(1.0 g, 1.5 mmol) and redistilled deoxygenated ethyl chloroformate (5 mL, 0.051 mol) in a manner identical with that described for **1** above to give 425 mg (38%) (an analytical sample was prepared by two recrystallizations from chloroform-petroleum ether): mass spectrum (relative intensities) 744 (M^+, 12), 700 (1), 680 (1), 671 (100); λ_{max} (CH_2Cl_2) 408, 527; ^1H NMR ($CDCl_3$, 100 MHz) δ -0.83 (t, 3 H, CH_3CH_2O), 1.40 (q, 2 H, CH_3CH_2O), 7.5-7.7 and 7.9-8.15 (m, 20 H, phenyl), 8.80 (s, 8 H, β-pyrrole). Anal. Calcd for $C_{47}H_{33}N_4O_2Co$: C, 75.80; H, 4.47; N, 7.52. Found: C, 75.61; H, 4.51; N, 7.44.

(*N*-(Ethoxycarbonyl)-5,10,15,20-tetraphenylporphinato)cobalt(II) (5). (Ethoxycarbonyl)(5,10,15,20-tetraphenylporphinato)cobalt(III) (**4**) (12.7 mg) was oxidized at 1.08 V and worked up as described above for the preparation of **2** from **1** to give 8.2 mg (~65%) of **5**: mass spectrum 744 (M^+, 5), 700 (1), 671 (100).

***N*-(Ethoxycarbonyl)-5,10,15,20-tetraphenylporphyrin (6).** Ethoxycarbonyl(5,10,15,20-tetraphenylporphinato)cobalt(III) (**4**) (39.6 mg, 0.053 mmol) in CH_2Cl_2 (10 mL containing 0.05 M *n*-Bu_4NPF_6) was electrolyzed at 1.08 V until 1.1 e/mol had been consumed. Trifluoroacetic acid was added to the solution to remove the cobalt. Supporting electrolyte was removed as described above for the preparation of **2**. The product was purified by chromatography in neutral alumina (grade II) and crystallized from CH_2Cl_2-MeOH to give **6** (27 mg, 80%) (an analytical sample was recrystallized from CH_2Cl_2-MeOH): mass spectrum 686 (M^+, 100) 642 (7), 614 (32); λ_{max} (CH_2Cl_2) 437, 493 (sh), 524, 566, 646, 714; ^1H NMR ($CDCl_3$) δ -1.22 (t, 3 H, ester CH_3), 0.88 (q, 2 H, ester CH_2), 7.44 and 8.1-8.34 (m, 20 H, phenyl), 8.02 (s, 2 H, β-pyrrole), 8.44 (s, 2 H, β-pyrrole), 8.47 (s, 2 H, β-pyrrole), 8.67 (s, 2 H, β-pyrrole). Anal. Calcd for $C_{47}H_{34}N_4O_2$: C, 82.19; H, 4.99; N, 8.16. Found: C, 81.47; H, 4.61; N, 8.34.

Ethyl-*d*$_5$-(5,10,15,20-tetraphenyl-*d*$_8$-porphinato)cobalt(III) (7). (5,10,15,20-Tetraphenyl-d_8-porphinato)cobalt(II) (prepared from 5,10,15,20-tetraphenyl-d_8-porphyrin[27]) (200 mg, 0.3 mmol) was reacted with ethyl-d_5 bromide (3 g, 37 mmol; Merck Sharp and Dohme of Canada Ltd., Isotopes Division) as described above for the preparation of **1** to give 110 mg (53%) of **7**: mass spectrum 713 (M^+, 8), 679 (100). During this reaction the deuterium content of the ethyl group (>95%) and that of the porphyrin (>92% at *o*-phenyls) were maintained.

(*N*-Ethyl-*d*$_5$-5,10,15,20-tetraphenyl-*d*$_8$-porphinato)cobalt(II) (8). Ethyl-d_5-(5,10,15,20-tetraphenyl-d_8-porphinato)cobalt(III) (**7**) (50 mg) was oxidized at 1.08 V as described in the preparation of **2** to give the product **8** (32 mg, 64%): mass spectrum 713 (M^+, 3), 679 (100).

Conversion of 8 to 7 by Reduction with Sodium Borohydride. (*N*-Ethyl-d_5-5,10,15,20-tetraphenyl-d_8-porphinato)cobalt(II) (**8**; 10 mg) in tetrahydrofuran (35 mL) was treated at room temperature with sodium borohydride (10 mg) under argon. The mixture was stirred for 0.5 h then and taken down to dryness at room temperature. The product was extracted into methylene dichloride and purified as described above for the preparation of **1** to give 6.8 mg (~65%) of a product identical with **7**: mass spectrum 713 (3), 708 (3), 705 (2), 700 (3), 671 (100).

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Registry No. **1**, 61730-43-6; **2**, 78638-41-2; **3**, 73568-09-9; **4**, 78638-40-1; **5**, 78638-42-3; **6**, 78656-78-7; **7**, 78638-43-4; **8**, 78638-44-5; $Co^{II}TPP$, 14172-90-8; $Co^{II}TPP$-d_8, 78638-45-6.

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Contribution from le Laboratoire de Chimie des Organométalliques, ERA du CNRS No. 477, et le Laboratoire de Chimie du Solide et Inorganique Moléculaire associé au CNRS No. 254, Université de Rennes, Campus de Beaulieu, 35042 Rennes Cedex, France

A New Bridging Ligand in Dinuclear Iron Carbonyl Species. Synthesis, Properties, and X-ray Structure Determination of Xanthate-$Fe_2(CO)_6$ Complexes

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The complexes μ-(alkoxymethanethione-*C,S*)-μ-(alkylthio)-1,1,1,2,2,2-hexacarbonyldiiron are obtained in good yield by reaction of *O*-alkyl *S*-alkyl dithiocarbonates (or xanthates) with diiron nonacarbonyl. These compounds were characterized by microanalysis and IR, ^1H and ^{13}C NMR, and mass spectroscopies. The structure of the complex obtained from *O*-(adamantylmethyl) *S*-methyl dithiocarbonate has been determined by single-crystal X-ray diffraction. The crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ and $a = 7.765$ (3) Å, $b = 11.025$ (2) Å, $c = 14.155$ (2) Å, $\alpha = 106.24$ (4)°, $\beta = 104.56$ (4)°, and $\gamma = 90.37$ (2)°. A full-matrix least-squares method refined the structure to $R = 0.033$ from 2715 nonzero independent reflections. The structure shows that fragmentation of the ligand has occurred and that one iron atom has inserted into the carbon-sulfur single bond, giving rise to two orthogonal bridges made from the thiocarbonyl function and by the *S*-alkyl group. This unexpected behavior of the xanthate ligand provides a convenient route to dissymmetrically bridged diiron hexacarbonyl species where the carbon of the bridge presents a carbenic character in agreement with the ^{13}C and X-ray data. Displacement of one or two carbonyls or removal of the *O*-alkyl group by a phosphorus ligand is also described, and the mass spectra of the complexes are discussed.

Introduction

In the course of our investigations concerning the design of organometallic combinations which can be used as templates[1] either in a chemical or photochemical manner, we have studied the behavior of new ligands toward metal carbonyls. Electron-rich sulfur-containing functional groups have been chosen for their well-known propensity to coordinate with transition metals, and we have already described complexation of trithiocarbonates[2] by $Fe_2(CO)_9$ and desulfurization of xanthates

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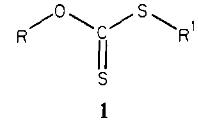
and dithioesters by $Co_2(CO)_8$ which afford a new and efficient route to synthetize a variety of tricobalt nonacarbonyl clusters.[3,4] In this article we describe the complexation of *O*-alkyl *S*-alkyl dithiocarbonates **1** (also called *S*-alkyl xanthates) by



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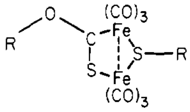

2

$Fe_2(CO)_9$. The xanthates are fragmented and lead to a new type of doubly bridged diiron hexacarbonyl complexes (**2**).

Experimental Section

Synthesis. General Methods. Infrared spectral determinations were made with a Unicam SP 1100 spectrophotometer. ^1H NMR spectra were recorded with a Varian EM 360 and ^{13}C NMR with a Bruker WP 80, with Me_4Si as an internal standard and $CDCl_3$ as solvent unless otherwise noted. Mass spectra were recorded with a Varian MAT 311 double-focusing spectrometer. Microanalyses were determined by CNRS, Lyon, and satisfactory analytical data (±0.4% for C, H, S, P, Fe) were reported for all new compounds. TLC was carried out on Merck Kieselgel plates (1 mm) with use of mixtures of solvents described in ratio of volume and petroleum ether refers to the fraction with bp 40–60 °C. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Me, Bz, *i*-Pr refer respectively to methyl, benzyl, and isopropyl.

Synthesis of Xanthates 1 (ROC(S)SR^1). Compounds **1** are obtained in almost quantitative yield according to Barton.[5] The alcohols are commercially available except for 3α-cholestanol which was prepared.[6] R = cholestanol (**1a**, R^1 = Me, mp 87 °C; **1b**, R^1 = Bz, mp 96 °C); R = 3α-cholestanol (**1c**, R^1 = Me, mp 133 °C; **1d**, R^1 = Bz, mp 72 °C); R = cholesterol (**1e**, R^1 = Me, mp 127 °C; **1f**, R^1 = Bz, mp 142 °C); R = ergosterol (**1g**, R^1 = Me, mp 143 °C; **1h**, R^1 = Bz, mp 110 °C; **1i**, R^1 = *i*-Pr, mp 112 °C); R = (−)-menthol (**1j**, R^1 = Me (oil); **1k**, R^1 = Bz, mp 52 °C); R = 2-indanol (**1l**, R^1 = Me, mp 62 °C); R = 1-adamantanemethanol (**1m**, R^1 = CH_3, mp 89 °C).

Synthesis of Complexes 2. To a solution of xanthate **1** (0.1 mol) in 30 mL of dry toluene warmed at 60 °C was introduced by portions freshly prepared $Fe_2(CO)_9$ (0.3 mol) over a period of 10 min. After another 5 min (TLC control showing complete disparition of the starting material), the solvent was removed under vacuum and the residue, dissolved in ether, was spread on silica plates eluted with petroleum ether (9/1). The crude products were crystallized from acetone (steroids) or pentane. Comparable results can also be obtained by allowing the same quantities of xanthate and $Fe_2(CO)_9$ to react in acetone (30 mL) for 24 h at room temperature under N_2 and in the dark. The yield of pure material varies from 62 to 84%.

2a: mp 110 °C; δ 5.06 (H^3), 2.37 (SMe). **2b**: mp 69 °C; δ 5.09 (H^3), 3.91 (SCH_2). **2c**: mp 99 °C, δ 5.42 (H^3), 2.49 (SMe). **2d**: mp 68 °C, δ 5.31 (H^3), 3.83 (SCH_2). **2e**: mp 126 °C; δ 5.40 (H^6), 4.93 (H^3), 2.42 (SMe). **2f**: mp 71 °C; δ 5.23 (H^6), 4.74 (H^3), 3.25 (SCH_2). **2g**: mp 68 °C; δ 5.30–5.04 (H^3, H^5, H^6, H^{22}, H^{23}), 2.37 (SMe). **2h**: mp 65 °C; δ 3.80 (SCH_2). **2k**: oil, δ 4.85 (H^2), 3.74 (SCH_2). **2l**: mp 126 °C, δ 5.78 (H^2), 2.44 (SMe). **2m**: mp 105 °C, δ 3.99 (CH_2), 2.47 (SMe).

Synthesis of Complexes 4–6. To 1 mmol of **2** in 30 mL of dry acetone was added 1 mmole of $P(OMe)_3$. After 10 h of stirring at 25 °C under N_2 in a dark room, the solvent was removed and the crude material purified by chromatography on silica plates (hexane–ether 1/1). The less polar compounds were identified as monophosphites **4** (60–70%) and crystallized from acetone at −20 °C. The more polar fractions were found to be compounds **5**. When an excess of phosphite (0.3 g) was added to 1 mmol of complex **2** dissolved into 20 mL of refluxing acetone (or toluene), the monophosphites **4** were obtained quantitatively after 20 min, and when relflux was maintained for 8–10 h, bis(phosphites) **6** were formed and purified as described above (elution with pure ether and crystallization from acetone).

Table I. Relevant Crystallographic Data

compd	$C_{19}H_{20}Fe_2O_7S_2$
fw	535.93
a	7.765 (2) Å
b	11.025 (3) Å
c	14.155 (3) Å
α	106.24 (4)°
β	104.56 (4)°
γ	90.37 (2)°
V	1122.3 Å^3
Z	2
density calcd	1.59 g cm^{-3}
abs coeff	15.416 cm^{-1}
space group	$P\bar{1}$
cryst dimens	(0.18 × 0.22 × 0.25) mm
temp	20 °C
radiation, monochromator	λ(Mo Kα) = 0.710 73 Å, graphite
scan angle	(1.10 + 0.35 tan θ)°
max scan time	60 s
receiving aperture	(2.3 + 0.40 tan θ) mm
crystal–counter dist	173 mm
no. of refined variables	272
unique data used	2715
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.033
$R = \lvert\Sigma w\lvert\Delta F\rvert^2/\Sigma wF_o{}^2\rvert^{1/2}$	0.035

4a: mp 123 °C; δ 5.10 (H^3), 2.59 (SMe), 4.00 ($P(OMe)_3$, *J* = 11.4 Hz). **4b**: mp 105 °C; δ 5.02 (H^3), 3.77 (SCH_2), 3.67 ($P(OMe)_3$, *J* = 11.1 Hz). **4c**: mp 109 °C; δ 5.31 (H^3), 2.57 (SMe), 3.82 ($P(OMe)_3$, *J* = 11.4 Hz). **4d**: mp 116 °C; δ 5.38 (H^3), 3.96 (SCH_2), 3.65 ($P(OMe)_3$, *J* = 11.2 Hz). **4e**: mp 73 °C; δ 5.59 (H^6), 5.02 (H^3), 2.62 (SMe), 3.66 ($P(OMe)_3$, *J* = 11.3 Hz). **4g**: mp 111 °C; δ 5.74–5.48 (H^3, H^6, H^7, H^{22}, H^{23}), 2.87 (SMe), 4.20 ($P(OMe)_3$, *J* = 10.7 Hz). **4h**: mp 150 °C; δ 3.75 (SCH_2), 3.66 ($P(OMe)_3$, *J* = 11 Hz). **4k**: oil, δ 5.09 (H^2), 3.84 (SCH_2), 3.75 ($P(OMe)_3$, *J* = 13.8 Hz). **4m**: oil; with $P(OPh)_3$ instead of $P(OMe)_3$; mp 148 °C. **6h**: mp 62 °C, δ 5.53–5.31 (H^3, H^6, H^7, H^{22}, H^{23}), 3.83 ($P(OMe)_3$, *J* = 11.7 Hz), 3.90 (SCH_2); ν_{CO} 1960, 1975, 2040, 1070 cm^{-1}. **6m**: mp 49 °C, δ 2.74 (SMe), 4.10 and 4.07 ($P(OMe)_3$, *J* = 11 Hz); ν_{CO}: 1960, 1980, 2040, 2075 cm^{-1}. **5** = $Fe_2(CO)_4(\mu\text{-}SR)_2[P(OMe)_3]_2$: R = Me, 35%, mp 61–62 °C, M^+ 565.89, δ 2.07 and 1.42 (SMe), 3.77 ($P(OMe)_3$, *J* = 11.7 Hz), ν_{CO} 1915, 1950, 1975, 2015 cm^{-1}; R = Bz, 28%, mp 128–129 °C, M^+ 717.96, δ 2.28 (SCH_2), 3.59 ($P(OMe)_3$, *J* = 11.8 Hz), ν_{CO} 1920, 1950, 1975, 2020 cm^{-1}.

X-ray Analysis. Collection and Reduction of X-ray Data. A crystal of **2m**, (*O*-(adamantylmethyl) *S*-methyl xanthate)diiron hexacarbonyl complex $C_{19}H_{20}O_7S_2Fe_2$, suitable for X-ray diffraction analysis was grown from hexane. Preliminary photographic data revealed that the crystal belongs to the triclinic system. Accurate cell parameters were obtained by a least-squares analysis of 25 carefully centered diffractometer reflections. Table I gives the pertinent crystal data and all the details of data collection.

Intensity data were collected with use of the ω/2θ scan technique on a Nonius CAD 4 automatic diffractometer. The scan range was increased by 25% at each end for background measurements. A total of 3623 independent reflections were measured from which 2715 were nonzero and used in the subsequent structure determination and refinement. The data were corrected for Lorentz and polarization effects with use of the program MAXE,[7] and absorption corrections were performed. The check of stability for the detection chain and for the crystal was done from three standard reflections measured after every hour of X-ray exposure.

Solution and Refinement. The position of the heaviest atoms were found in the *E* map calculated from the set with the highest figure of merit from MULTAN.[8] Subsequent three-dimensional electron density difference maps and least-squares refinement reveal the entire structure. Atomic scattering factors were taken from Moore's ta-

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Table II. Fractional Coordinates and Anisotropic Thermal Parameters[a] ($\times 10^4$) for Nonhydrogen Atoms

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	795 (1)	2892 (1)	1228 (1)	112 (1)	54 (1)	35 (1)	−5 (1)	18 (1)	7 (1)
Fe(2)	−913 (1)	2293 (1)	2432 (1)	135 (1)	61 (1)	38 (1)	−7 (1)	21 (1)	15 (1)
S(1)	1034 (1)	4017 (1)	3512 (1)	205 (2)	79 (1)	38 (1)	−33 (1)	25 (1)	7 (1)
S(2)	−1769 (1)	3643 (1)	1507 (1)	135 (2)	67 (1)	47 (1)	13 (1)	28 (1)	20 (1)
O(1)	3066 (3)	5012 (2)	2641 (2)	184 (6)	75 (3)	41 (2)	−49 (3)	31 (2)	−5 (2)
O(2)	−965 (4)	975 (3)	−710 (2)	264 (8)	113 (4)	57 (2)	−20 (4)	13 (3)	−16 (2)
O(3)	3838 (4)	1404 (3)	1714 (2)	161 (6)	128 (4)	99 (3)	42 (4)	31 (3)	39 (3)
O(4)	2061 (4)	4511 (3)	176 (2)	282 (8)	121 (4)	81 (2)	−7 (4)	59 (4)	49 (2)
O(5)	−3258 (5)	2805 (3)	3826 (2)	324 (9)	148 (4)	90 (3)	−14 (5)	115 (4)	17 (3)
O(6)	−3032 (4)	99 (3)	878 (2)	210 (7)	89 (3)	66 (2)	−29 (4)	16 (3)	8 (2)
O(7)	1545 (4)	514 (3)	3114 (2)	280 (8)	122 (4)	65 (2)	62 (4)	10 (3)	36 (2)
C(1)	6336 (7)	9421 (4)	3482 (4)	297 (12)	66 (4)	76 (3)	−10 (6)	34 (5)	20 (3)
C(2)	8695 (6)	8178 (5)	4159 (4)	194 (10)	118 (5)	99 (4)	−52 (6)	−4 (5)	42 (4)
C(3)	7268 (7)	7623 (4)	2279 (4)	315 (13)	105 (5)	78 (4)	−67 (7)	82 (6)	3 (4)
C(4)	7109 (6)	8894 (4)	4357 (3)	251 (11)	68 (4)	50 (3)	−44 (5)	13 (4)	1 (3)
C(5)	8106 (6)	7087 (4)	3157 (4)	173 (10)	90 (5)	115 (4)	−4 (5)	62 (5)	18 (4)
C(6)	5705 (7)	8337 (4)	2502 (3)	285 (12)	97 (5)	52 (3)	−28 (6)	18 (5)	29 (3)
C(7)	5698 (6)	7999 (4)	4472 (3)	225 (10)	78 (4)	48 (3)	−44 (5)	20 (4)	0 (3)
C(8)	6710 (5)	6181 (4)	3278 (3)	172 (9)	66 (4)	84 (3)	1 (5)	36 (4)	15 (3)
C(9)	4300 (5)	7442 (4)	2600 (3)	174 (9)	86 (4)	55 (3)	−7 (5)	10 (4)	19 (3)
C(10)	5113 (5)	6889 (3)	3486 (3)	142 (8)	57 (3)	41 (2)	−19 (4)	14 (3)	4 (2)
C(11)	3723 (5)	6007 (4)	3613 (3)	202 (1)	83 (2)	43 (1)	−49 (1)	24 (2)	−3 (2)
C(12)	−304 (5)	1704 (3)	52 (3)	156 (8)	75 (4)	44 (2)	−6 (4)	22 (4)	9 (2)
C(13)	2634 (5)	1973 (3)	1514 (3)	126 (8)	67 (4)	50 (2)	−8 (4)	20 (3)	7 (2)
C(14)	1548 (5)	3876 (3)	573 (3)	162 (8)	75 (4)	47 (2)	−2 (4)	31 (4)	16 (2)
C(15)	−2359 (5)	2590 (4)	3289 (3)	195 (9)	73 (4)	56 (3)	−13 (5)	40 (4)	16 (3)
C(16)	−2224 (5)	971 (3)	1475 (3)	152 (8)	74 (4)	52 (3)	0 (4)	24 (4)	22 (3)
C(17)	612 (5)	1233 (4)	2876 (3)	177 (9)	83 (4)	44 (2)	−4 (5)	14 (4)	20 (3)
C(18)	1832 (5)	4130 (3)	2544 (3)	141 (7)	56 (3)	43 (2)	−8 (4)	17 (3)	5 (2)
C(19)	−3709 (5)	3037 (4)	429 (3)	134 (8)	124 (5)	71 (3)	10 (5)	−1 (4)	44 (3)

[a] Parameters expressed in the form $\exp(-\Sigma_{i,j}B_{ij}h_ih_j)$.

Table III. Selected Interatomic Distances (Å)

C(1)–C(4)	1.507 (6)	C(11)–O(1)	1.470 (3)
C(1)–C(6)	1.525 (5)	S(2)–C(19)	1.813 (3)
C(2)–C(4)	1.512 (6)	Fe(1)–C(12)	1.811 (3)
C(2)–C(5)	1.546 (6)	Fe(1)–C(13)	1.788 (3)
C(3)–C(5)	1.526 (7)	Fe(1)–C(14)	1.795 (4)
C(3)–C(6)	1.505 (7)	Fe(2)–C(15)	1.819 (4)
C(4)–C(7)	1.541 (6)	Fe(2)–C(16)	1.787 (3)
C(5)–C(8)	1.545 (6)	Fe(2)–C(17)	1.799 (4)
C(6)–C(9)	1.527 (6)	C(12)–O(2)	1.144 (3)
C(7)–C(10)	1.543 (4)	C(13)–O(3)	1.151 (4)
C(8)–C(10)	1.519 (5)	C(14)–O(4)	1.140 (5)
C(9)–C(10)	1.544 (5)	C(15)–O(5)	1.136 (6)
C(10)–C(11)	1.528 (5)	C(16)–O(6)	1.444 (3)
		C(17)–O(7)	1.143 (5)

Table IV. Selected Bond Angles (Deg)

Fe(1)–Fe(2)–S(2)	54.33 (3)	Fe(2)–S(1)–C(18)	90.5 (1)
Fe(1)–Fe(2)–S(1)	76.67 (3)	Fe(1)–S(2)–Fe(2)	71.26 (5)
Fe(1)–Fe(2)–C(15)	154.31 (1)	Fe(1)–S(2)–C(19)	113.9 (1)
Fe(1)–Fe(2)–C(16)	95.25 (9)	Fe(2)–S(2)–C(19)	113.8 (1)
Fe(1)–Fe(2)–C(17)	97.9 (1)	C(11)–O(1)–C(18)	120.2 (3)
Fe(2)–Fe(1)–S(2)	54.42 (3)	C(10)–C(11)–O(1)	108.1 (3)
Fe(2)–Fe(1)–C(12)	98.73 (9)	Fe(1)–C(18)–O(1)	120.7 (2)
Fe(2)–Fe(1)–C(13)	95.56 (9)	Fe(1)–C(18)–S(1)	116.2 (2)
Fe(2)–Fe(1)–C(14)	156.73 (9)	S(1)–C(18)–O(1)	123.1 (3)
Fe(2)–Fe(1)–C(18)	76.65 (8)		

bulation[9] and anomalous dispersion terms $\Delta f'$ and $\Delta f''$ were included in the calculation of F_c.[10] The model was initially refined by full-matrix least-squares technique[11] with isotropic thermal parameters for all nonhydrogen atoms and then blocked into two molecular fragments each of which was refined by a full-matrix least-squares method with anisotropic thermal parameters and fixed isotropic B's equal to 5 Å^2 for the hydrogen atoms. Several cycles of refinement finally converged to $R = 0.033$ and $R_w = 0.035$. The weighting scheme used was based on counting statistics,[12] with the value of p being 0.04.

$$1/w = \sigma_F^2 = \tfrac{1}{4}((\sigma_I^2/I) + p^2I)$$

No significant peaks remained on a final Fourier difference map. The estimated standard deviation for an observation of unit weight was GOF = 1.015 with 272 refined variables. Table II lists the atomic parameters for the nonhydrogen atoms with their esd's. Bond distances and angles are given in Tables III and IV.

Results and Discussion

Xanthates **1** easily prepared from alcohols[5] are well-known as energy-rich groupings and as the starting materials for the Chugaev elimination.[13] This functional group may behave in a complex as a four- or a six-electron donor depending on the mode of coordination, and in principle competition can exist between oxygen and sulfur to lead to different complexes. Owing to our interest in the remote functionalization of natural products, we have chosen the alcohols among steroids and terpenes and prepared the corresponding xanthates. When $Fe_2(CO)_9$ is added to a solution of the xanthate in toluene (60 °C; inert atmosphere), we notice complete transformation of the starting material within a few minutes and a major complex **2** is isolated in 65–80% yield after chromatography. Although it was easy to establish that in every case the starting material had incorporated the $Fe_2(CO)_6$ group with all terminal carbonyls, two points remained confusing. Attempts at decomplexation by oxidative methods (addition of Fe^{3+} or Ce^{4+} to a solution of complex **2** in ethanol) lead to recovery of the starting alcohols with retention of configuration instead of the expected free ligand. On the other hand, the ^{13}C NMR data showed a considerable deshielding for the sp^2 carbon (293 ppm vs. 213 ppm in the starting material) to a value in the range of transition-metal-stabilized carbenes.

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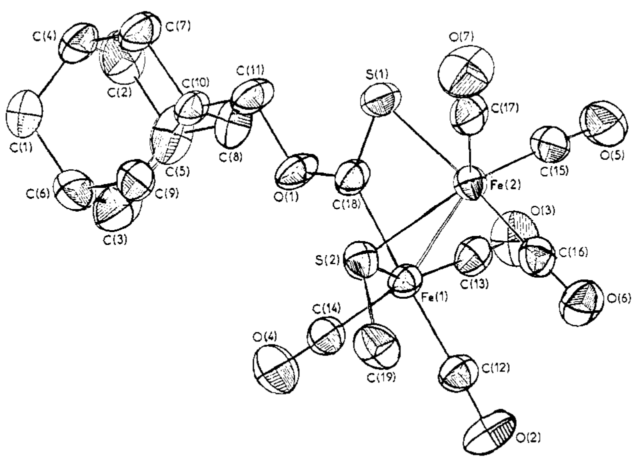


Figure 1. ORTEP drawing of compound **2m**.

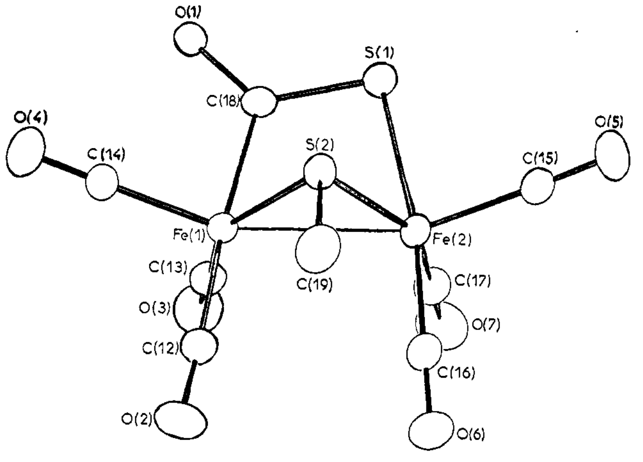


Figure 2. Bimetallic skeleton of compound **2m**.

The structure of complex **2m** prepared from xanthate **1m** has been established by X-ray diffraction; the ORTEP diagram is shown on Figure 1. The three-dimensional packing shows discrete molecules separated by normal Van der Waals contacts; for sake of clarity, the bimetallic skeleton has been represented in Figure 2.

The molecule contains the $Fe_2(CO)_6$ group in which the Fe–Fe distance is equal to 2.619 (0) Å; this value is in the range observed for other nonsymmetrically double-bridged complexes[14] but is significantly longer than those in complexes containing two identical thioalkyl or thioaryl bridges (2.516 (2) Å)[15,16] or a bicyclic dithiolate ligand (2.497 (4) Å).[17] The originality of our structure is found in the existence of the two bridges resulting from the effective insertion of an iron atom into the carbon-sulfur single bond of the xanthate. This gives rise to two nearly orthogonal bridging planes A which contains O(1), C(18), S(1), Fe(1), and Fe(2) and B which contains S(2), Fe(1), and Fe(2). The coplanarity of O(1) in plane A with both C(18) and S(1) and the values close to 120° for the angles centered at C(18) suggest that electron delocalization of the lone pairs of oxygen plays a role in the stabilization of the electron-deficient atom C(18). The Fe(1)–C(18) distance of 1.949 (2) Å corresponds to other iron-stabilized carbenes such as 1.950 Å for $(Ph\text{–}CO)_2Fe_2(CO)_6$[18] and is much shorter than the average Fe–C bond length of 2.151 Å in $Fe(CO)_4\text{-}C_{12}H_8$.[19] This carbenic character of C(18) agrees with its low-field resonance (293 ppm). Comparison of carbon–oxygen and carbon–sulfur bond lengths in the free ligand[20] and in the complex show that complexation does not significantly modify the carbon–oxygen single bond (1.325 (3) vs. 1.319 (4) Å). On the contrary, the C(18)–S(1) bond distance becomes longer (1.618 (2) vs. 1.673 (4) Å in the complex). From these data we can conclude that neither representation I nor II (Figure 3) provides an accurate description of the electron distribution but that formula III is in better agreement with our structural and spectral data and with recent EHT calculations.[21]

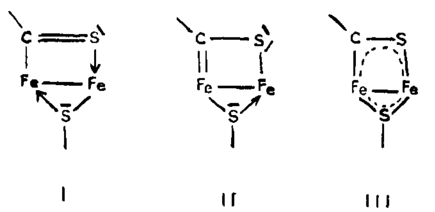
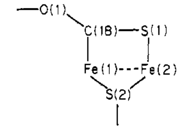
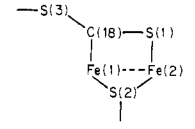


Figure 3. Alternative valence bond formulations of complexes of type **2**.

Table V. Comparison of Bond Lengths (Å) in Complexes 2 and 3

	 **2**	 **3**
C(18)-O(1)	1.319 (4) [1.325 (3)][a]	
C(18)-S(3)		1.698 (4) [1.743 (2)][a]
C(18)-S(1)	1.673 (4) [1.618 (2)][a]	1.658 (4) [1.634 (3)][a]
C(18)-Fe(1)	1.949 (2)	1.970 (3)
Fe(2)-S(1)	2.332 (1)	2.299 (1)
Fe(1)-S(2)	2.247 (1)	2.256 (1)
Fe(2)-S(2)	2.249 (1)	2.237 (1)
Fe(1)-Fe(2)	2.619 (1)	2.621 (1)

[a] The values in brackets refer to the bond lengths in the starting xanthates[20] or trithiocarbonates.[29]

The equidistance of the sulfur atom S(2) from both metal atoms (Table V) argues also in favor of formula III.

Although the gross features of this structure correspond to those of trithiocarbonate complex **3** that we have recently described[2] (Table V), several modifications appear to be related to replacement of oxygen by sulfur. For example, on the basis of the observed shortening of the C(18)–S(3) bond length in complex **3**, we can conclude to a stronger participation of S(3) compared to O(1) for stabilizing the electron-deficient C(18). On the contrary, the double-bond character of C(18)–S(1) is much more affected in complex **2** than in complex **3**. In fact, except for the unaltered iron–iron distance, all the other bond lengths are more or less modified, and, for example, the S(2) atom is no longer symmetrically bonded to the iron atoms in complex **3**. These modifications suggest a more important contribution of limit formula (I) to represent the electronic distribution in the trithiocarbonate complex.

The three carbonyls attached to each $Fe(CO)_3$ group have the usual ternary symmetry, and the Fe–C bond lengths are in the range of others in similar complexes (Table III). The iron–sulfur distances in the thiomethyl bridge are significantly shorter than those reported in symmetrical $Fe_2(CO)_6(SR)_2$,[15] but it seems important to notice that the S(1)–Fe(2) bond of

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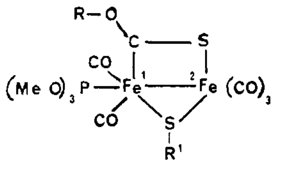
the biatomic bridge is by far the longest one.

Double-bridged $Fe_2(CO)_6$ complexes have been widely studied for their interesting properties. Except for a recent example,[17] all of the complexes reported so far are symmetrical so that each $Fe(CO)_3$ is spectroscopically identical. Although each $Fe(CO)_3$ group is stereochemically nonrigid, it remains uncertain whether carbonyl exchange can occur between the two $Fe(CO)_3$ units. Obviously our complexes are suitable examples of a dissymetrical environment for two iron atoms in the same molecule. The different electronic environment about Fe(1) and Fe(2) is demonstrated by the two quadrupole splittings measured in the Mössbauer spectra of complex **2**.[22] Furthermore only one $Fe(CO)_3$ group is stereochemically nonrigid, and we have demonstrated by ^{13}C NMR spectroscopy that the scrambling of carbonyls occurred exclusively at Fe(2). For definitive assignment of the exchange site, we have replaced one carbonyl by a phosphorus ligand and we have chosen trimethyl phosphite because alkyl- and arylphosphines gave unstable substitution products. By measuring the phosphorus–carbon coupling constants in the limiting low-temperature spectra we have shown that the phosphite ligand had replaced one carbonyl at Fe(1).[23]

When complex **2** reacts at room temperature with $P(OMe)_3$, compounds **4** and **5** are obtained, but in refluxing acetone the monosubstitution product is formed quantitatively after a few minutes and after 24 h the bis(phosphite) **6** is obtained. Treatment of **4** with excess $P(OMe)_3$ gives only **6**, showing that compound **5** is formed by an independent route. It has been mentioned that carbenes can afford addition products with amines or phosphines;[24] the intermediate ylide may not be stable enough in our case and liberates reactive species which recombine to afford complex **5**.



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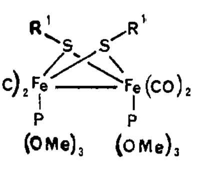

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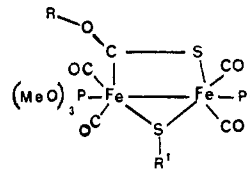
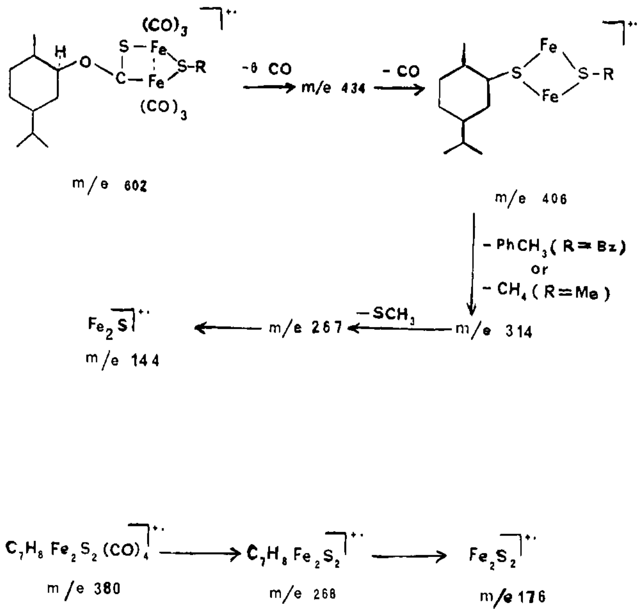


6

All the complexes described have been characterized by the usual techniques and, particularly, by mass spectroscopy. The molecular peaks could be measured in every case except for R^1 = steroid because in that particular case Chugaev elimination was too fast and the peak of higher mass always corresponds to the olefins. But in all the mass spectra we have found the peaks 176 $(Fe_2S_2)^+$ and 144 $(Fe_2S)^+$ which seem to be characteristic of all the sulfur double-bridged diiron carbonyl complexes. The fragment 144 has already been mentioned for thioketone complexes,[25] but we have never noticed the fragment 112 $(Fe_2)^+$ which is described as indicative of the presence of a metal–metal bond.[26] When the molecular peak could be measured, we found the successive loss of seven carbonyls for complexes **2**, of six carbonyls for complexes **4**, and five carbonyls for complexes **6**. This additional loss of one molecule of CO corresponds to the carbon oxygen fragment of the bridge. Other examples of decarbonylation under electron impact have been described,[27,28] and we have represented on Scheme I the two filiations giving rise to $(Fe_2S_2)^+$ and $(Fe_2S)^+$ for complex **2** (R = menthol, R^1 = benzyl). These two pathways are independent, but we have not found the filiation from the molecular peak to *m/e* 380.

Scheme I



Acknowledgment. We thank CNRS for financial support (A.T.P.) and Rhône-Poulenc Industries for a studentship to G.M.

Registry No. **1a**, 5211-17-6; **1b**, 70242-69-2; **1c**, 70286-38-3; **1d**, 79043-83-7; **1e**, 53496-46-1; **1f**, 70242-71-6; **1g**, 57852-44-5; **1h**, 79043-84-8; **1i**, 79043-85-9; **1j**, 5564-44-3; **1k**, 79043-86-0; **1l**, 79043-87-1; **1m**, 79057-62-8; **2a**, 79082-79-4; **2b**, 79082-78-3; **2c**, 79082-77-2; **2d**, 79043-56-4; **2e**, 78618-17-4; **2f**, 79043-44-0; **2g**, 79043-45-1; **2h**, 79043-46-2; **2k**, 79043-47-3; **2l**, 79043-48-4; **2m**, 79043-49-5; **4a**, 79082-73-8; **4b**, 79082-74-9; **4c**, 79082-75-0; **4d**, 79082-76-1; **4e**, 79043-50-8; **4g**, 79043-51-9; **4h**, 78618-19-6; **4k**, 79043-52-0; **4m**, 79043-53-1; **5**, R^1 = Me, 61688-14-0; **6h**, 79043-54-2; **6m**, 79043-55-3; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: Listings of structure factor amplitudes, least-squares planes, hydrogen atom coordinates, and anisotropic thermal parameters and the packing diagram (11 pages). Ordering information is given on any current masthead page.

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