Metal Tetrahydroborates and Tetrahydroborato Metalates, 20[◇]

Reactions of Cadmium Tetrahydroborate with Alcoholates and Phenolates – X-ray Structure of $[MeCd(OCMe_3)]_4$

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Cadmium tetrahydroborate reacts with alkali metal alcoholates or phenolates in THF solution either with formation of addition products $[Cd(BH_4)_2OR]^-$ or by ligand exchange to produce $Cd(BH_4)OR$. Different oligomers of the latter are formed depending on concentration. The reaction of $Cd(BH_4)_2$ with $Cd(Omes)_2$ (mes = mesityl) leads to an equilibrium of the starting materials with $Cd(BH_4)(Omes)$ as shown by ^{113}Cd-NMR spectroscopy. The crystal structure of $MeCd(OCMe_3)$, a molecule which can be regarded as a model for $Cd(OCMe_3)(BH_4)$, proved to be a tetramer with a cubane-type Cd_4O_4 core.

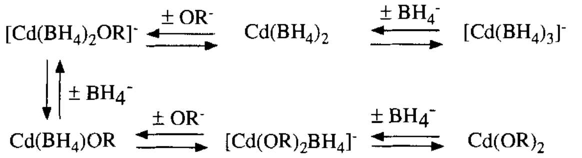
Alcohols are widely used as solvents for reductions of functional groups in organic molecules with alkali metal tetrahydroborates MBH_4. The reducing power can be tuned either by the choice of the alcohol or by the addition of metal halides. Reactions of MBH_4 with metal halides $M'X_n$ may result in the formation of $M'(BH_4)_n$ compounds, which, in turn, may react with a variety of Lewis bases. For instance, the reaction of $Cd(BH_4)_2$ with lithium tetrahydroborate leads to a wide variety of products[1]. In most cases complex equilibria[1–3] are established as shown by ^{11}B- and ^{113}Cd-NMR spectroscopy and occasionally by IR spectroscopy. Therefore, it was expected that $Cd(BH_4)_2$ would react not only with I^- or BH_4^-, but with various other anionic nucleophiles X^-. The present study reports on reactions of $Cd(BH_4)_2$ with several alkali metal alkoxides and phenolates.

Results

Interaction of $Cd(BH_4)_2$ with OR^- may result in: a) addition producing $[Cd(BH_4)_2OR]^-$, b) substitution leading to $Cd(BH_4)OR$ or $Cd(OR)_2$ and BH_4^- followed c) by addition of BH_4^- to $Cd(BH_4)_2$, $Cd(BH_4)OR$ and/or $Cd(OR)_2$ as shown in Scheme 1. Thus, a number of species may be present in solution. Each of these may give rise to a specific signal in the ^{113}Cd-NMR spectrum.

All ^{113}Cd-NMR signals observed in the systems investigated are summarized in Table 1 together with the coupling constants $^1J(CdH)$, which give information about the charge of the species[2]. These data and the multiplicity (hyperfine structure) of the signals can be used to assign the observed signals.

Scheme 1



As can be seen from Table 1, reactions of $Cd(BH_4)_2$ with lithium phenolate have been found to give a particular clear picture of the reactions involved. The ^{113}Cd-NMR spectrum of a THF solution containing $Cd(BH_4)_2$ and lithium phenolate exhibits a dominating signal at $\delta = -255$ and two further resonances at -170 and -447. Because the hyperfine structure is well resolved in this system, the assignment is clear. The resonance at $\delta = -170$ is a tridecet with $^1J(CdH) = 203$ Hz resulting from the interaction of twelve hydrogen nuclei with a ^{113}Cd center. Consequently this signal results from $[Cd(BH_4)_3]^-$. Although it is not possible to detect all 13 signals, the tridecet nature is deduced from the intensity ratio of the recorded signals. The ^{113}Cd resonance at $\delta = -255$ arises from a monoanion as ascertained by the value of the coupling constant $^1J(CdH) = 207$ Hz. Although only a septublet is observed, but the intensity of the recorded signal corresponds to a nonet and indicates the presence of two coordinated BH_4^- groups. Therefore, this signal is assigned to $[Cd(BH_4)_2OPh]^-$. The quintuplet at $\delta^{113}Cd = -447$ [$^1J(CdH) = 307$ Hz] suggests the presence of the neutral species $[(PhO)Cd(BH_4)]_n$ of unknown nuclearity. Reactions leading to these species are summarized in Eq. (1) to (3).

When the molar ratio of LiOPh to $Cd(BH_2)_4$ is increased, all signals disappear except the resonance of the anion $[Cd(BH_4)_2OPh]^-$. This phenoxybis(tetrahydroborato)cad-

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Table 1. δ^{113}Cd data for the signals observed in reactions of MOR (>1:1) with $Cd(BH_4)_2$ in THF solution. ^1J(CdH) in Hz. a) Tridecet, b) quintuplet, c) nonet

M	R	$Cd(BH_4)_2$	$[Cd(BH_4)_3]^-$ a)	$[ROCd(BH_4)]_n$ b)	$[Cd(BH_4)_2OR]^-$ c)
Li	Ph		−170 (203)	−447 (307)	−255 (207)
Li	mes	−335		−475 (278)	−257 (210)
Li	Et		−173 (203)	−361 −368 −374 −380	
Li	CMe_3			−326 (273) −294 (271) −307 (276) −325 (272)	−293 (270) −307 (289)
Na	CMe_3			−325 (270)	

$$Cd(BH_4)_2 + OR^- \rightleftharpoons [Cd(BH_4)_2(OR)]^- \quad (1)$$

$$[Cd(BH_4)_2(OR)]^- \rightleftharpoons Cd(BH_4)(OR) + BH_4^- \quad (2)$$

$$Cd(BH_4)_2 + BH_4 \rightleftharpoons [Cd(BH_4)_3]^- \quad (3)$$

R = Ph

mate, which forms by addition of PhO^- to $Cd(BH_4)_2$ as described in Eq. (1), is rapidly converted to the neutral phenoxycadmium(tetrahydroborate) [Eq. (2)] as long as an excess of $Cd(BH_4)_2$ can scavenge the liberated $LiBH_4$ as described by Eq. (3). Because the equilibrium constant for reaction (2) is small, an increasing concentration of LiOPh shifts the coupled equilibria to the side of the anion $[Cd(BH_4)_2OPh]^-$. It is surprising, however, that neither $[Cd(OPh)_2BH_4]^-$ nor an anion of type $[Cd(BH_4)_{4-n}(OPh)_n]^{2-}$ could be detected by ^{113}Cd-NMR spectroscopy even in the presence of a large excess of phenolate. This may be due to the ability of the cadmium center in $[Cd(BH_4)_2OPh]^-$ to coordinate THF or associate to form oligomers of yet unknown nuclearity.

Steric factors play an important role in the reaction of $Cd(BH_4)_2$ with phenolates. In contrast to the system LiOPh/$Cd(BH_4)_2$/THF, the equilibrium (1) lies on the side of the starting compounds in the system $Cd(BH_4)_2$/LiOmes (mes = 2,4,6-trimethylphenyl). The ^{113}Cd-NMR spectrum of a solution containing $Cd(BH_4)_2$ and LiOmes in a 2:1 molar ratio shows very little conversion: the most intense signal results from $Cd(BH_4)_2$ while the intensities of the signals of the products $Li[Cd(BH_4)_2(Omes)]$ ($\delta^{113}Cd = -257$) and $[Cd(BH_4)(Omes)]_n$ ($\delta^{113}Cd = -475$) are weak. This pattern changes considerably as one proceeds to a 1:1 ratio. Under these conditions, the ^{113}Cd resonance of the addition product $[Cd(BH_4)_2(Omes)]^-$ becomes the dominant signal. The signal of $[Cd(BH_4)(Omes)]_n$ is still present in low intensity, and disappears as the ratio of $Cd(BH_4)_2$ to LiOmes increases. A consequence of the greater steric demand of the $mesO^-$ anion as compared to the PhO^- group is that its addition to $Cd(BH_4)_2$ is hindered. Nevertheless, $[Cd(BH_4)_2(Omes)]^-$ is almost exclusively formed with $Cd(BH_4)(Omes)$ as a very minor by-product. This can only be understood if $Cd(BH_4)(Omes)$ is not present as a monomer.

To confirm the assignment of the ^{113}Cd-NMR signal at $\delta = -257$, a THF solution containing $Cd(BH_4)_2$ and $Cd(Omes)_2$ in a 1:1 molar ratio was investigated. Only the exchange reaction (4) was expected to occur:

$$Cd(BH_4)_2 + Cd(Omes)_2 \rightleftharpoons 2\,Cd(BH_4)(Omes) \quad (4)$$

The ^{113}Cd-NMR spectrum of the solution at 213 K shows that the equilibrium (4) lies to the right. This is deduced from the signal for $Cd(BH_4)(Omes)$ at $\delta^{113}Cd = -257$. In addition, a weak signal for $Cd(BH_4)_2$ at $\delta^{113}Cd = -335$ is found due to a slight excess of $Cd(BH_4)_2$.

The IR spectrum of this solution shows a pattern in the region of the B−H-stretching vibrations which is typical of η^2-bonded BH_4^- groups. Therefore, the compound must be described as $[(mesO)Cd[(\mu\text{-}H)_2BH_2]_n$. At 195 K crystals were obtained, but decomposed to a fine colorless powder on warming to ambient temperature. Thus we were unable to determined its molecular weight and information about its degree of association.

The ^{113}Cd-NMR spectra and especially the different negative NOEs (nuclear Overhauser effect) for the species in solution prevent a quantitative evaluation of equilibria in systems containing $Cd(BH_4)_2$ and alcoholates. This is particularly true for solutions prepared from $Cd(BH_4)_2$ and lithium ethanolate. In fact, due to the negative value of the gyromagnetic ratio γ of the ^{113}Cd nucleus, the change of the signal intensity on proton decoupling depends on the species observed. In proton-coupled spectra the intensity may be dissipated for high multiplicity signals, thus rendering the detection of minor signals difficult. This can lead to the total disappearance of signals.

In contrast to the $Cd(BH_4)_2$/LiOmes/THF system, up to six resonances are oberved in the ^{113}Cd-NMR spectrum of the $Cd(BH_4)_2$/LiOEt/THF system. One signal can be readily assigned: the resonance at $\delta^{113}Cd = -173$ results from $Cd(BH_4)_3^-$. Signals at $\delta^{113}Cd = -361, -368, -374$ and -380 all show fine structures with ^1J(CdH) = 257 Hz, and they are assigned tentatively to different oligomers of $Cd(OEt)BH_4$. The signal for the anion $[Cd(BH_4)_2(OEt)]^-$ can be detected at $\delta^{113}Cd = -221$ only at high EtO^- to Cd^{2+} ratios. Therefore, equilibria analogous to those described in Eq. (1) to (3) are also operative in the $Cd(BH_4)_2$/LiOEt solutions.

The presence of uncomplexed $LiBH_4$ in the mixtures is demonstrated by its characteristic signal in the ^{11}B-NMR spectra. No information on specific Cd tetrahydroborates is obtained from these spectra because all other signals are grouped around $\delta^{11}B = -50$.

How does the steric demand of the OR group influence its reactivity towards $Cd(BH_4)_2$? To answer this question and to elucidate the limits of resolution enhancement, LiOEt was replaced by $LiOCMe_3$. The ^{11}B- and ^{113}Cd-NMR resonances of the system $Cd(BH_4)_2/LiOCMe_3$ in THF are particularly well resolved. Data are summarized in Table 2. All ^{113}Cd signals are quintuplets with a coupling constant $^1J(CdH)$ of about 270 Hz. Therefore, all signals indicate the presence of a neutral species containing one BH_4^- group in the solutions. They are, therefore, assigned to different oligomers of $Cd(BH_4)(OCMe_3)$. No other Cd-containing species could be detected.

The use of $NaOCMe_3$ instead of $LiOCMe_3$ simplifies the $Cd(BH_4)_2/OR^-$ system: Only one quintuplet at $\delta^{113}Cd = -325$ with $^1J(CdH) = 270$ Hz is observed in this case. We attribute this resonance to the neutral species $[Cd(BH_4)(OCMe_3)]_n$. No free BH_4^- can be detected in the ^{11}B-NMR spectra of solutions containing $Cd(BH_4)_2$ and $NaOCMe_3$ in a 2:1 and 1:1 ratio. A signal due to the species $Cd(BH_4)_3^-$, which should form in analogy to equations (1) to (3), could not be detected. This is proably due the different influence of the NOE. At a relatively low Cd^{2+} content of the solution $[(Cd(BH_4)_2\text{: }NaOCMe_3 = 1:4)]$, the quintuplet $[^1J(CdH) = 256\text{ Hz}]$ points to the presence of a different oligomer of $[Cd(BH_4)(OCMe_3)]_m$ with $\delta^{113}Cd = -303$.

Finally, it should be noted that fairly rapid decomposition of all species detected in solution occurred at temperatures >250 K with formation of metallic Cd.

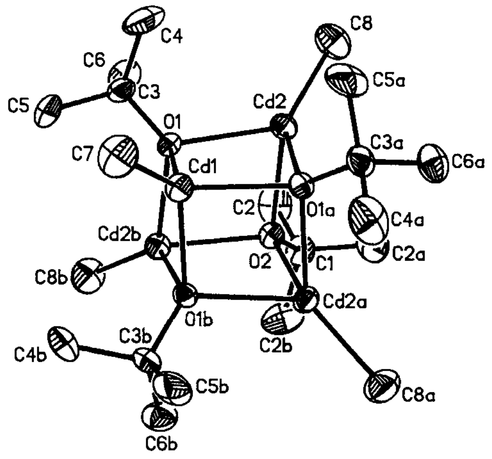
The Crystal Structure of $[MeCd(OCMe_3)]_4$

Because it was impossible to isolate any of the *tert*-butoxy tetrahydroborato-cadmium compounds due to rapid decomposition above 250 K, we attempted to prepare a compound that could be a model for $[(BH_4)Cd(OCMe_3)]_n$, and the best alternative is probably $[MeCdOCMe_3)]_n$. The methyl group is comparable to the tetrahydroborate group, and the respective compounds often have similar structures. For example, the methyl groups in $LiAlMe_4$[4] bridge the metal centers forming an infinite polymeric chain. Similarly, $LiAl(BH_4)_4$ which is isoelectronic with $LiAlMe_4$ also forms a polymer[5] probably involving bridging BH_4 groups because the structure of $Bu_4N[Al(BH_4)_4]$ demonstrates a tetrahedral disposition of the BH_4 groups around the Al center[5]. Therefore, $MeCdOCMe_3$ was synthesized according to Eq. (5)[5,7].

$$CdMe_2 + Me_3COH \rightarrow Me_3CO\text{-}CdMe + CH_4 \qquad (5)$$

^{113}Cd-NMR spectroscopy reveals the similarity between the methyl- and the tetrahydroborate compounds. Data are compiled in Table 3. The difference between the $\delta^{113}Cd$ data of analogous methyl and tetrahydroborate cadmium compounds is constant (the values were determined in different solvents and under various conditions). Though the bonding of the Me and BH_4 groups to the Cd center in the two classes of compound will be different, it can be supposed that they have similar molecular structures because the difference in the coupling constants remains constant for pairs of comparable compounds. Therefore, we assumed that the compounds $[(BH_4)CdOR]_n$ and $[CH_3CdOR]_n$ have analogous structures.

Figure 1. ORTEP plot of the molecular structure of $[tBuOCdMe]_4$. Thermal ellipsoids are represented on the 25% probability level. Esd values are given in parentheses[a]



[a] Selected bond lengths (in Å): Cd1−C7 2.13(1), Cd2−C8 2.10(3), Cd1−Cd2 3.456(2), Cd1−O1 2.287(6), Cd2−O1 2.291(6), Cd2−O2 2.289(6). − Selected bond angles (in °): O1−Cd1−C7 131.4(2), O1−Cd2−O2 81.5(3), Cd1−O1−Cd2 98.3(2), O1−Cd2−O1a 81.4(3), Cd1−O1−C3 118.4(6), Cd2−O2−C1 119.5(3).

The result of the X-ray structural determination of $CH_3Cd(OCMe_3)$ is shown in Figure 1. The compound is a cubane-shaped tetramer. The degree of oligomerization of this compound has been the subject of intense discussion. Coates and Lauder[6] postulated a dimer according to molecular weight data, but they did not give any experimental details. If this assumption is correct, the compound would be the only exception in the class of compounds [RCd(OR′)]. All other species (OR′ = OEt, $OCHMe_2$, OPh) are considered to be tetramers. On the other hand, Kennedy and McFarlaine[7] found only a small range of $\delta^{113}Cd$ values for methylcadmium alkoxides and postulated, that all of them are tetramers. They detected only one ^{113}Cd-NMR signal at ambient temperature. A reexamination at 223 K during our studies revealed, however, a second and less intense resonance at $\delta = -249$ besides the dominant signal at -244. This observation suggests, the presence of a second oligomer. The coupling constant $^2J(CdH)$ of $[MeCdOCMe_3]_n$ increases on cooling from 61 Hz at room temperature to 80 Hz at 223 K. This indicates either a change in conformation or a species with a time-averaged structure. The X-ray structural analysis of $MeCdOCMe_3$ proves it to be a tetramer in the solid state.

Figure 1 shows that the cadmium and oxygen atoms of $[MeCdOCMe_3)_4$ occupy the edges of a distorted cube. The molecule possesses a crystallographic three-fold axis which passes through Cd1, C7, O2, and C1. Therefore, the asymmetric unit consists only of Cd1, Cd2, O1, O2, C1, and C8. All other atoms are generated by symmetry operations. The

Table 2. ^{11}B- and ^{113}Cd-NMR data for reactions in the system $Cd(BH_4)_2$/LiOtBu in THF

$Cd(BH_4)_2$: $LiOCMe_3$	$\delta^{11}B$			$\delta^{113}Cd$		
2:1			−48.1 (q 83 Hz)	−326 (q, 273 Hz)		
1:1	−41.1 (q, 78 Hz)	−45.9 (q, 82 Hz)	−50.1	−293 (q 271 Hz)	−307 (q, 271 Hz)	−326 (272 Hz)
1:2	−41.7 (q, 81 Hz)			−293 (q, 270 Hz)	−307 (q, 289 Hz)	
1:4	−41.7 (q, 80 Hz)			−293 (q, 270 Hz)		

methyl groups at the cadmium center and the Me_3C groups at the oxygen atoms point away from the center of the tube, and the distortion is clearly indicated by the bond angles at the corner which are 81° at the cadmium centers and 98° at the oxygen atoms.

The structure of $[MeCdOCMe_3)]_4$ is interesting because it is, to our knowledge, the first reported X-ray structure of a cadmium alkoxide. The bond length for a covalent Cd−O single bond is estimated to be 217 pm by using covalent radii for a tetrahedral environment (148 pm for cadmium, 69 pm for oxygen,[8] (calculated 66 pm for an octahedral environment). If we assume that ionic bonds are present we must add the ionic radii of Cd^{2+} and O^{2-} (Cd^{2+}: 100 pm, O^{2-}: 147.4 pm[9]) which predicts a cadmium-oxygen distance of 247 pm. The observed value of 229 pm lies between these limits, and the ionic contribution to the bond can be estimated to be about 30% not taking into account the Shoemaker-Stevenson contraction. The Cd−O bond lengths are almost the same as the two shortest bonds found in the structure of bis(N,N-diethyl-N′-benzoylselenoureato)cadmium(II), although the Cd center is pentacoordinated in this compound[10].

Comparable structures with distorted cubane structures are quite common. Examples are $[MeZnOMe]_4$[11], $[Tl(OMe)]_4$[12], $[MeBe(OSiMe_3)]_4$[13] and some alkali metal alkoxides[14]. These structural units are part of the NaCl lattice, which is obviously stabilized by the organic groups. We expect that $Me_3COCdBH_4$ is also a tetramer with a Cd_4O_4 core, and the BH_4 group may either be μ_2- or μ_3-bonded to the Cd center.

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Experimental

All experiments were conducted under purified dry nitrogen. Anhydrous solvents were used throughout. Solutions of $Cd(BH_4)_2$ were synthesized according to literature procedures[1]. The concentration was determined as described in ref.[1]. Alkali metal alkoxides and phenoxides were prepared from the alkali metal and ROH.

A Bruker AC 200 instrument was used for the recording of NMR spectra. Conditions for measuring ^{113}Cd-NMR spectra are described in reference[2]. δ values refer to $CdMe_2$ and $BF_3 \cdot OEt_2$ as the standard, negative signs correspond to frequencies smaller than the standard.

The System $Cd(BH_4)_2$/LiOPh: A 0.56 M solution of $Cd(BH_4)_2$ and a 1.0 M solution of LiOPh in THF was used to prepare solutions containing $Cd(BH_4)_2$ and LiOPh in a molar ratio of 2:1, 1:1 and 1:2. The ^{11}B-NMR spectra show quintuplets at 213 K with $\delta^{11}B = -48$, while the ^{113}Cd-NMR spectra exhibit a single signal with a multiplicity of at least a septuplet at $\delta = -255$, $^1J(CdH) = 207$ Hz. The solution with a molar ratio of $Cd(BH_4)_2$: LiOPh = 2:1 shows two additional signals at $\delta^{113}Cd = -170$ ["septuplet", $^1J(CdH) = 203$ Hz] and −447, [$^1J(CdH) = 307$ Hz].

The System $Cd(BH_4)_2$/LiOmes: 2.05, 1.5, 1.0, and 0.50 ml respectively of a 0.81 M solution of $Cd(BH_4)_2$ in THF were combined with 0.96, 1.45 and 1.93 ml of a 0.84 M solution of Li(Omes) in THF corresponding to a $Cd(BH_4)_2$:LiOmes ratio of 2:1,1:1, 1:2 and 1:4. At 213 K the ^{11}B-NMR spectra contain a quintet at $\delta = -50$. The signals observed are summarized in Table 3.

Table 3. Comparison of $\delta^{113}Cd$ data for pairs of cadmium methyl compounds and cadmium tetrahydroborates recorded in THF solutions and Δδ values

R	RCdOEt	$RCdOCMe_3$	RCdOPh	RCdOmes
Me	−292	−244 (−249)	−383	−381[a]
BH_4	−373	(−294) −307 (−326)	−447	−475
Δδ	81	63	64	94

[a] value for 2,6-dimethylphenoxy

The System $Cd(BH_4)_2$/$Cd(Omes)_2$, 2,4,6-Trimethylphenoxycadmium Tetrahydroborate: a) A solution of mesOH (7.89 g, 57 mmol) in 30 ml of ether was added dropwise to 46 ml of a 0.62 M solution of $Cd(BH_4)_2$ in ether. A gas developed, and after 10 min a colorless precipitate formed. After the mixture had been stirred for 12 h, it was refluxed for 1 h. Then the solvent was evaporated in vacuo. Yield: 11.98 g of (BH_4)CdOmes. The product contained some THF. It was insoluble in ether, THF, benzene, and acetonitrile, but soluble in DMSO. − IR (nujol, ν in cm^{-1}): 1476 (st), 1433 (m), 1417 (m), 1371 (w), 1306 (s), 1224 (vst), 1148 (st), 1029 (w), 1005 (w), 956 (w), 878 (w), 851 (st), 787 (s), 744 (m), 588 (w), 488 (st), 445 (m), 368 (w), 329 (m). − $\delta^{13}C$ ([D$_6$]DMSO): 160.1, 128.3, 126.1, 122.1, 20.5, 18.2. − $\delta^{113}Cd$ (DMSO): −606. − $C_{18}H_{22}CdO_2$ (382.82): calc. C 56.47, H 5.80; found C 55.75, H 6.13. b) 8.40 ml of a 0.81 M solution of $Cd(BH_4)_2$ (6.84 mmol) in THF was added dropwise and with stirring to a solution of 2.64 g of $Cd(Omes)_2$ (6.83 mmol) in 5 ml of THF at 243 K. Whereupon a precipitate formed. The precipitate dissolved on warming the mixture to ambient temp. The resulting solution was quickly cooled below 250 K to avoid decomposition, and NMR spectra were then recorded at 213 K. − $\delta^{11}B$ (THF): −49.9 (quint, 83 Hz). − $\delta^{113}Cd$: −478 [quint, $^1J(CdH) = 279$ Hz]. − IR (cm^{-1}): 2393 (s), 2206 (w), 2107 (s) (νBH region).

The System $Cd(BH_4)_2$/LiOEt: An appropriate volume (2.0, 1.5, 1.0 and 1.0 ml) of a 0.56 M solution of $Cd(BH_4)_2$ in THF was added to 0.56, 0.84, 1.12, and 2.24 ml of a 1.0 M solution of LiOEt in THF, corresponding to a $Cd(BH_4)_2$:LiOEt ratio of 2:1, 1:1, 1:2

and 1:4. The NMR spectra were recorded at 213 K, and data are summarized in Table 1.

The System $Cd(BH_4)_2/NaOCMe_3$: 2.0, 2.0, 1.5, and 1.0 ml of a 0.20 M solution of $Cd(BH_4)_2$ in THF was added to 0.33, 0.66, 0.99, and 1.31 ml of a 0.61 M solution of $NaOCMe_3$ in THF, resulting in solutions containing a $Cd(BH_4)_2$:$NaOCMe_3$ ratio of 2:1, 1:1, 1:2 and 1:4. The ^{11}B-NMR spectra at 213 K show only one resonance at about $\delta = -49$ for the 2:1 and the 1:1 stoichiometry and a second resonance at $\delta = -46.8$ and -42.0 ppm respectively for the 1:2 and the 1:4 stoichiometry. The ^{113}Cd-NMR spectra at the same temperature show a quintet at $\delta = -325$ [^1J(CdH) = 271 Hz] independent of the composition of the solutions and a second resonance at $\delta = -303$ [q, ^1J(CdH) = 255 Hz] for the 1:4 solution.

The System $Cd(BH_4)_2/LiOCMe_3$: 2.0, 2.0, 1.5, and 1.0 ml of a 0.25 M solution of $Cd(BH_4)_2$ in THF were added to 0.25, 0.50, 0.75, and 2.00 ml of a 1.0 M solution of $LiOMe_3$ in THF, resulting in $Cd(BH_4)_2$:$LiOCMe_3$ ratios of 2:1, 1:1, 1:2, and 1:4. The NMR spectra were recorded at 213 K. The results are summarized in Table 1.

tert-Butoxymethylcadmium Tetramer: 123.3 ml of a 0.62 M solution of $CdMe_2$ was added dropwise to a solution of 1.07 g of Me_3COH in 20 ml of ether. The mixture was refluxed for 2 h. Then the solvent was removed in vacuo and the residue was recrystallized from ca. 20 ml of THF to give 1.52 g (54%) of colorless crystals of $(MeCdOCMe_3)_n$. – δ^{113}Cd (298 K): −252 [q, ^2J(CdH) = 61 Hz]; (213 K): −244 [q, ^2J(CdH) = 79 Hz], −249 [q, ^2J(CdH) = 80 Hz, small intensity].

Cadmium Dimesitylate: A solution of 2,4,6-trimethylphenol (7.89 g, 57 mmol) in 30 ml of diethyl ether was dropped into a stirred solution $CdMe_2$ in ether (46 ml, 0.62 M). Rapid evolution of gas was followed by the appearance of a precipitate after approximately 10 min. After the suspension had been stirred over night and kept at reflux for 1 h, the ether was evaporated in vacuo, the solid residue was washed with ether and dried. $Cd(Omes)_2$ was almost insoluble in ether, THF, benzene and acetonitrile, but soluble in DMSO. Yield: 10.9 g (99%). – δ^{113}Cd (DMSO): −606. – δ^{13}C: 160.1, 128.3, 126.1, 122.1, 20.5, 18.2. – $C_{18}H_{22}CdO_2$ (382.8); calc. C 56.47, H 5.80; found C 55.75, H 6.13.

Mesityoxycadmium Tetrahydroborate: To a suspension of $Cd(Omes)_2$ (2.64 g, 6.83 mmol) in 5 ml of THF was added a solution of $Cd(BH_4)_2$ (6.84 mmol, 8.4 ml of a 0.81 M solution) in THF at −30 °C. On warming the stirred mixture to ambient temp., a clear solution formed. No Cd metal separated when the solution of $Cd(Omes)BH_4$ was kept at −20 °C. – δ^{11}B (THF at 213 K): −49.9 [^1J(BH) = 83 Hz, quint]. – δ^{113}Cd: −478 [^1J(CdH) = 279 Hz]. – IR (cm^{-1}): 2393 (s), 2206 (m), 2107 (s) (BH_4).

X-Ray Structure Determination of $\{MeCd(OCMe_3)\}_4$: A Syntex R3 automated diffractometer using graphite-monochromated MoK_α radiation was used for cell determination and data collection. All calculations were performed with a micro-Vax computer using the SHELXT PLUS software package. Final refinement used the SHELX93 programs. Determination of the unit cell and data collection were performed at 298 K. *Crystal data:* $C_{20}H_{48}Cd_4O_4$ (802.2), colorless rhombus, size: 0.3 × 0.3 × 0.35 mm, trigonal, space group *P*-3c1 (no. 165), $a = 10.771(3)$, $c = 32.792(7)$ Å, $V = 3295(2)$ Å^3, $Z = 4$, $\mu = 2.56$ mm^{-1}, $F(000) = 1568$. *Data collection:* 2Θ range = 5.0–49.0°, variable scan speed: 2.4–29.3 °/min, scan range = 0.8°, 2 standard reflections after every 48 intensity measurements, 3955 reflections were measured, 1644 were found as independent, and 1295 were considered observed [$4\sigma(F)$ level]. – *Solution and refinement:* Direct methods, all non-hydrogen atoms refined anisotropically, hydrogen atoms, riding model with fixed isotropic U, $R = 0.047$, $wR2 = 0.147$, GOOF = 1.143, data-to-parameter ratio 14.2:1 [$F > 4\sigma(F_O)$], largest difference peak: 1.13 $e/10^6$ pm^3. This and two more are most likely due to a solvent molecule (THF)[15].

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[1] G. Linti, H. Nöth, M.Thomann, *Z. Naturforsch.* **1990**, *45b*, 1463–1471.

[2] H. Nöth, M. Thomann, *Z. Naturforsch.* **1990**, *45b*, 1472–1481.

[3] H. Nöth, M. Thomann, *Z. Naturforsch.* **1990**, *45b*, 1482–1486.

[4] H. Nöth, M. Thomann, G. Wagner, unpublished result.

[5] G. Emptoz, F. Huet, *J. Organomet. Chem.* **1973**, *55*, C61–C64; ibid **1974**, *85*, 264–267.

[6] G. E. Coates, A. Lauder, *J. Chem. Soc.* A, **1966**, 264–267.

[7] J. D. Kennedy, J. McFarlaine, *J. Chem. Soc., Perkin Trans 2*, **1977**, 1187–1191.

[8] Holleman-Wiberg: *Lehrbuch der Anorganischen Chemie*, Berlin, New York: Walther de Gruyter, 91–100. Edition, **1985**.

[9] W. Klever, *Einführung in die Kristallographie*, 16th edition, VEB Technik, Berlin, **1985**.

[10] W. Bensch, M. Schuster, *Z. Anorg. Allg. Chem.* **1993**, *619*, 791–795.

[11] H. M. M. Shearer, C. B. Spencer, *Acta Cryst.* **1980**, *B36*, 2046–2050.

[12] J. F. Dahl, G. L. Davies, D. L. Wampler, K. West, *J. Inorg. Nucl. Chem.* **1962**, *24*, 357.

[13] D. Mootz, A. Zinnius, B. Böttcher, *Angew. Chem.* **1969**, *81*, 398–399; *Angew. Chem. Int. Ed.* **1969**, *8*, 378–379.

[14] E. Weiss, H. Alsdorf, H. Kühr, *Angew. Chem.* **1967**, *79*, 816; *Angew. Chem.* Int. Ed. **1967**, *6*, 801.

[15] Further details of the crystal structure determination may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-401843, the names of the authors and the journal citation.

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