metal-organic compounds

Bis(η^5-pentamethylcyclopentadienyl)-cobalt(II)

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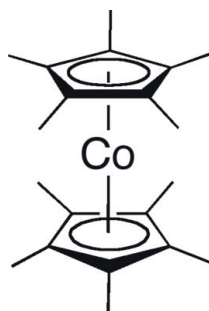Correspondence e-mail: brennessel@chem.rochester.edu

The crystal structure of the title compound, decamethyl-cobaltocene, $[Co(C_{10}H_{15})_2]$, has been determined. High-quality single crystals were grown from a cold saturated hexamethyldisiloxane solution. The structure is related to the manganese and iron analogs. The molecule has D_{5d} symmetry, with the Co atom in a crystallographic $2/m$ position. The cobalt–centroid(C_5) distance is 1.71Å and the centroid(C_5)–Co–centroid(C_5) angle is 180°, by symmetry.

Related literature

For the synthesis of the title compound and its electrochemical and magnetic properties, see: Robbins *et al.* (1982). For its formal potential and use as a reducing agent, see: Connelly & Geiger (1996). For the isotypic manganese and iron structures, see: Struchkov *et al.* (1978); Freyburg *et al.* (1979); Augart *et al.* (1991); Arrais *et al.* (2003).

Experimental

Crystal data

$[Co(C_{10}H_{15})_2]$	$V = 1737.0$ (3) Å^3
$M_r = 329.37$	$Z = 4$
Orthorhombic, $Cmca$	Mo $K\alpha$ radiation
$a = 15.0848$ (16) Å	$\mu = 0.98$ mm^{-1}
$b = 11.5031$ (12) Å	$T = 100$ K
$c = 10.0105$ (10) Å	$0.28 \times 0.28 \times 0.14$ mm

Data collection

Bruker APEXII CCD diffractometer	19672 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008*a*)	2386 independent reflections
	1903 reflections with $I > 2\sigma(I)$
$T_{min} = 0.771$, $T_{max} = 0.875$	$R_{int} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	84 parameters
$wR(F^2) = 0.089$	All H-atom parameters refined
$S = 1.07$	$\Delta\rho_{max} = 0.70$ e Å^{-3}
2386 reflections	$\Delta\rho_{min} = -0.74$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Co1—C1	2.0914 (12)	C1—C4	1.4961 (18)
Co1—C3	2.0956 (8)	C2—C3	1.4231 (12)
Co1—C2	2.1113 (8)	C2—C5	1.4935 (14)
C1—C2	1.4304 (12)	C3—C6	1.4950 (13)

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008*b*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008*b*); molecular graphics: *SHELXTL* (Sheldrick, 2008*b*); software used to prepare material for publication: *SHELXTL*.

References

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supporting information

Bis(η^5-pentamethylcyclopentadienyl)cobalt(II)

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S1. Comment

The structure of (I) has been conspicuously absent from the literature, despite its being a widely used reducing agent (Connelly & Geiger, 1996). Robbins and co-workers referred to a structural determination in 1982 (Robbins *et al.*, 1982), specifically its D_{5d} symmetry and its similarity to the manganese analog. However, no structural data were presented. Attempts to grow single crystals from toluene and hexane, the latter from which Robbins reported having grown crystals, resulted in very poor quality specimens that were unsuitable for X-ray diffraction experiments. A cold (-38 ° C) saturated hexamethyldisiloxane solution of (I) afforded excellent crystals that resulted in a high quality structural determination.

The structure is isomorphous to that of decamethylferrocene (refcodes DMFERR, Struchkov *et al.*, 1978, DMFERR01, Freyburg *et al.*, 1979, DMFERR02, Arrais *et al.*, 2003) and the low temperature polymorph of decamethylmanganocene (refcodes DMCPMN01 and DMCPMN02, Augart *et al.*, 1991), for which the metal atoms are in crystallographic *2/m* positions.

S2. Experimental

All operations were performed under an inert atmosphere (dinitrogen). Hexamethyldisiloxane was stirred over CaH_2 and vacuum transferred from sodium benzophenone ketyl. (I) was purchased from Sigma-Aldrich and used as is. Hexamethyldisiloxane (1 ml) was added to (I) (10 mg, 30 μmol), most of which dissolved over the course of a few hours at room temperature. After filtration through Celite, the filtrate was stored at -38 °C, resulting in dark yellow-brown crystals of (I) after a few hours.

S3. Refinement

Hydrogen atoms were found from the difference Fourier map and refined independently from their respective carbon atoms with individual isotropic displacement parameters.
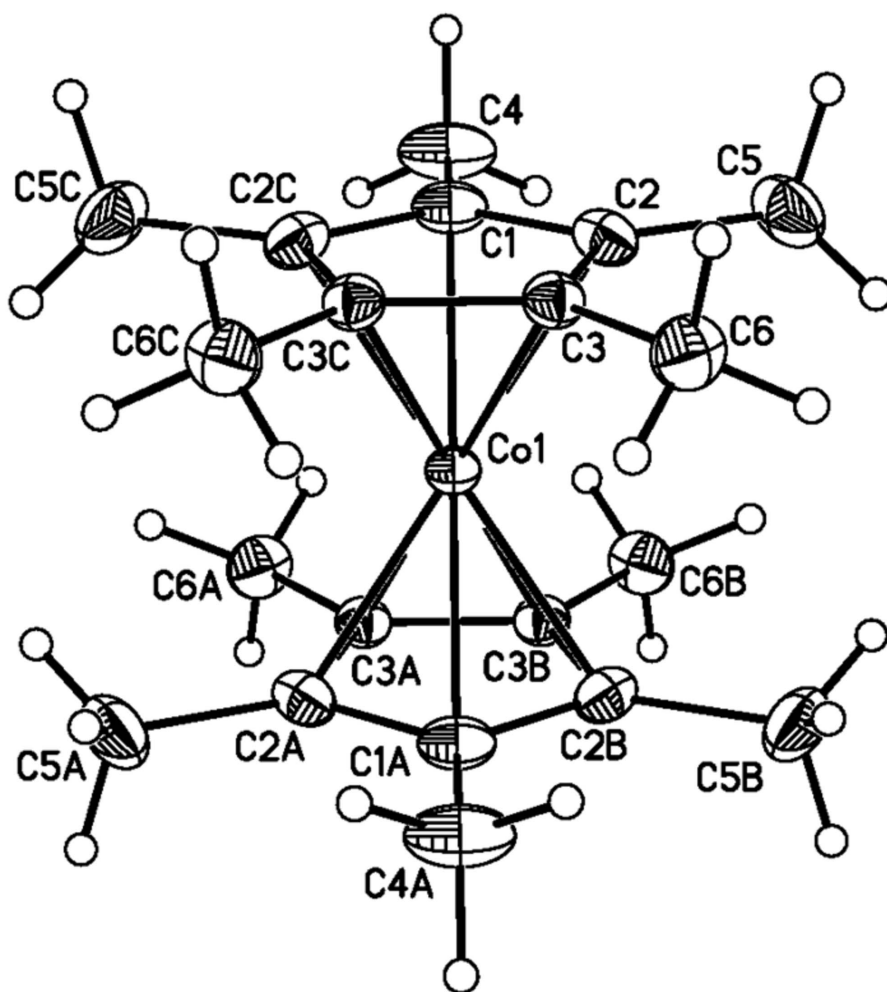
Figure 1

A displacement ellipsoid (50% probability) drawing of (I). The cobalt atom is in a crystallographic *2/m* position.

Bis(η^5-pentamethylcyclopentadienyl)cobalt(II)

Crystal data

[Co(C$_{10}$H$_{15}$)$_2$]	$F(000) = 708$
$M_r = 329.37$	$D_x = 1.259$ Mg m^{-3}
Orthorhombic, *Cmca*	Mo *Kα* radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2bc 2	Cell parameters from 4000 reflections
$a = 15.0848\,(16)$ Å	$\theta = 3.0\text{–}37.5°$
$b = 11.5031\,(12)$ Å	$\mu = 0.98$ mm^{-1}
$c = 10.0105\,(10)$ Å	$T = 100$ K
$V = 1737.0\,(3)$ Å^3	Block, dark yellow-brown
$Z = 4$	$0.28 \times 0.28 \times 0.14$ mm

Data collection

Bruker APEXII CCD diffractometer	19672 measured reflections
Radiation source: fine-focus sealed tube	2386 independent reflections
Graphite monochromator	1903 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.046$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008a)	$\theta_{max} = 38.0°$, $\theta_{min} = 2.7°$
	$h = -25 \rightarrow 25$
	$k = -19 \rightarrow 19$
$T_{min} = 0.771$, $T_{max} = 0.875$	$l = -16 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.031$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.089$	
$S = 1.07$	All H-atom parameters refined
2386 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 0.2743P]$
84 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.70$ e Å^{-3}
	$\Delta\rho_{min} = -0.74$ e Å^{-3}

Special details

Experimental. The crystal was examined under N$_2$ and affixed to the end of a glass capillary with viscous oil, which protected the crystal during transfer to the cold stream.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Co1	0.0000	0.0000	0.0000	0.01533 (7)
C1	0.0000	−0.17732 (10)	0.04617 (12)	0.0228 (2)
C2	−0.07677 (6)	−0.12416 (7)	0.10364 (8)	0.02149 (15)
C3	−0.04749 (5)	−0.03551 (7)	0.19244 (8)	0.01843 (13)
C4	0.0000	−0.27361 (12)	−0.05429 (14)	0.0348 (3)
H4A	0.0000	−0.352 (3)	−0.013 (2)	0.045 (8)*
H4B	−0.0486 (10)	−0.2711 (18)	−0.1133 (16)	0.063 (5)*
C5	−0.17089 (8)	−0.15651 (11)	0.07606 (12)	0.0340 (2)
H5A	−0.1798 (16)	−0.184 (2)	−0.0134 (18)	0.053 (6)*
H5B	−0.2119 (12)	−0.0926 (16)	0.0778 (19)	0.059 (5)*
H5C	−0.1896 (11)	−0.2189 (15)	0.1358 (16)	0.047 (4)*
C6	−0.10544 (7)	0.04079 (10)	0.27607 (9)	0.02731 (18)
H6A	−0.1134 (15)	0.0057 (13)	0.360 (3)	0.045 (6)*
H6B	−0.1638 (11)	0.0562 (13)	0.2287 (15)	0.039 (4)*

H6C	−0.0774 (11)	0.1158 (14)	0.2912 (14)	0.037 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.01811 (10)	0.01380 (9)	0.01409 (9)	0.000	0.000	−0.00032 (6)
C1	0.0353 (6)	0.0161 (4)	0.0170 (4)	0.000	0.000	−0.0004 (4)
C2	0.0245 (3)	0.0202 (3)	0.0198 (3)	−0.0054 (3)	−0.0013 (3)	0.0016 (3)
C3	0.0205 (3)	0.0180 (3)	0.0168 (3)	0.0002 (3)	0.0014 (2)	0.0006 (2)
C4	0.0653 (11)	0.0183 (5)	0.0206 (5)	0.000	0.000	−0.0029 (4)
C5	0.0290 (4)	0.0371 (5)	0.0359 (5)	−0.0147 (4)	−0.0069 (4)	0.0063 (4)
C6	0.0293 (4)	0.0292 (4)	0.0234 (4)	0.0056 (4)	0.0068 (3)	−0.0005 (3)

Geometric parameters (Å, º)

Co1—C1[i]	2.0914 (12)	C2—C3	1.4231 (12)
Co1—C1	2.0914 (12)	C2—C5	1.4935 (14)
Co1—C3[ii]	2.0955 (8)	C3—C3[ii]	1.4328 (17)
Co1—C3	2.0956 (8)	C3—C6	1.4950 (13)
Co1—C3[i]	2.0956 (8)	C4—H4A	0.99 (3)
Co1—C3[iii]	2.0956 (8)	C4—H4B	0.942 (16)
Co1—C2[iii]	2.1113 (8)	C5—H5A	0.960 (18)
Co1—C2	2.1113 (8)	C5—H5B	0.962 (18)
Co1—C2[ii]	2.1113 (8)	C5—H5C	0.976 (17)
Co1—C2[i]	2.1113 (8)	C6—H6A	0.94 (2)
C1—C2	1.4304 (12)	C6—H6B	1.016 (16)
C1—C2[ii]	1.4304 (12)	C6—H6C	0.973 (16)
C1—C4	1.4961 (18)		
C1[i]—Co1—C1	180.0	C3—Co1—C2[i]	140.46 (3)
C1[i]—Co1—C3[ii]	113.16 (4)	C3[i]—Co1—C2[i]	39.54 (3)
C1—Co1—C3[ii]	66.84 (4)	C3[iii]—Co1—C2[i]	66.67 (3)
C1[i]—Co1—C3	113.16 (4)	C2[iii]—Co1—C2[i]	66.53 (5)
C1—Co1—C3	66.84 (4)	C2—Co1—C2[i]	180.0
C3[ii]—Co1—C3	39.98 (5)	C2[ii]—Co1—C2[i]	113.47 (5)
C1[i]—Co1—C3[i]	66.84 (4)	C2—C1—C2[ii]	108.12 (10)
C1—Co1—C3[i]	113.16 (4)	C2—C1—C4	125.94 (5)
C3[ii]—Co1—C3[i]	140.02 (5)	C2[ii]—C1—C4	125.93 (5)
C3—Co1—C3[i]	180.0	C2—C1—Co1	70.85 (6)
C1[i]—Co1—C3[iii]	66.84 (4)	C2[ii]—C1—Co1	70.85 (6)
C1—Co1—C3[iii]	113.16 (4)	C4—C1—Co1	124.99 (9)
C3[ii]—Co1—C3[iii]	180.0	C3—C2—C1	107.84 (8)
C3—Co1—C3[iii]	140.02 (5)	C3—C2—C5	126.09 (9)
C3[i]—Co1—C3[iii]	39.98 (5)	C1—C2—C5	126.07 (9)
C1[i]—Co1—C2[iii]	39.79 (3)	C3—C2—Co1	69.63 (5)
C1—Co1—C2[iii]	140.21 (3)	C1—C2—Co1	69.36 (6)
C3[ii]—Co1—C2[iii]	140.46 (3)	C5—C2—Co1	126.81 (7)
C3—Co1—C2[iii]	113.34 (3)	C2—C3—C3[ii]	108.08 (5)

C3ⁱ—Co1—C2ⁱⁱⁱ	66.66 (3)	C2—C3—C6	126.09 (8)
C3ⁱⁱⁱ—Co1—C2ⁱⁱⁱ	39.54 (3)	C3ⁱⁱ—C3—C6	125.78 (5)
C1ⁱ—Co1—C2	140.21 (3)	C2—C3—Co1	70.82 (5)
C1—Co1—C2	39.79 (3)	C3ⁱⁱ—C3—Co1	70.01 (2)
C3ⁱⁱ—Co1—C2	66.67 (3)	C6—C3—Co1	126.88 (6)
C3—Co1—C2	39.54 (3)	C1—C4—H4A	112.8 (13)
C3ⁱ—Co1—C2	140.46 (3)	C1—C4—H4B	113.5 (11)
C3ⁱⁱⁱ—Co1—C2	113.33 (3)	H4A—C4—H4B	107.0 (15)
C2ⁱⁱⁱ—Co1—C2	113.47 (5)	C2—C5—H5A	112.8 (15)
C1ⁱ—Co1—C2ⁱⁱ	140.21 (3)	C2—C5—H5B	114.7 (11)
C1—Co1—C2ⁱⁱ	39.79 (3)	H5A—C5—H5B	100.5 (18)
C3ⁱⁱ—Co1—C2ⁱⁱ	39.54 (3)	C2—C5—H5C	110.1 (9)
C3—Co1—C2ⁱⁱ	66.67 (3)	H5A—C5—H5C	106.7 (16)
C3ⁱ—Co1—C2ⁱⁱ	113.33 (3)	H5B—C5—H5C	111.4 (14)
C3ⁱⁱⁱ—Co1—C2ⁱⁱ	140.46 (3)	C3—C6—H6A	109.0 (11)
C2ⁱⁱⁱ—Co1—C2ⁱⁱ	180.0	C3—C6—H6B	110.4 (9)
C2—Co1—C2ⁱⁱ	66.53 (5)	H6A—C6—H6B	112.4 (16)
C1ⁱ—Co1—C2ⁱ	39.79 (3)	C3—C6—H6C	110.7 (9)
C1—Co1—C2ⁱ	140.21 (3)	H6A—C6—H6C	107.2 (15)
C3ⁱⁱ—Co1—C2ⁱ	113.33 (3)	H6B—C6—H6C	107.2 (13)

C1ⁱ—Co1—C1—C2	22.38 (12)	C2ⁱⁱⁱ—Co1—C2—C1	141.96 (6)
C3ⁱⁱ—Co1—C1—C2	80.81 (6)	C2ⁱⁱ—Co1—C2—C1	−38.04 (6)
C3—Co1—C1—C2	37.16 (5)	C2ⁱ—Co1—C2—C1	−59.99 (6)
C3ⁱ—Co1—C1—C2	−142.84 (5)	C1ⁱ—Co1—C2—C5	59.74 (11)
C3ⁱⁱⁱ—Co1—C1—C2	−99.18 (6)	C1—Co1—C2—C5	−120.26 (11)
C2ⁱⁱⁱ—Co1—C1—C2	−62.03 (10)	C3ⁱⁱ—Co1—C2—C5	158.44 (10)
C2ⁱⁱ—Co1—C1—C2	117.97 (10)	C3—Co1—C2—C5	120.46 (11)
C2ⁱ—Co1—C1—C2	180.0	C3ⁱ—Co1—C2—C5	−59.54 (11)
C1ⁱ—Co1—C1—C2ⁱⁱ	−95.59 (13)	C3ⁱⁱⁱ—Co1—C2—C5	−21.56 (10)
C3ⁱⁱ—Co1—C1—C2ⁱⁱ	−37.16 (5)	C2ⁱⁱⁱ—Co1—C2—C5	21.70 (8)
C3—Co1—C1—C2ⁱⁱ	−80.82 (6)	C2ⁱⁱ—Co1—C2—C5	−158.30 (8)
C3ⁱ—Co1—C1—C2ⁱⁱ	99.18 (6)	C2ⁱ—Co1—C2—C5	179.75 (9)
C3ⁱⁱⁱ—Co1—C1—C2ⁱⁱ	142.84 (5)	C1—C2—C3—C3ⁱⁱ	−1.34 (8)
C2ⁱⁱⁱ—Co1—C1—C2ⁱⁱ	180.0	C5—C2—C3—C3ⁱⁱ	178.27 (8)
C2—Co1—C1—C2ⁱⁱ	−117.97 (10)	Co1—C2—C3—C3ⁱⁱ	−60.38 (2)
C2ⁱ—Co1—C1—C2ⁱⁱ	62.03 (10)	C1—C2—C3—C6	−178.77 (9)
C1ⁱ—Co1—C1—C4	143.40 (12)	C5—C2—C3—C6	0.85 (14)
C3ⁱⁱ—Co1—C1—C4	−158.17 (3)	Co1—C2—C3—C6	122.20 (9)
C3—Co1—C1—C4	158.17 (3)	C1—C2—C3—Co1	59.04 (7)
C3ⁱ—Co1—C1—C4	−21.83 (3)	C5—C2—C3—Co1	−121.35 (9)
C3ⁱⁱⁱ—Co1—C1—C4	21.83 (3)	C1ⁱ—Co1—C3—C2	142.61 (5)
C2ⁱⁱⁱ—Co1—C1—C4	58.98 (5)	C1—Co1—C3—C2	−37.39 (5)
C2—Co1—C1—C4	121.01 (5)	C3ⁱⁱ—Co1—C3—C2	−118.44 (5)
C2ⁱⁱ—Co1—C1—C4	−121.01 (5)	C3ⁱ—Co1—C3—C2	−112.12 (6)
C2ⁱ—Co1—C1—C4	−58.99 (5)	C3ⁱⁱⁱ—Co1—C3—C2	61.56 (5)
C2ⁱⁱ—C1—C2—C3	2.17 (13)	C2ⁱⁱⁱ—Co1—C3—C2	99.14 (7)
C4—C1—C2—C3	−179.08 (11)	C2ⁱⁱ—Co1—C3—C2	−80.87 (7)

Co1—C1—C2—C3	−59.21 (6)	C2ⁱ—Co1—C3—C2	180.0
C2ⁱⁱ—C1—C2—C5	−177.44 (7)	C1ⁱ—Co1—C3—C3ⁱⁱ	−98.952 (19)
C4—C1—C2—C5	1.30 (17)	C1—Co1—C3—C3ⁱⁱ	81.049 (19)
Co1—C1—C2—C5	121.18 (9)	C3ⁱ—Co1—C3—C3ⁱⁱ	6.32 (2)
C2ⁱⁱ—C1—C2—Co1	61.38 (8)	C3ⁱⁱⁱ—Co1—C3—C3ⁱⁱ	180.0
C4—C1—C2—Co1	−119.87 (12)	C2ⁱⁱⁱ—Co1—C3—C3ⁱⁱ	−142.43 (3)
C1ⁱ—Co1—C2—C3	−60.72 (8)	C2—Co1—C3—C3ⁱⁱ	118.44 (5)
C1—Co1—C2—C3	119.28 (8)	C2ⁱⁱ—Co1—C3—C3ⁱⁱ	37.57 (3)
C3ⁱⁱ—Co1—C2—C3	37.98 (5)	C2ⁱ—Co1—C3—C3ⁱⁱ	−61.56 (5)
C3ⁱ—Co1—C2—C3	180.0	C1ⁱ—Co1—C3—C6	21.37 (9)
C3ⁱⁱⁱ—Co1—C2—C3	−142.02 (5)	C1—Co1—C3—C6	−158.63 (9)
C2ⁱⁱⁱ—Co1—C2—C3	−98.77 (5)	C3ⁱⁱ—Co1—C3—C6	120.32 (8)
C2ⁱⁱ—Co1—C2—C3	81.24 (5)	C3ⁱ—Co1—C3—C6	126.64 (8)
C2ⁱ—Co1—C2—C3	59.29 (5)	C3ⁱⁱⁱ—Co1—C3—C6	−59.68 (8)
C1ⁱ—Co1—C2—C1	180.0	C2ⁱⁱⁱ—Co1—C3—C6	−22.11 (9)
C3ⁱⁱ—Co1—C2—C1	−81.30 (6)	C2—Co1—C3—C6	−121.24 (10)
C3—Co1—C2—C1	−119.28 (8)	C2ⁱⁱ—Co1—C3—C6	157.89 (9)
C3ⁱ—Co1—C2—C1	60.72 (8)	C2ⁱ—Co1—C3—C6	58.76 (10)
C3ⁱⁱⁱ—Co1—C2—C1	98.70 (6)		

Symmetry codes: (i) −*x*, −*y*, −*z*; (ii) −*x*, *y*, *z*; (iii) *x*, −*y*, −*z*.