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Notes

Facile Syntheses and Transformations of a Series of Tellurium−Iron Carbonyl Clusters: Crystal Structures of $[PhCH_2NMe_3]_2[Te_6Fe_8(CO)_{24}]$, $Fe_2(CO)_6(\mu\text{-}TeCHCl_2)_2$, and $Fe_2(CO)_6(\mu\text{-}TeCHPhTe)$

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Tellurium-rich metal compounds have attracted extensive attention since tellurides exhibit unusual structural and reactivity patterns and are potentially precursors for new solid-state materials.[1,2] As a result of recent work, $Te_2Fe_3(CO)_9$ and $Te_2Fe_2(CO)_6$ have been shown to be useful starting materials for cluster-building reactions.[3] Fewer anionic tellurium−iron carbonyl clusters are known.[4−7] The reaction of the oxyanion of tellurium(IV) with basic iron carbonyl solution followed by acidification was reported in 1958 to afford both $Te_2Fe_2(CO)_6$ and $Te_2Fe_3(CO)_9$.[8] Unfortunately, there has been little work reported on the anionic species in this reaction,[9] which plagued the understanding of chemical transformations of this system. In our research of mixed tellurium−iron carbonyl cluster system, we have recently communicated the isolation of an intermediate complex $[Te_6Fe_8(CO)_{24}]^{2-}$ (**I**) from Hieber's synthesis.[10] Here we describe the full details of the investigation of the formation of **I** and related clusters and its transformations and structural comparison to $Fe_2(CO)_6(\mu\text{-}TeCHCl_2)_2$ (**II**) and $Fe_2(CO)_6(\mu\text{-}TeCHPhTe)$ (**III**).

Experimental Section

All reactions were performed under an atmosphere of pure nitrogen by using standard Schlenk line techniques. Solvents were purified, dried, and distilled under nitrogen prior to use. $K_2TeO_3{\cdot}H_2O$ (Alfa), TeO_2 (Strem), $TeCl_4$ (Strem), and $Fe(CO)_5$ (Aldrich) were used as received. Infrared spectra were recorded on a Jasco 700 IR spectrometer using CaF_2 liquid cells. Mass spectra were obtained on a Finningan MATTSQ-46C mass spectrometer at 30 eV. ^1H NMR spectra were taken on a Jeol 400 (400 MHz) instrument.

Preparation of $[Te_6Fe_8(CO)_{24}]^{2-}$ (I). Method 1. To a solution of 2.0 g (7.4 mmol) of $K_2TeO_3{\cdot}H_2O$ in 50 mL of deionized H_2O was added a solution prepared from 1.33 mL (9.98 mmol) of $Fe(CO)_5$, 3.33 mL of 50% aqueous KOH, and 10 mL of MeOH. After being stirred for 2 h at room temperature, the solution was filtered and an aqueous solution of 1.86 g (10 mmol) of $[PhCH_2NMe_3]Cl$ added dropwise, precipitating the dark red product. This was collected by filtration, washed with H_2O, and dried under vacuum. Recrystallization from CH_2Cl_2 gave 2.60 g (1.19 mmol) of $[PhCH_2NMe_3]_2[Te_6Fe_8(CO)_{24}]$ ($[PhCH_2NMe_3]_2$[**I**]) (96% based on Te). IR (ν_{CO}, CH_2Cl_2) for $[PhCH_2NMe_3]_2$[**I**]: 2026 s, 2004 vs, 1956 m (br) cm^{-1}. Anal. Calcd (found) for $[PhCH_2NMe_3]_2$[**I**]: C, 24.12 (23.52); H, 1.47 (1.55); N, 1.28 (1.19). $[PhCH_2NMe_3]_2$[**I**] is soluble in THF and CH_2Cl_2 and sparingly soluble in $CHCl_3$ but insoluble in hexane.

Following a similar procedure, the $[PPN]_2$[**I**] and $[Et_4N]_2$[**I**] can also be isolated. $[PPN]_2$[**I**] is soluble in CH_2Cl_2, THF, and $CHCl_3$ and insoluble in hexane, and $[Et_4N]_2$[**I**] is soluble in CH_2Cl_2 and THF and sparingly soluble in $CHCl_3$ but insoluble in hexane.

Method 2. To a solution of 0.5 g (1.86 mmol) of $TeCl_4$ and 0.85 g (15.2 mmol) of KOH in 20 mL of MeOH was added 1.00 mL (7.6 mmol) of $Fe(CO)_5$. After being stirred for 3−4 h at room temperature, the solution was filtered and an aqueous solution of 0.80 g (3.81 mmol) of $[Et_4N]Br$ was added dropwise, precipitating the dark red product. This product was collected by filtration, washed with H_2O, dried under vacuum, and then extracted with several portions of diethyl ether to give 0.30 g (0.14 mmol) of $[Et_4N]_2[Te_6Fe_8(CO)_{24}]$ ($[Et_4N]_2$[**I**]) (45% based on Te), which was identified by its IR spectrum.

Method 3. To a mixture of 1.25 g (7.83 mmol) of TeO_2 in 1.2 g (21.4 mmol) of KOH was added 20 mL of MeOH. The mixed solution was stirred for 1 min, and 1.0 mL (7.61 mmol) of $Fe(CO)_5$ was then added. The mixed solution was stirred 3 h to give a reddish-brown solution. The solution was filtered, and an aqueous solution of 0.56 g (3.02 mmol) of $[PhCH_2NMe_3]Cl$ added dropwise, precipitating the dark brown product. This was collected by filtration, washed with H_2O, and dried under vacuum. Recrystallization by CH_2Cl_2/hexane gave 1.17 g (0.54 mmol) of $[PhCH_2NMe_3]_2[Te_6Fe_8(CO)_{24}]$ ($[PhCH_2NMe_3]_2$[**I**]) (56% based on $Fe(CO)_5$), which was identified by its IR spectrum.

Acidification of $[Te_6Fe_8(CO)_{24}]^{2-}$ (I). To a solution of 2.6 g (1.19 mmol) of $[PhCH_2NMe_3]_2$[**I**] in 60 mL of CH_2Cl_2 was cautiously added 6 M HCl in an ice bath. The resulting precipitate was filtered out, washed throughly with H_2O, and extracted into several portions of 20 mL of hexane. The extracts were chromatographed to give 1.00 g (1.48 mmol) of $Te_2Fe_3(CO)_9$ (41% based on Te) and very small amount of $Te_2Fe_2(CO)_6$.

Reduction of $Te_2Fe_3(CO)_9$ with $CoCp_2$. To a mixture of 0.5 g (0.74 mmol) of $Te_2Fe_3(CO)_9$ and 0.3 g (1.6 mmol) of $CoCp_2$ was added 50 mL of THF. The solution was allowed to stir at room temperature for 7 days. The infrared spectrum of the THF solution showed IR bands corresponding to $[Te_6Fe_8(CO)_{24}]^{2-}$ (**I**). The following workup gave 0.20 g (0.088 mmol) of $[CoCp_2]_2[Te_6Fe_8(CO)_{24}]$ ($[CoCp_2]_2$[**I**]) (35% based on Te).

Preparation of $Fe_2(CO)_6(\mu\text{-}TeCHCl_2)_2$ (II). To a sample of 0.5 g (0.16 mmol) of $[PPN]_2$[**I**] was added 50 mL of $CHCl_3$. The mixed solution was allowed to heat at 50−60 °C for 3 h. The orange-red solution was filtered and solvent removed under vacuum. The residue was extracted into hexane, and the hexane extracts were combined and chromatographed on a silica gel column using hexane as eluent. The first moving band was collected to give 0.11 g (0.157 mmol) of **II** (33% based on Te). IR (ν_{CO}, hexane): 2064 s, 2036 vs, 1996 s cm^{-1}. Anal. Calcd (found) for **II**: C, 13.67 (13.94); H, 0.29 (0.35). Mass (EI): $M^+ = 706$, $(M - nCO)^+ = 678, 650, 622, 594, 566, 538$ ($n = 1{-}6$), $(Te_2Fe_2CHCl_2)^+ = 455$, and $[Te_2Fe_2(CHCl_2)_2]^+ = 538$. ^1H NMR: δ 6.36 (s, 1H), δ 6.15 (s, 1H), Mp: 82 °C (dec).

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Table 1. Selected Crystallographic Data for $[PhCH_2NMe_3]_2[Te_6Fe_8(CO)_{24}]$ ($[PhCH_2NMe_3]_2$[**I**]), $Fe_2(CO)_6(\mu\text{-}TeCHCl_2)_2$ (**II**), and $Fe_2(CO)_6(\mu\text{-}TePhCHTe)$ (**III**)[a]

	$[PhCH_2NMe_3]_2$[**I**]	**II**	**III**
empirical formula	$Te_6Fe_8C_{44}H_{32}O_{24}N_2$	$Te_2Fe_2C_8O_6H_2Cl_4$	$Te_2Fe_2C_{13}O_6H_6$
fw	2185.12	702.80	625.07
cryst system	monoclinic	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	*Cc* (No. 9)	$P2_1/n$ (No. 14)
a, Å	20.694(7)	13.443(3)	8.254(3)
b, Å	14.649(4)	14.971(3)	22.432(8)
c, Å	22.813(7)	9.271(1)	9.078(2)
β, deg	101.45(3)	90.25(1)	95.01(3)
V, $Å^3$	6778(4)	1855(1)	1674(1)
Z	4	4	4
D(calc), Mg m^{-3}	2.290	2.123	2.480
abs coeff, mm^{-1}	4.28	5.26	5.19
T_{min}/T_{max}	0.50/1.00	0.82/1.00	0.60/1.00
residues:[b] *R*; R_w	0.050; 0.060	0.050; 0.056	0.072; 0.070

[a] All data are obtained from a Nonius (CAD-4) diffractometer with radiation (Mo Kα) of 0.7107 Å at 25 °C. [b] The functions minimized during least squares cycles were $R = \Sigma(F_o - F_c)/\Sigma F_o$, and $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2}$.

Preparation of $Fe_2(CO)_6(\mu\text{-}TeCHPhTe)$ (III). To a sample of 0.50 g (0.23 mmol) of $[PhCH_2NMe_3]_2$[**I**] in 50 mL of THF was added 0.5 mL (3.91 mmol) of $PhCHCl_2$. The solution was heated at 55 °C for 23 h to give an orange solution. The solution was filtered and solvent was removed under vacuum. The hexane extracts were chromatographed using hexane as eluent. The orange-band was collected to give 0.09 g (0.14 mmol) of **III** (20% based on Te). IR (ν_{CO}, hexane): 2056 s, 2020 vs, 1987 s cm^{-1}. Anal. Calcd (found) for **III**: C, 24.98 (24.62); H, 0.97 (0.91). Mass (EI): $M^+ = 630$, $(M - nCO)^+ = 602$, 574, 546, 518, 490, 462 (n = 1–6), and $(Te_2Fe_2CHPh)^+ = 462$. ^1H NMR: δ 4.02 (s, 1H), δ 7.44–7.63 (m, 5H), Mp: 136 °C (dec).

X-ray Structural Characterization of $[PhCH_2NMe_3]_2$[I], II, and III. A summary of selected crystallographic data for $[PhCH_2NMe_3]_2$[**I**], **II**, and **III** is given in Table 1. Data collection was carried out on a Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα 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,[11] and atomic scattering factors were taken from the *International Tables for X-ray Crystallography*.[12]

Reddish black crystals of $[PhCH_2NMe_3]_2$[**I**] suitable for X-ray analysis were grown from CH_2Cl_2 solution. A total of 4423 unique reflections were collected and corrected for absorption and decay. Systematic absences and intensity data indicated that the space group was centrosymmetric *C*2/*c* (No. 15). The structure of $[PhCH_2NMe_3]_2$[**I**] was solved by the heavy-atom method and refined by least-squares cycles and by fixed refinement for the two $[PhCH_2NMe_3]^+$ cations. All non-hydrogen atoms were refined with anisotropic thermal parameters. Full-matrix least-squares refinement of $[PhCH_2NMe_3]_2$[**I**] led to convergence with *R* = 5.0% and R_w = 6.0% for those reflections with $I > 2.0\sigma(I)$.

Orange-red crystals of **II** and **III** suitable for X-ray analysis were grown from a hexane solution. A total of 1622 and 2179 unique reflections were collected for **II** and **III**, respectively, and corrected for absorption and decay. The space group, *Cc* (No. 9), for **II** was indicated from the systematic absences and intensity statistics, and the space group, $P2_1/n$ (No. 14), for **III** was determined unambiguously from systematic absences. The structures of **II** and **III** were solved by direct methods which indicated the presence of Te and Fe atoms. The light atoms were found 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 **II** and **III** led to convergence with *R* = 5.0% and R_w = 5.6% and *R* = 7.2% and R_w = 7.0%, respectively, for those reflections with $I > 2.0\sigma(I)$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[PhCH_2NMe_3]_2[Te_6Fe_8(CO)_{24}]$ ($[PhCH_2NMe_3]_2$[**I**])

(A) Distances (Metal–Metal Bond Lengths)			
Te(1)–Te(1)′	3.267(2)	Te(1)–Fe(1)	2.552(3)
Te(1)–Fe(1)′	2.583(3)	Te(1)–Fe(2)	2.637(3)
Te(2)–Te(3)	3.123(2)	Te(2)–Fe(2)	2.633(3)
Te(2)–Fe(3)	2.563(3)	Te(2)–Fe(4)	2.564(3)
Te(3)–Fe(2)	2.639(3)	Te(3)–Fe(3)	2.572(3)
Te(3)–Fe(4)	2.569(3)	Fe(3)–Fe(4)	2.577(4)
Fe(1)–Fe(1)′	2.625(5)		
(B) Bond Angles			
Te(1)–Fe(1)–Te(1)′	79.02(8)	Te(2)–Fe(4)–Te(3)	74.96(8)
Te(1)–Fe(2)–Te(2)	162.92(11)	Te(1)–Fe(2)–Te(3)	91.08(8)
Te(2)–Fe(2)–Te(3)	72.67(7)	Te(2)–Fe(3)–Te(3)	74.94(9)

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $Fe_2(CO)_6(\mu\text{-}TeCHCl_2)_2$ (**II**)

(A) Distances			
Metal–Metal Bond Lengths			
Te(1)–Te(2)	3.382(2)	Te(1)–Fe(1)	2.517(3)
Te(1)–Fe(2)	2.522(3)	Te(2)–Fe(1)	2.530(4)
Te(2)–Fe(2)	2.550(4)	Fe(1)–Fe(2)	2.656(5)
Carbonyl Ranges			
Te–C	2.21(2)–2.24(2)	Fe–C	1.72(3)–1.85(3)
C–O	1.11(3)–1.22(3)	C–Cl	1.67(3)–1.77(3)
(B) Angles			
Te(2)–Te(1)–Fe(1)	48.10(8)	Te(2)–Te(1)–Fe(2)	48.54(9)
Fe(1)–Te(1)–Fe(2)	63.63(12)	Te(1)–Te(2)–Fe(1)	47.77(8)
Te(1)–Te(2)–Fe(2)	47.83(8)	Fe(1)–Te(2)–Fe(2)	63.05(11)
Te(1)–Fe(1)–Te(2)	84.13(11)	Te(1)–Fe(1)–Fe(2)	58.27(11)
Te(1)–Fe(1)–Fe(2)	58.27(11)	Te(2)–Fe(1)–Fe(2)	58.84(11)
Te(1)–Fe(2)–Te(2)	83.63(11)	Te(1)–Fe(2)–Fe(1)	58.11(10)
Te(2)–Fe(2)–Fe(1)	58.11(11)	Fe–C–O	168(3)–177.3(20)
Fe–Te–C	106.3(7)–109.6(7)		

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $Fe_2(CO)_6(\mu\text{-}TeCHPhTe)$ (**III**)

(A) Distances			
Metal–Metal Bond Lengths			
Te(1)–Te(2)	3.127(3)	Te(1)–Fe(1)	2.535(5)
Te(1)–Fe(2)	2.547(5)	Te(2)–Fe(1)	2.558(5)
Te(2)–Fe(2)	2.549(5)	Fe(1)–Fe(2)	2.585(6)
Carbonyl Ranges			
Te–C	2.16(3)–2.17(3)	Fe–C	1.75(4)–1.89(4)
C–O	1.06(4)–1.18(4)		
(B) Angles			
Te(2)–Te(1)–Fe(1)	52.47(12)	Te(2)–Te(1)–Fe(2)	52.17(12)
Fe(1)–Te(1)–Fe(2)	61.15(15)	Te(1)–Te(2)–Fe(1)	51.79(11)
Te(1)–Te(2)–Fe(2)	52.12(12)	Fe(1)–Te(2)–Fe(2)	60.81(15)
Te(1)–Fe(1)–Te(2)	75.74(14)	Te(1)–Fe(1)–Fe(2)	59.65(15)
Te(2)–Fe(1)–Fe(2)	59.41(15)	Te(1)–Fe(2)–Te(2)	75.70(14)
Te(1)–Fe(2)–Fe(1)	59.20(15)	Te(2)–Fe(2)–Fe(1)	59.78(15)
Te(1)–C(7)–Te(2)	92.5(11)	Fe–C–O	169(4)–179(3)
Te–C–C	115.1(19)–116.7(19)		

Selected bond distances and angles of $[PhCH_2NMe_3]_2$[**I**] are listed in Table 2, those of **II** are in Table 3, and those of **III** are included in Table 4. Additional crystallographic data are available as supplementary material.

Results

The novel complex $[Te_6Fe_8(CO)_{24}]^{2-}$ (**I**) can be isolated easily from the reaction $Fe(CO)_5$/KOH with 1 equiv or excess of K_2-

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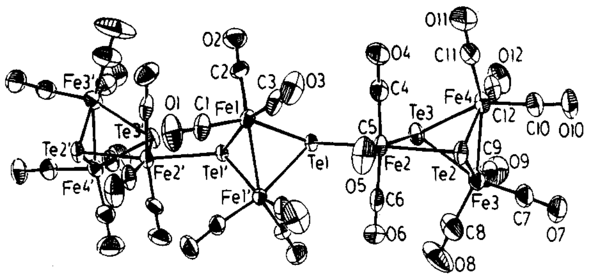

Figure 1. ORTEP diagram showing the structure and atom labeling for the dianion I.

TeO_3 in methanol solution. Alternatively, treatment of TeO_2/KOH with 1 equiv of $Fe(CO)_5$ in methanol affords the dianion I cleanly. The acidification of I forms the major product $Te_2Fe_3(CO)_9$ and the minor product $Te_2Fe_2(CO)_6$. Conversely, the reduction of $Te_2Fe_3(CO)_9$ with cobaltocene produces the dianion I. I is not stable in the reaction solutions and can be isolated as the $[PhCH_2NMe_3]^+$, $[Et_4N]^+$, and $[PPN]^+$ salts. These salts are quite stable in the solid state and can be used as good starting materials for further reactions. The infrared spectrum of the dianion I is composed of three major bands from 2026 to 1956 cm^{-1} indicative of the absorptions of terminal carbonyl groups. For a dianionic cluster, the absorption positions of I are quite high probably due to the delocalization of the charge over the large metal skeleton. A similar effect is also seen in the case of the cluster $[Te_{10}Fe_8(CO)_{20}]^{2-}$.[6]

The dianion I can be viewed as two $Te_2Fe_3(CO)_9$ clusters asymmetrically attached each to the two Te atoms of the anion $[Te_2Fe_2(CO)_6]^{2-}$. The ORTEP diagram of I is shown in Figure 1. The dianion is located on the crystallographic 2-fold axis which passes through the centers of Fe(1)−Fe(1)′ and Te(1)−Te(1)′, respectively. The average bond lengths for Te−Fe and Fe−Fe are 2.590 and 2.601 Å, respectively. It is noted that the Te(2)−Te(3) distance of 3.123(2) Å and Te(1)−Te(1)′ distance of 3.267(2) Å are indicative of the absence of direct Te−Te bonding; however, the long-range Te−Te interactions may be considered to be significant in this cluster.[13]

Unlike the reaction with refluxing CH_2Cl_2,[14] treatment of $[PPN]_2[I]$ in refluxing $CHCl_3$ forms the dialkyl complex, $Fe_2(CO)_6(\mu\text{-}TeCHCl_2)_2$ (**II**). Further reaction of I with $PhCHCl_2$ in THF forms a −TeCHPhTe− bridged iron cluster, $Fe_2(CO)_6(\mu\text{-}TeCHPhTe)$ (**III**). Clusters **II** and **III** are fully characterized by IR, ^1H NMR, and mass spectroscopic methods and further structurally characterized by X-ray analysis.

II shows a Te_2Fe_2 butterfly with each Te atom coordinated to one $CHCl_2$ group in which the butterfly dihedral angle is 103.5(1)° at the Fe−Fe crease. The $CHCl_2$ groups sit in the equatorial−axial positions of the Te_2Fe_2 butterfly structure. In **II**, the Te−Te distance of 3.382(2) Å is considered nonbonding. On the other hand, cluster **III** displays a Te_2Fe_2 butterfly geometry with the two Te atoms bridged by a CHPh group in which the Te−Te distance is 3.127(3) Å. The respective Fe−Fe distances in **II** and **III** are 2.656(5) and 2.585(6) Å, which are normal. The angles about C(7) atom in **III** are in the range of 92.5(1)−116.7(2)° indicative of a slightly distorted tetrahedral environment. The ORTEP diagrams of **II** and **III** are given in Figure 2 and 3, respectively.

Discussion

Formation of I and Related Clusters. The dianion I is isolated as an intermediate in Hieber's synthesis. The Te−Fe bond breakage and Te−Te and Fe−Fe bond formation of the dianion I account for the formation of $Te_2Fe_3(CO)_9$ and $Te_2Fe_2(CO)_6$ in Hieber's synthesis. Cluster I is an important anionic species in the Te−Fe−CO system and also can be obtained in the reduction of $Te_2Fe_3(CO)_9$ by cobaltocene. Alternatively, the synthesis of I can be accomplished by the reaction of TeO_2/KOH or $TeCl_4$/KOH with $Fe(CO)_5$ in MeOH solution. It is noted that the ratio of TeO_2/KOH to $Fe(CO)_5$ is a controlling factor in determining which product is produced from the reaction. The reaction of TeO_2/KOH with 1 equiv of $Fe(CO)_5$ in MeOH immediately forms the dianion I while treatment of TeO_2/KOH with 3 equiv of $Fe(CO)_5$ in MeOH leads to the formation of the tetrahedral complex $[TeFe_3(CO)_9]^{2-}$.

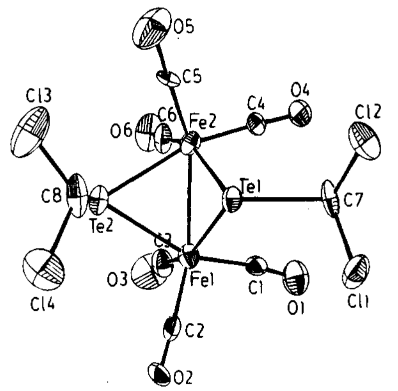

Figure 2. ORTEP diagram showing the structure and atom labeling for **II**.

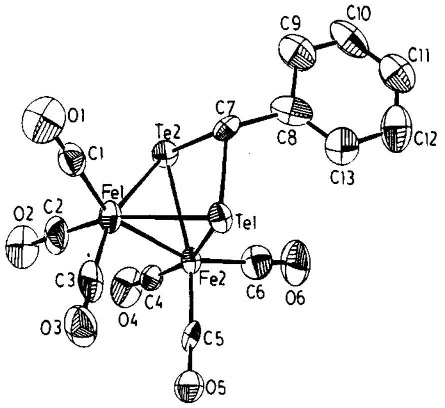

Figure 3. ORTEP diagram showing the structure and atom labeling for **III**.

The synthesis of $[TeFe_3(CO)_9]^{2-}$ from Te^{2-} and $Fe(CO)_5$ was recently reported.[15] $[TeFe_3(CO)_9]^{2-}$ was also reported to be prepared from the reaction of TeO_2 with 3 equiv of $Fe(CO)_5$/KOH in MeOH,[16] similar to the methodology we describe here. Surprisingly, we found that TeO_2 reacts very slowly with 1 equiv of $Fe(CO)_5$/KOH in MeOH to form the dianion I and an excess of KOH would increase the reaction rate. The Te−Fe−CO system is obviously very versatile, and subtle change of the reaction conditions may give rise to a different outcome. Detailed investigation into this issue is in progress.

Our previous study shows that cluster I can react readily with dihaloalkanes to form $-Te(CH_2)_nTe-$ bridged diiron complexes, $Fe_2(CO)_6(\mu\text{-}Te(CH_2)_nTe)$.[14] To study the extension of this usage, the reactions of I with geminal halides were investigated. The outcomes show that cluster I is a mild reducing reagent in these oxidative alkylations and can react with a wide range of organodihalides to form a series of organotellurium iron

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carbonyl clusters. In the reaction with $CHCl_3$, no $-TeCHClTe-$ bridged iron carbonyl complex is produced even under room temperature. The formation of dialkyl derivative **III** is probably attributed to the greater reactivity of $CHCl_3$. On the contrary, the reaction with the less reactive and bulky reagent $PhCHCl_2$ gives the $-CHPh-$ bridged $Te_2Fe_2(CO)_6$ complex in a similar fashion to that of the reaction with the mild reagent CH_2Cl_2.[14]

Structural Comparison of I–III. The Te(2)–Te(3) distance in **I** and the Te–Te length in **III** are 3.123(2) and 3.127(3) Å, respectively. These distances are long compared to 2.712 Å in Ph_2Te_2 for a typical single bond length[17] but are comparable to those found in $Cp_2Mo_2FeTe_2(CO)_7$ (3.142 Å),[13] $(CO)_6Fe_2(\mu_3\text{-}Te)_2Fe(CO)_3PPh_3$ (3.14 Å),[18] and $Fe_2(CO)_6(\mu\text{-}TeCH_2Te)$ (3.114 Å).[19] As for the bonding mode for the tellurium atoms in these clusters, the hypervalency of Te(2) and Te(3) in **I** and of the Te atoms in **III** may be suggested.

II is similar to the previously reported $Fe_2(CO)_6(TeMe)_2$.[7] The structural difference is that **II** adopts a butterfly geometry with an *anti*-conformation of $CHCl_2$ groups while $Fe_2(CO)_6(\mu\text{-}TeMe)_2$ has a *syn*-arrangement of methyl groups. The $Te-CHPh-Te$ bridging angle in **III** is 92.5(1)°, which is comparable to the corresponding angle of 92.1(4)° in $Fe_2(CO)_6(\mu\text{-}TeCH_2Te)$[19] but a bit smaller than the $S-CH_2-S$ angle of 94.6° reported for $Fe_2(CO)_6(\mu\text{-}SCH_2S)$.[20] In **I**, the Te(3)–Fe(4)–Te(2) and Te(3)–Fe(3)–Te(2) angles in the end Te_2Fe_2 skeletons average 74.95° and the corresponding angles in **III** have an average value of 75.7°. These angles are close to 75° found in $Fe_2(CO)_6(\mu\text{-}TeCH_2Te)$,[19] 75° in $(CO)_6Fe_2(\mu_3\text{-}Te)_2Fe(CO)_3PPh_3$,[18] and 79° in $Fe_2Te_2(CO)_6Ru_3(CO)_{11}$,[21] which is consistent with some degree of opening of the Te_2Fe_2 "tetrahedron" to accommodate the bridging groups.

Conclusion

The novel cluster $[Te_6Fe_8(CO)_{24}]^{2-}$ can be obtained in high yields from several facile methodologies. This cluster establishes interesting chemical transformations in the Te–Fe–CO system and is a useful reagent for the synthesis of a wide range of organotellurium iron carbonyl clusters.

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Supplementary Material Available: Complete listings of crystallographic data, atomic positional parameters, bond distances and angles, and anisotropic thermal parameters of clusters **I–III** (13 pages). Ordering information is given on any current masthead page.

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