ppm since the magnitudes of these shifts are in the range that is normally observed for terminal carbonyls bound to iron in a neutral cluster.[23] Of the three remaining sets of signals, carbonyl g is assigned to the signal of area 1 at 169.9 ppm. Since axial carbonyls in this type of cluster tend to have chemical shifts at lower field than equatorial carbonyls,[23] carbonyls h are assigned to the signal of area 2 at 174.6 ppm and carbonyls d are assigned to the signal of area 2 at 173.4 ppm. Variable-temperature ^{13}C NMR spectra of $(\mu\text{-H})_2Os_3Fe(CO)_{13}$, recorded from –60° to 70 °C, are consistent with those reported for $(\mu\text{-H})_2Ru_3Fe(CO)_{13}$.[22] The three distinct fluxional processes suggested for $(\mu\text{-H})_2Ru_3Fe(CO)_{13}$[22] are probably also operative in the case of $(\mu\text{-H})_2Os_3Fe(CO)_{13}$.

Acknowledgment. This work was supported by the National Science Foundation through Grants CHE80-23448 (M.R.C.) and CHE79-18148 (S.G.S.).

Registry No. $(\mu\text{-H})_2Os_3Fe(CO)_{13}$, 12563-74-5; $(\mu\text{-H})_2Os_3(CO)_{10}$, 41766-80-7; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: Listings of anisotropic thermal parameters (Table IIS), least-squares planes, and observed and calculated structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
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Comparison of the Redox Properties of Small Metallacarboranes with Those of Metallocenes and Large Metallacarborane Clusters

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Received September 25, 1981

Electrochemical data on six iron or cobalt metallacarborane clusters containing 5–7 vertices are presented. Cobalt compounds of the type $CpCo(C_2B_4H_6)$ undergo one oxidation and two reductions, all involving one electron. Only the first reduction, involving Co(II)/Co(I), is completely reversible. The *nido*-cobaltaborane $2\text{-}CpCoB_4H_8$ undergoes a reversible reduction to a Co(II) monoanion. $1,2,3\text{-}CpFe(C_2B_4H_6)$, isoelectronic with Cp_2Fe^+, is reversibly reduced to formal Fe(II) about 0.8 V negative of the metallocene wave; it also undergoes a one-electron oxidation, although that process is irreversible. Detailed comparison of $E°$ values for metallacarboranes and metallocenes supports the isoelectronic analogy between the two sets of compounds. Compared to their larger metal dicarbollide analogues, the small clusters stabilize high metal oxidation states and destabilize low oxidation states.

Electrochemical studies on metallacarborane clusters have proven to be a valuable probe for the understanding of metal oxidation states in these compounds. Hawthorne and coworkers have reported $E°$ potentials for a large number of metallocarboranes. These and related investigations, which have recently been reviewed,[1] have dealt exclusively with large clusters containing nine or more vertices. In this paper we report the results of an electrochemical investigation of six small metallacarboranes and metallaboranes (**1**–**6**; Figure 1) and compare their behavior with that of the electronically similar metallocenes and larger metallacarboranes.[2]

Electrochemical Methodology and Criteria for Reversibility

Each of the compounds was studied in at least two solvents (usually acetonitrile and dichloromethane) at both mercury and platinum electrodes. This gave a range from about +2.0 to about –2.8 V to search for oxidation or reduction processes. All compounds were investigated by dc polarography, cyclic voltammetry, and, in some cases, phase-selective ac polarography. Polarographic waves were tested for diffusion control by plotting the limiting plateau current against the square root of the mercury column height. Similarly, cyclic voltammetry (CV) measurements always included plots of peak current (i_p) as a function of the square root of the scan rate. Straight lines showed that each redox process studied was diffusion controlled.

Each wave observed was a one-electron process. This was shown by comparison of the diffusion current constant, I,[5] with that of the one-electron wave of $Cp_2Co^{+/0}$ in the appropriate solvent and by comparison of the CV peak currents with those of Cp_2Co^+ or Cp_2Fe at the same scan rate. Plots were made of $-E$ vs. $\log\,[i/(i_d - i)]$, and slopes of the linear plots were about 60 mV, typical of a reversible one-electron wave. Couples that are simply designated as reversible also displayed ΔE_p values of no greater than 65 mV at slow CV scan rates (ca. 50 mV/s) and had anodic to cathodic current ratios of about 1 at similar scan rates. Deviations from this behavior are pointed out. A fuller description of the voltammetric measurements is available.[6]

Cobaltacarboranes

In **1**–**3**, the cobalt atom may be viewed as being in a +3 oxidation state, since the CpCo moiety is bonded to a $C_2B_4H_6^{2-}$ (or $C_2B_4H_4(CH_3)_2^{2-}$) ligand. Therefore these compounds are isoelectronic with cobaltocenium ion, Cp_2Co^+. This analogy between metallacarboranes and metallocenes was first proposed by Hawthorne[7] and, in at least a qualitative sense, has stood the test of many experimental and theoretical probes over the last 15 years.[8–14] The three cobaltacarboranes are each re-

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[1] Geiger, W. E. In "Metal Interactions with Boron Clusters"; Grimes, R. N., Ed.; Plenum Press: New York, in press.

[2] Preliminary data on **1** and **2** were previously reported as part of a study ancillary to the investigation of triple-decker sandwich compounds.[3]

[3] Brennan, D. E.; Geiger, W. E. *J. Am. Chem. Soc.* **1979**, *101*, 3399.

[4] All potentials are reported vs. the aqueous saturated calomel electrode.

[5] $I = 706nD_o^{1/2} = i_d/Cm^{2/3}t^{1/6}$ (where n = number of electrons transferred, D_o = diffusion coefficient of electroactive species, C = bulk concentration, m = mercury flow rate, t = mercury capillary drop time).

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0020-1669/82/1321-1963$01.25/0

Table I. Redox Potentials[a,b] of Metal–Boron Clusters and Selected Metallocenes

(a) Cobalt Compounds

	Co(IV)/Co(III)	Co(III)/Co(II)	Co(II)/Co(I)	ref
1,2,3-$CpCo(C_2B_4H_6)$ (**1**)	+1.52[c]	−1.62	−2.50 (irrev)	this work
1,2,4-$CpCo(C_2B_4H_6)$ (**2**)	+1.70[c]	−1.43	<−2.75	this work
1,2,3-$CpCo\{C_2B_4H_4(CH_3)_2]$ (**3**)	+1.43[c]	−1.70	−2.70 (irrev)	this work
2-$CpCo(B_4H_8)$ (**4**)	+1.14 (irrev)	−1.40	−2.52 (irrev)	this work
Cp_2Co^+ (**7**)	*d*	−0.94	−1.88	15
1,2,3-$CpCo(C_2B_9H_{11})$ (**8**)	+2.07[c]	−1.21	−2.11	23, 27, this work
(1,2-$C_2B_9H_{11})_2Co^-$ (**9**)	+1.63	−1.36	−2.24	23, 28
(1,7-$C_2B_9H_{11})_2Co^-$ (**10**)	+1.68	−1.14	−2.52	23, 28

(b) Cyclopentadienyliron Compounds

	Fe(IV)/Fe(III)	Fe(III)/Fe(II)	ref
1,2,3-$CpFe(C_2B_4H_6)$ (**5**)	+1.20	−0.52	this work
1,2,3-$CpFe(C_2B_9H_{11})$ (**11**)	*d*	−0.08	23[e]
Cp_2Fe^+ (**12**)	+1.99	+0.31	22
$[C_5(CH_3)_5]_2Fe^+$ (**13**)	+1.39	−0.29	24

(c) Other Iron Carboranes

	reductns	ref
1,2,6-$(CO)_3Fe(C_2B_3H_5)$ (**6**)	−1.25 (rev), −1.89 (irrev)	this work

[a] Potentials are reported in volts vs. the aqueous saturated calomel electrode. $E°$ values are reported except for irreversible processes, in which case cathodic peak potentials (for reductions) from CV measurements are given. [b] Solvent is CH_3CN with tetraalkylammonium perchlorate or hexafluorophosphate added, unless otherwise noted. [c] Irreversible in CH_3CN; reversible in CH_2Cl_2. [d] Not detected and unreported. [e] Solvent was acetone/water with $LiClO_4$ as supporting electrolyte.

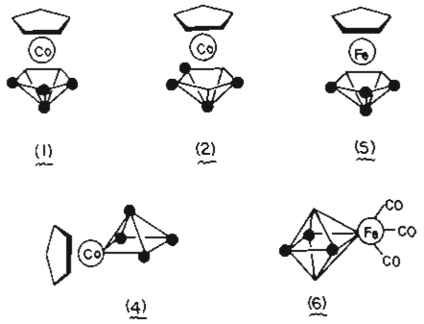

Figure 1. Some of the compounds studied in this work (● represents BH): **1** = 1,2,3-$CpCo(C_2B_4H_6)$; **2** = 1,2,4-$CpCo(C_2B_4H_6)$; **4** = 2-$CpCo(B_4H_8)$ (the four basal hydrogens are omitted in the figure); **5** = 1,2,3-$CpFe(C_2B_4H_6)$; **6** = 1,2,6-$(CO)_3Fe(C_2B_3H_5)$.

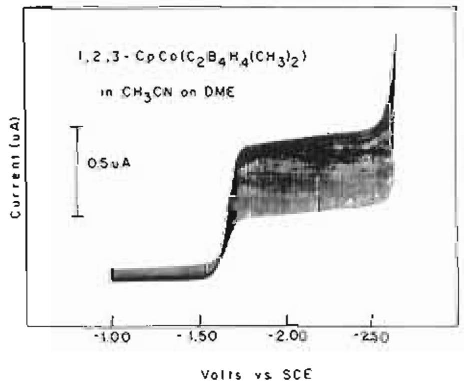

Figure 2. Dc polarogram of 3.0×10^{-4} M **3** in CH_3CN/Bu_4NPF_6: drop time = 2 s; scan rate = 2 mV/s.

versibly reduced to a Co(II) anion (Figure 2) but at potentials considerably more negative than that of Cp_2Co^+ (Table I). Compounds **1** and **3** can be reduced in a second one-electron step, apparently to the corresponding Co(I) dianion, but these reductions are quite close to the potential of the electrolyte breakdown (background) and were found to be irreversible by cyclic voltammetric measurements. The second reduction for **2** is in doubt, because polarographic measurements suggest a wave riding right on the edge of the background, but resolution was insufficient to attach certainty to the observation. We can say that the second reduction of **2** is at a potential more negative than −2.75 V. The irreversibility of the Co(II)/Co(I) wave contrasts with that of $Cp_2Co^{0/-}$, which is reversible in a variety of solvents.[15,16]

The lower electron affinity of the neutral cobaltacarboranes is due at least partially to the difference in charge between them and the cationic cobaltocenium ion. The lack of a positive charge in the cobaltacarboranes aids the oxidation to Co(IV). Although oxidation to the d^5 Co(IV) complex, Cp_2Co^{2+}, has not been observed,[17] Co(IV) is an accessible oxidation state for all of the small cobaltacarboranes. One-electron irreversible waves were observed in acetonitrile for **1**–**3** in the vicinity of +1.5 V. However, these waves were reversible in dichloromethane. Observation of reversibility for the Co(IV)/Co(III) couple is important not only because it establishes the viability of this high Co oxidation state in the carborane complexes but also because it allows us to attach thermodynamic significance to the electrode potentials for this couple.

A comparison of $E°$ potentials[18] for the various couples associated with these compounds and other cobaltacarboranes establishes that the spacings between successive redox processes are constant, giving yet another example of the electronic similarities of these molecules. Table II gives differences between successive $E°$ potentials for the compounds reported here as well as Co and Fe compounds reported previously. The separation between the Co(IV)/Co(III) and Co(III)/Co(II)

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(17) We have scanned to +2.2 V in both CH_2Cl_2 and CH_3CN without finding evidence for this oxidation.

(18) In Table I, each electrode potential given is an $E°$ value except for the three irreversible processes. To aid our comparison of potentials of electrode processes, we have assumed that the overpotentials associated with the irreversible processes are small and that the observed $E_{1/2}$ potential approximates the $E°$ value.

Table II. Differences in $E°$ between Successive Redox Processes of Some Metallocarboranes and Metallocenes

	$\Delta E°(4-2)^a$	$\Delta E°(3-1)^b$
(a) Cobalt Compounds with Adjacent Carbons in Ligand		
1,2,3-CpCo($C_2B_4H_6$) (**1**)	3.14	0.88
1,2,3-CpCo[$C_2B_4H_4(CH_3)_2$] (**3**)	3.13	1.00
Cp_2Co^+ (**7**)	*c*	0.94
1,2,3-CpCo($C_2B_9H_{11}$) (**8**)	3.28	0.90
(1,2-$C_2B_9H_{11}$)$_2$Co$^-$ (**9**)	2.99	0.88
(b) Cobalt Compounds with Nonadjacent Carbons in Ligand		
1,2,4-CpCo($C_2B_4H_6$) (**2**)	3.13	>1.3
(1,7-$C_2B_9H_{11}$)$_2$Co$^-$ (**10**)	2.82	1.38
(c) Iron Compounds		
1,2,3-CpFe($C_2B_4H_6$) (**5**)	1.72	
1,2,3-CpFe($C_2B_9H_{11}$) (**11**)	*c*	
Cp_2Fe^+ (**12**)	1.68	
[$C_5(CH_3)_5$]$_2$Fe$^+$ (**13**)	1.68	

[a] $E°$ for M(IV)/M(III) minus $E°$ for M(III)/M(II), in volts. [b] $E°$ for Co(III)/Co(II) minus $E°$ for Co(II)/Co(I), in volts. [c] Not available.

couples is 3.08 ± 0.14 V for the cobaltacarboranes. This suggests that the $E°$ value for $Cp_2Co^{+/2+}$ should lie at about +2.14 ± 0.14 V. The difference in potential between Co(III)/Co(II) and Co(II)/Co(I), including cobaltocene, is 0.92 ± 0.05 V for compounds **1**, **3**, and **7**–**9**. Compounds **2** and **10** stand out from this group by virtue of a Co(II)/Co(I) $E°$ value that is more negative than expected by at least 0.4 V. What these compounds have in common structurally is that the two carbon atoms in the pentagonal face bonded to the metal are in nonadjacent positions. If these compounds are indicative of a general trend, it would appear that this geometric arrangement leads to a destabilization of the Co(I) oxidation state.

2-CpCo(B_4H_8)

Very little voltammetric data has been published on metallaboranes, with the exception of several nickelaboranes. Closo clusters like 1-CpNi(B_9H_9)$^-$ display a reversible reduction[19] [formally Ni(IV)/Ni(III)] and an irreversible oxidation.[20] Nido clusters like CpNi($B_{10}H_{13}$), CpNi($B_{10}H_{12}$)$^-$, and $(B_{10}H_{12})_2Ni^{2-}$ undergo irreversible oxidations.[19,21] We find that the nido cluster 2-CpCoB_4H_8 has a voltammetric behavior roughly similar to that of the above small *closo*-cobaltacarboranes in that three waves (one oxidation and two reductions) were observed, with only the first reduction Co(III)/Co(II) being reversible in acetonitrile. The oxidation wave at +1.14 V is considerably less positive than those found for the closo clusters: the separation between $E°$ values[18] for the Co(IV)/Co(III) and Co(III)/Co(II) couples is only 2.54 V, compared to the value of 3.08 V found for the cobaltacarboranes. Hence the borane seems to lead to a thermodynamic stabilization of the Co(IV) oxidation state, although the irreversibility of the oxidation in CH_3CN shows that the Co(IV) cation is still a very reactive species.

Iron Compounds

1,2,3-CpFe($C_2B_4H_6$) (5). This compound is isoelectronic with ferrocenium ion, Cp_2Fe^+, and the mixed sandwich ferracarborane 1,2,3-CpFe($C_2B_9H_{11}$). These compounds display a highly reversible Fe(III)/Fe(II) couple at mild potentials, with **5** being about 0.8 V negative of the ferrocenium reduction[22] and $E°$ for 1,2,3-CpFe($C_2B_9H_{11}$) falling midway between these potentials.[23] Thus, we find that for both the Fe and the Co small carboranes studied, $E°$ potentials are shifted *negative* by ca. 0.4 V compared to those for the isoelectronic large metallacarboranes having the same overall charge. 1,2,3-CpFe($C_2B_4H_6$) also has a one-electron wave at E_p = +1.20 V, which represents oxidation to formal Fe(IV). Since this would be a very rare species for metal clusters or π complexes, it was disappointing to find the process irreversible in both CH_3CN and CH_2Cl_2. But knowing the potential of the process allows an interesting comparison to be made with the recent observations concerning the *second* oxidation of ferrocene and decamethylferrocene. Gale et al.[24] have studied the oxidation of these two compounds in basic melts of $AlCl_3$/1-butylpyridinium chloride. At fairly positive potentials, an irreversible, multielectron wave was observed for the oxidation of Cp_2Fe^+, but a one-electron reversible wave was found for $(C_5Me_5)Fe^{2+/+}$. The separation between the Fe(IV)/Fe(III) and Fe(III)/Fe(II) couples was found to be 1.68 V in each case. By comparison, the measured separation of the similar couples for 1,2,3-CpFe($C_2B_4H_6$) is virtually identical, 1.72 V. This is more evidence for similarities in electronic structure of the ferracarborane and the metallocenes. Furthermore, it argues that the orbitals involved in the redox processes have considerable metal character and suggests that the potentials observed in the $AlCl_3$ melts[24] have relevance to those obtained in more traditional nonaqueous media.

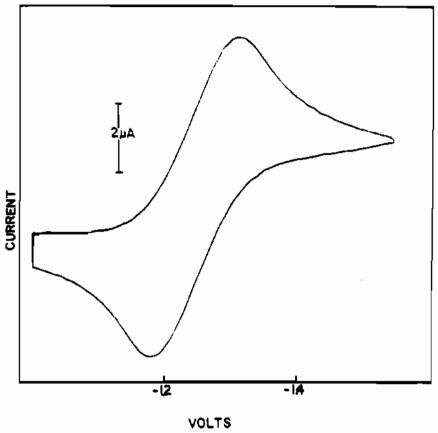

Figure 3. Cyclic voltammogram of 6 × 10^{-4} M **6** in THF/Bu_4NPF_6 at a hanging mercury drop electrode; scan rate = 287 mV/s.

1,2,6-(CO)$_3$Fe($C_2B_3H_5$) (6). The electrochemical data on **6** appears to be the first redox data available for a Fe(CO)$_3$ derivative of a carborane cage. Although redox measurements on the analogous non-metal-containing *closo*-$C_2B_4H_6$ have apparently not been reported, data on $C_2B_{10}H_{12}$ clusters suggest that *closo*-carboranes undergo irreversible reductions at quite negative potentials.[25,26] In contrast, (CO)$_3$Fe($C_2B_3H_5$) undergoes a reversible reduction at $E°$ = −1.25 V in THF (Figure 3). The monoanion produced is not as stable as that from cobaltacarboranes; CV scan rates in excess of 300 mV/s were necessary to outrun the effect of the decomposition reaction of the anion. Below this scan rate, the ratio of the anodic-to-cathodic currents fell below the value of 1.0 necessary for a completely chemically reversible reduction (i_a/i_c = 0.80 at v = 80 mV/s). Under the faster scan conditions, a second wave of equal height to the first was present at −1.89 V, due to the reduction of the monoanion of **6**. This wave was

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irreversible. Rapid repetitive CV scans past the second wave showed that an unidentified product with a reversible couple at $E^\circ = -1.15$ V was formed by the decomposition reaction of $(CO)_3Fe(C_2B_3H_5)^{2-}$.

Conclusions

The small cobalt and iron carboranes studied have E° values that are shifted negative from those of the metallocenes and large metallocarboranes. One may conclude that there is an overall destabilization of low metal oxidation states for small metallocarboranes; concomitantly, these compounds allow easier access to higher formal metal oxidation states. Comparison of the differences in potential between successive redox processes gives further credence to an isoelectronic model for metallocenes and metallacarboranes.

Data on $(CO_3)Fe(C_2B_3H_5)$ show that $(CO)_3Fe$ derivatives of *closo*-carboranes can be reversibly reduced at rather accessible potentials.

Experimental Section

Compounds **1**–**5** were supplied by Dr. R. N. Grimes of the University of Virginia, and **6** was obtained from Dr. T. P. Fehlner of Notre Dame University. Spectrograde CH_3CN and CH_2Cl_2 were distilled under vacuum from calcium hydride. Tetrahydrofuran was distilled first from lithium aluminum hydride and then from sodium–benzophenone ketyl in vacuo just before use. The supporting electrolyte was 0.1 M Bu_4NPF_6, and the concentration of electroactive compound was between 1.5×10^{-4} and 6.0×10^{-4} M. Electrochemical equipment and procedures were as described elsewhere.[27] $(CO)_3Fe(C_2B_3H_5)$, which is air sensitive, was investigated within a Vacuum Atmospheres drybox. Electrode potentials are reported vs. the aqueous saturated calomel electrode.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant No. CHE 80-04242) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We wish to thank Professors Grimes and Fehlner for providing the compounds to be studied and for enlightening conversations.

Registry No. **1**, 50860-25-8; **2**, 41660-23-5; **3**, 50932-66-6; **4**, 43061-99-0; **5**, 39980-35-7; **6**, 53363-10-3; **8**, 37100-20-2.

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Preparation and Analysis of Crystalline Alkalides

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Received September 1, 1981

The synthesis and analysis of crystalline salts which contain alkali-metal anions and alkali-metal cations, with the latter complexed by various cryptands or a crown ether, are described. Analysis included measurement of evolved hydrogen after decomposition with water, pH titration of OH^- and the cryptand, flame emission determination of alkali metals, and ^1H NMR spectra of the complexing agent. The analyses are in good agreement with the expected stoichiometry for $Cs^+C322{\cdot}Na^-$, $Cs^+18C6{\cdot}Na^-$, and $K^+C222{\cdot}Na^-$ in which C*mno* refers to the macrobicyclic cryptand [*m.n.o*] and 18C6 refers to the macrocyclic crown ether 18-crown-6. Analyses of $Rb^+C222{\cdot}Na^-$, $Li^+C211{\cdot}Na^-$, $Na^+C221{\cdot}Na^-$, $Rb^+C222{\cdot}Rb^-$, and $K^+18C6{\cdot}Na^-$ are in general accord with the proposed stoichiometry. However, in these cases some of the results are in poor agreement with the expectations, probably because of either partial decomposition of the complexant during the hydrogen evolution step or contamination of the crystals with excess metal. Crystals were also precipitated from solutions whose solution stoichiometry corresponded to $Cs^+C222{\cdot}Na^-$, $K^+C222{\cdot}K^-$, and $Cs^+C222{\cdot}Cs^-$. Nevertheless, for these crystals the analyses were poor and suggested decomposition prior to analysis and/or contamination by metal. A sample presumed to be $Cs^+C322{\cdot}Cs^-$ decomposed violently in vacuo at about −20 °C. Attempts to synthesize $Ba^{2+}C222{\cdot}(Na^-)_2$ failed to yield satisfactory analyses.

Introduction

Since the preparation and characterization of the first crystalline salt of an alkali-metal anion (Na^-) in 1974,[1,2] we have observed the formation of a number of other alkalide salts which, by analogy, presumably consist of alkali-metal *cations* trapped inside of the macrobicyclic cryptand [2.2.2][3] with alkali-metal *anions* outside.[4–12] We report here the preparation and analysis of a number of such crystalline alkalides as well as others which utilized cryptands [2.1.1], [2.2.1], and [3.2.2].[3] We also report the first synthesis of two sodide salts which contain the crown ether 18-crown-6.[13]

The crystal structure of the parent compound, $Na^+C222{\cdot}Na^-$, may be approximately described[2] as closest-packed large cryptated cations with sodium anions in the octahedral holes. Within the hexagonal unit cell, the cations pack in ABC··· repeat layers. Thermodynamic arguments[6,8] show that the stabilization of Na^- is largely due to the stability of the cryptated sodium cation which is resistant to reduction by Na^-. Because crystals of $Na^+C222{\cdot}Na^-$ can be grown isothermally in tetrahydrofuran in the presence of cryptand [2.2.2]and

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[1] Dye, J. L.; Ceraso, J. M.; Lok, M. T.; Barnett, B. L.; Tehan, F. J. *J. Am. Chem. Soc.* **1974**, *96*, 608.

[2] Tehan, F. J.; Barnett, B. L.; Dye, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 7203.

[3] IUPAC names for the cryptands are as follows: cryptand [2.2.2], 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, abbreviation C222; cryptand [2.2.1], 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane, abbreviation C221; cryptand [2.1.1], 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane, abbreviation C211; cryptand [3.2.2], 4,7,10,16,19,24,27-heptaoxa-1,13-diazabicyclo[11.8.8]nonacosane.

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[13] The IUPAC name of 18-crown-6 is 1,4,7,10,13,16-hexaoxacyclooctadecane; the abbreviation is 18C6.

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