

New C₂-symmetric cyclopentadiene dimer
from sodium naphthalenide reduction of
1,3,6-tri-*tert*-butylfulveneSarah Bragg,^a Jane E. B.
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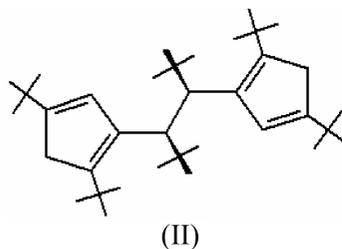
Key indicators

Single-crystal X-ray study
T = 173 K
Mean $\sigma(\text{C}-\text{C})$ = 0.002 Å
R factor = 0.060
wR factor = 0.158
Data-to-parameter ratio = 23.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The sodium naphthalenide reduction of 1,3,6-tri-*tert*-butylfulvene gave the dimer, *rac*-3,4-bis(1,4-di-*tert*-butylcyclopenta-1,3-dien-2-yl)-2,2,5,5-tetramethylhexane [C₃₆H₆₂, (II)] after protonation of the disodium salt of the bis(cyclopentadienyl-ethane) intermediate. Bond distances and angles for (II) are consistent with a bis(cyclopentadiene) structure. The ansa bridge bond is long, at 1.592 (2) Å. The substitution pattern on the cyclopentadiene rings, as well as the ansa bridge, result in an overall C₂ symmetry for (II).

Comment

The reductive dimerization of fulvenes to form bridged-cyclopentadienyl ligands is a versatile synthetic route to ansa-metallocene complexes, which are important in catalytic processes (Long, 1998; Brintzinger *et al.*, 1995; Gomez & Waymouth, 2002; Aitola *et al.*, 2002; Miller & Bercaw, 2002; Angermund *et al.*, 2000; Bogaert *et al.*, 2001; Ihara *et al.*, 2001; Shaltout & Corey, 1995). Methods most commonly used directly incorporate the metal into the ligand framework, and include reaction of fulvenes with activated Ca or Sr (Rieckhoff *et al.*, 1993; Sinnema *et al.*, 2002), Mg/CCl₄/TiCl₃·3THF or Na(Hg)/TiCl₃·3THF (Schwemlein & Brintzinger, 1983), activated lanthanide metals (Recknagel & Edelman, 1991; Fedushkin *et al.*, 2001), group IV divalent halides (Eisch *et al.*, 1998, 1999) and metal vapors at low temperature (Tacke, Dunne *et al.*, 2001). Fulvene radical anions are key intermediates, leading to dimerization in these reactions, and have been studied by theoretical and experimental methods (Tacke, Fox *et al.*, 2001).



Reduction of fulvenes with aromatic hydrocarbon radical anions has also been carried out. Reaction of 6,6-dimethylfulvene with sodium naphthalenide gave a dimer product, coupled at the C-1 position on the ring (Oku *et al.*, 1979), while reaction of 6,6-dimethylfulvene with sodium anthracenide followed by TiCl₃·3THF was reported to give exclusive formation of the bridged tetramethylethylene-titanocene dichloride (Schwemlein & Brintzinger, 1983). In the reductive coupling of substituted 6-dimethylaminofulvenes with lithium naphthalenide, deamination of proposed bis(cyclopenta-

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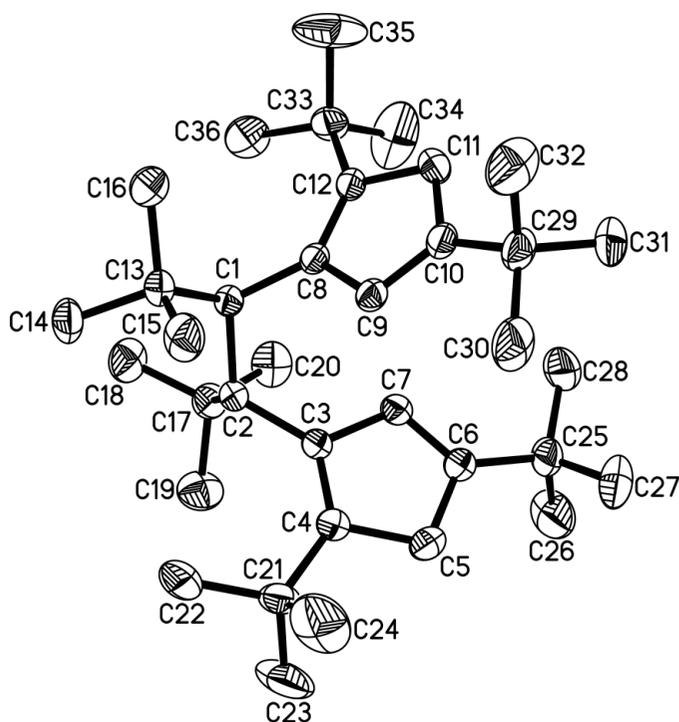


Figure 1
View of (II). Displacement ellipsoids are shown at the 50% probability level.

dienyl) intermediates led to the formation of substituted 6,6'-bifulvenyl compounds (Kawese *et al.*, 1989).

One of our research goals is to investigate the selectivity in reactions of aromatic hydrocarbon radical anions with various substituted fulvenes, with an emphasis on obtaining new bis(cyclopentadienyl) compounds useful as ligands for the formation of ansa-metallocene complexes. Recently, we carried out the aromatic hydrocarbon radical anion dimerization of the sterically demanding 1,3,6-tri-*tert*-butylfulvene, (I) (Johnson *et al.*, 1997). A unique feature of this chemistry is the almost exclusive formation of the racemic dimer (II) (79%), from the reaction of (I) and sodium naphthalenide. The dimer (II) is formed by protonation of the isolable bis(cyclopentadienylethane) intermediate. To our knowledge, the dimer (II) is the first reported case of a C_2 ansa-cyclopentadiene ligand synthesized by fulvene dimerization, using aromatic hydrocarbon radical anions. Research in our laboratory on the utility of (II) for the synthesis of ansa-metallocenes is in progress.

Single-crystal X-ray diffraction results for (II) show a nearly C_2 symmetric structure adopted as a result of selective coupling of two 1,3,6-tri-*tert*-butylfulvene units (Fig. 1 and Table 1). The cyclopentadiene rings are nearly eclipsed in (II) (Fig. 2), with a torsion angle of $119.0(1)^\circ$ between the *tert*-butyl groups of the ansa bridge. C—C bond distances in (II) are comparable to those in a recently reported crystal structure of the related ansa-cyclopentadiene ligand $C_5H_5CMe_2CMe_2C_5H_5$ (Tacke, Dunne *et al.*, 2001). The C1—C2 bond distance in (II) [$1.592(2) \text{ \AA}$] is slightly shorter than in $C_5H_5CMe_2CMe_2C_5H_5$ [$1.600(3) \text{ \AA}$], but consistent with an

elongated bridge bond from steric interaction of bulky *tert*-butyl groups.

Experimental

Sodium naphthalenide was prepared by combining naphthalene (1.63 g, 12.7 mmol) and sodium (0.31 g, 13 mmol) in dry THF (100 ml) under N_2 and allowing the dark-green solution to vigorously stir for 1 h. To the vigorously stirred sodium naphthalenide solution at 195 K was added, in one portion, a solution of 1,3,6-tri-*tert*-butylfulvene (3.00 g, 12.2 mmol) in dry THF (50 ml) at 195 K. The colour of the reaction mixture immediately faded from dark-green to red, and the red solution was allowed to stir for 30 min at 195 K under N_2 . The reaction mixture was allowed to slowly warm to room temperature, and THF removed under vacuum. Dry CH_3CN (50 ml) was added to the resulting crude orange solid under N_2 , and the mixture exposed to air. Ammonium chloride (3 ml, 5 M, 15 mmol) was added to the CH_3CN solution, resulting in the precipitation of a white solid. The white solid was filtered, washed with CH_3CN (30 ml), and dissolved in C_6H_6 (50 ml). Filtration of solids followed by removal of C_6H_6 and vacuum drying yielded 2.37 g (79%) of the dimer (II) as a white solid. Crystals suitable for single-crystal X-ray analysis were obtained from 50/50 MeOH/ C_6H_6 as colourless and transparent prisms with well defined faces. 1H NMR (200 MHz, C_6D_6 , 303 K, p.p.m.): δ 1.14, 1.15, 1.41 (s, 54H, 'Bu); 2.96 (broad s, 4H, ring CH_2); 3.43 (s, 2H, bridge CH' Bu); 5.86 (m, 2H, ring CH). ^{13}C NMR (75.5 MHz, C_6D_6 , 303 K, p.p.m.): δ 30.8, 31.2, 33.0 [$C(CH_3)_3$]; 32.7, 35.7, 36.9 [$C(CH_3)_3$]; 40.4 (ring CH_2); 45.7 (CH' Bu); 131.5 (ring CH); 139.4, 145.2, 148.1 (ring C). Selected FT-IR (KBr pellet, cm^{-1}): 3104 (w, ν_{ringCH}); 2958, 2903, 2866 (s, ν_{CH}); 1620 (m, $\nu_{C=C}$). M.p. = 433.1 K decomposition (DSC). The measured density at 173 K was obtained by correcting the measured density at room temperature (0.954 Mg m^{-3} , flotation) to 173 K using the room-temperature diffraction data [$a = 16.4307(10) \text{ \AA}$, $b = 10.5281(7) \text{ \AA}$, $c = 19.8552(12) \text{ \AA}$, $\beta = 96.2200(10)^\circ$ and $V = 3414.4(4) \text{ \AA}^3$].

Crystal data

$C_{36}H_{62}$
 $M_r = 494.89$
Monoclinic, $P2_1/c$
 $a = 16.279(1) \text{ \AA}$
 $b = 10.519(1) \text{ \AA}$
 $c = 19.680(2) \text{ \AA}$
 $\beta = 96.935(1)^\circ$
 $V = 3345.4(5) \text{ \AA}^3$
 $Z = 4$
 $D_x = 0.983 \text{ Mg m}^{-3}$
 $D_m = 0.974 \text{ Mg m}^{-3}$

D_m measured by correction from room temperature data
Mo $K\alpha$ radiation
Cell parameters from 4491 reflections
 $\theta = 2.3\text{--}22.6^\circ$
 $\mu = 0.05 \text{ mm}^{-1}$
 $T = 173(2) \text{ K}$
Prism, colorless
 $0.45 \times 0.27 \times 0.13 \text{ mm}$

Data collection

Bruker CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)
 $T_{min} = 0.84$, $T_{max} = 0.99$
28 797 measured reflections

7984 independent reflections
5492 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.047$
 $\theta_{max} = 28.4^\circ$
 $h = -20 \rightarrow 20$
 $k = -13 \rightarrow 13$
 $l = -25 \rightarrow 25$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.060$
 $wR(F^2) = 0.158$
 $S = 1.03$
7984 reflections
343 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0727P)^2 + 0.6485P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.006$
 $\Delta\rho_{max} = 0.29 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.17 \text{ e \AA}^{-3}$

Table 1
Selected geometric parameters (Å, °).

C1—C8	1.521 (2)	C13—C15	1.534 (2)
C1—C13	1.590 (2)	C13—C16	1.537 (2)
C1—C2	1.592 (2)	C13—C14	1.537 (2)
C2—C3	1.526 (2)	C17—C20	1.531 (2)
C2—C17	1.589 (2)	C17—C18	1.539 (2)
C3—C4	1.359 (2)	C17—C19	1.540 (2)
C3—C7	1.487 (2)	C21—C22	1.528 (2)
C4—C5	1.519 (2)	C21—C23	1.533 (3)
C4—C21	1.531 (2)	C21—C24	1.535 (3)
C5—C6	1.499 (2)	C25—C28	1.528 (3)
C6—C7	1.335 (2)	C25—C27	1.532 (3)
C6—C25	1.517 (2)	C25—C26	1.540 (3)
C8—C12	1.359 (2)	C29—C30	1.522 (2)
C8—C9	1.483 (2)	C29—C32	1.531 (2)
C9—C10	1.335 (2)	C29—C31	1.532 (2)
C10—C11	1.496 (2)	C33—C36	1.524 (2)
C10—C29	1.519 (2)	C33—C34	1.527 (3)
C11—C12	1.519 (2)	C33—C35	1.530 (3)
C12—C33	1.533 (2)		
C8—C1—C13	109.03 (11)	C16—C13—C1	109.38 (12)
C8—C1—C2	116.44 (11)	C14—C13—C1	111.34 (13)
C13—C1—C2	113.61 (11)	C20—C17—C18	108.22 (14)
C3—C2—C17	109.62 (12)	C20—C17—C19	107.62 (14)
C3—C2—C1	116.06 (11)	C18—C17—C19	106.43 (14)
C17—C2—C1	113.88 (11)	C20—C17—C2	113.86 (13)
C4—C3—C7	107.99 (12)	C18—C17—C2	111.73 (13)
C4—C3—C2	130.81 (13)	C19—C17—C2	108.65 (13)
C7—C3—C2	120.91 (12)	C22—C21—C4	116.80 (13)
C3—C4—C5	107.84 (13)	C22—C21—C23	106.73 (16)
C3—C4—C21	135.58 (14)	C4—C21—C23	109.36 (14)
C5—C4—C21	116.58 (13)	C22—C21—C24	106.98 (17)
C6—C5—C4	105.27 (12)	C4—C21—C24	108.19 (15)
C7—C6—C5	107.24 (13)	C23—C21—C24	108.52 (18)
C7—C6—C25	129.07 (15)	C6—C25—C28	110.70 (13)
C5—C6—C25	123.67 (13)	C6—C25—C27	110.27 (15)
C6—C7—C3	111.65 (13)	C28—C25—C27	109.36 (16)
C12—C8—C9	108.10 (12)	C6—C25—C26	108.97 (14)
C12—C8—C1	131.21 (12)	C28—C25—C26	108.60 (16)
C9—C8—C1	120.32 (12)	C27—C25—C26	108.91 (16)
C10—C9—C8	111.27 (12)	C10—C29—C30	110.88 (13)
C9—C10—C11	107.71 (12)	C10—C29—C32	108.89 (13)
C9—C10—C29	128.14 (14)	C30—C29—C32	109.06 (16)
C11—C10—C29	124.10 (13)	C10—C29—C31	109.95 (14)
C10—C11—C12	104.92 (11)	C30—C29—C31	109.73 (14)
C8—C12—C11	107.94 (12)	C32—C29—C31	108.27 (15)
C8—C12—C33	134.79 (13)	C36—C33—C34	106.93 (16)
C11—C12—C33	117.23 (12)	C36—C33—C35	106.15 (16)
C15—C13—C16	107.72 (14)	C34—C33—C35	109.76 (19)
C15—C13—C14	107.66 (13)	C36—C33—C12	116.43 (13)
C16—C13—C14	106.54 (13)	C34—C33—C12	107.72 (14)
C15—C13—C1	113.89 (12)	C35—C33—C12	109.72 (14)
C8—C1—C2—C3	15.63 (17)	C1—C2—C3—C4	127.04 (16)
C13—C1—C2—C17	118.99 (13)	C2—C1—C8—C12	124.79 (16)

H atoms on C atoms were placed in calculated positions and constrained to ride on the C atom with usual bond lengths. The U_{eq} values were 1.5 times (methyl groups) the U_{eq} values of the corresponding C atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINTE-Plus* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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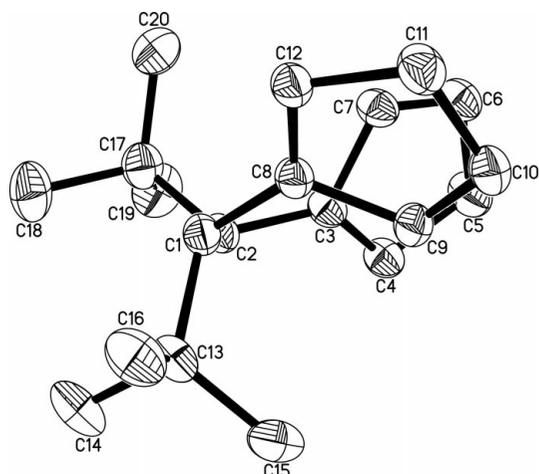


Figure 2
View of (II) along the C1—C2 bond axis. Ring *tert*-butyl groups have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

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