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Reaction of the Tellurium-Capped Triiron Cluster $[TeFe_3(CO)_9]^{2-}$ with the Bifunctional Propargyl Bromide: Formation of a Series of Novel Organic Te−Fe−CO Complexes

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When $[TeFe_3(CO)_9]^{2-}$ was treated with 1 equiv of propargyl bromide in MeCN, the novel acyl complex $[Et_4N][(\mu_3\text{-Te})Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-C(O)C(H)CCH}_2)]$ ($[Et_4N]$[**1**]) was obtained. Cluster **1** can be viewed to consist of a $TeFe_3$ core which is linked by the novel allylcarbonyl ligand $C(O)CHCCH_2$ in a $\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3$ fashion. Further oxidation of cluster **1** occurs via organo ligand loss and bond rearrangement to give the oxidation product $Te_2Fe_3(CO)_9$. In addition, when cluster **1** was methylated with CF_3SO_3Me, the Fischer-type carbene complex $(\mu_3\text{-Te})Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-C(OMe)C(H)CCH}_2)$ (**2**) was afforded. When the ratio of reactants and reaction solvent was varied, the detailed reaction of $[TeFe_3(CO)_9]^{2-}$ with propargyl bromide could be further investigated. When $[TeFe_3(CO)_9]^{2-}$ was treated with excess propargyl bromide in MeCN, the two new butterfly clusters $Te_2Fe_2(CO)_6(CH{=}C{=}CH_2)_2$ (**3**) and $Te_2Fe_2(CO)_6(CH_2C{\equiv}CH)(CH{=}C{=}CH_2)$ (**4**) were obtained along with cluster **1**. While cluster **3** displays a Te_2Fe_2 metal core with two allenyl ligands attached to the tellurium atoms in anti positions, cluster **4** consists of a Te_2Fe_2 core with each tellurium atom coordinated to one allenyl or one propargyl ligand in an anti position. Further investigation of $[TeFe_3(CO)_9]^{2-}$ with propargyl bromide in a molar ratio of 1:2 or 1:4 in CH_2Cl_2 showed that the oxidation product $(\mu_3\text{-Te})Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-C(Me)}{=}\text{CH})$ (**5**) was afforded, in addition to the formation of **1**, **3**, and **4**. Cluster **5** can be viewed to be composed of a $TeFe_3$ core coordinated with the propyne ligand $C(Me){\equiv}CH$, which acts as a 4e donor. This paper describes the detailed reactions of $[TeFe_3(CO)_9]^{2-}$ with the bifunctional propargyl bromide in terms of the reaction solvents, the ratio of the reactants, and the chalcogen effect, and the reactivities and structural features of the resultant clusters with the novel organo moieties are systematically compared and discussed.

Introduction

While chalcogen-containing transition-metal carbonyl complexes have attracted much attention, their interaction with organic moieties has been much less explored.[1] Such studies could reveal valuable information regarding the selective anchoring process on metal surfaces that could lead to nanomaterials with controlled properties.[1,2] A previous study on chalcogen-containing iron complexes with organic fragments only involved the reactions of such complexes with alkyl or alkyl-like reagents.[3] Vahremkamp et al. reported a series of heteronuclear metal complexes starting from the mononuclear acetylide complexes $LnMC{\equiv}CR$,[4] and Wojcicki et al. have studied metal clusters containing C_3 fragments by use of the mononuclear propargyl complexes $LnMCH_2C{\equiv}CR$ or the allenyl complexes $LnMCHC{=}C{=}CRR'$ with other transition-metal carbonyls.[5,6]Some polynuclear carbonyl clusters with simple alkynes have also been studied.[7] Nevertheless, reports of the incorporation of main-group-element-bridged transition-

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metal carbonyl clusters with unsaturated hydrocarbon fragments are scarce.[1−7] Recently, we reported the first isolation of two rotational isomers of a Fischer-type carbene cluster which was afforded from the reaction of $[SeFe_3(CO)_9]^{2-}$ with the bifunctional propargyl bromide followed by careful methylation.[8] This successful isolation was thought to be attributable to the existence of a continuous unsaturated conjugation system due to the introduction of the propargyl fragment. However, another important issue arises as to whether the chalcogen atom might also play an important role in the stability of the resultant complexes containing the unsaturated C_3 moieties. With the aim of addressing this issue, we extended our study to the tellurium system and investigated the reactions of the tetrahedral triiron cluster $[TeFe_3(CO)_9]^{2-}$ with propargyl bromide and their subsequent related reactions. The formations of the resultant complexes are studied in terms of the effects of solvent and different ratios of the reactants, and the preferred geometries of these complexes are also discussed in terms of the chalcogen effect, the electronic influence, and the steric demands.

Experimental Section

All reactions were performed under an atmosphere of pure nitrogen using standard Schlenk techniques.[9] Solvents were purified, dried, and distilled under nitrogen prior to use. $HC\equiv CCH_2Br$ (Merck) and CF_3SO_3Me (Aldrich) were used as received. $[Et_4N]_2[TeFe_3(CO)_9]$[3b,10] and $[Cu(MeCN)_4][BF_4]$[11] were prepared by the published methods. Infrared spectra were recorded on a Perkin-Elmer Paragon 500 IR spectrometer as solutions in CaF_2 cells. The ^1H and ^{13}C NMR spectra were taken on a JEOL 400 instrument at 399.78 and 100.53 MHz, respectively. Elemental analyses of C, H, and N were performed on a Perkin-Elmer 2400 analyzer at the NSC Regional Instrumental Center at National Taiwan University, Taipei, Taiwan. Calculations were performed using the DISCOVER Molecular Simulation Program, Version 2.95; the input file for DISCOVER was generated by INSIGHT II.

Reaction of $[Et_4N]_2[TeFe_3(CO)_9]$ with $HC\equiv CCH_2Br$ (∼1:1) in MeCN: Synthesis of $[Et_4N][(\mu_3\text{-Te})Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}C(O)C(H)CCH_2)]$ ($[Et_4N][1]$). To a solution of 1.08 g (1.34 mmol) of $[Et_4N]_2[TeFe_3(CO)_9]$ in 30 mL of MeCN was added 0.14 mL (1.58 mmol) of $HC\equiv CCH_2Br$. The resulting solution was stirred at 50 °C for 1 h to give a yellowish brown solution, which was filtered, and the solvent was removed under vacuum. The precipitate was washed with deionized water several times, extracted with CH_2Cl_2, and then recrystallized with hexanes/CH_2Cl_2 to give 0.61 g (0.82 mmol) of $[Et_4N][(\mu_3\text{-Te})Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}C(O)C(H)CCH_2)]$ ($[Et_4N][\mathbf{1}]$; 61% based on $[Et_4N]_2[TeFe_3(CO)_9]$). IR (ν_{CO}, CH_2Cl_2): 2051 w, 2022 vs, 1989 s, 1954 s, 1940 m, 1914 w, 1557 w cm^{-1}. Negative ion ESI-MS: m/z 614.8. Anal. Calcd for $[Et_4N][\mathbf{1}]$: C, 33.88; H, 3.11; N, 1.88. Found: C, 33.43; H, 2.73; N, 1.94. ^1H NMR (400 MHz, DMSO-d_6, 295 K): δ 3.70 (1 s, CH), 2.77, 2.59 (2 s, CH_2) (chemical shifts not given for $[Et_4N]^+$). ^{13}C NMR (100 MHz, DMSO-d_6, 295 K): δ 259.8 (FeC=O), 215.9, 214.5, 214.3, 214.1, 211.0, 208.3 (FeCO), 107.8 (CHCCH$_2$), 86.8 (CH), 56.9 (CH_2) (chemical shifts not given for $[Et_4N]^+$). $[Et_4N][\mathbf{1}]$ is soluble in ether, CH_2Cl_2, DMSO, THF, and MeCN but insoluble in hexanes. Crystals of $[Et_4N][\mathbf{1}]$ suitable for X-ray analysis were grown from hexanes/CH_2Cl_2 at −20 °C.

Reaction of $[Et_4N][1]$ with $[Cu(MeCN)_4][BF_4]$. To a mixture of 0.56 g (0.75 mmol) of $[Et_4N][\mathbf{1}]$ and 0.71 g (2.26 mmol) of $[Cu(MeCN)_4][BF_4]$ was added 30 mL of CH_2Cl_2. The reaction mixture was stirred in an ice−water bath for 132 h. The solution was filtered and solvent removed under vacuum. The residue was extracted with hexanes to give 0.07 g (0.10 mmol) of a brownish sample of $Te_2Fe_3(CO)_9$[12] (14% based on $[Et_4N][\mathbf{1}]$).

Reaction of $[Et_4N][1]$ with CF_3SO_3Me. To a solution of 0.52 g (0.70 mmol) of $[Et_4N][\mathbf{1}]$ in 30 mL of CH_2Cl_2 was added 0.12 mL (1.06 mmol) of CF_3SO_3Me in an ice−water bath. The resulting solution was stirred in the ice−water bath for 150 min to give a yellowish green solution, which was filtered, and the solvent was removed under vacuum. The residue was extracted with 20 mL of Et_2O. The Et_2O extract was redissolved in 2 mL of CH_2Cl_2 and 3 mL of hexanes, and this solution was chromatographed with hexanes using a Chromotron to give the first band of 0.06 g (0.09 mmol) of the known complex $Te_2Fe_3(CO)_9$ (13% based on $[Et_4N][\mathbf{1}]$) and then chromatographed with CH_2Cl_2/hexanes (1:3) to give a second red band of 0.10 g (0.16 mmol) of $(\mu_3\text{-Te})Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}C(OMe)C(H)CCH_2)$ (**2**; 23% based on $[Et_4N][\mathbf{1}]$). IR (ν_{CO}, CH_2Cl_2): 2073 w, 2048 vs, 2012 vs, 1995 s, 1978 m, 1954 w cm^{-1}. Negative ion ESI-MS: m/z 631.9. Mp: 140 °C dec. Anal. Calcd for **2**: C, 26.72; H, 0.96. Found: C, 26.65; H, 0.90. ^1H NMR (400 MHz, DMSO-d_6, 299 K): δ 5.81 (s, CH), 5.02, 4.75 (2 s, CH_2), 3.55 (s, OMe) (chemical shifts not given for $[Et_4N]^+$). ^{13}C NMR (100 MHz, DMSO-d_6, 297 K): δ 222.1, 219.4, 212.0 (FeCO), 209.0 (Fe=C), 139.1 (CHCCH$_2$), 103.2 (CH_2), 71.3 (CH), 59.8 (OCH_3) (chemical shifts not given for $[Et_4N]^+$). Complex **2** is soluble in hexanes, ether, CH_2Cl_2, THF, DMSO, and MeCN.

Reaction of $[Et_4N]_2[TeFe_3(CO)_9]$ with $HC\equiv CCH_2Br$ (1:16) in MeCN. Similar to the procedures for the 1:1 reaction in MeCN, the reaction solution was stirred at ambient temperature for 38 h. The reaction products were recrystallized with hexanes/CH_2Cl_2 to give the solid and the filtrate. The solvent of the filtrate was removed, which was further extracted with 20 mL of hexanes and redissolved in 1 mL of CH_2Cl_2 and 3 mL of hexanes. The solution was then chromatographed with hexanes to give the first band of $Te_2Fe_2(CO)_6(CH{=}C{=}CH_2)_2$ (**3**; 22% based on $[Et_4N]_2[TeFe_3(CO)_9]$). IR (ν_{CO}, CH_2Cl_2): 2058 m, 2025 s, 1900 s, 1976 w (sh), 1950 vw, 1932 w cm^{-1}. Mp: 87 °C dec. Anal. Calcd for **3**: C, 23.51; H, 0.99. Found: C, 23.76; H, 0.85. ^1H NMR (400 MHz, $CDCl_3$, 295 K): δ 6.12 (t, =CH, J = 6.84 Hz), 5.17 (t, =CH, J = 6.35 Hz), 4.91 (d, =CH_2, J = 6.84 Hz), 4.85 (d, =CH_2, J = 6.35 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 302 K): δ 211.6 ($=C_{(8)}=$), 209.1 ($=C_{(11)}=$), 210.6 (FeCO), 74.1 ($=C_{(12)}H_2$), 73.2 ($=C_{(9)}H_2$), 56.0 ($-C_{(10)}H=$), 35.3 ($-C_{(7)}H=$). **3** is soluble in hexanes, ether, CH_2Cl_2, DMSO, THF, and MeCN. The second band was collected to give $Te_2Fe_2(CO)_6(CH_2C\equiv CH)(CH{=}C{=}CH_2)$ (**4**; 13% based on $[Et_4N]_2[TeFe_3(CO)_9]$). IR (ν_{CO}, CH_2Cl_2): 2059 m, 2026 s, 1991 m, 1931 m cm^{-1}. Anal. Calcd for **4**: C, 23.51; H, 0.99. Found: C, 23.73; H, 0.95. Mp: 79.5 °C dec. ^1H NMR (400 MHz, DMSO-d_6, 295 K): δ 5.20 (t, CH, J = 6.35 Hz), 4.87 (d, CH_2, J = 6.35 Hz), 3.30 (d, CH_2, J = 2.92 Hz), 2.42 (t, $\equiv$CH, J = 2.92 Hz). ^{13}C NMR (100 MHz, DMSO-d_6, 302 K): δ 210.5 (FeCO), −7.7 ($-CH_2$), 82.6 ($-C\equiv$), 74.2 ($\equiv$CH), 72.9 ($=CH_2$), 211.8 ($=C=$), 35.4 ($=$CH). **4** is soluble in hexanes, ether, CH_2Cl_2, DMSO, THF, and MeCN. The solid was further purified as before to yield $[Et_4N][\mathbf{1}]$ (26% based on $[Et_4N]_2[TeFe_3(CO)_9]$).

Reaction of $[Et_4N]_2[TeFe_3(CO)_9]$ with $HC\equiv CCH_2Br$ (1:2) in CH_2Cl_2. Similar to the procedures for the 1:16 reaction

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Table 1. Crystallographic Data for [Et_4N][(μ_3-Te)$Fe_3(CO)_9$(μ_3-η^1:η^1:η^3-C(O)C(H)CCH_2)] ([Et_4N][1]), (μ_3-Te)$Fe_3(CO)_9$(μ_3-η^1:η^1:η^3-C(OMe)C(H)CCH_2) (2), $Te_2Fe_2(CO)_6(CH{=}C{=}CH_2)_2$ (3), $Te_2Fe_2(CO)_6(CH_2C{\equiv}CH)(CH{=}C{=}CH_2)$ (4), and (μ_3-Te)$Fe_3(CO)_9$(μ_3-η^1:η^2:η^1-C(Me)=CH) (5)

	[Et_4N][**1**]	**2**	**3**	**4**	**5**
empirical formula	$C_{21}H_{23}Fe_3NO_{10}Te$	$C_{14}H_6Fe_3O_{10}Te$	$C_{12}H_6Fe_2O_6Te_2$	$C_{12}H_6Fe_2O_6Te_2$	$C_{12}H_4Fe_3O_9Te$
fw	744.55	629.33	613.06	613.06	587.29
cryst syst	monoclinic	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
cryst dimens, mm	0.25 × 0.15 × 0.14	0.51 × 0.48 × 0.31	0.40 × 0.30 × 0.30	0.30 × 0.25 × 0.15	0.25 × 0.22 × 0.18
a, Å	11.556(5)	13.136(3)	9.265(2)	9.356(4)	7.666(3)
b, Å	19.835(5)	9.136(1)	9.811(1)	9.717(2)	9.014(4)
c, Å	12.722(2)	16.714(2)	10.375(2)	10.232(4)	13.373(2)
α, deg			71.00(1)	70.88(2)	98.75(2)
β, deg	110.01(3)	111.26(2)	75.08(1)	75.52(3)	99.92(2)
γ, deg			88.01(1)	87.04(3)	102.20(3)
V, Å^3	2740 (2)	1869.4(5)	860.4(2)	850.5(5)	872.5(5)
Z	4	4	2	2	2
D(calcd), g cm^{-3}	1.805	2.236	2.366	2.394	2.236
μ, mm^{-1}	2.66	3.88	5.03	5.09	4.14
diffractometer	Nonius (CAD4)	Nonius (CAD4)	Nonius (CAD4)	Nonius (CAD4)	Nonius (CAD4)
radiation (λ), Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
temp, K	298	298	298	298	298
θ range for data collecn, deg	1.5−24.93	1.5−24.94	2.15−22.42	1.5−24.92	1.5−24.92
T_{min}/T_{max}	0.49/0.56	0.33/0.43	0.24/0.31	0.22/0.34	0.36/0.41
no. of indep reflns	3104 ($I > 2.5\sigma(I)$)	2750 ($I > 2.5\sigma(I)$)	2240 ($I > 2\ \sigma(I)$)	2723 ($I > 2.5\sigma(I)$)	2671 ($I > 2.5\sigma(I)$)
$R^a/R_w{}^a$	0.028/0.029 ($I > 2.5\sigma(I)$)	0.021/0.22 ($I > 2.5\sigma(I)$)		0.024/0.027 ($I > 2.5\sigma(I)$)	0.023/0.027 ($I > 2.5\sigma(I)$)
$R^a/R_w{}^a$(all data)	0.074/0.076	0.030/0.032		0.028/0.029	0.030/0.033
R1^b/wR2^b			0.034/0.096 ($I > 2\sigma(I)$)		
R1^b/wR2^b(all data)			0.036/0.097		

[a] The functions minimized during least-squares cycles were $R = \sum|F_o - F_c|/\sum F_o$ and $R_w = [\sum w(F_o - F_c)^2/\sum w(F_o)^2]^{1/2}$. [b] The functions minimized during least-squares cycles were $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$.

in MeCN, the reaction products were recrystallized in hexanes/CH_2Cl_2 to give a solid and a filtrate. The filtrate was chromatographed with hexanes to give the first band of (μ_3-Te)$Fe_3(CO)_9$(μ_3-η^1:η^2:η^1-C(Me)=CH) (**5**; 5% based on [Et_4N]$_2$[$TeFe_3(CO)_9$]). IR (ν_{CO}, CH_2Cl_2): 2080 w, 2070 w, 2049 s, 2033 s, 2008 s, 1999 m cm^{-1}. Negative ion ESI-MS: m/z 589.6. Anal. Calcd for **5**: C, 24.54; H, 0.69. Found: C, 24.61; H, 0.68. ^{1}H NMR (400 MHz, DMSO-d_6, 297 K): δ 10.07 (s, CH), 3.24 (s, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6, 302 K): δ 220.2 (−C=), 213.0 (FeCO), 187.9 (=CH), 45.9 (CH_3). The second band was collected to give **3** (4% based on [Et_4N]$_2$[$TeFe_3(CO)_9$]), and the third band gave a sample of **4** (1% based on [Et_4N]$_2$[$TeFe_3(CO)_9$]). The solid was purified as before to give ([Et_4N][**1**]) (20% based on [Et_4N]$_2$[$TeFe_3(CO)_9$]).

X-ray Structural Characterization of [Et_4N][1] and 2−5. The selected crystallographic data for [Et_4N][**1**] and **2**−**5** are given in Table 1. All crystals were mounted on glass fibers with epoxy cement. Data collection for [Et_4N][**1**] and **2**−**5** was carried out on a Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation at 298 K in the 2θ range 2.0−50° using θ−2θ scans, and an empirical absorption correction by azimuthal (ψ) scans was applied.[13] The structures of [Et_4N][**1**], **2**, **4**, and **5** were solved by direct methods and refined with NRCC-SDP-VAX packages,[14]and the structure of **3** was refined with SHELXL-97.[15] All of the non-hydrogen atoms were refined with anisotropic temperature factors. The selected distances and angles for [Et_4N][**1**] and **2**−**5** are listed in Table 2. Additional crystallographic data as CIF files are available as Supporting Information.

Results

Synthesis of [Et_4N][(μ_3-Te)$Fe_3(CO)_9$(μ_3-η^1:η^1:η^3-C(O)C(H)CCH_2)] ([Et_4N][1]) and Its Subsequent Reactions with CF_3SO_3Me and [Cu(MeCN)$_4$]BF_4. When [Et_4N]$_2$[$TeFe_3(CO)_9$] was treated with 1 equiv of propargyl bromide in MeCN at 50 °C for 1 h, the novel acyl complex [Et_4N][(μ_3-Te)$Fe_3(CO)_9$(μ_3-η^1:η^1:η^3-C(O)-C(H)CCH_2)] ([Et_4N][**1**]) was obtained. The X-ray analysis (Figure 1) shows that the anion **1** consists of three Fe centers with one Fe−Fe bond, in which three Fe atoms are capped on opposite sides by a Te atom and by the allylcarbonyl ligand C(O)$CHCCH_2$ in a μ_3-η^1:η^1:η^3 fashion. The infrared spectrum of [Et_4N]-[**1**] shows absorptions characteristic of terminal carbonyl ligands in the region 2051−1914 cm^{-1}. The existence of the acyl group was further identified by an IR absorption at 1557 cm^{-1}, which can be compared to other acyl absorptions in related complexes.[5,16,17] Further, the presence of an acyl CO in **1** is spectroscopically indicated by a ^{13}C NMR resonance at 259.8 ppm. The ^{13}C−^{1}H COSY measurements unambiguously showed that the ^{1}H NMR resonances at δ 3.70 and 2.77, 2.59 correspond to the absorptions of CH and the CH_2 of the allyl group, respectively. In addition, elemental analysis and negative ion mass methods confirm the formula of cluster **1** as [(μ_3-Te)$Fe_3(CO)_9$(μ_3-η^1:η^1:η^3-C(O)C(H)CCH_2)]$^-$.

The subsequent reaction of cluster **1** with [Cu(MeCN)$_4$]-BF_4 in CH_2Cl_2 gave the oxidation product $Te_2Fe_3(CO)_9$. The cluster $Te_2Fe_3(CO)_9$ was previously characterized to have a square-pyramidal Te_2Fe_3 core with each iron coordinated to three carbonyl groups.[12] The formation of this product was proposed to occur via organo ligand

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[Et_4N][(\mu_3\text{-}Te)Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}C(O)C(H)CCH_2)$ ($[Et_4N][$1**$]$), $(\mu_3\text{-}Te)Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}C(OMe)C(H)CCH_2)$ (2), $Te_2Fe_2(CO)_6(CH{=}C{=}CH_2)_2$ (3), $Te_2Fe_2(CO)_6(CH_2C{\equiv}CH)(CH{=}C{=}CH_2)$ (4), and $(\mu_3\text{-}Te)Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C(Me){=}CH)$ (5)**

Compound $[Et_4N][$**1**$]$			
Te(1)−Fe(1)	2.632(1)	Te(1)−Fe(2)	2.493(1)
Te(1)−Fe(3)	2.515(1)	Fe(2)−Fe(3)	2.717(1)
Fe(3)−C(13)	2.038(5)	C(10)−C(11)	1.403(8)
C(11)−C(12)	1.428(8)	C(12)−C(13)	1.496(8)
Fe(1)−Te(1)−Fe(2)	91.71(4)	Fe(1)−Te(1)−Fe(3)	100.22(3)
Fe(2)−Te(1)−Fe(3)	65.71(3)	Fe(1)−C(11)−C(10)	72.0(3)
Fe(1)−C(11)−C(12)	69.9(3)	Fe(3)−C(13)−O(10)	123.3(4)
Fe(3)−C(13)−C(12)	118.7(4)		
Compound **2**			
Te−Fe(1)	2.6232(8)	Te−Fe(2)	2.4735(7)
Te−Fe(3)	2.5680(7)	Fe(2)−Fe(3)	2.7491(8)
Fe(3)−C(13)	1.944(4)	C(10)−C(11)	1.413(6)
C(11)−C(12)	1.419(5)	C(12)−C(13)	1.445(6)
O(10)−C(13)	1.324(5)		
Fe(1)−Te−Fe(2)	92.01(2)	Fe(1)−Te−Fe(3)	96.34(3)
Fe(2)−Te−Fe(3)	66.06(2)	Fe(1)−C(11)−C(10)	71.4(2)
Fe(1)−C(11)−C(12)	70.0(2)	Fe(3)−C(13)−O(10)	129.0(3)
Fe(3)−C(13)−C(12)	123.2(3)		
Compound **3**			
Te(1)−Fe(1)	2.5522(9)	Te(1)−Fe(2)	2.5341(9)
Te(2)−Fe(1)	2.5363(9)	Te(2)−Fe(2)	2.538(1)
Fe(1)−Fe(2)	2.620(1)	Te(1)−C(7)	2.138(7)
Te(2)−C(10)	2.128(7)	C(7)−C(8)	1.29(1)
C(8)−C(9)	1.30(1)	C(10)−C(11)	1.30(1)
C(11)−C(12)	1.28(1)		
Fe(1)−Te(1)−Fe(2)	62.02(3)	Fe(1)−Te(2)−Fe(2)	62.18(3)
Fe(1)−Te(1)−C(7)	105.0(2)	Fe(2)−Te(1)−C(7)	109.6(2)
Fe(1)−Te(2)−C(10)	107.5(2)	Fe(2)−Te(2)−C(10)	105.1(2)
Te(1)−C(7)−C(8)	123.4(5)	Te(2)−C(10)−C(11)	119.0(5)
C(7)−C(8)−C(9)	178.7(9)	C(10)−C(11)−C(12)	177.1(7)
Compound **4**			
Te(1)−Fe(1)	2.556(1)	Te(1)−Fe(2)	2.5347(9)
Te(2)−Fe(1)	2.536(1)	Te(2)−Fe(2)	2.528(1)
Fe(1)−Fe(2)	2.630(2)	Te(1)−C(7)	2.133(6)
Te(2)−C(10)	2.189(6)	C(7)−C(8)	1.296(9)
C(8)−C(9)	1.28(1)	C(10)−C(11)	1.42(1)
C(11)−C(12)	1.17(1)		
Fe(1)−Te(1)−Fe(2)	62.20(3)	Fe(1)−Te(2)−Fe(2)	62.57(4)
Fe(1)−Te(1)−C(7)	107.5(2)	Fe(2)−Te(1)−C(7)	110.1(2)
Fe(1)−Te(2)−C(10)	107.7(2)	Fe(2)−Te(2)−C(10)	107.1(2)
Te(1)−C(7)−C(8)	124.3(5)	Te(2)−C(10)−C(11)	111.3(4)
C(7)−C(8)−C(9)	179.3(7)	C(10)−C(11)−C(12)	178.9(7)
Compound **5**			
Te−Fe(1)	2.5798(9)	Te−Fe(2)	2.485(1)
Te−Fe(3)	2.5067(9)	Fe(1)−Fe(2)	2.672(1)
Fe(2)−Fe(3)	2.644(2)	Fe(1)−C(10)	2.109(4)
Fe(1)−C(11)	2.155(4)	Fe(2)−C(10)	1.952(5)
Fe(3)−C(11)	1.976(5)	C(10)−C(11)	1.381(7)
C(11)−C(12)	1.517(6)		
Fe(1)−Te−Fe(2)	63.65(3)	Fe(1)−Te−Fe(3)	62.62(3)
Fe(2)−Te−Fe(3)	102.05(4)	Fe(2)−Fe(1)−C(10)	46.4(1)
Fe(3)−Fe(1)−C(11)	47.3(1)	Fe(2)−C(10)−C(11)	133.2(3)
Fe(3)−C(11)−C(10)	125.9(3)	Fe(3)−C(11)−C(12)	118.4(3)
C(10)−Fe(1)−C(11)	37.8(2)	C(10)− C(11)−C(12)	115.7(4)

loss and bond rearrangement. However, careful methylation of cluster **1** with CF_3SO_3Me in CH_2Cl_2 formed the Fischer-type carbene complex $(\mu_3\text{-}Te)Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}C(OMe)C(H)CCH_2)$ (**2**) (Scheme 1). The X-ray analysis shows that cluster **2** is structurally related to the anion of **1**, except that the oxygen of the acyl group is methylated. Cluster **2** is further characterized by spectroscopic methods and elemental analysis. By the $^{13}C-^{1}H$ COSY measurements of **2**, the ^1H NMR resonances at δ 5.81, 3.55, and 4.75, 5.02 can be assigned to CH, OMe, and CH_2, respectively.

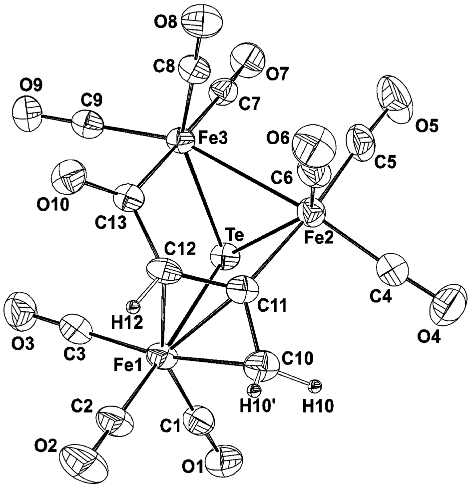

Figure 1. ORTEP diagram showing the structure and atom labeling for the anion **1**.

Reactions of $[Et_4N]_2[TeFe_3(CO)_9]$ with $HC{\equiv}CCH_2Br$. The varied ratios of $[Et_4N]_2[TeFe_3(CO)_9]$ with $HC{\equiv}CCH_2Br$ were investigated in MeCN or CH_2Cl_2, and the results are summarized in Scheme 2. As mentioned above, the 1:1 reaction in MeCN led to the formation of $[Et_4N][$**1**$]$ as the major product. If the reaction was conducted in a molar ratio of 1:16 in MeCN, the two butterfly clusters $Te_2Fe_2(CO)_6(CH{=}C{=}CH_2)_2$ (**3**) and $Te_2Fe_2(CO)_6(CH_2C{\equiv}CH)(CH{=}C{=}CH_2)$ (**4**) were produced in approximately equal amounts along with cluster **1**. In addition, when the reaction proceeded in MeCN for a prolonged period of time, cluster **4** could transform to cluster **3,** which may involve a 1,3-hydrogen shift of the propargyl ligand. A similar transformation of a propargyl ligand to an allenyl ligand was also seen in the literature.[18]

In contrast to those in MeCN, the reactions of $[Et_4N]_2[TeFe_3(CO)_9]$ with $HC{\equiv}CCH_2Br$ proceeded slowly and differently in CH_2Cl_2. When the reaction was performed in a molar ratio of 1:2 in CH_2Cl_2, the new neutral cluster $(\mu_3\text{-}Te)Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C(Me){=}CH)$ (**5**) was produced along with clusters **1**, **3**, and **4**. As the ratio is changed to 1:4 in CH_2Cl_2, the yield of cluster **5** decreased, accompanied by increased yields of **3** and **4**, indicative of the decreased stability of **5** compared with that of **3** and **4** under an excess of propargyl bromide in CH_2Cl_2. The reactions of $[Et_4N]_2[TeFe_3(CO)_9]$ with $HC{\equiv}CCH_2Br$ are summarized in Scheme 2. In addition, it is noted that cluster **1** could not transform to clusters **3**−**5** upon addition of propargyl bromide in either MeCN or CH_2Cl_2. This result indicates that the formation of clusters **3**−**5** may occur via other reactive intermediates rather than via cluster **1**.

Clusters **3**−**5** were fully characterized by spectroscopic methods and single-crystal X-ray analysis. The ^1H NMR spectrum of **3** gives triplet absorptions at δ 6.12 and 5.17, corresponding to those of the CH moieties of the two allenyl groups, and doublet reso-

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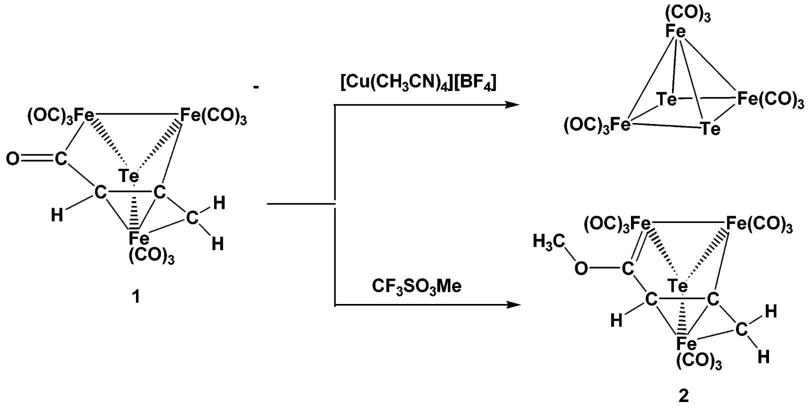
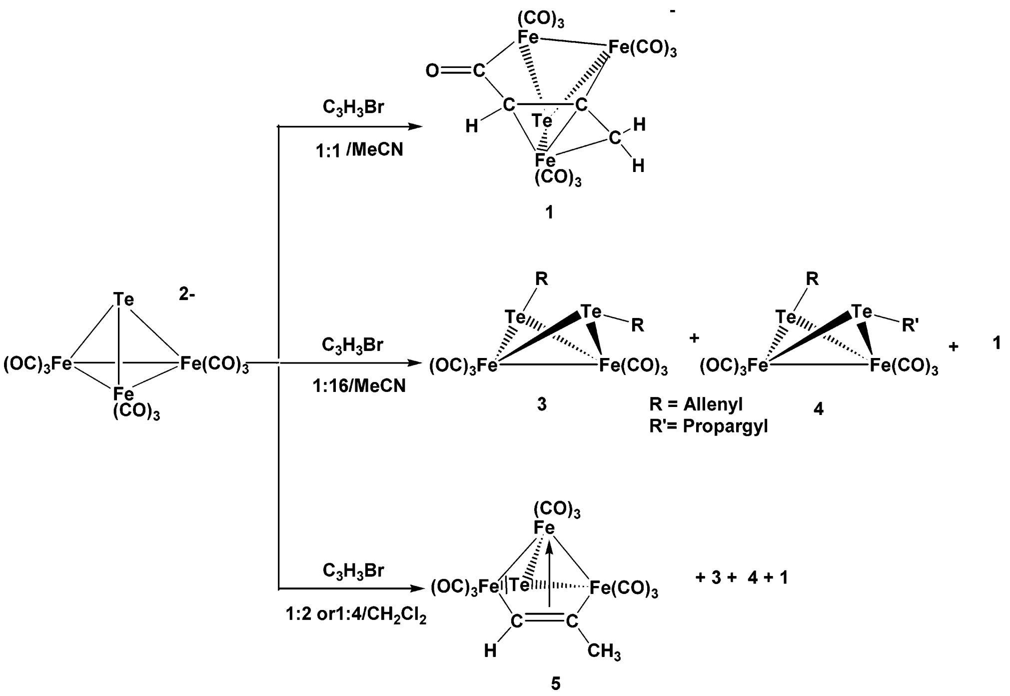
(18) Keng, R.-S.; Lin, Y.-C. *Organometallics* **1990**, *9*, 289 and references therein.

Scheme 1



Scheme 2



nances at δ 4.91 and 4.85, assignable to those of the CH_2 moieties of the two allenyl groups. The ^1H NMR spectrum of **4** shows resonances at δ 5.20 and 4.87, due to those of the CH and CH_2 for the allenyl ligand, and absorptions at δ 3.30 and 2.42, assignable to those of the CH_2 and CH moieties for the propargyl group, in which the values are also comparable to those reported in the literature.[18] In addition, the ^1H NMR spectrum of **5** gives absorptions at δ 10.07 and 3.24, corresponding to those of CH and CH_3 for the propyne ligand, respectively.

Structures of [Et$_4$N][1] and 2. The structures of [Et$_4$N][**1**] and **2** are depicted in Figures 1 and 2; selected bond lengths and angles are given in Table 2. The X-ray analyses show that clusters **1** and **2** each consist of three Fe centers with one Fe–Fe bond, in which three Fe atoms are capped on opposite sides by a Te atom and by an allylcarbonyl ligand C(O)CHCCH$_2$ or by a C(OMe)C(H)CCH$_2$ moiety, respectively, in a μ_3-η^1:η^1:η^3 fashion. In terms of electron counting, both the C(O)CHCCH$_2$ and C(OMe)C(H)CCH$_2$ ligands act as 5e donors and the apical Te atom contributes 4e to the bonding, which gives a total of 52e for the anion **1** or cluster **2**, respectively, consistent with one Fe–Fe bond in the Fe$_3$ cluster.

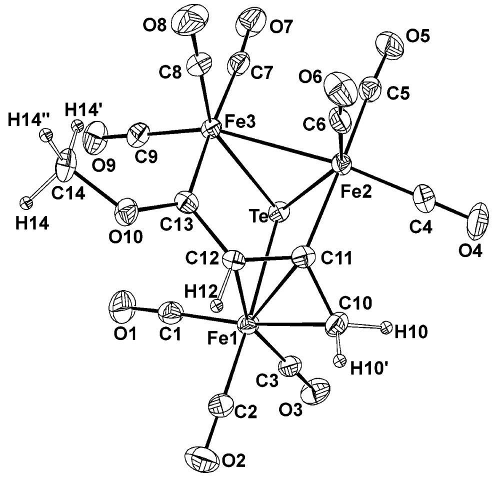


Figure 2. ORTEP diagram showing the structure and atom labeling for **2**.

The π-allyl complexes are well-known; however, those containing α-allylcarbonyl ligands are rare.[5,17,19,20] To

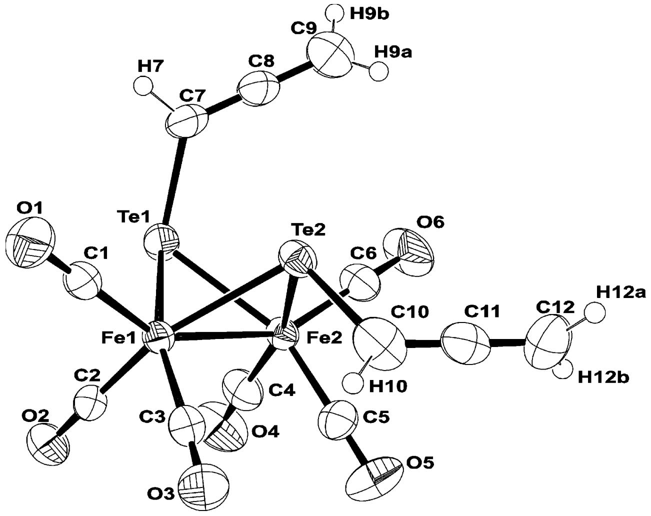


Figure 3. ORTEP diagram showing the structure and atom labeling for **3**.

the best of our knowledge, this type of μ_3-η^1:η^1:η^3-allylcarbonyl bonding mode is unprecedented before our study.[8] In **1**, the bond distances of C−C bonds in the allyl ligand are 1.403(8) and 1.428(8) Å, indicative of the double-bond character,[21] and are close to those (1.401(9) and 1.419(8) Å) in the related selenium complex $[Et_4N][(\mu_3\text{-}Se)Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}C(O)C(H)CCH_2)]$.[8] Complex **2** shows the continuous conjugated double-bonding character in the O−C$_{carbene}$, C$_{carbene}$-Fe, and C$_{carbene}$−allyl bonds. Like the Fischer-type carbene complexes, **2** has a C$_{carbene}$−O bond distance of 1.324(5) Å, comparable to the typical C−O distances (1.29−1.35 Å) in terminally coordinated alkoxycarbene complexes.[22] Further, the bond length of Fe−C$_{carbene}$ in **2** is 1.944(4) Å, which is similar to those (1.924(5) and 1.936(4) Å) in the isomers of $(\mu_3\text{-}Se)Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}C(OMe)C(H)CCH_2)$[8] but longer than that (1.856(5) Å) in the cluster carbene $Fe_3(\mu_3\text{-}NPh)_2(CO)_8\{C(OEt)Ph\}$.[23] In addition, the C$_{carbene}$−CH$_{allyl}$ distance (1.445(6) Å) in **2** is indicative of double-bond character as well.[21]

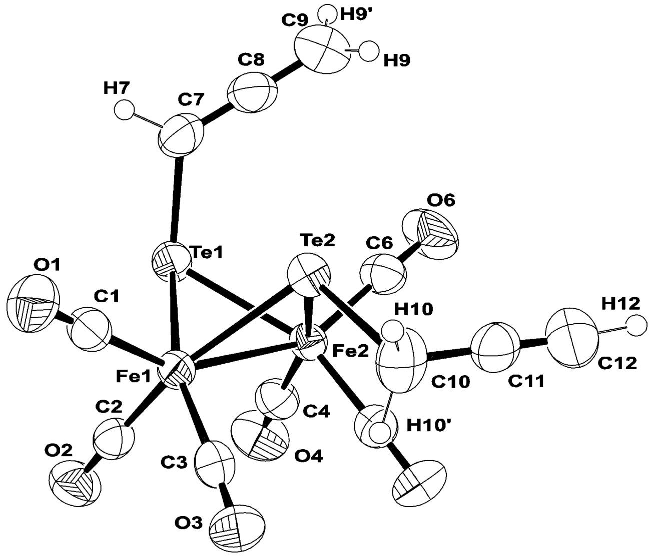


Figure 4. ORTEP diagram showing the structure and atom labeling for **4**.

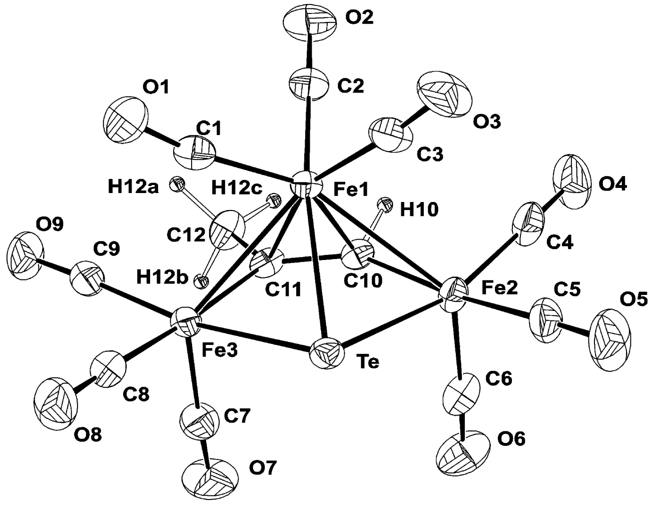


Figure 5. ORTEP diagram showing the structure and atom labeling for **5**.

Structures of 3−5. The structures of **3**−**5** are depicted in Figures 3−5; selected bond lengths and angles are listed in Table 2. Clusters **3** and **4** each display a butterfly geometry with the wingtips linked with the C_3 fragments. The metal core of cluster **3** contains a Te_2Fe_2 butterfly geometry with the wingtips of Te atoms bonded to two allenyl groups in the axial−equatorial positions, in which the butterfly dihedral angle is 101.85(5)° at the Fe−Fe crease. In **3**, the bond distances of 1.29(1) and 1.30(1) Å in the C−C bonds of the allenyl group in the axial position are comparable to those (1.30(1) and 1.28(1) Å) of the allenyl group in the equatorial position, which are characteristic of double bonding in the C−C bonds.[18] The C−C−C bond angles of the two allenyl ligands are 178.7(9) and 177.1(7)°, respectively, close to a linear arrangement.

On the other hand, the metal core of cluster **4** contains a Te_2Fe_2 butterfly geometry with the wingtips of the Te atoms connected to the allenyl and propargyl ligands, in which the former occupies an axial position and the latter an equatorial position. The dihedral angle of the Te_2Fe_2 butterfly is 102.35(3)° at the Fe−Fe crease. In **4**, while the bond distances of C−C bonds in the allenyl group are 1.296(9) and 1.28(1) Å, those in the propargyl ligand are 1.42(1) and 1.17(1) Å. In addition, the C−C−C bond angles of the allenyl and propargyl ligands are 179.3(7) and 178.9(7)°, respectively, which are in agreement with a linear carbon−carbon backbone. The C−C bond distances in the allenyl and propargyl moieties are consistent with those reported in $CpW(CO)_3CH_2C{\equiv}CH$ and $CpW(CO)_3CH{=}C{=}CH_2$.[19]

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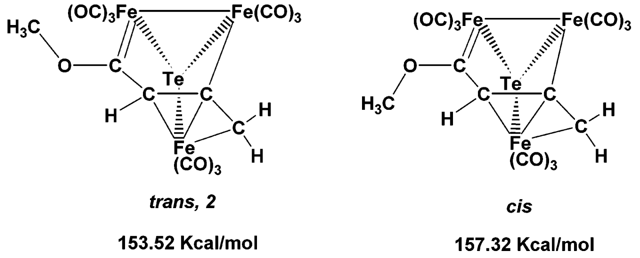
Chart 1



Cluster **5** consists of three Fe centers with two Fe−Fe bonds, in which three Fe atoms are capped on opposite sides by a Te atom and by the propyne ligand $HCCCH_3$ in a μ_3-η^1:η^2:η^1 fashion. In terms of electron counting, the $HCCCH_3$ ligand acts as a 4e donor and the capping Te atom contributes 4e in bonding, which gives a total of 50e for complex **5**, consistent with two Fe−Fe bonds in this Fe_3 cluster.

Discussion

Formation and Reactivities of [Et$_4$N][1]. The formation of complex **1** can be viewed to result from the nucleophilic attack of $[TeFe_3(CO)_9]^{2-}$ onto the propargyl bromide, followed by two Fe−Fe bond breakages and a CO insertion, in which the allylcarbonyl ligand donates its 3e to one iron center and 1e each to the other two iron atoms. Complex **1** is a CO insertion product, which can be supported by the fact that the yield of **1** was significantly increased (61% to 79%) if the reaction was conducted under a CO atmosphere.

When complex **1** was treated with $[Cu(MeCN)_4]BF_4$, severe bond breakage and formation occur to give the neutral product $Te_2Fe_3(CO)_9$. This indicates that the organic moiety of complex **1** was fragile and susceptible to oxidants. Since **1** is an acyl complex, **1** can be methylated to give the Fischer-type carbene cluster **2** when carefully methylated with CF_3SO_3Me. Cluster **2** is isolated in the trans form in the solid state, and the cis product is not obtained under our conditions, due to the greater stability of the trans form (Chart 1). This is in contrast to the related Se system, where the cis and trans forms are both isolable at room temperature due to greater rotational energy.[8] The INSIGHT II calculation showed that the total energy of cluster **2** (trans form) is 153.52 kcal/mol and that of the cis form is 157.32 kcal/mol, explaining the quick isomerization of these two forms in solution at room temperature and the successful isolation of cluster **2** in the trans form in the solid state at low temperature. The results suggest that the tellurium Fischer carbene complex should have a higher degree of free rotation about the $O-C_{carbene}$ bond compared with the corresponding selenium complex. This phenomenon could be rationalized by the better metallic character of the tellurium atom vs the selenium atom, which induces less electron demand in the $Fe-C_{carbene}$ bond than in the Se carbene case.

Due to the different degrees of ionization of $HC{\equiv}CCH_2Br$ in organic solvents, it was found that the reactions of $[Et_4N]_2[TeFe_3(CO)_9]$ with $HC{\equiv}CCH_2Br$ proceeded differently in different solvents. The reaction of $[Et_4N]_2[TeFe_3(CO)_9]$ with $HC{\equiv}CCH_2Br$ in MeCN basically produced clusters **1**, **3**, and **4**, depending on the different ratios of the reactants. However, apart from **1**, the reactions in CH_2Cl_2 gave low yields of clusters **3**−**5**. Cluster **5** possesses the propyne ligand $CHCCH_3$, which was a reduced product from propargyl bromide. Clusters **3**−**5** were proposed to result from cluster **1** with $HC{\equiv}CCH_2Br$. However, independent experiments showed that cluster **1** could not give rise to clusters **3**−**5** upon the reactions with $HC{\equiv}CCH_2Br$, suggesting that they are generated via the different reaction pathways. To rationalize the solvent effect on the reactions of $[Et_4N]_2[TeFe_3(CO)_9]$ with $HC{\equiv}CCH_2Br$, it is concluded that the better degree of ionization of $HC{\equiv}CCH_2Br$ in the polar solvent MeCN can facilitate the nucleophilic attack of $[TeFe_3(CO)_9]^{2-}$ on the propargyl bromide, whereas the poor degree of ionization of $HC{\equiv}CCH_2Br$ in CH_2Cl_2 makes $HC{\equiv}CCH_2Br$ a weak electrophile and probably also a proton donor.

Table 3. Average Bond Distances (Å) of [Et$_4$N][(μ_3-Te)Fe$_3$(CO)$_9$(μ_3-η^1:η^1:η^3-C(O)C(H)CCH$_2$) ([Et$_4$N][1]), (μ_3-Te)Fe$_3$(CO)$_9$(μ_3-η^1:η^1:η^3-C(OMe)C(H)CCH$_2$) (2), Te$_2$Fe$_2$(CO)$_6$(CH=C=CH$_2$)$_2$ (3), Te$_2$Fe$_2$(CO)$_6$(CH$_2$C≡CH)(CH=C=CH$_2$) (4), (μ_3-Te)Fe$_3$(CO)$_9$(μ_3-η^1:η^2:η^1-C(Me)=CH) (5), and Related Complexes

complex	Te−Fe, Å	Fe−Fe, Å	ref
$[Et_4N][(\mu_3\text{-}Te)Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}C(O)C(H)CCH_2)$ ([Et$_4$N][**1**])	2.547	2.717(1)	*a*
$(\mu_3\text{-}Te)Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}C(OMe)C(H)CCH_2)$ (**2**)	2.555	2.7491(8)	*a*
$Te_2Fe_2(CO)_6(CH{=}C{=}CH_2)_2$ (**3**)	2.540	2.620(1)	*a*
$Te_2Fe_2(CO)_6(CH_2C{\equiv}CH)(CH{=}C{=}CH_2)$ (**4**)	2.539	2.630(2)	*a*
$(\mu_3\text{-}Te)Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C(Me){=}CH)$ (**5**)	2.524	2.658	*a*
$[PhCH_2NMe_3]_2[Te_6Fe_8(CO)_{24}]$	2.590	2.601	24
$Fe_2(CO)_6(TeCHCl_2)_2$	2.530	2.656(5)	3c
$Fe_2(CO)_6(\mu\text{-}TeCHPhTe)$	2.547	2.585(6)	3c
$[(\mu_3\text{-}PhTe)Fe_2(CO)_6]_2(\mu\text{-}Te{-}Te\text{-}\mu)$	2.536	2.61	25
$Fe_2(CO)_6(\mu\text{-}TeMe)_2$	2.550	2.634(5)	26
$Fe_2(CO)_6[\mu\text{-}TeCH(CH_3)Te]_2$	2.533	2.606(1)	27
$\{Fe(CO)_3[\mu\text{-}TeRe(CO)_5]\}_2$	2.577	2.629	28
$[Et_4N][Cl]\cdot 2[Fe_2(CO)_6Te_2]$	2.543	2.645	29
$[(\mu\text{-}CH_3Te)Fe_2(CO)_6]_2[\mu\text{-}Te(CH_2)Te\text{-}\mu]$	2.553	2.613	30
$[PPh_4]_2[Fe_5Te_4(CO)_{14}]$	2.605	2.592(4)	31

[a] This work.

Structural Features of [Et$_4$N][1] and 2−5. The anionic cluster **1** and the neutral cluster **2** are structurally related, except that the oxygen atom of the acyl group of **2** is methylated. Clusters **3** and **4** exhibit a Te_2Fe_2-based butterfly geometry. Theoretically, the two allenyl groups of cluster **3** may have three configurations, which are in the axial−axial, axial−equatorial, and equatorial−equatorial positions. However, in practice, only cluster **3** (axial−equatorial isomer) is isolated and observed. A similar situation is also observed in the case of **4**, where the allenyl and propargyl groups are in the axial−equatorial positions. The preferred orientation of the C_3 ligands in the axial−equatorial positions should be attributable to the minimized steric repulsion and the effective crystal packing.

The average Te−Fe and Fe−Fe distances in clusters **1**−**5** and related complexes are given in Table 3.

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Basically, the Te–Fe distances in clusters **1**–**5** are in good agreement with those in related Te–Fe clusters. The average Te–Fe distances of **1** (2.547 Å) and **2** (2.555 Å) are close, despite the negative charge of **1**. The Te–Fe distances in clusters **3** (2.540 Å) and **4** (2.539 Å) are almost equal, indicative of the small effect of the organic ligands on the Te_2Fe_2 butterfly core. The average Fe–Fe distances of **1**–**5** are also comparable to those in the related clusters. Like the Te–Fe lengths, the Fe–Fe distance in **1** is comparable to that of **2**. Again, the Fe–Fe bond distances of **3** and **4** are almost the same, due to the similar Te_2Fe_2 butterfly core geometries.

Summary

In summary, a new series of organic Te–Fe–CO clusters has been synthesized from the reactions of the tellurium-capped triiron cluster $[TeFe_3(CO)_9]^{2-}$ with propargyl bromide and their related reactions. These organo-bridged complexes have been fully characterized by spectroscopic methods, and their structural features are systematically compared. The preferred geometries of the Fischer-type cluster carbene and the Te_2Fe_2-based organic complexes are discussed in terms of the chalcogen atom effect, the electronic influence, and the steric demands.

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Supporting Information Available: X-ray crystallographic files in CIF format for $[Et_4N][\mathbf{1}]$ and **2**–**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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