The Bis(allyl)bismuth Cation: A Reagent for Direct Allyl Transfer by Lewis Acid Activation and Controlled Radical Polymerization**

Crispin Lichtenberg, Fangfang Pan, Thomas P. Spaniol, Ulli Englert, and Jun Okuda*

Cationic organometallic compounds of Group 3 (including the lanthanoids), 4, or 13 elements show increased Lewis acidity and electrophilicity compared to their neutral parent compounds. They serve as efficient polymerization catalysts and as unique organometallic reagents for stoichiometric transformations.^[1-3] The Lewis acidity of neutral bismuth(III) compounds has been recognized and exploited in bismuthcatalyzed (co)polymerizations and organic transformations.^[4] However, the number of isolated and characterized cationic organobismuth(III) compounds is still limited, and detailed investigations concerning their reactivity have not been reported to date.^[5,6] Only two systems with chelating di(aryl) ligands have been applied as Lewis acid-base catalysts in organic transformations.^[6] Herein, we present the isolation and characterization of the bis(allyl)bismuth cation and its application as an efficient allyl transfer reagent and as initiator for the controlled radical polymerization of styrene.

Tris(allyl)bismuth (1) was first synthesized about 50 years ago and has later been used as a bismuth source for metalorganic chemical vapor deposition.^[7] The bonding mode of the allyl ligands has not been investigated to date. Compound 1 was synthesized according to a simplified literature procedure. The yellow liquid is temperature, light, air, and vacuum sensitive and slowly decomposes (over months) when stored under argon at -30 °C in the dark. The main decomposition pathway is radical coupling of allyl ligands with concomitant formation of a bismuth mirror.^[8] Attempts to crystallize 1 by cooling a sample in a sealed capillary on the diffractometer remained unsuccessful. Tris (methallyl)bismuth (2), which has been elusive to date, was isolated as a vellow liquid (m.p. = 176 K) in low yield (see the Supporting Information), and an in situ crystallization experiment afforded its solid-state structure (Scheme 1).^[9,37] The methallyl ligands coordinate to the metal center in an η^1 fashion and show localized single and double C-C bonds. The average Bi-C bond lengths (2.32(2) Å) are similar to the corresponding value reported for the only other fully characterized bismuth compound containing an allyl ligand, $[Bi(\eta^1-C_3H_3)\{2,6-(Me_2NCH_2)_2C_6H_3\}_2]$ (Bi-Callyl

[*] C. Lichtenberg, F. Pan, Dr. T. P. Spaniol, Prof. Dr. U. Englert, Prof. Dr. J. Okuda Institut für Anorganische Chemie, RWTH Aachen Landoltweg 1, 52056 Aachen (Germany) E-mail: jun.okuda@ac.rwth-aachen.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201206782.



Scheme 1. Synthesis of bis (allyl) bismuth cation **3**; $[A] = [B(C_6H_3Cl_2)_4]$. Molecular structure of **2** and cationic part of **3**. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. For **3**, only one of the two crystallographically independent cations is shown and discussed, as the structural parameters are highly similar. Selected bond lengths [Å] and angles [°]: **2**: Bi1–C1 2.324(16), Bi1–C5 2.310(17), Bi1–C9 2.309(16), C1–C2 1.44(2), C2–C3 1.32(2), C2–C4 1.51(3); C1-Bi1-C5 93.9(9). **3**: Bi1–C1 2.273(10), Bi1–C4 2.242(11), Bi1–O1 2.404(7), Bi1–O2 2.418(7), C1–C2 1.489(13), C2–C3 1.325(14); C1-Bi1-C4 92.2(4), C1-Bi1-O1 91.5(3), O1-Bi1-O2 171.9(3).

2.331(2) Å).^[5g] The coordination geometry around the bismuth center in **2** is trigonal pyramidal with small C-Bi-C angles of about 94°.^[10] Compound **2** is a typical molecular crystal without short directional interactions between neighboring molecules. Shortest intermolecular contacts are associated with Bi···H(methyl) distances of ca. 3.2 Å and owing to stacking along the crystallographic *b* axis (see Supporting Information). In comparison, intermolecular Bi···C interactions have been revealed for $[Bi(C_5H_5)_3]$ in the solid state.^[11] In solution, the allyl ligands of **1** and **2** show η^1 bonding modes without fluxionality at ambient temperature in contrast to $[Bi(C_5H_5)_3]$ in which the η^1 -bonded cyclopentadienyl ligands show fluxional behavior.^[11]

Organobismuth cations have so far been prepared by salt elimination reactions.^[5,12] However, this approach was not feasible using [Bi(C₃H₅)₂X] (X = halide) owing to their low stability (see the Supporting Information). A protonolysis reaction of **1** with the sufficiently strong Brønsted acid [PhNMe₂H][B(C₆H₃Cl₂)₄] allowed the isolation of the bis-(allyl)bismuth cation **3** as a yellow solid (Scheme 1). Compound **3** can be stored over months under inert gas atmosphere in the dark without decomposition. The solidstate structure of **3** was investigated by single-crystal X-ray analysis. Compound **3** crystallizes in the orthorhombic space group *Pbca* with Z = 16 (Scheme 1).^[37] The bismuth center adopts a bisphenoidal coordination geometry with the THF ligands occupying the axial positions. The allyl ligands in **3**

^[**] Generous financial support by Fonds der Chemischen Industrie (Kekulé Scholarship to C.L.) is gratefully acknowledged. The authors thank Dr. Klaus Beckerle for helpful discussions.

coordinate to the metal center in an η^1 fashion. Thus, the coordination mode of allyl ligands in allyl bismuth compounds is retained upon cationization (σ vs. π bonding), as observed for allyl complexes of other Lewis acidic metals (La,^[13a] Nd,^[13a] Zn,^[13b] Al,^[3c] Ga^[3e]).^[14] Steric factors can be ruled out as a reason for the lack of π -coordination, as bismuth cations with coordination numbers of up to eight have been reported.^[15] The Bi-C bond lengths are significantly shorter compared to 2, and this shortening is ascribed to the cationic charge in 3. Although similarities in the coordination chemistry of bismuth and the lighter lanthanides can be expected on the basis of similar charge-to-radius ratio, the higher electronegativity and the stereochemically active lone pair of bismuth can cause marked differences between lanthanide and bismuth compounds.^[16] In the case of allyl complexes, the coordination chemistry of 3 clearly differs from that of the bis(allyl)lanthanide cations $[Ln(\eta^3-C_3H_5)_2 (thf)_4$ ⁺ (Ln = La, Nd; π coordination of $(C_3H_5)^-$, C.N.(Ln) = 8).^[13a] In contrast, close structural similarities of **3** with the related Group 13 cations $[E(\eta^1-C_3H_5)_2(thf)_3]^+$ become apparent when taking into account the equal contribution of lone pairs and donor ligands to the steric number of a molecule $(E = Al, Ga; \sigma \text{ coordination of } (C_3H_5)^-, C.N.(E) = 5).^{[3c,e]}$

Compound 3 is soluble in THF, dichloromethane, and pyridine, but insoluble in diethyl ether and hydrocarbons. It shows an increased stability in solution compared to 1. Decomposition also occurs via radical pathways, as evident from the formation of 1,5-hexadiene as a degradation product.^[17] In the ¹H NMR spectrum of **3** in $[D_8]$ THF at 23 °C, the allyl ligands cause an A₄X pattern, indicating a fluxional behavior (Figure 1, top). Cooling this sample to -95°C showed an A2MNX pattern for the allyl ligands, revealing the η^1 bonding mode as the ground state of allyl coordination for compound 3 in solution (Figure 1, bottom). The allyl exchange was investigated by means of lineshape analysis (see the Supporting Information). Values of $\Delta G^{\pm,298\,\text{K}} = (40.9 \pm$ 5.0) kJ mol⁻¹, $\Delta H^{\pm} = (42.4 \pm 2.2)$ kJ mol⁻¹, $\Delta S^{\pm} = (5.0 \pm 10^{-1})$ 9.3) J mol⁻¹ K⁻¹ and an allyl exchange rate of $k = 4.3 \times$ 10⁵ Hz at 298 K were determined. The allvl exchange in THF of a few other allvl metal compounds, namely Mg- $(C_{3}H_{5})Hal]$, $[Ca(C_{3}H_{5})([18]crown-6)][Zn(C_{3}H_{5})_{3}]$, and [Zn-1] $(C_3H_5)_2$], has been investigated by lineshape analysis (Hal = Cl, Br) revealing exchange rates at 298 K of 1.0×10^4 Hz to 2.8×10^7 Hz.^[18] Notably, the ΔS^{\pm} values of (-16 to



Figure 1. Excerpts of ¹H NMR spectra of **3** in $[D_8]$ THF at 23 °C (top) and -95 °C (bottom); *: resonances that are due to THF ligands and $[D_8]$ THF.

-43) J mol⁻¹K⁻¹ determined for these compounds were significantly smaller than that of **3**. For [Zn(C₃H₅)₂], the negative activation entropy has been shown to Carbon to an intermolecular allyl exchange mechanism.^[18a,19,20] In turn, the positive ΔS^{+} value of **3** suggests an intramolecular allyl exchange mechanism for this compound.

The THF ligands in **3** are labile and can be substituted for stronger donors, as demonstrated by the synthesis of $[Bi-(C_3H_5)_2(HMPA)_2][B(C_6H_3Cl_2)_4]$ (**4**; HMPA = hexamethylphosphoramide). Single-crystal X-ray analysis of **4** revealed a molecular structure similar to that of **3** (see the Supporting Information).

Bismuth(III) catalysts have been used for the allylation of aldehydes.^[21,22] In these reactions, addition of a second component, such as an allyltin compound, an allyl silane (Sakurai reaction), or the combination of an allyl halide and Fe⁰, Zn⁰ or Sn⁰, was required.^[23] The direct carbometalation of a carbonyl substrate by a well-defined organobismuth(III) compound alone (such as [BiMe₃] or [BiPh₃]) has not been observed to date.^[24-26] In agreement with these earlier reports, tris(allyl)bismuth (1) did not react with benzaldehyde in THF at ambient temperature. Unexpectedly, 1 slowly reacted with benzaldehyde under carbometalation when the Lewis acid [BPh₃] was added, as detected by NMR spectroscopy (26 h, 23 °C, 81 % yield).^[27] These results prompted us to investigate the Lewis acidic bis(allyl)bismuth cation 3 as a direct allyl transfer reagent. Indeed, 3 quantitatively reacted with two equivalents of benzaldehyde in THF at ambient temperature to give the carbometalation product in a rapid reaction (Table 1, entry 1). Notably, coordination of aldehydes to an organobismuth cation with a chelating diaryl ligand has previously been reported.^[5d] Thus, we suggest, that not only is the Lewis acidity of the cationic bismuth center responsible for the carbometalation reaction to occur, but also the lability of the allyl ligands. From a mechanistic viewpoint, two different roles have been discussed for the bismuth center in

Table 1: Reaction of 3 with aldehydes, imines, and ketones.

3 +	$n \underset{\mathbb{R}^1}{\overset{X}{\amalg}} \mathbb{R}^2$	THF, RT,	$\begin{bmatrix} Bi \begin{pmatrix} X \\ R^1 & R^2 \end{pmatrix}_2 (thf)_2 \end{bmatrix} [A]$		
5a–m			6a–m		

Entry	n	R ¹	R^2	Х	Product	$Yield^{[a]}$
1	2	Ph	н	0	6a	>99
2	2	$4-FC_6H_4$	н	0	6 b	>99
3	2	4-CIC ₆ H ₄	н	0	6c	>99
4	2	4-BrC ₆ H₄	н	0	6 d	>99
5	2	$4-CF_3C_6H_4$	н	0	6e	>99
6	2	4-PhC ₆ H ₄	н	0	6 f	>99
7	2	1-napthyl	Н	0	6g	>99
8	2	4-CNC ₆ H ₄	Н	0	6h	>99
9	2	4-NO ₂ C ₆ H ₄	н	0	6i	>99
10	2	4-Me/4-MeOC ₆ H ₄	Н	0	6j/k	traces
11 ^[b]	2	Ph	Н	NTos	61	54
12	2	Ph	Ph	0	6 m	29 ^[c]
13	10	Ph	Ph	0	6 m	64 ^[c]
14	50	Ph	Ph	0	6 m	97 ^[c]

[a] Determined by NMR spectroscopy. [b] Reaction time: 3 h. [c] Yield based on monoinsertion product **6m** (see main text).

13012 www.angewandte.org

allylations of aldehydes with bismuth catalysts: 1) Lewis acid activation of the substrate;^[6c] and 2) transfer of the allyl ligand to the substrate (with possible simultaneous Lewis acid activation of the substrate).^[21i] Our results provide the first evidence for the direct carbometalation of a carbonyl compound by a well-defined organobismuth reagent.^[26] Furthermore, they show that Lewis acid activation of the substrate induced by cationization of the organobismuth reagent is essential.

We set out to investigate the electronic demand and functional-group tolerance of the carbometalation of aldehydes by 3. Electron-poor aldehydes 5b-i were quantitatively converted into the carbometalation products 6b-i (Table 1, entries 2-9). When electron-rich substrates were used, only traces of the carbometalation products were detected, major side reactions being polymerization of the substrate and the solvent.^[28] Reactions of **3** with aldehydes show an excellent functional group tolerance for electron poor substrates as they are compatible with halide, nitrile, and even nitro substituents (Table 1, entries 2-4,8,9). Substitution of the aromatic substrate in the ortho- and meta-position did not sterically inhibit the reaction (Table 1, entry 7). In all of these reactions, two sets of signals with a relative intensity of 1:1 were observed for the carbometalation products and ascribed to the R,R/S,S enantiomers and the R,S meso-compound. Substrates other than aldehydes were also studied. The Nprotected aldimine 51 gave the carbometalation product 61 in moderate yield (Table 1, entry 11).^[29] In reactions of 3 with benzophenone, the monoinsertion product $[Bi(C_3H_5)(OCPh_2 (C_3H_5)(thf)_2$ [A] (6m) was formed selectively (Table 1, entry 12). A yield of 29% was observed initially (determined spectroscopically), which did not increase after prolonged reaction times although unconverted starting materials remained unchanged. This indicates equilibrium conditions for this reaction. Accordingly, excess benzophenone shifted the equilibrium to the product side with formation or up 97 % of monoinsertion product 6m (Table 1, entries 13, 14).^[30]

Neutral organobismuth compounds have recently been reported to be unique initiators for the controlled living radical polymerizations of activated olefins, such as styrene.^[31] Neutral **1** and cationic species **3** were tested as initiators in polymerization reactions, as these compounds undergo homolysis of the Bi–C bond (see above). Compound **1** was active as an initiator in the bulk polymerization of styrene to give an atactic polymer with a broad molecular weight distribution (polydispersity index (PDI)=4.62; Table 2, entry 1). In contrast, under identical conditions cationic **3** as an initiator gave atactic polystyrene (PS) with a lower PDI of 1.62 (Table 2, entry 2). Under optimized reaction conditions, high yields of PS with consistently low PDI values of 1.3–1.4

Table 2: Bulk polymerization of styrene.^[a]

Entry	Initiator	<i>т</i> [°С]	<i>t</i> [h]	Yield [%]	<i>M_n</i> [g mol ⁻¹]	M_w/M_n
1	1	100	4.5	58	8400	4.62
2	3	100	4.5	67	9400	1.62
3	3	120	2	90	14900	1.38

[a] Monomer/initiator = 100:1 (molar ratio).

were obtained (Table 2, entry 3; Figure 2).^[32] End group analysis revealed an allyl moiety to be covalently bonded to the polymer chain. Reaction of **3** with $[Sn(nBu)_3H]$ in C_6D_6 at



Figure 2. Plot of M_n and M_w/M_n versus conversion for bulk polymerization of styrene at 120 °C using **3** as an initiator.

ambient temperature gave propene as a main product, suggesting that the allyl ligands of 3 are susceptible to homolysis. Thus, the polymerization of styrene initiated by 3 is likely to proceed by a controlled radical mechanism. A linear correlation between the polymer yield and the number average molecular weight revealed the living character of the polymerization (Figure 2). The bulk polymerization of styrene initiated by 3 was shown to follow first-order kinetics in the range of 80-120 °C with rate constants ranging from $(2.3 \pm 0.1) \times 10^{-5} \text{ s}^{-1}$ to $(2.5 \pm 0.5) \times 10^{-4} \text{ s}^{-1}$.^[33] Activation parameters of $\Delta H^{\pm} = (-64.9 \pm 0.8) \text{ kJ mol}^{-1}$ and $\Delta S^{\pm} =$ (150 ± 18) J mol⁻¹K⁻¹ were determined from an Eyring plot in the same temperature range (see the Supporting Information).^[34] In preliminary experiments with 1 and 3 as initiators, similar trends have been observed when other activated olefins, such as methyl methacrylate, were used as monomers (see the Supporting Information). These results provide the first example of a cationic main group organometallic compound to act as an initiator for controlled living radical polymerizations.[35,36]

In conclusion, we have presented the structurally characterized bis(allyl)bismuth cation, which is present in [Bi- $(C_3H_5)_2(thf)_2$][B($C_6H_3Cl_2$)₄] (**3**), that acts as a stoichiometric allyl transfer reagent and as an initiator for the controlled radical polymerization.

Received: August 21, 2012 Revised: September 21, 2012 Published online: November 14, 2012

Keywords: allyl ligands \cdot allylation \cdot bismuth \cdot cationic species \cdot radical polymerization

a) M. B. Harney, R. J. Keaton, J. C. Fettinger, L. R. Sita, J. Am. Chem. Soc. 2006, 128, 3420-3432; b) R. F. Jordan, Adv. Organomet. Chem. 1991, 32, 325-387; c) H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, Angew. Chem. 1995, 107, 1255-1283; Angew. Chem. Int. Ed. Engl. 1995, 34, 1143-

Angewandte Communications

1170; d) G. W. Coates, *Chem. Rev.* **2000**, *100*, 1223–1252; e) V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283–315.

- [2] a) P. M. Zeimentz, S. Arndt, B. R. Elvidge, J. Okuda, *Chem. Rev.* 2006, *106*, 2404–2433; b) M. U. Kramer, D. Robert, S. Arndt, P. M. Zeimentz, T. P. Spaniol, A. Yahia, L. Maron, O. Eisenstein, J. Okuda, *Inorg. Chem.* 2008, *47*, 9265–9278; c) A. Yahia, M. U. Kramer, J. Okuda, L. Maron, *J. Organomet. Chem.* 2010, *695*, 2789–2793.
- [3] a) D. A. Atwood, *Coord. Chem. Rev.* 1998, *176*, 407–430; b) S. Dagorne, D. A. Atwood, *Chem. Rev.* 2008, *108*, 4037–4071; c) C. Lichtenberg, D. Robert, T. P. Spaniol, J. Okuda, *Organometallics* 2010, *29*, 5714–5721; d) T. Klis, D. R. Powell, L. Wojtas, R. J. Wehmschulte, *Organometallics* 2011, *30*, 2563–2570; e) C. Lichtenberg, T. P. Spaniol, J. Okuda, *Inorg. Chem.* 2012, *51*, 2254–2262.
- [4] For reviews see: a) J. M. Bothwell, S. W. Krabbe, R. S. Mohan, *Chem. Soc. Rev.* 2011, 40, 4649-4707; b) N. M. Leonard, L. C. Wieland, R. S. Mohan, *Tetrahedron* 2002, 58, 8373-8397; c) H. R. Kricheldorf, *Chem. Rev.* 2009, 109, 5579-5594.
- [5] a) C. J. Carmalt, N. C. Norman, A. G. Orpen, S. E. Stratford, J. Organomet. Chem. 1993, 460, C22-C24; b) C. J. Carmalt, L. J. Farrugia, N. C. Norman, J. Chem. Soc. Dalton Trans. 1996, 443 454; c) C. J. Carmalt, D. Walsh, A. H. Cowley, N. C. Norman, Organometallics 1997, 16, 3597-3600; d) M. Bao, T. Hayashi, S. Shimada, Organometallics 2007, 26, 1816-1822; e) N. L. Kilah, S. Petrie, R. Stranger, J. W. Wielandt, A. C. Willis, S. B. Wild, Organometallics 2007, 26, 6106-6113; f) H. J. Breunig, M. G. Nema, C. Silvestru, A. P. Soran, R. A. Varga, Dalton Trans. 2010, 39, 11277-11284; g) I. J. Casely, J. W. Ziller, B. J. Mincher, W. J. Evans, Inorg. Chem. 2011, 50, 1513-1520; h) M. G. Nema, H. J. Breunig, A. Soran, C. Silvestru, J. Organomet. Chem. 2012, 705, 23-29.
- [6] a) R. Qiu, S. Yin, X. Zhang, J. Xia, X. Xu, S. Luo, *Chem. Commun.* 2009, 4759–4761; b) X. Zhang, S. Yin, R. Qiu, J. Xia, W. Dai, Z. Yu, C.-T. Au, W.-Y. Wong, *J. Organomet. Chem.* 2009, 694, 3559–3564; c) X. Zhang, R. Qiu, N. Tan, S. Yin, J. Xia, S. Luo, C.-T. Au, *Tetrahedron Lett.* 2010, 51, 153–156; d) R. Qiu, Y. Qiu, S. Yin, X. Xu, S. Luo, C.-T. Au, W.-Y. Wong, S. Shimada, *Adv. Synth. Catal.* 2010, 352, 153–162; e) R. Qiu, Y. Qiu, S. Yin, X. Xu, Xu, X. Zhang, S. Luo, C.-T. Au, W.-Y. Wong, *Green Chem.* 2010, 12, 1767–1771; f) R. Qiu, S. Yin, X. Song, Z. Meng, Y. Qiu, N. Tan, X. Xu, S. Liu, F.-R. Dai, C.-T. Au, W.-Y. Wong, *Dalton Trans.* 2011, 40, 9482–9489; g) N. Tan, S. Yin, Y. Li, R. Qiu, Z. Meng, X. Song, S. Liu, C.-T. Au, W.-Y. Wong, *J. Organomet. Chem.* 2011, 696, 1579–1583.
- [7] a) A. E. Borisov, M. A. Osipova, A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR Ser. Khim.* **1963**, 1507–1509 [*Chem. Abstr.* **1963**, *59*, 14021]; b) J.-Y. Hyeon, M. Lisker, M. Silinskas, E. Burte, F. T. Edelmann, *Chem. Vap. Deposition* **2005**, *11*, 213–218.
- [8] The formation of low-valent allyl bismuth species cannot be ruled out (see Ref. [11]). 1,5-Hexadiene is the only THF-soluble degradation product. 12% degradation was observed after 25 h at RT in THF.
- [9] The solid-state structure of the dibismuthine [Bi₂Et₄] has recently been established using a similar method: A. Kuczkowski, S. Heimann, A. Weber, S. Schulz, D. Bläser, C. Wölper, *Organometallics* **2011**, *30*, 4730–4735.
- [10] C. Silvestru, H. J. Breunig, H. Althaus, Chem. Rev. 1999, 99, 3277-3327.
- [11] J. Lorberth, W. Massa, S. Wocadlo, I. Sarraje, S.-H. Shin, X.-W. Li, J. Organomet. Chem. 1995, 485, 149–152.
- [12] One attempt to prepare an organobismuth cation by protonolysis has been reported: a mixture of the desired product and the starting material was isolated (Ref. [5g]).
- [13] a) D. Robert, E. Abinet, T. P. Spaniol, J. Okuda, *Chem. Eur. J.* 2009, 15, 11937–11947; b) C. Lichtenberg, T. P. Spaniol, J.

Okuda, Angew. Chem. 2012, 124, 8225-8229; Angew. Chem. Int. Ed. 2012, 51, 8101-8105.

- [14] In contrast, upon cationization the coordination mode of the allyl ligand in calcium compounds changes from η³ to μ₂-η¹:η¹: C. Lichtenberg, P. Jochmann, T. P. Spaniol, J. Okuda, *Angew. Chem.* **2011**, *123*, 5872–5875; *Angew. Chem. Int. Ed.* **2011**, *50*, 5753–5756.
- [15] a) N. W. Alcock, M. Ravindran, G. R. Willey, J. Chem. Soc. Chem. Commun. **1989**, 1063–1064; b) R. D. Rogers, A. H. Bond, S. Aguinaga, A. Reyes, J. Am. Chem. Soc. **1992**, 114, 2967–2977.
- [16] a) M. Mehring, Coord. Chem. Rev. 2007, 251, 974–1006; b) D. Mansfeld, M. Mehring, Z. Anorg. Allg. Chem. 2005, 631, 2429– 2432.
- [17] 6% degradation was observed after 36 h at RT in THF. During the degradation process, which proceeds at a slower rate in the dark, small amounts of black solid precipitate (Bi⁰ and/or lowvalent bismuth species). 1,5-Hexadiene is the only THF-soluble degradation product.
- [18] a) E. G. Hoffmann, H. Nehl, H. Lehmkuhl, K. Seevogel, W. Stempfle, *Chem. Ber.* **1984**, *117*, 1364–1377; b) A. E. Hill, W. A. Boyd, H. Desai, A. Darki, L. Bivens, *J. Organomet. Chem.* **1996**, *514*, 1–11; c) see citation in Ref. [14].
- [19] C. Lichtenberg, J. Engel, T. P. Spaniol, U. Englert, G. Raabe, J. Okuda, J. Am. Chem. Soc. 2012, 134, 9805–9811.
- [20] In noncoordinating solvents or neat substance (not specified), a ΔS⁺ value of -42 Jmol⁻¹K⁻¹ has been reported for the allyl exchange of [B(C₃H₅)₃] and an intramolecular mechanism has been suggested (the order of reaction was not determined): Y. N. Bubnov, M. E. Gurskii, I. D. Gridnev, A. V. Ignatenko, Y. A. Ustynyuk, V. I. Mstislavsky, *J. Organomet. Chem.* **1992**, 424, 127-132.
- [21] Some of the reactions were also performed with stoichiometric amounts of Bi compounds; in few cases, ketones were also used as substrates: a) M. Wada, H. Ohki, K. Akiba, Tetrahedron Lett. 1986, 27, 4771-4774; b) Z. Li, B. Plancq, T. Ollevier, Chem. Eur. J. 2012, 18, 3144-3147; c) B. Leroy, I. E. Markó, Tetrahedron Lett. 2001, 42, 8685-8688; d) S. Donnelly, E. J. Thomas, M. Fielding, Tetrahedron Lett. 2004, 45, 6779-6782; e) P. Sreekanth, J. K. Park, J. W. Kim, T. Hyeon, B. M. Kim, Catal. Lett. 2004, 96, 201-204; f) P. W. Anzalone, A. R. Baru, E. M. Danielson, P. D. Hayes, M. P. Nguyen, A. F. Panico, R. C. Smith, R. S. Mohan, J. Org. Chem. 2005, 70, 2091-2096; g) T. Ollevier, Z. Li, Eur. J. Org. Chem. 2007, 5665-5668; h) G. Sabitha, M. Bhikshapathi, S. Nayak, J. S. Yadav, R. Ravi, A. C. Kunwar, Tetrahedron Lett. 2008, 49, 5727-5731; i) S. Donnelly, E. J. Thomas, E. A. Arnott, Chem. Commun. 2003, 1460-1461; j) B. Alcaide, P. Almendros, R. Rodríguez-Acebes, J. Org. Chem. 2005, 70, 2713-2719; k) N. Bazar, S. Donnelly, H. Liu, E. J. Thomas, Synlett 2010, 575-578; 1) L. Zhao, D. J. Burnell, Tetrahedron Lett. 2006, 47, 3291-3294; m) M. Wada, M. Honna, Y. Kuramoto, N. Mivoshi, Bull. Chem. Soc. Jpn. 1997, 70, 2265-2267; n) see also Ref. [4a,b,6c].
- [22] The combination of [BiR₃] and a second organometallic reagent has also been used for the carbometalation of benzaldehyde:
 a) E. Kayahara, H. Yamada, S. Yamago, *Chem. Eur. J.* 2011, *17*, 5272–5280;
 b) I. Sato, Y. Toyota, N. Asakura, *Eur. J. Org. Chem.* 2007, 2608–2610;
 c) I. Sato, N. Asakura, T. Iwashita, *Tetrahedron: Asymmetry* 2007, *18*, 2638–2642.
- [23] Especially in the case of toxic allyltin, the need for co-reagents in stoichiometric amounts diminishes any possible environmental benefits owing to the use of a bismuth catalyst.
- [24] Bi⁰ has been used for the allylation of aldehydes, aldimines, and ketones in Grignard related reactions, in which the active species remained unidentified: a) M. Wada, K. Akiba, *Tetrahedron Lett.* **1985**, 26, 4211–4212; b) P. J. Bhuyan, D. Prajapati, J. S. Sandhu, *Tetrahedron Lett.* **1993**, 34, 7975–7976; c) M. Wada, H. Ohki, K.

Akiba, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1738–1747; d) X. Xu, Z. Zha, Q. Miao, Z. Wang, *Synlett* **2004**, 1171–1174.

- [25] Pentaorganobismuth(V) compounds do not undergo carbometalation with carbonyl compounds. [BiPh₅] reacts with enolizable carbonyl compounds in a two-step sequence of deprotonation followed by electrophilic arylation of the α-carbon, releasing benzene and [BiPh₃] as by-products; for example: D. H. R. Barton, J.-C. Blazejewski, B. Charpiot, J.-P. Finet, W. B. Motherwell, M. T. B. Papoula, S. P. Stanforth, J. Chem. Soc. Perkin Trans. 1 1985, 2667–2675.
- [26] The bismuth amide [1,8-C₁₀H₆(NSiMe₃)₂BiNMe₂] adds an NMe₂ group to alkenes, alkynes, aldehydes, and ketones: B. Nekoueishahraki, S. P. Sarish, H. W. Roesky, D. Stern, C. Schulzke, D. Stalke, *Angew. Chem.* 2009, *121*, 4587–4590; *Angew. Chem. Int. Ed.* 2009, *48*, 4517–4520.
- [27] No reaction (such as abstraction of an allyl ligand from 1) was observed between 1 and $[BPh_3]$ (molar ratio=1:3) in THF at ambient temperature, as detected by NMR spectroscopy.
- [28] Polymerization of aromatic aldehydes induced by light or Lewis acids (for example, [SbCl₅]) have previously been reported:
 a) G. R. De Maré, J. R. Fox, *J. Photochem.* 1986, *32*, 293–301;
 b) P. Kovacic, A. K. Sparks, *J. Org. Chem.* 1961, *26*, 2541–2542;
 c) R. Raff, J. L. Cook, B. V. Ettling, *J. Polym. Sci. Part A* 1965, *3*, 3511–3517.
- [29] A circa 60% conversion of **3** was observed; side products were presumably due to reaction of **3** with the tosyl group. Degradation of **61** was observed at prolonged reaction times of t > 6 h with the beginning of concomitant polymerization of the solvent.
- [30] Compound 1 did not react with benzophenone (3 equiv) regardless of the presence of $[BPh_3]$ (3 equiv).
- [31] a) S. Yamago, E. Kayahara, M. Kotani, B. Ray, Y. Kwak, A. Goto, T. Fukuda, *Angew. Chem.* 2007, *119*, 1326–1328; *Angew. Chem. Int. Ed.* 2007, *46*, 1304–1306; b) E. Kayahara, S. Yamago, *J. Am. Chem. Soc.* 2009, *131*, 2508–2513.

- [32] In a control experiment (styrene, 120 °C, 2 h, no catalyst), 7% of polystyrene were obtained with $M_n = 1.9 \times 10^5 \text{ g mol}^{-1}$ and $M_w/M_n = 2.56$.
- [33] a) Apparent rate constants k_{app} of $1 \times 10^{-5} \text{ s}^{-1}$ to $4 \times 10^{-5} \text{ s}^{-1}$ at 90 °C and 120 °C, respectively, and an activation energy E_A of 55 kJ mol⁻¹ have been reported for the nitroxide-catalyzed polymerization of styrene: C. R. Becer, R. M. Paulus, R. Hoogenboom, U. S. Schubert, *J. Polym. Sci. Part A* 2006, 44, 6202-6213; b) higher conversions at slightly shorter reaction times have been reported for the polymerization of styrene with [BiMe₂(CMe₂CO₂Me)], but the apparent rate of reaction was not explicitly mentioned: see Ref. [31a].
- [34] An activation energy of $E_A = 67.9 \text{ kJ mol}^{-1}$ has been determined from an Arrhenius plot; compare Ref. [33a].
- [35] Neutral main-group organometallic complexes and metal-free reagents have been reported as initiators or mediators in controlled living radical polymerizations, for example: a) *Handbook of Radical Polymerization* (Eds.: K. Matyjaszewski, T. P. Davis), Wiley-Interscience, New York, 2002; b) G. Moad, D. H. Solomon, *The Chemistry of Radical Polymerization*, Elsevier, Amsterdam, 2006; c) S. Yamago, *Proc. Jpn. Acad. Ser. B* 2005, *81*, 117–128; d) G. David, C. Boyer, J. Tonnar, B. Ameduri, P. Lacroix-Desmazes, B. Boutevin, *Chem. Rev.* 2006, *106*, 3936–3962; e) A. Goto, Y. Kwak, T. Fukuda, S. Yamago, K. Iida, M. Nakajima, J.-i. Yoshida, *J. Am. Chem. Soc.* 2003, *125*, 8720–8721; f) S. Yamago, K. Iida, J.-I. Yoshida, *J. Am. Chem. Soc.* 2002, *124*, 2874–2875; g) also see Ref. [31].
- [36] Cationic species, such as [Cu(bipy)₂][CF₃SO₃] (bipy = bipyridyl), are well-established in transition-metal-catalyzed controlled living radical polymerization, for example: T. Pintauer, K. Matyjaszewski, *Top. Organomet. Chem.* **2009**, 26, 221–251.
- [37] CCDC 897779 (2) and CCDC 897780 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.