

# Disodium Tetracarbonylferrate—A Transition-Metal Analog of a Grignard Reagent

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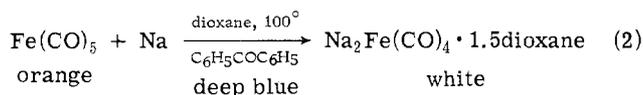
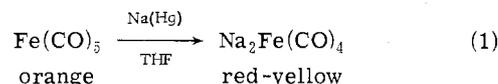
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With the expectation that significant synthetic methodologies will emerge from organotransition-metal chemistry, organic chemists are becoming increasingly interested in this rapidly growing field. To date, few truly useful new organotransition reagents have been developed.<sup>1</sup> However as new reactions are discovered and the underlying reaction mechanisms are slowly clarified, practical applications become more likely. In this Account, I summarize our research on  $\text{Na}_2\text{Fe}(\text{CO})_4$  as a reagent for organic synthesis.

This work had its origin in 1970 when my postdoctoral associate, M. Cooke, was searching for a method of forming Ge-Ge bonds by coupling  $\text{R}_3\text{GeCl}$  with two electron reductants such as  $\text{Na}_2\text{Fe}(\text{CO})_4$ . Being an organic chemist, Cooke tried methyl iodide in a model reaction. Treatment of  $\text{CH}_3\text{I}$  with  $\text{Na}_2\text{Fe}(\text{CO})_4$  followed by hydrolysis gave the characteristic odor of acetaldehyde. This lead was quickly developed into a general synthesis of homologous aldehydes.<sup>2</sup> Because of my past interest in oxidative addition,<sup>3</sup> reductive elimination,<sup>3b</sup> and migratory insertion,<sup>3b</sup> the potential of  $\text{Na}_2\text{Fe}(\text{CO})_4$  as a reagent for organic synthesis was evident, and the matter became vigorously pursued by my other students.

**Synthesis of the Reagent.** Our early experiments employed  $\text{Na}_2\text{Fe}(\text{CO})_4$  derived from  $\text{Fe}(\text{CO})_5$  and sodium-mercury amalgam (eq 1).<sup>2</sup> Because of the expense, difficulty in scale-up, and the presence of mercury salts and of colored polynuclear iron carbonyl impurities inherent in this procedure, we sought a

better method for preparing  $\text{Na}_2\text{Fe}(\text{CO})_4$ . Eventually we developed a very practical method<sup>4,5</sup> (eq 2)



employing  $\text{Fe}(\text{CO})_5$ , the least expensive iron carbonyl,<sup>6</sup> and metallic sodium, with an electron carrier (such as benzophenone ketyl) in an ethereal solvent under conditions where the sodium (mp 97.5°) is molten. At atmospheric pressure, boiling dioxane (bp 101°) is ideal, yielding a more soluble solvate (eq 2). This process is rapid, nearly quantitative, and easily scaled up. Present raw material costs in this preparation of  $\text{Na}_2\text{Fe}(\text{CO})_4$  depend substantially (~75%) on the current price of  $\text{Fe}(\text{CO})_5$ . However, if a large-scale application for  $\text{Fe}(\text{CO})_5$  were developed,<sup>7</sup> raw material costs could drop below those of Grignard re-

(1) Perhaps the most versatile and useful transition-metal reagents developed thus far are organocopper compounds: H. O. House, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, **17**, 101 (1973).

(2) M. P. Cooke, *J. Am. Chem. Soc.*, **92**, 6080 (1970).

(3) (a) J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **87**, 4008 (1965); (b) J. P. Collman, *Acc. Chem. Res.*, **1**, 136 (1968); (c) J. P. Collman and W. R. Roper, *Adv. Organometal. Chem.*, **7**, 54 (1968).

(4) J. P. Collman and R. G. Komoto, U.S. Patent Application filed June 11, 1973.

(5) (a) J. P. Collman, R. G. Komoto, W. O. Siegl, S. R. Winter, and D. R. Clark, unpublished results; (b) S. R. Winter, Ph.D. Dissertation, Stanford University, 1973; (c) R. G. Komoto, Ph.D. Dissertation, Stanford University, 1974.

(6) In fact,  $\text{Fe}(\text{CO})_5$  is the least toxic and least expensive transition-metal carbonyl. The other iron carbonyls,  $\text{Fe}_2(\text{CO})_9$  and  $\text{Fe}_3(\text{CO})_{12}$ , are derived from  $\text{Fe}(\text{CO})_5$  and thus are more expensive.

(7) For example, commercialization of a carbon monoxide process converting ilmenite to rutile would produce  $\text{Fe}(\text{CO})_5$  as a by-product: A. Vasnapu, B. C. Marek, and J. W. Jensen, Report of Investigations 7719, U.S. Department of the Interior, Bureau of the Mines, 1973.

Professor Collman's work covers a wide range of complex ion chemistry, from the classical coordination compounds to the newer organometallic combinations. He is a native of Nebraska, and studied at the University of Nebraska for his B.S. degree. Following receipt of the Ph.D. from the University of Illinois in 1958, he joined the faculty of University of North Carolina. In 1967, he moved to Stanford University, where he is professor of chemistry.

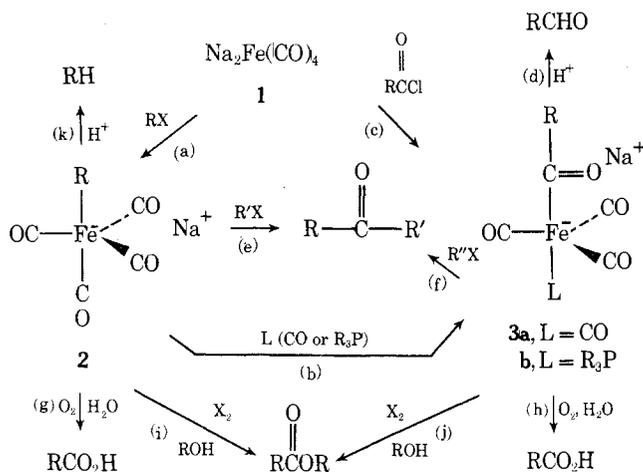


Figure 1.

agents, making  $\text{Na}_2\text{Fe}(\text{CO})_4$  competitive in fine chemicals manufacture. However, the extreme oxygen sensitivity of  $\text{Na}_2\text{Fe}(\text{CO})_4$  (spontaneously inflammable in air) will severely hinder its development on both industrial and laboratory scales.

**Scope of Synthetic Applications.** Conversions of aliphatic halides and sulfonates into aldehydes,<sup>2</sup> unsymmetric ketones,<sup>8</sup> carboxylic acids,<sup>9</sup> esters,<sup>9</sup> and amides<sup>9</sup> by means of  $\text{Na}_2\text{Fe}(\text{CO})_4$  (1) are outlined in Figure 1.<sup>10</sup> In a sense  $\text{Na}_2\text{Fe}(\text{CO})_4$  can be considered a transition-metal analog of a Grignard reagent. Principal advantages of these  $\text{Na}_2\text{Fe}(\text{CO})_4$  reactions are high yields, stereospecificity, and toleration of unmasked functional groups which would be attacked by the more reactive magnesium or lithium reagents. Limitations of  $\text{Na}_2\text{Fe}(\text{CO})_4$  derive from its basicity ( $\text{p}K_b$  about that of  $\text{OH}^-$ )<sup>11</sup> and the resulting tendency to cause eliminations. Thus for reaction a in Figure 1, tertiary substrates cannot be used, and secondary tosylates are preferred over secondary halides. Allylic halides cannot be employed since these afford stable 1,3-diene- $\text{Fe}(\text{CO})_3$  complexes rather than the acyliron(0) intermediate 2. The preparation of aldehydes goes through the acyliron(0) intermediates 3. Since pathway b, migratory insertion of the acyliron(0) 2 to the acyliron(0) 3, fails for alkyl groups bearing adjacent electronegative groups, the scope of aldehyde synthesis is limited to simple primary and secondary substrates. However, the acid chloride route (c) followed by (d) can also be employed.<sup>12</sup> Finally, alkylation of the alkyl or acyl intermediates 2 or 3 (steps e and f) affording ketones is restricted to reactive primary alkylating agents  $\text{R}'\text{X}$ ,  $\text{R}''\text{X}$  (usually a primary iodide).

In spite of these restrictions a wide range of useful synthetic reactions can be carried out in high yield using  $\text{Na}_2\text{Fe}(\text{CO})_4$ . Specific examples with yields are given in Figure 2. Reactions 3, 5, 6, and 9 illustrate

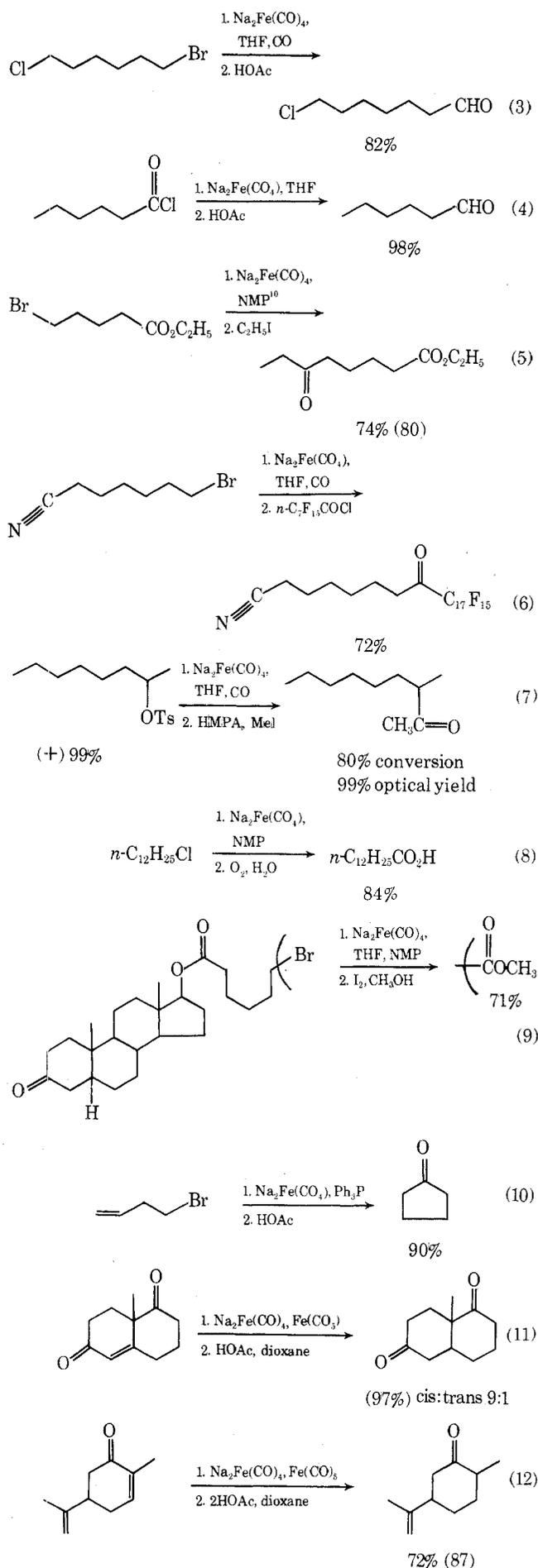
(8) J. P. Collman, S. R. Winter, and D. R. Clark, *J. Am. Chem. Soc.*, **94**, 1788 (1972).

(9) J. P. Collman, S. R. Winter, and R. G. Komoto, *J. Am. Chem. Soc.*, **95**, 249 (1973).

(10) The following abbreviations are used in this paper: L is a tertiary phosphine or CO,  $\text{X}_2$  is  $\text{Cl}_2$ , Br, or  $\text{I}_2$ , THF is tetrahydrofuran, NMP is *N*-methylpyrrolidone.

(11) P. Krumholtz and H. M. A. Stettiner, *J. Am. Chem. Soc.*, **71**, 3035 (1949).

(12) This route has been used for an aldehyde synthesis: Y. Watanabe, T. Mitsudo, M. Tanaka, K. Yamamoto, T. Okajima, and Y. Takegami, *Bull. Chem. Soc. Jpn.*, **44**, 2569 (1971).

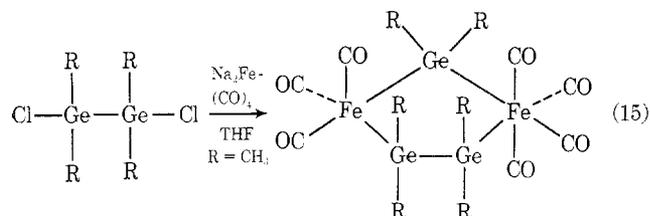
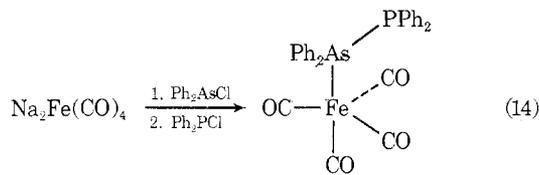
Figure 2. A survey of organic syntheses involving  $\text{Na}_2\text{Fe}(\text{CO})_4$ .

the toleration of other functional groups. Comparison of eq 3 and 8 shows how the reactivity of the alkylation step a in Figure 1 may be controlled by the choice of solvent. A special case, affording hemifluorinated ketones<sup>13</sup> (eq 6), involves treating an alkyliron(0) intermediate (2) with a perfluoroacid chloride; however, this process is not effective with simple acid chlorides. The synthesis of cyclopentanone from 1-bromo-3-butene (eq 10) is also a special case limited to five- and six-ring ketones<sup>5c,14</sup> and is not illustrated in Figure 1. The mechanism of (10) seems to involve a variation of step b in which the olefin acts as an intramolecular ligand, L.

Perhaps the most important synthetic application of  $\text{Na}_2\text{Fe}(\text{CO})_4$  is the highly selective reduction of conjugated olefins illustrated in eq 11 and 12.<sup>15</sup> These reactions may involve  $\text{Na}_2\text{Fe}_2(\text{CO})_8$ , prepared by reaction of  $\text{Na}_2\text{Fe}(\text{CO})_4$  with  $\text{Fe}(\text{CO})_5$  (eq 13) or generated in situ. Two equivalents of a mild acid are required. In terms of yield, stereoselectivity, and toleration of other functional groups (aldehyde, ketone, nitrile, unconjugated olefin, halides, and epoxides) this reagent<sup>15</sup> seems superior to other recently described reducing agents.<sup>16</sup>



The reagent  $\text{Na}_2\text{Fe}(\text{CO})_4$  is also useful for the synthesis of unusual inorganic substances. Two examples are shown in eq 14<sup>17</sup> and 15.<sup>18</sup> The latter is a complex reaction in which a Ge-Ge bond is cleaved.



**Mechanisms of Organic Syntheses Using  $\text{Na}_2\text{Fe}(\text{CO})_4$ .** Qualitative mechanistic patterns of organotransition-metal reactions<sup>3b</sup> were used as a guide for developing the synthetic applications of  $\text{Na}_2\text{Fe}(\text{CO})_4$ . However, unexpected results such as striking solvent effects<sup>19</sup> prompted us to explore the reaction mechanisms in depth.<sup>20</sup> These studies, although still

incomplete, provide a substantial understanding of the underlying mechanisms.

In Figure 1 pentacoordinate anionic alkyl- and acyliron(0) complexes (2 and 3) are shown as intermediates. In synthetic practice 2 and/or 3 are generated and used in situ. Several examples of these air-sensitive anionic iron(0) complexes have been isolated as air-stable crystalline  $[(\text{Ph}_3\text{P})_2\text{N}]^+$  salts,<sup>21</sup> characterized by elemental analyses and NMR and ir spectra, and demonstrated to undergo the individual steps b, d, e, f, g, and h illustrated in Figure 1.<sup>5,22</sup> The indicated trigonal-bipyramidal structures with bulky substituents in the apical position expected for five-coordinate  $d^8$  complexes ( $C_{3v}$  symmetry) are consistent with the pattern of  $\nu_{\text{CO}}$  frequencies exhibited by the isolated complexes. Proton and <sup>13</sup>C NMR spectra—especially for CO groups—suggest rapid equilibration of axial and equatorial groups, characteristic of many pentacoordinate complexes.

Let us next consider each reaction step and the evidence bearing on the corresponding mechanism. Reaction between an alkyl halide or sulfonate and  $\text{Na}_2\text{Fe}(\text{CO})_4$  forming a saturated  $d^8$  complex 2 (step a) can be considered an oxidative addition<sup>3</sup> of a coordinatively saturated  $d^{10}$  complex, 1, or equivalently as an  $\text{S}_{\text{N}}2$  attack at carbon by the nucleophilic reagent 1. Substrate reactivities ( $\text{CH}_3 > \text{RCH}_2 > \text{R}-\text{R}'\text{CH}$ , and  $\text{RI} > \text{RBr} > \text{ROT}s > \text{RCl}$ ) resemble classic  $\text{S}_{\text{N}}2$  reactions.<sup>20</sup> Furthermore, the observed stereochemistry (overall inversion<sup>8</sup>—eq 7, Figure 2) is consistent with inversion<sup>23</sup> in step a, Figure 1, followed by retention<sup>24</sup> in the migratory insertion, step b.

The form of the rate law for the oxidative-addition step a is also consistent with an  $\text{S}_{\text{N}}2$  reaction when account is taken of the dominant role which ion pairing plays in this step. The rate of step a is dramatically increased by employing more polar solvents.<sup>20,25</sup> For example, addition of 10% NMP to a THF solution of  $\text{Na}_2\text{Fe}(\text{CO})_4$  increases the rate of step a 100-fold. Synthetic applications for this solvent-dependent reactivity are illustrated in Figure 2. In THF primary chlorides are very slow (eq 3), whereas in NMP these are useful substrates (eq 8). Solvent effects on the rate of the alkylation step a have been examined quantitatively for THF and NMP. These results clearly indicate *the more dissociated species are kinetically more active*.

For NMP solutions of  $\text{Na}_2\text{Fe}(\text{CO})_4$  freezing-point-depression studies indicate that the dominant species is a uni-unielectrolyte.<sup>25</sup> For reaction a under pseudo-first-order conditions in iron, the observed second-order rate constant increases with decreasing  $[\text{Fe}]_{\text{T}}$  (total of  $\text{Na}_2\text{Fe}(\text{CO})_4$  concentration). The ob-

(13) J. P. Collman and N. W. Hoffman, *J. Am. Chem. Soc.*, **95**, 2689 (1973).

(14) (a) J. Y. Merom, J. L. Roustan, C. Charrier, and *J. Organometal. Chem.*, **51**, C24 (1973); (b) J. P. Collman, M. P. Coe, J. N. Cawse, and K. R. G. Komoto, unpublished results.

(15) J. P. Collman, R. G. Komoto, R. Wahren, and P. L. Matlock, unpublished results.

(16) (a) R. Noyori, I. Umeda, and T. Ishigami, *J. Org. Chem.*, **37**, 1542 (1972); (b) R. K. Boeckman and R. Michalak, *J. Am. Chem. Soc.*, **96**, 1623 (1974); (c) S. Masamune, G. S. Bates, and P. E. Georghiou, *ibid.*, **96**, 3686 (1974).

(17) J. P. Collman, R. G. Homoto, and W. O. Siegl, *J. Am. Chem. Soc.*, **94**, 5905 (1972).

(18) J. P. Collman and J. K. Hoyano, unpublished results.

(19) J. P. Collman, J. N. Cawse, and J. I. Brauman, *J. Am. Chem. Soc.*, **94**, 5905 (1972).

(20) J. P. Collman, J. I. Brauman, R. G. Finke, and J. N. Cawse, unpublished results.

(21) This ion is often useful in forming kinetically stable crystalline salts of oxygen-sensitive anions: J. K. Ruff and W. J. S. Chlitz, *Inorg. Syn.*, in press.

(22) W. O. Siegl and J. P. Collman, *J. Am. Chem. Soc.*, **94**, 2516 (1972).

(23) Other oxidative additions found to go by inversion at carbon include: (a) P. K. Wong, K. S. Y. Lau, and J. K. Stille, *J. Am. Chem. Soc.*, **96**, 3956 (1974), and references therein; (b) G. M. Whitesides and D. J. Boschetto, *ibid.*, **91**, 4313 (1969).

(24) All alkyl-acyl migratory insertions which have been studied with chiral centers proceed with retention at that center—see, for example, ref 23b.

(25) (a) J. N. Cawse, Ph.D. Dissertation, Stanford University, 1973. (b) In NMP the solvent-separated ion pair may be the kinetically dominant species.



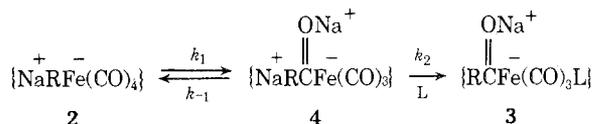


Figure 3. Rate =  $k_1 k_2 [2][L] / (k_{-1} + [L]k_2)$ . If  $k_{-1} \gg [L]k_2$ , rate =  $(k_1/k_{-1})k_2[2][L]$ . † † denotes tight ion pair.

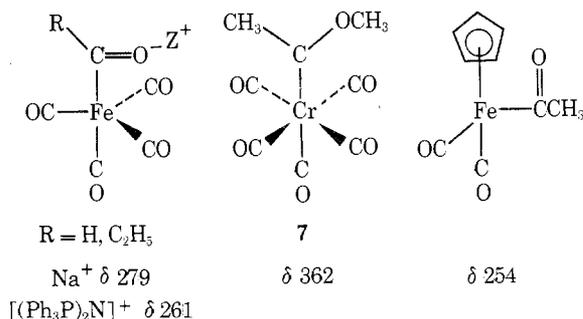
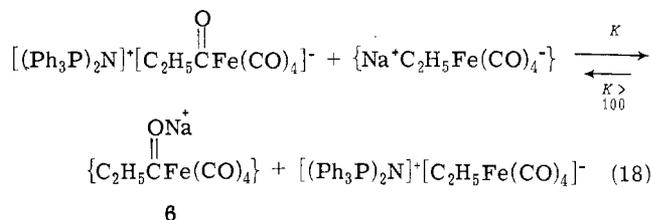


Figure 4.  $^{13}\text{C}$  chemical shifts for acyl and carbene carbon atoms in ppm relative to TMS.

dence for a two-step path in alkyl-acyl migratory insertions,<sup>27</sup> we prefer this mechanism in the present case. Furthermore, the near-zero activation entropy ( $\Delta S^\ddagger = -2$  eu) found for reaction b is inconsistent with a concerted mechanism. Nevertheless we have so far not been able to find conditions under which the rate law for (b) deviates from second-order behavior.

In THF the acyliron(0) complex 3 also forms a strong ion pair with  $\text{Na}^+$  (or  $\text{Li}^+$ ), as shown by conductometric titration (Figure 3), and the cation dependence of the acyl ir stretching mode. By using this change in the infrared spectrum, we were able to show that the acyl complex forms a more stable ion pair, 6, than that of the alkyl complex, 5 (eq 18). The



formation of the sodium-acyliron tight ion pair 6 is also easily detected by  $^{13}\text{C}$  NMR spectroscopy. The acyl carbon exhibits an 18-ppm chemical shift going from the tight ion pair to the free anion (Figure 4). Such a chemical shift occurs upon successive addition of aliquots of NMP to THF solutions of the sodium ion pair 3 until the value of the free acyl ion is reached.<sup>28</sup> The  $^{13}\text{C}$  NMR chemical shift of the CO groups (a sharp singlet) is insensitive to ion pairing, suggesting that the cation is associated with the acyl oxygen in 6. The acyl tight ion pair 6 may be considered structurally related to carbene complexes such as 7 (Figure 4) which exhibit a characteristically low-field  $^{13}\text{C}$  NMR signal for the carbene carbon.<sup>29</sup>

The reverse of step b which would involve conver-

(27) (a) I. S. Butler, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **6**, 2074 (1967); (b) R. W. Glyde and R. J. Mawby, *Inorg. Chim. Acta*, **4**, 331 (1970); **5**, 317 (1971); *Inorg. Chem.*, **10**, 854 (1971).

(28) This  $^{13}\text{C}$  chemical shift vs. NMP "titration curve" exhibits a breakpoint at 2.5 NMP per  $\text{Na}^+$ .

(29) C. G. Kreiter and V. Formacek, *Angew. Chem., Int. Ed. Engl.*, **11**, 141 (1972); G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. E. Wuller, and L. J. Todd, *Inorg. Chem.*, **12**, 1071 (1973).

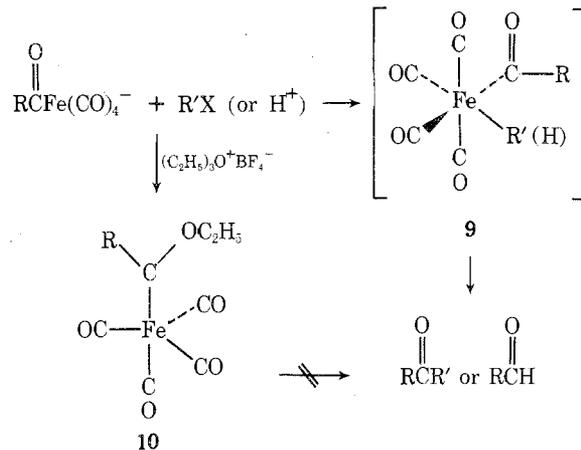
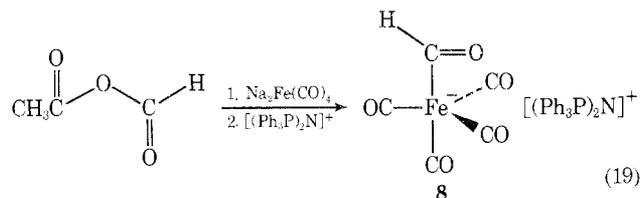


Figure 5.

sion of 3 to 4 in Figure 3 is very slow, as shown by the failure of the acyl complex 3 to exchange with  $^{13}\text{CO}$  under ambient conditions. This kinetic stability of acyl complexes was employed to prepare the thermodynamically unstable formyl complex 8 (eq 19)<sup>30</sup> by a variation of step c (Figure 1). Hitherto no formyl complex had been characterized. Apparently the failure of the hydride  $\text{NaHFe(CO)}_4$  to form the formyl complex under 1000 psi CO is due to an unfavorable equilibrium ( $K_1/K_{-1}$  very small in Figure 3,  $\text{R} = \text{H}$ ). A similar explanation can be advanced for the failure of electronegatively substituted alkyl groups (such as 11, eq 20) to migrate, thus limiting the scope of the sequence ((a), (b), (d)) forming aldehydes.



The transformation of acyl complexes into aldehydes (step d) is conceptually simple but mechanistically ill-resolved. Probably protonation of the iron, affording a six-coordinate iron(II) complex 9 ( $\text{R} = \text{H}$ ), is followed by rapid reductive elimination (Figure 4.). The acyl ketone synthesis (step f) (Figure 1) follows a second-order rate law and probably goes by a similar path (Figure 4). The ketone synthesis brought about by alkylating the alkyliron complex 2 (step e, Figure 1) is also a second-order reaction (100 times faster than step f; see Table I).<sup>20</sup> This "alkyl ketone synthesis" is more complex and must involve at least two intermediates. Alkyl-alkyl hydrocarbon coupling has not been detected.<sup>31</sup> That step e, Figure 1, does not involve the unsaturated acyl intermediate 4 (Figure 4) is certain because (e) does not show parallel kinetic responses due to the ion-pairing effects described above for the alkyl-acyl migration (see Table I). Intermediates such as 9 have not been detected. That alkylation at oxygen affording an oxy-carbene intermediate, 10, is not involved in step f is clear since 10<sup>32</sup> was found to be quite stable (Figure

(30) J. P. Collman and S. R. Winter, *J. Am. Chem. Soc.*, **95**, 4089 (1973).

(31) The reductive elimination of two saturated alkyl groups forming an alkane would be a most useful synthetic procedure; however, this seems to be an unfavorable process.

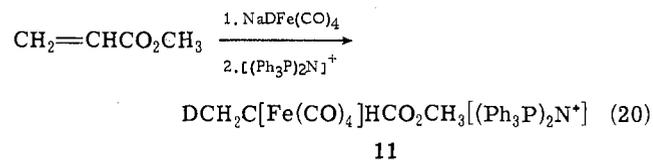
(32) (a) N. W. Hoffman, Ph.D. Dissertation, Stanford University, 1973; (b) H. L. Conder and M. Y. Darensbourg, *J. Organometal. Chem.*, **67**, 93 (1974).

5). Similar, stable acyloxy carbene complexes are formed by reaction of the anionic acyl complexes **3** with acid chlorides blocking a potential synthesis of  $\alpha$ -diketones.<sup>33</sup>

The mechanisms for paths g, h, i, and j (Figure 1) have not been studied. It seems probable that these involve oxidation of **2** or **3**, affording very reactive iron(III) acyl complexes. Oxidative enhancement of migratory insertion and solvolysis of oxidized acyls have precedents.<sup>34</sup>

Mechanisms for the reducing reactions (eq 11 and 12, Figure 2) are poorly understood. The coordinatively saturated hydride slowly adds to  $\alpha,\beta$ -unsaturated esters, affording the kinetically determined product **11** (eq 20) which is reduced by protonation (step k, Figure 1),<sup>5</sup> but the first step in eq 20 is too

slow to account for the rate of reductions in reactions such as eq 11 and 12 (Figure 2).



We are still investigating mechanisms for the reduction reactions (eq 11, 12) and oxidatively induced migration.<sup>34</sup> These may bring to a close our studies of this reagent.

*This Account is based on the experimental and intellectual efforts of my students and associates: J. Cawse, D. R. Clark, M. P. Cooke, R. Finke, N. W. Hoffman, R. G. Komoto, P. L. Matlock, W. O. Siegl, R. Wahren, and S. R. Winter; support was provided by the National Science Foundation (MPS70-01722-A03) and the Center for Materials Research (N00014-67-A-0112-0056 and DAHC15-73-G15). I am also indebted to my colleague J. I. Brauman for collaboration in the mechanistic studies discussed herein.*

(33) Low yields of  $\alpha$ -diketone have been found after destructive distillation mixtures formed from acid chlorides and the acyl complex: Y. Sawa, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **35**, 4183 (1970).

(34) (a) K. M. Nicholas and M. Rosenblum, *J. Am. Chem. Soc.*, **95**, 4449 (1973); (b) M. Rosenblum, *Acc. Chem. Res.*, **7**, 122 (1974).

# *Additions and Corrections*

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Page 343. In eq 7, (+)99% should read: (-)99%