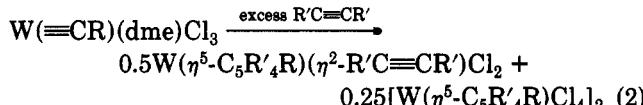


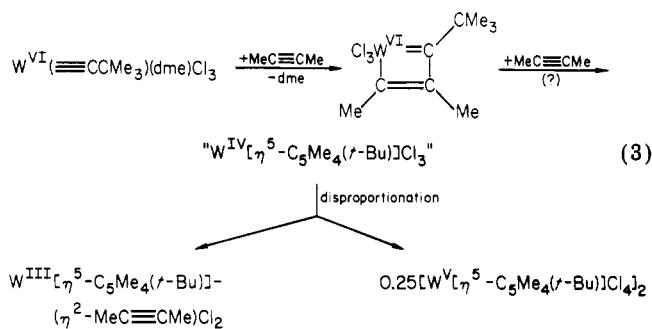
electron-donating) acetylenic ligand is found in a *paramagnetic* tungsten(III) complex. To the best of our knowledge, there is no other example of such a linkage in a paramagnetic species.

The second feature of interest concerns the occurrence of a pentasubstituted  $\eta^5$ -cyclopentadienyl ligand in the molecule. It should be noted that the production of highly substituted cyclopentadienyl systems is not straightforward and that much synthetic work in organometallic chemistry has been confined to the easily obtained  $C_5Me_5$  and  $C_5Me_4Et$  systems. The present  $\eta^5-C_5Me_4(t\text{-}Bu)$  ligand is clearly formed by the *net* coupling of one neopentylidyne ligand and two 2-butyne molecules. There are some indications<sup>4</sup> that this type of reaction can provide a rather general route to highly substituted  $\eta^5$ -cyclopentadienyl systems (see eq 2). Of course, unsymmetrical acetylenes



could be used (e.g.,  $R'C\equiv CR''$ ); the disadvantage here is that a mixture of isomeric cyclopentadienyl systems would be formed and separation could become a major problem. A further possibility is that functionalized acetylenes could be used, providing an entry into more complex cyclopentadienyl systems.

The pathway of the reaction is not firmly established. A possible sequence for the reaction of  $W(\equiv CCMe_3)(dme)Cl_3$  and 2-butyne is shown in eq 3. The intermediacy of the tungstenacyclobutadiene complex is established, as is the nature (and approximate relative quantities) of the



final products.<sup>4</sup> A disproportionation reaction clearly must occur, and an intermediate complex of stoichiometry  $W[\eta^5-C_5Me_4(t\text{-}Bu)]Cl_3$  provides perhaps the simplest possible intermediate. The disproportionation of a (presumably diamagnetic) tungsten(IV) complex into *paramagnetic* tungsten(III) and tungsten(V) complexes is, however, unusual in organometallic chemistry. Clearly, however, further work is required before this type of coupling reaction is understood in detail.

**Acknowledgment.** This work was supported by NSF Grant CHE80-23448 (M.R.C.). We thank Professor R. R. Schrock for providing the material studied.

**Registry No.**  $W[\eta^5-C_5Me_4(t\text{-}Bu)](\eta^2-MeC\equiv CMe)Cl_2$ , 83511-02-8.

**Supplementary Material Available:** Listings of observed and calculated structure factor amplitudes, calculated positions for hydrogen atoms (Table II-S), anisotropic thermal parameters (Table III-S), and least-squares planes (Table VI-S) (19 pages). Ordering information is given on any current masthead page.

## Stereospecific Additions of Dimethylsilylene and Diphenylsilylene to Olefins<sup>1,2</sup>

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Dimethyl- and diphenylsilylene add stereospecifically to *cis*- and *trans*-2-butene to give the corresponding siliranes. Easy additions to cyclopentene and cyclohexene indicate that the cycloadditions are *cis*. Opening of the siliranes by methanol also occurs in stereospecifically *cis* fashion.

### Introduction

Singlet carbenes add to olefins with retention of stereochemistry; triplets do not. Behind that simple sentence lies a rich, complex matrix of theory and experiment, in-

terwoven with liberal amounts of intuitive conjecture and occasional wishful thinking.<sup>5</sup> Even today, debate over both detailed mechanistic description<sup>5</sup> and, occasionally, the fundamental reaction pathways surfaces.<sup>6</sup> Never-

(1) We dedicate this paper to the memory of Professor Xu Jigong, Fudan University, Shanghai, People's Republic of China.

(2) A portion of this work has been previously communicated.<sup>3</sup> Other parts are taken from the Ph.D. Thesis of V. J. T., Princeton University, 1981. Presented, in part, by S.-h.W. at: "The Second Chinese-Japanese-United States Symposium on Organometallic and Inorganic Chemistry", Shanghai, June 14-18, 1981. Grateful acknowledgment is made to the National Science Foundation for support through Grants CHE-77-24625 and CHE-81-01212.

(3) Tortorelli, V. J.; Jones, M., Jr. *J. Am. Chem. Soc.* 1980, 102, 1425.

(4) Much of this work was done while Shi-hui Wu was at Princeton University, on leave from Fudan University, Shanghai, People's Republic of China.

(5) For a summary of recent developments see: (a) Moss, R. A.; Jones, M., Jr. In "Reactive Intermediates"; Wiley: New York, 1978; Vol. 1, Chapter 3, p 69. (b) *Ibid.*, 1981; Vol. 2, Chapter 3, p 59. (c) For history see: "Carbenes"; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973, 1975; Vols. I and II. W. Kirmse, "Carbene Chemistry", 2nd ed., Academic Press: New York, 1971.

(6) Jones, M., Jr.; Tortorelli, V. J.; Gaspar, P. P.; Lambert, J. B. *Tetrahedron Lett.* 1978, 4257 and references therein.

theless, the sentence beginning this paper is a reasonable summary of current knowledge. It does ignore the fact that some carbenes are reluctant to add to olefins at all, at least at ambient temperature.<sup>7</sup> For instance, diphenylcarbene adds efficiently only to olefins containing at least one terminal methylene group.<sup>8</sup> More highly substituted double bonds produce mostly the products of abstraction/recombination by triplet diphenylcarbene.

The chemistry of silylenes, the second-row counterparts of carbenes, has only begun to emerge in the last few years.<sup>9</sup> Although it has become clear that most, if not yet all, reactions of divalent carbon have their counterparts in silylene chemistry, our knowledge of these second-row species remains in a relatively primitive state. For instance, at the inception of this work the stereochemistry of silylene addition was unknown, despite the abundant evidence that siliranes could be formed from olefins and various silylene precursors.<sup>9,10</sup> The problem is that siliranes, unlike cyclopropanes, are quite unstable compounds, reacting rapidly with nucleophiles and even reverting thermally to their precursors.<sup>11</sup> We have been interested in carbene addition reactions for some years and, accordingly, set out to determine the stereochemistry of silylene addition. Since the beginning of our experiments,<sup>3</sup> the question has been approached both theoretically and experimentally by others.

There is general agreement that silylenes, unlike most carbenes, will have singlet ground states.<sup>9,12</sup> This implies that addition will probably proceed with retention of stereochemistry as it does for singlet carbenes.

An experiment of Ishikawa, Nakagawa, and Kumada strongly implies that addition of phenyltrimethylsilylsilylene is stereospecifically *cis*.<sup>13</sup> *trans*-2-Butene led to a single silirane, but addition to *cis*-2-butene led to two different adducts. All three products were opened by methanol to the same compound.

(7) For a summary of the behavior of arylcarbenes at low temperature and in solid matrices which often differs from room temperature chemistry, see ref 5b.

(8) Baron, W. J.; Hendrick, M. E.; Jones, M., Jr. *J. Am. Chem. Soc.* 1973, 95, 6286.

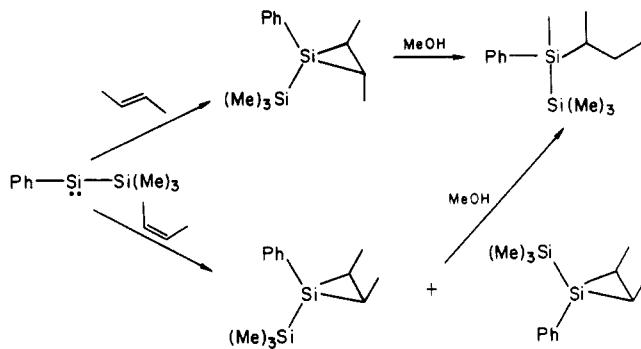
(9) For recent developments see: (a) Gaspar, P. P. In "Reactive Intermediates"; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1978; Vol. 1, p 229. (b) *Ibid.*, 1981; Vol. 2, p 335.

(10) (a) Ishikawa, M.; Ishiguro, M.; Kumada, M. *J. Organomet. Chem.* 1973, 49, C71. (b) Ishikawa, M.; Kumada, M. *Ibid.* 1974, 81, C3. (c) Ishikawa, M.; Ohi, F.; Kumada, M. *Tetrahedron Lett.* 1975, 645. (d) Seyerth, D.; Annarelli, D. C. *J. Organomet. Chem.* 1976, 117, C51. (e) Gaspar, P. P.; Hwang, R.-J. *J. Am. Chem. Soc.* 1974, 96, 6198. (f) Hwang, R.-J.; Conlin, R. T.; Gaspar, P. P. *J. Organomet. Chem.* 1975, 94, C38. (g) Ishikawa, M.; Nakagawa, K.-I.; Ishiguro, M.; Ohi, F.; Kumada, M. *Ibid.* 1978, 152, 155.

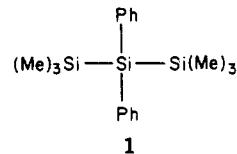
(11) Seyerth, D.; Haas, C. K.; Annarelli, D. C. *J. Organomet. Chem.* 1973, 56, C7. Seyerth, D.; Haas, C. K.; Lambert, R. L., Jr.; Annarelli, D. C. *Ibid.* 1978, 152, 131.

(12) (a) Drahak, T. J.; Michl, J.; West, R. *J. Am. Chem. Soc.* 1979, 101, 5247, and references therein. (b) Kasden, A.; Herbst, E.; Lineberger, W. C. *J. Chem. Phys.* 1975, 62, 541. (c) Zeck, O. F.; Su, Y. Y.; Gennaro, G. P.; Tang, Y.-N. *J. Am. Chem. Soc.* 1974, 96, 5967. (d) Synder, L. C.; Wasserman, Z. R. *Ibid.* 1979, 101, 5222. (e) Meadows, J. H.; Schaefer, H. F., III. *Ibid.* 1976, 98, 4383. (f) Gordon, M. S. *Chem. Phys. Lett.* 1978, 54, 9. (g) Barthelat, J.-C.; Trinquier, G.; Bertrand, G. *J. Am. Chem. Soc.* 1979, 101, 3785. (h) Dewar, M. J. S.; Lo, D. H.; Ramsden, C. A. *Ibid.* 1975, 97, 1311. (i) Harrison, J. F.; Liedtke, R. C.; Liebman, J. F. *J. Am. Chem. Soc.* 1979, 101, 7162. See also: (j) Strausz, O. P.; Gosavi, R. K.; Theodorakopoulos, G.; Csizmadia, I. G. *Chem. Phys. Lett.* 1978, 58, 43. (k) Gosavi, R. K.; Gunning, H. E.; Strausz, O. P. *Ibid.* 1978, 59, 321.

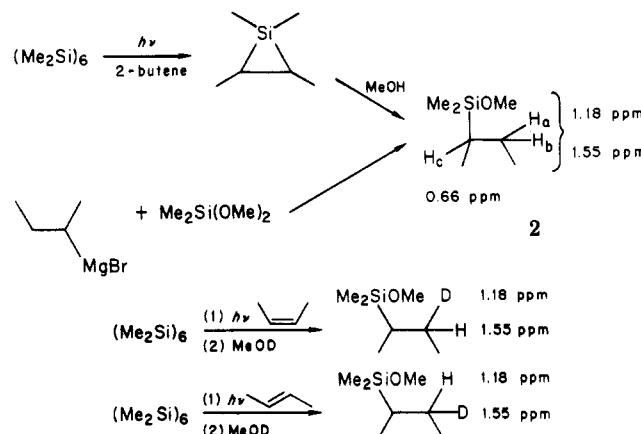
(13) Ishikawa, M.; Nakagawa, K.-I.; Kumada, M. *J. Organomet. Chem.* 1979, 178, 105. See also: Seyerth, D.; Annarelli, D. C.; Duncan, D. P. *Organometallics* 1982, 1, 1288.



We opted to study the simplest readily accessible system, dimethylsilylene and the 2-butenes. Dimethylsilylene is easily available from dodecamethylcyclohexasilane,<sup>12a</sup> and use of the 2-butenes maintains contact with classical carbene chemistry.<sup>5c</sup> We also decided to examine diphenylsilylene on the chance that it, like diphenylcarbene, would show unusual properties. Diphenylsilylene seemed likely to be available by photolysis of 2,2-diphenylhexamethyltrisilane (1).<sup>14</sup>



**Additions of Silylenes to the 2-Butenes.** It has been amply demonstrated that siliranes are produced on generation of silylenes in olefins.<sup>9,10</sup> We originally hoped that it would be possible to observe directly the silirane(s) produced from dimethylsilylene and the 2-butenes. Irradiation of dodecamethylcyclohexasilane (henceforth  $(Me_2Si)_6$ ) in olefin in a quartz NMR tube failed to yield an interpretable  $^1H$  NMR spectrum, however. Decomposition of the starting material was evident from collapse of the silicon-methyl singlet in the unirradiated sample, but the relatively low yield of silirane and large amount of side products made it necessary to monitor silirane formation indirectly. Addition of methanol to a previously irradiated sample of  $(Me_2Si)_6$  in *cis*- or *trans*-2-butene led to formation of 2 in each case. Authentic 2 could be made by treatment of dimethoxydimethylsilane with a single equivalent of 2-butylmagnesium bromide. In the  $^1H$  NMR

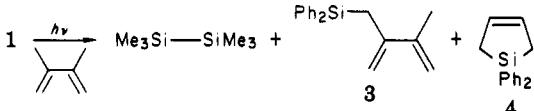


spectrum of 2,  $H_c$  appears as a broad multiplet at  $\delta$  0.66 and the diastereotopic  $H_a$  and  $H_b$  as multiplets centered

(14) For a review see: Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* 1981, 19, 51. That photolysis of 1 does lead to diphenylsilylene is mentioned in passing in the review cited above. Ishikawa, M.; Fujioka, F.; Okamura, A.; Kumada, M., unpublished work.

at  $\delta$  1.55 and 1.18. When the ring opening was carried out with methanol-*d*, *cis*-2-butene led to a monodeuterio 2 which retained a broad multiplet at  $\delta$  1.55, but which lacked the  $\delta$  1.18 signal. With *trans*-2-butene as the substrate the situation was reversed: the  $\delta$  1.18 multiplet remained and the  $\delta$  1.55 signal was missing. At this point it was clear that the addition reaction was largely stereospecific, but the difficulty of integrating the broad, nearly overlapping multiplets for  $H_b$  and  $H_a$  led us to another analytical method,  $^2\text{H}$  NMR spectroscopy.<sup>15</sup> Irradiation of  $(\text{Me}_2\text{Si})_6$  in *cis*-2-butene followed by quenching with  $\text{CH}_3\text{OD}$  led to a monodeuterio 2 in which the multiplet "missing" in the  $^1\text{H}$  NMR spectrum appeared as a singlet at  $\delta$  1.18. Similarly, *trans*-2-butene showed a signal in the  $^2\text{H}$  NMR spectrum at  $\delta$  1.55. No evidence for the peak corresponding to the product of methanolysis of 2 from *cis*-2-butene could be found in the material from *trans*-2-butene, but ca. 5% of the compound from *trans*-2-butene could be seen in the product isolated from the *cis* olefin. However, recovered *cis*-2-butene could be shown to be contaminated with 2–3% of the *trans* isomer, so the figure of 5% represents a generous upper limit to the nonstereospecificity of the reaction. Addition of dimethylsilylene is certainly highly stereospecific. At this point, though, it is not possible to say whether addition is stereospecifically *cis* or *trans*, although one's intuitive feeling is that it must be *cis*. We will return to this question later.

As mentioned earlier, diphenylcarbene adds only reluctantly to the butenes at room temperature. Most of the product consists of olefins produced by an abstraction/recombination reaction of the triplet carbene. We wondered if diphenylsilylene would be prone to the same kind of reaction. No such easy precursor as  $(\text{Me}_2\text{Si})_6$  was available, but trisilane 1 was known.<sup>14,16</sup> Our first goal was to show that diphenylsilylene could be generated from 1. One of the better reactions of silylenes is the addition to dienes to give a vinylsilsilane that rapidly rearranges to a silacyclopentene and a conjugated diene. This reaction sequence has been nicely worked out by Ishikawa, Ohi, and Kumada for methylphenylsilylene generated from the appropriate trisilane.<sup>17</sup> Irradiation of trisilane 1 in 2,3-dimethylbutadiene gave three products: hexamethyldisilane and the two expected compounds 3 and 4. Com-



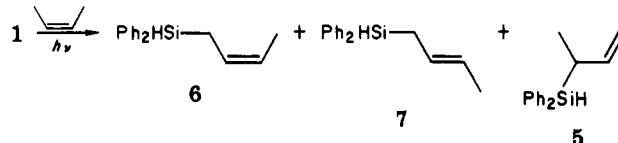
pounds 3 and 4 were identified by comparison of their spectra with those reported by the Japanese group for the related compounds produced from methylphenylsilylene.<sup>17</sup> Given that diphenylsilylene was available from 1, the next step was an examination of the reaction with the 2-butenes. Would addition or abstraction take place?

It first appeared that abstraction was the path preferred. Irradiation of 1 through quartz in *cis*-2-butene followed by quenching with methanol led to a complex mixture of products in which olefins (5–7) predominated. Olefins 5 and 6 could be rationalized through a series of abstraction and/or insertion reactions but *trans* product 7 cannot. In fact 6 and 7 were present in nearly 1:1 ratio. It is known

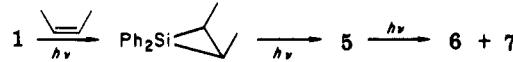
(15) Ms. Mary Baum of this department and Drs. M. Kelly and A. Evans of JEOL Analytical Instruments Division were most helpful in the determination of the  $^2\text{H}$  NMR spectra.

(16) Duffaut, N.; Dunogues, J.; Calas, R. *C. R. Hebd. Seances Acad. Sci., Ser. C* 1969, 268, 967.

(17) Ishikawa, M.; Ohi, F.; Kumada, M. *J. Organomet. Chem.* 1975, 86, C23.

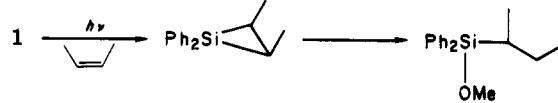


that the siliranes formed from methylphenylsilylene are photosensitive,<sup>14,18</sup> and products analogous to 5–7 were found by Kumada, Ishikawa, et al. when irradiation was performed through quartz. By analogy, we assume that the initially formed silirane is isomerizing to 5 which undergoes further photolysis to give 6 and 7 through a photoinduced 1,3 shift of silicon.<sup>19</sup> The Japanese were able

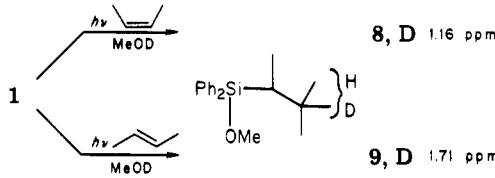


to circumvent this problem and trap the silirane with methanol when the irradiation was carried out using a Vycor filter. We were not. Irradiation of 1 in *cis*-2-butene through Vycor also led to 5–7. Presumably the diphenylsilylenes are even more photosensitive than the monophenyl ones.

The problem was solved by irradiating 1 in a solution of butene and trapping agent. Under these conditions the silirane is captured by methanol before substantial photolytic conversion to 5–7. Diphenylsilylene does add to



the butenes and is thus quite different from diphenylcarbene in this respect. The stereochemistry of addition was determined as before. Irradiation of 1 in *cis*-2-butene/methanol-*d* led to 8 and reaction with *trans*-2-butene/methanol-*d* to 9. Integration of the  $^2\text{H}$  NMR



spectra<sup>15</sup> showed that 9 was accompanied by ca. 6% 8. We could detect no 9 in the product from *cis*-2-butene, 8. High specificity is observed, and once more we guessed that both the addition of  $\text{Ph}_2\text{Si}$  and subsequent opening by methanol were stereospecifically *cis*.

As pointed out by a reviewer, the generation of a silylene in the presence of more than one potential trap introduces complications. In particular, it is a legitimate concern that diphenylsilylene might react first with methanol to generate diphenylmethoxysilane and then add photochemically across the double bond of the butene. Irradiation of diphenylmethoxysilane in 2-butene does not give adduct, however, and this pathway is ruled out.

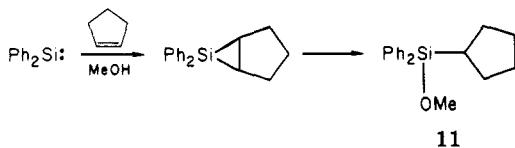
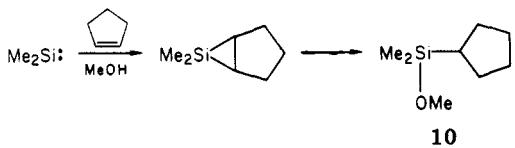
**Addition to Silylenes to Cyclic Olefins.** Years ago Kumada showed that methylphenylsilylene added to cyclohexene.<sup>9,20</sup> It certainly seemed likely that such additions must proceed in *cis* fashion. We have confirmed that  $\text{Me}_2\text{Si}$  and  $\text{Ph}_2\text{Si}$  also add to cyclohexene and to the even smaller cyclopentene. Once again dodecamethylcyclohexasilane and trisilane 1 were the silylene sources and

(18) Ishikawa, M.; Nakagawa, K.; Ishiguro, M.; Ohi, F.; Kumada, M. *J. Organomet. Chem.* 1978, 152, 155.

(19) We thank a referee for straightening out our muddled thinking on this point.

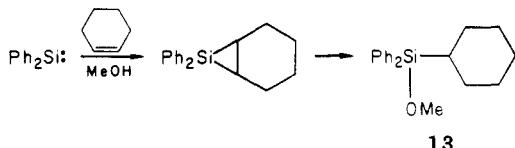
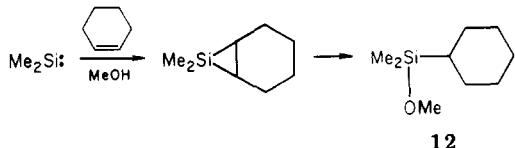
(20) Ishikawa, M.; Ishiguro, M.; Kumada, M. *J. Organomet. Chem.* 1973, 49, C71.

methanol the trapping agent. Generation of the silylenes in pentane solutions of cyclopentene and methanol led to cyclopentyldimethylmethoxysilane **10** and cyclopentyldiphenylmethoxysilane **11**. The structures were confirmed

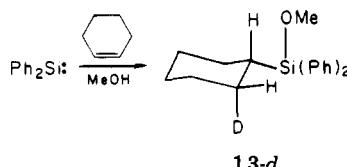
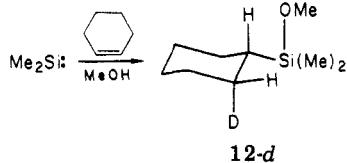


by conventional syntheses of authentic compounds. It now seems clear that the initial additions are *cis*, as are the analogous reactions of their cousins, singlet carbenes.

The additions to cyclohexene provide an opportunity to determine also the stereochemistry of ring opening by methanol-*d*. Irradiation of  $(\text{SiMe}_2)_6$  or 1 in cyclohexene and methanol led to adducts **12** and **13**.



If the  $\text{Me}_2\text{SiOCH}_3$  or  $\text{Ph}_2\text{SiOCH}_3$  group is assumed to occupy an equatorial position, then high-resolution  $^1\text{H}$  NMR spectroscopy should separate the axial from equatorial hydrogens and thus show which position carried the deuterium. Thus the stereochemistry of ring opening would become apparent. The axial positions are known to appear at ca. 0.1–0.6 ppm higher field.<sup>21</sup> In both **12-d** and **13-d** the ratio of equatorial hydrogens (**12**,  $\delta$  1.5–1.8; **13**,  $\delta$  1.45–1.57) to axial (**12**,  $\delta$  1.0–1.3; **13**,  $\delta$  1.18–1.26) was 5:4. Thus the deuterium in each case is axial and ring opening of the initially formed silirane is *cis*.



## Experimental Section

**General Data.** Melting points were determined by using a Thomas Hoover Unimelt apparatus and are uncorrected.

Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, GA 30366.

(21) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy"; Pergamon Press: New York, 1965; pp 696.

Routine nuclear magnetic resonance spectra were recorded on a Varian A-60A spectrometer (60 MHz), a Perkin-Elmer R-32 spectrometer (90 MHz) (continuous-wave operation), a Varian XL-100 spectrometer ( $^1\text{H}$ , 100.083 MHz;  $^{13}\text{C}$ , 25.196 MHz), or JEOLCO-JEOL FX 90 Q spectrometer ( $^1\text{H}$  NMR, 89.55 MHz;  $^{13}\text{C}$  22.50 MHz) (Fourier transform mode).<sup>15</sup> High-field (250-MHz) spectra were taken on a Bruker WM-250 spectrometer.

Infrared spectra were recorded on Perkin-Elmer 237B or 283 IR spectrophotometers.

Analytical gas chromatography was performed on a Varian 1400 gas chromatograph (flame ionization detector) with nitrogen as carrier gas, using  $1/8$ -in. stainless-steel columns. Preparative gas chromatography was performed on a Varian A-90A gas chromatograph (thermal conductivity detector) with helium as carrier gas, using  $1/4$ -in. copper or aluminum columns.

Mass spectra were obtained on an AEI MS-9 mass spectrometer (electron impact). GC/MS runs were conducted on a Du Pont 21-490 GC/MS interfaced to a Varian 1400 gas chromatograph.

**Dodecamethylcyclohexasilane.**<sup>12a</sup> To a mixture of lithium wire (1.6 g) in 100 mL of THF at 0 °C was slowly added (1.5 h) 13.0 g of dichlorodimethylsilane in 40 mL of THF with stirring under nitrogen. The reaction mixture was stirred for an additional 2 h at 0 °C and was left to stir overnight at room temperature. Cyclohexane (100 mL) was added and the precipitate isolated by filtration. The solvent was removed under reduced pressure and the residue extracted with 100 mL of cyclohexane. After filtration and evaporation of solvent, a solid product was obtained. The product was recrystallized from ethanol to yield 2.8 g (48%):  $^1\text{H}$  NMR (cyclohexane)  $\delta$  0.1 (s).

**Irradiation of Dodecamethylcyclohexasilane in *cis*- or *trans*-2-Butene Followed by Methanol Quenching.** Dodecamethylcyclohexasilane (0.174 g) was placed in a quartz tube equipped with a greaseless gas-tight Teflon vacuum stopcock. Either *cis*- or *trans*-2-butene was condensed in the tube. The tube was closed and allowed to warm to room temperature in the hood behind a safety shield. The reaction mixture was irradiated for 10–12 h in a water-cooled bath using a 450-W medium-pressure Hanovia mercury lamp. After irradiation, the tube was placed in a Dry Ice/acetone bath, opened, and quenched with methanol or with methanol-*d*. The tube was closed immediately, allowed to warm to room temperature, and shaken to ensure good mixing. The tube was again cooled in a Dry Ice/acetone bath, opened, and then allowed to warm to room temperature as the 2-butene evaporated. The butenes were collected for analysis of isomerization of the olefins.

If one does not quench the photolysis mixture immediately but allows the butenes to distill, the remaining residue when treated with methanol does not give the methoxy-trapped products as indicated by VPC analysis.

All VPC analyses and collections of the methoxy-trapped products were conducted on a 10-ft 15% SF96 column at a temperature of 130 °C. The injector was set at 210 °C and the detector at 240 °C with a helium flow rate of 60 mL/min.

The *cis*-2-butene reaction yielded 23.9% *sec*-butyldimethylmethoxysilane, and the *trans*-2-butene yielded 19.5% *sec*-butyldimethylmethoxysilane. Isolation of trapped methoxysilane using methanol-*d* showed proton spectra identical with that of the authentic sample, except the product from the *cis*-2-butene reaction mixture lacked the absorptions at  $\delta$  1.18, whereas the deuterated methoxysilane derived from *trans*-2-butene lacked the peak at  $\delta$  1.55.

**Analysis of *cis*- and *trans*-2-Butene.** A silver nitrate column was freshly prepared as follows: silver nitrate (3.8 g) dissolved in 9.7 g of benzyl cyanide was poured onto Chromosorb P 60/80 while being gently stirred with a glass rod. Stirring was continued until all of the silver nitrate/benzyl cyanide had been added, and mixing resulted in a homogeneous free-flowing support. A 12-ft, 0.25-in. copper column was packed in the dark. The column was used at room temperature with both the injector and detector heaters turned off. A helium flow rate of 40 mL/min was used to establish excellent separation. *trans*-2-Butene (from the lecture bottle) eluted first and was found to be 99.4% *trans* and 0.6% *cis*. After 12 h of irradiation the *trans*-2-butene was reanalyzed and found to contain 99.5% *trans* and 0.5% *cis*. *cis*-2-Butene (from the lecture bottle) was found to consist of 99.25% *cis* and 0.75% *trans*. After 12 h of irradiation the *cis*-2-butene was

reanalyzed and found to contain 97.3% cis and 2.70% trans. **Preparation of Authentic sec-Butyldimethylmethoxysilane.** A solution containing 13.0 g of sec-butyl bromide in 30 mL of dry ether was placed in a dropping funnel and added slowly to 2.5 g of magnesium in 30 mL of dry ether under nitrogen. After the initial reaction started, the remainder of the bromide was added over ca. 1 h, with stirring continuing for another hour after the addition ended. This Grignard reagent was added to an ether solution containing 13 mL of dimethoxydimethylsilane under a nitrogen atmosphere. After the addition was completed, the reaction mixture was stirred at room temperature for 1 h and then was refluxed for 10 h and allowed to stir at room temperature under nitrogen overnight. Addition of saturated ammonium chloride to the ice-cooled reaction mixture was followed by extraction with  $H_2O$ . The ether layer was separated and dried over  $Na_2SO_4$ . After filtration from the drying agent and careful removal of ether at reduced pressure, the residue was distilled. The product distilled at a head temperature of 125–127 °C, and sec-butyldimethylmethoxysilane was isolated in 93% pure yield by VPC. A sample submitted for mass spectral analysis gave a molecular ion at  $m/e$  146 and a base peak at  $m/e$  89. A pure sample was collected from a 10-ft 15% SF96 column:  $^{13}C$  NMR ( $CDCl_3$ ) δ –4.54 and –4.45 ( $SiCH_3$ ), 13.2 and 13.4 ( $CH_3$ ), 21.96 ( $CH$ ), 23.19 ( $CH_2$ ), 50.20 ( $OCH_3$ );  $^1H$  NMR (neat) δ –0.2 (s, 6), 0.2–1.5 (m, 9), 3.1 (s, 3).

Anal. Calcd for  $C_7H_{18}OSi$ : C, 57.47; H, 12.40. Found: C, 57.52; H, 12.37.

**2,2-Diphenylhexamethyltrisilane (1).**<sup>14</sup> In a 500-mL three-necked round-bottomed flask, 6.08 g (0.25 g-atom) of magnesium and 53.76 g (0.3 mol) of HMPA and 100 mL of dry THF were mixed. A mixture of 32.5 g (0.3 mol) of trimethylchlorosilane and 25.32 g (0.1 mol) of dichlorodiphenylsilane was added dropwise with stirring under nitrogen. When the reaction mixture was heated to 80 °C, the reaction started. The reaction mixture was heated and stirred for another 60 h. During this period the magnesium almost completely disappeared.

This reaction mixture was treated with water and extracted by ether and the ether solution dried with  $Na_2SO_4$ . After filtration and evaporation of solvent, the products were distilled under reduced pressure and four fractions were collected. Trisilane 1 distilled at 140–160 °C (1 mm); yield 12.4 g (37.8% based on diphenyldichlorosilane).

A pure sample was collected from a 10-ft 15% SF96 column:  $^{13}C$  NMR (acetone- $d_6$ ) δ –0.40 ( $SiCH_3$ ), 128.75, 129.14, 136.66 (phenyl);  $^1H$  NMR (acetone- $d_6$ ) δ 7.37 (m, 10), 0.18 (s, 18).

Precise mass calculated for  $C_{18}H_{19}Si_3$ : 328.1499. Found: 328.1504.

**Photolysis of 1 in 2,3-Dimethyl-1,3-butadiene.** A mixture of 240 mg (0.73 mmol) of 1, 5 g (85 mmol) of 2,3-dimethyl-1,3-butadiene, and 15 mL of *n*-pentane was placed in a quartz tube equipped with a greaseless gas-tight Teflon vacuum stopcock. This solution was repeatedly degassed by the freeze-thaw method. The reaction mixture was irradiated for 1 h in a water-cooled bath using a medium-pressure 450-W Hanovia mercury lamp. After irradiation, the tube was placed in a Dry Ice/acetone bath and opened and the solvent distilled under ordinary pressure.

The products were collected from a 10-ft 10% FFAP column with the column temperature set at 230 °C. Three products were obtained. The first one (43%) is hexamethydisilane. The second is 3 (29%):  $^1H$  NMR (acetone- $d_6$ ) δ 7.71–7.41 (m, 10), 5.02–5.01 (m, 4), 4.85 (t, 1), 2.43 (d, 2), 1.84 (s, 3); GC-MS parent peak 264.3, base peak 183.15. The third one is 4 (28%):  $^1H$  NMR ( $CD_2Cl_2$ ) δ 7.39 (m, 10), 1.78 (m, 6), 1.26 (m, 4); GC-MS parent peak 264.3, base peak 105.10.

**Photolysis of 1 in *cis*-2-Butene.** A solution of 240 mg of 1 (0.73 mmol) and 15 mL of *n*-pentane was placed in a quartz tube equipped with a greaseless gas-tight Teflon vacuum stopcock. About 5 mL of *cis*-2-butene was condensed in the tube. The tube was closed and allowed to warm to room temperature in the hood behind a safety shield. The reaction mixture was irradiated for 12 h in a water-cooled bath using a medium-pressure 400-W Hanovia mercury lamp. After irradiation, the tube was placed in a Dry Ice/acetone bath, opened, and quenched with methanol. The tube was closed immediately and allowed to warm to room temperature as the *cis*-2-butene distilled. The solvent was removed under ordinary pressure.

The products were separated and collected from a 6-ft Carbowax 20 M column with the column temperature set at 195 °C. Three peaks were collected. The first one was a mixture that contained starting material and 5 (52%). The second and third products were 6 (26%) and 7 (18%).

5:  $^1H$  NMR ( $CDCl_3$ ) δ 7.64–7.24 (m, 10, phenyl), 6.15–5.77 (m, 1,  $C=CH$ ), 4.96–4.70 (m, 3,  $SiH$  and  $=CH_2$ ), 2.30 (m, 1,  $CHC=$ ), 1.23, 1.15 (d, 3,  $CH_3CH$ ).

6:  $^1H$  NMR ( $CDCl_3$ ) δ 7.67–7.30 (m, 10, phenyl), 5.40–5.36 (m, 2,  $=CH$ ), 4.85–4.81 (t, 1,  $SiH$ ), 2.01 (m, 2,  $CH_2C=$ ), 1.53 (br s, 3,  $CH_3$ ).

7:  $^1H$  NMR ( $CDCl_3$ ) δ 7.62–7.31 (m, 10, phenyl), 5.45–5.38 (m, 2,  $CH=$ ), 4.82 (t, 1,  $SiH$ ), 2.15–2.05 (m, 2,  $CH_2C=$ ), 1.49–1.24 (m, 3,  $CH_3$ ).

**Irradiation of 1 in *cis*- or *trans*-2-Butene and Methanol or Methanol-*d*.** A solution of 250 mg of 1, 12 mL of *n*-pentane, and 1.2 mL of methanol (or methanol-*d*) was placed in a quartz tube equipped with a greaseless gas-tight Teflon vacuum stopcock. This reaction mixture was degassed by the freeze-thaw method, then either *cis*- or *trans*-2-butene (ca. 5 mL) was condensed in the tube. The tube was closed and allowed to warm to room temperature in the hood behind a safety shield. The reaction mixture was irradiated for 12 h in a water-cooled bath using a medium-pressure 450-W Hanovia mercury lamp. After irradiation, the tube was placed in a Dry Ice/acetone bath and opened. The 2-butene and most of the solvent was distilled under ordinary pressure. The residue was analyzed by VPC and a pure sample collected.

For VPC analysis and collections of the methoxy-trapped products, 15% SF96 and 15% Carbowax 20 M columns were used.

The overall yield of three steps (generation of diphenylsilylene, addition to 2-butene, and ring opening) was 2.5%.

Besides the sec-butyldiphenylmethoxysilane, small amounts of 5–7 were found.

**Irradiation of Diphenylmethoxysilane in *trans*-2-Butene.** A solution of 15 mg of diphenylmethoxysilane (made from diphenylchlorosilane and methanol) in 5 mL of pentane and 5 mL *trans*-2-butene was irradiated in a quartz vessel for 12 h with a 450-W Hanovia medium pressure mercury lamp. Analysis of the products by gas chromatography-mass spectrometry revealed starting material and no diphenyl-sec-butyldimethoxysilane.

**Irradiation of Dodecamethylcyclohexasilane in Cyclopentene and Methanol-*d*.** Dodecamethylcyclohexasilane (174 mg), 10 mL of *n*-pentane, 10 mL of cyclopentene, and 1 mL of methanol-*d* were placed in a quartz tube equipped with a greaseless gas-tight Teflon vacuum stopcock. This reaction mixture was degassed by the freeze-thaw method. The tube was closed under vacuum and allowed to warm to room temperature. The reaction mixture was irradiated for 12 h in a water-cooled bath using a medium-pressure 450-W Hanovia mercury lamp. After irradiation, the tube was placed in a Dry Ice/acetone bath and opened. Most of the solvent and cyclopentene were removed under ordinary pressure.

VPC analysis and collection of the product was conducted on a 20-ft 30% FFAP column at a column temperature of 70 °C:  $^1H$  NMR ( $CDCl_3$ ) δ 3.42 (s, 3,  $OCH_3$ ), 1.82–0.90 (m, 8, cyclopentyl hydrogen), 0.052 (s, 6,  $SiCH_3$ );  $^{13}C$  NMR ( $CDCl_3$ ) δ 50.51 ( $OCH_3$ ), 27.49, 27.05, 26.94, 25.91, 25.81 (cyclopentyl carbon), –4.05 ( $SiCH_3$ ).

**Irradiation of 1 in Cyclopentene and Methanol-*d*.** A solution of 250 mg of 1 in 10 mL of *n*-pentane, 10 mL of cyclopentene, and 1.2 mL of methanol-*d* was placed in a quartz tube equipped with a greaseless gas-tight Teflon vacuum stopcock. The same procedure was used as in the irradiation of dodecamethylcyclohexasilane.

VPC analysis and collection of the product were conducted on a 10-ft 15% SF96 column at a column temperature of 70 °C:  $^1H$  NMR ( $CDCl_3$ ) δ 7.65–7.33 (m, 10, phenyl), 3.51 (s, 3,  $OCH_3$ ), 1.98–1.04 (m, 8, cyclopentyl hydrogen).

**General Procedure for Synthesis of Authentic Compounds.** A solution containing 0.05 mol of alkyl halide in 15 mL of dry ether was placed in a dropping funnel and added slowly to 1.22 g (0.05 g-atom) of magnesium in 15 mL of dry ether with stirring under nitrogen. The halide was added over ca. 0.5 h with stirring which was continued for another hour after the addition ended. The Grignard reagent was added to an ether solution

containing 0.55 mol of dimethyldimethoxysilane (or diphenyl-dimethoxysilane or diphenylmethoxychlorosilane) under a nitrogen atmosphere. After the addition was completed, the reaction mixture was stirred at room temperature for 1 h and then refluxed for 5 h. It was then cooled by an ice-water bath. Addition of saturated ammonium chloride to the ice-cooled reaction mixture was followed by extraction with water. The ether layer was separated and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration from the drying agent and careful removal of ether, the residue was distilled.

The pure compounds were collected by VPC using a 15% SF96 column for diphenyl-*sec*-butylmethoxysilane and diphenyl-cyclopentylmethoxysilane and a 30% FFAP column for dimethylcyclopentylmethoxysilane.

**Diphenyl-*sec*-butylmethoxysilane:** yield 52.5% (based on diphenylmethoxychlorosilane);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.62-7.34 (m, 10), 3.48 (s, 3), 1.81-1.88 (m, 9);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  135.18, 129.17, 127.76 (phenyl carbon), 51.54 ( $\text{OCH}_3$ ), 24.02 ( $\text{CH}_2$ ), 20.12 (CH), 13.35 ( $\text{CH}_3$ ), 13.13 ( $\text{CH}_3$ ).

Anal. Calcd for  $\text{C}_{17}\text{H}_{22}\text{OSi}$ : C, 76.54; H, 7.85. Found: C, 76.57; H, 7.93.

**Cyclopentyldiphenylmethoxysilane:** yield 42.8% (based on diphenylmethoxysilane);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.59-7.38 (m, 10, phenyl), 3.52 (s, 3,  $\text{OCH}_3$ ), 1.99-1.51 (m, 9);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  135.13, 129.71, 217.76 (phenyl carbon), 51.59 ( $\text{OCH}_3$ ), 27.76, 27.00, 23.91 (cyclopentyl carbon).

Anal. Calcd for  $\text{C}_{18}\text{H}_{22}\text{OSi}$ : C, 75.50; H, 8.20. Found: C, 75.60; H, 8.26.

**Cyclopentyldimethylmethoxysilane:** yield 48.7% (based on dimethyldimethoxysilane);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.43 (s, 3,

$\text{OCH}_3$ ), 1.92-1.00 (m, 9), 0.06 (s, 6,  $\text{CH}_3\text{Si}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  50.56 ( $\text{OCH}_3$ ), 27.43, 27.00, 25.86 (cyclopentyl carbon), -3.82 ( $\text{CH}_3\text{Si}$ ).

Anal. Calcd for  $\text{C}_8\text{H}_{18}\text{OSi}$ : C, 60.69; H, 11.46. Found: C, 60.72; H, 11.47.

**Cyclohexyldiphenylmethoxysilane:** yield 47.5% (based on diphenylmethoxysilane);  $^1\text{H}$  NMR ( $\text{CDCl}_3$  250 MHz)  $\delta$  7.35-7.60 (m, 10, phenyl), 3.5 (s, 3,  $\text{OCH}_3$ ), 1.45-1.57 (br s, 5, eq), 1.18-1.26 (br s, 5, ax), 0.75-0.9 (m, 1,  $\alpha$ -Si).

Anal. Calcd for  $\text{C}_{19}\text{H}_{24}\text{OSi}$ : C, 77.02; H, 8.10. Found: C, 76.83; H, 7.98.

**Cyclohexyldimethylmethoxysilane:**<sup>10b</sup> yield 90% (based on dimethyldimethoxysilane);  $^1\text{H}$  NMR ( $\text{CDCl}_3$  250 MHz)  $\delta$  3.40 (s, 3,  $\text{OCH}_3$ ), 1.5-1.8 (m, 5, eq), 1.0-1.3 (m, 5, ax), 0.56-0.77 (m, 1,  $\alpha$ -Si), -0.1 to +0.1 (s,  $\text{Si-CH}_3$ ).

**Irradiations of Dodecamethylcyclohexasilane and 1 in Cyclohexene and Methanol-*d*.** These reactions were carried out as were the cyclopentene runs. Analysis of the 250-MHz  $^1\text{H}$  NMR spectra showed in each case that the ratio of equatorial to axial protons was 5/4.

**Registry No.** 1, 18549-83-2; 3, 84960-75-8; 4, 34106-93-9; 5, 84960-76-9; 6, 54008-70-7; 7, 54960-77-0; 10, 84960-80-5; 11, 84960-79-2; 12, 54731-56-5; 13, 84960-81-6; ( $\text{Me}_2\text{Si}$ )<sub>6</sub>, 4098-30-0;  $\text{Me}_3\text{Si-SiMe}_3$ , 1450-14-2; dichlorodimethylsilane, 75-78-5; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; *sec*-butyldimethylmethoxysilane, 73618-57-2; dichlorodiphenylsilane, 80-10-4; 2,3-dimethyl-1,3-butadiene, 513-81-5; cyclopentene, 142-29-0; diphenyl-*sec*-butylmethoxysilane, 84960-78-1; cyclohexene, 110-83-8; dimethylsilylene, 6376-86-9; diphenylsilylene, 84960-82-7.

## Communications

### Carbon-Hydrogen Bond Activation Using a Bis(phosphine)Iridium Carbonyl Hydride and the Carbonylation of Benzene

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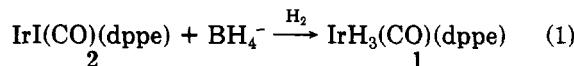
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**Summary:** The complex  $\text{IrH}_3(\text{CO})(\text{dppe})$  (dppe = 1,2-bis(diphenylphosphino)ethane) has been prepared from  $\text{IrI}(\text{CO})(\text{dppe}) + \text{BH}_4^-$  under  $\text{H}_2$ . Under irradiation or heating,  $\text{IrH}_3(\text{CO})(\text{dppe})$  eliminates  $\text{H}_2$ , yielding  $\text{IrD}_3(\text{CO})(\text{dppe})$  under  $\text{D}_2$  and  $\text{IrH}(\text{CO})_2(\text{dppe})$  under  $\text{CO}$ . In  $\text{C}_6\text{D}_6$  under vacuum,  $\text{IrH}_3(\text{CO})(\text{dppe})$  shows evidence of H/D exchange only upon irradiation, indicating arene carbon-hydrogen bond activation involving a photochemical process. When irradiation of  $\text{IrH}_3(\text{CO})(\text{dppe})$  in  $\text{C}_6\text{H}_6$  is performed under  $\text{CO}$  for longer times, benzaldehyde is produced as determined by NMR, GC, and organic derivatization methods. The amount of benzaldehyde formed appears to be limited thermodynamically and not kinetically. The equilibrium of the reaction  $\text{C}_6\text{H}_6(\text{l}) + \text{CO} = \text{C}_6\text{H}_5\text{CHO}(\text{l})$  is also approached by the decarbonylation of benzaldehyde. However, true equilibrium is not reached because of secondary reactions which occur upon prolonged photolysis.

Significant progress has been reported recently on the

activation of carbon-hydrogen bonds by transition metal complexes. Early reports of C-H activation were based primarily on the observation of H/D exchange in hydrocarbon substrates and on the isolation of *intramolecular* C-H addition products.<sup>1</sup> More recent studies, however, have described the formation of stable alkyl and aryl hydride complexes via the *intermolecular* oxidative addition of C-H bonds to low-valent metal systems.<sup>2</sup> In this communication we describe a system which not only activates aryl C-H bonds but also inserts CO, leading to the formation of benzaldehyde. The entry point to this unusual example of C-H bond functionalization is the previously unreported Ir(III) trihydride complex  $\text{IrH}_3(\text{CO})(\text{dppe})$ , 1 (dppe = 1,2-bis(diphenylphosphino)ethane).

Complex 1 is prepared by the reaction of  $\text{NaBH}_4$  and the previously unreported Ir(I) iodo complex  $\text{IrI}(\text{CO})(\text{dppe})$ , 2, in  $\text{CH}_2\text{Cl}_2/\text{EtOH}$  under  $\text{H}_2$  as shown in eq 1.<sup>3</sup>



(1) Parshall, G. W. *Acc. Chem. Res.* 1975, 8, 113.

(2) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* 1982, 104, 352. (b) Crabtree, R. H.; Mellea, M. F.; Mihelicic, J. M.; Quirk, J. M. *Ibid.* 1982, 104, 107 and references therein. (c) Hoyano, J. K.; Graham, W. A. *G. Ibid.* 1982, 104, 3723. (d) Barefield, E. K.; Parshall, G. W.; Tebbe, F. N. *Ibid.* 1970, 92, 5234. (e) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Am. Chem. Soc. Chem. Commun.* 1980, 1243. (f) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* 1982, 104, 4240. (g) Hill, G. L.; Schardt, B. C. *Ibid.* 1980, 102, 6374. (h) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; p 127 ff.