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Reduction of (μ_2-Te_2)$Fe_2(CO)_6$ and reaction of the dianion formed with metal dihalides, L_2MCl_2, (L = PPh_3, M = Pt, Pd, Ni; L = C_5H_5, M = Ti; L = Me, n-Bu, M = Sn)

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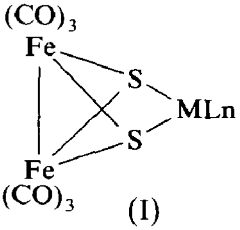
Abstract

Treatment of a THF solution of (μ_2-Te_2)$Fe_2(CO)_6$ with $LiEt_3BH$ at −78°C gives the dianion $[(\mu\text{-}Te)_2Fe_2(CO)_6]^{2-}$. The dianion reacts with the metal dihalides $(PPh_3)_2MCl_2$, M = Pt, Pd, Ni, to give the neutral compounds $(CO)_6Fe_2(\mu_3\text{-}Te)_2M(PPh_3)_2$, with Cp_2TiCl_2 to give $(CO)_6Fe_2(\mu_3\text{-}Te)_2TiCp_2$, or with R_2SnCl_2, R = Me, n-Bu to give $(CO)_6Fe_2(\mu_3\text{-}Te)_2SnR_2$.

Introduction

The compounds $E_2Fe_2(CO)_6$ (E = S, Se, Te) present interesting opportunities for studying the chemical reactivity [1–3]. In addition to the potentially reactive E–E and Fe–Fe bonds, the chalcogen atoms are good sites of reactivity towards electrophiles. Seyferth and co-workers [4] have shown that similarities exist in the reactivities of (μ-S_2)$Fe_2(CO)_6$ and the diorganodisulfides. Both are reduced by alkali metals and undergo nucleophilic S–S cleavage on reaction with simple and complex metal hydrides. The analogy between the organic and the inorganic disulfides has been extended to their behaviour towards coordinatively unsaturated low-valent transition metal species. Addition of the coordinatively unsaturated species into the S–S bond of both acyclic and cyclic organic disulfides is known. Several transition metal species have been shown to add readily across the reactive S–S bond in (μ-S_2)$Fe_2(CO)_6$ to form mixed metal complexes of the type $(CO)_6Fe_2(\mu_3\text{-}S)_2MLn$ (I) [5]. A high yield route based on complex hydride has been



(I)

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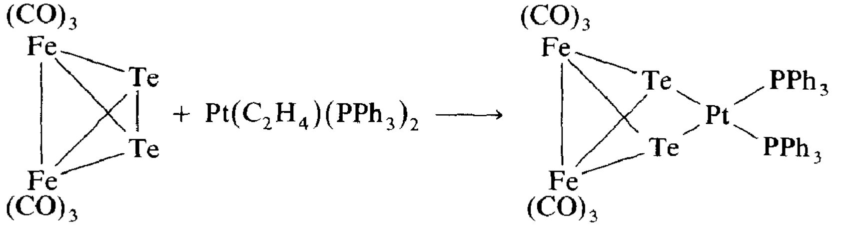
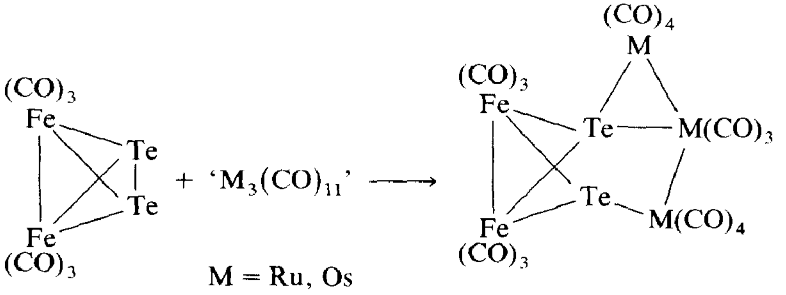
reported for the preparation of $[(\mu\text{-}S_2)Fe_2(CO)_6]^{2-}$, which has been shown to serve as a useful reagent for the synthesis of complexes of type I by reaction with metal dihalides [4].

We have been interested in the chemistry of $(\mu\text{-}Te_2)Fe_2(CO)_6$. Like the S–S bond in $(\mu\text{-}S_2)Fe_2(CO)_6$, the Te–Te bond in $(\mu\text{-}Te_2)Fe_2(CO)_6$ is very reactive and readily adds coordinatively unsaturated, low-valent, metal species to form complexes of type I ([6]. We recently showed that polynuclear metal carbonyl units can also be added across Te–Te bonds to give high nuclearity clusters in which the tellurium bridges the iron atom and the adding metal atom [7]. The high reactivity of the Te–Te bond in $(\mu_2\text{-}Te_2)Fe_2(CO)_6$ is evident from its reaction with $Ru_3(CO)_{12}$ and $Os_3(CO)_{11}(NCMe)$. Both of these reagents react at room temperature to give $Fe_2M_3(\mu_4\text{-}Te)(\mu_3\text{-}Te)(CO)_{17}$ (M = Ru, Os respectively) clusters [8]. Diaryl ditellurides react with low valent metal species to form complexes in which the metal species have inserted into the Te–Te bonds [9]. The organic ditellurides undergo reduction in the presence of common reducing agents to give RTe^- [10], which react readily with metal halide species, $LnMCl_m$ to give the neutral compounds $LnM(TeR)_m$ [11]. Such reductions, however, have not been studied for the inorganic ditellurides. Here, we report our studies on the reduction of $(\mu_2\text{-}Te_2)(CO)_6Fe_2$ and the reaction of the reactive dianion $[(\mu_2\text{-}Te_2)(CO)_6Fe_2]^{2-}$ made from the halides of nickel, palladium, platinum, tin and titanium.



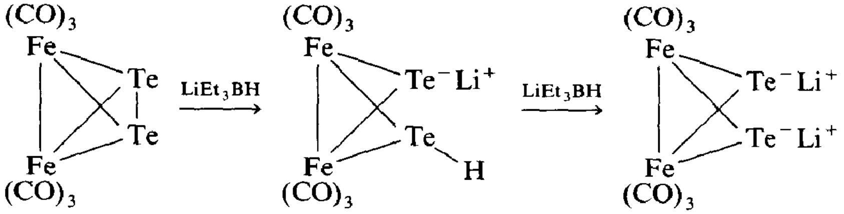


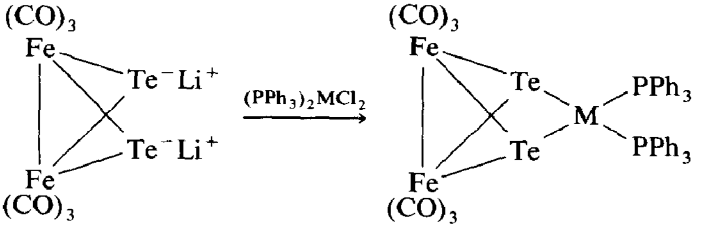
$$RTeTeR \xrightarrow{\text{Reduction}} RTe^- \xrightarrow{LnMCl_m} LnM(TeR)_m$$

Results and discussion

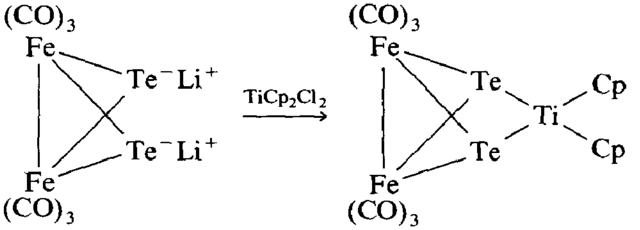
The addition of one molar equivalent of lithium triethylborohydride to the orange-red THF solution of $(\mu_2\text{-}Te_2)Fe_2(CO)_6$ at −78°C caused an immediate colour change to deep blue. When a second equivalent of the hydride was added, the solution turned dark red and the formation of the dianion $[(\mu_2\text{-}Te_2)Fe_2(CO)_6]^{2-}$

was confirmed from the formation of the neutral compounds of type I by addition of $LnMCl_2$ to the reaction mixture. The colour changes suggest that the reaction proceeds in two steps; the first corresponds to the formation of the anionic species, and the second to that of the dianion. A similar two step process has been reported for the formation of $[(\mu_2\text{-}S_2)Fe_2(CO)_6]^{2-}$ from the reaction of $(\mu_2\text{-}S_2)Fe_2(CO)_6$ and lithium triethylborohydride at low temperature. The dianion was found to be a useful reagent for the synthesis of multinuclear metal–tellurium complexes of type I. When the dianion solution was treated with $M(PPh_3)_2Cl_2$ (M = Ni, Pd, Pt), the neutral mixed metal complexes $(CO)_6Fe_2(\mu_3\text{-}Te)_2M(PPh_3)_2$ (II–IV) were formed in good yields. These mixed metal complexes were identified by comparison of their infrared spectra in the carbonyl region with those reported. The same compounds have previously been made from $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ and $M(PPh_3)_4$ in somewhat lower yields [6]. Addition of titanocene dichloride to the dianionic solution at −78° C resulted in the formation of the neutral compound $(CO)_6Fe_2(\mu_3\text{-}Te)_2TiCp_2$ (V) as characterised on the basis of infrared and ^1H NMR spectroscopy. The infrared spectrum of V in the carbonyl region shows bands at 2051 (m), 2016 (vs), 1976 (s) in a pattern typical of compounds of type I. The ^1H NMR spectrum in $CDCl_3$ shows a single peak due to the protons of the two Cp groups at 3.75 ppm





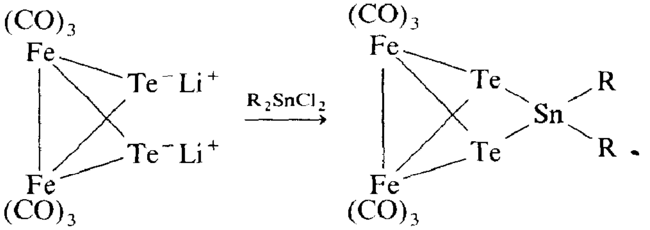
(II: M = Pt;
III: M = Pd;
IV: M = Ni)



(V)

(relative to TMS), which is 2.85 ppm upfield from the signal observed for the protons in the starting material – Cp_2TiCl_2. In contrast to compounds II–IV, compound V is markedly less stable; it slowly decomposes in solution, and all attempts to isolate it as a pure solid have so far been unsuccessful. The telluronium analogous of the dithiolene chelates have been prepared by the same procedure and show similar sensitivity towards air, moisture and light [12].

The dianion was found to react with main group metal halides with equal ease. It readily reacts with R_2SnCl_2 (R = Me, n-Bu) to give the compounds $(CO)_6Fe_2(\mu_3\text{-}Te)_2SnR_2$ (VI, VII). Both of these were characterised by infrared and ^1H NMR



(VI: R = Me;
VII: R = *n*-Bu)

spectroscopy. The infrared spectra showed carbonyl stretching frequencies at 2053 (m), 2020 (vs), 1981 (s) in a pattern typical of compounds of type I. The ^1H NMR spectrum of VI showed a single peak for the two equivalent methyl groups. VI and VII are sufficiently stable in solution, but attempts to recrystallise the product resulted in an oily mass.

The results described here show a similarity between the reactivity of $(\mu_2\text{-}Te_2)Fe_2(CO)_6$ and organic ditellurides. The high yield, complex hydride route for the preparation of $[(\mu_2\text{-}Te_2)Fe_2(CO)_6]^{2-}$ should allow fuller development of metal tellurium complexes.

Experimental

All operations were carried out under pure argon or nitrogen with the use of standard Schlenk techniques. The solvents were thoroughly purified, dried, and distilled under inert atmosphere immediately before use. The compound $(\mu_2\text{-}Te_2)Fe_2(CO)_6$ was prepared as previously described [3]. All other reagents were purchased and used as received. Proton nuclear magnetic resonance spectra were recorded at 300 MHz on a Varian Associates spectrometer. Infrared spectra were recorded on a Nicolet 5DXB Fourier Transform spectrometer. Solution samples were contained in 0.1-mm pathlength sodium chloride solution cells.

Reactions of $[(\mu_2\text{-}Te_2)Fe_2(CO)_6]^{2-}$ *

(a) With cis-bis(triphenylphosphine)platinum dichloride. A 200-ml Schlenk flask equipped with a rubber septum and a stir-bar was charged with 0.108 g (0.2 mmol) of $(\mu_2\text{-}Te_2)Fe_2(CO)_6$ and then flushed with nitrogen. Tetrahydrofuran (75 ml) was

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* Prepared by reduction of $(\mu_2\text{-}Te_2)Fe_2(CO)_6$ with $LiEt_3BH$.

added and the reaction solution cooled to −78° C. $LiEt_3BH$ (5.0 ml of 1.0 *M*) in THF (Aldrich) was added dropwise by syringe. The reaction solution turned from orange red to deep blue when one molar equivalent was added. Addition of the second equivalent of $LiEt_3BH$ caused a change in colour to dark-red. To this was added 0.158 g (0.2 mmol) of solid *cis*-$(PPh_3)_2PtCl_2$ and the reaction mixture was left to warm to room temperature while being stirred for 2 h. The red solution was filtered through a celite pad and evaporation of the solvent from the filtrate gave a dark-red residue. Chromatography of the residue on a silica gel column (20% dichloromethane/hexane) gave an air stable red solid, which was identified as $(CO)_6Fe_2(\mu_3\text{-}Te)_2Pt(PPh_3)_2$; Yield 0.14 g (88%), IR (hexane) in the carbonyl region (cm^{-1}): 2031 (s), 1991 (s), 1955 (s), 1947 (sh).

(b) With cis-bis(triphenylphosphine)palladium dichloride. The dianion solution was prepared as above. To 0.2 mmol of the reagent solution, maintained at −78° C was added 0.138 g (0.2 mmol) of solid *cis*-$(PPh_3)_2PdCl_2$. The reaction mixture was left to warm to room temperature, and was stirred for an additional one hour. Evaporation of the solvent in vacuo and chromatography of the residue on silica gel column with 30% dichloromethane/hexane yielded a single product, identified as $(CO)_6Fe_2(\mu_3\text{-}Te)_2Pd(PPh_3)_2$; yield 0.13 g (78%). IR (dichloromethane) in the carbonyl region (cm^{-1}): 2033 (s), 1991 (s), 1958 (s), 1948 (sh).

(c) With bis(triphenylphospine)nickel dichloride. To 0.2 mmol of the dianion solution, prepared as above, was added 0.11 g (0.2 mmol) of solid $Ni(PPh_3)_2Cl_2$. The reaction mixture was stirred for 1 h at room temperature. Removal of the solvent in vacuo and filtration chromatography of the red residue on a neutral alumina column with hexane as the eluant gave the red band of the product, $(CO)_6Fe_2(\mu_3\text{-}Te)_2Ni(PPh_3)_2$; Yield 0.05 g (29%). IR (hexane) in the carbonyl region (cm^{-1}): 2041 (m), 2016 (s), 1990 (m).

(d) With titanocene dichloride. To a solution containing 0.2 mmol of the dianion was added 0.048 g (0.2 mmol) of Cp_2TiCl_2, and the mixture was stirred at −78° C for one hour. The solution was left to warm to room temperature and the solvent was removed in vacuo. The red residue obtained was chromatographed on a silica gel column with hexane as eluant to afford to single red product, identified as $(CO)_6Fe_2(\mu_3\text{-}Te)_2TiCp_2$; IR (dichloromethane) in the carbonyl region (cm^{-1}): 2051 (m), 2016 (vs), 1976 (s). ^1H NMR ($CDCl_3$) δ 3.75 ppm (s, Cp).

(e) With dimethyltin dichloride. The dianion solution was prepared as above and to a 0.2 mmol portion of it was added 0.044 g (0.2 mmol) of Me_2SnCl_2. The reaction mixture was stirred at −78° C for 45 min and then left to warm to room temperature. Chromatographic work-up as above yielded a single red solid, which was identified as $(CO)_6Fe_2(\mu_3\text{-}Te)_2Sn(CH_3)_2$; Yield 0.06 g (47%). IR (hexane) in the carbonyl region (cm^{-1}): 2053 (m), 2020 (vs), 1981 (s). ^1H NMR ($CDCl_3$) δ 1.26 ppm (s with Sn satellites, $^2J(^{117/119}Sn\text{–}H)$ 68/72 Hz).

(f) With dibutyltin dichloride. To 0.2 mmol of the dianion solution, prepared as described above, 0.154 g (0.2 mmol) of $(n\text{-}Bu)_2SnCl_2$ was added, the solution was stirred for two hours, and chromatographic work-up as described above, gave a single product, identified as $(CO)_6Fe_2(\mu_3\text{-}Te)_2Sn(n\text{-}Bu)_2$; yield 0.05 g (35%). IR (hexane) in the carbonyl region (cm^{-1}): 2053 (m), 2020 (vs), 1981 (s). ^1H NMR ($CDCl_3$): δ 0.96 ppm (t, with weak Sn satellites, $Sn\text{-}CH_2CH_2CH_2CH_3$), 1.42 ppm (m, $CH_2CH_2CH_2CH_3$), δ 1.82 ppm (m, $CH_2CH_2CH_2CH_3$ and $CH_2CH_2CH_2CH_3$ overlapping).

Acknowledgements

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