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Review

Insertions into lanthanide–ligand bonds in organolanthanide chemistry

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Abstract

Insertions of small molecules into lanthanide–ligand bonds have led to a number of new organolanthanide derivatives. Many attractive catalytic transformations are also based on these insertion reactions. The focus of this review concerns these important stoichiometric and catalytic transformations. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Insertion; Catalysis; Organolanthanide; Review

1. Introduction

Insertion of an organic functional group into a metal–ligand bond represents a fundamental step for many metal-promoted functionalizations. The lanthanide metals are characterized by high electropositivity, very large ionic radii (resulting in high coordination numbers and coordinative unsaturation), relatively constrained/immobile yet tunable ancillary ligation, and facile bond activation via concerted four-centered σ-bond metathesis processes rather than by conventional two-electron oxidative addition/reductive elimination sequences [1–4]. These properties could impart unusual unique organometallic reactivity chemistry [5–7]. For example, certain types of "orbitally forbidden" reactions may be easy to accomplish at a lanthanide center due to no orbital constraints. Furthermore, in a catalytic cycle, some nonessential intermediate steps, which are necessitated by favorable orbital interactions in transition metal complexes, may be absent in lanthanide system, which, consequently, could favor a faster reaction rate. In a word, a great deal of investigation results confirm that organolanthanide complexes may provide the optimum geometrical environment for unique reaction chemistry.

Hence, the studies on insertions of organolanthanide complexes and their applications in organic synthesis and catalysis have experienced extremely important development during the last two decades. Many compounds with unprecedented structures and reactivity patterns have been isolated by these insertions, which generally proceed with high chemoselectivity and high levels of stereochemical control. It was realized that instead of being limitations, the lanthanide metals had the potential for some unique chemistry distinct from anything possible with main-group or transition metals [8]. The purpose of this article is to present a brief account of the developments in the insertion chemistry of organolanthanides during the last two decades.

2. Ln–H bond insertion chemistry

Lanthanide hydrides are highly reactive species due to the high unsaturation. A lot of investigation results have shown that a rich insertion chemistry is available through the Ln–H bond.

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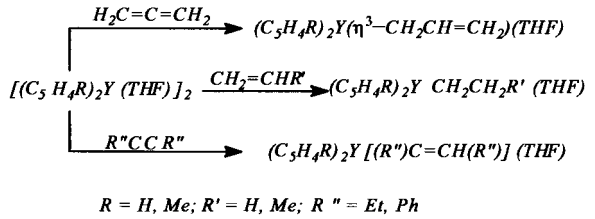


Scheme 1.

2.1. Unsaturated hydrocarbon insertion into a Ln–H bond

The basic insertion patterns of organolanthanide hydride complexes are firstly revealed by studying the reactivity of $[(C_5H_4R)_2YH(THF)]_2$ (R = H, Me) with unsaturated hydrocarbons as shown in Scheme 1. The hydrides react with terminal alkenes to form alkyl complexes, with 1,2-propadiene to form the allyl complex, and with the internal alkynes to form *cis*-alkenyl complexes [9].

Further investigation results demonstrate that the change of center metals and substrates and the modification of the ancillary ligands have strong effects on the property of the insertion products [10–32]. For example, in contrast to $[Cp_2YH(THF)]_2$, which reacts with terminal alkynes to give alkynide derivatives [9], treatment of $[Cp_2LuH(THF)]_2$ with phenylacetylene yields the 1,2-inserted product $Cp_2Lu(CH{=}CHPh)$ [10]. $[Cp^*_2LnH]_2$ (Ln = La, Y) react with trimethylvinylsilane or styrene to form 2,1-insertion products of the branched-type $Cp^*_2LnCH(R)CH_3$ (R = TMS, Ph) [11].

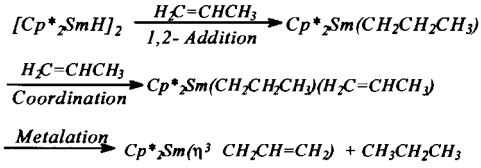
With the alkenes containing β-H, a number of allyl complexes are obtained (Eqs. (1) and (2)). It may be attributed to the steric unsaturation of the initial insertion product, which provides the opportunity for the sequent coordination of alkene and the metalation (Scheme 2). The relative Ln–H bond insertive transformation is also found in reactions of divalent $Cp^*_2Sm(THF)_{0/2}$ with alkenes or dienes. In addition, the η^3-crotyl complex $Cp^*_2Ln(\eta^3\text{-}CH_2CH{=}CHMe)$ can also be produced by the 1,4-addition of $[Cp^*_2LnH]_2$ (Ln = La, Sm) with butadiene [13,14].

$$1/2[Cp^*_2LnH]_2 + 2CH_2{=}CHCH_2R \longrightarrow CH_3CH_2CH_2R + Cp^*_2Ln(\eta^3\text{–}CH_2CH{=}CHR) \quad (1)$$

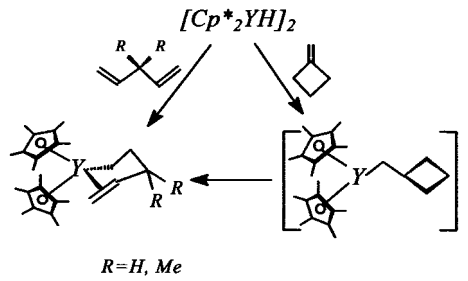
Ln = La, Nd, R = H, ^{n}Pr; Ln = Sm, R = H, Ph

$$1/2[Cp^*_2SmH]_2 + 2CH_3CH{=}CHCH_3 \longrightarrow Cp^*_2Sm(\eta^3\text{–}CH_2CH{=}CHMe) + CH_3CH_2CH_2CH_3 \quad (2)$$

Insertion of 1,4-pentadienes or methylenecyclobutane into the Y–H bond of $[Cp^*_2YH]_2$ gives the first d^0 transition metal–alkyl–alkene complexes (Scheme 3) [15–17]. It is found that the 4-pentenyl side chain



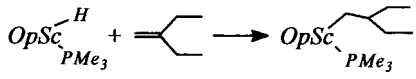
Scheme 2.



Scheme 3.

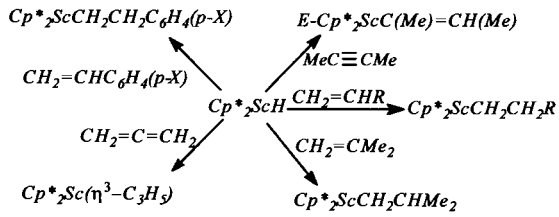
favors alkene complexation by the chelation effect, but the sequential intramolecular alkene insertion is thermodynamically disfavored due to the ring strain from the resulting cyclobutyl complex.

The insertion models of Cp^*_2ScH are similar to that of $[(C_5H_4R)_2YH(THF)]_2$, giving the 1,2-insertion products (Scheme 4) [18–22]. However, for the more open, linked bis(cyclopentadienyl) systems, an interesting new insertion chemistry is observed. $OpScH(PMe_3)$ (Op = $Me_2SiCp'_2$) reacts with 2-Et-1-butene to afford a single insertion product (Eq. (3)). But with the decrease of the size of alkenes, the initial monoinsertion products $OpSc[CH_2CH(R)Me]$ (R = H, Me) are readily complicated by a number of sequent transformations, decomposing into the methyl derivative $OpScMe(PMe_3)$ [23].

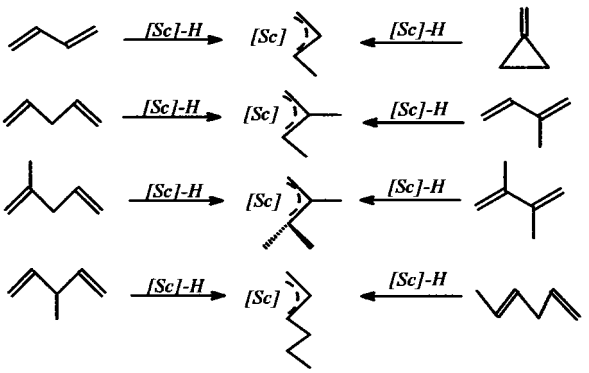


(3)

$(DpScH)_2$ [Dp = $Me_2Si(C_5H_3'Bu)_2$] reacts with a series of dienes and their corresponding isomers to give the allyl derivatives at 80 °C in C_6D_6 (Scheme 5) [19,24]. The tentative mechanisms involve a number of intramolecular olefin insertions and β-H/β-alkyl eliminations after the initial addition of Sc–H to the C=C bonds.



Scheme 4.



Scheme 5.

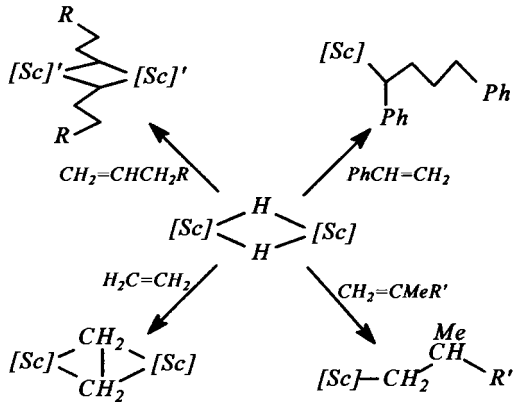
Contrary to the dimeric Cp^*_2Ln- and $Me_2SiCp''_2Ln$-based hydrides, which undergo rapid dissociation to yield active monomers, dissociation of $R_2SiCpCp''Ln$-based system is rather reluctant. Instead, they rearrange irreversibly to $–Ln(\mu\text{-}R_2SiCpCp'')_2Ln–$ forms, which slowly and reversibly undergo μ-hydrido single insertion toward α-olefins, generating the corresponding hydridoalkyls (Eq. (4)) [25]. In comparison to terminal hydride, the μ-H ligand is kinetically deactivated and the resulting single μ-H bond does not undergo secondary μ-alkyl transformation.

$$Ln(\mu\text{-}Et_2SiCpCp'')_2(\mu\text{-}H)_2Ln + \text{alkene } R \underset{>140^\circ C}{\overset{<80^\circ C}{\rightleftharpoons}} Ln(\mu\text{-}Et_2SiCpCp'')_2(\mu\text{-}H)(\mu\text{-}CH_2CH_2R)Ln \quad (4)$$

$Ln = Y, R = H, Me;\quad Ln = Lu, R = H, Me, {}^nBu$

When hard, electronegative ancillary ligands such as alkoxides and amido groups replace one cyclopentadienyl, an unusual insertion chemistry occurs. For example, the less crowded linked amido–Cp″ ligand derivative $[(Cp''SiMe_2N^tBu)(PMe_3)Sc]_2(\mu\text{-}H)_2$ reacts with ethylene to afford an unusual ethylene-bridged scandium dimer $[(SiMe_2Cp''N^tBu)(PMe_3)Sc]_2(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_2H_4)$. When it reacts with propylene and 1-butene, dinuclear alkyl-bridged complexes are obtained. However, for bulkier alkenes such as 2-methylpentene and isobutylene, the insertion products have monomer structures. Interestingly, reaction of styrene proceeds via a normal 1,2-insertion into the Sc–H, followed by a rapid and terminal 2,1-insertion to afford a unique double insertion product $(Cp''SiMe_2N^tBu)(PMe_3)$-$ScCH(Ph)(CH_2)_3Ph$ (Scheme 6) [26,27]. However, $[(Cp''SiMe_2N^tBu)(THF)Y]_2(\mu\text{-}H)_2$ reacts with styrene to form a well-defined monoinsertion product [28].

trans-$[YCp^*(OAr)(\mu\text{-}H)]_2$ reacts irreversibly with α-olefins to give the hydridoalkyl products *trans*-$[YCp^*(OAr)]_2(\mu\text{-}H)(\mu\text{-}CH_2CH_2R)$ [$Ar = C_6H^t_3Bu_2$-2,6; $R = H$, Me, Et, ^{n}Bu] [29,30]. In contrast to Cp^*_2Ln species, the reactivity is hampered by the kinetical inhibition of pre-equilibrium dissociation to a more reactive monomer due to the additional electropositivity afforded by the alkoxide groups.



$[Sc] = [(Cp''SiMe_2N^tBu)(PMe_3)Sc]$

$[Sc]' = [(Cp''SiMe_2N^tBu)Sc]$

$R = H, Me;\ R' = Me, {}^nPr$

Scheme 6.

As expected, the non-Cp supported complex $[(DADMB)Y(\mu\text{-}H)(THF)]_2$ (DADMB = 2,2′-bis[(*tert*-butyldimethylsilyl)amido]-6,6′-dimethylbiphenyl) reacts rapidly with ethylene or 1-hexene to give a single insertion product (Eq. (5)) [31]. $\{[PhC(N(TMS))_2]_2$-$ScH\}_2$ even reacts with PhC≡CPh to form $[PhC$-$(N(TMS))_2]_2Sc[C(Ph)=CHPh]$ in 40% isolated yield [32]. Moreover, insertion of tetramethylfulvalene into $[Cp^*_2SmH]_2$ gives the sterically hindered complex Cp^*_3Sm [76].

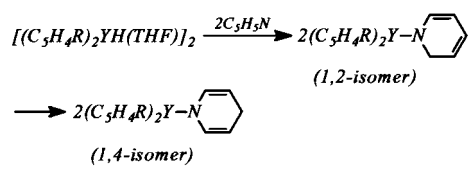
$$[(DADMB)YH(THF)]_2 \xrightarrow[THF]{2\ \text{alkene } R} 2(DADMB)Y(CH_2CH_2R)(THF)_2 \quad (5)$$

$R = H, {}^nBu$

2.2. C=N and C≡N insertion into a Ln–H bond

$[(C_5H_4R)_2YH(THF)]_2$ (R = H, Me) reacts with pyridine in polar solvent THF to afford the 1,2-insertion product, which subsequently rearranges to the 1,4-isomer, indicating that 1,4-insertion is thermodynamically more stable (Scheme 7). It is found that the isomerization can be effectively prohibited by the substituent at 4-position of pyridine [9].

Similarly, $[(DADMB)YH(THF)]_2$ reacts with pyridine to give a mixture of 1,2-insertion (major) and



Scheme 7.

1,4-insertion (minor) products [31]. Heating the mixture to 80 °C, complete conversion to 1,4-isomer occurs. But with $\{[PhC(N(TMS))_2]_2Y(\mu\text{-}H)\}_2$, 1,2-insertion product is cleanly formed, and subsequent thermal isomerization does not occur [33].

It is interesting to note that hydrogenolysis of bis(alkoxysilylamido)yttrium pyridyl $[Me_2Si(N^tBu)(O^tBu)]_2YPy$ rapidly forms 1,2-isomer $[Me_2Si(N^tBu)(O^tBu)]_2Y(NC_5H_6)$. The formation of the 1,2-isomer strongly suggests that the pyridyl complex is firstly hydrogenolyzed to the corresponding hydride, which subsequently inserts the adduct pyridine. Upon heating (65 °C), the 1,2-isomer rearranges to the 1,4-isomer by a 1,3-H shift. In the presence of excess hydrogen, the monoinsertion product is subsequently converted into the 2,3-dihydropyridyl complex as the final product, via hydrogenolysis of the Y–N bond accompanied by second 1,2-insertion (Scheme 8) [34]. Hydrogenolysis of Cp^*_2YPy directly forms 1,4-addition product $Cp^*_2Y(NC_5H_6)$ [35].

$[Cp^*_2LnH]_2$ reacts with *N*-benzylideneaniline PhN=CHPh, yielding insertion product $Cp^*_2Ln[N(Ph)CH_2Ph]$ (Ln = La, Sm). However, reaction of $[Cp^*_2SmH]_2$ with cyclic imines such as 2-phenyl-1-pyrroline gives the C–H activation product $Cp^*_2Sm[C_6H_4(o\text{-}2\text{-}NC_4H_6)]$ [37].

The yttrium hydrides $[(C_5H_4R)_2YH(THF)]_2$ react rapidly with nitriles to form dimeric alkylideneamido complexes (Eq. (6)) [9]. A similar nitrile insertion product $\{[PhC(N(TMS))_2]_2Y(\mu\text{-}N{=}C(H)Me)\}_2$ is obtained in the reaction of $\{[PhC(N(TMS))_2]_2Y(\text{-}H)\}_2$ with MeCN, but this insertion product is unstable [33].

$$[(C_5H_4R)_2YH(THF)]_2 + 2\,R'CN \longrightarrow (C_5H_4R)_2Y\langle^{N=CHR'}_{N=CHR'}\rangle Y(C_5H_4R)_2 \qquad (6)$$

$R = H, Me;\ R' = Me, {}^tBu$

Cp^*_2ScH reacts with nitriles to provide the insertion products $Cp^*_2ScNC(H)R$, which can be further hydrogenated to the amide complexes $Cp^*_2ScNHCH_2R$ (Eqs. (7) and (8)). A likely mechanism involves hydrogenolysis of the Sc–N bond and the resulting Sc–H intermediate addition to the imines [38]. Reaction of $[(Me_2SiCp''N^tBu)Y(THF)]_2(\mu\text{-}H)_2$ with acrylonitrile gives a 1,4-insertion product (Eq. (9)) [28]. The hydrides $[(C_5H_4R)_2Ln(\mu\text{-}H)(THF)]_2$ (Ln = Er, Y; R = H, Me) react with isocyanide ^tBuNC to form $[(C_5H_4R)_2Ln(\mu,\eta^2\text{-}HC{=}N^tBu)]_2$, in which both C and N formimidoyl atoms coordinate to the metal [39,40].

$$Cp^*_2ScH + RCN \longrightarrow Cp^*_2Sc{=}N{=}C\langle^{R}_{H} \qquad (7)$$

$R = {}^tBu, p\text{-}C_6H_4OMe, p\text{-}C_6H_4Me$

$$Cp^*_2Sc{=}N{=}C\langle^{H}_{R} \xrightarrow{H_2} \left[Cp^*_2Sc\langle^{H}_{N(H)CHR}\right] \longrightarrow Cp^*_2Sc{=}N\langle^{H}_{CH_2R} \qquad (8)$$

$R = {}^tBu, p\text{-}C_6H_4OMe$

$$[(Me_2SiCp''NCMe_3)YH(THF)]_2 + H_2C{=}CH{-}CN \longrightarrow [(Me_2SiCp''NCMe_3)Y(N{=}C{=}CHCH_3)]_2 \qquad (9)$$

2.3. Carbonyl insertion into a Ln–H bond

Reaction of $[Cp^*_2SmH]_2$ with CO leads to the formation of a *cis*-enediolate complex, isolated as a $OPPh_3$ adduct $[Cp^*_2(Ph_3PO)Sm]_2(\mu\text{-}OCH{=}CHO)$, which can isomerize to the *trans*-isomer [41]. The formation of the enediolate moiety demonstrates that the samarium hydride is capable of both reducing CO and inducing C=C double bond formation.

Treatment of $Cp^*_2ScH(THF)$ with carbonyl complexes $Cp_2M(CO)$ (M = Mo, W) or $CpM(CO)_2$ (M = Co, Rh) affords the carbonyl insertion products (Eqs. (10) and (11)) [42].

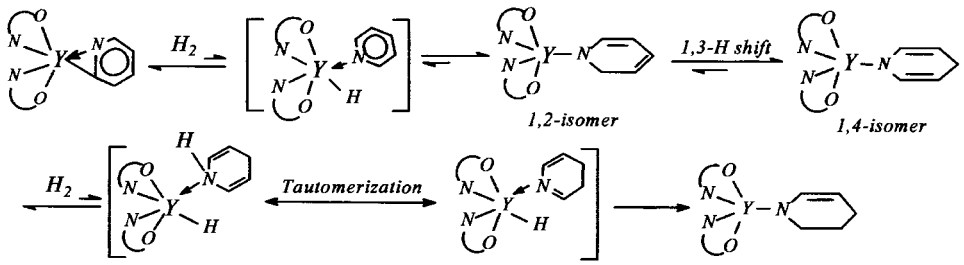
$$Cp^*_2ScR + Cp_2M{-}C{\equiv}O \rightleftharpoons \left[Cp^*_2Sc\langle^{R}_{O{=}C{=}MCp_2}\right] \longrightarrow Cp^*_2Sc{-}O{-}C\langle^{R}_{MCp_2} \qquad (10)$$

$R = H, Me;\ M = Mo, W$

$$Cp^*_2ScR + CpM(CO)_2 \longrightarrow Cp(CO)M{=}C(R)OScCp^*_2$$

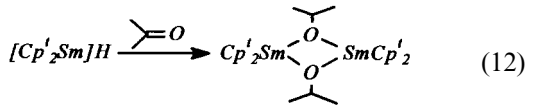
$$R = H, Me, CH_2CH_2Ph, NMe_2,\ M = Co;\ R = H, Me,\ M = Rh \qquad (11)$$

Insertions of ketones into a Ln–H bond are very similar to those occurring with CO, and the hydride is transferred to the carbonyl carbon atom, generating an



Scheme 8.

alkoxide ligand. Borohydrides $Cp^{Q}_{2}NdHBEt_3$ and $Cp^{Q}_{2}NdBH_4$ ($Cp^{Q} = C_5H_4CH_2CH_2OMe$) react with propanone or pivalone, yielding $Cp^{Q}_{2}NdOCHR_2$ (R = Me, ^{t}Bu) [43]. $[Cp'_2SmH]_2$, $Cp'_2SmH(PMe_3)_2$, $Cp'_2SmHBEt_3(THF)_2$, and $Cp'_2SmHBEt_3(PMe_3)_2$ react with propanone to afford the alkoxide derivative (Eq. (12)) [44]. Reaction of excess pivalone with $[Cp^{*}_{2}LaH]_2$ leads to the alkoxide–ketone adduct (Eq. (13)) [45]. Generally, a sterically hindered ketone is usually used to trap the highly reactive organolanthanide hydrides, which is a convincing reaction of the hydrido function [46]. However, fewer examples are with aldehydes. $[Cp_2LuH(THF)]_2$ reacts with benzaldehyde to yield $Cp_2Lu(OCH_2Ph)(THF)$ quantitatively [47].



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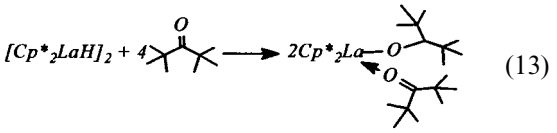


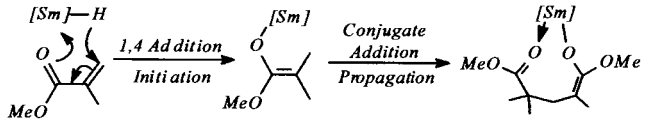
(13)

2.4. Other substrate insertion into a Ln–H bond

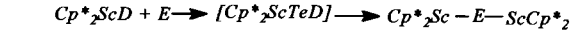
Reaction of $[Cp^{*}_{2}SmH]_2$ with MMA leads to the isolation of a keto enolate complex (Scheme 9), which establishes the mechanism for catalytic polymerization of MMA by organolanthanide hydrides [48,49]. The reaction may proceed by initial 1,4-addition of the hydride to conjugated ester, yielding the intermediate $Cp^{*}_{2}SmOC(OMe)=CMe_2$ which sequentially couples a second molecule of MMA to afford the eight-membered-ring product.

Ring opening of tetrahydrofuran by $[Cp^{*}_{2}LnH]_2$ leads to the formation of the butoxide derivatives $Cp^{*}_{2}LnO^{n}Bu$ (Ln = Sm [50], Y [12]), providing an example of saturated molecule insertion into a Ln–H bond. Reaction of $[Cp^{*}_{2}SmH]_2$ with azobenzene yields the insertion product $Cp^{*}_{2}Sm(PhNHNPh)$, which represents the first example of N=N insertion into a Ln–H bond [36].

Reaction of 0.5 equivalent of tellurium or selenium with the deuteride $Cp^{*}_{2}ScD$ results in elimination of D_2 and production of $[Cp^{*}_{2}Sc]_2(\mu\text{-E})$ (E = Te, Se) (Eq. (14)). Evidence that the production of chalcogenide dimer proceeds via $Cp^{*}_{2}ScTeD$ is presented [51].



Scheme 9.



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2.5. Catalytic reactions based on the Ln–H bond insertion mechanism

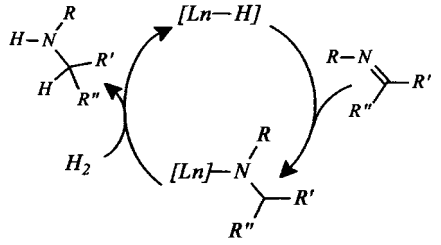
Many important organolanthanide mediated alkene/alkyne transformations, such as isomerization [18,19,24,52–54], hydroboration [56,57], hydrogenation [9,52,53,55,58–72], cyclization [18,19,67,73–75], and polymerization/oligomerization [13,14,19–22,26–30,33,46,61,69,70,76–104], generally involve the Ln–H bond insertion step. Since these related topics have been recently reviewed by Ephritikhine [7], we herein are interested in dimerization and cyclization/silylation of alkenes/alkynes as well as hydrogenation and hydrosilylation of imines promoted by the Ln–H bond insertion mechanisms.

2.5.1. Imine hydrogenation

In contrast to the catalytic hydrogenation of olefins, far less is known about the equally exothermic hydrogenation of imines. Precatalysts $Cp^{*}_{2}LnCH(TMS)_2$ (Ln = La, Sm, Lu) and $Me_2SiCp''_2SmCH(TMS)_2$ catalyze hydrogenation of acyclic imines to yield the corresponding amines (Scheme 10) [37]. Small amounts of $PhSiH_3$ accelerate the imine hydrogenation process by deamidation of the lanthanide center. However, cyclic imines only give trace yield, and *N*-aryl and *N*-TMS and imine C-methyl substitution are found to deactivate hydrogenation.

2.5.2. Hydrosilylation/cyclization of unsaturated organic molecules

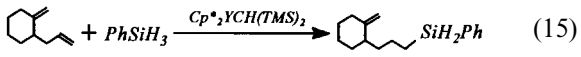
Since the first organolanthanide-catalyzed olefin hydrosilylation was reported by Tanaka and coworkers in 1991 [105], the area has experienced high development. The generally supported mechanism for organolanthanide-catalyzed hydrosilylation of alkenes involves [Ln–H]/alkene insertion and subsequent turnover-limiting Ln–C/Si–H transposition to complete the catalytic cycle, usually giving two types of products (1,2- and 2,1-insertion) as shown in Scheme 11 [106,107]. Re-



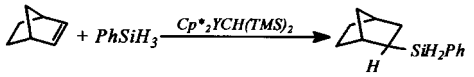
Scheme 10.

leased steric environment, such as larger metal size and reduced substitution on the cyclopentadienyl ligands, as well as more open coordination spheres favor unusual 2,1-insertion, especially for styrenic olefins [106,110].

$[Cp_2^*NdH]_2$ and $Cp_2^*LnCH(TMS)_2$ (Ln = Nd, Y) mediate the hydrosilylation of a variety of aliphatic alkenes with high regioselectivity for 1,2-addition-silyl delivered to the less hindered carbon of alkenes, yielding linear products (Eq. (15)) [105,108]. The results indicate that the reactivities are very sensitive to the nature and steric influence of the alkene substituents, and 1,1-disubstituted olefins are much less reactive than monosubstituted ones. As a consequence, excellent chemoselectivities can be achieved with dienes. Efficient hydrosilylation of norbornylene is the rare example for highly hindered alkenes (Eq. (16)) [108]. It is noteworthy that $Cp_2^*NdCH(TMS)_2$ catalyzes the hydrosilylation of 1,3-dienes to form the (*E*)-1,4-addition products selectively [109]. Recently, it is found that non-Cp lanthanide complex [DADMB]YMe$(THF)_2$ is an active precatalyst for regioselective hydrosilylation of olefins [112].



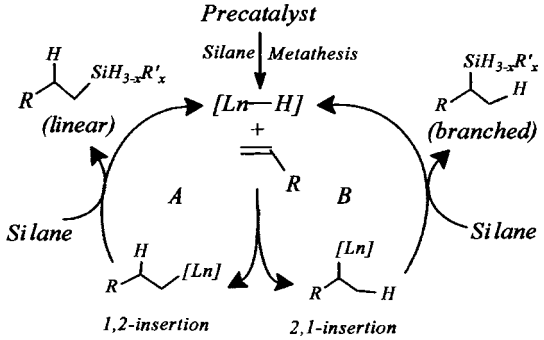
(15)



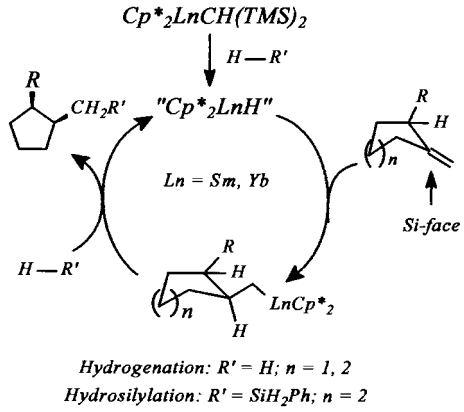
(16)

$Cp_2^*LnCH(TMS)_2$ (Ln = Sm, Y) catalyzes hydrosilylation of chiral exomethylenecyclohexanes, yielding the *cis*-substituted (phenylsilyl)methylcyclohexanes. Attack of the catalyst takes place largely from the less hindered Si-face, leading to the major *cis*-diastereomer. Additionally, the hydrosilylation is regiospecific, with the silyl placed exclusively at the terminal position of the double bond. The process is very similar to the catalytic hydrogenation of chiral exomethylene-substituted cyclopentanes and cyclohexanes (Scheme 12) [63].

Many examples of 2,1-insertion mode in which the silyl group adds to the more hindered carbon of alkenes

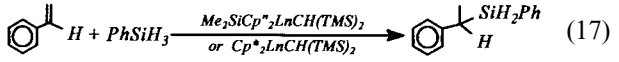


Scheme 11.

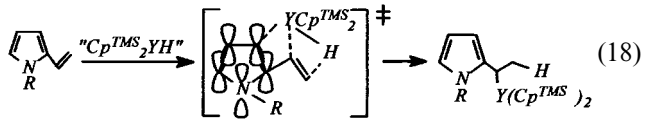


Scheme 12.

are found in organolanthanide-mediated hydrosilylation of styrenic and conjugated substrates (Eqs. (17) and (18)) [105,106,111–113]. These observed 2,1-regiochemistries for most aryl olefins suggest that electronic factors are important. The "aryl-directed" process proposed by Marks [106] infers that the aromatic moiety serves as a Lewis base, interacting with the Lewis acidic metal center. Thus the metals remain near the arene at the more hindered olefin site. Larger metal size and more "open" metal coordination environment afford enhanced 2,1-regiospecificity [106], whereas secondary silanes or bulky primary silanes reduce the "aryl-directed" effects [105,112].

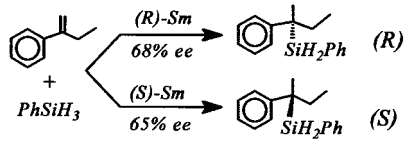


(17)



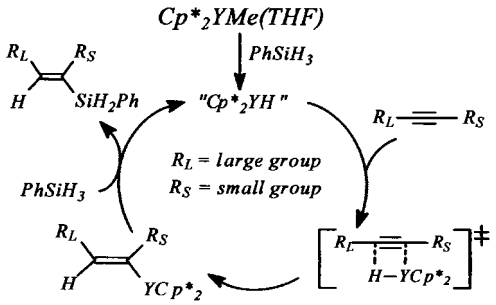
(18)

Asymmetric 2,1-hydrosilylation can be achieved by chiral precatalysts, (*R*)- and (*S*)-$Me_2SiCp''[(-)$-menthyl$C_5H_3]$SmCH$(TMS)_2$ (Eq. (19)) [106]. Recently, this work has been expanded to enantioselective hydrosilylation of norbornene by non-Cp chiral organolanthanide precatalyst (*S*)-[DADMB]YMe$(THF)_2$ (90% ee) [112].



(19)

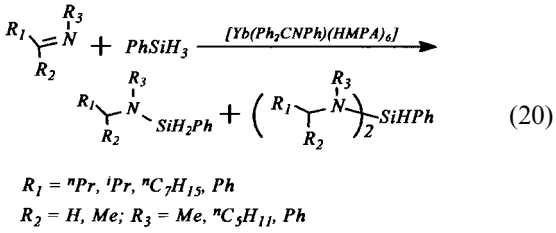
Furthermore, this transformation is further extended to the hydrosilylation of internal alkynes, in which the *cis*-addition products with the silyl at the less hindered carbon of the alkyne are obtained (Scheme 13) [114]. Further investigation results demonstrate that the regioselectivity is sensitive to the natures of the metal ion



Scheme 13.

and alkynes. $(C_5Me_4^iPr)_2LnMe(THF)$ (Ln = Y, Lu), $(C_5Me_4^iPr)_2LnCH(TMS)_2$ (Ln = Sm, Y) and $[(C_5H_4SiMe_2R)_2LnMe]_2$ (R = ^{t}Bu, Me; Ln = Sm, Y, Lu) also show high activity and regioselectivity in catalytic hydrosilylation of alkenes and alkynes [115,116].

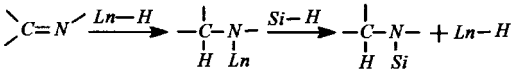
Another noteworthy aspect of organolanthanide-catalyzed hydrosilylation is imine hydrosilylations. Precatalysts [Yb(η^2-Ph_2CNAr)$(HMPA)_n$] (Ar = Ph, C_6H_4F-4) mediate hydrosilylations of imines with $PhSiH_3$, giving rise to mono- and di-aminosilanes (Eq. (20)) [117]. Imine hydrosilylation involves two key steps: insertion of imine into the Ln–H bond and silanolysis of the resulting Ln–N bond (Scheme 14).



(20)

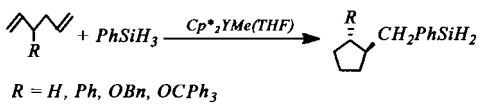
Significantly, if subsequent intramolecular insertion/cyclization could compete with Ln–C/Si–H metathesis after the initial C=C/C≡C insertion into the "Ln–H" bond, cyclization/silylation of dienes/trienes/enynes can be accomplished to allow rapid access to functionalized carbo- and heterocycles [106,109,113,118–122].

Cp_2^*YMe(THF)-catalyzed cyclization/silylation of various substituted 1,5- and 1,6-dienes give the corresponding cyclized organosilanes with excellent yields and diastereoselectivities (Eqs. (21) and (22)) [119]. The enhanced regioselectivity can be rationalized by initial addition of "Y–H" bond to the least sterically hindered and most electron rich C=C bond, followed by cyclization resulting in the formation of 1,2-disubstituted cyclopentanes for 1,5-dienes and 1,3-disubstituted cyclohexanes for 1,6-dienes. The diastereoselectivities are in line with the predicted chair-like transition state

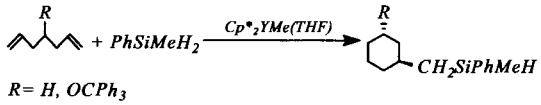


Scheme 14.

of cyclization step. In spite of the "extreme Lewis acidity" of the catalyst, functional groups survive the reaction intact.

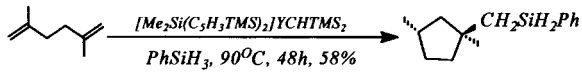


(21)

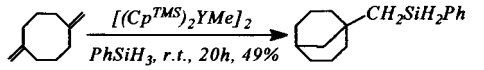


(22)

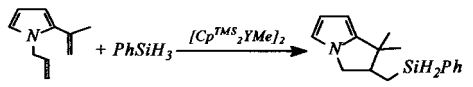
Cyclization/silylation has been extended to 1,1-disubstituted olefins by reducing the sterical hindrance of precatalysts (Eqs. (23) and (24)) [120]. Similar results are also observed in the reaction of heteroaromatic pyrrole and indole derivative dienes with arylsilanes mediated by $[Cp_2^{TMS}YMe]_2$ (Eq. (25)) [113]. In situ generated $Cp_2^{TMS}YH$ undergoes initial olefin insertion at the vinyl group with "aryl-directed" regioselectivity.



(23)

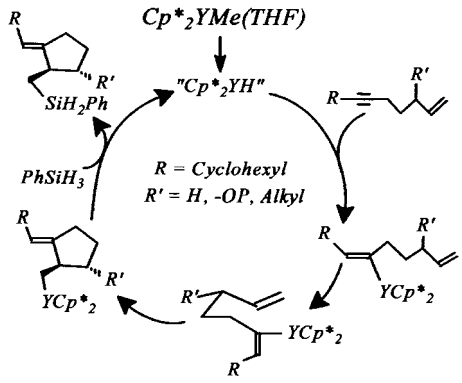


(24)



(25)

The utility of Cp_2^*YMe(THF) is yet further extended to the catalytic cyclization/silylation of 1,6-and 1,7-enynes (Scheme 15) [121]. The catalyst's ability to initially insert the alkyne in preference to the alkene in a regioselective manner (a cyclohexyl group serving as a regiocontrol element in the alkyne insertion), combined with the high diastereoselectivity of the intramolecular cyclization process (chairlike transition state favoring *trans*-diastereomer), affords the resulting exocyclic olefins with only one stereochemistry. In summary,



Scheme 15.

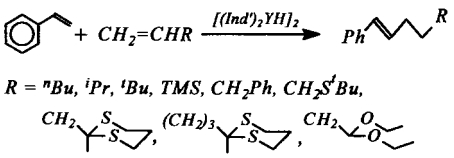
organolanthanide-catalyzed cyclization/silylation provides a versatile method for the selective preparation of complex ring systems. For example, this method has been utilized in the total synthesis of (±)-epilupinine [122].

2.5.3. Alkene dimerization

Organolanthanide-mediated dimerization of α-olefins is generally characterized by a second alkene insertion into the resulting Ln–C bond which is formed via the initial Ln–H/alkene addition, and then β-H elimination occurs much faster than a third alkene insertion.

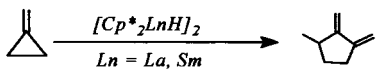
In contrast to the reaction of Cp^*_2ScH with CH_2=CHR which ultimately generates *trans*-Cp^*_2Sc–CH=CHR via σ-bond metathesis after the initial Sc–H/olefin addition, less sterically encumbered scandocene complexes OpScH, $[DpScH]_2$, Cp*CpScH(PMe_3) and Cp*($C_5H_2Me_3$)ScH(PMe_3) rapidly and selectively catalyze the dimerization of CH_2=CHR to the head-to-tail dimers, CH_2=C(R)CH_2CH_2R (R = Me, Et, *p*-C_6H_4Me) (> 98%) [18,19,73], indicating that the less encumbered environment preferentially affords the second olefin insertion before β-elimination. Furthermore, $[Cp^*_2LnH]_2$ and $[Me_2SiCp''_2LnH]$ react with 1-hexene under D_2 atmosphere, yielding the saturated head-to-tail dimerization product $DH_2CCH(^nBu)CH_2CHD^nBu$ in significant quantities [13,58,86].

The bis(2,4,7-trimethylindenyl)yttrium hydride $[(Ind')_2YH]_2$ affects the regio- and stereoselective dimerization with a range of α-olefins [11]. For 1-hexene and 3-methyl-1-butene, regular head-to-tail coupling (> 98%) is observed, whereas for trimethylvinylsilane and styrene, unusual head-to-head homodimerization products are isolated. Codimerization of styrene with α-olefins also yields head-to-head products (Eq. (26)). The codimerization is likely to proceed via initial 1,2-insertion of the α-olefin into the Y–H bond, followed by a 2,1-insertion of styrene into the resulting Y–C bond and subsequent β-H abstraction.



(26)

It is noteworthy that $[Cp^*_2LnH]_2$ (Ln = La, Sm) catalyze dimerization of methylenecyclopropane to yield the ring-expanding product with high chemoselectivity (Eq. (27)) [88]. A series of C=C double bond insertions, β-alkyl shift-based ring-opening and β-H eliminations may rationalize this transformation.



(27)

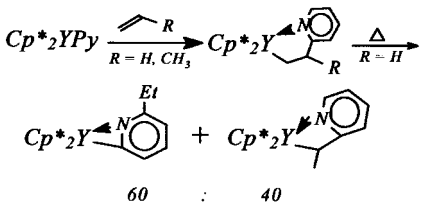
3. Ln–C bond insertion chemistry

3.1. Unsaturated hydrocarbon insertion into a Ln–C bond

Insertion of alkenes into a Ln–C bond is a most important elementary step in the catalytic polymerization of olefins. The complexes arising from the insertion of ethylene into a Ln–C bond are hardly isolated and characterized due to the disturbance from rapid successive insertions. Alternatively, the difference in the rate between first and second insertions permits propene to become the common substrate in stoichiometric insertive reactions. $Cp^*_2LnCH_3$ (Ln = Sc [20,21], Yb, Lu [77–79]) reacts with propylene to give the corresponding isobutyl derivative $Cp^*_2LnCH_2CHMe_2$. At elevated temperature, $Cp^*_2ScCH_2CHMe_2$ reacts with another propene to generate *trans*-Cp^*_2ScCH=CHMe, which is unreactive toward further insertion. $Cp^*_2LuCH_2CHMe_2$ undergoes the propylene insertion 1000-fold slower than the starting methyl complex due to the higher steric hindrance. No insertion of more than one propene molecule is observed in the case of Cp^*_2YMe(THF), probably due to the coordinated THF molecule suppressing further complexation of propene [80].

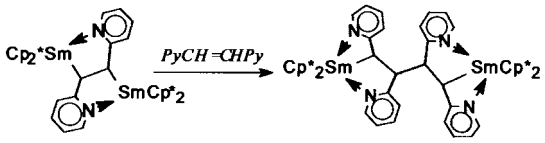
Bercaw and coworkers investigated the rate of ethylene insertion of Cp^*_2ScR system at −80 °C by ^{13}C NMR. The rate order is Sc–H ≫ Sc–^{n}Pr > Sc–Me > Sc–Et > Sc–Ph. A ground-state stabilizing β-agostic interaction retards the insertion into Sc–Et. It should be noted that ethylene inserts into the Sc–aryl bond much slower than into the Sc–alkyl bond [22].

Cp^*_2YPy reacts with ethylene/propene to give monoinsertion products $Cp^*_2YCH_2CH_2Py$ and $Cp^*_2Y[CH_2$-CH(Me)Py], respectively (Eq. (28)). $Cp^*_2YCH_2CH_2Py$ is thermally unstable and rearranges to the isomers $Cp^*_2Y[2$-$NC_5H_3(6$-Et)] and Cp^*_2Y[CH(Me)Py] at 80 °C [35]. Reaction of $[Me_2Si(N^tBu)(O^tBu)]_2$YPy with ethylene directly gives the rearranged insertion product $[Me_2Si(N^tBu)(O^tBu)]_2Y$[CH(Me)Py] [34].



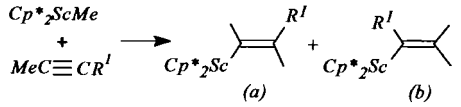
(28)

It is noteworthy that the treatment of $[Cp^*_2Sm]_2$(PyCHCHPy) with PyCH=CHPy affords a seemingly inserted product (Eq. (29)) [123]. This transformation raises the interesting question that the sterically and electronically saturated complex undergoes the large substrate insertion.



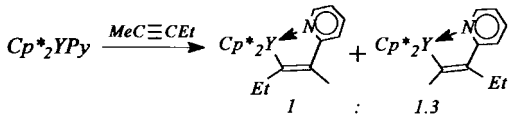
(29)

$Cp^*_2Sc–CH_3$ undergoes internal alkyne insertion to yield alkenyl derivatives which do not undergo further insertion even with excess alkynes. With unsymmetrical alkynes, a mixture of insertion products are obtained (Eq. (30)) [18,20,22]. Similar regioisomers are also isolated in reaction of yttrium pyridyl complex with 2-pentyne (Eq. (31)) [35]. These investigation results indicate that the steric factors favor the isomer with the larger alkyl substituent on the β-carbon. However, the reaction of $Cp^*_2ScCH_2CH_2R$ with internal alkynes does not give the insertion products due to β-H elimination occurring first [22].



(30)

R^1 = Me (a:b = 50:50); Et (68:32); Ph (61:39); ^{i}Pr (100:0)

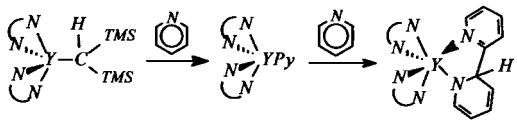


(31)

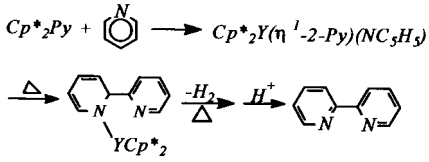
$Cp^*_2LnC{\equiv}CR$-type complexes undergo intermolecular ligand-coupling reaction to afford trienedyl complexes with the general formula $[Cp^*_2Ln]_2[\mu\text{-}\eta^2\text{:}\eta^2\text{-}RC{=}C{=}C{=}CR]$ (Ln = La, Ce, R = Me, ^{t}Bu, Ph; Ln = Nd, R = Ph; Ln = Sm, R = ^{i}Pr, $CH_2CH^i_2Pr$, CH_2CH_2Ph, Ph), which provides the first example of bonded alkyne insertion into a Ln–C bond (Scheme 16) [124–127].

3.2. C=N and C≡N insertion into a Ln–C bond

Insertions of pyridine into a Ln–C bond generally lead to the formation of amino ligands. $[PhC(N(TMS))_2]_2YR(THF)$ reacts with pyridine to form the 1,2-insertion product $[PhC(N(TMS))_2]_2Y(NC_5H_5\text{-}2\text{-}R)$ (R = CH_2Ph) [33]. With bulky alkyl complex $[PhC(N(TMS))_2]_2YCH(TMS)_2$, however, it initially undergoes the C–H activation to yield an orthometalated pyridyl intermediate which then undergoes the secondary substrate insertion to afford the 2,2′-bipyridyl complex (Eq. (32)) [33]. Similar intramolecular pyridyl migratory insertion is observed in the thermal decomposition of $Cp^*_2YPy(HPy)$ (Eq. (33)) [35].



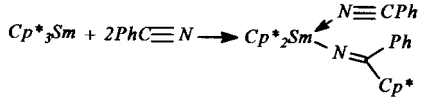
(32)



(33)

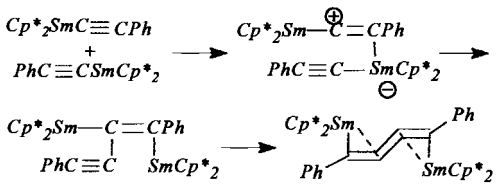
Marks and co-workers have studied imine insertions into the Ln–C bond. It is found that $Cp^*_2SmCH(TMS)_2$ reacts with two equivalents of *N*-benzylidene(methyl)-amine/2-methyl-1-pyrroline to yield the corresponding Cp^*_2Sm-imine–amido complexes, which invokes an orthometalation/C–H activation, followed by C=N insertion into the resulting Sm–C bond (Scheme 17) [37].

Insertions of nitriles into a Ln–C bond give a rich reactivity chemistry of organolanthanide complexes. Cp^*_2ScR reacts with nitriles R′C≡N to form the anticipated insertion product $Cp^*_2ScN{=}C(R)R'$ (R=R′=Me, C_6H_4(*p*-Me); R=Me, R′=^{t}Bu, CH=CH_2) [38]. Reaction of Cp^*_2YR (R=$CH(TMS)_2$, $CH_2C_6H_3Me_2$-3,5) with ^{t}BuCN gives the imide cyanide adducts $Cp^*_2Y[N{=}C(R)^tBu](^tBuCN)$ [128]. The benzonitrile insertion is observed for the sterically crowded Cp^*_3Sm (Eq. (34)), which represents a rare example of Ln–Cp* bond insertions [81].

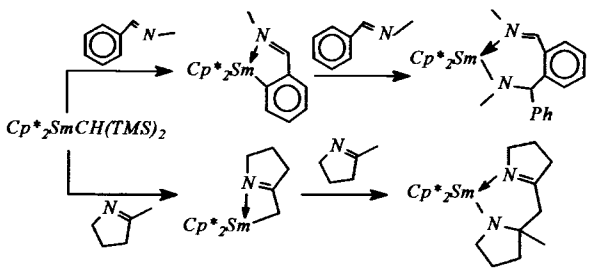


(34)

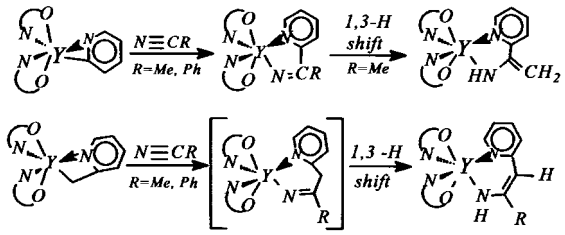
It is noteworthy that the reaction of $[Me_2Si(N^tBu)(O^tBu)]_2YR$ (R = Py, CH_2Py) with benzonitrile/acetonitrile forms insertion product isomers (Scheme 18) [34], indicating that the initial insertion is generally accompanied by sequential 1,3-H shift, except for reaction of $[Me_2Si(N^tBu)(O^tBu)]_2YPy$ with NCPh.



Scheme 16.

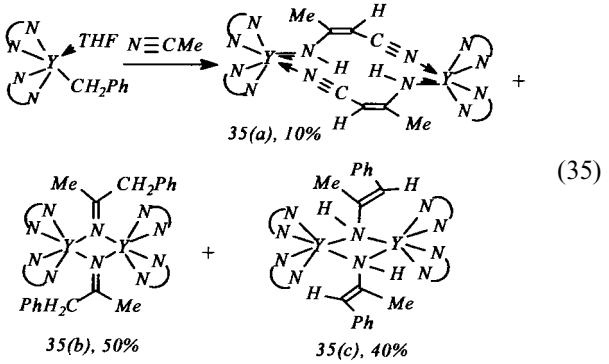


Scheme 17.



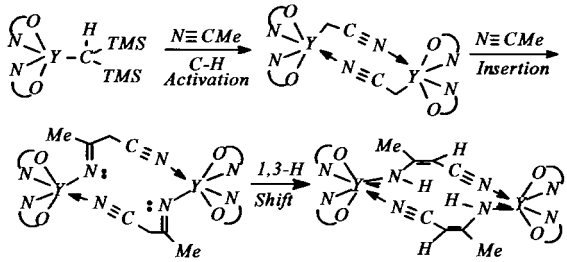
Scheme 18.

The reaction of $[Me_2Si(N^tBu)(O^tBu)]_2YCH(TMS)_2$ with excess MeCN shows a new feature. The results indicate that $[Me_2Si(N^tBu)(O^tBu)]_2YCH(TMS)_2$ initially undergoes metalation of the methyl group of MeCN to give a new alkyl complex, which then undergoes insertion of another MeCN into the resulting Y–C bond and subsequent 1,3-H shift to produce the crotononitrileamido complex (Scheme 19) [104]. The analogous insertion product is also obtained in the reaction of $[PhC(N(TMS))_2]_2YCH(TMS)_2$ with MeCN [33]. Interestingly, the reaction of $[PhC(N(TMS))_2]_2$-$Y(CH_2Ph)(THF)$ with acetonitrile yields a mixture of the insertion products (Eq. (35)). The majors are the direct nitrile insertion product (**35b**) and its imine–enamine tautomer (**35c**). The minor product (**35a**) resulting from the pathway paralleled with Scheme 19 is also obtained. The above results indicate that the benzyl CH_2Ph group is not as strong a Brønsted base as the bulky $CH(TMS)_2$ group in these organoyttrium complexes.

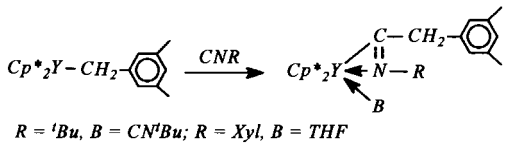


35(a), 10% + 35(b), 50% + 35(c), 40% (35)

Reaction of $Cp^*_2Y[CH_2C_6H_3Me_2\text{-}3,5]$ with isonitriles ^{t}BuNC or XylNC gives the iminoacyls (Eq. (36)) [128]. Insertion of isocyanide into the Y–C bond of $Cp^*_2YCH(TMS)_2$, however, does not take place under the same conditions. These results suggest that the steric bulk of the alkyl group has an important effect on the isocyanide insertions. Too large a ligand may prevent insertion, either by inhibiting the formation of adducts or by blocking the transition state for insertion.



Scheme 19.

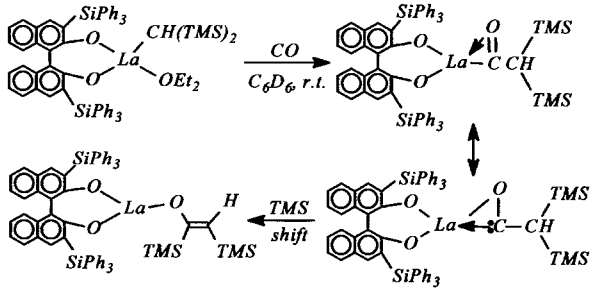


$R = {}^tBu$, $B = CN^tBu$; $R = Xyl$, $B = THF$ (36)

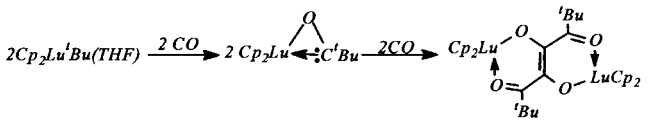
The neutral dialkyl–aryloxide complex $[(TMS)CH_2]_2$-$Y(OC_6H_3^tBu_2\text{-}2,6)(THF)_2$ is found to have reactivity comparable to the most reactive cyclopentadienyl lanthanide complexes. When treated with ^{t}BuNC, evidence for insertion into the Y–C bond was obtained from the mass spectra of deuterolyzed reaction mixture [82].

3.3. CO, CO_2 and the like insertion into a Ln–C bond

Insertion of CO into a Ln–C bond may give rise to six types of products, and the level of CO insertion may be controlled. 1,1-Monoinsertion affords the η^2-acyl complexes as illustrated by the reactions of $Cp_2Lu^tBu(THF)$ (Eq. (37)) [129], $La[CH(TMS)_2][1,1'$-$(2\text{-}OC_{10}H_5SiPh_3\text{-}3)_2](OEt_2)$ (Scheme 20) [130], or *trans*-$Y(MAC)[CH_2(TMS)]_2$ (MAC = deprotonated aza-18-crown-6) (Eq. (38)) [131] with CO. In most cases the acyl complexes are unstable and rearrange to the corresponding enolate complexes via 1,2-silyl migration promoted by the oxophilicity of lanthanides. Evidence for insertion of CO into the Ln–C bond is also obtained in $[(TMS)CH_2]_2Y(OC_6H_3^tBu_2\text{-}2,6)(THF)_2$ [82] and $Cp^*Lu(CH_2^tBu)_2(THF)$ with CO [132].



Scheme 20.



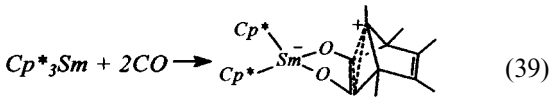
(37)

(38)

For $Cp_2Lu(^tBu)(THF)$ [129], when excess CO is used, surprisingly, a dimeric enedione diolate complex is isolated in which four CO molecules are coupled via one C=C double bond and two C–C single bonds (Eq. (37)). $Cp^*_2NdCH(TMS)_2$ reacts with excess CO, yielding the same enedionediolate structure complex [13].

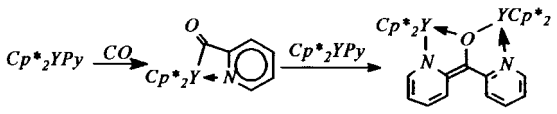
Cp^*_2YPy reacts with excess CO to give the unexpected insertion product $(Cp^*_2Y)_2[\mu\text{-}\eta^2\text{:}\eta^2\text{-}OCPy_2]$, rather than the above enolates or dinuclear enedione diolates (Scheme 21) [35]. Presumably, the product results from the nucleophilic attack of the starting compound on the acyl species. The same reaction pattern is found in $[Me_2Si(N^tBu)(O^tBu)]_2YPy$ with CO [34].

Treatment of Cp^*_3Sm [133–135] with CO results in another interesting CO coupled insertion into the Sm–C bond, in which a thermally stable nonclassical 7-norbornadienyl carbocation complex, $Cp^*_2Sm(OC)_2(C_5Me_5)$, is obtained (Eq. (39)) [136]. The formal positive charge is stabilized within the molecule by $[Cp^*_2Sm(OR)_2]^-$.

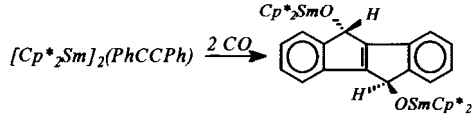


(39)

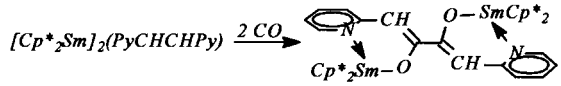
$Cp^*_2Sm(THF)_2$ reacts with a variety of unsaturated substrates to form $[Cp^*_2Sm]_2$(substrate) complexes [123], which have a remarkable insertion chemistry with CO. Reaction of $[Cp^*_2Sm]_2(PhCCPh)$ with CO leads to the formation of a tetracyclic indenoindene complex (Eq. (40)), which can be rationalized by CO insertion into the two Sm–C bonds and sequential adjacent C–H activation [137]. Reaction of $[Cp^*_2Sm]_2(PyCHCHPy)$ with CO results in an unusual insertion product $(Cp^*_2Sm)_2[\mu\text{-}\eta^4\text{-}PyCH{=}C(O)C(O){=}CHPy]$, in which the complete cleavage of the C=C double bond of the original substrate and the double CO insertions are observed (Eq. (41)) [123,138]. These results indicate that the powerful Sm(II) reagent can induce multiple-bound cleavage and reorganization to provide unusual transformations of multiply bonded species.



Scheme 21.



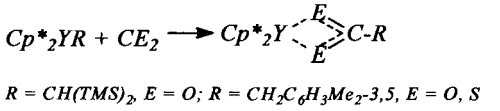
(40)



(41)

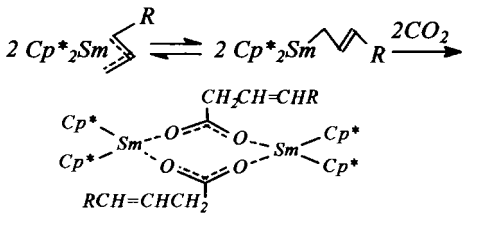
Furthermore, like Cp^*_2ScH, Cp^*_2ScR can induce the coordinated carbonyl insertion to afford alkyl-substituted "scandoxycarbene" complexes (Eqs. (10) and (11)) [42]. This may be explained by the increased Lewis acidity of the 14-electron Sc-center resulting in the activation of metal carbonyls.

Metathesis of $LuCl_3$, NaCp and $Li(CH_2)_3NMe_2$ in 1:2:1 molar ratio affords the lutetium alkyl complex $Cp_2Lu(CH_2)_3NMe_2$ [139]. Treatment of $YbCl_3$ with NaCp and $Li(CH_2)_3NMe_2$ in the same ratio under CO_2 results in the formation of a chelating carboxylate complex $Cp_2Y[\eta^2\text{-}O_2C(CH_2)_3NMe_2]$. Presumably, the latter may result from one CO_2 molecule insertion into the σ-Ln–C bond. Analogous insertion products are obtained in the reaction of Cp^*_2YR [R = $CH(TMS)_2$, 3,5-dimethylbenzyl] (Eq. (42)) [128]. $Et_2Sc[N(SiMe_2CH_2P^iPr_2)_2]$ reacts with CO_2, showing evidence for the formation of $Sc(O_2CEt)$ type residues by ^1H NMR, however, substantial decomposition is also observed [140].



(42)

Allyl complexes $Cp^*_2Sm(\eta^3\text{-}CH_2CH{=}CHR)$ react with CO_2 in non-coordinating solvents to form bimetallic insertion products $[Cp^*_2Sm(\mu\text{-}O_2CCH_2CH{=}CHR)]_2$ (R = H, Me, Et) at low temperature (Eq. (43)). These reactions confirm that the η^3-allyl unit can be converted to an η^1-$CH_2CH{=}CHR$ substituent attached to an inserted substrate. If the reaction is carried out at room temperature, branched products will be obtained due to the skeleton isomerization of alkenyl groups before CO_2 insertion. Non-allyl species Cp^*_2SmPh reacts with CO_2, giving the similar bimetallic insertion compound [141].

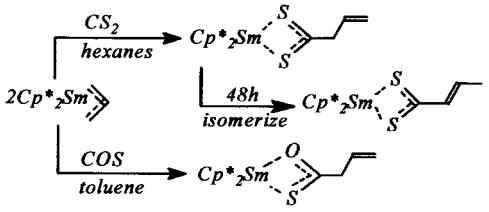


(43)

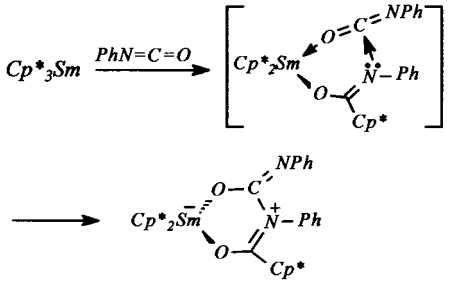
Isoelectronic CS_2 insertion into the Ln–C bond is observed in the treatment of $Cp^*_2Y(CH_2C_6H_3Me_2$-3,5) with CS_2 (Eq. (42)) [128]. With $Cp^*_2YCH(TMS)_2$, however, no CS_2 insertion is observed. This clearly demonstrates that the activation of CS_2 needs the central metal to possess a more "open" coordination environment as compared with that of CO_2, the smaller benzyl group provides a sufficient space for the pre-coordination of CS_2. Similar dithiocarboxylato complexes can also be obtained by CS_2 insertion into an organosamarium η^3-allyl moiety (Scheme 22) [141]. In contrast to the allyl carboxylate complexes, $Cp^*_2Sm(S_2CCH_2$-$CH{=}CH_2)$ can undergo the double bond isomerization to form $Cp^*_2Sm(S_2CCH{=}CHCH_3)$. Moreover, it also differs from the corresponding carboxylates in the binding model. For the latter, the carboxylate group can change from bridging to nonbridging structure depending on the nature of solvents, but the former forms only monometallic species. COS also participates in an insertion reaction with $Cp^*_2Sm(\eta^3$-$CH_2CH{=}CH_2)$ to form $Cp^*_2Sm[\eta^2$-$(OCS)CH_2CH{=}CH_2]$ (Scheme 22) [141].

3.4. Isocyanate/isothiocyanate insertion into a Ln–C bond

Insertions of isocyanates into main- and transition-metal–carbon bonds have been studied in some detail [142,143]. However, there are relatively few reports concerning the reactivity of isocyanates toward lanthanide–carbon bonds. Recently, Evans and co-workers showed that Cp^*_3Sm reacts with PhNCO to give the insertion product of two isocyanate molecules into one $Sm–C_5Me_5$ bond (Scheme 23) [81]. Further investigation results show that only one phenyl isocyanate inserts into the Ln–C σ-bond of $Cp'_2LnR(THF)$ ($R = {}^n$Bu, Np; Ln = Sm, Dy, Er), and excess PhNCO is catalyzed to form cyclotrimer by the mono-insertion product (Eq. (44)) [144].



Scheme 22.



Scheme 23.

$$Cp'_2LnR(THF) \xrightarrow{PhNCO} [Cp'_2Ln(OC(R)NPh)]_2 \quad (44)$$
$$R = {}^n Bu, Np;\ Ln = Sm, Dy, Er$$

The reactivity of monocyclopentadienyl lanthanide dialkyls is a little explored area in organolanthanide chemistry. Reaction of $Cp'Ho{}^nBu_2(THF)_n$ with two equivalents of PhNCO leads to PhNCO insertion into two Ln–C bonds (Eq. (45)) [144], indicating that lanthanide dialkyl(aryl) complexes exhibit higher activity to phenyl isocyanate than some transition-metal dialkyls, where only one of the M–C σ-bonds is reactive to isocyanate even under more drastic conditions for Cp_2ZrR_2 ($R = Me$, Ph, CH_2Ph) [145], $MoO_2(Mes)_2$ [146], $[Mn(CH_2{}^tBu)_2]_4$ and $[Mn(CH_2CMe_2Ph)_2]_2$ [147]. Insertion chemistry also occurs with $[(TMS)CH_2]_2$-$Y(OC_6H_3{}^tBu_2$-2,6)$(THF)_2$ and PhNCO [82].

$$Cp'HoCl_2(THF)_3 \xrightarrow[2)\ 2\ PhNCO, -10\ ^oC]{1)\ 2\ Li{}^nBu,\ THF} Cp'Ho[OC({}^nBu)NPh]_2(THF)_X \quad (45)$$

Very recently, the reactions of Cp_2LnR ($R = {}^n$Bu, Np; Ln = Gd, Dy, Ho, Y) with phenyl isothiocyanate are also studied. Insertions of isothiocyanate into Ln–C bonds are very similar to those occurring with isocyanates and the alkyl/aryl group is generally transferred to the isothiocyanate carbon atom to give the corresponding thiolate derivatives (Eq. (46)) [148]. Evidence for insertion of PhNCS into the Ln–C bond is also obtained from the mass spectra of deuterolyzed products of the reaction of $[(TMS)CH_2]_2Y(OC_6H_3{}^tBu_2$-2,6)$(THF)_2$ with PhNCS [82]. Furthermore, carbodiimide insertion into the Ln–C bond is observed in the treatment of $Cp_2Ln{}^nBu$ with ^{n}BuN=C=N^{n}Bu (Eq. (47)) [149].

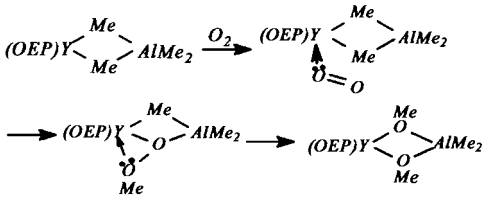
$$Cp_2LnR(THF) \xrightarrow{PhNCS} [Cp_2Ln(SC(R)NPh)]_2 \quad (46)$$
$$Ln = Gd, Dy, Ho, Y;\ R = {}^n Bu, Np$$

$$Cp_2Ln{}^nBu \xrightarrow[-10\ ^oC]{{}^tBuN=C=N{}^tBu} Cp_2LnN({}^tBu)C({}^nBu)N({}^tBu) \quad (47)$$

3.5. Other substrate insertion into a Ln–C bond

Like unsaturated organic molecules, THF reacts with Cp^*_3Sm to form $Cp^*_2Sm[O(CH_2)_4Cp^*](THF)$ via the ring-opening transformation, suggesting that Cp^*_3Sm is a bulky Cp^*_2SmR complex in disguise [81].

Porphyrin is another supporting ligand, in which large metals can be placed out of the N_4 porphyrin plane [150]. $(OEP)Y(\mu$-$Me)_2AlMe_2$ (OEP = porphyrin dianion) can selectively activate O_2 to afford $(OEP)Y(\mu$-$OMe)_2AlMe_2$ (Scheme 24) [151], which represents the



Scheme 24.

first oxygen insertion in organolanthanide chemistry. The mechanism demonstrates that the initial attack of O_2 prefers the more oxophilic, sterically less hindered yttrium center rather than the 4-coordinate aluminum.

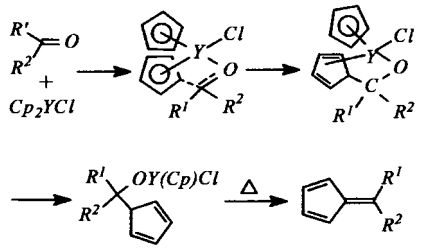
Metallic tellurium readily inserts into the Y–C σ-bond of $[Cp^x_2Ln(\mu\text{-}Me)]_2$ to form $[Cp^x_2Ln(\mu\text{-}TeMe)]_2$ ($Cp^x = Cp$, Cp^{TMS}, Ln = Lu; $Cp^x = Cp^t$, Ln = Lu, Y) [152]. Te or Te transfer agent $Te=P^nBu_3$ also reacts facially with Cp^*_2ScR to form the insertion product Cp^*_2ScTeR (R = Me, $CH_2(TMS)$, CH_2Ph, CH_2CH^tBu, $CH_2CHD(CH_2)_2CH{=}CMe_2$, Ph, $CH_2(c\text{-}C_5H_9)$ [51,153, 154]. These resulting tellurolates are thermally unstable toward further elimination of TeR_2, forming Cp^*_2Sc–Te–ScCp*. Selenium insertion is also observed for $Cp^*_2ScCH_2(TMS)$ to give Cp^*_2Sc–Se–CH_2(TMS) [51].

3.6. Catalytic reactions based on the Ln–C bond insertion mechanism

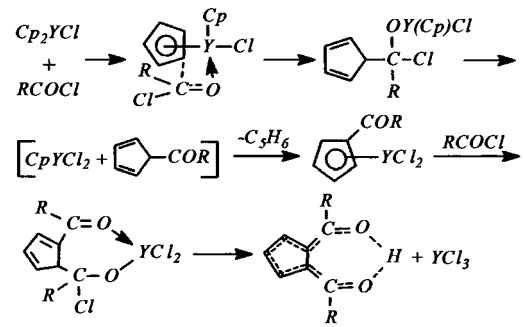
3.6.1. Organolanthanide alkyl mediated functionalization

Organolanthanide alkyl mediated organic functionalizations have been extensively investigated in organic synthesis. Since they have been reviewed in other literatures [5,155–161], we intentionally exclude these insertive transformations in this review. However, insertions of aldehydes and ketones into a Ln–Cp π-bond should be noted. Cp_2YCl reacts with aldehydes and ketones, generating fulvenes in excellent yield [162]. This transformation results from the insertion of carbonyl into the Y–Cp π-bond as shown in Scheme 25.

Evidence for another interesting insertion of carbonyl into the Ln–Cp π-bond is obtained in the reaction of Cp_2YCl with RCOCl, which affords 1,5-diacylcyclopentadienes and $RCO_2(CH_2)_4Cl$. The YCl_3 generation rationalizes the ring-opening product $RCO_2(CH_2)_4Cl$ in the whole reaction (Scheme 26) [163].



Scheme 25.



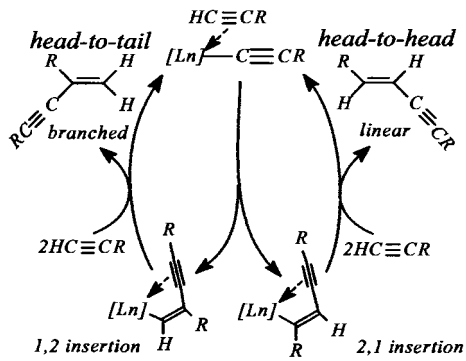
Scheme 26.

3.6.2. Alkyne dimerization/cyclization

1-Alkyne reacts with organolanthanide alkyls to form [Ln]–C≡CR, which undergoes sequential alkyne insertion, followed by σ-bond metathesis, resulting in the formation of enyne. The alkyne insertion pattern decides the head-to-tail and head-to-head arrangements of the resulting dimers (Scheme 27) [33]. In most cases, the Ln–C bond insertion step is also rate-determining.

Cp^*_2ScMe and $Cp^*_2YCH(TMS)_2$ catalyze the head-to-tail dimerization of HC≡CR (R = Me, ^{n}Pr, ^{t}Bu) with high regioselectivity [20,164,165]. However, in the case of $Cp^*_2LnCH(TMS)_2$ (Ln = La, Ce) corporating larger metals, higher head-to-tail oligomers are observed for smaller alkynes such as propyne or *n*-pentyne. $[PhC(N(TMS))_2]_2YR$ [R = $CH(TMS)_2$, $CH_2Ph(THF)$, H] are moderate active precatalysts for HC≡C^{t}Bu dimerization, but inactive for smaller 1-alkynes, HC≡CR (R = H, Me, ^{n}Pr) [33,166].

Regioselective head-to-tail dimerization for alkyl-substituted alkynes is sterically controlled, while the formation of a significant amount of head-to-head dimers for HC≡CPh and HC≡C(TMS) suggests that electronic factors are also important. The exclusive 2,1-insertion mode of HC≡C(TMS) dimerization is observed in catalytic systems of $Cp^*(OAr)YCH(TMS)_2$ ($Ar = C_6H_3{}^tBu_2$-2,6) [30] and $[PhC(N(TMS))_2]_2YR$ [R = $CH(TMS)_2$, $CH_2Ph(THF)$, H] [33,166], and a decreased activity is found. With HC≡CPh, however, the situation is complex. $[PhC(N(TMS))_2]_2YR$-catalyzed HC≡CPh



Scheme 27.

dimerization forms 100% head-to-tail product. Whereas in $Cp^*_2LnCH(TMS)_2$ catalytic systems, predominant head-to-tail dimer for Y and head-to-head one for La and Ce are found [165]. Additionally, $Cp^*_2Ln[N(TMS)_2]$ (Ln = Ce, Nd, Sm) react with excess HC≡CPh to afford PhCH=CH–C≡CPh [126].

$Cp^*_2LnCH(TMS)_2$ (Ln = La, Ce) are efficient precatalysts for the cyclodimerization of 2-alkynes MeC≡CR (R = Me, Et, ^{n}Pr) to 1,2-disubstituted 3-alkylidenecyclobutenes (Scheme 28). The first step is propargylic metalation of the α-methyl group on disubstituted alkynes. Rate-determining step is the alkyne insertion into Ln–CH_2C≡CR bonds. This step also determines the selectivity, i.e. isomeric ratios of asymmetrical 2-alkynes. With bulkier R groups, e.g. TMS and ^{t}Bu, only stoichiometric α-methyl C–H activation takes place without subsequent dimerization [167].

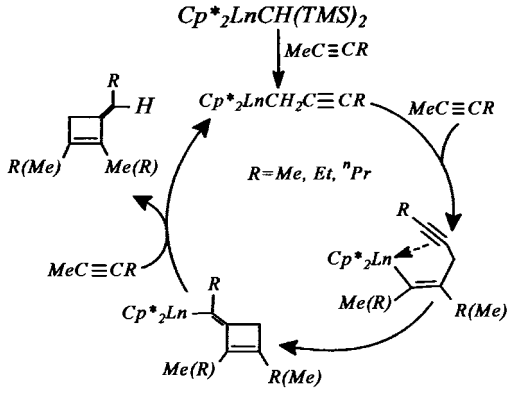
4. Ln–N bond insertion chemistry

4.1. Stoichiometric transformation

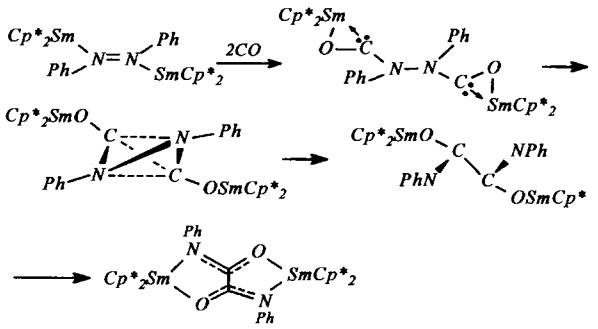
The reduction of CO by $[Cp^*_2Sm]_2(N_2Ph_2)$ provides an unusual example of the insertion of CO into a Sm–N bond. The formation of $[Cp^*_2Sm]_2[\mu,\eta^4$-(PhN)OCCO-(NPh)] indicates that two CO molecules have inserted into the N=N bond of azobenene and coupled (Scheme 29) [168–170]. Similarly, $[Cp^*_2Sm]_2[PhNN(C_6H_4NMe_2$-4)] and $[Cp^*_2Sm]_2[N_2(C_6H_4Me$-3)$_2]$ react with CO to form $[Cp^*_2Sm]_2[(PhN)OCCO(NC_6H_4NMe_2$-4)] and $[Cp^*_2Sm]_2[3$-$MeC_6H_4N](CO)]_2$, respectively [170].

$Cp^*_2ScNMe_2$ can activate the carbonyl of Cp-$Co(CO)_2$, resulting in amide-substituted "scandoxycarbene" complex $Cp(CO)Co{=}C(NMe_2)OScCp^*_2$ by nucleophilic attack of the NMe_2 group on the carbonyl carbon (Eq. (11)) [42].

The rich CO insertion chemistry prompts the investigation toward CO_2. In contrast to CO insertions, which typically form symmetrical double insertion products,

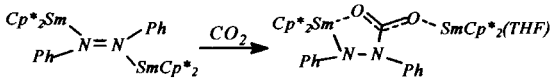


Scheme 28.



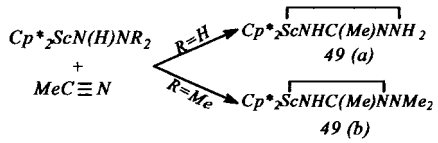
Scheme 29.

$[Cp^*_2Sm]_2(N_2Ph_2)$ reacts with excess CO_2 to yield the asymmetric monoinsertion product $Cp^*_2Sm[\mu$-η^2:η^1-PhNN(CO_2)Ph]$SmCp^*_2$(THF) (Eq. (48)) [171]. Isoelectronic analogue with CO_2, PhNCO reacts with Cp'_2Ln-(N^iPr_2)(THF) to form monoinsertion product Cp'_2Ln-[$OC(N^iPr_2)$NPh](THF) (Ln = Y, Er, Yb), which may be the real active species for PhNCO polymerization [172].



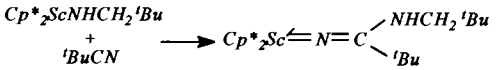
(48)

$Cp^*_2ScNHNR_2$ (R = H, Me) react with acetonitrile to form $Cp^*_2ScNHC(Me)NNR_2$ (Eq. (49)) [173]. One possible pathway may involve 1,3-$NHNR_2$ migration to give the nitrile insertion intermediate, followed by tautomerization via 1,3-H shift. The smaller ring size adopted by **49b** relative to **49a** is due to the steric bulk of the dimethylamino group.



(49)

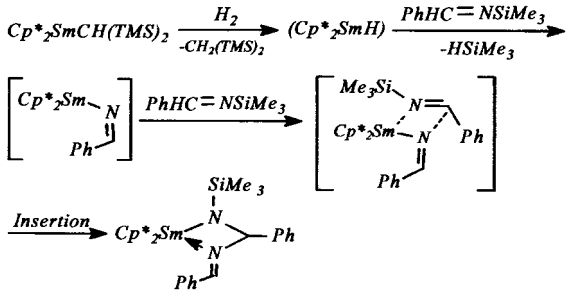
Nitrile insertion into the scandium–amide bond is also observed in the reaction of $Cp^*_2ScNHCH^t_2Bu$ with ^{t}BuCN (Eq. (50)) [38]. This irreversible reaction is a competing termination in catalytic hydrogenation of ^{t}BuCN by Cp^*_2ScH.



(50)

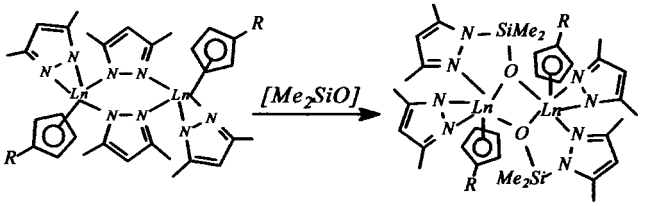
$Cp^*_2SmCH(TMS)_2$ reacts with PhCH=N(TMS) under H_2, quantitatively yielding an imine–amido complex $Cp^*_2Sm[N(TMS)CH(Ph)N{=}CHPh]$ which provides the evidence of imine insertion into the Sm–N bond [37]. A possible pathway is depicted as desilylation proceeding via σ-bond metathesis to yield a benzylidene–amido complex which undergoes subsequent C=N insertion (Scheme 30).

Me_2SiO insertion into an Ln–N bond is found in pyrazolate- and amino-type lanthanide complexes. $[(C_5H_4R)Ln(PzMe_2)_2]_2$ react with highly diluted dimethylsilicone grease to give the insertion products

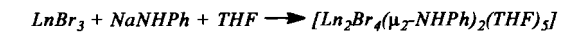


Scheme 30.

$[(C_5H_4R)Ln(\eta^2\text{-}PzMe_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}OSiMe_2PzMe_2)]_2$ (Eq. (51)). But no Me_2SiO insertion occurs for bis(cyclopentadienyl)lanthanide pyrazolates and tri(pyrazolate)lanthanide complexes [174–177]. Reaction of $[Ln_2X_4(\mu\text{-}NHR)_2(THF)_5]$ (R = Ph, ^{t}Bu) with $[Me_2SiO]_3$ leads to the formation of mono- and double-Me_2SiO insertion products (Eqs. (52), (53) and (54)) [178].



R = Me; Ln = Nd, Gd, Dy, Yb
R = H; Ln = Ho, Dy (51)



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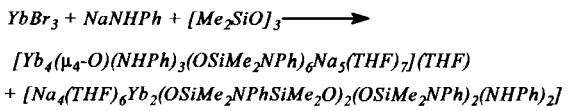
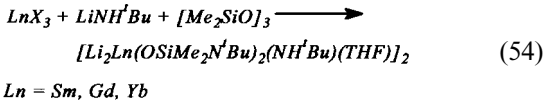


(53)



(54)

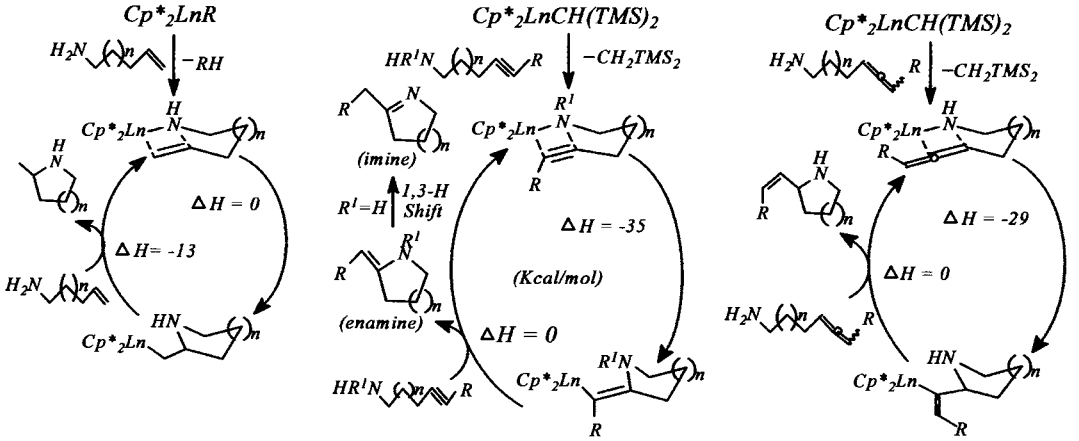
4.2. Catalytic transformation of unsaturated amines based on the Ln–N bond insertion mechanism

These works are pioneered by Marks' and Molander's groups. The general mechanism for hydroamination/cyclization of amino–alkene/alkyne/allene involves rapid protonolysis of the precatalysts to give a labile Ln–amido(amine) intermediate, which undergoes irreversible turnover-limiting intramolecular alkene/alkyne/allene insertion into the Ln–N bond, and then rapid protonolytic cleavage of the resulting Ln–C bond by free amine to give the nitrogen heterocycles (Scheme 31) [179–184]. The relative reaction rate for the resulting cycle is $5 > 6 \gg 7$.

4.2.1. Aminoalkene hydroamination/cyclization

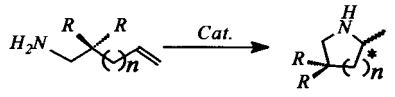
The catalytic cycle for the hydroaminotion/cyclization of aminoalkenes is represented in Scheme 31. Cp_2^*LnR (R = H, $CH(TMS)_2$, $\eta^3\text{-}C_3H_5$, $N(TMS)_2$; Ln = La, Nd, Sm, Y, Lu), $R_2SiCpCp''LnCH(TMS)_2$ (Ln = Y, Lu), $R_2SiCp''_2LnCH(TMS)_2$ (Ln = Nd, Sm, Y), (EBI)YbN$(TMS)_2$ (EBI = [ethylenebis(η^5-indenyl)]) and $Cp_2^*Sm(THF)_{0/2}$ are efficient precatalysts for the regiospecific cyclization of various aminoalkenes [179,180,185,187]. Since the turnover-limiting step is ring-forming olefin insertion, which is sensitive to the steric factors, so that larger metal size, less sterical hindrance and more "open" coordination environment enhance the reaction rate [180]. For example, more open silyl-linked amido complexes $[Me_2SiCp''N^tBu]$-LnE$(TMS)_2$ (Ln = Sm, Nd, Yb, Lu; E = CH, N) result in significantly enhanced hydroamination activity compared with the corresponding $Cp_2^*LnE(TMS)_2$ [186].

Chiral precatalysts C_1-symmetric $[Me_2SiCp''(C_5H_3\text{-}R^*)]LnE(TMS)_2$ (R* = (+)-neomenthyl, (−)-menthyl,



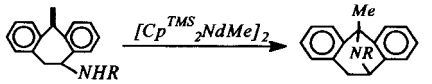
Scheme 31.

(−)-phenylmenthyl; Ln = La, Nd, Sm, Y, Lu; E = N, CH) can be used for the enantioselective hydroamination/cyclization of aminoolefins to chiral pyrrolidines and piperidines (Eq. (55)) [59,188]. The nonbonded repulsive interactions in the quasi-7-memberd cyclic chair-like transition state are expected to play a significant role in enantioselection (40–70% ee). These chiral precatalysts also mediate the diastereoselective cyclization of aminoalkenes. For example, (R)-$Me_2SiCp''(C_5H_3R^*)$SmR (R* = (+)-neomenthyl) mediates the cyclization of $H_2NCHMeCH_2CH_2CH{=}CH_2$ to *trans*-2,5-dimethypyrrolidine with >95% diastereoselectivity [188].



(55)

Consistent with the sterically sensitive rate-limiting cyclization step, less hindered catalyst systems $[Cp_2^{TMS}LnMe]_2$ (Ln = Sm, Nd) affect the cyclization of hindered 1,1-disubstituted aminoolefins and exocyclic alkenes, allowing the construction of monocyclic as well as fused and bridged heterocycles, by performing multiple alkene insertions (Eqs. (56) and (57)). However, endocyclic alkenes remain resistive to cyclization [189,190]. Furthermore, this transformation is yet extended to the synthesis of polycyclic products by performing multiple alkene insertions, in which the intermediate is a secondary amine [189].



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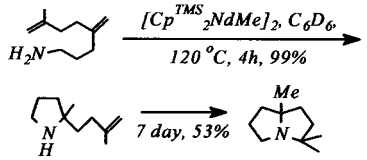


(57)

4.2.2. Aminoalkyne hydroamination/cyclization

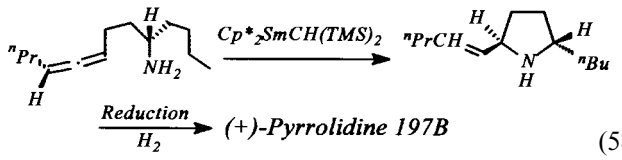
Analogous transformations are generated in hydroamination of aliphatic and aromatic aminoalkynes with the general formula $RC{\equiv}C(CH_2)_nNHR'$ (R′ = H, alkyl) by precatalysts $Cp_2^*LnCH(TMS)_2$ (Ln = La, Nd, Sm, Lu) and $Me_2SiCp''_2LnCH(TMS)_2$ (Ln = Nd, Sm), yielding the corresponding cyclic imines or enamines depending on the R′ substituents (Scheme 31) [181,182]. The present cyclizations are ~10–100 times more rapid than the corresponding aminoolefin transformations under the same conditions. The substituent R affects the cyclization rates: TMS ≫ H > Me ≥ Ph > 2-propenyl. The turnover-limiting step is an intramolecular alkyne insertion into the Ln–N bond (Scheme 31). However, the relative ordering of catalyst activities with metal size and ancillary ligation is different to that observed for lanthanide-centered olefin insertion processes. The use of larger metal and a more "open" coordination environment in the precatalysts results in a decreased hydroamination rate. These observations argue that the steric demands in the –C≡C– insertive transition state are relaxed compared with those of the analogous aminoolefin.

The cyclopentadienyl-free precatalysts mono- and bis-(*N*-isopropyl-2-(isopropylamino)troponiminato)-yttrium amides $[(^iPr)_2ATI]Y[N(TMS)_2]_2$ and $[(^iPr)_2ATI]_2Y[N(TMS)_2]$ exhibit moderate activities in aminoalkynes hydroamination [191]. It is noteworthy that no Cp^*LnR_2-type complexes were ever used as precatalysts in this reaction.

4.2.3. Aminoallene hydroamination/cyclization

Efficient cyclization of 1,2-disubstituted aminoalkenes for constructing azacycles bearing unsaturated α-substituents is elusive until choosing aminoallenes as substrates [183,184]. Organolanthanide complexes $Cp_2^*LnCH(TMS)_2$ (Ln = La, Sm, Y, Lu) serve as effective precatalysts for the rapid, regioselective and highly diastereoselective intramolecular hydroamination/cyclization of 1,3-disubstituted aminoallenes $RCH{=}C{=}CH(CH_2)_nCHR'NH_2$ to yield the corresponding pyrrolidines and piperidines (Scheme 31). Hydroamination/cyclization of monosubstituted aminoallenes (R = H; R′ = H, Me; *n* = 1, 2) is less regioselective, with tetrahydropyridines being the predominant products.

The above results indicate that hydroamination/cyclization of aminoallenes is significantly more rapid than that of the corresponding aminoalkenes but slower than the corresponding aminoalkynes. It is also suggested that the nonbonding interactions arising from congestion of the metal coordination sphere in the chair-like transition state determine the stereochemical outcome (Eqs. (58) and (59)) [184,186,192]. Based on these differences in the reactivities of unsaturated amines, less hindered $Me_2SiCp''(N^tBu)SmN(TMS)_2$ efficiently catalyzes the stereoselective tandem bicyclization of acyclic aminoallene–alkene to the bicyclic pyrrolizidine under mild conditions (Eq. (59)).



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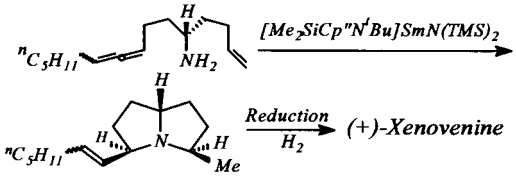
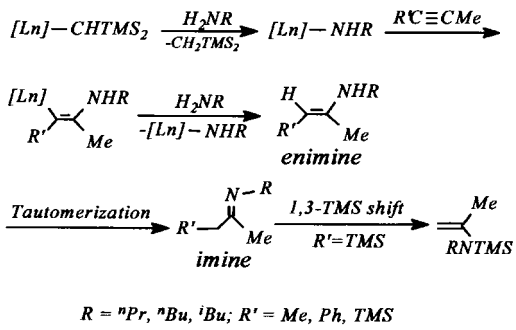


(59)

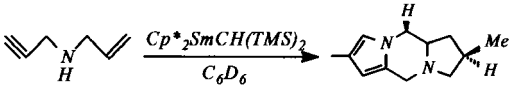
Analogous intramolecular hydroaminoation/bicyclization of acyclic aminoalkene–alkyne is obtained by using $Cp^*_2LnCH(TMS)_2$ and $Me_2SiCp''_2LnCH(TMS)_2$ as precatalysts [194,195]. The mechanism for such tandem C–N/C–C bond formations is postulated to involve turnover-limiting allene/alkyne insertion into the Ln–N functionality, followed by rapid intramolecular insertion of a pendant C=C/C≡C– containing functionality into the resulting Ln–C bond (prior to protonolysis).

4.2.4. Intermolecular alkene/alkyne hydroamination/cyclization

Significantly, Cp^*_2SmR and $Me_2SiCp''_2LnR$ (R = $CH(TMS)_2$; Ln = Nd, Sm, Lu) catalyze yet the regiospecific intermolecular addition of primary amines to acetylenic, olefinic and diene substrates (Scheme 32) [193]. The mechanism involves turnover-limiting intermolecular C≡C/C=C insertion into a Ln–N bond, followed by protonolysis of the resulting Ln–C bond. For example, in marked contrast to the aforementioned intramolecular coupled amine hydroaminotion/bicyclization, Cp^*_2SmR and $Me_2SiCp''_2NdR$ (R = $CH(TMS)_2$) catalyzed-hydroamination of $HC{\equiv}CCH_2NHR$ (R = $CH_2CH{=}CH_2$, ^{n}Pr, $(CH_2)_3CH{=}CH_2$) preferentially undergoes intermolecular rather than intramolecular hydroamonation, arguing for a more rapid intermolecular insertion of the terminal alkyne moiety into the Ln–N bond than intramolecular olefin insertion (intramolecular C≡C insertion would yield a highly strained 3-membered ring). This presents new regiospecific approaches to assemble pyrrole, pyrazine, and pyrrole–pyrazine–pyrrole skeletons (Eq. (60)) [195].



Scheme 32.



(60)

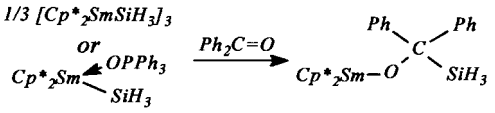
5. Ln–Si/Ge bonds insertion chemistry

Given the high insertion chemistry associated with hydride, alkyl and amido derivatives of rare earth metals, it seems somewhat surprising that few examples of insertions into Ln–Si/Ge bonds are reported. The development of this area has undoubtedly been slowed by the scarcity of lanthanide–silicon bonded compounds available for reactivity study [196].

The Tilley group has investigated in detail the reactivity of $Cp_2Sc(ER_3)(THF)$ [$ER_3 = Si(TMS)_3$ (**1a**), Si^tBuPh_2 (**1b**), $Ge(TMS)_3$ (**1c**)] toward CO, CO_2 and CNXyl, and finds that in a number of ways the reactivity patterns of scandocence silyl complexes are similar to those that have been observed previously for analogous alkyl derivatives, and the insertion level of unsaturated molecules into the Sc–Si bond is versatile (Scheme 33) [84,197,198].

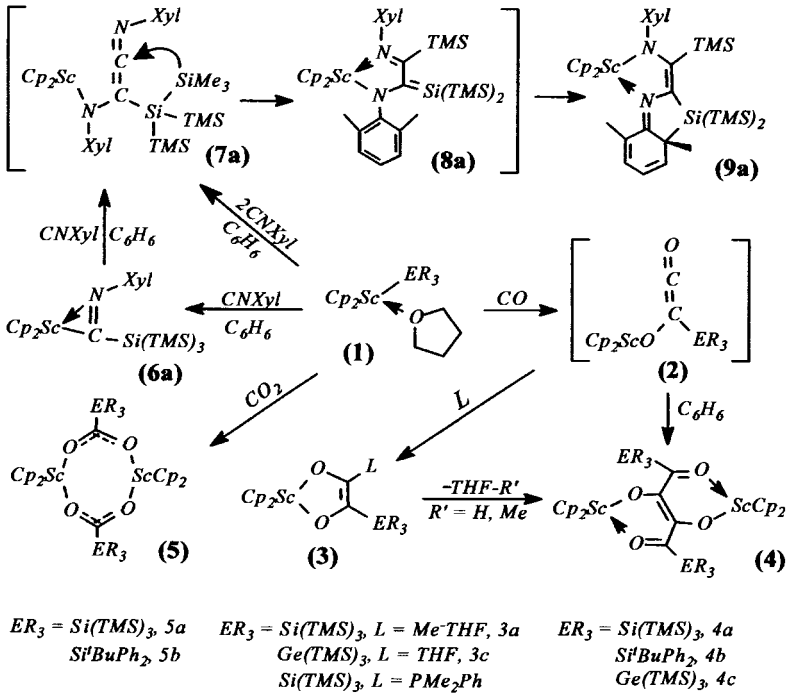
It is demonstrated that CO rapidly inserts into the Sc–Si bond to produce two types of CO–CO coupling insertion products depending on the nature of solvents. Complexes **1**(**a**, **b**) react with CO via CO–CO coupling processes, to give the scandoxyketene intermediates $(Cp_2ScO)(R_3E)C{=}C{=}O$ (**2**), which are trapped as the adducts (**3**) in the presence of Lewis base. Removal of the coordinated solvent from these adducts gives the enedione diolates **4**(**a**, **b**). In nonpolar solvent C_6H_6, however, carbonylation of **1**(**a**, **b**) directly gives **4**(**a**, **b**). Insertion of CO_2 into Sc–Si bond of **1**(**a**, **b**) forms the dimeric silanecarboxylate complexes **5**(**a**, **b**).

$Cp_2ScSi(TMS)_3(THF)$ (**1a**) reacts with one equivalent of CNXyl to form a stable monoinsertion η^2-iminosilaacyl complex (**6a**), which further reacts with a second equivalent of CNXyl to form an unusual product (**9a**). Complex **9a** appears to result from the rearrangement of the intermediate ketenimine $(Cp_2ScNXyl)[(TMS)_3Si]C{=}C{=}N(Xyl)$ (**7a**) via the migration of TMS from the $Si(TMS)_3$ group to the α-carbon of the ketenimine, followed by the cycloaddition of the resulting $C{=}Si(TMS)_2$ double bond in **8a** to an adjacent xylyl ring. Another example of the Ln–Si bond insertion chemistry is that benzophenone reacts with $[Cp^*_2SmSiH_3]_3$ or $Cp^*_2Sm(SiH_3)(OPPh_3)$ to produce $Cp^*_2SmOCPh_2(SiH_3)$ quantitatively (Eq. (61)) [199].



(61)

The insertion of CO into the Sc–Ge bond of $Cp_2ScGe(TMS)_3(THF)$ (**1c**) is comparable to those of silyl complexes, yielding the Lewis base adduct (**3c**) in THF and the enedione diolate complex (**4c**) in nonpolar media, but the carbonylation rate is noticeably slower than that of the corresponding silyl complexes **1**(**a**, **b**) (Scheme 33) [84].



Scheme 33.

6. Ln–P/As bonds insertion chemistry

The examples of organic molecules insertion into Ln–P/As bonds are very rare. The first structural characterized Ln–P bond insertion is the THF ring-opening reaction observed in the synthesis of Cp_2LuPPh_2 (Eq. (62)) [200]. A similar ring-opening reaction occurs for $(C_5Me_5)_2Sm(EPh_2)(THF)$ (E = P, As) (Eq. (63)) [201].

$$2/n\,[Cp_2LuPPh_2]_n \xrightarrow{2THF} [Cp_2Lu\{u\text{-}O(CH_2)_4PPh_2\}]_2 \quad (62)$$

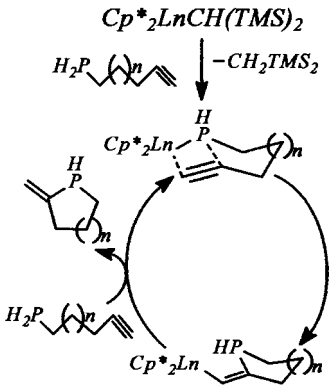
$$Cp^*_2Sm(EPh_2)(THF) \longrightarrow Cp^*_2Sm[O(CH_2)_4EPh_2](THF) \quad (63)$$

$E = P, As$

Recently, Marks et al. reported catalytic cyclization of phosphinoalkenes and phosphinoalkynes using $Cp^*_2LnCH(TMS)_2$ (Ln = La, Sm, Y) and $(Me_2SiCp''N^t\text{-}BuSmN(TMS)_2$ as precatalysts, which represents the first example of insertions of unsaturated organic molecules into the Ln–P bond (Scheme 34) [202,203].

7. Conclusions

The advances in organolanthanide insertion chemistry have demonstrated that organolanthanide complexes have an extensive, distinctive reactivity. It is clear that organolanthanide complexes are useful reagents in stoichiometric organic synthesis and catalytic transformations. The successful application of organolanthanide-catalyzed hydrosilylation and hydroamination/cyclization in synthesis of natural alkaloids under mild conditions provides a strong encouragement for the further development of new, highly reactive, and selective organolanthanide catalysts. Novel CO coupled insertions, including organolanthanide-promoted CO double insertion into C=C and N=N double bonds, constitutes some valuable new methods for regioselective carbonylations of organic molecules and synthesis of new organolanthanide derivatives. Organolanthanides effectively and high regio- and stereoselectively mediate a variety of transformations of unsaturated molecules, including isomerization, hydrogenation, hydrosilylation, hydroboration, hydrophosphination, polymerization, cyclization, and so on, have opened many new areas in organolanthanide chemistry and homogeneous catalysis. Studies on insertion chemistry



Scheme 34.

of organolanthanide complexes have considerable potential for generating novel reactivity patterns and revealing useful catalytic transformations in the future, since these reactions are sensitive to the electronic and steric characteristics of both the substrates and organolanthanide complexes. It should be possible to make further predictions that the development of new reactive and selective organolanthanide complexes and the design for new organolanthanide-catalyzed systems should lead to more and more novel insertions, and the applications of organolanthanide insertions in organic synthesis and catalytic asymmetric additions will surely increase.

8. List of abbreviations

Ln	lanthanide, rare earth metal
Me	methyl, CH_3
Et	ethyl, C_2H_5
Pr	propyl, C_3H_7
Bu	butyl, C_4H_9
Ph	phenyl, C_6H_5
Mes	mesitylenyl, C_6H_2-2,4,6-Me_3
Xyl	dimethylphenyl, C_6H_3-2,6-Me_2
Py	2-pyridyl, C_5H_4N
Pz	pyrazolate, $C_3N_2H_3$
Np	α-naphthyl, $C_{10}H_7$
OEP	octaethylporpyrin dianion
Cp	cyclopentadienyl, C_5H_5
Cp′	C_5H_4Me
Cp^t	$C_5H_4^tBu$
Cp^{TMS}	$C_5H_4SiMe_3$
Cp″	C_5Me_4
Cp*	pentamethylcydopentadienyl, C_5Me_5
Op	$Me_2SiCp''_2$
Dp	$Me_2Si(C_5H_3^tBu)_2$
n, *i*, *t*	normal, iso, tertiary
o-, *m*-, *p*-	*ortho*-, *meta*-, *para*-
THF	tetrahydrofuran
DMSO	dimethyl sulfoxide
HMPA	hexamethylphosphoramide, $(Me_2N)_3PO$
MMA	methyl methacrylate
r.t.	room temperature

Acknowledgements

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