Reaction of $[Te_6Fe_8(CO)_{24}]^{2-}$ with Dihaloalkanes: A New Route to Organotellurium Complexes of Iron

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Organotellurium hexacarbonyldiiron complexes, $Fe_2(CO)_6(\mu\text{-}Te(CH_2)_nTe)$ (n = 1, n = 2, **2**; n = 3, **3**), are synthesized by the reaction of $[Te_6Fe_8(CO)_{24}]^{2-}$ (**1**) with appropriate dihaloalkanes. When $[Et_4N]_2[\mathbf{1}]$ is treated with $Br(CH_2)_2Br$, an anionic cluster $[Et_4N][BrTe_2Fe_2(CO)_6]$ (**4**) is obtained. Clusters **2**–**4** were characterized by spectroscopic data and single-crystal X-ray analysis. Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with a = 7.194(1) Å, b = 13.179(4) Å, c = 14.644(3) Å, β = 91.57(2)°, V = 1387.9(6) Å^3, and Z = 4. Compound **3** is isomorphous with **2**: monoclinic, space group $P2_1/n$ with a = 7.455(1) Å, b = 13.312(1) Å, c = 15.097(3) Å, β = 91.48(2)°, V = 1497.7(4) Å^3, and Z = 4. Crystals of **4** are monoclinic, space group $P2_1/n$ with a = 13.304(2) Å, b = 13.022(3) Å, c = 13.372(5) Å, β = 93.70(2)°, V = 2311.6(1) Å^3, and Z = 4. Compound **2** or **3** displays a Te_2Fe_2 butterfly geometry with the Te atoms bridged by a $-(CH_2)_n-$ (n = 2, 3) group while the anionic cluster **4** exhibits a Te_2Fe_2 tetrahedral core with one Te bonded to an external Br atom. The anionic **1** has been shown to be a source of the dianion, $[Te_2Fe_2(CO)_6]^{2-}$, and provides a useful reagent for the preparation of organotellurium hexacarbonyldiiron complexes, $Fe_2(CO)_6(\mu\text{-}Te(CH_2)_nTe)$.

Introduction

Research in chalcogen-rich metal complexes has shown that the tellurides exhibit unique structural and reactivity patterns due to the large size, increased nucleophilicity, and the metallic character of the tellurium atom.[1] Of these complexes, $Te_2Fe_3(CO)_9$[2] and $Te_2Fe_2(CO)_6$[3] are known to be good starting materials for cluster building reactions.[4] Recently, a number of interesting anionic tellurium–iron clusters have been synthesized and structurally characterized, including $[Fe_2(CO)_6(Te)(Te)_2]^{2-}$,[5] $[Te_4Fe_5(CO)_{14}]^{2-}$,[6,7] and $[Te_{10}Fe_8(CO)_{20}]^{2-}$.[6,8] However, little is known about their reactivity.

More recently, we have isolated and characterized an unusual anionic cluster, $[Te_6Fe_8(CO)_{24}]^{2-}$ (**1**), from the reaction of K_2TeO_3 and $Fe(CO)_5$/KOH in methanol.[7] Cluster **1** can be viewed as composed of two $Te_2Fe_3(CO)_9$ fragments bridged by a $[Te_2Fe_2(CO)_6]^{2-}$ anion, which leads to the interesting question if cluster **1** can function as a $[Te_2Fe_2(CO)_6]^{2-}$ source in reaction with organic dihalides to form organotellurium complexes of iron. To answer this question, we have treated **1** with a series of dihaloalkanes and describe the synthesis and characterization of several $-Te(CH_2)_nTe-$ bridged diiron complexes, $Fe_2(CO)_6(\mu\text{-}Te(CH_2)_nTe)$ (n = 1;[9] n = 2, **2**; n = 3, **3**). The anionic complex, $[Et_4N][Te_2Fe_2(CO)_6Br]$ (**4**), is produced when $[Et_4N][\mathbf{1}]$ is treated with $Br(CH_2)_2Br$.

Experimental Section

All reactions were performed under an atmosphere of pure nitrogen using standard Schlenk line techniques. Solvents were purified, dried, and distilled under nitrogen prior to use: THF (Na/benzophenone); hexane (CaH_2); toluene ($LiAlH_4$); CH_2Cl_2 (P_2O_5). $K_2TeO_3\cdot xH_2O$ (Strem), $Fe(CO)_5$ (Aldrich), 1,2-dibromoethane (Janssen), 2-bromo-1-chloroethane (Kanto), 1,3-dichloropropane (Kanto), 1,2-dichloroethane (Kanto), and 3-bromo-1-chloropropane (Kanto) were used as received without further purification. Infrared spectra were recorded on a Jasco 700 IR spectrometer as solutions in CaF_2 cells. Mass spectra were obtained on a Finningan MATTSQ-46C mass spectrometer at 30 or 20 eV. ^1H NMR spectra were taken on a JEOL 400 (400 MHz) or a Bruker AC-300 (300 MHz) instrument. Elemental analyses were performed on a Perkin-Elmer 2400 analyzer at the NSC Regional Instrumental Center at National Taiwan University, Taipei, Taiwan. $[Te_6Fe_8(CO)_{24}]^{2-}$ (**1**) was prepared by the literature procedure.[7]

Reaction of $[Te_6Fe_8(CO)_{24}]^{2-}$ (1) with CH_2Cl_2. To a sample of 0.5 g (0.23 mmol) of $[PhCH_2NMe_3]_2[Te_6Fe_8(CO)_{24}]$ ($[PhCH_2NMe_3]_2[\mathbf{1}]$) was added 50 mL of CH_2Cl_2. The resulting solution was heated at 45 °C for 3 days. The orange-red solution was filtered and solvent removed under vacuum. The residue was extracted into hexane. The hexane extracts were chromatographed on a silica gel column using hexane as eluent to give a dark purple band from which was isolated 0.13 g (0.20 mmol) of $Te_2Fe_3(CO)_9$ (30% based on Te). IR (ν_{CO}, hexane): 2044 (s), 2022 (s), 2002 (s) cm^{-1}. A second orange-red band gave 0.08 g (0.15 mmol) of the previously known cluster $Fe_2(CO)_6(\mu\text{-}TeCH_2Te)$ (65% based on "$Te_2Fe_2(CO)_6^{2-}$" content),[9] which was identified by X-ray analysis. IR (ν_{CO}, hexane): 2058 (s), 2018 (vs), 1983 (s) cm^{-1}. Mass (EI, 20 eV): M$^+$ = m/z 554.

Reaction of $[Te_6Fe_8(CO)_{24}]^{2-}$ (1) with $Cl(CH_2)_2Br$. To a sample of 0.60 g (0.27 mmol) of $[PhCH_2NMe_3]_2[Te_6Fe_8(CO)_{24}]$

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Table 1. Selected Crystallographic Data for $Fe_2(CO)_6(\mu\text{-}TeCH_2CH_2Te)$ (2), $Fe_2(CO)_6(\mu\text{-}TeCH_2CH_2CH_2Te)$ (3), and $[Et_4N][BrTe_2Fe_2(CO)_6]$ (4)

	2	3	4
empirical formula	$Te_2Fe_2C_8O_6H_4$	$Te_2Fe_2C_9O_6H_6$	$Te_2Fe_2C_{14}O_6H_{20}NBr$
fw	563.02	577.03	745.11
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	7.194(1)	7.455(1)	13.304(2)
b, Å	13.179(4)	13.312(1)	13.022(3)
c, Å	14.644(3)	15.097(3)	13.372(5)
β, deg	91.57(2)	91.48(2)	93.70(2)
V, Å^3	1387.9(6)	1497.7(4)	2311.6(1)
Z	4	4	4
D(calc), Mg m^{-3}	2.70	2.56	2.14
abs coeff, mm^{-1}	6.24	5.78	3.75
diffractometer	Nonius (CAD-4)	Nonius (CAD-4)	Nonius (CAD-4)
radiation: λ(Mo Ka), Å	0.709 30	0.709 30	0.709 30
temp, °C	25	25	25
T_{min}/T_{max}	0.69/1.00	0.69/1.00	0.73/1.00
residuals: $R_F{}^a$; $R_w{}^a$	0.033; 0.031	0.026; 0.023	0.042; 0.041

[a] The function minimized during the least squares cycles was $R_F = \sum(F_o - F_c)/\sum F_o$, $R_w = [\sum w(F_o - F_c)^2/\sum w(F_o)^2]^{1/2}$.

($[PhCH_2NMe_3]_2[1]$) was added 0.8 mL (9.67 mmol) of $Cl(CH_2)_2Br$ in 50 mL of THF. The resulting solution was heated at 55–60 °C for 24 h. The orange-red solution was filtered and solvent removed under vacuum. The residue was extracted with hexane. The extracts were chromatographed on a silica gel column using hexane as eluent to give 0.07 g (0.12 mmol) of $Fe_2(CO)_6(\mu\text{-}TeCH_2CH_2Te)$ (2) (44% based on "$Te_2Fe_2(CO)_6{}^{2-}$" content). IR (ν_{CO}, hexane): 2060 (s), 2023 (vs), 1984 (s) cm^{-1}. Anal. Calcd. (found) for 2: C, 17.07 (17.90); H, 0.72 (0.80). Mass (EI, 30 eV): $M^+ = m/z$ 568 $(M - nCO)^+$ = 540, 512, 484, 456, 428, 462 (n = 1–6). ^1H NMR (300 MHz, $CDCl_3$): δ 2.20 (s). Mp: 109 °C dec.

Reaction of $[Te_6Fe_8(CO)_{24}]^{2-}$ (1) with $Cl(CH_2)_3Cl$. To a sample of 0.80 g (0.37 mmol) of $[PhCH_2NMe_3]_2[Te_6Fe_8(CO)_{24}]$ ($[PhCH_2NMe_3]_2[1]$) was added 1.0 mL (10.5 mmol) of $Cl(CH_2)_3Cl$ in 50 mL of THF. The resulting solution was heated at 55–60 °C for 24 h. The orange-red solution was filtered and solvent removed under vacuum. The residue was extracted with hexane. The extracts were chromatographed on a silica gel column using hexane as eluent. The fastest moving band was collected to give 0.13 g (0.23 mmol) of $Fe_2(CO)_6(\mu\text{-}TeCH_2CH_2CH_2Te)$ (3) (62% based on "$Te_2Fe_2(CO)_6{}^{2-}$" content). IR (ν_{CO}, hexane): 2058 (s), 2021 (vs), 1983 (s) cm^{-1}. Anal. Calcd. (found) for 3: C, 18.73 (19.01); H, 1.05 (0.98). Mass (EI, 20 eV): $M^+ = m/z$ 582, $(M - nCO)^+$ = 554, 526, 498, 470, 442, 414 (n = 1–6), $(Te_2Fe_2)^+$ = 372. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.30 (t, 4H, J = 5.2 Hz), 0.75 (m, 2H). Mp: 113 °C dec.

A similar reaction of 0.50 (0.23 mmol) of $[PhCH_2NMe_3]_2[Te_6Fe_8(CO)_{24}]$ ($[PhCH_2NMe_3]_2[1]$) with 1.0 mL (10.2 mmol) of $Cl(CH_2)_3Br$ in 50 mL of THF gave 0.103 g (0.18 mmol) of $Fe_2(CO)_6(\mu\text{-}TeCH_2CH_2CH_2Te)$ (3) (78% based on "$Te_2Fe_2(CO)_6{}^{2-}$" content). IR (ν_{CO}, hexane): 2056 (s), 2023 (vs), 1984 (s) cm^{-1}.

Reaction of $[Te_6Fe_8(CO)_{24}]^{2-}$ (1) with $Br(CH_2)_2Br$. To a sample of 0.50 g (0.23 mmol) of $[Et_4N]_2[Te_6Fe_8(CO)_{24}]$ ($[Et_4N]_2[1]$) was added 0.5 mL (5.8 mmol) of $Br(CH_2)_2Br$ in 50 mL of THF. The resulting solution was heated at 55–60 °C for 24 h. The orange-red solution was filtered and solvent removed under vacuum. The residue was washed with hexane and extracted with 20 mL of toluene to give 0.213 g (0.29 mmol) of $[Et_4N][BrTe_2Fe_2(CO)_6]$ (4) (42% based on Te). IR (ν_{CO}, toluene): 2060 (s), 2019 (vs), 1983 (s) cm^{-1}. Anal. Calcd. (found) for 4: C, 22.57 (22.1); H, 2.71 (2.69); N, 1.88 (1.77). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 3.43 (q, 2H, J = 7.8Hz), 1.38 (t, 3H, J = 7.8 Hz). Compound 4 is soluble in toluene, THF, CH_3CN, and CH_2Cl_2 and insoluble in hexane.

X-ray Structural Characterization of 2–4. A summary of selected crystallographic data for 2–4 is given in Table 1. Data collection was carried out on a Nonius CAD-4 diffractometer using graphite-monochromated Mo Ka radiation at 25 °C. All crystals were mounted on glass fibers with Epoxy cement. Data reduction and structural refinement were performed using the NRCC-SDP-VAX packages,[10] and atomic scattering factors were taken from ref 11.

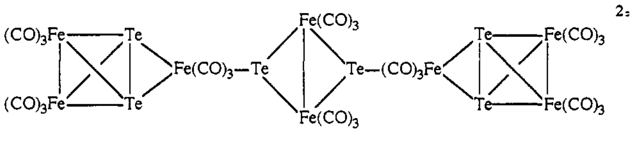
Orange-red crystals of 2 and 3 suitable for X-ray analysis were grown from hexane solution. A total of 3184 and 3429 unique reflections were collected for 2 and 3, respectively, and corrected for absorption and decay. The structures of 2 and 3, were solved by direct methods which indicated the presence of Te and Fe atoms. The light atoms were found by using successive least squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic thermal parameters. Full-matrix least squares refinement of 2 and 3 led to convergence with R_F = 3.3%, R_w = 3.1% and R_F = 6.5%, R_w = 3.3%, respectively, for those reflections with $I > 2.5\sigma(I)$.

Orange-red crystals of 4 suitable for X-ray analysis were grown from toluene solution. A total of 3002 unique reflections were collected and corrected for absorption and decay. The structure of 4 was solved by direct methods which indicated the presence of Te and Fe atoms. The light atoms were found by using successive least squares cycles and difference Fourier maps. All non-hydrogen atoms of 4 were refined with anisotropic thermal parameters. Full-matrix least squares refinement of 4 led to convergence with R_F = 4.2% and R_w = 4.1% for those reflections with $I > 2.5\sigma(I)$.

The selected atomic coordinates of 2–4 are given in Tables 2–4, respectively. Selected bond distances and angles of 2 and 3 are presented in Tables 5 and 6, respectively, and those of 4 are listed in Table 7. Additional crystallography data are available as supplementary material.

Results

As noted above, the core geometry of 1 can be viewed as a $Te_2Fe_2(CO)_6{}^{2-}$ anion connected to two $Te_2Fe_3(CO)_9$ clusters. When cluster 1 is refluxed in CH_2Cl_2, the known



(1)

$Fe_2(CO)_6(\mu\text{-}TeCH_2Te)$ and $Te_2Fe_3(CO)_9$ are generated. This indicates that cluster 1 can function as a $Te_2Fe_2(CO)_6{}^{2-}$ source. Further reaction of cluster 1 with $Cl(CH_2)_2$-

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Table 2. Selected Atomic Coordinates and Isotropic Displacement Coefficients for $Fe_2(CO)_6(\mu\text{-}TeCH_2CH_2Te)$ (2)

	x	y	z	B_{iso}, Å^2
Te(1)	0.76122(7)	0.22255(4)	0.29517(4)	3.114(22)
Te(2)	0.31440(7)	0.18881(4)	0.23043(4)	3.233(23)
Fe(1)	0.47408(15)	0.32724(8)	0.32301(8)	3.06(5)
Fe(2)	0.49618(15)	0.13609(8)	0.37269(8)	2.85(4)
O(1)	0.5069(10)	0.4808(5)	0.1808(5)	6.0(4)
O(2)	0.6714(10)	0.4219(6)	0.4768(6)	8.0(5)
O(3)	0.1200(9)	0.3899(6)	0.3988(5)	6.6(4)
O(4)	0.7274(9)	0.1495(6)	0.5389(5)	6.6(4)
O(5)	0.1559(9)	0.1259(6)	0.4759(4)	5.8(4)
O(6)	0.5514(10)	−0.0758(5)	0.3250(5)	6.2(4)
C(1)	0.4947(11)	0.4207(6)	0.2373(7)	4.0(4)
C(2)	0.5954(13)	0.3853(7)	0.4164(7)	4.8(4)
C(3)	0.2561(12)	0.3633(7)	0.3677(6)	4.3(4)
C(4)	0.6354(12)	0.1440(7)	0.4738(6)	4.3(4)
C(5)	0.2869(11)	0.1294(6)	0.4337(6)	3.7(4)
C(6)	0.5290(12)	0.0064(7)	0.3428(6)	4.2(4)
C(7)	0.7148(13)	0.1758(8)	0.1560(6)	4.9(5)
C(8)	0.5163(12)	0.1596(8)	0.1271(6)	4.6(5)

Table 3. Selected Atomic Coordinates and Isotropic Displacement Coefficients for $Fe_2(CO)_6(\mu\text{-}TeCH_2CH_2CH_2Te)$ (3)

	x	y	z	B_{iso}, Å^2
Te(1)	0.75382(4)	0.77071(3)	0.200989(25)	3.591(16)
Te(2)	0.31156(5)	0.80761(3)	0.26448(3)	4.095(18)
Fe(1)	0.46582(10)	0.67097(6)	0.17809(5)	3.76(4)
Fe(2)	0.48718(10)	0.86091(6)	0.13083(5)	3.57(3)
O(1)	0.5199(7)	0.5178(4)	0.3151(4)	7.9(3)
O(2)	0.6286(6)	0.5852(4)	0.0213(4)	8.3(3)
O(3)	0.1136(6)	0.6063(4)	0.1105(3)	7.2(3)
O(4)	0.6906(7)	0.8498(5)	−0.0314(3)	9.0(3)
O(5)	0.1494(6)	0.8772(5)	0.0292(3)	8.4(3)
O(6)	0.5483(7)	1.0712(3)	0.1770(3)	7.4(3)
C(1)	0.5005(8)	0.5772(5)	0.2620(5)	5.1(3)
C(2)	0.5689(8)	0.6187(5)	0.0836(4)	5.2(3)
C(3)	0.2490(8)	0.6329(4)	0.1373(4)	4.6(3)
C(4)	0.6117(9)	0.8540(5)	0.0321(4)	5.5(3)
C(5)	0.2798(8)	0.8709(5)	0.0699(4)	5.1(3)
C(6)	0.5261(9)	0.9889(5)	0.1585(4)	4.9(3)
C(7)	0.7858(8)	0.8132(5)	0.3377(4)	5.3(3)
C(8)	0.6465(9)	0.8812(6)	0.3756(4)	7.1(4)
C(9)	0.4653(8)	0.8406(5)	0.3841(4)	5.2(3)

Table 4. Selected Atomic Coordinates and Isotropic Displacement Coefficients for $[Et_4N][BrTe_2Fe_2(CO)_6]$ (4)

	x	y	z	B_{iso}, Å^2
Te(1)	0.81404(9)	0.14074(9)	0.22374(10)	4.07(6)
Te(2)	0.80690(9)	0.19074(9)	0.02501(10)	4.45(6)
Fe(1)	0.64890(18)	0.16558(19)	0.12281(19)	3.69(12)
Fe(2)	0.76843(18)	0.01062(18)	0.08803(19)	3.52(12)
Br	0.77117(16)	0.05003(17)	0.42302(17)	5.95(11)
O(1)	0.5234(10)	0.0570(11)	0.2600(11)	6.5(8)
O(2)	0.6011(11)	0.3779(10)	0.1721(11)	6.7(8)
O(3)	0.5120(11)	0.1372(13)	−0.0573(11)	7.3(9)
O(4)	0.6780(10)	−0.1399(11)	0.2134(10)	6.3(8)
O(5)	0.6683(10)	−0.0472(11)	−0.1033(10)	6.4(8)
O(6)	0.9554(10)	−0.0975(11)	0.0694(11)	7.0(9)
C(1)	0.5741(12)	0.0990(14)	0.2065(14)	4.1(9)
C(2)	0.6194(13)	0.2957(14)	0.1527(14)	4.2(9)
C(3)	0.5643(15)	0.1504(17)	0.0104(16)	5.5(11)
C(4)	0.7139(13)	−0.0800(13)	0.1642(15)	4.3(10)
C(5)	0.7098(14)	−0.0255(13)	−0.0275(16)	4.6(11)
C(6)	0.8810(16)	−0.0537(14)	0.0772(16)	5.8(12)

Br or $Cl(CH_2)_3Cl$ produces $Fe_2(CO)_6(\mu\text{-}TeCH_2CH_2Te)$ (2) and $Fe_2(CO)_6(\mu\text{-}TeCH_2CH_2CH_2Te)$ (3), respectively. In contrast, the reaction with $Br(CH_2)_2Br$ produces the anionic complex $[Et_4N][BrTe_2Fe_2(CO)_6]$ (4) as the major product.

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for $Fe_2(CO)_6(\mu\text{-}TeCH_2CH_2Te)$ (2)

(A) Distances			
Metal–Metal Bond Lengths			
Te(1)–Te(2)	3.3562(9)	Te(1)–Fe(1)	2.527(1)
Te(1)–Fe(2)	2.518(1)	Te(2)–Fe(1)	2.530(1)
Te(2)–Fe(2)	2.527(1)	Fe(1)–Fe(2)	2.626(2)
Other Bond Ranges			
Te–C	2.146(9)–2.160(9)	Fe–C	1.77(1)–1.78(1)
C–O	1.13(1)–1.15(1)		
(B) Angles			
Te(2)–Te(1)–Fe(1)	48.46(3)	Te(2)–Te(1)–Fe(2)	48.41(3)
Fe(1)–Te(1)–Fe(2)	62.73(4)	Te(1)–Te(2)–Fe(1)	48.37(3)
Te(1)–Te(2)–Fe(2)	48.19(3)	Fe(1)–Te(2)–Fe(2)	62.56(4)
Te(1)–Fe(1)–Te(2)	83.17(4)	Te(1)–Fe(1)–Fe(2)	58.48(4)
Te(2)–Fe(1)–Fe(2)	58.66(4)	Te(1)–Fe(2)–Te(2)	83.40(4)
Te(1)–Fe(2)–Fe(1)	58.79(4)	Te(2)–Fe(2)–Fe(1)	58.78(4)
Te(1)–C(7)–C(8)	115.7(6)	Te(2)–C(8)–C(7)	115.6(6)
Fe–C–O	176.9(8)–179.3(8)	Fe–Te–C	100.7(2)–101.7(2)

Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for $Fe_2(CO)_6(\mu\text{-}TeCH_2CH_2CH_2Te)$ (3)

(A) Distances			
Metal–Metal Bond Lengths			
Te(1)–Te(2)	3.4918(8)	Te(1)–Fe(1)	2.5404(9)
Te(1)–Fe(2)	2.5310(9)	Te(2)–Fe(1)	2.5317(9)
Te(2)–Fe(2)	2.535(1)	Fe(1)–Fe(2)	2.633(1)
Other Bond Ranges			
Te–C	2.147(6)–2.159(6)	Fe–C	1.776(7)–1.792(7)
C–O	1.133(8)–1.142(8)		
(B) Angles			
Te(2)–Te(1)–Fe(1)	46.39(2)	Te(2)–Te(1)–Fe(2)	46.47(2)
Fe(1)–Te(1)–Fe(2)	62.56(3)	Te(1)–Te(2)–Fe(1)	46.60(2)
Te(1)–Te(2)–Fe(2)	46.38(2)	Fe(1)–Te(2)–Fe(2)	62.63(3)
Te(1)–Fe(1)–Te(2)	87.01(3)	Te(1)–Fe(1)–Fe(2)	58.54(3)
Te(2)–Fe(1)–Fe(2)	58.74(3)	Te(1)–Fe(2)–Te(2)	87.15(3)
Te(1)–Fe(2)–Fe(1)	58.89(3)	Te(2)–Fe(2)–Fe(1)	58.63(3)
Te(1)–C(7)–C(8)	117.7(4)	C(7)–C(8)–C(9)	117.3(6)
Te(2)–C(9)–C(8)	118.2(4)	Fe–C–O	177.3(6)–179.6(6)
Fe–Te–C	109.6(2)–110.1(2)		

Table 7. Selected Bond Distances (Å) and Bond Angles (deg) for $[Et_4N][BrTe_2Fe_2(CO)_6]$ (4)

(A) Distances			
Metal–Metal Bond Lengths			
Te(1)–Te(2)	2.732(2)	Te(1)–Fe(1)	2.524(3)
Te(1)–Fe(2)	2.528(3)	Te(2)–Fe(1)	2.567(3)
Te(2)–Fe(2)	2.555(3)	Fe(1)–Fe(2)	2.629(3)
Other Bond Ranges			
Te(1)–Br	3.003(3)	Fe–C	1.73(2)–1.83(2)
C–O	1.12(3)–1.16(3)		
(B) Angles			
Te(2)–Te(1)–Fe(1)	58.32(7)	Te(2)–Te(1)–Fe(2)	57.98(7)
Te(2)–Te(1)–Br	163.81(7)	Fe(1)–Te(1)–Fe(2)	62.72(8)
Fe(1)–Te(1)–Br	108.44(8)	Fe(2)–Te(1)–Br	108.83(8)
Te(1)–Te(2)–Fe(1)	56.79(7)	Te(1)–Te(2)–Fe(2)	57.01(7)
Fe(1)–Te(2)–Fe(2)	61.76(8)	Te(1)–Fe(1)–Te(2)	64.89(7)
Te(1)–Fe(1)–Fe(2)	58.71(8)	Te(2)–Fe(1)–Fe(2)	58.89(8)
Te(1)–Fe(2)–Te(2)	65.01(7)	Te(1)–Fe(2)–Fe(1)	58.57(8)
Te(2)–Fe(2)–Fe(1)	59.34(8)	Fe–C–O	177.3(2)–179.6(1)

Clusters 2–4 are fully characterized by spectroscopic methods and elemental analysis. The infrared spectra of 2–4 show the absorptions characteristic of terminal carbonyl ligands in the region 2060–1984 cm^{-1}. The absorption pattern is indicative of a Te_2Fe_2 tetrahedron-like core geometry, as compared to those for $Fe_2Te_2(CO)_6$[3] and $Fe_2(CO)_6(\mu\text{-}TeCH_2Te)$. Moreover, the ^1H NMR spectra provide some useful structural information. The ^1H NMR spectrum of 2 exhibits a singlet peak at δ 2.20 indicative of fluxionality of the structure in solution. The methylene proton at δ 2.20 is compared to the reported value, δ 2.19, for bridged methylene in the case of $Fe_2(CO)_6(\mu\text{-}TeCH_2Te)$,[9] and is consistent with the chemical shifts of the μ-C(H)R moieties that are unsupported by

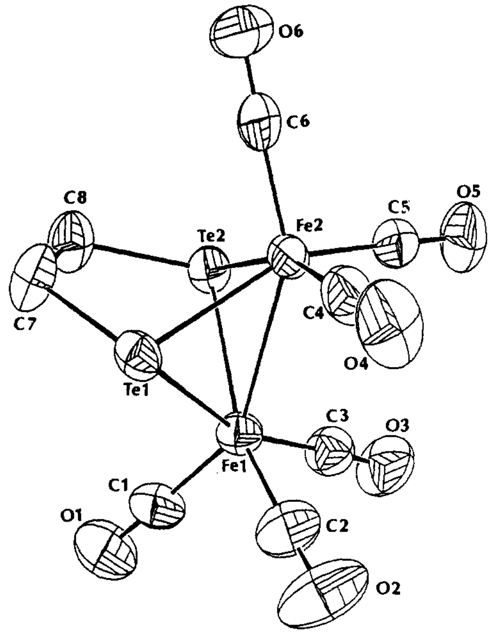

Figure 1. ORTEP diagram showing the structure and atom labeling for 2.

metal–metal bonds.[12] Similarly, the ^1H NMR spectrum of 3 consists of two resonances: one triplet at δ 2.30 for the methylene groups bonded to the Te atoms and the other multiplet at δ 0.75 for the middle methylene group.

The mass and elemental analysis confirm the formulas of 2 and 3. The mass spectrum of 2 shows the parent peaks in the region of *m/z* 560–568 centered at *m/z* 565 in a pattern consistent with the isotopic distribution for two tellurium atoms. The mass spectrum of 3 shows similar behavior with parent peaks centered at *m/z* 578 and the stepwise loss of six carbonyl groups.

Clusters 2–4 are further confirmed by single-crystal X-ray analysis. Basically, the core geometry of 2 or 3 displays a Te_2Fe_2 butterfly core with the $-(CH_2)_n-$ (n = 2, 3) bridging the two Te atoms. In 2 and 3, the Te–Te distances of 3.3562(9) and 3.4918(8) Å, respectively, are considered nonbonding.[13] The anion of 4 exhibits a Te_2Fe_2 tetrahedral geometry with one Te bonded to a Br atom. The Te–Te bond length in 4 is 2.732(2) Å, which shows a strong bonding interaction.[13] The ORTEP diagrams of 2–4 are given in Figures 1–3, respectively.

Discussion

Although the chemistry of the dianion of $S_2Fe_2(CO)_6$ has been extensively investigated,[14] the study on the tellurium analogue $Te_2Fe_2(CO)_6^{2-}$ is limited.[15] Cluster 1 can be easily obtained as a solid complex in high yield. The reaction of 1 with a series of dihaloalkanes shows that 1 is a good source of the dianion $Te_2Fe_2(CO)_6^{2-}$, and this availability allows further development of tellurium/iron chemistry.

Synthesis of 2–4. $Fe_2(CO)_6(\mu\text{-}Te(CH_2)_nTe)$ (n = 1; n = 2, **2**; n = 3, **3**) can be prepared from the reactions of 1 with suitable dihaloalkanes. It suggests that the reactivity of dihaloalkanes plays an important role in these reactions. It is likely that the alkylation of 1 with $Cl(CH_2)_2Br$ is kinetically more favorable than that with $Cl(CH_2)_2Cl$. The stronger electrophile $Br(CH_2)_2Br$ acts as an oxidizing agent to oxidize the dianion 1 to form the monoanion 4. We believe that the ease of the formation of 3 is probably ascribed to its relatively greater stability of the six membered ring $FeTe_2C_3$. The driving force to facilitate these reactions would be the greater basicity of the central Te_2Fe_2 fragment than that of the terminal Te_2Fe_3 moieties in the anion 1.

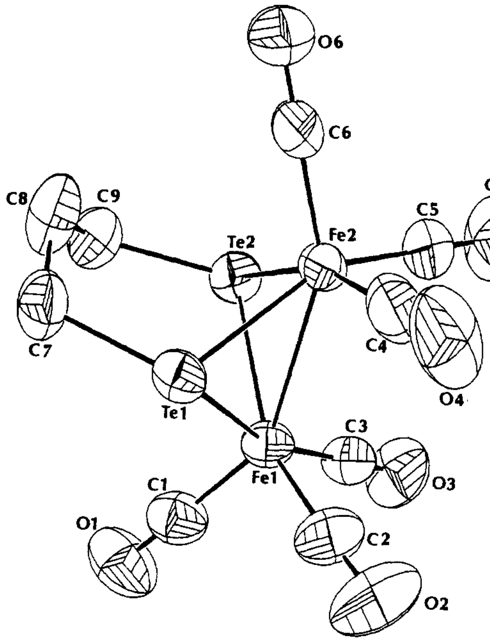

Figure 2. ORTEP diagram showing the structure and atom labeling for 3.

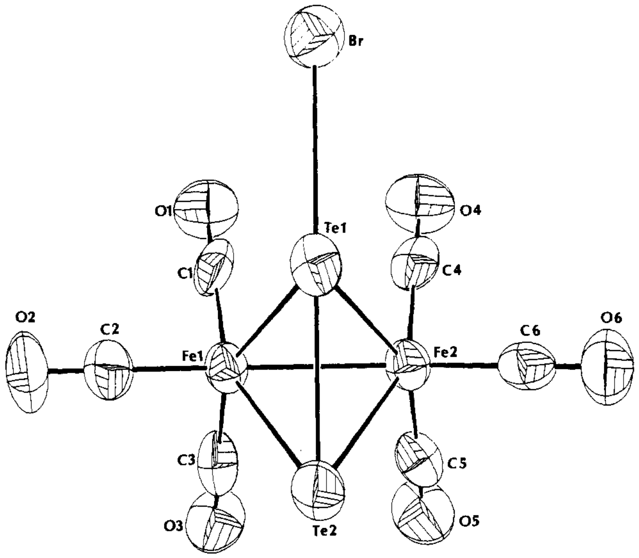

Figure 3. ORTEP diagram showing the structure and atom labeling for 4.

It is reported by Mathur and co-workers that $Fe(CO)_6$-(μ-$TeCH_2Te$) and 2 have been isolated from the reaction of $Te_2Fe_3(CO)_9$ with CH_2N_2.[9] Cluster 2 is a minor product from their reaction, and no structural data in the solid state are available. Our method described here provides a convenient route to 2, and X-ray structure determination is successful. Unlike the alkylation of $S_2Fe_2(CO)_6^{2-}$,[14] the

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usage of diiodoalkanes with 1 results in cluster fragmentation to form $Te_2Fe_3(CO)_9$.

Structures of 2–4. Cluster 2 is isomorphous with 3. The electron counting for 2 and 3 is conventional and obeys the EAN rules. The striking feature of complex 4 is the Te–Te–Br angle of 196° which indicates the presence of a stereochemically active lone pair at the four-coordinate Te(1). The coordination geometry of Te(1) resembles that found for $(RC_5H_4)MoFe(Te_2X)(CO)_5$.[16] Thus, the Te(1) atom is a "hypervalent" ten-electron center, which is seen in many tellurium containing metal clusters such as 1, $Cp_2Mo_2FeTe_2(CO)_7$,[13] $(CO)_6Fe_2(\mu_3\text{-}Te)_2Fe(CO)_3PPh_3$,[17] and $Fe_2(CO)_6(\mu\text{-}TeCH_2Te)$.[9]

It is of interest that the average Te–Fe–Te angle of 87.08(3)° in 3 is greater than that of 83.29(4)° in 2, and these angles are both larger than 75.4(1)° in $Fe_2(CO)_6(\mu\text{-}TeCH_2Te)$. It clearly indicates that the bond angle of Te–Fe–Te of the Te_2Fe_2 framework increases to accommodate the increased number of methylene groups. These angles are much greater than the corresponding angles in 4 (average 64.95(7)°), which is consistent with the opening of the $TeFe_2Te$ tetrahedron to possess the methylene groups.

The Fe–Fe and Te–Fe bond distances in clusters 2–4 are normal. The Te–Te distance of 3.3562(9) Å in 2 is less than that in 3 (3.4918(8) Å) and much greater than those in $Fe_2(CO)_6(\mu\text{-}TeCH_2Te)$ (3.114(1) Å and 4 (2.732(2) Å). The increased size of the bridging $-(CH_2)_n-$ is responsible for the increased Te–Te bond distance. In 4, the Te–Te bond length is 2.732(2) Å, which is quite short as compared to other tellurium containing complexes and indicative of a strong bonding.[13] The Te(1)–Br distance of 3.003(3) Å is greater than the sum of the covalent radii of Te (1.35 Å) and Br (1.14 Å) but significantly shorter than their van der Waals contact (i.e. 4.10 Å) and can be considered weak bonding.[18] In this point, 4 is intrinsically like a $Te_2Fe_2(CO)_6$ cluster, which may explain the high CO absorption frequencies for this compound. The angles about C(7) and C(8) in 2 are 115.7(6) and 115.6(6)°; and those about C(7), C(8), and C(9) in 3 are 117.7(4), 117.3(6), and 118.2(4)°, respectively. These angles deviate a bit from the perfect tetrahedral angle indicative of the sp^3-hybridzed carbons.

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Supplementary Material Available: Complete listings of crystallographic data, atomic positional parameters, bond distances and angles, and anisotropic thermal parameters (11 pages). Ordering information is given on any current masthead page.

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