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Inorganica Chimica Acta 345 (2003) 8–14
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Reaction chemistry of $[Pd_2(\mu\text{-}OH)_2L_4]^{2+}$ with aryl amines. Structures of $[Pd_2(\mu\text{-}OH)\{\mu\text{-}NH(p\text{-}tol)\}(PPh_3)_4](BF_4)_2$, $[Pd(\eta^3\text{-}CH_2C(NH(p\text{-}tol)CH_2)(PPh_3)_2](BF_4)$, and $[Pd(PMe_2Ph)_2(\mu\text{-}PF_2O_2)]_2(PF_6)_2$

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Received 8 April 2002; accepted 6 May 2002

Dedicated in honor of Professor Richard Schrock

Abstract

The reaction of $[Pd_2(\mu\text{-}OH)_2(PPh_3)_4](BF_4)_2$ (**1**) with aromatic amines (aniline and *p*-toluidine) in dichloromethane yields the dinuclear complexes $[Pd_2(\mu\text{-}OH)(\mu\text{-}NHAr)(PPh_3)_4](BF_4)_2$ (**2**) (Ar = Ph, *p*-tol). The same reaction in acetone gives the palladium(II) allyl complex, $[Pd(\eta^3\text{-}CH_2C(NHp\text{-}tol)CH_2)(PPh_3)_2](BF_4)$ (**3**). An attempt to prepare the PMe_2Ph analog of **1** as the PF_6^- salt yielded instead $[Pd(PMe_2Ph)_2(\mu\text{-}PF_2O_2)]_2(PF_6)_2$ (**7**).The structures of **2** (Ar = *p*-tol), **3**, and **7** have been determined by X-ray diffraction methods.

Keywords: Palladium; Hydroxo; Amido; Allyl; Phosphine

1. Introduction

Palladium complexes are important catalysts or catalyst precursors in organic syntheses [1]. Recently, they have found use in carbon–nitrogen bond formation [2], in acetalizations [3], in Mannich-type reactions [4] and in oxidation reactions [5]. Amido, alkoxo, and hydroxo complexes are proposed as intermediates in many of these processes. In addition, amido and hydroxo complexes are useful synthetic precursors taking advantage of their basicity [6]. They may also be deprotonated to give oxo and imido complexes [7]. As a continuation of our studies on the chemistry of hydroxo/oxo and amido/imido complexes of late-transition metal ions [7,8], we report the reactions of the triphenylphosphine palladium(II) hydroxo complex $[Pd_2(\mu\text{-}OH)_2(PPh_3)_4](BF_4)_2$ (**1**) [9] with aromatic amines and the unexpected formation of an amido allyl complex when the reaction is conducted in acetone.

2. Experimental

Reactions were conducted in air. Solvents and reagents were reagent grade and used as received. Ethanol was 95%. NMR spectra were recorded at ambient temperatures on a Bruker AMX-250 spectrometer, using internal $SiMe_4$ (^1H), external $CFCl_3$ (^{19}F), and external H_3PO_4 (^{31}P) as standards and are reported in ppm with negative shifts upfield of the standard. IR spectra (cm^{-1}) were recorded on a Nicolet 550 Magna FTIR spectrometer as mineral oil mulls between NaCl plates. M-H-W Laboratories, Arizona, carried out the elemental analyses. $[Pd_2(\mu\text{-}OH)_2(PPh_3)_4](BF_4)_2$ (**1**) [9] and $Pd(PMe_2Ph)_2Cl_2$ [10] were prepared by reported methods.

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0020-1693/02/$ - see front matter
PII: S0020-1693(02)01278-1

2.1. $[Pd_2(\mu\text{-}OH)(\mu\text{-}NHAr)(PPh_3)_4](BF_4)_2$ (2) (Ar = Ph, p-tol)

The amine (0.400 mmol) was slowly added to a stirred CH_2Cl_2 (5 ml) suspension of $[Pd_2(\mu\text{-}OH)_2(PPh_3)_4](BF_4)_2$ **1** (250 mg, 0.170 mmol) and the mixture was stirred overnight. The resulting clear red solution was evaporated to dryness in vacuo. The residue was extracted with CH_2Cl_2 (2 ml) and filtered. THF (3 ml) addition to the filtrate followed by cooling at −10 °C overnight gave a red–orange solid, which was filtered-off, washed with ether and dried in vacuo. Recrystallization from CH_2Cl_2/diglyme (diglyme = 2-methoxyethyl ether) gave red crystals suitable for X-ray diffraction (Ar = *p*-tol).

Ar = Ph. Yield: 210 mg (80%). IR: 3574 (OH), 3292 (NH). ^{1}H NMR (CD_2Cl_2): −3.20 (t, $^3J_{PH} = 2.5$ Hz, OH), 1.30 (br, NH), 7.1–7.4 (m, PPh_3 and NHPh). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 29.3, 29.9 (AB quartet, $^2J_{PP} = 19.5$ Hz). ^{19}F NMR (CD_2Cl_2): −151.3 (s). *Anal*. Calc. (Found) for $C_{78}H_{67}B_2F_8OP_4Pd_2N$·diglyme: C, 60.1 (60.0); H, 4.8 (4.5); N, 0.8 (1.0)%.

Ar = *p*-tol. Yield: 180 mg (68%). IR: 3582 (OH), 3301 (NH). ^{1}H NMR (CD_2Cl_2): −3.27 (t, $^3J_{PH} = 2.5$ Hz, OH), 1.28 (br s, NH), 2.41 (s, tol), 7.2–7.4 (m, PPh_3 and tol). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 29.0, 29.8 (AB quartet, $^2J_{PP} = 20.0$ Hz). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): −151.4 (s). *Anal*. Calc. (Found) for $C_{79}H_{69}B_2F_8NOP_4Pd_2$·0.5diglyme: C, 60.6 (60.5); H, 4.7 (4.8); N, 0.9 (0.9)%.

2.2. $[Pd(CH_2C\{NH(p\text{-}tol)\}CH_2)(PPh_3)_2](BF_4)$ (3)

(*a*) From $[Pd_2(\mu\text{-}OH)_2(PPh_3)_4](BF_4)_2$. *p*-Toluidine (45 mg, 0.42 mmol) was slowly added to a stirred acetone (5 ml) suspension of dihydroxo complex **1** (250 mg, 0.170 mmol). The mixture was stirred for 24 h after which time the clear yellow solution was filtered. The filtrate was concentrated to approximately 1 ml, layered with 2 ml of C_6H_{14} and cooled at −10 °C for 12 h. The resulting white solid was filtered-off, washed with C_6H_{14} and dried. Yield: 220 mg (75%). (*b*) From $[Pd_2(\mu\text{-}OH)(\mu\text{-}NHp\text{-}tol)(PPh_3)_4](BF_4)_2$. *p*-Toluidine (10 mg, 0.093 mmol) was slowly added to a stirred acetone (2 ml) solution of **2** (Ar = *p*-tol) (120 mg, 0.077 mmol). The solution was stirred for 2 h, layered with C_6H_{14} (4 ml), and cooled at −10 °C overnight. The white crystalline product was filtered-off, washed with C_6H_{14} and ether, and dried. Yield: 115 mg (91%). Crystals for the X-ray analysis were obtained from acetone/C_7H_{16}.

IR: 3348 (NH). ^{1}H NMR (CD_2Cl_2): 1.65 (br s, 1H, NH), 2.36 (s, 3H, tol), 2.64 (m, 2H, allyl *syn*-H), 3.24 (br d, $^2J_{HH} = 2.5$ Hz, 2H, allyl *anti*-H), 7.04–7.40 (m, 34H, PPh_3 and tol). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 26.1 (s). ^{19}F NMR (CD_2Cl_2): −151.8 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 21.0 (s, tol CH_3), 55.1 (dd, $J_{P-C} = 19.9$ and 39.8 Hz, allyl C_α), 123.6 (s, PPh_3 C_1), 129.15 (t, $J_{P-C} = 5.1$ Hz, PPh_3 $C_{2,6}$), 131.23 (s, PPh_3 C_4), 131.5 (s, tol C_1), 131.9 (s, tol $C_{2,6}$), 132.1 (s, tol $C_{3,5}$), 133.9 (t, $J_{P-C} = 6.5$ Hz, PPh_3 $C_{3,5}$), 135.6 (s, tol C_4), 136.1 (s, tol $C_{3,5}$) 148.8 (t, $J_{P-C} = 5.2$ Hz, allyl C_β). *Anal*. Calc. (Found) for $C_{46}H_{42}BF_4N_1P_2Pd$: C, 64.0 (63.9); H, 4.9 (5.0); N, 1.6 (1.6)%.

2.3. $[Pd(PMe_2Ph)_2(\mu\text{-}PF_2O_2)]_2(PF_6)_2$ (7)

An acetone solution of $AgPF_6$ (250 mg, 0.990 mmol) was added to a stirred suspension of $PdCl_2(PMe_2Ph)_2$ (220 mg, 0.486 mmol) in acetone containing few drops of water. The mixture was stirred for 2 h and then filtered to remove AgCl. The volatiles were removed in vacuo and the residue was extracted with CH_2Cl_2. The extract was filtered and the volume of the filtrate was reduced to 2 ml and layered with $C_6H_5CH_3$. Slow evaporation yielded yellow crystals of the product suitable for X-ray analysis. Yield: 210 mg (69%).

^{1}H NMR (d_6-acetone): 1.91 (d, 24H, $^2J_{PH} = 11.6$ Hz, PMe_2), 7.50–7.72 (m, 20H, PPh). ^{31}P NMR (d_6-acetone): 19.8 (s, PMe_2Ph), −13.5 (t, $^1J_{P-F} = 960$ Hz, PF_2O_2), 142.6 (sept, $^1J_{P-F} = 708$ Hz, PF_6). ^{19}F NMR (d_6-acetone): −71.6 (d, $^1J_{F-P} = 708$ Hz, PF_6), −80.6 (d, $^1J_{F-P} = 960$ Hz, PF_2O_2).

2.4. X-ray structure determinations

Crystals of the complexes were obtained as described above and were taken from the mother liquor and placed in an N_2 cold stream on a SMART CCD system. A summary of crystal data and data collection and processing is given in Table 1. Data collection and processing followed routine procedures. Details may be found in the supporting information.

3. Results and discussion

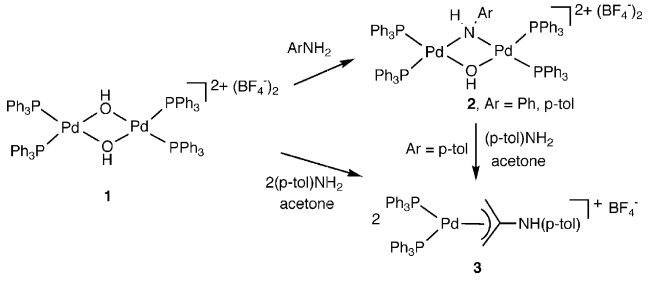
3.1. $[Pd_2(\mu\text{-}OH)(\mu\text{-}NHAr)(PPh_3)_4](BF_4)_2$ (2, Ar = Ph, p-tol)

Many Pt and Pd bridging amido complexes have been prepared by aminolysis of bridging hydroxo complexes [11,12]. Although this process has been applied to platinum complexes of the type $[Pt(\mu\text{-}OH)L_2]_2^{2+}$ (L = a phosphine, L_2 = a diphosphine), aminolysis reactions with the analogous Pd complexes have not been reported. As we previously reported with the Pt analog [12], the dihydroxo bridged palladium(II) compound $[Pd(\mu\text{-}OH)(Ph_3P)_2]_2(BF_4)_2$ (**1**) with aryl amines (Scheme 1) readily yields the hydroxo-amido bridged dinuclear palladium(II) complexes $[Pd_2(\mu\text{-}OH)(\mu\text{-}NHAr)(PPh_3)_4](BF_4)_2$ (**2**, Ar = Ph, *p*-tol). The spectroscopic properties of **2** closely resemble those reported for the Pt analogs with the exception that ^{195}Pt coupling in the NMR spectra is absent in **2**. The ^{31}P NMR spectra of **2** show a

Table 1
Crystallographic and data collection parameters at 173 K [a]

Complex	$[Pd_2(\mu\text{-}OH)(\mu\text{-}NHp\text{-}tol)(PPh_3)_4](BF_4)_2$ (**2**)	$[Pd(\eta^3\text{-}CH_2C(NHp\text{-}tol)CH_2)(PPh_3)_2](BF_4)$ (**3**)	$[Pd(PMe_2Ph)_2(\mu\text{-}PF_2O_2)]_2(PF_6)_2$ (**7**)
Formula	$C_{79}H_{69}B_2F_8NOP_4Pd_2\cdot 2.5CH_2Cl_2\cdot 0.5C_6H_{14}O_3$ [d]	$C_{46}H_{42}BF_4N_1P_2Pd$	$C_{32}H_{44}F_{16}O_4P_8Pd_2$
Color/habit	red/prism	colorless/rod	yellow/prism
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	16.8842(8)	11.1017(7)	8.8701(4)
b (Å)	23.4920(12)	13.9591(8)	16.6431(8)
c (Å)	21.6947(11)	14.6092(9)	16.8285(8)
α (°)		86.586(1)	72.812(1)
β (°)	96.102(1)	71.638(1)	85.223(1)
γ (°)		70.093(1)	84.191(1)
Z	4	2	2
Crystal size (mm)	0.3 × 0.3 × 0.2	0.3 × 0.2 × 0.1	0.3 × 0.3 × 0.2
Trans range (%)	100–78.64	100–81.84	100–83.05
Observed ($>2\sigma(I)$)	9901	7184	8348
Total/unique/R_{int}	45 520/18 077/0.0620	19 983/8743/0.0329	14 400/9931/0.0173
θ max/% measured	27.22/94.7	27.12/98.1	27.14/94.9
R_1 [b]/wR_2 [c]/S	0.0679/0.1953/0.997	0.0366/0.0788/1.023	0.0337/0.0875/1.030

[a] Siemens CCD system (omega scans), SADABS absorption correction.
[b] $R_1 = (\Sigma\ ||F_o|-|F_c||)/\Sigma\ |F_o|$.
[c] $wR_2 = [(\Sigma\ w(F_o^2-F_c^2)^2)/\Sigma\ w(F_c^2)^2]^{1/2}$.
[d] The half occupancy solvent molecules were disordered about an inversion center.



Scheme 1.

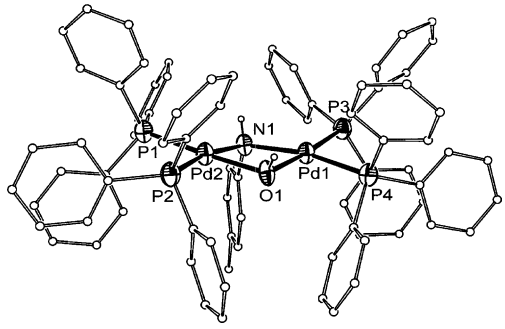


Fig. 1. Drawing of the cationic portion of $[Pd_2(\mu\text{-}OH)(\mu\text{-}NHAr)(PPh_3)_4](BF_4)_2$ (**2**) (Ar = *p*-tol). Aryl group hydrogen atoms are omitted for clarity. Arbitrary spheres represent hydrogen atoms and aryl group carbon atoms; all other atoms are represented by 50% probability thermal ellipsoids.

doublet of doublets with J_{P-P} of about 20 Hz indicating inequivalent phosphine ligands in a cis configuration. IR spectra show the presence of both hydroxo ($\nu_{OH} = 3574$, 3582 cm^{-1}) and amido groups ($\nu_{NH} = 3292$, 3301 cm^{-1}). The ^1H NMR spectrum shows the expected aromatic peaks and the tol methyl peak for **2**, Ar = *p*-tol. The OH proton triplet ($J_{PH} = 2.5$ Hz) shows that the OH group is coupled to only two of the phosphine ligands, presumably to one on each Pd center in a *trans* position to the OH group. The NH group signal could not be positively assigned.

An X-ray crystal structure determination confirms the identity of **2** (Ar = *p*-tol). A drawing of the cationic portion is given in Fig. 1. A summary of crystal and data collection parameters is given in Table 1. Selected distances and angles are listed in Table 2. Although the crystals of **2** are not isomorphous with those of the reported Pt analog [12], the structures of the cationic portions are nearly isostructural. The most notable

Table 2
Selected distances (Å) and angles (°) for $[Pd_2(\mu\text{-}OH)(\mu\text{-}NH(p\text{-}tol))(PPh_3)_4](BF_4)$ (**2**) (Ar = *p*-tol)

Bond distances			
Pd1–O1	2.122(4)	Pd2–N1	2.104(4)
Pd1–N1	2.134(4)	Pd2–P1	2.2556(15)
Pd1–P3	2.2530(15)	Pd2–P2	2.3042(15)
Pd1–P4	2.3134(15)	Pd1–Pd2	3.1985(6)
Pd2–O1	2.119(4)	N1–C51	1.443(7)
Bond angles			
Pd2–O1–Pd1	97.93(16)	N1–Pd2–O1	81.65(16)
Pd2–N1–Pd1	98.01(17)	P1–Pd2–P2	95.02(6)
O1–Pd1–N1	80.89(16)	C51–N1–Pd2	111.0(3)
P3–Pd1–P4	94.36(6)	C51–N1–Pd1	109.1(3)

difference is the near planarity of the Pd complex reported here. The fold along the common N–O edge of the two Pd square-planar coordination spheres is only 10.5° whereas that for the Pt analog is 31.1°. As a result, the Pd–Pd distance (3.1985(6) Å) in **2** is longer than that in the Pt complex (3.159(1) Å). Bond distances in **2** are longer than in the Pt complex or equal despite the greater covalent radius of Pt (1.28 vs. 1.30 Å). The greatest difference is in the M–O distances, which are significantly longer in **2** (2.119(4) and 2.124(4) Å) than in the Pt analog (2.059(6) and 2.066(6) Å).

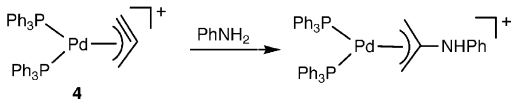
In some dihydroxo complexes related to **1**, it is possible to exchange both hydroxo groups for amido groups [12]. Attempts to do this and obtain the bis-amido compound $[Pd_2(\mu\text{-}NHAr)_2(PPh_3)_4](BF_4)_2$ failed. Excess aryl amine in a variety of solvents (CH_2Cl_2, $ClCH_2CH_2Cl$, THF, toluene) at room temperature gives only the amido-hydroxo complex **2**. Refluxing the mixtures gives palladium metal and triphenylphosphine oxide. The Pt analog of **2** also failed to give a diamido complex. This was attributed to steric factors, which also must apply here for Pd. An entirely different product is obtained when the reaction of **1** with aryl amines is conducted in acetone.

3.2. $[Pd(CH_2C\{NH(p\text{-}tol)\}CH_2)(PPh_3)_2](BF_4)$ (3)

The reaction of $[Pd(\mu\text{-}OH)(Ph_3P)_2]_2(BF_4)_2$ **1** with *p*-toluidine in acetone gives white crystalline $[Pd(\eta^3\text{-}CH_2C\{NH(p\text{-}tol)\}CH_2)(PPh_3)_2](BF_4)$ (**3**). The ^{31}P NMR spectrum of **3** shows a single resonance at 26.1 ppm. The IR spectrum shows the presence of an NH group but no OH group. The ^1H NMR spectrum shows the presence of aryl ring protons, a tol methyl group (δ 2.36, 3H) and two resonances at δ 2.65 (m, $J = 3$ Hz, 2H) and 3.24 (d, $J = 2.5$ Hz, 2H). The resonances at δ 2.65 and 3.24 could not be assigned from the ^1H NMR spectrum alone. The ^{13}C NMR spectrum shows the expected peaks for the PPh_3 and the tol group and two additional carbon peaks (δ 55.1 and 148.8), which are coupled to the phosphorus atoms. The identity of **3** as the mononuclear allyl complex $[Pd(\eta^3\text{-}CH_2C\{NH(p\text{-}tol)\}CH_2)(PPh_3)_2](BF_4)$ was revealed by an X-ray crystal structure determination (Scheme 1, Tables 1 and 3, Fig. 2). The unidentified resonances in the NMR spectra are assigned to the allyl group. An examination of the literature reveals that the analog of **3** has been previously prepared from the reaction of amines with the allenyl/propargyl complex $[Pd(\eta^3\text{-}CHCCH_2)(PPh_3)_2](BF_4)$ (**4**) (Scheme 2) [13]. This and related complexes have attracted attention for resonance contributions from metallacycle and heteroatom substituted trimethylenemethane complexes [13–17]. The phenyl analog of **3** has been structurally characterized and the metrical parameters are identical to those of **3** [13].

Table 3
Selected distances (Å) and angles (°) for $[Pd(\eta^3\text{-}CH_2C(NH(p\text{-}tol))CH_2)(PPh_3)_2](BF_4)$ (**3**)

Bond distances			
Pd1–C1	2.141(3)	N1–C3	1.368(3)
Pd1–C2	2.159(3)	N1–C71	1.420(3)
Pd1–C3	2.273(2)	C1–C3	1.415(4)
Pd1–P1	2.3049(7)	C2–C3	1.419(4)
Pd1–P2	2.3229(7)		
Bond angles			
C1–Pd1–C2	66.82(11)	C3–N1–C71	127.9(2)
C1–Pd1–C3	37.24(10)	C3–C1–Pd1	76.45(15)
C2–Pd1–C3	37.23(10)	C3–C2–Pd1	75.74(15)
C1–Pd1–P1	95.35(8)	N1–C3–C1	125.2(3)
C2–Pd1–P1	162.08(9)	N1–C3–C2	119.8(3)
C3–Pd1–P1	127.36(7)	C1–C3–C2	113.4(2)
C1–Pd1–P2	161.94(8)	N1–C3–Pd1	124.08(17)
C2–Pd1–P2	95.45(8)	C1–C3–Pd1	66.32(14)
C3–Pd1–P2	128.02(7)	C2–C3–Pd1	67.03(14)
P1–Pd1–P2	102.21(2)		



Scheme 2.

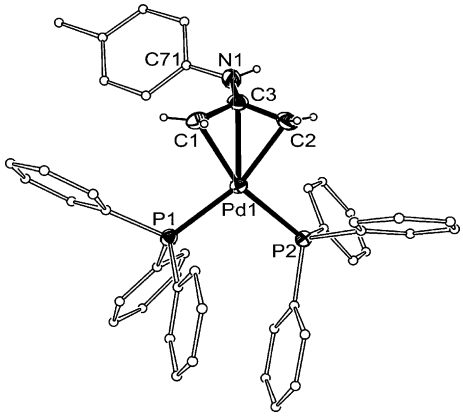
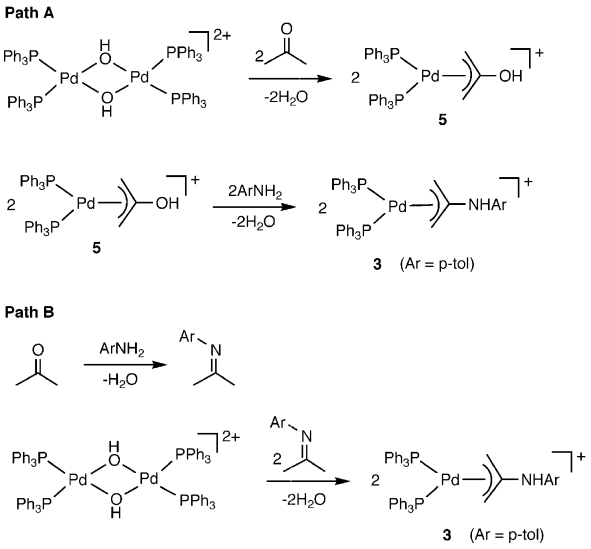


Fig. 2. Drawing of the cationic portion of $[Pd(\eta^3\text{-}CH_2C(NHp\text{-}tol)CH_2)(PPh_3)_2](BF_4)$ (**3**). Aryl group hydrogen atoms are omitted for clarity. Arbitrary spheres represent hydrogen atoms and aryl group carbon atoms; all other atoms are represented by 50% probability

Complex **3** is also obtained when the hydroxo amido complex **2** is treated with 1 equiv. of amine in acetone. Without the added amine, both **1** and **2** are stable in acetone for several days.

The source of the C_3 unit for the allyl must be acetone. Two possible pathways for the reaction are considered in Scheme 3. In path A, the reaction of acetone with the dihydroxo complex gives the hydroxo allyl complex **5** by hydroxo group deprotonation of acetone and tautomerization of the resulting enolate. Hydroxo complexes are effective deprotonating agents and Pd and Pt enolate complexes have been formed by



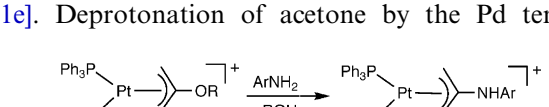
Scheme 3.

reactions with acetone [4,18]. Pd carbonate and dioxygen complexes, $L_2Pd(CO_3)$ and $L_2Pd(O_2)$, are also deprotonating agents and their reaction with the acidic ketone $AcCH_2C(O)CH_2Ac$ yields $L_2M(\eta^3$-AcCHC(O)CHAc), a deprotonated analog of **5** [17a,17b]. (Deprotonated **5**, $(Ph_3P)_2Pd(\eta^3$-$CH_2C(O)CH_2)$ is known [15b].) This reaction is essentially equivalent to the first reaction of path A except that there are 2 equiv. of base per metal with the carbonate and dioxygen complexes. As a result the deprotonated analog of **5** is isolated.

The second reaction of path A requires aminolysis of **5**. The Pt analog of **5** [14b] has been isolated (from the hydrolysis of the Pt analog of **4**) and, although reactions with amines have not been reported, the analogous alkoxo allyl complex **6** does react with amines to give Pt analogs of **3** (Scheme 4) [14c].

An obvious problem with path A is that the dihydroxo complex **1** and the hydroxo amido complex **2** are stable in acetone in the absence of added amine. (Complex **1** is prepared in an acetone/CH_2Cl_2 mixture.) Path A could still be followed if the reaction is amine catalyzed, probably by cleavage of the μ-hydroxo bridge [11e]. Deprotonation of acetone by the Pd terminal hydroxo complex $[Pd(PPh_3)_2(MeCN)(OH)]^+$ has been reported [18a].

In path B of Scheme 3, the absence of acetone reactivity with **1** and **2** is accommodated by prior reaction of aniline with acetone to form the imine. The imine, or its eneamine tautomer, then reacts with the dihydroxo complex **1** (or **2**) cleaving the bridge with loss of a proton to the hydroxo group. This reaction is essentially equivalent to the reported reactions of the carbonate and dioxygen complexes $L_2Pd(CO_3)$ and $L_2Pd(O_2)$ with $AcCH_2C(O)CH_2Ac$ except that there is one less base equivalent per metal with the bridging dihydroxo complex. As a result the protonated form, **3**, is isolated.



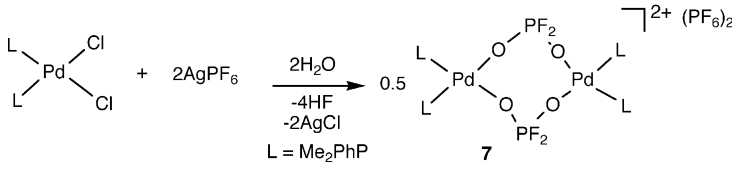
Scheme 4.

3.3. $[Pd(PMe_2Ph)_2(\mu\text{-}PF_2O_2)]_2(PF_6)_2$ (7)

In an attempt to prepare the PMe_2Ph analog of **1** as the PF_6^- salt, $Pd(PMe_2Ph)_2Cl_2$ was treated with $AgPF_6$ in wet acetone. The ^{31}P NMR spectrum of the isolated product is too complex for $[Pd(PMe_2Ph)_2(\mu\text{-}OH)]_2(PF_6)_2$ and an X-ray diffraction study reveals the product to be $[Pd(PMe_2Ph)_2(\mu\text{-}PF_2O_2)]_2(PF_6)_2$ (**7**), evidently formed by partial hydrolysis of half of the PF_6 anions (Scheme 5). Similar hydrolysis products have been previously reported [19]. A drawing of the cationic portion is given in Fig. 3. A summary of crystal and data collection parameters is given in Table 1. Selected distances and angles are listed in Table 4.

4. Conclusions

The dihydroxo bridged palladium complex behaves similarly to the Pt analog and reacts with 1 equiv. or excess aromatic amine in dichloromethane to yield only a single amido-hydroxo exchange giving the mixed bridge hydroxo amido complex. In acetone, the solvent participates in the reaction chemistry, most likely via amine catalyzed acetone deprotonation, and yields the amido allyl complex **3**. The isolation of **7** indicates that PF_6^- is susceptible to hydrolysis under conditions commonly used in the synthesis of bridged Pt and Pd hydroxo complexes. The hydrolysis product ($F_2PO_2^-$) may interfere with the formation of the hydroxo complex and should be avoided when a hydroxo complex is desired.



Scheme 5.

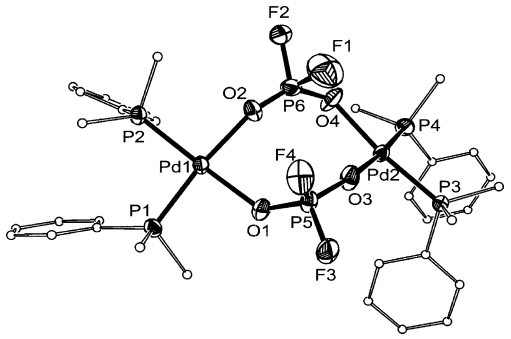


Fig. 3. Drawing of the cationic portion of $[Pd(PMe_2Ph)_2(\mu\text{-}PF_2O_2)]_2(PF_6)_2$ (**7**). Hydrogen atoms are omitted for clarity. Arbitrary spheres represent aryl group carbon atoms and hydrogen atoms; all other atoms are represented by 50% probability thermal ellipsoids.

Table 4
Selected distances (Å) and angles (°) for $[Pd(PMe_2Ph)_2(\mu\text{-}PF_2O_2)]_2(PF_6)_2$ (**7**)

Bond distances			
Pd1–P1	2.2282(8)	Pd1–P2	2.2349(8)
Pd1–O1	2.126(2)	Pd1–O2	2.122(2)
Pd2–O3	2.128(2)	Pd2–O4	2.118(2)
Pd2–P3	2.2333(8)	Pd2–P4	2.2280(8)
Bond angles			
P1–Pd1–P2	93.70(3)	P4–Pd2–P3	93.62(3)
O2–Pd1–O1	85.05(9)	O4–Pd2–P4	88.12(7)
O2–Pd1–P1	173.15(7)	O3–Pd2–P4	174.09(7)
O1–Pd1–P1	88.23(7)	O4–Pd2–P3	171.28(9)
O2–Pd1–P2	93.13(7)	O3–Pd2–P3	91.74(7)
O1–Pd1–P2	173.26(7)	O4–Pd2–O3	86.96(9)

5. Supplementary material

Full crystal structure information has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 185901–185903 for compounds **2**, **3** and **7**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Division of Chemical Sciences, Office of Basic Energy, Sciences, Office of Energy Research, U.S. Department of Energy (grant # DF-FG02-88ER13880) for support of this work. A grant from the National Science Foundation provided a portion of the funds for the purchase of X-ray (CHE-9011804) and NMR (PCM 8115599 and CHE 89-08304) equipment.

References

[1] (a) R.F. Heck, Palladium Reagents in Organic Synthesis, Academic Press, San Diego, 1985;
(b) J. Tsuji, Palladium Reagents and Catalysts, Wiley, New York, 1995.
[2] (a) J.F. Hartwig, Angew. Chem., Int. Ed. Engl. 37 (1998) 2047;
(b) J.P. Wolfe, S. Wagaw, J.F. Marcoux, S.L. Buchwald, Acc. Chem. Res. 31 (1998) 805.
[3] E. Nieddu, M. Cataldo, F. Pinna, G. Strukul, Tetrahedron Lett. 40 (1999) 6987.
[4] A. Fujii, E. Hagiwara, M. Sodeoka, J. Am. Chem. Soc. 121 (1999) 5450.
[5] R. Gavagnin, M. Cataldo, F. Pinna, G. Strukul, Organometallics 17 (1998) 661.
[6] (a) H.E. Bryndza, W. Tam, Chem. Rev. 88 (1988) 1163;
(b) M.D. Fryzuk, C.D. Montgomery, Coord. Chem. Rev. 95 (1989) 1.
[7] (a) P.R. Sharp, J. Chem. Soc., Dalton Trans. (2000) 2647;
(b) P.R. Sharp, Comments Inorg. Chem. 21 (1999) 85.
[8] S. Kannan, A.J. James, P.R. Sharp, J. Am. Chem. Soc. 120 (1998) 215.
[9] G.W. Bushnell, K.R. Dixon, R.G. Hunter, J.J. McFarland, Can. J. Chem. 50 (1972) 3694.
[10] E.A. Allen, W. Wilkinson, J. Inorg. Nucl. Chem. 36 (1974) 1663.
[11] (a) N.W. Alcock, P. Bergamini, T.J. Kemp, P.G. Pringle, S. Sostero, O. Traverso, Inorg. Chem. 30 (1991) 1594;
(b) J. Ruiz, M.T. Martínez, C. Vicente, G. García, G. López, P.A. Chaloner, P.B. Hitchcock, Organometallics 12 (1993) 4321;
(c) M.S. Driver, J.F. Hartwig, J. Am. Chem. Soc. 118 (1996) 4206;
(d) J. Ruiz, N. Cutillas, J. Samperdo, G. López, J.A. Hermoso, M. Martínez-Ripoll, J. Organomet. Chem. 526 (1996) 67;
(e) M.S. Driver, J.F. Hartwig, Organometallics 16 (1997) 5706;
(f) J. Ruiz, V. Rodriguez, G. Lopez, J. Casabo, E. Molins, C. Miravitlles, Organometallics 18 (1999) 1177;
(g) S. Kannan, A.J. James, P.R. Sharp, Polyhedron 19 (2000) 155.
[12] J.J. Li, W. Li, A.J. James, T. Holbert, T.P. Sharp, P.R. Sharp, Inorg. Chem. 38 (1999) 1563.
[13] A.J. Chen, C.C. Su, F.Y. Tsai, J.J. Lee, T.M. Huang, C.S. Yang, G.H. Lee, Y. Wang, J.T. Chen, J. Organomet. Chem. 569 (1998) 39.
[14] (a) T.M. Huang, J.T. Chen, G.H. Lee, Y. Wang, J. Am. Chem. Soc. 115 (1993) 1170;
(b) T.M. Huang, R.H. Hsu, C.S. Yang, J.T. Chen, G.H. Lee, Y. Wang, Organometallics 13 (1994) 3657;
(c) F.Y. Tsai, H.W. Chen, J.T. Chen, G.H. Lee, Y. Wang, Organometallics 16 (1997) 822;
(d) A.J. Chen, C.C. Su, F.Y. Tsai, J.J. Lee, T.M. Huang, C.S. Yang, G.H. Lee, Y. Wang, J.T. Chen, J. Organomet. Chem. 569 (1998) 39.
[15] (a) A. Ohsuka, T. Fujimori, T. Hirao, H. Kurosawa, I. Ikeda, J. Chem. Soc., Chem. Commun. (1993) 1039;
(b) A. Ohsuka, T. Hirao, H. Kurosawa, I. Ikeda, Organometallics 14 (1995) 2538;
(c) A. Ohsuka, T.W. Wardhana, H. Kurosawa, I. Ikeda, Organometallics 16 (1997) 3038.
[16] (a) M.W. Baize, J.L. Furilla, A. Wojcicki, Inorg. Chim. Acta 223 (1994) 1;
(b) M.W. Baize, V. Plantevin, J.C. Gallucci, A. Wojcicki, Inorg. Chim. Acta 235 (1995) 1;
(c) M.W. Baize, P.W. Blosser, V. Plantevin, D.G. Schimpff, J.C. Gallucci, A. Wojcicki, Organometallics 15 (1996) 164.
[17] (a) R.D.W. Kemmitt, P. McKenna, D.R. Russell, L.J.S. Sherry, J. Chem. Soc., Dalton Trans. (1985) 259;
(b) A. Imran, R.D.W. Kemmitt, A.J.W. Markwick, P. McKenna, D.R. Russell, L.J.S. Sherry, J. Chem. Soc., Dalton Trans. (1985)

549;
(c) M.D. Jones, R.D.W. Kemmitt, J. Fawcett, D.R. Russell, J. Chem. Soc., Chem. Commun. (1986) 427;
(d) K.W. Chiu, W. Henderson, R.D.W. Kemmitt, L.J.S. Prouse, D.R. Russell, J. Chem. Soc., Dalton Trans. (1988) 427;
(e) R.D.W. Kemmitt, P. McKenna, D.R. Russell, L.J.S. Prouse, J. Chem. Soc., Dalton Trans. (1989) 345.

[18] (a) A.C. Albeniz, N.M. Catalina, P. Espinet, R. Redon, Organometallics 18 (1999) 5571;
(b) J. Ruiz, V. Rodriguez, N. Cutillas, M. Pardo, J. Perez, G. Lopez, Organometallics 20 (2001) 1973;
(c) T.G. Appleton, M.A. Bennett, Inorg. Chem. 17 (1978) 738;
(d) D.P. Arnold, M.A. Bennett, J. Organomet. Chem. 199 (1980) 119.

[19] Leading references: (a) S. Mihan, K. Sunkel, W. Beck, Chem. Eur. J. 5 (1999) 745;
(b) K. Matsumoto, Y. Sano, M. Kawano, H. Uemura, J. Matsunami, T. Sato, Bull. Chem. Soc. Jpn. 70 (1997) 1239;
(c) S. Kitagawa, M. Kondo, S. Kawata, S. Wada, M. Maekawa, M. Munakata, Inorg. Chem. 34 (1995) 1455;
(d) N.G. Connelly, T. Einig, G.G. Herbosa, P.M. Hopkins, C. Mealli, A.G. Orpen, G.M. Rosair, F. Viguri, J. Chem. Soc., Dalton Trans. (1994) 2025.