indicate that these sites do not exchange. Other mechanisms[17] require the presence of good nucleophiles and they are not present.

(17) A. A. El-Anani, C. C. Greig, and C. D. Johnson, *Chem. Commun.*, 1024 (1970).

(18) For example, carbocation **2f** in the presence of the phenalenyl radical (**2f** + 1 electron) shows no ^{1}H NMR signals.

(19) R. M. Pagni, P. Easley, and R. Smith, unpublished results.

(20) This work was supported by the University of Tennessee.

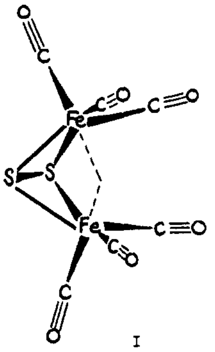
Richard M. Pagni,* Robert J. Smith
Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37916

Received August 25, 1978

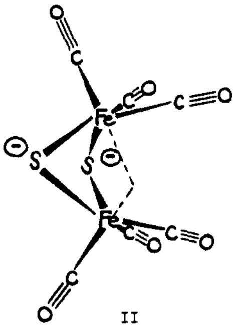
Novel Bridging Sulfide Anion Complexes of the Hexacarbonyldiiron Unit: a New Route to Alkylthio Complexes of Iron

Sir:

The interesting iron-sulfur cluster complex, μ-dithio-bis(tricarbonyliron), I, has been known for 20 years since its first preparation by Hieber and Gruber,[1] and its structure, as indicated in I, was determined by Wei and Dahl.[2] Although new procedures for the preparation of I have been developed recently by Russian workers,[3] only little work has been reported concerning the chemical transformations of this complex. Of some interest is the reaction of $S_2Fe_2(CO)_6$ with $GeCl_2$ precursors, which resulted, it was claimed, in the insertion of $GeCl_2$ into the Fe-Fe bond.[4]



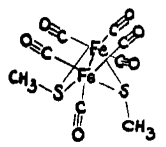
I



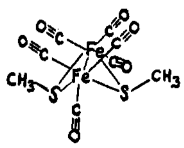
II

In an extension of our interest and activity in the area of heteroatom-containing transition metal carbonyl cluster complexes,[5] we have begun an investigation of the chemistry of $S_2Fe_2(CO)_6$. We report here some initial results.

The reaction of $S_2Fe_2(CO)_6$ with suitable reducing agents results in cleavage of the sulfur-sulfur bond, giving a dianion, presumably II, which has bridging sulfide anion ligands. Although structural studies have not been carried out as yet, the reactions of II suggest the assigned structure since reactions with alkyl iodides give products with bridging mercapto ligands. In a typical reaction, addition of 2.74 mmol of ruby-red crystals of $S_2Fe_2(CO)_6$ in THF to a suspension of 6.9 mmol of potassium hydride in THF (all operations under nitrogen in a drybox or using Schlenk apparatus) gave a dark red solution and caused gas evolution. Starting material was consumed (by TLC) within 4 h at room temperature. Filtration was followed by addition of 14.4 mmol of iodomethane to the red filtrate. After a reaction period of 12 h at room temperature, the solvent was removed and the residue was chromatographed (silicic acid-pentane) to give the known[6,7] isomers of $(CH_3S)_2Fe_2(CO)_6$ in 53% combined yield. This isomer mixture could be resolved by column chromatography into pure III, mp 65-67 °C (lit.[6] mp 65-67.5 °C), and IV, mp 101.5-102.5 °C (lit.[6] mp 101.5-103.5 °C). Isomers III and IV, whose structures had been assigned on the basis of considerations of the structure of $(C_2H_5S)_2Fe_2(CO)_6$ as determined by X-ray diffraction,[7] were formed in 2.7:1 ratio.



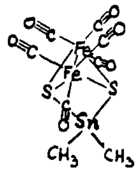
III



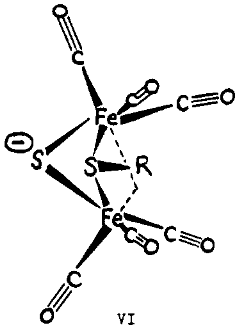
IV

Dianion II also could be formed by the reaction of $S_2Fe_2(CO)_6$ with sodium sand[8] or commercial sodium dispersion. Alkylation of II thus produced with iodomethane gave $(CH_3S)_2Fe_2(CO)_6$ (a mixture of III and IV in each case) in yields of 34 and 31%, respectively. Alkylation of II prepared by the sodium dispersion route with iodoethane resulted in formation of the known[7,9] $(C_2H_5S)_2Fe_2(CO)_6$ in 29% yield. The product, a dark red, air-stable solid, had mp 73-75 °C (lit.[9] mp 75.5 °C). The potassium hydride procedure gave this complex in 46% yield.

While complexes of type $(RS)_2Fe_2(CO)_6$ are more easily and directly prepared by reactions of thiols, sulfides, and disulfides with iron carbonyls,[10,11] dianion II nevertheless can have interesting and useful preparative applications. One example, its reaction with dimethyltin dichloride to give $(Me_2SnS_2)Fe_2(CO)_6$, a black-purple solid which is fairly air stable, mp 95 °C dec, presumably with structure V, serves to illustrate this. The ^{1}H NMR spectrum of V (in acetone-d_6) shows the CH_3 resonance as a singlet with ^{117}Sn and ^{119}Sn satellites (J = 30 and 32 Hz). The molecular ion was observed in the mass spectrum. Also observed were fragment ions due to successive loss of the six carbonyl ligands and the two methyl groups, giving finally the cluster ion $[Fe_2SnS_2]^+$.



V



VI

A monoanion derived from I (VI) also may be generated by reaction of $S_2Fe_2(CO)_6$ with an alkyllithium reagent, and in these homogeneous reactions much better product yields are obtained. For instance, the reaction of $S_2Fe_2(CO)_6$ in THF with an equimolar quantity of $CH_3Li/LiBr$ in diethyl ether (Alfa Inorganics) at −78 °C under nitrogen gave a green solution at the equivalence point. Addition of iodomethane, followed by a 12-h reaction time at room temperature, resulted in the formation of the two isomers of $(CH_3S)_2Fe_2(CO)_6$ in 82% yield (III/IV ratio, 3.1). A similar reaction in which anion VI (R = CH_3) was allowed to react with iodoethane gave $(CH_3S)(C_2H_5S)Fe_2(CO)_6$, an air-sensitive, dark red oil, bp 50 °C (0.2 Torr) (short-path still), in 77% yield. In another experiment, a THF solution of $S_2Fe_2(CO)_6$ at −78 °C was treated with n-butyllithium in hexane to give anion VI (R = n-C_4H_9). Reaction of the latter with CH_3I produced $(CH_3S)(n\text{-}C_4H_9S)Fe_2(CO)_6$, an air-sensitive red oil, which also could be distilled, in 70% yield.

μ-Dithio-bis(tricarbonyliron) thus has been shown to be a source of interesting sulfur-centered mono- and dianions. The monoanion provides a useful reagent for the preparation of unsymmetrical bis(alkylthio)hexacarbonyldiiron complexes, μ-(RS)-μ-(R′S)$Fe_2(CO)_6$, and the dianion should show interesting applications in the synthesis of acyclic and cyclic metal-sulfur-iron complexes. These applications, as well as further development of the chemistry of $S_2Fe_2(CO)_6$, are receiving our attention.

0002-7863/79/1501-0508$01.00/0

Acknowledgments. The authors are grateful to the National Science Foundation for support of this work (Grant CHE75-21215) and to Cincinnati Milacron Chemicals, Inc., for a gift of dimethyltin dichloride.

References and Notes

(1) W. Hieber and J. Gruber, *Z. Anorg. Allg. Chem.*, **296**, 91 (1958).
(2) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1 (1965).
(3) N. S. Nametkin, V. D. Tyurin, and M. A. Kukina, *J. Organomet. Chem.*, **149**, 355 (1978).
(4) N. S. Nametkin, V. D. Tyurin, O. V. Kuz'min, A. I. Nekhaev, and M. Mavlonov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2143 (1976).
(5) (a) D. Seyferth, *Adv. Organomet. Chem.*, **14**, 97 (1976); (b) D. Seyferth and J. S. Merola, *J. Am. Chem. Soc.*, **100**, 6783 (1978).
(6) R. B. King, *J. Am. Chem. Soc.*, **84**, 2460 (1962).
(7) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 328 (1963).
(8) W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1970, p 476.
(9) H. Reihlen, A. Gruhl, and G. Hessling, *Justus Liebigs Ann. Chem.*, **472** 268 (1929).
(10) E. W. Abel and B. C. Crosse, *Organomet. Chem. Rev.*, **2**, 443 (1967).
(11) H. Vahrenkamp, *Angew Chem.*, **87**, 363 (1975).

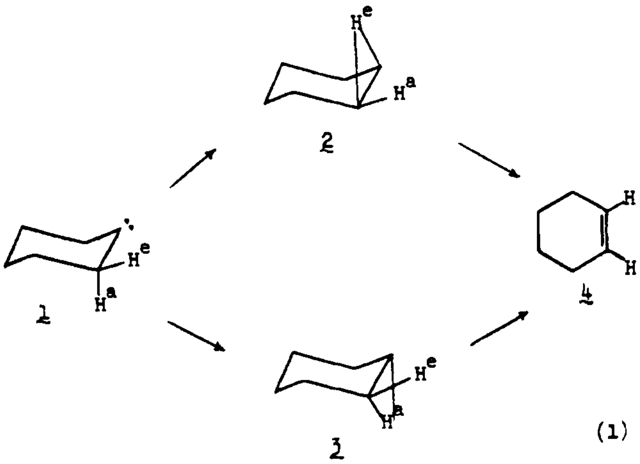
Dietmar Seyferth,* Richard S. Henderson
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received October 6, 1978

The Case for Stereoelectronic Axial Migration of Hydrogen in Nonrigid Cyclohexylidenes in Chair Conformation

Sir:

The stereochemistry of 1,2 rearrangements in carbenes is an important mechanistic question.[1] Brexan-5-ylidene, a rigid singlet cyclohexylidene in strained boat conformation, is presumed to undergo rearrangement of its exo α hydrogen 138 times faster than its endo hydrogen because migration is greatly favored for hydrogen which is nearly parallel to the vacant p orbital of the carbene.[1f] Subsequently, rearrangements of α-methine hydrogen and of α-phenyl occurring 1.46 and 0.20 times as extensively in *cis*- than in *trans*-4-*tert*-butyl-2-phenylcyclohexylidenes were interpreted to indicate that such migrations occur preferentially by axial processes.[1j] Recently, the migratory ratio, H(axial)/H(equatorial), of hydrogen from the 6 positions of 4-*tert*-butyl-2,2-dimethylcyclohexylidene was found to be 1.50.[1k] This result was theorized, however, to involve little stereoelectronic control during rearrangement. In conjunction with MINDO/3 or MNDO calculations,[11] it was then suggested that the activation energy for rearrangement of a nonrigid, chair-like cyclohexylidene (**1**) in which H^c migrates toward the empty carbenic orbital with realignment of H^a as in **2** is essentially equal to that to **3** or to alternate transition states.[11]

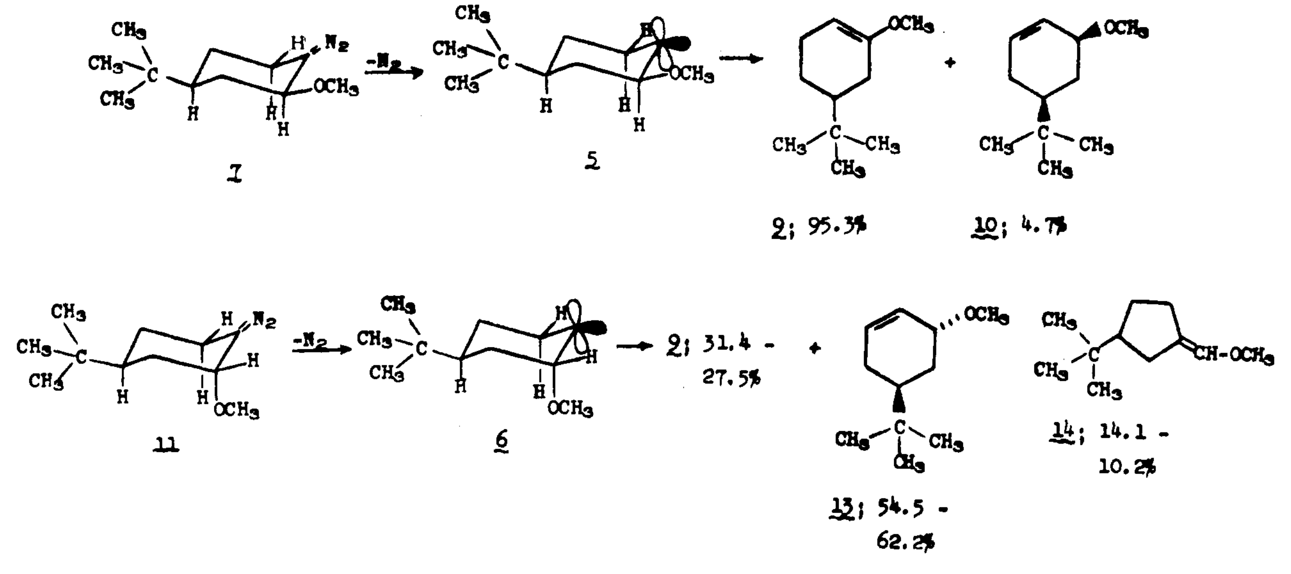


(1)

A study is now reported of the carbenic rearrangements of 4-*tert*-butyl-*cis*-2-methoxycyclohexylidene (**5**) and 4-*tert*-butyl-*trans*-2-methoxycyclohexylidene (**6**). These systems indicate clearly the significance of axial stereochemical preferences for migration in these conformationally restricted cyclohexylidenes. The results also (1) raise the question that the recent calculations for rearrangement of cyclohexylidene may be overextended[11] and (2) allow definition of factors in substituted flexible cyclohexylidenes which lead to rearrangement with apparent minimal stereoelectronic control.[1k,l]

Thus 1-diazo-2-methoxy-*cis*-4-*tert*-butylcyclohexane (**7**), generated in situ from sodium 2-methoxy-*cis*-4-*tert*-butylcyclohexanone *p*-tosylhydrazonate (**8**),[2a-c] decomposes in diglyme[2c] at 190 °C to 5-*tert*-butyl-1-methoxycyclohexene (**9**, 95.3%) and 5-*tert*-butyl-*cis*-3-methoxycyclohexene (**10**, 4.7%) (Scheme I), products of hydrogen migration from C-2 and C-6, respectively.[2d] Similar results are obtained by pyrolysis of dry **8** at 190 °C. In contrast, thermolysis of 1-diazo-2-methoxy-*trans*-4-*tert*-butylcyclohexane (**11**), as derived from sodium 2-methoxy-*trans*-4-*tert*-butylcyclohexanone *p*-tosylhydrazonate (**12**)[2a-c] at 190 °C in diglyme,[2c] gives **9** (31.4%) and 5-*tert*-butyl-*trans*-3-methoxycyclohexene (**13**, 54.5%) by hydrogen migration and 3-*tert*-butyl(methoxymethylene)cyclopentane (**14**, 14.1%) by ring contraction.[2d]

Scheme I



0002-7863/79/1501-0509$01.00/0