

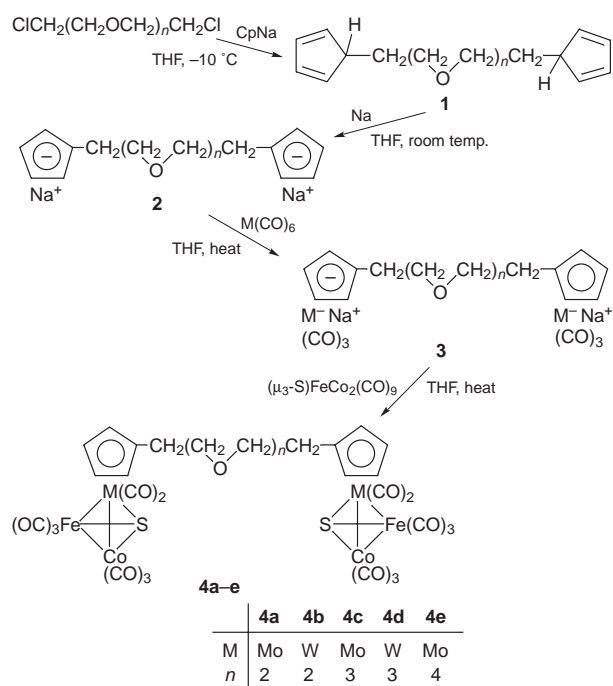
# Synthesis and Characterization of Novel Acyclic Polyethers Containing Two Tetrahedral Cluster Moieties as Terminal Groups†

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Five novel acyclic cluster polyethers  $[\eta^5\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5][\text{MFeCoS}(\text{CO})_8]_2$  ( $\text{M} = \text{Mo}, \text{W}; n = 2, 3; \text{M} = \text{Mo}, n = 4$ ) are synthesized through double isolobal displacement reaction of  $(\mu_3\text{-S})\text{FeCo}_2(\text{CO})_9$  with  $[\eta^5\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5][(\text{CO})_3\text{MNa}]_2$  and characterized by elemental analysis and spectroscopic techniques.

Since the 1970s acyclic polyethers with heteroatom-containing terminal groups have been receiving considerable attention.<sup>1</sup> Such polyethers possess both flexible open chains and donor atom-containing terminal groups, and they have been shown, similarly to crown ethers,<sup>2</sup> to be very useful as ionophores in solvent extraction,<sup>2</sup> ion transport<sup>3</sup> and phase-transfer catalysis.<sup>4</sup> However, among such known polyethers reported so far, none has terminal groups whose donor heteroatoms are involved in bonding to metal cluster cores. Herein we report the first examples of acyclic cluster polyethers, which have two sulfur-containing tetrahedral  $\text{MFeCoS}$  ( $\text{M} = \text{Mo}, \text{W}$ ) cluster cores at their terminal groups.



Scheme 1

We found that the new acyclic polyethers with general formula  $[\eta^5\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5][\text{MFeCoS}(\text{CO})_8]_2$  **4a-e** could be successfully prepared by the method shown in Scheme 1. First  $\text{ClCH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{Cl}$  ( $n = 2-4$ ) was treated with  $\text{CpNa}$  in THF at  $-10^\circ\text{C}$  to give oligoethylene glycol bridged dicyclopentadienes **1** which were then reacted with sodium sand

in THF at room temperature to afford THF solutions containing bridged dicyclopentadienyldisodium salts **2**. These were reacted with  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Mo}, \text{W}$ ) in THF or diglyme at reflux, followed by treatment of the intermediates  $[\eta^5\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5][(\text{CO})_3\text{MNa}]_2$  **3** ( $\text{M} = \text{Mo}, \text{W}; n = 2-4$ ) with  $(\mu_3\text{-S})\text{FeCo}_2(\text{CO})_9$  at reflux to yield the five acyclic cluster polyethers **4a-e**.

As can be seen from Scheme 1, the final two steps involve an isoelectronic ligand exchange<sup>5</sup> between **2** and  $\text{M}(\text{CO})_6$ , in which the two bridged 6e Cp ligands in **2** each substitute for three 2e CO ligands of  $\text{M}(\text{CO})_6$ , and then a double isolobal displacement<sup>6</sup> of two  $\text{Co}(\text{CO})_3$  ( $d^9 \text{ML}_3$ ) units in two molecules of  $(\mu_3\text{-S})\text{FeCo}_2(\text{CO})_9$  by the bridged double isolobal fragment  $(\text{CO})_2\text{M}[\eta^5\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5]\text{M}(\text{CO})_2$  ( $d^5 \text{ML}_5\text{-bridge-d}^5 \text{ML}_5$ ) generated *in situ* from **3**.

While single cluster complexes containing parent and monosubstituted cyclopentadienyl ligands  $\eta^5\text{-RC}_5\text{H}_4\text{M}(\text{CO})_2\text{FeCoS}(\text{CO})_8$  ( $\text{M} = \text{Mo}, \text{W}$ ) are intensely colored solids,<sup>6,7</sup> the double cluster polyethers **4a-e** are all red-brown viscous oils reflecting an influence of the bridged polyether chains upon the physical properties of the clusters. Products **4a-e** have been characterized by elemental analysis, IR and  $^1\text{H NMR}$  spectroscopies. For example, the IR spectra show four absorption bands in the range  $2071\text{-}1887 \text{ cm}^{-1}$  assigned to their terminal carbonyls and one absorption band at *ca.*  $1116 \text{ cm}^{-1}$  attributed to their ether functionalities, respectively. The  $^1\text{H NMR}$  spectra indicate the presence of all the hydrogen-containing organic groups. However, it is of note that although for **4a** and **4b** the triplets arising from the two  $\beta\text{-CH}_2$  groups indirectly bonded to Cp rings are partly overlapped with the singlets of  $\text{OCH}_2\text{CH}_2\text{O}$  groups, those for **4c-e** coalesce completely with the signals of  $\text{OCH}_2\text{CH}_2\text{O}$  groups to give one signal. In addition, for **4a-e** the four hydrogens on each substituted Cp ring all display an AA'BB' pattern of two singlets in a 3 : 1 intensity. Finally, it is of note that the oxygen atoms in **4a-e**, in contrast to those of mono-ether chain substituted cyclopentadienyl compounds,<sup>8,9</sup> cannot coordinate to the metals in their cluster cores, since these metals have achieved 18e configurations.

## Experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk and vacuum-line techniques. Tetrahydrofuran (THF) and diglyme were dried and deoxygenated by distillation from sodium benzophenone ketyl under nitrogen.  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  were purchased from Strem Chemicals Inc.  $\text{ClCH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{Cl}$  ( $n = 2-4$ )<sup>10,11</sup> and  $(\mu_3\text{-S})\text{FeCo}_2(\text{CO})_9$ <sup>12</sup> were prepared according to literature. IR and  $^1\text{H NMR}$  spectra were recorded on a Nicolet FT-IR 5DX spectrophotometer and a Bruker AC-P 200 spectrometer. Analyses (C, H) were performed using a Perkin-Elmer 240C model analyzer.

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**Preparations of Disodium Salts 2.**—A 100 ml two-necked flask equipped with a magnetic stir-bar, a serum cap and a nitrogen inlet tube, was charged with a THF solution of CpNa (30 ml, 81 mmol) prepared from sodium and cyclopentadiene and then was cooled to  $-10^{\circ}\text{C}$  by an ice salt bath.  $\text{ClCH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{Cl}$  ( $n = 2-4$ ) (40 mmol) was slowly added by syringe and then the mixture was stirred for 4 h at  $-10^{\circ}\text{C}$ . After removal of the precipitate by centrifugation, the centrifugate was diluted using THF (30 ml) and then stirred with a slight excess of sodium sand at room temp. for 15 h, to give, after filtration, THF solutions of  $[\eta^5\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5]\text{Na}_2$  **2** ( $n = 2-4$ ). Their concentrations were determined by titration using a standard HCl solution and they were kept under nitrogen for use in the preparations of **4a-e**.

**Preparation of 4a, 4c and 4e.**—A 100 ml two-necked flask fitted with a magnetic stir-bar, a serum cap and a reflux condenser topped with a nitrogen inlet tube, was charged with  $\text{Mo}(\text{CO})_6$  (792 mg, 3.0 mmol), the above-prepared THF solutions of disodium salts **2** ( $n = 2-4$ ) (1.5 mmol) and THF (20 ml). The mixture was stirred and refluxed for 20 h. Upon cooling this mixture to room temp.,  $(\mu_3\text{-S})\text{FeCo}_2(\text{CO})_9$  (1282 mg, 2.8 mmol) was added and the mixture was stirred and refluxed for 1 h. After removal of volatiles, the residue was subjected to TLC using 2 : 1  $\text{CH}_2\text{Cl}_2$ -light petroleum (bp  $30-60^{\circ}\text{C}$ ) for **4a**, 5 : 1  $\text{CH}_2\text{Cl}_2$ -light petroleum for **4c** and 100 : 1  $\text{CH}_2\text{Cl}_2$ -THF for **4e** as eluents. **4a**: brown-red oil, yield 24%;  $\nu_{\text{max}}/\text{cm}^{-1}$  2071, 2017, 1977, 1888 (CO), 1113 (C-O-C);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.69 (t,  $J = 5.8$  Hz, 4H,  $2\text{C}_5\text{H}_4\text{CH}_2$ ), 3.61 (s, 4H,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 3.63 (t,  $J = 5.8$  Hz, 4H,  $2\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2$ ), 5.27, 5.39 (s, s, 8H,  $2\text{C}_5\text{H}_4$ ) (Found: C, 32.82; H, 1.74.  $\text{C}_{32}\text{H}_{20}\text{Co}_2\text{Fe}_2\text{Mo}_2\text{O}_{18}\text{S}_2$  requires C, 32.63; H, 1.71%). **4c**: brown-red oil, yield 32%;  $\nu_{\text{max}}/\text{cm}^{-1}$  2070, 2022, 1980, 1889 (CO), 1118 (C-O-C);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.68 (t,  $J = 6.0$  Hz, 4H,  $2\text{C}_5\text{H}_4\text{CH}_2$ ), 3.62 (s, 12H,  $2\text{OCH}_2\text{CH}_2\text{O}$ ,  $2\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2$ ), 5.26, 5.40 (s, s, 8H,  $2\text{C}_5\text{H}_4$ ) (Found: C, 33.60; H, 2.00.  $\text{C}_{34}\text{H}_{24}\text{Co}_2\text{Fe}_2\text{Mo}_2\text{O}_{19}\text{S}_2$  requires C, 33.42; H, 1.98%). **4e**: brown-red oil, yield 30%;  $\nu_{\text{max}}/\text{cm}^{-1}$  2071, 2022, 2007, 1979, 1890 (CO), 1115 (C-O-C);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.68 (t,  $J = 6.0$  Hz, 4H,  $2\text{C}_5\text{H}_4\text{CH}_2$ ), 3.62 (s, 16H,  $3\text{OCH}_2\text{CH}_2\text{O}$ ,  $2\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2$ ), 5.26, 5.40 (s, s, 8H,  $2\text{C}_5\text{H}_4$ ) (Found: C, 34.40; H, 2.11.  $\text{C}_{36}\text{H}_{28}\text{Co}_2\text{Fe}_2\text{Mo}_2\text{O}_{20}\text{S}_2$  requires C, 34.15; H, 2.23%).

**Preparation of 4b and 4d.**—The equipped flask as described above was charged with  $\text{W}(\text{CO})_6$  (1056 mg, 3.0 mmol), the above-prepared THF solutions of disodium salts ( $n = 2, 3$ ) (1.5 mmol) and diglyme (20 ml). The mixture was stirred and refluxed for 6 h. After removal of diglyme,  $(\mu_3\text{-S})\text{FeCo}_2(\text{CO})_9$  (1282 mg, 2.8 mmol) and THF (20 ml) were added. The mixture was refluxed under stirring for 2 h. Solvent was removed and then the residue was subjected to TLC using 2 : 1  $\text{CH}_2\text{Cl}_2$ -light petroleum (bp  $30-60^{\circ}\text{C}$ ) for **4b** and 5 : 1

$\text{CH}_2\text{Cl}_2$ -light petroleum for **4d**. **4b**: brown-red oil, yield 14%;  $\nu_{\text{max}}/\text{cm}^{-1}$  2071, 2003, 1887 (CO), 1113 (C-O-C);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.78 (t,  $J = 5.4$  Hz, 4H,  $2\text{C}_5\text{H}_4\text{CH}_2$ ), 3.62 (s, 4H,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 3.65 (t,  $J = 5.4$  Hz, 4H,  $2\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2$ ), 5.31, 5.44 (s, s, 8H,  $2\text{C}_5\text{H}_4$ ) (Found: C, 28.75; H, 1.72.  $\text{C}_{32}\text{H}_{20}\text{Co}_2\text{Fe}_2\text{O}_{18}\text{S}_2\text{W}_2$  requires C, 28.39; H, 1.49%). **4d**: brown-red oil, yield 13%;  $\nu_{\text{max}}/\text{cm}^{-1}$  2069, 2021, 1972, 1892 (CO), 1118 (C-O-C);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.78 (t,  $J = 6.0$  Hz, 4H,  $2\text{C}_5\text{H}_4\text{CH}_2$ ), 3.63 (s, 12H,  $2\text{OCH}_2\text{CH}_2\text{O}$ ,  $2\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2$ ), 5.30, 5.46 (s, s, 8H,  $2\text{C}_5\text{H}_4$ ) (Found: C, 29.39; H, 2.04.  $\text{C}_{34}\text{H}_{24}\text{Co}_2\text{Fe}_2\text{O}_{19}\text{S}_2\text{W}_2$  requires C, 29.21; H, 1.73%).

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