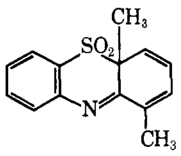
zenesulfonamide, is consistent with a structural assignment such as **2a**.[4]

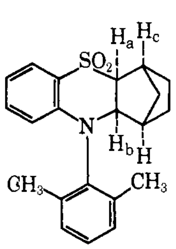
Subsequent irradiation[3] of crude **2a** at 30° in benzene solution ($10^{-2}M$) resulted in the formation of carbazole (**5**) by a process which formally represents the extrusion of sulfur dioxide and 1,5 cyclization of the intermediate syn diphenylamino diradical.[5] Since phenothiazine dioxide (**4**) is photochemically stable a possible route involving excitation of **2a** to the valence isomer **3a** with concomitant thermal cyclization to **4** may be excluded. However, **3a** is probably an intermediate in the rapid thermal conversion (30%) of **2a** to **4**[6] in *p*-xylene at 130°.

An increase in the conjugative stabilization of **2** relative to **3** should increase the endothermicity of the valence isomerization and thus permit purification and characterization of a benzothiazete 1,1-dioxide. Bulky ortho substituents carried by the *N*-phenyl group would cause a twisting about the C–N bond due to an ortho,ortho′ steric interaction and reduce the coplanarity of the π-electron system in **3** or the transition state from which it is derived. Such a hypothesis proved to be correct as evidenced by the following experiments.

Photolysis[3] of 2-(2,6-dimethylphenyl)-2*H*-1,2,3,4-benzothiatriazine 1,1-dioxide (**1b**)[4], mp 150–151° dec, in anhydrous benzene ($10^{-2}M$) at 30° afforded after crystallization from benzene 60% of **2b** as colorless prisms, mp 112–113° dec. The nmr spectrum ($CDCl_3$, 60 MHz) displayed a methyl singlet (6 H) at τ 7.68 and an aromatic proton multiplet (7 H) at 2.50–3.20, while the asymmetric and symmetric SO_2 stretching modes occurred at 1159 and 1345 cm^{-1} in the infrared. An exact mass determination gave 259.067 (calcd for $C_{14}H_{13}NO_2S$, 259.066) and prominent fragment ions occurred at $(M - SO_2)^+$ and $(M - SO_2N)^+$. The reactivity of **2b** toward nucleophiles paralleled **1a** but prolonged irradiation[3] in hexane solution failed to provide any monomeric products. Pyrolysis of **2b** in refluxing toluene afforded an isomer (exact mass of 259.066) as yellow needles, mp 83–84°. A structural assignment of **6** is consistent with the observed ir absorption at 1150 and 1305 cm^{-1} and nmr ($CDCl_3$, 60 MHz) signals centered at τ 2.38 (4 H) and 3.59 (3 H) as multiplets and 7.93 (3 H) and 8.40 (3 H) as singlets.



6



7

In a closely related thermolysis, **1b** in mesitylene (150°) gave **6** along with a trace of **2b**. Such transformations are readily explicable in terms of the valence isomerization of **2b** to the syn isomer of **3b** followed by electrocyclic closure. Evidence for the thermal production of **3b** was provided by the exclusive formation of cycloadduct **7**, mp 173–174°, when **2b** was refluxed in norbornene solution.[4] The assigned exo structure is based on the appearance in the nmr spectra ($CDCl_3$, 60 MHz) of a quartet at τ 3.74 for H_a with $J_{ab} = 8$ Hz and $J_{ac} < 1$ Hz and H_b at τ 3.15.[7] The bridge and bridgehead protons were found as multiplets centered at τ 8.50, 6.72, and 6.88 while the aromatic protons at 2.0–3.0 and a methyl singlet (6 H) at 7.83 completed the spectrum.

Acknowledgment. We wish to thank the National Science Foundation (GP-9411) and the National Institutes of Health (GM-2672) for support.

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[4] Spectroscopic analysis including exact mass determination for all new compounds was consistent with the assigned structures.

[5] This intermediate has previously been invoked in a related study of benzotriazole photochemistry: E. M. Burgess, R. Carithers, and L. McCullagh, *J. Amer. Chem. Soc.*, **90**, 1923 (1968).

[6] Identified by mixture melting point comparison with an authentic sample.

[7] P. Laszzlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

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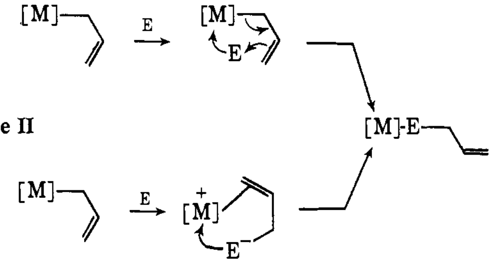
Metal-Assisted Cycloaddition Reactions

Sir:

The insertion of sulfur dioxide into metal–alkyl bonds to give alkyl-metal sulfones has been shown to be a rather general reaction for a number of transition metal complexes.[1] When these reactions are applied to metal–allyl complexes, they are often accompanied by an allylic rearrangement in which insertion occurs with 1,3 migration of the metal atom.[2] Although these rearrangements have been depicted as concerted processes[2] (Scheme I, E = SO_2), it is apparent that they may alternatively by pictured as proceeding stepwise through a dipolar intermediate A (Scheme II).

Scheme I[3]

Scheme II



A

In principle, this dipolar intermediate may alternatively collapse by addition of the anionic terminus to the coordinated double bond (Scheme III), but this

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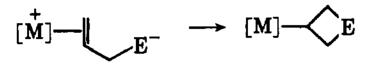
[1] J. P. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, **86**, 5051 (1964); A. Wojcicki and F. A. Hartman, *ibid.*, **88**, 844 (1966); J. P. Bibler and A. Wojcicki, *ibid.*, **88**, 4862 (1966); F. A. Hartman and A. Wojcicki, *Inorg. Chem.*, 7, 1504 (1968); S. E. Jacobson and A. Wojcicki, *J. Amer. Chem. Soc.*, **93**, 2535 (1971). A review of these reactions has recently been provided by W. Kitching and W. Fong, *Organometal. Chem. Rev.*, **5**, 315 (1970).

[2] F. A. Hartman, P. J. Pollick, R. L. Downs, and A. Wojcicki, *J. Amer. Chem. Soc.*, **89**, 2493 (1967); F. A. Hartman and A. Wojcicki, *Inorg. Chim. Acta*, **2**, 289 (1968); M. R. Churchill and J. Wormald, *Inorg. Chem.*, **10**, 573 (1971).

[3] The symbol [M] is used to denote a complex organometalic radical.

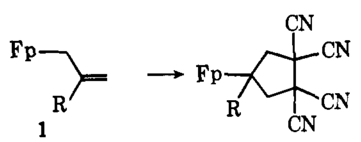
Scheme III



latter course of reaction has not apparently been observed when the electrophile is sulfur dioxide.[4]

We wish now to report several reactions of (h^5-cyclopentadienyl)(h^1-allyl)iron (**1**) and of (h^5-cyclopentadienyl)(h^1-cyclopropylmethyl)iron dicarbonyl (**2**) with electrophiles, which are best interpreted in terms of the formation of dipolar intermediates (A) and of their reaction according to Scheme III.

Treatment of the iron complex **1a** in 1,2-dichloroethane with 1 equiv of tetrachloroethane (TCNE) at room temperature led to the rapid formation of the adduct **3a** in good yield.[5,6]



1

3

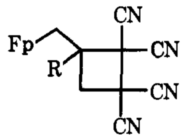
a, R = H

b, R = Me

Similarly, the methallyl complex **1b**, on treatment with TCNE in methylene chloride solution at room temperature, gave a quantitative yield of the adduct **3b**, in a reaction which was complete within 5 min. This latter complex represents the second known transition metal complex with a tertiary alkyl–metal bond.[7]

Both of the adducts exhibit strong ir absorption at 1940 and 2000 cm^{-1} (KBr) typical of (h^5-C_5H_5)$Fe(CO)_2$–alkyl complexes, in addition to a weak band at 2250 cm^{-1} (C≡N).

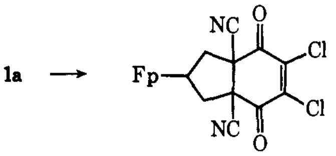
The possibility that these adducts possess structure **4** derived by (2 + 2) addition of TCNE[8] to the double bond in **1** may be excluded. Thus the nmr spectrum of **3a** fails to show alkyl resonance absorption above τ 8.0, indicative of the presence of a methylene group bound to the metal. The nmr spectrum of **3b** is more definitive. In addition to cyclopentadiene and methyl proton resonance at τ 4.87 and 8.35, respectively, the spectrum of this substance shows only a four-proton AB quartet centered at τ 6.78 (J_{AB} = 14.4 Hz), consistent with structure **3b** but not with **4b**.



4a, R = H

b, R = Me

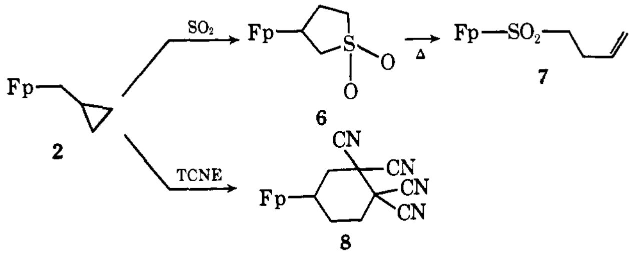
The allyl complex reacts rapidly with 2,3-dichloro-5,6-dicyanoquinone to give the adduct **5**, but no identifiable products could be obtained from the reaction of **1a** with either *p*-quinone or tetrachloro-*p*-quinone.[9]



5

(h^5-Cyclopentadienyl)(h^1-cyclopropylmethyl)iron dicarbonyl (**2**), prepared by the reaction of h^5-$C_5H_5Fe(CO)_2Na$ and cyclopropylmethyl benzenesulfonate, reacted with sulfur dioxide to give the sulfone **6**. The nmr spectrum of this substance exhibits complex alkyl proton absorption between τ 6.7 and 7.7 and cyclopentadienyl resonance at 5.0 typical of $C_5H_5Fe(CO)_2$–alkyl complexes. Its ir spectrum (KBr) shows, in addition to carbonyl absorptions at 1940 and 1980 cm^{-1}, two intense bands at 1110 and 1280 cm^{-1} characteristic of organic sulfones.[10] When **2** is heated at 125–130° for a brief period it is converted in 94% yield to the metal alkyl sulfone (**7**). In accord with this formulation, the substance exhibits cyclopentadienyl resonance at τ 4.70, intense ir absorption (KBr) at 1980 and 2059 cm^{-1} (C≡O), and strong absorption at 1040 and 1179 cm^{-1}.

Similarly complex **2** reacts with TCNE to give the



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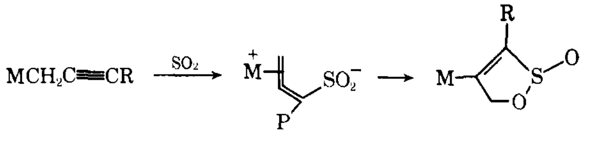
[4] The formation of a sulfine and of cyclic sulfinamides in the reaction of 2-propynylmanganese and -iron complexes with sulfur dioxide and *N*-phenylthionylamines [M. R. Churchill, T. Wormald, D. A. Ross, J. E. Thomasson, and A. Wojcicki, *J. Amer. Chem. Soc.*, **92**, 1795 (1970); P. W. Robinson and A. Wojcicki, *Chem. Commun.*, 951 (1970)] is readily accounted for in terms of the formation and closure of an allenic cation complex analogous to A



A similar formulation has very recently been proposed by W. D. Bannister, B. L. Booth, R. N. Haszeldine, and P. L. Loader for the reactions of $Mn(CO)_4LCH_2C{\equiv}CH$ complexes with carboxylic acids and sulfur dioxide (*J. Chem. Soc. A*, 930 (1971)).

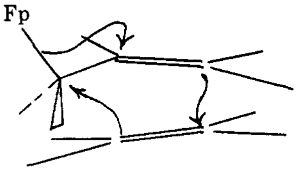
[5] Acceptable carbon and hydrogen analyses were obtained for all new substances reported.

[6] The symbol F_p is used to designate the complex organometallic radical (h^5-C_5H_5)$Fe(CO)_2$–.

[7] The first member of this class of organometallic complexes was reported recently: W. P. Giering and M. Rosenblum, *J. Organometal. Chem.*, **25**, C71 (1970).

[8] P. D. Bartlett, *Quart. Rev., Chem. Soc.*, **24**, 473 (1970).

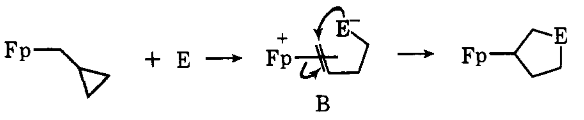
[9] The alternative formulation of these reactions as concerted $[_{\pi}2_a + _{\pi}2_s + _{\sigma}2_a]$ processes cannot be excluded. However, a mechanism involving a substantial ionic compound seems at present more likely in view of the ionic character of the reactions of TCNE with alkenes[8] and of the comparative stability of the F_p (olefin) cations: W. P. Giering and M. Rosenblum, *Chem. Commun.*, 441 (1971).



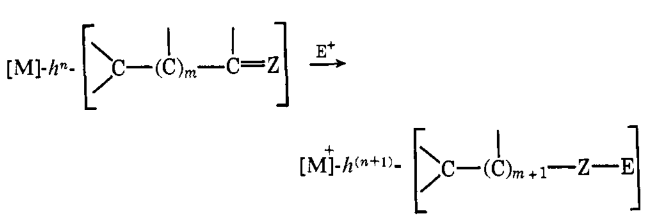
[10] P. M. G. Bavin, G. W. Gray, and A. Stephenson, *Spectrochim. Acta*, **16**, 1312 (1960).

adduct **8**: ir (KBr) 1945, 2009 (C≡O), 2250 cm^{-1} (C≡N); nmr (CD_3NO_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.



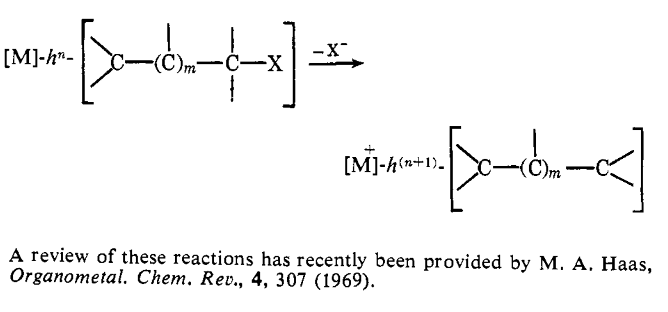
The *h*^{1}-allyl-metal complexes may be regarded as the simplest members of a large family of σ and π olefin–metal complexes constituting electron donor systems whose reactions with electrophiles may be formulated in general terms as[11]



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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Received June 28, 1971

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.

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

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

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-

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[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_2Cl_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_2Cl_2).

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