SHORT PAPER

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Reactions of dipropargyl oxalate with $Co_2(CO)_8$, $RuCo_2(CO)_{11}$ and crystal structure of $(COOCH_2C_2H\text{-}\mu)_2[Co_2(CO)_6]_2$[†]

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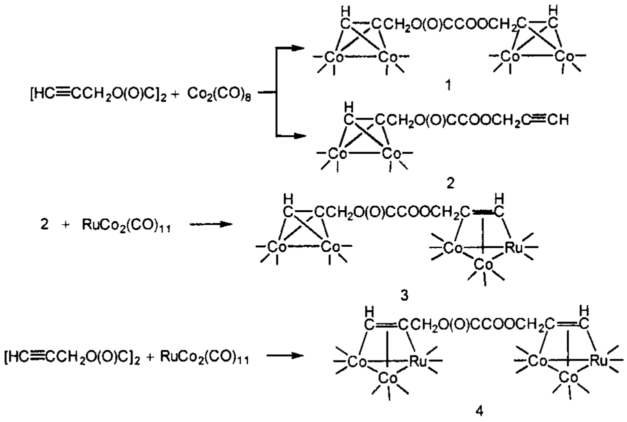
New compounds $(COOCH_2C_2H\text{-}\mu)_2[Co_2(CO)_6]_2$ **1**, $(HC_2CH_2O(O)CCOOCH_2C_2H\text{-}\mu)$ $[Co_2(CO)_6]$ **2**, $(COOCH_2C_2H\text{-}\mu)_2[RuCo_2(CO)_9][Co_2(CO)_6]$ **3** and $(COOCH_2C_2H\text{-}\mu)_2[RuCo_2(CO)_9]_2$ **4** were prepared by the reaction of $(COOCH_2C_2H)_2$ with $Co_2(CO)_8$ and $RuCo_2(CO)_{11}$, and the structure of **1** has been established by single-crystal X-ray diffraction methods.

Alkynes are able to coordinate to transition metals in a variety of bonding modes[1] and molecules containing two or three alkynyl groups can act as chelating ligands. [2] $Co_2(CO)_8$[3–5] and $RuCo_2(CO)_{11}$[6] can readily react with alkynes to give μ-alkyne complexes, but only a few reactions of the two compounds with diyne ligands have been reported, to our knowledge. In our attempt to study the reaction processes, four new complexes have been obtained by the reaction $(COOCH_2C_2H)_2$ with $Co_2(CO)_8$ and $RuCo_2(CO)_{11}$ in THF at room temperature (Scheme 1). Compounds **1** and **2** are air-stable both in solid and in solvent, however, clusters **3** and **4** are air-sensitive in solvents and hard to crystallise. Satisfactory C and H analysis were obtained for all compounds.



Scheme 1

In the IR spectra of these compounds, there are intense carbonyl absorption bands in the region 2100–1890 cm^{-1}. The strong absorption at 2100 cm^{-1} is characteristic of the $Co(CO)_3$ unit[7], and the weak absorption frequency around 1890 cm^{-1} in cluster **3** and **4** show that bridging or semi-bridging carbonyl exits in the $(\mathbf{C}_2H\text{-}\mu)[RuCo_2(CO)_9]$ group. The ester carbonyl bands are spit between 1775 and 1740 cm^{-1} upon the cluster formation. In the ^1H NMR spectrum, the terminal alkyne proton in $(\mathbf{C}_2H\text{-}\mu)[Co_2(CO)_6]$ appears at 6.10 ppm, and that in the $(C_2H\text{-}\mu)[RuCo_2(CO)_9]$ unit appears at 9.37 and 7.96 ppm as two signals. So the deshielding effects of metal units on alkyne proton follow the series $RuCo_2(CO)_9 > Co_2(CO)_6$. However, the effects are the contrary for the two protons in CH_2 unit.

The structure features of compound **1** have been established by X-ray diffraction analysis of a suitable crystal. As seen in Fig.1, cluster **1** consists of two C_2Co_2 cores connected *via* $(COOCH_2)_2$ as a bridging group. The C_2Co_2 core adopts a pseudo-tetrahedral geometry. The Co–Co bond lengths are 2.4675(8) and 2.4701(9) Å while the Co–C distances in C_2Co_2 core are in the range of 1.944(4)–1.957(4) Å, and the bond lengths of C(1)–C(2) and C(7)–C(8) are 1.328(5) and 1.320(5) Å respectively, all of which are comparable with the related dicobalt complexes.[4,8,9] The bond length of C(4)–C(5) is 1.522(6) Å, is slightly shorter than the normal C-C bond distance. The torsion angle of O(2)–C(4)–C(5)–O(4) is 32.8(7)°, so the two ester carbonyls are not located in one plane.

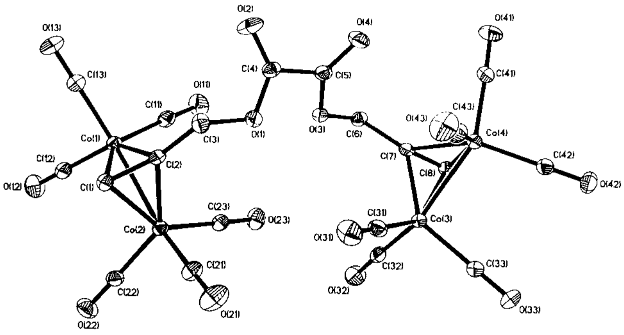


Fig. 1 Crystal structure of cluster 1. Selected bond lengths (Å) and angles (°): Co(1)–Co(2) 2.4675(8), Co(1)–C(1) 1.949(4), Co(1)–C(2) 1.950(4), Co(2)–C(1) 1.937(4), Co(2)–C(2) 1.948(4), Co(3)–Co(4) 2.4701(9), Co(3)–C(7) 1.954(4), Co(3)–C(8) 1.952(4), Co(4)–C(7) 1.957(4), Co(4)–C(8) 1.944(4), C(1)–C(2) 1.328(5), C(7)–C(8) 1.320(5), C(2)–C(3) 1.478(5), C(6)–C(7) 1.483(5), C(4)–C(5) 1.522(6); C(1)–C(2)–C(3) 143.0(4), C(8)–C(7)–C(6) 138.9(4), O(2)–C(4)–C(5) 120.8(4), O(2)–C(4)–O(1) 127.1(5), O(4)–C(5)–O(3) 126.7(4), O(4)–C(5)–C(4) 122.3(4)

Experimental

All operations were performed under a highly pure nitrogen atmosphere using standard Schlenk and vacuum techniques. Hexane, petroleum-ether (b.p. 60–90°C) and THF were distilled over sodium-benzophenone while CH_2Cl_2 was distilled over CaH_2. Column chromatography was carried out using 160–200 mesh silica gel. IR spectra were recorded on a Nicolet 10 DX spectrophotometer; ^1H NMR spectra on a Bruker AM-400MHz spectrometer and

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

elemental analysis (C, H) were performed on a Carlo Erba 1106-type analyser.

Preparation of cluster **1** *and* **2**: $Co_2(CO)_8$ (342 mg, 1mmol) was added to THF 25ml containing dipropargyl oxalate $(COOCH_2C_2H)_2$ (500 mg, 3.0mmol), the mixture was stirred at room temperature for 2h. A colour change from brown to purple was observed and monitoring by TLC showed the disappearance of the starting material. After the addition of a small amount of silica gel, the solvent was removed and the residue chromatographed. Elution with petroleum ether (b.p. 60–90°C)–CH_2Cl_2 (v/v = 4/3) afforded two red bands. From the first band, cluster **1** (60 mg, 16.3 %) was obtained as red crystals. Anal. Calc. for $C_{20}H_6O_{16}Co_4$: C, 32.55; H, 0.82%. Found: C, 32.56; H, 0.82%. IR (KBr disc): 2101s, 2076s, 2058vs, 2024vs (C≡O), 1775m, 1744w (C=O) cm^{-1}. δ_H ($CDCl_3$): 6.09 (s, 2H, 2CH), 5.50 (s, 4H, $2CH_2$). Compound **2** (270 mg, 46.5 %) was given from the second band. Anal. Calc. for $C_{14}H_6O_{10}Co_2$: C, 37.20; H, 1.34%. Found: C, 37.25; H, 1.30%. IR (KBr disc): 3258s (≡CH), 2133w (C≡C), 2099s, 2049vs, 2020vs (C≡O), 1773m, 1753m (C=O) cm^{-1}; δ_H ($CDCl_3$): 6.11 (s, 1H, CH), 5.51 (s, 2H, CH_2), 4.88 (s, 2H, CH_2), 2.55 (s, 1H, ≡CH).

Preparation of cluster **3**: A mixture of cluster **2** (135 mg, 3 mmol) and $RuCo_2(CO)_{11}$ (160 mg, 3 mmol) in THF 25 ml was allowed to react at room temperature for 2h. The solvent was removed *in vacuo*, and the residue was separated on a silica gel column. The main band was eluted with petroleum ether (b.p. 60–90°C)–CH_2Cl_2 (v/v = 2/1), from which cluster **3** (180 mg, 65.0 %) was obtained as a red solid. Anal. Calc. for $C_{23}H_6O_{19}Co_4Ru$: C, 29.93; H, 0.66%. Found: C, 29.87; H, 0.69%. IR (KBr disc): 2099s, 2062vs, 2033vs, 2006vs, 1994vs, 1899m (C≡O), 1770m (C=O) cm^{-1}; δ_H ($CDCl_3$): 9.36–7.96 (d, 1H, CH), 6.10 (s, 1H, CH), 5.51 (s, 2H, CH_2), 5.15–5.04 (d, 2H, CH_2).

Preparation of cluster **4**: The synthetic method for cluster **4** is similar to that for cluster **3**. A mixture of dipropargyl oxalate (83 mg, 0.5 mmol) and $RuCo_2(CO)_{11}$ (530 mg, 1.0 mmol) in 25 ml THF was stirred at room temperature for 2h. The main product was cluster **4** obtained as dark red solid (360 mg, 65.0 %). Anal. Calc. for $C_{26}H_6O_{22}Co_4Ru_2$: C, 28.18; H, 0.55%. Found: C, 28.23; H, 0.57%. IR (KBr disc): 2105s, 2037vs, 1892s (C≡O), 1679m, 1746m (C=O) cm^1; δ_H ($CDCl_3$): 9.37–7.96 (d, 2H, 2CH), 5.14-5.03 (d, 4H, $2CH_2$).

Crystal data for **1**: A Crystal of Cluster **1** ($C_{20}H_6Co_4O_{16}$, *Mr* = 737.97) was obtained from CH_2Cl_2–Hexane. The space group was P2(1)/c. The cell parameters were determined on a Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å): a = 7.3779(15), b = 18.011(4), c = 19.757(4) Å, α = 90°, β = 95.00(3)°, γ = 90°, Z = 4, V = 2615.5(9) Å, D_c = 1.874 g/m^{-3}, μ = 2.568 mm^{-1}, θ_{max} = 25.97° and $F(000)$ = 1448. Crystal size $0.9 \times 0.125 \times 0.1$ mm. Of the 5532 reflections observed at 20°C, 5119 were unique (R_{int} = 0.0179). The final cycle of full-matrix least-squares refinement was based on 3838 observed reflections [$I > 2\sigma(I)$] and 361 variable parameters and converged at final R = 0.0414, R_w = 0.0865. Minimum and maximum final densities are –0.371 and 0.355 e/Å^3. All the calculations were performed using the Enraf-Nonius Molen/VAX Software package of Molecular Structure Corporation. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

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