26. Compounds 12c and 13c were then transformed into the corresponding hydrazinothioazetidinones 17 and 18. Cyclization of 17 under the conditions described before, afforded **22**<sup>16</sup> ( $\Delta^2$  and  $\Delta^3$  mixture) in 20% yield and **23**<sup>17</sup> ( $\Delta^3$  isomer) in a very small amount. Instead, ring closure of 18 gave only the expected 24 (10% yield) with the corresponding  $\Delta^2$  isomer (20% yield). Synthesis of 3-thiomethyl-3-cephem derivatives from the bromides 5c and 6c is currently being investigated in our laboratories.

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  (6) Compound 1 (R = Ph, X = H) appeared not to undergo the ring opening
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# Free Radical Participation in the Reaction of Metalate Anions with Alkyl Halides<sup>1</sup>

Sir:

The displacement of halides and other groups from alkyl substrates by metalate anions represents one of the most important routes for the formation of metal-carbon  $\sigma$  bonds. The generally high stereoselectivity of these reactions has been widely interpreted as evidence against the intermediacy of free alkyl radicals and in favor of an S<sub>N</sub>2 pathway.<sup>2</sup> Other studies, particularly those of Traylor<sup>3</sup> and Kuivila,<sup>4</sup> have suggested the possibility that certain carbon-metal bond-forming reactions, considered to take place by nucleophilic substitution, may proceed by other pathways. Here we wish to describe spectroscopic and chemical evidence establishing that the reaction of certain metalate anions with the more reactive alkyl halides

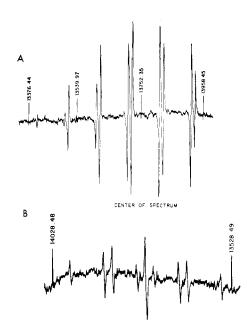


Figure 1. (A) ESR spectrum of the (CH<sub>3</sub>)<sub>2</sub>CH radical (septet of doublets) obtained by reacting CpFe(CO)<sub>2</sub>Na with isopropyl iodide in THF. (B) ESR spectrum of the CH<sub>2</sub>=CHCH<sub>2</sub>CH<sub>2</sub> radical (triplet of triplets) obtained by reacting CpFe(CO)<sub>2</sub>Na with cyclopropylcarbinyl iodide in THF. The proton NMR field markers are in kilohertz.

proceeds in substantial part through the intermediacy of free alkyl radicals produced by electron transfer. 5,6

An intense ESR spectrum of isopropyl radicals (Figure 1a) can be detected by mixing at room temperature 0.1 M THF solutions of sodium cyclopentadienyl(dicarbonyl)iron, 2, and isopropyl iodide in a flat mixing cell of simple design inserted into the ESR cavity so as to minimize the time between mixing and observation. The solutions were contained in 50-100-ml syringes and were driven by a dual syringe pump at a flow rate of about 9 ml/min. Radical concentration increased with increasing flow rates and concentrations of the starting solutions. Similar quality ESR spectra of ethyl, n-butyl, sec-butyl, and tert-butyl radicals were detected in reactions of 2 with the corresponding iodides under similar conditions. While the corresponding bromides and chlorides did not yield detectable concentrations of alkyl radicals, the more stable allyl and benzyl radicals were observed in the reactions of 2 with allyl and benzyl bromides, respectively. Significantly, reaction of 2 with tropylium tetrafluoroborate in THF/acetonitrile gave rise to an intense spectrum of the tropyl radical. No ESR signals attributable to organometallic radical species were observed in the above reactions, presumably because of the combined effects of short lifetimes, low steady-state concentrations, and the broad line widths expected for such species.

The foregoing results are insufficient to establish the extent to which alkyl radicals participate in the principal productforming reaction, although the high rates of generation required to produce detectable concentrations of such short-lived radicals argue against an insignificant role. Consequently, we have sought chemical evidence which would more quantitatively define the role of radical intermediates in these processes. Thus, the reaction of cyclopropylcarbinyl iodide, 1 (X = I), with sodium cyclopentadienyl(dicarbonyl)iron in THF at 0 °C, followed by an unexceptional workup, produces a 70:30 mixture of cyclopropyl- and allylcarbinyl(cyclopentadienyl) (dicarbonyl)iron, 3 and 4, respectively, as ascertained by their characteristic H<sup>1</sup> NMR spectra.<sup>8</sup> If this reaction is carried out in the ESR cavity, the spectrum of the allylcarbinyl radical is observed (Figure 1b).9 By contrast, the reaction of cyclopropylcarbinyl bromide with 2 yields, within the limits of detection (>3%), only 3.<sup>12</sup>

$$X + CpFe(CO)_2Na$$

1

2

Fe(CO)\_2Cp + Fe(CO)\_2Cp

 $X = I$ 
 $X = I$ 
 $X = Br$ 
 $Y = SPr$ 

Fe(CO)\_2Cp

 $Y = SPr$ 

Fe(CO)\_2Cp

 $Y = SPr$ 

Fe(CO)\_2Cp

In a related context we have also examined the reactions of lithium trimethyltin with cyclopropylcarbinyl halides. Again we observe the formation of rearranged product, trimethyl(allylcarbinyl)tin, the extent of formation of which depends, inter alia, on concentration, solvent, temperature, and the nature of the halide group. In all instances, control experiments established that neither 1 nor 3-6 are isomerized under the respective reaction conditions.<sup>13</sup>

Taken together, these results demonstrate that a substantial fraction of the reactions of  $CpFe(CO)_2Na$  and  $(CH_3)_3SnLi$  with certain alkyl halides occurs by a pathway involving free alkyl radicals. A reasonable mechanistic interpretation of these data is that *at least one* competing reaction is operating in addition to any direct  $S_N2$  displacement that may be occurring. Specifically, the spectroscopic and chemical results discussed above are consistent with either a reaction path involving an initial one-electron transfer, followed by nongeminate (and presumably also geminate) radical combination processes (Scheme I),  $^{14.15}$  or a radical chain process  $^{15}$  (eq 3–4). It follows that a minimum of 30 and 46%, respectively, of the substitution products produced by the reaction of  $CpFe(CO)_2Na$  and  $(CH_3)_3SnLi$  with 1 (X = I) results from nongeminate radical combinations.  $^{9.16}$ 

# Scheme I

RX • CpFe(CO)<sub>2</sub> 
$$\xrightarrow{R\cdot \bullet X^{-} \bullet} [CpFe(CO)_{2}]^{\bullet}$$

$$\downarrow S_{N^{2}} \qquad \qquad \downarrow k_{c} \qquad \qquad \downarrow k_{c}$$

$$RFe(CO)_{2}Cp + X^{-} \leftarrow R\cdot + X^{-} \bullet [CpFe(CO)_{2}]^{\bullet}$$

Finally, in the attempt to determine the role of electron transfer in the reactions of the other metalate anions with alkyl halides, we treated several simple alkyl iodides with solutions of Mn(CO)<sub>5</sub>Na, CpMo(CO)<sub>3</sub>Na, and Co(CO)<sub>4</sub>Na in THF under flow conditions. The fact that no alkyl radicals were detected by ESR is presumably attributable to the slower substitution rates and/or the less negative oxidation potentials observed for these anions, 18 since their treatment under similar conditions with tropylium (0.01 M) and trityl (0.001 M) tetrafluoroborates provides intense spectra of the tropyl and triphenylmethyl radicals, respectively. These results further establish the importance of metal radicals such as [Mn(CO)<sub>5</sub>];  $[CpMo(CO)_3]$ ,  $[Co(CO)_4]$  and  $[CpFe(CO)_2]$  as viable reaction intermediates in organometallic reactions. 19 Additional discussion of these and related studies will be presented in future papers.

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- (13) Control experiments establish that cyclopropylcarbinyl iodide and bromide are not significantly isomerized during the course of these reactions. Specifically, GLPC analysis of these halides reclaimed from the reaction of CpFe(CO)₂Na and (CH₃)₃SnLi with excess 1 (X = I, Br) indicate ≤ 4% isomerization to the corresponding allylcarbinyl halide. The extent of rearrangement of 1 under these conditions is influenced by a number of factors (e.g., concentration and efficiency of mixing) which suggest local concentration effects must be minimized to prevent significant rearrangement of these starting halides. The stability of 3 and 4 and of 5 and 6 under reaction conditions is suggested by the fact that they can be recovered unchanged after treatment with, respectively, CpFe(CO)₂Na and (CH₃)₃SnLi.
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- (15) Additional elementary steps as outlined in eq 1–4 cannot be completely dismissed. The exchange reaction (eq 1), originally proposed by Traylor<sup>3</sup> and Kuivila, <sup>4</sup> remains to be established. Under some circumstances eq 2 may be a viable reaction as suggested by the detection of an intense spectrum of the tert-butyl radical in the ESR-monitored reaction of tert-butyllithium with CpFe(CO)<sub>2</sub>I.

$$RX + CpFe(CO)_2^- \rightarrow R^- + CpFe(CO)_2X \rightarrow product$$
 (1)

$$R^- + CpFe(CO)_2X \xrightarrow{-X^-} R \cdot + [CpFe(CO)_2] \rightarrow product$$
 (2)

$$R \cdot + CpFe(CO)_2^- \rightarrow R^- + [CpFe(CO)_2]. \tag{3}$$

$$R \cdot + CpFe(CO)_2^- \rightarrow [RFe(CO)_2Cp] \cdot - \xrightarrow[-X^-]{RX} product + R \cdot$$
 (4)

(16) The rearrangement of cyclopropylcarbinyl anion to allylcarbinyl anion has been studied extensively by Roberts and co-workers. These authors report that the rearrangement of cyclopropylcarbinylmagnesium bromide to allylcarbinylmagnesium bromide is a first-order reaction with a half-life in dimethyl ether of 121 min at  $-24\,^{\circ}\mathrm{C}$ . It follows that the value of the rate constant for this process is  $k=9.5\times10^{-5}\,\mathrm{s}^{-1}$ . In the absence of rate data specific to the rearrangement of the cyclopropylcarbinyl anion under the conditions employed in our study, it is not possible to rigorously exclude the possibility that the rearrangement leading to the allylcarbinyl products

observed in the present investigations do not occur by way of intermediate carbanions such as might be generated by reactions similar to eq 1 and 3. It is important to note, however, that for such a process to be competitive with the rearrangement of the cyclopropylcarbinyl radical would require a minimum increase of >10<sup>10</sup> in the rate of rearrangement of the cyclopropylcarbinyl anion over that observed for cyclopropylcarbinylmagnesium bromide. While perhaps not impossible, an increase of such magnitude seems physically unreasonable under the present circumstances. We, therefore, feel justified in concluding that the rearrangement leading to 4 and 6 occurs essentially exclusively by a free radical pathway.

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$$t \cdot \text{BuN} = 0 + \dot{\text{M}} \text{n(CO)}_5 \longrightarrow t \cdot \text{BuNMn(CO)}_5$$

experiments with each reagent and *tert*-nitrosobutane did not yield nitroxide radicals under the same conditions.

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# Homogeneous Catalysis by Ruthenium Carbonyl in Alkaline Solution: the Water Gas Shift Reaction

Sir:

Methods of activating the reactions of carbon monoxide have long been a major area of catalysis research. Of particular interest, both from the standpoint of its fundamental chemistry and for its obvious commercial value, is the water gas shift reaction (eq 1).

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{1}$$

By this process, the reducing equivalents of CO can be converted to the more useable form of molecular hydrogen with relatively little loss in thermochemical potential.<sup>2</sup> Current methods for effecting this conversion involve heterogeneous catalysis at high temperature,3 and to our knowledge there are no published examples of systems which catalyze this reaction cleanly in homogeneous solution.4 In considering possible homogeneous catalysts, metal carbonyl complexes are logical candidates given the recent reports that certain coordinated carbonyls are activated toward nucleophilic attack of water.<sup>5</sup> In addition, various metal carbonyl clusters have been shown as homogeneous catalysts in the oxidation and/or reduction of carbon monoxide. In these contexts we are exploring the possible catalysis of the water gas shift reaction by metal carbonyl complexes, and here we describe conditions where a homogeneous solution prepared from triruthenium dodecacarbonyl [Ru<sub>3</sub>(CO)<sub>12</sub>] is an active catalyst under relatively mild conditions. It is additionally noteworthy that the catalyst is very active toward decomposition of formate to H<sub>2</sub> and CO<sub>2</sub> under conditions active for the water gas shift reaction.

For a run under typical conditions, the catalysis solution

contained the following components in 15 ml of purified ethoxyethanol solvent: Ru<sub>3</sub>(CO)<sub>12</sub> (0.126 g,  $2 \times 10^{-4}$  mol), KOH ( $\sim 0.5$  g,  $\sim 0.01$  mol), and H<sub>2</sub>O (1.0 g, 0.06 mol). When this solution was heated at 100 °C with stirring under 1 atm of carbon monoxide, the initially yellow color of the solution (attributed to the dissolved Ru<sub>3</sub>(CO)<sub>12</sub>) changed to a deep red-brown. Periodic sampling of the gaseous phase over the solution (total volume ~320 ml at 25 °C) and analysis by high resolution VPC (Hewlett Packard 5830A programmable GC) demonstrated conversion of the initially pure CO phase to one containing substantial amounts of H<sub>2</sub> and CO<sub>2</sub>. Analysis of the gas phase after 73 h gave a composition of 5.6% H<sub>2</sub>, 6.5% CO<sub>2</sub>, plus 88% CO, while analysis after 144 h gave 10.4% H<sub>2</sub>, 8.5% CO<sub>2</sub>, plus 77% CO. The latter figures indicate production of  $\sim 1.4 \times 10^{-3}$  mol of H<sub>2</sub> representing 7 mol of H<sub>2</sub> per mole of Ru<sub>3</sub>(CO)<sub>12</sub> initially added. The catalyst maintains an approximately constant activity over this sampling period with no observable changes in appearance. Also, the catalyst activity remains approximately constant or is perhaps slightly enhanced after flushing the system with fresh CO and restarting. (In contrast, carrying out the reaction under a N2 rather than a CO atmosphere leads to an apparently stoichiometric reaction giving some H<sub>2</sub> and CO<sub>2</sub> but also simultaneous catalyst decomposition to metallic ruthenium.) When the temperature of reaction solutions is raised to 110 °C the rate of H<sub>2</sub> formation is approximately quadrupled over that at 100 °C and a similar increase is noted again for the 10° raise to 120 °C. When the temperature was lowered back to 100 °C the catalyst activity returned approximately to that noted above. Over a period of 30 days the total hydrogen produced by this system equaled  $\sim 3 \times 10^{-2}$  mol, which represents a ratio of 150 mol of H<sub>2</sub> per mole of Ru<sub>3</sub>(CO)<sub>12</sub> initially added or 3 mol of H<sub>2</sub> per mole of KOH added.<sup>7</sup> Notably, the gas phase analyses also indicated trace quantities of a peak with the same retention time as methanol; however, GC analysis of the solvent at reaction conclusion showed no methanol as a solution phase product. Methane, another possible CO reduction product, was not found in either analysis.

The following observations support our conclusion that the described system is a homogeneous catalyst, for the water gas shift reaction. (1) The identity of the H<sub>2</sub> product was confirmed by mass spectrometry. (2) When the reaction was carried out with a solution prepared from deuterium exchanged solvent (CH<sub>3</sub>OD or C<sub>2</sub>H<sub>5</sub>OCH<sub>2</sub>CH<sub>2</sub>OD) and D<sub>2</sub>O,<sup>8</sup> D<sub>2</sub> (>90%), HD (4-8%), and H<sub>2</sub> (<2%) were the hydrogen products as analyzed by mass spectrometry. This confirms that water or water exchangeable hydrogen is the source of the molecular hydrogen produced and that this hydrogen is not the product of solvent decomposition.9 (3) Formation of H2 clearly exceeds the molar quantities of KOH and Ru<sub>3</sub>(CO)<sub>12</sub> added and thus cannot represent the stoichiometric reaction of base with coordinated carbon monoxide. That this system can be catalytic in base undoubtedly results from the fact that under the reaction conditions potassium bicarbonate in ethoxyethanol is unstable and decomposes to CO<sub>2</sub> plus KOH.<sup>10</sup> (4) Lastly, the homogeneity of the reaction solution is indicated by its clarity (no turbidity) when examined visually with a strong light and by the fact that an active catalyst solution displayed the same rate of H<sub>2</sub> production at 110 °C before and after filtration of the catalyst solution through a Fluoropore filter (FHLP, 0.5  $\mu$  pore size) under a purified nitrogen atmosphere.

Formate ion or formic acid are potential products or intermediates in a reaction system involving the oxidation of carbon monoxide by water.<sup>4,11</sup> Thus it is of interest to note that the present catalyst solution is very active toward the decomposition of formate to  $H_2$  plus  $CO_2$  (eq 2).

$$HCO_2H \rightarrow H_2 + CO_2$$
 (2)