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Preliminary communication

Molecular asymmetry of π-allylic compounds of transition metals. β-Ketoamine derivatives of π-allylpalladium complexes

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The molecular asymmetry of square planar π-allyl complexes of Pd^{II} has been discussed previously[1]. Complexes of the type I are chiral owing to the non planarity of the allyl ligand with the coordination plane of the metal atom. Moreover if an asymmetrically substituted allyl group is coordinated to the metal the allyl carbon atoms become chiral★. NMR studies carried out on diastereoisomeric complexes I (B = asymmetrical amine) have shown that the two expected diastereoisomers are present in equal amounts in the room temperature equilibrium[1].

We have found by NMR studies that in the room temperature equilibrium for the β-ketoamine complexes II in which the asymmetry is on the chelate ligand, one of the two halves of the allyl ligand may be preferentially bound to the metal. The ratio of the two diastereoisomers depends on the substituent R. As a typical example here we report briefly NMR and X-ray data for (π-methallyl)(2-(*R,S*)-α-phenylethylimino-3-penten-4-olato)palladium (II).

The PMR spectrum run at −50° with a solution of the complex made up in chloroform-*d* at the same temperature, is reported in Fig. 1. When the temperature is raised new signals show up which can be assigned to the other diastereoisomer. At room temperature the two diastereoisomers are present in approximately a 1/2 ratio.

The assignment indicated in Fig. 1 has been made on the ground that the allyl protons *cis* to the nitrogen might be expected to experience a larger difference in the chemical shifts than those *cis* to the oxygen owing to the magnetic anisotropy of the phenyl ring attached to the asymmetrical center of the chelate. According to this assignment the shift difference (0.9 ppm) for the *anti* protons α and α′ can be attributed to the magnetic anisotropy of the phenyl ring, since the α′ *anti* proton of the minor isomer should be closer to the phenyl ring than the corresponding α proton of the major isomer. On the other hand the methyl group of the major isomer is more shielded than that of the minor isomer. These findings can be rationalized assuming structures A and B (Fig. 1) for the major and minor isomer respectively★★. The solid must also have structure

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★Dissymmetrically substituted allyl complexes also give rise to a *syn–anti* isomerization[1,2] in solution.

★★Ring current arguments have recently been used to elucidate the stereochemistry of organometallic complexes[4].

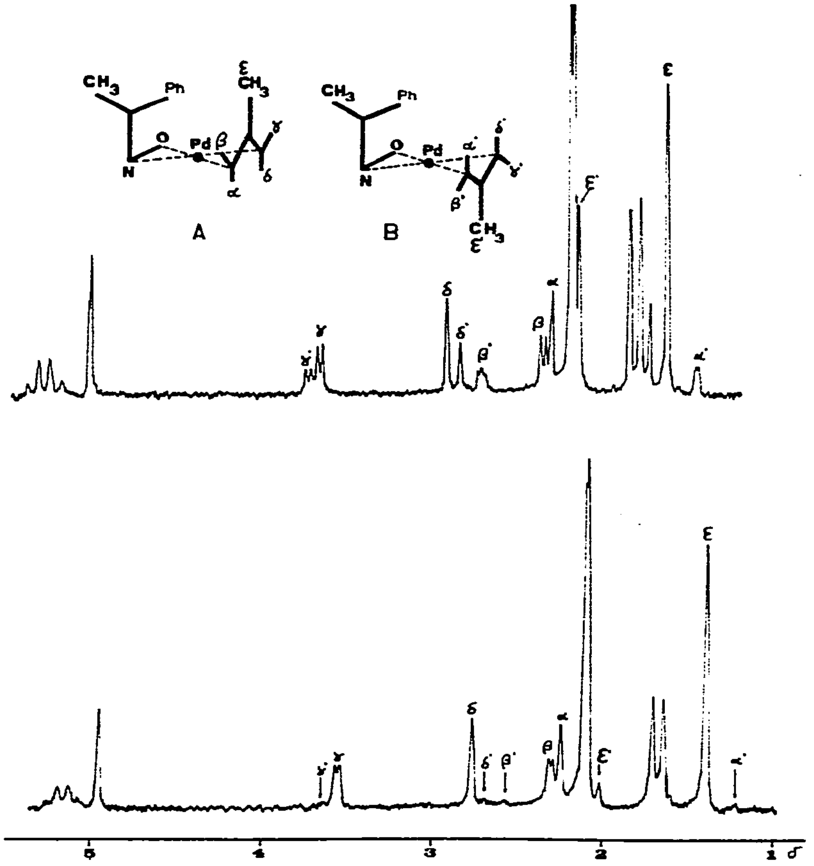


Fig. 1. 100 MHz PMR spectra of II (R = CH_3) in chloroform-*d*. The sample was dissolved at −50° (lower trace) and the solution warmed to room temperature (upper trace). The peaks not labelled belong to the β-ketoamine chelate.

A, since A is the only species present when the crystals are dissolved at low temperatures. This hypothesis has been confirmed by a preliminary X-ray study. The crystal data for $PdC_{17}H_{23}ON$ are : mol-wt. 363, yellow, prismatic, monoclinic; space group $P2_1/c$; a 9.85 ± 0.02, b 10.35 ± 0.02, c 19.34 ± 0.04 Å; β = 124° 13′ ± 15′; Z = 4; $D_{meas.}$ 1.47 $g \cdot cm^{-3}$. $D_{calc.}$ 1.48 $g \cdot cm^{-3}$. 1520 non zero independent reflections were measured with a Siemens four-circle automated diffractomer using Mo-*Kα* radiation. The structure factors were phased by the heavy atom method. The structure was refined by least squares calculations to an *R* value of 0.079. Refinement continues.

In Fig. 2 a preliminary molecular model is shown, and some geometrical parameters are reported. The coordination of Pd is distorted square planar. The conformation about the bond N–C(4) is skew (C(3)–N–C(4)–C(5))–118°, C(3)–N–C(4)–CH_3(4) 116°, as expected for a single bond adjacent to a double bond[3] (C(3)–N 1.28 Å). The phenyl ring and the methyl group CH_3(12) lie on the same side of the plane of coordina-

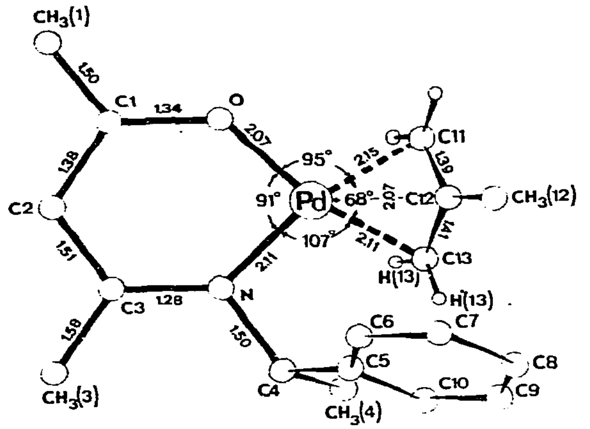
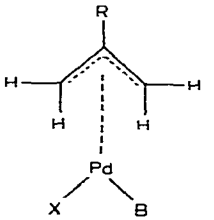
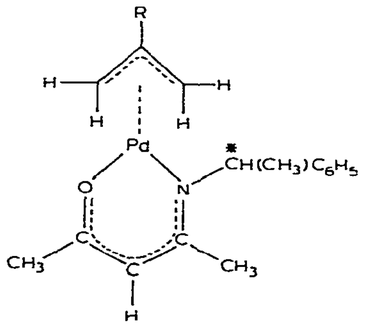


Fig. 2. Schematic structural model of II (R = CH$_3$).



(I)



(II)

tion of the metal atom. The contact distances between these two groups are greater than 4.0 Å. From the molecular conformation in Fig. 2 it turns out that the *syn*-hydrogen H′(13) of the allylic group has shorter contact distances with the phenyl ring than does the *anti*-hydrogen H(13). The structure in Fig. 2 is in agreement with that proposed by NMR for the major isomer which indicates that the NMR analysis of the complexes II will prove useful for establishing the stereochemistry of the coordinated allyl ligand.

Studies on symmetrically and unsymmetrically substituted π-allyl complexes of type II are in progress.

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