

$(\eta^6\text{-}N,N\text{-Diethylaniline})(\eta^4\text{-}1,2,3,4\text{-tetramethylcyclobutadiene})\text{cobalt(I) hexafluorophosphate}$

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Key indicators

Single-crystal X-ray study
 T = 120 K
 Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
 Disorder in main residue
 R factor = 0.052
 wR factor = 0.141
 Data-to-parameter ratio = 16.8

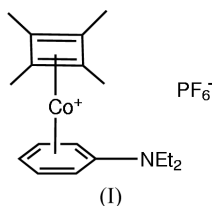
For details of how these key indicators were
 automatically derived from the article, see
<http://journals.iucr.org/e>.

The title isocobaltocenium salt, $[\text{Co}(\text{C}_8\text{H}_{12})(\text{C}_{10}\text{H}_{15}\text{N})]\text{PF}_6$, is shown to exist as discrete monomers with near equivalent C—C bonds in the cyclobutadiene ring.

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Comment

Isocobaltocenes are the series of compounds in which, in place of two cyclopentadienyl residues, the cobalt is π -bonded to one cyclobutadiene and one benzene ring. Species with bulky cyclobutadiene ring substituents have been known since the work of Maitlis & Efraty (1965) and have been widely crystallographically characterized. However, despite synthetic protocols being well known (Cook *et al.*, 1987), the only known structures of tetramethylcyclobutadiene-based isocobaltocenes are two species with unusual substituted boratabenzenes (Herberich *et al.*, 2002).



Reported here is the structure of (I), a tetramethylcyclobutadiene isocobaltocenium salt with a simple *N,N*-diethyl-

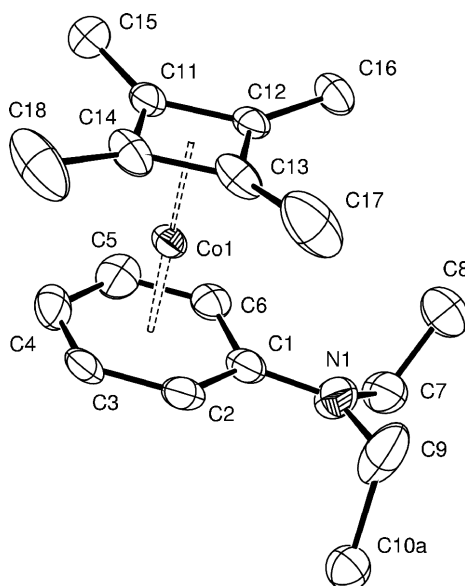


Figure 1
 The molecular structure of the cation of (I), shown with 50% probability displacement ellipsoids. H atoms and disordered fragments have been omitted for clarity.

aniline group as its arene component (Fig. 1). The centroid of the cyclobutadiene group lies further from Co1 than the centroid of the benzene ring (1.705 *versus* 1.592 Å) and this distance is also slightly longer than those found for the boratabenzene species (range 1.686–1.702 Å; Herberich *et al.*, 2002). However, it falls into the middle of the range found for nine general Co–tetramethylcyclobutadiene complexes found in a search of the Cambridge Structural Database (Version 5, with updates to December 2004; Allen, 2002). The cyclobutadiene ring C–C distances show only slight signs of alternate single- and double-bond nature (Table 1), indicating a high degree of aromaticity. The Co atom is placed over the centre of the cyclobutadiene ring but is displaced away from the amine-substituted C1 atom of the benzene ring. No strong intermolecular contacts were observed.

Experimental

The title compound was prepared according to the method of Cook *et al.* (1987).

Crystal data

[Co(C ₈ H ₁₂)(C ₁₀ H ₁₅ N)]PF ₆	$D_x = 1.519 \text{ Mg m}^{-3}$
$M_r = 461.31$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 21 381 reflections
$a = 8.4201(2) \text{ \AA}$	$\theta = 3.0\text{--}27.5^\circ$
$b = 16.2404(3) \text{ \AA}$	$\mu = 0.99 \text{ mm}^{-1}$
$c = 15.1960(4) \text{ \AA}$	$T = 120(2) \text{ K}$
$\beta = 103.844(1)^\circ$	Cut block, yellow
$V = 2017.63(8) \text{ \AA}^3$	$0.12 \times 0.10 \times 0.10 \text{ mm}$
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.078$
φ and ω scans	$\theta_{\text{max}} = 27.5^\circ$
21 381 measured reflections	$h = -10 \rightarrow 10$
4587 independent reflections	$k = -21 \rightarrow 21$
3068 reflections with $I > 2\sigma(I)$	$l = -17 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0681P)^2 + 0.6904P]$
$R[F^2 > 2\sigma(F^2)] = 0.052$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.141$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.49 \text{ e \AA}^{-3}$
4587 reflections	$\Delta\rho_{\text{min}} = -0.78 \text{ e \AA}^{-3}$
273 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Co1–C14	1.973 (3)	Co1–C2	2.109 (3)
Co1–C11	1.987 (3)	Co1–C6	2.126 (3)
Co1–C13	1.992 (3)	Co1–C1	2.241 (3)
Co1–C12	2.004 (3)	C11–C14	1.447 (5)
Co1–C3	2.077 (3)	C11–C12	1.450 (4)
Co1–C5	2.088 (4)	C12–C13	1.442 (4)
Co1–C4	2.101 (3)	C13–C14	1.452 (5)
C14–C11–C12	90.0 (3)	C12–C13–C14	90.1 (3)
C13–C12–C11	90.1 (3)	C11–C14–C13	89.8 (3)

H atoms were included in the riding-model approximation with C–H distances: CH₃ 0.98, CH₂ 0.99 and CH 0.95 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$. The PF₆[−] anion is rotationally disordered about the F3–P1–F4 axis. After several trial calculations, the remaining four F atoms were refined over 12 sites with set occupancies. The largest remaining electron-density peaks all occur near to the PF₆[−] anion. The C10 methyl group was refined as disordered over two sites with occupancies refined [0.52 (2):0.48 (2)]. The occupancies of atoms F1, F2, F5 and F6 were set at 0.5 and the occupancies of atoms F7–F12 were set at 0.25.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1988); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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