Reactivity Studies of Cationic Palladium(II) Phosphine Carboxylate Complexes with Lewis Bases: Substitution versus Cyclometalation

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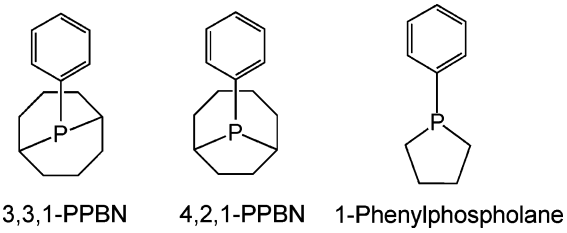
Two classes of cationic palladium(II) phosphine carboxylate complexes were isolated and characterized. Reactions of *trans*-$[(R_3P)_2Pd(O_2CR')_2]$ (**1**) with $[Li(OEt_2)_{2.5}][B(C_6F_5)_4]$ in MeCN led to carboxylate abstraction and formation of *trans*-$[(R_3P)_2Pd(O_2CR')(MeCN)][B(C_6F_5)_4]$ (**2**) in good to excellent yields. On the other hand, carboxylate abstraction reactions of **1** with $[Me_2(H)NPh][B(C_6F_5)_4]$ or *p*-toluenesulfonic acid ($HOTs\cdot H_2O$) in CH_2Cl_2 furnished the palladium cations $[(R_3P)_2Pd(\kappa^2\text{-}O,O\text{-}O_2CR')]^+$ (**3**). The reactions of **2** and **3** with Lewis bases were found to be different in some cases. For example, reactions of **2** with pyridine furnished the simple products of acetonitrile substitution, *trans*-$[(R_3P)_2Pd(O_2CR')(py)][B(C_6F_5)_4]$. In contrast, the reaction of **3e** ($R = {}^iPr$, $R' = CH_3$) with CD_3CN in the presence of excess sodium carbonate yielded a material derived from cyclometalation of one of the ^iPr arms of a $^iPr_3P$ ligand. New complexes were characterized by elemental analyses and NMR (^1H, ^{13}C, and ^{31}P) spectroscopic methods and in two cases by single-crystal X-ray structural methods.

Introduction

Admixtures of palladium acetate and phosphines, as well as discrete adducts of palladium acetate (and other palladium salts) with phosphines, constitute the basic ingredients for implementing a large number of important catalytic transformations.[1,2] Early investigations of the chemistry of palladium acetate and palladium carboxylates with phosphines date back to the 1960s. For example, Wilkinson and co-workers reported the isolation of the simple adducts *trans*-$[(Ph_3P)_2Pd(O_2CR')_2]$ ($R' = Me$, Et, Ph) from reactions involving $Pd(O_2CR')_2$ and PPh_3.[3] Interestingly, similar reactions performed using differing $Pd:PPh_3$ ratios afforded a dinuclear complex, $[(Ph_3P)Pd(O_2CMe)_2]_2$, which bears both terminal and bridging acetate moieties.[4] These reactions portended a chemistry for palladium phosphine carboxylate complexes richer than that first imagined. Complexes of the form $[(R_3P)_2Pd(O_2CMe)_2]$ can also show both cis and trans isomers. For example, Coles et al. have shown that the reaction of $Pd(O_2CMe)_2$ with 2 equiv of 3,3,1-PPBN and 4,2,1-PPBN (PPBN = 9-phenyl-9-phosphabicyclononane) gives *trans*-$[(R_3P)_2Pd(O_2CMe)_2]$ (PR_3 = 3,3,1-PPBN, 4,2,1-PPBN), whereas the same reaction with the similar but sterically less hindered 1-phenylphospholane gives *cis*-$[(R_3P)_2Pd(O_2CMe)_2]$ (PR_3 = 1-phenylphospholane).[5]



Further studies into the catalytically active species have revealed additional complexities. In careful studies aimed at determining the source of palladium(0) from mixtures of $Pd(O_2CMe)_2$ and PPh_3, anionic complexes have been identified as key intermediates. The oxidation of PPh_3 serves as the source of electrons necessary for the reduction of Pd(II).[6] Adding even more complexity to these reactions is the propensity of the palladium center to react with certain phosphines to yield cyclometalated complexes. In particular, reactions of $Pd(O_2CMe)_2$ with phosphines bearing at least an *o*-tolyl, mesityl, 1-naphthyl, or *tert*-butyl substituent or with (α-ferrocenylalkyl)-phosphines commonly afforded cyclopalladated acetate bridged dinuclear palladium complexes, some of which show great utility in catalysis.[7] Even being identified as such, these cyclometalated complexes can be also involved in dynamic equilibria with other

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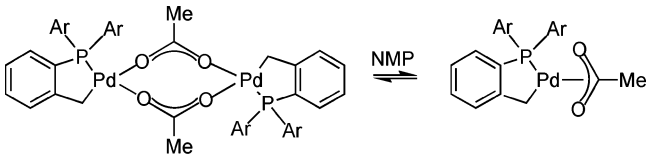
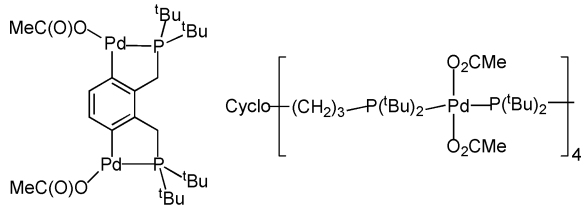
species. For example, the acetate-bridged dinuclear palladacycle **Ia** was shown to equilibrate with the monomer **Ib**.[8,9]

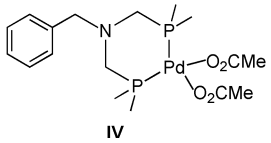


Ia **Ib**

Ar = *o*-tolyl

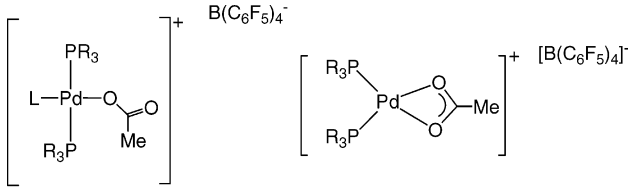
Studies of the reaction of $Pd(O_2CMe)_2$ with chelating phosphines revealed other possibilities. The specific products obtained were shown to depend on the nature of the substituents attached to phosphorus as well as on the nature of intervening atoms between two phosphorus donors. The reaction of $Pd(O_2CMe)_2$ with chelating diphosphines possessing sterically less hindered substituents on phosphorus can furnish mononuclear chelate complexes of the form *cis*-[(P-P)$Pd(O_2CMe)_2$] (P-P = chelating diphosphine).[10] In other cases, reactions with chelating phosphines (such as 1,2-bis((di-*tert*-butylphosphino)methyl)-benzene or 1,3-bis(di-*tert*-butylphosphino)propane) can afford the doubly ortho-palladated complexes **II** or cyclotetrameric complexes **III**.[11] However, the reaction of $Pd(O_2CMe)_2$ with bis(*tert*-butylaminomethylphosphine) was shown to furnish the mononuclear complex **IV**.[12]





The reactions of $Pd(O_2CMe)_2$ with chelating diphosphines have also shown their propensity to yield cationic complexes in reactions that are highly solvent dependent. Bianchini et al. found that the reaction of $Pd(O_2CMe)_2$ with dppe (dppe = 1,2-bis(diphenylphosphino)ethane) in MeOH-d_4 initially yields [(dppe)$Pd(O_2CMe)_2$] and that this complex subsequently undergoes a reversible autoionization to generate $[(dppe)_2Pd]^{2+}$, as shown by a ^{31}P NMR spectroscopic study.[10c] Subsequent work determined that the reaction of $Pd(O_2CMe)_2$ with dppe in CD_2Cl_2 produces the kinetic product $[(dppe)_2Pd]^{2+}$, which eventually yields the thermodynamically more stable [(dppe)-$Pd(O_2CMe)_2$] upon reaction with $Pd(O_2CMe)_2$.[13] The reaction of $Pd(O_2CMe)_2$ with dppp (dppp = 1,2-bis(diphenylphosphino)-propane) in MeOH/CF_3CO_2H, however, affords [(dppp)$Pd(\kappa^2$-*O*,*O*-$O_2CMe)]^+$, which upon reaction with an additional 1 equiv of dppp gives $[(dppp)_2Pd]^{2+}$.[14]

Clearly, these examples and others too numerous to detail here serve to illustrate the diversity and complexity of the fundamental chemistry of palladium carboxylates with phosphines. Recently, we communicated the syntheses and characterization of examples of two types of cationic palladium phosphine carboxylate complexes (**2** and **3**) that are derived by the action of lithium salts or acids on *trans*-$[(R_3P)_2Pd(O_2CMe)_2]$, as well as the conditions under which these complexes are susceptible to facile and reversible cyclometalation of coordinated phosphine ligands.[15]



2 **3**

The delightful diversity of products derived from palladium carboxylates with ligands extends to N-heterocylic carbenes (phosphine mimics).[16] Scheme 1 ($[BArF_{24}]^-$ = tetrakis[(3,5-trifluoromethyl)phenyl]borate; R = CH_3, CF_3) depicts some of the unusual products (**V**−**VII**) recently reported and their dependence on the choice of carboxylate abstraction reagent.[16a] As part of our continuing interest in understanding the factors that control the nature of products of palladium carboxylates with phosphines, we now give a full report on the syntheses and characterization of a wider family of complexes **2** and **3**, as well as an examination of their reactivity with Lewis bases.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk or drybox techniques, unless stated otherwise. Solvents were purified by standard procedures. $Pd(O_2CMe)_2$ (Strem, Johnson Matthey), P^iPr_3, PCy_3, $P(NMe_2)_3$ (Strem, Aldrich), $[Li(OEt_2)_{2.5}][B(C_6F_5)_4]$, $[Me_2(H)NPh][B(C_6F_5)_4]$ (Boulder Scientific), $HOTs\cdot H_2O$ (Fischer; Ts = tosyl), pyridine (Acros), 2,6-dimethylphenyl isocyanide (Fluka), 4-*tert*-butylpyridine, and DMAP (Aldrich) were used as received. $Pd(O_2CPh)_2$[17] and $Pd(O_2C^tBu)_2$[18] were prepared by following literature procedures. Elemental analyses were performed by Robertson Microlit Laboratories Inc. (Madison, NJ) after drying samples in a Fisher Isotemp 282A

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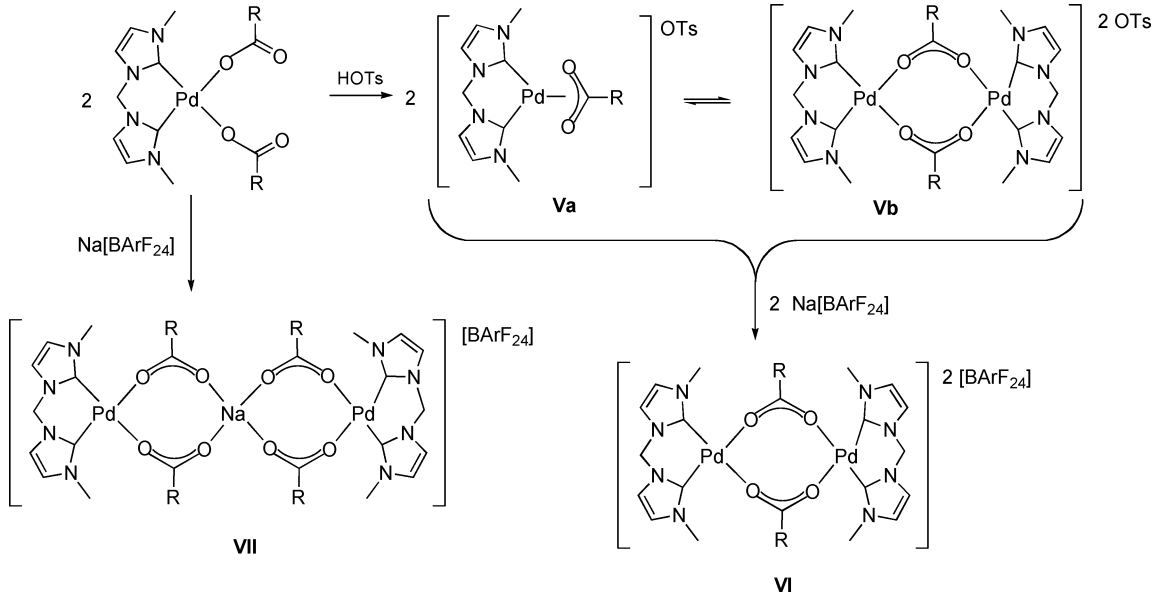
Scheme 1



vacuum oven under vacuum at 35 °C for 24 h. Proton and ^{13}C NMR spectra were recorded on Varian 300 and Varian 600 MHz NMR spectrometers, and the residual solvent proton signal served as a reference signal. The ^{31}P and ^{19}F NMR spectra were recorded on a Varian 300 spectrometer using 85% H_3PO_4 and trifluoroacetic acid, respectively, as the external standards.

***trans*-[(Cy$_3$P)$_2$Pd(O$_2$CMe)$_2$] (1a).** In a two-neck round-bottom flask equipped with an addition funnel, a reddish brown suspension of $Pd(O_2CMe)_2$ (5.00 g, 22.3 mmol) in dichloromethane (50 mL) was stirred at −78 °C. The addition funnel was charged with a dichloromethane solution (30 mL) of PCy_3 (13.12 g, 46.78 mmol), and this solution was then slowly added to the stirred suspension over the course of 15 min, resulting in a gradual change from reddish brown to yellow. After 1 h of stirring at −78 °C, the suspension was warmed to room temperature, stirred for an additional 2 h, and then diluted with hexanes (20 mL). The yellow solid was then collected by filtration, washed with pentane (5 × 10 mL), and dried under vacuum. A second crop was isolated by cooling the filtrate to 0 °C and filtering, washing, and drying. Yield: 15.42 g (88%). Anal. Calcd for $C_{40}H_{72}O_4P_2Pd$: C, 61.17; H, 9.24. Found: C, 61.44; H, 9.58. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 21.3. ^1H NMR (CD_2Cl_2): δ 1.15−1.34 (br m, 18H), 1.64−1.71 (br m, 18H), 1.80−1.82 (br m, 18H), 1.84 (s, 6H), 1.99 (br d, J = 14.4 Hz, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.9, 26.7, 28.2 (vt, $^2J_{CP} + {}^4J_{CP}$ = 5.3 Hz), 29.6, 33.2 (vt, $^1J_{CP} + {}^3J_{CP}$ = 8.8 Hz), 175.3.

***trans*-[(Cy$_3$P)$_2$Pd(O$_2$CPh)$_2$] (1b).** Complex **1b** was prepared from $Pd(O_2CPh)_2$ (1.380 g, 3.954 mmol) and PCy_3 (2.539 g, 9.054 mmol) in dichloromethane (10, 10 mL) in 74% yield (2.651 g) by a procedure analogous to that used for **1a**. Anal. Calcd for $C_{50}H_{76}O_4P_2Pd$: C, 66.03; H, 8.42. Found: C, 65.49; H, 8.51. The NMR (^1H and ^{31}P) spectral data of **1b** were consistent with previously reported values.[19]

***trans*-[(Cy$_3$P)$_2$Pd(O$_2$C^{t}Bu)$_2$] (1c).** Complex **1c** was prepared from $Pd(O_2C^tBu)_2$ (466 mg, 1.511 mmol) and PCy_3 (887 mg, 3.163 mmol) in dichloromethane (10 mL) in 74% yield (978 mg) by a procedure analogous to that used for **1a**. Anal. Calcd for $C_{46}H_{84}O_4P_2Pd\cdot C_4H_9CO_2H$: C, 63.04; H, 9.75. Found: C, 62.52; H, 9.71. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.4. ^1H NMR ($CDCl_3$): δ 1.08 (s, 18H), 1.20 (q, J = 12.6 Hz, 12H), 1.35 (qt, J = 12.6, 3.3 Hz, 4H), 1.68 (d, J = 12.6 Hz, 8H), 1.72 (d, J = 12.6 Hz, 10H), 1.78 (d, J = 13.2 Hz, 14H), 1.87−1.96 (m, 18H). $^{31}C\{^1H\}$ NMR ($CDCl_3$): δ 26.6, 27.9 (vt, $^2J_{PC} + {}^4J_{PC}$ = 5.0 Hz), 29.2, 32.0 (vt, $^1J_{PC} + {}^3J_{PC}$ = 8.5 Hz), 39.8, 182.4. The signal at δ_C 29.2 ppm arises due to the combination of resonances corresponding to the CH_3 nuclei of ^{t}Bu and one of the CH_2 nuclei of C_6H_{11}, as independently confirmed by two-dimensional HMQC experiments.

***trans*-[(Cy$_3$P)$_2$Pd(O$_2$CCF$_3$)$_2$] (1d).** Complex **1d** was prepared from $Pd(O_2CCF_3)_2$ (1.592 g, 4.79 mmol) and PCy_3 (2.859 g, 10.195 mmol) in dichloromethane (10, 16 mL) in 67% yield (2.86 g) by a procedure analogous to that used for **1a**. Anal. Calcd for $C_{40}H_{66}O_4P_2F_6Pd$: C, 53.78; H, 7.45. Found: C, 53.90; H, 7.24. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 24.5. ^1H NMR ($CDCl_3$): δ 1.08−1.38 (m, 18H), 1.56−1.86 (m, 36H), 1.94 (br d, J = 12.0 Hz, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.6, 27.8 (vt, $^2J_{PC} + {}^4J_{PC}$ = 5.4 Hz), 29.6, 32.7 (vt, $^1J_{PC} + {}^3J_{PC}$ = 9.1 Hz), 114.3 (q, $^1J_{CF}$ = 289.3 Hz, CF_3), 160.9 (q, $^2J_{CF}$ = 36.2 Hz, C=O). ^{19}F NMR ($CDCl_3$): δ 4.6.

***trans*-[(^{i}Pr$_3$P)$_2$Pd(O$_2$CMe)$_2$] (1e).** Complex **1e** was prepared from $Pd(O_2CMe)_2$ (5.00 g, 22.3 mmol) and P^iPr_3 (7.14 g, 44.6 mmol) in dichloromethane (20, 30 mL) in 90% yield (10.94 g) by a procedure analogous to that used for **1a**. Anal. Calcd for $C_{22}H_{48}O_4P_2Pd$: C, 48.49; H, 8.88. Found: C, 48.55; H, 8.85. ^1H NMR (CD_2Cl_2): δ 1.37 (m, 36H), 1.77 (s, 6H), 2.12 (br, 6H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 33.0. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.6, 23.7 (vt, $^1J_{CP} + {}^3J_{CP}$ = 9.2 Hz), 23.8, 175.9.

***trans*-{[(Me$_2$N)$_3$P)]$_2$Pd(O$_2$CMe)$_2$} (1f).** Complex **1f** was prepared from $Pd(O_2CMe)_2$ (368 mg, 1.719 mmol) and $P(NMe_2)_3$ (568 mg, 3.48 mmol) in 70% yield (664 mg) by a procedure analogous to that adopted for **1a**, except that the dichloromethane (3 mL) solution of $P(NMe_2)_3$ was added to the dichloromethane (3 mL) solution of $Pd(O_2CMe)_2$ at −35 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 93.3. ^1H NMR ($CDCl_3$): δ 1.85 (s, 6H, O_2CCH_3), 2.66 (apparent t, $^5J_{PH} + {}^3J_{PH}$ = 4.74 Hz, 36H, $N(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.6, 38.5, 177.4.

***trans*-[(PCy$_3$)$_2$Pd(O$_2$CMe)(MeCN)][B(C$_6$F$_5$)$_4$] (2a).** An acetonitrile (5 mL) solution of $[Li(Et_2O)_{2.5}][B(C_6F_5)_4]$ (864 mg, 0.992 mmol) was slowly added to the acetonitrile (40 mL) solution of **1a** (764 mg, 0.972 mmol), the reaction mixture stirred for 3 h, filtered through 0.45 μm filter and solvent removed under vacuum to furnish 1.40 g of **2a** (99%). Anal. Calcd. for $C_{64}H_{72}NO_2P_2BF_{20}Pd\cdot 1Et_2O$: C, 53.71; H, 5.44; N, 0.92%. Found: C, 53.85; H, 5.18; N, 0.93. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.7. ^1H NMR ($CDCl_3$): δ 1.12−1.22 (m, 12H), 1.28 (qt, J = 12.9 Hz, 3.2 Hz, 6H), 1.62 (q, J = 12.45 Hz, 12H), 1.77 (d, J = 12.6 Hz, 6H), 1.89 (d, J = 13.8 Hz, 14H), 1.93 (d, J = 11.4 Hz, 16H), 2.00 (s, 3H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 3.30, 23.4, 26.3, 27.9 (virtual t, $^2J_{CP}$ +

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$^4J_{CP}$ = 9 Hz), 29.9, 33.7 (virtual t, $^1J_{CP} + {}^3J_{CP}$ = 9.45 Hz), 124.5 (br), 127.2, 136.4 (d, $^1J_{CF}$ = 242 Hz), 138.4 (d, $^1J_{CF}$ = 244 Hz), 148.4 (d, $^1J_{CF}$ = 243 Hz), 175.5.

***trans*-[(Cy$_3$P)$_2$Pd(O$_2$CPh)(MeCN)][B(C$_6$F$_5$)$_4$] (2b).** Complex **2b** was prepared from an acetonitrile (10 mL) solution of [Li(OEt$_2$)$_{2.5}$][B(C$_6$F$_5$)$_4$] (142 mg, 0.164 mmol) and a dichloromethane (6 mL) solution of **1b** (146 mg, 0.161 mmol) in 98% yield (242 mg) by a procedure analogous to that used for **2a**, with the reaction time being 15 h. Anal. Calcd for $C_{69}H_{74}NO_2P_2PdBF_{20}$: C, 54.94; H, 4.94; N, 0.93. Found: C, 54.75; H, 4.75; N, 0.94. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.6. ^1H NMR ($CDCl_3$): δ 0.92−1.14 (m, 11H), 1.15−1.36 (m, 7H), 1.54−2.06 (m, 48H), 2.42 (s, 3H), 7.36 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.46 (t, $^3J_{HH}$ = 6.6 Hz, 1H), 7.88 (d, $^3J_{HH}$ = 8.1 Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 3.3, 26.2, 27.8 (vt, $^2J_{PC} + {}^4J_{PC}$ = 5.3 Hz), 29.9, 33.6 (vt, $^1J_{PC} + {}^3J_{PC}$ = 9.1 Hz), 124.5 (br), 127.3, 128.4, 129.8, 131.9, 133.6, 136.4 (d, $^1J_{CF}$ = 248 Hz), 138.4 (d, $^1J_{CF}$ = 242 Hz), 148.4 (d, $^1J_{CF}$ = 238 Hz), 170.8.

***trans*-[(Cy$_3$P)$_2$Pd(O$_2$C^{t}Bu)(MeCN)][B(C$_6$F$_5$)$_4$] (2c).** Complex **2c** was prepared from an acetonitrile (6 mL) solution of [Li(OEt$_2$)$_{2.5}$][B(C$_6$F$_5$)$_4$] (87.0 mg, 0.100 mmol) and a dichloromethane (6 mL) solution of **1c** (83.6 mg, 0.096 mmol) in 99% yield (142 mg) by a procedure analogous to that used for **2a** with the following exceptions. The reaction time was 5 h. The product was finally purified by triturating with pentane (10 mL) followed by vacuum drying. Anal. Calcd for $C_{67}H_{78}NO_2P_2BF_{20}Pd$: C, 54.06; H, 5.28; N, 0.94. Found: C, 53.59; H, 4.91; N, 0.77. $^{31}P\{^1H\}$ NMR (THF-d_8): δ 31.0. ^1H NMR (THF-d_8): δ 1.22 (s, 9H), 1.28−1.44 (m, 18H), 1.72−1.85 (m, 18H), 1.89 (br d, J = 11.4 Hz, 12H), 2.07 (br d, J = 12.0 Hz, 12H), 2.13 (t, J = 11.7 Hz, 6H), 2.77 (s, 3H). $^{31}C\{^1H\}$ NMR (THF-d_8): δ 3.1, 27.0, 28.4 (vt, $^2J_{PC} + {}^4J_{PC}$ = 5.6 Hz), 29.6, 30.5, 34.2 (vt, $^1J_{PC} + {}^3J_{PC}$ = 9.1 Hz), 40.6, 124.7 (br), 129.8, 137.1 (d, $^1J_{CF}$ = 245 Hz), 139.1 (d, $^1J_{CF}$ = 246 Hz), 149.2 (d, $^1J_{CF}$ = 234 Hz), 182.4.

***trans*-[(Cy$_3$P)$_2$Pd(O$_2$CCF$_3$)(MeCN)][B(C$_6$F$_5$)$_4$] (2d).** An acetonitrile solution (3 mL) of [Li(OEt$_2$)$_{2.5}$][B(C$_6$F$_5$)$_4$] (264 mg, 0.303 mmol) was slowly added to the acetonitrile (20 mL) solution of **1d** (266 mg, 0.298 mmol) with stirring. The ^{31}P NMR spectrum of the reaction product revealed peaks at 35.3 and 43.4 ppm in a 77:23 ratio; the former signal is attributed to **2d** (see below). After it was stirred for 12 h, the reaction mixture was filtered through a 0.45 μm filter. Evaporation of the solvent to a volume of 5 mL produced a pale brown powder, which after drying afforded **2d** in 59% yield (263 mg). Anal. Calcd for $C_{64}H_{69}NO_2P_2PdBF_{23}\cdot CH_3CN$: C, 51.43; H, 4.71; N, 1.82. Found: C, 51.27; H, 4.93; N, 1.94. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 35.0. ^1H NMR ($CDCl_3$): δ 1.08−1.38 (m, 18H), 1.63 (q, J = 11.7 Hz, 12H), 1.77 (br d, J = 10.2 Hz, 8H), 1.82−1.98 (br m, 28H), 2.45 (s, 3H). $^{31}C\{^1H\}$ NMR ($CDCl_3$): δ 3.5, 26.2, 27.7 (vt, $^2J_{PC} + {}^4J_{PC}$ = 5.3 Hz), 29.9, 33.6 (vt, $^1J_{PC} + {}^3J_{PC}$ = 9.4 Hz), 114.4 (q, $^1J_{CF}$ = 287.9 Hz, *C*F$_3$), 124.0 (br), 128.4, 136.4 (d, $^3J_{CF}$ = 244.8 Hz), 138.3 (d, $^3J_{CF}$ = 244.2 Hz), 148.3 (d, $^3J_{CF}$ = 241.5 Hz), 160.8 (q, $^2J_{CF}$ = 37.0 Hz, *C*═O). ^{19}F NMR ($CDCl_3$): δ −89.3 (br t, $^3J_{FF}$ = 17.1 Hz), −85.4 (t, $^3J_{FF}$ = 20.6 Hz), −54.9, 5.1.

***trans*-[(P^{i}Pr$_3$)$_2$Pd(O$_2$CMe)(MeCN)][B(C$_6$F$_5$)$_4$] (2e).** Complex **2e** was prepared from an acetonitrile (10 mL) solution of [Li(OEt$_2$)$_{2.5}$][B(C$_6$F$_5$)$_4$] (960 mg, 1.102 mmol) and an acetonitrile solution (20 mL) of **1e** (599 mg, 1.099 mmol) in quantitative yield (1.325 g) by a procedure analogous to that used for **2a**, with the following exceptions. The reaction time was 4 h. The final product was purified by triturating with pentane (10 mL) followed by vacuum drying. Interestingly, **2e** was also formed in quantitative yield from the reaction of **1e** (201 mg, 0.369 mmol) with [Me$_2$N(H)Ph][B(C$_6$F$_5$)$_4$] (302 mg, 0.377 mmol) in acetonitrile (15 mL) over 90 min, as revealed by ^{31}P NMR spectroscopy (δ 45.0 ppm). Anal. Calcd for $C_{46}H_{48}NO_2P_2BF_{20}Pd$: C, 45.81; H, 4.01; N, 1.16. Found: C, 46.00; H, 3.92; N, 1.18. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 44.5. ^1H NMR ($CDCl_3$): δ 1.37 (m, 36H), 1.92 (s, 3H), 2.22 (m, 6H), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 4.2, 19.6, 23.2, 24.5 (virtual t, $^1J_{CP} + {}^3J_{CP}$ = 10.1 Hz), 124.4 (br), 128.5, 136.9 (d, $^1J_{CF}$ = 248 Hz), 138.8 (d, $^1J_{CF}$ = 243 Hz), 148.7 (d, $^1J_{CF}$ = 240 Hz), 176.0.

[(Cy$_3$P)$_2$Pd(κ^2-*O*,*O*′-O$_2$CMe)][B(C$_6$F$_5$)$_4$] (3a). Method 1. A dichloromethane solution (25 mL) of [Me$_2$(H)NPh][B(C$_6$F$_5$)$_4$] (1.025 g, 1.279 mmol) was slowly added to a dichloromethane solution (50.0 mL) of **1a** (1.004 g, 1.273 mmol) at −35 °C. The reaction mixture was slowly raised to room temperature and stirred for 21 h. During the course of the reaction, the reaction mixture became deep orange. The volatiles from the reaction mixture were then removed under reduced pressure to give a paste, to which was added diethyl ether (ca. 30 mL) to induce the formation of an orange powder. The orange powder was collected by filtration, washed with acetonitrile (10.0 mL), and dried under reduced pressure to furnish **3a** as an air- and moisture-stable orange solid. Yield: 1.02 g (57%).

Method 2. Dichloromethane (5.0 mL) was syringed into the mixture of **1a** (333 mg, 424 μmol) and HOTs·H$_2$O (85.0 mg, 446 μmol). The resulting mixture was stirred for 22 h. A ^{31}P NMR spectrum of the reaction mixture revealed a new peak at δ 59.0. A dichloromethane (2.0 mL) solution of [Li(OEt$_2$)$_{2.5}$][B(C$_6$F$_5$)$_4$] (400 mg, 459 μmol) was then introduced into the above reaction mixture, stirred for 5 min, and filtered through a medium-porosity frit. The volatiles were removed under vacuum to give a foam that was triturated with hexane (5.0 mL) and dried under reduced pressure to give a yellow solid (577 mg). This solid was then sonicated in the presence of acetonitrile (2 × 3 mL), filtered, and dried under reduced pressure to give 471 mg of **3a** (79%). Anal. Calcd for $C_{62}H_{69}O_2P_2BF_{20}Pd$: C, 52.99; H, 4.95. Found: C, 53.29; H, 5.05. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 59.3. ^1H NMR ($CDCl_3$): δ 1.24−1.34 (m, 20H), 1.66 (q, J = 11.4 Hz, 12H), 1.80 (br, 6H), 1.90 (br, 12H), 1.96 (d, J = 13.8 Hz, 12H), 2.00 (d, J = 12.0 Hz, 4H), 2.04 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.1, 25.7, 27.2 (virtual t, $^2J_{CP} + {}^4J_{CP}$ = 5.5 Hz), 30.2, 34.7 (m), 124.2 (br), 136.2 (d, $^1J_{CF}$ = 248 Hz), 138.1 (d, $^1J_{CF}$ = 242 Hz), 148.2 (d, $^1J_{CF}$ = 239 Hz), 194.9.

Preparation of [(Cy$_3$P)$_2$Pd(κ^2-*O*,*O*-O$_2$CPh)][B(C$_6$F$_5$)$_4$] (3b). Method 1. The solid [Me$_2$(H)NPh][B(C$_6$F$_5$)$_4$] (162 mg, 0.203 mmol) was added in portions to a dispersion of **1b** (179 mg, 0.197 mmol) in diethyl ether (30 mL) in a 100 mL round-bottom flask, and the mixture was stirred for 72 h. The volume of the reaction mixture was then reduced to 10 mL and diluted with hexane (15 mL) to afford a gray solid. The gray solid was washed with acetonitrile (3 × 6 mL) and dried under vacuum to furnish **3b** as a yellow solid in 52% yield (150 mg).

Method 2. Dichloromethane (6 mL) was syringed into a 100 mL round-bottom flask that contained a mixture of **1b** (321 mg, 0.353 mmol) and HOTs·H$_2$O (76.5 mg, 0.402 mmol), and the resulting mixture was stirred for 22 h. A dichloromethane (3 mL) solution of [Li(OEt$_2$)$_{2.5}$][B(C$_6$F$_5$)$_4$] (373 mg, 0.428 mmol) was then introduced into the above reaction mixture, and the solution was stirred for 1 h and filtered. The volatiles from the filtrate were removed under vacuum to furnish a brown solid. The solid was sonicated in the presence of acetonitrile (3 × 3 mL) to facilitate precipitation of a powder. The powder was collected by filtration through a fine porous frit, washed with acetonitrile (3 mL), and dried under vacuum to furnish **3b** as a yellow solid in 80% yield (411 mg). Anal. Calcd for $C_{67}H_{71}O_2P_2PdBF_{20}$: C, 54.84; H, 4.88. Found: C, 54.72; H, 4.71. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 59.6. ^1H NMR ($CDCl_3$): δ 1.31 (br, 18H), 1.64−2.18 (m, 48H), 7.46 (t, $^3J_{HH}$ = 7.8 Hz, 2H), 7.61 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 7.95 (d, $^3J_{HH}$ = 7.2 Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.0, 27.5 (vt, $^2J_{CP} + {}^4J_{CP}$ = 5.6 Hz), 30.5, 35.1 (m), 124.7 (br), 128.7, 128.8, 131.8, 134.2, 136.4 (d, $^1J_{CF}$ = 238 Hz), 138.3 (d, $^1J_{CF}$ = 245 Hz), 148.4 (d, $^1J_{CF}$ = 239 Hz), 188.2.

Preparation of [(Cy$_3$P)$_2$Pd(κ^2-*O*,*O*-O$_2$C^{t}Bu)][B(C$_6$F$_5$)$_4$] (3c). Dichloromethane (18 mL) was syringed into a 100 mL round-bottom flask that contained a mixture of **1c** (448 mg, 0.515 mmol)

and HOTs·H_2O (107 mg, 0.563 mmol), and the resulting heterogeneous mixture was stirred for 24 h. During the course of the above period, the reaction mixture turned into a homogeneous yellow solution and the ^{31}P NMR spectrum of this solution revealed complete consumption of **1c** with the appearance of a new peak at δ 58.6. A dichloromethane (4 mL) solution of $[Li(OEt_2)_{2.5}][B(C_6F_5)_4]$ (512 mg, 588 mmol) was introduced into the above reaction mixture, and the mixture was stirred for 10 min and then filtered through filter paper. The volatiles from the filtrate were removed under vacuum to give a foam that was dissolved in the minimum amount of acetonitrile to give a yellow solution. The yellow solution was sonicated (to facilitate precipitate formation) until no more yellow solid deposited. The yellow solid was collected by filtration and dried under vacuum to furnish **3c** in 69% yield (517 mg). Anal. Calcd for $C_{65}H_{75}O_2P_2PdBF_{20}$: C, 53.94; H, 5.22. Found: C, 53.78; H, 4.98. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 58.4. ^1H NMR ($CDCl_3$): δ 1.13 (s, 9H), 1.20−1.40 (br m, 18H), 1.56−1.74 (br m, 12H), 1.76−2.10 (br m, 36H). $^{31}C\{^1H\}$ NMR ($CDCl_3$): δ 25.8, 26.1, 27.3 (vt, $^2J_{PC} + {}^4J_{PC} = 5.6$ Hz), 30.3, 34.8 (m), 41.1, 123.9 (br), 136.2 (d, $^1J_{CF} = 247$ Hz), 138.2 (d, $^1J_{CF} = 244$ Hz), 148.2 (d, $^1J_{CF} = 240$ Hz), 202.9.

Reaction of 1d with HOTs·H_2O. A dichloromethane solution (6 mL) of **1d** (231 mg, 0.256 mmol) was added to HOTs·H_2O (52 mg, 0.273 mmol), and the resulting heterogeneous mixture was stirred for 24 h. The ^{31}P NMR spectrum of the reaction product indicated the presence of **1d** (24.2 ppm, major) along with other unidentified species (27.7 (major) and 52.6, 54.8, and 56.8 ppm (all minor)).

[(^{i}Pr$_3$P)$_2$Pd(κ^2-*O,O′*-O$_2$CMe)][B(C$_6$F$_5$)$_4$] (3e). Method 1. A mixture of **1e** (51.0 mg, 93.6 μmol) and $[Me_2(H)NPh][B(C_6F_5)_4]$ (76.0 mg, 94.8 μmol) in dichloromethane (5.0 mL) was stirred at room temperature for 24 h. Removal of the volatile materials under reduced pressure yielded an orange gummy material. The ^{31}P NMR spectrum of the material revealed the presence of **3e** (δ 70) and many other unidentified products. Attempts to isolate **3e** from the reaction mixture were not successful.

Method 2. Dichloromethane (7.0 mL) was syringed into a mixture of **1e** (378 mg, 694 μmol) and HOTs·H_2O (137 mg, 720 μmol), and the mixture was stirred for 22 h. A ^{31}P NMR spectrum of the reaction mixture revealed a new peak at δ 70 (major) and smaller peaks at δ 37.1 and 54.0; no signal was observed for **1e**. A dichloromethane (4.0 mL) solution of $[Li(OEt_2)_{2.5}][B(C_6F_5)_4]$ (628 mg, 720 μmol) was then introduced into the reaction mixture. After the mixture was stirred for 5 min, solvent was removed under reduced pressure to give an orange solid. The orange solid was sonicated twice in the presence of diethyl ether (5 mL) to induce precipitation of a yellow powder. This powder was collected by filtration and dried under vacuum to furnish air- and moisture-stable **3e**. Yield: 645 mg (80%). Anal. Calcd. for $C_{44}H_{45}O_2P_2PdBF_{20}$: C, 45.36; H, 3.89. Found: C, 45.37; H, 3.88. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 69.4. ^1H NMR ($CDCl_3$): δ 1.45 (m, 36H), 2.02 (s, 3H), 2.26−2.39 (m, 6H).$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 20.1, 25.3, 26.3 (m), 124.4 (br), 136.9 (d, $^1J_{CF} = 241$ Hz), 138.8 (d, $^1J_{CF} = 243$ Hz), 148.8 (d, $^1J_{CF} = 237$ Hz), 196.1.

{[(Me$_2$N)$_3$P]$_2$Pd(κ^2-*O,O*-O$_2$CMe)}B(C$_6$F$_5$)$_4$ (3f). A diethyl ether (5 mL) solution of $[Me_2(H)NPh][B(C_6F_5)_4]$ (596 mg, 0.710 mmol) was slowly added to **1f** (371 mg, 0.673 mmol) that was also dispersed in diethyl ether (5 mL). The reaction mixture was stirred for 12 h at room temperature. The volatiles from the filtrate were removed under vacuum to give a yellow solid. The yellow solid was washed with the minimum amount of diethyl ether, collected by filtration, and dried under vacuum to furnish **3f** in 65% yield (515 mg). Anal. Calcd for $C_{38}H_{39}N_6O_2P_2BF_{20}Pd$: C. 38.98; H, 3.36; N, 7.18. Found: C, 39.04; H, 2.98; N, 7.16. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 88.9. ^1H NMR ($CDCl_3$): δ 1.99 (s, 3H, O_2CCH_3), 2.70 (apparent t, $^5J_{PH} + {}^3J_{HP} = 5.13$ Hz, 36H, P(N(CH_3)$_2$)$_3$).

***trans*-[(Cy$_3$P)$_2$Pd(O$_2$CMe)(C$_5$H$_5$N)][B(C$_6$F$_5$)$_4$] (4a).** Complex **2a** (198 mg, 0.137 mmol) and pyridine (61 mg, 0.77 mmol) were separately dissolved in toluene (4 and 1 mL, respectively) and cooled to −35 °C. The toluene solution of pyridine was added to the toluene solution of **2a**, and the mixture was stirred at room temperature for 100 min. The volatiles from the reaction mixture were removed under vacuum to furnish a residue that was subsequently triturated with hexane (3 × 10 mL) and collected by filtration. The solid was dried under vacuum to give **4a** in 99% yield (202 mg). Anal. Calcd for $C_{67}H_{74}NO_2P_2PdBF_{20}$: C, 54.21; H, 5.02; N, 0.94. Found: C, 54.34; H, 4.92; N, 0.83. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.1. ^1H NMR ($CDCl_3$): δ 1.04 (m, 12H), 1.22 (m, 6H), 1.50−1.70 (m, 18H), 1.71−1.90 (m, 30H), 2.00 (s, 3H), 7.54 (t, $^3J_{HH} = 7.0$ Hz, 2H), 7.98 (t, $^3J_{HH} = 7.8$ Hz, 1H), 8.77 (d, $^3J_{HH} = 4.8$ Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.6, 26.7, 28.2 (vt, $^2J_{CP} + {}^4J_{CP} = 5.0$ Hz), 30.2, 34.6 (vt, $^1J_{CP} + {}^3J_{CP} = 8.8$ Hz), 124.5 (br), 127.8, 136.8 (d, $^1J_{CF} = 253.5$ Hz), 138.8 (d, $^1J_{CF} = 244.3$ Hz), 140.8, 148.7 (d, $^1J_{CF} = 237.3$ Hz), 154.3, 176.0.

***trans*-[(Cy$_3$P)$_2$Pd(O$_2$CMe)(4-Me$_2$NC$_5$H$_4$N)][B(C$_6$F$_5$)$_4$] (4b).** Complex **4b** was prepared from **2a** (210 mg, 0.145 mmol) and DMAP (20 mg, 0.16 mmol) in THF (6 mL) in quantitative yield (221 mg) by a procedure analogous to that used to prepare **4a**. Anal. Calcd for $C_{69}H_{79}N_2O_2P_2PdBF_{20}$: C, 54.25; H, 5.21; N, 1.83. Found: C, 54.17; H, 5.03; N, 1.78. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.8. ^1H NMR ($CDCl_3$): δ 0.95−1.36 (m, 18H), 1.48−1.95 (m, 48H), 1.97 (s, 3H), 3.03 (s, 6H), 6.55 (d, $^3J_{HH} = 6.6$ Hz, 2H), 8.01 (d, $^3J_{HH} = 6.6$ Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.7, 26.3, 27.9 (vt, $^2J_{CP} + {}^4J_{CP} = 5.4$ Hz), 29.8, 34.0 (vt, $^1J_{CP} + {}^3J_{CP} = 8.8$ Hz), 39.4, 108.8, 124.2 (br), 136.4 (d, $^1J_{CF} = 242.2$ Hz), 138.3 (d, $^1J_{CF} = 243.6$ Hz), 148.4 (d, $^1J_{CF} = 237.9$ Hz), 151.6, 154.7, 176.0.

***trans*-[(Cy$_3$P)$_2$Pd(O$_2$CMe)(CNC$_6$H$_3$Me$_2$-2,6)][B(C$_6$F$_5$)$_4$] (4d).** Complex **4d** was obtained from **2a** (298 mg, 0.206 mmol) and 2,6-dimethylphenyl isocyanide (28 mg, 0.21 mmol) in THF (6 mL) in quantitative yield (316 mg) by a procedure analogous to that used to prepare **4a**. Anal. Calcd for $C_{71}H_{78}NO_2P_2PdBF_{20}\cdot C_4H_8O$: C, 55.99; H, 5.39; N, 0.87. Found: C, 56.23; H, 5.38; N, 0.78. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.6. ^1H NMR ($CDCl_3$): δ 1.10−1.38 (m, 18H), 1.60−1.80 (m, 18H), 1.87 (br d, $J = 12.0$ Hz, 12H), 2.03 (br d, $J = 12.0$ Hz, 12H), 2.06 (s, 3H), 2.16 (m, 6H), 2.47 (s, 6H), 7.24 (d, $^3J_{HH} = 7.3$ Hz, 2H), 7.37 (t, $^3J_{HH} = 7.3$ Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.9, 24.4, 26.6, 28.1 (vt, $^2J_{CP} + {}^4J_{CP} = 5.3$ Hz), 30.7, 35.6 (vt, $^1J_{CP} + {}^3J_{CP} = 9.4$ Hz), 36.7, 124.4 (br), 125.7, 129.8, 132.1, 135.4, 136.8 (d, $^1J_{CF} = 249.9$ Hz), 138.8 (d, $^1J_{CF} = 252.4$ Hz), 148.7 (d, $^1J_{CF} = 243.7$ Hz), 176.0.

***trans*-[(^{i}Pr$_3$P)$_2$Pd(O$_2$CMe)(C$_5$H$_5$N)][B(C$_6$F$_5$)$_4$] (4e).** Complex **4e** was prepared from **2e** (173 mg, 0.143 mmol) and pyridine (48 mg, 0.60 mmol) in dichloromethane (10 mL) in 99% yield (177 mg) by a procedure analogous to that used to prepare **4a**. Anal. Calcd for $C_{49}H_{50}NO_2P_2PdBF_{20}\cdot C_5H_5N$: C, 49.01; H, 4.19; N, 2.12. Found: C, 48.45; H, 3.93; N, 1.81. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 33.4. ^1H NMR (CD_2Cl_2): δ 1.27 (m, 36H), 1.91 (s, 3H), 1.98 (m, 6H), 7.57 (t, $^3J_{HH} = 7.2$ Hz, 2H), 7.96 (t, $^3J_{HH} = 7.8$ Hz, 1H), 8.78 (d, $^3J_{HH} = 4.8$ Hz, 2H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 19.6, 23.5, 24.9 (vt, $^1J_{CP} + {}^3J_{CP} = 9.7$ Hz), 124.2 (br), 128.0, 136.9 (d, $^1J_{CF} = 244.9$ Hz), 138.8 (d, $^1J_{CF} = 243.0$ Hz), 141.3, 148.7 (d, $^1J_{CF} = 236.8$ Hz), 154.2, 176.7.

***trans*-[(^{i}Pr$_3$P)$_2$Pd(O$_2$CMe)(CNC$_6$H$_3$Me$_2$-2,6)][B(C$_6$F$_5$)$_4$] (4f).** Complex **4f** was prepared from the reaction of 2,6-dimethylphenyl isocyanide with **2e** or **3e** as described below.

From 2e. Complex **2e** (98 mg, 84.1 μmol) and 2,6-dimethylphenyl isocyanide (13 mg, 99 μmol) were separately dissolved in THF (4 and 1 mL, respectively) and cooled to −35 °C. The THF solution of 2,6-dimethylphenyl isocyanide was added to the THF solution of **2e** and the reaction mixture stirred at ambient temperature for 2 h. The volatiles from the reaction mixture were removed under vacuum to furnish **4f** in 99% yield (108 mg).

From 3e. Complex **3e** (197 mg, 0.169 mmol) and 2,6-dimethylphenyl isocyanide (23 mg, 0.175 mmol) were separately dissolved in dichloromethane (6 and 4 mL, respectively). The dichloromethane solution of 2,6-dimethylphenyl isocyanide was added to the dichloromethane solution of **3e** at ambient temperature and stirred at the same temperature for 3 h. The volatiles from the reaction mixture were removed under vacuum to furnish **4f** as a light brown solid in 96% yield (210 mg). Anal. Calcd for $C_{53}H_{54}NO_2P_2PdBF_{20}$: C, 49.10; H, 4.20; N, 1.08. Found: C, 48.94; H, 3.88; N, 1.52. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 53.8. ^1H NMR (CD_2Cl_2): δ 1.42 (m, 36H), 1.96 (s, 3H), 2.43 (s, 6H), 2.47 (m, 6H), 7.22 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 7.36 (t, $^3J_{HH}$ = 7.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 19.1, 20.1, 24.1, 26.0 (vt, $^1J_{CP} + {}^3J_{CP}$ = 10.6 Hz), 124 (br), 125.5, 129.7, 132.1, 135.0 (br), 135.7, 136.9 (d, $^1J_{CF}$ = 243.0 Hz), 138.8 (d, $^1J_{CF}$ = 242.4 Hz), 148.7 (d, $^1J_{CF}$ = 239.9 Hz), 176.6.

Reaction of 3e with CD_3CN in the Presence of Sodium Carbonate. Sodium carbonate (191 mg, 1.806 mmol) was added to a CD_3CN solution (3.5 mL) of **3e** (162 mg, 0.139 mmol), and the resulting heterogeneous mixture was stirred for 15 h at room temperature. The reaction mixture was filtered, and the volatiles from the filtrate were removed under vacuum to give a waxy material of **5a** in 97% yield (155 mg). Elemental analysis could not be obtained for **5a** because of its waxy nature and the difficulty in obtaining an isolable solid. $^{31}P\{^1H\}$ NMR (CD_3CN): δ 51.7 (d, nonmetalated phosphorus), 43.2 (d, metalated phosphorus), $^2J_{PP}$ = 30.2 Hz. $^{31}P\{^1H\}$ NMR (THF-d_8): δ 52.4 (br, nonmetalated phosphorus), 44.0 (br, metalated phosphorus). ^1H NMR (THF-d_8): δ 1.29 (m, 18H), 1.46 (dd, J = 17.4, 15.3 Hz, 6H and d, J = 17.4 Hz, 6H), 1.63 (dd, J = 12.7, 9.7 Hz, 6H), 2.21 (m, 3H), 2.65 (m, 2H). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 1.33 (m), 20.1, 20.4 (d, J = 5.1 Hz), 20.5 (m), 21.9, 23.8 (br), 45.7 (br), 125.4 (br), 137.1 (d, $^1J_{CF}$ = 242.4 Hz), 139.1 (d, $^1J_{CF}$ = 243.0 Hz), 149.2 (d, $^1J_{CF}$ = 240.6 Hz). No peak was observed for CD_3CN. To the $CDCl_3$ (0.75 mL) solution of **5a** (50 mg, 43.5 μmol) was added acetic acid (3 μL), and NMR (^1H and ^{31}P) spectra were recorded immediately that indicated the formation of **3e** as the only product.

^1H NMR Monitoring of Cyclometalation Involving 3e and Pyridine. Complex **3e** (115 mg, 99 μmol) was dissolved in CD_2Cl_2 (0.4 mL). To the above solution was added a CD_2Cl_2 (0.3 mL) solution of pyridine (44 mg, 0.56 mmol) in a 5 mm screw-cap NMR tube; the contents of the NMR tube were shaken well and stored at ambient temperature for 4 h. NMR (^1H and ^{31}P) data for the above reaction products are given below. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 49.0 (d, nonmetalated phosphorus), 37.1 (d, metalated phosphorus), $^2J_{PP}$ = 32.7 Hz. ^1H NMR (CD_2Cl_2): δ 1.15−1.26 (m, 24H), 1.43 (dd, J = 7.2 Hz, 3.9 Hz, 6H), 1.49 (dd, J = 7.5 Hz, 3.9 Hz, 6H), 2.05 (m, 6H), 2.54 (m, 2H), 7.32 (br), 7.72 (br), 8.59 (br), 14.09 (s, 1H).

***cis*-[(^{i}Pr$_3$P)Pd(κ^2-*P*,*C*-P^{i}Pr$_2$CMe$_2$)(C_5H_5N)][$B(C_6F_5)_4$] (5b).** Complex **3e** (508 mg, 0.436 mmol) was dissolved in dichloromethane (6 mL), and the solution was stirred. To the above solution was added a dichloromethane (6 mL) solution of pyridine (164 mg, 2.073 mmol), and the mixture was stirred for 5 h. The initial light orange color slowly disappeared with the development of a colorless solution. The volatiles from the reaction mixture were removed under vacuum to furnish **5b** in quantitative yield (516 mg). Assignments of the ^1H and ^{13}C peaks were unambiguously made with the aid of two-dimensional COSY, HMQC, and HMBC NMR spectroscopic measurements. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 49.1 (d, nonmetallated phosphorus), 37.2 (d, metalated phosphorus), $^2J_{PP}$ = 29.3 Hz. ^1H NMR ($CDCl_3$): δ 1.14−1.21 (m, 24H, CH(CH_3)$_2$, ring C(CH_3)$_2$), 1.41−1.47 (m, 12H, CH(CH_3)$_2$), 2.00 (m, 3H, CH(CH$_3$)$_2$), 2.52 (m, 2H, CH(CH$_3$)$_2$), 7.50 (t, $^3J_{HH}$ = 6.3 Hz, 2H, C_5H_5N), 7.87 (t, $^3J_{HH}$ = 7.2 Hz, 1H, C_5H_5N), 8.51 (d, $^3J_{HH}$ = 4.2 Hz, 2H, C_5H_5N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 20.1, 20.3, 21.8, 22.5, 24.6 (d, $^1J_{CP}$ = 13.8 Hz), 24.8 (d, $^1J_{CP}$ = 26.8 Hz), 40.9 (dd, $^2J_{PC}$ = 46.0, 28.3 Hz, 1C, ring *C*(CH$_3$)$_2$), 124.1 (br), 126.2, 136.4 (d, $^1J_{CF}$ = 245.4 Hz), 138.4 (d, $^1J_{CF}$ = 244.2 Hz), 138.8, 148.4 (d, $^1J_{CF}$ = 237.3 Hz), 151.1. Anal. Calcd for $C_{47}H_{46}NP_2PdBF_{20}$: C, 47.67; H, 3.92; N, 1.18. Found: C, 47.67; H, 3.63; N, 1.17.

Table 1. Crystal Data and Structure Refinement Details for 2c and 4b

	2c	4b
empirical formula	$C_{67}H_{78}BF_{20}NO_2P_2Pd$	$C_{69}H_{79}BF_{20}N_2O_2P_2Pd$
formula wt	1488.45	1527.49
temp (K)	293(2)	293(2)
wavelength (Å)	0.710 73	0.710 73
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
unit cell dimens		
a (Å)	20.382(4)	14.910(3)
b (Å)	14.982(3)	15.0468(19)
c (Å)	23.225(5)	18.300(3)
α (deg)	90	69.387(10)
β (deg)	106.124(11)	67.634(12)
γ (deg)	90	88.773(12)
V (Å^3)	6813(2)	3523.5(9)
Z	4	2
calcd density (Mg/m^3)	1.451	1.440
abs coeff (mm^{-1})	0.418	0.407
F(000)	3056	1568
cryst size (mm)	0.24 × 0.20 × 0.10	0.30 × 0.30 × 0.25
cryst color, shape	yellow, irreg block	yellow, irreg block
θ range data collecn (deg)	1.80−24.01	1.91−24.00
limiting indices	$-23 \le h \le 1$ $-17 \le k \le 1$ $-25 \le l \le 26$	$-1 \le h \le 17$ $-15 \le k \le 15$ $-19 \le l \le 20$
no. of rflns collected	12 707	12 135
no. of indep rflns	10 686 (R_{int} = 0.0471)	10751 (R_{int} = 0.0370)
refinement method	full-matrix least squares on F^2	
no. of data/restraints/params	10 686/0/845	10 751/0/877
goodness of fit on F^2	1.013	1.032
final R indices ($I > 2\sigma(I)$)	R1 = 0.0644[a] wR2 = 0.1237[b]	R1 = 0.0647 wR2 = 0.1441
R indices (all data)	R1 = 0.1421 wR2 = 0.1529	R1 = 0.1150 wR2 = 0.1675

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.

Preparation of *cis*-[(^{i}Pr$_3$P)Pd(κ^2-*P*,*C*-P^{i}Pr$_2$CMe$_2$)(4-^{t}BuC$_5$H$_4$N)][$B(C_6F_5)_4$] (5c). Complex **5c** was prepared from **3e** (503 mg, 0.432 mmol) and 4-*tert*-butylpyridine (228 mg, 1.686 mmol) in dichloromethane (10 mL) in 95% yield (508 mg) by a procedure analogous to that used to prepare **5b**. Anal. Calcd for $C_{51}H_{54}NP_2PdBF_{20}$: C, 49.38; H, 4.39; N, 1.13. Found: C, 49.54; H, 4.15; N, 1.44. $^1P\{^1H\}$ NMR ($CDCl_3$): δ 49.2 (d, nonmetalated phosphorus), 36.4 (d, metalated phosphorus), $^2J_{PP}$ = 32.9 Hz. ^1H NMR ($CDCl_3$): δ 1.11−1.25 (m, 24H, CH(CH_3)$_2$, ring C(CH_3)$_2$), 1.33 (s, 9H, C(CH_3)$_3$), 1.40 (dd, J = 7.1 Hz, 4.9 Hz, 6H, CH(CH_3)$_2$), 1.46 (dd, J = 7.2, 5.1 Hz, 6H, CH(CH_3)$_2$), 1.99 (m, 3H, CH(CH$_3$)$_2$), 2.50 (m, 2H, CH(CH$_3$)$_2$), 7.48 (d, $^3J_{HH}$ = 6.0 Hz, 2H, 4-^{t}BuC$_5H_4$N), 8.36 (d, $^3J_{HH}$ = 6.0 Hz, 2H, 4-^{t}BuC$_5H_4$N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 20.2, 20.3 (d, $^2J_{PC}$ = 3.1 Hz), 21.9 (d, $^2J_{PC}$ = 2.5 Hz), 22.6 (m), 24.6 (d, $^1J_{CP}$ = 13.9 Hz), 24.7 (dd, $^1J_{CP}$ = 25.2 Hz, $^3J_{CP}$ = 3.1 Hz), 30.3, 35.4, 40.5 (dd, $^2J_{PC}$ = 46.2, 29.3 Hz, 1C, ring *C*(CH$_3$)$_2$), 123.3, 124.0 (br), 136.4 (d, $^1J_{CF}$ = 245.4 Hz), 138.4 (d, $^1J_{CF}$ = 244.8 Hz), 148.4 (d, $^1J_{CF}$ = 240.3 Hz), 150.6, 164.1.

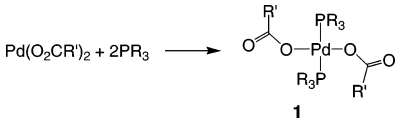
Reaction of 3a with Pyridine. Complex **3a** (147 mg, 0.105 mmol) was dissolved in dichloromethane (3 mL), and the solution was stirred. To the above solution was slowly added a dichloromethane (3 mL) solution of pyridine (70 mg, 2.07 mmol), and this mixture was stirred for 18 h. No new product was formed, as revealed by ^{31}P NMR spectroscopy. The reaction mixture was stirred for additional 76 h. The ^{31}P NMR spectrum of the reaction mixture indicated a pair of doublets (36.9 and 32.0 ppm (d, $^1J_{PP}$ = 22 Hz)) in addition to a broad singlet at 22.0 ppm.

X-ray Diffraction Studies. Details of the data collections and structure solutions are presented in Table 1. Further details may be found in the Supporting Information.

Results and Discussion

(a) Synthesis and Characterization of $[(R_3P)_2Pd(O_2CR')_2]$. The reactions of $Pd(O_2CR')_2$ with various PR_3 ligands in CH_2Cl_2 at −78 °C furnished air- and moisture-stable $[(R_3P)_2Pd(O_2CR')_2]$ (**1a**−**f**) as yellow crystalline solids in good yields (Scheme 2). Although **1a**[2] and **1e**[2a] have been noted, their

Scheme 2



1

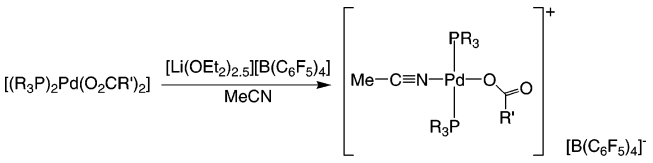
	R	R′	yield (%)	^{31}P NMR (δ)
1a	Cy	Me	88	21.3
1b	Cy	Ph	74	23.7
1c	Cy	^{t}Bu	74	17.4
1d	Cy	CF_3	67	24.5
1e	^{i}Pr	Me	90	33.0
1f	NMe_2	Me	70	93.3

characterization was partially reported. The formation of complexes **1a**−**e** was readily apparent from ^{31}P NMR spectra, which revealed a single peak shifted downfield as compared to that for the free ligand.

Specifically, the ^{31}P NMR signals for **1a**,**e** resonate at lower field as compared to those for uncoordinated PCy_3 (10.9 ppm) and P^iPr_3 (20.7 ppm), respectively.[20] The coordination chemical shifts $\Delta\delta$[21] for **1a**−**e** are 10.4, 12.8, 6.5, 13.6, and 12.3 ppm, respectively. The values, however, are somewhat smaller than that reported for *trans*-$[(Ph_3P)_2Pd(O_2CMe)_2]$ ($\Delta\delta$ 15.0).[22] In contrast, the ^{31}P NMR spectrum of **1f** revealed a resonance at δ 93.3 ppm which is upfield ($\Delta\delta$ −29.7) compared to free $P(NMe_2)_3$ (δ 123.0 ppm).[20] A positive coordination chemical shift was observed for $[Cy_3PAuCl]$ ($\Delta\delta$ 43.5)[23] and $[(^iPr_3P)AuCl]$ ($\Delta\delta$ 44.1),[23] whereas a negative coordination chemical shift ($\Delta\delta$ −12.3) was observed for $[(Me_2N)_3P]AuCl$.[24] The ^{13}C NMR spectra of **1a**,**c**,**e**,**f** revealed a characteristic singlet around 180 ppm for the carbonyl carbon of the carboxylate group, comparable to the value of 171.2 ppm previously established for **1b**,[19] and also for related bis(acetato)palladium(II) bis(carbene) complexes.[25] On the other hand, the ^{13}C NMR spectrum of **1d** revealed a quartet centered at δ 160.9 ($^2J_{CF}$ = 32.6 Hz) due to the coupling of a carbonyl carbon to C*F*$_3$ nuclei. In addition, the ^{13}C NMR spectrum of **1d** revealed a quartet centered at δ_C 114.3 ($^1J_{CF}$ = 289.3 Hz) assignable to coupling of the *C*F$_3$ carbon nucleus to three fluorine nuclei attached to it. The carbon chemical shifts for carbonyl and CF_3 carbons and the $^1J_{CF}$ value of **1d** are comparable to those reported for a bis(trifluoroacetato)palladium(II) bis(carbene) complex (carbonyl and CF_3 chemical shifts 163.9 and 116 ppm, respectively; $^1J_{CF}$ = 289.7 Hz).[25c] Compounds **1a**,**c**,**d** all exhibit four resonances for the Cy moieties, two of them being singlets and two others being virtual triplets due to the trans geometry of these complexes in solution, as was also reported for **1b**[18] and *trans*-$[(Cy_3P)_2PdCl_2]$.[26] The ^{13}C NMR spectrum of **1e** displays two resonances constituting a singlet for the methyl carbon and a virtual triplet for the methine carbon of ^{i}Pr moieties, again indicating a probable trans geometry. Compound **1a** displays some degree of thermal stability compared to *trans*-$[(Ph_3P)_2Pd(O_2CMe)_2]$,[22] for its ^{31}P and ^{1}H NMR spectra remained unchanged even after heating in toluene-d_8 solution at 63 °C for 23 h.

(b) Carboxylate Abstraction Reactions of $[(R_3P)_2Pd(O_2CR')_2]$. Studies have revealed that the primary mode of action of 1 equiv of $[Li(OEt_2)_{2.5}][B(C_6F_5)_4]$ or $[Me_2(H)NPh][B(C_6F_5)_4]$ on $[(R_3P)_2Pd(O_2CR')_2]$ is to abstract one of the carboxylate groups to generate cationic complexes. The specific products obtained vary, depending on solvent and reaction conditions. Reactions performed in acetonitrile with these reagents led to compounds **2a**−**e** (Scheme 3).

Scheme 3



2

	R	R′	yield (%)	^{31}P NMR (δ)
2a	Cy	Me	99	32.7
2b	Cy	Ph	98	32.6
2c	Cy	^{t}Bu	99	31.0
2d	Cy	CF_3	59	35.0
2e	^{i}Pr	Me	99	44.5

New complexes were characterized by ^{31}P NMR resonances that are notably shifted downfield relative to corresponding resonances determined for compounds **1a**−**e**. The ^{1}H NMR spectra of **2a**−**e** confirm the incorporation of one acetonitrile ligand per two phosphine ligands. These materials are air-stable crystalline compounds. In solution, these materials start to decompose above 60 °C, in contrast to the related carbene-supported cationic palladium carboxylates **Va** and **Vb** (Scheme 1), which are stable at 80 °C for at least 24 h.[16a]

The reactions of **1a**−**c**,**e** with $[Li(OEt_2)_{2.5}][B(C_6F_5)_4]$ in MeCN gave **2a**−**c**,**e** in nearly quantitative yield. However, the reaction of **1d** with $[Li(OEt_2)_{2.5}][B(C_6F_5)_4]$ in MeCN gave, in addition to **2d**, an unidentified species (^{31}P NMR: 43.4 ppm) in significant quantities, and thus the yield of 59% is diminished relative to those of the other reactions. Carboxylate abstractions from **1a**−**e** could also be performed using $[Me_2(H)NPh][B(C_6F_5)_4]$ in place of $[Li(OEt_2)_{2.5}][B(C_6F_5)_4]$, but isolation of pure materials from the reaction mixtures proved more difficult, despite the fact that ^{31}P NMR spectroscopy suggested that high yields of **2a**−**c** are produced.

Single crystals of compound **2c** were obtained by vapor diffusion of heptane into a diethyl ether solution of **2c**, and the results of an X-ray diffraction study are presented in Figure 1.

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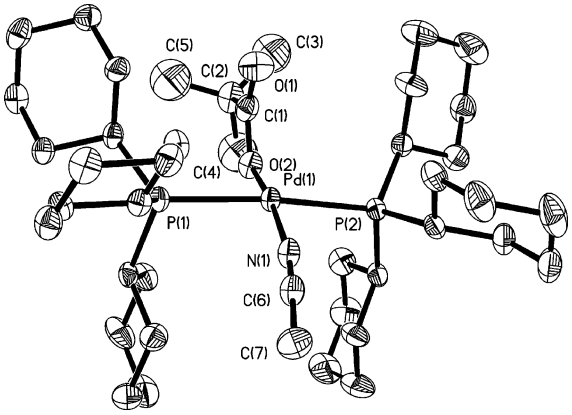
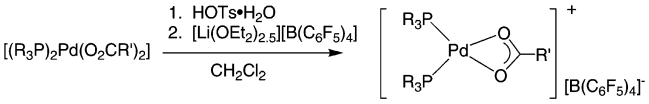


Figure 1. ORTEP representation of **2c** (hydrogen atoms and anion omitted for clarity). Selected bond distances (Å) and angles (deg): Pd(1)−O(2), 1.994(5); Pd(1)−N(1), 1.998(6); Pd(1)−P(2), 2.376(2); Pd(1)−P(1), 2.379(2); N(1)−C(6) 1.129(8); O(1)−C(1), 1.201(9); O(2)−C(1), 1.300(9); O(2)−Pd(1)−N(1), 169.7(2); O(2)−Pd(1)−P(2), 89.2(1); N(1)−Pd(1)−P(2), 91.0(2); O(2)−Pd(1)−P(1), 90.2(1); N(1)−Pd(1)−P(1), 88.6(2); P(2)−Pd(1)−P(1), 174.03(7).

Complexes **2a** and **2c** have essentially identical average Pd−P bond lengths (ca. 2.38 Å).[15] Compound **2c**, however, has shorter (possibly statistically insignificant) Pd−O bond lengths (1.994(5) vs 2.007(4) Å) and longer Pd−N bond lengths (1.998(6) vs 1.986(5) Å). This ever so slight bias of the parameters may be due to the fact that the pivalato group is a better donor for palladium than the acetato group, and thus in response, the binding of the acetonitrile is weaker in the pivalato complex. The remainder of the two structures are in close accord with one another and are within expectations for four-coordinate palladium(II) complexes.

Reactions of **1a**−**d**,**f** with $[Li(OEt_2)_{2.5}][B(C_6F_5)_4]$ or $[Me_2(H)NPh][B(C_6F_5)_4]$ in the noncoordinating solvent CH_2Cl_2, however, take a different course and produce the cationic complexes **3a**−**c**,**e**,**f** (Scheme 4) lacking the coordinating solvent

Scheme 4



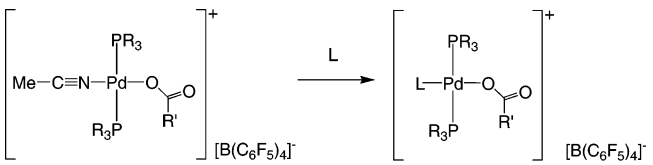
	R	R′	yield (%)	^{31}P NMR (δ)
3a	Cy	Me	79	59.3
3b	Cy	Ph	80	59.6
3c	Cy	^{t}Bu	69	58.4
3d	Cy	CF_3		
3e	^{i}Pr	Me	80	69.4
3f	NMe_2	Me	65	88.9

molecule. In order to satisfy the coordination needs of the palladium centers, these complexes feature κ^2-carboxylate ligands. By necessity, the two phosphine ligands are cis in these materials. Variations of reaction conditions led to the finding that higher yields (∼20% better) and easier product purification could be achieved if the reactions were performed via a two-step process. Specifically, addition of *p*-toluenesulfonic acid to $[(R_3P)_2Pd(O_2CR')_2]$ led to formation of $[(R_3P)_2Pd(\kappa^2\text{-}O,O\text{-}O_2CR')]OTs$, which upon addition of $[Li(OEt_2)_{2.5}][B(C_6F_5)_4]$ led to formation of $[(R_3P)_2Pd(\kappa^2\text{-}O,O\text{-}O_2CR')][B(C_6F_5)_4]$ (**3a**−**c**,**e**,**f**) in good yields. These intermediary tosylate salts were not fully characterized, but analysis of the reaction of **1c** with HOTs·H_2O in CH_2Cl_2 for 24 h showed that $[(Cy_3P)_2Pd(\kappa^2\text{-}O,O\text{-}O_2C\text{-}^tBu)]OTs$ (δ_P 58.6) is cleanly produced. The successful synthesis of carbene complexes **Va** also required an analogous two-step process.[16a] Attempts to isolate the trifluoroacetato analogue **3d** were unsuccessful by either reaction of **1d** with $[Me_2(H)NPh][B(C_6F_5)_4]$ or by reaction of **1d** with HOTs·H_2O/$[Li(OEt_2)_{2.5}][B(C_6F_5)_4]$. The ^{31}P NMR resonances of **3a**−**c**,**e** are markedly downfield compared to those of the analogous acetonitrile adducts **2a**−**e**. Interestingly, the magnitude of $\Delta\delta$ for **3f** is very small and is opposite in sign ($\Delta\delta$ −4.4). The ^{13}C NMR resonances for the carbonyl carbons of **3a**−**c**,**e** are consistently shifted about 20 ppm downfield (161−182 ppm) relative to those of the same atoms in **2a**−**c**,**e**.

(c) Reaction of Cationic Complexes with Lewis Bases. (i) Substitution Reactions. Our studies of the reactions of these complexes were prompted by the observation that the κ^2 complexes did not react with acetontrile to yield **2**. The presence of a labile acetonitrile ligand in complexes **2a**−**e**, as well as the known fluxionality of carboxylate ligands (between κ^2 and κ^1 binding modes), suggested that these complexes should be amenable to facile ligand substitution and addition reactions. Reactions of these materials were thus examined with some Lewis bases. During these investigations it was discovered that cyclometalation of the phosphine ligands can occur in preference to ligand addition. The substitution reactions are described first.

In general, reactions of **2a**,**b** with added ligands proceeded without difficulty to exchange the acetonitrile (Scheme 5). For

Scheme 5



	R	L	yield (%)	^{31}P NMR (δ)
4a	Cy	C_5H_5N	99	22.1
4b	Cy	$4\text{-}Me_2NC_5H_4N$	99	21.8
4c	Cy	NC_4H_4N	39 (NMR)	22.4
4d	Cy	$CNC_6H_3Me_2\text{-}2,6$	99	40.6
4e	^{i}Pr	C_5H_5N	99	33.4
4f	^{i}Pr	$CNC_6H_3Me_2\text{-}2,6$	99 [96][a]	53.8

[a] Yield from **3e** and $CNC_6H_3Me_2$-2,6.

example, the reaction of **2a** with pyridine in toluene and with DMAP in THF furnished **4a**,**b**, respectively, in nearly quantitative yields. Similarly, complex **2e** upon treatment with pyridine in dichloromethane gave **4e** in quantitative yield. The new palladium complexes **4** are stable to air and moisture for at least several days, like their precursors **2** and **3**.

The crystal structure of **4b** was determined by X-ray diffraction on a sample obtained by diffusing pentane into a THF solution of **4b**, and the results are depicted in Figure 2. The structure shows no unusual features and is closely related to the structures of **2a**[15] and **2c**. The coordination geometry around palladium in **4b** is square planar, with two PCy_3 ligands occupying trans positions. The Pd−P distances in **4b** of 2.40 Å are somewhat longer than those observed in **2a** and **2c** (2.38 Å). This observation may reflect the higher basicity of DMAP relative to acetonitrile. The longer Pd−O distance of 2.013(4) Å in **4b** is consistent with this proposal.

Attempts to isolate the product of reaction of **2a** with pyrazine in THF, however, were less productive. The desired pyrazine

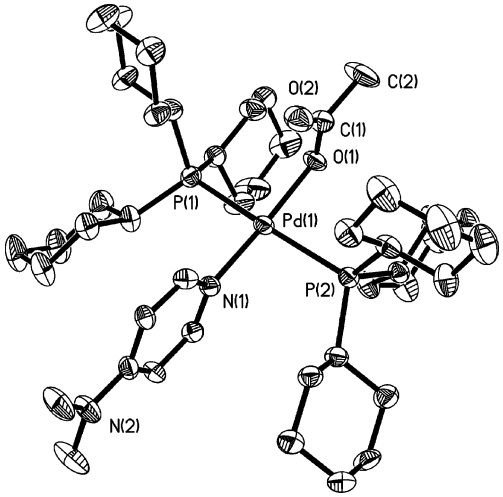


Figure 2. ORTEP representation of **4b** (hydrogen atoms and anion omitted for clarity). Selected bond distances (Å) and angles (deg): Pd(1)−O(1), 2.013(4); Pd(1)−N(1), 2.021(5); Pd(1)−P(1), 2.400(2); Pd(1)−P(2), 2.401(2); O(1)−Pd(1)−N(1), 172.1(2); O(1)−Pd(1)−P(1), 88.3(1); N(1)−Pd(1)−P(1), 92.7(2); O(1)−Pd(1)−P(2), 86.9(1); N(1)−Pd(1)−P(2), 93.7(2); P(1)−Pd(1)−P(2), 167.26(6).

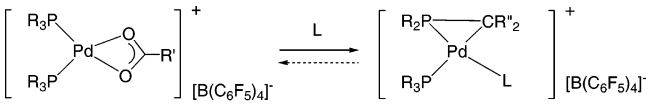
adduct **4c** is only produced in about 39% yield (as ascertained by ^{31}P NMR spectroscopy) upon addition of 1 equiv of pyrazine to **2a**. Longer reaction times (19 h) and the addition of 3 equiv of pyrazine to the reaction mixture did not significantly increase the amount of **4c** produced. Apparently, the weaker nucleophilicity of pyrazine as compared to that of MeCN and pyridine yields only an equilibrium mixture of **2a**, acetonitrile, pyrazine, and **4c**. The reaction of **2a** with 5 equiv of DABCO in dichloromethane yielded no new species, as revealed by ^{31}P NMR spectroscopy. This result might be due to unfavorable steric repulsion between PCy_3 in **2a** and the incoming DABCO.

The reactions of **2a**,**e** with 2,6-dimethylphenyl isocyanide afforded high yields of isocyanide complexes **4d**,**f**. These new adducts were identified by standard NMR spectroscopic methods, as well as elemental analysis. While complexes **4a,b**,**e** each revealed a ^{31}P NMR signal at higher field than for their respective parent complexes **2**, the isocyanide complexes, in contrast, have ^{31}P resonances at lower field relative to those of **2a**,**e**. The collective spectroscopic data support a trans geometry for palladium in all of the adducts **4**. Intriguingly, **4f** could also be obtained from the reaction of **3e** with 2,6-dimethylphenyl isocyanide in dichloromethane in 96% yield, whereas the reactions with N-centered Lewis bases produced different types of products (vide infra).

(ii) Cyclometalation Reactions. While reactions of the acetonitrile complexes **2** with pyridines gave the products of simple substitution, the reactions of complexes **3** are more complicated, despite the fact that these materials are effectively "acetonitrile-free" analogues of **2**. Cyclometalation of the $^{i}Pr_3P$ ligand of **3e** was discovered during attempts to convert complexes **3e** to **2e** by the addition of acetonitrile.

As previously noted, the cyclometalation reaction of **3e** occurs upon dissolution of **3e** in CD_3CN and affords an equilibrium mixture containing 30% of **5a** (Scheme 6).[15] Addition of sodium carbonate (as a convenient base) drives the reaction to completion. We also found that solutions of **3e** and pyridine provided the related complex **5b** as a crystalline solid, which was fully characterized. The reaction of **3e** can also be extended to derivative **5c** by using 4-*tert*-butylpyridine. Like the reaction of **3e** and pyridine, the yields of **5c** are maximal (95%) if more than 2 equiv of N-donor is used, so as to consume 1 equiv as proton scavenger of the proton from the cyclometalation process.

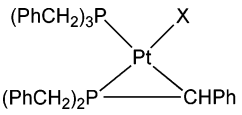
Scheme 6



5

	R	CR″$_2$	L	^{31}P NMR (δ)
5a	^{i}Pr	CMe_2	CD_3CN	51.7, 43.2 (J_{PP} = 30 Hz)
5b	^{i}Pr	CMe_2	C_5H_5N	49.1, 37.2 (J_{PP} = 29 Hz)
5c	^{i}Pr	CMe_2	4-^{t}BuC_5H_4N	49.2, 36.4 (J_{PP} = 33 Hz)
5d	Cy	$-C(CH_2)_5-$	C_5H_5N	36.9, 32.0 (J_{PP} = 22 Hz)

The properties of **5c** are in full accord with those of the previously reported analogue **5b**. Specifically, the ^{31}P NMR spectrum of **5c** displayed a pair of doublets centered at δ_P 49.2 and 36.4 for nonmetalated and metalated phosphorus, respectively.[21,27] These shifts are comparable to those reported for **5a** (δ_P 51.7 (nonmetalated phosphorus), 43.2 (metalated phosphorus)) and **5b** (δ_P 49.1 (nonmetalated phosphorus), 37.2 (metalated phosphorus)). The X-ray structure of **5b** unambiguously revealed a square-planar geometry around palladium in which the metalated phosphorus was located trans to pyridine.[15] We thus propose that both **5a** and **5c** possess structures analogous to that of **5b**. The cis disposition of phosphines in **5c** is also indicated by the small phosphorus−phosphorus coupling constant ($^2J_{PP}$ = 33 Hz), which is comparable to those values reported for **5a** ($^2J_{PP}$ = 30 Hz) and **5b** ($^2J_{PP}$ = 29 Hz). These values are also comparable to that of a related neutral platinum complex, **VIII** ($^2J_{PP}$ = 30 Hz).[28] Complexes **5b**,**c** each exhibit



X = 2Me-1,2-(sigma-$B_{10}C_2H_{10}$)

VIII

a characteristic pair of doublets centered at δ_P 40.9 ($^1J_{PC}$ = 46 Hz, $^2J_{PC}$ = 28 Hz) and at δ_P 40.5 ($^1J_{PC}$ = 46 Hz, $^2J_{PC}$ = 29 Hz), respectively, for the ring *C*Me$_2$ carbon, due to coupling with two nonequivalent phosphorus nuclei. These chemical shifts are in the region expected for the ring carbon in a three-membered palladacycle.[29]

Initial attempts to extend the cyclometalation reaction to complexes bearing the cyclohexyl groups are informative but inconclusive at this time. The reaction of **3a** and pyridine in dichloromethane was very slow, and two products appeared at the expense of perhaps half of **3a** after 4 days, as revealed by ^{31}P NMR spectroscopy. The material present in greater quantity

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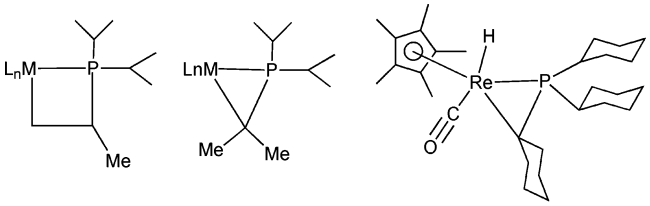
was identified by a pair of doublets centered at δ_P 36.9 and 32.0 ($^2J_{PP}$ = 22 Hz), and the minor product displayed a broad singlet at δ_P 22.0 ppm. The species displaying the pair of doublets is very likely to be the cyclometalated complex **5d**. A greater resistance to cyclometalation for compound **3a** compared to that for **3e** can probably be attributed to the formation of a spirocyclic ring system in a compound such as **5d**. The broad signal at 22 ppm is identified as the product of simple substitution, **4a**. Thus, for this material, substitution can occur competitively, albeit slowly, with cyclometalation.

Base-induced cyclometalation of alkylphosphines coordinated to transition metals is a well-known method to generate metallacycles. The C−H bond in P^iPr_3 coordinated to a transition metal can be activated in two ways, involving methyl or methine protons, the former process leading to either the four-membered metallacycle **IX** or the three-membered metallacycle **X**. While



IX **X** **XI**

numerous four-membered metallacycles are known in the literature, three-membered metallacycles are rarer. The reaction of *cis*-[$(Me_3P)_4Ru(O_2CMe)Cl$] or *cis*-[$(Me_3P)_4Ru(O_2CMe)_2$] with $LiN(SiMe_3)_2$ furnishes cyclometalated *cis*-[$(Me_3P)_3RuCl(\kappa^2$-*P*,*C*-$PMe_2CH_2)$] and spirocyclic *cis*-[$(Me_3P)_2Ru(\kappa^2$-*P*,*C*-$PMe_2CH_2)_2$], respectively.[31]Another closely related example reported in the literature involves activation of the ipso C−H bond of PCy_3 in [$(\eta^5$-$C_5Me_5)Re(CO)(N_2)(PCy_3)$] upon irradiation with UV light to furnish the cyclometalated **XI** in 66% yield, which was unambiguously characterized by X-ray crystallography.[32]

While addition of pyridine to **3e** provide the products of cyclometalation, addition of 2,6-dimethylphenyl isocyanide gives the only the product of substitution. Since **3a** provides both cyclometalation and substitution upon reaction with pyridine, one can ponder what specific factors control the type of product that is obtained. One possibility would involve interconversion of the κ^1- and κ^2-carboxylate complexes prior to ligand addition. Attempts to observe this interconversion, however, were only partially successful. ^{31}P NMR observation of solutions of **2a** and **2e** heated to greater than 60 °C reveal a slow decomposition of these materials to produce a mixture of Pd metal and PdH complexes (as suggested by the presence of ^{1}H NMR signals at around −15 ppm). Spectral signatures for significant amounts of the corresponding κ^2 complexes, however, are seen during these reactions. Heating solutions of **3a** and **3e** with acetonitrile under various conditions does not produce evidence for formation of acetonitrile adducts **2a** and **2e**. More work is required to properly explain the reasons for the product diversity and chemistry of these palladium complexes.

Conclusions

A diverse set of bis(carboxylato)palladium(II) bis(phosphine) complexes was isolated in high yield and characterized. Carboxylate abstraction reactions yielded cationic palladium carboxylate complexes, whose specific natures were very dependent on the choice of solvent. Reactions of *trans*-[$(R_3P)_2Pd(O_2CR')_2$] (**1**) with $[Li(OEt_2)_{2.5}][B(C_6F_5)_4]$ in MeCN led to carboxylate abstraction and formation of *trans*-[$(R_3P)_2Pd(O_2CR')(MeCN)$]-$[B(C_6F_5)_4]$ (**2**), while carboxylate abstraction reactions of **1** with $[Me_2(H)NPh][B(C_6F_5)_4]$ or *p*-toluenesulfonic acid ($HOTs\cdot H_2O$) in CH_2Cl_2 furnished cationic complexes of the form [$(R_3P)_2$-$Pd(\kappa^2$-*O*,*O*-$O_2CR')]^+$ (**3**). Reactions of these materials with pyridine gave two different types of products, either the products of acetonitrile substitution (**4**) or those of cyclometalation (**5**).

Acknowledgment. We thank Promerus LLC, for funding.

Supporting Information Available: CIF files giving crystallographic information for **2c** and **4b** and figures giving NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

OM070069G

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