## On the Mechanism of Cis–Trans Isomerization for Square Planar Complexes of the Type ML₂X₂

Sir:

Two different mechanisms have been proposed[1–9] for the cis–trans isomerization of square planar complexes of the type ML_2X_2 (M = Pd, Pt; X = uninegative anion and L is a monodentate phosphorus ligand). These are (1) consecutive displacement of anion[1–5] *via* the intermediate $[L_2L'MX]^+$, where L′ is a catalyzing base, and (2) fluxional rotation *via* the intermediate or transition state $[ML_2L'X_2]$ in which there exists a unique M–L′ bond.[6–9] We have found evidence which supports both of these mechanisms[5] as well as a third[5] involving consecutive displacement of the ligand, L. Job's law studies[10] show that when various bases are added to solutions containing ML_2X_2, new species are formed in solution. Conductometric titrations with the same reagents have shown that in some cases,[5,10] but not all, these new species are ionic, depending upon the solvent, the base, and the anion. In some cases, species of the type $[ML_2L'X]^+Y^-$ have been isolated utilizing large counterions Y⁻.[3–5] In these cases the isomerization is inhibited by addition of methanol,[3,4] a solvent which can stabilize the ionic intermediate. In other cases, isomerization is much faster than can be accounted for by the reaction[6,9]

$$[ML_3X]^+ + X^- \longrightarrow ML_2X_2 + L$$
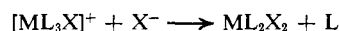
We wish to report herein ¹H nmr spectral data on catalyzed isomerization solutions for which conductometric titrations indicate the absence of ionic species. For solutions containing a 1:1 molar ratio of cis-$[(CH_3O)_3P]_2PdCl_2$ and cis- plus trans-$[CH_3P(C_6H_5)_2]_2$-$PdCl_2$ in $CDCl_3$ at 25°, it was found that within minutes, the ¹H nmr resonances of the original complexes disappeared and new resonances appeared (Figure 1B) which may be assigned to cis-$[(CH_3O)_3P][CH_3P(C_6H_5)_2]$-$PdCl_2$. This species can be isolated by evaporation of the $CDCl_3$ to yield a light yellow complex, mp 121–123° ($[(CH_3O)_3P]_2PdCl_2$, colorless, mp 128–129°; $[CH_3P-(C_6H_5)_2]_2PdCl_2$, yellow, mp 204–205°; mmp 95–140°). Similar results were also obtained with a 1:1 molar ratio of $[(CH_3O)_3P]_2PtCl_2$ and $[CH_3P(C_6H_5)_2]_2PtCl_2$ under the same conditions. Additionally, ¹H nmr demonstrates that solutions of $(CH_3O)_3P$ and $[CH_3P-(C_6H_5)_2]_2PdCl_2$ in various ratios (Figure 1C) contain the mixed complex. These data indicate that ligand mixing occurs such that *no* unique M–L′ bond is formed and in fact the mixed complexes are isolable and thermodynamically more stable and/or kinetically more inert than ML_2X_2!

An explanation which is consistent with all of the available data is that there is no unique isomerization

Figure 1. (A) The 100-MHz ¹H nmr spectrum for a $CDCl_3$ solution containing a 1:1 molar ratio of cis-$[(CH_3O)_3P]_2PdCl_2$ and cis-$[CH_3P(C_6H_5)_2]_2PtCl_2$ after 2 hr at 25°. Assignments are as follows: cis-$[(CH_3O)_3P]_2MCl_2$, M = Pd, δ 3.95, R. D. Bertrand, F. B. Ogilvie, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 1908 (1970); M = Pt, δ 3.95, F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 1916 (1970); cis- and trans-$[CH_3P(C_6H_5)_2]_2MCl_2$, M = Pd, δ 1.96 and 2.10, ref 11; M = Pt, δ 1.95, J. H. Nelson, unpublished results. For the phosphite resonances of $[(CH_3O)_3-P][CH_3P(C_6H_5)_2]MCl_2$, M = Pd, δ 3.68; M = Pt, δ 3.64, while for the phosphine resonances M = Pd, Pt, δ 2.33. (B) The 100-MHz ¹H nmr spectrum of a nearly complete redistribution of a 1:1 molar ratio of cis-$[(CH_3O)_3P]_2PdCl_2$ and cis- and trans-$[CH_3P(C_6H_5)_2]_2$-$PdCl_2$ in $CDCl_3$ at 25°. Assignments as in (A) above. (C) The 100-MHz ¹H nmr spectrum for a solution containing a 2:1 molar ratio of $(CH_3O)_3P$ and $[CH_3P(C_6H_5)_2]_2$ $PdCl_2$ after 1 hr at 25° in $CDCl_3$. The mixed complex phosphite resonances appear at δ 3.62. Note that other species are present in solution as well and that $CH_3P-(C_6H_5)_2$ is undergoing rapid exchange but $(CH_3O)_3P$ is not. All chemical shifts are relative to TMS internal standard and were recorded on a JEOLCO 4H-100 nmr spectrometer.

mechanism but rather each of the mechanisms outlined in eq 1 occur under various conditions.

$$\textit{cis-}ML_2X_2 + L' \rightleftharpoons$$

$$\textit{trans-}ML_2X_2 + L' \quad (1)$$

Pathway 1 is consecutive displacement of anion. This pathway should dominate in polar solvents, when X⁻ is poorly coordinating and L′ is a strong base. Pathway 3 is consecutive displacement of ligand and should dominate in nonpolar solvents when X⁻ is strongly coordinating. Pathway 2 is fluxional rotation and should dominate in nonpolar solvents when L and

(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 1st ed, Wiley, New York, N. Y., 1958, pp 249–254; see also 2nd ed, pp 423–427.
(2) L. Cattalini and M. Martelli, *J. Amer. Chem. Soc.*, **91**, 312 (1969).
(3) D. G. Cooper and J. Powell, *J. Amer. Chem. Soc.*, **95**, 1102 (1973).
(4) D. G. Cooper and J. Powell, *Can. J. Chem.*, **51**, 1634 (1973).
(5) D. A. Redfield, J. H. Nelson, R. A. Henry, D. W. Moore, and H. B. Jonassen, *J. Amer. Chem. Soc.*, in press.
(6) P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, **92**, 4996 (1970).
(7) P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, **92**, 5243 (1970).
(8) P. Haake and R. M. Pfeiffer, *Chem. Commun.*, 1330 (1969).
(9) W. J. Louw, *J. Chem. Soc., Chem. Commun.*, 353 (1974).
(10) D. A. Redfield, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, in press.
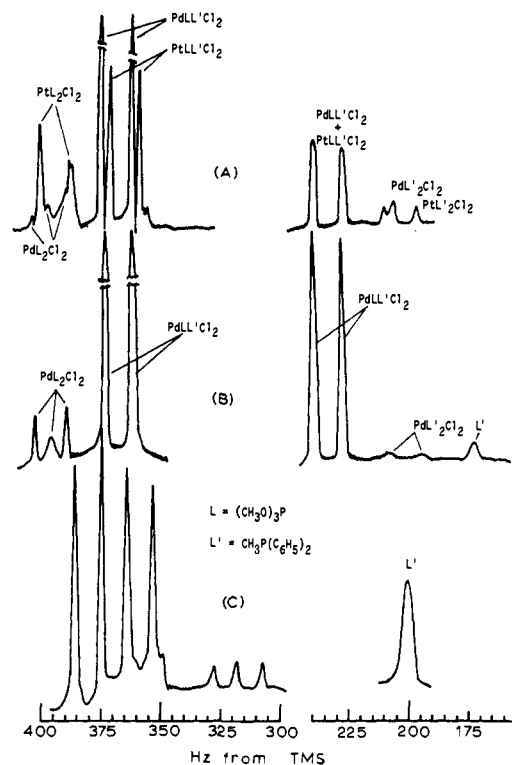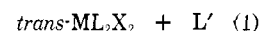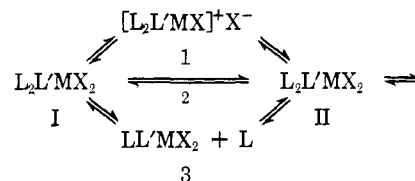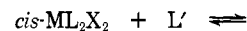
L' have nearly the same basicity and are small. Species I and II may be either transition states or intermediates and are not necessarily identical.

The overall mechanism is associative in nature as suggested by the following evidence. The isomerization rate decreases as L and L' increase in size and upon changing X⁻ from Cl⁻ to N_3^-.[10] cis-$[CH_3P(C_6H_5)_2]_2$-$PtCl_2$ is converted instantaneously at 25° in $CDCl_3$ to $trans$-$[CH_3P(C_6H_5)_2]_2PtCl_2$ by $(CH_3O)_3P$, and $[(CH_3O)_3$-$P][CH_3P(C_6H_5)_2]PtCl_2$ is present in solution, whereas with $(C_6H_5)_3P$ isomerization has not occurred for this complex within 48 hr to any measurable extent and $[(C_6H_5)_3P][CH_3P(C_6H_5)_2]PtCl_2$ is not present in this solution even after 48 hr. Moreover, equilibrium thermodynamics support the steric importance and solvent dependence of the mechanism.[5,10,11] This mechanism is also consistent with data obtained[5] for $[(C_6H_5)_2PCH_3]_2Pd(5$-CF_3-tetrazolate)$_2$ for which the pathway changes from (3) to (1) by addition of $(C_6H_5)_2$-PCH_3.

Thus, a third pathway for cis–trans-isomerization does exist and does predominate in at least some cases. We conclude, therefore, that the general mechanism contains three separate pathways whose importance varies as a function of the metal, solvent, coordinated ligand, catalyst (which may be solvent), and anion.

(11) D. A. Redfield and J. H. Nelson, *Inorg. Chem.*, **12**, 15 (1973).

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Chiral 1,2-Bisalkylidenecyclopentanes. Direct Formation *via* Cycloaddition Reactions of Chiral Substituted Alkenylidenecyclopropanes[1]

Sir:

2-Phenylisobutenylidenecyclopropane (**1**) undergoes cycloaddition reactions with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) and chlorosulfonylisocyanate (CSI) to form 1,2-bisalkylidenecyclopentane derivatives.[2,3] In a study of the stereochemical aspects of these cycloaddition reactions, (−)-(R)-**1** has been prepared[4] and reacted with PTAD and CSI at 0° in methylene chloride yielding adducts **2** and **3** and **4** and **5** respectively, *all of which are optically active.*

The configuration of **4b**, formed by the hydrolysis of **4a**, has been directly related to (+)-(S)-phenylglycine by ozonolysis and metaperiodate oxidation.[5] The absolute configuration of **2** is assigned the same as in **4**,

(1) (a) Cycloaddition Reactions of Cyclopropane-Containing Systems. VII. For the previous paper in this series see D. J. Pasto and A. F.-T. Chen, *Tetrahedron Lett.*, 713 (1973).

(2) D. J. Pasto and A. Chen, *J. Amer. Chem. Soc.*, **93**, 2562 (1971); D. J. Pasto, A. F.-T. Chen, and G. Binsch, *ibid.*, **95**, 1553 (1973).

(3) D. J. Pasto, A. F.-T. Chen, G. Ciurdaru, and L. A. Paquette, *J. Org. Chem.*, **38**, 1015 (1973).

(4) D. J. Pasto and J. K. Borchardt, *Tetrahedron Lett.*, 2517 (1973).

(5) The details of the stereochemical transformations and correlations will be reported in a future full article describing the mechanistic implications of the stereochemical studies.

(+)-(S)-**2**   (+)-**3**

PTAD

(−)-(R)-**1**

CSI
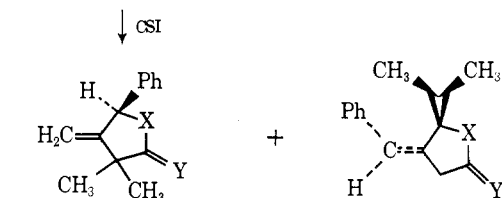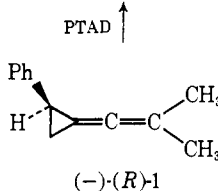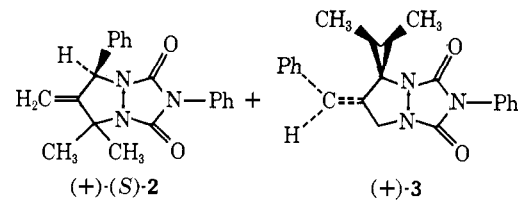
(+)-(S)-**4a**, X = NSO_2Cl; Y = O   (+)-**5a**, X = NSO_2Cl; Y = O
(+)-(S)-**4b**, X = NH; Y = O   (+)-**5b**, X = O; Y = NSO_2Cl
(+)-(S)-**4c**, X = O; Y = NSO_2Cl

the signs of rotation and the attachment atoms at the chiral carbon atoms in **2** and **4a** and **4b** being the same. The chirality of the dienes **3** and **5** are assigned as shown by comparison of the optical properties of the resulting PTAD adducts **6** and **7** (PTAD approaches the least

(+)-**3**

(−)-**6**

(+)-**5**   (−)-**7**
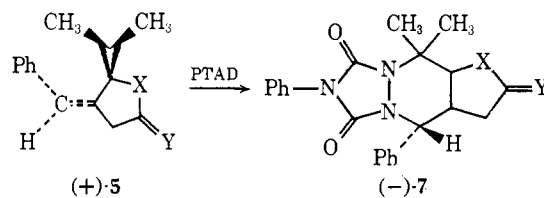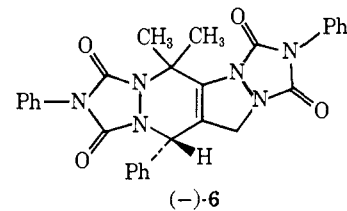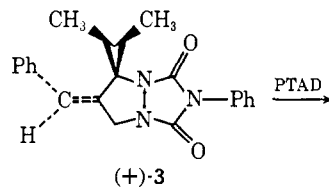
hindered face of the diene opposite the phenyl group)[2] which have opposite signs of rotation and configurations compared to **2** and **4a** and **4b**. Nmr analysis of **2** and **4b** in the presence of the chiral shift reagent tris-(trifluoroacetylcamphorato)europium(III) [Eu(tfac)$_3$] indicates that **2** and **4a** are formed stereospecifically.

To our knowledge **3** and **5** are the first examples of chiral, skewed 1,2-bisalkylidenecycloalkanes to be prepared. The chirality of the dienes arises from severe steric interactions between the phenyl and the "inside" methyl of the isopropylidene group forcing the diene to assume a nonplanar configuration. The extent of distortion of the diene chromophore is substantial as shown by X-ray structural studies carried out on an