

Priority communication

**The unexpected synthesis of a tricobalt cluster with ferrocenyl groups:
crystal structure and cyclic voltammetry of $\text{Co}_3(\text{CO})_7(\mu_3\text{-PFc})(\mu_2\text{-PFc}_2)$
($\text{Fc} = (\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)$)**

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Abstract

FcPcCl_2 is reacted with $\text{NaCo}(\text{CO})_4$ in THF at room temperature. Crystallization from CH_2Cl_2 -hexane affords dark-green diamagnetic rhombi in low yield. Single crystal X-ray analysis has shown that the structure is $[\text{Co}_3(\text{CO})_7(\mu_3\text{-PFc})(\mu_2\text{-PFc}_2)]$ (**1**). Cyclic voltammetry has shown that three iron atoms in **1** are oxidized at the same potential, but it exhibits two reversible reduction peaks. © 1997 Elsevier Science S.A.

Keywords: Cobalt cluster; Ferrocenyl groups; Cyclic voltammetry

RPCl_2 derivatives are important tethers for metal carbonyl groups to yield trimetallic clusters $\text{RPCo}_3(\text{CO})_9$ and/or mixed metal carbonyl clusters, $\text{RPMM}'(\text{CO})_x\text{L}$ and $\text{RPMM}'\text{M}''(\text{CO})_x\text{L}$ for simple R groups such as CH_3 , C_6H_{11} , C_6H_5 , t-Bu, and Et_2N when RPCl_2 is reacted with $\text{Co}_2(\text{CO})_8$ or $\text{NaCo}(\text{CO})_4$ in hexane [1,2]. However, a tetrametallic cluster, $\text{Co}_4(\text{CO})_{10}(\text{PPh})_2$, is obtained when PhPCl_2 is reacted with $\text{NaCo}(\text{CO})_4$ in toluene [3]. These results suggest that the reaction conditions, such as solvent and/or temperature, in addition to the choice of the substituent R affect whether trimetallic clusters or tetrametallic clusters are obtained in the reaction of RPCl_2 with $\text{NaCo}(\text{CO})_4$ or $\text{Co}_2(\text{CO})_8$. Recently, we have been interested in the synthesis of nanometer-sized higher-nuclearity clusters by using small cobalt clusters as building blocks [4,5] with the hope of applications to nano-technology [6–8]. In this context, tuning of the cluster is of fundamental importance and introduction of a redox-active substituent R is one of the primary strategies to achieve this. Therefore, the synthesis of $\text{FcPCo}_3(\text{CO})_9$ and/or $\text{FcPCo}_4(\text{CO})_{10}\text{PFc}$ ($\text{Fc} = (\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)$) as a building block is highly desirable for access to functionalized modules of higher-nuclearity cobalt clusters. Herein we

report the reaction of FcPcCl_2 with $\text{NaCo}(\text{CO})_4$ in THF and the isolation and X-ray analysis of the unexpected product.

The reaction of FcPcCl_2 [9] with $\text{NaCo}(\text{CO})_4$ in THF at room temperature affords, after column-chromatography on silica-gel (twice) and crystallization from hexane: CH_2Cl_2 (3:1), dark-green rhombi (**1**) in low yield.¹

¹ A THF solution (30 ml) in which FcPcCl_2 (3.4 mmol, 1.0 g) was dissolved and added slowly to a THF solution (30 ml) of $\text{NaCo}(\text{CO})_4$ prepared from $\text{Co}_2(\text{CO})_8$ (4.0 mmol, 1.36 g) over sodium-amalgam at room temperature. A red-brown solution was immediately produced. The mixture was stirred for 17 h at ambient temperature. Then the solvent was removed under reduced pressure leaving a dark green-brown oil. The oil was dissolved in benzene (30 ml) and the solution was loaded on a Yamazen YFLC-700 medium-pressure liquid chromatography instrument (Wako-gel C-200). The first dark brown main band was eluted with hexane:benzene (4:1), then a dark green-brown band was eluted with benzene. A dark green solid was left after evaporation of the solvent; this was again subjected to column-chromatography on the same instrument. The dark green band was eluted with a mixed solvent of benzene:hexane (4:1). Dark green rhombi (10 mg) were obtained after crystallization from CH_2Cl_2 :hexane (5 ml:15 ml). (The yield of the crude product is about 50 mg.) $\text{IR}(\nu(\text{CO}))$ /(KBr-disk): 2046(s), 1996(vs), 1982(vs), 1969(vs), 1952(vs) cm^{-1} . Absorption spectrum in CHCl_3 : 390, 450, and 630 nm (ϵ 4120, 4150, and 2670). The characterization of the main dark-brown product has not yet been accomplished.

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A single crystal X-ray study of **(1)** (Fig. 1)² reveals that the dark-green product **(1)** possesses a triangular cobalt cluster skeleton with a triply-bridging FcP group and a doubly-bridging Fc₂P group. The Co1–Co2 distance (2.564(1) Å) is significantly shorter than the Co1–Co3 distance (2.642(1) Å) and the Co2–Co3 distance (2.670(2) Å), suggesting that the Co1–Co2 bond has some double bond character. The cluster **(1)** has an overall electron count of 48. A powdered sample of **(1)** does not give rise to an ESR signal at room temperature, indicating that **(1)** is diamagnetic.

Fig. 2 shows a cyclic voltammogram of **(1)** in CH₂Cl₂.³ A reversible oxidation peak is observed at $E_{1/2} = +0.33$ V, which suggests that three iron atoms of the ferrocenyl groups are oxidized at the same potential [10] although the iron atoms are in two different ligands. In the reduction potential region, however, two

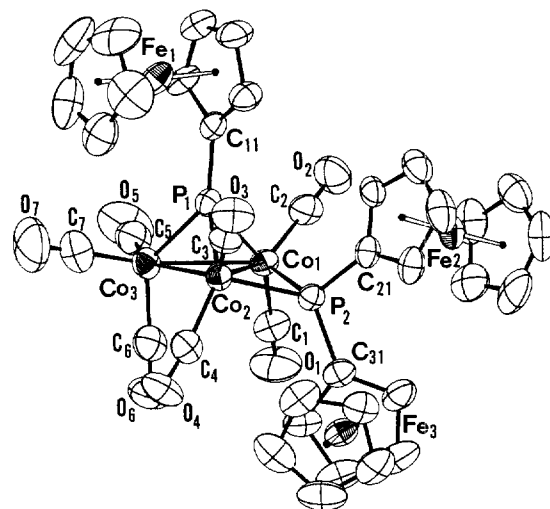


Fig. 1. X-ray molecular structure of the novel cobalt cluster **1** with the atom numbering scheme. Selected bond lengths (Å) and angles (deg). Estimated standard deviations in parentheses: Co1–Co2 2.564(1), Co1–Co3 2.642(1), Co2–Co3 2.670(2), P1–Co1 2.156(2), P1–Co2 2.123(2), P1–Co3 2.136(2), P2–Co1 2.193(2), P2–Co2 2.188(2), P1–C11 1.785(8), P2–C21 1.792(8), P2–C31 1.798(8); Co1–Co2–Co3 60.60(4), Co2–Co3–Co1 67.72(4), Co2–Co1–Co3 61.68(4), P1–Co1–Co2 52.61(6), P1–Co1–Co3 51.68(6), P1–Co2–Co1 53.78(6), P1–Co2–Co3 51.40(6), P1–Co3–Co1 52.34(6), P1–Co1–P2 95.93(8), P1–Co2–P2 97.04(8), Co1–Co2–P2 54.26(6), Co2–Co1–P2 54.08(6), Co1–P2–Co2 71.65(7).

² Crystal data: C₃₇H₂₇Co₃Fe₃O₇P₂, M = 989.9, monoclinic, space group $P2_{1/n}$ (No. 14), $a = 16.043(4)$, $b = 18.174(3)$, $c = 12.562(2)$ Å, $\beta = 91.45(2)^\circ$, $V = 3661(1)$ Å³, $Z = 4$, $D_c = 1.80$ g cm⁻³, Monochromated MoK α radiation, $\lambda = 0.71073$ Å, $\mu = 15.0$ cm⁻¹, $T = 298$ K. Data were collected using a crystal of ca. $0.55 \times 0.45 \times 0.20$ mm³, on a MAC Science MXC³ diffractometer, in the ω -scan mode. A total of 6441 unique reflections were measured for $3^\circ < 2\theta < 50^\circ$ and 4387 reflections with $|F_o| > 4\sigma(|F_o|)$ were used in refinement. No absorption correction was applied. The structure was solved by a direct method (SHELXS-86) and refined by full matrix least squares. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. The final residuals were $R = 0.055$ and $R_w = 0.075$. Programs from the MAC Science Crystan package were run on a Sun SP/Classic workstation.

³ Cyclic voltammetry was carried out under an argon atmosphere at 20°C using a BAS CV-50W electrochemical analyzer equipped with a platinum plate electrode as the working electrode and a platinum coil for the auxiliary electrode. A Ag/AgNO₃ in CH₃CN (0.01 M) electrode was employed as the reference electrode with 0.1 M *n*-Bu₄NClO₄ (TBAP) in CH₂Cl₂ (1 M = 1 mol dm⁻³). An approximate 10⁻³ M solution was prepared in CH₂Cl₂ which contained 0.1 M TBAP as a supporting electrolyte. A sweep rate of 200 mV s⁻¹ was used for cyclic voltammetry.

reversible peaks are observed at $E_{1/2} = -1.15$ and -1.34 V with $\Delta E_{1/2} = 190$ mV. For FcCCo₃-(CO)_{9-x}L_x and FcCCo₃(Cp)₃Cfc [10], only one metal core reduction peak is observed at around -1.0 V. In contrast, *p*-[(CO)₉Co₃-C]₂C₆H₄ shows two quasi-reversible reduction peaks at around -1.0 V with $\Delta E_{1/2} = 140$ mV which arise from the significant interaction between two cluster units when the core reduction potential is applied to this cluster [5]. When the CV measurements are made at -3°C the oxidation peak splits into two peaks (0.530 and 0.570 V). Temperature-dependent ¹H NMR measurements have

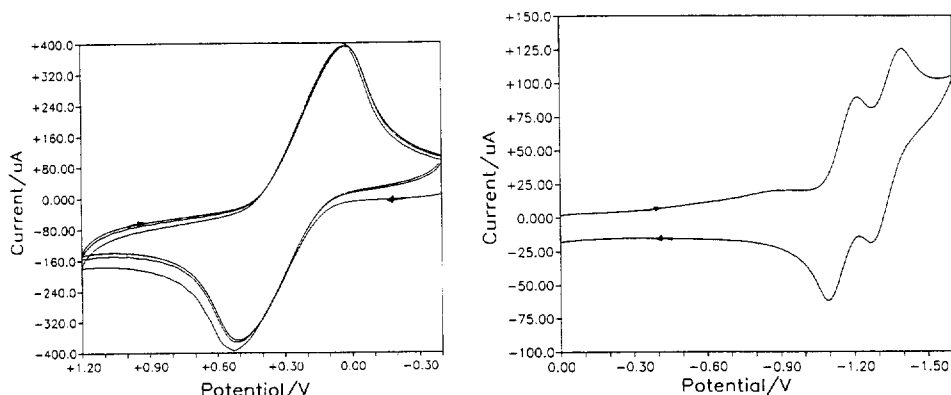


Fig. 2. Cyclic voltammograms of **1** in CH₂Cl₂ at 20°C; 200 mV s⁻¹, Pt plate (working electrode), Ag/Ag⁺ in CH₃CN (reference electrode).

shown significant changes on lowering the temperature from room temperature to -50°C . These observations suggest that the two reduction processes for (1) occur within the two core skeletal isomers. Exact analysis of these reduction processes must await future ESR studies using the species obtained from the bulk electrolysis of (1). To achieve this, the yield of this cluster should be improved. A plausible explanation of the formation of 1 is that a small amount of Fc_2PCL is contained in FcPCL_2 [9]. Thus, our effort is in continuing to improve the yield of this interesting cluster by reacting $\text{NaCo}(\text{CO})_4$ with a mixture of equimolar amounts of FcPCL_2 and Fc_2PCL .

Acknowledgements

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