g (95%); mass spectrum [m/e (relative intensity) with ref to ^{35}Cl] 305 (M$^+$, 21), 194 (Cp*Co$^+$, 50), 135 (Cp*, 33), 76 (PMe$_3$, 100). Anal. Calcd for C$_{13}$H$_{24}$ClCoP (304.7): C, 51.08; H, 7.91. Found: C, 50.94; H, 7.88.

Chloro(pentamethylcyclopentadienyl)(dimethylphenyl- phosphine)cobalt (2d) was prepared analogously to **3c** from 1.0 g (2.2 mmol) of **1a** and 0.69 g (5 mmol) of dimethylphenyl- phosphine: yield 1.45 g (90%); mass spectrum, m/e (relative intensity) 367 (M$^+$, 16), 229 (M – PPhMe$_2$$^+$, 100), 194 (Cp*Co$^+$, 52). Anal. Calcd for C$_{18}H_{26}$ClCoP (367.8): C, 58.79; H, 7.08. Found: C, 58.78; H, 7.05.

Bromo(pentamethylcyclopentadienyl)(dimethylphenyl- phosphine)cobalt (2e) was prepared analogously to **3c** from **1b** and dimethylphenylphosphine: yield 1.4 g (85%); mass spectrum, m/e (relative intensity) 411 (M$^+$, 13), 332 (M – Br$^+$, 40), 274 (M – PPhMe$_2$$^+$, 57), 194 (Cp*Co$^+$, 37). Anal. Calcd for C$_{18}H_{26}$BrCoP (412.2): C, 52.45; H, 6.36. Found: C, 52.12; H, 6.12.

Determination of EPR Intensities of 1a in Different Solvents. Equal portions (0.1 mL) of solutions containing 20 mg/mL of **1a** in pentane, toluene, or THF were transferred by syringe under nitrogen into two EPR quartz sample tubes. To one sample was added 0.1 mL of the respective solvent and to the other one were added the solvent (toluene for the case of the pentane solution to ensure dissolution at room temperature) and excess pyridine to make a total of 0.2 mL in either tube. The samples were shock frozen in liquid nitrogen and measured at the temperatures indicated in Table III.

Kinetics and Mechanism of the Reaction of [Et₄N][HFe(CO)₄] and Alkyl Halides. The Unexpected Formation of Acetone

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When [Et$_4$N][HFe(CO)$_4$] is treated with methyl iodide in CH$_3$CN at 25.0 ± 0.2 °C, a clean second-order reaction ensues as monitored via the change in the intensity of ν_{CO} of the metal carbonyl hydride. In all cases, yields of CH$_4$ were 85–100%. A second-order rate constant (first order in iron and in CH$_3$I) of (1.7 ± 0.1) × 10^{-2} M^{-1} s^{-1} was determined, and activation parameters of E_a = 11.2 ± 1.0 kcal/mol, $\Delta H^\ddagger$ = 10.6 ± 1.0 kcal/mol, and $\Delta S^\ddagger$ = –33 cal/(mol K) were found over the temperature range 15–35 °C. The iron product from this reaction is thought to be the unstable "Fe(CO)$_4$(NCCH$_3$)", which can also be generated from Fe(CO)$_5$ in CH$_3$CN by irradiation or use of (CH$_3$)$_3$NO. Reaction of iron hydride with 6-bromo-1-hexene produced only 1-hexene and no detectable methylcyclopentane. Reaction with cyclopropylcarbinyl bromide yielded primarily methylcyclopropane and lesser amounts of 1-butene and *cis*- and *trans*-2-butene, although evidence is presented to suggest nonrigorously that this is a side reaction. A simple nucleophilic substitution is proposed as the rate-determining step. During this study acetone was detected and confirmed as a reaction product by isotope-labeling studies. A mechanism for this latter observation is discussed.

Introduction

Transition-metal hydride anions can dehalogenate organic halides RX to RH through a variety of pathways. Among those available are electron transfer (SET) and nucleophilic displacement. Nucleophilic displacement reactions may occur via attack on the carbon atom by (1) the metal center (followed by reductive elimination) or by (2) the hydride ligand.

Kinney, Jones, and Bergman, in studying [CpV(CO)$_3$H]$^-$, saw evidence for both SET- and S$_N$2-type reactions depending on the organic substrate being dehalogenated.[1] M. Y. Darensbourg and co-workers have recently examined the group VI (6^{24}) metal hydride anions [HM(CO)$_4$L]$^-$ (M = Cr, Mo; L = CO, PR$_3$) as well as [HFe(CO)$_3$L]$^-$ (L = CO, PR$_3$) and some related complexes[2,3] and have developed

Scheme I
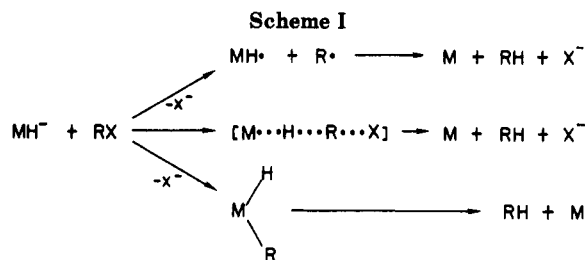
a reactivity scale based on these results. Again, SET or S$_N$2 processes were possibly dependent on the metal complex employed. Darensbourg's work suggested that the reactions of [HFe(CO)$_4$]$^-$ would likely proceed by SET processes.[3] We had begun our study of [HFe(CO)$_4$]$^-$ with alkyl iodides before Darensbourg's initial reports and found

(1) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902.
(2) Kao, S. C.; Darensbourg, M. Y. *Organometallics* **1984**, *3*, 646.

(3) Kao, S. C.; Spillet, C. T.; Ash, C.; Lusk, R.; Park, Y. K.; Darensbourg, M. Y. *Organometallics* **1985**, *4*, 83.

Table I. Sample Rate Data Obtained for the Reaction of [Et₄N][HFe(CO)₄] with CH₃I in CH₃CN[a]

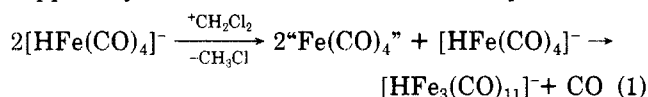| [CH₃I], M	$10^4 k'$,[b] s⁻¹	$10^2 k$,[c] M⁻¹ s⁻¹
$k_{av} = (1.7 \pm 0.1) \times 10^{-2}$ M⁻¹ s⁻¹		
0.053	8.9	1.7
0.080	13	1.6
0.107	18	1.7
0.134	22	1.6
0.160	28	1.8

[a] Reactions are pseudo-first-order with CH₃I in 14-fold excess (25 °C). [b] Pseudo-first-order rate constant. [c] Second-order rate constant.

Table II. Temperature Dependence of the Rate of Reaction of [Et₄N][HFe(CO)₄] with CH₃I in CH₃CN[a]

temp, °C	$10^3 k$, M⁻¹ s⁻¹	temp, °C	$10^3 k$, M⁻¹ s⁻¹
15	7.8	25	17
15	8.0	30	22
20	12	30	21
20	12	35	31
25	15	35	26

[a] Plots of ln k vs. $1/T$ gives $E_a = 11.2$ kcal/mol.

these reactions to proceed quite readily in contrast to the reported lack of reactivity of [HFe(CO)₄]⁻ with alkyl bromides. We also were aware that this ion decomposed, albeit slowly, in methylene chloride to yield [HFe₃(CO)₁₁]⁻,[4] supposedly via a reaction such as that in eq 1.

$$2[\text{HFe(CO)}_4]^- \xrightarrow[-\text{CH}_3\text{Cl}]{+\text{CH}_2\text{Cl}_2} 2\text{“Fe(CO)}_4\text{”} + [\text{HFe(CO)}_4]^- \rightarrow$$

$$[\text{HFe}_3(\text{CO})_{11}]^- + \text{CO} \quad (1)$$

The goal of this study was to determine the feasibility of preparing unstable hydrido–alkyl complexes HFe(CO)₄R. We expected such species to be intermediates in these reductions by analogy to the known, stable HOs(CO)₄R species.[5] The mechanistic question was of central importance to this problem, and we pursued our kinetic studies to determine if SET or S_N2 processes were operative in this reaction. Our results suggest a primarily S_N2-type process. These findings as well as the unexpected formation of acetone in the reaction of [HFe(CO)₄]⁻ and CH₃I are discussed.

Results

Kinetics of the Reaction of RX with [HFe(CO)₄]⁻.
The reaction of [Et₄N][HFe(CO)₄] with CH₃I in CH₃CN is a clean reaction which produces CH₄ (>85% yields) and an unstable complex thought to be "Fe(CO)₄(NCCH₃)". The kinetics were studied by monitoring the decrease in absorbance of the 1885 cm⁻¹ ν_{CO} of [HFe(CO)₄]⁻. Other noncoordinating solvents were not suitable because of the formation of unidentified, interfering metal carbonyls. The product Fe(CO)₄(NCCH₃) could not be isolated and extensively characterized; however, the same species was generated in situ from Fe(CO)₅ and trimethylamine N-oxide in CH₃CN and from Fe(CO)₅ upon irradiation in CH₃CN. A similar reaction producing Fe(CO)₄[N(CH₃)₃] has been reported.[6]

The infrared spectrum of "Fe(CO)₄(NCCH₃)" showed two bands (2060 (m), 1955 (s) cm⁻¹) which we have found characteristic of a large number of Fe(CO)₄L species. This complex is unstable in solution, and decomposition to Fe(CO)₅ can be noted after several hours. In the presence

(4) Whitmire, K. H.; Lee, T. R. *J. Organomet. Chem.* **1985**, *282*, 95.
(5) Carter, W. J.; Kelland, J. W.; Okrasinski, S. J.; Warner, K. E.; Norton, J. R. *Inorg. Chem.* **1982**, *21*, 3955.
(6) Elzinga, J.; Hogeveen, H. *J. Chem. Soc., Chem. Commun.* **1977**, 705.

Table III. Yield Data for the Reaction of [Et₄N][HFe(CO)₄] with CH₃I in CH₃CN

CH₃I, added mL	yield CH₄, mol/mol of Fe	yield acetone, mol/mol of Fe
0.10	1.00	0.22
0.20	0.86	0.25
0.20	0.90	0.33
0.30	0.91	0.33
0.40	0.88	0.32
0.40[a]	...	0.09
0.60	0.92	0.44
0.60[b]	...	0.00
1.00	0.94	0.26
1.50	0.91	0.19

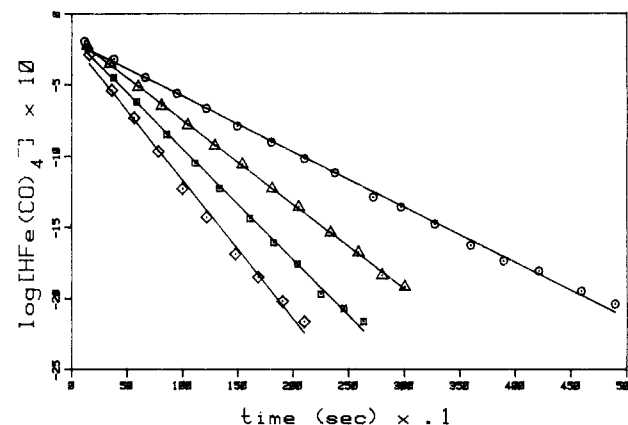[a] Under static P_{CO}. [b] Purge of CO.

Figure 1. First-order plots for the reaction of Methyl iodide with [Et₄N][HFe(CO)₄] at various concentrations of CH₃I. [CH₃I]: ⊙, 0.053 M; △, 0.080 M; ▫, 0.107 M; ◇, 0.134 M.
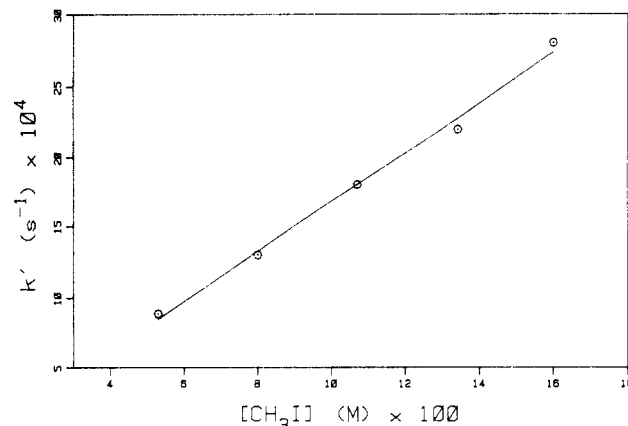

Figure 2. The pseudo-first-order rate constant k' plotted as a function of concentration of CH₃I for its reaction with [HFe(CO)₄]⁻.

of PPh₃, no significant formation of Fe(CO)₄PPh₃ is observed after 1 h; however, upon standing overnight no "Fe(CO)₄NCCH₃" remained and a mixture of Fe(CO)₄(PPh₃) and Fe(CO)₃(PPh₃)₂ was obtained.

The kinetic studies of RI with [HFe(CO)₄]⁻ were conducted under pseudo-first-order conditions (5–16-fold excess of RI) as summarized in Tables I–III and Figures 1 and 2. The data show that the reaction using CH₃I is obviously second order following the rate law

$$\frac{-d[\text{HFe(CO)}_4]^-}{dt} = k[\text{CH}_3\text{I}][\text{HFe(CO)}_4]^- \quad (2)$$

The second-order rate constant k was found to be (1.7 ± 0.1) × 10⁻² M⁻¹ s⁻¹ (Table I). The variation in rate with temperature (Table II and Figure 3) gives values of Arrhenius activation energy, $E_a = 11.2 \pm 1.0$ kcal/mol and
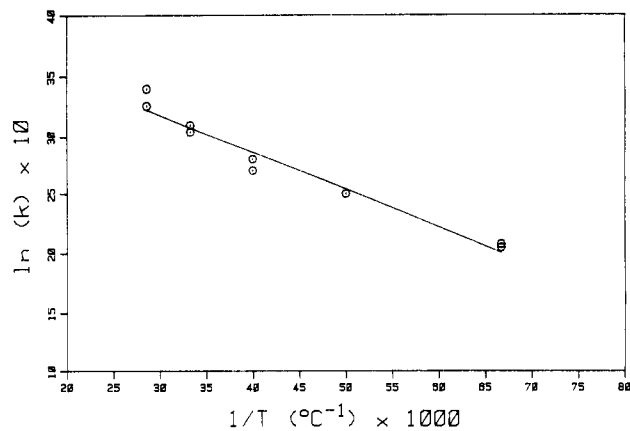
Figure 3. Arrhenius plot of the second order rate constant for the reaction of CH_3I with $[Et_4N][HFe(CO)_4]$.
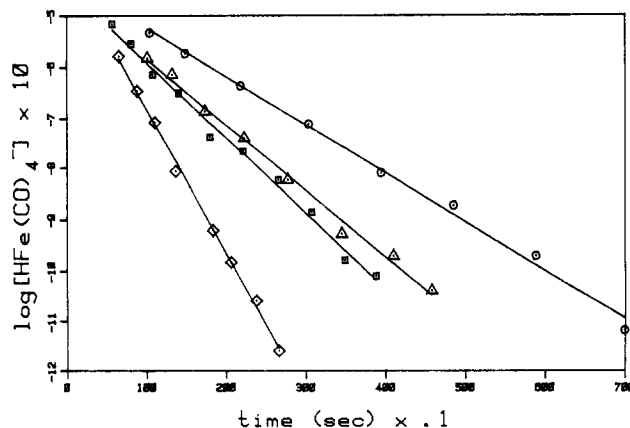

Figure 4. Sample plots of the pseudo-first-order rate data for the reaction of C_2H_5I with $[Et_4N][HFe(CO)_4]$ at various concentrations of C_2H_5I: ☉, 0.74 M; ▲, 1.12 M; ■, 1.49 M; ◇, 1.86 M.

$\Delta H^{\ddagger} = 10.6 \pm 1.0$ kcal/mol with $\Delta S^{\ddagger} = -33$ cal/(mol K). The value of $\Delta S^{\ddagger}$ is consistent with a bimolecular process. These parameters are very similar to those found by M. Y. Darensbourg for the $[HM(CO)_4L]^-$ systems.[2,3] No coupling of CH_3I units to form ethane was detected; however, acetone was found as a product. Discussion of experiments probing the origin of the acetone product will be deferred until after a presentation of the results from the mechanistic probes of the $[HFe(CO)_4]^-$ and RX reaction.

The rates of reaction using C_2H_5I, $(CH_3)_2CHI$, and $(CH_3)_2SO_4$ were also measured. While ethyl iodide, isopropyl iodide, and dimethyl sulfate showed pseudo-first-order kinetics as did CH_3I, that of C_2H_5I and $(CH_3)_2CHI$ were less satisfatory than hoped (Figures 4 and 5). Correlations of the least-squares plots were reasonable but lower (>96%); however, variation in $[C_2H_5I]$ and $[(CH_3)_2CHI]$ produced rather unexpected changes in rate. The data for C_2H_5I are summarized in Table IV. The data are complicated by the fact that "$Fe(CO)_4(NCCH_3)$" *was not* the product of this reaction. Instead an apparent intermediate was formed which reached a steady state and then decreased in concentration as the reaction proceeded. This unknown complex had a ν_{CO} which interfered with the ν_{CO} of $[HFe(CO)_4]^-$, which contributes to the less satisfactory nature of the correlations. Isopropyl iodide behaved similarly to ethyl iodide. A rough relative ordering for the reactions of $k_{CH_3I} \gg k_{C_2H_5I} > k_{(CH_3)_2SO_4}$ was evident such that $k_{rel} \approx 400:4:1$, respectively.

Mechanistic Probes. A number of reactions were undertaken to determine if the reaction occurs by electron transfer, hydride transfer, or attack by the metal center
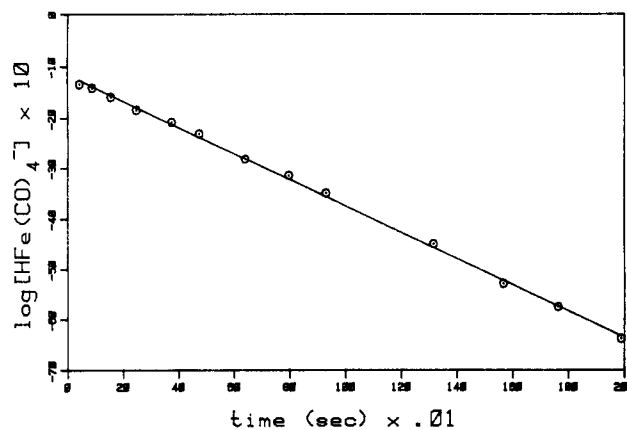
Figure 5. Sample plot for the pseudo first order reaction of $(CH_3)_2SO_4$ with $[Et_4N][HFe(CO)_4]$. $[(CH_3)_2SO_4] = 1.41$ M.

Table IV. Reaction of C_2H_5I with $[Et_4N][HFe(CO)_4]$ in CH_3CN

concn C_2H_5I, M	slope of plot of log A vs. t, $s^{-1} \times 10^4$	slope/$[C_2H_5I]$, s^{-1} $M^{-1} \times 10^4$
1.86	−2.84	−1.5
1.49	−1.48	−1.0
1.12	−1.30	−1.0
0.74	−0.95	−1.3
0.37	−0.63	−1.7
0.20	−0.61	−3.0
0.12	−0.69	−6.0
0.082	−0.52	−6.3

Table V. Yield Data for the C_4 Hydrocarbon Products Produced in the Reaction of (Bromomethyl)cyclopropane and 4-Bromo-1-hexene with $[Et_4N][HFe(CO)_4]$[a]

conditions	▷—CH₃	1-butene	2-butene	
			cis	*trans*
▷—CH₂Br	72	2	5	20
▷—CH₂Br	77	1	4	17
▷—CH₂Br	84	3	4	9
▷—CH₂Br (light excluded)	82	1	4	14
⩘⩗⩘Br		25	9	66

[a] Values are given as percent of total C_4 products.

on CH_3I. Standard ring-opening[7] and ring-closing probes[8] for this study were chosen with the awareness that such probes for free radical intermediates may be flawed. The lack of formation of ring-closure or ring-opening products may be a good indication that nucleophilic displacement (via either hydride transfer or metal attack) at the carbon center is the mechanism of choice, but the presence of ring closure and ring opening does not necessarily guarantee an electron-transfer process since nucleophilic displacement can also give rise to such products.[9]

In this system, ring closing for the reaction with 6-bromo-1-hexene was not observed; the product of simple

(7) Lal, D.; Griller, D.; Husband, S.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6355.

(8) San Filippo, J., Jr.; Silbermann, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834.

(9) (a) Garst, J. F.; Hines, J. B., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 6443. (b) Alanajjar, M. S.; Smith, G. F.; Kuivila, H. G. *J. Org. Chem.* **1984**, *49*, 1271. (c) Newcomb, M.; Smith, M. G. *J. Organomet. Chem.* **1982**, *228*, 61. (d) Newcomb, M.; Williams, W. G. *Tetrahedron Lett.* **1985**, *26*, 1179. (e) Newcomb, M.; Williams, W. G.; Crumpacker, E. L. *Tetrahedron Lett.* **1985**, *26*, 1183. (f) On the basis of data presented in 10d, Newcomb estimates that less than 1% of the reaction described in 10a proceeds via a radical process. Newcomb, M., personal communication, 1985.

Table VI. Methylcyclopropane vs. Butene Formation for the Reaction of [Et₄N][HFe(CO)₄] with (Bromomethyl)cyclopropane as a Function of Time

time, h	ratio of methylcyclopropane:total butenes	time, h	ratio of methylcyclopropane:total butenes
1.3	0.9	5.6	3.8
2.0	2.0	6.8	4.6
3.2	2.5	25.3	4.6
4.3	3.0	26.8	5.1

Table VII. Ratio of 1-Butene, *cis*-2-Butene, and *trans*-2-Butene from the Reaction of [HFe(CO)₄]⁻ with 4-Bromo-1-butene[a]

time, h	ratio of 1-butene:*cis*-2-butene:*trans*-2-butene	time, h	ratio of 1-butene:*cis*-2-butene:*trans*-2-butene
0.4	2.3:1:4.3	7.2	2.9:1:5.2
1.4	2.4:1:4.6	25.0	3.5:1:5.6
2.6	2.5:1:3.0	26.5	3.6:1:7.4
3.7	2.8:1:4.5	71.7	2.6:1:6.6
6.1	2.8:1:4.0		

[a] In all cases *cis*-2-butene was the minor products and values are referenced to it.

reduction was 1-hexene as determined by GC/MS. No methylcyclopentane was detected. When bromomethylcyclopropane was reduced, some ring opening to yield butenes was observed (Table V).

Further mechanistic information was obtained by monitoring the ratio of methylcyclopropane to total butenes as a function of time (Table VI). In addition to 1-butene, *cis*- and *trans*-2-butene were also observed which can be accounted for by the facility with which unsaturated iron carbonyl fragments can isomerize olefins.[10,11] As can be seen from the tables the amount of isomerized products, i.e., 1-butene and *cis*- and *trans*-2-butene, was dependent upon the conditions and length of reaction. The formation of butenes from the (bromomethyl)cyclopropane reaction occurs relatively quickly, and then the rate of production slows dramatically while the production of methylcyclopropane is slower at first but continues at a persistent (although slow) rate as seen by the increase in the ratio of methylcyclopropane to total butenes as a function of time. It is obvious, therefore, that the bulk of the butenes produced are derived from a mechanism different from that of methylcyclopropane.

The starting material, (bromomethyl)cyclopropane supplied by Aldrich Chemical Co., was checked for impurities by GC/MS and small amounts of a substance having the same mass spectrum but a different retention time from (bromomethyl)cyclopropane was observed. Its amount was estimated to be only 1–2% in agreement with Aldrich's reported purity. The impurity present is probably an isomeric bromobutene and could account, at least in part, for some of the butenes observed in this reaction.

The reaction of [HFe(CO)₄]⁻ with 4-bromo-1-butene was also carried out, and 1-butene and *cis*- and *trans*-2-butene were the observed products (Table VII). The presence of *cis*- and *trans*-2-butenes is in accord with the findings for the (bromomethyl)cyclopropane reactions. The ratio of 1-butene:*cis*-2-butene:*trans*-2-butene appeared to vary

(10) Graff, J. L.; Sanner, R. D.; Wrighton, M. S. *Organometallics* **1982**, *1*, 837.

(11) H₂Fe(CO)₄ is also known to catalyze the isomerization of olefins, but this is probably due to decomposition to H₂ and "Fe(CO)ₙ", see: Sternberg, H. W.; Marby, R.; Wender, I. *J. Am. Chem. Soc.* **1957**, *79*, 6116.

Table VIII. Concentration of Acetone as a Function of Time[a]

time, min	10²[acetone], M	time, min	10²[acetone], M
6	trace	144	2.6
16	0.5	200	3.3
50	1.5	396	5.0
86	2.2		

[a] Initial conditions are ca. 0.76 M CH₃I and 0.16 M [Et₄N][HFe(CO)₄] in CH₃CN at 29 °C.

from that obtained for the (bromomethyl)cyclopropane reaction; and the ratio varied slightly as a function of time.

Carrying out the reaction in the presence of a radical scavenger (2,6-di-*tert*-butylphenol) had no effect on the rate of reaction. Unfortunately this is inconclusive owing to the nature of the radical scavenger employed, which is more effective on oxygen radicals than carbon radicals. Other scavenging agents reacted very quickly with the iron complex and were not useful as mechanistic probes in this reaction. Carrying out the reaction in the dark or in a quartz tube (with no direct irradiation) produced no noticeable effect on the rate. Other added reagents including CO, NaBPh₄, Et₄NI, and H₂O had no noticeable effect on the rate.

With this in mind, a careful search for unsaturated or carbonyl products was carried out since the formation of a M–alkyl species might lead to β-elimination or methyl migration (CO insertion) reactions. No evidence for ethylene or propanal formation from the C₂H₅I reaction or acetaldehyde formation from the CH₃I reaction was obtained. In the case of 6-bromo-1-hexene, however, a small amount of hexadiene was found by GC/MS and may indicate a small amount of β-elimination from a M(H)R intermediate.
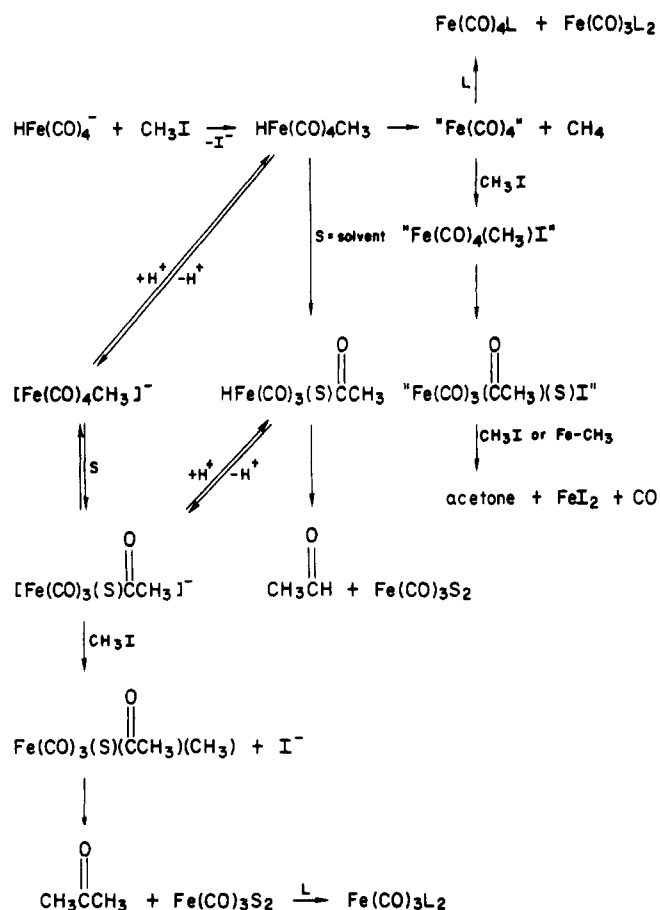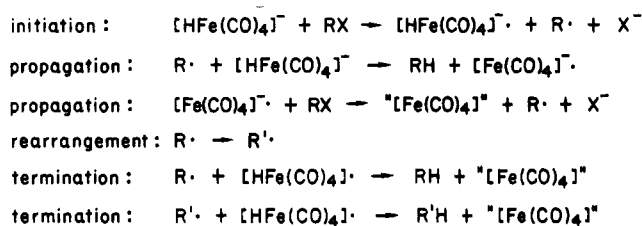
Acetone Formation from the Reaction of [HFe(CO)₄]⁻ and CH₃I. Acetone is also an observed product in the reaction of CH₃I with [HFe(CO)₄]⁻ in 25–44% yield after 24 h of reaction (Table III). The acetone produced originates from the CH₃I as indicated by the production of acetone-d₆ when CD₃I was employed in place of CH₃I. An approximate rate of reaction to form acetone can be obtained from Table VIII which shows the production of acetone as a function of time. It is observed that acetone formation is quite slow compared to consumption of [HFe(CO)₄]⁻ and CH₄ production. Under the conditions employed for the reaction presented in Table VIII, the [HFe(CO)₄]⁻ would be essentially completely reacted after the first 10 min, and acetone formation is just beginning at that time. When Fe(CO)₅ was irradiated in CH₃CN, the same complex resulting from the reaction of [HFe(CO)₄]⁻ with CH₃I in CH₃CN was obtained. Irradiating Fe(CO)₅ in NCCH₃ in the presence of CH₃I yielded acetone in moderate yields after 24 h (26% based on 1 mol of acetone/mol of Fe).

Discussion

The Mechanism of [HFe(CO)₄]⁻ Reaction with Alkyl Halides. As presented in Scheme I, there are a variety of pathways available for the reaction of metal hydride anions with alkyl halides. A more detailed presentation of the various reaction pathways is shown in Scheme II. The kinetic analysis of the reaction of [HFe(CO)₄]⁻ with CH₃I shows it to be a bimolecular process obeying the second-order rate law given in eq 2. Performing the reaction under 1 atm of CO produced no discernible effect on the rate of reaction, so major contributions to the rate of reaction based on a dissociative loss of CO from [HFe(CO)₄]⁻ are not significant. These findings, however, do not distinguish between possible radical or nucleophilic

Scheme II. Various Pathways Available for the Reaction of Alkyl Halides with [HFe(CO)₄]⁻

$$Fe(CO)_4L \;+\; Fe(CO)_3L_2$$

$$HFe(CO)_4^- \;+\; CH_3I \;\underset{-I^-}{\rightleftharpoons}\; HFe(CO)_4CH_3 \;\longrightarrow\; "Fe(CO)_4" \;+\; CH_4$$

$$\text{S = solvent} \quad "Fe(CO)_4(CH_3)I"$$

$$[Fe(CO)_4CH_3]^- \qquad HFe(CO)_3(S)\overset{O}{\overset{\|}{C}}CH_3 \qquad "Fe(CO)_3(\overset{O}{\overset{\|}{C}}CH_3)(S)I"$$

$$\text{acetone} \;+\; FeI_2 \;+\; CO$$

$$[Fe(CO)_3(S)\overset{O}{\overset{\|}{C}}CH_3]^- \qquad CH_3\overset{O}{\overset{\|}{C}}H \;+\; Fe(CO)_3S_2$$

$$Fe(CO)_3(S)(\overset{O}{\overset{\|}{C}}CH_3)(CH_3) \;+\; I^-$$

$$CH_3\overset{O}{\overset{\|}{C}}CH_3 \;+\; Fe(CO)_3S_2 \;\xrightarrow{L}\; Fe(CO)_3L_2$$

Scheme III. Conceivable Radical Chain Mechanism for the Reaction of [HFe(CO)₄]⁻ with RX

initiation : [HFe(CO)₄]⁻ + RX → [HFe(CO)₄]⁻· + R· + X⁻

propagation : R· + [HFe(CO)₄]⁻ → RH + [Fe(CO)₄]⁻·

propagation : [Fe(CO)₄]⁻· + RX → "[Fe(CO)₄]" + R· + X⁻

rearrangement : R· → R'·

termination : R· + [HFe(CO)₄]· → RH + "[Fe(CO)₄]"

termination : R'· + [HFe(CO)₄]· → R'H + "[Fe(CO)₄]"

displacement mechanisms so we turned to standard mechanistic probe reactions involving ring closing and ring opening to shed some light on this issue. The steps involved in a possible radical chain process are reviewed in Scheme III.

For radical reactions involving slow subsequent hydride abstraction, 6-bromo-1-hexene will yield a mixture of 1-hexene and methylcyclopentane via a ring closure process:

The rate of this rearrangement process is known to be 1 × 10⁵ s⁻¹.[1,12] In our experiments, no methylcyclopentane was observed, suggesting that either an S_N2 process or a radical process involving fast subsequent hydride extraction was likely. We then turned to the use of (bromomethyl)cyclopropane as a probe, since its ring opening is known to be much faster (k = 1.3 × 10⁸ s⁻¹).[1,13]

(12) Lal, D.; Griller, D.; Husband, S.; Ingold, K. U. *J. Am. Chem. Soc.* 1974, *96*, 6355.
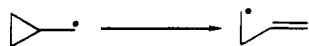
These experiments did show significant quantities of butenes (Table V). This suggested immediately that a radical process was involved; however, other aspects of the reaction are not in complete agreement with this hypothesis.

From the known rate of ring opening, the ratio of rearranged to unrearranged products, and the concentration of [HFe(CO)₄]⁻, one can calculate the rate of hydride abstraction (chain propogation) that must occur to produce the observed product distribution (eq 3). With use of the

$$\frac{k\text{(rearrangement)}}{k\text{(hydride abstraction)}} = \frac{\text{rearranged products}}{\text{nonrearranged products}}[HFe(CO)_4]^- \quad (3)$$

known value for cyclopropylmethyl radical ring opening of 1.3 × 10⁸ s⁻¹, [HFe(CO)₄⁻] = 0.17 M, and a ratio of rearranged to nonrearranged products of 1:4 (Table V), one estimates that the hydride abstraction must occur on the order of 2.3 × 10⁹ M⁻¹ s⁻¹. This value is very high compared to known values of abstraction from other metal hydride reagents and would be one of the fastest reported. For comparison, abstraction of hydride from (n-Bu)₃SnH by CH₃· occurs at about 6.3 × 10⁶ M⁻¹ s⁻¹.[14] One conclusion that can be drawn from these data is that simply not enough rearranged product is formed to support a radical chain mechanism. To explore this in more detail we measured the ratio of methylcyclopropane to total butenes as a function of time (Table VI). It is obvious from the GC traces obtained that the large portion of the butenes were formed in the first couple of hours (in comparable amount to the methylcyclopropane), but the methylcyclopropane was formed more slowly and much more persistently over the duration of the experiment. The conclusion we reached from this is that the bulk of the butenes are derived from a different mechanism than that of the methylcyclopropane. If this were not the case, the ratio of methylcyclopropane to butenes would be expected to be a constant over the time of the reaction. What cannot be determined accurately from the data is whether there is a lesser amount of butene formed concomitantly with the methylcyclopropane. If one considers the implication of this applied to the rate of hydride abstraction necessary to support the radical chain, it seems unlikely that this latter possibility is correct. The ratio of rearranged to unrearranged products would be much smaller, and upon substitution into eq 3, a value approximating the diffusion-controlled limit for the hydride abstraction process in a radical chain mechanism would be obtained.

What appears to be a more reasonable explanation is that some impurity present either in the iron carbonyl hydride or the (bromomethyl)cyclopropane gives rise to an alternate reaction pathway which produces butenes. We know the tetraethylammonium iron carbonyl hydride is extremely oxygen-sensitive and also light-sensitive, and it would not be surprising for oxidized, radical iron species to be present to a small extent. Carefully recrystallizing the iron hydride did not seem to alter the production of butenes significantly nor was any impurity detectable by infrared analysis of the starting material, so any impurity must be present only in small amounts. In fact, one reaction (run as per the conditions for reactions listed in Table VI), but which was inadvertently contaminated by O₂ (as seen by GC/MS), yielded much larger amounts of

(13) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* 1976, *98*, 7024.

(14) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* 1968, *90*, 7047.

butenes (ratio of ca. 3:1 butene to methylcyclopropane).

Having considered these aspects of the reaction we favor an interpretation by which methylcyclopropane is produced via an S_N2 halide displacement by the iron hydride followed by reductive elimination to yield the cyclic alkane. The relative ordering of the rates of reaction of [HFe(CO)$_4$]$^-$ with CH$_3$I, C$_2$H$_5$I, and (CH$_3$)$_2$SO$_4$ (ca. 400:4:1) is consistent with an S_N2 process although the ratio of methyl iodide to dimethyl sulfate rate is larger than has been found with other soft nucleophiles in aqueous solvents.[15] The butenes apparently are produced via a different mechanism arising from some undetectable and probably radical impurity in one of the starting reagents. This radical pathway appears to be short-lived in the absence of some radical initiator such as oxygen. This finding is in accord with studies by the research group of M. Y. Darensbourg which indicate that reaction of the substituted anions [HFe(CO)$_3$PR$_3$]$^-$ with alkyl halides probably proceeds via an S_N2 process.[16] One could suggest that an electron-transfer reaction followed by rapid hydrogen atom abstraction while the species are still in the solvent cage is possible; however, that process would be kinetically indistinguishable from any S_N2 process.

Acetone Formation. A mechanism for the production of acetone based on interaction of the CH$_3$I with [HFe(CO)$_4$]$^-$ can be envisioned and is shown in Scheme II. The ionic pathway is quite reasonable, but it is at odds with the experimental observations on several points. First, the pathway would require that the total yield of CH$_4$ and acetone never exceed 1 mol/mol of Fe complex used, which is obviously not the case (Table III). Secondly, acetaldehyde would be expected to be present in significant quantities from reductive elimination from an intermediate hydridoiron-acyl complex, although acetaldehyde could also arise from the binuclear reaction of [HFe(CO)$_4$]$^-$ with intermediate [Fe(CO)$_4$CH$_3$]$^-$ as recently observed by Barborak and Cann.[17] Further, when the reactions are carried out in the presence of CO, the yield of acetone is reduced or eliminated which is opposite to what one might expect for the CO insertion type mechanism. The presence of CO did not alter the rate at which the iron hydride was consumed.

An alternate mechanism and the one which we favor is that the acetone arises from reaction of CH$_3$I with the unsaturated "Fe(CO)$_4$" produced from the initial methane-yielding reaction (also shown in Scheme II). Oxidative addition followed by CO insertion would yield first Fe(CO)$_4$(CH$_3$)I and then Fe(CO)$_3$(C(O)CH$_3$)I(S) as possible intermediates. Further reaction with CH$_3$I (or another molecule of an iron-methyl complex) could yield acetone. This postulate was tested by irradiating Fe(CO)$_5$ with CH$_3$I in CH$_3$CN. The photodissociation of Fe(CO)$_5$ to "Fe(CO)$_4$" and CO is well-known, and the "Fe(CO)$_4$" produced was predicted to react with CH$_3$I in a fashion similar to that observed for the production of unsaturated iron carbonyls from the hydride reaction. Acetone was indeed produced from this reaction. It is surprising that the simple reaction of homoleptic metal carbonyls with alkyl halides to yield ketones had not hitherto been reported, although acetone production from the reaction of methyl iodide with Ni-(PMe$_3$)$_3$(CO) has been observed.[18] A previous report has indicated that Fe(CO)$_5$ does not react with CH$_3$I; however, the disubstituted Fe(CO)$_3$(PMe$_3$)$_2$ complex does produce
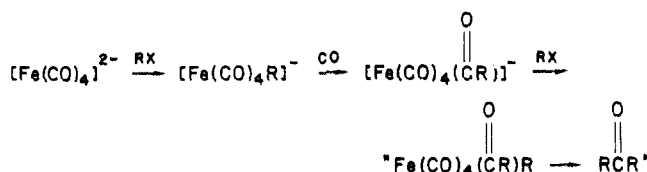
FeI(CO)$_2$(C(O)CH$_3$)(PMe$_3$)$_2$.[19] Similar chemistry has recently been reported for Fe(CO)$_3$(pdmp) (pdmp = [*O*-phenylenebis(dimethylphosphine)])[20] and Fe(CO)$_3$(diars).[21] Ketones were not reported as products of these reactions, which produced stable acyl complexes via alkylation followed by halide ion promoted CO insertion. In agreement with the earlier report, we found Fe(CO)$_5$ unreactive toward CH$_3$I unless irradiated. Another literature procedent is Collman and Cooke's production of ketones from [Fe(CO)$_4$]$^{2-}$ and alkyl halides (Scheme IV),[22] which obviously proceeds differently from our reaction.

As a further test of these ideas, the approximate rate of acetone formation was measured for comparison to the rate of [HFe(CO)$_4$]$^-$ disappearance. Under the conditions used, a pseudo-first-order half-life (large excess of CH$_3$I) of approximately 1 min is obtained, meaning that after about 10 min the [HFe(CO)$_4$]$^-$ is essentially gone. As can be seen in Table VIII, the acetone formation is much slower and indeed is only beginning to be appreciably observed after the iron hydride is consumed. This further substantiates our hypothesis that the acetone is being produced by the iron product of the [HFe(CO)$_4$]$^-$ and CH$_3$I reaction and not from [HFe(CO)$_4$]$^-$ directly.

These results led us to speculate that generation of "Fe(CO)$_4$" from CH$_3$I and [HFe(CO)$_4$]$^-$ might provide a potentially useful synthetic scheme for producing Fe(CO)$_4$L complexes, which are often produced as mixtures with their disubstituted counterparts. To test this hypothesis, Fe(CO)$_4$(NCCH$_3$) was generated from (CH$_3$)$_3$NO and Fe(CO)$_5$ in CH$_3$CN. Unfortunately, even though the synthesis of "Fe(CO)$_4$(NCCH$_3$)" proceeds cleanly, no formation of Fe(CO)$_4$(PPh$_3$) was observed several hours after adding a large excess of PPh$_3$; however, a mixture of Fe(CO)$_4$(PPh$_3$) and Fe(CO)$_3$(PPh$_3$)$_2$ was obtained after the solutions stood overnight. It was not possible to isolate the unstable "Fe(CO)$_4$(NCCH$_3$)". The reaction of [HFe(CO)$_4$]$^-$ with CH$_3$I was attempted in CH$_2$Cl$_2$ in the presence of PPh$_3$. Again a mixture of Fe(CO)$_4$L and Fe(CO)$_3$L$_2$ complexes resulted. The generation of Fe(CO)$_4$L and Fe(CO)$_3$L$_2$ species by this method may have some limited applications, but it does not appear to be particularly advantageous over known methods and is not being pursued. The observation of this product mixture has been suggested to arise by the intermediacy of "Fe$_2$(CO)$_8$-(NCCH$_3$)".[23] This is an interesting possibility which may have some bearing on the acetone formation reaction. This

Scheme IV

$$[Fe(CO)_4]^{2-} \xrightarrow{RX} [Fe(CO)_4R]^- \xrightarrow{CO} [Fe(CO)_4(\overset{O}{\overset{\|}{C}}R)]^- \xrightarrow{RX}$$

$$"Fe(CO)_4(\overset{O}{\overset{\|}{C}}R)R \longrightarrow R\overset{O}{\overset{\|}{C}}R"$$

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(20) Jablonski, C. R.; Wang, Y.-P. *Organometallics* 1985, *4*, 465.

(21) Jablonski, C. R. *Inorg. Chem.* 1981, *20*, 3940.

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(23) Collman, J. P.; Finke, R. G.; Matlock, P. L.; Wahren, R.; Komoto, R. G.; Brauman, J. I. *J. Am. Chem. Soc.* 1978, *100*, 1119.

(24) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III 3 and 13.)

intermediate avoids some of the oxidation state problems encountered in trying to propose a purely mononuclear mechanism. It is, however, unlikely that "$Fe_2(CO)_8(NCCH_3)$" is involved since its intermediacy would require the formation of $Fe(CO)_5$ in equal amounts to $Fe(CO)_3(PPh_3)_2$ and no $Fe(CO)_5$ was detected when the solvent–iron carbonyl complex was treated with PPh_3. This does not preclude, however, a bimolecular process for acetone formation, and that may indeed be a likely mechanism. The "$Fe(CO)_4(NCCH_3)$" species is unstable, and we were unable to isolate it and characterize it further.

Conclusions

The reaction of $[HFe(CO)_4]^-$ with alkyl halides appears to proceed primarily via an S_N2 nucleophilic displacement reaction with some electron-transfer component. The yield of CH_4 is high in all cases (>85%). Acetone is formed in this reaction via a mechanism independent of the nucleophilic attact of $[HFe(CO)_4]^-$ on CH_3I and probably arises from reaction of CH_3I with product "$Fe(CO)_4$".

Experimental Section

General Data. All manipulations were carried out under an inert atmosphere of $N_2(g)$ by using standard Schlenk and vacuum line techniques. Infrared spectra were obtained on a Perkin-Elmer 1430 infrared spectrometer. Acetonitrile was distilled from P_2O_5 and methanol from Mg/I_2 before use. Mass spectral analyses were obtained on a Finnigan 9500 GC/MS system. Gas chromatography were performed by using a Hewlett-Packard 5700A gas chromatograph using He as carrier gas.

Kinetic Measurements. The rates of reactions of $[Et_4N][HFe(CO)_4]$ with alkyl halides were followed by measuring the rate of decrease of the infrared (ν_{CO}) 1885 cm^{-1} band of the iron hydride. Measurements were made in transmittance and converted to absorbance owing to the limitations of the PE 1430 instrument used. All reactions were thermostated at the desired temperature to ±0.2 °C in a large volume constant temperature water bath. The reactions were conducted in Schlenk flasks fitted with rubber septa through which aliquots of the reaction were removed periodically via syringe. All runs of a series were conducted by using a constant amount of the iron complex (0.10 g) to a constant total solution volume (30 mL). Stock solutions of alkyl halide were prepared in CH_3CN and used for all runs of a given series. The iron hydride was first dissolved in a predetermined amount of CH_3CN, and then an amount of stock solution was added via syringe so that the solution volume totaled 30 mL. Timing was begun with the addition of the stock solution. The values of k for the reaction with varying amounts of CH_3I at 25.0 °C are given in Table I. Table II contains the values of k for the CH_3I reaction as a function of temperature over the range 15–35 °C. Plots of log (absorbance) vs. time yielded straight lines showing that the reactions were first order in iron hydride. Correlations for the CH_3I reaction were greater than 99.9% in all cases. A sample plot is shown in Figure 1. The concentration dependence on CH_3I showed the reaction to be first order in alkyl halide also. The rate constants given are second order and fit the rate law (2). The Arrhenius activation energy (E_a) and the enthalpy (ΔH^*) and entropy (ΔS^*) of activation were determined by standard methods.

The reaction kinetics using C_2H_5I, $(CH_3)_2CHI$, and $(CH_3)_2SO_4$ were carried out similarly; however, the data for ethyl iodide and isopropyl iodide were not nearly as well-behaved as that for CH_3I or $(CH_3)_2SO_4$. Plots of log A vs. time still showed first-order dependence on $[HFe(CO)_4]^-$, but the least-squares correlation coefficients were not as good as for CH_3I (>96.0% in all cases). Furthermore, concentration variations in C_2H_5I showed considerable scatter for the rate dependence of that reagent in a second-order analysis of the data. The kinetic measurements were complicated owing to the production of a different, unstable iron complex whose CO stretching frequencies interfered slightly with the ν_{CO} stretch of $[HFe(CO)_4]^-$ being monitored. The product in the case of CH_3I was obviously $Fe(CO)_4(NCCH_3)$ which we were able to generate in solution by other methods; however, this

product was not formed in the ethyl iodide or isopropyl iodide reactions. The $Fe(CO)_4(NCCH_3)$ generated in situ is too unstable to allow isolation. The ethyl iodide reaction is approximately an order of magnitude slower than that of CH_3I. Data are presented in Table IV. The rate for isopropyl iodide was similar to that of C_2H_5I.

In addition to the standard runs, various modifications of reaction conditions were attempted with no significant effect on the reaction rate. These included the addition of H_2O, Et_4NI, 2,6-di-*tert*-butylphenol, or $NaBPh_4$. In the latter case, the lack of effect on the rate may have been due to the limited solubility of $NaBPh_4$ in CH_3CN. Reactions were also performed in the dark and in a quartz tube (no irradiation) with no apparent effect on the rate.

Reactions of $[Et_4N][HFe(CO)_4]$ with 6-Bromo-1-hexene, (Bromomethyl)cyclopropane, and 4-Bromo-1-butene. Between 0.10 and 0.20 g of $[Et_4N][HFe(CO)_4]$ was weighed into a gas reaction flask, and approximately 2.0 mL of CH_3CN was vacuum transferred onto the iron complex. The flask was then transferred to a Schlenk line where, under a purge of N_2, 0.10 mL of the appropriate alkyl bromide was added via syringe to the still frozen solution. The flask was then reevacuated on the high vacuum line, closed, and allowed to warm to room temperature. The methylcyclopropane/1-butene/*cis,trans*-2-butene reaction product mixture was analyzed by GC and GC/MS (0.19% picric acid on graphpac support,$^1/_8$ in. × 6 ft SS, 50 °C) by sampling the gases above the solution. In the case of 6-bromo-1-hexene, the reaction solution itself was sampled and analyzed by GC/MS (3% SP2100 on 100/120 Supelcoport, $^1/_8$ in. × 6 ft nickel, 20–250 °C). The data are reported in Table V. The data in Tables VI and VII were obtained in the same manner except all quantities were doubled.

Yield Measurements from the Reactions of $[Et_4N][HFe(CO)_4]$ with CH_3I in CH_3CN. Gas flasks were prepared containing 0.10 g of $[Et_4N][HFe(CO)_4]$. An appropriate amount of CH_3I was placed in a small Schlenk tube, diluted to 2.50 mL with CH_3CN, and degassed on a high vacuum line. This solution was then vacuum transferred onto the iron carbonyl complex, and the flask was closed and allowed to warm slowly to room temperature. After 24 h the CO/CH_4 mixture was removed and quantitated by Toepler pumping the gas into a constant volume manometer. The percent of CH_4 in the gas was then determined by gas chromatography. The solution was warmed, and the volatiles were transferred to a trap under vacuum. The infrared of this solution showed $Fe(CO)_5$ and acetone which was quantitated by comparison to infrared data for standard acetone/acetonitrile solutions. (The presence of acetone was substantiated by the isotope-labeling and NMR studies described later.) The volatiles had to be removed to do this analysis because of interference by a band at 1735 cm^{-1} in the novolatile components which we believe to arise from the bridging carbonyl in the $[HFe_3(CO)_{11}]^-$ ion. The yield data so obtained is collected in Table III. The GC/mass spectrum of the volatiles confirmed the presence of acetone. No acetaldehyde was detected by GC and GC/MS analyses (Porapak Q, 6 ft × $^1/_8$ in. SS, 60–80 mesh, 150 °C).

Reaction of $[HFe(CO)_4]^-$ with CD_3I. These reactions were performed as described above for the CH_3I case using CD_3I prepared from CD_3OD and PI_3. The purity of this material was established by GC/MS. The volatiles from this experiment confirmed the presence of $CD_3C(O)CD_3$ (no mass 58 was observed), and the infrared showed the carbonyl stretch had shifted about 8 cm^{-1} to lower energy (from 1712 to 1704 cm^{-1}), also consistent with the presence of acetone-d_6 as established with an authentic sample in CH_3CN.

Reaction of $[HFe(CO)_4]^-$ with CH_3I in CD_3CN. Concentration conditions as given above were used except CD_3CN was used in place of CH_3CN. The volatiles were collected after approximately 24 h, and a ^1H NMR of these volatiles indicated the presence of unreacted CH_3I and acetone (δ 2.0) relative to internal Me_4Si as a standard.

Acetone Yield as a Function of Time. A solution of 1.00 g of $[Et_4N][HFe(CO)_4]$ in 20 mL of CH_3CN was prepared and transferred to a 50-mL round-bottom flask attached to a 1-L reservoir and a rubber septum through which aliquots could be withdrawn. The reaction was begun by syringing in 1.0 mL of CH_3I. Periodically 0.5–1.0 mL of the reaction mixture was

withdrawn and transferred to a flask attached to a trap. The volatiles were collected in this trap at −196 °C and then warmed to room temperature and analyzed by infrared spectroscopy. The results are summarized in Table VIII.

Preparation of CH₃CN Solutions of Fe(CO)₄(NCCH₃) Using (CH₃)₃NO. Trimethylamine N-oxide (40 mg, 0.53 mmol) was placed in a pressure-equalizing dropping funnel atop a standard Schlenk flask. The system was evacuated and purged with N₂ several times. Pentacarbonyliron (0.05 mL, 0.37 mmol) and CH₃CN (10 mL) were added via syringe to the Schlenk flask and CH₃CN (10 mL) to the dropping funnel. The (CH₃)₃NO solution was added dropwise to the Fe(CO)₅ solution with stirring. Slow addition results in clean conversion to a product showing ν_{CO} at 2060 (m) and 1955 (s, br) cm⁻¹.

The addition is continued until no Fe(CO)₅ remains as monitored by infrared. Attempts to isolate the product by removing the solvent under vacuum resulted in decomposition. Likewise, addition of water yielded a precipitate which also underwent decomposition. Addition of PPh₃ to the CH₃CN solution showed no production of Fe(CO)₄PPh₃ after an hour; however, upon standing overnight a mixture of Fe(CO)₄(PPh₃) and Fe(CO)₃-(PPh₃)₂ resulted. No Fe(CO)₅ was observed to form when PPh₃ was present.

Use of [HFe(CO)₄]⁻/CH₃I Solutions for Generation of Substituted Iron Carbonyls. To a solution of [Et₄N][HFe-(CO)₄] in CH₂Cl₂ (0.10 g in 10 mL) containing added ligand L (L = PPh₃) was added ca. 0.25 mL of MeI. The solutions very quickly changed to yellow, and infrared spectra were taken. A mixture of Fe(CO)₄L and Fe(CO)₃L₂ complexes was obtained.

Reaction of Fe(CO)₅ with CH₃I in CH₃CN. To an N₂-purged quartz reaction tube was placed in a water-cooled bath and irradiated with a 400-W Ace Hanovia mercury arc lamp for 24 h. At that time an aliquot was withdrawn and analyzed by quantitative infrared spectroscopy to give acetone in yields of 26 and 28% based on Fe(CO)₅ for two separate trials. In the absence of CH₃I, new metal carbonyl peaks at 2060 and 1955 cm⁻¹ grew in.

# Organoboranes. 44. A More Convenient, Practical Route To Achieve the Homologation of Boronic Esters

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A more practical procedure has been developed for the homologation of boronic esters, utilizing the in situ formation of (dichloromethyl)lithium at −78 °C from dichloromethane and one of the bases, lithium diisopropylamide (LDA) or lithium 2,2′,6,6′-tetramethylpiperidide (LTMP), followed by in situ reduction of the α-chloroboronic ester intermediates with potassium triisopropoxyborohydride (KIPBH). This procedure is relatively more practical for large-scale applications and avoids both the low temperature (−100 °C) and the use of an equivalent of alkyllithium required by the earlier procedure. The reaction is broadly applicable to many of the boronic esters tested with the earlier procedure.

Previously the homologation of organylboronic esters was achieved with (dichloromethyl)lithium[1] (prepared at −100 °C from dichloromethane and n-butyllithium), followed by reduction of the intermediate with KIPBH[2] (eq 1).
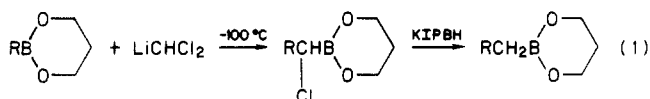
This reaction has proven to be of considerable value in permitting the syntheses of boron derivatives not available through hydroboration. Thus, the hydroboration of 2-methylenenorbornane would proceed from the exo direction to yield the endo product, while the homologation of

the hydroborated norbornene derivative affords the exo derivative (eq 2 and 3). Similarly, the hydroboration of

2-methylmethylenecyclopentane furnishes a mixture predominating in the cis isomer whereas the homologation of
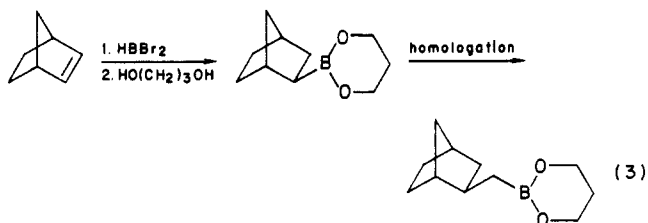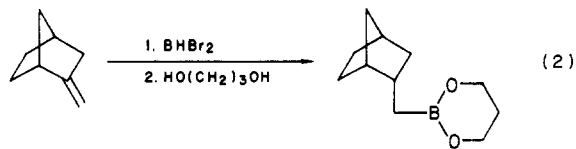
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