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Communications

Synthesis and Reactivity of Cationic Palladium Phosphine Carboxylate Complexes

Natesan Thirupathi,[†,‡] Dino Amoroso,[§] Andrew Bell,[§] and John D. Protasiewicz[*,†]

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, and
Promerus LLC, Brecksville, Ohio 44141

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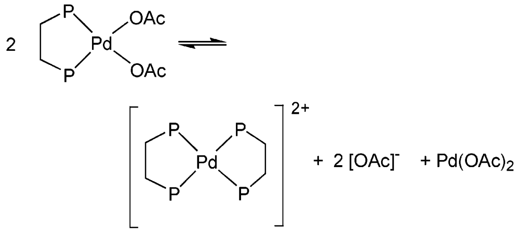
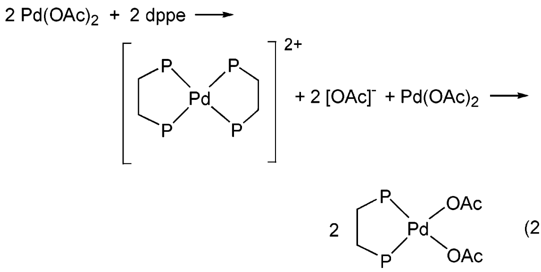
Summary: Simple routes to two new types of mononuclear cationic palladium phosphine acetate complexes featuring κ^1*- or* κ^2*-carboxylates have been developed, and the resulting materials have been characterized by single-crystal X-ray diffraction. In acetonitrile the complex* $[(^iPr_3P)_2Pd(\kappa^2O,O'\text{-}OAc)]^+$ *leads not to the independently prepared trans-*$[(^iPr_3P)_2Pd(MeCN)(OAc)]^+$ *but to reversible cyclometalation to form* $[(^iPr_3P)(MeCN)Pd(\kappa^2C,P\text{-}C(Me)_2P^iPr_2)]^+$.

Cationic palladium phosphine complexes are under active study, due to their role in an enormous number of important synthetic transformations and for the polymerization of polar and nonpolar olefins.[1−5] In particular, such complexes bearing acetate ligands have received added attention for catalysis of the copolymerization of carbon monoxide and olefins.[6−10] Studies of catalytic systems derived from mixtures of chelating diphosphines, $Pd(OAc)_2$, and acids have proved more complicated than was first envisioned. For example, the autoionization postulated in eq 1 was later revised to reflect the fact that $[(dppe)_2Pd]^{2+}$ was the kinetic product of addition of dppe (dppe = 1,2-bis(diphenylphosphino)ethane) to $Pd(OAc)_2$ in methanol, and a slower transformation of this material to the thermodynamically favored $[(dppe)Pd(OAc)_2]$ (eq 2).[11−13] The role of added acid in this system was suggested to sequester OAc^- ions that aided the transformation of $[(dppe)_2Pd]^{2+}$ to $[(dppe)Pd(OAc)_2]$.



(1)



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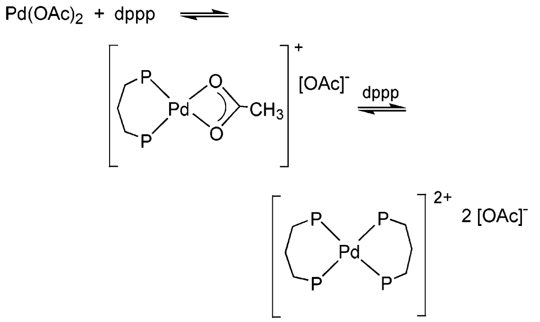

(3)

On the other hand, studies of the copolymerization of carbon monoxide and ethylene using the closely related system $[(dppp)Pd(OAc)_2]$ (dppp = 1,2-bis(diphenylphosphino)propane) have suggested that the spectroscopically detected $[(dppp)Pd(OAc)]^+$ (eq 3) is the catalytically important species in methanol/CF_3COOH mixtures.[14]

While these studies have been ongoing, the utility of nonchelating phosphines for polymerization catalysis is far less conspicuous. Our specific interest in cationic

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[†] Case Western Reserve University.

[‡] Current address: Department of Chemistry, University of Delhi, Delhi 110 007, India.

[§] Promerus LLC.

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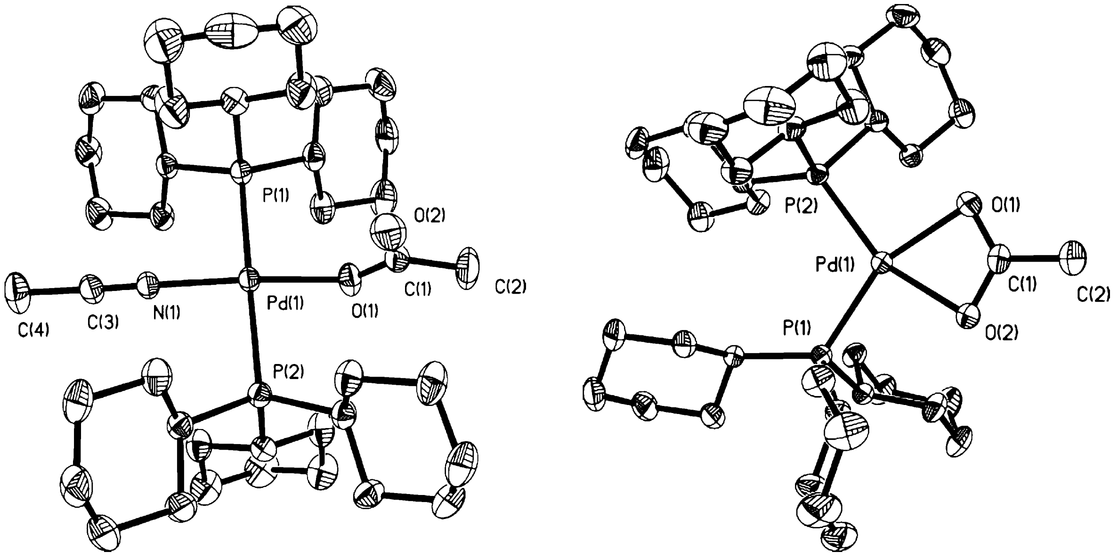
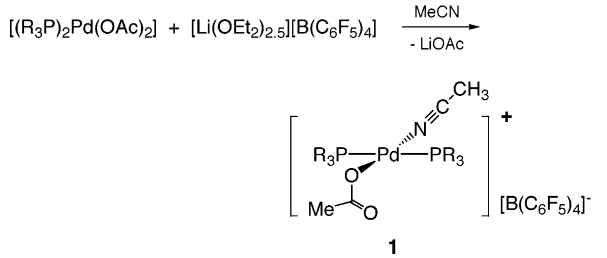


Figure 1. X-ray structural diagrams of **1a** (left) and **2a** (right), with the anions, solvent molecules, and hydrogen atoms omitted for clarity. Selected bond distances (Å) and angle (deg) for **1a**: Pd−P1, 2.376(2); Pd−P2, 2.376(2); Pd−N1, 1.986(5); Pd−O1, 2.007(4); P1−Pd−P2, 177.46(6). Selected bond distances (Å) and angle (deg) for **2a**: Pd−P1, 2.271(1); Pd−P2, 2.257(1); Pd−O1, 2.138(3); Pd−O2, 2.130(3); P1−Pd−P2, 107.14(4).

palladium complexes was initiated during recent efforts to ascertain how mixtures of *trans*-[$(R_3P)_2Pd(OAc)_2$] and [$Li(OEt_2)_{2.5}$][$B(C_6F_5)_4$] or [$Me_2(H)NPh$][$B(C_6F_5)_4$] promote the polymerization of norbornene.[15] Herein we present the synthesis and structural characterizations of several cationic palladium phosphine carboxylate complexes that are derived by the action of lithium salts or acids on *trans*-[$(R_3P)_2Pd(OAc)_2$]. These new monocationic species bridge the previously reported neutral *cis*-[$P_2Pd(OAc)_2$] and dicationic [P_4Pd]$^{2+}$ complexes. Furthermore, we show that the nature of these monocationic acetato complexes is very dependent on their mode of formation and that some of these complexes are susceptible to facile and reversible cyclometalation of coordinated triisopropylphosphine ligands.

Reactions of the palladium(II) acetate complexes *trans*-[$(R_3P)_2Pd(OAc)_2$] with [$Li(OEt_2)_{2.5}$][$B(C_6F_5)_4$] in acetonitrile led to the selective formation of *trans*-[$(R_3P)_2Pd(OAc)(MeCN)$][$B(C_6F_5)_4$] (R = Cy, **1a**; R = ^{i}Pr, **1b**), as judged by the appearance of new ^{31}P NMR signals ca. 9−14 ppm downfield from those of their respective neutral *trans*-[$(R_3P)_2Pd(OAc)_2$] precursors.[16]



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The pale yellow, air-stable crystalline products are isolated in near-quantitative yields. The results of the crystallographic analysis of **1a** are displayed in Figure 1 (left). The geometry of the palladium center in **1a** is square planar and features a palladium−oxygen bond length of 2.007(4) Å, which is slightly shorter than those found in structurally characterized *trans*-[$(R_3P)_2Pd(OAc)_2$][17] but comparable to palladium−oxygen bond lengths in cationic pyridine palladium acetate complexes.[18] Further studies of these reactions showed that not only were isolated yields dependent upon the reagent used to abstract the acetate units but also the identity of the products obtained depended on the choice of solvent. For example, changing the solvent for such reactions from acetonitrile to dichloromethane or THF led to an inseparable mixture of materials. Replacing [$Li(OEt_2)_{2.5}$][$B(C_6F_5)_4$] with [$Me_2(H)NPh$][$B(C_6F_5)_4$] and performing the reaction in dichloromethane, however, led to very different types of complexes. Studies of these reactions by ^{31}P NMR spectroscopy revealed new singlet resonances at approximately 25−27 ppm downfield from those signals observed for the corresponding products **1a**,**b**. From the reaction of *trans*-[$(Cy_3P)_2Pd(OAc)_2$] with [$Me_2(H)NPh$][$B(C_6F_5)_4$], [$(Cy_3P)_2Pd(\kappa^2 O,O'\text{-}OAc)$][$B(C_6F_5)_4$] (**2a**) was thus isolated in 57% yield (Scheme 1).[19]

A chelating acetate binding mode in **2a** was rigorously identified by a single-crystal X-ray diffraction study (Figure 1 (right)).[20] The P−Pd−P bond angle has nar-

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[16] **1a**: ^{31}P{^{1}H} NMR ($CDCl_3$) δ 32.7; ^{1}H NMR ($CDCl_3$) δ 1.12−1.22 (m, 12H), 1.24−1.33 (qt, *J* = 12.9 Hz; *J* = 3.15 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{^{1}H} NMR ($CDCl_3$) δ 3.3, 23.4, 26.3, 27.9 (virtual t, $^2J_{CP} + {}^4J_{CP}$ = 5.4 Hz), 29.9, 33.7 (virtual t, $^1J_{CP} + {}^3J_{CP}$ = 9.45 Hz), 124.5 (br), 127.2, 136.4 (d, $^1J_{CF}$ = 242.2 Hz), 138.4 (d, $^1J_{CF}$ = 244.0 Hz), 148.4 (d, $^1J_{CF}$ = 242.9 Hz), 175.5. Anal. Calcd for $C_{64}H_{72}NO_2P_2BF_{20}Pd\cdot Et_2O$: C, 53.71; H, 5.44; N, 0.92. Found: C, 53.85; H, 5.18; N, 0.93. **1b**: ^{31}P{^{1}H} NMR ($CDCl_3$) δ 44.5; ^{1}H NMR ($CDCl_3$) δ 1.37 (m, 36H), 1.92 (s, 3H), 2.22 (m, 6H), 2.34 (s, 3H); ^{13}C{^{1}H} 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, $^1J_{CF}$ = 247.9 Hz), 138.8 (d, $^1J_{CF}$ = 243.0 Hz), 148.7 (d, $^1J_{CF}$ = 239.8 Hz), 176.0. 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.

[17] Cambridge Crystallographic Database version 5.25, November 2003.

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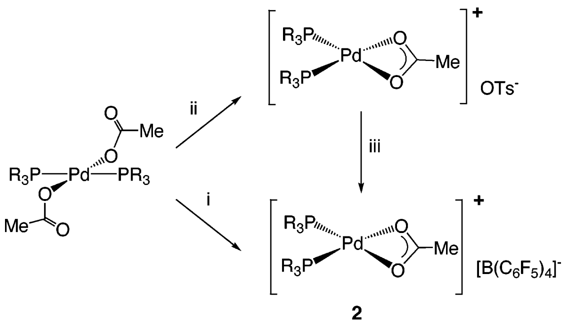
Scheme 1[a]



[a] Legend: (i) $[Me_2(H)NPh][B(C_6F_5)_4]$, CH_2Cl_2; (ii) $HOTs{\cdot}H_2O$, CH_2Cl_2; (iii) $[Li(OEt_2)_{2.5}][B(C_6F_5)_4]$, CH_2Cl_2.

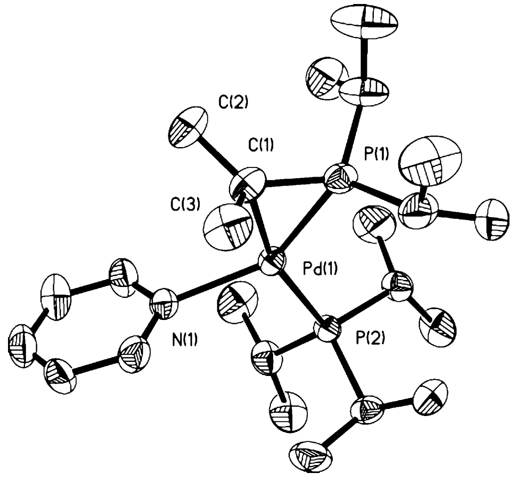


Figure 2. X-ray structural diagram of **3b**. Anion and hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg) for **3b**: Pd1–N1, 2.168(4); Pd1–C1, 2.171(5); Pd1–P1, 2.206(1); Pd1–P2, 2.376(1); P1–C1, 1.748(6); P1–C4, 1.846(6); P1–C7, 1.848(7); N1–Pd1–C1, 95.5(2); N1–Pd1–P1, 142.4(1); C1–Pd1–P1, 47.1(2); N1–Pd1–P2, 99.9(1); C1–Pd1–P2, 164.2(2); P1–Pd1–P2, 117.66(5); P1–C1–Pd1, 67.5(2); C1–P1–Pd1, 65.4(2).

rowed to 107.14(4)° from the 177.46(6)° seen in **1a**. Notably, the Pd–P bond distances increase by 0.11 Å on going from **2a** to **1a**, while the palladium–oxygen distances in **2a** are nearly identical with one another and are about 0.13 Å longer than the palladium–oxygen distance found in **1a**. Structurally characterized mononuclear palladium complexes possessing chelating carboxylates are rare,[21] but comparisons to our cationic derivative can be drawn to the recently reported neutral $[(IPr)Pd(OAc)(\kappa^2O,O'\text{-}OAc)]$ (IPr = *N,N'*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) complex, which contains both chelated and nonchelated acetate moieties.[22] For this complex palladium–oxygen distances of 2.005(4) Å for the nonchelated acetate and 2.034(4) and 2.163(4) Å for the chelated acetate group are realized.

In general, samples of pure $[(R_3P)_2Pd(\kappa^2O,O'\text{-}OAc)][B(C_6F_5)_4]$ (R = Cy; **2a**; R = ^{i}Pr; **2b**) were difficult to isolate in high yields using $[Me_2(H)NPh][B(C_6F_5)_4]$; therefore, a better carboxylate abstraction process was developed. Reaction of *trans*-$[(R_3P)_2Pd(OAc)_2]$ with *p*-toluenesulfonic acid ($HOTs{\cdot}H_2O$) was found to cleanly generate $[(R_3P)_2Pd(\kappa^2O,O'\text{-}OAc)]OTs$, having ^{31}P NMR signals nearly identical with those of **2** (not isolated; ^{31}P NMR δ 59 (R = Cy) and δ 70 (R = ^{i}Pr) ppm), which upon anion exchange leads to **2a** and **2b**.[19,23] The formation of **2** can be contrasted to the reaction of *trans*-$[(py)_2Pd(OAc)_2]$ and $[Li(OEt_2)_{2.5}][B(C_6F_5)_4]$ (1:1) in CH_2Cl_2, which leads to a dynamic mixture of *trans*-$[(py)_2Pd(OAc)_2]$, $[(py)_3Pd(OAc)]^+$, and $[(py)_4Pd]^{2+}$, from which the coordination polymer $[(py)_4Pd][(py)_2Pd(OAc)_2][B(C_6F_5)_4]_2$ can be crystallized and structurally characterized.[24]

While complexes **1** and **2** differ in composition by a molecule of acetonitrile, addition of acetonitrile to **2** does not lead to any detectable amounts of **1**. The ^{31}P NMR spectrum of **2b** in acetonitrile-d_3 after 23 h revealed two broad peaks (δ 52.1 and 43.6 ppm). Oddly, removal of acetonitrile-d_3 from the reaction product followed by dissolution of the resulting material in chloroform-*d* and analysis by ^{31}P NMR spectroscopy revealed the presence of a mixture of **2b** (ca. 70%) and a new species (**3a**). Stirring the acetontrile-d_3 solution of **2b** in the presence of excess sodium carbonate resulted in clean formation of a new species having more resolved NMR signals (δ 51.7 (d), 43.2 (d), $^2J_{PP}$ = 30 Hz). Complete purification of the complex, unfortunately, was hindered by its waxy nature, and thus other bases were examined. The ^{31}P NMR spectrum of a 1:2 mixture of **2b** and pyridine in dichloromethane revealed rapid and selective formation of a closely related complex showing similar NMR signals (δ 49.1 (d), 37.2 (d), $^2J_{PP}$ = 29 Hz). Reducing the amount of pyridine to 1:1, however, resulted in only 50% conversion of **2b** to the new complex. Under the former conditions the crystalline three-membered palladacycle **3b** (Scheme 2) was isolated in high yields.[25] Addition of pyridine to **3a** yields **3b** quantitatively. The identity of **3b** was established by single-crystal X-ray diffraction analysis, and the results are shown in Figure 2. The Pd–C and Pd–P bond distances of 2.1751(5) and

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[19] **2a**: $^{31}P\{^1H\}$ 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, $^1J_{CF}$ = 247.8 Hz), 138.1 (d, $^1J_{CF}$ = 241.8 Hz), 148.2 (d, $^1J_{CF}$ = 239.2 Hz), 194.9. 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. **2b**: $^{31}P\{^1H\}$ 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, $^1J_{CF}$ = 241.0 Hz), 138.8 (d, $^1J_{CF}$ = 243.0 Hz), 148.8 (d, $^1J_{CF}$ = 237.3 Hz), 196.1. Anal. Calcd for $C_{44}H_{45}O_2P_2PdBF_{20}$: C, 45.36; H, 3.89. Found: C, 45.37; H, 3.88.

[20] Details for the crystal structures are given in the Supporting Information in CIF format.

[21] Such structures have been suggested for supported catalysts: (a) Churruca, F.; SanMartin, R.; Tellitu, I.; Dominguez, E. *Tetrahedron Lett.* **2003**, *44*, 5925–5929. (b) Colacot, T. J.; Gore, E. S.; Kuber, A. *Organometallics* **2002**, *21*, 3301–3304.

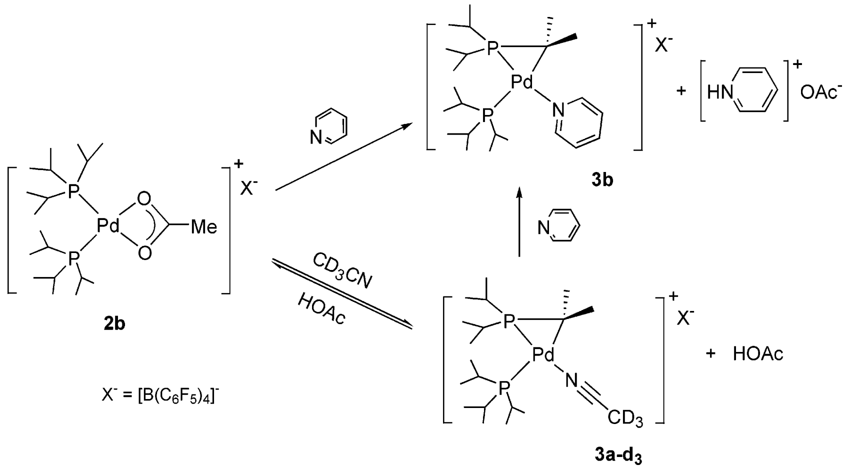
[22] Viciu, M. S.; Stevens, E. D.; Petersen, J. L.; Nolan, S. P. *Organometallics* **2004**, *23*, 3752–3755.

[23] In contrast, reactions of *p*-toluenesulfonic acid (2 equiv) with $[(Ar_3P)_2Pd(OAc)_2]$ have been reported to yield the neutral complex $[(Ar_3P)_2Pd(OTs)_2]$. See: Seayad, A.; Jayasree, S.; Damodaran, K.; Toniolo, L.; Chaudhari, R. V. *J. Organomet. Chem.* **2000**, *601*, 100–107.

[24] Ma, L.; Smith, R. C.; Protasiewicz, J. D. *Inorg. Chim. Acta*, in press.

[25] **3b**: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 49.1 (d, nonmetalated 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, $^3J_{HH}$ = 6.30 Hz, 2H, C_5H_5N), 7.87 (t, $^3J_{HH}$ = 7.20 Hz, 1H, C_5H_5N), 8.51 (d, $^3J_{HH}$ = 4.20 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.

Scheme 2



2.206(1) Å are comparable to values found in other three-membered palladacycles.[26,27]

Having rigorously identified **3b**, the nature of **3a** can be assigned as an analogous palladacyclic complex by spectroscopic comparisons to **3b**. The cis disposition of phosphines in these compounds is consistent with the small $^2J_{PP}$ coupling constants (29 and 30 Hz, respectively). While cyclopalladation reactions of palladium phosphine complexes are well-known,[28] it is interesting to note the mild and selective metalation for a mixture of acetonitrile and **2b**, in comparison to the case for compound **1a**, containing the these same two components.

The formation of **3** involves elimination of acetate as acetic acid and a β-hydrogen elimination from one of the Me_2CH groups of $^iPr_3P$ ligands. The process was found to be reversible, for addition of acetic acid to **3a**-d_3 generates **2b** quantitatively. Protonation of palladium metallacycles by acids has been discussed as the reversal of phosphine cyclometalation.[29] Also consistent with this concept, we have found that heating samples of **2b** in acetontrile-d_3 with CH_3COOD leads to the slow selective incorporation of deuterium at the isopropyl methine carbons and formation of $[((CH_3)_2CD)_3P)_2Pd(\kappa^2O,O'\text{-OAc})][B(C_6F_5)_4]$ (^1H NMR). Preliminary studies of the reaction of **1** with bases such as pyridine are found to yield the products of substitution of acetonitrile (i.e., *trans*-$[(R_3P)_2Pd(OAc)(L)][B(C_6F_5)_4]$), *not* the products of metalation. This work thus provides additional evidence of the inherent complexities associated with deceptively simple phosphine adducts of palladium acetate. Further efforts to delineate the generality of these reactions involving other phosphines and carboxylate ligands are underway.

Acknowledgment. We acknowledge Promerus LLC for support.

Supporting Information Available: Text giving full experimental details for all compounds and X-ray crystallographic files in CIF format for **1a**, **2a**, and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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