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# The contrasting roles of the various chalcogens in the synthesis of mixed metal complexes $(CO)_6Fe_2(\mu_3\text{-}E)_2M(PPh_3)_2$ (E = Te, Se, S; M = Ni, Pd, Pt))

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## Abstract

Reactions of $Fe_3E_2(CO)_9$ (E = S, Se) with $M(PPh_3)_4$ (M = Ni, Pd, Pt), at room temperature, show a marked contrast with the analogous reaction of $Fe_3Te_2(CO)_9$. Different mechanisms are suggested for the formation of the mixed-metal complexes, $Fe_2E_2(CO)_6M(PPh_3)_2$ (E = S, Se, Te; M = Pd, Pt, and E = Te; M = Ni), depending on the chalcogen atom involved. The size of the chalcogen and that of the heterometal atom play crucial roles in the outcome of the reaction.

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## Introduction

Recent developments in understanding the structure and bonding of transition metal cluster compounds may provide a basis for the development of rational syntheses. Though transition metal carbonyl clusters incorporating main group elements have been known for the last three decades, only recently has development begun [1] on the synthetic strategy, in which specific single atom ligands derived from the main groups of the Periodic Table, are used as bridges between the various metal fragments in cluster growth reaction. The lone pairs of electrons on the single atom ligands serve as useful initial points of contact for the incoming metal fragments. Another advantage of such ligands is that they can act as bridges, and so prevent degradative fragmentation, to which clusters are often susceptible when subjected to the rigorous conditions used during catalytic processes.

The most extensively used ligand in recent years has been the sulfido ligand, in particular for the preparation of numerous osmium, ruthenium, and some mixed metal clusters [2].

The lone pair of electrons in $Os_3S_2(CO)_9$ has been used for donation to other mononuclear metal fragments and hence the formation of higher nuclearity complexes such as $Os_3S_2(CO)_9W(CO)_5$ [3], $PtOs_3S_2(CO)_9(PMe_2Ph)_2$ [4] and $Os_4S_2(CO)_{13}$ [5]. Selenium has to a lesser extent, also been shown to serve as a

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useful bridge in some cluster building reactions. The formation of $Os_4Se_2(CO)_{13}$ from $Os_3Se_2(CO)_9$ and $Os(CO)_5$ indicates the similarity in the function of the selenium to that of sulfur in these cluster syntheses [6]. In contrast to the first two members of group 16, the use of tellurium as a bridge between metal fragments has been rare. Work by Rauchfuss et al. [7] and recent work carried out in our laboratory [8,9] indicates that the tellurium containing clusters may have structural features and reactivity which are different from those of the sulfur or selenium analogues. Here we describe the contrasting mechanisms for the preparation $Fe_2E_2(CO)_6M(PPh_3)_2$, (E = S, Se, Te; M = Pt, Pd, Ni); and the definite influence of the relative sizes of the chalcogen ligands and of the adding metal fragments.

## Results and discussions

The mixed metal complexes, $Fe_2E_2(CO)_6M(PPh_3)_2$, as well as the substituted derivatives, $Fe_3E_2(CO)_8(PPh_3)$ and $Fe_3E_2(CO)_7(PPh_3)_2$ can be isolated from solutions containing $Fe_3E_2(CO)_9$, (E = S, Se, Te,) and $M(PPh_3)_4$, (M = Ni, Pd, Pt) that have been stirred at room temperature. Though $M(C_2H_4)(PPh_3)_2$ readily reacts with $Fe_2E_2(CO)_6$ to form the same mixed metal complexes, the use of the ethylene complex as a source of $M(PPh_3)_2$, under the same conditions, in the reaction with $Fe_3E_2(CO)_9$ does not give the mixed metal products. It has however been reported that $M(C_2H_4)(PPh_3)_2$ reacts with $Fe_3E_2(CO)_9$, under vigorous conditions to give the mixed metal compounds, probably after the initial formation of $Fe_2E_2(CO)_6$ [10].

The complex $Fe_3Te_2(CO)_9$ is known to undergo substitution by Lewis bases under second order kinetics (first order in the cluster and first order in the Lewis base), whereas the sulfur and selenium analogues of $Fe_3Te_2(CO)_9$ undergo substitution primarily as a first order process [7]. This difference has been attributed to the larger size of the tellurium atom which results in a more strained Fe–Te–Fe angle in $Fe_3Te_3(CO)_9$ than in its S and Se analogues. Figure 1 shows how adduct formation can release the strain by cleavage of the bond between the apical and one of the basal iron atoms.

In an earlier report we have shown that the '$Fe(CO)_3(PPh_3)$' unit in $Fe_3Te_2(CO)_9PPh_3$ can be replaced by fragments of the type '$M(PPh_3)_2$' (M = Pt, Pd, Ni) [8]. We have found that the formation of the mixed metal complexes $Fe_2E_2(CO)_6M(PPh_3)_2$ (E = S and Se), from the reaction of the robust $Fe_3E_2(CO)_9$ with $M(PPh_3)_4$ takes place by a different mechanism. Though adduct formation is not observed for the S and Se analogues of $Fe_3Te_2(CO)_9$, the role played by the phosphine liberated from $M(PPh_3)_4$ could be significant.

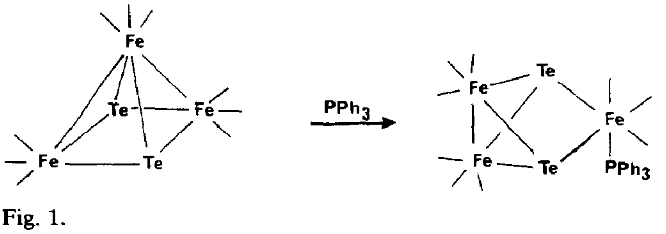
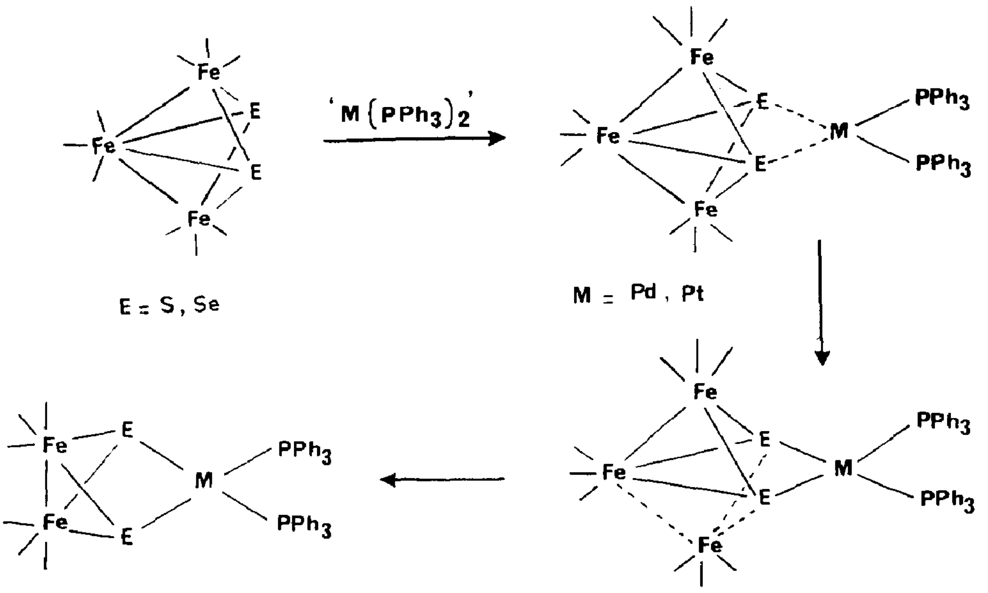


Fig. 1.



Scheme 1.

A likely mechanism for the reaction of $Fe_3E_2(CO)_9$, (E = S, Se) with $M(PPh_3)_4$ could involve initial contact of the '$M(PPh_3)_2$' fragment, generated from $M(PPh_3)_4$ in solution, with one or both chalcogen atoms in $Fe_3E_2(CO)_9$ (Scheme 1). This would result in a change in the chalcogen mode of bonding from triply bridged to quadruply bridged. In sulfido osmium clusters the versatility of the sulfido ligands in changing from triply bridging to quadruply bridging is well documented, and a study of the M–E bond lengths shows that the M–E distances in crease as the coordination number of the chalcogen changes from three to four [1].

The overall loss of a '$Fe(CO)_3$', fragment may be facilitated by a slight weakening of its contact with the chalcogens once they have taken on a quadruply bridging mode of bonding. The cleavage of one Fe–Fe bond and of the two Fe–E bonds required for the loss of the '$Fe(CO)_3$' fragment may also be facilitated by coordination to the iron atom of the free triphenyl phosphine liberated into solution by $M(PPh_3)_4$. The formation of the by-products, the monosubstituted derivative of $Fe_3E_2(CO)_9$, $Fe_3E_2(CO)_8(PPh_3)$ and the disubstituted derivative, $Fe_3E_2(CO)_7(PPh_3)_2$ is the result of the direct reaction of $Fe_3E_2(CO)_9$ with the free triphenylphosphine. The replacement of each carbonyl in $Fe_3E_2(CO)_9$ is catalysed by the presence of $M(PPh_3)_4$ in solution. The catalytic behaviour of $Pt(PPh_3)_4$ in the replacement of carbonyl groups by various ligands has recently been reported [11].

For the formation of $Fe_2Te_2(CO)_6M(PPh_3)_2$, adduct formation followed by replacement of the '$Fe(CO)_3PPh_3$' fragment by '$M(PPh_3)_2$' is more favoured than the general substitution of two $PPh_3$ in $Fe_3Te_2(CO)_9$ for CO. By contrast, for $Fe_2E_2(CO)_6M(PPh_3)_2$, (E = S, Se), release of strain in $Fe_3E_2(CO)_9$ is not as important as that in $Fe_3Te_2(CO)_9$, and is reflected in the absence of the adduct, and in the higher yields of the substituted products $Fe_3E_2(CO)_{(9-x)}(PPh_3)_x$ ($x = 1, 2$) relative to the mixed metal derivative. The relative stabilities of the $Fe_2E_2(CO)_6M(PPh_3)_2$ fall in the order E = Te > Se ≈ S and M = Pt ≈ Pd > Ni. The most stable compound is that in which the atoms of both E and M are large; that no nickel containing mixed metal product is formed for the smaller chalcogens, S and Se, supports this.

The ease of formation of bonds between the transition metals in transition metal–non metal clusters is related to the size of the non-metal, as has been discussed by Schmid [13]. Clusters containing intermediate sized non-metals can adopt either open or closed geometries. This is exemplified by germanium (1.22 Å)-containing clusters. The open cluster $PhGe[Co(CO)_4]_3$ readily decarbonylates to form $PhGe\{Co(CO)_4\}\{Co_2(CO)_7\}$ with one metal–metal bond. Further decarbonylation gives $PhGeCo_3(CO)_9$ with two metal–metal bonds. In our mixed metal complexes the presence of only one metal–metal bond in the tellurium (1.37 Å) derivative is therefore not surprising. The absence of additional metal–metal bonding for the smaller sulfur (1.03 Å) and selenium (1.17 Å) analogues may be due to the presence of the two bulky triphenylphosphine ligands on the heterotransition metal. For the complexes, $(CO)_6Fe_2(\mu_3\text{-}E)_2M(PPh_3)_2$, the size of the chalcogen determines the mechanism by which these complexes are formed. The smaller chalcogens, sulfur and selenium, thus readily undergo direct replacement of a '$Fe(CO)_3$' fragment by the '$M(PPh_3)_2$' whereas for the tellurium derivative, initial formation of the phosphine adduct takes place, and is followed by the replacement of the '$Fe(CO)_3(PPh_3)_2$' fragment by the '$M(PPh_3)_2$' unit.

## Experimental

All reactions were carried out under dry nitrogen or argon using standard Schlenk techniques. The solvents were purified and dried before use. $Fe_3Se_2(CO)_9$ and $Fe_3S_2(CO)_9$ were prepared as previously described [13]. $Pt(PPh_3)_4$, $Pd(PPh_3)_4$ (Fluka) and $Ni(PPh_3)_4$ (Aldrich) were used as received. Elemental analysis (See Table 1) were carried out in a Carlo Erba Strumentazione Mod. 1106 elemental analyser and the infrared spectra (See Table 2) were recorded with a 5DXB Nicolet FTIR spectrometer.

### *1. Reaction of $Fe_3Se_2(CO)_9$ with $Pt(PPh_3)_4$*

A solution of $Fe_3Se_2(CO)_9$ (0.0578 gm, 0.1 mmol) in benzene (50 ml) was stirred with $Pt(PPh_3)_4$ (0.1267 gm, 0.1 mmol) for 5 h at room temperature. The solvent was removed in vacuo and the residue was chromatographed on silica TLC plates. Elution with 20/80 dichloromethane/hexane separated the brown $Fe_3Se_2(CO)_8$-$(PPh_3)$ and the green $Fe_3Se_2(CO)_7(PPh_3)_2$ from the reddish brown $Fe_2Se_2(CO)_6Pt$-

Table 1

Elemental analyses

| Compound | C<br>(Found (calc) (%)) | H<br>(Found (calc) (%)) |
|---|---|---|
| $Fe_2Se_2(CO)_6Pt(PPh_3)_2$ | 43.31 (43.59) | 2.63 (2.61) |
| $Fe_2Se_2(CO)_6Pd(PPh_3)_2$ | 46.68 (47.11) | 3.00 (2.82) |
| $Fe_2S_2(CO)_6Pt(PPh_3)_2$ | 47.36 (47.43) | 2.86 (2.84) |
| $Fe_2S_2(CO)_6Pd(PPh_3)_2$ | 51.83 (51.75) | 3.33 (3.10) |

Table 2

Infrared spectral data in the carbonyl region (in $CH_2Cl_2$ solution unless otherwise indicated)

| Compound | $\nu$(CO) (cm$^{-1}$) |
|---|---|
| $Fe_2Te_2(CO)_6Ni(PPh_3)_2$ [a] | 2041(m), 2016(s), 1990(m) |
| $Fe_2Te_2(CO)_6Pd(PPh_3)_2$ | 2033(s), 1992(s), 1958(s), 1948(sh) |
| $Fe_2Te_2(CO)_6Pt(PPh_3)_2$ | 2031(s), 1991(s), 1955(s), 1947(sh) |
| $Fe_2Se_2(CO)_6Pd(PPh_3)_2$ | 2041(s), 2001(s), 1964(s), 1954(sh) |
| $Fe_2Se_2(CO)_6Pt(PPh_3)_2$ | 2041(s), 2001(s), 1963(s), 1954(sh) |
| $Fe_2S_2(CO)_6Pd(PPh_3)_2$ | 2047(s), 2006(s), 1970(s), 1956(s) |
| $Fe_2S_2(CO)_6Pt(PPh_3)_2$ | 2048(s), 2007(s), 1970(s), 1958(s) |
| $Fe_3Se_2(CO)_8(PPh_3)$ | 2065(s), 2026(s), 2004(s, br) |
| $Fe_3Se_2(CO)_7(PPh_3)_2$ | 2034(m), 1992(s), 1972(s), 1936(m) |
| $Fe_3S_2(CO)_8(PPh_3)$ | 2072(s), 2032(s), 2011(s, br) |
| $Fe_3S_2(CO)_7(PPh_3)_2$ | 2040(s), 1999(vs), 1978(sh), 1943(m) |

[a] In hexane solution.

$(PPh_3)_2$. Yield; $Fe_2Se_2(CO)_6Pt(PPh_3)_2$, 63%; $Fe_3Se_2(CO)_8(PPh_3)$, 15%; $Fe_3Se_2(CO)_7(PPh_3)_2$, 22%.

### 2. *Reaction of $Fe_3Se_2(CO)_9$ with $Pd(PPh_3)_4$*

A solution of $Fe_3Se_2(CO)_9$ (60 mg, 0.1 mmol) in benzene (50 ml) was stirred with $Pd(PPh_3)_4$ (100 mg, 0.1 mmol) at room temperature for 6 h. The solvent was removed under vacuo and the residue was chromatographed on a grade II alumina column. Elution with hexane gave the brown $Fe_3Se_2(CO)_8PPh_3)$, elution with 10/90 dichloromethane/hexane gave the green $Fe_3Se_2(CO)_7(PPh_3)_2$, and elution with 20/80 dichloromethane/hexane gave the reddish brown $Fe_2Se_2(CO)_6Pd(PPh_3)_2$ as the major product of the reaction. Recrystallisation from the same solvent mixture gave the major product as brown needles. Yield; $Fe_2Se_2(CO)_6Pd(PPh_3)_2$, 58%; $Fe_3Se_2(CO)_8(PPh_3)$, 22%; $Fe_3Se_2(CO)_7(PPh_3)_2$, 20%.

### 3. *Reaction of $Fe_3S_2(CO)_9$ with $Pt(PPh_3)_4$*

A solution of $Fe_3S_2(CO)_9$ (50 mg, 0.1 mmol) in benzene (50 ml) was stirred with $Pt(PPh_3)_4$ (126 mg, 0.1 mmol) at room temperature for 8 h. Chromatography on silica TLC plates separated the reddish brown $Fe_3S_2(CO)_8(PPh_3)$ and the dark purple $Fe_3S_2(CO)_7(PPh_3)_2$ from the red $Fe_2S_2(CO)_6Pt(PPh_3)_2$ on elution with 20/80 dichloromethane/hexane. Yield; $Fe_3S_2(CO)_8(PPh_3)$, 16%; $Fe_3S_2(CO)_7(PPh_3)_2$, 20%; $Fe_2S_2(CO)_6Pt(PPh_3)_2$, 64%.

### 4. *Reaction of $Fe_3S_2(CO)_9$ with $Pd(PPh_3)_4$*

To a solution of $Fe_3S_2(CO)_9$ (50 mg, 0.1 mmol) in benzene (50 ml) was added $Pd(PPh_3)_4$ (107 mg, 0.1 mmol) and the mixture was stirred at room temperature for 10 h. Chromatography of the mixture on a grade II alumina column with 20/80 dichloromethane/hexane as eluant separated $Fe_3S_2(CO)_8(PPh_3)$ and $Fe_3S_2(CO)_7(PPh_3)_2$ from $Fe_2S_2(CO)_6Pd(PPh_3)_2$. Yield; $Fe_3S_2(CO)_8(PPh_3)$, 22%; $Fe_3S_2(CO)_7(PPh_3)_2$, 30%; $Fe_2S_2(CO)_6Pd(PPh_3)_2$, 52%.

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