Organometallics **1994,** *13,* 2532-2535

Functionalization of a Diacetylene on the Mixed-Chalcogenide Compound $Fe_2(CO)_6(\mu\text{-STe})$. Structural Characterization of $(CO)_6Fe_2\{\mu\text{-SC}(C{\equiv}CCH_3){=}C(H)Te\}$

Pradeep Mathur,*[,1] Md. Munkir Hossain,[1] Sambhu N. Datta,[1]
Rama-Krishna Kondru,[1] and Mohan M. Bhadbhade[2]

Chemistry Department, Indian Institute of Technology, Powai, Bombay 400 076, India, and
Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002, India

Received January 14, 1994[⊗]

Summary: The room-temperature reaction of the mixed-chalcogenide complex $Fe_2(CO)_6(\mu\text{-STe})$ *with the diacetylene* $CH_3C{\equiv}CC{\equiv}CH$ *forms the new compound* $(CO)_6Fe_2\{\mu\text{-SC}(C{\equiv}CCH_3){=}C(H)Te\}$*. The structure of* $(CO)_6Fe_2\{\mu\text{-SC}(C{\equiv}CCH_3){=}C(H)Te\}$ *has been established by single-crystal X-ray diffraction methods:* $P\bar{1}$, a = *6.587(2) Å,* b = *10.689(3) Å,* c = *11.067(3) Å,* α = *92.74(2)°,* β = *92.77(2)°,* γ = *97.23(2)°,* V = *771(3) Å*^{3}*,* Z = *2,* R = *5.6%,* R_w = *6.8%. Molecular orbital calculations have been performed on the four possible isomers of* $(CO)_6Fe_2\{\mu\text{-SC}(C{\equiv}CCH_3){=}C(H)Te\}$ *which can be expected to form, and the formation of the experimentally found isomer has been rationalized.*

Introduction

The use of group 16 elements for the stabilization of transition-metal carbonyl compounds is now well established.[3] Moreover, certain contrasts have been observed in the structures and reactivity of compounds containing the smaller S or Se and the larger Te ligands.[4] In general, the class of compounds of the general form $Fe_2(CO)_6(\mu\text{-}E_2)$ where E = S, Se, or Te have served as useful starting materials for the addition of organic and inorganic moieties across the reactive E–E bonds. Seyferth has reported the reactions of alkynyllithium reagents with $Fe_2(CO)_6(\mu\text{-}S_2)$ and facile dithio ligand construction on the $Fe_2(CO)_6$ framework.[5] Recently, we have investigated the activation of acetylenes on $Fe_2(CO)_6(\mu\text{-}Se_2)$.[6] A new and convenient method to prepare the mixed-chalcogenide compounds $Fe_2(CO)_6(\mu\text{-EE}')$ has provided an opportunity to explore unique reactivity features of compounds which contain two different types of the chalcogenide ligand.[7] The reactivity of the compounds $Fe_2(CO)_6(\mu\text{-EE}')$ ($E \neq E'$) has been explored with respect to coordinatively unsaturated metal carbonyl fragments, and clusters of the form $Fe_{4-x}Ru_x(CO)_{11}(\mu_4\text{-E})(\mu_4\text{-E}')$ (x = 0–2) have been prepared. Here we report the functionalization of the diacetylene $CH_3C{\equiv}CC{\equiv}CH$ on $Fe_2(CO)_6(\mu\text{-STe})$ and the structural characterization of the product obtained. The reaction of the mixed-chalcogen complex $Fe_2(CO)_6STe$ with the diacetylene $CH_3C{\equiv}CC{\equiv}CH$ would be expected to give four possible isomers. Empirical (extended Hückel molecular orbital) calculations were performed on the four possible isomers.

Experimental Section

General Procedures. Reactions and manipulations were carried out under an inert atmosphere of argon by means of standard Schlenk techniques. Solvents were deoxygenated immediately prior to use. Infrared spectra were recorded on a Nicolet 5DXB FT spectrometer as hexane solutions in 0.1-mm-pathlength NaCl cells. NMR spectra were obtained on a Varian XL-300 spectrometer at 25 °C.

Preparation of 1. Compound 1 was prepared by a method modified from that reported earlier.[7] To an ice-cooled solution of Na_2TeO_3 (0.3 g, 1.4 mmol) and Na_2SO_3 (0.32 g, 2.5 mmol) in 40 mL of water was added a solution prepared from $Fe(CO)_5$ (0.55 mL, 4.1 mmol) and 4 mL of a 50% KOH solution in methanol. The mixture was stirred for 1.5 h and then acidified with 12 M HCl. A black precipitate was formed which was filtered in air, washed with distilled water, and dried in vacuo. The solid material was extracted with four 20-mL portions of CH_2Cl_2 and the combined extracts were filtered and evaporated to dryness to yield a mixture of the three compounds $Fe_3(CO)_9(\mu\text{-}S_2)$, $Fe_3(CO)_9(\mu\text{-STe})$, and $Fe_3(CO)_9(\mu\text{-}Te_2)$. The solid was added to a solution of NaOMe (1.5 g of Na in 200 mL of MeOH), and the mixture was stirred at room temperature for 2 h. The solution was diluted with hexane (50 mL) and water (50 mL) and acidified with 12 M HCl. After separation of the aqueous and organic layers, the aqueous phase was further washed with hexane and the combined organic extracts were washed with water and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated to 10 mL and subjected to chromatography on a silica gel column. Using hexane as eluent, two bands were

---

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1994.

(1) Organometallics Group (P.M. and M.M.H.) and Theory Group (S.N.D. and R.-K.K.), Indian Institute of Technology.

(2) Central Salt and Marine Chemicals Research Institute.

(3) Roof, L. C.; Kolis, J. W. *Chem. Rev.* **1993,** *93,* 1037. Linford, L.; Raubenheimer, H. G. *Adv. Organomet. Chem.* **1991,** *32,* 1. Compton, N. A.; Errington, R. J.; Norman, N. C. *Adv. Organomet. Chem.* **1990,** *31,* 91. Mathur, P.; Chakrabarty, D.; Hossain, M. M.; Rashid, R. S.; Rugmini, V.; Rheingold, A. L. *Inorg. Chem.* **1992,** *31,* 1106. Mathur, P.; Thimmappa, B. H. S.; Rheingold, A. L. *Inorg. Chem.* **1990,** *29,* 4658. Bogan, L. E.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985,** *107,* 3843. Mathur, P.; Mavunkal, I. J.; Rugmini, V.; Mahon, M. F. *Inorg. Chem.* **1990,** *29,* 4838. Fenske, D.; Ohmer, J.; Hachgenei, J.; Merzweiler, K. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 1277. Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990,** *100,* 223. Tatsumi, K.; Kawaguchi, H.; Tani, K. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 591. Boorman, P. M.; Kraatz, H.-B.; Parvez, M. *J. Chem. Soc., Dalton Trans.* **1992,** 3281. Layer, T. M.; Lewis, J.; Martin, A.; Raithby, P. R.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1992,** 3411. Johnson, B. F. G.; Lewis, J.; Lodge, P. G.; Raithby, R.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1979,** 719. Adams, R. D.; Horvath, I. T. *Inorg. Chem.* **1984,** *23,* 4718. Arce, A. J.; Machado, R.; Rivas, C.; de Sanctis, Y.; Deeming, A. J. *J. Organomet. Chem.* **1991,** *419,* 63.

(4) Bogan, L. E.; Lesch, D. A.; Rauchfuss, T. B. *J. Organomet. Chem.* **1983,** *50,* 429. Lesch, D. A.; Rauchfuss, T. B. *Organometallics* **1982,** *1,* 499.

(5) Seyferth, D.; Womack, G. B. *Organometallics* **1986,** *5,* 2360. Seyferth, D.; Womack, G. B.; Henderson, R. S.; Cowie, M. *Organometallics* **1986,** *5,* 1568. Seyferth, D.; Womack, G. B.; Song, L.-C. *Organometallics* **1983,** *2,* 776.

(6) Mathur, P.; Hossain, M. M. *Organometallics* **1993,** *12,* 2398. Mathur, P.; Hossain, M. M.; Das, K.; Sinha, U. C. *J. Chem. Soc., Chem. Commun.* **1993,** 46.

(7) Chakrabarty, D.; Hossain, M. M.; Mathur, P. *J. Organomet. Chem.* **1991,** *410,* 143. Mathur, P.; Chakrabarty, D.; Hossain, M. M. *J. Organomet. Chem.* **1991,** *401,* 167.

0276-7333/94/2313-2532$04.50/0

Table 1. Crystal Data Collection and Refinement Parameters[a]

formula	$C_{11}H_4O_6SFe_2Te$
fw	503.5
color	dark brown
lattice type	triclinic
space group	$P\bar{1}$
a, Å	6.587(2)
b, Å	10.689(3)
c, Å	11.067(3)
α, deg	92.74(2)
β, deg	92.77(2)
γ, deg	97.23(2)
V, Å^3	771(3)
Z	2
d_{calc}, g cm^{-3}	2.169
μ(Mo Kα) cm^{-1}	38.9
cryst dim, mm	0.12 × 0.16 × 0.06
collectn temp, °C	22
hkl ranges	$h = 8$, $k = -13$ to $+13$, $l = -14$ to $+14$
$2\theta_{max}$, deg	54
total no. of rflns	3201
no. of rflns obsd ($I_o > 5\sigma(I_o)$)	1837
intensity control rflns	3 per 60 min
orientation control rflns	3 per 200 rflns
T_{min}, T_{max}	69.8, 99.8
$R(F)$	0.056
$R_w(F)$	0.068
max Δ/σ, e Å^{-3}	0.03
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	+0.78, −0.80
GOF	1.66

[a] H atoms were not refined.

separated, in order of elution: $Fe_2(CO)_6(\mu\text{-}S_2)$ and a $Fe_2(CO)_6(\mu\text{-}STe)/Fe_2(CO)_6(\mu\text{-}Te_2)$ mixture. A second chromatographic workup on alumina using hexane as eluent gave complete separation of $Fe_2(CO)_6(\mu\text{-}STe)$ (1) and $Fe_2(CO)_6(\mu\text{-}Te_2)$. Approximate yield of 1 (based on $Fe(CO)_5$): 30%. IR (ν(CO), cm^{-1}): 2075 (m), 2036 (s), 2000 (s).

Preparation of 2. To a solution of 1 (1.1 mmol) in methanol (20 mL) was added 1,3-pentadiyne (1.5 mmol) and solid anhydrous sodium acetate (0.25 g). The mixture was stirred at room temperature for 24 h. The solvent was removed in vacuo, and the residue was redissolved in 5 mL of dichloromethane. The solution was filtered through Celite to remove insoluble material, and chromatographic workup using silica gel TLC plates and hexane as eluent yielded compound 2 (83 mg, 11%). Mp: 106–108 °C. IR (ν(CO), cm^{-1}): 2071 (m), 2036 (vs), 2002 (s), 1996 (s). ^{1}H NMR ($CDCl_3$; δ): 1.97 (s, CH_3), 7.31 (s, CH). ^{13}C NMR ($CDCl_3$, δ): 5.88 (CH_3), 78.08 ($\equiv C\text{—}CH_3$), 106.85 ($C\equiv C\text{—}CH_3$), 114.65 ($C\text{=}CH$), 153.65 (CH), 208.98 (CO). Anal. Calcd (found) for $C_{11}H_4Fe_2O_6STe$: C, 26.24 (26.35); H, 0.79 (0.82).

Crystal Structure Determination of 2. A dark brown crystal of approximate dimensions 0.12 × 0.16 × 0.06 mm^3 was selected for the X-ray diffraction study. The data were collected on an Enraf-Nonius CAD4 diffractometer generating Mo Kα radiation at room temperature, using the ω–2θ scan method. Unit cell parameters were determined and refined from 24 randomly selected reflections with a maximum θ value of 14° by the least-squares method. An empirical absorption correction (8 reflections near $\chi = 90$, ψ scan) was applied. The structure was solved by the heavy-atom method. The position of the heaviest atom, Te, was first located from the Patterson map. The few H atoms were located by subsequent Fourier syntheses and full-matrix least-squares refinements. The geometry of the methyl hydrogen atoms was regularized using the program HYDRO in the SDP package. All the computations were carried out on a PDP-11/73 computer using the Structure Determination Package (B.A. Frenz and Associates, 1985). The experimental conditions, crystal data, and summary of structural refinement are listed in Table 1. Final positional parameters on non-H atoms along with their isotropic equivalent temperature factors are recorded in Table 2. Selected bond distances and angles are given in Tables 3 and 4, respectively.

Table 2. Positional Parameters and Their Esd's

atom	x	y	z	B^a (Å^2)
Te1	0.8567	0.34739(7)	0.84615(7)	3.38(1)
Fe1	0.6733(2)	0.1257(1)	0.7878(2)	3.51(3)
Fe2	0.5766(2)	0.3149(2)	0.6788(1)	3.62(3)
S1	0.3967(4)	0.2225(3)	0.8272(2)	3.18(5)
O1	0.777(2)	0.027(1)	1.022(1)	7.0(3)
O2	1.004(1)	0.053(1)	0.647(1)	7.1(3)
O3	0.403(2)	−0.092(1)	0.681(1)	9.3(3)
O4	0.903(2)	0.351(1)	0.507(1)	8.7(3)
O5	0.295(2)	0.186(1)	0.4882(9)	8.5(3)
O6	0.422(2)	0.561(1)	0.678(1)	8.5(3)
C1	0.736(2)	0.063(1)	0.930(1)	4.4(3)
C2	0.879(2)	0.084(1)	0.702(1)	4.6(3)
C3	0.508(2)	−0.006(1)	0.722(1)	5.8(3)
C4	0.722(2)	0.336(2)	0.574(1)	5.8(3)
C5	0.402(2)	0.235(1)	0.563(1)	5.3(3)
C6	0.484(2)	0.466(1)	0.679(1)	5.2(3)
C7	0.655(2)	0.376(1)	0.985(1)	3.6(2)
C8	0.469(2)	0.314(1)	0.968(1)	3.3(2)
C9	0.315(2)	0.307(1)	1.056(1)	3.7(2)
C10	0.185(2)	0.294(1)	1.127(1)	3.9(2)
C11	0.036(2)	0.279(1)	1.220(1)	5.9(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table 3. Selected Bond Distances (Å)

Fe1–Te	2.555(2)	Fe2–Te	2.529(2)
Fe1–Fe2	2.538(2)	Fe1–S	2.258(3)
Fe2–S	2.264(4)	Te–C7	2.12(1)
S–C8	1.82(2)	C7–C8	1.31(1)
C8–C9	1.44(2)	C9–C10	1.19(2)

Table 4. Selected Bond Angles (deg)

Fe1–Te–Fe2	59.89(6)	Fe1–S–Fe2	68.3(1)
Te–Fe1–S	81.22(8)	C7–C8–C9	126(1)
C8–C9–C10	177(1)	C9–C10–C11	177(2)
Te–C7–C8	115.5(8)	S–C8–C9	114.9(7)
S–C8–C7	119.5(9)	Fe1–Te–C7	92.6(3)
Fe2–S–C8	108.5(3)	Fe1–S–C8	104.5(4)

Complete listings of bond distances and angles and anisotropic displacement parameters are included in the supplementary material.

Results and Discussion

A mixture containing $Fe_3(CO)_9S_2$, $Fe_3(CO)_9Te_2$, and $Fe_3(CO)_9STe$ was obtained when a KOH/methanol solution of $Fe(CO)_5$ was treated with a mixture of Na_2SO_3 and Na_2TeO_3, followed by acidification. When a solution containing the three compounds was stirred at room temperature with NaOMe, a mixture of $Fe_2(CO)_6(\mu\text{-}S_2)$, $Fe_2(CO)_6(\mu\text{-}Te_2)$, and $Fe_2(CO)_6(\mu\text{-}STe)$ was obtained, from which the desired mixed-chalcogenide compound 1 was obtained in pure form by chromatographic workup. Compound 1 is unstable in the solid form, like its Te_2 analog, and therefore the solution containing the freshly prepared 1 was used in subsequent reactions. When a methanol solution containing 1, $CH_3C\equiv CC\equiv CH$, and sodium acetate was stirred at room temperature for 24 h, a brown compound was isolated from the reaction medium and characterized as $(CO)_6Fe_2\{\mu\text{-}SC(C\equiv CCH_3)\text{=}C(H)\text{-}Te\}$ (2) on the basis of infrared and ^{1}H and ^{13}C NMR spectroscopy (Scheme 1). Its composition was confirmed by elemental analysis.

Brown crystals of 2 were grown from its hexane solution at −20 °C, and an X-ray analysis was undertaken. An ORTEP diagram of its molecular structure is shown in Figure 1. The molecule consists of a Fe_2STe butterfly core with the S and Te atoms bonded across the terminal

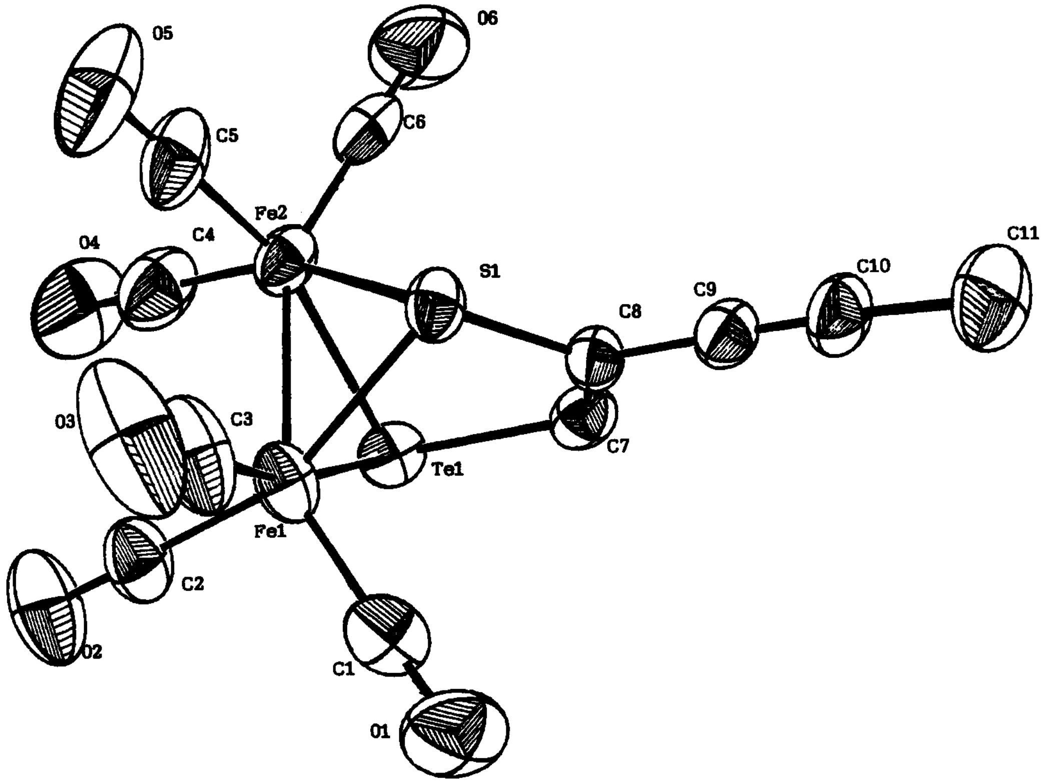
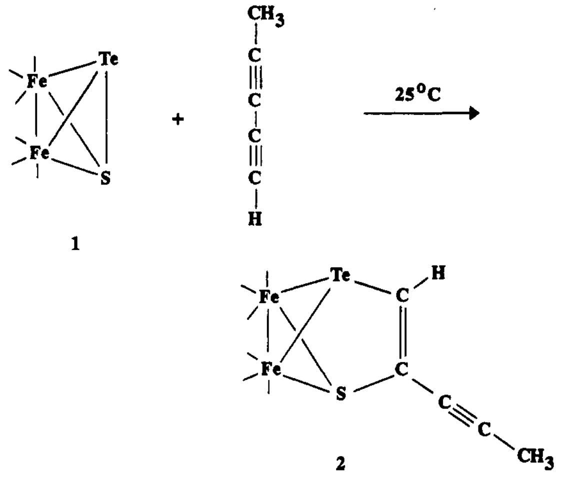


Figure 1.

Scheme 1



acetylenic bond of methyldiacetylene such that the methyl group is farthest away from the Te atom. Each Fe atom has three terminal carbonyl groups bonded to it. The Fe—Fe bond in **2** (2.538(2) Å) is slightly shorter than the Fe–Fe bond distances in related compounds: $Fe_2(CO)_6(\mu\text{-}S_2)$,[8] 2.552(2) Å; $Fe_2(CO)_6(\mu\text{-}Se_2)$,[9] 2.575(2) Å; $Fe_2(CO)_6(\mu\text{-}TeCH_2Te)$,[10] 2.587(2) Å. It is also much shorter than the Fe—Fe bond distance observed in the open-butterfly structure of $Fe_2(CO)_6(\mu\text{-}TeMe_2)$[11] (2.634(5) Å) but is comparable to that observed in $Fe_2(CO)_6(\mu\text{-}SEt)_2$ (2.537(10) Å).[12] The Te—Fe distances of **2** (2.555(2) and 2.529(2) Å) compare well with the previously reported values of Te—Fe bond distances: $Fe_2(CO)_6(\mu\text{-}TeCH_2Te)$, 2.551(2) and 2.546(2) Å; $Fe_3(CO)_9(\mu_3\text{-}Te)_2$,[13] 2.53 Å (av); $Fe_2Ru_3Te_2(CO)_{17}$,[14] 2.556 Å (av); $[Fe_2(CO)_6(\mu\text{-}Te)(\mu\text{-}Te)_2]^{2-}$,[15] 2.572 Å (av). The S—Fe bond distances in **2** (2.258(3) and 2.264(4) Å) compare well with the average S—Fe bond distances observed in $Fe_2(CO)_6(\mu\text{-}SEt)_2$ (2.259 Å) but are longer than the average S—Fe bond distance observed in $Fe_2(CO)_6(\mu\text{-}S_2)$ (2.228 Å). The C—C bond distance of the coordinated acetylenic bond (1.31(1) Å) is within the range observed for olefinic bonds but is somewhat shorter than the C—C bond distance of the coordinated acetylene in $(CO)_6Fe_2\{\mu\text{-}SeC(Ph){=}C(H)Se\}$[6] (1.331(7) Å) and in $(CO)_6Fe_2\{\mu\text{-}TeC(Ph){=}C(H)Te\}$[16] (1.34(1) Å). The C—C bond distance of the uncoordinated acetylenic bond (1.19(2) Å) is typical of a C—C triple-bond distance. The experimental results are, in principle, in agreement with extended Hückel molecular orbital calculations. The calculated binding energy and difference between the energies of the LUMO and HOMO for the four possible isomers of **2** indicate the experimentally isolated structure to be the most stable one, although the extended Hückel calculation does not show a substantial relative stability (Table 5). Details of calculations are available as supplementary material.

The addition of phenylacetylene across the Se—Se bond of $Fe_2(CO)_6(\mu\text{-}Se_2)$ occurs readily, and a product in which the acetylenic triple bond is reduced to a double bond is formed. In contrast, the addition of phenylacetylene across the Te—Te bond of $Fe_2(CO)_6(\mu\text{-}Te_2)$ is not observed; the analogous Te compound $Fe_2(CO)_6(\mu\text{-}TeC(H){=}C(Ph)Te)$ is obtained by refluxing a benzene solution of $Fe_3(CO)_9$-

---

[8] Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1.

[9] Campana, C. F.; Lo, F. W.-K.; Dahl, L. F. *Inorg. Chem.* **1979**, *18*, 3060.

[10] Mathur, P.; Reddy, V. D.; Bohra, R. *J. Organomet. Chem.* **1991**, *401*, 339.

[11] Bachman, R. E.; Whitmire, K. H. *Organometallics* **1993**, *12*, 1988.

[12] Dahl, L. F.; Wei, C. H. *Inorg. Chem.* **1963**, *2*, 328.

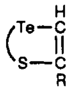
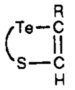
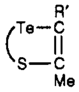
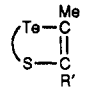
[13] Schumann, H.; Magaerstadt, M.; Pickardt, J. *J. Organomet. Chem.* **1982**, *240*, 407.

[14] Mathur, P.; Mavunkal, I. J.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1982**, 382.

[15] Eichorn, B. W.; Haushalter, R. C.; Merola, J. S. *Inorg. Chem.* **1990**, *29*, 728.

[16] Fassler, T.; Buchholz, D.; Huttner, G.; Zsolnai, I. *J. Organomet. Chem.* **1989**, *369*, 297.

Table 5. Energies of the LUMO and HOMO and Binding Energies of Four Possible Isomers of 2 in eV

	isomers[a]			
				
LUMO	−9.974	−9.828	−9.009	−9.646
HOMO	−10.274	−10.241	−9.975	−9.952
binding energy	−148.686	−148.532	−142.767	−142.952

[a] R = –C≡CMe; R′ = –C≡CH.

(μ_3-Te)$_2$ and phenylacetylene.[16] A similar contrast is observed between the reactivities of $Fe_2(CO)_6(\mu\text{-}S_2)$ and $Fe_2(CO)_6(\mu\text{-}Te_2)$ toward the diacetylene $CH_3C{\equiv}CC{\equiv}CH$. The S-compound forms a trace amount of a product from its reaction with $CH_3C{\equiv}CC{\equiv}CH$, which on the basis of comparison of its infrared spectrum with that of compound 2 may be identified as $(CO)_6Fe_2\{\mu\text{-}SC(H){=}C(C{\equiv}CCH_3)S\}$. Attempts to improve the yield of this compound to enable a fuller characterization have been unsuccessful. The formation of the Te_2 analog of compound 2 from the reaction of $Fe_2(CO)_6(\mu\text{-}Te_2)$ and the diacetylene was not observed. The polar character of the S—Te bond in compound 1 enables the functionalization of a diacetylene on the diiron dichalcogenide framework. The synthesis of cluster-functionalized polyacetylenes has been of interest for obtaining potentially high one-dimensional conductivities.[17] Compounds containing the Co_3C moiety incorporated in the alkyne backbone have been recognized as suitable precursors for conducting materials.[18] The generality of our facile method for the functionalization of polyacetylenes on the Fe_2STe framework is currently under investigation.

Acknowledgment. Financial support (to P.M.) by the Department of Atomic Energy, Government of India, is gratefully acknowledged.

Supplementary Material Available: Tables of bond distances and angles and anisotropic displacement coefficients for 2, text giving details of the molecular orbital calculations, and tables of extended Hückel molecular orbital energies, computed and total binding energies, net atomic charges, and comparison of the net overlap population between different atoms in the four possible isomers (10 pages). Ordering information is given on any current masthead page.

OM940034D

---

(17) Seymour, R. B., Ed. *Conductive Polymers*; Plenum: New York, 1981; Vol. 16.

(18) Worth, G. H.; Robinson, B. H.; Simpson, J. *Organometallics* **1992**, *11*, 501.