

Rare earth metal complexes that contain linked amido-cyclopentadienyl ligands: *ansa*-metallocene mimics and “constrained geometry” catalysts

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A survey of group 3 metal complexes that contain a linked amido-cyclopentadienyl ligand is given. Originally designed as *ansa*-metallocene analogues for the development of single-component olefin polymerization catalysts, variations in the metals and ligand substituents have allowed the synthetic access to new rare earth metal complexes including olefin polymerization initiators, divalent complexes and heterobimetallic metallocenes. The linked amido-cyclopentadienyl ligands have made half-sandwich complexes of group 3 metals accessible in a more systematic manner and provided a better understanding of the electronic and steric constraints of chelating ligands for the larger rare earth metal centres.

1 Introduction

The organometallic chemistry of the group 3 metals including the lanthanides (rare earth metals) has greatly benefited from

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Jun Okuda

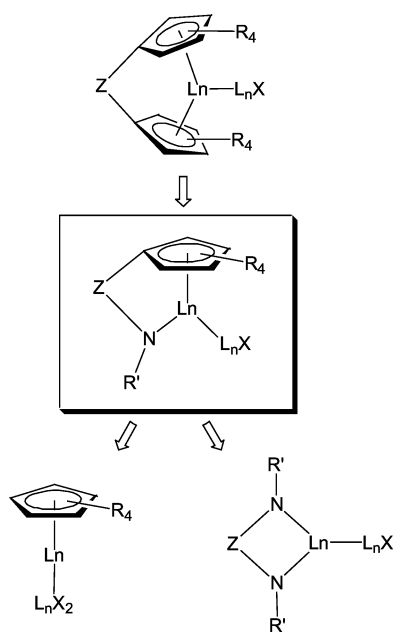
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the introduction of cyclopentadienyl and pentamethylcyclopentadienyl ligands.¹ The metallocene ligand framework occupying six metal orbitals and generating a well-defined reaction site of three frontier orbitals within the wedge has allowed the structural, reactivity and catalytic patterns of group 3 organometallic complexes to be established swiftly.² Lagging far behind are the half-sandwich complexes of these elements, not unexpectedly due to considerable synthetic difficulties as a result of the reduced steric shielding of the extremely Lewis acidic/electrophilic rare earth metal centres.³ One can, however, expect a fairly rich chemistry for lanthanide half-sandwich complexes, once the synthetic obstacles are overcome and the structural principles are systematized. One important step was the design of a chelating ligand [C₅R₄ZX] based on one cyclopentadienyl moiety C₅R₄ linked by a group Z to a pendant one-electron (or monoanionic) donor X.^{4,5} When such a bidentate ligand is introduced into the coordination sphere of a rare earth metal, a fairly well-controlled reaction site is created and the reactivity can be systematically investigated.

In the late 1980s Bercaw and Shapiro introduced the first complexes of bridged amido-cyclopentadienyl ligands⁶ in the context of developing single-component olefin polymerization catalysts. As electronically more unsaturated and sterically more accessible analogues of *ansa*-scandocene complexes, precursors for complexes of the type [Sc(η⁵:η¹-C₅Me₄SiMe₂N^tBu)X] (X = H, alkyl) were synthesized, and in fact shown to exhibit much higher reactivity towards α -olefins than the *ansa*-scandocenes [Sc(η⁵:η¹-C₅Me₄SiMe₂C₅Me₄)X].⁶ Iron and titanium complexes of the sterically demanding derivative of this ligand [(C₅H₃^tBu)SiMe₂N^tBu] were synthesized shortly thereafter.⁷ Based on these bridged amido-cyclopentadienyl ligands, the research laboratories of Dow Chemical and Exxon Chemical independently developed⁸ so-called “constrained geometry” catalysts of group 4 metals, including [Ti(η⁵:η¹-C₅Me₄SiMe₂N^tBu)Me]⁺, which has become one of the most versatile and industrially important single-site olefin polymerization catalysts.⁹

The linked amido-cyclopentadienyl ligand system [C₅R₄-ZNR'] constitutes an (L₃X₂)-type or eight-electron ligand (if the NR' group is treated as an LX-type three-electron donor) and can be conceived as a hybrid between a ten-electron *ansa*-bis(cyclopentadienyl) ligand and a chelating six-electron diamido ligand system (Scheme 1).¹⁰ It allows independent variation of all three substituent groups. Apart from the extensive variation of the ring substituent pattern C₅R₄, well known from zirconocene chemistry,¹¹ the bridge Z and the amido-substituent R' can also be broadly varied. In principle, therefore, a vast number of variations are possible. Those frequently reported in the literature for group 3 metal complexes and mentioned in this article are compiled in Chart 1.

In this article, the group 3 metal complexes with a linked amido-cyclopentadienyl ligand [Ln(η⁵:η¹-C₅R₄ZNR')XL_n] are described systematically, with some emphasis on their use as electronically and sterically more unsaturated catalysts. The structural types commonly encountered are derived from



Scheme 1

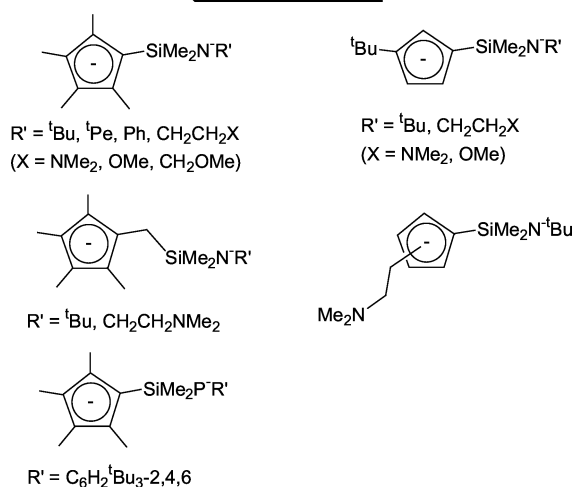
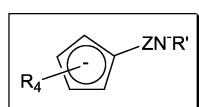


Chart 1

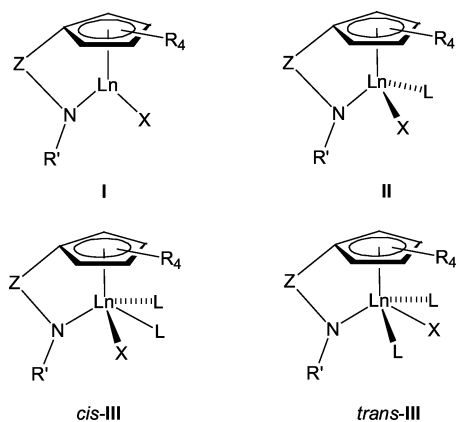


Chart 2

piano-stool configurations and are listed with increasing coordination/valence electron number in Chart 2. The structure for the dinuclear complexes are shown in Chart 3, where *cis* and *trans* refer to the relative arrangement of the cyclopentadienyl moieties and *homo* and *hetero* refer to the relative chiralities of the metal centres.

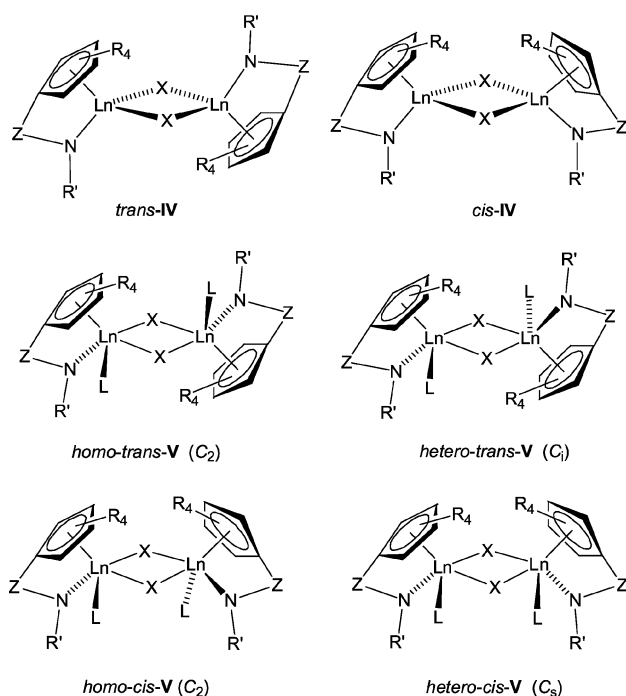
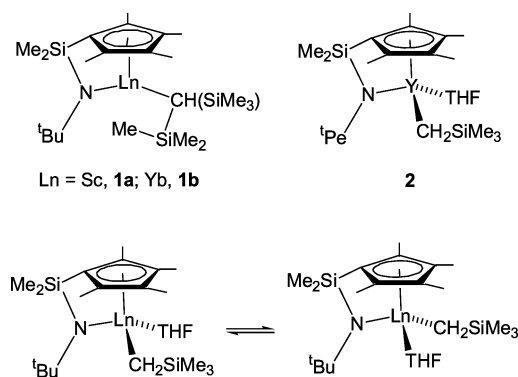


Chart 3

2 Hydrocarbyl complexes

2.1 Alkyl complexes

Group 3 metal alkyl complexes that contain a linked amido-cyclopentadienyl ligand are listed in Table 1 and two representative examples are depicted in Scheme 2. The Lewis base-free scandium bis(trimethylsilyl)methyl complex $[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{-SiMe}_2\text{N}^t\text{Bu})\{\text{CH}(\text{SiMe}_3)_2\}]$ (**1a**) was obtained by salt metathesis between the scandium chloro complex $[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\text{Cl}]_x$ and $\text{Li}\{\text{CH}(\text{SiMe}_3)_2\}$.^{6b} Analogous lutetium and ytterbium complexes $[\text{Ln}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\{\text{CH}(\text{SiMe}_3)_2\}]$ ($\text{Ln} = \text{Yb}$, **1b**, Lu) were synthesized by alkane elimination starting from the lanthanide tris(alkyl) $[\text{Ln}\{\text{CH}(\text{SiMe}_3)_2\}_3]$ and the linked amino-cyclopentadiene under forcing conditions.¹² The single-crystal X-ray diffraction study of the ytterbium complex **1b** shows a pseudo-trigonal configuration with an agostic $\text{Yb} \cdots \text{Me-Si}$ contact, a feature also commonly observed in metallocene derivatives $[\text{Ln}(\eta^5\text{-C}_5\text{R}_5)_2\{\text{CH}(\text{SiMe}_3)_2\}]$.¹³



Scheme 2

The trimethylsilylmethyl complexes $[\text{Ln}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{-SiMe}_2\text{N}^t\text{Bu})(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ ($\text{Ln} = \text{Y}$, Tb, Er, Yb, Lu) were obtained by alkane elimination starting from $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$ under mild conditions in high yields.^{14,15} There is, however, a trade-off between the smooth complexation and the use of the THF adduct $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$. The THF

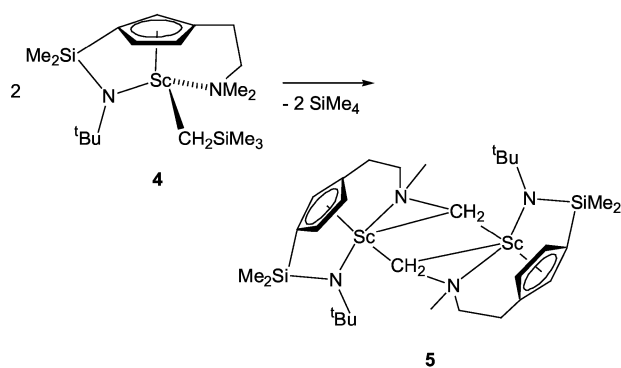
Table 1 Hydrocarbyl complexes

Compound	Structural type	Method of preparation	Characterization	Ref.
[Sc(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu){CH(SiMe ₃) ₂ }] 1a	I	Salt metathesis	¹ H NMR, IR	6b
[Ln(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu){CH(SiMe ₃) ₂ }] 1b ; Ln = Yb, Lu	I	Alkane elimination	X-Ray (Ln = Yb), ¹ H, ¹³ C NMR (Ln = Lu), MS	12
[Y(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ NR')(CH ₂ SiMe ₃)(THF)], R' = ^t Bu, ^t Pe, ^a 2	II	Alkane elimination	X-Ray (R = ^t Pe), ¹ H, ¹³ C, ²⁹ Si NMR	14
[Ln(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu)(CH ₂ SiMe ₃)(THF)], Ln = Yb, Lu	II	Alkane elimination	¹ H, ¹³ C, ²⁹ Si NMR (Ln = Lu)	15
[Y(η^5 : η^1 -C ₅ Me ₄ CH ₂ SiMe ₂ N ^t Bu)(CH ₂ SiMe ₃)(THF)]	II	Alkane elimination	X-Ray, ¹ H, ¹³ C, ⁸⁹ Y NMR	17
[Y(η^5 : η^1 -C ₉ H ₆ SiMe ₂ N ^t Bu)(CH ₂ SiMe ₃)(THF)]	II	Alkane elimination	¹ H, ¹³ C, ²⁹ Si NMR,	14b
[Y(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu)(CH ₂ SiMe ₃)(DME)]	III	Ligand exchange	¹ H, ¹³ C NMR	16
[Sc{ η^5 : η^1 : η^1 -C ₅ H ₃ (SiMe ₂ N ^t Bu)(CH ₂ CH ₂ NMe ₂)}(CH ₂ SiMe ₃) 3]	II	Alkane elimination	¹ H, ¹³ C NMR	18
[Y(η^5 : η^1 : η^1 -C ₅ Me ₄ CH ₂ SiMe ₂ NCH ₂ CH ₂ NMe ₂)-(CH ₂ SiMe ₃)(THF)]	III	Alkane elimination	X-Ray, ¹ H, ¹³ C NMR	19b
[Sc(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu)(PMe ₃) ₂ (μ - η^2 : η^2 -C ₂ H ₄) 7]	V	Alkane elimination	X-Ray (<i>trans</i>), ¹ H, ¹³ C, ³¹ P NMR	6b
[Sc(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu)(μ -(CH ₂) _n CH ₃) ₂ , n = 2, 8 ; 3]	IV	Insertion	X-Ray (n = 2, <i>trans</i>), ¹ H, ¹³ C NMR, IR	6b
[Sc(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu)(PMe ₃){CH ₂ CHMe(CH ₂) ₂ Me}]	II	Insertion	¹ H, ¹³ C, ³¹ P NMR, IR	6b
[Y(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ NR')(μ -CH ₂ CH ₂ R) ₂ , R' = ^t Bu, ^t Pe; R = ⁿ Et, 10 ; ⁿ Pr, ⁿ Bu]	IV	Insertion	X-Ray (<i>trans</i>), ¹ H, ¹³ C, ²⁹ Si NMR	20
[Y(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu)(CH ₂ CH ₂ R)(THF)], R = Et, ⁿ Bu]	II	Ligand exchange	¹ H, ¹³ C, ²⁹ Si NMR	20
[Y(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu)(CH ₂ CH ₂ R)(DME)], R = Et, 11 ; ⁿ Bu]	III	Ligand exchange	X-Ray (L = DME, <i>cis</i>), ¹ H, ¹³ C, ²⁹ Si NMR	20
[Yb(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu)(μ -CH ₂ CH ₂ ⁿ Bu)] ₂	IV	Insertion	X-Ray (<i>trans</i>)	20
[Sc(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu)(PMe ₃){CHPh(CH ₂) ₃ Ph}] 12	II	Insertion	¹ H, ¹³ C, ³¹ P NMR, IR	6b
[Y(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ NR')(CHMePh)(THF)], R' = ^t Bu, ^t Pe]	II	Insertion	¹ H, ¹³ C, ²⁹ Si NMR	14b
[Y(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Pe){CHMe(C ₆ H ₄ ^t Bu-4)}(THF)] 13	II	Insertion	X-Ray, ¹ H, ¹³ C, ²⁹ Si NMR	14b
[Y(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu){CHMe(C ₆ H ₄ OMe-4)}(THF)]	II	Insertion	¹ H, ¹³ C, ²⁹ Si NMR	14b
[Y(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu){CHMe(C ₆ H ₃ OMe-2,4)}(THF)]	II	Insertion	¹ H, ¹³ C, ²⁹ Si NMR	14b
[Y(η^5 : η^1 -C ₅ Me ₄ CH ₂ SiMe ₂ N ^t Bu)(CHMePh)(THF)]	II	Insertion	X-Ray, ¹ H, ¹³ C, ⁸⁹ Y NMR	17
[Y(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu)(μ -C ₄ H ₃ O)] ₂ , 16	(IV)^b	Alkane elimination	X-Ray, ¹ H, ¹³ C, ²⁹ Si NMR	16a,21
[Y(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu)(μ -C ₄ H ₃ O)] ₂	(IV)^b	Alkane elimination	¹ H, ¹³ C, ²⁹ Si NMR	21
[Y(η^5 : η^1 -C ₅ Me ₄ CH ₂ SiMe ₂ N ^t Bu)(C ₄ H ₃ O)(THF)]	II	Alkane elimination	X-Ray, ¹ H, ¹³ C, ⁸⁹ Y NMR	16a
[Y(η^5 : η^1 -C ₅ Me ₄ CH ₂ SiMe ₂ N ^t Bu)(μ -C ₄ H ₃ O)] ₂	(IV)^b	Alkane elimination	¹ H, ¹³ C, ⁸⁹ Y NMR	16a
[Y(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu){ μ -2-(OC ₄ H ₇ Me-5)}] ₂	(IV)^b	Alkane elimination	¹ H, ¹³ C NMR	16a
[Y(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu)(2-C ₄ H ₃ O)(DME)]	III	Alkane elimination	X-Ray, ¹ H, ¹³ C NMR	16a
[Y(η^5 : η^1 -C ₅ Me ₄ CH ₂ SiMe ₂ N ^t Bu)(2-C ₄ H ₄ OMe)(THF)]	<i>trans</i> - III	Alkane elimination	X-Ray, ¹ H, ¹³ C NMR	16b
[Li(THF)] ₂ [Y(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ NCH ₂ CH ₂ X)(o-C ₆ H ₄ CH ₂ NMe ₂ -(μ -Cl))] ₂ , X = NMe ₂ , OMe, CH ₂ OMe	III	Salt metathesis	X-Ray (X = OMe), ¹ H, ¹³ C, ²⁹ Si NMR	22

^a ^tPe = CMe₂Et. ^b LX-type bridging ligand.

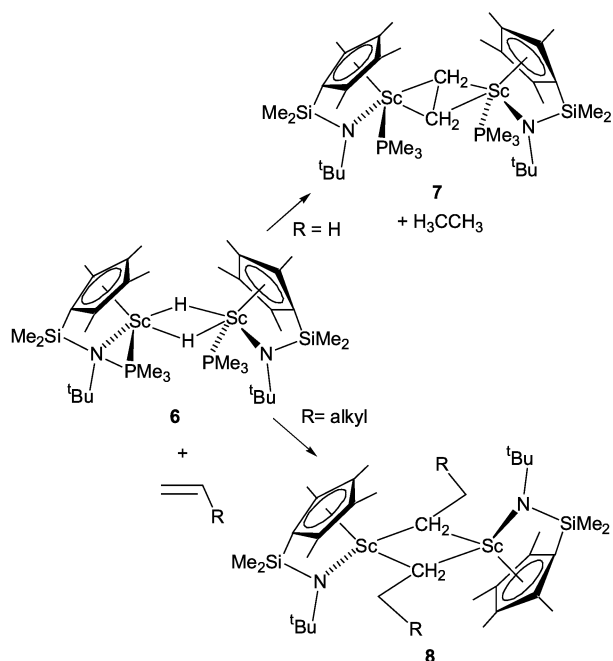
ligand in [Ln(η^5 : η^1 -C₅Me₄SiMe₂N^tBu)(CH₂SiMe₃)(THF)] is labile on the NMR timescale, more so for the larger yttrium than for the lutetium complex, although the dissociation constants are virtually the same (K_{diss} (25 °C) \approx 0.1). This lability of THF allows these complexes to be considered as “masked” forms of the 12-electron complex [Ln(η^5 : η^1 -C₅Me₄SiMe₂N^tBu)R]. By the same method, the crystallographically characterized complex [Y(η^5 : η^1 -C₅Me₄SiMe₂N^tPe)(CH₂SiMe₃)(THF)] (**2**) and the indenyl complex [Y(η^5 : η^1 -C₉H₆SiMe₂N^tBu)(CH₂SiMe₃)(THF)] were obtained.^{14b} The yttrium complex reacts with DME to give the substitutionally less labile 16-electron complex [Y(η^5 : η^1 -C₅Me₄SiMe₂N^tBu)(CH₂SiMe₃)(DME)].¹⁶ The reaction of the amino-cyclopentadiene (C₅Me₄H)CH₂SiMe₂NH^tBu that contains the longer bridge with [Y(CH₂SiMe₃)₂(THF)]₂ gave the complex [Y(η^5 : η^1 -C₅Me₄CH₂SiMe₂N^tBu)(CH₂SiMe₃)(THF)] (**3**) which according to X-ray crystallography contains a larger bite angle $\text{Cp}_{\text{cent}}\text{-Y-N}$ of 106.5(7)° compared to 97.1(2)° in **2**.¹⁷

The scandium complex [Sc{ η^5 : η^1 : η^1 -C₅H₃(SiMe₂N^tBu)(CH₂CH₂NMe₂)}(CH₂SiMe₃) (**4**)] was obtained by alkane elimination, from [Sc(CH₂SiMe₃)₂(THF)]₂ with an amino-cyclopentadiene functionalized with an intramolecular donor function.¹⁸ The reaction is completely diastereoselective, since only one pair of enantiomers was formed (in theory, two diastereomeric pairs of enantiomers are possible due to the chiral metal centre and the enantiotopic faces of the ligand). The molecular structure of the thermolysis product [Sc{ η^5 : η^1 : η^1 -C₅H₃(SiMe₂N^tBu){CH₂CH₂NMe(μ -CH₂)}}]₂ (**5**) formed by metalation involving one amino methyl group of the side-chain was determined by X-ray diffraction (Scheme 3).


Scheme 3

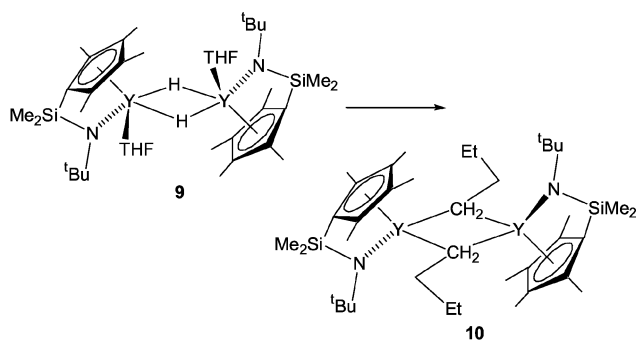
A significant number of alkyl complexes are obtained from insertion reactions of α -olefins with hydrido complexes. The reaction of the scandium hydride [Sc(η^5 : η^1 -C₅Me₄SiMe₂N^tBu)(PMe₃)(μ -H)]₂ (**6**) with 2 equiv. of ethylene generated the unusual ethylene-bridged dimer [Sc(η^5 : η^1 -C₅Me₄SiMe₂N^tBu)(PMe₃)₂(μ - η^2 : η^2 -C₂H₄) (**7**)] besides 1 equiv. of ethane. A single-crystal diffraction study showed an ethylene ligand bridging two [Sc(η^5 : η^1 -C₅Me₄SiMe₂N^tBu)(PMe₃)] fragments. The scandium hydride regioselectively reacted with propene to give the base-free alkyl-bridged dimer [Sc(η^5 : η^1 -C₅Me₄SiMe₂N^tBu)(μ -CH₂CH₂CH₃)]₂ (**8**), which was crystallographically characterized to show a structure of type *trans*-**IV** (Scheme 4).^{6b}

The yttrium hydride [Y(η^5 : η^1 -C₅Me₄SiMe₂N^tBu)(THF)(μ -H)]₂ (**9**) exhibited similar reactivity towards 1-alkenes, afford-

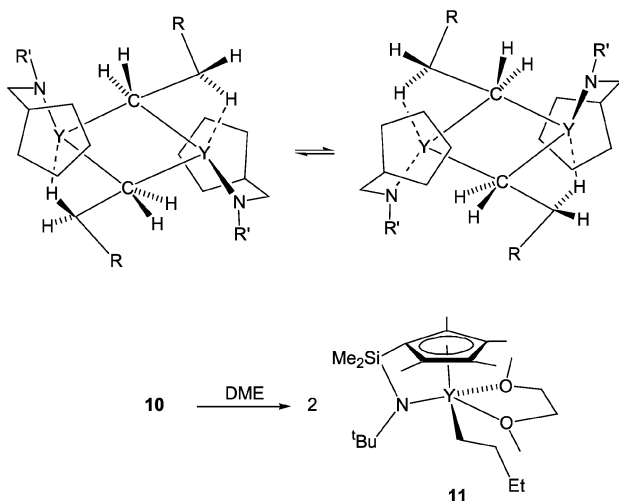


Scheme 4

ing a series of THF-free *n*-alkyl-bridged dimers $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NR}')\{\mu\text{-(CH}_2)_n\text{CH}_3\}]_2$ ($R' = \text{'Bu, 'Pe; } n = 3\text{--}5$). The initially unexpected loss of THF during the insertion of the 1-alkene can be explained by the presence of a dynamic β -agostic interaction of the alkyl chain's hydrogen atoms with the metal centre. Despite the high fluxionality in solution even at lower temperatures (Scheme 5) and disorder problems in the crystals, one of the β -hydrogen atoms of the alkyl group is oriented toward the metal centre, completing the usual pseudo-square-pyramidal configuration, as shown in the crystal



Scheme 5

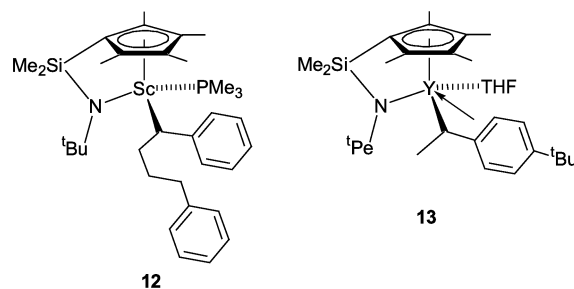


Scheme 6

structure of $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N'Bu})(\mu\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)]_2$ (**10**).²⁰

In the presence of THF a monomer–dimer equilibrium exists for the *n*-alkyl complexes. Although the THF adduct $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N'Bu})\{(\text{CH}_2)_n\text{CH}_3\}(\text{THF})]$ cannot be isolated, the *n*-butyl complex with a DME ligand $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N'Bu})(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)(\text{DME})]$ (**11**) could be crystallographically characterized, and was found to have the *cis*-III-type structure. In solution, this complex behaves fluxionally, with intramolecular exchange of the two oxygen atoms of the DME ligand.²⁰ The reaction of the dimeric hydride **9** with 1,5-hexadiene gave under cyclization the cyclopentylmethyl complex $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N'Bu})\{\text{CH}_2\text{CH}(\text{CH}_2)_4\}(\text{THF})]$.^{14b} Related $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N'Bu})\{\text{CH}_2\text{CH}(\text{CH}_2)_4\}(\text{THF})]$ was characterized by crystallography, confirming the presence of a cyclopentylmethyl group.^{19a}

Styrene reacted with the scandium hydride $[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N'Bu})(\text{PMe}_3)(\mu\text{-H})_2]$ to form orange $[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N'Bu})(\text{PMe}_3)\{\text{CHPh}(\text{CH}_2)_3\text{Ph}\}]$ (**12**) as the result of a primary (1,2) insertion followed by a secondary (2,1) insertion of styrene.^{6b} Contrary to this finding, the related yttrium hydrido complex **9** regioselectively underwent secondary insertion with styrenes with not more than one *ortho*-substituent to give the bright yellow mono(insertion) product (Scheme 6). An X-ray diffraction study of $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N'Pe})\{(\text{CHMe}(\text{C}_6\text{H}_4)\text{'Bu-4})\}(\text{THF})]$ (**13**) confirmed that the insertion occurred in a Markovnikov (2,1)-fashion and that the 1-phenethyl group is η^3 -coordinated. Variable-temperature NMR spectroscopy further revealed fluxional behaviour including THF dissociation, phenyl ring coordination, and rotation about the *ipso*- and α -carbon atom.^{14b} Interaction between the metal and the phenyl ring is not present in the related complex $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N'Bu})\{\text{CHMe}(\text{C}_6\text{H}_5)\}(\text{THF})]$ with a longer link.¹⁷

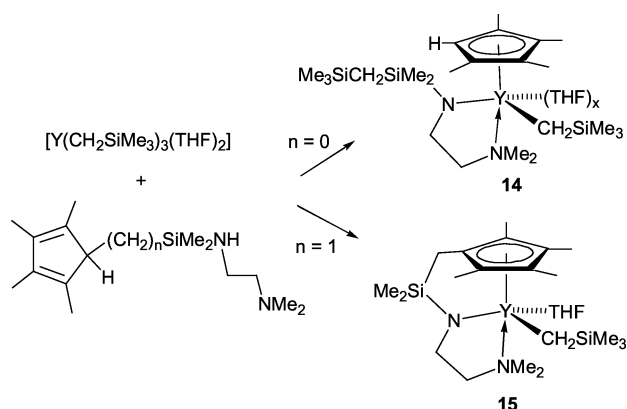


Scheme 6

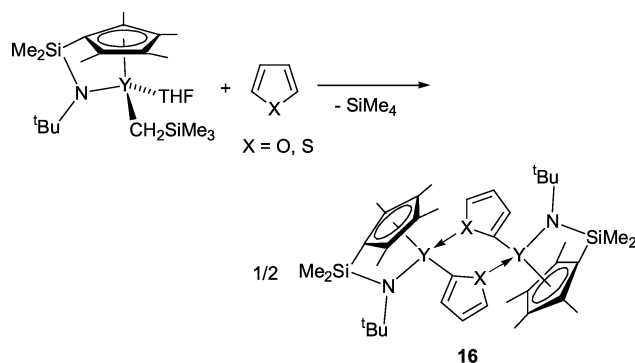
Synthesis of alkyl complexes derived from the tridentate ligand $[\text{C}_5\text{Me}_4\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{X}]$ ($X = \text{NMe}_2, \text{OMe}, \text{CH}_2\text{OMe}$) was hampered by the decomposition of the amino-cyclopentadiene ligand when reacted with $[Y(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$, to give, for instance, the tetramethylcyclopentadienyl complex **14**. The “ate” complex $[\text{Li}(\text{THF})][Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{OMe})(o\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)\text{Cl}]$ along with the related compounds $[\text{Li}(\text{THF})][Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{X})(o\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)(\mu\text{-Cl})]$ ($X = \text{NMe}_2, \text{CH}_2\text{OMe}$) formed by salt metathesis, but does not contain a tridentate ligand as shown by X-ray diffraction.²² The use of the $[\text{C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{NMe}_2]$ ligand eventually allowed the isolation of the alkyl complex $[Y(\eta^5\text{-}\eta^1\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ (**15**) (Scheme 7).^{19b}

2.2 Aryl complexes

The trimethylsilylmethyl yttrium complex $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N'Bu})(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ smoothly underwent σ -bond metathesis reactions with the five-membered heterocycles furan and thiophene (Scheme 8). Excess thiophene gave the sparingly soluble dinuclear 2-thienyl complex $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N'Bu})(\mu\text{-C}_4\text{H}_3\text{S})_2]$ (**16**), soluble only in bases such as THF and



Scheme 7



Scheme 8

pyridine. In agreement with the negative activation entropy and large kinetic isotope effect,²¹ this reaction appears to follow associative pathways, since the DME adducts of the alkyl complex $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{CH}_2\text{SiMe}_3)(\text{DME})]$ do not react with furan and thiophene. The crystal structure determination of the product confirmed a centrosymmetric dimeric structure with the ancillary ligands arranged in a transoidal fashion and two bridging 2-thienyl ligands forming a puckered six-membered ring core.^{16a,21} The related 2-furyl compounds $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\mu\text{-C}_4\text{H}_3\text{O})_2]$ and $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\{\mu\text{-}2\text{-(OC}_4\text{H}_2\text{Me-5)}\}]_2$ were obtained by the same method and characterized by NMR spectroscopy.^{16a,21} The monomeric furyl complex $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(2\text{-C}_4\text{H}_3\text{O})(\text{DME})]$ was crystallographically characterized to have the *cis*-III structure. In contrast to compound with the shorter bridge **16**, the 2-thienyl complex $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}^t\text{Bu})(2\text{-C}_4\text{H}_3\text{S})(\text{THF})]$ was isolated and crystallographically characterized as a monomeric THF adduct

of type II.^{16a} Anisole underwent *ortho*-metalation with **3** to give $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}^t\text{Bu})(2\text{-C}_6\text{H}_4\text{OMe})(\text{THF})]$ with *trans*-III structure.^{16b}

3 Hydrido Complexes

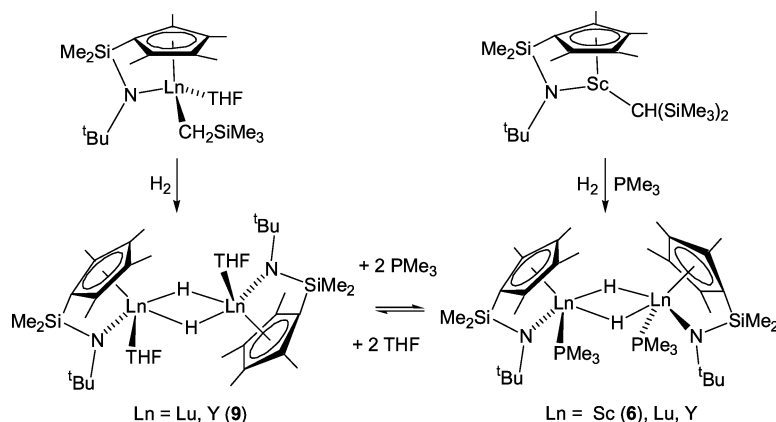
In contrast to the metallocene hydrides¹ and the aryloxy-supported yttrium complex $[Y(\eta^5\text{-C}_5\text{Me}_5)(\text{OC}_6\text{H}_3^t\text{Bu}_2\text{-}2,6\text{-}(\mu\text{-H}))_2]$,²³ the rare earth hydride $[\text{Ln}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{L})(\mu\text{-H})_2]$ containing the linked amido-cyclopentadienyl ligand is not accessible without the presence of a coordinating Lewis base (Table 2).^{6,14,15,17} Hydrogenolysis of $[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\{\text{CH}(\text{SiMe}_3)_2\}]$ in the presence of trimethylphosphine afforded $[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{PMe}_3)(\mu\text{-H})_2]$ (**6**). X-Ray crystal structure determination revealed a homochiral molecule of C_2 -symmetry with *cis*-arranged cyclopentadienyl ligands (*homo-cis* V in Chart 3). The ¹H NMR spectra are consistent with the presence of a single species over the temperature range of -80 to 25 °C, although in the ³¹P NMR spectrum at -66 °C two signals in a 4:1 ratio suggest the presence of diastereomers.

Isostructural yttrium and lutetium hydrides could be isolated by displacement of THF by PMe_3 in $[\text{Ln}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{THF})(\mu\text{-H})_2]$ ($\text{Ln} = \text{Lu}, \text{Y}$, **9**) (Scheme 9).¹⁵ For the lutetium complex, hydrogenolysis of the alkyl $[\text{Lu}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ in the presence of PMe_3 is also feasible. In the ³¹P NMR spectrum at -60 °C the lutetium complex gives rise to one signal, whereas two doublets in a 2 : 3 ratio are recorded for the yttrium complex, consistent with the presence of two diastereomers at lower temperatures.¹⁵

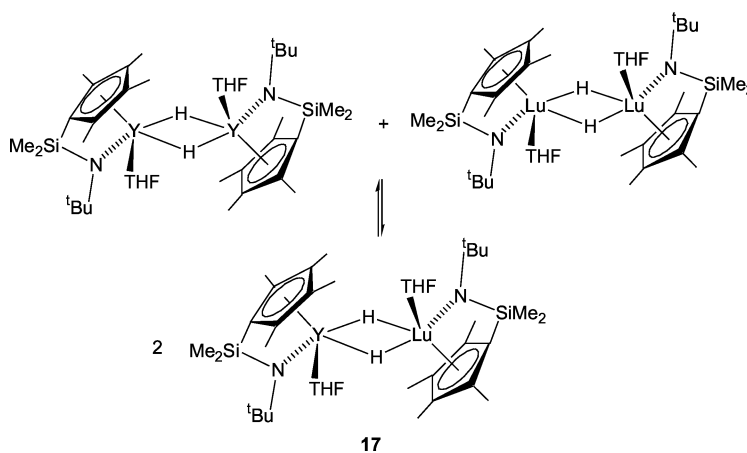
A series of hydrido complexes with THF as Lewis-base $[\text{Ln}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NR}')(\text{THF})(\mu\text{-H})_2]$ ($\text{Ln} = \text{Y}, \text{Yb}, \text{Lu}$; $\text{R}' = ^t\text{Bu}, ^t\text{Pe}$) was obtained by hydrogenolysis of the alkyls $[\text{Ln}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NR}')(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ with dihydrogen or phenylsilane at 25 °C.^{14,15} In contrast to the PMe_3 adducts, the THF complexes were shown by X-ray structural analysis to be C_2 -symmetric homochiral molecules with *trans* configured ancillary ligands (*homo-trans* V). At least within the series containing the metals scandium, lutetium, and yttrium, the nature of the Lewis base rather than the size of the metal centre seem to determine the configuration.¹⁵ ¹H Variable-temperature NMR spectra of the lutetium and yttrium complexes revealed dynamic behaviour as a result of fast dissociation of THF ligands. Furthermore, the dissociation into monomers was suggested by the formation of the heterobimetallic complex $[\text{LuY}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})_2(\text{THF})_2(\mu\text{-H})_2]$ (**17**) within 5 min, when equimolar amounts of the lutetium and yttrium hydrides were mixed in C_6D_6 at room temperature (Scheme 10).¹⁵

Table 2 Hydrido complexes

Compound	Structural type	Method of preparation	Characterization	Ref.
$[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{PMe}_3)(\mu\text{-H})_2]$, 6	V	Hydrogenolysis	X-Ray (<i>homo-cis</i>), ¹ H, ¹³ C, ³¹ P NMR, IR	6a,b
$[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{PMe}_3)(\mu\text{-H})_2]$	V	Ligand exchange	X-Ray (<i>homo-cis</i>), ¹ H, ¹³ C, ³¹ P NMR	15
$[\text{Lu}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{PMe}_3)(\mu\text{-H})_2]$	V	Hydrogenolysis	X-Ray (<i>homo-cis</i>), ¹ H, ¹³ C, ²⁹ Si, ³¹ P NMR	15
$[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NR}')(\text{THF})(\mu\text{-H})_2]$, $\text{R}' = ^t\text{Bu}$, 9 ; ^tPe	V	Hydrogenolysis	X-Ray ($\text{R} = ^t\text{Bu}$, <i>homo-trans</i>), ¹ H, ¹³ C, ²⁹ Si, ⁸⁹ Y ($\text{R} = ^t\text{Bu}$) NMR	14
$[\text{Yb}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NR}')(\text{THF})(\mu\text{-H})_2]$, $\text{R}' = ^t\text{Bu}, ^t\text{Pe}$	V	Hydrogenolysis	X-Ray ($\text{R} = ^t\text{Pe}$, <i>homo-trans</i>), ¹ H NMR	15
$[\text{Lu}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NR}')(\text{THF})(\mu\text{-H})_2]$, $\text{R}' = ^t\text{Bu}, ^t\text{Pe}$	V	Hydrogenolysis	¹ H, ¹³ C, ²⁹ Si NMR	15
$[\text{Y}(\eta^5\text{-}\eta^1\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)(\mu\text{-H})_2]$, 18	V	Hydrogenolysis	X-Ray (<i>homo-trans</i>), ¹ H, ¹³ C, NMR	19b
$[\text{Sc}\{\eta^5\text{-}\eta^1\text{-}\eta^1\text{-C}_5\text{H}_3(\text{SiMe}_2\text{N}^t\text{Bu})(\text{CH}_2\text{CH}_2\text{NMe}_2)\}(\mu\text{-H})_2]$	V	Hydrogenolysis	X-Ray, ¹ H, ¹³ C NMR	18
$[\text{Y}_2(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NR}')_2(\text{THF})_2(\mu\text{-H})(\mu\text{-Cl})]$, $\text{R}' = ^t\text{Bu}, ^t\text{Pe}$	V	Ligand scrambling	¹ H, ¹³ C, ²⁹ Si, ⁸⁹ Y NMR ($\text{R} = ^t\text{Bu}$)	15

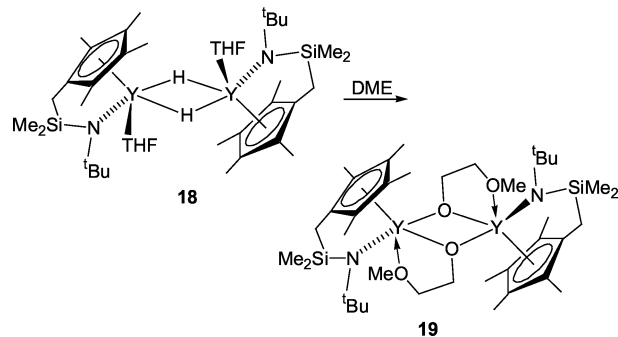


Scheme 9



Scheme 10

Hydrogenolysis of the alkyl $[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}^t\text{Bu})(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ with a CH_2 group added between the amido and the tetramethylcyclopentadienyl moieties in the bridge, also resulted in clean formation of the homochiral dimer $[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}^t\text{Bu})(\text{THF})(\mu\text{-H})_2]$ (**18**). X-Ray crystallography showed that the dimeric structure is intermediate between a *cis* and a *trans* arrangement of the ancillary ligands. In solution below -60°C the triplet decoalesces to three triplets in a ratio of 1 : 2.4 : 1, which are assigned to the C_2 -symmetric homochiral dimer and the centrosymmetric heterochiral dimer.¹⁷ Reaction of this hydride with DME resulted in the formation of a methoxyethanolato complex, $[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}^t\text{Bu})(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]$ (**19**), documenting the extreme electrophilicity of the monomeric hydride species $[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}^t\text{Bu})(\text{H})]$ (Scheme 11).^{19a} An example of a THF-free hydrido complex $[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)(\mu\text{-H})_2]$ was obtained by hydrogenolysis of the alkyl **15** and shown to have a distorted *homo-trans* configuration.^{19b}



Scheme 11

The scandium hydrido complex $[\text{Sc}\{\eta^5\text{-}\eta^1\text{-C}_5\text{H}_3(\text{SiMe}_2\text{N}^t\text{Bu})(\text{CH}_2\text{CH}_2\text{NMe}_2)\}(\mu\text{-H})_2]$ with the tridentate ligand $[\text{C}_5\text{H}_3(\text{SiMe}_2\text{N}^t\text{Bu})(\text{CH}_2\text{CH}_2\text{NMe}_2)]$ that contains both an amido group and a pendant amine donor was obtained upon hydrogenolysis of the alkyl $[\text{Sc}\{\eta^5\text{-}\eta^1\text{-C}_5\text{H}_3(\text{SiMe}_2\text{N}^t\text{Bu})(\text{CH}_2\text{CH}_2\text{NMe}_2)\}(\text{CH}_2\text{SiMe}_3)]$ in benzene at 70°C under elevated pressure.¹⁸ Due to the enantiotopic faces of the cyclopentadienyl ligand, complexation to the chiral metal centre results in four diastereomers, two of which are observed by ^1H and ^{13}C NMR spectroscopy. One of the two isomers was characterized by X-ray crystallography and found to be the heterochiral C_2 -symmetric dimer with *trans* arranged cyclopentadienyl units. The two isomers interconvert slowly, indicating a monomeric hydride in equilibrium with the dimers.

Scrambling reactions of the chloro complexes $[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NR}')(\text{THF})(\mu\text{-Cl})_2]$ ($\text{R}' = \text{'Bu, 'Pe}$) and the hydrido complexes $[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NR}')(\text{THF})(\mu\text{-H})_2]$ resulted in the formation of the mixed μ -hydrido- μ -chloro complexes $[\text{Y}_2(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NR}')_2(\text{THF})_2(\mu\text{-H})(\mu\text{-Cl})]$ that according to crystallography is isotypical to the dimeric hydride (*homo-trans V*).¹⁵

4 Pnictogenido, chalcogenido and halo complexes

Only a limited number of complexes of this class is known (Table 3), some of them mentioned in the following section, since they are derived by oxidation of the divalent complexes. A series of bis(trimethylsilyl)amido complexes containing a linked amido-cyclopentadienyl ligand $[\text{Ln}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\{\text{N}(\text{SiMe}_3)_2\}]$ ($\text{Ln} = \text{Y,}^{24} \text{Nd, Sm, Lu}^{12}$) was obtained by amine elimination starting from $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3]$ and the linked amino-cyclopentadiene (Scheme 12). For yttrium and samarium complexes **20a** and **20b** they were crystallographically characterized. In these complexes the π -donation by the two amido

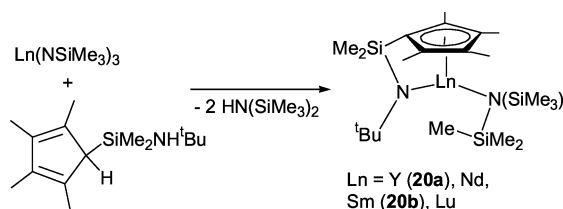
Table 3 Pnicogenido, chalcogenido and halo complexes

Compound	Structural type	Method of preparation	Characterization	Ref.
$[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\{\text{N}(\text{SiMe}_3)_2\}]$, 20a	I	Aminolysis	X-Ray, ^1H , ^{13}C NMR	24
$[\text{Ln}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\{\text{N}(\text{SiMe}_3)_2\}]$, Ln = Nd, Sm, 20b ; Lu	I	Aminolysis	X-Ray (Ln = Sm), ^1H , ^{13}C (Ln = Lu) NMR, MS	12
$[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{NC}_4\text{H}_4)_x]$		Alkane elimination	^1H , ^{13}C , ^{29}Si NMR	21
$[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{NC}_4\text{H}_4)(\text{DME})]$	III	Alkane elimination	X-Ray (<i>cis</i>), ^1H , ^{13}C NMR	16
$[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}^t\text{Bu})(\text{NC}_4\text{H}_4)_x]$		Alkane elimination	^1H , ^{13}C , ^{89}Y NMR	16
$[Yb_2(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh})_2(\mu\text{-}\eta^3\text{-}\eta^2\text{-N}_2\text{Ph}_2)(\text{THF})]$		Oxidation	X-Ray	25
$[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}^t\text{Bu})(\mu\text{-OCH}_2\text{CH}_2\text{OMe-}\kappa\text{O})]_2$, 19	V	Alkane elimination	X-Ray (<i>trans</i>), ^1H , ^{13}C NMR	19a
$[Yb(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh})(\text{THF})_2(\text{OC}_{13}\text{H}_8)]^a$, 25	III	Oxidation	X-Ray (<i>trans</i>)	25
$[Yb(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh})(\text{THF})_2(\mu\text{-O}_2\text{C}_6\text{H}_{16})^b$, 26	II		X-Ray	25
$[\text{Sm}\{\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{P}(\text{C}_6\text{H}_2\text{Bu}_3\text{-}2,4,6)\}(\text{THF})_2(\mu\text{-OCPh}_2)]$	III	Oxidation	X-Ray, ^1H NMR	26
$[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\text{Cl}]_x$		Salt metathesis	^1H NMR, IR	6b
$[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NR}')(\text{THF})(\mu\text{-Cl})_2]$, R' = ^tBu , ^tPe	V	Alkane elimination	X-Ray (R = ^tPe , <i>hetero-trans</i>), ^1H , ^{13}C , ^{29}Si NMR	15
$[\text{Sm}\{\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{P}(\text{C}_6\text{H}_2\text{Bu}_3\text{-}2,4,6)\}(\text{THF})(\mu\text{-I})_2]$	V	Oxidation	X-Ray (<i>hetero-trans</i>), ^1H NMR	26

^a OC₁₃H₈: Biphenyl-2,2'-diyl ketyl. ^b OC₂₆H₁₆: Bis(biphenyl-2,2'-diyl)pinacolato.

Table 4 Divalent complexes

Compound	Method of preparation	Characterization	Ref.
$[Yb(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh})(\text{THF})_3]$, 23	Aminolysis	X-Ray, ^1H NMR	25
$[Yb(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh})(\text{THF})_2]$, 24	Ligand elimination	X-Ray, ^1H NMR	25
$[\text{Sm}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh})(\text{THF})_n]$, n = 0, 1	Aminolysis	^1H NMR	25
$[Yb(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NHR})(\text{L})_n(\mu\text{-I})_2]$, R = Et, allyl, ^nPr , ^tBu ; L = THF, n = 2; L = DME, n = 1	Salt metathesis	X-Ray (R = ^tBu , L = THF), ^1H , ^{13}C NMR	28
$[Yb(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{THF})]$	Aminolysis	^1H NMR, IR	29
$[\text{Li}_0.5][Yb(\mu\text{-}\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}^t\text{Bu})(\text{THF})_2(\mu\text{-I})_0.5]$, 22	Salt metathesis	X-Ray, ^1H , ^{13}C NMR	28
$[\text{Sm}\{\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{P}(\text{C}_6\text{H}_2\text{Bu}_3\text{-}2,4,6)\}(\text{DME})_2]$	Ligand exchange	X-Ray, ^1H NMR	26
$[\text{Sm}\{\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{P}(\text{C}_6\text{H}_2\text{Bu}_3\text{-}2,4,6)\}(\text{HMPA})_2]$	Ligand exchange	X-Ray, ^1H NMR	26
$[\text{Ln}\{\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{P}(\text{C}_6\text{H}_2\text{Bu}_3\text{-}2,4,6)\}(\text{THF})_n]$, Ln = Sm, n = 3, 1, Ln = Yb, n = 3, 0	Salt metathesis	X-Ray (Ln = Yb, n = 3), ^1H NMR	26

**Scheme 12**

ligands alleviates the electron deficiency of the formally 10-electron valence shell.²⁴ Yttrium pyrrolo complexes $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{NC}_4\text{H}_4)_x]$ and $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}^t\text{Bu})(\text{NC}_4\text{H}_4)_x]$ were obtained by aminolysis of the trimethylsilylmethyl complex, and the DME adduct $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\eta^1\text{-NC}_4\text{H}_4\text{-}\kappa\text{N})(\text{DME})]$ was crystallographically shown to have a four-legged piano-stool geometry (*cis*-**III**).^{16,21}

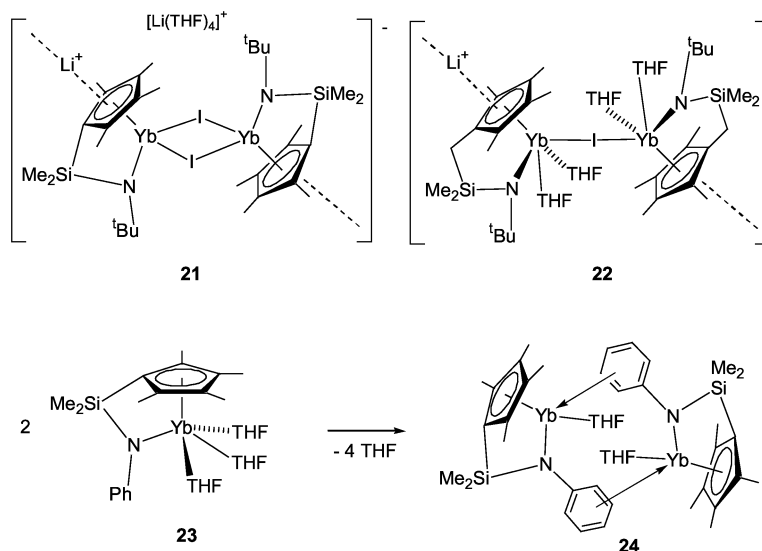
The reaction of $\text{Li}_2(\text{C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})$ with $\text{ScCl}_3(\text{THF})_3$ gave non-stoichiometric $[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\text{Cl}(\text{LiCl})(\text{THF})_x]$ ^{6b} (which probably contains an “ate” complex $[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\text{Cl}_2]^-$) from which LiCl and THF could be removed to give the chloro complex $[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\text{Cl}]$. The chloro-bridged dimers $[Y(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NR})(\text{THF})(\mu\text{-Cl})_2]$ (R = ^tBu , ^tPe) were obtained by alkane elimination from the *in situ* prepared “ $Y(\text{CH}_2\text{SiMe}_2)_2\text{Cl}(\text{THF})_x$ ”; and the linked amino-cyclopentadiene. X-Ray crystallography of the *tert*-pentylamido derivative showed a C_1 -symmetric heterochiral dimer (*hetero-trans* **V**).¹⁵

5 Divalent samarium and ytterbium complexes

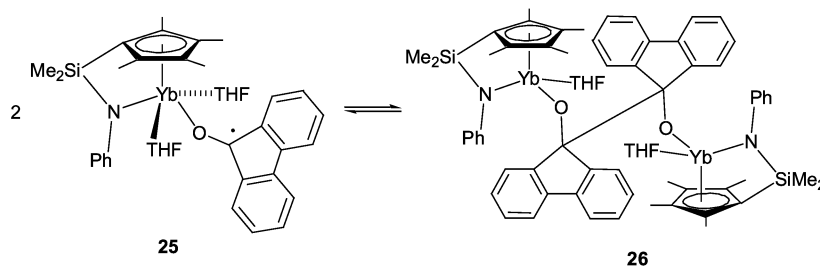
Linked cyclopentadienyl-pnicogenido complexes of the divalent lanthanides have become accessible only recently by

salt metathesis and amine elimination (Table 4).^{25–29} A critical feature, discovered by Hou *et al.*, is that only phenylamido-based ligands allow a straightforward entry into complexes that have the half-sandwich structure.^{25–27} Thus, the reaction of the alkali metal *tert*-butylamido-cyclopentadienide with ytterbium diiodide resulted in the formation of a polymeric “ate” complex $[\text{Li}(\text{THF})_4][\text{Li}\{\text{Yb}(\mu\text{-}\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\mu\text{-I})_2\}]$ (**21**)²⁷ or the half-sandwich complex $[\text{Yb}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NH}^t\text{Bu})(\text{THF})_2(\mu\text{-I})_2]$ containing an amino side chain.²⁸ The reaction of $[\text{Yb}(\text{C}_{10}\text{H}_8)(\text{THF})_2]/\text{LiI}$ with $(\text{C}_5\text{Me}_4\text{H})\text{CH}_2\text{-SiMe}_2\text{NH}^t\text{Bu}$ also gave a polymeric “ate” complex $\text{Li}\{[\text{Yb}(\mu\text{-}\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{SiMe}_2\text{N}^t\text{Bu})(\text{THF})_2]_2(\mu\text{-I})\}$ (**22**) (Scheme 13).²⁸ Although aminolysis of $(\text{C}_5\text{Me}_4\text{H})\text{SiMe}_2\text{NH}^t\text{Bu}$ using $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$ resulted in the formation of metallocene derivatives, $[\text{Ln}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NH}^t\text{Bu})_2(\text{THF})_n]$ (Ln = Sm, n = 0; Yb, n = 1), the less electron-rich aniline-derived ligand precursor $(\text{C}_5\text{Me}_4\text{H})\text{SiMe}_2\text{NPh}$ afforded the crystallographically characterized ytterbium complexes $[\text{Yb}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh})(\text{THF})_3]$ (**23**) as well as the samarium complexes $[\text{Sm}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh})(\text{THF})_n]$ (n = 0, 1).²⁵ Recrystallization of the ytterbium complex from toluene-hexane resulted in the formation of dimeric $[\text{Yb}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh})(\text{THF})_2]$ (**24**) with “intermolecular” interaction between the divalent ytterbium centre and the phenyl ring.

Whilst the reaction of the divalent ytterbium complex $[\text{Yb}(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{NPh})(\text{THF})_3]$ with azobenzene gave $[\text{Yb}_2(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh})_2(\mu\text{-}\eta^3\text{-}\eta^2\text{-N}_2\text{Ph}_2)(\text{THF})]$ with a somewhat distorted bridging 1,2-diphenylhydrazido(2–) ligand, the reaction with one equivalent of fluorenone gave the ketyl complex $[\text{Yb}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh})(\text{OC}_{13}\text{H}_8)(\text{THF})_2]$ (**25**) that has the *trans*-**III**-type structure.²⁵ Reversible formation of μ -pinacolato complex was observed for this ketyl complex, giving $[\text{Yb}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NPh})(\text{THF})_2(\mu\text{-O}_2\text{C}_6\text{H}_{16})]$ (**26**)



Scheme 13



Scheme 14

with a gauche conformation of the pinacolate ligand in hexane–diethyl ether (Scheme 14). Dissolving the μ -pinacolate complex in THF resulted in cleavage of the central C–C bond of the pinacolate unit and regenerated the ketyl complex quantitatively.²⁵

According to Hou *et al.*, the divalent phosphido-linked complexes $[\text{Ln}\{\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{P}(\text{C}_6\text{H}_2\text{tBu}_3\text{-2,4,6})\}(\text{THF})_3]$ ($\text{Ln} = \text{Sm}, \text{Yb}$) can be obtained by salt metathesis of $\text{LnI}_2(\text{THF})_2$ with $[\text{K}_2\{\mu\text{-}\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{P}(\text{C}_6\text{H}_2\text{tBu}_3\text{-2,4,6})\}\text{-}(\text{THF})_4]$, and were studied by X-ray diffraction for $\text{Ln} = \text{Sm}$ along with the HMPA and DME adducts $[\text{Sm}\{\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{P}(\text{C}_6\text{H}_2\text{tBu}_3\text{-2,4,6})\}(\text{L})_2]$ ($\text{L} = \text{HMPA}, \text{DME}$).²⁶ Oxidation of the divalent samarium complex $[\text{Sm}\{\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{P}(\text{C}_6\text{H}_2\text{tBu}_3\text{-2,4,6})\}(\text{THF})_3]$ with diiodoethane gave the dimeric iodo complex $[\text{Sm}\{\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{P}(\text{C}_6\text{H}_2\text{tBu}_3\text{-2,4,6})\}\text{-}(\text{THF})(\mu\text{-I})_2]$, which, according to an X-ray diffraction study, contains a centrosymmetric configuration of the type *heterotrans* V. The reaction with benzophenone gave the complex $[\text{Sm}\{\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{P}(\text{C}_6\text{H}_2\text{tBu}_3\text{-2,4,6})\}(\text{THF})_2(\mu\text{-}\eta^2\text{-OCPH}_2)]$, which was shown by X-ray diffraction to contain a bridging benzophenone dianion ligand.³⁰ No formation of a ketyl complex was observed.²⁶

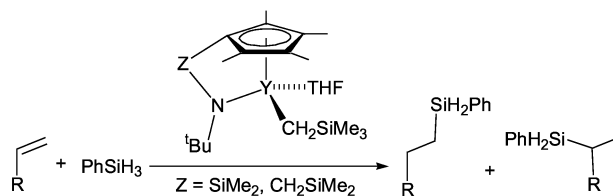
6 Catalysis

Lanthanocene derivatives have by now established themselves as highly efficient homogeneous catalysts in a variety of transformations of olefinic substrates.³¹ The corresponding reactive complexes with a linked amido-cyclopentadienyl ligand are emerging as alternatives for the various catalysed reactions.

6.1 Hydrometallation

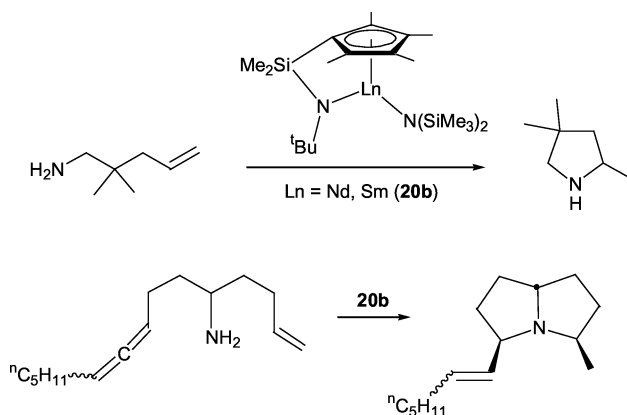
α -Olefins such as 1-decene can be efficiently hydrosilylated with PhSiH_3 by catalytic amounts of the hydride $[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{ZN}^t\text{Bu})(\mu\text{-H})(\text{THF})_2]$ ($\text{Z} = \text{SiMe}_2, \text{CH}_2\text{SiMe}_2$), conven-

iently generated *in situ* from the alkyl complexes $[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{ZN}^t\text{Bu})(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ (Scheme 15). The silane $^{10}\text{C}_{10}\text{H}_{23}\text{SiPhH}_2$ was formed regioselectively and could be oxidatively transformed into the corresponding alcohol. Exchange of the SiMe_2 linker by a longer CH_2SiMe_2 chain resulted in a significant increase in the activity under standard conditions (5 mol% catalyst, 25 °C). This somewhat unexpected finding, contradictory to the concept of “constrained geometry” catalysts, is ascribed to the shift of the dimer–monomer equilibrium of the dimeric hydride complex towards the reactive monomer with the longer backbone link. The hydrosilylation of styrene is more sluggish and results in a mixture of both terminal and internal regioisomers. An influence of the link on the regioselectivity is noted here as well.¹⁷ The efficiency and selectivity are comparable with lanthanocene-catalysed hydrosilylation methodology.³²



Scheme 15

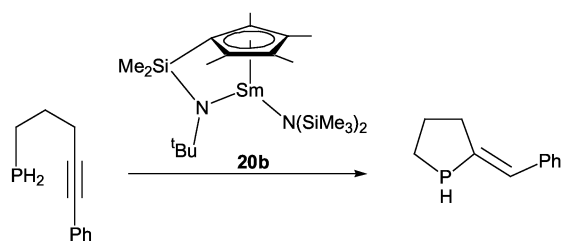
A series of lanthanide alkyl and amide complexes with a linked amido-cyclopentadienyl ligand $[\text{Ln}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\{\text{E}(\text{SiMe}_3)_2\}]$ ($\text{Ln} = \text{Nd}, \text{Sm}$, **20b**, Lu; E = N; Yb, **16b**, Lu, E = CH) was introduced as efficient hydroamination/cyclization catalysts for α,ω -aminoolefins, exhibiting significantly higher activity than the typical lanthanocene derivatives $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_5)_2\{\text{E}(\text{SiMe}_3)_2\}]$ (E = CH, N) (Scheme 16). During the total synthesis of the natural products pyrrolidine alkaloid (+)-197B



Scheme 16

and pyrrolizidine alkaloid (+)-xenovenine, the aminoallene (5*S*,8*S*)-5-aminotrideca-8,9-diene and the aminoallene-alkene (5*S*)-5-aminopentadeca-1,8,9-triene underwent intramolecular regio- and diastereoselective hydroamination/cyclization catalysed by $[\text{Ln}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\{\text{N}(\text{SiMe}_3)_2\}]$. The turnover-limiting step in these catalytic cycles is proposed to be intramolecular insertion into the Ln–N bond of the proximal allenic C=C linkage, followed by rapid protonolytic cleavage of the resulting Ln–C bond.^{12,33}

The amido complex $[\text{Sm}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\{\text{N}(\text{SiMe}_3)_2\}]$ (**20b**) catalysed the intramolecular hydrophosphination/cyclization of phosphinoalkenes and phosphinoalkynes (Scheme 17). Substrates such as $\text{H}_2\text{P}(\text{CH}_2)_3\text{C}\equiv\text{CPh}$ were converted into cyclized products 2-methylenephospholanes with a higher turnover number observed for **20b** compared with $[\text{Sm}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\{\text{CH}(\text{SiMe}_3)_2\}]$.³⁴

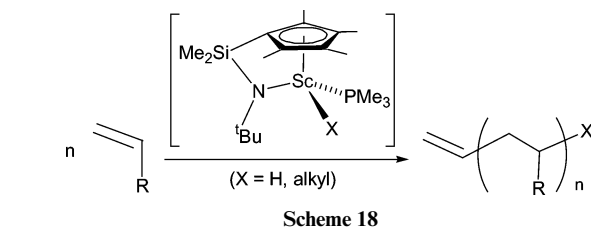


Scheme 17

6.2 Polymerization

Propene, 1-butene and 1-pentene were oligomerized by $[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{PMe}_3)(\mu\text{-H})_2]$ (**6**) with >99% “head-to-tail” coupling to produce linear, atactic poly(α -olefins) of low molecular weights ($M_n = 3000\text{--}7000$). Chain transfer was relatively slow and appears to occur by β -H elimination. The stoichiometric reaction between **6** and 2 equiv. of ethylene produced the unusual ethylene-bridged dimer $[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{PMe}_3)_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-C}_2\text{H}_4)]$ (**7**) (Scheme 4), whereas the same reaction with propene afforded the phosphine-free, alkyl-bridged scandium dimer $[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\mu\text{-CH}_2\text{CH}_2\text{CH}_3)_2]$ (**8**), which functioned as a more active olefin polymerization catalyst precursor. The structure of the catalytic intermediate was determined by low-temperature ¹³C NMR spectroscopic studies of the model complexes $[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\{\text{P}(\text{C}^{13}\text{CH}_3)_3\}\text{CH}_2\text{CH}(\text{C}^{13}\text{H}_3)\text{CH}_2\text{CH}_2\text{CH}_3]$ and $[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{PMe}_3)\text{C}^{13}\text{H}_2\text{CH}(\text{C}^{13}\text{CH}_3)_2]$ to be a monomeric, 12-electron, scandium alkyl complex $[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\text{X}]$ (X = H, alkyl) of the type I (Scheme 18).⁶⁶ The base-free alkyl complex $[\text{Sc}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\{\text{CH}(\text{SiMe}_3)_2\}]$ (**1a**) was also claimed to be an ethylene polymerization catalyst in the patent literature.³⁵

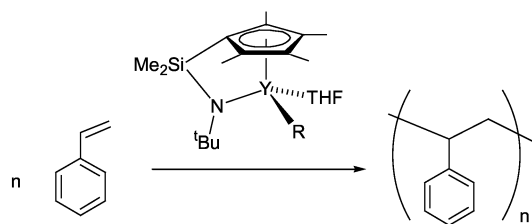
Ethylene underwent slow sequential insertion at low temperatures (<–30 °C) with the hydrido complex $[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\mu\text{-H})_2]$ (**9**) to give a mixture of *n*-alkyl complexes $[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\{\mu\text{-}(\text{CH}_2\text{CH}_2)_n\text{H}\}]_2$. The *n*-alkyl complexes could be synthesized independently by the reaction of the dimeric hydride with 1-alkenes. The THF-free dimeric alkyl complexes dissolved in THF or DME to give the monomeric *n*-alkyl complex $[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\{\text{CH}_2\text{CH}_2\text{CH}_3\}(\text{L})]$. Whereas ethylene was slowly polymerized by the hydrido complex at room temperature to give linear polyethylene ($T_m = 136$ °C), none of α -olefins, dienes, or styrene were polymerized. In all these cases stable mono(insertion) products could be isolated.^{14b,20} Divalent samarium complexes $[\text{Sm}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{THF})_n]$ were capable of polymerizing ethylene to give linear polyethylene with $M_n = 726\,000$ and $M_w/M_n = 1.58$, whilst the phosphido complex $[\text{Sm}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{PR}')(\text{THF})]$ very high molecular weight polyethylene with $M_n > 4 \cdot 10^6$.²⁵



Scheme 18

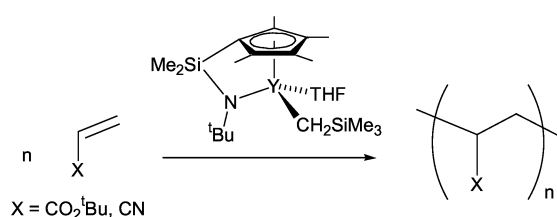
Styrenes reacted with the hydride **9** to give isolable 1-phenethyl complexes which failed to react further with styrene. However, the monomeric *n*-alkyl complex $[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\{\text{CH}_2\text{CH}_2\text{CH}_3\}(\text{THF})]$ polymerized styrene in a controlled manner to give atactic polystyrene with low polydispersity (Scheme 19). Thus, 50 equiv. of styrene gave with **9**, activated by 1-hexene, polystyrene with $M_n = 24\,100$ and $M_w/M_n = 1.10$, $rr = 70\%$.^{14b,20}

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Scheme 19

The alkyl complexes $[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ and the yttrium hydrido complex $[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})(\text{THF})(\mu\text{-H})_2]$ were found to polymerize the polar monomers *tert*-butyl acrylate and acrylonitrile (Scheme 20). *tert*-Butyl acrylate was polymerized at temperatures as low as –30 °C to give atactic poly(*tert*-butyl acrylate) in high yields and with molecular weights $M_n > 20\,000$ and molecular weight distributions in the range of $M_w/M_n = 1.5\text{--}2.0$. When acrylonitrile was added to a toluene solution of the hydride complex **9**, an intensely red solution developed and atactic poly(acrylonitrile)s with molecular weights in the range of 10^5 , but broad molecular distributions of $M_w/M_n > 5$, were obtained.^{14a,36} Synthesis of block copolymers such as poly(styrene-*co-tert*-butyl acrylate) was also possible, when the yttrium alkyl complex $[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\{\text{CH}_2\text{CH}_2\text{CH}_3\}(\text{THF})]$ (**10**) was used.^{14a,36}



Scheme 20

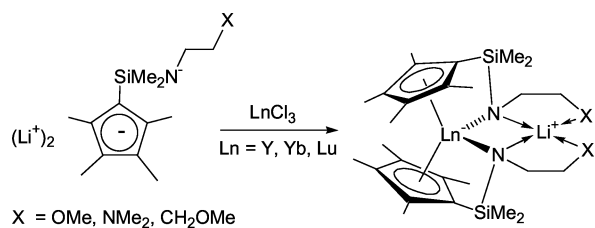
$\text{CH}_2)_n\text{H}\}(\text{THF})]$ is sequentially treated with styrene and *tert*-butyl acrylate.³⁷

7 Metallocene complexes that contain two linked amido-cyclopentadienyl ligands

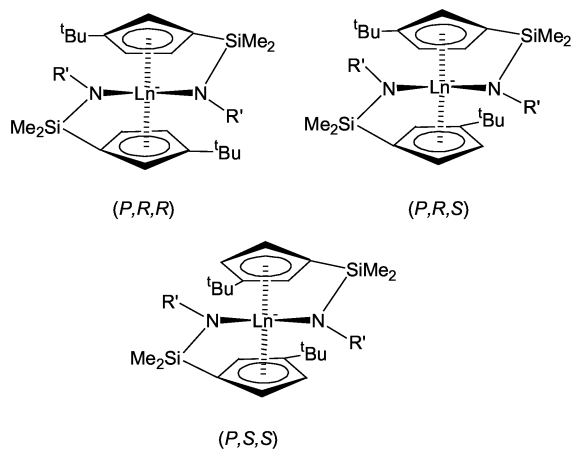
During the synthesis of group 4 metal half-sandwich complexes containing the linked amido-cyclopentadienyl ligands, it was occasionally noted that two of the ligands are coordinated at a metal centre to give C_2 -symmetric metallocenes $[\text{M}(\eta^5\text{:}\eta^1\text{-C}_5\text{R}_4\text{ZNR}')_2]$,^{38–40} as exemplified by the crystal structure of $[\text{Zr}(\eta^5\text{:}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{NPh})_2]$.³⁹ The double coordination of the linked amido-cyclopentadienyl ligands appears to be a result of the presence of excess ligand. The characteristically longer metal–amido nitrogen bonds indicate that the excess electrons of the formal 20-electron valence shell reside on the amido-nitrogen atoms. Thus, in a formal sense, one of the amido ligand acts as a one-electron X-type ligand without the π -donation, since only the $1a_1$ orbital of the Cp_2MX_2 can accept electrons.⁴¹

Group 3 metals give rise to anionic complexes of the type $[\text{M}(\eta^5\text{:}\eta^1\text{-C}_5\text{R}_4\text{ZNR}')_2]^-$. One structurally characterized example $[\text{K}(\text{DME})][\text{Yb}\{\eta^5\text{:}\eta^1\text{-C}_5\text{H}_3\text{tBu-3}\}\text{SiMe}_2\text{N}^t\text{Bu}\}_2]$ has a “super-sandwich” structure with infinite zigzag chains.²⁸ This type of “ate” complex is easily isolated when tridentate ligands of the type $[\text{C}_5\text{R}_4\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{X}]$ ($\text{X} = \text{OMe}, \text{NMe}_2$) with an additional donor group are used.⁴² The reaction of anhydrous rare earth trichlorides with $\text{Li}_2(\text{C}_5\text{R}_4\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{X})$ produced, in high yields, hydrocarbon-soluble heterobimetallic complexes of the composition $\text{Li}[\text{Ln}(\eta^5\text{:}\eta^1\text{-C}_5\text{R}_4\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{X})_2]$ ($\text{Ln} = \text{Y}, \text{Yb}, \text{Lu}$). As shown by the crystal structures of $\text{Li}[\text{Y}(\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{X})_2]$, the metallocene unit tightly coordinates the lithium ion together with the ligand side chains (Scheme 21). The amido nitrogen atoms exhibit a distorted tetrahedral geometry and a significantly longer yttrium–nitrogen bond than in $[\text{Y}(\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\{\text{N}(\text{SiMe}_2)_2\}]$.²⁴

When a *tert*-butylcyclopentadienyl ligand is used for C_5R_4 three diastereomeric pairs of enantiomers are expected (Scheme 22).⁴² Under kinetic control the sterically more constrained

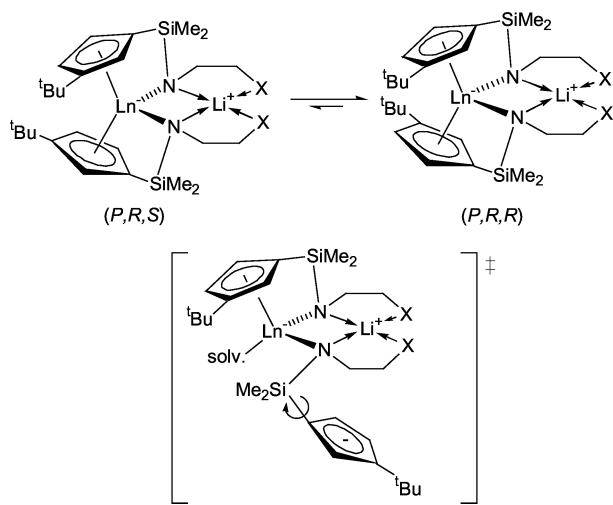


Scheme 21



Scheme 22

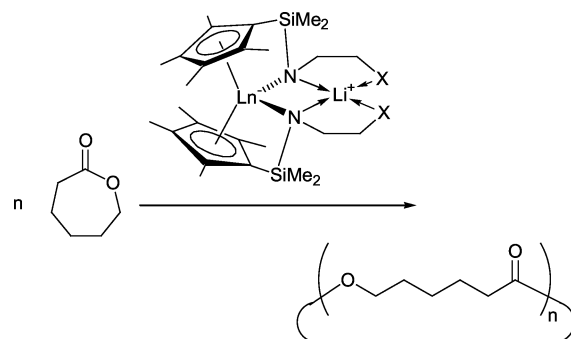
(*R,S*)-isomer was preferentially formed, and converted into the thermodynamically more stable C_2 -symmetric (*R,R*)-isomer in donor solvents such as THF at room temperature (Scheme 23). The interconversion is first-order and activation parameters indicate a fairly ordered transition state. It is noteworthy that this epimerization process requires the dissociation of one of the cyclopentadienyl moieties (most probably as a cyclopentadienyl anion) to allow the rotation about the ring carbon–silicon bond and recomplexation of the cyclopentadienyl ligand from the opposite diastereoface. Such processes are common for chiral lanthanocenes of the type $[\text{Ln}(\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{-C}_5\text{H}_3\text{R}^*)](\mu\text{-Cl})_2\text{Li}(\text{OEt})_2]$ with an optically active substituent R^* in donor solvents.^{43,44} Brintzinger-type *ansa*-zirconocenes are also known to undergo such epimerization processes.⁴⁵



Scheme 23

The reaction of the heterobimetallic complex $\text{Li}[\text{Y}(\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{OMe})_2]$ with phenylacetylene as a mild proton source gave, under protonation of the amido groups, a new complex $\text{Li}[\text{Y}(\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NHCH}_2\text{CH}_2\text{OMe})_2(\text{C}\equiv\text{CPh})_2]$ that contains bridging acetylide ligands.⁴⁰ A heterobimetallic complex $\text{Li}[\text{Y}(\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NC}_5\text{H}_4\text{N})_2]$ with a pyridyl group in the side chain of the linked amido-cyclopentadienyl ligand underwent a smooth metal exchange reaction with cuprous chloride to give a copper-containing complex $\text{Cu}[\text{Y}(\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NC}_5\text{H}_4\text{N})_2]$.⁴⁶

The heterobimetallic complexes are highly efficient ring-opening polymerization catalysts for ϵ -caprolactone and lactide, producing poly(ϵ -caprolactone) and poly(lactide) of high molecular weight ($M_n > 30\,000$) and moderate polydispersity ($M_w/M_n < 2.0$) (Scheme 24).^{47,48} Intriguingly, the lack of end



Scheme 24

groups in the polymer and NMR spectroscopic investigations suggest a mechanism that distinguishes itself fundamentally from the conventional metal alkoxide-initiated ring-opening polymerization that in many cases proceed as a living pseudo-anionic polymerization with defined end groups, good molec-

Table 5 Helical metallocene complexes

Compound	Method of preparation	Characterization	Ref.
Li[Y(η^5 : η^1 : η^1 -C ₅ Me ₄ SiMe ₂ NCH ₂ CH ₂ X) ₂], X = NMe ₂ , OMe, CH ₂ OMe	Salt metathesis	X-Ray (X = NMe ₂ , OMe), ¹ H, ¹³ C NMR	42
Li[Lu(η^5 : η^1 : η^1 -C ₅ Me ₄ SiMe ₂ NCH ₂ CH ₂ OMe) ₂]	Salt metathesis	X-Ray, ¹ H, ¹³ C NMR	42
Li[Y(η^5 : η^1 : η^1 -C ₅ H ₄ SiMe ₂ NCH ₂ CH ₂ OMe) ₂]	Salt metathesis	¹ H, ¹³ C NMR	42
Li[Y(η^5 : η^1 : η^1 -C ₅ H ₃ ^t Bu-3)SiMe ₂ NCH ₂ CH ₂ X) ₂], X = NMe ₂ , OMe	Salt metathesis	X-Ray (X = OMe, R,S; NMe ₂ , R,R), ¹ H, ¹³ C NMR	42
[K(DME)][Yb(η^5 : η^1 -C ₅ H ₃ ^t Bu-3)SiMe ₂ N ^t Bu) ₂]	Salt metathesis	X-Ray (R,R/S,S)	28
Li ₂ [Yb(η^5 : η^1 -C ₅ H ₃ ^t Bu-3)SiMe ₂ NH(CH ₂ CH ₂ NMe ₂) ₂ -(μ -Cl) ₂]	Salt metathesis	X-Ray, ¹ H, ¹³ C NMR	28
Li[Yb(η^5 : η^1 -C ₅ H ₃ ^t Bu-3)SiMe ₂ NCH ₂ CH ₂ X) ₂], X = NMe ₂ , OMe	Salt metathesis	X-Ray (X = NMe ₂ , R,R/S,S)	28
Li[Y(η^5 : η^1 : η^1 -C ₅ Me ₄ SiMe ₂ NC ₅ H ₄ N) ₂]	Salt metathesis	X-Ray, ¹ H, ⁶⁷ Li, ¹³ C, ²⁹ Si, ⁸⁹ Y NMR, MS	46
Li[Y(η^5 : η^1 : η^1 -C ₅ Me ₄ SiMe ₂ NHCH ₂ CH ₂ OMe) ₂ -(C=CPh) ₂]	Protonolysis	¹ H, ¹³ C, ²⁹ Si, NMR	40
Cu[Y(η^5 : η^1 : η^1 -C ₅ Me ₄ SiMe ₂ NC ₅ H ₄ N) ₂]	Metal exchange	X-Ray, ¹ H, ⁶⁷ Li, ¹³ C, ²⁹ Si, ⁸⁹ Y NMR, MS	46
[Sm(η^5 : η^1 -C ₅ Me ₄ SiMe ₂ N ^t Bu)(η^5 : η^1 -C ₅ Me ₄ -SiMe ₂ NH ^t Bu)]	Aminolysis	X-Ray	12

ular weight control, and narrow polydispersity indices.⁴⁹ The strongly nucleophilic amido group acts as the nucleophile-forming ligand-attached macrocycle that at a certain ring size forms the complex back, releasing the macrocyclic polymer. A related mechanism was recently proposed for the ring-opening metathesis polymerization (ROMP) of cyclooctene by a ruthenium alkylidene catalyst that contains a tethered heterocyclic carbene ligand.⁵⁰

8 Outlook

The seemingly limited class of group 3 metal complexes containing a linked amido-cyclopentadienyl ligand clearly paved the way for the systematic development of the synthetically challenging chemistry of half-sandwich complexes of these large metals. The linked amido-cyclopentadienyl ligand serves as an ancillary ligand that provides a consistent reaction site, reminiscent of the bis(cyclopentadienyl) framework in Brintzinger-type *ansa*-metallocenes. The higher degree of unsaturation in this (L₃X₂)-type ligand compared to the (L₄X₂)-type bis(cyclopentadienyl) ligand results in different reactivity patterns, which can be accounted for by the presence of a harder amido donor and/or the sterically more open ligand sphere. The absence of ligand scrambling of the cyclopentadienyl ligand (to eventually give thermodynamically stable metallocenes or flyover complexes) allows fine tuning of the reaction site through ligand modification. This may be crucial for the rational control of more subtle effects in homogeneous catalysts such as stereoselectivity. Given the increasing application of rare earth metallocene catalysts, group 3 metal complexes with a linked amido-cyclopentadienyl ligand [C₅R₄ZNR'] should be included in the repertoire of structurally well-defined homogeneous catalysts.^{51–54} In group 4 metal chemistry, numerous series of new ligand variations of this type have already been introduced.⁹

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