SHORT PAPER

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Synthesis of the chiral indenyl tetrahedral clusters [(μ_3-S)FeCoM(η^5-Ind)(CO)$_8$] (M=Mo,W) and the crystal structure of [(μ_3-S)FeCoW(η^5-Ind)(CO)$_8$]

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The new indenyl tetrahedral cluster [(μ_3-S)FeCoM (η^5-Ind)(CO)$_8$] (M=Mo **2** ,W **3**) have been isolated from the reaction of [(μ_3-S)FeCo$_2$(CO)$_9$] **1** and K$^+$[(η^5-Ind)M(CO)$_3$]$^-$ (M=Mo,W) under mild conditions and the crystal structure of [(μ_3-S)FeCoW(η^5-Ind)(CO)$_8$] **3** has been established, affording structural evidence for the ring slippage of the indenyl ligand.

Keywords: tetrahedral cluster, indenyl, ring slippage

Considerable efforts have been devoted to the synthesis of the chiral tetrahedral cluster, due to their unique structure and their potential application in asymmetric catalysis.[1] Among all the synthetic methods, the direct, one step, metal-exchange reaction using the reagent Na[η^5-CpM(CO)$_3$] is mostly utilised, therefore nearly all of the tetrahedral clusters reported are these containing Cp and its simple analogues.[2] Intrigued by the possibility that the replacement of Cp with an indenyl ligand would enhance the reactivity of the metal exchange reagent and also enable indenyl complexes to generate vacant coordinate sites during the catalysis procedure,[3] we set out to exploit an effective synthetic route to access the chiral indenyl tetrahedral clusters. Two novel chiral clusters [(μ_3-S)FeCoM (η^5-Ind)(CO)$_8$] (M=Mo,W), which have been obtained from the reactions of K[(η^5-Ind)M(CO)$_3$] (M=Mo,W) with the prochiral cluster [(μ_3-S)FeCo$_2$(CO)$_9$] in THF at room temperature (Scheme 1). Both clusters **2** and **3** are air stable dark crystals and soluble in polar solvents such as CH$_2$CI$_2$, THF and ether. Satisfactory C, H analyses were obtained for the two compounds.

The similar spectral characteristics of compounds **2** and **3** suggest the same configuration for these clusters. In the IR spectra there were several intense absorption bands in the range 2070–1860 cm^{-1}, characteristic absorption of carbonyl ligands bound to transition metals in the terminal mode, and characteristic absorption bands of indenyl ligand at –748 cm^{-1} and –520 cm^{-1}.[4] The ^{1}H NMR spectra of the compounds exhibited two independent sets of signals in the ratio 4:3. The resonances for benzene protons appear at 7.27–7.52ppm as characteristic AA'BB' multiplets. The set for the coordinating indenyl five membered ring single are three distinct AA'B type singlets and revealed that the indenyl ligands were bound asymmetrically, which indicates the presence of a chiral tetrahedral subcluster [SFeCoM](M=Mo,W).[5]

The structural features of theses two chiral indenyl cluster have been established by X-ray diffraction analysis of a suitable crystal of **3**. The structure unexpectedly reveals the presence of two enantiomeric molecule A. and B. in the unit cell, and each unit contains a tetrahedral skeleton composed of Fe, Co, W and S (Fig.1) in which the slightly distorted triangle(Fe, Co ,W,) is capped by an S ligand. The acute angles in the tetrahedral core about the basal atom range from 54.9 to 62.8°, and those about the capping atom S, average 74.4°, which deviates considerably from perfect tetrahedral geometry and reflects the relative atom size (W>Fe≈Co>S). The carbonyl ligands adopt the terminal mode of coordination. The W bonds to indenyl are certainly in the pentahapto mode and cluster **3** is electronically saturated, containing a total of 48 valence electrons.

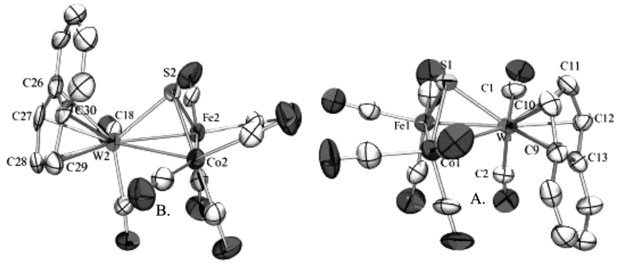
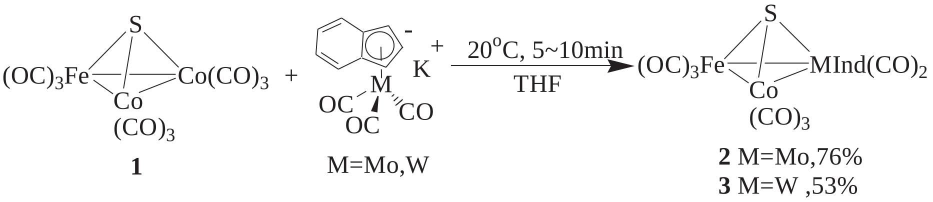


Fig. 1 The ORTEP plot of the molecular structure of cluster 3 showing the atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.



Scheme 1

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

There is structural evidence of ring slippage in the indenyl ligand of the basal W atom. The slip distortion of ally-ene bonding[6] to the indenyl ligand is further defined by values of (a_1) 0.13Å, (a_2) 0.06 Å for the difference between the average of the metal–C distances to C10, C11 and C12 and those to ring junction carbon C9 and C13, and the fold angles (b_1) 4.7° and (b_2) 3.5° between the planes defined by the carbons and the indenyl bezenoid ring.[7] Interestingly, to use the slip parameters Δ of Faller, Crabtree and Habib,[8] the W atom in molecule A has slipped a distance S=0.17 Å away from the centroid while S=0.09Å in molecule B. Whether the difference in S values results from the orientation of the indenyl ligand on the cluster or the chirality of the cluster skeleton needs further investigation.

Selected bond distance (Å) and angles (deg) of A.:Fe1–S1 2.187(3) Fe1–Co1 2.569(3) Co1–S1 2.187(3) W1–S1 2.348(3) W1–Co1 2.761(2) W1–Fe1 2.784(2) W1–C11 2.279(12) W1–C12 2.288(12) W1–C10 2.298(12) W1–C13 2.410(11) W1–C9 2.435(11) W1–Ind 2.012(5); S1–Co1–Fe1 54.02(8), S1–Co1–W1 55.17(8), Fe1–Co1–W1 62.84(5), S1–Fe1–W1 54.78(8), S1–Fe1–Co1 54.03(8), Co1–Fe1–W1 61.96(5), S1–W1–Fe1 49.56(7), S1–W1–Co1 49.89(7), Co1–W1–Fe1 55.20(4), Co1–S1–Fe1 71.95(9), Fe1–S1–W1 75.66(9), Co1–S1–W1 74.94(9)

Selected bond distance (Å) and angles (deg) of B.:Fe2–S2 2.178(3), Fe2–Co2 2.571(2), Co2–S2 2.192(3), W2–S2 2.332(3), W2–Co2 2.782(2), W2–Fe2 2.790(2), W2–C28 2.325(10), W2–C29 2.326(12), W2–C27 2.351(14), W2–C26 2.398(12), W2–C30 2.401(11), W2–Ind 2.018(5); S2–W2–Co2 49.82(7), S2–W2–Fe2 49.34(7), Co2–W2–Fe2 54.96(4), S2–Fe2–Co2 54.21(8), S2–Fe2–W2 54.30(7), Co2–Fe2–W2 62.35(5), S2–Co2–Fe2 53.71(8), S2–Co2–W2 54.36(7), Fe2–Co2–W2 62.69(5), Fe2–S2–Co2 72.08(10), Fe2–S2–W2 76.36(9), Co2–S2–W2 75.83(9)

Symmetry transformations used to generate equivalent atoms: **1** $-x,-y+1,-z+2$

Experimental

All reactions were performed under an atmosphere of pure N_2 by using standard Schlenk and vacuum-line techniques. Column chromatography was carried out by using silica gel of 160~200 mesh. Compounds $[Mo(CO)_6]$ and $[W(CO)_6]$ were purchased form Fluka and Aldrich Chem. Co. IR spectra were recorded on Nicolet FT-IR 10DX spectrometer; analysis (C,H) were performed on an 1106-type analyzer.

$K[(\eta^5\text{-Ind})\,M(CO)_3]$

To potassium sand (0.39g,10mmol) in DME (20ml) was added indene (1.16g,10mmol). The mixture was stirring at 0°C for 0.5h, resulting in a bright-yellow solution. After stirring for an additional 0.5h while warming to room temperature, $[M(CO)_6]$ (10mmol)(M=Mo,W) was added to the mixture and refluxed under nitrogen for 12h. The resulting red mixture was the DME solution of $K[(\eta^5\text{-Ind})M(CO)_3]$ (20ml, 0.5mmol/ml)

Preparation of $(\mu_3\text{-}S)FeCoMo(\eta^5\text{-}Ind)\,(CO)_8$: The cluster $(\mu_3\text{-S})FeCo_2(CO)_9$ (0.22g,0.5mmol) was dissolved in THF(15ml), and then the DME solution of $K[(\eta^5\text{-Ind})Mo(CO)_3]$ (1ml,0.5mmol) was added. The mixture was stirred at room temperature for 10min. The solvent was removed under vacuum and the residue was extracted by CH_2Cl_2. The extract was subjected to column chromatography. The main product was obtained as red dark solid (0.22g) in yield 76%. (Cal.for $SFeCoMoC_{17}H_7O_8$: C, 34.95; H, 1.21. Found: C, 34.73; H, 1.19%) IR (KBr disk): ν (CO) 2067S, 2023s, 1992sh; 827m 748s δ_H (400MHz,$CDCl_3$): 5.58(S,1H) 5.85(S,2H) 7.27–7.52(m,4H)

Preparation of $(\mu_3\text{-}S)FeCoW(\eta^5\text{-}Ind)\,(CO)_8$: The synthetic method for cluster **3** was the same as that for **2**. Yield: 53% (Cal.for $SFeCoWC_{17}H_7O_8$: C, 30.46; H, 1.05 Found: C,30.41;H,1.06%) IR (KBr disk): ν (CO) 2064s, 2026s, 1962sh; 838m, 753s δ_H (400MHz $CDCl_3$): 5.60(S,1H) 5.85(S,1H) 5.90(S,1H) 7.27–7.52(m,4H)

Crystal data for cluster **3**: Suitable crystals of cluster **3** ($C_{17}H_7O_8SCoFeW$) (Mr=669.92) were obtained from CH_2Cl_2–hexane at –20°C. The crystal system and space group was triclinic and *P–1* (no. 2), respectively. The cell parameters were determined on an Enraf-Nonius CAD-4 diffractometer with graphite- monochromated Mo-K_α radiation: a = 8.4995(6) Å, b = 11.4295(8) Å, c = 19.9498(15) Å, α = 93.37(0) °, β = 96.21(0) °, γ = 90.41(0) °V = 1923.13(20) $Å^3$, Z = 4, D_c = 2.314 g/cm^3, μ = 7.715 mm^{-1}, θ_{max} = 25.49° and $F(000)$ = 704. A total of 10279 reflections were collected with 7068 unique reflections (R_{int}=0.1245). The structure was solved by direct method and expanded using Fourier technique. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 7068 observed reflections [$I>2\sigma(I)$] and 524 variable parameters and converged with unweighted and weighted agreement factors of R = 0.0589, R_w = 0.14852. The minimum and maximum final electron densities were 4.038 and –2.698 eÅ^{-3}. All the calculations were performed using the SHELXL-97 crystallographic program package.

Full crystallographic details, excluding structure factors have been deposited at the Cambridge Crystallographic Data Center (CCDC deposition number 206140).

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