Pergamon

Tetrahedron Letters 41 (2000) 4923–4927

TETRAHEDRON LETTERS

# Convenient preparation of ytterbium(III) chalcogenolate complexes by insertion of ytterbium into chalcogen–chalcogen bonds. Application in the ring-opening of epoxides

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Received 3 April 2000; accepted 27 April 2000

**Abstract**

Convenient conditions are reported for the preparation of ytterbium(III) chalcogenolate complexes by insertion of ytterbium metal into the chalcogen–chalcogen bond of disulfides, diselenides, and ditellurides. The resulting complexes have been found to transfer arylsulfanyl, -selenanyl, and -telluranyl groups to epoxides in a facile ring-opening reaction. The ytterbium(III) chalcogenolate complexes appear to perform a dual role in both activating the epoxide, due to their Lewis acidic nature, and supplying a nucleophile to the coordinated substrate. 

*Keywords:* lanthanides; epoxides; sulfides; selenium and compounds; tellurium and compounds.

Organosulfur and selenium chemistry occupies an important place in organic synthesis.[1] The development of new methods for the introduction of sulfur-, selenium-, and tellurium-containing groups into organic molecules, particularly in a stereocontrolled manner, remains a significant challenge. Our interest in organolanthanide-mediated transformations[2] has led us to consider lanthanide(III) chalcogenolate complexes as reagents for the transfer of organosulfanyl, -selenanyl, and -telluranyl groups. We believed such complexes would be capable of performing a dual role in reactions with substrates: initial coordination of the substrate to the Lewis acidic lanthanide(III) centre would activate the substrate, and the complex would then provide a nucleophile for reaction with the activated substrate. We report here a convenient route to ytterbium(III) chalcogenolate complexes and their application in the ring-opening of epoxides.

Relatively few lanthanide(III) chalcogenolate complexes have been reported,[3–5] and their application in organic synthesis has been limited.[6,7] Lanthanide(III) chalcogenolate complexes have previously been prepared from dichalcogenides;[4,6f–h] however, few reports of their preparation by the insertion of lanthanide metals, with no metal co-reductant,[6f–h] into the chalcogen–chalocogen bond of dichalcogenides have appeared.[5f,7] Unfortunately, in all previous examples, unsatisfactory

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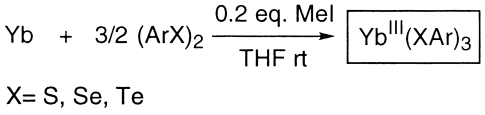
0040-4039/00/$ - see front matter 
PII: S0040-4039(00)00687-0

methods for metal-activation were employed. We wished to develop a more general and convenient method for the preparation of complexes, not only from disulfides, but also from diselenides and ditellurides, and examine their reactions with organic electrophiles.

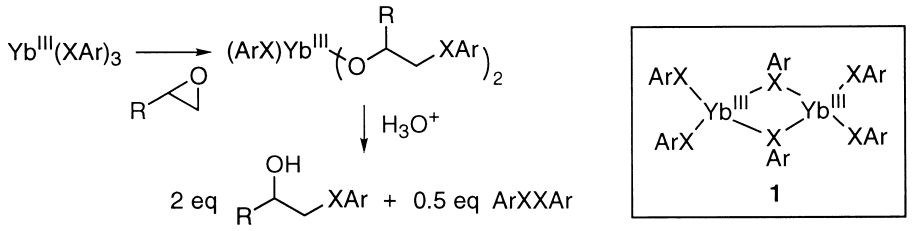
The condition of the metal surface in these reactions is crucial. In a related reaction, activation was achieved by the reversible complexation of the lanthanide metal to benzophenone in the presence of HMPA.[7a] We found that excellent results can be achieved by a much simpler approach which does not require the use of HMPA. Our approach involves mechanical activation[8] followed by the addition of iodomethane and is outlined in Scheme 1.




Scheme 1.

The exact structure of the resultant lanthanide(III) complexes has not yet been determined; however, homoleptic complexes as shown in Scheme 1 appear likely[3] and have previously been suggested.[7a] As we expected these lanthanide(III) chalcogenolate complexes to be Lewis acidic and also to act as a source of nucleophiles, we chose to examine their reaction with epoxides.

Typically, in the reaction with dichalcogenides, the metal is completely consumed after 1–2 h and a red/brown suspension is formed. Addition of neat epoxide to the complex results in an instantaneous colour change and the reaction is complete in less than 15 min. In most cases, approximately 0.5 equivalents of dichalcogenide was recovered from the reaction and up to 2 equivalents of the ring-opened product were obtained.[9] It is therefore clear that each complex is capable of transferring more than one ligand. From the apparent stoichiometry of the reaction, we believe that each complex transfers at least two ligands. Untransferred ligands may remain on the lanthanide centre until acidic work-up leads to the regeneration of the dichalcogenide (Scheme 2).

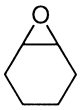
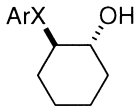
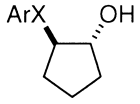
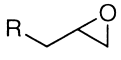
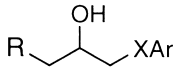
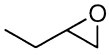
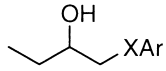
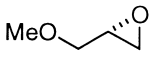
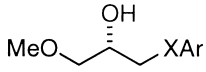
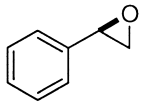
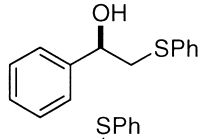



Scheme 2.

In order to attain steric and electronic saturation, many lanthanide(III) chalcogenolate complexes contain bridging chalcogenolate groups linking either two lanthanide centres, or a lanthanide and an alkali metal centre (ate complexes).[5] If a dimeric species, such as **1**, were formed here, then it might be expected that the bridging ligands would not be as readily transferred to the epoxide substrate. Thus, the stoichiometry of the reaction may give an indication as to the nature of the complex. Further studies aimed at confirming the structure of these complexes are currently underway.

A range of dichalcogenides and epoxides have been used in the reaction and our results are summarised in Table 1.[10] Cyclic epoxides are opened efficiently to give *anti*-β-hydroxy sulfides and selenides in excellent yield. Entries 7–15 show the expected regiochemical tendency for epoxide-opening at the least hindered position of the epoxide. One exception can be seen in entry 16, where the reaction of styrene oxide gives products arising mainly from attack at the benzylic position. Reaction with epichlorohydrin (entry 8) occurs chemoselectively to give only the product of epoxide-opening, even when an excess of reagent is used. This supports the idea that activation of the substrate by the reagent is crucial to the overall reaction.

Table 1

| entry | epoxide | dichalcogenide | product[a] | yield (%)[b] |
|---|---|---|---|---|
| 1<br>2<br>3 |  | PhSSPh<br>*p*TolSS*p*Tol<br>PhSeSePh |  | **1a** X= S, Ar= Ph, 67%<br>**1b** X= S, Ar= *p*Tol, 81%<br>**1c** X= Se, Ar= Ph, 85% |
| 4<br>5<br>6 |  | PhSSPh<br>PhSeSePh<br>*p*TolSS*p*Tol |  | **2a** X= S, Ar= Ph, 85%<br>**2b** X= Se, Ar=Ph, 97%<br>**2c** X= S, Ar= *p*Tol, 89% |
| 7<br>8 |  | PhSSPh<br>PhSeSePh |  | **3a** R= H, X= S, Ar= Ph, 78%<br>**3b** R= Cl, X= Se, Ar= Ph, 85% |
| 9<br>10<br>11<br>12 |  | PhSSPh<br>*p*TolSS*p*Tol<br>PhSeSePh<br>PhTeTePh |  | **4a** X= S, Ar= Ph, 75%<br>**4b** X= S, Ar= *p*Tol, 68%<br>**4c** X= Se, Ar= Ph, 82%<br>**4d** X= Te, Ar = Ph, 65% |
| 13<br>14<br>15 |  | PhSSPh<br>PhSeSePh<br>PhTeTePh |  | **5a** X= S, Ar= Ph, 85%<br>**5b** X= Se, Ar= Ph, 96%<br>**5c** X= Te, Ar= Ph, 70% |
| 16 |  | PhSSPh |  | **6aa**<br>73%, **6aa/6ab**, 1:4<br>**6ab** |

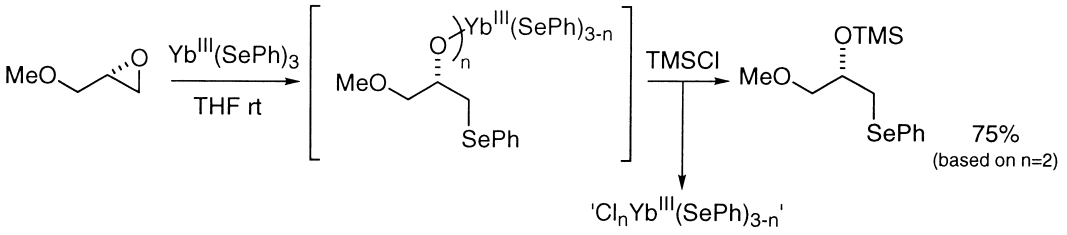
[a]For reaction conditions see typical procedure

[b]All yields are based on the transfer of two 'XAr' groups per metal.

The reaction of ytterbium(III) chalcogenolate complexes with enantiomerically pure epoxide substrates has also been studied (entries 13–16). The enantiomeric purity of the products **5a**, **5b**, **5c**, **6aa** and **6ab** has been determined.[11] The reaction of complexes with (*R*)-(–)-glycidyl methyl ether gives the expected products, **5a**, **5b** and **5c**, with no loss of enantiomeric purity. The reaction

of (*S*)-styrene oxide, however, gives **6ab** of considerably lower enantiomeric purity than the starting epoxide. From the same reaction, the minor product **6aa** is obtained with no loss of stereochemical integrity. This clearly illustrates that the reaction of styrene oxide proceeds, to a large extent, via the benzylic cation.

As shown in Scheme 2, the product prior to aqueous work-up is a ytterbium(III) alkoxide. Due to the oxophilicity of the lanthanides, the lanthanide–oxygen bond is relatively strong and its formation at the expense of the lanthanide–sulfur bond appears to represent the driving force for the epoxide insertion reaction. Previous reports have shown that successful cleavage of the lanthanide–oxygen bond can be achieved by treatment with TMSCl.[12] Trapping of the intermediate lanthanide(III) alkoxide, formed in reactions of (*R*)-(–)-glycidyl methyl ether, with TMSCl, was found to give the protected β-hydroxy selenides in good yield, via a ring-opening/protection sequence. Presumably the by-product from the reaction is a lanthanide(III) chloride species (Scheme 3).




Scheme 3.

Attempts to employ dialkyl disulfides in the epoxide-opening reaction gave less satisfactory results. With dibenzyl and dibutyl disulfide, reaction did occur but the ytterbium metal was not completely consumed. This suggests the reactions of dialkyldisulfides with ytterbium may follow a different stoichiometry. Separation of the resultant solution from the remaining metal, and reaction with 1,2-epoxybutane gave the expected sulfides in low yield.[13]

In summary, we have described a convenient method for the preparation of ytterbium(III) chalcogenolates by the insertion of ytterbium metal into the chalcogen–chalcogen bond of dichalcogenides. These complexes have been found to transfer arylsulfanyl, -selenanyl, and -telluranyl groups to epoxides in facile ring-opening reactions. We believe these Lewis acidic complexes perform a dual role in both activating the epoxide, and delivering a nucleophile to the coordinated substrate.

Studies aimed at confirming the structure of the ytterbium(III) chalcogenolate complexes and further exploring their applications in organic synthesis are currently underway in our laboratories.

**Typical procedure**: Ytterbium metal[14] (50 mg, 0.29 mmol, 2 equiv.) was stirred vigorously in a test tube under a stream of argon for 1 h with intermittent heating. Methyl iodide (4 μl) was then added followed by diphenyldiselenide (135 mg, 0.43 mmol, 3 equiv.) and the reaction mixture stirred vigorously at room temperature with intermittent heating. After 1–2 h, the metal was completely consumed and an orange suspension was formed. Additional THF (0.5 ml) was then added, followed by neat (*R*)-glycidyl methyl ether (78 μl, 0.87 mmol, 6 equiv.). After 15 min, aqueous saturated $NH_4Cl$ (3 ml) and $H_2O$ (3 ml) were added, followed by citric acid (182 mg, 0.87 mmol, 6 equiv.). After 10 min, 30% ethyl acetate/hexane (5 ml) was added and the aqueous layer separated and extracted with further portions of 30% ethyl acetate/hexane (2×5 ml). The combined organic layers were then dried ($Na_2SO_4$) and concentrated in vacuo. Purification

by Kugelrohr distillation (oven temp 75°C, 0.2 mmHg) gave **5b** (136 mg, 0.56 mmol, 96%) as a colourless oil.

## Acknowledgements

D.J.P. would like to thank Pfizer (FM) for the funding of a final year project.

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9. In some reactions, traces (< 5%) of the corresponding β-hydroxy iodides were detected in the crude product mixtures. We presume these by-products are formed by ring-opening with a 'Yb(III)-I' species arising from the initial formation of 'MeYb(II)I' during the activation process.
10. All new compounds were characterised by $^1H$ and $^{13}C$ NMR, IR and mass spectra, and gave satisfactory elemental analysis and/or accurate mass spectra.
11. The Mosher's acid esters of **5a**, **5b**, **6aa** and **6ab** were prepared and their $^1H$, $^{13}C$ and $^{19}F$ NMR spectra compared, where possible, to those of derivatives prepared from the corresponding racemic epoxides.
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13. The reactions of dibenzyldisulfide and dibutyldisulfide, with ytterbium and 1,2-epoxybutane, gave 1-benzylsulfanyl-butan-2-ol and 1-butylsulfanyl-butan-2-ol in 28 and 30% yields, respectively (based on ytterbium).
14. Ytterbium metal (40 mesh) was purchased from Acros Organics and stored under Argon.