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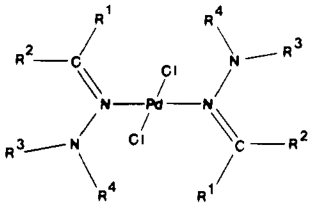
On the Dynamic Behavior of Trans-Dihalide-Bishydrazone-Palladium(II) Complexes

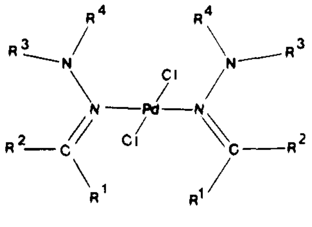
Sir:

A recent article[1] in this journal dealt with the dynamic behavior of *trans*-$PdCl_2(Me_2C{=}NNMePh)_2$ (I) and *trans*-$PdCl_2(Pr^iMeC{=}NNMePh)_2$ (II) and pointed out that (i) in compound I, at low temperature, the two hydrazones are unequivalent as a consequence of the alternating character of the palladium-alkyl interaction with the two ligands; (ii) compound II exists in two isomeric forms, II_1 and II_2, one of which (II_2) reveals unequivalence of the two ligands within the same molecule as I; (iii) a concerted intramolecular exchange mechanism occurring through oscillation of small amplitude about the Pd-N bond, rather than complete rotation of the two ligands about the metal-ligand bonds, is responsible for the fluxionality of I and II_2.

The same arguments[2] were used by those authors to challenge an independent note[3] of ours in which the two sets of NMR signals observed in I, as well as in a whole series of bishydrazone palladium derivatives, were assigned to two rotational isomers (each one having equivalent ligands) differing by mutual orientation of the two hydrazone molecules (isomers A and B).[3,4]



A



B

The two sets of signals of equal intensity observed in I could arise from the same molecular species (either A or B)[5] as well as from two isomers present in equal concentration. However, the presence in I of only one isomer should have been quite suspect since the authors themselves[1] admit that space-filling molecular models indicate that there is no obvious difference between A and B in compound I while isomer B appears more crowded than A in compound II, where both isomers are found in different concentration.

These sterical considerations are by themselves an argument in favor of the existence of the two rotational isomers in equal concentration in compound I; this is strongly supported by the subsequent observation that, by increasing the size of R^1 (R^1 = Me, Et, or Pr^i),[6] one set of signals becomes increasingly more intense ([A]/[B] = 1, 1.6, and 2.7, respectively).

We also looked for more compelling evidence and, assuming that the isomer ratio could be affected by a difference in the substituents at the hydrazone as well as by a difference in the halide ions, we have prepared the bromo analogue of I. The spectra, shown in Figure 1, indicate that the same sets of signals are present in both cases and, since they are not necessarily of equal intensity, they must belong to two isomeric species and not to a single molecule.

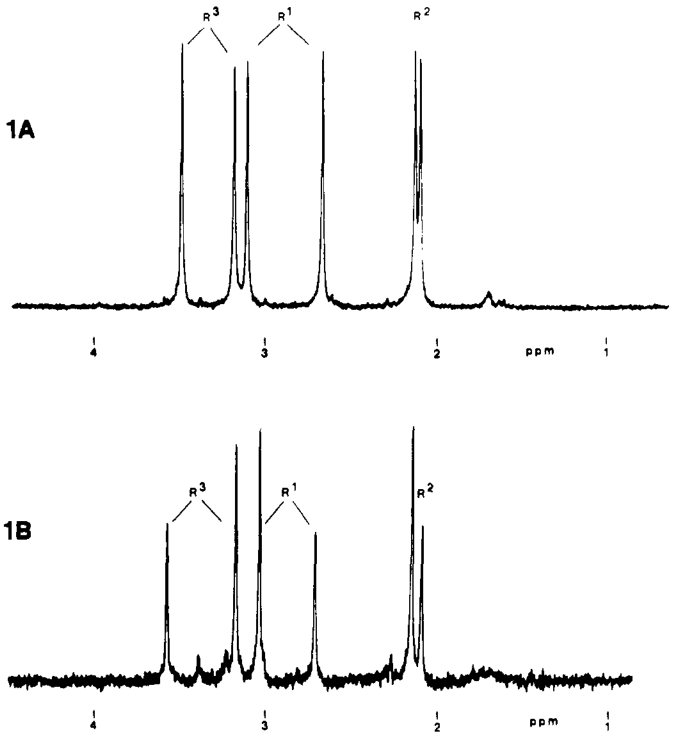


Figure 1. ^1H NMR spectra of *trans*-$PdCl_2(Me_2C{=}NNMePh)_2$ (A) and its bromo analogue *trans*-$PdBr_2(Me_2C{=}NNMePh)_2$ (B) at 90 MHz and 0 °C, solvent $CDCl_3$.

The different intensity of the two sets of signals in the bromo derivative[7] also allows an unequivocal assignment of the signals belonging to each set in compound I; this agrees with our previous assignment[3,4] and is in contrast with that of Postel et al.[1,2]

The behavior of compound II as described by Postel et al.[1,2] did not appear convincing since the only evidence for the presence of a third set of resonances in $CDCl_3$ (instead of the two observed in I and in all other analogous complexes investigated by us) was a splitting by 0.01 ppm in one resonance. They said that the three signals arising from each methyl group were better resolved when the spectra were run in toluene rather than in chloroform, but they did not gave the relative values. We have reinvestigated this compound and, in order to better ascertain any possible splitting, we have run the NMR spectra of solutions of this complex, whose purity was controlled by HPLC,[8] in deuteriochloroform and in deuteriotoluene, at 270 MHz on a Bruker HX 270 instrument.[9] The spectra, shown in Figure 2, indicate that only two sets of signals of intensity ratio 2.7:1 are present either in $CDCl_3$ or in C_7D_8.[10] Therefore, two isomers, none of which shows the dynamic process suggested by Postel, are present.

To show that the separation between the two sets of signals reflects the different situation of the ligands in the two isomers (as determined by the reciprocal influence of the trans ligands) rather than a difference between the two hydrazones in the same molecule, we have prepared the mixed complex *trans*-$PdCl_2(Me_2C{=}NNMePh)(Me_2C{=}NNMe_2)$.[8] The isomer split of the -NMePh hydrazone, which was large in compound I, is small in the mixed complex, since its protons face in both isomers a Me group from the trans ligand. On the contrary, the isomer split of the $-NMe_2$ hydrazone, which was small in *trans*-$PdCl_2(Me_2C{=}NNMe_2)_2$, is large in the present case, since the protons face alternately a Me and a Ph group from

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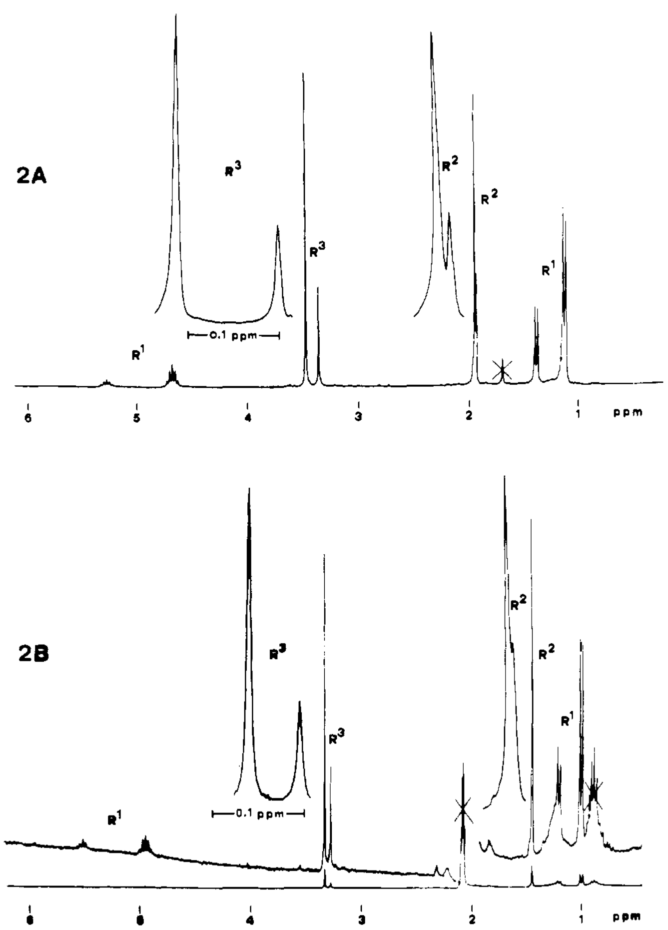

Figure 2. ^{1}H NMR spectra of *trans*-$PdCl_2(Pr^iMeC{=}NNMePh)_2$ at 270 MHz and −10 °C: solvent $CDCl_3$ (A) and C_7D_8 (1000 scans) (B).

the trans ligand.[11]

In conclusion only two sets of NMR signals are present in these complexes in the range of temperature explored. They belong to two rotational isomers, A and B, and not to an intereacting and to a noninteracting hydrazone within the same molecule. Their coalescence necessarily requires a 180° rotation of the ligands about the Pd–N bond. Finally, any discussion on the variation of the chemical shifts of R^1 with temperature cannot be based solely on changes in the paramagnetic contribution of the metal, but changes in the relative influence of the trans ligand must also be considered.

References and Notes

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(5) Authors of ref 1 and 2 say that compounds I and II_2 are expected to have the same structure but leave an open question if they have pseudoanti (A) or pseudosyn (B) conformation.
(6) R^1 = Me and Pr^i refer to compounds I and II of the present text, respectively. R^1 = Et refers to *trans*-$PdCl_2(Et_2C{=}NNMePh)_2$ earlier reported by us; see ref 3 and 4.
(7) Resonances (δ (ppm) from Me_4Si) of R^1, R^2, and R^3 are at 2.72, 2.10, and 3.57 in one set and at 3.04, 2.16, and 3.18 in the other. The first set is assigned to isomer A while the second set is assigned to B; the intensity ratio [A]/[B] is 0.6.
(8) High performance liquid chromatography was carried out under the following conditions: column, LiChrosorb DIOL 10μ, 50 × 0.42 cm i.d.; mobile phase, *n*-hexane–dichloromethane, 85:15 (v/v); flow rate, 2.0 cm^3/min at room temperature; detector R.I. The same technique was used to separate pure *trans*-$PdCl_2(Me_2C{=}NNMePh)(Me_2C{=}NNMe_2)$ from *trans*-$PdCl_2(Me_2C{=}NNMePh)_2$ and *trans*-$PdCl_2(Me_2C{=}NNMe_2)$; see below. F. Gasparrini, D. Misiti, G. Natile, and B. Galli, *J. Chromatogr.*, 161, 356 (1978).
(9) The half band width was <1.5 Hz corresponding to 0.005 ppm.
(10) The resonances in $CDCl_3$ solution (δ (ppm) from Me_4Si; the first value refers to isomer A, the second value to isomer B) of *trans*-$PdCl_2(Pr^iMeC{=}NNMePh)_2$ follow: R^1 (α-H), 4.96 and 5.29; R^1 (β-H), 1.13 and 1.39; R^2, 1.95 and 1.94; R^3, 3.48 and 3.37. The resonances (order same as above) of the same compound in C_7D_8 follow: R^1 (α-H), 4.93 and 5.50; R^1 (β-H), 0.99 and 1.19; R^2, 1.44 and 1.44_5; R^3, 3.32 and 3.27. The splitting of the R^2 protons was not observed by Postel et al.
(11) The resonances (δ (ppm) from Me_4Si; the first value refers to isomer A, the second value to isomer B) of $Me_2C{=}NNMePh$ hydrazone (in compound I) follow: R^1, 2.67 and 3.11; R^3, 3.49 and 3.18. In the mixed complex, they are as follows: R^1, 3.14 and 3.07; R^3, 3.45 and 3.41. The resonances of $Me_2C{=}NNMe_2$ hydrazone (in *trans*-$PdCl_2(Me_2C{=}NNMe_2)_2$) follow: R^1, 3.01 and 3.12; R^3, 2.95 and 2.90. In the mixed complex, they are as follows: R^1, 2.45 and 2.98; R^3, 2.83 and 2.45.

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Formation of Metal Chelates in Secondary Ion Mass Spectrometry. Comparisons with Solution Chemistry

Sir:

We report a new area of application of secondary ion mass spectrometry (SIMS) in that metal chelates can be generated by ion bombardment of surfaces comprised of mixtures of metal salts and organic ligands. Some parallels with organometallic chemistry in solution will also be shown.

Organic molecules can be ionized by metal ion[1] or proton attachment[2] using a primary bombarding ion beam. Admixture of the organic compound (M) with a transition or alkali metal (C) salt is a particularly convenient method of cationizing organic molecules in SIMS.[3] The procedure yields molecular weight information (mass of the cationized molecule $(C + M)^+$), and a fragmentation pattern from which the molecular structure and, in some cases, the site of metal attachment can be inferred.

The possibility of forming gas-phase chelates in this way was tested by admixing 1,10-phenanthroline with $CoCl_2$, bom-

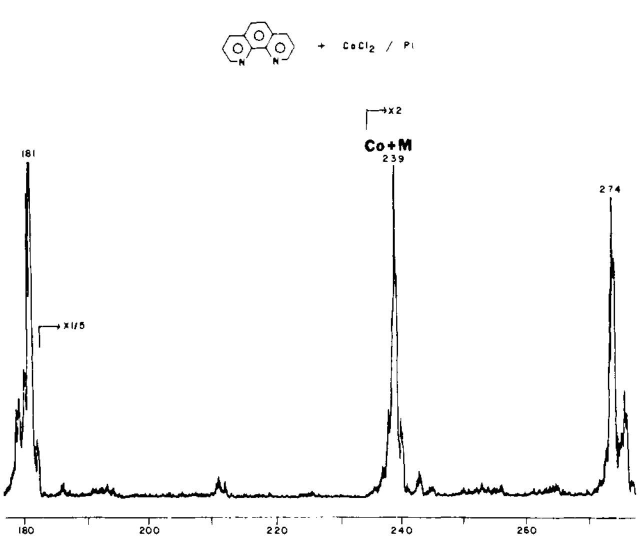

Figure 1. SIMS spectrum (partial) of 1,10-phenanthroline (M) mixed with $CoCl_2$ and supported on platinum showing (i) cationization, $(Co + M)^+$, *m/z* 239, (ii) attachment of a solvated cation to give *m/z* 274 $(CoCl + M)^+$, and (iii) protonation to yield *m/z* 181 $(H + M)^+$.

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