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# Molecular Asymmetry of π-Allylic Compounds of Transition Metals: Epimerization Mechanism of Chloro-(l-Acetyl-2-Methyl-π-Allyl)(S)-α-Phenylethylamine Palladium(II)

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*Received May 7, 1968*

*Molecular asymmetry is generated when a prochiral allyl ligand is π-bound to a transition metal. Intermediates in which the allyl ligand is σ bound to the metal or the allyl ligand and the metal are coplanar, are proposed as a rationale for the racemization of optically active π-allyl systems. Polarimetric and thermodynamic data are given for the chloro (1-acetyl-2-methyl-π-allyl) (S-α-phenylethylamine) Pd$^{II}$.*

## Introduction

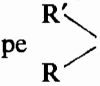
In previous publications[1-3] we have shown that olefins possessing symmetry other than $C_{2v}$ or $D_{2h}$ may be coordinated to a transition metal in two enantiomorphous ways. The same type of asymmetry can be foreseen for π-allylic systems.

A study on this kind of molecular asymmetry was considered worthwhile owing to the importance that π-allylic compounds have in the anionic polymerization of dienes.[4] It is not difficult to foresee that π-allylic compounds, in which the asymmetry is either on the allylic radical or in a substituent coordinated to the metal, might be used as an optically active initiator for stereospecific polymerization of *prochiral* dienes.[5]

Some preliminary data concerning the asymmetry of these types of compounds have been reported in a previous brief communication.[6]

Here we report the polarimetric and thermodynamic data concerning one of the two possible diastereoisomers of chloro-(1-acetyl-2-methyl-π-allyl) (*S*-α-phenylethylamine) palladium(II).

## Results and Discussion

Molecular asymmetry is induced in olefinic complexes when the transition metal atom is π-bonded to an olefin containing *prochiral* trigonal carbon atoms which have to be of the type  $\genfrac{}{}{0pt}{}{R'}{R}\!\!>\!C=$.[7] From this assumption it can be recognized that any 1-substituted allyl radical has to be considered *prochiral*. In Figure 1 only the syn[8] isomer of a *prochiral* allyl ligand is shown.

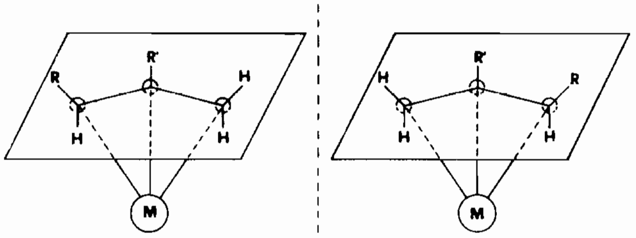


Figure 1. Enantiomers generated on coordination of a *prochiral* allyl ligand to a transition metal. Formally, each carbon atom is σ bonded to the metal.

The literature offered a large spectrum of π-allylic compounds[10] but only a few were suitable for our investigation.

We selected as model compounds the dimeric π-allylic compounds of Pd$^{II}$ with halogen bridges. These are the simplest compounds one can choose and are among the most stable. Furthermore by breaking the halogen bridges with a suitable optically active ligand (phosphine or amine) a mixture of the two possible diastereoisomers is readily obtained. Because the preparation of sufficient amounts of optically active phosphines is not a trivial task,[11] we found it more convenient, for our present purposes, to use the amine ligand α-phenylethylamine.[12]

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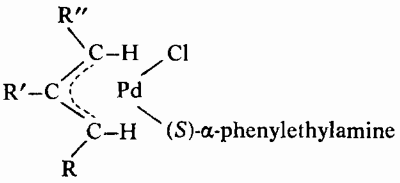
(1) G. Paiaro and A. Panunzi, *J. Am. Chem. Soc.*, *86*, 5148 (1964).
(2) A. Panunzi and G. Paiaro, *J. Am. Chem. Soc.*, *88*, 4843 (1966).
(3) G. Paiaro, R. Palumbo, A. Musco, and A. Panunzi, *Tetrahedron Letters*, *16*, 1067 (1965).
(4) L. Porri, G. Natta, and M. C. Gallazzi, *J. Polymer Sci.*, Part C, 2525 (1967).
(5) G. Natta, L. Porri, and S. Valenti, *Makromol. Chem.*, *67*, 225 (1963).
(6) P. Corradini, G. Maglio, A. Musco, and G. Paiaro, *Chem. Comm.*, 618 (1966).
(7) K. R. Hanson, *J. Am. Chem. Soc.*, *88*, 2731 (1966).
(8) Syn and anti define position of R relative to the substituent on the carbon atom 2. It is posisble to apply to these systems the sequence rules of Cahn, Ingold and Prelog[9] by considering each carbon atom of the allylic radical bonded with a single bond to the metal.
(9) R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem. Internat. Edit.*, *5*, 385 (1966).
(10) M. I. Lobach, B. D. Babitskii, and V. A. Kolner, *Russ. Chem. Rev.*, *36*, 476 (1967).
(11) O. Korpium, K. Mislow, *J. Am. Chem. Soc.*, *89*, 4784 (1967) and references quoted therein.
(12) H. Cruen and B. E. Norcross, *J. Chem. Ed.*, *42*, 268 (1965).

**Table I.** Properties of compounds of formula:



<table>
<tr><th></th><th>R</th><th>R′</th><th>R″</th><th>M.p. [b]<br>(C°)</th><th colspan="2">Pd%</th><th colspan="2">C%</th><th colspan="2">H%</th><th colspan="2">Cl%</th><th colspan="2">N%</th><th>Colour</th></tr>
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<tr><td>I</td><td>H</td><td>H</td><td>H</td><td>105-107</td><td>33.89</td><td>33.54</td><td>42.05</td><td>42.12</td><td>5.09</td><td>5.07</td><td>11.30</td><td>11.24</td><td>4.46</td><td>4.44</td><td>white</td></tr>
<tr><td>II</td><td>$CH_3$</td><td>H</td><td>H</td><td>90-91</td><td>33.47</td><td>33.63</td><td>45.29</td><td>45.09</td><td>5.66</td><td>5.68</td><td>11.67</td><td>11.05</td><td>4.40</td><td>4.52</td><td>white</td></tr>
<tr><td>III</td><td>H</td><td>$CH_3$</td><td>H</td><td>109-112</td><td>33.47</td><td>33.36</td><td>45.29</td><td>45.19</td><td>5.66</td><td>5.68</td><td>11.67</td><td>11.15</td><td>4.40</td><td>4.60</td><td>pale yellow</td></tr>
<tr><td>IV</td><td>H</td><td>$CH_3$</td><td>$COCH_3$[a]</td><td>77-79</td><td>24.34</td><td>23.66</td><td>39.84</td><td>37.83</td><td>4.61</td><td>4.44</td><td>24.33</td><td>24.12</td><td>3.20</td><td>3.34</td><td>yellow</td></tr>
</table>

[a] The compound was crystallized from $CCl_4$. The analytical data are in sufficient agreement with Chloro(1-acetyl-2-methyl-π-allyl) (*S*)-α-phenylethylamine palladium(II) 0.5 $CCl_4$. [b] The compounds melt with decomposition.

The (*S*)-α-phenylethylamine derivatives listed in Table I have been prepared simply by treating a benzene solution of the π-allyl dimeric complexes with stoichiometric amounts of the amine. The crude materials obtained upon evaporation of the solvent can be crystallized from a mixture of chloroform and cyclohexane. The ($\pi$-crotyl $PdCl)_2$ which contains the simplest prochiral allyl radical was found to be unsuitable for our investigation. We have been unable to fractionally crystallize the diastereoisomeric mixture obtained by reaction of the crotyl complex with the optically active amine. On the contrary, the amine derivative of the μ-dichloro-(1-acetyl-2-methyl-π-allyl) $Pd^{II}$ [13] has been resolved in one of the two diastereoisomers by a suitable choice of solvents. The mixture of diastereoisomers was crystallized from $CCl_4$ and gave yellow air-stable crystals which contained $CCl_4$ as an inclusion compound. Similarly, an inclusion compound containing cyclohexane was obtained by crystallizing the diastereoisomeric mixture from chloroform and cyclohexane. In both cases only the (—) diastereoisomer was quantitatively obtained through a «second order asymmetric transformation».[14]

These experimental results are not unusual,[1] however, since the two diastereoisomers have a very similar chemical potential in solution, but the formation of clathrate compound stabilizes preferentially only one of the two foreseeable diastereoisomers. The compound shows a high optical activity $[\alpha]^{-}{}_{D}{}^{70}$—465 (*c*, 3.2, acetone) only at low temperatures. At room temperature the diastereoisomer epimerizes very rapidly and the measured optical activity $[\alpha]_D^{25}$—31.6 (*c*, 3.2, acetone), is probably due only to the coordinated amine.

The rates of epimerization were measured in acetone solutions at various temperatures in the range from —30° to —5°. An agreement was found with the first order rate expression $\frac{dx}{dt} = k(a-x)$ where *x* is the amount of complex epimerized at time t, and *a* is the initial concentration. The integrated form $\log\frac{\alpha_0-\alpha_\infty}{\alpha_t-\alpha_\infty} = k(t-t_0)$ at —17.8°C is shown in Figure 2. $\alpha_0$ is the initial angle of rotation read at time $t_0$, $\alpha_t$ is the angle of rotation read at time t in minutes and $\alpha_\infty$ is the value of the angle of rotation of the completely epimerized product. The angles of rotation were measured at 436 mμ. Table II lists the values of the rate constant $k$[15] obtained at four different temperatures by using acetone as the solvent.

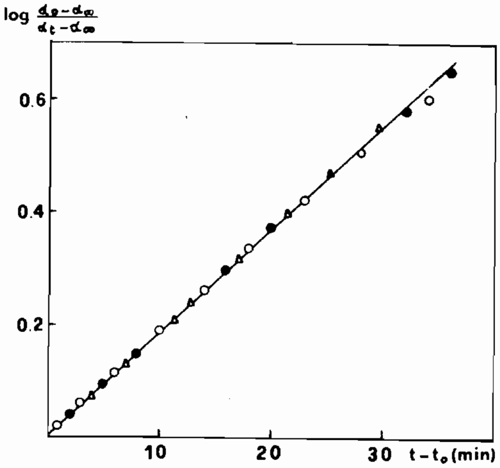

Figure 2. Determination of the reaction order for the epimerization of chloro(1-acetyl-2-methyl-π-allyl)((*S*)-α-phenylethylamine) palladium(II) at three different concentrations in acetone at 18±1°C. $\alpha_0$, $\alpha_t$, $\alpha_\infty$ are the angles of rotation at the times $t_0$, $t_t$, $t_\infty$. The concentrations are $1.16\times10^{-2}$ (○). $3.860\times10^{-3}$ (●), $7.72\times10^{-3}$ *M* (△).

**Table II.** Epimerization rates of Cl(1-acetyl-2-methyl-π-allyl) (*S*)-α-phenylethylamine)$Pd^{II}$

| Temp.<br>°C | $k\times10^3$<br>$sec^{-1}$ |
|---|---|
| — 9 | 2.41 |
| —12 | 1.46 |
| —18 | 0.69 |
| —27 | 0.11 |

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(13) G. W. Parshall and G. Wilkinson, *Inorg. Chem.*, *1*, 896 (1962).

(14) E. L. Eliel, «Stereochemistry of Carbon Compounds», McGraw-Hill, New York, p. 63 (1962).

(15) The first order rate constants were calculated by analysis of the data by a least-squares, first order rate equation program on the IBM 1620.

The Arrhenius activation energy was calculated to be 20.4 ± 1.4 Kcal/mole by plotting the logarithm of the rate constants $k$ as a function of the reciprocal of the absolute temperature (Figure 3). The frequency factor was estimated to be $2 \times 10^{14}$ sec.$^{-1}$. The enthalpy and free energy of activation were calculated at $-18°$: $\Delta H^* = 19.9 \pm 1.3$ Kcal/mole; $\Delta G^* = 18.6 \pm 1.3$ Kcal/mole. Within the accuracy of the data, the entropy of activation at $-18°$ was $\sim 5$ e.u.

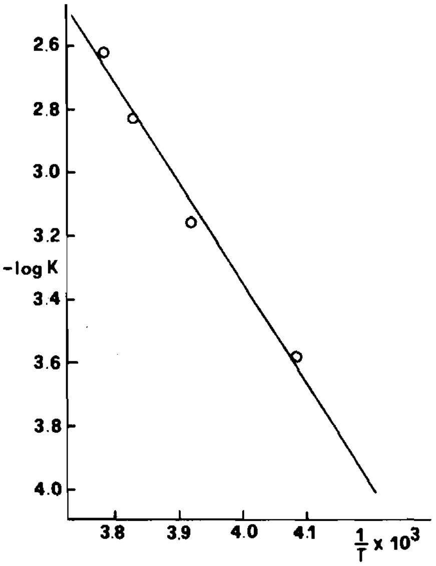


Figure 3. Arrhenius plot for the epimerization of chloro(1-acetyl-2-methyl-π-allyl)(*S*)-α-phenylethylamine) palladium(II).

In the previous short communication[6] an epimerization mechanism was proposed. A σ, π equilibrium was recognized to be operative on the basis of the NMR studies carried out by several workers[16] on the phosphine derivatives.

In order to assess the validity of our previous assumption an NMR study at variable temperature of the complex chloro (π-methallyl)(*S*-α-phenylethylamine) palladium(II) was undertaken.[17] The NMR data, obtained in $CDCl_3$ solution, are reported in Table III. The room temperature spectrum shows only two signals for the *syn* and *anti* protons, τ 6.60 and 7.50 respectively. As the temperature is lowered a symmetrical broadening of the two resonances is observed. At −40° which is the lowest temperature that can be reached before considerable crystallization of the compound occurs, each room temperature signal is split into two broad, but fairly distinct peaks. On the other hand, by rising the temperature up to 90°, even in presence of a fairly high excess of amine no change with respect to the room temperature spectrum is observed.

An exchange of the amine according to the following equilibria accounts for the variable temperature NMR spectra.

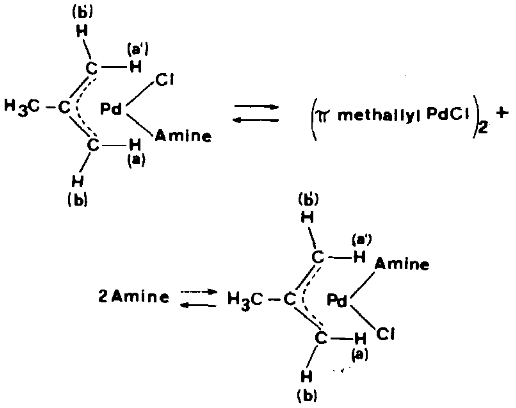
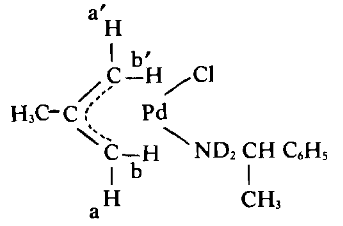


**Table III.** NMR parameters,[a,b] of chloro (π-methallyl) ((*S*)-α-phenylethylamine)[c] palladium(II)



| Temp.[d] °C | Chemical Shifts τ values | |
|---|---|---|
| | a,a' | b,b' |
| 40° | 6.60 | 7.50 |
| −40° | 6.40-6.75 | 7.40-7.60 |

[a] $CDCl_3$ solution. [b] Only the absorption of the methallyl ligand are reported. [c] In order to avoid overlap of the absorption of the $NH_2$ group with those of the syn and anti protons of the allyl ligand the amine has been deuterated by shaking a $CDCl_3$ of the complex with $D_2O$. [d] No change in the NMR spectrum is observed up to 90°.

At high temperature the exchange rate of the amine is fast enough to average the two *syn* and the two *anti* protons respectively. At low temperatures the rate of exchange is lowered so that all the four protons a,a',b,b' are distinguishable. The broadness of the signals at the lowest temperature can be due either to the slow exchange of the amine or to the presence of two diastereoisomers. The asymmetry of the amine allows for the existence of two diastereoisomer with the palladium coordinating on either side of the allyl ligand plane.[18] The base exchange process which is operative at high temperatures has been observed by K. Vrieze[23] *et al.* by using arsines and phosphines as ligands.

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(16) J. Powell and B. L. Shaw, *J. Chem. Soc.*, (A), 1839 (1967) provide a fair number of references on these systems.

(17) An NMR study of the chloro-(1-acetyl-2-methyl-π-allyl)((*S*)-α-phenylethylamine)palladium(II) was thwarted by the presence after several crystallizations of organic impurities which interferred with the genuine signals.

(18) The formation of diastereoisomeric compounds upon coordination of an olefin to the catalyst yelding stereoregular polymers has been put forward by Natta and his school.[19,20] Moreover conformational equilibria in π-allilic systems have been recognized by Davison and Rode[21] and are currently investigated by J. W. Faller.[22]

(19) G. Natta, M. Peraldo, M. Farina, and G. Bressan, *Makromol. Chem.*, 55, 139 (1962).

(20) G. Paiaro, P. Corradini, R. Palumbo, and A. Panunzi, *Makromol. Chem.*, 71, 184 (1964).

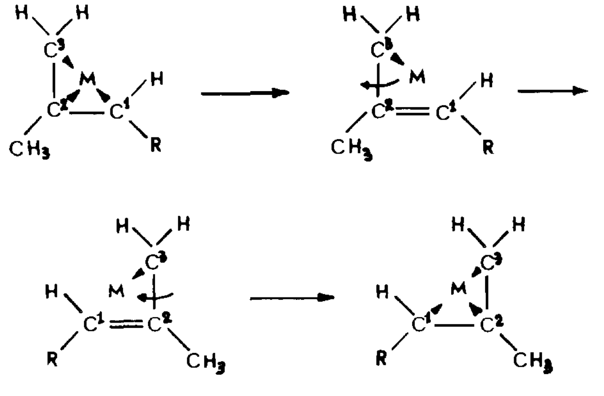
(21) A. Davison and W. C. Rode, *Inorg. Chem.*, 6, 2124 (1967).

(22) J. W. Faller, Yale University, private communication.

(23) K. Vrieze, P. Cossee, C. W. Hilbers, and A. P. Praat, *Rec. Trav. Chim.*, 85, 1077 (1966).

In our case a rapid base exchange does not account for the epimerization process of the chloro-(1-acetyl-2-methyl-π-allyl) ((*S*)-α-phenylethylamine) palladium(II).

Epimerization can occur either by a σ, π equilibrium as outlined in the scheme below or by a fast exchange of the allyl radical. A σ, π equilibrium



should average the *syn* and *anti* protons and give rise to an $A_4X_3$ nmr spectrum typical of a so-called dynamic allyl system. This equilibrium has been observed in presence of other basic ligands,[24] generally phosphines.

Kinetic data obtained polarimetrically on chloro (1-acetyl-2-methyl-π-allyl) (*S*-α-phenylethylamine) $Pd^{II}$ suggest that if a σ, π equilibrium were occurring in the methylallyl case, it should be observable on the n.m.r. time scale (coalescence temperature calculated to be around 100°C). Since no broadening of the n.m.r. peaks is observed on heating the methallyl complex to 90° and providing the two complexes epimerize at similar rates, a σ, π mechanism seems not to be operative. However, another possibility is that the epimerization involves an intermediate in which the allyl moiety becomes coplanar with the metal (Figure 4). Here averaging of *syn* and *anti* protons does not occur. It has been extensively proved by X-ray structural analysis that in (π-allyl $MX)_2$[25] (M = Pd, Ni; X = halogen) complexes the dihedral angle between the metal coordination plane and π-allyl ligand is 110-120°. Nevertheless, as pointed out by Kettle and Mason[26] in the configuration B where allyl ligand and Pd are coplanar, the molecular orbitals of the allyl ligand still overlap with orbitals centered on the metal. From the transition state B the complex can go back either to the configuration A or to the enantiomorphous configuration C.

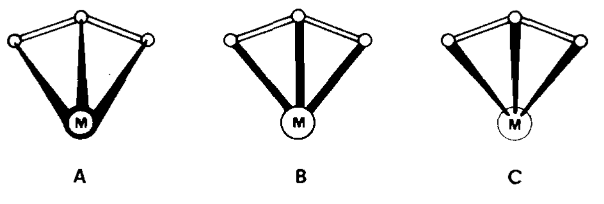


Figure 4. Possible racemization mechanism of a π-allyl complex. In each configuration the allyl ligand is in the plane of the paper. In configuration A the metal atom is above the plane of the allyl ligand. In configuration B, allyl ligand and metal are coplanar. In configuration C the metal atom is below the plane of the allyl ligand.

Further studies on amino derivatives of π-allyl complexes are underway in order to reach conclusive evidence for or against any of these two hypotheses.

## Eperimental Section

Te NMR spectra were measured using a Varian Associates A60A proton nuclear resonance spectrometer equipped with a variable temperature accessory.

The polarimetric measurements have been carried out by an automatic Perkin Elmer 141 polarimeter.

Elemental analyses were performed by A. Bernhardt, Mikroanalitische Laboratorium of the Max-Planck Institut, Mülheim.

*Kinetic Studies.* The temperature of the polarimetric cell was measured directly on the solution by a thermocouple system before and after each kinetic run. The temperature was kept constant within 1°C by circulating ligroin emanating from a conventional cryostat to the cell jacket. The cell windows were swept with nitrogen in order to avoid condensation of water on the surfaces. The chloro-(1-acetyl-2-methyl-π-allyl) (*S*-α-phenylethylamine) $Pd^{II}$ was dissolved in acetone at −70°C and was kept at this temperature until the polarimetric cell was perfectly thermostated.

*Materials.* The dimeric complexes $(\pi\text{-enyl PdCl})_2$ were prepared according to the standard methods (enyl=allyl, methallyl, crotyl,[27] 1-acetyl-2-methylallyl[13])

*Chloro*(*π-enyl*)(*S-α-phenylethylamine*) *Palladium*(*II*). As a typical preparation only the preparation of chloro (π-methallyl) (*S*-α-phenylethylamine) $Pd^{II}$ will be described. In an argon atmosphere 0.60 g of $(\pi\text{-methallyl PdCl})_2$ were dissolved in 15 ml of dry benzene. To the stirred solution 0.4 ml of *S*-α-phenylethylamine ($[\alpha]_D^{25}$ −38.2) were added. The solution was stirred at room temperature for 30 min., then the solvent was removed at reduced pressure. The residue, which is stable in the air, was crystallized from a mixture of chloroform and cyclohexane (1/3) yielding 0.83 g of very pale yellow crystals.

*Acknowledgments.* We are indebted to Professor P. Corradini and to Dr. P. A. Temussi for many helpful discussions and for critical reading of the manuscript.

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(24) F. A. Cotton, J. W. Faller, and A. Musco, *Inorg. Chem.*, *6*, 179 (1967).

(25) M. R. Churchill and T. O'Brien, *Inorg. Chem.*, 6, 1386 (1967) and references quoted therein.

(26) S. F. A. Kettle and R. Mason, *J. Organometal. Chem.*, *5*, 573 (1966).

(27) W. T. Dent, R. Long, and A. J. Wilikson, *J. Chem. Soc.*, 1585 (1964).