Dichloro-1,2-bis(isopropylseleno)ethanepalladium(II): a Conformational Study by Nuclear Magnetic Resonance

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Summary The temperature-dependent 90 MHz n.m.r. spectrum of dichloro-1,2-bis(isopropylseleno)ethanepalladium(II) has been examined and coalescence phenomena in the spectrum are explained by reference to total chelate ring inversion; the presence, below the coalescence temperature, of a metastable envelope conformation has been detected.

NUCLEAR MAGNETIC RESONANCE spectral studies, in which coalescence phenomena have been explained by reference to inversion about the ligand donor atoms, have recently appeared[1,2] for palladium(II) and platinum(II) complexes of 1,2-bis(alkylthio)ethane ligands. A similar inversion might also be expected to occur in the analogous chelate complexes of bidentate selenium ligands. However, we find that for dichloro-1,2-bis-(isopropylseleno)ethanepalladium(II), (I), an alternative explanation based on total chelate ring inversion is more plausible.

The room temperature 60 MHz n.m.r. spectrum of (I) has already been briefly reported[3] but little information could be obtained from it because of the low solubility of the compound in acetone and the relatively poor resolution of the spectrometer. Using better instrumentation we have examined the 90 MHz n.m.r. spectrum of nitrobenzene solutions of (I) over a wide temperature range up to and beyond the coalescence temperature. A spectrum, representative of those obtained well below the coalescence temperature, is shown in Figure 1. Three separate regions were apparent in this spectrum: absorptions arising from the isopropyl methyls at τ 8·0—8·3, those from the ring methylene protons at 6·1—6·8, and those from the isopropyl methine protons at 5·7—6·1. The methylene part of the spectrum consisted of two partially superimposed AA′BB′ multiplets, 1 and 2 of relative intensities 1 : 0·68, which coalesced to a single broad peak at about 380 K, thus giving $\Delta G_c^{\ddagger} \simeq$ 80 kJ mol^{-1}. The process was reversible on cooling the sample. Multiplet 1 closely resembled that reported for the 250 MHz n.m.r. spectrum of *N*-deuteriated $\mathrm{Co(en)_3}^{3+}$,[4] and was assigned to the intraconverting pseudo axial–equatorial protons of a puckered chelate ring system with staggered, *i.e. gauche*, methylene groups. Analysis gave the following values for chemical shifts and coupling constants for multiplet 1 at 340 K: $\Delta\nu_{ae}$ 39·6; J_{gem} −11·7; J_{aa}, 4·2; J_{ee}, 1·7; J_{ae}, 4·8 Hz. $\Delta\nu_{ae}$ was temperature dependent and reached a maximum value of 39·6 Hz.

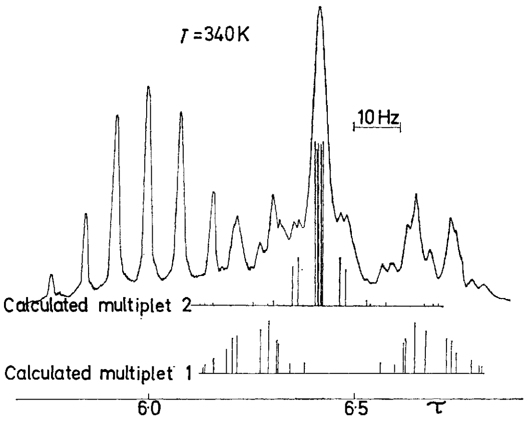

FIGURE 1. 90 MHz n.m.r. spectrum of dichloro-1,2-bis(isopropylseleno)ethanepalladium(II) in nitrobenzene showing absorptions arising from the chelate ring methylene protons and the isopropyl methine protons.

Almost identical multiplets would be expected for *gauche* methylene conformations whether the isopropyl groups were on the same side, *syn*, or on opposite sides, *anti*, of the chelate ring, and therefore the dissimilarity of the two observed multiplets strongly suggested that multiplet 2 could not be assigned to such a *gauche* conformation. Fewer lines could be identified for multiplet 2, and the analysis was necessarily less definite, but gave the following values: $\Delta\nu_{AB}$, 10·2; $J_{AB} = J_{gem}$, −12·1; $J_{AA'}$, 4·4; $J_{AB'}$, 13·1 Hz. The small value of $\Delta\nu_{AB}$ showed that all four protons were in a very similar environment, and the large value for $J_{AB'}$ (*cf.* J_{ae} for multiplet 1) suggested that the dihedral angle ϕ approached 0° for this system.[5] Accordingly we have assigned this multiplet to the eclipsed methylene protons of an envelope conformation with the two carbon atoms both above the $\mathrm{PdSe_2}$ plane, hence removing the protons from the anisotropic effects of the Pd–Se bonds.

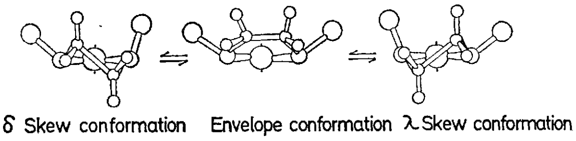

FIGURE 2. Postulated mechanism for the interconversion of the skew conformations.

The solid state molecular structure of (I) consists of a puckered chelate ring with *syn* isopropyl groups[6] and evidence that (I) retains this *syn* conformation in solution comes from a study of the isopropyl absorptions. The isopropyl methyl absorptions apparently consisted of three partially superimposed doublets with a common splitting of 6·9 Hz. The isopropyl methine absorptions superficially resembled a first-order septuplet. However, the relative intensities of the component lines were not as expected and decoupling by irradiation with the isopropyl methyl frequency revealed three absorptions with relative intensities approximately 1 : 1·8 : 1. Coincidentally the 12·7 Hz separations of these absorptions approximated to twice the isopropyl spin–spin splitting. Consequently spin–spin splitting would lead to overlap of the components and a spectrum calculated on such a basis agreed well with the measured component intensities. The centre absorption was assigned to the methine protons of the two identical isopropyl groups of the envelope conformation while the absorptions at higher and lower fields were assigned to the pseudo axial–equatorial isopropyl groups of the *gauche* conformations.

We believe that the observed process is as shown in Figure 2 where interconversion between the n.m.r.-indistinguishable enantiomeric δ and λ skew conformations occurs *via* the intermediate envelope conformation.

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