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Mixed chalcogen carbonyl compounds: synthesis and characterisation of $(CO)_6Fe_2(\mu_3\text{-}Se)(\mu_3\text{-}Te)Pt(PPh_3)_2$ and $Fe_3(CO)_7(PPh_3)_2(\mu_3\text{-}Se)(\mu_3\text{-}Te)$

Pradeep Mathur *, Debojit Chakrabarty and Md. Munkir Hossain
Chemistry Department, Indian Institute of Technology, Powai, Bombay 400 076 (India)

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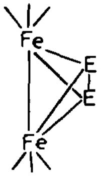
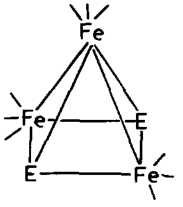
Abstract

An improved method for the isolation of pure $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ and $Fe_2(CO)_6(\mu\text{-}SeTe)$ has been developed. The mixed metal mixed chalcogenide complex $(CO)_6Fe_2(\mu_3\text{-}Se)(\mu_3\text{-}Te)Pt(PPh_3)_2$ is formed exclusively on treatment of $Fe_2(CO)_6(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ with $Pt(C_2H_4)(PPh_3)_2$, or along with $Fe_3(CO)_7(PPh_3)_2(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ when $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ is treated with $Pt(PPh_3)_4$. With PPh_3, $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ forms an adduct, $(CO)_6Fe_2(\mu_3\text{-}Se)(\mu_3\text{-}Te)Fe(CO)_3PPh_3$.

Introduction

By virtue of the diverse bonding modes exhibited by chalcogen ligands in clusters, they have been recognised as very useful bridging ligands in cluster growth reactions [1]. Although the sulfido ligand has been by far the most extensively used for this purpose [2], recent work on the use of the large chalcogens suggests that these may give rise to clusters with reactivity and structural patterns different from those of the sulfido clusters [3]. Two classes of compounds have served as convenient starting materials for cluster expansion purposes: the dinuclear $Fe_2(CO)_6(\mu\text{-}E_2)$ [4] and the trinuclear $M_3(CO)_9(\mu_3\text{-}E)_2$, ($E = S$, Se, Te; $M = Fe$, Ru, Os) [5].





The former have reactive E–E bonds across which mononuclear and polynuclear metal fragments can readily be added. In the second type of compounds, the lone pairs of electrons on E can act as initial points of contact for adding coordinatively unsaturated groups. While the reactivity of the dinuclear compound is independent of the nature of E, differences are observed in the reactivity of $M_3(CO)_9(\mu_3\text{-}E)_2$ for

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different metals and chalcogens. The most noticeable differences occur between compounds containing E = S or Se and E = Te, and also between M = Fe and M = Ru or Os. Differences between Fe and Ru/Os containing compounds arise primarily due to the difference in the M–M bond strengths. There are many examples which show that all $M_3(CO)_9(\mu_3\text{-}E)_2$ compounds can engage in metal addition reactions to give higher nuclearity clusters [5]. However, for the M = Fe compounds, generally, metal–metal exchange reactions are more common than when M = Ru or Os. When E = S or Se, $M_3(CO)_9(\mu_3\text{-}E)_2$ undergo substitution by Lewis bases primarily by first order processes whereas when E = Te, substitution occurs by a second order process [3].

We have been interested in looking at the reactivities of compounds containing different chalcogen ligands, and here we present results on $Fe_2(CO)_6(\mu\text{-}SeTe)$ and $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$.

Results and discussion

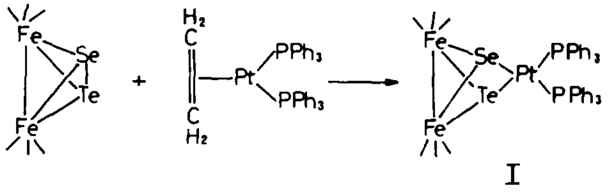
The chalcogen containing clusters, $Fe_3(CO)_9(\mu_3\text{-}E)_2$ (E = S, Se or Te) are obtainable from the reaction of EO_3^{2-} with $Fe(CO)_5$/KOH in methanol. The mixed chalcogen compound $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ is reported to be formed when a mixture of TeO_3^{2-} and SeO_3^{2-} are used [6]. This method also forms, in addition, $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ and $Fe_3(CO)_9(\mu_3\text{-}Se)_2$, and the separation of the three compounds poses much difficulty. We find that it is more convenient to treat the mixture of the three compounds with NaOMe, followed by acidification, which converts all three to the respective dinuclear derivatives, $Fe_2(CO)_6(\mu\text{-}EE')$ (E = E′ = Se; E = E′ = Te; E = Se, E′ = Te). Separation of the three dinuclear compounds is relatively much easier and $Fe_2(CO)_6(\mu\text{-}SeTe)$ can be obtained in pure form in good yields. Visible light irradiation of hexane solution containing $Fe_2(CO)_6(\mu\text{-}SeTe)$ and $Fe(CO)_5$ forms $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ almost quantitatively (Scheme 1).

Room temperature stirring of a benzene solution of $Fe_2(CO)_6(\mu\text{-}SeTe)$ and $Pt(C_2H_4)(PPh_3)_2$ forms the mixed metal mixed chalcogen complex $(CO)_6Fe_2(\mu_3\text{-}Se)(\mu_3\text{-}Te)Pt(PPh_3)_2$(I) in almost quantitative yield (Scheme 2). Compound I has been characterised by comparison of its infrared spectrum in the carbonyl region with those of the previously reported $(CO)_6Fe_2(\mu_3\text{-}E)_2Pt(PPh_3)_2$ [7] and on the basis of microanalytical data. The formation of I involves the addition of the coordinatively unsaturated '$Pt(PPh_3)_2$' group across the interchalcogen bond in $Fe_2(CO)_6(\mu\text{-}SeTe)$, thereby relieving some strain in the FeSeTeFe ring.

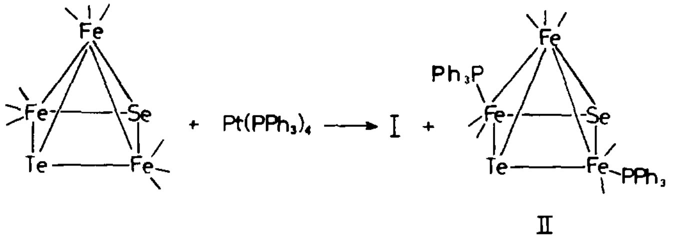
The trinuclear compound, $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3Te)$ remains unreactive towards $Pt(C_2H_4)(PPh_3)_2$ in benzene solvent for up to 5 hours. It does however, react with $Pt(PPh_3)_4$ at room temperature to form I, along with some $Fe_3(CO)_7(PPh_3)_2(\mu_3\text{-}$

$$\begin{tikzcd}
Fe(CO)_5 \arrow[r, "(i)"] & Fe_3(CO)_9(\mu_3\text{-}E)(\mu_3\text{-}E') \arrow[d, "(ii)"] \\
 & Fe_2(CO)_6(\mu\text{-}EE')
\end{tikzcd}$$

Scheme 1. E = E′ = Se, Te; E = Se, E′ = Te (i) KOH, EO_3^{2-}, H^+, or KOH, $EO_3^{2-}/E'O_3^{2-}$, H^+ (ii) NaOMe, H^+



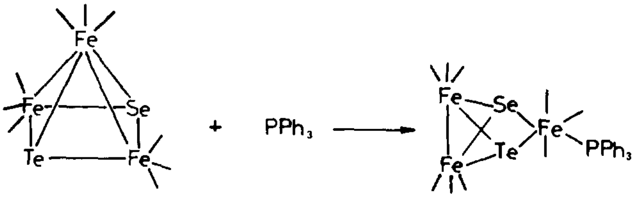
Scheme 2



Scheme 3

Se)(μ_3-Te) (Scheme 3). Compound II has been characterised by comparison of its infrared spectrum with that of the structurally characterised $Fe_3(CO)_7(PPh_3)_2(\mu_3$-$Te)_2$ [8], and on the basis of microanalytical data.

Formation of $(CO)_6Fe_2(\mu_3$-$Te)_2Pt(PPh_3)_2$ from the reaction of $Fe_3(CO)_9(\mu_3$-$Te)_2$ and $Pt(PPh_3)_4$ proceeds via an initial formation of the adduct $(CO)_6Fe_2(\mu_3$-$Te)_2Fe(CO)_3(PPh_3)$, followed by substitution of the $Fe(CO)_3(PPh_3)$ group by $Pt(PPh_3)_2$ group. On the other hand, adduct formation is not observed when $Fe_3(CO)_9(\mu_3$-$Se)_2$ is treated with $Pt(PPh_3)_4$ to give $(CO)_6Fe_2(\mu_3$-$Se)_2Pt(PPh_3)_2$. The mixed chalcogen compound $Fe_3(CO)_9(\mu_3$-Se)(μ_3-Te) seems to be more similar to the $Fe_3(CO)_9(\mu_3$-$Te)_2$ than $Fe_3(CO)_9(\mu_3$-$Se)_2$, because when $Fe_3(CO)_9(\mu_3$-Se)(μ_3-Te) is treated with PPh_3 and the solution stirred for 1 hour, the adduct, $(CO)_6Fe_2(\mu_3$-Se)(μ_3-Te)$Fe(CO)_3(PPh_3)$ and $Fe_3(CO)_7(PPh_3)_2(\mu_3$-Se)($\mu_3$-Te) are formed (Scheme 4). The mixed chalcogen adduct, $(CO)_6Fe_2(\mu_3$-Se)(μ_3-Te)$Fe(CO)_3$ (PPh_3) has been characterised on the basis of infrared spectral comparison with the tellurium analogue $(CO)_6Fe_2(\mu_3$-$Te)_2Fe(CO)_3(PPh_3)$ [3c]. In solution, $(CO)_6Fe_2$ (μ_3-Se)(μ_3-Te)$Fe(CO)_3(PPh_3)$ slowly converts to $Fe_3(CO)_7(PPh_3)_2(\mu_3$-Se)($\mu_3$-Te). If the stirring of solution containing $Fe_3(CO)_9(\mu_3$-Se)(μ_3-Te) and PPh_3 is continued for 5 hours, $Fe_3(CO)_7(PPh_3)_2(\mu_3$-Se)($\mu_3$-Te) is the sole product formed. Curiously, the monosubstituted compound, $Fe_3(CO)_8(PPh_3)(\mu_3$-Se)(μ_3-Te) is not observed. Characterisation of $Fe_3(CO)_7(PPh_3)_2(\mu_3$-Se)($\mu_3$-Te) has been made by comparison



Scheme 4

of its infrared spectrum with $Fe_3(CO)_7(PPh_3)_2(\mu_3\text{-}Te)_2$ and on the basis of microanalytical data.

We are presently investigating the possibility of using $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ for preparing the mixed chalcogen analogues of the electron deficient octahedral clusters, $M_4(CO)_{11}(\mu_4\text{-}E)_2$ [2d,5f].

Experimental

All reactions were carried out under argon using standard Schlenk techniques. The solvents were purified and dried before use. $Pt(PPh_3)_4$ and $Pt(C_2H_4)(PPh_3)_2$ (Aldrich) were used as received. Elemental analyses were carried out on a Carlo Erba automatic analyser and infrared spectra (Table 1) were recorded with a Nicolet 5DXB FTIR spectrometer.

Preparation of $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$

A solution of Na_2TeO_3 (0.6 g, 2.75 mmol) and Na_2SeO_3 (0.48 g, 2.75 mmol) in 75 mL of H_2O was added to a flask containing an ice cooled solution prepared from 1.1 mL (8.25 mmol) of $Fe(CO)_5$, 4 mL of 50% aq. KOH and 15 mL of MeOH. After stirring for 0.5 h at room temperature the reaction mixture was cooled to 0 °C and acidified with 12 *M* HCl. The resulting black precipitate was filtered in air, washed with distilled water and dried in vacuo. The solid was then extracted with four 25 mL portions of CH_2Cl_2. The combined extracts were filtered and evaporated to dryness. The mixture was added to a solution of NaOMe (3g Na in 400 mL MeOH) and the mixture was stirred at room temperature until complete dissolution had taken place. The solution was diluted with hexane (100 mL) and water (100 mL) and acidified with 12 *M* HCl. After separation of the layers, the aqueous phase was further extracted with hexane and the combined organic extracts were washed with H_2O and dried over anhydrous Na_2SO_4. The organic fraction was concentrated to 10 mL. Flash chromatography of the reaction mixture on silica gel column separated $Fe_2(CO)_6(\mu\text{-}Se_2)$ and $Fe_2(CO)_6(\mu\text{-}SeTe)$ as the major products, followed by a trace amount of $Fe_2(CO)_6(\mu\text{-}Te_2)$. To a hexane solution of $Fe_2(CO)_6(\mu\text{-}SeTe)$ was added $Fe(CO)_5$ and irradiation with a 40 watt light bulb for 15 minutes yielded $Fe_3(CO)_9(\mu_3\text{-}SeTe)$. Overall yield based on $Fe(CO)_5$: 0.43 g, 24%.

Reaction of $Fe_2(CO)_6(\mu\text{-}SeTe)$ with $Pt(C_2H_4)(PPh_3)_2$

To a benzene solution (15 mL) of $Fe_2(CO)_6(\mu\text{-}SeTe)$ (0.05 g, 0.1 mmol) was added $Pt(C_2H_4)(PPh_3)_2$ (0.08 g, 0.1 mmol) and the reaction mixture was stirred at room temperature for 4 hours. The solvent was removed in vacuo and the residue subjected to chromatographic work-up on a silica gel column. Elution with hexane/dichloromethane (80/20) afforded the red $(CO)_6Fe_2(\mu_3\text{-}Se)(\mu_3\text{-}Te)Pt(PPh_3)_2$. Yield: 0.12 g, 92%. Analysis: Calculated for $C_{42}H_{30}O_6P_2Fe_2PtSeTe$: C 41.86, H 2.50; Found: C 41.81, H 2.53%.

Reaction of $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ with $Pt(PPh_3)_4$

A benzene solution (15 mL) containing $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ (0.06 g, 0.1 mmol) and $Pt(PPh_3)_4$ (0.125 g, 0.1 mmol) was stirred at room temperature for 5 hours. The solvent was removed in vacuo and the residue was chromatographed on a silica gel column. Elution with hexane/dichloromethane (80/20) separated the

Table 1

Infrared spectral data in the carbonyl region (in hexane solution unless otherwise indicated)

Compound	ν(CO) (cm^{-1})
$Fe_2(CO)_6(\mu_2\text{-}SeTe)$	2073(s), 2033(vs), 1998(vs)
$Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$	2052(vs), 2034(s), 2011(s)
$Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)PPh_3$	2061(m), 2046(s), 2020(vs), 2002(m), 1984(m), 1968(w), 1953(w)
$(CO)_6Fe_2(\mu_3\text{-}Se)(\mu_3\text{-}Te)Pt(PPh_3)_2$ [a]	2036(vs), 1996(vs), 1959(s), 1951(s,sh)
$Fe_3(CO)_7(PPh_3)_2(\mu_3\text{-}Se)(\mu_3\text{-}Te)$	2061(s), 2053(w), 2023(vs), 2002(vs), 1980(w), 1946(s)

[a] In dichloromethane solution.

red $(CO)_6Fe_2(\mu_3\text{-}Se)(\mu_3\text{-}Te)Pt(PPh_3)_2$ (yield: 0.08 g, 70%) from $Fe_3(CO)_7(PPh_3)_2(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ (yield: 0.02 g, 21%; analysis: calculated for $C_{43}H_{30}O_7P_2FeSeTe$: C 47.23, H 2.76; found C 46.94, H 3.18%).

Reaction of $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ with PPh_3

A benzene solution (15 mL) of $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ (0.06 g, 0.1 mmol) and PPh_3 (0.03 g, 0.1 mmol) was stirred at room temperature for 1 hour. The solvent was evaporated off and chromatography of the residue on silica gel column using hexane/dichloromethane (80/20) separated the following bands in order of elution: $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$, $Fe_3(CO)_7(PPh)_3(\mu_3\text{-}Se)(\mu_3\text{-}Te)$, and $(CO)_6Fe_2(\mu_3\text{-}Se)(\mu_3\text{-}Te)Fe(CO)_3(PPh_3)$. 1

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