Complexes of Hydrazones with Dichloro(η-ethylene)platinum(II): Stereochemical and Conformational Analysis of the Co-ordinated Ligand

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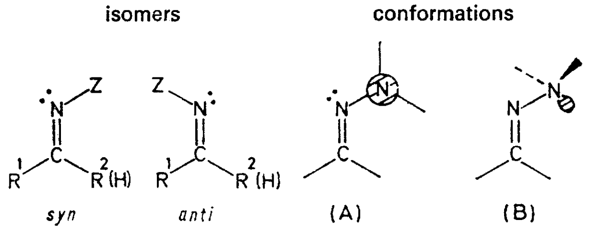
By reaction of the hydrazones (Me_2C:N·NMePh, L^1; MeHC:N·NMe_2, L^2; MeHC:N·NMePh, L^3; EtHC:N·NMe_2, L^4; EtHC:N·NMePh, L^5; and Me_2C:N·NHPh, L^6) with Zeise's salt, complexes of formula *trans*-[$Pt(C_2H_4)Cl_2$(hydrazone)] have been prepared in which the imino-nitrogen acts as donor atom. Of the hydrazones derived from aldehydes, which in the free state are present as pure *syn* isomers, L^2 and L^4 retain their configuration on co-ordination to the metal, while L^3 and L^5 give two isomeric complexes, in one of which the ligand keeps the *syn* configuration, whereas in the other isomerization to the *anti* form occurs (with respect to the C:N double bond). Evidence of rotational isomerism about the N·N bond has been found in the case of L^6. The coupling of the ligand protons with the ^{195}Pt nucleus has been measured and correlated with their relative *cis* or *trans* position about the C:N double bond. A coupling of *ca.* 74 and 27 Hz has been found for the aldehydic proton, *trans* and *cis* to platinum respectively. For the methyl substituents at the carbonylic carbon, a higher coupling constant (11—13 Hz) is observed when the methyl group is *cis* to platinum and a lower one (6—8 Hz) when it is *trans*. This result is discussed in connection with other literature data.

HYDRAZONES can give rise to different geometrical isomers depending on the relative position of the substituents about the C:N double bond. When Z = NHY



(Y = hydrogen, alkyl, or aryl) the hydrazones derived from aldehydes (R^2 = H) are present in solution as *syn* and *anti* isomers. On the other hand, when Z = NMe_2 or NMePh a single (*syn*) isomer is present that does not isomerize on heating or on treatment with acid. Hydrazones derived from ketones are present always as *syn* and *anti* isomers regardless of the nature of Z. On the basis of steric considerations it was assumed[1] that, when Z = NHY, *syn* and *anti* isomers of aldehyde and ketone derivatives have similar conformations, the unshared pair of electrons in both cases being parallel to and overlapping the π orbital of the azomethine bond [conformation (A)]. When Z = NMe_2 or NMePh, only the *syn* isomer of aldehyde derivatives can assume conformation (A); in the *anti* isomer, because of strong non-bonded interactions between R^1 and methyl or phenyl, the unshared electrons would not be parallel with the π orbital [conformation (B)].

In co-ordination to transition metals, hydrazones behave as nitrogen-donor ligands and there is conclusive evidence that the nitrogen atom involved in co-ordination is of imino-type.[2-5] However, it has never been investigated whether the co-ordination affects and/or is influenced by the geometrical and conformational isomerism of these ligands.

EXPERIMENTAL

Preparation of the Ligands.—Acetone methylphenylhydrazone, L^1, and acetone phenylhydrazone, L^6, were prepared according to the method of Marion and Oldfield.[6] They were purified by distillation under reduced pressure: L^1, b.p. 68—70 °C, 31 mmHg; L^6, b.p. 139 °C, 10 mmHg.† Acetaldehyde dimethylhydrazone, L^2, and acetaldehyde methylphenylhydrazone, L^3, were prepared according to reported procedures:[7,8] L^2, b.p. 91—93 °C, 760 mmHg; L^3, b.p. 136—137 °C, 25 mmHg. Propionaldehyde dimethylhydrazone, L^4, and propionaldehyde methylphenylhydrazone, L^5, were prepared in an analogous way to the acetaldehyde derivatives: L^4, b.p. 94—95 °C, 360 mmHg; L^5, b.p. 130 °C, 8 mmHg.

Preparation of Complexes.—The complexes *trans*-[$Pt(C_2H_4)Cl_2L$] (L = L^1, L^2, and L^3) were prepared by adding dropwise a methanolic solution of the pure hydrazone to a slight excess of Zeise's salt, K[$Pt(C_2H_4)Cl_3$], dissolved in the same solvent. After a few minutes, the solution was taken to dryness, the solid residue extracted with CH_2Cl_2, the solvent evaporated under reduced pressure, and the desired complex was obtained as a fine yellow powder. The complex *trans*-[$Pt(C_2H_4)Cl_2L^4$] was prepared in a similar way, but because of its lower thermal stability all solutions were kept at slightly below room temperature (10—15 °C) and a longer reaction time was used (*ca.* 1 h). The complexes *trans*-[$Pt(C_2H_4)Cl_2L$] (L = L^5 and L^6), which are not stable at temperatures above 0 °C, were prepared by reacting in chloroform at −5 °C stoicheiometric amounts of Zeise's dimer [{$Pt(C_2H_4)Cl_2$}$_2$] and the appropriate hydrazone. After stirring for 1 h, the solution was taken to dryness and the product obtained as a yellow powder; because of the instability of the complexes, no further purification was attempted.

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† 1 mmHg ≈ 13.6 × 9.8 Pa.

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Analytical and i.r. data are collected in Table 2. I.r. spectra in the range 300—4 000 cm^{-1} were recorded as KBr pellets with a Perkin-Elmer 456 spectrophotometer; spectra in the range 100—500 cm^{-1} were recorded as Nujol mulls or Polythene pellets with a Beckmann I.R.11 instrument. ^{1}H N.m.r. spectra were obtained with Varian NV 14 (60 MHz) and Bruker (90 MHz) spectrometers with CDCl$_3$ as solvent and tetramethylsilane as internal standard (Tables 1 and 3).

TABLE 1

Proton chemical shifts * (δ in p.p.m., downfield from SiMe$_4$) of free hydrazones

Compound	C$_6$H$_5$	H^1	N·CH$_3$	α(CH$_2$)	α(CH$_3$)	β(CH$_3$)
Me$_2$C:N·NMePh (L^1)	7.5—6.6		2.97		2.07, 1.90	
MeHC:N·NMe$_2$ (L^2)		6.73 (q) (5)	2.73		1.93 (d) (5)	
MeHC:N·NMePh (L^3)	7.5—6.6	6.77 (q) (5)	3.15		2.01 (d) (5)	
EtHC:N·NMe$_2$ (L^4)		6.67 (t) (5)	2.71	2.23 (m) (7, 5)		1.05 (t) (7)
EtHC:N·NMePh (L^5)	7.5—6.6	6.81 (t) (5)	3.17	2.38 (m) (7, 5)		1.15 (t) (7)
Me$_2$C:N·NHPh (L^6)	7.5—6.6				2.07, 1.88	

* All spectra were recorded in CDCl$_3$ solution; ^3J values (in Hz) are given in parentheses. The notation used to distinguish the various protons on the carbonyl residue is the following: (CH$_\alpha$CH$_\beta$)(H^1)C:NZ.

TABLE 2

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

Compound	C	H	N	Cl	$\bar{\nu}$(C:N)	$\bar{\nu}$(Pt·Cl)
trans-[Pt(C$_2$H$_4$)Cl$_2$(Me$_2$C:N·NMePh)] (I)	31.4 (31.6)	4.0 (4.0)	5.9 (6.1)	15.4 (15.5)	1 615m	340vs
trans-[Pt(C$_2$H$_4$)Cl$_2$(MeHC:N·NMe$_2$)] (II)	18.7 (18.9)	3.5 (3.7)	7.3 (7.4)	18.5 (18.6)	1 605m	342vs
trans-[Pt(C$_2$H$_4$)Cl$_2$(MeHC:N·NMePh)] (III)	29.9 (29.9)	3.7 (3.6)	6.2 (6.3)	16.0 (16.0)	1 615m	340vs
trans-[Pt(C$_2$H$_4$)Cl$_2$(EtHC:N·NMe$_2$)] (IV)	21.2 (21.3)	4.0 (4.1)	7.0 (7.1)	17.8 (18.0)	1 605m	345vs
trans-[Pt(C$_2$H$_4$)Cl$_2$(EtHC:N·NMePh)] (V)	31.3 (31.6)	3.8 (4.0)	5.9 (6.1)	15.5 (15.5)	b	
trans-[Pt(C$_2$H$_4$)Cl$_2$(Me$_2$C:N·NHPh)] (VI)	29.7 (29.9)	3.4 (3.6)	6.1 (6.3)	15.9 (16.0)	b	

^{a} Calculated values are given in parentheses. ^{b} Not recorded because of thermal instability of the complex.

TABLE 3

Proton chemical shifts ^{a} (δ in p.p.m., downfield from SiMe$_4$) of *trans*-[Pt(C$_2$H$_4$)Cl$_2$(hydrazone)] complexes

		Ligand protons						
Complex	θ_c/°C	C$_6$H$_5$	H^1	N·CH$_3$	α(CH$_2$)	α(CH$_3$)	β(CH$_3$)	Ethylene protons
(I)	r.t.^{b}	7.5—6.6		3.63		2.91 [^4J(PtH) 12], 2.32 [^4J(PtH) 7]		4.64 [J(PtH) 62]
(II)	−10		7.98 [^3J(HH) 6, ^3J(PtH) 73]	3.15		2.73 [^3J(HH) 6, ^4J(PtH) 13]		4.88 [J(PtH) 62]
(IIIa)	−10	7.7—6.8	7.85 [^3J(HH) 6, ^3J(PtH) 76]	3.68		2.74 [^3J(HH) 6, ^4J(PtH) 13]		4.71 [J(PtH) 63]
(IIIb)		7.7—6.8	8.37 [^3J(HH) 6, ^3J(PtH) 27]	3.60		2.30 [^3J(HH) 6, ^4J(PtH) 8]		4.63 (J(PtH) 62)
(IV)	−20		7.72 [^3J(HH) 6, ^3J(PtH) 74]	3.20	3.30 [^3J(HH) 7, 5]		1.29 [^3J(HH) 7]	4.88 [J(PtH) 62]
(Va)	−20	7.7—6.8	7.72 [^3J(HH) 7, ^3J(PtH) 74]	3.65	3.25 [^3J(HH) 7, 5]		1.25 [^3J(HH) 7]	4.68 [J(PtH) 63]
(Vb)		7.7—6.8	8.17 [^3J(HH) 7, ^3J(PtH) 27]	3.56	2.60 [^3J(HH) 7, 5]		1.22 [^3J(HH) 7]	4.60 [J(PtH) 62]
VI)	−5	7.6—6.6				2.87 [^4J(PtH) 11], 2.38 [^4J(PtH) 6]		4.70 [J(PtH) 61]
	−25	7.6—6.6				2.87, 2.83, 2.37, 2.33		4.68 [J(PtH) 61], 4.65 [J(PtH) 61]
	−45	7.6—6.6				2.88 [^4J(PtH) 11], 2.37 [^4J(PtH) 6]		4.70 [J(PtH) 60]

^{a} All spectra were recorded in CDCl$_3$ solution; J values in Hz. The notation used to distinguish the various protons of the carbonyl residue is the same as in Table 1. ^{b} r.t. = Room temperature.

RESULTS

As observed for osazones,[9] hydrazones do not react with bis(benzonitrile)dichloroplatinum(II) and at high temperature and with long reaction times only partial decomposition of the reagents occurs. However, they do react readily with Zeise's salt giving a 1 : 1 adduct of formula *trans*-[Pt(C$_2$H$_4$)Cl$_2$(hydrazone)] which does not react any further with excess of ligand. The i.r. spectra of the complexes (Table 2) showed, beside the bands due to co-ordinated organic ligand, only one metal–chlorine stretching frequency, indicating that the two halogens are *trans* to each other. The ^{1}H n.m.r. spectra are summarized in Table 3.

The hydrazone Me$_2$C:N·NMePh (L^1), derived from a symmetrical ketone, cannot give different geometrical isomers and according to what has been said previously it should have conformation (B). Its co-ordination to platinum, complex (I), does not cause any structural change and the n.m.r. spectrum showed, beside a complex resonance pattern in the region of aromatic protons (5 H), three signals of equal intensity (3 H) at δ 2.32, 2.91, and 3.63 p.p.m. The first two signals had satellites with ^4J(PtH) 7 and 12 Hz respectively and were assigned to C·Me groups; the third signal at δ 3.63 p.p.m. was assigned to the N·Me protons. Another signal at δ 4.64 p.p.m. [4 H, J(PtH) 62 Hz] was indicative of co-ordinated ethylene. On varying the temperature from −60 to 35 °C no changes or significant shifts of the n.m.r. signals were detected.

The hydrazone MeHC:N·NMe$_2$ (L^2) was prepared in the pure *syn* form; after co-ordination to platinum [complex (II)] it keeps the original *syn* configuration, as could be ascertained by a single-crystal *X*-ray examination [5] in the solid state and by the solution n.m.r. spectrum. The observed coupling constant between the aldehydic proton

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[9] L. Maresca, G. Natile, L. Cattalini, and F. Gasparrini, *J.C.S. Dalton*, 1975, 1601.

and platinum was 73 Hz, and that of the C·Me protons was 13 Hz. The chemical shift and coupling constant of this methyl group were very similar to those of one of the two C-methyls in complex (I), presumably the one *cis* to platinum.

The hydrazone MeHC:N·NMePh (L^3), as with L^2, was also prepared in the pure *syn* form; however, on co-ordination to platinum two isomeric complexes were obtained, which could not be separated in the pure state. The n.m.r. spectrum of the mixture showed two values of chemical shift for each group of equivalent protons. The separation between the two resonances was *ca.* 0.08 p.p.m. for the N·Me and the ethylenic protons and *ca.* 0.5 p.p.m. for the C·Me and the aldehydic protons. The relative intensity of the two different sets of signals did not vary on changing the temperature from −60 to 35 °C; the signals broadened at temperatures above 20 °C, and above 40 °C the complex started to decompose and no further investigation was possible. The coupling constants of the aldehydic and C·Me protons with platinum were 76 and 13 Hz respectively in one set of signals and 27 and 8 Hz in the other set. It is evident that one set of signals is very close to those found in complex (II), and therefore we suggest that they belong to an isomer in which the ligand has kept its original *syn* configuration [complex (IIIa)]. The other set of signals has C·Me resonances very similar to those of the C·Me group *trans* to platinum in complex (I), and the coupling between platinum and the aldehydic proton of only 27 Hz is indicative of their mutually *cis* position; therefore we conclude that the latter set of resonances belongs to a complex isomer in which the ligand has isomerized to the *anti* form [complex (IIIb)]. On treating the isomeric mixture with PPh_3 or $P(OMe)_3$, the free ligand was obtained in its original *syn* configuration.

The two hydrazones L^2 and L^3 differ only in the nature of a substituent at the amino-nitrogen (Me in L^2 and Ph in L^3), and this could be the cause of their different behaviour in co-ordination to platinum. In order to test this hypothesis we prepared two more hydrazones, derived from propionaldehyde, one with the NMe_2 group (L^4) and the other with the NMePh group (L^5). Both hydrazones were prepared as pure *syn* isomers, but whereas L^4 (analogous to L^2) gave only one complex isomer, (IV), the hydrazone L^5 (analogous to L^3) gave rise to two isomeric complexes, (Va) and (Vb), which differ in the configuration of the co-ordinated ligand which is *syn* in the isomer (Va) and *anti* in (Vb). In complex (IV) the coupling constant of the aldehydic proton with platinum is 74 Hz, indicating its *trans* position with respect to the metal atom. The methylenic protons gave a complex resonance in which a quartet of doublets, caused by coupling with the methyl and aldehydic protons, could be distinguished; however, the coupling of these protons with platinum could not be determined. In the isomeric complexes, (Va) and (Vb), the separation between the two resonances arising from each type of equivalent protons was *ca.* 0.08 p.p.m. for the N·Me and the ethylene protons, *ca.* 0.03 p.p.m. for the C·Me protons, and *ca.* 0.6 p.p.m. for the aldehydic and the methylenic protons. The coupling constant of the aldehydic proton with platinum was 74 Hz in (Va) and 27 Hz in (Vb). The relative abundance of the isomers in complex (III) was *ca.* 1 : 1; in complex (V), the ratio (Va) : (Vb) was 4 : 1.

The hydrazone Me_2C:N·NHPh (L^6), derived from a symmetrical ketone, cannot give different geometrical isomers and according to the introduction it should have conformation (A). We allowed this hydrazone to react with Zeise's salt and the n.m.r. spectrum of the complex obtained, *trans*-$[Pt(C_2H_4)Cl_2(Me_2C{:}N{\cdot}NHPh)]$, (VI), below −45 °C showed only one resonance for each type of equivalent protons. On increasing the temperature, another set of resonances appeared, separated by *ca.* 0.04 p.p.m. from the previous peaks. At −25 °C the relative intensity of the two sets was *ca.* 1 : 1 and at −5 °C only one set of resonances was again observed. We believe that the changes in the n.m.r. spectrum are associated with a change in the conformation of the ligand, involving a rotation about the N·N bond. It is likely that the steric repulsion between the phenyl and the other substituents on the metal atom forces the ligand to change its conformation [from (A) to (B)] at various temperatures. On the basis of the spectral data, other possible isomerisms involving the hydrazone [10] or the distribution of the ligands about the metal atom have been ruled out.

DISCUSSION

In previous work the configuration of the free ligands has been assigned mainly by consideration of steric effects and coupling between protons in the hydrazone molecule. In our complexes the ^{195}Pt nuclear spin allows observations of the coupling constant between the metal and the substituents at the carbonylic carbon, in particular ^3J(PtH) between platinum and the aldehydic proton and ^4J(PtH) between the metal and the protons of the substituents at the carbonylic carbon. In unsaturated systems such as organic amides [11] and olefins [12] a larger coupling constant for *trans* over *cis* substituents has been generally assumed. By analogy, in complexes *trans*-$[Pt\{C(O)(NMe_2)\}XL_2]$ (X = Cl, I, or NCO; L = PPh_3, $PMePh_2$, or $AsPh_3$) a value of ^4J(PtH) of less than 2.0 Hz was assigned to the *cis* configuration and a value in the range 5.2—6.3 Hz to the *trans*.[13] In the complexes *cis*-$[Pt\{C(NRH)(NMe_2)\}Cl(PMe_2Ph)_2]$ (R = Me or *p*-tolyl), of the two observed ^4J(PtH) couplings, the higher value (4.5—7.0 Hz) was assigned to the methyl group *trans* to platinum and the lower (3.3—5.4 Hz) to the methyl *cis* to the metal.[14] In *cis*-$[Pt\{C(NHPh)_2\}Cl_2(PPr^n_3)]$ and *trans*-$[Pt\{C(NHMe)_2\}ClL_2][ClO_4]$ (L = PMe_2Ph or PEt_3) the ranges given for ^4J(PtH) were 8—8.4 and 6.4—6.5 Hz respectively for the N·Me groups *trans* and *cis* to the metal. Similarly, the *trans* configuration was assigned to the PtCNH group with the larger coupling constant [^3J(PtH) 80—90 Hz] and the *cis* configuration to that with the smaller coupling (28—33 Hz).[14] Following the criterion of larger coupling for the *trans* group, the *cis* configuration (C) was assigned to the *N*-

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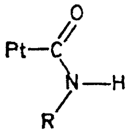
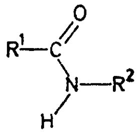
[14] B. Crociani and R. L. Richards, *J.C.S. Dalton*, 1974, 693.

alkylcarboxamido-complexes [Pt{C(O)(NHR)}Cl$(PPh_3)_2$] (R = Me, Et, or Pr^i),[13] in contrast to organic *N*-alkylamides which always have the *trans* configuration, (D), because of steric factors.[15]



(C)



(D)

According to the above suggestions, we would have always expected a larger coupling for substituents *trans* to platinum than for those *cis* to it; however, this does not seem to be the case. In fact, whereas the PtNCH group of hydrazone has a larger coupling constant (*ca.* 74 Hz) when it has the *trans* configuration, the reverse trend is observed for the PtNCCH group which has ^4J(PtH) greater than 11 Hz in the *cis* configuration and less than 8 Hz in the *trans*. Therefore the assumption of ^4J(PtH) being larger in *trans* than in the *cis* configuration is not generally valid, and in some cases, as in the *N*-alkylcarboxamido-complexes,[15] a different assumption concerning the relative magnitude of ^4J(PtH) would have led to less strident formulations.

Isomerization about the C:N bond has been observed for complexes (III) and (V) but not for the analogous (II) and (IV). Moreover, the ratio of the isomers was 1 : 1 in complex (III) and 4 : 1 in favour of the isomer with the ligand in its original *syn* configuration in (V). If the isomerization is caused by steric repulsion between the alkyl substituent at the carbonylic carbon and the metal group, we would have expected a predominance of isomer (Vb) over (Va) since the ethyl group of (V) exerts a higher steric hindrance than the methyl group of (III). The opposite trend is observed. Also the different behaviour of complex (II) with respect to (III) and of complex (IV) with respect to (V) cannot be explained on the basis of steric considerations. Complexes (III) and (V) have larger amino-groups (NMePh) than (II) and (IV) (NMe_2); if a steric interaction is assumed to exist between the amino-group and the alkyl substituents at the carbonylic carbon atom in the *anti* isomer, this configuration of the ligand would be more favoured in complexes (II) and (IV) than in (III) and (V); but this is not the case. Therefore we suggest that electronic rather than steric factors, due to the presence of a phenyl group in complexes (III) and (V), are mainly responsible for the observed phenomenon. In fact the isomerization, which probably occurs through an internal rotation about the C:N bond, requires rupture of the π-electron system and could be favoured by the participation of resonance structures involving the phenyl radical.

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