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Transition metals complexed to ordered mesophases

VIII *. Cyclopalladated *p*-azoxyanisole complexes. Crystal structure of [*N*-(phenyl)-2-salicylideneaminato]-[4′-(methoxyphenyl-*NNO*-azoxy-N^2)-4-methoxyphenyl-2-ato]palladium(II)

Mauro Ghedini *, Stefania Morrone, Giovanni De Munno and Alessandra Crispini
Dipartimento di Chimica, Università della Calabria, I-87036 Arcavacata (Cs) (Italy)

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Abstract

The synthesis and characterization of the cyclopalladated *p*-azoxyanisole chloro-bridged dimer $[Pd(Azoxy)Cl]_2$, **1**, is reported and its reactions with some salicylideneaniline derivatives (HL_{1-5}) are described. ^1H NMR spectral observations indicate that except for $[Pd(Azoxy)(L_4)]$ the mononuclear [Pd(Azoxy)(L)] products are ca 5:1 mixtures of *N-trans* and *N-cis* isomers. In the HL_4 case (HL_4 = salicylidene(2,4-dimethyl)aniline) the only product which was detected is the *N-trans* isomer. The crystal structure of *trans*-$[Pd(Azoxy)(L_1)]$ (HL_1 = salicylideneaniline) (**3**-*trans*) is monoclinic.

Introduction

Formation of Pd–C(sp^2) bonds from organic compounds containing an aromatic C–H bond and a heteroatom (e.g. nitrogen) in an appropriate position can be conveniently brought about by cyclopalladation [2]. Among the organic species meeting the above mentioned requirements is azobenzene the first species shown to undergo palladation [3], and related azo-compounds [4–9]. Although azoxybenzenes also have structural features meeting the requirements for cyclometallation they have been almost completely neglected as ligands, the complex di-μ-chloro-bis[(phenyl-*NNO*-azoxy-N^2)-phenyl-2-ato]palladium(II) being the only one reported up to now [10].

We previously reported the preparation of the metallated (*p*-azoanysole)-palladium-μ-chloro dimer and the molecular structure of its mononuclear 8-hydroxyquinolinato derivative [9]. In an extension of the investigation to azoxy compounds, we have carried out the synthesis and characterization of the palladated *p*-

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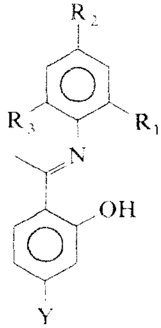
* For Part VII see ref. 1.

azoxyanisole chloro-bridged dimer (**1**) and some mononuclear complexes as described below. The latter complexes contain both the cyclopalladated *p*-azoxyanisole moiety and the $\overset{\frown}{\mathrm{O\ N}}$ chelate ring formed from the salicylideneaniline derivatives illustrated:



HL_1: $R_1 = R_2 = R_3 = Y = H$
HL_2: $R_1 = R_3 = CH_3$; $R_2 = Y = H$
HL_3: $R_1 = R_3 = H$; $R_2 = CH_3$; $Y = OC_{12}H_{25}$
HL_4: $R_1 = R_3 = H$; $R_2 = C_2H_5$; $Y = OC_{12}H_{25}$
HL_5: $R_1 = R_3 = H$; $R_2 = C_4H_9$; $Y = OC_{12}H_{25}$

The crystal structure has been determined of *trans*-[*N*-(phenyl)-2-salicylideneaminato][4′-(methoxyphenyl-*NNO*-azoxy-N^2)-4-methoxyphenyl-2-ato]palladium(II), which provides the first example of structurally characterized metallated azoxybenzene ligand.

Experimental

General procedures

All manipulations were carried out in air. The IR spectra were recorded for KBr pellets on a Perkin–Elmer spectrometer and the ^{1}H NMR spectra ($CDCl_3$, standard $SiMe_4$) on a Bruker WH 300 spectrometer. Conductivities were measured with an LKB 5300 B Conductolyser conductivity bridge. Elemental analyses were carried out by the Microanalysis Laboratory of this Department.

Preparation of compounds

The standard chemicals and *p*-azoxyanisole (Aldrich Chemical Co.) and $AgBF_4$ (Fluka A.G.) were used as supplied. $[Pd(PhCN)_2Cl_2]$ was prepared as previously reported [11]. Typical preparations were as follows. (All analogous compounds were prepared similarly.)

Salicylideneaniline, HL_1, and related ligands, HL_{2-5}

To a solution of salicylaldehyde or 2-hydroxy-4-n-dodecyloxybenzaldehyde (8.2 mmol) in absolute ethanol (10 cm^3) was added a stoichiometric amount of the appropriate aromatic amine. The resulting orange solution was stirred under reflux for 2 h. The yellow precipitate formed on cooling (0 °C) in the case of HL_1 and HL_{3-5}, was filtered off, washed with cold pentane, and vacuum dried. In the case of HL_2 a yellow oil was formed, and this was purified by chromatography on a silica gel column with a mixture of diethyl ether and petroleum ether as eluent (v/v, 50/50). Yields and selected ^{1}H NMR data (300 MHz, $CDCl_3$, standard $SiMe_4$) are:

HL_1: Yield 77%, m.p. 45 °C. δ_H 8.62 (s, 1H, C*H*=N).

HL_2: Yield 60%, oily. δ_H 8.62 (s, 1H, C*H*=N); 2.20 (s, 6H, $C_6H_3(CH_3)_2N=$).

HL_3: Yield 35%, m.p. 83 °C. δ_H 8.4 (s, 1H, C*H*=N); 3.90 (t, 2H, $J = 5$ Hz, OC*H*$_2$); 2.3 (s, 3H, C*H*$_3$C$_6$H$_4$N=).

HL_4: Yield 45%, m.p. 78 °C. δ_H 8.40 (s, 1H, C*H*=N); 3.90 (t, 2H, $J = 5$ Hz, OC*H*$_2$); 2.60 (q, 2H, $J = 5$ Hz, C*H*$_2$C$_6$H$_4$N=).

HL_5: Yield 45%, m.p. 86 °C. δ_H 8.40 (s, 1H, C*H*=N); 3.90 (t, 2H, $J = 5$ Hz, OC*H*$_2$); 2.30 (t, 2H, $J = 5$ Hz, C*H*$_2$C$_6$H$_4$N=).

[Pd(Azoxy)(μ-Cl)]$_2$, 1

To a suspension of [Pd(PhCN)$_2$Cl$_2$] (0.742 g, 1.94 mmol) in absolute ethanol (40 cm^3) was added *p*-azoxyanisole (HAzoxy) (500 mg, 1.94 mmol). The resulting brownish mixture was stirred under reflux for 4 h, then the greenish precipitate was filtered off, washed with diethyl ether, was purified by Soxhlet extraction into dichloromethane. The solvent was partly evaporated under reduced pressure and the resulting yellow solid filtered off, washed with diethyl ether, and vacuum dried: yield 0.465 g (60%), m.p. > 230 °C. Anal. Found: C, 41.84; H, 3.17; N, 6.83. $C_{28}H_{26}Cl_2N_4O_6Pd_2$ calcd.: C, 42.10; H, 3.28; N, 7.05%.

[Pd(Azoxy)(MeCN)$_2$]BF$_4$, 2

To a solution of $AgBF_4$ (0.097 g, 0.50 mmol) in MeCN (5 cm^3) was added complex **1** (0.200 g, 0.25 mmol). The suspension was stirred at room temperature for 12 h then filtered. The solvent was evaporated under reduced pressure and the resulting orange solid was washed with diethyl ether and vacuum dried (0.220 g, 90%). Anal. Found: C, 39.33; H, 3.51; N, 9.05. $C_{18}H_{19}BF_4N_4O_3Pd$ calcd.: C, 40.57; H, 3.59; N, 10.56%. IR (nujol mull): ν(CN) = 2285, ν(B–F) = 1050 cm^{-1}. Λ_M: 123.7 Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3}) in MeCN. ^{1}H NMR data (300 MHz, $CDCl_3$, standard $SiMe_4$) are: δ_H 6.64 (H(3), brs); 6.73 (H(5), brd, $J(H_5H_6) = 9$ Hz); 7.49 (H(6), d, $J(H_5H_6) = 9$ Hz).

[Pd(Azoxy)(L)], 3–7

To a suspension of complex **2** (0.200 g, 0.37 mmol) in absolute ethanol (10 cm^3), was added a stoichiometric amount of the appropriate HL ligand. The mixture was stirred for 3 h at room temperature. The resulting orange precipitate was filtered off, and shaken with $CHCl_3$ and the formed suspension was filtered through a short Florisil column. The solvent was removed from the filtrate under reduced pressure and the residual orange solid was filtered of and recrystallized from $CHCl_3$–diethyl ether to give an orange microcrystalline solid.

[Pd(Azoxy)(L$_1$)], **3**. Yield 70%, m.p. 220 °C. Anal. Found: C, 57.62; H, 4.09; N, 7.27. $C_{27}H_{23}N_3O_4Pd$ calcd.: C, 57.90; H, 4.14; N, 7.53%.

[Pd(Azoxy)(L$_2$)], **4**. Yield 46%, m.p. 192 °C. Anal. Found: C, 58.53; H, 4.49; N, 7.01. $C_{29}H_{29}N_3O_4Pd$ calcd.: C, 59.22; H, 4.63; N, 7.12%.

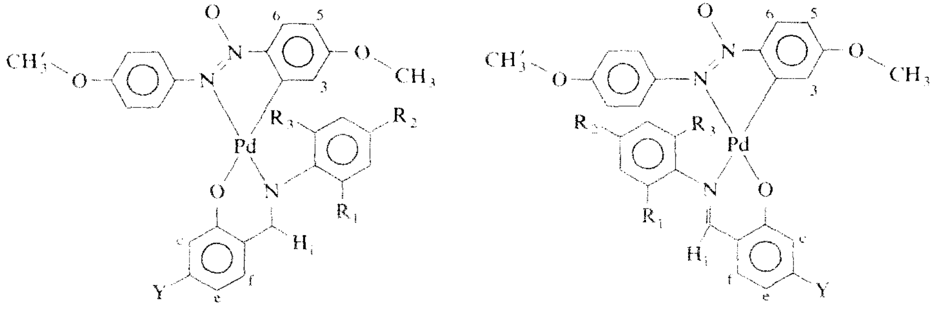
[Pd(Azoxy)(L$_3$)], **5**. Yield 50%, m.p. 137 °C. Anal. Found: C, 63.52; H, 6.61; N, 5.27. $C_{40}H_{51}N_3O_5Pd$ calcd.: C, 64.54; H, 6.9; N, 5.67%.

[Pd(Azoxy)(L$_4$)], **6**. Yield 51%, m.p. 135 °C. Anal. Found: C, 63.14; H, 6.53; N, 4.56. $C_{41}H_{53}N_3O_5Pd$ calcd.: C, 64.93; H, 7.04; N, 5.56%.

[Pd(Azoxy)(L$_5$)], **7**. Yield 53%, m.p. 130 °C. Anal. Found: C, 64.09; H, 6.87; N, 4.65. $C_{43}H_{57}N_3O_5Pd$ calcd.: C, 65.66; H, 7.30; N, 5.36%.

Table 1

Selected ^{1}H NMR data for complexes **1** and **3**–**7** [a]



(*trans*) (*cis*)

Compound	δ										J			
	H_3	H_5	H_6	H_c	H_d	H_e	H_f	H_i	OCH_3	OCH'_3	$J(H_6H_5)$	$J(H_5H_3)$	$J(H_cH_f)$	$J(H_cH_e)$
1	7.38d	6.84dd	7.49d	–	–	–	–	–	3.83	3.81	8.6	1.8	–	–
3-*trans*	5.37d	6.52dd	7.49d	7.21m	6.51m	6.51m	7.21m	8.01s	3.30	3.91	8.9	2.5	n.d.	n.d.
3-*cis*	[b]	6.75dd	[b]	[b]	[b]	[b]	[b]	7.91s	4.03	3.76	8.8	2.4	n.d.	n.d.
4-*trans* [c]	5.05d	6.57dd	7.55d	7.25m	6.48m	6.41m	7.11m	7.69s	3.35	3.91	8.9	2.5	n.d.	n.d.
5-*trans*	5.41d	6.51dd	7.49d	5.91d	–	6.15dd	7.05d	7.85s	3.27	3.90	8.9	2.5	8.8	2.3
5-*cis*	7.57d	6.72 [d]	[b]	6.62d	–	6.28dd	[b]	7.78s	4.03	3.73	n.d.	2.4	8.7	2.4
6-*trans*	5.49d	6.50dd	7.48d	5.92d	–	6.15dd	7.05d	7.85s	3.27	3.90	8.9	2.4	8.8	2.4
6-*cis*	7.57d	6.72dd	[b]	6.62d	–	6.27dd	7.06d	7.78s	4.03	3.73	8.6	2.3	8.9	2.6
7-*trans*	5.43d	6.51dd	[b]	5.92d		6.16dd	7.06d	7.94s	3.30	3.90	8.8	2.5	8.8	2.4
7-*cis*	7.56d	6.72dd	[b]	6.62d		6.28dd	[b]	7.79s	4.03	3.70	8.8	2.5	8.6	2.4

[a] In $CDCl_3$ at 300.13 MHz; δ in ppm with multiplicities in parenthesis J in Hz; key: d = doublet; dd = doublet of doublet; s = singlet; n.d. = J value not determined. [b] Signal obscured by more intense resonances. [c] Two singlets at 2.35 and 2.16 ppm arise from $R_1(CH_3)$ and $R_3(CH_3)$. No assignment could be made. [d] Unresolved multiplet.

Table 2

Selected distances (Å), angles (°) and torsion angles (°)

Bond distances			
Pd–N(1)	2.033(2)	Pd–O(1)	2.065(2)
Pd–C(9)	1.984(3)	Pd–N(3)	2.035(2)
N(1)–N(2)	1.300(3)	N(3)–C(21)	1.303(4)
N(2)–O(2)	1.258(3)	C(21)–C(22)	1.411(4)
N(2)–C(8)	1.429(3)	C(22)–C(23)	1.434(4)
C(8)–C(9)	1.385(4)	O(1)–C(23)	1.299(4)
Bond angles			
N(1)–Pd–C(9)	80.1(1)	N(3)–Pd–O(1)	86.7(1)
N(1)–Pd–N(3)	178.6(1)	O(1)–Pd–C(9)	172.8(1)
Pd–N(1)–N(2)	115.3(2)	Pd–N(3)–C(21)	119.9(2)
N(1)–N(2)–C(8)	115.5(2)	N(3)–C(21)–C(22)	127.2(3)
N(1)–N(2)–O(2)	123.4(2)	C(21)–C(22)–C(23)	121.6(3)
O(2)–N(2)–C(8)	121.1(2)	O(1)–C(23)–C(22)	123.4(3)
N(2)–C(8)–C(9)	115.5(2)	Pd–O(1)–C(23)	117.7(2)
Pd–C(9)–C(8)	113.5(2)		
Torsion angles			
Pd–N(1)–N(2)–O(2)	178.0(2)	Pd–N(3)–C(21)–C(22)	−10.3(4)
Pd–N(1)–N(2)–C(8)	−3.0(3)	N(3)–C(21)–C(22)–C(23)	−21.7(5)
N(1)–N(2)–C(8)–C(9)	−0.6(4)	C(21)–C(22)–C(23)–O(1)	6.3(5)
O(2)–N(2)–C(8)–C(9)	178.4(3)	C(22)–C(23)–O(1)–Pd	35.9(4)
N(2)–C(8)–C(9)–Pd	3.9(3)	C(23)–O(1)–Pd–N(3)	−49.5(2)
C(8)–C(9)–Pd–N(1)	−4.1(2)	O(1)–Pd–N(3)–C(21)	36.9(2)
C(9)–Pd–N(1)–N(2)	4.0(2)		

Determination of the crystal structure of complex 3-trans

Crystal data. $C_{27}H_{23}N_3O_4Pd$, $M = 559.9$, monoclinic, space group $P2_1/c$, $a = 11.208(2)$, $b = 16.834(3)$, $c = 12.550(3)$ Å, $\beta = 99.91(3)°$, $U = 2332.5(8)$ Å^3, $Z = 4$, $\lambda = 0.71069$ Å, $T = 298$ K, $D_c = 1.59$ g cm^{-3}, $F(000) = 1136$, $\mu(\text{Mo-}K_\alpha) = 8.22$ cm^{-1}.

A crystal of approximate dimensions 0.40 × 0.35 × 0.50 mm was used for the structure analysis. Absorption correction was ignored. For the data collection and processing a Siemens $R3m/V$ diffractometer was used in ω–2θ scan mode, using graphite-filtered Mo-K_α radiation; all the reflections with 2θ in the range 3.5–50° were measured. Of 4124 unique reflections, 3634, having $I > 3\sigma(I)$, were used in the analysis. For the structure solution and refinement Patterson and Fourier methods, were used. Hydrogen atoms were located one ΔF map and refined. Final R and R_w values were 0.033 and 0.036 respectively, $S = 1.31$. The weighting scheme used in the last cycles of refinement was $w = 1.000/\sigma^2(F_o + 0.001(F_o))^2$. All calculations were performed with SHELXTL PLUS [12] on a Microvax(II) computer. Selected bond distances, angles and torsion angles are given in Table 2, and final atomic coordinates for non-hydrogen atoms in Table 3. Other crystallographic details and complete lists of bond distances, bond angles, coordinates of H atoms, thermal parameters, and observed and calculated structure factors, are available from the authors.

Table 3

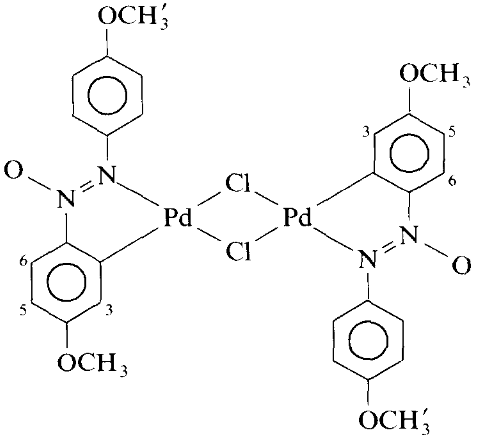
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$)

	x	y	z	U_{eq} [a]
Pd	892(1)	1447(1)	1198(1)	32(1)
N(1)	862(2)	581(1)	2323(2)	36(1)
N(2)	−23(2)	75(1)	2105(2)	39(1)
N(3)	895(2)	2298(1)	47(2)	35(1)
O(1)	2574(2)	1873(1)	1893(2)	47(1)
O(2)	−156(2)	−508(1)	2700(2)	56(1)
O(3)	4017(2)	639(2)	6253(2)	65(1)
O(4)	−3331(2)	694(1)	−1567(2)	52(1)
C(1)	1640(3)	526(2)	3354(2)	36(1)
C(2)	1165(3)	536(2)	4303(2)	38(1)
C(3)	1935(3)	583(2)	5294(2)	42(1)
C(4)	3173(3)	603(2)	5323(2)	45(1)
C(5)	3653(3)	570(2)	4382(3)	48(1)
C(6)	2880(3)	541(2)	3395(2)	43(1)
C(7)	3584(5)	757(4)	7237(3)	74(2)
C(8)	−870(3)	230(2)	1139(2)	36(1)
C(9)	−638(2)	901(2)	571(2)	34(1)
C(10)	−1469(3)	1057(2)	−371(2)	39(1)
C(11)	−2468(3)	569(2)	−669(2)	40(1)
C(12)	−2662(3)	−98(2)	−65(3)	45(1)
C(13)	−1837(3)	−273(2)	841(3)	44(1)
C(14)	−3123(4)	1307(3)	−2292(3)	61(1)
C(15)	−171(3)	2715(2)	−431(2)	35(1)
C(16)	−471(3)	2804(2)	−1551(3)	43(1)
C(17)	−1499(3)	3228(2)	−1974(3)	50(1)
C(18)	−2217(3)	3559(2)	−1315(3)	57(1)
C(19)	−1920(4)	3467(2)	−205(3)	56(1)
C(20)	−906(3)	3044(2)	225(3)	44(1)
C(21)	1900(3)	2476(2)	−288(2)	37(1)
C(22)	3081(3)	2229(2)	167(2)	39(1)
C(23)	3375(3)	1968(2)	1269(2)	42(1)
C(24)	4611(3)	1839(3)	1671(3)	62(1)
C(25)	5482(4)	1918(4)	1039(4)	80(2)
C(26)	5183(3)	2162(3)	−37(4)	73(2)
C(27)	4004(3)	2331(2)	−453(3)	53(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Results and discussion

Treatment of *p*-azoxyanisole (HAzoxy) with $[Pd(PhCN)_2Cl_2]$ in refluxing ethanol gave a good yield of the yellow solid, **1**, whose elemental analysis is consistent with the formulation $[Pd(Azoxy)Cl]_2$ like that of the dinuclear cyclometallated complex formed from azobenzenes under similar experimental conditions [3–9]. Palladation of the HAzoxy was confirmed by ^1H NMR spectroscopy. The ^1H NMR spectrum of **1** shows two resonances in the aliphatic region which can be assigned to non-equivalent methoxy groups. In the aromatic range two sets of signals were resolved by decoupling experiments. They arise from four and three protons, respectively, and are attributable to the free and the metallated phenyl ring. On the basis of the evidence we suggest for **1** the molecular structure reported in Scheme 1.



Scheme 1. Proposed molecular structure of **1**, and numbering of aromatic protons.

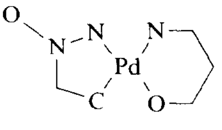
Balch suggested a similar structure [10] for di-μ-chloro-bis[(phenyl-*NNO*-azoxy-N^2)-phenyl-2-ato]palladium(II). He observed that azoxybenzene was less reactive than azoxybenzene and so could be classified as a poorer donor ligand [10].

As recently emphasized by Ryabov [2], the cyclopalladation reaction can be regarded as an electrophilic attack by the palladium centre on the organic molecule. In this light the high reactivity displayed by *p*-azoxyanisole can probably attributed to the presence of the methoxy substituents, which are strong activating groups for electrophilic substitution.

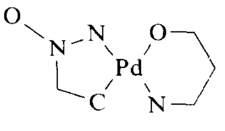
Mononuclear cyclopalladated complexes may be obtained by bridge-splitting reactions [13]. In the present case the salicylideneaminato derivatives **3**–**7** were prepared by reaction of the intermediate compound $[Pd(Azoxy)(MeCN)_2]BF_4$, **2**, with the Schiff bases HL_{1-5}.

Complex **2**, characterized spectroscopically and by conductivity measurements (Experimental section), was formed from **1** by cleavage of the chlorine bridge with $AgBF_4$ in acetonitrile solution and was isolated as an orange solid in 90% yield. When **2** was suspended in absolute ethanol in the presence of HL (1 : 1 molar ratio), at room temperature an orange precipitate was formed whose elemental analysis and IR data were in agreement with the formulation [Pd(Azoxy)(L)].

Compounds **3**–**7** should be able to adopt two different conformations, *cis* (I) and *trans* (II) as defined by the disposition of the two palladium-coordinated nitrogen atoms.



(I)



(II)

The presence of the two possible isomers is apparent from the ^{1}H NMR spectra of **3** and **5**–**7** (Table 1). The imine hydrogen gives rise to a pair of signals (integration ratio ca 5 : 1), which evidently arise from different species since two

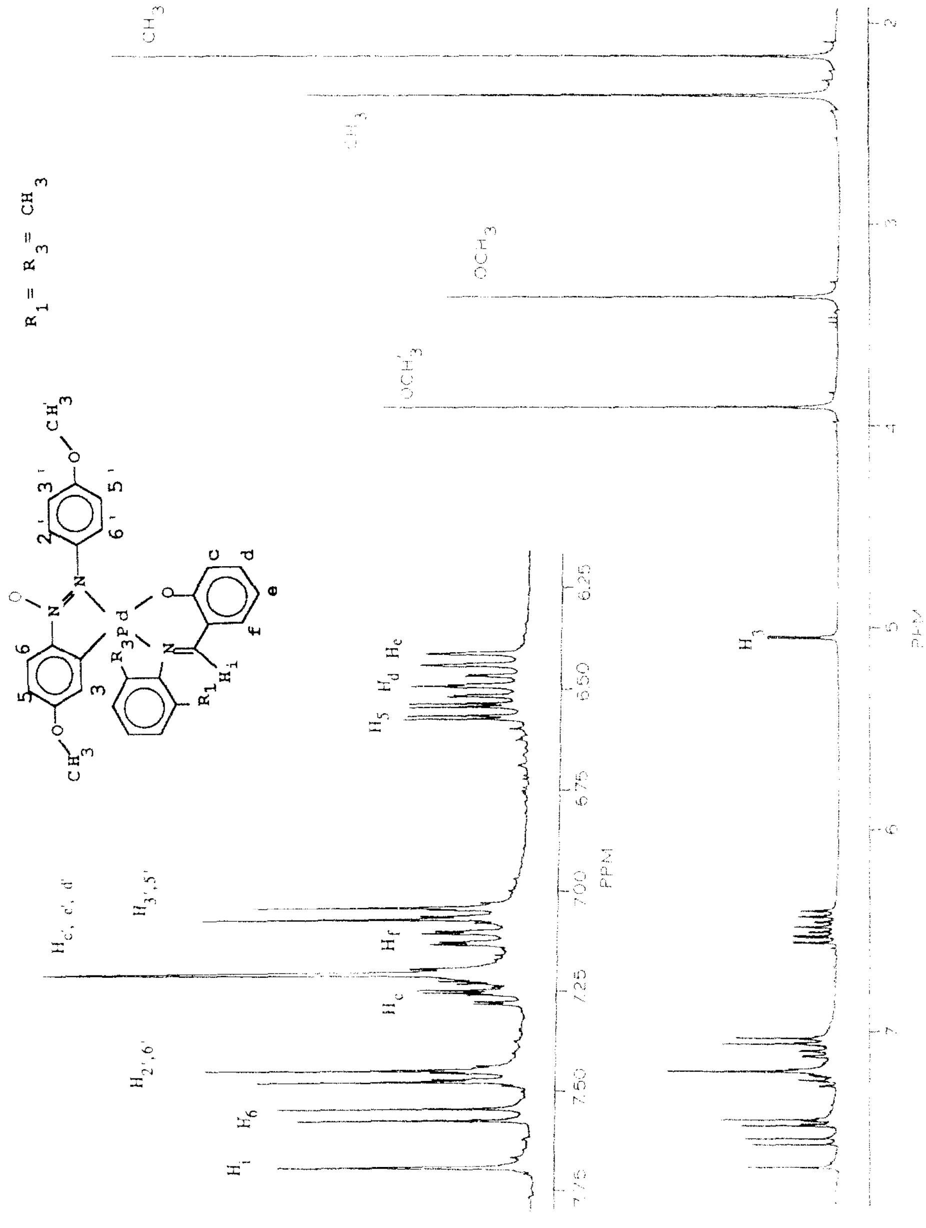


Fig. 1 ^1H NMR spectra of the complex $[Pd(Azoxy)(L_2)]$, 4.

pairs of nonequivalent methoxy groups with the same integration ratio (ca 5 : 1) are also present.

However, full assignment of the aromatic protons by decoupling experiments did not allow us to distinguish with certainty between *cis* and *trans* isomers, and so it could be helpful to consider the special structural features of *cis* and *trans* forms. In **3**–**7** four phenyl rings are present, two of which are involved in chelate rings (and therefore blocked) and two are free to rotate. As molecular models suggest, the less crowded structure seems to be the *trans* one, which the free-rotating phenyl rings lie on opposite sides, and so this isomer should be thermodynamically the more stable. Furthermore, bis-salicylideneaminato metal complexes usually adopt a *trans* arrangement of N (and O) donor atoms [14,15].

The ^{1}H NMR spectrum of **4** is straightforward, since only one isomer is present (Fig. 1). The chemical shift of H(3) at 5.05 ppm, is very unusual, and is the result of strong shielding by a neighbouring group. This behaviour can be accounted for if complex **4** is assigned the *trans* structure. In this isomer the freely rotating phenyl group is likely to generate magnetic anisotropy, causing the H(3) proton signal to move upfield. An upfield shift of the H(3) signal is also observed for the major species in all the isomeric mixtures, which is therefore also assigned the *trans* structure. This attribution is confirmed by the presence (for all the series) of a doublet at about 7.56 ppm assigned to H(3) in the *cis* form; for the *cis* isomer no major shielding effect is expected for the *ortho*-metallated ring protons.

Many attempts were made to grow single crystals from the isomeric mixtures. After several recrystallizations, crystals of a pure isomer of **3** suitable for an X-ray diffraction study were from chloroform–diethyl ether.

The molecular structure (Fig. 2) reveals the presence of discrete monomeric molecules in which the palladium atom has a slightly distorted square planar coordination geometry with a *trans* arrangement of the N donor atoms. Selected bond distances and angles are given in Table 2. Final atomic coordinates for the non-hydrogen atoms are listed in Table 3.

The azoxy fragment is bound to the palladium centre through an *ortho* carbon atom of a phenyl ring and a distant azoxy-nitrogen atom. The C(9)–C(8)–N(2)–[O(2)]–N(1) atoms are coplanar, with Pd out of this plane by 0.109(1) Å. The structural features within the $\overline{\text{C(9)–Pd–N(1)–N(2)–C(8)}}$ metallacycle can conveniently be discussed by comparing the data with those reported for the free ligand *p*-azoxyanisole [16] and related azobenzene palladium complexes [8b,9].

The Pd–C(9) (1.984(3) Å) and Pd–N(1) (2.033(2) Å) bond distances, as well as the bite angle N(1)–Pd–C(9) (80.1(1)°), are in good agreement with the corresponding values for (8-hydroxyquinolinato)[2-(4′-methoxyphenylazo-N^2)-5-methoxyphenyl]palladium(II) [9] and di-μ-chloro-bis[2′,6′-dimethyl(phenylazo-N^2)phenyl-2-ato] dipalladium(II) [8b]. As a result of extended conjugation, the N(1)–N(2) (1.300(3) Å) and N(2)–C(8) (1.429(3) Å) bond lengths are alternatively longer and shorter than those in the free ligand (1.218(5) and 1.496(5) Å, respectively). On the other hand, the nitrogen–oxygen bond distance (1.258(3) Å) is slightly affected by coordination of the molecule to the metal ion (1.279(4) Å in the free ligand). In addition, the bond angles at N(2) are more regular than in *p*-azoxyanisole; thus values in the range 115.5–123.4° are found in **3** (Table 2) compared to values in the range 111.8–130.3° for the ligand [16]. These effects can be accounted for by assuming that there is electronic conjugation involving the N–O group.

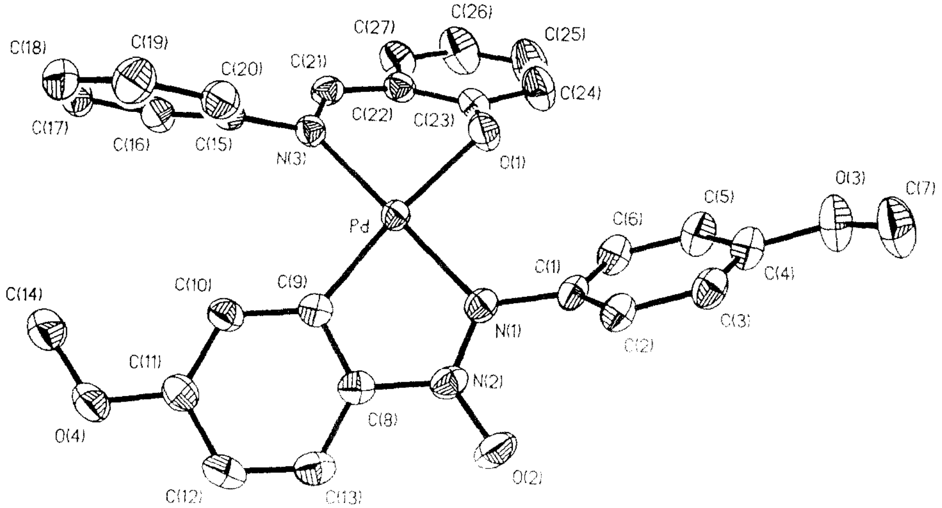


Fig. 2. ORTEP view of the complex $[Pd(Azoxy)(L_1)]$, **3**-*trans*, with the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

In the coordination polyhedron the salicylideneaminato group, although showing bond lengths and angles which agree well with those or palladium bis-salicylideneaminato complexes [14,15], does not show the expected planarity. The torsion angles for the O(1)–Pd–N(3)–C(21)–C(22)–C(23) cycle are reported in Table 2. A noteworthy feature is the length of the Pd–O(1) bond to C(9). Owing to the *trans* effect of the σ-bonded C atom this bond, with a length of 2.065(2) Å, is about 0.1 Å longer than those *trans* to O atoms [14,15].

The torsion angles about the C(1)–N(1) and C(15)–N(3) bonds are 52.2(1) and 75.4(1)°, respectively.

In keeping with the discussion above based on the crystallographic and NMR data, we suggest that the main product in the mixture of isomers of **3** is always the *trans* species.

Finally, the synthesis of mixed *p*-azoxyanisolesalicylideneaminate palladium complexes was successfully accomplished. Some of the ligands (namely HAzoxy and HL_{3-5}) are well known to give thermotropic nematic and/or smectic liquid crystals [17,18]. However, none of the new compounds displays liquid-crystalline properties.

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