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Formation of Organozincate Anions in LiCl-Mediated Zinc Insertion Reactions

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Tetrahydrofuran solutions of the products formed in LiCl-mediated zinc insertion reactions into various organic halides RHal were analyzed by anion-mode electrospray ionization (ESI) mass spectrometry. In all cases, organozincate anions were observed. The reactions with RHal, Hal = Br and I, yielded predominantly mononuclear complexes, such as $ZnRHal_2^-$ and $ZnRHalCl^-$, whereas for the reaction with benzylchloride abundant polynuclear organozincates, such as $Zn_2Bn_2Cl_3^-$ and $Zn_3Bn_3Cl_4^-$, were detected. The equilibria governing the stoichiometry and aggregation state of these complexes appear to be mainly controlled by the nature of the halide ions present in solution. It seems likely that the formation of organozincate complexes also changes the reactivity of the organozinc species, thus offering a rationale for the recently found pronounced effect of LiCl in organozinc chemistry. Additional preliminary studies suggest that organozincate anions as well as organozinc cations may moreover form in the absence of LiCl.

1. Introduction

Because of their excellent chemoselectivity and good compatibility with functional groups, organozinc compounds are valuable reagents in organic synthesis.[1,2] Functionalized organozinc halides R−Zn−Hal can be accessed via zinc insertion into the respective alkyl and aryl halides RHal (Hal = Br and I). However, this method suffers from some limitations in that not all alkyl and aryl halides readily undergo zinc insertion. In general, alkyl bromides only react with Rieke-zinc but not with commercially available zinc powder.[3,4] Rieke-zinc is also required for the conversion of aryl iodides[3] unless elevated temperatures are applied.[5]

Recently, Knochel and co-workers have found that the addition of stoichiometric amounts of lithium chloride greatly facilitates zinc insertion and significantly broadens the scope of this reaction.[6−9] In the presence of LiCl, alkyl bromides react smoothly with zinc powder,[6] and even allyl[7] and benzyl chlorides[9] give the respective organozinc chlorides. Recent findings of Oshima and co-workers moreover suggest that the addition of LiCl not only facilitates zinc insertion but also enhances the reactivity of the resulting organozinc halides toward transmetalation.[10] Furthermore, LiCl promotes important reactions in organomagnesium[11−14] and organoindium chemistry.[15]

Although the beneficial effects of LiCl in zinc insertion and subsequent transmetalation reactions are thus well documented, their molecular mode of action is unknown. Knochel and co-workers surmised that LiCl leads to the formation of R−Zn−Hal·LiCl complexes that are well-soluble in tetrahydrofuran (THF), the solvent of choice for zinc insertion reactions.[6] The formation of these dissolved complexes supposedly regenerates the free zinc surface, which can then react with further RHal molecules.[6] Similarly, Oshima and co-workers conjectured that LiCl enhances the reactivity of organozinc halides by coordination to the Zn center and formation of monomeric R−Zn−Hal·LiCl species.[10] These monomeric zinc species are expected to have a higher tendency toward transmetalation than larger aggregates. While the formulation as R−Zn−Hal·LiCl deliberately avoids a specific structural assignment of this putative intermediate, the well-known properties of zinc offer some clues to its likely structure. Zn(II) complexes with two ligands have an unsaturated coordination sphere and behave as strong Lewis acids that readily add a Lewis base. For instance, diorganylzinc species ZnR_2 react with organolithium compounds RLi to yield

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lithium triorganozincates $Li^+ZnR_3^-$;[16] these triorganozincates are more reactive than the corresponding diorganyl zinc compounds,[17] and they have therefore found applications in various important synthetic transformations, including Michael-type addition[18] and halogen–zinc exchange reactions.[19] One may expect organozinc halides R–Zn–Hal to react with LiCl in a similar way to produce $Li^+ZnRClHal^-$ complexes, in which the zinc center adopts a trigonal coordination geometry. In a strongly coordinating solvent such as THF, these complexes may at least partly dissociate into free Li^+ and $ZnRClHal^-$ ions (eq 1).

$$R{-}Zn{-}Hal + Li^+Cl^- \rightarrow Li^+ZnRClHal^- \rightleftharpoons Li^+ + ZnRClHal^- \quad (1)$$

Complexes of the type $ZnRHal_2^-$ have been observed in electrochemical studies,[20] but otherwise only very little was known about such species. This lack of information reflects experimental difficulties in the selective detection of charged organometallics. The advent of electrospray ionization (ESI) mass spectrometry has changed this situation, however, and made possible the identification of a manifold of organometallic ions.[21–23] Using this method, we could show that the reactions of $ZnCl_2$ with 1 equiv of RLi (RLi = CH_3Li, ^nBuLi, ^sBuLi, ^tBuLi, and 2-lithiothiophene) in THF produced free $ZnRCl_2^-$ ions (eq 2), along with related polynuclear complexes.[24] We also investigated the gas-phase reactivity of the $ZnBuCl_2^-$ anions found and compared it with that of their $ZnBu_2Cl^-$ and $ZnBu_3^-$ congeners[24] as well as with the behavior of previously studied organomagnesate[25] and organocuprate ions.[26,27]

$$ZnHal_2 + RLi \rightarrow Li^+ + ZnRHal_2^- \quad (2)$$

In our present contribution, we apply ESI mass spectrometry to demonstrate that similar organozincate anions are formed in LiCl-mediated zinc insertion reactions. For comparison, we also report preliminary results on organozinc ions produced by zinc insertion into benzylbromide in the *absence* of LiCl and analyze solutions of LiCl in THF. In addition, we probe the gas-phase reactivity of selected organozincate anions in order to achieve a more complete characterization.

2. Experimental Section

Synthetic Methods. The synthetic procedures were similar to those described by Knochel and co-workers[6,28] with the exception that we found it more convenient to use a solution of anhydrous LiCl in THF (distilled from potassium/benzophenone) rather than neat LiCl.

Typical procedure:[6] Zinc powder (7.0 mmol, Sigma-Aldrich) was placed in a flask and flame-dried under high vacuum. The flask was filled with Ar and allowed to cool down before the procedure was repeated twice. A total of 10 mL of a 0.5 M solution of anhydrous LiCl (5.0 mmol) in THF was added, and the resulting suspension was concentrated to a volume of 5 mL. The zinc was activated by the addition of 1,2-dibromoethane (0.020 mL), followed by a short boiling-up of the suspension, and of chlorotrimethylsilane (0.020 mL), again followed by a short boiling-up. The alkyl or aryl halide (5.0 mmol) was added dropwise and the suspension was stirred overnight at room temperature. The remaining zinc powder was allowed to precipitate, and an aliquot of the overlaying solution was diluted with THF before subjecting it to ESI mass spectrometric analysis. A solution of benzylzinc bromide in THF was prepared according to the method of Berk et al.[28]

ESI Mass Spectrometry. The ESI mass spectrometric experiments were analogous to those described previously in more detail.[24] In brief, sample solutions were transferred into a gastight syringe and administered into the ESI source of a TSQ 7000 multistage mass spectrometer (Thermo-Finnigan) at flow rates of approximately 10 $\mu L\ min^{-1}$. Nitrogen was used as sheath gas, and ESI voltages ranging from 3.0 to 4.3 kV were applied. In order to avoid unwanted fragmentation of possibly labile complexes, gentle ESI conditions were chosen (heated capillary at 60 °C, low potential difference between the heated capillary and the following electro-optical lens). The m/z ratios of the ions were then established by scanning the first quadrupole mass filter.

For the gas-phase reactivity studies, the first quadrupole mass filter was used to mass-select the organozincate ions of interest, which then passed an 18 cm long octopole ion guide. For studying the unimolecular reactivity of a mass-selected ion in a collision-induced dissociation (CID), argon (Linde, 99.998% purity) was added as collision gas into the octopole ($p(Ar) \approx 0.6$ mtorr as measured with a Convectron). The collision energy $E_{LABORATORY}$ was controlled by adjusting the voltage offset of the octopole. For the bimolecular reactions of the organozincate ions with methyl iodide and formic acid, these substrates were purified by repeated freeze–pump–thaw cycles before adding them into the octopole ($p \approx 0.4$ mtorr, uncorrected reading of the Convectron). The m/z ratios of the product ions formed by CID or ion–molecule reactions were then established by scanning the second quadrupole mass filter before the ions reached the detector.

3. Results

3.1. Stoichiometry of Organozincate Anions. The LiCl-mediated zinc insertion reaction was studied for a variety of alkyl and aryl halides RHal (RHal = CH_3I, ^iPrBr, ^iPrI, ^nBuI, BnCl, BnBr, and 4-EtOOC–C_6H_4I). In order to ensure full comparability of results, in all cases, 1 mM THF solutions (with respect to reactant RHal as well as to LiCl) were analyzed under very similar ESI conditions. In addition, we probed solutions of Bn–Zn–Br in THF and of LiCl in THF.

LiCl-Mediated Reaction of CH_3I with Zn. Anion-mode ESI of a solution of the products formed in the LiCl-mediated zinc insertion into CH_3I yielded, along with smaller amounts of I^-, several different zincate ions, such as $Zn(CH_3)ICl^-$, $Zn(CH_3)I_2^-$, ZnI_2Cl^-, and ZnI_3^- (Figure 1a). These zincate complexes could be easily identified thanks to their characteristic isotopic patterns,[29] as illustrated for $Zn(CH_3)I_2^-$ and ZnI_2Cl^- (Figure 1b). The identity of the organometallic $Zn(CH_3)I_2^-$ ion was further corroborated by a CID experiment, which produced I^- as ionic fragment together with neutral $Zn(CH_3)I$ (Supporting Information Table S1, entry 1).

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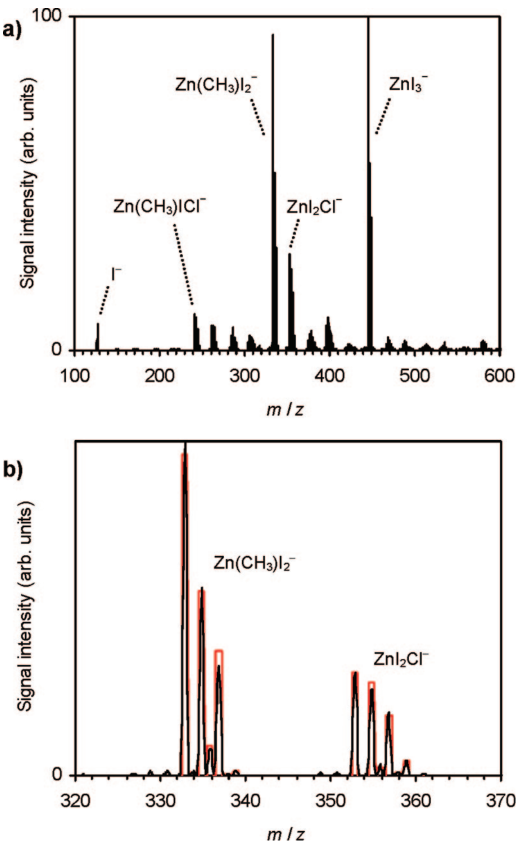

Figure 1. Anion-mode ESI mass spectrum of a 1 mM solution (with respect to reactant CH_3I and to LiCl) of the products formed in the LiCl-mediated reaction of methyliodide with zinc powder in THF: (a) overview and (b) comparison of observed (black) and expected isotopic patterns (red) for the low mass range.

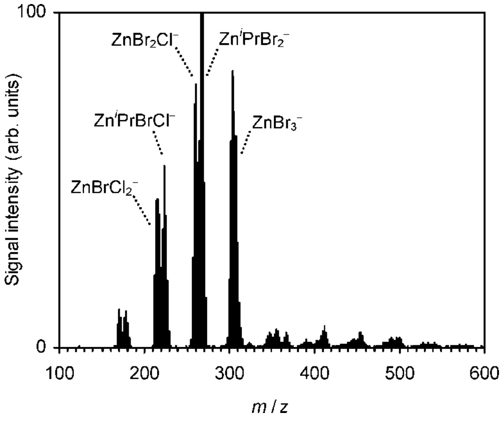

Figure 2. Anion-mode ESI mass spectrum of a 1 mM solution (with respect to reactant ${}^iPrBr$ and to LiCl) of the products formed in the LiCl-mediated reaction of isopropylbromide with zinc powder in THF.

LiCl-Mediated Reaction of ^{i}PrBr with Zn. Analysis of the reaction solution by anion-mode ESI mass spectrometry resulted in the detection of various zincate anions (Figure 2). Besides the purely inorganic complexes $ZnBr_{3-n}Cl_n^-$ ($n = 0$, 1, and 2), the organometallic species $Zn^iPrBrCl^-$ and $Zn^iPrBr_2^-$ were observed in significant abundance. Additional ions were detected at higher m/z ratios. Although their low signal intensities prevented their unambiguous identification, it seems very likely that these ions correspond to zincate complexes in higher aggregation states.

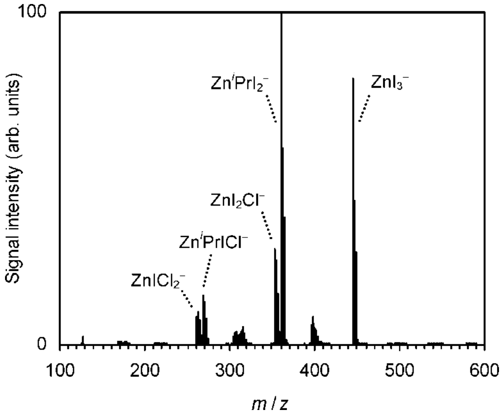

Figure 3. Anion-mode ESI mass spectrum of a 1 mM solution (with respect to reactant ${}^iPrI$ and to LiCl) of the products formed in the LiCl-mediated reaction of isopropyliodide with zinc powder in THF.

All of the mononuclear zincates listed above yielded predominantly Br^- upon fragmentation (Supporting Information Table S1, entries 2−6). For the heavier ions, however, additional fragment ions were found that pointed to the presence of $LiZnBrCl_3^-$, $LiZn^iPrBrCl_2^-$, and $LiZnBr_2Cl_2^-$ as parent ions (Supporting Information Table S1, entries 7−9). For instance, CID of the ion at $m/z = 259$ produced small amounts of ionic fragments at $m/z = 171$ and 173, which we assign to $ZnCl_3^-$. Obviously, $ZnCl_3^-$ cannot originate from $ZnBrCl_2^-$ but instead is formed by fragmentation of isobaric $LiZnBrCl_3^-$ ($M(Li^{35}Cl^{37}Cl^-) = M(^{79}Br^-)$). The parent ions at $m/z = 259$ thus correspond to a mixture of $ZnBrCl_2^-$ and $LiZnBrCl_3^-$. A careful analysis of the measured isotopic pattern suggests that $ZnBrCl_2^-$ strongly prevailed over $LiZnBrCl_3^-$ ($I(ZnBrCl_2^-)$: $I(LiZnBrCl_3^-) \geq 9{:}1$). Similarly, $Zn^iPrBr_2^-$ and $ZnBr_3^-$ were only slightly contaminated by $LiZn^iPrBrCl_2^-$ and $LiZnBr_2Cl_2^-$ species, respectively. The fact that the latter nevertheless left their signature in the CID experiments can be ascribed to their higher tendency toward dissociation. Our previous studies on organozincate ions showed that polynuclear zincate complexes fragment much more readily than their mononuclear congeners.[24]

LiCl-Mediated Reaction of ^{i}PrI with Zn. Anion-mode ESI mass spectra obtained for this reaction closely resemble those for the analogous reaction of ${}^iPrBr$. The most abundant ions detected, $ZnI_{3-n}Cl_n^-$ ($n = 0$, 1, and 2), Zn^iPrICl^-, and $Zn^iPrI_2^-$ (Figure 3), are all direct counterparts of the corresponding bromozincate complexes. In contrast to the latter, however, the iodozincate complexes apparently do not form higher aggregates, as no ions were observed at $m/z > 460$.

The organozincates Zn^iPrICl^- and $Zn^iPrI_2^-$ were also subjected to CID. Both complexes produced I^- as ionic fragment (Supporting Information Table S1, entries 10 and 11) and thus again behaved in complete analogy to the corresponding bromozincates.

LiCl-Mediated Reaction of ^{n}BuI with Zn. Analysis of the reaction solution by anion-mode ESI mass spectrometry again permitted the detection of the inorganic zincate complexes $ZnI_{3-n}Cl_n^-$ ($n = 0$ and 1) as well as of the organometallic species Zn^nBuICl^- and $Zn^nBuI_2^-$ (Figure 4). The latter two ions both gave I^- as ionic fragment upon CID (Supporting Information Table S1, entries 12 and 13).

LiCl-Mediated Reaction of BnCl with Zn. Anion-mode ESI of a solution of the products formed in the LiCl-mediated reaction between benzylchloride and zinc gave the expected

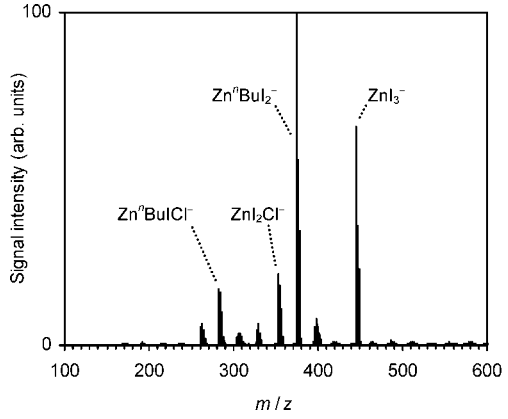

Figure 4. Anion-mode ESI mass spectrum of a 1 mM solution (with respect to reactant ^{n}BuI and to LiCl) of the products formed in the LiCl-mediated reaction of *n*-butyliodide with zinc powder in THF.

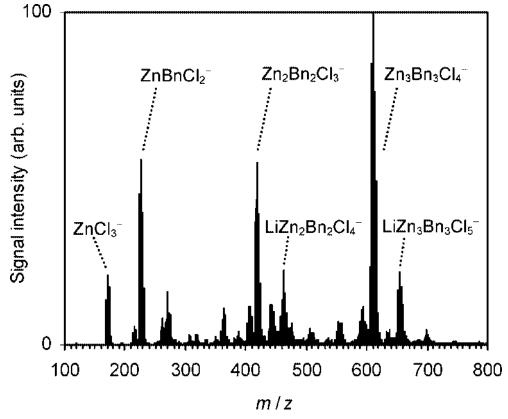

Figure 5. Anion-mode ESI mass spectrum of a 1 mM solution (with respect to reactant BnCl and to LiCl) of the products formed in the LiCl-mediated reaction of benzylchloride with zinc powder in THF.

mononuclear zincate anions $ZnCl_3^-$ and $ZnBnCl_2^-$ (Figure 5). In addition to these, abundant species occurred at higher *m*/*z* ratios.

The most prominent of these ions could be identified as $Zn_2Bn_2Cl_3^-$, $LiZn_2Bn_2Cl_4^-$, $Zn_3Bn_3Cl_4^-$, and $LiZn_3Bn_3Cl_5^-$. These assignments are based on a comparison between the observed and calculated isotopic patterns[29] and are also fully consistent with CID experiments performed for all of these ions (Supporting Information Table S1, entries 14−18). In comparison to their mononuclear counterparts, the polynuclear zincate complexes showed a much more diverse fragmentation behavior, which allows their unequivocal identification. For example, $Zn_3Bn_3Cl_4^-$ as the most abundant zincate anion observed yielded three different fragment ions upon CID (Supporting Information Figure S1) (eq 3a−3c).

$$Zn_3Bn_3Cl_4^- \rightarrow ZnCl_3^- + Zn_2Bn_3Cl \qquad (3a)$$

$$\rightarrow Zn_2BnCl_4^- + ZnBn_2 \qquad (3b)$$

$$\rightarrow Zn_2Bn_2Cl_3^- + ZnBnCl \qquad (3c)$$

It is interesting to note that the dissociation reactions tend to produce ionic fragments enriched in chloride ligands whereas the concomitantly formed neutrals contain a relatively higher number of benzyl groups. Similar fragmentation patterns were also observed for the other polynuclear zincates.

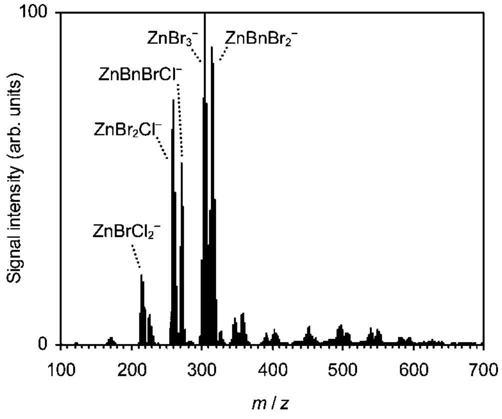

Figure 6. Anion-mode ESI mass spectrum of a 1 mM solution (with respect to reactant BnBr and to LiCl) of the products formed in the LiCl-mediated reaction of benzylbromide with zinc powder in THF.

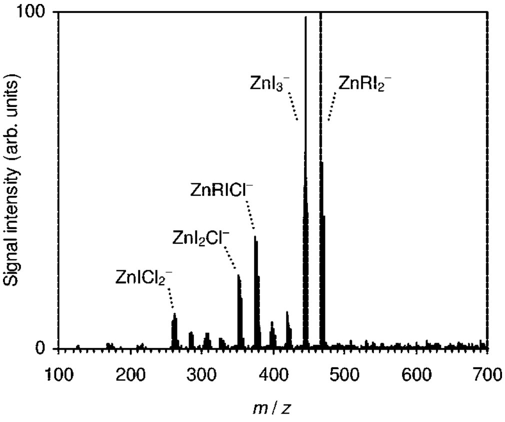

Figure 7. Anion-mode ESI mass spectrum of a 1 mM solution (with respect to reactant $EtOOC-C_6H_4I$ and to LiCl) of the products formed in the LiCl-mediated reaction of 4-iodo-ethylbenzoate (RI) with zinc powder in THF.

LiCl-Mediated Reaction of BnBr with Zn. Anion-mode ESI mass spectra obtained for this reaction show the presence of $ZnBr_{3-n}Cl_n^-$ ($n = 0$, 1, and 2), $ZnBnBrCl^-$, and $ZnBnBr_2^-$ (Figure 6) in the sampled solution. As expected, CID of these ions gave Br^- as ionic fragment (Supporting Information Table S1, entries 19−23). The detection of traces of additional fragment ions that cannot arise from these parent ions, however, again indicated the presence of isobaric contaminants, such as $LiZnCl_4^-$, $LiZnBnCl_3^-$, $LiZnBr_2Cl_2^-$, and $LiZnBnBrCl_2^-$ (Supporting Information Table S1, entries 24−27). A careful analysis of the measured isotopic patterns suggests that these isobaric contaminants account for only negligibly small fractions of the ion populations in question, though.

Additional ions observed at higher *m*/*z* ratios did not exhibit sufficient signal intensities for CID experiments and unambiguous identification. However, the measured isotopic patterns are consistent with those calculated for polynuclear zincate complexes, such as $LiZnBr_3Cl^-$, $LiZnBnBr_2Cl^-$, $Zn_2BnBr_{4-n}Cl_n^-$ ($n = 1$, 2, and 3), and $Zn_2Bn_2BrCl_2^-$.

LiCl-Mediated Reaction of 4-EtOOC-C_6H_4I with Zn. Anion-mode ESI mass spectrometry revealed that the LiCl-mediated zinc insertion into 4-iodo-ethylbenzoate (RI) afforded $ZnI_{3-n}Cl_n^-$ ($n = 0$, 1, and 2), $ZnRICl^-$, and $ZnRI_2^-$ as major ionic products (Figure 7). As expected, the latter produced I^-

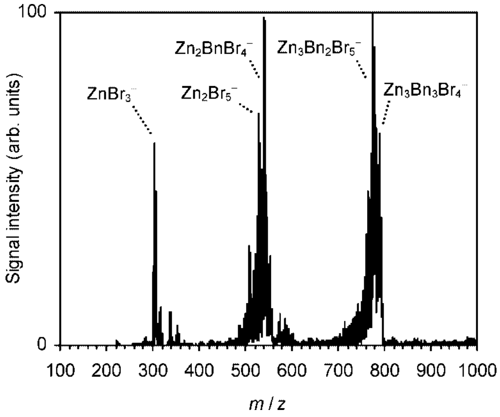

Figure 8. Anion-mode ESI mass spectrum of a 1 mM solution of Zn−Bn−Br in THF (without addition of LiCl).

as ionic fragment upon CID (Supporting Information Table S1, entry 28). No ions of significant intensity were detected for *m/z* > 480.

Reaction of BnBr with Zn in the Absence of LiCl. Analysis of the reaction solution by anion-mode ESI mass spectrometry resulted in the detection of $ZnBr_3^-$ and abundant polynuclear zincates (Figure 8). On the basis of their isotopic patterns and CID experiments (Supporting Information Table S1, entries 29 and 30), the most prominent of these zincates could be identified as $Zn_2Br_5^-$, $Zn_2BnBr_4^-$, $Zn_3Bn_2Br_5^-$, and $Zn_3Bn_3Br_4^-$.

LiCl in THF. Anion-mode ESI mass spectra of solutions of LiCl in THF gave only very weak genuine analyte signals, whereas, even after extensive cleaning and purging of the inlet system and the ESI source, contaminants such as $ZnCl_3^-$ and I^- remained visible. Only with optimized ESI conditions, acceptable signal intensities could be obtained for Cl^-, $LiCl_2^-$, and $Li_2Cl_3^-$ (Supporting Information Figure S2).

3.2. Concentration Dependence. All of the ESI mass spectrometric experiments presented so far sampled solutions with concentrations of $c = 1$ mmol L^{-1}, both in reactant RHal and in LiCl (except for the additional experiments on Bn−Zn−Br and LiCl solutions). The concentration of these species supposedly has a decisive influence on the equilibria between the different aggregation states, which the zincate ions adopt in solution. If ESI mass spectrometry really is capable of faithfully probing the aggregation state of the zincate complexes in solution, variation of the concentration should produce discernible effects in the ESI mass spectra. We thus investigated the concentration dependence of the relative ESI signal intensities of the different zincate ions to test our methodology and to learn more about the equilibria operative in solution. In doing so, we focused on the LiCl-mediated zinc insertion reactions into *n*-butyliodide, benzylchloride, and 4-iodo-ethylbenzoate.

The experiments presented above already applied gentle ESI conditions in order to avoid unwanted fragmentation of weakly bound complexes, particularly of polynuclear zincates, which are quite susceptible to dissociation.[24] Despite the gentle ESI conditions applied, we cannot rigorously rule out that fragmentations during the ESI process led to the relative scarcity of polynuclear zincates observed in all cases except for the insertion reactions into BnCl and BnBr. For the studies of the concentration dependence, we therefore chose even milder ESI conditions (lower potential difference between the heated capillary and the following electro-optical lens). While these extremely gentle ESI conditions reduced the overall signal intensity, they should permit the detection of intact labile polynuclear zincates complexes.

In general, an increase of the analyte concentration translates into higher absolute ESI signal intensities, although at the relatively high concentrations sampled in the present work saturation effects may come into play.[30] We indeed observed an increase in the overall absolute ESI signal intensities as a function of analyte concentration, but here we are interested in the *relative* ESI signal intensities of the different zincate complexes. For calculating these relative signal intensities, we considered the major isotopologues of the most abundant zincate ions detected (zincates of lower abundance were neglected). It is important to note that the ratio between the (relative) ESI signal intensities of different zincate complexes does not necessarily reflect their relative concentrations in solution because the ESI signal intensities also depend on the relative ESI response factors of the zincates. It is unknown how these ESI response factors differ for different zincate ions. Hence, we do not compare the relative ESI signal intensities of different zincates but instead analyze the concentration dependence for each zincate species separately.

LiCl-Mediated Reaction of ^{n}BuI with Zn. Even with extremely gentle ESI conditions, hardly any polynuclear zincates were detected for product solutions of $c = 1$ mmol L^{-1} (with respect to reactant ^{n}BuI and to LiCl). At higher concentrations, however, new species occurred at high *m/z* ratios (Supporting Information Figure S3a). Their pronounced isotopic patterns (Supporting Information Figure S3b) point to the presence of multiple zinc and chlorine atoms as ingredients of polynuclear zincate complexes.

The observed isotopic patterns of the two most prominent polynuclear zincates are best compatible with assignments as $Zn_2{}^nBuI_2Cl_2^-$ and $Zn_2{}^nBuI_3Cl^-$ (Supporting Information Figure S3b). These assignments also appear plausible in that the proposed polynuclear complexes $Zn_2{}^nBuI_2Cl_2^-$ and $Zn_2{}^nBuI_3Cl^-$ are closely related to the abundant mononuclear zincates ZnI_2Cl^-, $Zn^nBuI_2^-$, and ZnI_3^-. Unfortunately, the rather low signal intensities of the polynuclear ions did not permit confirmation of the given assignments by CID experiments. The poor signal-to-noise ratios also caused statistic fluctuations, which help to explain the deviations between the measured and the expected isotopic patterns. A particularly conspicuous deviation is seen for $m/z = 601$. Presumably, the higher than expected experimental signal intensity resulted from the presence of a second species besides $^{64}Zn_2{}^nBuI_3{}^{35}Cl^-$. The fact that considerable signal intensities were observed at the lower neighboring *m/z* ratios of $m/z = 597$ and 599 supports this assessment. We refrain from proposing assignments for this second species and for other additional ions at high *m/z* ratios.

The relative ESI signal intensities of the polynuclear zincates increased as a function of concentration (Figure 9). For the mononuclear zincates, the trend was less clear: the signal intensities of the purely inorganic complexes ZnI_2Cl^- and ZnI_2Cl^- first declined and then leveled off with increasing concentration, whereas that of $Zn^nBuI_2^-$ exhibited a pronounced maximum at an intermediate concentration of $c = 10$ mmol L^{-1}.

LiCl-Mediated Reaction of BnCl with Zn. For this reaction, abundant polynuclear zincates were already observed at a concentration of $c = 0.1$ mmol L^{-1} (with respect to reactant BnCl and to LiCl). The relative ESI signal intensity of $Zn_3Bn_3Cl_4^-$ considerably increased as a function of concentration, while those of $Zn_2Bn_2Cl_3^-$ and $LiZn_2Bn_2Cl_4^-$ showed only slight overall increases (Figure 10). In marked contrast, the

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[30] Cech, N. B.; Enke, C. G. *Mass Spectrom. Rev.* **2001**, *20*, 362.

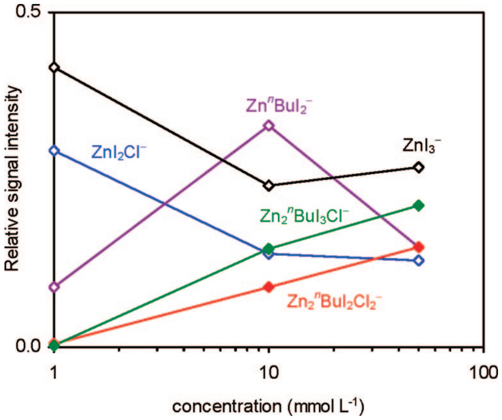

Figure 9. Relative signal intensities of zincate complexes produced by anion-mode ESI of 1, 10, and 50 mM solutions (with respect to reactant ^{n}BuI and to LiCl) of the products formed in the LiCl-mediated reaction of *n*-butyliodide with zinc powder in THF. Open symbols represent mononuclear complexes, and filled symbols represent polynuclear complexes.

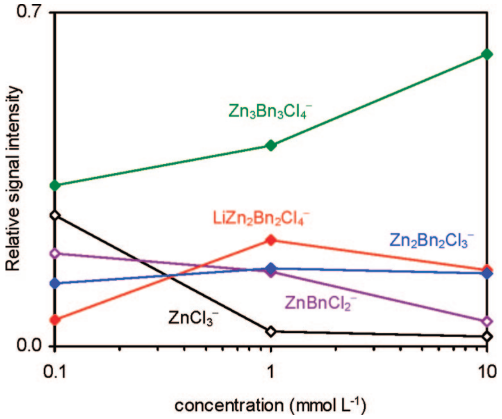

Figure 10. Relative signal intensities of zincate complexes produced by anion-mode ESI of 0.1, 1, and 10 mM solutions (with respect to reactant BnCl and to LiCl) of the products formed in the LiCl-mediated reaction of benzylchloride with zinc powder in THF. Open symbols represent mononuclear complexes, and filled symbols represent polynuclear complexes.

relative signal intensities of the mononuclear zincate complexes $ZnCl_3^-$ and $ZnBnCl_2^-$ decreased as function of concentration.

LiCl-Mediated Reaction of 4-EtOOC-C_6H_4I with Zn. No polynuclear zincate ions were detected even at the extremely gentle ESI conditions applied at a concentration of $c = 50$ mmol L^{-1} (with respect to reactant 4-EtOOC-C_6H_4I and to LiCl). The relative ESI signal intensities of the mononuclear zincates remained almost constant over the concentration range investigated ($1 \leq c \leq 50$ mmol L^{-1}, data not shown).

3.3. Observed Cations. The cation-mode ESI mass-spectra of the products from the LiCl-mediated zinc insertion reactions were completely dominated by $Li(THF)_3^+$ and $Li(THF)_4^+$ ions (compare Supporting Information Figure S4 for the case of Bn−Zn−Br·LiCl). Very similar results had previously been obtained for the reaction of $ZnCl_2$ with RLi (eq 2).[24] ESI of solutions of LiCl in THF also yielded $Li(THF)_3^+$ as the main peak but in addition gave the dinuclear species $Li_2Cl(THF)_n^+$, $n = 3$ and 4, and $Li_2Br(THF)_4^+$ (Supporting Information Figure S5). The latter apparently originated from a contamination of the inlet system and/or ESI source.

The high propensity of alkaline metal cations to form complexes with THF molecules is also evident from the ESI mass spectra measured for THF solutions of Bn−Zn−Br. Although for this case the zinc insertion occurred in the *absence* of LiCl and no sodium-containing compound was added either, $Li(THF)_3^+$ and $Na(THF)_n^+$, $n = 2$ and 3, yielded the highest signal intensities (Figure 11). We assume that these species stemmed from residual traces of Li^+ and Na^+ in the inlet system and/or ESI source.

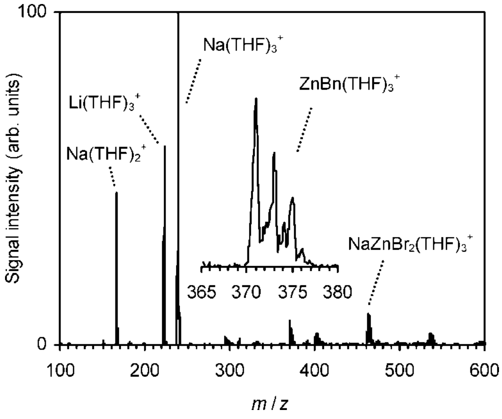

Figure 11. Cation-mode ESI mass spectrum of a 1 mM solution of Zn−Bn−Br in THF (without addition of LiCl). The solvated Li^+ and Na^+ ions result from a contamination. Inset: Enlarged part of the mass spectrum showing the isotopic pattern of $ZnBn(THF)_3^+$.

In addition, small amounts of cations were observed at higher *m*/*z* ratios. The ions with $m/z = 371-375$ displayed an isotopic pattern indicative of a mononuclear zinc complex (Figure 11, inset). CID resulted in the subsequent loss of up to three THF molecules and thus established the identity of this species as the organometallic cation $ZnBn(THF)_3^+$. In contrast, the other ions at high *m*/*z* ratios, such as $NaZnBr_2(THF)_3^+$, did not bear organyl groups.

3.4. Bimolecular Gas-Phase Reactivity. For the gas-phase reactivity studies, we focused on the mononuclear organozincates $Zn^nBuI_2^-$, $ZnBnCl_2^-$, and $ZnRI_2^-$ (derived from RI = 4-EtOOC-C_6H_4I) as selected examples. None of these species reacted with methyliodide (a prototypical carbon electrophile) or formic acid (a prototypical proton donor) at a measurable rate. From this finding, it can be estimated that the ion−molecule reactions of the organozincates both with CH_3I and HCOOH have efficiencies of less than 1% (less than 1 out of 100 collisions is productive; see ref 24 for details).

4. Discussion

General. For all LiCl-mediated zinc insertion reactions investigated, we observed the formation of organozincate anions. Together with purely inorganic $ZnHal_3^-$ complexes, these organozincates dominate the ESI mass spectra recorded. We therefore conclude that organozincate complexes represent major anionic constituents of THF solutions of the products from LiCl-mediated zinc insertion reactions. Preliminary results suggest that organozincate ions also form in zinc insertion reactions in the absence of LiCl. However, our experiments do not probe the absolute concentration of organozincate ions in solution nor the ratio between anionic and neutral organozinc species.

Mononuclear Organozincate Complexes. Mononuclear organozincate anions of the type $ZnRHal_2^-$ were produced in all reactions studied. These species correspond to those formed in the transmetalation reactions between $ZnHal_2$ and RLi (eq 2).[24] Both LiCl-mediated zinc insertion and transmetalation reactions thus apparently afford completely analogous organozinc species. Moreover, the $ZnRHal_2^-$ or, more specifically, the $ZnRHalCl^-$ anions observed can be linked to the R−Zn−Hal·LiCl complexes proposed by Knochel and co-workers as intermediates in LiCl-mediated zinc insertion reactions.[6] Our present findings provide support for the hypothesis of these authors and further suggest that the R−Zn−Hal·LiCl intermediates should be viewed as lithium zincates, which at least partly dissociate in THF (eq 4).

$$Li^+ZnRHalCl^- \rightleftharpoons Li^+ + ZnRHalCl^- \qquad (4)$$

A more detailed analysis takes into account the nature of the halogen. In the transmetalation reactions according to eq 2, only a single type of halogen is involved. The same holds true for the LiCl-mediated zinc insertion into benzylchloride. However, the situation is more complicated for the LiCl-mediated reactions of zinc with organic bromides and iodides, where two different halogen atoms are present. The original hypothesis of Knochel and co-workers assumed that R−Zn−Hal·LiCl intermediates contain the halogen from the reactant RHal (Hal = Br and I) as well as one chlorine atom stemming from LiCl. We indeed observed the corresponding $ZnRHalCl^-$ anions but, particularly for Hal = I, in considerably lower signal intensities than their $ZnRHal_2^-$ counterparts. Similarly, the signal intensities of the purely inorganic $ZnHal_{3-n}Cl_n^-$ complexes are the higher the less chloride ligands they contain, with this trend being more pronounced for the $ZnI_{3-n}Cl_n^-$ series than for the $ZnBr_{3-n}Cl_n^-$ series. The lower signal intensities of the chlorine-rich zincates may reflect lower ESI response factors and/or lower concentrations of these species in solution. Note that a putative lower concentration of chlorine-rich zincates could not simply result from a lower overall concentration of ionogenic chlorine compared to bromine or iodine, respectively, because in all experiments equimolar amounts of reactant RHal and LiCl and thus of Hal and Cl were employed (for incomplete conversion and remaining RHal, the concentration of ionogenic chlorine would be even higher than that of ionogenic bromine or iodine, respectively). Instead, we surmise that the concentration of free chlorine-rich zincate anions that are detectable by ESI mass spectrometry is significantly reduced by ion pairing with lithium cations (eq 4 for the case of $Li^+ZnRHalCl^-$). The lithium cation is well-known to be a hard Lewis acid, and so supposedly it preferentially interacts with hard Lewis bases. Because chloride is a harder Lewis base than bromide and iodide, the lithium cation should bind more strongly to chlorine-rich than to chlorine-free zincate anions. This stronger binding directly translates into a higher equilibrium concentration of contact ion pairs and thus a smaller fraction of free ions in the case of the chlorine-rich zincates. The strong tendency of lithium cations to form higher aggregates with chloride is also reflected in the low equivalent conductivity of LiCl in THF, which amounts to only 2% of the corresponding equivalent conductivity of LiBr (for $c(LiHal) \approx 10$ mmol L^{-1} at 298 K).[31]

The simultaneous presence of different zincate complexes, such as $ZnRHalCl^-$, $ZnRHal_2^-$, $ZnHal_2Cl^-$, and $ZnHal_3^-$, points to an extensive equilibration via exchange of halide ligands. Similar equilibration processes might conceivably also lead to the exchange of the organyl R (eq 5).

$$2\,ZnRHal_2^- \rightleftharpoons ZnR_2Hal^- + ZnHal_3^- \qquad (5)$$

At first sight, such Schlenk-type equilibria seem to rationalize the presence of $ZnHal_3^-$ complexes, which were observed in all cases. However, no ZnR_2Hal^- ions were found, which should be formed concomitantly with $ZnHal_3^-$ complexes according to eq 5. It seems rather unlikely that the absence of ZnR_2Hal^- in the mass spectra could be due to exceptionally low ESI response factors or to the complete formation of contact ion pairs between ZnR_2Hal^- and Li^+. More probably, the lack of ZnR_2Hal^- ions observed reflects the nonoccurrence of the disproportionation according to eq 5. For $ZnRHal_2^-$ obtained from transmetalation reactions, we did not find evidence for disproportionation reactions either and only for the dithiophenylzincate complex $Zn(C_4H_3S)_2Cl^-$ such a reaction appeared to take place;[24] for neutral organozinc species, similar disproportionation reactions are reported to be negligible in most,[32] but not in all, cases studied.[33] The $ZnHal_3^-$ complexes observed in the present experiments instead are ascribed to the partial decomposition of organozinc species by residual traces of moisture and/or oxygen (see below).

Polynuclear Organozincate Complexes. For the LiCl-mediated zinc insertion into *n*-butyliodide, significant amounts of polynuclear organozincates were observed only at higher analyte concentrations. This concentration dependence is consistent with the expected equilibria for the corresponding association reactions, such as eq 6a and 6b.

$$ZnI_2Cl^- + Zn^nBuCl \rightleftharpoons Zn_2{}^nBuI_2Cl_2^- \qquad (6a)$$

$$ZnI_3^- + Zn^nBuCl \rightleftharpoons Zn_2{}^nBuI_3Cl^- \qquad (6b)$$

The parallel decline of the relative ESI signal intensities of the mononuclear ZnI_2Cl^- and ZnI_3^- complexes at higher concentrations is also in line with this interpretation, whereas the intermediate increase observed for $Zn^nBuI_2^-$ clearly is not. Interestingly, the signal intensity of the analogous $Zn^nBuCl_2^-$ zincate generated from the transmetalation reaction of $ZnCl_2$ with ^nBuLi displayed very similar nonmonotonic concentration dependence.[24] We rationalized this behavior by the occurrence of hydrolysis and/or oxidation processes due to residual contamination by traces of moisture and/or oxygen. The depletion of the organozincate species due to these reactions should be most significant for low absolute concentrations. At higher concentrations, these decomposition processes affect only a small fraction of the organozincate ions whereas now depletion because of association reactions sets in.

The successive formation of higher aggregation states for increasing analyte concentrations can be seen even more clearly in the LiCl-mediated reaction between zinc and benzylchloride. Here, the increase of the relative signal intensity for the trinuclear organozincate $Zn_3Bn_3Cl_4^-$ is mirrored by decreases observed for mononuclear $ZnBnCl_2^-$ and $ZnCl_3^-$. The signal intensity for the intermediate dinuclear zincate $Zn_2Bn_2Cl_3^-$ (as well as the related $LiZn_2Bn_2Cl_4^-$) exhibits only weak concentration dependence because formation and depletion of this complex according to eq 7 apparently balance each other.

$$ZnBnCl_2^- + 2\,ZnBnCl \rightleftharpoons Zn_2Bn_2Cl_3^- + ZnBnCl \rightleftharpoons Zn_3Bn_3Cl_4^- \qquad (7)$$

Similar to the case of the transmetalation reaction between $ZnCl_2$ and ^nBuLi,[24] the observed concentration dependences thus well correlate with the expected shifts of the equilibria between

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[32] Evans, D. F.; Fazakerley, G. V. *J. Chem. Soc. A* **1971**, 182.

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different aggregation states in solution. This finding gives us further confidence that ESI mass spectrometry can be used to probe the different zincate complexes actually present in solution.

Although the reactions both with *n*-butyliodide and benzylchloride lead to the formation of polynuclear zincate anions, important differences exist. Whereas for the former reaction significant amounts of polynuclear zincates were only detected for concentrations of $c \geq 10$ mmol L^{-1} (with respect to reactant RHal and to LiCl), the latter gave abundant ESI signal intensities already for $c = 0.1$ mmol L^{-1}. Moreover, the reaction with *n*-butyliodide did not produce zincate complexes containing more than two metal centers, whereas for the reaction with benzylchloride the trinuclear complex $Zn_3Bn_3Cl_4^-$ gave the highest signal intensity. A comparison of these two reactions alone cannot differentiate whether these different tendencies toward formation of aggregates are governed by the organyl or the halogen of the RHal reactant. The fact that even for $c = 50$ mmol L^{-1} no polynuclear zincates were observed for the reaction of 4-iodo-ethylbenzoate can be viewed as a first indication that it is the exclusive presence of chlorine that facilitates the detection of higher aggregates.

This assessment is fully borne out by a comparison with the results from our previous study on organozincates generated by transmetalation according to eq 2. For the reaction of $ZnCl_2$ with ^{n}BuLi, we observed much more abundant polynuclear zincate complexes[24] than for the LiCl-mediated zinc insertion into ^{n}BuI, and this difference obviously results from the different properties of the two halogens. Reactions of $ZnCl_2$ with other alkyl lithium compounds RLi also led to polynuclear zincates.[24] All of these complexes displayed R/Zn ratios of ≤ 1, suggesting that a minimum number of chloride ligands is necessary for the formation of polynuclear zincates.[24] No polynuclear zincates were observed for the reactions of $ZnBr_2$ and ZnI_2 with ^{n}BuLi, although these reactions did yield lithium halide clusters of the type $Li_nHal_{n+1}^-$.[24] Apparently, chloride is more effective in forming bridging bonds between two zinc atoms than the heavier halides. This interpretation is also in line with findings on other halide-containing zinc complexes.[34] Note, however, that the zinc insertion into benzylbromide in the absence of LiCl led to significant amounts of polynuclear organozincates as well. This observation demonstrates that bromide is also capable of forming bridging bonds between zinc atoms if competition by chloride is excluded.

The fact that no abundant polynuclear zincates were detected when both chloride *and* bromide or iodide, respectively, were present in solution is probably related to the low relative ESI signal intensities also observed for mononuclear chlorine-rich zincates in these cases (see above). Presumably, the proposed higher tendency toward the formation of contact ion pairs is not limited to mononuclear chlorine-rich zincates but also applies to their polynuclear congeners and thus suppresses their ESI signal intensities in comparison to those of the (mononuclear) bromo- and iodozincates, respectively.

Besides the halide ligands, the organyl groups also have some influence on the tendency toward aggregation. While for the LiCl-mediated zinc insertion into *n*-butyliodide polynuclear zincates were detected at higher analyte concentrations, analogous complexes were not observed for the reaction with 4-iodo-ethylbenzoate. Similarly, the transmetalation reactions between $ZnCl_2$ and different organyl lithium compounds RLi also showed a dependence of the exact stoichiometry of the polynuclear organozincates produced on the nature of the organyl R.[24] These findings indicate that already subtle effects may influence the formation of polynuclear zincate complexes in a not easily predictable manner. In line with this assessment, a considerable variety of structural motifs is known for organozinc compounds in the literature.[35] However, no structural information is available that is directly relevant to the complexes found in the present work.

Cationic Species. In contrast to the anionic complexes observed, all of the detected cations contained at least two molecules of THF. Essentially the same behavior could be seen for transmetalation reactions between zinc halides and organyl lithium compounds in THF.[24] This difference clearly shows that the Lewis base THF has a high affinity toward cations whereas its interaction with anions apparently is not sufficiently strong to survive the ESI process, despite the mild conditions applied.[24]

The high affinity of THF toward cations also explains the formation of the organozinc cation $ZnBn(THF)_3^+$ from Bn−Zn−Br. This species closely resembles complexes of alkylzinc cations coordinated by dimethylformamide (DMF) molecules, which Caggiano et al. recently observed by ESI mass spectrometry of solutions of the corresponding alkylzinc iodides in DMF.[36] Theoretical calculations by these authors suggest that three molecules of DMF are necessary to achieve ionization of $CH_3{-}Zn{-}I$.[36] In the resultant $ZnCH_3(DMF)_3^+$ complex, the $ZnCH_3^+$ cation is stabilized by O-coordination.[36] It is remarkable that the system Bn−Zn−Br/THF apparently behaves very similarly although the two solvents DMF and THF have rather different properties (compare, e.g., ε(DMF) = 36.7 and ε(THF) = 7.4). Presumably, the ionization of Bn−Zn−Br is facilitated by the ability of the benzyl group to stabilize the cationic zinc center by its positive mesomeric effect.

We believe that the generation of the solvated $ZnBn^+$ cation is intimately linked to the formation of organozincate anions and can be understood as a disproportionation of neutral Bn−Zn−Br (eq 8).

$$n\,\mathrm{Bn{-}Zn{-}Br} \rightleftharpoons \mathrm{ZnBn}^+(\mathrm{solv}) + \mathrm{Zn}_{n-1}\mathrm{Bn}_{n-1}\mathrm{Br}_{n+1}^- \quad (8)$$

In line with this interpretation, the organozincates observed in general contained a higher number of bromine atoms than benzyl groups. For the LiCl-mediated zinc insertion reactions, the situation is different because here the addition of extra LiCl permits the formation of an organozincate complex without abstraction of a halide ion from the organylzinc compound. Indeed, no organozinc cations were detected for the LiCl-mediated zinc insertion reactions.

Gas-Phase Reactivity. In their unimolecular fragmentation reactions, the mononuclear organozincate complexes of the type $ZnRHal_2^-$ almost exclusively lost ZnRHal to produce Hal^- as ionic fragment (eq 9).

$$\mathrm{ZnRHal_2}^- \rightarrow \mathrm{Hal}^- + \mathrm{ZnRHal} \quad (9)$$

Similarly, the polynuclear organozincates from the LiCl-mediated reaction of zinc with benzylchloride fragmented in such a way that the chloride ligands preferentially remained in the ionic fragment whereas the benzyl groups accumulated in the neutral fragment. Analogous fragmentation patterns were observed for polynuclear organozincates produced in transmeta-

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lation reactions.[24] This asymmetric fragmentation maximizes the stabilization of the anionic fragment by virtue of the electron-withdrawing effect of the halogen atoms. Interestingly, these heterolytic dissociations differ from the behavior of the recently studied $MgBnCl_2^-$ anion. As O'Hair and co-workers reported,[37] this ion undergoes a homolytic bond cleavage upon CID (eq 10).

$$MgBnCl_2^- \rightarrow MgCl_2^{\bullet -} + Bn^{\bullet} \qquad (10)$$

The gas-phase experiments furthermore showed a rather low bimolecular reactivity of $ZnRHal_2^-$ complexes. This finding is fully consistent with the results of our previous gas-phase studies on analogous $ZnRCl_2^-$ species generated by transmetalation[24] and is also in line with the well-known moderate reactivity of organozinc compounds in solution.[1,2]

5. Conclusions

Anion-mode ESI mass spectrometry of THF solutions of the products from the LiCl-mediated zinc insertion reactions into organic halides RHal resulted in the detection of abundant organozincate anions, such as $ZnRHalCl^-$ and $ZnRHal_2^-$ (for Hal = Br and I). We identify the former with the dissociated form of the R−Zn−Hal·LiCl intermediate proposed by Knochel and co-workers.[6] The present results hence support the hypothesis put forward by these authors. The fact that not only $ZnRHalCl^-$ but also $ZnRHal_2^-$ ions were observed indicates extensive equilibration of the organozincate complexes by exchange of the halide ligands. The thus formed $ZnRHal_2^-$ ions yielded even higher ESI signal intensities than their $ZnRHalCl^-$ counterparts. This difference is ascribed to a smaller concentration of free $ZnRHalCl^-$ anions, of which presumably a larger fraction is tied up in contact ion pairs with Li^+. The nature of the halogen present in the zincate complexes also has a strong influence on their aggregation state. Whereas the reactions with iodides predominantly or exclusively afforded mononuclear zincates, abundant polynuclear zincates were detected for the LiCl-mediated zinc insertion into benzylchloride. The relative signal intensities of these polynuclear zincates increased as a function of concentration (relative to reactant BnCl and to LiCl), thus apparently reflecting the corresponding association equilibria operative in solution. The propensity of the organozinc chlorides to the formation of polynuclear zincates points to the ability of chlorine to bridge different zinc centers.

The observed coordination of halides ions to organozinc species is likely to influence the reactivity of the latter. Indeed, Oshima and co-workers found the addition of LiCl to accelerate the transmetalation of hexylzinc iodide and rationalized this effect by a putative deaggregation of the organozinc species.[10] In contrast, our present results indicate that chloride ions facilitate the formation of polynuclear organozincate complexes instead of causing deaggregation. Further work is needed to resolve this apparent contradiction.

Preliminary studies of the zinc insertion into benzylbromide show that organozincates also form in the absence of LiCl. The formation of organozincate anions most likely involves a disproportionation of neutral Bn−Zn−Br, thus generating organozinc cations as coproducts. This hypothesis is directly supported by the observation of the $ZnBn(thf)_3^+$ ion. The ionization of Bn−Zn−Br in THF mimics the recently reported heterolytic dissocation of alkylzinc iodides in DMF.[36] We are currently investigating zinc insertion reactions in the absence of LiCl in more detail.

Finally, the gas-phase reactivity of the organozincate complexes probed in the present work closely resembles that of analogous species investigated previously.[24] Mono- and polynuclear organozincates fragment by elimination of neutral zinc species. The partitioning of the organyl groups and halogen atoms in the ionic and neutral fragment is largely controlled by thermochemistry. The bimolecular gas-phase reactivity of the organozincate anions sampled is rather low, and this finding is in line with the moderate reactivity characteristic of organozinc compounds in solution.[1,2]

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Supporting Information Available: Table of CID experiments performed and figures showing additional mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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