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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/jo3020775 • Publication Date (Web): 30 Nov 2012

[bmim][Br], as a Solvent and Activator for the Ga-mediated Barbier Allylation: Direct Formation of a *N*-Heterocyclic Carbene from Ga-metal

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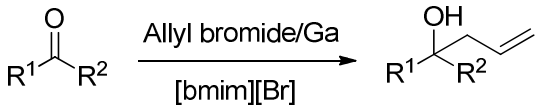


ABSTRACT: The room temperature ionic liquid (RTIL) [bmim][Br] has been found to be an excellent green and inexpensive medium for the Ga-mediated allylation of aromatic and aliphatic aldehydes and ketones. The RTIL activated the metal via formation of a Ga-N-heterocyclic carbene complex that assisted to carry out the reaction at an ambient temperature, and with only 0.5 equiv. of Ga and 1.2 equiv. of allyl bromide with respect to the carbonyl substrates. The present protocol required much shorter time than those reported in literature using other metals and solvents, and proceeded with good yields and excellent selectivity.

INTRODUCTION

Allylation of carbonyl compounds is a key carbon-carbon bond forming reaction in organic synthesis, and various protocols have been developed both in organic and aqueous media.[1] The Barbier type protocols involving *in situ* reaction of allylic halides with different metals are more convenient for this, since the reactive metal-allyl complexes are produced in organic, aqueous and room temperature ionic liquid (RTIL) media. More recently, indium has become the metal of choice for this reaction, and is being used extensively.[2] In contrast, reports

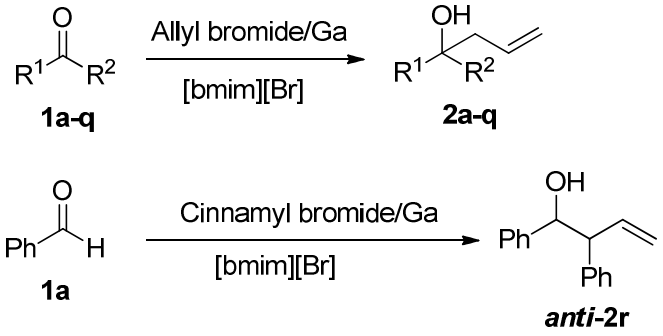
on the gallium-mediated allylation are limited, despite advantages such as low first ionization potential (5.99 eV), non-toxicity, ease of handling (as a liquid at room temperature), and less air and moisture-sensitivity of Ga. The earlier reports with Ga-mediated Barbier type reactions are primarily restricted to reactions in water and/ or organic solvents,[3] but not in RTIL. In addition, use of preformed allyl-Ga dihalides and allyl transfer reaction are also reported.[4a-c]

The key issue for this type of transformations is acceleration of the electron transfer from the metals to the allylic halides. This is generally accomplished by Rieke's activation method,[5a] the metal-graphite method[5b] as well as addition of a catalytic amount of a second metal to the target metal.[5c-h] The problem is severe with Ga requiring its activation by heating when carried out in THF,[3a,g] or sonication[3f] under solvent free conditions even in the presence of additional chemical activators. Currently, the RTILs have emerged as good, eco-friendly alternative reusable solvents for a wide range of organic transformations. These have excellent stability to air, moisture and heat, possess very low vapour pressure, and can dissolve various organic and inorganic materials.[6] Also, they can be prepared easily, and their properties can be tailored by changing the ionic components. In general, only the hydrophobic RTILs are used for the organic reactions including the Barbier-type protocols.[7,8] However, the hydrophilic RTILs such as [bmim][Br] appear better suited for the reaction. It was envisaged that the stronger oxidizing power of [bmim][Br] might facilitate a dipolar interaction between Ga metal and the imidazolium moiety of [bmim][Br], leading to the required metal activation. The standard reduction potential of [bmim][Br] (0.641 V, measured by cyclic voltammetry using a standard Calomel electrode as reference) was also suggestive of such an interaction. Hence we hypothesized that a combination of Ga and [bmim][Br] might trigger the allylation reaction without the need of any metal activation by chemical additives and/ or energy sources

(thermal/ultrasonic). In a preliminary communication, we have reported that the Ga-mediated allylation of (*R*)-cyclohexylideneglyceraldehyde can be achieved in [bmim][Br] within ~4-5 h with excellent diastereoselectivity.[9] The present study was primarily aimed to assess the potential of the allylation protocol with a large number of aliphatic/aromatic aldehydes and ketones and establish the mechanism of the reaction. This has also led to a novel method for activation of metallic Ga using [bmim][Br] as the solvent as well as a reacting partner, and gave some insights on the mechanism of the Ga activation.

RESULTS AND DISCUSSION

Our initial studies (**Scheme 1**, Table 1) carried out with benzaldehyde (**1a**) as the substrate in various media and under different conditions (stoichiometry, presence or absence of additives etc.) revealed [bmim][Br] as the most efficient medium for the Ga-mediated allylation.



Scheme 1.

The reaction carried out in H_2O or THF even in the presence of activators proceeded slowly giving the product **2a** in 63% and 49% yields respectively (Table 1, entries 1-3), while even under sonication in THF, **2a** was obtained in 71-73% yield (Table 1, entries 4,5) in 14-16 h. The reactions in H_2O or THF required a large excess of Ga (5 equiv.) and allyl bromide (3 equiv.) as well as extended reaction time, while reduction of these parameters led to significantly poorer results (data not shown).

Table 1. Effect of solvents and additives on Ga-mediated allylation of **1a**[a]

entry	allyl bromide (equiv.)	metal (equiv.)	solvent	Additive	time (h)	yield (%) of **2a**[b]
1	3.0	5.0	H_2O	LiCl+KI[c]	16	63
2	3.0	5.0	H_2O	--	24	47
3	3.0	5.0	THF	LiCl+KI[c]	24	49
4	3.0	5.0	THF	--	16 [d]	73
5	3.0	5.0	THF	LiCl+KI[c]	14 [d]	71
6	1.2	2.0	[bmim][BF_4]	--	20	64
7	1.2	2.0	[bmim][PF_6]	--	20	62
8	1.2	2.0	[bmim][BF_4]	[bmim]Br[c]	20	64
9	1.2	2.0	[bmim][Br]	--	4	82
10	1.2	1.0	[bmim][Br]	--	4	84
11	1.2	0.5	[bmim][Br]	--	4	84

[a]The reactions were carried out in 2 mmol scale. [b]Yield of isolated product. [c]1.0 equiv. of LiCl+KI or 20 mol% [bmim][Br]. [d]under ultrasonic irradiation.

The commonly used RTILs, [bmim][BF_4], and [bmim][PF_6], even in the presence of [bmim][Br] (20 mol%) as the activator furnished **2a** in 62-64% yields after 20 h (Table 1, entries 6-8). However, allylation of **1a** in [bmim][Br] was very fast (4 h) furnishing **2a** in 82-84% yield, without requiring any metal activator (Table 1, entries 9,10). Further, the reaction in [bmim][Br] could be accomplished with only 1.2 equiv. of the bromide and 1 equiv. of Ga. Subsequently the

allylation of **1a** was achieved using only 0.5 equiv. of Ga to obtain **2a** in a similar yield (Table 1, entry 11). The results are significant, considering that with sub-stoichiometric amounts of Sn, allylation of **1a** in [bmim][BF_4] proceeded with very poor yield.[8] To the best of our knowledge similar attempt with Ga has not been reported so far in any RTIL.

The scope of the sub-stoichiometric protocol (0.5 equiv. Ga) was further explored with several aromatic and aliphatic aldehydes **1b-k** as well as ketones **1l-q** (**Scheme 1**, Table 2). The protocol was equally effective with both aromatic and aliphatic aldehydes. With the aromatic aldehydes, the products **2b-h** were obtained in good (72-87%, Table 2, entries 1-7) yields, irrespective of the presence of any electron withdrawing or donating group, or a heteroatom in the aromatic ring. However, no reaction was observed with 2-hydroxy-4-ethoxybenzaldehyde, containing a free phenolic group (data not shown). This is consistent with a previous report where alkyl gallium compounds were reported to react preferably with the acidic phenolic moiety.[10] Likewise, the aliphatic aldehydes also furnished the corresponding allylated products **2i-2k** in high yields (Table 2, entries 8-10). The lower yield of **2i** might be due to its volatility. The protocol was also useful with aromatic or aliphatic ketones **1l-q** furnishing the products **2l-q** in 67-81% yields (Table 2, entries 11-16) without any significant role of the steric and/ or electronic factors. Earlier, the Zn, Bi, and In-mediated allylation of acetophenone (**1l**) under a solvent-free condition was largely unsuccessful,[8a] although the In-mediated allylation of **1l** and **1q** was reported in water.[8b] Earlier, the Ga-mediated allylation of ketones could be achieved only after metal activation.[3a,f] Thus, our protocol is more versatile and could be used even for the bulky and electronically demanding substrates such as **1m-1p**.

Table 2. Ga mediated allylation of aldehydes and ketones in [bmim][Br][a]

Entry	Substrate	R_1	R_2	Product	Time (h)	Yield (%)[b]
1	**1b**	3-OMe-C_6H_4	H	**2b**	6	84
2	**1c**	4-$(CH_3)_2CH$-C_6H_4	H	**2c**	5	87
3	**1d**	4-C_6H_5- C_6H_4	H	**2d**	5	83
4	**1e**	4-Br-C_6H_4	H	**2e**	6	77
5	**1f**	C_6F_5	H	**2f**	5	83
6	**1g**	3-Indolyl	H	**2g**	12	72
7	**1h**	C_6H_5CH=CH	H	**2h**	8	79
8	**1i**	$(CH_3)_2CH$	H	**2i**	6	67
9	**1j**	$CH_3(CH_2)_5$	H	**2j**	5	84
10	**1k**	$CH_3(CH_2)_8$	H	**2k**	5	95
11	**1l**	C_6H_5	CH_3	**2l**	10	71
12	**1m**	C_6H_5	C_6H_5	**2m**	16	67
13	**1n**	C_6H_5CO	C_6H_5	**2n**	8	77
14	**1o**	C_6H_5CH=CH	Ph	**2o**	8	81
15	**1p**	Cyclohexanone		**2p**	7	78
16	**1q**	2-Methylcyclohexanone		**2q**	7	77[c]
17	**1a**	C_6H_5	H	**2r**	7	65[d]

[a]The reactions were carried out in 2 mmol scale. [b]Yields of the isolated products. [c]Exclusively *trans*-product (H and OH *trans*) was obtained. [d]The reaction was carried out with *E*-$PhCH=CHCH_2Br$ to get *anti*-**2r** as the sole product.

Chemo- and stereoselective allylation of multifunctional compounds is one of the most fundamental goals in constructing complex molecules. Our new protocol of allylation proceeded with complete chemoselectivity with the conjugated carbonyls, **1h** and **1o**, furnishing the respective 1,2-addition products **2h** and **2o** only, while only the mono allylated product **2n** was obtained with the diketone **1n**. Interestingly, allylation of 2-methylcyclohexanone (**1q**) under the above conditions furnished *trans*-**2q** exclusively in excellent yield (Table 2, entry 16). Likewise, reaction of **1a** with cinnamyl bromide afforded the γ-addition product, *anti*-**2r** only (Table 2, entry 17). The products obtained from the allylation in [bmim][Br] could be conveniently isolated by extraction with Et_2O followed by concentration. The reactions proceeded smoothly without any side reactions such as reduction and coupling, and furnished the products devoid of side products and/ or starting materials. Only with the ketone **1m**, the reaction was incomplete allowing the recovery of 18% of the substrate. In general, the reaction yields were more than those reported in other solvents.

The above results clearly established [bmim][Br] as the best RTIL among those chosen for the Ga-mediated allylation. The reactions were much faster in [bmim][Br] even without any metal activator, and could be executed with only a sub-stoicheometric quantity of Ga, providing economic and environmental advantages. In contrast, excess reagents and toxic metal activators such as acid or fluoride are required in H_2O. Finally, unlike in H_2O or THF, the reaction in [bmim][Br] takes place at an ambient temperature, which is conducive while using more volatile reagents such as allyl bromide.

Mechanistic studies: For the mechanistic insight of the activating role of [bmim][Br], we probed the nature of the organometallic species responsible for the reaction. For this, the course of the reaction between Ga (1 mmol) and allyl bromide (1 mmol) in [bmim][Br] (2 mL) was

periodically followed up to 8 h, by ^{1}H NMR spectra. The intensity of the NMR peak due to the CH_2-Ga protons in the allyl-gallium species was quantified by comparing with that of the CH_2Br signal of allyl bromide.

The ^{1}H NMR spectra of the reaction mixtures obtained in [bmim][Br] showed a new doublet at δ 1.63 (J = 6.4 Hz) with simultaneous reduction of the signal at δ 3.9. In addition, new olefinic multiplets at δ 4.59 at the expense of that at δ 4.78 (of allyl bromide) also emerged, and these resonances together accounted for two protons over the entire period of studies. The ^{1}H NMR doublets for the CH_2-Ga protons suggested[5h] $(CH_2CH=CH_2)_2GaBr$ (**I**) as the active allyl-Ga species, which was confirmed by its isolation, followed by spectral (^{1}H and ^{13}C NMR), and chemical analyses. An analogous compound, $(CH_2CH=CH_2)_2GaCl$, synthesized following a reported procedure,[11] also provided a similar ^{1}H NMR spectrum. The sesquibromide, $(CH_2CH=CH_2)_3GaBr_3$, produced[5h] in THF, was not formed[12] in [bmim][Br]. The integration of the NMR signals for **I** reached a maximum (~48%) in ~ 3.5 h, and remained steady even up to 8 h. Addition of **1a** to the reaction mixture led to complete depletion of the signals, confirming **I** as the active organometallic species. The composition of **I** as $(CH_2CH=CH_2)_2GaBr$ also explains the need of only 0.5 equiv. of Ga for the reaction.

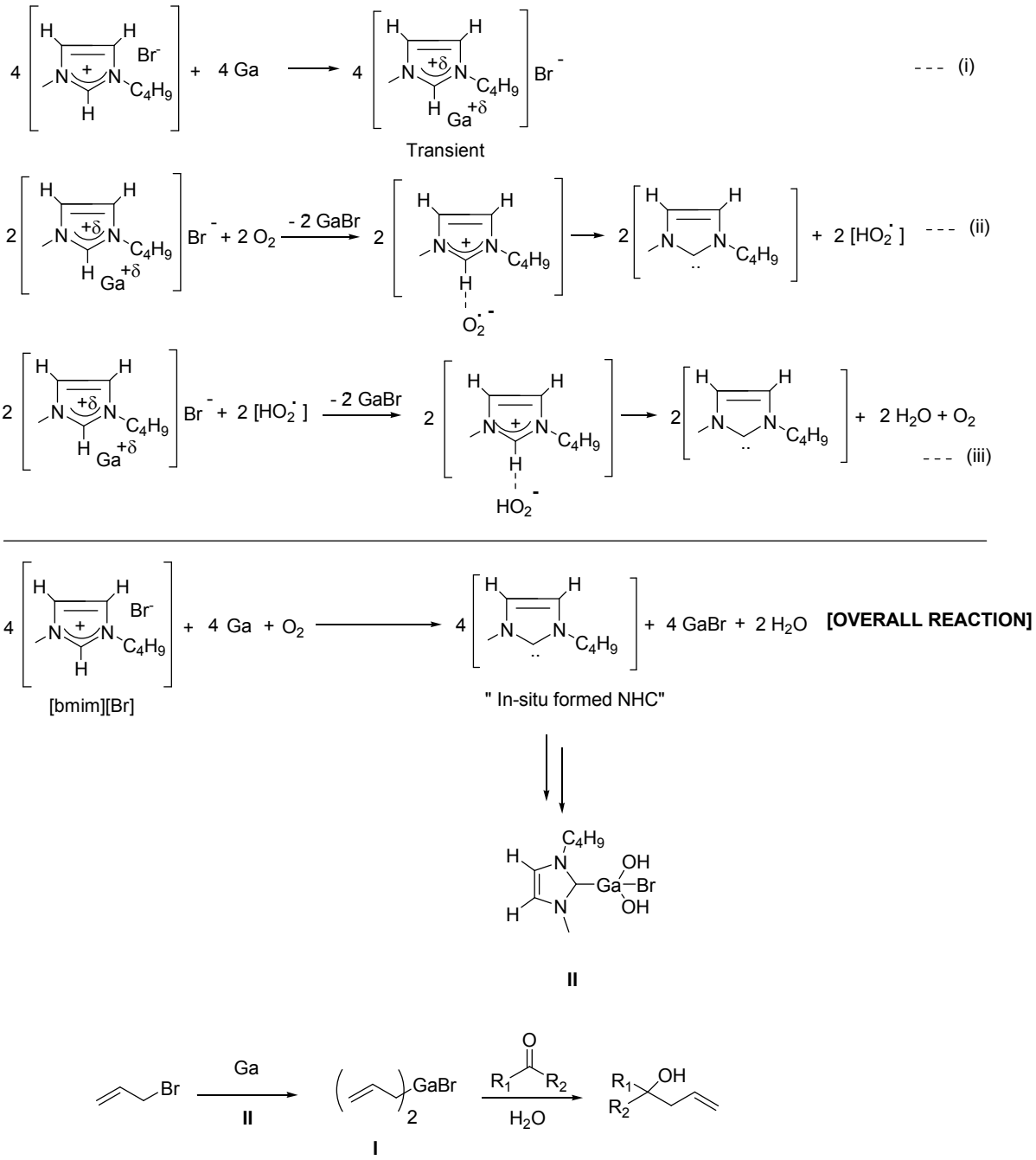
With regard to the activation of Ga metal, we envisaged a dipole induced dipole interaction with [bmim][Br]. After incubating for 10 min only, the ^{1}H NMR spectrum of the reaction mixture of [bmim][Br] (2 mL) and Ga (1.0 mmol) showed upfield shifts of the imidazole H-2 (3.8 Hz), and H-4 and H-5 (each 3.4 Hz) protons. Similar trends were also seen for the imidazole carbons, where an upfield shift of 10 Hz for C-2 and 6 Hz for both C-4 and C-5 were noticed. The shifts were more prominent at 30 min. These results suggested partial polarization of the Ga metal electrons towards the imidazolium core of [bmim][Br] which would

activate the Ga-metal. The shift followed the expected trend, considering maximum positive charge density at C-2 of the imidazole ring. The NMR shifts of similar magnitudes are generally attributed to the charge transfer phenomenon.[13] Possibly the combination of Ga and [bmim][Br] initially forms ion pairs or more complex ion-aggregates with an activated Ga. The results are consistent with the respective redox potentials of [bmim][Br] and Ga-metal. The metal-catalyzed Barbier reaction is proposed to be mediated through radicals on metal surface as well as metal surface activation especially in aqueous acidic media.[14] Earlier surface reaction with In metal in H_2O has been reported.[15] The occurrence of a charge transfer in RTILs is not unprecedented.[16a,b] Especially the imidazolium-based ILs have remarkable ability to promote electron transfer reactions.[16c] However, the direct involvement of a metal in this process is not reported so far.

On continued stirring for 1-1.5 h, the mixture of [bmim][Br] and Ga eventually produced a gray solid that can be purified by vacuum sublimation (bath temperature 40-45 ^{o}C/0.1 torr). Its IR spectrum (thin film) displayed a strong –O-H stretching band (3545 cm^{-1}), while a ^{1}H NMR singlet at δ 7.21 (2H) and the ^{13}C NMR resonances at δ 123.3 and δ 121.7 (olefin) along with δ 175.9 (carbene) revealed the presence of a *N*-heterocyclic carbene (NHC) moiety. The Raman spectrum confirmed the Ga-C (697 cm^{-1}) and Ga-O (330 and 662 cm^{-1}) bonds, while excluding any Ga-Ga and Ga-O-Ga bonds.[17a-c] The electron impact mass spectrum showed a [M^{+}-57] ion peak at m/z 262 (17%), a [M^{+}-Br] ion peak at m/z 240 (11%), and a major fragmentation peak at m/z 184 (18%) ($GaBr(OH)_2$) with appropriate isotopic patterns. In addition, the fragmentation peak at m/z 138 (19%) accounted for the NHC moiety. The studies on the thermal stability of the solid by differential scanning calorimetry (DSC) showed a gradual mass loss starting at ~120 ^{o}C accompanied by a large endothermic thermal transition at ~162 ^{o}C producing Ga metal. The broad DSC profile indicated the powder as a *N*-heterocyclic carbene (NHC)-Ga complex. Based

on these, the intermediate was assigned the structure [NHC-GaBr$(OH)_2$] (**II**) (**Scheme 2**). The NMR data was also clean without showing presence of any isomers, consistent with the proposed monocarbene structure of the complex. The XRD analysis of **II** was inconclusive except for showing its amorphous nature. Despite our intense efforts, we failed to isolate it in crystalline form. However, the spectral, elemental and thermal data of the solid established its proposed structure unambiguously.

The probable reaction sequence involved in the process of Ga-activation and the allylation reaction is shown in **Scheme 2**. Possibly, an electron transfer from Ga to O_2, present in the RTIL[18] occurs and results in the formation of Ga^+ and $O_2^{-\cdot}$, which is stabilized by the C2-hydrogen of [bmim].[19] The electron transfer is "facilitated" by an interaction between Ga and [bmim]. Subsequent transfer of the C2-proton from [bmim$^\cdot$] to [$O_2^{-\cdot}$] would then give the [bmim]-NHC and $HO_2^\cdot$. Another such cycle with [$HO_2^\cdot$] can also be envisaged to produce more [bmim]-NHC and H_2O. In view of its good σ-donating ability, the generated NHC would stabilize the Ga (I) species. Further, the poor stability of the sterically less hindered cyclic carbene and Ga(I) would eventually furnish the species **II** by oxidation. This type of reaction is well established in M-NHC chemistry, but the mechanism remains unclear.[20] To support the hypothesis, we incubated Ga in deaerated [bmim][Br], where the formation of **II** was not observed. As expected, purging the same reaction mixture with O_2 produced the same Ga-intermediate **II**, which is consistent with the proposed mechanism.



Scheme 2

Several authors have suggested a link for the fast chemical conversion of imidazolium ion to the NHC on the surface of a nanoparticle.[21] Our hypothesis of direct adduct formation of a NHC with Ga metal is consistent with this. This also corroborates with the results of theoretical DFT calculation wherein a similar oxidative addition of the imidazolium salts to Pt(0) has been

shown to be exothermic.[22] In this study, we have also carried out the experiments with [bmim][Br] (2 mL) and incremental amounts of Ga (up to 5.0 mmol). However, the gray solid **II** was obtained in 3-4% yields only. This suggested that compound **II** makes a coating on the Ga-metal, preventing its further reaction with [bmim][Br]. Addition of allyl bromide removes the coating of **II** making the activated Ga-metal available to continue the reaction.

Since their description by Wanzlick[23] and Arduengo,[24] stable NHCs have been a significant area of study and several crystalline and well-characterized NHC complexes with main group and especially transition metals have been synthesized.[25] The NHCs can stabilize thermally labile or low oxidation state metal fragments, and the complexes can be used for various organic transformations. The use of NHCs as good σ-donor molecules to stabilize trivalent group 13 compounds is well established.[25b, 26] Over the past few years, the chemistry of metastable gallium complexes has been an active research area in organometallic chemistry. A large number of NHC-complexes with metal (Al, In, and Ga) hydrides and halides have since been synthesized.[27] However, formation of Ga-NHC directly from the metal is novel and opens various new possibilities in organic synthesis as well as materials development. Sterically non-hindered NHCs are often sensitive to air and moisture, making their isolation and use difficult.[24a,28] However, in our case its formation was achieved in a hygroscopic RTIL, and also required O_2.

Earlier, the Pd-carbene complexes have been shown to catalyze the Heck and related C–C bond forming reactions.[29] We have also isolated the Ga-carbene complex **II** and reacted with allyl bromide to synthesize the active allylating Ga species **I**. The exact mechanism of the catalysis is at present, far from clear. It may in fact turn out to follow a much more complex pathway. The Ga-NHC complex might be the precursor, which would generate a zero-valent Ga-

NHC species as the likely active catalyst, as suggested for the Pd-catalyzed Heck reaction in [bmim][Br].

CONCLUSION

Overall, a novel method for Ga metal mediated allylation of carbonyls in [bmim][Br] has been accomplished. To the best of our knowledge, this is the first example of a Ga-mediated allylation of carbonyls in any RTIL. The imidazolium cation is usually considered as a simple inert component of a solvent system, and its possible involvement in a catalytic cycle, especially with a free a metal is rarely an issue. We have found that [bmim][Br] reacts with Ga to give the Ga-NHC complex (**II**). This also provides a method of base-free generation of NHCs through aerobic oxidation of a free metal, although a similar protocol has been reported with transition metal complexes.[15c] This is very interesting since strong bases can cause various side reactions. We expect the present results to open up many applications towards synthesizing stable NHCs in RTILs and applying those as versatile heterogeneous catalysts in many organic reactions.

EXPERIMENTAL SECTION

Typical procedure for the Ga-mediated allylation reaction in [bmim][Br]. A mixture of Ga and allyl bromide (quantities specified in Tables) in [bmim][Br] (2 mL/mmol) was stirred at room temperature for 1 h, followed by addition of the aldehyde. The reaction mixture was stirred at room temperature for the time specified in the Tables 1 and 2. After completion of the reaction (*cf*. TLC), the mixture was extracted with Et_2O (3 × 10 mL), the ether extract evaporated in vacuo and the residue purified by column chromatography (silica gel, hexane/EtOAc) to give the respective products. All the products were fully characterized by IR, ^1H and ^{13}C NMR spectra as well as elemental analysis. The Ga-mediated allylation was also carried out in H_2O and THF under the conditions specified in Table 1.

NMR experiments. A mixture of the Ga (1.0 mmol) and allyl bromide (1.0 mmol) in [bmim][Br] (2 mL) was magnetically stirred at room temperature. Aliquots (35 μL) of reaction mixture were taken at different time intervals, and the ^{1}H NMR spectra were recorded in $CDCl_3$ or D_2O.

1-Phenyl-but-3-en-1-ol 2a.[8] yield: 0.249 g (84%); colourless liquid; IR (flim): 3468, 922 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.92 (broad s, 1H), 2.45-2.56 (m, 2H), 4.74 (t, *J* = 6.8 Hz, 1H), 5.10-5.25 (m, 2H), 5.65-5.93 (m, 1H), 7.26-7.40 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 43.8, 73.2, 118.4, 125.8, 127.5, 128.4, 134.4, 143.8.

1-(3-Methoxyphenyl)-but-3-en-1-ol 2b.[30a] yield: 0.296 g (84%); colourless liquid; IR (flim): 3418, 916 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.18 (broad s, 1H), 2.49-2.53 (m, 2H), 3.80 (s, 3H), 4.69 (t, *J* = 6.2 Hz, 1H), 5.10-5.19 (m, 2H), 5.70-5.91 (m, 1H), 6.79-6.91 (m, 3H), 7.21-7.29 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 43.7, 55.2, 73.2, 111.3, 112.9, 118.1, 118.3, 129.4, 134.4, 145.6, 159.7.

1-(4-Isopropylphenyl)-but-3-en-1-ol 2c.[30b] yield: 0.331 g (87%); colourless liquid; IR (flim): 3388, 915 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.26 (d, *J* = 6.8 Hz, 6H), 2.08 (broad s, 1H), 2.51 (t, *J* = 6.6 Hz, 2H), 2.88-2.94 (m, 1H), 4.70 (t, *J* = 6.6 Hz, 1H), 5.12-5.21 (m, 2H), 5.76-5.84 (m, 1H), 7.26 (q, *J* = 8.0 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 24.0, 33.8, 43.7, 73.2, 112.0, 118.1, 125.8, 126.4, 134.7, 141.3, 148.2.

1-(4-Phenylphenyl)-but-3-en-1-ol 2d.[30c] yield: 0.372 g (83%); colourless liquid; IR (flim): 3583, 911 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.18 (broad s, 1H), 2.53-2.59 (m, 2H), 4.78 (t, *J* = 6.6 Hz, 1H), 5.15-5.24 (m, 2H), 5.75-5.95 (m, 1H), 7.24-7.41 (m, 5H), 7.45-7.61 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 43.8, 73.0, 118.5, 126.3, 127.0, 127.1, 127.3, 128.8, 134.4, 140.4, 140.8, 142.9.

1-(4-Bromophenyl)-but-3-en-1-ol 2e.[30d] yield: 0.350 g (77%); colourless liquid; IR (flim): 3389, 910 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 2.14 (broad s, 1H), 2.34-2.53 (m, 2H), 4.67 (t, *J* = 6.6 Hz, 1H), 5.10-5.17 (m, 2H), 5.65-5.86 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 43.8, 72.5, 118.8, 121.2, 127.5, 131.4, 133.9, 142.8.

1-Pentafluorophenyl-but-3-en-1-ol 2f.[30e] yield: 0.395 g (83%); colourless liquid; IR (flim): 3408, 926 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 2.50-2.82 (m, 3H), 5.05-5.17 (m, 3H), 5.62-5.79 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 41.1, 65.6, 116.3, 119.4, 132.4, 137.5, 140.5, 144.7.

1-(3-Indolyl)-but-3-en-1-ol 2g. yield: 0.269 g (72%); colourless liquid, IR (flim): 3458, 910 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 2.08 (broad s, 1H), 2.36-2.49 (m, 1H), 2.81-2.97 (m, 1H), 4.05-4.15 (m, 1H), 5.04-5.15 (m, 2H), 5.82-5.96 (m, 1H), 6.95-7.06 (m, 1H), 7.08-7.16 (m, 2H), 7.36-7.40 (m, 1H), 7.57-7.63 (m, 1H), 7.89-7.94 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 41.3, 60.3, 110.9, 114.5, 116.2, 118.8, 119.0, 121.0, 121.8, 138.7. Anal. Calcd. for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N 7.48%. Found: C, 76.81; H, 6.92; N, 7.34%.

(*E*)-1-Phenylhexa-1,5-dien-3-ol 2h.[3g] yield: 0.275 g (79%); colourless liquid; IR (flim): 3425, 916 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.84 (broad s, 1H), 2.33-2.42 (m, 2H), 4.31-4.41 (m, 1H), 5.13-5.22 (m, 2H), 5.75-5.93 (m, 1H), 6.18-6.29 (dd, *J* = 6.2 Hz and 16.0 Hz, 1H), 6.61 (d, *J* = 16.0 Hz, 1H), 7.23-7.40 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 41.8, 71.6, 118.3, 126.3, 127.5, 128.4, 130.2, 131.4, 133.9, 136.5.

2-Methylhex-5-en-3-ol 2i.[30f] yield: 0.153 g (67%); colourless liquid; IR (flim): 3419, 908 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.90 (d, *J* = 5.4 Hz, 6H), 1.61-1.70 (m, 1H), 2.01-2.16 (m, 2H), 2.22 (broad s, 1H), 3.31-3.38 (m, 1H), 5.06-5.14 (m, 2H), 5.71-5.92 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 17.5, 18.7, 33.0, 38.8, 75.3, 117.7, 135.4.

1-Decen-4-ol 2j.[30g] yield: 0.262 g (84%); colourless liquid; IR (flim): 3408, 912 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.85 (t, *J* = 6.4 Hz, 3H), 1.22-1.60 (m, 10H), 1.92 (broad s, 1H), 2.02-2.29 (m, 2H), 3.52-3.65 (m, 1H), 4.98-5.17 (m, 2H), 5.65-5.93 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.0, 22.6, 25.6, 29.3, 31.8, 36.8, 41.9, 70.6, 117.8, 134.9.

1-Tridecen-4-ol 2k.[30h] yield: 0.376 g (95%); colourless liquid; IR (flim): 3462, 908 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 0.91 (t, *J* = 6.4 Hz, 3H), 1.29-1.47 (m, 16H), 1.75 (broad s, 1H), 2.08-2.37 (m, 2H), 3.59-3.68 (m, 1H), 5.12-5.18 (m, 2H), 5.76-5.93 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.0, 22.6, 25.6, 29.3, 29.6, 31.8, 36.7, 41.8, 70.6, 117.7, 134.9.

2-Phenylpent-4-en-2-ol 2l.[3a] yield: 0.230 g (71%); colourless liquid, IR (flim): 3499, 925 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.54 (s, 3H), 1.98 (broad s, 1H), 2.44-2.74 (m, 2H), 5.08-5.18 (m, 2H), 5.56-5.64 (m, 1H), 7.23-7.46 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 29.8, 48.4, 73.6, 119.4, 124.7, 126.5, 128.1, 128.5, 133.6, 147.6.

1,1-Diphenylbut-3-en-1-ol 2m.[30i] yield: 0.300 g (67%); colourless liquid, IR (flim): 3434, 929 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 2.04 (broad s, 1H), 3.08 (d, *J* = 8 Hz, 2H), 5.15-5.28 (m, 2H), 5.56-5.73 (m, 1H), 7.21-7.35 (m, 7H), 7.43-7.47 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 46.5, 77.0, 120.3, 125.8, 126.7, 128.0, 133.2, 146.3.

2-Hydroxy-1,2-diphenylpent-4-en-1-one 2n.[30j] yield: 0.388 g (77%); colourless liquid, IR (flim): 3478, 917 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 2.16 (broad s, 1H), 2.91-3.19 (m, 2H), 4.96-5.13 (m, 2H), 5.63-5.80 (m, 1H), 7.24-7.52 (m, 8H), 7.71-7.75 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 43.7, 81.2, 111.9, 120.2, 125.4, 127.9, 128.7, 129.9, 132.1, 132.6, 134.3, 141.5, 200.6.

(*E*)-1,3-Diphenylhexa-1,5-dien-3-ol 2o. yield: 0.405 g (81%); colourless liquid; IR (flim): 3431, 911 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 2.17 (broad s, 1H), 2.82 (d, *J* = 6.8 Hz, 2H),

5.18-5.27 (m, 2H), 5.64-5.85 (m, 1H), 6.50-6.72 (m, 2H),7.23-7.42 (m, 8H),7.52-7.56 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 47.1, 75.7, 120.1, 125.0, 125.5, 126.4, 127.0, 127.3, 127.4, 127.8, 128.2, 128.3, 132.5, 135.2, 137.4, 145.3. Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25%. Found: C, 86.60; H, 7.01%.

1-Allylcyclohexanol 2p.[30k] yield: 0.218 g (78%); colourless liquid; IR (flim): 3451, 913 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.23 (broad s, 1H), 1.45-1.61 (m, 10H), 2.20 (d, *J* = 7.4 Hz, 2H), 5.04-5.14 (m, 2H), 5.77-5.98 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.5, 25.5, 30.3, 36.3, 37.9, 45.2, 72.5, 117.6, 134.0.

1-Allyl-2-methylcyclohexanol 2q.[30l] yield: 0.237 g (77%); colourless liquid; IR (flim): 3484, 908 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.79 (d, *J* = 2.4 Hz, 3H), 1.16-1.50 (m, 9H), 1.70 (broad s, 1H), 2.14 (d, *J* = 7.4 Hz, 2H), 4.93-4.99 (m, 2H), 5.65-5.82 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.6, 21.4, 25.4, 30.2, 35.8, 37.8, 45.1, 72.3, 117.5, 133.9.

1,2-Diphenylbut-3-en-1-ol 2r.[30m] yield: 0.291 g (65%); colourless liquid; IR (flim): 3429, 910 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.95 (broad s, 1H), 3.55 (t, *J* = 8.0 Hz, 1H), 4.84 (d, *J* = 7.8 Hz, 1H), 5.18-5.39 (m, 2H), 6.01-6.35 (m, 1H), 7.17-7.45 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 58.9, 77.0, 118.2, 126.1, 126.4, 126.5, 127.2, 127.5, 127.7, 128.2, 128.4, 137.7, 140.4, 141.7.

Diallylgallium bromide I. yield: 0.093 g (40%); colourless liquid; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.69 (d, *J* = 6.4 Hz, 4H), 4.91-5.06 (m, 4H), 5.71-5.91 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 33.1, 114.6, 138.1. EIMS: *m*/*z* (%) 152 [{M − Br}$^+$, 11].

***N*-Butyl-*N*-methyl-imidazolinylidinegalliumdihydroxybromide II**. yield: 0.013 g (4%); grey amorphous solid; mp: >250 ^{o}C; IR (KBr): 3545, 3466, 3229, 2853, 1616, 1187, 924, 637, 538, 479 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.99 (t, *J* = 7.4 Hz, 3H), 1.21-1.28 (m, 2H), 1.74 (broad

s, 2H), 1.87-1.92 (m, 2H), 4.03 (s, 3H), 4.24 (t, J = 7.4 Hz, 2H), 7.21 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 12.9, 18.9, 31.6, 36.2, 49.3, 121.7, 123.3, 175.9. EIMS: m/z (%) 264 [{M − C_4H_9}$^+$, 17], 241 [{M − Br}$^+$, 11], 184 [{$Ga(OH)_2Br$}$^+$, 18], 138 [{$C_8H_{14}N_2$}$^+$, 19]; Raman: 697, 330, 662, 980, 1079, 1332, 1374 cm^{-1}. Anal. Calcd. for $C_8H_{16}BrGaN_2O_2$: C, 29.85; H, 5.01; N, 8.70%. Found: C, 29.64; H, 5.18; N, 8.61%.

Supporting Information: ^{1}H and ^{13}C NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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