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ansa-Calcocenes: *trans*-$Ph_2(CH_3)_2C_2(\eta^5\text{-}C_5H_4)_2$-Ca(DME)

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Key indicators

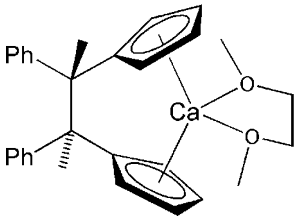
Single-crystal X-ray study
T = 213 K
Mean σ(C–C) = 0.004 Å
R factor = 0.062
wR factor = 0.117
Data-to-parameter ratio = 15.1

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

The title compound, (1,2-di-η^5-cyclopentadienyl-1,2-dimethyl-*trans*-1,2-diphenylethane)(1,2-dimethoxyethane)calcium, *trans*-$Ph_2(CH_3)_2C_2(\eta^5\text{-}C_5H_4)_2Ca(DME)$ or $[Ca(C_{26}H_{24})(C_4H_{10}O_2)]$, was synthesized by reductively coupling 6,6-methylphenylfulvene with activated calcium in the presence of dimethoxyethane (DME). The *trans* isomer was isolated by fractional crystallization. The Ca atom is four-coordinate and is η^5-bonded to both cyclopentadienyl rings [Ca—Cp(centroid) distance = 2.381 (3) Å] and the O atoms of the coordinated solvent chelate ligand [Ca—O = 2.350 (2) and 2.404 (2) Å].

Comment

The reductive coupling of fulvenes with active metals is a convenient method for generating ethanediyl-bridged dicyclopentadienyl-ligand frameworks for ansa-metallocene complexes (Tan *et al.*, 1975; Schwemlein & Brintzinger, 1983; Eisch & Shi, 1998). We have examined the reductive coupling of 6-methyl-6-phenylfulvene with activated calcium and report on the structure of the unusual calcocene: *trans*-$Ph_2(CH_3)_2$-$C_2(\eta^5\text{-}C_5H_4)_2Ca(DME)$, (I).



(I)

The Ca atom in (I) is in a four-coordinate environment, η^5-bonded $\eta$to both cyclopentadienyl (Cp) ligands and η^1-bonded to each O atom of the solvent ligand. Compound (I) has a Cp(centroid)—Ca distance of 2.381 (3) Å and a Cp—Ca—Cp angle of 121.3 (2)°. The Ca—O distances are slightly asymmetric [2.404 (2) and 2.350 (2) Å]. The O—Ca—O angle [69.66 (7)°] is distorted from the ideal tetrahedral angle due to the geometrical constraint of the chelate DME ligand. The dihedral angle between the two cyclopentadienyl rings is 59.6 (1)°.

There are few structurally determined ansa-bridged calcocenes for comparison. The closely related *cis* and *trans* ansa-calcocenes $Ph_2C_2H_2(\eta^5\text{-}C_5H_4)_2Ca(thf)_2$ have average Cp—Ca distances of 2.40 and 2.42 Å, respectively with a Cp—Ca—Cp angle of 120.4 and 119.9° (Matare *et al.*, 1998; Kane *et al.*, 1997). The only other structurally reported carbon-bridged ansa-calcocene consists of the diiminoethane (DIE) coordinated calcocene $(CH_3)_4C_2(\eta^5\text{-}C_5H_4)_2Ca(^t\!Bu_2DIE)$ which is closely related to (I) with asymmetric ligand N—Ca bonding of 2.503 (6) and 2.563 (6) Å, Cp—Ca distances of 2.396 (3) and 2.391 (3) Å, and a Cp—Ca—Cp angle of 119.0° (Reickhoff *et al.*, 1993).

Experimental

The title compound, (I), was prepared in the following manner: calcium granules (1.33 g, 33.19 mmol; preactivated with $HgCl_2$) were suspended in 100 ml of dry DME under an argon atmosphere. 6,6-Methylphenylfulvene (10.00 g, 59.44 mmol) was added gradually for a period of 15 min as the reaction was stirred at room temperature. The red color of the fulvene disappeared almost instantly and the reaction mixture appeared colorless within 6 h. The mixture was filtered to remove the gray precipitate and the solvent was removed under reduced pressure. The tan solid was washed with copious amounts of hexane yielding the product, a colorless solid (8.71 g, 61%). Roughly equal amounts of both the *cis* and *trans* isomers are present. The *trans* isomer was selectively precipitated as a colorless powder by dissolution and cooling to 195 K in a dry ice/acetone bath. Yield 2.66 g, 25%. X-ray quality crystals of the *trans* isomer were obtained from a saturated DME solution at room temperature after 3 d. ^{1}H NMR (200 MHz, DMSO-d_6): δ 1.92 (*s*, 6H, CH_3), 3.24 (*s*, 6H, CH_3-DME), 3.43 (*s*, 4H, CH_2-DME), 5.44 (*s*, 2H, Cp), 5.63–5.69 (*d*, 4H, Cp), 6.20 (*s*, 2H, Cp), 7.06–7.34 (*m*, 10H, Ph); $^{13}C\{^1H\}$ NMR (50.3 MHz, DMSO-d_6): δ 28.2 (CH_3), 52.8 (MeCPH), 58.9 (CH_3O-DME), 71.9 (OCH_2CH_2O), 104.1, 106.7, 107.5, 108.2, 125.5 (C_5H_4), 126.5, 128.6, 129.4, 130.3, 132.5, 150.0 (C_6H_5); $C_{30}H_{34}CaO_2$ (calc/found%): C 77.21/77.17, H 7.34/7.31.

Crystal data

$[Ca(C_{26}H_{24})(C_4H_{10}O_2)]$
$M_r = 466.65$
Monoclinic, $C2/c$
$a = 27.726$ (3) Å
$b = 12.412$ (2) Å
$c = 16.087$ (3) Å
$\beta = 110.46$ (2)°
$V = 5186.7$ (14) Å^3
$Z = 8$

$D_x = 1.195$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 1.8$–$25.0°$
$\mu = 0.27$ mm^{-1}
$T = 213$ (2) K
Block, colorless
0.25 × 0.20 × 0.15 mm

Data collection

Siemens SMART 1 K diffractometer
ω scans
Absorption correction: empirical (*XPREP*; Sheldrick, 1998)
$T_{min} = 0.937$, $T_{max} = 0.961$
14 054 measured reflections

4564 independent reflections
4294 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 25.0°$
$h = -32 \rightarrow 32$
$k = -7 \rightarrow 14$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.117$
$S = 1.29$
4564 reflections
302 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0165P)^2 + 8.9225P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

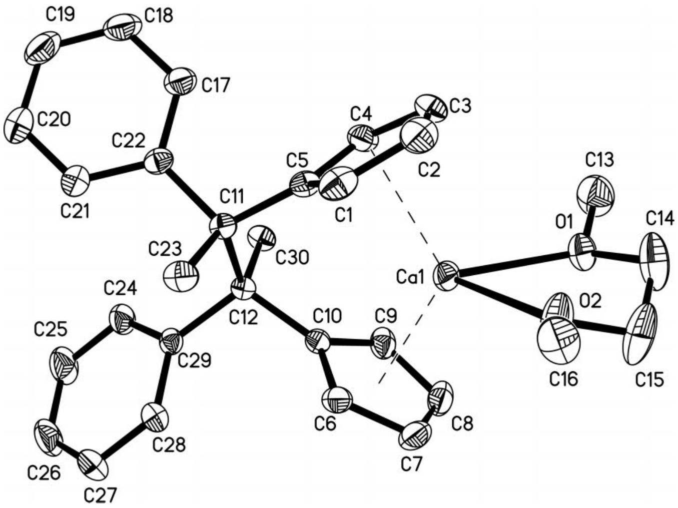


Figure 1
The molecular structure of (I) with 30% probability ellipsoids. H atoms have been omitted for clarity.

H atoms were placed geometrically and refined with a riding model, with U_{iso} constrained to be $1.2U_{eq}$ of the carrier atom. There are voids of 48 Å^3 present in (I).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *XS* (Sheldrick, 1998); program(s) used to refine structure: *XL* (Sheldrick, 1998); molecular graphics: *XP* (Sheldrick, 1998); software used to prepare material for publication: *XCIF* (Sheldrick, 1998).

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