Hindered Rotation about the Metal–Nitrogen Bond in *trans*-Dichlorodihydrazonepalladium(II) Complexes and *X*-Ray Crystal Structure of *trans*-Bis(acetone methylphenylhydrazone)dichloropalladium(II) [1]

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The complexes *trans*-[$PdCl_2L_2$] [L = $Me_2C{=}N{-}NMePh$ (L^1); $Et_2C{=}N{-}NMePh$ (L^2); $Pr^nMeC{=}N{-}NMePh$ (L^3); $MeHC{=}N{-}NMePh$ (L^4); $Me_2C{=}N{-}NMe_2$ (L^5); or $MeHC{=}N{-}NMe_2$ (L^6)] have been prepared by reaction of the hydrazone ligands with [$PdCl_2(NCPh)_2$]. The crystal and molecular structure of *trans*-[$PdCl_2(Me_2C{=}N{-}NMePh)_2$] has been determined from three-dimensional *X*-ray data. The complex crystallizes in the monoclinic space group $P2_1/n$ with two molecules in a cell of dimensions $a = 18.83(3)$, $b = 7.53(2)$, and $c = 7.76(2)$ Å, $\beta = 89.1(5)°$. The palladium atom lies at a centre of symmetry; consequently the four ligating atoms, *i.e.* the two chloride ions and the two imino-nitrogens of the hydrazones, are located rigorously in a plane passing through the central metal. The co-ordination plane is nearly perpendicular to the plane containing the non-hydrogen atoms of the hydrazone skeleton $Me_2C{=}N{-}N$. Significant bond distances are Pd–Cl 2.298(4) and Pd–N 2.047(2) Å. Another isomeric structure of this complex can be obtained by 180° rotation about the Pd–N bond of one of the two hydrazone ligands. This isomer is not centrosymmetric but contains a plane of symmetry which is perpendicular to the co-ordination plane and passes through the Cl–Pd–Cl axis. Both these isomers exist in equilibrium in solution for all the prepared complexes. Values of free energies of activation for the interconversion process have been obtained from temperatures of coalescence of the n.m.r. signals; they vary from 58 to 89 kJ mol^{-1} with the nature of the ligand substituents. In particular, complexes of hydrazones derived from aldehydes (L^4 and L^6) have $\Delta G^{\ddagger}$ 10—14 kJ mol^{-1} lower than those of analogous hydrazones derived from ketones (L^1—L^3 and L^5); complexes of hydrazones derived from methylphenylhydrazine (L^1—L^4) have $\Delta G^{\ddagger}$ 17—21 kJ mol^{-1} lower than those of analogous hydrazones derived from dimethylhydrazine (L^5 and L^6).

COMPLEXES of hydrazones ($R^1R^2C{=}N^1{-}N^2R^3R^4$) with transition metals have been reported. Generally the organic ligand co-ordinates through the iminic nitrogen (N^1); [2,3] however, at least in one case, it has been observed that the aminic nitrogen (N^2) can act as donor atom. (The latter configuration gives minimal steric interaction between the hydrazone and the complex residue.[4]) In a previous investigation we examined the co-ordination of hydrazones to platinum(II); [5,6] in all cases the iminic nitrogen was the donor atom and, in the solid state, the plane of the ligand molecule was perpendicular to that of co-ordination. Although a π interaction between the metal *d* orbitals and the iminic π system is possible, the *X*-ray data showed that the Pt–N bond distance was essentially that corresponding to a single bond.

The shape of a hydrazone molecule is such that when it is co-ordinated to a metal through the iminic nitrogen a hindered rotation about the metal–ligand bond is expected. If this hindered rotation occurs in complexes of the type *trans*-[MX_2(hydrazone)$_2$] (M = transition metal, X = anionic ligand) two isomeric structures could be obtained: one centrosymmetric and the other with a plane of symmetry perpendicular to that of co-ordination and passing through the X–M–X axis. We were unsuccessful in preparing complexes of type *trans*-[MX_2(hydrazone)$_2$] with M = Pt, but did prepare complexes with M = Pd and the results of this investigation are now reported.

EXPERIMENTAL

Preparations.—*Ligands.* All the ligands were prepared by the same procedure, treating the carbonyl compound ($R^1R^2C{=}O$) with the appropriate hydrazine ($H_2N{-}NR^3R^4$). The experimental conditions were those reported in the literature.[7] The purity of the ligands was tested by g.l.c. and t.l.c. and their formulation was in accord with the elemental analyses and ^1H n.m.r. spectra (Table 1).

Complexes. All the complexes were prepared in an analogous way. In a typical experiment, a solution of *trans*-[$PdCl_2(NCPh)_2$] [8] (1.18 g, 3.08 mmol) in benzene (30 cm^3) was added to a solution of the hydrazone (*e.g.* $Me_2C{=}N{-}NMePh$; 1.00 g, 6.17 mmol) in the same solvent (40 cm^3). The reaction mixture was stirred for 12 h then filtered, and the solvent was evaporated under reduced pressure. The solid residue was dissolved in warm CH_2Cl_2, the solution was filtered, and the product precipitated with hexane. The yield was always >60%. Analytical data, melting points (uncorrected), and molecular weights (measured by osmometry) are summarized in Table 2.

Apparatus.—Infrared spectra in the range 250—4 000 cm^{-1} were recorded as KBr pellets or Nujol mulls on a

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[1] For preliminary accounts see: F. Gasparrini, D. Misiti, and E. Cernia, *Inorg. Chim. Acta*, 1976, **17**, L3; G. Natile, L. Cattalini, and F. Gasparrini, *J.C.S. Chem. Comm.*, 1977, 89.

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Perkin-Elmer 457 spectrophotometer. Hydrogen-1 n.m.r. spectra were obtained with a Varian NV14 spectrometer. The probe temperature was adjusted with a variable temperature accessory and measured using the precalibrated internal chemical shift of a methanol sample. Free energies of activation for the isomerization process were calculated using the expression $\Delta G^\ddagger = -RT\ln(\pi\Delta\nu\boldsymbol{h}/2^{\frac{1}{2}}\boldsymbol{k}T)$ where $\Delta\nu$ represents the chemical shift of the coalescing peaks under conditions of slow isomerization, T the temperature of coalescence, and R, $\boldsymbol{k}$, and $\boldsymbol{h}$ have their normal thermodynamic significance.

TABLE 1

Proton chemical shifts * (δ/p.p.m. downfield from $SiMe_4$) of free hydrazones. The numbering of substituents in the hydrazone molecule is $R^1R^2C=N^1-N^2R^3R^4$

	R¹			R²			R³	R⁴	
Compound	γ(CH)	β(CH)	α(CH)	β(CH)	α(CH)	H	CH_3	CH_3	C_6H_5
$Me_2C=N-NMePh$ (L^1)			2.05		1.90		2.95		6.6—7.4
$Et_2C=N-NMePh$ (L^2)		1.17 (8)	2.33 (8)	0.93 (8)	2.27 (8)		2.90		6.3—7.3
$Pr^nMeC=N-NMePh$ (L^3)	0.93 (6.7)	1.54 (6.7, 7.5)	2.30 (7.5)		1.82		2.91		6.6—7.3
$MeHC=N-NMePh$ (L^4)			1.93 (5)			6.57 (5)	3.00		7.0—7.2
$Me_2C=N-NMe_2$ (L^5)			1.95		1.90		2.40	2.40	
$MeHC=N-NMe_2$ (L^6)			1.84 (5.3)			6.60 (5.3)	2.68	2.68	

* All the spectra were recorded in $CDCl_3$ solution; ^3J values (in Hz) are given in parentheses.

X-Ray Analysis.—Crystals of *trans*-[$PdCl_2(Me_2C=N-NMePh)_2$] are prismatic in shape. From a series of Weissenberg photographs the crystal appeared to be twinned, (100) being the twin plane. Monoclinic symmetry was observed with the following systematic absences: $h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$. The space group $P2_1/n$ (an alternative to $P2_1/c$) is the only one consistent with these conditions. The general positions are: x, y, z; $-x, -y, -z$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$. Unit-cell calibration was carried out by a least-squares fit of the angular parameters of 28 reflections, measured on the diffractometer. The crystal data are: $C_{20}H_{28}Cl_2N_4Pd$, $M = 501.8$, Monoclinic, $a = 18.83(3)$, $b = 7.53(2)$, $c = 7.76(2)$ Å, $\beta = 89.1(5)°$, $U = 1\,100.1$ Å^3, $Z = 2$, $D_c = 1.514$ g cm^{-3}. Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 11.7$ cm^{-1}.

The crystal was mounted with the c axis parallel to the spindle axis of a computer-controlled Siemens AED diffractometer. Intensities were measured for $\theta < 25°$, following the θ—2θ scan method and the 'five-points' technique;[9] zirconium-filtered Mo-K_α radiation was used. A standard reflection (400), measured every 15 reflections, was used to monitor the intensity variations, which did not exceed 3%. Intensities were corrected for this effect by means of a simple linear-interpolation method. A total of 2 065 reflections was collected comprising only one unique form ($\pm hkl$), the major part of which could be assigned to a single individual; 1 035 reflections with $I < 2.5\sigma(I)$ were rejected. Because of the twinning, the intensities of $hk0$ reflections, to which the two individuals A and B make comparable contributions [as established by intensity measurements of various $hkl(A)$ and $hkl(B)$ pairs], were halved. The $h0l$ reflections, which practically result from a nearly complete overlapping of $h0l(A)$ and $-h0l(B)$ pairs, were excluded from the refinement. The remaining reflections were assigned to a single individual, even though some overlapping was unavoidable, particularly for hkl with $l < 4$. The intensities were reduced to values of F^2 by applying Lorentz and polarization factors. Absorption corrections were applied according to the method of Busing and Levy.[10]

TABLE 2

Analytical (%) [a] and i.r. data (cm^{-1})

Complex	M.p. (θ_c/°C)	M [a]	C	H	N	Cl	ν(C=N), ν(C=C)	δ(C–H)	ν(Pd–Cl)
trans-[$PdCl_2L^1{}_2$]	153	496 (502)	47.7 (47.9)	5.6 (5.6)	11.1 (11.2)	14.4 (14.1)	1 620s, 1 590vs	780vs, 710vs	345s
trans-[$PdCl_2L^2{}_2$]	113	550 (558)	51.5 (51.7)	6.3 (6.5)	10.5 (10.0)	13.0 (12.7)	1 595vs, 1 575s	770vs, 700vs	340vs, br
trans-[$PdCl_2L^3{}_2$]	134	577 (558)	51.5 (51.7)	6.2 (6.5)	10.0 (10.0)	12.9 (12.7)	1 595vs, br	760pvs, 700vs	345s
trans-[$PdCl_2L^4{}_2$]	132	480 (474)	45.2 (45.6)	5.0 (5.1)	11.9 (11.8)	15.3 (15.0)	1 610m, 1 590vs, 1 580s	785vs, 705vs	335vs
trans-[$PdCl_2L^5{}_2$]	178	399 (378)	31.2 (31.8)	6.2 (6.4)	14.7 (14.8)	19.1 (18.8)	1 630vs		350vs
trans-[$PdCl_2L^6{}_2$]	146	372 (350)	27.4 (27.5)	5.8 (5.8)	16.0 (16.0)	20.1 (20.3)	1 645vs		345vs (365vs [b])

[a] Calculated values are given in parentheses. [b] Alternative assignment. vs = Very strong, s = strong, m = medium, and br = broad.

Structure Determination and Refinement.—The structure was solved by Patterson and Fourier methods and refined by block-matrix least squares. The function minimized was $\Sigma w(F_o - F_c)^2$ with Cruickshank's weighting scheme.[11] The atomic scattering factors used were those of Moore[12]

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[9] W. Hoppe, *Acta Cryst.*, 1969, **A25**, 67.

[10] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[11] D. W. J. Cruickshank, 'Computing Methods in Crystallography,' Pergamon, London, 1965, p. 114.

[12] F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

for non-hydrogen atoms and of Stewart *et al.*[13] for hydrogen. The positions of the hydrogen atoms were calculated according to the usual sp^2 or sp^3 geometry. In the final cycles of the refinement, the hydrogen-atom contributions to the structure factors were calculated from these fixed positions with isotropic thermal parameters of 6.0 Å^2. All the computer programs were written by Immirzi.[14] With two formula units per unit cell, the palladium atom can be located unambiguously at the origin with $\bar{1}$ site symmetry; this was clearly confirmed by the Patterson map. Two subsequent Fourier syntheses located all the other non-hydrogen atoms.

TABLE 3

Atomic fractional co-ordinates and thermal parameters of non-hydrogen atoms. Anisotropic thermal factors are defined by $\exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$

	x	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	0	0	0	3.08(5)	2.01(4)	2.93(6)	−0.27(8)	−0.42(4)	0.40(9)
Cl	0.004 3(3)	0.186 7(5)	−0.234 0(6)	6.31(24)	4.61(18)	3.72(22)	−1.50(17)	−1.60(20)	1.67(17)

	x	*y*	*z*	*B*		*x*	*y*	*z*	*B*
N(1)	0.072 2(6)	0.147 5(14)	0.132 6(17)	3.4(2)	C(5)	0.189 9(8)	0.253 0(19)	0.034 2(23)	3.7(3)
N(2)	0.144 7(7)	0.113 5(17)	0.108 1(20)	4.4(3)	C(6)	0.162 0(10)	0.386 5(24)	−0.063 7(29)	5.4(4)
C(1)	0.054 1(8)	0.264 9(19)	0.245 7(23)	4.0(3)	C(7)	0.210 1(11)	0.519 5(26)	−0.133 9(29)	6.2(4)
C(2)	0.107 0(11)	0.354 0(25)	0.357 7(31)	6.3(5)	C(8)	0.278 7(12)	0.518 4(27)	−0.092 4(31)	6.9(5)
C(3)	−0.023 1(9)	0.305 3(20)	0.269 0(24)	4.2(3)	C(9)	0.305 7(10)	0.394 2(22)	0.005 0(26)	5.0(4)
C(4)	0.164 0(10)	−0.061 0(22)	0.028 9(29)	5.2(4)	C(10)	0.260 8(10)	0.255 3(22)	0.078 5(27)	5.0(4)

TABLE 4

Calculated fractional co-ordinates (× 10^4) of the hydrogen atoms

	x	*y*	*z*
H′[C(2)]	1 598	3 091	3 228
H″[C(2)]	958	3 213	4 908
H‴[C(2)]	1 037	4 961	3 405
H′[C(3)]	−532	2 293	1 776
H″[C(3)]	−320	4 453	2 480
H‴[C(3)]	−399	2 705	3 983
H′[C(4)]	1 564	−548	−1 085
H″[C(4)]	1 306	−1 639	835
H‴[C(4)]	2 190	−906	545
H[C(6)]	1 057	3 926	−880
H[C(7)]	1 904	6 199	−2 202
H[C(8)]	3 129	6 230	−1 406
H[C(9)]	3 619	3 949	310
H[C(10)]	2 821	1 571	1 649

After a few cycles of isotropic refinement, some systematic discrepancies appeared, particularly for *hk*1 and *hk*2 reflections, which had systematically higher observed than calculated values. This effect had clearly to be ascribed to a partial overlapping of some *hkl*(*A*) and −*hkl*(*B*) pairs, which causes an overestimation of the experimental intensity of a reflection. Because of the practical impossibility of evaluating this effect for each reflection, the application of different scale factors to *F*(*hkl*), at different values of the *l* index, appeared reasonable. The resulting scale factors were in the ratio 0.77 (l = 1) : 0.90 (l = 2) : 0.97 (l = 3) : 1.0 (l = 0 and >4). The palladium and chlorine atoms were refined anisotropically, while the other non-hydrogen atoms were left isotropic. Least-squares refinement with 841 independent observations converged to *R* 0.09.

The final positional and thermal parameters of the non-hydrogen atoms are in Table 3, calculated hydrogen positions in Table 4, and selected geometrical parameters in Table 5. A perspective view of the molecule is shown in Figure 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 22055 (9 pp.).*

RESULTS AND DISCUSSION

By reaction of *trans*-[PdCl$_2$(NCPh)$_2$] with hydrazones (molar ratio 1 : 2) in benzene, complexes of formula *trans*-[PdCl$_2$L$_2$] [L = Me$_2$C=N-NMePh (L^1); Et$_2$-C=N-NMePh (L^2); Pr^{n}MeC=N-NMePh (L^3); MeHC=N-NMePh (L^4); Me$_2$C=N-NMe$_2$ (L^5); or MeHC=N-NMe$_2$ (L^6)] were obtained in high yield (⩾60%). The i.r. spectra (Table 2) show one band assignable to metal–chlorine stretching vibrations, indicating that the two chlorine atoms are mutually *trans*.[15] In the C=N stretching region all the complexes exhibit a strong absorption at *ca.* 1 600 cm^{-1} which indicates that the hydrazone is bonded through the lone pair of the iminic nitrogen.[16]

TABLE 5

Bond lengths (Å) and angles (°) with their estimated standard deviations in parentheses for *trans*-[PdCl$_2$(Me$_2$C=N-NMePh)$_2$]

Pd–Cl	2.298(4)	C(1)–C(3)	1.49(2)
Pd–N(1)	2.047(12)	C(5)–C(6)	1.37(2)
N(1)–N(2)	1.398(19)	C(5)–C(10)	1.38(2)
N(1)–C(1)	1.288(21)	C(6)–C(7)	1.45(2)
N(2)–C(4)	1.493(23)	C(7)–C(8)	1.34(3)
N(2)–C(5)	1.464(20)	C(8)–C(9)	1.31(3)
C(1)–C(2)	1.49(2)	C(9)–C(10)	1.45(2)
Cl–Pd–N(1)	92.9(2)	C(2)–C(1)–C(3)	119.7(7)
Cl–Pd–N(1′)	87.1(2)	N(2)–C(5)–C(6)	121.2(9)
Pd–N(1)–N(2)	119.2(7)	N(2)–C(5)–C(10)	118.0(8)
Pd–N(1)–C(1)	122.9(9)	C(6)–C(5)–C(10)	120.6(8)
N(2)–N(1)–C(1)	117.8(8)	C(5)–C(6)–C(7)	118.2(8)
N(1)–N(2)–C(4)	116.6(7)	C(6)–C(7)–C(8)	120.3(10)
N(1)–N(2)–C(5)	118.9(6)	C(7)–C(8)–C(9)	122.0(10)
C(4)–N(2)–C(5)	109.5(6)	C(8)–C(9)–C(10)	120.6(8)
N(1)–C(1)–C(2)	122.2(8)	C(5)–C(10)–C(9)	117.9(8)
N(1)–C(1)–C(3)	118.0(6)		

The molecular structure of one of these complexes, *trans*-[PdCl$_2$(Me$_2$C=N-NMePh)$_2$], was determined by *X*-ray analysis. The palladium atom lies at a centre of symmetry; consequently the four ligating atoms, *i.e.* the

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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two chloride ions and the two imino-nitrogens of the hydrazone ligands, are located rigorously in a plane passing through the central metal. This plane is nearly perpendicular to that containing the N(2)–N(1)=C(1)-[C(2)]C(3) atoms (Figure 1). The Pd–Cl bond distance [2.298(4) Å] is in good agreement with that found in various square-planar complexes of Pd^{II}.[17] The Pd–N bond length [2.047(2) Å] is comparable with that found in structurally analogous amine complexes of Pd^{II},[17] indicating that the palladium–hydrazone bond is essentially single. The N–N bond distance [1.398(19) Å] and the angle (*ca.* 40°) between the approximate direction of the lone pair of N(2) and the *p* orbitals of the N(1)=C(1) π system (*a* and *b* in Figure 2) indicate that the overlap of the *p* orbitals within the N–N bond is negligible. The N(2)–C(5) bond distance [1.464(20) Å] also corresponds to that of a single bond; in fact the directions of the phenyl π system and the aminic lone pair (*c* and *a* in Figure 2) make an angle of 67° which excludes any π contribution to this bond.

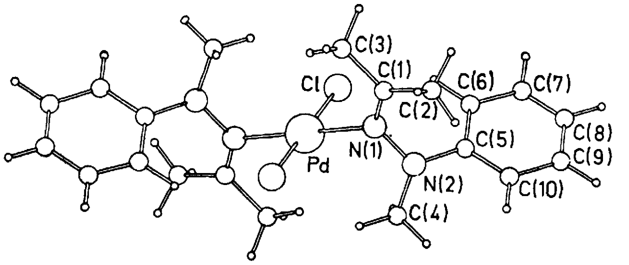

FIGURE 1 Projection of the molecular structure of *trans*-$[PdCl_2(Me_2C{=}N{-}NMePh)_2]$ together with the atom numbering scheme

TABLE 6

Proton chemical shifts [a] (δ/p.p.m., downfield from $SiMe_4$) of *trans*-$[PdCl_2(hydrazone)_2]$ complexes. Under conditions of slow exchange two resonances (upper and lower line) are observed for each type of equivalent proton. The free energy of activation for the isomerization process is also given

		R¹			R²			R³	R⁴		
Complex	θc/°C	γ(CH)	β(CH)	α(CH)	β(CH)	α(CH)	H	CH_3	CH_3	C_6H_5	ΔG‡ [b] kJ mol⁻¹
trans-$[PdCl_2L^1{}_2]$	0			2.67 3.10		2.09 2.12		3.50 3.19		6.8—7.5	67
trans-$[PdCl_2L^2{}_2]$	0		1.27 1.55	3.37 3.71	1.03 1.03	2.48 2.48		3.51 3.25		6.8—7.5	70
trans-$[PdCl_2L^3{}_2]$	0	0.99 1.24	1.5—2.2 [c]	3.39 3.67		2.07 2.09		3.59 3.27		6.8—7.5	68
trans-$[PdCl_2L^4{}_2]$	−30			2.40 2.91			*d*	3.60 3.33		7.0—7.6	58
trans-$[PdCl_2L^5{}_2]$	+25			3.04 3.15		2.26 2.28		2.98 2.93	2.98 2.93		89
trans-$[PdCl_2L^6{}_2]$	+25			2.90 2.96			7.40 7.36	3.11 3.11	3.11 3.11		75

[a] All the spectra were recorded in $CDCl_3$ solution. The notation used to distinguish the various protons is the same as in Table 1. [b] Errors are estimated to be *ca.* ±1.5 kJ mol⁻¹. [c] Because of overlap it is not possible to distinguish between the resonances of the two isomers. [d] Obscured by phenyl resonances.

The n.m.r. spectra of these complexes are summarized in Table 6. In each case, for each type of equivalent proton, we observed two resonances (in some cases the temperature of the n.m.r. probe had to be decreased to −30 °C); therefore an equilibrium between two isomeric complexes is present in solution. The assignment of the resonances was carried out by comparing the whole set of complexes and also referring to data for platinum hydrazone complexes *trans*-$[PtCl_2(C_2H_4)L]$.[6,18] The numbering of the hydrazone substituents is $R^1R^2C{=}N^1(Pd){-}N^2R^3R^4$. The mean resonance of the R^3 protons (R^3 is always Me) was shifted by *ca.* 0.40—0.55 p.p.m. to lower field after co-ordination. Similarly the mean resonance of the α-protons of R^2 was shifted by 0.20—0.40 p.p.m. to lower field after co-ordination. A larger shift (0.70—1.25 p.p.m.) was observed for the α-protons of R^1. The latter feature suggests that some interaction may occur between the α-protons of R^1 and the metal atom as a consequence of the fact that the R^1 group is forced to be *cis* to the metal. In the crystal structure of *trans*-$[PdCl_2L^1{}_2]$ the non-bonded distance Pd • • • H'[C(3)] (2.36 Å) is quite short.

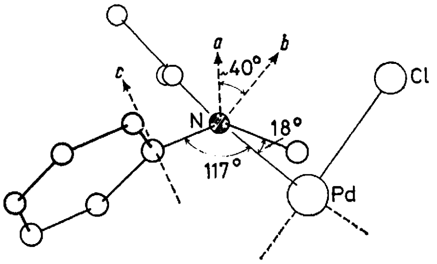

FIGURE 2 View of the molecule *trans*-$[PdCl_2(Me_2C{=}N{-}NMePh)_2]$ along the N(1)–N(2) bond. The approximate directions of the lone pair of electrons of the aminic nitrogen and of the *p* orbitals of the azomethine and phenyl π system are also shown and labelled *a*, *b*, and *c*, respectively

We also found that the isomer splitting of the α-protons of R^2 does not exceed 0.03 p.p.m. in each case. Moreover, in the complexes derived from methylphenylhydrazones (R^3 = Me, R^4 = Ph) the splitting of the R^1

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[17] F. R. Hartley, ' The Chemistry of Platinum and Palladium,' Applied Science, London, 1973.

[18] G. Natile, L. Maresca, and L. Cattalini, *J.C.S. Chem. Comm.*, 1976, 24.

resonance was 0.30—0.50 p.p.m. and that of the α-protons of R^3 was 0.25—0.30 p.p.m. On the other hand in the complexes derived from dimethylhydrazones ($R^3 = R^4 = Me$) the splitting of the α-protons of R^1 was at most 0.11 p.p.m. and that of R^3 was <0.05 p.p.m. Therefore the magnetic environment of R^2 is always very similar in the two different isomers, whereas that of R^1 and R^3 is quite different if $R^4 = Ph$ and similar if $R^4 = Me$.

Different causes could be responsible for the formation of the isomers, *i.e.* a change in the donating atom of the hydrazone ligands [iminic nitrogen (N^1) in one isomer and aminic nitrogen (N^2) in the other], a change in the geometry of the complex (*trans* in one case and *cis* in the other), or a different orientation of one hydrazone molecule with respect to the other [symmetrical in one case (*syn* isomer) and antisymmetrical in the other case (*anti* isomer)] (Figure 3). The first hypothesis can be ruled out on the basis that both isomers exhibit similar frequency shifts of the hydrazone protons on co-ordination; furthermore, according to this hypothesis the isomer splitting of the R^2 resonance should have been larger than that observed and the splitting of the R^1 and R^3 resonances should have been of the same magnitude with $R^4 = Ph$ or Me. We can also exclude a *cis–trans* isomerization of the complexes because this kind of structural change does not explain the trend observed in the isomer splitting of the various groups; moreover, isomerization in square-planar complexes generally occurs through substitution processes catalyzed by the presence of free ligand, which is not the case here. In fact, addition of free hydrazone to a solution of the complex caused no increase of the isomerization rate. Moreover the n.m.r. spectra of an equimolar mixture of *trans*-$[PdCl_2L^1_2]$ and L^2 recorded at different times did not show any ligand exchange.

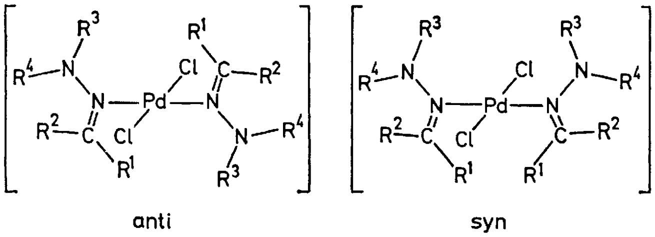

FIGURE 3 Antisymmetrical (*anti*) and symmetrical (*syn*) rotational isomers of the *trans*-$[PdCl_2(hydrazone)_2]$ complexes

The hypothesis of two isomeric complexes deriving from a hindered rotation of the organic ligands about the Pd–N bond accounts for all the experimental results. In this case, in fact, the isomer splitting of the R^2 resonance should be very small since this group, being *trans* to palladium, points away from the metal centre. On the other hand, the isomer splitting of the R^1 resonance should be larger than any other since, being *cis* to the metal, it interacts with that part of the *trans* ligand which it faces: R^1 in the *syn* isomer and NR^3R^4 in the *anti* isomer. The isomer splitting of the R^3 resonance should be intermediate between those of R^1 and R^2 since, because of free rotation about the N–N bond of the hydrazone, R^3 is in a situation intermediate between those of the previous two groups. Also the observation that the isomer splitting of the R^1 and R^3 resonances is much larger when $R^4 = Ph$ than Me is in accord with this interpretation; in fact, in the first case ($R^4 = Ph$) R^1 and R^3, alternately, face in one isomer a phenyl group (R^4 of the *trans* ligand) and in the other isomer an alkyl group (R^1 of the *trans* hydrazone) whereas in the second case ($R^4 = Me$) R^1 and R^3 always face an alkyl group. Indirect evidence for hindered rotation about the metal–ligand bond has been obtained in some complexes of platinum with carbene ligands which are structurally analogous with hydrazones.[19]

Free energies of activation for the isomerization process were calculated from the coalescence temperatures of the peaks corresponding to the two isomers (see Experimental section) and are reported in Table 6. It was found that $\Delta G^\ddagger$ for complexes of hydrazones derived from aldehydes (L^4 and L^6) is 10—14 kJ mol^{-1} lower than for the complexes of analogous hydrazones derived from ketones (L^1—L^3 and L^5). Moreover, the free energy of activation for the complexes of hydrazones derived from methylphenylhydrazine (L^1—L^4) is 17—21 kJ mol^{-1} lower than that for complexes with analogous hydrazones derived from dimethylhydrazone (L^5 and L^6).

The steric contribution to the rotational barrier is given by the difference between the maximum and minimum energy potential induced by the non-bonded interactions which are encountered as the hydrazone rotates about the metal–nitrogen axis. The steric-energy minima will occur when the plane of the hydrazone is perpendicular to that of co-ordination and corresponds to the configuration found in the solid state. The steric-energy maximum will occur when the hydrazone passes through the co-ordination plane and therefore interacts with the *cis*-chlorine atoms. Apparently the increase in $\Delta G^\ddagger$ values does not parallel the bulkiness of the ligand substituents (particularly R^1 and NR^3R^4). In fact, on changing the size of R^1 ($R^1 = Me$, Et, or Pr^n) $\Delta G^\ddagger$ remains practically the same; * on the other hand, a decrease in the size of R^2 ($R^2 = Me$ or H), which should be without significant effect, caused a decrease in $\Delta G^\ddagger$ of 10—14 kJ mol^{-1}. Furthermore, on increasing the size of NR^3R^4 ($NR^3R^4 = NMe_2$ or NMePh) $\Delta G^\ddagger$ does not increase, as could be expected, but decreases by 17—21 kJ mol^{-1}.

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* The free hydrazones L^1, L^2, L^3, L^4, L^5, and L^6 have $R^1 =$ Me, Et, Pr^n, Me, Me, and Me respectively.[20] This configuration is kept also after co-ordination (R^1 *cis* to the metal) as indicated by the downfield shift and isomer splitting of the R^1 resonances in the complexes.

[19] H. C. Clark and L. Manzer, *Inorg. Chem.*, 1972, **11**, 503 and refs. therein; B. Crociani and R. L. Richards, *J.C.S. Dalton*, 1974, 693.

[20] G. J. Karabatsos, R. A. Taller, and F. M. Vane, *Tetrahedron Letters*, 1964, **18**, 1081; G. J. Karabatsos, F. M. Vane, R. A. Taller, and N. Hsi, *J. Amer. Chem. Soc.*, 1964, **86**, 3351.

In our opinion the impediment to rotation of the hydrazone ligand does not depend solely on the bulkiness of its substituents but also on some interactions of the ligand hydrogens, which come in near proximity to the metal. More work is needed in order to see how the different substituents can alter the energetics of the process.

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