JOM 23711

Synthesis and characterization of hydroxo, pyrazolato and carboxylato derivatives of the $PdR(PPh_3)$ moiety ($R = C_6F_5$ or C_6Cl_5)

José Ruiz, Consuelo Vicente, José M. Martí, Natalia Cutillas, Gabriel García and Gregorio López

Departamento de Química Inorgánica, Universidad de Murcia, 30071-Murcia (Spain)

(Received February 2, 1993)

Abstract

The hydroxo-complexes $[\{PdR(PPh_3)(\mu\text{-}OH)\}_2]$ ($R = C_6F_5$ or C_6Cl_5) have been obtained by reaction of the corresponding $[\{PdR(PPh_3)(\mu\text{-}Cl)\}_2]$ complexes with NBu_4OH in acetone. In this solvent, the reaction of the hydroxo-bridged complexes with pyrazole (Hpz) and 3,5-dimethylpyrazole (Hdmpz) in 1:2 molar ratio leads to the formation of the new complexes $[\{Pd(C_6F_5)(PPh_3)(\mu\text{-azolate})\}_2]$ and $[\{Pd(C_6Cl_5)(PPh_3)\}_2(\mu\text{-}OH)(\mu\text{-azolate})]$ (azolate = pz or dmpz). The reaction of the bis(μ-hydroxo) complexes with Hpz and Hdmpz in acetone in 1:1 molar ratio has also been studied, and the resulting product depends on the organic radical (C_6F_5 or C_6Cl_5) as well as the azolate (pz or dmpz). The identity of the isomer obtained has been established in every case by NMR (^1H, ^{19}F and ^{31}P) spectroscopy. The reaction of the bis(μ-hydroxo) complexes with oxalic (H_2Ox) and acetic (HOAc) acids yields the binuclear complexes $[\{PdR(PPh_3)\}_2(\mu\text{-}Ox)]$ ($R = C_6F_5$ or C_6Cl_5) and $[\{Pd(C_6F_5)(PPh_3)(\mu\text{-}OAc)\}_2]$, respectively. $[\{Pd(C_6F_5)(PPh_3)(\mu\text{-}OH)\}_2]$ reacts with PPh_3 in acetone in 1:2 ratio giving the mononuclear complex *trans*-$[Pd(C_6F_5)(OH)(PPh_3)_2]$, whereas the pentachlorophenylhydroxo complex does not react with PPh_3, even under forcing conditions.

1. Introduction

The recent interest in the chemistry of late transition-metal hydroxides is due to their relevance to some catalytic organic syntheses, in which they are believed to be intermediates [1]. The syntheses of a number of hydroxo-bridged binuclear nickel, palladium, and platinum complexes of the types $[\{MR_2(\mu\text{-}OH)\}_2]^{2-}$ (M = Ni ($R = C_6F_5$) [2], Pd ($R = C_6F_5$ [3], C_6Cl_5 [4] or $C_6H_2F_3$-2,4,6 [5]) or Pt ($R = C_6F_5$ [6]) have recently been reported and their chemical behaviour towards some electrophiles has been studied. Some non-organometallic hydroxo-bridged binuclear complexes have also been reported [7,8]. Although some nickel complexes of the type $[\{NiLR(\mu\text{-}OH)\}_2]$ [L = PMe_3 (R = Me [9], $CH_2C_6H_4$-*o*-Me [10], CH_2SiMe_3, CH_2CMe_2Ph, $CH_2C_6H_5$ [11]), or PPh_3 (R = $CClCCl_2$) [12]] have been described, no binuclear uncharged hydroxo-palladium complex is known.

The aim of the present work was to obtain a better knowledge of the chemistry of the binuclear hydroxo-complexes of palladium. For this purpose new hydroxo-bridged binuclear palladium(II) complexes containing two different ligands *trans* to the OH bridges have now been prepared and their reactions with azoles, acetic and oxalic acids, and triphenylphosphine have been studied. A preliminary report of this work has been published [13].

Correspondence to: Professor G. López.

2. Results and discussion

The metathesis of chloride by hydroxide in the corresponding chloro-bridged complexes leads to the formation of the bis(μ-hydroxo) complexes **I** and **II**, according to eqn. (1).

$$[\{Pd(PPh_3)R(\mu\text{-}Cl)\}_2] + 2NBu_4OH \rightarrow [\{Pd(PPh_3)R(\mu\text{-}OH)\}_2] + 2NBu_4Cl \quad (1)$$

$R = C_6F_5$ (**I**) or C_6Cl_5 (**II**)

This method has previously been used for the preparation of other palladium and platinum hydroxo complexes [4,6,14].

Both complexes were characterized by partial elemental analyses and spectroscopic data (Tables 1 and 2). The IR spectra show the bands attributed to C_6F_5 (1500, 1450, 1050, 950 and 800 cm^{-1}) [15] and C_6Cl_5 (1315, 1285, 1220, 830, 670 and 610 cm^{-1}) [16], respectively. The bands at 800 (C_6F_5) and 830 (C_6Cl_5) cm^{-1} are derived from the so-called "X-sensitive" mode [15]

0022-328X/93/$6.00

TABLE 1. Analytical data, yields and physical properties for the palladium complexes

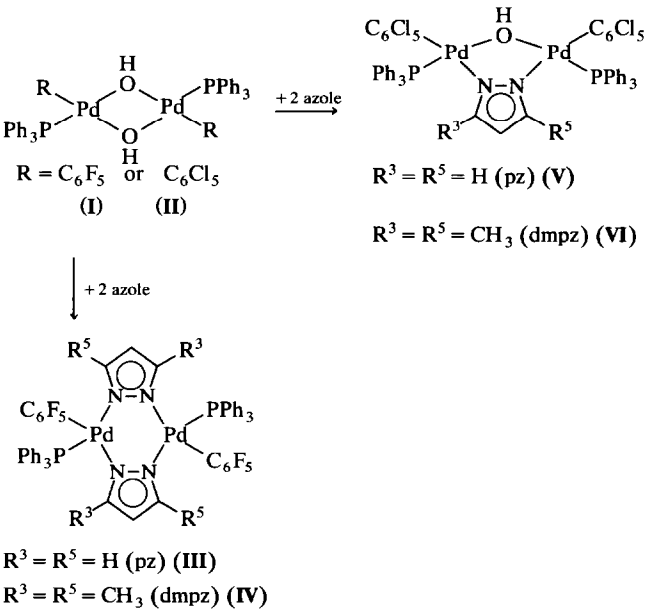
Complex	M.p. [a] (°C)	Analysis (%) [b]			Selected IR bands (cm^{-1}) [c]	
		C	H	N	X-sensitive	Others
I	173	52.8 (52.1)	3.4 (2.9)		790	3600 (ν(OH))
II	278	45.9 (45.4)	3.2 (2.5)		840	3620 (ν(OH))
III	292	53.4 (53.8)	3.6 (3.0)	4.6 (4.6)	790	
IV	287	55.9 (55.1)	4.2 (3.7)	4.0 (4.4)	780	
V	317	47.2 (46.4)	3.5 (2.6)	2.0 (2.1)	835	3600 (ν(OH))
VI	280	48.5 (47.2)	3.5 (2.8)	2.2 (2.1)	840	3620 (ν(OH))
VII	246	53.7 (53.0)	3.4 (3.0)	2.7 (2.4)	790	3600 (ν(OH))
IX	311	46.7 (46.4)	2.7 (2.6)	2.0 (2.1)	835	3600 (ν(OH))
XI	265	51.0 (51.8)	2.7 (2.6)		800	1605 ($\nu_a(CO_2^-)$) 1360 ($\nu_s(CO_2^-)$)
XII	301	45.2 (45.4)	2.4 (2.3)		840	1610 ($\nu_a(CO_2^-)$) 1365 ($\nu_s(CO_2^-)$)
XIII	185	52.4 (52.5)	3.3 (3.1)		790	1580 ($\nu_a(CO_2^-)$) 1420 ($\nu_s(CO_2^-)$)

[a] With decomposition. [b] Calculated values in parentheses. [c] Nujol mulls.

and behave like ν(Pd–C) bands. A medium band at 3610–3600 cm^{-1} is assigned to the stretching mode of the OH bridges. The ^1H, ^{19}F and $^{31}P\{^1H\}$ NMR data listed in Table 2 show unambiguously that **I** and **II** exist in chloroform solution exclusively as the *trans* isomers (Scheme 1), since the ^1H spectra exhibit a unique high-field resonance for the OH groups consisting of a doublet arising from coupling to ^{31}P of the phosphine *trans* to OH. No coupling to ^{31}P of the phosphine *cis* to OH is observed. The ^{19}F spectrum of complex **I** shows the expected NMR pattern for two equivalent C_6F_5 groups and the magnitude of J(PF) for the *ortho*-fluorine is consistent with the values found in other palladium complexes containing the *cis*-Pd($C_6F_3H_2$)(phosphine) arrangement [17].

The reaction of the bis(hydroxo) complexes $[\{MR_2(\mu\text{-OH})\}_2]^{2-}$ (M = Ni, Pd, or Pt) with protic electrophiles (HL or HLL) has previously been used for the synthesis of complexes of the types $[\{MR_2(\mu\text{-L}\}_2]^{2-}$, $[\{MR_2\}_2(\mu\text{-OH})(\mu\text{-L})]^{2-}$, and $[MR_2(LL)]^-$ [2,3,18–21]. Of the protic electrophiles, azoles have been most used because they produce the very versatile azolate anions on deprotonation, and these can act as mono- or bi-dentate ligands [22]. When complex **I** was treated with pyrazoles (Hpz) and 3,5-dimethylpyrazole (Hdmpz) in acetone in 1:2 molar ratio, it yielded the corresponding azolate-bridged complexes $[\{Pd(C_6F_5)(PPh_3)(\mu\text{-azolate})\}_2]$ (azolate = pz (**III**) or dmpz (**IV**)). If the C_{2h} symmetry is assigned to complex **III** (Scheme 1), a set of three signals arising from 3-, 4- and 5-H atoms of the pz ring should be observed in the ^1H spectrum (the C_{2v} isomer, with a long *cis* arrangement of the phosphines, should give two sets of signals, each consisting of two peaks with relative intensities of 2 (3- and 5-H):1 (4-H)) [23–25]. The observed spectrum (Table 2) shows two peaks at δ 6.25 and 5.57 assigned to 3- and 4-H, respectively, but a further peak was suspected to be masked by the multiplet signal from the *ortho*- and *para*-hydrogen atoms of the phenyl rings since its relative intensity (20 H) is greater than the theoretical value of 18 H. This was confirmed when a ^1H-^1H COSY experiment was performed; a third resonance at δ 7.37 (for 5-H) correlated to the 5.57 ppm signal. The signals from 3- and 4-H appear as a pseudotriplet and a pseudoquartet, respectively, due to coupling to the ^{31}P nucleus of the phosphine *trans* to the pyrazolate ring and the accidental coincidence of the coupling constants ($J(PH^3) \approx J(PH^4) \approx J(H^3H^4) \approx J(H^4H^5) = 1.5$–$2.1$ Hz; $J(H^3H^5) = 0$). On irradiation of the 4-H peak, the original pseudotriplet from 3-H was transformed into a well-resolved doublet ($J(PH^3) = 1.5$ Hz) and one of the peaks of the phenyl multiplet was affected. On irradiation of the signal at *ca.* 7.37 ppm (5-H), the peaks from 3- and 4-H were seen as pseudotriplets.

The dmpz complex **IV** showed one ^{31}P resonance and two different signals for the methyl protons of the dmpz ligand, but the presence of only one signal for the 4-H of the dmpz ring suggests that the *trans*



Scheme 1.

TABLE 2. NMR data (J in Hz) for the palladium complexes (in $CDCl_3$)

Complex	^1H $\delta(SiMe_4)$	^{31}P $\delta(H_3PO_4)$	^{19}F δ ($CFCl_3$)
I	7.6 (m, 12 H, H_o of Ph)	30.5 (t, J(PFo) = 9.9)	−117.2 (dd, 4 F_o, J(om) = 22.0, J(PFo) = 9.9)
	7.4 (m, 18 H, H_p + H_m of Ph)		−161.2 (t, 2 F_p, J(mp) = 19.8)
	−1.58 (d, 2 H, OH, J(PH) = 3.4)		−163.9 (m, 4 F_m)
II	7.7 (m, 12 H, H_o of Ph)	28.4 (s)	
	7.3 (m, 18 H, H_p + H_m of Ph)		
	−1.66 (d, 2 H, OH, J(PH) = 2.2)		
III [a]	7.4–7.3 (m, 20 H, H_p + H_o of Ph and 5-H of pz)	24.9 (s)	−113.0 (d, 2 F_o, J(om) = 25.9)
			−119.7 (d, 2 F_o, J(om) = 28.5)
	7.08 (m, 12 H, H_m of Ph)		−161.8 (t, 2 F_p, J(mp) = 20.0)
	6.25 (pseudo t, 2 H, 3-H of pz)		−162.7 (m, 2 F_m)
	5.57 (pseudo q, 2 H, 4-H of pz)		−163.2 (m, 2 F_m)
IV	7.2-7.0 (m, 30 H, Ph)	17.1 (s)	−104.7 (br, 2 F_o)
	5.32 (s, 2 H, 4-H of dmpz)		−114.8 (br, 2 F_o)
	2.31 (s, 3 H, 3-Me of dmpz)		−163.2 (br, 2 F_m + 2 F_p)
	1.36 (s, 3 H, 5-Me of dmpz)		−165.1 (br, 2 F_m)
V	7.46 (m, 12 H, H_o of Ph)	26.6 (s)	
	7.30 (m, 6 H, H_p of Ph)		
	7.13 (m, 12 H, H_m of Ph)		
	6.64 (dd, 2 H, 3- and 5-H of pz, J(HH) ≈ J(PH) = 2.0)		
	5.91 (tt, 1 H, 4-H of pz, J(HH) = 2.0, J(PH) = 1.8)		
	−2.96 (t, 1 H, OH, J(PH) = 1.7)		
VI	7.45 (m, 12 H, H_o of Ph)	28.0 (s)	
	7.26 (m, 6 H, H_p of Ph)		
	7.05 (m, 12 H, H_m of Ph)		
	5.61 (s, 1 H, 4-H of dmpz)		
	1.43 (s, 6 H, 3- and 5-Me of dmpz)		
	−3.09 (t, 1 H, OH, J(PH) = 1.7)		
VII	7.33 (m, 12 H, H_o of Ph)	28.5 (t, J(PFo) = 8.6)	−117.3 (dd, 4 F_o, J(om) = 28.2, J(PFo) = 8.6)
	7.23 (m, 6 H, H_o of Ph)		−161.5 (t, 2 F_p, J(mp) = 19.2)
	7.10 (m, 12 H, H_m of Ph)		−163.4 (m, 4 F_m)
	6.54 (dd, 2 H, 3- and 5-H of pz, J(HH) ≈ J(PH) = 2.0)		
	5.88 (tt, 1 H, 4-H of pz, J(HH) = 2.0; J(PH) = 1.8)		
	−2.57 (t, 1 H, OH, J(PH) = 2.0)		
VIII	7.7–7.1 (m, 30 H, Ph)	27.4 (s)	−117.1 (d, 2 F_o, J(om) = 31.6)
	6.60 (d, 1 H, 5-H of pz, J(HH) ≈ 2.0)	33.3 (s)	−119.1 (d, 2 F_o, J(om) = 30.2)
			−162.5 (t, 2 Fp, J(mp) = 20.6)
	6.23 (d, 1 H, 3-H of pz, J(HH) ≈ 1.7)		−164.6 (m, 4 F_m)
	5.55 (dd, 1 H, 4-H of pz)		
	−0.83 (br, 1 H, OH)		
IX	7.6–7.1 (m, 30 H, Ph)	32.0 (s)	
	6.74 (d, 1 H, 5-H of pz, J(HH) = 2.0)	25.2 (s)	
	6.27 (d, 1 H, 3-H of pz, J(HH) = 1.6)		
	5.56 (dd, 1 H, 4-H of pz)		
	−0.79 (br, 1 H, OH)		
X	7.6–7.1 (m, 30 H, Ph)	23.3 (s)	−116.9 (br, 2 F_o)
	7.05 (br, 2 H, 3-H and 5-H of pz)		−119.1 (d, 2 F_o, J(om) = 27.1)
	6.16 (d, 2 H, 3-H and 5-H of pz, J(HH) = 1.9)		−161.9 (t, 2 F_p, J(mp) = 20.0)
			−162.7 (m, 2 F_m)
	5.86 (br, 1 H, 4-H of pz)		−163.8 (m, 2 F_m)
	5.44 (t, 1 H, 4-H of pz, J(HH) = 1.9)		

TABLE 2 (*Continued*)

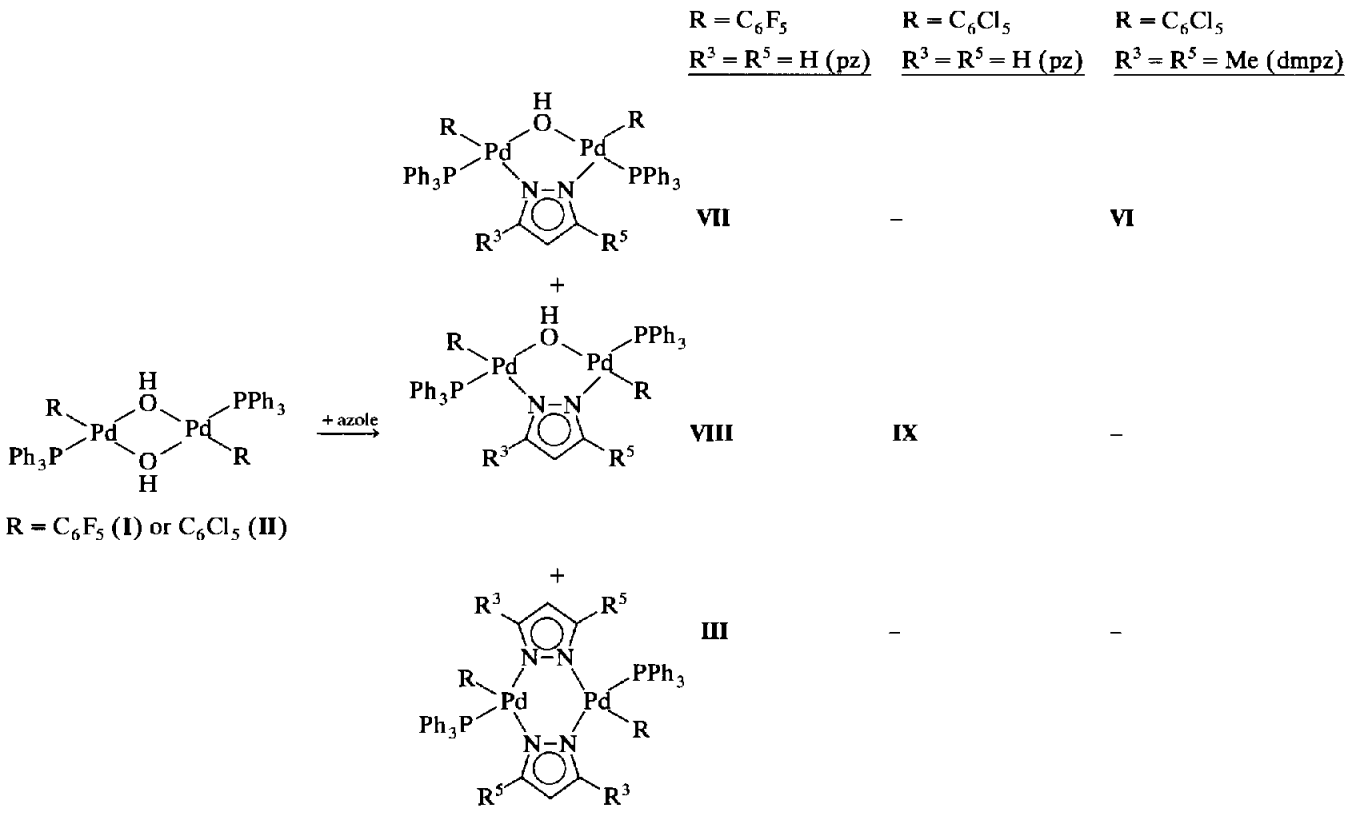
Complex	^{1}H δ(SiMe$_4$)	^{31}P δ(H$_3$PO$_4$)	^{19}F δ (CFCl$_3$)
XI	7.6–7.2 (m, 30 H, Ph)	30.3 (t, J(PFo) = 12.4)	−120.5 (dd, 4 F$_o$, J(om) = 22.0, J(PFo) = 12.4) −161.2 (t, 2 F$_p$, J(mp) = 19.2) −164.3 (m, 4 F$_m$)
XII	7.6–7.2 (m, 30 H, Ph)	27.9 (s)	
XIII	7.6–7.2 (m, 30 H, Ph) 1.89 (br, 6 H, OAc)	28.2 (s)	−117.2 (br, 4 F$_o$) −160.8 (br, 2 F$_p$) −163.4 (br, 4 F$_m$)

[a] See text for discussion of the ^{1}H NMR spectrum.

configuration (Scheme 1) should also be assigned to this complex. The two signals observed in the *ortho*- and *meta*-fluorine regions of the ^{19}F spectra of **III** and **IV** indicate that the rotation of the C_6F_5 groups around the Pd–C bond is hindered.

The reaction of complex **II** with Hpz and Hdmpz in 1:2 molar ratio always led to the corresponding complexes [{Pd(C_6Cl_5)(PPh$_3$)}$_2$(μ-OH)(μ-azolate)] (azolate = pz (**V**) or dmpz (**VI**) which were formulated as shown in Scheme 1, with the two C_6Cl_5 groups *cis* to the OH bridge. The ^{1}H NMR pattern observed in the spectra of complexes **V** and **VI** is consistent with this geometrical arrangement; a triplet due to the OH bridge with two phosphines *trans* to it and two signals with relative intensities of 1:2 (pz complex) or 1:6 (dmpz complex). The ^{31}P{^{1}H} spectra show a unique resonance which is also consistent with the *cis* configuration. Attempts to prepare the bis(μ-azolate) complexes similar to **III** and **IV** were unsuccessful.

The reactions of complexes **I** and **II** with pyrazole and 3,5-dimethylpyrazole in 1:1 molar ratio were also tried (Scheme 2). Complex **II** gives only the μ-hydroxo-μ-azolate complexes, **VI** and **IX**. Complex **IX** was identified by NMR spectroscopy as the geometrical isomer



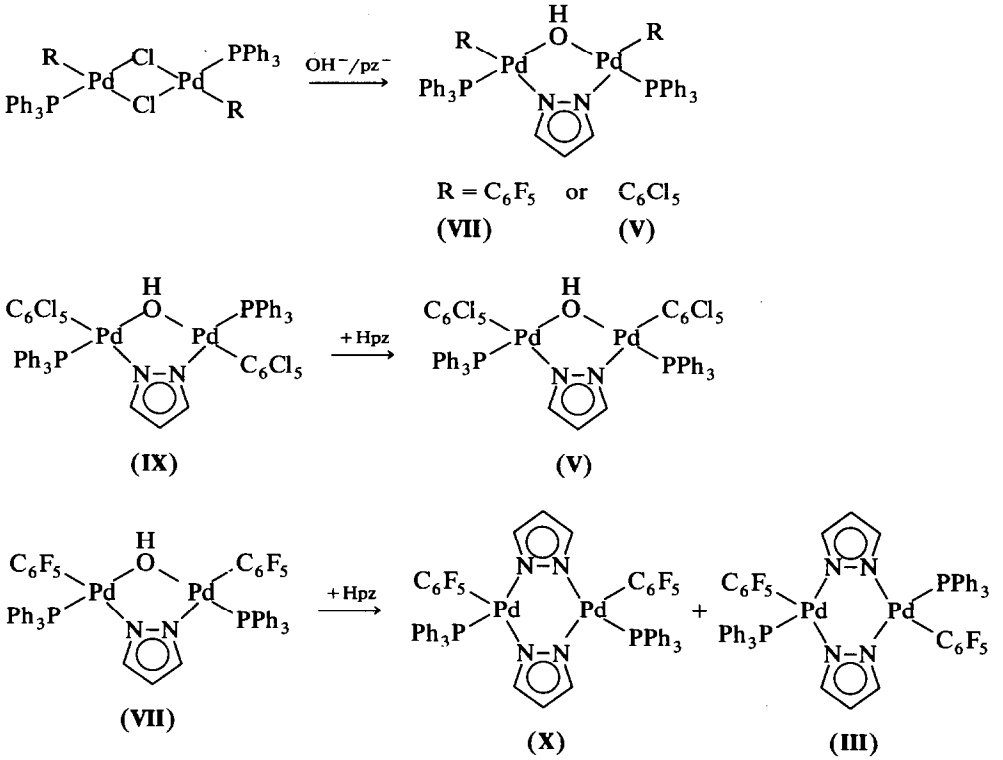
Scheme 2.

of **V** in Scheme 2, since it gives two signals in the ^{31}P spectrum and a set of three ^1H signals for the bridging pz. However, in the presence of pyrazole, **IX** is converted into the isomer **V** (Scheme 3) which is the reaction product obtained when the same reaction is carried out in 1:2 molar ratio.

A more complex result is obtained in the reaction of complex **I** with Hpz under the same conditions. The ^1H NMR spectrum of the isolated solid (see Experimental section) showed that it was a mixture of μ-hydroxo-μ-azolate and bis(μ-azolate) complexes (Scheme 2) which we were not able to separate. However, complex **VII** could be prepared as a pure compound by a different route, the metathesis of the bridging chlorides in $[\{Pd(PPh_3)R(\mu\text{-}Cl)\}_2]$ by OH^-/pz^-, and the same reaction with the pentachlorophenyl analogue yields complex **V** (Scheme 3). The *cis* configuration assigned to **VII** is consistent with its NMR data; only one ^{31}P resonance, a triplet signal for the OH bridge due to coupling to two phosphines *trans* to it, and the expected two signals (relative intensities of 2:1) for a symmetrical bridging pyrazolate. The ^1H, $^{31}P\{^1H\}$ and ^{19}F spectra of **VIII** show that there are three different protons in the pz ligand, two different phosphines and two different C_6F_5 groups. The NMR data of the solid isolated from the reaction of complex **I** with Hdmpz indicated the presence of a similar mixture but no attempts were made to study this complex mixture further because the unavailability of a genuine sample of μ-OH-μ-dmpz complex prevented us from making reliable assignments.

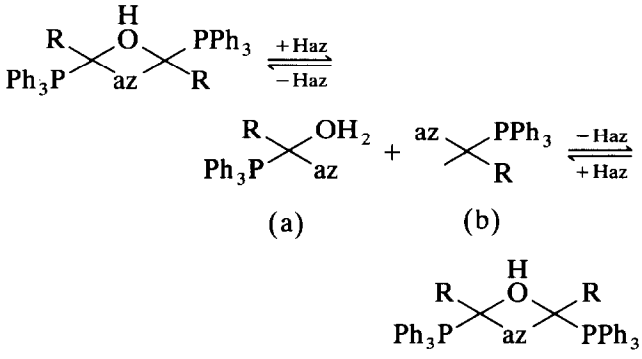
Rather unexpectedly, the reaction of complex **VII** with pyrazole (1:1 molar ratio) does not lead to the formation of **III** as the unique reaction product; instead a mixture of **III** and the new compound **X** is formed (Scheme 3). This mixture could not be resolved but **X** was identified by ^1H NMR spectroscopy. The ^1H NMR data in Table 2 show the presence of two different pz ligands in **X**, the signals at δ 7.05 and 5.86 being assigned to the pz ring *trans* to the phospine molecules.

A satisfactory interpretation of the experimental results implies the existence of a mechanism for *cis-trans* isomerization of the μ-hydroxo-μ-azolate complexes catalyzed by the azole (Haz). We suggest that the Haz-catalyzed interconversion of both isomers takes place *via* the monomeric intermediates $[R(PPh_3)Pd(az)(OH_2)]$ (a) and $[R(PPh_3)Pd(az)(solvent)]$ (b) resulting from the protonation of *trans*- or *cis*-$[R(PPh_3)Pd(\mu\text{-}OH)(\mu\text{-}az)Pd(PPh_3)R]$ by Haz. The elimination of Haz from (a) followed by recombination of the two



Scheme 3.

monomeric fragments gives the *cis* isomer, but elimination of Haz between (a) and (b) and subsequent recombination yields the *trans* isomer.



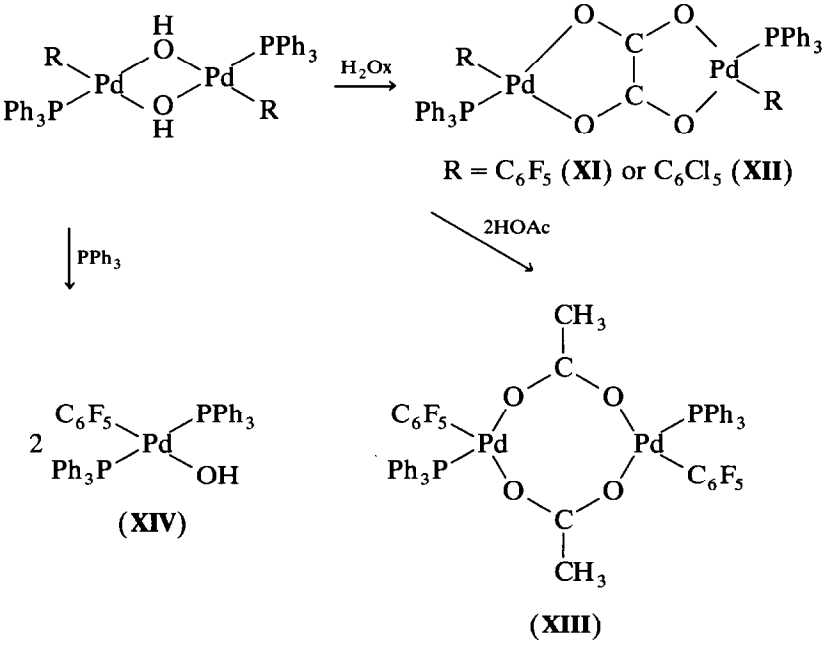
The result is a *cis–trans* mixture at equilibrium and the identity of the isolated solid will be dependent on the solvent as well as on the R (C_6F_5 or C_6Cl_5) and az.

The failure to observe bis(azolato) complexes with C_6Cl_5 may be attributed to the greater steric requirement of this group compared to C_6F_5. Both the formation of the *cis* complexes **V** and **VI** from **II** and the isomerization of **IX** to **V** are consistent with the suggested mechanism for isomerization, because the bulky C_6Cl_5 ligand should facilitate the elimination of Haz from the aqua complex (a) and, consequently, the formation of the *cis* isomer. The conversion of **VII** into **III** and **X** may be explained on the basis of the previous isomerization of **VII** (*cis*) to give an approximately equimolecular mixture of **VII** (*cis*) and **VIII** (*trans*); the deprotonation of these by Hpz leads to the formation of the corresponding bis(pyrazolato) complexes **X** (*cis*) and **III** (*trans*). Similar isomeric *cis–trans* mixtures have been reported from the conversion of hydroxo-bridged complexes to amido-bridged diplatinum(II) complexes [25].

The reactions of the di-μ-hydroxo complexes **I** and **II** with oxalic acid (H_2Ox) in 1:1 molar ratio led to the formation of the corresponding complexes $[\{Pd(PPh_3)R\}_2(\mu\text{-}Ox)]$ (R = C_6F_5 (**X1**), or C_6Cl_5 (**X11**)). Their IR spectra exhibit only two absorptions (Table 1) arising from the *asym* and *sym* ν(OCO) modes of doubly bridging tetradentate oxalate ($\Delta\nu = 245$ cm^{-1}) [26]. Accordingly, we propose the structure shown in Scheme 4 for them, which is similar to that found in $[\{Ni(Me)(PPh_3)\}_2(\mu\text{-}Ox)]$ [27]. Similarly, protonation of the OH bridges in complex **I** by acetic acid gives the bis(μ-acetato) complex **XIII** and concomitant release of water (Scheme 4). The value of $\Delta\nu$ ($\nu_{asym} - \nu_{sym} = 160$ cm^{-1}) for the carboxylate stretching modes appears to be consistent with the presence of bridging bidentate acetate [28].

We also tried the reaction of complex **II** with acetic acid but the NMR spectra showed that the isolated solids were non-reproducible mixtures of hydroxo and acetato complexes.

Complex **I** reacts with PPh_3 to give the mononuclear hydroxo complex $[Pd(C_6F_5)(OH)(PPh_3)_2]$ (**XIV**), which exhibits a unique resonance in the ^{31}P NMR spectrum indicating a *trans* configuration. This complex was



Scheme 4.

previously prepared by Yoshida *et al.* starting from *trans*-$[Pd(C_6F_5)Cl(PPh_3)_2]$ [12]. However, the analogue of **XIV** with the more steric demanding pentachlorophenyl ligand could not been obtained even working under reflux and with an excess of triphenylphosphine.

3. Experimental details

The C, H, and N analyses were carried out with a Perkin-Elmer 240 C microanalyser. Decomposition temperatures were determined on a Mettler TG-50 thermobalance with a heating rate of 10°C min^{-1}. The spectroscopic instruments used were Perkin-Elmer Model 1430 for IR spectra (Nujol mulls) and Varian Unity 300 or Bruker 200E for NMR spectra. The precursors $[\{R(PPh_3)Pd(\mu\text{-}Cl)\}_2]$ ($R = C_6F_5$ or C_6Cl_5) were prepared as described in the literature [29]. Solvents were dried by standard techniques before use.

3.1. Preparation of complexes I and II

To a suspension of $[\{R(PPh_3)Pd(\mu\text{-}Cl)\}_2]$ ($R = C_6F_5$ or C_6Cl_5) (0.088 mmol) in acetone (10 cm^3) was added 20% $[NBu_4]OH$ (aq) (0.176 mmol), with constant stirring for 30 min. After partial evaporation of the solvent under reduced pressure, small portions of methanol were added to precipitate complexes **I** or **II** as white solids which were filtered off and dried at 100°C. Yields: 70% and 87%, respectively.

3.2. Preparation of complexes III and IV from I

The corresponding azole (Hpz or Hdmpz; 0.180 mmol) was added to a solution of **I** (0.090 mmol) in acetone (6 cm^3) with constant stirring for 30 min. The solvent was partially evaporated under vacuum and small portions of water were added to precipitate complexes **III** and **IV** as white solids which were filtered off and air-dried. The ^1H NMR spectrum of complex **III** showed the presence of a small amount of **X**, but pure crystals of **III** were obtained after recrystallization from chloroform/hexane. Yields: 80% (**III**) and 90% (**IV**).

3.3. Preparation of complexes V and VI from II

The corresponding azole (0.168 mmol) was added to a solution of **II** (0.084 mmol) in dichloromethane (6 cm^3). After stirring for 30 min, the solution was concentrated under reduced pressure and addition of hexane caused the precipitation of **V** or **VI** as a white or yellow solid, respectively, which was filtered off and air-dried. Yields: 77% and 57%, respectively.

3.4. Preparation of complexes V and VII from $[\{R(PPh_3)Pd(\mu\text{-}Cl)\}_2]$ ($R = C_6F_5$ or C_6Cl_5)

The corresponding chloro-bridged complex (0.087 mmol) was added to a solution of a 0.087:0.087 molar mixture of pyrazolate and OH^- (prepared from 0.087 mmol of pyrazole and 0.174 mmol of NBu_4OH) in acetone (6 cm^3), and the suspension was stirred at room temperature for 30 min. After partial elimination of the solvent under reduced pressure, the white solid was filtered off and air-dried. Yield: 70% for both compounds.

3.5. Reaction of I and II with Hpz and Hdmpz in 1:1 molar ratio

The corresponding azole (0.090 mmol) was added to a solution of **I** or a suspension of **II** (0.090 mmol) in acetone (5 cm^3). The resulting solution was stirred for 30 min. The solvent was evaporated under vacuum and methanol was added (2 cm^3). The solid was filtered off and air-dried. The results are presented in Scheme 2. Complexes **VI** (yield 76%) and **IX** (yield 77%) were the only products obtained from the reaction of **II** with Hpz but the solid isolated from the reaction of **I** with Hpz (yield 70 mg) was identified by NMR spectroscopy as a mixture of complexes **III**, **VII** and **VIII** in the ratio 30:40:30%, respectively. The ^1H spectrum of the solid isolated from the reaction of **I** with Hdmpz (yield 60 mg) showed the presence of a similar mixture, but individual assignments were not possible.

3.6. Reaction of VII with Hpz

Pyrazole (0.087 mmol) was added to a solution of **VII** (0.087 mmol) in chloroform (5 cm^3). The resulting solution was stirred for 3 h and concentrated under reduced pressure. The addition of hexane precipitated a white solid (80 mg) which was identified by NMR spectroscopy as a mixture of **III** and **X** (55% and 45%, respectively).

3.7. Reaction of IX with Hpz

Pyrazole (0.045 mmol) was added to a suspension of complex **IX** (0.045 mmol) in acetone (30 cm^3). The suspension was boiled under reflux for 6 h and the resulting colourless solution was evaporated to dryness. A small amount of methanol was added and the white solid was filtered off and air-dried. Yield: 83%. The solid was identified as complex **V**.

3.8. Preparation of complex XI

Oxalic acid (0.054 mmol of the dihydrate) was added to a suspension of **I** (0.054 mmol) in acetone (6 cm^3). After stirring for 30 min, the solvent was partially evaporated and a small amount of water was added to complete the precipitation of **XI** as a white solid which was filtered off and air-dried. Yield: 70%.

3.9. Preparation of complex XII

Oxalic acid (0.066 mmol of the dihydrate) was added to a white suspension of **II** (0.066 mmol) in acetone (15

cm^3). The resulting yellowish suspension was stirred for 2.5 h and then the yellow solid **XII** was separated by filtration and air-dried. Yield: 71%.

3.10. Preparation of complex XIII

Acetic acid (0.180 mmol; 10 μl of 99.7% acetic acid) was added to a solution of **I** (0.090 mmol) in dichloromethane (6 cm^3), with constant stirring for 30 min. The solution was concentrated under reduced pressure and the addition of hexane resulted in the precipitation of complex **XIII** as a yellow solid, which was filtered off and air-dried. Yield: 84%.

3.11. Reaction of I with PPh_3

Triphenylphosphine (0.108 mmol) was added to a solution of **I** (0.054 mmol) in acetone (6 cm^3). The solution was stirred for 30 min and concentrated under reduced pressure. On addition of water, complex **XIV** precipitated as a white solid which was filtered off and air-dried. Yield: 60%. The experimental data [satisfactory C and H analysis; IR (Nujol, cm^{-1}): 3590 ν(OH), 795 (X-sensitive); NMR (solvent $CDCl_3$): ^1H $\delta(SiMe_4)$ 7.63 (m) and 7.32 (m) Ph, −2.31 (br) OH; ^{31}P $\delta(H_3PO_4)$ 22.81 (t, $J(PF_o)$ 6.1 Hz)] are consistent with those previously reported [12].

Acknowledgments

Financial support of this work by the DGICYT (project PB91-0574), Spain, is acknowledged. C.V. and J.M.M. thank the Dirección General de Educación y Universidad (Comunidad Autónoma de Murcia) and the Fundación O.N.C.E., respectively, for research grants.

References

1 H.E. Bryndza and W. Tam, *Chem. Rev., 88* (1988) 1163.
2 G. López, G. García, G. Sánchez, J. García, J. Ruiz, J.A. Hermoso, A. Vegas and M. Martínez Ripoll, *Inorg. Chem., 31* (1992) 1518.
3 G. López, J. Ruiz, G. García, C. Vicente, J. Casabó, E. Molins and C. Miravitlles, *Inorg. Chem., 30* (1991) 2605.
4 G. López, J. Ruiz, G. García, J.M. Martí, G. Sánchez and J. García, *J. Organomet. Chem., 412* (1991) 435.
5 G. López, G. García, G. Sánchez, M.D. Santana, J. Ruiz and J. García, *Inorg. Chim. Acta, 188* (1991) 195.
6 G. López, J. Ruiz, G. García, C. Vicente, J.M. Martí, J.A. Hermoso, A. Vegas and M. Martínez Ripoll, *J. Chem. Soc., Dalton Trans.*, (1992) 53.
7 S. Wimmer, P. Castan, F.L. Wimmer and N.P. Johnson, *J. Chem. Soc., Dalton Trans.*, (1989) 403.
8 A.L. Bandini, G. Banditelli, M.A. Cinellu, G. Sanna, G. Minghetti, F. Demartin and M. Manassero, *Inorg. Chem., 28* (1989) 404.
9 H.F. Klein, H.H. Karsch, *Chem. Ber.*, (1973) 1433.
10 E. Carmona, J.M. Marín, M. Paneque, and M.L. Poveda, *Organometallics, 6* (1987) 1757.
11 E. Carmona, J.M. Marín, P. Palma, M. Paneque, and M.L. Poveda, *Inorg. Chem., 28* (1989) 1985.
12 T. Yoshida, T. Okano and S. Otsuka, *J. Chem. Soc., Dalton Trans.*, (1976) 993.
13 G. López, J. Ruiz, G. García, C. Vicente, J.M. Martí and M.D. Santana, *J. Organomet. Chem., 393* (1990) C53.
14 G. López, G. García, J. Ruiz, G. Sánchez, J. García and C. Vicente, *J. Chem. Soc., Chem. Commun.*, (1989) 1045.
15 D.A. Long and D. Steel, *Spectrochim. Acta, 19* (1963) 1955.
16 J. Casabó, J.M. Coronas and J. Sales, *Inorg. Chim. Acta, 11* (1974) 5.
17 G. López, G. García, M.D. Santana, G. Sánchez, J. Ruiz, J.A. Hermoso, A. Vegas and M. Martínez-Ripoll, *J. Chem. Soc., Dalton Trans.*, (1990) 1621.
18 G. López, G. Sánchez, G. García, J. Ruiz, J. García, M. Martínez-Ripoll, A. Vegas and J.A. Hermoso, *Angew. Chem. Int. Ed. Engl., 30* (1991) 716.
19 G. López, J. Ruiz, G. García, C. Vicente, V. Rodríguez, G. Sánchez, J.A. Hermoso and M. Martínez-Ripoll, *J. Chem. Soc., Dalton Trans.*, (1992) 1681.
20 G. López, G. Sánchez, G. García, J. García, A. Martínez, J.A. Hermoso and M. Martínez-Ripoll, *J. Organomet. Chem., 435* (1992) 193.
21 G. López, G. Sánchez, G. García, J. García, A. Sanmartín and M.D. Santana, *Polyhedron, 10* (1991) 2821.
22 S. Trofimenko, *Prog. Inorg. Chem., 34* (1986) 115.
23 D. Carmona, J. Ferrer, F.J. Lahoz, L.A. Oro, J. Reyes and M. Esteban, *J. Chem. Soc., Dalton Trans.*, (1991) 2811.
24 D. Carmona, J. Ferrer, L.A. Oro, M.C. Apreda, C. Foces-Foces, F.H. Cano, J. Elguero, and M.L. Jimeno, *J. Chem. Soc., Dalton Trans.*, (1990) 1463 and refs. therein.
25 N.W. Alcock, P. Bergamini, T.J. Kemp, P.G. Pringle, S. Sostero and O. Traverso, *Inorg. Chem., 30* (1991) 1594.
26 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1986, p. 244.
27 H.F. Klein, T. Wiemer, M.J. Menu, M. Dartiguenave and Y. Dartiguenave, *Inorg. Chim. Acta, 154* (1988) 21.
28 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1986, p. 231.
29 R. Usón, J. Forniés, R. Navarro and M.P. García, *Inorg. Chim. Acta, 33* (1979) 69.