Headline Articles

Preparation of (Alkaneimidoyl)lanthanides and Their Reactions with Carbonyl Compounds

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(Received September 4, 1995)

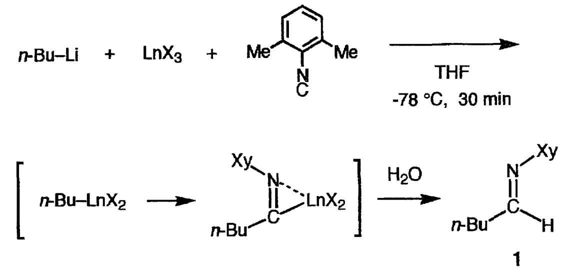
The preparation of (alkaneimidoyl)lanthanide(III) reagents and their reactions with carbonyl compounds were studied. Alkyllithium was added to a mixture of an anhydrous lanthanide salt and 2,6-xylyl isocyanide in tetrahydrofuran at −78 °C. Among a series of lanthanide salts, $CeCl_3$ effected the quantitative conversion of the isocyanide to afford an orange solution of (alkaneimidoyl)cerium(III). Although $LaCl_3$, SmI_3, and $Sm(OTf)_3$ were found to be highly reactive, multiple insertion of the isocyanide ensued. (Alkaneimidoyl)cerium(III) could also be prepared by the reaction of dialkylmagnesium with $CeCl_3$ and 2,6-xylyl isocyanide at −45 °C. The thus-prepared (alkaneimidoyl)cerium(III) reacted with a carbonyl compound to afford an addition product, i.e., an α-hydroxy imine. The present reactions for the preparation of (alkaneimidoyl)cerium(III) provide a convenient synthetic equivalent to a nucleophilic acyllanthanide species with a wide variation for the acyl group.

The migratory insertion of carbon monoxide into a metal–alkyl bond to furnish an acylmetal is one of the most fundamental elementary processes in organometallic chemistry. The isocyano carbon of an isocyanide also undergoes insertion into a metal–alkyl bond to afford an (alkaneimidoyl)metal compound (hereafter *alkaneimidoyl* is abbreviated to *imidoyl*), which has found successful synthetic applications.[1)] On the other hand, since the appearance of seminal papers by Luche[2)] and Kagan,[3)] ever-increasing research activities have been directed toward the use of lanthanide reagents for synthetic purposes.[4)] In many cases, however, the intermediate organolanthanide has not been established as being definitive. Hence, the preparative methods of new organolanthanide reagents, which are thermodynamically stable, are yet to be developed. Recently, we have found that the SmI_2-mediated coupling of aryl isocyanide with an alkyl halide furnishes an (imidoyl)samarium(III) species, which is reasonably stable up to 0 °C in the presence of hexamethylphosphoric triamide.[5)] The (imidoyl)samarium(III) disclosed unique chemical properties in terms of nucleophilicity and basicity, that set itself apart from the existing analogous imidoyl complexes of the main group and transition elements. Of much interest is the behavior of imidoyl complexes of other lanthanide series. This paper describes the results of our study on the preparation of (imidoyl)lanthanide(III) reagents and their reactions with carbonyl compounds.

Results and Discussion

Preparation of (Imidoyl)lanthanide by the Reaction of Isocyanide with a Lanthanide Salt and Organolithium. The reaction of a lanthanide(III) salt with organolithium has been assumed to generate the corresponding organolanthanide through transmetallation, although the precise structure of the intermediate is equivocal.[6)] Thus, butyllithium (1.0 equiv) was added to a white milky suspension of an anhydrous lanthanide(III) salt (1.1 equiv) and 2,6-xylyl isocyanide (1.0 equiv) in tetrahydrofuran (THF) at −78 °C. The reaction mixture was stirred for 30 min and then quenched with water. The results with a series of lanthanide salts are shown in Table 1. The use of $CeCl_3$ effected the complete conversion of the isocyanide to afford an orange solution with dissolution of the lanthanide salt and, after hydrolysis, an aldimine (**1**) was produced quantitatively (Run 2). We have reported that the reaction of butyllithium alone with 2,6-xylyl isocyanide at −78 °C results in the quantitative formation of an anomalous product through trimerization of the isocyanide.[7)] The fact that no such trimer was produced with $CeCl_3$ suggested that, prior to a direct reaction of free butyllithium with the isocyanide, a putative butylcerium(III) was formed by transmetallation between butyllithium and $CeCl_3$. Subsequently, an exclusive single insertion of 2,6-xylyl isocyanide into the C–Ce bond occurred to afford (imidoyl)cerium(III), for which we assumed a η^2-bound structure

Table 1. Reactions of Isocyanide with Lanthanide Salts and Butyllithium (Xy = 2,6-xylyl)



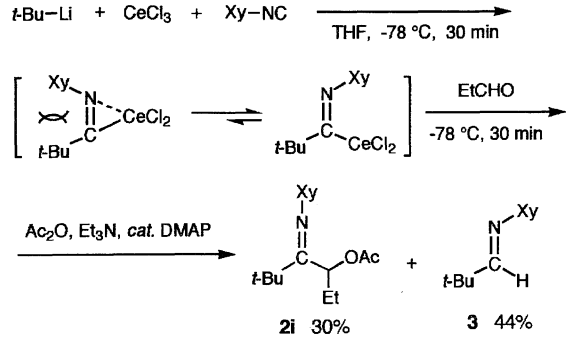
Run	LnX_3	Yield of **1** (%)	Yield of oligomers (%)
1	$LaCl_3$	68	21
2	$CeCl_3$	99	0
3	$SmCl_3$	14	0
4	SmI_3	43	30
5	$Sm(OTf)_3$	13	74
6	$EuCl_3$	0	0
7	$GdCl_3$	0	0
8	$YbCl_3$	21	4
9	$Yb(OTf)_3$	10	0

(vide infra).

Although $LaCl_3$, SmI_3, and $Sm(OTf)_3$ were found to also be highly reactive, multiple insertion of the isocyanide ensued (Runs 1, 4, and 5). In the cases of $EuCl_3$ and $GdCl_3$, the isocyanide remained unreacted after 30 min at −78 °C with the appearance of the white milky suspension being unchanged. After hydrolysis, no **1** was obtained (Runs 6 and 7). Since neither was produced the aforementioned trimer, it is unlikely that butyllithium remained unchanged. A "complexing salt" or "butyllanthanide," which encumbered the reaction with the isocyanide, might have been formed.

When 1,1,3,3-tetramethylbutyl isocyanide was used instead of 2,6-xylyl isocyanide under conditions analogous to those used in Run 2, no **1** was obtained after hydrolysis. This result disclosed that a tertiary alkyl isocyanide is less reactive toward organocerium(III) than an aromatic isocyanide.

Reactions of (Imidoyl)lanthanides with Carbonyl Compounds. The addition of other organolithium reagents to a mixture of 2,6-xylyl isocyanide and $CeCl_3$ also produced an orange solution of the corresponding (imidoyl)cerium(III). When a carbonyl compound was reacted with the (imidoyl)cerium(III) at −78 °C, an addition product, i.e., an α-hydroxy imine (**2**) was obtained in moderate to high yields. The (imidoyl)cerium(III) was stable at temperatures of up to −40 °C, and the reaction at higher temperature led to a gradual collapse of the intermediate to decrease the yield of **2**. Selected examples of the synthesis of α-hydroxy imines from a variety of organolithiums and carbonyl compounds are shown in Table 2. The methyl, phenyl, and vinyl groups were easily coupled with the isocyanide (Runs 1,6—8), whereas the incorporation of these groups in the skeleton of an α-hydroxy imine using organic halides as the source in SmI_2-mediated three-component coupling was unsuccessful.[5] An alkynylcerium failed to react with the isocyanide, in contrast to the reaction with carbonyl compounds.[6d] α-Hydroxy imines were obtained as well by the reaction with an aldehyde (Run 2), and even with cyclopentanone (Run 6), which is extremely susceptible to enolization when treated with nucleophilic organometallics. On the contrary, (imidoyl)lithium prepared from 1,1,3,3-tetramethylbutyl isocyanide with butyllithium according to Walborsky's procedure,[1a,1b,1c] failed to add to cyclopentanone. Thus, the low basicity of the (imidoyl)cerium(III) reagent is noteworthy. Like other organolanthanides, (imidoyl)cerium(III) underwent a selective 1,2-addition to an α,β-unsaturated ketone (Run 7).

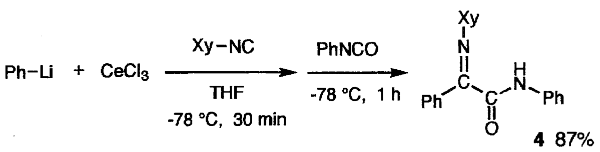


Scheme 1.

Whereas secondary as well as primary alkyllithium reagents furnished **2** in good yield, the reaction of (imidoyl)cerium(III) derived from t-butyllithium with propionaldehyde afforded **2i** in only 30% yield together with an aldimine **3** in 44% yield (Scheme 1). The low-yield coupling with the aldehyde might have been due to the collapse of the intermediate (imidoyl)cerium(III) species. We suspect that the steric repulsion between the bulky t-butyl group and the 2,6-xylyl group disfavors the η^2-bound structure. The t-butyl group is pushed away to the other side of the imino group, thereby rendering η^2-binding difficult. The enforced η^1-complex is less stable to decompose gradually, even at −78 °C.

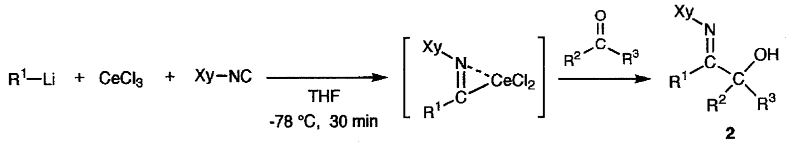
When phenyl isocyanate was reacted with the PhLi-derived (imidoyl)cerium(III), an amide **4** was produced in 87% yield (Scheme 2).

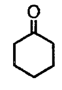
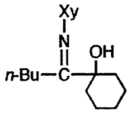
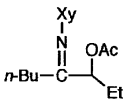
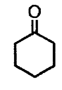
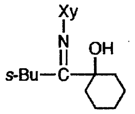
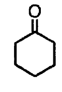
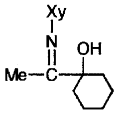
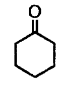
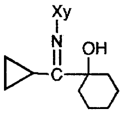
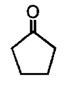
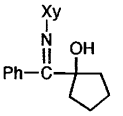
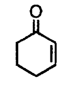
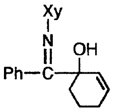
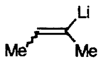
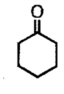
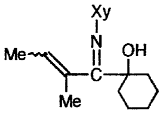
Preparation of (Imidoyl)cerium by the Reaction of Isocyanide with $CeCl_3$ and Dialkylmagnesium. The relative ease of formation of Grignard reagents (RMgX) from organic halides together with a wide variation of the group R led us to examine their use instead of alkyllithium. It has been reported that the use of the Grignard reagent–$CeCl_3$ system in reactions with carbonyl substrates affords the addition products in high yield.[8] However, an attempted reaction of the Grignard reagent with 2,6-xylyl isocyanide in the presence of $CeCl_3$ failed to proceed at temperatures ranging from −78 to 0 °C, possibly due to the sluggish process of



Scheme 2.

Table 2. Reactions of (Alkaneimidoyl)cerium(III) with Carbonyl Compounds (Xy = 2,6-xylyl)



Run	R^1–Li	$R^2R^3C=O$	Product (2)	Yield/%
1	*n*-Bu–Li		 **2a**	99
2	*n*-Bu–Li	EtCHO	 **2b**	95[a]
3	*s*-Bu–Li		 **2c**	90
4	Me–Li		 **2d**	68
5			 **2e**	54
6	Ph–Li		 **2f**	83
7	Ph–Li		 **2g**	80
8			 **2h**	87

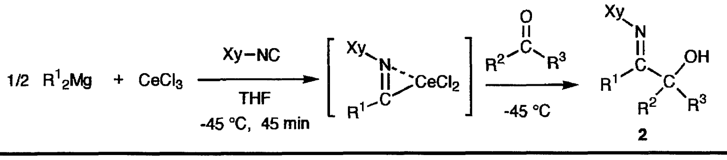
a) The reaction was quenched by adding Ac_2O, Et_3N, and 4-(dimethylamino)pyridine. The product was isolated as the acetylated derivative.

transmetallation.[9]

The use of dialkylmagnesium for transmetallation with a lanthanide salt has been documented,[6c,10] and was thus applied to a reaction with 2,6-xylyl isocyanide (Table 3). An ether solution of dibutylmagnesium (0.25 mmol) was added to a mixture of 2,6-xylyl isocyanide (0.50 mmol) and $CeCl_3$ (0.55 mmol) in THF at −78 °C. Being stirred at that temperature for 90 min, the reaction mixture also became orange, suggesting the formation of an (imidoyl)cerium(III) species. Subsequent quenching with water gave the aldimine (**1**) in 70% yield. Moreover, the addition of dibutylmagnesium at −45 °C led to a quantitative conversion of the isocyanide. Since no reaction occurred upon treatment of dibutylmagnesium alone with 2,6-xylyl isocyanide at temperatures up to 0 °C, it is likely that transmetallation between dibutylmagnesium and $CeCl_3$ proceeds quite efficiently at −45 °C, yielding butylcerium(III), which is then coupled with the isocyanide. Notably, both butyl groups of dibutylmagnesium were utilized in the coupling. These results may be accounted for by assuming the concurrent occurrence of transmetallation at both Mg–C linkages at −45 °C. Table 3 presents the results of the addition reactions of the diorganylmagnesium-derived (imidoyl)cerium(III) reagents to carbonyl compounds. Primary and secondary alkyl, phenyl, and vinyl groups were successfully coupled with the isocyano carbon in the initial C–C bond-forming step. The second coupling of the (imidoyl)lanthanides with carbonyl compounds proceeded efficiently to produce α-hydroxy imines in good yield. Di-*t*-butylmagnesium failed to undergo α-addition to the isocyanide.

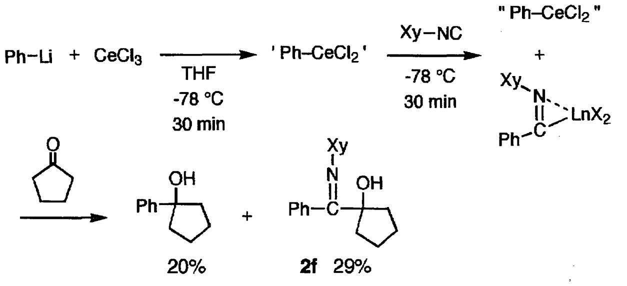
Mechanistic Features of Preparation of (Imidoyl)lanthanide. In the reported procedure of the organo-

Table 3. Reactions of $R^1{}_2Mg$-Derived (Imidoyl)cerium(III) with Carbonyl Compounds (Xy = 2,6-xylyl)

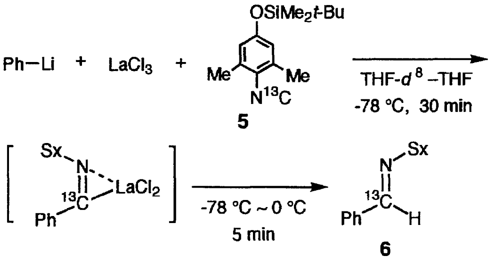


Run	$R^1{}_2Mg$	$R^2R^3C=O$	**2**	Yield (%)
1	n-Bu_2Mg	Cyclohexanone	**2a**	87
2	s-Bu_2Mg	Cyclohexanone	**2c**	89
3	Ph_2Mg	Et-CHO	**2j**	95[a)]
4	$(PhCH_2)_2Mg$	Cyclohexanone	**2k**	79
5	$(Me_2C{=}CH)_2Mg$	Cyclohexanone	**2l**	78

a) The reaction was quenched by addition of Ac_2O, Et_3N, and 4-(dimethylamino)pyridine. The product was isolated as the acetylated derivative.



Scheme 3.



Scheme 4.

lithium–$CeCl_3$ system for a carbonyl addition reaction, after organolithium was treated with $CeCl_3$ at −78 °C for 30 min, a carbonyl compound was added.[6a)] When phenyllithium was treated with $CeCl_3$ at −78 °C for 30 min, and then with the isocyanide at that temperature for an additional 30 min, the insertion reaction stopped halfway. However, the subsequent addition of cyclopentanone to the mixture furnished 1-phenylcyclopentanol in 20% yield together with the α-hydroxy imine (**2f**) in 29% yield (Scheme 3). Although evidence for a discussion of the nature of actual species involved in the reaction with the isocyanide is rather sparse, at least two different organocerium species can be assumed to explain this anomalous result. The transitory one initially formed is sufficiently reactive to undergo α-addition to the isocyanide, and is gradually converted to another species which is less reactive toward the isocyanide, but is still so reactive as to add to cyclopentanone.

On the basis of the structures of the related (formimidoyl)lanthanide complexes,[11)] a η^2-bound structure may be presumed for the (imidoyl)lanthanide(III) species. Whether it adopts a monomeric or aggregated form is unclear. In order to obtain structural information, a NMR study was carried out using a ^{13}C-labeled 4-(t-butyldimethylsiloxy)-2,6-xylyl (Sx) isocyanide (**5**).[12)] Thus, the isocyanide **5** was treated with phenyllithium and a diamagnetic salt, $LaCl_3$, at −78 °C for 30 min (Scheme 4). The ^{13}C NMR spectra (−78 °C) of the supernatant of the reaction mixture showed a distinct resonance at 271.6 ppm, which conformed to the expectation for the imidoyl carbon bound to La of the proposed (imidoyl)lanthanum structure. Notably, the signal at 271.6 ppm disappeared in the spectrum measured shortly after the temperature was raised to 0 °C over 5 min. Instead, there appeared a new peak at 163.5 ppm, which was ascribed to the formimidoyl carbon of an aldimine (**6**). It seemed that the thermal decomposition of an (imidoyl)lanthanum occurs via the abstraction of a hydrogen atom from THF or the 2,6-xylyl group.

Conclusion

The straightforward preparation of acyllanthanides has met difficulties from a synthetic point of view: A stable acylcerium(III) species is inaccessible by way of the carbonylation of alkylcerium(III).[13)] The generation of stable acylsamarium(III) reagents by the reduction of an acid chloride[14)] or by reductive carbonylation of an alkyl halide[15)] is limited to acyl groups having tertiary α-carbon atoms. Since the imino functionality of an imine can be easily converted to a carbonyl group by acidic hydrolysis, the present reactions for the preparation of (imidoyl)cerium(III) provide a convenient synthetic equivalent to a nucleophilic acyllanthanide species. As compared with the SmI_2-mediated three-component coupling,[5)] a wider variation for the acyl group becomes available by this procedure without the use of carcinogenic hexamethylphosphoric triamide.

Experimental

General. Column chromatography was performed with silica gel 60 (E. Merck, Darmstadt), 230—400 mesh. Preparative thin-layer chromatography (TLC) was performed with silica gel 60 PF_{254} (E. Merck, Darmstadt). ^1H and ^{13}C NMR spectra were acquired in chloroform-d at 200 and 50 MHz, respectively. The carbon chemical shifts were recorded relative to chloroform-*d* ($\delta = 77.0$). Na_2SO_4 was used to dry the organic layers after extraction. All of the reactions were performed under a dry nitrogen atmosphere. Unless otherwise noted, all materials were obtained from commercial sources. THF was distilled from sodium diphenylketyl. 2,6-Xylyl isocyanide was prepared according to the literature.[16] An ether solution of diorganylmagnesium was obtained by the addition of dioxane to an ether solution of a Grignard reagent.[17] A reaction vessel was immersed in a Dry Ice–MeCN bath to carry out the reaction at −45 °C.

Synthesis of 1-[1-(2,6-Xylylimino)pentyl]cyclohexanol (2a) by the Reaction of the BuLi-Derived (Imidoyl)cerium(III) with Cyclohexanone. Cerium trichloride heptahydrate (205 mg, 0.55 mmol) was dried under vacuum at 50 °C for 1 h and at 140 °C for 2 h. After being cooled to room temperature, THF (2 ml) was added and the mixture was vigorously stirred for 12 h. 2,6-Xylyl isocyanide (65 mg, 0.50 mmol) was added to the resulting milky white suspension, which was then cooled to −78 °C. To this was added a hexane solution of butyllithium (300 µl, 0.50 mmol). After the mixture was stirred at that temperature for 30 min, cyclohexanone (39 mg, 0.40 mmol) was added. The reaction mixture was stirred for additional 1 h. Then, the temperature was allowed to rise to room temperature. A drop of water was added, and the mixture was passed through a Florisil pad to remove insoluble materials. The filtrate was subjected to silica-gel column chromatography (ether : hexane = 1 : 10) to afford **2a** as oil (114 mg, 99%).

3-Acetoxy-4-(2,6-xylylimino)octane (2b). Pale-yellow oil. ^{1}H NMR $\delta = 0.76$ (t, $J = 7.0$ Hz, 3H), 1.10 (t, $J = 7.2$ Hz, 3H), 0.91—1.52 (m, 4H), 1.82—2.15 (m, 4H), 1.95 (s, 3H), 1.98 (s, 3H), 2.16 (s, 3H), 5.27 (dd, $J = 8.0$, 4.8 Hz, 3H), 6.81—7.00 (m, 3H); ^{13}C NMR $\delta = 10.5$, 13.5, 18.0, 18.1, 21.0, 23.0, 25.9, 27.7, 31.7, 77.0, 122.8, 125.1, 125.9, 127.7, 127.9, 147.4, 170.9, 172.6. Anal. Found: C, 74.44; H, 9.65; N, 4.62%. Calcd for $C_{18}H_{27}NO_2$: C, 74.70; H, 9.40; N, 4.84%.

1-[2-Methyl-1-(2,6-xylylimino)butyl]cyclohexanol (2c). Pale-yellow oil. ^{1}H NMR $\delta = 0.83$ (t, $J = 7.2$ Hz, 3H), 1.01 (d, $J = 7.1$ Hz, 3H), 1.10—1.95 (m, 12H), 2.04 (s, 6H), 2.45—2.67 (m, 1H), 5.30—5.65 (br, 1H), 6.85—7.05 (m, 3H); ^{13}C NMR $\delta = 12.8$, 15.5, 18.3, 21.8, 25.4, 25.9, 35.0, 35.1, 38.7, 75.9, 122.6, 125.2, 127.58, 127.63, 146.6, 180.2. Anal. Found: C, 79.40; H, 10.18; N, 4.79%. Calcd for $C_{19}H_{29}NO$: C, 79.39; H, 10.17; N, 4.87%.

1-[1-(2,6-Xylylimino)ethyl]cyclohexanol (2d). Colorless solid. ^{1}H NMR $\delta = 1.18$—1.45 (m, 1H), 1.54—2.05 (m, 9H), 1.71 (s, 3H), 1.97 (s, 6H), 5.36 (s, 1H), 6.87—7.09 (m, 3H); ^{13}C NMR $\delta = 14.7$, 17.5, 21.6, 25.4, 35.2, 74.5, 123.2, 125.9, 127.9, 146.7, 176.0. Anal. Found: C, 78.10; H, 9.54; N, 5.66%. Calcd for $C_{16}H_{23}NO$: C, 78.32; H, 9.45; N, 5.71%.

1-[Cyclopropyl(2,6-xylylimino)methyl] cyclohexanol (2e). Pale-yellow oil. ^{1}H NMR $\delta = 0.45$—0.72 (m, 4H), 1.17—1.97 (m, 11H), 2.01 (s, 6H), 5.54—5.68 (br, 1H), 6.83—7.01 (m, 3H); ^{13}C NMR $\delta = 6.9$, 13.0, 18.0, 22.0, 25.6, 36.1, 75.7, 122.8, 125.6, 127.6, 145.9, 176.2. Anal. Found: C, 79.93; H, 9.48; N, 4.93%. Calcd for $C_{18}H_{25}NO$: C, 79.66; H, 9.28; N, 5.16%.

1-[Phenyl(2,6-xylylimino)methyl]cyclopentanol (2f). Colorless solid. ^{1}H NMR $\delta = 1.60$—2.10 (m, 8H), 2.08 (s, 6H), 5.51 (s, 1H), 6.50—6.89 (m, 3H), 7.02—7.25 (m, 5H); ^{13}C NMR $\delta = 18.4$, 24.0, 38.9, 84.5, 123.1, 125.7, 126.3, 127.5, 127.7, 128.5, 135.1, 146.7, 175.7. Anal. Found: C, 82.16; H, 7.92; N, 4.77%. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77%.

1-[Phenyl(2,6-xylylimino)methyl]cyclohex-2-en-1-ol (2g). Colorless oil. ^{1}H NMR $\delta = 1.52$—2.24 (m, 6H), 1.87 (s, 3H), 2.23 (s, 3H), 5.89 (d, $J = 10.1$ Hz, 1H), 6.07—6.20 (m, 1H), 6.11 (s, 1H), 6.76—6.87 (m, 2H), 6.90—7.02 (m, 1H), 7.12—7.28 (m, 5H); ^{13}C NMR $\delta = 18.1$, 18.4, 18.5, 24.6, 34.9, 73.5, 123.4, 124.6, 126.8, 127.4, 127.7, 128.0, 128.9, 132.3, 135.1, 145.9, 174.6. Anal. Found: C, 82.32; H, 7.60; N, 4.59%. Calcd for $C_{21}H_{23}NO$: C, 82.59; H, 7.59; N, 4.59%.

1-[2-Methyl-1-(2,6-xylylimino)but-2-enyl]cyclohexanol (2h). Colorless oil. ^{1}H NMR $\delta = 1.12$—1.95 (m, 10H), 1.61 (s, 6H), 2.06 (s, 6H), 5.21 (s, 1H), 5.28—5.49 (m, 1H), 6.82—7.00 (m, 3H); ^{13}C NMR $\delta = 18.2$, 21.8, 22.0, 22.6, 25.4, 35.5, 76.7, 123.2, 126.3, 127.7, 130.9, 146.5, 179.1. Anal. Found: C, 79.87; H, 9.75; N, 4.81%. Calcd for $C_{19}H_{27}NO$: C, 79.95; H, 9.53; N, 4.91%.

4-Acetoxy-2,2-dimethyl-3-(2,6-xylylimino)hexane (2i). Pale-yellow oil. ^{1}H NMR $\delta = 0.75$ (t, $J = 7.4$ Hz, 3H), 1.31 (s, 9H), 1.50—1.61 (m, 2H), 1.98 (s, 3H), 1.99 (s, 3H), 2.02 (s, 3H), 5.54 (dd, $J = 9.4$, 3.6 Hz, 1H), 6.76—7.00 (m, 3H); ^{13}C NMR $\delta = 10.7$, 18.1, 18.2, 20.9, 26.3, 28.8, 41.2, 74.1, 121.9, 122.8, 124.7, 127.5, 127.9, 147.7, 170.2, 174.2. Anal. Found: C, 74.45; H, 9.39; N, 4.79%. Calcd for $C_{18}H_{27}NO_2$: C, 74.70; H, 9.40; N, 4.84%.

***N*,2-Diphenyl-2-(2,6-xylylimino)acetamide (4).** Yellow solid. ^{1}H NMR $\delta = 2.01$ (s, 6H), 6.51—7.00 (m, 3H), 7.12—7.45 (m, 8H), 7.71—7.80 (m, 2H), 9.82 (br s, 1H); ^{13}C NMR $\delta = 18.9$, 120.0, 124.8, 125.0, 126.0, 128.2, 128.6, 129.5, 129.7, 130.6, 132.2, 138.1, 146.4, 161.3, 161.4. Anal. Found: C, 80.21; H, 6.04; N, 8.34%. Calcd for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14; N, 8.53%.

Synthesis of 2c by the Reaction of the *s*-Bu$_2$Mg-Derived (Imidoyl)cerium(III) with Cyclohexanone. Cerium trichloride heptahydrate (205 mg, 0.55 mmol) was dried under vacuum at 50 °C for 1 h and at 140 °C for 2 h. After being cooled to room temperature, THF (2 ml) was added and the mixture was vigorously stirred for 12 h. 2,6-Xylyl isocyanide (65 mg, 0.50 mmol) was added to the resulting milky white suspension, which was then cooled to −45 °C. To this was added an ether solution of di-*s*-butylmagnesium (640 µl, 0.25 mmol). The mixture was stirred at that temperature for 45 min, and then cyclohexanone (39 mg, 0.40 mmol) was added. After the reaction mixture was stirred at −45 °C for 1 h, the temperature was allowed to rise to room temperature. A drop of water and ether (2 ml) were added, and the mixture was passed through a Florisil pad to remove insoluble materials. The filtrate was subjected to silica-gel column chromatography (ether : hexane = 1 : 10) to afford **2c** as oil (102 mg, 89%).

2-Acetoxy-1-phenyl-1-(2,6-xylylimino)butane (2j). Pale-yellow oil. ^{1}H NMR $\delta = 1.07$ (t, $J = 7.4$ Hz, 3H), 1.76 (s, 3H), 1.86—2.05 (m, 2H), 2.17 (s, 3H), 2.20 (s, 3H), 5.60 (t, $J = 6.2$, 1H), 6.74—6.85 (m, 2H), 6.87—7.00 (m, 1H), 7.15—7.32 (m, 5H); ^{13}C NMR $\delta = 10.3$, 18.1, 18.4, 21.0, 25.9, 78.2, 122.7, 124.5, 126.8, 127.1, 127.3, 128.0, 128.1, 129.3, 136.0, 147.5, 168.3, 171.1. Anal. Found: C, 77.87; H, 7.66; N, 4.49%. Calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53%.

1-[2-Phenyl-1-(2,6-xylylimino)ethyl]cyclohexanol (2k). Pale-yellow oil. ^{1}H NMR $\delta = 1.15$—1.40 (m, 1H), 1.58—1.92 (m, 9H), 1.87 (s, 6H), 3.56 (s, 2H), 5.15 (s, 1H), 6.74—6.81 (m, 2H), 6.87—6.94 (m, 3H), 7.02—7.11 (m, 3H); ^{13}C NMR $\delta = 18.3$, 22.3, 26.0, 36.4, 36.5, 76.1, 123.9, 126.6, 126.9, 128.4, 128.6, 129.9, 135.7, 146.7, 176.7. Anal. Found: C, 81.91; H, 8.44; N, 4.28%. Calcd for $C_{22}H_{27}NO$: C, 82.20; H, 8.47; N, 4.36%.

1-[3-Methyl-1-(2,6-xylylimino)but-2-enyl]cyclohexanol (2l). Pale-yellow oil. ^{1}H NMR $\delta = 1.18$ (s, 3H), 1.15—1.90 (m, 10H), 1.61 (d, $J = 1.2$ Hz, 3H), 2.06 (s, 6H), 5.43—5.61 (br, 1H), 5.62—5.68 (m, 1H), 6.82—7.03 (m, 3H); ^{13}C NMR $\delta = 18.3$, 20.4, 21.8, 25.4, 25.6, 35.8, 75.1, 117.7, 123.4, 126.8, 128.1, 140.4, 146.3, 175.0. Anal. Found: C, 79.95; H, 9.68; N, 4.72%. Calcd for $C_{19}H_{27}NO$: C, 79.95; H, 9.53; N, 4.91%.

The authors are grateful to The Ministry of Education, Science and Culture for a financial support on Priority Areas "New Development of Rare Earth Complexes" (No. 06241239).

References

1) a) G. E. Niznik, W. H. Morrison, and H. M. Walborsky, *J. Org. Chem.*, **39**, 600 (1974); b) M. J. Marks and H. M. Walborsky, *J. Org. Chem.*, **46**, 5405 (1981); c) M. J. Marks and H. M. Walborsky, *J. Org. Chem.*, **47**, 52 (1982); d) M. Murakami, H. Ito, and Y. Ito, *J. Org. Chem.*, **53**, 4158 (1988); e) M. Murakami, H. Ito, W. A. W. A. Bakar, A. B. Baba, and Y. Ito, *Chem. Lett.*, **1989**, 1603.

2) a) J. L. Luche, *J. Am. Chem. Soc.*, **100**, 2226 (1978); b) A. L. Gemal and J. L. Luche, *J. Am. Chem. Soc.*, **103**, 5454 (1981).

3) P. Girard, J. L. Namy, and H. B. Kagan, *J. Am. Chem. Soc.*, **102**, 2693 (1980).

4) a) H. B. Kagan and J. L. Namy, *Tetrahedron*, **24**, 6573 (1986); b) J. A. Soderquist, *Aldrichim. Acta*, **24**, 15 (1991); c) G. A. Molander, *Chem. Rev.*, **92**, 29 (1992); d) T. Imamoto, "Lanthanides in Organic Synthesis," Academic Press, London (1994).

5) a) M. Murakami, T. Kawano, H. Ito, and Y. Ito, *J. Org. Chem.*, **58**, 1458 (1993); b) M. Murakami, H. Ito, and Y. Ito, *J. Org. Chem.*, **58**, 6766 (1993).

6) a) T. Imamoto, T. Kusumoto, Y. Tawarayama, Y. Sugiura, T. Mita, Y. Hatanaka, and M. Yokoyama, *J. Org. Chem.*, **49**, 3904 (1984); b) S. Collins, Y. Hong, G. J. Hoover, and J. R. Veit, *J. Org. Chem.*, **55**, 3565 (1990); c) G. A. Molander, E. R. Burkhardt, and P. Weinig, *J. Org. Chem.*, **55**, 4990 (1990); d) K. Utimoto, A. Nakamura, and S. Matsubara, *J. Am. Chem. Soc.*, **112**, 8189 (1990).

7) M. Murakami, H. Ito, and Y. Ito, *Chem. Lett.*, **1996**, 7.

8) T. Imamoto, N. Takiyama, K. Nakamura, T. Hatajima, and Y. Kamiya, *J. Am. Chem. Soc.*, **111**, 4392 (1989).

9) It has been reported that the reactions of a Grignard reagents with tertiary alkyl isocyanide are generally less satisfactory than those of alkyllithium reagents.[1a)] We also observed that a Grignard reagent failed to react with 2,6-xylyl isocyanide at temperatures ranging from −78 °C to room temperature, in marked contrast to the case with alkyllithium.[7)]

10) S. Matsubara, A. Nakamura, and K. Utimoto, "37th Symposium on Organometallic Chemistry," Osaka, 1990, Abstr., No. PB106.

11) a) W. J. Evans, T. P. Hanusa, and J. H. Meadows, *Organometallics*, **6**, 295 (1987); b) W. J. Evans, J. H. Meadows, W. E. Hunter, and J. L. Atwood, *Organometallics*, **2**, 1252 (1983).

12) Synthesis and application of the ^{13}C-labeled isocyanide, see: M. Murakami, H. Ito, and Y. Ito, *Chem. Lett.*, in press.

13) T. Imamoto, Y. Kamiya, T. Hatajima, M. Yokoyama, *Kidorui*, **14**, 166 (1989).

14) J. Collin and H. B. Kagan, *Tetrahedron Lett.*, **29**, 6097 (1988).

15) a) J. Collin, J.-L. Namy, F. Dallemer, and H. B. Kagan, *J. Org. Chem.*, **56**, 3118 (1991); b) J.-L. Namy, M. Colomb, and H. B. Kagan, *Tetrahedron Lett.*, **35**, 1723 (1994).

16) I. Ugi and R. Meyr, "Organic Syntheses," ed by H. E. Baumgarten, Wiley, New York (1973), Coll. Vol. 5, p. 1060.

17) W. Schlenk, *Chem. Ber.*, **62**, 920 (1929).