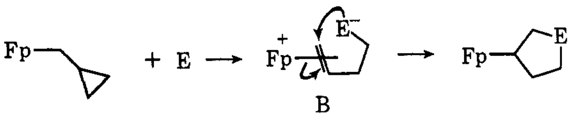
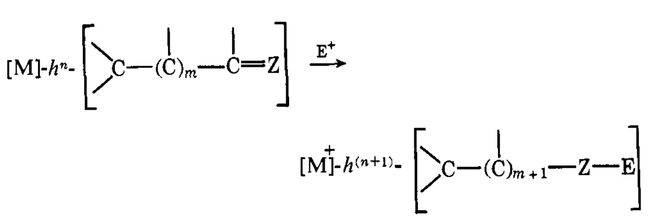
adduct **8**: ir (KBr) 1945, 2009 (C≡O), 2250 cm^{-1} (C≡N); nmr (CD$_3$NO$_2$) τ 4.97 (s, 5, Cp), 7.0–8.0 (m, 7, CH).

Each of these adducts may be accounted for in terms of metal-assisted electrophilic attack of the cyclopropyl ring resulting in the formation of the dipolar ion **B** analogous to **A**, and the subsequent collapse of this species by nucleophilic addition to the coordinated olefin.



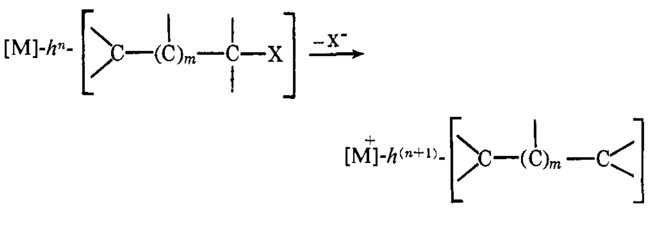
The h^1-allyl–metal complexes may be regarded as the simplest members of a large family of σ and π olefin–metal complexes constituting electron donor systems whose reactions with electrophiles may be formulated in general terms as[11]



The reactions of these and other allyl–metal complexes with electrophilic reagents are being investigated.

Acknowledgment. This work was supported by the National Institutes of Health (GM-16395) and by the National Science Foundation (GP-8714).

(11) The simplest of these reactions is exemplified by the protonation of h^1-allyl and 3-oxaallyl complexes: M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 889 (1963); M. L. H. Green and A. N. Stear, *J. Organometal. Chem.*, **1**, 230 (1964); M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963); M. L. H. Green and C. R. Hurley, *J. Organometal. Chem.*, **10**, 188 (1967). For other examples involving h^4 complexes and other electrophiles including protons see: F. M. Chandhari and P. L. Pauson, *ibid.*, **5**, 73 (1966); B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *Chem. Commun.*, 1273 (1969); M. Green, S. Tolson, J. Weaver, D. C. Wood, and P. Woodward, *ibid.*, 222 (1971); M. L. H. Green, A. G. Massey, J. T. Moelwyn-Hughes, and P. L. I. Nagy, *J. Organometal. Chem.*, **8**, 511 (1967); M. L. H. Green and P. L. I. Nagy, *Z. Naturforsch. B*, **18**, 162 (1963); N. J. Dauben and D. J. Bertelli, *J. Amer. Chem. Soc.*, **83**, 497 (1961); R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 594 (1961); E. Weiss and W. Hübel, *Chem. Ber.*, **95**, 1186 (1962). These reactions are closely related to processes resulting in the formation of a stabilized olefin–metal cation complex through elimination of an anion



A review of these reactions has recently been provided by M. A. Haas, *Organometal. Chem. Rev.*, 4, 307 (1969).

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Asymmetric Homogeneous Hydrosilylation with Platinum(II) Complexes of Chiral Phosphines

Sir:

There has been recent interest in hydrosilylation of olefins in the presence of some platinum(II) complexes as a homogeneous catalysis.[1–3]

Although few of the platinum complexes with phosphine ligands have been recorded so far in the literature as an effective catalyst for hydrosilylation,[4] we have recently found that some of them provide homogeneous catalysis within a rather limited case.[5]

We wish to report here the first example of asymmetric hydrosilylation[6] of some olefins catalyzed by platinum(II) complexes of chiral phosphines. Thus, addition of methyldichlorosilane (30 mmol) to α-methylstyrene (30 mmol) was carried out in the presence of *cis*-dichloro(ethylene)[(*R*)-benzylmethylphenylphosphine]platinum(II)[7] (2 × 10^{-2} mmol) in a degassed sealed glass tube at 40° over a period of 40 hr. The reaction mixture was distilled to give 2-phenylpropylmethyldichlorosilane[8] (43% yield), $[\alpha]^{15}\text{D}$ +1.93° (neat), along with some polymeric products. The addition product was methylated to give 2-phenylpropyltrimethylsilane,[8] $[\alpha]^{15}\text{D}$ +1.20° (neat); 5% enantiomeric excess of the *R* isomer. The authentic (+)-(*R*)-2-phenylpropyltrimethylsilane was prepared by the unambiguous route shown below.

$$\begin{array}{ccc} (R)\text{-PhCHMeCH}_2\text{OH}^{9} & \xrightarrow[\text{pyridine}]{\text{SOCl}_2} & (R)\text{-PhCHMeCH}_2\text{Cl}^{10} \\ {[\alpha]}^{20}\text{D}\ +16.6^\circ & & {[\alpha]}^{20}\text{D}\ +13.4^\circ \\ (95.4\%\ \text{optical purity}) & & \end{array}$$

$$\xrightarrow[\text{2. ClSiMe}_3]{\text{1. Mg-THF}} \begin{array}{c} (R)\text{-PhCHMeCH}_2\text{SiMe}_3 \\ {[\alpha]}^{20}\text{D}\ +23.3^\circ \end{array}$$

A marked decrease in optical yield of the product was observed when dichlorobis[(*R*)-methylphenyl-*n*-propylphosphine]di-μ-chloro-diplatinum(II)[11] was used as catalyst, as indicated in Table I.

Similarly, hydrosilylation of 2-methyl-1-butene gave 2-methylbutylmethyldichlorosilane,[12] with only 0.9% asymmetric bias of the *R* isomer. The authentic but enantiomeric substances were prepared from (+)-(*S*)-2-

(1) A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, **87**, 16 (1965).

(2) L. H. Sommer, J. E. Lyons, and H. Fujimoto, *ibid.*, **91**, 7051 (1969).

(3) For a relevant review: C. Eaborn and B. W. Bott in "Organometallic Compounds of the Group IV Elements," A. G. MacDiarmid, Ed., Vol. 1, Part 1, Marcel Dekker, New York, N. Y., 1968, pp 231–263.

(4) Chalk and Harrod[1] did not claim a catalytic activity of Pt(II)–phosphine complexes, though a reaction of silanes with phosphine complexes was examined: *cf.* A. J. Chalk, U. S. Patent 3,188,300 (1965); *Chem. Abstr.*, **63**, 7043d (1965). On the other hand, the Eaborn–Bott review[3] claims, based on a patent literature, that phosphine–platinum complexes are effective catalysts for the additions.

(5) K. Yamamoto, T. Hayashi, and M. Kumada, *J. Organometal. Chem.*, **28**, C37 (1971).

(6) There is only a brief description about an asymmetric hydrosilylation of menthyl *trans*-crotonate with triethylsilane. This is, however, not the case of a catalytic asymmetric synthesis: R. Calas, IUPAC International Symposium on Organosilicon Chemistry, Prague, 1965; Special Lectures, Butterworths, London, 1966, p 63.

(7) Prepared according to a procedure by J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1662 (1964); $[\alpha]^{15}\text{D}$ −49.4° (*c* 1.60, CH$_2$Cl$_2$).

(8) J. W. Ryan and J. L. Speier, *J. Org. Chem.*, 24, 2052 (1959).

(9) S. P. Bakshi and E. E. Turner, *J. Chem. Soc.*, 171 (1961); $[\alpha]^{15}\text{D}$ +17.4° (neat).

(10) Contaminated with *ca.* 7% of 1-phenyl-2-chloropropane, which did not interfere with the Grignard reaction.

(11) Prepared according to a procedure by A. C. Smithies, M. Rycheck, and M. Orchin, *J. Organometal. Chem.*, **12**, 199 (1968); $[\alpha]^{20}\text{D}$ −15.0° (*c* 1.00, CH$_2$Cl$_2$).

(12) J. Saam and J. L. Speier, *J. Amer. Chem. Soc.*, **83**, 1351 (1961).

Table I. Asymmetric Hydrosilylation of Olefins with $MeCl_2SiH$ Catalyzed by Chiral Phosphine–Platinum(II) Complexes at 40°

Olefin (30 mmol)	Catalyst (10 mg)	$[\alpha]^{15}D$, deg, of product	Yield, %	$[\alpha]^{15}D$, deg, methylated
$PhMeC{=}CH_2$	*cis*-$(C_2H_4)R_3P^*PtCl_2$[a]	+1.93	43	+1.20
$PhMeC{=}CH_2$	$[R'_3P^*PtCl_2]_2$[b]	+0.37	64	
$EtMeC{=}CH_2$	*cis*-$(C_2H_4)R_3P^*PtCl_2$[a]	−0.12	69	−0.14
$EtMeC{=}CH_2$	$[R'_3P^*PtCl_2]_2$	−0.08	55	

[a] R_3P^*: (+)-(*R*)-$(PhCH_2)MePhP$ (K. Neumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7102 (1969)) (81% optical purity). [b] R'_3P^*: (−)-(*R*)-MePh-*n*-PrP (see Neumann, *et al.*, footnote *a*) (93% optical purity).

methylbutyl chloride, $[\alpha]^{15}D$ +1.68° (neat) (98% optical purity),[13] (+)-(*S*)-$EtMeCHCH_2SiMeCl_2$, $[\alpha]^{15}D$ +12.8° (neat), and (+)-(*S*)-$EtMeCHCH_2SiMe_3$, $[\alpha]^{15}D$ +15.8° (neat).

cis-Dichloro(ethylene)[(*S*)-1-phenylethylamine]platinum(II), which is known to cause the asymmetric induction of the coordinated olefin by exchanging ethylene with such higher olefins as *tert*-butylethylene and *trans*-2-butene,[14] showed an efficient catalytic activity in hydrosilylation of α-methylstyrene (in essentially quantitative yield under the conditions used), but the adduct was racemic.

These observations are significant for several reasons. First, a system with one asymmetric center as close to the metal as possible is advantageous in order to sustain the asymmetric bias, though this is not always necessary for asymmetric synthesis[15] in general. Second, the stereochemical sequence of coordination of olefins followed by addition of a silicon hydride, which must take place at least within the coordination sphere of the platinum atom, is proved to be identical in all experiments.

Finally, we are aware of the mechanistic similarity between the present hydrosilylation and the asymmetric homogeneous hydrogenation,[15] which at present is restricted to the use of phosphine complexes of rhodium(I) as catalysts, presumably of the type L_3RhCl where L is the chiral ligand.

Further experiments with chiral phosphine complexes of other metals including nickel(II), palladium(II), and rhodium(I) are in progress.

Acknowledgment. We thank Professor S. Suga and Dr. T. Nakajima of Kanazawa University for a generous gift of (+)-(*R*)-2-phenylpropyl alcohol.

[13] L. Spialter and D. H. O'Brien, *J. Org. Chem.*, **31**, 3048 (1966); $[\alpha]^{18}D$ +1.71° (neat).

[14] A. Panunzi and G. Paiaro, *J. Amer. Chem. Soc.*, **88**, 4843 (1966).

[15] For the recent papers: J. D. Morrison, R. E. Burnett, A. M. Aguiar, C. J. Morrow, and C. Phillips, *ibid.*, **93**, 1301 (1971); T. P. Dang and H. B. Kagan, *Chem. Commun.*, 481 (1971).

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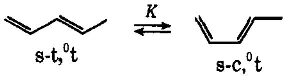
The Role of *s-cis*-1,3-Diene Triplets in Sensitized Cis–Trans Photoisomerization

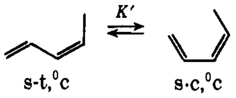
Sir:

Acyclic 1,3-diene-photosensitized cycloaddition products vary with sensitizer triplet energy.[1,2] High-energy sensitizers, >60 kcal/mol, excite s-cis and s-trans diene conformers indiscriminately producing mainly s-trans triplets which give cyclobutane products. Lower energy sensitizers, $60 > E_T > 50$ kcal/mol, favor excitation of s-cis conformations, yielding s-cis triplets which give chiefly cyclohexene products. The requirement is that s-cis and s-trans triplets do not interconvert. Although photostationary trans–cis ratios for the sensitized isomerization of the 1,3-pentadienes vary over the same triplet energy region, Figure 1, the role of s-cis triplets in cis–trans isomerization has not been evaluated.[3,4]

1,3-Pentadienes. A mechanism for sensitized 1,3-pentadiene cis-trans photoisomerization including the intermediacy of s-cis triplets is given by eq 1–8 (^{3}p



(1)



(2)

$$^3D + \text{s-t},^0t \xrightarrow{k_3} {}^0D + \text{s-t},^3p \quad (3)$$

$$^3D + \text{s-c},^0t \xrightarrow{k_4} {}^0D + \text{s-c},^3p \quad (4)$$

$$^3D + \text{s-t},^0c \xrightarrow{k_5} {}^0D + \text{s-t},^3p \quad (5)$$

$$^3D + \text{s-c},^0c \xrightarrow{k_6} {}^0D + \text{s-c},^3p \quad (6)$$

$$\text{s-t},^3p \xrightarrow{k_7} \alpha^0t + (1 - \alpha)^0c \quad (7)$$

$$\text{s-c},^3p \xrightarrow{k_8} \alpha'^0t + (1 - \alpha')^0c \quad (8)$$

denotes relaxed diene triplets). Using the steady-state approximation for all excited species, eq 9–11 are

$$\left(\frac{[t]}{[c]}\right)_s = \frac{1 + K}{1 + K'}\left(\frac{\alpha k_5 + \alpha' k_6 K'}{(1 - \alpha)k_3 + (1 - \alpha')k_4 K}\right) \quad (9)$$

$$\phi_{t\to c} = \frac{a}{k_3 + k_4 K}((1 - \alpha)k_3 + (1 - \alpha')k_4 K) \quad (10)$$

$$\phi_{c\to t} = \frac{a}{k_5 + k_6 K'}(\alpha k_5 + \alpha' k_6 K') \quad (11)$$

derived (*a* represents the sensitizer's intersystem crossing efficiency). Benzophenone, fluorenone, and pyrene photoisomerization data are compared in Table I. For high-energy sensitizers, $k_3 = k_4 = k_5 = k_6 = k_{\text{dif}}$ and since K and K' are small, terms containing α' are negligible. For fluorenone, $\phi_{c\to t}/a = 0.55 = \alpha$, indicating that s-cis triplets are not produced from *cis*-1,3-pentadiene, *i.e.*, $K' \ll 1$.[5] Since steric interactions in *s-cis*-1,3-butadiene and *s-cis,trans*-1,3-pentadiene are similar, the same distribution of s-cis and

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[1] R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965), and references cited therein.

[2] W. L. Dilling, R. D. Kroening, and J. C. Little, *ibid.*, **92**, 928 (1970).

[3] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, N. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).

[4] N. J. Turro, *Photochem. Photobiol.*, **9**, 555 (1969).

[5] Identical photodimer compositions are obtained from *cis*-1,3-pentadiene using benzophenone and fluorenone as sensitizers: J. Saltiel and D. Townsend, preliminary observations.