Journal of Organometallic Chemistry, 412 (1991) 435–443
Elsevier Sequoia S.A., Lausanne
JOM 21864

Synthesis and reactivity of the di-μ-hydroxo-bis[bis(pentachlorophenyl)palladate(II)] ion

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(Received February 4th, 1991)

Abstract

The binuclear hydroxo-pentachlorophenyl palladium complex $Q_2[\{Pd(C_6Cl_5)_2(\mu\text{-}OH)\}_2]$ (I) ($Q = NBu_4$) has been obtained by reaction between $Q_2[\{Pd(C_6Cl_5)_2(\mu\text{-}Cl)\}_2]$ and QOH in acetone. Reaction of the hydroxo-complex I with protic electrophiles HL gives complexes of the types $Q_2[\{Pd(C_6Cl_5)_2(\mu\text{-}L)\}_2]$ [L = pyrazolate (pz) (II), 3-methylpyrazolate (mpz) (III), indazolate (indz) (IV), or methoxo (V)], $Q_2[\{Pd(C_6Cl_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}dmpz)]$ (VI) (dmpz = 3,5-dimethylpyrazolate), or $[Pd(C_6Cl_5)_2L]$ [L = acetylacetonate (acac) (VII), benzoylacetonate (bzac) (VIII), or 8-hydoxyquinolinate (oxin) (IX)]. However, complex VI is best prepared by reaction of the above chloro-complex with QOH and Hdmpz. The neutral mononuclear complex *cis*-$[Pd(C_6Cl_5)_2(PhCN)_2]$ (X) has been obtained by treating complex I with benzonitrile in the presence of tetrafluoroboric acid. The lability of complex X is manifested by its reactivity towards aniline and 1,5-cyclooctadiene (cod), with which it gives the corresponding complexes *cis*-$[Pd(C_6Cl_5)_2(PhNH_2)_2]$ (XI) and $[Pd(C_6Cl_5)_2(cod)]$ (XII). The reaction between complex X and the chloro-complex $[PdCl_2(PEt_3)_2]$ yields the asymmetric binuclear complex $[(C_6Cl_5)_2Pd(\mu\text{-}Cl)_2Pd(PEt_3)_2]$ (XIII).

Introduction

The chemistry of monomeric hydroxo-complexes of late transition metals has been recently reviewed [1], and the interest in the chemistry of these compounds is doubtless related to their interesting reactions and their potential relevance to catalysis.

Previously reported organometallic hydroxo-bridged binuclear complexes of the nickel group elements include anionic or neutral compounds of the types $[\{M(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ (M = Ni, Pd, or Pt) [2] and $[\{MLR(\mu\text{-}OH)\}_2]$ (M = Ni, L = PMe_3 (R = CH_3 [3], $CH_2C_6H_4$-*o*-Me [4], CH_2SiMe_3, CH_2CMe_2Ph, or $CH_2C_6H_5$ [5]) or PPh_3 (R = $CClCCl_2$) [6]; M = Pd, L = PPh_3 (R = C_6F_5 or C_6Cl_5) [7]]. Non-organometallic hydroxo-bridged binuclear complexes have also been reported [8–12].

We describe below the synthesis of the pentachlorophenyl derivative $[\{Pd(C_6Cl_5)_2(\mu\text{-}OH)\}_2]^{2-}$ and its reactions with some protic electrophiles. This

0022-328X/91/$03.50

hydroxo-complex reacts with benzonitrile and HBF_4 to give *cis*-$[Pd(C_6Cl_5)_2(PhCN)_2]$, which has been used as a source of other pentachlorophenyl-palladium derivatives.

Experimental

C, H, and N analyses were performed with a Perkin–Elmer 240C microanalyzer. Decomposition temperatures were determined with a Mettler TG-50 thermobalance. Molar conductivities were measured in acetone solution ($c \approx 5 \times 10^{-4}$ mol L^{-1}) with a Philips PW 9501/01 conductimeter. The spectroscopic instruments were Perkin–Elmer Model 1430 for IR spectra (as Nujol mulls) and Bruker Model AC 200E for ^1H NMR spectra.

$Q_2[\{Pd(C_6Cl_5)_2(\mu\text{-}Cl)\}_2]$ [13] and $[PdCl_2(PEt_3)_2]$ [14] were prepared as previously described. Solvents were dried by standard methods.

$Q_2[\{Pd(C_6Cl_5)_2(\mu\text{-}OH)\}_2]$ (I)

A 20% aqueous solution of QOH (1.15 mmol) was added to an acetone solution (10 mL) of $Q_2[\{Pd(C_6Cl_5)_2(\mu\text{-}Cl)\}_2]$ (0.46 mmol). After 30 min stirring the solution was concentrated under reduced pressure until the expected hydroxo complex began to separate. Addition of a small amount of water then induced complete precipitation of yellowish white crystals of I, which were filtered off, washed with water, and air-dried; yield 91%.

$Q_2[\{Pd(C_6Cl_5)_2(\mu\text{-}L)\}_2]$ [L = pz (II), mpz (III), or indz (IV)]

The weak acid HL (0.08 mmol) was added to a solution of complex I (0.04 mmol) in methanol (ca. 2 mL). The mixture was stirred for 30 min, during which white crystals of the relevant title compound separated. The product was filtered off and dried in the air; yields 78–82%.

$Q_2[\{Pd(C_6Cl_5)_2(\mu\text{-}MeO)\}_2]$ (V)

Complex I (0.043 mmol) was dissolved in methanol (5 mL) and the solution stirred at room temperature. Within a few minutes a white precipitate was formed. The solid was filtered off and air-dried; yield 55%.

$Q_2[\{Pd(C_6Cl_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}dmpz)]$ (VI)

A 20% aqueous solution of QOH (0.12 mmol) was added to a methanol (3 mL) solution of 3,5-dimethylpyrazole (0.06 mmol). After 15 min stirring $Q_2[\{Pd(C_6Cl_5)_2(\mu\text{-}Cl)\}_2]$ (0.06 mmol) was added and the solution was stirred at room temperature for 1 h. The solvent was then partly evaporated under reduced pressure and water was slowly added until a white solid separated. This was filtered off and dried in the air; yield 83%.

$Q[Pd(C_6Cl_5)_2L]$ [L = acac (VII), bzac (VIII), or oxin (IX)]

HL (0.08 mmol) was added to a solution of complex I (0.04 mmol) in acetone (10 mL). The solution was stirred for 30 min, then concentrated under reduced pressure. Addition of water caused precipitation of complexes VII–IX as white (VII) or yellow (VIII, IX) solids. These were filtered off and air-dried; yields 65–75%.

Table 1

Analyses, decomposition temperatures, conductances and IR data for the palladium complexes

Complex	Analysis (%) [a]			M.p. [b] (°C)	Λ_M (Ω^{-1} cm^2 mol^{-1})	Relevant IR bands (cm^{-1})		
	C	H	N			X-sensitive	ν(Pd–C_6Cl_5)	Others
I	38.3 (38.3)	4.0 (4.3)	1.5 (1.6)	222	148	830, 825	615, 600	3590 (ν(OH)), 465, 425 (ν(PdO))
II	40.8 (40.7)	4.6 (4.3)	4.6 (4.6)	241	155	830, 825	610, 600	pz: 1060
III	41.0 41.4)	4.2 (4.5)	4.2 (4.5)	229	143	830 br	608 br	mpz: 1065, 770
IV	43.3 (43.6)	4.3 (4.4)	4.1 (4.4)	233	150	835, 825	610, 602	indz: 1065, 755
V	39.4 (39.6)	4.1 (4.4)	1.5 (1.6)	253	–	840, 830	618 sh, 610	1040 (ν(C–O))
VI	40.1 (40.5)	4.5 (4.7)	2.9 (3.1)	219	148	835, 825	610, 600	3600 (ν(OH))
VII	42.2 (42.0)	4.8 (4.6)	1.2 (1.5)	218	80	845, 835	600 br	acac: 1580, 1510, 1400, 430
VIII	45.0 (45.2)	4.6 (4.5)	1.4 (1.4)	231	81	835, 830	620, 607	bzac: 1590, 1560, 1500, 1400, 455, 435
IX	44.9 (44.8)	4.2 (4.3)	2.6 (2.8)	241	70	840, 825	622, 612	oxin: 1565, 800, 790
X	38.2 (38.5)	1.3 (1.2)	3.2 (3.5)	280	4	840, 835	622, 614	2270 (ν(C≡N))
XI	36.6 (36.4)	2.0 (1.8)	3.2 (3.5)	219	5	835, 830	620, 610	3320, 3250 (ν(N–H))
XII	33.6 (33.7)	1.9 (1.7)		203	–	840, 830	615, 605	cod: 1565, 1420
XIII	29.2 (29.3)	3.1 (3.0)		264	8	840 br	628 br	260 br (ν(Pd–Cl))

[a] Calculated values in parentheses. [b] Decompose.

cis-*[Pd(C_6Cl_5)$_2$(PhCN)$_2$] (X)*

To a solution of complex I (0.03 mmol) in tetrahydrofuran (4 mL) was added a 50% aqueous solution of HBF_4 (0.06 mmol) and PhCN (0.15 mmol). The solution was stirred for 1 h, then a mixture of H_2O–MeOH (10 mL : 10 mL) was added. The solution was concentrated under reduced pressure to give a precipitate of complex X, which was filtered off and air-dried; yield 72%.

cis-*[Pd(C_6Cl_5)$_2$($PhNH_2$)$_2$] (XI)*

Aniline (0.18 mmol) was added to a suspension of complex X (0.09 mmol) in dichloromethane (5 mL) and the resulting solution was stirred at room temperature for 30 min, then concentrated under reduced pressure. Complex XI was precipitated by addition of n-hexane, then filtered off and air-dried; yield 68%.

[Pd(C_6Cl_5)$_2$(cod)] (XII)

Addition of cod (0.09 mmol) to a suspension of complex X (0.06 mmol) in dichloromethane (4 mL) caused precipitation of XII as a white solid. It was filtered off and air-dried; yield 71%.

[(C_6Cl_5)$_2$Pd(μ-Cl)$_2$Pd(PEt_3)$_2$] (XIII)

To a suspension of complex X (0.06 mmol) in dichloromethane (4 mL) was added $[PdCl_2(PEt_3)_2]$ (0.06 mmol). The solution was stirred at room temperature for 15 min, then n-hexane was added to induce precipitation of XIII as a white solid. This was filtered off and dried in the air; yield 55%.

Analytical data and decomposition temperatures for all the palladium complexes are listed in Table 1.

Results and discussion

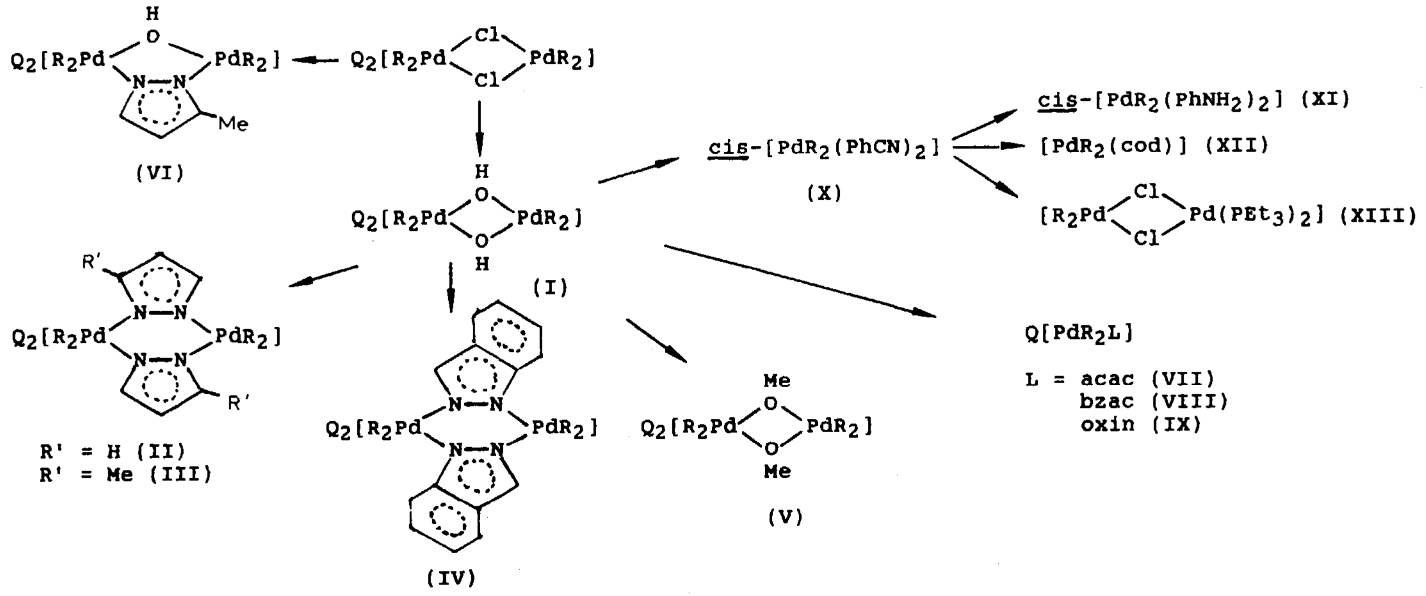
The results of our study are summarized in Scheme 1.

Synthesis and characterization of [(C_6Cl_5)$_2$Pd(μ-OH)$_2$Pd(C_6Cl_5)$_2$]$^{2-}$

The complex $Q_2[\{Pd(C_6Cl_5)_2(\mu\text{-}Cl)\}_2]$ in acetone reacts with 20% aqueous QOH to give the hydroxo-pentachlorophenyl palladium complex I (eq. 1), which was isolated as a pale yellow solid after precipitation with water.

$$Q_2[\{Pd(C_6Cl_5)_2(\mu\text{-}Cl)\}_2] + 2QOH \rightarrow \underset{(I)}{Q_2[\{Pd(C_6Cl_5)_2(\mu\text{-}OH)\}_2]} + 2\,QCl \qquad (1)$$

Complex I behaves in acetone (Table 1) as a 2 : 1 electrolyte [15]; the IR spectrum shows the absorptions attributed to the C_6Cl_5 group [16] at 1315, 1285, 1220, and 670 cm^{-1}. The absorption at ca. 830 cm^{-1}, which has previously been used for structural elucidation [13], is derived from the so-called "X-sensitive" mode in C_6Cl_5X (X = halogen) molecules [17,18], and in square-planar $M(C_6Cl_5)_2L_2$ complexes is related to the skeletal symmetry of the entire molecule [19] and behaves as ν(M–C) bands. Two split bands at ca. 830 cm^{-1} for the X-sensitive mode and ca. 610 cm^{-1} (ν(Pd–C)) [16] point to the presence of the *cis*-$Pd(C_6Cl_5)_2$ fragment. The IR absorptions at 3590 (OH stretch) [20], 465, and 425 cm^{-1} (Pd–O stretch) [21] are attributed to the OH bridges. The presence of the μ-OH groups is also supported by the resonance found at δ −2.68 in the ^1H spectrum of complex I, in good agreement with the data reported for compounds containing Pd–OH bonds [2,6].



Scheme 1. Synthesis of the pentachlorophenyl derivatives of palladium(II) ($Q = NBu_4$; $R = C_6Cl_5$).

Reactivity of complex I towards some weak acids

The high nucleophilicity of the OH bridges in complex I is indicated by the high-field proton resonance and the reactivity of the complex towards weak acids such as pyrazoles or methanol, with which it gives the corresponding pyrazolate or methoxo complexes with formation of water. Binuclear metal pyrazolate complexes have attracted considerable interest in recent years [22,23], and hydroxo complexes of nickel [2], rhodium [24], and iridium [25] have been used as starting materials for the synthesis of such complexes.

The reaction of complex I with pyrazoles or methanol in 1:2 molar ratio gives the new binuclear complexes II–V, according to eq. 2.

$$Q_2[\{Pd(C_6Cl_5)_2(\mu\text{-OH})\}_2] + 2HL \rightarrow Q_2[\{Pd(C_6Cl_5)_2(\mu\text{-L})\}_2] + 2H_2O \qquad (2)$$

(L = pz (II), mpz (III), indz (IV) or MeO (V))

However, the more sterically demanding 3,5-dimethylpyrazolate does not give a similar complex, but in the reaction of I with Hdmpz in 1:1 molar ratio the μ-OH-μ-dmpz complex (VI) was detected by ^{1}H NMR spectroscopy. Complex VI is best prepared by treating the di-μ-chloro complex with QOH and Hdmpz (1:2:1 molar ratio, respectively). The overall process is represented by eq. 3.

$$Q_2[\{Pd(C_6Cl_5)_2(\mu\text{-Cl})\}_2] + 2QOH + Hdmpz \rightarrow$$
$$Q_2[\{Pd(C_6Cl_5)_2\}_2(\mu\text{-OH})(\mu\text{-dmpz})] + 2QCl + H_2O \qquad (3)$$

The conductance data for complexes II–IV and VI (Table 1) are consistent with the formulae proposed for them, and the infrared spectra again show the characteristic bands assigned to the *cis*-$Pd(C_6Cl_5)_2$ moiety (Table 1). The ^{1}H NMR data (Table 2) are in agreement with those reported for compounds containing pyrazolates as bridging ligands [24], and the μ-OH ligand in VI gives an IR band at 3600 cm^{-1} (ν(OH)) and a proton resonance peak at δ − 1.68. Complex V gave a satisfactory analysis, and the IR spectrum provided evidence for the presence of the MeO groups, but unfortunately conductance and ^{1}H NMR data could not be obtained because it decomposes in solvents such as chloroform or acetone to regenerate the hydroxo-complex I.

Acetylacetone, benzoylacetone, and 8-hydroxyquinoline react with complex I to give the corresponding mononuclear anionic complexes VII–IX (eq. 4),

$$Q_2[\{Pd(C_6Cl_5)_2(\mu\text{-OH})\}_2] + 2HL \rightarrow 2Q[Pd(C_6Cl_5)_2L] + 2H_2O \qquad (4)$$

(L = acac (VII), bzac (VIII), or oxin (IX))

which were characterized from their conductivity and spectroscopic (IR and ^{1}H NMR) data. As expected, in these complexes L^- acts as a chelating bidentate ligand, and, consequently, complexes VII–IX behave as 1:1 electrolytes in acetone [15].

Synthesis of neutral mononuclear complexes

When complex I reacts with tetrafluoroboric acid in the presence of a coordinating species such as benzonitrile the corresponding complex X is obtained (eq. 5).

$$Q_2[\{Pd(C_6Cl_5)_2(\mu\text{-OH})\}_2] + 2\ HBF_4 + 4\ PhCN \rightarrow$$
$$2\ cis\text{-}[Pd(C_6Cl_5)_2(PhCN)_2] + 2\ QBF_4 + 2\ H_2O \qquad (5)$$

(X)

Table 2

^1H NMR data for the palladium complexes

Complex	δ (ppm) (reference $SiMe_4$) [a]
I [b]	−2.68 (s, 2H, OH)
II [b]	7.14 (d, 4H, 3- and 5-H, J 1.9 Hz) 5.59 (t, 2H, 4-H, J 1.9 Hz)
III [b]	7.25 (d, 2H, 4-H, J 1.7 Hz) 5.37 (d, 2H, 5-H, J 1.7 Hz) 2.22 (s, 6H, Me)
IV [b]	8.32 (dd, 2H, J 8.7 Hz, J′ 0.9 Hz) 8.02 (d, 2H, J 0.9 Hz) 7.23 (d, 2H, J 7.9 Hz) 6.70 (pseudotriplet, 2H, J 7.8 Hz) 6.49 (pseudotriplet, 2H, J 7.2 Hz)
VI [b]	5.35 (s, 1H, 4-H) 1.46 (s, 6H, Me) −1.67 (s, 1H, OH)
VII [b]	5.17 (s, 1H, CH) 1.72 (s, 6H, Me)
VIII [c]	7.69 (m, 2H, aromatic) 7.26 (m, 3H, aromatic) 5.82 (s, 1H, CH) 1.97 (s, 3H, Me)
IX [b]	8.20 (dd, 1H, J 7.5 Hz, J′ 1.5 Hz) 7.71 (dd, 1H, J 1.3 Hz, J′ 4.8 Hz) 7.24 (m, 2H) 6.74 (d, 1H, J 7.8 Hz) 6.62 (d, 1H, J 7.8 Hz)
X [c]	7.6 (m, 3H aromatic) 7.5 (m, 2H, aromatic)
XI [c]	7.5–6.9 (m, aromatic) 3.78 (br, NH_2)
XIII [c]	1.6 (dq, 12H, CH_2, J(PH) 10.6 Hz, J(HH) 7.5 Hz) 1.2 (dt, 18H, CH_3, J(PH) 18.8 Hz, J(HH) 7.5 Hz)

[a] Additional peaks from $[NBu_4]^+$ are found at δ ca. 3.3 (t, NCH_2), 1.7 (m, NCH_2CH_2), 1.4 (m, CH_2CH_3), and 1.0 (t, CH_3), the relative intensities being 16:16:16:24 (I–IV, VI) or 8:8:8:12 (VII–IX), respectively). [b] In $(CD_3)_2CO$. [c] In $CDCl_3$.

The IR spectrum of complex X shows the split band at ca. 830 cm^{-1} characteristic of the *cis*-$Pd(C_6Cl_5)_2$ moiety, and the presence of coordinated benzonitrile is confirmed by the band at 2270 cm^{-1} (free PhCN absorbs at 2230 cm^{-1} [26]).

The pentafluorophenyl and 2,4,6-trifluorophenyl analogues of complex X have been shown previously to be convenient starting materials for the synthesis of other organometallic palladium complexes [2,27–29]. The metathetical reaction of complex X with aniline or 1,5-cyclooctadiene can likewise be used to prepare the corresponding neutral complexes XI and XII, respectively. The insolubility of complex XII prevented us from obtaining its conductivity and ^1H NMR data.

Asymmetric binuclear complexes such as XIII can also be prepared by treating complex X with the appropriate halogeno-complex (eq. 6) in dichloromethane.

$$cis\text{-}[Pd(C_6Cl_5)_2(PhCN)_2] + [PdCl_2(PEt_3)_2] \rightarrow [(C_6Cl_5)_2Pd(\mu\text{-}Cl)_2Pd(PEt_3)_2] + 2PhCN \quad (6)$$

That the halogeno-complex is linked to the organometallic moiety is demonstrated by the absence of an IR band in the $\nu(C\equiv N)$ region and the presence of a band at 260 cm^{-1} attributed to $Pd(\mu\text{-}Cl)_2Pd$ (at 355 cm^{-1} in uncoordinated $Cl_2Pd(PEt_3)_2$). The $^{31}P\{^1H\}$ NMR spectrum of complex XIII exhibits a resonance at δ 30.2 (reference H_3PO_4). For the pentafluorophenyl analogue this resonance is found at δ 38.6 [30], in keeping with the higher electronegativity of the C_6F_5 group. The *cis* geometry of the $Pd(PEt_3)_2$ fragment is confirmed by the ^1H NMR spectrum (Table 2), since there is no virtual coupling with the phosphorus nuclei and the methylene and methyl groups give two overlapping quartets and two overlapping triplets, respectively, in agreement with previous results [31].

Acknowledgements

Financial support of this work by the DGICYT (project PB87-0690) Spain, is acknowledged. J.M.M. thanks the Fundación ONCE, Spain, for a research grant.

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