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Structure of Cyclopentadienyl(6,6-diphenylfulvene)cobalt

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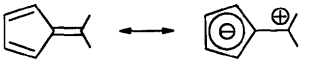
Abstract. $[Co(C_5H_5)(C_{18}H_{14})]$, $C_{23}H_{19}Co$, $M_r = 354{\cdot}34$, monoclinic, $C2/c$, $a = 26{\cdot}643\,(8)$, $b = 7{\cdot}577\,(1)$, $c = 18{\cdot}021\,(4)$ Å, $\beta = 107{\cdot}06\,(3)^\circ$, $V = 3478$ Å^3, $Z = 8$, $D_x = 1{\cdot}352$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 9{\cdot}8$ cm^{-1}, $F(000) = 1472$, ambient temperature, $R = 0{\cdot}044$ for 2510 unique observed reflections $[F_o > 2\sigma(F_o)]$. The fulvene ligand is η^4-coordinated to the CpCo group, with a fold angle of 17° and a short [1·372 (4) Å] exocyclic carbon—carbon bond.

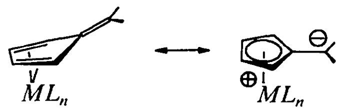
Introduction. Based on resonance between the limiting structures (I*a*) and (I*b*), pentafulvenes have been assigned an intermediate position between alkenes and the isomeric benzoid compounds (Hafner *et al.*, 1963). However, more recent theoretical, spectroscopic and crystallographic data indicate (I*a*) to be an adequate description of the ground state (Yates, 1968; Lloyd, 1984, and references cited therein; Burzlaff, Hartke & Salamon, 1970).



(I*a*) (I*b*)

In transition-metal complexes with a pentafulvene ligand serving as a six π-electron donor both η^6- and η^5-coordination, (II*a*) and (II*b*) respectively, have been found (Watts, 1981). In contrast to the latter, the η^6-coordination mode is always accompanied by a substantial folding of the fulvene ligand, thereby shortening the distance from the metal to the exocyclic carbon atom. A contribution of the η^5-resonance structure seems only significant with some metal fragments bearing a formal positive charge {*e.g.* $ML_n = [RhL_2]^+$, L_2 = cod (cod = cyclooctadiene) (Moran, Green & Orpen, 1983; Dauter, Hansen, Mawby, Probitts & Reynolds, 1985), $[P(PhO)_3]_2$ (Dauter, *et al.*, 1985)} or donor substituted fulvenes (Lubke & Behrens, 1978). For fulvenes functioning as four-electron ligands, a different kind of polarization can be envisaged as indicated in (III*a*)<—>(III*b*).

(II*a*) (II*b*)



(III*a*) (III*b*)

The crystal structures of $[(CO)_3Fe(6,6\text{-diphenylfulvene})]$ and [(cod)Ni(6,6-diphenylfulvene)] (Edelmann, Lubke & Behrens, 1982), however, do not indicate any participation of the resonance structure (III*b*). For ML_n = CpCo (Cp = η-cyclopentadienyl), (III*b*) corresponds to a substituted cobaltocenium ion; this bonding situation should possess a higher inherent stability (Kemmitt & Russell, 1982, and references cited therein). The related binuclear compounds $[CpCo(\mu\text{-}C_5H_4)Co(L)Cp]$ ($L = C_2H_4$, PR_3, $P(OR)_3$, CO, RNC), which can be formally derived from the fulvene complexes by substituting the exocyclic CR_2 group with the isolobal [CpCoL] fragment, are quite well described by two resonance structures analogous to (III*a*)<—>(III*b*) (Wadepohl & Pritzkow, 1987).

Experimental. The title compound was prepared from 6,6-diphenylfulvene and $[CpCo(C_2H_4)_2]$ as described elsewhere (Wadepohl, 1989; Rau & Behrens, 1990). Deep red crystals were grown from a petroleum ether (boiling range 303–333 K)/toluene (90:10, *v*:*v*) solution at 248 K. Analytical data: % calculated C 77·96, H 5·40; % found C 77·69, H 5·43. Space group and approximate cell constants were determined from precession and Weissenberg photographs. Exact cell constants were derived by a least-squares procedure from 18 reflections of a Guinier powder diffractogram. A plate-like crystal of

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approx. dimensions $0{\cdot}55 \times 0{\cdot}45 \times 0{\cdot}15$ mm was sealed in a Lindemann tube and used for intensity data collection on a Stoe Stadi-2 two-circle Weissenberg diffractometer $\{\omega$-scan, $3 < \theta < 25°$, $0 \le h \le 30$, $0 \le k \le 8$, $-21 \le l \le 20$; 2863 reflections measured, 2863 unique, 2510 observed $[F_o > 2\sigma(F_o)]\}$. Corrections were made for Lorentz–polarization and absorption effects (max. and min. transmission factors 0·894 and 0·858 respectively). The position of the Co atom was taken from a Patterson synthesis and all other atoms were located from subsequent difference Fourier syntheses. Refinement on F was carried out by blocked-matrix least squares with anisotropic thermal parameters for all non-H atoms (293 parameters). Final residuals were $R = 0{\cdot}044$, $wR = 0{\cdot}040$, $w = 1{\cdot}303/\sigma^2(F_o)$; $(\Delta/\sigma)_{\max} = 0{\cdot}2$. A final difference Fourier synthesis showed no features larger than $0{\cdot}3$ e Å^{-3}. The calculations were performed with the *SHELX76* program (Sheldrick, 1976) on an Atari 520ST$^+$ microcomputer fitted with a Motorola 68020/68881 processor board and on an IBM 3090-180 mainframe computer. Atomic scattering factors were taken from Cromer & Mann (1968).

Discussion. Atomic coordinates and $U_{\rm eq}$ values are listed in Table 1,* selected bond lengths and bond angles in Table 2. The molecular structure of [CpCo(6,6-diphenylfulvene)], together with the labelling scheme, is depicted in Fig. 1.

The fulvene ligand adopts the η^4-coordination to the (η^5-Cp)Co moiety *via* its planar (±0·004 Å) 1,3-diene system. Carbon—carbon bond lengths within the diene part are equal (1·40 Å) within experimental error; they are shorter than the distances C6—C7/10 (1·47 Å). The fulvene is folded away from the Co atom by 16° along C7···C10. As a consequence, the distance Co···C6 is elongated to 2·341 (3) Å. The vector C6—C11 is at an angle of 5° to the plane C6C7C10, inclined towards the Co atom. The exocyclic double bond C6═C11 [1·372 (4) Å] is only marginally longer than the corresponding distances found in free fulvenes (1·34–1·37 Å; Zeller, 1985, and references cited therein) without donor or acceptor substituents on the exocyclic C atom.

The pattern of bond lengths within the η^4-fulvene ligand of the title compound does not deviate much from that of [(CO)$_3$Fe(η^4-6,6-diphenylfulvene)], [(cod)Ni(η^4-6,6-diphenylfulvene)] (Edelmann, Lubke & Behrens, 1982) and {(indenyl)Rh[η^4-6,6-di(p-methylaminophenyl)fulvene]} (Rau & Behrens,

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic thermal parameters*

	x	y	z	$\overline{U}$ (Å^2)
Co1	0·31219 (2)	0·29759 (5)	0·39745 (2)	0·043
C1	0·37899 (18)	0·1539 (6)	0·4393 (3)	0·090
C2	0·37085 (16)	0·2505 (5)	0·4980 (2)	0·075
C3	0·32433 (16)	0·2005 (6)	0·5098 (2)	0·075
C4	0·30229 (18)	0·0752 (60	0·4579 (3)	0·091
C5	0·3337 (3)	0·0450 (5)	0·4099 (3)	0·102
C6	0·32609 (11)	0·4870 (3)	0·30275 (16)	0·041
C7	0·28716 (12)	0·3452 (4)	0·28086 (17)	0·049
C8	0·24714 (12)	0·3681 (5)	0·3162 (2)	0·057
C9	0·26328 (13)	0·5024 (4)	0·3714 (2)	0·055
C10	0·31350 (11)	0·5594 (4)	0·37060 (18)	0·045
C11	0·36684 (11)	0·5293 (4)	0·27387 (16)	0·044
C12	0·37548 (11)	0·4418 (4)	0·20601 (16)	0·044
C13	0·42567 (13)	0·4166 (5)	0·2000 (2)	0·064
C14	0·43450 (16)	0·3292 (5)	0·1373 (2)	0·080
C15	0·39393 (17)	0·2661 (5)	0·0787 (2)	0·071
C16	0·34340 (16)	0·2972 (5)	0·0812 (2)	0·070
C17	0·33452 (14)	0·3826 (5)	0·14352 (19)	0·061
C18	0·40753 (11)	0·6581 (4)	0·31591 (17)	0·047
C19	0·41990 (16)	0·8030 (5)	0·2792 (2)	0·073
C20	0·45923 (19)	0·9188 (5)	0·3173 (3)	0·092
C21	0·48690 (15)	0·8905 (6)	0·3937 (3)	0·081
C22	0·47493 (16)	0·7507 (6)	0·4312 (2)	0·079
C23	0·43531 (14)	0·6343 (5)	0·3930 (2)	0·063

Table 2. *Important bond lengths* (Å) *and angles* (°)

Co1—C1	2·033 (4)	C2—C3	1·371 (7)
Co1—C2	2·047 (4)	C3—C4	1·341 (6)
Co1—C3	2·088 (4)	C4—C5	1·389 (9)
Co1—C4	2·065 (5)	C6—C7	1·465 (4)
Co1—C5	1·992 (4)	C6—C10	1·466 (5)
Co1—C6	2·341 (3)	C6—C11	1·372 (5)
Co1—C7	2·041 (3)	C7—C8	1·404 (5)
Co1—C8	1·986 (3)	C8—C9	1·399 (5)
Co1—C9	1·992 (3)	C9—C10	1·410 (5)
Co1—C10	2·044 (3)	C11—C12	1·467 (4)
C1—C2	1·355 (7)	C11—C18	1·490 (4)
C1—C5	1·429 (7)		
C5—C1—C2	106·9 (4)	C8—C7—C6	111·1 (2)
C3—C2—C1	109·3 (3)	C9—C8—C7	107·2 (2)
C4—C3—C2	108·6 (4)	C10—C9—C8	108·1 (3)
C5—C4—C3	109·3 (4)	C9—C10—C6	110·1 (2)
C4—C5—C1	105·7 (3)	C12—C11—C6	123·1 (2)
C10—C6—C7	100·5 (2)	C18—C11—C6	119·9 (2)
C11—C6—C7	130·2 (2)	C18—C11—C12	116·8 (2)
C11—C6—C10	129·0 (2)		

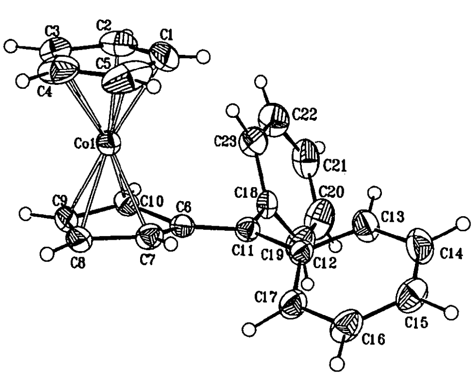

Fig. 1. *ORTEP* (Johnson, 1970) drawing of the molecule showing the labelling scheme for atoms.

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* Lists of structure factors, anisotropic thermal parameters, full bond lengths and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54182 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1990). The folding angles of the fulvene ligands in the above complexes vary from 8 to 22°. A correlation with the ability to stabilize a formal charge on the metal of the $(CO)_3Fe$, (cod)Ni, (indenyl)Rh and CpCo fragments is not, however, apparent. Hence, dipolar resonance structures do not seem to contribute very significantly to the electronic structure of these compounds. There is, however, a clear distinction between the η^4-coordination mode of the fulvenes donating four π electrons in these complexes and the above mentioned η^5- or η^6-coordination found for fulvenes functioning as six π-electron donors.

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Structure of Octaaquasaccharinatoneodymium Disaccharinate Hydrate*

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Abstract. $[Nd(C_7H_4NO_3S)(H_2O)_8]^{2+}.2C_7H_4NO_3S^-.H_2O$, $M_r = 852{\cdot}9$, monoclinic, $P2_1/c$, $a = 7{\cdot}730\ (4)$, $b = 13{\cdot}408\ (9)$, $c = 30{\cdot}59\ (3)$ Å, $\beta = 94{\cdot}90\ (7)°$, $V = 3159\ (4)$ Å^3, $Z = 4$, $D_m = 1{\cdot}79$, $D_x = 1{\cdot}793\ (2)$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}93$ mm^{-1}, $F(000) = 1716$, $T = 296\ (1)$ K, final $R = 0{\cdot}0482$ for 6059 reflections. The neodymium ions adopt a tricapped trigonal prismatic coordination defined by eight water oxygen atoms and the carbonyl oxygen atom of one of the three independent saccharinate anions.

Introduction. Saccharin and its metal complexes and salts have been the subject of rather extensive structural investigations (*e.g.* Hergold-Brundić, Kamenar & Jovanovski, 1989; Cotton, Falvello, Llusar, Libby, Murillo & Schwotzer, 1986, and references therein). We decided to investigate its neodymium complex as part of our study on lanthanide complexes with N-donor ligands.

Experimental. The title compound was prepared by adding freshly precipitated neodymium hydroxide to a warm aqueous suspension of saccharin. After a few days long violet needles were formed. A specimen, 0·6 × 0·45 × 0·2 mm, was cut from a larger crystal. D_m by flotation in $C_2H_4Br_2/CHCl_3$. Oscillation and Weissenberg photographs allowed the crystal system and space group to be established. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation for lattice parameters (15 reflections, $23 < 2\theta < 28°$), variable $\omega/2\theta$ scan, $5 < 2\theta < 57°$. Two standards every 50 reflections, mean relative e.s.d. of the control reflections 5·6%. 6147 of the 8206 intensities measured had $I \geq 3\sigma(I)$,

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* Saccharin is 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide.

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