Mono or Binuclear Orthopalladated ($\widehat{CN}$) Complexes ($\widehat{CN}$ = Phenylazophenyl-C^2,N^1; Dimethylbenzylamine-C^2,N; 8-Methylquinoline-C^8,N) Containing Terminal or Bridging SPR_3 Ligands

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Abstract

The reactions between $[Pd(\widehat{CN})(S)_2]^+$ ($\widehat{CN}$ = phenylazophenyl-C^2,N^1; dimethylbenzylamine-C^2,N; 8-methylquinoline-C^8,N; S = THF or acetone) and $SPPh_3$ or $SPMe_2Ph$ have been studied. The reactions in a 1:2 molar ratio render in all cases the corresponding $[Pd(\widehat{CN})(SPR_3)_2]ClO_4$. For a 1:1 molar ratio $SPPh_3$ gives either $[Pd(\widehat{CN})(SPPh_3)(S)]ClO_4$ or $[Pd(\widehat{CN})(OClO_3)(SPPh_3)]$ depending on the solvent used, while $SPMe_2Ph$ yields the binuclear $[Pd(\widehat{CN})(\mu\text{-}SPMe_2Ph)]_2(ClO_4)_2$ complexes. IR and ^{31}P NMR spectroscopy have been used for the characterization of the complexes. The structure of $[Pd(C_6H_4N{=}NC_6H_5)(OClO_3)(SPPh_3)]$ has been established by X-ray diffraction: monoclinic, space group $P2_1/n$, $a = 11.544(6)$, $b = 20.698(1)$, $c = 12.487(6)$ Å, $\beta = 105.022(4)°$; $Z = 4$; $D_c = 1.568$ g cm^{-3}. The structure was solved by Patterson and refined to residuals of $R = 0.043$, $R_w = 0.051$. The complex presents a distorted square planar coordination around the palladium atom.

Introduction

Recently we have described the synthesis of cationic species of the type $[Pd(\widehat{CN})(S)_2]^+$ ($\widehat{CN}$ = phenylazophenyl-C^2,N (az), dimethylbenzylamine-C^2,N (dmba), 8-methylquinoline-C^8,N (8-mq), S = THF (tetrahydrofuran), acetone or NCMe [1], having two weakly coordinated ligands S, which are suitable precursors for the synthesis of mono-and binuclear complexes containing the '$Pd(\widehat{CN})$' moieties. In the present paper we study the reactions of such species toward phosphine sulfides, which render mono- or binuclear complexes containing terminal or bridging phosphine sulfide depending on the molar ratio of the reactants or the phosphine sulfide used. The structure of the complexes have been established on the basis of IR and ^{31}P NMR spectra. $[Pd(C_6H_4N{=}NC_6H_5)(SPPh_3)OClO_3]$ has been characterized by single crystal X-ray diffraction.

Experimental

C, H and N analyses were carried out on a Perkin-Elmer 240B microanalyzer. IR spectra were recorded (in the 4000–200 cm^{-1} range) on a Perkin-Elmer 599 spectrophotometer, using Nujol mulls between polyethylene sheets. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL 200 instrument.

Literature methods were used to prepare the compounds $[Pd_2(\mu\text{-}Cl)_2(az)_2]$ [2], $[Pd_2(\mu\text{-}Cl)_2(dmba)_2]$ [3], $[Pd_2(\mu\text{-}Cl)_2(8\text{-}mq)_2]$ [4], $SPPh_3$ [5] and $SPMe_2Ph$ [5]. $CHCl_3$ solutions of $[Pd(\widehat{CN})(OCMe_2)_2]ClO_4$ were obtained by reacting the corresponding $[Pd_2(\mu\text{-}Cl)_2(\widehat{CN})_2]$ complexes with $AgClO_4$ in acetone (molar ratio 1:2), removal of the precipitated AgCl by filtration, evaporation of the resulting solution to dryness and addition of $CHCl_3$.

$[Pd(\widehat{CN})(OClO_3)(SPPh_3)]$ ($\widehat{CN}$ = az (1), dmba (2), 8-mq (3))

To a $CHCl_3$ (20 ml) solution of $[Pd(az)(OCMe_2)_2]ClO_4$ (0.309 mmol), $SPPh_3$ (0.090 g, 0.309 mmol) was added. The mixture was stirred for 10 min at room temperature and evaporated to dryness. Addition of ~20 ml of Et_2O rendered an orange solid, **1**, (81% yield).

Complexes **2** and **3** were obtained in a similar way by using $[Pd(dmba)(OCMe_2)_2]ClO_4$ and $[Pd(8\text{-}mq)(OCMe_2)_2]ClO_4$ respectively as starting materials. Yields: 81% (**2**), 88% (**3**).

$[Pd(dmba)(SPPh_3)(THF)]ClO_4$ (4)

To a solution of $[Pd(dmba)(THF)_2]ClO_4$ (0.724 mmol) in 10 ml of THF, $SPPh_3$ (0.213 g, 0.724 mmol) was added and the mixture was stirred at room temperature for 15 min. The resulting yellow solid was filtered and washed with Et_2O (~ 10 ml), **4**, 47% yield.

$[Pd(dmba)(SPPh_3)(OCMe_2)]ClO_4$ (5)

To a solution of $[Pd(dmba)(OCMe_2)_2]ClO_4$ (0.724 mmol) in 20 ml of acetone, $SPPh_3$ (0.213 g, 0.724 mmol) was added. The mixture was stirred for 30 min

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at room temperature and evaporated to $\sim$2 ml. Addition of $\sim$20 ml of Et_2O afforded **5**, 49% yield.

$[Pd(\widehat{CN})(\mu\text{-}SPMe_2Ph)]_2(ClO_4)_2$ ($\widehat{CN}$ = az (9), dmba (10))

To a solution of $[Pd(az)(OCMe_2)_2]ClO_4$ (0.309 mmol) in 20 ml of $CHCl_3$, $SPMe_2Ph$ (0.052 g, 0.309 mmol) was added. The mixture was stirred for 15 min at room temperature and evaporated to dryness. The residue was treated with $\sim$20 ml of Et_2O yielding **9**, 85% yield.

A similar reaction starting from $[Pd(dmba)(OCMe_2)_2]ClO_4$ rendered **10**, 56% yield.

$[Pd(\widehat{CN})(SPR_3)_2]ClO_4$ ($\widehat{CN}$ = az, SPR_3: $SPPh_3$ (6), $SPMe_2Ph$ (11); $\widehat{CN}$ = dmba, SPR_3: $SPPh_3$ (7); $\widehat{CN}$ = 8-mq, SPR_3: $SPPh_3$ (8), $SPMe_2Ph$ (12))

From $[Pd(\widehat{CN})(OCMe_2)_2]ClO_4$

To a solution of $[Pd(az)(OCMe_2)_2]ClO_4$ (0.309 mmol) in 20 ml of $CHCl_3$, $SPPh_3$ (0.183 g, 0.618 mmol) was added. The mixture was stirred for 10 min at room temperature and then evaporated to dryness. Addition of Et_2O ($\sim$20 ml) rendered an orange solid, **6**, 89% yield.

Complexes 7 and **8** were obtained in a similar way by using $[Pd(dmba)(OCMe_2)_2]ClO_4$ or $[Pd(8\text{-}mq)(OCMe_2)_2]ClO_4$ respectively as starting materials. Similar reactions between $[Pd(az)(OCMe_2)_2]ClO_4$ or $[Pd(8\text{-}mq)(OCMe_2)_2]ClO_4$ and $SPMe_2Ph$ rendered **11** or **12** respectively. Yields: **7** (90%), **8** (86%), **11** (80%), **12** (74%).

From $[Pd(\widehat{CN})(\mu\text{-}SPR_3)]_2(ClO_4)_2$

To a solution of $[Pd(az)(\mu\text{-}SPMe_2Ph)]_2(ClO_4)_2$ (0.1 g, 0.089 mmol) in 20 ml of CH_2Cl_2, $SPMe_2Ph$ (0.061 g, 0.358 mmol) was added. The mixture was stirred for 10 min at room temperature and evaporated to dryness. Addition of Et_2O (20 ml) gives a yellowish orange solid, **9**, 87% yield.

From $[Pd(\widehat{CN})(OClO_3)(SPPh_3)]$

To a solution of $[Pd(dmba)(OClO_3)(SPPh_3)]$ (0.1 g, 0.157 mmol) in 20 ml of CH_2Cl_2, $SPPh_3$ (0.092 g, 0.315 mmol) was added. After 10 min stirring, the resulting solution was evaporated to dryness; the oily residue was treated with Et_2O (20 ml) to give a yellow solid, **7**, 69% yield.

From $[Pd(\widehat{CN})(SPPh_3)(S)]ClO_4$

To a solution of $[Pd(dmba)(SPPh_3)(OCMe_2)]ClO_4$ (0.1 g, 0.144 mmol) in 20 ml of CH_2Cl_2, $SPPh_3$ (0.085 g, 0.288 mmol) was added. The mixture was stirred at room temperature for 10 min and evaporated to dryness. Addition of $\sim$20 ml of Et_2O afforded **7**, 65% yield.

X-ray Data Collection, Structure Solution and Refinement

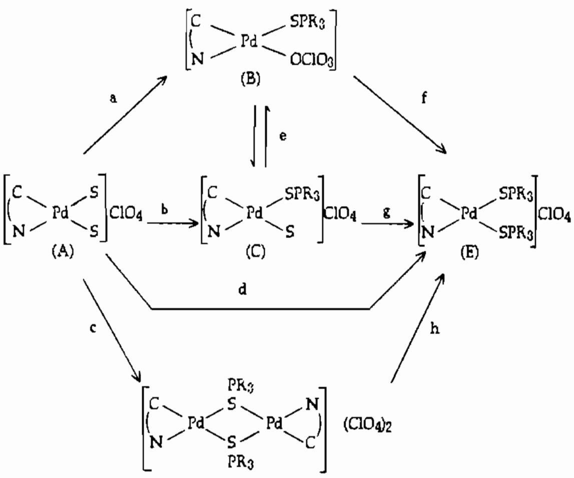
$PdClSPN_2C_{30}O_4H_{24}$, $M = 680.88$, monoclinic, space group $P2_1/n$, $a = 11.5444(6)$, $b = 20.698(1)$, $c = 12.4876(6)$ Å, $\beta = 105.022(4)^\circ$, $U = 2881.9$ Å^3, $D_c = 1.568$ g cm^{-3} for $Z = 4$, $F(000) = 1376$, μ_0(Mo Kα) = 8.4. Siemens/STOE AED2 diffractometer. A total of 4849 unique profile-fitted intensities [6] in the range $3^\circ < 2\theta < 50^\circ$ were collected using a ω–2θ scan technique and those 4212 reflections for which $|F| \geqslant 6\sigma(F)$ were used in the calculations.

The position of the Pd atom was located by Patterson methods. The three terminal oxygen atoms of the ClO_4 group were disordered between two sites (O_2, O_3, O_4 and O_2', O_3', O_4') with occupancies 0.63 and 0.37 respectively. The C_6H_5 rings were refined as idealized rigid groups with C–C = 1.395 Å and their hydrogen atoms were included in calculated positions (C–H = 1.08 Å) with one, overall refined $U_{iso} = 0.1015$ Å^2. All non-hydrogen atoms were assigned anisotropic vibrational parameters except for the oxygen atoms in disorder. The refinement converged at $R = 0.043$, $R_w = 0.051$, where $\omega^{-1} = \sigma^2(F) + 0.000757F^2$. The final difference Fourier only showed two peaks higher than 1 e/Å^3 (1.35 e/Å^3 and 1.20 e/Å^3). These peaks are closed to the ClO_4 group in disorder. Calculations were performed using SHELX-76 [7]. The final positional parameters are given in Table 1, while bond length and angle data are given in Table 2.

Results and Discussion

Analytical data are listed in Table 3. Relevant IR absorptions and ^{31}P NMR parameters are collected in Tables 4 and 5.

The methods of preparation of the complexes and the observed interconversions are summarized in Scheme 1.



Scheme 1.

TABLE 1. Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters and e.s.d.s for $[Pd(C_6H_4N{=}NC_6H_5)(OClO_3)(SPPh_3)]$

	x	y	z	B (Å^2)[a]
Pd	1969(0)	1398(0)	3176(0)	2.97(2)*
Cl	4247(1)	1566(1)	2112(1)	4.05(6)*
S	1156(1)	758(1)	1634(1)	3.64(6)*
P	1405(1)	−150(1)	2228(1)	3.23(6)*
O1	3802(3)	1236(2)	2971(3)	3.82(17)*
O2	4058(9)	1220(4)	1146(8)	8.07(19)
O3	5451(8)	1702(5)	2538(7)	7.57(21)
O4	3613(7)	2180(4)	1922(6)	6.73(15)
O2′	3340(11)	1755(6)	1239(10)	6.18(23)
O3′	4797(12)	1042(6)	1648(11)	6.68(26)
O4′	5220(12)	1992(7)	2634(11)	6.48(29)
N1	2483(3)	1893(2)	4640(3)	3.62(20)*
N2	1674(4)	2044(2)	5110(3)	4.46(24)*
C11	3669(2)	1990(2)	5301(3)	4.07(26)*
C12	4495(2)	2305(2)	4841(3)	4.77(30)*
C13	5657(2)	2420(2)	5485(3)	5.87(37)*
C14	5994(2)	2221(2)	6590(3)	6.42(39)*
C15	5169(2)	1906(2)	7050(3)	6.82(41)*
C16	4006(2)	1791(2)	6406(3)	5.42(33)*
H12	4233(2)	2459(2)	3985(3)	8.02(38)
H13	6296(2)	2664(2)	5129(3)	8.02(38)
H14	6894(2)	2310(2)	7089(3)	8.02(38)
H15	5430(2)	1752(2)	7905(3)	8.02(38)
H16	3368(2)	1547(2)	6762(3)	8.02(38)
C21	532(5)	1909(2)	4454(4)	4.25(27)*
C22	411(4)	1584(2)	3454(4)	3.62(24)*
C23	−754(5)	1461(3)	2806(5)	5.16(32)*
C24	−1743(5)	1661(3)	3170(6)	6.34(41)*
C25	−1598(6)	1984(3)	4164(7)	6.64(44)*
C26	−457(6)	2111(3)	4837(6)	5.87(38)*
C31	4(2)	−581(1)	1995(3)	3.52(23)*
C32	−1031(2)	−327(1)	1281(3)	4.51(27)*
C33	−2100(2)	−677(1)	1056(3)	5.58(33)*
C34	−2134(2)	−1281(1)	1544(3)	5.58(34)*
C35	−1098(2)	−1534(1)	2258(3)	5.83(38)*
C36	−30(2)	−1184(1)	2484(3)	5.12(31)*
H32	−1005(2)	140(1)	902(3)	8.02(38)
H33	−2901(2)	−481(1)	502(3)	8.02(38)
H34	−2961(2)	−1552(1)	1370(3)	8.02(38)
H35	−1124(2)	−2001(1)	2637(3)	8.02(38)
H36	772(2)	−1380(1)	3036(3)	8.02(38)
C41	2312(3)	−565(2)	1473(3)	3.91(25)*
C42	1879(3)	−1092(2)	788(3)	4.46(27)*
C43	2573(3)	−1360(2)	138(3)	5.81(38)*
C44	3699(3)	−1103(2)	174(3)	6.93(46)*
C45	4132(3)	−577(2)	859(3)	7.23(47)*
C46	3438(3)	−308(2)	1509(3)	5.55(35)*
H42	1007(3)	−1291(2)	761(3)	8.02(38)
H43	2238(3)	−1768(2)	−392(3)	8.02(38)
H44	4236(3)	−1311(2)	−329(3)	8.02(38)
H45	5004(3)	−378(2)	887(3)	8.02(38)
H46	3773(3)	99(2)	2039(3)	8.02(38)
C51	2095(3)	−205(2)	3693(2)	3.62(23)*
C52	1496(3)	67(2)	4421(2)	4.57(28)*
C53	2013(3)	48(2)	5561(2)	6.26(39)*
C54	3129(3)	−243(2)	5975(2)	7.10(43)*
C55	3729(3)	−515(2)	5247(2)	6.83(40)*
C56	3212(3)	−496(2)	4107(2)	5.37(31)*
H52	631(3)	292(2)	4101(2)	8.02(38)
H53	1549(3)	258(2)	6124(2)	8.02(38)
H54	3530(3)	−258(2)	6858(2)	8.02(38)
H55	4594(3)	−740(2)	5567(2)	8.02(38)
H56	3676(3)	−706(2)	3544(2)	8.02(38)

[a] Starred atoms were refined anisotropically.

Solutions of cationic $[Pd(\widehat{CN})(S)_2]^+$ derivatives in weakly coordinating solvents (S) such as THF (tetrahydrofuran) or acetone, have been obtained according to eqn. (1) [1].

$$[Pd(\widehat{CN})(\mu\text{-}Cl)]_2 + 2AgClO_4 \xrightarrow{S} 2[Pd(\widehat{CN})(S)_2]^+ + 2ClO_4^- + 2AgCl \qquad (1)$$

The reactions of $[Pd(\widehat{CN})(S)_2]^+$ derivatives with SPR_3 in a 1:1 molar ratio render mono- or binuclear derivatives, depending on the SPR_3 used. For $SPPh_3$, if the reaction is carried out in THF or acetone, the cationic mononuclear complexes $[Pd(\widehat{CN})(SPR_3)(S)]ClO_4$ (C, Scheme 1 b, $\widehat{CN}$ = dmba, $SPR_3 = SPPh_3$, S = THF (**4**), acetone (**5**)) are obtained. On the other hand, if the acetone or THF solutions of $[Pd(\widehat{CN})(S)_2]ClO_4$ (A) are evaporated to dryness and the residues in $CHCl_3$ are treated with $SPPh_3$ (molar ratio 1:1), the neutral mononuclear derivatives $[Pd(\widehat{CN})(OClO_3)(SPPh_3)]$ (B, Scheme 1 a, $\widehat{CN}$ = az (**1**), dmba (**2**), 8-mq (**3**)) are obtained $[Pd(dmba)(OClO_3)(SPPh_3)]$ (**2**) (B) can also be obtained when $CHCl_3$ solutions of **4** or **5** are evaporated to dryness and the residue treated with Et_2O. The treatment of **2** with THF or acetone renders as expected the cationic complexes **4** or **5** (Scheme 1 e).

For $SPMe_2Ph$, the cationic binuclear derivatives $[Pd(\widehat{CN})(\mu\text{-}SPMe_2Ph)]_2(ClO_4)_2$ (D, Scheme 1 c, $\widehat{CN}$ = az (**9**), dmba (**10**)) containing bridging $SPMe_2Ph$ are obtained by reacting the corresponding $[Pd(\widehat{CN})(S)_2]ClO_4$ with $SPMe_2Ph$ (molar ratio 1:1) either in donor (THF, acetone) or non-donor solvents ($CHCl_3$).

Finally, cationic mononuclear complexes containing two SPR_3 ligands (E) $[Pd(\widehat{CN})(SPR_3)_2]ClO_4$ ($\widehat{CN}$ = az, $SPR_3 = SPPh_3$ (**6**), $SPMe_2Ph$ (**11**); $\widehat{CN}$ = dmba, $SPR_3 = SPPh_3$ (**7**); $\widehat{CN}$ = 8-mq, $SPR_3 = SPPh_3$ (**8**), $SPMe_2Ph$ (**12**)) can be obtained by reacting either the $[Pd(\widehat{CN})(S)_2]ClO_4$ complexes (Scheme 1 d) or the intermediate (B, C, D) complexes containing one SPR_3 per palladium atom (Scheme 1 f, g, h) with SPR_3 in the appropriate molar ratio.

As can be seen from Scheme 1 in no case could binuclear complexes containing bridging μ-$SPPh_3$ ligand be obtained; this result is in contrast with the

TABLE 2. Bond distances (Å) and bond angles (°) and e.s.d.s for [Pd($C_6H_4N{=}NC_6H_5$)($OClO_3$)($SPPh_3$)]

S1---Pd	2.326 (0.001)	O1---Pd	2.222 (0.003)
N1---Pd	2.045 (0.004)	C22---Pd	1.957 (0.004)
O1---Cl1	1.472 (0.003)	O2---Cl1	1.371 (0.009)
O3---Cl1	1.382 (0.009)	O4---Cl1	1.455 (0.007)
O2'---Cl1	1.359 (0.012)	O3'---Cl1	1.451 (0.013)
O4'---Cl1	1.444 (0.013)	P1---S1	2.013 (0.002)
C31---P1	1.804 (0.002)	C41---P1	1.799 (0.002)
C51---P1	1.800 (0.002)	N2---N1	1.264 (0.005)
C11---N1	1.418 (0.004)	C21---N2	1.388 (0.007)
C22---C21	1.393 (0.007)	C26---C21	1.410 (0.007)
C23---C22	1.401 (0.007)	C24---C23	1.396 (0.008)
C25---C24	1.382 (0.010)	C26---C25	1.392 (0.010)
O1-Pd-S1	90.6 (0.1)	N1-Pd-S1	170.8 (0.1)
N1-Pd-O1	96.6 (0.1)	C22-Pd-S1	93.8 (0.1)
C22-Pd-O1	175.6 (0.2)	C22-Pd-N1	79.0 (0.2)
O2--Cl1-O1	113.1 (0.4)	O3-Cl1-O1	108.7 (0.4)
O3-Cl1-O2	111.0 (0.6)	O4-Cl1-O1	105.7 (0.3)
O4-Cl1-O2	110.7 (0.5)	O4-Cl1-O3	107.3 (0.5)
O2'-Cl1-O1	112.2 (0.5)	O3'-Cl1-O1	102.4 (0.5)
O3'-Cl1-O2'	102.7 (0.7)	O4'-Cl1-O1	109.4 (0.5)
O4'-Cl1-O2'	122.3 (0.8)	O4'-Cl1-O3'	105.5 (0.8)
P1-S1-Pd	103.7 (0.1)	C31-P1-S1	111.4 (0.1)
C41-P1-S1	107.5 (0.1)	C41-P1-C31	107.3 (0.2)
C51-P1-S1	114.6 (0.1)	C51-P1-C31	106.0 (0.2)
C51-P1-C41	109.8 (0.2)	Cl1-O1-Pd	122.4 (0.2)
N2-N1-Pd	117.4 (0.3)	C11-N1-Pd	127.1 (0.3)
C11-N1-N2	114.4 (0.4)	C21-N2-N1	112.3 (0.4)
C12-C11-N1	119.1 (0.2)	C16-C11-N1	120.9 (0.2)
C32-C31-P1	120.1 (0.1)	C36-C31-P1	119.8 (0.1)
C22-C21-N2	119.0 (0.4)	C26-C21-N2	117.9 (0.5)
C26-C21-C22	123.0 (0.5)	C21-C22-Pd	111.8 (0.4)
C23-C22-Pd	130.6 (0.4)	C23-C22-C21	117.6 (0.4)
C24-C23-C22	120.1 (0.6)	C25-C24-C23	121.1 (0.6)
C26-C25-C24	120.6 (0.5)	C25-C26-C21	117.5 (0.6)
C42-C41-P1	122.0 (0.1)	C46-C41-P1	117.7 (0.1)
C52-C51-P1	118.2 (0.1)	C56-C51-P1	121.8 (0.1)

TABLE 3. Analytical results for the complexes

		Found (calc.) (%)		
		C	H	N
1	[Pd(az)($OClO_3$)($SPPh_3$)]	52.25 (52.87)	3.82 (3.52)	4.15 (4.11)
2	[Pd(dmba)($OClO_3$)($SPPh_3$)]	51.06 (51.12)	3.95 (4.29)	2.21 (2.22)
3	[Pd(8-mq)($OClO_3$)($SPPh_3$)]	52.12 (52.35)	3.84 (3.61)	2.17 (2.18)
4	[Pd(dmba)($SPPh_3$)(THF)]ClO_4	52.69 (52.71)	5.29 (4.99)	2.00 (1.98)
5	[Pd(dmba)($SPPh_3$)($OCMe_2$)]ClO_4	51.95 (52.03)	5.20 (4.80)	2.09 (2.02)
6	[Pd(az)($SPPh_3$)$_2$]ClO_4	58.24 (59.10)	4.12 (4.00)	2.92 (2.90)

(continued)

TABLE 3. *(continued)*

		Found (calc.) (%)		
		C	H	N
7	$[Pd(dmba)(SPPh_3)_2]ClO_4$	57.89 (58.20)	4.94 (4.56)	1.53 (1.51)
8	$[Pd(8\text{-}mq)(SPPh_3)_2]ClO_4$	58.08 (58.98)	4.38 (4.09)	1.43 (1.49)
9	$[Pd(az)(\mu\text{-}SPMe_2Ph)]_2(ClO_4)_2$	42.74 (43.10)	3.40 (3.61)	4.85 (5.02)
10	$[Pd(dmba)(\mu\text{-}SPMe_2Ph)]_2(ClO_4)_2$	39.87 (40.00)	4.63 (4.54)	2.73 (2.74)
11	$[Pd(az)(SPMe_2Ph)_2](ClO_4)$	45.93 (46.23)	4.53 (4.53)	3.82 (3.85)
12	$[Pd(8\text{-}mq)(SPMe_2Ph)_2](ClO_4)$	45.59 (45.35)	4.67 (4.39)	1.83 (2.03)

TABLE 4. Relevant IR data and $^{31}P\{^1H\}$ NMR[a] data

	ν(P–S) (cm^{-1})	$\Delta\nu$[b] (cm^{-1})	δP (ppm)
$SPPh_3$	636		43.88
$SPMe_2Ph$	583		33.16
$[Pd(az)(OClO_3)(SPPh_3)]$ (1)	592	44	46.59
$[Pd(dmba)(OClO_3)(SPPh_3)]$ (2)	600	36	45.64
$[Pd(8\text{-}mq)(OClO_3)(SPPh_3)]$ (3)	603	33	44.92
$[Pd(dmba)(SPPh_3)(THF)]ClO_4$ (4)	594	42	45.71
$[Pd(dmba)(SPPh_3)(OCMe_2)]ClO_4$ (5)	594	42	45.67
$[Pd(az)(SPPh_3)_2]ClO_4$ (6)	600	36	45.44[c]
	588	48	44.94[c]
$[Pd(dmba)(SPPh_3)_2]ClO_4$ (7)	605	31	45.12
	595	41	44.21
$[Pd(8\text{-}mq)(SPPh_3)_2]ClO_4$ (8)	604	32	44.15[c]
	596	40	43.43[c]
$[Pd(az)(\mu\text{-}SPMe_2Ph)]_2(ClO_4)_2$ (9)	516	67	40.61
$[Pd(dmba)(\mu\text{-}SPMe_2Ph)]_2(ClO_4)_2$ (10)	514	69	39.66
$[Pd(az)(SPMe_2Ph)_2](ClO_4)$ (11)	562	29	40.71[c]
	554	21	39.37[c]
$[Pd(8\text{-}mq)(SPMe_2Ph)_2](ClO_4)$ (12)	562	29	39.32
	554	21	35.70

[a] Shifts are related to external 85% H_3PO_4, $CDCl_3$ solutions. [b] $\Delta\nu$: ν(P–S)(free SPR_3) – ν(P–S)(coordinated SPR_3). [c] Low temperature NMR (–50 °C).

behaviour of other palladium or platinum substrata towards $SPPh_3$, e.g. *cis*-$Pd(C_6F_5)_2(THF)_2$ or *cis*-$Pt(C_6F_5)_2(THF)_2$ react with $SPPh_3$ either in 1:1 or 2:1 molar ratio yielding only the corresponding binuclear derivatives: $(C_6F_5)_2M(\mu\text{-}SPPh_3)_2M(C_6F_5)_2$ (M = Pd, Pt) [8].

IR and ^{31}P NMR Spectra

The structures of the complexes were assigned on the basis of their IR (Table 4) and ^{31}P NMR spectra (Tables 4 and 5).

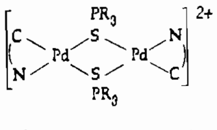
All the cationic complexes (**4**–**12**) containing the ClO_4^- anion (Td) show in the IR spectrum a very broad absorption at ~1100 cm^{-1} and a strong band at 620 cm^{-1}, while complexes **1**–**3** which contain the $-OClO_3$ ligand (C_{3v}) show bands at ~1140(s), ~1015(s), ~630(m) and ~615 cm^{-1} [9, 10].

The absorptions due to ν(P–S) deserve some comments. The formation of the Pd–S bond produces a lowering of the P–S bond order resulting in a decrease of the ν(P–S) respective to the free ligand [11] (see Table 4). The cationic mononuclear com-

TABLE 5. ^{31}P NMR $\{^1H\}$ data

		δ P (ppm)
(a)	[Pd(az)($OClO_3$)($SPPh_3$)]	46.56
(b)	[Pd(az)($OClO_3$)($SPPh_3$)] (3.0×10^{-3} M) + [Pd(az)($SPPh_3$)$_2$](ClO_4) (3.0×10^{-3} M)	45.83
(c)	[Pd(az)($SPPh_3$)$_2$](ClO_4) (4.0×10^{-3} M)	45.31
(d)	[Pd(az)($SPPh_3$)$_2$](ClO_4) (2.0×10^{-3} M)	44.70
(e)	[Pd(az)($SPPh_3$)$_2$](ClO_4) (4.0×10^{-3} M) + $SPPh_3$ (10^{-2} M)	44.45
(f)	$SPPh_3$	43.88

plexes containing two terminal SPR_3 groups (**6**–**8**, **11** **12**) show two absorptions to be assigned to ν(P–S) as a consequence of the coupling of both ν(P–S) vibrations via the coordination to the same metal centre (Cs, $2A_1$ both IR active). The binuclear complexes with two $SPMe_2Ph$ bridging groups (**9** and **10**) show only one IR absorption due to ν(P–S), in agreement with the geometry

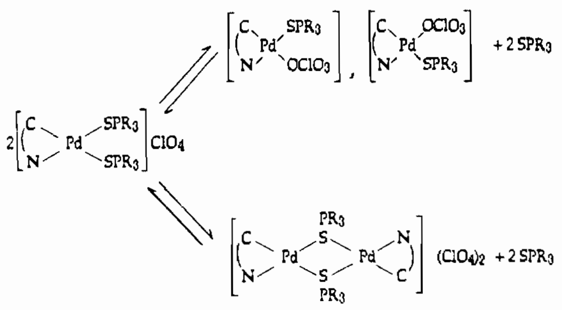


which presents the $\widehat{CN}$ groups mutually *trans* (C_{2h}, ν(P–S): $A_g + B_u$, only B_u IR active).

The Δν(P–S) (Table 4) is greater in complexes containing μ-SPR_3 bridging ligands than in complexes with terminal SPR_3, showing that the S–P bond is weaker when the ligand is acting as a bridge. A similar observation has been made for other palladium or platinum complexes [8].

The mononuclear complexes with one $SPPh_3$ coordinated group (**1**–**5**) show one signal in the ^{31}P NMR spectra. The values lie in the range 46.6–44.9 ppm, higher than the corresponding value of the free $SPPh_3$ (43.88 ppm). The dinuclear complexes with two μ-$SPMe_2Ph$ groups (**9** and **10**) also show only one ^{31}P NMR signal, indicating that both $SPMe_2Ph$ groups are equivalent.

A point that is worth commenting on is the behaviour of mononuclear complexes of the type [Pd($\widehat{CN}$)(SPR_3)$_2$]ClO_4 (**6**–**8**, **11** and **12**). In some cases (complexes **7** and **12**), the ^{31}P NMR in $CDCl_3$ at room temperature show two signals in agreement with the structure E (Scheme 1), which contains two inequivalent SPR_3 groups. By contrast complexes **6**, **8** and **9** show at room temperature only one signal (**6**: 45.31 ppm, **8**:44.12 ppm, **9**:38.90 ppm), but their ^{31}P NMR spectra at −50 °C present two signals (see Table 4) according to the static configuration E (Scheme 1). This behaviour suggests an exchange process involving dinuclear cationic [Pd(C N)(μ-SPR_3)]$_2$(ClO_4)$_2$, or mononuclear neutral [Pd($\widehat{CN}$)($OClO_3$)(SPR_3)] complexes, such as that represented in Scheme 2.



Scheme 2.

Table 5 collects the ^{31}P NMR chemical shifts of different samples: (a) complex **1**; (b) a mixture of complex **1** and complex **6**; (c) and (d) complex **6**; (e) a mixture of complex **6** and $SPPh_3$; (f) $SPPh_3$. The presence of only one ^{31}P NMR signal in all cases seems to confirm a exchange process like that indicated in Scheme 2.

X-ray Crystal Structure of [Pd(az)(OClO$_3$)(SPPh$_3$)]

Figure 1 shows the ORTEP [12] drawing of the molecule with the $OClO_3$ group in disorder. The palladium atom displays a distorted square planar environment formed by one $SPPh_3$ molecule, one $OClO_3$ group and a 2-(phenylazo)phenyl group. The 2-(phenylazo)phenyl group is bonded to the palladium atom through an *ortho* carbon of a phenyl

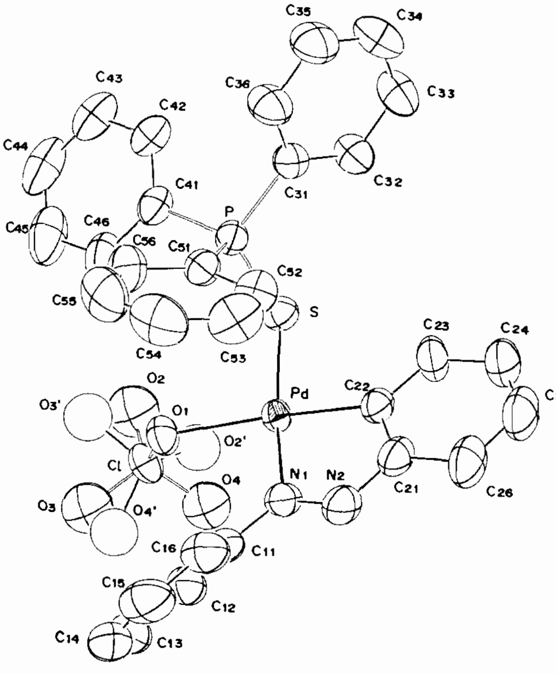


Fig. 1. ORTEP drawing of [Pd($C_6H_4N{=}NC_6H_5$)($OClO_3$)($SPPh_3$)].

ring (C_{22}) and the nitrogen atom (N_1) which is the distant azonitrogen to the C_{22}.

The dihedral angle formed by the planes $SPdO_1$ and $C_{22}PdN_1$ is 174.2(1)°. The angles between Pd–*cis* ligands bonds are in the range 79.0–96.6°. The small bite angle of the chelating ligand ($C_{22}PdN_1$, 79.0(2)°) distorts the environment of the metal atom and the adjacent angles become 93.8(1)° ($SPdC_{22}$) and 96.6(1)° (O_1PdN_1). The angle $C_{22}PdN_1$ (79.0(2)°) is the same within experimental error as the one observed in (phenylazophenyl) palladium hexafluoroacetylacetonate [13].

The Pd–S distance is 2.326(1) Å. The Pd–C_{22} distance is only 1.957(4) Å which is very short [14], however short distances like this one are usual in this kind of compounds [13]. Related to the short Pd–C_{22} bond distance is the long Pd–O_1 distance which is in *trans* position to the former one; this long Pd–O_1 distance can be due to the *trans* influence of the σ-bonded carbon combined with the low degree of nucleophilicity of the $OClO_3$ group. The Pd–N_1 distance (2.045(4) Å) is slightly longer than those observed in (phenylazophenyl) palladium hexafluoroacetylacetonate (1.994(4) Å) and *trans*-μ-dichlorobis-(phenylazophenyl-C^2,N) diplatinum(II) [15]. The chelating ring ($PdC_{22}C_{21}N_2N_1$) is not planar, the nitrogen atoms being one up (0.047(4) Å) and the other one below (0.041(4) Å) from the best weighted least-squares plane [16]. Pd and C_{21} atoms are almost in the plane. C_{22} is only 0.027(5) Å apart. This kind of distortion has already been reported [17]. Notwithstanding planar geometries for these rings have also been reported [15]. The dihedral angles formed by the free phenyl group with the best weighted least-squares plane of the palladium–azophenyl moiety is 53.09(9)°. The N_1–N_2 distance is 1.264(5) Å. This value is slightly longer than that observed for the N_1=N_2 bond in *trans*-azobenzene (1.236(6) Å) [18]. The N–C distances are also slightly different N_1–C_{11} being longer (1.418(4) Å) while the N_2–C_{21} distance is 1.388(7) Å.

Supplementary Material

Tables of anisotropic thermal factors and structure factors are available from the authors.

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