

Intramolecular C-H Insertion Reactions of (Cyclopentadienyl)dicarbonyliron Carbene Complexes

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Received June 13, 1989

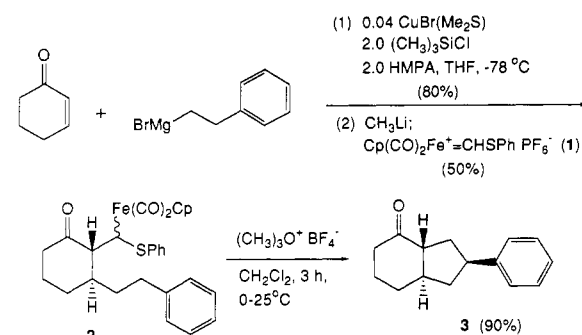
Carbene, or alkylidene, complexes of transition metals are well-known, thoroughly studied species.¹ Among the carbene complexes for which useful reactivity has been reported, the complexes containing the (η^5 -cyclopentadienyl)dicarbonyliron [or $\text{Cp}(\text{CO})_2\text{Fe}$] and related iron groups are especially prominent. Particularly well developed are the uses of these iron complexes in alkylidene transfer reactions with alkenes to give cyclopropanes.² Other reactions of these complexes have been developed much less extensively. Recently, we reported that these complexes can participate in cationic olefinic cyclization reactions,³ and now we report that these species can undergo intramolecular C-H insertion reactions.

We have previously reported the facile preparation and uses of the stable thiocarbene complex $\text{Cp}(\text{CO})_2\text{Fe}^+=\text{CHSPh PF}_6^-$ (**1**) as a reagent for the incorporation of prospective carbene centers into a variety of organic systems.⁴ These incorporations are accomplished by means of simple carbanionic addition reactions to **1**. Thus, copper-promoted addition of (2-phenylethyl)magnesium bromide to 2-cyclohexenone in the presence of trimethylsilyl chloride⁵ followed by enolate addition to **1** gives the adduct **2** as a mixture of diastereomers with respect to the iron-bearing carbon atom. Treatment with trimethyloxonium tetrafluoroborate under standard conditions for sulfonium salt formation and spontaneous carbene complex generation leads to direct, stereoselective formation of the cyclopentane-fused product **3** (Scheme I). This product is, at least formally speaking, the result of carbene insertion into a benzylic C-H bond of the substrate **2**.

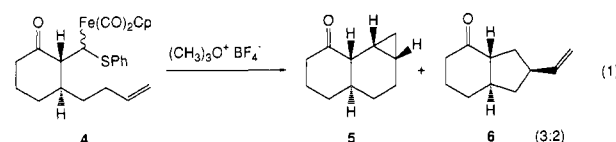
In this initial case, we have attempted to optimize the results of the cyclization step in order to set a reasonable upper limit for the yield of this key step. Through use of **2** that has been purified carefully by column chromatography (silica gel), cyclization product **3** is obtained in 90% yield.⁶ In the other brief, exploratory studies reported below, we have simply used the adducts corresponding to **2** in crude form and have determined only the overall yields from the silyl enol ethers resulting from the initial conjugate additions to the alkenone starting materials.

Iron carbene complexes have previously been shown to undergo intramolecular alkene cyclopropanation reactions.⁷ In the case of substrate **4** (obtained as in Scheme I, but with 3-butenyl-

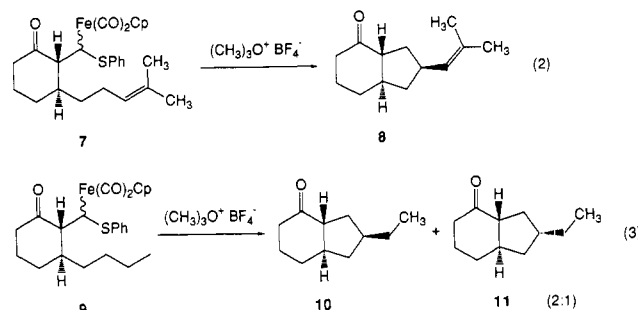
Scheme I



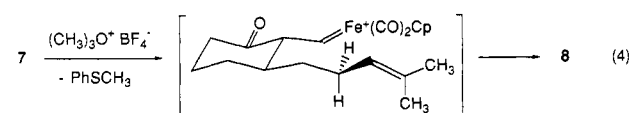
magnesium bromide as the Grignard reagent), intramolecular cyclopropanation and formal allylic C-H insertion occur competitively to give the products **5** and **6**, respectively, in a ratio of 3:2 (eq 1; 51% overall yield). On the other hand, substrate **7**



[obtained by using (4,4-dimethyl-3-butenyl)magnesium bromide], containing a more highly substituted and thus more hindered double bond, undergoes cyclopentane formation to give **8** exclusively within our limits of detection (<5% by ¹H NMR; eq 2; 51% overall yield). Formal insertion occurs, albeit less efficiently, even in the case of a substrate **9** (obtained by using *n*-butylmagnesium bromide) containing a simple saturated, alkyl side chain (eq 3; 36% overall yield).



The stereoselectivity seen in these reactions may tentatively be explained by assuming that the intermediate carbene complexes adopt a conformation such as that illustrated in the case of substrate **7** (eq 4). The delineation of the mechanism(s) for the further reaction of the intermediates to give the cyclization products must await further studies.



Insertions of carbenes and carbene complexes into C-H bonds are certainly well-known reactions,⁸ but they have not been developed previously for the above types of iron carbene complexes.⁹

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(8) (a) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971. (b) *Carbenes*; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. 1; *Ibid.* 1975; Vol. 2. (c) Wulfsberg, D. S.; Linstromelle, G.; Cooper, C. F. In *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: Chichester, 1978; Part 2, p 821. (d) Wulfsberg, D. S.; Poling, B. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. 1, p 321. (e) Wentrup, C. *Reactive Molecules*; Wiley: New York, 1984; p 162. (f) Moss, R. A.; Jones, M. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1985; Vol. 3, p 45 and the earlier volumes of this series. (g) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919. (h) Maas, G. *Top. Curr. Chem.* **1987**, *137*, 75.

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In recent years, the best-developed intramolecular C-H insertion reactions have been rhodium-catalyzed reactions of diazo carbonyl compounds, which are believed to occur via intermediate rhodium carbene complexes.¹⁰ In a comparison of the methods, useful complementarity exists between the iron carbene and the rhodium-catalyzed reactions. From the point of view of synthetic strategy, the rhodium-catalyzed ring closures proceed with carbon-carbon bond formation α to a carbonyl group, whereas the iron-based reactions result in ring closure β to a carbonyl group. Also, the iron carbene reactions produce cyclopentane rings bearing a substituent incorporated stereoselectively at a position γ to a carbonyl group, a position that is not normally subject to direct introduction of substituents. Another attractive feature of the iron-based reactions is the ease and directness with which fairly complex substrates are available from simple starting materials.

Further, in-depth studies of the iron carbene insertion reaction are clearly necessary to define the scope of this new method. The effects of other saturated and unsaturated side-chain substituents as well as heteroatomic substituents will be explored.

Acknowledgment. We thank Dr. James T. Carey, Prof. Anthony Serianni, and Donald Schifferl for extensive help with NMR data, Dr. T. K. Mishra of the Carnegie-Mellon NMR Laboratory for obtaining 620-MHz ¹H NMR data, and Dr. Bruce Plashko for mass spectrometric measurements. We are also very grateful to the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, for providing generous financial support of this research.

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Highly Efficient Complexation of a π -Acceptor by a Molecular Tweezer Containing Two π -Donors: The Role of Preorganization

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Received June 30, 1989

The stacking of aromatic systems has relevance to many areas of chemistry. For example, it has found recent use as a binding element in host-guest chemistry.² We have described a new class of hosts (e.g., *molecular tweezer 1*) which contain two acridine chromophores held syn cofacially by a rigid dibenz[*c,h*]acridine spacer.^{3,4} In chloroform, the acridines acted as π -donor chro-

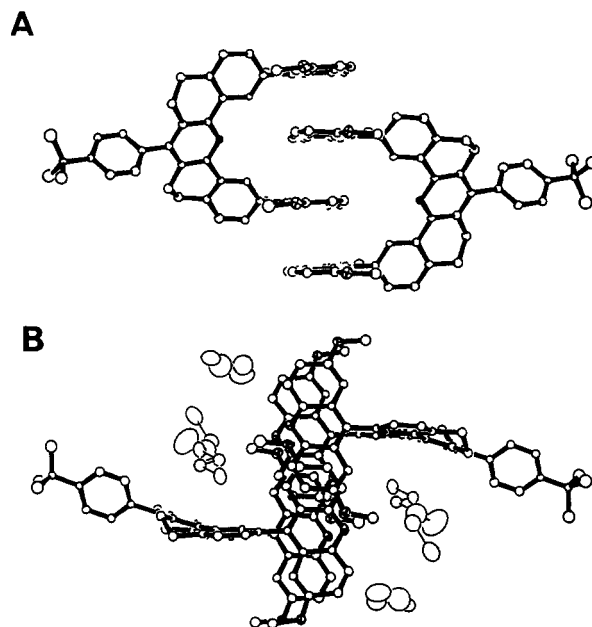


Figure 1. Side (A) and top (B) views of crystal packing of molecular tweezer 4. Solvent molecules (dichloroethane) have been omitted in A for clarity.

mophores to "cooperatively" sandwich a π -deficient (acceptor) aromatic guest.⁵ While efficient π -sandwiching is common when driven by the hydrophobic effect,⁶ it has not been well documented in cases where electron donor-acceptor (EDA) interactions are the primary binding force.⁷⁻⁹ In this communication we report

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(4) For a related approach, see: Wilcox, C. S.; Greer, L. M.; Lynch, V. *J. Am. Chem. Soc.* **1987**, *109*, 1865-1867. Harmata, M.; Murray, T. *J. Org. Chem.* **1989**, *54*, 3761-3763 and references therein.

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(8) Stoddart has reported several hosts with two π -donor or two π -acceptor chromophores. Although association constants have not been compared with monochromophoric analogues, there is clear evidence for cooperative π -sandwiching in acetone and acetonitrile: Colquhoun, H. M.; Goodings, E. P.; Maud, J. M.; Stoddart, J. F.; Williams, D. J.; Wolstenholme, J. B. *J. Chem. Soc., Chem. Commun.* **1983**, 1140-1142. Colquhoun, H. M.; Goodings, E. P.; Maud, J. M.; Stoddart, J. F.; Wolstenholme, J. B.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 2* **1985**, 607-624. Stoddart, J. F. *Pure Appl. Chem.* **1988**, *60*, 467-472. Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1547-1550.

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(2) Representative examples: Tabushi, I.; Sasaki, H.; Kuroda, Y. *J. Am. Chem. Soc.* **1976**, *98*, 5727-5728. Soga, T.; Odashima, K.; Koga, K. *Tetrahedron Lett.* **1980**, 4351-4354. Jarvi, E. T.; Whitlock, H. W., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 657-662. Diederich, F.; Dick, K. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 715-716. O'Krongly, D.; Denmeade, S. R.; Chiang, M. Y.; Breslow, R. *J. Am. Chem. Soc.* **1985**, *107*, 5544-5545. Rebek, J., Jr.; Nemeth, D. *Ibid.* **1985**, *107*, 6738-6739. Pirkle, W. H.; Pochapsky, T. C. *Ibid.* **1986**, *108*, 5627-5628. Sheppard, T. J.; Pettit, M. A.; Dougherty, D. A. *Ibid.* **1986**, *108*, 6085-6087. Wilcox, C. S.; Cowart, M. D. *Tetrahedron Lett.* **1986**, 5563-5566. Hamilton, A. D.; Van Engen, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 5035-5036. See also references 3, 8, and 9.