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Molecular Asymmetry of π-Allylic Compounds of Transition Metals: Temperature Dependence of the PMR Spectra of Chloro(π-Allyl)(Amine) Palladium(II) Complexes [1]

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The pmr spectra of π-allyl and π-methallylPdClamine (amine = (S)-α-phenylethylamine, benzylamine) are temperature dependent. In the range −60°, +35° the pmr spectra are interpretable with an amine-chlorine exchange. This exchange is responsible for the epimerization or racemization of π-allyl and symmetrically substituted π-allylPdClamine complexes. At higher temperatures (up to 70°) the optically active amine enables to evidence that a flip of the allylic ligand with respect to the coordination plane of the palladium atom is faster than a σ-π equilibrium.

Introduction

In previous publications[3,4] it has been shown that molecular asymmetry occurs whenever a *prochiral* allyl ligand is coordinated to a transition metal. Therefore if a *prochiral* allyl group and an optically active ligand are both coordinated to a transition metal diastereoisomeric compounds are formed. Our studies have been focused on dimeric through halogen bridges π-allyl complexes of Pd^{II} mainly for two reasons a) these compounds are stable b) diastereoisomeric mixtures are readily prepared by splitting the halogen bridges with an optically active ligand.

By crystallizing the diastereoisomeric mixture of chloro(1-acetyl-2-methyl-π-allyl)(*S*)-α-phenylethylamine palladium(II) (**1**) only one diastereoisomer is obtained in quantitative yield[4] through a second order asymmetric transformation.[5] A rapid epimerization is found to occur at room temperature.

A pmr study on (π-enylPdClamine) complexes was undertaken in order to clarify the rearrangment pathway by which the coordination upon the metal may occur on either side of the plane containing the allyl radical, the two positions being enantiomorphous.

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(2a) Università di Napoli.
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(2c) Politecnico di Milano.
(3) P. Corradini, G. Maglio, A. Musco, and G. Paiaro, *Chem. Commun.*, 618 (1966).
(4) F. De Candia, G. Maglio, A. Musco, and G. Paiaro, *Inorg. Chim. Acta*, 2, 233 (1968).
(5) E. L. Eliel « Stereochemistry of Carbon Compounds », McGraw-Hill, New York, N. Y., p. 63 (1962).

Experimental Section

(*S*)-α-phenylethylamine had an optical purity of 95%. The π-enylPdClamine complexes (enyl = allyl, 2-methylallyl; amine = (*S*)-α-phenylethylamine, benzylamine) were prepared according to the method previously described.[4] Nmr spectra were recorded on either a Varian A-60-A or HA-100 spectrometer equipped with a variable temperature probe. Calibration of the temperature control unit was accomplished by measuring peak separation in methanol or ethylene glycol samples. In order to avoid decompositions in the high temperature experiments, the nmr tubes were filled under an argon atmosphere.

Results

The pmr spectrum of π-allylPdCl(*S*)-α-phenylethylamine (**2**) is temperature dependent. Figure 1 shows the spectra registered at 100 MHz in $CDCl_3$ at room temperature and at −50° respectively. The same results aside from slight variations of the chemical shifts are obtained in methanol-d_4 solutions where lower temperatures may be reached. The spectrum at −50° either in CD_3OD or $CDCl_3$ may be considered as the limiting spectrum since no spectral variations are detected below −50° in CD_3OD.

The room temperature spectrum in $CDCl_3$ (Table I) shows one complex resonance for the *syn* protons of relative intensity 2 and two resonances (doublets) each one of relative intensity 1 for the *anti* protons. A better separation of the *syn* protons was achieved in CD_3OD. The entire ABCDX spectral pattern in this solvent has been calculated (Table II). Above 30° the two doublets assigned to the *anti* protons broaden and give rise to one broad doublet around 70° (Figure 2). No broadening is observed, within the experimental error, in the same temperature range for the *syn* protons. At temperatures higher than 70° extensive decomposition occurs. The measurements above room temperature have been performed at 60 MHz in $CDCl_3$, the separation of the *anti* proton absorptions being of 2.9 Hz in this solvent at room temperature. The low temperature spectrum is more complex. In

Table I. Chemical shifts in Hz from TMS of the allylic protons of π-allylPdClamine in $CDCl_3$ at 100 MHz.

Amine	H_x [a]	*syn* protons	Weighted average position *syn* protons	*anti* protons	Weighted average position *anti* protons	T°C
(*S*)-α-phenylethylamine	519.4	370.0	370.0	266.1 — 261.3	263.7	+31
(*S*)-α-phenylethylamine	518.7	395.5 — 357.3	372.2	280.8 — 259.7	266.4	−50
		395.0 — 341.3		280.8 — 244.5		
Benzylamine	523.4	394.6 — 359.4		281.2 — 261.4		−50

[a] H_x is the singular hydrogen of the allyl radical.

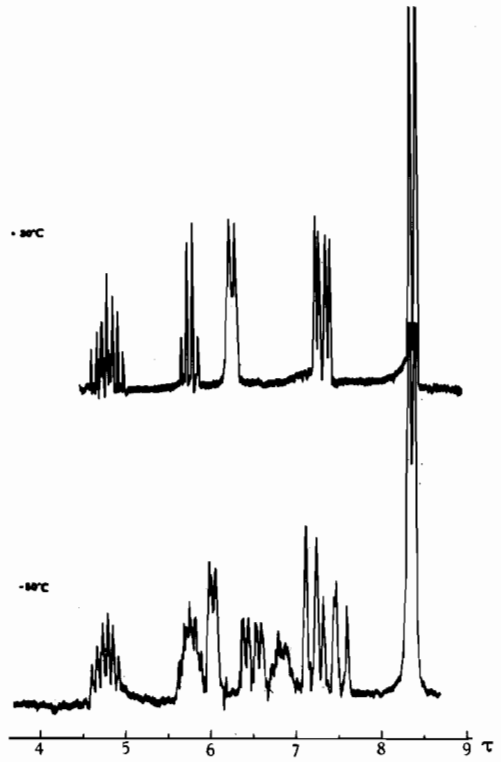
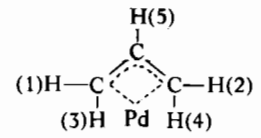


Figure 1. The 100 MHz pmr spectra of π-allylPdCl(*S*)-α-phenylethylamine in $CDCl_3$ at +30° and at −50°. See Table I for the assignment of the allylic protons. The $(\pi\text{-allylPdCl})_2$ absorptions which can be detected at −50° at high spectrometer gain are centered at 6.95 τ (*anti* protons) and 5.95 τ (*syn* protons). All the other absorptions are due to the (*S*)-α-phenylethylamine ligand. The $-NH_2$ protons have been exchanged with D_2O before running the spectra.

both the regions of *syn* and *anti* protons three resonance of relative intensity 2:1:1 appear (Figure 1). The presence of small amounts of π-allyl palladium chloride dimer give rise in the limiting spectrum to low intensity absorptions which disappear at higher temperatures. Owing to this monomer-dimer equilibrium the weighted averages of the chemical shifts of each set of absorptions at −50° slightly deviate from the values observed at room temperature (Table I). Analogous temperature dependence and monomer-dimer equilibrium are observed for π-methallylPdCl(*S*)-α-phenylethylamine (**3**) (Table III). In the limiting spectrum the amount of dimer detected (15%) is conspicuously larger than in the π-allyl case. Again, measurements above room temperature have been performed at 60 MHz. Methanol-d_4, where the separation of the *anti* protons absorptions is of 2.8 Hz at

Table II. Calculated 100 MHz spectrum [a] of π-allylPdCl(*S*)-α-phenylethylamine at 31° in methanol-d_4.



Chemical shifts, Hz (±0.02) from TMS	J Hz(±0.03)
$\nu_{H(1)}$ 320.67	J_{12} ∓2.05
$\nu_{H(2)}$ 316.38	J_{13} ∓0.01
$\nu_{H(3)}$ 204.64	J_{14} ∓0.01
$\nu_{H(4)}$ 212.59	J_{15} ±6.94
$\nu_{H(5)}$ 469.10	J_{23} ∓0.01
	J_{24} ∓0.01
	J_{25} ±6.63
	J_{34} ∓0.01
	J_{35} ±12.31
	J_{45} ±12.16

[a] RMS error 0.1 Hz; the spectrum has been calculated on the 21 experimental lines by using the Bothner-By and Castellano LAOCOON III computer program kindly provided by the authors.

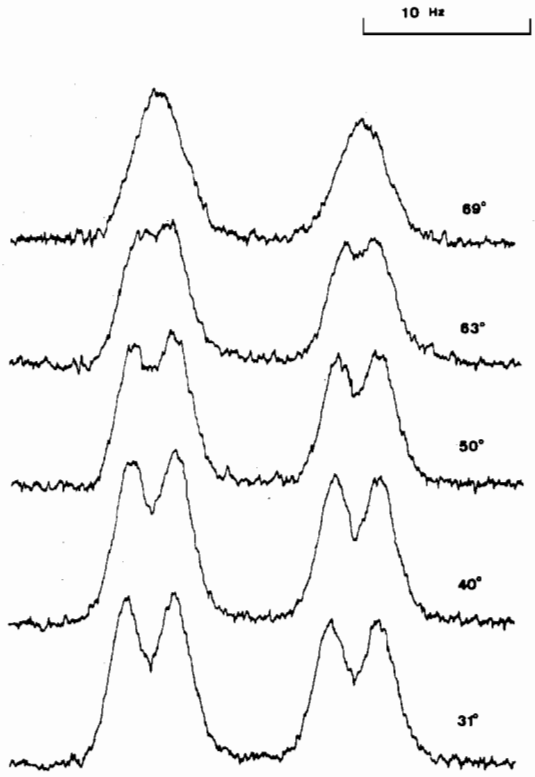


Figure 2. High temperature 60 MHz pmr spectra of the *anti* protons of π-allylPdCl(*S*)-α-phenylethylamine in $CDCl_3$.

Table III. Chemical shifts in Hz from TMS of the allylic protons of π-methallylPdClamine in $CDCl_3$.

Amine	CH_3	*syn* protons	Weighted average position *syn* protons	*anti* protons	Weighted average position *anti* protons	T°C
(*S*)-α-phenylethylamine	184	349.0	349.0	258.6 — 261.1	259.8	+31°
(*S*)-α-phenylethylamine	178	370 — 336 370 — 326	350.5	264 — 252 264 — 246	256.5	—50°
Benzylamine	187.4	373.1 —341.2		268.0 — 254.7		—50°

room temperature, was used as the solvent.[6] Up to 90° only a broadening of the *anti* protons is observed, but differently from (**2**) the coalescence has not yet been reached (Figure 3). At higher temperatures (**3**) decomposes.

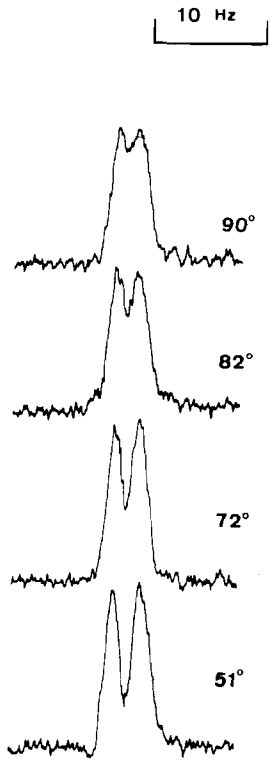


Figure 3. High temperature 60 MHz pmr spectra of the *anti* protons of π-methallylPdCl(*S*)-α-phenylethylamine in CD_3OD.

The room temperature pmr spectrum of π-allyl-PdCl-benzylamine (**4**) in $CDCl_3$ shows one absorption for the *syn* protons and one absorption for the *anti* protons. By increasing the temperature, at 80° a symmetrical, reversible broadening of both *syn* and *anti* protons resonances is quite evident (Figure 4). By lowering the temperature down to −50°, two absorptions for the *syn* protons and two absorptions for the *anti* protons are observed (Figure 5). π-MethallylPdClbenzylamine (**5**) shows analogous behaviour in the low temperature spectra (Table III), whereas no broadening of the *syn* and *anti* protons resonances is detected by rising the temperature up to 95°.

(6) In $CDCl_3$ at 60 MHz and room temperature the *anti* protons give rise to only one broad resonance.

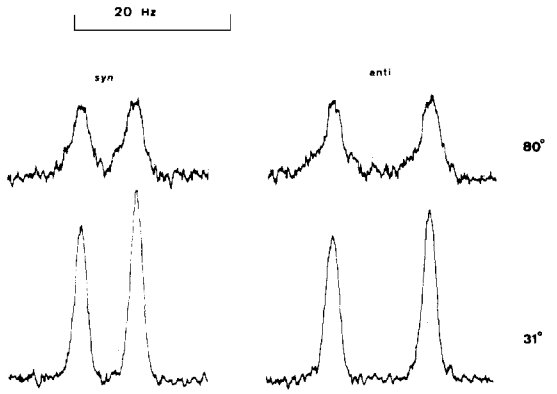


Figure 4. High temperature 60 MHz pmr spectra of the *syn* and *anti* protons of π-allylPdClbenzylamine in $CDCl_3$.

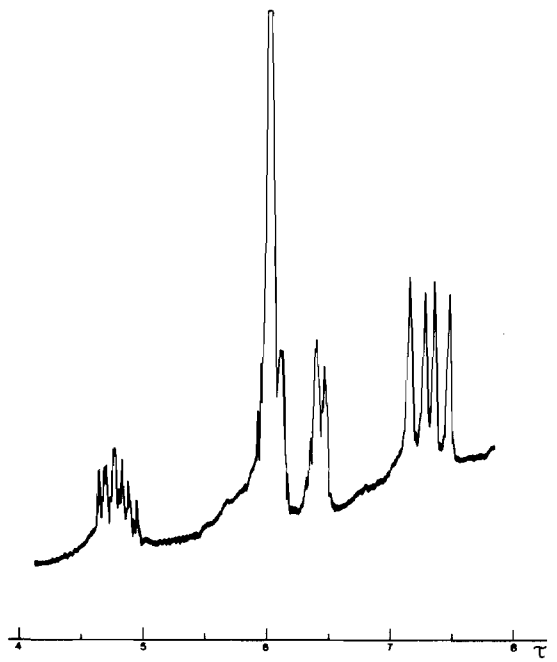


Figure 5. The 100 MHz pmr spectrum of π-allylPdClbenzylamine at −50° in $CDCl_3$. See Table I for the assignment of the allylic protons. The absorption of the methylenic protons of the amine at ~6 τ overlaps one line of the *syn* protons resonances. The $-NH_2$ protons have been exchanged with D_2O.

Discussion

The complex pmr spectrum observed at low temperatures for both (**2**) and (**3**) indicates that two diastereoisomers have to be present in practically equal

amounts (Figure 6; L = (*S*)-α-phenylethylamine). The pmr lines of (**4**) and (**5**) at −50° actually coincide with those of one of the two diastereoisomers of (**2**) and (**3**) respectively. Clearly by using a symmetrical ligand only a racemic mixture is formed (Figure 6; L = benzylamine). The two isomers, regardless of the nature of the ligand L, might more properly be called conformers since one isomer is brought into the other by rotation of 180° either about the vector from the metal to the allyl group,[7-11] or about the axis which contains the C_1 and C_3 carbon atoms. The former rotation is equivalent to an amine-chlorine exchange.

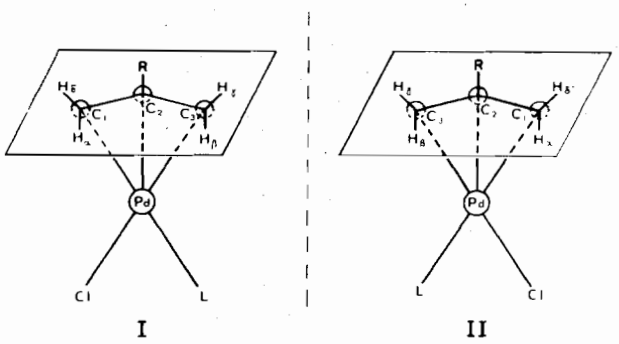


Figure 6. Sketch showing the molecular asymmetry of π-allylPdClamine complexes. R = H, CH_3; L = (*S*)-α-phenylethylamine, benzylamine. $\alpha \neq \alpha'$, $\beta \neq \beta'$, etc., when L is the optically active ligand.

The pmr spectra of (**2**) and (**3**) up to room temperature may be rationalized by an exchange of the two conformers by either one of the two rotations. On the other hand the room temperature spectra of (**4**) and (**5**) are readily interpreted by a rotation around the allyl-metal axis (or by a chlorine-amine exchange) since a rotation around the terminal carbon atoms of the allyl group will not produce any exchange of the protons of the allyl moiety. By analogy, the same kind of rotation might be involved for (**2**) and (**3**). Thus, protons α and β of conformer I exchange with protons β′ and α′, respectively of conformer II (Figure 6; L = (*S*)-α-phenylethylamine). The *syn* protons are involved in an analogous exchange.

Accordingly, the pmr spectra of (**2**) and (**3**) taken at room temperature show two absorptions for the *anti* protons and one broad absorption for the *syn* protons.[12]

Yet, we have to define whether a rotation of the allyl ligand about the allyl metal axis or an amine exchange is the correct exchange mechanism in the temperature range −50°, +35°. However the observation that at low temperatures the pmr spectra of both (**2**) and (**3**) reveal the absorptions of the dimeric π-allylic complexes which disappear by increasing the temperature, does support the amine-chlorine exchange as the most likely mechanism in the above temperature range.

The pmr spectra of (**2**) and (**3**) above room temperature suggest that another averaging mechanism supervenes besides the amine exchange. By increasing the temperature a coalescence of the *anti* protons of (**2**) and a broadening of the *anti* proton of (**3**) is observed, while the widths at half height of the *syn* protons absorptions of both (**2**) and (**3**) remain unchanged. The spectral variations of the *anti* proton absorptions may be explained assuming a rotation of the allyl group about the C_1–C_3 axis. By assuming for sake of simplicity the amine fixed during this rotation, according to Figure 6, (L = (*S*)-α-phenylethylamine), proton α exchanges with α′, β with β′ and since for the previous motion, *i.e.* exchange of the chlorine amine ligands, α exchanges with β′ and β with α′ only one absorption will be observed for the *anti* protons. Analogous spectral variations cannot be detected for the *syn* protons of (**2**) and (**3**) since at 60 MHz, even at room temperature, only one signal is observed for these protons. The rotation around the C_1–C_3 axis is not sterically unacceptable if the motion is observed through the steps indicated in Figure 7. It is known that the conformation of π-1,-

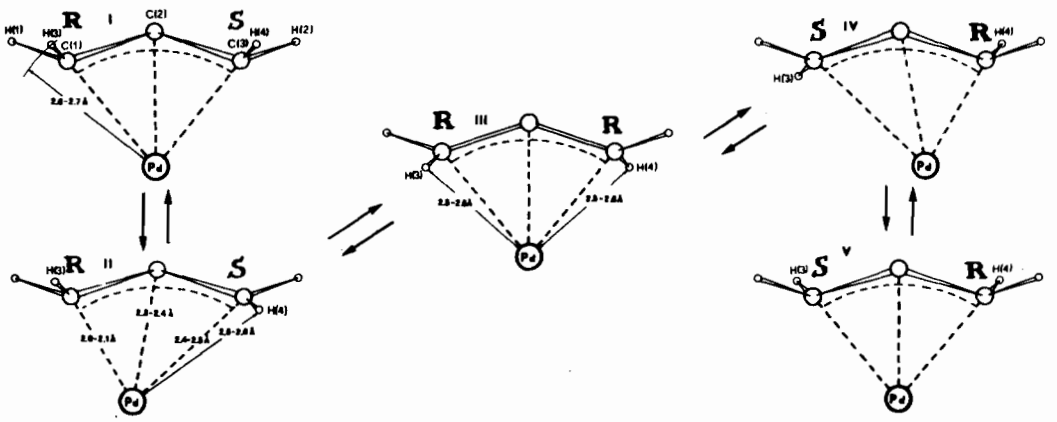


Figure 7. A schematic representation of a possible inversion mechanism of the allylic system by a flip movement. The intramolecular distances and the conformations shown are tentative. Larger or smaller distortions are possible.

(7) A. Davison and W. C. Rode, *Inorg. Chem.*, 6, 2124 (1967).
(8) J. W. Faller and M. J. Incorvia, *Inorg. Chem.*, 7, 840 (1968).
(9) H. Bonnemann, B. Bogdanovic, and G. Wilke, *Angew. Chem. internatl. Edit.*, 6, 804 (1967).
(10) A. N. Nesmeyanov, Yu. A. Ustynyuk, I. I. Kritiskaya, and G. A. Shchembalov,, *J. Organometal. Chem.*, *14*, 395 (1968).
(11) J. K. Becconsall and S. O'Brien, *Chem. Commun.*, 720 (1966).
(12) Actually the *syn* protons give rise to a complex pattern of lines in CD_3OD likely owing to the long range coupling constant J_{12} (see Table II).

1,3,3-tetramethylallylpalladiumchloride dimer[13] is characterized by a *cis* bending of the CH_3CCH_3 planes in such a way that the hybridization of the terminal carbon atoms is intermediate between sp^2 and sp^3. The nonplanarity of the allyl group may be due both to electronic effects as discussed by Kettle[14] for metalcyclic ligand bonds and to steric Pd...CH_3 interactions. Moreover the allyl group makes an angle of 120° with the coordination plane of Pd. By assuming a similar conformation for the amine derivatives an equilibrium may exist between conformations I and II. In conformation II by approaching the C_1 and Pd atoms a dissymetric bonding of the allyl group to the metal is assumed, while the bending in the other terminal carbon atom is strongly attenuated. By using bond angles and bond distances close to those found in literature it is possible to build up a model in which the bending of the $H_4C_3H_2$ plane completely disappears. Some relevant conformational parameters might be the following: Pd–C_1 2.0 - 2.1 Å, Pd–C_2 2.3 - 2.4 Å, Pd–C_3 2.4 - 2.5 Å. We note that the conformation of the allyl group in the step II is very similar to the one found for $C_4H_7PdClP(C_6H_5)_3$[15] and for $(C_6H_5CH_2)(\pi\text{-}C_3H_5)(CO)_2Mo$.[16]

Starting from conformation II and by rotating the $C_1C_2C_3$ plane around the C_1–C_3 axis until this plane becomes coplanar with the PdClamine grouping, the allyl group achieves a symmetrical π-allylic bond (conformation III) characterized by a *trans* bending of the HCH planes. During this rotation the shortest Pd–H distance is of 2.3-2.4 Å which is acceptable considering that in the ground state that distance is of 2.6-2.7 Å. From conformation III the process can continue either restoring conformation I without any inversion of the C_1 and C_3 configurations or, synergically with the amine exchange, going to conformation V through IV which is isoenergetic with II. The conformations V and I differ merely in the configurations of C_1 and C_3. The overall process does not cause any exchange between the *syn* and *anti* protons.

All the above considerations are referred to the results obtained at temperatures not higher than 70°. By further increasing of the temperature (**2**) decomposes, however by rising the temperature from 70° to 80°, (**4**) shows a symmetrical and reversible broadening of the *syn* and *anti* protons. This observation indicates the onset of a σ, π equilibrium for compound (**4**). No such effect can be detected for (**3**) and (**5**) up to 90°. Evidently for the methallyl derivatives the σ, π equilibrium at 90° is still too slow in the n.m.r. time scale to be detected.

Conclusions

The temperature dependence of the pmr spectra of π-allyl and π-methallyl palladium amine complexes evidences three different averaging mechanisms for the protons of the allyl moiety. The mechanism operative at low temperatures (−50°, +35°) merely consist of an exchange of the amine ligand. This exchange is responsible for the racemization (or epimerization) of symmetrically) substituted π-allylPdClamine complexes. The second mechanism which is operative at higher temperatures (+40°, +70°) consists of a flip of the allyl group. The onset a third mechanism, *i.e.* σ, π equilibrium, could be detected only for (**4**). Both the flip of the allyl ligand and the σ, π equilibrium can rationalize the epimerization of asymmetrically substituted π-allylPd complexes such as (**1**). However preliminary variable temperature p.m.r. studies[18] carried out on some asymmetrically substituted π-allyl palladium amine complexes indicate a σ, π equilibrium for these compounds and do not give evidences for a flip of the allyl group. Very likely the different behaviour of the two classes of compounds, *i.e.*, symmetrically and unsymmetrically substituted π-allyl complexes is due to electronic rather than to steric effects.[19]

(13) R. Mason and A. G. Wheeler, *J. Chem. Soc.*, (A) 2543 (1968).
(14) S. F. A. Kettle, *Inorg. Chim. Acta*, *1*, 303 (1967).
(15) R. Mason and D. R. Russel, *Chem. Commun.*, 26 (1966).
(16) F. A. Cotton and M. D. La Prade, *J. Am. Chem. Soc.*, *90*, 5418 (1968).

(17) A σ, π equilibrium in presence of other basic ligands such as phosphines and arsines has been observed by several authors. See for example: a) F. A. Cotton, J. W. Faller and A. Musco, *Inorg. Chem.*, *6*, 179 (1967); b) K. Vrieze, A. P. Pratt and P. Cossee, *J. Organometal. Chem.*, *12*, 533 (1968), and references therein.
(18) G. Maglio, A. Musco, and R. Palumbo, to be published.
(19) While this manuscript was ready for submission Professor J. W. Faller (Yale University) has informed one of us (A. M.) that a similar study was in progress in his laboratory. Our data and Professor Faller's data are in agreement as far as the low temperature range is considered.