Studies on the Synthesis and C–C Bond-Forming Reactions of Binuclear Iron Complexes: Evidence for Intramolecular Interactions between Organic Fragments Bonded to the Metal

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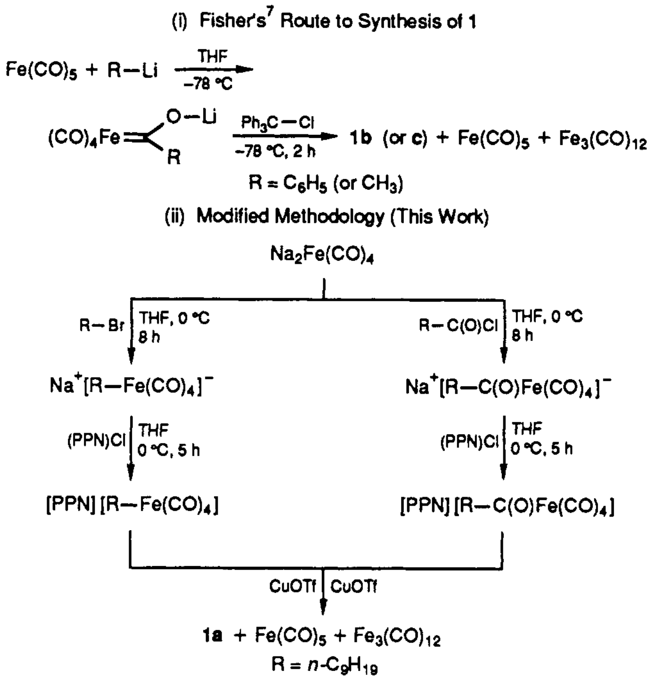
In an attempt to investigate the various reaction pathways available for C–C bond-forming reactions, the synthesis and study of the chemical behavior of the binuclear complex bis(μ,η^2-decanoyl)hexacarbonyldiiron was undertaken. Thermal decomposition of the complex in cyclohexane yields three organic products, *n*-octadecane, 10-nonadecanone, and 10,11-eicosadione. The principal organometallic product is $Fe(CO)_5$. The decomposition when monitored by FT-IR spectroscopy displays a clean first-order kinetics and is characterized by an unusually large negative entropy of activation, $\Delta S^{\ddagger} = -29.7$ eu (log $A = 6.07$). Absence of crossover products in the combined decomposition of mixtures of bis(acyl)diiron complexes indicates that the principal products are formed in processes that do not involve alkyl group scrambling and presumably occur by intramolecular pathways. Additional evidence for this postulate is derived from the observed kinetics of the reaction of the diiron complex with triphenylphosphine, implying a unimolecular rate-determining equilibrium step prior to a fast product-forming sequence. The reactivity of the bis(decanoyl)hexacarbonyldiiron complex with methyl iodide, methyl alcohol, and acetic acid is also briefly examined.

Introduction

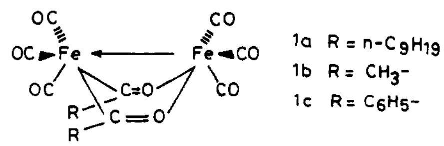
Binuclear complexes of transition metals derive their prominence in the recent literature[1] from the suggestion that their chemistry may serve as a bridge between that of mononuclear metal complexes, used extensively as homogeneous catalysts,[2] and those of multinuclear metal clusters, which may act as models for more complex systems like heterogeneous catalysts.[3] A crucial step in many of these reactions involves C–C or C–H bond formation. Several soluble metal complexes possess such reactivity on a stoichiometric basis, which can be exploited in model studies directed toward the elucidation of mechanisms of catalytic reactions.[4] A basic question that has to be answered in any such study is if these reactions proceed by *intra-* or *intermolecular* pathways.

Bergman and co-workers[5] investigated C–C bond-forming reactions of certain binuclear organocobalt complexes and demonstrated that the chemistry of these species is dominated by *intermolecular* alkyl exchange and by elimination of organic fragments from mononuclear intermediates or metal radicals. On the other hand, according to Norton,[6] elimination of methane from a hydridomethyl-

Scheme I



tetracarbonylosmium complex occurs via *intermolecular* pathway and by labeling studies it was shown that the alkane allegedly arose from a still-forming diosmium complex. It is pertinent here to note that Fischer and co-workers[7] have quite serendipitously synthesized complexes **1b** and **1c** while attempting to isolate oxycarbene



1a R = n-C9H19-
1b R = CH3-
1c R = C6H5-

complexes of iron, by a method proved successful earlier

(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; and references therein. (b) Birnbaum, J.; Laurie, J. C. V.; Dubois, M. R. *Organometallics* **1990**, *9*, 56. (c) Hogarth, G.; Kayser, F.; Knox, S. A. R.; Morton, D. A. V.; Orpen, A. G.; Turner, M. L. *J. Chem. Soc., Chem. Commun.* **1988**, 358. (d) Jacobsen, E. N.; Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3706.

(2) (a) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980. (b) Masters, C. *Homogeneous Transition Metal Catalysts*; Chapman and Hall: London, 1981. (c) For recent developments in homogeneous catalysis in the industry, see: Parshall, G. W.; Nugent, W. A. *Chemtech* **1988**, 184, 314, 376.

(3) (a) Muetterties, E. L.; Rhodin, P. N.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91. (b) Muetterties, E. L. *Chem. Soc. Rev.* **1982**, *11*, 283. (c) *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1985. (d) *Metal Clusters*; Muskovits, M., Ed.; John Wiley & Sons: New York, 1986; p 127 (e) Sundararajan, G. *J. Sci. Ind. Res.* **1989**, *48*, 417.

(4) (a) Christ, C. S., Jr.; Eyler, J. R.; Richardson, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 714. (b) Deutsch, P. P.; Eisenberg, R. *Ibid.* **1990**, *112*, 596. (c) Ghosh, C. K.; Graham, W. A. G. *Ibid.* **1989**, *111*, 375. (d) Watson, P. *Ibid.* **1983**, *105*, 6491.

(5) (a) Schore, N. E.; Ilenda, C. S.; White, M. A.; Bryndza, H. E.; Matturo, M. G.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *102, 7451.* (b) Evitt, E. R.; Bergman, R. G. *Ibid.* **1980**, *102*, 7003. (c) Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113.

(6) (a) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139. (b) Carter, W. J.; Okranski, S. J.; Norton, J. R. *Organometallics* **1980**, *4*, 1376.

(7) (a) Fischer, E. O.; Kiener, V.; Bunbury, D. St. P.; Frank, E.; Lindley, P. F.; Mills, O. S. *J. Chem. Soc., Chem. Commun.* **1968**, 1378. (b) Fischer, E. O.; Kiener, V. *J. Organomet. Chem.* **1970**, *23*, 215.

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Table I. Distribution of Products from the Thermal Decomposition of 1a

no.	complex	% yield of products[b-d] R-R	R-C(O)-R	R-C(O)-C(O)-R
1	**1a**	15	63	11
2	**1b**	10	58	16
3	**1c**	18	43	25

[a] [1] = 0.50 M. [b] No monomeric products like R(-H), R-H, or R-CH(O) were observed. [c] Yields were determined by GLPC with noninterfering internal standards. [d] Yields of $Fe(CO)_5$ were approximately 50% in all cases.

for group VI metal carbonyls. Thus, it appeared to us that bis(μ,η^2-acyl)hexacarbonyldiiron complexes **1** could be the obvious bridge between the systems described above. To facilitate an easy analysis of the products obtained from thermolysis and other reactions, we set out to examine the reactivity of **1a**, wherein the acyl groups attached to iron atoms are decanoyl moieties.[8]

Results and Discussion

Preparation of 1. 1b,c were prepared by Fischer and co-workers[7] via successive addition of the corresponding organolithium reagent to $Fe(CO)_5$ and an oxidizing agent like trityl chloride (we found copper triflate to be the best oxidizing agent for this purpose). For synthesis of **1a**, however, we had to devise a slightly different route utilizing the reaction between disodium tetracarbonylferrate and alkyl halides reported earlier by Collman[9] and oxidizing the thus-formed alkylferrate complexes or oxidizing the isolated nonyl- or decanoylferrate salts (vide Scheme I).

The diiron complex **1a** obtained after careful workup, unlike **1b,c**, could not be isolated as a solid and remained elusive to crystallization attempts. It also decomposed at room temperature over a few days or immediately on exposure to atmospheric oxygen. It, however, was readily soluble in nonpolar organic solvents. The spectral properties of **1a** compare well with those of **1b,c**, reported earlier by Fischer,[7] and also with those of analogous bis(acyl)diruthenium complexes, isolated by Kaesz.[10] On the basis of this supporting evidence, the diiron complex can be safely assigned as having a structure shown as **1**, where two acyl groups are attached to a *single* iron atom and the two iron atoms differ in their formal oxidation states.[7b] The common spectral data worth noting among **1a–c** are the four-band spectra found in the terminal carbonyl stretching frequency region in IR[11] spectroscopy and the η^2-acyl carbon chemical shift in ^{13}C-NMR spectroscopy, δ = 295.52 ppm relative to TMS, which is typical for oxycarbene metal complexes.[12] In fact, the iron atom bearing the two acyl groups can be thought of as an "acetylacetonate" type ligand binding a "$Fe(CO)_3$" moiety.[13] It is difficult to predict if indeed a metal–metal bond exists in this type of complex, but the distance between the two iron atoms in **1c** given as 2.568 Å, by single-crystal X-ray diffraction, corresponds to a normal single-bonded metal–metal distance in diiron complexes.[14] So it may not be very presumptuous to postulate that a single coordinate bond exists between the two iron atoms.[15]

(8) (a) For a preliminary communication on this study, see: Sundararajan, G.; San Filippo, J. *Organometallics* **1985**, *4*, 606. (b) Sundararajan, G. Doctoral Dissertation, Rutgers University, New Brunswick, NJ, 1985.
(9) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.
(10) Kampe, C. E.; Boag, N. M.; Kaesz, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 2896.
(11) Reference 1a, p 114.
(12) Mann, B. E.; Taylor, B. F. *^{13}C-NMR Data for Organometallic Compounds*; Academic Press: New York, 1981.
(13) Lukehart, C. M. *Adv. Organomet. Chem.* **1986**, *25*, 45.

Table II. Distribution of Products from the Thermal Decomposition of Mixtures of 1a–c

no.	complex mixture	R	% yield of products[b-d] R-R	R-C(O)-R	R-C(O)-C(O)-R
1	1a,b	CH_3	10	60	17
		n-C_9H_{19}	17	62	12
2	1b,c	C_6H_5	19	45	27
		CH_3	11	61	17
3	1a,c	C_6H_5	20	44	23
		n-C_9H_{19}	18	66	14

[a] [1] = 0.50 M. [b] Both monomeric products like R(-H), R-H or R-CH(O) and crossover products like R-R′, R-C(O)-R′, or R-C(O)-C(O)-R′ were not observed.

Thermal Decomposition of 1a. Compound **1a** is a red oil, thermally labile and extremely air-sensitive. When a 0.50 M solution of **1a** in cyclohexane was heated in an ampule sealed under nitrogen, it yielded $Fe(CO)_5$ as the principal IR-active organometallic product (yield = 48%). The reaction mixture when analyzed by GC–MS was found to contain only three compounds: *n*-octadecane, 10-nonadecanone, and 10,11-eicosadione (entry 1, Table I). Surprisingly, no monomeric organic compounds, like 1-nonene, *n*-nonane, and/or *n*-decaldehyde, were detected. For analogous complexes **1b,c**, when subjected to similar thermal decomposition, the individual reactions proceeded smoothly with the results in parallel with those of **1a** (vide Table I and eq 1). It can be envisaged that the products

$$1 \xrightarrow[55\ ^\circ C]{c\text{-}C_6H_{12}} \text{R-R} + \text{R-C(O)-R} + \text{R-C(O)-C(O)-R} + Fe(CO)_5 \quad (1)$$

of eq 1 can arise from any one or combination of the following pathways: (i) *intermolecular* alkyl (or acyl) transfer among acetyl groups attached to the iron atoms; (ii) *intramolecular* alkyl migration or reductive elimination preceded by migratory deinsertion of acylcarbonyls; (iii) *homolytic cleavage* of a metal–acyl bond leading to free acyl radicals, which might couple with or without losing CO. Premises i and iii can be checked by control studies for crossover products. Thus an equimolar mixture of **1a,b** (as well as **1b,c** and **1a,c**) when subjected to sealed ampule thermolysis gave rise to no crossover products (eq 2) and the distribution of the *dimeric* organic products remained the same irrespective of the presence of the other complex in solution (Table II).

$$[\text{R-C(O)}]_2Fe_2(CO)_6 + [\text{R}'\text{-C(O)}]_2Fe_2(CO)_6 \xrightarrow[55\ ^\circ C]{c\text{-}C_6H_{12}} \text{R-R}' + \text{R-C(O)-R}' + \text{R-C(O)-C(O)-R}' + Fe(CO)_5 \quad (2)$$

The found absence of crossover products might appear to nullify premises i and iii (however, see below) and might appear to suggest that the C–C bond-formed products from thermal decomposition of **1a** could arise out of pure intramolecular interactions alone. It then becomes imperative that the kinetics of the thermal decomposition reaction be examined.

Kinetic Studies on the Thermal Decomposition of 1a. The thermal decomposition in cyclohexane when monitored by FT-IR using a cell specially fabricated for

(14) Fehlhammer, W. P.; Stolzenberg, H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1981; Chapter 31.4.
(15) For a discussion on the difference between coordinate and covalent bonds, see: Haland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992.
(16) For a qualitative discussion on this observed pattern, see: Sundararajan, G. *Indian J. Chem. A* **1990**, *29*, 1060.

Table III. Kinetic Parameters Associated with the Thermal Decomposition of 1a

no.	temp. °C[b]	$10^4 k_{obs}$, s^{-1} [c]
1	30	0.15 ± 0.01
2	43	0.44 ± 0.01
3	62	1.09 ± 0.09
4	75	4.65 ± 0.05

[a] [1a] = 0.050 *M*. [b] The required temperature was obtained by using a preheated, precalibrated, thermostated IR cell (Foxboro-Analabs). [c] Values were obtained from the decrease in intensity of the band at 2080 cm^{-1}.

this purpose shows a clean conversion of **1a** to $Fe(CO)_5$ (~50%), the only IR-active soluble metal-containing product. The spectral changes in the stretching frequency region for coordinated terminal carbonyls are continuous starting with a four-band pattern (2080_m, 2035_s, 2004_s, 1968_m cm^{-1}) and resulting in a two-band absorption (2022_m, 2002_s cm^{-1}) reported terminal carbonyl stretching frequencies for $Fe(CO)_5$. During thermal decomposition, the bands at 2080 and 1979 cm^{-1} diminish in intensity while a new peak at 2064 cm^{-1} grows and recedes,[17] yielding finally the peaks characteristic of $Fe(CO)_5$. For kinetic studies the band at 2080 cm^{-1} was monitored, because unlike the other three bands, the bandwidth of this absorption remained constant throughout. IR spectra recorded in the region 2300–1800 cm^{-1} at different time intervals at 50 °C depict the decomposition path of **1a** to $Fe(CO)_5$.

The rate of disappearance of **1a** displayed clean first-order kinetics for more than 2 half-lives, over a range of temperatures. The resulting kinetic parameters[18] (the observed rate constants) associated with the decomposition of **1a** are shown in Table III. The activation parameters for this reaction thus become $\Delta S^{\ddagger} = -29.7 \pm 4.3$ eu and $\log A = 6.07 \pm 0.937$. The magnitude of the entropic term is clearly inconsistent with a rate-determining step that involves an elementary unimolecular process in which *two particles* originate from *one* in the transition state.[19,20] However, this observation is not unique. At least two other well-defined unimolecular processes display a comparable entropy of activation. Thus, the isomerization[21] of the dinuclear iron complex $[\mu\text{-}(C_6H_5)(CH_3)Sn]_2Fe_2(CO)_8$ and the automerization[22] of cyclobutadiene exhibit an entropy of activation of -25 ± 5 and -25 ± 7 eu, respectively. In the former case, the purported rate-determining step involves the scission of one of the iron–tin bonds. In the latter instance it was concluded that the abnormally low activation entropy associated with what is in fact a bond-shifting reaction reflects a reaction trajectory in which the extreme narrowness of the reaction barrier makes heavy-atom tunneling the dominant pathway.

To extrapolate and to assert that similar *intramolecular* processes are involved in the thermal decomposition of **1a** is difficult now,[23] but however, the absence of crossover products in the thermolysis of mixtures of **1** (eq 2) suggests a unimolecular pathway that may resemble the exceptions in the category of unimolecular processes with negative entropies of activation listed above. And of course, the crossover experiments become futile if the individual rates of decomposition of the two complexes are significantly different. For this reason, the thermal decomposition of **1b** was monitored by FT-IR and the decomposition of **1b** also follows clean first-order kinetics. The rate constants for the thermal decomposition of **1a,b** at 62 °C in cyclohexane, are, in that order, 1.09×10^{-4} and 1.35×10^{-4} s^{-1}. As it can be seen, the rates of thermolysis of **1a,b** are comparable, and hence the failure to observe any crossover product under these conditions (eq 2) supports the premise that the C–C bond-forming step in these reactions proceeds by *intramolecular* pathway and no *intermolecular* alkyl group transfer takes place during these transformations. To gain additional insight into the nature of the reactivity of **1**, we subjected **1a** to reaction with triphenylphosphine and followed its kinetics.

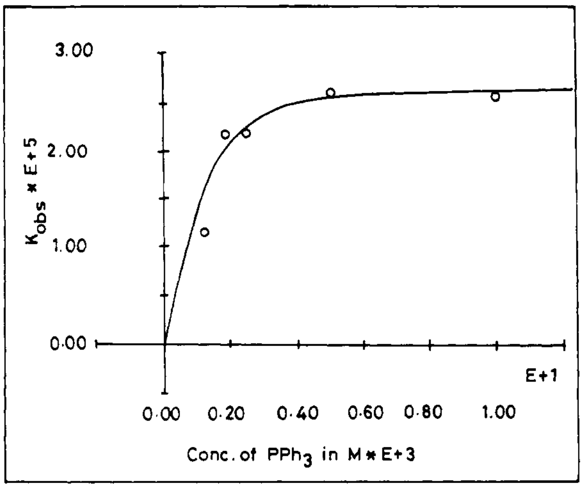


Figure 1. Influence of PPh_3 concentration on the observed rate constant for the reaction of **1a** with excess PPh_3 in cyclohexane at 25 °C.

Kinetics of the Reaction of 1a with Triphenylphosphine. Triphenylphosphine reacts rapidly with **1a** at room temperature to give an almost quantitative yield of 10-nonadecanone (98%) and three organometallic products in the ratio outlined in eq 3. A spectrophotometric study of the rate of this reaction revealed what appears to be two kinetic regimes (Figure 1). In the first regime the diappearance of **1a** shows a strong dependence on the concentration of phosphine. The second region occurs when there is an excess of phosphine. Under these conditions the observed reaction rate appears to become

$$\mathbf{1a} + PPh_3 \xrightarrow[25\ °C]{c\text{-}C_6H_{12}} \underset{98\%}{R\text{–}C(O)\text{–}R} + \underset{54\%}{Fe(CO)_4PPh_3} + \underset{22\%}{Fe(CO)_3(PPh_3)_2} + \underset{22\%}{Fe_3(CO)_{12}} \quad (3)$$

(17) One reviewer has raised the possibility that the peak at 2064 cm^{-1} could be the ^{13}CO satellite of $Fe(CO)_5$. However, in the IR spectrum $Fe(^{13}CO)_5$ has strong absorptions at 1973 and 1949 cm^{-1}, which are at lower frequencies than those for $Fe(CO)_5$, see: Jones, L. H.; McDowell, R. S.; Goldberg, M.; Swansan, B. I. *J. Chem. Phys.* **1952**, *57*, 2050.

(18) At 55 °C, the value of k_{obsd} showed only minor (ca. 10%) variation over the concentration range of [**6a**] = 0.050–0.50 M.

(19) (a) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1968; Chapter 3. (b) Benson, S. W.; O'Neal, H. E. *Kinetic Data on Gas Phase Unimolecular Reactions*; National Bureau of Standards: Washington, DC, 1970.

(20) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3996 and references therein.

(21) Grynkewich, G. W.; Marks, T. J. *Inorg. Chem.* **1976**, *15*, 1307.

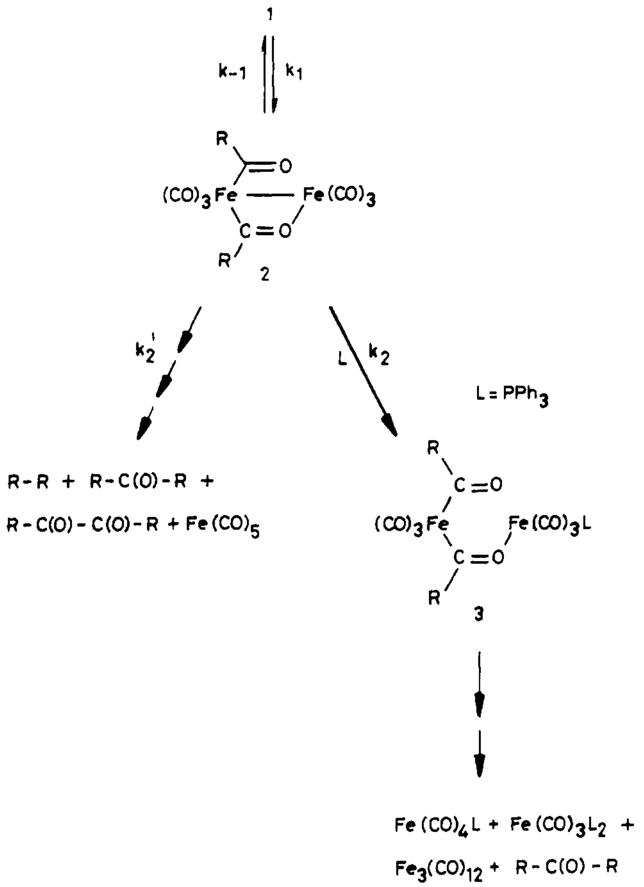
(22) (a) Whitman, D. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1982**, *104*, 647. (b) Carpenter, B. K. *J. Am. Chem. Soc.* **1982**, *105*, 1700.

(23) Classically, unimolecular isomerization involving a one-particle transition state (i.e. a process in which one particle is transferred into one particle) are characterized by log *A* values ranging from ca. 11 to 14.[19b] For examples of other processes that exhibit abnormally low log *A* values, see: (a) Huang, M. J.; Wolfsberg, M. *J. Am. Chem. Soc.* **1984**, *106*, 403. (b) Dewar, M. J. S.; Merz, K. M.; Stewart, J. J. P. *Ibid.* **1984**, *106*, 4040. (c) Dewar, M. J. S.; Wade, L. E. *Ibid.* **1979**, *99*, 4417.

(24) Pilling, M. J. *Reaction Kinetics*; Clarendon Press: Oxford, England, 1975; p 110.

(25) An equivalent scheme has been proposed by Bergman to account for similar observations in the reaction of certain binuclear cobalt compounds with triphenylphosphine: Bryndza, H. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 4766.

Scheme II



independent of added phosphine and the reaction exhibits pseudo-first-order kinetics. Such behavior is consistent with the reaction profile shown in Scheme II.

Scheme II details the possible mechanistic paths available for the formation of dimeric organic products from 1 during thermolysis and reaction with PPh_3. Herein, we suggest that the bis(acyl)hexacarbonyldiiron complexes 1, in a slow rate-determining equilibrium, converts to intermediates 2, in which one of the η^2-acyl ligands presumably transforms into a η^1-acyl moiety. Intramolecular reductive elimination at one of the iron atoms would lead to a 1,2-diketone, and an alkyl transfer from a η^1-acyl ligand can yield a ketone and hydrocarbon.[26]

For reaction with PPh_3, an alternate course, namely, a ligand-assisted cleavage of a metal–metal bond, is chosen forming 3 wherein the two iron atoms are held together by a μ-acyl moeity. This can further rearrange to give the observed products.

Finally, it should also be kept in mind that we still cannot exclude the possibility that mononuclear species arise in a post-rate-limiting sequence leading to product-forming events.

Under this proposed scheme, the rate constants[27] (Table IV) for the reaction of **1a** with PPh_3 become $k_1 = 2.79 \times 10^{-3}$ s^{-1} and $k_{-1}/k_2 = 0.56 \times 10^{-5}$ M^{-1}.

Selected Reactions of 1a. i. With Carbon Monoxide. At room temperature, under 60 psi of CO, **1a** is stable but decomposes readily when heated to 55 °C. The products

Table IV. Kinetic Parameters Associated with the Reactions of 1a with Triphenylphosphine

no.	$[PPh_3]/[\mathbf{1a}]$	$10^3[PPh_3]$, M	10^3k_{obs}
1	0.25	1.25	1.15 ± 0.01
2	0.33	1.88	2.18 ± 0.08
3	0.5	2.50	2.19 ± 0.06
4	1.0	5.0	2.61 ± 0.08
5	2.0	10.0	2.59 ± 0.09

[a] Rate constants were obtained by following the formation of $Fe_3(CO)_{12}$ from the absorption at λ = 600 nm. [b] [**1a**] = 0.50 M.

of the reaction are $Fe(CO)_5$, 10,11-eicosadione, and 10-nonadecanone (eq 4). Not surprising however, is the found absence of dimeric alkanes.

1a —(CO, 60 psi; c-C_6H_{12}, RT)→ no reaction

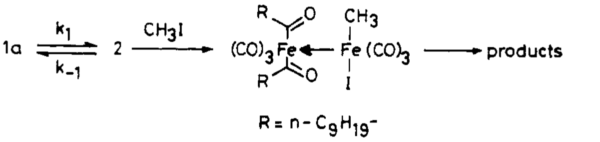
1a —(CO, 60 psi; c-C_6H_{12}, 55 °C)→ R–C(O)–R (76%) + R–C(O)–C(O)–R (11%) + R–R (<1%) + $Fe(CO)_5$ (52%) (4)

R = n-C_9H_{19}

ii. With Methyl Iodide. When **1a** was allowed to react with an excess of methyl iodide at ambient conditions under nitrogen, the reaction proceeded very smoothly and the mixture was found to contain $Fe(CO)_5$ as the principal organometallic product, in addition to organic products like 10-nonadecanone, n-decane, 2-undecanone, and n-nonyl iodide, as confirmed by GC-MS analysis (eq 5).

$$\mathbf{1a} \xrightarrow[CH_3I]{c\text{-}C_6H_{12},\ 25\ °C} \underset{11\%}{R\text{-}CH_3} + \underset{6\%}{R\text{-}C(O)\text{-}CH_3} + \underset{5\%}{R\text{-}I} + \underset{73\%}{R\text{-}C(O)\text{-}R} + \underset{46\%}{Fe(CO)_5} \quad (5)$$

The formation of these products can be explained if the initial step involves scission of a *single* metal–oxygen bond as described earlier in Scheme I, allowing one of the iron atoms to be coordinatively unsaturated to form 2, facilitating oxidative addition at this center. Subsequent reductive elimination at two metal centers provides reasonable concluding steps for this reaction (eq 6).



(6)

iii. With Protic Substrates. The ^{13}C NMR spectrum of **1a** has a signal at δ = 295.52 ppm (see Experimental Section). Since absorptions in this region are characteristic of metal–carbene complexes, an attempt to exploit the carbenic nature of **1a** was made, and **1a** was treated independently with methanol and acetic acid. The various products formed and their respective distribution are shown in eqs 7 and 8). It can be noted that the formation of secondary alcohols and esters offers some basis for the suggestion of the carbenic nature of the acyl–iron bond.

1a —(c-C_6H_{12}, 25 °C; CH_3OH)→ R–H (3%) + R–CHO (11%) + R–C(O)–R (65%) + R–C(O)–CH_3 (9%) + R_2CHOH (5%) + R–C(O)OCH_2R (5%) (7)

1a —(c-C_6H_{12}, 25 °C; HOAc)→ R–H (3%) + R–CHO (10%) + R_2CH(OH) (5%) + R–C(O)–OCH_2R (4%) + R–C(O)–R (60%) (8)

(26) Metal-formyl complexes can act as hydride donors; see: Gladysz, J.; Tom, W. *J. Am. Chem. Soc.* **1979**, *101*, 1589. Casey, C. P.; Newman, S. M. *Ibid.* **1978**, *100*, 2544. Precedence also exists for metal-acyl complexes to act as alkyl donors; see ref 5c.

(27) Obtained from a plot of $1/k_{obsd}$ vs $1/[L]$, disregarding the k_{obsd} value at the lowest phosphine concentration, which most reasonably does not fall in the pseudo-first-order kinetic regime.

Conclusions

It has been shown here that neutral bis(acyl)diiron complexes can be synthesized by one-electron oxidation of anionic alkyl- or acylferrate complexes. The reactivity of one of these complexes, viz. **1a**, has been explored in some detail. C–C bond-forming reactions in the thermolysis of **1a** have been shown to occur by *intramolecular* mechanism. Thus, the diiron complexes **1a–c** possess some novel properties, necessitating more studies of such systems, and more work will be deployed to fulfill this commitment.

Experimental Section

General Materials. All reactions were carried out under an atmosphere of prepurified nitrogen that had been passed through a 12-in. tube of Drierite. All solvents were reagent grade. THF and diethyl ether were purified by preliminary distillation from calcium hydride followed by a final distillation from lithium aluminium hydride. All transfers and manipulations of air-sensitive compounds were carried out in a nitrogen-filled Vacuum Atmosphere glovebox, and standard Schlenk techniques such as those described by Shriver[28] were routinely followed for handling air-sensitive materials.

$Na_2Fe(CO)_4 \cdot 1.5C_4H_8O_2$ was purchased from Alfa Inorganics Inc. and was also prepared in the laboratory by a literature procedure.[29] Both samples were found to behave identically, and hence no preference was made in its usage. (PPN)Cl was prepared as described elsewhere.[30] 1-Bromononane, decanal, phenyllithium, methyllithium, and trityl tetrafluoroborate were purchased from Aldrich Chemical Co. 1-Bromonanane and *n*-decyl bromide were distilled under reduced pressure prior to use. Copper(II) triflate was prepared from copper(II) carbonate and trifluoromethanesulfonic acid (Aldrich) as previously reported.[31]

Analytical GLC analyses of reaction products were performed on Hewlett-Packard 5750 and Varian Model 3380-A electronic integrators. Absolute yields of products were calculated from peak areas by using internal standard techniques with response factors obtained from authentic samples. Acetone, biacetyl, and ethane were analyzed by GLPC using a 24 ft × $^1/_8$ in. column of 10% SE-30 sorbent on Chromosorb W. Other organic products were analyzed by using a 6 ft × $^1/_8$ in. column of 3% SE-30 sorbent (80/100-Supelcoport). $Fe(CO)_5$ and $Fe_3(CO)_{12}$ were analyzed by HPLC using a μ-Poracil column (Waters) with isooctane as the eluant, and $Fe(CO)_4PPh_3$ was analyzed with a 70:30 isooctane–benzene mixture as the eluant.

GC-mass spectra were obtained by using a Hewlett-Packard 5985 GC–mass spectrometer. Routine proton NMR spectra were recorded on a Varian T-60 spectrometer; chemical shifts are reported in parts per million downfield from TMS. Infrared spectra were recorded in sodium chloride cells on a Perkin-Elmer 237 grating spectrometer. Infrared kinetic studies were carried out in an IBM Model No. 97 FT-IR spectrometer. Spectrophotometric data were obtained by using a Hewlett-Packard Model 8457-A diode-array UV–vis spectrometer. Elemental analyses were performed by Galbraith Laboratories.

Preparation of (PPN)(*n*-$C_9H_{19}Fe(CO)_4$). The procedure adopted was similar to the one described earlier by Siegl and Collman.[29] To a suspension of $Na_2Fe(CO)_4$ (2.18 g, 10 mmol) in 150 mL THF at 0 °C was added 1-bromononane (1.75 mL, 10 mmol) dropwise over a period of 15 min. Stirring was continued at 0 °C, and the reaction was monitored by removing aliquots periodically and examining the ν_{CO} region in the IR spectrum. The flask was then brought into the glovebox, and (PPN)Cl (3.46 g, 10 mmol) was added. Stirring was then recommenced, and the reaction temperature was maintained at 0 °C for an additional 5 h or until all the (PPN)Cl had dissolved. The resulting mixture was then filtered through dry Celite in a Schlenk vessel under nitrogen and concentrated under reduced pressure. When the volume of the filtrate reached ca. 25 mL, 75 mL of ether was added to the mixture, which was then placed in the freezer at −20 °C overnight. The yellowish brown solid that precipitated was filtered out under nitrogen and recrystallized from a methylene chloride–diethyl ether (75:25) mixture. The resulting reddish yellow crystals were dried in vacuo. Yield: 3.50 g (42%). Anal. Calcd for $C_{49}H_{49}NO_4P_2Fe$: C, 70.59; H, 5.88; N, 1.68. Found: C, 71.25; H, 5.69; N, 1.65. IR (THF) (cm^{-1}): $\nu_{CO,term}$ 1990_m, $1870_{br,s}$ (lit. IR for $(PPN)C_4H_9Fe(CO)_4$ ν_{CO} 1998_m, 1880_s, 1855_s).

Preparation of (PPN)(*n*-$C_9H_{19}C(O)Fe(CO)_4$). The procedure adopted was similar to the one described above for *n*-nonylferrate except $Na_2Fe(CO)_4$ (2.188 g, 10 mmol) in 150 mL of THF was mixed with *n*-decanoyl chloride (1.90 mL, 10 mmol). The yield of the reddish yellow crystals of the acylferrate is 4.20 g (49%). Anal. Calcd for $C_{50}H_{49}NO_5P_2Fe$: C, 69.69; H, 5.69; N, 1.63. Found: C, 70.02; H, 5.75; N, 1.72. IR (THF) (cm^{-1}): $\nu_{CO,term}$ 2005_m, 1905_s, 1887_{vs}; $\nu_{CO,acyl}$ $1612_{w,m}$ (lit. IR for $(PPN)(C_2H_5C(O)Fe(CO)_4)$ $\nu_{CO,term}$ 2000_m, $1900_{m,sh}$, 1880_s, 1861_s, $\nu_{CO,acyl}$ $1610_{w,m}$).

Preparation of 1a. i. One-Pot Synthesis. In a glovebox $Na_2Fe(CO)_4 \cdot 1.5C_4H_8O_2$ (5.00 g, 14.5 mmol) was added to a 500-mL three-necked, round-bottomed flask equipped with a 125-mL addition funnel. The flask was removed from the glovebox, and 250 mL of dry distilled THF was added via a cannula. The dispersion was cooled to 0 °C in an ice bath, and to this 1-bromononane (3.00 g, 14.5 mmol) in 50 mL of THF was added through an addition funnel over a period of 10 min. After being stirred for 5 h at 0 °C, the reaction mixture was cooled to −78 °C in a dry-ice/acetone bath and a copper(II) triflate solution (5.20 g, 14.5 mmol, in 50 mL of THF) was chilled to −78 °C and added through a cannula. The resulting mixture was then allowed to warm slowly to 0 °C, during which time the color of the solution changed from red to greenish orange. The mixture was then stirred for an additional 30 min, and the addition funnel was removed under a positive pressure of nitrogen. The vessel was chilled to 0 °C and the reaction mixture concentrated to dryness under reduced pressure. The resulting residue was extracted with three 50-mL portions of dry pentane, the solution was chilled to 0 °C, and the combined pentane extracts were filtered through a bed of dry Celite in a Schlenk vessel, under nitrogen. An infrared spectrum of this solution exhibited characteristic bands of the bis(acyl)diron complex reported earlier by Fischer,[8] as well as those of $Fe(CO)_5$ and $Fe_3(CO)_{12}$. The pentane filtrate was concentrated to dryness in vacuo at 0 °C and subjected to column chromatography over silica under nitrogen. Three distinct bands were observed and the components [in the order of elution, as identified by IR spectroscopy] were $Fe(CO)_5$ (yellow), $Fe_3(CO)_{12}$ (emerald green), and $[n\text{-}C_9H_{19}C(O)]_2Fe_2(CO)_6$ (golden yellow). The last fraction was collected and concentrated under reduced pressure at 0 °C, and the dark red oil that remained was stored under nitrogen at −20 °C. This oil showed no tendency to crystallize even at low temperature (−50 °C). It was however soluble in most nonpolar organic solvents. Yield: 1.20 g (28.1%). IR (pentane) (cm^{-1}): $\nu_{CO,term}$ 2080_m, 2033_s, 2002_s, 1968_m; $\nu_{CO,bridg}$ $1536_{br,w}$. ^1H NMR (C_6D_6): δ 2.5 (t, 2 H), 0.7–1.2 (m, 17 H). MS: *m/e* 590 (0.1%, M^+), 435 (22%), 280 (46%), 155 (100%, RC(O)). ^{13}C NMR: δ 295.52 (Fe–C(O)Fe), 215.00, 211.34 ($Fe(CO)_3$), 61.71 (CH_2–(C-O)–Fe), 32–23 (C_3–C_9), 14.25 (C_{10}).

ii. By Oxidation of Alkyl- or Acylferrates. In a nitrogen-filled glovebox, either $[PPN][n\text{-}C_9H_{19}Fe(CO)_4]$ (8.33 g, 10 mmol) or $[PPN][n\text{-}C_9H_{19}C(O)Fe(CO)_4]$ (8.61 g, 10 mmol) (see below) was placed in a 500-mL three-necked round-bottomed flask, and the flask was capped with rubber septa and removed from the glovebox. The solution was stirred at 0 °C for 1 h and then cooled to −78 °C in a dry-ice/acetone bath. Copper(II) triflate (3.4 g, 10 mmol) was dissolved in 50 mL of THF, and the solution chilled to −78 °C was added by a cannula to the ferrate solution. The resulting mixture was then slowly warmed to 0 °C, and the color of the solution changed from red to green-orange. The mixture was then stirred at 0 °C for an additional 1 h, after which time the flask, still cooled at 0 °C, was connected to a vacuum line and the solvent removed under reduced pressure. The resulting residue was extracted with three 50-mL portions of chilled pentane, and this pentane extract was filtered through a bed of Celite in a Schlenk vessel kept under nitrogen. The filtrate was worked up as mentioned earlier, and the red oil was identical with the one obtained by the method described above. The yield of

(28) Shriver, D. F.; Drezdzen, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; John Wiley & Sons: New York, 1986; Chapter 3.
(29) Siegl, W. O.; Collman, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 2516.
(30) Ruff, J. K. *Inorg. Chem.* **1968**, *7*, 1818.
(31) Jenkins, C. L.; Kochi, J. K. *J. Org. Chem.* **1971**, *36*, 3095.

1a based on alkylferrate was 1.80 g (30.5%), and that based on acylferrate was 2.10 g (35.6%).

Preparation of 1b,c. Compounds **1b,c** were prepared from the reaction of $Fe(CO)_5$ and the corresponding alkyllithium followed by oxidation and workup as reported earlier by Fischer and co-workers.[7] The method followed was outlined as "eintopverfahren" in their report. The only change made in the procedure was that the oxidant used in this case was copper(II) triflate instead of trityl chloride. The resulting solids for both **1b** and **1c** displayed spectroscopic properties identical with those earlier reported.

Thermal Decomposition of 1a. An oven-dried 5-mL ampule equipped with a Teflon-coated magnetic stirrer bar was charged with **1a** (0.30 g, 0.80 mmol) in the glovebox and stoppered with a rubber septum. The ampule was removed and placed in dry ice. Olefin-free cyclohexane (1 mL) and *n*-tridecane (100 μL, internal standard) were added by syringe, and the ampule was sealed with the aid of a torch. After it had warmed to room temperature, the ampule was placed in a test tube and immersed in an oil bath at 55 ± 1 °C for 4 h. The reaction mixture changed from red to pale yellow. The ampule was then removed from the oil bath, chilled to −78 °C, and opened. An IR spectrum of this mixture showed the absence of bands due to the starting material. There were, however, two new carbonyl bands at 2022 and 2002 cm^{-1}. The yield of the organic products were determined by GLPC, and the yield of $Fe(CO)_5$, by HPLC.

Thermal Decomposition of 1b,c. The procedure adopted was similar to the one observed for the thermal decomposition of **1a** except that 0.5 mmol of **1b** or **1c** was used for the decomposition studies.

Thermal Decomposition of a Mixture of 1a,b. The procedure adopted was similar to the ones described for thermal decomposition of **1a** except that 0.5 mmols each of **1a** and **1b** were added to the ampule and as internal standards *n*-tridecane and *n*-hexane were added.

Kinetics of the Thermal Decomposition of 1a. The thermal decomposition of **1a** was monitored by FT-IR spectroscopy by using a thermostated, variable-temperature cell purchased from Foxboro-Analabs. The cell thermostat was calibrated prior to use, and the cell was preheated to a preselected temperature and charged with a 0.50 M solution of **1a** in cyclohexane. The decrease in intensity of the band at 2080 cm^{-1} was recorded at predetermined intervals, and the rate constants were subsequently derived.

Reaction of 1a with Triphenylphosphine. An oven-dried 5-mL ampule containing a Teflon-coated magnetic stirrer bar was charged with 0.50 mmol of **1a** and stoppered with a rubber septum. The ampule was then removed from the glovebox and placed in dry ice. Olefin-free cyclohexane (0.5 mL), *n*-tridecane (100 μL), and a 1 M solution of triphenylphosphine in cyclohexane (0.50 mL) were added by syringe under an atmosphere of nitrogen. The ampule was then warmed to room temperature, and the mixture was stirred for 2 h, during which time the color of the solution changed from dark red to yellow-green. The ampule was then chilled to −78 °C and opened. An IR spectrum of the reaction mixture revealed absorptions at 2053_m, 2026_w, 1979_m, 1958_s, 1894_m, and 1725_m cm^{-1}. These absorptions correspond to the known ν_{CO} values for $Fe(CO)_4PPh_3$, $Fe(CO)_3(PPh_3)_2$, $Fe_3(CO)_{12}$, and 10-nonadecanone. The yields of organic products were determined by GLPC, and those of the organometallic products, by HPLC.

Kinetics of the Reaction of 1a with Triphenylphosphine. Solutions of **1a** (0.10 M) and triphenylphosphine (0.10 M) in cyclohexane were prepared and used for the kinetic studies. A UV cell equipped with a 3-cm stem was capped with a rubber septum and flame-dried under a flush of nitrogen. Cyclohexane (3.5 mL) and 200 μL of a 0.1 M solution of **1a** were added by syringe. The cell was placed in a Hewelett-Packard Model 8451A UV–vis spectrometer and the initial spectrum recorded. An appropriate volume of the 0.10 M solution of triphenylphosphine was added to this solution by syringe. Various ratios (0.25, 0.33, 0.5, 1.0 and, 2.0) of $[PPh_3]/[\mathbf{1a}]$ were thus obtained for kinetic studies. The increments in the absorption values of $\lambda = 600$ nm were followed at specified time intervals, and a plot of $\ln A/A_0$ was constructed from these values.

Reaction of 1a with Carbon Monoxide. A flame-dried Fisher–Porter pressure tube containing a Teflon-coated magnetic stirrer bar was charged with 0.5 mmol of **1a** and capped with a rubber septum. The tube was then taken out of the glovebox, and 5 mL of olefin-free cyclohexane and 100 μL of *n*-tridecane were added via syringe. The mixture was then pressurized with 60 psi of carbon monoxide and stirred at room temperature for 12 h. Aliquots were removed periodically and were examined by IR spectroscopy. The bands due to **1a** in the terminal carbonyl region showed no signs of diminution. The reaction vessel was then heated to 55 °C. After 3 h, the bands due to the starting material disappeared and those of $Fe(CO)_5$ became apparent. The organic products were identified. Their yields were determined by GLPC, and the yield of $Fe(CO)_5$, by HPLC.

Reaction of 1a with Methyl Iodide. In a glovebox, an oven-dried, 5-mL ampule was equipped with a Teflon-coated magnetic stirrer bar and charged with 0.5 mmol of **1a**. The ampule was stoppered with a rubber septum, removed from the glovebox, and chilled in dry ice. Olefin-free cyclohexane (1 mL), *n*-tridecane (100 μL), and methyl iodide (300 μL, 5.0 mmol) were added by syringe, and the ampule was sealed with the aid of a torch. After it had warmed to room temperature, the mixture was stirred for 3 h, over which period the color of the solution changed from red to yellow. The ampule was then chilled to −78 °C and opened, and the organic products were identified by GC–MS. Their yields were determined by GC. $Fe(CO)_5$, the principal organometallic product, was identified by IR spectroscopy, and its yield was determined by HPLC.

Reaction of 1a with Methyl Alcohol and Acetic Acid. The procedure adopted was similar to the one detailed above except 5 mmol of MeOH or HOAc was used for reaction with **1a**. The organic products were identified in the same manner by use of GC–MS, and their yields, by GC. No IR-active carbonyl-containing organometallic products were observed in both cases.

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Supplementary Material Available: Figures showing IR spectral changes associated with thermal decomposition of **1a** and kinetic plots (3 pages). Ordering information is given on any current masthead page.