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New 2,4,6-trinitrophenylpalladium(II) complexes. Crystal and molecular structure of *trans*-2,4,6-trinitrophenyl(chloro)bis(triphenylarsine)palladium(II)

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Abstract

The complex $Q_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]$ ($Q=(PhCH_2)PPh_3$; R= 2,4,6-trinitrophenyl) reacts with PPh_3 or $AsPh_3$ in molar ratio 1/2 to give the dinuclear complexes $[Pd_2R_2(\mu\text{-}Cl)_2L_2]$. Complexes of the type $[Pd(R)ClL_2]$ ($L=PPh_3$, $AsPh_3$, $SbPh_3$, tetrahydrothiophene (tht) or L_2=1,2-bis(diphenylphosphino)-ethane (dppe), 1,5-cyclooctadiene (COD), 2,2′-bipyridine (bipy), 2,2′-biquinolyl (bquin), 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (Me_2phen)) have been obtained using the stoichiometric amounts, or an excess, of the corresponding ligands. The complex $[Pd(R)Cl(py)_2]$ (py = pyridine) could only be isolated starting from those with L = tht or L_2 = COD. The crystal structure of $[Pd(R)Cl(AsPh_3)_2]$ has been determined by X-ray diffraction methods. Crystals are monoclinic, space group $P2_1/c$, $a=14.214(4)$, $b=20.588(6)$, $c=14.295(4)$ Å, $\beta=104.94(2)°$, $V=4042(2)$ Å^3, $Z=4$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to $R=0.720$ for 2455 observed reflections. In the square planar coordination around the Pd atom the two $AsPh_3$ ligands are in *trans* positions and the 2,4,6-trinitrophenyl ligand acts as monodentate through a carbon atom with the phenyl ring nearly perpendicular to the coordination plane.

Introduction

We are interested in the structural properties of nitroaryl complexes because we have found some unexpected results concerning the relationship between the electron-withdrawing properties of the nitro group and the structural parameters of the ligand 2-nitrophenyl. In addition, the synthesis of series of this family of complexes has allowed us to show the coordination ability of the nitro group along with spectroscopic and bonding properties of these complexes [1–4].

The number of nitroarylmetal complexes described is rather limited because the classical way of synthesis, using lithium or magnesium derivatives, is not easily accessible due to the thermal instability or to the unavailability of these intermediates. In fact, only a few complexes containing 2-nitrophenyl groups have been reported using the corresponding lithium derivative [5].

We have shown that organomercury derivatives are excellent intermediates in the synthesis of nitroaryl complexes of rhodium [1], gold [2], palladium [3] and platinum [4]. This route also allows the synthesis of complexes containing other ring substituents, in addition to the nitro group, incompatible with lithium or magnesium as is the case of the $-NH_2$ group [4] or with several nitro groups such as in the 2,4,6-trinitrophenyl ligand (R), of which we have reported the anionic complexes $[Pd_2R_2X_2(\mu\text{-}X)_2]^{2-}$ (X = Cl, Br) [3c] and $[Au(R)Cl]^-$ [6].

The synthesis of 2,4,6-trinitrophenyl complexes was designed to compare their properties with those of the 2-nitrophenyl ones and also to know if it is possible to prepare complexes containing one or both *ortho*-nitro groups coordinated to a metal. In this last case such complexes would be related to those obtained by van Koten and co-workers with the

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ligand 2,6-$(Me_2NCH_2)_2C_6H_3$ which have unusual and very interesting properties [7].

In this paper we report the results of the reactions between $Q_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]$ and neutral ligands along with the crystal structure of $[Pd(R)Cl(AsPh_3)_2]$.

Experimental

Recording of the IR spectra, the C, H and N analyses, conductance measurements, and the melting point determinations were performed as described elsewhere [3c]. NMR spectra (in $CDCl_3$ except for complex **8**, see below) were recorded in a Brucker 200AC spectrometer. Reactions were carried out with magnetic stirring without special precautions to exclude light or moisture. The recipes below are for the best yield method. All complexes are yellow in colour. Yields, elemental analyses, melting points and relevant spectroscopic data are included in Table 1.

$[Pd_2R_2(\mu\text{-}Cl)_2L_2]$ (L = PPh_3 (1), $AsPh_3$ (2))

After 3 h of stirring $Q_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]\cdot 2Me_2CO$ [3c] (120 mg, 0.075 mmol) and PPh_3 or $AsPh_3$ (molar ratio 1/2) in dichloromethane (8 cm^3) the resulting suspension was filtered to remove some decomposition products, the filtrate concentrated (2 cm^3) and ethanol (14 cm^3) added to precipitate **1** or **2**, which were washed with ethanol and recrystallized from dichloromethane/ethanol.

$[Pd(R)ClL_2]$ (3–12)

The following general method was used. To a suspension of $Q_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]\cdot 2Me_2CO$ (70–300 mg) in dichloromethane (5–10 cm^3) the ligand was added in molar ratio 1/2 for **7**, **10** and **12** and in 10–20% excess for all the others. After *c.* 1–4 h stirring for all except **8** (24 h) the mixture was concentrated (1–2 cm^3) and ethanol (for **8**, **9** and **11**) or methanol (10–15 cm^3) added to precipitate the corresponding complexes which were washed with the same precipitating agent (ROH) and recrystallized from dichloromethane/ROH except complexes **9** and **12** which were recrystallized from hot acetone. Complexes **4** and **11** were dried in an oven (80 °C, 3 and 5 h, respectively) to remove trace amounts of solvents.

trans-$[Pd(R)Cl(PPh_3)_2]$ (3t)

To a suspension of $[Pd(R)Cl(tht)_2]$ (**6**) (71.6 mg, 0.15 mmol) in dichloromethane (4 cm^3) solid PPh_3 (70.8 mg, 0.27 mmol) was added. The solution was stirred for 3 h, filtered and concentrated (to 1 cm^3). Addition of diethyl ether (15 cm^3) gave **3t** which was recrystallized from dichloromethane/diethyl ether.

$[Pd(R)Cl(py)_2]$ (13)

To a suspension of [PdRCl(COD)] (46.4 mg, 0.10 mmol) in dichloromethane (5 cm^3) an excess of pyridine (0.2 cm^3) was added and the resulting mixture stirred for 24 h and filtered. The filtrate was concentrated (1 cm^3) and diethyl ether added (8 cm^3) to precipitate **13** which was washed with diethyl ether (5 cm^3) and recrystallized from dichloromethane + pyridine (5 cm^3 + 1 drop)/diethyl ether (15 cm^3).

Crystal structure determination of the complex $[Pd(R)Cl(AsPh_3)_2]$ (4)

All crystals of **4** were of very poor quality and mostly twinned. A thin fragment of a larger crystal of approximate dimensions 0.05 × 0.20 × 0.30 mm was used for the X-ray data collection. Unit-cell parameters were obtained by least-squares refinement of the θ values of 30 carefully centred reflections (with θ in the range 20–39°).

Crystal data

$C_{42}H_{32}As_2ClN_3O_6Pd$, $M = 966.43$, monoclinic, space group $P2_1/c$, $a = 14.214(4)$, $b = 20.588(6)$, $c = 14.295(4)$ Å, $\beta = 104.94(2)°$, $V = 4042(2)$ Å^3, $Z = 4$, $D_c = 1.588$ g cm^{-3}, $F(000) = 1928$, μ(Cu Kα) = 66.58 cm^{-1}.

Data were collected at room temperature on a Siemens AED diffractometer using nickel filtered Cu Kα radiation ($\lambda = 1.54178$ Å) and the $\theta/2\theta$ scan technique, the individual profiles having been analyzed according to Lehmann and Larsen [8]. All reflections with θ in the range 3–65° were measured. Of 6914 independent reflections, 2455, having $I > 3\sigma(I)$, were considered observed and used in the analysis. The intensity of one standard reflection was measured after 50 reflections as a general check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. A correction for absorption effects was applied [9] using the program ABSORB [10] (maximum and minimum values for the transmission factors were 1.027 and 0.890). The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, first with isotropic and then with anisotropic thermal parameters for all non-hydrogen atoms excepting the carbons of the phenyl rings. The hydrogen atoms were placed at their geometrically calculated positions (C–H = 1.0 Å) and refined 'riding' on the corresponding carbon atoms. The SHELX system of computer programs was used

TABLE 1. Analytical, spectroscopic and other data for complexes **1**–**13**

Compound	^{1}H NMR^{a} δ (ppm) J(H–P) (Hz)	^{31}P NMR^{b} δ (ppm) J(P–P) (Hz)	ν(Pd–Cl) (cm^{-1})	Melting point (°C)	Analytical data found (calc.) (%)			Yield (%)
					C	H	N	
$[Pd_2R_2(\mu\text{-}Cl)_2(PPh_3)_2]$ (**1**)	8.56	24.98	290, 265	264^{d}	46.11 (46.78)	3.44 (2.78)	6.49 (6.82)	65
$[Pd_2R_2(\mu\text{-}Cl)_2(AsPh_3)_2]$ (**2**)	8.54		290, 265	270^{d}	44.90 (43.66)	2.86 (2.59)	6.54 (6.36)	66
$[Pd(R)Cl(PPh_3)_2]$ (**3**)	8.12^{b} 8.59^{c} ($J=2$)	19.68^{b} 23.5, 26.5^{c} ($J_{AB}=26.9$)	315	235^{d}	56.72 (57.42)	3.86 (3.67)	4.64 (4.78)	83
trans-$[Pd(R)Cl(PPh_3)_2$ (**3t**)	8.12	19.68	315	250^{d}	57.31 (57.42)	3.42 (3.67)	4.71 (4.78)	65
$[Pd(R)Cl(AsPh_3)_2]$ (**4**)	8.02		315	254	52.16 (52.20)	3.33 (3.33)	4.32 (4.35)	84
$[Pd(R)Cl(SbPh_3)_2]$ (**5**)	8.08		310	155^{d}	47.60 (47.50)	3.38 (3.04)	3.47 (3.96)	98
$[Pd(R)Cl(tht)_2]$ (**6**)	8.91		315	167	32.31 (31.71)	3.07 (3.42)	8.09 (7.92)	66
$[Pd(R)Cl(dppe)]$ (**7**)	8.77 ($J=2$)	56.0, 48.5 ($J=19$)	310	222	51.07 (51.08)	3.83 (3.48)	5.93 (5.88)	63
$[Pd(R)Cl(COD)]$ (**8**)	8.82, 8.67^{e}		^{e}	183^{d}	36.43 (36.38)	3.14 (3.05)	8.71 (9.09)	76
$[Pd(R)Cl(bipy)]$ (**9**)	^{e}		350	300	37.83 (37.67)	2.08 (1.97)	13.75 (13.73)	86
$[Pd(R)Cl(bquin)]$ (**10**)	^{e}		340	315^{d}	46.90 (47.24)	2.33 (2.31)	12.07 (11.48)	97
$[Pd(R)Cl(phen)]$ (**11**)	^{e}		350	315	39.51 (40.47)	2.09 (2.04)	13.03 (13.11)	92
$[Pd(R)Cl(Me_2phen)]$ (**12**)	^{e}		335	302^{d}	42.65 (42.73)	3.21 (2.51)	12.46 (12.46)	83
$[Pd(R)Cl(py)_2]$ (**13**)	^{e}		335, 310	253^{d}	37.57 (37.52)	2.33 (2.36)	13.42 (13.67)	71

^{a}Corresponding to H3 and H5 of the aryl ligand. ^{b}Corresponding to the *trans* isomer. ^{c}Corresponding to the *cis* isomer. ^{d}With decomposition. ^{e}See text.

[11]. In the last cycles of refinement a weighting scheme was used, $w=K[\sigma^2(F_o)+gF_o^2]^{-1}$, with $K=0.896$ and $g=0.004$ at the convergence. The final atomic coordinates for the non-hydrogen atoms are given in Table 2. Final R and R' values were 0.0720 and 0.0927, respectively. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 12. All calculations were performed on the GOULD POWERNODE 6040 computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma. See also 'Supplementary material'.

Results and discussion

Synthesis

We previously reported reactions of $Q_2[Pd_2R_2X_2(\mu\text{-}X)_2]$ (X = Cl, Br) with excess of dimethyl sulfoxide (dmso) to give the corresponding anionic complexes *cis*-$[Pd(R)X_2(dmso)]^-$ [3c]. However, PPh_3 or $AsPh_3$ behave differently because the substitution reaction products $[Pd_2R_2(\mu\text{-}Cl)_2L_2]$ (L = PPh_3 (**1**); $AsPh_3$ (**2**) or $[Pd(R)ClL_2]$ (L = PPh_3 (**3**); $AsPh_3$ (**4**)) are isolated when the molar ratio between reagents is 1/2 or an excess of the ligands is used, respectively.

When monodentate or bidentate ligands are reacted (1/4 or 1/2 molar ratios, respectively, or excess) with $Q_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]$ complexes of the type $[Pd(R)ClL_2]$ are also obtained (L = $SbPh_3$ (**5**), tetrahydrothiophene (tht) (**6**); L_2 = 1,2-bis(diphenyl phosphino)ethane (dppe) (**7**), 1,5-cyclooctadiene (COD) (**8**), 2,2'-bipyridine (bipy) (**9**), 2,2'-biquinolyl (bquin) (**10**), 1,10-phenanthroline (phen) (**11**), 2,9-dimethyl-1,10-phenanthroline (Me_2phen)] (**12**)). The corresponding reaction with pyridine (py) always leads to a mixture of compounds. However, $[Pd(R)Cl(py)_2]$ (**13**) could be isolated starting from

TABLE 2. Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of **4**

	x	*y*	*z*
Pd	1618(1)	814(1)	2299(1)
As(1)	254(2)	1504(1)	2304(2)
As(2)	3015(1)	180(1)	2158(2)
Cl	535(3)	−13(3)	1633(4)
O(1)	2029(24)	731(18)	4356(18)
O(2)	3308(24)	988(15)	5328(22)
O(3)	4747(21)	2998(15)	5182(26)
O(4)	4614(26)	3490(17)	3758(26)
O(5)	2553(22)	2567(13)	964(17)
O(6)	2135(17)	1621(11)	928(14)
N(1)	2720(22)	1046(17)	4536(20)
N(2)	4418(22)	3095(21)	4319(33)
N(3)	2488(16)	2076(14)	1368(19)
C(1)	2491(13)	1528(9)	2898(13)
C(2)	2935(16)	1568(12)	3904(17)
C(3)	3608(18)	2056(15)	4376(20)
C(4)	3752(18)	2534(13)	3807(28)
C(5)	3381(17)	2573(13)	2829(22)
C(6)	2817(15)	2016(12)	2418(18)
C(7)	534(13)	2424(9)	2500(14)
C(8)	1006(15)	2690(10)	3365(15)
C(9)	1295(18)	3328(12)	3446(19)
C(10)	1126(20)	3692(14)	2661(21)
C(11)	678(19)	3447(13)	1726(21)
C(12)	374(17)	2790(12)	1693(18)
C(13)	−750(14)	1531(10)	1061(14)
C(14)	−471(16)	1394(10)	194(15)
C(15)	−1187(15)	1469(10)	−664(16)
C(16)	−2109(16)	1670(10)	−707(16)
C(17)	−2330(17)	1775(11)	175(17)
C(18)	−1694(14)	1693(10)	1072(15)
C(19)	−405(14)	1276(10)	3277(14)
C(20)	−896(17)	1741(12)	3704(17)
C(21)	−1432(17)	1558(12)	4359(17)
C(22)	−1466(18)	910(12)	4588(18)
C(23)	−997(17)	463(12)	4176(17)
C(24)	−456(15)	644(10)	3480(15)
C(25)	4260(15)	598(10)	2673(16)
C(26)	4735(16)	515(12)	3673(17)
C(27)	5593(21)	882(14)	4045(23)
C(28)	5904(27)	1282(18)	3458(27)
C(29)	5503(20)	1402(14)	2507(21)
C(30)	4617(17)	1007(11)	2128(18)
C(31)	3024(12)	29(8)	844(12)
C(32)	2154(14)	75(10)	105(14)
C(33)	2140(16)	−89(11)	−855(16)
C(34)	2988(16)	−287(11)	−1075(17)
C(35)	3833(16)	−366(10)	−366(16)
C(36)	3852(16)	−252(10)	613(16)
C(37)	3207(14)	−648(10)	2767(15)
C(38)	4064(17)	−995(11)	2859(16)
C(39)	4213(17)	−1641(11)	3241(16)
C(40)	3448(18)	−1905(12)	3534(18)
C(41)	2561(16)	−1570(11)	3443(15)
C(42)	2466(14)	−951(10)	3074(14)

the tht or COD complexes **6** or **8**, respectively. Probably, reactions (1) and (2) are equilibria (L = py) and when a precipitating agent (e.g. MeOH) is added to isolate complex **13** a mixture of $Q_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]$ (the presence of the cation Q^+ in the obtained mixture is evident by IR and NMR spectroscopies), $[Pd_2R_2(\mu\text{-}Cl)_2(py)_2]$ and $[Pd(R)Cl(py)_2]$ is obtained. Reaction (2) (L = py) is proved to be an equilibrium by the fact that **13** must be recrystallized in the presence of added pyridine because otherwise a mixture of compounds is obtained. Probably reaction (2) is also an equilibrium for L = $AsPh_3$ because the dinuclear complex **2** (L = $AsPh_3$) can also be obtained by reacting $Q_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]$ and complex **4** (1/2) which could be interpreted as the result of the presence of enough $AsPh_3$ in equilibrium (2) to allow reaction (1) to occur.

$$[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]^{2-} + 2L \longrightarrow [Pd_2R_2(\mu\text{-}Cl)_2L_2] + 2Cl^- \quad (1)$$

$$[Pd_2R_2(\mu\text{-}Cl)_2L_2] + 2L \text{ (or } L_2) \longrightarrow 2[Pd(R)ClL_2] \quad (2)$$

The mononuclear nature of complex **7** has been confirmed in solution by measuring the molecular weight in chloroform (isopiestic method: found, 780; calc., 752).

Table 1 gives analytical and other data for complexes **1–13**. All complexes are non-conducting in acetone solutions.

NMR and IR spectra

The resonance corresponding to both H3 and H5 of the trinitrophenyl ligand appears at 8.0–9.0 ppm in the ^1H NMR spectra of complexes 1–13 (see Table 1). However, in complexes **9–12** other resonances in this region, corresponding to the neutral ligands, make the assignment unreliable.

NMR spectra (see Table 1) show that the dinuclear complexes **1** and **2** are only one of the possible isomers (unless a rapid interchange of ligands at room temperature occurs) and that complex **3** is a 2/1 mixture of *cis* and *trans* isomers.

The presence of shoulders in the two signals at 8.86 and 8.81 ppm in the ^1H NMR spectrum of the py complex **13** points to the probable presence in solution of other species in addition to the *cis* and *trans* isomers. It is likely that, as we assumed above, they are dimeric complexes formed through reaction (2).

Mononuclear complexes with $AsPh_3$, $SbPh_3$ and tht, **4–6**, contain only one isomer. In order to know the geometry of these complexes and to fulfill our previous objectives (see 'Introduction') we tried to grow single crystals but only in the case of **4** did we succeed (see below). The pattern of the ^1H NMR signals corresponding to CH_2 groups in complex **6** is very similar to that in the free tht ligand which suggests a *trans* geometry (as complex **4**) which is also supported, in the solid state, by IR spectroscopic data (see below).

Complex **8** is not soluble enough in non-coordinating solvents (although a solution is obtained when COD is added to a dichloromethane solution of $Q_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]$) as to permit recording of its ^1H NMR spectrum. When dissolved in d^6-dimethyl sulfoxide two different signals appear at 8.82 and 8.67 ppm which could be due to a mixture of **8** and $[Pd(R)Cl(d^6\text{-}dmso)_2]$. This complex, is neither obtainable from $Q_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]$ [3c] nor from a dmso solution of **8** because when ethanol was added to precipitate it, complex **8** was recovered.

Trying to prepare separately both isomers of **3** we carried out reactions between the *trans*-tht and *cis*-COD complexes **6** and **8** with excess of PPh_3. However, only the *trans* isomer **3t** is formed. Neither of the two isomers of **3** convert to each other when the mixture is heated for 2 h in chloroform but the molar ratio *cis*/*trans* increases slightly.

IR spectra of all complexes show bands at around 1530(vs) and 1330(vs) cm^{-1}, corresponding to $\nu_{asym}(NO_2)$ and $\nu_{sym}(NO_2)$, respectively. The absence of any medium to strong band in the 1250–1300 cm^{-1} region suggests that there is no coordinated nitro group [1–4, 6] as was later confirmed in the case of complex **4**. This means that complexes **1** and **2** should be dinuclear with chloro bridges, as formulated.

A medium band in the 350–250 cm^{-1} region can tentatively be assigned to the $\nu(Pd\text{–}Cl)$ mode. The observed values are according to the *trans* influence series. Thus, all complexes having chelating N-donor atoms and therefore of a *cis* geometry, **9**–**12**, show a medium band in the 335–350 cm^{-1} region assignable to $\nu(Pd\text{–}Cl)$ *trans* to N, a value which is similar to those found in complexes *cis*-$[Pd(R)ClL_2]$ ($R = C_6H_3Me\text{-}2, NO_2\text{-}6$; $L_2 =$ bipy, phen) [3b]. The band assignable to $\nu(Pd\text{–}Cl)$ *trans* to C appears at 315 cm^{-1} in complex **4**. Therefore, those appearing near this value in complexes **3t** (315 cm^{-1}), **5** (310 cm^{-1}) and **6** (315 cm^{-1}) could indicate a *trans* geometry for these complexes, also in the solid state. The strong band which complex **3** shows at 535 cm^{-1}, assignable to the *cis* isomer [3b, 13], is absent in **3t**. The presence of two bands at 335(m) ($\nu(Pd\text{–}Cl)$ *trans* to N) and 310(m) ($\nu(Pd\text{–}Cl)$ *trans* to C) cm^{-1} in the py complex **13** suggests the presence of both isomers in the solid state.

In both dimeric complexes **1** and **2** the two bands at 290 and 265 cm^{-1} can be assigned to $\nu(Pd\text{–}Cl)_{bridge}$ according to the expected lowering with respect to the above $\nu(Pd\text{–}Cl)_{terminal}$ bands. Both bands are 15–20 cm^{-1} shifted to higher wavenumber with respect to the corresponding ones in the starting complex $Q_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]$ [3c]. The anionic nature of this complex, which should decrease the strength of the $p_\pi(Cl) \rightarrow d_\pi(Pd)$, could be the reason for the lowering of the $\nu(Pd\text{–}Cl)_{bridge}$. We have observed a similar relationship in gold(III) complexes [14].

The band assignable to $\nu(Pd\text{–}Cl)$ *trans* to P in complex **7** appears at 310 cm^{-1}. A band at 880(m) cm^{-1} which is assigned to the presence of the chelating dppe ligand [15] proves that, as in solution, complex **7** is mononuclear. In complex **8** the presence of several bands in the 280–330 cm^{-1} region due to the neutral ligand makes the assignment of $\nu(Pd\text{–}Cl)$ difficult.

Description of the crystal structure of complex 4

The structure of **4** is represented in Fig. 1 together with the atomic numbering system; selected bond distances and angles are given in Table 3. The crystal structure consists of discrete units of neutral complexes $[Pd(R)Cl(AsPh_3)_2]$ in which the Pd atom is coordinated in a square planar fashion by two As atoms, in *trans* position, from $AsPh_3$ ligands, by a chlorine atom, and a carbon atom from the trinitrophenyl ligand. The square planar coordination is only slightly distorted as the C(1) atom deviates by 0.24(2) Å from the mean plane passing through the

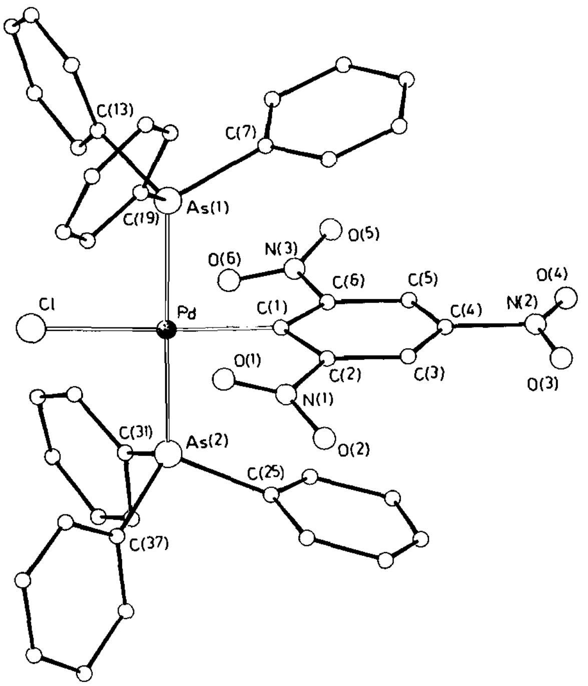

Fig. 1. View of the molecular structure of the complex $[Pd(R)Cl(AsPh_3)_2]$ ($R = 2,4,6$-trinitrophenyl) (**4**) with the atomic numbering system.

TABLE 3. Selected bond distances (Å) and angles (°) for **4**

Pd–As(1)	2.406(3)	Pd–As(2)	2.427(3)
Pd–Cl	2.329(5)	Pd–C(1)	1.97(2)
As(1)–C(7)	1.94(2)	As(2)–C(25)	1.93(2)
As(1)–C(13)	1.97(2)	As(2)–C(31)	1.91(2)
As(1)–C(19)	1.93(2)	As(2)–C(37)	1.90(2)
N(1)–O(1)	1.15(5)	N(3)–C(6)	1.46(3)
N(1)–O(2)	1.23(4)	C(1)–C(2)	1.42(3)
N(2)–O(3)	1.22(6)	C(2)–C(3)	1.43(4)
N(2)–O(4)	1.22(6)	C(3)–C(4)	1.33(5)
N(3)–O(5)	1.18(4)	C(4)–C(5)	1.36(5)
N(3)–O(6)	1.17(3)	C(5)–C(6)	1.44(3)
N(1)–C(2)	1.49(4)	C(1)–C(6)	1.36(3)
N(2)–C(4)	1.55(5)		
As(1)–Pd–As(2)	174.3(1)	Cl–Pd–C(1)	177.3(6)
As(1)–Pd–Cl	89.1(2)	As(1)–Pd–C(1)	88.6(6)
As(2)–Pd–Cl	92.4(2)	As(2)–Pd–C(1)	90.0(6)
Pd–As(1)–C(7)	116.2(6)	Pd–As(2)–C(25)	114.6(6)
Pd–As(1)–C(13)	114.2(6)	Pd–As(2)–C(31)	112.5(5)
Pd–As(1)–C(19)	113.6(6)	Pd–As(2)–C(37)	117.9(6)
Pd–C(1)–C(2)	123(2)	Pd–C(1)–C(6)	126(2)
C(2)–C(1)–C(6)	110(2)	N(1)–C(2)–C(1)	118(2)
C(1)–C(2)–C(3)	126(2)	N(1)–C(2)–C(3)	116(2)
C(2)–C(3)–C(4)	115(3)	N(2)–C(4)–C(3)	116(3)
C(3)–C(4)–C(5)	126(3)	N(2)–C(4)–C(5)	118(3)
C(4)–C(5)–C(6)	114(3)	N(3)–C(6)–C(1)	121(2)
C(5)–C(6)–C(1)	127(2)	N(3)–C(6)–C(5)	111(2)
O(1)–N(1)–O(2)	119(3)	O(4)–N(2)–C(4)	114(4)
O(1)–N(1)–C(2)	125(3)	O(5)–N(3)–O(6)	120(3)
O(2)–N(1)–C(2)	116(3)	O(5)–N(3)–C(6)	122(3)
O(3)–N(2)–O(4)	133(4)	O(6)–N(3)–C(6)	118(3)
O(3)–N(2)–C(4)	113(4)		

coordinated atoms (As(1), As(2) and Cl deviate by −0.004(2), −0.003(2) and 0.020(6) Å, respectively, with Pd out by 0.111(2) Å). The slight difference in the Pd–As(1) and Pd–As(2) bond distances (2.406(3) and 2.427(3) Å) seems due to steric hindrance effects. In fact, the C(7)–As(1)–Pd–C(1) and C(25)–As(2)–Pd–C(1) torsion angles of 16.0(8) and 1.4(9)° show that in both $AsPh_3$ groups an $As–C_{Ph}$ bond eclipses the Pd–C(1) bond and the longer Pd–As corresponds to the narrower torsion angle. The Pd–Cl bond, 2.329(5) Å, is significantly shorter than in *cis*-$[Pd(R)Cl_2\{S(O)Me_2\}]^-$, 2.365(1) Å [3c], and this could be attributed to the anionic nature of this complex, which, as mentioned above when the IR spectra were discussed, should decrease the strength of the $p_\pi(Cl) \rightarrow d_\pi(Pd)$ bonding. We have observed a similar relationship between the charge of two thallium(III) complexes and the Tl–Cl bond distances [16]. Also the Pd–C(1) bond, 1.97(2) Å, is shorter than in *cis*-$[Pd(R)Cl_2\{S(O)Me_2\}]^-$ (1.994(4) Å) but, in this case, the difference is not significant.

The trinitrophenyl group, with exception of the oxygen atoms, is planar (maximum deviation of 0.08(3) Å for C(3)) and forms an angle of 86.0(4)° with the mean coordination plane. The nearly perpendicular disposition of this ligand with respect to the coordination plane determines axial positions for oxygen atoms of two nitro groups (Pd–O(1), 2.85(3) Å and Pd–O(6) 2.81(2) Å). These distances are comparable to those found in *cis*-$[Pd(R)Cl_2\{S(O)Me_2\}]^-$ (2.910 and 2.911 Å) [3c] and in $[Pd_2(R')_2Cl_2(\mu\text{-}Cl)_2]^{2-}$ [R′ = 2-methyl-6-nitrophenyl; Pd–O, 2.893(6) Å] [3b]. In these three cases it is difficult to say if such Pd–O distances correspond to weak interactions or to geometrical constraints. In the complex *cis*-$[Pd(R'')_2(py)]$ (R″ = 2-nitrophenyl), in which one of the two nitrophenyls acts as monodentate ligand through the carbon and the other one chelates through one carbon and one oxygen atom, these geometrical constraints are missing but the Pd–O distance is always rather short, 2.888 Å [3a]. The three $C–NO_2$ groups are tilted ($CN(1)O_2$, 24(1)°; $CN(2)O_2$, 2(1)°; $CN(3)O_2$, 15(1)°) with respect to the mean phenyl plane, the one almost coplanar being the one not involved in the short contact with the Pd atom, as in *cis*-$[Pd(R)Cl_2\{S(O)Me_2\}]^-$ [3c].

The C–C bond distances within the phenyl ring, ranging from 1.33(5) to 1.44(3), even if with high e.s.d.s, seem to be normal as observed in other trinitrophenyl complexes [3c]. The presence of the three electron-withdrawing groups causes significant deformation in the bond angles rather than in bond distances of the ring. The endocyclic angles at C(2), C(4) and C(6), bonded to the nitro groups, are 126(2), 126(3) and 127(2)°, respectively, while those at C(1), C(3) and C(5) are 100(2), 115(3) and 114(3)°, a comparable trend having been observed also in *cis*-$[Pd(R)Cl_2\{S(O)Me_2\}]^-$ [3c] and in $[Au(R)(Me_2phen)]$ (Me_2phen = 2,9-dimethyl-1,10-phenanthroline) [6].

Supplementary material

Coordinates of the hydrogen atoms, thermal parameters and a list of observed and calculated structure factors are available from the authors on request.

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