metal-organic papers

Hexacarbonyldicobalt(0) complex of 5,6,11,12-tetradehydrodibenzo[a,e]-cyclooctene, [(η²-C₁₆H₈)Co₂(CO)₆]

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The title compound, [(η²-C₁₆H₈)Co₂(CO)₆], (I), has been prepared by treatment of 5,6,11,12-tetradehydrodibenzo[a,e]-cyclooctene, (II), with dicobalt octacarbonyl. Although one acetylene in (II) remains intact upon treatment with Co₂(CO)₈, the other is coordinated to Co₂(CO)₆, exhibiting a C≡C bond lengthened to 1.356 (2) Å and a C≡C—C bond angle contracted to 147.53 (16)°.

Comment

It has been recognized that 5,6,11,12-tetradehydrodibenzo-[a,e]cyclooctene, (II), contains the most strained acetylene groups (Destro *et al.*, 1975). Although these triple bonds are quite reactive because of their great strain energy, only one example of Pt complexed to the triple bonds has been reported so far (Shimada *et al.*, 1997). We have developed a new methodology for access to various acetylenes and succeeded in preparing a Co₂(CO)₆ complex of an acetylenic cyclophane (Orita *et al.*, 2002). We have been intrigued by the structural features of Co₂(CO)₆ complexes of the most strained acetylene 5,6,11,12-tetradehydrodibenzo[a,e]cyclo-octene, (II), and have carried out an investigation of the title compound, (I).

(I)   (II)
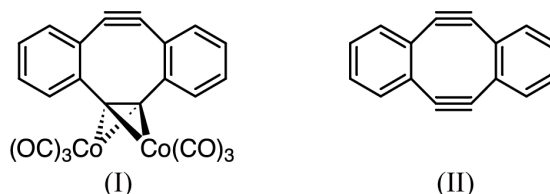
By X-ray analysis of the starting cyclophane (II), it has been shown that the triple bonds adopt a bond length of 1.195 (2) Å and a bond angle of 155.3 (1)° (Destro *et al.*, 1975). Coordination of the Co₂(CO)₆ moiety by the acetylene of (I) lengthens the C1—C2 bond to 1.356 (2) Å and contracts the bond angle C1—C2—C3 to 147.53 (16)°. In sharp contrast to these, the corresponding length and angle of the other acetylene group in (I) remain unchanged, with the same bond length [1.196 (2) Å] and angle [155.98 (18)°] as observed in (II). Interestingly, the lengths of the C1—C2, C2—C3 and C1—C16 bonds are almost the same as in the (η²-PhC≡CPh)–Co₂(CO)₆ complex (Gregson & Howard, 1983). The bond angle C1—C2—C3 [147.53 (16)°] is somewhat larger than the corresponding angle [140.2 (9)°] in diphenylacetylene–Co₂(CO)₆. Two cobalt atoms, Co1 and Co2, are located at the same distance from C1 and C2, but unsymmetrically displaced from the plane involving the eight-membered ring [Co1—C1—C2—C3 = 154.1 (4)° and Co2—C1—C2—C3 = −122.5 (4)°].

Table 1
Selected geometric parameters (Å, °).

Co1—Co2	2.4616 (3)	Co2—C20	1.8331 (18)
Co1—C1	1.9564 (17)	Co2—C1	1.9719 (16)
Co1—C2	1.9626 (16)	Co2—C2	1.9903 (18)
C1—C2	1.356 (2)	Co2—C22	1.8297 (18)
C2—C3	1.474 (2)	O2—C18	1.135 (2)
C8—C9	1.434 (2)	O1—C17	1.131 (2)
C9—C10	1.196 (2)	O3—C19	1.135 (2)
Co1—C19	1.8196 (19)	C8—C3	1.420 (2)
Co1—C18	1.8101 (19)	C10—C11	1.434 (2)
Co1—C17	1.8122 (18)	C1—C16	1.471 (2)
Co2—C21	1.7942 (19)	C11—C16	1.417 (2)
C1—C2—C3	147.53 (16)	Co2—C1—C2	70.7 (1)
C2—C3—C8	120.83 (14)	Co1—C1—C16	134.95 (12)
C3—C8—C9	114.39 (14)	Co2—C1—C16	127.31 (12)
C8—C9—C10	155.98 (18)	C2—C1—C16	147.67 (16)
Co1—Co2—C1	50.92 (5)	C10—C11—C16	113.79 (14)
C7—C8—C3	120.59 (15)	C1—C16—C11	121.30 (14)
C9—C10—C11	156.41 (18)	C8—C3—C4	118.17 (14)
Co1—C1—C2	70.0 (1)		
C1—C2—C3—C8	11.0 (6)	Co1—C1—C2—C3	154.1 (4)
C3—C8—C9—C10	−7.2 (7)	Co2—C1—C2—C3	−122.5 (4)
C16—C1—C2—C3	7.9 (7)	Co1—C1—C16—C15	33.3 (3)
C8—C9—C10—C11	3.0 (10)	Co2—C1—C16—C15	−79.0 (2)

The H atoms were located from difference density maps and refined isotropically with restraints, C—H 0.968 (3)–1.079 (3) Å.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Rigaku, 1999); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*3 for Windows (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* (Molecular Structure Corporation and Rigaku Corporation, 2001).

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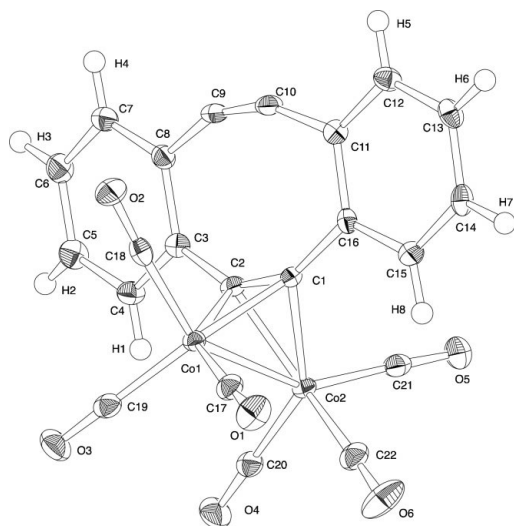

Figure 1
Molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

Experimental

To a flame-dried flask were added (II) (100.1 mg, 0.5 mmol), and $Co_2(CO)_8$ (512.9 mg, 0.5 mmol) and CH_2Cl_2 (10 ml); the mixture was stirred for 12 h at room temperature in the dark. After evaporation, hexane was added to the residual black solid and the resulting solution was filtered through a thin layer of silica gel. After evaporation of the filtrate, black crystals of (I) were obtained in 50–60% yield.

Crystal data

$[Co_2(C_{16}H_8)(CO)_6]$	$D_x = 1.742$ Mg m^{-3}
$M_r = 486.17$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 8782
$a = 16.2876$ (8) Å	reflections
$b = 7.4552$ (4) Å	$\theta = 4.0–27.5°$
$c = 17.1415$ (5) Å	$\mu = 1.83$ mm^{-1}
$\beta = 117.075$ (3)°	$T = 93.1$ K
$V = 1853.34$ (15) Å^3	Cuboid, black
$Z = 4$	$0.30 \times 0.30 \times 0.20$ mm

Data collection

Rigaku RAXIS-IV diffractometer	3763 reflections with $F^2 > 2\sigma(F^2)$
ω scans	$R_{int} = 0.037$
Absorption correction: multi-scan (Higashi, 1995)	$\theta_{max} = 27.5°$
$T_{min} = 0.471$, $T_{max} = 0.694$	$h = -21 \rightarrow 21$
14 932 measured reflections	$k = -9 \rightarrow 9$
4379 independent reflections	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.031$	$w = 1/[0.002F_o^2 + \sigma^2(F_o)]/(4F_o^2)$
$wR(F^2) = 0.090$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.99$	$\Delta\rho_{max} = 0.59$ e Å^{-3}
4090 reflections	$\Delta\rho_{min} = -0.90$ e Å^{-3}
279 parameters	