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# Barbier/Grignard-Type Allylation or Benzylolation Mediated by the Mischmetall/SmI<sub>2</sub>(cat.) System

Aurore Di Scala,<sup>[a]</sup> Stefania Garbacia,<sup>[a]</sup> Florence Hélicon,<sup>[a]</sup> Marie-Isabelle Lannou,<sup>[a]</sup> and Jean-Louis Namy\*<sup>[a]</sup>

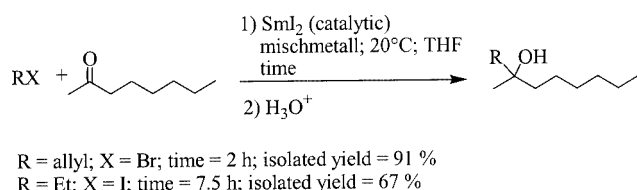
**Keywords:** Allylation / Catalysis / Lanthanides / Mischmetall / Samarium

Barbier- and Grignard-type allylation and benzylolation have been achieved by the use of samarium diiodide in catalytic amounts together with mischmetall (an alloy of the light lanthanides) as a coreductant. Plausible catalytic schemes are proposed. In addition, organocerium and -lanthanum reagents have been obtained from samarium diiodide catalysed reactions between organic halides and cerium or lan-

thanum metal, giving a new route to organolanthanoid compounds. It also appears that trivalent benzyl and allyl organometallic compounds of cerium and lanthanum are much more stable than the corresponding samarium ones.

## Introduction

We have recently reported the use of mischmetall (cerium mixed metal) as a coreductant for catalytic reactions of some organic substrates with samarium diiodide.<sup>[1]</sup> Mischmetall is an alloy of the light lanthanides, its typical composition being Ce 50%, La 33%, Nd 12%, Pr 4%, other lanthanides 1%. With the mischmetall/SmI<sub>2</sub>(cat.) system, for example, we were able to perform Barbier-type reactions between a ketone and several organic halides (Scheme 1).



Scheme 1

The procedure, as indicated above, can be designated by the abbreviation Catalytic BP (for Catalytic Barbier Procedure), while mischmetall is denoted below as Ln.

Barbier-type reactions have been performed with a variety of reductants,<sup>[2,3]</sup> and several mechanisms have been proposed. In particular, formation of products could result either from a ketyl radical/radical coupling or from addition of an organometallic species onto a carbonyl compound. In the case of lithium, it has been established that the Barbier reaction can occur without the in situ formation

of an organometallic compound.<sup>[4]</sup> In samarium(II)-mediated reactions, however, the formation of an organosamarium compound is likely.<sup>[5-7]</sup> It is consequently assumed in the following discussion that reaction occurs through formation of an organometallic species. According to our previous proposal,<sup>[1]</sup> two catalytic schemes can be considered. In the catalytic scheme I (Figure 1), an organosamarium compound RSmIX (or RSmX<sub>2</sub> or RSmI<sub>2</sub>) is formed first. Its addition to a carbonyl compound gives a samarium alkoxide. This in turn, through a reduction/transmetallation process with Ln, provides another lanthanide alkoxide, with the regeneration of SmI<sub>2</sub> (or SmX<sub>2</sub>).

In the catalytic scheme II (Figure 2), the initially formed RSmIX reacts with Ln to give another organometallic compound (LnR<sub>3</sub>; Ln ≠ Sm) through a reduction/transmetallation process, with the regeneration of SmI<sub>2</sub>. This organolanthanoid compound then adds to the carbonyl compound to furnish an alkoxide.

Alternatively, reduction of the initially produced radicals (from a reaction between organic halide and SmI<sub>2</sub>) with Ln

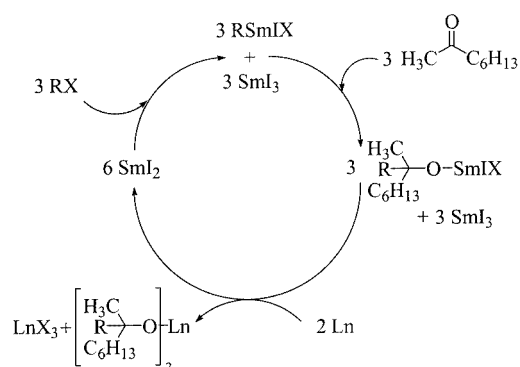


Figure 1. Catalytic scheme I

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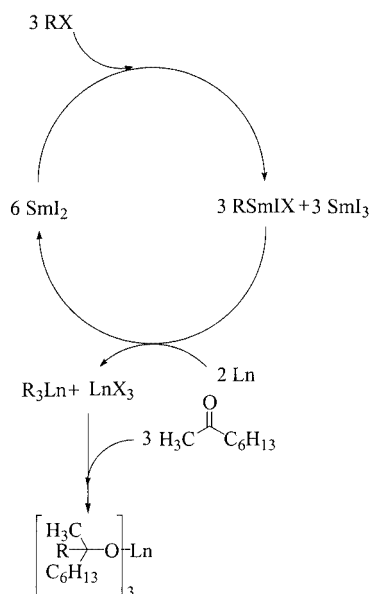


Figure 2. Catalytic scheme II

instead of  $\text{Sm}^{\text{II}}$  could give an organometallic compound ( $\text{R}_3\text{Ln}$ ) directly,  $\text{SmI}_2\text{X}$  being concomitantly reduced with  $\text{Ln}$  into  $\text{SmI}_2$ . This catalytic scheme III (Figure 3) should not require formation of an organosamarium compound. However, it can be seen as a variant of scheme II (Figure 2) since it also implies a reaction between  $\text{R}_3\text{Ln}$  ( $\text{Ln} \neq \text{Sm}$ ) and a carbonyl compound.

It is well known that organosamarium compounds obtained by means of the reaction between  $\text{SmX}_2$  ( $\text{X} = \text{I}, \text{Br}$ ) and organic halides are unstable and must be trapped immediately by an electrophile, which generally necessitates the use of a Barbier-type procedure (BP).<sup>[5,6]</sup> In some cases (reactions performed at low temperature and/or in the presence of HMPA, reactions with allylic or benzylic halides in

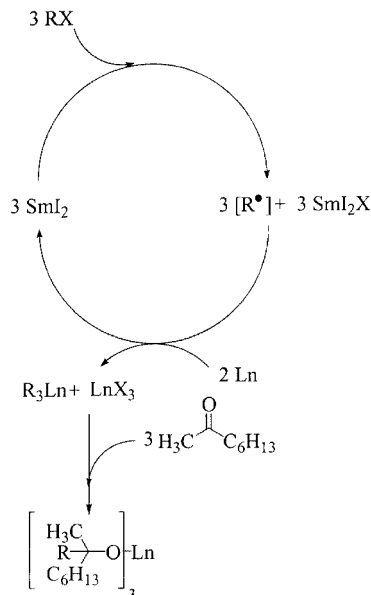


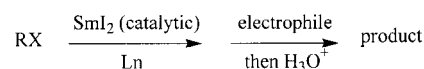
Figure 3. Catalytic scheme III

tetrahydropyran or with cyclopropyl halides<sup>[7–10]</sup>), however, a Grignard-type procedure (GP) may be used. According to this sequential procedure the electrophile is added after the organosamarium compound has been formed.

Here we report results that give some insights into the mechanisms of reactions that use mischmetall as a coreductant in samarium(II)-mediated reactions. The potential of mischmetall in organic synthesis is also investigated.

## Results and Discussion

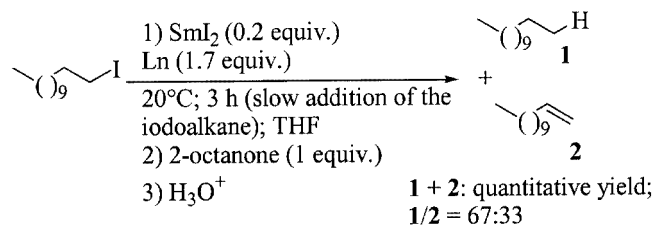
In order to assess the soundness of the catalytic schemes (Figure 1–3), we performed reactions according to the sequential procedure depicted below, which could be termed a Catalytic Grignard Procedure (Catalytic GP, Scheme 2).



Scheme 2

If the catalytic scheme I (Figure 1) were the only effective one, this procedure would not be able to provide the expected product (a tertiary alcohol if a ketone is the electrophile), as it is known that organosamarium compounds are unstable. On the other hand, the success of this procedure would agree well with catalytic schemes II or III (Figure 2 and 3), which imply formation of  $\text{R}_3\text{Ln}$ ,  $\text{R}_2\text{LnX}$  or  $\text{RLnX}_2$  ( $\text{Ln}$  other than  $\text{Sm}$ ). However, failure of this experiment would not mean that the catalytic schemes II or III would have to be ruled out, since these organometallic compounds might also be unstable, and consequently require a Barbier-type procedure.

At first, the experiment with 1-iodododecane as shown in Scheme 3 was performed.

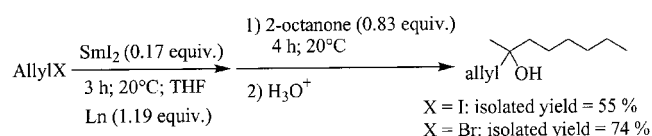


Scheme 3

Treatment of this alkyl halide with  $\text{SmI}_2$  (0.2 equiv.) and  $\text{Ln}$  in stoichiometric amounts for 3 h, followed by addition of 2-octanone, provided a 2:1 mixture of dodecane and 1-dodecene in quantitative yield, whereas the expected tertiary alcohol was not detected and the ketone was recovered unchanged. However, the presence of the alkene strongly suggests the formation of an organometallic compound, which would have undergone a  $\beta$ -elimination of hydrogen. It is worth noting that treatment of 1-iodododecane with a stoichiometric amount of  $\text{SmI}_2$  exclusively furnished dodecane.

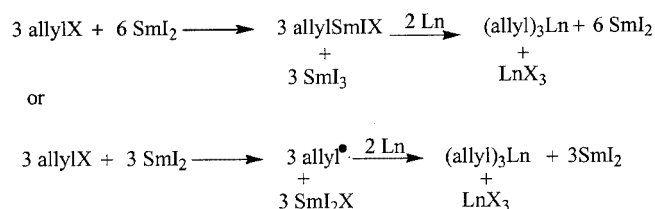
The reactions of allylic halides were examined next, since these are able to afford stable organolanthanoid species in

some cases.<sup>[8,11]</sup> Interestingly, the sequential procedure (treatment of allylX with SmI<sub>2</sub> in catalytic amounts and Ln in stoichiometric amounts for 3 h, followed by addition of 2-octanone) was successful, as shown below (Scheme 4).



Scheme 4

The tertiary alcohol was obtained in moderate (X = I) or good yields (X = Br). In contrast, the sequential procedure could not be used with samarium diiodide in stoichiometric amounts, the only products detected being the dienes arising from a Wurtz coupling.<sup>[12]</sup> In the absence of samarium diiodide no reaction occurred. Thus, the formation of a stable allyllanthanide reagent, according to either of the processes indicated below, is likely (Scheme 5).



Scheme 5

For prevention of Wurtz coupling, it must be assumed that Ln quickly reduces either allylSmX<sub>2</sub> or allyl radicals. These findings are in strong agreement with the catalytic schemes II or III (Figure 2 and 3) for the Catalytic BP. In a previous study, cerium was used to perform Grignard- or Barbier-type reactions. However, the metal had to be activated prior to use either with iodine<sup>[13]</sup> or with mercuric chloride.<sup>[14]</sup> Nevertheless, the reactions are very slow with allyl bromide, and the main products arise from pinacol-type coupling.

The catalytic reactions of allylic halides were tested with a variety of electrophiles: ketones, aldehydes and esters, according to both a Barbier-type procedure (Catalytic BP) and a Grignard-type one (Catalytic GP). The results are collected in Table 1.

Both procedures gave good results. Nevertheless, the yields were slightly better with the Catalytic BP (except for coumarin) than with the Catalytic GP. The structure of **3** [(Z) isomer] was established by <sup>1</sup>H NMR NOE experiments: irradiation of 1'-H (δ = 6.44 ppm) produced a nuclear Overhauser effect on 2'-H (δ = 5.79 ppm) and vice versa.

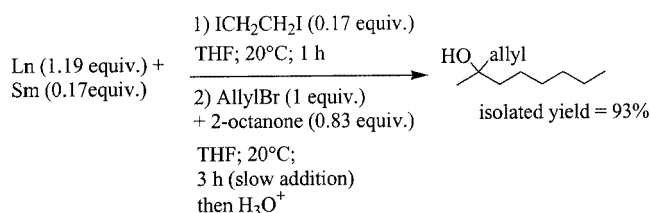
In addition, similar experiments were performed with 4-*tert*-butylcyclohexanone, affording the alcohol resulting from the equatorial attack of the allyl group as the major one in both procedures (Catalytic BP: 83:17; Catalytic GP: 81:19). These ratios are similar to those previously obtained for the stoichiometric Barbier-type reaction (87:13).<sup>[12]</sup>

Table 1. Catalytic reactions of allylic halides mediated by the mischmetall/SmI<sub>2</sub> system

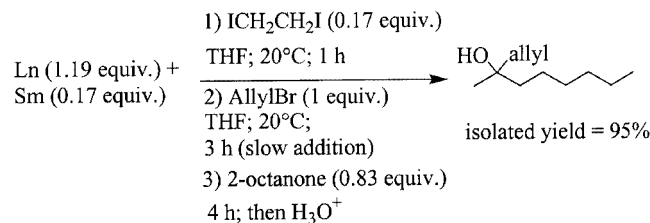
AllylX + electrophile		$\xrightarrow[2) H_3O^+]{1) Ln / SmI_2 (cat.)}$ product <sup>[a]</sup>	
X	Electrophile	Product: <sup>[a]</sup> Catalytic BP <sup>[b]</sup>	yield (%) Catalytic GP <sup>[b]</sup>
I	2-octanone	90	55
Br	2-octanone	92	74
Br	octanal	62	60
Br	acetophenone	85	75
Br	benzaldehyde	80	76
I	ethyl benzoate	74	54
Br	ethyl benzoate	68	73
Br	ethyl isobutyrate	64	50
I	ethyl isobutyrate	60	52
Br	coumarin	20 <sup>[c]</sup>	3 <sup>[c]</sup> ; 59

<sup>[a]</sup> Secondary alcohols from aldehydes and tertiary alcohols from ketones or esters. <sup>[b]</sup> Isolated yields, for experimental details, see the Exp. Sect. <sup>[c]</sup> 2-[(Z)-3-Allyl-3-hydroxyhexa-1,5-dienyl]phenol, see Scheme 9.

Interestingly, a simpler experimental procedure, starting from a mixture of samarium metal and mischmetall, could be used as depicted below (Scheme 6), while a sequential procedure also gave excellent results. Thus, it had been demonstrated that a stable organometallic compound was also formed under these experimental conditions (Scheme 7). In both cases the product was obtained in excellent yields.



Scheme 6



Scheme 7

Presumably, in situ formation of samarium diiodide occurs under these conditions. In addition, diiodoethane might activate mischmetall, thus facilitating the catalytic process (reduction/transmetallation of RSmIX – see catalytic scheme II, Figure 2 – or reduction of radicals – see catalytic scheme III, Figure 3). In the absence of samarium metal, the expected alcohol was obtained in low yield while pinacol coupling of the ketone was the main reaction.

Reactions of crotyl bromide and cinnamyl bromide were also studied. The results are summarized in Table 2.

Table 2. Catalytic reactions of crotyl bromide and cinnamyl bromide mediated by the mischmetal/ $\text{SmI}_2$  system

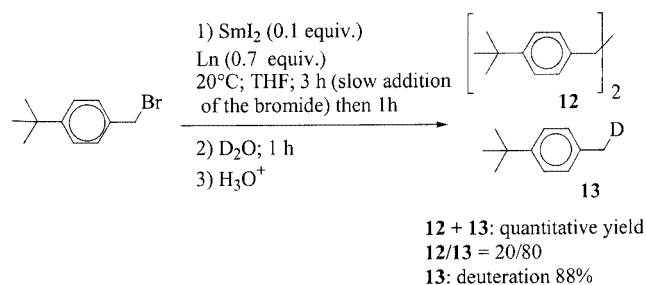
R	Electrophile	(A + B) <sup>[a]</sup> ; A/B <sup>[a][b]</sup>	
		Catalytic BP	Catalytic GP
CH <sub>3</sub>	2-octanone	66; 90:10	66; 90:10
CH <sub>3</sub>	octanal	46; 75:25	37; 90:10
CH <sub>3</sub>	acetophenone	40; 90:10	48; 80:20
CH <sub>3</sub>	benzaldehyde	20; 70:30	26; 70:30
C <sub>6</sub> H <sub>5</sub>	2-octanone	77; 45:55	45; 35:65
C <sub>6</sub> H <sub>5</sub>	nonanal	59; 80:20	53; 80:20
C <sub>6</sub> H <sub>5</sub>	acetophenone	71; 35:65	74; 20:80
C <sub>6</sub> H <sub>5</sub>	benzaldehyde	45; 60:40	56; 80:20

<sup>[a]</sup> Isolated yield (%); for experimental details, see the Exp. Sect. <sup>[b]</sup> Ratios were measured by GLC and <sup>1</sup>H NMR.

With crotyl bromide, both procedures gave alcohols in moderate yields. In every case, a mixture of two homoallylic alcohols was obtained, with the linear isomer (product A) as the major one. With cinnamyl bromide, both Catalytic BP and Catalytic GP allowed the formation of the alcohols in medium to good yield. Diols arising from pinacol coupling were found as by-products (trace amounts to 30% yield). Unexpectedly, while aldehydes preferentially gave the linear isomer, ketones afforded the more substituted isomer (product B). This latter result is in contrast with the obtained product distribution in stoichiometric Barbier-type conditions with  $\text{SmI}_2$  (the linear isomer is the major one in every case).<sup>[15]</sup> Finally, it should be noted that the A/B ratios depended only slightly on the procedure used.

Similar reactions were achieved with benzylic halides (Table 3).

Except in the case of coumarin, which gave a complex mixture of products in Catalytic BP, both procedures provided alcohols in good yields. In contrast, the Grignard-type procedure with samarium diiodide in stoichiometric amount exclusively give Wurtz coupling.<sup>[15]</sup> The formation of a stable organometallic species in Catalytic GP was demonstrated with 4-*tert*-butylbenzyl bromide, by quenching the reaction mixture with  $\text{D}_2\text{O}$ ; 4-*tert*-butyltoluene was then obtained in 80% yield, with incorporation of deuterium (88%). This result is also in agreement with the catalytic schemes II or III. A minor amount of 4,4'-di-*tert*-butylbenzyl (ca. 20%) was also detected (Scheme 8).



Scheme 8

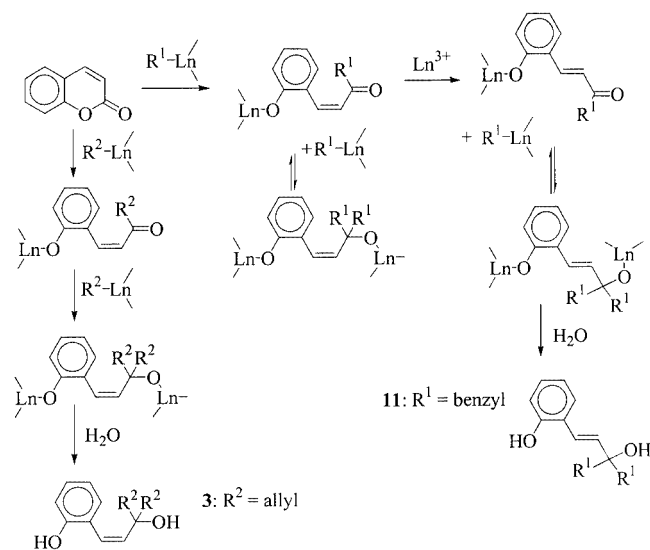
Surprisingly, the (*E*) isomer (product **11**; Table 3) was obtained from coumarin in the Catalytic GP. The structure of **11** was confirmed by 2D NMR NOESY experiments (correlation between 3-H and 2'-H was observed). This should result from the reaction of a benzylanthanoid species. The change in the configuration of the C–C double bond must be subsequent to the ring-opening of the lactone, which would initially provide an  $\alpha,\beta$ -unsaturated ketone. This isomerization could occur under the influence of  $\text{Ln}^{\text{III}}$  salts acting as Lewis acids. Nevertheless, no such transformation

Table 3. Catalytic reactions of benzylic halides mediated by the mischmetal/ $\text{SmI}_2$  system

ArCH <sub>2</sub> Br	R <sup>1</sup> ; R <sup>2</sup>	R <sup>3</sup> ; R <sup>4</sup>	Product: yield (%)	
			Catalytic BP <sup>[a]</sup>	Catalytic GP <sup>[a]</sup>
4-( <i>t</i> Bu)benzyl bromide	CH <sub>3</sub> ; C <sub>2</sub> H <sub>5</sub>	–	<b>4</b> : 93	67
4-( <i>t</i> Bu)benzyl bromide	<i>n</i> -C <sub>4</sub> H <sub>9</sub> ; H	–	<b>5</b> : 73	62
4-( <i>t</i> Bu)benzyl bromide	<i>n</i> -C <sub>7</sub> H <sub>15</sub> ; H	–	<b>6</b> : 82	58
4-( <i>t</i> Bu)benzyl bromide	C <sub>6</sub> H <sub>5</sub> ; CH <sub>3</sub>	–	<b>7</b> : 64	63
4-( <i>t</i> Bu)benzyl bromide	C <sub>6</sub> H <sub>5</sub> ; H	–	<b>8</b> : 37	46
4-( <i>t</i> Bu)benzyl bromide	cyclohexenone	–	<b>9</b> : 35 <sup>[b]</sup>	59 <sup>[b]</sup>
4-( <i>t</i> Bu)benzyl bromide	–	C <sub>6</sub> H <sub>5</sub> ; C <sub>2</sub> H <sub>5</sub>	<b>10</b> : 80	70
benzyl bromide	–	C <sub>6</sub> H <sub>5</sub> ; C <sub>2</sub> H <sub>5</sub>	71	55
benzyl bromide	–	CH <sub>3</sub> ; <i>tert</i> -C <sub>4</sub> H <sub>9</sub>	84	74
benzyl bromide	–	<i>i</i> C <sub>4</sub> H <sub>9</sub> ; C <sub>2</sub> H <sub>5</sub>	84	73
benzyl bromide	–	$\beta$ -propiolactone	56	71
benzyl bromide	–	$\gamma$ -butyrolactone	77	50
benzyl bromide	–	coumarin	0	<b>11</b> : 59 <sup>[c]</sup>

<sup>[a]</sup> Isolated yields (%); for experimental details, see the Exp. Sect. <sup>[b]</sup> 1-(4-*tert*-Butylbenzyl)cyclohex-2-enol. <sup>[c]</sup> 2-[(*E*)-3-Benzyl-3-hydroxy-4-phenylbut-1-enyl]phenol; see Scheme 9.

was observed with allyl bromide (Table 1; product **3**). To account for this, it might additionally be assumed that some reversibility applies in the addition of benzyl organometallic



Scheme 9

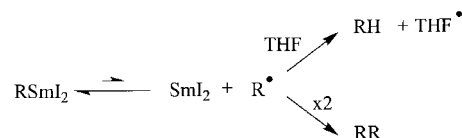
species to the unsaturated ketone (Scheme 9). Some examples of reversible addition of organometallic compounds to ketones are known, giving support to this assumption.<sup>[16,17]</sup>

As the main components of mischmetall are cerium and lanthanum, these were tested in both procedures in place of mischmetall under similar experimental conditions. Results of reactions of allyl halides or 4-*tert*-butylbenzyl bromide with some electrophiles are reported in Table 4.

It was found that cerium and lanthanum were both efficient coreductants in these reactions, as well in Catalytic BP and Catalytic GP. The results obtained either with Ce or with La were close to those described with mischmetall. In the absence of SmI<sub>2</sub>, the starting material was recovered unchanged. Neodymium was also tested in Catalytic BP and Catalytic GP for reactions of allyl bromide and 2-oc-

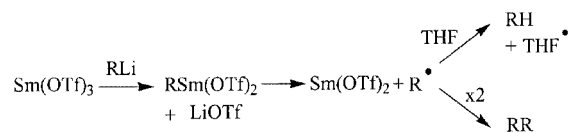
tanone and afforded the expected alcohol in 88% and 51% isolated yields, respectively. However, the alloy is much cheaper than cerium, lanthanum or neodymium, and moreover is less prone to oxidation. All this is in favour of the use of mischmetall instead of separated lanthanide metals.

In addition, our results underline that organolanthanum and -cerium compounds are much more stable than organosamarium compounds (in their +3 oxidation states). This interesting feature could be connected with the stability of the +2 oxidation state for samarium. Thus, it can be assumed that, in contrast to RCeX<sub>2</sub> and RLaX<sub>2</sub>, RSmX<sub>2</sub> could easily change into a samarium(II) compound and a radical species that would give organic compounds, according to the transformation shown in Scheme 10.



Scheme 10

A similar change has previously been observed in the preparation of samarium(II) triflate from samarium(III) triflate and an organolithium reagent.<sup>[18]</sup> In that case, it was proposed that the initially formed RSm(OTf)<sub>2</sub> afforded the divalent samarium species through reduction of the Sm<sup>III</sup> species by R<sup>-</sup> as shown in Scheme 11.



Scheme 11

In contrast, organosamarium(II) compounds such as allylSm<sup>II</sup>Br, the preparation of which from samarium metal and allyl bromide has recently been reported,<sup>[19]</sup> could be more stable than organosamarium(III) species, since reduction to Sm<sup>I</sup> compounds obviously cannot occur.

Table 4. Catalytic reactions of benzylic or allylic halides mediated by the cerium/SmI<sub>2</sub> system or the lanthanum/SmI<sub>2</sub> system

RX	Electrophile	Procedure <sup>[a][b]</sup>	product <sup>[a]</sup>		
			Lanthanum	Cerium	Mischmetall
allylI	2-octanone	Catalytic BP	88	84	83
allylBr	2-octanone	Catalytic BP	90	92	92
allylBr	2-octanone	Catalytic GP	68	65	73
allylBr	acetophenone	Catalytic BP	58	78	85
allylBr	acetophenone	Catalytic GP	70	59	75
allylBr	ethyl benzoate	Catalytic GP	54	67	74
4-( <i>t</i> Bu)benzyl bromide	Butanone	Catalytic GP	64	55	67
4-( <i>t</i> Bu)benzyl bromide	ethyl benzoate	Catalytic GP	79	55	70
4-( <i>t</i> Bu)benzyl bromide	pentanal	Catalytic BP	75	87	73

<sup>[a]</sup> Secondary alcohol from aldehydes and tertiary alcohol from ketones or esters. <sup>[b]</sup> For experimental details, see the Exp. Sect. <sup>[c]</sup> Isolated yields (%).

## Conclusion

We found that it was possible to use samarium diiodide in catalytic quantities with mischmetall as a coreductant in both Barbier- and Grignard-type reactions involving allylic and benzylic halides. Organocerium and -lanthanum compounds could be obtained through a reduction/transmetallation process of an organosamarium compound with cerium or lanthanum metal. However, they could be also produced directly, through reduction by lanthanide metals of initially formed radicals arising from reaction between organic halides and  $\text{SmI}_2$ . Thus, a new route to organolanthanoid compounds has been established. It was also shown that trivalent organometallic compounds of cerium and lanthanum are much more stable than samarium ones. Moreover, it was highlighted that in some cases there is no need to use separated lanthanides, since a mixture can at the very least give similar results. We are currently investigating further examples of the use of mischmetall as a reagent or as the starting material for preparation of cheap and efficient catalysts.

## Experimental Section

**General:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 250 MHz and 63 MHz, respectively, with a Bruker AM 250 instrument (unless otherwise stated). Chemical shifts are reported in parts per million ( $\delta$ ) downfield from TMS. Infrared (IR) spectra were recorded neat with an FTIR IFS 66 Bruker and are reported in  $\text{cm}^{-1}$ . Mass spectra (MS) were recorded with a GC/MS RiberMag R10-10 instrument. Electronic impact was performed at 70 eV. High-resolution mass spectra were recorded with a GC/MS Finningan-MAT-95-S. Flash chromatography was performed on silica gel (Merck 230–240 mesh; 0.0040–0.0630 mm). All commercially available organic compounds were distilled before use. Samarium, cerium and lanthanum were purchased from the Acros Company, and mischmetall (cerium mixed metal) from Fluka (about \$ 60 per 500 g). Mischmetall ingots (about 5 g) were easily powdered in air with a rasp; the powder was kept under argon (average molecular mass of mischmetall is 140). Tetrahydrofuran (THF) was distilled under argon from sodium benzophenone ketyl. Samarium diiodide was prepared as previously described.<sup>[8]</sup> All reactions were carried out under argon in Schlenk tubes by standard vacuum-line techniques.<sup>[7]</sup>

**Catalytic Barbier Procedure (Catalytic BP):** Mischmetall powder (0.7 g, 5 mmol) was suspended with  $\text{SmI}_2$  (0.7 mmol) in THF (7 mL) in a Schlenk tube under argon at room temperature. A solution of an electrophile (ketones or aldehydes: 3.5 mmol; esters: 2 mmol) and organic halide (allyl halides and benzyl halides: 4.2 mmol; crotyl bromide and cinnamyl bromide: 5 mmol) in THF (7 mL) was slowly added to the THF/ $\text{SmI}_2$ /mischmetall suspension over 2.5 h. The mixture was then stirred for an additional period of 0.5 h, diluted with ether, quenched with HCl (1 M) and stirred for 15 min to obtain a clear solution, which was extracted with ether. The combined extracts were washed with brine, aqueous sodium thiosulfate and brine again. The organic layer was dried with  $\text{MgSO}_4$ , and the solvents were removed under reduced pressure. The crude material was purified by flash chromatography on silica gel. The same procedure was used with cerium and lanthanum.

**Catalytic Grignard Procedure (Catalytic GP):** Mischmetall powder (0.7 g, 5 mmol) was suspended with  $\text{SmI}_2$  (0.7 mmol) in THF (7 mL) in a Schlenk tube under argon at room temperature. A solution of an organic halide (allyl halides and benzyl halides: 4.2 mmol; crotyl bromide and cinnamyl bromide: 5 mmol) in THF (7 mL) was slowly added over 3 h to the THF/ $\text{SmI}_2$ /mischmetall suspension. The mixture was then stirred for an additional period of 10 min. A solution of an electrophile (ketone or aldehyde: 3.5 mmol; ester: 2 mmol) in THF (5 mL) was added over 30 min. Stirring was maintained for 4 h. The mixture was then diluted with ether, quenched with HCl (1 M) and stirred for 15 min to obtain a clear solution, which was extracted with ether. The combined extracts were washed with brine, aqueous sodium thiosulfate and brine again. The organic layer was dried with  $\text{MgSO}_4$ , and the solvents were removed under reduced pressure. The crude material was purified by flash chromatography on silica gel. The same procedure was used with cerium and lanthanum.

### Spectroscopic Data

**2-[(Z)-3-Allyl-3-hydroxyhexa-1,5-dienyl]phenol (3):** Purification: eluent pentane/Et<sub>2</sub>O (70:30), yellow oil. Yield 271 mg (59%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 2.34 (s, 1 H, 3'-OH), 2.34 (d,  $J$  = 7.3 Hz, 4 H, 4'-H<sub>2</sub>,  $\text{CH}_2\text{-CH=CH}_2$ ), 5.13 (m,  $J_{\text{trans}}$  = 17.6 Hz,  $J_{\text{cis}}$  = 10.3 Hz, 5 H, 1-OH, 6'-H<sub>2</sub>,  $\text{CH}_2\text{-CH=CH}_2$ ), 5.79 (d,  $J_{1'-2'}$  = 12.7 Hz, 1 H, 2'-H), 5.85 (ddt,  $J_{\text{trans}}$  = 17.1 Hz,  $J_{\text{cis}}$  = 10.3 Hz,  $J$  = 7.3 Hz, 2 H, 5'-H,  $\text{CH}_2\text{-CH=CH}_2$ ), 6.44 (d,  $J_{1'-2'}$  = 12.7 Hz, 1 H, 1'-H), 6.85–6.91 and 7.05–7.25 (2 m, 4 H, 3-H, 4-H, 5-H, 6-H) ppm.  $^{13}\text{C}$  ( $\text{CDCl}_3$ ):  $\delta$  = 45.2 (C-4',  $\text{CH}_2\text{-CH=CH}_2$ ), 75.4 (C-3'), 116.7 (C-6), 119.4 (C-6',  $\text{CH}_2\text{-CH=CH}_2$ ), 120.2 (C-4), 124.7 (C-2), 125.2 (C-2'), 128.7 (C-3), 129.5 (C-5), 133.0 (C-5',  $\text{CH}_2\text{-CH=CH}_2$ ), 138.1 (C-1'), 152.5 (C-1) ppm. FTIR ( $\text{CaF}_2$ ):  $\tilde{\nu}_{\text{max}}$  = 3528, 3306, 3076, 3010, 2978, 2928 2849, 1838, 1698, 1640, 1604, 1586, 1576, 1502, 1450, 1414, 1364, 1228, 1170. GC-MS:  $m/z$  (%) = 41 (70), 77 (12), 91 (46), 103 (46), 115 (12), 147 (100), 171 (22), 189 (22), 230 (1). HRMS: calcd. for  $\text{C}_{15}\text{H}_{18}\text{O}_2$ : 230.1307; found 230.1310.

**1-(4-tert-Butylphenyl)-2-methylbutan-2-ol (4):** Purification: eluent pentane/EtOAc (90:10), white powder. Yield 716 mg (93%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.96 (t,  $J$  = 7.5 Hz, 3 H, 4-H<sub>3</sub>), 1.13 (s, 3 H, 2-CH<sub>3</sub>), 1.30 [s, 10 H, C(CH<sub>3</sub>)<sub>3</sub>, OH], 1.49 (q,  $J$  = 7.5 Hz, 2 H, 3-H<sub>2</sub>), 2.65 (d,  $J$  = 1.3 Hz, 1 H, 1-H<sub>a</sub>), 2.75 (d,  $J$  = 1.3 Hz, 1 H, 1-H<sub>b</sub>), 7.13 (d,  $J$  = 8.0 Hz, 2 H, Ar), 7.32 (d,  $J$  = 8.0 Hz, 2 H, Ar) ppm.  $^{13}\text{C}$  (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.4, 25.9, 31.4 [C(CH<sub>3</sub>)<sub>3</sub>], 34.1, 34.4 [C(CH<sub>3</sub>)<sub>3</sub>], 46.9 (C-1), 72.7 (C-2), 125.1, 130.2, 134.4, 149.2 ppm. HRMS (electrospray): calcd. for  $\text{C}_{15}\text{H}_{24}\text{NaO}$ : 243.1725; found 243.1712.  $\text{C}_{15}\text{H}_{24}\text{O}$  (220.4): calcd. C 81.76, H 10.98; found C 81.61, H 11.01.

**1-(4-tert-Butylphenyl)hexan-2-ol (5):** Purification: eluent pentane/EtOAc (95:5), colourless oil. Yield 600 mg (73%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.9 (t,  $J$  = 7.0 Hz, 3 H, 6-H<sub>3</sub>), 1.5 and 1.3 (2 m, 7 H, 3-H<sub>2</sub> to 5-H<sub>2</sub>, OH), 1.3 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 2.57 (dd,  $J_{\text{a-b}}$  = 13.5 Hz,  $J_{\text{a-2}}$  = 8 Hz, 1 H, 1-H<sub>b</sub>), 2.79 (dd,  $J_{\text{a-b}}$  = 13.5 Hz,  $J_{\text{a-2}}$  = 4 Hz, 1 H, 1-H<sub>a</sub>), 3.76 [m, 1 H, 2-H], 7.12 (d,  $J$  = 8.0 Hz, 2 H, Ar), 7.32 (d,  $J$  = 8.0 Hz, 2 H, Ar) ppm.  $^{13}\text{C}$  ( $\text{CDCl}_3$ ):  $\delta$  = 14.1 (C-6), 22.7, 28.0, 31.4 [C(CH<sub>3</sub>)<sub>3</sub>], 34.4 [C(CH<sub>3</sub>)<sub>3</sub>], 36.6, 43.5 (C-1), 72.7 (C-2), 125.5, 129.1, 135.5, 149.3 ppm. FTIR ( $\text{CaF}_2$ ):  $\tilde{\nu}_{\text{max}}$  = 3562, 3370, 2958, 1512, 1465, 1363, 1269. GC-MS:  $m/z$  (%) = 41 (22), 57 (38), 69 (11), 133 (100), 148 (27), 234 (2). HRMS (electrospray): calcd. for  $\text{C}_{16}\text{H}_{26}\text{NaO}$ : 257.1881; found 257.1884.

**1-(4-tert-Butylphenyl)nonan-2-ol (6):** Purification: eluent pentane/EtOAc (95:5), colourless oil. Yield 793 mg (82%)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.85 (t, 3 H, 9-H<sub>3</sub>), 1.26 (m, 10 H), 1.29 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.46–1.56 (m, 2 H, 3-H<sub>2</sub>), 1.56 (s, 1 H, OH), 2.67 (dd,

$J_{a-b} = 13.5$  Hz,  $J_{a-2} = 8.5$  Hz, 1 H, 1- $H_a$ ), 2.79 (dd,  $J_{a-b} = 13.5$  Hz,  $J_{b-2} = 4$  Hz, 1 H, 1- $H_b$ ), 3.76 (m, 1 H, 2-H), 7.13 (d,  $J = 8.0$  Hz, 2 H, Ar), 7.32 (d, Ar,  $J = 8.0$  Hz, 2 H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 14.1$  (C-9), 22.6, 25.8, 29.3, 29.6, 31.4 [ $\text{C}(\text{CH}_3)_3$ ], 31.8, 34.4 [ $\text{C}(\text{CH}_3)_3$ ], 36.7, 43.5 (C-1), 72.7 (C-2), 125.5, 129.1, 135.5, 149.2 ppm. FTIR ( $\text{CaF}_2$ ):  $\tilde{\nu}_{\text{max}} = 3559, 3369, 2958, 2928, 2870, 2857, 1902, 1789, 1513, 1465$ . GC-MS:  $m/z$  (%) = 41 (11), 57 (22), 69 (10), 92 (24), 133 (100), 148 (33), 276 (2). HRMS (electrospray): calcd. for  $\text{C}_{19}\text{H}_{32}\text{NaO}$ : 299.2351; found 299.2347.

**1-(4-*tert*-Butylphenyl)-2-phenylpropan-2-ol (7):** Purification: eluent pentane/EtOAc (95:5), white powder. Yield 602 mg (64%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.30$  [s, 9 H,  $\text{C}(\text{CH}_3)_3$ ], 1.53 (s, 3 H, 3- $H_3$ ), 1.88 (s, 1 H, OH), 2.97 (d,  $J = 8.0$  Hz, 1 H, 1- $H_a$ ), 3.10 (d,  $J = 8.0$  Hz, 1 H, 1- $H_b$ ), 6.95 (d,  $J = 8.0$  Hz, 2 H, Ar), 7.24 (d,  $J = 8.0$  Hz, 2 H, Ar), 7.24 to 7.45 (m, 5 H, Ph) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 29.4$  (C-3), 31.3 [ $\text{C}(\text{CH}_3)_3$ ], 34.4 [ $\text{C}(\text{CH}_3)_3$ ], 49.8 (C-1), 74.3 (C-2), 124.9, 125.0, 126.6, 128.0, 130.3, 133.5, 147.8, 149.5 ppm. FTIR ( $\text{CaF}_2/\text{CCl}_4$ ):  $\tilde{\nu}_{\text{max}} = 3603, 3571, 3090, 3060, 3028, 2967, 2932, 2906, 2870, 1603, 1516, 1494, 1476, 1447, 1374, 1364$ . GC-MS:  $m/z$  (%) = 43 (100), 121 (66), 133 (81), 148 (61), 250 (1). HRMS (electrospray): calcd. for  $\text{C}_{19}\text{H}_{24}\text{NaO}$ : 291.1725; found 291.1727.  $\text{C}_{19}\text{H}_{24}\text{O}$  (268.4): calcd. C 85.03, H 9.01; found C 84.52, H 9.04.

**2-(4-*tert*-Butylphenyl)-1-phenylethanol (8):** Purification: eluent pentane/EtOAc (97:3), white powder. Yield 405 mg (46%).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.30$  [s, 9 H,  $\text{C}(\text{CH}_3)_3$ ], 1.97 (d, 1 H, OH), 2.94 (dd,  $J_{a-b} = 14$  Hz,  $J_{a-1} = 9$  Hz, 1 H, 2- $H_a$ ), 3.03 (dd,  $J_{a-b} = 14$  Hz,  $J_{b-1} = 4.5$  Hz, 1 H, 2- $H_b$ ), 4.88 (m, 1 H, 1-H), 7.10–7.45 (m, 9 H, Ar) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 31.4$  [ $\text{C}(\text{CH}_3)_3$ ], 34.4 [ $\text{C}(\text{CH}_3)_3$ ], 45.7 (C-2), 75.2 (C-1), 125.5, 125.9, 127.6, 128.4, 129.1, 135.0, 144.0, 149.5 ppm. FTIR ( $\text{CaF}_2/\text{CCl}_4$ ):  $\tilde{\nu}_{\text{max}} = 3555, 3405, 3063, 3027, 2967, 2865, 1946, 1904, 1802, 1602, 1512, 1491, 1452, 1362, 1269$ . HRMS: calcd. for  $\text{C}_{18}\text{H}_{22}\text{O}$ : 254.1671; found 254.1675.  $\text{C}_{18}\text{H}_{22}\text{O}$  (254.4): calcd. C 84.99, H 8.72; found C 84.77, H 8.71.

**1-(4-*tert*-Butylbenzyl)cyclohex-2-enol (9):** Purification: eluent pentane/EtOAc (97:3), colourless oil. Yield 504 mg (59%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.30$  [s, 9 H,  $\text{C}(\text{CH}_3)_3$ ], 1.55 (d,  $J = 2.25$  Hz, 1 H, OH), 1.70 (m, 4 H, 5- $H_2$ , 6- $H_2$ ), 2.01 (m, 2 H, 4- $H_2$ ), 2.80 (s, 2 H,  $\text{CH}_2$ -Ar), 5.61 (dd,  $J_{2-3} = 10$  Hz,  $J = 2.25$  Hz, 1 H, 2-H), 5.82 (dt,  $J_{2-3} = 10$  Hz,  $J_{3-4} = 3.75$  Hz, 1 H, 3-H), 7.18 (d, 2 H, Ar), 7.33 (d, 2 H, Ar) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 19.1, 25.2, 31.4$  [ $\text{C}(\text{CH}_3)_3$ ], 34.4 [ $\text{C}(\text{CH}_3)_3$ ], 35.7, 47.6, 69.6 (C-1), 125.0, 129.8, 130.3, 132.3, 133.8, 149.2 ppm. FTIR ( $\text{CaF}_2$ ):  $\tilde{\nu}_{\text{max}} = 3551, 3427, 3022, 2961, 2867, 2829, 1904, 1793, 1705, 1647, 1513, 1458, 1439, 1411, 1393, 1363$ . GC-MS:  $m/z$  (%) = 41 (24), 57 (15), 77 (19), 79 (18), 91 (32), 117 (15), 133 (53), 148 (32), 169 (28), 211 (48), 226 (25). HRMS: calcd. for  $\text{C}_{17}\text{H}_{24}\text{O}$ : 244.1827; found 244.1833.

**1,3-Bis(4-*tert*-butylphenyl)-2-phenylpropan-2-ol (10):** Purification: eluent pentane/EtOAc (95:5), white powder. Yield 641 mg (80%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.25$  [s, 18 H,  $\text{C}(\text{CH}_3)_3$ ], 1.90 (s, 1 H, OH), 3.24 and 3.05 (2 d,  $J = 13.5$  Hz, 4 H, 1- $H_2$ , 3- $H_2$ ), 6.87 (d,  $J = 8.0$  Hz, 4 H, Ar), 7.16 (d,  $J = 8.0$  Hz, 4 H, Ar), 7.25 (m, 5 H, Ph) ppm.  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta = 31.3$  [ $\text{C}(\text{CH}_3)_3$ ], 34.3 [ $\text{C}(\text{CH}_3)_3$ ], 48.1 (C-1, C-3), 76.9 (C-2), 124.8, 125.9, 126.4, 127.7, 130.4, 133.3, 145.8, 149.2 ppm. FTIR ( $\text{CaF}_2$ ):  $\tilde{\nu}_{\text{max}} = 3563, 2962, 1675, 1604, 1514, 1446, 1363, 1268$ . GC-MS:  $m/z$  (%) = 41 (17), 57 (55), 77

(15), 91 (23), 105 (84), 119 (11), 133 (14), 147 (12), 197 (100), 253 (94), 382 (3). HRMS (electrospray): calcd. for  $\text{C}_{29}\text{H}_{36}\text{NaO}$ : 423.2664; found 423.2661.  $\text{C}_{29}\text{H}_{36}\text{O}$  (400.6): calcd. C 86.95, H 9.06; found. C 86.56, H 9.09.

**2-[(E)-3-Benzyl-3-hydroxy-4-phenylbut-1-enyl]phenol (11):** Purification: eluent heptane/EtOAc (80:20), yellow powder. Yield 272 mg (59%).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.94$  (s, 1 H, 3'-OH), 3.06 (s, 4 H, 4'- $H_2$ ,  $\text{CH}_2$ -Ph), 5.29 (s, 1 H, 1-OH), 6.25 (d,  $J_{1'-2'}$  = 16.1 Hz, 1 H, 2'-H), 6.41 (d,  $J_{1'-2'}$  = 16.1 Hz, 1 H, 1'-H), 6.81 (d,  $J_{5-6}$  = 7.8 Hz, 1 H, 6-H), 6.9 (dd,  $J_{5-6}$  = 7.8 Hz,  $J_{4-5}$  = 7.3 Hz, 1 H, 5-H), 6.94–7.39 (m, 12 H, 3-H, 4-H, 2 Ph) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 47.8$  (C-4',  $\text{CH}_2$ -Ph), 76.0 (C-3'), 115.9 (C-6), 120.6 (C-4), 123.5 (C-1'), 124.2 (C-2), 126.7, 127.3 (C-2'), 128.1, 128.5 (C-3), 130.7, 136.4, 137.2 (C-5), 152.9 (C-1) ppm. FTIR ( $\text{CaCl}_2$ ):  $\tilde{\nu}_{\text{max}} = 3527, 3477, 3031, 2924, 1603, 1582, 1492, 1335, 1269, 1217$ . GC-MS:  $m/z$  (%) = 91 (100), 203 (11), 221 (50), 239 (38), 312 (5). HRMS (electrospray): calcd. for  $\text{C}_{23}\text{H}_{22}\text{O}_2 - \text{H}_2\text{O}$ : 312.1512; found 312.1514.  $\text{C}_{23}\text{H}_{22}\text{O}_2$  (330.4): calcd. C 83.60, H 6.71; found C 83.24, H 6.77.

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- [1] F. Hélicon, J. L. Namy, *J. Org. Chem.* **1999**, *64*, 2944–2946.
- [2] C. Blomberg, *The Barbier Reaction and Related One-step Processes*, Springer-Verlag, Berlin, Heidelberg, **1993**.
- [3] A. Russo, *The Barbier Reaction (Handbook of Grignard Reagents)*, M. Dekker, Inc., New York, **1996**, p. 405–439.
- [4] G. Molle, P. Bauer, *J. Am. Chem. Soc.* **1982**, *104*, 3481–3487.
- [5] D. P. Curran, M. J. Totleben, *J. Am. Chem. Soc.* **1992**, *114*, 6050–6058.
- [6] D. P. Curran, T. L. Fevig, C. P. Jasperse, M. J. Totleben, *Synlett* **1992**, 943–961.
- [7] P. Wipf, S. Venkatraman, *J. Org. Chem.* **1993**, *58*, 3455–3459.
- [8] B. Gaudinet-Hamann, J. L. Namy, H. B. Kagan, *Tetrahedron Lett.* **1997**, *38*, 6585–6588.
- [9] G. A. Molander, J. A. Mckie, *J. Org. Chem.* **1992**, *57*, 3132–3139.
- [10] H. M. Walborsky, M. Topolski, *J. Org. Chem.* **1992**, *57*, 370–373.
- [11] C. Bied, J. Collin, H. B. Kagan, *Tetrahedron* **1992**, *48*, 3877–3890.
- [12] P. Girard, J. L. Namy, H. B. Kagan, *J. Am. Chem. Soc.* **1980**, *102*, 2693–2698.
- [13] S.-I. Fukuzawa, T. Fujinami, S. Sakai, *J. Organomet. Chem.* **1986**, *299*, 179–185.
- [14] T. Imamoto, T. Kusumoto, Y. Tawarayama, Y. Sugiura, T. Mita, Y. Hatanaka, M. Yokoyama, *J. Org. Chem.* **1984**, *49*, 3904–3912.
- [15] J. Soupe, J. L. Namy, H. B. Kagan, *Tetrahedron Lett.* **1982**, *23*, 3497–3500.
- [16] P. Miginiac, *Bull. Soc. Chim. Fr.* **1970**, 1077–1083.
- [17] R. A. Benkesser, P. Siklosi, *J. Org. Chem.* **1976**, *41*, 3212–3213.
- [18] S.-I. Fukuzawa, K. Mutoh, T. Tsuchimoto, T. Hiyama, *J. Org. Chem.* **1996**, *61*, 5400–5405.
- [19] Z. Li, Y. Zhang, *Tetrahedron Lett.* **2001**, *42*, 8507–8510.