Introduction

Many metal hydroborates are prepared by metathetical reactions from a metal halide and an alkali metal hydroborate [2]. The solvent, in many cases diethyl ether or tetrahydrofuran, plays an important role. As has been pointed out previously, reactions of cadmium halides CdX₂ with LiBH₄ or NaBH₄ result in the formation of hydroborato cadmates [3] Cd₂X₂⁺(BH₄)ₓ⁻ₓ⁺, rather than Cd(BH₄)₂ [4]. Anions of this type can be detected by ¹³Cd NMR spectroscopy in CdCl₂-MBH₄ solutions in dimethylformamide (DMF) [1]. The low solubility of CdCl₂ in this solvent allowed the recording of ¹³Cd NMR spectra only for a limited range of CdCl₂-MBH₄ ratios, and it failed completely in a solvent like dimethyl ether of diglycol (= diglyme). In contrast to CdCl₂, cadmium iodide dissolves readily in DMF. Its solubility at 20 °C exceeds 1.5 M. The ¹³Cd NMR spectrum of a 1.1 M solution shows only a single, fairly sharp signal at δ¹³Cd = -559.3 (see Fig. 1a). This corresponds to data reported for aqueous CdI₂ solutions (≈ -583 [5], -588 [6], -596 ppm [7]). Nevertheless, the observed signal does not represent a single species since it splits into four resonances at 213 K as depicted in Fig. 1b. The two high field signals are fairly broad. In accord with signals in CdCl₂-DMF solution the more intense signal at δ¹³Cd = -589 corresponds to Cd(DMF)₂⁻ while the resonance at δ¹³Cd = -671 results from solvated CdI(BH₄) and Cd(BH₄)₂. The other two signals arise from iodocadmates, and we assign the resonances at δ¹³Cd = -445 and -567 to CdI₂⁻ and CdI₂⁺, respectively. This latter value is closer to ¹³Cd resonances found for solid tetraiodocadmates (≈ -549, -562 ppm [8]) than for (Bu₄N)₂CdI₄ in CH₂Cl₂ at 208 K [9]. In the CdI₂ solution the two anions CdI₂⁻ and CdI₂⁺ are present in approximately a 6:4 ratio. Therefore, dissociation of CdI₂...
Addition of iodide (in the form of LiI) shifts these equilibria to the side of the iodocadmates. At room temperature addition of one mole equivalent of LiI leads to a $^{113}$Cd NMR signal at $-508$ ppm, and at $-557$ ppm on adding a second equivalent, corresponding to the formation of Li$_2$CdI$_4$. The sharp signals represent still an exchange situation as demonstrated by Fig. 1c and 1d. In the “LiCdI$_3$” solution at 213 K there is more CdI$_4^{2-}$ present at 213 K than CdI$_3^-$ [10]. Consequently Cd cations must be present. The same holds for the “Li$_2$CdI$_4$” solution which still contains a significant amount of CdI$_3^-$. The rather broad lines suggest that iodide exchange occurs even at 213 K, its rate increasing as more LiI is present. This indicates that the presence of solvated Li$^+$ is involved in this exchange process by an acid-base interaction with iodide. It is, therefore, also not unreasonable to assume that the Cd cations, which should still be present even in the Li$_2$CdI$_4$ solution, produce too broad a signal due to exchange processes to be detected.

The Sodium Hydroborate-Cadmium Iodide System in Dimethylformamide

Addition of a NaBH$_4$ solution in DMF to CdI$_2$ in the same solvent induces precipitation of NaI irrespective of the CdI$_2$:NaBH$_4$ ratio which was varied from 1:1 to 1:4. The $^{11}$B NMR spectra of these solutions at 305 K showed a single quintet, $\delta^{11}$B changing from $-46.1$ to $-43.3$ with increasing NaBH$_4$ content. Cooling these solutions to 213 K caused the fine structure to vanish around 250 K (this happens for the 1:1 solution at about 20 K a higher temperature than in the CdCl$_2$-NaBH$_4$ system [1]), and at 233 K a second resonance appears at $\delta^{11}$B $-36.1$ for solutions with CdI$_2$:NaBH$_4$ ratios 1:2, 1:3 and 1:4. The intensity ratio of the signals at $-36.1$ and $-44.8$ ppm approximates 1:2. Therefore, not all of the NaBH$_4$ added reacts with CdI$_2$, indicating competition of I$^-$ and BH$_4^-$ in complex formation. Fig. 2 depicts the changes in these spectra for the 1:2 solution. Due to the high-
Fig. 2. Temperature dependence of the $^{11}$B NMR spectrum of a \( \ce{NaCdI_2(BH_4)} \) solution in DMF.

Fig. 3. Temperature dependence of the \(^{113}\)Cd NMR spectra of a \( \ce{NaCdI_2(BH_4)} \) solution in DMF: a) at 305 K; b) the same solution proton-decoupled at 213 K; c) the same solution proton-coupled at 213 K.

Higher overall concentration possible for \( \ce{CdI_2−NaBH_4} \) solutions \(^{113}\)Cd NMR spectra allow a more definite detection and characterization of these complexes in solution. At ambient temperature only a single signal is recorded (see Fig. 3). However, on cooling several signals emerge. Good resolution is achieved at 213 K. For the 1:1 solution seven separate \(^{113}\)Cd resonances are present in the proton decoupled spectrum. They are found at \( \delta = -195, -246, -324, -446, -457 \) (weak), -570 and -593 ppm. In the 1:2 solution an additional signal at -259 ppm appears (Fig. 4), which vanishes as the BH\(_4^-\) proportion is increased (Fig. 5). The assignment of the \(^{113}\)Cd NMR signals at \( \delta = -593, -570 \) and -446 to the species \( \ce{Cd(DMF)_6^{2+}} \), \( \ce{CdI_2^{2−}} \) and \( \ce{CdI_3^{−}} \) is straightforward, not only on the basis of the \( \delta \) values but also on their remaining sharp in the absence of proton decoupling.

The \( \ce{Cd(DMF)_6^{2+}} \) cation can be detected only in solutions containing \( \ce{CdI_2} \) and \( \ce{NaBH_4} \) in a 1:1 ratio. In this solution the concentration of \( \ce{CdI_2^{2−}} \) exceeds that of \( \ce{CdI_3^{−}} \) by far as compared with the \( \ce{LiCdI_3} \) solution (see previous section). In addition to these two anions there are four BH\(_4^-\) containing species. The signal at \( \delta ^{113}\)Cd = -457 has a triplet
structure (see Fig. 4). This suggests the presence of one BH$_4^-$ group bound via two hydrogen atoms to the cadmium center. Since BH$_4^-$ groups cause a low field shift of the $^{113}$Cd resonance it is most likely by that this signal represents the anion CdI$_3$(BH$_4^-$)$_2^2^-$. The $^{113}$Cd resonance at $-324$ ppm has a quintet structure. Considering the chemical shift the most likely assignment is the anion CdI(BH$_4^-$)$_2^2^-$. The signal further downfield, $\delta$113Cd = $-246$, exhibits a septet structure in the proton-coupled NMR spectrum, and this septet is also readily recognized in the $^{113}$Cd NMR spectrum of the 1:3 solution. We assume that this signal results from the presence of CdI(BH$_4^-$)$_3^2^-$, while the remaining and very weak resonance at $\delta$113Cd $-195$ is due to Cd(BH$_4^-$)$_3^2^-$ (v.i.).

It is evident from these data that the most simple assumption for a reaction in a 1:1 molar ratio according to eq. (5) is not realized. Since large quantities of Na$_2$CdI$_4$ and a minor amount of NaCdI$_3$ is formed at this stoichiometry, it follows that reactions described by eq. (6) to (11) occur.

\[
\begin{align*}
\text{CdI}_2 + \text{NaBH}_4 & \rightarrow \text{Na}[\text{CdI}_2\text{BH}_4] \quad (5) \\
\text{CdI}_2 + \text{NaBH}_4 & \rightarrow \text{NaI} + \text{Cd}([\text{BH}_4]) \quad (6) \\
\text{Na}[\text{CdI}_2] + \text{NaI} & \rightarrow \text{Na}[\text{CdI}_2] \quad (7) \\
\text{Na}[\text{CdI}_3] + \text{NaI} & \rightarrow \text{Na}[\text{CdI}_3] \quad (8) \\
\text{Cd}([\text{BH}_4]) + \text{NaBH}_4 & \rightarrow \text{Na}[\text{CdI}([\text{BH}_4])] \quad (9) \\
\text{Na}[\text{CdI}([\text{BH}_4])] + \text{NaBH}_4 & \rightarrow \text{Na}[\text{CdI}([\text{BH}_4])] \quad (10) \\
\text{Na}[\text{CdI}([\text{BH}_4])] & \rightarrow \text{NaI} + \text{Na}[\text{CdI}([\text{BH}_4])] \quad (11)
\end{align*}
\]

It should be noted that about one third of the NaBH$_4$ in solution is present in uncomplexed form and only two thirds are incorporated in hydroborato cadmates. This corresponds with a reaction in a CdI$_2$:NaBH$_4$ ratio of 3:2.

The $^{113}$Cd NMR spectrum of the 1:2 solution is unique for the absence of CdI$_3^-$ and the presence of a quintet at $\delta$113Cd = $-347$. This chemical shift together with its fine structure points unequivocally to the presence of Cd(BH$_4^-$)$_2$I$_2^2^-$ [11]. In addition, there is also a new resonance at $\delta$113Cd = $-259$. The undecoupled spectrum reveals that this signal results from a BH$_4^-$-containing species. However, the multiplicity cannot be extracted unambiguously from the spectrum due to overlap with the signal at $\delta$113Cd = $-247$ ppm. Nevertheless, the width of the signal suggests it to be a septet (or even higher multiplicity). This and considering the chemical shift points to a second species CdI(BH$_4^-$)$_3^2^-$ [12]. Its nature (geometrical isomer, Na$^+$-bridged oligomer) remains speculative at the moment. Peculiarly, this species is only observed in the 1:2 solutions.
The $^{113}\text{Cd}$ NMR spectra also clearly demonstrate that more NaBH$_4$ in solution decreases the proportion of CdI$_2$$^{2-}$. Therefore, free NaI is formed as described by eq. (11), e.g. reactions (12) and (13) which are coupled with reactions according to eq. (7) and (8) become predominant.

\begin{align*}
\text{CdI}_2 + 3\text{NaBH}_4 & \rightleftharpoons \text{Na}_3[\text{Cd}(\text{BH}_4)_3] + \text{NaI} \quad (12) \\
\text{CdI}_2 + 3\text{NaBH}_4 & \rightleftharpoons \text{Na}[\text{Cd}(\text{BH}_4)_3] + 2\text{NaI} \quad (13)
\end{align*}

This is further ascertained by an intensity increase of the signals assigned to CdI(BH$_4$)$_3$$^{2-}$ and Cd(BH$_4$)$_3$$^{-}$. The multiplicity of these signals, as discussed above, is now more clearly recognizable.

The Lithium Hydroborate-Cadmium Iodide System in Dimethylformamide

Solutions containing CdI$_2$ and LiBH$_4$ in the molar ratios 1:1, 1:2, 1:3 and 1:4 in DMF show $^{11}$B NMR signals as described for the CdI$_2$-NaBH$_4$ system. In addition, a very broad $^{113}$Cd NMR signal was found for the 1:1 solution at $\delta^{113}\text{Cd} = -480$ (after 240000 pulses). This information is consistent with I$^-$/BH$_4$$^-$/DMF exchange at the Cd center.

$^{11}$B NMR spectra recorded at 213 K exhibit only a single broad signal around $-46$ ppm, except for the 1:2 solution, where a new signal appears as a shoulder at $-36$ ppm resolving at 223 K into a separate signal at $\delta^{11}\text{B} = -36.3$ at 213 K. This behaviour indicates that BH$_4$$^-$ is involved in an exchange process even close to 223 K, suggesting that the presence of Li$^+$ (instead of Na$^+$) accelerates this exchange.

The $^{113}$Cd NMR spectra recorded at 213 K reflect the same behaviour as described and discussed for the CdI$_2$-NaBH$_4$ solutions. However, the resolution of the fine structure of the $^{113}$Cd signals in the proton-coupled spectra leaves much to be desired and would lead to ambiguous assignments. The most notable feature is that the relative amount of CdI$_2$$^{2-}$ decreases by increasing the amount of LiBH$_4$ per CdI$_2$. The following species are present in 1:1 solutions: Cd(DMF)$_2$$^{2+}$, CdI$_4$$^{-}$, CdI$_2$(BH$_4$)$_2$$^{2-}$, CdI(BH$_4$)$_2$$^{-}$ and CdI(BH$_4$)$_3$$^{2-}$. As the BH$_4$$^-$/Cd$^{2+}$ ratio increases the relative amount of CdI(BH$_4$)$_3$$^{2-}$ and Cd(BH$_4$)$_3$$^{-}$ (first observed in the 1:2 solutions) grows at the expense of the other species. Since the $^{113}$Cd NMR signals are rather broad, even in the proton-decoupled spectra, I$^-$/BH$_4$$^-$/exchange processes keep going on even at 213 K at a much higher rate than in the CdI$_2$-NaBH$_4$ solutions. However, apart from this, the cadmium species present in the solutions of CdI$_2$ with either NaBH$_4$ or LiBH$_4$ in DMF are analogous.

Cadmium Iodide and Lithium Iodocadmates in Diglyme

Many of the reactions between cadmium halides and alkali metal hydroborates are conducted in ether type solvents. However, diethyl ether and even tetrahydrofuran dissolve these halides insufficiently to allow a recording of the $^{113}$Cd NMR spectra. An exception is diglyme, which dissolves CdI$_2$ to give a 0.48 M solution at ambient temperature. The dielectric constant of diglyme is only 5.7, and this solvent will, therefore, be less suited for dissociation as compared to DMF. On the other hand, it coordinates quite well with Li$^+$ or Na$^+$, and the formation of either ion pairs and/or solvent separated ion pairs is likely. Under these circumstances the systems CdI$_2$-LiI and CdI$_2$-MBH$_4$ in diglyme might be different from those in DMF.

A CdI$_2$ solution (0.48 M) in diglyme showed a single $^{113}$Cd resonance ($\delta = -537.5$) at 305 K. Cooling this solution to 218 K resulted in a shift of this signal to $-507$ ppm, without significantly changing the line width. This suggests that there is a single species present in solution, with some exchange (most likely with oxygen donor atoms of the solvent) occurring at ambient temperature. The $\delta$ value would be in accordance with a hexacoordinated Cd center. We assume that a CdI$_2$(diglyme)$_2$ species is responsible for this signal

On adding LiI to the CdI$_2$ solution, formally producing LiCdI$_3$, two additional signals due to CdI$_2$$^{2-}$ ($\delta^{113}\text{Cd} = -581$) and CdI$_4$$^{-}$ ($\delta^{113}\text{Cd} = -476$) appear, the latter being rather broad. This indicates reduced symmetry as compared with CdI$_4$$^{2-}$, or iodide exchange. Further addition of LiI to produce Li$_2$CdI$_4$ solutions results in the formation of an insoluble product, and no $^{113}$Cd NMR signals were recorded in the supernatant solution at 213 K.
The Cadmium Iodide-Sodium Hydroborate System in Diglyme

Clear solutions result on mixing diglyme solutions of CdI₂ with those of NaBH₄ irrespective of the CdI₂:NaBH₄ ratio which we varied from 1:1 to 1:4. ¹¹B NMR spectra of these solutions show the same behaviour as reported above for the CdI₂-NaBH₄ system in DMF. There is only a single quintet which moves from δ¹¹B = -46.0 for the 1:1 solution downfield to -43.7 ppm for the 1:4 solution concomitant with a decrease in the coupling constant.

Studying the ¹¹B and ¹³Cd NMR spectra at lower temperature, resulted in problems. Samples containing CdD₄ as a lock separated into two phases, the heavier one being rich in Cd and decomposing slowly with metal deposition even at low temperature. In addition, the viscosity of the heavy phase increases considerably, making NMR measurements obsolete. In the absence of CD₆ the solution separates from the solutions below 273 K, and this material melts at ~0 °C. Its composition has not been determined.

Under the given circumstances, only the lighter phase of the C₆D₄-containing samples was further investigated. At 213 K the phases obtained from 1:1 and 1:2 solutions produce a single, broad ¹¹B resonance at -48.8 and -46.9 ppm, respectively. For the corresponding phases of the 1:3 and 1:4 solutions an additional ¹¹B NMR signal of “free” NaBH₄ at δ¹¹B = -41 appears as a quintet. The high field signal suggests the presence of BH₄⁻ groups bound to Cd²⁺.

A ¹³Cd NMR spectrum could only be recorded for the supernatant phase of the 1:1 solution. Signals found at δ¹³Cd = -579 and -479 result from CdI(BH₄)₂ and CdI₃⁻. A resonance at δ¹³Cd = -331 may indicate the presence of solvated Cd(BH₄)₂⁻. Finally, two signals at δ¹³Cd = -405 and -232 show the presence of BH₄⁻ containing Cd species. Since these signals are rather broad in the proton-coupled spectra and in the absence of a reliable fine structure any assignment remains speculative. Most likely the resonance at -232 ppm is due to CdI(BH₄)₂⁻. The signal at δ¹³Cd = -405 suggests the presence of solvated CdI(BH₄)₂⁻. The ¹³Cd NMR signal of this species should be observed at a higher field than that for CdI(BH₄)₂⁻ due to the anisotropic shift resulting from the presence of iodide in the compound.

The Cadmium Iodide-Lithium Hydroborate System in Diglyme

Solution containing CdI₂ and LiBH₄ in diglyme are unstable at ambient temperature separating cadmium metal readily. The two solutions were, therefore, mixed in the appropriate molar ratios at 0 °C and kept at -78 °C before they were investigated by ¹¹B and ¹³Cd NMR. Clear solutions resulted only for ratios up to CdI₂:LiBH₄ = 1:1. If more LiBH₄ was added, a precipitate formed. ¹³Cd NMR spectra were, therefore, only recorded for 3:1, 2:1 and 1:1 solutions. These spectra are shown in Fig. 6. The corresponding ¹¹B NMR spectra at 218 K consist of single broad signals at δ¹¹B = -51.5, -48.4 and -50.6 ppm respectively.

As the LiBH₄ proportion increases the ¹³Cd NMR signal for CdI₂(diglym)ₙ vanishes at the 1:1 ratio and resonances for CdI⁻ and CdI₂⁻ gain in intensity, particularly the latter. The first BH₄⁻ containing species formed is CdI(BH₄) (δ¹³Cd = -405), suggesting reactions (14) and (15) to occur. The new signal emerging at δ¹³Cd = -335 in the solution containing CdI₂ and LiBH₄ in a 2:1 ratio is most likely due to Cd(BH₄)₂. Its proportion is about one half of that of CdI(BH₄) and there is still unreacted CdI available. In addition to reactions (14) and (15) reaction (16) and to a minor extent (17) now play also a role, the latter becoming more important, as the ratio approaches 1:1.

\[
\begin{align*}
\text{CdI} + \text{LiBH}_4 & \rightarrow \text{CdI}(\text{BH}_4)_2 + \text{Li} \quad (14) \\
\text{CdI} + \text{Li} & \rightarrow \text{LiCdI} \quad (15) \\
\text{LiCdI}_3 + 2\text{LiBH}_4 & \rightarrow \text{Cd}(\text{BH}_4)_2 + 3\text{Li} \quad (16) \\
\text{LiCdI}_3 + \text{Li} & \rightarrow \text{Li}_2\text{CdI}_4 \quad (17)
\end{align*}
\]

Under these conditions all CdI₂ has reacted. The new ¹³Cd NMR signal at -233 ppm is due to CdI(BH₄)₂⁻ (δ¹³Cd = -246 in DMF). This is in accord with the decrease in intensity of the signal assigned to CdI(BH₄) as well as with the high field resonance as compared with CdI(BH₄)₂⁻.

Discussion

It is evident from the description of the NMR spectra obtained for CdI₂-MBH₄ solutions in DMF and diglyme that the species formed are more strongly influenced by the solvent than by the cations M = Na, Li. In DMF as the more polar solvent the formation of both cations and anions is favoured, and, consequently, no or only minor quantities of solvated neutral CdI(BH₄) and Cd(BH₄)₂ are detected. In the presence of excess...
BH₄⁻ the predominant anionic species are CdI(BH₄)₃⁻ and Cd(BH₄)₃⁻.

It is interesting to note that two series of BH₄⁻ containing cadmates are formed: CdI₄₋(BH₄)₄⁻ and CdI₃₋(BH₄)₂⁻. In the first series the anion Cd(BH₄)₄⁻ is missing, in the second the anion CdI₂BH₄⁻. The absence of Cd(BH₄)₄⁻ may be due to the low Lewis acid character of the Cd(BH₄)₃⁻ ion. Steric effects can most likely be neglected since CdI₂⁻ is readily formed, I⁻ and BH₄⁻ having comparable effective ionic radii (2.20 Å versus 2.1 Å). The absence of CdI₂BH₄⁻ in the second series is less well understood. Its presence is most likely in solutions with a low BH₄⁻/CdI₂ ratio. However it could not be detected.

Assignment of the signals to the two series of iodosotetrahydroborato cadmates is based on the fine structure of the ¹¹³Cd resonance resulting from ¹¹³Cd−¹H coupling. While triplets or quintets result unequivocally from one or two BH₄⁻ groups bound via two hydride bridges to the Cd center, a septet structure may either arise from three BH₄⁻ groups involving two hydrogen atoms each in bonding, or from two BH₄⁻ groups exhibiting triple hydride bridges. Since the multiplicity of the ¹¹³Cd signals for Cd(BH₄)₃⁻ and CdI₃(BH₄)₂⁻ all involve double hydride bridges there seems to be no reason to assume that the type of bonding should change in these two series of anions. Therefore, we consider a septet structure as evidence for the presence of three BH₄⁻ groups in the complex anion. It should be noted that the shift difference between two adjacent members of the series CdI₄₋(BH₄)₄⁻ is approximately 110 ppm. Moreover, the two series of anions can be differentiated by their ¹/J(¹¹³Cd¹H) coupling constants. For the series CdI₃₋(BH₄)₂⁻ this value is ~200 Hz, and for the CdI₄₋(BH₄)₄⁻ series it is 157 Hz, the exception being CdI(BH₄)₄⁻ with ¹/J(¹¹³Cd¹H) = 198 Hz. On the basis of this argument, this species should belong to the CdI₃₋(BH₄)₂⁻ series. But the chemical shift data exclude an assignment to this series. CdI₅(BH₄)⁺, the missing link in this series should give rise to a high field signal, and the septet struc-
ture of the observed resonance demonstrates the presence of three double-bridged BH$_4^-$ ligands. The remaining alternative would be a CdI$_2$(BH$_4$)$_2$ species with the BH$_4$ groups bound via triple hydride bridges to the cadmium center as observed for Cd(BH$_4$)$_2$ [11]. However, in terms of the low activation barrier for intramolecular rotation of the BH$_4^-$ group in metal complexes [14] we consider this an unlikely possibility.

Diglyme is a less ionizing solvent than DMF. Therefore, even CdI$_2$ itself is present as a molecular entity, in contrast to its DMF solution, where it dissociates into Cd(DMF)$_6^{2+}$, CdI(DMF)$_5^+$, CdI$_3^-$ and CdI$_4^{2-}$. Reactions of CdI$_2$ with MBH$_4$ in diglyme lead to the solvated molecular units CdI(BH$_4$)$_2$ and Cd(BH$_4$)$_3$$. The formation of hydroborato cadmates sets in at CdI$_2$:LiBH$_4$ ratios < 1:2, and it is to be expected, for this reason, that species CdI(BH$_4$)$_3^{2-}$ and Cd(BH$_4$)$_3^-$ are formed in a larger proportion as this ratio approaches 1:4.

The present study clearly and convincingly shows, that the reactions of CdI$_2$ with alkali metal hydroborates does not follow a simple stoichiometry leading to a single or a predominant species. There are many species in equilibrium with one another, which can be detected only at a sufficiently low temperature. At ambient temperature there is rapid scrambling amongst all species involved in the realm of the NMR time scale.

In order to find out which is the most reactive species, e.g. for the reduction of carboxylic acid chlorides to aldehydes by a CdX$_2$-MBH$_4$ mixture, reaction conditions have to be designed which will allow to pursue such reactions e.g. by NMR methods. And it is apparent from the present results that the solvent will play an important part in such studies.

### Experimental Part

$^{11}$B and $^{113}$Cd NMR spectra were recorded as described in the preceding publication of the series [1]. Chemical shifts ($\delta$ in ppm) refer to external BF$_3$·OEt$_2$ and CdMe$_2$, respectively with the negative sign referring to lower frequencies than the standard. CdI$_2$, LiBH$_4$ and NaBH$_4$ were reagent grade chemicals, the purity of the tetrahydroborates were >96%. Solutions showed no other borane-containing compound in the $^{11}$B NMR spectrum. DMF and diglyme were dried by standard procedures and stored under dry oxygen-free dinitrogen gas.

**CdI$_2$ and CdI$_2$/LiI solutions in DMF:** A 1.1 M solution of CdI$_2$ was investigated at 305 K and 213 K. Solutions of “LiCdI$_3$” and “Li$_2$CdI$_4$” were prepared by adding 294.5 mg (or 589.0 mg LiI) to 2.0 ml of a 1.1 M solution of CdI$_2$. LiI dissolved readily with evolution of heat and an increase in viscosity.

<table>
<thead>
<tr>
<th>Solution</th>
<th>$\delta^{113}$Cd at 305 K</th>
<th>$\delta^{113}$Cd at 213 K</th>
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<tr>
<td>CdI$_2$</td>
<td>-559.3</td>
<td>-444.6</td>
</tr>
<tr>
<td>LiCdI$_3$</td>
<td>-507.7</td>
<td>-444.8</td>
</tr>
<tr>
<td>Li$_2$CdI$_4$</td>
<td>-557.0</td>
<td>-446.7</td>
</tr>
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**CdI$_2$/NaBH$_4$/DMF solutions:** Correct proportions of a 1.1 M CdI$_2$ solution in DMF (1.79, 0.89, 0.60, 0.45 ml) were added to 1.5 ml of a 1.25 M solution of NaBH$_4$ in the same solvent to obtain solutions with mole ratios CdI$_2$:NaBH$_4$ = 1:1, 1:2, 1:3 and 1:4 respectively. The solutions showed a single $^{11}$B NMR signal as a 1:4:6:4:1 quintet each at $\delta^{11}$B (J(BH) in Hz) -46.1 (86.8), -44.5 (86.0), -42.9 (86.0) and -42.3 (86.9) respectively. The $^{113}$Cd resonance for the 1:1 solution was found at -417 ppm. At 213 K the following $^{11}$B NMR spec-

<table>
<thead>
<tr>
<th>Solution</th>
<th>$\delta^{11}$B (J(BH)) at 213 K</th>
<th>$\delta^{113}$Cd at 305 K</th>
<th>$\delta^{113}$Cd at 213 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdI$_2$/NaBH$_4$ 1:1</td>
<td>-195</td>
<td>-446</td>
<td>-570</td>
</tr>
<tr>
<td>(m)$^{a,b}$</td>
<td>(q, 201)$^b$</td>
<td>(s)</td>
<td>(m)$^{a,b}$</td>
</tr>
<tr>
<td>CdI$_2$/NaBH$_4$ 1:2</td>
<td>-194</td>
<td>-457</td>
<td>-570</td>
</tr>
<tr>
<td>(m)$^a$</td>
<td>(m)$^a$</td>
<td>(q, 157)</td>
<td>(t, 157)</td>
</tr>
<tr>
<td>CdI$_2$/NaBH$_4$ 1:3</td>
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<td>-572</td>
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<tr>
<td>(sep. 195)</td>
<td>(q, 202)</td>
<td>(t, 200)</td>
<td>(t, 200)</td>
</tr>
<tr>
<td>CdI$_2$/NaBH$_4$ 1:4</td>
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<td>-570</td>
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<tr>
<td>(sep. 200)</td>
<td>(q, 199)</td>
<td>(t, 200)</td>
<td>(t, 200)</td>
</tr>
</tbody>
</table>

$^{a}$ Fine structure of the signal not well enough resolved to allow an unambiguous recognition of the multiplicity. This is primarily due to a low signal intensity (i.e. low concentration); $^{b}$ m = multiplet, q = quintet, t = triplet, sep = septet, s = singlet.
tra were recorded: 1:1 solution: $\delta^{11}B = -47.7, 1:2$ solution: $\delta^{11}B = -36.1, -44.8; 1:3$ solution: $\delta^{11}B = -37.0, -45.2; 1:4$ solution: $\delta^{11}B = -36.2, -45.0$. $^{113}\text{Cd}$ NMR spectra at 213 K: $\delta^{113}\text{Cd}$ ($^1J(\text{Cd}^{1}H)$) in Hz.

$\text{CdI}_2/\text{LiBH}_4/\text{DMF}$ solutions: Only freshly prepared solutions of LiBH$_4$ in DMF must be used [1]. Appropriate volumes (2.59, 1.30, 0.86 and 0.65 ml each) of a 0.7 M CdI$_2$ solution in DMF was added to 1.5 ml of a 1.21 M solution of LiBH$_4$ to make solutions containing these reagent in CdI$_2$:LiBH$_4$ ratios of 1:1, 1:2, 1:3 and 1:4. These showed unresolved $^{11}B$ NMR signals at $-46.1, -44.0, -42.0$ and $-41.0$ ppm respectively. At 213 K the $^{11}B$ NMR spectrum of the 1:1 solution shows a single signal at $\delta = -45.8$, and the 1:2 solution two signals at $-36.3$ and $-46.8$ ppm. The following $^{113}\text{Cd}$ NMR resonances were found at 213 K.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>$\delta^{113}\text{Cd}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>$-244$ $-323$ $-343$</td>
</tr>
<tr>
<td>1:2</td>
<td>$-243$ $-313$ $-343$</td>
</tr>
<tr>
<td>1:3</td>
<td>$-245$ $-323$ $-343$</td>
</tr>
<tr>
<td>1:4</td>
<td>$-234$ $-321$ $-343$</td>
</tr>
</tbody>
</table>

$^{113}\text{Cd}$ resonances (in ppm) at 213 K for various CdI$_2$:LiBH$_4$ ratios:

$\text{CdI}_2/\text{LiI}/\text{diglyme}$ solutions: $^{113}\text{Cd}$ NMR spectra were recorded of a 0.48 M CdI$_2$ solution in diglyme. To 2.0 ml of this solution was added 64 mg and 128 mg of LiI, corresponding to solutions of composition LiCd$_{3}I_{4}$ and LiCdI$_{3}$, respectively. 256 mg of LiI did not dissolve completely in 2.0 ml of the CdI$_2$ solution. Therefore, no $^{113}\text{Cd}$ NMR spectra were recorded of the supernatant solution.

$\text{CdI}_2/\text{LiBH}_4/\text{diglyme}$ solutions: To a 0.385 M solution of CdI$_2$ in diglyme was added the appropriate amount of a 0.56 M solution of NaBH$_4$ in diglyme to produce clear solutions having ratios CdI$_2$:NaBH$_4$ of 1:1, 1:2, 1:3, 1:4 with $^{11}B$ NMR signals at $-46.0 (83.4), -45.2 (82.5), -44.3 (81.7)$ and $-43.7 (81.3)$ ($^1J(\text{BH})$ in parenthesis). These spectra were recorded at 305 K. At 213 K these signals shifted to $-48.8$ and $-46.9$ ppm for the 1:1 and 1:2 solution, and the signals lost their quintet structure. The 1:3 solution gave two overlapping signals at $\delta = -41.0$ and $-46.2$, while the low field signal of the 1:4 solution ($\delta = -41.5$ ($^1J(\text{BH}) 77.1 \text{Hz}$)) showed a fairly well resolved quintet (free NaBH$_4$) besides a broad signal at $-46.6$ (ratio $\sim$1:3). These data refer to the supernatant liquid phase which formed on cooling of the solution after addition of C$_6$D$_6$ as an internal lock. $^{113}\text{Cd}$ could only be recorded for this phase resulting from the 1:1 solution. At 213 K signals were found $\delta^{113}\text{Cd} = -232, -331, -404, -478$ and $-578$ ppm.

$\text{CdI}_2/\text{LiBH}_4/\text{diglyme}$ solutions: The solutions must be prepared at temperatures not exceeding 0 °C, and it is advisable to keep them at $-78$ °C until their NMR spectra can be recorded. A 0.42 M CdI$_2$ solution and a 1.53 M solution of LiBH$_4$ were used to make Li,$\text{Cd}_{\text{m}}$(BH$_4$)$_{\text{n}}$ solutions of CdI$_2$:LiBH$_4$ ratios 3:1, 2:1 and 1:1. Additional LiBH$_4$ caused the formation of a precipitate not dissolving completely on adding diglyme. The following $^{113}\text{Cd}$ NMR signals were recorded at 218 K:

<table>
<thead>
<tr>
<th>Ratio</th>
<th>$\delta^{113}\text{Cd}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:1</td>
<td>$-405$ $-478$ $-503$</td>
</tr>
<tr>
<td>2:1</td>
<td>$-335$ $-404$ $-479$ $-503$</td>
</tr>
</tbody>
</table>

We thank Fonds der Chemischen Industrie and Chemetall GmbH for support of this study, and Dipl.-Chem. St. Böck for helpful suggestions regarding the operation of the NMR instrument.
[10] This statement rests on the assumption that the intensities are proportional to concentrations.
[12] The formation of Cd(BH$_4$)$_{2}^{-}$ can be ruled out, since no resonance at $\delta^{113}$Cd = -259 ppm is found in solution with a higher NaBH$_4$ content. A higher BH$_4^{-}$:Cd$^{2+}$ ratio should favour Cd(BH$_4$)$_{2}^{-}$ formation.
[13] If the signal at $\delta^{113}$Cd = -507 ppm would originate from Cd(diglyme)$_2^{2+}$, one would expect also the formation of CdI$_{2}^{-}$ and CdI$_{2}^{2-}$, which are, however, not observed.