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Mixed chalcogen carbonyl compounds

IV *. Reactivity of $Fe_2(CO)_6(\mu\text{-STe})$ and $Fe_3(CO)_9(\mu_3\text{-S})(\mu_3\text{-Te})$ towards coordinatively unsaturated species

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Abstract

Using $Fe_2(CO)_6(\mu\text{-STe})$ and $Fe_3(CO)_9(\mu_3\text{-S})(\mu_3\text{-Te})$ for the addition of coordinatively unsaturated species, the following new mixed metal, mixed chalcogen compounds have been obtained: $Fe_2(CO)_6(\mu_3\text{-S})(\mu_3\text{-Te})M(PPh_3)_2$ (M = Pt, Pd), $Fe_2Ru(CO)_9(\mu_3\text{-S})(\mu_3\text{-Te})$ and $Fe_{4-x}Ru_x(CO)_{11}(\mu_4\text{-S})(\mu_4\text{-Te})$ ($x = 0\text{–}2$). The formation of the triphenylphosphine derivatives, $Fe_3(CO)_{9-x}(PPh_3)_x(\mu_3\text{-S})(\mu_3\text{-Te})$ ($x = 1, 2$) and $Fe_3(CO)_9(PPh_3)(\mu_3\text{-S})(\mu_3\text{-Te})$ are also reported.

Introduction

The use of compounds of the form $Fe_2(CO)_6(\mu\text{-EE})$ and $Fe_3(CO)_9(\mu_3\text{-E})_2$, where E = S, Se or Te for the synthesis of new mixed metal complexes has been the subject of much interest in recent times [1]. Easy accessibility to the mixed chalcogen derivatives, $Fe_2(CO)_6(\mu\text{-EE}')$ and $Fe_3(CO)_9(\mu_3\text{-E})(\mu_3\text{-E}')$, where $E \neq E'$ has now provided an opportunity to investigate the contrasting influence of the bridging chalcogen ligands in metal carbonyl complexes [2]. In previous reports, we have described the chemistry of some complexes containing the mixed Se, Te bridges [2,3]. In general, the dinuclear $Fe_2(CO)_6(\mu\text{-SeTe})$ was demonstrated to add several coordinatively unsaturated metal species across the Se–Te bond to form open mixed metal, mixed chalcogen complexes, and to the μ_3-Se and μ_3-Te atoms in $Fe_3(CO)_9(\mu_3\text{-Se})(\mu_3\text{-Te})$ to form new tetranuclear, mixed chalcogen clusters which are electron deficient according to the 18-electron rule. We have extended the study of mixed chalcogen carbonyl complexes to the S, Te system, and here we report on the chemistry of $Fe_2(CO)_6(\mu\text{-STe})$ (Scheme 1) and $Fe_3(CO)_9(\mu_3\text{-S})(\mu_3\text{-Te})$ (Scheme 2) towards coordinatively unsaturated species.

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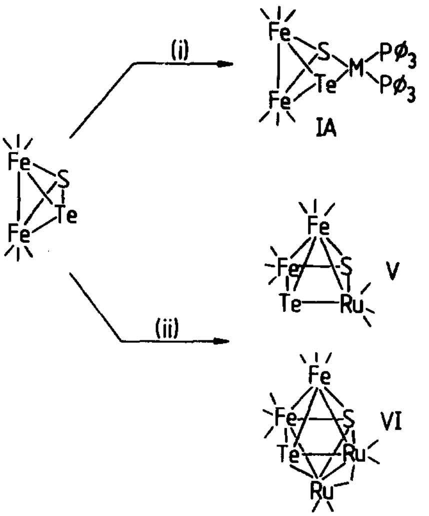
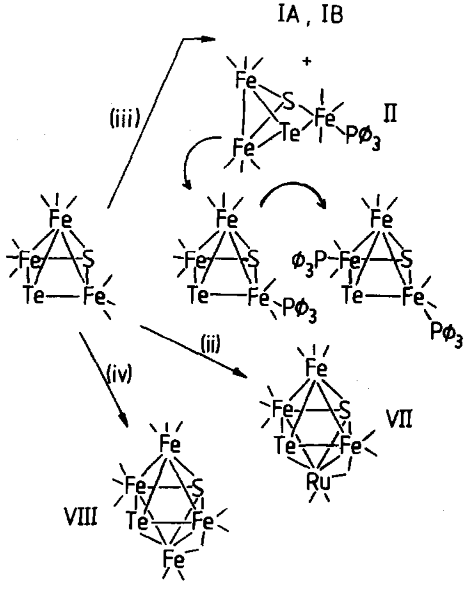
[*] For Part III, see ref. 8.

Results and discussion

The mixed chalcogenide compounds, $Fe_2(CO)_6(\mu\text{-STe})$ and $Fe_3(CO)_9(\mu_3\text{-S})(\mu_3\text{-Te})$, were obtained in pure form using the general method reported earlier for preparing $Fe_2(CO)_6(\mu\text{-SeTe})$ and $Fe_3(CO)_9(\mu_3\text{-Se})(\mu_3\text{-Te})$ [2]. When $Pt(C_2H_4)(PPh_3)_2$ was added to a solution containing $Fe_2(CO)_6(\mu\text{-STe})$, and the



Scheme 1. Reactions of $Fe_2(CO)_6(\mu\text{-STe})$; (i) $M(C_2H_4)(PPh_3)_2$, M = Pt; (ii) $Ru(C_2H_4)(CO)_4$.



Scheme 2. Reactions of $Fe_3(CO)_9(\mu_3\text{-S})(\mu_3\text{-Te})$; (ii) $Ru(C_2H_4)(CO)_4$; (iii) $M(PPh_3)_4$, M = Pt, Pd; (iv) $Fe(CO)_5$, photolysis.

Table 1

Infrared carbonyl stretching frequencies

Compound	Solvent [a]	ν(CO) (cm^{-1})
$Fe_2STe(CO)_6$	b	2075(m), 2036(s), 2000(s)
$Fe_2Pt(CO)_6STe(PPh_3)_2$ (IA)	a	2039(s), 1998(s), 1960(m), 1951(m,sh)
$Fe_2Pd(CO)_6STe(PPh_3)_2$ (IB)	a	2040(s), 1999(s), 1964(m), 1952(m,sh)
$Fe_3STe(CO)_9(PPh_3)$ (II)	a	2072(w), 2052(m), 2043(s), 2032(w,sh), 2011(m), 1995(w,sh)
$Fe_3STe(CO)_8(PPh_3)$ (III)	b	2065(m), 2027(s), 2005(vs), 2001(vs,sh), 1948(w)
$Fe_3STe(CO)_7(PPh_3)_2$ (IV)	a	2030(m), 1995(s,sh), 1988(vs), 1972(s), 1950(w,sh), 1943(m)
$Fe_2RuSTe(CO)_9$ (V)	b	2095(w), 2064(vs), 2056(w), 2049(w), 2036(vs), 2028(w), 2012(m), 1968(w,br)
$Fe_2Ru_2STe(CO)_{11}$ (VI)	a	2085(w), 2043(vs), 2012(w,sh), 1843(w), 1839(w)
$Fe_3RuSTe(CO)_{11}$ (VII)	a	2087(w), 2044(vs0, 2024(m,sh), 2007(w,sh), 1999(w,sh), 1837(w), 1826(w)
$Fe_4STe(CO)_{11}$ (VIII)	a	2082(w), 2035(vs), 2018(m,sh), 1997(w,sh), 1833(w)

[a] a, dichloromethane; b, hexane.

mixture stirred at room temperature, the mixed metal compound, $(CO)_6Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)Pt(PPh_3)_2$ (IA) was obtained as the sole product. Compound IA belongs the the general class of mixed metal compounds of the form $(CO)_6Fe_2(\mu_3\text{-}E)_2M(PPh_3)_2$, (E = S, Se or Te; M = Ni, Pd or Pt) [4], all of which display a characteristic carbonyl stretching pattern consisting of three strong bands and one shoulder in their infrared spectra. A useful feature of their infrared spectra is the regular decrease in the stretching frequencies of the corresponding bands along the series E = S, Se, Te. Accordingly, the stretching frequencies of IA lie between those of $(CO)_6Fe_2(\mu_3\text{-}S)_2Pt(PPh_3)_2$ and $(CO)_6Fe_2(\mu_3\text{-}Te)_2Pt(PPh_3)_2$ (Table 1). Elemental analysis confirmed the molecular formula of IA. $C_{42}H_{30}O_6P_2Fe_2PtSTe$ calc.: C, 43.5; H, 2.61. Found: C, 43.2; H, 2.96%. When $Pd(PPh_3)_4$ was used as a source of the coordinatively unsaturated $Pd(PPh_3)_2$ species, the mixed metal compound, $(CO)_6Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)Pd(PPh_3)_2$ (IB) was obtained, which was characterised by infrared spectral comparison and by elemental analysis. (calculated for $C_{42}H_{30}O_6P_2Fe_2PdSTe$ calc.: C, 47.1; H, 2.82. Found: C, 46.9; H, 3.11.

Formation of the mixed metal compounds $(CO)_6Fe_2(\mu_3\text{-}E)_2M(PPh_3)_2$ from $Fe_3(CO)_9(\mu_3\text{-}E)_2$ and $M(PPh_3)_4$ for E = S or Se proceeds by direct substitution of a $Fe(CO)_3$ fragment by a $M(PPh_3)_2$ fragment, whereas for E = Te, there is initially formation of the phosphine adduct, $(CO)_6Fe_2(\mu_3\text{-}Te)_2Fe(CO)_3(PPh_3)$, followed by replacement of the $Fe(CO)_3(PPh_3)$ group by $M(PPh_3)_2$. When a solution of $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}Te)$ was stirred with $M(PPh_3)_4$ (M = Pd or Pt), the mixed metal compounds $(CO)_6Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)M(PPh_3)_2$ (IA and IB) were obtained. Also, the phosphine adduct, $(CO)_6Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)Fe(CO)_3(PPh_3)$ (II) and the phosphine substituted compounds, $Fe_3(CO)_8(PPh_3)(\mu_3\text{-}S)(\mu_3\text{-}Te)$ (III) and

$Fe_3(CO)_7(PPh_3)_2(\mu_3\text{-S})(\mu_3\text{-Te})$ (IV) were isolated in both reactions. Compounds II and III could be identified on the basis of comparison of their infrared spectra with those of the previously reported $(\mu_3\text{-Te})_2$ compounds. In solution, II and III gradually convert to the bis-phosphine derivative, thereby preventing isolation of analytically pure samples of these two compounds. Compound IV was characterised by infrared spectroscopy and on the basis of elemental analysis. $C_{43}H_{30}O_7P_2Fe_3STe$ calc.: C, 52.4; H, 3.04. Found: C, 52.0; H, 3.40%. A similar type of conversion in solution between the phosphine adduct and the substituted derivatives was observed for the $(\mu_3\text{-Se})(\mu_3\text{-Te})$ compounds [2].

The mixed metal cluster, $Fe_2Ru(CO)_9(\mu_3\text{-S})(\mu_3\text{-Te})$ (V) was formed when a freshly prepared solution containing $Ru(CO)_4(C_2H_4)$ was added to a solution of $Fe_2(CO)_6(\mu\text{-STe})$ and the mixture was stirred at room temperature. Cluster V was found to add a second ruthenium carbonyl group on increasing the reaction time and the tetranuclear $Fe_2Ru_2(CO)_{11}(\mu_4\text{-S})(\mu_4\text{-Te})$ (VI) was isolated. Both V and VI were characterised by infrared spectroscopy, mass spectrometry and by elemental analysis. The infrared spectrum of V shows the typical carbonyl stretching pattern characteristic of molecules of the form $M_3(CO)_9(\mu_3\text{-E})_2$ [1b]. The mass spectrum showed peaks centred at *m/e* 627 corresponding to the molecular ion, $[Fe_2Ru(CO)_9(\mu_3\text{-S})(\mu_3\text{-Te})]^+$, and also peaks at *m/e* 599, 571, 543, 515, 487, 459, 431, 403 and 375 corresponding to fragments arising from the successive loss of nine carbonyl groups. Elemental analysis confirmed the molecular formula of V. $C_9O_9STeFe_2Ru$ calc.: C, 16.9. Found: C, 17.3%. The infrared spectrum of VI in the carbonyl region displays the characteristic absorption pattern observed for the previously reported octahedral tetranuclear undecacarbonyl dichalcogenide molecules [5]. The mass spectrum of VI showed peaks centred at *m/e* 753, corresponding to the $(M - 1CO)^+$ ion and also peaks at *m/e* 725, 697, 669, 641, 613, 585, 557, 529, 01 and 473 for the fragments arising from the loss of the remaining carbonyl groups. A good match was seen between the experimentally obtained and the computer simulated isotopic distribution pattern for the $Fe2Ru2STe^+$ ion. Elemental analysis confirmed the molecular formula of VI. $C_{11}O_{11}STeFe_2Ru_2$ calc.: C, 16.9. Found: C, 16.6%. Formation of V occurs by the addition of a coordinatively unsaturated ruthenium carbonyl group across the reactive S–Te bond in $Fe_2(CO)_6(\mu\text{-STe})$, whereas the formation of VI takes place by an initial addition of the coordinatively unsaturated ruthenium carbonyl fragment to the lone pairs of electrons on the S and Te ligands in $Fe_2Ru(CO)_9(\mu_3\text{-S})(\mu_3\text{-Te})$, followed by bond formation between iron and ruthenium atoms. In earlier reports, the reactive nature of the interchalcogen bonds and the tendency for the FeEEFe ring to be opened, even to the extent of accommodating polynuclear metal carbonyl fragments have been described [6]. For instance, the formation of the open clusters, $Fe_2M_3(CO)_{17}(\mu_3\text{-Te})(\mu_4\text{-Te})$ (M = Ru or Os) takes place by a mechanism involving cleavage of one Ru–Ru bond in $Ru_3(CO)_{12}$ [6] or Os–Os bond in $Os_3(CO)_{11}(NCMe)$ [7], and addition of the open Ru_3 or Os_3 fragment across the Te–Te bond of $Fe_2(CO)_6(\mu\text{-Te}_2)$. When the bis-acetonitrile derivatives, $Ru_3(CO)_{10}(NCMe)_2$ or $Os_3(CO)_{10}(NCMe)_2$ are added to $Fe_2(CO)_6(\mu\text{-Te}_2)$, it has been reported that an overall atom transfer reaction occurs and $Ru_3(CO)_9(\mu_3\text{-Te})_2$ and $Os_3(CO)_9(\mu_3\text{-Te})_2$ are formed respectively [7]. The formation of these trinuclear clusters would also involve overall the cleavage of one metal–metal bond in the triruthenium or triosmium framework. Our mixed chalcogen compound,

$Fe_2(CO)_6(\mu$-STe), however, when treated with $Ru_3(CO)_{10}(NCMe)_2$ formed the unexpected tetranuclear cluster VI. Mechanism of formation of VI from this reaction can in principle involve two pathways; fragmentation of the triruthenium compound to monoruthenium carbonyl fragments, which sequentially add to $Fe_2(CO)_6(\mu$-STe) to give VI via an initial formation of V, or alternatively, fragmentation of the triruthenium unit into a dinuclear carbonyl unit and a monoruthenium carbonyl unit, with only the diruthenium carbonyl unit adding to the $Fe_2(CO)_6(\mu$-STe) to form VI without formation of V as an intermediate. On close monitoring of our reaction by infrared spectroscopy the formation of V was not observed at any stage.

The trinuclear compound, $Fe_3(CO)_9(\mu_3$-S)(μ_3-Te) was found to utilise the lone pairs of electrons on its triply bridging chalcogen atoms to add a ruthenium carbonyl fragment, from $Ru(CO)_4(C_2H_4)$ to give $Fe_3Ru(CO)_{11}(\mu_4$-S)(μ_4-Te) (VII). Cluster VII was characterised by comparison of its infrared spectrum in the carbonyl region with other known related compounds and by elemental analysis. The infrared spectrum of VII gave the typical carbonyl stretching pattern observed for the previously reported clusters of the general formula $M_4(CO)_{11}(\mu_4\text{-E})_2$. Elemental analysis confirmed the molecular formula of VII. $C_{11}O_{11}STeFe_3Ru$ calc.: C, 17.9. Found: C, 17.5%. On visible light irradiation of a solution containing a mixture of $Fe_3(CO)_9(\mu_3$-S)(μ_3-Te) and $Fe(CO)_5$, $Fe_4(CO)_{11}(\mu_4$-S)(μ_4-Te) (VIII) was formed as the sole product. Its infrared spectrum in the carbonyl region displays the same stretching frequency pattern which has been commonly observed for all other $M_4(CO)_{11}(\mu_4\text{-E})_2$ compounds. Its mass spectrum showed peaks centred at m/e 663 corresponding to the $(M - 1CO)^+$ ion and also peaks at m/e 635, 607, 579, 551, 523, 495, 467, 439, 411 and 383 for ions formed by the successive loss of the remaining carbonyl groups. There is good agreement between the experimentally obtained and the computer simulated isotopic distribution pattern for the Fe_4STe^+ ion. Elemental analysis confirmed the molecular formula of VIII. $C_{11}O_{11}STeFe_4$ calc.: C, 19.1. Found: C, 18.5%.

Experimental

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. All solvents were thoroughly dried and distilled immediately before use. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrometer as solutions in NaCl cells. Mass spectral analysis was carried out using a Shimadzu QP1000 mass spectrometer operating at a potential of 70 eV. Elemental analyses were performed on a Carlo Erba automatic analyser. Photochemical reactions were carried out in a water-cooled double walled quartz vessel. A 125-W immersion type mercury lamp manufactured by Applied Photophysics Ltd. was used.

1. Preparation of $Fe_2(CO)_6(\mu$-STe) and $Fe_3(CO)_9(\mu_3$-S)(μ_3-Te)

A solution of Na_2TeO_3 (0.6 g, 2.75 mmol) and Na_2SO_3 (0.63 g, 5.0 mmol) in 75 mL of water was added to a flask containing an ice cooled solution prepared from $Fe(CO)_6$ (1.1 mL, 8.25 mmol), 4 mL of 50% KOH and methanol (15 mL). The mixture was stirred at room temperature for 0.5 h, then 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 solid residue was added to a solution of NaOMe (3 g of Na in 400 mL MeOH) and the mixture was stirred at room temperature until complete dissolution took 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 water and dried over anhydrous Na_2SO_4. The organic fraction was concentrated to 10 mL and subjected to chromatography on a silica gel column. Using hexane as the eluant, in order of elution, $Fe_2(CO)_6(\mu\text{-}S_2)$ and $Fe_2(CO)_6(\mu\text{-STe})$ and trace amount of $Fe_29CO)_6(\mu\text{-}Te_2)$ were obtained. A second column chromatographic work-up was found to be necessary to give complete separation between the last two fractions. Using a mixture of tetrahydrofuran and hexane (10:90, v/v) gave pure $Fe_2(CO)_6(\mu\text{-Te})_2$ and $Fe_2(CO)_6(\mu\text{-STe})$ in order of elution.

To a hexane solution of $Fe_2(CO)_6(\mu\text{-STe})$ was added $Fe(CO)_5$ and irradiation with a 40 W light bulb for 15 min yielded pure $Fe_3(CO)_9(\mu_3\text{-S})(\mu_3\text{-Te})$. Overall yield based on Fe(CO)5: 0.653 g, 41%.

2. *Reaction of $Fe_2(CO)_6(\mu\text{-STe})$ with $Pt(C_2H_4)(PPh_3)_2$*

To a benzene solution (25 mL) of $Fe_2(CO)_6(\mu\text{-STe})$ (0.11 mmol) was added $Pt(C_2H_4)(PPh_3)_2$ (0.082 g, 0.11 mmol), and the mixture was stirred at room temperature for 1.5 h. After removal of the solvent *in vacuo* the residue was subjected to chromatographic work-up on a silica gel column using hexane/dichloromethane solvent mixture (70:30, v/v) as eluant. The red $(CO)_6Fe_2(\mu_3\text{-S})(\mu_3\text{-Te})Pt(PPh_3)_2$ (IA) was obtained as the sole product. Yield: 0.85 g, 74%.

3. *Reaction of $Fe_2(CO)_6(\mu\text{-STe})$ with $Pt(PPh_3)_4$*

A benzene solution (25 mL) containing $Fe_2(CO)_6(\mu\text{-STe})$ (0.11 mmol) and $Pt(PPh_3)_4$ (0.137 g, 0.11 mmol) was stirred at room temperature for 0.5 h. Solvent removal and chromatographic work-up as above gave the red $(CO)_6Fe_2(\mu_3\text{-S})(\mu_3\text{-Te})Pt(PPh_3)_2$ (IA). Yield: 0.75 g, 65%.

4. *Reaction of $Fe_3(CO)_9(\mu_3\text{-S})(\mu_3\text{-Te})$ with $Pt(PPh_3)_4$*

A mixture of $Fe_3(CO)_9(\mu_3\text{-S})(\mu_3\text{-Te})$ (0.1 g, 0.17 mmol) and $Pt(PPh_3)_4$ (0.211 g, 0.17 mmol) in benzene solvent (25 mL) was stirred at room temperature for 4 h. The solvent was removed *in vacuo* and the residue was chromatographed on a silica gel column using a hexane/dichloromethane (30:70, v/v) mixture as eluant. In order of elution the following compounds were collected: grey $Fe_3(CO)_8(PPh_3)(\mu_3\text{-S})(\mu_3\text{-Te})$ (III) (0.021 g, 15%), green $Fe_3(CO)_7(PPh_3)_2(\mu_3\text{-S})(\mu_3\text{-Te})$ (IV) (0.009 g, 5%), and red $Fe_2Pt(CO)_6(\mu_3\text{-S})(\mu_3\text{-Te})(PPh_3)_2$ (IA) (0.116 g, 60%).

When the above reaction was carried out for only 1 h, in addition to compounds IA, III, and IV, the phosphine adduct, orange-red $Fe_3(CO)_9(PPh_3)(\mu_3\text{-S})(\mu_3\text{-Te})$ (II) was also obtained (this compound eluted first) and was identified by infrared spectroscopy. However, in solution it gradually converted to a mixture of III and IV. On carrying out the reaction for a longer period (12 h) a significantly greater proportion of the bis-phosphine derivative, IV was obtained: compound III (0.018 g, 15%), IV (0.054 g, 35%), I (0.098 g, 50%).

5. *Reaction of $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}Te)$ with $Pd(PPh_3)_4$*

A benzene solution (25 mL) of $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}Te)$ (0.1 g, 0.17 mmol) was stirred with $Pd(PPh_3)_4$ (0.196 g, 0.17 mmol) for 1 h at room temperature. The solvent was removed *in vacuo* and the residue was subjected to chromatographic work-up on a silica gel column using a 70:30 (v/v) hexane/dichloromethane mixture as eluant. In order of elution, the following fractions were collected: grey III (0.021 g, 15%), green IV (0.018 g, 10%), and red $(CO)_6Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)Pd(PPh_3)_2$ (IB) (0.1 g, 55%).

When the stirring of the reaction mixture was maintained for 12 h, after work-up, compounds III, IV and IB were obtained in yields of 10%, 35% and 30% respectively.

6. *Reaction of $Fe_2(CO)_6(\mu\text{-}STe)$ with $Pd(PPh_3)_4$*

A benzene solution (25 mL) of $Fe_2(CO)_6(\mu\text{-}STe)$ (0.05 g, 0.11 mmol) was stirred with $Pd(PPh_3)_4$ (0.127 g, 0.11 mmol) for 0.5 h at room temperature. The solvent was removed under vacuum and the red IB was obtained after chromatographic work-up using a silica gel column with a 80:20 (v/v) mixture as eluant. Yield: 0.081 g, 69%.

7. *Reaction of $Fe_2(CO)_6(\mu\text{-}STe)$ with $Ru(C_2H_4)(CO)_4$*

A hexane solution (120 mL) of $Ru_3(CO)_{12}$ (0.016 g, 0.025 mmol) was irradiated for 10 min under a constant purge of ethylene gas, and the colourless solution containing the $Ru(C_2H_4)(CO)_4$ so prepared was added to a 1:1 (v/v) hexane/benzene solvent mixture (100 mL) containing $Fe_2(CO)_6(\mu\text{-}S)(\mu\text{-}Te)$ (0.033 g, 0.075 mmol). The mixture was stirred for 1.5 h. The solvent was removed *in vacuo* and the red-violet $Fe_2Ru(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}Te)$ was obtained as the sole product on chromatographic work-up of the residue on a silica-gel column using hexane as eluant. Yield 0.024 g, 51%.

8. *Reaction $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}Te)$ with $Ru(C_2H_4)(CO)_4$*

A hexane solution (120 mL) of $Ru_3(CO)_{12}$ (0.016 g, 0.025 mmol) was irradiated for 10 min under a constant purge of ethylene gas, and the colourless solution containing the $Ru(C_2H_4)(CO)_4$ so prepared was added to a 1:1 (v/v) hexane/benzene solvent mixture (100 mL) containing $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}Te)$ (0.041 g, 0.07 mmol). The mixture was stirred for 10 min. The solvent was removed *in vacuo*, and the residue was chromatographed on a silica gel column using hexane/dichloromethane (80:20, v/v) mixture as eluant. The first two bands to elute were trace amounts of $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}Te)$ and $Ru_3(CO)_{12}$, followed by a greenish brown band of $Fe_3Ru(CO)_{11}(\mu_4\text{-}S)(\mu_4\text{-}Te)$. Yield 0.02 g, 39%.

9. *Reaction $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}Te)$ with $Fe(CO)_5$*

A hexane solution (80 mL) of $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}Te)$ (0.023 g, 0.04 mmol) and $Fe(CO)_5$ (0.2 mL, 16 mmol) was irradiated with UV light under an argon atmosphere for 8 min. The solvent was removed *in vacuo* and chromatographic work-up on a silica gel column using hexane/dichloromethane (80:20) (v/v) mixture as eluant gave the following bands, in order of elution: $Fe_3(CO)_{12}$ (trace amount), $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}Te)$ (trace amount) and the dark green $Fe_4(CO)_{11}(\mu_4\text{-}S)(\mu_4\text{-}Te)$. Yield: 0.006 g, 21%.

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