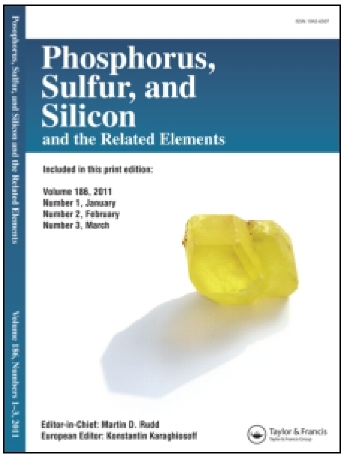

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TRANSITION METAL, NON-METAL CARBONYL CLUSTRS AS SUPPORTS FOR UNUSUAL ACETYLIDE REACTIVITY

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TRANSITION METAL, NON-METAL CARBONYL CLUSTRS AS SUPPORTS FOR UNUSUAL ACETYLIDE REACTIVITY

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Group 16 elements serve as useful bridging and stabilising single atom ligands in mixed-metal carbonyl complexes and impart unusual reactivity on coordinated acetylenic moieties. Reactions of $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = S, or Se) with mononuclear acetylide complexes, $[CpM(CO)_{3-x}(CCR)]$ (M = Mo or W, x = 0, R = Ph; M = Fe, x = 1, R = Ph or ferrocenyl) under facile conditions yield complexes featuring acetylide coupling, acetylide-flip and formation of oxo and acetylide-bridged complexes. In presence of free acetylenes, unusual ligand systems arising from C—S bond formation are observed and under certain conditions, formation of quinones by coupling of acetylenes with carbon monoxide is facilitated.

Keywords: Acetylide; carbonyl; chalcogen; cluster; mixed-metal

Mononuclear acetylide complexes serve as useful starting materials for mixed-metal clusters containing multi-site bound polycarbon units formed by coupling of acetylide ligands.[1] In our previous studies, we have investigated the reactions of the chalcogen-bridged complexes $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = S, Se or Te) with the acetylide complexes, $[CpM(CO)_3(CCPh)]$ (M = Mo or W) and noted the influence of the bridging chalcogen ligands in the overall reactions leading to different types of acetylide coupling on the mixed-metal frameworks.[2] Under certain conditions, mixed-metal clusters containing oxo and acetylide bridges have been obtained.[3] This article gives a brief review of the reactions of some chalcogen-bridged metal carbonyl clusters with mononuclear acetylide complexes with acetylide complexes under mild conditions to yield some new types of acetylide-bridged systems.

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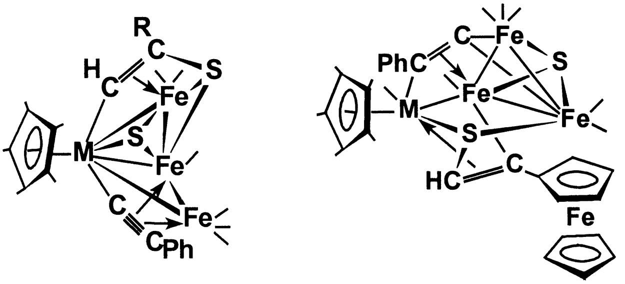

FIGURE 1 Clusters formed from photolysis of selected metal carbonyl alkyne mixtures.

DISCUSSION

When benzene solution containing $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$, $[Cp'M(CO)_3(CCPh)]$ ($Cp' = (\eta^5\text{-}C_5Me_5)$; M = Mo or W); and HC≡CR (R = Ph, n-Bu or Fc) is photolysed, two types of clusters formed: $[Cp'MFe_3(\mu_3\text{-}S)\{\mu_3\text{-}C(H){=}C(R)S\}(CO)_6(\mu_3\text{-}CCPh)]$ (M = Mo or W; R = Ph or n-Bu) and $[Cp'MFe_3(\mu_3\text{-}S)\{\mu_3\text{-}C(Fc){=}C(H)S\}(CO)_7(\mu_3\text{-}CCPh)]$ (M = Mo or W) (Figure 1), which feature unusual acetylide-S coupled ligand formation and an "acetylide-flip" respectively.

Photolysis of benzene solution containing $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = S or Se), $[(\eta^5\text{-}C_5R_5)Fe(CO)_2(CCR')]$ ($Cp' = (\eta^5\text{-}C_5Me_5)$, R = H or Me, R′ = Ph, Fc) and H_20/Et_3N results in formation of $[(\eta^5\text{-}C_5R_5)Fe_3(CO)_6(\mu_3\text{-}E)(\mu_3\text{-}ECCH_2R')]$. Under same conditions, $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ reacts with $[(\eta^5\text{-}C_5R_5)Mo(CO)_3(CCPh)]$ (R = H or Me) to yield mixed-metal clusters $[(\eta^5\text{-}C_5R_5)MoFe_2(CO)_6(\mu_3\text{-}S)(\mu\text{-}SCCH_2Ph)]$ (Figure 2). In both types of reactions acetylide-chalcogen bond formation occurs and the formation of a $(ECCH_2R')$ bound to either three or two metal atoms of the

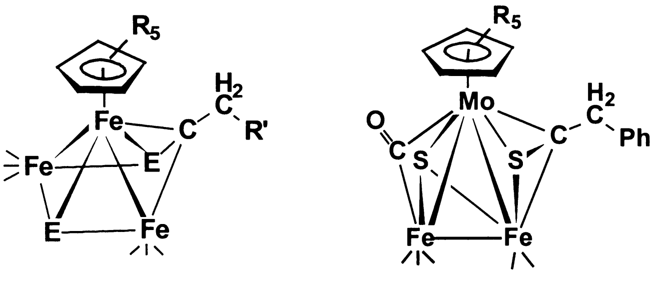

FIGURE 2 Mixed metal clusters.

cluster are observed. The unusual $\mu_2,\eta^2{:}\eta^2$-bonded $SCCH_2R'$ ligand can be thought of formally as being the anion of the thiocarbene $HSCCH_2R$.

Trimethylamine-N-oxide (TMNO) has been used as a source of an oxo group[4] as well as a mild decarbonylating agent in some of our cluster/acetylide reactivity studies.[5] An example of the latter type is the unprecedented formation of a cluster bearing a η^1-bound acetylide group. Mild thermolysis of an acetonitrile solution containing $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = Se or Te) and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(CCPh)]$ in presence of one equivalent of TMNO results in formation of $[(\eta^5\text{-}C_5H_5)MoFe_2(CO)_7(\eta^1\text{-}CCPh)]$. The uncoordinated triple bond of the acetylide group can be utilized for cluster expansion processes. For instance, room temperature reaction of $[(\eta^5\text{-}C_5H_5)MoFe_2(CO)_7(\eta^1\text{-}CCPh)]$ with $[Co_2(CO)_8]$ results in formation of $[(\eta^5\text{-}C_5H_5)MoFe_2Co_2(CO)_8(\mu_4\text{-}CCPh)]$ cluster.

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