SHORT PAPER

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Reactions of a chiral metal cluster containing a functionally substituted cyclopentadienyl ligand with hydrazines[†]

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Reaction of hydrazines with $SFeCoMo(CO)_8[\eta^5\text{-}C_5H_4C(O)CH_3]$ (**1**), gave four novel cluster hydrazones.

Clusters with a tetrahedral skeleton comprised of four different atoms have been receiving considerable attention in recent years, largely because they can provide unambiguous evidence for cluster catalysis through asymmetric induction.[1–3] Our interest in the resolution of racemic clusters prompted us to prepare chiral clusters containing functional substituted cyclopentadienyl ligands.[4–9] In this paper, we report the reactions of seven hydrazines with the chiral cluster $SFeCoMo(CO)_8[\eta^5\text{-}C_5H_4C(O)CH_3]$, four of which react to give novel metal cluster derivatives. The reactions are shown in Scheme 1.

The characterizational data for these cluster derivatives agree well with their proposed structures. In the IR spectra, very strong absorption bands in the region of 2076 – 1884 cm^{-1} can be assigned to the carbonyl ligands, suggesting that the metal framework is intact. The C=N vibrations are observed around 1600 cm^{-1} as weak bands, which are different for each of the four clusters. In cluster **4,** the bands at 1714 and 1672 cm^{-1} can be assigned to the two ketonic carbonyls, and in **5,** the band at 1708 cm^{-1} to the ester group. The ^1H NMR spectra of **2-5** are as expected.

The chemical shifts of the four protons in the cyclopentadienyl ligand are observed as triplet or quartet in the range of 5.95–5.40 ppm, and those of the three protons in methyl group appeared around 2.10 ppm as a singlet. In **2** the singlet at 8.30 ppm can be assigned to the N-H proton and the signal around 5.80 is assigned to the NH_2 group. The chemical shifts of the protons of the 2,4-dinitrophenyl groups in **3** are observed in the region of 11.22–1.85 ppm, consistent with the published results.[10] For cluster **4,** two singlets at 10.17 and 7.75 ppm are assigned to the two N–H units, the singlet at 7.35 is to the five protons in benzene ring, and the methylidyne protons are observed at 5.09, whilst the singlet at 1.61 ppm can be assigned to the protons of the methyl group near the benzene ring. In cluster **5,** the menthol group is observed at 4.71 – 0.81 ppm,[11] and the singlet at 7.78 ppm corresponds to the N-H proton. All of the four compounds are air-stable solids obtained in *ca* 50% yield, but could not be crystallized.

Reaction of the starting material with $PhNNNH_2$, $(H_2NNH)_2CO$ and H_2NNH_2 gave no isolable products.

Although in complexes **4** and **5** two kinds of optically active groups have been introduced into the racemic cluster, the mixture of diastereoisomers could not be separated by chromatography. The reason might be that the chiral carbon is too far away from the tetrahedral framework. Whatever, this should be a route to an optically active cluster. The study is being continued.

Experimental

All reactions were carried out under nitrogen. Commercial $NH_2NHC(S)NH_2$, 2,4-dinitrophenylhydrazine, $NH_2NH_2{\cdot}H_2O$ and $PhNHNH_2$ were used as received; $C(O)(NHNH_2)_2$, $SFeCoMo(CO)_8[\eta^5\text{-}C_5H_4C(O)CH_3]$,[5] (-)-5-(α-phenyl)semioxamazide (m.p. 167–169ºC, $[\alpha]^{25}_D = -107.6^\circ$, $CHCl_3$, *c* 0.1, *l* 1)[12] and L-(+)-menthydrazide (m.p. 94–95ºC, $[\Phi]^{25}_D = +173.3^\circ$, EtOH, *c* 1, *l* 1)[13] were prepared according to literature methods. IR and ^1H NMR spectra were recorded on Nicolet FT-IR 10DX and Bruker AM-400 MHz spectrometers respectively. C/H elemental analyses were performed on an 1106-type analyser.

Preparations: Compound **2:** A solution of thiosemicarbazide (0.2g, … mmol) in 2 ml 98% H_2SO_4, 10ml 95% EtOH and 2 ml H_2O was slowly added to a solution/suspension of **1** (0.1g, 0.17 mmol) in anhydrous EtOH (10ml), with stirring. After stirring at room temperature for 12 h, the ethanol was removed and the residue was separated on a silica gel column. Elution with CH_2Cl_2-hexane (v/v = 1:1) gave unreacted starting material (43 mg). Elution with CH_2Cl_2-ether (v/v = 50:1) afforded the main brown band; upon removing the solvent, compound **2** was obtained as brown solid. Yield 45% (50 mg) (Calc. for $C_{16}H_{10}O_8N_3S_2CoFeMo$: C, 29.70; H, 1.56. Found: C, 29.71; H, 1.59). IR (KBr disk): 2076vs, 2024vs, 1885w (C[O), 1588w, (C=N) cm^{-1}. δ_H ($CDCl_3$): 8.30 (s, 1H, N-H), 5.80-5.45 (m, 6H, $C_5H_4NH_2$), 2.34 (s, 3H, CH_3).

Compound **3:** The synthesis of cluster **3** was similar to that described above, except that 2,4-dinitrophenylhydrazine was used instead of thiosemicarbozide. CH_2Cl_2-hexane (v/v = 1:1) eluted the main band, from which compound **3** was obtained as a dark brown solid. (yield 47%) (Calc. for $C_{21}H_{11}O_{12}N_4SCoFeMo$: C, 33.45; H, 1.47. Found: C, 33.44; H, 1.47). IR (KBr disk): 3294w (*n*-H), 2076vs, 2021vs, 1996vs, 1973vs, 1957s, 1892m (C[O), 1614w (C=O) cm^{-1}. δ_H ($CDCl_3$): 11.22 (s, 1H, N–H), 9.08 (s, 1H, H^3 of benzene ring), 8.31 (d, 1H, *J* 9.6 Hz, H^5 of benzene ring), 7.87 (d, 1H, *J* 9.56 Hz, H^6 of benzene ring), 5.88–5.44 (q, 4H, C_5H_4), 2.20 (s, 3H, CH_3).

Compound **4:** Cluster **1** (200 mg, 0.35 mmol) and (-)-5-(α-phenylethyl)semioxamizide (80 mg, 0.36 mmol) were dissolved in 30 ml ethanol and 5 ml benzene, several drops of 98% H_2SO_4 were added and the mixture was stirred at room temperature for 1 day. The solvent was removed and the residue was separated on silica gel column. Elution with CH_2Cl_2-hexane (v/v = 1:1) gave the $SFeCoMo(CO)_8[\eta^5\text{-}C_5H_4C(O)CH_3]$. Elution with CH_2Cl_2-hexane-ether (v/v/v = 1:1:1) afforded the second band, from which compound **4** (123mg, 46%) was obtained. (Calc. for $C_{25}H_{18}O_{10}N_3SCoFeMo$: C, 39.34; H, 2.38. Found: C, 39.32; H, 2.37). IR (KBr disk): 2074vs, 2031vs, 1890w (C[O), 1714m, 1672m, (C=O), 1632w (C=N). δ_H ($CDCl_3$): 10.17 (s, 1H, N–H), 7.75 (s, 1H, N–H), 7.35 (s, 5H, C_6H_5), 5.95–5.45 (t, 4H, C_5H_4), 5.10 (s, 1H, CH), 2.14 (s, 3H, CH_3), 1.60 (s, 3H, CH_3).

Compound **5:** Cluster **1** (200 mg, 0.35 mmol) and L-(+)-menthydrazide (80 mg, 0.37 mmol) were dissolved in 15 ml ethanol. Three drops of 98% H_2SO_4 were added and the mixture was stirred at room temperature for 1 day. Then the mixture was concentrated and the residue was subjected to silica gel column chromatography. Elution with CH_2Cl_2-hexane (v/v = 2:1) afforded the product band. The solvent was removed, and the residue crystallized in CH_2Cl_2-hexane at –18ºC to give brown solid 142mg (53%) identified as compound **5** (Calc. for $C_{26}H_{27}O_{10}N_2SCoFeMo$: C, 40.54; H, 3.53. Found: C, 40.50; H, 3.52). IR (KBr disk): 2072vs, 2029vs, 1979vs, 1888m (C[O), 1703m, (C=O) cm^{-1}. δ_H ($CDCl_3$): 7.78 (s, 1H, N–H), 5.83–5.40 (q, 4H, C_5H_4), 4.71 (s, 1H, H^1 of menthol unit), 2.01–0.80 (m, 18H, protons of menthol unit).

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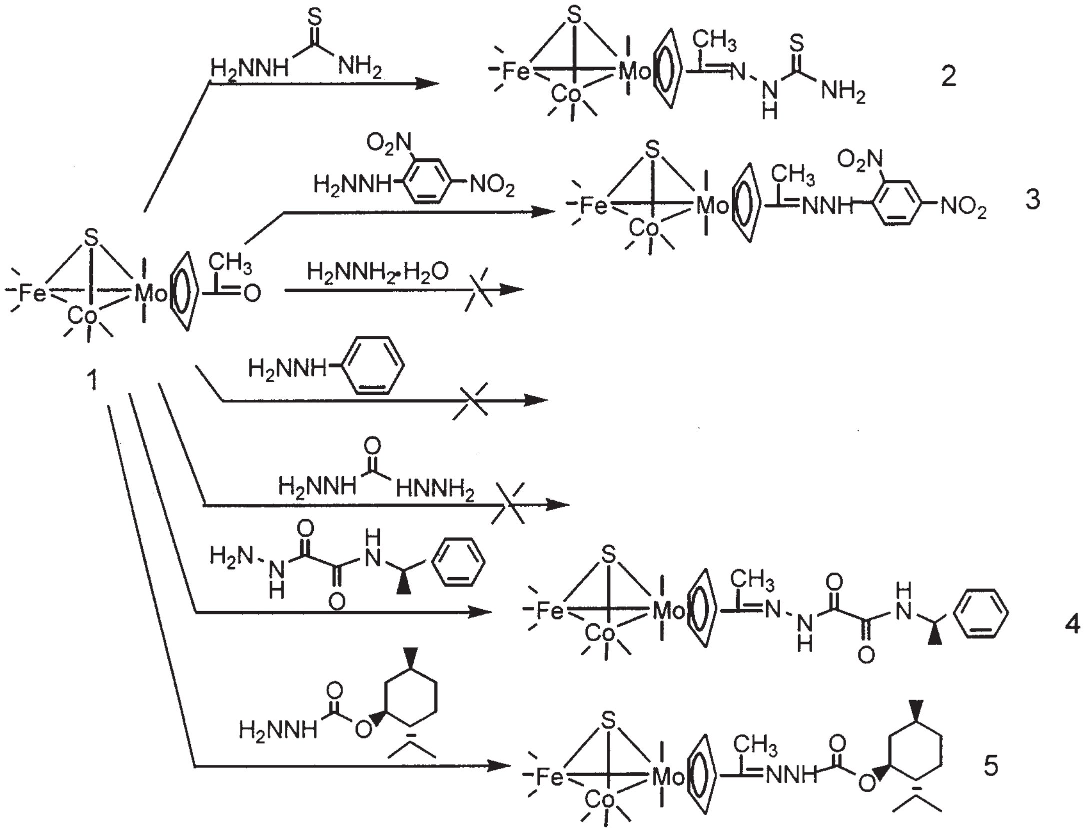
[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*



Scheme 1

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