supplementary material). Final atomic coordinates of the non-hydrogen atoms are noted in Table I. The anion is a dimer with a crystallographically imposed center of inversion. The Mn atoms are bridged by the terminal perthio atoms of perthiocarbonate ligands. One of the other terminal atoms of each perthiocarbonate coordinates to an axial site on each Mn to form five-membered SSCSMn chelate rings. Carbonyl ligands complete a distorted octahedral arrangement about each Mn atom. A view of the anion is given in Figure 1. Within the precision of this structure analysis there is no significant difference in the three Mn–S bond lengths (range 2.360 (4)–2.381 (4) Å).

The structures of a few other perthiocarbonates, which do not have carbonyl ligands, have been reported.[7,8] In $[(SCS_3)_2MoS]^{2-}$ and $[(SCS_3)Mo_2S_4(SCS)_3]^{2-}$ the perthiocarbonate is bidentate with the Mo–S (perthio) bond being significantly shorter than the other Mo–S bond to this ligand (ca. 0.06 Å for the former, but only ca. 0.02 Å for the latter).[8] Bond distances within the perthiocarbonate ligand of $[(Mn(CO)_3(SCS_3))_2]^{2-}$ closely parallel those of $[(SCS_3)_2MoS]^{2-}$: the S–S distance is somewhat long, the C–S bond to the uncoordinated S is short, indicating that the double bond is largely localized here and not delocalized into the chelate ring, and the C–S distances within the chelate ring are near equal.

Some comparisons can also be made with perthiolates[9] and S_4^{2-} complexes[10] as they, too, form five-membered chelate rings of the type SS(C or S)S(Metal). In these compounds the metal–S bonds may be near equal[9b,c,10a] or asymmetric,[9a,10b] a feature which is well-known for dithiocarbamates and dithiolates.[11] Perthiolates show shorter C–S bonds within the chelate ring than perthiocarbonates as the double bond is delocalized within the ring. The structure of a copper perthiolate has been reported in which the ligating S atoms bridge metal atoms.[9d]

The following procedure was used: to 3.0 mmol of $Mn(CO)_5Br$ in CH_2Cl_2 (50 mL) or 4-methyl-2-pentanone (25 mL) was added an equivalent volume of 5 N NaOH containing benzyltriethylammonium chloride. After the mixture was stirred for 30 min at 40 °C **1** was formed (IR identical with that reported previously),[4] elemental sulfur (0.32 g) was added, and stirring was continued at 40 °C for 3 h (CH_2Cl_2) or for 30 min at 70 °C (4-methyl-2-pentanone). The reaction mixture was cooled to room temperature, the phases were separated, and the organic phase was dried ($MgSO_4$). Hexane was added to the organic phase, and orange crystals of **2** were obtained after the solution was stored in a refrigerator; yield 46%. (Anal. Calcd for $C_{34}H_{44}Mn_2N_2O_6S_8$: C, 43.30; H, 4.70; S, 27.20. Found: C, 43.41; H, 4.61; S, 27.33.)

In conclusion, phase-transfer-catalyzed reaction of $Mn_2(CO)_9Br^-$ with sulfur affords a novel class of complexes. The mechanism of this intriguing reaction remains to be determined.

Acknowledgment. We are indebted to the Natural Sciences and Engineering Research Council of Canada for support of this work.

Supplementary Material Available: A description of the collection of the X-ray diffraction data and refinement of the structure, Figure 2, showing the cation, and tables listing crystal data, data collection and refinement, atomic coordinates and thermal parameters of the hydrogen atoms, interatomic distances and angles, least-squares planes and torsion angles, and observed calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Evidence for Intramolecular Pathways in C–C Bond-Forming Reactions Proceeding from Binuclear Iron Complexes[1]

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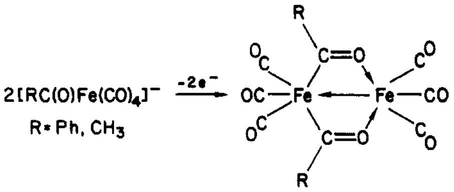
Summary: Decomposition of the binuclear iron complex **2** (R = *n*-C_9H_{19}) in THF or cyclohexane yields three products: *n*-octadecane, 10-nonadecanone, and 10,11-eicosodione. The principal organometallic product is $Fe(CO)_5$. Decomposition obeys first-order kinetics and is characterized by an unusually large, negative entropy of activation, $\Delta S^{\ddagger} = -29$ cal/(mol K) (log $A = 6.07$). The failure to observe any crossover products demonstrates that these decomposition products are produced in processes which do not involve alkyl group scrambling and presumably occur by intramolecular pathways. The reactivity of **2** with methyl iodide and triphenylphosphine has also been briefly examined.

Binuclear complexes would appear to afford an obvious bridge between the chemistry of mononuclear complexes and polynuclear clusters with interest in the latter deriving in part from the suggestion that their chemistry may serve as a model for the study of even more complex multimetal systems such as are found heterogeneous catalysts.[2] In fact, in their extensive studies of the C–C bond-forming reactions of certain simple binuclear organocobalt complexes, Bergman and co-workers demonstrated that the chemistry of these reagents is dominated by intermolecular mononuclear processes.[3-6] We report here the results of our investigation of the ostensibly similar reactions associated with certain binuclear organoiron complexes which, however, appear to occur by *intramolecular* pathways.

Oxidation of acyltetracarbonylferrates by any of several one-electron oxidants yields a neutral complex (eq 1),[7a] the



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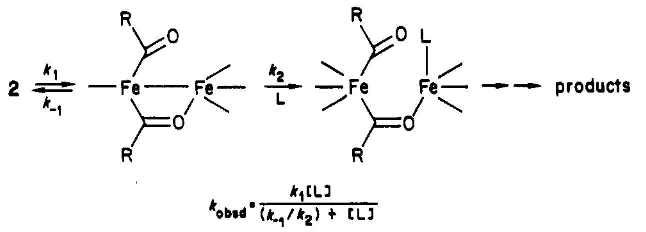
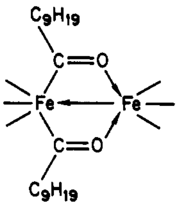
Scheme I



$$k_{obsd} = \frac{k_1[L]}{(k_{-1}/k_2) + [L]}$$

structure of which has been established by a single-crystal X-ray diffraction as the dinuclear compound 1 (R = Ph).[7b] In an extension of this procedure, we have observed that when the bis(triphenylphosphine)nitrogen(1+) salt of either *n*-nonoyl(tetracarbonyl)- or *n*-nonyl(tetracarbonyl)ferrate (3 and 4, respectively)[8a] is treated with 1.0 equiv of cupric triflate in THF at 25 °C and the subsequent reaction mixture subjected to column chromatography on silica gel under scrupulously air-free conditions, the pentane eluent contains a thermally labile, neutral complex to which, on the basis of comparison between its spectral properties and those of 1, R = Ph and CH_3,[7b] we assign the equivalent binuclear structure 2.

$$PPN[n\text{-}C_9H_{19}Fe(CO)_4] \text{ or } PPN[n\text{-}C_9H_{19}C(O)Fe(CO)_4] \xrightarrow[THF,\ 25\ °C]{Cu(OTF)_2}$$



(2)

2

We have explored the reactivity of this material by examining its reaction with several common substrates. Thus, 2 reacts readily with excess methyl iodide (eq 3). Analysis of the resulting product mixture reveals the symmetrical coupling product di-*n*-nonyl ketone as well as significant amounts of the cross-coupling products 2-undecanone, *n*-decane, and *n*-nonyl iodide.

$$2 \xrightarrow[c\text{-}C_6H_{12},\ 25\ °C]{CH_3I} \begin{array}{ccccccccc} RCH_3 & + & RC(O)CH_3 & + & RI & + & RC(O)R & + & Fe(CO)_5 \\ 11\% & & 6\% & & 5\% & & 73\% & & 46\% \end{array} \quad (3)$$

Treatment of 2 with a slight excess of triphenylphosphine in cyclohexane results in an immediate reaction, producing di-*n*-nonyl ketone and (triphenylphosphine)tetracarbonyliron as the major product (eq 4). A spectrophotometric study of the rate of this reaction revealed what appears to be two kinetic regimes. In the first regime the disappearance of 2 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 independent of phosphine (Figure 1), and the reaction exhibits pseudo-first-order kinetics. Such behavior is consistent with the reaction scheme shown in Scheme I.[9a] Analysis of the kinetic data yields $k_{-1}/k_2 = 0.56 \times 10^{-3}\ M^{-1}$ and $k_1 = 2.8 \times 10^{-3}\ s^{-1}$.[9b]

$$2 + Ph_3P \xrightarrow[c\text{-}C_6H_{12}]{25\ °C} \begin{array}{ccc} RC(O)R & + & Fe(CO)_4(PPh_3) + \\ 98\% & & 54\% \\ Fe_3(CO)_{12} & + & Fe(CO)_3(Ph_3P)_2 \\ 22\% & & 22\% \end{array} \quad (4)$$

In THF or cyclohexane, complex 2 decomposes slowly at room temperature. Three C–C bond-forming products are produced: *n*-octadecane, 10-nonadecanone, and 10,11-eicosodione (Table I). The principal organometallic

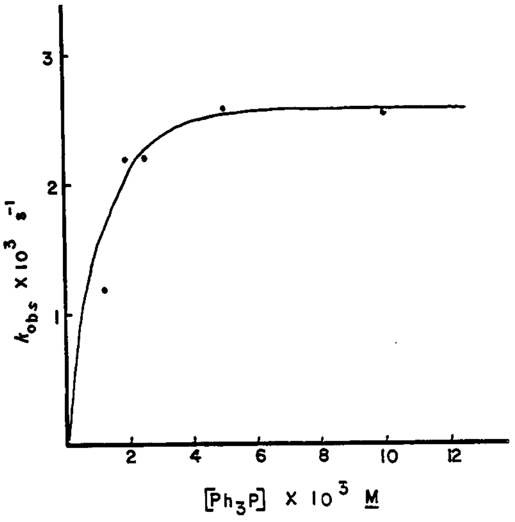


Figure 1. Influence of Ph_3P concentration on the observed rate constant for reaction of 2 with excess Ph_3P in cyclohexane at 25 °C.

Table I. Organic Products from the Thermal Decomposition of 2

$$[RC(O)]_2Fe_2(CO)_6 \xrightarrow[L]{c\text{-}C_6H_{12}}$$

R^a	L	products,[b,c] %		
		R-R	RC(O)R	RC(O)C(O)R
CH_3		10	58	16
C_6H_5		18	43	25
n-C_9H_{19}		15	63	11
n-C_9H_{19}	CO	<1	76	11
n-C_9H_{19}[d]	Ph_3P	<1	98	<1

[a] [2] = 0.5 M; unless otherwise noted, a reaction temperature of 55 °C was employed. [b] No monomeric organic products (i.e., RH, R(–H), or RCHO) were observed. [c] Yields were determined by GLPC employing unexceptional internal standard techniques. [d] Reaction temperature: 25 °C.

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(8) (a) Prepared by the dropwise addition of *n*-nonoyl chloride or nonyl bromide, respectively, to a well-stirred suspension of $[PPN]_2Fe(CO)_4$ (9.3 g, 13.2 mmol) in THF at 0 °C.[18] (b) Prepared by the slow addition of 1.0 equiv of anhydrous copper(II) triflate in THF to a well-stirred suspension of 3 in THF at –78 °C. The mixture was slowly warmed to 0 °C and concentrated to near dryness under reduced pressure. This residue was extracted with three, 50-mL portions of chilled (–50 °C) pentane. The combined pentane extracts were filtered through a bed of Celite; the filtrate was concentrated at 0 °C under reduced pressure and subjected to column chromatography over silica. Three distinct bands were observed. The last band to elute was collected and concentrated to dryness at 0 °C under reduced pressure to yield 2 as a dark red oil: IR (in pentane) ν(CO) 2079 (m), 2035 (s), 2004 (s), 1979 (m), 1536 (br w) cm^{-1}; ^1H NMR (δ, C_6D_6, Me_4Si) 2.5 (t, 2 H), 0.95 (m, 17 H); ^{13}C NMR (δ, C_6D_6, Me_4Si) 295.52 (*C*(O)), 215.00, 211.34 ($Fe(CO)_3$), 61.71 ($CH_2C(O)$), 23–33 (CH_2), 14.25 (CH_3); MS, *m/e* (relative intensity), 590 (0.1, M^+), 435 (0.1), 280 (6), 155 (100, $RC(O)^+$). The corresponding spectral properties of authentic 1, R = CH_3: IR (in pentane) ν(CO) 2088 (m), 2037 (s), 2002 (s), 1971 (m), 1543 (br, w) cm^{-1}; ^1H NMR (δ, C_6D_6, Me_4Si) 2.62; MS, *m/e* (relative intensity) 366 (M^+), 388 [M – (CO)], 323 [M – ($CH_3C(O)$)], 310 [M – 2(CO)], 280 [M – 2L($CH_3C(O)$)] (100%). 1, R = Ph: IR (in pentane) ν(CO) 2093 (m), 2040 (s), 2008 (s), 1972 (m), 1497 (br, w) cm^{-1}; ^1H NMR (δ, $CDCl_3$, Me_4Si) 6.65.

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

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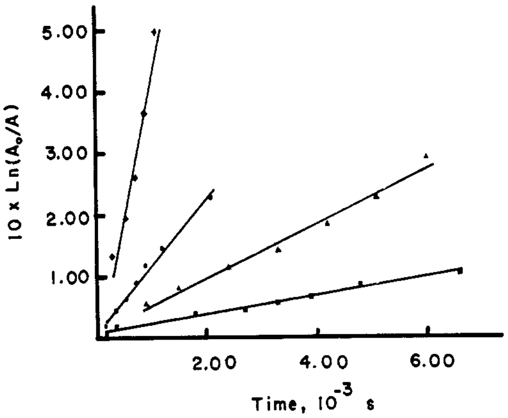

Figure 2. Plot of ln (A_0/A) vs. time for the decomposition **2** (R = n-C_9H_{19}) in cyclohexane solution: ♦, T = 75 °C; ●, T = 62 °C; ▲, T = 43 °C; ■, T = 30 °C.

Table II. Kinetic Parameters Associated with the Thermal Decomposition of **2**[a]

temp, °C	$10^4 k_{obsd}$,[b,c] s^{-1}	E_a, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol K)	log A
30	0.147 ± 0.005	15.1 ± 1.4	−29.7 ± 4.3	6.07
43	0.442 ± 0.002			
62	1.09 ± 0.05			
75	4.65 ± 0.05			

[a] See ref 10a. [b] $[\mathbf{2}]_0$ = 0.50 M. [c] At 55 °C, the value of k_{obsd} showed only minor (ca. 10%) variation over the concentration range of [**2**] = 0.050–0.50 M.

product is iron pentacarbonyl, $Fe(CO)_5$ (48%). The rate of disappearance of **2**, which can be conveniently monitored by infrared spectroscopy,[10a] obeys first-order kinetics for >2 half-lives and varies with temperature as shown in Figure 2. The same reaction performed under an atmosphere of CO (60 psi) yields only RC(O)R and RC(O)C(O)R.

The intra- vs. intermolecularity of the C–C bond-forming reactions was investigated by the use of crossover experiments. A sample containing a mixture of 50 mol % **2** and 50 mol % **1**, R = CH_3, was allowed to decompose in cyclohexane at 62 °C and the product mixture examined by capillary GC/mass spectrometry.[10b] No crossover products were observed from which we conclude these coupling products are formed in processes which do not involve alkyl group scrambling and presumably occur by intramolecular pathways.

The activation parameters associated with the thermal decomposition of **2** are informative. In particular, the magnitude of the entropic term, ΔS^*, 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.[11,12] However, similar entropies of activation are associated with at least two other well-defined unimolecular processes. Thus, the isomerization[13] of the dinuclear iron complex μ-$[(C_6H_5)(CH_3)Sn]_2Fe_2(CO)_8$ and the automerization of cyclobutadiene[14] exhibit an entropy of activation of −25 ± 5 and −25 ± 7 cal/(mol deg), respectively. In the former case, the purported rate-determining step involves the single scission of one of the bridging iron–tin bonds. In the latter instance it was concluded[15] that the abnormally low activation entropy associated with what is, in fact, a bondshifting reaction, reflects a reaction trajectory in which the extreme narrowness of the reaction barrier makes heavy-atom tunneling the dominant reaction pathway. Whether similar intramolecular processes are responsible for the unusually large negative entropy of reaction associated with the decomposition of **2** remains unknown.[16]

Collectively, the chemical behavior of **2** invites comparison to the process of oxidative addition, reductive elimination, ligand migration, and decarbonylation, all well-established reactions in the chemistry of mononuclear complexes. In fact, we cannot at present exclude the possibility that mononuclear species arise in a post-rate-limiting sequence leading to product-forming events. However, in part, the production of 1,2-diketones, which were not observed by Collman[17] in the decomposition of mononuclear iron complexes, mitigates against this possibility.

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(10) (a) Employing a calibrated, preheated, thermostated infrared cell (Foxboro/Analogs), the disappearance of the 2079-cm^{-1} band of a 0.5 M solution of **2** (R = n-C_9H_{19}) was monitored by FT-IR. (b) Under these conditions, the rate constant for the decomposition of **1**, R = CH_3, is 1.36 × 10^{-4} s^{-1} while that of **2**, R = n-C_9H_{19}, is 1.09 × 10^{-4} s^{-1}.

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(16) Classically, unimolecular isomerizations involving a one-particle transition state (i.e., a process in which one particle is transformed into one particle) are characterized by log A values ranging from ca. 11 to 14.[11b] Examples of other processes that exhibit abnormally low log A values have been cited elsewhere.[19]

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Synthesis of (Carbyne)metal Complexes by Oxide Abstraction from Acyl Ligands

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Summary: Stable carbyne complexes of the type *trans*-$X(CO)_2L_2M{\equiv}CR$ (M = Cr, Mo, W; R = C_6H_5, CH_3; X = Cl, Br, $CF_3C(O)O$, L_2 = 2 pyridine, tetramethylethylenediamine) are prepared in a single synthesis step by reaction of the respective acyl complexes $[NMe_4][(CO)_5MC(O)R]$ at low temperatures with $COCl_2$, $C_2O_2Cl_2$, $ClC(O)OCCl_3$, $C_2O_2Br_2$, or $(CF_3CO)_2O$ and subsequent addition of the nitrogenous ligands at warmer temperatures.

The chemistry of metal–carbon triple bonds has developed into an area of considerable interest. Metal alkylidyne, or carbyne, complexes are now established catalyst precursors for alkyne metathesis[1] and alkyne polymerization reactions.[2] Reactions of potential synthetic interest based on the coupling of carbyne and carbonyl ligands have been discovered.[3] Further exploration of this

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