(exptl)[b]	$\Delta G^\ddagger$(exptl)[b]	$\Delta S^\ddagger$(exptl)[c]
1	$(N-N)Pd(CH_3)(CH_2{=}CH_2)^+$	16.2		18.5(1)(−25 °C)	
2	$(N-N)Pd(C_2H_5)(CH_2{=}CH_2)^+$		18.5(6)	19.4(2)(−25 °C)	−3.7(2.0)
3	$(N-N)Pd(acyl)(CH_2{=}CH_2)^+$	18.2		16.6(1)(−46 °C)	
4	$(N-N)Pd(CH_3)(CO)^+$	14.9		15.4(1)(−66 °C)	
5	$(P-P)Pd(CH_3)(CH_2{=}CH_2)^+$		15.2(7)	16.6(1)(−45.6 °C)	−6.2(2.9)
6	$(P-P)Pd(C_2H_5)(CH_2{=}CH_2)^+$	15.6	15.9(8)	16.3(1)(−33.7 °C)	−1.6(3.7)
7	$(P-P)Pd(acyl)(CH_2{=}CH_2)^+$	13.9		12.3(1)(−103.1 °C)	
8	$(P-P)Pd(CH_3)(CO)^+$		14.8(7)	14.8(1)(−81.7 °C)	0.1(3.5)
9	$(P-P)Pd(C_2H_5)(CO)^+$	11.5		13.4(1)(−94.2 °C)	

[a] N−N is HN═CH−CH═NH for calculated values by Morokuma, et al.,[11] and 1,10-phenanthroline for experimental values by Rix;[1,2] P−P is $H_2PCH{=}CHPH_2$ for calculated values by Ziegler et al.,[9] and $(Ph)_2P(CH_2)_3P(Ph)_2$ for experimental values reported here. [b] In kcal·mol^{-1}. [c] In cal·mol^{-1}·K^{-1}.

Kinetics of conversion of **8** to the acyl carbonyl complex, **10**, were conveniently followed by low-temperature $^1H\{^{31}P\}$ NMR spectroscopy in CD_2Cl_2. The rate of conversion is independent of CO concentration and follows excellent first-order kinetics yielding $k_{obs} = 4.5 \times 10^{-5}$ s^{-1} and $\Delta G^\ddagger = 14.8(1)$ kcal/mol at −81.7 °C. The lack of dependence of the rate on CO concentration indicates that the migratory insertion step is rate-determining ($k_2[CO] > k_{-1}$), and thus the observed rate constant (k_{obs}) represents the true rate constant (k_1) for migratory insertion of the methyl carbonyl complex (eq 6). Eleven kinetic runs were carried out over a 19 °C temperature range (−82 to −63 °C) to give activation parameters of $\Delta H^\ddagger = 14.8(7)$ kcal/mol and $\Delta S^\ddagger = 0.1(3.5)$ eu. An Eyring plot of these data is provided in the Supporting Information.

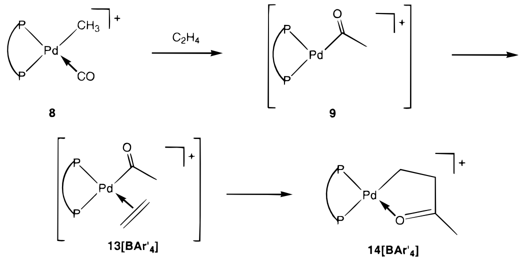
The barrier to migratory insertion of the ethyl carbonyl complex $(dppp)Pd(CH_2CH_3)(CO)^+$, **11**, was more difficult to obtain. As noted in the previous section, exposure of $(dppp)Pd(CH_3)(OEt_2)^+$, **5**, to excess ethylene eventually results in the formation of the ethyl ethylene complex, **7**, as the catalyst resting state for ethylene dimerization. Therefore, the ethyl carbonyl complex, **11**, was prepared by first generating **7** in situ and then treating it with CO (eq 7). The ^1H NMR spectrum is complicated by the presence of propene and butenes; however, with the help of ^{31}P decoupling, the resonances for the CH_2CH_3 could be located at δ 1.78 and δ 0.70. The $^{31}P\{^1H\}$ spectrum shows clean formation of **11** as indicated by resonances at δ 17.8 and δ −7.7 which are consistent with the shifts observed for the methyl carbonyl complex, **8**(δ 16.6 and δ −7.9). The rate of migratory insertion was followed by $^{31}P\{^1H\}$ NMR spectroscopy as **11** was converted to **12** with $^{31}P\{^1H\}$ signals at δ 2.8 and δ −9.2. The first-order rate constant for conversion was 1.5×10^{-4} s^{-1} at −94.2 °C, corresponding to a $\Delta G^\ddagger = 13.4(1)$ kcal/mol.



(7)

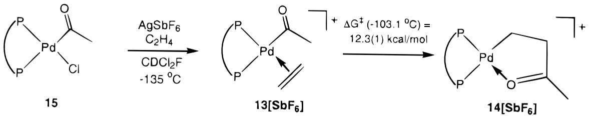
Generation and Migratory Insertion Reaction of $(dppp)Pd(COCH_3)(C_2H_4)^+ (X^-)$, $X^- = BAr'_4{}^-$ or $SbF_6{}^-$, 13[X].

In an attempt to generate the acyl ethylene complex, **13[BAr′4]**, the methyl carbonyl complex **8** was treated with excess ethylene at low temperatures with the intent of trapping the fourteen-electron acyl complex **9** (eq 8).



(8)

Although this approach was successful for the phenanthroline-based system,[1,2] in this case only the chelate complex **14[BAr′4]** is observed implying that the migratory insertion of **8** is slower than that of the acyl ethylene intermediate **13[BAr′4]**. In a second successful approach, chloride was abstracted from the acyl chloride complex, **15**, using $AgSbF_6$ in $CDCl_2F$ at −135 °C in the presence of excess ethylene (eq 9).[14] The resulting acyl ethylene complex **13[SbF6]** was characterized by ^1H and ^{31}P NMR spectroscopy. In the low-temperature ^1H NMR spectrum of **13[SbF6]** the rotation of the η^2-bound ethylene ligand is static on the NMR time scale, and the ethylene hydrogens appear as an AA′BB′ pattern centered at δ 4.9. The acyl methyl resonance is observed as a singlet at δ 1.58. Warming to −103.1 °C resulted in first-order migratory insertion to form chelate **14[SbF6]**, $k = 6.2 \times 10^{-4}$ s^{-1}, $\Delta G^\ddagger = 12.3(1)$ kcal/mol (eq 9).[15]



(9)

Summary of Migratory Insertion Barriers. It is of interest to compare the barriers determined here to those calculated for model systems. In some cases, the activation enthalpies were not measured experimentally; hence, we are left to compare calculated $\Delta H^\ddagger$ values with experimentally determined $\Delta G^\ddagger$ values for some complexes. To make more accurate comparisons, entropic contributions to the Gibbs free energy of activation must be accounted for. The experimentally determined $\Delta S^\ddagger$ for the migratory insertions of olefin complexes (Table 1, entries 2, 5, and 6) is small and negative. The $\Delta H^\ddagger$ values for the migratory insertion values would therefore be expected to be less than the experimentally observed $\Delta G^\ddagger$ by 0−1.5 kcal/

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(14) The $CDCl_2F$ solvent used in these halide abstraction experiments contained ~50% $CDClF_2$. The difluorinated compound is completely inert as is $CDCl_2F$.

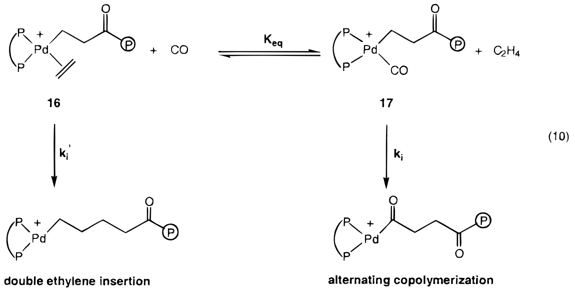
(15) Complex **14[SbF6]** and **14[BAr′4]** have identical spectroscopic data and are consistent with the previously reported triflate salt of this compound. Zuidveld, M. A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Klusener, P. A. A.; Stil, H. A.; Robeek, C. F. *J. Am. Chem. Soc.* **1998**, *120*, 7977.

mol. The entropic contribution for the migratory insertion reactions of carbonyl complexes (entries 4 and 9) would be expected to be even less significant due to less reorganization of the linear carbonyl ligand in the transition state. This is confirmed for complex **8** (entry 8) that has a $\Delta S^{\ddagger} \sim 0$.

Morokuma et al.[11] has used the simple diimine ligand HN═CH−CH═NH in modeling barriers for phenanthroline systems reported earlier.[1,2] Table 1 (entries 1−4) summarizes the observed barriers[1,2] for the 1,10-phenanthroline system together with the calculated barriers[11] at the B3LYP/I level. The methyl/CO barrier is calculated to be the lowest barrier in agreement with experiment, but the order of the methyl to ethylene (16.2 kcal/mol) and acyl to ethylene (18.2 kcal/mol) is reversed relative to the experimental numbers, 18.5 and 16.6 kcal/mol, respectively. The expected entropic contributions for these reactions fail to account for this reversal since for these olefin complexes (entries 1 and 3) the experimental $\Delta H^{\ddagger}$ would be expected to be slightly less than the $\Delta G^{\ddagger}$.

Most relevant to this work are studies by Margl and Ziegler who have used $H_2PCH{=}CHPH_2$ as a model ligand.[8,9] Table 1 summarizes comparison data. The calculated ethyl ethylene migratory insertion barrier closely matches the experimental barrier (15.6 vs 15.9 kcal/mol; $\Delta H^{\ddagger}$, entry 6); however, there is disagreement in the acyl ethylene and ethyl carbonyl barriers. The $\Delta H^{\ddagger}$ for the acyl ethylene complex (entry 7) would be expected to be slightly less than the $\Delta G^{\ddagger}$ of 12.3 kcal/mol, thus making the experimental and theoretical difference 2−3 kcal/mol. For the ethyl carbonyl complex (entry 9) the entropic contribution would be small so that the calculated and experimental difference remains at 1.5−2 kcal/mol. Qualitatively, calculations predict the lowest barrier to be that for the ethyl carbonyl complex, whereas experimentally, the acyl ethylene complex shows the lowest barrier.

The alternating copolymer of ethylene and CO prepared from Pd(II) complexes employing bidentate phosphine ligands exhibits a remarkable degree of fidelity with no detectable microstructures involving double insertions of ethylene.[3,4,16] A major factor, as previously noted,[17] which dictates the alternating nature of the copolymerization, is the much higher affinity of CO relative to that of ethylene for the Pd(II) center. Competition studies suggest the ratio of binding constants, K_{eq}, is $\sim 10^4$ at 25 °C.[2] The results obtained here provide further information concerning the factors which control the alternating insertion of monomers. Since CO and ethylene undergo rapid associative exchange relative to the rate of insertion, two factors control the extent of two consecutive insertions of ethylene: (1) the equilibrium ratio of the alkyl carbonyl and alkyl olefin complexes and (2) the relative rates of migratory insertion of these two species. This situation is illustrated in eq 10 and conforms to Curtin-Hammett kinetics.[18]



The ratio of normal propagation to double C_2H_4 insertion is given in eq 11.

$$\frac{\text{normal propagation}}{\text{double } C_2H_4 \text{ insertion}} = \left(\frac{[\mathbf{17}]}{[\mathbf{16}]}\right)\left(\frac{k_i}{k_i'}\right) = K_{eq}\left(\frac{[CO]}{[C_2H_4]}\right)\left(\frac{k_i}{k_i'}\right) \approx (10^4)\left(\frac{7.3 \times 10^{-3}\ \text{M}}{0.11\ \text{M}}\right)(10^2) \approx 10^5 \tag{11}$$

The ratio of [**17**]/[**16**] is estimated from the equilibrium constant, $K_{eq} \sim 10^4$, multiplied by the ratio of [CO]/[C_2H_4] in solution at 25 °C.[2] [CO] was determined from Bryndza's equation,[19] and [C_2H_4] was determined previously[2] for a 1:1 mixture of C_2H_4/CO gas at 1 atm and 25 °C. The ratio of the relative propagation rates k_i/k_i' at 25 °C can be estimated from the data above ($\Delta\Delta G^{\ddagger} \approx 2.6$ kcal/mol) as $\sim 10^2$.[20] Thus, only one double ethylene insertion will occur for every $\sim 10^5$ insertions of CO into the Pd−alkyl bond. This compares to a 1:10^6 ratio for the (1,10-phenanthroline)Pd(II) system.[2] These numbers indicate that in a polymerization producing a polymer with an average M_n of 20 000 g/mol (360 turnovers) there would be only one error (double ethylene insertion) per 200 chains. These studies make clear that the lower barrier of alkyl to CO migratory insertion in **17** relative to the alkyl to ethylene insertion barrier in **16** contributes significantly in establishing the essentially flawless nature of the alternating copolymerization.

Experimental Section

I. Synthesis. General Methods. All reactions, except where indicated, were carried out in flame-dried glassware under a dry, oxygen-free argon atmosphere, using standard Schlenk and drybox techniques. Acetone was degassed with argon and dried over 4 Å molecular sieves. All other solvents were either freshly distilled from sodium benzophenone (or P_2O_5 in the case of CH_2Cl_2) or deoxygenated and then dried by passing them through a column of activated alumina under nitrogen.[21] CD_2Cl_2 was purchased from Cambridge Isotope Laboratories, Inc. and dried over calcium hydride or P_4O_{10}. The CD_2Cl_2 was subjected to three freeze−pump−thaw cycles and vacuum transferred into glass Schlenk tubes fitted with high-vacuum Teflon plugs and then stored under Ar. $CDCl_2F$ was prepared using a literature procedure.[22] Air-sensitive complexes were handled in an argon-filled glovebox and stored under Ar at −30 °C. CP grade CO and ethylene were purchased from National Welders Supply and used as received.

Kinetics experiments were carried out under argon in NMR tubes equipped with septa. CD_2Cl_2 or $CDCl_2F$ was added to samples at −78 °C unless otherwise indicated, after which solids were dissolved at the lowest temperature possible. Kinetics experiments were carried out on a Bruker AMX-300 or Avance 300 spectrometer. NMR probe temperatures were measured using an anhydrous methanol sample except for temperatures below −95 °C, which were determined using a thermocouple.[23] ^1H and ^{13}C chemical shifts were referenced to residual ^1H signals and to the ^{13}C signals of the deuterated solvents, respectively.

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(16) Double CO insertion has been shown to be highly endothermic and does not occur in these copolymerizations. See: Chen, J.-T.; Sen, A. *J. Am. Chem. Soc*. **1984**, *106*, 1506 and Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *118*, 7337.

(17) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303.

(18) Monomer interchange is fast relative to the migratory insertion reactions of complexes **16** and **17**. This has been seen previously for bidentate nitrogen-based catalytic systems (ref 2). Low-temperature spectra (see Supporting Information) of complex **6** also indicate very rapid interchange of free and bound ethylene prior to migratory insertion.

(19) Bryndza, H. E. *Organometallics* **1985**, *4*, 1686.

(20) $\Delta\Delta G^{\ddagger}$ and k_i/k_i' estimated from Eyring data for **7**: $\Delta G^{\ddagger}$ (179 K) = 16.0 kcal/mol and kinetic data for **11**: $\Delta G^{\ddagger}$ (179 K) = 13.4 kcal/mol. For $\Delta\Delta G^{\ddagger} = 2.6$ kcal/mol, $k_i/k_i' \approx 100$.

(21) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(22) Siegel, J. S.; Anet, F. A. L. *J. Org. Chem.* **1988**, *53*, 2629.

(23) Ammann, C.; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319.

Elemental analyses were obtained from Oneida Research Services Inc., Whitesboro, NY, and Atlantic Microlabs Inc., Norcross GA.

$H(OEt_2)_2BAr'_4$,[24] (dppp)Pd(Me)(Cl), and $(TMEDA)Pd(Me)_2$ (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine),[25] were synthesized using published methods. 1,3-Bis-(diphenylphosphino)propane (dppp) (>98% purity) and $AgSbF_6$ were purchased from Aldrich and used as received.

The ^1H and ^{13}C NMR data attributed to the counterion BAr'^-_4 ($Ar' = 3,5(CF_3)_2C_6H_3$) are consistent for all cationic complexes examined and are not included in each compound characterized below. Full spectral details have been previously reported.[26]

$(dppp)Pd(Me)_2$,[27] 4. The following method was adapted from van Koten's synthesis of $(dmpe)PdMe_2$with only minor variations.[25] A solution of dppp, (2.00 g, 4.80 mmol) in acetone (15 mL) was added to a solution of $(TMEDA)PdMe_2$, (1.00 g, 3.96 mmol) in acetone (5 mL) and stirred for 18 h. The solvent was removed in vacuo at 0 °C to yield a white precipitate. The crude product was recrystallized from acetone at −30 °C. Repeated crystallizations from acetone yielded 1.7 g, 77% of **4** as colorless crystals. ^1H NMR (300 MHz, CD_2Cl_2, −20 °C) δ 7.33−7.51 (m, 20H, $(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$), 2.42 (m, 4H, $PCH_2CH_2CH_2P$), 1.73 (m, 2H, $PCH_2CH_2CH_2P$), −0.12 (d, $^3J_{HP}$ = 2, 6H, $Pd-(CH_3)_2$). $^{13}C\{^1H,^{31}P\}$ NMR (75 MHz, CD_2Cl_2, −20 °C) δ 132.9, 133.0, 127.9, 129.4 ($(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$), 27.5 ($PCH_2CH_2CH_2P$), 19.3 ($PCH_2CH_2CH_2P$), 5.84 ($Pd-(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, −20 °C) δ 7.2. Anal. ($C_{29}H_{32}P_2Pd$) calcd C, 63.45; H, 5.88; found C, 63.69; H, 5.71. An additional recrystallization in Et_2O/CH_2Cl_2 was often necessary to remove residual acetone.

$(dppp)PdMe(OEt_2)^+(BAr'_4)^-$, 5. The dimethyl complex, **4**, (0.256 g; 0.467 mmol) and $H(OEt_2)_2BAr'_4$ (0.505 g, 0.499 mmol) were suspended in ether (0.5 mL) and CH_2Cl_2 (1.5 mL) at −30 °C. The reaction mixture was stirred for 2 h followed by brief warming to 25 °C to dissolve all solids. The resulting light yellow solution was brought to 0 °C, cooled slowly, and ultimately stored overnight at −78 °C. The resulting crystals were filtered and washed with pentane (2 × 3 mL) to afforded clear, crystalline **5** (0.521 g; 76%) which was dried in vacuo. ^1H NMR (300 MHz, CD_2Cl_2, −60 °C) δ 7.27−7.51 (m, 20H, $(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$), 3.25 (br, 4H, $O(CH_2CH_3)_2$), 2.47 (m, 4H, $PCH_2CH_2CH_2P$), 1.67 (m, 2H, $PCH_2CH_2CH_2P$), 1.08 (br, 6H, $O(CH_2CH_3)_2$), 0.44 (d, $^3J_{HP}$ = 4.2, 3H, $Pd-CH_3$). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, −60 °C) δ see Supporting Information for aryl data ($(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$), 68.7 (s, $O(CH_2CH_3)_2$), 27.3 (br d, $^1J_{CP}$ = 32, ($PCH_2CH_2CH_2P$)), 26.5 (br d, $^1J_{CP}$ = 23, $PCH_2CH_2CH_2P$), 16.9 (br s, $PCH_2CH_2CH_2P$), 15.3 (s, $O(CH_2CH_3)_2$), 15.0 (d, $^2J_{CP}$ = 86.4, $Pd-CH_3$). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, −60 °C) δ 30.3 (d, $^2J_{PP}$ = 51), −0.21 (d, $^2J_{PP}$ = 51). Anal. ($C_{64}H_{51}BF_{24}OP_2Pd$) calcd C, 52.25; H, 3.49; found C, 52.10; H, 3.51.

$(dppp)Pd(Me)(CO)^+(BAr'_4)^-$, 8. The ether adduct, **5**, was produced in situ by the reaction of $dpppPdMe_2$, **4**, (0.256 g, 0.466 mmol) and $H(OEt_2)_2BAr'_4$ (0.479 g, 0.473 mmol) in CH_2Cl_2 (7 mL) at −30 °C. CO was precooled by passing the gas through approximately 3 m of nalgene tubing immersed in a −90 °C bath. The flask was cooled to −90 °C and vigorously purged with CO for 5 min. The solution was then purged with argon for 30 min. Hexane was added to precipitate **8** (0.612 g, 92%) as a light yellow powder. ^1H NMR (300 MHz, CD_2Cl_2, −70 °C) δ 7.24−7.53 (m, 20H, $(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$), 2.47 (br m, 4H, $PCH_2CH_2CH_2P$), 1.71 (br m, 2H, $PCH_2CH_2CH_2P$), 0.48 (dd, $^3J_{HP}$ = 6.0, $^3J_{HP}$ = 6.0, 3H, $Pd-CH_3$). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, −70 °C) δ 180.1 (dd, $^2J_{CP}$ = 118, $^2J_{CP}$ = 14, $Pd-CO$), see Supporting Information for aryl data ($(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$), 24.5 (br d, $^1J_{CP}$ = 17, $PCH_2CH_2CH_2P$), 24.3 (br d, $^1J_{CP}$ = 22, $PCH_2CH_2CH_2P$), 17.5 (br, $PCH_2CH_2CH_2P$), 4.8 (d, $^2J_{CP}$ = 70, $Pd-CH_3$). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, −70 °C) δ 16.6 (d, $^2J_{PP}$ = 60), −7.9 (d, $^2J_{PP}$ = 60). IR (CH_2Cl_2) ν_{CO} = 2132 cm^{-1}. Anal. ($C_{61}H_{41}BF_{24}OP_2Pd$) calcd C, 51.41; H, 2.90; found C, 51.53; H, 2.90.

$(dppp)Pd(CO)(COMe)^+(BAr'_4)^-$, 10. The methyl ether complex, **5**, (0.521 g, 0.354 mmol) was dissolved in CH_2Cl_2 (3.5 mL) under a CO atmosphere at −30 °C. The solution was then purged with CO for 5 min to ensure complete reaction followed by hexane (5 mL) to produce a yellow oil. To the oil was added CH_2Cl_2 (10 mL). The resulting yellow solution was filtered through Celite to remove some Pd(0). The filtrate was kept at −30 °C, and hexanes (50 mL) were layered slowly onto the CH_2Cl_2 solution under a CO atmosphere. The mixture was then stored at −30 °C until a large number of yellow crystals had formed. These crystals were filtered, washed with hexanes (2 × 10 mL), and dried in vacuo. Yellow crystals of **10** (0.17 g, 34%) were isolated. ^1H NMR (300 MHz, CD_2Cl_2, −70 °C) δ 7.37−7.55 (m, 20H, $(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$), 2.74 (br m, 2H, $PCH_2CH_2CH_2P$), 2.55 (br m, 2H, $PCH_2CH_2CH_2P$), 1.97 (br m, 2H, $PCH_2CH_2CH_2P$), 1.85 (s, 3H, $Pd-COCH_3$). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, −70 °C) δ 232.0 (dd, $^2J_{CP}$ = 85, $^2J_{CP}$ = 8.5, $Pd-COCH_3$), 175.7 (dd, $^2J_{CP}$ = 83, $^2J_{CP}$ = 20, $Pd-CO$), see Supporting Information for aryl data ($(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$), 42.1 (dd, $^3J_{CP}$ = 25, $^3J_{CP}$ = 24, $Pd-COCH_3$), 24.9 (br, $PCH_2CH_2CH_2P$), 24.8 (br, $PCH_2CH_2CH_2P$), 17.9 (br m, $PCH_2CH_2CH_2P$). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, −70 °C) δ 2.2 (d, $^2J_{PP}$ = 84), −8.0 (d, $^2J_{PP}$ = 84). IR (CH_2Cl_2) ν_{CO} = 2130 cm^{-1}, ν_{acyl} = 1715 cm $^{-1}$. Anal. ($C_{62}H_{41}BF_{24}O_2P_2Pd$) calcd C, 51.25; H, 2.84; found C, 51.64; H, 2.53).

(dppp)Pd(COMe)(Cl), 15. $dpppPd(CH_3)(Cl)$ (0.765 g, 1.34 mmol) was dissolved in CH_2Cl_2 (20 mL) at room temperature with stirring. A stream of CO was purged through the solution for 30 min and stirring was continued for another 2 h. The solution was filtered through Celite to remove traces of Pd black that had formed. The solvent was removed in vacuo to yield a glassy residue. The residue was washed with pentane (5 × 5 mL) to yield **15**, as a cream colored powder (0.55 g, 69%). The product was characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and agreed with data previously reported.[5] Anal. ($C_{29}H_{29}OP_2Pd$) calcd C, 58.31; H, 4.89; found C, 58.37; H, 5.00).

$(dppp)\overline{Pd(CH_2CH_2CO}CH_3)^+(BAr'_4)^-$, 14[BAr′4]. $(dppp)PdMe(OEt_2)^+(BAr'_4)^-$, **5**, (0.237 g, 0.161 mmol) was dissolved in CH_2Cl_2 (7.0 mL) and diethyl ether (1.0 mL) at −78 °C. A gentle stream of CO was purged through the solution for 2−3 min followed by an argon purge for 30 min. C_2H_4 (20 mL, ~0.8 mmol) was added via syringe, and the solution was warmed to −30 °C. The solvent was removed in vacuo to give a yellow foam. This yellow foam was redissolved in diethyl ether (0.5 mL) and CH_2Cl_2 and stored at −78 °C overnight to give a white precipitate. This precipitate was filtered, rinsed with hexanes (2 × 2 mL), and dried in vacuo to give **14[BAr′4]** as a white powder. ^1H NMR (300 MHz, CD_2Cl_2, −80 °C) δ 7.34−7.48 (m, 20H, $(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$), 3.13(m, 2H, $Pd-CH_2CH_2COCH_3$), 2.55, (m, 2H, $PCH_2CH_2CH_2P$), 2.47 (m, 2H, $PCH_2CH_2CH_2P$), 2.32(s, 3H, $Pd-CH_2CH_2COCH_3$), 1.84 (m, 2H, $Pd-CH_2CH_2COCH_3$), 1.32 (br m, 2H, $PCH_2CH_2CH_2P$). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, −80 °C) δ 238.3 (d, $^3J_{CP}$ = 12, $Pd-CH_2CH_2COCH_3$), see Supporting Information for aryl data ($(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$), 51.2 (d, $^3J_{CP}$ = 6, $Pd-CH_2CH_2COCH_3$), 35.8 (d, $^2J_{CP}$ = 89, $Pd-CH_2CH_2COCH_3$), 28.2 (s, $Pd-CH_2CH_2COCH_3$), 26.9 (dd, $^1J_{CP}$ = 34, $^3J_{CP}$ = 8, $PCH_2CH_2CH_2P$), 25.5 (d, $^1J_{CP}$ = 23, $PCH_2CH_2CH_2P$), 17.9 (br, $PCH_2CH_2CH_2P$). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, −80 °C) δ 28.2 (d, $^2J_{PP}$ = 55), −6.0 (d, $^2J_{PP}$ = 55). Anal. ($C_{63}H_{46}BF_{24}OP_2Pd$) calcd C 52.07; H, 3.12; found C, 52.34; H, 3.17).

II. Kinetics. *β*-Methyl Migratory Insertion Reaction of $(dppp)Pd(CH_3)(C_2H_4)^+(BAr'_4)^-$, 6. (a) Spectroscopic Characterization of 6: NMR data: ^1H NMR (300 MHz, CD_2Cl_2, −80 °C) δ 7.28−7.51 (m, 20H, $(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$), 5.19 (br, 4H, $Pd-\eta^2-C_2H_4$), 2.60 (m, 4H, $PCH_2CH_2CH_2P$), 1.83 (m, 2H, $PCH_2CH_2CH_2P$), 0.32 (dd, 3H, $^3J_{PH}$ = 7, $^3J_{PH}$ = 4, $Pd-CH_3$). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, −70 °C) δ see Supporting Information for aryl data ($(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$), 108.6 (br d, $^2J_{CP}$ = 5, $Pd-\eta^2-C_2H_4$), 25.5 (br d, $^1J_{CP}$ = 38, $PCH_2CH_2CH_2P$), 25.2 (br d, $^1J_{CP}$ = 23, $PCH_2CH_2CH_2P$), 17.4 (br s, $PCH_2CH_2CH_2P$), 17.3 (dd, $^2J_{CP}$ = 91, $^2J_{CP}$ = 7, $Pd-CH_3$). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, −70 °C) δ 17.3 (d, $^2J_{PP}$ = 56), −2.0 (d, $^2J_{PP}$ = 56).

(b) Kinetic Measurements. The ether adduct, **5** (10 mg, ~6.8 μmol) was dissolved in CD_2Cl_2 (0.7 mL) at −78 °C. The addition of C_2H_4 (4.25 mL, ~170 μmol, ~25 equiv) by gastight syringe afforded **6**. The sample was placed in a precooled NMR probe and the decrease in

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[27] Ozawa, F.; Yamamoto, A. *Nippon Kagaku Kaishi* **1987**, *5*, 773.

intensity of the Pd−Me peak of **6** was followed by $^{1}H\{^{31}P\}$ NMR spectroscopy. The slope of the line defined by the ln(Pd−CH_3) of **6** vs time afforded the first-order rate constant for the reaction. Spectra were taken at intervals of 1−15 min, depending on conditions. Propene and the ethyl ethylene complex **7** was produced as the reaction proceeded. The reaction was observed for 2−4 half-lives. The averaged rate constant (4.9×10^{-5} at −45.6 °C) for the β-methyl migratory insertion reaction of **6** was employed to determine the $\Delta G^{\ddagger}$ (16.6(1) kcal/mol) for the reaction. This experiment was repeated with varying concentrations of ethylene to determine the order of the reaction in C_2H_4. These data reveal that the rate of the reaction is independent of $[C_2H_4]$.[12]

(c) Activation Parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) for the β-Methyl Migratory Insertion Reaction of 6. A series of experiments conducted over a 20 °C temperature range afforded a good linear fit from the Eyring plot of 1/T (K) vs ln{k_{me}/T (K)} (see Supporting Information). These data give a $\Delta S^{\ddagger} = -6.2(2.9)$ eu and a $\Delta H^{\ddagger} = 15.(7)$ kcal/mol.

β-Ethyl Migratory Insertion Reaction of (dppp)Pd(CH_2CH_3)(C_2H_4)$^+$(BAr′$_4$)$^-$, 7. (a) Spectroscopic Characterization of 7. Generated from the dimerization of C_2H_4 with the methyl ether adduct, **5**, as described below. NMR data: ^{1}H NMR (300 MHz, CD_2Cl_2, −70 °C) δ 7.35−7.50 (m, 20H, $(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$), (Pd−$\eta^2$-$C_2H_4$, not observed), 2.78 (br m, 2H, $PCH_2CH_2CH_2P$), 2.58 (br m, 2H, $PCH_2CH_2CH_2P$), 1.88 (m, 2H, $PCH_2CH_2CH_2P$), 1.41 (m, 2H, Pd−CH_2CH_3), 0.40 (m, 3H, Pd−CH_2CH_3). $^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2, −50 °C) δ 17.7 (br d, $^{2}J_{PP} = 60$), −2.0 (d, $^{2}J_{PP} = 60$). Selected ^{1}H data for **7** with ^{31}P decoupling. $^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_2F$, −70 °C) δ 1.41 (q, $^{3}J_{HH} = 7$, 2H, Pd−CH_2CH_3), 0.43 (t, $^{3}J_{HH} = 7$, 3H, Pd−CH_2CH_3).

(b) Rate Constant and Free Energy of Activation ($\Delta G^{\ddagger}$). The ether adduct, **5** (10 mg, ∼6.8 μmol) was dissolved in CD_2Cl_2 (0.7 mL) at −78 °C. The addition of C_2H_4 (4.25 mL, ∼170 μmol, ∼25 equiv) by gastight syringe afforded **6**. The sample was placed in a precooled NMR probe, and care was taken to make sure that **6** was completely converted to **7** before measurements were taken. The integrals of the methyl peaks of *trans*-, *cis*-, and 1-butene were observed by $^{1}H\{^{31}P\}$ NMR spectroscopy and plotted against time to determine the turnover frequency for butene formation. From the turnover frequency of butene formation ($k_{obs} = 5.5 \times 10^{-3}$ at −33.7 °C) the $\Delta G^{\ddagger}$ (16.3(1) kcal/mol) could be determined.

(c) Activation Parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) for the β-Ethyl Migratory Insertion Reaction of 7. A series of experiments conducted over a 23 °C temperature range afforded a good linear fit from the Eyring plot of 1/T (K) vs ln{k_{Et}/T (K)} (see Supporting Information). These data give a $\Delta S^{\ddagger} = -1.6(3.7)$ eu and a $\Delta H^{\ddagger} = 15.9(8)$ kcal/mol.

α-Methyl Migratory Insertion Reaction of (dppp)Pd(CH_3)(CO)$^+$(BAr′$_4$)$^-$, 8. (a) Rate Constant and Gibbs Free Energy of Activation($\Delta G^{\ddagger}$). The ether adduct, **5** (5 mg, ∼3.4 μmol) was dissolved in 0.7 mL of CD_2Cl_2 at −78 °C. Purging the solution with CO at −90 °C for 1−5 min yielded **8**. The sample was placed in a precooled NMR probe at −81.6 °C, and the decay of the Pd−CH_3 peak of **8** monitored by $^{1}H\{^{31}P\}$ NMR spectroscopy. The slope of the line defined by the ln(Pd−CH_3) signal of **8** vs time afforded the first-order rate constant for the reaction. Spectra were taken at intervals of 1−15 min, depending on conditions. The acyl carbonyl complex **10** was produced cleanly as the only product throughout the reaction. The reaction was monitored for 2−4 half-lives. The averaged rate constant k_{obs} (4.5×10^{-5} s^{-1} at −81.7 °C) for the migratory insertion reaction of **8** was employed to determine the $\Delta G^{\ddagger}$ (14.8(1) kcal/mol) for this reaction. Higher concentrations of **8** resulted in incomplete conversion to **10** due to insufficient concentrations of CO in solution.

(b) Activation Parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) for the Migratory Insertion Reaction of 8. A series of experiments conducted as above over a 20 °C temperature range afforded a good linear fit from the Eyring plot of 1/T (K) vs ln{k_{Me}/T (K)} (see Supporting Information). These data gave a $\Delta S^{\ddagger} = 0.1(3.5$ eu), $\Delta H^{\ddagger} = 14.8(7)$ kcal/mol.

α-Ethyl Migratory Insertion Reaction of (dppp)Pd(CH_2CH_3)(CO)$^+$(BAr′$_4$)$^-$, 11. (a) Spectroscopic Characterization of 11. Generated from the addition of CO to **7** as described below. NMR data: $^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_2F$, −110 °C) δ 7.25−7.50 (m, 20H, $(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$), 2.59 (br m, 2H, $PCH_2CH_2CH_2P$), 2.50 (br m, 2H, $PCH_2CH_2CH_2P$), 1.89 (m, 2H, $PCH_2CH_2CH_2P$), 1.78 (q, $^{3}J_{HH} = 7$, 2H, Pd−CH_2CH_3), 0.70 (t, $^{3}J_{HH} = 7$, 3H, Pd−CH_2CH_3). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_2F$, −94.2 °C) δ 17.8 (d, $^{2}J_{PP} = 67$), −7.7 (d, $^{2}J_{PP} = 67$).

(b) Spectroscopic Characterization of 12. Generated from the migratory insertion of **11**. NMR data: $^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_2F$, −60 °C) δ 7.25−7.50 (m, 20H, $(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$), 2.64 (br m, 2H, $PCH_2CH_2CH_2P$), 2.44 (br m, 2H, $PCH_2CH_2CH_2P$), 2.29 (q, $^{3}J_{HH} = 7$, 2H, Pd−$COCH_2CH_3$), 1.93 (br m, 2H, $PCH_2CH_2CH_2P$), 0.38 (t, $^{3}J_{HH} = 7$, 3H, Pd−$COCH_2CH_3$). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_2F$, −94.2 °C) δ 2.8 (d, $^{2}J_{PP} = 83$), −9.2 (d, $^{2}J_{PP} = 83$).

(c) Rate Constant and Free Energy of Activation ($\Delta G^{\ddagger}$). The ether adduct, **5** (10 mg, ∼6.8 μmol) was dissolved in 0.7 mL of $CDCl_2F$ in a screw-capped NMR tube at −78 °C. A capillary tube containing tricyclohexyl phosphine dissolved in CD_2Cl_2 had also been added to the NMR tube as an internal standard for kinetic analysis. Ethylene (3.5 mL, ∼20 equiv) was added via syringe at −78 °C to afford the methyl ethlene complex **6**. The solution was monitored by ^{1}H NMR spectroscopy at 245 K until all of complex **6** was converted to the ethyl ethylene complex **7**. Purging the solution with carbon monoxide at −110 °C for 2 min yielded **11**. The sample was placed in a precooled NMR probe at −94.2 °C, and the decay of the resonance at δ 17.7 in the $^{31}P\{^{1}H\}$ NMR spectrum was monitored as a function of time. The slope of the line defined by the ln(integral of peak at δ 17.7) signal of **11** vs time afforded the first-order rate constant for the reaction. Spectra were taken at intervals of 1−15 min, depending on conditions. The acyl carbonyl complex **12** was produced cleanly as the only product throughout the reaction. The reaction was monitored for 2−4 half-lives. The rate constant k_{obs} (1.47×10^{-4} s^{-1} at −94.2 °C) for the migratory insertion reaction of **11** was employed to determine the $\Delta G^{\ddagger}$ (13.4(1) kcal/mol) for this reaction.

α-Acyl Migratory Insertion Reaction of (dppp)Pd(C(O)CH_3)(C_2H_4)$^+$(SbF_6), 13[SbF_6]. (a) Spectroscopic Characterization of 13-[SbF_6]: NMR data: ^{1}H NMR (300 MHz, $CDCl_2F$, −115 °C) δ 7.09−7.85 (m, 20H, $(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2$), 5.0, 4.8 (br, 4H, Pd−$\eta^2$-$C_2H_4$, rotation frozen out), 2.53 (br m, 4H, $PCH_2CH_2CH_2P$), 1.6 (br m, 2H, $PCH_2CH_2CH_2P$), 1.58 (s, 3H, Pd−$COCH_3$). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_2F$, −115 °C) δ −0.62 (d, $^{2}J_{PP} = 84$), −2.08 (d, $^{2}J_{PP} = 84$).

(b) Rate Constant and Free Energy of Activation ($\Delta G^{\ddagger}$). The acyl chloride complex, **15** (10 mg, ∼17 μm) and $AgSbF_6$ (5.7 mg, ∼17 μmol, ∼1.2 equiv) were added to an NMR tube under an inert atmosphere and were cooled to −135 °C. C_2H_4 (1 mL, ∼41 μmol, ∼2.4 equiv) was added by gastight syringe to the NMR tube followed by $CDCl_2F$ (0.6 mL) again at −135 °C. The sample was agitated slightly and placed in a precooled NMR probe. Complete conversion of the acyl chloride complex **15** to the acyl ethylene complex **13[SbF$_6$]** was not observed. The amount of **13[SbF$_6$]** generated was highly variable (∼60−85%); however, once it was placed in the NMR probe, the formation of **13[SbF$_6$]** had ceased and did not continue throughout the kinetic run. The sample was warmed to −103.1 °C to follow the conversion of **13[SbF$_6$]** to **14[SbF$_6$]**. The slope of the line defined by the ln(Pd−C_2H_4) signal of **13[SbF$_6$]** vs time afforded the first-order rate constant ($k_{obs} = 6.24 \times 10^{-4}$ s^{-1} at −103.1 °C) from which the $\Delta G^{\ddagger}$ (12.3(1) kcal/mol) could be determined.

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Supporting Information Available: Eyring plots for the migratory insertion reactions of **6**, **7**, and **8**, selected ^{13}C NMR data for complexes **5**, **6**, **8**, **10**, and **14[BAr′$_4$]**, and representative ^{1}H and ^{31}P NMR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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