Reductive Coupling of Allylic Esters with Carbonyl Compounds Mediated by the Mischmetall/[SmI_2/$Pd^0{}_{cat.'}$]$_{cat.}$ System

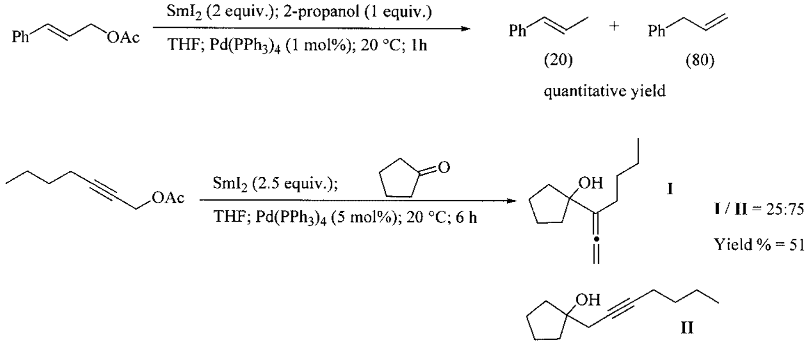
Sédami Médégan,[a] Florence Hélion,[a] and Jean-Louis Namy*[a]

Keywords: Allylation / Catalysis / Mischmetall / Samarium / Palladium

The mischmetall/[SmI_2/$Pd^0{}_{cat.'}$]$_{cat.}$ system has been used to mediate the allylation of ketones using a variety of allylic esters (acetates, carbonates and phosphates). Thus, a "two-stage catalysis" has been carried out using SmI_2 and $Pd(PPh_3)_4$ in catalytic amounts together with mischmetall (an alloy of the light lanthanides) as a co-reductant. A catalytic scheme that takes into account previously reported reactions of SmI_2/$Pd^0{}_{cat.}$ and mischmetall/$SmI_{2,cat.}$ systems is proposed. It has also been shown that palladium complexes catalyse the addition of organolanthanide species to ketones.

Introduction

The reduction of allylic and propargylic esters in the presence of an alcohol, as well as the coupling of these substrates with carbonyl compounds, using a combination of SmI_2 and catalytic Pd^0 have been widely studied.[1–10] Some examples of these reactions are shown in Scheme 1.

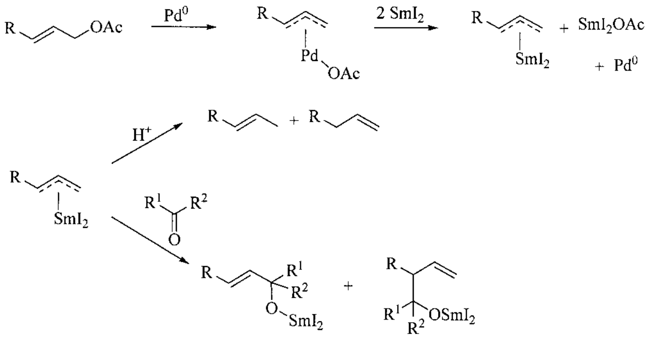


Scheme 1.

Mischmetall, an alloy of the light lanthanides (Ce, La, Nd and Pr), also known as cerium mixed metal, is obtained from bastnaesite (a lanthanide ore). It is an industrial material used in steelmaking which is available in large quantities at a low price since the elements are not separated (an expensive process).

In these reactions, the formation of a (π-allyl)palladium species, which is subsequently reduced to an organosamarium compound with the regeneration of Pd^0, is likely (Scheme 2).

In addition, we have recently reported the use of mischmetall as a co-reductant in the catalytic reactions of some organic substrates with samarium diiodide.[11,12] For example, Barbier-type reactions have been studied[13] (Scheme 3).



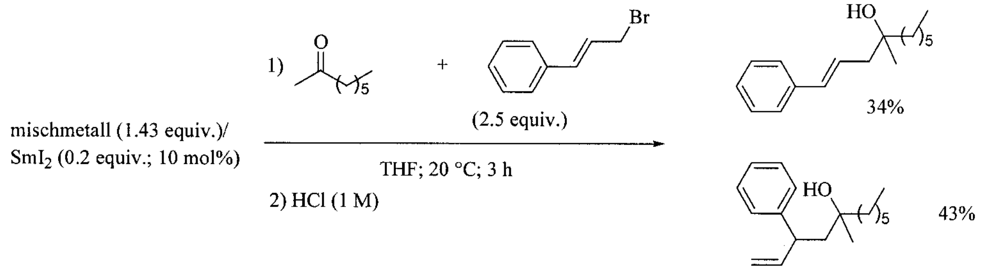
Scheme 2.

Two mechanisms for this transformation are conceivable (Figures 1 and 2). In the first mechanism (Figure 1), an or

---

[a] Laboratoire de Catalyse Moléculaire, associé au CNRS,
ICMMO, Bat 420, Université Paris-Sud,
91405, Orsay, France
Fax: +33-1-69154680
E-mail: jelonamy@icmo.u-psud.fr

DOI: 10.1002/ejoc.200500291



Scheme 3.

ganosamarium compound, RSmIX (or $RSmX_2$ or $RSmI_2$) is formed first. Its addition to a carbonyl compound gives a samarium alkoxide. This in turn, through reduction/transmetallation with the lanthanide, gives lanthanide alkoxide with the regeneration of SmI_2 (or SmX_2). In the second mechanism (Figure 2), the initially formed RSmIX reacts with lanthanide to give another organometallic compound (LnR_3; Ln ≠ Sm) through reduction/transmetallation with the regeneration of SmI_2. This organolanthanide compound then adds to the carbonyl compound to furnish an alkoxide.

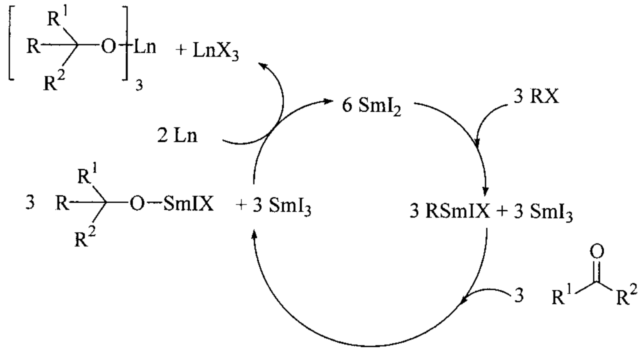


Figure 1. Catalytic scheme I.

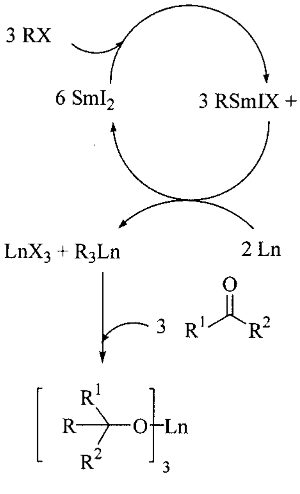


Figure 2. Catalytic scheme II.

Evidence[13] that allylation reactions with cinnamyl bromide can be performed sequentially (addition of cinnamyl bromide, then the ketone), even though trivalent allylic samarium species are unstable, leads us to conclude that the second mechanism is more plausible.

We wondered whether it would be possible to allylate carbonyl compounds with allylic esters using the mischmetall/$[SmI_2/Pd^0{}_{cat.'}]_{cat.}$ system (with mischmetall as a co-reductant, catalytic amounts of SmI_2 with respect to mischmetall and catalytic amounts of Pd^0 with respect to SmI_2). This system is comparable to the mischmetall/$[SmI_2/NiI_{2,cat.'}]_{cat.}$ one, which has been used to alkylate lactones, and would amount to a "two-stage catalysis".[14] This catalytic process could also be related to "concurrent tandem catalysis" since it involves the cooperative action of two catalytic cycles in a single reactor.[15]

Results and Discussion

A variety of allylic acetates (with the exception of allyl acetate) have been used to allylate carbonyl compounds (ketones and aldehydes); an intramolecular reaction has also been reported.[2] To the best of our knowledge the use of allylic carbonates in these reactions have not been tested whereas allylic phosphates have been studied but in the absence of Pd^0.[16] However, it has been mentioned that these latter substrates should be more reactive in the presence of $Pd(PPh_3)_4$.[17]

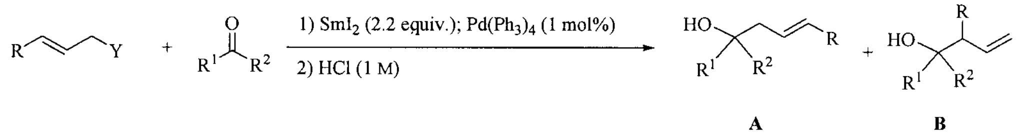
Since our aim was to test a large variety of substrates in reactions mediated by the mischmetall/$[SmI_2/Pd^0{}_{cat.'}]_{cat.}$ system, we first studied the reactions of some allylic esters (carbonates, phosphates and acetates) using the $SmI_2/Pd^0{}_{cat.}$ system.

Some examples of the allylation rections of ketones are gathered in Table 1.

With cinnamyl carbonate, the yields of the homoallylic alcohols were satisfactory. Except in the case of 5-nonanone (Entry 3), mixtures of two homoallylic alcohols were obtained with the linear isomer (product **A**) as the major product. In all cases, dienes arising from the coupling of the cinnamyl moiety were formed as by-products (1,4-diphenylhexa-1,5-diene, 1,6-diphenylhexa-1,5-diene and 3,4-diphenylhexa-1,5-diene). The alcohols were also observed in the absence of palladium; the reaction was slower but the **A**/**B** ratios are only slightly dependent on the presence of the catalyst (Entries 1 and 2).

With allyl carbonate the yields of the expected alcohols were lower; hexa-1,5-diene was almost certainly the main by-product, but unfortunately this compound (b.p. 59.5 °C)

Table 1. Allylation reactions with allylic esters.[a]



Entry	Y	R^1, R^2	Isolated yield (%) of **A** + **B** (**A/B**)	
			R = phenyl	R = H (**A** = **B**)
1	$-OC(O)_2CH_3$	$-(CH_2)_5-$	74 (2.8)	27
2[b]	$-OC(O)_2CH_3$	$-(CH_2)_5-$	49 (2.65)	n.d.
3	$-OC(O)_2CH_3$	n-C_4H_9, n-C_4H_9	68 (0.8)	45
4	$-OC(O)_2CH_3$	CH_3, n-C_6H_{13}	78 (3.12)	52
5	$-OC(O)_2CH_3$	$C_6H_5CH_2CH_2$, CH_3	63 (6.54)	complex mixture
6[c]	$-OPO(OC_2H_5)_2$	$-(CH_2)_5-$	64 (2.24)	n.d.
7[d]	$-OPO(OC_2H_5)_2$	$-(CH_2)_5-$	51 (2.40)	n.d.
8[c]	$-OCOCH_3$	$-(CH_2)_5-$	77 (2.44)	n.d.

[a] Conditions: THF, 20 °C, 3 h. [b] Without $Pd(Ph_3)_4$; 16 h. [c] Reaction time: 1 h. [d] Without $Pd(PPh_3)_4$; 1 h.

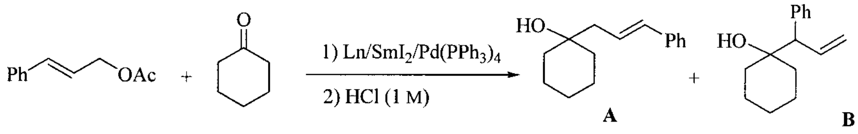
could not be observed easily under our experimental conditions. With cinnamyl phosphate (Entries 6 and 7) the presence of Pd^0 led to a significant increase in the yield of alcohol (64% in the presence of Pd^0 compared with 51% in its absence) but the **A/B** ratios were similar (2.24 and 2.40). Unexpectedly, we obtained better isolated yields of the alcohols than has previously been reported in the literature (51 compared with 37%).[16] With cinnamyl acetate and cyclohexanone, (Entry 8), in contrast to previously reported results,[5] we obtained linear and branched isomeric alcohols (**A/B** = 2.44).

Coupling between cinnamyl acetate and cyclohexanone mediated by mischmetall/$[SmI_2/Pd^0_{cat.'}]_{cat.}$ was studied under a variety of experimental conditions (Table 2).

This system could be used to carry out this reaction efficiently, all the components of the catalytic system (mischmetall/SmI_2/Pd^0) being essential (Entries 9 and 10). Mixtures of homoallylic alcohols (linear and branched) were formed; the **A/B** ratio was close to 1 with a slight preponderance of the linear isomer **A**. The use of 2.5 mol-% $Pd(PPh_3)_4$ was found to give satisfactory results. Note that a sequential procedure failed, the expected alcohols not being detected; instead, 1,4-diphenylhexa-1,5-diene was observed as a single product (Scheme 4). This result is in contrast with the coupling reaction between cinnamyl bromide and carbonyl compounds mediated by the mischmetall/$SmI_{2,cat.}$system.[13] Finally, the experimental conditions shown in Entry 2 were found to give the best results (Table 2).

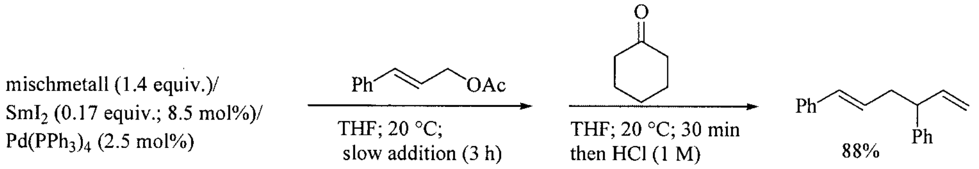
It is also important to note that the **A/B** ratios obtained under both samarium diiodide catalytic (Table 2, Entry 2) and stoichiometric conditions (Table 1, Entry 8) differ sig-

Table 2. Allylation of cyclohexanone under a variety of experimental conditions.[a]



Entry	Ln[b]	Cinnamyl acetate [mmol]	Cyclohexanone [mmol]	$Pd(PPh_3)_4$ [mol-%][c]	Isolated yield (%) **A** + **B** (**A/B**)
1	mischmetall	3	5	2.5	49 (1.2)
2	mischmetall	4	4	2.5	68 (1.12)
3[d]	mischmetall	4	4	2.5	60 (1.04)
4	mischmetall	5	3.5	2.5	62 (1.0)
5[d]	mischmetall	5	3.5	2.5	54 (1.06)
6[e]	mischmetall	4	4	2.5	50 (1.0)
7	mischmetall	5	3.5	1	34 (1.04)
8	mischmetall	4	4	1[f]	45 (1.07)
9[g]	mischmetall	5	3.5	2.5	0
10	mischmetall	5	3.5	0	0
11	La	4	4	2.5	36 (0.8)
12	Ce	4	4	2.5	33 (1.0)
13	Gd	4	4	2.5	10 (2.40)

[a] The ester and cyclohexanone in THF (5 mL) were added to mischmetall/SmI_2/Pd^0 over 3 h, and stirring was then continued for 12 h at 20 °C. [b] Ln (1.4 equiv.), SmI_2 (0.17 equiv.) according to substrate (cinnamyl acetate or cyclohexanone) in the lesser quantity. [c] In mol-% according to substrate (cinnamyl acetate or cyclohexanone) in the lesser quantity. [d] Substrates were added over 9 h. [e] Substrates were added over 1 h, and then stirring was continued for a further 1 h. [f] With PPh_3 (30 mol-%). [g] Without SmI_2.



Scheme 4.

nificantly (1.12 and 2.44), which could be indicative of the involvement of different organometallic species.

As the main components of mischmetall are cerium and lanthanum, these were tested instead of mischmetall under similar experimental conditions. In addition we used gadolinium, an element that follows samarium in the lanthanide group (Table 2, Entries 11–13).

With cerium and lanthanum, the expected homoallylic alcohols were obtained in moderate yields (lower than those obtained with mischmetall), the **A**/**B** ratios being close to 1, as with the alloy, whereas gadolinium gave the products in low yields (10%) with an **A**/**B** ratio of 2.40. In the latter case the formation of alcohols could mainly be ascribed to a stoichiometric reaction with samarium diiodide.

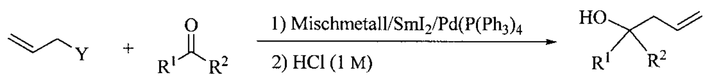
The mischmetall/[SmI_2/$Pd^0{}_{cat.'}$]$_{cat.}$ system was also used to allylate ketones and aldehydes with allyl esters (acetate, carbonate and phosphate) under the optimised experimental conditions (Table 2, Entry 2). The results are collected in Table 3. Homoallylic alcohols were produced in moderate yields, as with the SmI_2/Pd^0cat. system. Allyl phosphate gave the best results.

The coupling of a variety of ketones with cinnamyl esters was also studied (Table 4).

With these esters, similar yields of homoallylic alcohols were obtained which were, on the whole, satisfactory. In all these cases, mixtures of two homoallylic alcohols were obtained. The **A**/**B** ratios depend on the esters and ketones. Linear alcohols predominate, except with 4-nonanone. In the absence of Pd^0, the allylation of cyclohexanone with cinnamyl phosphate occurred but the alcohols were produced in poor yields (25% instead of 63% with palladium).

By considering the results and interpretations suggested above (Scheme 2 and Figure 2), the following catalytic scheme III can be proposed for the reactions mediated by the mischmetall/[SmI_2/$Pd^0{}_{cat.'}$]$_{cat.}$ system (Figure 3).

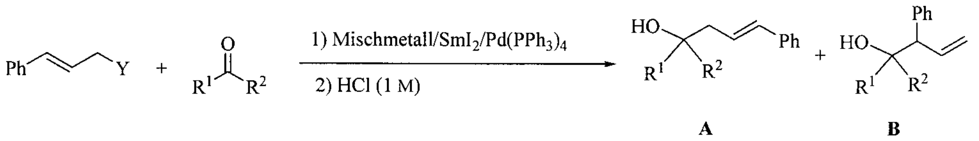
Table 3. Allylation of ketones with allyl esters.[a]



Entry	R^1, R^2	Product: isolated yield (%)		
		Y = $–OCOCH_3$	Y = $–OPO(OC_2H_5)_2$	Y = $–OC(O)_2CH_3$
1	$–(CH_2)_5–$	43	47	34
2	4-*t*Bu-cyclohexanone	47[b]	46[b]	40[b]
3	CH_3, n-C_6H_{13}	36	45	18
4	n-C_4H_9, n-C_4H_9	43	46	52
5	CH_3, $PhCH_2CH_2$	26	60	23
6	Ph, H	complex mixture	34	complex mixture

[a] SmI_2 (0.17 equiv.), mischmetall (1.4 equiv.), $Pd(PPh_3)_4$ (2.5 mol-%); ester (4 mmol) and ketone (4 mmol) in THF (5 mL) were added to mischmetall/SmI_2/Pd^0 over 3 h, and stirring was then continued at 20 °C for 12 h. [b] OH_{ax}/OH_{eq} = 2.7 (acetate); 2.5 (phosphate); 0.93 (carbonate).

Table 4. Coupling of ketones with cinnamyl esters.[a]



Entry	R^1, R^2	Isolated yields (%) **A** + **B** (**A**/**B**)		
		Y = $–OCOCH_3$	Y = $–OPO(OC_2H_5)_2$	Y = $–OC(O)_2CH_3$
1	$–(CH_2)_5–$	68 (1.12)	63 (1.83)	62 (1.26)
2	4-*t*Bu-cyclohexanone	25 (1.8)	31 (1.26)	n.d.
3	CH_3, n-C_6H_{13}	29 (1.6)	18 (1.35)	19 (1.85)
4	n-C_4H_9, n-C_4H_9	70 (0.36)	77 (0.58)	73 (0.6)
5	CH_3, $PhCH_2CH_2$	51 (1.4)	40 (1.18)	54 (1.85)

[a] SmI_2 (0.17 equiv.), mischmetall (1.4 equiv.), $Pd(PPh_3)_4$ (2.5 mol-%); ester (4 mmol) and ketone (4 mmol) in THF (5 mL) were added to mischmetall/SmI_2/Pd^0 over 3 h, and stirring was then continued at 20 °C for 12 h.

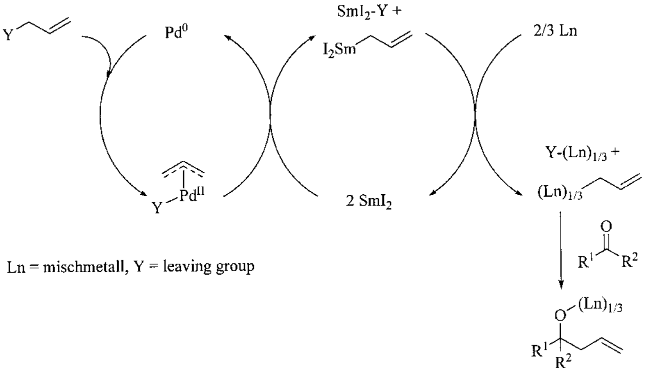


Figure 3. Catalytic scheme III.

It involves the formation of an allylic lanthanide compound (Ln ≠ Sm), which adds to a carbonyl compound. Since it has been shown that the organometallic species prepared by the reaction of cinnamyl bromide with the mischmetall/$SmI_{2,cat.}$ system is stable,[13] it is somewhat surprising that a sequential procedure could not be carried out with cinnamyl esters and the mischmetall/$[SmI_2/Pd^0{}_{cat.'}]_{cat.}$ system (Scheme 4). An alternative catalytic scheme IV can be proposed which supposes the addition of an allylic samarium compound onto the carbonyl compound (Figure 4).

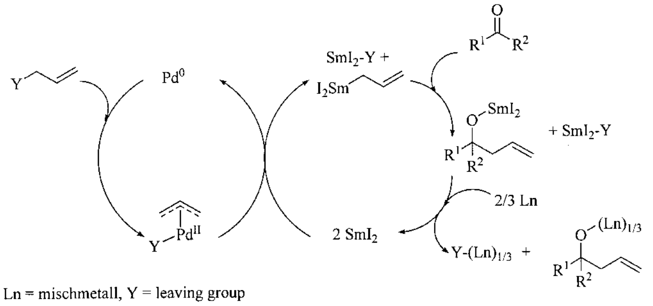


Figure 4. Catalytic scheme IV.

However, this mechanism seems unlikely since the **A/B** ratios (linear/branched) obtained under stoichiometric ($SmI_2/Pd^0{}_{cat.}$) conditions differ significantly to those obtained under catalytic conditions (mischmetall/$[SmI_2/Pd^0{}_{cat.'}]_{cat.}$), which probably indicates that it is not the organosamarium species that adds to the ketone under catalytic conditions.

Presumably, the failure of the sequential procedure (formation of a diene) results from an easy reaction between an allylic lanthanide compound and a π-allylic complex of palladium. Such couplings are well known in palladium chemistry: “hard” nucleophiles first attack the palladium atom to give a neutral complex which liberates the coupling product through reductive elimination.[18] This coupling reaction also accounts for the moderate yields of alcohols obtained with allyl esters.

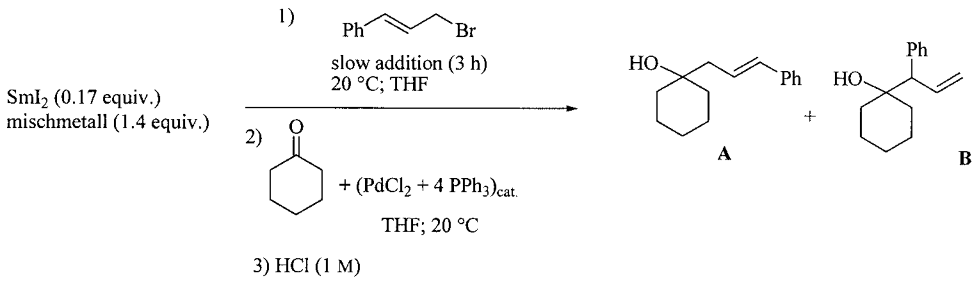
Since Yamamoto and co-workers have found that bis(π-allyl)palladium complexes are able to react with electrophiles such as aldehydes and imines,[19] we will consider the possibility that such a species could be involved in reactions mediated by the Ln/$[SmI_2/Pd^0{}_{cat.'}]_{cat.}$ or $SmI_2/Pd^0{}_{cat.}$ systems.

To gain further information regarding this possibility, we first prepared an organolanthanide compound from cinnamyl bromide[13] and then studied its reaction with cyclohexanone in the presence of catalytic amounts of $PdCl_2$ and triphenylphosphane. Since Sm^{II} derivatives are also present during this second step, reduction to Pd^0 species is likely. The results and experimental conditions are given in Table 5.

The following comments can be made: (1) the addition of the organometallic species to cyclohexanone is slow with several hours needed to reach completion, (2) the presence of palladium complexes has a significant effect on the yields of the alcohols, and (3) the beneficial effect is moderate and the **A/B** ratios do not vary in the presence or absence of palladium complexes.

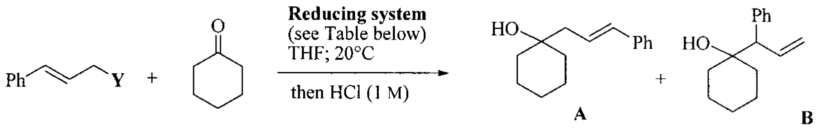
This means that palladium complexes are involved in several steps of the reactions (the formation of organometal-

Table 5. Addition of cinnamyllanthanide compounds to cyclohexanone in the presence of palladium complexes.



Entry	($PdCl_2$ + 4 PPh_3) [mol-%]	Reaction time [h]	Isolated yield [%] **A** + **B** (**A/B**)
1	0	0.5	16 (0.88)
2	2.5	0.5	27 (0.84)
3	0	1.5	52 (0.96)
4	2.5	1.5	80 (0.95)

Table 6. Dependence of **A**/**B** ratios on reaction conditions.

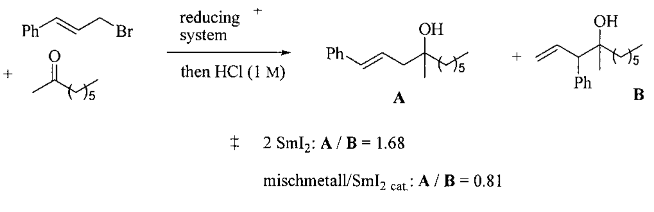


Entry	Reducing system	Y	**A/B**
1	SmI_2	$-OCOCH_3$	n.r.
2	SmI_2	$-OPO(OC_2H_5)_2$	2.24
4	SmI_2	$-OC(O)_2CH_3$	2.65
4	SmI_2	–Br	2.76
5	$SmI_2/Pd^0_{cat.}$	$-OCOCH_3$	2.44
6	$SmI_2/Pd^0_{cat.}$	$-OPO(OC_2H_5)_2$	2.40
7	$SmI_2/Pd^0_{cat.}$	$-OC(O)_2CH_3$	2.80
8	$SmI_2/Pd^0_{cat.}$	–Br	2.85
9	mischmetall/$SmI_{2,cat.}$	$-OCOCH_3$	n.r.
10	mischmetall/$SmI_{2,cat.}$	$-OPO(OC_2H_5)_2$	0.96
11	mischmetall/$SmI_{2,cat.}$	$-OC(O)_2CH_3$	n.r.
12	mischmetall/$SmI_{2,cat.}$	–Br	0.96
13	mischmetall/$[SmI_2/Pd^0_{cat.'}]_{cat.}$	$-OCOCH_3$	1.12
14	mischmetall/$[SmI_2/Pd^0_{cat.'}]_{cat.}$	$-OPO(OC_2H_5)_2$	1.83
15	mischmetall/$[SmI_2/Pd^0_{cat.'}]_{cat.}$	$-OC(O)_2CH_3$	1.26
16	mischmetall/$[SmI_2/Pd^0_{cat.'}]_{cat.}$	–Br	0.95
17	La/$[SmI_2/Pd^0_{cat.'}]_{cat.}$	$-OCOCH_3$	0.8
18	Ce/$[SmI_2/Pd^0_{cat.'}]_{cat.}$	$-OCOCH_3$	1.0

lics from allylic esters and the reactions of these species with electrophiles). However, the addition to carbonyl compounds probably does not proceed through a bis(π-allyl)-palladium species.

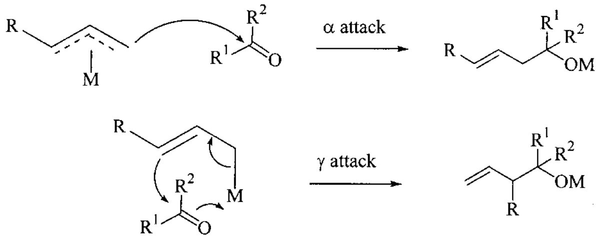
In the reactions involving cinnamyl esters, homoallylic alcohols were obtained as mixtures of linear (**A**) and branched (**B**) isomers. The **A/B** ratio varies widely according to the substrates and reducing systems used. The results obtained from the reactions with cyclohexanone are collected in Table 6; those concerning cinnamyl bromide and this ketone have been included for an exhaustive comparison (Table 6).

The **A/B** ratios are between 2.24 and 2.85 when samarium diiodide is used in stoichiometric amounts, whereas they are in the range of 0.8–1.26 when samarium diiodide is used in catalytic amounts with mischmetall, lanthanum or cerium as co-reductants (with the exception of cinnamyl phosphate, Entry 14). In the first case it is likely that an organosamarium compound is formed, which adds to the ketone; in the second case, homoallylic alcohols should result from the reaction of an organolanthanum and/or an organocerium compound. This feature is also observed in the reactions of 2-octanone (Table 1, Entry 4; Table 4, Entry 4; ref.[20] and Scheme 5).



Scheme 5.

In previous reports,[21,22] α-adducts (isomer **A**), in which the allylic group is linked through the less hindered position, are considered to form through the reaction of organometallic species possessing an η^3-allyl moiety. In contrast, γ-adducts (isomer **B**), in which the allyllic group is attached through the more highly substituted position, result from the reaction of an organometallic species with an η^1-allyl structure (Scheme 6).



Scheme 6.

On the basis of this assumption, it could be considered that cinnamylsamarium compounds possess an η^3-allyl moiety whilst cinnamyllanthanum and -cerium compounds could mainly have an η^1-allyl structure. This result somewhat conflicts with recent results concerning crotyl Grignard reagent/$LnCl_3$ systems.[23] However, other factors such as steric hindrance (organometallic, electrophile) could also affect the product distribution. Besides, comparison with the reactivity of organolanthanides prepared by another procedure is inconclusive.

Conclusions

To conclude, we have studied some new reactions of allylic esters with the $SmI_2/Pd^0_{cat.}$ system and we have demonstrated that it is possible to use the mischmetall/[SmI_2/$Pd^0_{cat.'}$]$_{cat.}$ system to mediate the allylation of carbonyl compounds with allylic esters. Thus a "two-stage catalysis" was carried out using a cheap alloy of the light lanthanides as a co-reductant. Several experimental facts remain to be explained, especially the product distribution of the homoallylic alcohols.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded at 250 and 63 MHz, respectively, with a Bruker AC 250 instrument (unless otherwise stated). IR spectra were recorded with an FTIR IFS 66 Bruker spectrometer. MS data were determined with a GC/MS Fison 8000 instrument. EI was performed at 70 eV. HRMS data and electrospray mass spectra were recorded with a GC/MS Finningan-MAT-95-S spectrometer. Flash chromatography was performed on silica gel (Merck 230–240 mesh; 0.0040–0.0630 mm). All the compounds (homoallylic alcohols and dienes), which were obtained in the reactions indicated above, were identified by comparison with previously published spectroscopic data. All commercially available organic compounds were distilled before use. Lanthanide metals (ingots) 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 (***CAUTION!*** Mischmetall powder is pyrophoric, the ingot may give out sparks when it is scraped, powder must be collected in a flask filled with argon). The powder was kept under argon in a Schlenk tube, the average molecular weight of mischmetall is 140. Tetrahydrofuran (THF) was distilled under argon from sodium benzophenone ketyl. Samarium diiodide was prepared as described previously.[20] Allylic carbonates were prepared according to the procedure of Trost et al.;[24] allylic phosphates were prepared using the same procedure.[25] All reactions were carried out under argon in Schlenk tubes using standard vacuum-line techniques.

Reaction Procedure Using SmI_2: A solution of allylic compound (2 mmol) and ketone (2 mmol) in THF (7 mL) was slowly added to a solution of SmI_2 (4.4 mmol) in THF (44 mL) in a Schlenk tube under argon at room temperature over 3 h. The mixture was then stirred for an additional period of 12 h, diluted with diethyl ether, quenched with HCl (1 M) and stirred for 15 min to obtain a clear solution, which was extracted with diethyl ether. The combined extracts were washed with brine, sodium thiosulfate and brine again. The organic layer was dried with $MgSO_4$ and the solvents were removed under reduced pressure. The crude material was purified by flash chromatography on silica gel.

Reaction Procedure Using the SmI_2/$Pd^0_{cat.}$ System: Tetrakis(triphenylphosphane)palladium (23.4 g, 0.02 mmol) was suspended in THF (44 mL) with SmI_2 (4.4 mmol) in a Schlenk tube under argon at room temperature for 5 min. A solution of an allylic compound (2 mmol) and ketone (2 mmol) in THF (7 mL) was then slowly added to the THF/SmI_2/$Pd(PPh_3)_4$ suspension over 3 h. This mixture was stirred for an additional period of 12 h, diluted with diethyl ether, quenched with HCl (1 M) and stirred for 15 min to obtain a clear solution, which was extracted with diethyl ether. The combined extracts were washed with brine, sodium thiosulfate and brine again. The organic layer was dried with $MgSO_4$ and the solvents were removed under reduced pressure. The crude material was purified by flash chromatography on silica gel.

Reaction Procedure Using the Mischmetall/$SmI_{2,cat.}$ System: Mischmetall powder (0.7 g, 5 mmol) was suspended in THF (7 mL) with SmI_2 (0.7 mmol) in a Schlenk tube under argon at room temperature. A solution of an allylic compound (4 mmol) and ketone (4 mmol) in THF (7 mL) was slowly added to the THF/SmI_2/mischmetall suspension over 3 h. The mixture was then stirred for an additional period of 12 h, diluted with diethyl ether, quenched with HCl (1 M) and stirred for 15 min to obtain a clear solution, which was extracted with diethyl ether. The combined extracts were washed with brine, sodium thiosulfate and brine again. The organic layer was dried with $MgSO_4$ and the solvents were removed under reduced pressure. The crude material was purified by flash chromatography on silica gel.

Reaction Procedure Using Ln/[SmI_2/$Pd^0_{cat.'}$]$_{cat.}$ Systems: Lanthanide powder (Ln = mischmetall, La, Ce or Gd, 5 mmol), tetrakis(triphenylphosphane)palladium (115 g, 0.1 mmol) and SmI_2 (0.7 mmol) were stirred in THF (7 mL), in a Schlenk tube under argon at room temperature for 5 min. A solution of an allylic compound (4 mmol) and ketone (4 mmol) in THF (7 mL) was slowly added to the THF/SmI_2/$Pd[P(Ph)_3]_4$/lanthanide suspension over 3 h. The mixture was then stirred for an additional period of 12 h, diluted with diethyl ether, quenched with HCl (1 M) and stirred for 15 min to obtain a clear solution, which was extracted with diethyl ether. The combined extracts were washed with brine, sodium thiosulfate and brine again. The organic layer was dried with $MgSO_4$ and the solvents were removed under reduced pressure. The crude material was purified by flash chromatography on silica gel.

Sequential Procedure Using the Mischmetall/[SmI_2/$Pd^0_{cat.'}$]$_{cat.}$ System: Mischmetall powder (0.7 g, 5 mmol), tetrakis(triphenylphosphane)palladium (115 g, 0.1 mmol) and SmI_2 (0.7 mmol) were stirred in THF (7 mL) in a Schlenk tube under argon at room temperature for 5 min. A solution of an allylic compound (4 mmol) in THF (7 mL) was slowly added to the THF/SmI_2/$Pd[P(Ph)_3]_4$/mischmetall suspension over 3 h. A solution of a ketone (4 mmol) in THF (5 mL) was then quickly added. The mixture was then stirred for an additional period of 12 h, diluted with diethyl ether, quenched with HCl (1 M) and stirred for 15 min to obtain a clear solution, which was extracted with diethyl ether. The combined extracts were washed with brine, sodium thiosulfate and brine again. The organic layer was dried with $MgSO_4$, and the solvents were removed under reduced pressure. The crude material was purified by flash chromatography on silica gel.

Preparation of Cinnamyllanthanide Compounds and Addition to Cyclohexanone in the Presence of $PdCl_2$/PPh_3: Mischmetall powder (0.7 g, 5 mmol) was suspended in THF (7 mL) with SmI_2 (0.7 mmol) in a Schlenk tube under argon at room temperature. A solution of cinnamyl bromide (702 mg, 4 mmol) in THF (7 mL) was slowly added to the THF/SmI_2/mischmetall suspension over 3 h. Palladium chloride (17.7 mg, 0.1 mmol) suspended in THF (7 mL) with triphenylphosphane (105 mg, 0.4 mmol) and cyclohexanone (392 mg, 4 mmol) was then quickly added. The mixture was then stirred for an additional period of 0.5 or 1.5 h, diluted with diethyl ether, quenched with HCl (1 M) and stirred for 15 min to obtain a clear solution, which was extracted with diethyl ether. The combined extracts were washed with brine, sodium thiosulfate and brine again. The organic layer was dried with $MgSO_4$ and the solvents were removed under reduced pressure. The crude material was purified by flash chromatography on silica gel.

Acknowledgments

We are indebted to Professor J. C. Fiaud for fruitful discussions. We thank the University of Paris-Sud and the CNRS for their financial support.

---

[1] T. Tabuchi, J. Inanaga, M. Yamaguchi, *Tetrahedron Lett.* **1986**, *27*, 601–602.

[2] T. Tabuchi, J. Inanaga, M. Yamaguchi, *Tetrahedron Lett.* **1986**, *27*, 5237–5240.

[3] K. Mikami, A. Yoshida, *Tetrahedron* **2001**, *57*, 889–898.

[4] A. Yoshida, T. Hanamoto, J. Inanaga, K. Mikami, *Tetrahedron Lett.* **1998**, *39*, 1777–1780.

[5] T. Tabuchi, J. Inanaga, M. Yamaguchi, *Tetrahedron Lett.* **1986**, *27*, 1195–1196.

[6] K. Mikami, A. Yoshida, S. Matsumoto, F. Feng, Y. Matsumoto, A. Sugino, T. Hanamoto, J. Inanaga, *Tetrahedron Lett.* **1995**, *36*, 907–908.

[7] T. Tabuchi, J. Inanaga, M. Yamaguchi, *Chem. Lett.* **1987**, 2275–2278.

[8] J. M. Aurrecoechea, R. Fañanás-San-Antón, *J. Org. Chem.* **1994**, *59*, 702–704.

[9] J. M. Aurrecoechea, R. Fañanás, M. Arrate, J. M. Gorgojo, N. Aurrekoetxea, *J. Org. Chem.* **1999**, *64*, 1893–1901.

[10] J. M. Aurrecoechea, J. H. Gil, B. López, *Tetrahedron* **2003**, *59*, 7111–7121.

[11] F. Hélion, J. L. Namy, *J. Org. Chem.* **1999**, *64*, 2944–2946.

[12] M. I. Lannou, F. Hélion, J. L. Namy, *Tetrahedron* **2003**, *59*, 10551–10565.

[13] A. Di Scala, S. Garbacia, F. Hélion, M. I. Lannou, J. L. Namy, *Eur. J. Org. Chem.* **2002**, 2989–2995.

[14] M. I. Lannou, F. Hélion, J. L. Namy, *Tetrahedron Lett.* **2002**, *43*, 8007–8010.

[15] J. C. Wasilke, S. J. Obrey, R. T. Baker, G. C. Bazan, *Chem. Rev.* **2005**, *105*, 1001–1020.

[16] S. Araki, M. Ho, H. Ito, Y. Butsugan, *J. Organomet. Chem.* **1987**, *333*, 329–335.

[17] T. Hanamoto, A. So, T. Kikukawa, J. Inanaga, *Bull. Soc. Chim. Fr.* **1997**, *134*, 391–394.

[18] a) H. Matsuhita, E. I. Negishi, *J. Chem. Soc., Chem. Commun.* **1982**, 160–161; b) J. C. Fiaud, J. Y. Legros, *J. Org. Chem.* **1987**, *52*, 1907–1911.

[19] H. Nakamura, H. Iwama, Y. Yamamoto, *J. Am. Chem. Soc.* **1996**, *118*, 6641–6647.

[20] P. Girard, J. L. Namy, H. B. Kagan, *J. Am. Chem. Soc.* **1980**, *102*, 2693–2698.

[21] W. R. Roush in *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming, C. H. Heathcock), Pergamon Press, Oxford, **1991**, vol. 2, p. 1–53.

[22] Y. Yamamoto, N. Asao, *Chem. Rev.* **1993**, *93*, 2207–2293.

[23] S. Matsukawa, Y. Funabashi, T. Imamoto, *Tetrahedron Lett.* **2003**, *44*, 1007–1010.

[24] B. M. Trost, L. Li, S. D. Guile, *J. Am. Chem. Soc.* **1992**, *114*, 8745–8747.

[25] a) J. Y. Legros, M. Toffano, J. C. Fiaud, *Tetrahedron* **1995**, *51*, 3235–3246; b) M. Toffano, Thesis, University Paris-Sud, France, **1996**.

Received: April 26, 2005