The $^4J_{PtH}$ Coupling Constant in Platinum–Hydrazone Complexes: Relative Magnitude of the Coupling Constant between an Alkyl Group and a Metal Atom which are Mutually *cis*- and *trans*- with Respect to the Azomethine Double Bond

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Summary The coupling constant between the alkyl protons and the platinum nucleus in $[Pt(C_2H_4)Cl_2(R^1R^2C{:}N{\cdot}NR^3R^4)]$ complexes is higher when the alkyl group is *cis*- to the metal, with respect to the azomethine double bond, than when it is *trans*- to it.

HYDRAZONES are very common condensation products of carbonyl compounds with hydrazines and contain the azomethine bond ($>C{=}N{-}$). The problem of stereoisomerism and the factors which affect isomerization about this bond have already received attention from many authors.[1] Hydrazones co-ordinate to transition metals through imino-type nitrogen[2] giving complex molecules which have some structural analogy with carbene ligands.[3,4]

We have now prepared, by reaction of Zeise's salt with the appropriate hydrazone in methanol, the complexes: *trans*-$[Pt(C_2H_4)Cl_2(Me_2C{:}N{\cdot}NMePh)]$, (**1**); *trans*-$[Pt(C_2H_4)Cl_2(MeHC{:}N{\cdot}NMePh)]$, (**2**); *trans*-$[Pt(C_2H_4)Cl_2(MeHC{:}N{\cdot}NMe_2)]$, (**3**); *trans*-$[Pt(C_2H_4)Cl_2(EtHC{:}N{\cdot}NMe_2)]$, (**4**); and *trans*-$[Pt(C_2H_4)Cl_2(EtHC{:}N{\cdot}NMePh)]$, (**5**). Compounds (**4**) and (**5**) were not stable in solution at room temperature and their preparation and isolation was performed at temperatures near 0 °C. Except for $Me_2C{:}N{\cdot}NMePh$ all the other hydrazones used could give, in the free state, two isomeric forms with the aminic nitrogen *cis*- or *trans*- to the aldehydic proton; isomers *syn*- and *anti*- respectively. However it has been found that in the condensation reaction between aldehydes and hydrazines only the *syn*-isomer is formed, which can assume, without steric strain, the conformation with the aminic lone-pair parallel to and overlapping with the π-orbital of the C:N double bond.[5] Thus we have prepared the complexes starting from the pure *syn*-isomers.

Solution n.m.r. spectra (Table) allow observation of the coupling constant between platinum and the substituents at the carbonylic carbon and these can be related to the geometry of the organic ligand.

Compounds (**1**), (**3**) and (**4**) are present in a unique form in which the ligand keeps its original *syn*-configuration [an *X*-ray crystal structure of complex (**3**) has confirmed this situation of the ligand molecule].[6] Therefore with respect to the C=N double bond the aldehydic proton is *trans*- to platinum [$^3J_{PtH}$ 73 (**3**) and 74 (**4**) Hz] and the methyl group of the acetaldehyde residue *cis*- to it [$^4J_{PtH}$ 13 Hz (**3**)].

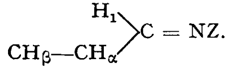
Complexes (**2**) and (**5**), on the contrary, showed a more complex n.m.r. pattern. Two resonances were observed for each type of equivalent protons, therefore two isomers, (**a**) and (**b**), were present in solution. The isomers (**2a**) and (**5a**) had n.m.r. signals strictly analogous, for chemical shift and coupling constant, to those observed in (**3**) and (**4**) respectively and we conclude that in the isomers (**a**) the ligands have kept their original *syn*-configuration. The isomers (**2b**) and (**5b**) showed a $^3J_{PtH}$ of 27 Hz, much smaller than those observed in the (**a**) isomers, which indicates that the aldehydic protons are *cis*- to platinum and that isomerization of the ligand about the C=N double bond occurred.

What at first appears unusual is that the $^4J_{PtH}$ between the methyl group of acetaldehyde and platinum is 8 Hz in (**2b**) and 13 Hz in (**2a**), although in the former case the methyl would be *trans*- to platinum and in the latter case *cis*- to it. Therefore the coupling constant is higher for the *trans*- over the *cis*-isomer for the aldehydic proton, whereas for the methyl group the reverse trend is observed. The correctness of our assignment is confirmed

Table. Proton chemical shift[a] (δ downfield from Me_4Si) of *trans*-$[Pt(C_2H_4)Cl_2(hydrazone)]$ complexes.

		Ligand protons						Ethylene protons
Compound	T/°C	Ph	H_1($^3J_{HH}$,$^3J_{PtH}$/Hz)	N·Me	α-CH_2($^3J_{HH}$/Hz)	α-Me($^3J_{HH}$,$^4J_{PtH}$/Hz)	β-Me($^3J_{HH}$/Hz)	(J_{PtH}/Hz)
(1)	room temp.	7·5–6·6		3·63		2·91 (–, 12), 2·32 (–, 7)		4·64 (62)
(2a)	–10	7·7–6·8	7·85 (6, 76)	3·68		2·74 (6, 13)		4·71 (63)
(2b)		7·7–6·8	8·37 (6, 27)	3·60		2·30 (6, 8)		4·63 (62)
(3)	–10		7·98 (6, 73)	3·15		2·73 (6, 13)		4·88 (62)
(4)	–20		7·72 (6, 74)	3·20	3·30 (7, 5)		1·29 (7)	4·88 (62)
(5a)	–20	7·7–6·8	7·72 (7, 74)	3·65	3·25 (7, 5)		1·25 (7)	4·68 (63)
(5b)		7·7–6·8	8·17 (7, 27)	3·57	2·60 (7, 5)		1·22 (7)	4·60 (62)

[a] All spectra were recorded in $CDCl_3$ solution. The notation used to distinguish the various protons on the carbonyl residue is:



by the n.m.r. spectrum of compound (**1**); in this case the carbonyl residue bears two methyls one *cis*- and the other *trans*- to platinum (this has been also confirmed by *X*-ray crystal data[6]). The spectrum shows two resonances for the methyl protons, one has a chemical shift and coupling constant similar to those of the CMe group in (**2a**) and therefore belongs to the methyl *cis*- to platinum, the other has chemical shift and coupling constant similar to the CMe group in (**2b**) and cannot be other than the resonance of the methyl *trans*- to platinum.

In unsaturated organic molecules such as amides[7] and olefins[8] and in platinum complexes with carboxamido[9] and carbene[4] ligands a higher coupling constant for *trans*- over *cis*-substituents has always been assumed. However, as our results show, this is not always the case.

Compounds (**3**) and (**4**) differ from (**2**) and (**5**), only in having a methyl instead of a phenyl substituent at the aminic nitrogen; we think that in the complexes (**2**) and (**5**) the isomerization about the C=N bond is favoured by the participation of the phenyl radical in the transition state.

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