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Direct Observation of the Conversion of a Palladium 5-Hexenyl Chelate Complex to a Palladium Cyclopentylmethyl Complex

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Summary: Warming a solution of $\{(\mathrm{phen})\mathrm{Pd}[\eta^1{:}\eta^2\text{-}\mathrm{CH}(\mathrm{CH_2SiEt_3})\mathrm{CH_2C}(\mathrm{CO_2Me})_2\mathrm{CH_2CH{=}CH_2}]\}^+[\mathrm{BAr_4}]^-$ (**4**) *at* -41 °C *led to first-order decay* ($k = (4.7 \pm 0.3) \times 10^{-4}$ M s^{-1}, $\Delta G^{\ddagger} = 17.1 \pm 0.1$ kcal mol^{-1}) *with formation of the palladium cyclopentylmethyl complex* $\{(\mathrm{phen})\mathrm{Pd}[\mathrm{CH_2}\overline{\mathrm{CHCH_2C}(\mathrm{CO_2Me})_2\mathrm{CH_2CH}}\mathrm{CH_2SiEt_3}](\mathrm{NCAr})\}^+[\mathrm{BAr_4}]^-$ (**5**) *in 96 ± 10% yield* (^{1}H NMR).

The β-migratory insertion of a coordinated olefin into the M−C bond of a transition-metal alkyl olefin chelate complex is the presumed C−C bond forming process in numerous transition-metal-mediated and -catalyzed annulation protocols.[1] In contrast, the majority of well-characterized transition-metal alkyl olefin chelate complexes are unreactive toward insertion.[2] In two rare exceptions, insertion of Pt[3] and Y[4] 4-pentenyl chelate complexes was implicated by the scrambling of deuterium atoms between the C(1) and C(3) carbon atoms of the pentenyl ligand. However, in neither case was the presumed cyclobutylmethyl insertion product observed.[3,4] Although β-migratory insertion has been directly observed in a small number of nonchelated alkyl olefin complexes,[5] the effect of the chelate backbone on β-migratory insertion remains unknown and may be significant due to the geometric constraints of this transformation.[6] Here we report the first direct observation of the β-migratory insertion of a coordinated olefin into the M−C bond of a transition-metal alkyl olefin chelate complex.

We have developed several related procedures for the cyclization/hydrosilylation of functionalized dienes catalyzed by cationic palladium phenanthroline[7] and optically active palladium pyridine−oxazoline complexes.[8] Based on the work of Brookhart,[9] we have proposed a mechanism for palladium-catalyzed diene cyclization/hydrosilylation initiated by insertion of one of the double

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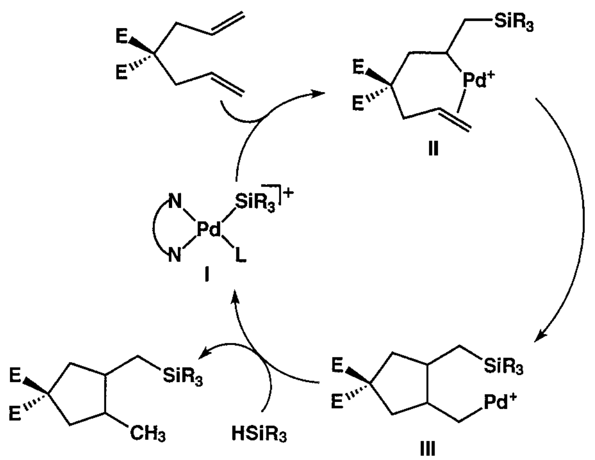
Scheme 1

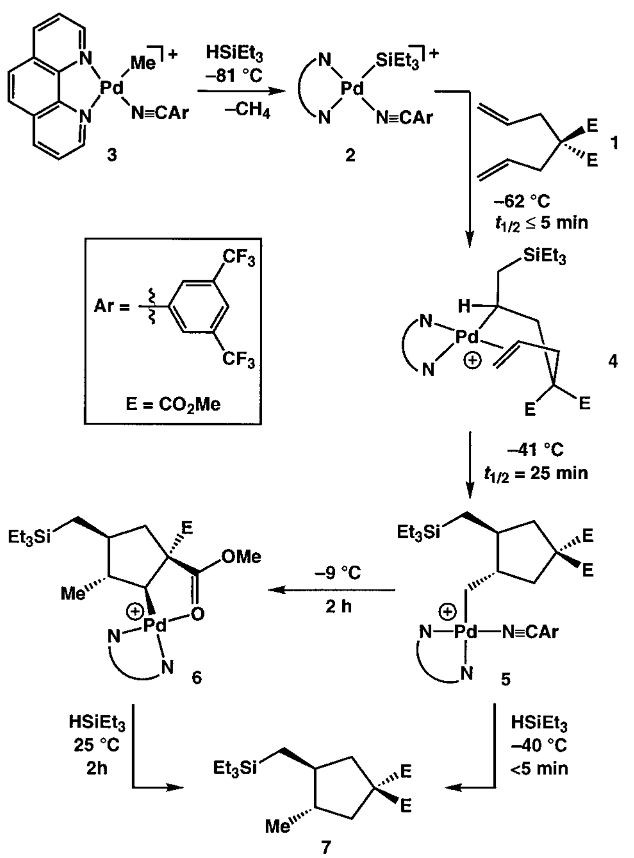


bonds of the diene into the Pd−Si bond of the palladium silyl complex **I** to form the palladium alkyl olefin chelate complex **II** (Scheme 1).[7] β-Migratory insertion of the coordinated olefin into the Pd−C bond of **II** could form the palladium cyclopentylmethyl intermediate **III**, which could react with silane to release the carbocycle and regenerate **I**.

In an effort to support our proposed cyclization/hydrosilylation mechanism, we have investigated the reaction of dimethyl diallylmalonate (**1**) with the cationic palladium silyl complex $[(phen)Pd(SiEt_3)(NCAr)]^+[BAr_4]^-$ (Ar = 3,5-$C_6H_3(CF_3)_2$) (**2**) by low-temperature NMR spectroscopy. Thermally sensitive **2** was generated in quantitative yield (101 ± 10% by ^{1}H NMR) by addition of $HSiEt_3$ (1 equiv) to a CD_2Cl_2 solution of $[(phen)Pd(Me)(NCAr)]^+[BAr_4]^-$ (**3**) (42 mM) at −81 °C and was characterized in solution by ^{1}H NMR spectroscopy (Scheme 2).[10] Silylation of **3** was established by the disappearance of the Pd−CH_3 resonance of **3** (δ 1.23) and the appearance of the Pd−$SiEt_3$ resonances of **2** (δ 0.97 (q), 1.06 (t), $J = 7.5$ Hz) and free methane (δ 0.21) in the ^{1}H NMR spectrum.

Addition of **1** (1 equiv) to a solution of **2** at −62 °C led to rapid ($t_{1/2} \leq 5$ min) formation of the palladium 2-((triethylsilyl)methyl)-5-hexenyl chelate complex $\{(phen)Pd[\eta^1:\eta^2\text{-}CH(CH_2SiEt_3)CH_2C(CO_2Me)_2CH_2CH{=}CH_2]\}^+[BAr_4]^-$ (**4**) in 84 ± 10% yield by ^{1}H NMR spectroscopy as a single diastereomer.[11] Thermally sensitive **4** was characterized in solution at −62 °C by NMR spectroscopy.[12] The ^{1}H NMR spectrum of **4** displayed a one-proton multiplet at δ 2.66 (Pd−C*H*), a one-proton doublet of doublets at δ 1.11 ($J = 3$, 13 Hz, −C*H*HSiEt$_3$), and a one-proton triplet at δ 1.23 ($J = 13$ Hz, −CH*H*SiEt$_3$), which together established insertion of an olefin of **1** into the Pd−Si bond of **2**. Olefin coordination was established by the large difference of the ^{1}H NMR chemical shifts of the olefinic protons of **4** (δ 6.41 (m), 5.44 ($J_{cis} = 9$ Hz), and 4.22 ($J_{trans} = 16$ Hz)) relative to the corresponding olefinic resonances of uncomplexed **1** (δ 5.53, 5.09, and 5.06). Olefin coordination was further supported by the large difference of the ^{13}C NMR chemical shifts and reduced $J_{C=C}$ coupling constant[13] of the olefinic carbon atoms of $\{(phen)Pd[\eta^1:\eta^2\text{-}^{13}CH(^{13}CH_2SiEt_3)^{13}CH_2C(CO_2Me)_2{}^{13}CH_2{}^{13}CH{=}^{13}CH_2]\}^+[BAr_4]^-$ (**4**-$^{13}C_6$) (δ 103.7 (dd), 87.5 (d), $J_{C=C} = 47$ Hz), relative to the olefinic carbon atoms of uncomplexed **1**-$^{13}C_6$ (δ 131.4 (dd), 119.7 (d), $J_{C=C} = 69$ Hz) under identical conditions. We assign **4** an axial boatlike conformation on the basis of DFT calculations of the hypothetical palladium hexenyl chelate complex $\{(NH{=}CHCH{=}NH)Pd[\eta^1:\eta^2\text{-}CH(CH_2Me)CH_2C(Me)_2CH_2CH{=}CH_2]\}^+$ (**4a**).[14]

Scheme 2



Warming a solution of **4** and NCAr (released in the formation of **4**) at −41 °C for 2 h led to β-migratory insertion and formation of the palladium cyclopentylmethyl complex $\{(phen)Pd[CH_2CHCH_2C(CO_2Me)_2CH_2CHCH_2SiEt_3](NCAr)\}^+[BAr_4]^-$ (**5**) in 96 ± 10% yield by ^{1}H NMR spectroscopy as a single diastereomer. Thermally sensitive **5** was characterized in solution by ^{1}H and ^{13}C NMR spectroscopy at −41 °C.[11,12] The ^{1}H NMR spectrum of **5** displayed two one-proton multiplets at δ 1.67 and 1.80, assigned to the cyclopentyl methine protons, and two one-proton doublets of doublets at δ 2.09 ($J = 8$, 11 Hz) and 2.52 ($J = 4$, 8 Hz), assigned to the palladium-bound methylene group, which together established β-migratory insertion and cyclopentyl ring

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(10) Similar palladium silyl complexes have been reported.[9]

(11) No byproducts were observed in any of these transformations. The formation of **6** in 93% overall yield from **3** suggests that the yield for the conversion of **2** to **4** was higher than indicated by ^{1}H NMR.

(12) Assignment of ^{1}H NMR resonances and determination of J_{HH} coupling constants for **4** and **5** was facilitated by spectroscopic analysis of $\{(phen)Pd[\eta^1:\eta^2\text{-}CD(CH_2SiEt_3)CH_2C(CO_2Me)_2CH_2CD{=}CH_2]\}^+[BAr_4]^-$ (**4**-d_2), $\{(phen)Pd[\eta^1:\eta^2\text{-}CH(CH_2SiEt_3)CD_2C(CO_2Me)_2CD_2CH{=}CH_2]\}^+[BAr_4]^-$ (**4**-d_4), $\{(phen)Pd[CH_2CDCH_2C(CO_2Me)_2CH_2CDCH_2SiEt_3](NCAr)\}^+[BAr_4]^-$ (**5**-d_2), and $\{(phen)Pd[CH_2CHCD_2C(CO_2Me)_2CD_2CHCH_2SiEt_3](NCAr)\}^+[BAr_4]^-$ (**5**-d_4) and through ^{1}H COSY analysis of **4** and **5**.

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formation. Disappearance of **4** at −41 °C obeyed first-order kinetics to >3 half-lives with a rate constant of $k = (4.7 \pm 0.3) \times 10^{-4}$ M s^{-1} ($\Delta G^{\ddagger} = 17.1 \pm 0.1$ kcal mol^{-1}). The barrier for β-migratory insertion of **4** to form **5** was significantly lower than the insertion barriers of unchelated (phen)Pd(R)(ethylene)$^+$ complexes, which range from 18.5 to 19.4 kcal mol^{-1}.[15]

Warming a solution of **5** at −9 °C for 2 h led to rearrangement and formation of the thermally stable cyclopentyl chelate complex $\{(\mathrm{phen})\mathrm{Pd}[\mathrm{CHCH(Me)CH(CH_2SiEt_3)CH_2C(COOMe)(COOMe)}]\}^+[\mathrm{BAr_4}]^-$ (**6**) in 110 ± 10% yield (93 ± 10% from **3**) by ^{1}H NMR spectroscopy as a single diastereomer (Scheme 2).[15] Complex **6** was subsequently isolated in 78% yield from the preparative-scale reaction of $[(\mathrm{phen})\mathrm{Pd(Me)(CH_3CN)}]^+[\mathrm{BAr_4}]^-$ (**3a**), **1**, and $\mathrm{HSiEt_3}$ and was characterized by spectroscopy and elemental analysis. The ^{1}H NMR spectrum of **6** displayed a one-proton doublet at δ 2.47 ($J = 10.5$ Hz, Pd−C*H*) and a three-proton doublet at δ 1.20 ($J = 6.5$ Hz, CH−CH_3), which together established migration of the palladium atom from the exocyclic methylene carbon to the cyclopentyl ring.

Cyclopentylmethyl complex **5** reacted with $\mathrm{HSiEt_3}$ (1.6 equiv) within 5 min at −40 °C to form a 1:1 mixture of **2** and 1,1-dicarbomethoxy-3-((triethylsilyl)methyl)-4-methylcyclopentane (**7**) as the exclusive products (Scheme 2). In comparison, reaction of **6** with $\mathrm{HSiEt_3}$ required 2 h at room temperature to form **7** as the exclusive organic product (Scheme 2).[16] The facile silylation of **5** coupled with the slow isomerization of **5** to **6** precludes the intermediacy of **6** in the palladium-catalyzed cyclization/hydrosilylation of **1**.

In summary, conversion of the palladium 5-hexenyl chelate complex **4** to the palladium cyclopentylmethyl complex **5** represents the first direct observation of the β-migratory insertion of a coordinated olefin into the M−C bond of a transition-metal alkyl olefin chelate complex. In addition, the experiments described above provide direct support for the intermediacy of complexes **2**, **4**, and **5** and rule out the intermediacy of cyclopentyl chelate complex **6** in the palladium-catalyzed cyclization/hydrosilylation of **1**.

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Supporting Information Available: Text and figures giving experimental procedures and spectroscopic data for the synthesis of new compounds and isotopomers and kinetic data for the conversion of **4** to **5** and of **5** to **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) We assume complex **2** was also formed in this reaction. However, the low thermal stability of **2** precluded its detection under these conditions.