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Article

Competitive Benzene C−H Bond Activation versus Olefin Insertion in a (Monomethyl)palladium(II) β-Diketiminate Complex

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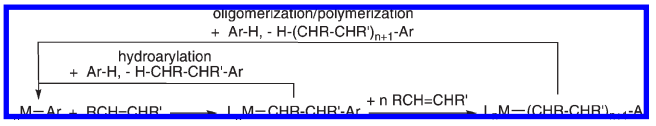
The monomethylpalladium(II) complex (COD)Pd(CH_3)Cl (COD = 1,5-cyclooctadiene) is found to undergo both benzene C−H activation and migratory insertion of olefin, with the former faster than the latter, at room temperature in the presence of an anionic β-diketiminate ligand, to yield η^3-(6-R-cyclooctenyl)palladium(II) β-diketiminate (R = methyl or phenyl). The reaction is proposed to take place via the formation of a (monomethyl)palladium(II) β-diketiminate with COD as the fourth ligand, followed by competitive benzene C−H activation and migratory insertion of olefin. The proposed mechanism is supported by density functional theory calculations upon a simplified model system.

Coupling of arenes and olefins via aromatic C−H activation by transition metal complexes provides an efficient and atom-economic way to construct C−C bonds.[1] Most arene−olefin coupling reactions are limited to activated olefins and arenes with chelation assistance;[2] however, there have been several recent reports of hydroarylation involving simple arenes (e.g., benzene and toluene) and nonactivated olefins at elevated temperatures, using catalysts based on Ir, Ru, and Pt.[3] In general, these reactions proceed by aromatic C−H activation followed by migratory insertion of olefin into the resulting metal−aryl bond, to generate a β-aryl-alkyl complex; this key intermediate can undergo aromatic C−H activation to liberate the C−C coupled product and regenerate the aryl complex.[4] However, it can also undergo additional olefin insertions, so that olefin oligmerization/polymerization can be a competing side reaction (Scheme 1). Understanding the factors controlling the relative rates of these two reactions, which determine the selectivity for olefin hydroarylation,[3,4] is essential for rational design of improved catalysts. (Side reactions presumably involving β-hydride elimination of the β-aryl-alkyl complex or olefinic C−H activation have also been observed under harsh conditions, e.g., 180 °C reaction temperature).[3d,3e]

Scheme 1



The results for platinum suggest that palladium might also be a promising metal for catalyzing olefin hydroarylation, and indeed C−H activation of simple arenes by monomethylpalladium(II) has been demonstrated.[5] However, related monomethylpalladium(II) complexes often are highly active for olefin oligomerization/polymerization,[6] so the competition of Scheme 1 may well be unfavorable in many cases. Herein, we report a monomethylpalladium(II) system for which benzene C−H activation and migratory insertion of olefins are competitive, with the former faster at room temperature, along with experimental and computational findings relevant to the mechanism.

Results and Discussion

Addition of lithium β-diketiminate **2** to a CD_2Cl_2 solution containing 1 equiv of (COD)Pd(CH_3)Cl (**1**, COD = 1, 5-

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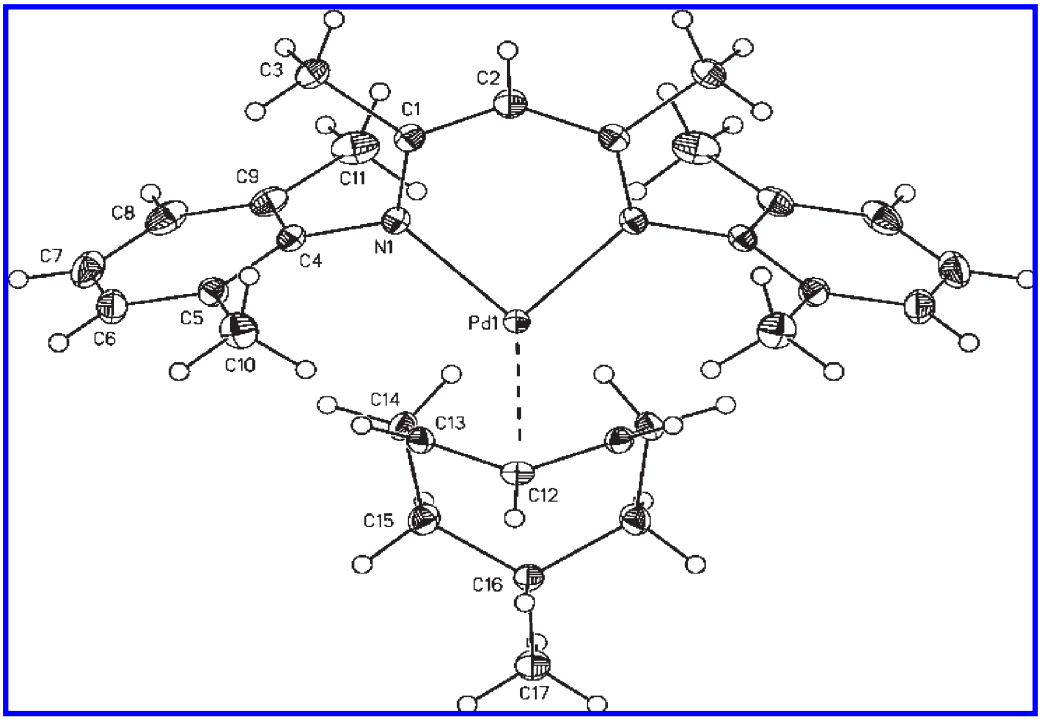
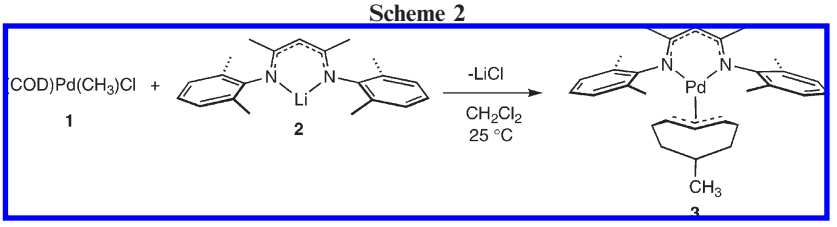
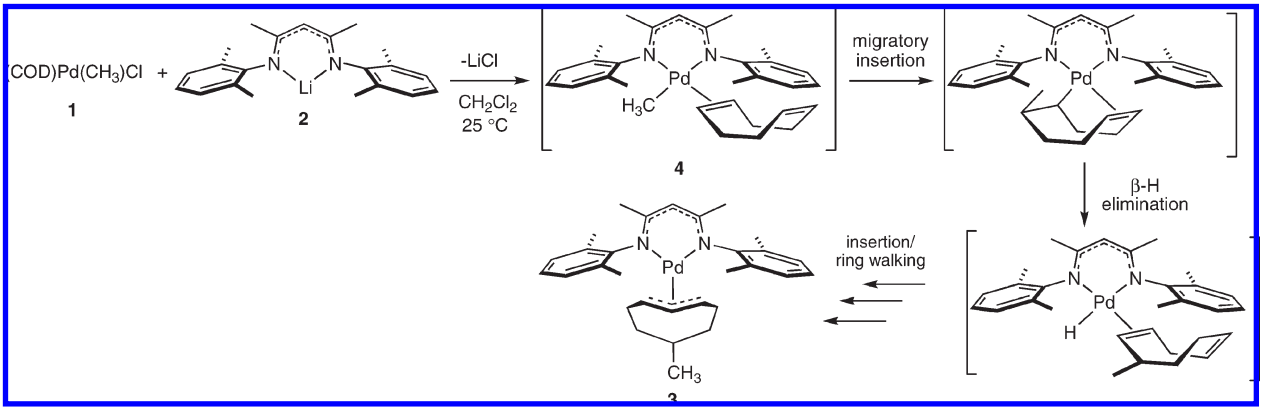


Figure 1. X-ray crystal structure of compound **3** (CCDC 295981). Selected bond distances (Å): Pd(1)−N(1), 2.0708(10); Pd(1)−C(12), 2.0932(16); Pd(1)−C(13), 2.1696(11).

Scheme 2



Scheme 3

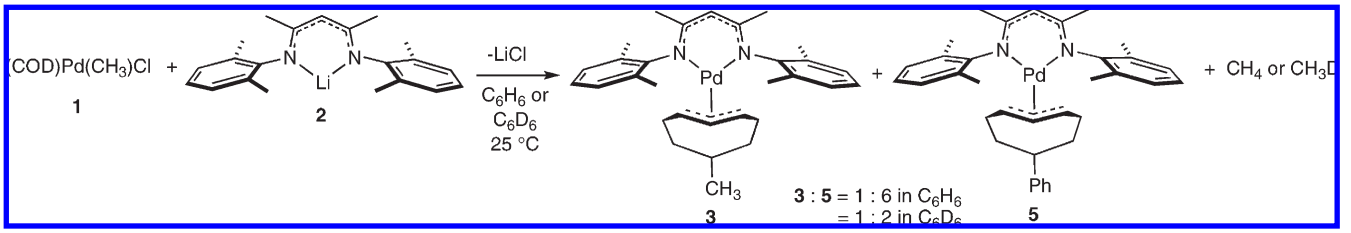


cyclooctadiene), at room temperature under nitrogen, results in a yellow solution with some black precipitate. Crystals obtained from solution were identified by ^{1}H NMR and X-ray crystallography as η^3-(6-methylcyclooctenyl)palladium(II) β-diketiminate (**3**, Scheme 2). The ^{1}H NMR spectrum, particularly the characteristic triplet, singlet, and doublet at δ_H = 5.03 (the proton at the central carbon of the η^3-allyl fragment), 4.53 (the proton at the central carbon of the β-diketiminate backbone), and 0.43 (the proton of the methyl group on the cyclooctenyl moiety) respectively,[7] indicates that the complex is symmetrical about the plane bisecting the diketiminate ligand, while the crystal structure (Figure 1) shows that the methyl group on the cyclooctenyl moiety is *cis* to Pd.

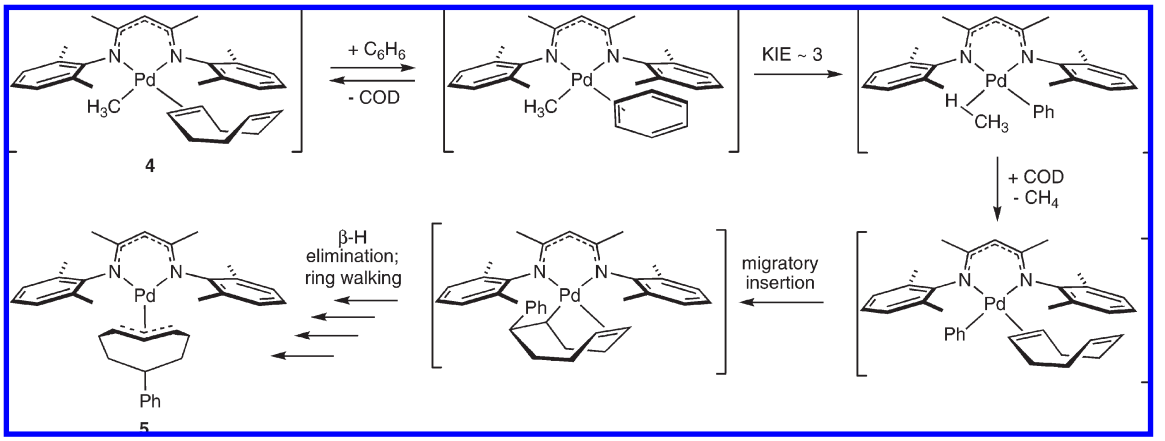
A mechanism for the formation of **3** is proposed in Scheme 3. Salt metathesis between (COD)Pd(CH$_3$)Cl and

(7) Synthesis of (η^3-propenyl)palladium(II) β-diketiminates have recently been reported: Tian, X.; Goddard, R.; Porschke, K. R. *Organometallics* **2006**, *25*, 5854–5862.

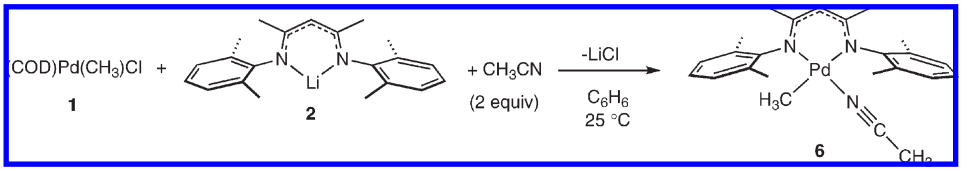
Scheme 4



Scheme 5



Scheme 6



lithium β-diketiminate affords COD-coordinated monomethylpalladium(II) β-diketiminate (**4**). Migratory insertion of COD into the Pd−CH_3 bond leads to η^1-methylcyclooctenylpalladium(II), which further undergoes a series of β-hydride eliminations and migratory insertions to form the η^3-allyl species **3**, presumably thermodynamically preferred among all the isomers in the ring-walking process. The *cis* conformation of **3** suggests that dissociation of coordinated olefins from the Pd(olefin)(H) intermediates does not occur.

When the reaction is carried out in benzene (C_6H_6) instead of CD_2Cl_2, some **3** still forms, but the ^{1}H NMR indicates the presence of a new species **5** as well. The new ^{1}H NMR signals assigned to **5** (in CD_2Cl_2) are similar to those of **1**, with a triplet at δ_H 5.42 and a singlet at δ_H 4.76; there are also several new signals in the aromatic region. If the same reaction is carried out in a closed NMR tube using C_6D_6 as the solvent, formation of CH_3D was observed, indicating benzene C−D bond activation by monomethylpalladium(II), and the new aromatic signals are absent. (The formation of a small amount of CH_4 is observed, presumably due to competing C−H bond activation of COD or β-diketiminate.) These findings strongly suggest that **5** is the phenyl analogue of **3**, η^3-(6-phenylcyclooctenyl)palladium(II) β-diketiminate (Scheme 4). The assignment is further supported by high-resolution FAB+ mass spectroscopy, which gives signals corresponding to the molecular cation and the cation of the molecule minus the phenylcyclooctenyl moiety.

Because sharp ^{1}H NMR signals are observed for N-aryl methyl groups of both **3** and **5**, rotation of the allyl moiety appears to be slow on the NMR time scale, which is in sharp contrast to many other (η^3-allyl)palladium(II) systems.[8] Slow apparent rotation has also been recently noted for (η^3-propenyl)palladium(II) β-diketiminates.[7]

The ratio of products **3** and **5**, by NMR, is approximately 1:6 for the reaction in C_6H_6 and 1:2 in C_6D_6. Since these ratios reflect the relative rates of benzene C−H/C−D activation by monomethylpalladium(II) and insertion of COD into the Pd−CH_3 bond, and because the latter is isotope insensitive, the ratio (~3) reflects the kinetic isotope effect (KIE) for benzene C−H activation. This suggests that C−H bond breaking is the rate-determining step in the formation of **5**. Scheme 5 shows the proposed mechanism: after formation of intermediate **4**, displacement of COD by benzene takes place, followed by C−H activation to form phenylpalladium(II) and release methane. The resultant phenylpalladium(II) then undergoes migratory insertion with COD and forms an η^1-(phenylcyclooctenyl)palladium(II); the ring-walking process discussed above leads to the η^3-allyl species **5**.

(8) For a review involving discussions of apparent rotation in (η^3-allyl)palladium(II) systems and its mechanisms, see: Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395–422.

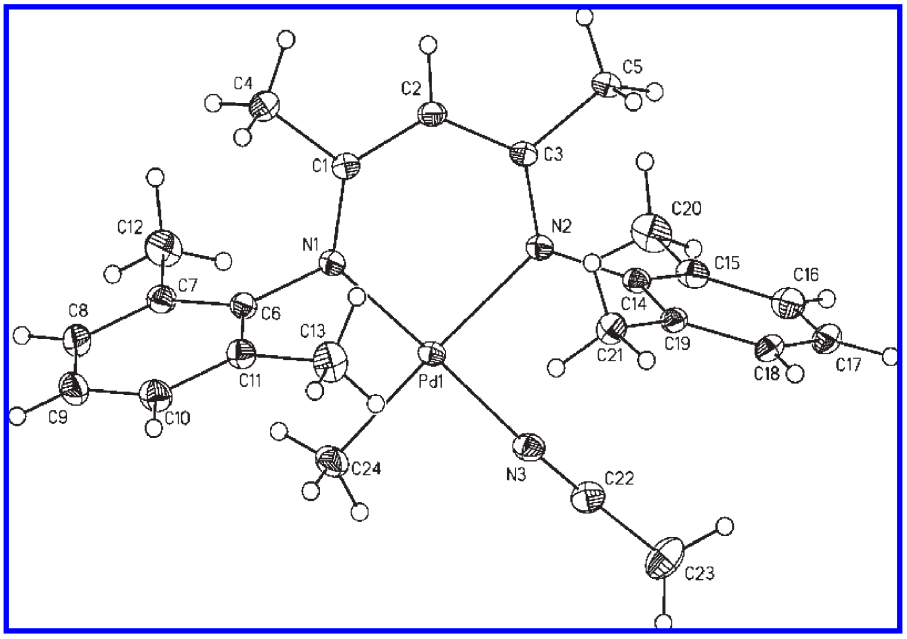
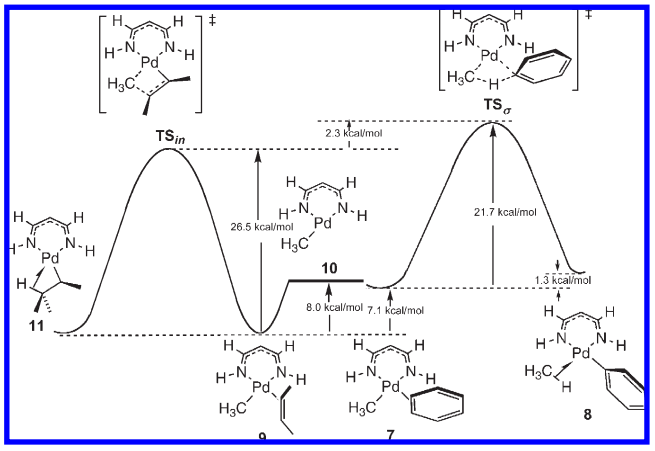


Figure 2. X-ray crystal structure of compound **6** (CCDC 296075). Selected bond distances (Å): Pd(1)−N(3), 2.0135(9); Pd(1)−N(1), 2.0262(8); Pd(1)−C(24), 2.0526(9); Pd(1)−N(2), 2.1113(7).

Scheme 7



If 2 equiv of acetonitrile is added to the reaction mixture containing **1** and **2** in benzene, neither **3** nor **5** is formed; instead monomethylpalladium(II)(acetonitrile) complex **6** is obtained nearly quantitatively (Scheme 6). The crystal structure of **6** (Figure 2) shows that (in contrast to **3** and **5**) the coordination plane is a plane of symmetry, consistent with the ^{1}H NMR spectrum. Related monomethylpalladium(II) β-diketiminates have been previously reported.[7,9] Although **6** is fairly stable in C_6D_6 at room temperature, it decomposes to a mixture of uncharacterized products at 80 °C with the formation of a significant amount of CH_3D, indicative of the activation of a benzene C−D bond. This is in sharp contrast to a related acetonitrile-ligated monomethylplatinum(II) complex supported by another monoanionic N,N-based ligand, which is stable in refluxing benzene.[10]

The mechanism for benzene C−H activation could involve either σ-bond metathesis or oxidative addition followed by reductive elimination. Pd^{IV}-*H* is generally considered to be a high-energy intermediate, which might argue against the latter, but it cannot be firmly excluded. To compare these two mechanisms, density functional theory (DFT) calculations at the level of rB3LYP/LACVP**[11] were performed on a model system with a simplified β-diketiminate ligand. The computational results suggest that σ-bond metathesis is indeed preferred over oxidative addition for the conversion of **7** to **8**, with the activation free energy of the former (21.7 kcal/mol) lower than that of the latter by 9.6 kcal/mol and the product, methane adduct **8**, slightly less stable (by 1.3 kcal/mol) than benzene adduct **7**.

The competition between benzene C−H activation via σ-bond metathesis (TS$_\sigma$) and migratory insertion (TS$_{in}$) was subsequently investigated by DFT for the same system, using *cis*-2-butene as a simplified model for COD. Coordination of benzene is calculated to be 7.1 kcal/mol weaker than that of *cis*-2-butene (**9** + C_6H_6 to **7** + *cis*-2-butene, Scheme 7). Although a transition state for associative displacement of *cis*-2-butene by benzene (a mechanism tentatively suggested by experimental observations)[12] was not located, the activation barrier for the dissociative mechanism, which should be approximately equal to the dissociation free energy of coordinated *cis*-2-butene from **7**, 8.0 kcal/mol, can be taken as an upper limit. Hence displacement of olefin by benzene should be fast compared to breaking the benzene C−H bond, which is consistent with the experimentally observed KIE of about 3.

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(11) *Jaguar*, version 6.5 ; Schrodinger, LLC: New York, 2005.
(12) Use of the sterically bulkier *N*,*N*′-2,6-diisopropylphenyl-substituted β-diketiminate instead of **2** for the reaction in C_6D_6 gives only a trace amount of CH_3D, indicating that the activation of the benzene C−D bond is significantly suppressed. This suggests that the displacement of COD by benzene in Scheme 5 is associative; however, in the absence of any well-characterized products from this reaction, no firm conclusion can be drawn. The formation of a significant amount of CH_4 is also observed, presumably due to the competing C−H bond activation of COD or β-diketiminate. Further characterization of the palladium products is needed to identify the source of the CH_4.

Further calculations indicate that migratory insertion of *cis*-2-butene into Pd−CH_3 (**9** to **11**, Scheme 7) is nearly thermoneutral and has a 26.5 kcal/mol activation free energy, lower than that of TS_σ by 2.3 kcal/mol. This small difference appears consistent with the experimental observation of competitive C−H activation vs migratory insertion, given the imprecision of DFT calculations as well as the simplified model system.

In summary, we have demonstrated that our monomethylpalladium(II) β-diketiminate can undergo both benzene C−H activation and migratory insertion of olefin at room temperature. The simultaneous observation of these two reactions for metal alkyls has previously only been demonstrated in the catalytic hydroarylation of olefins at elevated temperatures.[3] In addition, unlike other monomethylpalladium(II) systems, where olefin oligomerizations and polymerizations dominate, benzene C−H activation is somewhat favored in our system. DFT calculations on a simplified model system suggest that the C−H activation occurs through a σ-bond metathesis mechanism. Further work is underway to investigate effects of various anionic ligands on the competition between benzene C−H activation and migratory insertion at monomethylpalladium(II), with the goal of gaining insights leading to the design of Pd(II)-based catalysts for hydroarylation of olefins.

Experimental Section

General Information. All air- and/or moisture-sensitive compounds were manipulated by using standard Schlenk techniques or in a glovebox under a nitrogen atmosphere. All starting materials are commercially available and used as received without further purification. Solvents were dried with appropriate methods before use and stored under nitrogen. (COD)Pd(CH_3)Cl was synthesized according to the literature procedure.[13] A modified literature procedure was used for the synthesis of THF-free lithium β-diketiminates.[14] All NMR spectra were recorded at room temperature using a Varian Mercury 300 spectrometer. NMR spectra were referenced to TMS using the residual impurities of the given solvent. Chemical shifts are reported using the standard δ notation in parts per million; positive chemical shifts are to a higher frequency from TMS, and coupling constants are reported in Hz. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of triplets (dt), triplet (t), quartet (q), multiplet (m), broad resonance (br). The Caltech X-ray Crystallography Laboratory provided the X-ray analysis. High-resolution mass spectra were obtained at Caltech Mass Spectrometry Laboratory.

Preparation of Compound 3. Lithium *N*,*N*′-2,6-dimethylphenyl-substituted β-diketiminate **2** (11.8 mg, 0.0374 mmol) and (COD)Pd(CH_3)Cl (10 mg, 0.0377 mmol) was mixed with 0.7 mL of CD_2Cl_2 at room temperature under nitrogen in a J-Young tube. The solution turned yellow immediately upon mixing with slow precipitation of a black solid. The reaction was complete after 24 h, with **3** as the major product (NMR yield: 90%). After removal of the precipitate, crystals suitable for X-ray structural analysis were obtained by thermal diffusion of petroleum ether into the filtrate in the refrigerator. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 6.85−6.80 (m, 4H), 6.69−6.63 (m, 2H), 5.03 (t, J = 7.9, 1H), 4.53 (s, 1H), 2.40 (q, J = 8.0, 2H), 2.02 (s, 6H), 1.95 (s, 6H), 1.34 (s, 6H), 0.97−0.49 (m, 9H), 0.43 (d, J = 6.6, 3H). ^{13}C NMR (75 MHz, CH_2Cl_2): δ 158.30, 155.20, 131.26, 129.67, 127.75, 127.72, 123.23, 109.13, 93.99, 73.65, 34.64, 29.19, 27.78, 22.13, 21.96, 18.66, 18.41. HRMS (FAB+): *m*/*z* calcd for $C_{30}H_{40}N_2Pd$ 534.2227, found 534.2207.

Preparation of Compound 5. Lithium *N*,*N*′-2,6-dimethylphenyl-substituted β-diketiminate **2** (11.8 mg, 0.0374 mmol) and (COD)Pd(CH_3)Cl (10 mg, 0.0377 mmol) were dissolved in 0.5 mL of C_6H_6 and stirred overnight at room temperature under nitrogen. The solution turned yellow immediately upon mixing with slow precipitation of a black solid. After the removal of the precipitate and the solvent, a yellow solid was obtained. The ^{1}H NMR spectrum of the solid in CD_2Cl_2 shows that compound **5** is the major product (NMR yield: 81%), which was further characterized by high-resolution mass spectroscopy. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.20−6.81 (m, 11H), 5.42 (t, J = 7.9, 1H), 4.76 (s, 1H), 2.79 (tt, J = 2.8, 12, 1H), 2.66 (q, J = 8.0, 2H), 2.27 (s, 6H), 2.19 (s, 6H), 1.57 (s, 6H), 1.39−0.98 (m, 8H). HRMS (FAB+): *m*/*z* calcd for $C_{35}H_{42}N_2Pd$ 596.2383, found 596.2424; [M − phenylcyclooctenyl]$^+$ calcd for $C_{21}H_{28}N_2Pd$ 414.13, found 414.1061.

Preparation of Compound 6. Lithium *N*,*N*′-2,6-dimethylphenyl-substituted β-diketiminate **2** (11.8 mg, 0.0374 mmol), (COD)Pd(CH_3)Cl (10 mg, 0.0377 mmol), and ∼2 equiv of acetonitrile were dissolved in 0.7 mL of C_6H_6 and stirred overnight at room temperature under nitrogen. The solution turned yellow immediately upon mixing with slow precipitation of a black solid. After 24 h, the solution was filtered to remove the precipitate and volatiles were removed under vacuum. A yellow solid was obtained, consisting entirely (^{1}H NMR, $CDCl_3$) of **6**. Crystals suitable for X-ray structural analysis were obtained by thermal diffusion of petroleum ether into the filtrate in a refrigerator (isolated yield > 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04 (d, J = 7.4, 4H), 6.97−6.78 (m, 2H), 4.72 (s, 1H), 2.32 (s, 6H), 2.22 (s, 6H), 1.57 (s, 3H), 1.53 (s, 3H), 1.53 (s, 3H), −0.57 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.53, 159.91, 154.56, 147.69, 134.99, 134.77, 131.57, 130.14, 129.90, 126.21, 125.70, 96.08, 27.27, 25.47, 21.45, 21.28, 4.69, 0.63. HRMS (FAB+): *m*/*z* calcd for $C_{24}H_{31}N_3Pd$ 467.1553, found 467.1571.

Computational Methodology. All the structures were fully optimized by using the restricted hybrid density functional theory B3LYP method as implemented in the Jaguar 6.5 program package.[11] The Pd was described by LACVP**, a basis set consisting of the Wadt and Hay[15] relativistic effective core potentials (RECPs) and valence double-ζ contraction functions. A modified variant of Pople's[16] all-electron basis set, 6-31G**, where the six d functions have been reduced to five, was used for all other atoms. It should be noted that the computation method used in this study is commonly more reliable in studying trends than providing absolute numbers for the reactions, although model calculations with similar methods have been demonstrated to afford remarkably accurate figures in absolute terms for migratory insertions.[17]

All species were treated as singlets. Harmonic vibrational frequencies were calculated with the B3LYP method for the optimized geometries. Zero-point vibrational energy corrections and thermodynamic corrections were obtained by using unscaled frequencies. Free energies were calculated for each species at 298 K and 1 atm in the gas phase. All transition structures possess one and only one imaginary frequency and

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were further confirmed by following the corresponding normal mode toward each product and reactant.

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Supporting Information Available: Detailed experimental and computational data. This material is available free of charge via the Internet at http://pubs.acs.org.