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Anionic 2,4,6-trinitrophenylpalladium(II) complexes. Crystal structure of *cis*-$[PdCl_2\{2,4,6\text{-}C_6H_2(NO_2)_3\}\{S(O)Me_2\}]^-$

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Abstract

Treatment of $[(PhCH_2)PPh_3]_2[Pd_2Cl_4(\mu\text{-}Cl)_2]$ with HgR_2 (R = 2,4,6-trinitrophenyl) (1/2) in refluxing acetone gives $[(PhCH_2)PPh_3]_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]\cdot 2Me_2CO$ (**1**). Reaction of **1** with an excess of NaX gives $[(PhCH_2)PPh_3]_2[Pd_2R_2X_2(\mu\text{-}X)_2]$[X = Br (**2**), I (**3**)]. Reactions of **1** or **2** with dimethylsulfoxide give the complexes *cis*-$[(PhCH_2)PPh_3][Pd(R)X_2\{S(O)Me_2\}]$ (X = Cl (**4**) or Br (**5**)). An X-ray diffraction study of complex **4** has revealed a square-planar coordination around the palladium atom, with mutually *cis* chloro ligands and a S-bonded coordination of dimethylsulfoxide. The shortest Pd–O distances (2.911 and 2.910 Å) are too long to imply intramolecular coordination.

Introduction

We have used arylmercury(II) compounds as transmetallating agents in the preparations of aryl complexes of gold(I) and gold(III) [1], palladium(II) [2], platinum(II) [3], rhodium(III) [4], and tin(IV) [5]. Most recently we extended the method to thallium(III) [6].

One of the types of aryl groups we transfer bear *ortho*-nitro groups [1c,d,g,2,3a,b,4]. We are interested in using transmetallation involving these aryl groups in order to obtain complexes which permit study of the coordination properties of the nitro group, and also to establish the range of synthetic application of the corresponding mercury derivatives in preparation of functionalized aryl complexes that are not accessible through the usual organolithium or Grignard routes.

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Many applications of organomercury compounds in organic synthesis use stoichiometric or catalytic amounts of $Li_2[PdCl_4]$. Organopalladium complexes are suggested to be intermediates [7]. Because most of these organopalladium derivatives have not been isolated, we thought it of interest to study mercury-to-palladium transmetallation reactions and to isolate the products.

We describe here the synthesis of the anionic palladium(II) complexes $[Pd_2R_2X_2(\mu\text{-}X)_2]^{2-}$ in which R is 2,4,6-trinitrophenyl. The only previously reported complexes of this type are those we recently described which have R = C_6H_3Me-2, NO_2-6 [2a]. We chose the trinitrophenyl group for several reasons, one of them being that it has both *ortho* positions occupied and the products could be expected to be stable owing to the well known *ortho*-effect [8]. Additionally, we wished to know if the aryl group could act as a chelating ligand to give one or two five-membered metallacycles. Another reason was that there are very few 2,4,6-trinitrophenyl complexes, and the only involving a transition element is $[Pt(R)\{N(C_6H_5)_2\}(PPh_3)_2]$ [9], obtained by treating $Pt(PPh_3)_4$ with $(Ph)_2N\dot{N}R$.

Results and discussion

When an acetone suspension containing $[HgR_2]$ (R = 2,4,6-$C_6H_2(NO_2)_3$) and $[(PhCH_2)PPh_3]_2[Pd_2Cl_4(\mu\text{-}Cl)_2]$ (2/1) is refluxed, an orange solution is obtained. When this is cooled to room temperature the orange complex $[(PhCH_2)PPh_3]_2[Pd_2R_2Cl_2(\mu\text{-}Cl_2] \cdot 2Me_2CO$ (**1**) separates. It can be freed from solvent keeping it at 60 °C for 40 h.

We recently reported [2b] the synthesis of *ortho*-nitrophenylpalladium(II) complexes containing chelating and/or monodentate *ortho*-nitrophenyl ligands. These complexes are prepared from those obtained by treating bis(*o*-nitrophenyl)mercury with $PdCl_2$. Depending on whether a molar ratio of 2/1 or 1/1 is used the complexes *cis*-$[Pd\{o\text{-}C_6H_4N(O)O\}_2]$ or $[Pd\{o\text{-}C_6H_4N(O)O\}(\mu\text{-}Cl)]_2$, respectively, are formed. However, no reactions were observed between $[HgR_2]$ (R = 2,4,6-trinitrophenyl) and $PdCl_2$ (1/1, in refluxing ethanol) or $[PdCl_2(NCMe)_2]$ (1/1, room temperature in acetonitrile, 5 days) or $[PdCl_2(NCPh)_2]$ (1/1, room temperature in acetone, 3 days). This behaviour is the same as that described previously for reactions between $[HgR_2]$ (R = C_6H_3Me-2, NO_2-6) and $PdCl_2$ [2a].

Complex **1** reacts with an excess of NaX salts to give $[(PhCH_2)PPh_3]_2[Pd_2R_2X_2(\mu\text{-}X)_2]$, with X = Br (**2**) or I (**3**).

When dimethylsulfoxide is added to orange suspensions of complexes **1** and **2** in acetone, yellow solutions are obtained from which complexes $[(PhCH_2)PPh_3][Pd(R)X_2\{S(O)Me_2\}]$ (X = Cl (**4**) or Br (**5**)) can be isolated. However, there is no change in the colour of the orange solution of **3** in acetone when dimethylsulfoxide is added, and complex **3** can be recovered unchanged. These mononuclear anionic complexes correspond to a rarely found stoicheiometry in the organometallic chemistry of palladium. As far as we know the only aryl complexes similar to **4**–**5** are $[Pd\{o\text{-}C_6H_4C(Me)\text{=}NNHPh\}Cl(Br)]$ [10] and the complex $[(PhCH_2)PPh_3][Pd(R)X_2\{S(O)Me_2\}]$ (R = C_6H_3Me-2, NO_2-6) that we described recently [2a].

Complex **4** is stable in the solid state, but addition of diethyl ether to its acetone solutions gave a mixture of **4** and **1**.

Table 1 gives analytical and other data for complexes **1**–**5**.

IR and NMR spectra

The IR spectra of complexes **1–5** show a band in the 1330–1340(s) cm^{-1} region assignable to the $\nu_{sym}(NO_2)$ mode of the nitro groups. This is the expected region for a non-coordinated nitro group [1c,d,g,2b,11]. When it is bonded through an oxygen atom, giving a five-membered ring, the band appears at a lower frequency of ca. 1260 cm^{-1} [2b,3a,b,4,12]. Furthermore, complexes **1–5** show three bands in the 1580–1590(s), 1510–1535(s), and 815–820(m) cm^{-1} regions assignable to vibrations of a substituted phenyl ring, $\nu_{asym}(NO_2)$, and the deformation vibration $\delta(NO_2)$, respectively.

We previously reported the synthesis, IR study, and crystal structure of *trans*-$[(PhCH_2)PPh_3]_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2] \cdot 2Me_2CO$ ($R = C_6H_3Me\text{-}2, NO_2\text{-}6$) [2a]. This complex shows bands at 335(m), 280(w) and 240(w) cm^{-1} which are assignable to $\nu(PdCl)$ modes corresponding to terminal and bridging chloro ligands, respectively. Complex **1** also shows three bands at 335(m), 270(w) and 250(w) cm^{-1}, which suggests the same *trans* geometry for **1**. Complexes **2** and **3** show similar IR spectra to those of the solvent-free form of complex **1**, except in the 400–200 cm^{-1} region. Those bands assigned in **1** to $\nu(Pd\text{–}Cl)$ disappear in **2**, and two others at 230 and 245 cm^{-1} are observed, which can be assigned to $\nu(Pd\text{–}Br)$, while no bands are observed for **3** in this region.

The presence of acetone in **1** accounts for an IR band at 1700(s) cm^{-1} and a signal at 2.07 ppm in its ^1H NMR spectrum, in dimethylsulfoxide solutions. This ^1H NMR spectrum and the analytical data allows us to formulate **1** as containing two acetone molecules per dimer, which is also the ratio found for its analogue with $R = C_6H_3Me\text{-}2, NO_2\text{-}6$.

The IR spectrum of $[(PhCH_2)PPh_3][Pd(R)X_2\{S(O)Me_2\}]$ (**4**) shows a band at 1115(s) cm^{-1} that we assigned [13] to the $\nu(S{=}O)$ mode in the S-bonded coordination. The related complex with $R = C_6H_3Me\text{-}2, NO_2\text{-}6$, shows a band at 1130 cm^{-1} which we assigned to the same $\nu(S{=}O)$ mode. The crystal structure of **4** (see below) supports our previous IR and structural assignments. The IR spectrum of **5** is similar to that of **4** except for the presence in **4** of three additional bands at 325, 305 and 290 cm^{-1}, two of which must be associated with $\nu(Pd\text{–}Cl)$ modes. From these similarities we think that **5** is also the *cis*-isomer in the solid state.

The NMR spectra of complexes **1–5** show a singlet corresponding to both protons of the trinitrophenyl group at around δ 8.5 ppm. Complex **2** shows two signals in this region, which could be due to the presence in solution of the two possible isomers (*cis* and *trans*) in a 1/1 ratio. The CH_2 group of the cation gives rise to a doublet at around δ 5 ppm (J(P-H) 14–15 Hz) in all the complexes.

Crystal structure of complex 4

Figure 1 shows a perspective view of the structure of the anion and cation (for clarity, only the non-hydrogen atoms are shown). Final atom coordinates are listed in Table 2, and Tables 3 and 4 give the bond distances and bond angles. Table 5 shows selected non-bonded interatomic distances.

In the anion, the Pd atom has a square planar coordination with two *cis* Cl, one C, and one S atoms. The shortest Pd–O distances (2.911 and 2.910 Å) are too long to imply intramolecular coordination. These Pd–O distances are significantly longer than those reported for complexes containing chelating *ortho*-nitrophenyl ligands, such as those in *cis*-$[Pd\{o\text{-}C_6H_4N(O)O\}_2]$ (2.158(5) and 2.136(5) Å) and in *cis*-

Table 1

Analytical and other data for complexes 1–5

Compound [a]	^{1}H NMR [b] δ(ppm) J(H–P) (Hz)	M.p. (°C)	Λ_M [c]	Analytical data (found(calc.) (%)) C	H	N	Yield (%)
$Q_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]\cdot 2Me_2CO$ (1)	8.38; 7.81–7.02; 5.06 (J 14.8)	119	165	50.42 (50.77)	4.02 (3.76)	5.35 (5.22)	84
$Q_2[Pd_2R_2Br_2(\mu\text{-}Br)_2]$ (2)	8.66, 8.46; 7.87–7.07; 5.05 (J 14.9)	110	207	44.76 (45.07)	2.91 (3.71)	5.05 (4.73)	79
$Q_2[Pd_2R_2I_2(\mu\text{-}I)_2]$ (3)	8.58; 7.88–7.12; 5.06 (J 14.9)	110	208	40.22 (40.98)	2.61 (3.03)	4.54 (3.97)	76
cis-$Q[Pd(R)Cl_2\{S(O)Me_2\}]$ (4)	8.66; 7.64–7.07; 4.83 (J 14.0)	161	101	48.28 (48.84)	3.68 (3.88)	5.12 (5.15)	80
$Q[Pd(R)Br_2\{S(O)Me_2\}]$ (5)	8.60; 7.65–7.04; 4.72 (J 14.02)	137	110	45.15 (45.51)	3.44 (3.51)	4.79 (4.76)	69

[a] $Q = (PhCH_2)PPh_3$. [b] See text. [c] Molar conductivities of ca. 10^{-4} M solutions in acetone (Ω^{-1} cm^2 mol^{-1}).

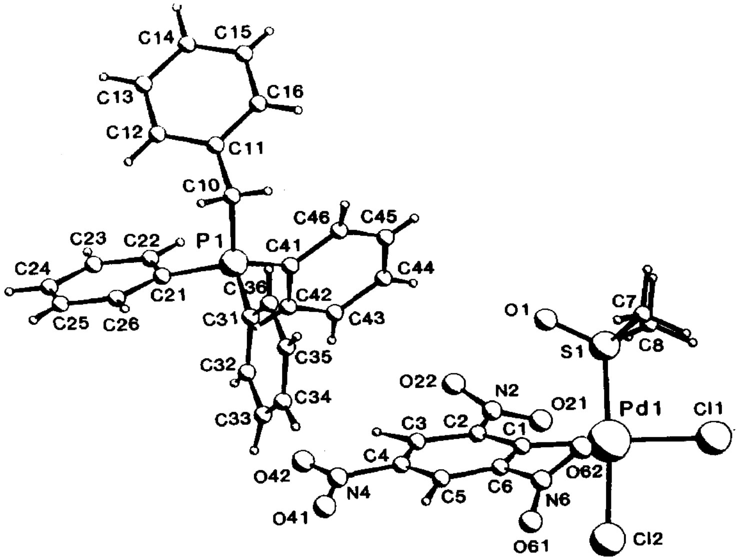

Fig. 1. Molecular structure of *cis*-[$(PhCH_2)PPh_3$][$Pd(R)Cl_2\{S(O)Me_2\}$] (4).

[$Pd\{o\text{-}C_6H_4N(O)O\}(o\text{-}C_6H_4NO_2)(py)$] (2.138(3) Å) [2b]. On the other hand, in this type of complex, the phenyl and nitro groups are almost coplanar [2b,3a,b,4], whereas in **4** the NO_2 planes form angles of 25.3 (N(2)), 11.0 (N(4)) and 38.8° (N(6)) with the plane of the phenyl ring. However, the planarity of the nitrophenyl group seems to be a necessary, but not the only condition, for the coordination to occur, since in *cis*-[$Pt(2\text{-}C_6H_4NO_2)_2(PPh_3)_2$] [15] or in [$Au(2\text{-}C_6H_4NO_2)(AsPh_3)$] [11] the nitrophenyl ligands are monodentate and nearly planar.

The C–C bond distances in the trinitrophenyl group (mean 1.39(1) Å) are normal, which is unexpected for an aryl group with three electron-withdrawing substituents. We have, previously, observed the same mean C–C bond distance in chelating and monodentate [2,3a,b] *ortho*-nitrophenyl groups of several palladium and platinum complexes. The only exceptions to such constancy are [$Au(2\text{-}C_6H_4NO_2)(AsPh_3)$] [11] ($Rh\{2\text{-}C_6H_4N(O)O\}_2Cl(PPh_3)$] [16] and [$Rh\{2\text{-}C_6H_4\text{-}N(O)O\}_2Cl(CO)$] [4], in which there are C–C bond distances as short as 1.233(7) Å or as long as 1.568(6) Å.

The Pd–Cl bond distance *trans* to R (2.365(1) Å) is longer than that *trans* to dimethylsulfoxide (2.330(1) Å), and both are shorter than that found in *trans*-[$PdCl_2\{S(O)Me_2\}_2$] (2.287 Å) [17]. The order of *trans* influence is thus aryl > dimethylsulfoxide ≫ Cl.

The Pd–S bond distance (2.249(1) Å) is shorter than that in *trans*-[$PdCl_2\{S(O)Me_2\}_2$] (2.298 Å) [17], in accord with the above *trans* influence scale. The Pd–C length (1.994(4) Å) is longer than that found in [$(PhCH_2)PPh_3]_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2$] ($R = C_6H_3Me\text{-}2, NO_2\text{-}6$; 1.958(8) Å) [2a].

The O–N (mean 1.217(7) Å), and C–N (mean 1.477(5) Å) bond lengths are in the range found for other monocoordinated nitrophenyl groups. When O-coordination occurs, the N–O(M) and C–N bond distances are increased and shortened, respectively [2b,3a,b,4].

Table 2

Fractional atomic coordinates ($\times 10^4$) with their e.s.d.'s. and equivalent temperature factors

	x	y	z	B_{eq}
Pd(1)	3406(0)	1217(0)	2226(0)	3.26
Cl(1)	4518(1)	195(1)	1399(1)	4.66
Cl(2)	1282(1)	1705(1)	1235(1)	5.08
S(1)	5472(1)	954(1)	3101(1)	4.01
O(1)	5529(3)	1538(2)	3733(2)	5.50
O(21)	3974(3)	3375(2)	1638(2)	6.05
O(22)	3976(3)	4194(2)	2591(2)	6.05
O(41)	−1378(3)	3154(3)	4857(2)	6.85
O(42)	−32(3)	4341(3)	4478(3)	7.23
O(61)	−173(3)	248(2)	3858(2)	5.93
O(62)	2090(3)	−270(2)	3905(3)	6.49
N(2)	3567(3)	3540(2)	2352(2)	4.29
N(4)	−317(3)	3523(3)	4502(2)	4.91
N(6)	1052(3)	411(2)	3795(2)	4.40
C(1)	2361(3)	1942(2)	3009(2)	3.26
C(2)	2505(3)	2938(3)	2967(2)	3.45
C(3)	1686(4)	3454(3)	3475(3)	3.84
C(4)	635(4)	2955(3)	4026(2)	3.87
C(5)	398(4)	1967(3)	4129(2)	3.91
C(6)	1297(3)	1492(3)	3629(2)	3.50
C(7)	6098(5)	−427(3)	3848(3)	5.81
C(8)	6831(4)	1280(4)	2237(3)	5.45
P(1)	2989(1)	2953(1)	7987(1)	3.11
C(10)	4148(4)	2149(3)	9109(3)	3.63
C(11)	5387(3)	2616(3)	9284(2)	3.50
C(12)	5190(4)	3420(3)	9615(3)	4.33
C(13)	6352(5)	3792(3)	9827(3)	4.91
C(14)	7720(5)	3347(4)	9735(3)	5.35
C(15)	7911(4)	2531(4)	9439(4)	5.94
C(16)	6757(4)	2169(4)	9214(3)	4.94
C(21)	2261(3)	4214(3)	8007(2)	3.34
C(22)	2952(4)	5089(3)	7566(3)	4.05
C(23)	2454(4)	6024(3)	7658(3)	4.74
C(24)	1285(5)	6094(3)	8189(3)	4.91
C(25)	599(5)	5233(4)	8636(3)	5.18
C(26)	1081(4)	4285(3)	8555(3)	4.40
C(31)	1571(3)	2230(3)	7999(3)	3.69
C(32)	436(5)	2734(4)	7296(3)	5.82
C(33)	−616(5)	2170(6)	7253(4)	7.19
C(34)	−537(5)	1133(5)	7893(4)	6.47
C(35)	561(6)	631(4)	8599(5)	6.80
C(36)	1634(4)	1177(3)	8667(4)	5.39
C(41)	3884(3)	3189(2)	6848(2)	3.20
C(42)	3270(4)	4002(3)	5941(3)	4.09
C(43)	3875(5)	4100(3)	5055(3)	4.72
C(44)	5056(4)	3400(3)	5061(3)	4.67
C(45)	5668(4)	2606(3)	5953(3)	4.75
C(46)	5094(4)	2493(3)	6853(3)	3.93

Table 3

Bond lengths in Å with their esd's

Cl(1)-Pd(1)	2.365(1)	C(11)-C(10)	1.509(6)
Cl(2)-Pd(1)	2.330(1)	C(12)-C(11)	1.386(6)
S(1)-Pd(1)	2.249(1)	C(16)-C(11)	1.377(5)
C(1)-Pd(1)	1.994(4)	C(13)-C(12)	1.385(7)
O(1)-S(1)	1.476(4)	C(14)-C(13)	1.383(6)
C(7)-S(1)	1.773(4)	C(15)-C(14)	1.367(9)
C(8)-S(1)	1.784(4)	C(16)-C(15)	1.379(7)
N(2)-O(21)	1.212(5)	C(22)-C(21)	1.393(5)
N(2)-O(22)	1.223(5)	C(26)-C(21)	1.394(5)
N(4)-O(41)	1.223(5)	C(23)-C(22)	1.378(6)
N(4)-O(42)	1.203(6)	C(24)-C(23)	1.370(6)
N(6)-O(61)	1.221(5)	C(25)-C(24)	1.375(6)
N(6)-O(62)	1.216(4)	C(26)-C(25)	1.385(7)
C(2)-N(2)	1.475(4)	C(32)-C(31)	1.374(5)
C(4)-N(4)	1.472(6)	C(36)-C(31)	1.376(5)
C(6)-N(6)	1.484(5)	C(33)-C(32)	1.389(9)
C(2)-C(1)	1.397(5)	C(34)-C(33)	1.345(8)
C(6)-C(1)	1.403(4)	C(35)-C(34)	1.350(7)
C(3)-C(2)	1.396(6)	C(36)-C(35)	1.398(8)
C(4)-C(3)	1.373(5)	C(42)-C(41)	1.390(4)
C(5)-C(4)	1.380(6)	C(46)-C(41)	1.381(5)
C(6)-C(5)	1.389(5)	C(43)-C(42)	1.382(6)
C(10)-P(1)	1.806(3)	C(44)-C(43)	1.365(6)
C(21)-P(1)	1.798(4)	C(45)-C(44)	1.365(5)
C(31)-P(1)	1.809(4)	C(46)-C(45)	1.385(6)
C(41)-P(1)	1.801(3)		

The geometry of the dimethylsulfoxide moiety is virtually unaffected by S-coordination, except that the S–O bond (1.476(4) Å) is shorter than that in solid dimethylsulfoxide (1.531 Å) [18].

Experimental

Recording of the IR and NMR spectra, the C, H, and N analyses, the conductance measurements, and the melting point determinations were performed as described elsewhere [19]. Reactions were carried out with magnetic stirring without special precautions to exclude light or moisture. The starting mercury compound was made by a published method [20], and $[(PhCH_2)PPh_3]_2[Pd_2Cl_4(\mu\text{-}Cl)_2]$ was prepared by refluxing an ethanol suspension of equimolar amounts of $PdCl_2$ and $[(PhCH_2)PPh_3]Cl$. The red solid obtained was filtered off and washed with ethanol. NMR spectra were recorded for solutions in $(CD_3)_2CO$ (complexes **1**–**3**) or $CDCl_3$ (complexes **4**–**5**). Values of δ are in ppm relative to TMS. Molar conductivities (Λ_M) are in Ω^{-1} cm^2 mol^{-1}.

$[(PhCH_2)PPh_3]_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2] \cdot 2Me_2CO$ (*1*)

A suspension of HgR_2 (240 mg, 0.38 mmol) and $[PPh_3(CH_2Ph)]_2[Pd_2Cl_4(\mu\text{-}Cl)_2]$ (217.5 mg, 0.19 mmol) in acetone (20 cm^3) was refluxed for 2.5 h. The hot solution was then filtered and concentrated to 5 cm^3. An orange solid that separated was

Table 4

Bond angles in degrees with their esd's

Cl(2)–Pd(1)–Cl(1)	92.5(0)	C(31)–P(1)–C(21)	110.0(2)
S(1)–Pd(1)–Cl(1)	90.6(0)	C(41)–P(1)–C(10)	112.9(2)
S(1)–Pd(1)–Cl(2)	173.2(0)	C(41)–P(1)–C(21)	109.5(1)
C(1)–Pd(1)–Cl(1)	173.7(1)	C(41)–P(1)–C(31)	107.9(2)
C(1)–Pd(1)–Cl(2)	86.3(1)	C(11)–C(10)–P(1)	117.0(2)
C(1)–Pd(1)–S(1)	91.3(1)	C(12)–C(11)–C(10)	121.3(3)
O(1)–S(1)–Pd(1)	118.1(1)	C(16)–C(11)–C(10)	119.7(4)
C(7)–S(1)–Pd(1)	111.3(2)	C(16)–C(11)–C(12)	118.7(4)
C(7)–S(1)–O(1)	108.6(2)	C(13)–C(12)–C(11)	120.2(4)
C(8)–S(1)–Pd(1)	108.3(1)	C(14)–C(13)–C(12)	120.3(5)
C(8)–S(1)–O(1)	107.9(2)	C(15)–C(14)–C(13)	119.2(5)
C(8)–S(1)–C(7)	101.2(2)	C(16)–C(15)–C(14)	120.6(4)
O(22)–N(2)–O(21)	123.6(3)	C(15)–C(16)–C(11)	120.9(5)
C(2)–N(2)–O(21)	119.1(4)	C(22)–C(21)–P(1)	120.4(3)
C(2)–N(2)–O(22)	117.2(3)	C(26)–C(21)–P(1)	119.6(3)
O(42)–N(4)–O(41)	124.4(4)	C(26)–C(21)–C(22)	119.6(4)
C(4)–N(4)–O(41)	117.6(4)	C(23)–C(22)–C(21)	120.0(4)
C(4)–N(4)–O(42)	117.9(3)	C(24)–C(23)–C(22)	120.2(4)
O(62)–N(6)–O(61)	124.1(4)	C(25)–C(24)–C(23)	120.5(4)
C(6)–N(6)–O(61)	117.9(3)	C(26)–C(25)–C(24)	120.4(4)
C(6)–N(6)–O(62)	117.8(3)	C(25)–C(26)–C(21)	119.3(4)
C(2)–C(1)–Pd(1)	126.3(2)	C(32)–C(31)–P(1)	119.0(3)
C(6)–C(1)–Pd(1)	120.7(3)	C(36)–C(31)–P(1)	121.5(3)
C(6)–C(1)–C(2)	112.9(3)	C(36)–C(31)–C(32)	119.5(4)
C(1)–C(2)–N(2)	121.0(3)	C(33)–C(32)–C(31)	119.7(4)
C(3)–C(2)–N(2)	114.3(3)	C(34)–C(33)–C(32)	120.7(5)
C(3)–C(2)–C(1)	124.7(3)	C(35)–C(34)–C(33)	120.2(6)
C(4)–C(3)–C(2)	117.1(4)	C(36)–C(35)–C(34)	120.6(5)
C(3)–C(4)–N(4)	118.0(4)	C(35)–C(36)–C(31)	119.2(4)
C(5)–C(4)–N(4)	118.5(3)	C(42)–C(41)–P(1)	119.8(3)
C(5)–C(4)–C(3)	123.4(4)	C(46)–C(41)–P(1)	120.2(2)
C(6)–C(5)–C(4)	115.7(3)	C(46)–C(41)–C(42)	119.6(3)
C(1)–C(6)–N(6)	119.8(3)	C(43)–C(42)–C(41)	119.5(3)
C(5)–C(6)–N(6)	114.1(3)	C(44)–C(43)–C(42)	120.7(3)
C(5)–C(6)–C(1)	126.2(3)	C(45)–C(44)–C(43)	119.8(4)
C(21)–P(1)–C(10)	109.0(2)	C(46)–C(45)–C(44)	120.8(4)
C(31)–P(1)–C(10)	107.5(2)	C(45)–C(46)–C(41)	119.6(3)

Table 5

Selected interatomic distances in Å

O(21)...Pd(1) [a]	2.911
O(62)...Pd(1) [a]	2.910
C(22)...O(22) [b]	3.221
C(23)...O(22) [b]	3.398
C(12)...O(21) [c]	3.162
C(33)...O(41) [b]	3.231
C(44)...O(41) [d]	3.385
C(45)...O(41) [d]	2.869

[a] x, y, z. [b] $1-x, 1-y, 1-z$. [c] $x, y, 1+z$. [d] $1+x, y, z$.

filtered off, and washed with acetone (5 cm^3) to give **1** (181 mg, 0.11 mmol). Slow addition of diethyl ether to the filtrate gave further orange solid, which was filtered off and washed with diethyl ether (5 cm^3) to give additional **1** (95.3 mg, 0.06 mmol). Heating of the solid at 60 °C for 40 h gave solvent-free **1**.

$[(PhCH_2)PPh_3]_2[Pd_2R_2Br_2(\mu\text{-}Br)_2]$ (2)

A suspension of **1** (192 mg, 0.12 mmol) and NaBr (213.8 mg, 2.08 mmol) in acetone (15 cm^3) was refluxed for 8 h, then concentrated to dryness, and dichloromethane (20 cm^3) added. The resulting orange suspension was filtered and the filtrate concentrated (2 cm^2). Addition of diethyl ether (15 cm^3) gave an orange solid, which was filtered off and recrystallized from dichloromethane/diethyl ether.

$[(PhCH_2)PPh_3]_2[Pd_2R_2I_2(\mu\text{-}I)_2]$ (3)

When solid NaI (358.5 mg, 2.39 mmol) was added to a suspension of **1** (222.1 mg, 0.14 mmol) in acetone (8 cm^3), a red suspension was obtained. After 3 h under reflux the solution was concentrated to dryness and dichloromethane added. The resulting suspension was filtered and the filtrate concentrated to 2 cm^3. Addition of diethyl ether (20 cm^3) gave a red solid, which was recrystallized from dichloromethane/diethyl ether.

cis-$[(PhCH_2)PPh_3][Pd(R)Cl_2\{S(O)Me_2\}]$ (4)

Two drops of dimethylsulfoxide (an excess) were added to a suspension of **1** (85.2 mg, 0.05 mmol) in acetone (5 cm^3). After 3 h, the solution was concentrated and diethyl ether added to give an oil, which was converted into a yellow solid after 12 h of stirring. It was filtered off and washed with diethyl ether to give **4**.

Single crystals of **4** were obtained by slow diffusion of diethyl ether into a solution of **4** in dichloromethane (4 cm^3) containing a drop of dimethylsulfoxide.

$[(PhCH_2)PPh_3][Pd(R)Br_2\{S(O)Me_2\}]$ (5)

Four drops of dimethylsulfoxide were added to a suspension of 2 (60 mg, 0.04 mmol) in acetone (2 cm^3). After 1.5 h stirring, the solution was concentrated (1 cm^3) and diethyl ether added (10 cm^3) to give an oil, which became a solid upon stirring. It was filtered off, washed with diethyl ether, and recrystallized by addition of diethyl ether to a solution of the solid in acetone/dimethylsulfoxide (4 drops of dimethylsulfoxide/4 cm^3 acetone) to give the yellow complex **5**.

X-ray crystal structure of complex 4

A crystal of 0.37 × 0.20 × 0.26 mm was used. Cell constants and data collections were determined with an Enraf–Nonius CAD4 diffractometer. Space group: triclinic $P\bar{1}$. Cell parameters (from least squares-analyses of 25 reflections): a 9.529(3), b 13.974(4), c 14.678(2) Å, α 65.19(2), β 89.70(2), γ 80.72(3)°, V 1746 $Å^3$, T 294 K, $Z = 2$, D_x 1.56 Mg m^{-3} $F(000) = 800$, $\mu(\text{Mo-}K_\alpha)$ 8.3 cm^{-1}. The intensity data were collected in the ω–2θ scan mode, no significant variations were observed in standard reflections (0.8%). 6150 independent reflections ($2\theta < 50°$) were measured, $-11 \leq h \leq 11$; $-16 \leq k \leq 16$; $0 \leq l \leq 17$, 5874 were considered as observed [$F > 4\sigma(F)$] and used in the subsequent analysis. Corrections for Lorentz and polarization effects were applied, but not for absorption.

The structure was solved by direct methods involving the MULTAN-11/84 program [21]. The two palladium atoms of the cell were located by using the non-centrosymmetric space group $P1$. These coordinates then allowed location of the centre of symmetry of the cell. A subsequent weighted Fourier synthesis in the $P\bar{1}$ space group revealed all the non-hydrogen atoms. Full-matrix refinement on F of positional and thermal parameters were performed with the SHELX-76 System [22]. Difference Fourier maps in the final cycles showed the positions of 26 hydrogen atoms. The remaining H atoms were introduced in calculated positions. Refinement converged at $R = 0.046$ and $R_w = 0.040$ ($w^{-1} = \sigma^2(F) + 0.000268F^2$) by use of 507 refined parameters. Non-hydrogen atoms were refined anisotropically and hydrogen atoms with an overall isotropic temperature factor. Scattering factors for the non-hydrogen atoms were taken from ref. 23, and those for hydrogen atoms from ref. 14. No significant shift/error values were observed in the final least-squares cycles. Maximum and minimum difference Fourier peaks were 0.5 and -0.4 eA^{-3}, respectively.

List of structures factors, anisotropic thermal parameters and H atom coordinates are available from the authors.

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