Synthesis and Crystal Structure of a Dinuclear Palladium Complex Containing C,O-Bridging Ester−Enolato Moieties

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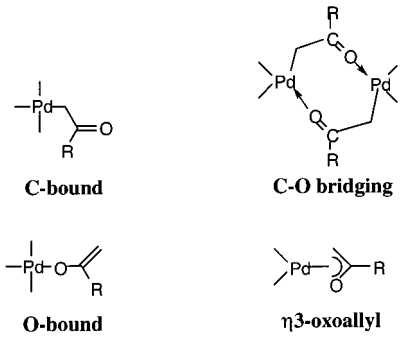
Palladium ester enolates have been prepared and characterized using IR, NMR, and single-crystal X-ray diffraction techniques. The X-ray diffraction established a dimeric crystal structure for complex $\{[N\hat{}N]PdCH_2C(O)OCH_3\}_2$ (N^N = 1-[1-(5-methylpyrrole-2-yl)ethylidne]-amino-2,6-diisopropylbenzene), **2**, which contains C,O-bridging enolato groups. Upon reaction with donor molecules (acetonitrile, phosphines), the dimeric **2** cleaves to form monometallic C-bound enolate complexes, **3′** and **4**.

The formation of palladium enolates is assumed to be a crucial step in numerous organic transformations. Examples include the direct arylation of esters and ketones,[1] aldol-like and Mannich-type reactions,[2,3] and the arylation of acrylates (Heck reactions).[4] Palladium ester enolates have also been proposed as key intermediates in the copolymerzation of ethylene and acrylates.[5] Evidence for the presence of palladium enolates in these organic reactions and polymerizations rests mainly on spectroscopic data.[3a,6] Some palladium enolates have been isolated and characterized, and various bonding modes are found for the enolato groups (Chart 1). Unlike early transition metal and rare earth enolates, carbon-bound enolates are the most common binding mode found in palladium complexes due largely to the low oxophility of palladium.[7] When a second coordination site is available, the C,O-bridging[7a,c,8] or η^3-oxoallyl enolate[9] can also be seen. The O-bound enolates, although very scarce in late metal complexes, can also be found in palladium complexes.[10]

Chart 1



Among the isolated and well-characterized palladium enolates, most of them are ketonyl complexes. Only a few examples are known for palladium ester enolates, and no crystal structure is available to date.[7f,11] Herein, we report the synthesis and the first crystal structure of palladium ester enolates.

During our studies on group VIII complexes for olefin copolymerizations with polar monomers, we discovered that palladium-based neutral complexes possessing 2-iminopyrrole ligands were highly active initiators for methylacrylate homopolymerization and copolymerization with olefins (e.g., 1-hexene, norbornene).[12] Realizing that palladium ester enolates could be reasonable

(1) Palucki, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 11108−11109.

(2) (a) Ito, Y.; Aoyama, H.; Hirao, T.; Mochizuki, A.; Saegusa, T. *J. Am. Chem. Soc.* **1979**, *101*, 494−496. (b) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011−1013.

(3) (a) Fujii, A.; Hagiwara, E.; Sodeoka, M. *J. Am. Chem. Soc.* **1999**, *121*, 5450−5458. (b) Hagiwar, E.; Fuji, A.; Sodeoka, M. *J. Am. Chem. Soc.* **1998**, *120*, 2474−2475.

(4) (a) Cabri, W.; Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2−7. (b) Meijere, A. de; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379−2411.

(5) (a) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 899. (b) Brookhart, M.; Johnson, L. K.; Killian, C. M.; Arthur, S. D.; Feldman, J.; McCord, E. F.; Mclain, S. J.; Kreutzer, K. A.; Bennett, A. M.; Coughlin, B. E.; Ittel, S. D.; Parthasarethy, A.; Tempel, D. J. Pat. Appl. WO 96/23010, 1996.

(6) (a) Brown, J. M.; Hii, K. K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 657−659. (b) Sodeoka, M.; Ohrai, K.; Shibasaki, M. *J. Org. Chem.* **1995**, *60*, 2648−2649.

(7) (a) Albeniz, A. C.; Catalina, N. M.; Espinet, P.; Redon, R. *Organometallics* **1999**, *18*, 5571−5576. (b) Vicente, J.; Abad, J. A.; Chicote, M.-T.; Abrisqueta, M.-D.; Lorca, J.-A.; de Arellano, M. C. R. *Organometallics* **1998**, *17*, 1564−1568. (c) Veya, P.; Floriani, C. *Organometallics* **1993**, *12*, 4899−4907. (d) Suzuki, K.; Yamamoto, H. *Inorg. Chim. Acta* **1993**, *208*, 225−229. (e) Byers, P. K.; Canty, A. J.; Skelton, B. W.; Traill, P. R.; Watson, A. A.; White, A. H. *Organometallics* **1992**, *11*, 3085−3088. (f) Burkhardt, E. R.; Bergman, R. G.; Heathcock, C. H. *Organometallics* **1990**, *9*, 30−44. (g) Wanat, R. A.; Collum, D. B. *Organometallics* **1986**, *5*, 120−127. (h) Bertani, R.; Castellani, C. B.; Crociani, B. *J. Organomet. Chem.* **1984**, *269*, C15−C18.

(8) (a) Vicente, J.; Arcas, A.; Fernandez-Hernandex, J. M.; Bautista, D. *Organometallics* **2001**, *20*, 2767. (b) Ruiz, J.; Rodriguez, V.; Cutillas, N.; Pardo, M.; Perez, J.; Lopez, G. *Organometallics* **2001**, *20*, 1973−1982.

(9) (a) Lemke, F. R.; Kubiak, C. P. *J. Organomet. Chem.* **1989**, *373*, 391−400. (b) Yanase, N.; Nakamura, Y.; Kawaguchi, S. *Inorg. Chem.* **1980**, *19*, 1575−1581. (c) Yanase, N.; Nakamura, Y.; Kawaguchi, S. *Chem. Lett.* **1979**, *5*, 591−594. (d) Yoshimura, N.; Murahashi, S.-I.; Moritani, I. *J. Organomet. Chem.* **1973**, *52*, C58−C60.

(10) (a) Culkin, D. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 5816−5817. (b) Bohm, A.; Beck, W. *J. Organomet. Chem.* **1998**, *588*, 247−255.

(11) Kayaki, Y.; Shimizu, I.; Yamamoto, A. *Chem. Lett.* **1995**, 1089−1090.

(12) Tian, G.; Boone, H. W.; Novak, B. M. *Macromolecules* **2001**, *34*, 7656.

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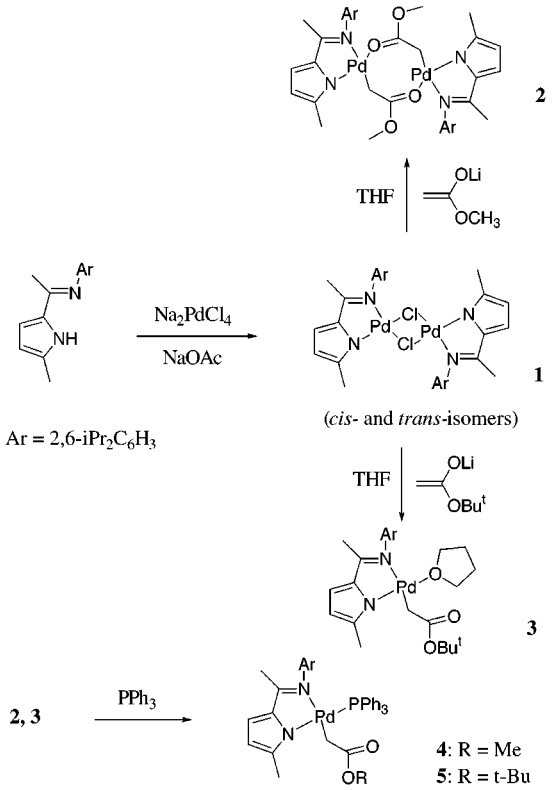
Scheme 1



intermediates in a propagation mechanism involving acrylates, we sought to independently synthesize and study their behavior. Our first attempts to prepare ester enolates by the insertion of methyl acrylate into complexes possessing Pd−CH_3 bonds (e.g., (N^N)Pd(CH_3)L, where N^N = 1-[1-(5-methylpyrrole-2-yl)ethylidne]-amino-2,6-diisopropylbenzene, and L = triphenylphosphine (PPh_3), trimethylphosphine (PMe_3), or pyridine) failed, with nonspecific decomposition and reductive elimination occurring in all attempts. We later found out that the Pd−CH_3 bond in these neutral palladium complexes is relatively inert toward the insertion of methyl acrylate. Therefore, we used the reaction of lithium enolates with palladium chloride to prepare our palladium ester enolates.

The palladium chloride dimer **1**, obtained from the reaction of Na_2PdCl_4 with the N^N bidentate ligand in methanol, proved to be a convenient starting material to prepare the palladium ester enolates. When complex **1** was allowed to react with the lithium enolate of methyl acetate in THF, a new complex, **2**, is formed (Scheme 1). Complex **2** was later shown to be a palladium dimer that has the ester-enolato ligands bridging the palladium centers. The THF used in the reaction does not compete with the enolate carbonyl group for coordination as far as the isolated solid product is concerned. However, the reaction of complex **1** and the lithium enolate of *tert*-butyl acetate gave the monomeric C-bound compound **3** rather than a dimeric complex. Complex **3** was isolated as a yellow solid that displays low thermal stability. Substituting the bound THF for triphenylphosphine stabilizes the complex (vide infra). Again, the preferred reaction pathway is away from an η^3-oxoallyl enolate and toward the C-bond species. We attribute the inhibition of dimer formation in this case to the steric effects introduced by the *tert*-butyl group.

The IR spectrum of **2** exhibits a strong ν(C═O) absorption shifted down to 1594 cm^{-1} (KBr), suggesting the coordination of the carbonyl group with a palladium center. In the ^1H NMR spectrum ($CDCl_3$) the methylene protons of complex **2** appear as two doublets at δ 3.10 and 3.00 ppm (J_{H-H} = 6.0 Hz). The resonance of the methoxy protons is observed at δ 2.54 ppm, which is significantly shifted with respect to organic methyl esters. This shift is due to shielding by the aromatic groups that are held in close proximity through the coordination of the carbonyl group by the second palladium center. The signals for the isopropyl groups consist of two septets for the C*H* and four doublets for the CH_3 groups. The observed NMR pattern is a consequence of the absence of a molecular symmetry plane in each fragment of the dimer **2**, which has now been confirmed by the X-ray diffraction (vide infra). In the ^{13}C NMR spectrum, the resonances at δ 193.1 and 9.1 ppm can be ascribed to the carbonyl carbon and the CH_2 bound to the Pd, the former being shifted downfield owing to the coordination with palladium. All of these spectroscopic data are consistent with either a chelated monomeric η^3-oxoallyl complex or a dimer complex held together by bridging enolates.

Lopez and co-workers have recently reported that the dimeric complex $\{(AsPh_3)(C_6F_5)Pd\}_2\{\mu\text{-}CH_2C(O)CH_3\}_2$, **A**, undergoes dissociation to give two η^3-oxoallyl monomeric complexes in chloroform solution.[8b] The dimer:monomer ratio increases as the temperature decreases. In contrast, there is no direct evidence indicating the dissociation of dimer **2** in noncoordinating solvents (e.g., chloroform and benzene). No change was found in the variable-temperature NMR spectra of complex **2** in chloroform solution (up to 50 °C). In the IR spectrum, the value of ν(C═O) absorption measured in chloroform solution (1595 cm^{-1}) is essentially the same as that recorded in the solid state. These studies lead us to conclude that the dimeric structure of **2** is very robust in noncoordinating solvents. We were, however, able to observe dissociation in the presence of a coordinating solvent. The IR spectrum of complex **2** in $CHCl_3/CH_3CN$ (ca. 10:1) displays the complete disappearance of the absorbance at 1595 cm^{-1} and the appearance of a strong carbonyl absorption at 1680 cm^{-1}, indicating that the coordinated carbonyl group is dissociated, forming the solvated monomeric palladium complex, **3′**. This interpretation is further supported by the ^1H NMR spectrum of **2** in $CDCl_3/CD_3CN$, which consists of a singlet (δ 2.54 ppm) for Pd-CH_2, a septet (δ 3.30 ppm) for the isopropyl C*H* groups, and a singlet at δ 3.50 ppm for CH_3O group. No resonances are observed in the vinylic region of the spectrum, indicating that no O-bound species is formed.

The dissociation of the dimer **2** can also be achieved by adding a strong coordination ligand like PPh_3. The resulting air- and moisture-stable monomeric product has been isolated as complex **4**. The C-bound structure is assigned on the basis of NMR and infrared data. The phosphorus−proton coupling (J_{P-H} = 5.1 Hz) and phosphorus−carbon coupling (J_{P-C} = 11.4 Hz) are observed for the methylene groups in the ^1H and ^{13}C NMR spectra, respectively. The ν(C═O) absorption in the IR spectrum (1695 cm^{-1}, KBr) is also consistent with the C-bound enolate structure. Similarly, addition of PPh_3

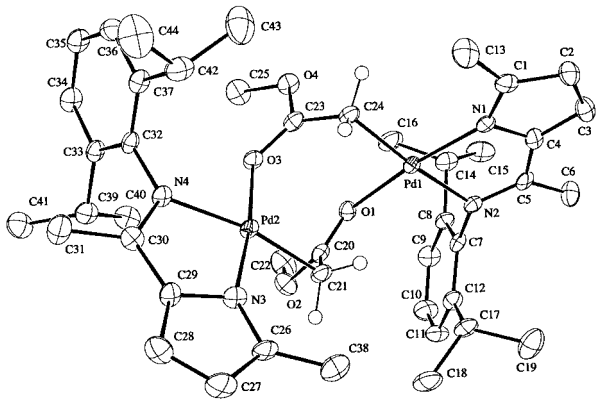


Figure 1. X-ray crystal structure of complex **2**. Selected bond lengths (Å) and angles (deg): Pd1−O1 2.053(3), Pd1−N1 2.003(4), Pd1−N2 2.083(4), Pd1−C24 2.075(4), C23−C24 1.448(7), C23−O3 1.252(6), C23−O4 1.337(5), N1−Pd1−O1 171.46(13), N2−Pd1−C24 174.26(16), C20−O1−Pd1 122.0(3), O1−Pd1−C24 91.85(15), Pd1−C24−C23 107.8(3), C24−C23−O3 127.3 (4). The bond lengths and angles in the other Pd unit are essentially the same as above.

into the solution of **3** resulted in the replacement of THF by PPh_3 and produced C-bound enolate **5** as a air- and moisture-stable solid.

An X-ray crystallographic study ultimately established the crystal structure of **2** as the dimer.[13] A view of the molecule is given in Figure 1, and selected bond lengths and angels are listed in the caption. The ester-enolato groups connect two palladium atoms with a head-to-tail arrangement, giving rise to an eight-membered ring. Each palladium atom is in a square planar coordination geometry with a slight tetrahedral distortion. The two palladium coordination planes are mutually perpendicular, forming a dihedral angle of 93.27(10)°. The two nonsymmetric N^N ligands are related by a pseudo C_2 symmetry axis. Finally, the Pd−C bond occupies the position *trans* to the imino nitrogen atom. The dimeric structure of complex **2** is comparable with the recently reported ketonyl-bridged palladium enolates, **A** and $[\{Pd(PPh_3)_2\}_2(\mu\text{-}\{CH_2C(O)\text{-}Ph\})_2][CF_3SO_3]_2$, **B**.[7c,8b] However, the following points must be stressed: (i) The Pd−C distances (2.074(5) and 2.075(4) Å) are shorter in **2** than in other dimeric palladium complexes **A** (2.106(10) and 2.130(11) Å) and **B** (2.162(10) and 2.134(10) Å), thus suggesting that the *trans*-influence of nitrogen is much smaller than that of phosphorus or arsenic. The Pd−O distances, 2.053-(3) and 2.051(3) Å, are also relatively shorter in complex **2**. (ii) The corresponding bond distances in the two independent units of complex **2** are essential identical. But somewhat different bond distances, especially Pd−C and Pd−O, are found in the two units of complexes **A** and **B**, respectively. (iii) The enolato groups are twisted out of the palladium coordination plane with a torsion angle N1−Pd1−C24−C23 of 160.1(6)°. The free rotation of the enolato group around the Pd−C bond is arrested by the formation of the eight-membered ring. As a result, the two protons on each enolato methylene group are in a different chemical environment, which is displayed in the ^{1}H NMR spectrum.

It is worthwhile to point out that the NMR and IR data are insufficient to determine the structure of complex **2**, since both η^3-oxoallyl and C,O-bridging binding mode would be consistent with these data. On the other hand, the former binding mode for enolato, though often invoked in palladium chemistry, has never been proven structurally. The characterization of the dimeric structure of complex **2** implies that a dinuclear process might be a plausible pathway for some palladium-catalyzed reactions and polymerizations, which have been assumed to proceed through a η^3-oxoallyl intermediate.

In conclusion we have prepared and characterized palladium ester enolates. The results indicate that of the four possible binding modes, the ester-enolato group in this study prefers to coordinate with palladium through either a C-bound or a C,O-bridging binding mode. The C,O-bridging structure of complex **2** has been confirmed by X-ray diffraction. As far as we know, this is the first crystal structure of palladium ester enolates. Since the relevant reactions and polymerizations have been widely used in organic and polymer chemistry, this study should contribute to a better understanding of the reaction mechanism and provide valuable guidelines to improve catalyst design and reaction yield.

Experimental Section

All manipulations of air- and/or water-sensitive compounds were performed using standard Schlenk techniques. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a GE-300 or Varian Gemini-300 spectrometer (300 MHz for ^{1}H) unless otherwise specified. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced using internal solvent resonances and are reported relative to tetramethylsilane. The ^{31}P NMR spectra were referenced to external H_3PO_4. Infrared spectra were recorded on a Jasco FT/IR-410 Series Fourier transform infrared spectrometer. Elemental analysis was performed by Atlantic Microlab, Inc.

Anhydrous solvents were passed through columns packed with Q5 catalysts and molecular sieves prior to use. Benzene-d_6 was dried over CaH_2, vacuum-transferred, degassed by repeated freeze−pump−thaw cycles, and stored over 4 Å molecular sieves. Chloroform-*d* was dried over 4 Å molecular sieves. The N^N bidentate ligand (1-[1-(5-methylpyrrole-2-yl)-ethylidne]amino-2,6-diisopropylbenzene) was prepared according to the procedure reported before.[12] Unless otherwise noted, all compounds were purchased from Aldrich Chemical Co. and used as received.

Preparation of {[N^N]PdCl}$_2$ (1). $Na_2[PdCl_4]$ (2.0 mmol), prepared in situ from $PdCl_2$ and NaCl, was dissolved in 10 mL of methanol and cooled to −40 °C. The N^N bidentate ligand (0.564 g, 2.0 mmol) and sodium acetate (0.164 g, 2.0 mmol) in methanol (10 mL) were transferred to the above solution via cannula. The resulting mixture was warmed and stirred at room temperature for 12 h. The red solid formed during this period was collected by filtration, washed twice with methanol (ca. 20 mL), and air-dried. Recrystallization from CH_2Cl_2/methanol afforded 0.770 g (91% yield) of **1**. The product consisted of two isomers (*cis* and *trans*) in the ratio of 77:23. It was used in the following preparation without further separation. Major isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26−7.24 (m, 2 H, ph-*H*^{4}), 7.08 (d, 4 H, ph-*H*^{3,5}), 6.56 (d, 2 H, pyrrole-*H*^{3}), 5.74 (d, 2 H, pyrrole-*H*^{4}), 3.41 (m, 4 H, *i*Pr−C*H*), 1.89 (s, 6 H, pyrrole-CH_3), 1.80 (s, 6 H, N=C-CH_3), 1.47 (d, 12 H, J_{H-H}

(13) Crystal data for **2**: 0.34 × 0.32 × 0.30 mm, monoclinic, *P*21/*c*, a = 12.0009(13) Å, b = 14.6436(9) Å, c = 28.262(2) Å, β = 100.087-(11)°, V = 4889.9(7) Å^3, Z = 4, D_c = 1.350 g·cm^{-3}, μ = 0.78 mm^{-1}, λ = 0.71073 Å, 2θ = 49.8°, F(000) = 2065.01, T = 148 K, reflections measured 8536, of which 8536 were independent, residuals R_f = 0.049, R_w = 0.063.

= 6.8, *i*Pr-CH_3), 1.18 (d, 12 H, J_{H-H} = 6.8, *i*Pr-CH_3); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 169.6 (*C*═N), 149.5, 143.2, 141.3, 140.3, 127.9, 123,7, 117.9, 110.5 (pyrrole- and ph-C), 28.6 (*i*Pr-*C*H), 24.2, 24.1 (*i*Pr-*C*H_3), 15.7, 15.6 (pyrrole- and imine-*C*H_3). Minor isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26−7.24 (m, 2 H, ph-*H*^{4}), 6.90 (d, 4 H, ph-*H*^{3,5}), 6.56 (d, 2 H, pyrrole-*H*^{3}), 5.81 (d, 2 H, pyrrole-*H*^{4}), 3.16 (m, 4 H, *i*Pr−C*H*), 2.24 (s, 6 H, pyrrole-CH_3), 1.85 (s, 6 H, N═C-CH_3), 1.21 (d, 12 H, J_{HH} = 6.8, *i*Pr-CH_3), 1.04 (d, 12 H, J_{HH} = 6.8, *i*Pr-CH_3); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 169.6 (*C*═N), 149.1, 143.2, 141.3, 140.3, 127.7, 123,5, 118.0, 110.7 (pyrrole- and ph-C), 28.5 (*i*Pr-*C*H), 24.2, 24.1(*i*Pr-*C*H_3), 16.2, 15.8 (pyrrole- and imine-*C*H_3). Anal. Calcd for $C_{38}H_{50}Cl_2N_4Pd_2$: C, 53.91; H, 5.95; N, 6.62. Found: C, 53.74; H, 5.96; N, 6.58. MS(FAB): *m/e* 844 (M^+).

Preparation of {[N^N]PdCH$_2$CO$_2$CH$_3$}$_2$ (2). A solution of complex **1** (0.423 g, 0.50 mmol) in 5.0 mL of THF was added to the solution of lithium enolate generated in situ from the reaction of LDA (1.0 mmol) and methyl acetate (1.0 mmol) in THF (5.0 mL) at −78 °C. The resulting mixture was stirred at −78 °C for 2 h and then allowed to warm to room temperature over a period of 12 h. The solvent was removed under vacuum, and the residue was taken in 10 mL of benzene. After filtration, the solvent of the clear filtrate was evaporated to afford a yellow solid. Recrystallization from benzene/pentane afforded 0.202 g (44% yield) of **2**. ^{1}H NMR (C_6D_6): δ 7.15−6.90 (m, 6 H, ph-*H*), 6.80 (d, 2 H, pyrrole-*H*^{3}), 6.16 (d, 2 H, pyrrole-*H*^{4}), 3.58 (m, 2 H, *i*Pr-C*H*), 3.52 (d, 2 H, J_{H-H} = 6.0 Hz, Pd-CH_2), 3.38 (d, 2 H, J_{H-H} = 6.0 Hz, Pd-CH_2), 3.36 (m, 2 H, *i*Pr-C*H*), 2.57 (s, 6 H, CH_3O), 2.31 (s, 6 H, pyrrole-CH_3), 1.69 (s, 6 H, N═C-CH_3), 1.25 (d, 6 H, *i*Pr-CH_3), 1.16 (d, 6 H, *i*Pr-CH_3), 1.03 (d, 6 H, *i*Pr-CH_3), 0.87 (d, 6 H, *i*Pr-CH_3). ^{1}H NMR ($CDCl_3$): δ 7.20−7.00 (m, 6 H, ph-*H*), 6.64 (d, 2 H, pyrrole-*H*^{3}), 5.91 (d, 2 H, pyrrole-*H*^{4}), 3.53 (m, 2 H, *i*Pr-C*H*), 3.26 (m, 2 H, *i*Pr-C*H*), 3.10 (d, 2 H, J_{H-H} = 6.0 Hz, Pd-CH_2), 3.01 (d, 2 H, J_{H-H} = 6.0 Hz, Pd-CH_2), 2.54 (s, 6 H, CH_3O), 2.18 (s, 6 H, pyrrole-CH_3), 1.93 (s, 6 H, N═C-CH_3), 1.22 (d, 6 H, *i*Pr-CH_3), 1.18 (d, 6 H, *i*Pr-CH_3), 1.17 (d, 6 H, *i*Pr-CH_3), 1.03 (d, 6 H, *i*Pr-CH_3). ^{13}C NMR (C_6D_6): δ 193.1 (*C*═O), 167.5 (*C*═N), 148.3, 143.2, 143.1, 143.0, 142.9, 126.3, 123.6, 118.0, 112.3 (pyrrole- and ph-C), 52.9 (*C*H_3O), 28.8, 28.5 (*i*Pr-*C*H), 24.8, 24.3, 23.7, 23.4 (*i*Pr-*C*H_3), 17.5, 16.1 (pyrrole- and imine-*C*H_3), 9.1 (Pd-*C*H_2). IR (KBr): 1595 (s, C═O), and 1559 cm^{-1} (s, C═N). IR ($CHCl_3$): 1596 (s, C═O), and 1564 cm^{-1} (s, C═N). IR ($CHCl_3$/CH_3CN = 10:1): 1680 (s, C═O), and 1565 cm^{-1} (s, C═N). Anal. Calcd for $C_{44}H_{60}N_4O_4Pd_2$: C, 57.33; H, 6.56; N, 6.08. Found: C, 57.87; H, 6.61; N, 5.95.

Preparation of [N^N](THF)PdCH$_2$CO$_2$Bu^t (3). A mixture of complex **1** (0.423 g, 0.50 mmol), lithium enolate of *tert*-butyl acetate (1.0 mmol), and THF (10.0 mL) was stirred at −78 °C for 2 h and then at room temperature for 12 h. The solvent was removed under vacuum, and the residue was taken in 10 mL of ether. After filtration, the solvent of the clear filtrate was evaporated to afford a yellow oil, which solidified upon addition of pentane. The obtained yellow solid, complex **3**, showed low thermal stability and gradually decomposed in solution even under nitrogen atmosphere. Yield: 0.489 g (85%). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.10−7.08 (m, 3 H, ph-*H*), 6.81 (d, 1 H, pyrrole-*H*^{3}), 6.25 (d, 1 H, pyrrole-*H*^{4}), 3.56 (m, 2 H, *i*Pr-C*H*), 3.48 (m, 4 H, thf-CH_2O), 2.88 (s, 2 H, Pd-CH_2), 2.81 (s, 3 H, pyrrole-CH_3), 1.76 (s, 1 H, N═C-CH_3), 1.48 (s, 9 H, C(CH_3)$_3$), 1.44 (d, 6 H, *i*Pr-CH_3), 1.38 (m, 4 H, thf-CH_2), 1.13 (d, 6 H, *i*Pr-CH_3). ^{13}C NMR (C_6D_6, 400 MHz): δ 186.2 (*C*═O), 167.0 (*C*═N), 148.4, 144.5, 143.7, 142.7, 126.0, 123.3, 117.4, 112.1 (pyrrole- and ph-C), 80.2 (O*C*(CH$_3$)$_3$), 68.8 (thf-*C*H$_2$O), 28.8 (*i*Pr-*C*H), 28.5 (−C(*C*H$_3$)$_3$), 25.7 (thf-*C*H$_2$), 24.5, 24.4 (*i*Pr-*C*H$_3$), 18.2, 16.7 (pyrrole- and imine-*C*H$_3$), 6.2 (Pd-*C*H$_2$).

Preparation of [N^N](Ph$_3$P)PdCH$_2$CO$_2$CH$_3$ (4). A mixture of complex **1** (0.423 g, 0.50 mmol), lithium enolate of methyl acetate (1.0 mmol), PPh_3 (0.262 g, 1.0 mmol), and THF (10.0 mL) was stirred at −78 °C for 2 h and then at room temperature for 12 h. The solvent was removed under vacuum, and the residue was taken in 10 mL of benzene. After filtration, the solvent of the clear filtrate was evaporated to afford a yellow solid. Recrystallization from ether/pentane afforded 0.448 g (62% yield) of **4**. The complex can also be prepared in quantitative yield by adding PPh_3 into the benzene solution of **2**. ^{1}H NMR (C_6D_6): δ 8.00−7.85 (m, 6 H, PPh_3-*H*), 7.15−7.10 (m, 3 H, ph-*H*), 7.02 (d, 1 H, pyrrole-*H*^{3}), 7.00−6.90 (m, 9 H, PPh_3-*H*), 6.17 (d, 1 H, pyrrole-*H*^{4}), 3.75 (m, 2 H, *i*Pr-C*H*), 3.05 (s, 3 H, CH_3O), 1.99 (s, 3 H, pyrrole-CH_3), 1.50 (d, 2 H, J_{P-H} = 5.1 Hz, Pd-CH_2), 1.34 (s, 3 H, N═C-CH_3), 1.28 (d, 6 H, *i*Pr-CH_3), 1.14 (d, 6 H, *i*Pr-CH_3). ^{13}C NMR (C_6D_6, 400 MHz): δ 177.7 (*C*═O), 169.8 (*C*═N), 148.2, 144.0, 143.3, 142.0, 136.0 (d, J_{P-C} = 11.4 Hz), 130.9, 128.9, 128.5, 126.9, 124.2, 119.8, 112.7 (pyrrole- and ph-C), 50.4 (*C*H_3O), 28.8, (*i*Pr-*C*H), 24.7, 24.0 (*i*Pr-*C*H_3), 24.6 (d, J_{P-C} = 9.1 Hz, Pd-*C*H_2), 18.4, 18.3 (pyrrole- and imine-*C*H_3). ^{31}P NMR (C_6D_6): δ 35.2 (s). IR (KBr): 1695 (s, C═O), and 1553 cm^{-1} (s, C═N). Anal. Calcd for $C_{40}H_{45}N_2O_2PPd$: C, 66.43; H, 6.27; N, 3.87. Found: C, 66.43; H, 6.36; N, 3.78.

Preparation of [N^N](Ph$_3$P)PdCH$_2$CO$_2$Bu^t (5). A mixture of complex **1** (0.423 g, 0.50 mmol), lithium enolate of *tert*-butyl acetate (1.0 mmol), PPh_3 (0.262 g, 1.0 mmol), and THF (10.0 mL) was stirred at −78 °C for 2 h and then at room temperature for 12 h. The solvent was removed under vacuum, the residue was taken in 10 mL of hexane, and, after filtration, the solvent was evaporated to afford a yellow solid. Recrystallization from hexane at −20 °C afforded 0.590 g (76% yield) of **5**. The complex can also be prepared in high yield by adding PPh_3 into the benzene solution of **3**. ^{1}H NMR (C_6D_6): δ 8.00−7.80 (m, 6 H, PPh_3-*H*), 7.15−7.10 (m, 3H, ph-*H*), 7.03 (d, 1 H, pyrrole-*H*^{3}), 7.00−6.90 (m, 9 H, PPh_3-*H*), 6.20 (d, 1 H, pyrrole-*H*^{4}), 3.78 (m, 2 H, *i*Pr−C*H*), 2.00 (s, 3 H, pyrrole-CH_3), 1.51 (d, 2 H, J_{P-H} = 4.1 Hz, Pd-CH_2), 1.37 (s, 3 H, N═C-CH_3), 1.31 (d, 6 H, *i*Pr-CH_3), 1.13 (d, 6 H, *i*Pr-CH_3), 1.09 (s, 9 H, *t*Bu). ^{13}C NMR (C_6D_6): δ 177.1 (*C*═O), 169.6 (*C*═N), 148.2, 144.1, 143.4, 142.1, 136.1 (d, J_{P-C} = 12.2 Hz), 130.9, 128.9, 128.6, 126.8, 124.2, 119.7, 112.8 (pyrrole- and ph-C), 78.0 (O*C*(CH$_3$)$_3$), 28.8, (*i*Pr-*C*H), 28.6 (−C(*C*H$_3$)$_3$), 26.6 (d, J_{P-C} = 9.8 Hz, Pd-*C*H$_2$), 24.6, 24.3 (*i*Pr-*C*H$_3$), 18.5, 18.3 (pyrrole- and imine-*C*H$_3$). ^{31}P NMR (C_6D_6): δ 34.0 (s). IR (KBr): 1689 (s, C═O), and 1554 cm^{-1} (s, C═N). Anal. Calcd for $C_{43}H_{51}N_2O_2PPd$: C, 67.49; H, 6.72; N, 3.66. Found: C, 68.14; H, 6.94; N, 3.50.

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Supporting Information Available: X-ray structure information for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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