Organometallics **2000,** *19,* 4127−4133

Synthesis and Characterization of Novel Iron(0) Complexes Derived from α,*β*-Unsaturated-Ketone Analogues with *β*-Positioned Heteroatoms Containing Covalent and Coordination Bonds

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Received May 22, 2000

Synthesis of novel mono- and dinuclear complexes of Fe(0) are reported displaying both coordination and organometallic bonds. **5**−**11** were prepared by allowing the new ligands **1**−**4** to react with $Fe_2(CO)_9$. The structures of the complexes were determined by spectroscopic methods (IR, MS, HR-MS, ^{1}H and ^{13}C NMR) and confirmed by single-crystal X-ray analysis.

Introduction

The ever-growing and longstanding interest in Fe(0) complexes stems mainly from their structural diversity and widespread applications. Nowadays, the utility of such compounds—mainly issued from conventional α,*β*-unsaturated systems—ranges, inter alia, from potential new applications in organic synthetic chemistry to the usual efforts in understanding fundamental chemistry and physical properties.[1−8]

Also, most attention on this subject has so far been aimed at synthesizing novel complexes derived from a wide-ranging assortment of functionalized ligands with the aim of exploring novel coordination patterns and their reactivity, and, as a part of an ongoing project centered on the preparation and reactivity of such complexes, we are currently focusing our efforts on the coordination ability of Fe(0) toward α,*β*-unsaturated-ketone analogues, mainly with *β*-positioned heteroatoms.

Thus, recently we have reported the synthesis of new dinuclear Fe(0) complexes obtained from the reaction of $Fe_2(CO)_9$ with 1,2-dicarbonyl monohydrazones conceived as α,*β*-unsaturated-ketone analogues with heteroatoms in *β*-position.[9] Also, building on the success achieved by varying the functional groups attached to α,*β*-unsaturated ketones, we extended our studies to include the dithiol group *β*-positioned on α,*β*-unsaturated carbonylic compounds, and we succeeded in the preparation of new dinuclear Fe(0) complexes derived from *para*-substituted derivatives of benzoyldithioacetic acid displaying a σ-S coordination instead of the usual η^2 or η^4 π-coordination upon the α,*β*-unsaturated system of the ligands.[10] On the other hand, previous work on the synthesis and structural characterization of related Fe(0) complexes of α,*β*-unsaturated imines has been recently reported.[11−13]

A logical extension concerning the reactivity of these classes of ligands was therefore considering compounds in which an additional conjugated double bond is present, such as 4-phenyl-1-(1,3-dithiolane-2-ylidene)-3*E*-butenone, **1**, 4-(2-pyridyl)-1-(1,3-dithiolane-2-ylidene)-3*E*-butenone, **2**, *N*,*N*-dimethyl hydrazono-1-(1,3-dithiolane-2-ylidene)-propan-2-one, **3**, and *N*,*N*-dimethyl hydrazono-1-(1,3-dithiane-2-yliden)-propan-2-one, **4** (Scheme 1), and herein we report the preparation of novel mono- and dinuclear Fe(0) complexes **5**−**11** starting from these new ligands **1**−**4**.

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10.1021/om0004702 CCC: $19.00
Publication on Web 09/02/2000

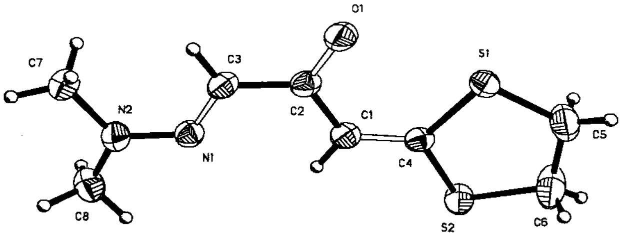
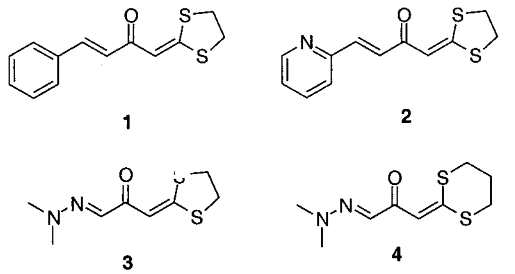


Figure 1. ORTEP drawing of compound **3**. Thermal ellipsoids at 30% probability level.

Scheme 1



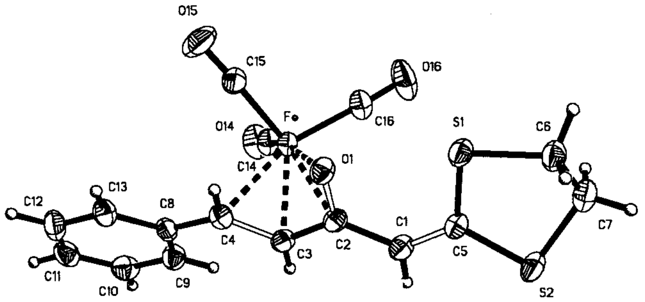
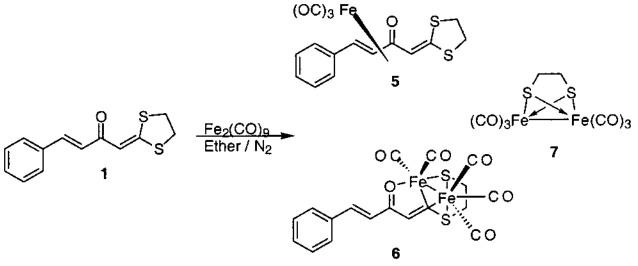


Figure 2. ORTEP drawing of complex **5**. Thermal ellipsoids at 30% probability level.

Scheme 2



Results and Discussion

The ligands **1** and **2** were conveniently prepared by a condensation reaction from the 1-(1,3-dithiolane-2-ylidene) acetone derivative and benzaldehyde or 2-pyridinecarboxaldehyde using known procedures.[14] On the other hand, compounds **3** and **4** were prepared by condensation of the pyruvaldehyde hydrazone and CS_2 and further alkylation, by a modification of Larson's method.[15]

As far as we are aware, there are no reports concerning the synthesis of compounds **2**, **3**, and **4**. For **3**, a single crystal was obtained, and Figure 1 shows that the molecule is essentially planar, with the 1,3-dithiolane ring adopting an envelope conformation with the carbon atom C6 as a flap (−0.291 Å out of the mean plane) and displaying an *s-trans* conformation for the ketoimine moiety, probably stabilized by an intramolecular C−H···N interaction between the N1 and H1 (2.48 Å) (Figure 1). The shortening in the N1−N2 bond length (Table 2) and the sum of bond angles around N2 ($\Sigma = 359.1°$) indicate an extensive interaction of the lone pair of the dimethyl amino nitrogen atom with the ketoimine system.

Magnetic stirring of a solution of **1** and $Fe_2(CO)_9$ in anhydrous diethyl ether led to the formation of complexes **5**−**7**, which were isolated by silica gel chromatography after the usual workup (Scheme 2).

The new complex **5**, obtained as an air-stable red crystalline solid, was characterized by spectroscopic methods and the structure fully confirmed by single-crystal X-ray analysis. Thus, the IR spectrum showed absorption bands in the ν(M−CO) region at 2062, 2004, and 1985 cm^{-1}, and a band at 1601 cm^{-1}, assigned to a coordinated α,β-unsaturated CO group, was also observed. The ^{1}H NMR spectrum (300 MHz, $CDCl_3$) exhibited signals—besides those corresponding to the aromatic protons at δ 7.25 ppm—at δ 7.5 and 5.9 of an AB system integrating for 2H (J = 7.4 Hz) assigned to the coordinated double bond of the α,β-unsaturated carbonylic system, appearing shifted upfield with respect to those of the ligand, and also two other signals: a doublet at δ 3.4 (4H) and a singlet at 6.7 (1H), belonging to the methylene groups joined to the sulfur atoms and the vinylic proton from the noncoordinated double bond, respectively. From the ^{13}C NMR data (75 MHz, $CDCl_3$), the presence of the metallic M−CO groups and the coordinated double bond was also confirmed by the signals at δ 211.6, 74.8, and 61.2 ppm, respectively, with the rest of the molecule appearing in a normal mode; that is, the signals are quite similar to those of the ligand. In the mass spectrum a peak is noticed at m/z 360 assigned to the fragment [M$^+$−28] and the successive loss of two CO groups along with the iron atom and the peak base at m/z 248 owing to the molecular weight of the free ligand. To ascertain the precise nature of **5**, an X-ray crystallographic study was carried out. As can be seen in Figure 2, the planar enone moiety and the phenyl ring make a dihedral angle of 27.5°, and the 1,3-dithiolane ring adopts an envelope conformation with the C7 carbon atom as a flap (0.645 Å). The $Fe(CO)_3$ fragment binds to the ligand in an η^4 fashion through the atom of the enone moiety O1−C2−C3−C4 (Figure 2). The coordination polyhedron can be best described as a trigonal bipyramid with two carbonyl groups and the C3=C4 double bond in the equatorial position and the O1 oxygen atom of the enone and the remaining carbonyl group in apical positions. This latter group seems to suffer the *trans* effect of O1, as judging by the differences among the Fe−C$_{\text{carbonyl}}$ distances (Table 3).

The second complex, **6**, obtained as a deep-red crystalline solid, exhibited in its IR spectrum absorption bands in the ν(M−CO) region at 2060, 2020, and 1953 cm^{-1}. The ^{1}H NMR spectrum (300 MHz, $CDCl_3$) showed, as the relevant features, two signals at δ 7.5 and 6.8 ppm (d, 1H, J = 15 Hz) assigned to the noncoordinated double bond as well as two multiplets at δ 3.3 and 2.1 ppm (2H for each signal) corresponding to the methylene group bearing the sulfur atoms. Finally, a singlet at 2.25

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Table 1. Summary of Crystal Data, Data Collection, and Refinement Details

	3	**5**	**6**	**8**	**9**
formula	$C_8H_{12}N_2OS_2$	$C_{16}H_{12}FeO_4S_2$	$C_{18}H_{12}Fe_2O_6S_2$	$C_{16}H_{11}FeNO_5S_2$	$C_{14}H_{1}2Fe_2N_2O_7S_2$
description	yellow block	red prism	deep-red prism	orange prism	deep-red plate
cryst size (mm)	0.60 × 0.60 × 0.40	0.32 × 0.20 × 0.20	0.60 × 0.44 × 0.40	0.56 × 0.24 × 0.20	0.44 × 0.18 × 0.04
a (Å)	8.335(1)	7.416(2)	8.411(1)	7.467(2)	16.072(6)
b (Å)	11.940(1)	10.182(3)	17.236(2)	10.255(2)	9.680(2)
c (Å)	11.324(3)	11.486(4)	14.038(3)	12.199(3)	13.174(3)
α (deg)	90	75.62(2)	90	82.16(2)	90
β (deg)	110.43(1)	87.70(2)	101.05(2)	73.35(3)	107.00(2
γ (deg)	90	80.13(2)	90	82.55(2)	90
U (Å^3)	1056.1(3)	827.7(4)	1997.4(5)	882.6(4)	1960.0(9)
F(000)	384	396	1008	424	1000
cryst syst	monoclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
Z	4	2	4	2	4
D_{calc} (Mg/m^3)	1.361	1.558	1.663	1.570	1.681
μ (mm^{-1})	0.468	1.178	1.693	1.117	1.730
T_{max}, T_{min}	0.730, 0.782	0.489, 0.595	0.382, 0.450	0.730, 0.754	0.654, 0.947
θ range (deg)	1.50−25.00	1.50−25.00	1.50−25.00	1.50−25.00	1.50−25.00
index ranges	$0 \leq h \leq 9$	$0 \leq h \leq 8$	$0 \leq h \leq 10$	$0 \leq h \leq 8$	$-19 \leq h \leq 18$
	$0 \leq k \leq 14$	$-11 \leq k \leq 11$	$0 \leq k \leq 20$	$-12 \leq k \leq 12$	$-11 \leq k \leq 0$
	$-13 \leq l \leq 12$	$-13 \leq l \leq 13$	$-16 \leq l \leq 16$	$-13 \leq l \leq 14$	$0 \leq l \leq 15$
no. reflns collected	1994	5140	3761	3370	3380
no. ind reflns	1861	4796	3506	3108	3220
R_{int}	0.0333	0.0343	0.0322	0.0350	0.0584
no. data/params	1861/119	4798/217	3506/253	3108/226	3220/245
GooF on F^2	1.040	0.923	1.063	1.087	1.050
R1, wR2 [$I \geq 2\sigma(I)$]	0.0491, 0.1183	0.0455, 0.1004	0.0443, 0.1092	0.0531, 0.1536	0.0618, 0.1530
R1, wR2 [all data]	0.0745, 0.1346	0.0868, 0.1119	0.0798, 0.1254	0.0777, 0.2018	0.1191, 0.1868
residuals	−0.342, 0.491	−0.333, 0.431	−0.260, 0.327	−0.414, 0.551	−0.491, 0.892

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 3

O1−C2	1.233(4)	N1−C3	1.299(4)
N1−N2	1.323(4)	N2−C7	1.439(5)
N2−C8	1.441(5)	C1−C2	1.453(5)
C1−C4	1.335(5)	C2−C3	1.452(5)
C5−C6	1.377(7)		
C3−N1−N2	120.9(3)	N1−N2−C7	123.0(3)
N1−N2−C8	115.9(3)	C7−N2−C8	120.1(3)
C4−C1−C2	123.0(3)	O1−C2−C3	119.2(3)
O1−C2−C1	121.5(3)	C3−C2−C1	119.2(3)
N1−C3−C2	119.7(3)	C1−C4−S1	124.7(3)
C1−C4−S2	121.6(3)	S1−C4−S2	113.65(19)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 5

Fe−C14	1.778(4)	Fe−C15	1.818(4)
Fe−C16	1.822(4)	Fe−O1	2.019(3)
Fe−C2	2.134(3)	Fe−C3	2.064(4)
Fe−C4	2.126(4)	O1−C2	1.315(4)
C1−C2	1.462(5)	C1−C5	1.343(5)
C2−C3	1.412(5)	C3−C4	1.418(5)
C14−Fe−C1	597.9(2)	O1−C2−C3	115.3(3)
C14−Fe−C16	89.01(19)	O1−C2−C1	121.2(3)
C15−Fe−C16	104.6(2)	S2−C5−S1	114.0(2)
C14−Fe−O1	164.25(15)	C1−C5−S1	124.8(3)
C15−Fe−O1	97.08(16)	C1−C5−S2	121.2(3)
C16−Fe−O1	92.06(16)	C2−C3−C4	117.3(3)
C14−Fe−C2	127.46(17)	C3−C2−C1	123.4(3)
C16−Fe−C2	93.81(17)	C14−Fe−C3	97.49(17)
C15−Fe−C3	131.07(17)	C15−Fe−C2	131.44(17)
C14−Fe−C4	95.33(16)	C15−Fe−C4	92.90(16)
C16−Fe−C4	161.25(17)	C5−S1−C6	96.77(18)
C16−Fe−C3	121.85(18)		

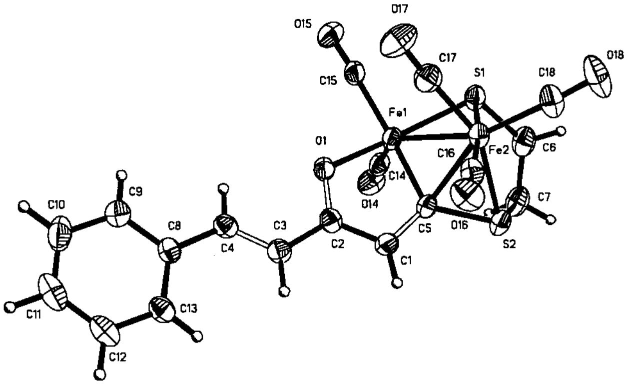


Figure 3. ORTEP drawing of complex **6**. Thermal ellipsoids at 30% probability level.

(1H) corresponding to the other vinylic proton is also observed. The ^{13}C NMR spectrum (75 MHz, $CDCl_3$) displayed signals at δ 213 and 211 ppm for the M−CO groups, at δ 189 for the CO group, at δ 188 for the vinylic carbon joined to the sulfur atoms, at 136.4−122.7 ppm for aromatic carbons, and, finally, at δ 36.2 and 31.0 ppm for the methylene groups bearing the sulfur atoms. In regard to mass spectrometry, the molecular ion at m/z of 500 is noticed as well as the peaks for successive loss of five CO groups, all these data suggesting the formation of a dinuclear complex. This fact was unequivocally established by X-ray diffraction studies and the molecular structure, and the numbering schemes are given in Figure 3.

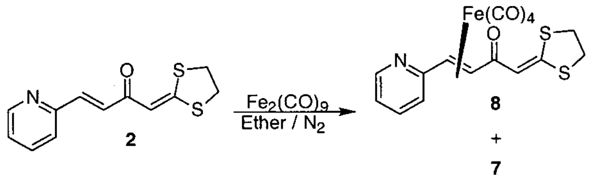
The ylidenbutenone backbone of the ligand is essentially planar with the phenyl ring just slightly tilted (angle between planes 8.9°). In the binuclear iron unit the Fe−Fe bond distance [2.6280(12) Å] is in agreement with a single metal−metal bond. One of the iron atoms (Fe1) is surrounded by two terminal carbonyl groups and the other (Fe2) by three terminal carbonyl groups (Table 4).

The most salient feature of the structure is the bridging μ-C and μ-S nature of the ligand toward the binuclear iron fragment as a result of the 1,3-dithiolane ring aperture. The S1 atom bridges the two iron atoms nearly symmetrically [Fe1−S1 2.213(2), Fe2−S1 2.260(2) Å], while the C5 atom is more tightly bonded to Fe1 [Fe1−C5 1.931(5), Fe2−C5 2.252(5) Å]. The rest

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compound 6

Fe1−Fe2	2.628(1)	Fe1−C14	1.754(6)
Fe1−C15	1.839(6)	Fe1−C5	1.931(5)
Fe1−O1	1.954(4)	Fe1−S1	2.213(2)
Fe2−C16	1.810(6)	Fe2−C17	1.786(7)
Fe2−C18	1.807(7)	Fe2−C5	2.252(5)
Fe2−S1	2.260(2)	Fe2−S2	2.328(2)
S1−C6	1.837(7)	S2−C5	1.741(5)
S2−C7	1.822(6)	O1−C2	1.301(7)
C1−C2	1.382(8)	C1−C5	1.399(8)
C2−C3	1.455(7)	C3−C4	1.334(8)
C14−Fe1−C15	96.1(3)	C14−Fe1−C5	97.7(2)
C15−Fe1−C5	164.1(2)	C14−Fe1−O1	98.9(2)
C15−Fe1−O1	89.2(2)	C5−Fe1−O1	80.9(2)
C14−Fe1−S1	101.8(2)	C15−Fe1−S1	91.9(2)
C5−Fe1−S1	92.9(2)	O1−Fe1−S1	159.1(1)
C14−Fe1−Fe2	139.5(2)	C15−Fe1−Fe2	115.3(2)
C5−Fe1−Fe2	56.8(2)	O1−Fe1−Fe2	106.1(1)
S1−Fe1−Fe2	54.8(5)	C16−Fe2−C17	89.1(3)
C16−Fe2−C18	95.7(3)	C17−Fe2−C18	102.0(3)
C16−Fe2−C5	90.6(2)	C17−Fe2−C5	108.7(3)
C18−Fe2−C5	148.8(3)	C16−Fe2−S1	172.8(2)
C17−Fe2−S1	88.6(2)	C18−Fe2−S1	91.4(2)
C5−Fe2−S1	83.7(1)	C16−Fe2−S2	91.2(2)
C17−Fe2−S2	153.3(2)	C18−Fe2−S2	104.5(3)
C5−Fe2−S2	44.6(13)	S1−Fe2−S2	87.8(6)
C16−Fe2−Fe1	119.6(2)	C17−Fe2−Fe1	74.4(2)
C18−Fe2−Fe1	144.1(2)	C5−Fe2−Fe1	45.8(1)
S1−Fe2−Fe1	53.2(4)	S2−Fe2−Fe1	82.4(5)
Fe1−S1−Fe2	71.9(5)	C5−S2−Fe2	65.3(2)
C2−O1−Fe1	114.5(3)	C2−C1−C5	112.3(5)
O1−C2−C1	117.6(5)	O1−C2−C3	119.1(5)
C1−C2−C3	123.3(5)	C4−C3−C2	122.0(5)
C1−C5−S2	119.8(4)	C1−C5−Fe1	114.1(4)
S2−C5−Fe1	125.9(3)	C1−C5−Fe2	124.5(4)
S2−C5−Fe2	70.0(2)	Fe1−C5−Fe2	77.4(2)

Scheme 3



of the coordination in the case of Fe1 is accomplished by a σ-O bond by the ketone oxygen atom O1 and by a σ-S (S2) bond of the opened dithiolane ring (Figure 3).

Thus the reaction between ligand **1** and $Fe_2(CO)_9$ leads to the formation of the new complexes **5** and **6**, along with complex **7**, which has also been obtained by other procedures.[16,17] Complex **6** could be proposed as an intermediate in the formation of **7**, on the basis of considering the early rupture of the C−S bond leading to the unexpected organometallic core of **6**, which displays, as can be seen, both organometallic and coordination bonds. Similar fragmentations are known as decarbansulfurization reactions.[18]

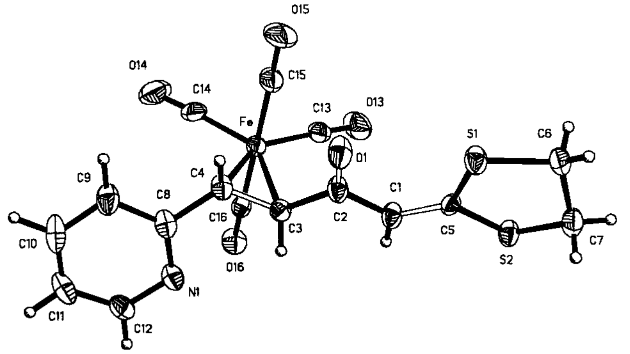


Figure 4. ORTEP drawing of complex **8**. Thermal ellipsoids at 30% probability level.

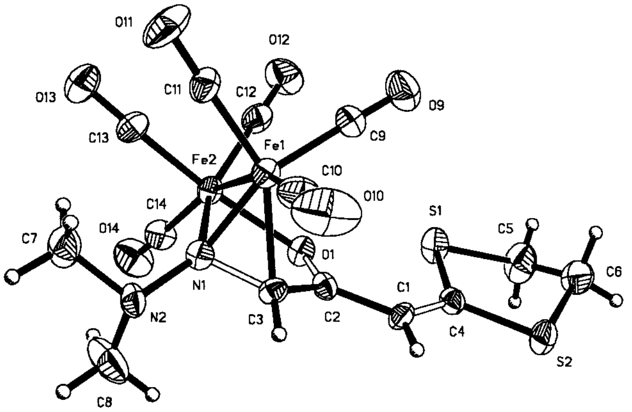


Figure 5. ORTEP drawing of complex **9**. Thermal ellipsoids at 30% probability level.

On the other hand, when **2** was reacted with $Fe_2(CO)_9$ in the aforementioned conditions (Scheme 3), complex η^2-**8** was obtained as an orange solid, displaying in its IR spectrum strong bands at 2094, 2030, and 1990 cm^{-1} corresponding to ν(M−CO) frequency absorptions. The ^1H NMR data (300 MHz, $CDCl_3$) of this complex indicated signals at δ 6.9 as a singlet for the free double bond and at δ 4.8 ppm an AB system (J = 10.5 Hz) owing to the coordinated double bond as the main spectroscopic features. The ^{13}C NMR spectrum (75 MHz, $CDCl_3$) disclosed the same pattern of signals—besides those corresponding to the aromatic carbons—as for **5**, i.e., at δ 206.8, 191.5, 164.0, and 161.6 ppm for the M−CO, CO groups, the C bearing the S atoms and the other C of this double bond, respectively, as well as the signals for the coordinated double bond at δ 57.0 and 55.4 and, finally, at 39.0 and 35.4 for the ethylene group. The mass spectrum (EI) exhibited a peak at m/z 389 assigned to M^+−CO and the successive loss of other three CO groups along with an iron atom. Also the peak base is clearly observed at m/z 249, corresponding to the molecular weight of the free ligand. Complex **7** was also obtained in low yield (>5%) and apparently is formed by a fragmentation reaction as for complex **6**, but such an intermediate complex was not isolated. The structure of complex **8** was fully confirmed by a single-crystal X-ray diffraction study, displaying that the $Fe(CO)_4$ unit is η^2-bonded to the vinyl group C3−C4 (Figure 4). The conventional features of the bonding mode of this moiety are observed, the ligand occupying an equatorial position in a trigonal bipyramid with the C3−C4 bond distance typically of a π-coordinated carbon−carbon double bond and corresponding to a bond order in the range 1−2. The pyridine ring is tilted 26.4°, and the 1,3-dithiolane ring, as in the previous structures, adopts the envelope conformation with C7 as a flap (0.633 Å out of plane) (Table 5).

When the same reaction was carried out on **3**, complex **9** was isolated as a deep-red solid (Scheme 4). The IR spectrum showed bands in the ν(M−CO) region at 2063,

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[16] Dahl, F.; Suan, C. H. *Inorg. Chem.* **1965**, *4*, 1.

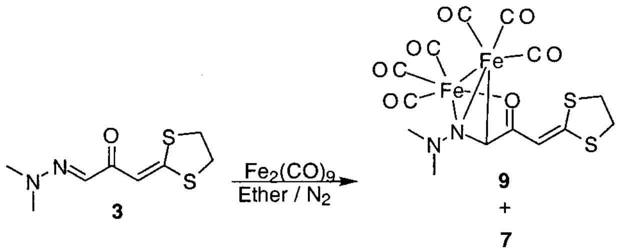
[17] Hughes, D. L.; Leigh, G. L.; Paulson, D. *Inorg. Chim. Acta* **1986**, *120*, 191.

[18] Shawer, A.; Fitzpatrick, P. J.; Steliow, K.; Butter, I. S. *J. Am. Chem. Soc.* **1979**, *101*, 1313.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Compound 8

Fe−C13	1.814(7)	Fe−C14	1.811(7)
Fe−C15	1.826(7)	Fe−C16	1.818(6)
Fe−C3	2.151(6)	Fe−C4	2.147(6)
O1−C2	1.227(7)	C1−C2	1.456(8)
C1−C5	1.364(8)	C2−C3	1.497(7)
C3−C4	1.416(8)		
C13−Fe−C14	112.9(4)	C15−Fe−C3	95.4(3)
C13−Fe−C15	89.6(3)	C16−Fe−C3	85.9(2)
C13−Fe−C16	90.1(3)	C13−Fe−C4	143.5(3)
C14−Fe−C15	90.4(3)	C14−Fe−C4	103.3(3)
C14−Fe−C16	88.5(3)	C15−Fe−C4	86.5(3)
C15−Fe−C16	178.7(3)	C16−Fe−C4	94.6(2)
C13−Fe−C3	106.2(3)	C4−Fe−C3	38.5(2)
C14−Fe−C3	140.4(3)	C4−C3−Fe	70.6(3)
C3−C4−Fe	70.9(3)	C4−C3−C2	122.8(5)
C5−C1−C2	123.9(5)	O1−C2−C1	122.4(5)
O1−C2−C3	123.9(5)	C1−C2−C3	113.7(5)
C1−C5−S1	125.4(4)	C1−C5−S2	120.0(4)
S1−C5−S2	114.6(3)		

Scheme 4



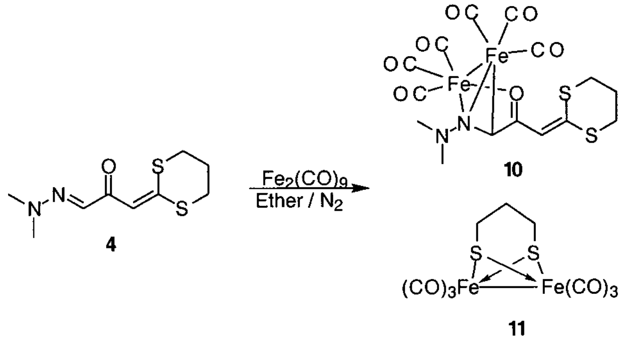
2015, 1990, and 1978 cm^{-1}. In regard to the ^{1}H NMR spectrum (300 MHz, $CDCl_3$), signals quite similar to those of the ligand were observed, and just the signal of the proton of the coordinated double bond appeared shifted upfield at δ 4.0 ppm. The ^{13}C NMR spectrum (75 MHz, $CDCl_3$) exhibited clearly all the relevant signals, appearing at δ 212.7, 196.3, and 167.1 ppm, the peaks corresponding to the M−CO, CO, and CSS carbons, respectively, as well as at δ 105.6 and 71.3 ppm, the peaks for both the carbons adjacent to the CO group, the latter signal being due to the carbon bearing the hydrazono group, and finally at δ 39.4 and 36.4 ppm, peaks belonging to the ethylene group. By high-resolution mass spectrometry with FAB ion mode technique the molecular weight of the complex was confirmed at *m*/*z* 497.

As in the preceding case, we were able to obtain good quality single crystals of complex **9** for X-ray structural confirmation. This complex closely resembles the binuclear complex reported by Alvarez.[19] Upon complex formation the *s-trans* configuration of the ketoimine moiety rearranges to an *s-cis* configuration. The C3−N1 group can be described as an imine group η^2-bonded to Fe1 and σ-N bonded to Fe2. The N1 atom bridges the two iron atoms unsymmetrically and is more tightly bonded to Fe1 [Fe1−N1 1.914(7), Fe2−N1 1.970(7) Å] than to Fe2. The C1−N1 distance is consistent with a C=N π-coordinated double bond, and the geometric parameters (Table 6) around N2 are now consistent with an sp^3 hybridization.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Compound 9

Fe1−C9	1.795(10)	Fe1−C10	1.771(11)
Fe1−C11	1.799(9)	Fe1−N1	1.914(7)
Fe1−C3	2.049(8)	Fe1−Fe2	2.586 (2)
Fe2−C12	1.816(11)	Fe2−C13	1.773(10)
Fe2−C14	1.843(9)	Fe2−N1	1.970(7)
Fe2−O1	1.995(6)	O1−C2	1.268(11)
N1−C3	1.387(11)	N1−N2	1.460(10)
N2−C7	1.446(14)	N2−C8	1.458(16)
C1−C2	1.432(12)	C1−C4	1.376(12)
C2−C3	1.463(12)	C3−C4	1.416(8)
C9−Fe1−C10	101.6(5)	C9−Fe1−C11	98.3(5)
C10−Fe1−C11	92.5(5)	C9−Fe1−N1	132.3(4)
C10−Fe1−N1	113.3(4)	C11−Fe1−N1	111.1(4)
C9−Fe1−C3	109.5(4)	C10−Fe1−C3	92.4(4)
C11−Fe1−C3	150.1(4)	N1−Fe1−C3	40.8(3)
C9−Fe1−Fe2	91.5(3)	N1−Fe1−Fe2	49.2(2)
C10−Fe1−Fe2	162.1(4)	C3−Fe1−Fe2	71.5(2)
C11−Fe1−Fe2	97.7(3)	C14−Fe2−O1	92.4(4)
C12−Fe2−C13	89.8(5)	N1−Fe2−O1	83.9(3)
C12−Fe2−C14	100.7(4)	C13−Fe2−Fe1	91.9(3)
C13−Fe2−C14	92.3(5)	C12−Fe2−Fe1	102.8(3)
C12−Fe2−N1	149.2(4)	N1−Fe2−Fe1	47.3(2)
C13−Fe2−N1	97.6(4)	C14−Fe2−N1	108.8(4)
C12−Fe2−O1	86.2(4)	C13−Fe2−O1	174.3(4)
C14−Fe2−Fe1	156.1(3)	O1−Fe2−Fe1	85.1(2)
C4−S1−C5	94.3(5)	C4−S2−C6	96.1(5)
C3−N1−Fe1	74.8(5)	C3−N1−Fe2	108.4(5)
C3−N1−N2	111.3(7)	N2−N1−Fe1	126.9(5)
N2−N1−Fe2	134.9(6)	Fe1−N1−Fe2	83.5(3)
C7−N2−C8	111.2(11)	C7−N2−N1	110.8(8)
C8−N2−N1	109.7(8)	C4−C1−C2	123.3(8)
O1−C2−C1	121.8(7)	O1−C2−C3	118.4(8)
C1−C2−C3	119.6(8)	N1−C3−C2	114.8(7)
N1−C3−Fe1	64.4(4)	C2−C3−Fe1	103.0(6)
C1−C4−S1	124.6(7)	C1−C4−S2	119.7(7)
S1−C4−S2	115.5(5)		

Scheme 5



In the binuclear unit each iron atom is surrounded by three terminal carbonyl groups, and the rest of the coordination in one case (Fe1) is achieved as stated before by an η^2-CN bond, while in the other case (Fe2) the coordination sphere is completed by a σ-N bond of the same group and a σ-O bond by the ketone oxygen atom O1.

In this case, complex **7** was also obtained additionally in traces, arising from the dithiolane fragmentation as above (vide supra), but such rupture is disfavored since the Fe atom coordinates on the hydrazono moiety, giving rise to a stable core exhibiting both covalent and coordination bondings.

Finally, when **4** reacted with $Fe_2(CO)_9$ under the same conditions, two new complexes, **10** and **11**—quite similar to complexes **9** and **7**, respectively—were obtained (Scheme 5).

Complex **10**, isolated as a crystalline red solid in 26% yield, exhibited in its IR spectrum frequency absorption bands in the M−CO region at 2062, 2014, 1985, and

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(19) Alvarez-Toledano, C.; Gutiérrez-Pérez, R.; Toscano, R. A.; Moya-Cabrera, M.; Haquet, T.; Ortega, M. C.; Cabrera, A. *Polyhedron* (accepted).

1951 $\mathrm{cm^{-1}}$. The ^{1}H NMR spectrum (300 MHz, $\mathrm{CDCl_3}$) showed a pattern quite similar to those of complex **9**; thus the relevant features are a signal at δ 4 ppm assessed to the proton of the coordinated double bond and a signal at δ 2.15 ppm owing to the methyl groups of the nitrogen atom. The ^{13}C NMR spectrum (75 MHz, $\mathrm{CDCl_3}$) showed signals at δ 213 and 207 corresponding to the metallic CO groups, along with two other peaks at δ 114 and 72 ppm, owing to the vinylic carbon of the noncoordinated double bond and to the coordinated iminic carbon, respectively. In the HR-MS (FAB ion mode technique) spectrum the molecular ion at m/z 511 is clearly observed and also the successive loss of six CO groups.

As for **7**, complex **11** was also isolated as a brown solid with a 3.4% yield, and similarly this complex has been obtained by other methods.[20] On the other hand, the presence of an intermediate similar to **6** can be inferred since in the reaction mixture some other products are detected.

Comparing with the results gathered in preceding studies, the noteworthy feature is the fact that the presence of an additional C═C double bond implies a different reactivity since the formation of the dinuclear Fe(0) complex **6** gives rise to a unique organometallic framework in the sulfur-containing moiety. In regard to complex **9**, the outstanding point is that there is no rupture in the N−N bond of the ligand, as it was reported[9] with just the 1,2-dicarbonylic monohydrazones, i.e., in the absence of an additional conjugated double bond present in the conjugated system. For the mononuclear Fe(0) complexes **5** and **8**, usual η^2- and η^4-coordinations of the iron atom are observed.

Conclusion

The new complexes η^2 and η^4 **5** and **8** were isolated displaying typical Fe(0) coordination patterns of α,β-unsaturated ketones, independently of the other functionalization in the molecule. In regard to the new dinuclear complex **6** the sulfur-containing moiety also reacted separately, giving rise to a novel organometallic core. This complex could be proposed as an intermediate in the formation of **7**. Complexes **9** and **10** showed a dinuclear iron unit displaying at one end both σ-N and σ-O coordination, and the sulfur-containing moiety remains unaffected.

Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian 300S spectrometer, using $\mathrm{CDCl_3}$ as solvent and TMS as internal reference. IR spectra were performed on a Perkin-Elmer 283 B or 1420 spectrometer. The FAB spectra were obtained on a JEOL JMS SX 102A mass spectrometer operating at an accelerating voltage of 10 kV. Samples were desorbed from a nitrobenzyl alcohol matrix using 6 keV xenon atoms. The electronic impact (EI) ionization mass spectra were acquired on a JEOL JMS-AX505 HA mass spectrometer operating in the positive ion mode. The acquisition conditions were ion source temperature 230 °C, ionization energy 70 eV, emission current 0.14 μA, and ionization current 100 μA. Mass measurements in FAB are performed at 10 000 resolution using electrical field scans and poly(ethylene glycol) ions as reference material. Melting points were measured using a Mel-Temp II apparatus and are uncorrected. All reagents were obtained from commercial suppliers and used as received. Reactions were perfomed under nitrogen atmosphere in carefully dried glassware. Diethyl ether was distilled from sodium−benzophenone ketyl under argon and/or nitrogen atmosphere. Column chromatography was performed with Merck silica gel (70−230 mesh) using ethyl acetate/hexane in different ratios as eluent. Elemental analyses were performed by Galbraith Laboratories, Inc.

Synthesis of Ligands. Ligands **1** and **2** were prepared by a condensation reaction between 1-(1,3-dithiolan-2-ylidene)-acetone[14] (0.1 mol) and benzaldehyde or 2-pyridincarboxaldehyde (0.1 mol) using an ethanolic solution of 0.1 N NaOH (150 mL) during 24 h. The reaction mixture was filtered off, and the product was recrystallized from ethanol, affording **1** and **2** with yields of 70 and 85%, respectively.

Ligands 3 and 4. To a solution of potassium *tert*-butoxide (0.03 mol) in dry THF was added dropwise a mixture of pyruvaldehyde dimethyhydrazone (0.015 mol) and carbon disulfide (0.015 mol), with magnetic stirring for 40 min. Afterward, the alkylating reagent (0.015 mol) was added maintaining the agitation for 4 h. Finally, AcOEt and water (3 × 40 mL) were also added, extracting the organic phase, drying with $\mathrm{Na_2SO_4}$, and removing the volatiles in vacuo. The reaction mixture was purified by column chromatography, using hexane/AcOEt in different ratios as eluent. Yields obtained are 45 and 30% for **3** and **4**, respectively, based on the pure products isolated.

Synthesis of Complexes. A solution of the ligands **1**−**4** (15.3 mmol) in anhydrous diethyl ether (150 mL) was treated with $\mathrm{Fe_2(CO)_9}$ (45.9 mmol) with magnetic stirring at room temperature for 24 h under an inert atmosphere. After the reaction was complete, the crude was filtered off through an alumina column, and the solvent was evaporated under vacuum. The reaction mixture was chromatographed on silica gel, and elution with hexane/ethyl acetate in a 98/2 ratio gave the corresponding Fe(0) complexes **5**−**11**, with yields of 35, 28, 9, 38, 25, and 25%, respectively, based on the pure products isolated.

Ligand 4-(2-Pyridyl)-1-(1,3-dithiolane-2-ylidene)-3*E*-butenone, 2: yellow solid (85% yield), mp147−149 °C; IR ν_{max} ($\mathrm{CHCl_3}$) $\mathrm{cm^{-1}}$ 3030 ($\mathrm{C_{Sp2}}$ pyr-H); 1591.1 (CO); 1516.0 (C═SS); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ8.62 (d, 1H, $\mathrm{NCH_{arom}}$); 7.68 (td, 1H, NCHCHC*H*); 7.42 (d, 1H, NCC*H*); 7.23 (m, 1H, NCHC*H*); 7.59 and 7.26 (AB system, 2H, J = 15.4 Hz, C*H*C*H*CO); 6.87 (s, 1H, C*H*CSS); 3.46 and 3.36 (m, 4H, $\mathrm{SC}H_2\mathrm{C}H_2$) ppm; ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 184.6 (*C*O); 167.9(HC*C*SS); 153.74 (H*C*CSS); 140 and 130.8 (H*CC*H); 150.1, 136.8, 124.7, 123.9, 112.2 ($C\mathrm{H_{arom}}$); 39.11 and 35.5 ($\mathrm{S}C\mathrm{H_2}C\mathrm{H_2S}$) ppm; MS-EI ($m/z$) 249 ($\mathrm{M^+}$).

Ligand *N*,*N*-Dimethylhydrazono-1-(1,3-dithiolane-2-ylidene)propene-2-one, 3: 45% yield, orange crystals, mp 109−112 °C; IR ν_{max} ($\mathrm{CHCl_3}$) $\mathrm{cm^{-1}}$ 2931.7($\mathrm{C_{Sp3}}$ −H); 2868($\mathrm{C_{Sp2}}$ −H); 1600.8 (CO); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) 7.35 (s, 1H, NC*H*); 6.65 (s, 1H, C*H*CSS); 3.41 and 3.30 (m, 4H, $\mathrm{SC}H_2\mathrm{C}H_2\mathrm{S}$); 3.1 (s, 6H, $\mathrm{C}H_3$) ppm; ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 184.3(*C*O); 161.54(HC*C*SS); 128.49(N*C*H); 108.48 (H*C*CSS); 42.56($C\mathrm{H_3}$); 38.9 and 35.28 ($\mathrm{S}C\mathrm{H_2}C\mathrm{H_2S}$) ppm; MS-EI ($m/z$) 216 ($\mathrm{M^+}$).

Ligand *N*,*N*-Dimethylhydrazono-1-(1,3-dithiane-2-ylidene)propan-2-one, 4: 25% yield, yellow crystalline solid, mp 65−67 °C; IR ν_{max} ($\mathrm{CHCl_3}$) $\mathrm{cm^{-1}}$ 3003.56 ($\mathrm{C_{Sp3}}$−H); 2928.84 ($\mathrm{C_{Sp2}}$−H); 1602.9 (CO); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) 7.36 (s, 1H, NC*H*); 6.61 (s, 1H, C*H*CSS); 3.11 (s, 6H, $\mathrm{C}H_3$); 3.01 (t, 2H, $\mathrm{SC}H_2$); 2.94 (t, 2H, $\mathrm{CH_2C}H_2\mathrm{S}$); 2.22 (m, 2H, $\mathrm{SCH_2C}H_2$) ppm; ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 184 (*C*O); 157 (HC*C*SS); 128 (N*C*H); 117 (H*C*CSS); 42.4 ($C\mathrm{H_3}$); 28 and 27 ($\mathrm{S}C\mathrm{H_2CH_2}C\mathrm{H_2S}$); 23.7 ($\mathrm{SCH_2}C\mathrm{H_2CH_2S}$) ppm; MS-EI ($m/z$) 230 ($\mathrm{M^+}$).

Complex η^4-[4-Phenyl-1-(1,3-dithiolane-2-ylidene)-3*E*-butene-2-one]Fe(CO)$_3$, 5: red crystals, 35% yield, mp 105 °C

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(20) (a) Seyferth, D.; Womack, G. B.; Gallangher, M. K. *Organometallic* **1987**, *6*, 283. (b) Winter, A.; Zsolnai, L.; Huttner, G. Z. *Naturfosch, B., Anorg. Chem., Org. Chem.* **1982**, *37B*, 1430.

(dec); IR ν_{max}(KBr)/cm^{-1} 2062, 2004, 1985 (M−CO); 1601 (CO); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, 1H, C*H*CHCO); 7.25 (m, 5H, CH_{arom}); 6.72 (s, 1H, C*H*═CSSC$_2$H$_4$); 5.94 (d, 1H, *J* = 7.41 Hz, CHC*H*CO); 3.42 (d, 4H, SSC_2H_4) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.6 (M−CO); 165.7 (*C*O); 154.3 ($CSSC_2H_4$); 140.5, 139.4, 128.8, 126.8 (CH_{arom}); 105.7 (*C*H−CSS); 74.8 (*C*H−CO), 61.2 (*C*HCHCO)); 35.8 (SSC_2H_4) ppm; MS-EI (*m*/*z*) 360 (M$^+$−CO); 332 (M$^+$−2CO); 304 (M$^+$−3CO); 248 (M$^+$−Fe(CO)$_3$); HR-MS (FAB$^+$) $C_{16}H_{13}O_4S_2Fe$, found 388.9613, calcd 388.9605. Anal. Calcd C, 49.49; H, 3.09; S, 16.49. Found: C, 49.36; H, 3.62; S, 15.10.

Complex [4-Phenyl-1-(1,3-dithiolane-2-ylidene)-3*E*-butene-2-one]Fe$_2$(CO)$_7$, 6: black solid, 28% yield, mp 82 °C; IR ν_{max}(KBr)/cm^{-1} 2060, 2020, 1953 (M−CO); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, 1H, *J* = 15 Hz, C*H*CHCO), 7.31 (m, 5H, CH_{arom}), 6.8 (d, 1H, *J* = 15 Hz, CHC*H*CO), 3.3 (m, 2H,-$CSCH_2$), 2.2 (s,1H, C*H*CSS), 2.1 (m, 2H, $FeSCH_2$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 213 (M−CO); 189 (CO); 136.4, 135.4, 128.7, 127.3, 124.3, 122.7 (CH_{arom}); 65.4, 36.2, 31.0, 15.4 ppm; MS-EI (*m*/*z*) 500 (M$^+$); HR-MS (FAB$^+$) $C_{18}H_{13}O_6S_2Fe_2$, found 500.8847, calcd 500.8852.

Complex η^2-[4-(2-Pyridyl)-1-(1,3-dithiolane-2-ylidene)-3*E*-butene-2-one]Fe(CO)$_4$, 8: crystals, 38% yield, mp 38 °C (dec); IR ν_{max}($CDCl_3$)/cm^{-1} 2094, 2030, 1990 (M−CO); 1600 (CO); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31(d, 1H, NCH_{arom}); 7.57−6.95 (m, 4H, CH_{arom}); 6.92 (s, 1H, C*H*CSS); 4.81 (Sistema AB, 2H, *J* = 10.7 Hz, ArC*H*═C*H*); 3.36 (dd, 4H, SSC_2H_4) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.8 (M−CO); 191.5 (CO); 164.0 ($CSSC_2H_4$); 161.6 ($CH{=}CSSC_2H_4$); 136.5, 123.0, 121.1, 112.7 (CH_{arom}); 57.0 (CO−*C*H); 55.4 (Ar*C*H), 39.0, 35.4 (SCH_2CH_2S) ppm; MS-EI (*m*/*z*) 389 (M$^+$−CO); HR-MS (FAB$^+$) (M$^+$−CO), $C_{15}H_{11}O_4NS_2Fe$, found 388.9497, calcd 388.9479; (M$^+$−2CO), $C_{14}H_{12}O_3NS_2Fe$, found 361.9615, calcd 361.9608; (M$^+$−3CO), $C_{13}H_{11}O_2NS_2Fe$, found 332.9583, calcd 332.9581; (M$^+$−4CO), $C_{12}H_{11}ONS_2Fe$, found 304.9631, calcd 304.9631.

Complex [*N*,*N*-Dimethylhydrazono-1-(1,3-dithiolane-2-ylidene)propene-2-one]Fe$_2$(CO)$_6$, 9: brown solid, 25% yield, mp 106−110 °C (dec); IR ν_{max}($CDCl_3$)/cm^{-1} 2063, 2015, 1990, 1978 (M−CO); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.34 (s, 1H, C═C*H*CO); 4.00 (s, 2H, N═CC*H*); 3.38 (m, 4H, SSC_2H_4); 2.76 (s, 6H, NCH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.7 (M−CO); 196.3 (CO); 167.1($CSSC_2H_4$); 105.6 (CO*C*H═C); 71.3 (N═*C*HCO); 39.4, 36.4 (SCH_2CH_2S) ppm; MS-EI (*m*/*z*) 497 (M$^+$+1) 468 (M$^+$−CO); 440 (M$^+$−2CO); 384 (M$^+$−Fe(CO)$_2$); 356 (M$^+$−Fe(CO)$_3$); 328 (M$^+$−Fe(CO)$_4$); 272 (M$^+$−Fe$_2$(CO)$_4$). Anal. Calcd C, 33.87; H, 2.41; N. 5.65; S, 12.90. Found: C, 34.48; H, 2.77; N, 5.62; S, 12.97.

Complex [*N*,*N*-Dimethylhydrazono-1-(1,3-dithiane-2-ylidene)propan-2-one]Fe$_2$(CO)$_6$, 10: red dark solid, 26% yield, mp 156−158 °C (dec); IR ν_{max}($CDCl_3$)/cm^{-1} 2062, 2014, 1985, 1951 (M−CO); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.27 (s, 1H, C═C*H*CO); 4.02 (s, 1H, N═CC*H*); 2.93 (s, 2H, SCH_2); 2.16 (s, 6H, NCH_3); 1.63 (s, 2H, SCH_2); 1.23 (s, 2H, $CH_2CH_2CH_2$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.7, 207.6 (M−CO); 195.X (CO); 169.2 ($CSSC_2H_4$); 114.3 (CO*C*H═C); 72.3 (N═*C*HCO); 56.5 (N*C*H$_3$); 29.0, 28.6 ($SCH_2CH_2CH_2S$) ppm; MS (FAB$^+$) (M$^+$+1) 511 *m*/*z* HR-MS (FAB$^+$) (M$^+$−2CO), $C_{13}H_{14}O_5N_2S_2Fe_2$, found 453.9056, calcd 453.9043; (M$^+$−4CO), $C_{11}H_{14}O_3N_2S_2Fe_2$, found: 397.9170, calcd 397.9145. Anal. Calcd C, 35.30; H, 2.75; N. 5.49; S, 12.55. Found: C, 37.31; H, 3.56; N, 5.35; S, 12.93.

X-ray Crystal Structure Determinations of Compounds 3, 5, 6, 8, and 9. Data collection and refinement parameters are summarized in Table 1. The diffraction data were collected on a Siemens P4/PC diffractometer with Mo Kα radiation, λ = 0.71063 Å. Each data set was corrected for Lorentz and polarization effects, and empirical absorption corrections based on ψ-scans were applied. The structures were solved by direct methods,[21] and each structure was refined by full-matrix least-squares on F^2 using all data with all non-hydrogen atoms assigned anisotropic displacement parameters and hydrogen atoms bound to carbon atoms inserted at calculated positions with isotropic temperature factors 1.2 times the U_{iso} of the parent carbon atom. The program used in the final refinements was SHELXL-97.[22] Selected bond lengths and bond angles are shown in Tables 2−6.

Acknowledgment. We thank Conacyt (27500E) for financial support and Rocío Patiño and Javier Pérez for their technical assistance in collecting spectroscopic data.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM0004702

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