second option has its origins in the conformation-reactivity relationships of triplet olefins.[19]

The preceding considerations assume, of course, that the reaction chronology bypasses the intervention of *syn*-sesquinorbornatrienes. This question remains under active investigation.

Acknowledgment. We are grateful to the National Institutes of Health for financial support of this work (Grant CA-12115).

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Reaction of sp^2 C-H Bonds in Unactivated Alkenes with Bis(diphosphine) Complexes of Iron

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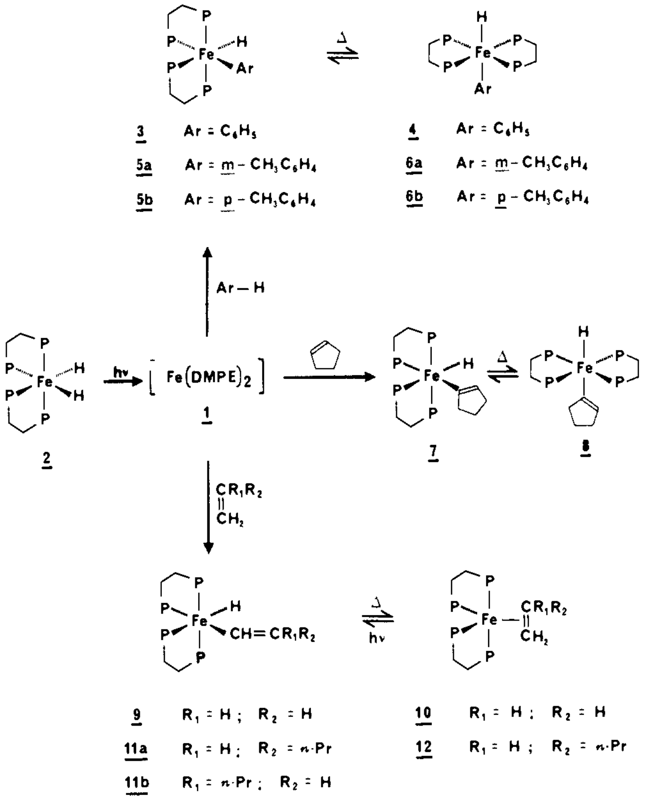
Over the last 10 years, there has been much interest in the chemistry of coordinatively unsaturated transition-metal complexes, particularly in the activation of alkyl C-H bonds by complexes of Ir,[1] Rh,[1b,2] Re,[3] and W.[4] Some early fundamental work[5a-c] in the area of C-H bond activation involved $Fe(DMPE)_2$ (**1**) [DMPE = 1,2-bis(dimethylphosphino)ethane], a reactive intermediate generated by reductive elimination of naphthalene from *cis*-$FeH(Np)(DMPE)_2$ [Np = 2-naphthyl]; however, this system was limited in that only substrates with a reactivity greater than (or comparable to) that of the naphthalene byproduct could be examined. In addition, this route to **1** necessarily required reaction temperatures close to room temperature, where any thermally labile products may not have been sufficiently stable to be observed or characterized.

An alternative, more versatile route to **1** is by photolysis of the dihydride $FeH_2(DMPE)_2$[6] (**2**). We have examined the reactions of **1**, generated photochemically at low temperature, with hydrocarbons, and report here the formation of products arising from Fe insertion into sp^2 C-H bonds of *unactivated* alkenes.

Irradiation[7] of a dilute solution of **2** in benzene at room temperature led to elimination of dihydrogen and formation of a mixture of *cis*-$FeH(C_6H_5)(DMPE)_2$ (**3**) and *trans*-$FeH(C_6H_5)(DMPE)_2$ (**4**)[8] (Scheme I). Irradiation of a solution of **2** in toluene at -80 °C similarly led to elimination of dihydrogen and initially afforded a mixture of the *cis*-tolyl hydrides **5a** and **5b**.[9] On warming to 0 °C, **5a** and **5b** isomerized to give an equilibrium mixture containing **5a** and **5b** as well as the trans isomers **6a** and **6b**. The complexes **3**-**6** have been reported previously as products formed on elimination of naphthalene from $FeH(Np)(DMPE)_2$ in benzene or toluene.[5c] It has been reported recently that photolysis of **2** in toluene at room temperature affords the DMPE-bridged dimer $Fe_2(DMPE)_5$.[10] In our experience, this product is only obtained in the presence of excess DMPE.

Scheme I



Photolysis of **2** in solutions containing alkenes led primarily to the formation of products arising from insertion of **1** into an sp^2 C-H bond. On irradiation of **2** at -80 °C in a solution of cyclopentene (5% in cyclopentane) a single cis product formed quantitatively. This compound was assigned the structure **7**, and on warming to 0 °C it isomerized to give an equilibrium mixture of *cis*- and *trans*-cyclopentenyl hydrides **7** and **8** in a 1:3 ratio. When the reaction mixture was quenched with 2 equiv of deuteriotrifluoroacetic acid in THF at -78 °C, cyclopentene was liberated with deuterium incorporated only at the vinylic positions.

Photolysis of **2** in a solution of ethylene (4% in pentane or cyclopentane) at -80 °C afforded a 10:1 mixture of the *cis*-vinyl hydride **9** and the known π-complex **10**.[5a] When warmed to room temperature, the C-H insertion product **9** isomerized to the π-complex. Similarly, photolysis of **2** in a solution of 1-pentene (5% in pentane) at -80 °C led to two major products in approximately equal amounts, and we assign these as the *Z* and *E* isomers **11a** and **11b**, which would arise by insertion of **1** into the terminal sp^2 bonds of 1-pentene.[11] Small amounts of the π-complex **12** were always present (ca. 5-10%) in the reaction mixture, and when the sample was warmed to room temperature, both **11a** and **11b** isomerized to **12**. This sequence is analogous to that reported[12] for the reaction of ethylene with the coordinatively unsaturated iridium species $(\eta^5\text{-}Me_5C_5)Ir(PMe_3)$, where the concurrent formation of a π-complex and a C-H insertion product has been demonstrated.

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(1) (a) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190-7191 and references cited therein. (b) Janowicz, A. H; Periana, R. A.; Buchanan, J. M.; Kovac, C. A.; Stryker, J. M.; Wax, M. J.; Bergman, R. G. *Pure Appl. Chem.* **1984**, *56*, 13-23 and references cited therein.

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(3) Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, *25*, 1283-1286 and references cited therein.

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(5) (a) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4080-4089. (b) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577-7585. (c) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742-1751.

(6) Meakin, P.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 75-88.

(7) Samples were irradiated in Pyrex NMR tubes, positioned ca. 10 cm from a 125-W mercury vapor lamp. The tubes were supported within a quartz cylinder and cooled by a stream of nitrogen gas.

(8) Attempts to isolate the complexes arising from direct C-H bond cleavage failed, apparently due to facile elimination of arene or alkene.

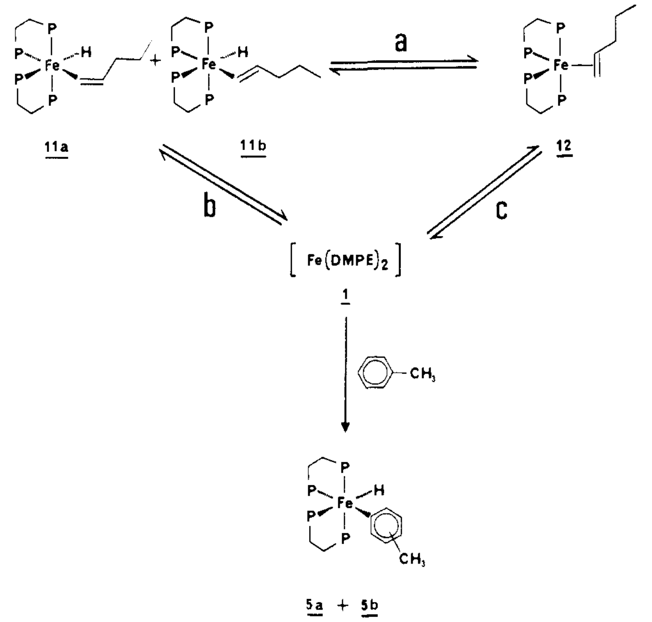
(9) The initial formation of exclusively cis addition products is consistent with an oxidative addition which proceeds via a three-center transition state see ref 5b.

(10) Bergamini, P.; Sostero, S.; Traverso, O. *J. Organomet. Chem.* **1986**, *299*, C11-C14.

(11) Analogous products are obtained on reaction of **1** with propylene, 1-butene, and isobutylene.

(12) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581-4582.

Scheme II



Treatment of a reaction mixture containing the vinyl hydride **9** with $CHCl_3$[13] afforded the thermally stable derivative *trans*-$\mathrm{ClFe(CH{=}CH_2)(DMPE)_2}$ (**13**), while treatment with CH_2Br_2 afforded *trans*-$\mathrm{BrFe(CH{=}CH_2)(DMPE)_2}$ (**14**). Similarly, treatment of a mixture of the cyclopentenyl iron hydrides **7** and **8** with CH_2Br_2 afforded the corresponding bromide, *trans*-$\mathrm{BrFe(\overline{C{=}CHCH_2CH_2CH_2})(DMPE)_2}$ (**15**). We have evidence that the *cis*-alkenyl iron hydrides react with $CHCl_3$ or CH_2Br_2 to form *cis*-halo derivatives initially, and these isomerize to the trans complexes on warming. After they were quenched with the haloalkanes, the reaction mixtures always contained *trans*-$\mathrm{Br_2Fe(DMPE)_2}$ or *trans*-$\mathrm{Cl_2Fe(DMPE)_2}$[14] in varying amounts.

The π-complex **12** is fluxional on the NMR time scale at room temperature, but this is not unexpected as the analogous π-complexes of ethylene, propylene, 1-butene, and styrene also exhibit dynamic behavior on the NMR time scale.[5a] **12** is photochemically labile, and photolysis at -80 °C in the presence of excess 1-pentene leads to the reformation of a mixture which contains **11a** and **11b** as dominant products. In a sealed tube, the cycle **11a** + **11b** (warm) → **12** ($h\nu$, -80 °C) → **11a** + **11b** was repeated 6 times with no significant degradation of the sample.

Irradiation of either **12** or a mixture of **11a** and **11b** at -80 °C in the presence of toluene led to formation of the tolyl iron hydrides **5a** and **5b**. This suggests that, under photolytic conditions, each of the complexes **11a**, **11b**, and **12** affords the coordinatively unsaturated intermediate **1** which reacts with the added arene. In Scheme II, at least two of the three pathways a, b, or c must operate under photochemical conditions. At present, we have no evidence to indicate whether **12** is an intermediate in the conversion of **11a** and **11b** to **1** or vice versa.[15]

Acknowledgment. We gratefully acknowledge financial support from the Australian Research Grants Scheme and the Australian Government for a Commonwealth Postgraduate Award (M.V.B.).

Supplementary Material Available: ^1H and ^{31}P NMR spectral data for compounds **3**–**15** (4 pages). Ordering information is given on any current masthead page.

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[13] In a typical experiment, 2-4 equiv of a solution of $CHCl_3$ or CH_2Br_2 (0.2 M in pentane) was added to a sample of an alkenyl iron hydride in pentane at -78 °C. The sample was warmed to room temperature, stripped of solvent under vacuum, and extracted into deuteriobenzene.

[14] Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 5507-5511.

[15] The coordinatively unsaturated intermediate $\mathrm{Fe(DEPE)_2}$ [DEPE = 1,2-bis(diethylphosphino)ethane], an analogue of **1**, reacts with C-H bonds in ethylene *without* prior formation of the π-complex. Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.*, in press.

Conformer Selection by Monolayer Compression

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Cyclization of nerol (**1a**) and its derivatives is a well-known reaction in terpene chemistry. Zeitschel[1] proved the cis configuration for nerol by showing that it cyclizes to α-terpineol (**4**), 9 times faster than geraniol (**2**) in dilute sulfuric acid. Several kinetic studies have shown that neryl derivatives solvolyze with π-participation of the remote double bond.[2-7] This participation imposes considerable restraints upon the transition state in terms of partial gauche butane-like interactions and a loss of rotational entropy estimated to be ca. 5.5 eu,[6] leading to only modest rate enhancements relative to the geranyl isomers which react to give largely acyclic products.

In the present study the ability of nerol and geraniol to form monolayers as a consequence of their amphipathic nature has been exploited to select conformers. In the monolayer the OH group is incorporated into the aqueous subphase and the hydrocarbon chain oriented away from it. When the monolayer is compressed to a high surface pressure, the hydrocarbon chains are forced out into a vertical position, while at low surface pressures the monolayer is in an expanded state, the hydrophobic chains are less oriented, and the molecules lie randomly on the surface. This difference has been used to select conformers of compressed and expanded films over dilute sulfuric acid, using a modified Langmuir trough consisting of a thermostated multicompartmental PTFE trough with a Wilhelmy plate balance.[8] The subphases (in this case 5% H_2SO_4 and water) could be confined in different compartments and the monolayers transferred from one to the other with minimal mixing. In a typical experiment 100 μL of a 0.1 M solution of the alcohol in hexane was spread on water, compressed to over 20 dyn cm^{-1} and transferred to 5% H_2SO_4 at 25 °C. After 5 min the layer was transferred to water, the monolayer material extracted into hexane, and the products determined by GLC. For the expanded films the monolayer was spread directly over the acid and allowed to react for 5 min. Since the surface pressures were as low as 2 dyn cm^{-1}, the films were compressed before transfer over water and extraction.[10]

Compressed nerol films remain largely unreacted giving <5% α-terpineol. By contrast expanded films with the same exposure time gave >90% cyclization to α-terpineol and <10% nerol. Clearly in compressed films existence of conformers **1b** leading to **1c** (Scheme I) is strongly disfavored and the monolayer may be considered to consist largely of extended conformers of the type **1a**. With expanded films conformer **1b** is accessible, despite being at least 1.5 kcal higher in energy than the extended conformers,[6] and may be stabilized by hydrophilic interaction of the remote double bond with the aqueous subphase.[9] Formation of transition state **1c** is thereby strongly favored. Interestingly <2% linalol (**3**) is formed in either film, and this points to negligible "slipping" of extended conformers to the allylically delocalized cation in the compressed films. In expanded films the factors favoring reaction of conformer **1b** to cyclic products seem overwhelming, in contrast to the behavior of neryl cations in bulk-phase hydrolyses where

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[2] Valenzuela, P.; Cori, O. *Tetrahedron Lett.* **1967**, 3089.

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[6] Astin, K. B.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1160.

[7] Bunton, C. A.; Cori, O.; Hachey, D.; Leresche, J.-P. *J. Org. Chem.* **1979**, *44*, 3238.

[8] Fromherz, P. *Rev. Sci. Instrum.* **1975**, *46*, 1380.

[9] E.g.: Davies, J. T.; Rideal, E. K. *Interfacial Phenomena*; Academic Press: New York, 1963; p 284.

[10] In view of the low alcohol concentrations required for the monolayer studies, overall yields could not be reliably assessed. However, reaction times were maintained strictly constant and our conclusions regarding relative reactivities of the conformers retain their validity.

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