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Evidence for Multiple Palladium–Hydrogen Short-range Interactions in Dichlorobis(1,3-dimethyl-1,4,5,6-tetrahydropyridazine)palladium(II)

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In previous work [1] dealing with the interpretation of n.m.r. spectra of palladium–hydrazone complexes of formula *trans*-[PdCl$_2$(R^{1}R^{2}C=N–NR^{3}R^4)$_2$] we suggested that the metal had a large deshielding effect on the alkyl hydrogens whenever they were held close to the axial co-ordination sites, and alkyl groups from both hydrazones could simultaneously experience this effect.

To support this view we have prepared a complex with a cyclic hydrazone, *trans*-[PdCl$_2$(CH$_2$CH$_2$CH$_2$-CMe=N–NMe)$_2$]. In this case the rotation about the N–N bond is blocked and both C–Me and N–Me groups of each hydrazone are held rigidly close to the axial coordination sites. The n.m.r. spectra already showed that both C- and N-bonded methyls exhibited a large downfield shift which for the N-Me groups were the largest ever observed in this type of compounds.

However, by determining the X-ray crystal structure of this complex and by locating the hydrogen atoms, we believed it would be possible to see if, beyond the steric constrictions which force the methyls to be close to palladium, there was also a specific attractive interaction between the metal and a hydrogen atom of each methyl group.

Crystals are monoclinic, space group $C2/m$ (from systematic absences and structural analysis), with a = 11.504(9), b = 9.639(8), c = 8.163(8) Å, β = 110.53(8)°; U = 847.7 Å^3, Z = 2, D_c = 1.57 g cm^{-3}, μ(Mo-Kα) = 13.92 cm^{-1}. The intensities were collected with the θ–2θ scan technique using the Nb-filtered Mo-Kα radiation on a Siemens AED single-crystal diffractometer. 1186 independent reflectioms were measured (with θ in the range 2.5–29.0°) 1081 of which, having $I > 2\sigma(I)$, were used in the analysis. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, anisotropically for Pd, Cl, N, and C, isotropically for H atoms. All the H atoms were clearly localized in a ΔF synthesis. The conventional R value was 0.033 (observed reflections only). The atomic fractional coordinates and thermal parameters are given in Table I.

In the centric $C2/m$ space group the cyclic hydrazone has an imposed crystallographic m symmetry, so that the carbon C(1) and the nitrogen N(2) atoms are indistinguishable. This result can be explained

TABLE I. Fractional Atomic Coordinates (×10^4 for non hydrogen atoms and ×10^3 for H atoms) and Thermal Parameters (×10^3) with e.s.d.'s in Parentheses. Anisotropic thermal parameters are in the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{13})]$.

	x/a	y/b	z/c	U_{11} or U	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	5000	5000	0	477(4)	356(3)	494(4)	0	283(3)	0
Cl(1)	3211(2)	5000	–2402(2)	573(10)	536(10)	591(11)	0	247(9)	0
N(1)	3953(5)	5000	1563(8)	521(31)	419(28)	555(32)	0	308(27)	0
C(1), N(2)	3520(5)	3810(5)	1922(8)	846(37)	402(25)	945(41)	89(26)	688(35)	50(25)
C(2)	2805(6)	3753(6)	3089(9)	730(38)	555(31)	733(39)	–4(29)	466(34)	–80(29)
C(3)	2003(9)	5000	2894(15)	642(52)	717(50)	820(68)	0	481(54)	0
C(4)	4224(7)	2547(6)	1873(11)	906(42)	439(27)	992(51)	32(30)	614(40)	–7(28)
H(31)	138(7)	500	168(10)	53(24)					
H(32)	170(7)	500	383(10)	73(22)					
H(21)	340(5)	378(6)	425(7)	75(16)					
H(22)	236(5)	295(6)	290(7)	95(15)					
H(41)	376(5)	164(6)	182(7)	110(16)					
H(42)	462(5)	265(6)	107(7)	119(15)					
H(43)	458(5)	230(6)	296(7)	131(17)					

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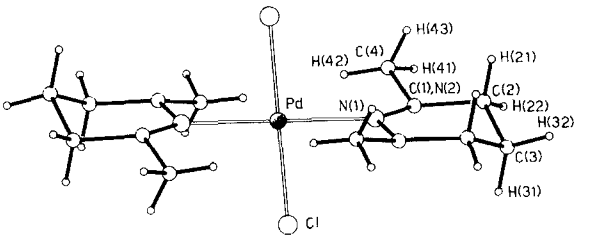

Fig. 1. View of the complex with the atomic numbering scheme. Bond distances are: Pd–Cl, 2.291(3); Pd–N(1), 2.039(7); N(1)–C(1), N(2), 1.324(6); C(1), N(2)–C(2), 1.462(9); C(2)–C(3), 1.489(9) Å. Bond angles are: Cl–Pd–N(1), 89.1(2); C(1), N(2)–N(1)–C(1′), N(2′), 120.1(6); N(1)–C(1), N(2)–C(2), 121.2(5); C(1), N(2)–C(2)–C(3), 111.7(6); C(2)–C(3)–C(2′), 107.6(8)°. The apex indicates an atom related by the *m* symmetry plane.

only if the hydrazone is disordered with C(1) and N(2) statistically interchanged between two positions with an occupancy factor of 0.5. The peak due to this couple of atoms is so well defined (the corresponding thermal U_{ij} parameters are low and comparable with those of the other atoms) that the distances N(1)–C(1) and N(1)–N(2) must be very close indicating a double-bond delocalization over the –(Me)N–N=C(Me)– moiety.

The structure of the complex, having 2/*m* symmetry, is shown in Fig. 1 with the more relevant bond distances and angles. Two Cl atoms and two N atoms from cyclic hydrazone ligands are *trans*-coordinated to the Pd atom in a square-planar arrangement. The cyclic ligand adopts a 'sofa' conformation with five atoms nearly co-planar and C(3) out of the mean plane passing through the others, this plane is perpendicular to the coordination plane.

There are four equivalent H(42)···Pd contacts of only 2.52 Å. All these short contact would be avoided by a 60° rotation of the methyl groups about the C(1), N(2)–C(4) bond suggesting that these interactions are attractive in nature [2] and showing that palladium can interact with as many as four hydrogens simultaneously.

Concerning the *quasi* planarity of the hydrazone moiety (excluding C(3) and the hydrogen atoms) it is to be noted that although other related molecules as N-nitrosoamines, $R_2N^1–N^2=O$ [3–8], adopt in their ground state a planar conformation with the lone-pair of the N^1 nitrogen parallel to and overlapping the π-orbital of the nitrosyl moiety, in contrast the hydrazones, $R_2N^1–N^2=CR_2$, do not assume such a conformation [9–11] even in coordination compounds, as confirmed by X-ray structural studies [12–15].

Therefore this appears to be the first example in which, probably because of sterical constriction, a nearly complete conjugation between the aminic lone-pair and the ketiminyl π-system is attained.

If such a conformation of the ligand would hold in the free hydrazone or is induced by co-ordination to the metal cannot be said at this stage; however it would be interesting to clarify this point in connection with studies on interactions of metal atoms with biological substrates containing pyridazine residues.

Acknowledgments

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References

1 G. Natile, F. Gasparrini, L. Caglioti, B. Galli and D. Misiti, *J. Chem. Soc. Dalton*, 1262 (1979) and references therein.
2 A. G. Constable, W. S. McDonald and B. L. Shaw, *J. Chem. Soc. Dalton*, 1109 (1979).
3 L. E. Looney, W. D. Phillips and L. Reilly, *J. Am. Chem. Soc.*, *79*, 6136 (1957).
4 R. K. Harris and R. A. Spragg, *J. Mol. Spectroscopy*, *23*, 158 (1967).
5 Y. L. Chow, C. J. Colon and J. M. S. Tam, *Can. J. Chem.*, *46*, 2821 (1968).
6 J. D. Cooney, S. K. Brownstein and J. W. ApSimon, *Can. J. Chem.*, *52*, 3028 (1974).
7 H. W. Brown and D. P. Hollis, *J. Mol. Spectroscopy*, *13*, 305 (1964).
8 G. J. Karabatsos and R. A. Taller, *J. Am. Chem. Soc.*, *86*, 4373 (1964).
9 G. J. Karabatsos, R. A. Taller and F. M. Vane, *Tetrahedron Letters*, 1081 (1964).
10 A. Mannschreck and U. Koelle, *Tetrahedron Letters*, 863 (1967).
11 G. J. Karabatsos and R. A. Taller, *Tetrahedron*, *24*, 3923 (1968).
12 N. Bresciani Pahor, M. Calligaris, P. Delise, L. Randaccio, L. Maresca and G. Natile, *Inorg. Chim. Acta*, *19*, 45 (1976).
13 G. Natile, F. Gasparrini, D. Misiti and G. Perego, *J. Chem. Soc. Dalton*, 1747 (1977).
14 M. Biagini Cingi, G. Natile, A. Tiripicchio and F. Gasparrini, *J. Chem. Research*, (S) 98, (M) 1321 (1979).
15 A. M. Manotti Lanfredi, A. Tiripicchio, G. Natile, F. Gasparrini and B. Galli, *Cryst. Struct. Comm.*, *8*, 611 (1979).