Synthesis of Clusters containing Two C_2Co_2 Cores†

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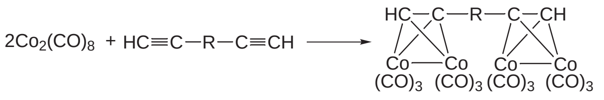
New clusters $[Co_2(CO)_6]_2(\mu\text{-}HC_2RC_2H)$ [R=$C_6H_4(CO_2CH_2)_2$-1,2 **2**, CH_2OCH_2 **3**, $(CH_2)_5$ **4**] have been isolated from the reaction of $Co_2(CO)_8$ **1** with diyne ligands HC≡CRC≡CH, and the structure of **2** has been established by single-crystal X-ray diffraction methods.

It is known that 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] Octacarbonyldicobalt reacts readily with alkynes to give μ-alkyne complexes $(RC{\equiv}CR)Co_2(CO)_6$,[3–5] but only a few reactions of $Co_2(CO)_8$ with diynes have been reported.[6,7] Here, new double tetrahedral clusters $[Co_2(CO)_6]_2(\mu\text{-}HC_2RC_2H)$ **2**–**4** have been obtained by reactions of $Co_2(CO)_8$ **1** with diyne ligands HC≡CRC≡CH in benzene or hexane at room temperature (Scheme 1). Clusters **2** and **3** are stable in air in the solid state and are soluble in common organic solvents while cluster **4** is a red oil. Satisfactory C and H analyses were obtained for all compounds.



Scheme 1 Synthesis of clusters **2**–**4**

The similar spectral features of **2**–**4** suggest that all the clusters have the same configuration. The IR spectra of clusters **2**–**4** show intense terminal carbonyl absorption bands in the range 2012–1873 cm^{-1} and in **2** the ester carbonyl band is split (1737, 1715 cm^{-1}) upon cluster formation. The ^1H NMR spectra of **2**–**4** show single peaks at δ 6.14–6.02 which can be assigned to the protons of the terminal alkynes (C_2H) and a single peak at δ 5.52–2.89 which can be assigned to methylene protons (CH_2) adjacent to C≡CH.

The structural features of this new series of clusters have been established by X-ray diffraction analysis of a suitable crystal of **2**. In the molecule two tetrahedral cores (C_2Co_2) are connected *via* $C_6H_4(CO_2CH_2)_2$-1,2 as a bridging unit (Fig. 1). The C_2Co_2 core adopts a pseudo-tetrahedral geometry. The overall conformations of the two Co_2C_2 moieties in **2** are similar. The Co–Co bond lengths are 2.472(1) and 2.475(1) Å while the Co–Co bond distances in the Co_2C_2 core are in the range 1.926(7)–1.956(6) Å, comparable with those of related dicobalt complexes.[4] The C(7)–C(8) and C(19)–(20) distances are 1.319(8) and 1.317(9) Å, respectively, typical for μ-alkyne- hexacarbonyldicobalt complexes. The bond angles C(9)–C(8)–C(7), C(8)–C(7)–H(1), C(18)–C(19)–C(20) and C(19)–C(20)–H(10) are 140.9(6), 141(4), 143.3(6) and 140(3)°, respectively, which also lie in the normal range.[4]

The distance C(11)–C(12) is longer than C(14)–C(15) while the bond angles C(13)–C(14)–C(15) and C(14)–C(15)–C(16) are greater than C(11)–C(12)–C(13) and C(16)–C(11)–C(12). The difference of bond lengths and angles are likely to depend on the effect of the two large $CO_2CH_2C_2Co_2$ groups.

Experimental

All operations were carried out under a highly pure nitrogen atmosphere using standard Schlenk and vacuum techniques. Hexane, petroleum ether (bp 60–90 °C) and benzene 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 FT-IR 10 DX spectrophotometer; ^1H NMR spectra on a Bruker AM-300 MHz spectrometer and elemental analyses (C, H) were performed on a Carlo Erba 1106-type analyzer.

Preparation of Cluster **2**.–A mixture of $[Co_2(CO)_8]$ (684 mg, 2 mmol) and dipropargyl phthalate $C_6H_4(CO_2CH_2C_2H)_2$-1,2 (242 mg, 1 mmol) in benzene (40 cm^3) was allowed to react at room temperature for 2 h. A colour change from brown to purple was observed and monitoring by TLC monitoring showed the disappearance of the starting complex. After the addition of a small amount of silica the solvent was removed and the residue chromatographed. Elution with benzene gave a red band of cluster **2**. Recrystallization from hexane–benzene give red prismatic crystals (648 mg, 79.6%). IR (KBr): ν(C=O) 1737m, 1715m; ν(CO) 2098s, 2055vs, 2022vs, 2016vs, 2002vs (terminal CO) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.81–7.57 (m, 4H, C_6H_4), 6.14 (s, 2H, 2CH) and 5.52 (s, 4H, $2CH_2$).

Preparation of Cluster **3**.—In a similar reaction to above, dipropargyl ether $O(CH_2C_2H)_2$ (94 mg, 1 mmol) and $[Co_2(CO)_8]$ (684 mg, 2 mmol) were allowed to react in hexane (40 cm^3) at room temperature for 2 h. The solvent was removed under reduced pressure and the residue purified by silica gel column with petroleum ether CH_2Cl_2 (1:1) as eluent to give red product **3** (546 mg, 82.0%). IR (KBr): ν(CO) 2012s, 2095s, 2060vs, 2038vs, 2022vs, 1995vs (terminal CO) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.07 (s, 2H, 2CH) and 4.85 (s, 4H, $2CH_2$).

Preparation of Cluster **4**.—A mixture of 1,8-nonadiyne $CH_2(CH_2CH_2C_2H)_2$ (120 mg, 1 mmol) and $[Co_2(CO)_8]$ (684 mg, 2 mmol) was dissolved in hexane (40 cm^3) and allowed to react at room temperature for 2 h. The main product was cluster **4** obtained as a red oil (482 mg, 69.7%). IR (KBr): ν(CO) 2093s, 2049vs, 2017vs, 1940w, 1873w (terminal CO) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.02 (s, 2H, 2CH), 2.89 (s, 4H, $2CH_2$) and 1.68 (m, 6H, $CH_2CH_2CH_2$).

Crystal Data for **2**.—A crystal of compound **2** ($C_{26}H_{10}O_{16}Co_4$) ($M_r = 814.09$) was obtained from benzene–hexane. The space group was $P2_1/a$, and the cell parameters were determined on a Rigaku AFC7R diffractometer with graphite-monochromated, Mo-Kα radiation: $a = 8.521(2)$, $b = 29.143(6)$, $c = 12.918(7)$ Å, $\beta = 100.12(3)°$, $V = 3158(2)$ Å^3, $Z = 4$, $D_c = 1.712$ g cm^{-3}, $\mu = 21.37$ cm^{-1}, $2\theta_{max} = 51.0°$, and $F(000) = 1608.00$. The crystal size is 0.20 × 0.20 × 0.40 mm. Of the 5610 reflections collected, 5194 were unique ($R_{int} = 0.028$). The intensities of three representative reflections were measured every 200. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 3151 observed reflections [$I > 2.00\sigma(I)$] and 455 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.044$, $R_w = 0.048$. Minimum and maximum final

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† 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)*.

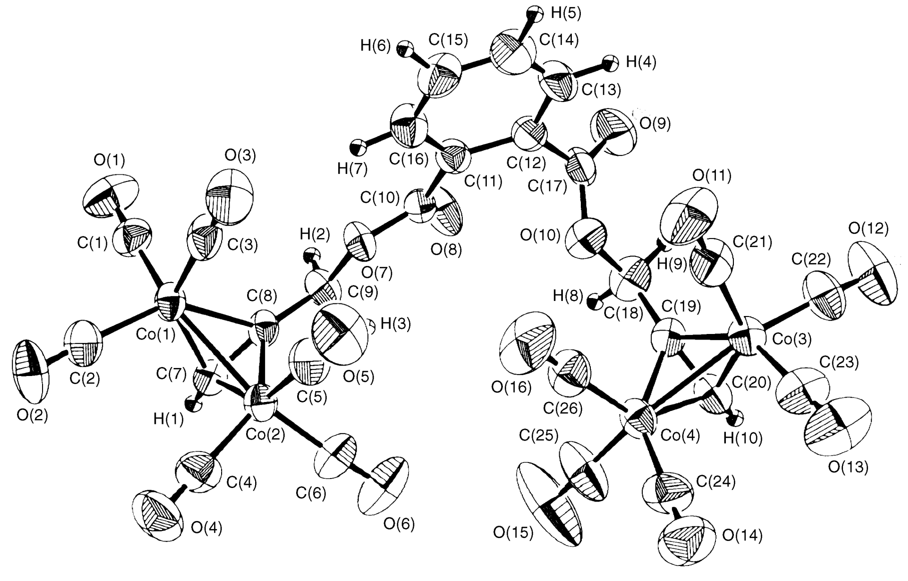

Fig. 1 Crystal structure of cluster **2**: selected bond distances (Å) and angles (°): Co(1)–C(7) 1.951(6), Co(3)–C(19) 1.956(6), Co(1)–C(8) 1.955(6), Co(3)–C(20) 1.937(7), Co(2)–C(7) 1.937(6), Co(4)–C(19) 1.937(7), Co(2)–C(8) 1.942(6), Co(4)–C(20) 1.926(7), C(14)–C(15) 1.36(1), C(11)–C(12) 1.403(8); C(11)–C(12)–C(13) 119.4(7), C(13)–C(14)–C(15) 120.6(8), C(12)–C(11)–C(16) 119.2(6), C(14)–C(15)–C(16) 120.7(8). Other selected band lengths and angles are quoted in the text

electron densities were −0.29 and 0.49 e $Å^{-3}$. The calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation. 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 for this material should quote the full literature citation and the reference number 423/15.

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