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Award Accounts

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Half-Sandwich Rare Earth Metal Complexes as Novel Catalysts for Olefin Polymerization and Other Chemical Transformations

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This article describes our recent studies on the synthesis and chemistry of mono(cyclopentadienyl)-ligated rare earth metal alkyl and hydride complexes. The half-sandwich mono- and dialkyl rare earth metal complexes are prepared either by alkane elimination reactions between trialkyl rare earth complexes and the neutral cyclopentadiene derivatives or by metathetical reactions of rare earth trichlorides with the alkali metal salts of the corresponding ligands. The reaction of the dialkyl complexes with an equivalent of a borate compound such as $[Ph_3C][B(C_6F_5)_4]$ or $[PhNMe_2H][B(C_6F_5)_4]$ generates easily the corresponding cationic monoalkyl species, which serve as excellent catalysts for the polymerization and copolymerization of a variety of olefins to yield a new family of polymer materials that show novel properties but are difficult to prepare by other catalysts. The half-sandwich monoalkyl rare earth complexes bearing the silylene-linked cyclopentadienyl–arylamido ligands act as excellent catalysts for the catalytic dimerization of terminal alkynes, cross coupling of terminal alkynes with isocyanides, and the catalytic addition of terminal alkyne C–H, amine N–H, and phosphine P–H bonds to carbodiimides. The hydrogenolysis of the dialkyl rare earth complexes with H_2 affords a new class of polynuclear rare earth metal polyhydride complexes, which show unique features in both structure and reactivity.

1. Introduction

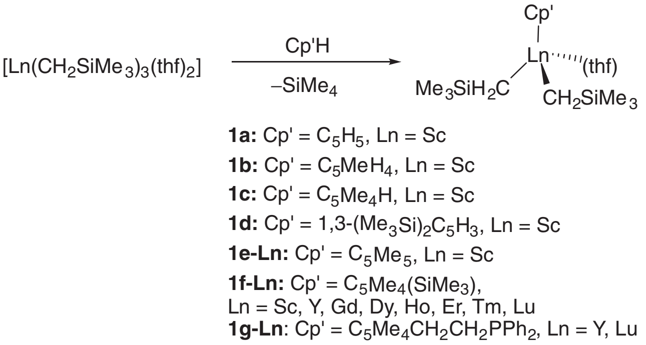
Rare earth elements, which include scandium, yttrium, and the lanthanides (La–Lu), possess unique chemical and physical properties, and constitute one of the last frontiers in the periodic table. Generally, rare earth metal–carbon and –hydride bonds are extremely reactive, and their reactivity can be fine-tuned not only by modifying the ancillary ligands but also by changing the central metal ions in a series of complexes with similar structures, thanks to the lanthanide contraction. Moreover, rare earth elements usually adopt the 3+ oxidation state as the most stable oxidation state, which is not easily changed to other oxidation states under usual conditions, in contrast to most d-block transition metals which can adopt different, easily inter-convertible oxidation states. These features make rare earth metals unique candidates for the formation of true "single-site" catalysts for polymerization and other chemical transformations.

Previously, most studies on the organometallic chemistry of the rare earth elements have focused on complexes bearing two cyclopentadienyl ligands (e.g., $[Ln(C_5Me_5)_2R]$).[1] Recently, half-sandwich rare earth complexes bearing mono(cyclopentadienyl) ligands, especially the dialkyl and dihydride complexes, have received significant attention because of their unique and diverse reactivities. This account is intended to give an overview of our recent studies on mono(cyclopentadienyl)-ligated rare earth alkyl and hydride complexes.[2,3]

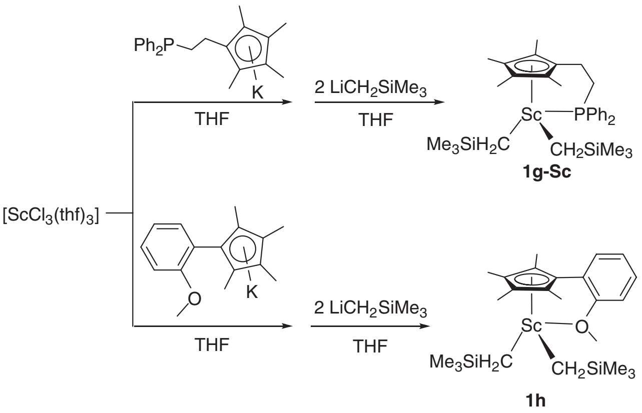
2. Cationic Rare Earth Metal Alkyls as Novel Catalysts for Olefin Polymerization and Related Reactions

2.1 Synthesis of Rare Earth Metal Dialkyl Complexes.

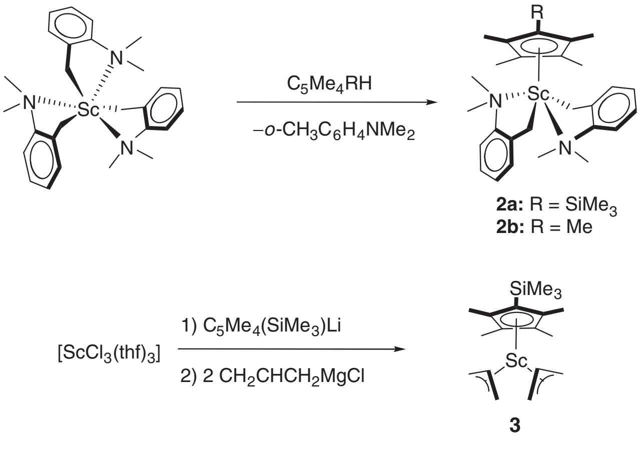
The isolation of a half-sandwich rare earth metal dialkyl complex bearing one cyclopentadienyl ligand is generally much more difficult than that of a monoalkyl complex with two cyclopentadienyl ligands, because of ligand disproportionation problems. The use of an appropriate metal/ligand combination is rather critical. By combining the sterically demanding cyclopentadienyl ligand $C_5Me_4SiMe_3$ with trimethylsilylmethyl CH_2SiMe_3, we have succeeded in the isolation and structural characterization of a series of the corresponding half-sandwich rare earth dialkyl complexes $[Ln(CH_2SiMe_3)_2(C_5Me_4SiMe_3)(thf)]$ (**1f-Ln**: Ln = Sc, Y, Gd, Dy, Ho, Er, Tm, and Lu) (Scheme 1).[2c,4,5] The bis(trimethylsilylmethyl) rare earth complexes bearing other cyclopentadienyl groups such as C_5H_5 (**1a**),[6] C_5MeH_4 (**1b**),[6] C_5Me_4H (**1c**),[6] 1,3-$(Me_3Si)_2C_5H_3$ (**1d**),[7] C_5Me_5 (**1e–Ln**),[6] and $C_5Me_4CH_2CH_2PPh_2$ (**1g-Ln**)[8] have also been prepared similarly (Scheme 1). The analogous complexes bearing the cyclopentadienyl ligands with a phosphine or ether side arm such as $C_5Me_4CH_2CH_2PPh_2$ (**1g**)[6] and $C_5Me_4C_6H_4OMe$-*o* (**1h**)[6] are obtained by the one-pot metathetical reactions of $[ScCl_3(thf)_3]$ with 1 equivalent of the potassium salts of the ligands and 2 equivalents of $LiCH_2SiMe_3$ (Scheme 2). The half-sandwich bis(aminobenzyl) scandium complex $[Sc(CH_2C_6H_4NMe_2\text{-}o)_2(C_5Me_4R)]$ (**2a**: R = $SiMe_3$,



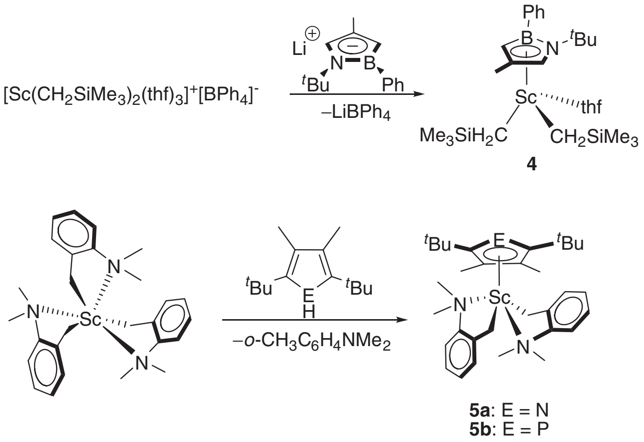
Scheme 1. Synthesis of half-sandwich rare earth metal dialkyl complexes.



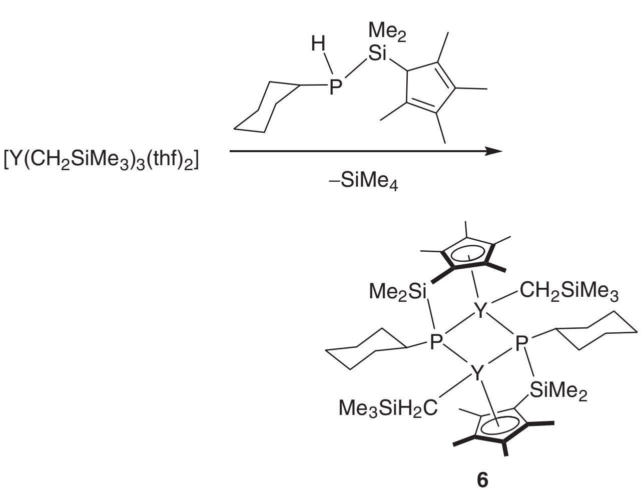
Scheme 2. Synthesis of half-sandwich scandium dialkyl complexes bearing cyclopentadienyl ligands with a phosphine or ether side arm.



Scheme 3. Synthesis of THF-free half-sandwich rare earth metal bis(aminobenzyl) and bis(allyl) complexes.



Scheme 4. Synthesis of rare earth metal dialkyl complexes bearing heteroatom-containing cyclopentadienyl ligands.



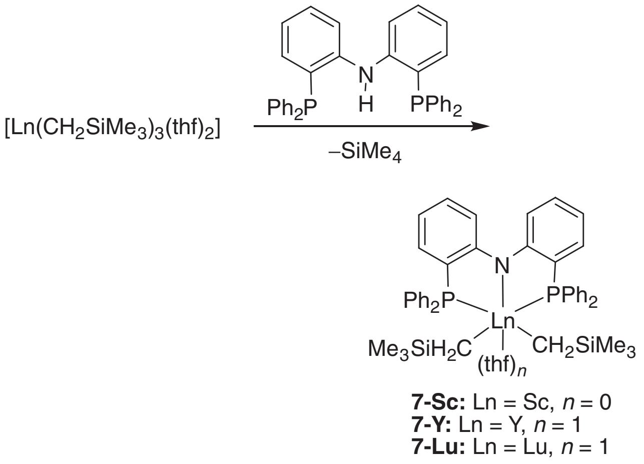
Scheme 5. Synthesis of a binuclear yttrium dialkyl complex bearing the silylene-linked cyclopentadienyl–phosphido ligand.

2b: R = Me) is easily obtained by the acid–base reaction of the tris(aminobenzyl) complex [Sc($CH_2C_6H_4NMe_2$-*o*)$_3$] with C_5Me_4H(R) (Scheme 3).[9] Complexes **1g**, **1h**, **2a**, and **2b** do not contain a THF ligand though being isolated from a THF solution, because of the intramolecular coordination of the hetero-atom groups. The THF-free half-sandwich di-allyl scandium complex [Sc(η^3-CH_2CHCH_2)$_2$($C_5Me_4SiMe_3$)] (**3**) has been prepared by the one-pot metathetical reactions of [$ScCl_3$(thf)$_3$] with $C_5Me_4SiMe_3Li$ and allylmagnesium chloride in THF (Scheme 3).[10] The analogous half-sandwich rare earth metal dialkyl complexes bearing heteroatom-containing cyclopentadienyl groups such as azaborolyl (**4**),[11] pyrrolyl (**5a**),[12] and phospholyl (**5b**)[13] as ancillary ligands have also been obtained in similar ways (Scheme 4).

The alkane elimination reaction of [Y(CH_2SiMe_3)$_3$(thf)$_2$] with one equivalent of the silylene-linked cyclopentadienyl–phosphine $Me_2Si(C_5Me_4H)PH(Cy)$ (Cy = cyclohexyl) yields the binuclear dialkyl complex [Me_2Si(η^5-C_5Me_4)(μ-PCy)Y(CH_2SiMe_3)]$_2$ (**6**), in which the two yttrium metal atoms are bridged by two phosphido groups (Scheme 5).[14] In contrast with the analogous cyclopentadienyl–amido complexes, the phosphido complexes adopt a dimeric structure through phosphido-bridging, whereas the alkyl ligand is placed in a terminal position.

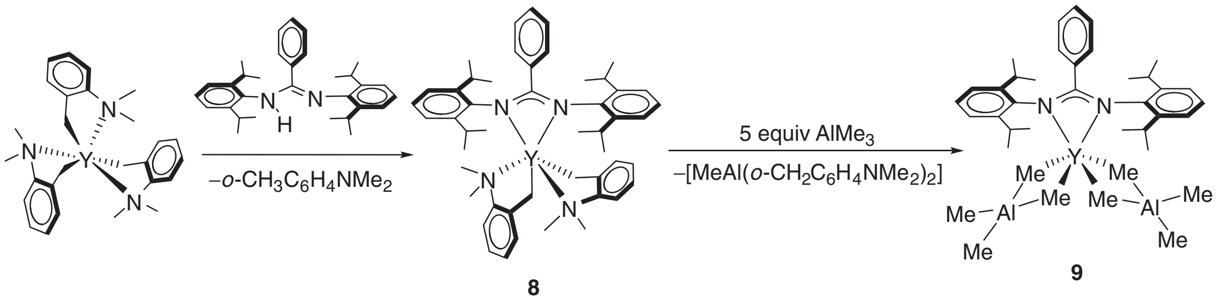
The rare earth dialkyl complexes bearing monoanionic, non-cyclopentadienyl ligands have also been prepared by similar alkane elimination or metathesis reactions. The reaction between [Ln(CH_2SiMe_3)$_3$(thf)$_2$] and 1 equivalent of [2-(Ph_2P)C_6H_4]$_2$NH (Hpnp) yields straightforwardly the corresponding bis(phosphinoamido)-ligated dialkyl complexes

$[Ln(CH_2SiMe_3)_2(pnp)(thf)_n]$ (**7-Sc**: Ln = Sc, $n = 0$; **7-Y**: Ln = Y, $n = 1$; and **7-Lu**: Ln = Lu, $n = 1$) (Scheme 6).[15] Similarly, the acid–base reaction of $[Y(CH_2C_6H_4NMe_2\text{-}o)_3]$ with $(PhC[N(2,6\text{-}^iPr_2C_6H_3)]_2)H$ (Hncn) gives the THF-free bis(aminobenzyl) complex $[Y(CH_2C_6H_4NMe_2\text{-}o)_2(ncn)]$ (**8**) (Scheme 7).[16] The reaction of the yttrium bis(aminobenzyl) complex **8** with an excess of $AlMe_3$ yields the Y/Al heterotrimetallic complex $[Y(AlMe_4)_2(ncn)]$ (**9**) via Me/aminobenzyl exchange and release of $[MeAl(CH_2C_6H_4NMe_2\text{-}o)_2]$.[16] The reaction of **1g-Y,Lu** with $[PtMe_2(cod)]$ (cod = 1,5-cyclooctadiene) affords the Ln/Pt heterobinuclear complexes $[\{Ln(CH_2SiMe_3)_2(C_5Me_4CH_2CH_2PPh_2)(thf)\}PtMe_2]$ (**1i-Y**: Ln = Y and **1i-Lu**: Ln = Lu) through replacement of the COD ligand at the Pt atom with the phosphine side arm in **1g-Y,Lu** (Scheme 8).[8] The reactions of half-sandwich complexes **1f-Y,Lu** with transition metal hydride complexes such as $[Ru(C_5Me_5)H_3(PPh_3)]$ and $[\{Os(C_5Me_5)H_2\}_2]$ afford the corresponding heteromultimetallic hydride complexes.[17]

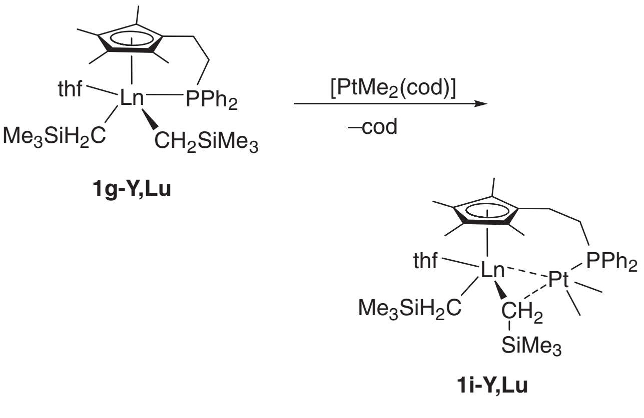


Scheme 6. Synthesis of an yttrium dialkyl complex bearing the [pnp] ligand.

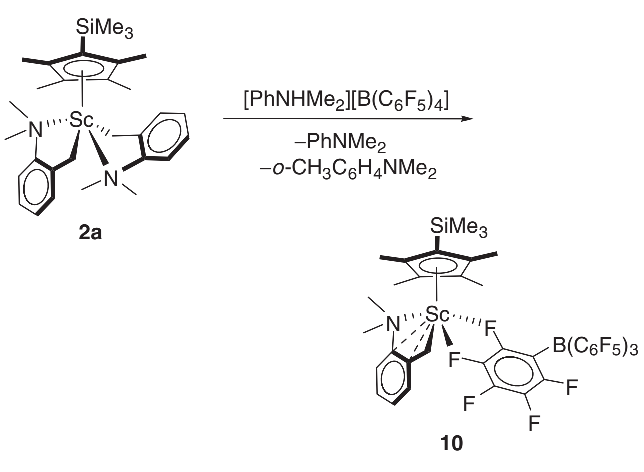
2.2 Generation of Cationic Rare Earth Metal Alkyls from Dialkyl Complexes. Generally, the reaction of dialkyl rare earth complexes with an equimolar amount of a borate compound can yield the corresponding cationic monoalkyl species. However, the cationic rare earth alkyl species are usually much less stable and more difficult to isolate because of facile ligand scrambling and other decomposition reactions.[18] Most of the cationic rare earth alkyl species reported so far are solvent-separated ion pairs, which contain extra Lewis bases such as THF as stabilization ligands.[6,15,18] We have recently isolated the first external Lewis base-free, cationic rare earth alkyl complex $[Sc(CH_2C_6H_4NMe_2\text{-}o)(C_5Me_4SiMe_3)(\kappa^2F\text{-}C_6F_5)B(C_6F_5)_3]$ (**10**) by reaction of the THF-free bis(aminobenzyl) complex $[Sc(CH_2C_6H_4NMe_2\text{-}o)_2(C_5Me_4SiMe_3)]$ (**2a**) with $[PhNMe_2H][B(C_6F_5)_4]$ (Scheme 9).[9] This complex is a contact ion-pair, in which weak interactions between the metal center and two adjacent F atoms (ortho and meta) in the borate anion unit $[B(C_6F_5)_4]$ are observed. Similarly, the reaction of the di-allyl scandium complex $[Sc(\eta^3\text{-}CH_2CHCH_2)_2(C_5Me_4SiMe_3)]$ (**3**) with one equivalent of $[PhNMe_2H][B(C_6F_5)_4]$ affords the cationic mono-allyl complex **11**, in which *N,N*-



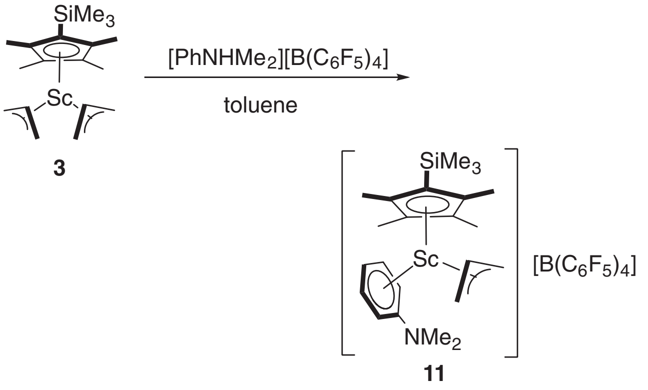
Scheme 7. Synthesis of a [ncn]-ligated yttrium dialkyl complex and its transformation to an Y/Al heterotrinuclear complex.



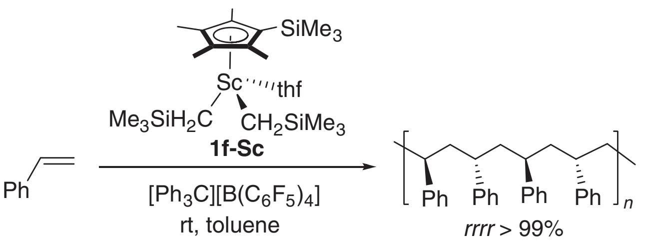
Scheme 8. Synthesis of rare-earth/platinum heterobinuclear alkyl complexes.



Scheme 9. Synthesis of a contact ion-pair scandium aminobenzyl complex.



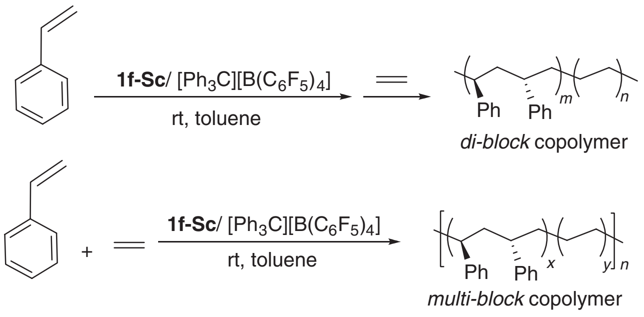
Scheme 10. Synthesis of a cationic scandium allyl complex bearing a weak Lewis base ligand.



Scheme 11. Scandium-catalyzed syndiospecific living polymerization of styrene.

dimethylaniline (a co-product of the deprotonation reaction) is trapped to the metal center through coordination of the phenyl ring in an η^6-fashion (Scheme 10).[10] This is the first example of a structurally characterized cationic metal complex that unambiguously shows an interaction between *N*,*N*-dimethylaniline and a metal center via the phenyl ring rather than via the amino group.

2.3 Syndiospecific Polymerization and Copolymerization of Styrene with Ethylene. The neutral half-sandwich rare earth metal bis(alkyl) complexes $[Ln(CH_2SiMe_3)_2(C_5Me_4SiMe_3)(thf)]$ (**1f-Ln**, Ln = Sc, Y, Gd, Dy, Ho, Er, Tm, and Lu) alone do not show any activity for styrene polymerization at room temperature. However, when treated with 1 equivalent of $[Ph_3C][B(C_6F_5)_4]$, all of these complexes become active for the syndiospecific polymerization of styrene, with the activity being dependent on both the ion size of the central metals and the ancillary ligands.[4] Among these complexes, the scandium complex $[Sc(CH_2SiMe_3)_2(C_5Me_4SiMe_3)(thf)]$ (**1f-Sc**) shows the highest activity (Scheme 11). In the present polymerization, neither atactic nor isotactic polystyrene is observed, and therefore, solvent fractionation is not required to obtain pure syndiotactic polystyrene (sPS) (*rrrr* > 99%). More remarkably, the molecular weight of the resulting polymers increases almost linearly as the monomer-to-catalyst ratio is increased, while the molecular weight distribution remains narrow, suggesting that this catalyst system has a living character. This is the first example of syndiospecific, living polymerization of styrene at room temperature.[19] Under similar conditions, the scandium aminobenzyl complexes bearing azaborolyl (**4**),[11] η^5-coordinated pyrrolyl (**5a**),[12] and phosphoryl (**5b**)[13] ligands also show high activity for the syndiospecific polymerization of styrene. In contrast, the counterpart of the $\eta^1(\sigma)$-coordinated pyrrolyl ligand showed no polymerization activity under the same conditions,[12] suggesting that an η^5-π-bonding ligand system is superior to an η^1-bonding analog for the present polymerization systems. The THF-free, cationic half-sandwich scandium aminobenzyl complex **10**, as a single component, has also shown high activity for the syndiospecific polymerization of styrene.[9]

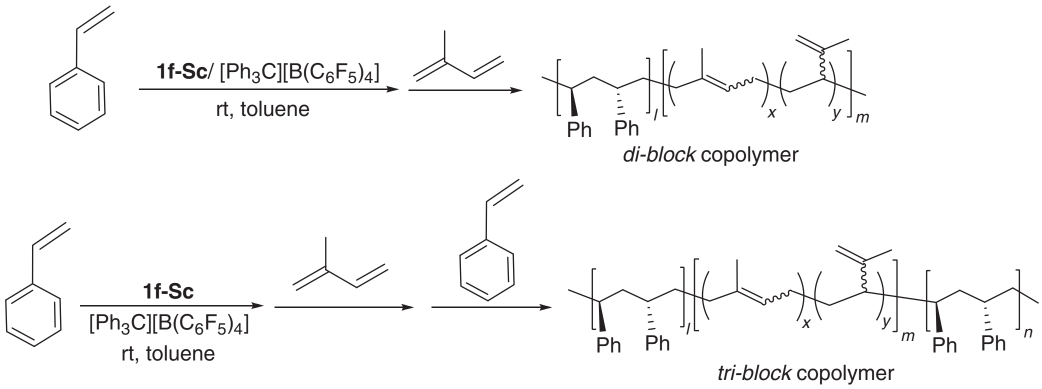


Scheme 12. Scandium-catalyzed syndiospecific copolymerization of styrene with ethylene.

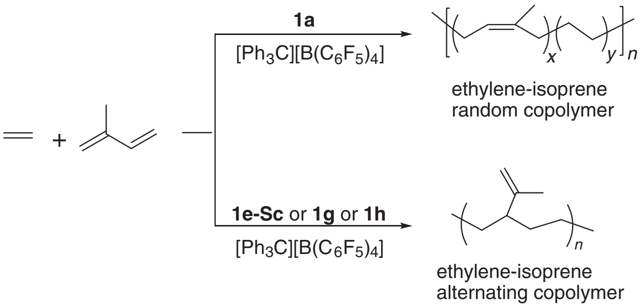
Consistent with the excellent livingness for the polymerization of styrene, the cationic half-sandwich scandium-based catalyst system shows excellent activity and selectivity for the syndiospecific copolymerization of styrene with ethylene as well (Scheme 12).[4] Introduction of ethylene (1 atm) into a completed styrene polymerization reaction mixture affords the diblock styrene–ethylene copolymer having a sPS block. When the copolymerization is carried out in the presence of both styrene and ethylene, multi-block styrene–ethylene copolymers with sPS blocks connected by polyethylene units are obtained selectively. These reactions represent the first example of syndiospecific copolymerization of styrene with ethylene.[20] The resulting copolymers possess high potential for various practical applications, because of their much improved properties compared with homo-sPS.

2.4 Syndiospecific, Living Copolymerization of Styrene with Isoprene. The **1f-Sc**/$[Ph_3C][B(C_6F_5)_4]$ catalyst system shows excellent livingness not only for the polymerization of styrene and isoprene but also for the copolymerization of these two monomers, affording for the first time styrene–isoprene block copolymers which possess stereoregular syndiotactic polystyrene blocks, such as styrene–isoprene AB-type diblock copolymers, styrene–isoprene–styrene ABA-type triblock copolymers (Scheme 13).[21] These copolymers possess both hard syndiotactic polystyrene blocks and soft polyisoprene blocks, and are expected to show unique physical and mechanical properties.

2.5 Alternating and Random Copolymerization of Isoprene with Ethylene. The copolymerization of isoprene and ethylene has been examined in detail by use of the cationic half-sandwich Sc alkyl catalysts bearing various cyclopentadienyl ligands. Significant influences of the substitutents at the cyclopentadienyl ligands of the catalysts on polymerization activity and selectivity have been observed.[6] The catalyst system $[Sc(CH_2SiMe_3)_2(C_5H_5)(thf)]$ (**1a**)/$[Ph_3C][B(C_6F_5)_4]$ gives the random isoprene–ethylene copolymers with high isoprene contents (up to 90%) and predominant *cis*-1,4-



Scheme 13. Synthesis of styrene–isoprene copolymers having syndiotactic polystyrene blocks.



Scheme 14. Random and alternating copolymerization of isoprene with ethylene.

polyisoprene microstructures (up to 90%), which constitutes the first example of *cis*-1,4-selective copolymerization of isoprene with ethylene (Scheme 14). In contrast, the catalyst systems based on [$Sc(CH_2SiMe_3)_2(C_5Me_5)(thf)$] (**1e-Sc**) or the side-arm-containing cyclopentadienyl scandium complexes **1g** and **1h** have afforded, for the first time, almost perfect alternating isoprene–ethylene copolymers with predominant 3,4-polyisoprene microstructures (Scheme 14).

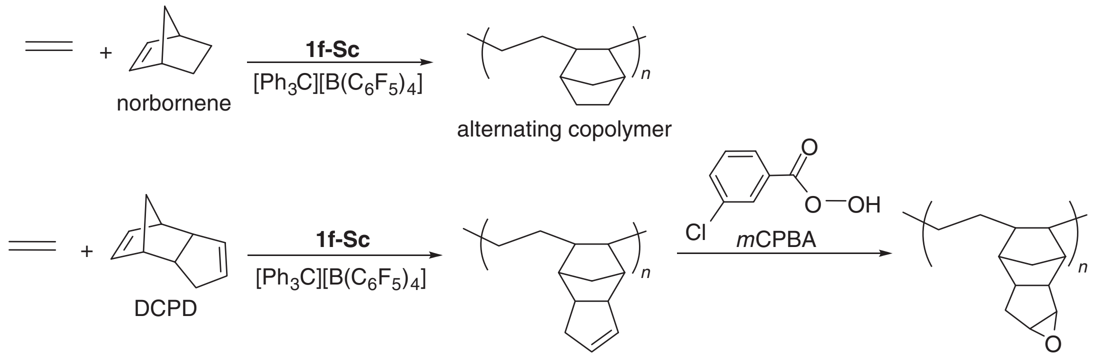
2.6 Alternating Copolymerization of Cyclic Olefins with Ethylene. The cationic scandium species generated from the reaction of the half-sandwich scandium complex **1f-Sc** with [Ph_3C][$B(C_6F_5)_4$] also serves as an excellent catalyst system for the alternating copolymerization of norbornene and ethylene (Scheme 15).[7] A strong dependence of the copolymerization activity on the monomer concentration (or the ethylene/norbornene molar ratio in the reaction solution) is observed. Under appropriate (ethylene/norbornene molar ratio) conditions, the catalytic activity reaches as high as 25.2×10^3 kg/(mol-Sc h atm), which is among the highest ever reported for the copolymerization of ethylene and norbornene. Possibly due to steric hindrance, successive norbornene insertion or homopolymerization of norbornene is sluggish in the present catalyst system. However, the insertion of a norbornene monomer into a $Sc–CH_2CH_2R$ bond and that of an ethylene monomer into a Sc–norbornyl bond can be very fast, and the former can be even more preferred to successive ethylene insertion when an adequate amount of norbornene is present. This unique nature leads to rapid and exclusive formation of the alternating ethylene–norbornene copolymer under appropriate ethylene/norbornene molar ratios.

Moreover, cationic half-sandwich scandium catalyst systems such as **1f-Sc**/[Ph_3C][$B(C_6F_5)_4$] can also serve as an excellent catalyst for the alternating copolymerization of DCPD with ethylene, which not only shows high activity but can also distinguish the norbornene unit from the cyclopentene unit in DCPD, thus constituting the first example of the alternating copolymerization of DCPD with ethylene (Scheme 15).[22] In the presence of **1f-Sc**/[Ph_3C][$B(C_6F_5)_4$] in toluene, the copolymerization of DCPD with ethylene takes place very rapidly at a wide range of temperatures (0–70 °C) to yield the corresponding alternating copolymers. The DCPD content of the resulting copolymers increases as the DCPD monomer feed is raised under 1 atm of ethylene and can reach as high as 45 mol %. Similar to norbornene–ethylene copolymerization, the copolymerization of the two monomers (DCPD and ethylene) is preferred to the homopolymerization of either monomer.

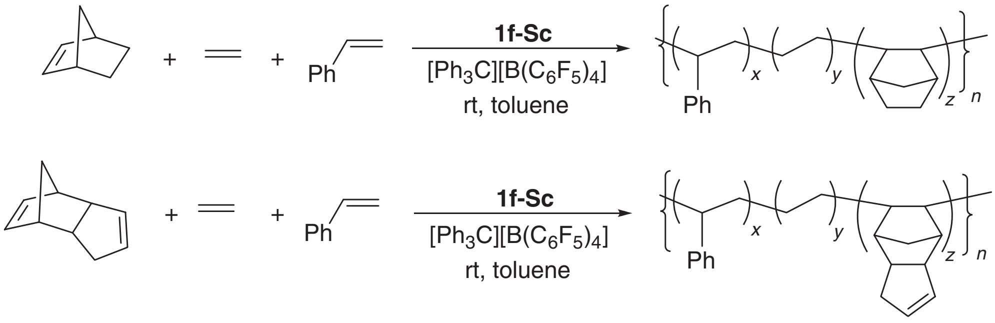
The epoxidation of an ethylene–DCPD alternating copolymer is easily achieved by use of *m*-chloroperbenzoic acid (*m*CPBA) as an oxidant, converting quantitatively the olefinic groups into epoxy groups (Scheme 15).

2.7 Terpolymerization of Styrene, Ethylene, and Cyclic Olefins. By use of **1f-Sc**/[Ph_3C][$B(C_6F_5)_4$] as a catalyst, we have also achieved for the first time the terpolymerization of styrene, ethylene, and a cyclic olefin such as norbornene or DCPD (Scheme 16).[22] The terpolymers with styrene content of 4–57 mol % and DCPD content of 5–26 mol % can be easily prepared by changing the DCPD/styrene feed ratio under 1 atm of ethylene. ^{13}C NMR analyses revealed that the terpolymers are random copolymers that contain isolated or alternating DCPD units, isolated and syndiotactic styrene–styrene sequences, while no styrene–DCPD sequences are observed. As far as we are aware, this is the first, and remains to date the only, example of the stereoselective terpolymerization of styrene, ethylene, and a cyclic olefin. The resulting terpolymers show unique optical, mechanical, and physical properties.

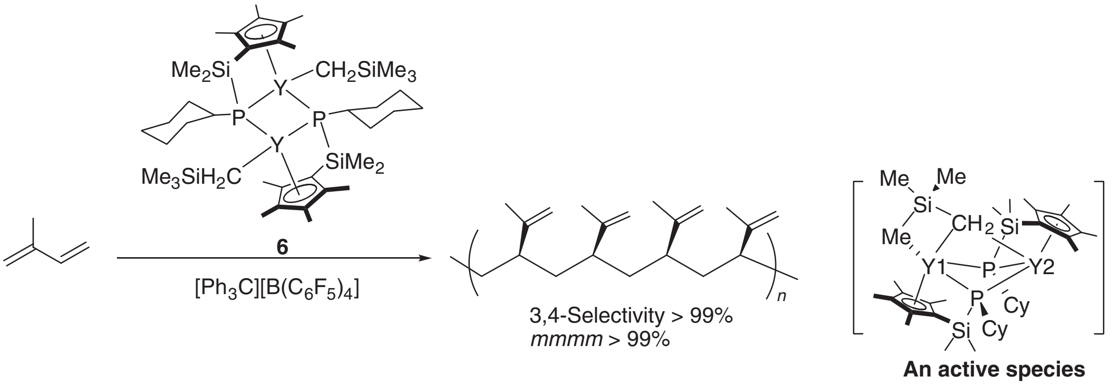
2.8 Isospecific 3,4-Polymerization of Isoprene. By use of the cationic alkyl species generated in the reaction of the binuclear yttrium dialkyl complex [$Me_2Si(\eta^5\text{-}C_5Me_4)(\mu\text{-}PCy)Y(CH_2SiMe_3)]_2$ (**6**) with an equimolar amount of [Ph_3C][$B(C_6F_5)_4$], we have achieved for the first time the isospecific 3,4-polymerization of isoprene (Scheme 17).[14b] When the polymerization is carried out at −20 °C, a polyisoprene polymer with almost perfect isotactic 3,4-microstructure (3,4-selectivity 100%, *mmmm* > 99%), high molecu-



Scheme 15. Alternating copolymerization of cyclic olefins with ethylene.



Scheme 16. Terpolymerization of styrene, ethylene, and cyclic olefins.

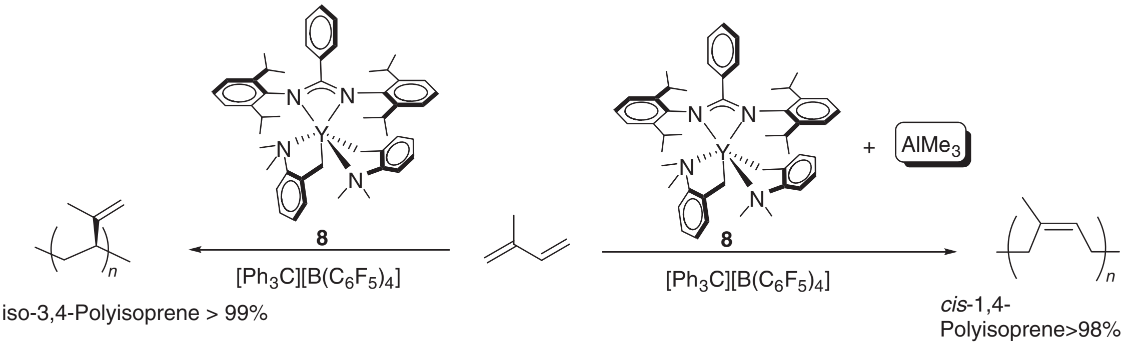


Scheme 17. Isospecific 3,4-polymerization of isoprene catalyzed by a binuclear yttrium catalyst.

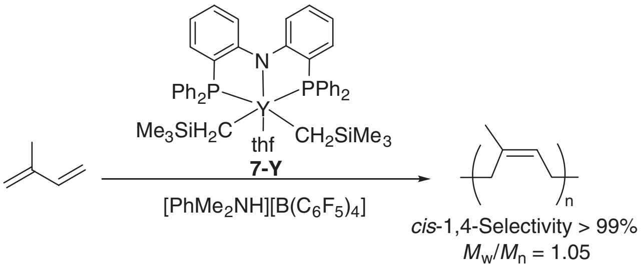
lar weight ($M_n = 5 \times 10^5$), and narrow molecular weight distribution ($M_w/M_n = 1.6$) is obtained. The isotactic 3,4-polyisoprene obtained is a new polymer, which is crystalline as shown by XRD, and has a melting point at 162 °C. DFT calculations suggest that a binuclear monocationic monoalkyl species, such as $[Me_2Si(C_5Me_4)(\mu\text{-PCy})Y(\mu\text{-CH}_2SiMe_3)Y(\mu\text{-PCy})(C_5Me_4)SiMe_2]^+$, in which the alkyl group bridges the two metal centers, is the true catalyst species.[14c]

The amidinate-ligated yttrium bis(aminobenzyl) complex $[Y(CH_2C_6H_4NMe_2\text{-}o)_2(ncn)]$ (**8**), in combination with $[Ph_3C][B(C_6F_5)_4]$, also shows excellent activity and selectivity for the isospecific 3,4-polymerization of isoprene (Scheme 18, left).[16] Moreover, if the polymerization is carried out in the presence of a small amount of $AlMe_3$ (3–5 equivalents to Y), the regio- and stereoselectivity is dramatically switched from 3,4-isospecific to 1,4-*cis*-selective (Scheme 18, right).[16] The Y/Al heterometallic complex $[Y(AlMe_4)_2(ncn)]$ (**9**), isolated from the reaction of **8** with $AlMe_3$, also shows *cis*-1,4-selectivity in the presence of $[Ph_3C][B(C_6F_5)_4]$, suggesting that the active species for the 1,4-*cis*-polymerization in the **8**/$[Ph_3C][B(C_6F_5)_4]$/$AlMe_3$ system should be a cationic Y/Al heteromultimetallic complex. Although alkylaluminum compounds have often been used as additives or co-catalysts in various isoprene polymerization catalyst systems, this is the first example to unambiguously show that the incorporation of an alkylaluminum species can dramatically change the regio- and stereoselectivity of a catalyst system.

2.9 Living *cis*-1,4-Polymerization and Copolymerization of Isoprene and Butadiene. The combination of the bis(phosphinophenyl)amido (pnp)-ligated yttrium dialkyl complex $[Y(CH_2SiMe_3)_2(pnp)(thf)]$ (**7-Y**) and $[PhMe_2NH][B(C_6F_5)_4]$ has proved to be an excellent catalyst system for the *cis*-1,4 living polymerization of isoprene, which affords, for the first time, polyisoprene with both extremely high *cis*-1,4-



Scheme 18. Switching the polymerization of isoprene from 3,4-isospecific to 1,4-*cis*-selective by addition of $AlMe_3$.



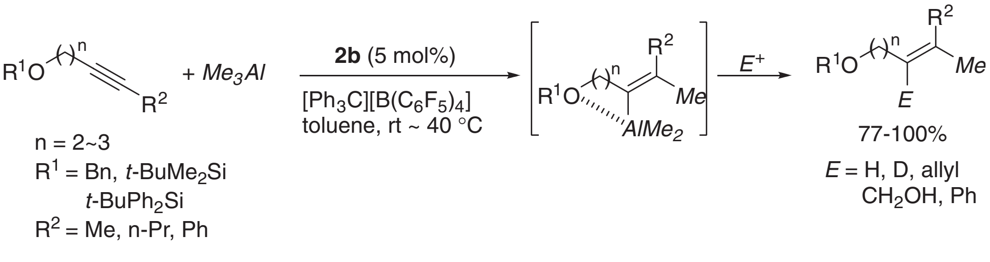
Scheme 19. *cis*-1,4-Living polymerization of isoprene by a pnp-ligated yttrium catalyst.

content (>99%) and very narrow molecular weight distribution ($M_w/M_n < 1.10$) (Scheme 19).[15] The excellent livingness and high *cis*-1,4-selectivity of the catalyst can be maintained even at high temperatures ($M_w/M_n = 1.05$–1.08, *cis*-1,4-selectivity >98.5%, at 50–80 °C). The copolymerization of isoprene with butadiene has also been achieved for the first time in a *cis*-1,4-living fashion by use of this catalyst system.

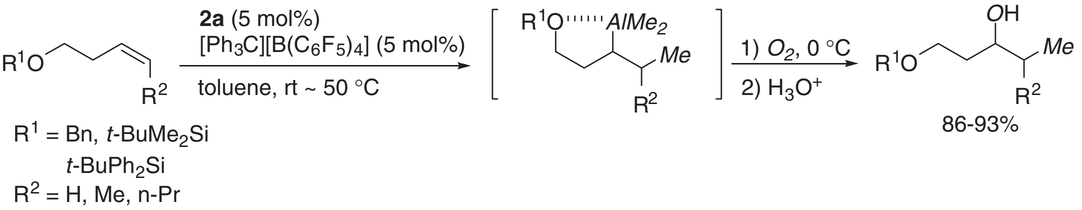
The cationic monoalkyl species generated by the reaction of the analogous lutetium dialkyl complex $[Lu(CH_2SiMe_3)_2(pnp)(thf)]$ (**7-Lu**) with $[PhMe_2NH][B(C_6F_5)_4]$ has been isolated and structurally characterized. A computational study has revealed that the coordination of isoprene to the cationic metal center in a *cis*-1,4-fashion is about 5–7 kcal mol^{-1} more favored than that in a 3,4-fashion; *trans*-1,4-coordination is not accessible. This could thus account for the high *cis*-1,4-selectivity in the present polymerization system.

2.10 Regio- and Stereospecific Methylalumination of Silyloxy/Alkoxy-Substituted Alkynes and Alkenes.

Carboalumination of alkynes is one of the most efficient methods for the synthesis of polysubstituted alkenes, especially those with branching methyl groups (an important class of structural units that are found in many biologically active natural compounds). However, its application to internal alkynes has been hardly explored due to the difficulty in controlling the regioselectivity. By use of the combination of a half-sandwich scandium bis(alkyl) complex such as **2a** or **2b** and an equimolar amount of $[Ph_3C][B(C_6F_5)_4]$ as a catalyst system, we have achieved the regio- and stereoselective *syn*-methylalumination of the silyloxy- or alkoxy-substituted internal alkynes (Scheme 20).[23] The regiospecific methylalumination of terminal and internal alkenes has also been achieved similarly (Scheme 21). In these reactions, the tethered oxygen atom in the alkynes or alkenes seems to play a crucially important role, possibly through its coordination to the metal center. This regio- and stereoselectivity is unique to the scandium catalysts and could not be achieved by previous group 4 metal catalysts.



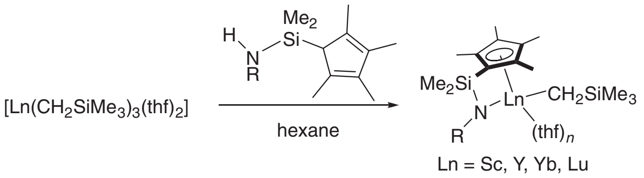
Scheme 20. Scandium-catalyzed regio- and stereoselective methylalumination of internal alkynes.



Scheme 21. Scandium-catalyzed regioselective methylalumination of alkenes.

3. Neutral Half-Sandwich Rare Earth Metal Alkyls as Novel Catalysts for Selective Chemical Transformations

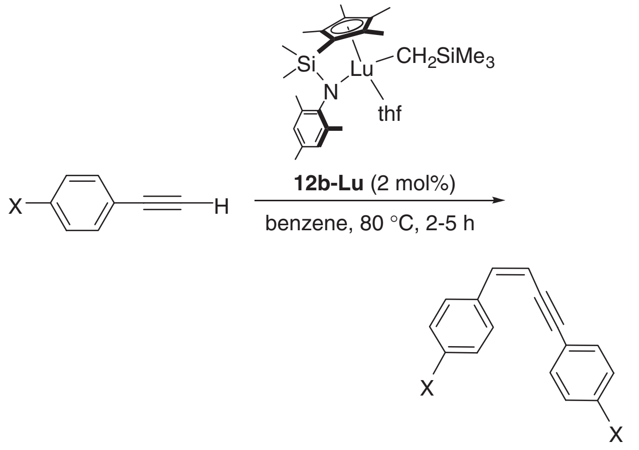
3.1 Synthesis of Half-Sandwich Rare Earth Metal Alkyl Complexes Bearing Silylene-Linked Cyclopentadienyl–Amido Ligands. The acid–base reactions between the rare earth metal tris(trimethylsilylmethyl) complexes [Ln(CH$_2$SiMe$_3$)$_3$(thf)$_2$] and the cyclopentadienyl aryl amine ligands (C$_5$Me$_4$H)SiMe$_2$NHR give straightforwardly the cyclopentadienyl–arylamido alkyl complexes [Ln(CH$_2$SiMe$_3$){Me$_2$Si(C$_5$Me$_4$)(NR)}(thf)$_n$] (**12a-Ln**: R = Ph, Ln = Y, Yb, Lu, n = 2; **12b-Ln**: R = C$_6$H$_2$Me$_3$-2,4,6, Ln = Y, Lu, n = 1; and **12c**: C$_6$H$_3$Me$_2$-2,6, Ln = Lu, n = 1) as shown in Scheme 22.[24,25] The use of the aminobenzyl group CH$_2$C$_6$H$_4$NMe$_2$-*o* instead of trimethylsilylmethyl (CH$_2$SiMe$_3$) has enabled the first successful synthesis of the half-sandwich complexes over the whole size range of the rare earth metal series. In most cases, the desired complexes [Ln(CH$_2$C$_6$H$_4$NMe$_2$-*o*){Me$_2$Si(C$_5$Me$_4$)(NC$_6$H$_2$Me$_3$-2,4,6)}(thf)] (**13-Ln**: Ln = Y, La, Pr, Nd, Sm, Gd, and Lu) can be easily prepared by the reaction of [Ln(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$] with the corresponding cyclopentadienyl–amine ligands (Scheme 23).[26] However, in the case of scandium (**13-Sc**) (the smallest ion in the rare earth series), the one-pot metathetical reactions of ScCl$_3$(thf)$_3$ with 1 equivalent of the dilithium salt of the ligand and 1 equivalent of LiCH$_2$C$_6$H$_4$NMe$_2$-*o* prove to be a more appropriate synthetic route (Scheme 23).[26]



12a-Ln: R = Ph, Ln = Y, Yb, Lu, n = 2
12b-Ln: R = C$_6$H$_2$Me$_3$-2,4,6, Ln = Y, Lu, n = 1
12c: R = C$_6$H$_3$Me$_2$-2,6, Ln = Lu, n = 1

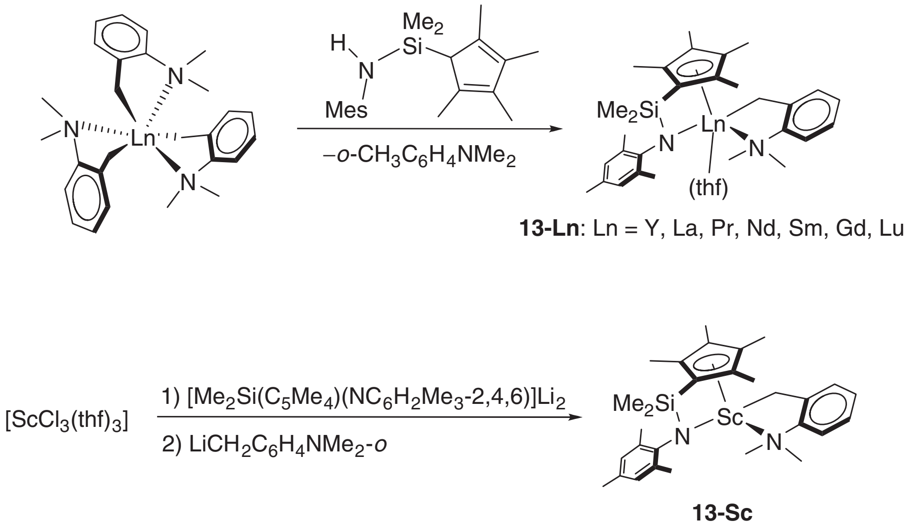
Scheme 22. Synthesis of rare-earth metal alkyl complexes bearing silylene-linked cyclopentadienyl–amido ligands.

3.2 Regio- and Stereoselective Dimerization of Terminal Alkynes. The dimerization of terminal alkynes is a straightforward, atom-economical route to conjugated enynes, which are important building blocks for organic synthesis and significant components in various biologically active compounds. Although various transition metal catalysts are known to catalyze the dimerization of terminal alkynes, in most cases a mixture of regio (head-to-head vs. head-to-tail)- and stereo (E/Z-head-to-head)-isomers is obtained. By use of the half-sandwich lutetium alkyl complex [Lu(CH$_2$SiMe$_3$){Me$_2$Si(C$_5$Me$_4$)(NC$_6$H$_2$Me$_3$-2,4,6)}(thf)] (**12b-Lu**) as a catalyst precursor, we have realized for the first time the regio- and stereoselective head-to-head (Z)-dimerization of various aromatic terminal alkynes (Scheme 24).[25a] Aromatic C–Cl, C–Br, and C–I bonds, which are known to be susceptible to reductive cleavage by transition metals, have survived the reaction conditions. An alkynide-bridged binuclear complex such as **A** is confirmed to be the true catalyst species (Scheme 25). More remarkably, the alkynide catalyst species can be recovered from a completed reaction mixture and reused without loss of



X = H, Me, OMe, F, Cl, Br, I

Scheme 24. Regio- and stereoselective head-to-head (Z)-dimerization of terminal alkynes.



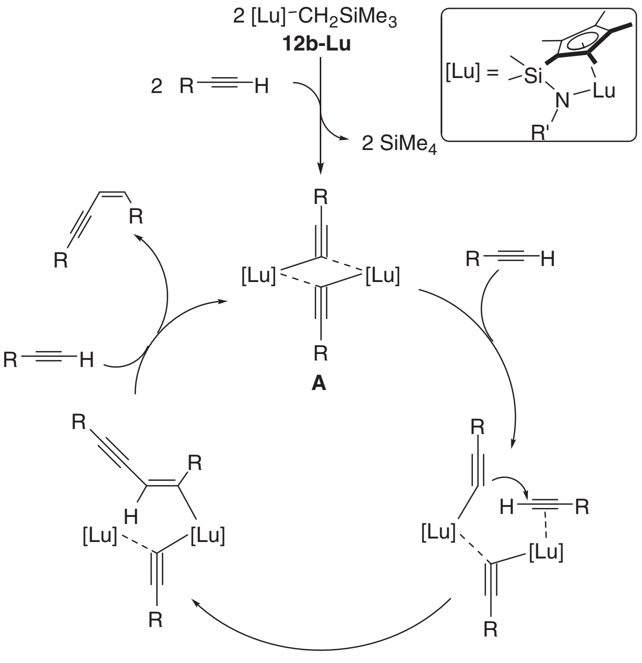
Scheme 23. Synthesis of rare-earth metal aminobenzyl complexes bearing silylene-linked cyclopentadienyl–amido ligands.

activity and selectivity. This is a rare example of catalyst recycling in a homogeneous catalytic system. The dimerization reaction probably takes place at the binuclear metal center and thus leads to the unprecedented (*Z*)-selectivity (Scheme 25).

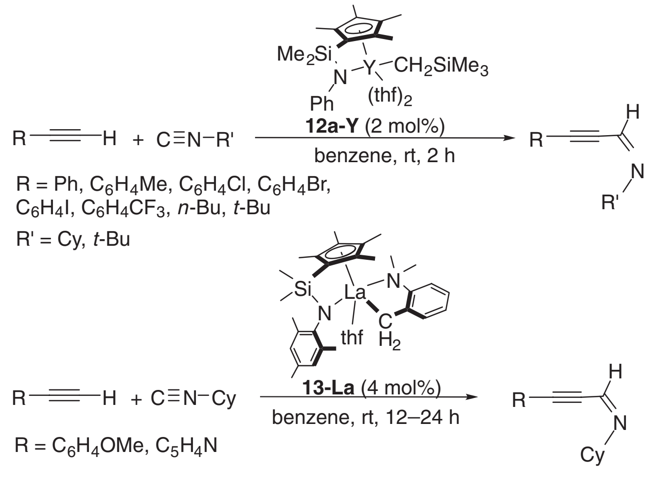
In the dimerization of the carbazoly-substituted phenylacetylene, the lanthanum metallocene catalyst [La{CH($SiMe_3$)$_2$}(C_5Me_5)$_2$] shows excellent *E*-selectivity, in contrast with the *Z*-selective half-sandwich lutetium catalyst **12c** (Scheme 26).[27] The resulting *Z*-enyne compound shows excellent white electroluminescence as a unique single-emitting component.

3.3 Stereoselective Cross-Coupling of Terminal Alkynes with Isocyanides. The 1,1-insertion of isocyanides into the C–H bond of terminal alkynes is a straightforward, atom-economical route to conjugated 1-aza-1,3-enynes (RC≡C–CH=NR′). However, few catalysts were known to promote the catalytic coupling of isocyanides with terminal alkynes and none showed high selectivity. By using the half-sandwich rare earth alkyl complexes as a catalyst, we have achieved for the first time the (*Z*)-selective cross-coupling of terminal alkynes with isocyanides to afford the corresponding (*Z*)-1-aza-1,3-enynes under mild conditions (Scheme 27).[28] Usually, the yttrium complexes such as [Y(CH_2SiMe_3){$Me_2Si(C_5Me_4)$(NPh)}(thf)$_2$] (**12a-Y**) are highly effective for various phenylacetylene derivatives and alkyl alkynes. However, in the case of the less reactive terminal alkynes with a strongly electron-donating substituent such as 4-methoxyphenylacetylene and pyridylacetylene, the larger lanthanum complex (**13-La**) exhibits higher activity.

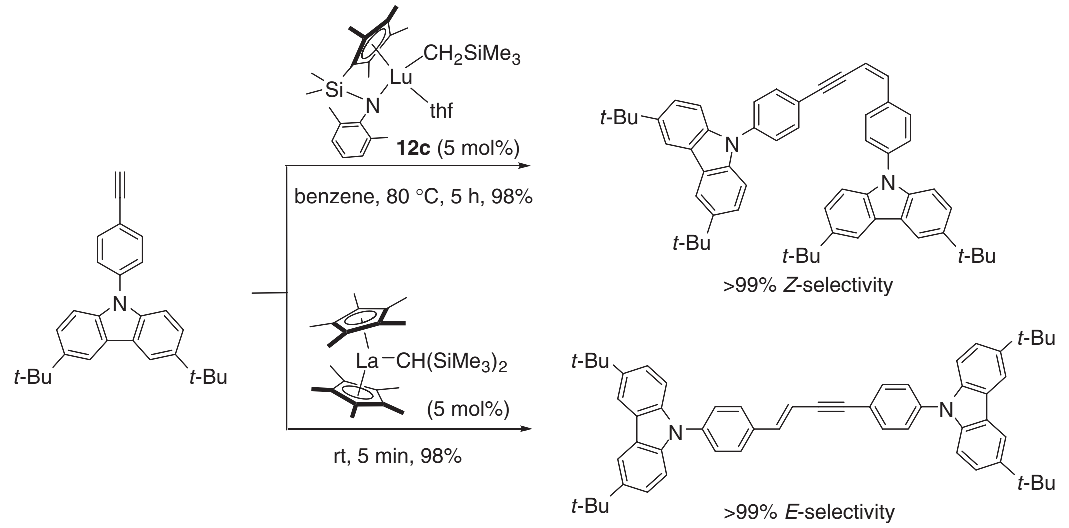
Similar to the homo-dimerization of terminal alkynes described above (Section **3.2**), the selective formation of (*Z*)-1-aza-1,3-enynes in the present reaction of terminal alkynes with isocyanides could also be rationalized by a possible binuclear reaction mechanism as shown in Scheme 28.



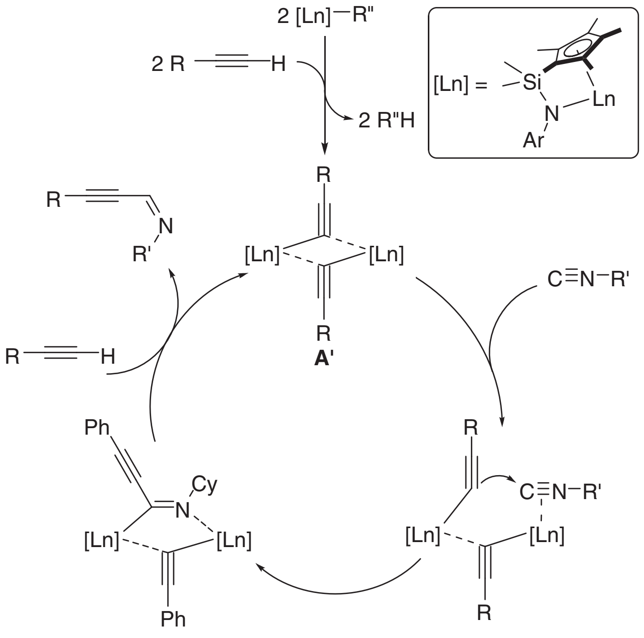
Scheme 25. A possible mechanism of the (*Z*)-selective dimerization of terminal alkynes at a binuclear metal center.



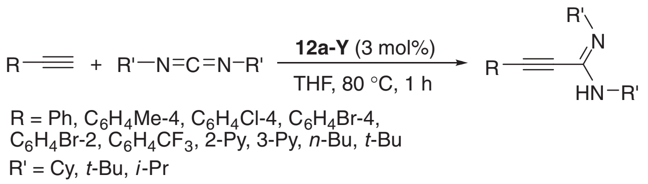
Scheme 27. Catalytic cross-coupling of isocyanides with terminal alkynes.



Scheme 26. Regio- and stereoselective synthesis of conjugated enynes.



Scheme 28. A possible mechanism of catalytic cross-coupling of terminal alkynes with isocyanides.

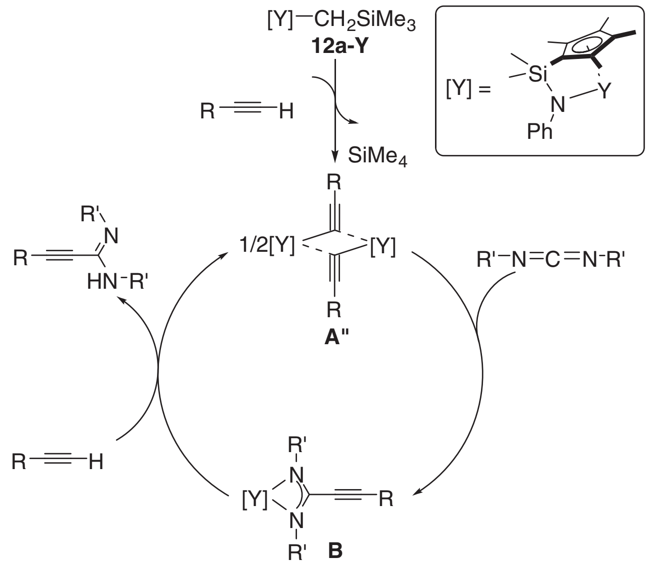


R = Ph, C_6H_4Me-4, C_6H_4Cl-4, C_6H_4Br-4, C_6H_4Br-2, $C_6H_4CF_3$, 2-Py, 3-Py, *n*-Bu, *t*-Bu
R' = Cy, *t*-Bu, *i*-Pr

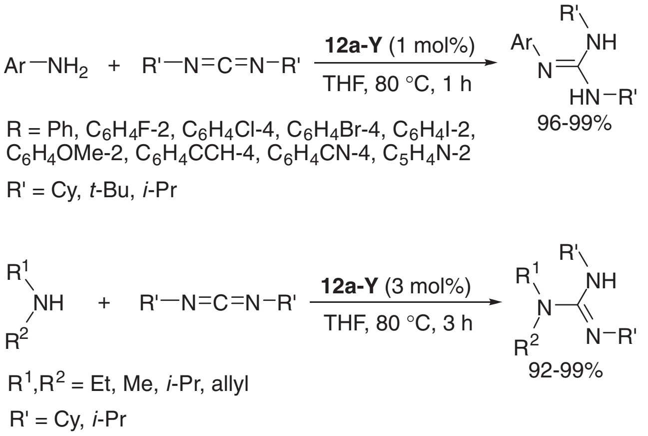
Scheme 29. Catalytic addition of terminal alkynes to carbodiimides.

3.4 Catalytic Addition of Terminal Alkynes to Carbodiimides. By use of the half-sandwich yttrium complex **12a-Y** as a catalyst, we have achieved for the first time the catalytic addition of terminal alkynes to carbodiimides to afford *N*,*N'*-disubstituted propiolamidines R'N=C(C≡CR)(NHR'), a new family of amidines which contain a conjugated C–C triple bond and were difficult to prepare previously (Scheme 29).[29] A wide range of terminal alkynes can be used for this catalytic cross-coupling reaction. The reaction is not affected by either electron-withdrawing or -donating substituents or their positions at the phenyl ring of an aromatic alkyne. The aromatic C–Cl and C–Br bonds can survive in the present reactions. Heteroatom-containing alkynes such as pyridylacetylenes are also applicable.

A catalytic cycle for the present addition reaction is shown in Scheme 30. Nucleophilic addition of an alkynide species such as **A''** to a carbodiimide affords the amidinate species **B**, which on abstraction of a proton from another molecule of alkyne would yield the corresponding amidine and regenerate the alkynide **A''**. Although a large number of amidinate complexes of various metals have been reported previously, this is the first example of the catalytic transformation of an amidinate species.



Scheme 30. A possible mechanism of catalytic addition of terminal alkynes to carbodiimides.



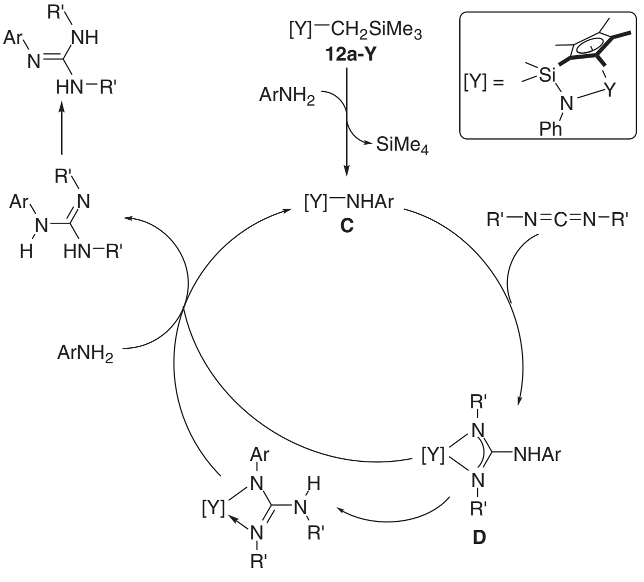
R = Ph, C_6H_4F-2, C_6H_4Cl-4, C_6H_4Br-4, C_6H_4I-2, C_6H_4OMe-2, C_6H_4CCH-4, C_6H_4CN-4, C_5H_4N-2
R' = Cy, *t*-Bu, *i*-Pr

R^1,R^2 = Et, Me, *i*-Pr, allyl
R' = Cy, *i*-Pr

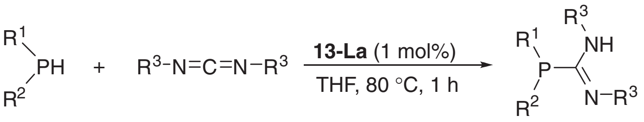
Scheme 31. Catalytic addition of amines N–H bonds to carbodiimides.

3.5 Catalytic Addition of Amine N–H Bonds to Carbodiimides. Multi-substituted guanidines are useful building blocks for many biologically relevant compounds. Although addition of amine N–H bonds to carbodiimides could provide a straightforward and atom-economical route to guanidines, such catalytic reactions are rather limited. Primary aliphatic amines were known to undergo direct guanylation with carbodiimides to yield *N*,*N'*,*N''*-trialkylguanidines under rather forcing conditions. However, less nucleophilic aromatic amines or secondary amines hardly react with carbodiimides under the same or harsher conditions. We have found that the half-sandwich yttrium alkyl complex [Y(CH_2SiMe_3){$Me_2Si(C_5Me_4)$(NPh)}$(thf)_2$] (**12a-Y**) can work as an efficient catalyst for the catalytic addition of various aromatic primary amines and secondary amines to carbodiimides to afford the corresponding guanidines with a wide range of substituents on the nitrogen atoms (Scheme 31).[25c,25d] Substrates with functional groups such as C≡N, C≡CH, and aromatic C–X (X: F, Cl, Br, and I) bonds can be applied to this catalytic addition reaction.

Some key reaction intermediates or true catalyst species, such as the amido complex **C** and the guanidinate complex **D** have been isolated and structurally characterized (Scheme 32). Reactivity studies on these complexes suggest that the present



Scheme 32. A possible mechanism of catalytic addition of amine N–H bonds to carbodiimides.



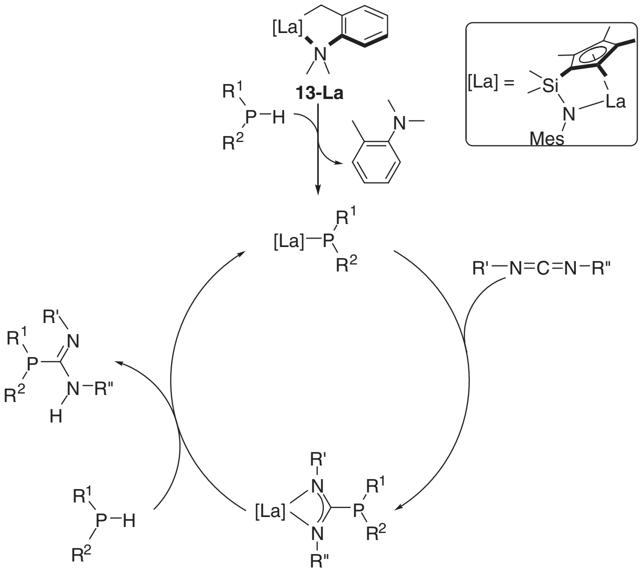
R^1,R^2 = Ph, C_6H_4Me-4, C_6H_4Cl-4, C_6H_4Br-4, C_6H_4OMe-4, $C_6H_3Cl_2$-3, 5, Cy, H

R^3 = Cy, *t*-Bu, *i*-Pr

Scheme 33. Catalytic addition of phosphine P–H bonds to carbodiimides.

catalytic formation of a guanidine compound proceeds through nucleophilic addition of an amido species, which is formed by the acid–base reaction between a rare earth metal alkyl bond and an amine N–H bond, to a carbodiimide, followed by amine protonolysis of the resultant guanidinate species, as shown in Scheme 32.

3.6 Catalytic Addition of Phosphine P–H Bonds to Carbodiimides. The half-sandwich rare earth metal aminobenzyl complexes (**13-La**, **-Pr**, **-Nd**, **-Sm**, **-Gd**, and **-Lu**) serve as efficient catalysts for the addition of phosphine P–H bonds to carbodiimides to afford a new family of phosphaguanidines with various substituents (Scheme 33).[26] The catalytic activity of these complexes increases as the metal size becomes larger (La > Pr > Nd > Sm > Gd > Lu), and therefore, the largest lanthanum complex **13-La** shows the highest activity. A wide range of arylphosphines can be used as the nucleophiles. Aromatic C–Cl and C–Br bonds have survived in the catalytic conditions to yield selectively the corresponding halogen-substituted phosphaguanidines, a new class of phosphaguanidine building blocks that could be useful for construction of further larger phosphaguanidine derivatives. Similar to the addition of amines to carbodiimides described above (Section **3.5**), the formation of phosphaguanidines in the present phosphine addition reactions could also be explained by an addition–deprotonation mechanism through a phosphaguanidinate species as a key intermediate, as shown in Scheme 34.



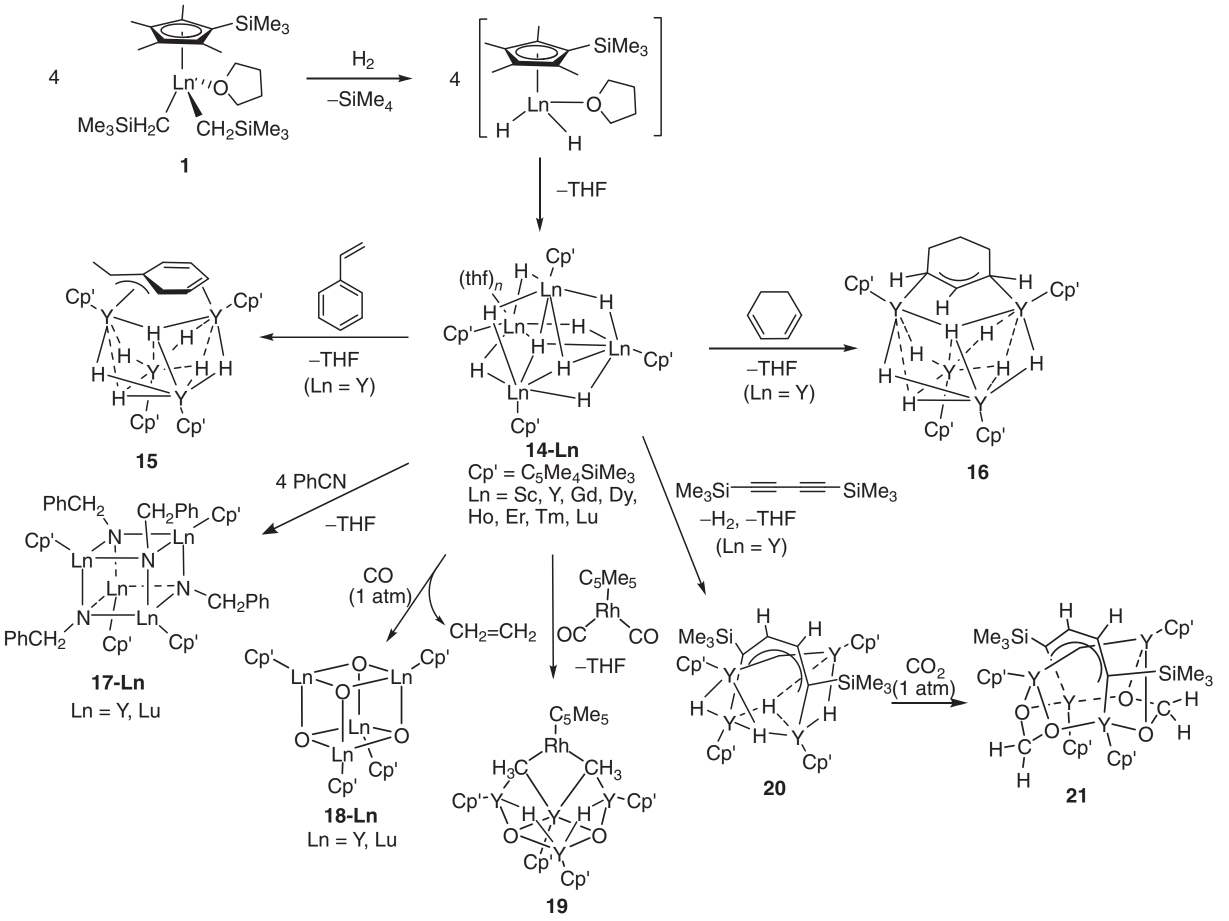
Scheme 34. A possible mechanism of catalytic addition of phosphine P–H bonds to carbodiimides.

In parallel to the study on the lanthanide-catalyzed addition reactions, we have found that alkali metal amido compounds such as $KN(SiMe_3)_2$ can also serve as efficient catalysts for the addition of phosphines to carbodiimides under mild conditions.[30]

4. Synthesis and Novel Reactivity of Rare Earth Metal Polyhydrides

Metal hydrides are fundamental components in a wide range of stoichiometric and catalytic reactions. Their importance in modern inorganic and organic chemistries cannot be overemphasized. So far, a large number of monohydride complexes of the general type "L_2MH" or "(L)(L′)MH," which are supported by two anionic ancillary ligands per metal, have been synthesized and extensively studied. In contrast, dihydrido rare earth metal complexes of type "LMH_2," which bear one anionic ancillary ligand per metal, have remained unexplored, even though such complexes are of much interest both structurally and chemically in comparison with the analogous monohydrido rare earth metal complexes. By use of the $C_5Me_4SiMe_3$-ligated half-sandwich dialkyl complexes $[Ln(CH_2SiMe_3)_2(C_5Me_4SiMe_3)(thf)]$ (**1f–Ln**, Ln = Sc, Y, Gd, Dy, Ho, Er, Tm, and Lu) as precursors, we have succeeded in the isolation and structural characterization of a series of polynuclear polyhydrido rare earth metal complexes that contain the "$(C_5Me_4SiMe_3)LnH_2$" units. These polyhydrido rare earth metal complexes show unique reactivities that differ from those of the conventional monohydride complexes.

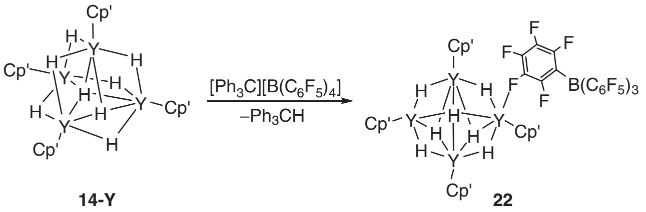
On hydrogenolysis with H_2, the half-sandwich rare earth dialkyl complexes **1f** can be transformed into a new class of tetranuclear octahydride complexes of a general formula $[\{Ln(C_5Me_4SiMe_3)(\mu\text{-}H)_2\}_4(thf)_n]$ (**14-Sc**: Ln = Sc, $n = 0$; **14-Y**: Ln = Y, $n = 0$, 1, 2; and **14-Ln**: Ln = Gd, Dy, Ho, Er, Tm, Lu; $n = 1$), which can be viewed as being the result of a self-assembly of the dihydride units "$(C_5Me_4SiMe_3)LnH_2$" through "intramolecular" Ln–H bonding interactions (Scheme 35).[2c,31] A unique 4-coordinate hydrogen atom is



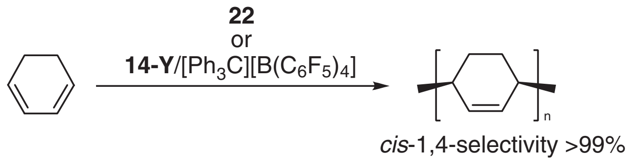
Scheme 35. Synthesis and representative reactions of rare-earth polyhydride complexes.

found at the center of the tetrahedron by X-ray and neutron diffraction analyses and computational studies, when the THF ligand number is less than two. These hydride clusters are soluble in common organic solvents such as THF, toluene, and hexane, and can maintain their tetranuclear framework in solution. The polyhydride complexes exhibit unique and high reactivity toward various unsaturated substrates, such as hydrogenation of the C–N triple bond of a nitrile compound into the C–N single bond,[31c,31e] reduction of carbon dioxide (CO_2) into a methylene diolate species,[31d] deoxygenative C–C coupling of carbon monoxide (CO) into ethylene,[31g] and reduction of metal-coordinated carbon monoxide (CO) into a methyl group.[31i] Some representative examples are shown in Scheme 35.

The reaction of the neutral yttrium hydride cluster $[\{Y(C_5Me_4SiMe_3)(\mu\text{-}H)_2\}_4]$ (**14-Y**) with an equimolar amount of $[Ph_3C][B(C_6F_5)_4]$ affords the structurally characterizable cationic polyhydride complex $[Y_4(C_5Me_4SiMe_3)_4H_7][B(C_6F_5)_4]$ (**22**), in which a direct bonding interaction between the $[Y_4(C_5Me_4SiMe_3)_4H_7]^+$ cation and the $[B(C_6F_5)_4]^-$ anion via a Y–F bond is observed (Scheme 36).[32] This is the first example of a well-defined, cationic hydrido rare earth metal complex. The cationic hydride cluster **22** or the combination of **14-Y** and $[Ph_3C][B(C_6F_5)_4]$ shows moderate activity for the syndiospecific polymerization of styrene and regio- and stereospecific *cis*-1,4-polymerization of 1,3-cyclohexadiene (Scheme 37), in contrast with the reactions of the neutral hydride **14-Y** with styrene and 1,3-cyclohexadiene, which give only the 1:1 addition products **15** and **16**, respectively (Scheme 35).



Scheme 36. Synthesis of a cationic yttrium polyhydride complex.



Scheme 37. *cis*-1,4-Selective polymerization of cyclohexadiene by a cationic yttrium polyhydride complex.

5. Conclusion

This work has demonstrated that half-sandwich rare earth metal alkyl and hydride complexes bearing mono(cyclopentadienyl) or related monoanionic ligands can show unique reactivity in various chemical transformations. Treatment of the dialkyl complexes with an equivalent of a borate compound such as $[Ph_3C][B(C_6F_5)_4]$ or $[PhMe_2NH][B(C_6F_5)_4]$ has afforded easily the corresponding cationic monoalkyl species which show unprecedented activity and selectivity for the polymerization and copolymerization of a variety of olefins. The half-sandwich rare earth metal alkyl complexes bearing the silylene-linked cyclopentadienyl–amido ligands have shown unique activity and selectivity for various coupling reactions such as the catalytic dimerization of terminal alkynes, cross-coupling of terminal alkynes with isocyanides, and addition of terminal alkyne C–H, amine N–H, and phosphine P–H bonds to carbodiimides. The hydrogenolysis of the half-sandwich rare earth dialkyl complexes has generated a new family of well defined, extremely reactive polyhydride complexes, thus opening a new frontier in rare earth metal hydride chemistry. A further exciting and prosperous future in this area can be reasonably expected.

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