Metal Telluride Clusters — From Small Molecules to Polyhedral Structures

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Dedicated to Professor Dr. Henri Brunner on the occasion of his retirement

Keywords: Niobium / Tellurium / Polymetallic complexes / Clusters / Structures / Reactivity

Niobocene ditelluride complexes [(tBuC$_5$H$_4$)$_2$Nb(Te$_2$)H] (**1**) and [(C$_5$Me$_5$)$_2$Nb(Te$_2$H)] (**2**) are useful starting materials for the synthesis of heterometallic telluride complexes and clusters. The presence of free electron pairs, the propensity for Te–Te bond cleavage and the ability to eliminate Te ligands allow stepwise formation of polyhedral structures in reactions with binary transition metal carbonyl complexes or reactive organometallic fragments. Among the products are the first examples of organometallic derivatives of the elusive [MTe$_4$]$^{2-}$ ion. Ligand cross-transfer (CO versus Te) from one metal center to the other and subsequent charge separation lead to the formation of anionic metal telluride clusters and cationic carbonylniobocene species. The latter play a decisive role in tuning the electronic properties of the cluster units. Whereas the 17-electron fragment (tBuC$_5$H$_4$)$_2$Nb(CO) is directly anchored at the cluster cores by Te bridges, the 18-electron cation [Cp$^*_2$Nb(CO)$_2$]$^+$ (Cp* = C$_5$Me$_5$) formed in situ is able to stabilize large and differently charged cluster anions. This is particularly the case in cobalt telluride cluster chemistry which is characterized by hexacapped cubic Co@Co$_8$ or heptacapped pentagonal-prismatic Co@Co$_{10}$ polyhedra. These compounds exhibit pronounced electron-sponge behavior, and crystallographic studies of differently charged clusters allow a correlation of different cluster charges and bond parameters important for understanding electronic structures.

Introduction

Metal telluride complexes are characterized by a wide and impressive structural variety[1] and recent developments focus on their ability for cluster aggregation.[2,3] Our interest in tellurium complex chemistry stems from the chemistry of chalcogen-rich organometallic complexes and the diversity of sulfur- and selenium-derived ligands.[4] During these studies we have found that bent dicyclopentadienylmetal fragments of the early transition metals are ideal organometallic substrates for the incorporation of chalcogenide ligands.[5] However, only a few comparative investigations have been carried out in which the coordination behavior of different chalcogens has been studied with the same transition metal,[6] although they reveal gradual but distinct changes when going from sulfur to tellurium.

It is a particular feature of the heavier group 5 metallocene fragments that they incorporate two chalcogenide ligands along with hydrogen in different coordination modes **A**−**C** (Scheme 1).[7,8] Obviously, the assembly of the main-group ligands not only depends on the nature of the chalcogen, but also on the substituents at the cyclopentadienyl ligand. Ligand rearrangements by breaking chalcogen−hydrogen and/or chalcogen−chalcogen bonds may lead to interconversion of one form into another. For example, [Cp*$_2$Nb(η-Se$_2$H)] (form **A**) may be easily converted by light into the corresponding forms **B** and **C**.[8b]

The presence of free electron pairs in metallocene dichalcogenides is an important prerequisite for the formation of

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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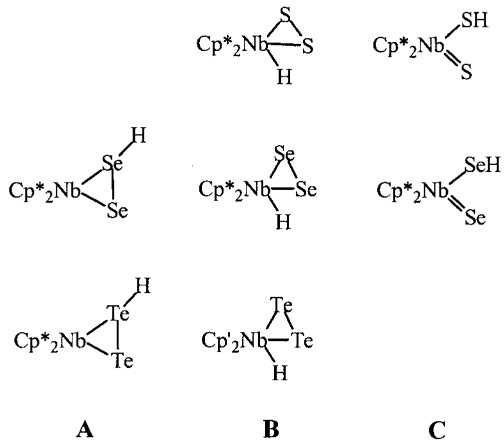
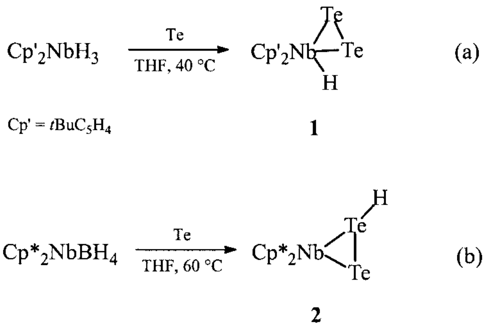


Scheme 1. Examples of the coordination modes of dichalcogenide ligands in [$Cp^*{}_2NbX_2H$] complexes ($Cp^* = C_5Me_5$; X = S, Se, Te) and [($t$$BuC_5H_4)_2Nb(Te_2)H$]

polymetallic compounds,[9] whereas the role of the different coordination modes of the hydrogen ligands is not yet fully understood. A specific feature, particularly in niobocene ditelluride chemistry, is the elimination of Te^0 or Te^{2-} building blocks and their transfer onto reactive organometallic compounds followed by the assembly of polyhedral clusters. The diversity of the obtained results is summarized in this microreview.

Activation of Elemental Tellurium in Hydridic Niobocene Derivatives

Convenient synthetic methods involve the use of hydride or boranate ligands containing alkyl-substituted niobocene derivatives. In both cases identical results are obtained. Thus, reaction of [($t$$BuC_5H_4)_2NbH_3$] or [($t$$BuC_5H_4)_2NbBH_4$] with elemental tellurium in THF forms [($t$$BuC_5H_4)_2Nb(Te_2)H$] (**1**) in good yields [Equation (1a)].[10] Replacement of the $t$$BuC_5H_4$ ligand by the more electron-rich peralkylated Cp* ligand in the analogous reactions gives [$Cp^*{}_2Nb(Te_2H)$] (**2**) in excellent yields [Equation (1b)].[11] These results show that the formation of the structure types **A** or **B** for **1** and **2** depends more on the nature of the cyclopentadienyl ligands than on the nature of the hydride source.



(1)

NMR spectroscopy alone is not suitable to assign complexes **1** and **2** to one of the structural types shown in Scheme 1. However, the presence of a Te_2 ligand along with a hydride ion in the dark orange [($t$$BuC_5H_4)_2Nb(Te_2)H$] (**1**) follows definitively from the crystal structure of [($t$$BuC_5H_4)_2Nb(Te_2)H{\cdot}Cr(CO)_5$] (**3**), which is the product of the addition of the Lewis acid fragment $Cr(CO)_5$ to **1** (Scheme 2a). Structural analogues of **1** are [$Cp^*{}_2Nb(S_2)H$],[7] [($t$$BuC_5H_4)_2Ta(S_2)H$],[12] and [$Cp^*{}_2Ta(Te_2)H$].[13]

The orange complex [$Cp^*{}_2Nb(Te_2H)$] (**2**) exhibits in its ^1H NMR spectrum a hydride resonance at $\delta = -3.55$ ppm, whereas in the ^{125}Te NMR spectrum only one resonance ($\delta = -207.9$ ppm) is found, probably due to partially relaxed scalar ^{125}Te-^{93}Nb interactions.[11] The ^1H NMR spectrum of [$(C_5Me_4Et)_2Nb(Te_2H)$] exhibits a symmetrical 14-line signal for the diastereotopic CH_2 protons of both ethyl groups, in agreement with a chiral center at one of the Te atoms.[14] A nearly identical pattern has been observed in [$(C_5Me_4Et)_2Nb(Se_2H)$].[8b]

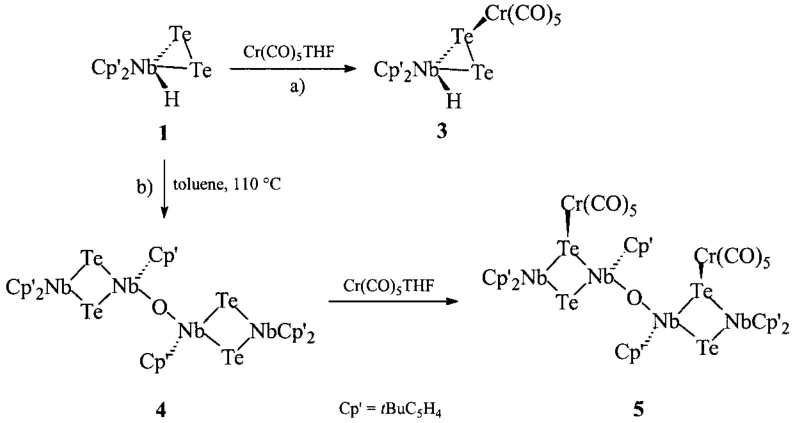
Polymetallic Telluride Complexes from [($t$$BuC_5H_4)_2Nb(Te_2)H$]

As already noted, [($t$$BuC_5H_4)_2Nb(Te_2)H$] reacts with [$Cr(CO)_5THF$] to give the dimetallic adduct [($t$$BuC_5H_4)_2Nb(Te_2)H{\cdot}Cr(CO)_5$] (**3**) in 90% yield. The crystal structure of **3** provides evidence for the presence of a $\mu,\eta^{1:2}$-Te_2 ligand and allows unambiguous localization of the hydride ion directly bonded to the Nb center (Figure 1).[10] Therefore, complex **3** is one of the few structurally characterized ditelluride complexes of the structural type **B**. The Te−Te distance of 2.695(1) Å is similar to those in other complexes containing side-on coordinated η^2-Te_2.[6b,6e,15]

A side-product in the synthesis of **1** is the homonuclear polymetallic complex [($t$$BuC_5H_4)_6Nb_4Te_4O$] (**4**), the formation of which depends on the residual concentration of air in the reaction mixture. Small amounts of **4** also form upon heating solutions of **1** (Scheme 2b).

The crystal structure of **4** shows two planar Nb_2Te_2 rings (Figure 2) connected by a linear oxygen bridge. Each of the "outer" Nb atoms [Nb(1), Nb(4)] is part of a niobocene fragment, whereas the coordination sphere of the "inner" Nb atoms [Nb(2), Nb(3)] is completed by only one ($t$$BuC_5H_4$) ligand. The linearity of the Nb−O−Nb bridge [angle (Nb−O−Nb) = 177.1(1)°] and the electron deficiency of the "inner" Nb atoms [Nb(2), Nb(3)] suggests the contribution of p_π oxygen orbitals. A similar structure has been found in [($t$$BuC_5H_4)_6V_4S_4O$].[16]

Formally, complex **4** contains four Nb^{IV} centers, but ^1H NMR spectroscopy indicates the diamagnetic nature of the molecule. This behavior seems to be characteristic for compounds with four-membered Nb_2Te_2 rings and may be explained by through-space Nb−Nb coupling (see below). In the case of **4** the Nb−Nb distances (3.43 Å) are only slightly longer than those in the related diamagnetic complex [$(C_5H_5)_2Nb(\mu\text{-}S)]_2$ [d(Nb−Nb) 3.2340(8) Å].[17]



Scheme 2

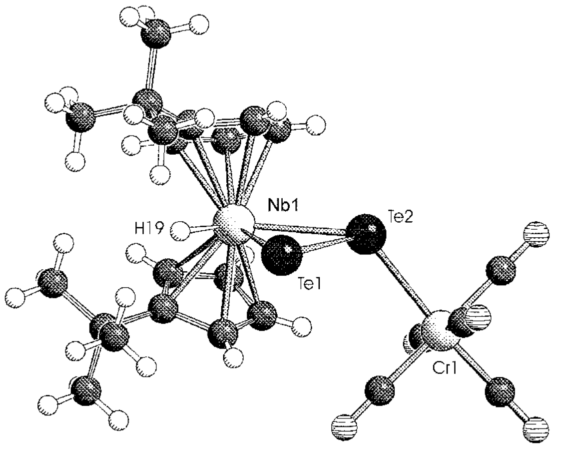


Figure 1. Molecular structure of $[(t\text{BuC}_5\text{H}_4)_2\text{Nb}(\text{Te}_2)\text{H}\cdot\text{Cr(CO)}_5]$ (**3**)

The Te bridges of **4** are still accessible for the addition of two Cr(CO)_5 fragments although the steric situation of the bridges seems to be rather crowded (Scheme 2b). In the resulting complex $[(t\text{BuC}_5\text{H}_4)_6\text{Nb}_4\text{Te}_4\text{O}\cdot2\text{Cr(CO)}_5]$ (**5**) the overall geometry of the starting complex has been preserved, but now the bulky Cr(CO)_5 groups are able to block the rotation around the Cp′−Nb bonds at room temperature, as follows from ^{1}H NMR spectroscopy.[10]

The reaction of $[(t\text{BuC}_5\text{H}_4)_2\text{Nb}(\text{Te}_2)\text{H}]$ (**1**) with $[\text{Fe}_2(\text{CO})_9]$ formally proceeds with insertion of an $\text{Fe}_2(\text{CO})_6$ unit into the Te−Te bond of **1** (Scheme 3).[18] The resulting heterotrimetallic compound $[\{(t\text{BuC}_5\text{H}_4)_2\text{NbH(Te)}_2\}\text{-Fe}_2(\text{CO})_6]$ (**6**) forms the monoadduct $[\{(t\text{BuC}_5\text{H}_4)_2\text{NbH(Te)}_2\text{Fe}_2(\text{CO})_6\}\cdot\text{Cr(CO)}_5]$ (**7**) with $[\text{Cr(CO)}_5\text{THF}]$ in nearly quantitative yield. ^{1}H NMR investigations reveal the presence of two isomers at room temperature in nearly equal amounts. Crystallization at −24 °C affords separation of the sterically more crowded *vic*-**7**. Its crystal structure (Figure 3) proves that the incoming Cr(CO)_5 fragment is

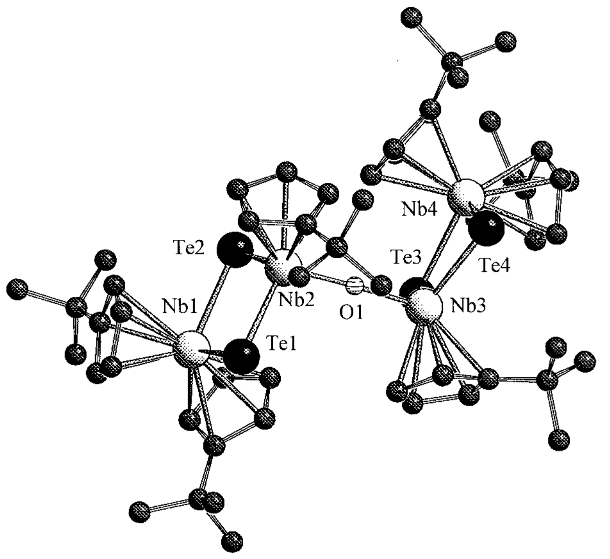
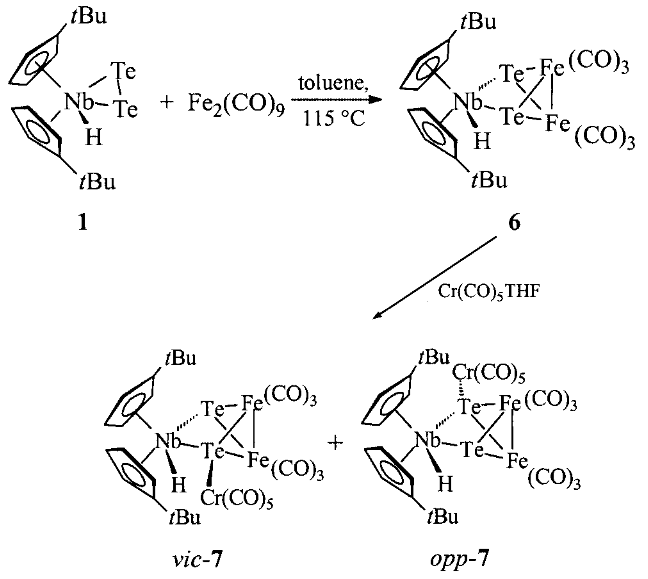


Figure 2. Molecular structure of $[(t\text{BuC}_5\text{H}_4)_6\text{Nb}_4\text{Te}_4\text{O}]$ (**4**)



Scheme 3

attached at the central Te atom and in the vicinity (*vic*) of the Nb−H moiety. Although the latter could not be localized directly, its presence follows from its stereochemical activity in the structure and from the ^1H NMR spectra.

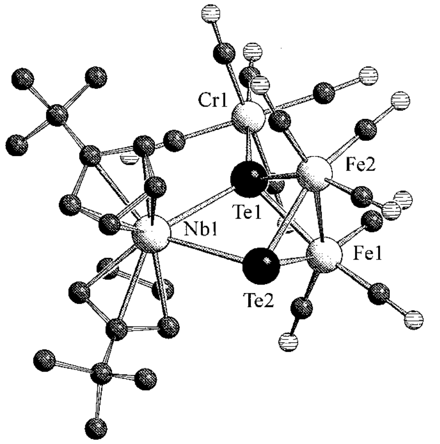
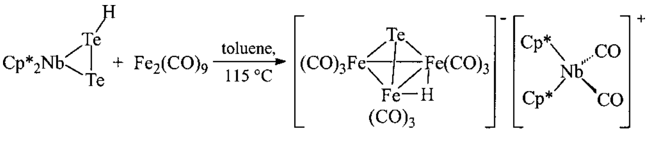


Figure 3. Molecular structure of *vic*-[{(tBuC$_5$H$_4$)$_2$-NbH(Te)$_2$Fe$_2$(CO)$_6$}·Cr(CO)$_5$] (*vic*-**7**); the hydrogen atom at Nb(1) may be located close to Te(1)[18]

Complexes **6** and **7** are some more examples of compounds with an Fe_2Te_2 core.[19] Generally, such derivatives are formal insertion products of a two-electron metal fragment into the Te−Te bond of [$Fe_2(\mu\text{-}Te_2)(CO)_6$].[20]

The stability of the $NbTe_2Fe_2$ framework in **6** and **7** occurs for different reasons, because replacement of tBuC$_5$H$_4$ by the Cp* ligand results in a ligand (CO, Te) cross-transfer from one metal center to the other. A concomitant charge separation leads to the formation of distinct [$Cp^*_2Nb(CO)_2$]$^+$ and [$Fe_3H(\mu_3\text{-}Te)(CO)_9$]$^-$ ions [Equation (2)].[21] CO-containing intermediate products, which may be analogues of **6**, can be observed by IR spectroscopy, but they are not stable enough for isolation.



2 **8**

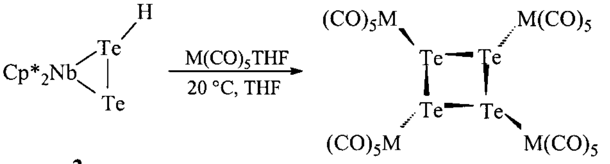
(2)

Oxidative Elimination of Active Te^0 from [Cp*$_2$Nb(Te$_2$H)] (2)

Solutions of **2** are stable towards rearrangement into structural forms **B** and **C**. They are also stable with respect to spontaneous Te elimination, but with PPh_3 the corresponding phosphane oxide and elemental tellurium are formed, probably due to the presence of traces of air. No proof has been found for the existence of pseudo-tetrahedral [$Cp^*_2Nb(=Te)H$], although the structurally related [$Cp^*_2Ta(=Te)H$] is accessible in a similar reaction from [$Cp^*_2Ta(Te_2)H$].[13]

In the presence of reactive transition metal fragments there is no precipitation of grey tellurium. Instead, depending on the reaction conditions a series of homo- and heterometallic telluride complexes or even clusters is formed which are the subject of the following sections.

A nice example of the elimination of Te^0 from [$Cp^*_2Nb(Te_2H)$] is its reaction with an excess of [$M(CO)_5(THF)$] (M = Cr, W).[11] The resulting red-brown compounds *cyclo*-Te$_4$[M(CO)$_5$]$_4$ (**8**) are the first organometallic derivatives of a neutral molecular tellurium ring [Equation (3)].[12] The central feature of the structure of **8**-Cr is a Te_4 ring [d(Te−Te) = 2.854(3) Å mean], which is forced by the attached $Cr(CO)_5$ fragments into D_{2d} butterfly geometry (Figure 4). EHMO calculations carried out on the free hypothetical *cyclo*-Te$_4$ ring show that the square-planar (D_{4h}) structure is only 0.2 eV less favorable in total energies than the folded (D_{2d}) structure.[11]



(3)

2 **8**

M = Cr, W

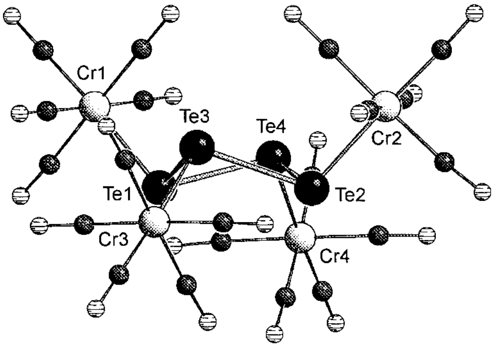
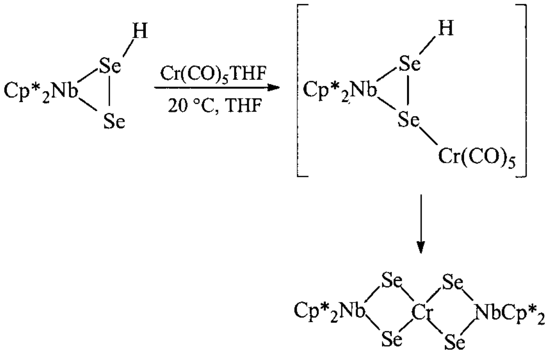


Figure 4. Side view of the structure of *cyclo*-Te$_4$[Cr(CO)$_5$]$_4$ (**8**-Cr)[11]

Another example of the incorporation of Te^0 from **2** into a Lewis acid metal fragment was observed in the reaction of **2** with [$(C_5H_5)Mn(CO)_2(THF)$], which gave [$\{(C_5H_5)Mn(CO)_2\}_3(\mu_3\text{-}Te)$] in 80% yield.[25] This complex, which was first synthesized 1983 by Herberhold et al., possesses a trigonal-planar Te center.[26]

Interestingly, [$Cp^*_2Nb(Se_2H)$], which is isostructural with **2**, gives a completely different result under identical reaction conditions: the carbonyl-free heterotrimetallic complex **9** is formed as the final product [Equation (4)],[23] which belongs to the class of *pseudo*-tetrahedral MX_4 compounds and which will be discussed shortly.[23,24] The observation of CO absorptions during the reaction by IR spectroscopy may be a hint for the addition of $Cr(CO)_5$ to one or more lone-pair electrons of the $Nb(Se_2H)$ moiety [Equation (4)]. By contrast, the sterically less demanding tBuC$_5$H$_4$ ligand in **1** allows formation of a stable $Cr(CO)_5$ adduct

(Scheme 2). The related complex [(tBuC$_5$H$_4$)$_2$Ta(S$_2$)H] can even add two Cr(CO)$_5$ fragments.[9]



(4)

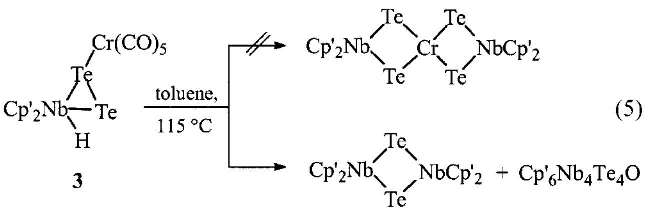
9

The Quest for Derivatives of the Tetratellurometalate Ion

Molecular polymetallic chalcogenido complexes containing a central *pseudo*-tetrahedral MX$_4$ (X = S, Se) unit show interesting electronic and optical properties.[27,28] Although it is known that replacement of sulfur by selenium increases nonlinear optical properties by a heavy metal effect,[29] the corresponding tetratellurometalates are still unknown. Examples of tellurometalates with coordination number four, in which the metal center is surrounded by polytelluride ligands, like in [AuTe$_7$]$^{3-}$, are known.[30]

Dimetallic tetrathio- and tetraselenometalates of the type [(Cp*$_2$Nb)$_2$MX$_4$] (M = Cr, Mo; X = S, Se) may be prepared from [Cp*$_2$Nb(η^2-X$_2$)H] derivatives and binary carbonyl transition metal complexes {e.g. [M(CO)$_6$], [Fe$_2$(CO)$_9$], [Co$_2$(CO)$_8$]} in boiling toluene.[23,24] An alternative route is the thermal decomposition of solutions of [(tBuC$_5$H$_4$)$_2$-Ta(S$_2$)H·Cr(CO)$_5$],[9] [Cp*$_2$Nb(S$_2$)H·Cr(CO)$_5$],[31] and the elusive [Cp*$_2$Nb(Se$_2$)H·Cr(CO)$_5$], respectively [Equation (4)].

Attempts to convert solutions of **3** in boiling toluene into [(Cp*$_2$Nb)$_2$CrTe$_4$] end up with green-black [(tBuC$_5$H$_4$)$_4$Nb$_2$Te$_2$] (**10**) along with small amounts of **4** [Equation (5)]. Complex **10** may be obtained in still better yield from the reaction of **1** with [Cr(CO)$_6$] in boiling toluene.[31] The crystal structure of **10** contains a planar rhombohedral Nb$_2$Te$_2$ core to which four Cp′ ligands are coordinated. The conformation of the (tBuC$_5$H$_4$) ligands is that of the achiral *meso* diastereomer (Figure 5). ^{1}H NMR spectroscopic investigations reveal a restricted rotation around the (tBuC$_5$H$_4$)−Nb bonds at −90 °C. Although a similar conformation has been found in the related complex [(tBuC$_5$H$_4$)$_4$Zr$_2$Te$_2$], there is no spectroscopic evidence for a restricted rotation around the (tBuC$_5$H$_4$)−Zr axis.[32]



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3 **10** **4**

Cp' = tBuC$_5$H$_4$

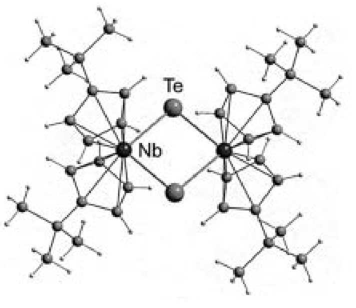
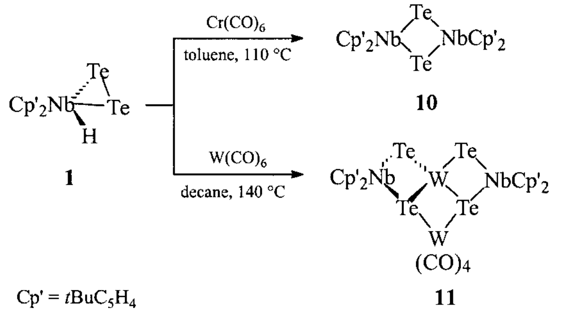


Figure 5. Molecular structure of [(tBuC$_5$H$_4$)$_4$Nb$_2$Te$_2$] (**10**)[31]

The bonding system within the four-membered Nb$_2$Te$_2$ ring in **10** is defined by a long transannular Te−Te distance [d = 4.262(1) Å] of nonbonding character and an Nb−Nb distance [3.647(1) Å], which is still longer than d(Nb−Nb) in **4**, but which is again consistent, according to DFT calculations,[10] with a through-space Nb−Nb coupling.

The μ$_2$-Te bridges in **10** exhibit nucleophilic character. Thus, reaction of **10** with MeI gives the violet salts [(tBuC$_5$H$_4$)$_4$Nb$_2$Te(MeTe)]I or [Cp′$_4$Nb$_2$(MeTe)$_2$]I$_2$ according to the employed stoichiometry (1 or 2 equiv. of MeI).[10] Crystallographic studies of the cations reveal that addition of the electrophiles does not significantly affect the intraannular forces between opposite atoms in the Nb$_2$Te$_2$ ring.

Whereas reaction of **1** with [Cr(CO)$_6$] in boiling toluene gives chromium-free **10** [Equation (6)], [W(CO)$_6$] does not react under similar conditions. However, in decane at 140 °C the red tetrametallic complex [{(tBuC$_5$H$_4$)$_4$Nb$_2$WTe$_4$}W(CO)$_4$] (**11**) is formed in 54% yield [Equation (6)].[31] According to X-ray crystallography, complex **11** contains a slightly distorted WTe$_4$ tetrahedron to which two niobocene fragments are coordinated (Figure 6). A W(CO)$_4$ fragment is inserted between two of the Te bridges of the central WTe$_4$ tetrahedron. Formally, complex **11** may be described as an organometallic derivative of the hitherto unknown [WTe$_4$]$^{2-}$ ion. This view is in agreement with W−Te bond lengths [average 2.574(2) Å] around W(1) in the range of W−Te double bonds and a *pseudo*-tetrahedral arrangement of the Te atoms around W(1).[33] Accordingly, the distances W(2)−Te(2) and W(2)−Te(3) are longer by 0.25 Å. The description of the entire metal−ligand bond system needs to take into account delocalization over the heavy atom skeleton, except for W(2).[31]



(6)

1 **10** **11**

Cp' = tBuC$_5$H$_4$

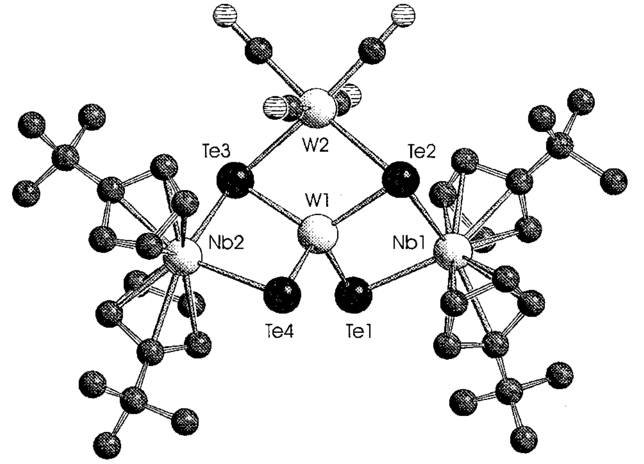


Figure 6. Molecular structure of $[\{(t\mathrm{BuC_5H_4})_4\mathrm{Nb_2WTe_4}\}\mathrm{W(CO)_4}]$ (**11**)[31]

A second example of a tetratellurometalate complex is $[(\mathrm{Cp^*{}_2Nb})_2\mathrm{NiTe_4}]$ (**12**). The black-violet diamagnetic compound is accessible from the reaction of $[\mathrm{Ni(COD)_2}]$ with $[\mathrm{Cp^*{}_2Nb(Te_2H)}]$ in boiling toluene. The reaction with $[(t\mathrm{BuC_5H_4})_2\mathrm{Nb(Te_2)H}]$ under analogous conditions does not give well-defined products.[34]

At first glance the molecular structure of **12** resembles those of the above-described bis(niobocene) tetrachalcogenidometalates. However, there is a remarkable distortion of the central $\mathrm{NiTe_4}$ tetrahedron (Figure 7). This is expressed by Te−Ni−Te angles which split into three different groups between 78.2(1) and 139.2(1)° when compared to the $\mathrm{WTe_4}$ core in **11**. The distortion is also expressed by interannular Te1···Te3 and Te2···Te4 distances of 3.100(7) and 3.122(7) Å, which may even be bonding interactions. In contrast, the transannular Te···Te distances within each of the $\mathrm{NiNbTe_2}$ cycles are much longer (4.19 Å mean). Interestingly, complexes involving $\mathrm{Ni_2Te_2}$ four-membered rings, like $[\{(\mathrm{triphos})\mathrm{Ni}\}_2(\mu\text{-Te})_2]$ [*d*(Te−Te) = 2.802(1) Å][35] and $[\{(\mathrm{C_5H}i\mathrm{Pr_4})\mathrm{Ni}\}_2(\mu\text{-Te})_2]$ [*d*(Te−Te) = 3.052(5) Å] exhibit Te−Te distances that clearly have bonding character.[36]

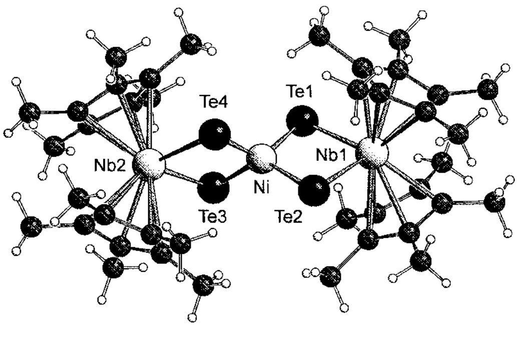


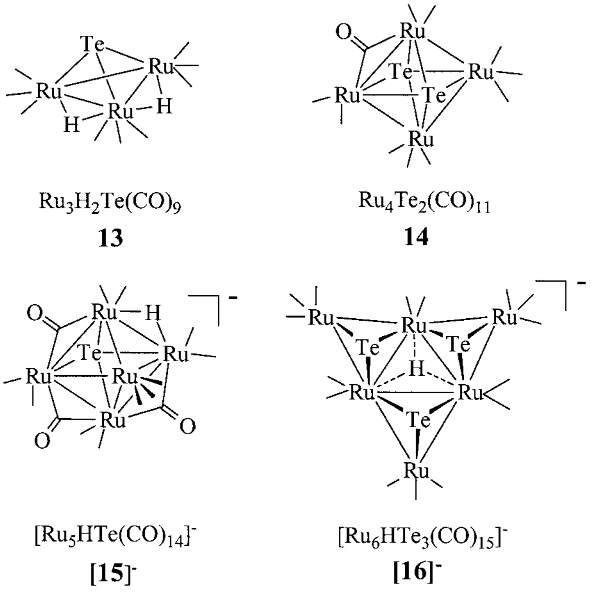
Figure 7. Molecular structure of $[(\mathrm{Cp^*{}_2Nb})_2\mathrm{NiTe_4}]$ (**12**)[34]

Like $[(\mathrm{Cp^*{}_2Nb})_2\mathrm{CrSe_4}]$ (**9**),[23] complex **12** is able to undergo two reversible oxidation steps and two reversible reduction steps in cyclic voltammetry.[37] The corresponding paramagnetic cation $[\mathbf{12}]^+$ has been obtained by oxidation of **12** with $[\mathrm{C_5H_5})_2\mathrm{Fe}]^+$, but only in the presence of a chemically relatively inert anion, like $[\mathrm{BPh_4}]^-$.

Formation of Metal Telluride Clusters

It has already been shown that insertion of an $\mathrm{Fe_2(CO)_6}$ unit from $[\mathrm{Fe_2(CO)_9}]$ into the Te−Te bond of **1** gives the heterotrimetallic complex **6** (Scheme 3). However, the $\mathrm{NbTe_2Fe_2}$ framework seems to be destabilized by introduction of the Cp* ligand. Thus, reaction of **2** with $[\mathrm{Fe_2(CO)_9}]$ finally results in a reductive elimination of $\mathrm{Te^{2-}}$, which serves as a glue for the formation of the $[\mathrm{Fe_3H}(\mu_3\text{-Te})(\mathrm{CO})_9]^-$ cluster anion [Equation (2)].[19b,19g,38] The counterion is the rather stable $[\mathrm{Cp^*{}_2Nb(CO)_2}]^+$ ion, which may have been formed by CO ligand transfer from enneacarbonyldiiron onto the niobocene fragment. In the following sections we will show that the in situ formation of this $\mathrm{Nb^{III}}$ cation exerts a considerable stabilization effect on anionic transition metal telluride clusters. It is striking that a corresponding $[(t\mathrm{BuC_5H_4})_2\mathrm{Nb(CO)_2}]^+$ ion has not yet been observed thus far.

The reaction of **2** with $[\mathrm{Ru_3(CO)_{12}}]$ in boiling toluene gives a rather heterogeneous mixture of neutral and salt-like carbonylruthenium clusters with tellurido and hydrido ligands (Scheme 4).[39] $[\mathrm{Ru_3}(\mu_2\text{-H})_2(\mu_3\text{-Te})(\mathrm{CO})_9]$[40] (**13**; 11% yield) has been characterized indirectly by crystallography of $[\mathrm{Ru_3}(\mu_2\text{-H})_2(\mu_3\text{-Te})(\mathrm{CO})_7(\mathrm{dppm})]$, which is a CO substitution product from the reaction of **13** with bis(diphenylphosphanyl)methane (dppm). Along with the already known cluster $[\mathrm{Ru_4}(\mu_4\text{-Te})_2(\mathrm{CO})_{11}]$ (**14**; 27%),[41] $[\mathrm{Cp^*{}_2Nb(CO)_2}][\mathrm{Ru_5H}(\mu_4\text{-Te})(\mathrm{CO})_{14}]$ $\{[\mathrm{Cp^*{}_2Nb(CO)_2}][\mathbf{15}]$; 31%} and $[\mathrm{Cp^*{}_2Nb(CO)_2}][\mathrm{Ru_6H}(\mu_3\text{-Te})_3(\mathrm{CO})_{15}]$ $\{[\mathrm{Cp^*{}_2Nb(CO)_2}][\mathbf{16}]$; 4%} have been isolated and characterized by X-ray crystallography. Cluster **14** exhibits inter-



Scheme 4. Neutral and anionic clusters from the reaction of **2** with $[\mathrm{Ru_3(CO)_{12}}]$ in boiling toluene; the corresponding cation in the case of $[\mathbf{15}]^-$ and $[\mathbf{16}]^-$ is $[\mathrm{Cp^*{}_2Nb(CO)_2}]^+$

esting redox properties: The reversible uptake of up to four electrons may be accompanied by structural rearrangements as suggested by theoretical studies.[39]

These structural motifs extend the knowledge of carbonylruthenium chalcogenide clusters.[42] The structure of the 74-electron anion [**15**]$^-$ may be described by a slightly distorted Ru_5 square pyramid spanned by a μ_4-Te ligand. Thus, it belongs to the class of $[Ru_5X(CO)_{15}]$ clusters (X = S, Se, Te), of which only $[Ru_5S(CO)_{15}]$ has been synthesized thus far.[43] The triangular structure of [**16**]$^-$ is mainly composed of three edge-linked Ru_3Te tetrahedra, in close analogy to the structure of $[Ru_6HS_3(CO)_{15}]^-$.[44]

It is striking that the CO/Ru ratio in all compounds is much higher than two, although attempts to increase the tellurium content by varying the stoichiometry and reaction conditions were not successful. The origin of the hydrido ligands in **13**, [**15**]$^-$ and [**16**]$^-$ may rather be ascribed to abstraction from the solvent[40,45] than hydrogen transfer from **2**. In this context it may be of interest that $[(t\text{Bu}C_5H_4)_2Nb(Te_2)H]$ does not give reasonable results under analogous reaction conditions.[46]

Another still more complex system concerns the reaction of $[Cp^*{}_2Nb(Te_2H)]$ {or $[(C_5Me_4Et)_2Nb(Te_2H)]$ for the purpose of better crystallization} with $[Co_2(CO)_8]$. This reaction is temperature-dependent and, contrary to other systems, it has been possible to isolate intermediate products, such as **17** and **18**, at 0 °C. These disappear at higher temperatures forming highly connected and symmetric molecular carbonylcobalt telluride cluster anions (Scheme 5).[47]

The bicapped trigonal-bipyramidal cobalt telluride cluster **17** consists of a triangular 47-electron $Co_3(CO)_6Te_2$ core [d(Co−Co) = 2.513(3) Å] to which a 17-electron $Cp^*{}_2Nb(CO)$ fragment is attached by a covalent Te−Nb bridge (Figure 8). This structural motif is more current for niobocene derivatives comprising the $t\text{Bu}C_5H_4$ ligand, as will be shown later. Cluster **17** is the only example of an intermediate in which peralkylated niobocene telluride and carbonylcobalt building blocks are arranged together into a small covalent cluster. For this reason it may also be considered as the first step en route to polyhedral structures or even solid-state compounds.[48]

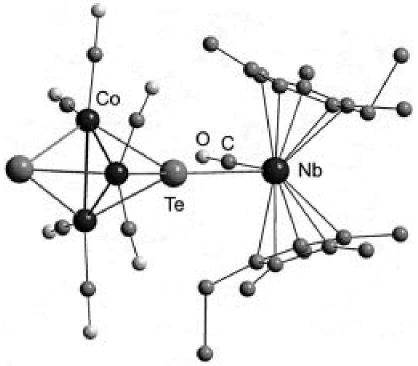
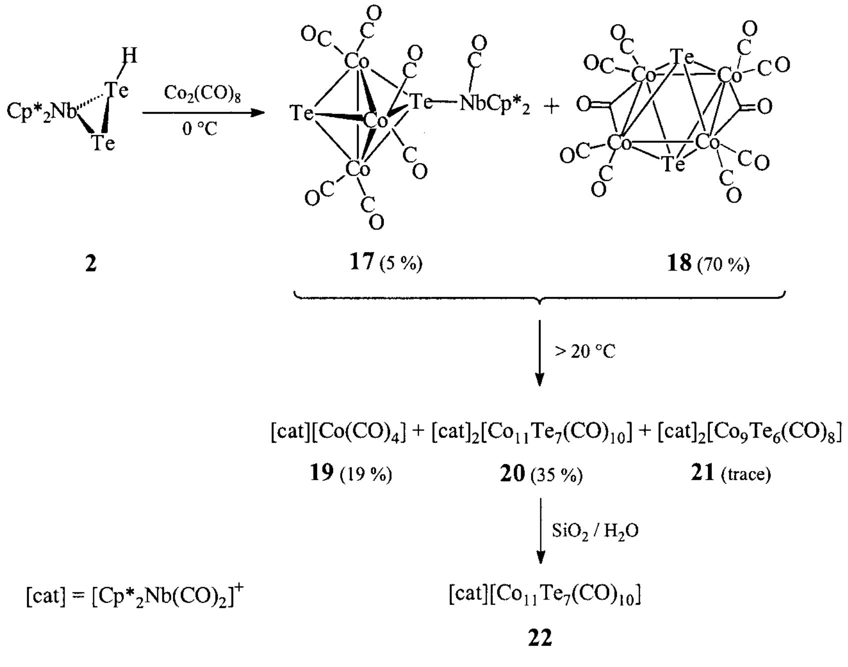


Figure 8. Molecular structure of $[(C_5Me_4Et)_2NbTe_2Co_3(CO)_7]$ (**17**)[47]

The second product is the already known tetragonal-bipyramidal $[Co_4(\mu_4\text{-Te})_2(\mu_2\text{-CO})_2(CO)_8]$ (**18**),[49] which forms in remarkably good yield. However, at room temperature there is a considerable decrease of the yields of **17** and **18** and the ionic compounds **19**−**21**, the formation of which is completed by refluxing the mixture in toluene for 3 h, are formed instead (Scheme 5). From the fact that **18** does not react with **2** in an independent experiment one may conclude that as-yet-unidentified reactive niobocene telluride particles exist in solution and that these are responsible for the disappearance of **18** when raising the temperature.



Scheme 5

The mixture of **19**, **20** and **21** was separated by fractional crystallization and the resulting crystals were examined by X-ray crystallography. The structure of the yellow salt **19** consists of distinct $[Cp^*_2Nb(CO)_2]^+$ and $[Co(CO)_4]^-$ ions in a 1:1 ratio, whereas the cation/anion ratio is 2:1 in **20** and **21**. The structure of the dianion in **20** resembles that of the monoanion (see below). It may be described by a heptacapped pentagonal-prismatic Co_{10} polyhedron (Figure 9), while that in **21** is a hexacapped Co_8 cube (Figure 10). In addition, each of the two polyhedra contains an interstitial Co atom.[47]

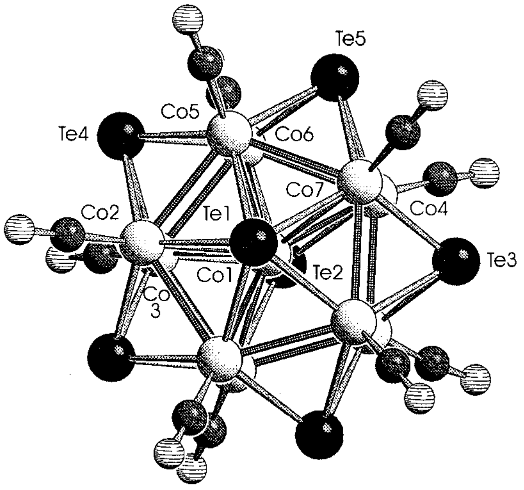


Figure 9. Structure of the $[Co_{11}Te_7(CO)_{10}]^-$ ion in **22**[47]

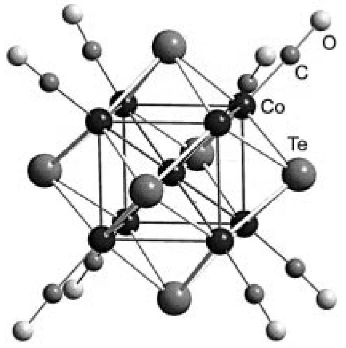


Figure 10. Structure of the $[Co_9Te_6(CO)_8]^{2-}$ ion in **21**[47]

The omnipresence of the $[Cp^*_2Nb(CO)_2]^+$ cation in the structures of compounds **19**−**22** is striking. The remarkably stable Nb^{III} derivative extends the series of dicarbonyl early transition metallocene complexes, for example $[Cp^*_2M(CO)_2]$ (M = Ti, Zr, Hf)[50] and $[(C_5H_5)_2V(CO)_2]^+$.[51] Furthermore, it takes the role of an organometallic template in the formation of cluster anions.

Although the cluster salt **21** is formed in only trace amounts its existence is important because it contains the first cobalt- and tellurium-containing representative in the class of metal-centered hexacapped $[M_9(\mu_4\text{-}E)_6L_8]$ clusters (M = Ni, Pd; E = GeEt, As, Te).[3a,52] According to various combinations of metals and ligands metal valence electron (MVE) counts of between 120 and 130 MVEs have been realized. No cluster has been described in different oxidation states thus far.[53] The anion in **21** contains 123 MVEs, but other electron counts have been realized by varying the cluster charges, as will be shown below.

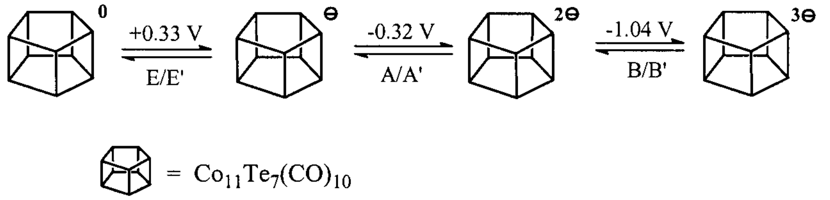
Compound **20** contains the same dianion $[Co_{11}Te_7(CO)_{10}]^{2-}$ as has already been found in $[Ph_4P]_2[Co_{11}Te_7(CO)_{10}]$. This compound was synthesized from $[Co_2(CO)_8]$, Na_2Te_2 and Ph_4PCl in methanol under solvothermal conditions.[54] Chromatography of **20** results in the formation of $[Cp^*_2Nb(CO)_2][Co_{11}Te_7(CO)_{10}]$ (**22**; Scheme 5). The loss of one $[Cp^*_2Nb(CO)_2]^+$ ion during the transfer **20** → **22** corresponds to a one-electron oxidation of $[Co_{11}Te_7(CO)_{10}]^{2-}$ by H^+. Electrochemical investigations confirm three reversible electron-transfer steps regardless of the charge of the anions (Scheme 6).[47] Concomitantly, the ν(CO) frequencies are a function of cluster charge n and decrease from 1961 ($n = -1$) to 1897 ($n = -3$) cm^{-1}, whereas the neutral species ($n = 0$) is too unstable in solution.

The redox behavior of the anions $[Co_{11}Te_7(CO)_{10}]^{1-,2-}$ is in agreement with considerable metallic interactions within the cluster core, which is also expressed by the small HOMO−LUMO gaps for both compounds.[47] According to DFT calculations the oxidized product ($n = 0$) should be less stable than the anions.

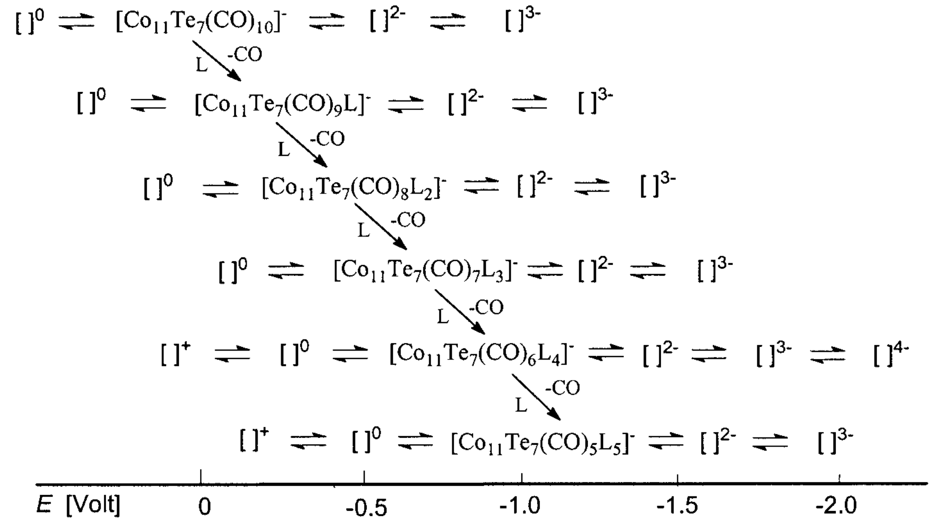
The structure of the $[Co_{11}Te_7(CO)_{10}]^-$ ion in **22** is that of a pentagonal prism formed by ten Co atoms in the center of which resides a further Co atom (Figure 9). All faces are capped by Te bridges. Alternatively, the $Co_{11}Te_7$ cage may be thought to be composed of five edge-sharing Co_5Te octahedra which are arranged around the fivefold Te(1)−Co(1)−Te(2) axis, with Co(1) as common vertex. These octahedra are nearly perfect, with Co−Te and Co−Co bond lengths of approximately equal order (between 2.50 and 2.61 Å).

Neutral clusters comprising the intact $Co_{11}Te_7$ cage are accessible by the reaction of phosphanes L with the salts **20** or **22** and subsequent chromatography on silica gel. In a very complex reaction the substituted clusters $[Co_{11}Te_7(CO)_{10-m}L_m]$ (m = 3, 4, 5) are formed, regardless of the charge of the initial cluster anion.[55] Electrochemical studies of the reaction of **22** with L = PMe_2Ph reveal that there is a stepwise substitution of CO groups, in which differently substituted cluster anions $[Co_{11}Te_7(CO)_{10-m}(PMe_2Ph)_m]^{n-}$ ($m = 1-5$, n = 1, 2) may be formed as intermediate products. Each of these intermediates exhibits at least three electron-transfer processes, leading to a total of 21 redox couples with 27 electroactive species. It is noteworthy that each replacement of a CO ligand by PMe_2Ph in $[\mathbf{1}]^-$ causes a shift of about 200 mV towards more negative potentials (Scheme 7).[55] As a consequence, reduction becomes more difficult and oxidation easier. Traces of oxygen or water (from SiO_2) are thought to be responsible for the oxidation.

The molecular structure of $[Co_{11}Te_7(CO)_5(PMe_2Ph)_5]$ contains the same cluster geometry as the precursor anion $[Co_{11}Te_7(CO)_{10}]^-$.[55] The replacement of five π-acceptor



Scheme 6. Schematic representation of the electrochemistry of the $[Co_{11}Te_7(CO)_{10}]^{n-}$ anions ($n = 0-3$)



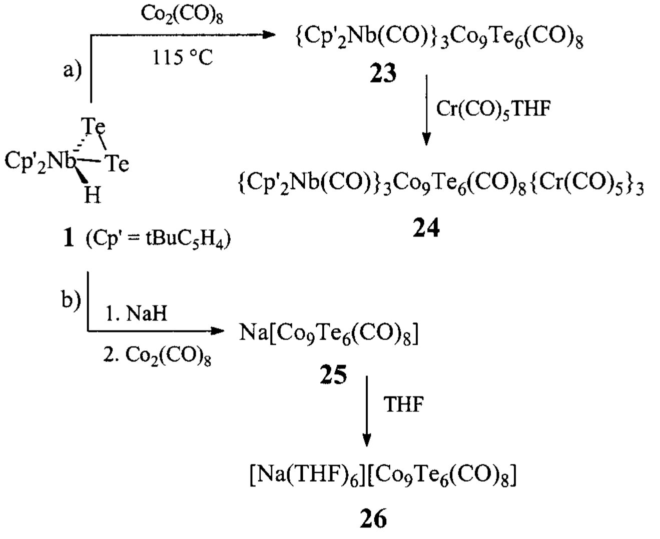
Scheme 7. Schematic summary of the electrochemical studies of the system $[Cp^*{}_2Nb(CO)_2][Co_{11}Te_7(CO)_{10}]/L$ (L = PMe_2Ph); compounds $[Co_{11}Te_7(CO)_{10-m}L_m]^0$ (m = 3, 4, 5) are accessible by synthetic means[55]

CO ligands by PMe_2Ph and the oxidation of the cluster core by one electron do not affect significantly the bond parameters in the $Co_{11}Te_7$ core when compared to the parent cluster anions. This is again in agreement with a *quasi-metallic* electron distribution within the cluster skeleton.

The rich redox chemistry of the $Co_{11}Te_7$ core resembles to some extent the electron-sink behavior of homoleptic carbonylmetal cluster anions.[56] A similar behavior may be expected for the cubic Co_9Te_6 core in **21** (Figure 10). This compound is not available in sufficient amounts (Scheme 5), but if $[(t\text{Bu}C_5H_4)_2Nb(Te_2)H]$ (**1**) is used as starting material instead of **2** the neutral cluster $[\{(t\text{Bu}C_5H_4)_2Nb(CO)\}_3Co_9Te_6(CO)_8]$ (**23**) forms in good yield (Scheme 8a).[57] This product contains a Co_9Te_6 core, to which three 17-electron $(t\text{Bu}C_5H_4)_2Nb(CO)$ fragments are attached by three of the six μ_4-Te ligands. No charge separation into distinct ionic building blocks, as described in Scheme 5, is observed. Interestingly, the reaction seems to proceed at 0 °C in an analogous manner to that of peralkylated **2** (Scheme 5). Accordingly, $[(t\text{Bu}C_5H_4)_2NbTe_2Co_3(CO)_7]$, an analogue of **17**, and $[Co_4Te_2(CO)_{10}]$ (**18**) are formed, although in low yields.[57][58]

For the purpose of crystallization it was necessary to treat **23** with $[Cr(CO)_5THF]$ (Scheme 8a). The central feature of the structure of the resulting cluster **24** is a Co@Co_8 cube. Its faces are bridged by six Te ligands to which three $(t\text{Bu}C_5H_4)_2Nb(CO)$ and three $Cr(CO)_5$ fragments are coordinated in a meridional manner with respect to the Te_6 octahedron (Figure 11).[57] The resulting outer octahedral shell of metal atoms has an average diameter of 11.6 Å, which means an expansion of the inner cubic shell by about 6.7 Å.

A somewhat different result is obtained when **1** is reduced with NaH. It is not yet clear if this reaction proceeds with hydride abstraction or with cleavage of the Te−Te bond. In the subsequent reaction of the obtained solution with $[Co_2(CO)_8]$ at 20 °C dark-brown $Na[Co_9Te_6(CO)_8]$ (**25**) is formed (Scheme 8b). Compound **25** crystallizes with THF as salt **26**, which is composed of $[Co_9Te_6(CO)_8]^-$ and $[Na(THF)_6]^+$ ions in a 1:1 ratio.[59] This means that **26** con-



Scheme 8

Figure 11. Molecular structure of $[\{(tBuC_5H_4)_2Nb(CO)\}_3Co_9Te_6(CO)_8\{Cr(CO)_5\}_3]$ (**24**); two of the $Cr(CO)_5$ fragments, attached at the "free" μ_4-Te ligands, are omitted for the sake of clarity[57]

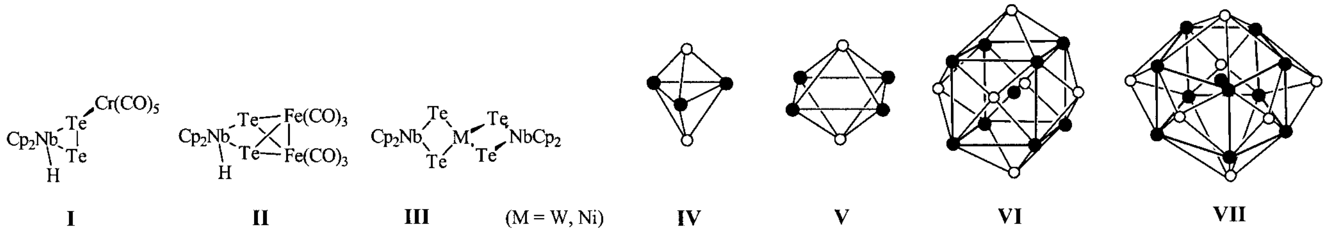
tains an oxidized form (122 MVEs) of the Co_9Te_6 cage with respect to that in **21** (123 MVEs). The metric parameters of both cubes and of the Co@Co_8 cage in **24** (124 MVEs) are very similar. This fact is currently under investigation from a theoretical point of view.

Conclusions

This microreview deals with synthesis and structure of niobocene ditelluride complexes and their application in cluster synthesis. The presence of free electron pairs, the propensity for Te−Te bond cleavage and the ability to eliminate Te^0 or Te^{2-} make them ideal molecular building blocks for the synthesis of polymetallic telluride complexes and clusters. Thus, in reactions with several binary carbonyl transition metal complexes a series of new homo- and heterometallic complexes and cluster compounds are formed, which range from simple adducts to polyhedral cluster frameworks (Scheme 9).

The stepwise build-up of telluride clusters may be facilitated by ligand (CO, Te) cross-transfer from one metal atom to the other. The carbonylniobocene species $[(tBuC_5H_4)_2Nb(CO)]$ and $[Cp^*_2Nb(CO)_2]^+$, the formation of which is directed by the organic substituents, play a decisive role in tuning the electronic properties of the cluster units: Whereas the 17-electron fragment may be directly anchored to the cluster core by Te bridges, the in situ formed 18-electron cation is able to stabilize large and differently charged cluster anions. An outstanding property of clusters derived from all-capped Co@Co_8 (type **VI**) and Co@Co_{10} (type **VII**) polyhedra is their pronounced electron-sponge behavior. Crystal structure analyses allow correlation of cluster charge and bond parameters, and theoretical studies will provide insights into their electronic structures.

It has already been demonstrated that metal telluride complexes may be an important molecular basis for the preparation of binary solid-state phases such as β-CoTe[3b] and NiTe.[3a] Another area of interest may be the extension of polyhedral structures into supramolecular architectures. In this context it was suggested as early as 1985 to combine "discrete clusters into small aggregates" by means of covalent bridges that exist in the solid state.[60] This idea has been stimulated by the observation that the discrete cubic cluster $[Co_8S_6(SPh)_8]^{4-,5-}$ may be considered as a small solubilized fraction of the solid-state structure of pentlandite minerals, in which Co_8S_6 cubes are linked together by octahedral Co centers and sulfide bridges. Very recently it has been observed that octahedral $[Re_6(\mu_2\text{-}Se)_8]^{2+}$ core-containing clusters bearing ligands susceptible for self-organization of functional groups by hydrogen bonds arrange into zigzag chains of hydrogen-bonded cluster polymers.[61] A realization of these ideas with respect to our metal telluride clus-



Scheme 9. Examples of heteropolymetallic telluride complexes (**I−III**) and cobalt telluride cluster frameworks (**IV−VII**; o =Te, • = Co)

ters may envisage the facile CO substitution in the cluster anions in **20** and **22**. Thus, it should be possible to connect individual polyhedra by appropriate bifunctional donor ligands. On the other hand, reaction of the nucleophilic Te vertices with tellurophilic metal cations[2] may lead to the formation of inorganic networks.

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