

η^5 -(3)-1-Methyl-1,2-dicarbollyl- η^5 - 2',5'-dimethylpyrrolylcobalt(III)

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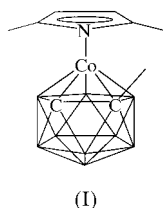
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In the title compound, (η^5 -2,5-dimethylpyrrolyl)[(7,8,9,10,11- η)-7-methyl-7,8-dicarba-*nido*-undecaborato]cobalt(III), [3-Co{ η^5 -[2,5-(CH₃)₂-NC₄H₂]}-1-CH₃-1,2-C₂B₉H₁₀] or [Co(C₃H₁₃B₉)-(C₆H₈N)], the Co^{III} atom is sandwiched between the pentagonal faces of the pyrrolyl and dicarbollide ligands, resulting in a neutral molecule. The C—C distance in the dicarbollide cage is 1.649 (3) Å.

Comment

Our studies concerning 1,2-dicarba-*closo*-dodecaborane(12)s have shown that the C1—C2 (C_c—C_c) distance in the cage can be modified by substituting the cluster C atoms (Sillanpää *et al.*, 1996). We have previously prepared mixed cobalt pyrrolyl/dicarbollide *closo* compounds (Bertran *et al.*, 1997; Gómez *et al.*, 1997; Lamrani *et al.*, 1996; Teixidor *et al.*, 1997). It seems that from a structural point of view the cobaltacarborane cluster in these compounds resembles normal *closo* architecture. In order to obtain more information on the C_c—C_c distances as a function of the C_c substituent in mixed cobalt pyrrolyl/dicarbollide *closo* compounds, the crystal structure of [3-Co{ η^5 -[2,5-(CH₃)₂-NC₄H₂]}-1-CH₃-1,2-C₂B₉H₁₀], (I), is now reported.



(I)

A perspective view of the title compound is shown in Fig. 1. The metal is sandwiched by pentagonal faces of the mono-anionic 2,5-dimethylpyrrolyl and dianionic dicarbollide ligands so that the conformation of the faces is staggered with the pyrrolyl N13 atom being placed between the cluster C atoms. Theoretical calculations show that this is the most stable conformation for [3-Co{ η^5 -(NC₄H₄)}-1,2-C₂B₉H₁₁],

even though the energy difference between different rotamers is low (Teixidor *et al.*, 2000).

Bond lengths in (I) from the five-membered rings to Co3 are normal, varying from 2.013 (2) to 2.079 (2) Å. The coordinated pentagonal faces are not exactly parallel as the dihedral angle between the planes through the faces is 6.9 (1)°. In (I), the C_c—C_c distance of 1.649 (3) Å agrees with the value of 1.640 (7) Å in [3-Co{ η^5 -(NC₄H₄)}-1,2-C₂B₉H₁₁] (Lamrani *et al.*, 1996), but is slightly shorter than the values in the C_c—C_c-disubstituted compounds [3-Co{ η^5 -(NC₄H₄)}-1-CH₃-2-*n*C₄H₉-1,2-C₂B₉H₉] [1.671 (7) Å], [3-Co{ η^5 -(NC₄H₄)}-1-C₆H₅-2-C₃H₅-1,2-C₂B₉H₉] [1.737 (4) Å] (Teixidor *et al.*, 1997) and [3-Co{ η^5 -(NC₄H₅)}-1-CH₃-2-(C₃H₆NC₄H₄)-1,2-C₂B₉H₉] [1.692 (7) Å; Gómez *et al.*, 1997].

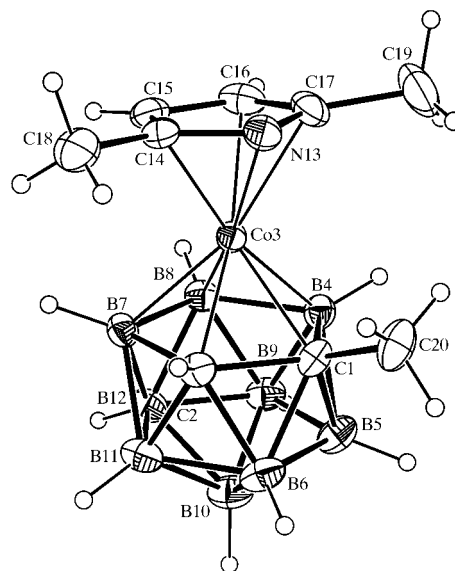


Figure 1

ORTEP-3 (Farrugia, 1997) plot of (I). Only the heavy atoms have been labelled. Displacement ellipsoids are drawn at the 30% probability level.

This observation is in line with the effect of reported C_c substituents on the lengthening of the C_c—C_c distance for *o*-carborane derivatives. In accordance with this, the effect of C_c monosubstitution on the lengthening of the C_c—C_c distance is smaller than that of disubstitution.

Experimental

Compound (I) was synthesized by two methods. Method A: 1-CH₃-1,2-C₂B₁₀H₁₁ (0.20 g, 1.20 mmol) was dissolved in a suspension of K[2,5-(CH₃)₂NC₄H₂] (1.90 g, 14.3 mmol) in tetrahydrofuran (THF) (100 ml). After 4 h of stirring under reflux, anhydrous CoCl₂ (0.79 g, 6.0 mmol) was added. The reaction mixture was refluxed for a further 48 h. After cooling, the solvent was evaporated *in vacuo*, and the resulting dark solid was treated with CH₂Cl₂ (80 ml). The suspension was filtered and the orange solution was concentrated to 1 ml. Chromatography of the crude orange solution using CH₂Cl₂/C₆H₁₄ (6:4) as the mobile phase provided a pure orange complex [*R*_F(prep) = 0.65] (yield 0.23 g, 61%). Method B: to a potassium (0.51 g, 13.0 mmol) suspension in deoxygenated and dry THF (100 ml), 2,5-dimethylpyrrole (1.30 ml, 13.0 mmol) was added. Then, [N(CH₃)₄][7-CH₃-7,8-C₂B₉H₁₁] (0.44 g, 1.98 mmol) was incorporated into the

mixture. After 4 h of stirring under reflux, anhydrous CoCl_2 (0.70 g, 5.30 mmol) was added. From this point, the work-up was as for method A (yield 0.35 g, 59%). IR (KBr, ν , cm^{-1}): 3120 (C—H), 3029 (C—H), 2598, 2538, 2524 (B—H). ^1H NMR: δ = 6.0 (s, $\text{C}_{\text{pyr}}\text{—H}$, 1H), 5.8 (s, $\text{C}_{\text{pyr}}\text{—H}$, 1H), 3.9 (*br s*, $\text{C}_c\text{—H}$, 1H), 3.5–1.0 (*br s*, B—H), 2.4 (s, $\text{C}_{\text{pyr}}\text{—CH}_3$, 6H), 2.3 (s, CH_3 , 3H). $^1\text{H}\{^{11}\text{B}\}$ NMR: δ = 6.0 (s, $\text{C}_{\text{pyr}}\text{—H}$, 1H), 5.8 (s, $\text{C}_{\text{pyr}}\text{—H}$, 1H), 3.9 (*br s*, $\text{C}_c\text{—H}$, 1H), 3.1 (*br s*, B—H, 4H), 1.8 (*br s*, B—H, 5H), 2.4 (s, $\text{C}_{\text{pyr}}\text{—CH}_3$, 6H), 2.3 (s, CH_3 , 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ = 124.7 (s, N— C_{pyr}), 124.2 (s, N— C_{pyr}), 89.6 (s, $\text{C}_{\text{pyr}}\text{—C}_{\text{pyr}}$), 87.6 (s, $\text{C}_{\text{pyr}}\text{—C}_{\text{pyr}}$), 74.9 (s, $\text{C}_c\text{—CH}_3$), 60.8 (s, $\text{C}_c\text{—H}$), 31.6 (s, $\text{C}_c\text{—CH}_3$), 13.6 ($\text{C}_{\text{pyr}}\text{—CH}_3$). ^{11}B NMR: δ = 6.2 (*d*, $^1J_{\text{B,H}} = 149$, 1B), 3.6 (*d*, $^1J_{\text{B,H}} = 147$, 1B), 0.2 (*d*, $^1J_{\text{B,H}} = 153$, 1B), -3.8 (*d*, $^1J_{\text{B,H}} = 138$, 2B), -4.3 (*d*, $^1J_{\text{B,H}} = 161$, 1B), -7.1 (*d*, $^1J_{\text{B,H}} = 148$, 1B), -11.8 (*d*, $^1J_{\text{B,H}} = 160$, 1B), -15.9 (*d*, $^1J_{\text{B,H}} = 159$, 1B). Analysis calculated for $\text{C}_9\text{H}_{21}\text{B}_9\text{CoN}$: C 36.09, H 7.07, N 4.68%; found: C 36.20, H 7.00, N 4.85%.

Crystal data

$[\text{Co}(\text{C}_3\text{H}_3\text{B}_9)(\text{C}_6\text{H}_8\text{N})]$
 $M_r = 299.49$
 Monoclinic, $P2_1/n$
 $a = 8.1630$ (11) Å
 $b = 16.3957$ (10) Å
 $c = 11.5686$ (14) Å
 $\beta = 98.622$ (11)°
 $V = 1530.8$ (3) Å³
 $Z = 4$

$D_x = 1.299$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 19.3\text{--}22.6^\circ$
 $\mu = 1.10$ mm⁻¹
 $T = 294$ (2) K
 Prism, pale yellow
 $0.36 \times 0.34 \times 0.28$ mm

Data collection

Rigaku AFC-5S diffractometer
 $\omega/2\theta$ scans
 2894 measured reflections
 2695 independent reflections
 2187 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.012$
 $\theta_{\text{max}} = 25.0^\circ$

$h = 0 \rightarrow 10$
 $k = 0 \rightarrow 20$
 $l = -14 \rightarrow 14$
 3 standard reflections
 every 150 reflections
 intensity decay: 0.8%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.077$
 $S = 1.06$
 2695 reflections
 211 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 0.4100P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.24$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³

H atoms on the C atoms were treated as riding, with C—H distances in the range 0.93–0.96 Å. H atoms on B atoms were refined with fixed isotropic displacement parameters, giving B—H distances in the range 1.04 (3)–1.12 (3) Å.

Table 1

Selected bond lengths (Å).

Co3—C2	2.013 (2)	Co3—C17	2.072 (2)
Co3—C15	2.037 (2)	Co3—B8	2.072 (3)
Co3—C1	2.039 (2)	Co3—B4	2.074 (3)
Co3—C16	2.042 (3)	Co3—N13	2.079 (2)
Co3—C14	2.056 (2)	C1—C2	1.649 (3)
Co3—B7	2.064 (3)		

Data collection: *MSC/AFC-5S Diffractometer Control Software* (Molecular Structure Corporation, 1995); cell refinement: *MSC/AFC-5S Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1152). Services for accessing these data are described at the back of the journal.

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