The room-temperature reaction of \([\text{Fe}_2(\text{CO})_6(\mu-\text{S})_2(\mu-\text{Se})_2)]\) with two equiv. of \([\text{Mo}(\text{CO})_5(\text{thf})]\) yields the mixed-metal, mixed-chalcogenide cluster \([\text{Fe}_2\text{Mo}(\text{CO})_6(\mu-\text{Se})_2(\mu-\text{Te})_2]\), which has an unusual structure as established by single-crystal X-ray diffraction.

The class of compounds \([\text{Fe}_2(\text{CO})_6(\mu-E)]\) (E = S, Se, Te) have served as useful starting materials for numerous types of cluster-growth reactions. Under favorable conditions, addition of mono- and poly-nuclear metal carbonyl species occurs across the E=E bond to yield mixed-metal clusters. Mostly, the addition of mononuclear metal carbonyl species across the E=E bond is accompanied by formation of one new bond between an iron atom and the adding metal atom to give clusters (structure 4) with a square-pyramidal core of the three metal atoms and the two chalcogens, in which one of the iron atoms occupies the apical site. However, a few instances are recorded where the addition of the heterometal atom across the E=E bond is accompanied by Fe-Fe bond cleavage and two new Fe-heterometal atom bond formations, resulting in a square-pyramidal core in which the heterometal atom occupies the apical site. In continuation of our interest in mixed-metal clusters of form 5, we have investigated the reaction of the mixed-chalcogenide compound \([\text{Fe}_2(\text{CO})_6(\mu-\text{SeTe})]\) with \([\text{Mo}(\text{CO})_5(\text{thf})]\).

When equimolar amounts of \([\text{Fe}_2(\text{CO})_6(\mu-\text{SeTe})]\) and \([\text{Mo}(\text{CO})_5(\text{thf})]\) were stirred in hexane solvent at room temperature, the reaction mixture changed from orange to maroon and IR spectroscopy indicated some new bands in the CO region with a pattern and stretching frequencies comparable with those of the previously reported compounds \([\text{Fe}_2\text{M}(\text{CO})_6(\mu-E)]\) (M = W, E = Te; M = Mo, W, E = Se). During chromatographic work-up, in addition to the unreacted \([\text{Fe}_2(\text{CO})_6(\mu-\text{SeTe})]\) and \([\text{Mo}(\text{CO})_5(\text{thf})]\), two new bands were observed: a major maroon band (6) and a much smaller amount of a green band (7). The maroon band was found to gradually convert to the green compound (7) during the chromatography. The reaction of 2 equiv. of \([\text{Fe}_2(\text{CO})_6(\mu-\text{SeTe})]\) and \([\text{Mo}(\text{CO})_5(\text{thf})]\) yielded a much better yield of (7) (Scheme 1). The molecular structure of 7 was established by a single-crystal X-ray structure analysis (Fig. 1). The Mo atom occupies the common apical site of two distorted square-pyramidal cores in each of which the two Fe atoms, one Se atom and one Te atom occupy the basal sites.
clusters stabilized by chalcogen ligands,6 whereas the fourth bond is somewhat long [Mo–Fe(3), 3.083(5) Å], making one of the square pyramids more distorted than the other. While the two Mo–Se distances are similar [2.567(4), 2.622(4) Å], there is a slightly greater difference in the two Mo–Te bond lengths [2.792(4), 2.701(4) Å].

A contrast in the influence of the chalcogens in the cluster expansion is seen in the reactions of [Fe₂(CO)₆(μ-Se₆)] and [Fe₂(CO)₆(μ-Te₆)]. The former readily reacts with [Mo(CO)₆(thf)] (M = Mo or W) to form [Fe₂Mo(CO)₁₀(μ-μ₄-Se₆)]; on the other hand, [Fe₂(CO)₆(μ-μ₄-Se₆)] reacts with the tungsten compound only to form [Fe₂W(CO)₁₀(μ₃-Se₆)(μ₃-Te₆)].

Conversion to the unusual compound [Fe₂M(CO)₁₄(p₃-Se₆)(p₃-Te₆)] has so far been unsuccessful. We are currently investigating the possibility of adding coordinatively unsaturated metal carbyl species to the two open FeSeFeTe faces of 7.

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Footnotes

1Synthesis of 6 and 7: a thf solution (120 ml) of [Mo(CO)₆] (0.068 g, 0.26 mmol) was irradiated with 366 nm UV light in an immersion-type photolysis instrument for 10 min under a constant argon purge. The yellow-green solution of [Mo(CO)₆(thf)] was added to a hexane solution (50 ml) containing [Fe₂(CO)₆(μ-μ₄-Se₆)] (0.125 g, 0.26 mmol). The reaction mixture was stirred at room temperature for 3 h. The solvent was removed and the residue was subjected to chromatographic work-up on a silica gel chromatography column. Elution with hexane yielded a trace amount of [Mo(CO)₆(thf)] consumed; IR [hexane, ν(CO)/cm⁻¹]: 2086w, 2052vs, 2010s, 1969w. Analysis of the solid showed that it was [Fe₂Mo(CO)₁₀(μ₃-Se₆)(μ₃-Te₆)].

References


6For example: [(η⁵-C₅H₅Me₂O₂Fe₂(CO)₁₂]₂[Si(η⁵-C₅H₅)]₂] 2.853(3) Á, B. Bowler, J. A. Noddick and M. R. DeBois, Organometallics, 1993, 2, 931; [η⁵-C₅H₅MoFe₂Co₂(CO)(η⁵-PPh₂Me)-Si(η⁵-C₅H₅)] 2.793(2) Á, A. Richter and H. Vahrenkamp, Chem. Ber., 1982, 115, 3243; [η⁵-C₅H₅MoFe₂(OCH₂CH₂OC(OCH₂CH₂)n)] 2.801(1) Á, L.-C. Song, J.-Y. Shen, Q.-M. Hu and X.-Y. Huang, Organometallics, 1995, 14, 98; [η⁵-C₅H₅MoFe₂(OCH₂CH₂)n][CO(CO)₆] 2.816(5) Á, P. D. Williams, M. D. Curtis, D. N. Duffy and W. M. Butler, Organometallics, 1983, 2, 165.

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