

Syntheses and Characterization of Palladium Complexes with a Hemilabile “PCO” Pincer Ligand

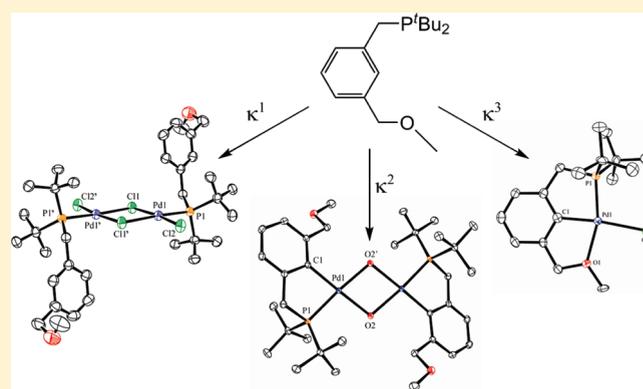
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S Supporting Information

ABSTRACT: The synthesis of a new pincer ligand (^tBuPCO = 2-(CH₂P^tBu₂)-6-(CH₂OCH₃)C₆H₃) is reported. This ligand has been observed to coordinate in three different modes to palladium. The ^tBuPCO ligand coordinates in a monodentate fashion through the phosphine moiety in the dimeric [(^tBuPCO)Pd(Cl)(μ-Cl)]₂. Bidentate coordination is observed through the phosphine and the aryl ring in the binuclear [(^tBuPCO)Pd(μ-OH)]₂. The traditional tridentate coordination mode of a pincer is observed in the monomeric complex (^tBuPCO)PdCl, wherein the ether oxygen provides the third point of attachment. Each of these novel palladium(II) complexes was characterized by NMR spectroscopy, elemental analyses, and single-crystal X-ray crystallography. A variety of other palladium(II) complexes of ^tBuPCO have also been prepared and characterized, including the hydroxide complex (^tBuPCO)PdOH. The reactivity of the hydroxide complex with CO₂, CO, and H₂ is reported.



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INTRODUCTION

The seminal work of Moulton and Shaw's first monoanionic tridentate pincer ligands opened the door to an extremely useful class of organometallic complexes.¹ Due to the ability to readily tune the electronics and sterics of these ligands, as well as the robust nature of pincer metal complexes, this family of compounds has been extensively studied and used in numerous late transition metal-catalyzed reactions.^{2,3} The traditional coordination mode of a monoanionic pincer ligand is tridentate, and the high stability of many pincer metal species under a variety of reaction conditions is typically attributed to this strong and rigid tridentate coordination. While the first monoanionic pincer ligands were largely symmetric with a central anionic donor atom flanked by two identical neutral donor atom arms (e.g., so-called PCP- or NCN-type ligands), recently new, unsymmetric pincer complexes wherein the neutral donor arms are different from one another or in which the anionic donor species is located on one of the arms rather than the central position of the pincer have been prepared.⁴ The unique electronic, steric, and coordination environments provided by these unsymmetric pincer ligands have enabled new modes of reactivity.^{4a,5} The inclusion of a donor moiety on one arm of the pincer that does not bind tightly to the metal provides potential access to an open site in the coordination sphere. This hemilabile attribute of the ligand allows for the ligand to coordinate in a tridentate configuration in some situations and in a bidentate configuration in others.

The new monoanionic pincer complex 2-(CH₂P^tBu₂)-6-(CH₂OCH₃)C₆H₃ (^tBuPCO, Figure 1, complex 1) has been synthesized and used to prepare a variety of palladium(II) complexes. Similar to the chemistry reported for a PCO analogue (1,3,5-tris-(CH₃)-2-(CH₂P^tBu₂)-6-(CH₂OCH₃)C₆H₃, Figure 1, complex 2) by Milstein and co-workers,^{5f} the hemilability of the ether arm as compared to the phosphine was expected to allow the unsymmetrical ligand to function as both a bidentate “PC” chelate and a tridentate “PCO” system. Indeed, the palladium complexes prepared with the new ^tBuPCO ligand show a range of coordination from monodentate to bidentate and tridentate ligation. The reactivities of (^tBuPCO)Pd-type complexes are described herein and compared to that of the symmetric PCP analogue.

RESULTS AND DISCUSSION

Synthesis of ^tBuPCO Complexes. The ^tBuPCO ligand was synthesized according to a literature preparation for a similar compound from α,α' -dibromo-*m*-xylene by successive nucleophilic displacements with sodium methoxide and di-*tert*-butylphosphine (Scheme 1).^{5f}

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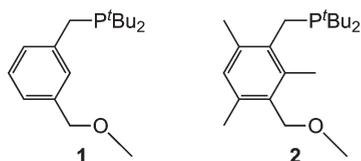
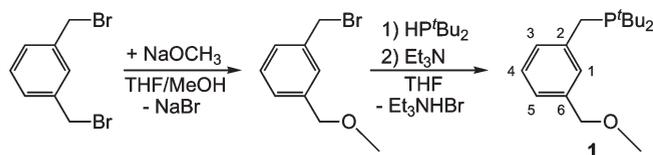
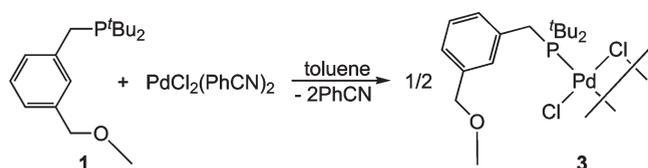


Figure 1. ^tBu₂PCO ligand, 2-(CH₂P^tBu₂)-6-(CH₂OCH₃)C₆H₃ (**1**), and Milstein's PCO ligand, 1,3,5-tris-(CH₃)-2-(CH₂P^tBu₂)-6-(CH₂O-CH₃)C₆H₃ (**2**).^{5f}

Scheme 1



Scheme 2



Reaction of the ^tBu₂PCO ligand with bis(benzonitrile)palladium(II) chloride resulted in the formation of a new phosphorus-containing compound with a single ³¹P{¹H} NMR resonance at 70.5 ppm. Additionally, the presence of four aromatic protons as established by integration of the ¹H NMR signals argues against coordination of the aryl ring to the palladium center through the *ipso*-carbon. This product was isolated by crystallization from a toluene–pentane solution and analyzed by X-ray crystallography. The orange-colored product of this reaction was determined to be the dimeric species [(^tBu₂PCO)Pd(Cl)(μ-Cl)]₂ (**3**), as illustrated in Scheme 2. An ORTEP of **3** is shown in Figure 2. Of note is that the potentially multidentate ligand is coordinated only in a monodentate fashion. κ^1 -Coordination to palladium through the phosphine arm is observed, and the other three sites of the typical square-planar local geometry about palladium are occupied by two bridging and one terminal chloride. For a list of selected bond distances and angles for **3**, see Table 1.

When a toluene solution of **3** was heated to 100 °C for an hour, the solution color changed from orange to bright yellow. Analysis by ³¹P{¹H} NMR spectroscopy revealed complete conversion of complex **3** (signal at 70.5 ppm) to a new complex, **4**, with a resonance at 106.1 ppm. However, when the solution was allowed to cool to room temperature, the signal at 106.1 ppm was observed to decrease over the course of 12 h as the 70.5 ppm signal for **3** returned to its former intensity. Complex **4** was observed by ¹H NMR spectroscopy to contain only three aromatic proton resonances, suggesting that C–H bond activation and coordination of the aryl ring to the metal center had occurred. Furthermore, a downfield shift for the –OCH₃ protons (from 3.21 to 3.53 ppm) was observed, suggesting coordination of the ether group to the palladium. On the basis of the NMR data, it was suspected that the reaction depicted in Scheme 3 was occurring.

The equilibrium between **3** and **4** shown in Scheme 3 implies that if a base were to be added to consume the HCl produced in

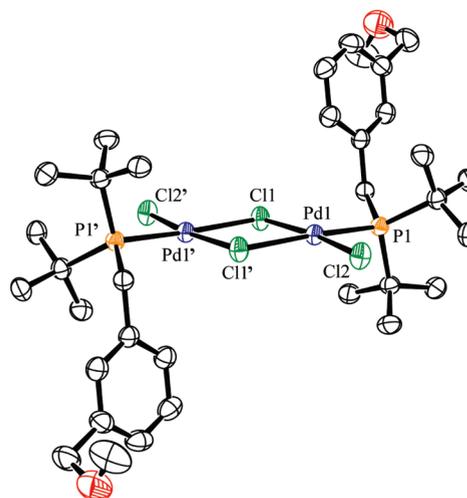
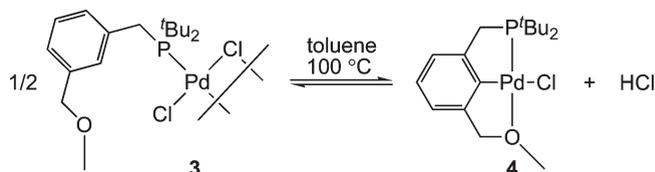


Figure 2. ORTEP of complex [(^tBu₂PCO)Pd(Cl)(μ-Cl)]₂ (**3**). Ellipsoids are shown at 50% probability, and hydrogen atoms and a toluene solvent molecule are omitted for clarity.

Table 1. Selected Bond Lengths and Angles for Complex **3**

bond	length (Å)	bond	angle (deg)
Pd1–P1	2.2765(7)	P1–Pd1–Cl1	94.27(2)
Pd1–Cl1	2.3192(7)	P1–Pd1–Cl2	94.95(2)
Pd1–Cl2	2.2849(7)	Cl1–Pd1–Cl2	170.62(2)
Pd1–Cl1'	2.4442(6)	P1–Pd1–Cl1'	175.24(3)
Pd1···Pd1'	3.567(9)	Cl1–Pd1–Cl1'	83.04(3)

Scheme 3



the conversion of **3** to **4**, the reaction could be driven to the right. Indeed, heating a toluene solution of **3** in the presence of potassium carbonate allowed for the isolation of the yellow-colored **4**, which was characterized by NMR spectroscopy, elemental analysis, and X-ray diffraction. An ORTEP of the monomeric, tridentate pincer complex (^tBu₂PCO)PdCl (**4**) is shown in Figure 3. Selected bond lengths and angles of **4** are given in Table 2. Additionally, the reaction shown in Scheme 3 can also be pushed to the left. The addition of HCl to a benzene-*d*₆ (C₆D₆) solution of **4** results in the formation of **3**.

In an attempt to remove the chloride from complex **4**, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]boron (NaB(Ar^F)₄) was added to solutions of **4** in both the noncoordinating solvent C₆D₆ and the more-coordinating solvent tetrahydrofuran-*d*₈ (THF-*d*₈). In both cases, however, only the palladium product [(^tBu₂PCO)Pd]₂(μ-Cl)[B(Ar^F)₄] (**5**), a binuclear species with a bridging chloride group, was observed to form (Scheme 4). After filtering the excess NaB(Ar^F)₄ from the solution, integration of the ¹H NMR spectrum revealed one equivalent of B(Ar^F)₄ resonances for every two equivalents of ligand backbone resonances.

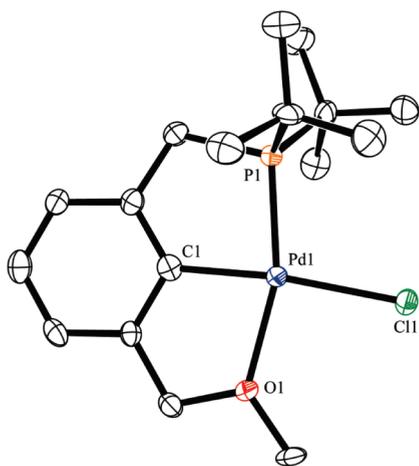
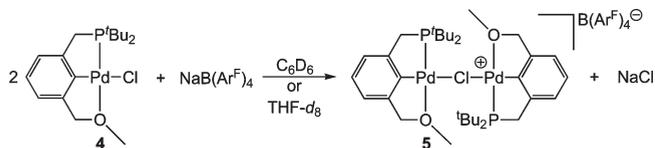


Figure 3. ORTEP of complex $(^t\text{BuPCO})\text{PdCl}$ (**4**). Ellipsoids are shown at 50% probability, and hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths and Angles for Complex 4

bond	length (Å)	bond	angle (deg)
Pd1–P1	2.2055(12)	P1–Pd1–O1	162.08(8)
Pd1–Cl1	2.4047(11)	C1–Pd1–Cl1	172.85(14)
Pd1–C1	1.978(4)	C1–Pd1–O1	80.07(16)
Pd1–O1	2.146(3)	C1–Pd1–P1	82.86(14)

Scheme 4



It would appear that once a chloride anion is removed from one molecule of **4**, the resulting three-coordinate species scavenges a second molecule of **4** to form the Cl-bridged binuclear palladium species, **5**. Complex **5** is quite resistant to removal of a second chloride by $\text{NaB}(\text{Ar}^{\text{F}})_4$. Heating a C_6D_6 solution of **5** to 150°C with excess $\text{NaB}(\text{Ar}^{\text{F}})_4$ present did not result in abstraction of the chloride.

When KOH was added to a solution of **5** in $\text{THF}-d_8$, conversion to a new species was observed by NMR spectroscopy. The spectroscopic data were consistent with assignment of the product as the hydroxide-bridged binuclear palladium species $[(^t\text{BuPCO})\text{Pd}]_2(\mu\text{-OH})[\text{B}(\text{Ar}^{\text{F}})_4]$ (**6**). As with **5**, integration of the ^1H NMR spectrum for complex **6** revealed two equivalents of ligand backbone resonances and only one equivalent of $\text{B}(\text{Ar}^{\text{F}})_4$ resonances. However, the ^1H NMR spectrum of **6** also contained a resonance for one hydroxide proton (-1.97 ppm). Complex **6** was further characterized by X-ray diffraction, and the ORTEP is shown in Figure 4. Bond distances and angles of **6** are listed in Table 3. Further heating of solutions of **6**, even in the presence of excess KOH, produced no changes in either the ^1H or ^{31}P NMR spectra.

When silver trifluoromethanesulfonate (AgOTf) was used to abstract the chloride from **4**, a monomer product was observed. Starting with a THF solution of **4**, AgOTf was added, and the

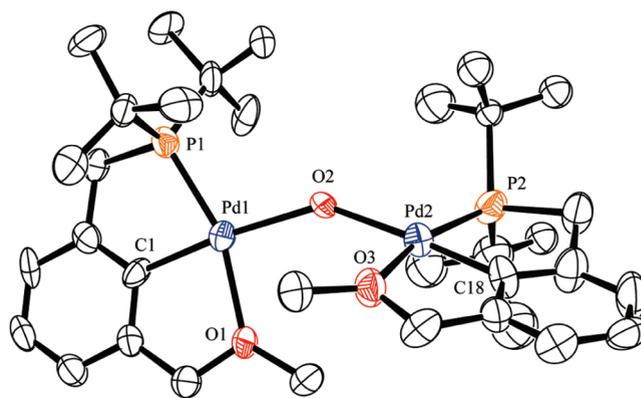
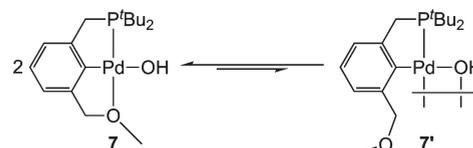


Figure 4. ORTEP of complex $[(^t\text{BuPCO})\text{Pd}]_2(\mu\text{-OH})[\text{B}(\text{Ar}^{\text{F}})_4]$ (**6**). Ellipsoids are shown at 50% probability, and the $[\text{B}(\text{Ar}^{\text{F}})_4]^-$ counterion, toluene solvent molecule, and hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths and Angles for Complex 6

bond	length (Å)	bond	angle (deg)
Pd1–P1	2.211(3)	P1–Pd1–O1	160.70(2)
Pd1–C1	1.948(11)	C1–Pd1–O2	173.30(4)
Pd1–O1	2.180(7)	C1–Pd1–O1	79.2(4)
Pd1–O2	2.149(7)	C1–Pd1–P1	81.6(3)
Pd2–O2	2.113(6)	Pd1–O2–Pd2	142.2(3)

Scheme 5



in situ formation of $(^t\text{BuPCO})\text{PdOTf}$ was observed by ^1H and ^{31}P NMR spectroscopies. Potassium hydroxide was then added to form a new hydroxide species, $(^t\text{BuPCO})\text{PdOH}$ (**7**), which exhibits a hydroxide resonance in the ^1H NMR spectrum at 1.00 ppm in C_6D_6 . Additionally, a small set of peaks, including a hydroxide resonance at -3.09 ppm, was also detected. This minor species ($<5\%$) was assigned as a $(^t\text{BuPCO})$ palladium(II) hydroxide dimer (**7'**) on the basis of the ^1H NMR data. Complex **7'** has a diagnostic upfield chemical shift for the $-\text{OCH}_3$ protons, suggesting the ether arm is not coordinated to the metal center (Scheme 5).

When a solution of **7** and **7'** was heated to 50°C , the two sets of resonances coalesced into single, broader sets of peaks, suggestive of a monomer–dimer equilibrium as shown in Scheme 5. From a benzene–pentane solution of **7** and **7'**, a single crystal was grown, and its structure was determined by X-ray diffraction. The ORTEP of the dimeric species **7'** is shown in Figure 5. Consistent with the NMR data, the structure of **7'** contains an “opened arm” bidentate coordination of the PCO ligand with two bridging hydroxides to form $[(^t\text{BuPCO})\text{Pd}(\mu\text{-OH})]_2$ (**7'**). Selected bond lengths and angles of complex **7'** are listed in Table 4.

While in the solid state the $(^t\text{BuPCO})$ palladium(II) hydroxide complex exists as a dimer, this configuration does not appear to

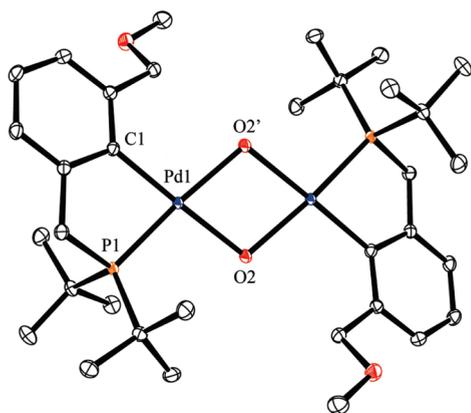


Figure 5. ORTEP of complex $[(^t\text{BuPCO})\text{Pd}(\mu\text{-OH})_2]$ (**7'**). Ellipsoids are shown at 50% probability, and hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Lengths and Angles for Complex **7'**

bond	length (Å)	bond	angle (deg)
Pd1–P1	2.2023(3)	C1–Pd1–O2	178.36(4)
Pd1–C1	2.0208(10)	P1–Pd1–O2'	172.56(2)
Pd1–O2	2.1101(8)	P1–Pd1–O2	99.06(2)
Pd1–O2'	2.1009(8)	Pd1–O2–Pd1'	102.01(3)

be maintained in solution. Strong evidence that it is primarily the monomer **7** that exists in solution at room temperature was obtained by determining the molecular weight (M) of the hydroxide complex. Using a Signer apparatus,⁶ the molecular weight for the (^tBuPCO)palladium(II) hydroxide complex in a benzene solution was found to be $M = 4.00 \times 10^2 \text{ g mol}^{-1}$, in good agreement with the expected monomeric $M_7 = 4.03 \times 10^2 \text{ g mol}^{-1}$ and not dimeric $M_{7'} = 8.06 \times 10^2 \text{ g mol}^{-1}$. The monomer form is also consistent with the downfield chemical shift of the ¹H NMR resonance for the $-\text{OCH}_3$ protons (3.34 ppm) of the major solution species, indicating a coordinated methoxy group. In contrast the $-\text{OCH}_3$ protons of the minor species appear farther upfield (3.24 ppm), as expected for a methoxy group that is not coordinated to the metal center, as would be the case for the dimeric structure **7'**.

Reactivity of (^tBuPCO)PdOH with H₂, CO₂, and CO. The reactivity of the palladium hydroxide complex **7** with a variety of small molecules was investigated. When benzene-*d*₆ solutions of **7** were degassed and placed under an atmosphere of carbon dioxide, signals for **7** were completely absent in the ¹H NMR spectrum. Quantitative conversion to two new palladium species, **8** and **9**, was observed. Notably, ¹³C{¹H} NMR spectrum in C₆D₆ contained new signals, which included free CO₂ at 124.8 ppm,⁷ and singlets at 164.2 and 173.7 ppm corresponding to complexes **8** and **9**, respectively. CO₂ insertion into palladium(II) hydroxides is precedented,⁸ and in the cases where η¹-bicarbonate complexes are formed,^{8a,b} a diagnostic ¹³C NMR resonance at δ 161–164 ppm ($-\text{OCOOH}$) is observed. Thus, the signal at 164.2 ppm would be consistent with a palladium(II) η¹-bicarbonate species. The resonances for both complexes were observed to be quite broad, suggesting that the species were in equilibrium. The ratio of the species (as determined by changes in the integrals of the ¹H NMR signals for each) changed with temperature, and at 25 °C complex **8** was present in greater

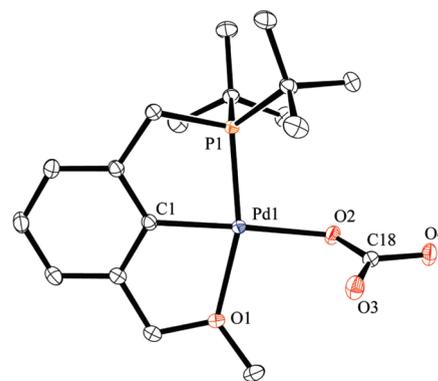


Figure 6. ORTEP of complex $(^t\text{BuPCO})\text{PdO}(\text{CO})\text{OH}$ (**8**). Ellipsoids are shown at 50% probability, and hydrogen atoms and benzene solvent molecule are omitted for clarity.

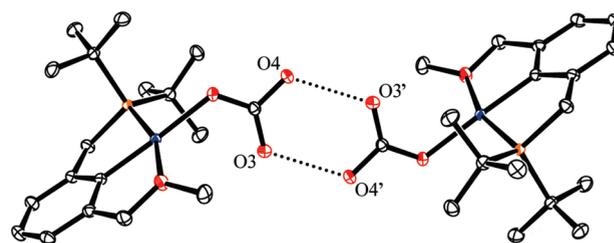


Figure 7. ORTEP exhibiting hydrogen bonding between molecules of **8**. Ellipsoids are shown at 50% probability, and hydrogen atoms and benzene solvent molecules are omitted for clarity.

Table 5. Selected Bond Lengths and Angles for Complex **8**

bond	length (Å)	bond	angle (deg)
Pd1–P1	2.2038(3)	P1–Pd1–O1	162.03(2)
Pd1–C1	1.9617(10)	C1–Pd1–O2	174.83(4)
Pd1–O1	2.1665(8)	C1–Pd1–O1	80.69(4)
Pd1–O2	2.1148(8)	C1–Pd1–P1	82.49(3)
O4···O3'	2.584(12)	O2–C18–O3	123.07(10)
O3···O4'	2.584(12)	O2–C18–O4	116.22(9)

concentration. Cooling the CO₂-concentrated solution enabled crystallization of the complex with the ¹³C signal at 164.2 ppm. X-ray crystallography verified the assignment of this complex as the η¹-bicarbonate species (^tBuPCO)PdO(CO)OH (**8**, Figure 6).

Like its ^tBuPCP analogue,^{8a} **8** displays intermolecular hydrogen bonding in the solid state between the bicarbonate $-\text{OH}$ and a neighboring bicarbonate $\text{C}=\text{O}$ (see oxygen atoms O4 and O3' in Figure 7), which bridges two independent units of **8** to form a dimer. The distances O4···O3' and O3···O4' of 2.584(12) Å are characterized as “moderate” hydrogen bonds according to the classification of Jeffrey.⁹ Additional bond lengths and angles for complex **8** are given in Table 5.

Higher temperatures favored the product with the ¹³C NMR singlet at 174 ppm, which was designated as complex **9**, and at 50 °C, all of complex **8** had been converted to **9**. Complex **9** was also isolated from the CO₂ reaction by removing the volatiles from the reaction mixture. After redissolving the resulting residue in fresh C₆D₆, the ¹H and ³¹P NMR resonances for **9** are observed to be much sharper, suggesting that when CO₂ is

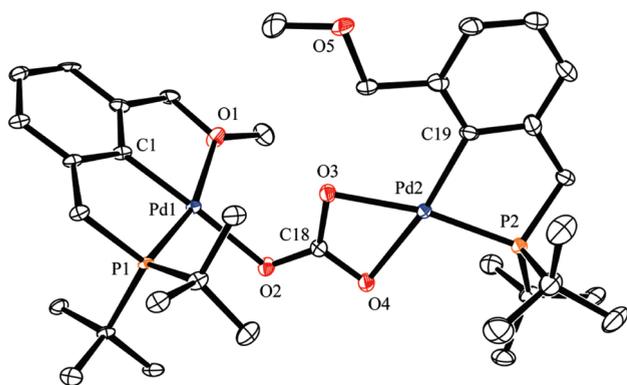


Figure 8. ORTEP of binuclear complex $[(^t\text{BuPCO})\text{Pd}]_2(\mu\text{-CO}_3)$ (**9**). Ellipsoids are shown at 50% probability, and non-bicarbonate hydrogen atoms and benzene solvent molecule are omitted for clarity.

Table 6. Selected Bond Lengths and Angles for Complex **9**

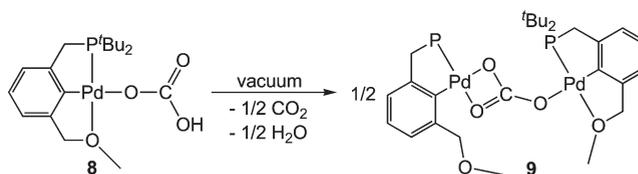
bond	length (Å)	bond	angle (deg)
Pd1–P1	2.1970(17)	P1–Pd1–O1	162.93(14)
Pd1–C1	1.966(6)	C1–Pd1–O2	175.2(2)
Pd1–O1	2.155(5)	C1–Pd1–O1	79.8(2)
Pd1–O2	2.127(5)	C1–Pd1–P1	83.23(19)
Pd2–C19	2.018(7)	Pd1–O2–C18	114.7(4)
Pd2–O3	2.135(5)	C19–Pd2–O3	109.5(2)
Pd2–O4	2.143(5)	C19–Pd2–O4	171.3(2)

absent, there is no equilibrium in solution between **8** and **9**. Crystals of the new species were obtained through the slow diffusion of pentane into a concentrated sample in benzene, and the solid-state structure was determined by X-ray diffraction as the μ -bridged binuclear palladium carbonate species $[(^t\text{BuPCO})\text{Pd}]_2(\mu\text{-CO}_3)$ (**9**). As illustrated in Figure 8, the CO_3 moiety in complex **9** is η^2 - and η^1 -bound to an “opened arm” and a “closed arm” $(^t\text{BuPCO})\text{Pd}$ unit, respectively. Only one other example of this type of binuclear palladium complex is reported,¹⁰ though similar examples for other late transition metals are known.¹¹ Additional bond distances and angles for complex **9** are listed in Table 6.

With knowledge of the structures of complexes **8** and **9**, the equilibrium between these two species in the presence of CO_2 can now be better understood. In particular, the exclusive formation of **9** upon removal of the volatiles from the product mixture containing **8** and **9** is consistent with the reaction shown in Scheme 6. Evaporation of the C_6D_6 solution would be accompanied by the removal of CO_2 and H_2O , which are required for the conversion of **9** to **8**.

Of note, only one set of NMR resonances was observed for the PCO ligand when analyzing solutions of **9**, which could suggest a rapid equilibrium between the binding of O3 to either Pd1 or Pd2 (see Figure 8). However, this change in the κ^1 or κ^2 binding of the CO_3 moiety between the two Pd centers would also have to be accompanied by the “opening” and “closing” of the respective $(^t\text{BuPCO})\text{Pd}$ ether arms. Another option is that the species in solution is an $\eta^1, \eta^1, \mu\text{-CO}_3$ binuclear palladium complex where both $(^t\text{BuPCO})\text{Pd}$ ligands are in the “closed arm” configuration.^{8c} Similar to how the hydroxide complex **7** is a dimer in the solid state with a κ^2 -PCO ligand and a monomer in solution with a κ^3 -PCO ligand, complex **9** could exist as the symmetric species

Scheme 6



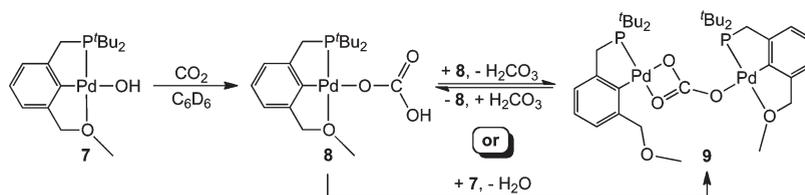
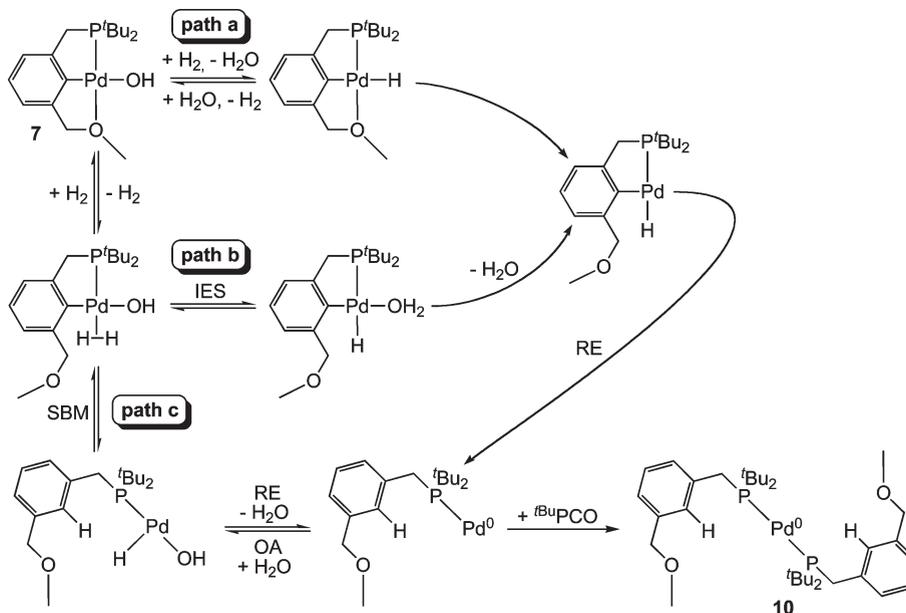
when dissolved, accounting for the single set of NMR signals observed. When variable-temperature NMR spectroscopy was attempted at -90°C in toluene- d_8 to further investigate potential fluxionality, line broadening was noted for the ether arm resonance, but only one set of signals corresponding to the protons in **9** was observed.

With complexes **8** and **9** characterized, the reaction of **7** with CO_2 can be depicted as shown in Scheme 7. Initially, as preceded for other late metal hydroxide complexes,⁸ carbon dioxide inserts into the hydroxide bond to form **8**. The formation of **9** can be achieved through the reaction of two units of **8**, where an equivalent of carbonic acid is released. The carbonic acid side-product can convert to carbon dioxide and water and can be eliminated if the mixture is subjected to vacuum to remove the volatiles. Alternatively, the binuclear carbonate complex **9** could also be formed via an acid–base reaction between **8** and unreacted hydroxo complex **7** with the release of water. Notably, when substoichiometric amounts of CO_2 were added to solutions of **7**, only the product **9** was observed by NMR spectroscopy, along with starting material.

Reactions of the related $(^t\text{BuPCP})\text{Pd}(\text{II})$ hydroxide complex with hydrogen gas leads to clean conversion to the corresponding palladium(II) hydride and water.¹² In contrast, reactions of **7** with H_2 resulted in some demetalation of the ligand and the formation of a black precipitate, presumably palladium(0). The reaction was monitored by NMR spectroscopy, but no hydride-containing products were detected. Instead, a new species was evident with virtual triplets resonating for the *tert*-butyl and phosphine methylene arm protons. These spectral data would be consistent with a product containing two $(^t\text{BuPCO})\text{Pd}$ ligands with *trans*-coordinated phosphines. A resonance in the ^1H NMR spectrum corresponding to a proton bound to the *ipso*-carbon of the benzene backbone was also observed. The new species was identified as $(^t\text{BuPCO})_2\text{Pd}^0$ (**10**), which was confirmed by the independent synthesis of the palladium(0) product. When bis-(dibenzylideneacetone)palladium(0) was added to two equivalents of $(^t\text{BuPCO})\text{Pd}$ ligand, the resulting product exhibited identical NMR resonances to the H_2 reaction product. Of note, in a similar palladium system reported by Hartwig and co-workers, the β -hydride elimination (BHE) of an alkylamine ligand results in the proposed formation of a palladium hydride species $(\text{PC})\text{Pd}-\text{H}$ ($\text{PC} = 2\text{-}(\text{CH}_2\text{P}^t\text{Bu}_2)\text{C}_6\text{H}_4$), which then decomposes presumably through reductive elimination (RE) to a product analogous to **10**.¹³

As illustrated in Scheme 8, several mechanisms for the formation of complex **10** can be considered. One mechanism (Scheme 8, path a) is the generation of a palladium hydride complex similar to the $(^t\text{BuPCP})\text{Pd}$ system,¹² followed by RE of the C–H bond of the ligand backbone. Notably, the hemilabile ether arm could dissociate, which would allow the hydride ligand to rearrange to a position *cis* to the Pd–C bond, facilitating the C–H reductive elimination. The $(^t\text{BuPCO})\text{Pd}^0$ could scavenge free $(^t\text{BuPCO})\text{Pd}^0$ ligand and form **10**. The presence of Pd(0) indicates that phosphine is released from some Pd centers. The other two

Scheme 7. Possible Reaction Pathways for the Production of 9

Scheme 8. Possible Mechanisms for the Reaction of 7 with H_2 , Formation of $(\text{t}^{\text{Bu}}\text{PCO})_2\text{Pd}^0$ (10)

mechanisms proceed via H_2 displacement of the ether arm and formation of a Pd(II) dihydrogen species.¹⁴ The hydrogen could then add across the Pd–O bond through a four-center internal electrophilic substitution (IES)¹⁵ pathway (Scheme 8, path b) to form a palladium(II) hydrido aquo complex or across the Pd–C bond through a four-center σ -bond metathesis (SBM)¹⁶ pathway (Scheme 8, path c) to form a three-coordinate palladium(II) hydrido hydroxo species. It is notable that the reaction of 7 with H_2 proceeds to completion in a matter of hours compared to the $\text{t}^{\text{Bu}}\text{PCP}$ system, which takes over three days. It is possible that the sterics of the ligand or even the electronics of the complex allow for a faster reaction with hydrogen. However, the decrease in reaction time may also be explained by the operation of mechanisms b or c, which involve the ability of the hemilabile ligand in complex 7 to open a coordination site and allow for efficient binding of the hydrogen.

To verify that the proton source for complex 10's *ipso*-carbon was indeed from H_2 , a separate experiment was performed in C_6H_6 using deuterium gas. Following the reaction of 7 and D_2 by ^2H NMR spectroscopy, it was discovered that a broad singlet first appeared at 1.09 ppm, corresponding to the palladium deuterio-oxide signal of $(\text{t}^{\text{Bu}}\text{PCO})\text{PdOD}$ (7- d_1). Later, the appearance of another ^2H signal was noted at 7.90 ppm, corresponding to a deuterium bound to the *ipso*-carbon of the ligand backbone for $(\text{t}^{\text{Bu}}\text{PCO}-d_1)_2\text{Pd}^0$ (10- d_2), confirming that H_2 (or D_2) is the

source of the C–H (or D). Additionally, when a C_6D_6 solution of 7 was treated with D_2 , HD gas was detected by ^1H NMR spectroscopy as a 1:1:1 triplet (4.43 ppm, $^1J_{\text{HD}} = 42.8$ Hz), as deuterium was observed to scramble into the PdO–H bond. The two products 7- d_1 and 10- d_2 and the starting material 7 were also detected by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy at 94.6, 59.5, and 94.5 ppm, respectively. The scrambling of deuterium into the PdO–H bond of 7 and the production of HD gas argue against path c, as the scrambling by this mechanism would require multiple successive steps to be reversible. The relevant scrambling would not occur until the last H–OH reductive elimination, which would also have to be reversible. Scrambling could occur via path a, if the C–H RE of the ligand backbone were the slow step of the reaction. Notably no palladium hydride complex was detected by NMR spectroscopy. Path b, wherein the scrambling occurs in a reversible IES step, would be the simplest explanation.

The reactivity of 7 with carbon monoxide was also investigated. Within minutes of CO exposure to 7, the colorless palladium(II) hydroxide solution changed to an intense orange color. Quantitative conversion of compound 7 to a thermally unstable species 11 was observed by NMR spectroscopy. It was not possible to definitively establish the identity of 11. The initial ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra contain resonances that would be consistent with a palladium(II) hydroxycarbonyl species

(^tBuPCO)PdCOOH, as preceded in the ^tBuPCP system,^{8a} and like the ^tBuPCP analogue, no proton resonance for the hydroxy group was observed. A less likely assignment for **11** would be an asymmetrically bridged binuclear compound, [(^tBuPCO)Pd]₂(μ-CO₂), analogous to the ^tBuPCP system,¹⁷ since only one ³¹P NMR resonance is seen. Distinct from the (^tBuPCP)PdCOOH chemistry, where CO₂ loss and palladium hydride formation occurred after heating the hydroxycarbonyl complex,^{8a} when **11** is heated or placed under vacuum, decomposition to **10** is observed. A potential pathway for the formation of **10** involves carbon dioxide evolution from **11** to form a palladium(II) hydride species, (^tBuPCO)PdH. Similar to the reactions shown in Scheme 8 for the later steps of the hydrogenolysis of **7**, reductive elimination of the C–H bond of the ligand backbone and association of additional ligand would result in **10**. Attempts to isolate and further characterize **11** were unsuccessful.

SUMMARY

In summary, we have prepared and characterized a new series of unsymmetric palladium pincer complexes. Among the various new compounds synthesized, examples of mono-, bi-, and tridentate coordination modes have been demonstrated for the ^tBuPCO ligand. Monodentate binding is observed through the phosphine in the dimeric [(^tBuPCO)Pd(Cl)(μ-Cl)]₂ complex **3**. The ^tBuPCO ligand can also function as a bidentate chelate through the phosphine and the aryl ring in the dimeric [(^tBuPCO)Pd(μ-OH)]₂ complex **7'**. Additionally, the traditional tridentate pincer coordination is observed in the monomeric (^tBuPCO)PdCl complex **4**, wherein the ether oxygen provides the third point of attachment. In some cases, equilibrium mixtures are observed that confirm the ether arm as a hemilabile donor. The (^tBuPCO)PdOH complex **7** was observed to react with CO₂ to form both the η¹-bicarbonate species (^tBuPCO)PdO(CO)OH, **8**, and the μ-bridged binuclear palladium carbonato complex [(^tBuPCO)Pd]₂(μ-CO₃), **9**. Hydrogenolysis reactions involving **7** resulted in the Pd(0) decomposition product (^tBuPCO)₂Pd⁰, **10**, presumably via the reductive elimination of the C–H bond of the ligand backbone, palladium(0) precipitation, and incorporation of released ^tBuPCO ligand.

It is notable that although the κ³-(^tBuPCO) palladium chloride and hydroxide complexes could be synthesized, isolated, and characterized, we were unable to prepare the corresponding hydride. It appears that C–H reductive elimination involving the central C position of the aryl ring of the ^tBuPCO ligand is rapid enough to prevent any observation of a Pd(II) hydride in this system. This facile C–H reductive elimination may be related to the hemilabile nature of the ether functionality, which can provide a low-energy pathway to a three-coordinate geometry and a *cis* configuration of the M–C and M–H bonds. Understanding reactivity trends for hemilabile ligands will aid in future design of new ligands for catalytic reactions.

EXPERIMENTAL SECTION

Unless specified otherwise, all manipulations were carried out under nitrogen using conventional vacuum line techniques and a glovebox equipped with a –35 °C freezer. Solvents were purified before use. THF, benzene, and pentane were purified by passage through columns of activated alumina and molecular sieves. C₆D₆, toluene-*d*₈, and THF-*d*₈ were dried over sodium metal–benzophenone. All other reagents were used as obtained from commercial suppliers, unless otherwise noted. ¹H

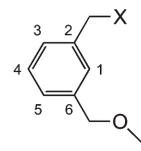


Figure 9. Aromatic carbon-numbering scheme for ligand (X = P^tBu₂) and its precursor (X = Br).

NMR, ²H NMR, ¹³C NMR, ³¹P NMR, 1D nuclear Overhauser effect (NOE) difference, and ¹H–¹³C gradient-selected heteronuclear multiple-quantum coherence (gsHMQC) NMR spectra were recorded at room temperature using a Bruker Avance 500 MHz spectrometer, and all were referenced to the residual solvent signal (reported in ppm), with the exception of ³¹P NMR spectra, which were referenced to an external standard of 85% H₃PO₄ set to 0 ppm. All ¹³C NMR and ³¹P NMR data were collected proton-decoupled (¹³C{¹H} and ³¹P{¹H}). Multiplicity is reported as s, singlet; d, doublet; t, triplet; vt, virtual triplet; q, quartet; br, broad. Electrospray ionization (ESI) mass spectrometry was performed using a Bruker Esquire liquid chromatograph–ion trap. Elemental analyses were carried out by Atlantic Microlab, Inc. of Norcross, GA. The complex bis(benzonitrile)palladium(II)chloride (PdCl₂(C₆H₅CN)₂) was prepared according to a published procedure.¹⁸

2-(CH₂Br)-6-(CH₂OCH₃)C₆H₃. α,α'-Dibromo-*m*-xylene (5.122 g, 19.6 mmol) and sodium methoxide (1.060 g, 19.6 mmol) were added to a round-bottom flask and dissolved in THF. The solution was cooled to 0 °C, whereupon methanol (1.00 mL, 24.7 mmol) was added. The reaction was stirred for 12 h, resulting in precipitation of a white solid. The volatiles were removed under reduced pressure, and the product was extracted with pentane and filtered through a Teflon filter. The volatiles were removed from the filtrate under vacuum, revealing a colorless oil, which was purified by column chromatography (SiO₂, CH₂Cl₂). Yield: 2.048 g (49.1%). ¹H NMR (C₆D₆, 500 MHz): 7.15 (s, 1H, H1), 7.07 (d, 1H, J_{HH} = 7.4 Hz, H5), 6.99 (t, 1H, J_{HH} = 7.5 Hz, H4), 6.96 (d, 1H, J_{HH} = 7.6 Hz, H3), 4.11 (s, 2H, CH₂O), 4.00 (s, 2H, CH₂Br), 3.08 (s, 3H, OCH₃). ¹³C{¹H} NMR (C₆D₆, 126 MHz): 139.7 (s, C4), 138.3 (s, C2), 128.8 (s, C6), 128.4 (s, C1), 128.3 (s, C3), 127.5 (s, C5), 74.1 (s, CH₂O), 57.8 (s, OCH₃), 33.4 (s, CH₂Br).

^tBuPCO = 2-(CH₂P^tBu₂)-6-(CH₂OCH₃)C₆H₃ (1). A round-bottom flask was charged with 2-(CH₂Br)-6-(CH₂OCH₃)C₆H₃ (1.262 g, 5.92 mmol) and methanol (20 mL). The solution was cooled to 0 °C, and di-*tert*-butylphosphine (0.866 g, 5.92 mmol) was added dropwise to the reaction. The reaction was allowed to warm to room temperature and stirred for 12 h. A slight excess of triethylamine (0.65 g, 6.4 mmol) was added to the colorless liquid. The reaction was stirred for an additional 12 h. The volatiles were removed under reduced pressure, revealing an oily, white solid residue. The product was extracted with pentane and filtered through a Teflon filter. The solvent was removed from the filtrate under vacuum, and the ^tBuPCO complex was isolated as a highly viscous, colorless oil. Yield: 1.253 g (75.9%). ¹H NMR (C₆D₆, 500 MHz): 7.53 (s, 1H, H1), 7.35 (d, 1H, J_{HH} = 7.3 Hz, H3), 7.17 (t, 1H, J_{HH} = 7.5 Hz, H4), 7.13 (d, 1H, J_{HH} = 7.5 Hz, H5), 4.28 (s, 2H, CH₂O), 3.15 (s, 3H, OCH₃), 2.75 (d, 2H, J_{HP} = 2.2 Hz, CH₂P), 1.06 (d, 18H, J_{HP} = 10.6 Hz, C(CH₃)₃). ¹³C{¹H} NMR (C₆D₆, 126 MHz): 142.2 (d, J_{CP} = 12.7 Hz, C2), 139.1 (s, C6), 128.5 (s, C5), 129.3 (d, J_{CP} = 8.8 Hz, C1), 129.2 (d, J_{CP} = 8.8 Hz, C3), 128.47 (s, C4), 125.0 (s, C5), 74.7 (s, CH₂O), 57.7 (s, OCH₃), 31.8 (d, J_{CP} = 24.2 Hz, C(CH₃)₃), 30.0 (d, J_{CP} = 13.6 Hz, C(CH₃)₃), 29.0 (d, J_{CP} = 25.5 Hz, CH₂P). ³¹P{¹H} NMR (C₆D₆, 203 MHz): 33.6.

[(^tBuPCO)Pd(Cl)(μ-Cl)]₂ (3). The ^tBuPCO ligand **1** (1.20 g, 4.3 mmol) and PdCl₂(C₆H₅CN)₂ (1.65 g, 4.3 mmol) were placed into a round-bottom flask, and toluene (30 mL) was added. The resulting solution was heated to 100 °C and stirred for 4 h, upon which the solution turned deep red in color. The reaction was allowed to cool to

room temperature over the course of 12 h. A large amount of an orange, powdery solid precipitated out of solution. The solid was isolated on a glass frit, rinsed with cold pentane, and dried on a high-vacuum line for 12 h. Yield: 1.53 g (77.7%). A small amount of the product (20 mg, 22 μmol) was redissolved in a minimum of toluene and layered with pentane, which resulted in the growth of red-orange crystals suitable for X-ray crystallography. ^1H NMR (C_6D_6 , 500 MHz): 8.28 (m, 2H, H4), 7.83 (s, 2H, H1), 7.07 (m, 4H, H3,5), 4.35 (br s, 4H, CH_2O), 3.25 (br s, 4H, CH_2P), 3.21 (br s, 6H, OCH_3), 1.28 (d, 36H, $^3J_{\text{HP}} = 14.6$ Hz, $\text{C}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 203 MHz): 70.5 (br s).

($^t\text{BuPCO}$)PdCl (4). Complex 3 (1.53 g, 1.67 mmol) and an excess of potassium carbonate (1.31 g, 9.48 mmol) were added to a round-bottom flask, and THF (30 mL) was added. The solution was heated at 100 $^\circ\text{C}$ and stirred for 12 h. The solution was filtered through a Teflon filter to reveal a bright, yellow-orange-colored solution. The volatiles were removed under reduced pressure, and the resulting yellow-orange solid was dissolved in a minimum of benzene. A pentane-vapor diffusion chamber was used to crystallize the desired product. The resulting yellow-colored crystals, which were suitable for X-ray crystallography, were isolated. Yield: 1.05 g (74.5%). ^1H NMR (C_6D_6 , 500 MHz): 6.98 (t, 1H, $^3J_{\text{HH}} = 7.5$ Hz, H4), 6.85 (d, 1H, $^3J_{\text{HH}} = 7.4$ Hz, H3), 6.52 (d, 1H, $^3J_{\text{HH}} = 7.5$ Hz, H5), 4.41 (s, 2H, CH_2O), 3.53 (s, 3H, OCH_3), 2.87 (d, 2H, $^2J_{\text{HP}} = 9.7$ Hz, CH_2P), 1.26 (d, 18H, $^3J_{\text{HP}} = 14.5$ Hz, $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 126 MHz): 158.0 (s, C1), 147.7 (d, $^2J_{\text{CP}} = 12.8$ Hz, C2), 145.2 (s, C6), 124.8 (s, C4), 122.1 (d, $^3J_{\text{CP}} = 22.0$ Hz, C3), 118.6 (s, C5), 84.2 (s, CH_2O), 60.3 (s, OCH_3), 35.8 (d, $^1J_{\text{CP}} = 29.9$ Hz, CH_2P), 35.5 (d, $^1J_{\text{CP}} = 19.4$ Hz, $\text{C}(\text{CH}_3)_3$), 29.0 (d, $^2J_{\text{CP}} = 4.2$ Hz, $\text{C}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 203 MHz): 106.1. Anal. Calcd for $\text{C}_{17}\text{H}_{28}\text{OPClPd}$: C, 48.48; H, 6.70. Found: C, 48.49; H, 6.61.

Reaction of 4 with $\text{NaB}(\text{Ar}^F)_4$ Generating [$(^t\text{BuPCO})\text{Pd}$] $_2(\mu\text{-Cl})[\text{B}(\text{Ar}^F)_4]$ (5). Complex 4 (2.0 mg, 4.7 μmol) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]boron ($\text{NaB}(\text{Ar}^F)_4$, 4.2 mg, 4.7 μmol) were added to a medium-walled NMR tube fitted with a resealable Teflon valve. The solids were dissolved in C_6D_6 (0.40 mL), and the solution was shaken vigorously. After 5 min, the solution was filtered through a Teflon filter. The filtrate was examined by NMR spectroscopy, which revealed the formation of the binuclear species 5. ^1H NMR (C_6D_6 , 500 MHz): 8.40 (s, 8H, $\text{Ar}^F\text{-H}_{2,6}$), 7.66 (s, 4H, $\text{Ar}^F\text{-H}_4$), 6.90 (t, 2H, $^3J_{\text{HH}} = 7.5$ Hz, H4), 6.73 (d, 2H, $^3J_{\text{HH}} = 7.5$ Hz, H3), 6.41 (d, 2H, $^3J_{\text{HH}} = 7.5$ Hz, H5), 4.32 (s, 4H, CH_2O), 3.42 (s, 6H, OCH_3), 2.74 (d, 4H, $^2J_{\text{HP}} = 9.9$ Hz, CH_2P), 1.04 (d, 36H, $^3J_{\text{HP}} = 14.8$ Hz, $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 126 MHz): 162.8 (q, $^1J_{\text{CB}} = 49.9$ Hz, $\text{Ar}^F\text{-C1}$), 152.2 (s, C1), 147.3 (d, $J_{\text{CP}} = 11.8$ Hz, C2), 143.9 (s, C6), 135.5 (s, $\text{Ar}^F\text{-C}_{2,6}$), 129.9 (q, $^3J_{\text{CF}} = 28.7$ Hz, $\text{Ar}^F\text{-C}_{3,5}$), 126.4 (s, C4), 125.3 (q, $^1J_{\text{CF}} = 27.5$ Hz, $\text{Ar}^F\text{-CF}_3$), 123.3 (d, $^3J_{\text{CP}} = 23.0$ Hz, C3), 119.4 (s, $\text{Ar}^F\text{-C}_4$), 118.1 (s, C5), 83.9 (s, CH_2O), 61.5 (s, OCH_3), 35.8 (d, $^1J_{\text{CP}} = 19.0$ Hz, $\text{C}(\text{CH}_3)_3$), 34.2 (d, $^1J_{\text{CP}} = 31.6$ Hz, CH_2P), 28.5 (d, $^2J_{\text{CP}} = 3.8$ Hz, $\text{C}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 203 MHz): 106.1. ESI-MS (methanol solution): M^+ found 807.3, calcd for $\text{C}_{34}\text{H}_{56}\text{O}_2\text{P}_2\text{ClPd}_2$ 807.1 (no solvent molecules or $\text{B}(\text{Ar}^F)_4$ are present).

Reaction of 5 with KOH Generating [$(^t\text{BuPCO})\text{Pd}$] $_2(\mu\text{-OH})[\text{B}(\text{Ar}^F)_4]$ (6). Complex 5 (12.5 mg, 7.5 μmol) and an excess of potassium hydroxide (3.5 mg, 62 μmol) were added to an NMR fitted with a resealable Teflon valve. C_6D_6 (0.40 mL) was added to the tube, and the vessel was placed in a sonic bath for 5 h. The solution was filtered through a Teflon filter, and the filtrate was examined by NMR spectroscopy, which revealed the formation of the dimeric hydroxide species 6. The solution was concentrated and layered with pentane, resulting in the formation of X-ray quality crystals as colorless plates. ^1H NMR (C_6D_6 , 500 MHz): 8.41 (s, 8H, $\text{Ar}^F\text{-H}_{2,6}$), 7.68 (s, 4H, $\text{Ar}^F\text{-H}_4$), 6.91 (t, 2H, $^3J = 7.4$ Hz, H4), 6.75 (d, 2H, $^3J = 7.4$ Hz, H3), 6.44 (d, 2H, $^3J = 7.4$ Hz, H5), 4.36 (s, 4H, CH_2O), 3.53 (s, 6H, OCH_3), 2.74 (d, 4H, $^2J = 9.8$ Hz, CH_2P), 0.98 (d, 36H, $^3J = 14.6$ Hz, $\text{C}(\text{CH}_3)_3$), -1.97 (s, 1H, OH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 126 MHz): 162.8 (q, $^1J_{\text{CB}} = 49.9$ Hz, $\text{Ar}^F\text{-C1}$),

150.8 (s, C1), 147.3 (d, $J_{\text{CP}} = 12.2$ Hz, C2), 144.0 (s, C6), 135.5 (s, $\text{Ar}^F\text{-C}_{2,6}$), 129.9 (q, $^3J_{\text{CF}} = 28.7$ Hz, $\text{Ar}^F\text{-C}_{3,5}$), 125.8 (s, C4), 125.3 (q, $^1J_{\text{CF}} = 27.5$ Hz, $\text{Ar}^F\text{-CF}_3$), 123.0 (d, $^3J_{\text{CP}} = 22.4$ Hz, C3), 119.1 (s, $\text{Ar}^F\text{-C}_4$), 118.1 (s, C5), 83.8 (s, CH_2O), 61.6 (s, OCH_3), 35.3 (d, $^1J_{\text{CP}} = 19.0$ Hz, $\text{C}(\text{CH}_3)_3$), 34.5 (d, $^1J_{\text{CP}} = 32.0$ Hz, CH_2P), 28.5 (d, $^2J_{\text{CP}} = 4.1$ Hz, $\text{C}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 203 MHz): 103.2.

Preparation of ($^t\text{BuPCO}$)PdOH (7). The Pd(II) triflate complex ($^t\text{BuPCO}$)PdOTf was formed in situ from the reaction of 4 and silver trifluoromethanesulfonate (AgOTf). Into a round-bottom flask were placed 4 (727.0 mg, 1.73 mmol) and AgOTf (450.0 mg, 1.75 mmol) followed by benzene (25 mL). The yellow solution became cloudy white in color. The flask was covered in aluminum foil, and the reaction was stirred in the dark for 12 h. The solution was filtered through a Teflon filter to reveal a champagne-colored solution. A portion of the solid product (2.2 mg) was added to an NMR tube and dissolved in C_6D_6 . The generation of the palladium triflate complex was confirmed by ^1H and ^{31}P NMR spectroscopies. ^1H NMR (C_6D_6 , 500 MHz): 6.87 (t, 1H, $^3J_{\text{HH}} = 7.5$ Hz, H4), 6.66 (d, 1H, $^3J_{\text{HH}} = 7.5$ Hz, H3), 6.32 (d, 1H, $^3J_{\text{HH}} = 7.5$ Hz, H5), 4.11 (s, 2H, CH_2O), 3.53 (s, 3H, OCH_3), 2.59 (d, 2H, $^2J_{\text{HP}} = 9.9$ Hz, CH_2P), 1.10 (d, 18H, $^3J_{\text{HP}} = 14.9$ Hz, $\text{C}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 203 MHz): 103.4. To the benzene solution of the palladium triflate complex ($^t\text{BuPCO}$)PdOTf (1.73 mmol) was added two equivalents of KOH (194.0 mg, 3.46 mmol). The reaction was stirred at ambient temperature for 12 h, upon which the solution was filtered through a Teflon filter. The faintly yellow-colored filtrate was stripped of its volatiles, resulting in the formation of a white solid. Yield: 520.4 mg (74.7%). X-ray quality crystals were obtained from a benzene solution as colorless plates by pentane-vapor diffusion. Data for monomer ("closed arm" 7): ^1H NMR (C_6D_6 , 500 MHz): 7.22 (d, 1H, $^3J_{\text{HH}} = 7.2$ Hz, H5), 7.05 (t, 1H, $^3J_{\text{HH}} = 7.2$ Hz, H4), 6.96 (d, 1H, $^3J_{\text{HH}} = 7.2$ Hz, H3), 5.06 (s, 2H, OCH_2), 3.34 (s, 3H, OCH_3), 2.91 (d, 2H, $^2J_{\text{HP}} = 9.9$ Hz, CH_2P), 1.13 (d, 18H, $^3J_{\text{HP}} = 13.3$ Hz, $\text{C}(\text{CH}_3)_3$), 1.00 (br s, 1H, OH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 126 MHz): 153.2 (s, C1), 149.4 (d, $^2J_{\text{CP}} = 16.5$ Hz, C2), 144.8 (s, C6), 128.7 (s, C5), 123.8 (s, C4), 122.8 (d, $^3J_{\text{CP}} = 19.3$ Hz, C3), 77.8 (s, OCH_2), 56.9 (s, OCH_3), 35.1 (d, $^1J_{\text{CP}} = 26.4$ Hz, CH_2P), 34.4 (d, $^1J_{\text{CP}} = 17.3$ Hz, $\text{C}(\text{CH}_3)_3$), 29.3 (s, $\text{C}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 203 MHz): 94.5. Anal. Calcd for $\text{C}_{34}\text{H}_{58}\text{O}_4\text{P}_2\text{Pd}_2$: C, 50.69; H, 7.25. Found: C, 50.62; H, 7.17. [$(^t\text{BuPCO})\text{Pd}(\mu\text{-OH})$] $_2$ (7'). Data for dimer ("opened arm"): ^1H NMR (C_6D_6 , 500 MHz): 5.20 (br s, 2H, OCH_2), 3.24 (br s, 3H, OCH_3), 2.91 (buried under 5, 2H, CH_2P), 1.13 (buried under 5, 18H, $\text{C}(\text{CH}_3)_3$), -3.09 (br s, 1H, OH). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 203 MHz): 93.4.

Molecular Weight Determination of 7 Using a Signer Apparatus. Applying Raoult's law, the molecular weight of 7 can be calculated from the following formula (eq 1):

$$M_x = \frac{G_x M_{\text{std}} V_{\text{std}}}{G_{\text{std}} V_x} \quad (1)$$

The variables M_{std} , V_{std} , and G_{std} are the molecular weight, volume of solution, and mass of a ferrocene standard, respectively, and M_x , V_x , and G_x are the corresponding values for complex 7. Using a Signer apparatus, one bulb was filled with a benzene solution of freshly sublimed ferrocene ($M_{\text{std}} = 1.86 \times 10^2$ g mol $^{-1}$, $V_{\text{std}} = 1.04$ mL, $G_{\text{std}} = 1.76$ mg). The other bulb was charged with crystals of complex 7, which were dissolved in benzene ($V_x = 0.86$ mL, $G_x = 5.20$ mg). The solutions were degassed with three freeze-pump-thaw cycles, and the apparatus was placed in a dark, draft-free cabinet for two weeks under isothermal conditions. Volumes were recorded every 1–3 days until they became constant, whereupon the molecular weight was calculated to be 4.00×10^2 g mol $^{-1}$ ($V_{\text{std}} = 1.10$ mL, $V_x = 0.80$ mL), which is consistent with the monomeric palladium(II) hydroxide structure ($M_7 = 4.03 \times 10^2$ g mol $^{-1}$).

Reaction of 7 with CO_2 Generating ($^t\text{BuPCO}$)PdO(CO)OH (8) and [$(^t\text{BuPCO})\text{Pd}$] $_2(\mu\text{-CO}_3)$ (9). An NMR tube fitted with a resealable Teflon valve was charged with complex 7 (12.2 mg, 30.3 μmol) and

dissolved in C_6D_6 (0.40 mL). The solution was degassed and then placed under an atmosphere of carbon dioxide. The quantitative conversion of **7** to **8** and **9** was observed within minutes by 1H NMR spectroscopy. X-ray quality crystals of **8** were obtained as colorless prisms by vacuum transferring hexane over the mixture and then filling the tube with CO_2 (1 atm). Elemental analysis of **8** was impractical since **9** cocrystallized with **8**. By NMR spectroscopy, both sets of resonances for **8** and **9** were broad; however, when the sample was cooled to $10^\circ C$, the peaks for **8** grew in intensity and sharpened. (^{tBu}PCO)PdO(CO)OH (**8**). 1H NMR (C_6D_6 , 500 MHz): 6.97 (t, 1H, $^3J_{HH} = 7.3$ Hz, H4), 6.80 (d, 1H, $^3J_{HH} = 7.3$ Hz, H3), 6.44 (d, 1H, $^3J = 7.3$ Hz, H5), 4.28 (s, 2H, CH_2O), 3.43 (s, 3H, OCH_3), 2.73 (d, 2H, $^2J_{HP} = 9.5$ Hz, CH_2P), 1.18 (d, 18H, $^3J_{HP} = 14.5$ Hz, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6 , 126 MHz): 164.2 (s, $OCOOH$), 152.9 (s, C1), 148.4 (d, $^2J_{CP} = 13.4$ Hz, C2), 145.6 (s, C6), 124.7 (s, C4), 122.2 (d, $^3J_{CP} = 22.1$ Hz, C3), 118.6 (s, C5), 83.2 (s, CH_2O), 61.7 (s, OCH_3), 35.4 (d, $^1J_{CP} = 19.1$ Hz, $C(CH_3)_3$), 34.3 (d, $^1J_{CP} = 30.7$ Hz, CH_2P), 28.7 (d, $^2J_{CP} = 3.8$ Hz, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6 , 203 MHz): 100.5.

[(^{tBu}PCO)Pd] $_{2}(\mu-CO_3)$ (**9**). A C_6D_6 solution of **8** and **9**, obtained through the reaction of **7** (14.0 mg, 34.8 μ mol) and CO_2 (1 atm), was stripped of its volatiles using a vacuum line. The resulting residue was redissolved in C_6D_6 and analyzed by NMR spectroscopy, confirming the exclusive, quantitative formation of **9**. The solution was layered with pentane and kept under vacuum. Over the course of two days, X-ray quality crystals formed as colorless prisms. Yield: 13.2 mg (91.4%). 1H NMR (C_6D_6 , 500 MHz): 7.07 (d, 2H, $^3J_{HH} = 3.6$ Hz, H3,5), 6.89 (t, 1H, $^3J_{HH} = 4.4$ Hz, H4), 4.94 (s, 2H, CH_2O), 3.56 (s, 3H, OCH_3), 2.82 (d, 2H, $^2J_{HP} = 9.7$ Hz, CH_2P), 1.21 (d, 18H, $^3J_{HP} = 14.1$ Hz, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6 , 126 MHz): 173.7 (s, CO_3), 151.2 (d, $^3J_{CP} = 2.8$ Hz, C1), 148.8 (d, $^2J_{CP} = 14.6$ Hz, C2), 146.7 (d, $^4J_{CP} = 2.0$ Hz, C6), 124.7 (s, C4), 122.3 (d, $^3J_{CP} = 21.1$ Hz, C3), 121.5 (s, C5), 79.5 (s, CH_2O), 59.9 (s, OCH_3), 35.2 (d, $^1J_{CP} = 18.8$ Hz, $C(CH_3)_3$), 33.8 (d, $^1J_{CP} = 29.5$ Hz, CH_2P), 29.0 (d, $^2J_{CP} = 4.3$ Hz, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6 , 203 MHz): 102.4. Anal. Calcd for $C_{35}H_{56}O_5P_2Pd_2$: C, 50.55; H, 6.79. Found: C, 50.59; H, 6.83.

Reaction of 7 with H_2 Yielding (^{tBu}PCO) $_2$ Pd 0 (10**).** Complex **7** (5.1 mg, 13 μ mol) and C_6D_6 (0.40 mL) were added to an NMR tube fitted with a resealable Teflon valve. The solution was degassed and the tube was pressurized with hydrogen gas (7.0 atm). Over the course of an hour, the reaction mixture changed from colorless to a dark brown-colored solution with a black precipitate. Resonances for the *tert*-butyl and phosphine methylene protons appeared as virtual triplets in the 1H NMR spectrum. This coupling pattern is indicative of *trans*-phosphine ligands coordinated to a metal center, consistent with the assignment of the complex as **10**. 1H NMR (C_6D_6 , 500 MHz): 8.34 (d, 2H, $^3J_{HH} = 7.1$ Hz, H3), 7.91 (s, 2H, H1), 7.22 (t, 2H, $^3J_{HH} = 7.3$ Hz, H4), 7.20 (d, 2H, $^3J_{HH} = 7.3$ Hz, H5), 4.33 (s, 4H, CH_2O), 3.17 (s, 6H, OCH_3), 2.97 (vt, 4H, $^2J_{HP} = 2.6$ Hz, CH_2P), 1.32 (vt, 36H, $^3J_{HP} = 6.1$ Hz, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6 , 203 MHz): 59.5.

(^{tBu}PCO) $_2$ Pd 0 (**10**). ^{tBu}PCO ligand **1** (21.5 mg, 77.2 μ mol) and bis(dibenzylideneacetone)palladium(0) (Pd(dba) $_2$, 22.2 mg, 38.6 μ mol) were added to an NMR tube fitted with a resealable Teflon valve, and the compounds were dissolved in C_6D_6 (0.40 mL). At room temperature, the tube was shaken until the solution color changed from deep purple to bright yellow. The volatiles were removed under reduced pressure, revealing a yellow-colored solid. The desired product was extracted with pentane, leaving behind the insoluble dba. 1H NMR (C_6D_6 , 500 MHz): 8.34 (d, 2H, $^3J_{HH} = 7.1$ Hz, H3), 7.91 (s, 2H, H1), 7.22 (t, 2H, $^3J_{HH} = 7.3$ Hz, H4), 7.20 (d, 2H, $^3J_{HH} = 7.3$ Hz, H5), 4.33 (s, 4H, CH_2O), 3.17 (s, 6H, OCH_3), 2.97 (vt, 4H, $^2J_{HP} = 2.6$ Hz, CH_2P), 1.32 (vt, 36H, $^3J_{HP} = 6.1$ Hz, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6 , 203 MHz): 59.5.

Reaction of 5 with D_2 Yielding ($^{tBu}PCO-d_1$) $_2$ Pd 0 (10-d₂**) and (^{tBu}PCO)PdOD (**7-d₁**).** Complex **7** (5.0 mg, 12 μ mol) was dissolved in C_6H_6 (0.40 mL) in an NMR tube fitted with a resealable Teflon valve.

The solution was degassed and then pressurized with deuterium gas (3.5 atm). Over the course of 3 h, the reaction was monitored by 2H and $^{31}P\{^1H\}$ NMR spectroscopies, confirming the formations of **10-d₂** and **7-d₁**. A separate experiment was run with **7** (4.2 mg, 10 μ mol) dissolved in C_6D_6 (0.40 mL), which was pressurized with D_2 (3.5 atm). The reaction was followed by 1H and $^{31}P\{^1H\}$ NMR spectroscopies, and the resonances for **10-d₂** (the H1 peak was absent) and **7-d₁** (the OH peak had greatly decreased in intensity) were detected, as well as HD gas (δ 4.43, 1:1:1 t, $^1J_{HD} = 42.8$ Hz). ($^{tBu}PCO-d_1$) $_2$ Pd 0 (**10-d₂**). 2H NMR (C_6H_6 , 76.7 MHz): 7.90 (s, D1). $^{31}P\{^1H\}$ NMR (C_6D_6 , 203 MHz): 59.5. (^{tBu}PCO)PdOD (**7-d₁**). 2H NMR (C_6H_6 , 76.7 MHz): 1.09 (s, OD). $^{31}P\{^1H\}$ NMR (C_6D_6 , 203 MHz): 94.6.

Reaction of 7 with CO. Formation of 11. A J. Young NMR tube was charged with **7** and C_6D_6 , and the subsequent colorless solution was degassed. Using a gas manifold, 1 atm of CO was added to the tube. Upon shaking the tube, within minutes the solution began to change in color to a bright orange. By NMR spectroscopy, the major species in solution was characterized as the CO insertion product **11**; however, upon heating the sample or placing the solution under vacuum, decomposition of **11** to **10** was observed. 1H NMR (C_6D_6 , 500 MHz): 6.97 (t, 1H, $^3J_{HH} = 7.5$ Hz, H4), 6.81 (d, 1H, $^3J_{HH} = 7.6$ Hz, H3), 6.50 (d, 1H, $^3J_{HH} = 7.5$ Hz, H5), 5.09 (s, 2H, CH_2O), 3.35 (s, 3H, OCH_3), 2.79 (d, 2H, $^2J_{HP} = 9.8$ Hz, CH_2P), 1.19 (d, 18H, $^3J_{HP} = 14.5$ Hz, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6 , 203 MHz): 101.2.

■ ASSOCIATED CONTENT

S Supporting Information. X-ray crystallographic data, including tables of bond lengths and angles, as well as files in CIF format for **3**, **4**, **6**, **7'**, **8**, and **9** and NMR spectra of non-isolated complexes are available free of charge via the Internet at <http://pubs.acs.org>.

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