Lithium Cobalt–Bis-Dicarbollide: A Novel Lewis Acid Catalyst for the Conjugate Addition of Silyl Ketene Acetals to Hindered α,β-Unsaturated Carbonyl Compounds

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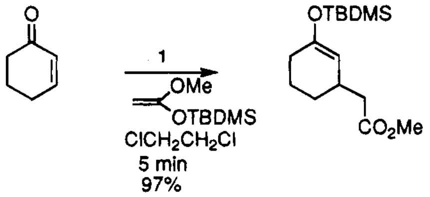
Summary: The novel Lewis acid, lithium cobalt–bis-dicarbollide (**1**), in which the lithium ion is weakly coordinated to the $Co(B_9C_2H_{11})_2^{1-}$ anion, is an effective, soluble catalyst for Mukaiyama–Michael reactions.

The limitations associated with the conjugate addition of silyl ketene acetals to α,β-unsaturated carbonyl systems under either conventional conditions (thermal and Lewis acid catalyzed)[1] or ultrahigh pressure[2] led us to explore the use of concentrated solutions of lithium perchlorate in diethyl ether[3] for promoting sensitive, sterically demanding Mukaiyama–Michael reactions. We report below on the use of lithium cobalt–bis-dicarbollide $[LiCo(B_9C_2H_{11})_2]$ (**1**)[4] as a mild and efficient Lewis acid for catalyzing the conjugate addition of silyl ketene acetals to α,β-unsaturated carbonyl compounds (eq 1).

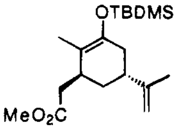
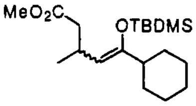
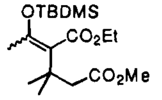
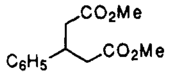
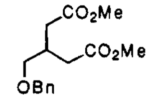


(1)

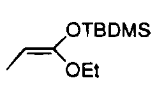
In searching for a substitute for lithium perchlorate in diethyl ether, we focused on anions that are more weakly coordinating than perchlorate, tetrafluoroborate, and hexafluorophosphate[5] which would presumably impart enhanced Lewis acidity to the cationic metal complex. In view of the ready solubility of lithium cobalt–bis-dicarbollide (**1**) in a number of organic solvents,[6] we chose to examine the conjugate addition of 1-methoxy-1-((*tert*-butyldimethylsilyl)oxy)ethylene to α,β-unsaturated enones in the presence of **1**. Addition of 10 mol % of **1**[7] to a 0.1 M solution of cyclohexenone in 1,2-dichloroethane containing 2.0 equiv of silyl ketene acetal gave rise (5 min) to a 97% yield of 1,4-addition product (eq 1). The reaction proceeds equally fast in diethyl ether or methylene chloride in the presence of 10 mol % of **1**. In the absence of catalyst there is no reaction.

Encouraged by the above result, a number of substrates were investigated (Table 1). Reactions are typically carried out at ambient temperature and pressure in the presence of 10 mol % of **1** in 1,2-dichloroethane. Reaction times range from several minutes to a few hours, and excellent yields are obtained ranging from 86 to 95%. The general conditions outlined in Table 1 could also be employed with the substituted silyl ketene acetals **2** and **3**. Treatment of a 0.1 M solution of cyclohexenone in 1,2-dichloroethane with 2.0 equiv of **2** in the presence of 10 mol % of **1** gave rise (5 min) to a 98% yield of the 1,4-adduct **4**. Under identical conditions employing cyclohexenone and the more substituted silyl ketene acetal **3**, the reaction required 1 h to go to completion giving rise to **5** in 99% yield.

Table 1. Lithium Cobalt–Bis-Dicarbollide Catalyzed Conjugate Addition of 1-Methoxy-1-((*tert*-butyldimethylsilyl)oxy)ethylene to α,β-Unsaturated Carbonyl Compounds[a]

product	time	%yield[b]
	5 min	99%
	10 min	94%
	24 h	84%[c]
	25 min	86%
	30 min	93%

[a] All reactions were conducted at ambient temperature and pressure employing a 0.1 M solution of substrate in 1,2-dichloroethane, 10 mol % $LiCo(B_9C_2H_{11})_2$, and 2.0 equiv of silyl ketene acetal. [b] Isolated yields. [c] Ca. 5% of the 1,2-adduct was isolated.



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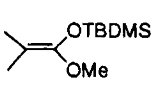

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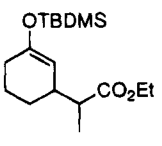

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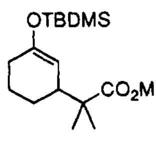

5

In a number of cases, particularly in sterically encumbered enones, the major product was found to be the

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[1] Kita, Y.; Segawa, J.; Haruta, J.; Fujii, T.; Tamura, Y. *Tetrahedron Lett.* **1980**, *21*, 3779. Saigo, K.; Osaki, M.; Mukaiyama, T. *Chem. Lett.* **1976**, 163. Danishefsky, S.; Vaughan, K.; Gadwood, R.; Tsuzuki, K. J. *J. Am. Chem. Soc.* **1981**, *103*, 4136. RajanBabu, T. V. *J. Org. Chem.* **1984**, *49*, 2083. Mukaiyama, T.; Tamura, M.; Kobayashi, S. *Chem. Lett.* **1986**, 1817. Otera, J.; Wakahara, Y.; Kamei, H.; Sato, T.; Nozaki, H.; Fukuzumi, S. *Tetrahedron Lett.* **1991**, *21*, 2405. Sato, T.; Wakahara, Y.; Otera, J.; Nozaki, H.; Fukuzumi, S. *J. Am. Chem. Soc.* **1991**, *113*, 4028.

[2] Matsumoto, K. *Angew. Chem., Int., Ed. Engl.* **1980**, *19*, 1013. Bunce, R. A.; Schlecht, M. F.; Dauben, W. G.; Heathcock, C. H. *Tetrahedron Lett.* **1983**, *24*, 4943.

[3] Grieco, P. A.; Cooke, R. J.; Henry, K. J.; VanderRoest, J. M. *Tetrahedron Lett.* **1991**, *32*, 4665.

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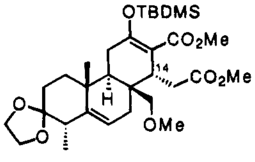
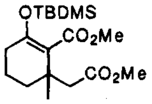
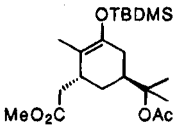
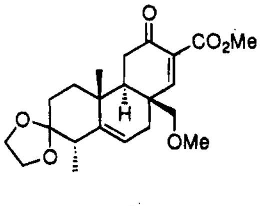
Table 2. Lithium Cobalt–Bis-Dicarbollide Catalyzed Conjugate Addition of 1-Methoxy-1-((*tert*-butyldimethylsilyl)oxy)ethylene to Enones in the Presence of HMPA[a]

product	time	%yield[b]
	32 h	96[c]
	24 h	86[d]
	25 h	95[e]

[a] All reactions were conducted at ambient temperature and pressure employing 0.1 M solution of substrate in 1,2-dichloroethane containing 10 mol % HMPA, 10 mol % $LiCo(B_9C_2H_{11})_2$, and 2.0 equiv of silyl ketene acetal unless noted otherwise. [b] Isolated yields. [c] The product contains ca. 10% of the C(14) epimeric 1,4-addition product. [d] Product contains ca. 15% of the 1,2-adduct. [e] 10 mol % DMPU was employed in place of HMPA.

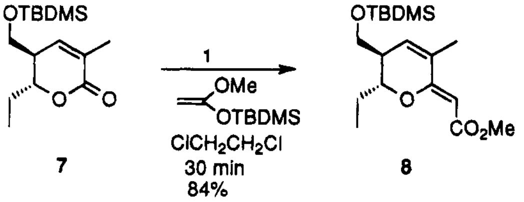
result of 1,2-addition. Upon treatment (20 min) of a 0.1 M solution of enone **6** in 1,2-dichloroethane with 2.0 equiv



6

of 1-methoxy-1-((*tert*-butyldimethylsilyl)oxy)ethylene in the presence of 10 mol % of **1**, a 95% yield of a 6:1 mixture of the 1,2- to 1,4-addition products was obtained. *In general, the ratio of the 1,2- to 1,4-adducts could be dramatically reversed by the addition of 10 mol % of HMPA* (Table 2). Thus, in the case of substrate **6**, addition of 10 mol % of HMPA to the above reaction mixture (Table 2, entry 1) gives rise (96%) to exclusive 1,4-addition. Note that in the cases where HMPA is employed to promote 1,4-addition, the reactions are slowed appreciably.

Lithium cobalt–bis-dicarbollide (**1**) also catalyzes the 1,4-addition of silyl ketene acetals to α,β-unsaturated esters (Table 1); however, it failed on an unsaturated lactone.[7] For example, treatment of a 0.1 M solution of **7**



in 1,2-dichloroethane with 2.0 equiv of silyl ketene acetal in the presence of 10 mol % of **1** afforded (30 min) an 84% yield of **8** as the sole product. When 10 mol % of HMPA was added to the above reaction in an attempt to promote 1,4-addition, no reaction was observed.

Acknowledgment. This investigation was supported by a Public Health Service Research Grant from the National Institutes of General Medical Sciences (GM 33605). We thank Bart Wild for preparing **1**.

Supplementary Material Available: Experimental and characterization data including NMR spectra and a stereoview of the $Co(B_9C_2H_{11})_2^{1-}$ anion (29 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal and can be ordered from the ACS; see any current masthead page for ordering information.

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(4) According to Chemical Abstracts nomenclature, the correct name for **1** is Lithium, cobaltate(1−), bis[(7,8,9,10,11-η)-undecahydro-7,8-dicarbaundecarborato(2−)]. The $B_9C_2H_{11}^{2-}$ dianion was given the common name "dicarbollide" ion by Fred Hawthorne who first discovered the interesting metal complexes of this ligand (Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F., Jr.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879). For a stereoview of the $Co(B_9C_2H_{11})_2^{1-}$ anion which was obtained from single-crystal X-ray analysis of **1** (Molecular Structure Report No. 94068, Indiana University), see the supplementary material.

(5) The chemistry of weakly coordinating anions has been the subject of much interest recently (Strauss S. H. *Chem. Rev.* **1993**, *93*, 927). The $B_{11}CH_{12}^{1-}$ anion and related carborane anions have been extensively studied in this regard (Liston, D. J.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 6643).

(6) The solubility of a number of salts of the cobalt–bis-dicarbollide anion has been noted previously [Plesek, J.; Base, K.; Mares, F.; Hanousek, F.; Stíbr, B.; Hermánek, S. *Collect. Czech. Chem. Commun.* **1984**, *49*, 2776].

(7) The lithium cobalt–bis-dicarbollide (**1**) was prepared from sodium cobalt–bis-dicarbollide (available from Strem Chemicals, Newburyport, MA 01950) by passing through a column of Mallinckrodt Amberlite IR-120H C.P. sulfonated polystyrene cation exchange resin which had been previously treated with excess aqueous lithium chloride. Prior to use, **1** was dried for 12 h under vacuum at 150 °C. The lithium cobalt–bis-dicarbollide has good shelflife; however, it will hydrate upon exposure to moisture. The cesium salt is available from KATCHEM, Ltd., El Krasnohorske 6, 110 00 Praha 1, Czech Republic.