Unexpected Reactions of Anionic Intermediates [(μ-RE)(μ-S=CS)Fe$_2$(CO)$_6$]$^-$ with SO$_2$Cl$_2$. Synthesis and Characterization of Novel Dithioformato-Bridged Double Clusters [(μ-RE)Fe$_2$(CO)$_6$]$_2$(μ-S=CS-μ) (E = S, Se)

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Received September 9, 1996[⊗]

The dithioformato-bridged anionic salts [Et$_3$NH][(μ-RE)(μ-S=CS)Fe$_2$(CO)$_6$], generated from CO-bridged anionic complexes [Et$_3$NH][μ-RE)(μ-CO)Fe$_2$(CO)$_6$] and carbon disulfide, reacted in situ with SO$_2$Cl$_2$ in THF to afford a series of novel dithioformato-bridged double clusters [(μ-RE)Fe$_2$(CO)$_6$]$_2$(μ-S=CS-μ) (3**a**−**e**) (3**a**, RE = EtS; 3**b**, n-PrS; 3**c**, t-BuS; 3**d**, PhSe; 3**e**, p-MeC$_6$H$_4$Se). A single-crystal diffraction analysis of 3**c** was undertaken and has confirmed the proposed structure.

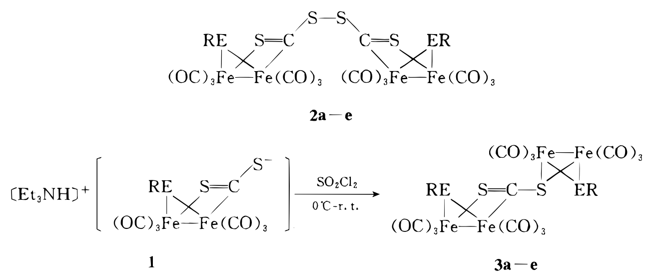
Introduction

In recent years, the Seyferth group and we have reported the synthesis of dithioformato-bridged anionic salts [Et$_3$NH][(μ-RE)(μ-S=CS)Fe$_2$(CO)$_6$] (E = S, Se) and their reactions with various organic and organometallic electrophiles.[1,2] All the reactions of [(μ-RE)(μ-S=CS)-Fe$_2$(CO)$_6$]$^-$ anions can be rationalized in terms of their action as exo sulfur-centered nucleophiles to give corresponding dithioformato-bridged, neutral transition-metal complexes in which the organic or organometallic group has been attached to the exo sulfur atom of these anions.[1,2] As a continuation of this project, we further investigated the reactivity of the anions [(μ-RE)(μ-S=CS)Fe$_2$(CO)$_6$]$^-$ toward an inorganic electrophile SO$_2$Cl$_2$. Now, we describe the unexpected synthesis of the dithioformato-bridged double clusters [(μ-RE)Fe$_2$(CO)$_6$]-[μ-S=CS-μ) (E = S, Se) from the reactions studied and an X-ray diffraction analysis for one representative cluster [(μ-t-BuS)Fe$_2$(CO)$_6$]$_2$(μ-S=CS-μ).

Results and Discussion

As seen from the Experimental Section below, a cherry-red THF solution of the anionic salts [Et$_3$NH]-[(μ-RE)(μ-S=CS)Fe$_2$(CO)$_6$] (**1**) was first generated by reaction of an excess of CS$_2$ and the CO-bridged anionic salts [Et$_3$NH][(μ-RE)(μ-CO)Fe$_2$(CO)$_6$] formed in situ from Fe$_3$(CO)$_{12}$/REH/Et$_3$N reagents (E = S, Se). Then, to this solution of the salts was added at 0 °C a given amount of inorganic electrophile SO$_2$Cl$_2$ and a color change to red-brown occurred. After the reaction mixture had been stirred for 2 h from 0 °C to room temperature followed by TLC separation, five CS$_2$-bridged clusters [(μ-RE)Fe$_2$(CO)$_6$]$_2$(μ-S=CS-μ) (**3a**−**e**) were obtained rather than (CS$_2$)$_2$-bridged clusters [(μ-RE)Fe$_2$(CO)$_6$]$_2$(μ-S=CSSC=S-μ) (**2a**−**e**), which were originally expected to be formed in view of SO$_2$Cl$_2$ being a good oxidative coupling reagent for sulfur-centered anions such as (μ-RE)(μ-S)Fe$_2$(CO)$_6$ (E = S, Se)[3] (Scheme 1).

Scheme 1



3	a	b	c	d	e
RE	EtS	n-PrS	t-BuS	PhSe	p-MeC$_6$H$_4$Se

Clusters **3a**−**e** have been characterized by C/H analysis and IR and ^{1}H NMR spectroscopy, as well as for **3c** by an X-ray diffraction method. The IR spectra of **3a**−**e** showed three to four strong absorption bands in the region of 1950−2100 cm^{-1} and one medium-absorption band at around 980 cm^{-1}. Apparently, the former bands were attributed to terminal carbonyls attached to iron atoms, whereas the latter was attributed to a thiocarbonyl C=S group in the bridged CS$_2$ ligand. The C=S vibrational band in free CS$_2$ is situated at 1533 cm^{-1}, but in CS$_2$ complexes it is usually shifted down to the region of 860−1120 cm^{-1}.[4] Although the ^{1}H NMR spectra of **3a**−**e** all exhibited the presence of their respective organic groups R, the axial or equatorial orientations of two R groups on the bridged E atoms[5] could not be assigned in terms of their ^{1}H NMR data.

[⊗] Abstract published in *Advance ACS Abstracts*, January 1, 1997.

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S0276-7333(96)00775-3 CCC: $14.00

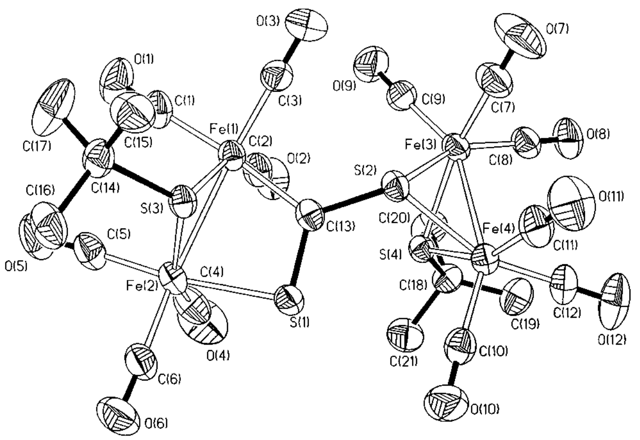

Figure 1. ORTEP view of **3c**, drawn with 35% probability ellipsoids.

Table 1. Selected Bond Lengths (Å) for 3c

Fe(1)−Fe(2)	2.620(1)	Fe(3)−Fe(4)	2.536(1)
Fe(1)−C(1)	1.828(5)	Fe(3)−C(7)	1.800(6)
Fe(1)−C(2)	1.792(5)	Fe(3)−C(8)	1.774(5)
Fe(1)−C(3)	1.800(5)	Fe(3)−C(9)	1.812(5)
Fe(1)−C(13)	1.942(4)	Fe(3)−S(2)	2.278(1)
Fe(1)−S(3)	2.256(1)	Fe(3)−S(4)	2.256(1)
Fe(2)−C(4)	1.797(6)	Fe(4)−C(10)	1.802(5)
Fe(2)−C(5)	1.773(5)	Fe(4)−C(11)	1.793(5)
Fe(2)−C(6)	1.809(6)	Fe(4)−C(12)	1.775(6)
Fe(2)−S(1)	2.295(1)	Fe(4)−S(2)	2.257(1)
Fe(2)−S(3)	2.252(1)	Fe(4)−S(4)	2.280(1)
C(13)−S(1)	1.654(4)	S(3)−C(14)	1.873(5)
C(13)−S(2)	1.759(4)	S(4)−C(18)	1.871(5)

Table 2. Selected Bond Angles (deg) for 3c

Fe(2)−Fe(1)−C(13)	77.3(1)	Fe(2)−Fe(1)−S(3)	54.4(1)
C(13)−Fe(1)−S(3)	81.2	Fe(1)−Fe(2)−S(3)	54.5(1)
S(1)−Fe(2)−S(3)	81.9(1)	Fe(4)−Fe(3)−S(2)	55.6(1)
Fe(4)−Fe(3)−S(4)	56.5(1)	S(2)−Fe(3)−S(4)	78.0(1)
S(2)−Fe(4)−S(4)	77.9(1)	Fe(1)−C(13)−S(1)	114.0(2)
Fe(1)−C(13)−S(2)	125.9(2)	S(1)−C(13)−S(2)	119.5(2)
Fe(2)−S(1)−C(13)	93.1(2)	Fe(3)−S(2)−Fe(4)	68.0(1)
Fe(3)−S(2)−C(13)	114.8(1)	Fe(4)−S(2)−C(13)	116.8(2)
Fe(1)−S(3)−Fe(2)	71.1(1)	Fe(1)−S(3)−C(14)	122.9(2)
Fe(2)−S(3)−C(14)	122.7(2)	Fe(3)−S(4)−Fe(4)	68.0(1)
Fe(3)−S(4)−C(18)	121.5(2)	Fe(4)−S(4)−C(18)	125.6(1)

At present we are not clear about the pathway for formation of the bridged clusters **3a**−**e**. Since SO_2Cl_2 is a good oxidative coupling reagent for various types of sulfur-centered anions such as RS^-,[6] (μ-S^-)$_2Fe_2(CO)_6$,[5] and (μ-RE)(μ-S^-)$Fe_2(CO)_6$ (E = S, Se),[3] the reaction of **1** with SO_2Cl_2 might first give the unstable oxidative coupling intermediate products **2a**−**e**, which would then afford the final products **3a**−**e** by extrusion of one molecule of CS_2. However, this pathway is mainly speculative and further work about the pathway still remains to be done in the future.

In order to confirm the structures of **3a**−**e**, an X-ray crystallographic study of **3c** was undertaken. The study demonstrates that crystals of **3c** consist of discrete molecules of **3c** separated by normal van der Waals distances. The crystal structure of **3c** is shown in Figure 1. Selected bond lengths and angles are given in Tables 1 and 2, respectively.

As seen from Figure 1, **3c** is composed of two identical subcluster units (μ-t-BuS)$Fe_2(CO)_6$ and a bridging CS_2 ligand. In the bridging S(2)C(13)=S(1) ligand the thiocarbonyl C(13)=S(1) is bridged to Fe(1) via a σ-bond [Fe(1)−C(13) = 1.942(4) Å] and to Fe(2) via the donation of an unshared electron pair on S(1) [Fe(2)−S(1) = 2.295(1) Å]. The double bond C(13)=S(1) extends to 1.654(4) Å from the bond length of 1.554 Å in free CS_2.[7] This coordination mode of C(13)=S(1) in the bridging S(2)C(13)=S(1) is the same as that in (μ-PhSe) (μ-S=$CSCH_2Ph$)$Fe_2(CO)_6$ (abbreviated as Psf hereafter).[2] For Psf corresponding Fe(1)−C(13), Fe(2)−S(1), and C(13)=S(1) are equal to 1.98(1), 2.307(5), and 1.63(1) Å, respectively. However, the coordination mode of sulfur atom S (2) in the bridging S(2)C(13)=S(1) of **3c** is completely different from corresponding S(2) in Psf; that is, the S(2) of **3c** is bridged to Fe(3) and Fe(4) of another subcluster rather than bonded to the benzyl group as in Psf. In **3c**, the single bond C(13)−S(2) equals 1.759(4) Å (corresponding C(13)−S(2) = 1.71(2) Å in Psf), which is slightly shorter than normal single C−S bond.[8] All the bond angles around C(13) are 114.0(2)° [(Fe(1)−C(13)−S(1)], 125.9(2)° [Fe(1)−C(13)−S(2)], and 119.5(2)° [S(1)−C(13)−S(2)], which are close to the theoretical value for a sp^2-hybridized carbon atom. It follows that this type of coordination of S(2)C(13)=S(1), to our knowledge, is unprecedent in all the reported transition metal complexes containing CS_2 as a ligand.[2,9] The six coordinated atoms or groups around each iron atom display as a distorted octahedron. The Fe(1)−Fe(2) distance of 2.620(1) Å in **3c** is almost the same as that of 2.648(3) Å in Psf [2] but slightly longer than the Fe(3)−Fe(4) distance of 2.536(1) Å and the Fe−Fe distance in double-bridged complexes containing two identical alkylthio or arylthio bridges.[10,11] While the S(3) atom is symmetrically bridged to Fe(1) and Fe(2) [Fe(1)−S(3) = 2.256(1) Å, Fe(2)−S(3) = 2.252(1) Å] in one subcluster, S(2) and S(4) atoms in the other subcluster are unsymmetrically bridged to Fe(3) and Fe(4) [Fe(3)−S(2) = 2.278(1) Å, Fe(4)−S(2) = 2.257(1) Å; Fe(3)−S(4) = 2.256(1) Å, Fe(4)−S(4) = 2.280(1) Å]. **3c** can be also viewed as consisting of two butterfly subclusters Fe(1)Fe(2)S(1)C(13)S(3) and Fe(3)Fe(4)S(2)S(4) joined together through a bond of C(13)−S(2). The dihedral angle between Fe(1)−Fe(2)−S(3) and Fe(1)−Fe(2)−S(1)−C(13) is 90.6°, while that between Fe(3)−Fe(4)−S(2) and Fe(3)−Fe(4)−S(4) is 81.2°. In addition, from Figure 1 it can be intuitively seen that the subcluster Fe(1)Fe(2)S(1)C(13)S(3) is bonded to S(2) by an axial type of bond, whereas two tertiary butyl groups are bound to S(3) and S(4) by an equatorial type of bond.[5]

Finally, it is worth pointing out that clusters **3a**−**e** are the first examples of double clusters containing a CS_2 ligand bridged to four iron atoms. Other examples involving a ligand to four iron atoms are well-known, such as [(μ-PhSe)$Fe_2(CO)_6$]$_2$ [(1,3-(μ-S=$CSCH_2$)$_2C_6H_4$],[2] [$(CO)_4Fe$]$_4$(μ_4-E) (E = Ge,[12] Sn,[13] Pb[14]), [(μ-Cl)$(CO)_8Fe_2$-(μ_4-E)]$Fe_2(CO)_6$ (E = P, As),[15] [$(CO)_8Fe_2$ (μ_4-As)]$_2Fe_2$-

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$(CO)_6$,[16] $[(CO)_8Fe_2(\mu_4\text{-Sb})]_2Fe_2(CO)_6$,[17] $[Fe(CO)_4]_4(\mu_4\text{-E})^{3-}$ (E=Sb,[18] Bi[19]), $[(\mu\text{-RE})Fe_2(CO)_6]_2(\mu_4\text{-E})$ (E = S,[20] Se[3]), $[(\mu\text{-RE})Fe_2(CO)_6](\mu\text{-SS-}\mu)$,[3,4] and $[(\mu\text{-RS})Fe_2(CO)_6]_2(\mu\text{-Z-}\mu)$ [Z = S $(CH_2)_4S$,[21] $SCH_2C_6H_4CH_2S$,[22] $SC(O)C_6H_4C(O)S$,[23] MeAsAsMe,[24] $C(O)C_6H_4C(O)$[25]].

Experimental Section

1. General Comments. All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl, triethylamine from potassium hydroxide, carbon disulfide from calcium chloride. Ethyl, n-propyl, and t-butyl mercaptans, and sulfuryl chloride were of commercial origin and used without further purification. Triiron dodecacarbonyl,[26] benzeneselenol[27] and 4-methylbenzeneselenol[27] were prepared by literature procedures.

The progress of reactions was monitored by thin-layer chromatography (TLC). Products were purified by TLC (20 × 25 × 0.025 cm, silica gel G) and recrystallized from deoxygenated, mixed solvents of CH_2Cl_2/petroleum ether. Chromatography was completed without exclusion of atmospheric oxygen and moisture. The eluents were light petroleum ether (60−90 °C) and methylene chloride, which were chemical reagents and used without further purification. The yields of products **3a**−**e** were calculated based on starting material $Fe_3(CO)_{12}$.

Melting points were determined on a Yanaco MP-500 melting point apparatus and were uncorrected. Combustion analysis was performed on a 240C model analyzer. ^1H NMR spectra were recorded on a JEOL FX-90Q spectrometer with a $CDCl_3$ solvent and a TMS internal standard. Infrared spectra were obtained on a Nicolet FT-IR 5DX spectrometer with a KBr disk.

2. Preparation of 3a. A 100 mL three-necked flask equipped with a stir bar, a N_2 inlet tube, and serum caps was charged with 1.00 g (1.98 mmol) of $Fe_3(CO)_{12}$ and 30 mL of THF. To the resulting green solution were added 0.28 mL (2.00 mmol) of triethylamine and 0.15 mL (2.00 mmol) of ethyl mercaptan. The solution was stirred at room temperature for 30 min, during which time the solution turned red-brown and the CO-bridged anionic salt $[Et_3NH][\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6]$ (RE = EtS) was formed. To this solution was added 0.36 mL (6.0 mmol) of carbon disulfide, and the new solution was stirred for an additional 30 min. The solution turned cherry-red, and IR spectroscopy showed that the $[Et_3NH][(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6]$ (RE = EtS) salt had been consumed since the μ-CO frequency at 1743 cm^{-1} had disappeared.[1] The dithioformato-bridged anionic salt $[Et_3NH][(\mu\text{-RE})(\mu\text{-S=CS})Fe_2(CO)_6]$ (RE = EtS) was made and then was cooled to 0 °C, to which was added 0.10 mL (1.23 mmol) of sulfuryl chloride. The reaction mixture was allowed to warm to room temperature and stirred for additional 2 h. The solvent was removed in vacuo to give a dark-red residue, which was extracted thoroughly with light petroleum ether. The extracts were concentrated and purified by TLC. Elution with petroleum ether gave two red bands. The first red band gave 0.087 g (11%) of $(\mu\text{-EtS})_2Fe_2(CO)_6$, which was identified by comparison of its melting point and ^1H NMR spectrum with those given in the literature.[28] The second major red band gave 0.157 g (21%) of $[(\mu\text{-EtS})Fe_2(CO)_6]_2(\mu\text{-S=CS-}\mu)$ (**3a**) as a dark-red solid. Mp: 68−70 °C. Anal. Calcd for $C_{17}H_{10}Fe_4O_{12}S_4$: C, 26.94; H, 1.33. Found: C, 27.39; H, 1.36. IR: $\nu_{C\equiv O}$ 2057 (s), 2041 (s), 1991 (vs), 1957 (s), $\nu_{C=S}$ 982 (m) cm^{-1}. ^1H NMR: δ 1.08−1.64 (m, 6H, $2CH_3$), 2.16−2.76 (m, 4H, $2CH_2$) ppm.

3. Preparation of 3b. The same procedure as for **3a** was followed, but 0.19 mL (2.00 mmol) of n-propyl mercaptan was used instead of ethyl mercaptan. The first red band gave 0.082 g (10%) of $(\mu\text{-n-PrS})_2Fe_2(CO)_6$.[28] The second red band gave 0.102 g (13%) of $[(\mu\text{-n-PrS})_2Fe_2(CO)_6]_2(\mu\text{-S=CS-}\mu)$ (**3b**) as a dark-red solid. Mp: 74−75 °C. Anal. Calcd for $C_{19}H_{14}Fe_4O_{12}S_4$: C, 29.04; H, 1.79. Found: C, 29.24; H, 1.72. IR: $\nu_{C\equiv O}$ 2057 (s), 2008 (vs), 1983 (vs), $\nu_{C=S}$ 982 (m) cm^{-1}. ^1H NMR: δ 0.76−1.28 (m, 6H, $2CH_3$), 1.44−1.82 (m, 4H, $2CH_2$), 2.16−2.64 (m, 4H, $2SCH_2$) ppm.

4. Preparation of 3c. The same procedure as for **3a** was followed, but 0.22 mL (2.00 mmol) of t-butyl mercaptan was used instead of ethyl mercaptan. The first red band gave very slight $(\mu\text{-t-BuS})_2Fe_2(CO)_6$.[28] The second red band gave 0.232 g (29%) of $[(\mu\text{-t-BuS})_2Fe_2(CO)_6]_2(\mu\text{-S=C-S-}\mu)$ (**3c**) as a dark-red solid. Mp: 105−106 °C. Anal. Calcd for $C_{21}H_{18}Fe_4O_{12}S_4$: C, 30.99; H, 2.23. Found: 31.25; H, 2.39. IR: $\nu_{C\equiv O}$ 2057 (s), 2041 (vs), 1991 (vs), 1967 (s), $\nu_{C=S}$ 990 (m) cm^{-1}. ^1H NMR: δ 1.36, 1.44 (s, s, 2 $(CH_3)_3$) ppm.

5. Preparation of 3d. The same procedure as for **3a** was followed, but 0.21 mL (2.00 mmol) of benzeneselenol was used instead of ethyl mercaptan. Just like the case for the preparation of **3a**, after addition of CS_2 to the CO-bridged anionic salt $[Et_3NH][(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6]$ (RE = PhSe) for 30 min, the solution turned cherry-red and IR spectroscopy showed the μ-CO frequency of the salt at 1740 cm^{-1} had disappeared.[29] It indicated that the dithioformato-bridged anionic salt $[Et_3NH]$-$[(\mu\text{-RE})(\mu\text{-S=CS})Fe_2(CO)_6]$ (RE = PhSe) was formed. The first red band gave 0.355 g (30%) of $(\mu\text{-PhSe})_2Fe_2(CO)_6$.[29] The second red band gave 0.133 g (14%) of $[(\mu\text{-PhSe})_2Fe_2(CO)_6]_2$-$(\mu\text{-S=CS-}\mu)$ (**3d**) as a brown-red solid. Mp: 138 °C (dec). Anal. Calcd for $C_{25}H_{10}Fe_4O_{12}S_2Se_2$: C, 31.68; H, 1.06. Found: C, 31.81; H, 1.13. IR: $\nu_{C\equiv O}$ 2065 (s), 2041 (s), 1991 (vs), $\nu_{C=S}$ 974 (m) cm^{-1}. ^1H NMR: δ 7.16 (s, 10H, $2C_6H_5$) ppm.

6. Preparation of 3e. The same procedure as for **3a** was followed, except that 0.342 g (2.00 mmol) of 4-methylbenzeneselenol was used instead of ethyl mercaptan. The first red band gave 0.362 g (30%) of $(\mu\text{-p-}CH_3C_6H_4Se)_2Fe_2(CO)_6$.[2] The second red band gave 0.072 g (8%) of $[(\mu\text{-p-}CH_3C_6H_4Se)_2Fe_2$-$(CO)_6]_2(\mu\text{-S=CS-}\mu)$ as a brown-red solid. Mp: 56−58 °C. Anal. Calcd for $C_{27}H_{14}Fe_4O_{12}S_2Se_2$: C, 33.23; H, 1.45. Found: C, 33.02; H, 1.38. IR: $\nu_{C\equiv O}$ 2065 (vs), 2041 (vs), 2000 (vs), $\nu_{C=S}$ 974 (m) cm^{-1}. ^1H NMR: δ 2.20 (s, 6H, $2CH_3$), 6.84−7.28 (m, 8H, $2C_6H_4$) ppm.

7. X-ray Crystallography of 3c. Details of crystal parameters, data collection, and structure refinement are listed in Table 3. Raw intensities were collected on a Rigaku AFC7R diffractometer with a rotating anode source (50 kV, 150 mA) at room temperature (293 K). Patterson superposition yielded the positions of all non-hydrogen atoms, which were subjected to anisotropic refinement. All hydrogens were

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Table 3. Crystal Data Collection and Refinement for 3c

mol formula	$C_{21}H_{18}O_{12}S_4Fe_4$
mol wt	813.99
cryst syst	monoclinic
space group	$P2_1/c$
a/Å	14.529(3)
b/Å	9.270(2)
c/Å	23.847(3)
β/deg	96.780(10)
V/Å^3	3189.3
Z	4
D_c/g cm^{-3}	1.695
$F(000)$	1632
diffractometer	Rigaku AFC7R
temp/°C	20
radiation	graphite-monochromatized Mo Kα, $\lambda = 0.0710\ 73$ Å
scan type	ω scan
$2\theta_{max}$/deg	55
no. observns, n	4494
no. variables, p	371
$R_F = \sum\|\|F_o\| - \|F_o\|\|/\sum\|F_o\|$	0.039
$R_w = [\sum W^2(\|F_o\| - \|F_c\|)^2/\sum W^2\|F_o\|^2]^{1/2}$	0.050
$S = [\sum W(\|F_o\| - \|F_c\|)^2/(n - p)]^{1/2}$	1.14
largest Δ/σ in final cycle	0.001
largest peak in final diff map/e Å^{-3}	0.35

generated geometrically (C−H bonds fixed at 0.96 Å) and allowed to ride on their respective parent C atoms; they were assigned the same isotropic temperature factors ($\mu = 0.08$ Å^2) and included in the structure factor calculations. Computations were performed using the SHELXTL PC program package on a PC 486 computer. Analytical expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.[30]

Acknowledgment. We are grateful to the National Natural Science Foundation of China, the State Key Laboratory of Structural Chemistry, and the Laboratory of Organometallic Chemistry for financial support of this project.

Supporting Information Available: Text describing X-ray procedures and tables of crystallographic data, positional and thermal parameters including hydrogen atoms, and anisotropic parameters (7 pages). Ordering information is given on any current masthead page.

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