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Oxidation State, Aggregation, and Heterolytic Dissociation of Allyl Indium Reagents

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Abstract: Solutions of allyl indium reagents formed in the reactions of indium with allyl bromide and allyl iodide, respectively, in *N*,*N*-dimethylformamide, tetrahydrofuran, and water were analyzed by a combination of electrospray-ionization mass spectrometry, temperature-dependent ^{1}H NMR spectroscopy, and electrical conductivity measurements. Additional mass spectrometric experiments probed charge-tagged derivatives of the allyl indium reagents. The results obtained indicate the presence of allyl indium(+3) species, which undergo heterolytic dissociation to yield ions such as $InR_2(solv)^+$ and $InRX_3^-$ with R = allyl and X = Br and I. The extent of dissociation is greatest for *N*,*N*-dimethylformamide, whereas aggregation effects are more pronounced for the less polar tetrahydrofuran. The heterolytic dissociation of the allyl indium reagents supposedly enhances their reactivity by simultaneously providing highly Lewis acidic allyl indium cations and nucleophilic allyl indate anions.

1. Introduction

Allyl indium reagents were first introduced into organic synthesis by Araki, Ito, and Butsugan.[1] As these authors showed in 1988, indium suspended in *N*,*N*-dimethylformamide (DMF) readily inserts into the carbon−halogen bond of allyl bromide and allyl iodide.[1] The resulting in situ formed allyl indium reagents smoothly add to aldehydes and ketones to yield the corresponding homoallylic alcohols in Barbier-type processes.[1] Further work extended the scope of these allylation reactions to other important substrate classes, such as acid anhydrides,[2] cyclic imides,[3] quinones,[4] alkynes,[5] imines,[6] and nitriles.[7] Most of these studies employed DMF as solvent, thus resembling the original reaction conditions of Araki et al.,[1] or alternatively used tetrahydrofuran (THF).[5c,d,7] In a seminal contribution, Li and Chan then demonstrated the suitability of aqueous media for indium-mediated allylation reactions under Barbier conditions.[8] The use of water not only offers advantages in terms of environmental benignity and procedural safety but also allows the direct conversion of water-soluble compounds without the need for tedious derivatization steps. Therefore, indium-mediated allylation reactions in aqueous media have been particularly valuable in carbohydrate chemistry.[9] With the additional development of catalytic[10] and stereoselective[11] reaction variants, allyl indium reagents today form an essential part of the synthetic organic chemist's armory.[12]

Despite their practical utility, current mechanistic understanding of indium-mediated allylation reactions is far from satisfactory. While a substituted allyl indium(+3) compound prepared by transmetalation has recently been structurally characterized,[13] such detailed information is lacking in the case of the in situ generated allyl indium reagents. For these, even the most basic properties, such as their stoichiometry and the oxidation state of the metal, have not been established unequivocally. In their initial study,[1] Araki et al. used ^{1}H NMR spectroscopy to probe the species formed upon reaction of indium with allyl iodide in DMF and observed two sets of allylic protons at δ 1.75 and 2.02 ppm in a ratio of 2:1. By determining the yield of the

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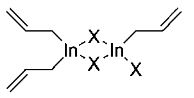
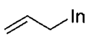
allylation of 2-octanone as a function of reactant stoichiometry, these authors moreover found that indium reacts with allyl iodide in a ratio of 2:3.[1] On the basis of these results, they tentatively proposed the sesquihalide structure **1** for the allyl indium reagent formed in DMF ($X = I$).[1] In contrast, Chan and Yang arrived at different conclusions for the reaction of indium with allyl bromide.[14] While theses authors also observed two sets of allylic protons for the allyl indium reagent generated in DMF, δ 1.7 and 2.15 ppm, they interpreted the signal at δ 1.7 ppm as the signature of the indium(+1) species **2**.[14] In brief, this assignment is based on the fact that the same chemical shift of δ 1.7 ppm was observed for allyl indium reagents prepared from indium and diallyl mercury as well as from indium(+1) iodide and diallyl mercury, for which structure **2** appears likely.[14] Chan and Yang further concluded that the reaction of indium with allyl bromide in water provides exclusively the indium(+1) species **2** because the thus formed reagent showed only one set of allylic protons at δ 1.7 ppm and exhibited a reactivity identical to that of the allyl indium reagents derived from diallyl mercury.[14] Recently, Bowyer and co-workers have revisited the reaction between indium and allyl bromide and iodide, respectively, in aqueous solution.[15] Besides establishing that these heterogeneous reactions proceed under diffusion control, they also showed that indium reacts with the allyl halides in a ratio of 2:3.[15] This finding is at odds with the formation of the indium(+1) species **2** assumed by Chan and Yang[14] but rather points to the generation of an indium(+3) compound, such as **1**. For DMF solutions, Singaram and co-workers have also proposed the presence of an indium(+3) compound as the active allylating species.[16] Finally, essentially nothing is known about the possible operation of aggregation and dissociation equilibria of the allyl indium reagents in the different solvents, although such phenomena can have a strong effect on the reactivity of organometallics.[17]



1, X = Br, I



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The apparent discrepancies in the literature clearly show the limitations of ^{1}H NMR spectroscopy, the chief method used so far for the investigation of allyl indium reagents, and call for alternative analytical techniques. In the present contribution, I use a combination of electrospray-ionization (ESI) mass spectrometry, ^{1}H NMR spectroscopy, and electrical conductivity measurements to probe the allyl indium reagents formed in the reactions of indium metal with allyl bromide and allyl iodide, respectively, in DMF, THF, and water (for the latter, no conductivity measurements were performed because of the limited stability of allyl indium reagents toward hydrolysis; see below). ESI mass spectrometry is increasingly recognized as one of the most powerful methods for the characterization of organometallics.[18] Specifically, it promises to determine the stoichiometry of the compounds in question and reveal trends in their aggregation and solvation behavior, if due care is taken to avoid possible artifacts resulting from the ESI process itself (see below). Hence, this method should be particularly useful in the present case. At the same time, ESI mass spectrometry exclusively detects *charged* species that are already preformed in solution. This restriction opens the opportunity to study the ionic products from heterolytic dissociations with high selectivity, as will be shown below. However, it also poses a severe limitation in that no direct information on neutral species can be obtained. To overcome this limitation, the present study not only samples the allyl indium reagents derived from allyl bromide and iodide but also includes related compounds that bear a quaternary phosphonium group as a charged tag. This charged tag should make undissociated and, thus, quasi-neutral species amenable to detection by ESI mass spectrometry.[19] The information gained from the ESI mass spectrometric experiments will then be compared to the results from temperature-dependent ^{1}H NMR spectroscopic studies and conductivity measurements. These well-established methods can yield quantitative data, which ESI mass spectrometry alone cannot provide, and thus complement the detailed but qualitative information afforded by the latter. Although the combination of these different analytical methods thus should hold substantial advantages for understanding dynamic phenomena and equilibria in solution,[20] this approach has hardly been realized in the field of organometallics so far.

2. Experimental Section

2.1. Synthetic Methods. For the materials used, see Supporting Information. Standard Schlenk techniques were applied in all cases to exclude oxygen and moisture (for the reactions in DMF and THF). While not necessary for synthetic studies, such precautions ensured the well-defined conditions needed for the present purpose.

Typical procedure for the indium insertion reactions in DMF and THF: A flame-dried flask filled with argon was loaded with indium powder (0.50 mmol) and 2.0 mL of the respective solvent. Allyl bromide or iodide (0.75 mmol), respectively, was added and the suspension was stirred for 1 h, during which time the indium metal largely or completely dissolved. Iodometric titration[21] of the resulting solution determined the reaction yield to 60−85% on the basis of an assumed $In_2R_3X_3$ ($R =$ allyl) product stoichiometry and an assumed consumption of all three R groups (note, however, that Araki, Ito, and Butsugan found the putative $In_2R_3X_3$ reagent in DMF to transfer only two of the three R groups to 2-octanone).[1]

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Typical procedure for the indium insertion reactions in water: An oven-dried flask filled with argon was loaded with indium powder (0.05 mmol) and 5.0 mL of water. Allyl bromide or iodide (0.075 mmol), respectively, was added, and the suspension was vigorously stirred for 7 min, during which time the indium metal did *not* dissolve completely.

The procedure for the reaction of indium with (*E*)-4-bromo-2-butenyltriphenylphosphonium bromide in DMF resembled that given for the reaction with the simple allyl halides. For the reactions in THF and water, in which the phosphonium salt is only very sparingly soluble, suspensions of indium metal and the phosphonium salt were stirred overnight in the case of THF and for 1 h in the case of water.

2.2. ESI Mass Spectrometry. Aliquots of the solutions containing the allyl indium reagents were diluted with the respective solvent to the desired concentration and then introduced into the ESI source of a TSQ 7000 tandem mass spectrometer or of a HCT quadrupole ion trap, respectively, via gastight syringes at typical flow rates of 5 μL min^{-1}. DMF solutions were only analyzed with the TSQ instrument to avoid contamination of the ESI source of the HCT ion trap. Complete removal of DMF from the ESI source of the TSQ instrument proved impossible. Instead a new ESI source had to be used for performing experiments under DMF-free conditions. A detailed description of the mass spectrometers and the instrumental settings used is given in the Supporting Information. Preparatory studies also probed solutions of In(+3)Cl_3 and In(+1)I to test whether the ESI process itself might electrochemically alter the oxidation state of indium species (see Supporting Information).

2.3. ^{1}H NMR Spectroscopy. Sample solutions of the allyl indium reagents in DMF-D_7 and THF-D_8 were added through rubber caps into flame-dried NMR tubes filled with argon whereas oven-dried NMR tubes were used for the sample solutions in D_2O. ^{1}H NMR spectra were recorded with 400-MHz Varian VNMRS and 200-MHz Varian Mercury instruments. The chemical shifts are given relative to the signals of the solvents (δ 2.75, 1.73, and 4.65 ppm for DMF, THF, and water, respectively).

2.4. Conductivity Measurements. Electrical conductivity measurements were performed with a CDM230 instrument (Radiometer Analytical) and a standard platinum-electrode cell (cell constant $\kappa_{\text{cell}} = 1$ cm^{-1}), which was calibrated against a 0.1 M solution of aqueous potassium chloride. Pure DMF or THF, respectively, was kept in a flame-dried flask under an argon atmosphere and was held at 25.0 ± 0.1 °C by means of a circulating water bath. Portions of a stock solution of the allyl indium reagent in the respective solvent were then added under stirring, and the increase in conductivity was measured. The obtained data were corrected for the background specific conductivities of the pure solvents (0.12−2.5 μS cm^{-1} for DMF and 0.003−0.26 μS cm^{-1} for THF). No conductometric measurements were performed for aqueous solutions because the relatively fast hydrolysis of allyl indium reagents in water would result in ill-defined experimental conditions, thus prohibiting a meaningful quantitative analysis.

3. Results

3.1. ESI Mass Spectrometry. 3.1.1. Reactions of Indium with Allyl Halides in DMF. The cation-mode ESI mass spectrum of formal $In_2R_3Br_3$ (R = allyl) in DMF was dominated by $InR_2(DMF)_n^+$, $n = 2$ and 3, and $InRBr(DMF)_3^+$ (Figure 1). In addition, $InR(DMF)_5^{2+}$ was clearly visible and showed the isotope pattern characteristic of a dication (Figure S9). The identity of these and all other organoindium ions observed in this study was confirmed by fragmentation reactions (see Supporting Information). The relative ESI signal intensities of the detected ions changed only very little when the concentration $c(In_2R_3Br_3)$ was varied in the range 0.5−15 mmol L^{-1}. Moreover, variation of the ESI conditions of the TSQ instrument over a wide range did not have a strong effect either.[22] Note that the ions observed comprise indium in an oxidation state of +3. Control experiments indicated that the ESI process itself does not artifactually alter the oxidation state of indium species under the conditions applied (see Supporting Information).

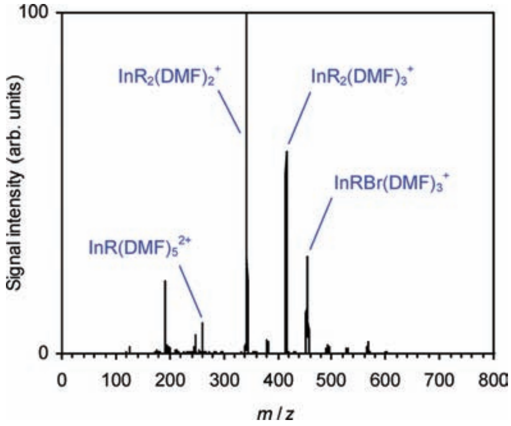

Figure 1. Cation-mode ESI mass spectrum of an approximately 3 mM solution of formal $In_2R_3Br_3$ (R = allyl) in DMF measured with the TSQ 7000 instrument. The ion at $m/z = 192$ corresponds to $H_2N(CH_3)_2(DMF)_2^+$, which results from decomposition of the solvent.

Upon cation-mode ESI of formal $In_2R_3I_3$ in DMF (Figure S10), ions identical or completely analogous to those obtained from $In_2R_3Br_3$ were observed for concentrations $c(In_2R_3I_3) =$ 0.5−20 mmol L^{-1} and for various different ESI conditions. After standing overnight, the solution showed a relative increase of $InR(DMF)_5^{2+}$ and $InRI(DMF)_3^+$ at the expense of $InR_2(DMF)_n^+$, $n = 2$ and 3, as well as the new formation of $InI_2(DMF)_3^+$ (Figure S11). These changes point to the occurrence of (partial) hydrolysis and/or oxidation reactions by traces of moisture and/or oxygen.

Anion-mode ESI of formal $In_2R_3Br_3$ in DMF mainly yielded the ate complex $InRBr_3^-$ along with smaller amounts of $InR_2Br_2^-$ and traces of the dinuclear $In_2R_2Br_5^-$ ion (Figure 2) for concentrations $c(In_2R_3Br_3) = 0.5{-}15$ mmol L^{-1} and different ESI conditions. As in the case of the cations, these species contain In(+3) centers. For formal $In_2R_3I_3$, analogous iodine-containing ions were observed (Figure S12) and apparently remained visible for concentrations as low as $c(In_2R_3I_3) \approx 2$ μmol L^{-1} (Figure S13). The same species were also detected for solutions kept overnight, although the relative signal intensity of the $InR_2I_2^-$ ion was decreased, presumably due to the occurrence of hydrolysis and/or oxidation reactions (Figure S14). For harsher ESI conditions, I^-, In(+1)I_2^-, and In(+2)I_3^- formed by decomposition of $InR_2I_2^-$ and $InRI_3^-$ during the ESI process,[23] as was verified by independent fragmentation of mass-selected $InR_2I_2^-$ and $InRI_3^-$ (see Supporting Information).

3.1.2. Reactions of Indium with Allyl Halides in THF. Cation-mode ESI of formal $In_2R_3Br_3$ in THF produced allyl indium(+3)

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(22) Specifically, the following parameters of the ESI source of the TSQ 7000 instrument were varied systematically: backing pressure of the sheath gas ($p(N_2) = 0.7{-}3.5$ bar), voltage of the ESI capillary ($V_{\text{ESI}} = 3.5{-}5.0$ kV), voltage of the heated capillary ($V_{\text{hc}} = 20{-}140$ V), and voltage of the tube lens ($V_{\text{tl}} = 29{-}149$ V). In addition, the flow rate of the sample solution was varied in a range of 5−30 μL min^{-1}. DMF containing solutions were deliberately *not* introduced into the HCT ion trap instrument to prevent long-lasting contamination of its ion source.

(23) The critical parameters were found to be the voltage of the heated capillary, V_{hc}, and the voltage of the tube lens, V_{tl}. Fragmentation during the ESI process was observed for $V_{\text{hc}} \leq -60$ V and $V_{\text{tl}} \leq -110$ V.

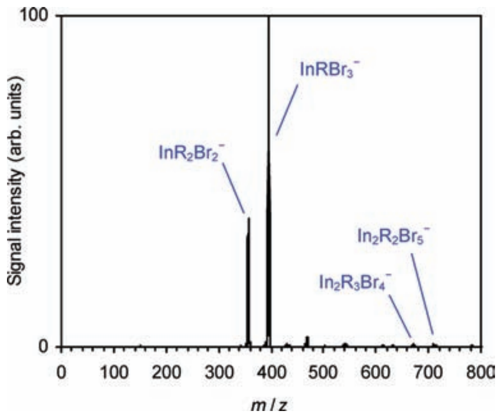

Figure 2. Anion-mode ESI mass spectrum of an approximately 3 mM solution of formal $In_2R_3Br_3$ (R = allyl) in DMF measured with the TSQ 7000 instrument.

species with both the TSQ instrument and the HCT ion trap. However, the former only yielded mononuclear $InR_2(THF)_2^+$ and $InRBr(THF)_2^+$ (Figure S15), whereas the latter mainly afforded the dinuclear species $In_2R_{5-n}Br_n^+$, $n = 1$ and 2 (Figure S16). This deviating performance was observed for the complete range of ESI parameters probed for the two instruments. Apart from this difference, it was consistently found that more energetic ESI conditions led to the partial decomposition of allyl indium(+3) cations and the formation of $In(+1)(THF)_n^+$, $n = 0-2$.[24] This decomposition was particularly pronounced for the HCT instrument if the ion transfer from the ESI source into the quadrupole trap was not controlled carefully. To avoid the artifactual production of $In(+1)(THF)_n^+$, the voltage of the first transfer octopole had to be significantly changed from the default value of the Compass software (Figure S17). The high propensity of $InR_2(THF)^+$ toward reductive elimination was also evident from fragmentation of the mass-selected ions (see Supporting Information).

Completely analogous results were obtained for solutions of formal $In_2R_3I_3$ in THF. Only the mononuclear species $InR_2(THF)_2^+$ and $InRI(THF)_2^+$ were observed with the TSQ instrument (Figure S18), while analysis with the HCT ion trap also yielded the dinuclear ions $In_2R_{5-n}I_n^+$, $n = 1$ and 2 (Figure S19). As in the case of formal $In_2R_3Br_3$ solutions, a change to harsher ESI conditions resulted in the formation of $In(+1)(THF)_n^+$, $n = 0 - 2$, in both instruments.

Anion-mode ESI of solutions of formal $In_2R_3Br_3$ in THF produced several mono- and polynuclear indium(+3) anions, the most prominent being $InRBr_3^-$, $In_2R_3Br_4^-$, $In_2R_2Br_5^-$, and $In_3R_4Br_6^-$. With the gentle ESI conditions typically applied, quite similar spectra were obtained with both the TSQ instrument (Figure 3) and the HCT ion trap (Figure S20). At somewhat more energetic ESI conditions, the relative signal intensities of the polynuclear anions were decreased because of fragmentation reactions. At even harsher conditions, formation of $In(+2)Br_3^-$ occurred.[25] The amount of polynuclear anions detected also depended on the concentration and increased as a function of $c(In_2R_3Br_3)$ (Figure S21). An analogous behavior was found for solutions of formal $In_2R_3I_3$ in THF although the amount of polynuclear anions formed was lower under comparable ESI conditions (Figures S22−S24).

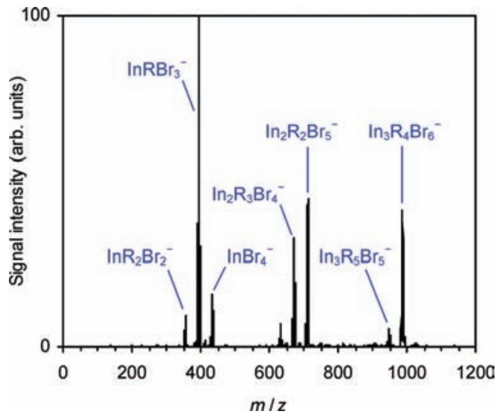

Figure 3. Anion-mode ESI mass spectrum of an approximately 5 mM solution of formal $In_2R_3Br_3$ (R = allyl) in THF measured with the TSQ 7000 instrument. The ions centered at $m/z = 634$ correspond to $In_2R_4Br_3^-$.

3.1.3. Reactions of Indium with Allyl Halides in Water. Because of the poor solubility of allyl halides in water and the instability of allyl indium reagents toward hydrolysis,[14,16] the relative concentration of the latter in water is inherently small, thus making their analysis more difficult. Additional problems specific to ESI of solutions of pure water arise from their high surface tension, which impairs the formation of a stable spray,[26] and less facile desolvation, particularly at the low source temperatures used in the present study. These factors are probably the reason why no conclusive cation-mode ESI mass spectra could be obtained for solutions of formal $In_2R_3Br_3$ in water. In the case of formal $In_2R_3I_3$, ESI with the TSQ instrument did not produce meaningful results for solutions in pure water either,[27] but only for a 1:1 mixture of water and DMF. The resulting cation-mode ESI mass spectrum exhibits the dications $InR(DMF)_5^{2+}$ and $InI(DMF)_5^{2+}$ as well as the related monocations $InRI(DMF)_n^+$, $n = 2$ and 3, and $InI_2(DMF)_n^+$, $n = 2-4$ (Figure S25). All of these species contain In(+3) centers. With the HCT ion trap, ESI of formal $In_2R_3I_3$ in *pure* water proved informative as well and showed the presence of dinuclear $In_2R_{5-n}I_n^+$, $n = 2$ and 3, in the cation mode (Figure S26). Additional peaks of smaller signal intensity most likely correspond to the related organoindium(+3) ions $InR(OH)(H_2O)^+$ and $InR(OR)(H_2O)^+$ (or possibly a tautomer of the latter). However, an alternative assignment as coordinated In^+ cations, i.e. $In(ROH)(H_2O)^+$ and $In(ROH)_2^+$, cannot be excluded because the fragmentation behavior (see Supporting Information) would also be compatible with this type of structure. Similarly to the case of allyl indium reagents in THF, the formation of bare In^+ was observed if the ion transfer from the ESI source into the quadrupole ion trap was not controlled carefully.

With the HCT ion trap, formal $In_2R_3Br_3$ in water showed the presence of Br^- and the In(+3) ions $InRBr_3^-$ and $InBr_4^-$ upon anion-mode ESI (Figure S27). The analogous iodine-containing anions were detected for solutions of $In_2R_3I_3$ in a 1:1 mixture of water/DMF (TSQ instrument, Figure S28) and pure water (HCT ion trap, Figure S29).

3.1.4. Reaction of Indium with (*E*)-4-Bromo-2-butenyltriphenylphosphonium Bromide. ESI mass spectrometry showed that the main cation formed in the reaction of indium with (*E*)-

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(24) For the TSQ 7000 instrument, such fragmentation during the ESI process was observed for $V_{hc} \geq 70$ V and $V_{tl} \geq 80$ V.

(25) For the TSQ 7000 instrument, formation of $InBr_3^-$ was observed for $V_{tl} \leq -80$ V. For the HCT ion trap, it occurred if skimmer voltages $V_{sk} \leq -60$ V were applied.

(26) Cech, N. B.; Enke, C. G. *Mass Spectrom. Rev.* **2001**, *20*, 362–387.

(27) The mass spectra recorded showed hardly any In-containing ions but were dominated by H_2O adducts in the cation mode and I_3^- and I_5^- in the anion mode.

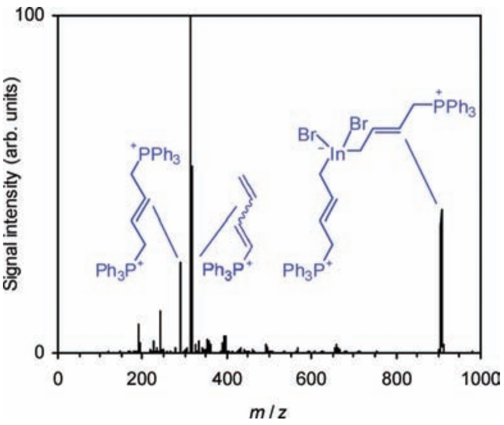
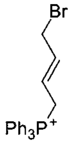


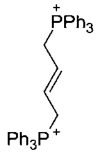
Figure 4. Cation-mode ESI mass spectrum of a solution of the products formed in the reaction of indium with (*E*)-4-bromo-2-butenyltriphenylphosphonium (**3**) bromide in DMF measured with the TSQ 7000 instrument. The ion at $m/z = 192$ corresponds to $H_2N(CH_3)_2(DMF)_2^+$, which results from decomposition of the solvent, and the ion at $m/z = 246.5$ corresponds to $Mn(DMF)_6^{2+}$, which originates from a contamination of the ESI source. The ions at $m/z = 395$ and 397 correspond to remaining reactant (*E*)-4-bromo-2-butenyltriphenylphosphonium cation (**3**).

4-bromo-2-butenyltriphenylphosphonium (**3**) bromide in DMF corresponds to **4** (Figure 4). This species results from a formal 1,4-elimination of HBr from **3**, which should be facilitated by the acidifying effect of the phosponium group. The elimination was significantly slowed down in the absence of indium, which suggests the involvement of organoindium species. These organoindium species could either induce an actual 1,4-elimination of HBr by deprotonatation of **3** or they might form **4** in the vinylogue variant of a β-H type elimination.[28] Organoindium species are probably also involved in the formation of the diphosphonium ion **5**, although its exact origin is unclear.

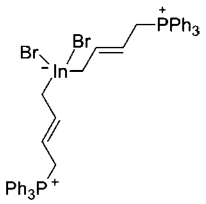


3

4



5



6

The observation of an ion compatible with the structure **6** provides strong evidence for the presence of an organoindium species derived from **3**. The measured isotope pattern matches that theoretically predicted for **6** almost perfectly (Figure S30), although the question of possible structural isomers remains (see below). Irrespective of this problem, there is little doubt that the ion in question corresponds to an In(+3) species. The organoindium ion **6** (or a possible isomer thereof), along with the elimination product **4**, was also observed for the reaction in THF (Figure S31) but not in aqueous solution (Figure S32).

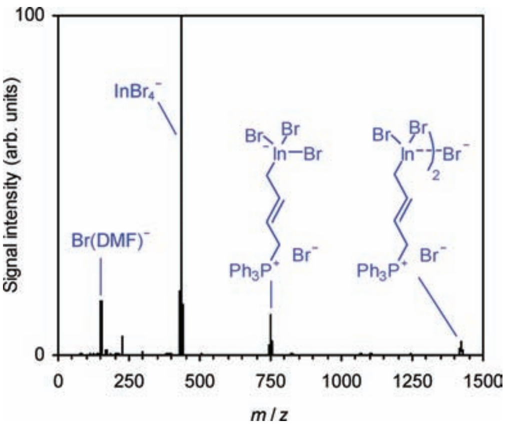
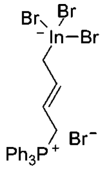
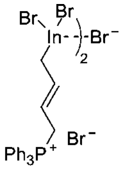


Figure 5. Anion-mode ESI mass spectrum of a solution of the products formed in the reaction of indium with (*E*)-4-bromo-2-butenyltriphenylphosphonium (**3**) bromide in DMF measured with the TSQ 7000 instrument. The ions at $m/z = 225$ and 227 correspond to $Br(DMF)_2^-$.

ESI mass spectrometric analysis of the anions formed in the reaction of indium with **3** in DMF indicated the presence of $Br(DMF)_n^-$, $n = 1$ and 2, $InBr_4^-$, and organoindium(+3) species (Figure 5), which are assigned to the complexes **7** and **8** (or possible isomers, see below). The high number of bromine atoms in the proposed structure **8** gives rise to a pronounced isotope pattern (Figure S33).



7



8

The anion **7** (or an isomer thereof) was also observed in THF (Figure S34) and in aqueous solution (Figure S35) where it was found to be stable against hydrolysis for >1 h.

3.2. ^{1}H NMR Spectroscopy. 3.2.1. Reactions of Indium with Allyl Halides in DMF. For the analysis, the focus is on the high-field regions of the spectra, which display the allylic protons of the allyl indium reagents (the full room-temperature spectra are given in the Supporting Information). The direct adjacency to the metal results in a relatively strong shielding of these protons such that they absorb in a range little congested with other spectral features and, thus, are easy to identify. At room temperature, formal $In_2R_3Br_3$ in DMF shows two sets of allylic protons at δ 1.75 and 1.95 ppm. Slightly deviating shifts of δ 1.82 and 2.10 ppm are observed for formal $In_2R_3I_3$. These results are by and large consistent with the data reported in the literature (see above).[1,14,16] Interestingly, the ^{1}H NMR spectra of both indium allyl reagents display a pronounced temperature dependence (Figure 6 and Figure S73). In both cases, the low-field doublet ($J = 9$ Hz) visible at room temperature shifts significantly upfield with decreasing temperature and is extremely broadened. Increasing the temperature leads to a broadening of both doublets and their complete merging at 333 K (at 353 K, decomposition occurs). The well-resolved multiplet simultaneously observed for the signal of propene (resulting from hydrolysis of the indium allyl reagents by traces of moisture) indicates that this merging of the signals of the allylic protons reflects a dynamic behavior of the allyl indium reagent and not just a loss of homogeneity of the sample. After standing overnight, the room-temperature sample of formal $In_2R_3I_3$ showed a decrease of the signal at δ 1.82 ppm, in line with the observations of Chan and Yang for the related formal $In_2R_3Br_3$ system.[14]

3.2.2. Reactions of Indium with Allyl Halides in THF. Solutions of formal $In_2R_3Br_3$ (Figure 7) and $In_2R_3I_3$ (Figure S74)

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(28) β-H eliminations from indium compounds have been reported before: Foos, E. E.; Wells, R. L.; Rheingold, A. L. *J. Cluster Sci.* **1999**, *10*, 121–131.

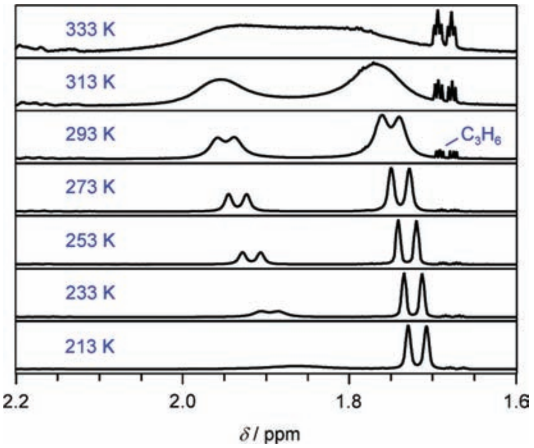

Figure 6. High-field section from the 400-MHz ^{1}H NMR spectrum of a solution of the products formed in the reaction of indium with allyl bromide in DMF-D$_7$ recorded at different temperatures. The detected propene results from hydrolysis of the allyl indium reagent by traces of moisture.

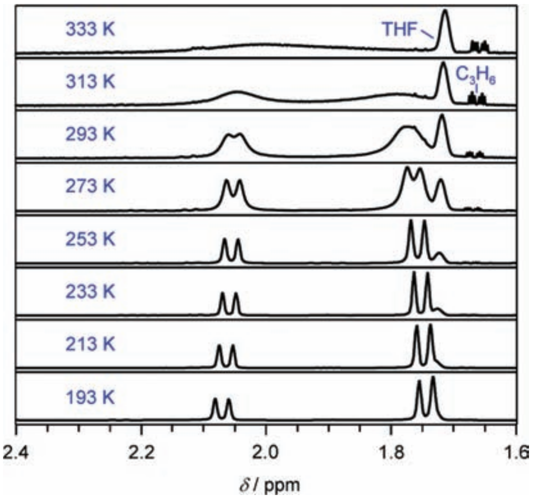

Figure 7. High-field section from the 400-MHz ^{1}H NMR spectrum of a solution of the products formed in the reaction of indium with allyl bromide in THF-D$_8$ recorded at different temperatures. The detected propene results from hydrolysis of the allyl indium reagent by traces of moisture.

in THF gave similar ^{1}H NMR spectra, which at low temperature show two clearly resolved doublets (J = 9 Hz) indicative of the allylic protons of the allyl indium reagent. Raising the temperature above 253 K leads to the broadening of both signals until they are completely merged at 333 K.

3.2.3. Reactions of Indium with Allyl Halides in Water. As reported in the literature,[14,15] the ^{1}H NMR spectra of aqueous solutions of allyl indium reagents display only a single set of allylic protons at δ 1.7 ppm indicative of an organoindium species (Figures S71 and S72). Variation of the temperature in the range T = 278−313 K did not have a pronounced effect for an aqueous solution of formal $In_2R_3I_3$. In comparison to the DMF and THF solutions, the formation of propene was accelerated, as expected for a hydrolysis reaction.

3.3. Conductivity Measurements. 3.3.1. Reactions of Indium with Allyl Halides in DMF. Solutions of formal $In_2R_3Br_3$ and particularly $In_2R_3I_3$ in DMF at 298 K exhibited significant specific electrical conductivities. In each case, three independent titration experiments were performed (see Experimental Section for details), using independently prepared stock solutions of allyl indium reagents, whose concentrations were determined by iodometric titration. The resulting molar conductivities plotted against the square root of the concentration showed a satisfactory internal consistency of the data (Figure 8) and thus lend support to their validity. Already at a qualitative level, it is obvious that heterolytic dissociation of formal $In_2R_3I_3$ occurs to a much greater extent than that of $In_2R_3Br_3$.

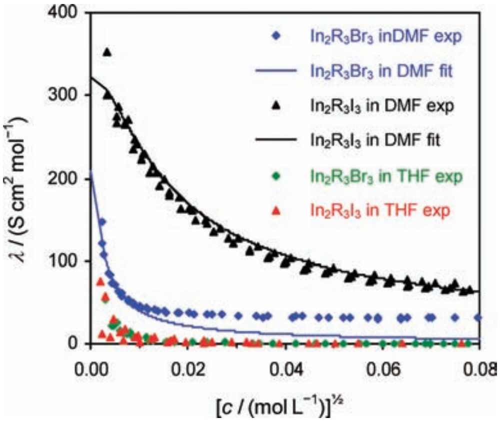

Figure 8. Measured molar conductivities λ of solutions of allyl indium reagents as functions of the square roots of their concentrations at 298 K. For the conductivity data in DMF, theoretical fits are shown as well (fitting parameters used: ($In_2R_3Br_3$) λ_0 = 208 S cm^2 mol^{-1}, K_{diss} = 4.46 × 10^{-6} mol L^{-1}; ($In_2R_3I_3$) λ_0 = 323 S cm^2 mol^{-1}, K_{diss} = 1.98 × 10^{-4} mol L^{-1}; activity coefficients were calculated according to ref 29).

For a quantitative analysis, the method of Fuoss[29] is applied. This method corrects Ostwald's simple dilution law according to the Debye−Hückel limiting law and provides a parametrized approach for straightforward implementation. Specifically, heterolytic dissociation according to eq 1 is assumed to be the predominant equilibrium operative in solution.

$$In_2R_3X_3 \rightleftharpoons InR_2^+ + InRX_3^- \tag{1}$$

This assumption certainly is rather simplistic given that the ESI mass-spectrometric experiments have revealed the presence of additional ions in solutions of allyl indium reagents in DMF. As the measured conductivity represents the averaged contributions of all ions present in solution, the quantitative analysis will only provide one averaged dissociation constant K_{diss}. For solutions of formal $In_2R_3Br_3$ in DMF, the measured data up to a concentration of $c(In_2R_3Br_3) = 10^{-4}$ mol L^{-1} were considered for the quantitative evaluation. At higher concentrations, the experimental data did no longer follow the rule predicted by Fuoss for low concentrations (in terms of the original nomenclature used by Fuoss,[29] the plot of F/Λ against $c\Lambda f^2/F$ started to deviate from linearity). The analysis yields a limiting molar conductivity of $\lambda_0 \approx 200$ S cm^2 mol^{-1} and a dissociation constant of $K_{diss} \approx 4 \times 10^{-6}$ mol L^{-1}. Fitting the measured data on the basis of these results only reproduces the molar conductivities at the lowest concentrations (Figure 8). For solutions of formal $In_2R_3I_3$ in DMF, the experimental data up to a concentration of $c(In_2R_3I_3) = 10^{-3}$ mol L^{-1} could be included for the quantitative evaluation, affording $\lambda_0 \approx 300$ S cm^2 mol^{-1} and a dissociation constant of $K_{diss} \approx 2 \times 10^{-4}$ mol L^{-1}. A fit based on these values agrees reasonably well with the measured conductivities over the entire concentration range sampled.

3.3.2. Reactions of Indium with Allyl Halides in THF. Solutions of allyl indium reagents derived from allyl bromide

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(29) Fuoss, R. M. *J. Am. Chem. Soc.* **1935**, *57*, 488–489.

and iodide in THF exhibited much lower conductivities than those of the corresponding solutions in DMF. Furthermore, the measured values were not completely stable but showed a slow increase with time. This increase apparently reflects the occurrence of unknown background reactions. As a result, the scattering in the data, particularly for the $In_2R_3I_3$ system, is considerable and does not permit a meaningful quantitative analysis.

4. Discussion

4.1. Oxidations States of Allyl Indium Reagents. The ESI mass spectra of allyl indium reagents in DMF, THF, and water showed the presence of allyl indium ions, all of which contain indium in an oxidation state of +3. The same holds true for the organoindium species derived from the phosphonium-tagged precursor **3**. These results strongly suggest the preferential formation of allyl indium(+3) species in the reactions of indium with allyl bromide and iodide in these solvents. Thus, they agree with the early conclusions of Araki et al.[1] for the system In/RI/DMF and the recent findings of Bowyer and co-workers[15] for the allyl indium reagents formed in aqueous solution. Moreover, the prevalence of allyl indium(+3) species is in line with organoindium chemistry in general, which almost exclusively comprises indium(+3) compounds.[30]

The present findings seem to disagree with the assessment of Chan and Yang who proposed the formation of the allyl indium(+1) species InR (**2**) in DMF and water.[14] If **2** was generated under the present conditions, one would expect to observe related ions, such as In_2R^+ or $InRX^-$, by ESI mass spectrometry, which was not the case (for example, the analogous ion InI_2^- was detected for solutions of InI; see Supporting Information). Similarly, the use of the phosphonium-tagged precursor **3** did not result in the observation of organoindium(+1) species either. Additional and complementary information on the accessibility of different oxidation states of allyl indium species is provided by the gas-phase fragmentation experiments. These experiments show that the allyl indium ions readily undergo reductive eliminations and lose R_2 and/or RX (see Supporting Information). However, in no case allyl indium(+1) species, such as In_2R^+, $InRX^-$, or InR_2^-, but only purely inorganic In(+1) ions, such as In_2X^+ and InX_2^-, are produced. This finding indicates that the formation of allyl indium(+1) ions is intrinsically unfavorable.

4.2. Aggregation and Heterolytic Dissociation of Allyl Indium Reagents. The high ESI signal intensities observed for allyl indium ions suggest that the allyl indium reagents formed in solution easily undergo heterolytic dissociation. This result is in line with the well-documented tendency of In(+3) compounds to behave as Lewis acids and add halides, thus yielding ate complexes.[31] For solid $In(CH_3)I_2$, e.g., the ionic structure $In(CH_3)_2^+InI_4^-$ has been proposed on the basis of its IR and Raman spectra.[32] The present findings show that the extent to which dissociation occurs strongly depends on the solvent. Valuable qualitative information on this dependence is provided by the ESI mass spectrometric results although it is clear that the ions observed do not simply reflect the ionic components present in solution. For example, the absence or presence of dinuclear allyl indium cations in the mass spectra measured with the TSQ instrument and the HCT ion trap, respectively, demonstrates that the ESI process itself can have a crucial influence on the aggregation state of the detected species. Therefore, the present analysis will focus on *trends* derived from a comparison of ESI mass spectra recorded under the same conditions (TSQ instrument for DMF and THF solutions and HCT ion trap for THF and aqueous solutions).

A first difference between solutions of allyl indium reagents in DMF and THF is given by their different tendencies toward the formation of dications. In DMF solutions, significant quantities of dicationic $InR(DMF)_5^{2+}$ were observed while analogous species could not be detected for THF solutions. The ability of DMF to stabilize the highly charged InR^{2+} core is testament to its particular donor strength.[33] The high Lewis basicity of DMF also prohibits the formation of larger aggregates and explains why predominantly mononuclear allyl indium ions were found over the entire concentration range sampled. In line with its significantly lower donor strength,[33] many more polynuclear anions were observed in THF. In this solvent, the transition from mononuclear to dinuclear complexes could actually be enforced by increasing the concentration of formal $In_2R_3X_3$, X = Br and I. The resulting enhanced relative ESI signal intensities of $In_2R_2X_5^-$ apparently correlate with a shift of the equilibrium according to the law of mass action, eq 2. A comparison between $In_2R_3Br_3$ and $In_2R_3I_3$ moreover showed a higher tendency toward aggregation for the former. Dinuclear allyl indium species were also observed in water.

$$InRX_3^- + InRX_2 \rightleftharpoons In_2R_2X_5^- \qquad (2)$$

The ESI mass spectrometric results are fully supported by the conductivity studies, which furthermore provide quantitative information. First, the conductivity data unambiguously show that heterolytic dissociation indeed occurs much more readily in DMF than in THF. They also allow a detailed comparison of the behavior of formal $In_2R_3Br_3$ and $In_2R_3I_3$ reagents in DMF. For both of these reagents, roughly similar limiting molar conductivities were determined, as expected. The obtained values of $\lambda_0 \approx 200-300$ S cm^2 mol^{-1} are approximately twice as high as those of DMF solutions of typical 1:1 electrolytes at ambient temperature.[34] A possible reason for this discrepancy might be that the quantitative analysis does not take into account all dissociation processes operative. As described above, the simplified model applied only considers a heterolytic dissociation according to eq 1. If the resulting product ions undergo further dissociation, the actual concentration of charged species is higher than assumed in the analysis, which thus overestimates the limiting molar conductivity. The observation of dicationic $InR(DMF)_5^{2+}$ by ESI mass spectrometry provides direct evidence for the proposed heterolytic dissociation of monocations. Given the complexity of the system and the simplicity of the model, only a limited accuracy of the obtained numerical data can be expected. Notwithstanding this uncertainty, the analysis clearly shows that formal $In_2R_3Br_3$ has a much lower tendency toward heterolytic dissociation than its iodine congener. This finding agrees with its higher tendency toward aggregation derived from the ESI mass spectrometric experiments. The

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(30) Weidlein, J. In *Gmelin Handbook of Inorganic and Organometallic Chemistry: Organoindium Compounds 1*, 8th ed.; Petz, W., Ed.; Springer: Berlin, 1991.

(31) Downs, A. J., Ed. *Chemistry of Aluminium, Gallium, Indium and Thallium*; Blackie Academic: London, 1993.

(32) Gynane, M. J. S.; Waterworth, L. G.; Worrall, I. J. *J. Organomet. Chem.* **1972**, *43*, 257–264.

(33) Reichhardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; Wiley-VCH: Weinheim, 2003; pp 19−27.

(34) Izutsu, K. *Electrochemistry in Nonaqueous Solutions*; Wiley-VCH: Weinheim, 2002; pp 214−215.

dissociation constant of formal $In_2R_3I_3$ in DMF, $K_{diss} \approx 2 \times 10^{-4}$ mol L^{-1}, exceeds that of acetic acid in water, which implies that heterolytic dissociation of this allyl indium reagent certainly is significant.[35]

Besides the quantitative analysis of dissociation equilibria, the exact identity of the formed ions is of interest as well. The ESI mass spectra show that the heterolysis reactions do not proceed in a symmetric fashion but that they produce cations enriched in allyl substituents and anions enriched in halogen atoms. This pattern was consistently found for both formal $In_2R_3Br_3$ and $In_2R_3I_3$ and for all three solvents. It markedly resembles the partitioning of the substituents in $In(CH_3)_2^+InI_4^-$ (see above)[32] and also parallels the behavior of alkylzinc halides, such as butylzinc iodide, which yields $ZnBu^+$(solv) and $ZnBuI_2^-$ in a putative disproportionation reaction.[36] In all of these cases, the enrichment of the halogen atoms in the anions leads to a stabilization of the negative charge by virtue of their high electronegativity while their relative depletion in the cations minimizes destabilization of the positive charge. This explanation also rationalizes the fragmentation pattern observed for the dinuclear allyl indium ions, which produce halogen-enriched mononuclear anions (see Supporting Information). An analogous fragmentation behavior has been observed for polynuclear organozincate[37] and organomagnesate[38] ions.

Interestingly, the asymmetric partitioning of the organyl and halogen substituents in the cations and anions also applies to the organoindium species derived from the phosphonium-tagged precursor **3**: For the cation observed, the ratio organyl:Br corresponds to 1:1 whereas ratios of 1:4 and 2:7, respectively, are found for the anions. The two organyl substituents in the cation must obviously bind to the In center, but it cannot be inferred unequivocally whether the two Br atoms also bind to the metal, thus forming the indate structure **6** or, when formulated as Br^- anions, interact electrostatically with the two cationic phosphonium groups.[39] The high number of bromine atoms detected for the organoindium anions can only be accounted for if complexation between the phosphonium groups and Br^- ions is postulated, unless coordination numbers > 4 are assumed for the In centers.[40] The assignment of the mononuclear anion to structure **7** thus seems quite plausible whereas the mode of connection between the two In centers in the dinuclear ion is less clear and structure **8** only represents one possibility. Despite this ambiguity, the predominance of the indate motif for the phosphonium-tagged organoindium species is evident and compares well with the situation for the unsubstituted allyl indium reagents.

In contrast to the manifold of different allyl indium species observed by ESI mass spectrometry, the ^{1}H NMR spectra do not exhibit a comparable richness. Lipshutz and co-workers found a similar situation for the case of lithium organocuprates.[41] They rationalized this seeming contradiction by the lower concentrations sampled in the ESI mass spectrometric studies and by the relatively slow time scale of the NMR experiments, which can result in the averaging of dynamic features.[41] Such an averaging is seen in the temperature-dependent NMR measurements of DMF and THF solutions of formal $In_2R_3X_3$. At elevated temperatures, inter- or intramolecular exchange processes apparently occur too fast to be resolved by NMR spectroscopy. This finding cautions against the direct equation of the number of NMR signal sets with the number of different species present in solution. Nevertheless, distinct parallels between the ^{1}H NMR and ESI mass spectra of solutions of allyl indium reagents in DMF and THF are evident. Araki et al. interpreted the two sets of allylic protons observed for $In_2R_3I_3$ in DMF as indication of In(+3) centers binding one and two allyl groups, respectively.[1] The ESI mass spectra also show the presence of such moieties. After standing overnight, the NMR signal at highest field, which had been assigned to the allylic protons of the $In(+3)R_2$ center of the sesquihalide **1**,[1] was strongly decreased and a similar loss in intensity also occurred for the peaks of diallyl indium(+3) species detected by ESI mass spectrometry, such as $InR_2(DMF)_n^+$ and $InR_2I_2^-$. Thus, both ^{1}H NMR spectroscopy and ESI mass spectrometry apparently point to the higher hydrolysis sensitivity of diallyl indium(+3) compared to monoallyl indium(+3) centers. In aqueous solution, the accelerated hydrolysis should greatly reduce the amount of diallyl indium(+3) species. The detection of only a single set of allylic protons by NMR spectroscopy seems to agree with this assumption and point to the exclusive presence of monoallyl indium(+3) centers. However, the observed chemical shift at δ 1.7 ppm deviates from the values measured for solutions of $In_2R_3X_3$ in DMF and THF at room temperature; for these, the putative In(+3)R centers give rise to signals at δ 1.95−2.18 ppm. The apparent deviation might result from different solvation as the chemical shifts observed in DMF and THF do not perfectly agree either. Moreover, the situation might be complicated by unresolved dynamic processes. Note again that Chan and Yang arrived at different conclusions and proposed the presence of the In(+1) species **2**, as discussed above.[14]

4.3. Implications for Reactivity. Indium(+3) compounds are typical Lewis acids.[31] The Lewis acidity should be further enhanced for monocationic and even more for dicationic species, which were observed for solutions of allyl indium reagents in DMF. At the same time, the negative charge of the likewise detected allyl indate complexes should enhance their nucleophilic character. The high nucleophilic reactivity of related tetraalkyl indate species supports this view.[42] One may thus surmise that the participation of both cationic and anionic species could lead to a double activation in the addition of allyl indium reagents to polar electrophiles, such as aldehydes. By coordination to the oxygen of the carbonyl group, allyl indium cations might further polarize the C−O bond and increase its electrophilic character. At the same time, the extra negative charge in the allyl indate anions could facilitate the nucleophilic addition

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(35) The derived dissociation constant of $K_{diss} \approx 2 \times 10^{-4}$ mol L^{-1} implies that, for $c(In_2R_3I_3) = 1$ mmol L^{-1}, 36% of the allyl indium reagent is dissociated (based on an activity coefficient of $f = 1$). For $c(In_2R_3I_3) = 0.5$ mol L^{-1}, a concentration more typical of synthetic applications, the degree of dissociation still amounts to ∼2%.

(36) Fleckenstein, J. E.; Koszinowski, K. *Chem.—Eur. J.* **2009**, *15*, 12745–12753.

(37) Koszinowski, K.; Böhrer, P. *Organometallics* **2009**, *28*, 100–110.

(38) Khairallah, G. N.; Thum, C.; O'Hair, R. A. J. *Organometallics* **2009**, *28*, 5002–5011.

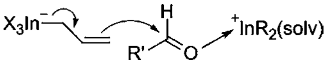
(39) The second possibility is considered less likely, however, because the absence of a peak corresponding to the adduct of dicationic **5** and Br^- in the mass spectrum (Figure 4) indicates that no stable complexes between the phosphonium group and Br^- form under the cation-mode ESI conditions applied.

(40) Although usually coordination numbers ≤ 4 are assumed, the observation of a fivefold coordinated In(+3) center (see ref 13) indicates that higher coordination numbers are accessible and might indeed not be uncommon for In(+3) compounds.

(41) Lipshutz, B. H.; Keith, J.; Buzard, D. J. *Organometallics* **1999**, *18*, 1571–1574.

(42) Araki, S.; Shimizu, T.; Jin, S.-J.; Butsugan, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 824–825.

Scheme 1. Push−Pull Activation Suggested for the Addition of Allyl Indium Reagents to Aldehydes (X = Br, I and R = Allyl)



of the allyl moiety to the carbonyl group, thus giving rise to a push−pull situation (Scheme 1). The realization of such a scenario depends on the availability of allyl indium cations and anions, whose concentration is highest for polar solvents, such as DMF and water. Indeed, these are the preferred solvents for the addition of allyl indium reagents to polar electrophiles. In contrast, the allylation of alkynes, for which an analogous push−pull activation seems much less probable, proceeds best in less polar THF.[5c,d] As the present results show, the degree of heterolytic dissociation can be controlled not only by the choice of the solvent but also by variation of the halogen. The higher tendency toward dissociation observed for $In_2R_3I_3$ in comparison to its bromine congener might suggest the favorable use of the former for the addition to more polar electrophiles.

5. Conclusions

ESI mass spectrometry of solutions of formal $In_2R_3X_3$, R = allyl and X = Br and I, in DMF, THF, and water permitted the detection of allyl indium(+3) cations and anions, such as $InR_2(solv)^+$ and $InRX_3^-$. Analogous organoindium(+3) ions were observed for related organoindium reagents derived from the phosphonium-tagged precursor **3**. Allyl indium chemistry in these solvents thus is apparently dominated by In(+3) species. The formation of undetected transient organoindium(+1) species cannot be excluded, however.

Heterolytic dissociation is most pronounced for DMF, which even stabilizes dicationic InR^{2+} and largely prevents aggregation. In contrast, polynuclear allyl indium ions form more readily in THF. The occurrence of dynamic dissociation equilibria can also be inferred from the temperature-dependent ^1H NMR studies and, in particular, from the conductivity measurements. From these measurements, an approximate dissociation constant of $K_{diss} \approx 2 \times 10^{-4}$ mol L^{-1} is derived for solutions of $In_2R_3I_3$ in DMF at ambient temperature. The tendency of the allyl indium reagents toward heterolytic dissociation might have important consequences for their reactivity. Possibly, the allylation of polar electrophiles, such as aldehydes, is facilitated by the coordination of Lewis acidic allyl indium cations to the oxygen of the carbonyl group, while the negative charge of the allyl indate complexes should activate them for nucleophilic addition.

The present results were obtained by a combination of ESI mass spectrometry, NMR spectroscopy, and conductivity measurements. ESI mass spectrometry does not provide reliable quantitative information, but it gives detailed qualitative insight into the nature of the ions derived from allyl indium reagents. While it is restricted to the detection of ions, this limitation can be largely overcome by the use of charge-tagged precursors. NMR spectroscopy, in turn, promises to afford both qualitative and quantitative information. However, the present case shows that determining the aggregation state and the coordination number of NMR-silent nuclei can be difficult based on this method alone. Moreover, the relatively slow time scale of NMR experiments can lead to the averaging of dynamic features. Finally, conductivity measurements are limited to charged species and provide little qualitative but valuable quantitative insight. Clearly, a combination of these different analytical methods with their complementary strengths and weaknesses is best suited to identify and characterize complex organometallic reagents and intermediates.

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Supporting Information Available: Details of the materials employed, detailed description of the ESI mass spectrometers used, results of preparatory ESI mass spectrometric experiments on solutions of $InCl_3$ and InI, additional ESI mass spectra, tables of observed fragmentation reactions, mass spectra of mass-selected parent and fragment ions, discussion of fragmentation reactions, room-temperature ^1H NMR spectra, and additional temperature dependent ^1H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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