Synthesis and Spectroscopic Characterization of μ_4-S-Containing Double- and Triple-Butterfly Iron Carbonyl Complexes. Crystal Structures of $[(\mu\text{-EtTe})Fe_2(CO)_6]_2(\mu_4\text{-S})$, $(\mu\text{-PhS})[\mu\text{-Cp}(CO)_2FeSC{=}S][Fe_2(CO)_6]_2(\mu_4\text{-S})$, and $(\mu\text{-}p\text{-MeC}_6H_4S)[\mu\text{-Cp}(CO)_2FeS]\,[Fe_2(CO)_6]_3(\mu_4\text{-S})_2$

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We first investigated the nucleophilic reactivities of the complex anions $[(\mu\text{-RTe})(\mu\text{-CO})\text{-}Fe_2(CO)_6]^-$ (**1**), $\{(\mu\text{-RS})(\mu\text{-S}{=}CS)[Fe_2(CO)_6]_2(\mu_4\text{-S})\}^-$ (**3**), and $\{(\mu\text{-RS})(\mu\text{-S})[Fe_2(CO)_6]_3(\mu_4\text{-S})_2\}^-$ (**5**) toward the electrophiles SCl_2 and $Cp(CO)_2FeI$, respectively. Interestingly, while anions **1** undergo a new type of double nucleophilic substitution reaction with SCl_2 to give the series of one-μ_4-S-containing double-butterfly iron carbonyl complexes $[(\mu\text{-RTe})Fe_2(CO)_6]_2(\mu_4\text{-S})$ (**2a**, R = Et; **2b**, R = Ph; **2c**, R = *p*-MeC_6H_4; **2d**, R = *o*-MeC_6H_4; **2e**, R = α-$C_{10}H_7$), the single nucleophilic substitution reactions of anions **3** and **5** with $Cp(CO)_2FeI$ afford the one-μ_4-S-containing double-butterfly iron carbonyl complexes $(\mu\text{-RS})[\mu\text{-Cp}(CO)_2FeSC{=}S][Fe_2(CO)_6]_2\text{-}(\mu_4\text{-S})$ (**4a**, R = Me; **4b**, R = Et; **4c**, R = Ph; **4d**, R = *p*-MeC_6H_4) and the two-μ_4-S-containing triple-butterfly iron carbonyl complexes $(\mu\text{-RS})[\mu\text{-Cp}(CO)_2FeS][Fe_2(CO)_6]_3(\mu_4\text{-S})_2$ (**6a**, R = Me; **6b**, R = Ph; **6c**, R = *p*-MeC_6H_4), respectively. All the new complexes **2a**−**e, 4a**−**d,** and **6a**−**c** have been characterized by elemental analysis and IR and ^{1}H NMR spectroscopy, **2a**−**e** have been characterized as well by ^{125}Te NMR spectroscopy, and **2a, 4c**, and **6c** have been characterized by crystal X-ray diffraction techniques.

Introduction

In 1967, Dahl and co-workers prepared the first μ_4-S-containing double-butterfly iron carbonyl complex $[(\mu\text{-MeS})Fe_2(CO)_6]_2(\mu_4\text{-S})$ in ∼1% yield.[1] Later on, Carleton[2] and Glidewell[3] also prepared this μ_4-S-containing compound by other methods, but the yield is still very low (13% and ∼1%, respectively). In 1990 de Beer and co-workers[4] prepared another μ_4-S-containing double-butterfly iron carbonyl complex, $[(\mu\text{-}t\text{-BuS})Fe_2(CO)_6]_2(\mu_4\text{-S})$, in 5% yield; however, to our knowledge, no other μ_4-S-containing butterfly iron carbonyl complexes had been known before 1988, when we reported a general and convenient procedure for the synthesis of such double-butterfly complexes with the general formula $[(\mu\text{-RS})\text{-}Fe_2(CO)_6]_2(\mu_4\text{-S})$ (R= Me, Et, $PhCH_2$, *p*-MeC_6H_4, PhC≡C) in high yield (61−91%).[5] In view of the novelty and diversity of structures and reactivities of μ_4-S-containing iron carbonyl complexes, we have been interested in studying both μ_4-S-forming reactions and the reactions with μ_4-S-containing reactive intermediates, which has so far led us to obtain a great variety of double-, triple-, and even multiple-butterfly iron carbonyl complexes.[6−10] This article will describe a new type of μ_4-S-forming reaction to give the series of double-butterfly complexes $[(\mu\text{-RTe})Fe_2(CO)_6]_2(\mu_4\text{-S})$, and the nucleophilic reactions of the μ_4-S-containing anionic intermediates $\{(\mu\text{-RS})(\mu\text{-S}{=}CS)[Fe_2(CO)_6]_2(\mu_4\text{-S})\}^-$ and $\{(\mu\text{-RS})(\mu\text{-S})[Fe_2(CO)_6]_3(\mu_4\text{-S})_2\}^-$ to afford the double- and triple-butterfly complexes $(\mu\text{-RS})[\mu\text{-Cp}(CO)_2\text{-}FeSC{=}S][Fe_2(CO)_6]_2(\mu_4\text{-S})$ and $(\mu\text{-RS})[\mu\text{-Cp}\ (CO)_2FeS]\text{-}[Fe_2(CO)_6]_3(\mu_4\text{-S})_2$. In addition, structural characterizations of these new μ_4-S-containing complexes, particularly by X-ray diffraction techniques, are also described.

Results and Discussion

Syntheses via Reactions of the Anions $[(\mu\text{-RTe})\text{-}(\mu\text{-CO})Fe_2(CO)_6]^-$ (1) and Characterization of $[(\mu$-

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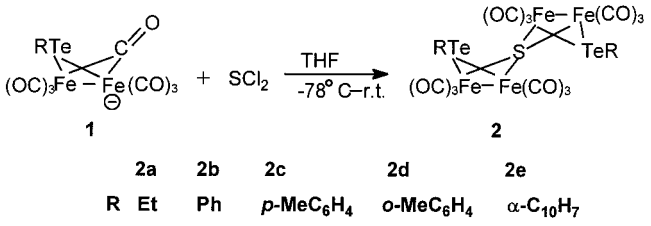
Scheme 1



RTe)$Fe_2(CO)_6]_2(\mu_4$-S) (2a−e). Crystal Structure of 2a (R = Et). We found that the $[MgBr]^+$ salts of anions **1**, formed from an insertion reaction of elemental Te with Grignard reagents RMgBr followed by reaction of the intermediates RTeMgBr with $Fe_3(CO)_{12}$,[11] could react with an excess amount of SCl_2 from −78 °C to room temperature in THF, through a type of μ_4-S-forming reaction to give the series of μ_4-S-containing double-butterfly iron carbonyl complexes **2a**−**e** (Scheme 1).

It is worth pointing out that both the μ_4-S-forming reaction of **1** with SCl_2 and the μ_4-S-containing double-butterfly $Fe_4Te_2(\mu_4$-S) products **2a**−**e** are new, although the μ_4-S-containing analogues with a double-butterfly core $Fe_4S_2(\mu_4$-S)[1−5] and $Fe_4Se_2(\mu_4$-S)[6] and the corresponding μ_4-S-forming reactions[1−6] were previously reported. Complexes **2a**−**e** have been characterized by combustion analysis and IR, ^{1}H NMR, and ^{125}Te NMR spectroscopy, as well as by X-ray diffraction techniques. ^{125}Te NMR spectroscopy has been developed as an important tool for characterizing Te-containing organometallic compounds.[12−14] We found that the ^{125}Te NMR spectra of **2a**−**e** each displayed a singlet in the region 168.5−309.5 ppm for their two bridged identical Te atoms. The ^{125}Te NMR resonance signal of **2a** (168.5 ppm) appeared at much higher field than those of **2b**−**e** (242.3−309.5 ppm), which is obviously due to the fact that the Et group in **2a** is an electron-donating group, whereas the aromatic R groups in **2b**−**e** are electron-withdrawing.

It is noteworthy that the reaction of the $[MgBr]^+$ salts of anions **1** with SCl_2 also afforded the corresponding single-butterfly complexes $(\mu$-RTe$)_2Fe_2(CO)_6$. This is not surprising, since reactions involving anions of type **1** were previously reported to produce the same type of complexes $(\mu$-RTe$)_2Fe_2(CO)_6$, possibly generated through decomposition of anions **1** followed by dimerization of the intermediate fragment $(\mu$-RTe)Fe$(CO)_3$.[15] The known complexes $(\mu$-RTe$)_2Fe_2(CO)_6$ (R = Et,[11] Ph,[15,16] *p*-MeC_6H_4,[15] *o*-MeC_6H_4[15]) were identified by comparison of their IR and ^{1}H NMR spectra with those of authentic samples, whereas the new complex (R = α-$C_{10}H_7$) was characterized by C/H analysis and IR and ^{1}H NMR spectroscopy.

The mechanism for the μ_4-S-forming reaction to produce the double-butterfly complexes **2a**−**e** can be proposed on the basis of similarity with the reactions of anions **1** with other electrophiles[11] (Scheme 2). Apparently, this mechanism involves a double nucleophilic attack of the negatively charged Fe atom in **1** at the S atom in SCl_2 to eliminate two Cl^- anions and a double coordination of the lone electron pairs on the S atom to the neighboring Fe atoms with concomitant loss of two μ-CO ligands.

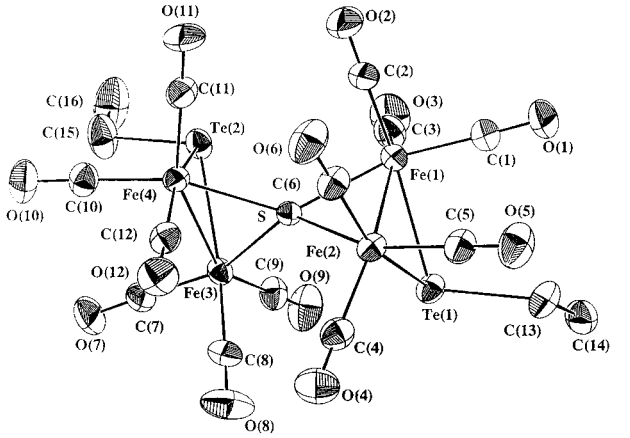


Figure 1. ORTEP drawing of **2a** with atom-labeling scheme.

Scheme 2

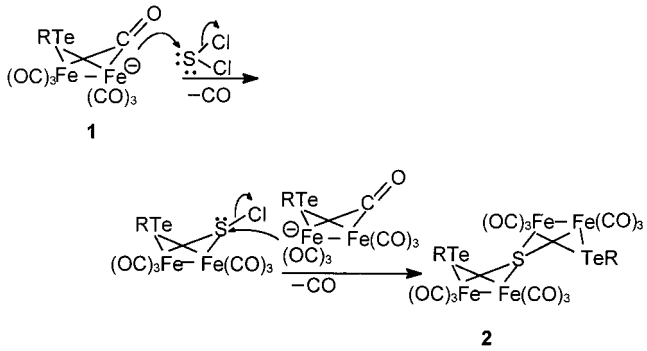


Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2a

Te(1)−Fe(2)	2.546(2)	Te(1)−Fe(1)	2.563(1)
Te(2)−Fe(4)	2.533(2)	Te(2)−Fe(3)	2.555(1)
Fe(4)−S	2.241(2)	Fe(1)−S	2.248(2)
Fe(2)−S	2.240(2)	Fe(1)−Fe(2)	2.572(2)
Fe(3)−S	2.243(2)	Fe(3)−Fe(4)	2.577(2)
Fe(4)−S−Fe(3)	70.17(6)	Fe(3)−S−Fe(1)	129.15(8)
Fe(4)−S−Fe(2)	129.32(8)	Fe(1)−S−Fe(2)	69.93(6)
Fe(1)−Te(1)−Fe(2)	60.45(4)	Fe(3)−Te(2)−Fe(4)	60.86(4)
S−Fe(1)−Te(1)	78.82(6)	S−Fe(1)−Fe(2)	54.88(5)
S−Fe(3)−Te(2)	78.98(5)	S−Fe(3)−Fe(4)	54.87(5)
Te(2)−Fe(3)−Fe(4)	59.14(4)	Te(1)−Fe(1)−Fe(2)	59.45(4)

To unequivocally confirm the double-butterfly structures of the products obtained from the above new type of reaction, a single-crystal X-ray diffraction analysis for $[(\mu$-EtTe$)Fe_2(CO)_6]_2(\mu_4$-S) (**2a**) was performed. While Figure 1 shows its structure, Table 1 lists the selected bond lengths and angles. The X-ray diffraction study revealed that **2a** consists of the two butterfly cores Fe(1)Fe(2)Te(1)S and Fe(3)Fe(4)Te(2)S joined to a spiro type of S atom, the dihedral angle between Fe(1)−Fe(2)−S and Fe(3)−Fe(4)−S is 96.6°, each Fe atom

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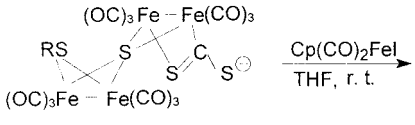
Scheme 3



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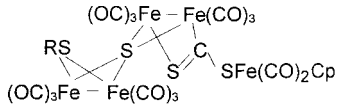

4

	4a	**4b**	**4c**	**4d**
R	Me	Et	Ph	*p*-MeC_6H_4

carries three terminal carbonyls, and both Te atoms are attached to Et groups by an equatorial type of bond.[17] Thus, this structure is completely similar to those of its analogues [(μ-MeS)$Fe_2(CO)_6]_2(\mu_4$-S)[1] and [(μ-EtS)$Fe_2(CO)_6]_2(\mu_4$-S).[5] The similarity can be also seen from the comparable parameters between **2a** and its two above-mentioned analogues. For instance, in **2a** the bond lengths Fe(1)−Fe(2) and Fe(3)−Fe(4) are 2.572(2) and 2.577(2) Å, whereas in [(μ-EtS)$Fe_2(CO)_6]_2(\mu_4$-S) the corresponding bond lengths are 2.542(2) and 2.538(2) Å. In addition, in **2a** the bond angles Fe(1)−S−Fe(2) and Fe(3)−S−Fe(4) are 69.93(6) and 70.17(6)°, whereas in the latter the corresponding angles are 69.04(7) and 68.69(7)°. The minor differences in parameters between **2a** and [(μ-EtS)$Fe_2(CO)_6]_2(\mu_4$-S) are apparently due to replacement of the two wing-tip S atoms in the butterfly core of [(μ-EtS)$Fe_2(CO)_6]_2(\mu_4$-S) by two Te atoms.

Syntheses via Reactions of the Anions {(μ-RS)(μ-S=CS)$[Fe_2(CO)_6]_2(\mu_4$-S)}$^-$ (3) and Characterization of (μ-RS)[μ-Cp$(CO)_2$FeSC=S]$[Fe_2(CO)_6]_2(\mu_4$-S) (4a−d). Crystal Structure of 4c (R = Ph). Interestingly, we have further found that the novel μ_4-S-containing anionic intermediates **3**, which were prepared as their $[MgX]^+$ (X = Br, I) salts from a sequential reaction of μ-$S_2Fe_2(CO)_6$ with the Grignard reagents RMgX, $Fe_3(CO)_{12}$, and CS_2,[9] could undergo nucleophilic substitution reactions with $Cp(CO)_2FeI$ in THF at room temperature, affording the S-functionalized double-butterfly iron carbonyl conplexes **4a**−**d**, as shown in Scheme 3.

Complexes **4a**−**d** were characterized by elemental analysis, spectroscopy, and X-ray crystal diffraction analysis. For example, the IR spectra of **4a**−**d** showed one absorption band in the region 1020−999 cm^{-1} for the coordinated C=S double bond,[18] whereas the ^{1}H NMR spectra of **4a**−**d** exhibited a singlet in the range 5.03−5.38 ppm for their Cp groups. To unambiguously confirm the double-butterfly structures of the products generated from anions **3**, a single-crystal X-ray diffraction analysis for (μ-PhS)[μ-Cp$(CO)_2$FeSC=S]$[Fe_2(CO)_6]_2$-(μ_4-S) (**4c**) was undertaken. The molecular structure of **4c** is shown in Figure 2, whereas its selected bond lengths and angles are given in Table 2. The X-ray diffraction study showed that **4c** consists of the two butterfly subcluster cores Fe(1)Fe(2)S(1)S(2) and Fe(3)Fe(4)S(1)C(15)S(3) joined to a spiro type of S(1) atom. The dihedral angle between Fe(1)−Fe(2)−S(1) and Fe(3)−Fe(4)−S(1) is 97.1°, while the S(2) atom is bonded to C(16) of the phenyl group by an equatorial type of bond.[17] The S(4) atom is bound to C(15) as well as Fe(5) of the $Cp(CO)_2Fe$ group; in addition, all 12 carbonyls attached to the Fe(1)−Fe(5) atoms are terminal. The geometric parameters of **4c** are similar to those of its analogue (μ-MeS)(μ-MeSC=S)$[Fe_2(CO)_6]_2(\mu_4$-S).[9] For example, in **4c** the bond lengths Fe(1)−Fe(2) and Fe(3)−Fe(4) are 2.5356(6) and 2.6234(5) Å, whereas in (μ-MeS)(μ-MeSC=S)$[Fe_2(CO)_6]_2(\mu_4$-S) the corresponding lengths are 2.5376(8) and 2.6496(7) Å. In addition, in **4c** the coordinated thiocarbonyl C(15)=S(3) is 1.671-(3) Å, whereas the corresponding thiocarbonyl in (μ-MeS)(μ-MeSC=S)$[Fe_2(CO)_6]_2(\mu_4$-S) is 1.672(4) Å. Apparently, the coordinated thiocarbonyls in **4c** and (μ-MeS)-(μ-MeSC=S)$[Fe_2(CO)_6]_2(\mu_4$-S) are just slightly longer than the corresponding thiocarbonyl in (μ-PhSe)-(μ-$PhCH_2SC$=S)$Fe_2(CO)_6$ (1.63(1) Å)[19] but are much longer than the uncoordinated C=S double bond in free CS_2 (1.554 Å).[20]

Syntheses via Reactions of Anions {(μ-RS)(μ-S)-$[Fe_2(CO)_6]_3(\mu_4$-S)$_2$}$^-$ (5) and Characterization of (μ-RS)[μ-Cp$(CO)_2$FeS]$[Fe_2(CO)_6]_3(\mu_4$-S)$_2$ (6a−c). Crystal Structure of 6c (R = *p*-MeC_6H_4). More interestingly, we have found that the $[MgX]^+$ (X = Br, I) salts of the novel two-μ_4-S-containing triple-butterfly anions **5**, prepared from the sequential reaction of μ-S_2-$Fe_2(CO)_6$ with the Grignard reagents RMgX, $Fe_3(CO)_{12}$ and μ-$S_2Fe_2(CO)_6$,[9] could also undergo nucleophilic substitution reactions with the electrophile $Cp(CO)_2FeI$ in THF at room temperature to give the triple-butterfly iron carbonyl complexes **6a**−**c**, as shown in Scheme 4.

Products **6a**−**c** were chatacterized by elemental analysis, spectroscopy, and X-ray crystal diffraction analysis. For example, the IR spectra of **6a**−**c** displayed three absorption bands in the range 2086−1988 cm^{-1} for their terminal carbonyls, whereas the ^{1}H NMR spectra of **6a**−**c** exhibited a singlet at ca. 5.47 ppm for their Cp groups. In principle, the R and $Cp(CO)_2Fe$ groups in **6a**−**c** should be attached to the bridged S atoms by an equatorial type of bond, to avoid the sterically strong repulsions between these groups and the structural moieties axially bonded to their neighboring bridged S atoms.[6,7] Fortunately, this has been confirmed by crystal X-ray diffraction analysis of **6c**. The molecular structure of **6c** is shown in Figure 3, whereas its selected bond lengths and angles are given in Table 3.

As shown in Figure 3, **6c** contains the three butterfly cores Fe(2)Fe(3)S(1)S(2), Fe(4)Fe(5)S(2)S(3), and Fe(6)Fe(7)S(3)S(4) joined together by two μ_4-S atoms of S(2) and S(3). In addition, except for Fe(1) with two terminal carbonyls, each of the Fe atoms from Fe(2) to Fe(7) is linked to three terminal carbonyls, and the Cp-$(CO)_2$Fe and *p*-MeC_6H_4 groups are bonded to the bridged S atoms of S(1) and S(4) by an equatorial type of bond, respectively. It is worthy of note that in the three butterfly cores the geometric parameters of the middle core are slightly different from those of the two side cores. For example, the bond length of Fe(2)−Fe(3) (2.5059(11) Å) or Fe(6)−Fe(7) (2.5094(11) Å) is shorter

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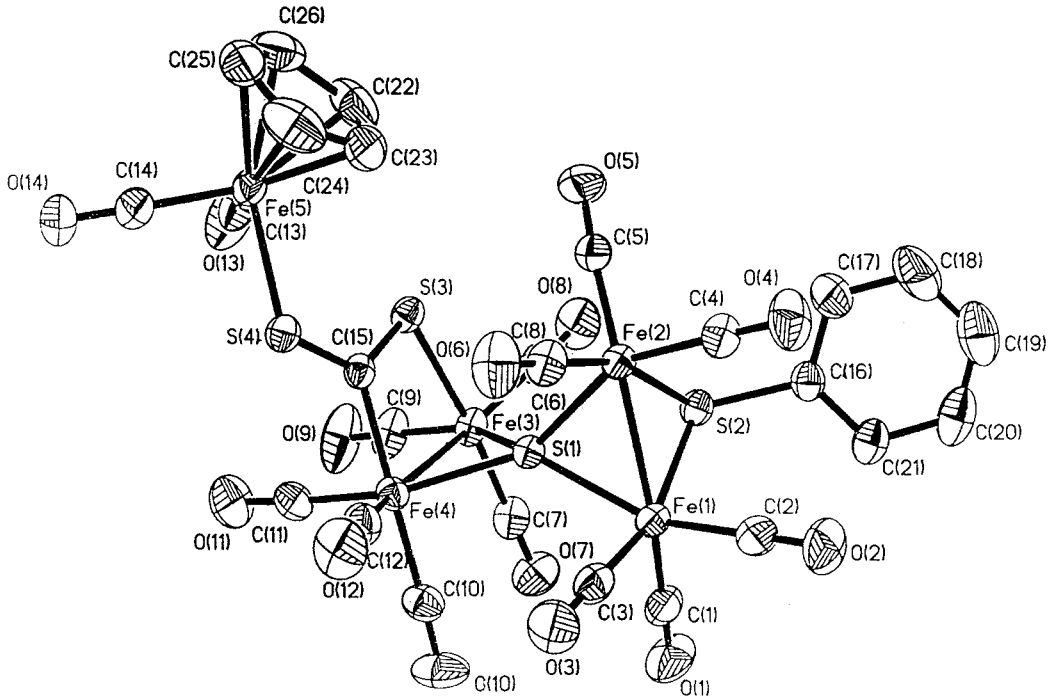
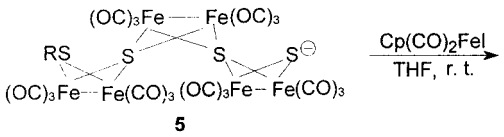


Figure 2. ORTEP drawing of **4c** with atom-labeling scheme.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4c

Fe(1)−S(1)	2.2532(7)	Fe(1)−S(2)	2.2748(8)
Fe(1)−Fe(2)	2.5356(6)	Fe(2)−S(1)	2.2480(7)
Fe(2)−S(2)	2.2784(8)	Fe(3)−S(1)	2.2366(7)
Fe(3)−S(3)	2.3119(8)	Fe(3)−Fe(4)	2.6234(5)
Fe(5)−S(4)	2.2631(8)	S(1)−Fe(4)	2.2411(7)
C(15)−S(3)	1.671(3)	C(15)−S(4)	1.683(3)
S(1)−Fe(1)−S(2)	76.57(3)	Fe(3)−S(1)−Fe(4)	71.73(2)
Fe(3)−S(1)−Fe(2)	126.97(3)	Fe(4)−S(1)−Fe(2)	137.08(3)
Fe(3)−S(1)−Fe(1)	133.41(3)	S(1)−Fe(2)−Fe(1)	55.81(2)
S(1)−Fe(1)−Fe(2)	55.62(2)	S(2)−Fe(2)−Fe(1)	56.09(2)
S(2)−Fe(1)−Fe(2)	56.23(2)	S(1)−Fe(2)−S(2)	76.60(3)
Fe(1)−S(2)−Fe(2)	67.68(2)	Fe(4)−S(1)−Fe(1)	130.85(3)
S(3)−Fe(3)−Fe(4)	75.67(2)	S(1)−Fe(4)−Fe(3)	54.056(19)

Scheme 4



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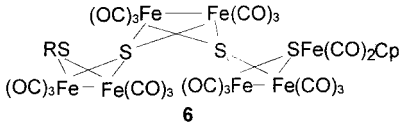

6

	6a	**6b**	**6c**
R	Me	Ph	*p*-MeC_6H_4

than that of Fe(4)−Fe(5) (2.5684(11) Å), and the dihedral angle between Fe(2)−Fe(3)−S(1) and Fe(2)−Fe(3)−(2) (85.02°) or Fe(6)−Fe(7)−S(3) and Fe(6)−Fe(7)−S(4) (84.00°) is larger than that between Fe(4)−Fe(5)−S(2) and Fe(4)−Fe(5)−S(3) (73.53°). In fact, the basic geometric parameters of **6c** are comparable with those of the butterfly Fe/S cluster complexes, such as $[(\mu\text{-PhS})Fe_2(CO)_6(\mu\text{-S})]_2$[21] and $(\mu\text{-PhCH}_2S)_2[Fe_2(CO)_6]_3(\mu_4\text{-S})_2$.[9]

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen using standard Schlenk and vacuum-line techniques. Tetrahydrofuran (THF) was distilled from Na/benzophenone ketyl under nitrogen. $Fe_3(CO)_{12}$,[22] $\mu\text{-}S_2Fe_2(CO)_6$,[23] the Grignard reagents RMgX,[24] SCl_2,[25] and $Cp(CO)_2FeI$[26] were prepared according to literature procedures, whereas the others used in this paper were of commercial origin and used without further purification. Preparative TLC was carried out on glass plates (26 × 20 × 0.25 cm) coated with silica gel H (10−40 μm). IR spectra were recorded on a Nicolet 170SX FT-IR or Bruker Vector 22 infrared spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AC-P 200 NMR spectrometer. ^{125}Te NMR spectra were recorded on a Varian Unity-Plus 400 NMR spectrometer with Ph_2Te_2 as external standard, and the chemical shifts are referenced to Me_2Te (δ 0). C/H analyses were performed on a Yanaco CHN Corder MT-3 analyzer or a Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus and were uncorrected.

Standard in Situ Preparation of $[MgBr]^+$ Salts of the Anions $[(\mu\text{-RTe})[(\mu\text{-CO})Fe_2(CO)_6]^-$ (1). A 100 mL two-necked flask equipped with a stir bar, a serum cap, and a reflux condenser topped with a nitrogen inlet tube was charged with 0.511 g (4.0 mmol) of tellurium powder, 25 mL of THF, and 4.0 mmol of RMgBr (R = Et, Ph, *p*-MeC_6H_4, *o*-MeC_6H_4, α-$C_{10}H_7$) in Et_2O. The mixture was refluxed for 2 h to give a slight gray solution of RTeMgBr. When the solution was cooled to room temperature, 2.0 g (3.96 mmol) of $Fe_3(CO)_{12}$ was added and the reaction mixture was stirred for ca. 0.5 h to produce a brown-red solution containing the salt of **1**[MgBr] (R = Et,

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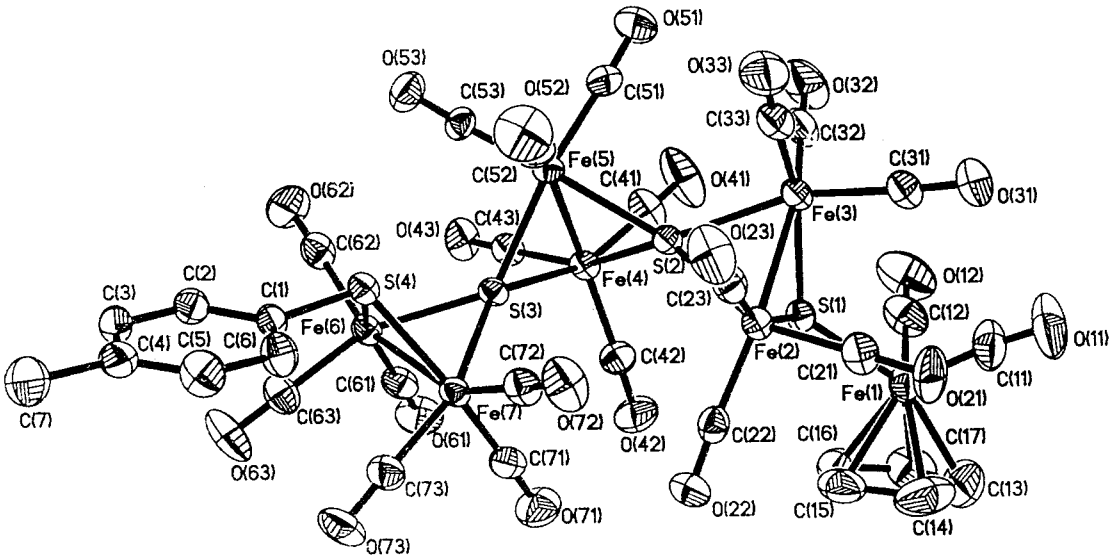

Figure 3. ORTEP drawing of **6c** with atom-labeling scheme.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 6c

Fe(1)−S(1)	2.3008(18)	S(1)−Fe(2)	2.2806(16)
Fe(2)−S(2)	2.2827(15)	Fe(2)−Fe(3)	2.5059(11)
Fe(7)−S(3)	2.2632(14)	Fe(7)−S(4)	2.2769(17)
Fe(3)−S(2)	2.2809(15)	Fe(3)−S(1)	2.2887(17)
Fe(4)−S(3)	2.2492(15)	S(2)−Fe(4)	2.2642(15)
Fe(4)−Fe(5)	2.5684(11)	Fe(6)−Fe(7)	2.5094(11)
S(3)−Fe(6)−S(4)	76.55(5)	S(3)−Fe(6)−Fe(7)	56.29(4)
S(4)−Fe(6)−Fe(7)	56.63(4)	S(3)−Fe(7)−S(4)	76.50(5)
S(3)−Fe(7)−Fe(6)	56.44(4)	S(4)−Fe(7)−Fe(6)	56.39(4)
Fe(2)−S(1)−Fe(3)	66.52(5)	Fe(2)−S(1)−Fe(1)	125.02(7)
Fe(3)−S(1)−Fe(1)	131.15(7)	Fe(5)−S(2)−Fe(4)	69.12(5)
Fe(5)−S(2)−Fe(3)	129.27(6)	Fe(4)−S(2)−Fe(3)	129.37(7)

Ph, *p*-MeC_6H_4, *o*-MeC_6H_4, α-$C_{10}H_7$), which was employed immediately in the preparations of **2a**−**e**.

Preparation of [(μ-EtTe)$Fe_2(CO)_6$]$_2$(μ$_4$-S) (2a). To the above prepared solution of **1**[MgBr] (R = Et), which had been cooled to −78 °C by a dry ice/acetone bath, was added 0.10 mL (1.5 mmol) of SCl_2, and this mixture was stirred for 20 min. After the dry ice/acetone bath was removed, the mixture was naturally warmed to room temperature and then continued to be stirred for 4 h. The solvent was removed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 1:20) as eluent. From the first main red band was obtained 0.289 g (24%) of (μ-$EtTe)_2Fe_2(CO)_6$.[11] The second main brown-red band afforded 0.129 g (10%) of **2a** as a red solid. Mp: 113.5 °C dec. Anal. Calcd for $C_{16}H_{10}Fe_4O_{12}STe_2$: C, 21.24; H, 1.11. Found: C, 20.97; H, 1.00. IR (KBr disk): $\nu_{C\equiv O}$ 2090 (m), 2046 (s), 2042 (vs), 1981 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 1.50−1.64 (m, 6H, $2CH_3$), 2.75−2.85 (m, 4H, $2CH_2$) ppm. ^{125}Te NMR ($CDCl_3$): 168.5 (s) ppm.

Preparation of [(μ-PhTe)$Fe_2(CO)_6$]$_2$(μ$_4$-S) (2b). The same procedure as that for **2a** was followed, but **1**[MgBr] (R = Ph) was used instead of **1**[MgBr] (R = Et). From the first main orange-red band was obtained 0.202 g (15%) of (μ-$PhTe)_2Fe_2(CO)_6$.[15] The second main orange-red band afforded 0.304 g (20%) of **2b** as a red solid. Mp: 202 °C dec. Anal. Calcd for $C_{24}H_{10}Fe_4O_{12}STe_2$: C, 28.80; H, 1.01. Found: C, 28.65; H, 1.14. IR (KBr disk): $\nu_{C\equiv O}$ 2082 (s), 2044 (vs), 2026 (vs), 1985 (vs), 1966 (vs) cm^{-1}. ^{1}H NMR (acetone-d_6): 7.10−7.64 (m, 10H, $2C_6H_5$) ppm. ^{125}Te NMR ($CDCl_3$): 309.5(s) ppm.

Preparation of [(μ-*p*-MeC_6H_4Te)$Fe_2(CO)_6$]$_2$(μ$_4$-S) (2c). The same procedure as that for **2a** was followed, but **1**[MgBr] (R = *p*-MeC_6H_4) was used instead of **1**[MgBr] (R = Et). From the first main red band was obtained 0.521 g (36%) of (μ-*p*-$MeC_6H_4Te)_2Fe_2(CO)_6$.[15] The second main dark red band afforded 0.324 g (21%) of **2c** as a dark red solid. Mp: 215 °C dec. Anal. Calcd for $C_{26}H_{14}Fe_4O_{12}STe_2$: C, 30.34; H, 1.37. Found: C, 30.30; H, 1.24. IR (KBr disk): $\nu_{C\equiv O}$ 2074 (s), 2045 (s), 2034 (vs), 1989 (vs), 1970 (vs) cm^{-1}. ^{1}H NMR (acetone-d_6): 2.30 (s. 6H, $2CH_3$), 7.30 (q, AA′BB′, *J* = 7.8 Hz, 8H, $2C_6H_4$) ppm. ^{125}Te NMR ($CDCl_3$): 306.3 (s) ppm.

Preparation of [(μ-*o*-MeC_6H_4Te)$Fe_2(CO)_6$]$_2$(μ$_4$-S) (2d). The same procedure as that for **2a** was followed, but **1**[MgBr] (R = *o*-MeC_6H_4) was used instead of **1**[MgBr] (R = Et). From the first main orange-red band was obtained 0.240 g (17%) of (μ-*o*-$MeC_6H_4Te)_2Fe_2(CO)_6$.[15] The second main brown-red band afforded 0.318 g (21%) of **2d** as a red solid. Mp: 216 °C dec. Anal. Calcd for $C_{26}H_{14}Fe_4O_{12}STe_2$: C, 30.34; H, 1.37. Found: C, 30.36; H, 1.45. IR (KBr disk): $\nu_{C\equiv O}$ 2082 (s), 2026 (vs), 2010 (s), 1989 (vs), 1973 (vs), 1958 (vs) cm^{-1}. ^{1}H NMR (acetone-d_6): 2.54 (s. 6H, $2CH_3$), 7.07−7.67 (m, 8H, $2C_6H_4$) ppm. ^{125}Te NMR ($CDCl_3$): 266.2 (s) ppm.

Preparation of [(μ-α-$C_{10}H_7Te$)$Fe_2(CO)_6$]$_2$(μ$_4$-S) (2e). The same procedure as that for **2a** was followed, but **1**[MgBr] (R = α-$C_{10}H_7$) was used instead of **1**[MgBr] (R = Et). From the first main red band was obtained 0.240 g (15%) of (μ-α-$C_{10}H_7$-$Te)_2Fe_2(CO)_6$ as a red solid. Mp: 145−148 °C. Anal. Calcd for $C_{26}H_{14}Fe_2O_6Te_2$: C, 39.57; H, 1.79. Found: C, 39.29; H, 1.55. IR (KBr disk): $\nu_{C\equiv O}$ 2060 (s), 2032 (vs), 1988 (vs), 1963 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.00−8.15 (m, 14H, $2C_{10}H_7$) ppm. The second main brown-red band afforded 0.286 g (17%) of **2e** as a dark red solid. Mp: 205 °C dec. Anal. Calcd for $C_{32}H_{14}Fe_4O_{12}$-$SeTe_2$: C, 34.90; H, 1.28. Found: C, 34.77; H, 1.50. IR (KBr disk): $\nu_{C\equiv O}$ 2082 (s), 2050 (vs), 2018 (vs), 1993 (vs), 1977 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.01−8.13 (m, 14H, $2C_{10}H_7$) ppm. ^{125}Te NMR ($CDCl_3$): 242.3 (s) ppm.

Standard in Situ Preparation of [MgX]$^+$ Salts of the Anions {(μ-RS)(μ-S=CS)[$Fe_2(CO)_6$]$_2$(μ$_4$-S)}$^-$ (3). A 100 mL two-necked flask equipped with a stir bar, an N_2 inlet tube, and a serum cap was charged with 0.172 g (0.5 mmol) of μ-$S_2Fe_2(CO)_6$ and 20 mL of THF. The resulting red solution was stirred and cooled to −78 °C using a dry ice/acetone bath. Into this solution was injected a given amount of RMgX (R = Me, Et, Ph, *p*-MeC_6H_4) in Et_2O by a syringe until the mixture turned to emerald green to give a solution of the [MgX]$^+$ salts of the anions [(μ-RS)(μ-S)$Fe_2(CO)_6$]$^-$. To this solution was added 0.252 g (0.5 mmol) of $Fe_3(CO)_{12}$, and then the mixture was warmed to room temperature by removing the dry ice/acetone bath and was stirred at this temperature for 1 h to give a solution of the [MgX]$^+$ salts of the anions {(μ-RS)-(μ-CO)[$Fe_2(CO)_6$]$_2$(μ$_4$-S)}$^-$. To this solution was added 0.10 mL (1.8 mmol) of CS_2, and the mixture was stirred at room temperature for 1 h to give a red-brown solution containing

the salt **3**[MgX] (R = Me, Et, Ph, *p*-MeC_6H_4; X = Br, I), which was immediately used for preparations of **4a**−**d.**

Preparation of (μ-MeS)[μ-Cp(CO)$_2$FeSC=S][Fe$_2$(CO)$_6$]$_2$-(μ_4-S) (4a). To the above prepared solution of **3**[MgX] (R = Me; X = I) was added 0.152 g (0.5 mmol) of $Cp(CO)_2FeI$. After the mixture was stirred for 12 h, the solvent was removed under reduced pressure to give a residue, which was subjected to TLC separation using CH_2Cl_2/petroleum ether (2/5 v/v) as eluent. From the main orange-red band 0.161 g (36%) of **4a** was obtained as an orange-red solid. Mp: 145 °C dec. Anal. Calcd for $C_{21}H_8Fe_5O_{14}S_4$: C, 28.28; H, 0.90. Found: C, 27.98; H, 0.89. IR (KBr disk): $\nu_{C\equiv O}$ 2077 (s), 2051 (vs), 2027 (vs), 1991 (vs); $\nu_{C=S}$ 1005 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.23 (s, 3H, CH_3), 5.05 (s, 5H, C_5H_5) ppm.

Preparation of (μ-EtS)[μ-Cp(CO)$_2$FeSC=S][Fe$_2$(CO)$_6$]$_2$-(μ_4-S) (4b). The same procedure as that for **4a** was followed, but **3**[MgX] (R = Et; X = Br) was used instead of **3**[MgX] (R = Me; X = I). From the main orange-red band 0.169 g (37%) of **4b** was obtained as a red solid. Mp: 143 °C dec. Anal. Calcd for $C_{22}H_{10}Fe_5O_{14}S_4$: C, 29.17; H, 1.11. Found: C, 28.99; H, 1.30. IR (KBr disk): $\nu_{C\equiv O}$ 2077 (s), 2048 (vs), 2029 (vs), 1987 (vs); $\nu_{C=S}$ 1001 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 1.42 (br s, 3H, CH_3), 2.55 (br s, 2H, CH_2), 5.05 (s, 5H, C_5H_5) ppm.

Preparation of (μ-PhS)[μ-Cp(CO)$_2$FeSC=S][Fe$_2$(CO)$_6$]$_2$-(μ_4-S) (4c). The same procedure as that for **4a** was followed, but **3**[MgX] (R = Ph; X = Br) was used instead of **3**[MgX] (R = Me; X = I). From the main orange-red band 0.178 g (37%) of **4c** was obtained as a red solid. Mp: 154 °C dec. Anal. Calcd for $C_{26}H_{10}Fe_5O_{14}S_4$: C, 32.74; H, 1.06. Found: C, 32.56; H, 1.04. IR (KBr disk): $\nu_{C\equiv O}$ 2078 (s), 2051 (vs), 2032 (vs), 1988 (vs); $\nu_{C=S}$ 1006 (s) cm^{-1}. ^{1}H NMR (acetone-d_6): 5.38 (s, 5H, C_5H_5), 7.25−7.65 (m, 5H, C_6H_5) ppm.

Preparation of (μ-*p*-MeC$_6$H$_4$S)[μ-Cp(CO)$_2$FeSC=S][Fe$_2$-(CO)$_6$]$_2$(μ_4-S) (4d). The same procedure as that for **4a** was followed, but **3**[MgX] (R = *p*-MeC_6H_4; X = Br) was used instead of **3**[MgX] (R = Me; X = I). From the main orange-red band 0.186 g (38%) of **4d** was obtained as a red solid. Mp: 141 °C dec. Anal. Calcd for $C_{27}H_{12}Fe_5O_{14}S_4$: C, 33.51; H, 1.25. Found: C, 33.56; H, 1.15. IR (KBr disk): $\nu_{C\equiv O}$ 2077 (s), 2053 (vs), 2032 (vs), 1994 (vs); $\nu_{C=S}$ 999 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.29 (s, 3H, CH_3), 5.03 (s, 5H, C_5H_5), 7.00−7.45 (m, 4H, C_6H_4) ppm.

Standard in Situ Preparation of [MgX]$^+$ Salts of the Anions {[(μ-RS)(μ-S)[Fe$_2$(CO)$_6$]$_3$(μ_4-S)$_2$}$^-$ (5). To the $[MgX]^+$ salts of the intermediate anions {(μ-RS)(μ-CO)[$Fe_2(CO)_6$]$_2$(μ_4-S)}$^-$ (R = Me, Ph, *p*-MeC_6H_4; X = Br, I) prepared as described above in the preparation of $[MgX]^+$ salts of anions **3** was added 0.172 g (0.5 mmol) of μ-$S_2Fe_2(CO)_6$. The mixture was stirred for 2 h at room temperature to give a solution containing the salt **5**[MgX] (R = Me, Ph, *p*-MeC_6H_4; X = Br, I), which was utilized in the following preparations for **6a**−**c**.

Preparation of (μ-MeS)[μ-CpFe(CO)$_2$S][Fe$_2$(CO)$_6$]$_3$(μ_4-S)$_2$ (6a). To the above prepared solution of **5**[MgX] (R = Me; X = I) was added 0.258 g (0.75 mmol) of $Cp(CO)_2FeI$. The new mixture was stirred overnight. Solvent was removed under reduced pressure to give a residue, which was subjected to TLC separation using CH_2Cl_2/petroleum ether (1/7 v/v) as eluent. From the main red band 0.123 g (21%) of **6a** was obtained as a black solid. Mp: 162 °C dec. Anal. Calcd for $C_{26}H_8Fe_7O_{20}S_4$: C, 26.93; H, 0.70. Found: C, 26.50; H, 0.93. IR (KBr disk): $\nu_{C\equiv O}$ 2086 (s), 2041 (vs), 1988 (vs) cm^{-1}. ^{1}H NMR (acetone-d_6): 2.32 (s, 3H, CH_3), 5.46 (s, 5H, C_5H_5) ppm.

Preparation of (μ-PhS)[μ-CpFe(CO)$_2$S][Fe$_2$(CO)$_6$]$_3$(μ_4-S)$_2$ (6b). The same procedure as that for **6a** was followed, but **5**[MgX] (R = Ph; X = Br) was used instead of **5**[MgX] (R = Me; X = I). From the main red band 0.138 g (23%) of **6b** was obtained as a black solid. Mp: 156 °C dec. Anal. Calcd for $C_{31}H_{10}Fe_7O_{20}S_4$: C, 30.48; H, 0.83. Found: C, 30.20; H, 1.02. IR (KBr disk): $\nu_{C\equiv O}$ 2060 (s), 2040 (vs), 1998 (vs) cm^{-1}. ^{1}H NMR (acetone-d_6): 5.48 (s, 5H, C_5H_5), 7.33−7.51 (m, 5H, C_6H_5) ppm.

Preparation of (μ-*p*-MeC$_6$H$_4$S)[μ-CpFe(CO)$_2$S][Fe$_2$-(CO)$_6$]$_3$(μ_4-S)$_2$ (6c). The same procedure as that for **6a** was followed, except that **5**[MgX] (R = *p*-MeC_6H_4; X = Br) was used instead of **5**[MgX] (R = Me; X = I). From the main red band 0.182 g (29%) of **6c** was obtained as a black solid. Mp: 160 °C dec. Anal. Calcd for $C_{32}H_{12}Fe_7O_{20}S_4$: C, 31.11; H, 0.98. Found: C, 30.96; H, 1.08. IR (KBr disk): $\nu_{C\equiv O}$ 2056 (s), 2038 (vs), 1997 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.29 (s, 3H, CH_3), 5.48 (s, 5H, C_5H_5), 7.15, 7.19, 7.37, 7.41 (q, AA′BB′, 4H, C_6H_4) ppm.

Table 4. Crystal Data and Structural Refinement Details for 2a, 4c, and 6c

	2a	4c	6c
mol formula	$C_{16}H_{10}Fe_4O_{12}STe_2$	$C_{26}H_{10}Fe_5O_{14}S_4$	$C_{32}H_{12}Fe_7O_{20}S_4\cdot CH_2Cl_2$
mol wt	904.90	953.83	1320.53
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (#2)	$P2_1/n$	$P2_1/n$
a/Å	9.042(3)	15.9464(16)	9.2669(6)
b/Å	10.046(3)	9.6578(10)	22.5961(15)
c/Å	16.228(6)	23.912(2)	22.5997(14)
α/deg	94.46(3)	90	90
β/deg	105.52(3)	105.178(2)	95.8210(10)
γ/deg	108.87(3)	90	90
V/Å^3	1322.0(9)	3554.2(6)	4707.9(5)
Z	2	4	4
D_c/g cm^{-3}	2.273	1.783	1.863
F(000)	852	1888	2608
abs coeff/mm^{-1}	4.452	2.289	2.460
temp/K	296	293	293
wavelength/Å	0.710 69	0.710 73	0.710 73
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
$2\theta_{max}$/deg	53.9	50.06	50.06
no. of observns	4643	4940	5581
no. of variables	316	442	595
R	0.048	0.0265	0.0453
R_w	0.059	0.0609	0.1240
goodness of fit	1.63	1.008	0.897
largest diff peak/e Å^{-3}	1.45 (near to Te1)	0.369	0.853

X-ray Structure Determinations of 2a, 4c, and 6c. Single crystals of **2a**, **4c**, and **6c** suitable for X-ray diffraction analyses were grown by slow evaporation of their CH_2Cl_2/hexane solutions at about 4 °C. Each crystal was mounted on an Enraf-Nonius CAD4 or a Bruker SMART 1000 automated diffractometer with a graphite monochromator with Mo Kα radiation (λ = 0.710 69 or 0.710 73 Å). The structures were solved by direct methods and expanded by Fourier techniques. The final refinements were accomplished by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were located by using the geometric method. The calculations were performed using the TEXSAN crystallographic software package of the Molecular Structure Corp. for **2a** and the SHELXTL-97 program for **4c** and **6c**. Details of the crystal data, data collections, and structure refinements are summarized in Table 4.

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Supporting Information Available: Full tables of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles for **2a**, **4c**, and **6c**. This material is available free of charge via the Internet at http://pubs. acs.org.

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