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Short Communication

Synthesis of the thermally unstable arachno cluster $Fe_2(CO)_6(\mu_3\text{-}S)_2Ni(1,5\text{-}COD)$ and observation of facile decomposition to FeNiS

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Abstract

The reaction between $Fe_2(CO)_6(\mu_2\text{-}S)_2$ and $(1,5\text{-}COD)_2Ni$ gives the arachno cluster $Fe_2(CO)_6(\mu_3\text{-}S)_2Ni(1,5\text{-}COD)$ at −78 °C in toluene. This new cluster is stable at low temperature and has been characterized by low-temperature IR spectroscopy. Cluster decomposition occurs upon warming to yield amorphous FeNiS, which has been characterized by energy-dispersive X-ray analysis (EDAX).

Introduction

The oxidative addition of unsaturated metal fragments into the reactive S–S bond of $Fe_2(CO)_6(\mu_2\text{-}S)_2$ (**1**) has been used as one method for the preparation of heterometallic arachno clusters $Fe_2(CO)_6(\mu_3\text{-}S)_2ML_x$ [1–5]. Recently, we reported the synthesis and redox reactivity of the mixed-metal cluster $Fe_2(CO)_6(\mu_3\text{-}S)_2CuCp^*$ (**2**) (where $Cp^* = \eta^5\text{-}C_5Me_5$) from **1** and Cp*Cu(THF) [6]. The reaction proceeds by the insertion of the carbene equivalent 'Cp*Cu' into the S–S bond of **1**. Unfortunately, the mixed-metal cluster **2** was too unstable to isolate, decomposing to give a small amount of **1** and $Fe_3(CO)_9(\mu_3\text{-}S)_2$ along with amorphous CuS/FeS. Given the isolobal relationship between the 'Cp*Cu' fragment ($d^{10}\text{-}ML_3$) and the '(1,5-COD)Ni' fragment ($d^{10}\text{-}ML_2$; where 1,5-COD = 1,5-cyclooctadiene) [7,8], we next examined the reaction between **1** and $(1,5\text{-}COD)_2Ni$ in an effort to prepare the corresponding mixed-metal cluster $Fe_2(CO)_6(\mu_3\text{-}S)_2Ni(1,5\text{-}COD)$ (**3**). The complex $(1,5\text{-}COD)_2Ni$ was chosen because it is a known precursor to the reactive carbene fragment '(1,5-COD)Ni' [9] and it would allow us to make reactivity comparisons with the corresponding platinum (1,5-COD) cluster $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(1,5\text{-}COD)$, which has recently been prepared in our laboratory [10].

Results and discussion

Treatment of $Fe_2(CO)_6(\mu_2\text{-}S)_2$ [11] with $(1,5\text{-}COD)_2Ni$ [12] in toluene at room temperature leads to the immediate precipitation of a black solid. This solid is insoluble in all common organic solvents and IR analysis (KBr pellet) revealed no metal carbonyl bands, which suggests that all of the ancillary CO groups have been lost during the reaction. Indeed, an extremely low carbon and hydrogen content was observed (*c.* 3% and 1%, respectively) when this material was analyzed by combustion analysis, supporting the notion that the black solid is predominantly inorganic in nature. The cluster $Fe_3(CO)_9(\mu_3\text{-}S)_2$ [11] and **1** were the only observed compounds (<25% combined yield) in the toluene solution. The deposit of an insoluble precipitate is reminiscent of the reaction between **1** and Cp*Cu(THF), which has been shown to give a mixture of insoluble metal sulfides [6]. Accordingly, we believe that the isolated black precipitate from **1** and $(1,5\text{-}COD)_2Ni$ is best represented as FeNiS (*vide infra*).

We next examined the same reaction at −78 °C using low-temperature IR spectroscopy. When **1** and $(1,5\text{-}COD)_2Ni$ were combined (1:1 ratio) at −78 °C, we observed the presence of new ν(CO) bands at 2058(s), 2013(vs), 1983(s) and 1966(m) cm^{-1}, which are attributed to the mixed-metal arachno cluster $Fe_2(CO)_6(\mu_3\text{-}S)_2Ni(1,5\text{-}COD)$ (**3**). These ν(CO) bands are virtually identical with those observed in the fully characterized platinum analog, $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(1,5\text{-}COD)$ (**4**) (cf. (THF at −78 °C) 2057(s), 2016(vs), 1976(s), 1956(m) cm^{-1}) [10]. However, unlike cluster **4**, which is readily isolable, cluster **3** decomposes upon warm-up to give the same black, insoluble material as the reaction conducted at room temperature. Our observation of **3** is interesting because the corresponding diphos-substituted cluster $Fe_2(CO)_6(\mu_3\text{-}S)_2Ni(diphos)$ has been isolated and characterized by Seyferth et al. [1, 2]. Thus, it appears that the presence of the ancillary 1,5-COD ligand in **3** promotes cluster decomposition, presumably through an initial olefin dissociation sequence. Accordingly, we propose that the reaction proceeds by the sequence of events shown in eqn. (1).

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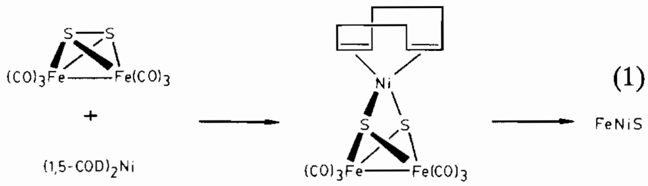

(1)

The composition of the presumed solid FeNiS was confirmed by using energy-dispersive X-ray analysis (EDAX). EDAX analysis revealed a homogeneous distribution of Fe, Ni and S in the solid sample in addition to establishing an Fe/Ni/S ratio of 1:1:1.

Our future studies will examine the low-temperature substitution chemistry of **3** along with the redox and possible catalytic activity of **3**.

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