Samarium(III) Tris(2,6-di-*tert*-butyl-4-methylphenoxide): Preparation, Properties, and Catalytic Activity in the Michael Type Reaction

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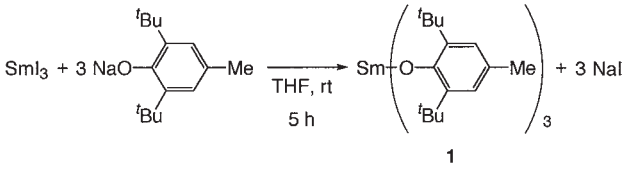
Samarium(III) tris(2,6-di-*tert*-butyl-4-methylphenoxide) (**1**), which is a highly coordinatively unsaturated complex, was prepared by the reaction of samarium(III) iodide with sodium 2,6-di-*tert*-butyl-4-methylphenoxide, and the crystal structure of its acetonitrile complex was determined by X-ray analysis. Complex **1** catalyzed the sequential Michael-Michael-aldol reaction of 3,3-dimethyl-2-butanone with benzalacetophenone.

Lanthanide elements are capable of forming complexes with high coordination numbers, and this property is one of the origins of the unique reactivity of lanthanide reagents in organic transformations.[1] Trivalent samarium ion can function as Lewis acid to promote a variety of reactions such as aldol reaction,[2] Diels–Alder reaction,[3] Meerwein reduction,[4] Tishchenko reaction,[5] and tandem Michael–aldol reaction.[6] Shibasaki *et al.* reported that optically active $LaLi_3$tris(binaphthoxide) (LLB) and related complexes effectively catalyzed asymmetric reactions such as nitroaldol reaction and Michael addition reaction. Furthermore, they recently found that the similar complexes promoted the asymmetric direct aldol reaction of unmodified ketones with aldehydes.[7] The highly sophisticated catalysts used in those reactions involve the metal centers coordinated with six phenoxide moieties. On the other hand, tri-coordinate lanthanide–phenoxide complexes[8] have been rarely used in organic synthesis, despite their anticipated high catalytic activity. Here we wish to report some preliminary results of the preparation of a samarium(III) triphenoxide complex and its use in the Michael type reaction of carbonyl compounds with benzalacetophenone.

For the preparation of the desired highly coordinatively unsaturated phenoxide complexes, we chose 2,6-di-*tert*-butyl-4-methylphenol as a sterically hindered phenoxide component. At first, samarium(III) tris(2,6-di-*tert*-butyl-4-methylphenoxide) (**1**) was prepared by the reaction of anhydrous samarium(III) iodide with three molar equivalents of sodium 2,6-di-*tert*-butyl-4-methylphenoxide in dry THF (Scheme 1).



Scheme 1.

The NMR analysis of this product indicates that the complex contains no coordinated THF or water.[9] Analysis of samarium content by chelatometric titration suggests that the ratio of the phenoxide ligand to samarium metal is three. Attempted recrystallization from THF to obtain single crystals for X-ray analysis was unsuccessful. Recrystallization from a mixed solvent of THF and acetonitrile gave yellow cubes, which were subjected to X-ray analysis.[10] Its molecular structure and selected coordination lengths and angles are shown in Figure 1. It is clear that this complex **2** contains three aryloxide ligands and two acetonitrile molecules to form a penta-coordinate structure. A characteristic feature of this molecular structure is manifested in the N1–Sm1–N2 bond angle (67.2 °). The extremely small bond angle in comparison with others in the same complex is ascribed to the limited coordination sphere for the acetonitrile molecules. It is noted that complex **2** liberated the coordinated acetonitriles on standing in vacuum at room temperature for a few hours to form complex **1**. This fact strongly supports that the initially formed complex **1** is a tri-coordinated complex without any solvent ligands.

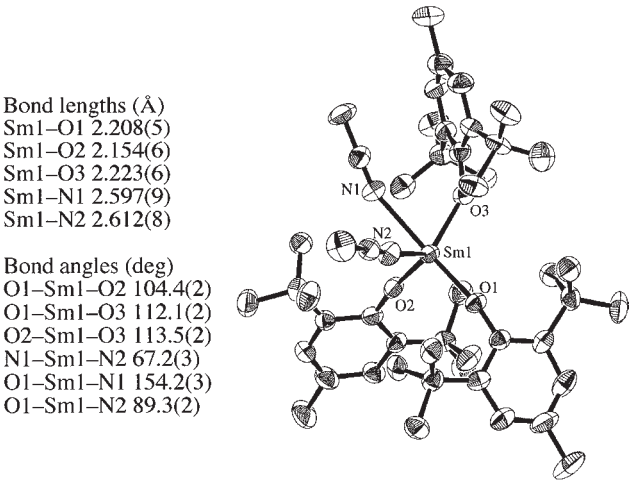
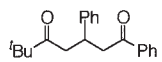
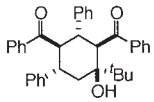
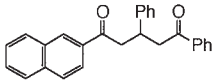
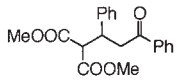
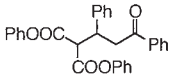
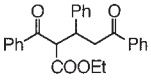
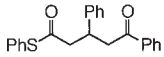


Figure 1. ORTEP drawing of complex **2** with 30% probability thermal ellipsolds.

The catalytic activity of complex **1** was tested for the direct Michael addition of several representative carbonyl compounds having methyl group or methylene component to benzalacetophenone. The reactions were carried out by employing exactly 1 : 1 ratio of the carbonyl compounds and benzalacetophenone except a few cases. The results are summarized in Table 1. The addition reaction of 3,3-dimethyl-2-butanone to benzalacetophenoe proceeded in THF, toluene, hexane, or dichloromethane to give 6,6-dimethyl-1,3-diphenyl-1,5-heptanedione (**3**) and 2,4-dibenzoyl-3,5-diphenyl-1-*tert*-butylcyclo-hexanol (**4**)[11] (entries 1, 2, 6, and 7). It is reasonable to consider that the latter compound **4** is produced via sequential Michael– Michael–aldol reaction. Thus, the initially formed Michael adduct **3** reacts with another molecule of benzalacetophenone, followed by intramolecular aldol reaction, to afford compound **4**. This compound was obtained as major product when the reaction was carried out at 0 °C using 3,3-dimethyl-2-butanone and benzalacetophenone in 1 : 2 ratio (entry 5).

On the other hand, the reaction in acetonitlrile or nitromethane resulted in the formation of complex mixture (entries 8 and 9).

Table 1. Reactions of Michael donors with benzalacetophenone in the presence of catalyst **1**[a]

Entry	Michael donor	Solvent	Time / h	Products / %[b]			
1	^{t}BuCOCH$_3$	THF	7		**3** (57)		**4** (21)
2	"	Toluene	7	"	**3** (62)	"	**4** (19)
3[c]	"	Toluene	10	"	**3** (83)	"	**4** (7)
4[d]	"	Toluene	4	"	**3** (27)	"	**4** (73)
5[e]	"	Toluene	5	"	**3** (15)	"	**4** (84)
6	"	Hexane	7	"	**3** (45)	"	**4** (27)
7	"	CH_2Cl_2	30	"	**3** (70)	"	**4** (15)
8	"	CH_3CN	30	complex mixture			
9	"	CH_3NO_2	10	complex mixture			
10	(β-naphthyl)COCH$_3$	THF	8		(78)		
11[f]	$CH_2(CO_2Me)_2$	THF	24		(85)		
12	$CH_2(CO_2CH_2Ph)_2$	THF	66		(55)		
13	$PhCOCH_2CO_2Et$	THF	66		(58)		
14[c]	$PhSCOCH_3$	Toluene	10		(94)		

[a] The reactions were carried out at rt by using 1 mmol of Michael donor, 1 mmol of benzalacetophenone, and 10 mol% of catalyst **1**, unless otherwise stated. [b] Yields were calculated based on Michael donor. [c] The reaction was carried out at 100 °C. [d] Two equivalents of benzalacetophenone were used. [e] The reaction was carried out at 0 °C by using 1 mmol of 3,3-dimethyl-2-butanone and 2 mmol of benzalacetophenone. [f] The reaction was carried out by using 1.5 mmol of Michael donor, 1 mmol of benzalacetophenone, and 20 mol% of catalyst **1**.

These results are ascribed to that the used solvent CH_3CN or CH_3NO_2 also reacted with benzalacetophenone.[12] Other carbonyl compounds including active methylene compounds reacted with benzal-acetophenone to give the corresponding Michael adduct in good to high yield. It is noted that the Michael reaction of β-naphthylmethyl ketone and thioacetic acid *S*-phenyl ester proceeded smoothly to give 1-β-naphthyl-3,5-diphenyl-1,5-pentanedione and 1,3-diphenyl-5-thiophenyl-1,5-pentanedione (entries 10 and 14).

In summary, we prepared samarium(III) tris(2,6-di-*tert*-butyl-4-methylphenoxide) (**1**) and found that the complex catalyzed the Michael type reaction of some representative carbonyl compounds to benzalacetophenone.

Dedicated to Prof. Teruaki Mukaiyama on the occasion of his 75th birthday.

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9 ^{1}H NMR (C_6D_6, 400 MHz, 25 °C) δ 0.86 (s, *t*Bu, 54H), δ 2.84 (s, Me, 9H), δ 8.17 (s, Ar-H, 6H).

10 Crystal data of **2**: C53H81O3N4Sm, M = 972.65, triclinic, space group *P*1 (#2), a = 12.627(9) Å, b = 21.20(1) Å, c = 11.230(4) Å, α = 91.02(3)°, β = 109.84(3)°, γ = 76.00(3)° V = 2736(2) cm^3, Z = 2, Dcala = 1.180 g/cm^{-3}, μ(MoKα) = 11.16 cm^{-1}, T = 278 K, R = 0.085, Rw = 0.142.

11 4-Dibenzoyl-3,5-diphenyl-1-*tert*-butylcyclohexanol (**4**); mp 222–223 °C (AcOEt/hexane (1 : 5)). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 0.15 (s, *t*Bu, 9H), δ 2.17 (dd, J = 3.42, 13.90 ,Hz, 1H), δ 2.48 (dd, J = 13.90, 13.40 Hz, 1H), δ 3.94 (dd, J = 11.24, 11.44 Hz, 1H), δ 3.97 (ddd, J = 3.42, 11.44, 13.40 Hz, 1H), δ 4.07 (d, J = 11.72 Hz, 1H), δ 4.15 (dd, J = 11.24, 11.72 Hz, 1H), δ 5.35 (s, OH, 1H), δ 6.89–7.56 (m, 20H). IR (KBr) 3460 (s), 1670 (s).

12 In a separate experiment, we found that benzalacetophenone on treatment with 1 equivalent of complex **1** in CH_3CN at room temperature for 24 h lead to 1-cyanomethyl-1,3-diphenyl-2-propen-1-ol in 60% yield. The reaction of benzal-acetophenone in CH_3NO_2 under similar conditions afforded 4-nitro-1,3-diphenyl-1-butanone in 98% yield.