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The Bonding of Hydrazones in Transition Metal Complexes. Crystal and Molecular Structure of *trans*-Dichloro-ethylene-acetonemethylphenylhydrazone- and *trans*-Dichloro-ethylene-acetaldehydedimethylhydrazone-platinum(II) Complexes

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The X-ray structures of trans-$[Pt(C_2H_4)Cl_2(Me_2C{=}N{-}NMePh)]$*, I, and trans-*$[Pt(C_2H_4)Cl_2(MeHC{=}N{-}NMe_2)]$*, II, have been determined. They were solved by conventional Patterson and Fourier methods giving conventional discrepancy factors of* $R = 0.066$ *for 1476 reflections in compound I and* $R = 0.065$ *for 866 reflections in compound II. Compound I crystallizes in the space group* $P2_1/c$ *with four formula weights in a cell measuring* $a = 9.488(8)$, $b = 11.315(8)$, $c = 14.726(9)$ Å; $\beta = 105.2°$; *compound II crystallizes in the space group* $P2_1$ *with two formula weights per unit cell having* $a = 6.652(7)$, $b = 11.961(8)$, $c = 7.143(7)$ Å; $\beta = 98.8°$. *Crystal densities are 1.987* g/cm^3 *and 2.31* g/cm^3 *for compound I and II respectively. The structures consist of individual monomeric molecules with the platinum atom in a four coordinate arrangement. The hydrazone molecule coordinates through the iminic nitrogen; the two nitrogen atoms and the skeleton of the carbonylic residue lie essentially in a plane which forms a dihedral angle with the coordination plane of 70.3° in compound I and of 87.7° in compound II. The geometry around the aminic nitrogen, N(2), is pyramidal and in both cases its methyl substituent is directed towards the metal. The structural data are compared with those of the palladium complex trans-*$[PdCl_2(Me_2C{=}N{-}NMePh)_2]$.

Introduction

Complexes of hydrazones with transition metals have been already reported and generally the coordination occurs through the iminic nitrogen,[1–5] but at least in one case it has been shown that also the aminic nitrogen, instead of the iminic one, can coordinate to the metal.[6] The bonding in these complexes has not been fully investigated; in particular, when the hydrazone coordinates through the –N=C nitrogen, the best overlap between the metal orbitals and the C=N π-system should be obtained for the hydrazone plane perpendicular and parallel to the plane of coordination; however the actual orientation of the ligand molecule could be determined by sterical more than electronic factors as found in carbene complexes.[7,8]

Moreover the hydrazones derived from aldehydes and disubstituted hydrazines are present, in the free state, only as the isomer having the aminic nitrogen *syn* to the aldehydic proton.[9,10]

In this particular isomer, in fact, the substituents at the aminic nitrogen (R^1, R^2) can lie in the same plane of the carbonylic residue allowing the aminic lone pair to become parallel to and overlapping with the –N=C π-system giving rise to hyperconjugation (in the *syn* isomer R^1 does not interact sterically with the aldehydic proton, but it would interact with the R^3 group in the *anti* isomer). The coordination to a metal atom, however, can alter the sterical equilibrium and in some cases it is found that starting from the pure *syn* isomer of an aldehydic hydrazone two isomeric complexes, one with the ligand in the original *syn* configuration and the other with the ligand in the *anti* form, are obtained.[11]

The isomerization of the ligand after complexation has been observed only in the hydrazones with a phenyl radical on the aminic nitrogen, in the other cases the original *syn* configuration is retained.

In order to clarify these points we have carried out the crystal and molecular structure of two platinum–hydrazone complexes: *trans*-[$Pt(C_2H_4)Cl_2(Me_2C=N-NMePh)$] and *trans*-[$Pt(C_2H_4)Cl_2(MeHC=N-NMe_2)$].

Experimental

Preparation of Compounds

The complexes were prepared by reacting in methanol at room temperature Zeise's salt with the appropriate hydrazone. A slight excess of $K[Pt(C_2H_4)Cl_3]$ was always used. After half an hour's stirring the methanolic solution was taken to dryness and the solid residue extracted with dichloromethane. Evaporation of the solvent afforded the desired compound, which was crystallized from diethylether. The analytical data showed them to be pure.

Crystal Data

a) *trans*-[$Pt(C_2H_4)Cl_2(Me_2C=N-NMePh)$], I, M = 456.3, monoclinic, $a = 9.488(8)$ Å, $b = 11.315(8)$ Å, $c = 14.726(9)$ Å, $\beta = 105.2°$, V = 1525.7 Å^3, Z = 4, $D_c = 1.987$, $\mu(\text{Mo-}K\alpha) = 100.0\ \text{cm}^{-1}$, $\mu R = 1.26$, space group $P2_1/c$. b) *trans*-[$Pt(C_2H_4)Cl_2(MeHC=N-NMe_2)$], II, M = 380.2, monoclinic, $a = 6.652(7)$ Å, $b = 11.961(8)$ Å, $c = 7.143(7)$ Å, $\beta = 98.8°$, V = 561.6 Å^3, Z = 2, $D_c = 2.31$, $\mu(\text{Mo-}K\alpha) = 138.96\ \text{cm}^{-1}$, $\mu R = 4.17$, space group $P2_1$.

Intensity Measurements

Three dimensional intensity data were collected on a Siemens diffractometer by the $\Theta-2\Theta$ scan technique with

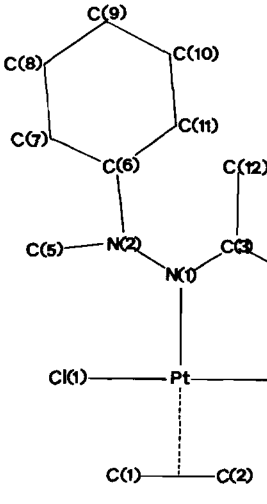


Figure 1. Numbering scheme for complexes *trans*-[$Pt(C_2H_4)Cl_2(Me_2C=N-NMePh)$] and *trans*-[$Pt(C_2H_4)Cl_2(MeHC=N-NMePh)$].

TABLE I. Fractional Parameters (× 10^4) and Temperature Factors for *trans*-[$Pt(C_2H_4)Cl_2(Me_2C=N-NMePh)$] together with Their e.s.d.'s in Parentheses.

	X	Y	Z	B
Pt	2783(1)	1371(1)	1552(1)	[a]
Cl(1)	3812(8)	1450(8)	3140(4)	[a]
Cl(2)	1759(8)	1250(9)	–39(5)	[a]
N(1)	4772(18)	1661(15)	1291(12)	3.4(3)
N(2)	5888(19)	800(19)	1482(13)	4.3(4)
C(1)	676(34)	1548(28)	1750(22)	6.7(7)
C(2)	938(36)	393(30)	1779(23)	7.3(8)
C(3)	5104(24)	2639(22)	877(16)	4.2(5)
C(4)	4042(31)	3658(27)	681(20)	6.1(6)
C(5)	5232(27)	–429(23)	1249(18)	4.8(5)
C(6)	7001(24)	887(23)	2348(16)	4.2(4)
C(7)	7862(26)	–112(23)	2631(17)	4.8(5)
C(8)	9058(31)	40(27)	3499(20)	6.1(6)
C(9)	9294(30)	1116(25)	3942(19)	5.7(6)
C(10)	8431(28)	2098(26)	3655(19)	5.5(6)
C(11)	7206(31)	2004(29)	2850(20)	6.3(7)
C(12)	6481(29)	2805(25)	565(18)	5.5(6)

[a] Anisotropic thermal parameters (× 10^4) are in the form: $\exp[-(B_{11}h^2 + B_{12}hk + B_{13}hl + B_{22}k^2 + B_{23}kl + B_{33}l^2)]$

B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
104(1)	–7(2)	34(1)	111(1)	1(1)	39(1)
185(8)	–40(17)	53(7)	181(9)	10(9)	40(3)
157(9)	–87(19)	–32(9)	269(13)	–10(12)	43(3)

TABLE II. Fractional Coordinates (× 10^3) and Temperature Factors for *trans*-[$Pt(C_2H_4)Cl_2(MeHC=N-NMe_2)$], together with Their e.s.d.'s in Parentheses.

	X	Y	Z	B
Pt	118.1 (2)	250.0	455.0(2)	[a]
Cl(1)	370 (2)	325 (2)	672 (2)	[a]
Cl(2)	–115 (2)	163 (1)	226 (2)	[a]
N(1)	269 (5)	307 (3)	242 (5)	3.3(6)
N(2)	222 (6)	412 (4)	152 (5)	3.8(7)
C(1)	29 (10)	139 (6)	671 (9)	5.8(13)
C(2)	–82 (7)	267 (5)	679 (7)	4.9(10)
C(3)	400 (5)	236 (4)	154 (5)	2.8(6)
C(4)	465 (9)	134 (6)	236 (8)	5.7(12)
C(5)	382 (10)	486 (6)	247 (9)	6.0(13)
C(6)	24 (7)	448 (4)	141 (6)	3.5(8)

[a] Anisotropic thermal parameters (× 10^4) are in the form: $\exp[-(B_{11}h^2 + B_{12}hk + B_{13}hl + B_{22}k^2 + B_{23}kl + B_{33}l^2)]$

B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
174(2)	33(7)	69(3)	52(1)	–23(7)	104(2)
386(36)	–215(38)	55(45)	162(15)	–22(32)	119(20)
287(31)	–91(32)	0(52)	91/(10)	10(33)	257(29)

Mo-$K\alpha$ radiation for a maximum of $2\Theta = 50°$ for I and $2\Theta = 54°$ for II. Since the crystals of compound II tend to decompose under irradiation, a good set of intensity data could not be collected and the structural data are largely affected by errors. It is however still possible to get useful information about the whole geometry of the compound. After discarding reflections having $I_o < 3\sigma(I_o)$ the remaining 1476 (for I) and 866 (for II) independent reflections were corrected for the Lorentz polarization factor. Correction for absorption was applied only for II.

Structure Determination and Refinement

The two structures were solved by conventional Patterson and Fourier methods. The final full matrix refinement (with anisotropic thermal factors for Pt and Cl atoms) gave a conventional index R = 0.066 for I and 0.065 for II. The final weighting schemes were $1/(A + B|F_o| + C|F_o|^2)$ where $A = 30.0$, $B = 1$, $C = 0.0033$ for I and $A = 12.0$, $B = 1$, $C = 0.0077$ for II. The constants were chosen such as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $\sin\Theta/\lambda$.

The numbering scheme for the atoms of both complexes is shown in Figure 1.

The final atomic parameters are listed in Tables I and II, together with their estimated standard deviations, calculated from the residuals and the diagonal elements of the inverse matrix of the last least squares cycle.[12] Atomic scattering factors were calculated according to ref. 13.

Results and Discussion

The crystal structure of both compounds consists of individual monomeric molecules in which the platinum atom is four-coordinate with *trans* chlorine atoms. The hydrazone ligand coordinates through its iminic nitrogen atom, the fourth coordination site being occupied by the ethylene molecule. A view of the molecules along the direction of the platinum–nitrogen bond is shown in Figure 2.

In both cases the N(2)–N(1)=C(3)–C(4) C(12) grouping is nearly planar (0.09°) and the plane passing through its non-hydrogen atoms makes a dihedral angle with the plane of the Pt, Cl(1), Cl(2), N(1) atoms of 70.3° in compound I and 87.7° in compound II. This result shows that intramolecular steric interactions play an important role in determining the orientation of the ligand plane. In fact the different orientation found in compounds I and II is probably due to the different steric requirements of the N-bonded phenyl and methyl groups. Whereas in compound II the balance of the steric interactions among Cl and Me groups determines an angle close to 90° which is also the *a priori* expected one, in compound I the steric interaction between the phenyl and chlorine groups makes the hydrazone ligand deviate by about 20° from the normal orientation.

In Figure 3 the torsional angles around the N–N bond are reported together with those found in the complex *trans*-[$PdCl_2(Me_2C{=}N{-}NMePh)_2$], III.[1]

The approximate directions of the lone pair of the aminic nitrogen atom and of the p-orbitals of the –N=C

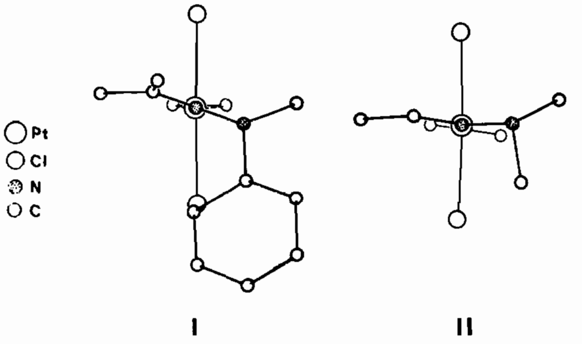


Figure 2. Views of *trans*-[$Pt(C_2H_4)Cl_2(Me_2C{=}N{-}NMePh)$], I, and *trans*-[$Pt(C_2H_4)Cl_2(MeHC{=}N{-}NMe_2)$], II, along the Pt–N(1) bond.

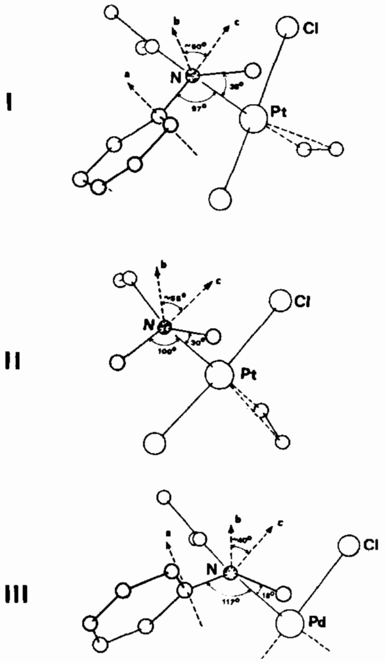


Figure 3. Views of *trans*-[$Pt(C_2H_4)Cl_2(Me_2C{=}N{-}NMePh)$], I, *trans*-[$Pt(C_2H_4)Cl_2(MeHC{=}N{-}NMe_2$], II, and *trans*-[$PdCl_2$ ($Me_2C{=}N{-}NMePh)_2$], III, along the N(1)–N(2) bond. Torsional angles of interest are also reported.

TABLE III. Bond Lengths (Å) and Angles (°) of Interest with Their Estimated Standard Deviations in Parentheses for *trans*-[Pt(C_2H_4)Cl_2(Me_2C=N–NMePh)], I, *trans*-[Pt(C_2H_4)Cl_2(MeHC=N–NMe_2)], II, and *trans*-[PdCl_2(Me_2C=N–NMePh)$_2$], III. For the phenyl group mean values are reported.

	I	II	III
Bond Lengths (Å)			
M–Cl(1)	2.288(6)	2.29(1)	2.298(4)
M–Cl(2)	2.293(7)	2.31(1)	
M–N(1)	2.05(2)	2.07(4)	2.047(12)
M–C(1)	2.10(3)	2.24(5)	
M–C(2)	2.17(3)	2.19(7)	
N(1)–N(2)	1.41(3)	1.41(5)	1.398(19)
N(1)–C(3)	1.34(3)	1.43(5)	1.288(21)
N(2)–C(5)	1.53(3)	1.47(7)	1.493(23)
N(2)–C(6)	1.43(3)	1.37(6)	1.464(20)
C(1)–C(2)	1.33(5)	1.71(9)	
C(3)–C(4)	1.51(4)	1.40(8)	1.49(2)
C(3)–C(12)	1.51(4)		1.49(2)
C–C (phenyl)	1.42(4)		1.38(2)
Bond Angles (°)			
Cl(1)–M–N(1)	91.0(5)	88.8(1)	92.9(2)
Cl(2)–M–N(1)	89.0(5)	88.7(1)	
Cl(1)–M–N(1)^I			87.1(2)
M–N(1)–N(2)	122(1)	122(2)	119.2(7)
M–N(1)–C(3)	123(1)	122(3)	122.9(9)
N(2)–N(1)–C(3)	114(2)	116(3)	117.8(8)
N(1)–N(2)–C(5)	110(2)	103(4)	116.6(7)
N(1)–N(2)–C(6)	118(2)	117(4)	118.9(6)
C(5)–N(2)–C(6)	115(2)	117(4)	109.5(6)
N(1)–C(3)–C(4)	120(2)	120(2)	118.0(6)
N(1)–C(3)–C(12)	125(2)		122.2(8)
C(4)–C(3)–C(12)	116(2)		119.7(7)
N(2)–C(6)–C(7)	117(2)		121.2(9)
N(2)–C(6)–C(11)	119(2)		118.0(8)
C–C–C (phenyl)	120(2)		119.9(9)

and phenyl π-systems are also reported and labelled *b*, *c*, and *a* respectively.

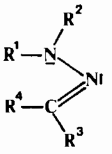
Inspection of the figure shows that in all cases the overlap of the *p*-orbitals within the N–N bond is negligible. Whereas this was the situation of free ligand in Me_2C=N–NMePh (compounds I and III), for MeHC=N–NMe_2 (compound II) a configuration with the aminic lone pair overlapping with the –N=C π-system was assumed to exist in the free state. Therefore it is evident that after complexation also in the latter ligand the aminic group (C(5)–N(2)–C(6)) is no longer coplanar with the carbonylic residue (N(1)=C(3)–C(4)) and there is no reason why only the *syn* isomer of the ligand should exist.

As a matter of fact, with the hydrazone MeHC=N–NMePh the presence after coordination of both the *syn* and *anti* isomers has been observed in solution.[11] With the hydrazone MeHC=N–NMe_2, however, only compound II with the ligand in its original *syn* configuration was obtained either in solid or in solution. In the former case the isomerization, which involves the rupture of a –N=C double bond, could be favoured by the participation of resonance structures with the phenyl radical. The crystal data do not give a clear answer to this point. In fact, while in compound I the angle between directions *a* and *b* is only 14° and could allow a π contribution to the N(2)–C(6) bond, in the compound of the same ligand with palladium (compound III) an angle of 67° was observed.

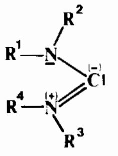
In Table III the bond lengths and angles of interest for compounds I, II, and III are reported.

In compound I the N(1)–N(2) and N(1)–C(3) bond lengths of 1.41(3) and 1.34(3) Å respectively are in accord with the former bond being essentially single and the latter double. In fact for a N–N double bond a value of 1.24(1) Å has been found in a platinum complex with 1-fluorophenyldiazene,[14] and a value of 1.30(1) Å is found in formamidoxime for a nearly double N–C(sp^2) bond.[15] The values reported for the palladium derivative are also in accord with these conclusions.

As far as the platinum–hydrazone bond is concerned, we want to point out that the length of the Pt–N(1) bond which is 2.05(2) and 2.07(4) Å in complexes I and II respectively is comparable with that found in structurally analogous amine complexes of platinum (II), *e. g.* 2.02(19) Å in *trans*-[Pt(C_2H_4)Cl_2($NHMe_2$)],[16] 2.14(3) Å in *cis*-[Pt(*trans*-CH_3CH = $CHCH_3$)Cl_2{(S)-α-phenethylamine}],[17] and 2.076(15) Å in *cis*-[Pt{(S)-1-CH_3CH_2CH = CH_2}Cl_2{(S)-α-phenethylamine}].[18] Therefore the platinum–hydrazone bond has essentially single bond character. It is worth noting that the hydrazone molecule has some structural analogy with carbene ligand.



hydrazone



limiting formula of a carbene

and also in the latter case a platinum–carbon bond length compatible with a substantial single bond character was found.[19]

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