Synthesis and Characterization of Novel Metallocarborane Triple-decker Complexes†

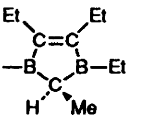
Jennifer M. Forward,[a] **D. Michael P. Mingos,***[,b] **Walter Siebert,**[c] **Jan Hauss**[c] **and Harold R. Powell**[d]
[a] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK*
[b] *Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK*
[c] *Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-6900 Heidelberg, Germany*
[d] *Protein Engineering Department, AFRC Institute of Food Research, Earley Gate, Whiteknights Road, Reading RG6 2EF, UK*

The syntheses of two novel triple-decker complexes are described where the $[C_2B_9H_{11}]^{2-}$ dianion is utilized for the first time as a terminal ligand. The sandwich anion $[Co(C_5H_5)(C_3B_2MeEt_4)]^-$ ($C_3B_2MeEt_4$ = 1,3,4,5-tetraethyl-1*H*-2,3-dihydro-2-methyl-1,3-diborol-2-yl) reacts with the $[C_2B_9H_{11}]^{2-}$ dianion and bis(pentane-2,4-dionato)nickel(II) to give the symmetrical tetradecker complex $[Ni\{(C_3B_2MeEt_4)Co(C_5H_5)\}_2]$ and the two unsymmetrical triple-decker complexes $[(C_5H_5)Co(C_3B_2MeEt_4)Ni(C_2B_9H_{11})]$ and $[(C_5H_5)Co(C_3B_2MeEt_4)Co(C_2B_9H_{11})]$. The molecular structures of the three complexes were established from elemental analyses and ^1H and ^{11}B-$\{^1H\}$ NMR and mass spectroscopic studies. In addition, the single-crystal X-ray analyses of the unsymmetrical ones were performed. Both complexes crystallize in the orthorhombic space group $P2_12_12_1$ (no. 19) with cell dimensions: for CoNi, a = 10.077(4), b = 13.880(1), c = 18.318(2); for CoCo, a = 9.973(3), b = 13.885(3), c = 18.280(5) Å. The CoCo triple-decker was also synthesised in higher yield from the reaction of the $[Co(C_5H_5)(C_3B_2MeEt_4)]^-$ anion with the $[C_2B_9H_{11}]^{2-}$ dianion and cobalt(II) chloride. The redox properties of the triple-decker complexes were studied by cyclic voltammetry.

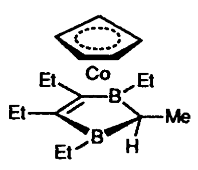
In 1972 Werner and Salzer[1] identified the first triple-decker complex, $[(C_5H_5)Ni(C_5H_5)Ni(C_5H_5)]^+$, in which both nickel atoms are sandwiched between two cyclopentadienyl rings. Complexes with benzene as the bridging ligand have also been characterized, the first being the divanadium complex $[(C_5H_5)V(C_6H_6)V(C_5H_5)]$, synthesized by Jonas and co-workers[2] in 1983. It was found that the presence of boron in the central ring of the triple-decker complexes helped to stabilize these structure and this discovery led to the synthesis of a whole series of complexes based on this principle. The first neutral triple-decker complex, $[(C_5H_5)Co(C_2B_3H_5)Co(C_5H_5)]$, was characterized by Grimes and co-workers[3] in 1973. In addition a wide range of tetra-, penta- and hexa-decker complexes have been synthesised subsequently.[4] This paper describes the synthesis of the first series of triple-decker complexes based on the carborane dianion $[C_2B_9H_{11}]^{2-}$.

Results and Discussion

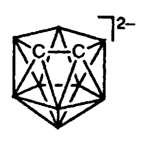
Reaction of 1,3,4,5-tetraethyl-1*H*-2,3-dihydro-2-methyl-1,3-diborole ligand, $C_3B_2HMeEt_4$, with η-cyclopentadienylbis(ethene)cobalt leads to the formation of the sandwich complex **1**.[4] This complex was deprotonated with *n*-butyllithium in tetrahydrofuran (thf) at −78 °C forming the anion $[Co(C_5H_5)(C_3B_2MeEt_4)]^-$ **2**. This anion was added to a thf solution of the carborane dianion $[7,8\text{-}C_2B_9H_{11}]^{2-}$, also at −78 °C. The carborane dianion was formed *in situ* by deprotonation of $K[7,8\text{-}C_2B_9H_{12}]$ using LiBu^n. To this mixture of the two anions 1 equivalent of bis(pentane-2,4-dionato)nickel(II) was added. Separation on Al_2O_3 gave compounds **3**–**5**.



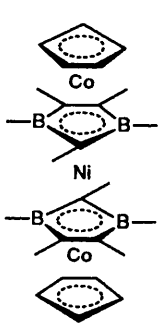
$C_3B_2HMeEt_4$



1



$[7,8\text{-}C_2B_9H_{11}]^{2-}$



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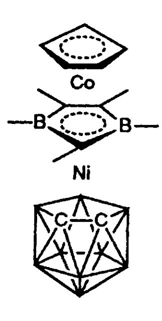

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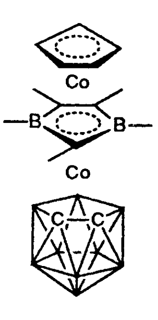

5

The dark green product $[Ni\{(C_3B_2MeEt_4)Co(C_5H_5)\}_2]$ **3** (yield = 15%) was recrystallized from a concentrated methanol solution at −20 °C. Confirmation of this stoichiometry was obtained from the mass spectrum which showed the $[M]^+$ parent ion peak at m/z 685. A computer simulation of the expected mass spectra for the tetradecker parent-ion peak, $[M]^+$, showed the same isotope distribution pattern as observed in the experimental data. The ^1H NMR spectrum of **3** contained a number of broad peaks in the range δ 27 to −38

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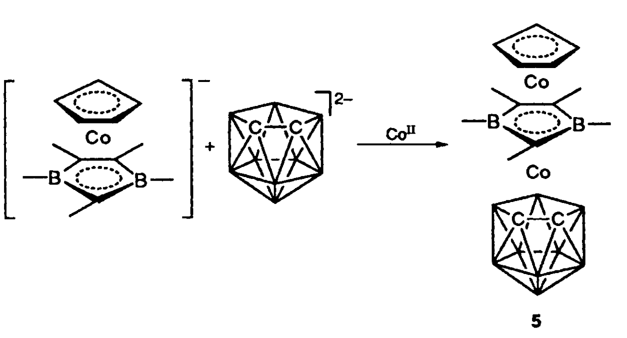
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

implying that the compound was paramagnetic. The complex has 44 valence electrons, two of which are unpaired in low-lying antibonding orbitals according to theoretical calculations.[5] Siebert and co-workers[6,7] first synthesised this complex in 1982 from the reaction of 2 equivalents of the $[Co(C_5H_5)(C_3B_2MeEt_4)]^-$ anion with $[\{Ni(C_5H_5)(CO)\}_2]$. The crystal structure of the analogous tetradecker complex with the 4,5-diethyl-1,3-dimethyl-1,3-diborolyl ligand has been solved and shows that, as expected, the 1,3-diborolyl rings are antiperiplanar.[6]

The purple product analysed correctly for the triple-decker complex $[(C_5H_5)Co(C_3B_2MeEt_4)Ni(C_2B_9H_{11})]$ **4** (yield = 35%) and was recrystallized from a concentrated methanol solution at −20 °C. The mass spectrum confirmed this formulation showing the $[M]^+$ parent ion peak at *m/z* 505 and a peak at *m/z* 371 assigned to the $[M - C_2B_9H_{11}]^+$ ion. The isotope peak distribution was simulated along with the peak distributions for two related triple-decker complexes $[(C_5H_5)Ni(C_3B_2MeEt_4)Ni(C_2B_9H_{11})]$ and $[(C_5H_5)Co(C_3B_2MeEt_4)Co(C_2B_9H_{11})]$ which have the same relative molecular mass. All three show the same basic pattern of peaks but the peak heights are sufficiently different to allow the complexes to be distinguished. The peak intensities of the experimental data matched the simulated pattern for the triple-decker complex $[(C_6H_5)Co(C_3B_2MeEt_4)Ni(C_2B_9H_{11})]$. The infrared spectrum showed a strong broad peak at 2530 cm^{-1} assigned to the B–H stretching mode of the carborane ligand. The ^1H NMR spectrum has a number of broad peaks that could not be assigned to individual proton resonances in the range δ 14 to −2. This implies that the compound is paramagnetic as would be expected for 31-electron complex.

The olive-green product **5** was recrystallized from a concentrated methanol solution at −20 °C (yield = 8%) and gave similar C and H analyses to those obtained for the purple triple-decker complex **4**. The FAB mass spectrum also showed the same two main peaks: a $[M]^+$ parent-ion peak at *m/z* 504 and a peak assigned to $[M - C_2B_9H_{11}]^+$ at *m/z* 372. The infrared spectrum had the same strong peak due to the B–H stretching mode of the carborane ligand, at 2525 cm^{-1}. However, the peak widths in the ^1H and ^{11}B-$\{^1H\}$ NMR spectra indicated that the compound is diamagnetic in contrast to **4**. The details of the NMR spectra are discussed below. The experimental data are consistent with the triple-decker complex $[(C_5H_5)Co(C_3B_2MeEt_4)Co(C_2B_9H_{11})]$ **5**. The atomic weights of cobalt and nickel are almost identical, 58.9 and 58.7 respectively, which explains the similarity in the mass spectra and the analyses obtained. Complex **5** has 30 valence electrons and therefore has the stable closed-shell configuration with its highest occupied molecular orbital being the fully occupied bonding orbital a_2'' as predicted by extended-Hückel calculations, which explains the diamagnetic ^1H and ^{11}B-$\{^1H\}$ NMR spectra obtained.[5] Unambiguous confirmation of the correct formulation of the two complexes was obtained from metal analyses performed on single crystals using X-ray fluorescence techniques.[8] Analysis of the purple single crystals of **4** confirmed the presence of both nickel and cobalt in an approximate 1 : 1 ratio, while analysis of the olive-green single crystals of **5** showed cobalt to be the only metal present.

The formation of the CoNi triple-decker complex **4** and the CoNiCo tetradecker complex **3** is expected from the combination of the reagents used. However, formation of the CoCo triple-decker complex **5** implies that degradation of the $[Co(C_5H_5)(C_3B_2MeEt_4)]^-$ anion has taken place. One possible explanation is oxidation of the latter on exposure of the reaction mixture to small amounts of oxygen. The neutral radical formed will quickly degrade to the free ligand and a $(C_5H_5)Co$ fragment so allowing the formation of the $[(C_5H_5)Co(C_3B_2MeEt_4)Co(C_2B_9H_{11})]$ triple-decker complex. The CoCo triple-decker was synthesised in higher yield from the reaction of $[Co(C_5H_5)(C_3B_2MeEt_4)]^-$ with $[7,8\text{-}C_2B_9H_{11}]^{2-}$ and Co^{II} (Scheme 1).



Scheme 1

Anhydrous cobalt(II) chloride was added to a mixture of the two anions $[Co(C_5H_5)(C_3B_2MeEt_4)]^-$ and $[7,8\text{-}C_2B_9H_{11}]^{2-}$ in thf at −78 °C. The air-sensitive anion $[Co(C_5H_5)(C_3B_2MeEt_4)]^-$ was formed by deprotonation of the sandwich complex **1** with $LiBu^n$; the dianion $[7,8\text{-}C_2B_9H_{11}]^{2-}$ was also formed *in situ* by deprotonation of $K[7,8\text{-}C_2B_9H_{12}]$ with $LiBu^n$. After warming to room temperature, the crude reaction product was chromatographed on Al_2O_3 plates as before using benzene–hexane (1 : 1) as eluent, but only one product was isolated. This olive-green crystalline compound analysed correctly for the triple-decker complex $[(C_5H_5)Co(C_3B_2MeEt_4)Co(C_2B_9H_{11})]$, formed as a side-product in the reaction described above. The ^1H and ^{11}B-$\{^1H\}$ NMR spectra also confirmed this. The relative stability of this complex may explain why the formation of the paramagnetic 43-electron tetradecker $[Co\{(C_3B_2MeEt_4)Co(C_5H_5)\}_2]$ is not observed.

The novel triple-decker complexes containing the $[C_2B_9H_{11}]^{2-}$ dianion as a terminal ligand have some different and interesting properties compared to previously characterized triple-decker complexes containing the C_5H_5 ligand. For example, the $[C_2B_9H_{11}]^{2-}$ dianion has the ability to stabilize the metal in a high oxidation state.[9] For the triple-decker complex **4**, if the $(C_5H_5)Co(C_3B_2MeEt_4)^-$ unit is considered as a monoanion and the $C_2B_9H_{11}{}^{2-}$ unit as a dianion the nickel is in a formal +3 oxidation state. As the initial reaction involved the two anions and Ni^{II} this implies that although the anion $[(C_5H_5)Co(C_3B_2MeEt_4)Ni(C_2B_9H_{11})]^-$ may have been formed initially, it was rapidly oxidized to the more stable neutral triple-decker complex containing Ni^{III}. For the triple-decker complex **5** the cobalt is also in a +3 oxidation state. This can be compared with the formation of the analogous complexes $[(C_5H_5)Co(C_3B_2MeEt_4)M(C_5H_5)]$ (M = Ni, Co or Fe), where reaction of $[Co(C_5H_5)(C_3B_2MeEt_4)]^-$ with $(C_5H_5)M^{II}$ fragments forms stable triple-decker complexes with the metal in the +2 oxidation state.[4] In addition, the reaction of 2 equivalents of $[Co(C_5H_5)(C_3B_2MeEt_4)]^-$ with a series of M^{2+} ions forms the tetradecker sandwich compounds $[M\{C_3B_2MeEt_4)Co(C_5H_5)\}_2]$ (M = Cr, Mn, Fe, Co, Ni, Cu or Zn) where M is also in a +2 oxidation state. Thus, the introduction of the $[C_2B_9H_{11}]^{2-}$ ligand has enabled the formation of air-stable triple-decker complexes where the metal is in the higher +3 oxidation state.

Proton and ^{11}B-$\{^1H\}$ *NMR Studies of Complex* **5**.—In the ^1H spectrum (in $CDCl_3$) the singlets at δ 5.01 (intensity 5) and 2.13(3) are assigned to the C_5H_5 and ring methyl groups respectively. The two triplets at δ 1.46(6) and 1.62(6) are assigned to the methyl protons of the CEt group and the BEt respectively. The two methylene protons of the CEt group are diastereotopic and constitute an ABX_3 spin system in which each proton might be expected to appear as a doublet of quartets, but as these are overlapping not all of the peaks are resolved. The multiplets at δ 3.10(2) and 2.41(2) are each assigned to one of these methylene protons. This assignment was confirmed by irradiation of the methyl protons of the CEt group at δ 1.46 which caused each of the multiplets to collapse towards a singlet. The two methylene protons of the BEt group are also non-equivalent, but appear as a complex multiplet in the spectrum at δ 2.10(4). As expected, irradiation of the methyl

Table 1 Selected crystal data of the triple-decker sandwiches **4** and **5**

Compound	**4**	**5**
Formula	$C_{19}H_{39}B_{11}CoNi$	$C_{19}H_{39}B_{11}Co$
M	504.06	504.08
Crystal dimensions/mm	1.0 × 0.22 × 0.22	1.14 × 0.66 × 0.15
a/Å	10.077(4)	9.973(3)
b/Å	13.880(1)	13.885(3)
c/Å	18.318(2)	18.280(5)
U/Å^3	2562.2	2531.3
D_c/g cm^{-3}	1.306	1.323
Radiation (λ/Å)	Cu-Kα (1.5401)	Mo-Kα (0.710 73)
θ_{max}/°	74.0	24.0
μ/cm^{-1}	62.34	13.15
F(000)	1052	1048
Total data collected	4370	2969
Total observed data ($I > 3\sigma$)	1001	2250
Minimum, maximum absorption correction	2.65, 4.73	1.16, 1.41
Weights	20.2, −11.5, 14.6	8.84, −0.36, 5.73
R	0.0551	0.0313
R′	0.0637	0.0340

Details in common; orthorhombic, space group $P2_12_12_1$, $Z = 4$.

Table 2 Fractional coordinates for complex **4**

Atom	*X/a*	*Y/b*	*Z/c*
Co(1)	−0.2930(2)	−0.1051(2)	0.1680(1)
Ni(303)	−0.0365(2)	−0.0055(2)	0.0853(1)
C(212)	−0.332(3)	0.174(2)	0.221(2)
C(11)	−0.413(2)	−0.229(1)	0.172(1)
C(12)	−0.365(2)	−0.204(1)	0.245(1)
C(13)	−0.411(2)	−0.111(2)	0.261(1)
C(14)	−0.483(2)	−0.074(1)	0.203(1)
C(15)	−0.486(2)	−0.145(1)	0.148(1)
C(22)	−0.250(1)	−0.005(1)	0.0892(8)
C(24)	−0.104(1)	−0.1361(9)	0.1321(7)
C(25)	−0.099(1)	−0.060(1)	0.1867(7)
C(211)	−0.199(2)	0.125(1)	0.2080(9)
C(221)	−0.347(2)	0.054(1)	0.0419(8)
C(231)	−0.227(2)	−0.175(1)	−0.004(1)
C(232)	−0.223(2)	−0.139(2)	−0.077(1)
C(241)	−0.018(2)	−0.225(1)	0.1357(8)
C(242)	−0.092(2)	−0.319(1)	0.146(1)
C(251)	−0.011(2)	−0.058(1)	0.2553(9)
C(252)	−0.068(2)	−0.099(2)	0.320(1)
C(301)	0.003(2)	0.050(1)	−0.0183(8)
C(302)	0.010(1)	0.131(1)	0.0431(8)
B(21)	−0.191(2)	0.030(1)	0.1621(9)
B(23)	−0.194(2)	−0.106(1)	0.0648(8)
B(304)	0.101(2)	−0.049(1)	0.004(1)
B(305)	0.155(2)	0.039(1)	−0.059(1)
B(306)	0.093(2)	0.152(2)	−0.038(1)
B(307)	0.107(2)	0.097(1)	0.114(1)
B(308)	0.176(2)	−0.014(1)	0.0903(9)
B(309)	0.267(2)	0.001(2)	0.0087(9)
B(310)	0.255(2)	0.125(2)	−0.018(1)
B(311)	0.153(2)	0.183(1)	0.049(1)
B(312)	0.269(2)	0.094(1)	0.076(1)

protons of the BEt group at δ 1.62 caused the multiplet at δ 2.10 to collapse towards a singlet. The protons in the $[C_2B_9H_{11}]^{2-}$ cage are fluxional and are often not observed in the ^1H NMR spectrum except as an extremely broad spread of peaks between δ 0 and 4. No peaks were observed in the ^1H NMR spectrum of **5** that could be assigned to the cage protons.

In the ^{11}B-{^1H} NMR spectrum (in $CDCl_3$) the peak at δ 17.0 is assigned to the two boron atoms of the C_3B_2 ring. The remaining six peaks at δ 6.3, −0.7, −5.7, −7.2, −18.7 and −23.7 of approximate relative intensities of 1:1:2:2:2:1 are assigned to the boron atoms in the $[C_2B_9H_{11}]^{2-}$ cage. When the ^{11}B NMR spectrum is run with no proton decoupling all of the six peaks, with the exception of that at δ −7.18, appear as doublets. The doublet at δ −7.18 is not resolved. These doublets arise from coupling of the boron to the terminal hydrogen atoms, J_{BH} = 138–156 Hz.

Table 3 Fractional coordinates for complex **5**

Atom	*X/a*	*Y/b*	*Z/c*
Co(1)	−0.287 87(6)	−0.101 36(5)	0.166 15(4)
Co(303)	−0.037 21(5)	−0.003 18(4)	0.084 64(3)
C(11)	−0.406 2(6)	−0.223 1(5)	0.169 9(4)
C(12)	−0.358 7(6)	−0.201 0(5)	0.240 4(4)
C(13)	−0.405 9(7)	−0.107 9(7)	0.258 6(4)
C(14)	−0.478 4(6)	−0.071 7(7)	0.198 3(5)
C(15)	−0.479 6(7)	−0.142 9(7)	0.145 7(4)
C(22)	−0.245 8(4)	−0.001 5(4)	0.087 1(3)
C(24)	−0.095 4(4)	−0.132 2(3)	0.130 0(3)
C(25)	−0.092 6(4)	−0.056 1(3)	0.185 2(2)
C(211)	−0.200 5(8)	0.129 9(5)	0.207 4(4)
C(212)	−0.331(1)	0.175(1)	0.217 8(6)
C(221)	−0.342 6(5)	0.056 6(5)	0.041 9(4)
C(231)	−0.228 8(9)	−0.169 8(5)	−0.003 4(4)
C(232)	−0.214(1)	−0.138 6(7)	−0.079 3(4)
C(241)	−0.013 2(6)	−0.223 0(3)	0.134 0(3)
C(242)	−0.087 3(7)	−0.315 3(4)	0.145 8(4)
C(251)	−0.006 1(6)	−0.057 6(4)	0.252 8(3)
C(252)	−0.063 6(8)	−0.100 3(7)	0.319 5(3)
C(301)	0.000 5(5)	0.046 1(4)	−0.017 0(3)
C(302)	0.005 7(5)	0.129 8(3)	0.046 2(3)
B(21)	−0.186 9(5)	0.031 7(4)	0.161 8(3)
B(23)	−0.192 7(5)	−0.104 1(4)	0.063 2(3)
B(304)	0.102 1(5)	−0.049 4(4)	0.005 7(3)
B(305)	0.153 4(7)	0.039 1(5)	−0.059 7(4)
B(306)	0.087 4(7)	0.151 7(5)	−0.034 7(4)
B(307)	0.105 8(5)	0.097 1(4)	0.115 8(3)
B(308)	0.174 9(5)	−0.016 4(4)	0.091 8(3)
B(309)	0.265 8(5)	0.000 3(6)	0.009 9(3)
B(310)	0.256 2(6)	0.124 8(5)	−0.016 2(4)
B(311)	0.158 3(7)	0.183 8(4)	0.050 3(4)
B(312)	0.268 3(6)	0.090 9(5)	0.077 9(4)

X-Ray Analysis.—Crystal data and details of the structure determinations of complexes **4** and **5** are given in Table 1 and their fractional coordinates in Tables 2 and 3. In Fig. 1 the triple-decker sandwich structure of the CoCo compound **5** is illustrated, and the important interatomic distances for **4** and **5** are summarized in Table 4. The two isomorphous structures consist of discrete triple-decker molecules, in which both metal atoms are η^5 bound to the central 1,3-diborolyl ligand. The two five-membered rings, C_5H_5 and $C_3B_2MeEt_4$, are both planar within ±0.01 Å, parallel and lie antiperiplanar to one another as has been observed in previously characterized triple- and tetra-decker complexes containing the 1,3-diborolyl ligand. The $[C_2B_9H_{11}]^{2-}$ ligand is co-ordinated to the metal (Ni, Co) *via* a five-membered bonding face, C_2B_3, forming a twelve-vertex metallacarborane unit $M(C_2B_9H_{11})$. The bonding face is planar where the deviations from planarity are ±0.02 Å in $[(C_5H_5)Co(C_3B_2MeEt_4)Co(C_2B_9H_{11})]$ and ±0.04 Å in $[(C_5H_5)Co(C_3B_2MeEt_4)Ni(C_2B_9H_{11})]$. Both of the crystal structures show typical values for C–C (1.38–1.43 Å), C–B (1.57–1.75 Å) and B–B bonds (1.72–1.87 Å). The interesting variations are observed in the metal-to-ligand distances as shown in Table 5.

The metal–ring distances, d_1 and d_2, in the (C_5H_5)Co(diborolyl) unit are similar for all three complexes. This is a feature that has been observed in all of the previously characterized triple-, tetra- and penta-decker complexes where the metal–ring distances in this unit remain approximately the same regardless of the metal to which it is co-ordinated. However, a large variation in d_3 and d_4 is observed for all these complexes where d_3 is the distance between the metal M and the

Table 4 Selected bond lengths (Å) and angles (°)

(*a*) $[(C_5H_5)Co(C_3B_2MeEt_4)Ni(C_2B_9H_{11})]$ **4**

Co(1)–C(11)	2.10(2)	Ni(303)–B(307)	2.09(2)
Co(1)–C(12)	2.10(2)	Ni(303)–B(308)	2.15(2)
Co(1)–C(13)	2.08(2)	C(11)–C(12)	1.46(3)
Co(1)–C(14)	2.06(2)	C(12)–C(13)	1.41(2)
Co(1)–C(15)	2.06(2)	C(13)–C(14)	1.39(2)
Co(1)–B(21)	2.14(2)	C(14)–C(15)	1.40(2)
Co(1)–C(22)	2.05(2)	C(15)–C(11)	1.44(2)
Co(1)–B(23)	2.13(2)	B(21)–C(22)	1.54(2)
Co(1)–C(24)	2.06(1)	C(22)–B(23)	1.57(2)
Co(1)–C(25)	2.08(1)	B(23)–C(24)	1.59(2)
Ni(303)–B(21)	2.15(2)	C(24)–C(25)	1.46(2)
Ni(303)–C(22)	2.16(1)	C(25)–B(21)	1.62(2)
Ni(303)–B(23)	2.15(2)	C(301)–C(302)	1.59(2)
Ni(303)–C(24)	2.12(1)	C(302)–B(307)	1.69(2)
Ni(303)–C(25)	2.10(1)	B(307)–B(308)	1.75(3)
Ni(303)–C(301)	2.09(2)	B(308)–B(304)	1.82(2)
Ni(303)–C(302)	2.10(1)	B(304)–C(301)	1.74(2)
Ni(303)–B(304)	2.12(2)		
C(15)–C(11)–C(12)	104.9(17)	B(23)–C(24)–C(25)	111.0(11)
C(11)–C(12)–C(13)	107.7(18)	C(24)–C(25)–B(21)	110.3(10)
C(12)–C(13)–C(14)	109.7(20)	B(304)–C(301)–C(302)	111.5(11)
C(13)–C(14)–C(15)	107.9(18)	C(301)–C(302)–B(307)	111.7(12)
C(14)–C(15)–C(11)	109.8(16)	C(302)–B(307)–B(308)	106.7(12)
C(25)–B(21)–C(22)	103.2(11)	B(307)–B(308)–B(304)	106.4(12)
B(21)–C(22)–B(23)	112.6(12)	B(308)–B(304)–C(301)	103.4(12)
C(22)–B(23)–C(24)	102.8(11)		

(*b*) $[(C_5H_5)Co(C_3B_2MeEt_4)Co(C_2B_9H_{11})]$ **5**

Co(1)–C(11)	2.062(6)	Co(303)–B(307)	2.073(5)
Co(1)–C(12)	2.064(6)	Co(303)–B(308)	2.127(5)
Co(1)–C(13)	2.062(6)	C(11)–C(12)	1.41(1)
Co(1)–C(14)	2.031(6)	C(12)–C(13)	1.42(1)
Co(1)–C(15)	2.046(5)	C(13)–C(14)	1.41(1)
Co(1)–B(21)	2.106(5)	C(14)–C(15)	1.38(1)
Co(1)–C(22)	2.046(5)	C(15)–C(11)	1.41(1)
Co(1)–B(23)	2.107(5)	B(21)–C(22)	1.556(8)
Co(1)–C(24)	2.075(4)	C(22)–B(23)	1.581(8)
Co(1)–C(25)	2.076(4)	B(23)–C(24)	1.608(7)
Co(303)–B(21)	2.110(5)	C(24)–C(25)	1.461(6)
Co(303)–C(22)	2.081(4)	C(25)–B(21)	1.598(7)
Co(303)–B(23)	2.126(5)	C(301)–C(302)	1.679(8)
Co(303)–C(24)	2.057(4)	C(302)–B(307)	1.639(7)
Co(303)–C(25)	2.056(4)	B(307)–B(308)	1.775(7)
Co(303)–C(301)	2.016(5)	B(308)–B(304)	1.793(8)
Co(303)–C(302)	2.021(4)	B(304)–C(301)	1.720(7)
Co(303)–B(304)	2.103(5)		
C(15)–C(11)–C(12)	107.0(7)	B(23)–C(24)–C(25)	111.1(4)
C(11)–C(12)–C(13)	107.6(7)	C(24)–C(25)–B(21)	110.8(4)
C(12)–C(13)–C(14)	108.1(8)	B(304)–C(301)–C(302)	111.0(4)
C(13)–C(14)–C(15)	107.1(7)	C(301)–C(302)–B(307)	111.2(4)
C(14)–C(15)–C(11)	110.1(7)	C(302)–B(307)–B(308)	106.5(4)
C(25)–B(21)–C(22)	103.4(4)	B(307)–B(308)–B(304)	106.7(4)
B(21)–C(22)–B(23)	112.5(4)	B(308)–B(304)–C(301)	104.7(4)
C(22)–B(23)–C(24)	102.2(15)		

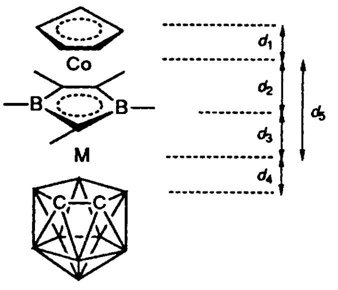


Table 5 Metal–ligand distances in triple-decker complexes

Distance (Å)	M = Ni **4**	M = Co **5**
d_1	1.69	1.67
d_2	1.62	1.60
d_3	1.67	1.61
d_4	1.52	1.46
d_5	3.29	3.21

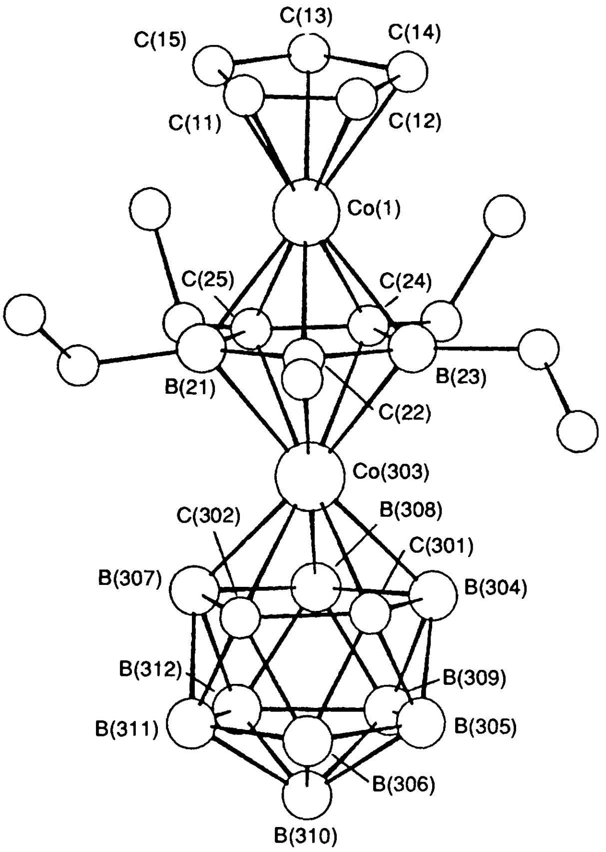


Fig. 1 Molecular structure of $[(C_5H_5)Co(C_3B_2MeEt_4)Co(C_2B_9H_{11})]$. The hydrogen atoms have been omitted for clarity

C_3B_2 ring and d_4 is the distance between the metal M and the $C_2B_9H_{11}$ ligand. Both d_3 and d_4 increase in going from **5** to **4**. This trend can be explained by looking at the formal oxidation state of the metal M and its number of d electrons. For the triple-decker complexes $[(C_5H_5)Co(C_3B_2MeEt_4)M(C_2B_9H_{11})]$ (M = Co or Ni) the cobalt and the nickel are in a formal +3 oxidation state with six and seven d electrons respectively. As mentioned above, complex **5** with 30 valence electrons has as its HOMO the fully occupied a_2'' orbital. For the 31-valence electron complex **4** the extra d electron goes into the antibonding e_1' orbital set. This weakens the bonding and causes lengthening of the metal–ring distances and the distance between the two metals (d_5).

The effect of the co-ordination of the $[C_2B_9H_{11}]^{2-}$ ligand is seen clearly in the distances d_3 and d_4. For both of the triple-decker complexes, $[(C_5H_5)Co(C_2B_2MeEt_4)M(C_2B_9H_{11})]$ (M = Co or Ni), containing this ligand, d_4 is significantly shorter than d_3. This reflects the larger opening of the C_2B_3 rim and in part the higher charge of the $[C_2B_9H_{11}]^{2-}$ dianion and its stronger bonding to the metal M compared to the C_3B_2 ring of the monoanion $[Co(C_5H_5)(C_3B_2MeEt_4)]^-$.

Electrochemical Behaviour.—Fig. 2 shows the cyclic voltammograms measured for $[(C_5H_5)Co(C_3B_2MeEt_4)Co(C_2B_9H_{11})]$ and $[(C_5H_5)Co(C_3B_2MeEt_4)Ni(C_2B_9H_{11})]$. The latter shows one quasi-reversible oxidation at +0.58 V (*vs.* saturated

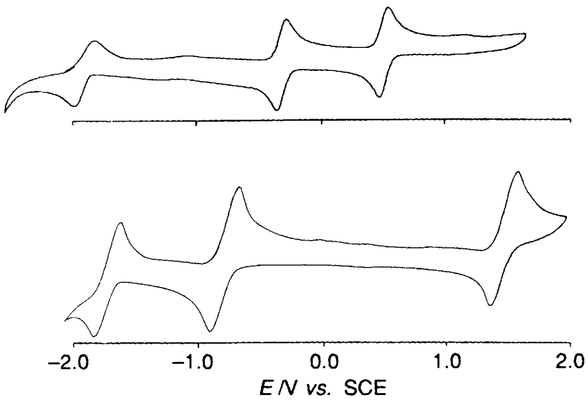


Fig. 2 Cyclic voltammograms measured for $[(C_5H_5)Co(C_3B_2MeEt_4)Ni(C_2B_9H_{11})]$ (top) and $[(C_5H_5)Co(C_3B_2MeEt_4)Co(C_2B_9H_{11})]$ (bottom). Conditions: MeCN–0.1 mol dm^{-3} NBu_4PF_6 solution, platinum electrode, room temperature

calomel electrode, SCE), one reversible reduction at −0.28 V and one quasi-reversible reduction at −1.93 V. The former shows one oxidation at +1.44 V, one reduction at −0.79 V and one reduction at −1.73 V. All three peaks are symmetric and remain symmetric at the three different scan rates used (500, 200 and 100m V s^{-1}), but a plot of the peak height against the square root of the scan rate for each couple does not give a straight line, indicating that all three redox couples are only quasi-reversible.

These data demonstrate that a 30-electron triple-decker complex with a closed-shell configuration is a highly stable species as predicted by extended-Hückel calculations. The 30-electron neutral triple-decker complex $[(C_5H_5)Co(C_3B_2MeEt_4)Co(C_2B_9H_{11})]$ is both difficult to oxidize (+1.44 V) and difficult to reduce (−0.79 V), where oxidation involves the loss of an electron from the bonding orbital a_2'' and reduction involves placing an extra electron into an antibonding orbital set e_1'. In both situations an open-shell paramagnetic species is formed. For the 31-electron neutral triple-decker $[(C_5H_5)Co(C_3B_2MeEt_4)Ni(C_2B_9H_{11})]$ the oxidation to the cation occurs at a much lower potential (+0.48 V) compared to the dicobalt complex because the electron removed would be from an antibonding orbital and the cation formed would have the stable 30-electron closed-shell configuration.

Two new triple-decker complexes, $[NMe_4][(C_5H_5)Co(C_3B_2MeEt_4)M(C_2B_{10}H_{12})]$ (M = Ni or Fe), containing the $[C_2B_{10}H_{12}]^{2-}$ dianion have also been synthesised and characterized from mass spectral and analytical data. These complexes are formed readily but are less stable and crystalline than those containing the $[C_2B_9H_{11}]^{2-}$ dianion. It should be possible to extend this series of novel complexes forming triple-deckers with different metal ions and also tetra-, penta- and hexa-decker complexes.

Experimental

Methods.—All reactions and manipulations, with the exception of the separation of the products on Al_2O_3 chromatographic plates, were carried out under an atmosphere of purified and dried dinitrogen by using standard Schlenk-type glassware. Solvents were pre-dried by standing over activated molecular sieves, and were subsequently refluxed over and distilled from a suitable drying agent under an inert atmosphere of dinitrogen.

Synthesis.—The 1,3-diborole, $[Co(C_5H_5)(C_3B_2HMeEt_4)]$ **1**,[10] $[Co(C_5H_5)(C_2H_4)_2]$[2] and $K[C_2B_9H_{12}]$[11] were synthesised *via* published procedures.

Reaction of $[C_2B_9H_{11}]^{2-}$, $[Co(C_5H_5)(C_3B_2MeEt_4)]^-$ *and Bis(pentane-2,4-dionato)nickel(II).*—The salt $K[C_2B_9H_{12}]$ (0.056 g, 0.32 mmol) was stirred in thf (30 cm^3). *n*-Butyllithium (0.4 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 0.6 mmol) was added and the reaction mixture stirred for 60 min. The solution was then cooled to −78 °C. In a separate Schlenk tube, complex **1** (0.1 g, 0.32 mmol) was dissolved in thf (20 cm^3) and cooled to −78 °C. *n*-Butyllithium (0.25 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 0.4 mmol) was added. The red-brown solution of **1** immediately changed to yellow-brown on formation of the $[Co(C_5H_5)(C_3B_2MeEt_4)]^-$ anion. The mixture was stirred at −78 °C for 20 min and then added to the thf solution of $[C_2B_9H_{11}]^{2-}$. Bis(pentane-2,4-dionato)nickel(II) (0.082 g, 0.32 mmol) was dissolved in thf (15 cm^3) to form a light green solution and added slowly to the stirred thf solution of the two anions, $[Co(C_5H_5)(C_3B_2MeEt_4)]^-$ and $[C_2B_9H_{11}]^{2-}$, at −78 °C. As the reaction mixture warmed slowly to room temperature the colour changed from yellow-brown to dark brown. The solvent was removed under reduced pressure and the residue chromatographed by PLC on Al_2O_3 plates, eluting with benzene–hexane (1:1). Three bands were observed: top band, dark green; middle band, brown-purple; and bottom band, olive-green. Each was removed from the plates and the products extracted from the Al_2O_3 with thf.

$[(C_5H_5)Co(C_3B_2MeEt_4)Ni(C_3B_2MeEt_4)Co(C_5H_5)]$ **3**. The product from the top dark green band was recrystallized from methanol to give dark green crystals of $[(C_5H_5)Co(C_3B_2MeEt_4)Ni(C_3B_2MeEt_4)Co(C_5H_5)]$ (yield = 15%), m.p. 180 °C. Mass spectrum: *m*/*z* (relative intensity) 685 (M^+, 100%). ^1H NMR (CD_3CN, $SiMe_4$): δ 26.9, 15.4, −12.6, −22.5, −31.7 and −37.5 (Found: C, 59.8; H, 8.2. Calc. for $C_{34}H_{56}B_4Co_2Ni$: C, 59.6; H, 8.2%).

$[(C_5H_5)Co(C_3B_2MeEt_4)Ni(C_2B_9H_{11})]$ **4**. The product from the middle brown-purple band was recrystallized from methanol to give purple crystals of $[(C_5H_5)Co(C_3B_2MeEt_4)Ni(C_2B_9H_{11})]$ (yield = 35%), m.p. 200 °C. Mass spectrum: *m*/*z* (relative intensity) 505 (M^+, 22%). ^1H NMR ($CDCl_3$, $SiMe_4$): δ 13.3, 3.7, 2.2, −0.84 and −1.6 (Found: C, 45.2; H, 8.4. Calc. for $C_{19}H_{39}B_{11}CoNi$: C, 45.2; H, 7.8%).

$[(C_5H_5)Co(C_3B_2MeEt_4)Co(C_2B_9H_{11})]$ **5**. The product from the third olive-green band was recrystallized from methanol to give olive-green crystals of $[(C_5H_5)Co(C_3B_2MeEt_4)Co(C_2B_9H_{11})]$ (yield = 8%), m.p. 150 °C. Mass spectrum: *m*/*z* (relative intensity) 504 (M^+, 100%). NMR: ^1H ($CDCl_3$, $SiMe_4$), 5.01 (s, 5 H), 3.10 (m, 2 H), 2.41 (m, 2 H), 2.13 (s, 3 H), 2.10 (m, 4 H), 1.62 (t, 6 H) and 1.46 (t, 6 H); $^{11}B-\{^1H\}$ ($CDCl_3$), δ 17.02, 6.34, −0.66, −5.68, −7.18, −18.70 and −23.69 (Found: C, 45.1; H, 8.5. Calc. for $C_{19}H_{39}B_{11}Co_2$: C, 45.2; H, 7.8%).

Reaction of $[C_2B_9H_{11}]^{2-}$, $[Co(C_5H_5)(C_3B_2MeEt_4)]^-$ *and Cobalt(II) Chloride.*—The $[C_2B_9H_{11}]^{2-}$ dianion and $[Co(C_5H_5)(C_3B_2MeEt_4)]^-$ anion were prepared as described for the previous reaction from $K[C_2B_9H_{12}]$ (0.056 g, 0.32 mmol) and $[Co(C_5H_5)(C_3B_2MeEt_4)]^-$ (0.10 g, 0.32 mmol). Cobalt(II) chloride (0.04 g, 0.32 mmol) was added to a solution of the two anions in thf (30 cm^3) at −78 °C. As the reaction mixture warmed slowly to room temperature it changed from yellow-brown to dark brown. The solvent was removed under reduced pressure and the residue chromatographed as before on Al_2O_3 plates, eluting with benzene–hexane (1:1). Only one band was observed and this was removed from the plates and extracted from the Al_2O_3 with thf. The product was recrystallized from methanol to give olive-green crystals of $[(C_5H_5)Co(C_3B_2MeEt_4)Co(C_2B_9H_{11})]$ **5** (yield = 45%).

Crystal Structure Determinations.—*Complex* **4**. Data were collected at room temperature on Enraf-Nonius CAD-4 automatic four-circle diffractometers, operating in the ω–2θ scan mode. Absorption correction curves were calculated from ψ scan reflections with $\chi \approx 90°$.

The coordinates of the cobalt and nickel atoms were determined by the automatic interpretation by SHELXS 86[12] of a Patterson synthesis. All further processing of the data was performed using the CRYSTALS package.[13] The remaining non-hydrogen atoms were located from subsequent $2F_o - F_c$

syntheses and their positional parameters refined by full-matrix least-squares refinement. The boron and carbon atoms in the carborane cage and in the C_3B_2 ring were identified from their isotropic thermal displacement parameters.

The coordinates of the hydrogen atoms attached to the atoms of the carborane cluster were calculated for idealized positions and were not refined, but a common isotropic thermal parameter was refined to a final value of 0.09 Å^2. Hydrogen-atom coordinates for the aliphatic groups on the C_3B_2 ring were calculated for idealized positions, and these were allowed to 'ride' on those of the appropriate carbon atoms; a common isotropic thermal parameter for these hydrogen atoms refined to a final value of 0.14 Å^2. Hydrogen atoms bonded to the η^5-cyclopentadienyl ring could not be located with certainty from Fourier syntheses so were not included in the model. A large amount of disorder was found to be associated with C(212), one of the ethyl carbons on the C_3B_2 ring, but examination of F_o syntheses with this atom omitted from the model did not allow the identification of more than one position for this atom. The cobalt, nickel and C(212) atom were assigned anisotropic thermal parameters in the final cycles of full-matrix refinement with a three-term Tukey and Prince weighting scheme. The largest residual electron-density peak which could not be assigned to an atom was 1.0 e Å^{-3}.

Complex **5**. The coordinates of the nickel and cobalt atoms from the final structure of **4** were put into the solution of **5** as two cobalt atoms. Subsequent Fourier-difference syntheses gave the positions of the remaining non-hydrogen atoms. The carbon and boron atoms in the carborane cage and in the C_3B_2 ring were identified from the bond lengths and the isotropic thermal parameters. The hydrogen atoms attached to the atoms of the cyclopentadienyl ligand and carborane cluster were located from Fourier-difference syntheses. The hydrogen-atom positions for the aliphatic groups on the C_3B_2 ring were calculated in idealized positions. All of the hydrogen atoms on the aliphatic groups on the C_3B_2 ring were allowed to 'ride' on those of the appropriate carbon or boron atoms. In the final cycles of full-matrix least-squares refinement all of the non-hydrogen atoms were assigned anisotropic thermal parameters. A three-term Tukey and Prince weighting scheme was applied. No residual electron density was observed above 1.0 e Å^{-3}. An absorption correction for the crystal was computed using ψ scans.

Additional material available for both structures from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

NMR Measurements.—The ^1H and ^{11}B-{^1H} NMR spectra were recorded using a Bruker AM-300 spectrometer operating at 300 and 96.25 MHz respectively.

Acknowledgements

The SERC is thanked for financial support and the British Council for sponsoring the collaboration between the English and German research groups.

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Received 25th *January* 1993; *Paper* 3/00438D