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Bismuth(III) Chloride or Triflate-Catalyzed Dienophilic Activity of α-Ethylenic Aldehydes and Ketones

Bernard Garrigues, Ferdinand Gonzaga,
Hélène Robert, and Jacques Dubac*

*Hétérochimie Fondamentale et Appliquée
(UPRES(A) 5069 CNRS), Université Paul-Sabatier,
118 route de Narbonne, 31062 Toulouse Cédex, France*

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The weak shielding of the 4f shell (lanthanoid contraction) and the relativistic effects responsible for the stabilization of 6s orbital (inert pair) confer to bismuth(III) a potential Lewis acidity, many complexes of which have been reported.[1] Curiously, the catalytic properties of bismuth compounds, in particular those of Bi(III) as Lewis acids, was developed only recently, although the applications in organic synthesis of the organobismuthanes derived from Bi(V) are well known.[2] Some recent results in this area, including some from our laboratory, concern the catalytic activity of Lewis acids derived from Bi(III) for Mukaiyama−aldol[3] and −Michael reactions,[3a,b] halosilane activation,[4] carbonyl-ene reaction,[5] and acylations,[6] especially Friedel−Crafts acylation.[6d,e] Catalytic properties of Bi(III) compounds are also known for other reactions like the oxidation of alkenes,[7] α-ketols,[8] or epoxides,[9] and for the Knoevenagel condensation.[10]

This new attraction to bismuth is understandable. Increasingly, catalysts and the processes using them should be consistent with ecological standards. Bismuth is the least toxic of the heavy elements.[11] Biochemistry,[12] toxicology,[13] and environmental effects[14] of bismuth compounds have been recently reported. Bismuth compounds are already used as industrial catalysts (manufacture of acrolein,[7a] acrylonitrile)[7b] and are employed in pharmaceutical products.[12]

Table 1. Diels−Alder Reactions Catalyzed by Various Lewis Acids

entry	reaction	catalyst (mol %)	experimental conditions[a]	product and isomers	% yield[b]
1	**1** + **4**	Sc(OTf)$_3$ (10)	0 °C; 12 h	**8** (89/11)[d]	96[c]
2	**1** + **4**	Bi(OTf)$_3$ (1)	0 °C; 4 h	**8** (93/7)[d]	87
3	**1** + **4**	BiCl$_3$ (10)	0 °C; 2 h	**8** (95/5)[d]	86
4	**2** + **5**	[TiCp*$_2$(H$_2$O)]-(OTf)$_2$	25 °C; 13 h	**9**	90[c]
5	**2** + **5**	Bi(OTf)$_3$ (0.1)	25 °C; 14 h	**9**	85
6	**2** + **5**	Bi(OTf)$_3$ (1)	25 °C; 3 h	**9**	82
7	**2** + **5**	BiCl$_3$ (10)	25 °C; 45 min	**9**	82
8	**2** + **6**	Yb (fod)$_3$ (1)	rt; 24 h	**10**	60[c]
9	**2** + **6**	Bi (0Tf)$_3$ (1)	25 °C; 3 h	**10**	69
10	**2** + **6**	BiCl$_3$ (10)	25 °C; 2 h	**10**	62
11	**3** + **7**	SmI$_2$ (5)	25 °C; 24 h	**11** (90/10)[e]	65[e]
12	**3** + **7**	Bi (OTf)$_3$ (1)	25 °C; 20 h	**11** (98/2)[e]	88
13	**3** + **7**	BiCl$_3$ (10)	25 °C; 15 h	**11** (97/3)[e]	61

[a] Solvent CH_2Cl_2, except entry 8 (none); 1 M solutions, diene and dienophile in equimolar amounts, except for entries 1−3 (diene 0.12 M, dienophile 0.4 M), and entry 11−13 (diene 1 M, dienophile 0.5 M). [b] Yields in isolated product. [c] References: entries 1,[15] 4,[16] 8,[17] 11.[18] [d] *endo*/*exo*. [e] 1,4/1,3 isomers.

We present here the first examples of Diels−Alder reactions catalyzed by bismuth(III) derivatives, bismuth trichloride, or bismuth tris(triflate), in comparison with some analogous Lewis acids well-known for their efficient catalytic activity. The reactivity of standard dienes, cyclopentadiene (**1**), 2,3-dimethylbutadiene (**2**), and isoprene (**3**) has been examined with four dienophiles, methyl vinyl ketone (**4**), ethyl vinyl ketone (**5**), acrolein (**6**), and methacrolein (**7**).

Results and Discussion

In the case of the Diels−Alder cycloaddition between **1** and **4**, scandium triflate (10% mol, 12 h, 96% yield) is a better catalyst than ytterbium or yttrium triflates.[15] Under the same conditions, 1% of Bi(OTf)$_3$ gave an 87% yield of **8** after 4 h (Table 1, entry 2), and 10% of BiCl$_3$ gave the same yield after only 2 h (entry 3). The *endo/exo* selectivity was a little higher (93/7 and 95/5, respectively) than with Sc(OTf)$_3$ (89/11).

The same two Bi-catalysts were compared with [TiCp*$_2$(H$_2$O)](OTf)$_2$ in the case of the reaction between **2** and **5**[16] (Table 1, entries 4−7). BiCl$_3$ (10% mol) led to a convenient result (45 min, 82% yield), and Bi(OTf)$_3$ proved more efficient than the Ti-catalyst; 0.1% of Bi(OTf)$_3$ and 2% of the Ti-catalyst gave a comparable result.

The bismuth catalysts were also found to be more efficient than an ytterbium catalyst, Yb(fod)$_3$. In the

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(1) Lange, K. C. H.; Klapötke, T. M. In *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*; Patai, S., Ed.; J. Wiley: New York, 1994; pp 315−366.

(2) (a) Barton, D. H. R. *Pure Appl. Chem.* **1987**, *59*, 937. (b) Finet, J. P. *Chem. Rev.* **1989**, *89*, 1487 and refences therein.

(3) (a) Wada, M.; Takeichi, E.; Matsumoto, T. *Bull. Chem. Soc. Jpn.* **1991**, *69*, 990. (b) Le Roux, C.; Gaspard-Iloughmane, H.; Dubac, J.; Jaud, J.; Vignaux, P. *J. Org. Chem.* **1993**, *58*, 1835. (c) Le Roux, C.; Gaspard-Iloughmane, H.; Dubac, J. *Bull. Soc. Chim. Fr.* **1993**, *130*, 832. (d) Le Roux, C.; Gaspard-Iloughmane, H.; Dubac, J. *J. Org. Chem.* **1994**, *59*, 2238. (e) Fontaine, E.; Baltas, M.; Escudier, J. M.; Gorrichon, L. *Mon. Chem.* **1996**, *127*, 519.

(4) (a) Labrouillère, M.; Le Roux, C.; Gaspard-Iloughmane, H; Dubac, J. *Synlett* **1994**, 723. (b) Labrouillère, M.; Le Roux, C.; Oussaid, A.; Gaspard-Iloughmane, H.; Dubac, J. *Bull. Soc. Chim. Fr.* **1995**, *132*, 522. (c) Montero, J. L.; Winum, J. Y.; Leydet, A.; Kamal, M.; Pavia, A. A.; Roque, J. P. *Carbohyd. Res.* **1997**, in press.

(5) Peidro, L.; Le Roux, C.; Laporterie, A.; Dubac, J. *J. Organomet. Chem.* **1996**, *521*, 397.

(6) (a) Dubac, J.; Le Roux, C.; Gaspard-Iloughmane, H. In *Progress in Organosilicon Chemistry*; Marciniec, B., Chojnowski, J., Eds.; Gordon and Breach: Basel, Switzerland, 1995; pp 325−343. (b) Le Roux, C.; Mandrou, S.; Dubac, J. *J. Org. Chem.* **1996**, *61*, 3885. (c) Le Roux, C.; Dubac, J. *Organometallics* **1996**, *15*, 4646. (d) Dubac, J.; Labrouillère, M.; Laporterie, A.; Desmurs, J. R. (Rhône-Poulenc Chimie) **1996**, *Eur. Pat. Appl.* EP 698,593 (FR Appl. 94/10,523, 24 Aug 1994) (*Chem. Abstr.* **1996**, *124*, 316758y). (e) Desmurs, J. R.; Labrouillère, M.; Dubac, J.; Laporterie, A.; Gaspard, H.; Metz, F. In *The Roots of Organic Development*; Desmurs, J. R., Ratton, S., Eds.; Elsevier: Amsterdam, The Netherlands, 1996, pp 15−28.

(7) (a) Ohara, T.; Sato, T.; Shimizu, N. In *Ullman's Encyclopedia of Industrial Chemistry*; Gerhartz, W., Ed.; VCH: Weinheim (Germany), 1985; Vol. A1, pp 149−160. (b) Langvardt, P. W. In *Ullman's Encyclopedia of Industrial Chemistry*; Gerhartz,W., Ed.; VCH: Weinheim (Germany), 1985; Vol. A1, pp 177−184.

(8) Le Boisselier, V.; Coin, C.; Postel, M.; Dunach, E. *Tetrahedron Lett.* **1995**, *51*, 4991.

(9) (a) Zevaco, T.; Dunach, E.; Postel, M. *Tetrahedron Lett.* **1993**, *34*, 2601. (b) Le Boisselier, V.; Dunach, E.; Postel, M. *J. Organomet. Chem.* **1994**, *482*, 119.

(10) Prajapati, D.; Sandhu, J. S. *Chem. Lett.* **1992**, 1945.

(11) Irwing-Sax, N.; Bewis, R. J. *Dangerous Properties of Industrial Materials*; Van Nostrand Reinhold: New York, 1989; pp 283, 284, 522, and 523.

(12) Dill, K.; McGown, E. L. In *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*; Patai, S., Ed.; J. Wiley: New York, 1994; pp 695−713.

(13) Wormser U.; Nir I. In *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*; Patai, S., Ed.; J. Wiley: New York, 1994; pp 715−723.

(14) Maeda, S. In *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*; Patai, S., Ed.; J. Wiley: New York, 1994; pp 725−759.

(15) Kobayashi, S.; Hachiya, I.; Araki, M.; Ishitani, H. *Tetrahedron Lett.* **1993**, *34*, 3755.

(16) Hollis, K. T.; Robinson, N. P.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 5464.

S0022-3263(97)00389-7 CCC: $14.00

reaction between **2** and **6**, Yb(fod)$_3$ (10% mol) was used without solvent at rt.[17] In 1 M dichloromethane solution with the same reagents, Bi(OTf)$_3$ (1% mol) and BiCl$_3$ (10% mol) led to an equivalent yield after a shorter time (Table 1, entries 8−10).

The activity of bismuth catalysts was compared with that of samarium(II) iodide for the reaction between **3** and **7**[18] (Table 1, entries 11−13). In this reaction, the use of a Lewis acid as catalyst strongly increase the 1,4-regioselectivity.[16] Although with SmI$_2$ this regioselectivity was already high (90%), with Bi-catalysis it increased up to 97−98%. Even though BiCl$_3$ appeared a little less active than SmI$_2$, Bi(OTf)$_3$ was much more efficient.

Finally, several other reactions between the dienes **1**−**3** and the dienophiles **4**−**7** have been carried out in dichloromethane as solvent, in the presence of Bi(OTf)$_3$ (1%), and led to the expected adducts in very good yields. For example, 2-methylbicyclo[2.2.1]-5-heptene-2-carboxaldehyde (**12**) (*endo*/*exo* = 5/95) was formed in 96% yield from **1** and **7** at 0 °C after 4 h, and 4-methyl-3-cyclohexen-1-yl methyl ketone (**13**) was isolated in 90% yield (0 °C; 24 h) from **3** and **4**.

The soft Lewis acidity of Bi(III) compounds, especially if the bismuth bears electronegative atoms,[19] results in low stability of carbonyl complexes.[1] An intramolecular complex in which the bismuth is coordinated to a carbonyl group has been recently isolated.[20] Other experiments have shown the Bi-acyl chloride interactions,[6e] that lead to effectively catalyzed acylation reactions.[6] An electrophilic assistance has been put forward with aldehydes and ketones involved in the Bi-catalyzed Mukaiyama−aldol, −Michael,[3] and carbonyl-ene reactions.[5]

The activation of α-carbonyl ethylenic dienophiles like **4**−**7** is promoted by the Lewis acid coordination with the carbonyl group.[21] The results presented here show that the two Bi(III) salts, BiCl$_3$ and especially Bi(OTf)$_3$, in which the Lewis acidity of bismuth is amplified by three strong electron-withdrawing groups, are strong, effective Lewis acids. At the same time, these catalysts are selective for [4 + 2] cycloadditions. We have not observed, for the dienes or for the dienophiles, the polymerization frequently involved with strong Lewis acids.[22]

Unlike BiCl$_3$, which is commercially available, the synthesis and the use of Bi(OTf)$_3$ requires some comments. Bismuth(III) triflate is a known compound, which has been prepared from bismuth trifluoroacetate or bismuth oxide.[23] These previous works have not reported the existence of hydrates, whereas the crystalline structure of a nonahydrate has been recently established.[24] A controlled dehydration between rt to 80 °C allowed us to identify three hydrates: Bi(OTf)$_3$·nH$_2$O, n = 9, 4, 2.[25] For temperatures higher than 80 °C, the dihydrate led a loss of weight, but a beginning of decomposition appeared; thus the pure anhydrous bismuth triflate has not been isolated. Unlike triflates of transition elements,[26] bismuth(III) triflate is not decomposed by water; therefore, it is recoverable after aqueous workup, and reusable, as we have shown (see Experimental Section).

Conclusion

The use of Bi(III) salts as Lewis acid catalysts has primarily concerned halides.[3−6] This work extends their field of application to [4 + 2] cycloadditions involving α-carbonyl ethylenic dienophiles. In comparison with other Sc-, Ti-, Sm-, or Yb-based efficient catalysts they show higher reactivity and selectivity. Bismuth (III) triflate, the strong catalytic activity of which we have also observed in the Mukaiyama−aldol reaction,[27] appears as a useful competitor to transition metal triflates,[26b] both because of its properties, i.e. catalytic power, water-stable and reusable catalyst, and also low cost.

The extension of this work into other Lewis acid mediated catalytic syntheses and the development of chiral bismuth-based catalysts is currently in progress.

Experimental Section

General. Dichloromethane was purified and dried using known procedures.[28] Bismuth(III) chloride and oxide, trifluoromethanesulfonic acid, dienes **2**, **3**, and dienophiles **4**−**7** were purchased and used without further purification. BiCl$_3$ was preserved in a desiccator. Cyclopentadiene (**1**) was distilled from its dimer just before use.

Typical Procedure. A solution of dienophile (16 mmol) in 8 mL of dichloromethane was introduced into a thermostated 100 mL double-walled flask, equipped with a septum inlet and a magnetic stirbar and connected to a drying agent (calcium chloride). The catalyst, bismuth triflate dihydrate (110 mg, 0.16 mmol) or bismuth chloride (504 mg, 1.6 mmol), was transferred in a glovebag to the reaction flask, and the mixture was agitated for 15 min. A solution of diene (16 mmol) in 8 mL of dichloromethane was added dropwise, and the reaction was kept under agitation during the time indicated in the table. The reaction mixture was quenched with 10 mL of a saturated sodium carbonate aqueous solution. The layers were separated, and the aqueous layer was washed three times with 10 mL of dichloromethane. The organic layers were combined, dried over sodium sulfate, and concentrated under reduced pressure. The crude product was analyzed according to previously described methods;[15−18] in particular, all compounds obtained had ^{1}H NMR spectra identical to those previously reported: **8**,[29] **9**,[16] **10**,[16] **11**.[30]

The isomers of adducts **8** and **11** were identified from products obtained by thermal Diels−Alder addition (**8**: *endo*/*exo* = 62/38;[31] **11**: 1,4/1,3 isomers = 70/30).[16] Their ratios were determined by GC with *n*-alkanes as internal standards.

Bismuth(III) Trifluoromethanesulfonate. Bismuth triflate was prepared from previous described procedure from bismuth oxide or bismuth(III) acetate.[23] The solid obtained was heated at 60 °C under reduced pressure (0.1 mmHg) until a constant weight was obtained. Elemental analysis was in agreement with a mixture of hydrated forms of bismuth tri-

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[17] Danishefsky, S.; Bernardski, M. *Tetrahedron Lett.* **1985**, *26*, 2507.

[18] Van de Weghe, P.; Collin, J. *Tetrahedron Lett.* **1994**, *35*, 2545.

[19] (a) Reese, A. L.; McMartin, K.; Miller, D.; Wickham, P. P. *J. Org. Chem.* **1973**, *38*, 764. (b) Nakamura, E.; Shimada, J.; Kuwajima, I. *Organometallics* **1985**, *4*, 646.

[20] Murafuji, T.; Mutoh, T.; Satoh, K.; Tsunenari, K. J. *Organometallics* **1995**, *14*, 3848.

[21] (a) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; J. Wiley: New York, 1976; pp 161−165. (b) Houk, K. N. *J. Am. Chem. Soc.* **1973**, *95*, 4092.

[22] (a) Brandup, J.; Immergut, E. H. In *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989; pp 295−363. (b) Liao, S.; Yu, S.; Chen, Z.; Yu, D. *J. Mol. Catal.* **1992**, *72*, 209.

[23] (a) Singh, S.; Verma, A. R. D. *Ind. J. Chem.* **1983**, *22A*, 814. (b) Niyogi, D. G.; Singh, S.; Gill, S.; Verma, R. D. *J. Fluorine Chem.* **1990**, *48*, 421.

[24] Frank, W.; Reiss, G. J.; Schneider, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2416.

[25] Louër, M.; Le Roux, C.; Dubac, J. To be published.

[26] (a) Kowall, T.; Foglia, F.; Helm, L.; Merbach, A. E. *Chem. Eur.* **1996**, *2*, 285. (b) Kobayashi, S. *Synlett* **1994**, 689; and refences therein.

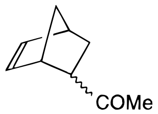
[27] Le Roux, C.; Robert, H.; Laporterie, A.; Dubac, J. XIth International Symposium on Organosilicon Chemistry, Université Montpellier II, 1−6 Sept 1996, Abstract OC5.

[28] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1992.

[29] Laszlo, P.; Schleyer, P. *J. Am. Chem. Soc.* **1963**, *85*, 2709.

[30] Van de Weghe, P. Thesis, Université Paris XI, Orsay, 1995.

[31] Dinwiddie, J. G., Jr.; McManus, S. P. *J. Org. Chem.* **1965**, *30*, 766.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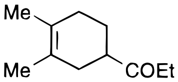
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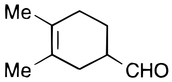
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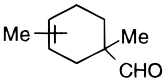
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flate. Another heating between 60 °C and 80 °C under reduced pressure of this crude powder led to a loss of weight, with formation of a low hydrated form of bismuth triflate, $Bi(OTf)_3\cdot 2H_2O$. Anal. Calcd for $C_3H_4BiF_9O_{11}S_3$: C, 5.20; H, 0.58; Bi, 30.19; F, 24.70; S, 13.90. Found: C, 5.25; H, 0.67; Bi, 30.23; F, 24.71; S, 13.92. ^{13}C NMR (CD_3COCD_3): 120 ppm (from TMS), quartet, ^1J ($^{13}C/^{19}F$) = 321 Hz; ^{19}F NMR (CD_3COCD_3): 0.84 ppm (from CF_3COOH); IR (nujol), ν (cm^{-1}): 3450−3550 (mb), 1230−1290 (vs), 1180 (s), 1034 (s), 1028 (sh), 650 (sh), 643 (s).

The catalytic power of these various hydrated forms of bismuth triflate for the described reactions was comparable.

An aqueous suspension (40 mmol L^{-1}) of bismuth triflate dihydrate was agitated over 24 h at rt and filtered and the resulting powder heated at 80 °C under reduced pressure. The product obtained gave elemental analysis and NMR spectra (^{13}C and ^{19}F) identical to those of the starting material. Their catalytic activity, compared for two reactions (Table 1, entries 2 and 12) is analogous.

The recovery of a substantial amount of bismuth triflate in a 5% molar catalytic experiment from **2** and **5** was carried out as above, by filtration after reaction and aqueous workup. The catalytic activity of the recovered bismuth triflate was unchanged.

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