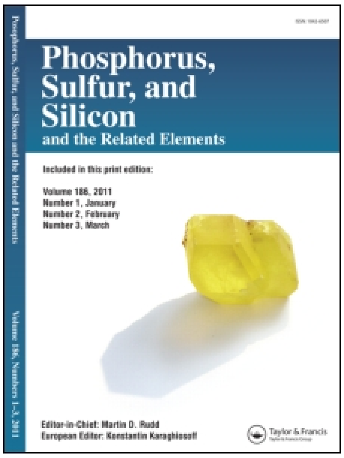

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DESIGNED CONSTRUCTION OF MIXED-METAL, MIXED CHALCOGENIDE CLUSTERS

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Room temperature reactions between $Fe_2(CO)_6(\mu\text{-EE'})$, (E and E' = S, Se or Te) and $M(CO)_5(thf)$, M = Cr, Mo or W yield three types of clusters, the formation of each type clearly dependent on the nature of E and E' present in $Fe_2(CO)_6(\mu\text{-EE'})$ and on the nature of M in $M(CO)_5(thf)$. While the Mo and W adducts are based on square pyramidal heavy atom cores, the Cr adduct has an unusual structure and can be considered as an inorganic analog of quadricyclane.

Keyword: cluster; chalcogen; mixed-metal

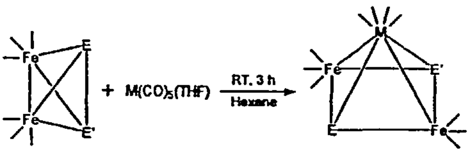
INTRODUCTION

There has been a growing interest in recent times in the use of single atom ligands derived from Group 16 elements.[1] Several methods have been developed for incorporation of chalcogens in metal clusters and several types of homo- and heterometallic clusters have been obtained in which chalcogens bridge the metal atoms. Versatility shown by S, Se and Te in engaging in different types of bonding and in their ability to bond to a wide variety of inorganic and organic units has been a major factor for their wide usage in development of synthesis of chalcogen-bridged organometallic compounds. It has been observed that in most cases S and Se show similar ligating behaviour but the large Te atom displays unique bonding and reactivity features. However, more recently, it has been shown that in some instances, it is the Se ligand which is different from both S and Te.[2] Contrasting behaviour of the three chalcogens has generated interest in the development of synthesis of mixed-chalcogen-bridged systems.

Successful synthesis of $Fe_3(CO)_9(\mu_3\text{-}E)(\mu_3\text{-}E')$ and $Fe_2(CO)_6(\mu\text{-}EE')$, where E = E' and E ≠ E' for E, E' = S, Se or Te has enabled the use of these compounds as starting materials for the synthesis of several types of cluster compounds and for the addition of small organic moieties.[3] This paper gives a brief review of the synthesis of some recently prepared and structurally characterised chalcogen-bridged metal carbonyl clusters, in which the contrasting roles of different metal/chalcogen combinations is revealed.

DISCUSSION

Compounds of the type $Fe_2(CO)_6(\mu\text{-}EE')$, E, E' = S, Se or Te are convenient starting materials for cluster growth reactions. Numerous metal units have been added across the reactive chalcogen-chalcogen bonds in these compounds. A series of compounds of the form $Fe_2M(CO)_{10}(\mu_3\text{-}E)(\mu_3\text{-}E')$ have been prepared at room temperature by reacting equimolar amounts of $Fe_2(CO)_6(\mu\text{-}EE')$ with $M(CO)_5(thf)$, M = Mo or W (Scheme 1).[4]



Scheme 1

The additions have been found to be dependent on the nature of E and E'. For instance, tungsten carbonyl unit readily adds to all possible E, E' combinations in $Fe_2(CO)_6(\mu\text{-}EE')$, whereas, the molybdenum carbonyl unit adds only when E, E' are Se, Se; S, Te or Se, Te. Crystal structures of representative compounds reveals that regardless of whether M is molybdenum or tungsten or on the nature of E and E', the structure consists of a square pyramidal core of Fe_2MEE' in which the heterometal atom M always occupies the apical site. Reaction of an equimolar amount of $Fe_2(CO)_6(\mu\text{-}EE')$ with $Cr(CO)_5(thf)$ did not yield any new mixed-metal cluster. However, when a 2:1 molar ratio of $Fe_2(CO)_6(\mu\text{-}E_2)$ (only for E = S or Se) and $Cr(CO)_5(thf)$ is used, an unusual "picnic-basket" shaped cluster, $Fe_4Cr(CO)_{10}(\mu\text{-}E_2)$ is formed (Figure 1a).[5]

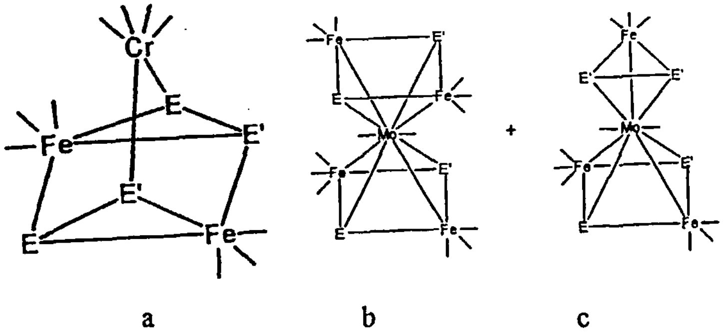


Figure 1

When a 2:1 molar ratio of $Fe_2(CO)_6(\mu\text{-}EE')$ and $Mo(CO)_5(thf)$ is reacted, clusters of the types $Fe_4Mo(CO)_{14}(\mu_3\text{-}E)_2(\mu_3\text{-}E')_2$ (Figure 1b) or $Fe_3Mo(CO)_{11}(\mu_3\text{-}E)(\mu_3\text{-}E')(\mu\text{-}E')_2$ (Figure 1c) are formed, and once again, the formation of one or the other being dependent on the nature of E and E' present in the parent molecule $Fe_2(CO)_6(\mu\text{-}EE')$.[6] Moreover, it is observed that the formation of $Fe_4Mo(CO)_{14}(\mu_3\text{-}E)_2(\mu_3\text{-}E')_2$ occurs in a stepwise formation via the square pyramidal cluster $Fe_2M(CO)_{10}(\mu_3\text{-}E)(\mu_3\text{-}E')$. Curiously, the formation of either $Fe_4W(CO)_{14}(\mu_3\text{-}E)_2(\mu_3\text{-}E')_2$ or $Fe_3W(CO)_{11}(\mu_3\text{-}E)(\mu_3\text{-}E')(\mu\text{-}E')_2$ is not observed.

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