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Selective complexation of functionalised 1-thia-3-azabutadienes with iron carbonyl

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Abstract

1-Thia-3-aza-butadienes $R^2C(S)N{=}C(CO_2C_2H_5)N(CH_3)_2$ bearing an aromatic substituent R^2 in position 2 ($R^2 = C_6H_5$), react selectively with $Fe_2(CO)_9$ to afford monoiron tricarbonyl and diiron hexacarbonyl complexes with retention of the heteroatomic chain. Oxidative decomplexation demonstrates the reversibility, with no loss of sulphur, of the reaction. In the case of the thiaazadiene bearing a thioalkyl group in position 2 ($R^2 = C_6H_5CH_2S$), complexation with $Fe_2(CO)_9$ involves the sulphur atom, to give a major product with a metallocarbene structure. ^{13}C NMR and Infrared spectral data are consistent with the structures of the complexes determined by X-ray diffractometry.

Introduction

Substituted butadiene-iron carbonyl complexes are of interest as synthetic intermediates [1]. The formation of complexes between oxa- and aza-butadienes and iron carbonyl has been particularly well-documented [2]. On the other hand, no study has been carried out on the complexation of functionalised 1-thia-3-azabutadienes compounds (I) for which numerous synthetic applications are known [3]. Our previously described syntheses of substituted 4-dimethylamino-4-ethoxycarbonyl-1-thia-3-azabutadienes. $[R^2C(S)N{=}C(CO_2C_2H_5)N(CH_3)_2]$ with an aromatic (Ia, $R^2 =$

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C_6H_5) [4] or a thioalkyl (Ib, $R^2 = C_6H_5CH_2S$) [5] substituent in position 2, prompted us to study the influence of heteroatoms and unsatured systems of these compounds on their photochemical and thermal complexations with [$Fe(CO)_5$] and [$Fe_2(CO)_9$], respectively.

Results and discussions

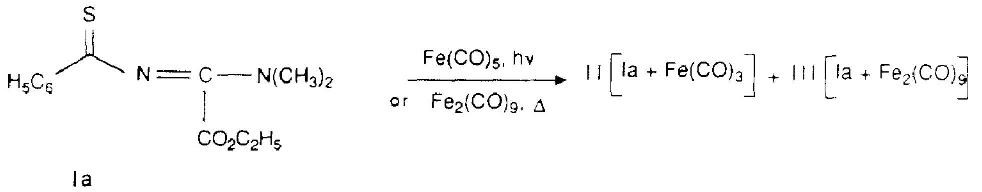
I. Complexation of substituted 1-thia-3-azabutadiene (Ia)

Photochemical reaction of compound Ia, with an excess of $Fe(CO)_5$ in toluene gave monoiron tricarbonyl (II) and diiron hexacarbonyl (III) complexes. When the reactions with $Fe_2(CO)_9$ (3 equivalents) was carried out thermally at 40 °C in toluene it also gave complexes II (54%) and III (27%) (Scheme 1). The mono- and bi-metallic complexes obtained photochemically and thermally were identified from their high-resolution infrared spectra.

The similar results obtained in the two methods led us to continue our study using the thermal complexation method only. We found that it is possible to obtain each complex selectively. Thus thermal treatment of Ia with $Fe_2(CO)_9$ (1 equiv.) afforded the monoiron tricarbonyl complex II (65%) exclusively, and further treatment of complex II in toluene with $Fe_2(CO)_9$ (2 equiv.) at 40 °C gave the diiron hexacarbonyl complex III (65%). We also found that when compound III was heated at 80 °C in toluene it gave complex II and the heterodiene Ia, as shown in Scheme 2. The structure of the monometallic compound II, was determined by X-ray diffraction (Fig. 1). The principal bond lengths and angles are given in Tables 1 and 2.

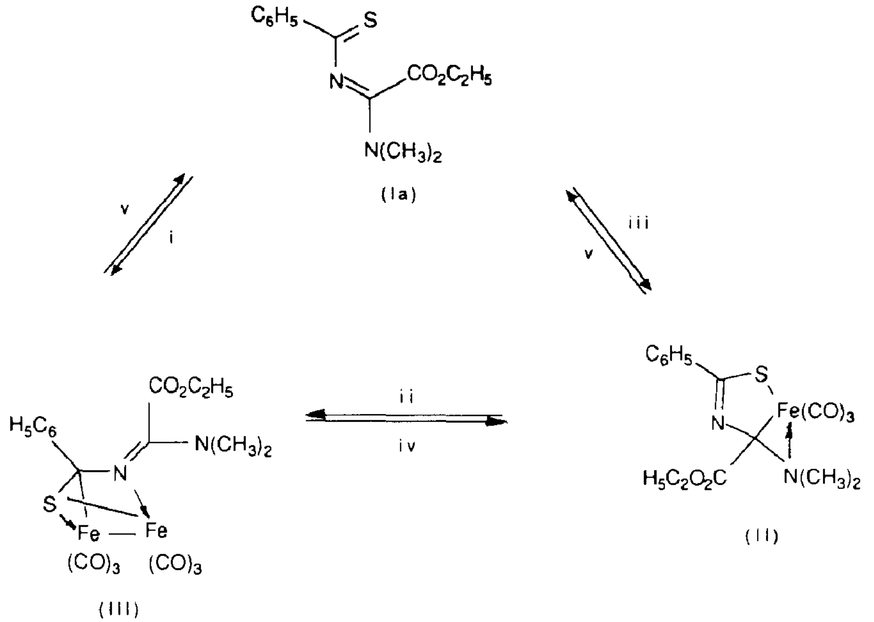
The iron atom and the S–C(10)–N(1)–C(7) chain lie in the same plane, and this planarity must contribute to the stability of the complex. Formation of the imine function, characterised by a C(10)–N(1) bond length of 1.279 Å [6], accounts for the non-equivalence of the aromatic protons displayed in the ^1H NMR spectrum. Restricted rotation of the nitrogen atom N(2) due to the formation of a dative bond between nitrogen and the iron atom [7] accounts for the magnetic non-equivalence observed for the *N*-dimethylamino groups (δ(C(8)) and δ(C(9)) 43.7 and 56.3 ppm). The chemical shift for carbon C(7) ($\delta = 98.5$ ppm) is in good agreement with values in the literature for an iron-coordinated tetrahedral carbon [8]. The mass spectrum showed a molecular ion peak, $m/z = 404$ (M^{+}), and fragmentations corresponding to the loss of CO, characteristics of iron tricarbonyl complexes [9].

The molecular structure of the diiron hexacarbonyl complex III is shown in Fig. 2. Principal bond lengths and angles are given in Tables 3 and 4. In this complex, the coordination provided by the S–C(4)–N(2) chain, also observed in the case of substituted thioamides [10], stabilises the bimetallic skeleton by contributing 6



Ia

Scheme 1



Scheme 2. i, $Fe_2(CO)_9$ 3 equiv.; ii, $Fe_2(CO)_9$ 2 equiv.; iii, $Fe_2(CO)_9$ 1 equiv.; iv, Δ; v, $(CH_3)_3NO\cdot 2H_2O$.

Table 1

Principal bond lengths (Å) in compound II

Fe–N(2)	2.007(3)	O(5)–C(6)	1.167(5)
Fe–C(1)	1.816(4)	N(1)–C(7)	1.405(4)
Fe–C(2)	1.777(4)	N(1)–C(10)	1.279(4)
Fe–C(3)	1.785(4)	N(2)–C(7)	1.452(4)
Fe–C(7)	2.019(3)	N(2)–C(8)	1.498(5)
S–C(10)	1.742(4)	N(2)–C(9)	1.495(4)
Fe–S	2.301(2)	C(6)–C(7)	1.508(4)
O(1)–C(1)	1.128(5)	C(10)–C(11)	1.489(5)
O(2)–C(2)	1.155(5)	C(11)–C(12)	1.386(5)
O(3)–C(3)	1.136(5)	C(11)–C(16)	1.389(5)
O(4)–C(6)	1.291(4)	C(12)–C(13)	1.377(6)

Table 2

Principal bond angles (°) in compound II

N(2)–Fe–C(7)	42.3(1)	C(7)–N(2)–C(8)	120.8(3)
C(1)–Fe–C(2)	104.9(2)	C(7)–N(2)–C(9)	118.4(3)
C(1)–Fe–C(3)	94.2(2)	C(8)–N(2)–C(9)	107.1(2)
C(1)–Fe–C(7)	145.0(1)	Fe–C(1)–O(1)	174.5(4)
C(2)–Fe–C(3)	88.5(2)	Fe–C(2)–O(2)	178.0(4)
C(2)–Fe–C(7)	108.0(2)	Fe–C(3)–O(3)	174.1(4)
C(3)–Fe–C(7)	98.1(2)	O(4)–C(6)–O(5)	122.1(3)
C(5)–O(4)–C(6)	119.0(3)	O(4)–C(6)–C(7)	110.1(3)
C(7)–N(1)–C(10)	118.1(3)	O(5)–C(6)–C(7)	127.6(3)
S–C(10)–N(1)	122.6(3)	N(1)–C(7)–C(6)	109.5(3)
Fe–N(2)–C(7)	69.3(2)	Fe–C(7)–N(1)	118.0(2)
Fe–N(2)–C(8)	116.8(2)	Fe–C(7)–N(2)	68.4(2)
Fe–N(2)–C(9)	121.1(2)	Fe–C(7)–C(6)	119.9(2)
N(2)–C(7)–C(6)	117.9(3)	N(1)–C(7)–N(2)	118.1(2)
S–C(10)–C(11)	118.9(3)	C(10)–C(11)–C(12)	120.0(3)

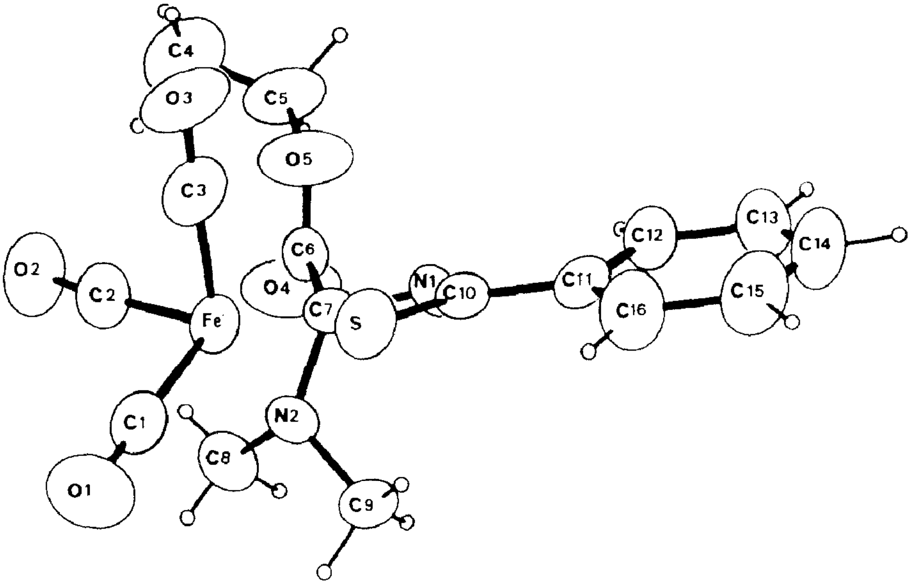


Fig. 1. Structure of compound II.

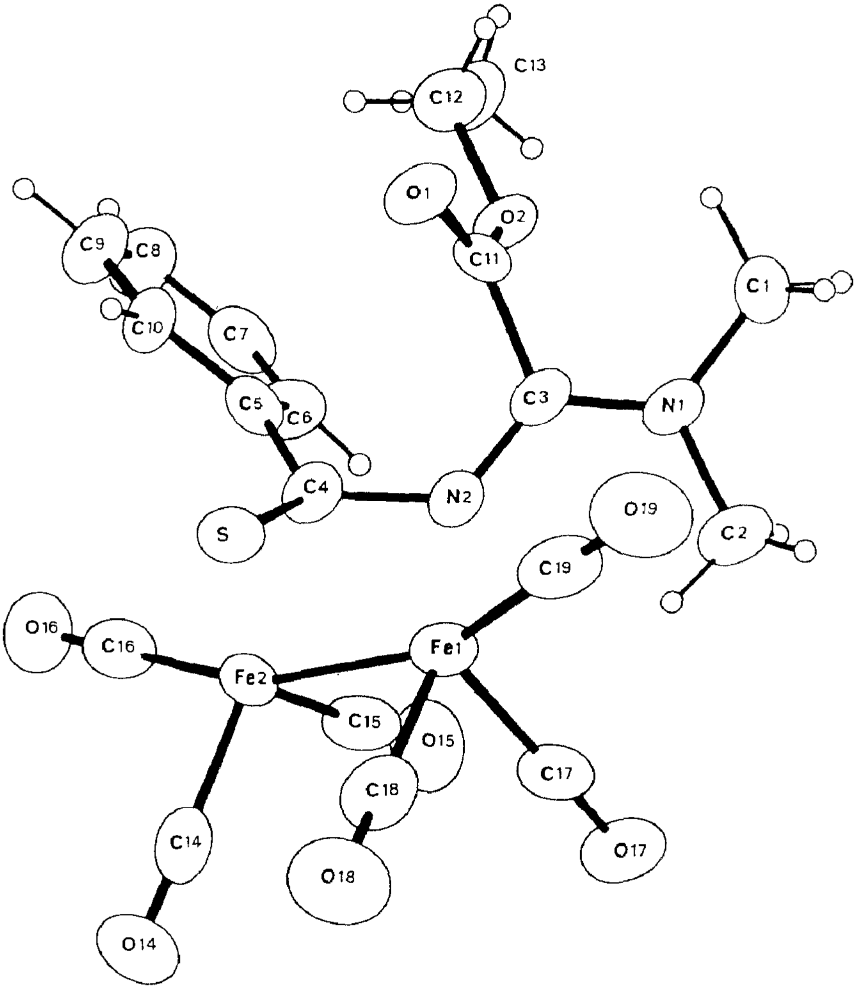


Fig. 2. Structure of compound III.

Table 3

Principal bond lengths (Å) in compound III

Fe(1)–Fe(2)	2.588(2)	S–N(2)	2.568(8)
Fe(1)–S	2.277(3)	S–C(4)	1.774(10)
Fe(1)–N(2)	2.049(8)	S–C(4)	1.774(10)
Fe(1)–C(4)	2.587(10)	O(1)–C(11)	1.197(11)
Fe(1)–C(17)	1.809(10)	O(2)–C(11)	1.316(11)
Fe(1)–C(18)	1.781(12)	O(2)–C(12)	1.468(11)
Fe(1)–C(19)	1.769(13)	N(1)–C(1)	1.462(12)
Fe(2)–S	2.176(3)	N(1)–C(2)	1.436(12)
Fe(2)–C(4)	2.026(10)	N(1)–C(3)	1.335(12)
Fe(2)–C(14)	1.823(14)	N(2)–C(3)	1.312(11)
Fe(2)–C(15)	1.781(13)	N(2)–C(4)	1.457(11)
Fe(2)–C(16)	1.741(13)	C(3)–C(11)	1.534(13)
C(12)–C(13)	1.477(14)	C(4)–C(5)	1.458(13)

electrons. The complexation of the organic ligand results in a lengthening of bonds (S–C(4) 1.774 Å and C(4)–N(2) 1.457 Å) compared to those in the heterodiene, precursor Ia (S–C(4) 1.667 Å and C(4)–N(2) 1.300 Å) [11].

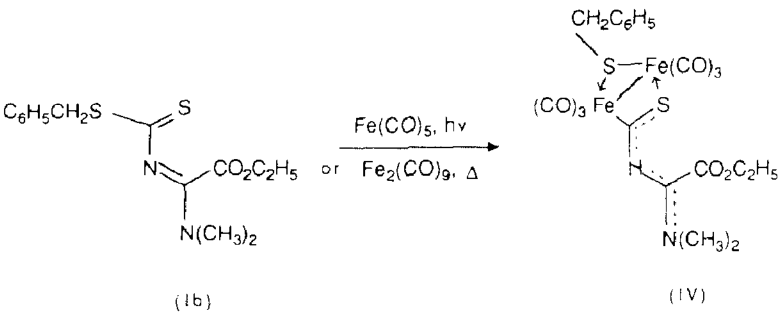
The amidinic system is only very slightly influenced by the complex formation: compared to the values recorded for compound Ia [11], there are small variations in bond lengths and no change in the stretching frequency of the ester function (ν(CO) 1731 cm^{-1}). The sp^3 state of hybridization for carbon C(4) was confirmed by ^{13}C NMR (δ 92.3 ppm) and by the distance (C(4)–Fe(2) 2.026 Å, which corresponds to the value calculated for an iron–carbon σ bond of this type [12]. The mass spectrum showed a molecular ion peak, $m/z = 554$ ($M^{+\cdot}$), and an ion at $m/z = 144$ $(Fe_2S)^+$, characteristic of a sulphur atom coordinated to two iron atoms [13].

It is noteworthy that the crystalline complexes II and III are relatively stable in air. Oxidation of the complexes in methylene chloride by use of a large excess of trimethylamine-*N*-oxide dihydrate (16 equiv.) regenerated the heterodiene ligand Ia. The structure was confirmed by mass spectrometry and ^{1}H NMR spectroscopy.

Table 4

Principal bond angles (°) in compound III

Fe(2)–Fe(1)–S	52.66(8)	Fe(1)–S–N(2)	49.6(2)
Fe(2)–Fe(1)–N(2)	73.3(2)	Fe(1)–S–C(4)	78.3(4)
Fe(2)–Fe(1)–C(4)	46.1(2)	Fe(2)–S–N(2)	71.9(2)
S–Fe(1)–N(2)	72.6(2)	Fe(2)–S–C(4)	60.7(3)
S–Fe(1)–C(4)	42.2(2)	C(11)–O(2)–C(12)	116.1(9)
N(2)–Fe(1)–C(4)	34.2(3)	C(1)–N(1)–C(2)	117.3(9)
Fe(1)–Fe(2)–S	56.30(9)	C(1)–N(1)–C(3)	121.3(9)
Fe(1)–Fe(2)–C(4)	66.9(3)	C(2)–N(1)–C(3)	121.4(9)
S–Fe(2)–C(4)	49.8(3)	C(3)–N(2)–C(4)	124.6(9)
Fe(1)–S–Fe(2)	71.0(1)	N(1)–C(3)–N(2)	124.2(9)
N(1)–C(3)–C(11)	116.(1)	N(2)–C(3)–C(11)	120.(1)
S–C(4)–N(2)	104.8(7)	S–C(4)–C(5)	123.8(8)
N(2)–C(4)–C(5)	122.0(9)	O(1)–C(11)–O(2)	127.(1)
O(1)–C(11)–O(2)	127.(1)	O(1)–C(11)–C(3)	122.(1)
O(2)–C(11)–C(3)	111.(1)	O(2)–C(12)–C(13)	107.5(9)



Scheme 3

Treatment of these two complexes with $Ce(NH_4)_2(NO_3)_6$ in methylene chloride did not give the heterodiene Ia because the latter reacts with ceric ammonium nitrate.

II. Complexation of substituted 1-thia-3-azabutadiene (Ib)

The complexation of 1-thia-3-azabutadiene bearing a thiobenzyl group in position 2 was carried out photochemically using $Fe(CO)_5$ or thermally using $Fe_2(CO)_9$ in toluene, and gave a diiron hexacarbonyl complex IV, $m/z = 590$ (M^{+}) as the major product (Scheme 3).

Comparison of the high-resolution infrared spectra confirmed the identity of the products IV obtained by the two methods.The spectra of IV showed several major differences from those of compound III described above. For complex IV the ^1H NMR spectrum showed an upfield shift of signals from the SCH_2 protons ($\delta(CH_2)$

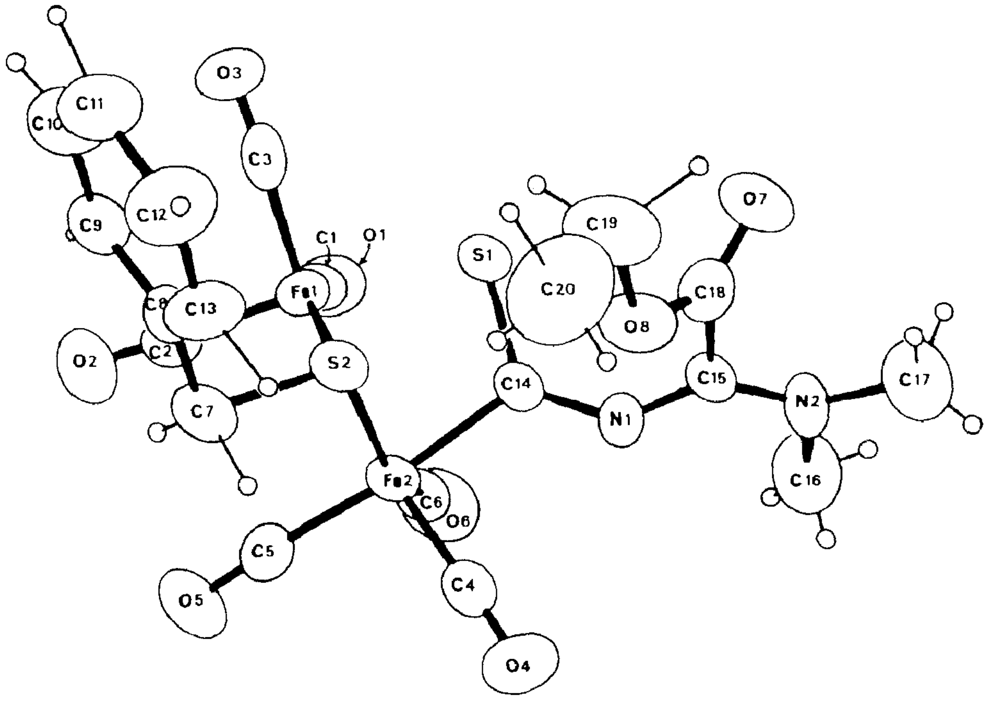


Fig. 3. Structure of compound IV.

Table 5

Principal bond lengths (Å) in compound IV

Fe(1)–S(1)	2.309(2)	Fe(1)–Fe(2)	2.22(6)
Fe(1)–S(2)	2.242(2)	S(2)–C(7)	1.847(7)
Fe(1)–C(1)	1.781(8)	S(1)–C(14)	1.715(7)
Fe(1)–C(2)	1.759(8)	N(1)–C(14)	1.309(7)
Fe(1)–C(3)	1.812(7)	N(1)–C(15)	1.306(9)
Fe(2)–S(2)	2.244(2)	N(2)–C(15)	1.299(7)
Fe(2)–C(4)	1.786(8)	N(2)–C(16)	1.424(11)
Fe(2)–C(5)	1.822(9)	N(2)–C(17)	1.447(12)
Fe(2)–C(6)	1.743(8)	C(7)–C(8)	1.483(9)
Fe(2)–C(14)	1.964(8)	C(15)–C(18)	1.528(10)
		C(19)–C(20)	1.44(2)

3.8 ppm) compared to those for compound Ib ($\delta(CH_2)$ 4.2 ppm). The ^{13}C NMR spectrum contained a signal strongly shifted downfield (δ 274 ppm). From a comparison of these results with the data in the literature for the complexation of xanthates [13] and trithiocarbonates [14], a structure corresponding to a metallocarbene complex could be assigned to compound IV. This structure was confirmed by X-ray diffraction (Fig. 3). Principal bond lengths and angles are given Tables 5 and 6.

This structure indicates that complex formation between compound Ib and $Fe_2(CO)_9$ involves the two sulphur atoms, and not the thiaazadiene system as it does in the case of heterodiene Ia. Formation of compound IV results from the cleavage of the C(14)–SCH_2Ar bond, followed by formation of a C(14) iron σ bond. It is noteworthy that atoms Fe(1) and Fe(2) and those of the heteroatomic chain S(1)–C(14)–N(1) lie in the same plane. This planarity, and the conjugation of the N(2)–C(15)–N(1)–C(14) system, which results in similar bond lengths (N(2)–C(15) 1.299 Å; C(15)–N(1) 1.306 Å; N(1)–C(14) 1.309 Å), contribute to the stability of the isolated bimetallic system.

The results obtained from studying the complexation of thiaazabutadienes, Ia and Ib, with iron carbonyl derivatives have demonstrated that in the case of a

Table 6

Principal bond angles (°) in compound IV

S(1)–Fe(1)–S(2)	82.02(8)	Fe(1)–S(2)–C(7)	113.8(3)
S(2)–Fe(1)–C(1)	152.6(2)	Fe(2)–S(2)–C(7)	114.6(3)
S(2)–Fe(1)–C(2)	95.5(3)	C(18)–O(8)–C(19)	115.0(7)
S(2)–Fe(1)–C(3)	103.5(3)	C(14)–N(1)–C(15)	131.4(6)
C(1)–Fe(1)–C(3)	102.1(4)	C(15)–N(2)–C(16)	119.8(7)
C(2)–Fe(1)–C(3)	94.2(3)	C(15)–N(2)–C(17)	124.2(6)
S(2)–Fe(2)–C(4)	105.8(3)	C(16)–N(2)–C(17)	115.7(6)
S(2)–Fe(2)–C(5)	95.8(2)	S(1)–C(14)–N(1)	122.3(6)
S(2)–Fe(2)–C(6)	149.9(3)	N(1)–C(15)–N(2)	121.0(6)
C(4)–Fe(2)–C(5)	94.3(4)	N(1)–C(15)–C(18)	120.2(5)
C(4)–Fe(2)–C(6)	101.7(4)	N(2)–C(15)–C(18)	118.8(6)
C(5)–Fe(2)–C(6)	94.1(4)	O(7)–C(18)–O(8)	126.5(6)
Fe(1)–S(2)–Fe(2)	71.54(7)	O(8)–C(18)–C(15)	110.8(7)

heterodiene bearing a thioalkyl group, complex formation is governed by the two sulphur groups (to give compound IV), whereas when position 2 bears an aromatic group the complexation involves the heterobutadiene system (to give compounds II and III). In the latter case the reversibility of the reactions, achieved by oxidative decomplexation, means that complexes II and III are potentially useful in organic synthesis. Modifying the substituents in positions 2 and 4 of the complexes would, after oxidation, generate new substituted-1-thia-3-azabutadienes. Physico-chemical studies including Mössbauer effects. currently being carried out on these compounds, should enable determination of the oxidation mechanism.

Experimental

^1H and ^{13}C NMR spectra were recorded at 90 and 22.5 MHz (Jeol Instrument), respectively; chemical shift are given in ppm with respect to TMS as internal standard for $CDCl_3$ as solvent. IR spectra were recorded on a IFS 85 Brucker TF spectrophotometer on samples dispersed in KBr. Mass spectra were recorded with a Varian spectrometer 112 at 70 eV. Melting point were determinated with an "RCH" (C. Reichert) microscope fitted with a Kofler heating stage. The ultraviolet irradiation was carried out with an "Hanovia" reactor at room temperature (mercury lamp, wavelengths 254, 265, 297, 373, and 366 mμ). The silica gel used for chromatography was Merck Kieselgel 60 (70–230 mesh ASTM). The preparation of $Fe_2(CO)_9$ from commercial $Fe(CO)_5$ (Fluka) was carried out as described in [15]. The substituted 1-thia-3-azabutadienes Ia and Ib were prepared by published procedures [4,5]. All reactions were carried out under nitrogen.

Complexes II, III and IV: general procedure

Photochemical complexation (method A). An excess of $Fe(CO)_5$ was added to a solution of substituted-4-dimethylamino-1-thia-3-azabutadienes (Ia or Ib) (1.9 mmol) in dry toluene (230 ml). The stirred mixture was irradiated for 7 h. The progress of the reaction was followed by TLC. The solution was filtered through Hyflo and concentrated under reduced pressure. The residue was chromatographed (eluant: toluene) to give complexes II (32%) and III (32%) from Ia, and complex IV (37%) yield from IIb.

Thermal complexation (method B). $Fe_2(CO)_9$ (5.7 mmol) was added to a solution of substituted-4-dimethylamino-1-thia-3-azabutadienes (Ia or Ib) (1.9 mmol) in dry toluene (40 ml). The solution was stirred at 40 ° C. The progress of the reaction was monitored by TLC. After filtration through Hyflo and concentration of the solution under vacuum the residue was chromatographed on silica gel (eluant: toluene). Complexe II and III: 54 and 27% yield from Ia. Complex IV: 28% yield from Ib.

Complex II (65% yield) can be selectively obtained from Ia (1.9 mmol) with $Fe_2(CO)_9$ (1.9 mmol) by use of the conditions described above for thermal complexation.

Complex III (65% yield) can be selectively obtained from complex II (1 mmol) and $Fe_2(CO)_9$ (2 mmol) by the same procedure described above.

Complex II (crystallized from hexane), m.p. 93° C. ^1H NMR δ: 1.36(t, 3H), 2.40 and 3.39 [s, 6H, $N(CH_3)_2$], 4.38(m, 2H), 7.39(m, 3H), 8.13(m, 2H) ppm. ^{13}C NMR δ. 209.9(CO), 206.4(CO), 185.6 and 169.8 (C(10) and C(6)), 136.5(C(11)), 131.1(C(14)), 128.7 and 128.2 (C(12) to C(16)), 98.1 (C(7)), 62.2(C(5), $^1J(^{13}C{-}H)$ 149 Hz), 56.3 and 43.7(C(8) and C(9) $^1J(^{13}C{-}H)$ 143 Hz), 14.0(C(4), $^1J(^{13}C{-}H)$ 128 Hz) ppm. IR: υ (cm^{-1}) 2059, 1994, 1975(CO), 1719(CO$_2$C$_2$H$_5$). Mass spectrum *mz* (%): 404($M^{+\cdot}$), 348(32), 320(45), 292(12), 249(14), *248(100)*, 247(11), 222(12), 221(77), 203(24), 178(75), 160(13), 145(21), 144(21), 133(13), 130(14), 127(17), 121(76), 105(72), 104(13), 103(22),100(14), 89(16), 88(29), 77(72), 76(15), 72(14), 71(14), 57(28), 56(55), 51(20), 45(12), 44(30).

Complex III (recrystallized from diethyl ether); ^{1}H NMR: δ 1.03(t, 3H), 2.83 [s, 6H, N(CH$_3$)$_2$], 3.39(m, 2H), 7.08(se, 5H) ppm. ^{13}C NMR: δ 212.5(CO), 161.1 and 160.6(C(3)),C(11)), 147.8(C(5)), 127.8, 126.8, 125.8, 125(C(6) to C(10)), 92.7(C(4)), 62.7(C(12), $^1J(^{13}C{-}H)$ 150 Hz), 40.1(C(1) and C(2), $^1J(^{13}C{-}H)$ 139.8 Hz), 13.4(C(13), $^1J(^{13}C{-}H)$ 127.9 Hz) ppm. IR: ν (cm^{-1}) 2054, 2015, 2000, 1987, 1966, 1950(CO), 1731(CO$_2$C$_2$H$_5$). Mass spectrum *m/z* (%): 544($M^{+\cdot}$), 488(11), 432(12), 404(16), 376(45), 333(23), 304(14), 248(17), 230(22), 203(39), 186(30), 145(17), 144(32), *105(100)*, 103(13), 77(32), 57(32), 45(11). Anal. Found: C, 41.15; H, 3.07; S, 6.01; Fe, 20.91. $C_{19}H_{16}Fe_2N_2O_8S$ calc.: C, 41.90; H, 2.94; S, 5.88; Fe, 20.58%.

Complex IV (recrystallized from diethyl ether); ^{1}H NMR: δ 1.31(t, 3H), 3.12[se, N(CH$_3$)$_2$], 3.85(s, CH$_2$S), 4.31(m, CH$_2$), 7.44(se, 5H) ppm. ^{13}C NMR: δ 274.5(C(14)), 213.4, 211.4, 210.9, 208.2(CO), 159.5(C(18)), 140.4(C(8)), 137.1(C(15)), 128.8, 127.4(C(9) to C(13)), 63.4(C(19), $^1J(^{13}C{-}H)$ 149.3 Hz), 45.7(C(7), $^1J(^{13}C{-}H)$

Table 7

Atomic coordinates for complex II

Atom	*x*	*y*	*z*	*B* (Å^2)
Fe	0.16705(5)	0.11775(7)	0.39599(2)	3.74(1)
S	0.22789(9)	0.1461(1)	0.30948(4)	4.25(2)
O(1)	0.0103(3)	−0.2015(4)	0.3488(2)	8.1(1)
O(2)	0.4258(3)	−0.0105(6)	0.4356(2)	8.5(1)
O(3)	0.1519(3)	0.0598(5)	0.5172(1)	7.99(9)
O(4)	0.3238(3)	0.4916(5)	0.4759(1)	7.62(8)
O(5)	0.1387(3)	0.5858(5)	0.4738(1)	8.55(9)
N(1)	0.2250(2)	0.4818(4)	0.3540(1)	3.26(6)
N(2)	0.0448(2)	0.3258(4)	0.3747(1)	3.54(6)
C(1)	0.0754(4)	−0.0847(5)	0.3675(2)	5.0(1)
C(2)	0.3232(4)	0.0370(6)	0.4203(2)	5.3(1)
C(3)	0.1521(4)	0.0875(6)	0.4695(2)	5.2(1)
C(4)	0.4057(6)	0.4456(8)	0.5791(3)	9.5(2)
C(5)	0.3765(4)	0.5845(7)	0.5324(2)	7.1(1)
C(6)	0.2050(3)	0.5000(5)	0.4526(1)	3.55(7)
C(7)	0.1714(3)	0.3952(4)	0.3952(1)	3.22(6)
C(8)	−0.0468(3)	0.3479(6)	0.4114(2)	5.3(1)
C(9)	−0.0246(3)	0.3608(5)	0.3119(2)	4.52(9)
C(10)	0.2488(3)	0.3836(5)	0.3130(1)	3.26(7)
C(11)	0.2955(3)	0.4756(5)	0.2661(1)	3.79(8)
C(12)	0.3376(3)	0.6556(6)	0.2736(2)	4.73(9)
C(13)	0.3843(4)	0.7414(6)	0.2315(2)	5.9(1)
C(14)	0.3889(4)	0.6501(8)	0.1810(2)	7.3(1)
C(15)	0.3455(4)	0.4789(8)	0.1723(2)	7.6(1)
C(16)	0.2990(4)	0.3858(7)	0.2142(2)	5.8(1)

140.8 Hz), 38.4(C(16) and C(17), $^1J(^{13}C-H)$ 140.8 Hz), 13.8(C(20), $^1J(^{13}C-H)$ 128 Hz) ppm. IR: ν (cm^{-1}) 2056, 2026, 1981, 1972, 1961, 1953(CO), 1739($CO_2C_2H_5$). Anal. Found: C, 39.22; H, 3.01; S, 10.55 Fe; 19.59. $C_{20}H_{18}Fe_2N_2O_8S_2$ calc.: C, 40.71; H, 3.32; S, 10.88; Fe: 19.59%.

Oxidative decomplexation of compounds II and III

$(CH_3)_3NO/2H_2O$ (18 mmol) was added to a solution of complex II or III (1 mmol) in methylene chloride (30 ml). The mixture was refluxed for 17 h with stirring. Filtration through silica gel and concentration under vaccum gave 4-dimethylamino-2-phenyl-1-thia-3-azabutadiene, Ia, which was purified by chromatography (Ia was obtained in 92 and 88% yield from II and III, respectively).

X-ray data collection and refinement

Crystals of complex II. $C_{16}H_{16}FeN_2O_5S$, $M = 404.2$, monoclinic, space group $P2_1/c$ with a 11.084(4), b 7.273(4), c 23.431(7) Å, β 104.88(3)°, $Z = 4$, μ 9.6 cm^{-1}.

Table 8

Atomic coordinates for complex III

Atom	x	y	z	B (Å^2)
Fe(1)	0.92903(4)	0.1425(1)	0.5493(1)	3.05(3)
Fe(2)	0.84992(4)	0.1330(1)	0.5909(1)	3.18(3)
S	0.90363(9)	0.2276(2)	0.6835(2)	3.30(7)
O(1)	0.9292(2)	0.5453(5)	0.5861(4)	3.5(2)
O(2)	0.8816(2)	0.5882(5)	0.4451(4)	3.1(2)
O(14)	0.8489(3)	−0.1171(6)	0.6631(5)	6.9(2)
O(15)	0.8109(2)	0.1129(7)	0.3773(5)	6.4(2)
O(16)	0.7701(2)	0.1919(6)	0.6705(5)	5.8(2)
O(17)	0.9112(3)	−0.0062(6)	0.3655(5)	6.0(2)
O(18)	0.9586(3)	−0.0735(6)	0.6615(5)	7.0(2)
O(19)	1.0192(2)	0.2233(7)	0.5501(6)	6.7(2)
N(1)	0.9329(2)	0.3932(6)	0.3757(5)	3.2(2)
N(2)	0.8990(2)	0.3002(6)	0.4999(5)	2.3(2)
C(1)	0.9597(3)	0.4937(9)	0.3509(7)	3.8(3)
C(2)	0.9308(4)	0.2895(9)	0.3117(7)	5.1(3)
C(3)	0.9131(3)	0.3956(7)	0.4575(6)	2.6(2)
C(4)	0.8720(3)	0.3026(8)	0.5798(6)	2.6(2)
C(5)	0.8422(3)	0.4016(8)	0.5908(7)	2.8(2)
C(6)	0.8428(3)	0.4611(9)	0.6830(7)	3.7(3)
C(7)	0.8135(3)	0.5477(9)	0.6964(8)	5.2(3)
C(8)	0.7806(3)	0.5777(9)	0.6182(9)	5.5(3)
C(9)	0.7794(3)	0.5215(9)	0.5250(8)	4.7(3)
C(10)	0.8100(3)	0.4337(8)	0.5131(8)	3.9(3)
C(11)	0.9087(3)	0.5189(8)	0.5053(7)	2.6(2)
C(12)	0.8726(3)	0.7059(9)	0.4859(8)	4.2(3)
C(13)	0.8377(3)	0.7628(9)	0.4128(7)	4.4(3)
C(14)	0.8497(4)	−0.0218(9)	0.6337(7)	4.4(3)
C(15)	0.8262(3)	0.1189(8)	0.4610(7)	4.0(3)
C(16)	0.8021(3)	0.1695(8)	0.6381(7)	4.0(3)
C(17)	0.9175(3)	0.0538(8)	0.4349(7)	4.1(3)
C(18)	0.9471(3)	0.0102(9)	0.6179(7)	4.4(3)
C(19)	0.9832(3)	0.1946(8)	0.5484(8)	3.9(3)

Table 9

Atomic coordinates for complex IV

Atom	x	y	z	B (Å^2)
Fe(1)	0.85045(7)	0.3351(1)	0.54147(6)	3.26(2)
Fe(2)	0.90179(7)	0.3455(1)	0.70234(6)	3.46(2)
S(1)	0.9900(1)	0.4593(2)	0.5894(1)	3.80(5)
S(2)	0.8025(1)	0.4844(2)	0.6083(1)	3.38(4)
O(1)	0.9771(4)	0.1219(6)	0.5382(4)	7.1(2)
O(2)	0.6859(4)	0.1626(6)	0.5060(4)	6.9(2)
O(3)	0.7701(4)	0.4328(6)	0.3693(3)	5.4(2)
O(4)	0.9411(5)	0.4608(6)	0.8646(3)	7.9(2)
O(5)	0.7476(4)	0.1764(6)	0.7089(3)	7.2(2)
O(6)	1.0474(4)	0.1432(6)	0.7464(4)	7.9(2)
O(7)	1.1036(4)	0.7848(6)	0.6565(3)	5.9(2)
O(8)	0.5241(3)	0.2398(5)	0.8122(3)	4.3(1)
N(1)	1.0756(4)	−0.4923(6)	0.7512(3)	3.7(2)
N(2)	0.7060(4)	0.8606(6)	0.3110(4)	4.2(2)
C(1)	0.9269(5)	0.2061(8)	0.5387(4)	4.3(2)
C(2)	0.7508(5)	0.2318(8)	0.5214(4)	4.2(2)
C(3)	0.8048(5)	0.3956(8)	0.4361(4)	3.9(2)
C(4)	0.9265(6)	0.4151(8)	0.8014(4)	5.1(2)
C(5)	0.8053(5)	0.2410(8)	0.7037(5)	4.8(2)
C(6)	0.9882(5)	0.2229(8)	0.7286(5)	5.0(2)
C(7)	0.6728(5)	0.4714(8)	0.5901(4)	4.2(2)
C(8)	0.6176(4)	0.5611(7)	0.5216(4)	3.3(2)
C(9)	0.5853(5)	0.5206(8)	0.4395(4)	4.2(2)
C(10)	0.4611(5)	0.3960(9)	0.6246(5)	5.0(2)
C(11)	0.4805(5)	0.2710(9)	0.6087(5)	5.5(2)
C(12)	0.4499(6)	0.2312(9)	0.5274(5)	5.4(2)
C(13)	0.5975(5)	0.6847(8)	0.5355(4)	4.6(2)
C(14)	0.4968(4)	−0.0480(7)	0.8096(4)	3.2(2)
C(15)	0.3815(5)	0.1183(7)	0.7447(4)	3.4(2)
C(16)	1.2607(7)	−0.463(1)	0.8624(7)	8.1(3)
C(17)	1.2504(6)	−0.235(1)	0.8317(6)	7.6(3)
C(18)	0.4340(5)	0.2255(7)	0.8059(4)	3.9(2)
C(19)	0.9159(6)	0.8263(9)	0.6231(6)	6.8(3)
C(20)	0.8342(8)	0.870(1)	0.6383(7)	9.5(4)

Number of independent reflexions used: 1965 ($R_{\text{int}} = 0.023$, $I > 2\sigma(I)$), $R = 0.043$, $R_{\text{w}} = 0.035$.

Crystals of complex III. $C_{19}H_{16}Fe_2N_2O_8S$, $M = 544.1$ monoclinic, space group $C2/c$ with a 30.819(9), b 11.173(6), c 13.365(5) Å, β 99.2(3)°, $Z = 8$, μ 14.1 cm^{-1}. Number of independent reflexions used: 1287 ($R_{\text{int}} = 0.028$, $I > \sigma(I)$), $R = 0.051$, $R_{\text{w}} = 0.040$.

Crystals of complex IV. $C_{20}H_{18}Fe_2N_2O_8S_2$, $M = 590.2$, monoclinic, space group $P2_1/n$ with a 15.048(6), b 10.399(4), c 17.661(9) Å, β 114.26(4)°, $Z = 4$, μ 13.54 cm^{-1}. Number of independent reflexions used: 2133 ($R_{\text{int}} = 0.024$, $I > \sigma$ (I)), $R = 0.054$, $R_{\text{w}} = 0.048$.

Data for all structures were collected on an Enraf–Nonius CAD-4 diffractometer with Mo-K_α graphite monochromated radiation (λ 0.71073 Å). The structure were solved by the Patterson method followed by isotropic and anisotropic refinements.

The best full matrix least-square refinement (x, y, z, β_{ij} for C, Fe, N, O and S atoms; x, y, z for H atoms) gives R and R_w. Lists of atomic coordinates are given in Tables 7–9. Tables of thermal parameters and lists of structure factors are available from the authors.

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