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Air-stable hypervalent organobismuth (III) tetrafluoroborate as effective and reusable catalyst for the allylation of aldehyde with tetraallyltin

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The allylation of different aldehydes with tetraallyltin was successfully operated over hypervalent organobismuth (III) tetrafluoroborate catalyst in a medium of aqueous methanol, giving the corresponding homoallylic alcohols in excellent chemoselectivity and yields.
Air-stable hypervalent organobismuth (III) tetrafluoroborate as effective and reusable catalyst for the allylation of aldehyde with tetraallyltin

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Abstract—Air-stable hypervalent organobismuth (III) tetrafluoroborate (C 6H11N(CH2C6H4)2BiBF4) was synthesized and characterized by spectroscopic and X-ray crystallographic techniques. The compound shows good catalytic efficiency in the allylation reaction of different aldehydes with tetraallyltin in a medium of aqueous methanol, giving the corresponding homoallylic alcohols in excellent chemoselectivity and yields. © 2011 Elsevier Science. All rights reserved

Keywords—Organobismuth, Tetrafluoroborate, Lewis acid, Catalysis, Allylation

Bismuth compounds are not toxic and relatively cheap, and have been widely used in catalysis and organic synthesis. In the past two decades, bismuth(III) compounds (e.g., BiCl3, BiBr3, Bi(OTf)3, Bi(NO3)3) have been used as catalysts in various organic reactions 1,2. However, up till now, there are only several reports on the use of organobismuth compounds as catalysts in organic synthesis, possibly due to the unstable nature of bismuth compounds 3. With environmental concerns and ‘green reagents’ in mind, we have been synthesizing stable bismuth compounds for potential uses. For example, organobismuth oxide, hydroxide, methoxide and bismuth compounds bearing a sulfur-bridged bis(phenolato) ligand were synthesized and found to be good reagents and catalysts for CO2 chemical fixation 4. Very recently we reported that certain organobismuth chlorides and their triphenylgermyl-proponate derivatives show good in vitro antiproliferative activity 5, and that organobismuth perfluoroocanesulfonate and perchlorate exhibit high catalytic efficiency towards one-pot Mannich-type reaction of ketones with aromatic aldehydes and aromatic amines in water 6. We have also developed a series of novel Lewis acids by incorporating large electron-withdrawing groups (e.g., -C6F5SO3, -C8F17SO3) into organometallic (e.g., Ti, Zr, Hf) compounds, and found that they are catalytically active towards many organic reactions in aqueous media as well as in various organic solvents 7. It is know that the Lewis acid-catalyzed allylation of carbonyl compounds to produce homoallylic alcohols is a versatile organic reaction 8. The allylation reaction can be promoted by the addition of a Lewis acid 9 or enhanced by the rise of reaction temperature or pressure 10. On the other hand, there is a growing body of evidence that under certain circumstances, the solvent (THF-HCl 10) or methanol 11) and ionic liquids 12 can facilitate allyl transfer from tetraallylstannane to alkanals or alkanoles.

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In this paper, we report the synthesis and characterization of an air-stable compound, viz. hypervalent organobismuth (III) tetrafluoroborate and its use in the allylation of carbonyl compounds with tetraallyltin in aqueous media.

Shown in Scheme 1 is the synthesis of hypervalent organobismuth (III) tetrafluoroborate. Treatment of C₆H₁₁N(CH₂C₆H₄)₂BiCl with silver tetrafluoroborate (AgBF₄) (1 equiv) in THF yields the target complex. The crystal structure of compound 1 was confirmed by X-ray analysis technique. An ORTEP representation of the structure of compound 1, as well as selected bonds and angles is shown in Fig. 1. One can see that the central bismuth-containing part shows a pseudo-trigonal bipyramidal (TBP) structure, where both the C(1) and C(8) atoms exist in the equatorial position of the TBP structure along with a lone electron pair of bismuth, and the N(1) and F(1) atoms are at the apical positions. The N(1)–Bi–F(1) bond angle is 153.9° while the C(1)–Bi–C(8) angle is 94.1°.

As reported previously, the Bi–N coordination distance in 5,6,7,12-tetrahydrodibenzo[c,f][1,5]aza-bismocines flexibly changes in response to the electronic nature of bismuth. The Bi–F bond is 2.502 Å in length, longer than that (2.190 Å) in ‘BuN(CH₂C₆H₄)₂BiF₄ and that (2.088 Å) in Ph₄BiF₄, but shorter than the Bi⋯F distance in ‘BuN(CH₂C₆H₄)₂Bi[B(C₆F₅)₄] (2.971 Å). The organobismuth tetrafluoroborate remained as dry crystals and suffered no color change in a test of one year in air. It is apparent that it is resistant to moisture and oxygen.

Attached to the Bi atom of compound 1 is a strongly electron-withdrawing tetrafluoroborate (BF₄⁻) and compound 1 shows Lewis acid strength of 3.3 < H° ≤ 4.8, stronger than that of (C₆H₁₁N(CH₂C₆H₄)₂Bi(OSO₂C₈F₁₇)₆. In addition, compound 1 is highly soluble in methanol and in aqueous solutions of common polar organic molecules. The thermal stability of compound 1 was investigated by TG-DSC analysis under N₂ atmosphere (Fig. 2). One can see that the material is stable up to about 259 °C. With all these positive features in mind, we proceeded to evaluate compound 1 as a Lewis acid catalyst for the allylation of aldehydes and ketones with tetraallyltin.

In most cases of the utilization of metal reagents, the allylation reactions have to be conducted under dry condition and/or in an inert atmosphere. It is not so in the handling of tetraallyltin. Another reason for adopting tetraallyltin for allylation in this study is that the substance is inexpensive and readily available. The reaction of tetraallyltin with benzaldehyde using 4 mol % of C₆H₁₁N(CH₂C₆H₄)₂BiBF₄ was examined in various solvents in a period of one hour (Table 1).

In order to demonstrate the excellent catalytic activity of 1, aliphatic aldehyde as well as aromatic aldehydes with electron-donating and electron-withdrawing groups were examined (Table 2). Allylation of both aromatic and
aliphatic aldehydes at ca. 30 °C in the presence of 4 mol% of the compound 1 proceeds smoothly to generate the corresponding homoallyl alcohols 2 in good to excellent yields. It is interesting to note that the aryl aldehydes with electron-withdrawing and electron-donating groups show similar allylation rate, suggesting that the presence of the electron-withdrawing or electron-donating group of the compound 1 has little effect on the reaction.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeOH</td>
<td>1</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>MeOH:H₂O = 9:1</td>
<td>1</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td>MeOH:H₂O = 4:1</td>
<td>1</td>
<td>96</td>
</tr>
<tr>
<td>4</td>
<td>MeOH:H₂O = 7:3</td>
<td>1</td>
<td>90</td>
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<td>5</td>
<td>MeOH:H₂O = 3:2</td>
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<td>70</td>
</tr>
<tr>
<td>6</td>
<td>MeOH:H₂O = 1:1</td>
<td>1</td>
<td>58</td>
</tr>
<tr>
<td>7</td>
<td>C₂H₅OH</td>
<td>1</td>
<td>92</td>
</tr>
<tr>
<td>8</td>
<td>THF</td>
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<td>90</td>
</tr>
<tr>
<td>9</td>
<td>CH₃CN</td>
<td>1</td>
<td>93</td>
</tr>
<tr>
<td>10</td>
<td>DMSO</td>
<td>1</td>
<td>84</td>
</tr>
<tr>
<td>11</td>
<td>CH₂Cl₂</td>
<td>6</td>
<td>80</td>
</tr>
<tr>
<td>12</td>
<td>Toluene</td>
<td>6</td>
<td>56</td>
</tr>
<tr>
<td>13</td>
<td>Hexane</td>
<td>12</td>
<td>30</td>
</tr>
</tbody>
</table>

[a] PhCHO 1.0 mmol, tetraallyltin 0.3 mmol, 0.04 mmol, RT, 2 mL solvent.  
[b] Isolated yield.

Furthermore, we observed no formation of homoallylic alcohol in the case of acetophenone even after prolonged period of reaction (not shown). In other words, high chemoselectivity between aldehydes and ketones is possible in this approach of catalytic allylation. Such degree of chemoselectivity is impossible with the commonly used allylation reagents such as allylmagnesium bromide, allyllithium and allyltinyltin/BF₃·OEt₂. It is apparent that compared to the catalysts reported in the literatures, compound 1 has the advantages of being high in activity, selectivity, stability, and reusability.

According to the concepts suggested by Cokley et al. and Lingaiah et al. and based on the experimental data reported so far, the mechanism of the allylation reaction over compound 1 in aqueous methanol solution is postulated (Scheme 2). With compound 1, tetraallyltin and an aldehyde dissolved in aqueous methanol, the aldehyde coordinates with the bismuth atom and is activated. Then tetrallytin attacks the activated aldehyde to form a six-membered intermediate. Meanwhile methanol and water coordinate to tin to form (RO)nSn(CH₂-CH=CH₂)n (n = 1, 2, 3).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (4 mol %)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>no Cat.</td>
<td>12</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>C₆H₅N(CH₂C₆H₄)₂BiCl</td>
<td>4</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>C₆H₅N(CH₂C₆H₄)₂BiBF₄</td>
<td>1</td>
<td>96</td>
</tr>
<tr>
<td>4</td>
<td>[Sn(CH₂C₆H₄)₂Bi(OH₂)]+[CIO₄]⁻</td>
<td>1</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>C₆H₅N(CH₂C₆H₄)₂Bi[OCO(CH₂)₂GePh₃]</td>
<td>4</td>
<td>88</td>
</tr>
<tr>
<td>6</td>
<td>C₆H₅N(CH₂C₆H₄)₂Bi[OCO(CH₂)₂GePh₃]</td>
<td>4</td>
<td>85</td>
</tr>
<tr>
<td>7</td>
<td>Bu₂N(CH₂C₆H₄)₂Bi[OCO(CH₂)₂GePh₃]</td>
<td>4</td>
<td>75</td>
</tr>
<tr>
<td>8</td>
<td>Bi(OSO₂CF₃)₃</td>
<td>3</td>
<td>50</td>
</tr>
<tr>
<td>9</td>
<td>S(CH₂C₆H₄)₂BiCl</td>
<td>4</td>
<td>77</td>
</tr>
<tr>
<td>11</td>
<td>BiCl₃</td>
<td>3</td>
<td>68</td>
</tr>
</tbody>
</table>

[a] PhCHO 1.0 mmol, tetraallyltin 0.3 mmol, 0.04 mmol, RT, 2 mL solvent (CH₃OH/H₂O=9:1).  
[b] Isolated yield.

To examine the reusability of the catalyst, compound 1 was subject to cycles of allylation reaction of benzaldehyde with tetraallyltin. In a test of 5 cycles, the change of product yield is minimal (isolated yield slightly declined from 96% to 94%), indicating that the catalyst is stable and reusable (details will be reported in a full paper).
2, 3, 4; R=H or CH3), producing the homoallyl alcohol. With the cleavage of the coordinate bond, compound 1 is regenerated and is ready for the next catalytic cycle.

In summary, we have synthesized and characterized air-stable hypervalent organobismuth (III) tetrafluoroborate as an efficient Lewis-acidity catalyst that shows high activity and good selectivity to homoallyl alcohols in the allylation of aromatic and aliphatic aldehydes with tetraallyltin in aqueous methanol.

Acknowledgements

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References and notes


13. Synthesis of compound 1: CH3N(CH2CH2)2BCl2 (2.61 g, 5.0 mmol) was dissolved in 90.0 mL THF, then a solution of AgBF4 (0.97 g, 5.0 mol) was added. After the mixture was stirred in the dark at room temperature for 3 h, it was filtered. The filtrate mixed with 10.0 mL hexane was refrigerated for 24 h, giving colorless crystals (2.74 g, 95.6%). Compound 1: HNMR (Daceton, 400 MHz, TMS): δ 1.19 (1H, td, J=13.6 Hz, 7.6 Hz, 3.13-4.24 (H, m), J=1.51-2.59 (H, m), 3.84 (H, d, J=12.0 Hz, 2.68 (H, d, J=12.0 Hz, 3.50 (H, t, J=12.0 Hz, 5.02 (H, d, J=15.6 Hz, 7.42 (H, td, J=7.6 Hz, 7.58 (H, t, J=7.6 Hz, 7.76 (H, d, J=7.6 Hz, and 8.09 (H, d, J=7.2 Hz); 13C NMR (Daceton, 100 MHz); δ 25.89, 26.16, 26.29, 32.03, 65.07, 67.75, 68.06, 129.28, 129.55, 131.58, 137.77, and 154.44; 19F NMR (Daceton, 376 MHz): -154.437(H); HRMS calculated for C23H32BF4Bi2N: 657.3419, found: 657.3414; Crystallographic data for 1: C23H32BF4Bi2N, colorless prism, formula weight 657.34, monoclinic, P2(1)/n, a = 10.9011(12), b = 16.0649 (18), c = 14.2625 (15), V = 2457.3, Z = 4, Dcalc = 1.777 g·cm -3, Rwp = 0.069, R = 0.056, GOF = 0.86, CCDC No. 746982.


16. Typical procedure for the allylation reaction: To a solution of 1 (0.04 mmol, 23.9 mg) in 2.0 mL solvent (CH3OH/H2O = 9:1), PhCHO (106.1 mg, 1 mmol) and tetraallyltin (0.3 mmol, 84.9 mg) were added. Then the mixture was stirred at room temperature and subject to TLC analysis for one hour. The resulted solution was subject to evaporation and the residue was dissolved in Et2O (20 mL). The catalyst precipitated and was filtered out, and could be immediately reused in the next reaction. The organic layer was mixed with methanol and 2N HCl (1 mL) and stirred for 15 minutes, and then NaHCO3 (10%) was added for neutralization. After filtration, the aqueous layer was washed with Et2O (10 mL × 3), and the organic layers were combined and washed with brine, then dried with Na2SO4. The resulted solution was subject to evaporation, whereas the residue was subject to silica gel column chromatography (ethyl acetate/petroleum ether = 1:8). The collected colorless oil showed an isolated yield of 142.0 mg, 96%. All aldehydes, acetophenone and tetraallyltin are commercially available. All homoallylic alcohols 2a-2j have been reported, and 1H NMR spectra data of the products are consistent with our previously results (see references 7a,7b) and those of Jiang et al. and Zhao and Cai (see references 19a, 19b).

1-Phenyl-3-buten-1-ol (2a): H NMR(CDC13, 400 MHz, TMS): δ 2.01 (1H, bs), 2.49-2.52 (2H, m), 4.75 (1H, t, J = 5.5 Hz), 5.14-5.20 (2H, m), 5.82 (1H, m), 7.25-7.43 (5H, m). 2-methylhex-5-en-3-ol (2b): H NMR(CDCl3, 400 MHz, TMS): δ 0.91 (6H, d, J=7.2 Hz), 2.12-2.17 (1H, m), 2.32-3.42 (2H, m), 3.30-3.42 (1H, m), 5.02 (2H, d, J=7.8 Hz), 5.08 (1H, s), 5.89-6.02 (1H, m).
1-(p-Chlorophenyl)-3-buten-1-ol (2c) $^1$H NMR(CDCl$_3$, 400 MHz, TMS): $\delta$ 2.16 (1H, s), 2.41-2.50 (2H, m), 4.71 (1H, dd, $J$=6.8 Hz), 5.13-5.17 (2H, m), 5.73-5.80 (1H, m), 7.26-7.32 (4H, m).

1-(p-Trifluoromethylphenyl)-3-buten-1-ol (2d) $^1$H NMR(CDCl$_3$, 400 MHz, TMS): $\delta$ 2.21 (1H, s), 2.57-2.43 (2H, m), 4.80 (1H, m), 5.18 (2H, m), 5.75-5.83 (1H, m), 7.47 (2H, d, $J$=8.2 Hz), 7.61 (2H, d, $J$=8.2 Hz).

1-(4-nitrophenyl)but-3-en-1-ol (2e) $^1$H NMR(CDCl$_3$, 400 MHz, TMS): $\delta$ 2.13 (1H, br), 2.42-2.49 (1H, m), 2.54-2.60 (1H, m), 4.86-4.89 (1H, m), 5.17-5.22 (2H, m), 5.74-5.84 (1H, m), 7.54 (2H, d, $J$=8.8 Hz), 8.21 (2H, d, $J$=8.8 Hz).

1-(p-Methoxyphenyl)-3-buten-1-ol (2f) $^1$H NMR(CDCl$_3$, 400 MHz, TMS): $\delta$ 1.94 (1H, bs), 2.50 (1H, bs), 2.50 (2H, m), 2.62-2.51 (2H, m), 4.69 (1H, t, $J$=6.6 Hz), 5.17-5.18 (2H, m), 5.80 (1H, m), 6.89 (2H, d, $J$=8.8 Hz), 7.27 (2H, d, $J$=8.8 Hz).

1-(p-Methylphenyl)-3-buten-1-ol (2g) $^1$H NMR(CDCl$_3$, 400 MHz, TMS): $\delta$ 1.94 (1H, bs), 2.33 (3H, s), 2.48-2.51 (2H, m), 4.69 (1H, t, $J$=6.6 Hz), 5.11-5.17 (2H, m), 5.76-5.81 (1H, m), 7.14 (2H, d, $J$=7.8 Hz), 7.24 (2H, d, $J$=7.8 Hz).

Undec-1-en-4-ol (2h) $^1$H NMR(CDCl$_3$, 400 MHz, TMS): $\delta$ 0.88 (3H, t, $J$=7.0 Hz), 1.28 (12H, bs), 1.44-1.48 (2H, m), 1.84 (1H, s), 2.11-2.17 (1H, m, one proton of CH$_2$), 2.27-2.32 (1H, m, one proton of CH$_2$), 3.62-3.66 (1H, m), 5.79-5.87 (1H, m).

1-Phenylpent-4-en-2-ol (2i) $^1$H NMR(CDCl$_3$, 400 MHz, TMS): $\delta$ 1.83 (1H, s), 2.20-2.26 (1H, m), 2.30-2.35 (1H, m), 2.72 (1H, dd, $J$=13.6 Hz), 2.81 (1H, dd, $J$=4.0 Hz), 3.87 (2H, m), 5.13-5.18 (2H, m), 5.86 (1H, m), 7.21-7.26 (3H, m), 7.29-7.34 (2H, m).

1-(furan-2-yl)but-3-en-1-ol (2j) $^1$H NMR(CDCl$_3$, 400 MHz, TMS): $\delta$ 1.93-2.12 (1H, br), 2.61-2.66 (2H, m), 4.76 (1H, t, $J$=6.1 Hz), 5.14-5.22 (2H, m), 5.74-5.84 (1H, m), 6.25 (1H, d, $J$=2.6 Hz), 6.33 (1H, q, $J$=2.6 Hz), 7.39 (1H, d, $J$=1.5 Hz).

