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Triple-decker complexes

XIV *. Reactions of iron carbonyls with the triple-decker sandwich complexes $(\eta^5\text{-}C_5H_5)Ni(\mu,\eta^5\text{-}C_2B_2C)M(\eta^5\text{-}C_5H_5)$, (M = Co, Ni). Replacement of $(\eta^5\text{-}C_5H_5)Ni$ by and insertion of the $Fe(CO)_3$ fragment into the $(\eta^5\text{-}C_5H_5)$–Ni bond **

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Abstract

The reactions of $Fe_2(CO)_9$ with triple-decker sandwich complexes containing the 2-methyl-1,3,4,5-tetraethyl or the 4,5-diethyl-1,3-dimethyl derivatives of the 2,3-dihydro-1,3-diborole heterocycle C_2B_2C (**4a,b**) as a bridging ligand have been investigated. The paramagnetic triple-deckers, 32 valence electron (VE) $[(\eta^5\text{-}C_5H_5)Ni(\mu,\eta^5\text{-}C_2B_2C)Co(\eta^5\text{-}C_5H_5)]$ (**8a**) and 33 VE $[(\eta^5\text{-}C_5H_5)Ni(\mu,\eta^5\text{-}C_2B_2C)Ni(\eta^5\text{-}C_5H_5)]$ (**9b**) react with $Fe_2(CO)_9$ to give products resulting either from replacement of a $(\eta^5\text{-}C_5H_5)Ni$ fragment by $Fe(CO)_3$, or insertion of $Fe(CO)_3$ into the $(\eta^5\text{-}C_5H_5)$–Ni bond. Thus, reaction of **8a** with $Fe_2(CO)_9$ proceeds via $Fe(CO)_3$ insertion into the $(\eta^5\text{-}C_5H_5)$–Ni bond to yield the trinuclear carbonyl-bridged complex $[(\eta^5\text{-}C_5H_5)FeCO(\mu\text{-}CO)_2Ni(\mu,\eta^5\text{-}C_2B_2C)Co(\eta^5\text{-}C_5H_5)]$ (**10a**), and subsequently the tetranuclear $[\{(\eta^5\text{-}C_5H_5)Co(\mu,\eta^5\text{-}C_2B_2C)Ni(\mu\text{-}CO)\}_2]$ (**12a**), and also via replacement of $(\eta^5\text{-}C_5H_5)Ni$ to give the triple-decker $[(\eta^5\text{-}C_5H_5)Co(\mu,\eta^5\text{-}C_2B_2C)Fe(CO)_3]$ (**13a**). 33 VE **9b** reacts with $Fe_2(CO)_9$ to give initially $[(\eta^5\text{-}C_5H_5)Ni(\mu,\eta^5\text{-}C_2B_2C)Fe(CO)_3]$ (**14b**); subsequent reactions lead to the carbonyl-bridged $[(\eta^5\text{-}C_5H_5)Fe(CO)(\mu\text{-}CO)_2Ni(\mu,\eta^5\text{-}C_2B_2C)Fe(CO)_3]$ (**15b**), the tetra-decker $[\{(CO)_3Fe(\mu,\eta^5\text{-}C_2B_2C)\}_2Ni]$ (**16b**), and the triple-decker $[(\eta^5\text{-}C_5H_5)Fe(\mu,\eta^5\text{-}C_2B_2C)Fe(CO)_3]$ (**17b**). The unsymmetrical triple-decker complexes **14a** and **14b** have been made independently by stacking the Ni-sandwich complexes **20a** and **20b** with an $Fe(CO)_3$ fragment. A close chemical relationship between 32 VE **8a** and 20

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* For Part XIII see ref. 1.

** Dedicated to Professor Gordon Stone on the occasion of his 65th birthday.

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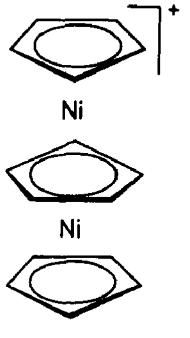
VE nickelocene has been established, and may be rationalised by consideration of electronic structures.

Introduction

The synthesis of the first triple-decker sandwich complex, 34 VE $[(\eta^5\text{-}C_5H_5)Ni(\mu,\eta^5\text{-}C_5H_5)Ni(\eta^5\text{-}C_5H_5)]^+$ (**1**) was reported by Werner and Salzer [2] in 1972, and this was closely followed by a report by Grimes et al. [3] of the preparation of the first neutral 30 VE triple-deckers **2** and **3**. Subsequently Hoffmann et al. [4] analysed the electronic structure of $[(\eta^5\text{-}C_5H_5)M(\mu,\eta^5\text{-}C_5H_5)M(\eta^5\text{-}C_5H_5)]$ and $[(CO)_3M(\mu,\eta^5\text{-}C_5H_5)M(CO)_3]$ triple-deckers.

More recently, investigations into the ligand properties of the 1,3-diborole heterocycle **4**, which by elimination of a hydrogen atom yields the three-electron 1,3-diborolyl ligand **4**$^\bullet$, resulted in the synthesis [5–7] of a series of neutral triple-decker complexes **5**–**9**. Complex **6** is diamagnetic, whereas the others represent the first examples of paramagnetic triple-decker sandwich complexes with 29, 31, 32, and 33 VE respectively [8].

It is instructive to compare the electronic structure [5] of these triple-decker species with that of the bis(cyclopentadienyl)metal sandwich complexes $[(\eta^5\text{-}C_5H_5)_2M]$, (M = Fe, Co, Ni). The diamagnetic complex **6** may be regarded as a ferrocene analogue, from which it is formally derived by insertion of a 12 VE stack,



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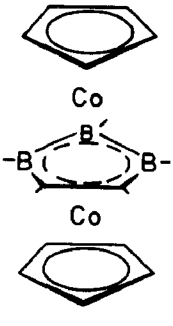

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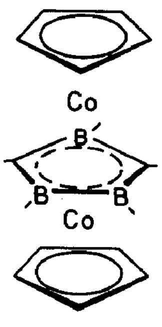

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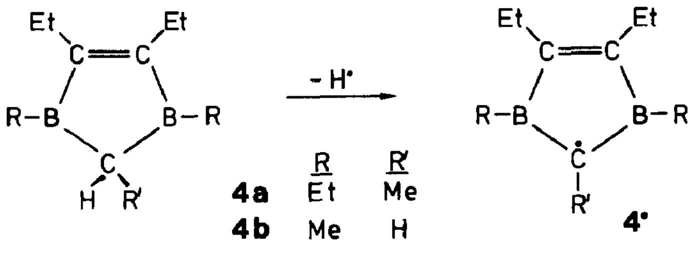
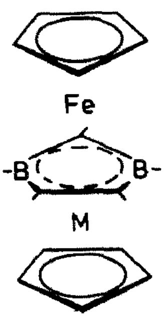
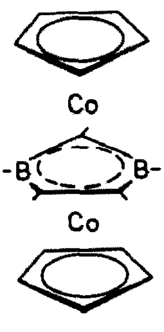


	R	R'
4a	Et	Me
4b	Me	H

4$^\bullet$



5 M=Fe
6 M=Co



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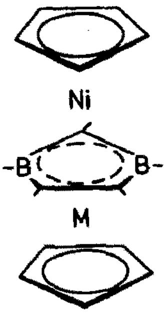


8 M=Co
9 M=Ni

Co(C_2B_2C), between C_5H_5 and Fe. Similarly the paramagnetic complex **7**, with one unpaired electron, represents the electronic extension of cobaltocene. Complex **8** has two unpaired electrons in a triplet ground state, and is therefore a direct analogue of nickelocene. Finally, **9** with one unpaired electron, would be the analogue of a 21 VE bis(cyclopentadienyl)metal complex.

Cobaltocene and nickelocene exhibit a rich and diverse chemistry [9]; and in many cases their unusual reactivities may be attributed to the presence of unpaired electrons. It therefore seemed to us of interest to examine how far the reactions of the paramagnetic triple-deckers, **7**, **8**, and **9**, can be considered to parallel those of $[(\eta^5\text{-}C_5H_5)_2M]$ (M = Co, Ni). In this paper we present details of a study of the reactions of $Fe_2(CO)_9$ with **8a** and with **9b**, which has revealed a close chemical relationship between nickelocene and 32 VE triple-decker complexes possessing two unpaired electrons.

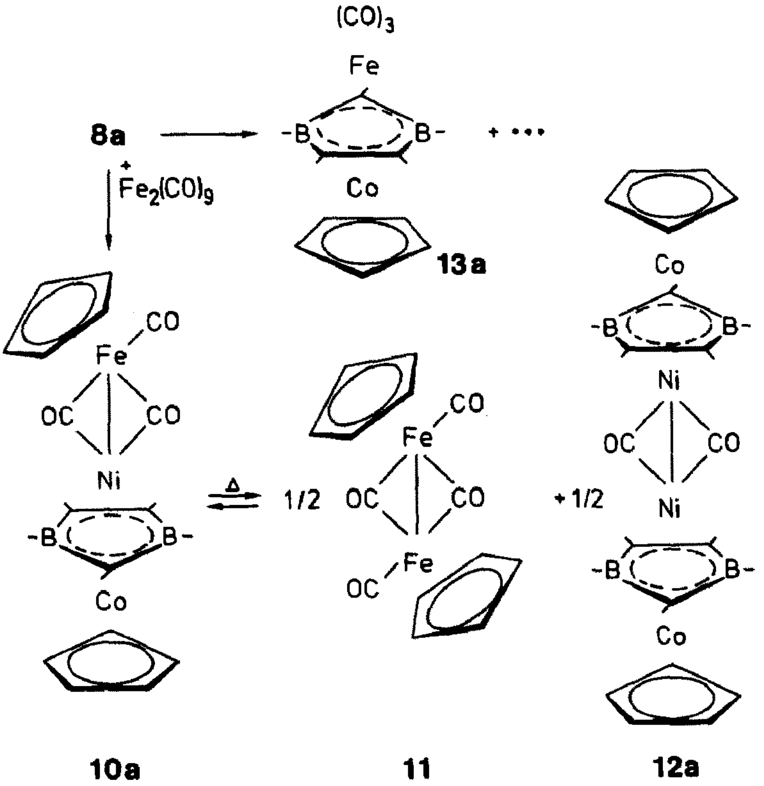
Results and discussion

*Reactions of the NiCo triple-decker **8a** with $Fe_2(CO)_9$*

It has long been known that nickelocene reacts with $Fe(CO)_5$ to give carbonyl-bridged $[(\eta^5\text{-}C_5H_5)FeCO(\mu\text{-}CO)_2Ni(\eta^5\text{-}C_5H_5)]$ by insertion of an $Fe(CO)_3$ fragment into the cyclopentadienyl–Ni bond [10]. We find that, in refluxing toluene, **8a** reacts similarly with an excess of $Fe_2(CO)_9$ to give the carbonyl-bridged trinuclear complex **10a** together with three other products **11**, **12a**, and **13a** (Scheme 1). The products were separated by column chromatography on silica gel.

Trinuclear, 46VE **10a** formed by electrophilic insertion of an $Fe(CO)_3$ fragment into the cyclopentadienyl–Ni bond of **8a** is a clear analogue of $[(\eta^5\text{-}C_5H_5)FeCO(\mu\text{-}CO)_2Ni(\eta^5\text{-}C_5H_5)]$. The diamagnetic complex **10a** was isolated as an air-sensitive, dark brown solid, and characterised by elemental analysis, mass spectrometry and infra-red and NMR spectroscopy. The ^{11}B NMR spectrum shows a singlet at 16.8 ppm, indicating that the 1,3-diborolyl ligand **4a'** is in a bridging position. The inequivalence of the two terminal cyclopentadienyl groups is clearly apparent in the 400 MHz ^1H NMR spectrum.

The carbonyl-bridged complex **10a** is thermally sensitive, and under the reaction conditions described undergoes cleavage to yield cyclopentadienyl–irondicarbonyl

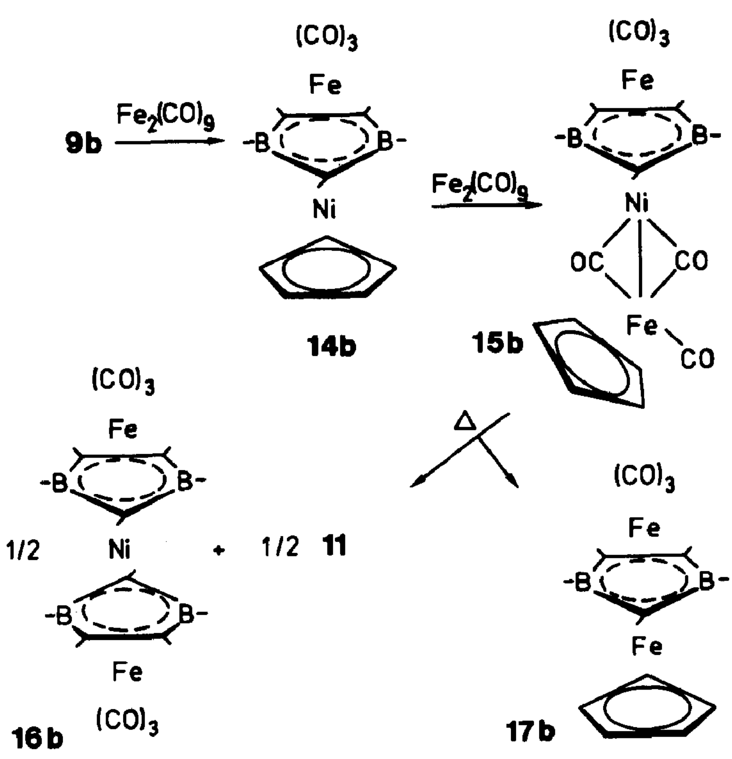


Scheme 1

dimer **11** and the novel, carbonyl-bridged, tetranuclear complex $[\{(\eta^5\text{-}C_5H_5)Co(\mu,\eta^5\text{-}C_2B_2C)Ni(\mu\text{-}CO)\}_2]$ (**12a**). Complexes **11** and **12a** were shown to be formed in a separate reaction of pure **10a** in refluxing toluene.

Details of the characterisation of diamagnetic 58 VE complex **12a** are given in the Experimental Section. The tetranuclear complex **12a** is of considerable interest, not only because of its synthetic potential, but also because of its close analogy to the carbonyl-bridged cyclopentadienyl-nickelcarbonyl dimer, from which **12a** is formally derived by insertion of two 12 VE $Co(C_2B_2C)$ fragments into the cyclopentadienyl–nickel bonds. Both **12a** and $[\{(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}CO)\}_2]$ give deep red solutions but are dark green as solids. However, the latter complex decomposes rapidly to nickelocene in refluxing toluene, whereas **12a** is stable even in refluxing mesitylene. No decomposition of **12a** to the tetra-decker sandwich complex [11] $[\{(\eta^5\text{-}C_5H_5)Co(\mu,\eta\text{-}C_2B_2C)\}_2Ni]$, the analogue of nickelocene, was observed. Furthermore **12a** is much less air-sensitive than $[\{(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}CO)\}_2]$. Although complexes **11** and **12a** are indeed formed by thermal decomposition of the trinuclear **10a**, complete conversion of **10a** into products was not be achieved even in refluxing mesitylene. The inference that there is equilibrium was confirmed by reaction of equimolar quantities of **11** and **12a** in refluxing toluene. Trinuclear **10a** was formed in 60% yield and tetranuclear **12a** recovered in 33% yield.

In addition to bringing about $Fe(CO)_3$ insertion into the cyclopentadienyl–nickel bond, $Fe_2(CO)_9$ can also react with **8a** by replacement of $(\eta^5\text{-}C_5H_5)Ni$ by $Fe(CO)_3$



Scheme 2

to give the 31 VE tripledecker [(η^5-C_5H_5)Co(μ,η^5-C_2B_2C)Fe(CO)$_3$] (**13a**). This is a brown air-sensitive solid which was characterised only by infra-red (ν(CO) 2052, 1988 cm^{-1} in petrol ether) and field desorption mass spectroscopy ($m/z = 453, M^+, 17\%$ relative intensity). Further characterisation was hampered by its progressive conversion, even in the solid state under dry nitrogen, into a deep purple solid, which is thought to be [{(η^5-C_5H_5)Co(μ,η^5-C_2B_2C)Fe(CO)$_2$}$_2$], the analogue of **11**.

Interestingly, the products of the reaction between **8a** and $Fe_2(CO)_9$ are to some extent dependent upon the reaction conditions and work-up procedure. For example, reaction of **8a** with an excess of $Fe_2(CO)_9$ in refluxing mesitylene, followed by removal of solvent and sublimation of the residue, gave the 30 VE [(η^5-C_5H_5)Fe(μ,η^5-C_2B_2C)Co(η^5-C_5H_5)] (**6a**) as the sublimate [5]. The tetranuclear complex **12a** was isolated from the residue in low yield.

*Reactions of the NiNi triple-decker **9b** with $Fe_2(CO)_9$*

The paramagnetic 33 VE triple-decker complex **9b** contains two (η^5-C_5H_5)Ni groups, and hence several products might be expected from its reaction with $Fe_2(CO)_9$ by fragment exchange or alternatively by electrophilic insertion of an Fe(CO)$_3$ fragment. Reaction of **9b** with an excess of $Fe_2(CO)_9$ in refluxing toluene gave a deep-red reaction mixture from which five compounds, **14b**, **15b**, **16b**, **17b** and **11** (Scheme 2) were isolated via chromatography on silica gel. The key complex in understanding this reaction is the 32 VE unsymmetrical triple-decker [(η^5-C_5H_5)Ni(μ,η^5-C_2B_2C)Fe(CO)$_3$] (**14b**), which is formed as the initial product by replacement of one (η^5-C_5H_5)Ni fragment by Fe(CO)$_3$. This appears to be the sole mode of reaction between $Fe_2(CO)_9$ and the 33 VE complex **9b**, whereas the corresponding reaction with **8a** give rise to both fragment exchange and electrophilic Fe(CO)$_3$ insertion. Stacking of the Ni-sandwich complexes **20** with an Fe(CO)$_3$ fragment also leads to the triple-decker complexes **14a** and **14b**.

The second step in this reaction sequence involves the reaction of the 32 VE complexes **14a** and **14b** with $Fe_2(CO)_9$ by Fe(CO)$_3$ insertion into the cyclopentadienyl–nickel bond to give the trinuclear carbonyl-bridged complex **15a** and **15b**. This was confirmed by carrying out a separate reaction of **14a** with $Fe_2(CO)_9$ in refluxing toluene, which yielded **15a** as the major product.

Formation of **11** and **16b** may be accounted for in terms of the thermal cleavage of the 46 VE carbonyl-bridged species **15b**, which occurs in a similar manner to that previously described for trinuclear, carbonyl-bridged **10a**. Interestingly, however, whilst **10a** yields, in addition to **11**, the tetranuclear carbonyl-bridged [{(η^5-C_5H_5)Co(μ,η^5-C_2B_2C)Ni(μCO)}$_2$] (**12a**), **15b** yields the tetra-decker complex [{(CO)$_3$Fe(μ,η^5-C_2B_2C)}$_2$Ni] (**16b**) together with **11**.

It seems probable that the formation of the 30 VE triple-decker complex [(η^5-C_5H_5)Fe(μ,η^5-C_2B_2C)Fe(CO)$_3$] (**17b**) may be attributed to an alternative thermal decomposition of **15b** involving loss of Ni and CO. Details of the characterisation of **14a,b**, **15a,b**, and **16b** by elemental analysis, infra-red, and mass spectroscopy and, where appropriate, NMR spectroscopy are given in the Experimental Section. The ^{1}H NMR signals from the paramagnetic **14b** and **16b** were not assigned.

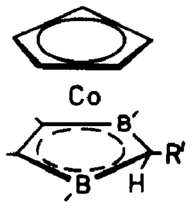
Conclusions

The results described demonstrate that there are two distinct modes of reaction between $Fe_2(CO)_9$ and triple-decker sandwich complexes:

1. Replacement of a (η^5-C_5H_5)Ni fragment by Fe(CO)$_3$, and
2. Insertion of an Fe(CO)$_3$ group into the cyclopentadienyl–nickel bond.

Both modes of reaction exhibit a marked specificity. Firstly, only the (η^5-C_5H_5)Ni fragment can be replaced by Fe(CO)$_3$. In the reaction between NiCo triple-decker-sandwich **8a** and $Fe_2(CO)_9$ there was no evidence for replacement of the (η^5-C_5H_5)Co fragment by Fe(CO)$_3$, which would have resulted in the formation of [(η^5-C_5H_5)Ni(μ,η^5-C_2B_2C)Fe(CO)$_3$] (**14a**). Furthermore, the FeCo and CoCo triple-decker sandwich complexes **6a** and **7a** are unreactive towards $Fe_2(CO)_9$, thereby confirming that the (η^5-C_5H_5)Co and (η^5-C_5H_5)Fe groups are inert towards exchange with Fe(CO)$_3$. Secondly, Fe(CO)$_3$ insertion occurs only at the cyclopentadienyl–nickel bond, and appears to be restricted to reactions involving 32 VE triple-decker complexes having two unpaired electrons.

There is a striking similarity between the reactions of $Fe_2(CO)_9$ with the 32 VE complexes **8a** and **14a,b** and that between Fe(CO)$_5$ and nickelocene. This similarity is expected from consideration of isolobal fragments [12], and supports the view that the 17 VE complex radicals cyclopentadienylcobalt-1,3-diborolyl and tricarbonyliron-1,3-diborolyl, derived from **18** and **19**, respectively, by hydrogen abstraction, may be regarded as a formally equivalent to the cyclopentadienyl radical $C_5H_5^{\cdot}$. The formal equivalence of [(η^5-C_5H_5)Co(C_2B_2C)]$^{\cdot}$ and cyclopentadienyl radicals is further substantiated by the close correspondence in the reactivity of [{(η^5-C_5H_5)Ni(μ-CO)}$_2$ and its tetranuclear analogue [{(η^5-C_5H_5)Co(μ,η^5-



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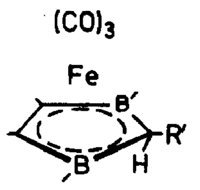

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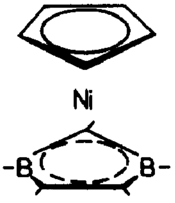

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$C_2B_2C)Ni(\mu$-$CO)\}_2]$ (**12a**). In this latter case the equivalence was exploited in the synthesis of the first penta-decker sandwich complex [13].

Experimental

The preparation, purification, and reactions of the complexes described were carried out under dry nitrogen in Schlenk-type glassware. Petroleum ether (b.p. 40–60 ° C), benzene, toluene, and diethyl ether were purified by slow passage through an alumina column, followed by boiling for one day over sodium-potassium alloy, then careful distillation under nitrogen. Column chromatography was carried out on Woelm silica gel activated by being heated to 160 ° C for three days in vacuo. The compounds 2-methyl-1,3,4,5-tetraethyl-1,3-diborole (**4a**) [14], 4,5-diethyl-1,3-dimethyl-1,3-diborole (**4b**) [5], the triple-decker sandwich complexes **8** and **9** [5] were prepared by published methods. $[\{(\eta^5$-$C_5H_5)Fe(CO)_2\}_2]$ (**11**) was purchased from the Ventron Chemical Company. The ^1H NMR spectra (δ, Me_4Si) were recorded on a Varian EM-360, a Varian XL-100, or a JEOL 300 spectrometer, and the ^{11}B NMR spectra (δ,Et_2OBF_3) on a Varian XL-100 spectrometer. The mass spectra were obtained with a Varian MAT CH7, a MAT 711, or a VEGE 7070 spectrometer. Microanalyses were performed at the Microanalytical Service of the Fachbereich Chemie, Universität Marburg, and the Organisch-Chemisches Institut, Universität Heidelberg. Melting points were determined with a Reichert melting point apparatus and are uncorrected.

*Reaction of **8a** with $Fe_2(CO)_9$ in refluxing toluene*

A stirred mixture of **8a** (0.50 g, 1.15 mmol) and $Fe_2(CO)_9$ (1.89 g, 5.19 mmol) in toluene (30 ml) was heated under reflux for 4.5 h. The solvent was removed under vacuum and the resulting brown residue was dissolved in petroleum ether (15 ml) and transferred to a silica–petroleum ether column. Five separate bands were eluted by progressive increase in the solvent polarity. Elution with petroleum ether gave the brown $[(\eta^5$-$C_5H_5)Co(\mu,\eta^5$-$C_2B_2C)Fe(CO)_3]$ (**13a**: 0.07 g, 13%), followed immediately by a blue-green band which yielded unchanged **8a** (0.29 g, 58%). The purple-red $[\{(\eta^5$-$C_5H_5)Co(\mu,\eta^5$-$C_2B_2C)Ni(\mu$-$CO)\}_2]$ (**12a**: 0.02 g, 4%, m.p. 256–258 ° C) was eluted with petroleum ether–benzene (20/1), and the brown **10a** (0.13 g, 20%, m.p. 126–128 ° C) with in petroleum ether–benzene (1/1). Finally $[\{(\eta^5$-$C_5H_5)Fe(CO)_2\}_2]$ (**11**: 0.01 g, 5%) was eluted by passing neat benzene through the column.

13a: MS (EI) m/z (rel. int.): 453(17). IR(ν(CO) cm^{-1}, C_2Cl_4): 2052, 1988. **12a**: ^{1}H NMR (300 MHz, C_6D_6): δ 4.07 (s,5H), 2.2 (m,2H), 2.1 (m,2H), 1.78 (s,3H) 1.5 (m,4H), 1.4 (m,6H), 1.2 (m,6H). ^{11}B NMR(C_6D_6): δ 14.6. Anal. Found: C, 53.87; H, 7.02. $C_{36}H_{56}B_4Co_2Ni_2O_2$ (799.62) calcd.: C, 54.10; H. 7.07%. MS (FD) m/z (rel. Int): 798(100). IR (ν(CO) cm^{-1}, C_2Cl_4): 1852. **10a**: ^{1}H NMR (300 MHz, C_6D_6): δ 16.8. Anal. Found: C, 51.94; H, 5.89. $C_{25}H_{33}B_2CoFeNiO_3$(576.62) calcd.: C, 52.07; 4, 5.77%. MS(FD) m/z (rel. int.): 576(100). IR (ν(CO) cm^{-1}, C_2Cl_4): 2011, 1828.

*Thermal cleavage of (η^5-cyclopentadienyl)iron(carbonyl)bis(μ-carbonyl(nickel(μ,η^5-2-methyl-1,3,4,5-tetraethyl-1,3-diborolyl)(η^5-cyclopentadienyl)cobalt (**10a**)*

A brown solution of **10a** (0.18 g, 0.31 mmol) in toluene (15 ml), was heated under reflux for 1.5 h. The resulting deep purple solution was evaporated to dryness and the residue was dissolved in petroleum (10 ml) and transferred to a silica–petroleum ether column. Elution with petroleum ether gave a green band containing small quantities of an unidentified product. Complexes **12a** (0.02 g, 16%), **10a** (0.10 g, 56%) and then complex **11** (0.01 g, 18%) were eluted (in their equilibrium ratio) by gradually increasing the polarity of the petroleum ether-benzene eluent.

*Reaction of bis[(η^5-cyclopentadienyl)cobalt(μ,η^5-2-methyl-1,3,4,5-tetraethyl-1,3-diborolyl)nickel(μ-carbonyl)] (**12a**) with [{(η^5-C_5H_5)Fe(CO)$_2$}$_2$] (**11**)*

A stirred mixture of **12a** (0.18 g, 0.23 mmol) and **11** (0.08 g, 0.23 mmol) in toluene (20 ml) was heated under reflux for 2.5 h. The solvent was removed under vacuum, and column chromatography of the residue by the procedure described above gave **12a** (0.06 g, 33%), **10a** (0.16 g, 60%), and **11**.

*Reaction of **9b** with $Fe_2(CO)_9$*

Reactions in refluxing toluene gave five products, and these were isolated by chromatography on a silica–petroleum ether column [5]. Successive bands gave the red-brown **16b** (26%, m.p. 172° C), a red mixture of **14b** and **17b** (50%), **15b** (11%), and **11**. **16b**: ^{1}H NMR (300 MHz, C_6D_6): δ 84(br), 17.8(s), 10.3(s), −3.8(br). Anal. Found: C, 45.12; H, 5.31. $C_{24}H_{34}B_4Fe_2NiO_6$ (632.15) calcd.: C, 45.60; H, 5.42%. MS(EI) m/z (rel. int.): 632 (9). IR (ν(CO) cm^{-1}, C_2Cl_4): 2052, 2000, 1991. **15b**: ^{1}H NMR (300 MHz, C_6D_6): δ 4.07 (s, 5H), 2.26 (s,1H), 2.2 (m,4H), 1.14 (t,6H), 1.02 (s,6H). ^{11}B NMR (C_6D_6): δ 16. MS (EI) m/z (rel. int.): 550 (33). IR (ν(CO) cm^{-1}, C_2Cl_4): 2056, 2020, 1988, 1983, 1834.

*Tricarbonyliron(μ,η^5-4,5-diethyl-1,3-dimethyl-1,3-diborolyl)(η^5-cyclopentadienyl)nickel (**14b**)*

A solution of the Ni-sandwich **20b** (0.46 g, 1.7 mmol) [5] and $Fe_2(CO)_9$ (1.0 g, 2.75 mmol) in toluene (20 ml) was kept at 80–90 °C for 0.5 h and then evaporated to dryness. The residue was sublimed at 80–90 °C/0.01 Torr to yield 0.53 g of the red **14b** (76%).

^{1}H NMR (300 MHz,C_6D_6): δ 74(br), 20.0(s), −0.6(s), −33.7(s). Anal. Found: C, 48.91; H, 5.21. $C_{17}H_{22}B_2FeNiO_3$ (410.52) calcd.: C, 49.74; H, 5.40%. MS (FD) m/z (rel. int.): 410 (100). IR (ν(CO) cm^{-1}, C_2Cl_4): 2038, 1978, 1972.

*Tricarbonyliron(μ,η^5-2-methyl-1,3,4,5-tetraethyl-1,3-diborolyl)-(η^5-cyclopentadienyl)-nickel (**14a**)*

The reaction between **20a** (0.39g, 1.25 mmol) and $Fe_2(CO)_9$ (1.10 g, 3.02 mmol) was carried out as described for **14b**. Distillation at 80–90 ° C/0.01 Torr afforded a red-brown product, which was chromatographed on silica. A red-brown band was eluted with petroleum ether and a green-brown band with ether. Both fractions were chromatographed again to yield **20a** (0.14 g, 35%), **14a** (0.12 g, 21%). MS (FD) *m/z*: 552 (M^+, 100); IR(ν(CO) cm^{-1}, C_2Cl_4): 2040(s), 1980 (vs); $(C_5H_5)_2Ni$ (10 mg) and deep-red **15a** (0.05 g, 7%). MS(EI) *m/z*: 592 (M^+,100). Anal. Found: C, 46.46; H, 4.59. $C_{23}H_{28}B_2Fe_2NiO_6$ (592.47) calcd.: C, 46.63; H, 4.76%.

Reaction of ***14a*** *with* $Fe_2(CO)_9$

A solution of **14a** (0.40 g, 0.89 mmol) and $Fe_2(CO)_9$ (0.44 g, 1.2 mmol) in mesitylene (10 ml) was kept at 120 °C for 1.5 h, then at 160 °C for a further 1.5 h. The solvent was removed in vacuo and the residue chromatographed on a silica–hexane column. The first fraction contained the red **14a** (0.06 g, 15%). A n-C_6H_{14}/C_6H_6 mixture (5/1) eluted another red product, which was identified as **15a** (0.20 g, 38%, m.p. 86 °C). Benzene eluted as a third fraction a small amount of **11**.

Thermal cleavage of ***15a***

A solution of the trinuclear **15a** (0.04 g, 0.07 mmol) was in mesitylene was kept at 160 °C for 1 h. The solvent was then removed and the residue chromatographed on silica. The brown fraction eluted by petroleum ether contained the dinuclear **17a**, MS (FD) *m/z*: 450 (100) and a trinuclear complex, MS (FD) *m/z*: 698(100), presumably $(\eta^5\text{-}C_5H_5)M(\mu,\eta^5\text{-}C_2B_2C)M'(\mu,\eta^5\text{-}C_2B_2C)Fe(CO)_3$ (MM' = NiFe or FeNi).

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