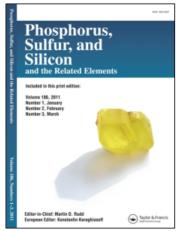
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TRANSITION METAL, NON-METAL CARBONYL CLUSTRS AS SUPPORTS FOR UNUSUAL ACETYLIDE REACTIVITY

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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 $[Fe_3(CO)_9(\mu_3-E)_2]$ (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. In our previous studies, we have investigated the reactions of the chalcogen-bridged complexes $[Fe_3(CO)_9(\mu_3-E)_2]$ (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. Under certain conditions, mixed-metal clusters containing oxo and acetylide bridges have been obtained. 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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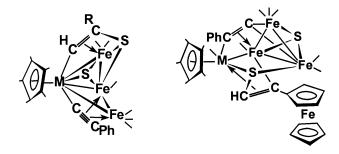


FIGURE 1 Clusters formed from photolysis of selected metal carbonyl alkyne mixtures.

DISCUSSION

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

Photolysis of benzene solution containing [Fe₃(CO)₉(μ_3 -E)₂] (E = S or Se), [(η^5 -C₅R₅)Fe(CO)₂(CCR')] (Cp' = (η^5 -C₅Me₅), R = H or Me, R' = Ph, Fc) and H₂0/Et₃N results in formation of [(η^5 -C₅R₅)Fe₃(CO)₆(μ_3 -E)(μ_3 -ECCH₂R')]. Under same conditions, [Fe₃(CO)₉(μ_3 -S)₂] reacts with [(η^5 -C₅R₅)Mo(CO)₃(CCPh)] (R = H or Me) to yield mixed-metal clusters [(η^5 -C₅R₅)MoFe₂(CO)₆(μ_3 -S)(μ -SCCH₂Ph)] (Figure 2). In both types of reactions acetylide-chalcogen bond formation occurs and the formation of a (ECCH₂R') bound to either three or two metal atoms of the

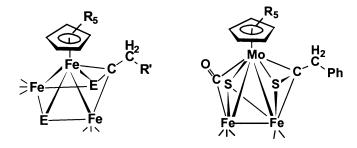


FIGURE 2 Mixed metal clusters.

cluster are observed. The unusual $\mu_2, \eta^2: \eta^2$ -bonded SCCH₂R' ligand can be thought of formally as being the anion of the thiocarbene HSCCH₂R.

Trimethylamine-N-oxide (TMNO) has been used as a source of an oxo group as well as a mild decarbonylating agent in some of our cluster/acetylide reactivity studies. 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 [Fe₃(CO)₉(μ_3 -E)₂] (E = Se or Te) and [(η^5 -C₅H₅)Mo(CO)₃(CCPh)] in presence of one equivalent of TMNO results in formation of [(η^5 -C₅H₅)MoFe₂(CO)₇(η^1 -CCPh)]. The uncoordinated triple bond of the acetylide group can be utilized for cluster expansion processes. For instance, room temperature reaction of [(η^5 -C₅H₅)MoFe₂(CO)₇(η^1 -CCPh)] with [Co₂(CO)₈] results in formation of [(η^5 -C₅H₅)MoFe₂Co₂(CO)₈(μ_4 -CCPh)] cluster.

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