

# Synthesis, Reactivity and Crystal Structure of a Novel Cluster $[\text{Co}_3(\text{CO})_9(\mu_3\text{-C})\text{C}(\text{O})\text{OCH}_2]_2$ †

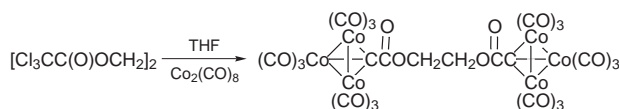
Ji Zhang,<sup>a</sup> Xue-Nian Chen,<sup>a</sup> Er-Run Ding,<sup>a</sup> Yuan-Qi-Yin<sup>\*a</sup> and Jie Sun<sup>b</sup>

<sup>a</sup>State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China

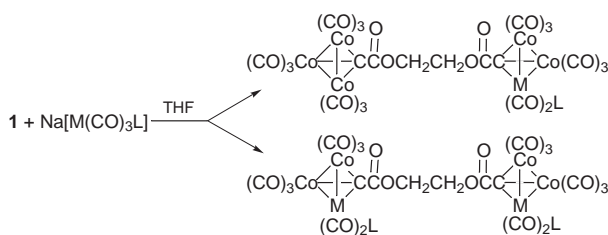
<sup>b</sup>Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, 200032, China

The higher-nuclearity cluster compound  $[\text{Co}_3(\text{CO})_9(\mu_3\text{-C})\text{C}(\text{O})\text{OCH}_2]_2$  **1** has been isolated from the reaction of  $[\text{Cl}_3\text{CC}(\text{O})\text{OCH}_2]_2$  and  $\text{Co}_2(\text{CO})_8$ , and its metal exchange reaction with  $\text{Na}[\text{M}(\text{CO})_3\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})\text{OMe}\}]$  (M=Mo or W) has been discussed together with its structure determination by single-crystal X-ray diffraction methods.

Being one of the most convenient processes to synthesize heterometal cluster compounds, metal exchange reactions have been systematically studied and extensively used since the 1980s.<sup>1–5</sup> However metal exchange reactions of higher-nuclearity cluster compounds has been less reported. In our attempt to study such processes, we have synthesized the double tetrahedral cluster **1**, which has two independent  $\text{Co}_3\text{C}$  skeletons in one molecule, by the reaction of  $[\text{Cl}_3\text{CC}(\text{O})\text{OCH}_2]_2$  with  $\text{Co}_2(\text{CO})_8$  in THF (Scheme 1). After treating **1** with metal exchange reagents  $\text{Na}[\text{M}(\text{CO})_3\{\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})\text{OMe}\}]$  (M=Mo or W), four novel double tetrahedral clusters  $[\text{Co}_2\text{M}^1(\text{CO})_8\text{L}^1(\mu_3\text{-C})\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OC}(\text{O})(\mu_3\text{-C})\text{Co}_2\text{M}^2(\text{CO})_8\text{L}^2](\text{M}^1=\text{Co}, \text{L}^1=\text{CO}, \text{M}^2=\text{Mo}, \text{L}^2=\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})\text{OMe} **2**;  $\text{M}^1=\text{Co}, \text{L}^1=\text{CO}, \text{M}^2=\text{W}, \text{L}^2=\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})\text{OCH}_3$  **3**;  $\text{M}^1=\text{M}^2=\text{Mo}, \text{L}^1=\text{L}^2=\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})\text{OMe}$  **4**;  $\text{M}^1=\text{M}^2=\text{W}, \text{L}^1=\text{L}^2=\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})\text{OMe}$  **5**) have been obtained (Scheme 2). Compounds **1–5** are air-stable solids at room temperature. They are soluble in polar solvents like THF and  $\text{CH}_2\text{Cl}_2$ . Satisfactory C, H analyses were obtained for all the compounds.$



Scheme 1



Scheme 2

The spectral characterization of compounds **2** and **3** as well as **4** and **5** is similar. This suggests the same configuration for **2** and **3** or **4** and **5**. Compared with **4** and **5**, the IR spectra of clusters **1–3** show a terminal carbonyl

absorption band at  $2112\text{ cm}^{-1}$ , which proved to be the characteristic of the  $\text{Co}_3(\text{CO})_9(\mu_3\text{-C})$  unit.<sup>6</sup> The weak absorption bands around  $1900\text{ cm}^{-1}$  in the IR spectra of clusters **2–5** correspond to the terminal carbonyls coordinated to the Mo or W atoms. For all the compounds, owing to the electronic effect of the metal cluster cores, the vibration bands of the  $\text{C}=\text{O}$  group in the  $\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OC}(\text{O})$  bridge occur around  $1670\text{ cm}^{-1}$ , much lower than expected for a  $\text{C}=\text{O}$  group in a normal ester complex. For the two  $\text{CH}_2$  groups in the  $\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OC}(\text{O})$  bridge, compounds **1**, **4** and **5** show one singlet at  $\delta$  4.58, 4.49 and 4.46 respectively, in their  $^1\text{H}$  NMR spectra, while compounds **2** and **3**, owing to the two different cluster cores (one is  $\text{Co}_3\text{C}$  and the other is  $\text{Co}_2\text{MC}$ ) in their molecules, show two singlets at  $\delta$  4.55, 4.53 and  $\delta$  4.54, 4.51, respectively. It should be noted that in the metal exchange reactions of cluster **1**, no compound of the type  $\text{Co}_3(\text{CO})_9(\mu_3\text{-C})\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OC}(\text{O})(\mu_3\text{-C})\text{CoM}_2(\text{CO})_7\text{L}_2$  was obtained. This indicates that the  $\text{Co}(\text{CO})_3$  group in different cluster cores has a different reactivity: that in the  $\text{Co}_3\text{C}$  core can be replaced more easily than that in the  $\text{Co}_2\text{MC}$  core.

The structure features of compound **1** have been established by X-ray diffraction analysis of a suitable crystal. As seen in Fig. 1, the molecule of compound **1** is centrosymmetric and contains two  $\text{CCo}_3$  tetrahedral skeleton cores connected through a  $\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OC}(\text{O})$  bridge. In the  $\text{CCo}_3$  tetrahedral skeleton core, each cobalt atom bears three terminal carbonyls. The average  $\text{Co–Co}$  bond length ( $2.47\text{ \AA}$ ) is equal to that of the simple  $\text{CCo}_3$  skeleton cluster while the average  $\text{Co–C}$  bond length is slightly shorter ( $1.89\text{ cf. }1.92\text{ \AA}$ ).<sup>7</sup> The  $\text{C}(3)\text{–C}(3^*)$  distance as well as the  $\text{C}(1)\text{–C}(2)$  distance is much shorter than the normal value of a  $\text{C–C}$  single bond ( $1.54\text{ \AA}$ ).

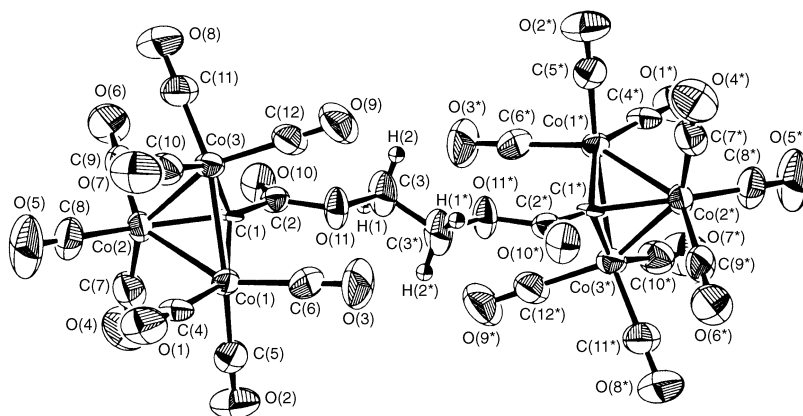
## Experimental

Apart from the synthesis of the starting material  $[\text{Cl}_3\text{CC}(\text{O})\text{OCH}_2]_2$ , all reactions and manipulations were performed under an atmosphere of pure nitrogen using standard Schlenk or vacuum-line techniques. Column chromatography was carried out by using silica gel of 160–200 mesh.  $\text{Co}_2(\text{CO})_8$  was from our laboratory.  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  were purchased from Fluka and Aldrich Chemical Co. The starting material  $[\text{Cl}_3\text{CC}(\text{O})\text{OCH}_2]_2$  was obtained by the esterification of glycol with excess  $\text{Cl}_3\text{CCO}_2\text{H}$ . IR spectra were recorded on a Nicolet FT-IR 10 DX spectrophotometer;  $^1\text{H}$  NMR spectra were recorded on a Bruker AM-300 MHz spectrometer; analyses (C, H) were performed on a Carlo Erba 1106-type analyzer.

**Preparation of Cluster 1.**  $2.13\text{ g}$  ( $6.23\text{ mmol}$ ) of  $\text{Co}_2(\text{CO})_8$  and  $0.60\text{ g}$  ( $1.70\text{ mmol}$ ) of  $[\text{Cl}_3\text{CC}(\text{O})\text{OCH}_2]_2$  were dissolved in  $50\text{ cm}^3$  of THF. The reaction mixture was stirred at  $40\text{--}50^\circ\text{C}$  for 8 h. Upon cooling to room temperature, the solvent was evaporated at reduced pressure and the residue was extracted with  $10\text{ cm}^3$  of  $\text{CH}_2\text{Cl}_2$ . The extracts were subjected to chromatographic separation on a silica gel column.

\*To receive any correspondence.

† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.



**Fig. 1** Crystal structure of cluster **1**. Selected bond distances (Å) and angles (°): Co(1)–Co(2) 2.477(1), Co(2)–Co(3) 2.467(1), Co(1)–Co(3) 2.464(1), C(1)–Co(1) 1.885(6), C(1)–Co(2) 1.878(7), C(1)–Co(3) 1.907(6), C(1)–C(2) 1.483(9), C(2)–O(11) 1.331(8), C(3)–O(11) 1.450(9) and C(3)–C(3\*) 1.45(2); Co(2)–Co(1)–C(1) 48.7(2), Co(3)–Co(1)–C(1) 49.9(2), Co(3)–Co(1)–Co(2) 59.90(4), Co(1)–Co(2)–Co(3) 59.79(4), Co(1)–Co(2)–C(1) 49.0(2), C(1)–Co(2)–Co(3) 49.8(2), Co(1)–Co(3)–Co(2) 60.31(4), Co(1)–Co(3)–C(1) 49.1(2), Co(2)–Co(3)–C(1) 48.8(2), Co(1)–C(1)–Co(2) 82.3(2), Co(1)–C(1)–Co(3) 81.1(2) and Co(2)–C(1)–Co(3) 81.3(3)

After elution with petroleum ether–CH<sub>2</sub>Cl<sub>2</sub> (1:9) followed by evaporation of solvents, 0.88 g (52%) of product as a dark purple solid was obtained. IR(KBr disc): 2112m, 2062vs, 2031vs, 2020s, 1989w and 1672m cm<sup>-1</sup>.  $\delta_{\text{H}}$ (CDCl<sub>3</sub>, 300 MHz) 4.58(s, 4H, 2CH<sub>2</sub>).

**Preparation of Na[M(CO)<sub>3</sub>{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>C(O)C<sub>6</sub>H<sub>4</sub>C(O)OMe}]** (M=Mo or W).—The compound Na(C<sub>5</sub>H<sub>5</sub>) (88 mg, 1.0 mmol) and dimethyl terephthalate (194 mg, 1.0 mmol) were dissolved in THF (50 cm<sup>3</sup>). After the mixture was refluxed for 8 h, M(CO)<sub>6</sub> (1.0 mmol) was added and refluxing continued for 12 (Mo) or 24 h (W). The solvent was removed under reduced pressure and the residue was washed with pentane; it can be used directly in the following reactions.

**Reaction of Cluster 1 with Na[Mo(CO)<sub>3</sub>{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>C(O)C<sub>6</sub>H<sub>4</sub>C(O)OMe}].**—Cluster **1** (300 mg, 0.3 mmol) and Na[Mo(CO)<sub>3</sub>{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>C(O)C<sub>6</sub>H<sub>4</sub>C(O)OMe}] (129 mg, 0.3 mmol) were dissolved in THF (20 cm<sup>3</sup>). After the mixture was stirred at room temperature for 10 h, the solution was evaporated to dryness. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) and then the extracts were subjected to column chromatography. Elution with CH<sub>2</sub>Cl<sub>2</sub> and then CH<sub>2</sub>Cl<sub>2</sub>–diethyl ether (2:1) gave three brown bands: (i) unreacted **1**, 90 mg; (ii) compound **2**, 72 mg (19.4%). IR (KBr disc): 2112m, 2093m, 2045vs, 2012s, 1971m, 1943m, 1895m, 1724m, 1672m and 1650m cm<sup>-1</sup>.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 300 MHz) 3.95 (s, 3H, CH<sub>3</sub>), 4.53 (s, 2H, CH<sub>2</sub>), 4.55 (s, 2H, CH<sub>2</sub>), 5.61 and 6.05 (d, 4H, C<sub>6</sub>H<sub>4</sub>), 7.83 and 8.15 (d, 4H, C<sub>6</sub>H<sub>4</sub>); (iii) compound **4**, 54 mg (12.2%). IR (KBr disc): 2093s, 2034s, 1946m, 1897m, 1726m, and 1671m cm<sup>-1</sup>.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 300 MHz) 3.96 (s, 6H, 2CH<sub>3</sub>), 4.49 (s, 4H, 2CH<sub>2</sub>), 5.63 and 6.05 (d, 8H, 2C<sub>6</sub>H<sub>4</sub>), 7.84 and 8.15 (d, 8H, 2C<sub>6</sub>H<sub>4</sub>).

**Reaction of Cluster 1 with Na[W(CO)<sub>3</sub>{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>C(O)C<sub>6</sub>H<sub>4</sub>C(O)OMe}].**—The manipulations were the same as described above. The three brown bands: (i) unreacted **1**, 96 mg; (ii) compound **3**, 88 mg (22.2%). IR (KBr disc): 2112m, 2091m, 2042vs, 2012s, 1962m, 1943m, 1891m, 1721m, 1672m and 1653m cm<sup>-1</sup>.  $\delta_{\text{H}}$ (CDCl<sub>3</sub>, 300 MHz) 3.96 (s, 3H, CH<sub>3</sub>), 4.51 (s, 2H, CH<sub>2</sub>), 4.54 (s, 2H, CH<sub>2</sub>), 5.72 and 6.07 (d, 4H, C<sub>6</sub>H<sub>4</sub>), 7.83 and 8.15 (d, 4H, C<sub>6</sub>H<sub>4</sub>); (iii) compound **5**, 98 mg (19.8%). IR (KBr disc): 2091s, 2031s, 1941m, 1890m, 1725m and 1669m cm<sup>-1</sup>.  $\delta_{\text{H}}$ (CDCl<sub>3</sub>, 300 MHz) 3.95 (s, 6H, 2CH<sub>3</sub>), 4.46 (s, 4H, 2CH<sub>2</sub>), 5.72 and 6.07 (d, 8H, 2C<sub>6</sub>H<sub>4</sub>), 7.84 and 8.15 (d, 8H, 2C<sub>6</sub>H<sub>4</sub>).

**Crystal Data for 1.**—A crystal of compound **1** (C<sub>24</sub>H<sub>4</sub>O<sub>22</sub>Co<sub>6</sub>, *M<sub>r</sub>* = 997.88) was grown from a petroleum ether–CH<sub>2</sub>Cl<sub>2</sub> solution at –20 °C. The space group was *P*2<sub>1</sub>/*n*(no. 14). The cell parameters were determined on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-K $\alpha$  radiation:

*a* = 9.330(2), *b* = 15.197(4), *c* = 11.783(4) Å,  $\beta$  = 91.16(2)°, *Z* = 2, *V* = 1670.4(7) Å<sup>3</sup>, *D<sub>c</sub>* = 1.984 g cm<sup>-3</sup>,  $\mu$  = 30.01 cm<sup>-1</sup>, *2* $\theta_{\text{max}}$  = 50.0° and *F*(000) = 972.00. Crystal size 0.20 × 0.20 × 0.30 mm. Of the 3119 reflections collected, 2926 were unique (*R*<sub>int</sub> = 0.086). The intensities of three representative reflections were measured every 200. The final cycle of full-matrix least-squares refinement was based on 1936 observed reflections [*I* > 2.00σ(*I*)] and 243 variable parameters and converged at final *R* = 0.045, *R<sub>w</sub>* = 0.051. Minimum and maximum final electron densities –0.43 and 0.66 e Å<sup>-3</sup>. All the calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation. The non-hydrogen atoms were refined anisotropically while hydrogen atoms were refined isotropically. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Research (S)*, 1999, Issue 1. Any request to the CCDC or this material should quote the full literature citation and the reference number 423/16.

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