

Articles

Synthesis and Reactivity of a Palladium(I)–Palladium(I)-Bonded μ -Hydroxo Complex Supported by a Bridging Butadiene Ligand

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The first Pd–Pd bonded hydroxo-bridged organopalladium dinuclear complex, $[\text{Pd}_2(\mu\text{-OH})(\text{THF})(\mu\text{-}\eta^2\text{:}\eta^2\text{-1,3-C}_4\text{H}_6)(\text{PPh}_3)_2][\text{PF}_6]$ (**1**·THF), was synthesized by a reaction of the sandwich-type complex $[\text{Pd}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-1,3-C}_4\text{H}_6)_2(\text{PPh}_3)_2][\text{PF}_6]_2$ with sodium hydroxide in tetrahydrofuran. Reactions of **1**·THF with *p*-toluidine, 3,5-dimethylpyrazole (Hdmpz), benzenethiol, isopropyl alcohol, and *p*-cresol afforded a series of heteroatom-bridged dinuclear complexes with the general formula $[\text{Pd}_2(\mu\text{-E})(\mu\text{-}\eta^2\text{:}\eta^2\text{-1,3-C}_4\text{H}_6)(\text{PPh}_3)_2][\text{PF}_6]$ (E = $\text{NHC}_6\text{H}_4\text{Me-}p$ (**2**), Hdmpz (**3**), SPh (**4**), $\text{OCH}(\text{CH}_3)_2$ (**5**), $\text{OC}_6\text{H}_4\text{Me-}p$ (**6**)). However, the μ -alkoxo complex **5** was unstable and rapidly decomposed via β -hydrogen elimination by releasing acetone. The complexes **1**·THF and **2** were structurally characterized by single-crystal X-ray diffraction analyses. X-ray crystallography of **1**·THF revealed that the complex molecule contained a tetrahydrofuran molecule that was associated with the bridging hydroxide through $\text{O}\cdots\text{H}-\text{O}$ hydrogen bonding. The complex **6** was reversibly converted to a hydroxo-bridged complex in the presence of excess water.

Introduction

Late-transition-metal hydroxo, alkoxo, and amido complexes have attracted recent interest for their diverse reactivity and relevance to catalytic reactions.¹ These species are thought to be involved in many catalytic processes.² There has been a common perception that the late-transition-metal–oxygen or –nitrogen bonds are unstable, due to a mismatch of the hard basic ligands with soft metal centers according to the HASB principle.³ However, a recent study suggests that such linkages are comparable to those of M–H or M–C bonds in terms of bond strength⁴ but reactive enough to demonstrate interesting reactivities that are usually absent in metal alkyls or hydrides.⁵

Until recently several hydroxo-bridged dinuclear organopalladium(II) complexes have been reported. These dinuclear structural types are $[\text{Pd}_2\text{R}_4(\mu\text{-OH})_2]^{2-}$ (R = C_6F_5 ,⁶ C_6Cl_5 ,⁷ $\text{C}_6\text{F}_3\text{H}_2\text{-2,4,6}^8$), $[\text{Pd}_2\text{R}_2\text{L}_2(\mu\text{-OH})_2]$ (L = PPh_3 ; R = Me,⁹ Ph,¹⁰ C_6F_5 , C_6Cl_5 ¹¹), and $[\text{Pd}_2(\text{L-L}^*)(\mu\text{-X})(\mu\text{-OH})]$ (L–L* = 2-(dimethylaminomethyl)phenyl, X = Br;¹² L–L* = 8-quinolylmethyl, X = carboxylate¹³), having the common $\text{Pd}^{\text{II}}(\mu\text{-OH})_2\text{Pd}^{\text{II}}$ dinuclear core without any Pd–Pd interaction. They can react with various amines, alcohols, nitriles, ketones, and other protic electrolytes and have been proven as excellent precursors for preparing related important heteroatom-bridged dinuclear derivatives.^{6,7,14–19} Some of these

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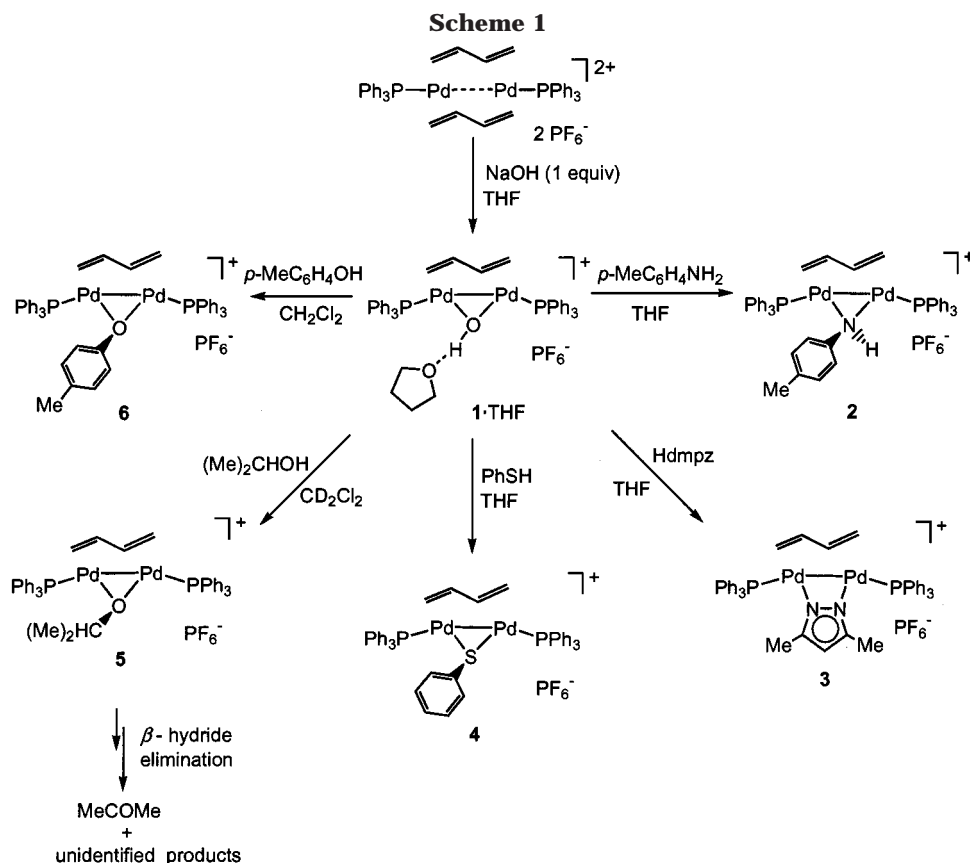
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hydroxo complexes and their derivatives are potential catalysts or intermediates in some organic transformations.^{10,20} To expand the scope of applications of the late-transition-metal hydroxo complexes, it is important to develop other new systems. In recent years metal-metal-bonded di- or polynuclear palladium and platinum complex systems have attracted a great deal of interest because they have the potential to promote homogeneous catalytic reactions due to the cooperative activation of the coordinated substrate molecule by multiple metal centers.²¹ Thus, the chemical behavior of the hydroxo group on a metal-metal bond of the late transition metals is of particular interest. As part of our recent interest in metal-metal-bonded di- and polynuclear organopalladium complexes,²² we report here the first example of a hydroxo-bridged organopalladium complex having a Pd(I)-Pd(I) bond and its reactions with various organic molecules containing N-H, O-H, and S-H bonds.

Results and Discussion

Synthesis and Characterization of the μ -Hydroxo Complex **1·THF.** Recently our group reported a sandwich-type bis(1,3-butadiene)dipalladium(I) complex, $[\text{Pd}_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-1,3-C}_4\text{H}_6)_2(\text{PPh}_3)_2][\text{PF}_6]_2$,²³ which we found as an excellent precursor for preparing a new type of metal-metal-bonded hydroxo-bridged organopalladium complex. Addition of 1 equiv of sodium hydroxide to $[\text{Pd}_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-1,3-C}_4\text{H}_6)_2(\text{PPh}_3)_2][\text{PF}_6]_2$ in tetrahydrofuran at room temperature led to facile release of one butadiene ligand and formation of the hydroxo-bridged complex **1·THF**, as outlined in Scheme 1.

Recrystallization from tetrahydrofuran and hexane gave **1·THF** as an orange crystalline solid in 80% yield. A ¹H NMR monitoring experiment revealed that no hydroxo addition to the μ -butadiene ligand occurred during this reaction. The isolated orange crystals were slowly converted to black within few days when they were stored at room temperature but were unchanged for several months in a refrigerator. The ¹H NMR spectrum of **1·THF** in CD₂Cl₂ showed a singlet at δ 3.92 for the OH proton, whose position was much less shielded than those in the corresponding Pd-Pd-nonbonded dinuclear hydroxo-bridged complexes (δ -1.0 to -3.0).⁶⁻¹² The proton resonances for 1,3-butadiene were observed at higher fields (δ 3.39, 3.15, and 2.57) than

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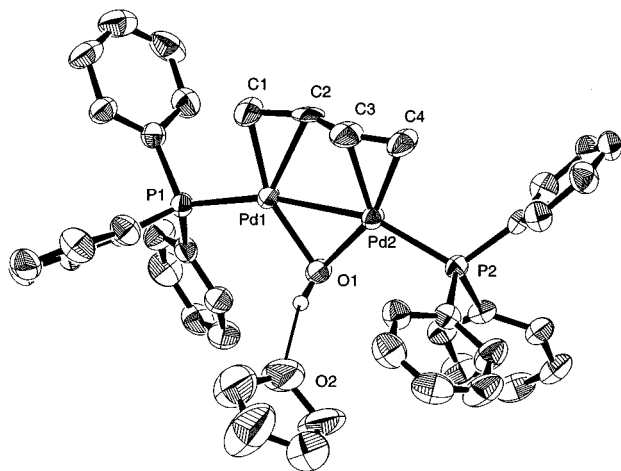


Figure 1. ORTEP view of **1**·THF with 50% probability ellipsoids. The counteranion and another set of disordered carbon atoms (C2 and C3) were omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for **1·THF**

Pd–Pd	2.5854(5)	Pd2–P2	2.282(1)
Pd1–P1	2.280(1)	Pd2–O1	2.077(3)
Pd1–O1	2.075(3)	Pd2–C3	2.20(3)
Pd1–C1	2.101(6)	Pd2–C4	2.112(6)
Pd1–C2	2.27(2)	O1···O2	2.661(7)
Pd1–Pd2–P2	159.62(4)	P2–Pd2–C4	92.5(2)
Pd2–Pd1–P1	161.97(4)	P2–Pd2–O1	108.21(10)
Pd1–O1–Pd2	77.0(1)	C1–C2–C3	141.0(7)
P1–Pd1–O1	110.70(10)	C2–C3–C4	138.0(7)
P1–Pd1–C1	91.7(2)		

those for the free diene (δ 7.0–5.0). The spectrum also confirmed the presence of one tetrahydrofuran molecule in the complex molecule. The ^{31}P signal was observed at δ 30.61 as a singlet. We also have prepared a tetrahydrofuran-free hydroxo complex by a heterogeneous reaction between the bis(1,3-butadiene) complex and solid sodium hydroxide in dichloromethane, but the yield was very low. The OH proton signal of the tetrahydrofuran-free complex was observed at the same position as that of the previous one (δ 3.93), indicating that in solution the tetrahydrofuran molecule in **1**·THF was not so strongly associated with the OH group. In the solid state, however, it was strongly associated with the OH group through hydrogen bonding, which was confirmed by a single-crystal X-ray analysis.

An ORTEP diagram of the complex cation of **1**·THF is provided in Figure 1, and selected bond distances (Å) and angles (deg) are listed in Table 1.

The X-ray crystallography revealed that the complex molecule contains a tetrahydrofuran molecule that is associated with the bridging hydroxo ligand through $\text{O}\cdots\text{H}-\text{O}$ hydrogen bonding ($\text{O1}\cdots\text{O2} = 2.661(7)$ Å). The two palladium ions are doubly bridged by a hydroxo group and a butadiene ligand, where the Pd–Pd distance is 2.5854(5) Å. The average Pd–O distance is 2.076(4) Å, which is very similar to those of other reported bridging $\text{Pd}^{\text{II}}-\text{OH}$ bonds.^{6,8,10} However, the Pd1–O1–Pd2 angle ($77.6(2)^\circ$) is significantly smaller compared to the corresponding angles of Pd–Pd-nonbonded dipalladium complexes (~ 90 – 100°).^{6,8,10} The two phosphine ligands are bent toward the hydroxyl group, $\text{P1}-\text{Pd1}-\text{Pd2} = 161.97(4)^\circ$ and $\text{P2}-\text{Pd2}-\text{Pd1} = 159.62(4)^\circ$, presumably as a consequence of steric repulsions

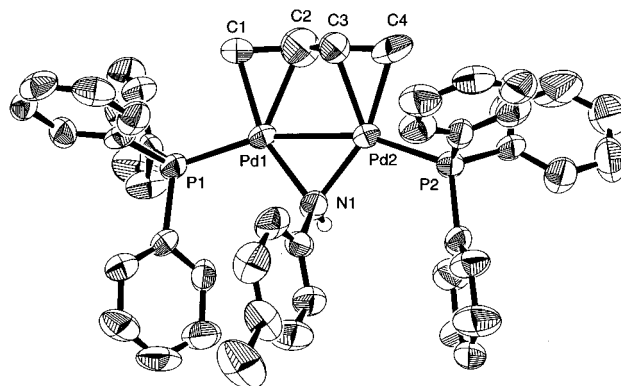


Figure 2. ORTEP view of **2** with 50% probability ellipsoids. The counteranion and another set of disordered carbon atoms (C2, C3) were omitted for clarity.

between phosphines and the coordinated butadiene. However, two palladium and two phosphorus atoms are virtually on the same plane. A detailed discussion on the structural parameters of the 1,3-butadiene ligand is limited, due to the disorder of its central two carbon atoms, C2 and C3, with an almost equal occupancy (51:49).⁹ However, the geometry is deduced to be $\eta^2:\eta^2$ -*s-trans* by the distance (3.8 Å) between the nondisordered terminal atoms C1 and C4. It should be noted here that structurally well-characterized hydrogen-bonded late-transition-metal hydroxo complexes are quite rare.²⁴ On the other hand, hydrogen-bonded alkoxo or aryloxo complexes are well documented.²⁵ It should be also mentioned that the proton of the hydroxo ligand was directly involved in the hydrogen bonding.

Reactivity of **1** with Various Organic Molecules.

When **1**·THF was stirred with 1 equiv of *p*-toluidine in tetrahydrofuran for 1 h, the air-stable amido-bridged complex $[\text{Pd}_2(\mu\text{-NHC}_6\text{H}_4\text{Me-}p)(\mu\text{-}\eta^2\text{-}\eta^2\text{-1,3-C}_4\text{H}_6)(\text{PPh}_3)_2][\text{PF}_6]$ (**2**) was formed in 84% isolated yield (Scheme 1). Several Pd–Pd-nonbonded bis(μ -hydroxo)palladium(II) complexes were also reported to react similarly with amines; however, in most cases an excess amount of amine was necessary for shifting the equilibrium toward palladium amides.¹⁰ The ^1H NMR spectrum of **2** in $\text{CD}_2\text{-Cl}_2$ showed that all protons of butadiene are nonequivalent, and the ^{31}P NMR spectrum showed two doublets at δ 25.30 and 25.34 ($J_{\text{PP}} = 55.4$ Hz), indicating the restricted inversion of the configuration at the amido nitrogen atom, since it has no symmetry element.

The molecular structure of **2** has been confirmed by a single-crystal X-ray diffraction analysis. An ORTEP diagram of the complex cation of **2** is shown in Figure 2, and selected bond distances and angles are listed in Table 2.

The structural features of **2** are almost similar to those of **1**·THF, but the μ -amido group is not involved in any hydrogen bonding. The average Pd–N distance is 2.105(1) Å, which is slightly longer than the average Pd–O distance in **1**. However, the Pd–Pd distance

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Table 2. Selected Bond Distances (Å) and Angles (deg) for **2**

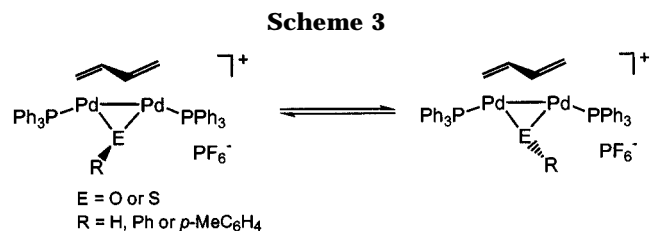
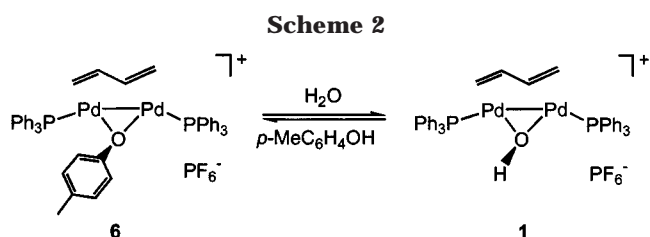
Pd–Pd	2.594(2)	Pd2–P2	2.273(4)
Pd1–P1	2.292(4)	Pd2–N1	2.12(1)
Pd1–N1	2.09(1)	Pd2–C3	2.25(5)
Pd1–C1	2.13(2)	Pd2–C4	2.17(2)
Pd1–C2	2.31(6)		
Pd1–Pd2–P2	161.4(1)	P2–Pd2–C4	89.4(6)
Pd2–Pd1–P1	161.8(1)	P2–Pd2–N1	110.4(3)
Pd1–N1–Pd2	76.0(4)	C1–C2–C3	119.0(6)
P1–Pd1–N1	109.4(4)	C2–C3–C4	126.0(7)
P1–Pd1–C1	91.9(5)		

(2.594(2) Å) and the Pd(1)–N(1)–Pd(2) angle (76.0(4)°) are almost similar to those of the hydroxo complex **1**·THF. The butadiene ligand is again disordered here with an unequal occupancy (59:41) and adopts the same geometry, $\eta^2:\eta^2$ -*s*-trans, as in **1**·THF.

The azolate-bridged complex $[\text{Pd}_2(\mu\text{-dmpz})(\mu\text{-}\eta^2:\eta^2\text{-1,3-C}_4\text{H}_6)(\text{PPh}_3)_2][\text{PF}_6]$ (**3**) has been obtained in a similar manner by reacting **1**·THF with 3,5-dimethylpyrazole (Hdmpz) in tetrahydrofuran (Scheme 1). The complex precipitated out as a deep orange powder from its tetrahydrofuran solution upon layering with diethyl ether. The analytical and spectroscopic data are consistent with the proposed structure. The ^1H NMR spectrum showed two singlets at δ 5.78 and 1.34 for H-4 and the methyl protons of coordinated dmpz, respectively. The ^{31}P resonance was observed at δ 27.42 as a singlet.

Similar treatment of **1**·THF with benzenethiol in tetrahydrofuran afforded the air-stable, thiolate-bridged complex $[\text{Pd}_2(\mu\text{-SPh})(\mu\text{-}\eta^2:\eta^2\text{-1,3-C}_4\text{H}_6)(\text{PPh}_3)_2][\text{PF}_6]$ (**4**) in 74% yield (Scheme 1).²⁶ The NMR spectra and the analytical data are consistent with the proposed structure. Three resonances in a ratio of 2:2:1 were observed for three magnetically different types of aryl protons of the coordinated thiolate group (one doublet at δ 6.39 for *o*-H, one triplet at δ 6.75 for *m*-H, and one triplet at δ 6.96 for *p*-H). The spectra showed three peaks for butadiene protons at δ 3.85, 3.36, and 3.00 and a singlet ^{31}P resonance at δ 30.51, suggesting that the inversion of the configuration at the sulfur atom was faster than the NMR time scale at room temperature.

The alkoxo-bridged complex $[\text{Pd}_2(\mu\text{-OCH}(\text{CH}_3)_2)(\mu\text{-}\eta^2:\eta^2\text{-1,3-C}_4\text{H}_6)(\text{PPh}_3)_2][\text{PF}_6]$ (**5**) could also be produced by the same metathesis technique. However, this was unstable and decomposed through β -hydrogen elimination. Therefore, an NMR tube reaction was performed for characterizations of this alkoxo complex and its decomposition products. Thus, solution of **1**·THF in $\text{CD}_2\text{-Cl}_2$ was treated with a 5-fold excess of isopropyl alcohol, and the reaction mixture was subjected to study for NMR measurements at different intervals. Immediately after the reaction, the yield of the corresponding alkoxo complex **5** was about 36%, as estimated by ^{31}P NMR spectroscopy (δ 29.60 (s)). Coordination of the isopropoxo group to the palladium atoms was confirmed from its NMR data. The ^1H NMR spectrum showed that two methyls of the isopropoxo group were magnetically inequivalent, due to the chiral geometry of the complex molecule; two diastereotopic methyl peaks appeared at δ 0.43 and 0.51 as doublets and a complex multiplet for



methyne (CH) proton at δ 1.40. NMR spectra recorded at different intervals revealed the gradual disappearance of those resonances for the isopropoxo group and simultaneous appearance of a new peak at δ 2.11, which can be assigned to free acetone, produced via β -hydrogen elimination. Unfortunately, we failed to characterize metal-containing products. Several ^{31}P resonances were observed after 2 days, indicating the presence of more than one decomposition product.

The hydroxo complex **1**·THF has also been reacted with excess *p*-cresol. The reaction of **1**·THF with 5 equiv of *p*-cresol gave the complex **6** in 82% isolated yield.²⁷ The formation of the cresolate-bridged complex became directly evident from its ^1H spectrum, in which the ortho and meta aryl protons of the cresolato ligand were observed at higher field (δ 6.05 and 6.27) compared to those of the free *p*-cresol (δ 7.03 and 6.72). The ^{31}P resonance was observed at δ 28.49 as a singlet. Interestingly, the complex **6** was reversibly converted to a hydroxo complex in the presence of excess water, which was confirmed by NMR experiments (Scheme 2). Successive addition of water increased the formation of the hydroxo complex and free cresol. For instance, 72% hydroxo complex was formed by addition of about 50 equiv of water to the cresolato complex **6** in CD_2Cl_2 containing a few drops of acetone-*d*₆ for better solubility.

VT NMR Experiments. As discussed above, the inversion of configuration at the nitrogen atom in the μ -amido complex **2** was slower than the NMR time scale at room temperature, which made all butadiene protons and two ^{31}P nuclei magnetically nonequivalent. On the other hand, **1**·THF, **4**, and **6** gave only three butadiene proton peaks and one ^{31}P signal, due to the fast inversion of the configuration (Scheme 3) compared to the NMR time scale at room temperature. Therefore, **1**·THF, **4**, and **6** were subjected to study for low-temperature NMR experiments in order to clarify whether the rate of their configurational changes at the heteroatom would be slowed or not with respect to the NMR time scale. The VT NMR studies of **1**·THF and **6** in CD_2Cl_2 revealed that their configurational changes remained faster than the NMR time scale even at -90

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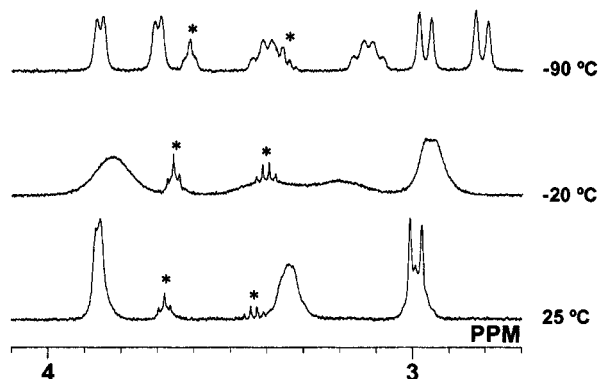


Figure 3. VT ^1H NMR spectra of complex **4** in the butadiene region (the asterisks denote solvent peaks).

$^{\circ}\text{C}$, the lowest available temperature. In contrast, the configurational change at the sulfur atom in **4** became slower than the NMR time scale at $-60\text{ }^{\circ}\text{C}$ and the spectrum showed six different proton signals with an equal intensity at the butadiene region depicted in Figure 3. Similarly, the singlet ^{31}P resonance also split into two AB systems (δ 30.31 and 30.84, $J_{\text{PP}} = 74.5\text{ Hz}$).

Conclusion

We have synthesized and characterized the first stable Pd–Pd-bonded hydroxo-bridged organopalladium complex and demonstrated its reactivity with several organic compounds having N–H, S–H, and O–H bonds. The study revealed that this novel hydroxide-bridged complex **1**·THF reacted with the organic molecules in a manner similar to that reported for Pd–Pd-nonbonded bis(μ -hydroxo) complexes. In the present metathesis reaction the Pd–Pd bond remains intact in the resultant complexes, which allowed us to prepare a new family of dinuclear complexes. This new system will be particularly useful in view of our present objectives to examine the behavior of various active bridging functional groups, including hydroxo, amido, and alkoxo, coordinated to metal–metal fragments.

Experimental Section

All reactions were carried out under a nitrogen atmosphere with standard Schlenk techniques. Solvents were dried and freshly distilled prior to use. Other chemicals were of reagent grade and used as received. The sandwich 1,3-butadiene complex $[\text{Pd}_2(\mu\text{-}\eta^2\text{-}1,3\text{-C}_4\text{H}_6)_2(\text{PPh}_3)_2][\text{PF}_6]_2$ was prepared by the method already reported by us.²³

NMR spectra were recorded on a JEOL GSX-270 spectrometer operating at 270 MHz for ^1H and 109.4 MHz for ^{31}P nuclei. ^{13}C and VT NMR studies were conducted on a JEOL JMT-C 400 MHz spectrometer. The elemental analyses were performed by the microanalytical service within our department.

Synthesis of $[\text{Pd}_2(\mu\text{-OH})(\text{THF})(\mu\text{-}\eta^2\text{-}1,3\text{-C}_4\text{H}_6)(\text{PPh}_3)_2][\text{PF}_6]$ (1**·THF).** To a stirred solution of $\text{Pd}_2(\mu\text{-}\eta^2\text{-}1,3\text{-C}_4\text{H}_6)_2(\text{PPh}_3)_2[\text{PF}_6]_2$ (400 mg, 0.352 mmol) in THF (60 mL) was added 0.1 M NaOH (aqueous; 3.5 mL, 0.350 mmol) by a syringe, and the mixture was allowed to stand for 1 h. After removal of all volatiles by a rotary evaporator, the residual solid was dissolved in THF (10 mL) and the solution filtered. Orange crystals of **1**·THF were obtained from the THF solution upon layering hexane, collecting by decantation, and drying under vacuum. Yield: 290 mg (80%). ^1H NMR (270 MHz, CD_2Cl_2): δ 7.59–7.48 (m, 30H, Ph), 3.92 (s, 1H, OH), 3.39 (br m, 2H, diene), 3.15 (br m, 2H, diene), 2.57 (br d, 2H, diene). ^{13}C NMR

Table 3. Crystallographic Data for **1**·THF and **2**

	1 ·THF	2
empirical formula	$\text{Pd}_2\text{C}_{46}\text{H}_{41}\text{OP}_3\text{F}_6$	$\text{Pd}_2\text{C}_{47}\text{H}_{44}\text{NP}_3\text{F}_6$
fw	1025.54	1042.58
cryst syst	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P1$ (No. 2)
$a/\text{\AA}$	10.0739(2)	12.802(2)
$b/\text{\AA}$	22.2119(7)	18.157(3)
$c/\text{\AA}$	19.5390(4)	10.550(2)
α/deg		93.197(6)
β/deg	91.875(1)	91.875(1)
γ/deg		99.219(6)
$V/\text{\AA}^3$	4369.7(2)	2219.5(7)
$D_{\text{calcd}}/(\text{g}/\text{cm}^3)$	1.565	1.560
$\mu(\text{Mo K}\alpha)/\text{cm}^{-1}$	9.93	9.78
T/K	–50	–50
Z	4	2
no. of rflns measd	39763	11147
no. of unique rflns	9893	9368
R	0.030	0.086
R_w	0.034	0.092

(CD_2Cl_2): δ 67.8 (s, CH_2 , diene), 91.6 (s, CH, diene), 129.2–133.9 (m, CH, Ar). ^{31}P NMR (109.4 MHz, external H_3PO_4 , CD_2Cl_2): δ 30.61 (s). Anal. Calcd for $\text{Pd}_2\text{C}_{44}\text{H}_{45}\text{O}_2\text{P}_3\text{F}_6$: C, 51.73; H, 4.05. Found: C, 51.33; H, 4.42.

Synthesis of $[\text{Pd}_2(\mu\text{-NHC}_6\text{H}_4\text{Me-}p)(\mu\text{-}\eta^2\text{-}1,3\text{-C}_4\text{H}_6)(\text{PPh}_3)_2][\text{PF}_6]$ (2**).** To a solution of **1**·THF (200 mg, 0.195 mmol) in THF (20 mL) was added *p*-toluidine (21 mg, 0.196 mmol), and the mixture was stirred at room temperature for 1 h. After removal of all volatiles by a rotary evaporator, the residual solid was dissolved in THF (10 mL) and the solution filtered. Orange-red crystals of **2** were obtained from the filtrate upon layering hexane, collecting by decantation, and drying under vacuum. Yield: 170 mg (84%). ^1H NMR (270 MHz, CD_2Cl_2): δ 7.50–7.20 (m, 30H, Ph), 6.48 (d, 2H, $J = 8.1\text{ Hz}$, *p*-tol), 5.81 (d, 2H, $J = 8.1\text{ Hz}$, *p*-tol), 3.65 (br d, 1H, diene), 3.48 (br d, 1H, diene), 3.34 (br m, 1H, diene), 3.28 (br m, 1H, diene), 2.69 (br d, 1H, diene), 2.51 (br d, 1H, diene), 2.07 (s, 3H, CH_3). ^{13}C NMR (CDCl_3): δ 20.8 (s, CH_3), 54.3, 56.6 (s, CH_2 , diene), 90.4, 92.2 (s, CH, diene), 121.7 (s, CH, *p*-tol), 128.9–133.4 (m, CH, Ar and *p*-tol), 152.1 (s, CH, *p*-tol). ^{31}P NMR (109.4 MHz, external H_3PO_4 , CD_2Cl_2): δ 25.30 and 25.34 (d, $J = 55.4\text{ Hz}$). Anal. Calcd for $\text{Pd}_2\text{C}_{47}\text{H}_{44}\text{NP}_3\text{F}_6$: C, 54.14; H, 4.28; N, 1.21. Found: C, 54.11; H, 4.36; N, 1.37.

Synthesis of $[\text{Pd}_2(\mu\text{-dmpz})(\mu\text{-}\eta^2\text{-}1,3\text{-C}_4\text{H}_6)(\text{PPh}_3)_2][\text{PF}_6]$ (3**).** Through the same procedure described for the synthesis of **2**, **3** was obtained as an orange-red solid from the reaction of **1**·THF (200 mg, 0.195 mmol) with 3,5-dimethylpyrazole (18.75 mg, 0.195 mmol) in THF (20 mL). Yield: 156 mg (78%). ^1H NMR (270 MHz, CD_2Cl_2): δ 7.56–7.28 (m, 30H, Ph), 5.78 (s, 1H, dmpz), 3.32 (br m, 2H, diene), 3.18 (br m, 2H, diene), 3.28 (br m, 1H, diene), 2.32 (br d, 2H, diene), 1.34 (s, 6H, Me). ^{13}C NMR (CD_2Cl_2): δ 13.1 (s, CH_3), 57.7 (s, CH_2 , diene), 92.4 (s, CH, diene), 109.2 (s, CH, dmpz), 129.0–134.0 (m, CH, Ar), 152.2 (s, CH, dmpz). ^{31}P NMR (109.4 MHz, external H_3PO_4 , CD_2Cl_2): δ 27.42 (s). Anal. Calcd for $\text{Pd}_2\text{C}_{45}\text{H}_{43}\text{N}_2\text{P}_3\text{F}_6$: C, 52.39; H, 4.20; N, 2.72. Found: C, 51.97; H, 4.43; N, 3.07.

Synthesis of $[\text{Pd}_2(\mu\text{-SPh})(\mu\text{-}\eta^2\text{-}1,3\text{-C}_4\text{H}_6)(\text{PPh}_3)_2][\text{PF}_6]$ (4**).** Following the same procedure described for the synthesis of **2**, **4** was obtained as a red solid from the reaction of **1**·THF (200 mg, 0.195 mmol) with benzenethiol (20 μL , 0.195 mmol) in THF (20 mL). Yield: 150 mg (74%). ^1H NMR (270 MHz, CD_2Cl_2 , 25 $^{\circ}\text{C}$): δ 7.46–7.33 (m, 30H, Ph), 6.96 (br t, 1H, SPh), 6.75 (br t, 2H, SPh), 6.39 (br d, 2H, SPh), 3.85 (br m, 2H, diene), 3.36 (br m, 2H, diene), 3.00 (br d, 2H, diene). ^{13}C NMR (CD_2Cl_2): δ 62.9 (s, CH_2 , diene), 93.2 (s, CH, diene), 128.9–133.5 (m, CH, Ar). ^{31}P NMR (109.4 MHz, external H_3PO_4 , CD_2Cl_2 , 25 $^{\circ}\text{C}$): δ 30.51 (s). Anal. Calcd for $\text{Pd}_2\text{C}_{46}\text{H}_{41}\text{SP}_3\text{F}_6$: C, 52.84; H, 3.95. Found: C, 52.81; H, 4.10.

NMR Tube Reactions of **1 with Isopropyl Alcohol To Form **5**.** To **1**·THF (7 mg, 6.8×10^{-3} mmol) in 0.6 mL of CD_2Cl_2

Cl₂ in an NMR tube was added isopropyl alcohol (2.6 μ L, 0.034 mmol), and NMR spectra were recorded at different intervals. Immediately after the reaction the conversion of **1**·THF into **5** was estimated to be 36%. **5**: ¹H NMR (270 MHz, CD₂Cl₂) δ 7.65–7.47 (m, 30H, Ph), 3.38 (br m, 2H, diene) 3.12 (br m, 2H, diene), 2.58 (br m, 2H, diene), 1.40 (m, 1H, CH), 0.52 (d, 3H, ²J_{HH} = 5.9 Hz, Me), 0.43(d, 3H, ²J_{HH} = 6.2 Hz, Me); ³¹P NMR (109.4 MHz, external H₃PO₄, CD₂Cl₂): δ 29.60 (s).

Synthesis of [Pd₂(μ -OC₆H₄Me-*p*)(μ - η^2 : η^2 -1,3-C₄H₆)(PPh₃)₂]-[PF₆] (6**).** To a solution of **1**·THF (300 mg, 0.29 mmol) in dichloromethane (20 mL) was added *p*-cresol (156 mg, 1.45 mmol), and the mixture was stirred at room temperature for 3 h. The volume of the reaction mixture was reduced to about 5 mL, and hexane was added to afford a red powder of **6**. Yield: 258 mg (82%). ¹H NMR (270 MHz, CD₂Cl₂): δ 7.59–7.33 (m, 30H, Ph), 6.27 (d, 2H, ²J_{HH} = 8.1 Hz, OC₆H₄Me), 6.05 (d, 2H, ²J_{HH} = 8.1 Hz, OC₆H₄Me), 3.39 (br m, 4H, diene), 2.68 (br d, 2H, diene), 1.99 (s, 3H, Me). ³¹P NMR (109 MHz, external H₃PO₄, CD₂Cl₂): δ 28.49 (s). Anal. Calcd for Pd₂C₄₇H₄₃·OP₃F₆·0.5CH₂Cl₂: C, 52.53; H, 4.08. Found: C, 52.26; H, 4.09.

X-ray Crystallographic Studies. The crystallographic data are summarized in Table 3. Crystals of **1**·THF were grown from a solution of the complex in tetrahydrofuran/hexane. Crystals of **2** were grown by slow evaporation of its methanol solution. All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochro-

ated Mo K α radiation at –50 °C. Indexing was performed from two oscillation images, which were exposed for 4.2 and 3.3 min for **1**·THF and **2**, respectively. Data for both crystals were processed by the PROCESS-AUTO program package and corrected for Lorentz and polarization effects. Symmetry-related absorption corrections were applied using the program ABSCOR. Both structures were solved by heavy-atom Patterson methods and expanded using Fourier techniques.

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1**·THF and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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