

Isolobal displacement methodology for the synthesis of transition-metal cluster complexes containing various biscyclopentadienyl ligands*

Li-Cheng Song[†] and Dian-Shun Guo

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

Abstract: The isolobal displacement methodology for the synthesis of biscyclopentadienyl-bridged transition-metal cluster complexes has been developed. This methodology involves various isolobal displacement reactions between tetrahedral cluster substrates and Mo/W-containing isolobal reagents, leading to a series of linear biscyclopentadienyl-bridged cluster complexes and cyclic biscyclopentadienyl-bridged cluster crown ethers, respectively.

INTRODUCTION

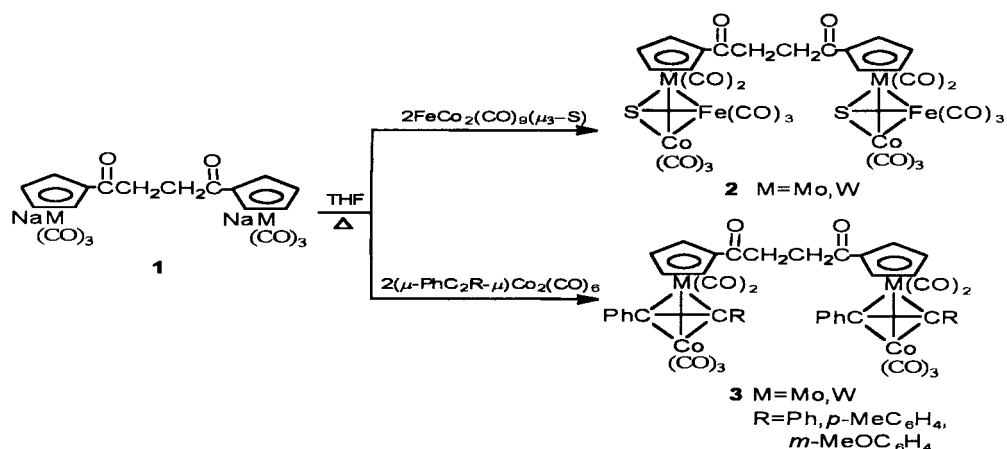
Since the mid-1970s transition-metal cluster complexes have been intensively studied, largely because of their potential applications such as in catalysis, as well as the novelty and diversity of their structures and reactions [1–4]. Among the reactions studied so far, the isolobal displacement reactions have been shown to be very useful for the rational synthesis of various transition-metal cluster complexes [3–23], particularly for the synthesis of those cluster complexes containing the bridging biscyclopentadienyl ligands [24–30]. In this paper, we wish to summarize our recent work related to isolobal displacement methodology for the synthesis of the biscyclopentadienyl-bridged cluster complexes.

SYNTHESIS OF DOUBLE CLUSTER COMPLEXES CONTAINING VARIOUS BRIDGING BISCYCLOPENTADIENYL LIGANDS

We found that reaction of 1,4-succinylbiscyclopentadienyldisodium with $M(\text{CO})_6$ ($M = \text{Mo}, \text{W}$) can produce M /disodium salts **1**, which react further with two molecules of tetrahedral cluster $\text{FeCo}_2(\text{CO})_9(\mu_3\text{-S})$ in refluxing tetrahydrofuran (THF) to give double clusters containing 1,4-succinylbis-cyclopentadienyl ligands **2** [24] (Scheme 1). Similarly, if the salts **1** react *in situ* with two molecules of tetrahedral clusters $(\mu\text{-PhC}_2\text{R-}\mu)\text{Co}_2(\text{CO})_6$ in THF at reflux, then double clusters **3**, containing the same bridging biscyclopentadienyl ligand, can be yielded [25] (Scheme 1). Interestingly, these bridged double clusters **2** and **3** are actually produced through a double isolobal displacement of two $\text{Co}(\text{CO})_3$ ($d^9\text{ML}_3$) units in two molecules of such tetrahedral clusters $\text{FeCo}_2(\text{CO})_9(\mu_3\text{-S})$ and $(\mu\text{-PhC}_2\text{R-}\mu)\text{Co}_2(\text{CO})_6$ by the bridging double isolobal fragments $(\text{CO})_2\text{M}[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_2]_2\text{M}(\text{CO})_2$ ($d^5\text{ML}_5$ -bridge- $d^5\text{ML}_5$) generated *in situ* from **1** [24, 25].

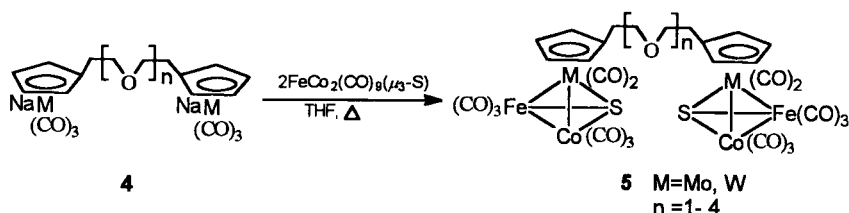
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[†]Corresponding author: E-mail: lcsong@public.tpt.tj.cn



Scheme 1

We also found [28,29] that reaction of the ether chain-bridged biscyclopentadienyl disodium salts with $\text{M}(\text{CO})_6$ ($\text{M} = \text{Mo}, \text{W}$), followed by treatment of the intermediate $\text{M}/\text{disodium}$ salts **4** with cluster $\text{FeCo}_2(\text{CO})_9(\mu_3\text{-S})$ in THF yields a series of double clusters **5**, containing the corresponding length-varied, ether chain-bridged biscyclopentadienyl ligands, as shown in Scheme 2.



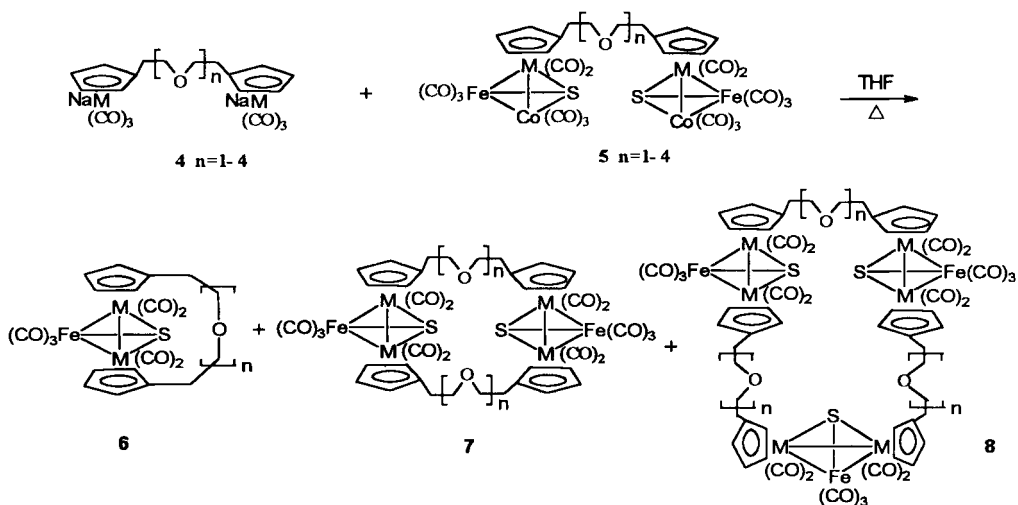
Scheme 2

Obviously, double clusters **5** are produced, similar to **2** and **3**, through a double isolobal displacement of two $\text{Co}(\text{CO})_3$ ($d^9\text{ML}_3$) units in two molecules of $\text{FeCo}_2(\text{CO})_9(\mu_3\text{-S})$ by the bridged double isolobal fragments $(\text{CO})_2\text{M}[\eta^5\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5]\text{M}(\text{CO})_2$ ($d^5\text{ML}_5$ -bridge- $d^5\text{ML}_5$) generated *in situ* from **4** [28,29]. Similarly, the double clusters containing other organic chain-bridged biscyclopentadienyl ligands can be also synthesized by such a type of double displacement reactions[25].

SYNTHESIS OF TRANSITION-METAL CLUSTER CROWN ETHERS CONTAINING BRIDGING BISCYCLOPENTADIENYL LIGAND

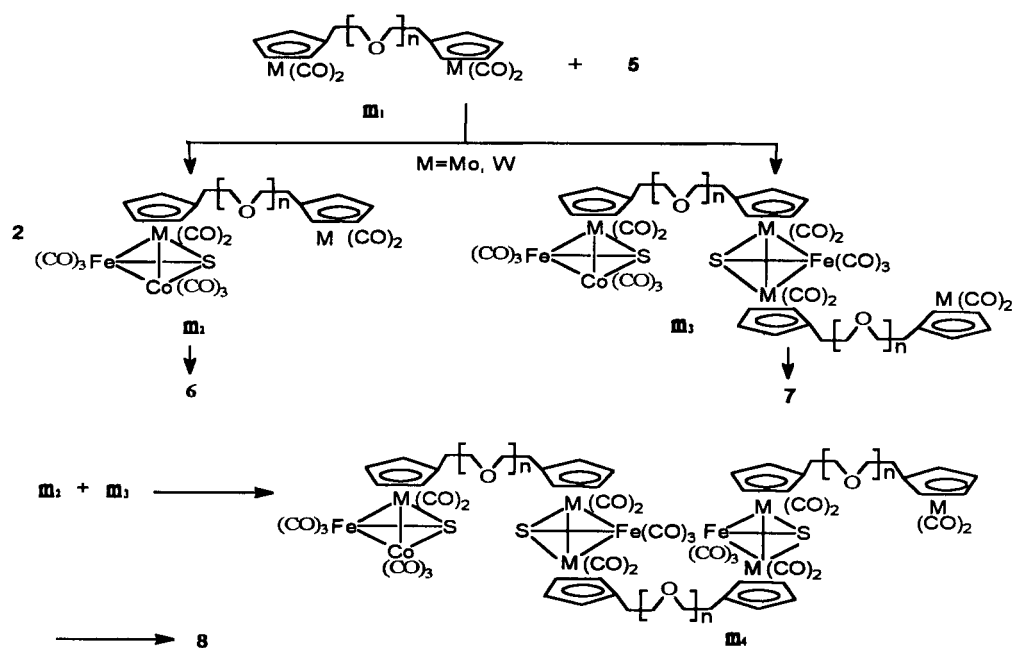
We found [30,31] that the ether chain-bridged biscyclopentadienyl M/Na salts **4** react with the same chain-bridged biscyclopentadienyl double clusters **5** in THF at reflux to afford a series of single, double, and triple cluster crown ethers **6–8**, all containing tetrahedral $\text{M}_2\text{Fe}(\mu_3\text{-S})$ cluster cores and the ether-chain bridged biscyclopentadienyl ligands (Scheme 3).

In the first step of the suggested pathway [30,31] (Scheme 4), the bridged M/Na salts **4** can be converted into their decarbonylated intermediates \mathbf{m}_1 . Then, while these intermediates react further with double clusters **5** through intermolecular single isolobal $d^5\text{ML}_5/d^5\text{ML}_5$ displacement to give two molecules of intermediates \mathbf{m}_2 , the reactions of \mathbf{m}_1 with **5** via intermolecular single isolobal $d^5\text{ML}_5/d^9\text{ML}_3$



Scheme 3

displacement give intermediates \mathbf{m}_3 . While \mathbf{m}_2 undergo an intramolecular $d^5\text{ML}_5/d^9\text{ML}_3$ single isolobal displacement to give the single cluster crown ethers **6**, the intramolecular single isolobal $d^5\text{ML}_5/d^9\text{ML}_3$ displacement of \mathbf{m}_3 affords the double cluster crown ethers **7**. However, if \mathbf{m}_2 react with \mathbf{m}_3 through intermolecular $d^5\text{ML}_5/d^9\text{ML}_3$ single isolobal displacement, then the intermediates \mathbf{m}_4 will be produced. Finally, the intramolecular single isolobal $d^5\text{ML}_5/d^9\text{ML}_3$ displacement of \mathbf{m}_4 yields the triple cluster crown ethers **8**.



Scheme 4

CONCLUSION

We have briefly summarized some of our recent new findings, which include the first synthesis of a series of linear biscyclopentadienyl-bridged tetrahedral $MCoFe(\mu_3-S)$ and $MCoC_2$ ($M = Mo, W$) cluster complexes and cyclic biscyclopentadienyl-bridged tetrahedral $M_2Fe(\mu_3-S)$ ($M = Mo, W$) cluster crown ethers by using isolobal displacement methodology. Apparently, this methodology for synthesis of such linear and cyclic cluster complexes is novel and would have more wider applications for synthesis of valuable transition-metal cluster complexes by using other cluster substrates and isolobal displacement reagents, particularly the bridging dinuclear and even polynuclear isolobal displacement reagents [27].

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