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A Facile Generation of Organosamarium η^3-Allyl Complexes by Reductive Cleavage of Allylic Ethers with $(C_5Me_5)_2Sm(THF)_n$

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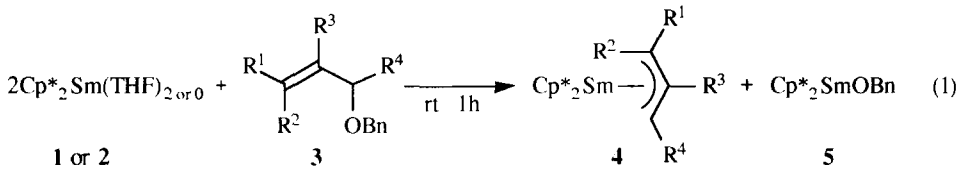
Abstract: Reductive C-O bond cleavage of allylic benzyl ethers with two equivalents of $(C_5Me_5)_2Sm(THF)_n$ (n=2 or 0) takes place selectively to generate $(C_5Me_5)_2Sm(\eta^3$-allyl) complexes in high yields along with equimolar amounts of the samarium benzyloxide.

Allylic organometal reagents have played an important role in organic synthesis.[1] Of the allylic metals, chemical property of lanthanide allyl complexes has been less known, compared to transition metal analogues. They are usually generated *in situ* by halogen-metal exchange using samarium diiodide[2] or cerium amalgam[3] and by transmetallation like allylic lithium with cerium trichloride[4] and allylic palladium with samarium diiodide.[5] In addition, biscyclopentadienyl(Cp_2) and bispentamethyl-cyclopentadienyl(Cp^*_2)lanthanide allyl complexes have been also prepared from alkenes with $[Cp^*_2LnH]_2$ (Ln=La, Nd)[6] or Cp^*_2Sm[7], allylmagnesium bromide with Cp_2LnCl (Ln=Sm, Ho, Er)[8], and allylic chlorides with Cp_2Sm.[9] However, structure of the allylic lanthanides has been unambiguously determined in few cases.[6, 7, 10]

For the preparation of Cp^*_2Sm(allyl) complexes, allylic ethers would be potentially useful precursors, since they are able to coordinate from the internal oxygen to the low-valent lanthanide metal , even in the case of the readily available solvated complex, $Cp^*_2Sm(THF)_2$, which is followed by reductive cleavage of the C-O bond to yield the allylic complexes and alkoxides.[11] We describe herein a new synthetic method for the organosamarium η^3-allyl complexes from allylic ethers and determination of their structures by NMR.

When allyl benzyl ether (**3a**) was added to a solution of two equivalents of $Cp^*_2Sm(THF)_2$ (**1**) in toluene, the colour of the mixture changed immediately to deep red. On quenching with dilute hydrochloric acid after stirring for 2 h at room temperature, benzyl alcohol was obtained in 83% yield along with **3a** (10%) and Cp*H (>99%), but allyl alcohol was not detected. In the gas phase, propene was detected by GLC, indicating the selective C-O bond cleavage of allylic ether, not of benzylic ether. Similar results were obtained in the reaction using various solvents such as cyclohexane, benzene, THF, and hexane.[12] Then the reaction was carried out in an NMR tube with cyclohexane-d_{12} to determine the intermediate. Two major sets of signals in ^1H and ^{13}C NMR were observed in nearly equal intensities together with minor signals of **3a**, one of which was assignable to $Cp^*_2Sm(\eta^3$-allyl) (**4a**) and the other to $Cp^*_2Sm(OCH_2Ph)$ (**5**).[13] In addition, the reaction of nonsolvated complex, Cp^*_2Sm (**2**), gave the η^3-allyl complex **4a** and benzyloxide **5** quantitatively. But NMR spectra of **4a** generated from **1** and **2** are different. In the former case four terminal

protons of the allyl moiety and two C5*Me*5 appeared as one signal at δ 5.70 and δ 1.16, respectively, whereas *anti*-CH_2 and *syn*-CH_2 were separated at δ 7.09 and 3.65, respectively and two signals for C5*Me*5 were split at δ 1.24 and 1.04 in the latter reaction. Similar difference between the two was also observed in ^{13}C NMR spectra.[13] These results indicate clearly that **4a** generated from **1** is a fluxional η^3-allyl complex, being in equilibrium with η^1-allyl caused by the coordination of THF, but on the other hand **4a** formed from **2** is a static η^3-allyl complex.[7]



a; R^1=R^2=R^3=R^4=H
b; R^1=Me, R^2=R^3=R^4=H
c; R^1=R^2=R^3=H, R^4=Me
d; R^1=Ph, R^2=R^3=R^4=H
e; R^1=R^2=H, R^3=Me, R^4=H
f; R^1=Me, R^2=R^3=H, R^4=Me
g; R^1=R^2=Me, R^3=R^4=H
h; R^1=R^2=Me, R^3=H, R^4=Me

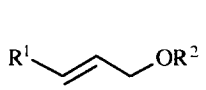
Table 1. Reaction of allylic benzyl ethers **3** with $(C_5Me_5)_2Sm(THF)_2$ (**1**) or $(C_5Me_5)_2Sm$ (**2**)

Run	Allylic Benzyl Ether	Samarium Complex	Solvent[a]	Product[b]	Yield(%)[c]
1	**3a**	**1**	A	**4a**[d]	82
2	**3a**	**2**	B	**4a**[e]	quant.
3	**3b**	**1**	A	**4b**[d]	86
4	**3b**	**2**	A	**4b**[e]	quant.
5	**3c**	**1**	A	**4b**[d]	80
6	**3d**	**1**	A	**4d**[d]	95
7	**3d**	**2**	B	**4d**[e]	quant.
8	**3e**	**1**	B	**4e**[d]	86
9	**3e**	**2**	B	**4e**[e]	quant.
10	**3f**	**1**	A	**4f**[e]	82
11	**3f**	**2**	A	**4f**[e]	quant.
12	**3g**	**1**	B	**4g**[d]	80[f]
13	**3h**	**1**	B	no reaction	

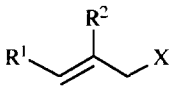
[a] A: cyclohexane-d_{12}, B: benzene-d_6. [b] Equimolar amount of **5** was also formed. [c] Determined by ^1H NMR after stirring for 1h at room temperature. [d] A fluxional η^3-allyl complex. [e] A static η^3-allyl complex. [f] Measured after 20 h.

The reaction of other allylic benzyl ethers **3** with **1** or **2** was carried out in the sealed tube and monitored by NMR (Eq. 1). These results are summarized in Table 1. Mono- and di-substituted allylic ethers **3b-g** were converted to the corresponding η^3-allyl complexes **4b-g** in high yields (runs 3-12). Crotyl ether **3b** and 1-methylallyl ether **3c** gave the same η^3-allyl complex **4b** as expected (runs 3 and 5). However trisubstituted allylic ether **3h** remained unchanged (run 13). With respect to the structure of the η^3-allyl complexes **4**, the reaction with **2** afforded static η^3-allyl complexes wherein the terminal methylenes were split into anti and syn protons as described above. In contrast, equivalence of the methylene protons proved a fluxional structure in the reaction with **1**. The complex **4f**, however, showed the same spectra in the two cases, being probably a static η^3-allyl complex (runs 10 and 11).[14]

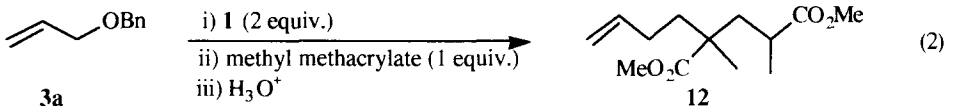
Other leaving groups on the allylic moiety instead of benzyl ether were investigated. Cinnamyl methyl ether (**6**) and diallyl ether (**7**) reacted with **1** to yield the complexes **4d** and **4a**, respectively, together with the corresponding samarium alkoxides quantitatively. Crotyl methoxymethyl ether (**8**) and crotyl acetate (**9**) were changed to very complex mixtures on treatment with **1**, in which no signals assignable to **4b** were observed in ^{1}H NMR spectra. The reaction of allyl chloride (**10**) and 3-chloro-2-methylpropene (**11**) with **1** in C_6D_6 took place rapidly, but minor signals of **4a** and **4e**, compared to those of $Cp^*_2SmCl(THF)$, were observed. The reaction with more reactive complex **2** gave rise to untractable mixtures. The allylic compounds **8-11** seem to be too reactive to **1** and **2** under the present conditions.



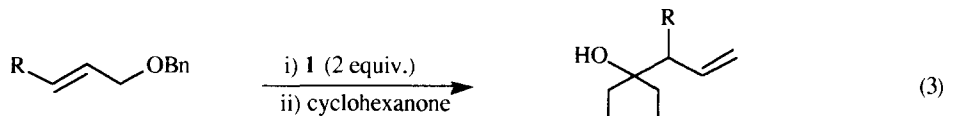
6; R^1=Ph, R^2=Me
7; R^1=H, R^2=$CH_2CH{=}CH_2$



8; R^1=Me, R^2=H, X=OCH_2OMe
9; R^1=Me, R^2=H, X=OAc
10; R^1=R^2=H, X=Cl
11; R^1=H, R^2=Me, X=Cl



3a **12** (2)



3b; R=Me
d; R=Ph

13b, **d** (3)

Then the generation of the η^3-allyl complexes **4** was further confirmed by the subsequent reaction with carbonyl compounds. Treatment of **3a** with **1** in toluene for 1h at room temperature, followed by addition of methyl methacrylate gave dimethyl 2-(3-butenyl)-2,4-dimethylglutarate (**12**) in 45% (Eq. 2).[15] The reaction

of **4b**, generated from **3b** and **1**, with cyclohexanone afforded branched homoallylic alcohol **13b** in quantitative yield, but corresponding linear homoallylic alcohol was not formed (Eq. 3). Similarly, the alcohol **13b** was exclusively obtained starting from **3c**. The allylic ether **3d** was also converted to the alcohol **13d** quantitatively.

Thus, the reductive cleavage of allylic ethers with $Cp^*_2Sm(THF)_n$ provides an efficient route to structurally defined organosamarium η^3-allyl complexes. Isolation of the complexes and their synthetic application are under investigation.

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12. In hexane, the mixture seems to deteriorate slightly on standing.
13. **4a**: fluxional: ^{1}H NMR (C_6D_{12}) δ 15.25 (1H, br s, CH), 5.70 (4H, v br s, $2CH_2$), 1.16 (30H, s, $2C_5Me_5$); ^{13}C NMR (C_6D_{12}) δ 178.0 (CH), 116.2 ($2C_5Me_5$), 20.9 ($2CH_2$), 16.6 ($2C_5\mathit{Me}_5$): static: ^{1}H NMR (C_6D_6) δ 15.75 (1H, br s, CH), 7.09 (2H, br s, 2anti-C*H*H), 3.65 (2H, br s, 2syn-CH*H*), 1.24 (15H, s, C_5Me_5), 1.04 (15H, s, C_5Me_5); ^{13}C NMR (C_6D_6) δ 176.6 (CH), 116.6 (C_5Me_5), 114.7 (C_5Me_5), 20.1 ($2CH_2$), 16.1 ($C_5\mathit{Me}_5$), 15.8 ($C_5\mathit{Me}_5$). **5**: ^{1}H NMR (C_6D_{12}) δ 8.61 (2H, d, J = 7.2 Hz, *o*-Ph), 7.41 (2H, t, J = 7.2 Hz, *m*-Ph), 7.25 (1H, t, J = 7.2 Hz, *p*-Ph), 6.23 (2H, s, CH_2Ph), 1.25 (30H, s, $2C_5Me_5$); ^{13}C NMR (C_6D_{12}) δ 146.8, 130.2, 129.1, 127.0, 114.7 ($2C_5Me_5$), 76.3 (CH_2Ph), 18.6 ($2C_5\mathit{Me}_5$).
14. **4f**: ^{1}H NMR (C_6D_{12}) δ 15.15 (1H, br s, CH), 9.18 (2H, br s, 2C*H*Me), 1.15 (15H, s, C_5Me_5), 1.11 (15H, s, C_5Me_5), -3.10 (6H, s, 2CH*Me*).
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