

Preliminary communication

**IRON–MOLYBDENUM AND IRON–TUNGSTEN SULPHIDO CLUSTERS
 CONTAINING HYDRAZIDO(2 –) LIGANDS**

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Summary

Reaction of $[\text{Fe}_2(\mu_2\text{-SLi})_2(\text{CO})_6]$ with $[\text{MCl}(\text{NNRR}')_2(\text{PPh}_3)_2]\text{Cl}$ ($\text{M} = \text{Mo}, \text{W}$; $\text{R}, \text{R}' = \text{Me}_2, \text{MePh}$) gives the trinuclear clusters $[\{\text{Fe}(\text{CO})_3(\mu_3\text{-S})\}_2\text{M}(\text{NNRR}')_2(\text{PPh}_3)]$ in good yield. Mössbauer spectroscopy confirms the absence of Fe–Mo or Fe–W bonds. Reaction with alkyl-substituted phosphines leads to replacement of the triphenylphosphine without change of structure.

Iron–molybdenum sulphido clusters are of considerable current interest as possible models for the iron–molybdenum co-factor of the enzyme nitrogenase. However, none of the clusters reported to date contain ligands such as dinitrogen (N_2), diazenide (N_2R) or hydrazido(2 –) (NNR_2). Such ligands are proven intermediates in the protonation and alkylation reactions of dinitrogen at a molybdenum site. We have now extended previous studies of complexes of such ligands [1–3] to the synthesis of the first reported iron–molybdenum and iron–tungsten sulphido-bridged cluster containing hydrazido(2 –) ligands.

It has previously been shown that $[\text{Fe}_2(\mu_2\text{-SLi})_2(\text{CO})_6]$ (I), prepared by $\text{Li}[\text{Et}_3\text{BH}]$ reduction of $[\text{Fe}_2(\mu_2\text{-S})_2(\text{CO})_6]$, reacts with a variety of metal and non-metal halides L_nMX_2 to give clusters of general type $[\text{Fe}_2(\text{CO})_6(\mu_3\text{-S})_2\text{ML}_n]$ [3–9]. The dilithium salt I reacts with the hydrazido(2 –) complexes $[\text{MCl}(\text{NNRR}')_2(\text{PPh}_3)_2]\text{Cl}$ ($\text{M} = \text{Mo}, \text{W}$; $\text{R}, \text{R}' = \text{Me}_2, \text{MePh}$) to give the clusters $[\text{Fe}_2(\text{CO})_6(\mu_3\text{-S})_2\text{M}(\text{NNRR}')_2(\text{PPh}_3)]$ with elimination of PPh_3 . The reaction proceeds in high yield (60–70%) for $\text{M} = \text{Mo}$, but yields are lower (ca. 40%) for $\text{M} = \text{W}$.

The identity of the complexes was established unequivocally by elemental analysis, $^{31}\text{P}\{^1\text{H}\}$ NMR, ^1H NMR, IR, and Mössbauer spectroscopy. The complexes show IR bands characteristic of the NNR_2 group and the $\text{Fe}_2(\text{CO})_6$ fragment ($\sim 1590, 1960\text{s}, 2046\text{s}, 2004\text{s}, 1973\text{sh cm}^{-1}$), in CH_2Cl_2 . The ^1H NMR confirms the presence of the hydrazido(2 –) groups and a single tertiary phosphine ligand, the latter giving the expected singlet in the $^{31}\text{P}\{^1\text{H}\}$ spectra. The parameters for the

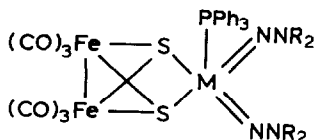


Fig. 1.

room temperature Mössbauer spectra of the hydrazido(2-) clusters were close to those observed for $[\{Fe(CO)_3(\mu_3-S)_2\}_2Ni(Ph_2PCH_2CH_2PPh_2)]Fe-Fe$ (doublet, δ 0.051 mm/s, Δ 0.723 mm/s. For $[Fe_2(CO)_6S(\mu_2-S)_2M(NNMePh)_2(PPh_3)]$, $M = W$; doublet, δ 0.090 mm/s, Δ 0.786 mm/s; $M = Mo$; doublet, δ 0.064 mm/s, Δ 0.752 mm/s. This strongly suggests the absence of Mo-Fe or W-Fe bonding and is entirely consistent with the structure in Fig. 1*. This would then be analogous to the structurally characterised complex $[S_2MoS_2Mo(NNMe_2)_2(PPh_3)]$ [3].

Reaction of the triphenylphosphine complexes with an excess of trimethylphosphine at room temperature leads to simple metathesis of the phosphine ligand and formation of the analogous trimethylphosphine derivatives. The bis[hydrazido(2-)] clusters do not react cleanly with acids, and an interactable mixture of products is formed. The possibilities of the synthesis of new clusters from other hydrazido(2-) and diazenido precursors is currently under investigation. It appears that the electronic flexibility and stability of the hydrazido(2-) derivatives permit the formation of clusters from $[Fe_2(\mu_2-SLi)_2(CO)_6]$ without the redox chemistry that frequently complicates the methathesis chemistry of the di-anion.

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* *Note added in proof.* The structure shown in Fig. 1 has now been verified by an X-ray crystal structure determination.