Applied Organometallic Chemistry (1990) 4 297–310

0268-2605/90/040297-14$07.00

REVIEW

The Exploitation of New Synthetic Reactions by Means of Rare Earth Metals

Ken Takaki and Yuzo Fujiwara*
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 724, Japan

Received 27 December 1989 *Accepted 12 April 1990*

This review deals with lanthanoid mediated organic reactions investigated by the authors. The scope of the lanthanoid-mediated reactions are discussed under the following topics:

(a) Reactions of Yb metal umpoled diaryl ketones with electrophiles;
(b) Reactions of Yb metal with imines;
(c) Reactions of Yb metal with C–C multiple bonds;
(d) Reactions of Sm metal with nitroarenes;
(e) Reactions of Yb metal with *α*, *β*-unsaturated carbonyl compounds;
(f) Reactions of a PhYbI *σ*-complex;
(g) Reactions of $LnCl_3$ as Friedel-Crafts catalyst.

Keywords: organic synthesis by lanthanoids, ytterbium, umpolung of ketones, imines

INTRODUCTION

The rare earth group is the biggest in the Periodic Table, consisting of 17 elements, and has characteristic properties resulting from the lanthanoid contraction and the electronic structures. The lanthanoid contraction is the phenomenon that the atomic radius of lanthanoids decreases from lanthanum(III) (1.061 Å) to lutetium(III) (0.848 Å) with increasing atomic number, owing to poor 4*f* orbitals shielding.[1] We have been interested in rare earths having these phenomena, and started our research on the exploitation of lanthanoid reagents for organic synthesis about ten years ago. At that time, Kagan reported pioneering work on SmI_2-mediated organic synthesis.[2]

Usually, trivalent compounds of rare earths are the most stable and there are also some stable divalent compounds such as those of samarium (Sm), europium (Eu), and ytterbium (Yb). Cerium (IV) is a powerful oxidant. Of the metals themselves, Sm and Yb are stable enough to be handled in air, owing to formation of an oxide coating. These metals have a strong reducing potential ($Yb^0/Yb^{3+} = -2.27$; $Sm^0/Sm^{3+} = -2.41$)[1] and are oxidized by the reaction. Generally rare earth metals have an oxophilic nature and their complexes are strong Lewis acids. We found several synthetic organic reactions using these specific properties of rare earths. In this article we describe our results on lanthanoid-mediated reactions.

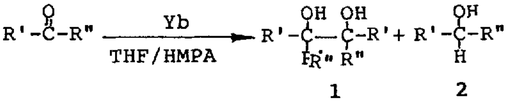
1 ORGANIC SYNTHESIS BY YTTERBIUM OR SAMARIUM METALS

Ytterbium metal (40-mesh, activated by treatment with 1–2 drops of methyl iodide or allyl iodide) reacts with an equimolar amount of benzophenone in THF/HMPA (HMPA = hexamethylphosphoric triamide) to give an initiallly blue and finally dark red solution, which on treatment with water gives benzhydrol (**2**) quantitatively. On the other hand, Yb with two equivalents of benzophenone gives benzopinacohol (**1**) quantitatively. By this reaction one can prepare various symmetrical 1,2-diols from various aromatic ketones (Eqn [1] and Table 1).

Quenching the dark red solution of Yb and one equivalent of benzophenone in THF/HMPA, with D_2O gave *C*-deuterated benzhydrol (PhDCPhOH) (D content 100% by NMR) quantitatively as shown in Scheme 1. This result shows that a dianionic intermediate such as metallaoxirane **A** is formed in the solution. IR spectra of this solution give a new band at 1566 cm^{-1} (b in Fig. 1) and the carbonyl absorption of benzophenone at

---

† Author to whom correspondence should be addressed.



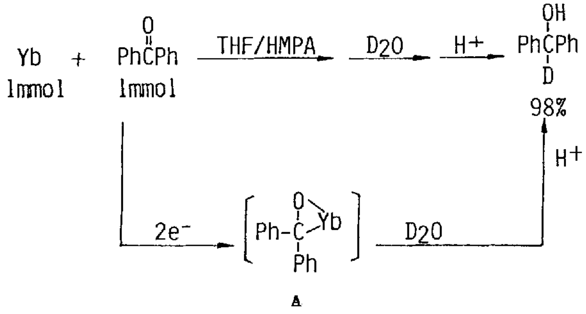
$$R'-\overset{O}{\overset{\|}{C}}-R'' \xrightarrow[\text{THF/HMPA}]{\text{Yb}} R'-\underset{R''}{\overset{OH}{C}}-\underset{R''}{\overset{OH}{C}}-R' + R'-\underset{H}{\overset{OH}{C}}-R'' \quad [1]$$

Table 1 Homo-coupling of carbonyl compounds by Yb Metal[a]

R′	R″	Yb:R′COR″ (mmol: mmol)	Reaction time	Product yield (%)[b] 1	2
Ph	Ph	1:2	<5 min	97	—
Ph	Ph	1:1	10 min	—	98
Ph	Me	1:2	5 h	73[c]	—
p-NCC_6H_4	Me	1:1	3 h	58	—
p-$MeOC_6H_4$	Me	1:1	4 h	71[c]	—
p-$MeOC_6H_4$	H	1:1	7 h	99[c]	—
2-Naphthyl	Me	1:2	2 h	96	—
n-C_6H_{13}	Me	1:1	18 h	—[d]	

[a]All reacctions were carried out at room temperature in THF ($4\ cm^3$)/HMPA ($2\ cm^3$). [b]Isolated yields based on the carbonyl compounds. [c]DL isomer. [d]The starting substrate was recovered.

1664 cm^{-1} (a in Fig. 1) disappears. This new band at 1566 cm^{-1} disappears on quenching with water (c in Fig. 1), and the carbonyl absorption of benzophenone at 1664 cm^{-1} again appears on exposing the solution to air. These results suggest that a metallaoxirane like **A** is formed *in situ* in the reaction of Yb with benzophenone. In fact, evaporation of the solvent *in vacuo* gives a reddish-black solid which exhibits an IR absorption band at 1563 cm^{-1} similar to that of the solution, and gives benzhydrol when exposed to air, and benzophenone when subjected to vacuum. The reddish-black solid gives also 1-(diphenylhydroxymethyl)cyclohexanol when allowed to react with cyclohexanone. These results support the formation of the metalloxirane **A** in the reaction of Yb and benzophenone. Miyashita *et al.* reported that the three-membered metallacycle $[Ni(\eta^2-O{=}C{=}CMe_2Ph)]$ exhibits an IR band at 1590 cm^{-1}.[3]



Scheme 1

However, the real structure of **A** may be more complex. Analysis of the hydrolysis products of the reaction intermediate of benzophenone (1 mmol) and Yb metal (1 mmol) showed that the ratio of benzhydrol to ytterbium was 1.0:0.92. Unchanged Yb metal was also recovered in 7% yield (0.07 mmol). These results suggest that besides the divalent ytterbium species, there should be a small amount of trivalent species in the intermediate.[4]

Based on the above experimental results, a possible mechanism of the reaction of benzophenone with Yb metal has been proposed as

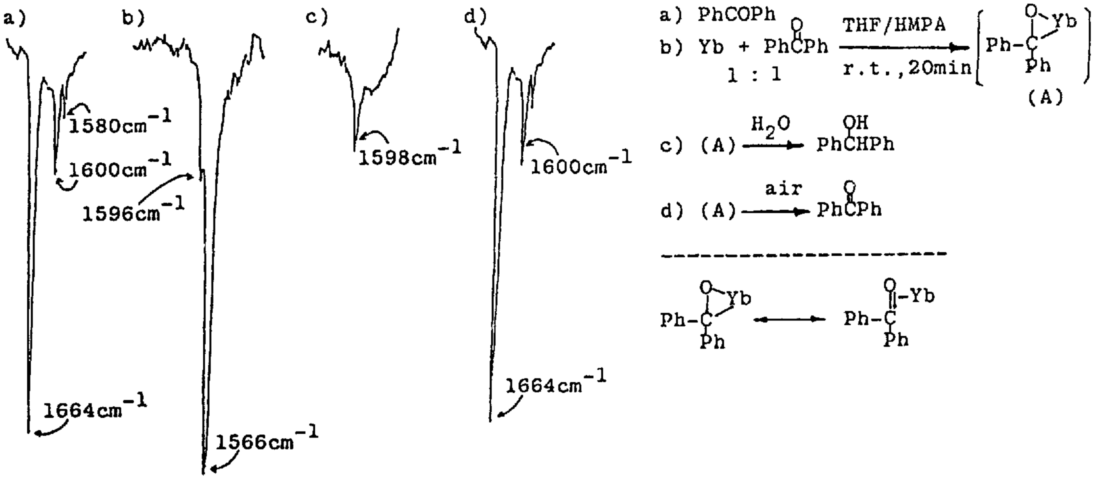
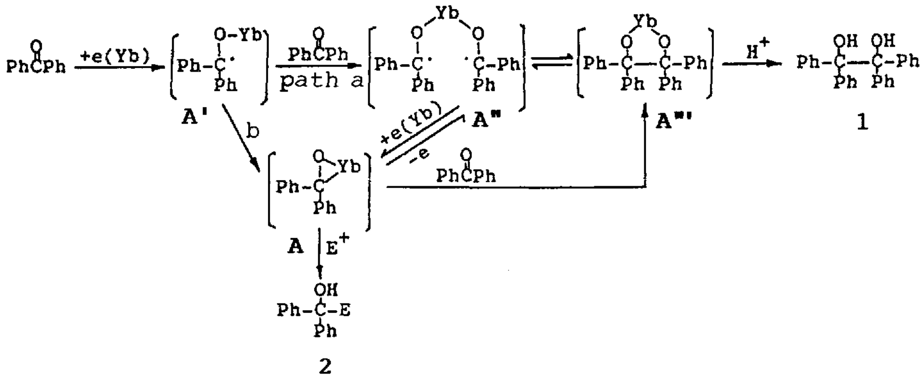


Figure 1



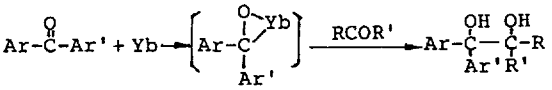
Scheme 2

depicted in Scheme 2. One-electron transfer from Yb metal to the benzophenone gives the univalent ytterbium intermediate (A′). There would be two paths from here. The highly reactive A′ would immediately react with another molecule of benzophenone to give A″ which couples into A‴ (Path a). The latter turns into **1** after hydrolysis. Alternatively, A′ undergoes intramolecular reaction to give **A** which then adds to another molecule of benzophenone to give A‴ (Path b). When an equivalent or excess of Yb metal is used, A″ or A‴ is further reduced by Yb metal into **A** which gives **2** after hydrolysis. This shows that the carbonyl carbon is umpoled from electrophilic to nucleophilic by Yb metal.

The metallaoxirane intermediates like **A** are also formed in the reaction of Yb metal with diaryl ketones such as phenyl naphthyl ketone and 9-fluorenone, and react with a wide variety of electrophiles such as ketones and aldehydes leading to unsymmetrical 1,2-diols, esters, nitriles, and amides to α-hydroxy ketones, epoxides to 1,3-diols, carbon dioxide to α-hydroxycarboxylic acids, isocyanates to α-hydroxyacetamides, acetylenes to allyl alcohols, silyl halides to α-silylalykl silyl ethers, alkyl halides to tertiary alcohols, and acid chlorides to esters.

1.1 Reaction with ketones: synthesis of unsymmetrical pinacols

At room temperature, addition of ketones to the diaryl ketone/Yb mixture gives the corresponding cross-coupled products (**3**) in high yields with small amounts of reduction products (Eqn [2] and Table 2).[4] Reaction of benzophenone with 4-t-butylcyclohexanone gives a mixture of the corresponding axial alcohol and equatorial alcohol (66:44). Under the same conditions Sm metal shows lower reactivity than Yb. In the Sm-promoted reaction of benzophenone with acetone only 38% yield of cross-coupled product was obtained and the homo-coupled product, benzopinacol, was also formed in 40% yield. The Yb and Sm metals used here were activated by treatment with 1–2 drops of methyl iodide or allyl iodide. Since the Sm metals surface is more inactivated, more effective activation methods are required for higher reactivity.



[2]

3

Table 2 Cross-coupling of diaryl ketones with other ketones to give unsymmetrical pinacols[a]

Diaryl ketone		Ketone		Yield of
Ar	Ar′	R	R′	3 (%)[b]
Ph	Ph	Me	Me	60
Ph	Ph	Me	Me	38[c]
Ph	Ph	Me	n-C_6H_{13}	90
Ph	Ph	$-(CH_2)_5-$		91
Ph	Ph	$-(CH_2)_2CH(t\text{-Bu})(CH_2)_2-$		83[d]
Ph	2-Naphthyl	Me	Me[e]	72
Ph	2-Naphthyl	Me	n-C_6H_{13}[e]	80
Ph	2-Naphthyl	$-(CH_2)_5-$[e]		90
Biphenyl-2,2′-diyl		Me	Me	91
Biphenyl-2,2′-diyl		Me	n-C_6H_{13}	88
Biphenyl-2,2′-diyl		$-(CH_2)_5-$		81

[a] Yb:diaryl ketone:ketone = 1:1:1; room temperature, 10–20 min. Small amounts (3–18%) of the corresponding reduction products were also formed. [b] Isolated yield based on the diaryl ketones. [c] Sm metal (2 equiv.) was used instead of Yb. [d] Ratio of axial alcohol to equatorial alcohol = 66:44. [e] 2 equiv. of Yb metal used.

Few reports on the cross-coupling reaction between different carbonyl compounds could be found.[5] Since a statistical product mixture was usually formed,[5d] it was thought to be difficult to obtain the corresponding unsymmetrical pinacols selectively from the reactions between two different carbonyl compounds. It was reported that in the presence of titanium metal the selective cross-coupling reaction between diaryl ketones and other ketones occurred, but the products were unsymmetrical olefins rather than pinacols.[5a,b] The reaction of disodiobenzophenones with benzaldehydes was reported to afford the corresponding unsymmetrical pinacols.[5a,b] However the results in the case of aliphatic carbonyl compounds were not given. Since disodiobenzophenones are very basic reagents, α-proton abstraction might occur in the reactions with aliphatic carbonyl compounds to give complex products.

In contrast, none of these side reactions was observed in the present lanthanoid-mediated cross-coupling reactions. Furthermore, because of their high yield, mild conditions, and simplicity, the present reactions constitute a useful method for the synthesis of unsymmetrical pinacols.

1.2 Reaction with nitriles: synthesis of α-hydroxy ketones

Both aromatic and aliphatic nitriles react well with diaryl ketones to give the corresponding addition products, α-hydroxy ketones (4) in good yields (Eqn [3] and Table 3).[4]

It seems that the intermediate **A** derived from reaction of diaryl ketones with Yb metal possesses an even higher reactivity toward nitriles than Grignard reagents and lithium reagents.[6] Addition of Grignard reagents to nitriles requires higher temperature and low yields of the addition products are usually obtained because of α-proton abstraction by Grignard reagents. In the reactions of lithium reagents with acetonitrile and phenylacetonitrile, α-proton removal is faster than the normal addition. Reaction of disodiobenzophenone with benzonitriles in liquid ammonia was reported to give α-arylbenzoins; however, results in the case of nitriles bearing α-protons were not given.[5b] The present Yb metal-promoted reactions of diaryl ketones with nitriles should be a convenient method for synthesis of α-hydroxy ketones.

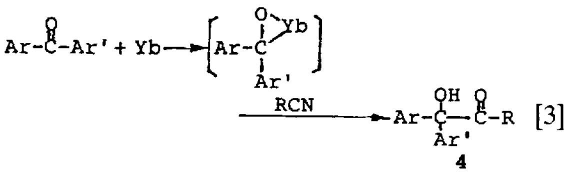


Table 3 Reaction of diaryl ketones with nitriles[a]

Diaryl ketone Ar	Ar′	Nitrile R	Yield of 4 (%)[b]
Ph	Ph	Ph	76
Ph	Ph	$PhCH_2$	65
Ph	Ph	Me	72
Ph	Ph	Me_2CH	82
Ph	2-Naphthyl[c]	Ph	92
	2-Naphthyl[c]	$PhCH_2$	60
Ph	2-Naphthyl[c]	Me	76
Biphenyl-2,2′-diyl		Ph	55
Biphenyl-2,2′-diyl		$PhCH_2$	83
Biphenyl-2,2′-diyl		Me	53

[a] Yb: diaryl ketone:nitrile = 1:1:1; room temperature, 4 h. Small amounts of reduction products were also formed. [b] Isolated yield based on the diaryl ketones. [c] 2 equiv. of Yb used.

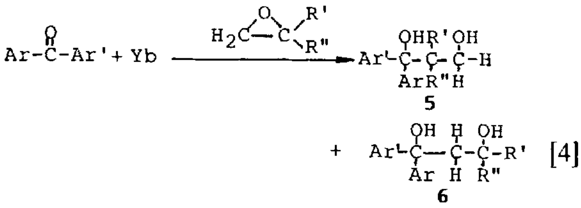


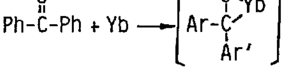
Table 4 Preparation of 1,3-diols from epoxides and diaryl ketones[a]

Diaryl ketone	Epoxide	Yield (%)[b] 5	6
Benzophenone	Cyclohexene oxide	67	—
Benzophenone	Styrene oxide	64	—
Benzophenone	Isobutylene oxide	Trace	56
Benzophenone	Butene oxide	38	37
Phenyl 2-naphthyl ketone[c]	Cyclohexene oxide	77	—
Phenyl 2-naphthyl ketone[c]	Styrene oxide	77	—
Phenyl 2-naphthyl ketone[c]	Isobutylene oxide	Trace	65
Phenyl 2-naphthyl ketone[c]	Butene oxide	42	26
9-Fluorenone	Cyclohexene oxide	58	—
9-Fluorenone	Styrene oxide	61	—
9-Fluorenone	Isobutylene oxide	Trace	47
9-Fluorenone	Butene oxide	54	20

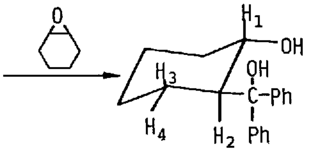
[a] Yb:diaryl ketone:epoxide = 1:1:2; room temperature, 2 h. Small amounts of reduction products were also formed. [b] Isolated yields based on the diaryl ketones. [c] 2 equiv. of Yb metal used. [d] —, Not detected.

1.3 Reaction with epoxides: synthesis of chiral 1,3-diols

In this case, since epoxides can react with Yb metal to give complex products (one of them is the corresponding alcohol), the diaryl ketone/Yb mixture was first transferred by a cannula to another vessel to obviate the influence of the unchanged Yb metal, and the epoxides were then added. As shown in Eqn [4] and Table 4, the corresponding cross-coupled products, 1,3-diols **5** and **6**, are formed in good yields.[4] In the reaction of benzophenone with cyclohexene oxide, only one stereoisomer (**5a**) is obtained. ^{1}H NMR (400 MHz) spectra show that **5a** has a *trans* structure ($J_{12} = 9.7$, $J_{23} = 12.5$, $J_{24} = 2.7$ Hz) (Eqn [5]).



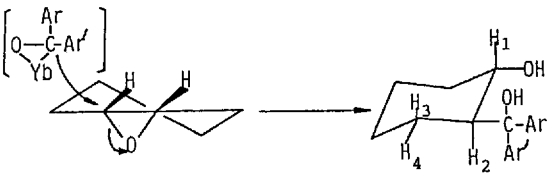
$$\mathrm{Ph\text{-}\overset{\overset{O}{\|}}{C}\text{-}Ph + Yb \longrightarrow \left[Ar\text{-}\overset{O\frown Yb}{C}\text{-}Ar'\right]}$$



[5]

5a

Similarly, 1,3-diols obtained from the reactions of cyclohexene oxide with phenyl 2-naphthyl ketone and 9-fluorenone have *trans* structures. These results mean that backside attack of the metallacycle intermediate **A** to the epoxide is operative here (Scheme 3).

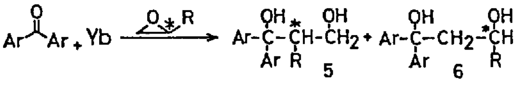


Scheme 3

In the case of styrene oxide, C–C bond formation occurs predominantly on the more substituted carbon atom, whereas in the case of isobutylene oxide it occurs on the less hindered one. A product mixture derived from attack at both carbon atoms was obtained in the reaction of 1-butene oxide. The present reactions constitute the first example of the cross-coupling reaction between ketones and epoxides and should be a good method for synthesis of 1,3-diols.

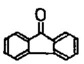
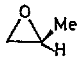
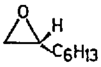
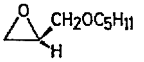
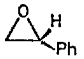
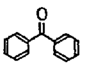
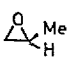
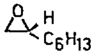
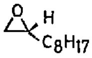
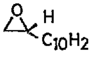
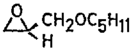
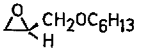
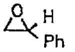
Since the reaction is found to proceed stereospecifically in an S_N2 manner, the reaction of chiral epoxides with diaryl ketones should afford chiral 1,3-diols. In fact the reactions of benzophenone and 9-fluorenone with chiral epoxides give chiral 1,3-diols as shown in Eqn [6] and Table 5.[7]

For example, reaction of (*S*)-(−)-propylene oxide with 9-fluorenone gives 2-(9-hydroxy-9-fluorenyl)-2-methylethanol (99%e,e) and 2-(9-hydroxy-9-fluorenyl)-2-propanol (90%e,e) in 40 and 37% yields, respectively. The optical purity was determined by HPLC analysis using chiral columns. By this method one can easily prepare chiral 1,3-diols which are important starting materials for synthesis of biologically active macrolides, ionophores, monosaccharides, and various medicines.

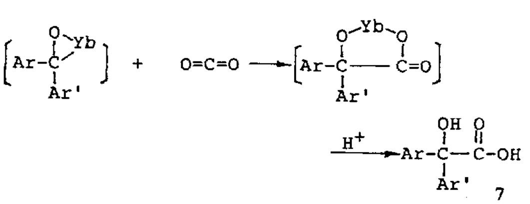


$$\mathrm{Ar\overset{O}{\overset{\|}{C}}Ar + Yb \longrightarrow Ar\text{-}\underset{Ar}{\overset{OH}{C}}\text{-}\underset{R}{\overset{*}{C}H}\text{-}\overset{OH}{CH_2} + Ar\text{-}\underset{Ar}{\overset{OH}{C}}\text{-}CH_2\text{-}\underset{R}{\overset{OH}{\overset{*}{C}H}}} \qquad [6]$$

Table 5 Reaction of diaryl ketone with chiral epoxides[a]

Educt		Product yield (%) [α]$^{20}_{D}$(THF) (%e,e)			
Ketone	Epoxide	**5**		**6**	
		40	+ 13.5(99) (*c*0.89)	37	− 12.5(90) (*c*0.53)
		21	− 32.4 (*c*0.46)	42	− 23.5(93) (*c*0.50)
		10	− 4.5	30	+ 20.5 (*c*0.40)
		61	− 6.0 (*c*0.61)	—	
		46	+ 1.5(90) (*c*0.40)	37	+ 18.5 (*c*0.40)
		24	− 1.98(87) (*c*0.59)	50	− 4.42(90) (*c*0.52)
		20	− 0.90 (*c*0.66)	58	+ 0.96 (*c*0.66)
		31	+ 0.89 (*c*0.56)	49	+ 3.31 (*c*0.66)
		23	+ 14.5 (*c*0.39)	62	+ 6.09 (*c*0.67)
		13		57	+ 7.91 (*c*0.68)
		64	+ 19.3(67) (*c*0.82)	—	

[a] Yb:ketone: epoxide = 1:1:1.5, THF/HMPA(4:1), r.t., 2 ~ 18 h. [b] —, not detected.



[7]

7

Table 6 Synthesis of α-hydroxy-carboxylic acids[a]

Diaryl ketone	Yield of 7 (%)[b]
Benzophenone	61
Phenyl 2-naphthyl ketone[c]	68
9-Fluorenone	61

[a] Yb: diaryl ketone = 1:1; CO_2 1 atm; room temperature, 30 min. [b] Isolated yields based on the diaryl ketones. [c] Yb:ketone = 2:1.

1.4 Reaction with CO_2: synthesis of α-hydroxycarboxylic acids

Bubbling CO_2 through the reaction mixture of diaryl ketones and Yb metal gives the corresponding carboxylation products (7) in good yields (Eqn [7] and Table 6).[4c]

1.5 Reaction with other electrophiles

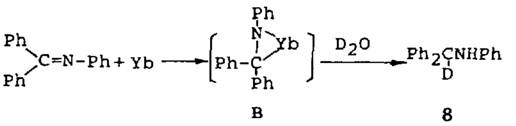
In the presence of Yb metal, benzophenone also reacts with acetaldehyde, phenyl isocyanate, and ethyl acetate to give 1,1-diphenylpropane-1,2-diol, *N*-phenyldiphenylhydroxyacetamide, and 2-oxo-1,1-diphenylpropan-1-ol in 82, 58, and 43% yields, respectively. A similar addition reaction occurs even in the case of *N*,*N*-dimethylformamide and diphenylacetylene to give diphenylhydroxyacetaldehyde and 1,1,2,3-tetraphenylprop-2-en-1-ol in considerable yields. In the case of diphenylacetylene, D_2O treatment of the reaction mixture gave the corresponding deuterated product, 1,1,2,3-tetraphenyl-3-deuterioprop-2-en-1-ol.[4c]

Alkylation of benzophenone using methyl iodide, allyl bromide, and benzyl chloride in the presence of Yb takes place selectively at the carbonyl carbon to lead to alkyl(aryl)diphenylmethyl alcohols in 30–60% yields, whereas acylation using acetyl chloride, propionyl chloride, and benzoyl chloride affords the corresponding esters of diphenylmethanol in 15–30% yields.

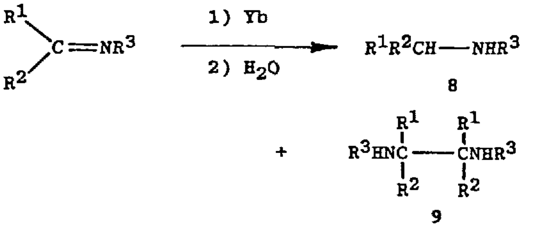
Reaction of benzophenone with trimethylsilyl chloride and t-butyldimethylsilyl chloride gives silyldiphenylmethyl silyl ethers as major products in 20–45% yields along with *O*-monosilylated products in 5–20% yields, providing additional evidence for the generation of A.[8]

1.6 Reaction of imines with Yb metal: coupling of aldimines and reduction of ketimines

Arylimines such as *N*-diphenylmethyleneaniline react also with Yb metal in THF/HMPA to give a dark red solution.[9] When *N*-diphenylmethyleneaniline is treated with an equimolar amount of Yb metal and quenched with water, *N*-diphenylmethylaniline (8) is obtained in 92% yield.



[8]



[9]

a: R^1= Ph, R^2= Ph, R^3= Ph
b: R^1= Ph, R^2= Ph, R^3= H
c: R^1= Ph, R^2= H , R^3= Ph
d: R^1= Ph, R^2= H , R^3= CH_2Ph

Table 7 Reduction and coupling reaction of Imines promoted by ytterbium metal

Run	Imine	Molar ratio [Imine]:[Yb]	Product yield (%)[a] **8**	**9**
1	**a**	1.0	92	0
2	**a**	2.5	(120)	0
3	**b**	1.0	93 (99)	0
4	**b**	2.5	(112)	0
5	**c**	1.0	32	23[b]
6	**c**	2.5	0	81 (98)
7	**d**	1.0	0	46[b]
8	**d**	2.5	0	61

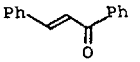
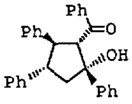
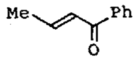
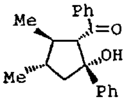
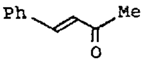
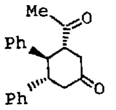
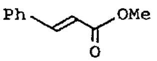
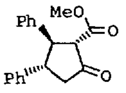
[a] Isolated yields (GC yields) based on Yb. [b] Diasteromer ratios were 70:30 for **9c** and 100:0 for **9d**, determined by ^{13}C NMR.

Quenching with deuterium gave *C*-deuterated **8** (Eqn [8]). These results suggest that a three-membered metallacyclic intermediate like **B** is also formed, and the imine carbon is umpoled to nucleophilic. The results of the reaction of ketimines and aldimines with Yb metal are listed in Table 7 and Eqn [9]. Ketimines are readily reduced to the corresponding amines (**8**) whereas reductive coupling of aldimines takes place to give predominantly 1,2-diaminoethanes (**9**). Compared with carbonyl functions, the reductive coupling of imines is less common in spite of the utility of the resulting vicinal diamines.[10] This reaction provides a convenient method for coupling and reduction of imines.

1.7 Reaction of *α,β*-unsaturated carbonyl compounds with Yb: regio- and stereo-selective synthesis of cyclopentanol, cyclopentanone and cyclohexanol derivatives

Yb metal promotes a cyclodimerization of *α,β*-unsaturated ketones and esters, leading to cyclopentanol, cyclopentanone, or cyclohexanone derivatives, regio- and stereo-selectively.[11] Table 8 summarizes the results.

Table 8 Cyclodimerization of *α*, *β*-unsaturated carbonyl compounds promoted by ytterbium metal[a]

Carbonyl compound	Product	Yield (%)[b]
	 10	73
	 11	38 (74)
	 12	44
	 13	36 (76)

[a]Carbonyl compound:Yb = 2.5:1. [b]Isolated yields (GC yields).

C D

Figure 2

When 2.5 equivalents of chalcone was treated with Yb metal in THF/HMPA (4:1) at room temperature, the mixture changed to green, then dark red, which was quenched with water after 3.5 h period to give (1*R**, 2*S**, 3*R**, 4*S**)-2-benzoyl-1,3,4-triphenylcyclopentanol (**10**) and benzylacetophenone in 73 and 35% yields based on Yb, respectively. Other regio- and stereoisomers were not detected. The reaction of 1-phenyl-2-buten-1-one gave the cyclopentanol (**11**), whereas 4-phenyl-3-buten-2-one was converted to 4,5-diphenyl-3-acetylcyclohexanone (**12**). The formation of **12** is interesting, since reduction does not take place formally as in the former two cases. Methyl cinnamate was reductively dimerized by Yb metal to afford 3,4-diphenyl-2-methoxycarbonylcyclopentanone (**13**).

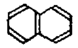
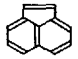
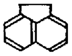
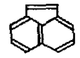
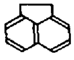
In the case of chalcone, the reaction is confirmed, by treatment with D_2O and Me_3SiCl, to proceed via a radical enolate (**C**) and the dianion intermediate (**D**) (Fig. 2), formed by electron transfer from Yb to chalcone: **C** then undergoes radical cyclization followed by anionic ring closure to give the cyclodimerization products.

The present Yb-promoted cyclodimerization of *α,β*-unsaturated carbonyl compounds has never been achieved by other metals or by electrochemistry.

1.8 Reduction by Yb of C—C multiple bonds conjugated with aromatic rings

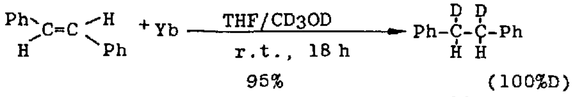
Yb metal with methanol can selectively reduce C–C multiple bonds conjugated with aromatic rings and leave the aromatic rings unaffected. Reactions of a variety of substrates with Yb metal and a PhYbI *σ*-complex are summarized in Table 9.[12] Three equivalent amounts of Yb metal reduce styrene to ethylbenzene quantitatively (Run 2) in marked contrast to the case of alkali metals.[13] Diphenylacetylene is reduced by three equivalents of Yb to a mixture of bibenzyl and stilbenes (Run 6). However, further excess of the Yb metal gave only bibenzyl, the completely reduced product, in high yield (Run 7). Reduction of (*E,E*)-1,4-diphenyl-1,3-butadiene gave 1,4-diphenyl-2-butene as a final product whose C–C double bond

Table 9 Reduction of C–C multiple bounds by Yb metal[a]

Run	Substrate (mmol)	Reducing agent (mmol)	Product[b]	Yield (%)[c]
1	$Ph_2C{=}CH_2$ (0.5)	PhYbI (1.0)[d,e]	Ph_2CHCH_3	(94)[f]
2	$PhCH{=}CH_2$ (1.0)	Yb (3.0)[e,g]	$PhCH_2CH_3$	(98)
3	$Ph(CH_3)C{=}CH_2$ (0.5)	Yb (1.5)	$PhCH(CH_3)_2$	54
4	$Ph(CH_3)C{=}CH_2$ (0.5)	Yb (2.0)	$PhCH(CH_3)_2$	78
5	n-$C_8H_{17}CH{=}CH_2$ (1.0)	Yb (2.0)	No reaction	
6	$PhC{\equiv}CPh$ (0.5)	Yb (1.5)[e]	$PhCH_2CH_2Ph$	47
			Z-PhCH=CHph	11[g]
			E-PhCH=CHPh	20[g]
7	$PhC{\equiv}CPh$ (0.5)	Yb (3.0)[e]	$PhCH_2CH_2Ph$	(87)
8	(*E*, *E*)-PhCH=CHCH=CHPh	Yb (2.0)	$PhCH_2CH{=}CHCH_2Ph$	(92)
9	 (0.5)	Yb (1.0)	No reaction	
10	 (0.5)	Yb (1.0)		53
11	 (0.5)	Yb (2.0)		73
12	PhCH=CHPh (0.5)	Sm (1.5)	No reaction	
13	PhCH=CHPh (0.5)	Ce (2.0)	No reaction	
14	PhCH=CHPh (0.5)	YbI_2 (1.0)	No reaction	
15	PhCH=CHPh (0.5)	SmI_2 (1.0)	No reaction	

[a] THF 4 cm^3, MeOH 0.5 cm^3, room temperature, 18 h. [b] Products were identified by comparison of GC retention time. The reactions were very clean and only a small amount of by-product could be detected apart from the unreacted starting materials. [c] NMR yield based on the substrate. [d] PhYbI was prepared using Yb (1.5 mmol) and PhI (1.0 mmol). [e] HMPA (hexamethylphosphoric triamide, 2 cm^3) was also used as a cosolvent. [f] Numbers in parentheses are yields isolated. [g] Determined by GC.

could not be further reduced (Run 8). The metal cannot reduce naphthalene under the present conditions, showing its different reactivity compared with alkali metals[14] and Yb in liquid ammonia.[15] Furthermore, the fact that the naphthalene ring does not suffer the reduction, enables it to reduce acenaphthylene to acenaphthene selectively (Runs 10 and 11). A PhYbI σ-complex (see Section 2) can also reduce C–C multiple bonds, but cerium (Ce) and samarium (Sm) were found to be inactive for the reaction under the same conditions. Either SmI_2 or YbI_2 was also inert toward the olefin (Runs 14 and 15). It was also found that in the case of (*E*)-stilbene, if CD_3OD was used instead of CH_3OH, the dideuterated reduction product (**14**) was obtained almost quantitatively (Eqn [10]).



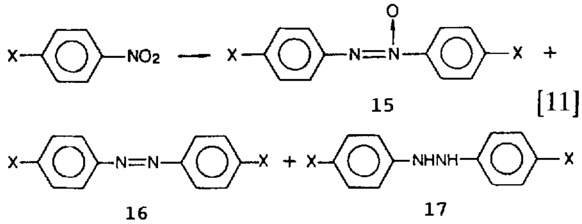
14

[10]

1.9 Reaction of nitroarenes with Sm: synthesis of azoxy compounds

There are many methods for preparation of azoxy compounds by reduction of nitro compounds.[16] However, since side reaction (e.g. dehalogenation, polymerization, etc.) usually accompany the reductions, their use is limited. We found that Sm metal can reduce various nitroarenes to give the corresponding azoxy compounds (**15**) selectively; a bromine, iodine, or carbonyl group in the substrates is retained. Equation [11] and Table 10 summarize the results of the Sm or Yb metal-mediated reduction of various nitroarenes.[17]

One can see from Table 10 that, under proper conditions, a variety of nitroarenes can be selectively reduced by Sm metal to their corresponding azoxy compounds (**15**). It also appears that Sm is more suitable than Yb for synthesis of azoxy compounds (Runs 1 vs 2 and 3 vs 4, Table 10). Interestingly, the bromine and iodine in the substrates remain unaffected during the reaction (Runs 8 and 9, Table 10), although iodobenzene



[11]

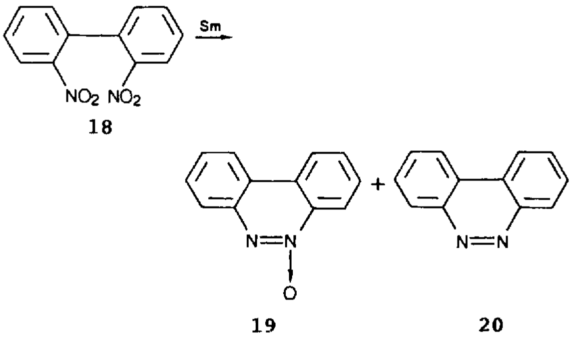
Table 10 Reduction of nitroarenes with lanthanide metals[a]

Run	Ln	X	Ln:Nitroarene (mmol:mmol)	Product yield (%)[b] 15	16	17
1	Sm	Me	1.5:0.5	79	5	—
2	Yb	Me	2.5:0.5[c]	36[d]	—	—
3	Sm	MeO	1.5:0.5	55	—	—
4	Yb	MeO	2.0:0.5[c]	45[e]	—	—
5	Sm	Cl	1.0:0.5	83	—	—
6	Sm	Cl	1.5:0.5	59	10	30
7	Sm	Cl	2.0:0.5	11	14	71
8	Sm	Br	1.0:0.5	83	—	—
9	Sm	I	1.0:0.5	81	—	—
10	Sm	CN	1.0:0.5[f]	55	6	—
11	Sm	MeCO	1.0:0.5[g]	70	—	—
12	Sm	$EtO_2CCH{=}CH$	1.0:0.5	[h]	—	—

[a] All reactions were carried out at room temperature for 18 h in THF (4 cm^3)/HMPA (0.5 cm^3)/MeOH (2 cm^3) unless otherwise noted. [b] Isolated yield. [c] MeOH (0.5 cm^3). No HMPA used. [d] *p*-Toluidine was also formed in 22% yield. [e] *p*-Anisidine was also formed in 36% yield. [f] Room temperature, 2.5 h. Prolonged reaction time gave complex products. [g] Room temperature, 4 h. [h] The corresponding ester-exchanged azoxy compound *p*-$MeO_2CCH{=}CHC_6H_4N{=}N(\rightarrow O)C_6H_4CH{=}CHCO_2Me$ was formed in 90% yield.

itself reacts easily with Sm metal at room temperature.[18,19] In the case of *p*-nitroacetophenone (Run 11, Table 10), the reaction occurred selectively at the nitro group rather than the carbonyl group, which is in marked contrast to the reaction with SmI_2. In the latter case, the carbonyl group was preferentially reduced.[20] In the reaction of ethyl 4-nitrocinnamate (Run 12, Table 10), the ester-exchanged azoxy derivative was obtained, and the C–C double bond in the substrate was not affected, although C–C multiple bounds conjugated with aromatic rings can be easily reduced by Yb metal as described above. In the case of *p*-chloronitrobenzene, two equivalents of Sm gave the azoxy compounds **15** selectively (Run 5, Table 10), whereas four equivalents of Sm resulted in the formation of the corresponding hydrazine compound **17** as a main product (Run 7, Table 10). This result shows that it is possible to obtain different reduction products simply by changing the ratio of Sm metal to nitro compounds.

It was also found that reaction of 2,2′-dinitrobiphenyl (**18**) with eight equivalents of Sm metal gave benzo[*c*]cinnoline *N*-oxide (**19**) and benzo[*c*]cinnoline (**20**) in 65 and 22% yields, respectively (Scheme 4).



Sm : 18	18	19	20
2 : 0.5	18%	24%	40%
4 : 0.5	12%	65%	22%

Scheme 4

The present method, because of its simplicity and high selectivity, constitutes a useful alternative to the commonly accepted procedures for the synthesis of azoxy compounds.

2 REACTION OF RLnI σ-COMPLEXES

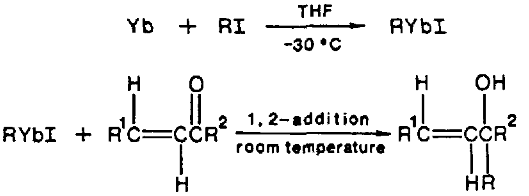
The first divalent organolanthanoid σ-complexes of the type RLnI were prepared from lanthanoid metals and organic iodides (RI) in THF by Evans *et al.*[19] We are interested in the reactions of lanthanoids with a view to exploring new synthetic reactions, and we investigated some reactions of organolanthanoids (RLnI) with ketones, aldehydes, nitriles, and acid chlorides.[21] We have shown that although the complexes RLnI are similar to the Grignard reagent (RMgX) in formula, they have rather different reactivities: the reaction of RLnI (Ln = Yb, Eu) with esters gives ketones as main products rather than tertiary alcohols[21a] and the reaction with aldehydes results in the formation of Tishchenko condensation products (Ln = Sm, Pr, Nd, Dy).[21f] Reaction of PhYbI with CO, followed by addition of alkyl halides (RX), afforded a tertiary alcohol

(Ph_2RCOH) or a ketone (Ph(CO)R, R = t-butyl), indicating the *in situ* formation of Ph(CO)YbI which is equivalent to an acyl anion, $Ph(CO)^-$.[7]

Here we describe the reactions of RLnI with α,β-unsaturated carbonyl compounds and allyl alcohols in which formation and/or cleavage of C–C bonds takes place depending upon reaction conditions.

2.1 Reaction of RLnI with α,β-unsaturated carbonyl compounds: selective 1,2-addition

Addition of an equivalent amount of α,β-unsaturated carbonyl compounds to the RYbI complexes, prepared *in situ* from Yb metal and RI, gave 1,2-addition products (**21**) exclusively (Eqn [12] and Table 11).[18] These results are in sharp contrast to those in the case of the Grignard reagent, which usually gives mixtures of 1,2- and 1,4-addition products.[22] Similar regioselectivity was reported by Beletskaya[23] and Imamoto *et al.*[24] This unique regioselectivity could be explained by the Hard and Soft Acid and Base (HSAB) theory. According to the HSAB theory, the lanthanoid complexes (RLnI) are harder than the Grignard reagents and in the conjugated enone system the carbonyl C is harder than α- and β-olefinic carbons.[25] Thus the attack of RYbI is enhanced at the harder site, i.e. carbonyl C, to give 1,2-addition products selectively.



[12]

21 a, R = R¹ = R² = Ph
b, R = Ph, R¹ = H, R² = H
c, R = Ph, R¹ = H, R² = Me
d, R = R¹ = Ph, R² = Me
e, R = Me, R¹, R² = $(CH_2)_3$

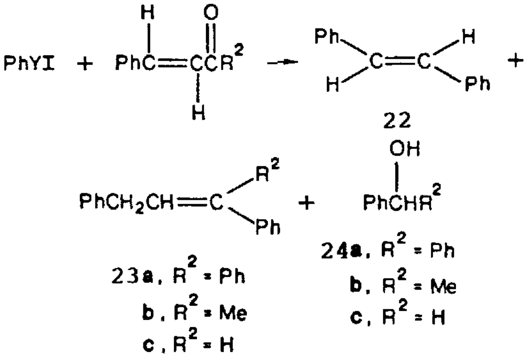
Table 11 Reactions of RYbI with α,β-unsaturated carbonyl compounds[a]

Run	RYbI	Carbonyl compound	Yield (%[b]) 1,2-Addition product
1	PhYbI	Chalcone[c]	**21a** 62
2	PhYbI	Acrolein	**21b** 66
3	PhYbI	Methyl vinyl ketone	**21c** 37
4	PhYbI	Benzalacetone	**21d** 43
5	MeYbI	2-Cyclohexen-1-one	**21e** 39

[a] Yb/RI/carbonyl compound = 0.5:0.75:0.5, in mmol; room temperature; 18 h. [b] GC yields based on the substrate. [c] Yb/PhI/chalcone = 1.25:1.0:1.0; −30°C, 1 h, and then room temperature, 18 h.

2.2 Effect of the molar ratio on the reaction of PhYbI with chalcone

As described above, the reaction of an equimolar amount of PhYbI with chalcone gives a 1,2-addition product (**21**) selectively, but interestingly enough, as the ratio of PhYbI to chalcone increases, (*E*)-stilbene (**22**), the C–C bond cleavage product, or triphenylpropene (**23**), the deoxygenation product, becomes the main product instead of **21** (Eqn [13]). When the PhYbI/chalcone ratio is 3:1, **22** and **23** were obtained in 31 and 30% yields, respectively, with diphenylmethanol (**24a**, 30%). In any reactions where **22** was obtained, an almost equimolar amount of diphenylmethanol (**24a**) was also formed. It was confirmed that **22** was formed via cleavage of the acyl–vinyl bond of chalcone and addition of a phenyl group of PhYbI, by a control experiment using *p*-methylphenylytterbium iodide (p-MeC_6H_4YbI). This is the first example of the formation of stilbene via C–C bond cleavage of chalcone activated by organolanthanoids, and there is no previous example even in *d*-block transition metal chemistry.

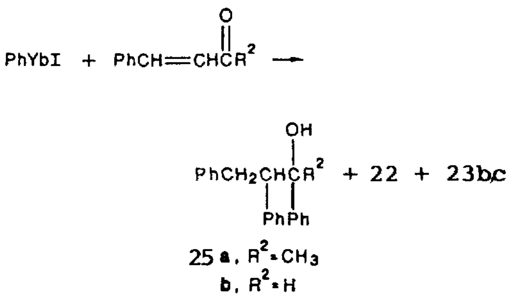


[13]

2.3 Reaction of excess PhYbI with benzalacetone, cinnamaldehyde and allylic alcohol

Besides **22** (1%) and **23b** (28%), the reaction of excess PhYbI with benzalacetone gave an unexpected compound **25a** as a main product (43%)

derived from the addition of PhYbI to the C–C double bond of the substrate (Eqn [14]).

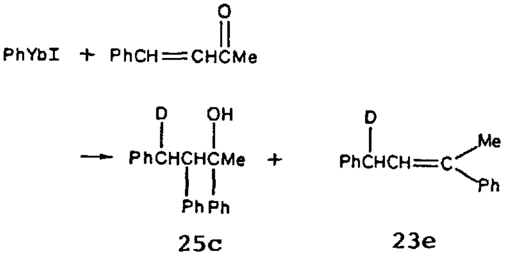


$$\mathrm{PhYbI} + \mathrm{PhCH{=}CH\overset{O}{\overset{\|}{C}}R^2} \longrightarrow \mathrm{PhCH_2\underset{Ph}{C}H\underset{Ph}{\overset{OH}{C}}R^2} + 22 + 23b,c \qquad [14]$$

25 a, $R^2 = CH_3$
b, $R^2 = H$

In the case of cinnamaldehyde, the addition product **25b** (12%) was also obtained with **23c** (16%), and **22** could not be detected.

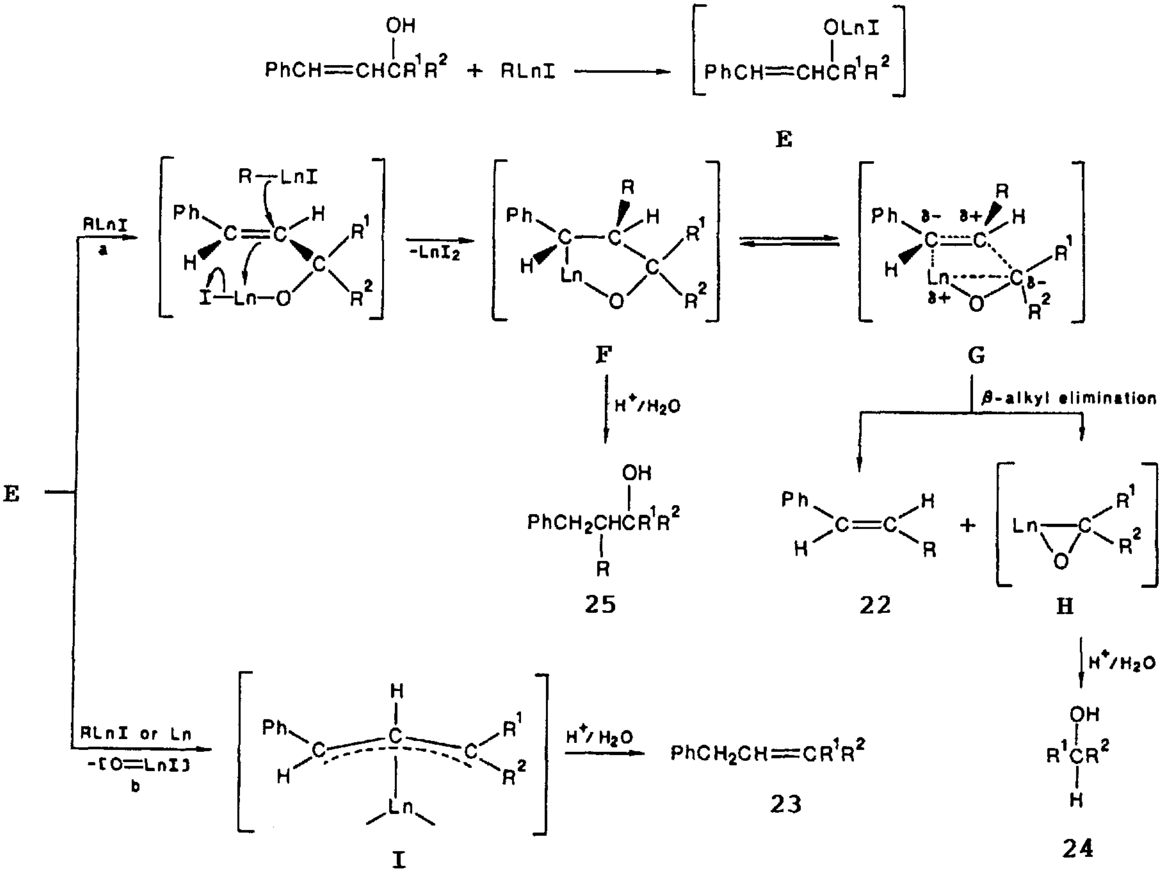
It was also found that quenching the reaction of PhYbI with benzalacetone with D_2O gave the deuterated products **25c** and **23e** in 40 and 27% yields, respectively (Eqn [15]).



$$\mathrm{PhYbI} + \mathrm{PhCH{=}CH\overset{O}{\overset{\|}{C}}Me} \longrightarrow \mathrm{Ph\overset{D}{C}H\underset{Ph}{C}H\underset{Ph}{\overset{OH}{C}}Me} + \mathrm{Ph\overset{D}{C}HCH{=}C(Me)Ph} \qquad [15]$$

25c 23e

Reaction of excess PhYbI with 1,1,3-triphenylprop-2-en-1-ol gave **22**, **23a**, and **24a** in 22, 48, and 19% yields, respectively, and quenching of the reaction with D_2O gave **22** and deuterated products, $PhDCHCH=CPh_2$ and Ph_2DCOH, in 20, 47, and 17% yields, respectively.



Scheme 5

2.4 Mechanism of the reaction of excess RLnI with allylic alcohols and *α,β*-unsaturated carbonyl compounds

On the basis of the above results, we suggest the reaction mechanism shown in Scheme 5. First, RLnI reacts with the allylic alcohol to give an Ln–alkoxide complex **E** which another molecule of RLnI attacks to give the metallacyclic intermediate **F** (Path a). **E** also corresponds to the intermediate of the reaction of RLnI with *α,β*-unsaturated carbonyl compounds. **F** would exist in equilibrium with **G**, whose bonds are more polarized than those of **F**. Hydrolysis of **F** would give the addition product **25**. In the case of chalcone and triphenylallyl alcohol ($R^1 = R^2 = Ph$ in **G**), the equilibrium between **F** and **G** would move to the right by stabilization of phenyl resonance in **G**. **G** would undergo *β*-alkyl elimination to give **22**, the C–C bond cleavage product, and the three-membered metallacycle **H**, which would give alcohol **24** after hydrolysis. *β*-Alkyl elimination and the three-membered metallacycle of this type are reported in the reaction of *f*-block transition metal compounds.[26] With excess of RLnI or Ln metals, **E** also undergoes C–O bond cleavage and electron transfer from RLnI or Ln metals to give the *π*-complex **I**, which would give **23** after hydrolysis (Path b).

Addition of organometal complexes RMX (M = metal) to the C–C double bond of *α,β*-unsaturated carbonyl compounds and allylic alcohols is rare,[27] and the C–C bond cleavage of these compounds by PhYbI complex has not been reported. The data presented here demonstrate that the organolanthanoid *σ*-complexes RLnI have very unusual reactivity which Grignard reagents or *d*-block transition metals do not have. They are not only able to form a C–C bond but also to cleave it, as well as to act as powerful reducing agents

3 TRICHLOROLANTHANOIDS AS FRIEDEL–CRAFTS CATALYSTS

Usually, trivalent compounds are most stable among the lanthanoid compounds, and $LnCl_3$, a typical compound of this type, has been found to serve as an efficient Friedel–Crafts catalyst for alkylation and acylation of arenes, and to be available for re-use after the reaction (Eqn [16]).[28] Numerous Lewis acids, such as $AlCl_3$, have been used to mediate the alkylation and acylation of arenes in Friedel–Crafts reactions. A common problem, particularly in industrial processes, is that catalysts cannot be re-used after the usual aqueous work-up.[29]

$$\mathrm{ArH} + \mathrm{RX} \xrightarrow{\mathrm{LnCl_3}} \mathrm{Ar{-}R} \qquad [16]$$

(Ln=Sc,Y,La,Ce,Pr,Nd,Sm,Eu,
Gd,Tb,Dy,Ho,Er,Tm,Yb,Lu)

$LnCl_3$-catalysed alkylation of arenes is carried out using the arene itself as solvent, alkyl halide (RX) and $LnCl_3 \cdot xH_2O$ as a catalyst at *ca* 0.3 molar equivalent in relation to RX at 75°C. $LnCl_3 \cdot xH_2O$ was dried by heating at 150°C *in vacuo* for 2 h. The reaction is heterogeneous and proceeds with evolution of HCl gas, but addition of solvents such as THF to give homogeneous solutions resulted in lower yields of alkylation

Table 12 $LnCl_3$-catalysed alkylation of benzene with benzyl halides (RX) to give diphenylmethane[a]

Run	$LnCl_3$	X in RX	Reaction time (h)	Yield of diphenylmethane (%)[b]
1	$ScCl_3$	Cl	18	8(20)
2	YCl_3	Cl	18	52(137)
3	$LaCl_3$	Cl	18	3(7)
4	$CeCl_3$	Cl	18	56(149)
5	$PrCl_3$	Cl	18	64(172)
6	$NdCl_3$	Cl	18	63(170)
7	$SmCl_3$	Cl	18	60(161)
8	$EuCl_3$	Cl	18	45(118)
9	$GdCl_3$	Cl	18	65(173)
10	$GdCl_3$	Br	18	61(163)
11	$TbCl_3$	Cl	18	25(67)
12	$DyCl_3$	Cl	1	74(196)
13	$DyCl_3$	Br	2	57(154)
14	$DyCl_3 \cdot 6H_2O$	Cl	18	Trace
15	$HoCl_3$	Cl	18	72(192)
16	$HoCl_3$	Br	18	49(135)
17	$ErCl_3$	Cl	18	63(171)
18	$ErCl_3$	Br	18	61(163)
19	$TmCl_3$	Cl	0.5	70(188)
20	$TmCl_3$	Br	18	57(159)
21	$YbCl_3$	Cl	3	62(166)
22	$YbCl_3$	Br	18	55(148)
23	$LuCl_3$	Cl	3	69(186)

[a] Reaction were carried out by using $LnCl_3$ (0.5 mmol), RX(1.34 mmol), and benzene (2 cm^3) with stirring at 75°C. In addition to diphenylmethane, dibenzylbenzenes were also formed in yields of several per cent. [b] GC yields based on RX; the numbers in parentheses are yields based on $LnCl_3$, i.e. catalytic yields.

product. Table 12 summarizes the $LnCl_3$-catalysed alkylation of benzene with benzyl halides.

All rare earth trichlorides, except $ScCl_3$, $LaCl_3$ and $PmCl_3$ (radioactive) are good catalysts and the later lanthanoids, especially $DyCl_3$, $TmCl_3$ and $LuCl_3$, have high activity. If trichlorolanthanoid hydrates are used without prior dehydration by heating, the reaction is greatly retarded, indicating that the presence of water decreases the yield (Run 14, Table 12). Drying of catalysts is essential in this reaction and anhydrous $LnCl_3$, prepared from lanthanoid oxides and NH_4Cl under water-free conditions, has higher activity than hydrated chlorides. The catalytic activity of these anhydrous lanthanoid chlorides is a little lower than that of $AlCl_3$ and almost the same as that of $AlCl_3/CH_3NO_2$.

These lanthanoid chloride catalysts have an advantage over the usual Lewis acid catalysts such as $AlCl_3$ in that they can be recovered and re-used several times. They can be recovered after the reaction by quenching of the reaction by aqueous acid, evaporation of the aqueous layer containing the lanthanoid chloride after separation of the products by ether, and addition of several drops of concentrated HCl.

Lanthanoid chlorides are also active catalysts for acylation of arenes. For example, reaction of anisole (40 mmol) and benzoyl chloride (40 mmol) at 130°C for 5 h is catalysed by $YbCl_3$ (1 mmol) to give *p*-methoxybenzophenone in 824% yield based on $YbCl_3$.[30]

Acknowledgements The authors thank the colleagues who appear in the literature cited below for the achievements of this pioneering research on lanthanoid-mediated organic reactions, and we are also grateful for the support by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan.

REFERENCES

1. Marks, T J *Prog. Inorg. Chem.*, 1978, 24: 51
2. Girard, P, Namy, J L and Kagan, H B *J. Am. Chem. Soc.*; 1980, 102: 2693
3. Sugai, R, Miyashita, A and Nohira, H *Chem. Lett.*, 1988, 1403
4. (a) Hou, Z, Takamine, K, Fujiwara, Y and Taniguchi, H *Chem. Lett.*, 1987, 2061; (b) Hou, Z, Takamine, K, Aoki, O, Shiraishi, H, Fujiwara, Y and Taniguchi, H *J. Chem. Soc., Chem. Commun.*, 1988, 668; (c) Hou, Z, Takamine, K, Aoki, O, Shiraishi, H, Fujiwara, Y and Taniguchi, H *J. Org. Chem.*, 1988, 53: 6077
5. (a) Hamrick, P J, Jr and Hauser, C R *J. Am. Chem. Soc.*, 1959, 81: 493; (b) Selman, S and Easthan, J F *J. Org. Chem.*, 1965, 30: 3804; (c) McMurry, J E, Fleming, M P, Kees, K L and Krepski, L R *ibid.*, 1979, 43: 3255; (d) Corey, E J, Danheiser, R L and Chadrasekaran, S *ibid.*, 1976, 41: 260
6. Stowell J C *Carbanions in Organic Synthesis*, John Wiley, New York, 1987, p 58
7. Takamine, K, Tanaka, S, Tsubaki, Y, Beppu, F, Takaki, K and Fujiwara, Y *Chem. Lett.* (in press)
8. Tanaka, S, Tsubaki, Y, Beppu, F, Takaki K and Fujiwara Y (unpublished results)
9. Takaki, K, Tsubaki, Y, Tanaka, S. Beppu, F and Fujiwara, Y *Chem. Lett.*, 1990, 203
10. Roskamp, E J and Pedersen, S F *J. Am. Chem. Soc.*, 1987, 109: 3152
11. Takaki, K, Beppu, F, Tanaka, S, Tsubaki, Y, Jintoku, T and Fujiwara, Y *J. Chem. Soc., Chem. Commun.*, 1990, 516
12. Hou, Z, Taniguchi, H and Fujiwara, Y *Chem. Lett.*, 1987, 305
13. Benkeser, R A, Arnold, C, Jr, Lambert, R F and Thomas, O H *J. Am. Chem. Soc.*, 1955, 77: 6042
14. Birch, A J, Murry, A R and Smith, H *J. Chem. Soc.*, 1951, 1945
15. White, J D and Larson, G L *J. Org. Chem.*, 1978, 43: 4555
16. Smith, P A S *Open-Chain Nitrogen Compounds*, vol 2, Benjamin, New York, 1966, p321
17. Hou, Z, Fujiwara, Y and Taniguchi, H *J. Org. Chem.*, 1988, 53: 3118
18. (a) Yokoo, K, Yamanaka, Y, Fukagawa, T, Taniguchi, H and Fujiwara, Y *Chem. Lett.*, 1983, 1301; (b) Hou, Z, Mine, N, Fujiwara, Y and Taniguchi, H *J. Chem. Soc., Chem. Commun.*, 1985, 1700; (c) Hou, Z, Fujiwara, Y, Jintoku, T, Mine, N, Yokoo, K, and Taniguchi, H *J. Org. Chem.*, 1987, 52: 3524
19. (a) Evans, D F, Fazakerley, G V and Phillips, R F *J. Chem. Soc. D* 1970, 244; (b) *idem J. Chem. Soc. A* 1971, 1932
20. (a) Souppe, J, Dannon, L, Namy, J K and Kagan, H B *J. Organomet. Chem.*, 1983, 205: 227; (b) Namy, J L, Souppe, J and Kagan, H B *Tetrahedron Lett.*, 1983, 24: 765; (c) Zhang, Y and Lin, R *Synth. Commun.*, 1987, 17: 329
21. (a) Fukagawa, T, Fujiwara, Y, Yokoo, K and Taniguchi, Y *Chem. Lett.*, 1981, 1771; (b) Fukagawa, T, Fujiwara, Y and Taniguchi, H *ibid.*, 1982, 601; (c) Yokoo, K, Fujiwara, Y, Fukagawa, T and Taniguchi, H *Polyhedron*, 1983, 2: 1101; (d) Yokoo, K, Kijima, Y, Fujiwara, Y and Haniguchi, H *Chem. Lett.*, 1984, 1321; (e) Yokoo, K, Fukagawa, T, Yamanak, Y, Taniguchi, H and Fujiwara, Y *J. Org. Chem.*, 1984, 49: 3237; (f) Yokoo, K, Mine, N, Taniguchi, H and Fujiwara, Y *J. Organomet. Chem.*, 1985, 279: C19; (g) Mine, N, Fujiwara, Y and Taniguchi, H *Chem. Lett.*, 1986, 357
22. Kohler, E P and Peterson, W D *J. Am. Chem. Soc.*, 1933, 55: 1073
23. Beletskaya, I P *Izv. Akad. Nauk SSSR, Ser. Khim.* 1983; 2615

24. Imamoto, T, Kusumoto, T, Tawarayama, Y, Sygiura, Y, Hatanaka, Y and Yakoyama, M *J. Org. Chem.*, 1984, 44: 3904

25. Ho, T-L *Hard and Soft Acids and Bases Principle in Organic Chemistry,* Academic Press, New York, 1977

26. (a) Watson, P L and Roe, D C *J. Am. Chem. Soc.*, 1982, 104: 6471; (b) Moly, K G, Marks, T J and Day, V W *ibid.*, 1983, 105: 5696

27. (a) Cherest, M, Felkin, H, Frajernan, C, Lion, C, Roussi, G and Swierczewski, G *Tetrahedron Lett.*, 1966, 875; (b) Felkin, H and Swierczewski, G *Tetrahedron*, 1975, 31: 2735; (c) Nagashima, H, Sato, K and Tsuji, J *Chem. Lett.*, 1981, 1605

28. Mine, N, Fujiwara, Y and Taniguchi, H *Chem. Lett.*, 1986, 357

29. Keim, W and Roper, M *Ullman: Encyclopedia of Industrial Chemistry*, 5th edn, vol A1, VCH Verlag, Weinheim, 1985 p 185

30. Mine, N, Takaki, K and Fujiwara, Y (unpublished results)