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Reactions of Butterfly Complex Anions of the Type $[(\mu\text{-RTe})(\mu\text{-CO})Fe_2(CO)_6]^-$ with Electrophiles. A New Route to μ_4-Se-Containing Double-Butterfly Clusters. Crystal Structures of $(\mu\text{-}p\text{-MeC}_6H_4Te)(\mu\text{-PhCH}_2SC{=}S)Fe_2(CO)_6$ and $[(\mu\text{-RTe})Fe_2(CO)_6]_2(\mu_4\text{-Se})$ (R = Ph, *p*-BrC_6H_4)

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The nucleophilic reaction of anions $[(\mu\text{-RTe})(\mu\text{-CO})Fe_2(CO)_6]^-$ (**3**) with CS_2 and subsequent treatment with organic halides R′X gave a series of R′S-containing single-butterfly complexes $(\mu\text{-RTe})(\mu\text{-R'SC{=}S})Fe_2(CO)_6$ (**4a**−**d**, R = Ph, *p*-MeC_6H_4; R′ = Me, $PhCH_2$), whereas **3** reacted with R′NCS followed by treatment with CF_3CO_2H or MeI to afford the R′HN- and R′MeN-containing single-butterfly complexes $(\mu\text{-RTe})(\mu\text{-R'HNC{=}S})Fe_2(CO)_6$ and $(\mu\text{-RTe})(\mu\text{-R'MeNC{=}S})Fe_2(CO)_6$ (**5a**−**d,** R = Ph, *p*-MeC_6H_4; R′ = Ph, $PhCH_2$). Interestingly, a series of double-butterfly μ_4-Se-containing complexes $[(\mu\text{-RTe})Fe_2(CO)_6]_2$ (μ_4-Se) (**6a**−**e**, R = Et, Ph, *p*-MeC_6H_4, *o*-MeC_6H_4, *p*-BrC_6H_4) could be produced via a simple and new synthetic route involving a doubly nucleophilic reaction of anions **3** with an electrophile $SeCl_2$. New complexes **4a**−**d**, **5a**−**d**, and **6a**−**e** derived from anions **3** have been fully characterized by elemental analysis and IR, ^1H NMR, ^{125}Te NMR, and ^{77}Se NMR (for **6a**−**e**) spectroscopies. The ^{125}Te NMR spectra of the new complexes displayed only one singlet, indicating that they consist of only one isomer, either *a*(R) or *e*(R). This has been confirmed by crystal X-ray diffraction analyses of **4d** (R = *p*-MeC_6H_4; R′ = $PhCH_2$), **6b** (R = Ph), and **6e** (R = *p*-BrC_6H_4), in which the R groups are attached to bridged Te atoms by an equatorial type of bond.

Introduction

The butterfly complex anions containing a μ-CO ligand $[(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6]^-$ [**1**, E = S; **2**, E = Se; **3**, E = Te] are very useful versatile synthons in the synthesis of a great variety of butterfly Fe/E cluster complexes.[1−13] Among the three types of anions, however, anions **3** are much less studied than anions **1** and **2**, most likely due to anions **3** being prepared much later and with more complicated chemistry.[7] To further develop the chemistry of anions **3**, we recently initiated a study on reactivities of anions **3** toward electrophiles CS_2/R′X, R′NCS/CF_3CO_2H, R′NCS/MeI, and $SeCl_2$. Interestingly, while anions **3** reacted with $SeCl_2$ to give a novel type of double-butterfly Fe_4SeTe_2 cluster complexes, reactions of **3** with the other electrophiles mentioned above afforded single-butterfly $Fe_2Te(C{=}S)$ cluster complexes. Herein we report the synthesis and spectroscopic (particularly ^{125}Te and ^{77}Se NMR) characterization of these new single- and double-butterfly cluster compounds, as well as the X-ray crystal diffraction analyses for clusters $(\mu\text{-}p\text{-MeC}_6H_4Te)(\mu\text{-PhCH}_2SC{=}S)Fe_2(CO)_6$ (**4d**), $[(\mu\text{-PhTe})Fe_2(CO)_6]_2(\mu_4\text{-Se})$ (**6b**), and $[(\mu\text{-}p\text{-BrC}_6H_4Te)Fe_2(CO)_6]_2(\mu_4\text{-Se})$ (**6e**).

Results and Discussion

Reactions of 3 with CS_2/R′X or R′NCS/CF_3CO_2H-(MeI) and Structural Characterization of 4a−d

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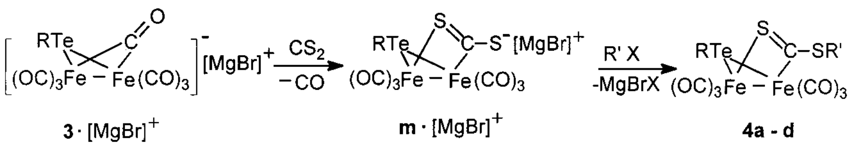
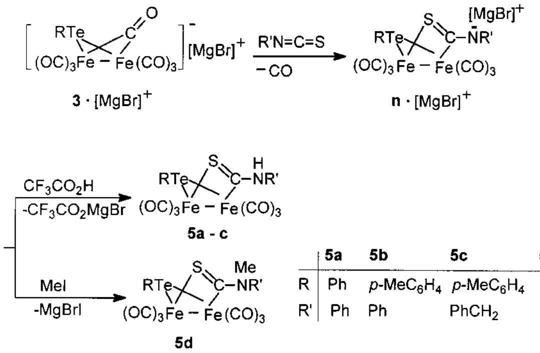
Scheme 1



	4a	4b	4c	4d
R	Ph	p-MeC$_6$H$_4$	Ph	p-MeC$_6$H$_4$
R'	Me	Me	PhCH$_2$	PhCH$_2$

Scheme 2



	5a	5b	5c	5d
R	Ph	p-MeC$_6$H$_4$	p-MeC$_6$H$_4$	p-MeC$_6$H$_4$
R'	Ph	Ph	PhCH$_2$	Ph

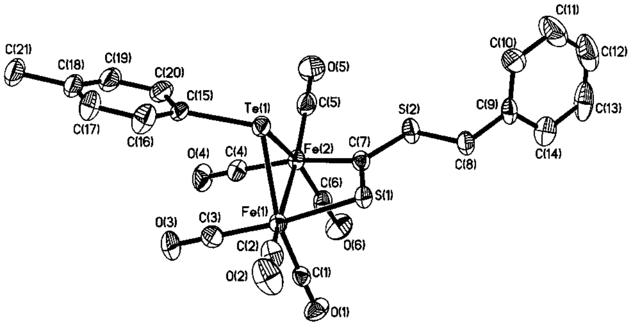


Figure 1. ORTEP drawing of **4d** with atom-labeling scheme.

and 5a−d. Up to now, there is still no report in the literature concerning the reactions of anions **3** with heterocumulenes CS$_2$ and R′NCS, although the reactions of anions **1** and **2** with such heterocumulenes have been previously reported.[2,14,15] So, it is interesting to study the reactions of anions **3** with CS$_2$ and R′NCS to compare the nucleophilicity of these three types of anions and in order to prepare the corresponding μ-RTe-containing analogues. We have now found that the [MgBr]$^+$ salts of anions **3** reacted with carbon disulfide CS$_2$ followed by treatment of the intermediate [MgBr]$^+$ salts of the S-centered anions (μ-RTe)(μ-S=CS$^-$)Fe$_2$(CO)$_6$ (**m**)[2] with organic halides R′X to afford a series of single-butterfly Fe$_2$Te(C=S) cluster complexes (μ-RTe)(μ-R′SC=S)Fe$_2$(CO)$_6$ (**4a−d**) (Scheme 1).

We have also found that reactions of the [MgX]$^+$ salts of anions **3** with isothiocyanates R′NCS and subsequent treatment of the intermediate [MgBr]$^+$ salts of the N-centered anions (μ-RTe)(μ-S=C(R′)N$^-$)Fe$_2$(CO)$_6$ (**n**)[2] with electrophile CF$_3$CO$_2$H or MeI afforded another series of single-butterfly cluster complexes (μ-RTe)(μ-R′HNC=S)Fe$_2$(CO)$_6$ (**5a−c**) and (μ-RTe)(μ-R′MeNC=S)Fe$_2$(CO)$_6$ (**5d**) (Scheme 2).

It is worth pointing out that the reactions described above not only gave rise to single-butterfly Fe$_2$Te(C=S) clusters **4a−d** and **5a−d** but also afforded the corresponding single-butterfly Fe$_2$Te$_2$ clusters (μ-RTe)$_2$Fe$_2$(CO)$_6$ (R = Ph, p-MeC$_6$H$_4$), possibly produced by decomposition of anions **3** and subsequent dimerization of the intermediate fragment RTeFe(CO)$_3$.[7] In addition, it is worthy of note that the yields of **4a−d** and **5a−d** (11−16%) derived from anions **3** are lower than the reported yields of their Se analogues (35−47%) derived from anions **2**,[14,15] which are in turn lower than their S analogues (59% to quantitative) derived from anions **1**[2] by the same type of reactions. This is most likely due to the increased nucleophilicity of the anions in the order **3** < **2** < **1** (it should be noted that the yields of anions **1−3** are generally comparable since the IR spectra of anions **1−3** showed comparable μ-CO intensities). While (μ-RTe)$_2$Fe$_2$(CO)$_6$ (R = Ph,[7] p-MeC$_6$H$_4$[7]) are known, **4a−d** and **5a−d** are new and have been fully characterized by elemental analysis, IR, ^{1}H NMR, and ^{125}Te NMR spectroscopy. For instance, the IR spectra of **4a−d** and **5a−d** display three to four absorption bands in the range 2066−1948 cm^{-1} for their terminal carbonyls. In addition, while the ^{1}H NMR spectra of **4a−d** and **5a−d** exhibit the signals assigned to their R and R′ groups, the ^{125}Te NMR spectra of **4a−d** and **5a−d** display a singlet in the region 745−712 ppm attributed to their bridged Te atoms. It is noteworthy that products **4a−d** and **5a−d** might exist theoretically as two isomers, one with an equatorial R and the other with an axial R.[2,14] However, since the ^{125}Te NMR spectra of these products show only one signal (a singlet) for their bridged Te atoms, they should exist as only one isomer, either a(R) or e(R). Fortunately, this has been proved by crystal X-ray diffraction analysis of **4d**, in which the substituent R is attached to the bridged Te atom by an equatorial type of bond.

The molecular structure of **4d** is shown in Figure 1. Table 1 lists its selected bond lengths and angles. As can be seen in Figure 1, **4a** has two ligands, p-MeC$_6$H$_4$-Te and PhCH$_2$SC=S, that are bridged to two Fe atoms of the two Fe(CO)$_3$ structural units to form the iron carbonyl complex with a single-butterfly Fe$_2$TeC=S cluster core; in addition, the p-MeC$_6$H$_4$Te ligand is indeed attached to the bridged Te atom of the butterfly core by an equatorial type of bond. So, the structure of **4d** is totally similar to that of its Se analogue (μ-PhSe)(μ-PhCH$_2$SC=S)Fe$_2$(CO)$_6$.[14] It is noteworthy that the carbon C(7) of the S(2)−C(7)−S(1) bridge in **4d** possesses a carbene character[16] with an Fe(2)−C(7) bond equal to 1.955(6) Å. This bond length is very close to

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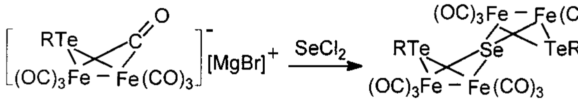
Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4d

S(1)−Fe(1)	2.3053(18)	S(1)−C(7)	1.666(6)
Te(1)−Fe(1)	2.5307(11)	Fe(2)−Te(1)	2.5474(11)
C(7)−Fe(2)	1.955(6)	S(2)−C(7)	1.694(6)
C(15)−Te(1)	2.150(6)	Fe(1)−Fe(2)	2.6665(214
S(2)−C(8)	1.818(6)	C(18)−C(21)	1.527(10)
S(1)−Fe(1)−Te(1)	82.14(5)	S(1)−Fe(1)−Fe(2)	75.32(5)
Te(1)−Fe(1)−Fe(2)	58.63(3)	C(7)−Fe(2)−Te(1)	83.76(18)
Fe(1)−Te(1)−Fe(2)	63.35(3)	C(7)−S(1)−Fe(1)	93.3(2)
Te(1)−Fe(2)−Fe(1)	58.02(3)	S(2)−C(7)−Fe(2)	122.3(3)
S(1)−C(7)−S(2)	123.1(4)	S(1)−C(7)−Fe(2)	114.6(3)

Scheme 3



3 · [MgBr]$^+$ **6a-e**

	6a	**6b**	**6c**	**6d**	**6e**
R	Et	Ph	*p*-MeC$_6$H$_4$	*o*-MeC$_6$H$_4$	*p*-BrC$_6$H$_4$

the bond length (1.969 Å) of the Fe−C (carbene) bond in an iron-carbene-stabilized compound.[17] In addition, in **4d** the Fe−Te bond lengths (Fe(1)−Te(1) = 2.5307(11) Å, Fe(2)−Te(1) = 2.5474(11) Å) and the Fe−Te−Fe bond angle (Fe(1)−Te(1)−Fe(2) = 63.35(3)°) are almost the same as the corresponding ones (2.548(2) Å, 2.551(3) Å, 62.3(1)°, and 62.2(1)°) in butterfly Fe_2Te_2 complex (μ-MeTe)$_2$ $Fe_2(CO)_6$,[18] respectively.

Reactions of 3 with SeCl$_2$ and Structural Charactrization of 6a−e. More interestingly, it has been found that the [MgBr]$^+$ salts of anions **3** reacted with $SeCl_2$ from −78 °C to room temperature in THF to give a new series of μ_4-Se-containing double-butterfly cluster complexes [(μ-RTe)$Fe_2(CO)_6$]$_2$(μ_4-Se) (**6a**−**e**) (Scheme 3).

It should be mentioned that the reactions of the [MgBr]$^+$ salts of anions **3** with $SeCl_2$, similar to those with CS_2/R′X and R′NCS/CF_3CO_2H(MeI), also gave the corresponding single-butterfly complexes (μ-RTe)$_2$$Fe_2(CO)_6$, generated by decomposition of **3** and subsequent dimerization of the intermediate fragment RTeFe(CO)$_3$.[7] In these complexes, while (μ-RTe)$_2$$Fe_2(CO)_6$ (R = Et,[15] Ph,[7] *P*-MeC$_6$H$_4$,[7] *o*-MeC$_6$H$_4$[7]) were previously reported, (μ-RTe)$_2$$Fe_2(CO)_6$ (R = *p*-BrC$_6$H$_4$) is new and has been characterized by elemental analysis and spectroscopy. In addition, we have proposed a pathway to account for the formation of double-butterfly complexes **6a**−**e**, on the basis of similarity with the reactions of anions **3** with other electrophiles containing a leaving group[15] (Scheme 4). Apparently, this pathway involves a double nucleophilic attack of the negatively charged Fe atom in **3** at the Se atom in $SeCl_2$ to eliminate two Cl$^-$ anions and a double coordination of the lone electron pairs on the Se atom to the neighboring Fe atoms with concurrent loss of two μ-CO ligands.

It is worth pointing out that the reactions of anions **3** with $SeCl_2$ provide a simple and new synthetic route for μ_4-Se-containing double-butterfly cluster complexes, although the more complicated routes leading to μ_4-Se-containing complexes with a double-butterfly cluster core Fe_4E_2(μ_4-Se) (E = S, Se),[5] Fe_4ESe(μ_4-Se) (E = S, Se, Te),[9] or Fe_4SSe(μ_4-Se)[19] were previously reported.

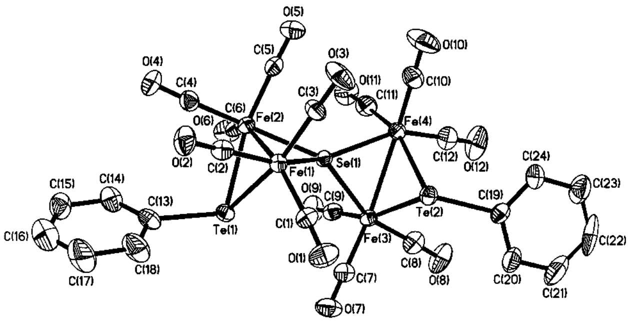


Figure 2. ORTEP drawing of **6b** with atom-labeling scheme.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 6b

Se(1)−Fe(4)	2.3370(18)	Se(1)−Fe(2)	2.3458(18)
Te(1)−Fe(2)	2.5418(16)	Fe(4)−Te(2)	2.5494(18)
Te(2)−Fe(3)	2.5716(17)	Se(1)−Fe(1)	2.3508(17)
Fe(3)−Se(1)	2.3551(18)	Te(1)−Fe(1)	2.5565(16)
Fe(1)−Fe(2)	2.611(2)	Fe(3)−Fe(4)	2.607(2)
Se(1)−Fe(3)−Te(2)	78.62(5)	Te(1)−Fe(1)−Fe(2)	58.91(5)
Se(1)−Fe(2)−Te(1)	78.62(6)	Fe(2)−Te(1)−Fe(1)	61.62(5)
Fe(1)−Se(1)−Fe(3)	127.85(6)	Se(1)−Fe(1)−Te(1)	78.23(5)
Fe(4)−Se(1)−Fe(3)	67.51(6)	Se(1)−Fe(1)−Fe(2)	56.13(5)
Fe(1)−Se(1)−Fe(2)	67.56(6)	Fe(1)−Se(1)−Fe(4)	138.39(7)

Products **6a**−**e** are new and have been characterized by combustion analysis and IR and ^{1}H (^{77}Se, ^{125}Te) NMR spectroscopy, as well as by X-ray diffraction analysis. The ^{77}Se NMR spectra of **6a**−**e** show a singlet in the range 296−239 ppm for their μ_4-Se atom, which resembles the corresponding ones of their analogues (μ-RTe)(μ-R′Se)[$Fe_2(CO)_6$]$_2$ (μ_4-Se).[9] In addition, the ^{125}Te NMR spectra of **6a**−**e** also display a singlet, which lies in the range 336−201 ppm (note the remarkably different ^{125}Te NMR values from those of **4a**−**d** and **5a**−**d** due to different structural types!) for their bridged Te atoms bonded to R groups with an equatorial type of bond.[5,9] It is worthy of note that the ^{125}Te NMR signal of **6a** (201.37 ppm) appeared at much higher field than the signals of **6b**−**e** (335.83−290.58 ppm), which is obviously due to an Et group in **6a** being an electron-donating group and the aromatic R groups in **6b**−**e** being electron-withdrawing.

To unambiguously confirm the structures of the double-butterfly complexes **6a**−**e** obtained from the above new type of reactions, we carried out the crystal X-ray diffraction analyses for **6b** and **6e**. Since **6b** is isostructural with **6e**, only the ORTEP drawing of the molecular structure of **6b** is shown in Figure 2. Table 2 lists its selected bond lengths and angles. As shown in Figure 2, **6b** consists of two butterfly cores, Fe(1)Fe(2)-Te(1)Se(1) and Fe(3)Fe(4)Te(2)Se(1), joined to a spiro type of Se(1) atom; each Fe atom carries three terminal carbonyls, and both Te atoms are attached to Ph groups by an equatorial type of bond.[5,9] In fact, the double-butterfly complex **6b** is very similar to the double-butterfly μ_4-Se complexes [(μ-EtS)$Fe_2(CO)_6$]$_2$(μ_4-Se)[5] and (μ-*p*-MeC$_6$H$_4$Te)(μ-MeSe)[$Fe_2(CO)_6$]$_2$(μ_4-Se),[9] structurally.

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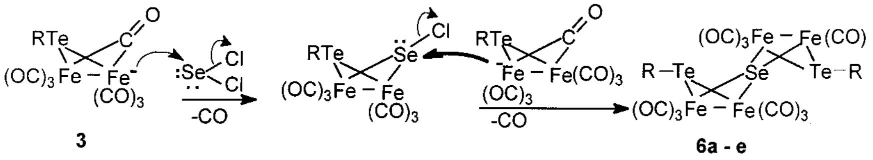
Scheme 4



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. Se powder, Te powder, CH_3I, $PhCH_2Br$, PhNCS, $PhCH_2NCS$, CF_3CO_2H, and CS_2 were of commercial origin and used without further purification. $Fe_3(CO)_{12}$,[20] Grignard reagents RMgBr,[21] and a THF solution of $SeCl_2$[22] were prepared according to literature procedures. 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, ^{77}Se NMR, and ^{125}Te NMR spectra were recorded on a Bruker AC-P 200 NMR spectrometer and a Varian Unity-Plus 400 NMR spectrometer with Ph_2Se_2 and Ph_2Te_2 as external standards, and the chemical shifts are referenced to Me_2Se ($\delta = 0$) and Me_2Te ($\delta = 0$), respectively. C/H analyses were performed on an elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus and were uncorrected.

General Procedure for in Situ Preparation of Intermediate Salts [(μ-RTe)(μ-CO)$Fe_2(CO)_6$]$^-$[MgBr]$^+$ (3·[MgBr]$^+$: R = Et, Ph, *p*-MeC_6H_4, *o*-MeC_6H_4, *p*-BrC_6H_4). A 100 mL three-necked flask equipped with a magnetic stir-bar, a rubber septum, and a reflux condenser topped with a N_2 inlet tube was charged with 0.255 g (2.0 mmol) of tellurium powder, 20 mL of THF, and 2.0 mmol of RMgBr (R = Et, Ph, *p*-MeC_6H_4, *o*-MeC_6H_4, *p*-BrC_6H_4) in Et_2O. The mixture was refluxed for 2 h to give a slightly gray solution of RTeMgBr. Upon cooling the solution to room temperature, 1.00 g (2.0 mmol) of $Fe_3(CO)_{12}$ was added and the mixture was stirred for 1 h to produce a brown-red solution of the intermediate salts **3**·[MgBr]$^+$, which was utilized immediately in the following preparations.

Preparation of (μ-PhTe)(μ-MeSC=S)$Fe_2(CO)_6$ (4a). To the above prepared solution of salt **3**·[MgBr]$^+$ (R = Ph) was added 0.15 mL (2.6 mmol) of CS_2, and the mixture was stirred at room temperature for 1 h. Then, 0.15 mL (2.6 mmol) of MeI was added, and the mixture was continuously stirred for 15 h. 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 band was obtained 0.103 g (15%) of (μ-PhTe)$_2$$Fe_2(CO)_6$.[7] The second main band afforded 0.185 g (16%) of **4a** as a red oil. Anal. Calcd for $C_{14}H_8Fe_2O_6S_2Te$: C, 29.21; H, 1.40. Found: C, 29.31; H, 1.41. IR (KBr disk): $\nu_{C\equiv O}$ 2058 (vs), 2026 (vs), 1993 (vs), 1970 (vs); $\nu_{C=S}$ 1010 (s) cm^{-1} . ^{1}H NMR ($CDCl_3$): 2.57 (s, 3H, CH_3), 7.48 (s, 5H, C_6H_5) ppm. ^{125}Te NMR ($CDCl_3$): 744.20 (s) ppm.

Preparation of (μ-*p*-MeC_6H_4Te)(μ-MeSC=S)$Fe_2(CO)_6$ (4b). Similarly, 0.220 g (31%) of (μ-*p*-MeC_6H_4Te)$_2$$Fe_2(CO)_6$[7] and 0.174 g (15%) of **4b** were obtained. **4b**: a red oil. Anal. Calcd for $C_{15}H_{10}Fe_2O_6S_2Te$: C, 30.55; H, 1.71. Found: C, 30.70; H, 1.75. IR (KBr disk): $\nu_{C\equiv O}$ 2042 (vs), 2010 (vs), 1973 (vs); $\nu_{C=S}$ 1006 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.33 (s, 3H, CH_3), 2.56 (s, 3H, CH_3SC=S), 7.48 (s, 4H, C_6H_4) ppm. ^{125}Te NMR ($CDCl_3$): 742.00 (s) ppm.

Preparation of (μ-PhTe)(μ-$PhCH_2SC$=S)$Fe_2(CO)_6$ (4c). Similarly, 0.245 g (35%) of (μ-PhTe)$_2$$Fe_2(CO)_6$[7] and 0.170 g (13%) of **4c** were obtained. **4c:** an orange-red solid, mp 121−122 °C. Anal. Calcd for $C_{20}H_{12}Fe_2O_6S_2Te$: C, 36.86; H, 1.86. Found: C, 36.70; H, 1.87. IR (KBr disk): $\nu_{C\equiv O}$ 2066 (s), 2010 (vs), 1981 (s), 1958 (vs); $\nu_{C=S}$ 998 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 4.34 (s, 2H, CH_2), 7.01−7.46 (m, 10H, 2C_6H_5) ppm. ^{125}Te NMR ($CDCl_3$): 744.76 (s) ppm.

Preparation of (μ-*p*-MeC_6H_4Te)(μ-$PhCH_2SC$=S)$Fe_2(CO)_6$ (4d). Similarly, 0.154 g (21%) of (μ-*p*-MeC_6H_4Te)$_2$$Fe_2(CO)_6$[7] and 0.166 g (13%) of **4d** were obtained. **4d**: an orange-red solid, mp 130−131 °C. Anal. Calcd for $C_{21}H_{14}Fe_2O_6S_2Te$: C, 37.89; H, 2.12. Found: C, 37.86; H, 2.20. IR (KBr disk): $\nu_{C\equiv O}$ 2058 (vs), 2018 (vs), 1981 (vs), 1958 (vs); $\nu_{C=S}$ 998 (s) cm^{-1} . ^{1}H NMR ($CDCl_3$): 2.29 (s, 3H, CH_3), 4.34 (s, 2H, CH_2), 6.99−7.45 (m, 9H, C_6H_5, C_6H_4) ppm. ^{125}Te NMR ($CDCl_3$): 744.71 (s) ppm.

Preparation of [(μ-PhTe)(μ-PhNHC=S)$Fe_2(CO)_6$ (5a). To the above prepared solution of salt **3**·[MgBr]$^+$ (R = Ph) was added 0.24 mL (2.0 mmol) of PhNCS, and the mixture was stirred at room temperature for 16 h. Then, 0.16 mL (2.1 mmol) of CF_3CO_2H was added, and the mixture was continuously stirred for 2 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 1:5) as eluent. From the first main band was obtained 0.241 g (31%) of (μ-PhTe)$_2$$Fe_2(CO)_6$.[7] The second main band afforded 0.172 g (14%) of **5a** as a red solid, mp 50−52 °C. Anal. Calcd for $C_{19}H_{11}Fe_2NO_6STe$: C, 36.76; H, 1.77; N, 2.26. Found: C, 36.65; H, 1.83; N, 2.30. IR (KBr disk): $\nu_{C\equiv O}$ 2057 (s), 2013 (vs), 1970 (s), 1948 (s); ν_{NH} 3337 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.34−7.56 (m, 10H, 2C_6H_5), 8.90 (s, 1H, NH) ppm. ^{125}Te NMR ($CDCl_3$): 722.02 (s) ppm.

Preparation of [(μ-*p*-MeC_6H_4Te)(μ-PhNHC=S)$Fe_2(CO)_6$ (5b). Similarly, 0.230 g (32%) of (μ-*p*-MeC_6H_4Te)$_2$$Fe_2(CO)_6$[7] and 0.136 g (11%) of **5b** were obtained. **5b**: a red solid, mp 124−126 °C. Anal. Calcd for $C_{20}H_{13}Fe_2NO_6STe$: C, 37.84; H, 2.05; N, 2.21. Found: C, 37.51; H, 2.07; N, 2.25. IR (KBr disk): $\nu_{C\equiv O}$ 2056 (s), 2014 (vs), 1996 (vs), 1987 (s), 1970 (s), 1948 (s); ν_{NH} 3339 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.31 (s, 3H, CH_3), 7.01−7.43 (m, 9H, C_6H_5, C_6H_4), 8.90 (s, 1H, NH) ppm. ^{125}Te NMR ($CDCl_3$): 719.60 (s) ppm.

Preparation of [(μ-*p*-MeC_6H_4Te)(μ-$PhCH_2NHC$=S)$Fe_2(CO)_6$ (5c). Similarly, 0.268 g (37%) of (μ-*p*-MeC_6H_4Te)$_2$$Fe_2(CO)_6$[7] and 0.146 g (11%) of **5c** were obtained. **5c**: a red solid, mp 99−101 °C. Anal. Calcd for $C_{21}H_{15}Fe_2NO_6STe$: C, 38.87; H, 2.31; N, 2.16. Found: C, 38.88; H, 2.37; N, 2.12. IR (KBr disk): $\nu_{C\equiv O}$ 2057 (s), 2014 (vs), 1991 (s), 1948 (s); ν_{NH} 3352 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.30 (s, 3H, CH_3), 4.61 (q,q, ${}^{2}J$ = 14.6 Hz, ${}^{3}J$ = 4.2 Hz, 2H, CH_2), 6.94−7.42 (m, 9H, C_6H_5, C_6H_4), 7.54 (br s, 1H, NH) ppm. ^{125}Te NMR ($CDCl_3$): 712.50 (s) ppm.

Preparation of [(μ-*p*-MeC_6H_4Te)(μ-PhMeNC=S)$Fe_2(CO)_6$ (5d). To the above prepared solution of salt **3**·[MgBr]$^+$ (R = *p*-MeC_6H_4) was added 0.24 mL (2.0 mmol) of PhNCS, and the mixture was stirred at room temperature for 1 h. Then, 0.13 mL (2.0 mmol) of MeI was added, and the mixture was continuously stirred for 15 h. The mixture was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 1:20) as eluent. From the first main band was obtained 0.240 g (34%) of (μ-*p*-MeC_6H_4Te)$_2$$Fe_2(CO)_6$.[7] The second main band afforded 0.156 g (12%) of **5d** as a red solid, mp 120 °C (dec). Anal. Calcd for $C_{21}H_{15}Fe_2NO_6STe$: C, 38.87; H, 2.31; N, 2.16. Found: C, 38.68; H, 2.34; N, 2.33. IR (KBr disk): $\nu_{C\equiv O}$ 2122 (m), 2057

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Table 3. Crystal Data and Structural Refinements Details for 4d, 6b, and 6e

	4d	**6b**	**6e**
mol formula	$C_{21}H_{14}Fe_2O_6S_2Te$	$C_{24}H_{10}Fe_4O_{12}SeTe_2$	$C_{24}H_8Br_2Fe_4O_{12}SeTe_2$
mol wt	665.74	1047.88	1205.68
cryst syst	monoclinic	monoclinic	monoclinic
space group	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*c*
a/Å	12.414(3)	9.041(3)	19.499(6)
b/Å	8.891(2)	13.156(5)	9.537(3)
c/Å	23.421(6)	27.322(9)	18.409(6)
β/deg	104.910(4)	98.392(6)	91.941(7)
V/Å^3	2498.0(11)	3215(2)	3421.5(19)
Z	4	4	4
D_c/g cm^{-3}	1.770	2.165	2.341
F(000)	1296	1968	2240
abs coeff/mm^{-1}	2.506	4.736	6.788
temp/K	293	298	293
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
$2\theta_{max}$/deg	50.04	50.06	50.04
no. of reflns	10104	13060	13808
no. of indep reflns	4408	5676	6039
R_{int}	0.0493	0.0675	0.1072
no. of data/restraints/ params	4408/0/289	5676/0/388	6039/0/406
R	0.0357	0.0422	0.0508
R_w	0.0662	0.0891	0.1104
goodness of fit	1.086	0.979	0.967
largest diff peak and hole/e Å^{-3}	0.590 and −0.595	0.862 and −1.085	0.816 and −0.990

(s), 2015 (vs), 1987 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.30 (s, 3H, CH_3), 3.34 (s, 3H, NCH_3), 7.08−7.58 (m, 9H, C_6H_5, C_6H_4) ppm. ^{125}Te NMR ($CDCl_3$): 716.92 (s) ppm.

Preparation of [(μ-EtTe)$Fe_2(CO)_6$]$_2$(μ_4-Se) (6a). To the above prepared solution of salt **3**·[MgBr]$^+$ (R = Et) cooled to −78 °C by a dry ice/acetone bath was added ca. 1 mmol of $SeCl_2$ in 5 mL of THF, which was prepared from Se powder and SO_2Cl_2 according to literature.[22] The mixture was stirred for 30 min at this temperature. After the bath was removed, the mixture was naturally warmed to room temperature and then was continuously stirred for 12 h. The mixture was subjected to TLC separation using petroleum ether as eluent. From the first main red band was obtained 0.040 g (7%) of (μ-EtTe)$_2Fe_2(CO)_6$.[15] The second main dark red band afforded 0.160 g (17%) of **6a** as a dark red solid, mp 110 °C (dec). Anal. Calcd for $C_{16}H_{10}Fe_4O_{12}SeTe_2$: C, 20.19; H, 1.06. Found: C, 19.86; H, 1.11. IR (KBr disk): $\nu_{C\equiv O}$ 2082 (s), 2026 (vs), 1997 (vs), 1981 (vs), 1966 (vs)cm^{-1}. ^{1}H NMR ($CDCl_3$): 1.53 (br s, 6H, 2CH_3), 2.78 (br s, 4H, 2CH_2) ppm. ^{77}Se NMR ($CDCl_3$): 295.56 (s) ppm. ^{125}Te NMR ($CDCl_3$): 201.37 (s) ppm.

Preparation of [(μ-PhTe)$Fe_2(CO)_6$]$_2$(μ_4-Se) (6b). Similarly, 0.180 g (26%) of (μ-PhTe)$_2Fe_2(CO)_6$[7] and 0.160 g (15%) of **6b** were obtained. **6b**: a dark red solid, mp 190−192 °C (dec). Anal. Calcd for $C_{24}H_{10}Fe_4O_{12}SeTe_2$: C, 27.50; H, 0.96. Found: C, 27.13; H, 1.00. IR (KBr disk): $\nu_{C\equiv O}$ 2082 (s), 2050 (vs), 2018 (vs), 1985 (vs), 1966 (vs) cm^{-1}. ^{1}H NMR (acetone-d_6): 7.17−7.66 (m, 10H, 2C_6H_5) ppm. ^{77}Se NMR ($CDCl_3$): 252.52 (s) ppm. ^{125}Te NMR ($CDCl_3$): 335.83(s) ppm.

Preparation of [(μ-*p*-MeC_6H_4Te)$Fe_2(CO)_6$]$_2$(μ_4-Se) (6c). Similarly, 0.160 g (22%) of (μ-*p*-MeC_6H_4Te)$_2Fe_2(CO)_6$[7] and 0.120 g (11%) of **6c** were obtained. **6c**: a dark red solid, mp 150 °C (dec). Anal. Calcd for $C_{26}H_{14}Fe_4O_{12}SeTe_2$: C, 29.02; H, 1.31. Found: C, 28.78; H, 1.29. IR (KBr disk): $\nu_{C\equiv O}$ 2082 (s), 2026 (vs), 1997 (s), 1981 (vs), 1962 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.32 (s. 6H, 2CH_3) 6.90−7.30 (m, 8H, 2C_6H_4) ppm. ^{77}Se NMR ($CDCl_3$): 258.44 (s) ppm. ^{125}Te NMR ($CDCl_3$): 332.40 (s) ppm.

Preparation of [(μ-*o*-MeC_6H_4Te)$Fe_2(CO)_6$]$_2$(μ_4-Se) (6d). Similarly, 0.100 g (14%) of (μ-*o*-MeC_6H_4Te)$_2Fe_2(CO)_6$[7] and 0.288 g (27%) of **6d** were obtained. **6d**: a dark red solid, mp 108 °C (dec). Anal. Calcd for $C_{26}H_{14}Fe_4O_{12}SeTe_2$: C, 29.02; H, 1.31. Found: C, 28.63; H, 1.31. IR (KBr disk): $\nu_{C\equiv O}$ 2050 (vs), 2018 (vs), 1993 (vs), 1977 (vs), 1958 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.40−2.65 (m. 6H, 2CH_3), 6.95−7.55 (m, 8H, 2C_6H_4) ppm. ^{77}Se NMR ($CDCl_3$): 270.38 (s) ppm. ^{125}Te NMR ($CDCl_3$): 290.58 (s) ppm.

Preparation of [(μ-*p*-BrC_6H_4Te)$Fe_2(CO)_6$]$_2$(μ_4-Se) (6e). Similarly, 0.070 g (8%) of (μ-*p*-BrC_6H_4Te)$_2Fe_2(CO)_6$ and 0.270 g (22%) of **6e** were obtained. (μ-*p*-BrC_6H_4Te)$_2Fe_2(CO)_6$: a red solid, mp 120−125 °C. Anal. Calcd for $C_{18}H_8Br_2Fe_2O_6Te_2$: C, 25.52; H, 0.95. Found: C, 25.46; H, 0.93. IR (KBr disk): $\nu_{C\equiv O}$ 2058 (vs), 2010 (vs), 1985 (vs), 1962 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.10 (s, 8H, 2C_6H_4) ppm. **6e**: a dark red solid, mp >300 °C. Anal. Calcd for $C_{24}H_8Br_2Fe_4O_{12}SeTe_2$: C, 23.91; H, 0.67. Found: C, 23.91; H, 0.69. IR (KBr disk): $\nu_{C\equiv O}$ 2074 (s), 2018 (vs), 1985 (vs), 1966 (s) cm^{-1}. ^{1}H NMR (acetone-d_6): 7.54 (q, AA′BB′, J = 8.0 Hz, 8H, 2C_6H_4) ppm. ^{77}Se NMR ($CDCl_3$): 239.42 (s) ppm. ^{125}Te NMR ($CDCl_3$): 330.83 (s) ppm.

X-ray Structure Determinations of 4d, 6b, and 6e. Single-crystals of **4d**, **6b**, and **6e** 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 a Bruker SMART 1000 automated diffractometer with a graphite monochromator with Mo Kα radiation (λ = 0.71073 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 SHELXTL-97 program. Details of the crystal data, data collections, and structure refinements are summarized in Table 3.

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

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