change shows that for these two and probably most other substituents $\Delta S_1 \approx \Delta S_{\text{rot.s.}}$. The ΔH_1 values shown in Table I were obtained under this assumption. Also shown in Table I are the STO-3G calculated[2] energy changes ΔE_1. A comparison between these ΔH_1 and ΔE_1 changes is given in Figure 1a, while Figure 1b gives a plot of the ΔH_1 and ΔE_1 values vs. the constants $\sigma_p{}^+$ of Brown and Okamoto[8] for para substituents.

Examination of Figure 1a shows on the whole a very good agreement between the experimental ΔH_1 and the theoretical ΔE_1. In Figure 1b again a good correlation is obtained between the ΔH_1 and the substituent constants $\sigma_p{}^+$, except for nitro-, cyanobenzene, and benzaldehyde, which are way out. Evidently protonation for these three compounds occurs not on the ring but on the substituent. All these substituents have lone pairs which can accommodate the proton. More importantly they are strongly electron-withdrawing substituents which destabilize the ring protonated ion. The good agreement of the results in Figure 1a and 1b show that in all other cases ring protonation in para position to the substituent can be occurring. For the alkyl and halo substituents and even HO- and CH_3O- this is not a surprising finding; however, the possibility of ring protonation in aniline is rather unexpected. The hydroxy, methoxy, and amino group are substituents that strongly stabilize the benzenium ion; on the other hand, phenyl is electron withdrawing and thus destabilizing for substituent protonation. Thus the protonation occurs on the ring and takes advantage of the stabilizing effect of the substituent. Ring protonation in -OH and $-OCH_3$ is in agreement with an earlier investigation of deuterium exchange by Beauchamp[9] and a recent correlation of oxygen 1s core electron energies with proton affinities by Harrison.[10] On the other hand Buttrill,[11] in a recent investigation, has come to the conclusion that substituent protonation occurs for those compounds. Buttrill observed strongly bonded $XC_6H_7{}^+\cdot OH_2$ hydrates for X = OH and CH_3O and argued that this would happen only if there is substituent protonation. In view of the present results, Buttrill's experiments can be interpreted as showing that the site of protonation is solvent dependent. It is known from NMR experiments in solution[12] that hydrogen-bonding solvents promote substituent protonation because of the strong hydrogen bonds that can be formed. For the same reason aniline is substituent protonated in polar solvents. Probably the proton affinity for N protonation of aniline is very close to that for ring protonation.[13] A correlation similar to that by Harrison,[10] but for 1s energies of N atoms, may be expected to provide the answer.

The values for OH in Figure 1 show considerable deviation from the σ correlation. It has been pointed out previously that this is due to the hydrogen bonding of the OH group to the solvent.[1,12] The reason for the disagreement between the ΔH and ΔE results for the OH and OCH_3 substituents (Figure 1a) is not clear.

References and Notes

(1) W. J. Hehre, D. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **92,** 4796 (1970).

(2) W. J. Hehre, R. T. McIver Jr., J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96,** 7162 (1974).

(3) J. M. McKelvey, S. Alexandratos, A. Streitwieser, Jr., J. L. M. Abboud, and W. J. Hehre, *J. Am. Chem. Soc.*, **98,** 244 (1976).

(4) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98,** 1320 (1976).

(5) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48,** 955 (1970) for ionization potential of t-C_4H_9 and W. Tsang, *J. Phys. Chem.*, **76,** 143 (1972), for $D(t\text{-}C_4H_9 - H)$.

(6) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **95,** 3504 (1973).

(7) The value for $\Delta H_{f298}(H^+)$ = 367 kcal/mol from *Natl. Bur. Stand.* (*U.S.*), *Tech. Note*, **No. 270-3** (19xx) is 1 kcal/mol higher than the often used value of 366 kcal/mol based on the compilation by J. L. Franklin, et al., Ed., *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26,** 1 (1969).

(8) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80,** 4979 (1958).

(9) B. S. Freiser, R. L. Woodin, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97,** 6893 (1975).

(10) F. M. Benoit and A. G. Harrison, in a paper presented at 59th Canadian Chemical Conference in London (Ontario), June 1976, have shown that a very good linear correlation is obtained when proton affinities of related oxygen bases (from ref 4) are plotted vs. 1s core electron energies of the oxygen atoms. The proton affinity of benzaldehyde, measured in the present work, fitted the correlation, but that of anisole was too high. Phenol was not investigated.

(11) D. P. Martinsen and S. E. Buttrill Jr., *Org. Mass Spectrom.*, **11,** 762 (1976).

(12) H. H. Jaffe, *Chem. Rev.*, **53,** 191 (1953).

(13) A theoretical calculation (STO-3G) for ΔE of the reaction $PhNH_3{}^+ + NH_3 = PhNH_2 + NH_4{}^+$ was found to be in very close agreement with experimentally measured $\Delta G°$ for proton transfer between aniline and ammonia (see R. W. Taft in "Proton Transfer Reactions", E. F. Caldin and V. Gold, Ed., Wiley-Halstead, New York, N.Y., 1975, p 61.

Yan K. Lau, Paul Kebarle*
Chemistry Department, University of Alberta
Edmonton, Alberta, Canada T6G 2E1

Received July 2, 1976

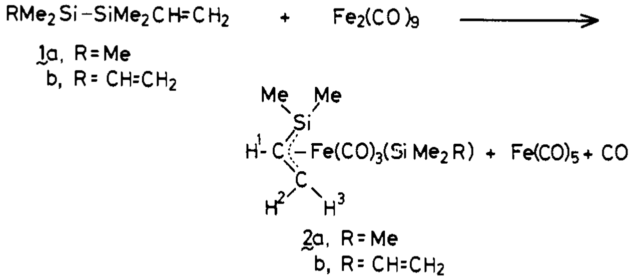
η^3-1-Silapropenyltricarbonyliron Complexes. The First Stable Compound of Doubly Bonded Silicon[1]

Sir:

It is well known that a transition metal can stabilize highly unstable molecules such as the allyl radical, cyclobutadiene, trimethylenemethane, and pentalene by forming stable complexes.[2] Although various attempts have been made also to stabilize unstable organosilicon species like silaethene[3] and "π-silaallyl" [4] by coordination with a transition metal, no success has been reported.

We report here the first preparation of η^3-1-silapropenyl complexes of iron. These complexes are the silicon analogues of π-allyl complexes and represent the first stable compounds of "doubly bonded silicon".

Enneacarbonyldiiron (200 mg, 0.55 mmol) and vinylpentamethyldisilane (**1a**, 230 mg, 1.45 mmol) were mixed with dry benzene (10 ml), and the yellow suspension was stirred at room temperature during 17 h under an argon atmosphere. A yellow-brown homogeneous solution was obtained at the end of the reaction. The solvent and volatile materials were evaporated and the residue was distilled under reduced pressure (~10^{-3} mmHg) to give a yellow-brown oil. A hexane solution of the oil was purified by preparative TLC on silica gel. After elution with hexane and evaporation, the residual oil was fractionated with a short column to give 100 mg (61.1% yield) of an analytically pure complex (**2a**), bp 45.0 °C (5 × 10^{-3} mmHg). The yellow complex, **2a,** was air sensitive and decomposed gradually on exposure to air, but was fairly stable thermally up to 80 °C.



The structure of the complex was determined on the basis of various spectroscopic studies to be (η^3-1,1-dimethyl-1-silapropenyl)(trimethylsilyl)tricarbonyliron as follows. The proton NMR spectrum of **1a** in carbon disulfide (Figure 1a) shows three Si–CH_3 signals at δ 0.15, 0.27, and 0.38 ppm with relative intensity of 1:3:1. These signals can be assigned to the *anti*-CH_3Si, $(CH_3)_3$Si, and *syn*-CH_3Si, respectively, in reference to the spectral data of the related π-allyliron complexes.[5] Vinyl protons of **2a** appear at higher field than the free

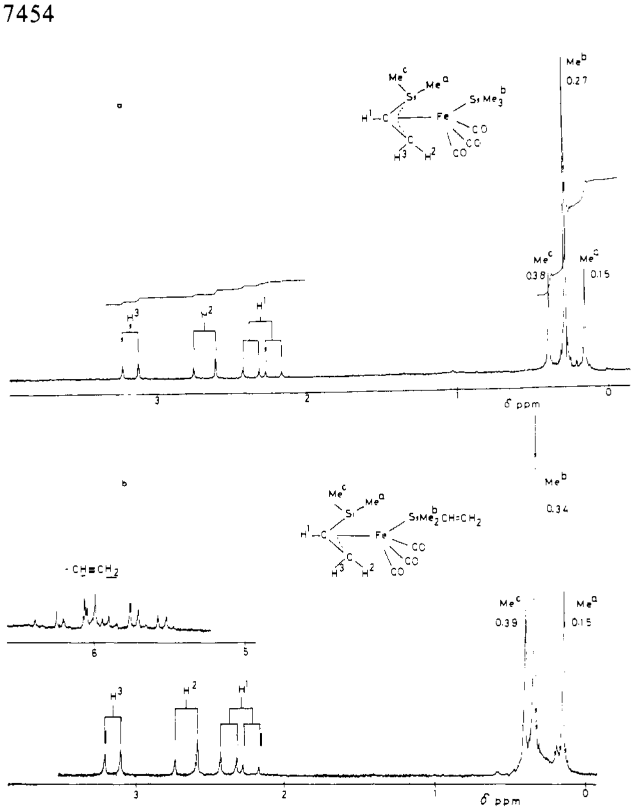


Figure 1. The ^{1}H NMR spectra of (a) **2a** and (b) **2b**.

vinyl protons because of the coordination to the iron atom. Thus, H^1 is observed at δ 2.29 ppm as a doublet of doublets with spin-spin coupling constants of 15.0 and 10.0 Hz. The chemical shifts of other vinyl protons, H^2 and H^3, are observed at δ 2.68 (doublet, $J = 15.0$ Hz) and 3.17 (doublet, $J = 10.0$ Hz), respectively. The proton decoupled ^{13}C NMR spectrum showed three C-Si signals at δ (vs. $Me_4Si = 0$) $-$ 3.0, -1.0, and 0.0 with relative intensity of 1:3:1, two vinyl carbons at δ 43.0 and 46.0 and carbonyl carbons at δ 212. A mass spectrum of **2a** (25 eV) showed inter alia the molecular ion $C_{10}H_{18}O_3Si_2Fe^+$ at m/e 298 and ions corresponding to the successive loss of three CO at m/e 270, 242, and 214. In its IR spectrum (film) three $\nu_{C=O}$ bands were observed at 2025, 1995, and 1975 cm^{-1}. These bands correspond nicely to those of π-allyltricarbonyliron halides which reportedly exhibited three $\nu_{C=O}$ bands between 2095 and 1980 cm^{-1}.[6] An absorption at 1315 cm^{-1} with medium intensity is interesting to note. The $\nu_{C=C}$ frequency of the coordinated double bond in the π-allyl complex is known to appear at about 100 cm^{-1} lower frequency than that of the free C=C.[7] Therefore, if the $\nu_{Si=C}$ value at 1407 cm^{-1} reported by Barton and McIntosh[8] is valid.[9] the absorption at 1315 cm^{-1} can be assigned to the frequency of the coordinated Si=C bond.

By a similar treatment with enneacarbonyldiiron (190 mg, 0.52 mmol) 1,2-divinyltetramethyldisilane (**1b**, 190 mg, 1.12 mmol) gave the corresponding yellow complex (**2b**) in 60% yield, bp 42.0 °C (10^{-3} mmHg). The ^{1}H spectrum of **2b** (Figure 1b) showed three CH_3-Si signals at δ 0.15 (3 H, s), 0.34 (6 H, s), and 0.39 (3 H, s) and three coordinated vinyl protons at δ 2.27 (1 H, dd, $J = 14.0$ and 10.0 Hz, H^1), 2.66 (1 H, d, $J = 14.0$ Hz, H^2), and 3.15 (1 H, d, $J = 10.0$ Hz, H^3). In addition to these signals, **2b** showed a multiplet at δ 5.50–6.50 (3 H) corresponding to a free vinyl group. The molecular ion, $C_{11}H_{18}O_3Si_2Fe^+$ at m/e 310, which loses three CO successively, was also observed. The IR spectrum of **2b** exhibited three $\nu_{C=O}$ at 2025, 1995, and 1975 cm^{-1}, an absorption at 1310 cm^{-1} (vide supra), and absorptions due to a free vinyl group at 1600 and 940 cm^{-1}. Again these spectroscopic data are fully in agreement with the structure indicated. Anal. Calcd for **2a** ($C_{10}H_{18}Si_2O_3Fe$): C, 40.27; H, 6.08. Found: C, 40.43; H, 5.86. Calcd for **2b** ($C_{11}H_{18}Si_2O_3Fe$): C, 42.58; H, 5.85. Found: C, 42.86; H, 5.67.

The spectroscopic evidence reported here suggests strongly that compounds **2a** and **2b** do indeed contain the η^3-1-silapropenyl ligand. However, ultimate proof of the structure should be given by an x-ray crystal-structure determination. Actually, we have examined the reaction of enneacarbonyldiiron with a variety of vinyldisilanes to obtain crystalline derivatives, but at this moment analytically pure samples have been obtained only for **2a** and **2b**. The reaction of **2** with other donors, for example, with triphenylphospine, resulted in the substitution of η^3-1-silapropenyl and silyl groups rather than CO to give bis(triphenylphosphine)tricarbonyliron.

$$\mathbf{2} + 2PPh_3 \rightarrow Fe(CO)_3(PPh_3)_2$$

Acknowledgment. We thank Toshiba Silicone Co., Ltd., for gifts of chlorosilanes. We also thank O. L. Chapman for a preprint.[10]

References and Notes

(1) Chemistry of Organosilicon Compounds 95.
(2) W. le Noble, "Highlights of Organic Chemistry", Marcel Dekker, New York, N.Y., 1974, Chapter 10.
(3) J. E. Bulkowski, N. D. Miro, D. Sepelak, and C. H. Van Dyke, *J. Organomet. Chem.*, **101**, 267 (1974).
(4) W. Malisch and P. Panster, *J. Organomet. Chem.*, **64**, C5 (1974).
(5) (a) F. J. Impastato and K. G. Ihrman, *J. Am. Chem. Soc.*, **83**, 3726 (1961); (b) M. L. H. Green and P. L. Nagy, *J. Chem. Soc.*, 189 (1963); (c) R. F. Heck and C. R. Boss, *J. Am. Chem. Soc.*, **86**, 2580 (1964); (d) F. M. Chaudhari, G. R. Knox, and P. L. Pauson, *J. Chem. Soc. C*, 2255 (1967); (e) D. H. Gibson and D. K. Erwin, *J. Organomet. Chem.*, **86**, C31 (1975); (f) A. N. Nesmeyanov, Yu. A. Ustynyuk, I. I. Kritskaya, and G. A. Shchembelov, *ibid.*, **14**, 395 (1968).
(6) H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **226**, 1927 (1962).
(7) M. L. H. Green, "Organometallic Compounds", Vol. 2, Methuen, London, 1968, Chapter 2.
(8) T. J. Barton and C. L. McIntosh, *J. Chem. Soc., Chem. Commun.*, 861 (1972).
(9) The result of Barton and McIntosh has been questioned.[10] However, the ab initio calculation predicted the stretching vibration of Si=C for $H_2Si{=}CH_2$ to be 1490 cm^{-1}.[11]
(10) O. L. Chapman, C.-C. Chang, J. Kolc, M. E. Jung, J. A. Lowe, T. J. Barton, and M. L. Tumey, *J. Am. Chem. Soc.*, in press.
(11) H. B. Schlegel, S. Wolfe, and K. Mislow, *J. Chem. Soc., Chem. Commun.*, 246 (1975).

Hideki Sakurai,* Yoshiyasu Kamiyama, Yasuhiro Nakadaira
Department of Chemistry, Tohoku University
Sendai 980, Japan

Received June 23, 1976

Copper(I) Catalysis of Olefin Photoreactions. Photorearrangement and Photofragmentation of 7-Methylenenorcarane

Sir:

Recently we have been concerned with discovering and understanding organic photochemical reactions which require transition metals as catalysts.[1] Olefin photoreactions which are catalyzed by salts of copper(I)[2] are especially interesting since the salts form isolable olefin complexes,[3] and since the olefin–metal interaction almost certainly plays a key role in the photochemical process. We now report that the photochemistry of 7-methylenenorcarane (**1**) in the presence of copper(I) is characterized by a plethora of novel molecular transformations involving carbon skeletal reorganizations, a new class of copper catalyzed photochemical process.

Our previous studies elucidated some mechanistic details of olefin photodimerization catalyzed by copper(I) salts.[1d] However, the precise nature of the olefin–catalyst–light interaction responsible for reaction is not known. The present study of photolysis of methylene cyclopropane **1** in the presence