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Transition-Metal Heterocyclic Chemistry. 10.[1] A Dimeric Selenoketoketene Complex and Doubly Reduced Thioketohydrazonato Complexes from Reactions of 1,2,3-Selena- and 1,2,3-Thiadiazoles with Diiron Enneacarbonyl in the Presence of Alcohol†

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When the reactions of 1,2,3-selena- and 1,2,3-thiadiazoles with Fe$_2$(CO)$_9$ are carried out in the presence of ethanol, two new complexes, a bis(selenoketoketene) complex with two of the organic ligands connected by two iron tricarbonyl fragments from the selenadiazole (**3**) and a thiolato–hydrazonato complex (**7**) from the ring-opened and doubly reduced thiadiazole, are obtained. The presence of alcohol is essential to generate these complexes. It is thought that the potential of alcohols to function as reducing reagents as well as labile ligands in intermediate iron complexes contribute to a reaction pattern different from previously reported results.

Introduction

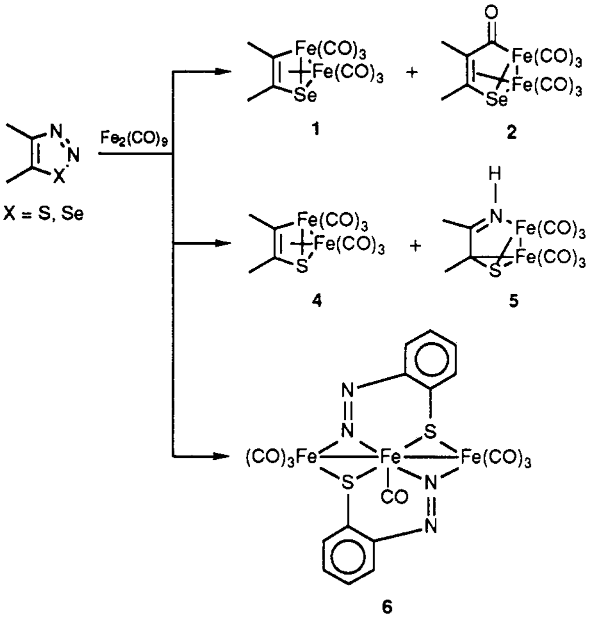
1,2,3-Selena- and 1,2,3-thiadiazoles are the cyclic analogues of α-diazocarbonyl compounds. Herrmann has extensively studied the reactions of the diazocarbonyl compounds with reactive molybdenum and manganese carbonyl complexes and reported the formation of carbene complexes (N$_2$ elimination),[2] ketene complexes (N$_2$ elimination and CO insertion),[3] imine complexes (reductive elimination of "N"),[3,4] and complexes from the unfragmented diazo compound.[5] The chemistry of the heteroaromatic diazoles with reactive transition-metal carbonyls has been investigated by several researchers[6-15] and was found to follow similar reaction pathways. Thus, reactions of 1,2,3-selena- and 1,2,3-thiadiazoles with Fe$_2$(CO)$_9$ in hexane led to complexes where nitrogen has been either entirely or in part eliminated from the heterocyclic aromatic system to produce carbene (**1**, **4**),[6,7,11,12] ketene (**2**),[11] and imine diiron hexacarbonyl complexes (**5**).[13] In the case of 1,2,3-benzothiadiazole a linear triiron cluster (**6**) with two attached ring-opened but otherwise intact diazole molecules, i.e. α-diazo thioketone moieties, was formed.[14] On the basis of these findings, the initial step in the reactions of the heterocyclic diazoles was suggested to be a transition-metal-initiated ring cleavage of the diazole followed by reactions similar to those of α-diazocarbonyl compounds.

Results and Discussion

The reaction of cyclohexa-1,2,3-selenadiazole with Fe$_2$(CO)$_9$ in 20% ethanol/hexane led not only to the formation of the products already obtained from the same reaction in hexane (**1a** and **2a**) but also to a new complex that was identified by single-crystal X-ray techniques as the bis(selenoketoketene) complex **3a**.

Complex **3a** is structurally related to the selenoketoketene complex **2a**[11] in regard to the organic ligand. The most striking feature of the new compound is the syn arrangement of the two selenoketoketene fragments about a shared and almost perfectly square Fe$_2$Se$_2$ unit with the iron atoms in a slightly distorted octahedral environment

Scheme I



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† Dedicated to Professor Gottfried Märkl on the occasion of his 60th birthday.

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Table I. Spectroscopic Data of Complexes 2a[a] and 3a

	IR ν(CO),[b] cm^{-1}	^{1}H NMR,[c] ppm	^{13}C NMR,[c] ppm
2a	2084, 2041, 2012, 2002, 1614	1.50–2.30 (m, 6 H), 2.90–3.30 (m, 2 H)	20.38, 23.88, 28.08, 35.32, 105.04, 130.08, 203.21, 207.33, 208.96, 209.42
3a	2083, 2068, 2026, 2017, 2003, 1641	1.50–2.70 (m)	20.96, 24.36, 27.90, 30.50, 148.78, 153.12, 201.05, 202.65, 205.08, 251.80

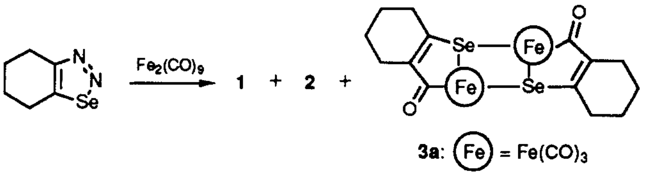
[a] For comparison. [b] In hexane. [c] In CDCl$_3$.

Table II. Spectroscopic Data of Complexes 5a,b[a] and 7a–e

	IR ν(CO), (ν(NH)),[b] cm^{-1}	^{1}H NMR,[c] ppm	^{13}C NMR,[c] ppm
5b	2079, 2021, 1999, 1990, 1960, (3353)	2.08 (s, 3 H), 2.92 (d, 1 H), 5.80 (s, 1 H)	22.52, 23.47, 35.53, 39.07, 66.72, 199.26, 212.87
5c	2078, 2020, 1998, 1989, 1966, (3354)	1.18 (s, 9 H), 3.31 (d, 1 H), 6.00 (s, 1 H)	27.97, 40.08, 48.12, 198.72, 213.24
7a	2073, 2036, 1995, 1990, (3341)	1.06–2.30 (m, 9 H), 6.90 (s, 1 H)	26.29, 26.92, 31.44, 34.45, 37.10, 161.00, 208.30
7b	2073, 2036, 1997, 1992, (3338)	1.88 (s, 3 H), 2.23 (s, 3 H), 7.20 (s, 1 H)	21.14 (t), 25.30 (q), 156.08 (s), 208.26 (s)
7c	2073, 2037, 1993, 1989, (3341)	1.16 (s, 9 H), 2.43 (s, 2 H), 7.10 (s, 1 H)	16.27 (t), 28.72 (q), 165.05 (s), 208.38 (s)
7d	2073, 2037, 1998, 1995, (3345)	2.65 (s, 2 H), 7.09–7.50 (m, 6 H)	18.75, 154.67, 125.22, 126.87, 130.17, 137.10, 207.75
7e	2074, 2038, 1997, 1994, (3338)	2.57 (s, 2 H), 6.86, 6.76, 6.58, 6.49 (AB-q, 2 H), 7.27–7.40 (m, 6 H)	18.04, 156.08, 127.02, 127.83, 128.84, 135.51, 130.98, 131.87, 208.12

[a] For comparison (from ref 13). [b] In hexane (dichloromethane). [c] In CDCl$_3$.

Scheme II



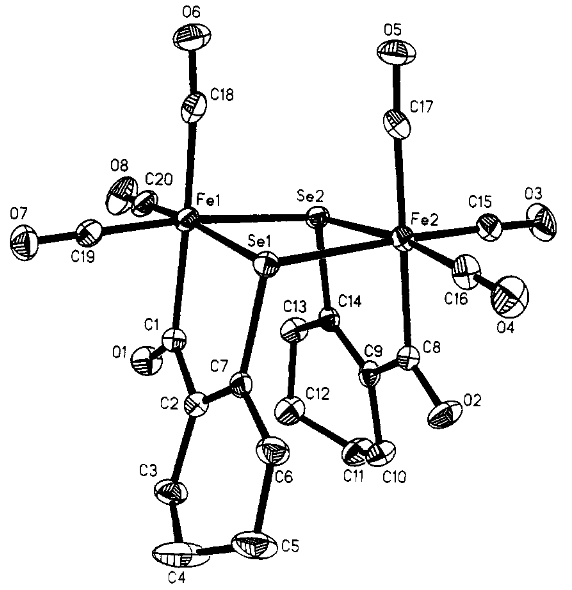
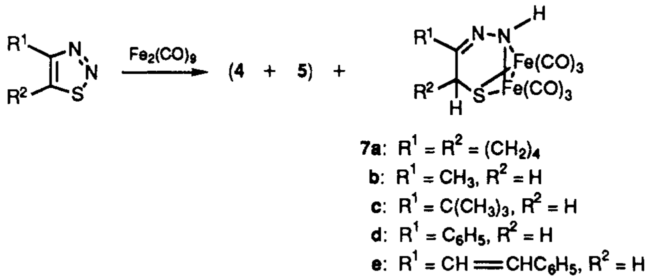


Figure 1. ORTEP representation of complex **3a**. Thermal ellipsoids are shown for the 25% probability level.

Scheme III



(see Figure 1). The position of one CO ligand almost exactly trans to the acyl group is responsible for the deshielding of the acyl carbon in ^{13}C NMR (251.80 ppm, Table II). With the exception of the C=C bond, which functions as a π-donor fragment in **2** but not in **3** [bond lengths 1.378 (12) Å for **2a** vs 1.329 (9) Å for **3a**], characteristic bond lengths and angles are rather similar for the organic ligands in the two complexes (structural data for **2a** in ref 11). The ^{13}C chemical shifts in the NMR spectra of the complexes also confirm the π-donor character of the C=C double bond only in **2**: 105.04, 130.08 ppm for **2a** vs 148.78, 153.12 ppm for **3a**. At 300 K, the carbonyl ligands at iron are not fluxional as indicated by the three distinct carbonyl signals in the ^{13}C NMR spectra of **2a** and **3a** (Table II).

One unexpected property of **3** is its thermal stability: whereas the elimination of CO is facile for **2** (activation energies of about 15 kcal/mol were determined for the thermal reaction of **2** → **1**, depending on the substituents[15]), the bis(selenoketoketene) complex **3a** does not decarbonylate under similar conditions. Thermal treatment led to indiscriminant decomposition, and a similar result was observed when a hexane solution of **3a** was irradiated over a prolonged period of time.

When 1,2,3-thiadiazoles are reacted with Fe$_2$(CO)$_9$ in the presence of alcohol, thioketohydrazonato complexes **7** are formed. The yields of **7** depend on the quantity of alcohol in the solvent mixture: in pure hexane the products are **4** and **5**,[13] in ethanol complex **7** is almost exclusively formed, and in alcohol/hexane mixtures all three complexes are produced.

The X-ray structure (Figure 2) shows complex **7b** to contain a doubly hydrogenated and ring-opened thiadiazole

Table III. Analytical Data and Melting Points of Compounds 3a and 7a–e

	mol wt	anal.[a] C	H	N	mp, °C
3a	653.96 ($C_{20}H_{16}Fe_2O_8Se_2$)	36.96 (36.73)	2.52 (2.47)		>200 dec (red prisms)
7a	421.98 ($C_{12}H_{10}Fe_2N_2O_6S$)	34.24 (34.16)	2.40 (2.39)	6.65 (6.63)	166–168 (red prisms)
7b	381.91 ($C_9H_6Fe_2N_2O_6S$)	28.21 (28.30)	1.51 (1.58)	7.42 (7.33)	154–156 (red prisms)
7c	423.99 ($C_{12}H_{12}Fe_2N_2O_6S$)	34.13 (33.99)	2.93 (2.85)	6.61 (6.61)	120–121 (red prisms)
7d	443.98 ($C_{14}H_8Fe_2N_2O_6S$)	38.01 (37.87)	1.87 (1.82)	6.32 (6.31)	144–145 (red prisms)
7e	470.02 ($C_{16}H_{10}Fe_2N_2O_6S$)	41.11 (40.89)	2.28 (2.14)	5.98 (5.96)	154–156 (red prisms)

[a] Calculated values in parentheses.

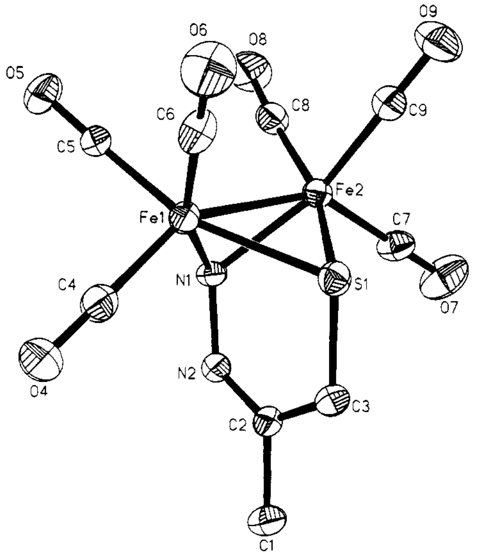


Figure 2. ORTEP representation of complex **7b**. Thermal ellipsoids correspond to 25% probability. There are two molecules in the asymmetric unit which differ slightly in orientation of the CO ligands. Bond lengths and angles are similar.

Table IV. Structure Determination Summary for Compounds 3a and 7b

	3a	**7b**
	Crystal Data	
empirical formula	$C_{20}H_{16}O_8Fe_2Se_2$	$C_9H_6N_2O_6SFe_2$
color, habit	red, prism	red, prism
cryst size, mm	0.16 × 0.16 × 0.14	0.12 × 0.46 × 0.50
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
unit cell dimensns		
a, Å	9.605 (3)	12.207 (4)
b, Å	9.462 (3)	10.493 (3)
c, Å	24.691 (9)	23.076 (8)
β, deg	95.64 (3)	96.29 (3)
V, Å^3	2233.1 (12)	2938 (2)
Z	4	8
fw	653.9	381.9
D(calcd), Mg/m^3	1.945	1.727
abs coeff, mm^{-1}	4.278	2.133
F(000)	1280	1520
	Solution and Refinement	
system used	Nicolet SHELXTL PLUS (MicroVAX II)	Nicolet SHELXTL PLUS (MicroVAX II)
soln	direct methods	direct methods
refinement method	full-matrix least squares	full-matrix least squares
quantity minimized	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$
absolute configuration	N/A	N/A
extinctn correctn	$\chi = 0.000\,23\ (3)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$	$\chi = 0.000\,14\ (3)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
hydrogen atoms	riding model, fixed isotropic U	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0001F^2$	$w^{-1} = \sigma^2(F) + 0.0003F^2$
final R indices (obsd data)	$R = 3.71$, w$R = 3.18$	$R = 3.65$, w$R = 3.90$
R indicies (all data)	$R = 5.15$, w$R = 3.34$	$R = 6.03$, w$R = 14.84$
goodness-of-fit	1.24	1.12
largest and mean Δ/σ	0.973, −0.001	0.296, 0.009
data-to-parameter Ratio	8.3:1	7.7:1
largest diff peak, e Å^{-3}	0.55	0.66
largest diff hole, e Å^{-3}	−0.47	−0.26
	Data Collection	
diffractometer used	Nicolet R3m/V	Nicolet R3m/V
radiatn	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
temp, K	298	298
monochromator	highly oriented graphite crystal	highly oriented graphite crystal
2θ range, deg	3.5–45.0	3.5–45.0
scan type	ω	ω
scan speed, deg/min	variable; 3.00–15.00 in ω	variable; 3.00–15.00 in ω
scan range (ω), deg	1.40	1.20
bkgnd measurement	stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time	stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
std reflctns	2 measd every 50 reflctns	2 measd every 100 reflctns
index ranges	$-1 \leq h \leq 10, -3 \leq k \leq 10, -26 \leq l \leq 26$	0 <eq $h \leq 13, 0 \leq k \leq 11, -24 \leq l \leq 24$
reflctns collected	3493	4411
independent reflctns	2917 (R_{int} = 0.89%)	3838 (R_{int} = 1.28%)
obsd reflctns	2400 ($R > 3.0\sigma(F)$)	2804 ($F > 4.0\sigma(F)$
abs correctn	N/A	semiempirical
min/max transmission		0.284/0.355

where the $Fe_2(CO)_6$ unit is held perpendicular to the perfect plane of the NNCCS fragment. C2N2 are connected by a double bond, evident from the bond distance of 1.27 Å and the carbon resonance in ^{13}C NMR. The chemical shift of the imine vs the hydrazone carbon in the ^{13}C NMR spectrum (about 200 ppm in **5** compared with 150 ppm in **7**) seems diagnostic. At 300 K, the CO ligands in complexes **5** and **7** are fluxional as indicated by only one sharp single carbon resonance (see Table II for NMR data).

The selenadiazoles produced in general only iron complexes where nitrogen was entirely eliminated (**1**, **2**, **3**), whereas the ability of the thiadiazoles to produce nitrogen-containing complexes is demonstrated by the formation of the imino complexes **5**, the trinuclear cluster **6**, and the thioketohydrazonato complexes **7** from 1,2,3-thiadiazoles and iron enneacarbonyl. That the selenium and sulfur heterocyclic compounds, despite their similar constitutions, are dramatically different in their reactivities toward transition-metal complexes is not surprising, however, when the donor qualities of the chalcogen atoms are considered.

Why the product formation in the described reactions depends on the presence or the absence of alcohol is not entirely understood. Since we have previously shown that with selenadiazoles, an insertion of CO to produce the mono(selenoketoketene) complex **2** takes place in the absence of alcohol,[11] it is reasonable to assume that in the selenadiazole reaction the alcohol is stabilizing an intermediate iron complex responsible for the formation of the dimeric selenoketoketene complex **3**, thus altering the reaction pathway. On the other hand, the double reduction of the thiadiazole to produce hydrazonato complexes **7** suggests that the alcohol was functioning as a reducing reagent and a source of hydrogen. Indeed, **7** is not formed when the same reaction is carried out in the presence of THF instead of ethanol.

Experimental Section

Published procedures[16-18] were followed to synthesize the 1,2,3-selena- and 1,2,3-thiadiazoles. All reactions with $Fe_2(CO)_9$ were carried out in dry and N_2-saturated solvents under an inert atmosphere, employing conventional Schlenck techniques. The reported melting points are uncorrected. Elemental analyses were carried out by Galbraith Laboratories Inc., Knoxville, TN. Spectra were measured with the following instruments: Perkin-Elmer PE-580 (IR), IBM-Bruker WP-200SY (NMR).

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Table V. Bond Lengths and Bond Angles for 3a

Bond Lengths (Å)			
Se(1)–Fe(1)	2.403 (1)	Se(1)–Fe(2)	2.462 (1)
Se(1)–C(7)	1.911 (6)	Se(2)–Fe(1)	2.462 (1)
Se(2)–Fe(2)	2.399 (1)	Se(2)–C(14)	1.913 (6)
Fe(1)–C(1)	2.042 (6)	Fe(1)–C(18)	1.858 (7)
Fe(1)–C(19)	1.788 (6)	Fe(1)–C(20)	1.797 (7)
Fe(2)–C(17)	1.860 (7)	Fe(2)–C(16)	1.806 (7)
Fe(2)–C(8)	2.035 (6)	Fe(2)–C(15)	1.785 (7)
O(5)–C(17)	1.132 (8)	O(3)–C(15)	1.129 (9)
C(14)–C(9)	1.338 (8)	C(14)–C(13)	1.510 (9)
O(4)–C(16)	1.125 (9)	C(1)–C(2)	1.504 (9)
C(1)–O(1)	1.214 (8)	C(9)–C(8)	1.509 (9)
C(9)–C(10)	1.503 (9)	O(7)–C(19)	1.137 (8)
O(8)–C(20)	1.134 (9)	C(7)–C(2)	1.329 (9)
C(7)–C(6)	1.504 (9)	C(2)–C(3)	1.495 (9)
O(6)–C(18)	1.143 (9)	C(8)–O(2)	1.206 (8)
C(10)–C(11)	1.532 (10)	C(3)–C(4)	1.504 (12)
C(13)–C(12)	1.515 (9)	C(6)–C(5)	1.516 (11)
C(12)–C(11)	1.477 (10)	C(4)–C(5)	1.387 (12)
Bond Angles (deg)			
Fe(1)–Se(1)–Fe(2)	95.9 (1)	Fe(1)–Se(1)–C(7)	95.5 (2)
Fe(2)–Se(1)–C(7)	107.5 (2)	Fe(1)–Se(2)–Fe(2)	96.0 (1)
Fe(1)–Se(2)–C(14)	104.7 (2)	Fe(2)–Se(2)–C(14)	95.8 (2)
Se(1)–Fe(1)–Se(2)	83.4 (1)	Se(1)–Fe(1)–C(1)	85.9 (2)
Se(2)–Fe(1)–C(1)	92.1 (2)	Se(1)–Fe(1)–C(18)	92.4 (2)
Se(2)–Fe(1)–C(18)	91.7 (2)	C(1)–Fe(1)–C(18)	175.6 (3)
Se(1)–Fe(1)–C(19)	91.0 (2)	Se(2)–Fe(1)–C(19)	172.7 (2)
C(1)–Fe(1)–C(19)	82.9 (3)	C(18)–Fe(1)–C(19)	93.1 (3)
Se(1)–Fe(1)–C(20)	169.1 (2)	Se(2)–Fe(1)–C(20)	89.3 (2)
C(1)–Fe(1)–C(20)	86.4 (3)	C(18)–Fe(1)–C(20)	95.9 (3)
C(19)–Fe(1)–C(20)	95.6 (3)	Se(1)–Fe(2)–Se(2)	83.5 (1)
Se(1)–Fe(2)–C(17)	88.6 (2)	Se(2)–Fe(2)–C(17)	91.8 (2)
Se(1)–Fe(2)–C(16)	91.3 (2)	Se(2)–Fe(2)–C(16)	171.7 (2)
C(17)–Fe(2)–C(16)	94.4 (3)	Se(1)–Fe(2)–C(8)	92.0 (2)
Se(2)–Fe(2)–C(8)	86.4 (2)	C(17)–Fe(2)–C(8)	178.0 (3)
C(16)–Fe(2)–C(8)	87.5 (3)	Se(1)–Fe(2)–C(15)	173.2 (2)
Se(2)–Fe(2)–C(15)	91.0 (2)	C(17)–Fe(2)–C(15)	95.6 (3)
C(16)–Fe(2)–C(15)	93.8 (3)	C(8)–Fe(2)–C(15)	83.6 (3)
Se(2)–C(14)–C(9)	118.8 (4)	Se(2)–C(14)–C(13)	116.8 (4)
C(9)–C(14)–C(13)	124.5 (5)	Fe(1)–C(1)–C(2)	117.8 (4)
Fe(1)–C(1)–O(1)	123.1 (5)	C(2)–C(1)–O(1)	119.0 (5)
C(14)–C(9)–C(8)	120.4 (5)	C(14)–C(9)–C(10)	122.3 (6)
C(8)–C(9)–C(10)	117.3 (5)	Fe(2)–C(17)–O(5)	177.4 (6)
Se(1)–C(7)–C(2)	119.1 (4)	Se(1)–C(7)–C(6)	116.3 (4)
C(2)–C(7)–C(6)	124.5 (5)	Fe(2)–C(16)–O(4)	177.8 (7)
C(1)–C(2)–C(7)	120.2 (5)	C(1)–C(2)–C(3)	117.1 (5)
C(7)–C(2)–C(3)	122.7 (6)	Fe(1)–C(18)–O(6)	174.7 (6)
Fe(2)–C(8)–C(9)	118.2 (4)	Fe(2)–C(8)–O(2)	123.3 (5)
C(9)–C(8)–O(2)	118.4 (5)	Fe(1)–C(19)–O(7)	179.5 (6)
Fe(1)–C(20)–O(8)	177.3 (6)	C(9)–C(10)–C(11)	111.9 (5)
Fe(2)–C(15)–O(3)	178.4 (6)	C(2)–C(3)–C(4)	111.0 (6)
C(14)–C(13)–C(12)	110.7 (5)	C(7)–C(6)–C(5)	110.8 (6)
C(13)–C(12)–C(11)	112.5 (6)	C(10)–C(11)–C(12)	112.7 (6)
C(3)–C(4)–C(5)	117.3 (7)	C(6)–C(5)–C(4)	116.8 (8)

Table VI. Bond Lengths and Bond Angles for 7b.

Bond Lengths (Å)			
Fe(1)–Fe(2)	2.459 (1)	Fe(1)–S(1)	2.253 (2)
Fe(1)–N(1)	1.964 (4)	Fe(1)–C(5)	1.807 (6)
Fe(1)–C(4)	1.792 (6)	Fe(1)–C(6)	1.798 (7)
Fe(2)–S(1)	2.245 (2)	Fe(2)–N(1)	1.973 (4)
Fe(2)–C(8)	1.796 (6)	Fe(2)–C(9)	1.782 (6)
Fe(2)–C(7)	1.783 (6)	S(1)–C(3)	1.789 (6)
N(1)–N(2)	1.425 (6)	N(2)–C(2)	1.268 (7)
C(1)–C(2)	1.513 (8)	C(2)–C(3)	1.498 (8)
O(6)–C(6)	1.133 (8)	O(7)–C(7)	1.135 (8)
O(8)–C(8)	1.134 (8)	O(4)–C(4)	1.146 (8)
C(9)–O(9)	1.144 (8)	O(5)–C(5)	1.120 (7)
Bond Angles (deg)			
Fe(2)–Fe(1)–S(1)	56.7 (1)	Fe(2)–Fe(1)–N(1)	51.5 (1)
S(1)–Fe(1)–N(1)	80.4 (1)	Fe(2)–Fe(1)–C(5)	102.6 (2)
S(1)–Fe(1)–C(5)	158.0 (2)	N(1)–Fe(1)–C(5)	92.2 (2)
Fe(2)–Fe(1)–C(4)	148.2 (2)	S(1)–Fe(1)–C(4)	104.7 (2)
N(1)–Fe(1)–C(4)	103.5 (2)	C(5)–Fe(1)–C(4)	97.1 (3)
Fe(2)–Fe(1)–C(6)	106.7 (2)	S(1)–Fe(1)–C(6)	89.2 (2)
N(1)–Fe(1)–C(6)	158.0 (2)	C(5)–Fe(1)–C(6)	90.4 (3)
C(4)–Fe(1)–C(6)	97.9 (3)	Fe(1)–Fe(2)–S(1)	57.0 (1)
Fe(1)–Fe(2)–N(1)	51.2 (1)	S(1)–Fe(2)–N(1)	80.4 (1)
Fe(1)–Fe(2)–C(8)	103.6 (2)	S(1)–Fe(2)–C(8)	159.6 (2)
N(1)–Fe(2)–C(8)	91.9 (2)	Fe(1)–Fe(2)–C(9)	106.4 (2)
S(1)–Fe(2)–C(9)	89.2 (2)	N(1)–Fe(2)–C(9)	157.4 (2)
C(8)–Fe(2)–C(9)	91.0 (3)	Fe(1)–Fe(2)–C(7)	145.6 (2)
S(1)–Fe(2)–C(7)	101.5 (2)	N(1)–Fe(2)–C(7)	102.7 (2)
C(8)–Fe(2)–C(7)	98.6 (3)	C(9)–Fe(2)–C(7)	99.0 (3)
Fe(1)–S(1)–Fe(2)	66.3 (1)	Fe(1)–S(1)–C(3)	107.6 (2)
Fe(2)–S(1)–C(3)	105.3 (2)	Fe(1)–N(1)–Fe(2)	77.3 (2)
Fe(1)–N(1)–N(2)	124.7 (3)	Fe(2)–N(1)–N(2)	125.2 (3)
N(1)–N(2)–C(2)	120.2 (4)	N(2)–C(2)–C(1)	117.0 (5)
N(2)–C(2)–C(3)	127.9 (5)	C(1)–C(2)–C(3)	115.0 (5)
S(1)–C(3)–C(2)	119.2 (4)	Fe(2)–C(8)–O(8)	176.5 (5)
Fe(2)–C(9)–O(9)	179.7 (7)	Fe(1)–C(5)–O(5)	177.6 (5)
Fe(1)–C(4)–O(4)	178.7 (6)	Fe(1)–C(6)–O(6)	178.1 (6)
Fe(2)–C(7)–O(7)	178.9 (6)		

(a) Reaction of Cyclohexa-1,2,3-selenadiazole with $Fe_2(CO)_9$. A solution of 1.0 g (5.3 mmol) of cyclohexa-1,2,3-selenadiazole in 50 mL of hexane and 20 mL of ethanol was stirred with 5.0 g of $Fe_2(CO)_9$ (13.7 mmol) at ambient temperature until the iron carbonyl was completely consumed (about 12 h). The solvent was stripped off under reduced pressure and the dark residue dissolved in a small amount of dichloromethane and chromatographed on an alumina column (2 × 30 cm). The following fractions are obtained: the (selenoketocarbene)diiron complex **1a** as an orange band (eluted with pure hexane; 0.23 g, 10%), the selenonoketoketene complex **2a** as a reddish brown band (eluted with hexane/dichloromethane (1:1); 0.30 g, 12%), and the bis(selenoketoketene)diiron complex **3a** as a brick-red band (eluted with hexane/dichloromethane (1:5) and recrystallized from hexane/CH_2Cl_2 (4:1) at −30 °C; 0.24 g, 14%). The physical and spectral properties of complexes **1a** and **2a** match the reported data.[11,12] See Table III for complex **3a**.

(b) Reaction of Cyclohexa-1,2,3-thiadiazole with $Fe_2(CO)_9$. A solution of 1.0 g (7.1 mmol) of cyclohexa-1,2,3-thiadiazole in 50 mL of ethanol was stirred with 8.0 g of $Fe_2(CO)_9$ (22 mmol) at room temperature for 12 h. The solvent was distilled off and the dark residue dissolved in the minimum amount of CH_2Cl_2 and placed on an alumina column (2 × 30 cm). Following trace amounts of other complexes (complex **4a** was identified by IR) an orange-red band was eluted with hexane/dichloromethane (1:4). After the solvent was evaporated in vacuo, complex **7a** was recrystallized from hexane/CH_2Cl_2 (9:1) at −30 °C (1.20 g, 40%). The reactions of 4-substituted 1,2,3-thiadiazoles were carried out under similar conditions and led to the formation of complexes **7b** (R = CH_3; 34%), **7c** (R = $C(CH_3)_3$; 38%), **7d** (R = C_6H_5; 42%), and **7e** (R = $CH{=}CHC_6H_5$; 36%). The analytical data and the melting points of **3a** and **7a** to **7e** are listed in Table III.

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Supplementary Material Available: Tables giving the structure determination summary, final atomic coordinates, thermal parameters, bond lengths and angles, and hydrogen atom coordinates for **3a** and **7b** and an ORTEP drawing of **7b** (19 pages); tables of final observed and calculated structure factors for **3a** and **7b** (25 pages). Ordering information is given on any current masthead page.