C−S Bond Activation of Two Novel Asymmetric α-*azo*-Ketenedithioacetals Using $Fe_2(CO)_9$

M. Carmen Ortega-Alfaro,*,[†] Olga Alcantara,[†] Manuel Orrala,[†] José G. López-Cortés,[‡]
Ruben A. Toscano,[‡] and Cecilio Alvarez-Toledano*,[‡]

Departamento Química Orgánica, Facultad de Química-UNAM, Circuito Exterior, Ciudad Universitaria, Coyoacán C.P. 04510, México D.F., Mexico, and Instituto de Química UNAM, Circuito Exterior, Ciudad Universitaria, Coyoacán, C.P. 04510 México D.F., Mexico

Received October 16, 2006

Two novel asymmetric *azo*-aliphatic compounds $[(CH_3)_3CN{=}NC(S(CH_2)_nS)C(O)CH_3$, $n = 2$ (**5**) and $n = 3$ (**6**)] have been synthesized via a tandem procedure. The reaction of **5** and **6** with $Fe_2(CO)_9$ affords three novel dinuclear iron complexes displaying C−S bond activation (**5b**, **5c**, and **6c**). **5b** and **5c** exhibit an unusual stereochemistry about the Fe_2 unit, as revealed by X-ray diffraction analyses. Additionally, two alquildithiolate-bridged iron hexacarbonyl complexes (**5a** and **6a**) were obtained as a result of a double C−S bond activation from **5** and **6**, respectively. The structures of **5**, **5b**, and **5c** were fully established by X-ray diffraction analyses.

Introduction

Tricarbonyl(η^4-1,3-diene) iron complexes have had many useful applications in synthetic organic chemistry and have shown themselves to represent excellent starting materials for the stereoselective synthesis of natural products.[1] We are interested in the synthesis of novel 1,3-heterodiene compounds with the aim of studying their reactivity toward $Fe_2(CO)_9$. In previous studies, we have evidenced that heterodienic systems, such as α,β-unsaturated carbonyl compounds with heteroatoms in position β toward $Fe_2(CO)_9$, display novel coordination patterns (Chart 1). Thus, when α,β-unsaturated ligands with a dithiol group react with diiron nonacarbonyl, they generate dinuclear complexes **1**.[2] However, ligands that contain an additional conjugated double bond, such as 4-phenyl-1-(1,3-dithiolane-2-ylidene)-3*E*-butenone, produce dinuclear Fe(0) complex **2** displaying C−S bond activation.[3] We previously reported that this activation depends on the electronic density of the heterodienic moiety.[3b] An attempt to understand the activation mechanism of these systems led us to the synthesis of α,β-unsaturated ketones with a sulfoxide group in β-position, which were regioselectively reacted with $Fe_2(CO)_9$, leading to dinuclear Fe(0) complexes **3**.[4] However, when the corresponding thiazolidine analogues **4**[5] were reacted with $Fe_2(CO)_9$, no stable products were obtained.[6] In order to further research the C−S bond activation mechanism of α,β-unsaturated carbonyl compounds β-positioned with sulfur atoms, we here report the synthesis of two novel cross-conjugated *azo*-ligands, **5** and **6**, and their reactivity behavior toward $Fe_2(CO)_9$.

Results and Discussion

Although, the literature describes that aldehydic arylhydrazones can be considered enamine analogues and that they, in appropriate conditions, promote the formation of arylazo compounds,[7] only a few examples of these compounds are reported.[8,9] Recently, L. El Kaïm et al. have reported the synthesis of several heterocyclic compounds via unstable azoalkenes trapped *in situ* by various nucleophiles.[10]

Taking into account this previous report, the novel ligands **5** and **6** were prepared by a tandem reaction from piruvaldehyde *tert*-butylhydrazone, CS_2, and the corresponding alkyldihalide in good yields (Scheme 1).

As far as we are aware, no reports relating to the synthesis of **5** and **6** by other methods exist, and our results represent some of the few examples of asymmetric *azo*-aliphatic compounds produced to date. Additionally, these compounds have

---

* Corresponding authors. E-mail: marycarm@correo.unam.mx. Tel: +52 5556223704. Fax: +52 5556223756. E-mail: cecilio@servidor.unam.mx. Tel: +52 5556224513. Fax: +52 5556162217.

[†] Facultad de Química-UNAM.

[‡] Instituto de Química-UNAM.

[1] For reviews, see: (a) Pearson, A. J. *Acc. Chem. Rev.* **1980**, *13*, 463. (b) Pearson, A. J. In *Comprehensive Organometallic Chemistry, Vol. 8*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 58. (c) Pearson, A. J. *Metallo-organic Chemistry*; Wiley: Chichester, 1985; Chapters 7 and 8. (d) Knölker, H. J. *Chem. Soc. Rev.* **1999**, *28*, 151. (e) Ley, S. V.; Cox, L. R.; Meek, G. *Chem. Rev.* **1996**, *96*, 423. (f) Pearson, A. J.; Alimardanov, A. *Organometallics* **1998**, *17*, 3739.

[2] Alvarez-Toledano, C.; Enríquez, J.; Toscano, R. A.; Martínez-García, M.; Cortés-Cortés, E.; Osornio, Y.; García, O.; Gutiérrez-Pérez, R. *J. Organomet. Chem.* **1999**, *577*, 38.

[3] (a) Ortega-Jiménez, F.; Ortega-Alfaro, M. C.; López-Cortés, J. G.; Velasco-Ibarra, L.; Peña-Cabrera, E.; Alvarez-Toledano, C. *Organometallics* **2000**, *19*, 4127. (b) Ortega-Alfaro, M. C.; López-Cortés, J. G.; Toscano, R. A.; Alvarez-Toledano, C. J. *Braz. Chem. Soc.* **2005**, *16*, 362−371. Ortega-Alfaro, M. C.; López-Cortés, J. G.; Toscano, R. A.; Alvarez-Toledano, C. J. *J. Mex. Chem. Soc.* **2005**, *49*, 124−133.

[4] Ortega-Alfaro, M. C.; Hernández, N.; Cerna, I.; López-Cortés, J. G.; Gómez, E.; Toscano, R. A.; Alvarez-Toledano, C. *J. Organomet. Chem.* **2004**, *689*, 885−893.

[5] Ortega-Alfaro, M. C.; López-Cortés, J. G.; Rangel Sánchez, H.; Toscano, R. A.; Penieres Carrillo, G.; Álvarez-Toledano, C. *Arkivoc* **2005**, *vi*, 356.

[6] Ortega-Alfaro, M. C. Estudio de la Reactividad del $Fe_2(CO)_9$, frente a ligantes carbonílicos α,β-insaturados. Nuevos arreglos estructurales. Ph.D. Thesis, 2004, UNAM.

[7] (a) Hegraly, A. F.; Scott, F. L. *J. Org. Chem.* **1967**, *32*, 1957. (b) Hegraly, A. F.; Scott, F. L. *J. Chem. Soc (B)* **1966**, 672.

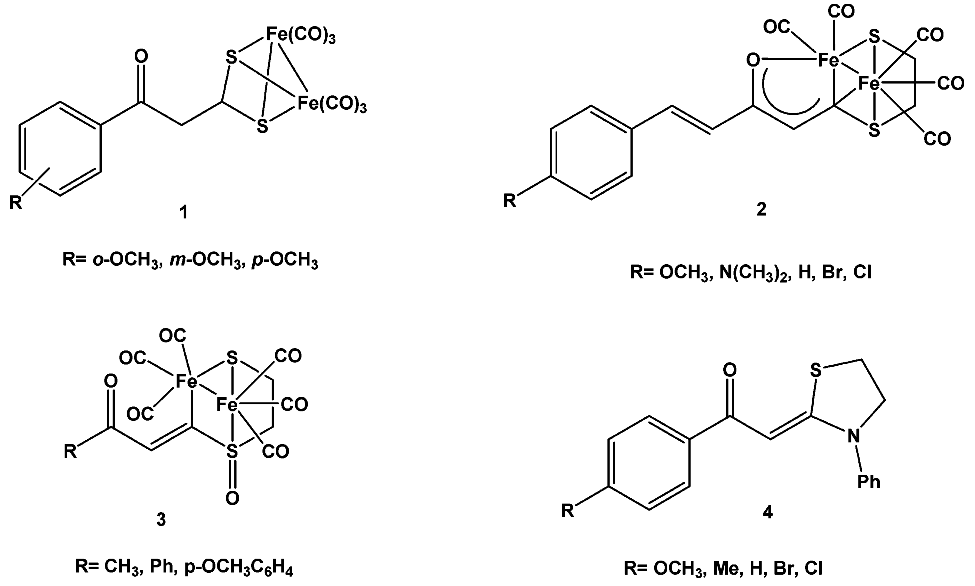
[8] Tronchet, J. M. J.; Baehler, B.; Lehong, N.; Livio, P. F. *Helv. Chim. Acta* **1971**, *54*, 921.

[9] Tahr, E.; Rupp, H. D. *Ann. Chem.* **1968**, *93*, 712.

[10] (a) Bailliez, V.; El Kaïm, L.; Michaut, V. *Synth. Commun.* **2004**, *34*, 109, and references therein. (b) Atlan, V.; El Kaïm, L.; Grimaud, L.; Jana, N. K.; Majee, A. *Synlett*, **2002**, 352. (c) Atlan, V.; Bienaymé, H.; El Kaïm, L.; Majee, A. *Chem. Commun.* **2000**, 1585. (d) Atlan, V.; El Kaim, L.; Supiot, C. *Chem. Commun.* **2000**, 1385. (f) Atlan, V.; El Kaïm, L.; Lacroix, S.; Morgentin, R. *Chem. Commun.* **1999**, 1893.

10.1021/om060953r CCC: $37.00

Chart 1. Coordination Modes in Iron Complexes



1

R= *o*-OCH$_3$, *m*-OCH$_3$, *p*-OCH$_3$

2

R= OCH$_3$, N(CH$_3$)$_2$, H, Br, Cl

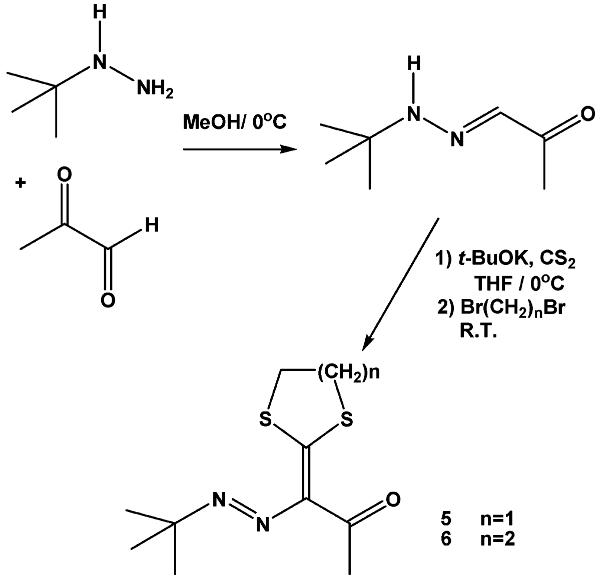
3

R= CH$_3$, Ph, p-OCH$_3$C$_6$H$_4$

4

R= OCH$_3$, Me, H, Br, Cl

Scheme 1. Synthesis of *azo*-Compounds 5 and 6



high functionalization, which will permit us to study their coordination behavior toward Fe$_2$(CO)$_9$.

These ligands were characterized by IR, MS, and ^{1}H and ^{13}C NMR and have some similarities in their ^{1}H and ^{13}C NMR spectra, such as a single signal around 1.35 ppm that corresponds to the methyls of the *tert*-butyl group, a simple signal at 2.55 ppm assigned to the acetyl group, and a multiple signal around 3.0 ppm that corresponds to the methylene groups. In ^{13}C NMR, two signals are exhibited at 139 and 158 ppm, corresponding to the N*C*═*C*SS. The structure of **5** was fully established by X-ray diffraction analysis (Figure 1). The *azo*-group shows a *trans* conformation displaying a smaller N═N bond distance compared with other aliphatic *azo*-compounds, while the angle N2−N1−C1 is in accord with the literature.[11] The distances S1−O1 [2.652(4) Å] and S2−N2 [2.617(4) Å] are shorter than the sum of the van der Waals radii. These features indicate that two interactions, S−O and S−N, which impart structural rigidity to the molecule, are present via the conjugated systems.[12] The 1,3-dithiolane ring adopts a twist conformation with a pseudo-C_2 axis over C4. Additionally, this moiety and the *tert*-butyl group present disorder, generating two orientations in 51:49 ratio. Only the major contributor is shown in Figure 1.

A suspension of **5** and Fe$_2$(CO)$_9$ in anhydrous ether (Scheme 2) led to the formation of **5a**−**c**, which were isolated on preparative TLC plates, after the usual workup. Complex **5a** was obtained in a trace amount. This compound has been obtained by other methods[13] and as subproduct of α,*β*-unsaturated ketone analogues in reactions brought about under similar conditions.[3,4] The novel complexes **5b** and **5c** are the principal products, and they arise from the C−S bond activation of **5**. This activation is not selective, as compared with complexes **2** and **3**.

Complex **5b** was obtained as a black, crystalline solid and shows, in its IR spectrum, absorption bands in the *ν*(M−CO) region at 1948, 1967, 2017, and 2062 cm^{-1}. The ^{1}H NMR spectrum (300 MHz, CDCl$_3$) exhibited a single signal at 1.31 ppm (9H), corresponding to a *tert*-butyl group, three multiplet signals at 1.68 (1H), 2.20 (1H), and 2.88 (2H) ppm, assigned

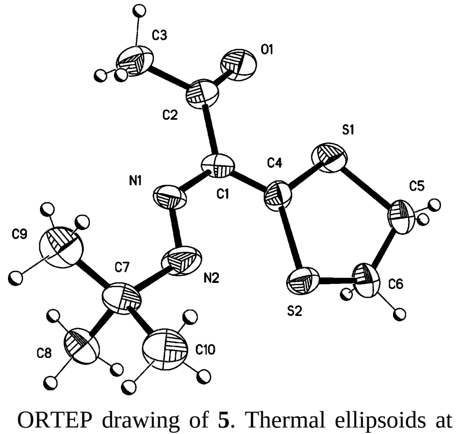
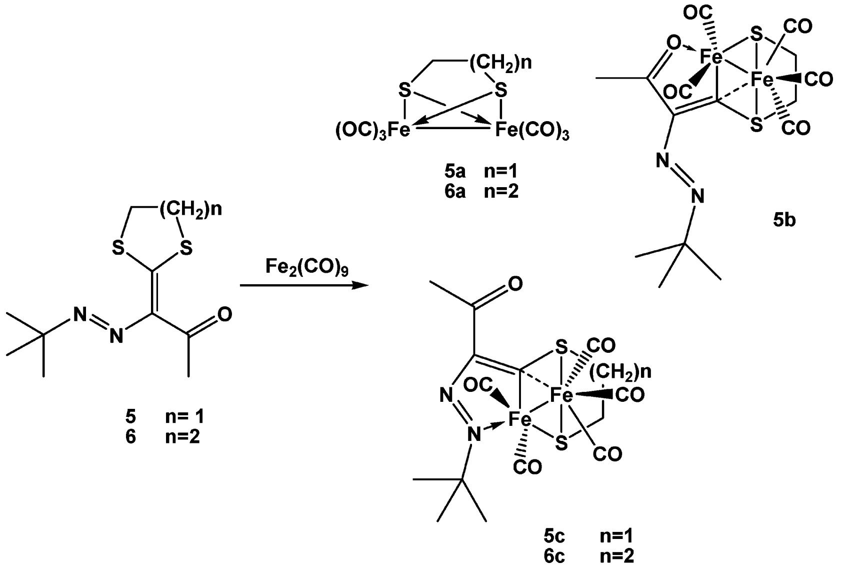


Figure 1. ORTEP drawing of **5**. Thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): S(1)−C(4) 1.755(4), S(2)−C(4) 1.748(4), N(1)−N(2) 1.220(5), N(1)−C(1) 1.408(5), N(2)−C(7) 1.503(11), O(1)−C(2) 1.213(5), C(1)−C(4) 1.365(6), C(1)−C(2) 1.472(5), C(4)−S(1)−O(1) 76.11(15), C(4)−S(2)−N(2) 73.15(16), N(2)−N(1)−C(1) 115.6(3), N(1)−N(2)−C(7) 113.3(6), N(1)−N(2)−S(2) 103.2(3), C(2)−O(1)−S(1) 98.8(3), C(4)−C(1)−N(1) 123.3(3).

---

[11] (a) Brown, C. J. *Acta Crystallogr.* **1966**, *21*, 146. (b) Chang, C. H.; Porter, R. F.; Baver, S. H. *J. Am. Chem. Soc.* **1970**, *92*, 5313. (c) Allmann, R. In PATAI, *The Chemistry of Diazonium and Diazo Groups,* part 1; Wiley: New York, 1975; p 23.

Scheme 2. Coordination Reaction of 5 and 6 and $Fe_2(CO)_9$



to the methylene groups bonded to sulfur atoms, and one simple signal at 2.44 ppm, for CH_3C(O). From the ^{13}C NMR data (75 MHz, $CDCl_3$), the presence of metallic M−CO groups was confirmed by the signals at 209.7 and 213.2 ppm. The signals assigned to *C*SFe and CH_3*C*(O), which are shifted upfield, $\Delta\delta \approx 10$ and $\Delta\delta \approx 20$, were observed at 146.2 and 174.8 ppm, respectively. These signals prompted us to propose the formation of a dinuclear complex, where the oxygen of the ketone group completes the coordination sphere of one iron atom, similar to that described for analogues of dinuclear iron complexes.[3] In regard to mass spectrometry, the molecular ion at 496 *m/z* and the peaks for the successive losses of five CO groups are noted. All these data suggest the formation of a dinuclear iron complex.

The structural arrangement for **5b** was unequivocally established by X-ray diffraction analysis (Figure 2). The complex **5b** displays C−S bond activation and is analogous to **2** and [1-(1,3-dithiolan-2-yliden)-*p*-methoxyacetophenone)$Fe_2(CO)_5$], previously reported.[3,4,6.] The most salient feature of the structure is the nearly symmetrical μ-S [Fe1−S1: 2.337(1) Å, Fe2−S1: 2.337(1) Å] and totally asymmetrically μ-C [Fe1−C4: 2.193(4) Å, Fe2−C4: 1.933(4) Å] nature of the ligand toward the binuclear iron moiety, as a result of the 1,3-dithiolane ring expansion. Additionally, the distance N1−N2 was slightly increased with respect to the ligand [**5b**, N1−N2 (1.257 Å); **5**, N1−N2 (1.220 Å)], maintaining a weak bond interaction N2−S2 (2.846 Å). The structure presents disorder in the *tert*-butyl group, generating two orientations in 64:36 ratio. Only the major contributor is shown in Figure 2.

Complex **5c** was obtained as a black, crystalline solid. The IR spectrum reveals three bands at 1945, 2005, and 2068 cm^{-1}, for ν(M−CO). The ^{1}H NMR displays a singlet at 1.68 ppm, corresponding to the *tert*-butyl group (9H), shifted to low field, $\Delta\delta \approx 0.4$, with respect to **5** and **5b**. At 2.22 (2H) and 3.14 (2H) ppm, two multiple signals for the methylene groups were observed. In the ^{13}C NMR spectrum, the most affected chemical shifts are the N*C*═CSFe (153.7 ppm) and the *C*═*C*SFe (167.9 ppm); both signals displayed higher frequencies ($\Delta\delta \approx 15$ and 10, respectively) compared to the ligand. Additionally, five M−CO were observed up to 200 ppm. In the mass spectrum (FAB$^+$) of **5c**, the [M$^+$ + 1] appeared at $m/z = 497$, which corresponded with a dinuclear complex.

The structure of **5c** was fully established by X-ray diffraction analysis (Figure 3). This complex shows C−S bond activation, forming a new six-membered ring, again displaying a nearly symmetrical μ-S [Fe2−S2: 2.235(1) Å, Fe1−S2: 2.254(1) Å] and a totally asymmetrical μ-C, denoting that C4 is more tightly bonded to Fe2 [Fe2−C4: 1.928(3) Å, Fe1−C4: 2.175(3) Å]. The distance Fe1−Fe2 [2.6491(7) Å] corresponds with a single metal−metal bond. The coordination sphere of Fe1 is completed by a σ-S (S1) bond and three terminal CO groups, while for Fe2, the completion is made by a σ-N bond of the *azo* moiety and two terminal CO groups. The elongation of distances N1−N2 and C1−C4 and the decrease of distance N1−C1 with respect to **5** are certainly due to the σ-N coordination and the strong interaction between Fe1 and C4. Taking into account the X-ray diffraction analysis for **5b** and **5c**, we can propose that these complexes are better described as the resonance hybrids **A** and **B**, respectively, similar to complexes reported elsewhere[3,4] (Chart 2).

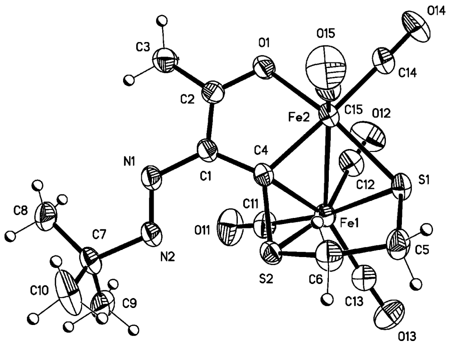


Figure 2. ORTEP drawing of **5b**. Thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Fe(1)−C(4) 2.193(4), Fe(1)−S(1) 2.263(1), Fe(1)−S(2) 2.337(1), Fe(1)−Fe(2) 2.623(1), Fe(2)−C(4) 1.933(4), Fe(2)−O(1) 1.966(3), Fe(2)−S(1) 2.214(1), S(2)−C(4) 1.744(4), O(1)−C(2) 1.281(5), N(1)−N(2) 1.257(5), C(1)−C(2) 1.392(6), C(1)−C(4) 1.428(5), C(4)−Fe(1)−S(1) 84.79(10), S(1)−Fe(1)−S(2) 87.64(4), C(4)−Fe(1)−Fe(2) 46.26(10), S(1)−Fe(1)−Fe(2) 53.26(3), S(2)−Fe(1)−Fe(2) 82.33(3), O(1)−Fe(2)−S(1) 158.27(10), C(4)−Fe(2)−Fe(1) 55.08(11), O(1)−Fe(2)−Fe(1) 105.87(9), S(1)−Fe(2)−Fe(1) 55.00(3), Fe(1)−S(2)−N(2) 101.96(8), N(1)−N(2)−S(2) 97.6(2), Fe(2)−S(1)−Fe(1) 71.73(4), Fe(2)−C(4)−Fe(1) 78.66(13).

---

[12] Dieter, R. K. *Tetrahedron* **1986**, *42*, 3029. Yates, P.; Lynch, T. R.; Moore, D. R. *Can. J. Chem.* **1971**, *49*, 1467.

[13] (a) Huges, D. L.; Leigh, G. L.; Paulson, D. *Inorg. Chim. Acta* **1986**, *120*, 191. (b) King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1584.

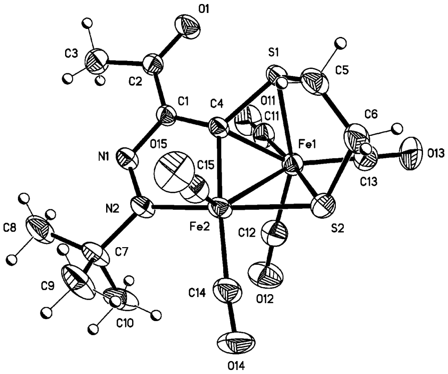


Figure 3. ORTEP drawing of **5c**. Thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Fe(1)−C(4) 2.175(3), Fe(1)−S(2) 2.254(1), Fe(1)−S(1) 2.299(1), Fe(1)−Fe(2) 2.6491(7), Fe(2)−C(4) 1.928(3), Fe(2)−N(2) 1.955(3), Fe(2)−S(2) 2.235(1), S(1)−C(4) 1.742(3), N(1)−N(2) 1.294(4), N(1)−C(1) 1.346(4), C(1)−C(4) 1.413(5), C(1)−C(2) 1.453(5), C(4)−Fe(1)−S(2) 84.83(9), C(4)−Fe(1)−S(1) 45.72(9), S(2)−Fe(1)−S(1) 87.79(4), C(4)−Fe(1)−Fe(2) 45.81(8), S(2)−Fe(1)−Fe(2) 53.51(3), S(1)−Fe(1)−Fe(2) 82.46(3), C(4)−Fe(2)−S(2) 91.42(10), N(2)−Fe(2)−S(2) 157.60(9), C(4)−Fe(2)−Fe(1) 54.00(10), N(2)−Fe(2)−Fe(1) 104.83(9), C(4)−S(1)−Fe(1) 63.38(11), C(4)−S(1)−O(1) 75.36(12), N(2)−N(1)−C(1) 113.9(3), N(1)−N(2)−Fe(2) 118.2(2), N(1)−C(1)−C(4) 115.3(3), C(1)−C(4)−Fe(1) 120.8(2), Fe(2)−C(4)−Fe(1) 80.18(12), Fe(2)−S(2)−Fe(1) 72.33(3).

Chart 2

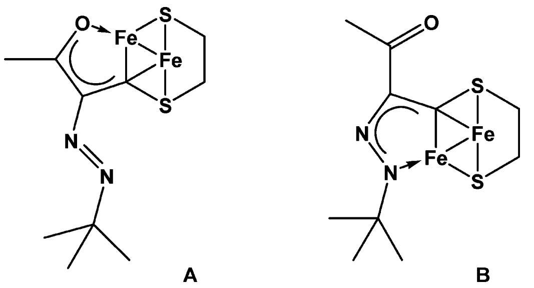


Table 1. Reaction of 5 and $Fe_2(CO)_9$ under Different Conditions

entry	condition reaction[a]	% yield	% **5**[b]	ratio **5a**:**5b**:**5c**
1	hexane	36.0	60.0	−:1:1
2	ether	28.0	68.2	1:4:7
3	THF	24.6	70	4:1:−
4	EtOH	26.3	29.8	6:1:2
5	acetonitrile	17.1	54	3:7:1

[a] Room temperature, 18 h. [b]Unreacted ligand.

We have carried out some experiments with the aim of analyzing different reaction conditions (Table 1). We observe a similar total yield of the reaction, but a different ratio of **5a**−**c**, which evidences that C−S bond activation is sensitive to the polarity of the solvent. Thus, the formation of dinuclear complexes **5b** and **5c** is favored in nonpolar solvents in the same ratio (entry 1), whereas **5a** is favored in polar solvents (entry 3). The latter compound could come from **5b** and/or **5c** via a second C−S bond activation. If a strong coordinating solvent such as acetonitrile is used, the reaction leads to more products that are very unstable, and it is not possible to isolate them.

With the aim of knowing the influence of ring size on the C−S bond activation, we reacted **6** and $Fe_2(CO)_9$, which resulted in the formation of two complexes (Scheme 2). Complex **6a** was the minor product,[14] while complex **6c** was totally analogous to **5c**, displaying regioselective carbon−sulfur bond activation. This activation occurs *syn* at the nitrogen atom. As in the previous experiment, we carried out this reaction under different conditions (Table 2), obtaining similar results to **5**. Nonpolar solvent promotes the formation of the dinuclear complex **6c**; however, polar solvents produce low yields of **6a** and **6c** and favor side-products. Comparing these results with those for **5** (Table 1), we can observe that ring size in **6** favors the formation of only one regioisomer complex, probably due to the conformational arrangement in the six-membered ring. The low yield of **6a** should indicate that its formation does not depend on **6c**. To gain a deeper insight into the formation of **5a** and **6a**, the isolated complexes **5b**,**c** and **6c** were stirred in boiling THF, under N_2. After 24 h, **5b**,**c** and **6c** were partially transformed into unstable side-products, and no evidence of **5a** and **6a** was obtained using TLC.

Table 2. Reaction of 6 and $Fe_2(CO)_9$ under Different Conditions

entry	condition reaction[a]	% yield	% **6**[b]	ratio **6a**:**6c**
1	hexane	48	12	1:10
2	ether	80.0	20.0	1:15
3	THF	19.0	8.0	1:18
4	EtOH	17.0		1:2

[a] Room temperature, 18 h. [b]Unreacted ligand.

In summary, we report the synthesis of two novel asymmetric *azo*-aliphatic compounds, in good yields, by a tandem procedure. These ligands are cross-conjugated systems, and this feature allowed us to study their reactivity toward $Fe_2(CO)_9$, leading to the formation of three novel dinuclear iron complexes (**5b**, **5c**, and **6c**). These complexes display one C−S bond activation. **5b** and **5c** exhibit an unusual stereochemistry about the Fe_2 unit. Additionally, two $Fe_2(SR)_2$ butterfly complexes (**5a** and **6a**) were obtained as result of a double C−S bond activation from **5** and **6**, respectively. The polarity of the solvents influences the formation of these complexes and their ratio. In nonpolar solvents, **5b**, **5c**, and **6c** are predominantly formed, while the formation of **5a** and **6a** is favored in polar solvents. Further studies using other metallic carbonyls are now being carried out in our laboratories.

Experimental Section

Materials. THF, ether, and hexane were distilled from benzophenone, under a nitrogen atmosphere. All reagents and solvents were obtained from commercial suppliers and used without further purification. $Fe_2(CO)_9$ was synthesized from $Fe(CO)_5$ according to the literature.[15] All compounds were characterized by IR spectra, recorded on a Perkin-Elmer 283B or 1420 spectrophotometer, by KBr technique, and all data are expressed in wavenumbers (cm^{-1}). Melting points were obtained on a Melt-Temp II apparatus and are uncorrected. NMR spectra were measured with a Jeol Eclipse +300, using $CDCl_3$ as solvent. Chemical shifts are in ppm (δ), relative to TMS. The MS-FAB and MS-EI spectra were obtained on a JEOL SX 102A. Elemental analyses were performed by the Analysis Service at the Faculty of Chemistry (UNAM).

(a) Synthesis of Ligands 5 and 6. A mixture of piruvaldehyde *tert*-butylhydrazone (3.6 g, 25.3 mmol) and carbon disulfide (3.1 mL, 51.4 mmol) was added, dropwise, to a suspension of potassium *tert*-butoxide (6.3 g, 51.4 mmol) in 50 mL of anhydrous THF, in 15 mL of THF, at 0 °C. The mixture was stirred for 45 min and the temperature allowed to rise slowly to room temperature. Subsequently, the alkylating reagent (51.4 mmol) was added.

---

(14) **6a** has been synthesized by other methods (see: Winter, A.; Zsolnai, L.; Huttner, G. Z. *Z. Naturforsch. Anorg. Chem*. **1982**, *37B*, 1430) and obtained by us as a subproduct from α,β-unsaturated ketone analogues in reactions brought about under similar conditions (ref 3).

(15) Braye, E. H.; Hübel, W. *Inorg. Synth.* **1966**, *8*, 178.

Table 3. Summary of Crystal Data, Data Collection, and Refinement Details

	5	**5b**	**5c**
formula	$C_{10}H_{16}N_2OS_2$	$C_{15}H_{16}Fe_2N_2O_6S_2$	$C_{15}H_{16}Fe_2N_2O_6S_2$
MW	244.37	496.12	496.12
cryst size (mm)	0.366 × 0.178 × 0.062	0.186 × 0.168 × 0.024	0.302 × 0.132 × 0.074
color	yellow plate	deep red plate	deep red prism
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
cell params (Å, deg)	$a = 5.832(3)$, $\alpha = 84.71$	$a = 7.519(1)$, $\alpha = 97.179(2)$	$a = 10.926(1)$, $\alpha = 90$
	$b = 5.833(3)$, $\beta = 84.73(1)$	$b = 7.918(1)$, $\beta = 94.098(2)$	$b = 7.197(1)$, $\beta = 98.153(1)$
	$c = 19.326(4)$, $\delta = 80.61(1)$	$c = 19.177(1)$, $\gamma = 113.176$	$c = 26.184(2)$, $\gamma = 90$
V (Å^3)	643.9(5)	1032.2(1)	2038.2(4)
Z	2	2	4
D_{calc} (g cm^{-3})	1.260	1.596	1.617
no. collected reflns	5230	12 266	16 133
no. indep reflns, R_{int}	2308, 0.0337	3635, 0.0426	3613, 0.0385
no. data/params	2308/200	3635/279	3613/248
R final, wR2[$I > 2\sigma(I)$]	0.0697, 0.1500	0.0501, 0.1087	0.0460, 0.1008
R1, wR2 (all data)	0.1070, 0.1069	0.0667, 0.1161	0.0575, 0.1064
GOOF on F^2	1.025	1.059	1.072

Finally, 30 mL of saturated solution in NaCl was added and the product extracted with CH_2Cl_2 (2 × 50 mL). The organic layer was dried with anhydrous Na_2SO_4, and the solvent was removed *in vacuo*. The product was purified by silica gel (70−230 mesh) chromatography, using hexane/ethyl acetate, in different ratios, as eluent, to obtain crystalline orange solids.

1-*N-tert*-Butylazo-1-(1,3-dithiolan-2-ylidene)propan-2-one (5): $C_{10}H_{16}N_2SO_2$, orange solid, 54% yield, mp 91−93 °C. IR ($CHCl_3$) ν_{max}, cm^{-1}: 2980 (C−H), 1649 (C═O), 1413 (C═S). MS-FAB *m/z* (%): 244 [M+] (100), 187 (83), 57 (100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.35 [s, 9H, C(C*H*$_3$)$_3$]; 2.55 [s, 3H, C(O)C*H*$_3$]; 3.18 [m, 4H, −(C*H*$_2$)$_2$]. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 27.3 [C(O)*C*H$_3$]; 28.1 [C(*C*H$_3$)$_3$]; 36.4 and 36.6 [−(*C*H$_2$)$_2$−]; 67.2 [*C*(CH$_3$)$_3$]; 139.9 [N*C*C(O)]; 158.1 (*C*SS); 195.5 (*C*O). Anal. Calcd for $C_{10}H_{16}N_2OS_2$: C, 49.15; H, 6.60; N, 11.46; S, 26.24. Found: C, 51.05; H, 6.95; N, 10.31; S, 26.24.

1-*N-tert*-Butylazo-1-(1,3-dithian-2-ylidene)propan-2-one (6): $C_{11}H_{18}N_2S_2O$, orange solid, 35% yield, mp 74−77 °C. IR ($CHCl_3$) ν_{max}, cm^{-1}: 2970, 2925, 2868 (C−H), 1655 (C═O), 1407 (C═S). MS-EI *m/z* (%): 258 [M+] (50), 201 (100), 173 (35), 57 (70). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.31 [s, 9H, C(C*H*$_3$)$_3$]; 2.23 [m, 2H, (CH$_2$)$_2$−C*H*$_2$−]; 2.34 [s, 3H, C(O)C*H*$_3$]; 2.69 and 2.85 [t, 4H, (C*H*$_2$)$_2$−CH$_2$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 25.6 [(CH$_2$)$_2$−*C*H$_2$]; 28.1 [C(*C*H$_3$)$_3$]; 28.8 [C(O)*C*H$_3$]; 29.8 and 30.1 [(*C*H$_2$)$_2$−CH$_2$]; 68.0 [*C*(CH$_3$)$_3$]; 145.8 [N*C*C(O)]; 157.8 (*C*SS); 194.7 (*C*O). Anal. Calcd for $C_{11}H_{18}N_2OS_2$: C, 51.13; H, 7.02; N, 10.84; S, 24.82. Found: C, 50.62; H, 6.98; N, 10.50; S, 25.26.

(b) Synthesis of Complexes. A solution of the ligands **5** and **6** (0.82 mmol) in anhydrous ethyl ether (30 mL) was treated with $Fe_2(CO)_9$ (2.46 mmol), with magnetic stirring at room temperature, for 18 h, under an inert atmosphere. After the reaction was complete, the crude was filtered off through an alumina column (5 cm long), and the solvent was evaporated under vacuum. The reaction mixture was chromatographed on preparative silica gel TLC plates, and elution with hexane/ethyl acetate in different ratios produced the corresponding iron complexes **5**,**6**(**a**−**c**). The yields are based on the pure products isolated.

5b: $C_{15}H_{16}Fe_2N_2O_6S_2$, black solid, mp 108 °C. IR ($CHCl_3$) ν_{max} cm^{-1}: 1948, 1967, 2017, 2062 (M − *C*O). MS-EI *m/z* (%): 496 [M$^+$] (10), 328 (100), 243 (64). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.31 [s, 9H, C(C*H*$_3$)$_3$]; 1.68, 2.20, and 2.88 [m, 4H, −(C*H*$_2$)$_2$]; 2.44 [s, 3H, C(O)C*H*$_3$]. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 28.2 [C(O)*C*H$_3$]; 29.8 [C(*C*H$_3$)$_3$]; 34.5 and 37.1 [−(*C*H$_2$)$_2$−]; 65.7 [*C*(CH$_3$)$_3$]; 137.7 [N*C*C(O)]; 146.2 (*C*SFe); 174.8 (*C*O); 209.7 and 213.2 (M − *C*O).

5c: $C_{15}H_{16}Fe_2N_2O_6S_2$, black solid, mp 126 °C. IR ($CHCl_3$) ν_{max}, cm^{-1}: 1945, 2005, 2068 (M − *C*O). MS-FAB$^+$ *m/z* (%): 497 [M + 1] (30), 440 (100), 57 (81). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.68 [s, 9H, C(C*H*$_3$)$_3$]; 2.22 and 3.14 [m, 4H, −(C*H*$_2$)$_2$]; 2.56 [s, 3H, C(O)C*H*$_3$]. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 28.1 [C(O)*C*H$_3$]; 31.8 [C(*C*H$_3$)$_3$]; 32.5 and 37.3 [−(*C*H$_2$)$_2$−]; 71.2 [*C*(CH$_3$)$_3$]; 153.7 [N*C*C(O)]; 167.9 (*C*SFe); 189.4 (*C*O); 201.6, 205.7, 209.7, 211.2, and 211.8 (M − *C*O).

6c: $C_{16}H_{18}Fe_2N_2O_6S_2$, black solid, mp 135 °C (dec). IR ($CHCl_3$) ν_{max}, cm^{-1}: 2969, 2926, 2854 (C−H); 2066, 2002, 2943 (M − *C*O); 1647 (CO). MS-FAB$^+$ *m/z*, (%): 511 [M$^+$+1] (5); 483 (7); 454 (20); 398 (5); 370 (12). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.82 and 2.11 (m, 2H, FeSC*H*$_2$); 2.53 [s, 3H, C*H*$_3$C(O)]; 2.40 (m, 2H, CSC*H*$_2$); 1.69 [s, 9H, C(C*H*$_3$)$_3$]; 1.62[m, 2H, (CH$_2$)$_2$−C*H*$_2$]. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 23.8 (CS*C*H$_2$); 26.2 [(CH$_2$)$_2$−*C*H$_2$]; 28.3 [*C*H$_3$C(O)]; 30.5 (FeS*C*H$_2$); 31.8 [C(*C*H$_3$)$_3$]; 71.9 [*C*(CH$_3$)$_3$]; 152.6 [N*C*C(O)]; 167.8 (*C*SFe); 189.7 (*C*O); 211.6 and 214.3 (M − *C*O). Anal. Calcd for $C_{16}H_{18}Fe_2N_2O_6S_2$: C, 37.65; H, 3.56; N, 5.49; S, 12.54. Found: C, 37.98; H, 3.75; N, 5.43; S, 12.80.

X-ray Crystallography Structure Determination. Suitable X-ray quality crystals of **5**, **5b**, and **5c** were grown by slow evaporation of an ether/*n*-hexane solvent mixture at −5 °C. A single orange crystal of compound **5** and single deep red crystals of compounds **5b** and **5c** were mounted on a glass fiber at room temperature. The crystals were then placed on a Bruker Smart Apex CCD diffractometer, equipped with Mo Kα radiation; decay was negligible in both cases. Details of crystallographic data collected on compounds **5**, **5b**, and **5c** are provided in Table 3. Systematic absences and intensity statistics were used in space group determination. All structures were solved using direct methods.[16] Anisotropic structure refinements were achieved using full-matrix, least-squares techniques on all non-hydrogen atoms. All hydrogen atoms were placed in idealized positions, based on hybridization, with isotropic thermal parameters fixed at 1.2 times the value of the attached atom. Structure solutions and refinements were performed using SHELXTL V 6.10.[17]

Acknowledgment. The authors appreciate the technical assistance of Erendira García, Georgina Duarte, Luis Velasco, Javier Pérez, and Nayeli López. They also wish to thank the CONACyT 46824Q project.

Supporting Information Available: Crystallographic data for **5**, **5b**, and **5c** are available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060953R

---

(16) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Canalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(17) *SHELXTL*, version 6.10; Bruker Analytical X-ray Systems: Madison, WI, 2000.