Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1-[2-(Dimethylaminomethyl)phenyl]-2,3,4,5-tetraphenylcyclopentadien-1-ol

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Received 12 December 2006
Accepted 22 December 2006

The crystal structure of the title compound, $C_{38}H_{33}NO$, shows that the OH group interacts with the N atom of the dimethylamino group *via* an intramolecular hydrogen bond, resulting in the formation of a seven-membered ring. The presence of this interaction, the poor nucleofugal properties of the hydroxy function and the particularly high steric hindrance decrease the ability of the OH group for substitution by other nucleophiles. The crystal packing exhibits no classical intermolecular hydrogen bonds.

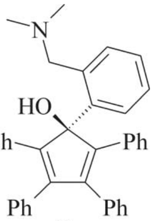
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.045
wR factor = 0.119
Data-to-parameter ratio = 17.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

It is well known that the properties of metallocene-related complexes can be easily modified by the introduction of various substituents at the cyclopentadienyl ring. Pentaphenylcyclopentadiene has a unique combination of steric and electronic properties, and a series of metal complexes bearing this ligand are known (Field *et al.*, 1992). In order to prepare new bulky cyclopentadienyl ligands with nitrogen-donating ability, we have synthesized the title compound, (I). Unfortunately, all our attempts to convert (I) into the respective cyclopentadiene were unsuccessful, and we tried to find some explanation for the observed inertness to nucleophilic substitution at the sp^3 C atom of the C_5 ring. For this purpose, we have determined the crystal structure of the title compound.



(I)

The molecular structure of (I) is shown in Fig. 1, and selected bond distances and angles are given in Table 1. The cyclopentadienyl and aromatic rings are almost planar, with maximum deviations from planarity of 0.0366 (14) and 0.054 (15) Å, respectively. The C—C bond lengths in the C_5 ring are very close to those reported for 1,2,3,4,5-pentaphenylcyclopentadien-1-ol, (II) (Bourne *et al.*, 1992). The average C—C—C angle at the sp^2 C atoms of the Cp ring is 109.4 (1)°, whereas the corresponding angle at the sp^3-hybridized C atom is only 102.06 (10)°. The O1—C1—C11 angle of 114.76 (10)° is significantly larger than the corresponding angle in (II) [107.62 (17)°], due to steric pressure exerted by the aminomethyl-substituted phenyl ring. Phenyl *ipso* atoms

doi:10.1107/S1600536806056170

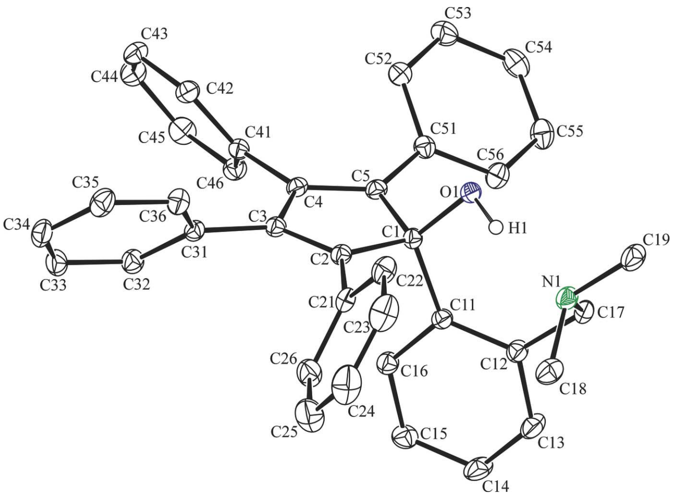


Figure 1
A view of the title compound, with displacement ellipsoids drawn at the 30% probability level. For clarity, only one H atom (H1), which is involved in an intramolecular hydrogen bond, is shown.

C21, C31 and C41 are displaced slightly [0.0079 (13)–0.0400 (13) Å] out of the Cp ring plane; *ipso* atom C51 is displaced out of the C_5 plane by 0.2616 (13) Å. The benzene *ipso* C atom bonded to the sp^3-hybridized atom C1 lies 1.4104 (13) Å out of the Cp ring plane, and this benzene ring is almost perpendicular [88.38 (8)°] to the Cp ring plane. The remaining phenyl substituents are canted relative to the cyclopentadienyl ring at angles of between 32.59 (7) and 65.43 (8)°.

The crystal structure of (I) shows that the OH group interacts with the N atom of the 2-(*N*,*N*-dimethylaminomethyl)phenyl substituent bonded to the sp^3 C atom, generating a seven-membered ring (Table 2). This interaction displaces the pendant dimethylaminomethyl arm close to the OH group and this, together with the large steric hindrance of the adjacent phenyl rings, prevents substitution of the OH group by nucleophiles.

Experimental

To a suspension of {2-[(*N*,*N*-dimethylamino)methyl]phenyl} lithium (3.46 g, 24.52 mmol) prepared from *N*,*N*-dimethylbenzylamine (Aldrich) and BuLi (Aldrich) in benzene (100 ml), 2,3,4,5-tetraphenylcyclopentadienone (5.45 g, 14.19 mmol, Aldrich) dissolved in benzene (100 ml) was added dropwise. After stirring for 12 h, the reaction mixture was poured into water (200 ml) and the pH was adjusted to a value of 8–9 using 1 *M* H_2SO_4. The light-pink organic layer was separated off, washed with brine (2 × 50 ml) and dried over Na_2SO_4, and the solvent was removed under vacuum, leaving an oily residue. Hexane (60 ml) was added with stirring, and the white crystals which precipitated were filtered off, washed with cold hexane (2 × 20 ml) and dried in a vacuum (yield 5.40 g, 73%; m.p. 427–428 K). Further purification can be performed using extraction with boiling hexane in a Soxhlet apparatus. Upon slow cooling of a hexane solution to 280 K, colourless crystals of (I) suitable for X-ray diffraction measurements were formed.

Attempts to convert (I) into the respective cyclopentadiene using methods described for 2,3,4,5-tetraphenylcyclopentadien-1-ol (Bandara *et al.*, 1974), 1,2,3,4,5-pentaphenylcyclopentadien-1-ol (Ziegler & Schnell, 1925; Chambers *et al.*, 1986) or 1-(*m*-tolyl)-2,3,4,5-tetraphenylcyclopentadien-1-ol (Greene *et al.* 2003) have failed. Similarly, the substitution of the OH group with a halide by the reaction of (I) with HCl, HBr, BBr_3, PBr_3/pyridine or $SOCl_2$/pyridine was not successful and only the starting compound, (I), was isolated from the reaction mixtures.

Crystal data

$C_{38}H_{33}NO$
$M_r = 519.65$
Triclinic, $P\overline{1}$
$a = 10.1507$ (3) Å
$b = 11.1701$ (3) Å
$c = 14.3299$ (3) Å
$\alpha = 91.3388$ (16)°
$\beta = 100.0688$ (17)°
$\gamma = 115.4451$ (11)°

$V = 1435.69$ (6) Å^3
$Z = 2$
$D_x = 1.202$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 0.07$ mm^{-1}
$T = 150$ (2) K
Prism, colourless
0.4 × 0.25 × 0.18 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: none
23210 measured reflections

6577 independent reflections
4982 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\rm max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.119$
$S = 1.02$
6577 reflections
367 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 0.4091P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cp is the cyclopentadiene ring plane defined by atoms C1–C5. Ph1, Ph2, Ph3, Ph4 and Ph5 are the aromatic ring planes defined by atoms C11–C16, C21–C26, C31–C36, C41–C46 and C51–C56, respectively. Cp—Phn values are the dihedral angles between the Cp and phenyl rings.

C1—C2	1.536 (2)	Cp—Ph1	88.38 (8)
C2—C3	1.3458 (18)	Cp—Ph2	65.43 (8)
C3—C4	1.487 (2)	Cp—Ph3	56.26 (7)
C1—O1	1.4138 (14)	Cp—Ph4	54.26 (7)
C2—C1—C5	102.06 (10)	Cp—Ph5	32.59 (7)
O1—C1—C11	114.76 (10)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.95 (2)	1.80 (2)	2.7089 (14)	157.6 (18)

Carbon-bound H atoms were positioned geometrically, with C—H = 0.93–0.97 Å, and refined as riding, with $U_{\rm iso}({\rm H}) = 1.2–1.5U_{\rm eq}({\rm C})$. The H atom of the –OH group was found in a difference Fourier map and freely refined with an isotropic displacement parameter.

Data collection: *COLLECT* (Nonius, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

The authors thank the Ministry of Education, Youth and Sports of the Czech Republic for financial support of this work within the framework of research project MSM 0021627501.

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