Synthesis and Redox Reactivity of the Thermally Unstable Mixed-metal Arachno Cluster $Fe_2(CO)_6(\mu_3\text{-}S)_2Cu(\eta^5\text{-}Cp^*)$

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Abstract

The reaction between $Fe_2(CO)_6(\mu_2\text{-}S)_2$ (**1**) and $(THF)Cu(\eta^5\text{-}Cp^*)$ (where $Cp^* = C_5Me_5$) has been examined in THF at −78 °C. Rapid and efficient insertion of the carbene like fragment $Cu(\eta^5\text{-}Cp^*)$ into the S–S bond of **1** affords the mixed-metal arachno cluster $Fe_2(CO)_6(\mu_3\text{-}S)_2Cu(\eta^5\text{-}Cp^*)$ (**2**). Reaction of **1** with $LiEt_3BH$ and MeLi at −78 °C gives the corresponding cluster radical anion $Fe_2(CO)_6(\mu_3\text{-}S)_2Cu(\eta^5\text{-}Cp^*)^{\cdot-}$ (**3**) without the spectroscopic intermediacy of CO-based reduction products. The thermal stability of **2** and **3** is described.

Introduction

The preparation and characterization of heteronuclear copper-containing clusters remains an underdeveloped area of cluster chemistry [1, 2]. Interest in such systems stems from their ability to function as models for alloy catalysts [3] and in the manufacture of mixed-metal thin films [4] by chemical vapor deposition (CVD) processes [5]. Copper-containing mixed-metal thin films are particularly attractive in connection with shape memory effect (SME) alloy films and their ultimate replacement of the more expensive SME alloys based on Ni–Ti (Nitinol) [6].

Mixed-metal clusters derived from $Fe_2(CO)_6(\mu_2\text{-}S)$ have been described and are easily formed from the insertion of low-valent organometallic complexes into the S–S bond of **1** [7–11]. Such reactions are analogous to the insertion reactions involving carbenes [12] since the majority of the organometallic complexes used afford metal fragments that are isolobal with CH_2 [13]. Given our interest in mixed-metal copper clusters and the high reactivity of the S–S bond in **1** towards carbene equivalents, we report our results for the reaction between $(THF)Cu(\eta^5\text{-}Cp^*)$ and $Fe_2(CO)_6(\mu_2\text{-}S)_2$ to give $Fe_2(CO)_6(\mu_3\text{-}S)_2Cu(\eta^5\text{-}Cp^*)$. The solvated copper complex is an excellent low-temperature source of the carbene equivalent '$Cu(\eta^5\text{-}Cp^*)$' (formally a d^{10} ML_3 fragment) [13] that has been used in other cluster assembly reactions [14].

Results and Discussion

Synthesis of $Fe_2(CO)_6(\mu_3\text{-}S)_2Cu(\eta^5\text{-}Cp^*)$

The reaction between $Fe_2(CO)_6(\mu_2\text{-}S)_2$ [15] and $(THF)Cu(\eta^5\text{-}Cp^*)$ in THF at −78 °C proceeds rapidly to give a red solution containing the arachno cluster $Fe_2(CO)_6(\mu_3\text{-}S)_2Cu(\eta^5\text{-}Cp^*)$. The formation of **2** is best viewed by insertion of the $Cu(\eta^5\text{-}Cp^*)$ fragment into the S–S bond of **1**. Low-temperature FT-IR analysis indicates that **2** forms in quantitative yield upon the addition of **1** to $(THF)Cu(\eta^5\text{-}Cp^*)$. Figure 1(a) shows the low-temperature IR spectrum of **2** where carbonyl stretching bands at 2043(s), 2011(vs), 1969(s) and 1958(s) cm^{-1} are observed. The shift in the CO bands of **2** to lower frequency

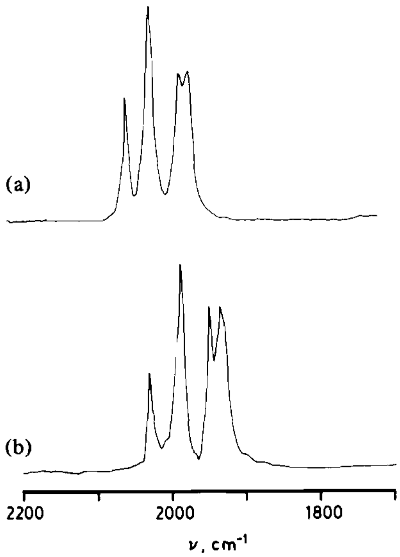

Fig. 1. Infrared spectra of the carbonyl region for (a) $Fe_2(CO)_6(\mu_3\text{-}S)_2Cu(\eta^5\text{-}Cp^*)$ (**2**) and (b) $Fe_2(CO)_6(\mu_3\text{-}S)_2Cu(\eta^5\text{-}Cp^*)^{\cdot-}$ (**3**). Both spectra were recorded in THF at −70 °C.

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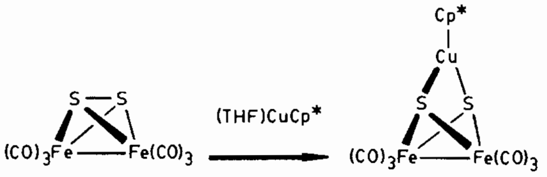
relative to 1 coupled with the spectral similarity to other reported mixed-metal arachno clusters of this genre supports the structure of 2 as shown in eqn. (1) [7, 8a, 16, 17]. Furthermore, the polyhedral skeletal electron pair (PSEP) theory also predicts the formation of an arachno cluster geometry upon Cu(η^5-Cp*) insertion into the S–S bond of 1 [18, 19].



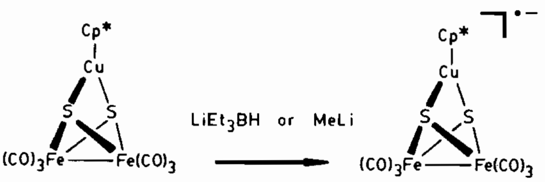
1 NIDO

2 ARACHNO (1)

2 was observed to be stable at −78 °C for a period of one month (less than 5% decomposition). The isolation of 2 has been hampered due to its decomposition at room temperature. IR spectral analysis of the solution containing decomposed 2 revealed minor amounts of 1 and $Fe_3(CO)_9(\mu_3\text{-}S)_2$ [15] as the only identifiable carbonyl-containing materials. The accompanying insoluble black precipitate has not been fully characterized and is possibly some form of copper and/or iron sulfide ($Cu_{1,2}S$ or $Fe_{1,2}S$) [20]. Efforts are being made to characterize this unknown solid material.

Redox Reactivity of $Fe_2(CO)_6(\mu_3\text{-}S)_2Cu(\eta^5\text{-}Cp^*)$

Next we examined the reaction between 2 and reducing agents as part of our interest in polynuclear reduction processes [21]. Treatment of 2 in THF at −78 °C with 1.0 eq. of $LiEt_3BH$ led to the generation of a new species in essentially quantitative yield based on IR analysis. The low-temperature IR spectrum (−70 °C) exhibited four carbonyl stretching bands at 2030(s), 1986(vs), 1949(s) and 1934(s) cm^{-1}. Use of MeLi (1.0 eq.) also gave the same IR spectrum. Based on the absence of a low frequency formyl(acyl) C–O stretching band between 1650–1500 cm^{-1} [22], we can rule out a CO reduction pathway (i.e. $Fe\text{–}CO \rightarrow Fe\text{–}C(O)\text{–}H(Me)^-$). The similarity of both IR spectra suggests that both reactions proceed by a single-electron transfer mechanism to give the corresponding cluster radical anion $Fe_2(CO)_6(\mu_3\text{-}S)_2Cu(\eta^5\text{-}Cp^*)^{\bullet-}$ (3) as shown in eqn. (2).



2

3 (2)

At no point in these reactions was any evidence obtained for the spectroscopic intermediacy of reduction products derived from CO, μ_3-S or direct metal (Fe or Cu) attack. Such intermediates could, however, serve as precursors to 3. While hydrides and RLi reagents typically function as two-electron reducing agents, there is ample literature precedence where these reagents function as single-electron reagents [23]. Moreover, we have observed similar reduction behavior with the known clusters $XCCo_3(CO)_9$ (where X = Ph, Me, Cl and Br) and $PhPFeCo_2(CO)_9$ [24]. Low-temperature IR studies (−78 °C) have shown that alkyl(aryl) lithiums and Grignard reagents react to give the known polynuclear radical anions [25].

Confirmatory proof for the existence of 3 derives from its independent generation using a known one-electron reducing agent. For example, 2 reacts with sodium naphthalide (1.0 eq.) in THF at −78 °C to give an IR spectrum identical to that obtained using $LiEt_3BH$ and MeLi. Figure 1(b) shows the low-temperature IR spectrum of 3 recorded using sodium naphthalide. The IR spectrum of 3 resembles that of 2, except for the expected low frequency shift in the CO bands of 3 relative to 2. The spectral similarity between 2 and 3 indicates that 3 maintains an arachno polyhedron upon electron accession. This trend is well documented in other chemical and electrochemical reduction reactions involving *closo* and *nido* clusters [25].

The highest frequency CO band in 3 is ~13 cm^{-1} lower in frequency while the other three bands are ~22 cm^{-1} lower in frequency relative to 2. Interestingly enough, this same trend is also observed in the related paramagnetic arachno clusters $Fe_2(CO)_6(\mu_3\text{-}S)_2Pt(L\text{–}L)^{\bullet-}$ (where L–L = 1,5-COD, 2,2′-bpy and 1,10-phen) [24]. Other well-documented examples of paramagnetic clusters reveal a ~60 cm^{-1} shift in the C–O stretching bands to lower frequency relative to the neutral parent cluster [21a, 26]. The magnitude of the observed CO shift in the latter paramagnetic clusters is presumably a manifestation of complete electron delocalization over the polyhedral core, consistent with such clusters functioning as class III charge-transfer complexes [27]. Although the exact reason(s) why the CO bands of 3 and the related arachno platinum analogues (*vide supra*) do not exhibit a 60 cm^{-1} low frequency shift is not known, we suspect that the odd electron is not completely delocalized over the two $Fe(CO)_3$ centers. Such a situation would minimize the amount of π^* backbonding available to the $Fe(CO)_3$, resulting in only small CO frequency shifts. The extent of electron delocalization in this family of paramagnetic clusters is currently being examined using electrochemical and EPR techniques.

3 is less stable than 2 as 3 decomposes over a period of one week at −78 °C to give 2 with material

loss. **3** may be oxidized back to **2** using $[Cp_2Fe][BF_4]$ (1.1 eq.) in 88% yield and, thus, reinforces the paramagnetic nature of **3**. Finally, since the electron-transfer between **2** and cobaltocene was unsuccessful, we can assume that the reduction potential for $\mathbf{2} \rightarrow \mathbf{3}$ must lie in the range of ~ -1.0 to -2.0 V versus SCE [28].

The synthesis of other mixed-metal iron–copper clusters is planned and the redox reactivity of these systems and the related iron–platinum clusters will be reported in due course.

Experimental

Materials

$Fe_2(CO)_6(\mu_2\text{-}S)_2$ was prepared according to the procedure of Hieber and Gruber [15]. $LiEt_3BH$ (1.0 M in THF), MeLi (1.4 M in Et_2O) and CuCl were purchased from Aldrich and used as received. Pentamethylcyclopentadiene was prepared from known literature procedures [29]. 0.5 M sodium naphthalide (in THF) was prepared according to the method of Fieser and Fieser [30] while $[Cp_2Fe][BF_4]$ was synthesized using the procedure of Gray and coworkers [31]. All reactions were conducted under argon using Schlenk techniques [32] or in a nitrogen filled Vacuum Atmosphere DL series inert-atmosphere Dri-box. THF was distilled from sodium/benzophenone ketyl and stored under argon in Schlenk vessels.

Routine infrared spectra were recorded on a Nicolet 20SXB FT-IR spectrometer in 0.1 mm NaCl cells. Low-temperature IR spectra were recorded on the same spectrometer with a Specac Model P/N 21.000 variable-temperature cell equipped with inner and outer CaF_2 windows. Dry ice/acetone was used as coolant, and the reported cell temperature, taken to be accurate to ±1 °C, was determined with a copper–constantan thermocouple.

Synthesis of $Fe_2(CO)_6(\mu_3\text{-}S)_2Cu(\eta^5\text{-}Cp^*)$

To 50 ml of THF containing 0.30 mmol of (THF)-$Cu(\eta^5\text{-}Cp^*)$ at -78 °C was added 0.1 g (0.29 mmol) of $Fe_2(CO)_6(\mu_2\text{-}S)_2$ under argon flush. The solution was stirred at -78 °C for one hour, and then monitored by IR spectroscopy. Due to the thermal instability of $Fe_2(CO)_6(\mu_3\text{-}S)_2Cu(\eta^5\text{-}Cp^*)$, no attempt was made to isolate the product. IR (THF, -70 °C): νCO 2043(s), 2011(vs), 1969(s) and 1958(s) cm^{-1}.

Reaction of 2 with Reducing Agents

In a typical experiment, 0.035 mmol of $Fe_2(CO)_6(\mu_3\text{-}S)_2Cu(\eta^5\text{-}Cp^*)$ in ~20 ml of THF at -78 °C was treated with 1.0 mol eq. of the desired reducing agent. The reaction giving paramagnetic **3** was monitored by low-temperature IR spectroscopy. IR (THF, -70 °C): νCO 2030(s), 1986(vs), 1949(s) and 1939(s) cm^{-1}.

$[Cp_2Fe][BF_4]$ Oxidation of $Fe_2(CO)_6(\mu_3\text{-}S)_2Cu(\eta^5\text{-}Cp^*)$

To the solution obtained above using sodium naphthalide in THF at -78 °C was added 9.6 mg (0.035 mmol) of $[Cp_2Fe][BF_4]$ under argon flush. The oxidation reaction was judged to be instantaneous based on immediate IR monitoring of the solution which indicated the presence of cluster **2** (88%). The yield of **2** was calculated by using the initial and final absorbance value of the 2043 cm^{-1} CO band of **2**.

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