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Synthesis of Tetradecker Sandwich Complex with 1,4-Dialkyl-1,4-dibora-2,5-cyclohexadiene

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A tetradecker sandwich complex (**7a**) was synthesized in low yield by the reaction of a tripledecker, bis(η^5 -cyclopentadienyl)- μ -(η^6 -1,2,3,4-tetramethyl 1,4-dibora-2,5-cyclohexadiene) dinickel (**5a**) with potassium and $\text{FeCl}_2 \cdot 2\text{THF}$. The reaction of another tripledecker, bis(η^5 -cyclopentadienyl)- μ -(η^6 -2,3-diethyl-1,4-dimethyl-1,4-dibora-2,5-cyclohexadiene) dicobalt (**4a**) with potassium and $\text{FeCl}_2 \cdot 2\text{THF}$ at room temperature produced a doubledecker complex (**2b**) via the decomposition of the dark green crystal.

Introduction

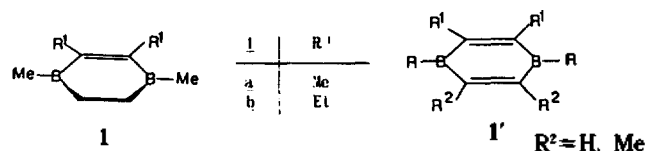
An unstable 1,4-dialkyl-1,4-dibora-2,5-cyclohexadiene (**1'**) rearranges to give a nido-tetracarbahexaborane because the electron-deficient boron atoms are included in it¹. We synthesized the stable 1,2,3,4-tetraalkyl-1,4-dibora-2-cyclohexene (**1**) acted as the precursor **1'** by the elimination of two hydrogen atoms². The complexes of **1'** with transition metals are comparatively stable to be separated and identified under inert gas atmosphere at room temperature. These stable doubledecker and tripledecker sandwich complexes were reported by Herberich² and our research team³ for the first time. However the multidecker complexes over tetradecker have not been known until now. On the other hand Siebert and his coworkers synthesized another kinds of multidecker compounds including many kinds of tetradeckers with the 1,3-diborolene as a ligand⁴. In this paper we report the preparation of tetradecker complex with 1,2,3,4-tetraalkyl-1,4-dibora-2,5-cyclohexadiene.

Experimental

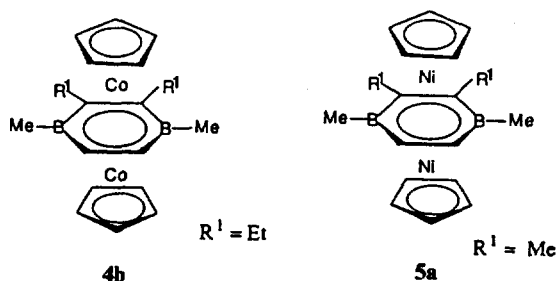
All reactions and manipulation were carried out under an atmosphere of purified and dried nitrogen or argon by using Schlenk type glassware. The solvents for preparation were dried by standard methods, distilled over potassium and benzophenone under argon atmosphere.

¹H-NMR spectra (δ , Me_4Si) were recorded on a Bruker AM 300, Bruker WP 80 SY spectrometer, ¹¹B-NMR (δ , $\text{BF}_3 \cdot \text{OEt}_2$) spectra were obtained on a JEOL FX-90Q. Mass spectra were recorded on a Varian MATCH 7 and a Kratos MS 25RFA in EI method. Melting points were determined on a Gallen Kamp M.P. Apparatus.

2,3-Dialkyl-1,4-dimethyl-1,4-dibora-2-cyclohexene (**1**) was synthesized by the reported methods². (η^5 -Cyclopentadienyl) bis(ethylene) cobalt (Jonas reagent) was synthesized by the



Jonas method⁵. Cobalt tripledecker complex (**4b**), bis-[(η^5 -cyclopentadienyl)- μ -(carbonyl) nickel] and nickel tripledecker complex (**5a**) were synthesized by the previously described methods⁶⁻⁸.



Reaction of **4b** with Potassium and $\text{FeCl}_2 \cdot 2\text{THF}$.

A 100 ml Schlenk tube was mirrored with 57 mg of potassium (1.46 mmol) in vacuum and was filled with argon gas. The solution of 270 mg of **4b** (0.66 mmol) in 20 ml THF was put into this tube and stirred vigorously at room temperature. After 5 hours this reaction solution was filtered to remove the excess potassium and reacted with solid 280 mg of $\text{FeCl}_2 \cdot 2\text{THF}$ (1.03 mmol). After 2 more hours reaction, the solvent was removed and the residue was extracted with petroleum ether (PE) and a dark brown solution was obtained. The product was separated by column chromatography on silicagel eluting with PE. A dark green solid was obtained and recrystallized at -30°C . The product amounted to 80 mg. This decomposed to an orange-colored solid at room temperature during identification.

Table 1. Main Fragment-Cations of 7a in Mass-Spectrum

Identity	m/e (relative intensity)	Identity	m/e (relative intensity)
M ⁺	566 (27.9)	L ⁺	132 (2.2)
(CpNiLFeL) ⁺	443 (4.9)	(CpNi) ⁺	123 (13.2)
(Cp ₂ Ni ₂ LFe) ⁺	434 (6.3)	Cp ⁺	65 (8.0)
(CpNi ₂ LFe) ⁺	370 (10.9)	Ni ⁺	57.2 (100.0)
(CpNiLFe) ⁺	311 (6.6)	Fe ⁺	55 (66.0)
(CpNiL) ⁺	255 (5.4)	(BMe ₂ H ₂) ⁺	43 (100.0)
(Cp ₂ Ni) ⁺	188 (7.2)	(BMe ₂) ⁺	41 (45.2)
or		(BMe ₂ H ₂) ⁺	28 (100.0)
(LFe) ⁺			

L = 1a - 1H, Cp = (η⁵-Cyclopentadienyl)

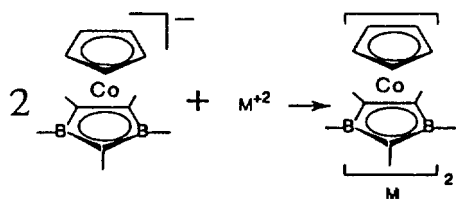
Reaction of 5a with Potassium and FeCl₂·2THF.

The reaction with 5a was carried out by the similar method described above. The mixture of 150 mg of potassium (3.84 mmol) and 350 mg of 5a (0.92 mmol) was reacted with 731 mg of FeCl₂·2THF (2.7 mmol). For chromatography toluene was used as an eluent. A dark green solid was obtained by the recrystallization with PE at -30°C. The yield was 15.9% (90 mg). mp. 186°C.

¹H-NMR(δ, C₆D₆): 4.39(s, 10H), 3.89(s, 4H), 1.96(s, 12H), 1.14(s, 12H); ¹¹B-NMR(δ, C₆D₆): 3.1 ppm; EI-MS: m/e 566 (M⁺, 27.9), see Table 1.

Results and Discussion

The first tetradeccker sandwich complex with 1,3-diborolene as a ligand was synthesized by Siebert research team in 1977⁹. Since then, many kinds of tetradeccker complexes were prepared by the following methods⁴.

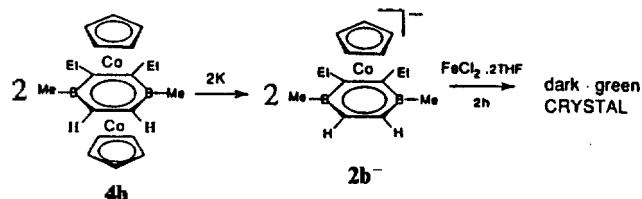


(M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Sn)

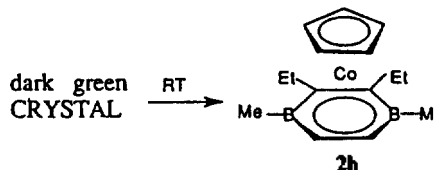
We tried to form the tetradeccker complex with 2,3-dialkyl-1,4-dimethyl-1,4-dibora-2,5-cyclohexadiene(1') as the similar way shown above. The complex 2b was reacted with potassium to form 2b anion and was reacted with FeCl₂·2THF solution of THF consecutively. We could not obtain the desirable Co, Fe-tetradeccker complex from the doubledecker complex (2b). The doubledecker anion, however, formed from the tripledecker complex was relatively stable and reacted with FeCl₂·2THF to give a tetradeccker complex as the similar case of the 1,3-diborolene tetradeccker complex⁴. It is supposed that the anion formed from the doubledecker 2b does not exist long enough to react with metal cation to form a tetradeccker complex.

Product from 4b with Potassium and FeCl₂·2THF. A tripledecker complex, 4b reacted with excess potassium and FeCl₂·2THF and gave a dark green solid. This

solid was probably a tetradeccker complex⁴. This compound was unstable as another 1,3-diborolene Fe, Co-tetradeccker^{4,10}.



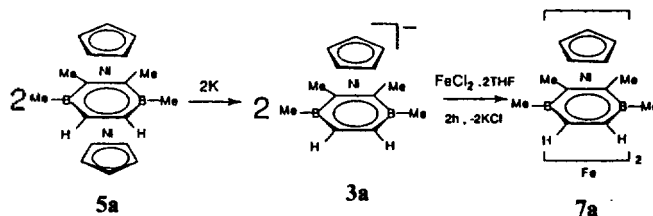
Via the decomposition of this dark green crystal, a double-decker sandwich complex was produced as follows.



¹H-NMR(δ, C₆D₆): 4.94(s, 2H), 3.95(s, 5H), 2.10(q, 4H), 1.24(t, 6H), 1.08(s, 6H); ¹¹B-NMR (δ, C₆D₆): 24.5 ppm; EI-MS: m/e 284(M⁺, 25.7), 246[(M-BCMe)⁺, 96]_[L=1b-2H], 232[(M-BC₂H₂Me)⁺, 22], 217[(M-BCEtMe)⁺, 25.5], 187[(M-C₂Et₂Me)⁺, 7.9], 142[M²⁺, 6.5], 160[L⁺, 3.2], 124[CpCo⁺, 7.2], 65(Cp⁺, 8.2), 59(Co⁺, 4.5).

This doubledecker complex (2b) was further confirmed by the synthesis of 2b using another known method⁶.

Tetradeccker Sandwich Complex (7a). A tripledecker (5a) reacted with potassium and FeCl₂·2THF to give a tetradeccker complex (7a). A radical anion (3a^{·-}) which was obtained by the decomposition of 5a with potassium at -60°C was identified⁶ and reduced to anion (3a⁻) by the excess potassium at room temperature. The reaction of anion with Fe²⁺ in solution produced a tetradeccker 7a. 7a having 46 valence electrons was diamagnetic and was identified by ¹H-NMR. This spectrum was compared with that of 5a⁸ and could be identified as 7a. On the other hand the value of ¹¹B-NMR was shifted to higher field according to the higher coordination number and the number of valence electron^{6,8} as in 1a, 5a and 7a. The complex 7a was further confirmed by mass spectrum. Figure 1 shows the result. The relative isotope existence near the mol peaks was shown in Figure 2. Their peak intensities were coincident with the theoretical isotope abundance peaks. The identities and intensities of main peaks were represented in Table 1.



Conclusion

The reaction of a doubledecker anion with metal cation was carried out to obtain a tetradeccker sandwich complex with 2,3-dialkyl-1,4-dimethyl-1,4-dibora-2,5-cyclohexadiene as a ligand. A dark green crystal was obtained by the reaction of a triple-decker complex, bis-(η⁵-cyclopentadienyl)-μ-(η⁶-2,3-

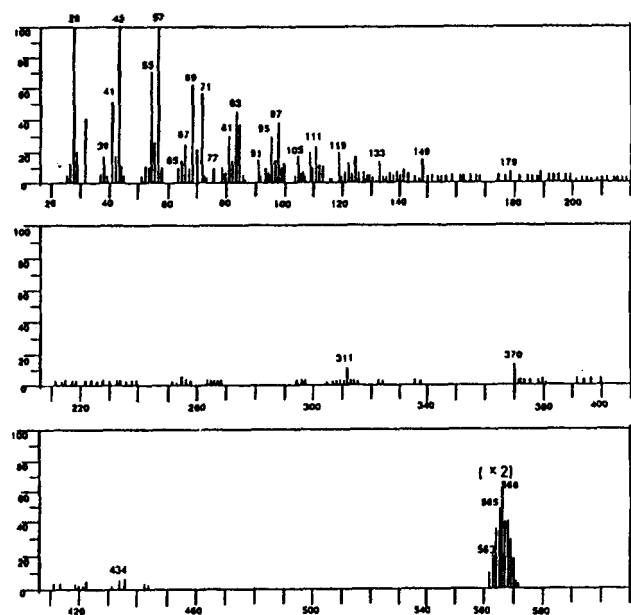


Figure 1. El-mass-spectrum of 7a.

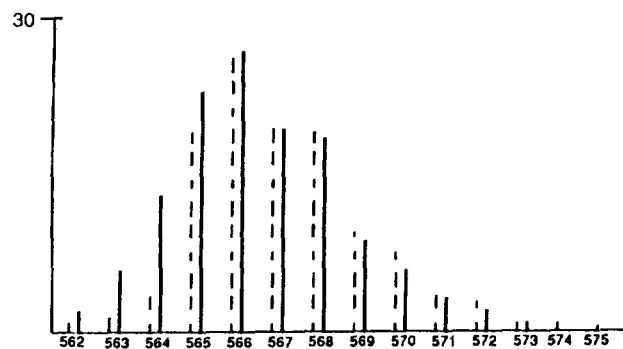


Figure 2. Calculated (---) and found (—) isotope existence for mol. peaks of 7a.

diethyl-1,4-dimethyl-1,4-dibora-2,5-cyclohexadiene) dicobalt (4b) with excess potassium and $\text{FeCl}_2 \cdot 2\text{THF}$. A double-decker

complex (2b) was produced during the identification of the dark green crystal at room temperature. A tetradecker complex (7a) was produced by the reaction of another tripledecker, bis-(η^5 -cyclopentadienyl)- μ -(η^6 -1,2,3,4-tetramethyl-1,4-dibora-2,5-cyclohexadiene) dinickel (5a) with excess potassium and $\text{FeCl}_2 \cdot 2\text{THF}$ at room temperature. This compound was identified by NMR and mass spectrometer.

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