ω scans

Absorption correction:
empirical (*SADABS*;
Sheldrick, 1996)
$T_{min} = 0.680$, $T_{max} = 0.858$
21 436 measured reflections
4893 independent reflections

$R_{int} = 0.026$
$\theta_{max} = 26.32°$
$h = -18 \rightarrow 18$
$k = -11 \rightarrow 11$
$l = -17 \rightarrow 20$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.067$
$S = 1.138$
4893 reflections
322 parameters
H atoms treated by a
mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2 + 1.8145P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.794$ e Å^{-3}
$\Delta\rho_{min} = -0.699$ e Å^{-3}
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pd1—N21	2.031 (2)	Pd1—Cl2	2.3107 (6)
Pd1—N31	2.0416 (19)	Pd1—Cl1	2.3110 (6)
N21—Pd1—N31	79.90 (8)	N21—Pd1—Cl1	95.77 (5)
N21—Pd1—Cl2	170.98 (5)	N31—Pd1—Cl1	169.39 (6)
N31—Pd1—Cl2	94.74 (6)	Cl2—Pd1—Cl1	90.70 (2)

The data collection nominally covered over a sphere of reciprocal space, by a combination of four sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 5.95 cm. Coverage of the unique set is over 99% complete to at least 26° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. All non-H atoms, except for C9′, were refined anisotropically. Due to disorder, the bond lengths O8—C9, O8—C9′, O11—C10, O11—C12, O11′—C10 and O11′—C12′ were restrained to 1.430 (3) Å, and C9—C10, C9′—C10, C12—C13 and C12′—C13 to 1.510 (3) Å. H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [U(H) = 1.2U_{eq}(C)] using a riding model with C—H(secondary) = 0.99 or C—H(aromatic) = 0.95 Å.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1272). Services for accessing these data are described at the back of the journal.

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[(1,2,5,6-η)-Cyclooctatetraene](η5-cyclopentadienyl)cobalt

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Abstract

In the title complex, [Co(C$_5$H$_5$)(C$_8$H$_8$)], the cycooctatetraene ligand coordinates to the Co atom through two non-adjacent C=C double bonds. A tub-like shape is adopted by the polyolefin ligand.

Comment

For a η^4-bonded C$_8$H$_8$ ligand, two coordination geometries are possible (Deganello, 1979). In the cyclooctadiene-like 1,2,5,6-η coordination mode, the polyolefin is bonded to the metal through two non-adjacent C=C double bonds ('1,5-isomer'). The second coordination isomer has a 1–4-η-coordinated butadiene-like substructure, where bonding to the metal occurs through two adjacent double bonds ('1,3-isomer'). Several complexes are known in which both isomers have been observed in solution (Deganello, 1979).

The structural preferences and electronic structure of [Co(C₅H₅)(C₈H₈)], (I), and its radical anion have been studied extensively (Albright *et al.*, 1981; Geiger *et al.*, 1986, 1993; Geiger, 1995). Both isomers are present in solutions of neutral (I). At ambient temperature, the concentration of the $(1,2,5,6-\eta)$-C₈H₈ complex, (1,5-I), is about three to four times that of the $(1-4-\eta)$-C₈H₈ isomer, (1,3-I) (Moraczewski & Geiger, 1979; Geiger, 1995). This equilibrium changes dramatically upon reduction of the solution. Both isomers were found to be reducible by one electron to give the radical anions ([1,5-I]⁻) and ([1,3-I]⁻). However, in marked contrast to the neutral complex, the $1,2,5,6-\eta$ coordination of the cyclooctatetraene is greatly destabilized in the anion, which rapidly and irreversibly transforms into the 1,3-isomer (Moraczewski & Geiger, 1981).

(I)
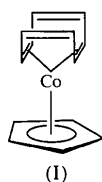
Surprisingly, no crystal structure of a neutral mononuclear complex of cyclooctatetraene with a metal of the cobalt group has been reported to date. Hence, details of the coordination geometry in either of the two above-mentioned coordination modes of cyclooctatetraene were not available.

Crystals of (I), obtained by vacuum sublimation of the solid at 373 K, were found to be composed of the $(1,2,5,6-\eta)$-C₈H₈ isomer, (1,5-I). The crystal structure is quite similar to that of [(C₅H₅)Co(η^4-1,5-cyclooctadiene)] (Ondráček *et al.*, 1990), which also has a similar molecular shape. A tub-like geometry is attained by the cyclooctatetraene ligand in (1,5-I) (Fig. 1). Compared with the free ligand, the C₈-tub is less 'open': fold angles (dihedral angles) along the transannular vectors C1···C6 and C2···C5 are

125.9(2) and 126.1(2)°, respectively, in the complex and 138.4° in the free ligand (Claus & Krüger, 1988). Consequently, the transannular distance between the centres of opposite double bonds is shorter in (1,5-I) [2.714(11) and 2.974(12) Å for the metal-coordinated and free C=C double bonds, respectively] than in the free ligand (3.085 Å). The lengths of the two non-coordinated C=C double bonds within the C₈ ring [1.314(6) and 1.342(5) Å] compare well with the corresponding distance in the free ligand [1.333(2) Å; Claus & Krüger, 1988]. Interaction with the metal atom causes the two remaining double bonds to be lengthened by about 0.1 Å. The coordination planes of the cyclooctatetraene and cyclopentadienyl ligands are nearly parallel to each other [angle between normals to the best planes 1.3(2)°]. The Co atom is at distances of 1.317(1) and 1.718(1) Å, respectively, from these two planes.

Experimental

Complex (I) was prepared as described in the literature (Fritz & Keller, 1961). Deep-red single crystals were obtained by slow vacuum sublimation [0.03 mbar (1 mbar = 100 Pa), 373 K].

Crystal data

[Co(C₅H₅)(C₈H₈)]	Mo $K\alpha$ radiation
$M_r = 228.16$	$\lambda = 0.7107$ Å
Monoclinic	Cell parameters from 23
$P2_1/c$	reflections
$a = 12.302\,(8)$ Å	$\theta = 14.7–17.1°$
$b = 7.461\,(4)$ Å	$\mu = 1.656$ mm⁻¹
$c = 11.203\,(8)$ Å	$T = 203\,(2)$ K
$\beta = 101.70\,(5)°$	Plate
$V = 1006.9\,(11)$ Å³	$0.30 \times 0.30 \times 0.15$ mm
$Z = 4$	Red
$D_x = 1.505$ Mg m⁻³	
D_m not measured	

Data collection

Siemens Stoe AED-2 diffractometer	1846 reflections with $I > 2\sigma(I)$
ω scans	$\theta_{max} = 28.04°$
Absorption correction:	$h = 0 \to 16$
ψ scan (Stoe & Cie, 1989b)	$k = -9 \to 0$
	$l = -14 \to 14$
$T_{min} = 0.675$, $T_{max} = 0.780$	3 standard reflections
2423 measured reflections	frequency: 120 min
2423 independent reflections	intensity decay: 2%

Refinement

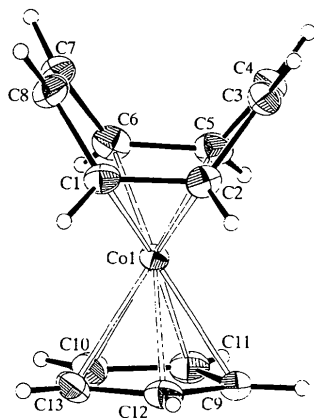|	
Refinement on F^2	$\Delta\rho_{max} = 0.701$ e Å⁻³
$R[F^2 > 2\sigma(F^2)] = 0.040$	$\Delta\rho_{min} = -0.557$ e Å⁻³
$wR(F^2) = 0.104$	Extinction correction:
$S = 1.024$	*SHELXL97* (Sheldrick,
2423 reflections	1997)
180 parameters	Extinction coefficient:
H atoms refined	0.0139 (14)

Fig. 1. The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level.

$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.3933P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Co1—C2	2.014 (3)	C2—C3	1.495 (5)
Co1—C1	2.015 (3)	C3—C4	1.314 (6)
Co1—C5	2.024 (3)	C4—C5	1.485 (6)
Co1—C6	2.029 (3)	C5—C6	1.426 (5)
C1—C2	1.418 (5)	C6—C7	1.492 (6)
C1—C8	1.494 (5)	C7—C8	1.342 (5)
C2—C1—C8	121.2 (3)	C6—C5—C4	120.7 (3)
C1—C2—C3	122.0 (3)	C5—C6—C7	121.6 (3)
C4—C3—C2	117.8 (3)	C8—C7—C6	117.6 (3)
C3—C4—C5	118.2 (3)	C7—C8—C1	117.1 (3)

Data collection: *DIF*4 (Stoe & Cie, 1989*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1989*c*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

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6,6-Bis[3-(dimethylamino)-1,1-dimethylpropyl]-2,2,4,4-tetramethyl-1,3,5-trioxa-2,4-disila-6-stannacyclohexane

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Abstract

The title compound, bis(3-dimethylamino-1,1-dimethylpropyl-C^1,N)(disiloxanediolato-O,O')tin(IV), [Sn(C_4H_{12}-O_3Si_2)($C_7H_{16}N$)$_2$], is the first stannasiloxane with hexacoordinate tin. The intramolecular Sn—N distances are 2.879 (3) and 2.957 (3) Å.

Comment

In an attempt to synthesize [$Me_2N(CH_2)_2CMe_2$]$_2$SnO as a functionally substituted analogue of ($^tBu_2$SnO)$_3$ (Puff *et al.*, 1984) by reaction of [$Me_2N(CH_2)_2CMe_2$]$_2$-SnCl$_2$ (Jurkschat *et al.*, 1989) with sodium hydroxide, we obtained the title compound, [$Me_2N(CH_2)_2CMe_2$]$_2$-Sn(OSiMe$_2$)$_2$O, (1). The synthesis of (1) can be rationalized by reaction of sodium hydroxide and silicon grease, accidentally present in the reaction mixture, with [$Me_2N(CH_2)_2CMe_2$]$_2$SnCl$_2$. The formation of stannasiloxanes from reactions in the presence of silicon grease has been noticed by other groups (Churchill *et al.*, 1993; Eaborn *et al.*, 1995; Cervantes-Lee *et al.*, 1998).

(1)
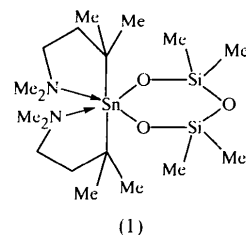
The molecular structure of (1) is shown in Fig. 1. The Sn atom is coordinated by two C, two O and two N atoms, resulting in a distorted octahedral configuration. The C atoms are in mutually *trans* positions, whereas the O and N atoms are *cis*. This configuration at tin is the same as in the structure determined for [$Me_2N(CH_2)_3$]$_2$Sn(OPh)$_2$ (Pieper *et al.*, 1998), but it is different from the all-*trans* configuration observed for the Sn atoms in the related derivatives [$Me_2N(CH_2)_2CMe_2$]$_2$SnCl$_2$ (Schollmeyer *et al.*,