Journal of Organometallic Chemistry, 476 (1994) 111–120

Reactivity of acetate-bridged cyclopalladated complexes. ^{1}H and ^{13}C NMR studies of some monomeric derivatives of *N*-(4-methoxyphenyl)-α-benzoylbenzylideneamine

José L. García-Ruano, Isabel López-Solera, José R. Masaguer, M.A. Monge *, Carmen Navarro-Ranninger and Jesús H. Rodríguez

Departamento de Química, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid (Spain)

(Received August 1993; in revised form November 11, 1993)

Abstract

The reactions have been studied of acetate-bridged cyclopalladated complexes with different reagents to yield monomeric structures. The relative reactivity is even higher than that of the corresponding chloro- and bromo-dimers, usually obtained from the acetates and used as starting materials in bridge-cleavage reactions. The ^{1}H and ^{13}C NMR spectra of the monomeric complexes have allowed evaluation of the influence of the palladium on the chemical shifts of the surrounding nuclei. The slow crystallization of $[\{Pd(\mu\text{-}Br)(4\text{-}MeOC_6H_4N{=}C(COC_6H_5)C_6H_4)\}_2]$ from DMSO induces a bridge-splitting reaction to afford $[Pd(4\text{-}MeOC_6H_4N{=}C(COC_6H_5)C_6H_4)(DMSO)Br]$.

Key words: Acetate; Nuclear magnetic resonance; Orthometallation; Palladium

1. Introduction

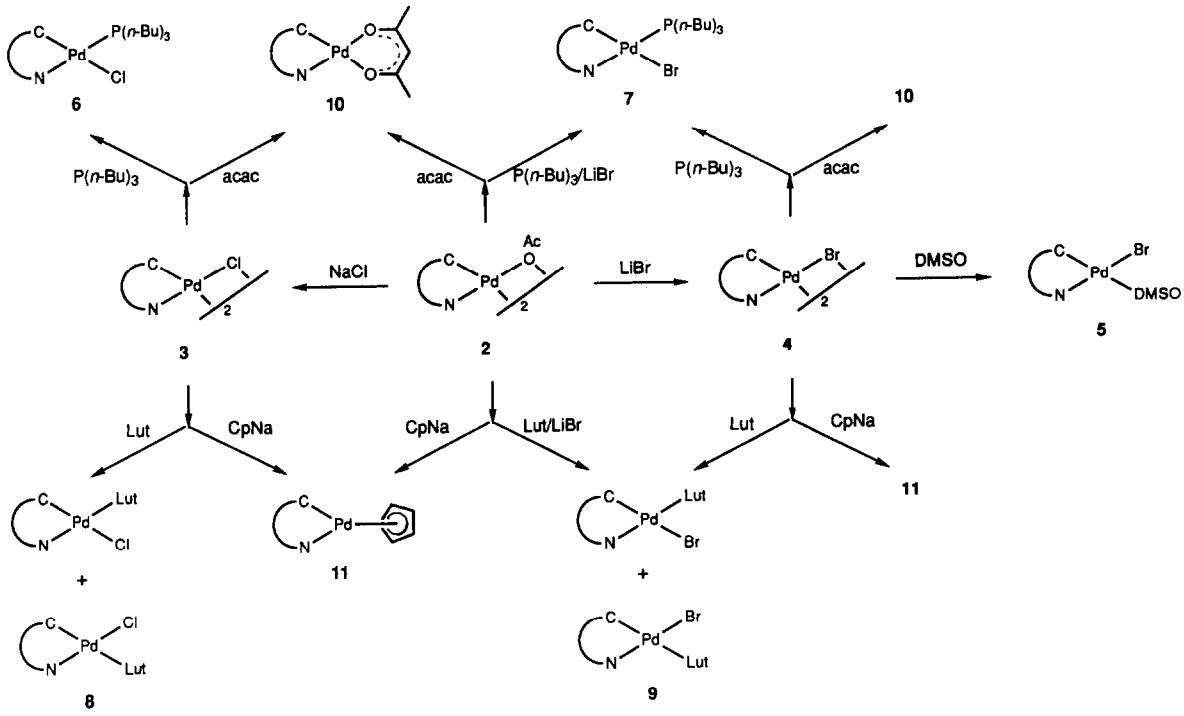
There are many studies of *ortho*-palladation reactions of imines and related compounds [1,2]. However the studies have concentrated mainly on insertion into Pd–C bonds. Monomeric cyclometallated derivatives are usually synthesized by bridge-cleavage reactions from their corresponding chloro- and bromo-bridged cyclometallated dimers, which in turn are prepared from the acetate-bridged derivatives. Nevertheless, the reactivity of these last dimers has hardly been studied. We are interested in the relative reactivity of acetate-, chloro- and bromo-bridge cyclometallated complexes compared to the corresponding monomeric complexes. The reported ^{1}H and ^{13}C NMR spectra of these compounds are few, and the chemical shift of the aromatic carbon atom directly joined to the metal is not described in most of the papers [3].

Recently, we have described the *ortho*-palladation reactions of benzoylbenzylideneamines [4,5]. Although the unequivocal structural characterization of the cyclometallated compounds had been made by X-ray diffraction, we also studied the ^{1}H and ^{13}C NMR spectra. Unfortunately, the folded structure of the acetate-bridge complexes caused the aromatic ring proton signals to be broadened, probably due to the anisotropic effect of the ring currents, precluding detailed study of *ortho*-metallation effects on the proton and carbon chemical shifts of the nearest nuclei. In order to overcome this we decided to synthesize and study chloro- and bromo-bridge complexes, whose unfolded structure precluded the broadening of the signals. Nevertheless, the low solubility of these complexes allowed us to record the NMR spectra only in DMSO, which sometimes affords bridge-splitting reactions [5]. Therefore we synthesized and studied cyclometallated monomers, which do not pose all these problems.

Correspondence to: Dr. J.L. García-Ruano and Dr. C. Navarro-Ranninger.

* Present address: Instituto de Ciencia de Materiales, CSIC Serrano 113, 28006-Madrid, and Laboratorio de Difracción de Rayos X, Facultad de Ciencias Químicas, UCM, 28040-Madrid, Spain.

0022-328X/94/$7.00
SSDI 0022-328X(93)24314-U



Scheme 1.

Here we report the synthesis and spectroscopic properties of the complexes **3–11**, derived from *N*-(4-methoxyphenyl)-α-benzoylbenzylidene amine (**1**) (Scheme 1). The monomeric compounds **5–11** were obtained both from the dimeric acetate (**2**) and from the corresponding chlorine (**3**) and bromine (**4**) derivatives. The unfolded structure of **3** and **4** and the monomeric structure of **5–11** prevents broadening of the signals. Furthermore, whereas **3** and **4** are sparingly soluble in $CDCl_3$, the monomeric complexes are soluble.

2. Results and discussion

Acetate-chloride exchange reaction of any two acetate-bridged cyclometallated atropisomers (**2**) with NaCl (there are two chiral axes [4]) leads to a unique chloro-bridged cyclometallated complex **3**, probably due to free rotation around the CO–CN bond in these complexes, which exhibit an unfolded structure. This complex has also been prepared by direct treatment of the benzylideneamine with $K_2[PdCl_4]$[6]. Similarly, the reaction between **2** and LiBr affords the bromo-bridged derivative **4**. The chloro- and bromo-bridged complexes are insoluble in most organic solvents, except DMSO, DMF and CH_3CN. Crystallization of complex **4** from DMSO causes bridge-splitting to afford [PdL(DMSO)-Br] (L = the benzylideneamine) (**5**) the analogous chloro-bridged complex [6] (Scheme 1).

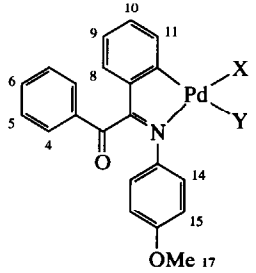
The reaction of dimeric complexes **3** and **4** with tri(n-butyl)phosphine yielded the corresponding halo-complexes **6** and **7**, respectively. Analogously, the reaction with 3,5-lutidine afforded **8** and **9** respectively, as mixtures of stereoisomers. Compounds **10** and **11** were obtained from chlorine and bromine derivatives by reaction with sodium 2,4-pentanedionate and sodium cyclopentadienide, respectively.

We then studied the reactions of the dimeric acetate complex **2** with the bases, in order to obtain our products in only one step. The results are compared in Table 1. The yields obtained from **2** are usually higher

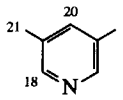
TABLE 1. Yields obtained for monomeric complexes

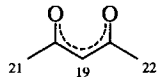
Starting Material	Reagent	Product	Yield (%)
2	$P(n\text{-}Bu)_3$/NaCl	**6**	82
3	$P(n\text{-}Bu)_3$	**6**	85
2	$P(n\text{-}Bu)_3$/LiBr	**7**	87
4	$P(n\text{-}Bu)_3$	**7**	85
2	Lut/NaCl	**8**	89
3	Lut	**8**	76
2	Lut/LiBr	**9**	94
4	Lut	**9**	84
2	acac	**10**	81
3	acac	**10**	79
4	acac	**10**	81
2	NaCp	**11**	76
3	NaCp	**11**	68
4	NaCp	**11**	71

TABLE 2. ^{1}H NMR Parameters (δ, ppm)



5	6	7	8	9	10	11
Br DMSO	$P(n\text{-}Bu)_3$ Cl	$P(n\text{-}Bu)_3$ Br	Lut Cl	+ Cl Lut + Lut Br	+ Br Lut	Cp





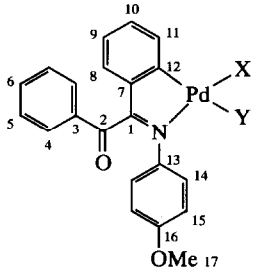
	1	3 [a]	4 [a]	5 [a]	6	7	8	9	10	11
H4	7.84, m, 2H	7.75, m, 2H	7.79, m, 2H	7.79, m, 2H	7.75, m, 2H	7.74, m, 2H	7.79, m, 4H	7.78, m, 4H	7.76, m, 2H	7.67, m, 2H
H5	7.35, m, 2H	7.48, m, 2H	7.49, m, 2H	7.50, m, 2H	7.36, m, 2H	7.36, m, 2H	7.35, m, 4H	7.38, m, 4H	7.33, m, 2H	7.29, m, 2H
H6	7.46, m, 1H	7.65, m, 1H	7.67, m, 1H	7.67, m, 1H	7.51, m, 1H	7.52, m, 1H	7.55, m, 2H	7.56, m, 2H	7.48, m, 1H	7.46, m, 1H
H8	7.75, m, 2H	6.83, dd, 1H	6.84, dd, 1H	6.85, dd, 1H	7.04, m [b]	7.03, m [b]	6.21, d, 1H	6.13, d, 1H	7.00, m [b]	6.92, m [b]
		J = 1.4, 8.1	J = 1.7, 7.5	J = 2.1, 7.7			J = 7.5	J = 7.1		
H9	7.31, m, 2H	6.99, dt, 1H	6.98, dt, 1H	6.98, t, 1H	7.04, m [b]	7.03, m [b]	7.00, m [b]	6.98, m [b]	7.00, m [b]	6.92, m [b]
		J = 1.4, 8.1	J = 1.7, 7.5	J = 7.7						
H10	7.42, m, 1H	7.14, t, 1H	7.10, dt, 1H	7.10 [b], t, 1H	7.19, dt, 1H	7.22, dt, 1H	7.15, m [b]	7.19, m [b]	7.25, m, 1H	7.23, m, 1H
		J = 8.1	J = 1.7, 7.5	J = 7.7	J = 1.9, 7.2	J = 2.3, 7.5	7.00, m [b]	6.98, m [b]		
H11	(see H9)	7.87, d, 1H	8.05, dd, 1H	8.03, dd, 1H	7.32, dd, 1H	7.36, m [b]	8.16, d, 1H	8.44, d, 1H	7.69, d, 1H	7.79, m, 1H
		J = 8.1	J = 1.7, 7.5	J = 2.1, 7.7	J = 1.9, 7.2		J = 7.5	J = 7.1	J = 7.6	
H14,14 [c]	6.88, 2H	7.03, 2H	7.07, 2H	7.07 [b], 2H	7.02, 2H	6.99, 2H	7.15 [b]	7.13 [b]	7.16, 2H	7.12, 2H
H15,15 [c]	6.65, 2H	6.72, 2H	6.76, 2H	6.76, 2H	6.63, 2H	6.63, 2H	6.63, 4H	6.63, 4H	6.65, 2H	6.61, 2H
H17	3.51, s, 3H	3.63, s, 3H	3.63, s, 3H	3.63, s, 3H	3.64, s, 3H	3.65, s, 3H	3.64, s, 3H	3.66, s, 3H	3.66, s, 3H	3.67, s, 3H
							3.58, s, 3H	3.59, s, 3H		
H18					2.05, m, 2H	2.08, m, 2H	8.60, s, 2H	8.61, s, 2H		
							7.94, s, 2H	7.94, s, 2H		
H19					1.63, m, 2H	1.63, m, 2H			5.34, s, 1H	
H20					1.44, m, 2H	1.43, m, 2H	7.48, s, 1H	7.48, s, 1H		
							7.15, m [b]	7.19, m [b]		
H21					0.92, t, 3H	0.92, t, 3H	2.35, s, 6H	2.36, s, 6H	2.01, s, 3H	
					J = 7.3	J = 7.1				
							2.05, s, 6H	2.06, s, 6H		
H22									1.78, s, 3H	
Other				2.53, s, 6H [e]						5.73, s, 5H [d]

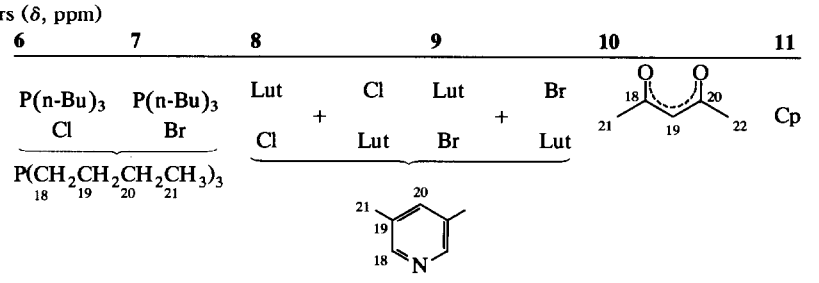
[a] DMSO-d_6; [b] Overlapped signal. [c] AA'BB' system. [d] Cp. [e] DMSO. s, singlet; s br, singlet broadened; d, doublet; t, triplet; dd, double doublet; dt, double triplet; m, multiplet. J(Hz).

than those from **3** or **4**. Although the reactions seem to be very rapid the yields depend on the reaction time, being best after 24 h. These results indicate that it is not necessary to prepare the chloro- and bromo-bridged complexes, the acetates being better starting materials.

The microanalytical data for all these complexes (see Experimental section) are consistent with the proposed structures. The IR spectra of these complexes show a shift of the ν(C=O) vibrations towards higher wavenumbers and a shift of the ν(C=N) vibrations towards lower frequency, indicating that the palladium atom is always bonded to the nitrogen atom of the C=N group [2]. The IR spectrum of complex **3** exhibits two asymmetric stretching absorption at 312 and 308 cm^{-1} assignable to ν(Pd–Cl) (bridging). The ν(Pd–Br) (bridging) in complex **4** cannot be observed since they are below 200 cm^{-1}. The complex **5** shows a band at 968 cm^{-1}, *ca.* 100 cm^{-1} lower than in free DMSO

TABLE 3. ^{13}C NMR Parameters (δ, ppm)





	1	3 [a]	4 [a]	6	7	8	9	10	11
C1	165.3	180.1	179.9	180.7	181.2, d J = 3.9	182.5	182.6	180.6	175.2
C2	198.5	192.6	192.4	194.3	194.2, d J = 2.9	192.4	192.4	192.9	193.5
C3	134.5	133.1	133.1	134.2	134.1	133.7 133.5	133.8 133.5	133.8	134.4
C4,4′	128.7	129.2	129.2	129.3	129.2	129.1	129.2	129.3	129.2
C5,5′	127.9	129.5	129.5	128.8	128.8	128.8	128.8	128.8	128.7
C6	134.2	135.6	135.6	135.7	134.6	135.0 134.9	135.0 134.9	134.7	134.4
C7	135.3	145.7	145.8	147.7	147.6	146.1	146.1	145.8	144.5
C8	128.8	128.3	128.5	129.8	129.7	132.6	132.5	128.0	127.4
C9	129.2	124.4	124.2	124.2	124.3	128.6 124.4	128.7 124.5	124.4	122.9
C10	131.3	131.1	131.3	131.6, d J = 4.5	131.7, d J = 5.0	131.8 131.5	131.8 131.6	131.0	130.8
C11	129.2	135.9	138.7	135.7, d J = 8.2	135.6, d J = 8.2	136.9	136.9	131.4	141.4
C12	128.8	155.8	154.4	160.3	161.4	158.1 157.9	158.0 [b]	158.6	172.1
C13	142.3	138.1	137.7	138.9	139.6	139.1	n.o.	137.8	143.8
C14,14′	122.2	125.7	125.6	125.6	125.7	125.6	125.7	125.8	124.6
C15,15′	113.9	113.0	113.2	112.8	112.6	113.1 112.8	113.1 112.9	113.0	113.4
C16	157.0	158.0	158.1	157.8	157.7	159.4	158.0	158.6	158.2
C17	55.1	55.2	55.2	55.1	55.0	55.2 55.0	55.2 55.0	55.2	55.2
C18				24.2, d J = 28.4	25.3, d J = 29.0	150.0 147.6	150.1 147.7	185.8	
C19				26.9	26.9	n.o.	n.o.	100.3	
C20				24.1, d J = 14.1	24.1, d J = 14.4	139.5 138.1	139.5 138.1	188.5	
C21				13.6	13.6	18.1 18.0	18.2 18.0	27.3	
C22								27.7	
Other									95.9 [c]

[a] DMSO-d_6; [b] overlapped signal; [c] Cp. $J(^{13}C/^{31}P)$ in Hz. n.o. = not observed.

(1055 cm^{-1}), which indicates *O*-coordination of DMSO [7]. Complex [PdL(Pn-Bu_3)Cl] (**6**) shows only one (Pd–Cl) band at 309 cm^{-1} indicating that only one isomer has been formed, probably with chloride *trans* to the Pd–C bond, since the ν(Pd–Cl) that has disappeared compared to that of chloro-bridge dimer is the higher frequency one. This should also be true for [PdL(Pn-Bu_3)Br] (**7**), but neither the Pd–Br nor the Pd–P stretching vibrations can be observed. Complex **8** shows two bands at 326 and 286 cm^{-1} attributed to ν(Pd–Cl) indicating two possible isomers (chlorine *trans* to carbon or *trans* to the imine nitrogen). On the basis of higher *trans*-influence of a σ-bonded carbon compared with that of a nitrogen atom, the higher frequency band was attributed to the stretching vibration ν(Pd–Cl) *trans* to the nitrogen atom and the lower frequency one to ν(Pd–Cl) *trans* to the σ-bonded carbon. The IR spectrum of **10** shows two bands at 1517 and 1398 cm^{-1} corresponding to ν(C–O) of the acac group [8].

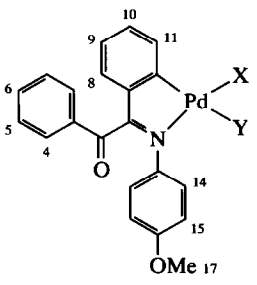
The low solubility of **3** and **4** in $CDCl_3$ made it necessary to record the NMR spectra in DMSO-d_6 [9*].

The ^1H and ^{13}C NMR parameters for **1** and its *ortho*-palladated complexes **3–11** are in Tables 2 and 3, respectively. The spectra were assigned on the basis of chemical shift, spin-spin coupling information, heteronuclear 2D correlation spectroscopy [10] and, for quaternary carbon atoms, by using the heteronuclear NOE effect [11]. The ^1H parameters were confirmed by selective proton decoupling. The small differences observed in the aromatic ring signals joined to the CO group and to imine nitrogen from those of the free benzylideneamine suggest that these rings are not involved in the *ortho*-metallation. The large change for the chemical shift of the protons H8–H11 and the carbons C7–C12 in the phenyl ring joined to the C=N group as well as those of C1 and C2, shows the cyclometallation is induced in this ring.

The aromatic region in the ^1H NMR spectrum of complex **5** is identical to that of complex **4**. The signal at 2.53 ppm suggests bridge-splitting by DMSO has occurred which is confirmed by X-ray diffraction. H11 seems to be affected by halogen, appearing more deshielded ($\sim$0.2 ppm) in bromo-derivatives which have the bromine and nitrogen atoms *trans*. The doubling of some of the signals in the ^1H and ^{13}C NMR spectra of complexes **8** and **9** confirms the existence of *cis* and *trans* isomers (ratio 1:1). The lower frequencies could be due to the isomer with lutidine *trans* to nitrogen. Complex **10** gives two different signals (1.78 and 2.01 ppm in the ^1H NMR spectrum and 18.2 and 18.0 ppm in the ^{13}C NMR spectrum) for the methyl groups of acac, indicating that they are not equivalent. Complex **11** shows a unique signal at 5.75 ppm (^1H NMR) and at 95.9 ppm (^{13}C NMR) for the cyclopentadienyl ring, suggesting that protons and carbons are equivalent and palladium coordination is through cyclopentadienyl π-bonding. Complexes **6** and **7** show a coupling constant $J(^{31}P/^{13}C)$ for carbons C10 and C11 consistent with the phosphorus and nitrogen atoms being *trans* [12].

Tables 4 and 5 show $\Delta\delta = \delta_{complex} - \delta_{ligand}$ for the complexes **3–11**. In the *N*-phenyl ring, a significant change of shift of the H15, H15′ protons is not observed; however the H14, 14′ protons show a significant deshielding. This may be attributed to Pd $\cdots$ N coordination, which would preclude delocalization of the lone pair at N on the aromatic ring π-system, causing a large charge-density decrease at the *ortho* position. This effect has been observed at C14, 14′. The down-field shielding of the carbon atom C12 joined directly to the palladium atom could be due to the Pd–C back-bonding, since an increase in M–C bond order increases the deshielding term, σ^{para}, in Pople's equation [13]. The proton *ortho* to the Pd–C bond, H11, is strongly deshielded after cyclopalladation except in the complexes **6** and **7** where this effect would be compensated for by phosphine. This can be explained the by proximity to the metallated sites of the

TABLE 4. ^1H-NMR ($\Delta\delta = \delta_{complex} - \delta_{ligand}$)



	X	Y
6	P(n-Bu)$_3$	Cl
7	P(n-Bu)$_3$	Br
8	Lut + Cl / Cl + Lut	
9	Lut + Br / Br + Lut	
10	acac	
11	Cp	

	H8	H9	H10	H11	H14,14′	H15,15′
3	−0.90	−0.47	−0.39	+0.41	+0.19	−0.03
4	−0.89	−0.48	−0.43	+0.59	+0.23	+0.01
5	−0.88	−0.48	−0.43	+0.57	+0.23	+0.01
6	−0.71	−0.27	−0.23	+0.01	+0.14	−0.02
7	−0.72	−0.28	−0.20	+0.05	+0.11	−0.02
8	−1.54	−0.31	−0.27 −0.42	+0.85	+0.27	−0.02
9	−1.62	−0.33	−0.23 −0.44	+1.13	+0.25	−0.02
10	−0.75	−0.31	−0.17	+0.38	+0.28	0
11	−0.83	−0.39	−0.19	+0.48	+0.24	−0.04

* Reference number with asterisk indicates a note in the list of references.

electron delocalization in the chelate ring [14] or by the increase of C-substitution [15]. However, we observed different deshielding values of H11 and C11 depending on the ligand linked to the palladium atom. Thus $\Delta\delta$ H11 ranges from +0.01 in complex **6** to +1.13 in complex **9**, and $\Delta\delta$ C11 ranges between +2.2 in acac derivative and +12.2 in Cp monomer, which could be a consequence of the steric effect of the ligands.

Although the H8 and H10 protons, *meta* to palladium, should be less affected by cyclometallation, the great shielding observed for H8 could be due to anisotropic effects of the benzoyl group, whose arrangement in the complexes must be different to that when the benzylideneamine is uncoordinated. The upfield shift observed for H9 and C9, *para* to palladium and unaffected by steric interactions, clearly indicates some metal–ligand back-bonding [16]. The high deshielding effect observed for C1 and C7 must be attributed to cyclometallation. The coordination nitrogen to palladium, which decreases the electronic density at the nitrogen, could explain the higher effect observed at C1. The negative value of $\Delta\delta$-C13 observed in all compounds (except complex **11**) is quite surprising and can only be understood by assuming that only the steric effects are operative. Similarly, C2 carbon is shielded by *ca.* 5 or 6 ppm.

The slow crystallization (*ca.* 3 months) of compound **4** from DMSO solution affords complex **5**. The molecular structure of **5** has been determined by X-ray diffraction. The crystal consists of discrete molecules separated by van der Waals distances. The palladium atom is bonded to four atoms: the nitrogen, the *ortho*-carbon atom of the phenyl ring supporting the imine carbon, the bromine and the oxygen atom of dimethylsulphoxide, in a distorted square-planar coordination approaching tetrahedral geometry. The dihedral angle between planes C3–Pd–N and Br–Pd–O1 is 5.8(1)°. The five-membered chelate ring has an envelope form, with the Pd atom out of the mean plane passing through the other four atoms by +0.2236 Å.

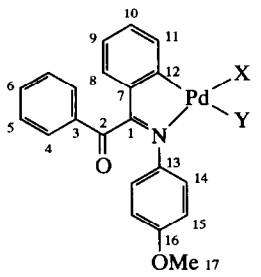
Final positional and thermal parameters for all non-hydrogen atoms are listed in Table 6, bond distances and angles are summarized in Table 7 and an ORTEP drawing with the scheme used for labeling atoms is shown in Fig. 1.

The Pd–C3 [1.967(5) Å], Pd–N [2.033(4) Å] and Pd–Br [2.420(1) Å] bond lengths are similar to those found for other cyclometallated complexes [4,5,17]. Figure 1 shows that DMSO is *O*-bonded. There are three reported X-ray structures of DMSO *O*-bonded to Pd [18–20], and only one structure of a cyclometallated complex [5]. Sulfoxides should *S*-bond to palladium(II)

TABLE 6. Positional parameters and equivalent thermal parameters for the non-hydrogen atoms and their estimated standard deviations for 5

	x	*y*	*z*	U_{eq}
Pd	0.31745(2)	0.21821(4)	0.31211(5)	353(1)
Br	0.41267(4)	0.09615(7)	0.24156(9)	594(3)
S	0.42109(9)	0.28067(17)	0.67957(22)	614(6)
O1	0.40280(20)	0.35356(38)	0.48165(50)	490(13)
O14	0.31067(27)	0.74146(44)	0.83320(58)	724(18)
O17	0.12704(23)	0.49842(47)	0.07832(56)	685(17)
N	0.23673(21)	0.32835(40)	0.34084(52)	363(13)
C1	0.17595(25)	0.29983(51)	0.22941(61)	372(15)
C2	0.17134(27)	0.17967(52)	0.12262(61)	393(16)
C3	0.23415(28)	0.11437(53)	0.15285(64)	412(16)
C4	0.23078(33)	−0.00957(60)	0.06865(77)	533(20)
C5	0.16693(37)	−0.06386(67)	−0.04582(86)	620(23)
C6	0.10728(34)	0.00534(70)	−0.08107(79)	613(23)
C7	0.10863(29)	0.12699(62)	0.00393(71)	496(19)
C8	0.24880(26)	0.44000(51)	0.45884(65)	378(16)
C9	0.24394(31)	0.39296(54)	0.65498(70)	476(18)
C10	0.26332(34)	0.49760(59)	0.77410(73)	548(21)
C11	0.28951(31)	0.64957(58)	0.70056(78)	514(20)
C12	0.29253(33)	0.69585(56)	0.50627(80)	532(20)
C13	0.27214(31)	0.59168(54)	0.38514(72)	480(19)
C15	0.35318(48)	0.89087(76)	0.76805(111)	954(34)
C16	0.11633(28)	0.38910(57)	0.20224(69)	444(18)
C18	0.04655(26)	0.33899(53)	0.32096(66)	402(16)
C19	−0.01194(31)	0.41145(64)	0.27696(76)	526(20)
C20	−0.07858(34)	0.36632(77)	0.38042(89)	649(25)
C21	−0.08612(34)	0.24641(81)	0.52952(92)	692(26)
C22	−0.02881(35)	0.17631(71)	0.57316(86)	652(24)
C23	0.03867(30)	0.21919(60)	0.47016(75)	512(19)
C24	0.51226(48)	0.24926(88)	0.67105(115)	947(37)
C25	0.44991(43)	0.42892(85)	0.81243(98)	822(31)

TABLE 5. ^{13}C-NMR ($\Delta\delta = \delta_{complex} - \delta_{ligand}$)



	X	Y
6	$P(n\text{-}Bu)_3$	Cl
7	$P(n\text{-}Bu)_3$	Br
8	Lut + Cl / Cl + Lut	
9	Lut + Br / Br + Lut	
10	acac	
11	Cp	

	C1	C2	C7	C8	C9	C10	C11	C12	C13
3	+15.4	−5.2	+11.1	+0.6	−4.8	−0.5	+6.7	+28.4	−3.6
4	+15.2	−5.4	+11.2	−0.4	−5.0	−0.3	+9.5	+27.0	−4.0
6	+15.4	−4.2	+12.4	+1.0	−5.0	+0.3	+6.5	+31.5	−3.4
7	+15.9	−4.3	+12.3	+0.9	−4.9	+0.4	+6.4	+32.6	−2.7
8	+17.2	−6.1	+10.8	+3.8	−0.6	+0.5	+7.7	+29.3	−3.2
					−4.8	+0.2		+29.1	
9	+17.3	−6.1	+10.8	+3.7	−0.5	+0.5	+7.7	+29.2	
					−4.7	+0.3			
10	+15.3	−5.6	+10.5	−0.8	−4.8	−0.3	+2.2	+29.8	−4.5
11	+9.9	−5.0	+9.2	−1.4	−6.3	−0.5	+12.2	+43.3	+1.5

TABLE 7. Selected bond distances (Å) and Angles (deg.) for **5**

Distances	
Pd–Br	2.420(1)
Pd–O1	2.165(3)
Pd–N	2.033(4)
Pd–C3	1.967(5)
N–C1	1.302(5)
C1–C2	1.455(7)
C1–C16	1.507(8)
C2–C3	1.407(8)
C2–C7	1.397(7)
C3–C4	1.390(8)
C4–C5	1.397(8)
C5–C6	1.379(10)
C6–C7	1.383(9)
S–O1	1.512(4)
S–C24	1.745(9)
S–C25	1.770(8)
O17–C16	1.209(6)
C16–C18	1.484(7)
Angles	
N–Pd–C3	81.2(2)
O1–Pd–N	92.7(1)
Br–Pd–C3	95.6(1)
Br–Pd–O1	90.3(1)
Pd–O1–S	117.6(2)
Pd–N–C1	114.8(3)
N–C1–C2	115.2(4)
C1–C2–C3	114.9(4)
Pd–C3–C2	113.0(3)

unless there are steric reasons to prevent this [21], in which case *O*-bonding would be observed [22]. Therefore, when back-bonding to sulfur is not possible, *O*-bonding might be expected. In complex **5** Pd atom is involved in a strong back-bonding to the aromatic ring favouring *O*-coordination.

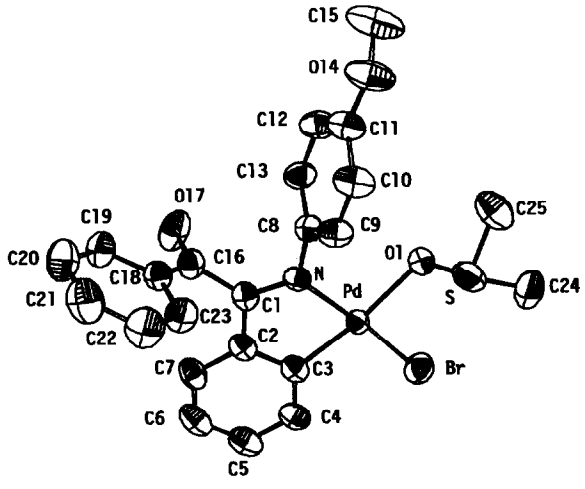


Fig. 1. The molecular structure of **5** showing the atom numbering scheme. H-atoms have been omitted for clarity.

The Pd–O1 bond distance of 2.165(3) Å is longer than that observed in other reported complexes [19,20] but similar to that found for the other cyclometallated complex [5]. The weakening of the Pd–O bond must be a consequence of the *trans*-effect of the Pd–C bond.

3. Experimental section

Infrared spectra were recorded on both Perkin Elmer 283 (4000–600 cm^{-1}) and Perkin Elmer 580-B (600–200 cm^{-1}) spectrophotometers. The samples were ground with KBr at a concentration of *ca.* 2% by weight and then pressed into pellets. For the region 600–200 cm^{-1}, the samples were prepared as Nujol on CsI windows. NMR spectra were recorded with $CDCl_3$ and DMSO-d_6 solutions by using a Bruker WP-200-SY. Elemental analysis was performed on a Perkin Elmer 240B analyzer. All the complexes gave satisfactory elemental analyses.

All solvents were purified prior to use by standard methods [23]. Palladium(II) chloride was purchased from Johnson-Matthey. The reagents were used without further purification. The benzylideneamine was synthesized by published methods [24].

3.1. Synthesis of [{PdL(μ-Cl)}$_2$] (3)

Method 1. To a solution of the acetate-bridged dimer **2** (0.240 g, 0.25 mmol) in acetone was added a 10^{-2} M solution of NaCl (0.032 g, 0.55 mmol). The solid obtained after stirring for 24 h was filtered, washed with water and acetone and dried *in vacuo* (yield 95%). Method 2. To a solution of 4-$OMeC_6H_4$-N=C(COC_6H_5)C_6H_5 (0.173 g, 0.55 mmol) in MeOH was added a solution of $K_2[PdCl_4]$ (0.163 g, 0.50 mmol) in water. After stirring for 4 days at 25°C, the solid obtained, was filtered, washed with water and MeOH and dried *in vacuo*, (26%). Anal. Calcd.: C, 55.33, H, 3.57, N, 3.02. Found: C, 55.28, H, 3.51, N, 3.07%. Melting point: 282–283°C (with decomposition); IR: ν_{max} 1673, 1606, 441, 596, 312, 308 cm^{-1}.

3.2. Synthesis of [{PdL(μ-Br)}$_2$] (4)

To a solution of the acetate-bridged dimer **2** (0.240 g, 0.25 mmol) in chloroform was added LiBr (0.048 g, 0.55 mmol). The solid obtained after stirring for 24 h was filtered, washed with water and chloroform and dried *in vacuo* (yield 97%). Anal. Calcd.: C, 50.37, H, 3.20, N, 2.80. Found: C, 50.38, H, 3.16, N, 2.77%. Melting point 277–278°C (with decomposition); IR: ν_{max} 1673, 1605, 444, 593 cm^{-1}.

3.3. Synthesis of [PdL(P(n-Bu)$_3$)Cl] (6)

Method 1. To a solution of **2** (0.240 g, 0.25 mmol) in acetone was added tri(n-butyl)phosphine (0.111 g, 0.55

mmol) and NaCl (0.032, 0.55 mmol) in water, 10^{-2} mol l^{-1}, after stirring for 24 h at 25°C, was concentrated under reduced pressure. Addition of acetone/water (1/3) gave a yellow solid, which was filtered, washed with acetone/water and dried *in vacuo* (yield 82%). Method 2. Tri(n-butyl)phosphine (0.111 g, 0.55 mmol) was added to acetone suspension of **3** (0.228 g, 0.25 mmol). A clear solution was formed after 10 min, which was concentrated after stirring for 24 h at 25°C. Addition of acetone/water (1/3) gave a yellow solid, which was filtered, washed with acetone/water and dried *in vacuo* (yield 85%). Anal. Calcd.: C, 55.06, H, 4.64, N, 2.55. Found: C, 55.16, H, 4.60, N, 2.57%. Melting point: 139–142°C; IR: ν_{max} 1674, 1606, 448, 589, 309 cm^{-1}.

3.4. Synthesis of [PdL(P(n-Bu)$_3$)Br] (7)

Method 1. To a solution of **2** (0.240 g, 0.25 mmol) was added tri(n-butyl)phosphine (0.111 g, 0.55 mmol) and LiBr (0.048 g, 0.55 mmol), to give immediately a yellow solution, which was stirred for 24 h at 25°C. Addition of acetone/water (1/3) gave a yellow solid, which was filtered, washed with acetone/water and dried *in vacuo* (yield: 87%). Method 2. Tri(n-butyl)phosphine (0.111 g, 0.55 mmol) was added to an acetone suspension of **4** (0.252 g, 0.25 mmol). A clear solution was formed immediately which was concentrated after stirring for 24 h at 25°C. Addition of acetone/water (1/3) gave a yellow solid, which was filtered off, washed with acetone/water and dried *in vacuo* (yield 85%). Anal. Calcd.: C, 50.97, H, 4.19, N, 2.43. Found: C, 51.00, H, 4.25, N, 2.38%. Melting point: 135–138°C; IR: ν_{max} 1672, 1600, 444, 591 cm^{-1}.

3.5. Synthesis of [PdL(Lut)Cl] (8)

Method 1. To a solution of **2** (0.240 g, 0.25 mmol) in acetone was added 3,5-lutidine (0.059 g, 0.55 mmol) and NaCl (0.032 g, 0.55 mmol) in water 10^{-2} mol l^{-1}. After stirring for 24 h at 25°C, it was concentrated under reduced pressure. Addition of diethyl ether gave a yellow solid, which was filtered, washed with diethyl ether and dried *in vacuo* (yield 89%). Method 2. 3,5-Lutidine (0.059 g, 0.55 mmol) was added to an acetone suspension of **3** (0.224 g, 0.25 mmol). A clear solution formed after 30 min, which was concentrated after stirring for 24 h at 25°C. When diethyl ether was added, the product immediately precipitated as a yellow solid, which was filtered, washed with diethyl ether and dried *in vacuo*. The solid was then recrystallized in dichloromethane/diethyl ether (yield 76%). Anal. Calcd.: C, 59.86, H, 4.56, N, 5.03. Found: C, 59.70, H, 4.44, N, 4.97%. IR: ν_{max} 1669, 1602, 453, 598, 326, 286 cm^{-1}.

3.6. Synthesis of [PdL(Lut)Br] (9)

Method 1. To a solution of **2** (0.240 g, 0.25 mmol) in acetone was added 3,5-lutidine (0.059 g, 0.55 mmol) and LiBr (0.048 g, 0.55 mmol), which was concentrated after stirring for 24 h at 25°C. When diethyl ether was added, the product precipitated as a yellow solid, which was filtered, washed with diethyl ether and dried *in vacuo*. The solid was then recrystallized from dichloromethane/diethyl ether (yield 94%). Method 2. 3,5-Lutidine (0.059 g, 0.55 mmol) was added to an acetone suspension of **4** (0.252 g, 0.25 mmol). A clear solution formed immediately, which was concentrated under reduced pressure after stirring for 24 h at 25°C. When diethyl ether was added, a yellow solid precipitated, which was filtered, washed with diethyl ether and dried *in vacuo*. The solid was then recrystallized in dichloromethane/diethyl ether (yield 84%). Anal. Calcd.: C, 55.29, H, 4.13, N, 4.67. Found: C, 55.32, H, 4.12, N, 4.61%; IR: ν_{max} 1672, 1603, 448, 596 cm^{-1}.

3.7. Synthesis of [PdLacac] (10)

Method 1. To a solution of **2** (0.240 g, 0.25 mmol) in acetone was added a solution of NaOMe (0.030 g, 0.55 mmol) and acetylacetone (0.055 g, 0.55 mmol) in MeOH, which was concentrated after stirring for 24 h at 25°C. The solid was filtered, washed with methanol and dried *in vacuo*. The solid was then recrystallized from dichloromethane/petroleum ether (yield: 81%). Method 2. As method 1 using complex **3** (0.228 g, 0.25 mmol) as starting material, (yield: 79%). Method 3. As method 1 using complex **4** (0.252 g, 0.25 mmol), as starting material, (yield: 81%). Anal. Calcd.: C, 60.09, H, 4.32, N, 2.74. Found: C, 59.92, H, 4.42, N, 2.69%. Melting point: 140–143°C; IR: ν_{max} 1672, 1602, 444, 599, 1517, 1398 cm^{-1}.

3.8. Synthesis of [PdLCp] (11)

Method 1. To a solution of NaCp (0.048 g, 0.55 mmol) (0.5 M in THF) was added the acetate-bridged **2** (0.240 g, 0.25 mmol) in THF. The orange solution formed was stirring for 24 h at 25°C. The solvent was removed *in vacuo*. The complex was extracted with dichloromethane and the extract concentrated under reduced pressure. When hexane was added the product precipitated as a yellow solid, which was filtered, washed with hexane and dried *in vacuo*. The solid was then recrystallized from dichloromethane/hexane (yield: 76%). Method 2. As method 1 using complex **3** (0.228 g, 0.25 mmol) as starting material, (yield: 68%). Method 3. As method 1 using complex **4** (0.252 g, 0.25 mmol) as starting material, (yield 71%). Anal. Calcd.: C, 64.32, H, 4.35, N, 2.90. Found: C, 64.28, H, 4.33, N, 2.88%. Melting point: 149–151°C; IR: ν_{max} 1672, 1601, 443, 595 cm^{-1}.

TABLE 8. Crystal and refinement data for **5**

Formula	$C_{23}H_{22}BrNO_3PdS$
Symmetry	Triclinic, $P\bar{1}$
Unit cell dimensions:	
a	17.936(2) Å
b	9.380(1) Å
c	7.161(4) Å
α	79.48(3)°
β	94.07(2)°
γ	105.50(1)°
Packing:	
V (Å^3), Z	1141.1(7), 2
D_0 (g cm^{-3}), M, $F(0,0,0)$	1.68, 578.3, 576
μ (cm^{-1})	26.5
Technique	Enraf-Nonius CAD4 diffractometer Graphite oriented monochromator Mo Kα (λ = 0.71069 Å) Scan, $\Omega/2\theta$
Number of reflections:	
Measured	4947
Observed (I) $\geq 2\sigma(I)$	3634
Range of hkl	−22 22, −12 12, 0 9
Value of R_{int} (%)	0.8
Standard reflections	3/105 rflns, no variation
Solution	Patterson
Refinement	Least-squares on F_0
H atoms	Geometric calculations
Final R and R_W	0.035, 0.037
Average shift/error	0.11

3.9. Structure determination and refinement of [PdL(DMSO)Br] (5)

The slow crystallization (*ca.* 3 months) of compound **4** from DMSO solution produced yellow crystals. Due to the sensitivity of the crystal to air, the crystal used for data collection was epoxy-coated and mounted in a kappa diffractometer. A summary of the crystal data is given in Table 8. The cell dimensions were refined by least-squares fitting the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Pd, Br and S were taken from the International Tables for X-Ray Crystallography [25]. The structure was solved by Patterson and Fourier methods. An empirical absorption correction [26] was applied at the end of the isotropic refinement. No trend in F *versus* F or $\sin\theta/\lambda$ was observed.

Final mixed refinement was with unit weights and fixed isotropic factors and coordinates for H atoms. The final synthesis showed no significantly electron density.

Most of the calculations were carried out with the X-Ray 80 system [27] and with PARST [28], on a VAX 11/750 computer.

Acknowledgement

We thank the CICYT (Grant FAR 516/90) for financial support.

Supplementary Material Available

Listings of anisotropic thermal parameters for non-hydrogen atoms, positional and isotropic thermal parameters for hydrogen atoms, and all bond distances and angles for **5** are available from the Cambridge Crystallographic Data Centre.

References and notes

1 (a) I. Omae, *J. Organomet. Chem., 18* (1986) 35; (b) J. Albert, J. Granell and J. Sales, *J. Synth. React. Inorg. Met. Org. Chem., 19* (1989) 1009.
2 I. Omae, *Chem. Rev., 79* (1979) 287.
3 (a) P.W. Clark and S.F. Dyke, *J. Organomet. Chem., 276* (1984) 421; (b) K. Hiraki, Y. Fuchita and K. Takechi, *Inorg. Chem., 20* (1981) 4316; (c) G.B. Caygill and P.J. Steel, *J. Organomet. Chem., 327* (1987) 101.
4 J.L. García-Ruano, I. López-Solera, J.R. Masaguer, C. Navarro-Ranninger, J. Rodríguez and S. Martínez-Carrera, *Organometallics, 11* (1992) 3013.
5 Navarro-Ranninger, I. López-Solera, A. Alvarez-Valdés, J. Rodríguez, J.R. Masaguer, J.L. Garía-Ruano and X. Solans, *Organometallics, 12* (1993) 4104.
6 This complex has also been synthesized by an alternative route. C. Navarro-Ranninger, A. Alvarez-Valdés, M.J. Camazón, J. Román and R. Lozano, *J. Organomet. Chem., 331* (1987) 107.
7 (a) W. Kitchin, C.J. Moore and D. Doddrell, *Inorg. Chem., 9* (1970) 541; (b) B.B. Wayland and R.F. Schramm, *Inorg. Chem., 8* (1969) 971.
8 K. Nakamoto, *IR and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., Wiley Interscience, New York, 1986.
9 The ^{1}H NMR spectra of **3** and **4**, obtained in $CDCl_3$ and CD_3CN show a low signal/noise ratio due to their insolubility. Nevertheless, the data obtained are similar to those observed in DMSO-d_6, which suggests that the chloro- and bromo-bridge-splitting reaction by DMSO must be slow. Furthermore complexes **3** and **4** remain unaltered upon treatment with DMSO at reflux (12 h).
10 A. Bax and G.A. Morris, *J. Magn. Reson., 42* (1981) 501.
11 F. Sánchez-Farrando, *Mag. Resonance Chem., 23* (1985) 185.
12 P.S. Pregosin, F. Wombacher, A. Albinati and F. Lianza, *J. Organomet. Chem., 418* (1991) 249.
13 B. Crociani, F. Di Bianca and A. Giovenco, *J. Organomet. Chem., 251* (1983) 393.
14 S. Chakladar, P. Paul, K. Venkatsubramanian and K. Nag, *J. Chem. Soc., Dalton Trans.*, (1991) 2669.
15 G.R. Newkome, K.J. Theriot, F.R. Fronczek and B. Villar, *Organometallics, 8* (1989) 2513.
16 M.A. Gutiérrez and G.R. Newkome, *J. Organomet. Chem., 202* (1980) 341.
17 (a) M.R. Churchill, H.J. Wasserman and G.J. Young, *Inorg. Chem., 19* (1980) 762; (b) V.W. Hiller, A. Castiñeiras, J.M. Vila, A. Suárez, M.T. Pereira and M. Gayoso, *Acta Cryst., C42* (1986) 1136; (c) J. Granell, D. Sainz, J. Sales, X. Solans and M. Font-Altaba, *J. Chem. Soc., Dalton Trans.*, (1986) 1785; (d) J. Albert, M.

Gómez, J. Granell and J. Sales, X. Solans, *Organometallics, 9* (1990) 1405.
18 D.P. Bancroft, F.A. Cotton and M. Verbruggen, *Acta Cryst., C45* (1989) 1289.
19 G. Anniibale, L. Cattalini, V. Bertolasi, V. Ferretti, G. Gilli and M.L. Tobe, *J. Chem. Soc., Dalton Trans.*, (1989) 1265.
20 B.F.G. Johnson, J. Puga and P.R. Raithby, *Acta Cryst., B37* (1981) 953.
21 F.R. Hartley, *The Chemistry of Platinum and Palladium*, Applied Science, London, 1973 and references therein.
22 R. Romeo and M.L. Tobe, *Inorg. Chem., 13* (1974) 1991.
23 D.D. Perrin, W.L.F. Armarego and D.R. Perrin, *Purification of Laboratory Chemicals*, 2nd Ed, Pergamon Press, Oxford, 1980.
24 B. Alcaide, M.A. León-Santiago, R. Pérez-Ossorio, J. Plumet, M.A. Sierra and M. De la Torre, *Synthesis*, (1982) 989.
25 *International Tables of X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1972.
26 N. Walker and D. Stuart, *Acta Cryst., A39* (1983) 158.
27 M. Stewarts, G.S. Kruger, H.L. Amomon, C. Dichirson and S.R. Hall, Techn. Report TR, 446, University of Maryland, 1976.
28 M. Nardelli, *Comput. Chem., 7* (1983) 96.