that of **4e** indicate strongly that **1e** and **2e** adopt structures analogous to that of **4e**.

The observation that phyrolysis of the phenyltolylacetylene complex **3a** gives only **3d** and none of the **1d** or **2d** implies that the alkyne scission process occurs without extensive fragmentation of the metal framework. Further details, however, are sketchy at best. Preliminary work suggests that initial decarbonylation with Me_3NO/MeCN occurs at Os(1) or Os(2),[17] but the overall result requires complete decarbonylation at tungsten. Thus, further carbonyl exchange, either intramolecular or intermolecular, is involved.

The presence of the tungsten atom in the cluster certainly appears to facilitate alkyne scission.[3d] It has been suggested by Fehlner and co-workers that the carbon-carbon bond scission of alkyne moieties in metal clusters, in carboranes, and on metal surfaces is driven by charge transfer (M → π*) from the relatively electropositive metal or boron atoms to the resulting alkylidyne ligands.[18] The tungsten atom in the dialkylidyne complex $CpWOs_3(CO)_9(CR)(CR')$ can be viewed as being bound to six anionic ligands ($C_5H_5^-$, H^-, $2C^-$, $2Os^-$) and a neutral donor Os center. The formal oxidation state of the tungsten center is +6. Thus, the results involving alkyne scission on the tungsten-triosmium clusters appear to be consistent with this idea in that the alkylidyne ligands are coordinated to a relatively oxidized, more electropositive, tungsten. The results of Fehlner and co-workers also suggest that the degree of M → π* charge transfer increases as the number of metal atoms to which the alkyne is coordinated increases and that the sites permitting the greatest number of metal-alkylidyne carbon interactions will be most effective in carrying out scission of the coordinated alkyne. Therefore a pseudoctahedral species with configuration I (probably unsaturated) may be an important intermediate in the alkyne scission reaction.

Registry No. **1a**, 86885-45-2; **1a***, 116025-81-1; **1d**, 86885-48-5; **1e**, 116052-47-2; **2a**, 86885-46-3; **2a***, 116025-82-2; **2d**, 86885-49-6; **2d***, 116025-83-3; **2e**, 116052-48-3; **3a**, 86885-47-4; **3d**, 86885-50-9; **5a**, 116025-75-3; **5b**, 116025-76-4; **5c**, 116126-24-0; **6a**, 116025-77-5; **6b**, 116025-78-6; **7a**, 116025-79-7; **7b**, 116025-80-0; $CpWO_{53}(CO)_{12}H$, 68796-10-1; $CPWO_{53}(CO)_{12}H$ (^{13}C enriched), 116102-23-9; Os, 7440-04-2; W, 7440-33-7; di-*p*-tolylacetylene, 2789-88-0; diphenylacetylene, 501-65-5; phenyl-*p*-tolylacetylene, 3287-02-3; ethyl phenylpropiolate, 2216-94-6; diethyl acetylenedicarboxylate, 762-21-0; hexafluoro-2-butyne, 692-50-2.

Supplementary Material Available: Tables of anisotropic thermal parameters for **1a** and **6b** and additional distances and angles for **1a** (5 pages); listings of structure factors **1a** and **6b** (56 pages). Ordering information is given on any current masthead page.

---

[17] Koerner, P. J. M.S. Thesis, University of Illinois, 1987.

[18] Deshmukh, P.; Dutta, T. K.; Hwang, J. L.-S.; Housecroft, C. E.; Fehlner, T. P. *J. Am. Chem. Soc.* 1982, *104*, 1740.

Electronic Structures and Reactivities of (η^5-2,3,5-Tricarbahexaboranyl)nickel Sandwich Complexes. A Combined Electrochemical, Preparative, and NMR Spectroscopic Approach[1]

Joachim Zwecker, Thomas Kuhlmann, Hans Pritzkow, Walter Siebert,* and Ulrich Zenneck*

Anorganisch Chemisches Institut der Universität, D-6900 Heidelberg, Federal Republic of Germany

Received February 29, 1988

(μ-η^5-1,3-Dimethyl-4,5-diethyl-2,3-dihydro-1,3-diborolyl)bis[(η^5-1,4,6-trimethyl-2,3-diethyl-2,3,5-tricarbahexaboranyl)nickel] (**1**) may be cleaved in the presence of 1,5-cyclooctadiene by chemical or electrochemical oxidation to form (η^5-1,4,6-trimethyl-2,3-diethyl-2,3,5-tricarbahexaboranyl)(η^5-1,3-dimethyl-4,5-diethyl-2,3-dihydro-1,3-diborolyl)nickel (**4**) and (η^5-1,4,6-trimethyl-2,3-diethyl-2,3,5-tricarbahexaboranyl)(1,5-cyclooctadiene)nickel(1+) ($\mathbf{5^+}$) in good yields. This reaction has been monitored by cyclic voltammetry, coulometry, and controlled potential electrolysis. **4** and $\mathbf{5^+}BF_4^-$ have been characterized fully, including single-crystal X-ray diffraction studies. 4: space group $P\bar{1}$, $Z = 2$, $a = 9.055$ (3) Å, $b = 11.140$ (4) Å, $c = 13.406$ (4) Å, $\alpha = 103.36$ (3)°, $\beta = 105.61$ (2)°, $\gamma = 109.91$ (3)°, $V = 1144.1$ Å^3, $R = 0.034$, $R_w = 0.030$. $\mathbf{5^+}BF_4^-$: space group $C2/c$, $Z = 8$, $a = 15.418$ (2) Å, $b = 14.331$ (3) Å, $c = 19.809$ (5) Å, $\alpha = 90°$, $\beta = 103.78$ (2)°, $\gamma = 90°$, $V = 4250.9$ Å^3, $R = 0.056$, $R_w = 0.048$. The reaction of 4 and bis(carbonylcyclopentadienylnickel) yields the asymmetric triple-decker complex (μ-η^5-1,3-dimethyl-4,5-diethyl-2,3-dihydrodiborolyl)(η^5-1,4,6-trimethyl-2,3-diethyl-2,3,5-tricarbahexaboranyl)nickel(η^5-cyclopentadienyl)nickel (**8**). The combination of electrochemistry and paramagnetic NMR spectroscopy on **1**, **8**, and (μ-η^5-1,3-dimethyl-4,5-diethyl-2,3-dihydro-1,3-diborolyl)bis(cyclopentadienylnickel) (**2**) as well as electrochemistry of **4** and $\mathbf{5^+}$ and ESR spectroscopy of their redox products allows a precise description of the properties of the 1,4,6-trimethyl-2,3-diethyl-2,3,5-tricarbahexaboranyl ligand. It is isolobal in respect to the cyclopentadienyl ligand, and the energies of the MO's involved in metal-ligand bonding are nearly identical for both ligands.

Introduction

Electrochemistry now is a well-established tool to investigate electron-transfer reactions even of precious organometallics like polynuclear organotransition-metal complexes[3] or metallaborane cage compounds.[4] In prin-

---

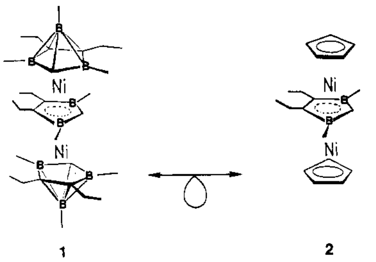
[1] Redox Chemistry of Transition-Metal π-Complexes. 1. (Tricarbahexaboranyl)metal Complexes. 2. Part 1: see ref 2.

[2] Zwecker, J.; Pritzkow, H.; Zenneck, U.; Siebert, W. *Angew. Chem.* 1986, *98*, 1129; *Angew. Chem., Int. Ed. Engl.* 1986, *25*, 1099.

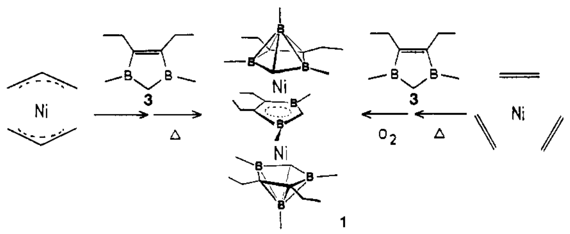
[3] Geiger, W. E.; Connelly, N. G. *Adv. Organomet. Chem.* 1984, *123*, 1; 1985, *124*, 86.

0276-7333/88/2307-2316$01.50/0 © 1988 American Chemical Society

Scheme I



Scheme II



ciple this method affords some experimental insight into the electronic structure of molecules.

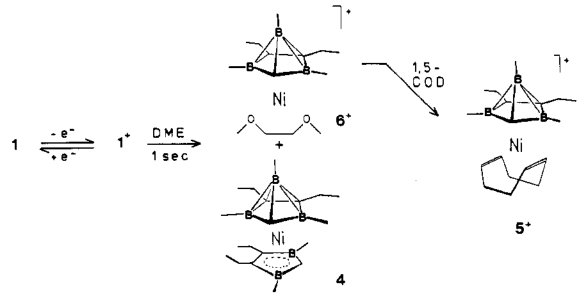
In this paper we describe a combined approach to reversible redox reactions which utilizes electrochemistry and NMR spectroscopy. This combination allows us to correlate the NMR spectra of different redox states, including those of a paramagnetic species. As the paramagnetic NMR spectra are directly dependent on the type of the partly filled orbital, this approach offers additional independent information on the same subject. On the other hand, partly reversible and irreversible redox processes are directly correlated with the reactivity of the redox products.

Oligodecker sandwich complexes have a rich redox chemistry. A detailed investigation on a series of tripledecker compounds of type **2** has been published.[5] A new type of nickel oligodecker sandwich complexes contains terminal η^5-2,3,5-tricarbahexaboranyl and bridging 2,3-dihydro-1*H*-1,3-diborolyl ligands.[6] Qualitative MO considerations support an isolobal relationship[7] between the cyclopentadienyl (C_5H_5) and the capping $C_3B_3R_6$ ligands (Scheme I). The most accessible of the 2,3,5-tricarbahexaboranylnickel oligodecker sandwiches is the dinickel triple-decker **1**,[6] an electronic analogue of **2**.[5] It is our aim to investigate this analogy in order to define its limitations with the methods mentioned above and to use **1** as a potential starting material for the synthesis of new complexes with 2,3,5-tricarbahexaboranyl ligands.

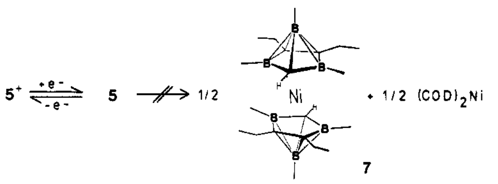
Results

Syntheses and Reactions of 1. The triple-decker **1** was synthesized according to a published procedure[6] from diallylnickel and 1,3-dimethyl-4,5-diethyl-2,3-dihydro-1*H*-1,3-diborole (**3**). Alternatively **1** may be obtained from tris(ethene)nickel[8] and **3**. Treatment of the reaction mixture with some air improves the yield of **1**. In the first step the sandwich Ni(**3**)$_2$ is formed,[6] which by methylboranediyl transfer and stacking yields **1** and higher oligodecker complexes. The mechanism of its formation still has to be clarified (Scheme II).

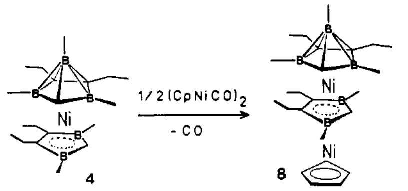
Scheme III



Scheme IV



Scheme V



Oxidation of **1**, either electrochemically by controlled potential electrolysis or by chemical methods using Ag^+ salts, results in the cleavage of **1** to give the (η^5-2,3,5-tricarbahexaboranyl)(η^5-2,3-dihydro-1,3-diborolyl)nickel derivative **4** and the cationic intermediate $\mathbf{6}^+$. The latter may be stabilized by four-electron-donor ligands such as 1,5-cyclooctadiene (COD) with formation of $\mathbf{5}^+$.

If 1,2-dimethoxyethane (DME) is used as a solvent and $AgBF_4$ as the oxidant, **4** and $\mathbf{5}^+BF_4^-$ are obtained in good yield. Separation of both products is simple, as **4** is highly soluble in petroleum ether while $\mathbf{5}^+BF_4^-$ dissolves only in polar solvents. Other four-electron ligands such as 1,2-bis(diphenylphosphino)ethane, cyclopentadiene, and pentamethylcyclopentadiene have also been used. Although **4** was isolated in all cases, we failed to isolate the corresponding complex salts (Scheme III).

Following the isolobal relationship $\mathbf{5}^+$ might be expected to undergo reactions like those of the $[(C_5H_5)Ni(COD)]^+$ cation.[10] Geiger and Lane[11] have reported a disproportion of its 19-valence electron (VE) reduction product at room temperature, and consistent observations have been published by Kölle and Werner.[12]

$$[\mathrm{CpNi(COD)}]^+ \underset{-e^-}{\overset{+e^-}{\Leftrightarrow}} \mathrm{CpNi(COD)} \rightarrow \tfrac{1}{2}\mathrm{Cp_2Ni} + \tfrac{1}{2}\mathrm{Ni(COD)_2}$$

---

[4] Geiger, W. E. In *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum: New York, 1982, Chapter 6, pp 239–268.

[5] Edwin, J.; Bochmann, M.; Böhm, M. C.; Brennan, D. E.; Geiger, W. E.; Krüger, C.; Pebler, J.; Pritzkow, H.; Siebert, W.; Swiridoff, W.; Wadepohl, H.; Weiss, J.; Zenneck, U. *J. Am. Chem. Soc.* **1983**, *105*, 2582.

[6] Kuhlmann, T.; Pritzkow, H.; Zenneck, U.; Siebert, W. *Angew. Chem.* **1984**, *96*, 994; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 965. Siebert, W. *Angew. Chem.* **1985**, *97*, 928; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 925.

[7] Hoffmann, R. *Angew. Chem.* **1982**, *94*, 725; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

[8] Fischer, K.; Jonas, K.; Wilke, G. *Angew. Chem.* **1973**, *85*, 620; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 565.

[9] Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219.

[10] Salzer, A.; Court, T. L.; Werner, H. *J. Organomet. Chem.* **1973**, *54*, 325.

[11] Lane, G.; Geiger, W. E. *Organometallics* **1982**, *1*, 401.

[12] Kölle, U.; Werner, H. *J. Organomet. Chem.* **1981**, *221*, 367.

Table I. Atomic Parameters for 4

atom	x	y	z	$\bar{U}$, Å^2
Ni	0.51973 (4)	0.15610 (4)	0.26569 (3)	0.040
B1a	0.6065 (4)	0.3366 (3)	0.1535 (3)	0.046
C2a	0.6520 (3)	0.3600 (3)	0.2923 (2)	0.043
C3a	0.4717 (3)	0.3116 (2)	0.2249 (2)	0.048
B4a	0.4111 (4)	0.1859 (3)	0.1172 (3)	0.044
C5a	0.5788 (3)	0.1759 (3)	0.1256 (2)	0.050
B6a	0.7294 (4)	0.2700 (3)	0.2360 (3)	0.050
C7a	0.6580 (4)	0.4385 (3)	0.0924 (3)	0.072
C8a	0.7517 (4)	0.4857 (3)	0.3976 (3)	0.065
C9a	0.8396 (5)	0.6164 (3)	0.3804 (3)	0.089
C10a	0.3647 (4)	0.3827 (3)	0.2521 (3)	0.084
C11a	0.3311 (5)	0.4674 (4)	0.1853 (3)	0.134
C12a	0.2344 (4)	0.1194 (3)	0.0173 (2)	0.065
C13a	0.9248 (4)	0.3007 (4)	0.2735 (3)	0.096
B1b	0.5364 (4)	−0.0317 (3)	0.2806 (3)	0.055
C2b	0.6437 (3)	0.0965 (3)	0.3829 (2)	0.054
B3b	0.5315 (5)	0.1458 (3)	0.4296 (3)	0.060
C4b	0.3527 (3)	0.0643 (3)	0.3338 (2)	0.060
C5b	0.3558 (3)	−0.0355 (3)	0.2485 (2)	0.048
C6b	0.5923 (4)	−0.1327 (3)	0.2144 (3)	0.093
C7b	0.5762 (5)	0.2590 (4)	0.5421 (3)	0.094
C8b	0.1960 (4)	0.0862 (3)	0.3320 (3)	0.092
C9b	0.1110 (5)	0.0098 (4)	0.3983 (4)	0.135
C10b	0.2062 (4)	−0.1339 (3)	0.1426 (3)	0.063
C11b	0.1168 (5)	−0.2705 (4)	0.1538 (3)	0.097

In our case, such a sequence would allow the synthesis of bis(η^5-2,3,5-tricarbahexaboranyl)nickel (**7**), a nickelocene analogue. Recently we obtained **7** although in relatively low yield[2] (Scheme IV).

The 19 VE complex **5** is formed quite easily by potassium reduction or electrolysis; however, it is stable for days at room temperature; **7** does not form. ESR spectra of **5** show an axial **g** tensor. The ESR data of **5** ($g_{\parallel}$ = 2.184, $g_{\perp}$ = 2.022) and CpNi(COD) ($g_{\parallel}$ = 2.182, $g_{\perp}$ = 2.025)[11] are nearly identical.

In analogy to the synthesis of **2** from $(C_5H_5)Ni[(EtC)_2(MeB)_2CH]$[5] and $(CpNiCO)_2$, **4** may be used as a starting material for the preparation of the asymmetric triple-decker sandwich complex **8**. Having both types of terminal ligands, cyclopentadienyl and 2,3,5-tricarbahexaboranyl, **8**, links together the complex types **1** and **2**. The reaction proceeds readily, affording a reasonable yield (45%) of green **8** (Scheme V).

X-ray Structures of 4 and 5$^+$BF$_4^-$. A view of the sandwich molecule **4** with the atom numbering is shown in Figure 1. The atom parameters are given in Table I and some important interatomic distances and angles in Table II. The best planes through the basis of the carbaboranyl (maximum deviation 0.06 Å) and the dihydrodiborolyl ring (maximum deviation 0.09 Å) are almost parallel. The two ligands are rotated by ca. 90°; thus the boron atoms are trans to the donor centers (the C=C bonds and the atoms C5a and C2b). The distance from the carbaboranyl basis to the nickel is 1.64 Å with B4a and B6a shifted toward nickel and from the dihydrodiborolyl ring 1.68 Å with B1b and B3b shifted away from the nickel atom. A view of the sandwich cation **5**$^+$ showing the atom numbering is illustrated in Figure 2. Atom parameters are collected in Table III and interatomic distances and angles in Table IV. A projection of the cell down the b axis (Figure 3) shows that the crystal is built up by sheets of cations parallel to the b–c plane with the BF_4^- anions between these sheets. There are no unusually short contacts between atoms of cations and anions. In the cation the best plane through the four carbons of the COD bonded to the nickel (maximum deviation from the plane

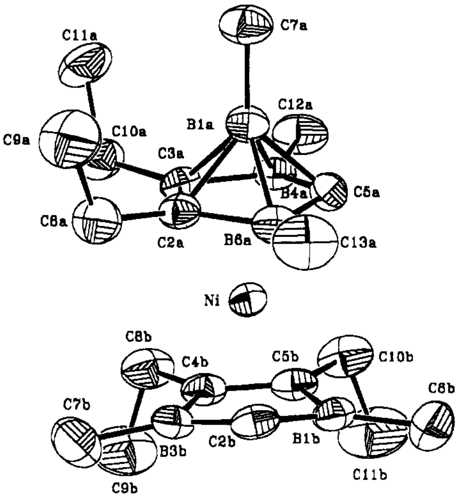


Figure 1. Molecular structure of **4**. The hydrogen atoms have been omitted for clarity.

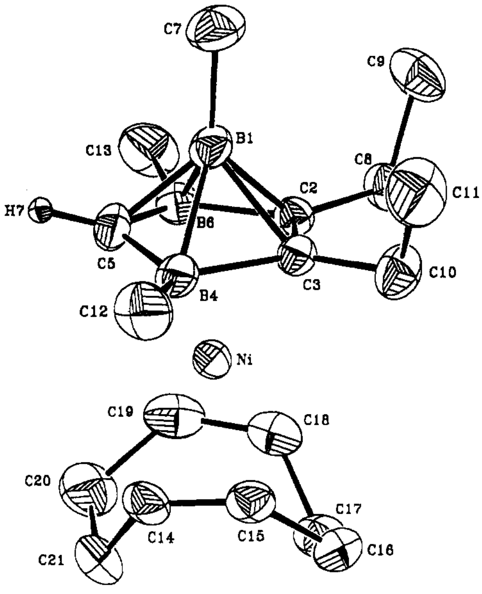


Figure 2. Molecular structure of **5**$^+$. The hydrogen atoms have been omitted for clarity, except H7.

Table II. Selected Bond Distances (Å) and Angles (Deg) for 4

Ni–C2a	2.065 (3)	Ni–C5b	2.060 (3)	C3a–B4a	1.569 (4)
Ni–C3a	2.077 (3)	B1a–C2a	1.729 (4)	B4a–C5a	1.536 (5)
Ni–B4a	2.124 (3)	B1a–C3a	1.734 (5)	C5a–B6a	1.540 (3)
Ni–C5a	2.124 (3)	B1a–B4a	1.822 (4)	B1b–C2b	1.516 (3)
Ni–B6a	2.090 (4)	B1a–C5a	1.655 (5)	B1b–C5b	1.558 (5)
Ni–B1b	2.198 (4)	B1a–B6a	1.815 (5)	C2b–B3b	1.513 (6)
Ni–C2b	2.052 (3)	B1a–C7a	1.566 (5)	B3b–C4b	1.561 (4)
Ni–B3b	2.203 (4)	C2a–C3a	1.468 (3)	C4b–C5b	1.414 (4)
Ni–C4b	2.071 (3)	C2a–B6a	1.574 (5)		
B6a–C2a–C3a	110.7 (1)	C5a–B6a–C2a	101.3 (2)	C4b–B3b–C2b	103.4 (2)
C5a–B4a–C3a	101.3 (1)	C5b–B1b–C2b	103.7 (2)	C5b–C4b–B3b	110.4 (2)
B6a–C5a–B4a	114.9 (2)	B3b–C2b–B1b	110.4 (2)	C4b–C5b–B1b	109.9 (2)

Table III. Atomic Parameters for $5^+BF_4^-$

atom	x	y	z	$\bar{U}$, Å^2
Ni	0.26808 (2)	0.01722 (2)	0.11110 (2)	0.034
B1	0.2446 (2)	0.1147 (2)	0.23080 (17)	0.041
C2	0.17066 (17)	0.08364 (18)	0.15335 (14)	0.035
C3	0.20846 (17)	0.00535 (18)	0.19599 (13)	0.036
B4	0.3145 (2)	0.0151 (3)	0.22174 (17)	0.044
C5	0.33079 (19)	0.1122 (2)	0.19510 (15)	0.046
B6	0.2480 (2)	0.1547 (2)	0.14376 (17)	0.041
C7	0.2274 (3)	0.1663 (2)	0.29574 (18)	0.065
C8	0.0714 (2)	0.0986 (2)	0.12375 (17)	0.050
C9	0.0312 (3)	0.1767 (3)	0.1552 (2)	0.081
C10	0.1555 (2)	−0.0727 (2)	0.21749 (16)	0.049
C11	0.1275 (3)	−0.0536 (3)	0.28408 (19)	0.070
C12	0.3760 (3)	−0.0491 (4)	0.2781 (2)	0.067
C13	0.2324 (3)	0.2513 (2)	0.10622 (19)	0.065
C14	0.2978 (2)	0.0628 (2)	0.01752 (15)	0.050
C15	0.2083 (2)	0.0465 (2)	0.00618 (14)	0.045
C16	0.1597 (2)	−0.0413 (3)	−0.02318 (16)	0.056
C17	0.2118 (3)	−0.1297 (2)	0.00193 (18)	0.063
C18	0.2616 (2)	−0.1229 (2)	0.07742 (17)	0.054
C19	0.3484 (3)	−0.0964 (2)	0.10043 (17)	0.060
C20	0.4106 (2)	−0.0631 (3)	0.0574 (2)	0.079
C21	0.3657 (2)	−0.0004 (3)	−0.00232 (19)	0.070
B	0.5092 (4)	0.2566 (4)	0.0798 (3)	0.080
F1a	0.5908 (7)	0.2274 (7)	0.0837 (7)	0.138
F2a	0.4475 (6)	0.2199 (9)	0.0361 (7)	0.198
F3a	0.5031 (6)	0.2502 (6)	0.1489 (4)	0.168
F4a	0.5098 (6)	0.3553 (3)	0.0659 (3)	0.120
F1b	0.4998 (12)	0.1626 (16)	0.1030 (13)	0.245
F2b	0.4739 (13)	0.2342 (11)	0.0104 (8)	0.152
F3b	0.4575 (14)	0.303 (2)	0.0997 (11)	0.273
F4b	0.5876 (13)	0.2703 (14)	0.0824 (13)	0.166

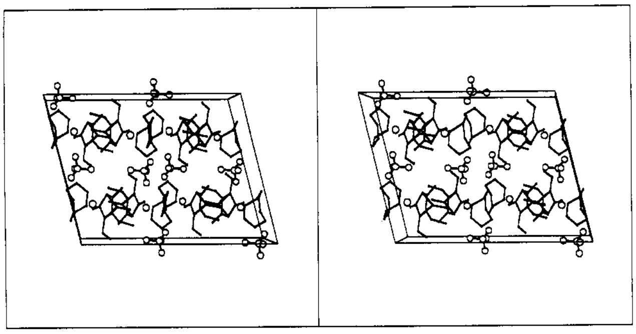


Figure 3. Stereoscopic view of the elemental cell of $5^+BF_4^-$.

0.07 Å) is almost parallel to the plane through the basis of the carbaboranyl (maximum deviation 0.08 Å). The two boron atoms in the basis are shifted toward the nickel, while the carbon C5 is shifted away from the nickel, yielding a dihedral angle between B4–C5–B6 and B4–C3–C2–B6 of 10.6°. The double bonds C14–C15 and C18–C19 in the COD are approximately perpendicular to the double bond in the carbaboranyl, thus yielding the Lewis acidic boron atoms trans to the donor centers. The BF_4^- anion is severely disordered, and the distances and angles for the two sets of fluorine atoms differ very much from the expected values.

The Ni–C and Ni–B distances in both structures lie in the range found for other 18 VE complexes like bis(dicarbollide)nickel,[14] $(C_5H_5)Ni[(EtC)_2(EtB)_2CMe)]$,[15] (CO-

Table IV. Selected Bond Distances (Å) and Angles (deg) for $5^+BF_4^-$

Ni–C2	2.112 (3)	B1–C5	1.647 (5)	C17–C18	1.512 (4)
Ni–C3	2.107 (3)	B1–B6	1.830 (5)	C18–C19	1.362 (5)
Ni–B4	2.138 (3)	B1–C7	1.561 (5)	C19–C20	1.505 (6)
Ni–C5	2.188 (3)	C2–C3	1.441 (4)	C20–C21	1.516 (5)
Ni–B6	2.120 (3)	C2–B6	1.614 (5)	B–F1a	1.311 (12)
Ni–C14	2.116 (3)	C3–B4	1.599 (4)	B–F2a	1.240 (12)
Ni–C15	2.105 (3)	B4–C5	1.529 (5)	B–F3a	1.396 (10)
Ni–C18	2.112 (3)	C5–B6	1.555 (4)	B–F4a	1.442 (8)
Ni–C19	2.087 (4)	C14–C15	1.363 (5)	B–F1b	1.441 (25)
B1–C2	1.738 (4)	C14–C21	1.506 (5)	B–F2b	1.391 (16)
B1–C3	1.749 (4)	C15–C16	1.509 (4)	B–F3b	1.176 (27)
B1–B4	1.822 (5)	C16–C17	1.519 (5)	B–F4b	1.214 (21)
B6–C2–C3	110.7 (2)	C18–C17–C16	112.0 (2)	F4a–B–F1a	105.9 (6)
B4–C3–C2	111.0 (2)	C19–C18–C17	125.1 (3)	F4a–B–F2a	108.7 (7)
C5–B4–C3	102.1 (2)	C20–C19–C18	127.4 (3)	F4a–B–F3a	104.9 (5)
B6–C5–B4	113.9 (2)	C21–C20–C19	113.3 (3)	F3b–B–F1b	107.2 (17)
C5–B6–C2	100.9 (2)	C20–C21–C14	111.7 (3)	F3b–B–F2b	109.0 (12)
C21–C14–C15	126.4 (2)	F2a–B–F1a	118.2 (8)	F4b–B–F1b	108.2 (12)
C16–C15–C14	126.6 (2)	F3a–B–F1a	102.1 (7)	F4b–B–F2b	103.4 (15)
C17–C16–C15	113.2 (2)	F3a–B–F2a	115.9 (8)	F4b–B–F3b	129.9 (16)

Table V. Cyclic Voltammetric Data[a]

compd	couple	$E°$,[b] V	ΔE_p[c]	current ratio[d]	v[e]	solv	electrolyte
1	1−/0	−1.30	61	1	0.2	CH_2Cl_2	Bu_4NPF_6
	0/1+	+0.12	62	1			
	1+/2+	+1.40	*f*				
1	1−/0	−1.05	68	1	0.1	DME	Bu_4NClO_4
	0/1+	+0.40	*f, g*				
1	1−/0	−1.07	170	1.1	5	DME	Bu_4NClO_4
	0/1+	+0.32	140	0.9			
8	1−/0	−1.34	66	1.1			
	0/1+	−0.03	63	1	0.2	CH_2Cl_2	Bu_4NPF_6
	1+/2+	+1.30	67	1			
8	1−/0	−1.12	63	0.7	0.2	DME	Bu_4NPF_6
	0/1+	+0.25	*f, g*				
4	1−/0	−1.47	125	0.9	0.2	DME	Bu_4NClO_4
	0/1+	+0.98	*f*				
$5^+BF_4^-$	0/1+	−0.50	123	1.0	0.2	CH_2Cl_2	Bu_4NPF_6

[a] Data reported for Pt electrodes at room temperature; electrolyte concentration is 0.1 M. [b] Volt vs. aqueous SCE; $E°$ reported for reversible systems; E(peak) reported for irreversible systems. [c] Separation in mV of cathodic and anodic peaks. [d] i_a/i_c for reductions; i_c/i_a for oxidations. [e] Scan rate in V/s. [f] Irreversible. [g] Irreversible in propionitrile/Bu_4NPF_6 too.

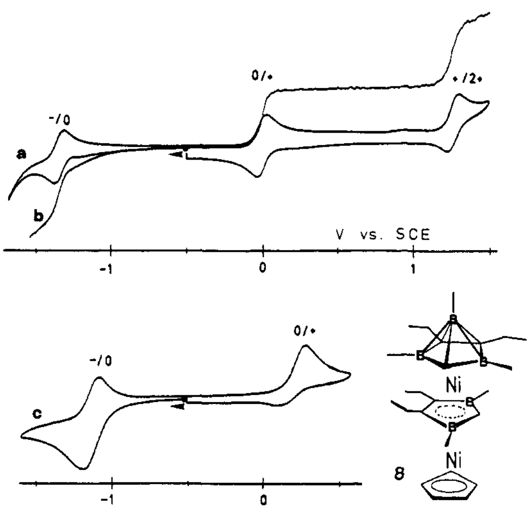


Figure 4. a. Cyclic voltammogram of 8 in $CH_2Cl_2/n\text{-}Bu_4NPF_6/0.2$ V/s; Pt disk electrode. b. Polarogram of the same solution at the RDE. c. Cyclic voltammogram of 8 in $DME/n\text{-}Bu_4NClO_4/0.1$ V/s.

$D)_2Ni$,[16a] $(COT)_2Ni$,[16b] and $(Br)(Ph_3P)Ni(Et_2C_2B_4H_3{}^+\text{-}PPh_3)$[17a] but are significantly shorter than in 20 VE compounds 7[2] and nickelocene.[13] Especially the complex $(C_5H_5)Ni[(EtC)_2(EtB)_2CMe)]$ and 4 show a great similarity emphasizing the analogy between the cyclopentadienyl and the 2,3,5-tricarbahexaboranyl ligands. Howard and Grimes[17b] first described this electronic analogy for the isomeric 2,3,4-tricarbahexaboranyl ligands in tricarbonylmanganese complexes.

The geometry of the carbaboranyl in 5^+ shows small differences compared with other known structures of this ligand in 1, 4, and 7: the bonds C2–B6 and C3–B4 are somewhat elongated (1.60, 1.61 vs 1.56–1.57 Å) and C2–C3 is somewhat shorter (1.44 vs 1.47–1.49 Å). The boron atoms in the basis of the carbaboranyl are shifted in all structures toward the nickel.

Electrochemistry. The compounds were investigated by cyclic voltammetry, polarography at a rotating disk electrode, and controlled potential coulometry. Cyclic voltammetric data suggest that the electron-transfer reactions are very rapid, i.e. electrochemically reversible. In support of this contention, the differences between cathodic and anodic peak potentials of a redox couple, ΔE_p, were generally 60–70 mV at moderate scan rates (0.1–0.2 V/s). Specific data are given in Table V. The represented waves are all one-electron transfers.

Within experimental error, the $E_{1/2}$ values in polarography are the same as the $E°$ values. The diffusion currents are much the same for different redox couples of one species, thus indicating the same number of electrons to be transferred in all cases and the diffusion constants to be nearly independent of the redox state. The determination of the number of the transferred electrons not only is based on electrochemistry but also is supported by spectroscopic monitoring of the redox processes by NMR and ESR. The two triple-deckers 1 and 8 show a closely related redox behavior, which is remarkably dependent on the solvent. A noncoordinating solvent like CH_2Cl_2 leads to the formation of four species, which in the case of 8 are all stable under the conditions of the experiment (Figure 4), while 1^{2+} is a transient species only.

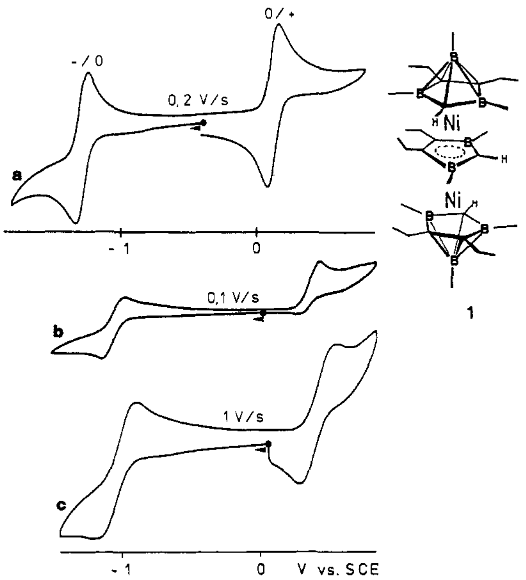


Figure 5. Cyclic voltammograms of 1 at Pt electrodes: a, $CH_2Cl_2/n\text{-}Bu_4NPF_6/0.2$ V/s; b, $DME/n\text{-}Bu_4NClO_4/0.1$ V/s; c, $DME/n\text{-}Bu_4NClO_4/1$ V/s.

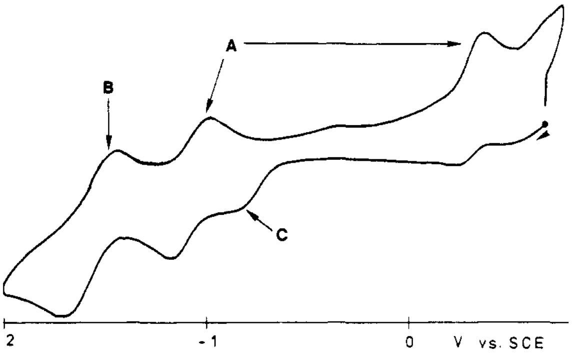


Figure 6. Cyclic voltammogram of 1 in $DME/n\text{-}Bu_4NClO_4/0.5$ V/s; start potential is +0.7 V. Signals A are stemming from 1; for signals B and C, see text.

The same has been observed for the cyclopentadienyl analogue 2; the $E°$ values are much the same[5] (2–/2, –1.31, reversible; $2/2^+$, –0.13, reversible; $2^+/2^{2+}$, +1.26, irreversible). Counting the valence electrons (VE) in these species, we may summarize this redox behavior for the three dinickel triple-decker sandwich complexes 1, 2, and 8.

$$\underset{34\ VE}{NiNi^-} \Leftrightarrow \underset{33\ VE}{NINI} \Leftrightarrow \underset{32\ VE}{NiNi^+} \Leftrightarrow \underset{31\ VE}{NiNi^{2+}}$$

The 34 VE rule[9] is obeyed in all cases; no further reductions are observable up to –2.7 V. Even a potassium mirror in dry THF does not reduce 1^- or 8^-. In propionitrile or DME solutions, the lifetimes of the monocations 1^+ and 8^+ decrease, and at normal scan rates the first oxidations of 1 and 8 are irreversible (Figure 5). Complex 2^+ does not show this effect. Increasing the scan rates allow the observation of reduction waves of the cations 1^+ and 8^+. Within 1 s at room temperature the concentration of the monocations in DME decrease to approximately 50%.

---

(13) Seiler, P.; Dunitz, J. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 2255.

(14) Wing, R. M. *J. Am. Chem. Soc.* **1970**, *92*, 1187.

(15) Siebert, W.; Bochmann, M.; Edwin, J.; Krüger, C.; Tsay, Y. H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1410.

(16) (a) Dierks, H.; Dietrich, H. *Z. Kristallogr.* **1965**, *122*, 1. (b) Gausing, W.; Wilke, G.; Krüger, C.; Liu, L. K. *J. Organomet. Chem.* **1980**, *199*, 137.

(17) (a) Boyter, H. A.; Swisher, R. G.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1985**, *24*, 3810. (b) Howard, J. W.; Grimes, R. N. *Inorg. Chem.* **1972**, *11*, 263. Bramlett, C. L.; Grimes, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 4269. (c) Grimes, R. N. *Pure Appl. Chem.* **1987**, *59*, 847 and references therein.

Table VI. ^{1}H NMR Data of Mixtures 1/1$^-$

f_p[b]	1[a]	2	3	4	5	6	7	8	9/10	11
1.000	71.1	13.0	30.0	62.3	20.4	5.37	20.4	−52.0	−24.7	7.64
0.984	69.8	12.5	29.1	61.1	20.0	5.32	20.0	−51.3	−24.6	7.55
0.862	60.9	11.4	25.6	53.7	18.2	4.72	18.2	−43.6	−20.4	6.68
0.686	47.9	9.59	20.3	42.7	14.6	3.97	14.6	−35.0	−16.2	5.56
0.469	32.3	7.27	14.13	29.85	10.6	3.05	10.00	−23.65	−10.60	4.18
0.325	22.01	5.76	9.90	21.27	7.89	2.42	7.08	−16.21	−6.84	3.24
0.108	6.16	3.46	3.33	7.73	3.70	1.46	3.46	−4.50	−0.98	1.81
0.000	−0.85	2.26	0.44	1.86	1.87	1.03	0.55	0.63	1.61	1.18
integral	6	2	12	4	4	12	1	6	4	6
r[c]	0.9998	0.9993	0.9997	0.9998	0.9995	0.9997	0.9993	0.9995	0.9992	0.9997

[a] For assignments, see Figure 7. [b] Paramagnetic mole fraction: $f_p = 1$, solution contains only 1; $f_p = 0$, solution contains only 1$^-$. [c] Correlation coefficient of the least-squares fit function $\delta = -\delta_p f_p + \delta_d$.[20]

To investigate the fate of 1$^+$, the starting point of the cyclic voltammogram was set beyond the formation of this species and the working electrode was held at that potential for several minutes. The result is presented in Figure 6. Only small amounts of 1 remain in the electrical double layer (A), and two new electroactive species are observable. One shows a reversible reduction at −1.55 V (B) and the other an irreversible reduction at −0.8 V (C). Species B was identified as complex 4 while C is believed to be the cationic (tricarbahexaboranyl)nickel dimethoxyethane complex 6$^+$. In order to prove this assumption, we conducted the oxidation as a controlled potential electrolysis at +0.54 V under coulometric control. Stabilization of the labile complex 6$^+$ was achieved by the addition of 1,5-COD to replace DME. 1,5-COD is a good ligand to stabilize the cyclopentadienylnickel cation fragment,[10] but it does not attack 1$^+$ effectively in noncoordinating solvents.

Progress of the reaction was monitored by cyclic voltammetry. In this manner we observed the exclusive formation of 4 and 5$^+$ out of 1, whereby one electron is transferred per molecule of 1. 4 may be extracted by petroleum ether after the removal of DME, but 5$^+$PF$_6^-$ could not be separated from the supporting electrolyte. Electrochemical reduction of 5$^+$ to form the stable radical 5, extraction with petroleum ether, and ESR spectroscopy of this species gave clear evidence of the proposed reaction sequence. On the basis of these results the preparative oxidation of 1 by AgBF$_4$ was developed. This eliminated the problem of separating a complex salt from the supporting electrolyte.

Electrochemistry of the two mononuclear complexes 4 and 5$^+$ points out the reversible formation of the two 19 VE complex radicals 4$^-$ and 5 (Table V). 4$^-$ is not stable enough to be characterized by ESR. The same is true for its analogue, the [cyclopentadienyl(tetraethylmethyl-2,3-dihydro-1,3-diborolyl)nickel] anion, which is formed at −1.74 V in acetonitrile from its neutral precursor. The $E°$ value of the redox couple [CpNi(COD)]$^+$/CpNi(COD) is −0.46 V in CH$_2$Cl$_2$.[11,12]

NMR Spectroscopy. If radicals show rapid electron relaxation, NMR spectroscopy is a useful tool for investigations, while ESR signals are difficult to obtain. This condition is fulfilled for the triple-deckers 1, 2, and 8. We failed to obtain ESR spectra, but NMR spectra are of good quality. According to the 34 VE rule for triple-decker complexes,[9] the reduction of 1 and 8 should lead to diamagnetic complex anions. This has been proven for two derivatives of 2.[18,19] If we correlate paramagnetic and diamagnetic NMR spectra of 1 and 8 with 1$^-$ and 8$^-$, respectively, we are able to assign the paramagnetic spectra, a nontrivial matter otherwise. The differences in the δ values of the paramagnetic and the diamagnetic line positions represent the paramagnetic shifts δ_p. These paramagnetic shifts are dependent on the electronic structures of the HOMO's of the radicals;[20] thus similarities or differences between the paramagnetic shifts of equivalent nuclei serve to illuminate electronic relations between molecules of the same electron count and the same principal structure.

Table VII. ^{1}H NMR Data of Mixtures 8/8$^-$

f_p[b]	1[a]	2	3	4	5	6	7	8	9	10	11	12
1.000	67.0	4.20	30.8	64.9	19.2	4.28	13.50	−55.1	13.40	−40.9	8.76	−56.2
0.675	44.5	3.20	20.8	44.5	13.54	3.22	9.30	−36.5	9.29	−26.93	6.27	−36.5
0.250	16.7	2.58	8.24	18.05	6.34	1.89	3.97	−13.9	4.47	−9.20	3.13	−10.90
0.000	−0.88	2.20	0.42	1.44	1.83	1.06	0.55	0.50	1.44	1.83	1.18	4.88
integral	3	1	6	2	2	6	1	6	2	2	6	5
r[c]	0.9993	0.9668	0.9992	0.9993	0.9993	0.9993	0.9993	0.9994	0.9996	0.9992	0.9992	0.9992

[a] For assignments, see Figure 8. [b] Paramagnetic mole fraction: $f_p = 1$, solution contains only 8; $f_p = 0$, solution contains only 8$^-$. [c] Correlation coefficient of the least-squares fit function $\delta = -\delta_p f_p + \delta d$.[20]

Solutions of 1 and 8 in deuteriated THF were prepared with a potassium mirror in a sealed NMR sample tube. Spectra of solutions that had no contact with the potassium show only the signals for the paramagnetic neutral complexes. Short contact between the potassium mirror and the solution leads to stepwise reduction, and mixtures with increasing fractions of the diamagnetic anions are produced until the reaction stops with the complete conversion of the sample. These diamagnetic spectra of 1$^-$ or 8$^-$ are easily assigned. No further reduction is observed, but 8$^-$ decomposes slowly in the presence of potassium and C$_5$H$_5^-$K$^+$ is formed. The same observation was made with 2$^-$, but 1$^-$ is absolutely inert; no carbaboranyl anion, C$_3$B$_3$R$_6^-$, is formed this way. In all cases the ^{1}H NMR spectra show only one signal for each set of nuclei (Tables VI and VII). Rapid electron exchange between the neutral complexes and their anions takes place which averages the signals of both species. Consequently linear correlations are found for the plots δ versus f_p, the paramagnetic mole

---

(18) Köhler, F. H.; Zenneck, U.; Edwin, J.; Siebert, W. *J. Organomet. Chem.* **1981**, *208*, 137.

(19) Siebert, W. In *Transition Metal Chemistry*; Müller, A., Diemann, E., Eds.; Verlag Chemie: Weinheim FRG, 1981; p 157.

(20) LeMar, G. N., Horrocks, W., Jr., Holm, R. H., Eds. *NMR of Paramagnetic Molecules*; Academic: New York. 1973.

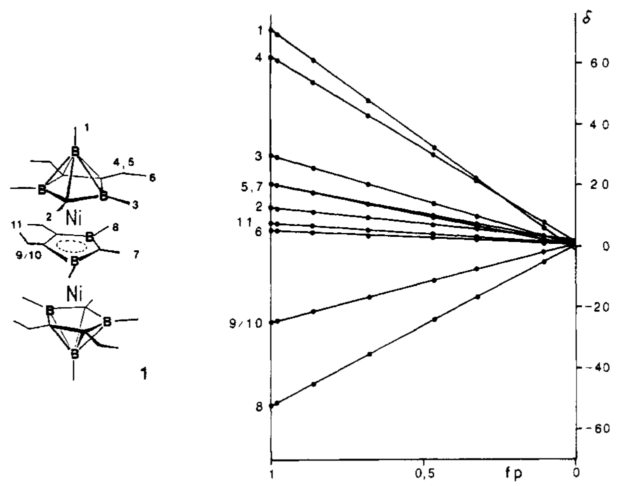


Figure 7. Correlation diagram for ^1H NMR signals of mixtures $1/1^-$: $f_p = 0$, 1^-; $f_p = 1$, 1. For data, see Table VI.

Table VIII. ^1H NMR Paramagnetic Shifts δ_p of 1, 2, and 8

complex	1[a]	2	3	4	5	6
1	-72.2[b]	-10.6	-29.4	-60.5	-18.7	-4.4
2[c]						
8	-67.6	-1.9	-30.7	-63.3	-17.3	-3.2
complex	7[a]	8	9	10	11	12
1	-19.7	52.6	26.4		-6.5	
2[c]	-7.0	57.7	14.8		-7.6	52.6
8	-12.9	55.3	-11.9	42.6	-7.6	61.0

[a] Numbering of H analogous to 8. [b] Least-squares fit data of the function $\delta = -\delta_p/f_p + \delta_d$;[20] positive values of δ_p represent high field shift (see Tables VI and VII). [c] For data, see ref 5.

fraction (Figures 7 and 8). Linear regression[21] proves nearly perfect linearity (Tables VI and VII). The negative slopes of the linear functions represent the regression values of the paramagnetic shifts δ_p. A comparison of the paramagnetic shifts of 1, 2, and 8 is presented in Table VIII.

The result is striking: the shift directions of equivalent nuclei are identical in all cases. The methylene protons 9 and 10 of the central ring of 8 are no exception. If we average both δ_p values, we yield nearly exactly the same value as for 2 (δ_p(average) 15.5). The splitting of set 9 and 10 to different shifts directions, which is impossible for 1 and 2 because of higher symmetry, indicates complex spin transfer mechanisms. The pseudocontact part of δ_p[20] can be ruled out as the reason for this finding. The methylene groups rotate free in the NMR time scale, and both protons have nearly the same orbits. Thus their average distance and angle in respect to the paramagnetic centers, most probably the nickel atoms, are the same. If we compare the numerical δ_p values, most of them are close to each other with the exception of the two sets 2 and 7. These positions have the closest contacts with the metals; thus any influence of the pseudocontact term has a maximum at these positions.

To summarize the NMR results we can state the following. The assignments of all signals are straightforward. Electron relaxation time is very short. Electron exchange between neutral complexes and anions is rapid; thus both redox states represent closely related structures. The same type of MO plays the role of the HOMO in all three cases, 1, 2, and 8, and the differences are small. There is no sign of inequivalence for the two ends of the symmetrical species 1 and 2, in spite of these being mixed-valence

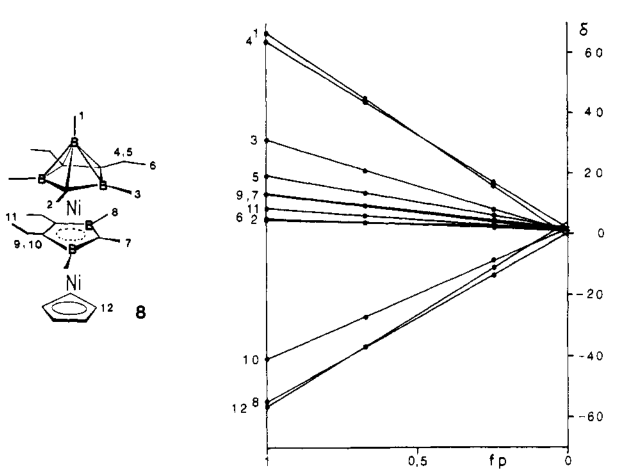


Figure 8. Correlation diagram for ^1H NMR signals of mixtures $8/8^-$: $f_p = 0$, 8^-; $f_p = 1$, 8. For data, see Table VII.

compounds. Thus the unpaired electron is delocalized over the whole molecule on the NMR time scale. The 34 VE rule is fulfilled strictly, and the complex anions are all closed-shell compounds.

Discussion

All methods that are sensitive to electronic structures—electrochemistry, ESR, and paramagnetic NMR spectroscopy—clearly point out the very close relationship between the cyclopentadienyl complexes and their 2,3,5-tricarbahexaboranyl analogues. The number of redox states for both groups of compounds, 1, 4, 5 versus 2, cyclopentadienyl(tetraethylmethyl-2,3-dihydro-1,3-diborolyl)nickel, and [(C_5H_5)Ni(COD)], respectively, are identical. Their redox potentials are the same within ±0.2 V, and the similarities of the ESR and paramagnetic NMR data have been mentioned already. As a result we not only have shown the isolobal relationship between the 2,3,5-tricarbahexaboranyl and the cyclopentadienyl ligands but also have established that the energies of the MO's involved in the metal–ligand bonding are nearly identical.

Differences occur only if kinetic factors come into play. Thus 1^+ and 8^+ are attacked rapidly by a hard base like DME, which does not cleave 2^+. From the steric point of view, the nickel atoms of 2^+ are relatively open to attack from any approaching base, while the alkyl substituents of the 2,3,5-tricarbahexaboranyl should shield the metals of 1^+ much more effectively. The existence of such a steric effect is proven by the inhibition of the direct attack of COD on 1^+.

The chemistry of 1^+ resembles that of the well-known 34 VE triple-decker $Cp_3Ni_2^+$ cation of Werner and Salzer.[22] However, cleavage of $Cp_3Ni_2^+$ leads to the 20 VE sandwich nickelocene and the 18 VE complexes $CpNiL_2^+$, while 32 VE 1^+ yields two 18 VE species upon reaction with ligands. In other cases the 2,3,5-tricarbahexaboranyl ligand can stabilize a complex relative to its cyclopentadienyl analogue, which is shown by the stability of 8^{2+} and 5, while the corresponding complexes 2^{2+} and [(C_5H_5)Ni(COD)] decompose much quicker. It should be mentioned that the stability of [(C_5H_5)Ni(COD)] is supposed to bery high,[11] which emphasizes the stability of 5. Also, the C_2B_4 ligand, as the C_3B_3, stabilizes transition-metal-organometallic complexes, as Grimes has pointed out.[17c] Further reaction is remarkably different in both groups of compounds. 2^-

---

(21) Fix, B. NMR Correlation Program, Heidelberg, 1986.

(22) Werner, H.; Salzer, A. *Synth. Inorg. Met.-Org. Chem.* **1972**, *2*, 239. Salzer, A.; Werner, H. *Angew. Chem.* **1972**, *84*, 949; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 930.

and 8^- are attacked by potassium, and $C_5H_5^-K^+$ is formed. This is a general property of metallocenes whose utility has been demonstrated by Jonas.[23] The tricarbahexaboranyl anion should be stable too, but its formation is not observed this way.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of purified and dried nitrogen or argon by using Schlenk-type glassware. The solvents for preparative use were dried by standard methods, distilled from potassium/benzophenone ketyl, and kept under nitrogen. Microanalyses were performed by the microanalysis laboratory of the Chemische Institute der Universität Heidelberg.

Spectral measurements: ^1H NMR (δ, Me_4Si), Brüker AC 200, Bruker WH 300, and Bruker WX 360; ^{11}B NMR (δ, $BF_3 \cdot OEt_2$), JEOL FX-90 Q, Bruker AC 200; X-band ESR, Varian E3, standard LiTCNQ; MS, MAT CH7 (EI), MAT 711 /FD (Universität Marburg).

Electrochemical equipment: Princeton Applied Research (PAR) Model 173 potentiostat, Model 179 digital coulometer, Model 175 function generator; Methrom electrochemical cell; Methrom rotating disk electrode (RDE) for polarography and for cyclic voltammetry (without rotating). Otherwise self-constructed platinum electrodes (wires 5 mm long, 0.5 mm diameter) were used. Bulk coulometry: PAR two-compartment cell M 377a with a stirring motor and Pt net electrodes. Reference electrodes: self-constructed SCE, Methrom SCE, and Methrom Ag/Ag^+ electrode (0.01 N $AgNO_3$ in propionitrile or acetonitrile). Moderate sweep rate cyclic voltammograms were recorded on a Houston Instruments Series 2000 x-y recorder and rapid scan rate data on a Hameg HM 208 two-channel digital storage oszilloscope which is connected with a Commodore 8032 SK microcomputer by an IEC-Bus and an Itoh CX-6000 plotter.

Electrochemical Procedures. Purifications of electrolytes and solvents are done under nitrogen, and the measurements are performed under argon. n-Bu_4NClO_4 is made from n-Bu_4NBr (Fluka, puriss) and $HClO_4$. The precipitated product is washed by cold water until all HBr is eliminated, recrystallized three times from EtOH/petroleum ether (1:4), and recrystallized finally from DME/petroleum ether (1:1). After 20 h at 100 °C (1 Pa) the material is dry. n-Bu_4NPF_6 (Fluka, purum) is recrystallized three times from refluxing EtOH (absolute). n-Bu_4NBF_4 (Fluka, puriss) is recrystallized three times from EtOH (absolute)/petroleum ether (1:4). Both are dried at 100 °C for 20 h in vacuo. CH_2Cl_2 (Merck, p.a.) is fractionated three times over $CaCl_2$ and stored over molecular sieves (4 Å). DME (Aldrich, 99%) is refluxed over K/Na alloy until the solvent turns blue in the cold and fractionated again. Propionitrile (Fluka, 98%) is refluxed over CaH_2 for a day, stored another day over highly activated Al_2O_3 neutral (activated at 280 °C (1 Pa)/2 days) and distilled into the storage flask. Freshly prepared solutions of the electrolytes are stored over activated Al_2O_3 in grease-free Schlenk tubes that are closed by Teflon valves. The electrochemical cells are rinsed with EtOH and acetic acid methyl ester and are stored at +60 °C. Prior to the measurements dry argon is blown through the warm cells. The glass parts of the cells are heated to more than 100 °C for several minutes. After cooling, the electrodes are set into the cell in a stream of argon. The RDE is polished before use with Al_2O_3 powder, and platinum wire electrodes are heated in a flame. If wide electrochemical windows are required, the cell is washed twice with the solvent/electrolyte. If the compounds are not absorbed by activated alumina, that material may be added to the solution. The measurements start with the iR compensation and determination of the width of the electrochemical window. If these cyclic voltammograms are stored in the computer, they may be subtracted from the experimental curves by using a smoothing program which has been proven helpful.[24]

X-ray Structure Determination. Structure Determination of 4. Cell parameters and intensities were measured with a Syntex R3 diffractometer from a crystal sealed in a glass capillary. An empirical absorption correction was applied. The structure was solved by the heavy-atom method and refined by least squares with weights $w = 1/\sigma_F^2$. Hydrogen atoms could be located in difference Fourier maps and were isotropically refined, and all other atoms were anisotropically refined.

Table IX. Summary of Crystal Data

	$5^+BF_4^-$	4
formula	$C_{18}H_{32}B_4F_4Ni$	$C_{19}H_{37}B_5Ni$
M_r	426.4	378.3
cryst system	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$
cell parameters		
a, Å	15.418 (2)	9.055 (3)
b, Å	14.331 (3)	11.140 (4)
c, Å	19.809 (5)	13.406 (4)
α, deg	90	103.36 (3)
β, deg	103.78 (2)	105.61 (2)
γ, deg	90	109.91 (3)
cell vol V, Å^3	4250.9	1144.1
molecules/cell	$Z = 8$	$Z = 2$
d(calcd), g cm^{-3}	1.33	1.10
radiatn	Mo Kα, $\lambda = 0.7107$ Å, graphite monochromator	
2θ limit, deg	6–60	3–60
hkl limits	21,19,±27	13,±16,±19
scan mode	ω scan	$\theta/2\theta$ scan
scan speed, deg min^{-1}	1	variable (2.5–29.3)
no. of measd reflctns	5112	3031
no. of obsd reflctns	4286 ($I > \sigma_I$)	3031 ($I > 2\sigma_I$)
cryst size	0.47 × 0.40 × 0.08 mm	0.67 × 0.40 × 0.13 mm
absorptn factor, cm^{-1}	μ(Mo Kα) = 9.5	μ(Mo Kα) = 8.5
transmissn factor	0.68 < T < 0.93	(empirical absorptn correctn)
final residuals	$R = 0.056$ $R_w = 0.048$ ($w = \sigma_F^{-2}$)	$R = 0.034$ $R_w = 0.030$ ($w = \sigma_F^{-2}$)
no. of variables	423	374

Structure Determination of $5^+BF_4^-$. Green, platelike crystals were sealed in glass capillaries for diffraction studies. The cell parameters were determined by precession photographs and refined with the indexed lines of a Guinier photograph (Cu Kα_1 radiation, $\lambda = 1.54051$ Å). Intensity data were measured with a STOE Weissenberg diffractometer and corrected numerically for absorption. The structure was solved by the heavy-atom method and refined by the least-squares method with weights $w = 1/\sigma_F^2$. The BF_4^- anion is disordered, and two sets of four F atoms were found and refined. Non-hydrogen atoms were refined anisotropically. All hydrogens besides those of one methyl group (which was treated as a rigid group with C–H = 0.95 Å) could be located and were refined isotropically. The SHELX-76[25] program system was used. Atomic scattering factors were those given by Cromer and Mann,[26] anomalous dispersion factors were taken from ref 27.

(μ-η^5-1,3-Dimethyl-4,5-diethyl-2,3-dihydro-1,3-diborolyl)-bis[(η^5-1,4,6-trimethyl-2,3-diethyl-2,3,5-tricarbahexaboranyl)nickel] (1). Toluene solutions of $Ni(C_2H_4)_3$[8] are prepared according to the Timms procedure from nickel/toluene cocondensation products.[28] The synthesis of the ligand **3** has been published.[5,29] **3** (0.8 g, 5.4 mmol) in 20 mL of toluene and 3.2 mL of a solution of $Ni(C_2H_4)_3$ in toluene (1.9 mmol, determined by reaction with $P(OCH_3)_3$ or COD) are stirred in the temperature range of −80 to +20 °C within 1 h. After 1 h of refluxing, the solvent is removed in vacuo and the residue is heated to 180 °C for 1 h, while some air is used to oxidize the mixture partly. The color turns from dark brown to green. **1** is the only product which is isolable by sublimation at 70 °C (1 Pa): yield 150 mg (0.25

---

[23] Jonas, K. *Angew. Chem.* **1985**, *97*, 292; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295.

[24] Fix, B. Cyclic Voltammogram Program, Heidelberg, 1986.

[25] Sheldrick, G. M. SHELX76, A Program for Crystal Structure Determination, Cambridge, 1976.

[26] Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968** *A24*, 321.

[27] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, 1974; Vol. IV, p 149.

[28] Atkins, R. M.; Mackenzie, R.; Timms, P. L.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* **1975**, 764.

[29] Siebert, W.; Ender, U.; Herter, W. *Z. Naturforsch.* **1985**, *40B*, 326.

mmol; 18%); mp 81 °C. Anal. Calcd for $C_{29}H_{57}B_8Ni_2$ (609.8): C, 57.13; H, 9.42. Found: C, 57.21; H, 9.69. For spectroscopic data, see ref 2.

(η^5-1,4,6-Trimethyl-2,3-diethyl-2,3,5-tricarbahexaboranyl)(η^5-1,3-dimethyl-4,5-diethyl-2,3-dihydro-1,3-diborolyl)nickel (4) and (η^5-1,4,6-Trimethyl-2,3-diethyl-2,3,5-tricarbahexaboranyl)(1,5-cyclooctadiene)nickel Tetrafluoroborate ($5^+BF_4^-$). 1 (70 mg, 0.11 mmol) and 1.3 g (12 mmol) of 1,5-cyclooctadiene in 10 mL of DME are treated dropwise with a dilute solution of $AgBF_4$ in DME until the color changes from green to red-brown. The mixture is filtered, and the solvent is removed in vacuo. Addition of 20 mL of low-boiling petroleum ether allows the extraction of 4 which is purified by distillation at 65 °C (1 Pa) and recrystallization: yield 25 mg (0.06 mmol; 60%); mp 47 °C. Anal. Calcd for $C_{19}H_{37}B_5Ni$ (378.3): C, 60.33; H, 9.86. Found: C, 59.76; H, 9.45. For spectroscopic data of 4, see ref 2.

The residue is dissolved in 1 mL of THF, and $5^+BF_4^-$ is precipitated by the addition of petroleum ether. Recrystallization from DME yields 35 mg of $5^+BF_4^-$ (0.08 mmol, 75%): ^1H NMR (CD_3NO_2) δ -0.12 (s, 3, B-CH_3 apex), 0.42 (s, 6, B-CH_3 basal), 1.32 (t, 6, CH_2CH_3), 2.6 (m, 2, CH_2-CH_3), 2.7 (m, 8, CH_2 (COD)), 2.9 (m, 2, CH_2-CH_3), 5.03 (m, 4, CH (COD)), 5.53 (s, 1, CH); ^{11}B NMR (64.17 MHz, CD_3NO_2) δ 6.3 (br), 1.8 (s, BF_4); FD mass spectrum, *m/z* (relative intensity) 339 (M^+, 100). Anal. Calcd for $C_{18}H_{32}B_4F_4Ni$ (426.4): C, 50.7; H, 7.56. Found: C, 50.9; H, 7.76.

(μ-η^5-1,3-Dimethyl-4,5-diethyl-2,3-dihydrodiborolyl)(η^5-1,4,6-trimethyl-2,3-diethyl-2,3,5-tricarbahexaboranyl)nickel(η^5-cyclopentadienyl)nickel (8). 4 (80 mg, 0.2 mmol) and 65 mg (0.22 mmol) of $[(C_5H_5)Ni(CO)]_2$ are refluxed in toluene for 3 h. Chromatography on silica gel/petroleum ether and distillation at 100 °C (1 Pa) yield 60 mg (0.12 mmol, 60%) of 8 as a green oil. FD mass spectrum: *m/z* (relative intensity) 502 (M^+, 100), no fragmentation. EI mass spectrum (70 eV): *m/z* (relative intensity) 378 (4^+, 20); 148 (tricarbahexaboranyl(1+), 100); 123 ($CpNi^+$, 12). NMR data and assignments, see Tables VII and VIII.

Acknowledgment. This research was supported by the Deutsche Forschungsgemeinschaft, by the Fonds der Chemischen Industrie and the BASF AG, and by generous grant from the Stiftung Volkswagenwerk. We are grateful to Dr. K. Steinbach (Marburg) and Dr. R. Geist for recording the mass spectra, Dr. P. Kunzelmann and Mrs. G. Rissmann for recording the NMR spectra, and Mr. R. Gänzler for performing elemental analyses.

Registry No. 1, 93782-60-6; 1^-, 116663-32-2; 1^+, 116663-33-3; 3, 81620-71-5; 4, 93782-63-9; 4^-, 116634-57-2; 5, 116634-58-3; 5(BF_4), 116634-53-8; 8, 116634-54-9; 8^-, 116663-34-4; 8^+, 116634-55-0; 8^{2+}, 116634-56-1; $Ni(C_2H_4)_3$, 50696-82-7; $[(C_5H_5)Ni(CO)]_2$, 12170-92-2.

Supplementary Material Available: Tables of atom parameters (with anisotropic thermal parameters and parameters for hydrogen atoms), a complete list of distances and angles, and tables of the best planes (13 pages); listings of structure factors (18 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, and Reactions of (1-Ethoxyethyl)zirconocene Chloride, a Stable Acyclic Secondary Zirconocene Alkyl

Stephen L. Buchwald,* Ralph B. Nielsen, and John C. Dewan

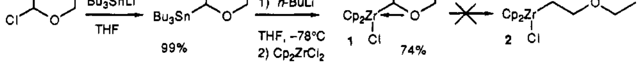
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received March 18, 1988

The title compound 1 ($Cp_2Zr(Cl)CH(CH_3)OCH_2CH_3$, Cp = η^5-C_5H_5) has been prepared in good yield by treatment of Cp_2ZrCl_2 with (1-ethoxyethyl)lithium. Compound 1 is the first example of a stable, structurally characterized secondary zirconocene alkyl derivative which shows no tendency to rearrange to the primary alkyl derivative at room temperature. Carbon monoxide and isocyanides react with 1 to give migratory insertion products without rearrangement of the 1-ethoxyethyl fragment. At high temperatures, 1 decomposes to give ethylene and $Cp_2Zr(Cl)OCH_2CH_3$, the same products obtained at ambient conditions from the reaction of Cp_2ZrHCl (Schwartz's reagent) with ethyl vinyl ether.

Hydrozirconation[1] of olefins using Cp_2ZrHCl (Schwartz's reagent) is a well-studied organometallic reaction. A distinctive feature of the hydrozirconation of acyclic olefins is that only primary alkylzirconocene products are observed. The absence of stable secondary alkyls is due both to the greater thermodynamic stability of the primary zirconocene alkyls and to the ease of the β-hydride elimination/hydrozirconation processes which migrate the Cp_2ZrCl fragment to the primary position.[1a] We now report the preparation and X-ray crystal structure of an acyclic secondary alkyl zirconocene chloride stabilized by an α-alkoxy substituent which acts as a ligand for the metal center.

Scheme I



Compound 1, (1-ethoxyethyl)zirconocene chloride, was synthesized in 74% yield (Scheme I) by treatment of Cp_2ZrCl_2 with (1-ethoxyethyl)lithium. The lithium reagent[2] was readily obtained from *n*-butyllithium and (1-

---

[1] (a) Schwartz, J.; Hart, D. W. *J. Am. Chem. Soc.* 1974, *96*, 8115. (b) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* 1976, *15*, 333. (c) Negishi, E.; Takahashi, T. *Aldrichchim. Acta* 1985, *18*, 31 and references therein. (d) Buchwald, S. L.; LaMaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* 1987, *28*, 3895.

[2] Still, W. C. *J. Am. Chem. Soc.* 1978, *100*, 1481.

0276-7333/88/2307-2324$01.50/0 © 1988 American Chemical Society