Journal of Organometallic Chemistry, 441 (1992) 487–498
Elsevier Sequoia S.A., Lausanne
JOM 22993

Some attempts to prepare chelating nitrophenylpalladium(II) complexes. Synthesis of covalent arylpalladium(II) perchlorate complexes. Crystal and molecular structure of *catena-trans*-$\{[Pd\{C_6H_2(NO_2)_3\text{-}2,4,6\}(tht)_2(H_2O)]ClO_4\}_n$ (tht = tetrahydrothiophene)

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(Received February 28, 1992)

Abstract

Complexes $[Pd(R)ClL_2]$ [R = $C_6H_2(NO_2)_3$-2,4,6, L = tetrahydrothiophene (tht) or PPh_3, or L_2 = 1,5-cyclooctadiene (COD); R = C_6H_3Me-2,NO_2-6, L_2 = 1,10-phenanthroline (phen) or 2,2′-bipyridyl (bipy)] react with $AgClO_4$ to give the corresponding perchlorato-complexes $[Pd(R)(OClO_3)L_2]$. Of these only some could be isolated and characterized [R = $C_6H_2(NO_2)_3$-2,4,6, L = tht (**1**); R = C_6H_3Me-2-NO_2-6, L_2 = phen (**2**) or bipy (**3**)]. These complexes, and solutions of the other non-isolated perchlorato-complexes, react with different neutral ligands to give cationic complexes $[Pd(R)L_2L']ClO_4$ [R = $C_6H_2(NO_2)_3$-2,4,6, L = tht, L′ = H_2O (**4**); L′ = PPh_3, L_2 = phen (**5**) or COD (**6**); R = C_6H_3Me-2-NO_2-6, L′ = PPh_3, L_2 = phen (**7**)]. The complex $(PhCH_2PPh_3)[Pd(R)Cl_2(dmso)]$ (R = $C_6H_2(NO_2)_3$-2,4,6, dmso = dimethyl sulphoxide) reacts with $Ag_2(ox)$ (ox = oxalate) to give $(PhCH_2PPh_3)[Pd(R)(ox)(dmso)]$ (**8**) and $(NMe_4)_2[Pd_2(R)_2Cl_2(\mu\text{-}Cl)_2]$ (R = C_6H_3Me-2-NO_2-6) reacts with Tl(acac) (acacH = acetylacetone) to give [Pd(R)(acac)] (**9**). IR studies suggest that in this complex the aryl ligand is chelating. The crystal structure of *trans*-$[Pd\{C_6H_2(NO_2)_3\text{-}2,4,6\}(tht)_2(H_2O)]ClO_4$ shows that each perchlorate anion bridges two cations using two different oxygen atoms which gives a *catena* structure with a helical frame. The anion–cation interaction seems to be through hydrogen bonding with the coordinated water molecule. C–C bond angles in the trinitrophenyl group support suggestions that nitro groups exert a −I inductive effect rather than a −M effect on the ring electron density.

Introduction

There is a very interesting controversy concerning the bonding ability of nitro groups in arenes. The relative importances of the inductive and mesomeric effects

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of this group have been discussed [1]. We used X-ray diffraction data from several 2-nitrophenylmetal-complexes in discussing structural aspects of this problem [1a,b]. In this paper we extend our previous observations to aryl groups containing two more nitro groups, or an additional methyl group, on the ring.

The use of weakly coordinating anions as precursors or in catalysis is still a subject of great interest [2]. Perchlorate is certainly the best studied of these anions [2,3]. Because of their high lability, relatively few of these complexes have been isolated. In most cases, they are used *in situ* with the donor one wishes to be coordinated. We have successfully used this technique in many cases [4a]. In this paper we report three isolated perchlorate-complexes of palladium.

Crystal structures of aqua-complexes of palladium(II) are limited to those of $[Pd(C_6H_4CH_2NMe\text{-}2)(benzoquinoline)(H_2O)]ClO_4$ [4b] and the very recently described $[Pd(R)(ONO_2)(H_2O)]ClO_4 \cdot H_2O$ (R = 1-methyl-2,2′-bipyridin-3-ylium) [4c]. We report in this paper the crystal structure of an aqua-complex which is similar to the above complexes but also interestingly different.

We are currently engaged on the synthesis of functionalized aryl complexes using organomercury compounds as transmetallating agents [5]. As a part of this project, we prepared 2-nitroaryl complexes [6] and showed that chelating 2-nitrophenyl complexes of Rh^{III} [1a,b], Pd^{II} [7], Pt^{II} [8], and Pt^{IV} [9] can be obtained. The IR data, reactivity and crystal structures of these complexes have interesting features, concerning, for example, the π-acceptor ability of the nitro group, the different strengths of the metal–oxygen bond, and the IR criteria for determining whether the 2-nitrophenyl group is chelating or not. We have prepared new aryl complexes to determine whether other substituents affect the ability of the *ortho*-nitroaryl group to coordinate. Gold [10] and palladium [11,12] complexes with two such groups, $-C_6H_2(NO_2)_3$-2,4,6 and $-C_6H_3Me$-2-NO_2-6, are now being studied. The interest of the first is that one or both *ortho*-nitro groups may co-ordinate. Complexes containing it would be related to those obtained by van Koten with $C_6H_3(CH_2NMe_2)_2$-2,6, which have unusual properties [13]. The second group would allow us to determine the influence of a methyl group on the ability of electron withdrawing nitro groups to chelate. In this paper we describe our attempts to prepare chelating nitrophenylpalladium(II) complexes by reaction of the corresponding chloro-complexes with various silver and thallium salts, and the crystal structure of one of the products.

Results and discussion

Synthesis

In attempting to prepare chelate-C,O-2-nitroarylpalladium complexes, neutral $[Pd(R)(OClO_3)L_2]$, anionic $[Pd(R)XL]^-$, and cationic $[Pd(R)L_2L']^+$ complexes [R = $C_6H_2(NO_2)_3$-2,4,6, or C_6H_3Me-2,NO_2-6; L, L_2 and L′ = neutral ligands; X = dianionic ligand] have been isolated. The methods used are summarized in Scheme 1.

Arylpalladium(II) complexes containing the aryl groups $-C_6H_2(NO_2)_3$-2,4,6 (R_{TN}) and $-C_6H_3Me$-2-NO_2-6 (R_{Me}) were obtained through a transmetallation reaction [11,12a].

$$[Pd_2Cl_4(\mu\text{-}Cl)_2]^{2-} + 2[HgR_2] \longrightarrow [Pd_2(R)_2Cl_2(\mu\text{-}Cl)_2]^{2-} + 2[HgRCl]$$
$(R = R_{TN} \text{ or } R_{Me})$

$[Pd(R)ClL_2] + AgClO_4$

$\downarrow -AgCl$

$[Pd(R)(OClO_3)L_2]$ (**1–3**)

$\downarrow +L'$

$[Pd(R)L_2L']ClO_4$ (**4–7**)

Complex	R	L	L_2	L′
1	R_{TN}	tht		
2	R_{Me}		phen	
3	R_{Me}		bipy	
4	R_{TN}	tht		H_2O
5	R_{TN}		phen	PPh_3

$Q[Pd(R)Cl_2(dmso)] + Ag_2(OX)$

$\downarrow -2AgCl$

$Q[Pd(R)(ox)(dmso)]$ (**8**)

$Q'_2[Pd_2(R)_2Cl_2(\mu\text{-}Cl)_2]$

$\downarrow \begin{array}{l} +2Tl(acac) \\ -2Q'Cl\ -2TlCl \end{array}$

$2[Pd(R)(acac)]$ (**9**)

Complex	R	L_2	L′
6	R_{TN}	COD	PPh_3
7	R_{Me}	phen	PPh_3
8	R_{TN}		
9	R_{Me}		

Scheme 1. Summary of reactions [$R_{TN} = C_6H_2(NO_2)_3$-2,4,6; $R_{Me} = C_6H_3Me$-2-NO_2-6; Q = $PhCH_2$-PPh_3; Q′ = NMe_4]

Molecular structures of $[Pd_2(R_{Me})_2Cl_2(\mu\text{-}Cl)_2]^{2-}$ [11], $[Pd(R_{TN})Cl_2(dmso)]^-$ [12a], (dmso = dimethyl sulphoxide), and $[Pd(R_{TN})Cl(AsPh_3)_2]$ [12b] show no Pd–O bonds. The IR data of all the derivatives obtained [11,12] by reaction of $[Pd_2(R)_2Cl_2(\mu\text{-}Cl)_2]^{2-}$ with anionic (X) or neutral ligands (L or L_2), *e.g.*, $[Pd_2(R)_2X_2(\mu\text{-}X)_2]^{2-}$, $[Pd(R)Cl_2L]^-$, $[Pd_2(R)_2(L)_2(\mu\text{-}Cl)_2]$ and $[Pd(R)ClL_2]$, show that R group never chelates. Therefore, because an R group is unable to coordinate *via* the *ortho*-nitro group(s) by replacing ligand(s) *cis* to it the synthetic route chosen was to replace a chloride by a good leaving group such as ClO_4^-.

Complexes $[Pd(R)ClL_2]$ [R = R_{TN}; L = tetrahydrothiophene (tht) or PPh_3; L_2 = 1,5-cyclooctadiene (COD); R = R_{Me}, L = 1,10-phenanthroline (phen) or 2,2′-bipyridyl (bipy)] react with $AgClO_4$ to give the corresponding perchlorato-complexes $[Pd(R)(OClO_3)L_2]$ of which only some are sufficiently stable to be isolated and characterized (see Scheme 1). IR data (see below) show clearly that ClO_4^- is coordinated while the nitro groups are not. The perchlorate remains coordinate in dichloromethane (Λ_M = 1–6 Ω^{-1} cm^2 mol^{-1}; see Experimental) but it is replaced by the solvent in acetone solutions (Λ_M = 87–135 Ω^{-1} cm^2 mol^{-1}). However, only complex **1** is stable enough in solution to permit NMR measurements.

Complexes **1–3**, and solutions of the other non-isolated perchlorato-complexes, react with neutral donors to give cationic complexes $[Pd(R)L_2L']ClO_4$ (see Scheme 1). Complex **4** [R = R_{TN}, L = tht, L′ = H_2O] is obtained only when a precipitating solvent (diethyl ether, hexane) is allowed to diffuse slowly into an acetone or dichloromethane solution of **1** in the air. If the same precipitating agents are added rapidly to stirred solutions of **1** in acetone or in acetone/water or in dichloromethane, complex **1** is recovered.

Table 1

NMR data for complexes [a]

Compound	^{1}H NMR δ (ppm)	^{31}P NMR δ (ppm)
1 $[Pd(R_{TN})(OClO_3)(tht)_2]$	8.98, [b] 3.00 (m, 4H, tht), 2.05 (m, 4H, tht)	
4 $\{[Pd(R_{TN})(tht)_2(H_2O)]ClO_4\}$	8.96, [b] 2.97 (m, 4H, tht), 2.02 (m, 4H, tht), 1.80 (s, 2H, H_2O)	
5 $[Pd(R_{TN})(phen)(PPh_3)]ClO_4$	[c]	33.45 (s) [d]
6 $[Pd(R_{TN})(COD)(PPh_3)]ClO_4$	8.60, [b] 7.56–7.36 (m, 15H, PPh_3), 5.49 (m, 4H, COD), 2.31 (m, 8H, COD)] [d]	23.73 (s) [e,f]
7 $[Pd(R_{Me})(phen)(PPh_3)]ClO_4$	8.89–7.00 (m, R_{Me}, PPh_3, phen), 2.66 (s, 3H, Me)	29.26 (s)
8 $[PhCH_2PPh_3][Pd(R_{TN})(ox)(dmso)]$	8.79, [b] 7.78–6.85 (m, Ph), 4.89 [d, ^2J(H–P) = 10 Hz, CH_2], 3.27 (s, 6H, dmso)	

[a] In $CDCl_3$ unless otherwise stated. [b] Singlet corresponding to H3 and H5 of the aryl ligand. [c] Several multiplets, that obscure the H3 and H5 resonances of the aryl ligand. [d] In acetone. [e] See text. [f] In dmso.

Cationic complexes **6** and **7** are the result of the replacement of the perchlorate by PPh_3 in complexes $[Pd(R)(OClO_3)L_2]$ ($R = R_{TN}$, L_2 = COD; $R = R_{Me}$, L_2 = phen). However, when trying to prepare a penta-coordinate complex by reaction of $[Pd(R_{TN})(OClO_3)(PPh_3)_2]$ with phen both ClO_4^- and one PPh_3 were replaced, giving **5**. Other reactions were attempted using $NaBPh_4$ instead of $AgClO_4$ to force the coordination of the nitro group but the products were so unstable that they could not be isolated.

These unsuccessful attempts to prepare chelating nitrophenyl complexes may be the result of the steric hindrance exerted by the ligand *trans* to the position to be occupied by the nitro group, over the substituent in the other *ortho* position (Me or NO_2), because coordination of the nitro group forces the aryl ligand to be in the coordination plane. Several experiments were devised to prove this using ligands which we presumed would allow the bonding of the nitro group. These led to only two isolable and stable complexes, only one of which was the expected chelated complex.

The complex *cis*-$(PhCH_2PPh_3)[Pd(R_{TN})Cl_2(dmso)]$ (dmso = dimethyl sulphoxide) [12a] reacts with $Ag_2(ox)$ (ox = oxalate) to give $(PhCH_2PPh_3)[Pd(R_{TN})(ox)(dmso)]$ (**8**). The reaction of $(NMe_4)_2[Pd_2(R_{Me})_2Cl_2(\mu\text{-}Cl)_2]$ with Tl(acac) (acacH = acetylacetone) gives $[Pd(R_{Me})(acac)]$ (**9**). This complex is formed thanks to the insolubility of NMe_4Cl and TlCl in dichloromethane and to the low steric requirement of the acac ligand that allows the aryl ligand to chelate.

NMR data are presented in Table 1. Analytical and other data for the new complexes are given in the Experimental section.

IR bands due to $\nu(NO_2)$ modes (in the regions 1530–1500 and 1340–1320 cm^{-1}) are in all complexes except **9**, which means that generally there are no Pd $\cdots$ O interactions, as evident from the X-ray structure of complex **4** [1a,b]. In complex **9**, no 1330 cm^{-1} band is present, but two additional ones are observed at 1310 and 1250 cm^{-1}. One of them can be assigned to a combination band $[\nu(C{-}CH_3) + \nu(C{=}C)]$ which appears at 1272 cm^{-1} in $[Pd(acac)_2]$ [16], the other can be assigned to the $\nu_{sym}(NO_2)$ mode in a chelating 2-nitrophenyl ligand. The IR

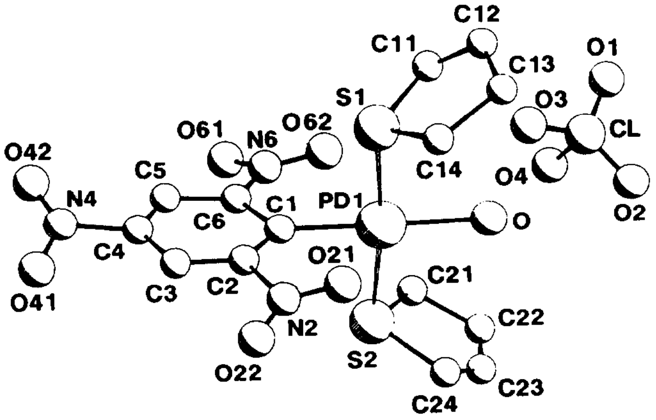

Fig. 1. A perspective view of one cation and one anion of complex 4.

spectrum of **9** is similar to that of [Pd(2-$C_6H_4N(O)O$)(acac)] [7] in the 1200–1350 cm^{-1} region and to [$AuMe_2$(acac)] [17] in the 1600–1500 cm^{-1} region where ν(CO) is expected, which indicates that both ligands chelate.

Structures of complexes

The palladium atom in complex **4** is in a square-planar environment (see Fig. 1 and Table 2) with the Pd atom 0.02 Å out of the mean plane defined by Pd, S(1), S(2), C(1) and O and with the tetrahydrothiophene ligands in a mutually *trans*

Table 2

Selected bond lengths (Å), bond angles (°) and intermolecular distances (Å) with esd's for complex 4

Bond lengths					
Pd–S1	2.341(4)	N4–O42	1.203(16)	C1–C2	1.392(12)
Pd–S2	2.326(4)	N6–O61	1.229(15)	C2–C3	1.365(12)
Pd–O	2.115(9)	N6–O62	1.206(13)	C3–C4	1.366(12)
Pd–C1	1.976(11)	C2–N2	1.464(16)	C4–C5	1.389(12)
N2–O21	1.224(15)	C4–N4	1.483(17)	C5–C6	1.387(12)
N2–O22	1.163(11)	C6–N6	1.458(16)	C6–C1	1.394(12)
N4–O41	1.221(16)				
Bond angles					
S1–Pd–S2	173.3(1)	O62–N6–O61	121.2(13)		
O–Pd–S1	93.4(3)	C6–C1–C2	113.7(10)		
O–Pd–S2	93.2(3)	C1–C2–C3	125.0(12)		
C1–Pd–S1	86.6(3)	C2–C3–C4	118.1(12)		
C1–Pd–S2	86.7(3)	C3–C4–C5	121.7(12)		
C1–Pd–O	178.4(4)	C4–C5–C6	117.0(11)		
O22–N2–O21	120.2(13)	C1–C6–C5	124.4(11)		
O42–N4–O41	128.0(15)				
Intermolecular distances					
$O4 \cdots HO2^{i}$	1.97(1)	$O3 \cdots HO1^{ii}$	1.94(1)	$O8 \cdots HO2^{i}$	1.88(1)
$O6 \cdots HO1^{ii}$	1.69(1)	$O4 \cdots O^{i}$	2.62(1)	$O3 \cdots O^{ii}$	2.80(1)
$O8 \cdots O^{i}$	2.85(1)	$O6 \cdots O^{ii}$	2.44(1)		

$i = 4/3 - x, 2/3 - y, 2/3 - z$; $ii = 2/3 + y, 1/3 + y - x, 1/3 - z$.

position. The molecular planes of the tetrahydrothiophene ligands are perpendicular to this plane and they make an angle of 57.3°. The aryl skeleton plane, which is also perpendicular to the coordination plane, forms angles of 19.9 ($N(2)O_2$), 17.7 ($N(4)O_2$) and 20.7° ($N(6)O_2$) with their own nitro groups, with O(62) and O(21) atoms at 2.75(1) and 2.83(1) Å from the Pd atom. These distances are comparable to those found in *cis*-$[Pd(R_{TN})Cl_2(dmso)]^-$ (2.910 and 2.911 Å) [12a], and *trans*-$[Pd(R_{TN})Cl(AsPh_3)_2]$ (2.85(3), 2.81(2) Å) [12b] but much longer than that found between Pd and the coordinated oxygen in $[Pd(C_6H_5N(O)O\text{-}2)(C_6H_5NO_2\text{-}2)(PPh_3)]$ (2.138(3) Å) [7] supporting the non-bonding Pd–ON(R)O interaction. The Pd–C (1.976(11) Å) and the Pd–S bond distances (2.326(4), 2.341(4) Å) are similar to those found in other related arylpalladium complexes [7,11,12] and in $[Pd(thiourea)_4]Cl_2$ (2.334(11) Å) [18a]. The $Pd\text{–}OH_2$ bond length [2.115(9) Å] is similar to that found in $[Pd(R)(ONO_2)(H_2O)]ClO_4 \cdot H_2O$ (R = 1-methyl-2,2′-bipyridin-3-ylium) [4c] but shorter than that in $[Pd(C_6H_4CH_2NMe\text{-}2)(benzoquinoline)(H_2O)]ClO_4$ (2.20(1) Å) [4b]. This occurs although **1** and the two aqua-complexes have the aryl ligand *trans* the water.

The C–C bond distances within the phenyl ring (1.365(12)–1.394(12) Å), C–N (1.458(16)–1.483(17) Å) and N–O (1.163(11)–1.229(15) Å) are normal compared to other trinitrophenyl complexes [10–12]. The presence of the three electron-withdrawing groups causes significant deformation in the bond angles rather than in the bond distances of the ring. The endocyclic angles at C(2), C(4), and C(6), bonded to the nitro groups, are 125.0(12), 121.7(12), and 124.4(11)°, respectively, while those at C(1), C(3), and C(5) are 113.7(10), 118.1(12), and 117.0(11)°. A comparable situation was observed in *cis*-$[Pd(R_{TN})Cl_2(dmso)]^-$ [12], *trans*-$[Pd(R_{TN})Cl(AsPh_3)_2]$, and $[Au(R_{TN})(Me_2phen)]$ (Me_2phen = 2,9-dimethyl-1,10-phenanthroline) [10b]. These differences can be rationalized using the isovalent hybridization concept [18b]. Thus, a nitro group, for example $N(2)O_2$, will demand greater *p* character of the C(2) hybrid than will a hydrogen atom because it is more electronegative. Therefore, C(2) will use hybrids with more *s* character than sp^2 for the C(1)–C(2)–C(3) bonds, giving rise to an angle wider than 120°. In addition, C(2) and C(4), because they use more electronegative orbitals to bond to C(3) will demand more *p* character of both hybrid orbitals of C(3) and thus the C(2)–C(3)–C(4) angle will be less than 120°. These data support suggestions [1] that nitro groups exert a −I inductive effect rather than a −M effect on the ring electron density. In addition, if this mesomeric effect exists, not only should the C–C bond distances be longer, but the partial C=N double bond character should close the $C\text{–}C(NO_2)\text{–}C$ angles rather than open them.

Each ClO_4^- bridges two cations using two different oxygen atoms which point to oxygen atoms of the co-ordinated water molecules giving a *catena* structure with a helical frame (see Fig. 2). The O···O bond distances (see Table 3) are similar to those in water [2.76 Å] [19], which suggests strong hydrogen bonds. Crystal structures of several aqua-complexes show similar hydrogen bridges between water and anions such as BF_4^-, AsF_6^-, and OTs^- [20]. As far as we know there is no previous example of such bonding in a complex containing ClO_4^-. Even the very similar complexes $[Pd(C_6H_4CH_2NMe_2\text{-}2)(benzoquinoline)(H_2O)]$ ClO_4 [4b] and $[Pd(R)(ONO_2)(H_2O)]ClO_4 \cdot H_2O$ (R = 1-methyl-2,2′-bipyridin-3-ylium) [4c] do not have this same hydrogen bonding, which is, however, found in anhydrous ClO_4H [21].

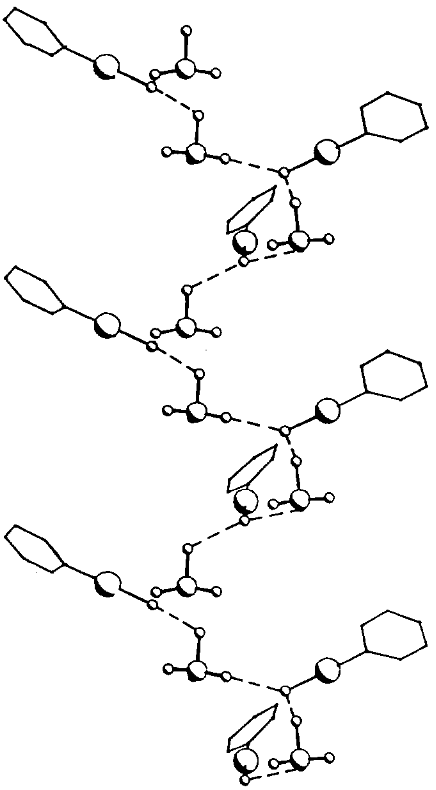

Fig. 2. A perspective view of the chain formed between cations and anions in complex 4. Tetrahydrothiophene and substituents of the aryl group are omitted for clarity. Pd, Cl and O atoms are represented with circles, of area proportionate to atomic number.

Consistent with the lowering of symmetry of the ClO_4^- in complex **4** (C_{2v}), compared to free $ClO_4^-(T_d)$, the usual bands corresponding to ν and $\delta(ClO_4)$ modes, appearing at around 1100 and 620 cm^{-1} in **5–7** are split (1150, 1010 and 620, 610 cm^{-1}, respectively). In addition, the band corresponding to the now IR active mode $\nu(A_1)$ appears at 870 cm^{-1}. The isolated perchlorate complexes **1–3** show IR spectra in these regions similar to those of complex **4**.

The only complexes with suitable solubility and stability in solution to allow us to record their NMR spectra are **1**, **4–8**. The equivalent 3- and 5-protons in the ^1H

Table 3

Crystallographic data for complex **4**

Formula $C_{14}H_{20}ClN_3O_{11}PdS_2$		V, Å^3	10264
Space group $R\bar{3}$		Z	18
F.W. 612.30		D_c, g cm^{-3}	1.78
Cell params. (hexagonal)		R	0.058
a, Å	34.245(6)	R_w [a]	0.058
c, Å	10.106(4)		

[a] $w = [\sigma^2(F) + 0.000613F^2]^{-1}$ over 1697 observed reflexions [$I > 2.5\sigma(I)$].

NMR spectra of trinitrophenyl-complexes appear in the 8.4–9 ppm region. ^1H and $^{31}P\{H\}$ NMR spectral data are shown in Table 1.

Experimental section

Recording of the IR spectra, the C, H, and N analyses, conductance measurements and melting point determinations were performed as described elsewhere [10b]. ^1H and ^{31}P NMR spectra (in $CDCl_3$) were recorded on a Bruker 200AC and on a Varian FT80 spectrometer, respectively. Chemical shifts in ppm are referenced to TMS and H_3PO_4, respectively (see Table 1). Reactions were carried out with magnetic stirring at room temperature and without special precautions to exclude light or moisture unless otherwise stated. The aryl groups will be represented, in general, as R but R_{TN} or R_{Me} when applying to $-C_6H_2(NO_2)_3$-2,4,6 or $-C_6H_3Me$-2-NO_2-6, respectively. Complexes $[Pd(R_{Me})Cl(phen)]$, $[Pd(R_{Me})Cl(bipy)]$ [11], $[Pd(R_{TN})Cl(tht)_2]$, $[Pd(R_{TN})Cl(PPh_3)_2]$, $[Pd(R_{TN})Cl(COD)]$ [12b], and $[PhCH_2PPh_3][Pd(R_{TN})Cl_2(dmso)]$ [12a] were obtained as reported.

$[NMe_4]_2[Pd_2(R_{Me})_2Cl_2(\mu\text{-}Cl)_2]$

A suspension of $[NMe_4]_2[Pd_2Cl_4(\mu\text{-}Cl)_2]$ (102.3 mg, 0.18 mmol) and $(R_{Me})_2Hg$ (168 mg, 0.35 mmol) in acetone (11 cm^3) was heated under reflux. After 1 h an orange solid precipitated and the suspension was filtered while hot and the solid washed with hot acetone (5 cm^3). Yield: 92%, m.p. 240°C, Λ_M, 198 Ω^{-1} cm^2 mol^{-1} (in acetone) (Found: C, 33.88; H, 4.56; N, 6.78. $C_{22}H_{36}Cl_4N_4O_4Pd_2$ calc.: C, 34.09; H, 4.68; N, 7.23%).

$[Pd(R)(OClO_3)L_2]$ (1–3)

To a solution of the corresponding $[Pd(R)ClL_2]$ (*ca.* 0.1–0.2 mmol) in acetone (5–10 cm^3) solid $AgClO_4$ (1:1.1, 1:1, and 1:1.8 molar ratios) was added. The suspension was then concentrated to dryness and the residue extracted with dichloromethane (20 cm^3). After filtering off the AgCl and the excess of $AgClO_4$, the resulting solution was concentrated (to *ca.* 2 cm^3) and addition of diethyl ether gave yellow crystals of complexes **1**, **2**, or **3**, respectively. Yields: 67, 67, 81%, m.p. 165 (decomp.), 202 (decomp.), 190 (decomp.) °C, Λ_M: 135, 87, 108 Ω^{-1} cm^2 mol^{-1} (in acetone) and 6, 1.5, 2 Ω^{-1} cm^2 mol^{-1} (in dichloromethane), respectively [(**1**) Found: C, 28.82; H, 2.93; N, 6.65. $C_{14}H_{18}ClN_3O_{10}PdS_2$ calc.: C, 28.29; H, 3.05; N, 7.07%. (**2**) Found: C, 42.44; H, 2.83; N, 7.58. $C_{19}H_{14}ClN_3O_6Pd$ calc.: C, 43.70; H, 2.70; N, 8.05%. (**3**) Found: C, 41.66; H, 3.13; N, 7.70. $C_{17}H_{14}ClN_3O_6Pd$ calc.: C, 40.99; H, 2.83; N, 8.43%].

$\{[Pd(R_{TN})(tht)_2(H_2O)]ClO_4\}$ (4)

Single crystals of **4**, suitable for X-ray diffraction study, were obtained by slow diffusion on hexane (4 cm^3) into a saturated solution of **1** (7.8 mg, 0.01 mmol) in dichloromethane (1 cm^3). Yield: 90%, m.p. 170°C, Λ_M: 121 Ω^{-1} cm^2 mol^{-1} (in acetone); Λ_M: 15 Ω^{-1} cm^2 mol^{-1} (in dichloromethane) (Found: C, 28.05; H, 3.05; N, 7.07. $C_{14}H_{20}ClN_3O_{11}PdS_2$ calc.: C, 27.46; H, 3.29; N, 6.86%).

$[Pd(R)L_2L']ClO_4$ (5–7)

To a suspension of *trans*-$[Pd(R_{TN})Cl(PPh_3)_2]$ (102.1 mg, 0.12 mmol), or of $[Pd(R_{TN})Cl(COD)]$ (110.5 mg, 0.24 mmol), or to a solution of $[Pd(R_{Me})Cl(phen)]$

(35.4 mg, 0.08 mmol) in acetone (4 cm^3) solid $AgClO_4$ (42.2 mg, 0.20 mmol, or 70 mg, 0.34 mmol, or 16 mg, 0.08 mmol, respectively) was added. After 15, 45, or 15 min, respectively, the suspension was concentrated to dryness, the residue extracted with dichloromethane (15 cm^3) and the suspension filtered. To the filtrate phen (42.3 mg, 0.23 mmol), or PPh_3 (63.2 mg, 0.24 mmol), or PPh_3 (28 mg, 0.10 mmol), respectively, was added. After 3 h the solution was concentrated (1–2 cm^3) and addition of diethyl ether (10–15 cm^3) gave yellow crystals of complex **5**, **6**, or **7**. Yield: 82, 66, 17%, m.p. 147, 151, 157°C, Λ_M: 125, 91, 90 Ω^{-1} cm^2 mol^{-1} (in acetone), respectively. [(**5**) Found: C, 49.94; H, 3.18; N, 8.47. $C_{36}H_{25}ClN_5O_{10}PPd$ calc.: C, 50.25; H, 2.93; N, 8.14%. (**6**) Found: C, 47.98; H, 4.08; N, 5.01. $C_{32}H_{29}ClN_3O_{10}PPd$ calc.: C, 48.75; H, 3.70; N, 5.33%. (**7**) Found: C, 56.78; H, 4.19; N, 5.35. $C_{37}H_{29}ClN_3O_6PPd$ calc.: C, 56.65; H, 3.73; N, 5.35%].

$[PhCH_2PPh_3][Pd(R_{TN})(ox)(dmso)]$ (8)

To a solution of $[PhCH_2PPh_3][Pd(R_{TN})Cl_2(dmso)]$ (127.4 mg, 0.15 mmol) in acetone (10 cm^3) silver oxalate (69.7 mg, 0.23 mmol) was added. After 24 h the suspension was concentrated to dryness, the residue extracted with dichloromethane (20 cm^3) and the resulting suspension filtered. The filtrate was concentrated (to 1 cm^3) and addition of diethyl ether (10 cm^3) gave yellow crystals of complex **8**. Yield: 43%, m.p. 119°C, Λ_M: 92 Ω^{-1} cm^2 mol^{-1} (in acetone) (Found: C, 51.14; H, 3.68; N, 5.11. $C_{35}H_{30}N_3O_{11}PPdS$ calc.: C, 50.16; H, 3.61; N, 5.01%).

$[Pd(R_{Me})(acac)]$ (9)

Tl(acac) (61.5 mg, 0.20 mmol) was added to a suspension of $[NMe_4]_2[Pd_2(R_{Me})_2Cl_2(\mu\text{-}Cl)_2]$ (67.6 mg, 0.09 mmol) in dichloromethane (6 cm^3). After 72 h under dry nitrogen the resulting suspension was filtered. The red filtrate was concentrated (2 cm^3) and hexane added. The resulting precipitate was filtered off and recrystallized from dichloromethane/hexane to give **9** as a red solid. Yield: 25%, m.p. 123°C, Λ_M: 0 Ω^{-1} cm^2 mol^{-1} (in acetone) (Found: C, 42.04; H, 4.18; N, 4.07. $C_{12}H_{13}NO_4Pd$ calc.: C, 42.19; H, 3.83; N, 4.10%).

Crystal structure determination of $[Pd(R_{TN})(tht)_2(H_2O)]ClO_4$ (4)

A summary of crystallographic data is presented in Table 3. The crystals were yellow needles. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with Mo-K_α radiation ($\mu = 11.5$ cm^{-1}) in the range $1 < \theta < 25°$; for minimizing absorption effects and due to the needle habit of the crystals, reflections were measured at the azimuth position corresponding to a minimum absorption using an imaginary crystal with finite but small thickness and infinitely large length (needle PSI mode); data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using MULTAN-11/84 [14] refined by full-matrix least-squares technique with SHELX-76 [15]. Hydrogen atoms were introduced in calculated positions, except those of water molecule (HO1 and HO2) which were located by difference Fourier synthesis. The O(1)–O(4) atoms were refined with an occupation factor of 0.67 and O(5)–O(8) with 0.33 in order to reproduce the orientational disorder of the perchlorate group. The maximum and minimum peaks in the last difference Fourier synthesis were 0.63 and −0.53 e Å^{-3}. Anisotropic thermal parameters were refined for non-hydrogen atoms and two global isotropic thermal parameters for the hydrogen atoms. Table 2 gives

Table 4

Fractional atomic coordinates ($\times 10^4$) with the equivalent temperature factors for complex **4**

Atom	x	y	z	B_{eq}
Pd1	4469.3(4)	2800.9(4)	1923(1)	5.02
S1	4358(1)	2277(1)	3580(4)	6.17
S2	4633(2)	3294(2)	155(5)	8.04
O21	5310(5)	3293(5)	3220(18)	12.54
O22	5951(4)	3506(5)	2498(14)	11.37
O42	5691(5)	1940(5)	−959(15)	10.67
O41	6257(5)	2584(6)	−330(13)	10.26
O61	4291(4)	1896(5)	−1403(13)	9.60
O62	4033(4)	2075(4)	252(14)	8.14
O	3974(4)	2934(4)	2695(11)	6.85
N2	5564(5)	3260(5)	2434(14)	6.90
N4	5857(6)	2304(6)	−436(14)	7.74
N6	4345(5)	2083(4)	−328(15)	6.60
C1	4919(4)	2663(4)	1168(12)	4.43
C2	5373(4)	2880(5)	1512(13)	4.81
C3	5684(5)	2785(5)	989(14)	5.60
C4	5538(4)	2436(5)	113(14)	5.22
C5	5092(4)	2197(4)	−304(13)	5.28
C6	4799(4)	2324(4)	228(13)	4.90
C11	3747(4)	1907(5)	3677(17)	7.66
C12	3619(7)	1958(9)	5037(18)	12.39
C13	3960(7)	2346(7)	5766(19)	11.63
C14	4414(6)	2563(6)	5154(15)	8.45
C21	4158(7)	3050(6)	−902(20)	13.62
C22	3903(6)	3268(8)	−548(20)	16.25
C23	4198(8)	3701(8)	25(28)	14.94
C24	4596(8)	3758(6)	748(20)	11.27
Cl	9037(2)	2929(2)	1403(5)	7.49
O1 [a]	8654(6)	2976(7)	1462(29)	12.46
O2 [a]	9399(7)	3241(7)	707(24)	15.84
O3 [a]	8901(8)	2467(5)	1213(25)	13.06
O4 [a]	9196(9)	2982(9)	2810(18)	15.87
O5 [a]	8772(13)	2821(14)	2563(30)	16.99
O6 [a]	9073(11)	2574(10)	813(44)	13.22
O7 [a]	8827(11)	3070(13)	371(35)	13.37
O8 [a]	9470(8)	3315(8)	1674(31)	8.27
HO1	3730(36)	2622(17)	2582(98)	9.60
HO2	3921(46)	3041(42)	3539(67)	9.60

[a] Partial occupation factor. See text.

selected bond lengths, angles and intermolecular distances. Atomic coordinates are given in Table 4. Anisotropic thermal parameters, a complete list of bond lengths and angles and observed and calculated structure factors are available from the authors.

Summary and conclusions

2-Nitroaryl ligands do not chelate to Pd^{II} when the 6 position of the aryl group is occupied by a substituent such as $-Me$ or $-NO_2$, because these groups interact with the ligand *trans* to the position which would be occupied by the nitro group. When such interference does not exist, (complex **9**), chelation occurs.

The crystal structure of complex **4** suggests that nitro groups exert a $-I$ rather than a $-M$ effect. This is the first *catena* structure of a Pd^{II} complex formed by hydrogen-bonding between coordinated water and the perchlorate anion and one of the few aqua-complexes of Pd^{II}.

Acknowledgments

We thank Dirección General de Investigación Científica y Técnica (Spain) (PB89-0430 and MAT 88-0268-CO2-02) for financial support; M.V.B. is grateful for a grant from the Ministerio de Educacion y Ciencia.

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