Synthesis and Reactions of a Metallathiacyclopentanone

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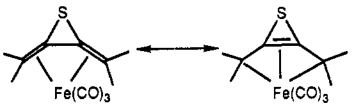
Summary: The reaction of diisopropylidenethiirane with $Fe_2(CO)_9$ results in the formation of a novel metallathiacyclopentanone 4 in high yield. Unexpectedly, 4 is converted into (tetramethylbutadienedithiolato)iron complex 7 by a thermal reaction. Both structures were determined by single crystal X-ray diffraction analysis.

We have previously shown that compounds of the type (η^4-thioallyl)$Fe(CO)_3$ can readily be prepared by treating allene episulfides with $Fe_2(CO)_9$.[1] Therefore it was expected to get the thiirene complex 1 or the alkylidene homologue of (β-thioallyl)$Fe(CO)_3$ 2 in a similar reaction of diisopropylidenethiirane with $Fe_2(CO)_9$. Nevertheless, the only isolated product was the metallathiacyclopentanone dimer 4, which can be regarded as the carbonyl insertion product of a metallathietane intermediate. We report herein the synthesis and reactions of this novel metallathiacyclopentanone dimer 4.

A solution of diisopropylidenethiirane (3)[2] and $Fe_2(CO)_9$ in 15 mL of benzene was heated to 60–70 °C for 10 min. After removal of solvent and purification of the residue by the preparative GPC, the metallathiacyclopentanone 4 was obtained in crystalline form in 77% isolated yield (eq 1). The ^{13}C NMR spectrum of 4 exhibits two terminal carbonyl peaks (202.3 and 204.1 ppm) and one characteristic carbonyl resonance at 249.9 ppm.[3] Recrystallization from benzene afforded crystals suitable for X-ray analysis; crystallographic data of the diffraction studies are listed in Table 1. As can be seen from the ORTEP drawing (Figure 1), compound 4 is a dimer of two ferrothiacyclopentanone subunits in a half-chair conformation, bridged over the heteroatoms. The bond distances and angles of these metallathiacyclopentanone skeletons resemble those of corresponding metallaselenacyclopentanone and metallathiacyclopentanone derivatives.[1b,4] A conceivable mechanism for the formation of 4 is depicted in Scheme 1. Initial nucleophilic attack of the thiirane sulfur atom on the iron atom produces a thioallyl cation complex 5, which collapses to metallathietane 6. Suc-



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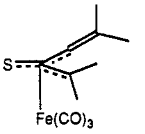

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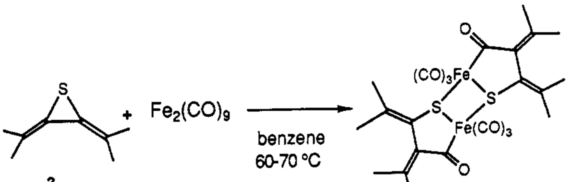

(1)

3

4

Table 1. Crystallographic Data for Diffraction Studies

compd	4	7
empirical formula	$C_{24}H_{24}O_8S_2Fe_2$	$C_{14}H_{12}O_6S_2Fe_2$
fw	616.28	452.07
cryst syst	monoclinic	monoclinic
lattice params		
a, Å	16.053(1)	12.616(2)
b, Å	9.864(1)	15.616(1)
c, Å	18.058(2)	19.207(2)
β, deg	109.10(1)	100.83(1)
V, Å^3	2702.0	3716.6
space group	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)
Z value	4	8
D_{calc}, g/cm^3	1.51	1.62
F_{000}	1264	1824
μ(Mo Kα), cm^{-1}	12.6	18.0
temp, °C	23	23
$2\theta_{max}$, deg	50	50
no. of observns ($I > 3\sigma(I)$)	1517	2686
no. of variables	163	433
residuals: R, R_w	0.043, 0.059	0.049, 0.059
goodness of fit indicator	1.96	4.22
max shift in final cycle	0.59	0.44
largest peak in final diff map, e/Å^3	0.26	0.51

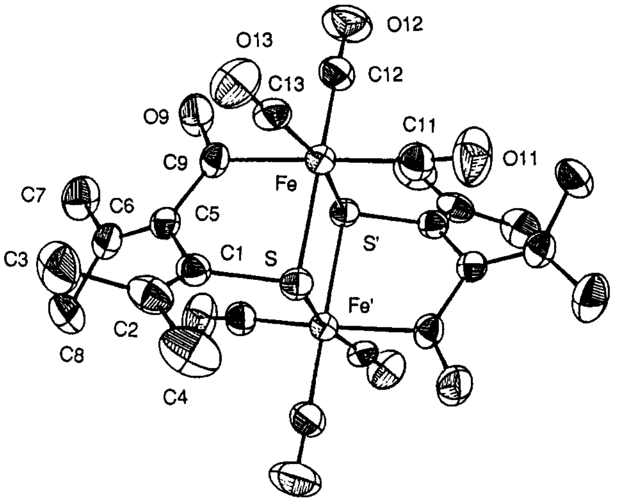

Figure 1. ORTEP drawing of 4. Selected bond lengths (Å) and angles (deg) are as follows: Fe–S 2.300(2), S–C(1) 1.785(7), C(1)–C(5) 1.486(9), C(5)–C(9) 1.51(1), C(9)–O(9) 1.205(9), C(1)–C(2) 1.36(1), C(5)–C(6) 1.356(8), C(9)–Fe 2.050(6), Fe–C(11) 1.863(6), Fe–C(12) 1.805(8), Fe–C(13) 1.802(8), C–O(av) 1.13; S–Fe–C(9) 86.1(2), Fe–S–C(1) 94.7(2), S–C(1)–C(5) 112.5(5), S–C(1)–C(2) 119.8(5), C(1)–C(9)–O(9) 121.0(5), C(5)–C(9)–Fe 115.0(4).

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[2] Ando, W.; Hanyu, Y.; Kumamoto, Y.; Takata, T. *Tetrahedron* **1986**, *42*, 1989.

[3] The carbonyl resonance of 4 is comparable to chemical shifts of bridging ligands $[Fe(\mu\text{-}CO)(CO)Cp]_2$ (293.2 ppm),[3a] $Fe_2(CNEt)_9$ (255.7 ppm),[3b] and $Fe(CO)_3(PPh_3)S(C{=}CPh_2)C(H)^tBuCO$ (252.1 ppm).[1b] (a) Gansow, O. A.; Burke, A. R.; Vernon, W. D. *J. Am. Chem. Soc.* **1976**, *98*, 5817. (b) Bassett, J.-M.; Baker, G. K.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Wolsey, W. C. *J. Chem. Soc., Dalton Trans.* **1981**, 219.

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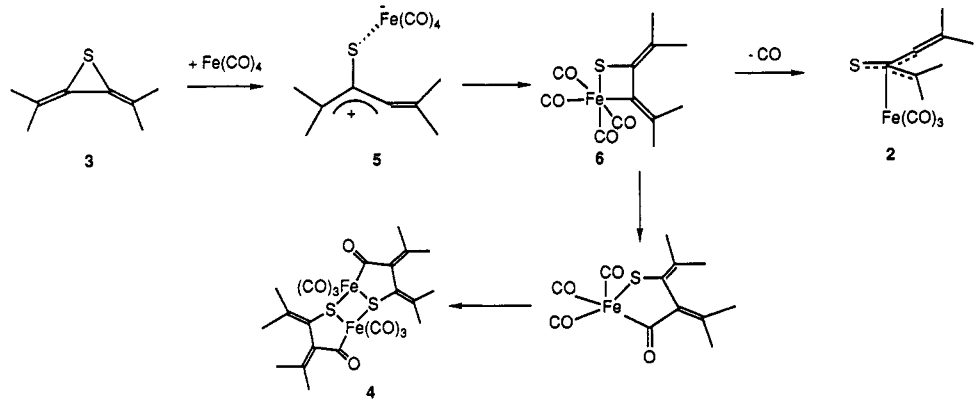
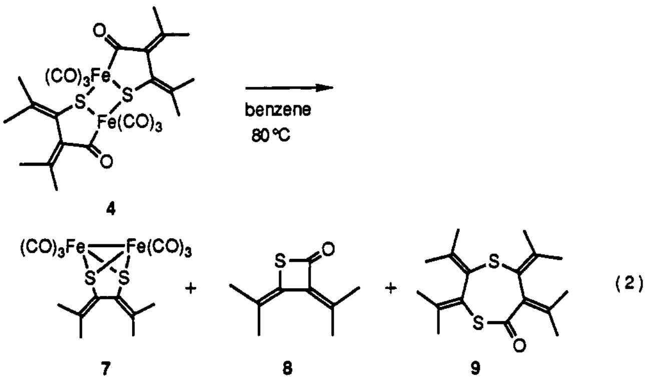
Scheme 1



cessive CO insertion then leads to a metallathiacyclopentanone which dimerizes to 4, while loss of a CO ligand would have resulted in formation of the (thioallyl)iron complex 2.

The thermolysis of 4 was carried out by refluxing it in benzene solution. Chromatographic purification afforded (tetramethylbutadienedithiolato)iron complex 7, 3,4-bis(isopropylidene)thietan-2-one (8), and 3,4,6,7-tetrakis(isopropylidene)-2,5-dithiacycloheptanone (9) in 20%, 15%, and 10% respective isolated yields (eq 2). The structure of 7 was unequivocally determined by single crystal X-ray diffraction. An ORTEP drawing, selected structural parameters, and crystallographic data for diffraction studies are shown in Figure 2 and Table 1. The bond lengths as well as angles of the bridging (μ-dithiolato)iron moiety are similar to those of other structurally related (μ-dithiolato)iron complexes.[1,5,6] The structural assignment of 8 and 9 was made by comparison of the ^{1}H and ^{13}C NMR as well as IR spectroscopic data with those of structurally related compounds.[7] A plausible mechanism for the thermolysis of 4 is illustrated in Scheme 2. Elimination of CO followed by extrusion of butatriene would give complex 7; on the other hand reductive elimination of iron would lead to the formation of 8 and 9.



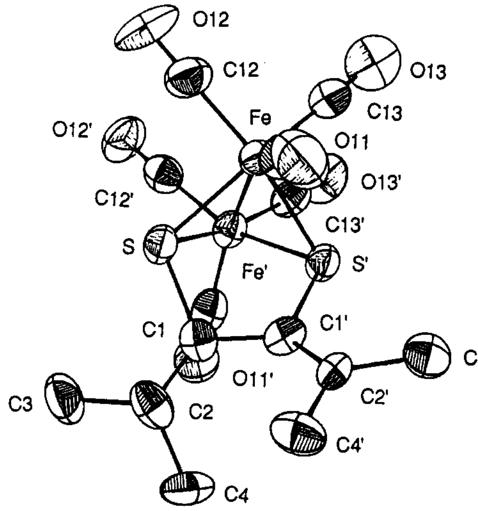


Figure 2. ORTEP drawing of 7. Selected bond lengths (Å) and angles (deg) are as follows: Fe-S 2.263(4), Fe-S' 2.267(4), Fe-Fe' 2.498(3), S-C(1) 1.80(1), C(1)-C(2) 1.36(2), C(1)-C(1') 1.48(2), Fe-C(av) 1.82, C-O(av) 1.12; Fe-S-Fe' 66.9(1), S-Fe-S' 80.5(1), Fe-S-C(1) 67.3(1), S-C(1)-C(2) 119.7(9), S-C(1)-C(1') 110.4(7).

Further investigation to elucidate the mechanisms of these reactions are in progress.

Experimental Section

General Data. All solvents and reagents were purified by standard procedures. Bis(isopropylidene)thiirane (3) was prepared according to ref 3. All reactions were performed under an argon atmosphere. Gel permeation chromatography (preparative GPC) was performed on a series of JAIGEL 1H and 2H columns with a flow of chloroform on an LC-08 liquid chromatograph of Japan Analytical Industry Co. Ltd. Infrared spectra were recorded on a JASCO FT/IR-5000 spectrometer. NMR spectra were run on a Bruker AC400 operating at 400 MHz. Elemental analyses were carried out by the Chemical Analytical Center of the University of Tsukuba. Mass spectra and high resolution mass spectra were obtained on a JEOL JMS SX102A mass spectrometer by EI at 70 eV. All melting points are uncorrected.

Reaction of Bis(isopropylidene)thiirane (3) with $Fe_2(CO)_9$. A solution of bis(isopropylidene)thiirane (3) (140 mg, 1.0 mmol) and $Fe_2(CO)_9$ (364 mg, 1.0 mmol) in 15 mL of benzene was heated to 60-70 °C for 10 min. The reaction mixture was filtered through Celite, and the solvent was removed under reduced pressure. Purification of the red residue by preparative GPC (eluent: $CHCl_3$) gave metallathiacyclopentanone 4 (236 mg, 0.38 mmol, 77%).

For 4: orange crystals, mp 108-109 °C dec; ^{1}H NMR (C_6D_6, 400 MHz) δ 1.35 (s, 6H), 1.53 (s 6 H), 1.41 (s, 6H), 2.03 (s, 6H);

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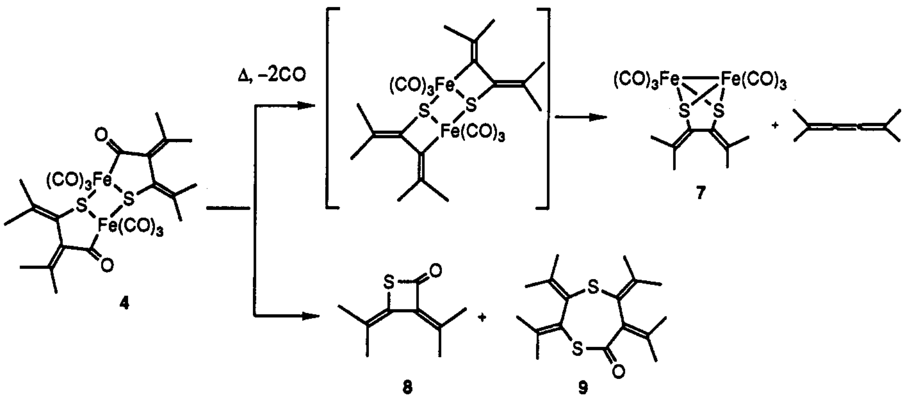
[7] (a) Gotthardt, H. *Tetrahedron Lett.* **1973**, *15*, 1221. (b) Krabsack, A. J.; Higa, T.; Slack, W. E. *J. Am. Chem. Soc.* **1970**, *92*, 5258. (c) Kooi, J.; Wynberg, H.; Kellogg, R. M. *Tetrahedron* **1973**, *29*, 2135.

Scheme 2



^{13}C NMR (C_6D_6, 100 MHz) δ 22.7 (q), 23.2 (q), 23.8 (q), 27.9 (q), 132.0 (s), 139.9 (s), 140.2 (s), 145.9 (s), 202.3 (s), 204.1 (s), 249.9 (s); IR (KBr) ν 2064 (s), 2010 (s), 1970 (m, sh), 1647 (s) cm^{-1}; MS *m/z* 436 (M^+ - $Fe(CO)_4$, 14.5%), 108 (100). Anal. Calcd for $C_{24}H_{24}O_8S_2Fe_2$: C, 46.81; H, 3.93. Found: C, 46.73; H, 3.89.

Thermolysis of 4. A solution of 4 (84 mg, 0.136 mmol) in 10 mL of benzene was heated to reflux. The course of the reaction was monitored by TLC, after 2.5 h 4 was completely consumed. Preparative TLC afforded (tetramethylbutadienedithiolato)iron complex 7 (16.0 mg, 0.027 mmol), 3,4-bis(isopropylidene)thietan-2-one (8) (4.5 mg, 0.027 mmol), and 3,4,6,7-tetrakis(isopropylidene)-2,5-dithiacycloheptanone (9) (5.2 mg, 0.017 mmol) in 20, 15, and 10% yields, respectively.

For 7: orange crystals, mp 114–115 °C dec; ^{1}H NMR (C_6D_6, 400 MHz) δ 1.29 (s, 6H), 1.84 (s, 6H); ^{13}C NMR (C_6D_6, 100 MHz) δ 23.4 (q), 25.2 (q), 117.2 (s), 135.9 (s), 210.2 (s); IR (NaCl) ν 2074 (s), 2034 (s), 1995 (s, br) cm^{-1}; MS *m/z* 452 (M^+, 6%), 284 (100). Anal. Calcd for $C_{14}H_{12}O_6S_2Fe_2$: C, 37.17; H, 2.65. Found: C, 36.99; H, 2.59.

For 8: pale yellow solid; ^{1}H NMR (C_6D_6, 400 MHz) δ 1.33 (s, 3H), 1.50 (s, 3H), 1.53 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (C_6D_6, 100 MHz) δ 21.7 (q), 22.7 (q), 23.4 (q), 24.9 (q), 122.3 (s), 123.7 (s), 137.3 (s), 143.2 (s) 182.0 (s); IR (KBr) ν 1756 (s) (CO) cm^{-1}; MS *m/z* 168 (M^+, 88.8%), 125 (53.0), 108 (24.1), 107 (54.5), 28 (100); HRMS calcd for $C_9H_{12}OS$ *m/z* 168.0609, found *m/z* 168.0645.

For 9: pale yellow solid; ^{1}H NMR (C_6D_6, 400 MHz) δ 1.59 (s, 3H), 1.60 (s, 3H), 1.62 (s, 3H), 1.67 (s, 3H), 1.69 (s 3H), 1.79 (s, 3 H), 1.81 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (C_6D_6, 100 MHz) δ 21.1 (q), 21.6 (q × 2), 21.75 (q), 21.84 (q), 21.9 (q), 22.1 (q), 22.2 (q), 123.2 (s), 126.0 (s), 126.4 (s), 129.0 (s), 132.8 (s), 137.5 (s), 141.5 (s), 145.8 (s), 193.5 (s); IR (KBr) ν 1651 (s) (CO) cm^{-1}; MS *m/z* 308 (M^+, 100%), 280 (20.7), 265 (20.6), 140 (16.9), 125 (33.1), 108 (64.0), 107 (91.1), 28 (81.7); HRMS calcd for $C_{17}H_{24}OS_2$ *m/z* 308.1269, found *m/z* 308.1290.

Crystallographic Analysis. Orange crystals of dimensions 0.2 × 0.2 × 0.4 mm for 4 and 0.2 × 0.2 × 0.3 mm for 7, obtained from slow evaporation of a benzene solution at 25 °C, were used for X-ray analyses. Diffraction measurements were made on an Enraf-Nonius CAD4 computer controlled Kappa axis diffractometer by using graphite-monochromatized Mo Kα. Unit cell was determined and refined from 25 randomly selected reflections obtained by using the CAD4 automatic search, center, index, and least-squares routines. Crystal data and data collection parameters and results of the analyses are listed in Table 1. All data processing was performed on a Micro VAX 3100 computer by using the MolEN structure solving program obtained from Enraf Nonius Corp., Delft, Netherlands. The ω–2θ scan technique was adopted by varying the ω scan width as function of θ [ω scan width = $(0.7 + 0.350 \tan \theta)°$]. All intensities were corrected for Lorentz and polarization corrections as well as decay corrections (–0.3% for 4, and –3.6% for 7). An empirical absorption correction based on a series of ψ scans was also applied to the data. Neutral atom scattering factors were calculation by the standard procedures.[8a] An anomalous dispersion correction was applied to all non-hydrogen atoms.[8b] Full-matrix least-squares refinements minimized the function $\Sigma\omega(|F_o| - |F_c|)^2$, $w = 1$.

Compound 4 crystallized in the monoclinic crystal system. The systematic absences observed during the collection of data (hkl, $h + k = 2n$; $h0l$, $hl = 2n$) are consistent with either the centrosymmetric space group $C2/c$ or the noncentrosymmetric space group Cc. The successful solution and refinement of the structure confirmed the crystal belonged to the centrosymmetric space group $C2/c$. The coordination of metal atoms was obtained by direct methods (MULTAN), and the remaining non-hydrogen atoms were subsequently obtained from difference electron density syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Compound 7 crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified uniquely on the basis of the systematic absences observed during the collection of data ($h0l$, $h + l = 2n$; $0k0$, $k = 2n$). The structure was solved by a combination of direct methods (MULTAN) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters.

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Supplementary Material Available: Textual presentation of experimental procedures, tables of crystallographic data, positional and thermal parameters, root-mean-square amplitudes of thermal vibration, and interatomic distances and angles, and ORTEP diagrams for 4 and 7 (42 pages). Ordering information is given on any current masthead page.

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[8] (a) *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99–101. (b) *International Tables for X-Ray Crystallography*; The Kynoch Press; Birmingham, England, 1975; Vol. IV, Table 2.3.1, pp 149–150.