High Barrier to Rotation about the Pd–N Bond in *trans*-Dichloro-dihydrazone-palladium(II) Complexes

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Summary Newly synthesized *trans*-$[PdCl_2(R^1R^2C{=}N^1{-}N^2R^3R^4)_2]$ complexes have a high Pd–N^1 rotational barrier which, in solution, gives rise to two isomers depending on the relative orientations of the hydrazone molecules with respect to each other (symmetrical in one isomer and asymmetrical in the other).

A FEW examples have been reported in which a co-ordinated monodentate molecule exhibits restricted rotation about the bond axis;[1] the molecular size and the presence of bulky metal-substituents in adjacent positions appear to be critical in creating this steric barrier. We report the first example of isomerism in *trans*-$[MX_2L_2]$ complexes (X = Cl, L = hydrazone) generated by hindered rotation about the M–L bond.

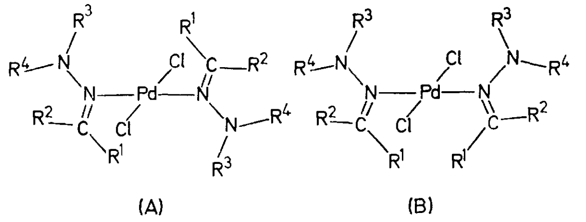

FIGURE.

The complexes *trans*-$[PdCl_2L_2]$ (L^1 = $Me_2C{=}N{-}NMePh$; L^2 = $Et_2C{=}N{-}NMePh$; L^3 = $MePr^nC{=}N{-}NMePh$; L^4 = $MeHC{=}N{-}NMePh$; L^5 = $Me_2C{=}N{-}NMe_2$; L^6 = $MeHC{=}N{-}NMe_2$) were prepared by substitution of the benzonitrile ligands with hydrazones in *trans*-$[PdCl_2(NCPh)_2]$. The *X*-ray structure of *trans*-$[PdCl_2(Me_2C{=}N{-}NMePh)_2]$[2] has shown that in the solid the palladium atom lies at a centre of symmetry; consequently the four ligating atoms, *i.e.* the two chloride ions and the two imino-type nitrogen atoms, are located in the plane passing through the central metal atom. This plane is almost perpendicular to that containing the non-hydrogen atoms of the $Me_2C{=}N{-}N$ unit (Figure, A).

In this complex if one hydrazone molecule is rotated by 180° about the Pd–N bond the centre of symmetry is lost and a different isomer having a plane of symmetry perpendicular to the co-ordination plane and passing through the Cl–Pd–Cl axis is obtained (Figure, B). Both these isomers appeared to exist in equilibrium in solution.

The n.m.r. spectra of all complexes (Table) showed the presence of two resonances for each type of equivalent proton (in some cases the n.m.r. probe had to be kept at temperatures as low as −30 °C in order to observe the splitting of the proton resonances due to the isomers). These signals generally had comparable intensity, but in some cases (as with L^5) definite deviations from equality were observed.

In each complex the n.m.r. signals were assigned by comparison with known spectra of other hydrazone complexes of palladium(II) and platinum(II).[3]

The observed chemical shift and isomer splitting of the proton resonances are in accord with an isomerism arising from a hindered rotation of the organic ligand about the Pd–N bond. In fact the isomer splitting of the R^2 reson-

TABLE

Proton chemical shifts[a] (δ, downfield from Me_4Si) of *trans*-$[PdCl_2(R^1R^2C{=}N^1{-}N^2R^3R^4)_2]$ complexes. In the conditions of slow exchange two resonances (upper and lower line) are observed for each type of equivalent protons. The free energy of activation for the isomerization process is also given.

		R^1			R^2			R^3	R^4		$\Delta G^{\ddagger b}$ kJ mol^{-1}
Compound	Temp./°C	γ(CH)	β(CH)	α(CH)	β(CH)	α(CH)	H	Me	Me	Ph	
trans-$[PdCl_2(L^1)_2]$	0	—	—	2·67	—	2·09	—	3·50	—	6·8—	67
		—	—	3·10	—	2·12	—	3·19	—	7·5	
trans-$[PdCl_2(L^2)_2]$	0	—	1·27	3·37	1·03	2·48	—	3·51	—	6·8—	70
		—	1·55	3·71	1·03	2·48	—	3·25	—	7·5	
trans-$[PdCl_2(L^3)_2]$	0	0·99	1·5—	3·39	—	2·07	—	3·59	—	6·8—	68
		1·24	2·2[c]	3·67	—	2·09	—	3·27	—	7·5	
trans-$[PdCl_2(L^4)_2]$	−30	—	—	2·40	—	—	—	3·60	—	7·0—	58
		—	—	2·91	—	—[d]	—	3·33	—	7·6	
trans-$[PdCl_2(L^5)_2]$	+25	—	—	3·04	—	2·26	—	2·98	2·98	—	89
		—	—	3·15	—	2·28	—	2·93	2·93		
trans-$[PdCl_2(L^6)_2]$	+25	—	—	2·90	—	—	7·40	3·11	3·11	—	75
		—	—	2·96	—	—	7·36	3·11	3·11		

[a] All spectra were recorded in $CDCl_3$ solution. The notation used to distinguish the various protons is the same as in the text. [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.

ance is always small since the R^2 group, being *trans* to palladium with respect to the azomethine double-bond, does not interact with the other metal-bonded ligands; on the other hand the isomer splitting of R^1 is bigger than that of the other groups since, being *cis* to the metal, it interacts through space with that portion of the *trans* ligand which comes in near proximity (NR^3R^4 in the isomer A and R^1 in the isomer B). The isomer splitting of R^3 is intermediate between those of R^1 and R^2 since, because of free rotation about the N–N bond, it is in a situation intermediate between those of the other two radicals. The ring current exerted by the phenyl group when $R^4 = Ph$ explains also why the isomer splitting of R^1 and R^3 is much bigger in the phenyl derivatives than in those with $R^4 = Me$.

An isomerism arising from a change in the donor atom of the ligand (N^2 in place of N^1) is ruled out on the basis of the observed trend in proton chemical shift and isomer splitting of complexed hydrazones.

Moreover the observed trend in this splitting of the proton resonances also excludes an isomerism arising from a change in the geometry of the complex (from *trans* to *cis*). It is also to be noted that the *cis* $\rightleftharpoons$ *trans* isomerization of square-planar complexes generally occurs through substitution processes catalysed by the free ligand.[4] We observed that the rate of isomerization of these complexes is not affected by the presence of free hydrazone and, furthermore, an equimolar mixture of *trans*-$[PdCl_2(L^1)_2]$ and L^2 did not show any ligand exchange after one day at room temperature.

The possibility of an isomerization arising from a restricted rotation about the N–N bond of the hydrazone ligand is also ruled out since no isomers should have been observed in the cases where $R^4 = R^3$.

Chemical evidence which supports, indirectly, the rotational isomerism in these complexes has been obtained from reactions of equimolar solutions of the compounds and triphenylphosphine. Although phosphines display a very high nucleophilic reactivity towards Pd^{II} and Pt^{II},[5] in $CDCl_3$ at 30 °C, the extent of substitution was $< 10\%$ after 1 h and could be considered complete only after one day. The factor controlling the rate is certainly the steric hindrance created by the hydrazone molecules above and below the co-ordination plane which prevents the phosphine ligand from reaching the metal centre.

Approximate values of the free energy of activation for the isomerization process could be obtained from the temperature of coalescence of the n.m.r. signals due to the two isomers; the data are reported in the Table. The steric contribution to $\Delta G^‡$ is given by the difference between the maximum and minimum energy potential induced by nonbonded interactions which are encountered as the hydrazone rotates about the metal–nitrogen axis. The steric energy minimum will occur when the hydrazone molecule is almost perpendicular to the plane of co-ordination, while the maximum will occur when the hydrazone molecule passes through the co-ordination plane and interacts with the *cis* chlorine atoms.

Apparently the observed changes in $\Delta G^‡$ do not parallel the bulkiness of the ligand substituents *cis* to palladium (R^1 and NR^3R^4). It can be seen that the steric interaction of the hydrazone molecule with the *cis* chlorines does not depend exclusively on its size but also on its sterical rigidity; therefore the influence of the hydrazone substituents on both these two properties of the ligand molecule should be taken in consideration.[3,6]

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