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Formation of Novel Tellurium-Containing Anions [(μ-RTe)(μ-CO)Fe$_2$(CO)$_6^-$] and Synthesis of Fe/Te Clusters (μ-RTe)(μ-σ,π-PhC=CH$_2$)Fe$_2$(CO)$_6$, (μ-RTe)$_2$Fe$_2$(CO)$_6$, and [(μ-RTe)Fe$_2$(CO)$_6$]$_2$(μ-Te−Te-μ). X-ray Crystal Structure of [(μ-PhTe)Fe$_2$(CO)$_6$]$_2$(μ-Te−Te-μ)

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A series of lithium salts of the anions [(μ-RTe)(μ-CO)Fe$_2$(CO)$_6^-$] (R = *n*-Bu, Ph, *o*-MeC$_6$H$_4$, *p*-MeC$_6$H$_4$) were prepared by reaction of organolithium reagents with elemental tellurium, followed by treatment of the intermediates RTeLi with Fe$_3$(CO)$_{12}$ in THF at room temperature. Further treatment of the lithium salt [(μ-RTe)(μ-CO)Fe$_2$(CO)$_6^-$]Li$^+$ (R = *n*-Bu) in situ with PhC≡CH at room temperature yielded Fe$_2$Te$_2$ and Fe$_2$Te clusters (μ-*n*-BuTe)$_2$Fe$_2$(CO)$_6$ (**1**) and (μ-*n*-BuTe)(μ-σ,π-PhC=CH$_2$)Fe$_2$(CO)$_6$ (**2**), whereas the lithium salts [(μ-RTe)(μ-CO)Fe$_2$(CO)$_6^-$]Li$^+$ (R = *n*-Bu, Ph, *o*-MeC$_6$H$_4$, *p*-MeC$_6$H$_4$) were treated in situ with acid chlorides, such as MeC(O)Cl and *p*-MeC$_6$H$_4$SO$_2$Cl, to afford Fe$_2$Te$_2$ clusters (μ-RTe)$_2$Fe$_2$(CO)$_6$ (R = *n*-Bu (**1**), Ph (**4**), *o*-MeC$_6$H$_4$ (**6**), *p*-MeC$_6$H$_4$ (**8**) and double Fe$_2$Te$_2$ clusters [(μ-RTe)Fe$_2$(CO)$_6$]$_2$(μ-Te−Te-μ) (R = *n*-Bu (**3**), Ph (**5**), *o*-MeC$_6$H$_4$ (**7**), *p*-MeC$_6$H$_4$ (**9**)). In addition, the new single clusters, except 1, were separated into ae and ee (where a = axial and e = equatorial) isomers and characterized individually, whereas the new double clusters were isolated and characterized mostly as isomer mixtures. Possible pathways for the formation of such clusters have been proposed, and the crystal structure of the double cluster **5** was determined by X-ray diffraction analysis.

Introduction

Since the first preparations of the anions [(μ-RS)(μ-CO)Fe$_2$(CO)$_6^-$][1] and [(μ-RSe)(μ-CO)Fe$_2$(CO)$_6^-$],[2] the chemical reactivities concerning such types of anions have been intensively studied and widely used in the synthesis of novel Fe/S and Fe/Se cluster complexes.[1−4] However, up to now, tellurium analogs of those anions, i.e., [(μ-RTe)(μ-CO)Fe$_2$(CO)$_6^-$], have not been reported in the literature, although the element Te is in the same group with S and Se in the periodic table. One might ask if the Te analogs could be made by similar procedures and if they would have chemical behavior similar to that of [(μ-RE)(μ-CO)Fe$_2$(CO)$_6^-$] (E = S, Se). In this paper we will answer some of these questions by describing the preparation of the anions [(μ-RTe)(μ-CO)Fe$_2$(CO)$_6^-$], as well as their reactions with some electrophiles to give a series of Fe/Te cluster complexes.

Results and Discussion

Tellurols, RTeH, in contrast to REH (E = S, Se), are not commercially available and their preparation is more difficult. However, their derived salts, RTeM (M = Li, MgX), can be readily prepared by the reaction of elemental Te with organolithium or Grignard reagents.[5] Although the anions [(μ-RE)(μ-CO)Fe$_2$(CO)$_6^-$] (E = S, Se) can be prepared by both the Fe$_3$(CO)$_{12}$/Et$_3$N/REH (E = S, Se)[1,2] and Fe$_3$(CO)$_{12}$/REM (M = Li, MgX) methods,[3b,4d,h] the practical preparation of their Te analogs, [(μ-RTe)(μ-CO)Fe$_2$(CO)$_6^-$], is restricted to the latter method. Tellurol salts, RTeLi (R = *n*-Bu, Ph, *o*-MeC$_6$H$_4$, *p*-MeC$_6$H$_4$), prepared from the corresponding lithium reagents and tellurium powder in THF, react with Fe$_3$(CO)$_{12}$ at room temperature to give the corresponding lithium salts of the expected anions [(μ-RTe)(μ-CO)Fe$_2$(CO)$_6^-$] (R = *n*-Bu, Ph, *o*-MeC$_6$H$_4$, *p*-MeC$_6$H$_4$, the salts are denoted as ZLi) (eq 1).

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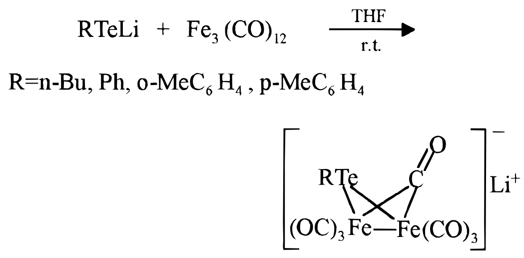
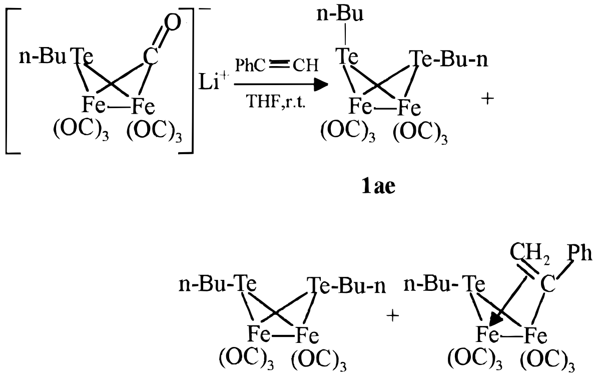


(1)

ZLi

It is noteworthy that during the course of the reactions a gas (CO) was continuously evolved until no green $Fe_3(CO)_{12}$ remained. This observation also was made in the case of reactions of RELi (E = S, Se) with $Fe_3(CO)_{12}$.[3b] The formation of ZLi was further demonstrated by IR spectroscopy. For example, the IR spectrum of the anion Z (R = Ph), i.e., $[(\mu\text{-PhTe})(\mu\text{-CO})Fe_2(CO)_6{}^-]$, in THF showed a μ-CO absorption band at 1745 cm^{-1}, which is very close to those of its analogs $[(\mu\text{-EtS})(\mu\text{-CO})Fe_2(CO)_6{}^-]$[1] and $[(\mu\text{-PhSe})(\mu\text{-CO})Fe_2(CO)_6{}^-]$[4f] at 1743 and 1740 cm^{-1}, respectively.

The lithium salts ZLi, similar to the salts of the anions $[(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6{}^-]$ (E = S, Se), are quite air sensitive and thermally unstable, so it is best to carry out their reactions in situ. When an electrophile phenylacetylene was added to a THF solution of ZLi (*R* = *n*-Bu) and the mixture was stirred at room temperature for 4 h, TLC showed two major products were formed, and from the reaction mixture a single Fe_2Te_2 cluster **1** and a single Fe_2Te cluster **2** could be isolated (eq 2).



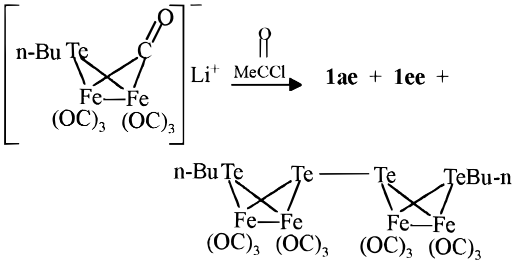
1ae

1ee **2**

(2)

The formation of new clusters **1** and **2** is not surprising since the corresponding reactions with $[(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6{}^-]Et_3NH^+$ (E = S, Se) gave the same types of products.[3g,4f] However, it should be noted (i) that the very complicated ^1H NMR patterns of the butyl groups indicated that product **1** exists as a mixture of two isomers **1ae** and **1ee** (where a = axial and e = equatorrial). For the former two alkyl groups are attached to the two Te atoms, respectively, by an axial and equatorial bond, whereas for the latter both are attached to the two Te atoms by equatorial bonds. (ii) For **2**, the *n*-butyl group is most likely attached to the Te atom by an equatorial bond and the two protons on the C=C double bond are both located on the β-carbon atom, since the ^1H NMR spectrum of the α-CH_2 of the *n*-butyl group showed one triplet at 2.87 ppm and the two protons exhibited two doublets at 2.07 and 3.55 ppm with J = 3.6 Hz, respectively. That there are two protons on the β-carbon implies that anion Z (*R* = *n*-Bu), as an iron-centered nucleophile, attacked at the α-carbon atom of PhC≡CH to give a β-carbanion intermediate. This intermediate would then displace the bridging CO by coordination of its C=C double bond, followed by abstraction of one proton obviously from PhC≡CH to give product **2**. This proposed pathway for the formation of **2** is shown in Scheme 1 and is similar to that proposed for reactions of $[(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6{}^-]$ with acetylenes.[3g,4f]

In order to further compare the chemical behavior of anions Z with that of $[(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6{}^-]$ (E = S, Se), the reaction of ZLi (*R* = *n*-Bu) with MeC(O)Cl was carried out. A single cluster **1**, as a mixture of two isomers **1ae** and **1ee**, and a double Fe_2Te_2 cluster $[(\mu\text{-}n\text{-BuTe})Fe_2(CO)_6]_2(\mu\text{-Te}-\text{Te-}\mu)$ (**3**) were formed in this reaction (eq 3).



(3)

3

It was reported previously that the reaction of $[(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6{}^-]$ with MeC(O)Cl produced $(\mu\text{-RS})_2Fe_2(CO)_6$ and μ-acyl derivatives,[4b] whereas the reaction of $[(\mu\text{-RSe})(\mu\text{-CO})Fe_2(CO)_6{}^-]$ with MeC(O)Cl gave only $(\mu\text{-RSe})_2Fe_2(CO)_6$ as isolable products,[4f] and in neither case were the analogs of cluster **3**, namely $[(\mu\text{-RE})Fe_2(CO)_6]_2$ $(\mu\text{-E-E-}\mu)$ (E = S, Se), formed. In order to know if the formation of such double clusters $[(\mu\text{-RTe})Fe_2(CO)_6]_2(\mu\text{-Te}-\text{Te-}\mu)$ is general, we carried out further the reactions of the lithium salts ZLi (R = Ph, *o*-MeC_6H_4, *p*-MeC_6H_4) with MeC(O)Cl. The results showed that the same type of double clusters **5**, **7**, and **9** were obtained along with single clusters **4**, **6**, and **8** (Scheme 2).

In contrast to the single cluster **1**, the single clusters **4**, **6**, and **8** can be separated into ae and ee isomers by TLC (although **4** was previously prepared by another route,[6] it was not separated into such two isomers). These isomers have been individually characterized by elemental analysis, IR and ^1H NMR spectroscopies, and MS. In the ^1H NMR spectra of isomers **4ae** and **4ee**, the phenyl groups all showed one complicated multiplet with a different shape and δ value. For isomers **6ae** and **6ee**, the ^1H NMR spectra of the eight protons of the two *ortho*-substituted benzene rings also showed a complicated multiplet with a different shape and δ value. In addition, the ^1H NMR spectrum of **6ae** showed one singlet at 2.50 ppm assigned to its two methyl groups on the substituted benzene rings bound to Te atoms by an equatorial bond and an axial bond, respectively, whereas that of **6ee** exhibited one singlet at 2.55 ppm attributed to its two methyl groups on the substituted benzene rings bound to Te atoms by an equatorial bond. That only one resonance was observed

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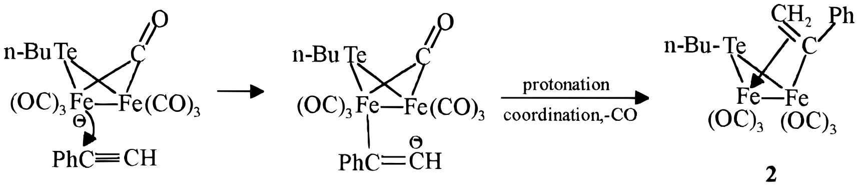
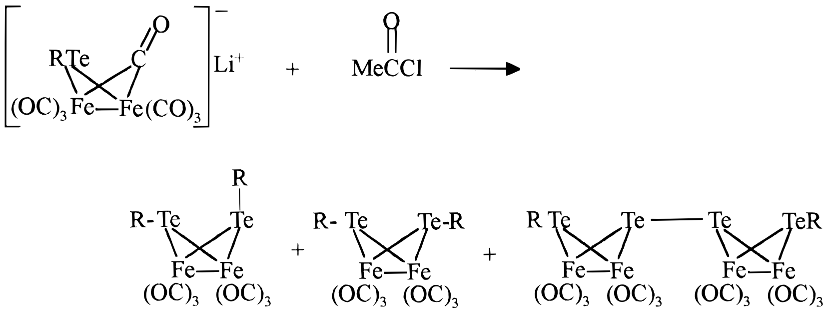
Scheme 1



2

Scheme 2



R=Ph	**4ae**	**4ee**	**5**
R=o-MeC$_6$H$_4$	**6ae**	**6ee**	**7**
R=p-MeC$_6$H$_4$	**8ae**	**8ee**	**9**

for the two methyl substituents in isomer **6ae** might be attributed to the fact that they are more distant from the axially and equatorially bonded benzene rings. For isomer **8ae**, the eight protons of the two substituted benzene rings showed two sets of AA′BB′ quartets between 6.96 and 7.28 ppm whereas the six protons of the two *para*-substituted methyl groups exhibited one singlet at 2.34 ppm. Apparently, this is consistent with the two *p*-MeC$_6$H$_4$ groups being attached to two Te atoms via an axial bond and an equatorial bond. For isomer **8ee**, those protons of the substituted benzene rings showed an AA′BB′ quartet between 7.01 and 7.41 ppm whereas the protons of the *para*-substituted methyl groups exhibited one singlet at 2.36 ppm. This is consistent with the two *p*-MeC$_6$H$_4$ groups being attached to Te atoms via an equatorial type of bond. In addition, since the yield ratios are **4ae**/**4ee** = 3:1, **6ae**/**6ee** = 8:1, **8ae**/**8ee** = 3:1, the ae isomers should be more stable than ee isomers. This was also commonly observed for isomers of (μ-RE)$_2$Fe$_2$(CO)$_6$ (E = S, Se) and related complexes.[4,7]

The double clusters **3**, **5**, **7**, and **9** [(μ-RTe)Fe$_2$(CO)$_6$]$_2$-(μ-Te−Te-μ) are the first examples of such organometallic clusters with a ditelluride bridge, although some dinuclear organometallic molecules with a ditelluride bridge such as [Cp(Et$_3$P)(CO)Fe]$_2$(μ-Te−Te-μ)[8a] and [(Et$_3$P)$_2$(CO)$_3$Mn]$_2$(μ-Te−Te-μ),[8b] are known. For **3** and **9**, the elemental analysis data and the IR and ^{1}H NMR spectra are in good agreement with the structures proposed above. However, for **5** and **7**, the elemental analysis and ^{1}H NMR spectra show them to contain one molecule of pentane, which has been further confirmed for **5** by an X-ray crystal diffraction analysis (vide infra). The pentane molecules which combined with **5** and **7**, evidently this originated from the petroleum ether used in the chromatographic separation and recrystallization, had not been completely removed during vacuum drying. In principle, double clusters **3**, **5**, **7**, and **9** should have more isomers than single clusters **1**, **4**, **6**, and **8**.[4g] According to the ^{1}H NMR spectra, we may conclude that **3**, **5**, and **7** are all isomer mixtures whereas **9** is one single isomer. This is because the ^{1}H NMR spectra for group R of **3**, **5**, and **7** are very complicated and the ^{1}H NMR spectrum for group R of **9** is simple: one singlet at 2.50 ppm assigned to the six protons of the two *para*-substituted methyl groups and an AA′BB′ quartet between 7.56 and 8.16 ppm for the eight protons of the substituted benzene rings. On the basis of the isomer analysis for its analogs, [(μ-RE)Fe$_2$(CO)$_6$](μ-S-S-μ) (E = S, Se),[4g] **9** could exist possibly as one of the three isomers, namely e(p-MeC$_6$H$_4$) e(p-MeC$_6$H$_4$) with an axial bond between two bridged Te atoms a(p-MeC$_6$H$_4$) a(p-MeC$_6$H$_4$), or e(p-MeC$_6$H$_4$) e(p-MeC$_6$H$_4$) with an equatorial bond between the two Te atoms, as shown in Scheme 3.

In the reactions mentioned above, the formation of single clusters **1**, **4**, **6**, and **8** is not unusual, since the reactions involving analogs of anions Z, i.e., [(μ-RE)(μ-CO)Fe$_2$(CO)$_6^-$] (E = S, Se), produced the same type of single clusters (μ-RE)$_2$Fe$_2$(CO)$_6$ (E = S, Se).[14] Clusters of the type (μ-RTe)$_2$Fe$_2$(CO)$_6$ might be generated through decomposition of the anions [(μ-RTe)(μ-CO)Fe$_2$(CO)$_6^-$], followed by dimerization of the intermediate fragments (μ-RTe)Fe(CO)$_3$. This is because (i) TLC showed that the appearance of (μ-RTe)$_2$Fe$_2$(CO)$_6$ comes after the formation of [(μ-RTe)(μ-CO)Fe$_2$(CO)$_6^-$], which rules out the possibility of (μ-RTe)$_2$Fe$_2$(CO)$_6$ being formed directly

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Scheme 3

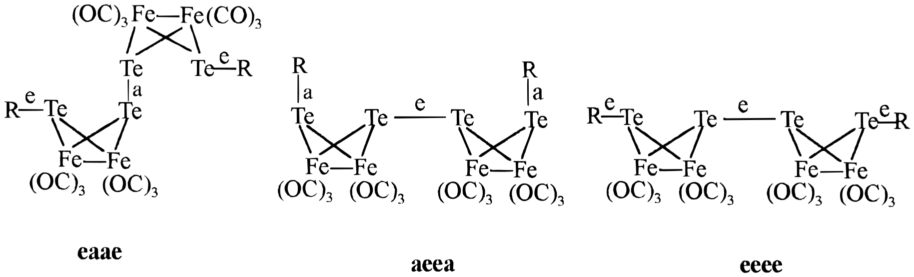

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 5

Te(1)−Fe(2)	2.516(9)	O(4)−C(4)	1.08(6)
Te(1)−Fe(1)	2.53(1)	O(5)−C(5)	1.0(1)
Te(2)−Fe(1)	2.532(8)	O(6)−C(6)	1.15(8)
Te(2)−Fe(2)	2.543(9)	O(7)−C(7)	1.16(7)
Te(2)−Te(3)	2.826(5)	O(8)−C(8)	1.14(6)
Te(3)−Fe(4)	2.524(8)	O(9)−C(9)	1.21(5)
Te(3)−Fe(3)	2.57(1)	O(10)−C(10)	1.13(5)
Te(4)−Fe(3)	2.528(9)	Fe(2)−C(4)	1.77(6)
Te(4)−Fe(4)	2.546(9)	Fe(2)−C(5)	1.8(1)
Fe(1)−Fe(2)	2.61(1)	Fe(3)−C(9)	1.68(5)
Fe(3)−Fe(4)	2.61(1)	Fe(3)−C(7)	1.77(7)
Te(1)−C(13)	2.18(4)	Fe(3)−C(8)	1.78(5)
Te(4)−C(19)	2.33(6)	Fe(4)−C(12)	1.64(6)
Fe(1)−C(2)	1.75(6)	Fe(4)−C(11)	1.76(6)
Fe(1)−C(1)	1.88(7)	Fe(4)−C(10)	1.77(5)
Fe(1)−C(3)	1.92(6)		
Fe(2)−Te(1)−Fe(1)	62.3(3)	C(1)−Fe(1)−Fe(2)	105(2)
Fe(1)−Te(2)−Fe(2)	61.9(3)	C(3)−Fe(1)−Te(2)	100(2)
Fe(1)−Te(2)−Te(3)	104.8(2)	C(3)−Fe(1)−Te(1)	109(2)
Fe(2)−Te(2)−Te(3)	114.4(2)	C(3)−Fe(1)−Fe(2)	156(2)
Fe(4)−Te(3)−Fe(3)	61.7(3)	C(6)−Fe(2)−Te(1)	97(3)
Fe(4)−Te(3)−Te(2)	103.3(2)	C(6)−Fe(2)−Te(2)	104(3)
Fe(3)−Te(3)−Te(2)	113.6(2)	C(6)−Fe(2)−Fe(1)	151(3)
Fe(3)−Te(4)−Fe(4)	62.0(3)	C(4)−Fe(2)−Te(1)	89(2)
Te(2)−Fe(1)−Te(1)	82.6(3)	C(4)−Fe(2)−Te(2)	163(2)
Te(2)−Fe(1)−Fe(2)	59.3(3)	C(4)−Fe(2)−Fe(1)	104(2)
Te(1)−Fe(1)−Fe(2)	58.6(3)	C(5)−Fe(2)−Te(1)	159(3)
Te(1)−Fe(2)−Te(2)	82.7(3)	C(5)−Fe(2)−Te(2)	85(3)
Te(1)−Fe(2)−Fe(1)	59.2(3)	C(5)−Fe(2)−Fe(1)	100(3)
Te(2)−Fe(2)−Fe(1)	58.9(3)	C(2)−Fe(1)−Te(2)	154(2)
Te(4)−Fe(3)−Te(3)	82.6(3)	C(2)−Fe(1)−Te(1)	89(2)
Te(4)−Fe(3)−Fe(4)	59.4(3)	C(2)−Fe(1)−Fe(2)	95(2)
Te(3)−Fe(3)−Fe(4)	58.3(3)	C(1)−Fe(1)−Te(2)	86(2)
C(13)−Te(1)−Fe(2)	112(1)	C(1)−Fe(1)−Te(1)	163(2)
C(13)−Te(1)−Fe(1)	107(1)		

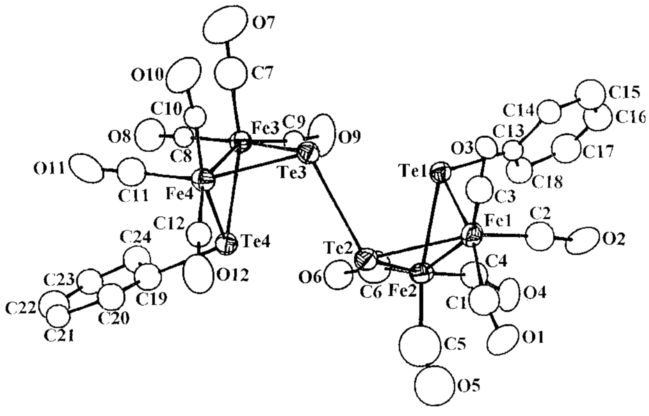

Figure 1. ORTEP view of **5** with atom-labeling scheme.

from RTeLi and $Fe_3(CO)_{12}$. (ii) Generally, in all the products from such reactions, the greater the amount of $(\mu\text{-RTe})_2Fe_2(CO)_6$, the less of the other products. (iii) $[(\mu\text{-RTe})(\mu\text{-CO})Fe_2(CO)_6{}^-]$ alone afforded considerable amounts of $(\mu\text{-RTe})_2Fe_2(CO)_6$. While the formation of $(\mu\text{-RTe})_2Fe_2(CO)_6$ might be expected in such reactions, the formation of double clusers **3**, **5**, **7**, and **9** is quite unusual and particularly interesting but at this time not understood. Since the anions Z alone gave only single clusters $(\mu\text{-RTe})_2Fe_2(CO)_6$, the added electrophiles MeC(O)Cl or p-$MeC_6H_4SO_2Cl$ must play an important role in the formation of the double clusters.

In order to further confirm the structures of such double clusters, an X-ray diffraction analysis for **5** was undertaken. One molecule of pentane was found to be present. Selected bond lengths and angles are given in Table 1. An ORTEP drawing with the numbering scheme is shown in Figure 1. As seen from Figure 1, **5** has two butterfly-shaped Fe_2Te_2 units joined together through an axial μ-Te−Te-μ bond; In addition, each Fe atom is attached to three terminal carbonyl ligands and the other two Te atoms are bound to phenyl groups, both by an equatorial type of bond. This molecule actually has a structure analogous to that of $[(\mu\text{-PhS})Fe_2(CO)_6]_2(\mu\text{-S-S-}\mu)$[9] with the Te atoms replacing the S atoms. However, for the latter, two phenyl groups are attached to S atoms, both by an axial bond, and the two butterfly Fe_2S_2 structural units are joined together by an equatorial μ-S-S-μ bond. The Fe−Fe bond lengths in **5** (Fe(1)−Fe(2) = Fe(3)−Fe(4) = 2.61(1) Å) are close to those in $[(\mu\text{-PhS})Fe_2(CO)_6]_2(\mu\text{-S−S-}\mu)$ (2.525(1) and 2.520(1) Å)[9] and are basically the same as those in other Te/$Fe_2(CO)_6$ compounds, such as 2.614(4) Å in $[(\mu\text{-Te})(\mu\text{-Te})_2Fe_2(CO)_6]^{-2}$,[10] 2.607(6) and 2.619(7) Å in $[(MeTe)Fe_2(CO)_6]_2(TeCH_2Te)$,[11] and 2.634(5) Å in $(\mu\text{-MeTe})_2Fe_2(CO)_6$.[12] Likewise, the average Fe−Te bond length, 2.536 Å, agrees very well with the 2.549 Å (average) bond length in $(\mu\text{-MeTe})_2Fe_2(CO)_6$,[12] 2.548 Å (average) in $(Te_2CH_2)Fe_2(CO)_6$,[13] 2.53 Å (average) bond length in $Te_2Fe_3(CO)_9$[14] and 2.572 Å (average) in $[(\mu\text{-Te})(\mu\text{-Te})_2Fe_2(CO)_6]^{-2}$.[10] The Te−Te bond length, 2.826(5) Å, is close to that in Ph_2Te_2 (2.712(2) Å)[15] and in other iron carbonyl compounds containing a Te−Te bond, such as 2.705(3) Å in $[(\mu\text{-Te})(\mu\text{-Te})_2Fe_2(CO)_6]^{-2}$,[10] 2.807(1) Å in $CpMoFe(CO)_5Te_2Br$,[16] and 2.700(4) and 2.719(4) Å in $(Et_4NCl)[(\mu\text{-Te})_2Fe_2(CO)_6]_2$.[17] In addition, it is worth noting (i) that the bond angles around the Te atoms of **5** (Fe(1)−Te(1)−Fe(2) = 62.2(3)°, Fe(2)−Te(2)−Fe(1) = 61.9(3)°, Fe(3)−Te(3)−Fe(4) = 61.7(3)°, and Fe(4)−Te(4)−Fe(3) = 62.0(3)°) are virtually the same as those of $(\mu\text{-MeTe})_2Fe_2(CO)_6$ (Fe(1)−Te(1)−Fe(1A) = 62.3(1)° and Fe(1)−Te(2)−Fe(1A) = 62.2(1)°).[12] (ii) The dihedral angle between the two wings of each butterfly Fe_2Te_2 skeleton of **5** are equal to 100.82° and 100.95°,

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[16] Bogan, L. E., Jr.; Rauchfuss, T. B.; Rheingold, A. L. *Inorg. Chem.* **1985**, *24*, 3720.

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which is somewhat greater than that of $(\mu\text{-MeTe})_2Fe_2(CO)_6$ (96.66°).[12]

Experimental Section

All reactions were carried out under an atmosphere of prepurified nitrogen using standard Schlenk techniques and monitored by TLC. Tetrahydrofuran and diethyl ether were distilled from sodium-benzophenone ketyl under nitrogen. Elemental Te, MeC(O)Cl, and $p\text{-MeC}_6H_4SO_2Cl$ were of commerical origin and used without further purification. $Fe_3(CO)_{12}$,[18] PhC≡CH,[19] BuLi,[20] PhLi,[20] $o\text{-CH}_3C_6H_4Li$,[21] and $p\text{-CH}_3C_6H_4Li$[21] were prepared according to literature methods.The products were separated first by a short column with a ca. 10 cm-high-bed of 300−400 mesh silica gel and then by TLC (20 × 25 × 0.25 cm, silica gel G). The products for analysis were further purified by recrystallization from CH_2Cl_2/petroleum ether. The yields were calculated after TLC and based on elemental Te. IR spectra were recorded on a Nicolet FT-IR 5DX spectrophotometer; ^1H NMR spectra were obtained on a Jeol FX-90 Q NMR spectrometer. C/H analyses and MS determinations were performed on a Perkin-Elmer model 240C analyzer and an HP 5988A mass spectrometer, respectively. Melting points were determined on a Yanaco MP-500 apparatus.

Preparation of 1 and 2. To a 100 mL three-necked flask fitted with a magnetic stir bar, a rubber septum, and a reflux condenser topped with a nitrogen inlet tube was added 0.255 g (2.0 mmol) of tellurium powder, 30 mL of THF, and 2 mL (1.06 M, 2.1 mol) of n-BuLi/Et_2O solution. The reaction mixture was stirred at room temperature for 2 h, and then stirred at reflux for 30 min to give a brown solution. After the solution was cooled to room temperature, 1.00 g (2.0 mmol) of $Fe_3(CO)_{12}$ was added and the reaction mixture was stirred for about 30 min (until no green $Fe_3(CO)_{12}$ remained) to give an intermediate salt $[(\mu\text{-RTe})(\mu\text{-CO})Fe_2(CO)_6{}^-]Li^+$ ($R = n$-Bu). To this was added 0.22 mL (2.0 mmol) of phenylacetylene, and the reaction mixture was stirred at room temperature for 10 h. The solvent was removed under reduced pressure, and the residue was subjected to short-column chromatography and then to TLC separation using petroleum ether as eluent. From the first band was obtained 0.073 g (11%) of **1** as a red liquid. Anal. Calcd for $C_{14}H_{18}Fe_2O_6Te_2$: C, 25.90; H, 2.79. Found: C, 26.05; H, 2.84. IR (KBr disk): $\nu_{C\equiv O}$ 2049 (s), 2016 (vs), 1975 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.64−2.72 (m, 18H, $2CH_2CH_2CH_2CH_3$) ppm. From the second band was obtained 0.110 g (10%) of **2** as a red solid. mp 76−77 °C. Anal. Calcd for $C_{18}H_{16}Fe_2O_6Te$: C, 38.09; H, 2.84. Found: C, 37.72; H, 2.52. IR (KBr disk):$\nu_{C\equiv O}$ 2057 (s), 2016 (vs), 1991 (s) 1967 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.96 (t, 3H, $J = 7.2$ Hz, CH_3), 1.21−1.93 (m, 4H, $CH_2C\mathbf{H}_2C\mathbf{H}_2CH_3$), 2.07 (d, 1H, $J = 3.6$ Hz), 2.87 (t, 2H, $J = 7.2$ Hz, $TeCH_2$), 3.55 (d, 1H, $J = 3.6$ Hz), 7.23 (s, 5H, C_6H_5) ppm. MS (EI, Te^{130}), m/z (relative intensity): 570 (M^+, 1.0), 542 ($M^+ -$ CO, 5.8), 514 ($M^+ -$ 2CO, 4.2), 486 ($M^+ -$ 3CO, 8.9), 458 ($M^+ -$ 4CO, 1.4), 430 ($M^+ -$ 5CO, 8.7), 402 ($M^+ -$ 6CO, 11.5), 346 ($(Fe_2(TeH)(CH_2{=}CPh)^+$, 86.3), 242 (Fe_2Te^+, 76.8), 215 ($Fe_2CH_2{=}CPh^+$, 4.6), 187 ($C_4H_9Te^+$, 7.4), 112 ($Fe_2{}^+$, 15.6), 103 ($PhC{=}CH_2{}^+$, 100), 77 ($C_6H_5{}^+$, 33.7), 57 ($C_4H_9{}^+$, 17.3), 56 (Fe^+, 44.7).

Preparation of 1 and 3. To the intermediate salt $[(\mu\text{-RTe})(\mu\text{-CO})Fe_2(CO)_6{}^-]Li^+$($R = n$-Bu) solution prepared as described above was added 0.60 mL (8.5 mmol) of MeC(O)Cl. The reaction mixture was stirred at room temperature for 4 h. After workup, as in the preparation of **1** and **2**, 0.141 g (22%) of **1** and 0.087 g (15%) of **3**, a red-brown solid, were obtained from the first and the second band, respectively. **3**: mp 125−126 °C. Anal. Calcd for $C_{20}H_{18}Fe_4O_{12}Te_4$: C, 20.29; H, 1.53. Found: C, 20.48; H, 1.47. IR (KBr, disk): $\nu_{C\equiv O}$ 2041 (vs), 2008 (vs), 1983 (s) 1967 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.73−3.17 (m, 18H, $2CH_2CH_2CH_2CH_3$) ppm. MS (EI, Te^{130}), m/z (relative intensity): 500 ($Fe_2TeHSC_4H_9(CO)_6{}^+$, 0.7), 472 ($Fe_2TeHSC_4H_9(CO)_5{}^+$, 0.6), 444 ($Fe_2TeHSC_4H_9(CO)_4{}^+$, 0.8), 416 ($Fe_2TeHSC_4H_9(CO)_3{}^+$, 2.5), 388 ($Fe_2TeHSC_4H_9(CO)_2{}^+$, 2.2), 332 ($Fe_2TeHSC_4H_9{}^+$, 1.0), 331 ($Fe_2TeSC_4H_9{}^+$, 1.4), 274 (Fe_2STe^+, 7.5), 242 (Fe_2Te^+, 1.2), 186 ($FeTe^+$, 0.3), 144 (Fe_2S^+, 9.0), 112 ($Fe_2{}^+$, 1.7), 90 ($C_4H_9SH^+$, 13.1), 57 ($C_4H_9{}^+$, 38.4), 56 (Fe^+, 27.0), 41 ($CH_2{=}CHCH_2{}^+$, 58), 28 (CO^+, 100).

Preparation of 4ae, 4ee, and 5. The intermediate salt $[(\mu\text{-PhTe})(\mu\text{-CO})Fe_2(CO)_6{}^-]Li^+$ was prepared by the same procedure as that used for $[(\mu\text{-}n\text{-BuTe})(\mu\text{-CO})Fe_2(CO)_6{}^-]Li^+$ using 4 mL (0.609 M, 2.4 mmol) of a PhLi/Et_2O solution. To this salt was added 0.6 mL of MeC(O)Cl and the mixture was stirred at room temperature. After workup, as in the preparation of **1** and **2**, 0.302 g (44%) of **4ae**, a red solid, was obtained from the first band. **4ae**: mp 104−106 °C. Anal. Calcd for $C_{18}H_{10}Fe_2O_6Te_2$: C, 31.37; H, 1.46. Found: C, 31.62; H, 1.36. IR (KBr, disk): $\nu_{C\equiv O}$ 2057 (s), 2000 (s), 1975 (s) 1950 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.88−7.48 (m, 10H, $2C_6H_5$) ppm. From the second band was obtained 0.090 g (13%) of **4ee** as a red solid. **4ee**: mp 158−160 °C. Anal. Calcd for $C_{18}H_{10}Fe_2O_6Te_2$: C, 31.37; H, 1.46. Found: C, 31.53; H, 1.41. IR (KBr, disk): $\nu_{C\equiv O}$ 2057 (s), 2016 (vs), 1991 (s) 1959 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.96−7.64 (m, 10H, $2C_6H_5$) ppm. MS(EI, Te^{130}), m/z (relative intensity): 610 ($M^+ -$ 3CO, 0.7), 582 ($M^+ -$ 4CO, 0.4), 554 ($M^+ -$ 5CO, 0.7), 526 ($M^+ -$ 6CO, 6.1), 372 ($Fe_2Te_2{}^+$, 27.1), 319 ($Fe_2TeC_6H_5{}^+$, 4.7), 242 (Fe_2Te^+, 11.4), 207 ($C_6H_5Te^+$, 11.3), 186 ($FeTe^+$, 5.1), 154 ($C_6H_5C_6H_5{}^+$,100), 112 ($Fe_2{}^+$, 4.9), 77 ($C_6H_5{}^+$, 68.3), 56 (Fe^+, 32.8). From the third band was obtained 0.096 g (16%) of **5**, a red solid, mp 109−110 °C. Anal. Calcd for $C_{24}H_{10}Fe_4O_{12}Te_4{\cdot}C_5H_{12}$: C, 26.87; H, 1.71. Found: C, 26.32; H, 1.48. IR (KBr, disk): $\nu_{C\equiv O}$ 2049 (vs), 2024 (vs), 1967 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.80−1.40 (m, 12H, $2C_5H_{12}$), 7.12−7.76 (m, 10H, $2C_6H_5$) ppm. MS (EI, Te^{130}), m/z (relative intensity): 505 ($Fe_2Te_2C_6H_5(CO)_2{}^+$, 0.7), 372 ($Fe_2Te_2{}^+$, 14.8), 319 ($Fe_2TeC_6H_5{}^+$, 1.6), 242 (Fe_2Te^+, 7.8), 207 ($C_6H_5Te^+$, 12.9), 186 ($FeTe^+$, 4.6), 154 ($C_6H_5C_6H_5{}^+$, 91.5), 112 ($Fe_2{}^+$, 3.0), 77 ($C_6H_5{}^+$, 76.3), 56 (Fe^+, 21.7).

Preparation of 6ae, 6ee and 7. Method i: The intermediate salt $[(\mu\text{-}o\text{-MeC}_6H_4Te)(\mu\text{-CO})Fe_2(CO)_6{}^-]Li^+$ was prepared using 3 mL (0.678 M, 2.0 mmol) of a $o\text{-MeC}_6H_4Li/Et_2O$ solution. To this salt was added 0.60 mL of MeC(O)Cl, and the mixture was stirred for 4 h at room temperature. After workup, as described above, 0.453 g (63%) of **6ae**, a red solid, was obtained from the first band. **6ae**: mp 74−76 °C. Anal. Calcd for $C_{20}H_{14}Fe_2O_6Te_2$: C, 33.49; H, 1.97. Found: C, 33.49; H, 1.96. IR (KBr, disk): $\nu_{C\equiv O}$ 2057 (s), 2016 (s), 1983 (s) 1959 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.50 (s, 6H, $2CH_3$), 6.82−7.60 (m, 8H, $2C_6H_4$) ppm. From the second band was obtained 0.063 g (9%) of **6ee**, a red solid, mp 136−138 °C. Anal. Calcd for $C_{20}H_{14}Fe_2O_6Te_2$: C, 33.49; H, 1.97. Found: C, 33.52; H, 2.07. IR (KBr, disk): $\nu_{C\equiv O}$ 2057 (s), 2024 (s), 1983 (s) 1959 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.55 (s, 6H, $2CH_3$), 6.92−7.64 (m, 8H, $2C_6H_4$) ppm. From the third band was obtained 0.034 g (5%) of **7**, a deep red solid, mp 80−82 °C. Anal. Calcd for $C_{26}H_{14}Fe_4O_{12}Te_4{\cdot}C_5H_{12}$: C, 28.11; H, 1.97. Found: C, 27.93; H, 1.53. IR (KBr, disk): $\nu_{C\equiv O}$ 2049 (s), 2024 (vs), 1975 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.76−1.52 (m, 12H, C_5H_{12}), 2.28−2.74 (m, 6H, $2CH_3$), 6.86−7.60 (m, 8H, $2C_6H_4$) ppm.

Method ii: The same procedure as described in Method i was used, but 0.788 g (4.15 mmol) of $p\text{-MeC}_6H_4SO_2Cl$ instead of MeC(O)Cl was added to give 0.477 g (67%) of a mixture of **6ae** and **6ee** and 0.048 g (7%) of **7**.

Preparation of 8ae, 8ee, and 9. The intermediate salt $[(\mu\text{-}p\text{-MeC}_6H_4Te)(\mu\text{-CO})Fe_2(CO)_6{}^-]Li^+$ was prepared using 3 mL (0.824 M, 2.5 mmol) of a $p\text{-MeC}_6H_4Li/Et_2O$ solution. To this salt was added 0.60 mL of MeC(O)Cl, and the mixture was

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Table 2. Crystal Data Collection and Refinement of 5

mol form	$C_{29}H_{22}Fe_4O_{12}Te_4$
mol wt	1296.27
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	11.570(7)
b, Å	11.94(1)
c, Å	15.69(1)
α, deg	106.64(6)
β, deg	102.45(6)
γ, deg	81.43(6)
V, Å^3	2020(3)
Z	2
density (calcd), g·cm^{-3}	2.13
F(000)	1208
μ(Mo Kα), cm^{-1}	43.01
diffractometer	Enraf-Nonius CAD4
temp, °C	23
radiation	Mo Kα(λ = 0.710 69 Å)
scan type	$\omega/2\theta$
2θ max, deg	50
no. of obs, n	1937
no. of variables, p	300
R	0.090
R_w	0.093
goodness-of-fit indicator	1.65
max shift in final cycle	0.25
largest peak in final diff map, e Å^{-3}	1.24

stirred for 4 h at room temperature. After workup, as described above, 0.270 g (38%) of **8ae**, a red solid, was obtained from the first band. **8ae**: mp 136−137 °C. Anal. Calcd for $C_{20}H_{14}Fe_2O_6Te_2$: C, 33.49; H, 1.97. Found: C, 33.35; H, 1.77. IR (KBr, disk): $\nu_{C\equiv O}$ 2049 (s), 2024 (s), 1983 (vs) 1967 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.31 (s, 6H, $2CH_3$), 6.93, 6.97, 7.12, 7.16 (AA′BB′ quartet, 4H, C_6H_4), 7.00, 7.04, 7.24, 7.28 (AA′BB′ quartet, 4H, C_6H_4) ppm. From the second band was obtained 0.098 g (14%) of **8ee**, a red solid, mp 129−130 °C. Anal. Calcd for $C_{20}H_{14}Fe_2O_6Te_2$: C, 33.49; H, 1.97. Found: C, 33.08; H, 1.70. IR (KBr, disk): $\nu_{C\equiv O}$ 2057 (s), 2016 (s), 1967 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.36 (s, 6H, $2CH_3$), 7.01, 7.11, 7.31, 7.41 (AA′BB′ quartet, 8H, $2C_6H_4$) ppm. From the third band was obtained 0.073 g (12%) of **9**, a red solid, mp 128 °C (dec). Anal. Calcd for $C_{26}H_{14}Fe_4O_{12}Te_4$: C, 24.94; H, 1.13. Found: C, 25.09; H, 1.22. IR (KBr, disk): $\nu_{C\equiv O}$ 2049 (vs), 2024 (vs), 1983 (vs) 1959 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.50 (s, 6H, $2CH_3$), 7.56, 7.66, 8.06, 8.16 (AA′BB′ quartet, 8H, $2C_6H_4$) ppm.

Single-Crystal Structure Determination of 5. Single crystals of **5** suitable for X-ray diffraction were obtained by slow evaporation of its CH_2Cl_2/petroleum ether solution. A crystal measuring 0.25 × 0.40 × 0.65 mm was mounted on a glass fiber and placed on an Enraf-Nonius CAD4 diffractometer with a graphite monochromator. A total of 7062 independent reflections were collected at 23 °C with Mo Kα (λ = 0.710 69 Å) radiation by a $\omega-2\theta$ scan mode. Of the total number of independent reflections, 1937 with $I \geq 3\sigma(I)$ were considered to be observed and used in subsequent refinement. Data were corrected for Lp factors. The crystal belongs to the triclinic space group $P\bar{1}$ (No. 2), with a = 11.570(7) Å, b = 11.94(1) Å, c = 15.69(1) Å; α = 106.64(6)°, β = 102.45(6)°, γ = 81.43(6)°; V = 2020(3) Å^3; Z = 2; D_c = 2.13 g·cm^{-3}; μ = 43.01 cm^{-1}; F(000) = 1208.

The structure was solved by direct methods. Fe atoms, Te atoms, and most of the oxygen atoms were subjected to the structure refinement with anisotropic temperature factors. All carbon atoms and the O(5) atom were subjected to structure refinement with isotropic temperature factors. All hydrogen atoms of the molecule except pentane were generated geometrically and allowed to ride on their respective parent C atoms. The unweighted and weighted agreement factors are 0.090 (R) and 0.093 (R_w), respectively. The highest peak on the final difference Fourier map has a height of 1.24 eÅ^{-3}. All calculations were performed on a Micro-Vax 3100 computer using the TEXSAN program system. Details of crystal parameters, data collection, and structure refinement are given in Table 2.

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Supporting Information Available: Text giving crystallographic experimental data and tables of data collection and processing parameters, positional and thermal parameters, bond lengths, and bond angles for **5** (5 pages). Ordering information is given on any current masthead page.

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