

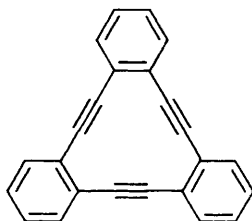
The Synthesis and Structural Characterization of a Novel Tetracobalt Cluster of 5,6,11,12,17,18-Hexadehydrotribenzo[*a,e,i*]cyclododecine

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The interaction of octacarbonyldicobalt with 5,6,11,12,17,18-hexadehydrotribenzo[*a,e,i*]cyclododecine (tbc) yields the sixty-six electron cluster $\text{Co}_4(\text{tbc})(\text{CO})_9$ whose structure may model the transition state during metal catalysed $[2 + 2]$ cyclootrimerization of alkynes.

Octacarbonyldicobalt forms complexes with alkynes by the net replacement of the bridging carbonyl groups with one alkyne unit.¹ In these complexes the alkyne is a 4-electron donor and uses both π orbitals to bridge the two cobalts. The versatility of the cyclic trialkyne ligand tbc² (**1**) is exemplified in its chemistry with copper(I) trifluoromethanesulphonate (triflate).³ The ligand tbc can co-ordinate a $\text{CuOSO}_2\text{CF}_3$ moiety to the three alkynes in its cavity, or it can act as a template co-ordinating three $\text{Cu}(\mu^2\text{-O}_2\text{SO}_2\text{CF}_3)$ moieties to the three alkynes. The latter mode of co-ordination suggested that tbc could act as a template for the formation of metal clusters and the known stability of cobalt alkyne complexes¹ prompted the choice of this metal.



(1) tbc

The reaction of tbc (0.333 mmol) and $\text{Co}_2(\text{CO})_8$ (0.666 mmol) in Et_2O at room temperature resulted in the formation of a tetracobalt cluster $\text{Co}_4(\text{tbc})(\text{CO})_9$ in 60% yield. Recrystallization from Et_2O provided crystals suitable for X-ray crystallography. The product showed CO stretching i.r. absorptions at 2069, 2042, 2031, 2003, and 1987 cm^{-1} . The $\text{C}\equiv\text{C}$ stretching absorptions were not observed. Satisfactory elemental analyses were obtained.

X-Ray analysis[†] of $\text{Co}_4(\text{tbc})(\text{CO})_9$ showed an unusual arrangement of cobalt atoms (Figure 2).⁴ One cobalt [Co(1)] lies above the centre of the tbc cavity (0.700 Å from the plane defined by the three alkynes), bound to the three alkynes and to each of the three other cobalt atoms [Co(2–4)]. Co(2–4) are also each bound to three carbonyl groups and to one alkyne of the tbc ligand but not to each other. Thereby, each

[†] Crystal data: $\text{Co}_4(\text{tbc})(\text{CO})_9$, monoclinic, space group $P2_1/c$, $a = 15.405(3)$, $b = 13.841(3)$, $c = 14.677(2)$ Å, $\beta = 105.59(2)^\circ$, $Z = 4$, $U = 3014(1)$ Å³, $D_c = 1.92$ g cm^{-3} , Mo- K_α radiation, $\lambda = 0.71073$ Å, $3 \leq 2\theta \leq 50^\circ$, Syntex P2₁ diffractometer. 7733 Reflections were collected of which 3097 unique reflections [$I \geq 3\sigma(I)$] were used for refinement (415 parameters), converging to $R = 0.040$ and $R_w = 0.042$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

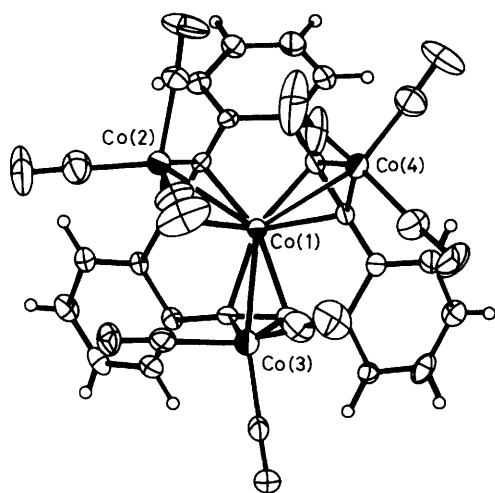


Figure 1. ORTEP diagram of $\text{Co}_4(\text{tbc})(\text{CO})_9$ with 20% thermal probability ellipsoids.

alkyne is bound in a $\mu^2\text{-}\eta^2$ -fashion to two cobalt atoms. In $\text{Co}_4(\text{tbc})(\text{CO})_9$, the tbc ligand simultaneously co-ordinates the four cobalt atoms using both modes that have been observed with copper(I) triflate.³ A similar arrangement of four metal atoms occurs in $\text{Bi}[\text{Co}(\text{CO})_4]_3$ (ref. 5) and other main group tricobalt complexes, but this is the first example of such an arrangement of four cobalt atoms. The distances from the central cobalt to the other three cobalts are 2.639(1), 2.651(1), and 2.690(1) Å with the nonbonding distances between Co(2—4) in the range 4.182(1)—4.349(1) Å. The six Co(1)—C(alkyne) distances range from 2.047(5) to 2.069(5) Å, with the other Co—C(alkyne) distances in the range 1.962(5)—1.977(6) Å. For comparison, the Co—Co distances in $\text{Co}_2(\text{CO})_6(\mu^2\text{-}\eta^2\text{-PhC}\equiv\text{CPh})_6$ and $\text{Co}_2(\text{CO})_8$ (ref. 7) are 2.47 and 2.524 Å, respectively, and the Co—C(alkyne) distances in $\text{Co}_2(\text{CO})_6(\mu^2\text{-}\eta^2\text{-PhC}\equiv\text{CPh})_4$ are 1.89—2.02 Å. The distance from a carbon of one alkyne to the nearest carbon on an adjacent alkyne averages 2.505(9) Å; a significant reduction

from the 2.86(1) Å found in free tbc⁸ but longer than the value calculated for the transition state during the [2 + 2 + 2] cyclotrimerization of alkynes to arenes (~2.2 Å).⁹ The complex $\text{Co}_4(\text{CO})_{12}$ is a catalyst for alkyne cyclotrimerizations.¹⁰ The cyclotrimerization of the alkynes of tbc and related ligands has not been observed but the reverse process takes place at high temperatures.¹¹

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