

Notes

Reactivity of the Triple-decker Complex, Bis(cyclopentadienylnickel)- μ -1,2,3,4-Tetramethyl-1,4-dibora-2,5-cyclohexadiene

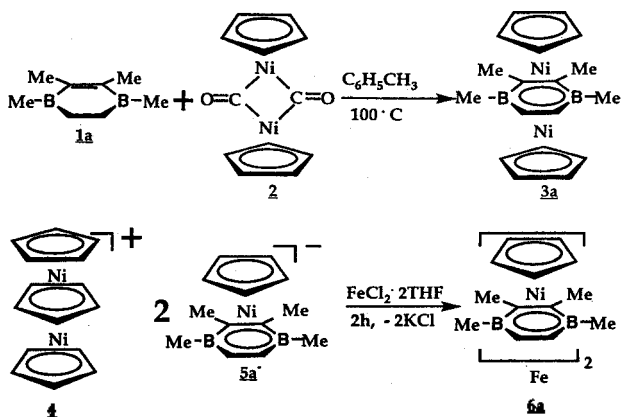
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Received November 2, 1995

The first triple-decker complex, $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-C}_4\text{H}_4\text{B}_2\text{Me}_2)\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)]^{2+}$ with a bridging 1,4-dibora-2,5-cyclohexadiene heterocycle was reported by Herberich *et al.*¹ We have studied the ligand properties of the 1,2,3,4-tetramethyl-1,4-dibora-2-cyclohexene (**1a**)² in its reaction with $[(\text{C}_5\text{H}_5)\text{Ni}(\text{CO})_2]$ (**2**). Via dehydrogenation of **1a** during complex formation we obtained the diamagnetic triple-decker sandwich **3a**.³ This 34 valence electron (VE) dinuclear complex is isoelectronic with $[\text{Ni}_2(\text{C}_5\text{H}_5)_3]^+$ (**4**)⁴ and thus should also exhibit a high reactivity due to anti-bonding HOMOs⁵ which are occupied by four electrons. We have shown that in THF **3a** is cleaved by potassium to yield the sandwich anion **5a**⁻, which reacts with FeCl_2 to give the diamagnetic tetra-decker complex **6a**.⁶ In this paper we would report the electrochemical results of **3a** and a destacking reaction of **3a** with 3-hexyne.



Result and Discussion

ESR and Electrochemistry. Cleavage of **3a** by potassium mirror in THF at -60°C yields a radical anion of **5a** in a red solution, which is identified with the ESR spectrometer.^{2c} This radical showed its spectrum in Figure 1 with $\langle g \rangle = 2.063$, $g_1 = 2.17$, $g_2 = 2.03$ and $g_3 = 1.99$ gauss. The ESR data of **5a** are almost identical with those of the 19 VE complex, $[(\text{C}_5\text{H}_5)\text{Ni}(\text{EtC})_2(\text{MeB})_2\text{S}]$.⁷

This radical anion is reduced in excess potassium to give **5a**⁻ at room temperature, a nickelocene analogue, which has

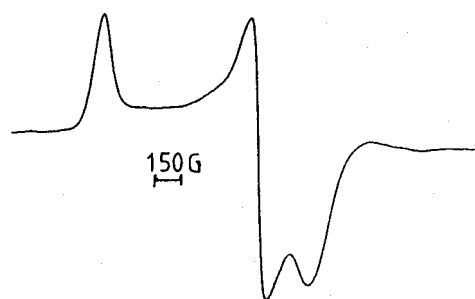


Figure 1. ESR spectrum of **5a** radical anion at 213 K generated via K metal reduction in THF.

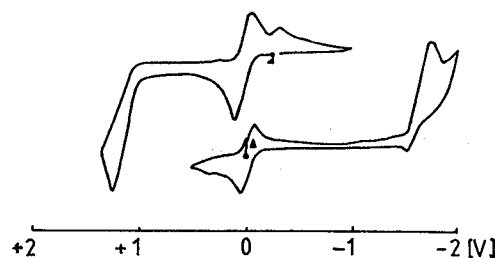


Figure 2. Cyclic voltammogram of **3a** at the Pt electrode in $\text{CH}_2\text{Cl}_2/(\text{n-Bu})_4\text{NPF}_6$; $v = 200$ mV/s.

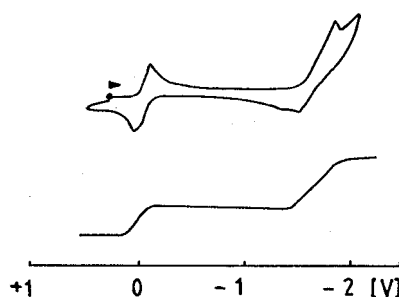


Figure 3. A dc polarogram of **3a** (0.3 mM) in $\text{CH}_2\text{Cl}_2/(\text{n-Bu})_4\text{NPF}_6$ at the DME; $v = 2$ mV/s; $t = 2$ s.

been used for the synthesis of the tetra-decker, **6a**.

In order to get information on the oxidation of **3a**, its cyclic voltammetry was studied in CH_2Cl_2 with $(\text{n-Butyl})_4\text{N}^+\text{PF}_6^-$ as an electrolyte. It showed that **3a** is oxidized reversibly, whereas reduction and second oxidation are irreversible processes.¹²

The cation **3a**⁺ with 33 VE is a stable triple-decker, however, the anion **3a**⁻ with 35 VE is unstable and decomposes to give **5a** anion and a $(\text{C}_5\text{H}_5)\text{Ni}$ fragment. This decomposed anion (**5a**⁻) was identified as the same compound produced by the reaction of **3a** with excess potassium at room temperature. The cyclic voltammetric and polarographic data were showed in ref. 11.

Degradation of 3a. It was noted^{2c} that crystalline **3a** slowly decomposed at 0°C within three weeks, accompanied by a color change from deep yellow to orange. On heating,

3a melts at 112 °C and turns into a dark green product on heating to 200 °C. The change of the color could indicate a dissociation of **3a** into **5a** and $[\text{Ni}(\text{C}_5\text{H}_5)]_n$. In order to trap possible complex fragments we have carried out a reaction between **3a** and 3-hexyne in n-hexane for 6 h at 68 °C. The solution turned deep green and by chromatographic work-up, only nickelocene (40%) could be isolated. Neither **5a** nor the 1,4-diboracyclohexadiene (or its C_4B_2 carborane) was detected.

Degradation of **3a** to nickelocene in the presence of 3-hexyne indicates that the bonding in this 34 VE triple-decker between the $\text{Ni}(\text{C}_5\text{H}_5)$ fragments and the bridging ligand is weak. In contrast to the 14 VE, $\text{Co}(\text{C}_5\text{H}_5)$ and $\text{Fe}(\text{C}_7\text{H}_5)$ moieties, which react with alkynes to produce substituted benzenes^{8,9} via (2+2+2) cycloaddition reactions, the 15 VE, $\text{Ni}(\text{C}_5\text{H}_5)$ fragment does not catalyze the oligomerization of alkynes.

Experimental Section

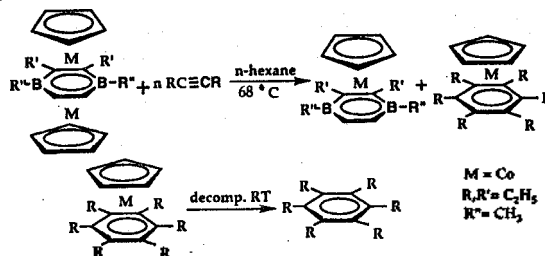
All reaction and manipulations were carried out under an atmosphere of purified and dried argon by using Schlenk type glassware. Solvents for preparation were dried by standard method, distilled over potassium and benzophenone under argon atmosphere. Melting points were measured by an M.P. Apparatus of Gallen Kamp Co. ¹H NMR spectra (δ , Me_4Si) were obtained by a Bruker AC 200, Bruker AM 300 Spectrometer, ¹¹B NMR (δ , $\text{BF}_3 \cdot \text{OEt}_2$) were checked on a JEOL-FX-90Q, Mass spectra were recorded on a Varian MATCH7 and a Kratos MS 25 RFA in EI method. X-band ESR spectrum was obtained by a Varian E3 in standard LiT-CNQ. Electrochemical equipments, Princeton Applied Research (PAR) Model 173 potentiostat, Model 179 digital coulometer, Model 175 function generator, Methrom rotating disk electrode (RDE) for cyclic voltammetry were used for electrochemical procedures. **2**¹⁰ was prepared from $\text{Ni}(\text{C}_5\text{H}_5)_2$ and $\text{Ni}(\text{CO})_4$.

Degradation of 3a. 150 mg **3a** (0.4 mmol) and 0.65 g 3-hexyne (7.9 mmol) were reacted in 30 mL n-hexane for 6 h at 68 °C. The deep green solution was chromatographed on a silicagel column. The compound was identified as nickelocene (30 mg, 40%) by the M.S. and melting point.

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- Wörner, K. F.; Uhm, J. K.; Pritzkow, H.; Siebert, W. *Chem. Ber.* **1990**, *123*, 1239. **3a** was obtained in 54% yield by the reaction of **1a** (7.5 mmol, 1 g) with **2** (7.5 mmol, 2.25 g) in 50 mL toluene for 4h at 100 °C. ¹H NMR (δ , C_6D_6) 4.80 (s, C_5H_5) 3.88 (s, C-H) 1.44 (s, C- CH_3) 1.10 (s, B- CH_3); ¹¹B NMR (δ , C_6D_6) 7.0 ppm; MS m/e [relative intensity] 378 (M^+ , 100), 313 [$(\text{M}-\text{Cp})^+$, 8.2], 255 [$(\text{M}-\text{NiCp})^+$, 8.7], 246 [$(\text{Cp}_2\text{Ni}_2)^+$, 50.7], 188 [$(\text{Cp}_2\text{Ni})^+$, 28.8],

- 132 [$(\text{M}-\text{Cp}_2\text{Ni}_2)$, 1.7], 123 [$(\text{CpNi})^+$, 21.3], 65 (Cp^+ , 3.5), 58 (Ni^+ , 6.3); Anal. found (calad. for $\text{C}_{18}\text{H}_{24}\text{Ni}_2$): C, 56.85 (56.98); H, 6.39 (6.38); Crystal structure of **3a** was reported in the above ref. 4. (a) Werner, H.; Salzer, A. *Synth. Inorg. Met. Org. Chem.* **1972**, *2*, 239 (b) Werner, H.; Ulrich, B.; Salzer, A. *J. Organomet. Chem.* **1977**, *141*, 334.
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- Cyclic voltammograms were measured at room temperature in CH_2Cl_2 with $(n\text{-butyl})_4\text{N}^+\text{PF}_6^-$ as an electrolyte (0.1 M). Working electrode, platinum rotating disc; auxiliary electrode, platinum wire; reference electrode, Ag/Ag^+ .

Cyclic Voltammetric Data

couple :	+2/+1	+1/0	0/-1
E_0 (V) :	1.10 (irrev.)	-0.02 (rev.)	-1.75 (irrev.)
ΔE_p (mV) :		100	
current ratio (I_R/I_0) :		1	
scan rate (V/s) :	0.2		

Polarographic Data

couple :	+1/0	0/-1
$E_{1/2}$ (V) :	-0.01 V (n=0.68),	-1.76 V (n=0.43)
Electrolyte :	0.1 M n-Bu ₄ NPF ₆ in CH_2Cl_2	

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NiNi^-	NiNi	NiNi^+	NiNi^{2+}
34VE	33VE	32VE	31VE
-1.37(V)	-0.06	+1.48(irr)	