First observation of π-bonding in triple decker pyrrolyl complexes. Crystal structure of [(η^5-tetramethylpyrrolyl)Co]$_2$($C_2Et_2B_3H_3$)

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Abstract

The binuclear, triple decker sandwich compound $[(\eta^5\text{-}NC_4Me_4)Co]_2(C_2Et_2B_3H_3)$ has a $C_2Et_2B_3H_3$ ring at the center stabilizing a π-pyrrolyl–Co group on either side. The compound is the first π-bond triple decker pyrrolyl complex and the structure is the first of a π pyrrolyl–metal complex. Crystal data: monoclinic, space group $P2_1/c$, $Z=4$, $a=14.973(3)$; $b=9.029(2)$; $c=18.659(5)$ Å; $\beta=106.38(4)°$. $R=3.8\%$ for 1387 reflections.

Introduction

Five-membered rings are important and much-used ligands, with π-bonding being common with cyclopentadiene (cp) [1], while σ-bonding is preferred when hetero atoms like nitrogen are present. The powerful σ-bonding capacity of nitrogen donor atoms has been used to design ligands and complexes for particular properties [2]. Thus, σ-bridged polynucleation via ring nitrogens can put pairs of metals in magnetic and electrical contact and enable electron transfer, e.g. in metalloenzyme models [3]. Polynucleation via π-bonds [4, 5] further expands the range of electron transfer potential, and expands the range between σ-bridging (weakest) and direct metal–metal bonding (strongest). π-Bonding sandwich compounds involving C_4N ring complexes are rare [6]. This paper reports the first structural characterization of a π-bonded pyrrolyl complex [7].

nido-$R_2C_2B_4H_4^-$ (**1**) is an excellent π-bonding ligand, attaching to Co(cp) or Co(C_5Me_5) as shown in **2**; further examples using this ligand follow [1, 4, 8]. Removal of the apical BH provides another π-bonding site on the other side of the ring affording sandwich complexes, **3**. Wider π-bond separation is possible with two intervening $R_2C_2B_4H_4$ rings (**4**). The chemistry can be tailored for weaker electronic communication between metals using offset stacks such as **5**. This method was used by Chase and Grimes [7, 9] to produce the novel pyrollyl complex, the structure of which is reported here. The sample was provided by Chase and Grimes.

Results and discussion

Figure 1 shows the structure and the atomic coordinates and selected bond lengths and angles are shown in Tables 1 and 2, respectively. The structures clearly show that the powerful σ-bonding capacity of nitrogen ligands does not prevail to form a σ-N-bonded complex. Instead, a π-bonded sandwich compound is formed, in which the pyrrolyl ring behaves like η^5-C_5H_5 [10, 11] and η^5-C_5Me_5 [12], the resemblance being closer to the ring-substituted C_5R_5 type.

The assignment of η^5 coordination is based on the similarity of the Co–N distance (2.046 Å) and the average of the Co–C distance (2.063 Å). The slightly smaller shorter bond length for Co–N is as expected and reflects the smaller size of the nitrogen atom.

The complex has two π-pyrrolyl–Co groups, one on either side of a central $C_2Et_2B_3H_3$ ring which stabilizes the approach of the two metal atoms to form the triple decker sandwich. The three rings are highly planar, each atom being under 0.01 Å from the mean plane, and the pyrrolyl rings are slightly canted with respect to the central $Et_2C_2B_3H_3$ ring, with dihedral angles of

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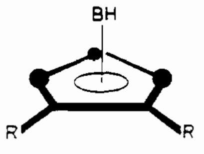

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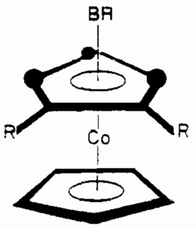

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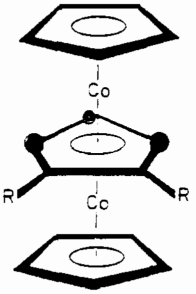

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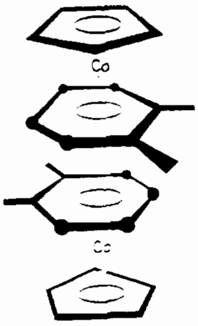

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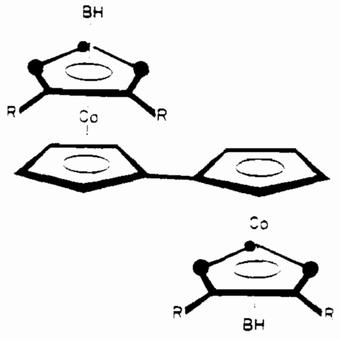

5

● = BH

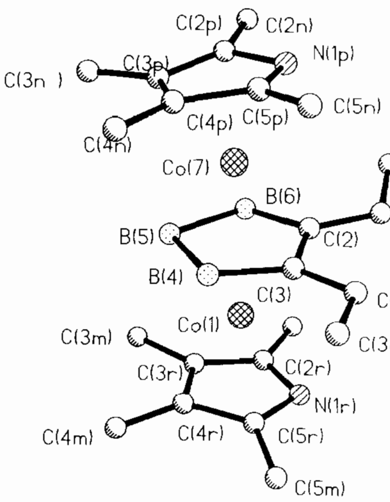

Fig. 1. Structure of $[(\eta^5\text{-pyrrolyl})\text{Co}]_2(\text{C}_2\text{Et}_2\text{B}_3\text{H}_3)$; H atoms omitted for clarity.

0.9 and 2.6°. The pyrrolyl nitrogens approximately eclipse the C_2Et_2 end of the central ring, thereby minimizing the interaction of the C-ethyls with the pyrrolyl methyl groups.

This is the first such structure characterized, and it establishes the molecule as a triple decker sandwich compound. Diagrams **1**–**5** give just a glimpse of the richness of polyhedral carbaborane chemistry, which is further diversified by heteroatom substitution in $C_5H_xR_{5-x}$. Some dramatic differences in properties result from the introduction of ring substituents on cp compounds. The further differences created by the introduction of heteroatoms are an important area for study.

Experimental

Crystal data and data collection

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U_{eq}[a]
Co(1)	8439(1)	791(3)	8214(1)	50(1)
Co(7)	6978(1)	784(3)	6632(1)	52(1)
N(1R)	8769(12)	1383(20)	9316(10)	67(7)
C(2R)	9396(14)	2066(24)	8966(11)	66(8)
C(3R)	9854(12)	913(31)	8675(9)	61(7)
C(4R)	9525(15)	−451(22)	8871(10)	59(7)
C(5R)	8856(16)	−118(24)	9279(10)	61(8)
C(2M)	9523(15)	3612(19)	9005(12)	84(10)
C(3M)	10591(12)	1172(22)	8280(9)	78(8)
C(4M)	9865(13)	−1982(22)	8715(11)	80(9)
C(5M)	8369(16)	−1241(24)	9608(9)	83(10)
N(1P)	5809(13)	1715(22)	5892(9)	73(7)
C(2P)	6571(15)	1863(30)	5618(10)	74(9)
C(3P)	6979(14)	439(22)	5549(10)	61(8)
C(4P)	6394(14)	−574(22)	5764(9)	58(7)
C(5P)	5684(15)	157(27)	5983(11)	61(8)
C(2N)	6865(17)	3410(23)	5452(11)	90(10)
C(3N)	7774(14)	245(25)	5240(11)	88(9)
C(4N)	6431(17)	−2232(22)	5713(11)	97(11)
C(5N)	4866(13)	−408(29)	6193(10)	88(10)
B(4)	7585(14)	−653(28)	7491(10)	54(7)
B(5)	8361(16)	335(22)	7123(11)	55(9)
B(6)	8069(18)	2116(25)	7269(11)	58(8)
C(2)	7241(14)	1975(18)	7636(9)	46(6)
C(3)	7034(12)	471(21)	7756(9)	50(7)
C(2Q)	6777(14)	3215(19)	7845(10)	68(8)
C(2E)	6912(22)	4642(28)	7574(19)	165(21)
C(3Q)	6259(13)	171(24)	8116(10)	70(8)
C(3E)	5963(16)	−1419(25)	8195(12)	96(10)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

$C_{22}H_{31}B_3Co_2N_2$, $M = 474$. The prismatic red crystal chosen for data collection had dimensions $0.32 \times 0.23 \times 0.18$ mm. Cell dimensions and space group data were obtained by rotation photographs and scans on a Siemens R3m/V four-circle diffractometer [13]. Monoclinic, space group $P2_1/c$, $Z = 4$, $a = 14.973(3)$, $b = 9.029(2)$, $c = 18.659(5)$ Å, $\beta = 106.38(4)°$, $V = 2420(2)$ Å^3, $D_c = 1.30$ g cm^{-3}, $\mu(\text{Mo K}\alpha) = 1.38$ cm^{-1}, F(000) =

TABLE 2. Selected bond lengths (Å) and Angles (°) with e.s.d.s. in parentheses

Co(1)–N(1R)	2.046(17)	Co(7)–B(6)	2.106(22)
Co(1)–C(2R)	2.053(19)	N(1R)–C(2R)	1.427(30)
Co(1)–C(3R)	2.053(17)	N(1R)–C(5R)	1.366(29)
Co(1)–C(4R)	2.069(19)	C(2R)–C(3R)	1.434(33)
Co(1)–C(5R)	2.076(19)	C(3R)–C(4R)	1.412(33)
Co(1)–C(2)	2.105(17)	C(4R)–C(5R)	1.449(34)
Co(1)–C(3)	2.056(16)	N(1P)–C(2P)	1.382(32)
Co(1)–B(4)	2.046(21)	N(1P)–C(5P)	1.435(32)
Co(1)–B(5)	2.047(21)	C(2P)–C(3P)	1.445(33)
Co(1)–B(6)	2.073(21)	C(3P)–C(4P)	1.400(30)
Co(7)–N(1P)	2.076(17)	C(4P)–C(5P)	1.406(33)
Co(7)–C(2P)	2.061(20)	C(2)–C(3)	1.425(25)
Co(7)–C(3P)	2.044(19)	C(2)–B(6)	1.581(35)
Co(7)–C(4P)	2.023(18)	C(3)–B(4)	1.478(30)
Co(7)–C(5P)	2.053(20)	B(4)–B(5)	1.751(34)
Co(7)–C(2)	2.099(17)	B(5)–B(6)	1.709(31
Co(7)–C(3)	2.094(17)	B(4)–H(4)	1.25(8)
Co(7)–B(4)	2.063(20)	B(5)–H(5)	1.37(8)
Co(7)–B(5)	2.055(22)	B(6)–H(6)	1.25(8)
Co(1)–C(2)–Co(7)	96.6(8)	C(2R)–N(1R)–C(5R)	108.6(19)
Co(1)–C(3)–Co(7)	98.3(8)	N(1R)–C(2R)–C(3R)	107.9(19)
Co(1)–B(4)–Co(7)	99.7(11)	C(2R)–C(3R)–C(4R)	107.2(18)
Co(1)–B(5)–Co(7)	99.9(11)	C(3R)–C(4R)–C(5R)	107.4(18)
Co(1)–B(6)–Co(7)	97.4(10)	N(1R)–C(5R)–C(4R)	108.9(19)
C(3)–C(2)–B(6)	112.1(16)	C(2p)–N(1P)–C(5P)	106.7(20)
C(2)–C(3)–B(4)	115.8(18)	N(1P)–C(2P)–C(3P)	111.2(21)
C(3)–B(4)–B(5)	106.0(17)	C(2P)–C(3P)–C(4P)	104.0(19)
B(4)–B(5)–C(6)	100.9(18)	C(3P)–C(4P)–C(5P)	111.2(19)
C(2)–B(6)–B(5)	105.1(17)	N(1P)–C(5P)–C(4P)	106.9(20)

984, $T = 292$ K. θ–2θ scans were used to record the intensities for all non-equivalent reflections for which $3.5 < 2\theta < 55°$.

The intensities of three standard reflections showed no greater fluctuations than expected form Poisson statistics. The data were corrected for Lorentz–polarization effects and empirically (DIFABS) for absorption. Of the 4730 independent intensities, there were 1387 with $F_o^2 \geqslant 2.8\sigma(F_o^2)$, $\sigma(F_o^2)$ being estimated from counting statistics [14].

Structure determination and refinement

The structure was solved by Patterson and Fourier methods, followed by full-matrix least-squares refinement (SHELXTL PLUS) [13, 15]. When anisotropic temperature factors were introduced, further Fourier difference syntheses permitted location of the hydrogen atoms attached to boron and these were included in the refinement. Other hydrogen atoms were included at their calculated positions with C–H bonds of 0.96 Å. The model converged with $R = 3.8\%$ and $R_w = 4.9\%$. Final Fourier difference functions showed no peaks higher than 0.30 e/Å^3.

Acknowledgements

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