and $\psi^2(0)$ are no doubt quite similar for tin and lead in the various molecules examined (except for a simple constant numerical factor (ca. 1.7) in the case of the latter) but because the s-overlap integrals can be rather small, especially in the case of lead, small differences in these are able to produce large apparent anomalies in the pattern of coupling constants. This is well illustrated by the Pb–Pb, Sn–Sn, and Pb–Sn bonds, as would also be expected on general chemical grounds. We conclude therefore that relations of the type of (1) cannot describe ${}^1K_{PbX}$ or ${}^1K_{SnX}$ and that attempts to obtain sets of parameters analogous to the Malinowski parameters[14] for ${}^1J_{{}^{13}C-H}$ cannot succeed.

The other coupling constants listed in Table I serve largely to confirm the foregoing conclusion. Thus ${}^2J_{{}^{207}Pb-H}$ varies in a systematic way largely in response to changes in the electronegativity of X, having its most negative values when the electronegativity of X is greatest. This behavior parallels that of other geminal coupling constants involving protons and a heavier element and supports the idea that α^2 and $\psi^2(0)$ for the lead atom are varying in the manner which chemical intuition would suggest. Some care must be used in the interpretation of the vicinal couplings ${}^3J_{Pb-H}$ since these probably have a marked stereochemical dependence, as will ${}^4J_{{}^{207}Pb-H}$. This last point is demonstrated vividly by the different values of the four-bond couplings to CH_3 and to CH_2 in $Me_3PbB(NMeCH_2-)_2$.

The lead chemical shifts are consistent with the view that heavy-atom substituents produce shifts to higher applied magnetic field when they possess one or more electron lone pairs but shifts to lower field when they do not. Similar conclusions have been drawn from work on ${}^{195}Pt$ shielding,[15] and the ${}^{11}B$ chemical shifts for the species $(-CH_2MeN)_2BX$ are also consistent with this. Thus for the series X = Cl, Br, and I the boron chemical shift moves to higher field as the atomic number of X increases,[16] whereas for X = C, Si, Sn, and Pb it moves to lower field.[5,17] These results indicate that the neighboring diamagnetic contribution to the shielding cannot be a dominant factor.[18]

It is clear from this preliminary survey that the coupling constants ${}^1J_{PbX}$ between lead and a directly bound element X are extraordinarily sensitive to the nature of the Pb–X bond (compare for example the widely different values of ${}^1J_{{}^{207}Pb-{}^{119}Sn}$ in $Me_3PbSnMe_3$ and $Me_3PbSnPh_3$). While this behavior has the disadvantage that it cannot be explained simply in terms of variations of α_s^2 and $\psi^2(0)$ for Pb and/or X, it does provide an extremely sensitive probe for the study of these bonds and no doubt will be greatly utilized with the growing availability of Fourier transform spectrometers.[19]

In connection with the structural uses of this type of measurement it is important to be aware that there is in general no close parallel between coupling constants involving tin and those involving lead and further that any attempts to extrapolate from the large body of carbon-13 data to lead may go seriously astray.

Acknowledgment. We thank the SRC, the Deutsche Forschungsgemeinschaft, and the University of London Central Research Fund for financial support and Mr. G. S. Pyne for a sample of $Ph^{15}NMeH$.

Registry No. Me_3SnH, 1631-73-8; Me_3PbH, 7442-13-9; $Me_3SnB(NMeCH_2-)_2$, 36333-59-2; $Me_3PbB(NMeCH_2-)_2$, 58747-16-3; Me_3SnCH_3, 594-27-4; Me_3PbCH_3, 75-74-1; $Me_3SnNMePh$, 1076-10-4; $Me_3PbNMePh$, 58747-17-4; Me_3SnPPh_2, 1213-51-0; Me_3PbPPh_2, 58747-18-5; $Me_3SnSeMe$, 17719-49-2; $Me_3PbSeMe$, 58747-19-6; $Me_3SnSnMe_3$, 661-69-8; $Me_3PbSnMe_3$, 58747-20-9; $Me_3SnSnPh_3$, 1235-18-3; $Me_3PbSnPh_3$, 58747-21-0; $Me_3PbPbMe_3$, 6713-83-3; Me_3PbNEt_2, 58747-22-1; dimethyldiselenium, 7101-31-7; trimethyllead bromide, 6148-48-7; $ClB(NMeCH_2-)_2$, 17739-11-6; ${}^{11}B$, 14798-13-1; ${}^{13}C$, 14762-74-4; ${}^{15}N$, 14390-96-6; ${}^{77}Se$, 14681-72-2; ${}^{119}Sn$, 14314-35-3; ${}^{207}Pb$, 14119-29-0.

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Organolanthanide Tetrahydroborates. Ligation Geometry and Coordinative Saturation

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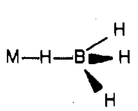
This work reports the synthesis and spectral (infrared, Raman) characterization of the series of compounds $(\eta^5\text{-}C_5H_5)_2LnBH_4\cdot THF$, where Ln = Sm, Er, Yb. Vibrational spectra indicate that the mode of BH_4^- coordination is sensitive to the metal ionic radius. The Ln = Sm compound is proposed to have tridentate BH_4^- ligation, whereas the Ln = Yb compound is proposed to have bidentate ligation. The tetrahydrofuran can be removed for Ln = Yb and Er to yield complexes of the composition $(\eta^5\text{-}C_5H_5)_2LnBH_4$. Vibrational spectra are similar to those of $Be(BH_4)_2$ and $CH_3Zn(BH_4)$, suggesting a polymeric structure with bridging BH_4^- groups. All data suggest appreciable ionic character in the bonding of the tetrahydroborate ligand to the trivalent lanthanides.

In recent years there has been a growing interest in the chemistry and bonding properties of the tetrahydroborate ligand, BH_4^-.[3] Organometallic tetrahydroborates are known for a large number of main group, transition metal, and actinide elements. Only the lanthanide series has remained virtually untouched in this respect.[3-5] Tetrahydroborate can conceivably adopt any of four different bonding modes (structures I–IV) in mononuclear complexes. Vibrational spectroscopy (infrared and laser Raman) can usually provide a straightforward method of distinguishing these.[7,8] Neutron diffraction, of course, provides the most precise geometric data, with x-ray and electron diffraction being of lesser accuracy.[3] Despite the prodigious growth of structural information over the past several years, the factors which influence the relative stabilities of the BH_4^- bonding modes (only II and III have been identified for covalent compounds) remain less than well understood.



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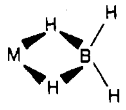

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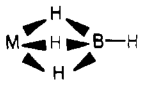


III

$M^+ BH_4^-$

IV

One simple yet untested consideration which may influence the orientation adopted by the BH_4^- is the size of the coordination site available. The ionic radius as well as the presence of other ligands (especially bulky ones) in the metal coordination sphere could be as important or even more important than electronic factors in dictating the ligation geometry.[9] With the hope of testing this hypothesis, we have chosen to synthesize and spectroscopically characterize a series of bis(η^5-cyclopentadienyl)tetrahydroboratolanthanides. Here, a monotonic variation in the metal ion size is available and the charge of the central metal ion does not vary. Thus, the effect of the lanthanide contraction[10] on the coordinative properties of the BH_4^- functionality could be tested. Presented here is a discussion of our chemical and vibrational spectroscopic studies which include the preparation of the first series of organometallic tetrahydroborates for tripositive lanthanides and some ascertainment of the influence of the lanthanide contraction and preferred coordination number upon the $M-BH_4^-$ interaction.

Experimental Section

The precautions involved in handling the highly air- and moisture-sensitive compounds for this study included the strict maintenance of anaerobic and anhydrous conditions. All operations were carried out under prepurified nitrogen or argon or in vacuo; solvents were thoroughly dried and were distilled under inert atmosphere immediately prior to use. Anhydrous $ErCl_3$ and $SmCl_3$ were obtained from Great Western Inorganics, Golden, Colo. Elemental analyses were performed by either Schwarzkopf Microanalytical Laboratories, Inc., Woodside, N.Y., or Dornis und Kolbe Mikroanalytisches Laboratorium, West Germany.

The syntheses of bis(η^5-cyclopentadienyl)lanthanide chlorides were carried out by a modification of the literature procedure[11a] in which C_5H_5Tl was substituted for NaC_5H_5. The procedure given below for $(\eta^5\text{-}C_5H_5)_2YbCl$ is also applicable to $(\eta^5\text{-}C_5H_5)_2MCl$, M = Sm, Er.

Bis(η^5-cyclopentadienyl)ytterbium Chloride. Prior to use, C_5H_5Tl was dried in vacuo at room temperature for 4 h. A slurry of 13.90 g (49.7 mmol) of anhydrous $YbCl_3$[12] in 150 ml of tetrahydrofuran (THF) was prepared in a 300-ml three-necked flask. Under nitrogen, an addition tube containing the C_5H_5Tl (26.77 g, 99.5 mmol) was attached to the flask and the C_5H_5Tl added in portions with stirring to the slurry over a period of 1 h; the reaction mixture was then allowed to stir overnight. After this time the reaction mixture was suction filtered to remove TlCl, and the THF removed in vacuo. The resultant orange solid was rinsed with three 10-ml portions of pentane; yield 8.73 g (51.9%). This compound and its homologues were identified by reported spectral properties.[11]

Bis(η^5-cyclopentadienyl)tetrahydroboratoytterbium. Bis(η^5-cyclopentadienyl)ytterbium chloride (2.16 g, 6.39 mmol) was placed in a 250-ml three-necked flask under nitrogen and dissolved in 125 ml of THF. Sodium borohydride (0.33 g, 8.68 mmol) was weighed quickly in air and added with stirring to the orange solution. The reaction mixture was allowed to stir for 2 days, filtered, and then the THF was removed in vacuo. The orange solid product was purified by sublimation (190 °C (10^{-3} Torr)) for 36 h. (Care was taken in this step not to allow the sublimation to proceed too long because thermal decomposition upon prolonged heating yields the green tris(η^5-cyclopentadienyl)ytterbium, which cosublimes under these conditions.) The yield is 0.71 g (35%) of dark orange solid. Anal. Calcd for $C_{10}H_{14}YbB$: C, 37.76; H, 4.44. Found: C, 37.43; H, 4.46.

Bis(η^5-cyclopentadienyl)tetrahydroboratoytterbium Tetrahydrofuranate. A small amount (0.27 g, 0.85 mmol) of pure bis(η^5-cyclopentadienyl)tetrahydroboratoytterbium was dissolved in 50 ml of THF, and the THF was immediately removed in vacuo at room temperature to yield 0.31 g (93%) of the orange powder bis(η^5-cyclopentadienyl)tetrahydroboratoytterbium tetrahydrofuranate. It was found that this compound would revert to the THF-free starting material by heating at 70–80 °C in vacuo for 3 h. Anal. Calcd for $C_{14}H_{22}YbBO$: C, 43.09; H, 5.68. Found: C, 42.84; H, 5.43. ^1H NMR (THF): broad cyclopentadienyl resonance at δ −36.3.

Bis(η^5-cyclopentadienyl)tetrahydroboratoerbium Tetrahydrofuranate. Bis(η^5-cyclopentadienyl)erbium chloride (4.77 g, 14.3 mmol) was weighed under nitrogen into a 500-ml three-necked flask, dissolved in 250 ml of THF, and $NaBH_4$ (0.63 g, 16.7 mmol, weighed quickly in air) was added with stirring. The reaction mixture was allowed to stir for 2 days after which time it was filtered and the THF was removed in vacuo. The peach-colored solid was rinsed with two 20-ml portions of pentane and dried under high vacuum. The compound was then sublimed (190 °C (10^{-3} Torr)) and the pink sublimate was extracted with THF to remove residual C_5H_5Tl via the following procedure. The compound was dissolved in a minimal amount of THF and the volume was reduced until precipitation occurred (the initial precipitate was yellow). The precipitate was allowed to settle and the supernatant was withdrawn via syringe and reserved. The THF was then removed in vacuo at room temperature to yield 0.88 g (16%) of a peach-colored solid. Anal.[13] Calcd for $C_{14}H_{22}ErBO$: Er, 43.51. Found: Er, 43.03.

Due to the facile loss of THF from this compound (vide infra), no parent ion was observed in the mass spectrum; however, an envelope[33] of peaks (*m/e* centered at 312) corresponding to an ion which had lost THF from the parent molecule was observed. Fragments ascribable to THF were also observed as were fragments corresponding to progressive loss of BH_4 and C_5H_5 from the THF-free compound. Furthermore, higher mass ions were observed, which, considering the apparent polymeric nature of the THF-free derivative (see Results and Discussion) is not surprising; under the high-vacuum and -temperature conditions of the mass spectrometer sample probe, the THF would quickly become detached from the molecule.

Bis(η^5-cyclopentadienyl)tetrahydroboratoerbium. A small portion (0.48 g, 1.25 mmol) of bis(η^5-cyclopentadienyl)tetrahydroboratoerbium tetrahydrofuranate was placed in a Schlenk tube and heated in vacuo at 70 °C for 1 h. This procedure removed the THF to yield 0.38 g (97%) of pink bis(η^5-cyclopentadienyl)tetrahydroboratoerbium. Anal.[13] Calcd for $C_{10}H_{14}ErB$: Er, 53.56. Found: Er, 52.49.

In the mass spectrum of this compound, an envelope[33] of peaks centered at *m/e* 312, which would correspond to the parent ion of the monomer $(\eta^5\text{-}C_5H_5)_2ErBH_4$, was observed. The relative intensities of these peaks confirm the presence of one erbium and one boron. Also observed were envelopes corresponding to progressive loss of BH_4 and C_5H_5 from the central metal. High-mass fragments were also present, corresponding to ions containing at least two erbiums. Since infrared data suggest that this compound has a polymeric nature (see Results and Discussion), the observation of these high-mass fragments is reasonable.

Bis(η^5-cyclopentadienyl)tetrahydroboratosamarium Tetrahydrofuranate. A 4.67-g (14.8-mmol) portion of bis(η^5-cyclopentadienyl)samarium chloride in a 500-ml three-neck flask was dissolved in 200 ml of THF. To this solution $NaBH_4$ (0.73 g, 19.3 mmol) was added, and the reaction mixture was allowed to stir for 3 days. After this time the reaction mixture was filtered under nitrogen and the solvent was removed in vacuo. The product was rinsed with three 5-ml portions of pentane to afford 3.76 g (69%) of a yellow

Table I. Infrared-Active Fundamental Vibrational Transitions Commonly Observed for Mononuclear MBH_4 Configurations

Structure	Approx freq, cm^{-1}	Type of internal coordinate change	Symmetry type	Comments
I	2300–2450	B-H_t str	A_1, E	Strong, probably a doublet
	~2000	B-H_b str	A_1	Strong
	~2000–1700	M-H_b str	A_1	May be broad
	1000–1150	BH_3 def	A_1, E	Strong band possibly with weaker one at slightly higher frequency
II	2400–2600	B-H_t str	A_1, B_1	Strong doublet, 50–80 cm^{-1} splitting
	1650–2150	B-H_b str	A_1, B_2	Strong band, possibly shoulder or second band
	1300–1500	Bridge str	A_1	Strong, broad
	1100–1200	BH_2 def	B_2	Strong
III	2450–2600	B-H_t str	A_1	Strong singlet
	2100–2200	B-H_b str	A_1, E	Doublet, 50–80 cm^{-1} splitting
	1150–1250	Bridge def	E	Strong
IV	2200–2300	B-H_t str	T_2	Strong, broad
	1050–1150	BH_2 def	T_2	Strong broad

powder. Attempts to remove the adducted THF from this compound either by sublimation or by heating in vacuo resulted in decomposition to tris(η^5-cyclopentadienyl)samarium.[14] Anal.[13] Calcd for $C_{14}H_{22}SmBO$: Sm, 40.91. Found: Sm, 41.26.

A mass spectrum (other than released THF and C_5H_5) could only be observed at relatively high probe temperatures (>200 °C). Under these conditions, the parent ion of $(\eta^5\text{-}C_5H_5)_3Sm$[33,34] was the only observable high-mass species; it is presumably a pyrolysis product (vide supra).

Borodeuteride Derivatives. All of the BD_4^- complexes prepared for this study were synthesized on a small scale in a manner totally analogous to the preparation of their BH_4^- counterparts. The $NaBD_4$ employed was obtained from Stohler Isotope Chemicals.

Instrumental Measurements. Infrared spectra were recorded with a Beckman IR-5 or IR-9 or a Perkin-Elmer Model 267 spectrophotometer and were calibrated with polystyrene film. Nujol mulls were prepared in a nitrogen-filled glovebox using dry, degassed Nujol. Solution spectra were obtained in benzene using a balanced set of Barnes Engineering 1.0-mm path length NaCl cells, sealed from the atmosphere as previously described,[15] and in THF using a balanced set of International Crystal Labs CaF_2 nitrogen-flushed cells with a 0.1-mm path length. Samples were checked for possible decomposition by making several scans of each compound, and samples were routinely exposed to air and spectra rerecorded to ascertain the effect of contact with the atmosphere.

Raman studies were performed with a Spex 1400II double monochromator using photon-counting detection. Excitation was by Spectra Physics Model 164 argon and krypton lasers. Samples were spun at 1800 rpm in sealed Pyrex tubes.

Nuclear magnetic resonance spectra were recorded using a Hitachi Perkin-Elmer R20-B (60-MHz) spectrometer. Samples were prepared in nitrogen-filled, serum-capped 5-mm NMR tubes.

Mass spectra were recorded with a Hewlett-Packard Model 5930A mass spectrometer at ionizing voltages of both 9 and 70 eV. The probe temperature was generally ca. 220 °C. Capillary sample containers were loaded in a nitrogen-filled glovebox and stored under N_2 until needed, at which time they were quickly inserted into the spectrometer probe. We thank Dr. L. A. Raphaelian for assistance with these measurements.

Results and Discussion

Table II. Borohydride Vibrational Frequencies (cm^{-1}) in Bis(η^5-cyclopentadienyl)tetrahydroboratolanthanide Tetrahydrofuranates and Their Borodeuteride Analogues in the Solid State as Nujol Mulls[a,b]

Cp_2-$YbBH_4$·THF	Cp_2-$YbBD_4$·THF	ν_H/ν_D	Cp_2-$ErBH_4$·THF	Cp_2-$SmBH_4$·THF	Cp_2-$SmBD_4$·THF	ν_H/ν_D
2393 m	1797 s	1.33	2380 br	2428 br	1800 br	1.35
2353 s	1735 s	1.36	2290 w	2279 br	1661 br	1.37
2238 w			2230 w	2223 sh	1640 sh	1.36
2171 s	1589 s	1.37	2175 s	1174 br	*d*	
2135 s	1539 s	1.39	2128 s			
1347 br	~950 br	1.42	1350 br			
1123 br	*c*		1120 br			

[a] Cp = η^5-C_5H_5. [b] Key: s, strong; m, medium; w, weak; br, broad; sh, shoulder. [c] This absorbance is buried underneath either the 844-cm^{-1} THF mode or the 800-cm^{-1} Cp mode. [d] This absorbance is probably under the 844-cm^{-1} THF mode.

$$LnCl_3 + 2C_5H_5Tl \xrightarrow{THF} (\eta^5\text{-}C_5H_5)_2LnCl + 2TlCl \qquad (1)$$

$$(\eta^5\text{-}C_5H_5)_2LnCl + \text{excess } NaBH_4 \xrightarrow{THF} (\eta^5\text{-}C_5H_5)_2LnBH_4\cdot THF + NaCl \quad (Ln = Sm, Er, Yb) \qquad (2)$$

$$(\eta^5\text{-}C_5H_5)_2LnBH_4\cdot THF \rightleftarrows (\eta^5\text{-}C_5H_5)_2LnBH_4 + THF \quad (Ln = Er, Yb) \qquad (3)$$

Chemistry. The reasons behind choosing lanthanide complexes for a spectroscopic investigation of the relationship between the size of the central metal ion and the bonding mode of the tetrahydroborate ligand have already been related. Although $Ln(BH_4)_3\cdot n$THF[16] and $Ln(BH_4)_2Cl\cdot n$THF[17] compounds are known, the likelihood of ligand redistribution reactions[18] and polymeric solid-state structures (cf. $U(BH_4)_4$[19]) rendered them an unappealing choice for such an investigation. It was therefore decided to synthesize tetrahydroborate derivatives of bis(η^5-cyclopentadienyl)lanthanides. Synthetic pathways to the desired compounds are shown in eq 1–3. Thallium cyclopentadienide is a more convenient choice of reagents for transformation 1 than the previously employed[11a] sodium cyclopentadienide because of the air and moisture stability of the former. The initial products of reaction 2 are tetrahydrofuran (THF) adducts, as deduced from chemical analysis and spectral (infrared, mass) studies. The coordinated THF can be removed by heating under high vacuum, to yield $(\eta^5\text{-}C_5H_5)_2LnBH_4$ complexes for Ln = Er and Yb. Addition of THF regenerates the adducts.

Vibrational Spectra. Solid-state infrared spectra of the tetrahydroborate derivatives synthesized for this study are shown in Figure 1. Infrared bands due to an η^5-C_5H_5 moiety are typically in the region of 790 (vs) (A_1 and E_1 out-of-plane wagging) and 1020 (m) cm^{-1} (E_1 in-plane wagging) and are easily identified in the spectra.[20] Other weaker features associated with $(\eta^5\text{-}C_5H_5)M$ are seen at 1780 (w), 1660 (br), and 1550 (w) cm^{-1}. Likewise, features arising from coordinated tetrahydrofuran can be identified by examining the spectrum of the THF complex of $YbCl_3$, shown in Figure 1I. Infrared absorptions are observed at 1350 (w), 1180 (m), 1040 (w), 920 (m), and 850 (s) cm^{-1}. When these data are subtracted from the experimental spectra, the characteristic vibrational transitions of the complexed tetrahydroborate functionality remain (see Tables I, II). As already noted, the tetrahydroborate ligand can adopt any of four different ligation patterns (I–IV) in mononuclear complexes. In most cases it is possible to differentiate these modes by analysis of the vibrational spectra. For convenience in the ensuing discussion, we summarize some general observations for infrared spectral features in the structurally diagnostic region of the spectrum[3b,7b] (Table I). The bidentate (structure II) and tridentate (structure III) coordination configurations are well documented for metal complexes.[3] The monodentate structure

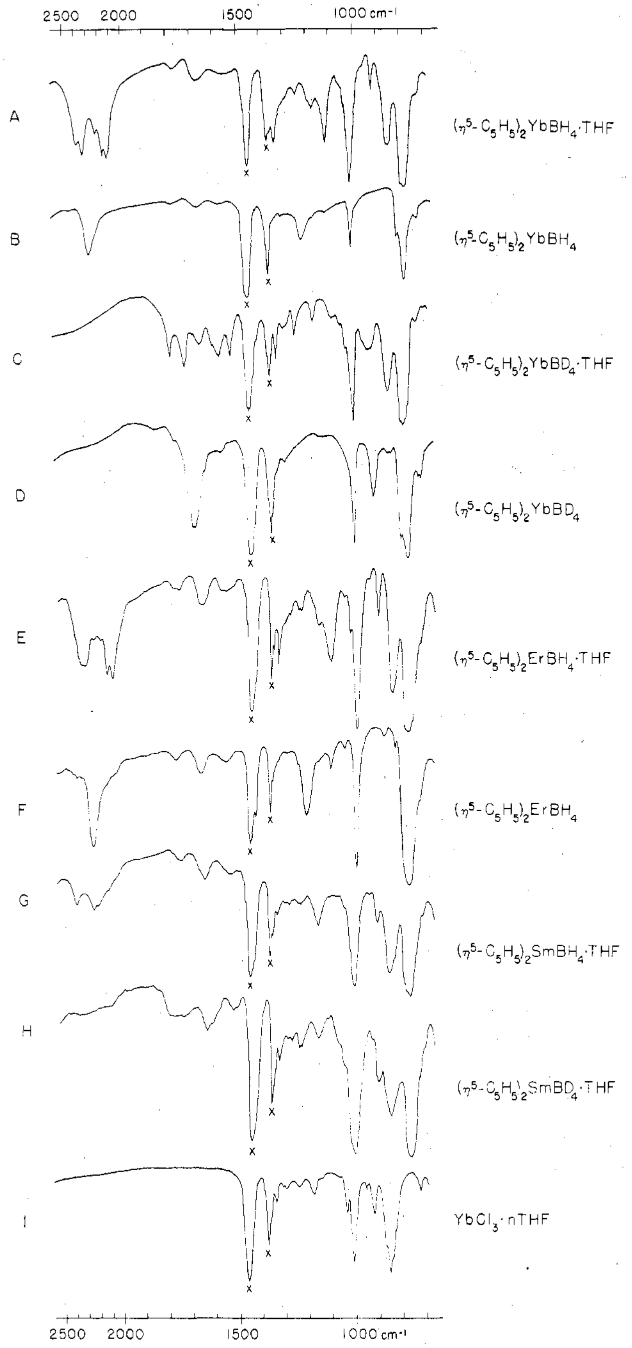


Figure 1. Solid-state (Nujol mull) infrared spectra of the lanthanide borohydride and borodeuteride complexes. Absorbances due to Nujol are indicated by X.

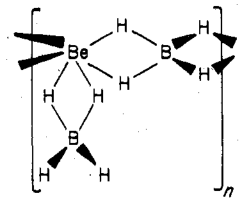
I is not established for metal complexes but is analogous to the singly hydrogen-bridged structures proposed for $B_2H_7^-$ and $(R_3B)_2H^-$.[21]

Table III. Borohydride Vibrational Frequencies (cm^{-1}) in Bis(η^5-cyclopentadienyl)tetrahydroboratolanthanide Compounds in the Solid State as Nujol Mulls[a,b]

Cp_2YbBH_4	Cp_2YbBD_4	ν_H/ν_D	Cp_2ErBH_4
2278 br	1700 br	1.34	2281 br
1227 br	929 br	1.32	1225 br

[a] $Cp = \eta^5\text{-}C_5H_5$. [b] br = broad.

As can be readily seen (Figure 1), the $(\eta^5\text{-}C_5H_5)_2LnBH_4\cdot THF$ and $(\eta^5\text{-}C_5H_5)_2LnBH_4$ series differ markedly in structure. For example, the tetrahydrofuranates exhibit terminal and bridging ν_{B-H} bands characteristic of any mononuclear BH_4 metal complex. On the other hand, removal of THF collapses the B–H stretching pattern to a single peak (ca. 2280 cm^{-1}). The only other tetrahydroborate band observed is found in the B–H deformation region, ca. 1225 cm^{-1}. These conclusions are further confirmed by deuteration (Figure 1D, Table III). The infrared pattern exhibited by the $(\eta^5\text{-}C_5H_5)_2LnBH_4$ complexes is strikingly reminiscent of that observed for $Be(BH_4)_2$[22] and $CH_3Zn(BH_4)$[23] in the solid state. The former has been shown to possess a polymeric structure V;[24] structure VI has been proposed for the latter.[23]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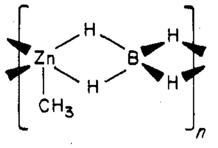
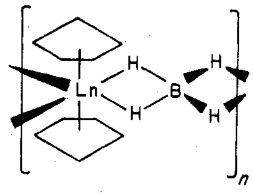

VI

The bridging BH_4^- segment of $Be(BH_4)_2$ exhibits major bands in the infrared spectrum at 2350, 2330, 1320, and 1130 cm^{-1}, which are compatible, when supplemented by Raman data, with a reduction in the BH_4^- symmetry from T_d to D_{2d}.[23] For $CH_3Zn(BH_4)$, the major infrared bands are at 2215 and 1236 cm^{-1}, with weaker bands at 2255 and 1096 cm^{-1}, also indicating some distortion (perhaps ±10° for the HBH angle) from T_d to D_{2d}.[23] These conclusions were supported by laser Raman spectra and normal-coordinate analysis. The distortion in $CH_3Zn(BH_4)$ appears to be less than in the beryllium compound, and this has been attributed to the greater ionic character of the bonding in the former.[23] By similar reasoning, the infrared spectra of the present $(\eta^5\text{-}C_5H_5)_2LnBH_4$ compounds are also compatible with a polymeric structure, such as VII. Here there is no spectral evidence for the infrared-active T_2 (T_d) B–H stretch splitting to B_2 and E bands (D_{2d}) nor of the infrared-active T_2 (T_d) deformation giving rise to B_2 and E modes, under reduced (D_{2d}) symmetry. Further attempts to corroborate these findings with laser Raman studies (using several Ar^+ and Kr^+ exciting lines) were frustrated by severe fluorescence. For $(\eta^5\text{-}C_5H_5)_2ErBH_4$ (5145-Å Ar^+ excitation), it was possible to identify $\eta^5\text{-}C_5H_5$ emissions[20b,25,35] at 1125 cm^{-1} (A_1 ring breathing) and 3116 cm^{-1} (A_1 C–H stretching) with certainty; there also appeared to be a weak B–H stretch at 2283 cm^{-1} (A_1?).[26] The H:D ratios of 1.34 for the infrared-active B–H stretches and 1.32 for the deformations are in agreement with product rule expectations for either T_2 vibrations or the corresponding irreducible representations in the D_{2d} subgroup.[23] Interestingly, the mass spectra (see Experimental Section for details) reveal association of the monomeric units even in the gas phase.


VII

The vibrational analysis for the $(\eta^5\text{-}C_5H_5)_2LnBH_4\cdot THF$ compounds is somewhat more complex. All infrared spectra show $B\text{-}H_{terminal}$ and $B\text{-}H_{bridge}$ vibrations. The spectrum of the ytterbium compound (Figure 1A) appears to be in best agreement with a bidentate (structure II) as opposed to a tridentate (structure III) ligation geometry. Besides a BH_2 deformation at 1123 cm^{-1} (Figure 1, Table II), the characteristic bidentate bridge expansion mode is observed at 1347 cm^{-1}, which shifts to 950 cm^{-1} upon deuteration (H:D = 1.42).

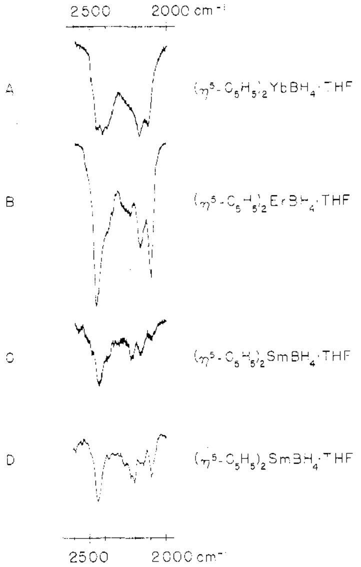


Figure 2. Solution infrared spectra of bis(η^5-cyclopentadienyl)-tetrahydroboratolanthanide tetrahydrofuranates. A–C in THF; D in benzene.

The H:D ratio can be compared to that for the corresponding band in $Be(BH_4)_2$ (1.43),[22] in $Al(BH_4)_3$ (1.37),[27,28] and in (η^5-C_5H_5)$_2$$VBH_4$ (1.35).[7a] The infrared spectra in solution (Figure 2) exhibit a broad, incompletely resolved ν_{B-H_t} multiplet at ca. 2410 cm^{-1} in both THF and benzene. For a bidentate structure, a doublet is expected. On progressing to the erbium and samarium compounds, noteworthy changes occur in the spectra. In solutions (Figure 2) the B–H$_{\text{terminal}}$ stretch absorption sharpens to a singlet, which is more characteristic of a tridentate configuration. There may also be further splitting of the ν_{B-H_b} absorptions. Similar trends are observed in the solid. Especially in the case of samarium, a decrease in the intensity (or disappearence) of the bridge expansion mode at ca. 1350 cm^{-1} is observed. Also, the BH_2 deformation mode increases in frequency from 1123 to 1174 cm^{-1}. If these trends are interpreted in terms of structural stereotypes II and III, then the samarium spectra are most compatible with a tridentate geometry. The intermediate erbium case is less clear-cut since the solid-state results are similar to the ytterbium spectra, while the solution transitions (which were identical in THF and benzene) are most like those of the samarium. Attempts to obtain corroboratory laser Raman spectra were again complicated by intense fluorescence, and only weak η^5-C_5H_5 vibrations were detected.

The rather small difference in frequency between the bridge and terminal B–H stretches for the (η^5-C_5H_5)$_2$$LnBH_4$·THF complexes (ca. 250 cm^{-1}) can be understood in terms of a smaller purturbation of the ligand from an isolated tetrahedral BH_4^- ion (here the modes are degenerate[28]) than is found in covalent transition metal tetrahydroborates.[3] In these complexes the separation between stretching modes (average of symmetric and antisymmetric) is usually on the order of 400–500 cm^{-1}, with (η^5-C_5H_5)$_2$$VBH_4$ (732 cm^{-1})[7a] and (η^5-C_5H_5)$_2$$Zr(BH_4)_2$ (ca. 280 cm^{-1})[7b] representing the extremes. In contrast, ion-paired Li^+ and BH_4^- exhibit a splitting of only ca. 120 cm^{-1} in diethyl ether solution.[29] The relatively small separation in the present case is in accord with other evidence for the predominantly electrostatic character of the bonding in organolanthanides.[4,30]

Conclusions

This study provides evidence that metal ion radius and coordinative saturation have a strong influence on the nature of BH_4^- coordination in organolanthanides. For the series of compounds (η^5-C_5H_5)$_2$$LnBH_4$·THF the contraction in ionic radius[31,32] on going from samarium (effective ionic radius 1.09 Å) to ytterbium (0.98 Å) appears to be accompanied by a change from tridentate (structure III) to bidentate (structure II) BH_4^- ligation. Removal of the tetrahydrofuran produces a reduction in the lanthanide coordination number which is compensated for by the formation of a polymeric, borohydride-bridged structure, similar to $Be(BH_4)_2$ and $CH_3Zn(BH_4)$. This apparently allows the lanthanide to maintain its coordination number at a preferred level. It is difficult to predict just how transferable the results of this investigation will be to transition metal chemistry. The bonding in organolanthanides appears to be significantly ionic, so that the restrictions of proper orbital overlap are far less important. However, it is also clear from this work that ionic radius effects should not be ignored in any type of tetrahydroborate complex.

Acknowledgment. We are grateful to the National Science Foundation (Grant MPS-10341 A01) and to NATO (Grant 776) for generous support of this work. We thank the Northwestern Materials Research Center for access to the Raman facility.

Registry No. Cp_2YbBH_4·THF, 58602-10-1; Cp_2YbBH_4, 58602-18-9; Cp_2YbBD_4·THF, 58602-11-2; Cp_2YbBD_4, 58602-20-3; Cp_2ErBH_4·THF, 58602-12-3; Cp_2ErBH_4, 58602-16-7; Cp_2SmBH_4·THF, 58602-13-4; Cp_2SmBD_4·THF, 58602-14-5; Cp_2YbCl, 42612-73-7; Cp_2ErCl, 53224-35-4; Cp_2SmCl, 56200-25-0.

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Nuclear Magnetic Resonance Study of Structural Dynamics in μ-Carbonyl-bis-μ-stannylene-diiron Hexacarbonyl Clusters

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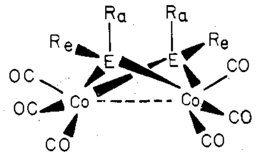
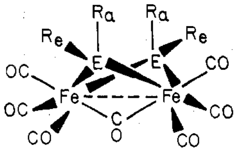
The compound $[\mu\text{-}(C_6H_5)(CH_3)Sn]_2Fe_2(CO)_7$ was synthesized to differentiate bridge deformation from iron–tin bond cleavage in R group interchange processes of stereochemically nonrigid $[\mu\text{-}R_2Sn]_2Fe_2(CO)_7$ complexes. It is found from proton NMR studies that both processes can occur, the former with $\Delta G^\ddagger = 11.8 \pm 0.6$ kcal/mol (298 K) and the latter with $\Delta G^\ddagger = 19.2 \pm 0.9$ kcal/mol (298 K). The bridge deformation in the related, more soluble molecule $[(n\text{-}C_4H_9)_2Sn]_2Fe_2(CO)_7$ occurs with simultaneous, stereospecific interchange of bridge and terminal carbonyl ligands, as monitored by ^{13}C NMR spectra. The complex $[(C_6H_5)(CH_3)SnFe(CO)_4]_2$ exists in two isomeric forms which interconvert in solution with $\Delta G^\ddagger = 25.5 \pm 0.7$ kcal/mol (298 K). The iron–tin bond cleavages are proposed to yield $R_2Sn \rightarrow Fe$ stannylene intermediates.

The process which interchanges axial (R_a) and equatorial (R_e) groups at a rate fast on the proton NMR time scale in $(R_2E)_2Co_2(CO)_6$ (A) and $(R_2E)_2Fe_2(CO)_7$ (B) cluster compounds has been discussed in terms of two distinct mechanistic patterns. One possible process is a "flapping" or deformation of the R_2E bridges, in which passage through a planar Co_2E_2 or Fe_2E_2 intermediate or transition state would serve to permute R_e and R_a moieties.[3,5] The other possible process would involve scission of Co_2–E and Fe_2–E bridges, to form $R_2E \rightarrow Co$ and $R_2E \rightarrow Fe$ species.[3–5] These are analogous to carbene complexes,[6,18] and rotation about the E→Co and E→Fe bonds, followed by closure of the bridge, would provide a pathway for R_e–R_a interconversion. Though the flapping process might seem plausible for molecules of type A, the observation that R_e–R_a interchange takes place at nearly the same rate in type B complexes[5] appears contradictory, since the presence of a fixed, bridging carbonyl would surely present some obstruction to "flapping". Our interest in bond-breaking reactions of group 4 metal–transition metal complexes[7,8] and in the nature of silylene, germylene, and stannylene analogues of carbene complexes,[8] has prompted our investigation of the above problem. Our goal has been to map out the relative energetic requirements of the two processes discussed above for a type B molecule, which on the surface presents the greatest potential contradiction in terms of mechanistic information.



A

E = Ge, Sn
R = CH_3



B

E = Si, Ge, Sn
R = CH_3, $n\text{-}C_4H_9$, C_6H_5

Experimental Section

The synthesis and handling of all compounds were carried out in an atmosphere of prepurified nitrogen or argon. Solvents were thoroughly dried in a manner appropriate to each and distilled under nitrogen immediately prior to use (except where otherwise noted). Elemental analyses were performed by either Ms. H. Beck (Northwestern University Analytical Services Laboratory) or Schwarzkopf Microanalytical Laboratory (Woodside, N.Y.).

Phenylmethyltin Dichloride. Triphenylmethyltin[9] (10.46 g, 28.6 mmol) was placed in a 300-ml three-necked flask and dissolved in 100 ml of ether. Approximately 12.7 ml (ca. 57.2 mmol) of a saturated solution (4.5 M at room temperature) of HCl in ether was syringed into a dropping funnel attached to the flask and was diluted with 25 ml of ether. This solution was added dropwise with stirring to the $(C_6H_5)_3SnCH_3$ solution over a period of 2 h, and the reaction mixture then allowed to stir overnight. Next, the ether and benzene were removed in vacuo, yielding at this point a white solid which was "wet" with a yellow, nonvolatile oil. Purification was accomplished by "sublimation" of the solid–liquid mixture at 10^{-3} Torr and 35 °C onto a water-cooled cold finger. This afforded 5.48 g (68%) of colorless crystals of phenylmethyltin dichloride, mp 46–47.5 °C. Anal. Calcd for $C_7H_8SnCl_2$: C, 29.78; H, 2.86. Found: C, 29.24; H, 3.01. ^{1}H NMR ($CDCl_3$): multiplet centered at δ 7.5 (5 H); singlet at δ 1.23 (3 H), $J_{^{117,119}Sn\text{-}CH_3} = 68$ Hz.

Bis-μ-phenylmethylstannylene-diiron Octacarbonyl, $[(C_6H_5)(CH_3)SnFe(CO)_4]_2$. To a slurry of 7.39 g (21.4 mmol) of $Na_2Fe(CO)_4 \cdot 1.5(\text{dioxane})$[10] in 100 ml of benzene at room temperature was added 5.48 g (19.45 mmol) of $(C_6H_5)(CH_3)SnCl_2$. The mixture was allowed to stir for 5 days, after which time the solvent (and released dioxane) were removed in vacuo. The resultant yellow-orange powder was recrystallized twice from 4:1 hexane–pentane in the following manner. A saturated solution was prepared in the mixed solvent. The