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A ^{11}B NMR Study of Substituted Dicarba-*closo*-undecaborane(11) Derivatives

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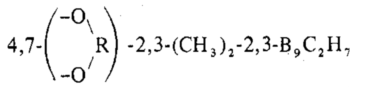
The 70.6-MHz ^{11}B NMR spectrum of 2,3-$(CH_3)_2$-2,3-$B_9C_2H_9$ consists of four doublets of relative intensity 4:2:2:1 reading upfield which are assigned to B(4,5,6,7), B(8,9), B(10,11), and B(1), respectively. The ^{11}B NMR spectrum of 4,7-$(OH)_2$-2,3-$(CH_3)_2$-2,3-$B_9C_2H_7$ consists of five doublets of relative intensity 1:2:1:2:1 reading upfield which are assigned to B(1), B(8,9), B(11), B(5,6), and B(10), respectively. The spectrum also contains a low-field singlet for B(4,7). The assignments are based on the synthesis of specifically labeled deuterio and brominated derivatives of the general class of molecules 4,7-(ORO)-2,3-$(CH_3)_2$-2,3-$B_9C_2H_7$ in which the divalent radical R bridges the two adjacent boron–oxygen units. The chemical shifts associated with the skeletal boron atoms in the octadecahedron appear to be affected by both the change in the exopolyhedral substituents as well as by the distortion in the cage structure which occurs upon substitution.

Introduction

The synthesis and structural assignments for a large number of B-substituted derivatives of 2,3-$(CH_3)_2$-2,3-$B_9C_2H_9$ have been completed.[2–5] These derivatives are members of the general class



$$4,7\text{-}\left(\begin{matrix}-O\\ R\\ -O\end{matrix}\right)\text{-}2,3\text{-}(CH_3)_2\text{-}2,3\text{-}B_9C_2H_7$$

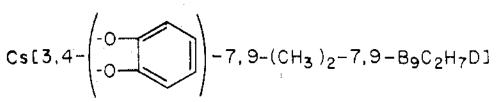
where the divalent radical R group bridges the two adjacent boron–oxygen units (hereafter designated as ORO) in the closo octadecahedron, Figure 1. The symmetry of these derivatives can be uniquely determined by the application of proton NMR spectral data and high-resolution ^{11}B NMR data. All the ^{11}B NMR spectra typically have a pattern of one low-field singlet of intensity 2 followed by a set of five doublets of intensity 1:2:1:2:1 reading upfield.

With the advent of high-field Fourier transform NMR instruments and such associated techniques as line narrowing, the ^{11}B spectra are of sufficient resolution to consider the specific assignment of each boron resonance to a particular boron atom in the molecule. This information will be of further use concerning the development of structure–chemical shift relationships in ^{11}B NMR. In this paper we describe the ^{11}B NMR spectra of certain derivatives of *closo*-dicarbaundecaborane and have synthesized specifically substituted derivatives in order to assign the boron atom-to-chemical shift relationships of most of the *closo*-dicarbaundecarborane derivatives.

Experimental Section

The ^{11}B NMR spectra were measured on equipment consisting of a pulsed NMR apparatus built in the Department of Chemistry, Indiana University, operating at 70.6 MHz, a Varian 51.7-kG superconducting magnet, and a 16K Nicolet 1080 series computer. Additional details have been reported elsewhere.[6] The ^{11}B NMR spectra were measured in methylene chloride solvent externally referenced to $BF_3 \cdot O(C_2H_5)_2$. A revised sign convention for boron-11 NMR chemical shifts, with positive sign denoting shift to lower field but with the retention of boron trifluoride etherate as the zero standard (thus reversing the signs based on the old convention), was agreed to in the plenary session at the Third International Meeting on Boron Chemistry, Munich and Ettal, West Germany, July 1976. This action brings boron-11 NMR in line with the sign convention employed for other commonly reported nuclei. Mass spectra were recorded on an MS-902 instrument.

The synthesis of 4,7-$(OH)_2$-2,3-$(CH_3)_2$-2,3-$B_9C_2H_7$ and the associated condensation products 4,7-(ORO)-2,3-$(CH_3)_2$-2,3-$B_9C_2H_7$ have been reported elsewhere.[2–5] The deuterated derivatives were prepared by the method of Hawthorne[7] using $[(C_6H_5)_3P]_2Rh(H)$-π-$B_9C_2H_{11}$ as a catalyst. The method for preparing



(where the two oxygens on the phenyl group will hereafter be represented as OC_6H_4O) by reaction of $LiAlD_4$ with 4,7-(OC_6H_4O)-2,3-$(CH_3)_2$-2,3-$B_9C_2H_7$ has been reported elsewhere.[2] Synthesis of 4,7-$(OH)_2$-10-Br-2,3-$(CH_3)_2$-2,3-$B_9C_2H_6$ has been previously reported.[2]

4,7-(OC_6H_4O)-2,3-$(CH_3)_2$-2,3-$B_9C_2H_3D_4$. In a 500-mL Parr vessel 0.268 g (1.0 mmol) of 4,7-(OC_6H_4O)-2,3-$(CH_3)_2$-2,3-$B_9C_2H_7$ and 0.38 g (0.05 mmol) of $[(C_6H_5)_3P]_2Rh(H)$-π-$B_9C_2H_{11}$ were dissolved in 20 mL of dry, degassed benzene. By use of a previously described hydrogenation apparatus,[8] the Parr vessel was flushed twice with dry nitrogen and then charged with deuterium at 45 psi. The solution was stirred for 32 h. Upon completion of the reaction, the Parr vessel was vented and the benzene solution filtered and transferred to a round-bottom flask. After removal of the solvent in vacuo at 60 °C, the final product was isolated by sublimation. No further purification was necessary. 4,7-(OC_6H_4O)-2,3-$(CH_3)_2$-2,3-$B_9C_2H_3D_4$ (147 mg) was isolated (54% yield, mp 103–105 °C). The final product had a parent peak at *m/e* 272 corresponding to $^{12}C_{10}{}^{1}H_{13}{}^{2}D_4{}^{11}B_9{}^{16}O_2$.

$[(C_4H_9)_4N]$-7,9-$(CH_3)_2$-3,4-(OC_6H_4O)-7,9-$B_9C_2H_4D_4$. In a Schlenk tube 4,7-(OC_6H_4O)-2,3-$(CH_3)_2$-2,3-$B_9C_2H_3D_4$ (0.19 g, 0.64 mmol) was added to sodium amalgam (0.05 g of Na, 15 g of Hg) in 30 mL of dry tetrahydrofuran and stirred under nitrogen for 18 h. The slurry was filtered under a N_2 blanket through Celite and the solvent removed in vacuo. The crude salt was dissolved in a minimum of water and then added to a saturated aqueous solution of tetrabutylammonium chloride. The final product was isolated by filtration and dried and recrystallized from methylene chloride. Anal. Calcd for $B_9C_{26}H_{50}D_4NO_2$: C, 60.58; H, D, 11.26; N, 2.72. Found: C, 59.94; H, D, 10.50; N, 2.62.

4,7-(OC_6H_4O)-2,3-$(CH_3)_2$-2,3-$B_9C_2H_6D$. In a dry Schlenk tube flushed with N_2, 4,7-(OC_6H_4O)-2,3-$(CH_3)_2$-2,3-$B_9C_2H_7$ (0.4 g, 1.4 mmol) was dissolved in 40 mL of dry tetrahydrofuran. $LiAlD_4$ (0.2 g) was added and the solution stirred at −40 °C for 12 h. The resulting slurry was Schlenk-filtered under N_2 into a second Schlenk tube containing sodium hydride, 0.17 g. The slurry was stirred at reflux for 10 h, cooled, and filtered again into a Schlenk tube containing 0.5 g of $SnCl_2$. Although the precipitation of tin was immediate, the solution was stirred at reflux for 12 h. After the solution was cooled, the tin was removed by filtration and the solvent evaporated in vacuo. After sublimation of the residue followed by recrystallization from acetonitrile, 0.22 g of product was isolated in 54.6% yield; mp 102–105 °C. The final product had a parent peak at *m/e* 269 corresponding to $^{12}C_{10}{}^{1}H_{16}{}^{2}D_1{}^{11}B_9{}^{16}O_2$.

2-C_2H_5-3-CH_3-2,3-$B_9C_2H_9$. A 250-mL Schlenk tube was evacuated, dried, and flushed with N_2, and 10 g (0.063 mol) of 1-CH_3-1,2-$C_2B_{10}H_{11}$ and 100 mL of freshly distilled tetrahydrofuran were added. The solution was cooled to −80 °C by use of a dry ice/ethanol bath. Then 3.8 mL of 1.7 M phenyllithium was added to the solution and stirred for 2 h at −80 °C. Ethyl iodide (5.03 mL) was added by syringe, and the solution was stirred for 1 h at −80 °C and then warmed

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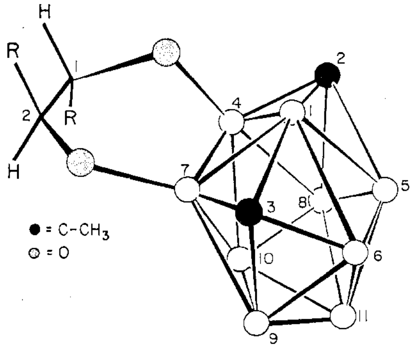


Figure 1. Numbering scheme for the condensation products 4,7-(ORO)-2,3-$(CH_3)_2$-2,3-$B_9C_2H_7$, in which the divalent radical R group bridges two adjacent boron–oxygen units.

Table I. ^{11}B NMR Data for C-Substituted 2,3-$B_9C_2H_{11}$ Derivatives[a]

compd	chem shift, ppm (*J*, Hz)	rel area
2,3-$B_9C_2H_{11}$	−1.2 (164)	4
	−7.3 (169)	2
	−10.5 (169)	2
	−17.3 (169)	1
2,3-$(CH_3)_2$-2,3-$B_9C_2H_9$	−2.9 (169)	4
	−6.8 (169)	2
	−10.5[a]	2
	−11.0[a]	1
2,3-$(C_2H_5)_2$-2,3-$B_9C_2H_9$	−4.9[a]	4
	−7.7[a]	2
	−12.6[a]	2
	−14.1[a]	1
2,3-$(C_6H_5)_2$-2,3-$B_9C_2H_9$	−4.5[a]	4
	−6.6[a]	2
	−10.3[a]	2
	−11.8[a]	1
2-C_2H_5-3-CH_3-2,3-$B_9C_2H_9$	−4.0[a]	2
	−4.6[a]	2
	−7.1[a]	1
	−8.4[a]	1
	−11.7[a]	2
	−13.0[a]	1

[a] Values are approximate due to overlap of signals. All resonances are doublets.

gradually to room temperature. The THF was removed in vacuo and the carborane sublimed at 60 °C (0.01 mm) to a −80 °C cold finger to give 11 g of 1-CH_3-2-C_2H_5-$C_2B_{10}H_{10}$ in 93% yield. The 1-CH_3-2-C_2H_5-$C_2B_{10}H_{10}$ was added to 200 mL of absolute ethanol containing 6.5 g of potassium hydroxide (100% molar excess) and stirred at reflux for 20 h under a nitrogen atmosphere. After the solution was cooled, excess potassium hydroxide was removed by the addition of CO_2 gas and converted to potassium carbonate. The slurry was filtered and the solution evaporated in vacuo to dryness to give a quantitative yield of K[7-CH_3-8-C_2H_5-7,8-$B_9C_2H_{10}$], 12.1 g. The potassium salt was thoroughly dried by azeotropic distillation.

A 300-mL three-neck round-bottom flask was equipped with a condenser, a nitrogen inlet, and a mechanical stirrer, and 12.1 g (0.058 mol) of 7-CH_3-9-C_2H_5-7,9-$B_9C_2H_{10}^-$ and 150 mL of freshly distilled toluene were added under N_2 to the reaction flask. The solution was heated to 60 °C and stirred. Polyphosphoric acid (60 g) was added to the solution which was heated to 110–120 °C and stirred vigorously for 2 h. After the solution was cooled, the toluene layer was decanted under nitrogen to a 500-mL round-bottom flask. Freshly distilled toluene (30 mL) was added to the polyphosphoric acid residue and stirred at 110–120 °C for 30 min. It was cooled and decanted under nitrogen and combined with the previous fraction. The toluene was removed in vacuo and the carborane sublimed at 30 °C (0.01 mm) to a −80 °C cold finger to give 7.1 g (0.041 mol) of 2-C_2H_5-3-CH_3-2,3-$B_9C_2H_9$ in 70% yield; mp 74 °C. The final product had a parent peak at *m/e* 176 corresponding to $^{12}C_5{}^1H_{17}{}^{11}B_9$.

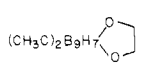
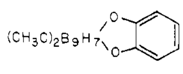
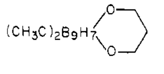
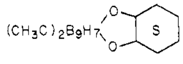
Results and Discussion

The 70.6-MHz ^{11}B NMR spectrum of *closo*-2,3-$B_9C_2H_{11}$ consists of a set of four doublets of relative intensity 4:2:2:1. The chemical shift values for 2,3-$B_9C_2H_{11}$ and some *C*-alkyl and *C*-aryl derivatives are found in Table I. The relative intensities have identified the large low-field doublet as the B(4,5,6,7) skeletal atoms and the high-field doublet of intensity 1 as the B(1) skeletal atom (see Figure 1 for numbering). The remaining doublets of intensity 2 are assigned to the B(8,9) boron atoms and the B(10,11) boron atoms. The B(8,9) pair has been assigned to the low-field doublet of intensity 2 on the basis of the synthesis of 2-Et-3-Me-2,3-*closo*-$B_9C_2H_9$ and analysis of its ^{11}B NMR spectrum. The chemical shift data of the *C*-ethyl-*C′*-methyl derivatives are found in Table I. As expected, the doublet of intensity 4 assigned to the B(4,5,6,7) boron atoms splits into two doublets of intensity 2 assigned to the B(4,5) and B(6,7) boron atoms. The lowest field doublet of intensity 2 in the parent $B_9C_2H_{11}$ splits in the *C*-ethyl-*C′*-methyl derivative to two doublets of intensity 1 each. The lowest field doublet of intensity 2 in the $B_9C_2H_{11}$ is then assigned to the B(8,9) boron atoms. In the *C*-ethyl-*C′*-methyl derivative, the B(8) and B(9) boron atoms would be nonequivalent while the B(10,11) pair would be equivalent, being reflected across the sole mirror plane remaining in the *C*-ethyl-*C′*-methyl derivative.

Compared to the rather simple and condensed ^{11}B NMR spectrum of the 2,3-$(CH_3)_2$-2,3-$B_9C_2H_9$ (I) (8–16 ppm), the spectra of 4,7-$(OH)_2$-2,3-$(CH_3)_2$-2,3-$B_9C_2H_7$ (II) and its condensation products 4,7-(ORO)-2,3-$(CH_3)_2$-2,3-$B_9C_2H_7$ extend over a range of 35–40 ppm accompanied by severe changes in the chemical shifts of some particular resonances relative to I. Table II lists the assignments and chemical shifts for a number of these derivatives.

Partial deuteration of 4,7-(OC_6H_4O)-2,3-$(CH_3)_2$-2,3-$B_9C_2H_7$ (III) using the Hawthorne catalyst[7] resulted in the substitution by four deuterium atoms. The doublets in the ^{11}B NMR spectrum of III (Figure 2) centered at −4.7 (2B), −11.1

Table II. ^{11}B NMR Data for 4,7-Substituted 2,3-$(CH_3)_2$-2,3-$B_9C_2H_7$ Derivatives[a]

compd	B(4,7)	B(1)	B(8,9)	B(11)	B(5,6)	B(10)
$(CH_3C)_2B_9H_7(OH)_2$	18.6	−0.9 (190)	−3.4 (169)	−9.4 (146)	−21.3 (162)	−22.6 (137)
	16.3	−1.8 (161)	−4.2 (168)	−11.6 (144)	∼−23.1[b]	
	14.5	−0.3 (177)	−4.7 (163)	−11.1 (151)	∼−21.5[b]	
	19.5	∼−1.2[b]	∼−3.7[b]	−12.1 (142)	−23.3 (161)	−26.6 (142)
	14.9	−2.9 (171)	−5.3 (166)	−12.4 (149)	∼−24.1[b]	

[a] Chemical shifts are in ppm. *J* values in Hz are in parentheses. [b] Values are approximate due to overlap of signals.

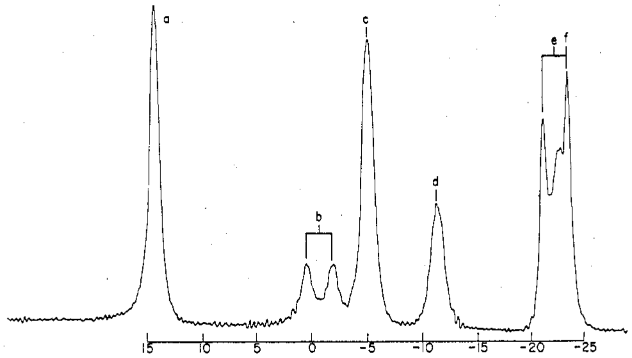


Figure 2. 70.6-MHz ^{11}B NMR spectrum of 4,7-(OC_6H_4O)-2,3-$(CH_3)_2$-2,3-$B_9C_2H_3D_4$.

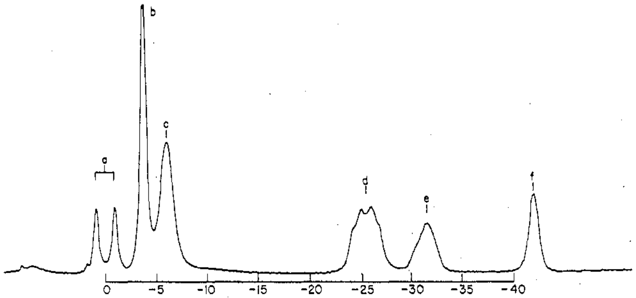


Figure 3. 70.6-MHz ^{11}B NMR spectrum of the tetramethylammonium salt of $[3,4\text{-}(OC_6H_4O)\text{-}1,2,5,6\text{-}D_4\text{-}7,9\text{-}(CH_3)_2\text{-}7,9\text{-}B_9C_2H_4]^-$ with resonances centered at (a) 0.2, (b) −3.7, (c) −6.0, (d) −25.6, (e) −32, and (f) −42.0 ppm.

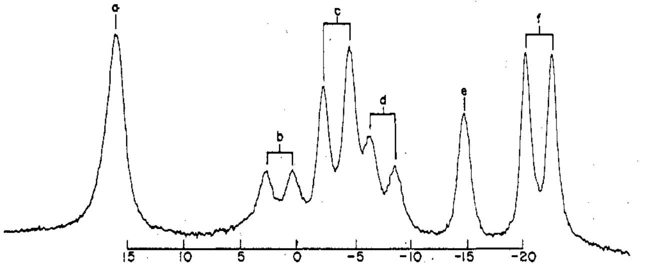


Figure 4. 70.6-MHz ^{11}B NMR spectrum [chemical shift, ppm (J_{BH}, Hz)] of 10-Br-4,7-$(OH)_2$-2,3-$(CH_3)_2$-2,3-$B_9C_2H_6$: (a) 16.1, (b) 1.5 (126), (c) −3.4 (156), (d) −7.5 (119), (e) −14.8 (f) −21.4 (161).

(1B), and −21.5 ppm (1B) show nearly complete substitution by deuterium. Reduction and subsequent hydrolysis of deuterated III as described previously demonstrated that in the reductive cage opening of I the unique B(1) atom moves away from the entering hydride ion to the side of the cage containing the bis(oxyphenyl) radical.[3] This generates a derivative, IV, of the *nido*-7,9-$B_9C_2H_{12}^-$ ion with the "B–O" units located at the B(3,4) skeletal positions and the terminal deuterium atoms at B(2,5), B(1), and B(6), Figure 3, based on the previously established boron atom-to-chemical shift relationships for the *nido*-7,9-$B_9C_2H_{12}^-$ ion.[9] On the basis of the proposed cage-opening mechanism for the conversion of III → IV and the assignment of IV, the ^{11}B NMR chemical shifts of III are assigned as follows. The doublet at −4.7 ppm (2B) for III is assigned to B(8,9). By elimination, the high-field doublet of area 2 at −21.5 ppm in III is assigned to the B(5,6) positions. The remaining chemical shifts at −11.1 ppm (1B) and −21.5 ppm (1B) for III are then assigned to the B(10) and B(11) positions, but cannot be specifically assigned on the basis of this deuteration data alone.

The ^{11}B NMR spectrum of 10-Br-4,7-$(OH)_2$-2,3-$(CH_3)_2$-2,3-$B_9C_2H_6$ (Figure 4) exhibits a singlet of unit area at high field. On the basis of the X-ray crystal structure analysis of this bromo derivative, the bromine substituent is located at B(10).[10,11] These results suggest that the highest field doublet of unit area in the spectrum of III is due to B(10). By elimination, the doublet of unit area at −11.1 ppm for III is assigned to B(11) and the doublet of unit area at lowest field, −0.3 ppm, to B(1). As further support for this latter assignment, the reaction of III with $LiAlD_4$ yielded the nido anion $[3,4\text{-}(OC_6H_4O)\text{-}8\text{-}D\text{-}7,9\text{-}(CH_3)_2\text{-}7,9\text{-}B_9C_2H_7]^-$, V. Hydride attack on III would be favored at either B(1) or B(4,5,6,7). The ^{11}B NMR of V, Figure 5, clearly indicates deuterium incorporation only at the B(8) position of V, which corresponds to the B(1) position in III. This contrasts with the attack of 2,3-$B_9C_2H_{11}$ by anionic reagents such as $CH(CN)_2^-$ and $C_2H_5O^-$ which leads to B(10)-substituted products.[12] Reaction of V with sodium hydride and then $SnCl_2$ in tetrahydrofuran[12] results in oxidative closure to give the monodeuterated derivative of III. The ^{11}B NMR spectrum of this closo product clearly shows the collapse of the unit area doublet at lowest field. On the assumption that no migration of the deuterium label during the oxidative-closure reaction occurs, the B(1) resonance is then definitely assigned to this low-field doublet.

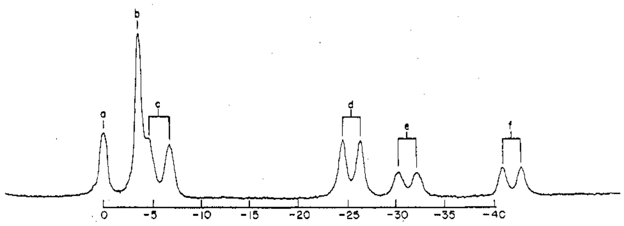


Figure 5. 70.6-MHz ^{11}B NMR spectrum [chemical shift, ppm (J_{BH}, Hz)] of the tetramethylammonium salt of $[3,4\text{-}(OC_6H_4O)\text{-}8\text{-}D\text{-}7,9\text{-}(CH_3)_2\text{-}7,9\text{-}B_9C_2H_7]^-$: (a) 0.3, (b) −3.5, (c) −5.5 (143), (d) −25.0, (e) −30.4 (129), (f) −40.8 (128).

To summarize, the ^{11}B NMR spectrum of III and related derivatives consists of six resonances of relative intensities 2:1:2:1:2:1, reading upfield, which can be assigned to B(4,7), B(1), B(8,9), B(11), B(5,6), and B(10), respectively. In comparison to the chemical shift positions for *closo*-2,3-$(CH_3)_2$-2,3-$B_9C_2H_9$, the substitution of oxygen atoms at the B(4,7) positions causes a significant but expected shift of the B(4,7) resonance to much lower field. The B(5,6) pair, which are in a remote (antipodal) position to B(4,7), are shifted upfield by approximately 19 ppm. This is similar to the effect seen in icosahedral molecules. It has been observed for a large number of icosahedral systems that an increase in the electron withdrawing ability of a cage atom causes an increase in the shielding of the antipodal polyhedral nucleus (seen in both ^{11}B and ^{13}C NMR spectra).[13-15] The B(1) and the B(8,9) positions in these octadecahedral molecules are shifted to lower field upon substitution of oxygen atoms at B(4,7). Likewise, for icosahedral molecules it has been observed that an increase in the electron-withdrawing ability of a polyhedral atom results in a deshielding perturbation of ^{11}B and ^{13}C resonances of polyhedral atoms ortho to them.[14,15]

In the case of the B(10) resonance of the B_9C_2 derivatives, the change upon substitution does not follow the ortho-effect rule stated above. This unusual shielding effect may be linked to the distortion in the structure of the substituted octadecahedron. This result serves as a warning that the empirical shielding rules developed for icosahedral molecules should be used with caution in other polyhedral systems.

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(11) The X-ray analysis of the boron-brominated derivative reveals some distortion from the idealized geometry shown in Figure 1. The unique B(1) atom remains on the mirror plane reflecting the two cage carbon atoms but is shifted on that mirror plane toward the B(5,6) boron pair. The resulting B(1)–B(4) distance is 2.30 Å, and the B(1)–B(5) distance is 1.95 Å. This distortion causes the structure to resemble that of a nido, 11-atom polyhedral fragment.
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Carbon-13 Magnetic Resonance Spectra of Diamagnetic Cyano Complexes

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Fourier transform ^{13}C NMR spectra are reported for 19 diamagnetic cyano complexes in D_2O solution. Data are included for $M(CN)_6^{n-}$ complexes of nd^6 electron configuration where M = Fe(II), Ru(II), Os(II), Co(III), Rh(III), Ir(III), Pd(IV), or Pt(IV); square-planar $M(CN)_4^{n-}$ complexes of nd^8 configuration where M = Ni(II), Pd(II), Pt(II), or Au(III); tetrahedral $M(CN)_4^{n-}$ complexes of nd^{10} configuration where M = Cu(I), Zn(II), Cd(II), or Hg(II); and linear $M(CN)_2^{n-}$ complexes of nd^{10} configuration where M = Ag(I), Au(I), or Hg(II). Except for $Fe(CN)_6^{4-}$, the ^{13}C resonance in all the cyano complexes is found at higher field than uncomplexed CN^-, and the range of chemical shifts spans 92.5 ppm. Chemical-shift differences are discussed in terms of changes in σ and π bonding of CN^- to the metal ion. Metal–^{13}C spin coupling was observed for $Co(CN)_6^{3-}$ (126.0 Hz), $Rh(CN)_6^{3-}$ (33.6 Hz), $Pt(CN)_6^{2-}$ (808 Hz), and $Pt(CN)_4^{2-}$ (1034 Hz). Relaxation times T_1 and T_2 are reported for enriched (45% ^{13}C) samples of $Fe(CN)_6^{4-}$, $M(CN)_4^{n-}$ (where M = Ni(II), Pd(II), Pt(II), Au(III), Zn(II), Cd(II), or Hg(II)), $M(CN)_2^-$ (where M = Ag(I) or Au(I)), and $Co(CN)_6^{3-}$ (60% ^{13}C). In addition T_1 values for these complexes were measured at 10 °C temperature intervals between 30 and 70 °C. The mechanism of relaxation of the ^{13}C nucleus in the cyano complexes is discussed with the data in most cases consistent with scalar coupling to ^{14}N.

Introduction

As Fourier transform instrumentation has become widespread, the use of ^{13}C magnetic resonance as a spectroscopic tool for the investigation of metal complexes with carbon-containing ligands has become extensive.[2] Ligands with carbon directly bonded to the metal have attracted the greatest interest since large chemical shifts are often observed, and if the metal has a nuclear spin, spin coupling is also often measurable. Among the simplest such ligands are CO and CN^-. Although carbonyl complexes have been extensively and widely studied, comparatively little has been reported for cyano complexes. Hirota et al.[3] reported chemical shifts for a number of cyano complexes, and several Fe(II), Co(III), and Pt(IV) octahedral cyano complexes have been investigated.[4-9] The lack of more extensive investigation of diamagnetic cyano complexes seems surprising in view of the abundance of easily synthesized examples in several different molecular geometries. Further, many octahedral or square-planar cyano complexes of the late transition-metal ions and tetrahedral or linear complexes of the coinage or zinc family metal ions are very stable and resistant to hydrolysis in the absence of acid.[10] Thus a systematic investigation of ^{13}C NMR of these cyano complexes offers the interesting prospects of examining the ^{13}C resonance in several well-defined structural and electronic environments. Consequently, prompted in part by our interest in the electronic and structural features of cyano complexes generally and in part by our wish to further the understanding of the factors which affect ^{13}C resonance in metal complexes, we report here ^{13}C NMR spectra for 19 high-symmetry cyano complexes. Our study includes octahedral $M(CN)_6^{n-}$ complexes of nd^6 electronic configuration, square-planar $M(CN)_4^{n-}$ complexes of nd^8, and tetrahedral $M(CN)_4^{n-}$ and linear $M(CN)_2^{n-}$ complexes of nd^{10}. In addition, selected examples of each geometry were synthesized using $K^{13}CN$ (90% ^{13}C). The isotopically enriched complexes allowed the measurement of relaxation times for the ^{13}C nucleus. Metal–^{13}C spin coupling was observed for Pt in $Pt(CN)_6^{2-}$ and $Pt(CN)_4^{2-}$, Rh in $Rh(CN)_6^{3-}$, and Co in $Co(CN)_6^{3-}$, and coupling constants were determined in each case.

Experimental Section

Preparation of Compounds. The complexes studied here are all known complexes,[10] and most were prepared by standard methods. The compounds $K_4[Os(CN)_6]$[11] and $K_3[Rh(CN)_6]$[12] were prepared by fusion of $(NH_4)_2[OsCl_6]$[13] and $RhCl_3$, respectively, with KCN; the resulting mixtures were extracted with water, and the products were crystallized and recrystallized from water. Solution syntheses were employed for $K_3[Co(CN)_6]$,[14] $K_2[Pd(CN)_6]$,[15] $K_2[Pt(CN)_6]$,[16] $K_2[Ni(CN)_4]$,[17] $K_2[Pd(CN)_4]$,[18] $K_2[Pt(CN)_4]$,[19] $K[Au(CN)_4]$,[20] $K[Ag(CN)_2]$,[21] $K[Au(CN)_2]$,[22] $K_3[Cu(CN)_4]$,[23] and $K_2[M(CN)_4]$ (M = Zn, Cd, or Hg).[10] $K_4[Fe(CN)_6]$ was reagent grade, $K_4[Ru(CN)_6]$ was purchased from Alfa Inorganics (Danvers, MA), and $K_3[Ir(CN)_6]$ was purchased from D. F. Goldsmith (Evanston, IL).

Isotopically enriched complexes were prepared with $K^{13}CN$ (90% ^{13}C; Merck Sharp and Dohme, Canada). Small quantities of $M(CN)_2$ (M = Ni,[17] Pd,[18] Pt,[19] Zn,[10] or Hg), $Cd(OH)_2$, MCN (M = Ag or Au[24]), or *trans*-$[Au(CN)_2Br_2]^-$[20] were treated with stoichiometric amounts of $K^{13}CN$ in neutral, aqueous solution to produce $M(CN)_4^{n-}$ or $M(CN)_2^{n-}$ complexes containing 45% ^{13}CN. A sample of $K_4[Fe(CN)_6]$, 45% enriched with ^{13}C, was prepared by adding a concentrated aqueous solution of $FeCl_2 \cdot 4H_2O$ to a boiling aqueous solution of 1:1 KCN and $K^{13}CN$. The product was precipitated with ethanol and purified by dissolving in water and reprecipitating with ethanol. Isotopically enriched $K_3[Co(CN)_6]$ (60% ^{13}C) was prepared by dissolving $Co(CN)_2$ in aqueous $K^{13}CN$ solution.[14] The solution was concentrated, and the product crystallized as the solution was cooled. Because of concern for paramagnetic impurities, the sample was recrystallized from water four times.

Solutions for NMR spectra of the complexes with natural-abundance ^{13}C were nearly saturated (0.5–1.0 M) D_2O solutions; the

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