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Crystal Structure of the Complex of Palladium(II) with the N-methyl, N-phenyl-Hydrazone of Acetone

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It is known that substituted phenylhydrazones can yield, when used as ligands, different types of co-ordination compounds.[1,2] When the complex is formed, hydrazones may subsequently undergo a number of chemical changes.[3,4] In this paper we report the results of our study on the structure determination of the complex obtained when acetone-N-methyl,N-phenyl-hydrazone and $Pd(PhCN)_2Cl_2$[5] react in benzene. The obtained complex (69%) shows m.p. 168–171° dec. and elemental analysis in agreement with the formula $Pd(L_I)_2Cl_2$. Molecular weight (by osmometry): 496 (calculated: 501). The i.r. spectrum shows at 340 cm^{-1} the antisymmetrical stretching band of the Pd–Cl bond, in agreement with the data reported in the literature for the *trans* structure.[6] The n.m.r. spectrum shows signals at (δ): 7.40–6.80 (m, 10H, 2 $-C_6H_5$); 3.33 (b, 3H, $-\underset{|}{N}-CH_3$); 3.20 (b, 3H, $-\underset{|}{N}-CH_3$); 3.06 (b, 3H, $CH_3-\underset{|}{C}=N-$); 2.70 (b, 3H, $CH_3-\underset{|}{C}=N-$); 2.06 (s, 6H, $2CH_3-\underset{|}{C}=N-$), ppm. The assignment of the signals corresponding to the $-\underset{|}{N}-CH_3$ group was carried out by comparing the n.m.r. spectrum of complex (I) to that of *trans*-$Pd(L_{II})_2Cl_2$ (L_{II} = diethylketone-N-methyl,N-phenyl-hydrazone in which the signals due to $CH_3-\underset{|}{C}=N-$ are absent while signals arising from the $CH_3-CH_2-\underset{|}{C}=N-$ group are present. The n.m.r. spectra of complex (I) with increasing temperature show first coalescence of the signals at δ 3.33 and 3.20 (Δν = 14 Hz) ppm and then of those at δ 3.06 and 2,70 (Δν = 22 Hz) ppm. Moreover, n.m.r. spectra of an equimolecular mixture of complex (I) and L_{II} recorded at different times show no intermolecular exchange. On the basis of the reported data we assume that the co-ordination centre is the "lone pair" of the sp^2-hybridized nitrogen atom. The splitting and the broadening of the above signals may be explained by the magnetic non-equivalence of the $-\underset{|}{N}-CH_3$ and $CH_3-\underset{|}{C}=N-$ groups probably arising from a partly hindered rotation. It is of interest to note that it is possible to recover quantitatively the ligand by reaction with Ph_3P. The above spectroscopic data are confirmed by X-ray analysis of complex (I).

TABLE I. Bond Distances (Å) and Angles (°)

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 crystal and molecular structure of complex (I) have been determined from three-dimensional X-ray data, collected by counter method, using Zr-filtered Mo Kα radiation. Because of the twinning of the crystals (twin law (100)), 1768 of the 2065 measured reflections were assigned to a single individual, even though some overlapping was unavoidable. Of these reflections, excluding the whole *h 0 l* set, 841 with $I > 2.5\ \sigma(I)$ were used in the refinement. The crystal data are: monoclinic space group $P2_1/n$; a = 18.83(3), b = 7.53(2), c = 7.76(2) Å, β = 89.1 (5)°; Z = 2; V = 1100.6 $Å^3$; D_X = 1.513 g/cm^3. The structure was solved by means of Patterson and Fourier techniques, and refined with block-diagonal least-squares, using anisotropic thermal parameters for the Pd and Cl atoms, isotropic for the N and C atoms and fixed contributions of the hydrogen atoms (placed in calculated positions); moreover, each *l* layer was scaled individually. The final conventional R factor was 9%.

The bond lengths and angles are given in Table I. A projection of the molecular structure is shown in Fig. 1. The Pd atom lies on a centre of symmetry, consequently the four ligating atoms, *i.e.* Cl, Cl′, N(1) and N(1′), are located rigorously in the plane passing through the central metal atom. This plane is

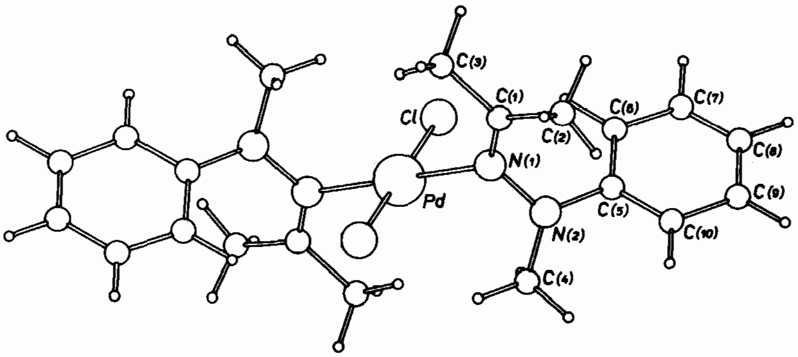

Fig. 1. A projection of the molecular structure.

nearly perpendicular to that containing the N(1), N(2), C(1), C(2) and C(3) atoms. The plane of the phenyl group is angled away from the latter, the torsion angle about the central bond of the sequence N(1)–N(2)–C(5)–C(6) being *ca.* 337°. The carbon atoms of this group display distances from the least-squares plane not exceeding 0.02 Å. The difference between the N(1)–Pd–Cl (92.9°) and Cl–Pd–N(1′) (87.1°) angles is somewhat large, however the values of the Pd–Cl and Pd–N bond distances (2.298(4) and 2.047(2) Å respectively) are in good agreement with others found in various square planar complexes of palladium.[7] The other geometrical parameters of the molecule do not show unusual volumes. On the other hand too many detailed considerations are probably not significant in view of the relatively low accuracy of the structure determination.

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