FpSi(CH$_3$)$_{2-n}$Cl$_n$CH$_2$Cl $\longrightarrow$ FpCH$_2$Si(CH$_3$)$_{2-n}$Cl$_{n+1}$

1, $n = 0$	**4**, $n = 0$
2, $n = 1$	**5**, $n = 1$
3, $n = 2$	**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	CH$_2$	Me	Cp
–SiMe$_2$CH$_2$Cl	1	30–31	7.02	9.56	5.30
–SiMeClCH$_2$Cl	2	34–36	6.80 (AB)	9.16	5.15
			($J = 12$ Hz)		
–SiCl$_2$CH$_2$Cl	3	89–90	6.63		5.04
–CH$_2$SiMe$_3$^{b}		28–30	10.28	9.94	5.38
–CH$_2$SiMe$_2$Cl	4	40–42	10.21	9.59	5.19
–CH$_2$SiMeCl$_2$	5	28–29	10.05	9.25	5.15
–CH$_2$SiCl$_3$	6	23–24	9.87		5.13
–SiMe$_2$CH$_2$Br	7	c	7.22	9.51	5.29
–CH$_2$SiMe$_2$Br	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 FpCH$_2$SiMe$_3$.[2a]
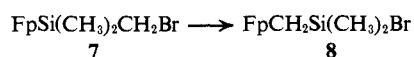
The rearrangement of the halomethylsilyl complexes (**1** and **2**) to the halosilylmethyl complexes (**4** and **5**) is in direct opposition to what would have been predicted intuitively and on the basis of the reported M–C and M–Si bond dissociation energies;[11,12] the migration of chlorine from 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

FpSi(CH$_3$)$_2$CH$_2$Br $\longrightarrow$ FpCH$_2$Si(CH$_3$)$_2$Br

| **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 π_{CC} 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
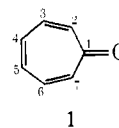
The pe spectrum[6] of tropone (**1**) is shown in Figure 1 along with an expanded portion of the first band. The IP's[7] are collected in Table I together with the results of several semiempirical MO calculations. The first IP at 8.90 eV is assigned to removal of an electron from the $b_1(\pi)$ level. The vibrational spacings of 1530, 800, and 315 cm^{-1} in this band[8] can be correlated with bands at 1651 and 1613 ($\pi_{C=C}$ and $\pi_{C=O}$), 1010 or 930 (ν_{C-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

(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 (Me$_3$SiCl), 96[12a] and 88 $\pm$ 2;[12b] Si–Br (Me$_3$SiBr), 79.8[12c] and 78.5 $\pm$ 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).

(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.
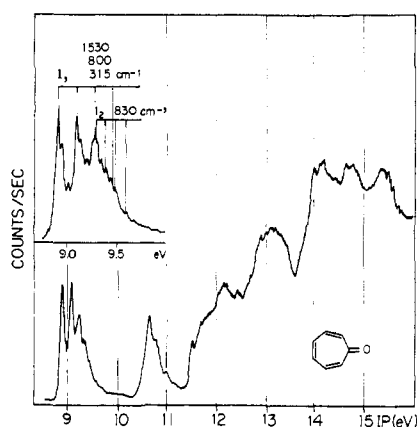
(8) The vibrational spacings are ± 50 cm^{-1}.

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

Table I. Vertical IP's (eV) of Tropone (1)[a]

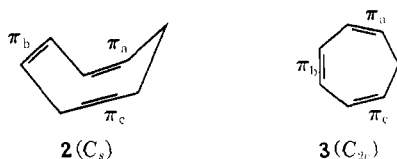| Measured[7]	Assignment	Calcd EH[b]	Calcd CNDO/2[c]	Calcd INDO[d]	Calcd CNDO/S[e]
8.90	$b_1(\pi)$	−11.78(b_2)	−10.96(b_2)	−10.38(b_2)	−9.87(b_1)
9.27	$b_2(n + \sigma)$	−12.75(b_1)	−11.33(b_1)	−10.98(b_1)	−10.59(b_2)
10.67	$a_2(\pi)$	−13.34(a_2)	−14.32(b_2)	−13.28(b_2)	−11.44(b_2)
11.54	$b_1(\pi)$ or σ	−13.65(a_1)	−15.00(a_1)	−14.61(a_1)	−12.10(a_2)
11.8	σ or $b_1(\pi)$	−13.65(b_2)	−16.63(a_1)	−15.91(a_1)	−13.78(b_1)
f		−14.22(b_1)	−16.74(a_2)	−16.27(a_2)	
			−16.85(b_2)	−16.50(b_2)	
			−18.09(b_1)	−17.65(b_1)	

[a] Geometry of tropone from C. L. Norris, R. C. Benson, P. Beak, and W. H. Flygare, *J. Amer. Chem. Soc.*, **95**, 2766 (1973). [b] Extended Hückel; see R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), using a hydrogen Slater exponent of 1.3. [c] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966). [d] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967). [e] J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807, 4050 (1968). [f] Other maxima at 12.2, 13.2, 14.1, 14.7, and 15.4 eV.

Figure 1. The photoelectron spectrum of tropone (1).

Figure 2. Correlation of the π levels in **1**, **2**, and **3**.

IP of benzene[10] and 1,3,5-hexatriene.[11] The second IP at 9.27 eV is assigned to ionization from the b_2 level. The vibrational spacing of 830 ± 80 cm^{-1} observed for this IP can be correlated with 827 and 882 (C–H bend) or 934 cm^{-1} (ν_{C-C}) in tropone.[9] Because of the complexity and overlapping of the first two IP's, the vibrational assignments are tentative.

The third IP at 10.67 eV is assigned to ionization from the $a_2(\pi)$ level. Although we cannot totally rule out the possibility of an additional ionization in this band, corresponding to one of the shoulders, we do not consider it likely. There appears to be a vertical IP at 11.54 eV and this is assigned either to the second $b_1(\pi)$ IP or to a σ IP. However, we feel that this is probably the second $b_1(\pi)$ ionization which is in keeping with the pes assignments for cis- and trans-1,3,5-hexatriene,[11] cyclooctatetraene,[12] 1,3,5-cyclooctatriene,[12] and heptafulvene.[13]

From the pes data of cycloheptatriene (**2**) and its

$$\mathbf{2}\,(C_s) \qquad \mathbf{3}\,(C_{2v})$$

hydrogenated derivatives, Batich, *et al.*, suggest that the energy of the unperturbed π levels in **2** are $\pi_a{}^0 = \pi_c{}^0 =$

(10) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970.

(11) M. Beez, G. Bieri, H. Bock, and E. Heilbronner, *Helv. Chim. Acta*, **56**, 1028 (1973).

(12) C. Batich, P. Bischof, and E. Heilbronner, *J. Electron Spectrosc. Relat. Phenomena*, **1**, 333 (1972).

(13) E. Heilbronner, private communication, 1973.

−9.57 eV and $\pi_b{}^0 = −9.74$ eV.[12] In addition, they find that $B_{ab} = B_{bc} = −0.85$ eV and $B_{ac} = −0.05$ eV. Using these parameters to solve the secular determinant for the π levels in **2** gives values $−\epsilon_i$ to be 8.48, 9.52, and 10.88 eV which can be compared to the measured IP's of 8.57, 9.52, and 10.96 eV.[12] Before we correlate the π levels of **2** with those of tropone (**1**), we must consider the effect of forcing the π-bonds of **2** into the planar cycloheptatriene (**3**). At present we have no way of accurately estimating the effect of θ (angle of twist between the double bonds) on B_{ac} and since it has been found to be small in a number of related cases[11,12] we shall neglect this term. Batich, *et al.*,[12] have found that

$$B_{ab} = −1.31 \cos \theta \qquad (1)$$

Now solving the secular determinant for the three π levels of planar cycloheptatriene (**3**) using

$$\pi_a{}^0 = \pi_c{}^0 = −9.57 \text{ eV}$$
$$\pi_b{}^0 = −9.74 \text{ eV}$$
$$B_{ab} = B_{bc} = −1.31 \text{ eV} \qquad (2)$$
$$B_{ac} = 0.00 \text{ eV}$$

we obtain $\epsilon(\pi_1) = −7.80$ eV, $\epsilon(\pi_2) = −9.57$ eV, and $\epsilon(\pi_3) = −11.51$ eV. This treatment also neglects the σ,π interactions in **2**. However, with these limitations we can construct the correlation diagram in Figure 2 for the π levels of **1**, **2**, and **3**. If the only effects on the π

levels of **3** in going to tropone (**1**) are the inductive effect of a carbonyl group (I_t) and the π_{CC}, π_{CO} interaction (R_1), we obtain

$$\epsilon(b_1) = -7.80 + I_1 + R_1 = -8.90$$

$$\epsilon(a_2) = -9.57 + I_2 = -10.67 \qquad (3)$$

$$\epsilon(b_1) = -11.51 + I_3 + R_3 \leq -11.54$$

In this treatment we consider the inductive effect to be a perturbation of the Coulomb integrals of the terminal atoms of the triene only. More sophisticated treatments would consider the perturbations at all atoms; however, they are much smaller than the perturbations at the terminal atoms[14] and the gross assumptions of the above model do not justify their inclusion. Symmetry precludes any resonance interaction between the $a_2(\pi_{CC})$ level and the $b_1(\pi_{CO})$ level in **1**, hence $I_2 = -1.10$ eV. If

$$I_t = 2C_{t2}{}^2 I_0 \qquad (4)$$

and $C_{12}{}^2 = 0.271$, $C_{22}{}^2 = 0.175$, and $C_{32}{}^2 = 0.054$,[15] then

$$I_0 = -3.14 \text{ eV} \qquad (5)$$

and

$$I_1 = -1.70 \text{ and } I_3 = -0.34 \text{ eV}$$

$$R_t = -\frac{(C_{t2}C_{CO}\beta + C_{t7}C_{CO}\beta)^2}{\epsilon(\pi_t) - \epsilon(\pi_{CO})}$$

$$= -\frac{C_{t2}{}^2}{\epsilon(\pi_t) - \epsilon(\pi_{CO})} 4C_{CO}{}^2\beta^2 \qquad (6)$$

The energy of π_{CO} is not known with certainty, but it has been estimated at 13.5 eV.[16] Then, if $C_{CO} \simeq 1/\sqrt{2}$, $R_1 = +0.60$ eV and $|\beta| = 2.6$ eV and $R_3 = +0.31$ eV and $|\beta| = 3.1$ eV. The values of $|\beta|$ are in reasonable agreement considering all of the approximations used. A similar correlation diagram and calculation can be obtained starting with cis-1,3,5-hexatriene.[11]

Using the above values of I_0, an average value for $|\beta|$, eq 4 and 6, and $\pi_{CC}{}^0 = -9.18$ eV,[17] to calculate the πIP of 2-cyclopentenone, one gets

$$\epsilon(\pi_{CC}) = \pi_{CC}{}^0 + I + R$$

$$= -9.18 - 1.57 + 0.47 = -10.28$$

to be compared with the measured value of 10.10 eV.[3] We have not included any contribution for the inductive effect of the carbonyl group transmitted to C-3 of 2-cyclopentenone via the saturated carbons.[18]

This calculated inductive parameter, eq 5, only applies to α,β-unsaturated ketones and it actually contains both the inductive effect and the change in σ,π interactions $R_t^{\sigma,\pi}$.[18] In fact, from CNDO/2 calculations on **1, 2, 3**, and heptafulvalene (**4**), it appears that

(14) J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "Valence Theory," 2nd ed, Wiley, London, 1970, Chapter 16.

(15) The C_{t2} are the coefficients of π_t at carbon 2 (and 7) from the simple Hückel treatment of cycloheptatriene (**2**). Note the numbering system to correlate with **1**.

(16) C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, J. Amer. Chem. Soc., **94**, 1451 (1972).

(17) P. Bischof and E. Heilbronner, Helv. Chim. Acta, **53**, 1677 (1970).

(18) This point will be dealt with in subsequent papers.

4

the inductive effect of the oxygen atom in **1** is small when comparing **1** and **4** as suggested earlier.[3]
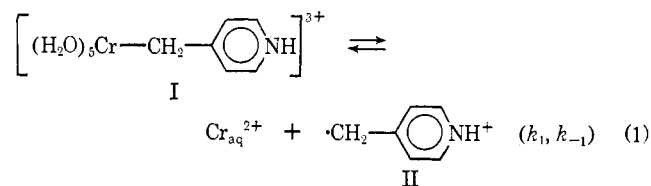
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Bimolecular Alkyl Transfer between Chromium(II) and the 4-Pyridinomethylchromium(III) Cation

Sir:

The thermal decomposition of 4-pyridinomethyl-chromium(III) ion, I, was proposed to proceed by an initial homolytic dissociation (eq 1) in aqueous per-

chloric acid solutions under aerobic conditions.[1] Studies of Schmidt and Swaddle[2] lent support to the same reaction under anaerobic conditions.

We undertook to examine further aspects of this purported homolysis through a study of (a) the rate of exchange of chromium atoms between I and $^{51}\text{Cr}_{aq}{}^{2+}$, for which reaction 1 would provide a pathway and (b) the rate of radical recombination, k_{-1} of eq 1.

The present studies were carried out under the same conditions used in the earlier work,[1,2] 55° and 1.00 F HClO$_4$. Solutions of I were prepared and purified as before,[1,2] and the exchange initiated by addition of ^{51}Cr-tagged Cr^{2+} in a rigorously oxygen-free environment. Samples were withdrawn by syringe at appropriate intervals, and quenched by oxidation of Cr^{2+}.[3-5] For each experiment a plot was constructed of log (1 − fraction exchange) vs. time according to the McKay equation,[6] permitting computation of the ex-

(1) (a) R. G. Coombes, M. D. Johnson, and N. Winterton, J. Chem. Soc., 7029 (1965); (b) R. G. Coombes and M. D. Johnson, J. Chem. Soc. A, 177 (1966).

(2) A. R. Schmidt and T. W. Swaddle, J. Chem. Soc. A, 1927 (1970).

(3) A convenient oxidizing agent was [Co(NH₃)₅Br]Br₂, although in early experiments oxygen was used with comparable results.

(4) The procedure consisted of chromatography of each sample on a 7-cm column of Dowex 50W-X2 cation exchange resin, eluting I with 2 F HClO₄. The purest and most concentrated fractions of I were combined and oxidized to chromate with alkaline peroxide. In this form the specific activity of I was determined from the measured Cr-51 activity and the spectrophotometric analysis as chromate.

(5) A sample was withdrawn early and late in each run to analyze for [Cr²⁺]; this served to measure the exact concentration of Cr²⁺ present, and its constancy confirmed the absence of net reactions which consume Cr²⁺.

(6) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 2nd ed, McGraw-Hill, New York, N. Y., 1961, pp 192–193.