because the nine methyl hydrogens result in a greater cross-section for the desired reaction.

It has been established[2,3] that reactions of F with primary C–H bonds are characterized by $\%E_v = 60 \pm 5$. For the reaction F + mesitylene-d_3 we find $\%E_v = 47$; this lowered fraction of energy released to HF$^+$ is a very sensitive indicator of the presence of radical stabilization since it describes the shape of the detailed vibrational energy distribution of the HF$^+$ product.

The constancy of $\%E_v$ for other R–CH$_3$ reactions[2,3] indicates that the entrance valleys of the surfaces for this class of reaction are nearly invariant and suggests that the relaxation of benzyl occurs on a slower time scale (hence later on the reaction coordinate) than the H atom transfer. The methylene torsion is expected to be the slowest component in the reorganization of benzyl and this serves to establish the relaxation time at *ca.* 10^{-13} sec. Three-body (R–H + F) trajectory calculations on a LEPS type potential energy surface indicate that the time scale for direct H atom abstraction by F is less than 10^{-14} sec.[9,10]

An unfortunate complication is that some reactive collisions are expected to occur by indirect encounters,[9,11] either complex encounters where the separation of HF$^+$ from R is not simple or encounters where the initially formed HF$^+$ undergoes a second collision with R.[9] In such encounters some of the stabilization energy of the R fragment may be transferred to HF$^+$. Because of this problem and the possibility that H atom transfer and the relaxation of the radical fragment may not be completely separated, even for simple collisions, we infer that our experimental measurement of E_{stab}. (C$_6$H$_5$CH$_2$) must represent a lower limit.[12]

Although these problems detract from the quantitative interpretation of our data, the present experiments represent the first direct[12] dynamical evidence concerning the disposal of the resonance stabilization energy of the radical fragment produced by an H atom abstraction reaction and, consequently, of the time scale for release of this energy. The method provides a straightforward and sensitive test for the presence of stabilization energy in polyatomic radicals.

(9) R. L. Johnson, K. C. Kim, and D. W. Setser, *J. Phys. Chem.*, **77**, 2499 (1973).

(10) The time scale for the atom transfer process is strongly dependent upon the mass of the central atom as well as other dynamical features. In general the fastest process is transfer of an H atom (the lightest possible mass) with a low threshold energy. Thus RH + F reactions are ideal probes for radical stabilization energy, E_{stab}(R).

(11) For a discussion see J. C. Polanyi, *Accounts Chem. Res.*, **5**, 161 (1972).

(12) Benson, *et al.* (ref 1), have found D_{298}(C$_6$H$_5$CH$_2$–H) = 85 kcal mol^{-1} which is anomalously low for a primary C–H bond. They have obtained the estimate, E_{stab}(C$_6$H$_5$CH$_2$) = 13 ± 1 kcal mol^{-1}, based upon comparison of the above value with D_{298}(CH$_3$CH$_2$–H) = 98 kcal mol^{-1}. Our lower limit of 11.2 kcal mol^{-1} is in good agreement with the above estimate. The well-known low reactivity of benzyl (and other resonance stabilized radicals) provides further indirect evidence. For discussion, see M. Szwarc, *Chem Rev.*, **47**, 75 (1950), and references therein.

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Relative Iron–Carbon and Iron–Silicon Bond Strengths in Derivatives of (η-Cyclopentadienyl)dicarbonyliron

Sir:

The transition metal–silicon σ-bond[1] has generally been considered to be substantially stronger than the corresponding metal–carbon σ-bond, presumably due to metal–silicon d$_\pi$–d$_\pi$ bonding.[2] This hypothesis appears to be supported by the known bond dissociation energies for transition metal–silicon and –carbon σ-bonds, which indicate the former to be stronger by 60–80 kcal,[3–5] and the instability of many alkyl complexes which have well-behaved organosilyl analogs. Recently, however, it has been proposed that the instability of many alkyl complexes is not a consequence of an inherently low metal–carbon bond strength but is rather due to the availability of a number of low energy degradative pathways.[6] Notable among these pathways is alkene formation *via* elimination of the transition metal and a β-hydrogen as the metal hydride. Since derivatives of silaethylene are apparently extremely reactive and or unstable, it has been proposed that part of the thermal stability of organosilyl complexes must be attributed to the reluctance of these complexes to decompose by elimination of the metal hydride.[7] We now wish to present chemical evidence which demonstrates that, in the case of derivatives of (η-cyclopentadienyl)dicarbonyliron, the iron–carbon and the iron–silicon σ-bond strengths are not significantly different and the possibility that the iron–carbon is stronger must be considered.

Our interest in the transition metal chemistry of strained and reactive olefins led us to prepare complexes **1, 2,** and **3** with a view toward transforming these substances into cationic silaisobutylene complexes. The silyl complexes (**1–3**) were prepared by distilling an equimolar quantity of chlorosilane, ClCH$_2$Si(CH$_3$)$_{3-n}$-Cl$_n$ (n = 1, 2, or 3), under vacuum onto a 0.4 M solution of sodium (η-cyclopentadienyl)dicarbonylferrate in tetrahydrofuran at $-196°$, warming the reaction mixture to room temperature, and stirring magnetically for 30 min. Complexes **1** and **2** were isolated by vacuum distilling the solvent at 0°, extracting the residue with *n*-hexane, and recrystallizing from *n*-hexane at $-78°$. Vacuum (10^{-5} mm) sublimation of the residue gave **3**. The yields were about 60% in all cases.[8]

(1) Silyl and silylmethyl complexes have been recently reviewed; C. S. Cundy, B. M. Kingston, and M. F. Lappert, *Advan. Organometal. Chem.*, **11**, 253 (1973).

(2) (a) R. B. King, K. H. Pannell, C. R. Bennett, and M. Ishag, *J. Organometal. Chem.*, **19**, 327 (1969); (b) A. G. Robiette, G. M. Sheldrick, R. N. F. Simpson, B. J. Aylett, and J. M. Campbell, *ibid.*, **14**, 279 (1968).

(3) The bond dissociation energies for Cl$_3$Si–, F$_2$MeSi–, and F$_3$Si–Co(CO)$_4$ have been reported as 126 ± 25, 127 ± 15, and 105 ± 12 kcal. The bond energies are dependent on the value used for $\Delta H_f°$ of Co$_2$(CO)$_8$ and may therefore be approximately 30 kcal lower. F. E. Saalfield, M. V. McDowell, and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, **92**, 2324 (1970).
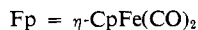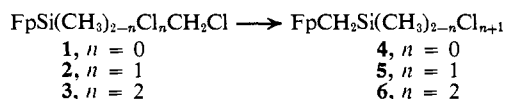
(4) Very few transition metal–carbon σ-bond dissociation energies have been determined and these are listed below: Me–Pt (CpPtMe$_3$), 39 ± 5;[5a] Et–Ti (Cp$_2$TiClEt), 36 kcal.[5b]

(5) (a) K. W. Egger, *J. Organometal. Chem.*, **24**, 501 (1970); (b) E. A. Fushman, E. D. Potyagalio, and N. M. Chirkov, *Izv. Akad. Nauk SSSR, Ser. Kim.*, 715 (1971).

(6) G. Wilkinson, *Pure Appl. Chem.*, **30**, 627 (1972).

(7) A. G. MacDiarmid, Y. L. Baay, J. F. Bald, A. D. Berry, S. K. Gondal, A. P. Hagen, M. A. Nasta, F. E. Saalfield, and M. V. MacDowell, *Pure Appl. Chem.*, **19**, 431 (1969).

(8) Satisfactory carbon, hydrogen, and/or halogen analyses have been obtained for all new compounds.

FpSi(CH₃)₂₋ₙClₙCH₂Cl ⟶ FpCH₂Si(CH₃)₂₋ₙClₙ₊₁

1, $n = 0$
2, $n = 1$
3, $n = 2$

4, $n = 0$
5, $n = 1$
6, $n = 2$

Fp = η-CpFe(CO)₂

Surprisingly, both **1** and **2** readily and quantitatively rearrange at 100° to the chlorosilylmethyl complexes **4** and **5**, respectively.[9] Although **3** does not rearrange under these conditions, it may be catalytically rearranged at room temperature by aluminum chloride in methylene chloride to **6** in 25% yield.[10] The melting points and nmr data for the complexes are presented in Table I.

Table I. Melting Points (°C) and Nmr Data[a] (τ) for FpR

R		Mp	CH₂	Me	Cp
–SiMe₂CH₂Cl	1	30–31	7.02	9.56	5.30
–SiMeClCH₂Cl	2	34–36	6.80 (AB)	9.16	5.15
			(J = 12 Hz)		
–SiCl₂CH₂Cl	3	89–90	6.63		5.04
–CH₂SiMe₃[b]		28–30	10.28	9.94	5.38
–CH₂SiMe₂Cl	4	40–42	10.21	9.59	5.19
–CH₂SiMeCl₂	5	28–29	10.05	9.25	5.15
–CH₂SiCl₃	6	23–24	9.87		5.13
–SiMe₂CH₂Br	7	c	7.22	9.51	5.29
–CH₂SiMe₂Br	8	43–45	10.02	9.45	5.20

[a] Determined in cyclohexane. The relative intensities agree with the assignments. [b] Reference 2a. [c] Too unstable to measure.

The identities of the Fe–Si and Fe–C isomers were established by comparison of the chemical shifts of the methylene resonances in the nmr spectra of **1–3** and **4–6**. Thus in the spectra of **1–3** this resonance was observed between τ 7.02 and 6.63, characteristic of a chloromethyl group. Moreover in the spectrum of **2** the methylene resonances exhibited by **4–6** occur in the region between τ 10.21 and 9.87 in accord with the methylene resonance reported for FpCH₂SiMe₃.[2a]

The rearrangement of the halomethylsilyl complexes (**1** and **2**) to the halosilylmethyl complexes (**4** and **5**) is in direct opposition to what would have been predicted intuitively and on the basis of the reported M–C and M–Si bond dissociation energies;[11,12] the migration of chlorine from carbon to silicon in the transformation of **1** to **4** would be expected to be exothermic by approximately 12–14 kcal. Since the equilibrium constant for the system **1** → **4** is greater than 200 in favor of **4**, the Fe–Si bond in **1** can be no more than 9–11 kcal stronger than the Fe–C bond in **4** if the entropy change is negligible. Pure bromomethylsilyl complex **7**, prepared from bromomethyldimethylbromosilane at −20°, rearranges quantitatively to the bromomethylsilyl complex **8** at 0°. Since the difference in Si–Br and

(9) The rate of rearrangement (determined by nmr spectroscopy) of **1** to **4** is first order in **1** and independent of concentration. The rate constants (65°) for this reaction are as follows: $k = 0.038 \pm 0.004$ hr⁻¹ (hexane); 0.53 ± 0.05 hr⁻¹ (methylene chloride); 0.099 ± 0.009 hr⁻¹ (tetrahydrofuran).

(10) The remaining 75% of **3** is transformed to unidentified products.

(11) The following bond dissociation energies have been reported: Si–Cl (Me₃SiCl), 96[12a] and 88 ± 2;[12b] Si–Br (Me₃SiBr), 79.8[12c] and 78.5 ± 2;[12b] C–Cl and C–Br (Me–X) 83.5 and 69 kcal.[12d]

(12) J. C. Baldwin, M. F. Lappert, J. B. Pedley, and J. S. Poland, *J. Chem. Soc., Dalton Trans.*, 1943 (1972); (b) S. J. Band, I. M. T. Davidson, C. A. Lambert, and I. L. Stephenson, *Chem. Commun.* 723 (1967); (c) J. C. Baldwin, M. F. Lappert, J. B. Pedley, and J. A. Treverton, *J. Chem. Soc.*, 1980 (1967); (d) J. M. Williams and W. A. Hamill, *J. Chem. Phys.*, 49, 4467 (1968).

FpSi(CH₃)₂CH₂Br ⟶ FpCH₂Si(CH₃)₂Br
7   **8**
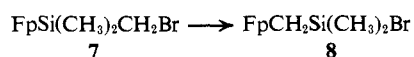
C–Br bond strengths is only 8–10 kcal,[11] the Fe–Si bond in **7** can be no more than 5–7 kcal stronger than the Fe–C bond in **8**.

The data allow an estimate of an upper limit to the difference in the bond energies of Fe–Si and Fe–C bonds and do not preclude the possibility that the Fe–Si bond may be indeed weaker than the Fe–C bond.

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Photoelectron Spectrum of Tropone. Inductive Effect of Carbonyl Group

Sir:

Sometime ago we became interested in the electronic properties of ketones as measured by photoelectron spectroscopy (pes). These original studies[1,2] required that we make some estimate of the inductive effect of a carbonyl group on a πCC level. Recently it has been suggested that we underestimated this inductive effect[3–5] and we would now like to report the pes study of tropone (**1**) which sheds some light on this problem.

1
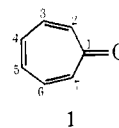
The pe spectrum[6] of tropone (**1**) is shown in Figure 1 along with an expanded portion of the first band. The IP's[7] are collected in Table I together with the results of several semiempirical MO calculations. The first IP at 8.90 eV is assigned to removal of an electron from the b₁(π) level. The vibrational spacings of 1530, 800, and 315 cm⁻¹ in this band[8] can be correlated with bands at 1651 and 1613 (πC=C and πC=O), 1010 or 930 (νC–C), and 577 or a series 329–396 cm⁻¹ (skeletal deformation) in the ir and/or Raman spectra of tropone.[9] The general shape of this pe band is quite similar to the first

(1) D. Chadwick, D. C. Frost, and L. Weiler, *J. Amer. Chem. Soc.*, 93, 4320 (1971).

(2) D. Chadwick, D. C. Frost, and L. Weiler, *J. Amer. Chem. Soc.*, 93, 4962 (1971).

(3) E. Heilbronner and H.-D. Martin, *Helv. Chim. Acta*, 55, 1490 (1972).

(4) K. N. Houk, L. P. Davis, G. R. Newkome, R. E. Duke, Jr., and R. V. Nauman, *J. Amer. Chem. Soc.*, 95, 8364 (1973).

(5) W. Schäfer, A. Schweig, G. Maier, and T. Sayrac, *J. Amer. Chem. Soc.*, 96, 279 (1973).

(6) For a description of the spectrometer see, J. C. Bünzli, D. C. Frost, and C. A. McDowell, *J. Electron Spectrosc. Relat. Phenomena*, 1, 481 (1972).

(7) The IP's measured in this work were calibrated using xenon and those reported to two decimal places are ±0.02 eV and those reported to one decimal place are ±0.1 eV.

(8) The vibrational spacings are ±50 cm⁻¹.

(9) Y. Ikegami, *Bull. Chem. Soc. Jap.*, 35, 967 (1962).