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Molecular Asymmetry of π-Allylic Compounds of Transition Metals: A Variable Temperature PMR Investigation on Amine Derivatives of Unsymmetrically Substituted π-Allyl Palladium Complexes

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The pmr spectra of unsymmetrically substituted π-allylPdClamine complexes (amine = (S)-α-phenylethylamine, benzylamine) are temperature dependent. The epimerization or racemization of these compounds, differently from the analogous π-allyl and π-methallyl complexes is interpreted in terms of σ, π-equilibrium.

Introduction

The molecular asymmetry of π-allyl palladium amine complexes has been reported in previous publications.[1,2,3]

One of the two foreseeable diastereoisomers of chloro (1-acetyl-2-methyl-π-allyl)(*S*)-α-phenylethylamine-palladium(II)(**1**) was isolated and found to epimerize rapidly ($\tau \sim 4$ sec) at room temperature.[1,2] In order to clarify the epimerization mechanism by which the allyl group may present either face on coordination to the metal a study on the temperature dependence of the pmr spectra of chloro (π-enyl)(*S*)-α-phenylethylamine Pd^{II} complexes was undertaken. The nmr investigation gave some evidences that for the π-allyl and π-methallyl derivatives a flip of the allyl ligand with respect to the coordination plane of the palladium atom is faster than a σ, π equilibrium.[3a] The proposed flip motion does not exchange *syn* and *anti* substituents differently from the σ, π equilibrium. Here we present an extension of the previous nmr study to unsymmetrically substituted π-allyl complexes, *i.e.*, to systems which are closely related to (**1**).

Experimental Section

NMR spectra were recorded on a Varian A-60 A spectrometer. Calibration of the temperature control unit was accomplished by measuring peak separation of an ethylenglycol sample. The nmr tubes were filled under argon atmosphere.

Materials. The preparations of (1-methyl-π-allylPdCl)$_2$[4] and (1-acetyl-2-methyl-π-allylPdCl)$_2$[5] have been performed according to the procedure described. (1-Phenyl-π-allylPdCl)$_2$, (1-phenyl-2-methyl-π-allylPdCl)$_2$, and (1-carbomethoxy-π-allylPdCl)$_2$ were prepared according to the method described by Dent *et al.*[4] The preparation of the carbomethoxy derivative deserves the following comments: (a) 1,3-dichloropropene was used as the olefin, (b) the reaction time was sufficiently long (18 h) to allow complete carbonylation of the (1-chloro-π-allylPdCl)$_2$ complex firstly formed. The crude reaction product was crystallized from hot toluene.

The purity of all the dimeric compounds was controlled by elemental analysis and nmr spectra.

The amine derivatives of the dimeric π-enylPdCl complexes were generally prepared *in loco* in the nmr tubes by adding stoichiometric amounts of the amine to a chloroform suspension of the dimer. (*S*)-α-phenylethylamine had an optical purity of 95%. Before running the nmr spectra the chloroform solutions have been shaked with D_2O in order to eliminate the $-NH_2$ resonance.

Results and Discussion

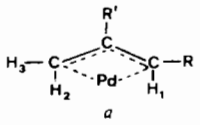
In this section the variable temperature nmr data of some amine derivatives of unsymmetrically substituted π-allylPd complexes will be presented and interpreted with regard to the sterical non rigidity of the coordinated allyl ligand.

The chemical shifts at room temperature and the relative assignments of the benzylamine and (*S*)-α-phenylethylamine derivatives are reported in the Table I and II respectively.

As a general behaviour of all these compounds the signals of the pmr spectra broaden below 0° which

(1) P. Corradini, G. Maglio, A. Musco, and G. Paiaro, *Chem. Commun.*, 618 (1966).
(2) F. De Candia, G. Maglio, A. Musco, and G. Paiaro, *Inorg. Chim. Acta*, 2, 233 (1968).
(3) (a) P. Ganis, G. Maglio, A. Musco, and A. L. Segre, *Inorg. Chim. Acta*, 3, 266 (1969); (b) J. W. Faller, M. J. Incorvia, and M. E. Thomsen, *J. Am. Chem. Soc.*, 91, 518 (1969).
(4) W. T. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.*, 1585 (1964).
(5) G. W. Parshall and G. Wilkinson, *Inorg. Chem.*, 1, 896 (1962).

Table I. Chemical shifts in H_z from TMS of the allylic protons of π-enylPdClbenzylamine in $CDCl_3$ at 60 MH_z



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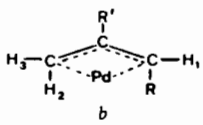
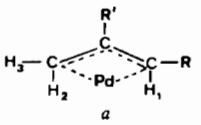


b

π-enyl	H_1	H_2	H_3	R	R′	$J_{1,4}$	$J_{2,4}$	$J_{3,4}$
syn-1-phenyl-π-allyl (*a*, R′=H, R=C_6H_5)	248	228	168	—	341	11.5	12	7
syn-1-phenyl-2-methyl-π-allyl (*a*, R′=CH_3, R=C_6H_5)	232	156	212	—	118	—	—	—
anti-1-phenyl-2-methyl-π-allyl (*b*, R′=CH_3, R=C_6H_5)	330	179	212	—	109	—	—	—
syn-1-methyl-π-allyl (*a*, R′=H, R=CH_3)	207 [a]	145	208	87 [a]	301	12	12	6
syn-1-acetyl-2-methyl-π-allyl (*a*, R′=CH_3, R=$COCH_3$)	204	160	211	132	130	—	—	—
anti-1-acetyl-2-methyl-π-allyl (*b*, R′=CH_3, R=$COCH_3$)	273	226 [b]	221 [b]	132	106	—	—	—

[a] $J_{H_1,CH_3} \sim 6$ H_z; [b] The assignment has been made considering that the H_1 and H_3 resonances have to be broader than the H_2 resonance owing to the long range coupling between *syn* protons. This effect has been previously observed for π-allylPdCl(*S*)-α-phenylethylamine.[3a].

Table II. Chemical shifts in H_z from TMS of the allylic protons of π-enylPdCl(*S*)-α-phenylethylamine in $CDCl_3$ at 60 MH_z



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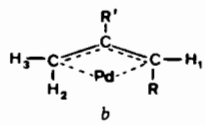


b

	H_1	H_2	H_3	R	R′	$J_{1,4}$	$J_{2,4}$	$J_{3,4}$
syn-1-phenyl-π-allyl (*a*, R′=H, R=C_6H_5)	259-247	169	230	—	343	11	11	7
syn-1-methyl-π-allyl (*a*, R′=H, R=CH_3)	197 [a]	130-133	196	119 [a]	287	12	12	6
syn-1-carbomethoxy-π-allyl (*a*, R′=H, R= $-COOCH_3$)	196	160-172	226	217	347	11	11	7
syn-1-phenyl-2-methyl-π-allyl (*a*, R′=CH_3, R=C_6H_5)	237-244	160-163	217	—	122-125	—	—	—
anti-1-phenyl-2-methyl-π-allyl (*b*, R′=CH_3, R=C_6H_5)	325	260-266	217	—	113-115	—	—	—
syn-1-acetyl-2-methyl-π-allyl (*a*, R′=CH_3, R=$COCH_3$)	207	158-161	207	237	132	—	—	—
anti-1-acetyl-2-methyl-π-allyl (*b*, R′=CH_3, R=$COCH_3$)	274	225-227	214-218	237	106-108	—	—	—

[a] $J_{H_1,CH_3} \sim 6$ H_z.

is an indication that analogously to the π-allyl and π-methallyl complexes, the amine derivatives of unsymmetrically substituted π-allyl complexes are involved in equilibria with the free ligand and the allyl palladium halide dimer.[6] At temperatures as low as −55° in chloroform the amine exchange is still too fast to record the limiting spectrum, thus we cannot say whether and at what extent the amine ligand is *cis* or *trans* with respect to the asymmetrical carbon atom of the allyl group. However, this is not a limitation in our investigation since the amine exchange will not bring about inversion of configuration on the asymmetrical carbon atoms of the allylic group coordinated to the metal.

1-Phenyl-π-allylPdCl(S)-α-*phenylethylamine*(**2**). The pmr spectra of (**2**) at variable temperature are shown in Figure 1. The room temperature spectrum shows that the two diastereoisomers of (**2**) are present within the experimental error in equal amounts. The resonances of H_2, H_3, and H_4 are not differentiated for the two diastereoisomers, whilst H_1 gives rise to an apparent triplet which is the combination of two doublets ($J_{1,4} \sim 12$ H_z) separated by ~ 12 H_z. At higher temperatures[7] (up to 90°) one signal is observed for H_1 while the H_2 and H_3 signals symmetrically collapse. The benzylamine analog of (**2**) behaves in a similar way in the same temperature range, *i.e.* the

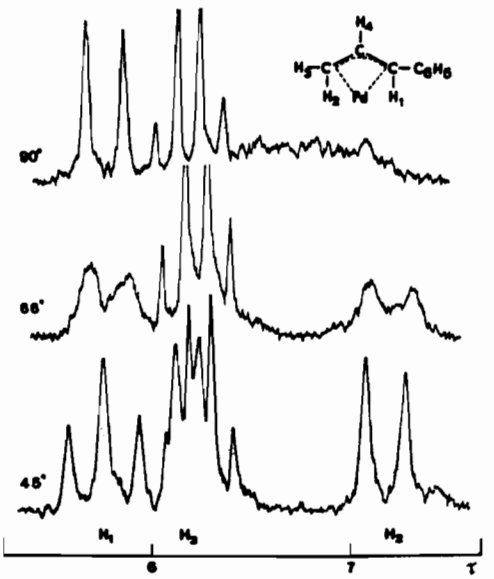


Figure 1. Pmr spectra of 1-phenyl-π-allylPdCl(*S*)-α-phenylethylamine in $CDCl_3$. Only the relevant resonances of the allyl group are shown. The resonance of the amine —CH group is centered at ~6.3 τ.

(6) J. W. Faller and M. J. Incorvia, *J. Organometal. Chem.*, *19*, P 13 (1969).
(7) Hereafter the high temperature limit is to be considered the temperature above which an extensive decomposition occurs.

H_2 and H_3 signals collapse while the H_1 signal remains unchanged. These results suggest that (a) the two diastereoisomers epimerize *via* a σ, π equilibrium; (b) in the short lived σ intermediate the Pd atom is σ bound to the less substituted carbon atom.

1-Carbomethoxy-π-allylPdCl(S)-*α-phenylethylamine*(**3**). The pmr spectra of the diastereoisomeric mixture of (**3**) are reported in Figure 2. Only the H_2 proton shows two different signals separated by ~ 12 H_z for the two diastereoisomers. By increasing the temperature up to 70° a simultaneous collapse of the H_3 and H_2 resonances is observed while no substantial change for the H_1 resonance occurs. Conclusions analogous to those of (**2**) can be drawn from these results. The epimerization of the two diastereoisomers of (**3**) may occurr through a σ, π equilibrium the less substituted carbon atom being σ-bound to the metal in the short lived σ-allyl intermediate.

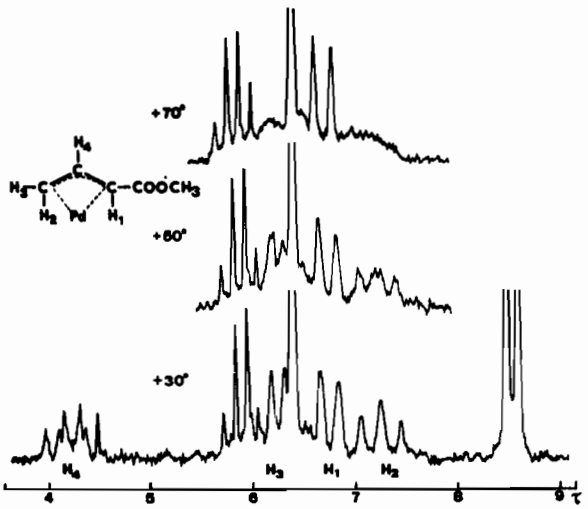


Figure 2. Pmr spectra of 1-carbomethoxy-π-allylPdCl(*S*)-α-phenylethylamine in $CDCl_3$.

1-Methyl-π-allylPdCl(S)-*α-phenylethylamine*(**4**). Analogously to (**3**) at room temperature, only the H_2 protons of the two diastereoisomers of (**4**) are differentiated, the separation being of 3 H_z. At higher temperatures ($\sim 60°$) the H_2 resonances broaden. This broadening, which has been confirmed on the benzylamine analog of (**4**), is due to the onset of the exchange of the H_2 and H_3 protons through a σ, π equilibrium analogous to that proposed for (**2**) and (**3**).

1-Phenyl-2-methyl-π-allylPdCl(S)-*α-phenylethylamine*(**5**). The pmr spectrum of a freshly prepared chloroform solution of (1-phenyl-2-methyl-π-allylPdCl)$_2$ (**6**) is reported in Table III. The assignments have been made by comparing the positions of the resonances of (**6**) with those of (1-phenyl-π-allylPdCl)$_2$. On standing at the probe temperature, other absorptions show up. Half on hour after the solution has been made these absorptions account for about 30% of the intensity of the initial spectrum and do not increase appreciably on further standing. The new absorptions can be assigned to the *anti* isomer of (**6**). An analogous *syn, anti* isomerism has been recently observed by Fong and Kitching for 1-acetyl-2-methyl-π-allyl-PdCl-triphenylphosphine[8] (*vide infra*).

Owing to this *syn, anti* isomerism the room temperature pmr spectrum of (**5**) shows the resonances of two couples of diastereoisomers (Figure 3). However, an assignment (Table II) can be made with sufficient confidence for each resonance. For sake of semplicity we can focus our attention on the resonances of the diastereoisomeric mixture which is generated from the more abundant *syn* isomer of (**6**).

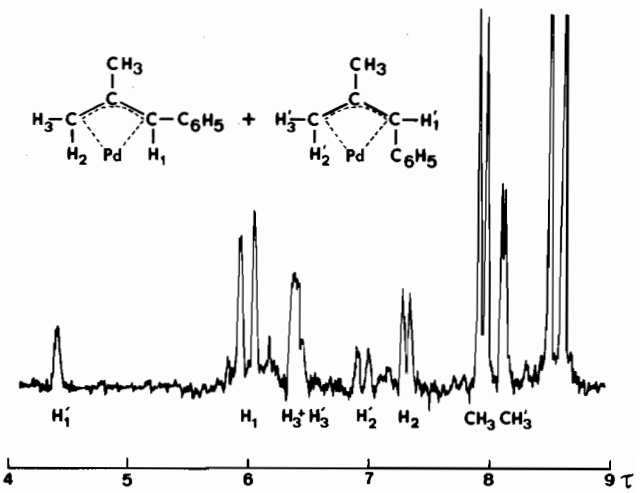


Figure 3. The room temperature pmr spectrum of 1-phenyl-2-methyl-π-allylPdCl(*S*)-α-phenylethylamine in $CDCl_3$.

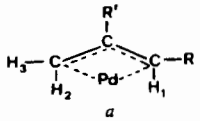
At room temperature two signals separated by 3 H_z for the $-CH_3$ group and two signals separated by 3H_z for the H_2 proton are observed. Proton H_3 is not differentiated for the two diastereoisomers. The H_1 resonance overlap the resonance of the –CH group of the amine. By increasing the temperature ($\sim 100°$) the $-CH_3$ and H_2 resonances merge to only one signal respectively. On the other hand the quality of the spectra is not sufficiently high to establish whether there is any variation of the width at half height for the H_3 resonance. The temperature dependence of the $-CH_3$ and H_2 resonances can be explained either by a σ, π equilibrium or through a rotation of the allyl ligand around the axis containing the terminal carbon atoms. In the case of a σ, π equilibrium there should be an exchange between protons H_2 and H_3 while in the case of a flip motion of the allyl group one signal for the H_2 proton and eventually a sharpening for H_1 and H_3 resonances should be observed.

The possibility of a flip motion of the allyl group has been ruled out by the pmr spectrum of 1-phenyl-2-methyl-π-allylPdClbenzylamine which at 100° is readily interpreted by the onset of a σ, π equilibrium exchanging protons H_2 and H_3.

1-Acetyl-2-methyl-π-allylPdCl(S)-*α-phenylethylamine*(**1**). The room temperature spectrum of (**1**) (Figu-

(8) C. W. Fong and W. Kitching, *Aust. J. Chem.*, 22, 477 (1969).

Table III. Chemical shifts in H_z from TMS of the allylic protons of (π—enylPdCl)$_2$ in $CDCl_3$ at 60 MH_z



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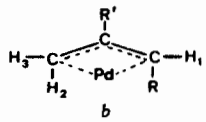


b

	H_1	H_2	H_3	R′
(*syn*-1-phenyl-π-allylPdCl)$_2$ (*a*, R′=H, R=C_6H_5) [a]	265	162	224	328
(*syn*-1-phenyl-2-methyl-π-allylPdCl)$_2$ (*a*, R′=CH_3, R=C_6H_5)	257	157	215	110
(*anti*-1-phenyl-2-methyl-π-allylPdCl)$_2$ (*b*, R′=CH_3, R=C_6H_5)	335	191	224	110

[a] $J_{1,4}\sim 12$ H_z, $J_{2,4}\sim 12$ H_z, $J_{3,4}\sim 6$ H_z.

Table IV. Rate constants [a] and activation free energies [b] for the σ, π rearrangement of π-enylPdClamine complexes

	Temp.	k	ΔF*
syn-1-phenyl-2-methyl-π-allylPdCl(*S*)-α-phenylethylamine	83°	14.1	19.0±0.4
syn-1-phenyl-π-allylPdCl(*S*)-α-phenylethylamine	74°	67.2	17.4±0.4
anti-1-acetyl-2-methyl-π-allylPdCl(*S*)-α-phenylethylamine	62°	32.5	17.4±0.4
anti-1-acetyl-2-methyl-π-allylPdClbenzylamine	67°	26.8	17.8±0.4

[a] sec^{-1}; [b] Kcal/mole.

re (4) shows a *syn, anti* isomerism analogous to that observed for (**5**), thus the signals of two couples of diastereoisomers are observed.[9]

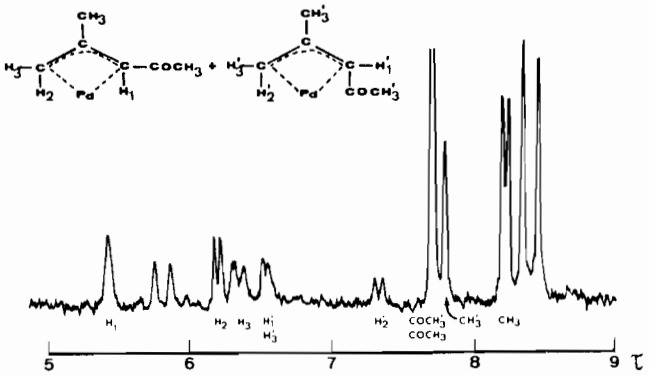


Figure 4. The room temperature pmr spectrum of 1-acetyl-2-methyl-π-allylPdCl(*S*)-α-phenylethylamine in $CDCl_3$.

According to the study made by Fong and Kitching[8] on the triphenylphosphine analog of (**1**) the more abundant isomer should have the acetyl group in *anti* with respect to the methyl group. By increasing the temperature ($\sim$60°) the pmr spectrum of (**1**) undergoes variations similar to those observed for (**5**), *i.e.*, the two signals of the $-CH_3$ group of the central carbon atom merge to only one signal while the H_2 and H_3 resonances coalesce to one broad peak. The high temperature pmr spectra of the benzylamine derivative which are more easily interpretable than those of (**1**) clearly show the onset of a σ, π equilibrium at $\sim$65° (Figure 5).

A complete line shape analysis on the pmr spectra of the compounds here reported was prevented by the difficulty of exploring a sufficiently large range of temperature owing to the low thermal stability of the samples. The rates of the σ, π rearrangement at the coalescence temperature for some of the compounds have been calculated by using the Gutowsky-Holm equation $k = 2^{-1/2}\,\pi\delta\nu$ and are reported in Table IV together with the ΔF* values. It may be pertinent to notice that the value of ΔF* (18.1±1.3 Kcal/mole at 62°) found for (**1**) using the polarimetric data is in sufficient agreement with the pmr value of 17.4± 0.4 Kcal/mole.

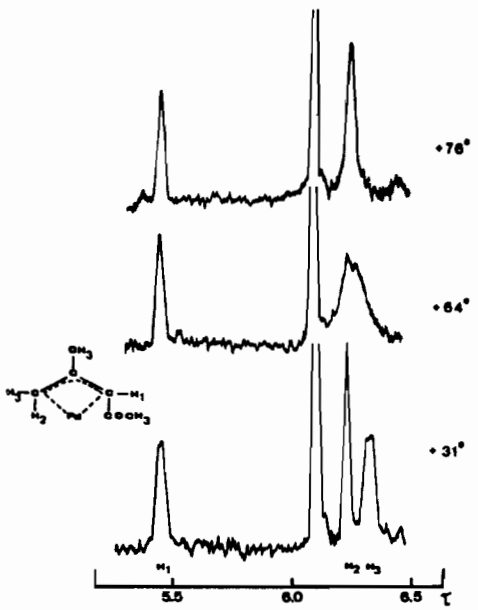


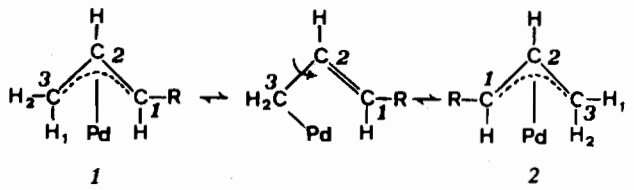
Figure 5. Pmr spectra of 1-acetyl-2-methyl-π-allylPdCl-benzylamine in $CDCl_3$. Only the relevant allyl resonances of the *anti* isomer are shown.

(9) In the early stage of our research[2] a satisfactory explanation for the low intensity absorptions was not given.

Conclusions

The racemization of 1-substituted π-allyl complexes may occurr by any mechanism which allow the allyl group to be alternatively coordinated by either face to the metal.

A racemization mechanism which can be easily visualized is a σ, π equilibrium[10] according to the scheme:



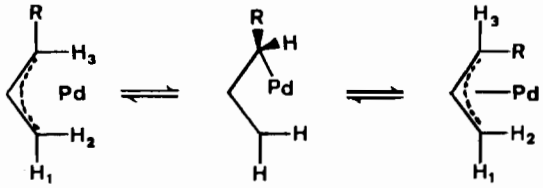
1 *2*

Assuming that in the σ-intermediate the less substituted carbon atom is σ-bound to the metal a rotation around the C_3–C_2 bond brings configuration *1* into the enantiomorphous configuration *2*. For effect of this equilibrium the two hydrogens on C_3 become magnetically equivalent. Another racemization pathway might be a rotation of the allyl ligand around the terminal carbon atoms. At first sight this rotation might appear sterically unacceptable, however it might occurr by a convenient rehybridization of the carbon atoms of the allyl group as it has been proposed for π-allyl and π-methallylPdCl(*S*)-α-phenylethylamine.[3a] A way to test the occurrence of the flip motion of the allyl ligand is to have an optically active ligand coordinated to the metal. The asymmetrical ligand (in our case (*S*)-α-phenylethylamine) is able to discern which face of the allyl ligand is coordinated to the metal.

(10) For a recent paper on σ, π equilibrium of π-allylPd complexes in presence of basic ligands see K. Vrieze, A. P. Praat, and P. Cossee, *J. Organometal. Chem.*, *12*, 533 (1968).

The experimental results here reported on the 1-substituted π-allyl complexes do not show any evidence for a flip of the allyl ligand, but only for a σ, π equilibrium.

Evidences for the rotation of the allyl group around the terminal carbon atoms have been obtained only for symmetrically substituted π-allyl complexes such as π-allyl and π-methallylPdClamine. Probably for the flip motion having a larger rate than the σ, π rearrangement the situations on the terminal carbon atoms of the allyl group have to be perfectly equivalent so that the same rehybridization may occurr on both carbon atoms with the same rate. Finally it might be pertinent to note that the *syn, anti* isomerization reaction for compounds (**1**) and (**5**) occurs very likely through an intermediate in which the asymmetrical carbon atom is σ bound to the metal according to the scheme:



However, the isomerization reaction proceeds at rates much smaller than the σ, π epimerization reaction, since no exchange of the *syn* and *anti* isomers could be observed up to the decomposition temperature of the samples.

Acknowledgments. We thank Mr. N. Lanzetta for extensive assistance in the preparation of the compounds.