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Synthesis, molecular structures, Mössbauer and electrochemical investigation of ferrocenyltelluride derivatives: $(Fc_2Te_2)Fe(CO)_3I_2$ $[(CO)_3IFe(\mu\text{-}TeFc)]_2$, $CpFe(CO)_2TeFc$, $CpFe(CO)_2TeX_2Fc$ (X = Br, I) and $CpFe(CO)_2(\mu\text{-}TeFc)Fe(CO)_3I_2$

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ABSTRACT

Depending on the ratio of the starting reagents, the interaction of [FcTeI] with $Fe(CO)_5$ gave complex $(Fc_2Te_2)Fe(CO)_3I_2$ (**1**) bearing an Fc_2Te_2 ligand, or a dimeric complex $[(CO)_3IFe(\mu\text{-}TeFc)]_2$ (**2**). An interaction of equimolar amounts of $[CpFe(CO)_2]_2$ and Fc_2Te_2 under the thermal conditions in toluene afforded $CpFe(CO)_2TeFc$ (**3**). Complex **3** can be easily halogenated at the Te center by elemental bromine and iodine to give monomeric $CpFe(CO)_2TeX_2Fc$ (X = Br (**4**), I (**5**)). Complex **5** can be prepared alternatively via formal insertion of [FcTeI] into Fc–I bond of $CpFe(CO)_2I$. Complex **3** readily substitutes one carbonyl in $Fe(CO)_4I_2$ to give the adduct $CpFe(CO)_2(\mu\text{-}TeFc)Fe(CO)_3I_2$ (**6**).

Introduction

Transition metal tellurides can be obtained by pyrolysis of organotellurium complex precursors incorporating the desired elements in the required ratio. The solid state structures of the precursors could be determined by XRD techniques and such compounds are generally stable in organic solvents, allowing them to be deposited on the various supporting materials. For example the deposition of cluster $(C_8H_{12})PtTe_2Fe_2(CO)_6$ from CH_2Cl_2 on Ketjen Black Carbon and subsequent pyrolysis at 300 °C, followed by elimination of cyclodiene and four CO molecules to give the composition $PtTe_2Fe_2(C)_2(O)_2$, which is a methanol-tolerant nano-sized catalyst for oxygen reduction in the direct methanol fuel cell [1].

We have obtained various inorganic transition metal tellurides starting from transition metal carbonyls with bridging and terminal diphenylditellurium or phenyltelluride ligands.

In the presence of the aromatic fragments in the molecule, we do not observe the formation of carbides and oxides during the thermolyses. For example, all carbonyl groups in the Mo/Ph_2Te_2 complex are eliminated so that Te–Te and Te–Ph bonds of Ph_2Te_2 ligands are cleaved to give polymeric cubane Mo_4Te_4 clusters, which can be subsequently transformed to the known monomeric anionic cyanide cluster [2] (Scheme 1).

Substitution of the phenyl group for ferrocenyl group should have some interesting consequences. Firstly, this led us to introduce

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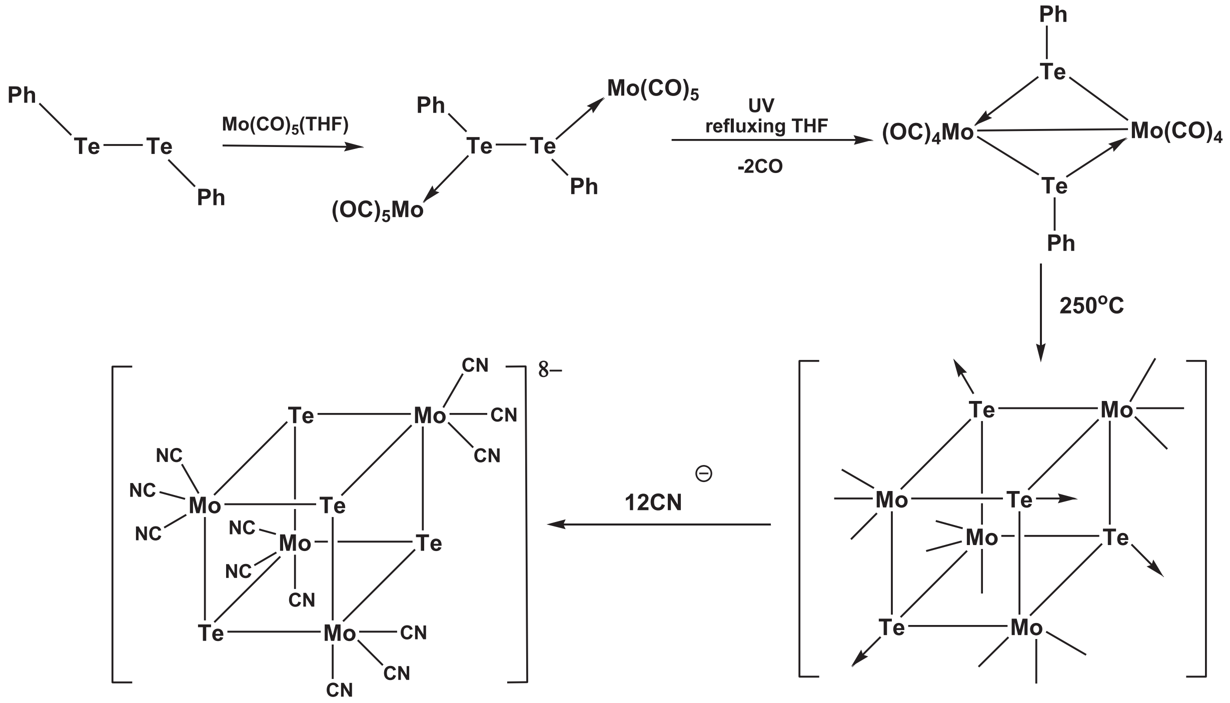


Scheme 1. Formation and thermolyses of Ph_2Te_2 complexes of Mo-carbonyls.

additional iron atoms into a molecule of the precursor. Secondly, the electron-donating ferrocenyl fragment increases the nucleophilicity of the associated tellurium atom. Finally, the ferrocenyl group can be easily oxidized electrochemically or by oxidative agents. Our recent investigation of diferrocenyl–ditelluride complexes of VI group carbonyls demonstrated general similarity with their phenyl congeners, particularly the electron-compensating cleavage of the Te–Te bond during the photochemical decarbonylation (Scheme 2) [3] (Fig. 1).

It was also interesting to compare the reactivity of [FcTeI] towards $Fe(CO)_5$ with that of its phenyl congener [PhTeI] [4] and investigate the decarbonylation of $CpFe(CO)_2TeFc$ and of its use as a possible metalloligand.

Results and discussion

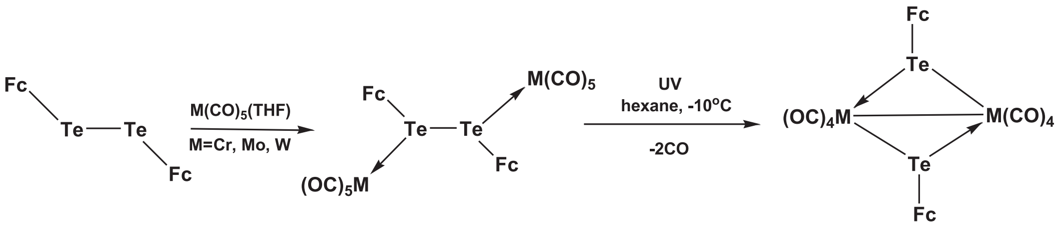
Depending on the ratio of the starting reagents an interaction between $FcTe{-}TeI_2Fc$ and $Fe(CO)_5$ gives the monomeric complex $(Fc_2Te_2)Fe(CO)_3I_2$ (**1**) or the dimeric complex $[(CO)_3IFe(\mu\text{-}TeFc)]_2$ (**2**) if an excess of $Fe(CO)_5$ was used (Scheme 3):

In complex **1** the molecule of diferrocenylditelluride is coordinated only by one tellurium atom completing the octahedral coordination surrounding of the iron atom. The iron–tellurium distance is shortened (Te1–Fe1 2.580(1) Å) as compared to the CRS (2.70 Å) [5], similarly to the rest of known transition metal organotellurides. This shortening is usually rationalized in terms of additional back donation M → Te [6] and is accompanied by the consequent elongation of the Te–Te distance (2.770(1) Å as compared to 2.704–2.721 Å in a “free” Fc_2Te_2 [7,8]. It is interesting that in **1** the “dropping” of Te(2) atom from the cyclopentadienyl plane to the iron atom of the ferrocenyl fragment takes place ($\alpha = 11.8°$). In the dimeric complex **2** (Fig. 2), iodide and bridging telluroferrocenyl ligands were found at the same (as in **1**) distances from the iron centers. The same similarity we have noticed in the pair of their phenyl congeners: $(CO)_3FeI_2(Ph_2Te_2)$ and $[(CO)_3IFeTePh]_2$ [9].

Complex $CpFe(CO)_2TeFc$ **3** (Fig. 3) containing the terminal ferrocenyltelluride ligand instead of the iodine atom was obtained as a brown crystalline product of the thermal interaction between $[Cp(CO)_2Fe]_2$ and Fc_2Te_2, by analogy with the preparation of $CpFe(CO)_2TePh$ [10].

In **3** the Fe–Te distance (2.589(3) Å) is significantly longer as compared to that in $CpFe(CO)_2TePh$ (Fe–Te 2.528 Å), since the additional Fe → Te back donation is reduced because an electron withdrawing phenyl is substituted for electron donating ferrocenyl group.

The cyclic voltammogram (CV) for complex 3 (Fig. 4, curve 1) demonstrates a quasi-reversible one-electron oxidation wave at 0.24 V apparently, arising from the ferrocenyl fragment oxidation, and the quasi-reversible two-electron oxidation wave at 0.76 V,



Scheme 2. Formation and transformation of Fc_2Te_2 – complexes of Cr-, Mo- and W-carbonyls.