

Energetics of Migratory Insertion Reactions in Pd(II) Acyl Ethylene, Alkyl Ethylene, and Alkyl Carbonyl Complexes

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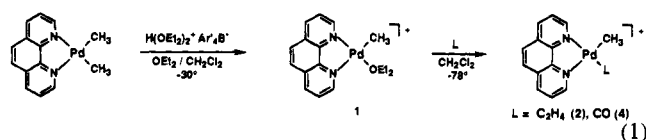
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Migratory insertion reactions of transition metal alkyl carbonyl, alkyl olefin, and acyl olefin complexes are key steps in numerous catalytic cycles.¹ While conversions of alkyl carbonyl to acyl complexes abound,¹ direct detection of migratory insertion reactions of alkyl olefin complexes² is rare, and such detection of acyl olefin complexes is unknown. The Pd(II)-mediated formation of perfectly alternating olefin/CO copolymers is an intriguing catalytic system which must involve alternating migratory insertion reactions of palladium alkyl carbonyl and palladium acyl olefin complexes.³ Such systems provide an opportunity to examine and compare fundamental migratory insertion reactions in square-planar d⁸ complexes. Simple insertion products have been isolated from certain catalytic systems; they are generally complexes of the type (L₂)-

Pd—CHR—CHR'—C(O)R''⁺,^{4,5} An *in situ* NMR study of the copolymerization of *p*-*tert*-butylstyrene/CO initiated with (2,2'-bipyridine)Pd(CH₃)(NCMe)⁺ established the acyl carbonyl complex as the catalyst resting state.⁵ In none of these studies has the key olefin intermediate, the acyl olefin complex, been observed nor the barrier to its β -migratory insertion measured. We report here studies which have allowed the first direct observation of the migratory insertion of an acyl olefin complex, (1,10-phenanthroline)Pd(C(O)CH₃)(C₂H₄)⁺, and the quantitative comparison of its migratory insertion aptitude with that of related alkyl ethylene and alkyl carbonyl palladium(II) complexes.

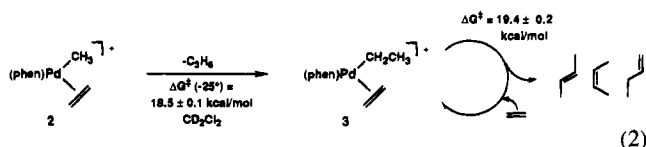
A convenient starting point for the low-temperature preparation of acyl and alkyl olefin complexes is the isolable cationic ether complex (phen)Pd(CH₃)(OEt₂)⁺Ar'₄B⁻ (**1**) (phen = 1,10-phenanthroline; Ar' = 3,5-(CF₃)₂C₆H₃). Complex **1** was isolated as a crystalline solid, stable for months at -30 °C, upon treatment of (phen)Pd(CH₃)₂⁶ with H⁺(OEt₂)₂ Ar'₄B⁻⁷ in CH₂Cl₂, Et₂O at -30 °C (eq 1). Its structure has been confirmed



by X-ray analysis. At -80 °C, the ¹H NMR resonances of the methylene hydrogens are nonequivalent, indicating hindered rotation around the Pd—O bond. These signals broaden and merge above -52 °C. Line shape analysis yields $k_{\text{rot}} = 14 \pm 3 \text{ s}^{-1}$ at -61 °C, $\Delta G^{\ddagger}_{\text{rot}} = 11.2 \pm 0.1 \text{ kcal/mol}$.

The methyl ethylene complex **2** was generated *in situ* by adding ethylene to a -78 °C CD₂Cl₂ or CD₂Cl₂/CDCl₂F solution of **1** and characterized by low-temperature NMR spectroscopy. Slightly less than 1 equiv of ethylene must be used to observe the coupling pattern of coordinated ethylene, otherwise a rapid associative exchange of Pd-bound and free ethylene occurs, averaging the two resonances. Samples prepared in this manner displayed ¹H resonances for coordinated ethylene at δ 5.11 and 4.93 (AA'BB' pattern, -110 °C) and a ¹³C resonance at δ 86.4 ($J_{\text{CH}} = 163 \text{ Hz}$).⁸

In the presence of excess ethylene, the clean conversion of **2** to propene and the ethyl ethylene complex, (phen)Pd(C₂H₅)(C₂H₄)⁺Ar'₄B⁻ (**3**) occurs at -25 °C. Complex **3** is the resting state of a catalytic system for ethylene dimerization (eq 2).⁹



The characterization of **3** is complicated since the observed NMR resonances represent an average of several exchanging olefin complexes due to the presence of propene, excess ethylene, and butenes. This problem was overcome by condensing propane directly into a -78 °C CD₂Cl₂ solution of a working dimerization system and precipitating **3** as a thermally unstable off-white solid. After the solid was washed twice with propane and vacuum dried at -78 °C, ¹H and ¹³C NMR analysis confirmed the presence of pure **3**. NMR data are similar to those for **2**, ¹H (δ 5.14, 4.79, -110 °C), ¹³C (δ 87.0, $J_{\text{CH}} = 161 \text{ Hz}$, -85 °C).

Complexes **2** and **3** allow direct comparison of the energetics of Me and Et group migrations to ethylene. The rate constant for Me migration was determined from the first-order decay of **2** by ¹H NMR spectroscopy.¹⁰ Since **3** is the resting state of an ethylene dimerization cycle, the rate constant for migratory insertion was calculated from the turnover frequency of the catalytic cycle (eq 2).¹¹ Rate constants and ΔG^{\ddagger} values at -25 °C are $k_{\text{Me} \rightarrow \text{C}_2\text{H}_4} = (2.8 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$, $\Delta G^{\ddagger}_{\text{Me} \rightarrow \text{C}_2\text{H}_4} = 18.5 \pm 0.1 \text{ kcal/mol}$; $k_{\text{Et} \rightarrow \text{C}_2\text{H}_4} = (4.7 \pm 0.6) \times 10^{-5} \text{ s}^{-1}$, $\Delta G^{\ddagger}_{\text{Et} \rightarrow \text{C}_2\text{H}_4} = 19.4 \pm 0.1 \text{ kcal/mol}$.¹² Rate constants for ethyl migration

(8) **2**: ¹H NMR (400 MHz, -110 °C, CD₂Cl₂/CDCl₂F) δ 8.82–7.8 (phen), 8.82 (d, $J = 5.2 \text{ Hz}$, 1H), 8.54 (d, $J = 8.4 \text{ Hz}$, 1H), 8.41 (d, $J = 8.4 \text{ Hz}$, 1H), 8.33 (d, $J = 4.8 \text{ Hz}$, 1H), 7.92 (dd, $J = 8.4 \text{ Hz}$, $J = 4.8 \text{ Hz}$, 1H), 7.90 (d, $J = 8.8 \text{ Hz}$, 1H), 7.87 (d, $J = 8.8 \text{ Hz}$, 1H), 7.8 (m, 9H, Ar'-H₃ + phen), 7.49 (s, 4H, Ar'-H₂), 5.11 (m, 2H, H_AH_BC=CH_AH_B), 4.93 (m, 2H, H_AH_BC=CH_AH_B), 0.920 (s, 3H, CH₃); ¹³C NMR (75 MHz, -85 °C, CD₂Cl₂) δ 86.4 (t, $J_{\text{CH}} = 163.2 \text{ Hz}$, C₂H₄). Site exchange of the ethylene ¹H resonances occurred at higher temperatures, $T_{\text{coal}} = -81 \text{ °C}$, $\Delta G^{\ddagger} = 9.2 \pm 0.2 \text{ kcal/mol}$.

(9) Butene composition is not constant during the dimerization but follows the trend *trans*- > *cis*- > 1-butene. Complete conversion of butenes into higher order oligomers occurs after ethylene is consumed.

(10) This rate constant is invariant to the presence of 5, 12, or 20 equiv of ethylene, verifying that the insertion reaction is not bimolecular between catalyst and ethylene.

(11) Linear plots of butene formation versus time were obtained even at high (80–100%) conversion of ethylene, indicating that there is no [ethylene] dependence in the turnover-limiting step.

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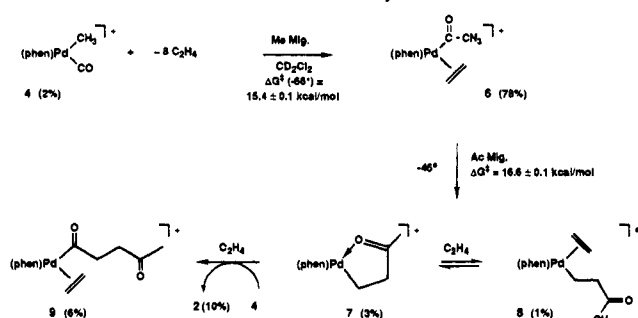
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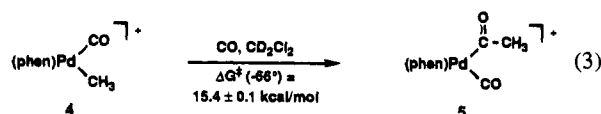
(7) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.

Scheme 1. Reaction Products of **4** Plus Ethylene^a

^a Percentage shown in parentheses represents observed products after 98% conversion of **4** at $-66^\circ C$.

were determined over a $54^\circ C$ temperature range ($-25^\circ C$ to $+29^\circ C$); an Eyring plot gave $\Delta H^\ddagger = 18.5 \pm 0.6$ kcal/mol, $\Delta S^\ddagger = -3.7 \pm 2.0$ eu. The small value of ΔS^\ddagger is consistent with other reports that $\Delta S^\ddagger \sim 0$ for alkyl^{2c,d} and hydride^{2a,13} migration to olefins.

The cationic methyl carbonyl complex **4** was formed at $-78^\circ C$ upon addition of CO to **1**¹⁴ (eq 3). This isolable complex is



a useful precursor to both *cis*-acetyl(carbonyl)- and *cis*-acetyl(ethylene)palladium complexes. Warming a $-78^\circ C$ solution of **4** and CO to $-66^\circ C$ yields the acyl carbonyl complex, $(phen)Pd(C(O)Me)(CO)^+Ar_4B^-$ (**5**). Under conditions of saturation kinetics at $-66^\circ C$, $k = (2.4 \pm 0.2) \times 10^{-4} s^{-1}$, $\Delta G^\ddagger_{Me \rightarrow CO} = 15.4(0.1)$ kcal/mol.^{15,16} Complex **5** has been isolated as $5 \cdot CH_2Cl_2$ by crystallization from CH_2Cl_2 /hexanes under a CO atmosphere at $-50^\circ C$; its structure has been confirmed by X-ray analysis.

Reaction of **4** at $-66^\circ C$ with excess (*ca.* 8 equiv) ethylene gives the unprecedented *cis*-acetyl(ethylene) species, $(phen)Pd(C(O)Me)(C_2H_4)^+Ar_4B^-$ (**6**) (78%) as well as products arising from the subsequent acetyl migration: **7** + **8** (total 4%) and $(phen)Pd(C(O)CH_2CH_2C(O)Me)(C_2H_4)^+$ (**9**) (6%) after 98% consumption of **4** (Scheme 1). The rate of conversion of **4** to **6** using ethylene as a trapping ligand ($k = (2.2 \pm 0.1) \times 10^{-4} s^{-1}$, $\Delta G^\ddagger = 15.4 \pm 0.1$ kcal/mol, saturation kinetics apply¹⁵) is unchanged¹⁷ from that determined using CO as the trap. Since conversion of **4** to **6** is only slightly faster than migratory insertion of **6**, complete conversion of **4** results in some production of **7**, **8**, and **9** at $-66^\circ C$.¹⁸ Complex **9** incorporates 2 equiv of CO, and thus **2** (*ca.* 10%) appears as the (required) non-CO-containing Pd complex.¹⁹

Ethylene-free solutions of **6** were obtained by holding the solution under vacuum at $-78^\circ C$ for 15 h. Key spectroscopic data for **6**, obtained under these conditions, include broad coordinated ethylene resonances at δ 5.25 in the 1H ($-100^\circ C$) and at δ 94 ($J_{CH} = 165 \pm 5$ Hz, $W_{1/2} = 35$ Hz, $-100^\circ C$) in the ^{13}C NMR.²⁰ The 1H resonance remains a singlet at $-120^\circ C$. These chemical shifts are similar to those observed in **2** and **3**. The acetyl carbonyl absorbs at δ 223.0, slightly downfield from the analogous carbonyl resonance in **5**, δ 216.5.

Migration of the acetyl group to ethylene was observed *in situ* by 1H NMR spectroscopy at $-46^\circ C$. In the presence of *ca.* 10 equiv of ethylene, **6** yields an equilibrating pair of complexes, the 5-membered chelate **7**, and its ethylene-coordinated open form **8**. The first-order rate constant for acetyl

migration was $k_{Ac \rightarrow C_2H_4} = (4.8 \pm 0.4) \times 10^{-4} s^{-1}$, $\Delta G^\ddagger_{Ac \rightarrow C_2H_4} = 16.6(0.1)$ kcal/mol. In the absence of free ethylene, the rearrangement of **6** to **7** occurs at the same rate, $k = 4.7 \times 10^{-4} s^{-1}$. The metallacycle **7** was independently prepared by the addition of ethylene to **4** at $20^\circ C$, followed by crystallization from CH_2Cl_2 . Subsequent exposure of **7** to ethylene confirmed generation of an equilibrating mixture of **7** and **8**. The temperature-dependent equilibrium, $7 + C_2H_4 \rightleftharpoons 8$, is studied in CD_2Cl_2 from $-92^\circ C$ to $-57^\circ C$, giving $\Delta H^\circ = -7.8 \pm 0.5$ kcal/mol, $\Delta S^\circ = -36 \pm 5$ eu.

A unique series of Pd(II) complexes has been developed which allows the first direct observation of three related migratory insertion reactions at the same metal center. These include alkyl migrations to CO and to olefin as well as the previously unobserved acyl migration to olefin. The ΔG^\ddagger for these reactions increase in the order $\Delta G^\ddagger_{Me \rightarrow CO} = 15.4 \pm 0.1$ kcal/mol ($-66^\circ C$) < $\Delta G^\ddagger_{Ac \rightarrow C_2H_4} = 16.6 \pm 0.1$ kcal/mol ($-46^\circ C$) < $\Delta G^\ddagger_{R \rightarrow C_2H_4} = ca. 19$ kcal/mol ($-25^\circ C$). These aptitudes are consistent with *in situ* low-temperature NMR studies which indicated that acyl migration to *p-tert*-butylstyrene was the rate-determining step in this copolymerization. They also suggest that a relatively high barrier for alkyl olefin migratory insertion relative to alkyl carbonyl migratory insertion plays a role in enforcing the alternating nature of the chain growth in addition to the preferred binding of CO (relative to olefins) to the palladium alkyl complex as noted by Sen.^{3a}

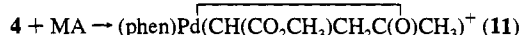
Acknowledgement is made to the National Science Foundation (CHE-8705534) and the Department of Energy for support of this work. F.C.R. was supported in part by a Department of Education Fellowship.

Supplementary Material Available: Details of syntheses and spectral data for complexes **1–11** and kinetics of migratory insertion reactions and equilibrium studies (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

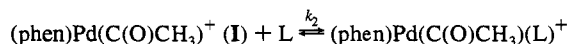
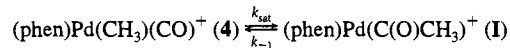
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(14) **4**: 1H NMR (300 MHz, CD_2Cl_2 , $20^\circ C$) δ 8.97–7.99 (phen), 8.97 (d, $J = 5.1$ Hz, 2H), 8.74 (d, $J = 8.4$ Hz, 1H), 8.69 (d, $J = 8.4$ Hz, 1H), 8.10 (s, 2H), 8.06 (dd, $J = 8.4$ Hz, $J = 5.4$ Hz, 1H), 7.99 (dd, $J = 8.4$ Hz, $J = 5.1$ Hz, 2H), 7.72 (s, 8H, $Ar'-H_o$), 7.54 (s, 4H, $Ar'-H_p$), 1.66 (s, 3H, CH_3); ^{13}C NMR (75 MHz, CD_2Cl_2 , $20^\circ C$) δ 176.3 (s, CO); IR (CH_2Cl_2) $\nu_{CO} = 2130$ cm^{-1} .

(15) The reaction of **4** with methyl acrylate (MA),



displays saturation kinetics: k_{obs} increases to a limiting value with increasing [MA]. (A saturation plot and complete experimental details are provided in the supplementary material.) No intermediates were observed. The limiting rate constant, $k_{sat} = (2.4(0.3)) \times 10^{-4} s^{-1}$, $\Delta G^\ddagger = 15.4(0.1)$ kcal/mol. The reaction of **4** with either excess CO or C_2H_4 occurs at the *same* rate. The origin of this effect lies in two competing reactions of the unsaturated Pd-acyl intermediate, I: (1) reversion to **4** by the microscopic reverse of migratory insertion, rate = $k_{-1}[I]$; (2) bimolecular trapping of I with a ligand, L, rate = $k_2[I][L]$. Thus, when $k_2[I][L] \gg k_{-1}[I]$, as must be the case for L = CO or ethylene, $k_{obs} = k_{sat}$.



(16) Similar chemistry has been reported for bipyridine,⁵ chelated diphosphine, and phosphine-amine Pd systems. For leading references, see: Tóth, I.; Elsevier, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 10388.

(17) This is the initial rate for one half-life before **2**, **7**, **8**, or **9** is observable and may include some trapping from trace CO. Small amounts of free CO, produced in a preequilibrium between **4** and **2**, equilibrate **6** and **5** at initial stages of the reaction. These fast (NMR time scale) equilibria are driven to **6** as CO is consumed in the migratory insertion.¹⁹

(18) At low $[C_2H_4]$, the equilibrium, $9 \rightleftharpoons (phen)Pd(C(O)CH_2CH_2C(O)CH_3)^+ (10) + C_2H_4$, is visible.

(19) Unaccounted for CO (4%) is likely exchanging with present olefin complexes.

(20) **6**: 1H NMR (400 MHz, $CD_2Cl_2/CDCl_2F$, $-100^\circ C$) δ 8.58 (d, $J = 8$ Hz, 1H), 8.51 (d, $J = 4.7$ Hz, 1H), 8.44 (d, $J = 8.6$ Hz, 1H), 8.31 (d, $J = 4.7$ Hz, 1H), 7.86 (m, 4H), 7.7 (m, 8H, $Ar'-H_o$), 7.5 (s, 4H, $Ar'-H_p$), 5.25 (br s, 4H, C_2H_4), 2.74 (s, 3H, CH_3).

(12) The opposite migratory aptitudes were observed for $Cp^*(MeO)_3P-Rh(R)(C_2H_4)^+$ ($R = Me, Et$).^{2b}

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