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Metal–Alkyl Interactions in Some Fluxional *Trans*-Dichlorodihydrazonepalladium(II) Complexes

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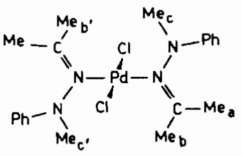
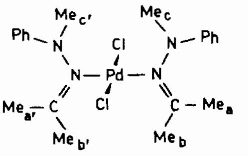
Coordination compounds of hydrazones with transition metals have received considerable attention; many studies have been concerned (i) with bonding and the relations between bonding and the geometrical and conformational isomerisation of the hydrazone ligand [1] and (ii) with metallation reactions [2].

We have already reported the dynamic behaviour of some dichlorobis(hydrazone) complexes of Pd(II) in solution [3]. The recent publication by Natile *et al.* [4] of a variable-temperature NMR study of several such compounds prompts us to publish evidence for a metal–alkyl interaction in some of them, as well as a different interpretation of the NMR evidence.

One interesting feature of the NMR spectra of *trans*-$PdCl_2(Me_2C{=}N{-}NMePh)_2$, **I**, in $CDCl_3$, is that each of the three methyl resonances splits into two signals of equal area upon cooling. This splitting has been assigned by Natile to the existence, in dynamic equilibrium, of the two isomers *syn* ($\mathbf{I_A}$) and *anti* ($\mathbf{I_B}$), which would be generated by a hindered rotation about the Pd–N bonds. But this splitting could just as well originate from the inequivalence of the two hydrazone ligands in any one of the two isomers $\mathbf{I_A}$ and $\mathbf{I_B}$.



I_A



I_B

We checked that all six low-temperature methyl signals keep equal areas throughout the accessible concentration range (0.18 to 0.013 *M*) and that there are no detectable changes in relative peak area when the polarity of the solvent is changed ($CDCl_3$, Toluene, CD_3NO_2), as would be expected if the two sets of signals were due to isomers $\mathbf{I_A}$ and $\mathbf{I_B}$. This strongly indicates that all the signals are likely to belong to the same molecular species, which would then exhibit two non-equivalent hydrazone ligands at low temperature in the solution.

Another feature which deserves attention concerns the differences (Δ) in chemical shifts between the free and coordinated ligands (Table I) which show important antishielding effects, the major cause of which is assigned to the anisotropy of the magnetic susceptibility of palladium. The paramagnetic contribution is indeed known to be a predominant contribution in the ^1H chemical shifts for d^8 planar compounds, and to cause a downfield shift of the protons which are close to the metal and above its coordination plane [5].

The data of Table I show that methyl groups a and a′ experience little influence from the metal. This and the fact that protons a and b (a′ and b′) remain inequivalent even at 90 °C imply that the rotation about the N=C bond is restricted, so that the a(a′) methyl group always remains far from the metal.

The most interesting clue, however, is given by the significantly larger low-field shift observed for proton b and to an even greater extent for proton b′ (respectively 0.64 and 0.95 ppm from the free ligand's shift). This means that they are closer and lie in a more suitable position above the metal's coordination plane, to undergo its antishielding effect. The contact between Pd and H_b in the solid, as calculated from the X-ray structure determination by Natile [6], is very short indeed (2.42 Å).

Thus both the NMR data and the Pd–H_b distance in the solid point to the existence of a so-called "non-bonded" interaction between palladium and protons b′ in compound **I**. Such interactions have already been found in complexes of transition metals with azo or azomethine ligands by Vrieze *et al.* [7], and it was shown by Cotton *et al.* that they can be of considerable strength; thus in $Et_2B(pz)_2$-$Mo(CO)_2(\eta^3$-allyl), for example, the strength of the Mo–H interaction was estimated at 70 kJ mol^{-1} [8]. On the other hand, such interactions are thought to play a part in intermediate stages of the metallation reaction which occurs in palladium complexes of hydrazones bearing an aromatic ketone residue [2].

The originality of the present situation is that compound **I** contains two chemically identical hydrazone ligands which can compete with each other with respect to this metal–alkyl interaction. As a result, at any given moment only one of the two ligands experiences a strong Pd–Me interaction in the solution, as shown by the larger value of Δ measured for b′ than for b protons at –10 °C. The two ligand planes thus form different angles with the

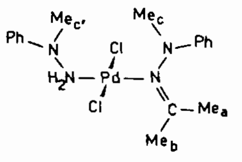
TABLE I. ^{1}H NMR Data for *Trans*-$\mathrm{PdCl_2[PhNMeN{=}CMeR]_2}$ (I, R = Me; III, R = $\mathrm{CHMe_2}$) and *Trans*-$\mathrm{PdCl_2[PhNMeN{=}CMe_2][PhNMeNH_2]}$ (II), in $\mathrm{CDCl_3}$.

Compound		Temp. °C	$\mathrm{C{-}CH_{3b}}$ or $\mathrm{C\mathit{H}(CH_3)_2}$	$\mathrm{C{-}CH_{3a}}$	$\mathrm{CH(\mathit{CH}_3)_2}$***	$\mathrm{N{-}CH_3}$	$\mathrm{NH_2}$
I	δ*	82	2.85	1.98		3.29	
	δ	0	2.70(b) 3.01(b′)	2.30(a) 2.07(a′)		3.20(c) 3.33(c′)	
	Δ**	0	0.64(b) 0.95(b′)	0.13(a) 0.17(a′)		0.25(c) 0.38(c′)	
II	δ	82	3.02	2.12		3.22 (hydrazine) 3.37 (hydrazone)	4.90
	δ	0	3.02	2.20		3.17 (hydrazine) 3.35 (hydrazone)	4.92
	Δ	0	0.96	0.30			
$\mathrm{III_1}$	δ	−13	4.63	1.93	1.13	3.45	
	Δ**	−13	2.09				
$\mathrm{III_2}$	δ	−13	4.63(b) 5.20(b′)	1.93 1.93	1.13(b) 1.37(b′)	3.34(c) 3.44(c′)	
	Δ	−13	2.09(b) 2.70(b′)				

*In ppm relative to TMS. **Δ refers to the chemical shift difference between the resonances of the complex and the free hydrazone. ***$^3J_{\mathrm{H-H}}$ = 6.5 Hz.

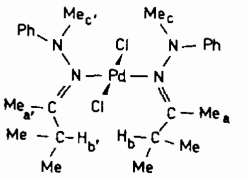
metal coordination plane, and are inequivalent. The ^{1}H NMR enables us to detect, at low temperatures, such a preferential interaction of one of the two ligands. The difference is obliterated above 50 °C, when the resonances of the two ligands have coalesced, indicating that they exchange roles rapidly on the NMR time-scale, with respect to the Pd–Me interaction.

In order to support this interpretation further, we prepared and investigated compound II, *trans*-$\mathrm{PdCl_2(Me_2C{=}N{-}NMePh)(H_2N{-}MePh)}$, in which only one hydrazone ligand is coordinated to palladium so that there is no possible competition between the two ligands with respect to a Pd–Me interaction. It was indeed found that the Pd–$\mathrm{Me_b}$ interaction is strong (Δ = 0.96 ppm). Moreover Δ has the same value as that measured for the most shifted signal b′ in compound I in its "frozen" low-temperature structure. It is also noteworthy that the same chemical shifts were found for N–Me in II and for N–$\mathrm{Me_c}$ in I, while they differ for C–$\mathrm{Me_a}$ in II and C–$\mathrm{Me_a}$ in I. This clearly illustrates that the chemical shifts of $\mathrm{Me_b}$ and $\mathrm{Me_c}$ are primarily influenced by their position with respect to the metal, while the paramagnetic contribution is lower for $\mathrm{Me_a}$, which stands further away from the metal, so that its chemical shift is more sensitive to a change of the ligand in *trans* position on the metal. This interpretation of the differences in chemical shifts is in contradiction to Natile's interpretation, which is essentially based on interactions between ligands.



II

Still further evidence for an intramolecular Pd–$\mathrm{H_b}$ interaction in the hydrazone complexes **I** and **II** was obtained from the study of *trans*-$\mathrm{PdCl_2(PhNMe{-}N{=}CMeiPr)_2}$, **III**, in which two of the C–Me groups had been substituted by isopropyl groups. In this case, and in this case only, do the low-temperature ^{1}H NMR spectra indicate the presence of two isomers in a *ca.* 55/45 ratio in $\mathrm{CDCl_3}$. One of them, $\mathrm{III_2}$, the less abundant, exhibits two sets of signals of equal area, which means that the two



III

ligands are again non-equivalent. In this case the isopropylic proton of one of the non-equivalent ligands undergoes a drastic downfield shift ($\Delta = 2.70$ ppm), and as expected if its origin is due to a Pd–H interaction, this shift is three times larger than in **I** where the effect is averaged on the three protons of the fast-rotating methyl group. The ligands are equivalent in the other isomer, $\mathbf{III}_1$, as shown by the single set of signals observed in the low-temperature NMR. The Me_a groups remain far from the metal in both isomers. The single set of signals detected in the NMR of compound **II** even at low temperature rules out an isomerisation arising from restricted rotation about the N–N bond of the hydrazone ligands. Finally the NMR spectrum of **III** remains unchanged on adding free ligand so that a *cis–trans* isomerisation can also be excluded [9]. This leaves two possible isomers: pseudo-*syn* and pseudo-*anti*, but no obvious assignment of which is which can be made on the basis of the NMR data. Likewise, the NMR data for the only detected isomer of compound **I** are compatible with both pseudo-*syn* and pseudo-*anti* structures in solution.

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