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The Reactions of Organosulfur Transfer Reagents with $Fe_2(CO)_9$ and the Synthesis of the $Fe_2(CO)_6$ Derivative of α-Lipoic Acid

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Abstract

Treatment of $Fe_2(CO)_9$ with sulfur-transfer reagents of the types Imide–S–S–Imide and RS–S–Imide where H-imide = phthalimide, succinimide, benzimidazole, morpholine and piperazine, and R = CH_2Ph and CMe_3 leads to cleavage of both the sulfur–sulfur bond and the sulfur–nitrogen bond to give $Fe_3(CO)_9S_2$ in varying yields, some $Fe_2(CO)_6S_2$ plus low yields of the appropriate dimers of the type $Fe_2(CO)_6(SR)(SR')$, where R = R' = phthal imido, CH_2Ph, CMe_3 and R = CH_2Ph, CMe_3, R' = phthalimido. The naturally occurring cyclic disulfide D,L-α-lipoic acid, its methyl ester and amide react with $Fe_2(CO)_9$ to give $Fe_2(CO)_6$ derivatives wherein the sulfur–sulfur bond has been broken.

Introduction

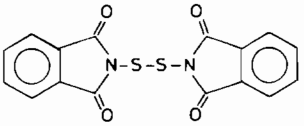
During studies into the preparation of complexes containing catenated polysulfur species of the type MS_xR where $x > 1$, extensive application of sulfur-transfer reagents of the types Imide–S_x–Imide and RS_x–Imide, where H-imide = phthalimide, benzimidazole; R = organic residue; x = 1,2 has proved successful [1]. Such reagents were initially developed to prepare organic polysulfanes as shown in eqn. (1) [2]. It is well known that organic disulfides react with $Fe_2(CO)_9$ to give complexes of the type $Fe_2(CO)_6(SR)_2$, where cleavage of the S–S bond has occurred (eqn. (2)) [3]. Thus it seemed reasonable that reaction of sulfur-transfer reagents, where x = 2, would give similar complexes which would contain the reactive S–Imide species. These compounds should, in turn, be precursors to catenated sulfur ligands upon reaction with thiols. In such reactions, we have found trace amounts of the desired complexes; however, the dominant reactivity in these systems includes cleavage of the S–Imide bond leading to the isolation of the known [4] complexes $Fe_3(CO)_9S_2$ and $Fe_2(CO)_6S_2$.

$$RS_x\text{–Imide} + R'SH \longrightarrow RS_x\text{–}SR' + \text{H–Imide} \quad (1)$$

$$RS\text{–}SR + Fe_2(CO)_9 \longrightarrow (CO)_3Fe\text{–}\mu,\mu'\text{-}(SR)_2Fe(CO)_3 \quad (2)$$

In addition, we report the facile preparation of $Fe_2(CO)_6$ derivatives of the important naturally occurring cyclic disulfide D,L-α-lipoic acid its methyl ester and amide. It has been shown that complexes of the type μ,μ'-$(SR)_2Fe_2(CO)_6$ are precursors to sulfides or disulfides (oxidation) and mercaptans (reduction) [6]. Thus these novel derivatives are of interest as possible intermediates for development of the medicinal chemistry of lipoic acid.

Results and Discussion



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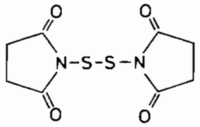

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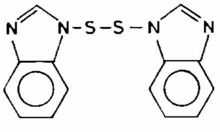

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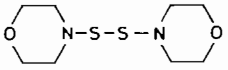

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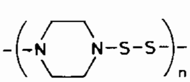

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The five sulfur-transfer reagents **1**–**5** were treated with $Fe_2(CO)_9$ in THF solvent under various experimental conditions. Upon evaporation of the reaction mixture the residue was extracted with pentane then $CHCl_3$ leaving a large amount of brown inorganic residue (ferric oxide). The pentane extract

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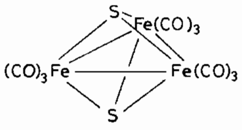
TABLE I. Yield of $Fe_3(CO)_9S_2$ as a Function of Sulfur Transfer Reagent

Sulfur transfer reagent	Yield (%)
1	23
2	48
3	20
4	20
5[a]	<1
9a	12

[a] **5** was recovered in 90% yield.

was evaporated to give $Fe_3(CO)_9S_2$ (**6**) in varying yields from **1**–**5** (Table I) plus some $Fe_2(CO)_6S_2$ (**7**), usually in negligible amounts (<1%), from **1** and **4**. The identities of **6** and **7** were confirmed by comparison to authentic samples prepared by published procedures [4]. In the case of **1** the chloroform extract contained small amounts (3%) of the desired product **8a** contaminated by **6**. The infrared spectrum of **8a** in the terminal carbonyl stretching region gave the characteristic pattern of four bands reported for complexes of type **8** [7]. The parent ion was not detected in the mass spectrum; however the ion ($M^+ - 2CO$) and those corresponding to successive loss of CO ligands were observed. The presence of two intense peaks at m/e 468($M^+ - 6CO$, 63%) and 404($M^+ - 6CO - 2S$, 68%) are consistent with the presence of the thiophthalimido groups. Peaks due to the fragmentation of the phthalimido moiety are also present.



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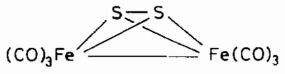

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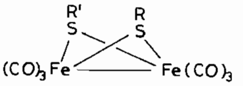
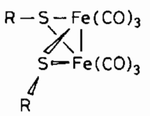
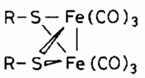


8a, R = R' = phthalimido
b, R = R' = CH_2Ph
c, R = CH_2Ph, R' = phthalimido
d, R = R' = CMe_3
e, R = CMe_3, R' = phthalimido

The ^1H NMR spectrum of complex **8a** in $CDCl_3$ is consistent with the formulation and its simplicity implies the existence of one isomer [9] of the complex in solution. It is reasonable to suggest that this isomer corresponds to that of an equatorial–equatorial (ee) conformation due to steric considerations although the axial–equatorial (ae) conformation cannot be completely ruled out. While the elemental analysis for C, H and N supports the formulation $C_{22}Fe_2H_8N_2O_{10}S_2$, that for sulfur is only about half of theory, an inconsistency often observed when metals are present [1a].



ae



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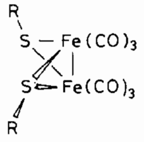
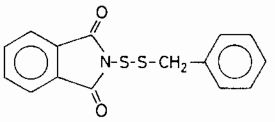


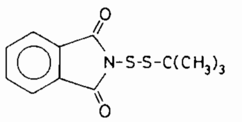
ee

Species similar to **8** were not isolated from **3** or **4** but their presence in very low yields were detected by infrared spectroscopy. There was no indication by infrared of the formation of dimeric complexes from **2** or **5**. Thus, the five reagents do not give the expected species when treated with $Fe_2(CO)_9$. This behaviour sharply contrasts with that of simple organic disulfides which invariably lead to dimers **8**. The cluster $Fe_3(CO)_9S_2$ is a common product from reactions between $Fe_2(CO)_9$ and sulfur compounds [3].

The sulfur transfer reagents RS–S–phthalimide, where R = CH_2Ph (**9a**) and (**9b**), have only one active S–N bond and therefore might be expected to give the desired $Fe_2(CO)_6$ dimers. However, treatment of **9a** with $Fe_2(CO)_9$ unexpectedly gave **8b** [6, 10] (35%) plus **6** (12%), **7** (<1%) and the expected dimer **8c** (<1%). The identity of complex **8b** was confirmed by comparison of its infrared spectrum to that of an authentic sample prepared from benzyl disulfide. Complex **8c** was identified on the basis of its IR, NMR and mass spectra.

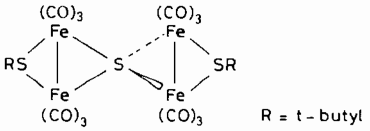


9a



9b

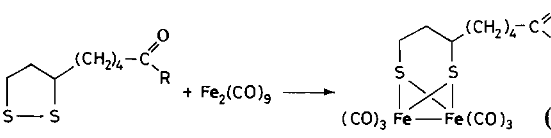
The major product from the reaction of **9b** with $Fe_2(CO)_9$ was t-butyldisulfide (23%) along with traces (4%) of **7**, **8d**, **8e** and **10** [11], the latter tentatively identified on the basis of its mass spectrum. The formation of t-butyldisulfide may have occurred via recombination of t-butyl thiyl radicals generated in the reaction thus accounting for the low yields of **8d** and **8e**.



10

Reactions of DL-α-Lipoic Acid and Derivatives with $Fe_2(CO)_9$

In tetrahydrofuran, $Fe_2(CO)_9$ reacts smoothly with D,L-α-lipoic acid, its methyl ester and amide, at room temperature, to give complexes **11a–c** in higher than 80% yield (eqn. (3)). These complexes are stable red oils which were purified by chromatography and identified spectroscopically and by



(3)

R = OH, OCH_3, NH_2

11a, R = OH
b, R = OCH_3
c, R = NH_2

elemental analysis. The infrared spectra of the three complexes in the carbonyl region show the five peaks characteristic of $[Fe(CO)_3SR]_2$ compounds in addition to the respective carboxyl group stretching absorptions. The mass spectra are very similar to that of related dimeric complexes [8]. The respective parent ions lose carbonyl groups stepwise as previously observed. Compounds **11b** and **11c** display peaks at *m/e* 304($M^+ - 7CO$) and 289($M^+ - 7CO$), respectively, consistent with loss of the organic carbonyl group. Other peaks in the spectra correspond to fragments of the organic framework and combinations of iron and sulfur atoms such as $Fe_2S_2^+$ and Fe_2S^+. The ^1H NMR spectra are consistent with the three complexes occurring as single compounds and contain peaks easily related to the constituent organic residues. Other by-products of the reactions were isolated but in such low-yield that their identification was not persued. Complexes of type **11** are the first metal carbonyl derivatives of these important natural products. The facile cleavage of the disulfide linkage is of interest; the reactivity of these novel compounds awaits exploration.

Experimental

Chemical reagents obtained commercially included diiron nonacarbonyl (Pressure Chemical Company), *N,N'*-dithiodimorpholine, D,L-α-lipoic acid and D,L-α-lipoamide, (Aldrich) all of which were used without further purification. The preparation of *N,N'*-dithiobisphthalimide and *N,N'*-thiobisphthalimide followed the procedure described by Kalnins [12]. Further purification and crystallization of these two compounds, as well as the synthesis of *N*-(benzyldithio)phthalimide, *N,N'*-dithiobisbenzimidazole, *N,N'*-dithiobissuccinimide and 1,4-epidithiopiperazine, were performed according to the procedures of Steliou [13]. *N*-(t-butyldithio)phthalimide was prepared by the procedure reported by Ash [14]. The preparation of methyl(±)-α-lipoate followed the general procedure described by Lorette and Brown [15]. Melting points were determined in open capillaries using a Thomas Hoover capillary melting point apparatus and are uncorrected. Thin layer chromatography was performed on pre-coated TLC sheets: SILICA GEL 60 F-254 (Layer thickness 0.2 mm) and Eastman Chromatogram sheets: 13181 SILICA GEL with fluorescent indicator (No. 6060). Column chromatography was carried out using F-100 Florisil 60–100 Mesh (Fisher Scientific Co.), Alumina Activated 80–200 MESH (Anachemica) and SILICA GEL 60 70–230 mesh ASTM. 0.063 - 0.200 mm (BDH Chemicals Ltd.). Infrared spectra were taken on Perkin-Elmer infrared spectrophotometers models 297 and 251 (expanded scale). Spectra were calibrated with polystyrene at 1601 cm^{-1}. The abbreviations used in describing the bands are: w (weak), m (medium), s (strong), vs (very strong), b (broad). Nuclear magnetic resonance (^1H NMR) spectra were obtained on a Varian T-60 instrument for routine work and a Varian XL-200 NMR spectrometer using tetramethylsilane (TMS) as internal standard. Mass spectra were obtained at 70 eV using an LKB 9000 Mass Spectrometer with a direct insertion probe at the Biomedical Mass Spectrometry Unit of McGill University and a Dupont No. 21492B high resolution mass spectrometer located in the Chemistry Department. Elemental analyses were performed by Midwest Microanalytical, Indianapolis, Indiana and Galbraith Laboratories, Inc. Knoxville, Tennessee. All reactions and manipulations were carried out under either nitrogen or argon atmosphere using standard inert atmosphere techniques [16]. Evaporation of the solvents was performed *in vacuo*. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone just before use. Diiron nonacarbonyl was washed just before use with freshly distilled tetrahydrofuran under nitrogen to remove traces of acid remaining from its preparation [17].

Reactions of $Fe_2(CO)_9$ with Sulfur Transfer Reagents

(a) N,N'-Dithiobisphthalimide (1)

$Fe_2(CO)_9$ (14.3 g, 3.92×10^{-2} mol), in a 500 ml round-bottom flask, was washed with 3 × 40 ml aliquots of freshly distilled THF. After removing the washings, the sulfur transfer reagent *N,N'*-dithiobisphthalimide (5.10 g, 1.43×10^{-2} mol) and 250 ml of freshly distilled THF were added. The orange slurry was stirred and became darker in colour within five minutes. The reaction was stirred 20 h at room temperature while its progress was monitored by TLC. Evaporation of the volatiles *in vacuo* gave a dark solid residue. The flask was filled with nitrogen and put into a nitrogen-filled glove bag where the residue was placed in a cellulose soxhlet thimble which was contained in a second larger thimble previously filled with florisil and transferred to a soxhlet extractor. The residue was extracted with boiling pentane (300 ml) under nitrogen for 9 h until the extracts were nearly colorless. The dark-red pentane solution was evaporated to dryness to give $Fe_3(CO)_9S_2$ (**6**) (1.20 g, 23% yield with respect to the sulfur reagent) as red–purple needles which decomposed at 109–112 °C (lit. [4] 114 °C) to a black shiny material; IR (hexane) ν(CO): 2082(w), 2063(vs), 2044(vs), 2023(s), 2007(m), 1988(w) cm^{-1}. These values are consistent with literature data [16a, 1b, 9a] and those of authentic $Fe_3(CO)_9S_2$ prepared according to the procedure of Hieber and Gruber [4]; mass spectrum: *m/e* 484(M^+), 456(M^+ – CO), 428(M^+ – 2CO), 400(M^+ – 3CO), 372(M^+ – 4CO), 344(M^+ – 5CO), 316(M^+ – 6CO), 288(M^+ – 7CO), 260(M^+ – 8CO), 232(M^+ – 9CO), 176($Fe_2S_2^+$), 144(Fe_2S^+), 56(Fe^+), lit. [18].

The residue left in the thimble after the pentane extraction was crushed under $CHCl_3$ in air. The dark red solution was filtered and the filtrate evaporated to give 0.58 g of a brown solid. This was redissolved in a minimum of ethyl acetate and transferred to a chromatography column (25 cm × 2 cm) filled with florisil. Elution of the column with hexane gave a brown band from which orange-red needles crystallized, melting point (m.p.) 166–169 °C. These were shown by TLC to be slightly contaminated with **6**. After evaporation of the solvent *in vacuo* and washing the crystals with pentane to remove **6**, 0.071 g of air-stable, orange crystals were collected. Elution of the column with chloroform gave a band from which more orange product contaminated with **6**, $Fe_3(CO)_{12}$ and $Fe_2(CO)_6S_2$ (**7**) was obtained. This was redissolved in $CHCl_3$ and rechromatographed on florisil in another column of the same dimensions. Careful elution with hexane afforded **7** (1%; m.p. 46–47 °C, lit. [4] 46.5 °C); IR (hexane) ν(CO): 2082(s), 2042(vs), 2005(vs), 1990(w), 1963(w), 1952(w) cm^{-1} and traces of **6** and $Fe_3(CO)_{12}$. The infrared spectrum of **7** agreed with those reported in the literature [4] and that of authentic $Fe_2(CO)_6S_2$ obtained as reported by Hieber and Gruber [4]. Finally, elution with $CHCl_3$ gave the orange compound which was found to be spectroscopically identical to the orange crystals. The powder was recrystallized from CH_2Cl_2/hexane to give **8a** (3%), m.p. 158–166 °C; IR (toluene) ν(CO): 2089(m), 2063(s), 2026(s), 2007(m), 1734(s) cm^{-1}; ^1H NMR ($CDCl_3$): 7.73(b) ppm; mass spectrum: *m/e* 580(M^+ – 2CO), 552(M^+ – 3CO), 524(M^+ – 4CO), 496(M^+ – 5CO), 468(M^+ – 6CO), 344($Fe_2(CO)_6S_2^+$), 316($Fe_2(CO)_5S_2^+$), 288($Fe_2(CO)_4S_2^+$), 260($Fe_2(CO)_3S_2^+$), 232($Fe_2(CO)_2S_2^+$), 204($Fe_2(CO)S_2^+$), 176($Fe_2S_2^+$), 147(phthalimide$^+$), 104($C_6H_4CO^+$), 76($C_6H_4^+$), 64(S_2^+). *Anal.* Calc. for $C_{22}Fe_2H_8N_2O_{10}S_2$: C, 41.5; H, 1.25; N, 4.40; S, 10.0. Found: C, 41.9; H, 1.53; N, 4.75; S, 5.57, 5.61%.

(b) N-(Benzyldithio)phthalimide (9a)

$Fe_2(CO)_9$ (14.1 g, 3.87×10^{-2} mol), *N*-(benzyldithio)phthalimide (4.3 g, 1.43×10^{-2} mol) and THF (190 ml) were stirred for 14 h. The residue was extracted in a soxhlet apparatus with absolute ether. The dark solution obtained was concentrated to a small volume and transferred to a florisil column (30 cm × 3.2 cm). Hexane eluted $Fe_2(CO)_6S_2$, (<1%) and $Fe_3(CO)_9S_2$, (12%). Ethyl acetate eluted 1.5 g (35%) of a sticky red material which was identified [10] as $[Fe(CO_3SCH_2Ph]_2$, IR (hexane) ν(CO): 2070(m), 2038(vs), 2002(s), 1990(s) cm^{-1}, ^1H NMR ($CDCl_3$): 7.26(s), 3.6(s) ppm; mass spectrum: *m/e* 526(M^+), 442(M^+ – 3CO), 414(M^+ – 4CO), 386(M^+ – 5CO), 358(M^+ – 6CO), 267($PhCH_2S_2Fe^+$), 246($PhCH_2SSCH_2Ph^+$), 214($PhCH_2SCH_2Ph^+$), 181($PhCH_2SSCH_2Ph$-HS_2^+), 92($C_7H_8^+$), 91($C_7H_7^+$), 77($C_6H_5^+$), 65($C_5H_5^+$), 51($C_4H_3^+$), 45(H–C=S^+), 39($C_3H_3^+$). Attempts to sublime this material led to decomposition and isolation of colorless crystals, m.p. 65–67 °C which had an infrared spectrum identical to that of benzyldisulfide, m.p. 70–72 °C. Further elution with ethyl acetate gave 0.18 g of another sticky reddish material. This was rechromatographed on florisil. Elution with hexane removed traces of $Fe_3(CO)_9S_2$ and $Fe_2(CO)_6S_2$. Ethyl acetate afforded orange–reddish crystals, (<1%), m.p. 125–130 °C dec., identified as $Fe_2(CO)_6[C_8H_4NO_2S][SCH_2Ph]$, (**8c**). IR (hexane) ν(CO): 2078(m), 2048(vs), 2011 and 2005(s), 1994(w), 1733(w) cm^{-1}; ^1H NMR ($CDCl_3$): 7.8–7.86(b), 7.26(s), 3.18(s) ppm; mass spectrum: *m/e* 553(M^+ – CO) 525(M^+ – 2CO) 497(M^+ – 3CO), 469(M^+ – 4CO), 441(M^+ – 5CO), 413(M^+ – 6CO), 322(M^+ – 6CO – $PhCH_2$), 290(M^+ – 6CO – $PhCH_2$ – Fe), 266(M^+ – 6CO – $PhCH_2$ – Fe), 214($PhCH_2SCH_2Ph^+$), 176($Fe_2S_2^+$), 147($C_8H_5NO_2$), 123(Ph-CH_2S^+), 91($C_7H_7^+$), 76($C_6H_4^+$), 65($C_5H_5^+$). There was insufficient sample for elemental analysis.

(c) N-(t-Butyldithio)phthalimide (9b)

$Fe_2(CO)_9$ (12.9 g, 3.54×10^{-2} mol), THF (250 ml) and *N*-(t-butyldithio)phthalimide (10.98 g, 4.11×10^{-2} mol) were stirred for 24 h. The dark solution was concentrated *in vacuo* to a small volume and transferred to an alumina column (40 cm × 2.5 cm). Hexane eluted two yellow bands A and B. Ethyl acetate afforded a very small amount of $Fe_2(CO)_6S_2$. The malodorous dark oil obtained from band A was rechromatographed on florisil. Hexane afforded 2.6 g of t-butyl disulfide contaminated with some $[Fe(CO)_3(S\text{-}t\text{-}C_4H_9)]_2$ **8d**, as indicated by infrared analysis [11a]. IR (hexane) ν(CO): 2070(s), 2036(vs), 2005 and 1994(s) cm^{-1}. Ethyl acetate eluted a small quantity of red–orange crystals identified as $Fe_2(CO)_6[C_8H_4NO_2S][S\text{-}t\text{-}C_4H_9]$, (**8e**). m.p. 131–140 °C dec.; IR (hexane) ν(CO): 2080(m), 2047(vs), 2039(sh), 2010(vs), 2007(sh), 1993(sh), 1732(m) cm^{-1}; ^{1}H NMR ($CDCl_3$): 7.78(b), 1.3(s) ppm; mass spectrum: m/e 519($M^+ - CO$), 491($M^+ - 2CO$), 463($M^+ - 3CO$), 435($M^+ - 4CO$), 407($M^+ - 5CO$), 379($M^+ - 6CO$), 323($M^+ - 6CO - Fe$), 290($M^+ - 6CO - Fe - SH$), 176($Fe_2S_2^+$), 147-($C_8H_5NO_2^+$), 104($C_6H_4CO^+$), 76($C_6H_4^+$), 57($C_4H_9^+$), 41($C_3H_5^+$), 39 ($C_3H_3^+$), 29(HCO^+), 15(CH_3^+). The small amount of red–orange oil obtained from band B, was tentatively identified [11] as $Fe_4(CO)_{12}(S)(S\text{-}t\text{-}C_4H_9)_2$, (**10**). IR (hexane) ν(CO); 2080(w), 2071(w), 2053(m), 2041(vs), 2036(w), 2005(m), 1997(w), 1991(m) cm^{-1}; mass spectrum: m/e 713($M^+ - t\text{-}C_4H_9$), 685($M^+ - 57 - CO$), 657(M$^+$ $- 57 - 2CO$, 629($M^+ - 57 - 3CO$), 601($M^+ - 57 - 4CO$), 573($M^+ - 57 - 5CO$), 545($M^+ - 57 - 6CO$), 517($M^+ - 57 - 7CO$), 489($M^+ - 57 - 8CO$), 461($M^+ - 57 - 9CO$), 433($M^+ - 57 - 10CO$), 377($M^+ - 57 - 12CO$), 375($Fe_4S_3C_4H_7^+$), 319($Fe_3S_3C_4H_7^+$), 57-($C_4H_9^+$).

Reaction of $Fe_2(CO)_9$ with D,L-α-lipoic Acid Derivatives

(d) D,L-α-Lipoic Acid

D,L-α-lipoic acid (1.02 g, 4.95 × 10^{-3} mol), $Fe_2(CO)_9$ (1.6 g, 4.39 × 10^{-3} mol) and 120 ml of freshly distilled tetrahydrofuran (THF) were stirred for 17 h. The volatiles were removed to give a dark red, oily mass. This was dissolved in a small volume of acetone and transferred to a silica-gel column (40 cm × 2.5 cm). Elution with CH_2Cl_2–1% acetone (99:1) produced a red band which, after evaporation of the solvent, gave 0.9g (88% yield based on D,L-α-lipoic acid) of a dark red oil identified as μ(S), μ'(S)-hexacarbonyldiiron(±)lipoic acid, (**11a**); IR (hexane) ν(CO): 2070(s), 2030(vs), 2001(s), 1986(s), 1978(w), 1708(m) cm^{-1}; ^{1}H NMR ($CDCl_3$): 3.58(t,1), 2.68–2.22(m,4), 2.2–1.32(m,6), 1.26(s,2), >9.16(b,1) ppm; mass spectrum: m/e 486(M^+), 430($M^+ - 2CO$), 402($M^+ - 3CO$), 374($M^+ - 4CO$), 346($M^+ - 5CO$), 318($M^+ - 6CO$), 206($C_8H_{14}O_2S_2^+$), 174($C_8H_{14}O_2S^+$), 123($C_7H_7S^+$), 97($C_8H_{14}O_2S_2 - COOH - 2S^+$), 81($C_8H_{14}O_2S_2 - CH_3COOH - 2S - H^+$). *Anal.* Calc. for $C_{14}Fe_2H_{14}O_8S_2$: C, 34.5; H, 2.88, S, 13.2. Found: C, 33.6; H, 3.61; S, 13.4%.

(e) Methyl(±)-α-lipoate

Methyl(±)-α-lipoate (1.75 g, 7.95 × 10^{-3} mol) in toluene (5 ml), $Fe_2(CO)_9$ (5.0 g, 1.37 × 10^{-2} mol) and THF (100 ml), were stirred under nitrogen for 21 h. The volatiles were removed under vacuo to give a dark red slurry which in toluene (5–10 ml) was transferred to a column (40 cm × 2.5 cm) of activated alumina. Elution with toluene/n-heptane (1:1) provided a yellow band. Removal of the solvent gave 1.5 g (86% yield) of a red oil identified as μ(S), μ'(S)-hexacarbonyldiiron(±)methyl lipoate (**11b**); IR (hexane) ν(CO): 2074(s), 2034(vs), 2005(vs), 1990(vs), 1982(m), 1753(m) cm^{-1}; mass spectrum: m/e 500(M^+), 472($M^+ - CO$), 444($M^+ - 2CO$), 416($M^+ - 3CO$), 388($M^+ - 4CO$), 360($M^+ - 5CO$), 332($M^+ - 6CO$), 304($M^+ - 7CO$), 176($Fe_2S_2^+$), 144(Fe_2S^+), 112(Fe_2^+), 87($CH_2{=}CH{-}C(OH^+)$-OMe). *Anal.* Calc. for $C_{15}H_{16}Fe_2O_8S_2$: C, 36.0; H, 3.20; S, 12.8. Found: C, 36.3; H, 3.53; S, 12.2%. ^{1}H NMR ($CDCl_3$): 3.68(s,3), 2.68–2.48(m,1), 2.46–2.22(t,2), 2.20–1.76(m,4), 1.74–1.14(m,6) ppm.

A second band (purple) was eluted with ethyl acetate to give a solution which after evaporation of the volatiles gave a dark oily residue contaminated with the major product **11b**. The residue was repeatedly chromatographed six times on alumina (25 cm × 2 cm). Elution with toluene removed traces of **11b**. Elution with ethyl acetate or methanol gave the purple band containing 0.15 g of a deep red oil; IR (hexane) ν(CO): 2070(s), 2036(vs), 2013(m), 1996(m), 1977(s), 1752(m) cm^{-1}; mass spectrum: m/e 500($Fe_2(CO)_6 \cdot C_9H_{16}O_2S_2^+$), 469($Fe_2(CO)_6 \cdot C_8H_{13}OS_2^+$), 444($Fe_2(CO)_4 \cdot C_9H_{16}O_2S_2^+$), 416($Fe_2(CO)_3 \cdot C_9H_{16}O_2S_2^+$), 388($Fe_2(CO)_2 \cdot C_9H_{16}O_2S_2^+$), 360($Fe_2(CO) \cdot C_9H_{16}O_2S_2^+$), 332($Fe_2C_9H_{16}O_2S_2^+$), 304($Fe_2C_8H_{16}OS_2^+$), 176($Fe_2S_2^+$), 144($Fe_2S^+$), 112-($Fe_2^+$), 87($C_4H_7O_2^+$). ^{1}H NMR ($CDCl_3$): 3.66(s,3), 3.23–3.02(t,2), 2.68–1.23(b,10); *Anal.* Found: C, 41.6; 37.4; H, 5.54, 4.70; S, 18.6, 17.1, 16.9%.

(f) D,L-α-lipoamide

D,L-α-lipoamide (3.05 g, 1.48 × 10^{-2} mol), $Fe_2(CO)_9$ (10.6 g, 2.91 × 10^{-2} mol) 200 ml of THF were stirred for 15 h. The volatiles were removed *in vacuo* and the resultant dark oil was extracted with ethyl acetate (50 ml). This dark red solution was filtered, leaving behind an insoluble dark material which was discarded. The filtrate was concentrated to 4 ml and transferred to a florisil column (40 cm × 2.5 cm). Elution with ethyl acetate gave an oragne band which was collected. The solvent was removed to give 3.8 g (80% yield) of a pure red-orange oil identified as μ(S), μ'(S)-hexacarbonyldiiron(±)-lipoamide (**11c**); IR (hexane) ν(CO): 2072(s), 2032(vs), 2003(s), 1990(s), 1980(w), 1751(w) cm^{-1}; mass spectrum: m/e 429($M^+ - 2CO$), 401($M^+ - 3CO$), 373($M^+ - 4CO$), 345($M^+ - 5CO$), 317($M^+ - 6CO$), 289($M^+ - 7CO$), 176($Fe_2S_2^+$), 59($CH_2{=}C(OH)NH_2^+$). ^{1}H NMR ($CDCl_3$): 5.48(b,2), 2.68–2.46(m,1), 2.38–1.80(m,6), 1.76–1.34(m,6). *Anal.* Calc. for $C_{14}Fe_2H_{15}NO_7S_2$: C, 34.6; H, 3.09; S, 13.2. Found: C, 34.2; H, 3.25; S, 12.9%.

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