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Synthesis and reactivity of bimetallic palladium(II) methyl complexes with new functional phosphine ligands

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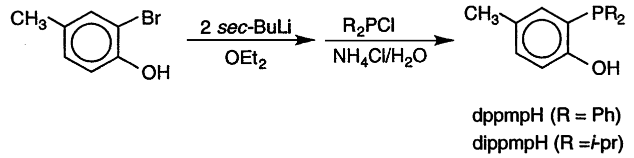
Bimetallic palladium(II) methyl complexes, $[Pd(dppmpH)(CH_3)(\mu\text{-}Cl)]_2$ (**1**) and $[Pd(dippmpH)(CH_3)(\mu\text{-}Cl)]_2$ (**2**) were synthesized by the reaction of $(COD)Pd(CH_3)(Cl)$ (COD = 1,5-cyclooctadiene) with the new functional phosphine ligands 2-diphenylphosphino-4-methylphenol (dppmpH) and 2-diisopropylphosphino-4-methylphenol (dippmpH). The homolytic cleavage of the CH_3–Pd bond was found to occur when complexes **1** and **2** were heated or photolyzed to form a methyl radical and the corresponding oxygen-bridged bimetallic palladium(II) complexes, $[Pd(dppmp)(Cl)]_2$ (**3**) and $[Pd(dippmp)(Cl)]_2$ (**4**), respectively. The molecular structures of complexes **1**, **3** and **4** were determined by single-crystal X-ray diffraction. Reaction of small molecules, such as CO, SO_2 and $CH_2{=}CH_2$, with complexes **1** and **2** was observed and characterized by IR, ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectroscopy.

Hybrid P/O ligands are of current interest from several different standpoints.[1] First, many exhibit hemilabile character with the ligating oxygen dissociating readily from the metal center. Second, the relatively "hard" oxygen atom and the "soft" phosphorus atom can exert a very different *trans* influence in compounds incorporating such hybrid ligands. Finally, because of the bridging ability of the oxygen atom, the use of P/O ligands often leads to the formation of dimeric species. Herein, we describe the chemistry of palladium(II) complexes incorporating two new P/O ligands.

Results and discussion

Synthesis of the monodentate phosphine ligands and palladium methyl complexes

An adaptation of the published procedure was used for the syntheses of the new monodentate phosphine ligands 2-diphenylphosphino-4-methylphenol (dppmpH) and 2-diisopropylphosphino-4-methylphenol (dippmpH) (Scheme 1).[2]



Scheme 1

They were analyzed by ^1H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy as described in the Experimental section. The ^{31}P NMR spectra of dppmpH and dippmpH exhibit a singlet at -25.6 and -22.9 ppm, respectively. The bimetallic palladium methyl complexes **1** and **2** were prepared by the reaction of $(COD)Pd(CH_3)(Cl)$ with the corresponding phosphine ligands. The complexes are stable in the solid state but undergo loss of the methyl group in solution.

Structural characterization of $[Pd(dppmpH)(CH_3)(\mu\text{-}Cl)]_2$ (1)

Due to their thermal and photochemical sensitivity, complexes **1** and **2** tend to decompose in solution by Pd–CH_3 bond cleavage to yield the oxygen-bridged dimetallic palladium complexes **3** and **4**, respectively. Fortunately, we were able to obtain a small amount of X-ray quality crystals of **1** by diffusion of diethyl ether into a concentrated chloroform solution.

The molecular structure of complex **1** with atomic labeling is shown in Fig. 1. Selected bond distances and angles are listed in Table 1. As anticipated from ^1H NMR spectroscopy and elemental analysis, two diethyl ether molecules were found in the unit cell of the dimer complex. As shown in Fig. 1, complex **1** is a neutral dimer in which each palladium metal center can be described in terms of a distorted square-planar geometry with phosphorus, methyl and two chloride atoms bound to the metal. The two halves are isostructural with an inversion center in the Pd_2Cl_2 rhombus. The distance between the palladium and the oxygen atom on the phenyl ring is 3.551 Å discounting any significant interaction between these atoms. The Pd–CH_3 bond distance is 2.100 Å which is similar to other known Pd complexes having a Pd–carbon σ-bond.[3,4] The Pd–Cl and Pd–P bond distances also fall within the literature range.[4] The Pd–Cl distance (2.4482 Å) *trans* to methyl is slightly longer than the Pd–Cl distance (2.4023 Å) *trans* to the phosphine moiety, suggesting a higher *trans* effect of the alkyl group. A similar result was found in comparable cyclometallated palladium

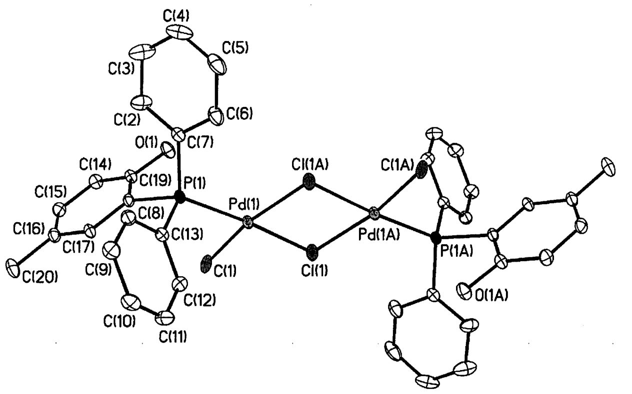


Fig. 1 ORTEP[17] view of $[Pd(dppmpH)(CH_3)(\mu\text{-}Cl)]_2{\cdot}2OEt_2$, (**1**)·$2OEt_2$ with atom labeling scheme. Hydrogens and solvent molecules are omitted for clarity.

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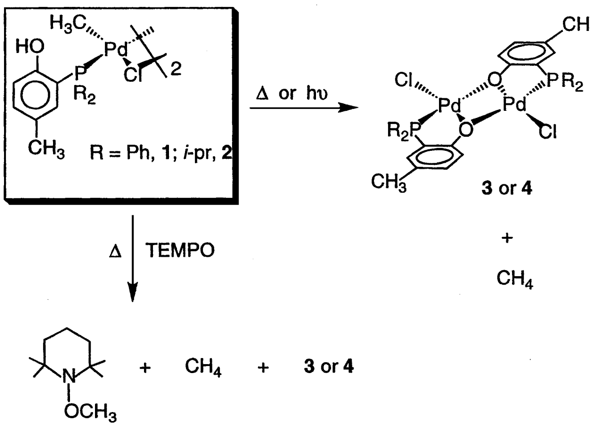
Table 1 Selected bond distances (Å) and bond angles (°) for $[Pd(dppmpH)(CH_3)(\mu\text{-}Cl)]_2\cdot 2OEt_2$ (**1**)$\cdot 2OEt_2$

Pd(1)–C(1)	2.100(4)	Pd(1)–Cl(1)	2.4023(11)
Pd(1)–P(1)	2.2463(11)	Pd(1)–Cl(1A)	2.4482(11)
P(1)–C(7)	1.830(5)	P(1)–C(13)	1.816(5)
P(1)–C(18)	1.831(4)	C(18)–C(19)	1.392(7)
C(19)–O(1)	1.358(5)	C(16)–C(20)	1.509(6)
C(1)–Pd(1)–P(1)	87.04(12)	C(1)–Pd(1)–Cl(1)	88.09(12)
P(1)–Pd(1)–Cl(1)	175.13(4)	C(1)–Pd(1)–Cl(1A)	170.31(13)
Cl(1)–Pd(1)–Cl(1A)	83.32(4)	P(1)–Pd(1)–Cl(1A)	101.51(4)
Pd(1)–P(1)–C(7)	117.94(14)	Pd(1)–Cl(1)–Pd(1A)	96.68(4)
Pd(1)–P(1)–C(18)	115.26(14)	Pd(1)–P(1)–C(13)	110.1(2)
P(1)–C(18)–C(17)	121.5(4)	P(1)–C(18)–C(19)	118.8(3)
O(1)–C(19)–C(18)	117.3(4)	O(1)–C(19)–C(14)	123.2(4)

dimer complexes.[5] The Cl–Pd–Cl angle is 83.32°, the smallest around the metal center, which is consistent with other reported complexes with $Pd(\mu\text{-}Cl)_2Pd$ bridging systems.[5]

Thermal and photochemical reactions of the palladium methyl complexes, $[Pd(dppmpH)(CH_3)(\mu\text{-}Cl)]_2$ (1) and $[Pd(dippmpH)(CH_3)(\mu\text{-}Cl)]_2$ (2)

Complexes **1** and **2** undergo photochemical and thermal $Pd–CH_3$ bond homolysis to produce methane and the corresponding oxygen-bridged palladium(II) dimer complexes **3** and **4**, respectively (Scheme 2). Complex **2** is particularly sensitive in solution and good elemental analysis data could not be obtained. The molecular structures of complexes **3** and **4** with atomic labeling are shown in Figs. 2 and 3, respectively. Selected bond distances and angles are listed in Tables 2 and 3.



Scheme 2

Compared to ambient light under which both complexes underwent slow loss of the methyl group, UV light induced a rapid reaction. For example, in 10 h 35% of complex **2** was decomposed under ambient light at 65 °C to give the corresponding oxygen-bridged palladium(II) dimer and methane. However, photolysis of this complex with UV light (350 nm) for 4 h left only 5% of the unreacted complex at 40 °C. The formation of methyl radicals during the photolysis of both **1** and **2** was suggested by the observation of CH_3D when $CDCl_3$ was used as the solvent. The occurrence of $Pd–CH_3$ bond homolysis was further confirmed by carrying out the thermolysis of **2** in the presence of the radical trap, TEMPO. In the presence of 2.0 equiv. of TEMPO, thermolysis of **2** at 65 °C yielded complex **4**, methane and 2,2,6,6-tetramethyl-1-piperidinyl-methoxide (TEMPO-Me) (Scheme 2). The identity of TEMPO-Me was established by ^1H NMR and GC/MS spectroscopy.[6] The ^1H NMR spectrum of the reaction solution showed a singlet peak due to the methoxy group of TEMPO-Me at 3.60 ppm and GC/MS data of TEMPO-Me were consistent with that reported in the literature.[7]

Palladium–alkyl complexes that are simultaneously heat and light-sensitive have been previously reported.[8–10] As in our systems, the alkyl radical was the intermediate in the formation of the observed organic products.

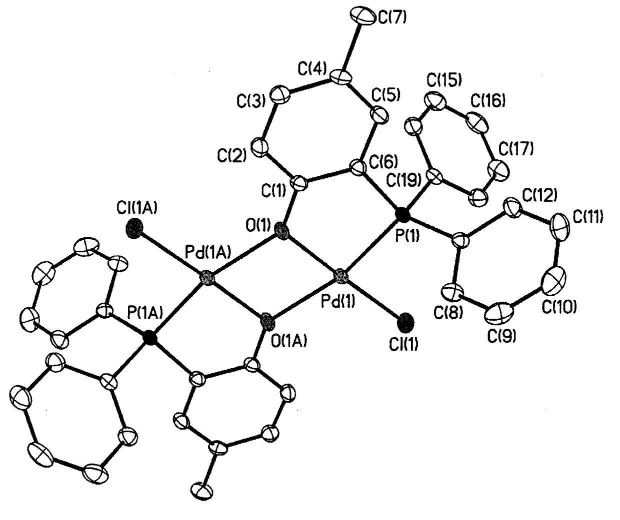


Fig. 2 ORTEP view of $[Pd(dppmp)(Cl)]_2\cdot 2CHCl_3$, (**3**)$\cdot 2CHCl_3$ with atom labeling scheme. Hydrogens and solvent molecules are omitted for clarity.

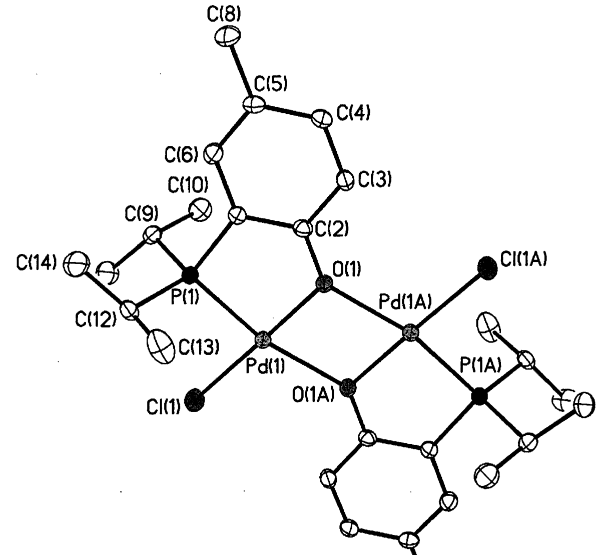


Fig. 3 ORTEP view of $[Pd(dippmp)(Cl)]_2$ (**4**) with atom labeling scheme. Hydrogens are omitted for clarity.

The reaction of $[Pd(dppmpH)(CH_3)(\mu\text{-}Cl)]_2$ (1) and $[Pd(dippmpH)(CH_3)(\mu\text{-}Cl)]_2$ (2) with small molecules

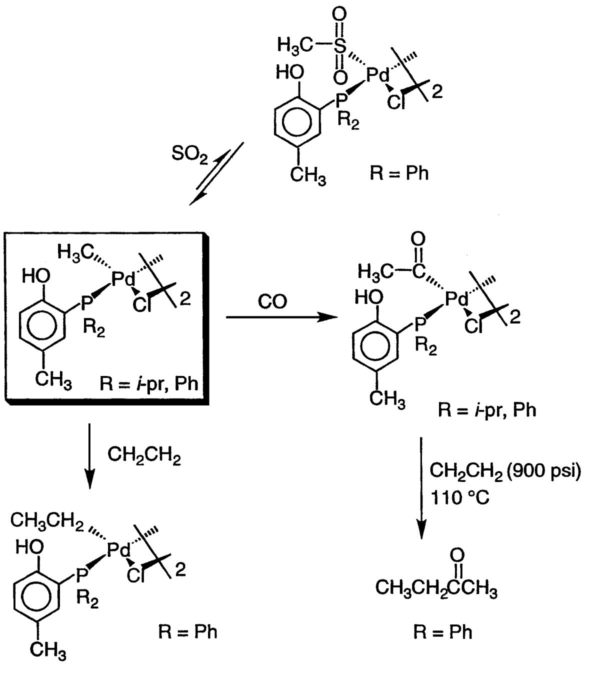
The reactions of carbon monoxide, sulfur dioxide and ethene with compounds **1** and **2** were examined (Scheme 3). Both **1** and

Table 2 Selected bond distances (Å) and bond angles (°) for $[Pd(dppmp)(Cl)]_2 \cdot 2CHCl_3$ (**3**)·$2CHCl_3$

Pd(1)–O(1)	2.022(2)	Pd(1)–O(1A)	2.146(2)
Pd(1)–P(1)	2.1721(6)	Pd(1)–Cl(1)	2.2723(6)
Pd(1)–Pd(1A)	3.2207(5)	P(1)–C(6)	1.793(2)
P(1)–C(13)	1.803(2)	P(1)–C(19)	1.798(2)
C(4)–C(7)	1.504(3)	C(1)–O(1)	1.350(2)
C(1)–C(6)	1.395(3)		
O(1)–Pd(1)–O(1A)	78.84(7)	O(1)–Pd(1)–P(1)	86.78(5)
O(1A)–Pd(1)–P(1)	165.59(5)	O(1)–Pd(1)–Cl(1)	178.09(4)
O(1A)–Pd(1)–Cl(1)	103.06(5)	P(1)–Pd(1)–Cl(1)	91.31(2)
O(1)–Pd(1)–Pd(1A)	40.82(4)	O(1A)–Pd(1)–Pd(1A)	38.02(5)
P(1)–Pd(1)–Pd(1A)	127.59(2)	Cl(1)–Pd(1)–Pd(1A)	141.08(2)
Pd(1)–P(1)–C(6)	99.62(7)	Pd(1)–P(1)–C(13)	116.37(7)
Pd(1)–P(1)–C(19)	116.10(7)	Pd(1)–O(1)–C(1)	117.91(13)
Pd(1A)–O(1)–C(1)	140.93(13)	Pd(1)–O(1)–Pd(1A)	101.16(7)
P(1)–C(6)–C(5)	122.9(2)	P(1)–C(6)–C(1)	116.2(2)
O(1)–C(1)–C(2)	121.7(2)	O(1)–C(1)–C(6)	119.5(2)

Table 3 Selected bond distances (Å) and bond angles (°) for $[Pd(dippmp)(Cl)]_2$ (**4**)

Pd(1)–O(1)	2.022(2)	Pd(1)–O(1A)	2.168(2)
Pd(1)–P(1)	2.1805(8)	Pd(1)–Cl(1)	2.2711 (9)
Pd(1)–Pd(1A)	3.2357(6)	P(1)–C(7)	1.804(3)
P(1)–C(12)	1.819(3)	P(1)–C(19)	1.824(3)
C(2)–C(7)	1.396(4)	C(2)–O(1)	1.340(4)
C(5)–C(8)	1.509(4)		
O(1)–Pd(1)–O(1A)	78.96(9)	O(1)–Pd(1)–P(1)	86.47(6)
O(1A)–Pd(1)–P(1)	165.39(6)	O(1)–Pd(1)–Cl(1)	177.54(7)
O(1A)–Pd(1)–Cl(1)	102.75(6)	P(1)–Pd(1)–Cl(1)	91.78(3)
O(1)–Pd(1)–Pd(1A)	41.12(6)	O(1A)–Pd(1)–Pd(1A)	37.84(6)
P(1)–Pd(1)–Pd(1A)	127.58(3)	Cl(1)–Pd(1)–Pd(1A)	140.56(3)
Pd(1)–P(1)–C(7)	105.56(14)	Pd(1)–P(1)–C(9)	118.46(11)
Pd(1)–P(1)–C(12)	112.21(11)	Pd(1)–O(1)–C(2)	118.3(2)
Pd(1A)–O(1)–C(2)	140.5(2)	Pd(1)–O(1)–Pd(1A)	101.04(9)
P(1)–C(7)–C(6)	124.4(2)	P(1)–C(7)–C(2)	115.5(2)
O(1)–C(2)–C(3)	121.3(3)	O(1)–C(2)–C(7)	119.9(3)



Scheme 3

2, in chloroform, react with carbon monoxide (1 atm) at ambient temperature to yield the corresponding acetyl complexes.[11] The formation of the latter was confirmed by ^1H and ^{13}C NMR spectroscopy (see Experimental section). The acetyl complex containing the dppmpH ligand was found to react further with ethene under high pressure (900 psi) at 110 °C to afford 2-butanone as the major product. Unlike carbon monoxide, the reaction of sulfur dioxide (1 atm) with **1** to form the corresponding sulfonyl complex proceeds only to a limited extent (approx. 40%). The formation of the sulfonyl complex was established by monitoring the reaction by ^1H and ^{13}C NMR spectroscopy. Interestingly, the insertion of sulfur dioxide was found to be reversible as demonstrated by the reformation of **1** when sulfur dioxide in the NMR tube was replaced by Ar gas (1 atm).

Complex **1** did not react when exposed to 1 atm of ethene at 60 °C. However, reaction was observed when the reaction solution was placed under 700 psi of ethene. The major palladium species formed is the dimeric palladium ethyl complex, $[Pd(dppmpH)(CH_3CH_2)(\mu\text{-}Cl)]_2$. Additionally, a small amount of 1-butene and propene were observed. The ^1H NMR spectrum for product mixture is shown in Fig. 4 and the overall transformation is presented in Scheme 4. The ^{31}P NMR spectrum of $[Pd(dppmpH)(CH_3CH_2)(\mu\text{-}Cl)]_2$ consists of a singlet at 29.8 ppm which is close to that of the corresponding dimeric methyl complex **1** (31.5 ppm). The presence of the ethyl group was suggested by the $^1H\{^{31}P\}$NMR spectrum which exhibited a quartet for the methylene and a triplet for the methyl fragment. Like complex **1**, the ethyl palladium complex also underwent reaction with carbon monoxide to generate an acyl complex (Scheme 4). The ^{31}P NMR spectrum of this species showed a singlet at 14.1 ppm which is again close to that of the acetyl complex (13.9 ppm) formed by the carbonylation of complex **1**.

As suggested in Scheme 4, the palladium propyl complex is the logical initial species formed by the reaction of ethene with complex **1**. ß-Hydrogen abstraction from this compound would yield a palladium hydride and propylene. The formation of the latter was confirmed by the ^1H NMR spectroscopy. The palladium hydride would be expected to rapidly insert ethene to generate the observed palladium ethyl complex. Further inser-

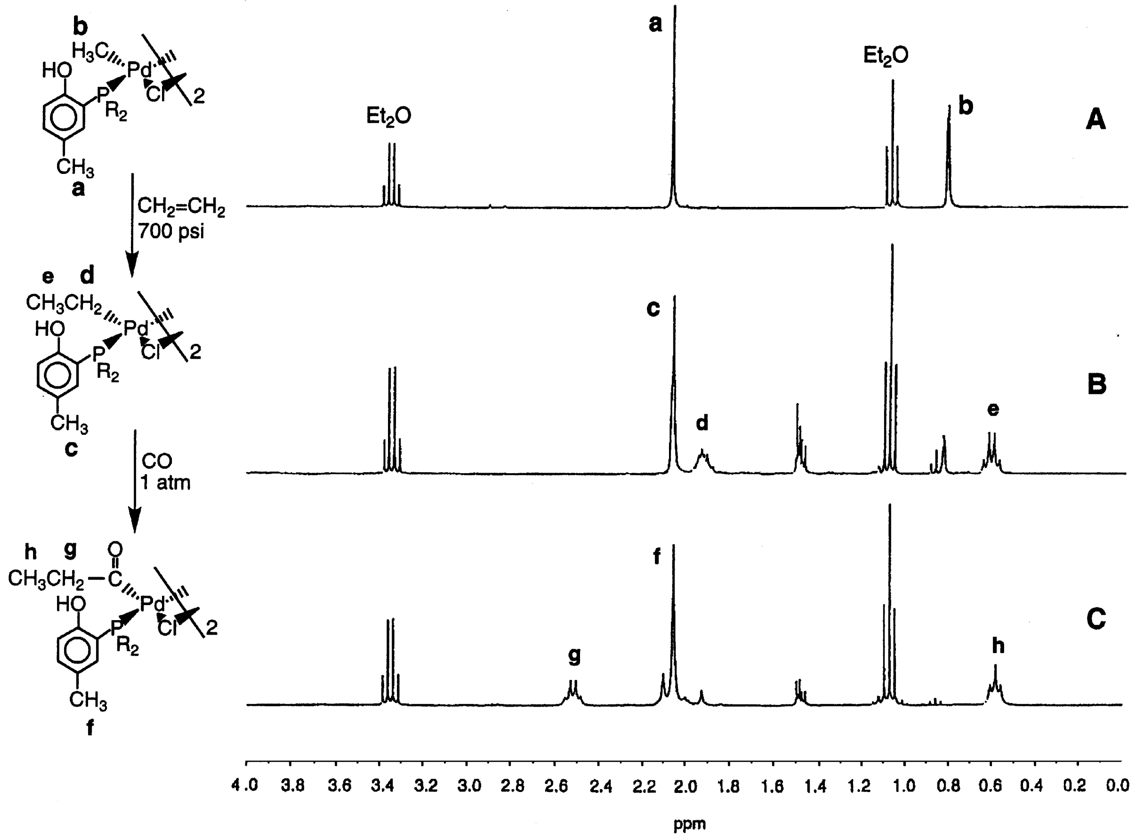
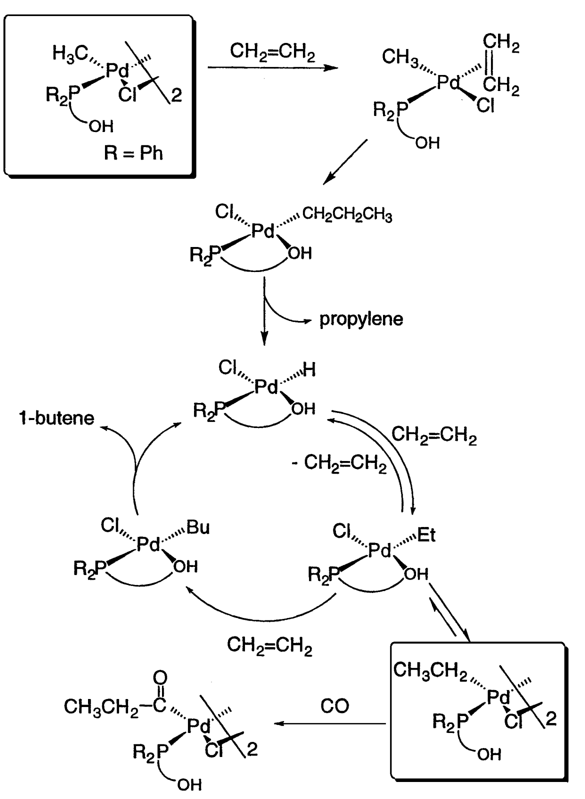


Fig. 4 ^{1}H NMR spectra of (A) $[Pd(dppmpH)(CH_3)(\mu\text{-}Cl)]_2$ (**1**), (B) $[Pd(dppmpH)(CH_2CH_3)(\mu\text{-}Cl)]_2$ and (C) $[Pd(dppmpH)(COCH_2CH_3)(\mu\text{-}Cl)]_2$.



Scheme 4

tion of ethene can and does occur to some extent as shown by the formation of 1-butene, the ß-hydrogen abstraction product from a palladium–butyl complex. Why are we able to observe the palladium ethyl complex but not the corresponding propyl and butyl species? If the ß-hydrogen abstraction from the palladium alkyl species is reversible, then in the presence of ethene all other palladium alkyl species will eventually form the ethyl compound.

Structural characterization of $[Pd(dppmp)(Cl)]_2$ (3) and $[Pd(dippmp)(Cl)]_2$ (4)

As shown in Scheme 2, $[Pd(dppmp)(Cl)]_2$ (**3**) and $[Pd(dippmp)(Cl)]_2$ (**4**) were produced as orange crystals by Pd–CH_3 bond homolysis in the bimetallic palladium methyl complexes **1** and **2**, respectively, in chloroform. Compared to the stable palladium(II) thiolate complexes,[12] only a few well characterized palladium(II) alkoxide or aryloxide compounds have been reported in the literature, in part due to their instability.[13] Indeed, complexes **3** and **4** are the first examples of stable dimeric palladium(II) aryloxides compounds with P,O-donor ligands.

The structures of complexes **3** and **4** with the atomic labeling are shown in Figs. 2 and 3, respectively. The selected bond distances and angles are listed in Tables 2 and 3; the bond distances and angles of the remaining phenyl groups are consonant with typical phenyl rings. Both palladium aryloxide dimers have a distorted square-planar geometry with the palladium metal coordinated to phosphorous, chloride, and two bridging-oxygen atoms. Each complex has an inversion center in the Pd_2O_2 rhombus. The distance between the two palladium atoms in the Pd_2O_2 rhombus are 3.2207 Å and 3.2357 Å, respectively. As found in dimeric palladium thiolate complexes,[12] the shortness of the Pd–Pd interaction and the reduced folding along the O–O axis of complexes **3** and **4**, compared to those in complex **1**, suggest a significant bonding between the two palladium centers. The Pd–Cl and Pd–P bond distances fall within the literature ranges.[13] As in complex **1**, a *trans* effect was evident in complexes **3** and **4**.[5] In both complexes, the Pd–O distances *trans* to chloride are slightly shorter than the Pd–O distances *trans* to phosphorus. Similar to complex **1**, the O–Pd–O angles were found to be the smallest around the metal centers.

Experimental

Materials

(COD)Pd(CH_3)(Cl) was prepared according to the literature procedure with little modification.[14] An adaptation of the published procedure was used for the syntheses of 2-diphenylphosphino-4-methylphenol (dppmpH) and 2-diisopropylphosphino-4-methylphenol (dippmpH).[2] Palladium chloride, 1-bromo-4-methylphenol, 1,5-cyclooctadiene, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), chlorodiphenylphosphine, *sec*-buthyllithium and $CDCl_3$ (all from Aldrich) were used as received. Diethyl ether and THF were dried over sodium/benzophenone under an argon atmosphere. Chloroform and chlorobenzene were dried over P_2O_5 and stored under an argon atmosphere.

Measurements

The ^1H, ^{31}P and ^{13}C NMR spectra were obtained on a Bruker AM300 FT-NMR spectrometer. The chemical shifts were referenced to an internal standard in a sealed capillary tube or to the solvent resonance at the appropriate frequency. GC/MS data were obtained on a Hewlett-Packard, HP 5890 gas chromatograph with a HP 5971 mass selective detector, and a HP cross-linked methyl silicone capillary column (20 m; 0.2 mm, film thickness 0.033 mm). Photochemical reactions were conducted with a Raynonet photochemical reactor having a Hg lamp (350 nm), all manufactured by the Southern N.E. Ultraviolet Co. Elemental analysis were performed by Galbraith Laboratories, Knoxville, TN.

2-Diphenylphosphino-4-methylphenol (dppmpH)

To a flask containing 120.0 mL of anhydrous diethyl ether and 15.0 g (80.2 mmol) of 2-bromo-4-methylphenol at −50 °C (acetone/liquid N_2 bath) was added a solution of 64.2 mL (2.5 M) of *sec*-butyllithium. The solution was allowed to warm to room temperature and stirred for 8 h resulting in a cloudy white solution. After cooling the reaction solution to −50 °C, 20 mL of diethyl ether solution containing 17.7 g (80.2 mmol) of chlorodiphenylphosphine was slowly added and stirred overnight at room temperature. The reaction mixture was treated with aq. NH_4Cl solution and the organic layer was separated. The solvents were removed by distillation to give a yellow oily liquid. Trituration of the sticky compound in methanol gave a white precipitate. Drying under vacuum yielded 16.6 g (71%) of dppmpH; mp 78 °C. ^1H NMR ($CDCl_3$) (ppm): 2.10, (s, CH_3, 3 H), 6.60–7.25 (m, phenyl, 13 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 21.0 (s, CH_3), 115.5–157.0 (m, phenyl). $^{31}P\{^1H\}$ NMR ($CDCl_3$) (ppm): −25.6.

2-Diisopropylphosphino-4-methylphenol (dippmpH)

To a flask containing 100.0 mL of anhydrous diethyl ether and 6.80 g (36.4 mmol) of 2-bromo-4-methylphenol at −50 °C (acetone/liquid N_2 bath) was added a solution of 56.0 mL (1.3 M) of *sec*-butyllithium. The solution was allowed to warm to room temperature and stirred for 8 h resulting in a cloudy white solution. After cooling the reaction solution to −50 °C, 20 mL of diethyl ether containing 5.55 g (36.4 mmol) of chlorodiisopropylphosphine was slowly added and stirred overnight at room temperature. The reaction mixture was treated with the degassed aq. NH_4Cl solution and the organic layer was separated. The solvents were removed by distillation to give a yellow oily liquid. Vacuum distillation (100–105 °C/0.7 torr) of the yellow oily liquid gave 4.80g (59%) of colorless liquid. ^1H NMR ($CDCl_3$) (ppm): 1.10, (dd, J_{HH} = 12.0 Hz, J_{PH} = 7.0 Hz, CH_3, 6 H), 1.19, (dd, J_{HH} = 16.0 Hz, J_{PH} = 7.0 Hz, CH_3, 6 H), 2.32 (sept d, J_{HH} = 7.0 Hz, J_{PH} = 4.0 Hz, CH, 2 H), 2.45 (s, CH_3, 3H), 6.90–7.37 (m, phenyl, 3 H), 7.37 (br s, OH, H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 18.9 (d, J_{PC} = 8.0 Hz, CH_3), 20.1 (d, J_{PC} = 17.0 Hz, CH_3), 20.7 (s, CH_3), 23.1 (d, J_{PC} = 7.0 Hz, CH), 115.0, 128.0, 130.2, 130.4, 158.5, 159.0(phenyl). $^{31}P\{^1H\}$ NMR ($CDCl_3$) (ppm): −22.9. Anal. calcd. (found) for $POC_{13}H_{21}$: C, 69.6 (68.7); H, 9.4 (9.1%).

[Pd(dppmpH)(CH_3)(μ-Cl)]$_2$ (1)

To a flask containing 0.20 g (0.76 mmol) of (COD)Pd(CH_3)(Cl) and 0.22 g (0.76 mmol) of dppmpH was added 10 mL of THF. The resulting yellow solution was stirred overnight and dried under vacuum to provide a yellow solid. The yellow solid was washed with 20.0 mL of diethyl ether, and then dried under vacuum to yield 0.30 g (99%) of [Pd(dppmpH)(CH_3)(μ-Cl)]$_2$. ^1H NMR ($CDCl_3$) (ppm): 0.97 (d, J_{PH} = 3.1 Hz, $PdCH_3$, 3 H), 2.22 (s, CH_3, 3 H), 6.95–7.60 (m, phenyl, 23 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 15.5 (s, $PdCH_3$), 66.0 (s, CH_3), 115.0–134.0 (m, phenyl). $^{31}P\{^1H\}$ NMR ($CDCl_3$) (ppm): 31.5. Anal. calcd. (found) for $Pd_2P_2O_2C_{36}H_{28}Cl_2$: C, 67.0 (66.0); H, 4.34 (4.26%).

[Pd(dippmpH)(CH_3)(μ-Cl)]$_2$ (2)

To a flask containing 0.20 g (0.76 mmol) of (COD)Pd(CH_3)(Cl) and 10 mL of diethyl ether, was added 0.17 g (0.76 mmol) of dippmpH in 2 mL of diethyl ether. The resulting yellow solution was stirred for 4 h to give a white solid. The white solid was filtered off, washed three times with 15.0 mL of diethyl ether, and then dried under vacuum to yield 0.17 g (65%) of [Pd(dippmpH)(CH_3)(μ-Cl)]$_2$. ^1H NMR ($CDCl_3$) (ppm): 0.81 (d, J_{PH} = 2 Hz, $PdCH_3$, 6 H), 1.08 (dd, J_{HH} = 15 Hz, J_{PH} = 7 Hz, CH_3, 12 H) 1.27 (dd, J_{HH} = 18 Hz, J_{PH} = 7 Hz, CH_3, 12 H), 2.30 (s, CH_3, 6 H), 2.50 (sept d, J_{HH} = 7 Hz, J_{PH} = 2 Hz, CH, 4 H), 6.95–7.20 (m, phenyl, 6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 18.0 (s, CH_3), 19.2 (d, J_{PC} = 4.0 Hz, CH_3), 20.9 (s, CH_3), 24.9 (d, J_{PC} = 28 Hz, CH), 117.0 (d, J_{PC} = 6 Hz), 130.5.0, 131.4, 134.0, 158.5, 159.0 (phenyl). $^{31}P\{^1H\}$ NMR ($CDCl_3$) (ppm): 80.9.

Reaction of [Pd(dppmpH)(CH_3)(μ-Cl)]$_2$ (1) with ethene, CO and SO_2

The reactions were performed in a 125 mL stirred autoclave manufactured by the Parr Instrument Company. In a typical reaction, 20.0 mg of **1** was placed in a 5.0 mL glass liner equipped with a small magnetic stirrer and dissolved in 1.0 mL of $CDCl_3$. In the reaction with ethene, the glass liner was inserted into the autoclave which was then pressurized to 700 psi of ethene. However, the autoclave was pressurized to 1 atm for CO and SO_2. After stirring at 60 °C for 1 h, the unreacted gas was released and the reaction mixture was transferrred *via* a double tipped needle into an NMR tube for analysis.

NMR data for [Pd(dppmpH)(CH_2CH_3)(μ-Cl)]$_2$:^1H NMR ($CDCl_3$) (ppm): 0.68 (m, Pd–CH_2CH_3, 3 H), 1.98 (m, Pd–CH_2CH_3, 2 H), 2.15 (s, CH_3, 3 H), 6.95–7.60 (m, phenyl, 23 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$) (ppm): 29.8.

NMR data for [Pd(dppmpH)((CO)CH_3)(μ-Cl)]$_2$: ^1H NMR ($CDCl_3$) (ppm): 2.12 (s, PdC(O)CH_3, 3 H), 2.17 (s, CH_3-phenyl, 3 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 36.8 (d, J_{PC} = 22.5 Hz, PdC(O)CH_3), 20.7 (s, CH_3-phenyl). ^{31}P NMR: 13.9 ppm.

NMR data for [Pd(dppmpH){(SO_2)CH_3}(μ-Cl)]$_2$: ^1H NMR ($CDCl_3$) (ppm): 2.12 (s, Pd){(SO_2)CH_3}, 3 H), 2.16 (s, CH_3-phenyl, 3 H). ^{31}P NMR: 15.6 ppm.

Acetyl complex from the reaction of [Pd(dippmpH)(CH_3)(μ-Cl)]$_2$ (2) with CO

^1H NMR ($CDCl_3$) (ppm): 2.60 (s, Pd–C(O)CH_3, 3 H), 2.25 (s, CH_3-phenyl, 3 H), $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 40.9 (d, J_{PC} = 19.5 Hz, Pd–C(O)CH_3), 20.8, (s, CH_3-phenyl). ^{31}P NMR: 39.6 ppm.

X-Ray structure determination

All pertinent crystallographic details are summarized in Table 4. The single crystal X-ray diffraction experiments were

Table 4 Crystallographic data for [Pd(dppmpH)(CH_3)(μ-Cl)]$_2$·2OEt$_2$ (**1**)·2OEt$_2$, [Pd(dppmp)(Cl)]$_2$·2CHCl$_3$ (**3**)·2CHCl$_3$ and [Pd(dippmp)(Cl)]$_2$ (**4**)

	1·2OEt$_2$	**3**·2CHCl$_3$	**4**
Formula	$C_{48}H_{60}Cl_2O_4P_2Pd_2$	$C_{40}H_{34}Cl_8O_2P_2Pd_2$	$C_{26}H_{40}Cl_2O_2P_2Pd_2$
M	1046.64	1105.05	730.22
Crystal habit	Yellow rod	Orange square plate	Orange square plate
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	10.1411(5)	8.7474(10)	11.078(2)
b/Å	11.0177(6)	9.2402(7)	11.830(2)
c/Å	12.0000(6)	13.0338(12)	11.619(2)
α/°	77.848(2)	94.835(5)°	
β/°	83.3270(10)	90.362(11)°	108.695(12)°
γ/°	64.9250(10)	91.245(10)°	
V/Å^3	1186.65(11)	1049.39(14)	1442.4(3)
μ(Mo–Kα)/cm^{-1}	9.79	14.78	15.65
T/K	173(2)	243(2)	243(2)
$R(F)^a$ (%)	4.27	3.25	3.39
$R(wF^2)^a$ (%)	12.11	10.30	8.46

[a] Quantity minimized = $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$. $R = \Sigma\Delta/\Sigma(F_o)\Delta = |F_o - F_c|$.

performed on a Siemens P4/CCD for complex **1**, and on a P4 diffractometer for complexes **3** and **4**.

The systematic absences in the diffraction data were consistent with the reported space groups. For complexes **1** and **3** either of the triclinic space groups $P1$ or $P\bar{1}$was indicated; in both cases the latter centrosymmetric space group was preferred based on the chemically reasonable and computationally stable results of refinement. The structures were solved using direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures. The data for complex **1** were corrected for absorption by using the program DIFABS.[15] Absorption corrections were not required for complexes **3** and **4** because the variation in the integrated ψ-scan intensities was less than 10%. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. In complex **4**, the molecule of the complex resides on an inversion center. In case of complexes **1** and **3**, the molecule of the complex resides on an inversion center and there is one solvate molecule of diethyl ether (**1**) and chloroform (**3**), respectively, in the asymmetric unit.

All software and sources of the scattering factors are contained in SHELXTL.[16]

CCDC reference numbers 171711–171713.

See http://www.rsc.org/suppdata/dt/b2/b208060p/ for crystallographic data in CIF or other electronic format.

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