The Behaviour of *trans*-Dihalogenobis(hydrazone)palladium(II) Complexes: Rotational Isomerism or Non-equivalence of the Two Ligands Within the Same Molecule?

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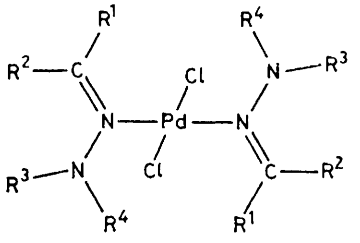
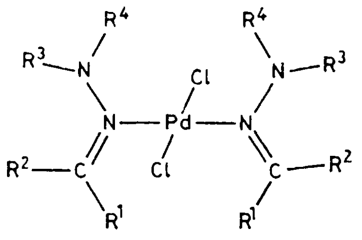
A detailed ^{1}H n.m.r. analysis of a series of *trans*-dihalogenobis(hydrazone)palladium(II) complexes has been made in order to demonstrate unequivocally the presence of two rotational isomers differing in the mutual orientation of the co-ordinated ligands.

HYDRAZONES and their co-ordination compounds with metals have received much attention in recent years with respect to: (*i*) bonding in the hydrazone molecule;[1,2] (*ii*) geometrical and conformational isomerism in co-ordinated hydrazones;[3-6] and (*iii*) metal–alkyl interaction and metallation reactions.[7-9]

The *trans*-[PdCl$_2$(R^{1}R^{2}C=NNR^{3}R^4)$_2$] complexes have ^{1}H n.m.r. spectra showing two sets of signals that coalesce on increasing the temperature; this feature was ascribed by us to the presence of two isomeric forms, (A) and (B) differing in the mutual orientation of the organic ligands.[10,11] Meanwhile, other workers have studied some of these complexes and assigned the two sets of resonances to a single molecular species in which the two hydrazones, chemically equivalent, compete with each other for metal–alkyl interaction.[12,13]



(A)



(B)

In this paper we report the results of some more experiments which have been performed with the aim of clarifying this controversial point.

EXPERIMENTAL

Preparations.—Ligands. All linear hydrazones were prepared by the same procedure, treating the carbonyl compound (R^{1}R^{2}C=O) with the appropriate hydrazine (H$_2$NNR^{3}R^4).[14]

The cyclic hydrazone $\overline{\mathrm{CH_2CH_2CH_2CMe{=}N{-}N}}\mathrm{Me}$ was prepared by dropwise addition, with stirring, of a solution of *N*-methylhydrazine (3.8 g) in diethyl ether (30 cm^3) to a solution of 3-chloropropyl methyl ketone (5.0 g) in the same solvent (30 cm^3) containing a small amount of acetic acid (0.5 cm^3). After refluxing for 2 h over molecular sieves the reaction mixture was treated with Na$_2$[CO$_3$] and distilled under reduced pressure, b.p. 48 °C (15 mmHg),† yield *ca.* 70%.

The purity of the ligands was checked by g.l.c., t.l.c., elemental analyses, and ^{1}H n.m.r. spectra.

Complexes. The chloro-complexes *trans*-[PdCl$_2$(hydrazone)$_2$] were prepared, as previously described, by treating stoicheiometric amounts of *trans*-[PdCl$_2$(NCPh)$_2$] with the appropriate ligand (ratio 1 : 2). The crude product was crystallized from chloroform–n-pentane.[11] The bromo-complex *trans*-[PdBr$_2$(Me$_2$C=NNMePh)$_2$] was prepared in an analogous manner using *trans*-[PdBr$_2$(NCPh)$_2$] as starting material.

The mixed hydrazone complex *trans*-[PdCl$_2$(Me$_2$C=NNMePh)(Me$_2$C=NNMe$_2$)] was prepared in dichloromethane from *trans*-[PdCl$_2$(NCPh)$_2$], Me$_2$C=NNMePh, and Me$_2$C=NNMe$_2$ in the ratio 1 : 1 : 1. After 1 d at room temperature the solution was taken to dryness and the oily residue, treated with n-pentane, was stirred for several hours. The resulting yellow solid, separated by filtration of the n-pentane solution, was analyzed by h.p.l.c.[15] and shown to be a mixture of *trans*-[PdCl$_2$(Me$_2$C=NNMePh)$_2$], *trans*-[PdCl$_2$(Me$_2$C=NNMe$_2$)$_2$], and *trans*-[PdCl$_2$(Me$_2$C=NNMePh)(Me$_2$C=NNMe$_2$)] in the ratio *ca.* 1 : 1 : 2. A small quantity of the mixed hydrazone complex (for elemental analysis, and i.r. and n.m.r. spectra) was separated by h.p.l.c. using the following conditions: column, LiChrosorb DIOL 10 μm, 50 × 0.42 cm internal diameter; mobile phase, n-hexane–dichloromethane (85 : 15 v/v); flow rate, 2.0 cm^3 min^{-1} at room temperature; refractive-index detector.

Analytical data, melting points (uncorrected), and molecular weights (measured by osmometry) of the complexes not previously described by us are summarized in Table 1.

Apparatus.—Separations by liquid chromatography were performed on a Waters model ALC/GPC-202 chromatograph (Waters Associates, Mildford, Massachusetts, U.S.A.)

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† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

TABLE 1

Analytical (%) and i.r. data (cm^{-1}) *

Complex	M.p. (θ_c/°C)	M	Analysis C	H	N	X	ν(C=N), ν(C=C)	δ(C–H)	ν(Pd–X)
trans-[PdBr$_2$(Me$_2$C=NNMePh)$_2$]	170	549	39.8	4.50	9.70	28.0	1 615m,	775s,	260s
		(590.6)	(40.65)	(4.80)	(9.50)	(27.05)	1 590s	710s	
trans-[PdCl$_2$(Pr^{i}MeC=NNMePh)$_2$]	160	541	51.2	6.90	10.4	13.0	1 595s,	765s,	340s
	(decomp.)	(557.8)	(51.65)	(6.50)	(10.05)	(12.7)	1 575m	700s	
trans-[PdCl$_2$(CH$_2$CH$_2$CH$_2$CMe=NNMe)$_2$]	160	398	36.0	6.10	14.0	18.0	1 610m		365s
	(decomp.)	(401.6)	(35.9)	(6.00)	(13.95)	(17.65)			
trans-[PdCl$_2$(Me$_2$C=NNMePh)(Me$_2$C=NNMe$_2$)]	90		41.3	6.10	12.9	16.5	1 620s,	760s,	350s
			(41.0)	(5.95)	(12.75)	(16.1)	1 590s	695s	

* Calculated values are given in parentheses. s = Strong, m = medium.

TABLE 2

Proton chemical shifts [a] (δ downfield from SiMe$_4$) of *trans*-[PdX$_2$(R^{1}R^{2}C=NNR^{3}R^4)$_2$] (X = Cl or Br) complexes. Under conditions of slow exchange, two resonances (upper and lower line) were observed for each type of equivalent protons and were assigned respectively to the *anti*-(A) and *syn*-(B) isomers. The chemical-shift difference (Δ) between the resonances of complexed and free hydrazone is given in parentheses. The isomer ratio [A] : [B] is also given

Complex		θ_c/°C	R^1 β(CH)	R^1 α(CH)	R^2 γ(CH)	R^2 β(CH)	R^2 α(CH)	R^3 CH$_3$	R^4 CH$_3$	R^4 C$_6$H$_5$	Ratio [A] : [B]
(1) *trans*-[PdCl$_2$(Me$_2$C=NNMePh)$_2$]		0		2.67			2.10	3.49			1
				(0.55)			(0.13)	(0.50)		6.8—	
				3.11			2.13	3.18		7.5	
				(0.99)			(0.16)	(0.19)			
(2) *trans*-[PdCl$_2$(Pr^{i}MeC=NNMePh)$_2$]	*a*	−10	1.13	4.69			1.95	3.48			2.7
			(−0.07)	(1.97)			(0.05)	(0.50)		6.8—	
			1.39	5.29			1.94	3.37		7.5	
			(0.19)	(2.57)			(0.04)	(0.39)			
	b		0.99	4.93				3.32			
			(−0.03)	(2.55)			1.44	(0.60)			
			1.19	5.50			(−0.11) [c]	3.27			
			(0.17)	(3.12)				(0.55)			
(3) *trans*-[PdBr$_2$(Me$_2$C=NNMePh)$_2$]		0		2.72			2.10	3.57			0.6
				(0.60)			(0.13)	(0.58)		6.8—	
				3.04			2.16	3.18		7.5	
				(0.92)			(0.19)	(0.19)			
(4) *trans*-[PdCl$_2$(CH$_2$CH$_2$CH$_2$CMe=NNMe)$_2$]		+34		2.99				3.79			1
				(1.14) [d]	2.88	1.90	2.36	(1.02) [d]			
				3.01	(0.22)	(−0.1)	(0.36)	3.77			
				(1.16) [d]				(1.00) [d]			
(5) *trans*-[PdCl$_2$(Me$_2$C=NNMe$_2$)$_2$]		+34		3.01			2.21	2.95	2.95		*e*
				(1.04)			(0.28)	(0.52)	(0.52)		
				3.12			2.23	2.90	2.90		
				(1.15)			(0.30)	(0.47)	(0.47)		
(6) *trans*-[PdCl$_2$(Me$_2$C=NNMePh)(Me$_2$C=NNMe$_2$)]	L^1	0		3.14			2.12	3.45			0.7
				(1.02)			(0.15)	(0.46)		6.9—	
				3.07			2.16	3.41		7.5	
				(0.95)			(0.19)	(0.42)			
	L^2			2.45			2.24	2.83	2.83		
				(0.47)			(0.29)	(0.38)	(0.38)		
				2.98			2.25	2.45	2.45		
				(1.00)			(0.30)	(0.00)	(0.00)		

[a] All spectra were recorded in CDCl$_3$ solution unless otherwise stated. [b] Spectrum recorded in C$_7$D$_8$ solution. [c] The separation between the resonances arising from the two isomers is *ca.* 0.005 p.p.m. [d] The assignment of the resonances to each set is tentative. [e] The two sets have intensity ratio *ca.* 1.5 : 1 but we cannot be certain of the attribution of each set to the parent isomer.

equipped with U6-K universal injector, model M6000 solvent-delivery system, 254-nm differential u.v. detector, and model 401 refractive-index detector.

Infrared spectra in the range 250—4 000 cm^{-1} were recorded as KBr or Polythene pellets on a Perkin-Elmer 457 spectrophotometer. Hydrogen-1 n.m.r. spectra were obtained with a Varian EM 390 spectrometer. Spectra of [PdCl$_2$(Pr^{i}MeC=NNMePh)$_2$] were also run on a Bruker HX 270 instrument. They are summarized in Table 2.

RESULTS AND DISCUSSION

In a previous paper we explained the presence of two sets of ^{1}H n.m.r. resonances observed in a whole series of *trans*-[PdCl$_2$(R^{1}R^{2}C=NNR^{3}R^4)$_2$] complexes as due to the existence of two geometric isomers, (A) and (B), differing in the mutual orientation of the two hydrazone molecules with respect to the co-ordination plane. The complex *trans*-[PdCl$_2$(Me$_2$C=NNMePh)$_2$] (1) was also investigated by Postel *et al.*[12] Their n.m.r. data agree with ours, but they gave a different explanation for the appearance of the two sets of resonances. Being of equal intensity, the two sets of signals were assigned to a single molecular species [it could be either (A) or (B)] in which there was competition, for metal–alkyl interaction, between the two chemically equivalent hydrazones. Thus, since at any time only one hydrazone could strongly interact with the metal, the two ligands formed different angles with the co-ordination plane, being therefore inequivalent. The same workers also investigated the complex *trans*-$[PdCl_2(Pr^iMeC{=}NNMePh)_2]$ (2) for which they observed three sets of signals, two of them having equal intensity being assigned to an isomer behaving as complex (1), the third set being assigned to a second isomer having magnetically equivalent hydrazones.

However, the correctness of our previous interpretation is also supported by the new results reported here. As far as complex (1) is concerned, unambiguous evidence in favour of the existence in solution of two geometric isomers, and not of a single molecular species with inequivalent ligands, comes from the study of the bromo-analogue, complex (3). The spectra of (1) and (3) in Figure 1 indicate that the same sets of signals are present in both complexes; however, in the bromo-complex the intensity ratio is not 1 : 1, as demanded by the suggestion of Postel *et al.*, but 0.6 : 1 which can only be accounted for by assuming the existence of geometric isomers. Moreover, the different intensities of the resonances belonging to each set make the n.m.r. assignment of complex (3) unequivocal. The same assignment must apply, by analogy, also to complex (1); this is in accord with our previous assignment [10,11] and contradicts that of Postel *et al.*[12,13]

The behaviour of complex (2) as described by Postel *et al.*[12] did not appear convincing since the only evidence for the presence of a third set of resonances [instead of the two observed for (1) and for all analogous complexes investigated by us] was the presence of three resonances, assignable to the NMe protons (R^3), at δ 3.34, 3.44, and 3.45 respectively; two of these were separated by only 0.01 p.p.m. Postel *et al.* reported that the three signals arising from each methyl group were better resolved when the spectra were run in toluene than in chloroform, but they did not give the relative values.

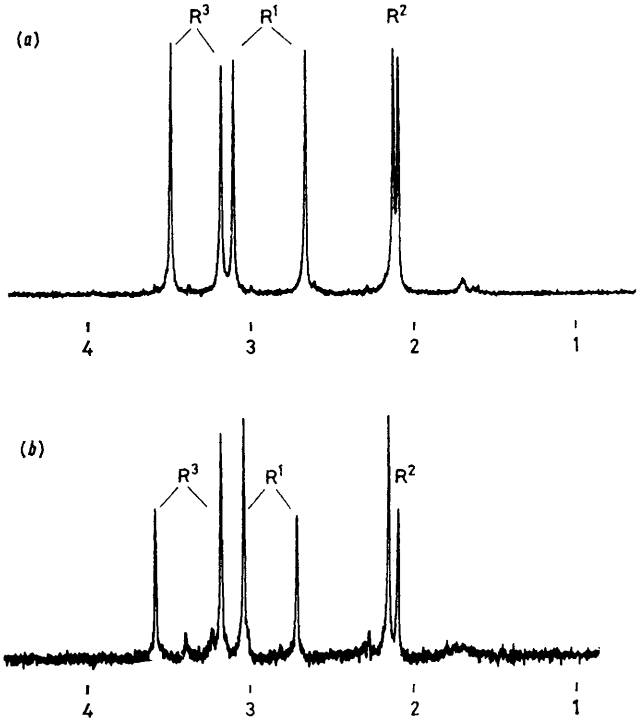

FIGURE 1 Hydrogen-1 n.m.r. spectra of (*a*) *trans*-$[PdCl_2(Me_2C{=}NNMePh)_2]$ and (*b*) of its bromo-analogue *trans*-$[PdBr_2(Me_2C{=}NNMePh)_2]$ at 90 MHz and 0 °C, solvent $CDCl_3$

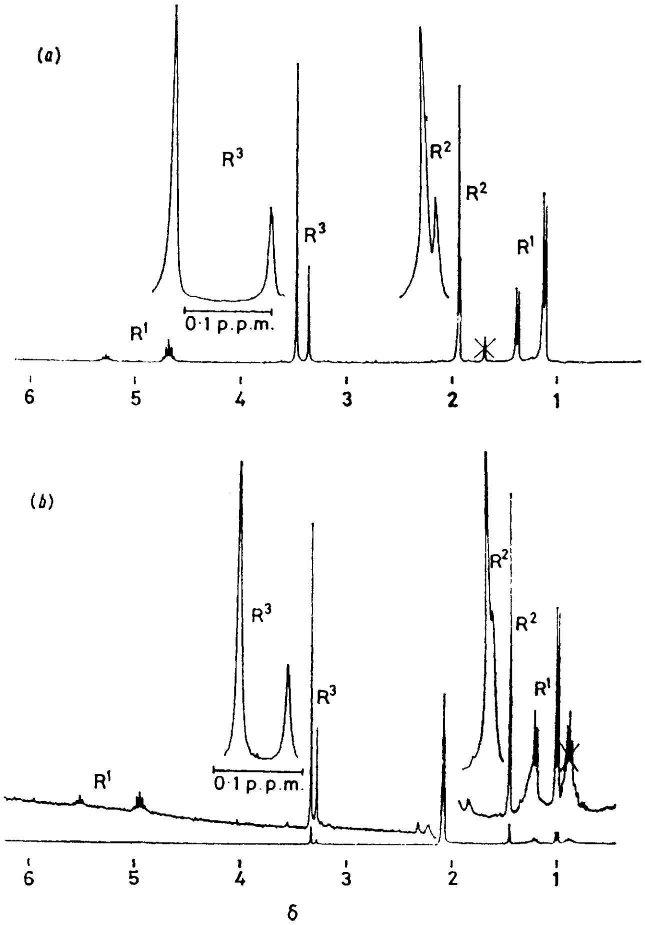

FIGURE 2 Hydrogen-1 n.m.r. spectra of *trans*-$[PdCl_2(Pr^iMeC{=}NNMePh)_2]$ in (*a*) $CDCl_3$ and (*b*) in deuteriotoluene at 270 MHz and −10 °C

We reinvestigated complex (2) and in order to get a better resolution we ran the n.m.r. spectra of deuteriochloroform and deuteriotoluene solutions of this complex on a Bruker HX 270 (270 MHz) instrument. The spectra are reported in Figure 2. Superficially they are the same as those shown in Figure 2 of ref. 12, but the 0.01 p.p.m. (3 Hz at 270 MHz) splitting on the signal at δ 3.45 is not resolved while the two signals for R^2, which were not resolved by Postel *et al.*, are resolved, and, in toluene solution, are separated by even less than 0.01 p.p.m. Therefore, since in both solvents only two sets of resonances of different intensity are present, we must conclude that they belong to two geometric isomers each one having equivalent hydrazones.

The complexes with $R^1R^2C{=}NNMe_2$ have already been shown to exhibit two sets of resonances, very close to one another, both resulting in a large downfield shift with respect to the free ligand. On the other hand the complexes with $R^1R^2C{=}NNMePh$ hydrazones behaved differently in the sense that corresponding resonances of the two sets had quite different chemical shifts, and whereas one set exhibited a large downfield shift for R^1 and a small downfield shift for R^3, opposite trends were observed for the other set. (Postel *et al.* erroneously assigned both the resonances of R^1 and R^3, exhibiting larger downfield shifts, to the same set, which was attributed to a single hydrazone interacting with the metal.)

Our explanations of these features are as follows. We suggest that the metal has a large deshielding effect on the alkyl hydrogens whenever they are held close to the axial co-ordination sites of the metal, and alkyl groups from both hydrazones can simultaneously experience this effect. In support of this we have prepared the complex with the cyclic hydrazone *trans*-$[PdCl_2(\overline{CH_2CH_2CH_2CMe{=}N{-}N}Me)_2]$ (4). In this case the rotation about the N–N bond is blocked and both R^1 and R^3 groups of each hydrazone are held rigid close to the axial co-ordination sites. Also, two sets of resonances corresponding to isomers (A) and (B) were observed, the chemical shifts of the two sets being close to one another as for all other complexes with all-alkyl hydrazones such as complex (5). The R^1 groups exhibited a large downfield shift similar to that observed for the other complexes of the series. The R^3 groups exhibited a downfield shift slightly smaller than that of R^1 and, on average, twice that observed for complexes with non-cyclic hydrazones where, because of the free rotation about the N–N bond, each NMe group spends only half its time in a position close to the axial co-ordination site of the metal.

The trend observed in the chemical shift of the alkyl resonances in complexes with $R^1R^2C{=}NNMePh$ ligands can be understood in terms of the phenyl substituent on one hydrazone shielding the R^1 substituent of the other ligand in isomer (A), and the NMe group of the other ligand in isomer (B). This has the effect of moving a resonance from its downfield-shifted position (as a consequence of its proximity to an axial co-ordination site of the metal) back to a position not far removed from that of the R group in the free ligand.

To obtain further support for this assumption we have prepared the mixed hydrazone complex *trans*-$[PdCl_2(Me_2C{=}NNMePh)(Me_2C{=}NNMe_2)]$ (6). In this complex the $Me_2C{=}NNMePh$ ligand, being *trans* to a hydrazone *not bearing* a phenyl group exhibits two sets of resonances close to one another and with large downfield shifts both for R^1 and R^3 [as is observed for complexes, such as (5), having two all-alkyl hydrazones]. In contrast, the $Me_2C{=}NNMe_2$ ligand, being *trans* to a hydrazone *bearing* a phenyl group, exhibits two sets of signals which show quite different chemical shifts for the same alkyl protons, and while one set exhibits a large downfield shift only for R^1 the other set exhibits a large downfield shift only for R^3 [as is observed for complexes, such as (1), having two phenylhydrazone ligands].

In conclusion, we must emphasize that all the features of the ^1H n.m.r. spectra of a wide series of *trans*-$[PdCl_2(R^1R^2C{=}NNR^3R^4)_2]$ complexes can be accounted for only by assuming the existence of two rotational isomers such as (A) and (B).

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