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Mono(cyclopentadienyl) Complexes of the Rare-Earth Metals

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I. Introduction

Organometallic complexes of the rare-earth metals are conventionally supported by bis(cyclopentadienyl) ligand frameworks,[1−8] in particular if such complexes are used as precursors in homogeneously catalyzed transformations.[9] Previously published reviews therefore clearly reflect the relative dominance of this class of compounds over the half-sandwich complexes that contain only one cyclopentadienyl ligand. Due to the smaller number of such mono(cyclopentadienyl) complexes, their complete coverage in the literature was possible until 1994/1995. Given the tremendous importance of d-block transition-metal half-sandwich complexes,[10] it is somewhat surprising that to date not many systematic investigations on the chemistry and application of mono(cyclopentadienyl) rare-earth complexes have been undertaken. The present review article summarizes the literature on this class of complexes with emphasis on the literature from 1994/1995 until 2000/2001. The complexes are organized according to the ligands other than the cyclopentadienyl moiety. Synthesis, structure, and properties of halo, chalcogenido, pnicogenido, hydrocarbyl, and hydrido ligands will be considered, followed by an

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overview of the application of some of these compounds in homogeneous catalysis.

II. Overview of Synthesis, Structure, and Properties

A. Synthetic Methods

The selective synthesis of the half-sandwich complexes $[Ln(\eta^5\text{-}C_5R_5)X_mL_n]$ is generally made difficult by the usual greater thermodynamic stability of the corresponding metallocene derivatives $[Ln(\eta^5\text{-}C_5R_5)_2X_{m-1}L_n]$. When the steric bulk of the cyclopentadienyl ligand C_5R_5 is small, the metallocene formation is virtually exclusive and no mono(cyclopentadienyl) complexes are available. Furthermore, the high electropositivity of the rare-earth metal centers results in more ionic ring−metal bonding and in facile ligand scrambling, a situation normal for the even more electropositive alkaline-earth metal complexes.[11,12] Moreover, compared to the lanthanocene derivatives, the electronically more unsaturated and sterically more open mono(cyclopentadienyl) complexes are significantly more difficult to handle due to tenacious Lewis base complexation (basic solvents, alkali-metal halide), air and moisture sensitivity, and thermal instability. As a consequence, methods of synthesis somewhat more sophisticated than the usual salt metathesis are commonly employed. Depending on the additional monoanionic ligands, different synthetic reactions are used. Those most frequently encountered in this survey are summarized in Scheme 1 and listed in Table 1. They will be referred to with their corresponding keys for the individual compounds in Tables 2−12.

Scheme 1

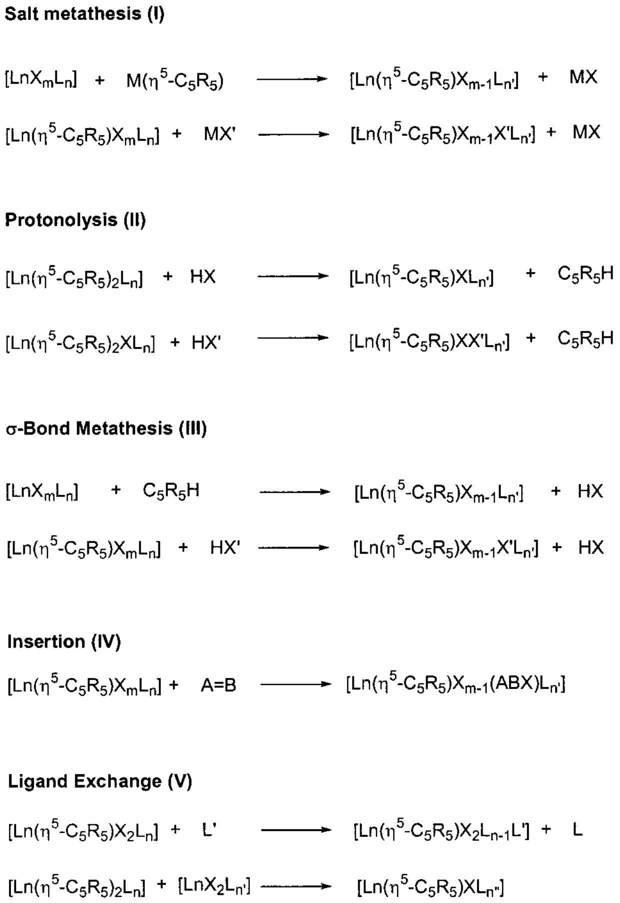


Table 1. Synthetic Methods for the Preparation of Mono(cyclopentadienyl) Rare-Earth Metal Complexes

key	method
I	salt metathesis (transmetalation)
II	protonolysis
III	σ-bond metathesis[a]
IV	insertion
V	ligand exchange[b]/addition of Lewis base
VI	oxidation
VII	reduction

[a] Including hydrogenolysis and C−H bond activation reactions (alkane elimination, amine elimination). [b] Including ligand comproportionation reactions.

Chart 1

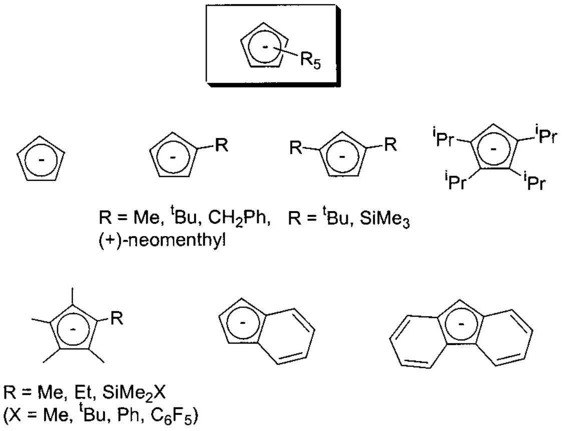


Chart 2

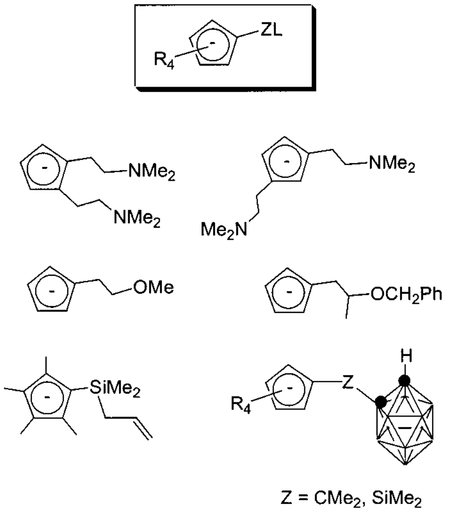


Chart 3

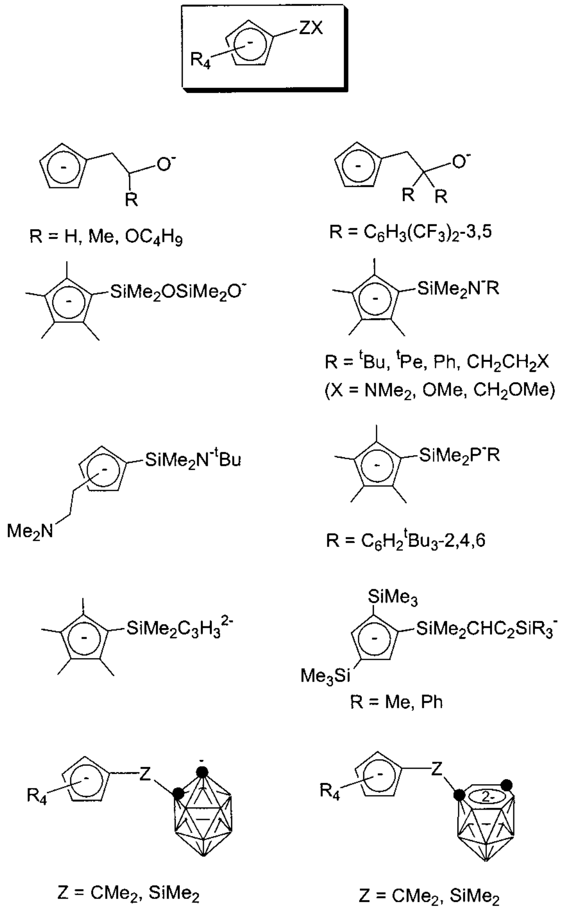
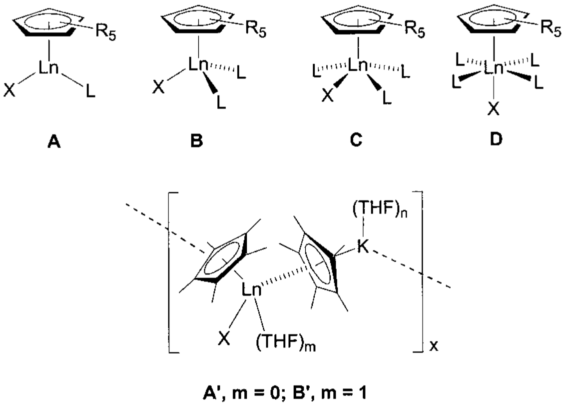


Chart 4



B. Ligands and Structures

The present review organizes the mono(cyclopentadienyl) rare-earth metal complexes $[\mathrm{Ln}(\eta^5\text{-}\mathrm{C_5R_5})\mathrm{X}_m\mathrm{L}_n]$ ($m = 1{,}2$; $n = 0-4$) according to the nature of the monoanionic ligand X other than the ancillary cyclopentadienyl ligand C_5R_5. The most common types of cyclopentadienyl ligands C_5R_5 are summarized in Charts 1−3. Cyclopentadienyl ligands containing functional side chains[13−15] have been extensively used in the development of organolanthanide chemistry and are compiled in Charts 2 and 3. The ligands X and L correspond to a monoanionic, one-electron ligand and a neutral, two-electron ligand, respectively, as defined by the systematizing scheme introduced by Green.[16] The halo, chalcogenido, pnicogenido, hydrocarbyl, and hydrido complexes will be dealt with in this order, corresponding to the decreasing group number of the monoanionic donor atom. In cases where the pendant donor group attached to cyclopentadienyl is a monoanionic ligand (Chart 3), the complexes will be classified according to this donor group. Thus, the fairly numerous complexes that contain a the linked amido−cyclopentadienyl ligand $(C_5R_4ZNR)^-$ [13,17] will be treated as amido complexes as long as they do not feature hydrocarbyl or hydrido ligands. Fairly extensive chemistry has evolved around the novel cyclopentadienyl ligand systems with a pendant *o*-dicarbollide group $(C_5R_4ZC_2B_{10}H_{11})^-$. The 1,2-dicarbadecaborane fragment $(C_2B_{10}H_{11})$ can act as a neutral (*closo*-type), dianionic (*nido*-type), or tetraanionic (*arachno*-type) ligand moiety.[18] A related *nido*-type monoanionic group $(C_2B_{10}H_{10})$ is also known.

The majority of structural types encountered in this review are generally identical to those described in the earlier, more comprehensive reviews.[2,3] The mononuclear divalent derivatives are compiled in Chart 4 and fall into the following categories: $[\mathrm{Ln}(\eta^5\text{-}\mathrm{C_5R_5})\mathrm{XL}_n]$, **A**, $n = 1$; **B**, $n = 2$; **C**, $n = 3$; **D**, $n = 4$. The structures of the dinuclear derivatives $[\mathrm{Ln}(\eta^5\text{-}\mathrm{C_5R_5})\mathrm{L}_n(\mu\text{-}\mathrm{X})]_2$, **E**, $n = 0$; **F**, $n = 1$; **G**, $n = 2$ are summarized in Chart 5. The formal valence electron count ranges from 12 for complexes of type **A** to 18

Chart 5

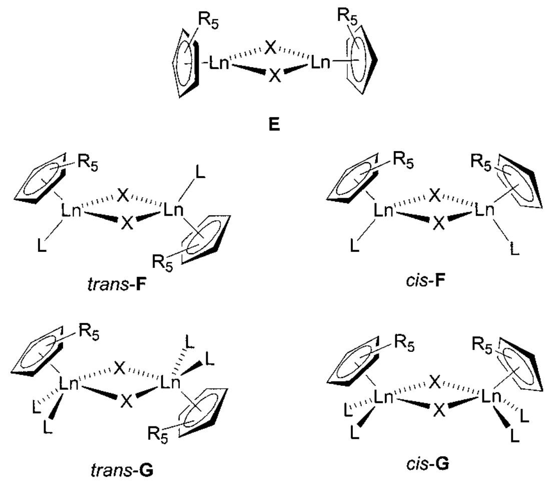
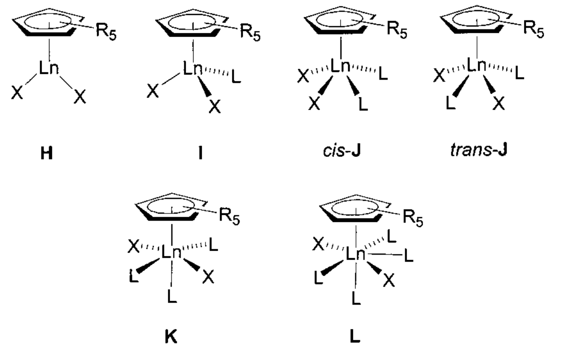


Chart 6



for complexes of type **D**. A somewhat special family of divalent complexes adopts polymeric structures designated as **A′** and **B′**, where [K(η^5-C_5R_5)(THF)$_n$] acts as one L-type ligand.

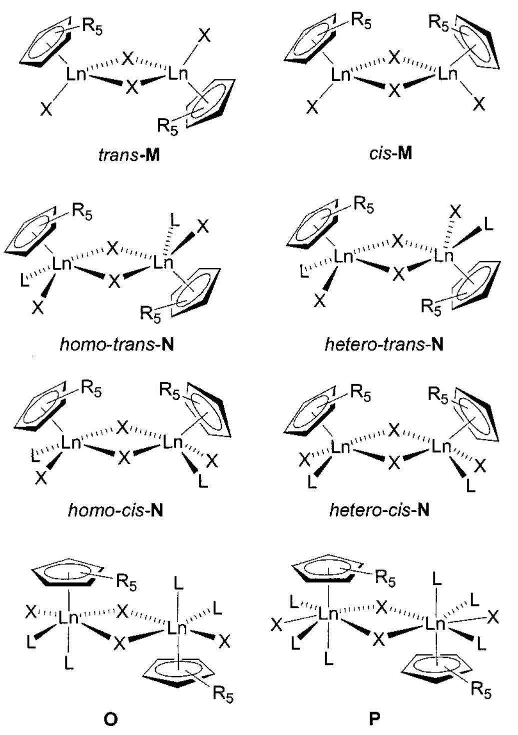
The trivalent complexes adopt structures that are classified as [Ln(η^5-C_5R_5)X_2L_n], **H**, $n = 0$; **I**, $n = 1$; **J**, $n = 2$; **K**, $n = 3$; **L**, $n = 4$, or [Ln(η^5-C_5R_5)(X)L_n(μ-X)]$_2$, **M**, $n = 0$; **N**, $n = 1$; **O**, $n = 2$; **P**, $n = 3$. The mononuclear derivatives are depicted in Chart 6, while dinuclear complexes are compiled in Chart 7. The formal valence electron count ranges from 10 for the complex type **H** with pseudotrigonal configuration to 18 for complex type **L** or **P** with pentagonal bipyramidal coordination geometry. For both oxidation states, larger clusters with more than two mono(cyclopentadienyl) metal fragments have been reported,[19,20] but they will not be considered in detail here. Some ionic species are also known and will be dealt with individually. Their structures can be normally derived from those of the neutral complexes by formally substituting an L-type ligand by an anionic X^- ligand.

III. Halo Complexes

A. General

Two types of half-sandwich halo complexes are prevalent: dinuclear derivatives of divalent samarium and ytterbium [Ln(η^5-C_5R_5)L_2(μ-X)]$_2$ of the structural type **G** and trivalent lanthanide complexes of the general formula [Ln(η^5-C_5R_5)X_2L_3] (X = Cl, Br, I), which normally adopt the structure of type **K**. These halo complexes are listed in Table 2.

Chart 7



B. Divalent Halo Complexes

The salt metathesis of lanthanide diiodide does not always afford the expected half-sandwich iodo complex of the type [Ln(η^5-C_5R_5)L_2(μ-I)]$_2$. Thus, the reaction of 1 equiv of Li($C_5Me_4SiMe_2{}^tBu$) with YbI_2 resulted in the formation of a cluster [Li(THF)$_4$]$_2$[{Yb($C_5Me_4SiMe_2{}^tBu$)}$_6I_8$] that contains a hexanuclear dianion.[21] The samarium(II) half-sandwich complexes [Sm(η^5-C_5Me_4R)(THF)$_2$(μ-I)]$_2$ (R = Me, Et) were used as starting materials for the preparation of sandwich complexes and triple-decker complexes containing a bridging cyclooctatetraene ligand.[22] The utility of electrospray mass spectrometry was examined for the characterization of acetonitrile solutions of [Ln(η^5-C_5Me_5)(THF)$_2$(μ-I)]$_2$ (Ln = Sm, Eu, Yb), giving differing sets of ions, depending on the specific metal.[23] The dimeric iodo complex [Yb(η^5-$C_9H_6SiMe_2C_2B_{10}H_{11}$)(THF)$_2$($\mu$-I)]$_2$, which contains an indenyl ligand attached to the neutral carboranyl group, was investigated by NMR spectroscopy.[24]

The reaction of a mixture of the potassium salts K{$C_5H_3(CH_2CH_2NMe_2)_2$-1,2} and K{$C_5H_3(CH_2CH_2NMe_2)_2$-1,3} with $YbI_2(THF)_2$ was reported to give the sparingly soluble, crystallographically characterized complex [Yb{η^5:η^1:η^1-$C_5H_3(CH_2CH_2NMe_2)_2$-1,2}I(THF)$_2$]. Its reaction with Na($C_5H_4{}^tBu$) or K(C_5Me_5) resulted in the formation of the mixed sandwich complexes [Yb{η^5:η^1:η^1-$C_5H_3(CH_2CH_2NMe_2)_2$-1,2}(η^5-$C_5H_4{}^tBu$)] or [Yb{η^5:η^1:η^1-$C_5H_3(CH_2CH_2NMe_2)_2$-1,2}(η^5-C_5Me_5)], respectively. The 1,3-isomer left in solution reacted with Na(C_5Me_5), forming the polymeric ate complex [NaYb{μ_2-η^5:η^1:η^1-$C_5H_3(CH_2CH_2NMe_2)_2$-1,3}(η^5-C_5Me_5)(μ_2-I)Yb{μ_2-η^5:η^1:η^1-$C_5H_3(CH_2CH_2NMe_2)_2$-1,3}(η^5-C_5Me_5)]$_n$.[25]

Table 2. Mono(cyclopentadienyl) Halo Rare-Earth Metal Complexes

compound	type	methods of preparation	characterization	ref
		Divalent Complexes		
$[\mathrm{Sm}(\eta^5\text{-}\mathrm{C_5{}^iPr_4H})(\mathrm{THF})_2(\mu\text{-}\mathrm{I})]_2$, Ln = Sm, Yb, Eu	**G**	I, V	X-ray, ^{1}H NMR	118
$[\mathrm{Yb}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{L})_2(\mu\text{-}\mathrm{I})]_2$, L = THF, L_2 = DME	**G**			21
$[\mathrm{Ln}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{THF})_2(\mu\text{-}\mathrm{I})]_2$, Ln = Sm, Eu, Yb	**G**		ESI MS	23
$[\mathrm{Yb}\{\eta^5{:}\eta^1{:}\eta^1\text{-}\mathrm{C_5H_3(CH_2CH_2NMe_2)_2\text{-}1,2}\}\mathrm{I}(\mathrm{THF})_2]$	**D**	I	X-ray, ^{1}H, ^{13}C NMR, MS	25
$[\mathrm{Yb}(\eta^5\text{-}\mathrm{C_9H_6SiMe_2C_2B_{10}H_{11}})(\mathrm{THF})_2(\mu\text{-}\mathrm{I})]_2$	**G**	I	^{1}H, ^{13}C, ^{11}B NMR, IR	24
		Trivalent Complexes		
$[\mathrm{Y}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Cl_2}(\mathrm{THF})_3]$	**K**	I	X-ray	27
$[\mathrm{Eu}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Cl_2}(\mathrm{THF})_3]$	**K**		X-ray, Mössbauer	29
$[\mathrm{Sm}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Cl_2}(\mathrm{THF})_3]$	**K**	I	X-ray	28
$[\mathrm{Sm}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{X_2}(\mathrm{THF})_3]$, X = Br, I	**K**	VI	X-ray	26
$[\mathrm{Eu}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{NCO})_2(\mathrm{THF})_x]$			Mössbauer	29
$[\mathrm{Eu}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{NCS})_2(\mathrm{THF})_3]$	**K**		Mössbauer	29
$[\mathrm{Er}(\eta^5\text{-}\mathrm{C_5H_4Me})\mathrm{Cl_2}(\mathrm{THF})_3]$	**K**	I	X-ray, MS, IR	119
$[\mathrm{Ln}(\eta^5\text{-}\mathrm{C_5H_4Me})\mathrm{Cl_2}(\mathrm{THF})_3]$, Ln = Sm, Eu, Gd, Tb, Dy, Ho, Y	**K**	I	MS, IR	119
$[\mathrm{Ln}(\eta^5\text{-}\mathrm{C_5H_4CH_2Ph})\mathrm{Cl_2}(\mathrm{THF})_x]$, Ln = Nd, Gd		I	no information available	120,121
$[\mathrm{Er}(\eta^5\text{-}\mathrm{C_5H_4CH_2Ph})\mathrm{Cl_2}(\mathrm{THF})_3]$	**K**		X-ray	122
$[\mathrm{Ln}\{\eta^5\text{-}\mathrm{C_5H_4(C_5H_9)}\}\mathrm{Cl_2}(\mathrm{THF})_x]$, Ln = Nd, Gd		I		123
$[\mathrm{Ho}(\eta^5\text{-}\mathrm{C_9H_7})\mathrm{Cl_2}(\mathrm{THF})_3]$	**K**	I	X-ray, IR	30
$[\mathrm{Sm}(\eta^5\text{-}\mathrm{C_9H_7})\mathrm{I_2}(\mathrm{THF})_2]$	**J**	VI	X-ray, ^{1}H, ^{13}C NMR, IR	31
$[\mathrm{Sm}(\eta^5\text{-}\mathrm{C_9H_7})\mathrm{I_2}(\mathrm{THF})_3]$	**K**	VI	X-ray	31
$[\mathrm{Nd}(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{I_2}(\mathrm{THF})_3]$	**K**	I	IR	32
$[\mathrm{Nd}(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{I_2}(\mathrm{py})_3]$	**K**	V	X-ray, IR	32
$[\mathrm{Y}(\eta^5\text{-}\mathrm{C_5Me_5})\{\eta^2\text{-}\mathrm{PhC(NSiMe_3)_2}\}(\mu\text{-}\mathrm{Cl})]_2$	**N**	I	^{1}H, ^{13}C NMR, IR	49
$[\mathrm{Ln}\{\eta^5\text{-}(+)\mathrm{neomenthylC_5H_4}\}\mathrm{I_2}(\mathrm{THF})_3]$, Ln = Sm, Yb	**K**	I	X-ray, ^{1}H NMR (Ln = Sm)	33
$[\mathrm{Ln}\{\eta^5\text{-}(+)\mathrm{neomenthylC_5H_4}\}\mathrm{Cl_2}(\mathrm{THF})_3]$, Ln = Sm, Gd, Yb, Lu, Y	**K**	I	^{1}H NMR (Ln = Y, Lu), MS	33
$[\mathrm{Ln}(\eta^5\text{-}\mathrm{C_5H_4CH{=}CH_2})\mathrm{Cl_2}]$, Ln = Nd, Tb		I	IR	124
$[\mathrm{Ln}(\eta^5\text{-}\mathrm{C_5H_4CMe{}^nPrCH_2CH{=}CH_2})\mathrm{Cl_2}(\mathrm{MgCl_2})(\mathrm{THF})]$, Ln = La, Nd, Sm, Gd		I	^{1}H NMR, MS, IR	125
$[\mathrm{Sm}(\eta^5{:}\eta^1\text{-}\mathrm{C_5H_4CH_2CH_2OCH_3})\mathrm{I_2}(\mathrm{THF})_2]$	**K**	I	X-ray	126
$[\mathrm{Sm}\{(\mathrm{S})\text{-}\eta^5\text{-}\mathrm{C_5H_4CH_2CHMeOCH_2Ph}\}\mathrm{I_2}(\mathrm{THF})_3]$	**K**	I	^{1}H, ^{13}C NMR, IR	34
$[\mathrm{La}\{(\mathrm{S})\text{-}\eta^5\text{-}\mathrm{C_5H_4CH_2CHMeOCH_2Ph}\}\mathrm{I_2}(\mathrm{THF})_2]$	**K**	I	^{1}H, ^{13}C, ^{139}La NMR, IR	34
$[\mathrm{Nd}(\eta^5\text{-}\mathrm{C_5H_4CMe_2C_2B_{10}H_{11}})\mathrm{Cl_2}(\mathrm{DME})_2]$	**L**	I	^{1}H, ^{13}C, ^{11}B NMR, IR	36
$[\mathrm{Sm}(\eta^5\text{-}\mathrm{C_5H_4CMe_2C_2B_{10}H_{11}})\mathrm{Cl_2}(\mathrm{THF})_3]$	**K**	I	^{1}H, ^{13}C, ^{11}B NMR, IR	36
$[\mathrm{Er}(\eta^5\text{-}\mathrm{C_5H_4CMe_2C_2B_{10}H_{11}})\mathrm{Cl_2}(\mathrm{THF})_3]$	**K**	I	^{1}H, ^{13}C, ^{11}B NMR, IR	36,37
$[\mathrm{Ln}(\eta^5\text{-}\mathrm{C_5H_4SiMe_2C_2B_{10}H_{11}})\mathrm{Cl_2}(\mathrm{THF})_3]$, Ln = Nd, Sm, Er, Yb	**K**	I	X-ray (Ln = Nd, Yb), ^{1}H, ^{11}B NMR, IR	35
$[\mathrm{La}\{\eta^5{:}\eta^1{:}\eta^1\text{-}\mathrm{C_5H_3(CH_2CH_2NMe_2)_2\text{-}1,3}\}\mathrm{I_2}(\mathrm{THF})]$	**K**	I	X-ray, ^{1}H, ^{13}C NMR, MS	25
$[\mathrm{La}\{\eta^5{:}\eta^1{:}\eta^1\text{-}\mathrm{C_5H_3(CH_2CH_2NMe_2)_2\text{-}1,2}\}\mathrm{I_2}(\mathrm{THF})]$	**K**	I	X-ray, ^{1}H, ^{13}C NMR, MS	25
$[\mathrm{Gd}(\eta^5\text{-}\mathrm{C_9H_6CMe_2C_2B_{10}H_{11}})\mathrm{Cl_2}(\mathrm{THF})_2]$	**J**	I	^{11}B NMR, IR	75
$[\mathrm{Ln}(\eta^5\text{-}\mathrm{C_9H_6SiMe_2C_2B_{10}H_{11}})\mathrm{Cl_2}(\mathrm{THF})_3]$, Ln = Nd, Er	**K**	I	^{1}H, ^{13}C, ^{11}B NMR, IR	74

C. Trivalent Halo Complexes

Half-sandwich complexes of the general type $[\mathrm{Ln}(\eta^5\text{-}\mathrm{C_5R_5})\mathrm{X_2}(\mathrm{L})_3]$ (X = Cl, Br, I) continue to be studied intensely because of their potential utility, e.g., in the synthesis of mixed metallocenes featuring two different ring ligands $[\mathrm{Ln}(\eta^5\text{-}\mathrm{C_5R_5})(\eta^5\text{-}\mathrm{C_5R'_5})\mathrm{X}_m(\mathrm{L})_n]$. The preparation usually follows the salt metathesis method (I). One notable exception is the reaction of $[\mathrm{Sm}(\eta^5\text{-}\mathrm{C_5H_5})_2(\mathrm{THF})]$ with $\mathrm{XCH_2CH_2X}$ (X = Br, I), leading to an equimolar mixture of $[\mathrm{Sm}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{X_2}(\mathrm{THF})_3]$ (X = Br, I) and $[\mathrm{Sm}(\eta^5\text{-}\mathrm{C_5H_5})_3(\mathrm{THF})]$.[26] The X-ray crystallographically determined molecular structures show a typical pseudo-octahedral coordination geometry around the formally eight-coordinate rare-earth metal atom with the two halo ligands in trans positions and the centroid of the $\mathrm{C_5H_5}$-ring and one L in the apical positions (*mer-trans* configuration of type **K**). In all cases the trans halo ligands bend away from the $\mathrm{C_5R_5}$ ligand, the angles X−Ln−X being in the 153−158° range. Within the parent series $[\mathrm{Ln}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Cl_2}(\mathrm{THF})_3]$, yttrium[27] and samarium[28] complexes have been added to the isostructural complexes with Ln = Nd, Gd, Ho, Er, and Yb.

The ^{151}Eu Mössbauer spectra of $[\mathrm{Eu}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Cl_2}(\mathrm{THF})_3]$, along with the pseudohalides $[\mathrm{Eu}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{NCO})_2(\mathrm{THF})_x]$ and $[\mathrm{Eu}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{NCS})_2(\mathrm{THF})_3]$, were measured at 4.2 K and show hyperfine parameters which are normal for organoeuropium(III) compounds. The isomer shifts correspond to the transfer of ca. 0.14 electrons from the cyclopentadienyl ligands into the 4f orbitals of europium via covalent bonding. These electrons polarize the partially occupied europium 4f orbitals and produce a large valence contribution to the electric field gradient at the europium nucleus; this suggests a strong covalent interaction between the ligands and the 4f orbitals of europium.[29]

The indenyl complex $[\mathrm{Ho}(\eta^5\text{-}\mathrm{C_9H_7})\mathrm{Cl_2}(\mathrm{THF})_3]$ was synthesized from $\mathrm{HoCl_3}$ and $\mathrm{Na(C_9H_7)}$ in THF, and its molecular structure was characterized by single-crystal X-ray diffraction, showing the holmium atom with the common distorted octahedral, *mer-trans* configuration of type **K**.[30]

In analogy to the reactions of related samarocene complexes $[\mathrm{Sm}(\eta^5\text{-}\mathrm{C_5R_5})_2(\mathrm{THF})_x]$, 2 equiv of indenyl samarium(II) complex $[\mathrm{Sm}(\eta^5\text{-}\mathrm{C_9H_7})_2(\mathrm{THF})_x]$ reacted with 1 equiv of 1,2-diiodoethane in THF to give [Sm-

$(\eta^5$-$C_9H_7)I_2(THF)_2]$ and $[Sm(\eta^5$-$C_9H_7)_3(THF)]$. While bulk samples of $[Sm(\eta^5$-$C_9H_7)I_2(THF)_2]$ were isolated as the bis(THF) complex (presumably of type **J**), crystallization from hexane/THF generated single crystals of the tris(THF) complex $[Sm(\eta^5$-$C_9H_7)I_2(THF)_3]$, displaying the common **K**-type configuration.[31]

$NdI_3(THF)_x$ reacted with 1 equiv of $K(C_5Me_5)$ to produce the mono(pentamethylcyclopentadienyl) complex $[Nd(\eta^5$-$C_5Me_5)I_2(THF)_3]$ in moderate yield, which upon treatment with an excess of pyridine in toluene led to displacement of all the THF ligands and formation of the tris-pyridine adduct $[Nd(\eta^5$-$C_5Me_5)I_2(py)_3]$. According to a single-crystal X-ray diffraction study, $[Nd(\eta^5$-$C_5Me_5)I_2(py)_3]$ adopts the pseudo-octahedral geometry of type **K** in the crystalline state.[32]

With half-sandwich complexes that contain a modified cyclopentadienyl ligand, the related trivalent lanthanide (+)-neomenthylcyclopentadienyl complexes $[Ln\{\eta^5$-(+)-neomenthyl$C_5H_4\}X_2(THF)_3]$ ($X = Cl$, $Ln = Sm$, Gd, Yb, Lu, Y; $X = I$, $Ln = Sm$, Yb) were prepared by metathesis of lanthanide halides with the appropriate alkali-metal (+)-neomenthylcyclopentadienyl reagents. X-ray structural analysis revealed that the compound $[Sm\{\eta^5$-(+)-neomenthyl-$C_5H_4\}I_2(THF)_3]$ adopts the usual pseudo-octahedral geometry of type **K** with the two trans iodo ligands.[33] Among the mono(cyclopentadienyl) lanthanide iodo complexes $[Ln\{(S)$-η^5-$C_5H_4CH_2CHMeOCH_2Ph)\}I_2(THF)_n]$ ($Ln = Sm$, $n = 3$; $Ln = La$, $n = 2$) containing a chiral cyclopentadienyl ligand $C_5H_4CH_2CHMeOCH_2$-Ph, intramolecular coordination has only been observed for the lanthanum complex.[34]

A mixture of the potassium salts $K\{C_5H_3(CH_2CH_2NMe_2)_2$-1,2$\}$ and $K\{C_5H_3(CH_2CH_2NMe_2)_2$-1,3$\}$ reacted with $LaI_3(THF)_3$ in THF to give the half-sandwich diiodo complexes $[La\{\eta^5{:}\eta^1{:}\eta^1$-$C_5H_3(CH_2CH_2NMe_2)_2$-1,2$\}I_2(THF)]$ and $[La\{\eta^5{:}\eta^1{:}\eta^1$-$C_5H_3(CH_2CH_2NMe_2)_2$-1,3$\}I_2(THF)]$, which were manually separated. X-ray crystallography revealed their pseudo-octahedral coordination geometry.[25]

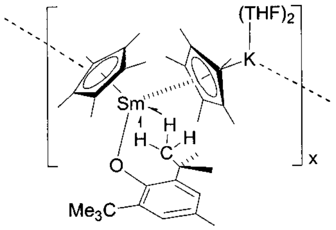
The structurally characterized complexes $[Ln(\eta^5$-$C_5H_4SiMe_2C_2B_{10}H_{11})Cl_2(THF)_3]$ ($Ln = Nd$, Yb) containing the silylene-bridged C_5H_4-carboranyl ligand adopt the structure of type **K**. The analogous samarium and erbium compounds[35] as well as complexes $[Ln(\eta^5$-$C_5H_4CMe_2C_2B_{10}H_{11})Cl_2(THF)_3]$ ($Ln = Sm$, Er)[36,37] and $[Nd(\eta^5$-$C_5H_4CMe_2C_2B_{10}H_{11})Cl_2(DME)_2]$ (type **L**) containing the isopropylidene bridged ligand system have also been described.[36]

IV. Chalcogenido Complexes

A. General

Both divalent and trivalent lanthanide complexes with sterically demanding phenolato ligands such as 2,6-di-*tert*-butyl-4-methylphenol ($HOC_6H_2{}^tBu_2$-2,6-Me-4) have been extensively studied. As synthetic methods, salt metathesis (I) and protonolysis reaction (II) predominate. The complexes of this class are listed in Table 3.

Scheme 2



B. Divalent Chalcogenido Complexes

Reaction of $[Sm(\eta^5$-$C_5Me_5)_2(THF)_2]$ with 1 equiv of $HOC_6H_2{}^tBu_2$-2,6-R-4 ($R = H$, Me, ${}^tBu$) or $[Sm(OC_6H_2{}^tBu_2$-2,6-R-4$)_2(THF)_3]$ in toluene gave, almost quantitatively, the heteroleptic unsolvated dimeric complexes of type **E**, $[Sm(\eta^5$-$C_5Me_5)(\mu_2$-$OC_6H_2{}^tBu_2$-2,6-R-4$)]_2$ ($R = H$, Me, ${}^tBu$), which did not undergo ligand redistribution in toluene. Addition of 4 equiv of hexamethylphosphoric triamide (HMPA) to a THF solution gave the monomeric HMPA complexes of type **B** $[Sm(\eta^5$-$C_5Me_5)(OC_6H_2{}^tBu_2$-2,6-R-4$)(HMPA)_2]$ in 90−94% isolated yields.[38] Reaction of $[Sm(OC_6H_2{}^tBu_2$-2,6-Me-4$)I(THF)_3]$ with $K(C_5Me_5)$ in THF/HMPA also gave $[Sm(\eta^5$-$C_5Me_5)(OC_6H_2{}^tBu_2$-2,6-Me-4$)(HMPA)_2]$.[39,40]

Reaction of $[Sm(\eta^5$-$C_5Me_5)(\mu$-$OC_6H_2{}^tBu_2$-2,6-R-4$)]_2$ with 2 equiv of $K(C_5Me_5)$ in THF gave the polymeric complexes $[Sm(\mu_2$-$\eta^5{:}\eta^5$-$C_5Me_5)(OC_6H_2{}^tBu_2$-2,6-R-4$)\{K(\mu_2$-$\eta^5{:}\eta^5$-$C_5Me_5)(THF)_2\}]_x$, in which the $K(C_5Me_5)(THF)_2$ unit acts as a neutral coordination ligand L (structural type **A′**). Metathesis reaction of $[Sm(OC_6H_2{}^tBu_2$-2,6-R-4$)_2(THF)_3]$ with $K(C_5Me_5)$ or $[Sm(\eta^5$-$C_5Me_5)_2(THF)_2]$ with $K(OC_6H_2{}^tBu_2$-2,6-R-4$)$ also gave the complexes $[Sm(\mu_2$-$\eta^5{:}\eta^5$-$C_5Me_5)(OC_6H_2{}^tBu_2$-2,6-R-4$)\{K(\mu_2$-$\eta^5{:}\eta^5$-$C_5Me_5)(THF)_2\}]_x$ in excellent yields. In the crystal structures of $[Sm(\mu_2$-$\eta^5{:}\eta^5$-$C_5Me_5)(OC_6H_2{}^tBu_2$-2,6-R-4$)\{K(\mu_2$-$\eta^5{:}\eta^5$-$C_5Me_5)(THF)_2\}]_x$, the $OC_6H_2{}^tBu_2$-2,6-R-4 ligand is severely bent toward the central samarium atom with a Sm−O−C(*ipso*) angle of 126.7(5)°, with an agostic interaction between the samarium atom and a methyl group of the *o-tert*-butyl substituent (Scheme 2). Depolymerization with HMPA in THF gave $[Sm(\eta^5$-$C_5Me_5)(OC_6H_2{}^tBu_2$-2,6-R-4$)(HMPA)_2]$ in 90−95% isolated yields.[38]

Reaction of $[Sm(\eta^5$-$C_5Me_5)_2(THF)_2]$ with 1 equiv of $K(SC_6H_2{}^iPr_3$-2,4,6$)$ in THF gave, in high yields, the thiophenolate complexes $[Sm(\mu_2$-$\eta^5{:}\eta^5$-$C_5Me_5)(SC_6H_2{}^iPr_3$-2,4,6$)(THF)\{K(\mu_2$-$\eta^5{:}\eta^5$-$C_5Me_5)(THF)_n\}]_x$, in which the $K(C_5Me_5)(THF)_n$ unit acts as a neutral coordination ligand L, bonded to the Sm(II) center. This polymeric structure can be classified as **B′**.[41]

The reaction of the silylene-linked bis(tetramethylcyclopentadienyl) samarium(II) complex $[Me_2Si(\eta^5$-$C_5Me_4)_2Sm(THF)_2]$ with 1 equiv of $K(OC_6H_2{}^tBu_2$-2,6-R-4$)$ in THF yielded $[Sm(OC_6H_2{}^tBu_2$-2,6-R-4$)\{(\mu_2$-$\eta^5{:}\eta^5)_2$-$C_5Me_4SiMe_2C_5Me_4\}\{K(THF)_n\}]_x$ ($R = Me$, ${}^tBu$, $n = 1, 2$), which can be viewed as a ($C_5Me_4/OC_6H_2{}^tBu_2$-2,6-R-4)-ligated Sm(II) species coordinated by the silylene-linked, neutral "$K(C_5Me_4)$" ligand.[41]

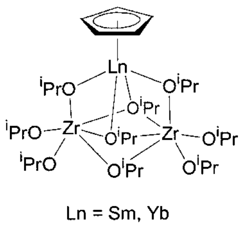
The dizirconium nona(isopropoxo) ligand $[Zr_2(O^iPr)_9]^-$ as an ancillary ligand in organolanthanide complexes has been shown to be compatible with cyclopentadienyl reagents and to enhance the solubility of divalent lanthanide organometallic species

Table 3. Mono(cyclopentadienyl) Chalcogenido Rare-Earth Metal Complexes

compound	type	methods of preparation	characterization	ref
		Divalent Complexes		
$[Ln(\eta^5\text{-}C_5H_5)\{Zr_2(O^iPr)_9\}]$, Ln = Sm, Yb	**C**	I	X -ray, ^1H, ^{13}C NMR, UV/Vis, IR, ESI MS	23,42
$[Sm_2(\eta^5\text{-}C_5Me_5)\{\mu\text{-}OSi(O^tBu)_3\}_3]$		II	X-ray	43
$[Sm(\eta^5\text{-}C_5Me_5)(OC_6H_2{}^tBu_2\text{-}2,6\text{-}Me\text{-}4)(HMPA)_2]$	**B**	I, V	X-ray	39−41
$[Sm(\eta^5\text{-}C_5Me_5)(OC_6H_2{}^tBu_2\text{-}2,6\text{-}R\text{-}4)(HMPA)_2]$, R = H, Me, ^tBu	**B**	V	^1H NMR	38
$[Sm(\eta^5\text{-}C_5Me_5)(\mu\text{-}OC_6H_2{}^tBu_2\text{-}2,6\text{-}R\text{-}4)]_2$, R = H, Me, ^tBu	**E**	I or II	X-ray (R = ^tBu), ^1H NMR	38
$[Sm(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(OC_6H_2{}^tBu_2\text{-}2,6\text{-}R\text{-}4)\{K(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(THF)_2\}]_x$, R = H, Me, ^tBu	**A′**	I	^1H NMR, X-ray (R = H, Me)	38,41
$[Sm(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(OC_6H_3{}^iPr_2\text{-}2,6)(THF)\{K(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(THF)_2\}]_x$	**B′**	I	X-ray	41
$[Sm(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(OC_6H_3{}^iPr_2\text{-}2,6)\{K(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(THF)\}]_x$	**A′**	I	no information available	41
$[Sm(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(SC_6H_2{}^iPr_3\text{-}2,4,6)(THF)\{K(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(THF)\}]_x$	**B′**	I	X-ray	41
$[Sm(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(SC_6H_2{}^iPr_3\text{-}2,4,6)\{K(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(THF)\}]_x$	**A′**	I	no information available	41
$[Sm(OC_6H_2{}^tBu_2\text{-}2,6\text{-}Me\text{-}4)\{(\mu_2\text{-}\eta^5{:}\eta^5)_2\text{-}C_5Me_4SiMe_2C_5Me_4\}\{K(THF)_2\}]_x$	**A′**	I	X-ray	41
$[Sm(OC_6H_3{}^tBu_2\text{-}2,6)\{(\mu_2\text{-}\eta^5{:}\eta^5)_2\text{-}C_5Me_4SiMe_2C_5Me_4\}\{K(THF)\}]_x$	**A′**	I	X-ray	41
$[Yb\{\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH(R)O\}(THF)]$, R = H, Me, $CH_2OC_4H_9$	**A**	II and III	^1H, ^{13}C NMR, IR	44
$[Yb(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2O)(DME)]$	**B**	II and III	^1H, ^{13}C NMR, IR	44
$[Yb\{\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2OSiMe_2(\mu\text{-}O)\}(THF)]_2$	**F**	II and III	X-ray, ^1H NMR, IR	45
		Trivalent Complexes		
$[Ln(\eta^5\text{-}C_5H_5)(ONCPh_2)(OC_9H_5N)]_2$, Ln = Gd, Tb, Dy, Ho, Er, Tm, Yb			MS, IR	127
$[\{Yb(\eta^5\text{-}C_5H_5)(\mu\text{-}OC_{20}H_{20}N_2O)\}_2(\mu\text{-}THF)](THF)$[a]		I	X-ray, IR	52
$[\{Sm(\eta^5\text{-}C_5H_5)(\mu\text{-}OC_{20}H_{20}N_2O)\}_2(\mu\text{-}THF)(THF)_2]$[a]		I	X-ray	53
$[Ln(\eta^5\text{-}C_5H_5)(O_3SMe)_2L_n]$, Ln = La, Pr, Nd, Eu, Yb, L = THF, PPh_3		I	IR	104
$[Pr(\eta^5\text{-}C_5H_5)\{CH(COOEt)_2\}_2]_2$	**P**	II	X-ray	51
$[Yb(\eta^5\text{-}C_5H_4Me)(OC_6H_2{}^tBu_2\text{-}2,6\text{-}Me\text{-}4)_2(THF)]$	**I**		X-ray	128
$[Ln(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2OMe)(\mu\text{-}OC_{20}H_{20}N_2O)]_2$,[a] Ln = Sm, Dy		I	X-ray, MS (Ln = Sm)	54
$[Sm(\eta^5\text{-}C_5{}^iPr_4H)(O^tBu)I(THF)]$	**I**	I	^1H NMR	118
$[Eu(\eta^5\text{-}C_5Me_5)(O^tBu)(\mu\text{-}O^tBu)]_2$	**M**	I	X-ray	46
$[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)_2]$	**H**	I	^1H, ^{13}C NMR	91
$[Sm(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)_2(THF)]$	I	I	X-ray	47
$[Sm(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^iPr_2\text{-}2,6)(\mu\text{-}OC_6H_3{}^iPr_2\text{-}2,6)_2Li(THF)]$		I	X-ray	47
$[Ce(\eta^5\text{-}C_5Me_5)(O_2CC_4H_6CO_2)]$		IV	^1H, ^{13}C NMR, MS, IR	61
$[Y(\eta^5\text{-}C_5Me_5)\{\eta^2\text{-}PhC(NSiMe_3)_2\}(OC_6H_3{}^tBu_2\text{-}2,6)]$	**I**	II	^1H, ^{13}C NMR	49
$[Sm(\eta^5\text{-}C_5Me_5)\{S_2P(OMe)_2\}_2]_2$	**P**		X-ray	56
$[Na(THF)_6]^+[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3Me_2\text{-}2,6)_3]^-$		I	X-ray	48
$[Sm(\eta^5\text{-}C_5Me_5)(OC_6H_2{}^tBu_2\text{-}2,6\text{-}Me\text{-}4)(OC_{13}H_8)(HMPA)]$[b]	**I**	VI	X-ray	110
$[Y(\eta^5\text{-}C_5Me_4SiMe_2CH_2CHCH_2)\{O(\mu\text{-}O)CCH_2SiMe_3\}\{\mu\text{-}(O_2CCH_2SiMe_3)\}]_2$	**O**	IV	X-ray	133
$[Sm\{(S)\text{-}\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH(Me)O\}I(THF)]$	**I**	I	^1H NMR, IR	55
$[La\{(S)\text{-}\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH(Me)O\}I(THF)_2]$	**J**	I	^1H NMR, IR	55
$[Y\{\eta^5{:}\eta^1\text{-}C_5H_4CH_2CR_2O\}Cl(THF)_2]$, R = $C_6H_3(CF_3)_2\text{-}3,5$	**J**	II and III	^1H, ^{13}C, ^{19}F NMR	132
$[Y\{\eta^5{:}\eta^1\text{-}C_5H_4CH_2CR_2O\}(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2]$, R = $C_6H_3(CF_3)_2\text{-}3,5$	**J**	II and III	X-ray, ^1H, ^{13}C, ^{19}F NMR	132

[a] $OC_{20}H_{20}N_2O$: *trans*-(±)-*N*,*N*′-bis(salicylidene)-1,2-cyclohexanediamine. [b] $OC_{13}H_8$: biphenyl-2,2′-diyl ketyl.

Scheme 3



in comparison with C_5H_5 analogues. Thus, $[Ln\{Zr_2(O^iPr)_9\}I_2]$ reacted with $Na(C_5H_5)$ to form the hexane-soluble divalent lanthanide complexes $[Ln(\eta^5\text{-}C_5H_5)\{Zr_2(O^iPr)_9\}]$ (Ln = Sm, Yb). In these complexes, the monoanionic $[Zr_2(O^iPr)_9]^-$ unit is attached to the lanthanide metal in a tetradentate fashion according to the crystal structure of $[Ln(\eta^5\text{-}C_5H_5)\{Zr_2(O^iPr)_9\}]$.[42] Electrospray mass spectra showed the unsolvated parent ion $[Ln(\eta^5\text{-}C_5H_5)\{Zr_2(O^iPr)_9\}]^+$.[23]The reaction of $[Sm(\eta^5\text{-}C_5Me_5)_2(THF)_2]$ with $(^tBuO)_3SiOH$ gave the dinuclear samarium(II) complex $[Sm_2(\eta^5\text{-}C_5Me_5)\{\mu\text{-}OSi(O^tBu)_3\}_3]$ in 85% yield, in which a samarium−samarium interaction of 3.465 Å was observed. It reacted with $[Sm\{OSi(O^tBu)_3\}_3]$ or $[Sm\{OSi(O^tBu)_3\}_3(THF)_2]$ to give a trinuclear mixed-valence samarium complex $[\{OSi(O^tBu)_3\}_3Sm(III)(\mu\text{-}C_5Me_5)Sm(II)_2(\mu\text{-}\{OSi(O^tBu)_3\}_3]$ in high yield.[43]

The reactions of ytterbium naphthalene complex $[Yb(C_{10}H_8)(THF)_2]$ with 2-cyclopentadienylethanol, 1-cyclopentadienylpropan-2-ol, and 3-cyclopentadienyl-1-butoxypropan-2-ol were reported to give divalent ytterbium complexes with bifunctional cyclopentadienyl ligands $[Yb\{\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH(R)O\}(THF)]$ (R = H, Me, $CH_2OC_4H_9$) and $[Yb(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2O)(DME)]$.[44] The crystal structure of the related dinuclear complex $[Yb\{\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2OSiMe_2(\mu\text{-}O)\}(THF)]_2$ containing a linked tetramethylcyclopentadienyl−silanolate ligand shows a configuration of type **F**.[45]

C. Trivalent Chalcogenido Complexes

A number of alkoxo complexes have been prepared by salt metathesis. The yttrium tris(aryloxo) complex $Y(OR)_3$ reacted with $K(C_5Me_5)$ to give $[Y(\eta^5\text{-}C_5Me_5)(OR)_2]$ (R = $C_6H_3{}^tBu_2\text{-}2,6$).[91] $[Eu_3(O^tBu)_7Cl_2(THF)_2]$ reacted with $K(C_5Me_5)$ to form $[Eu(\eta^5\text{-}C_5Me_5)(O^tBu)(\mu\text{-}O^tBu)]_2$, in 60% yield. The two europium atoms and the two oxygen atoms of the bridging ligands form a plane perpendicular to the plane defined by the two cis-oriented C_5Me_5 rings and the oxygen atoms of the terminal *tert*-butoxo ligands (type *cis*-**M**).[46]

$[Sm(OC_6H_2{}^tBu_2\text{-}2,6)_3(THF)]$ underwent a metathesis reaction with 1 equiv of $Li(C_5Me_5)$ to form the mono(pentamethylcyclopentadienyl) aryloxide derivative $[Sm(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)_2(THF)]$ featuring a three-legged piano-stool geometry of type **I**, with Sm−O distances to the aryloxide ligands of 2.133(6) and 2.188(6) Å and a Sm−O(THF) distance of 2.435(7) Å. In contrast, the analogous reaction of $Li(C_5Me_5)$ with the less bulky 2,6-di-isopropylphenoxide complex $[Sm(\mu\text{-}OC_6H_2{}^iPr_2\text{-}2,6)_3(THF)]$ led to the ate complex $[Sm(\eta^5\text{-}C_5H_5)(OC_6H_3{}^iPr_2\text{-}2,6)(\mu\text{-}OC_6H_3\text{-}{}^iPr_2\text{-}2,6)_2Li(THF)]$ with a three-legged piano-stool geometry with two of the aryloxide oxygen atoms coordinated to a lithium metal center.[47] $[Y(OC_6H_2Me_2\text{-}2,6)_3(THF)_3]$ was converted to the 'ate' salt $[Na(THF)_6]^+[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3Me_2\text{-}2,6)_3]^-$ with $Na(C_5Me_5)$, which contains an isolated hexasolvated cation and a pseudo-six-coordinate yttrium atom.[48]

The chiral complexes $[La\{(S)\text{-}\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH(Me)O\}I(THF)_2]$ and $Sm\{(S)\text{-}\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH(Me)O\}I(THF)]$ were synthesized from the dipotassium salt of enantiopure β-hydroxycyclopentadiene $C_5H_5CH_2CHMeOH$ and lanthanum or samarium iodides in high yields.[55]

Protonolysis is a straightforward method for the preparation of phenolato complexes. The benzimidate phenolate complex $[Y(\eta^5\text{-}C_5Me_5)\{\eta^2\text{-}PhC(NSiMe_3)_2\}(OC_6H_3{}^tBu_2\text{-}2,6)]$ was formed by protonolysis of $[Y(\eta^5\text{-}C_5Me_5)\{PhC(NSiMe_3)_2\}(\mu\text{-}Me)_2Li(TMEDA)]$ with $HOC_6H_3{}^tBu_2\text{-}2,6$.[49] The bis(malonato) complexes $[Ln(\eta^5\text{-}C_5H_5)\{CH(COOEt)\}_2]_2$ (Ln = Pr, Eu) were prepared by protonolyis of $[Ln(\eta^5\text{-}C_5H_5)_3]$ and the use of diethyl malonate and were shown by X-ray crystallography to adopt dimeric structures with pentagonal bipyramidally coordinated metal centers (structural type **P**).[50,51]

Treatment of $[Yb(\eta^5\text{-}C_5H_5)_3]$ with *trans*-(±)-*N,N′*-bis(salicylidene)-1,2-cyclohexanediamine gave the mono(cyclopentadienyl) Schiff base lanthanide complex, $[\{Yb(\eta^5\text{-}C_5H_5)(\mu\text{-}OC_{20}H_{20}N_2O)\}_2(\mu\text{-}THF)](THF)$. The molecular structure showed that it is a dimer in which the two $[Yb(\eta^5\text{-}C_5H_5)(\mu\text{-}OC_{20}H_{20}N_2O)]_2$ units connect via a bridging THF oxygen and two bridging oxygen atoms of the Schiff base ligand.[52] $[\{Sm(\eta^5\text{-}C_5H_5)(\mu\text{-}OC_{20}H_{20}N_2O)\}_2(\mu\text{-}THF)(THF)_2]$ has a similar dimeric structure.[53] In the structure of the related dinuclear complex $[Ln(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2OMe)(\mu\text{-}OC_{20}H_{20}N_2O)]_2$ (Ln = Sm, Yb), two $[Ln(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2OMe)]$ fragments are connected by two bridging O atoms of the Schiff base ligand.[54]

The oxidative reaction of $[Sm(\eta^5\text{-}C_5Me_5)_2(THF)_2]$ with the disulfide $\{SP({=}S)(OMe)_2\}_2$ resulted in the elimination of a C_5Me_5 ligand and formation of the dinuclear complex $[Sm(\eta^5\text{-}C_5Me_5)\{S_2P(OMe)_2\}_2]_2$. The X-ray diffraction showed as a notable structural feature the presence of triply bridging *O,O′*-dimethyldithiophosphate ligands with one of the methoxy groups completing the pentagonal bipyramidal coordination (type **P**) at each of the samarium atoms.[56]

The dinuclear mixed chloro/amido complex $[Y\{N(SiMe_3)_2\}_2(THF)(\mu\text{-}Cl)]_2$ underwent protonolysis/amine elimination with $C_5H_5CH_2C(OH)\{C_6H_3(CF_3)_2\text{-}3,5\}_2$ to give the NMR spectroscopically characterized linked cyclopentadienyl alkoxo complex $[Y\{\eta^5{:}\eta^1\text{-}C_5H_4CH_2CR_2O\}Cl(THF)_2]$, R = $C_6H_3(CF_3)_2\text{-}3,5$. The diprotio ligand also reacted with $[Y(OC_6H_3{}^tBu_2\text{-}2,6)\{CH(SiMe_3)_2\}(THF)_2]$ yielding the X-ray crystallographically characterized aryloxo complex of type *cis*-**J** $[Y\{\eta^5{:}\eta^1\text{-}C_5H_4CH_2CR_2O\}(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2]$.[132]

The dialkyl complex $[Y(\eta^5\text{-}C_5Me_4SiMe_2CH_2CHCH_2)(CH_2SiMe_3)_2(THF)_2]$ reacted via CO_2 insertion to form the crystallographically characterized dimer $[Y(\eta^5\text{-}C_5Me_4SiMe_2CH_2CHCH_2)\{O(\mu\text{-}O)CCH_2SiMe_3\}\{\mu\text{-}(O_2CCH_2SiMe_3)\}]_2$.[133]

V. Pnicogenido Complexes

A. General

After the divalent lanthanide amides $[Ln(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(NR_2)(THF)_m\{M(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(THF)_n\}]_x$ (M = K, Na),[41] the trivalent amido complexes comprise the majority of the compounds to be discussed in this section (Table 4). They are classified according to the ligands other than C_5R_5 and in the order bis(amido), mixed amido/alkoxo, and mixed amido/chloro complexes. Among the compounds with two lanthanide−amido nitrogen bonds, homo- and heteroleptic bis(amides) including linked amido−cyclopentadienyl amido complexes will be discussed. This class of complexes also includes azobenzene and pyrazolato compounds.

B. Divalent Amido and Phosphido Complexes

In analogy to the polymeric aryloxo and thiophenolato compounds $[Sm(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(X)\{K(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(THF)_2\}]_x$ (see section IV.B), a series of divalent lanthanide amides were synthesized in which the mono(pentamethylcyclopentadienyl) amido lanthanide units are coordinated to neutral $M(C_5Me_5)$ (M = K or Na) groups.[41] Reaction between $[Ln(\eta^5\text{-}C_5Me_5)_2(THF)_2]$ (Ln = Sm, Yb) and the potassium salt of the appropriate amine in THF gave polymeric $[Ln(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(X)\{K(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(THF)_2\}]_x$ (Ln = Sm, X = $NHC_6H_2{}^tBu_3\text{-}2,4,6$; Ln = Sm, Yb, X = $N(SiMe_3)_2$) in yields of ca. 90%. X-ray crystallographic characterization of the samarium complexes revealed linear polymers of type **A′** in which every C_5Me_5 ligand is linking a samarium and a potassium atom in an η^5 fashion. A linear coordination polymer of a different structure, in which the C_5Me_5 ligands and phosphorus atoms link the samarium and potassium atoms in an alternating manner, is found in the samarium phosphide $[Sm(\eta^5\text{-}C_5Me_5)(\mu_2\text{-}PHC_6H_2{}^tBu_3\text{-}2,4,6)(THF)\{K(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(THF)\}]_x$. This compound was obtained in 85% yield by a method analogous to that used for the amides. Interestingly, replacement of the "$K(C_5Me_5)$" ligand by a "$Na(C_5Me_5)$" unit gave dinuclear complexes instead of coordination polymers. The reactions of $[Ln(\eta^5\text{-}C_5Me_5)_2(THF)_2]$ (Ln = Sm, Yb) with $NaN(SiMe_3)_2$ in THF gave the crystallographically characterized complexes $[Ln(\eta^5\text{-}C_5Me_5)\{N(SiMe_3)_2\}\{Na(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5\text{-}$

Table 4. Mono(cyclopentadienyl) Pnicogenido Rare-Earth Metal Complexes

compound	type	methods of preparation	characterization	ref
Divalent Complexes				
$[Sm(\mu_2-\eta^5:\eta^5-C_5Me_5)(NHC_6H_2{}^tBu_3-2,4,6)\{K(\mu_2-\eta^5:\eta^5-C_5Me_5)(THF)_2\}]_x$	**A′**	I	X-ray	41
$[Sm(\mu_2-\eta^5:\eta^5-C_5Me_5)\{N(SiMe_3)_2\}\{K(\mu_2-\eta^5:\eta^5-C_5Me_5)(THF)_2\}]_x$	**A′**	I	X-ray	41
$[Yb(\mu_2-\eta^5:\eta^5-C_5Me_5)\{N(SiMe_3)_2\}\{K(\mu_2-\eta^5:\eta^5-C_5Me_5)(THF)_2\}]_x$	**A′**	I	^1H NMR	41
$[Sm(\eta^5-C_5Me_5)(\mu_2-PHC_6H_2{}^tBu_3-2,4,6)(THF)\{K(\mu_2-\eta^5:\eta^5-C_5Me_5)(THF)\}]_x$		I	X-ray	41
$[Sm(\eta^5-C_5Me_5)\{N(SiMe_3)_2\}(HMPA)_2]$	**B**	V	X-ray	41
$[Sm(\eta^5-C_5Me_5)\{N(SiMe_3)_2\}\{Na(\mu_2-\eta^5:\eta^5-C_5Me_5)(THF)_3\}]$	**A**	I	X-ray	41
$[Sm(\eta^5-C_5Me_5)\{N(SiMe_3)_2\}\{Na(\mu_2-\eta^5:\eta^5-C_5Me_5)(THF)\}]$	**A**	I	no information available	41
$[Yb(\eta^5-C_5Me_5)\{N(SiMe_3)_2\}\{Na(\mu_2-\eta^5:\eta^5-C_5Me_5)(THF)_3\}]$	**A**	I	X-ray	41
$[Yb(\eta^5-C_5Me_5)\{N(SiMe_3)_2\}\{Na(\mu_2-\eta^5:\eta^5-C_5Me_5)(THF)\}]$	**A**	I	no information available	41
$[Yb(\eta^5:\eta^1-C_5H_4SiMe_2N{}^tBu)(THF)]$	**A**	II and III	^1H NMR, IR	44
$[Yb(\eta^5:\eta^1-C_5H_4SiMe_2NPh)(THF)_3]$	**C**	II	X-ray, ^1H NMR	129
$[Yb(\eta^5:\eta^1-C_5H_4SiMe_2NPh)(THF)]_2$		V	X-ray, ^1H NMR	129
$[Sm(\eta^5:\eta^1-C_5H_4SiMe_2NPh)(THF)_n]$, $n = 0,1$		II	^1H NMR	129
$[Ln\{\eta^5:\eta^1-C_5Me_4SiMe_2P(C_6H_2{}^tBu_3-2,4,6)\}(THF)_n]$, Ln = Sm, Yb; $n = 1, 3$	**C**	I	X-ray, ^1H, ^{31}P NMR	134
$[Sm\{\eta^5:\eta^1-C_5Me_4SiMe_2P(C_6H_2{}^tBu_3-2,4,6)\}(HMPA)_2]$	**B**	V	X-ray, ^1H NMR	134
$[Sm\{\eta^5:\eta^1-C_5Me_4SiMe_2P(C_6H_2{}^tBu_3-2,4,6)\}(DME)_2]$	**D**	V	X-ray, ^1H NMR	134
Trivalent Complexes				
$[Ln(\eta^5-C_5H_5)(C_3N_2HMe_2-3,5)_2]$, Ln = Dy, Ho		II	MS, IR	69
$[Ln(\eta^5-C_5H_5)(\eta^2-C_3N_2HMe_2-3,5)(\mu-OSiMe_2C_3N_2HMe_2-3,5)]_2$, Ln = Dy, Ho	**O**	IV	X-ray (Ln = Ho), MS, IR	69
$[Sc(\eta^5-C_5H_5)\{N(SiMe_2CH_2P{}^iPr_2)_2\}Cl]$	**J**	I	X-ray, ^1H, ^{31}P NMR, MS	65
$[Sc(\eta^5-C_5H_5)\{N(SiMe_2CH_2P{}^iPr_2)_2\}(NHC_6H_5)]$	**J**	I or II	^1H, ^{31}P NMR	65
$[Sc(\eta^5-C_5H_5)\{N(SiMe_2CH_2P{}^iPr_2)_2\}(NH{}^tBu)]$	**J**	I or II	^1H, ^{31}P NMR	65
$[Lu(\eta^5-C_5H_5)(THF)(\mu-\eta^2:\eta^2-N_2Ph_2)]_2$			X-ray, ^1H NMR	67,68
$[Yb(\eta^5-C_5H_5)_2(\mu-NPPh_3)_2Yb(\eta^5-C_5H_5)(NPPh_3)]$		I	X-ray	66
$[Y(\eta^5-C_5H_5)(NPPh_3)(\mu-OSiMe_2NPPh_3)]_2$	**N**	IV	X-ray	66
$[Ln(\eta^5-C_5H_4Me)(C_3N_2HMe_2-3,5)_2]$,Ln = Nd, Gd, Dy		II	MS, IR	71
$[Ln(\eta^5-C_5H_4Me)(\eta^2-C_3N_2HMe_2-3,5)(\mu-OSiMe_2C_3N_2HMe_2-3,5)]_2$, Ln = Nd, Gd, Dy	**O**	IV	X-ray (Ln = Dy), IR	71
$[Ln(\eta^5-C_5H_4Me)(\eta^2-C_3N_2HMe_2-3,5)_2]_2$, Ln = Sm, Tb		II	MS, IR	70
$[Ln(\eta^5-C_5H_4Me)(\eta^2-C_3N_2HMe_2-3,5)(\mu-OSiMe_2C_3N_2HMe_2-3,5)]_2$, Ln = Sm, Tb	**O**	IV	X-ray (Ln = Tb), IR, MS	70
$[Li(THF)_4]^+[Yb(\eta^5-C_5H_4{}^tBu)(NPh_2)_3]^-$		I	X-ray, ^1H NMR, MS, IR	63,64
$[Sm(\eta^5-C_9H_7)(N_2Ph_2)(THF)]_x$		VI	IR	31
$[Nd(\eta^5-C_5Me_5)(NPh_2)_2(HNPh_2)]$	**I**	II	^1H, ^{13}C NMR, MS, IR	61
$[Ln(\eta^5:\eta^1-C_5H_4CH_2CH_2OMe)\{N(SiMe_3)_2\}_2]$, Ln = Y, Yb	**I**	I	^1H NMR (Ln = Y), MS, IR	62
$[Y\{\eta^5:\eta^1-C_5H_4CH_2CR_2O\}\{N(SiMe_3)_2\}(THF)_n]$, $R = C_6H_3(CF_3)_2-3,5$; $n = 1, 2$	**I**	I	^1H, ^{13}C, ^{19}F, ^{29}Si NMR	132
$[Y\{\eta^5:\eta^1-C_5H_4CH_2CR_2O\}\{\mu-N(SiMe_3)_2\}_2Na(THF)_2]$,$R = C_6H_3(CF_3)_2-3,5$		V	^1H, ^{13}C, ^{19}F, ^{29}Si NMR	132
$[Sc(\eta^5:\eta^1-C_5Me_4SiMe_2N{}^tBu)Cl]_x$		I	^1H NMR, IR	94
$[Y(\eta^5:\eta^1-C_5Me_4SiMe_2NR)(THF)(\mu-Cl)]_2$, R = ^{t}Bu, ^{t}Pe	**N**	III	X-ray (R = ^{t}Pe), ^1H, ^{13}C, ^{29}Si (R = ^{t}Pe) NMR	72
$[Yb(\eta^5:\eta^1-C_5Me_4SiMe_2NPh(THF)_2(OC_{13}H_8)]$[a]	**J**	VI	X-ray	129
$[Yb(\eta^5:\eta^1-C_5Me_4SiMe_2NPh)(THF)]_2(\mu-O_2C_{26}H_{16})$[b]			X-ray	129
$[Yb_2(\eta^5:\eta^1-C_5Me_4SiMe_2NPh)_2(\mu-\eta^3:\eta^2-N_2Ph_2)(THF)]$		VI	X-ray	129
$[Y(\eta^5:\eta^1-C_5Me_4SiMe_2N{}^tBu)\{N(SiMe_3)_2\}]$	**H**	III	X-ray, ^1H, ^{13}C NMR	57
$[Ln(\eta^5:\eta^1-C_5Me_4SiMe_2N{}^tBu)\{N(SiMe_3)_2\}]$, Ln = Nd, Sm, Lu	**H**	III	X-ray (Ln = Sm), ^1H, ^{13}C (Ln = Lu) NMR, MS	58
$[Y(\eta^5:\eta^1-C_5Me_4SiMe_2N{}^tBu)(NC_4H_4)]_x$		II	^1H, ^{13}C, ^{29}Si NMR	60
$[Y(\eta^5:\eta^1-C_5Me_4SiMe_2N{}^tBu)(NC_4H_4)(DME)]$	**J**	II, V	X-ray, ^1H, ^{13}C NMR	59
$[Y(\eta^5:\eta^1-C_5Me_4CH_2SiMe_2N{}^tBu)(NC_4H_4)]$	**H**	II	^1H, ^{13}C, ^{89}Y NMR	59

[a] $OC_{13}H_8$: biphenyl-2,2′-diyl ketyl. [b] $OC_{26}H_{16}$: 1,2-bis(biphenyl-2,2′-diyl)pinacolate.

$Me_5)(THF)_3\}]$ (Ln = Sm, Yb) in 90% yield. When polymeric $[Sm(\mu_2-\eta^5:\eta^5-C_5Me_5)\{N(SiMe_3)_2\}\{K(\mu_2-\eta^5:\eta^5-C_5Me_5)(THF)_2\}]_x$ was treated with HMPA in THF, crystallographically characterized mononuclear $[Sm(\eta^5-C_5Me_5)\{N(SiMe_3)_2\}(HMPA)_2]$ of structural type **B** was isolated.

Recently, linked cyclopentadienyl pnicogenido complexes of the divalent lanthanides were reported to be accessible by amine elimination and salt metathesis reactions.[129,134] Besides the crystallographically characterized ytterbium complexes $[Yb(\eta^5:\eta^1-C_5H_4SiMe_2NPh)(THF)_3]$ and $[Yb(\eta^5:\eta^1-C_5H_4SiMe_2NPh)(THF)]_2$, the NMR spectroscopically analyzed samarium complexes $[Sm(\eta^5:\eta^1-C_5H_4SiMe_2NPh)(THF)_n]$, $n = 0, 1$, were reported.[129] The type **C** complexes $[Ln\{\eta^5:\eta^1-C_5Me_4SiMe_2P(C_6H_2{}^tBu_3-2,4,6)\}(THF)_3]$, Ln = Sm, Yb, were studied by X-ray diffraction, as were the HMPA and DME adducts $[Sm\{\eta^5:\eta^1-C_5Me_4SiMe_2P(C_6H_2{}^tBu_3-2,4,6)\}(HMPA)_2]$ and $[Sm\{\eta^5:\eta^1-C_5Me_4SiMe_2P(C_6H_2{}^tBu_3-2,4,6)\}(DME)_2]$.[134]

C. Trivalent Pnicogenido Complexes

1. Bis(amido) Complexes

Linked Amido–Cyclopentadienyl Complexes. Base-free bis(trimethylsilyl)amido complexes containing a linked amido–cyclopentadienyl ligand $[Ln(\eta^5:\eta^1-C_5Me_4SiMe_2N{}^tBu)\{N(SiMe_3)_2\}]$ (Ln = Y[57], Lu, Sm, Nd[58]) having the structure **H** were obtained by amine elimination starting from $[Ln\{N(SiMe_3)_2\}_3]$

and the linked amino–cyclopentadiene. Structures of type **H** were crystallographically characterized for Ln = Y and Sm. In these complexes the strong π-donation of the amido ligands alleviates the electron deficiency of the formally 10-electron valence shell.[58] Yttrium pyrrolido complexes containing a linked amido–cyclopentadienyl ligand $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(NC_4H_4)]_x$ and $[Y(\eta^5:\eta^1\text{-}C_5Me_4CH_2SiMe_2N^tBu)(NC_4H_4)]_x$ were obtained by aminolysis of the trimethylsilylmethyl complex.[59,60] The DME adduct $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(NC_4H_4)(DME)]$ was crystallographically shown to have a four-legged piano-stool geometry of type *cis*-**J**.

Bis(amido), Bis(phosphoraneiminato), and Anionic Tris(amido) Complexes. Kretschmer et al. reported the protonolysis of the (pentamethylcyclopentadienyl)neodymium butadiene complex with diphenylamine to give the NMR spectroscopically characterized bis(amido) derivative $[Nd(\eta^5\text{-}C_5Me_5)(NPh_2)_2(HNPh_2)]$.[61] Yttrium and ytterbium bis(amido) complexes $[Ln(\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2OMe)\{N(SiMe_3)_2\}_2]$ (Ln = Y, Yb) containing a donor-functionalized cyclopentadienyl ligand were obtained by salt metathesis.[62] The reaction of $[Yb(\eta^5\text{-}C_5H_4{}^tBu)Cl_2]$ with 3 equiv of $LiNPh_2$ generated the ate complex $[Li(THF)_4]^+[Yb(\eta^5\text{-}C_5H_4{}^tBu)(NPh_2)_3]^-$, which was characterized by X-ray crystallography.[63,64] Heteroleptic bis(amido) complexes $[Sc(\eta^5\text{-}C_5H_5)\{N(SiMe_2CH_2P\text{-}{}^iPr_2)_2\}(NHC_6H_5)]$ and $[Sc(\eta^5\text{-}C_5H_5)\{N(SiMe_2CH_2P\text{-}{}^iPr_2)_2\}(NH^tBu)]$ were synthesized from the methyl complex $[Sc(\eta^5\text{-}C_5H_5)\{N(SiMe_2CH_2P^iPr_2)_2Me]$ by protonolysis as well as by salt metathesis using the chloro complex $[Sc(\eta^5\text{-}C_5H_5)\{N(SiMe_2CH_2P^iPr_2)_2Cl]$. They were characterized by ^1H and ^{31}P NMR spectroscopy.[65] The reaction of ytterbocene chloride with lithium triphenylphosphoraneimidate in toluene gave the crystallographically characterized homobimetallic complex $[Yb(\eta^5\text{-}C_5H_5)_2(\mu\text{-}NPPh_3)_2Yb(\eta^5\text{-}C_5H_5)(NPPh_3)]$ in which an ytterbocene phosphoraneimidate fragment is connected to a mono(cyclopentadienyl) bis(phosphoraneiminato) ytterbium fragment through two bridging phosphoraneiminato nitrogen atoms.[66]

Azobenzene Complexes. Oxidation of $[Sm(\eta^5\text{-}C_9H_7)_2(THF)_x]$ with azobenzene gave a compound of composition $[Sm(\eta^5\text{-}C_9H_7)(N_2Ph_2)(THF)]_x$, which is expected to be analogous to the previously structurally characterized C_5Me_5 analogue $[Sm(\eta^5\text{-}C_5Me_5)(THF)(\mu\text{-}\eta^2:\eta^2\text{-}N_2Ph_2)]_2$.[31] The crystallographically characterized[67] dimeric lutetium complex $[Lu(\eta^5\text{-}C_5H_5)(THF)(\mu\text{-}\eta^2:\eta^2\text{-}N_2Ph_2)]_2$ was obtained by reaction between the naphthalenide complex $[Lu(\eta^5\text{-}C_5H_5)(C_{10}H_8)(THF)_2]$[68] or the anthracenide complex $[Lu(\eta^5\text{-}C_5H_5)(C_{14}H_{10})(THF)_2]$[67] and azobenzene in THF and can be regarded as an analogous complex containing two bridging 1,2-diphenylhydrazido(2−) ligands.

A somewhat distorted ligand of this type is observed in the product of the reaction of the ytterbium complex $[Yb(\eta^5:\eta^1\text{-}C_5H_4SiMe_2NPh)(THF)_3]$ with azobenzene, giving $[Yb_2(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NPh)_2(\mu\text{-}\eta^3:\eta^2\text{-}N_2Ph_2)(THF)]$.[129]

Pyrazolato Complexes. (Methylcyclopentadienyl)bis(3,5-dimethylpyrazolato) complexes of the rare-earth metals were synthesized by the reaction of the tris(cyclopentadienides) with 2 equiv of 3,5-dimethylpyrazole in THF. The number of C_5H_5 groups eliminated from $[Ln(C_5H_5)_3]$ strongly depends on the size of the lanthanide ion. Structural details from X-ray crystallography are not available. Cyclopentadienyl dysprosium and holmium complexes $[Ln(\eta^5\text{-}C_5H_5)(C_3N_2HMe_2\text{-}3,5)_2]$ (Ln = Dy, Ho)[69] and methylcyclopentadienyl samarium, terbium,[70] neodymium, gadolinium, and dysprosium[71] compounds $[Ln(\eta^5\text{-}C_5H_4Me)(C_3N_2HMe_2\text{-}3,5)_2]$ (Ln = Nd, Sm, Gd, Tb, Dy) were reported.

2. Mixed Halo and Chalcogenido Complexes

The amido–chloro complex $[Sc(\eta^5\text{-}C_5H_5)\{N(SiMe_2CH_2P^iPr_2)_2\}Cl]$ was obtained by reaction between $[Sc\{N(SiMe_2CH_2P^iPr_2)_2\}Cl_2(THF)]$ and $[Na(DME)(C_5H_5)]$ and was crystallographically characterized as having a structure of type **J**.[65] The chloro-bridged dimers $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NR)(THF)(\mu\text{-}Cl)]_2$ (R = ^{t}Bu, ^{t}Pe) were obtained by alkane elimination and use of "$Y(CH_2SiMe_3)_2Cl(THF)_x$" and linked amino–cyclopentadiene. X-ray crystallography of the *tert*-pentylamido derivative showed a C_i-symmetric heterochiral dimer of type *hetero-trans*-**N**.[72]

The mono(cyclopentadienyl) complexes containing both amido and alkoxo ligands were formed accidentally by insertion of poly(dimethylsiloxane) (silicon grease) fragments into the lanthanide–nitrogen bonds. The reaction of $[Y(\eta^5\text{-}C_5H_5)Cl_2]$ with lithium triphenylphosphoraneimidate in the presence of poly(dimethylsiloxane) gave the crystallographically characterized siloxo-bridged dimer $[Y(\eta^5\text{-}C_5H_5)(NPPh_3)\{\mu\text{-}OSiMe_2NPPh_3\}]_2$.[66] A series of crystallographically characterized "dimethylsilanone" insertion products of cyclopentadienyl–pyrazolato complexes were also reported. All of them are centrosymmetric dimers with two bridging oxygen atoms connecting the lanthanide metal centers. In addition, the lanthanide atoms are coordinated to a C_5R_5 ligand, a chelating pyrazolato ligand, and a bridging pyrazolato ligand, completing a distorted octahedral geometry of type **O**. (Cyclopentadienyl)holmium and dysprosium complexes $[Ln(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_3N_2HMe_2\text{-}3,5)(\mu\text{-}OSiMe_2C_3N_2HMe_2\text{-}3,5)]_2$ (Ln = Ho, Dy), of which the holmium complex had been crystallographically characterized, were reported.[69] Among the methylcyclopentadienyl complexes $[Ln(\eta^5\text{-}C_5H_4Me)(\eta^2\text{-}C_3N_2HMe_2\text{-}3,5)(\mu\text{-}OSiMe_2C_3N_2HMe_2\text{-}3,5)]_2$, terbium and dysprosium compounds were crystallographically characterized.[70,71]

The linked alkoxo–cyclopentadienyl complex $[Y\{\eta^5:\eta^1\text{-}C_5H_4CH_2CR_2O\}Cl(THF)_2]$, R = $C_6H_3(CF_3)_2\text{-}3,5$, underwent a salt metathesis reaction with $NaN(SiMe_3)_2$ to give the NMR spectroscopically characterized amido complexes $[Y\{\eta^5:\eta^1\text{-}C_5H_4CH_2CR_2O\{N(SiMe_3)_2\}(THF)_n]$, $n = 1, 2$. In the presence of a second equiv of $NaN(SiMe_3)_2$, the heterobimetallic complex $[Y\{\eta^5:\eta^1\text{-}C_5H_4CH_2CR_2O\}\{\mu\text{-}N(SiMe_3)_2\}_2Na(THF)_2]$ was formed.[132]

Oxidation of the divalent samarium complex $[Sm\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2P(C_6H_2{}^tBu_3\text{-}2,4,6)\}(THF)_3]$ with diiodoethane gave the dimeric *hetero-trans*-**N**-type cyclopentadienyl phosphido complex $[Sm\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2P(C_6H_2{}^tBu_3\text{-}2,4,6)\}(THF)(\mu\text{-}I)]_2$, which was studied by X-ray diffraction.[134]

Table 5. Mono(cyclopentadienyl) Hydrocarbyl and Silyl Rare-Earth Metal Complexes

compound	type	methods of preparation	characterization	ref
Divalent Complexes				
$[Yb(\eta^5\text{-}C_5Me_5)\{Si(SiMe_3)_3\}(THF)_2]$	**B**	I	X-ray, ^{171}Yb, ^{29}Si NMR	78
Trivalent Complexes				
$[La(\eta^5\text{-}C_5H_5)\{CH(SiMe_3)_2\}_2]$	**H**		density-functional study	79,80
$[Sc(\eta^5\text{-}C_5H_5)\{N(SiMe_2CH_2P^iPr_2)_2\}Ph]$	**J**	I	^1H, ^{31}P NMR, MS	65
$[Sc(\eta^5\text{-}C_5H_5)\{N(SiMe_2CH_2P^iPr_2)_2\}Me]$	**J**	I	^1H, ^{31}P NMR, MS	65
$[\{Lu(\eta^5\text{-}C_5H_5)(DME)\}_2\{\mu\text{-}1,1,4,4\text{-}(Ph)C(Ph)C{=}C(Ph)C(Ph)\}]$			X-ray, IR	68
$[La(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}_2]$	**H**		neutron diffraction	79,80
$[Gd(\eta^5\text{-}C_5Me_5)(CH_2Ph)_2(THF)]$	**I**	I	X-ray	82
$[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)(\mu\text{-}Me)]_2$	**M**	I	^1H, ^{13}C NMR	91
$[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)Me(THF)_2]$	**J**	V	^1H, ^{13}C NMR	91
$[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)Me(THF)_2]$	**J**	V	^1H, ^{13}C NMR	91
$[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)\{CH(SiMe_3)_2\}]$	**H**	I	X-ray, neutron diffraction	79,80,91
$[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)(C{\equiv}CSiMe_3)]$	**H**	III	^1H NMR	91
$[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)(C{\equiv}CSiMe_3)(THF)_2]$	**J**	V	^1H NMR	91
$[Y(\eta^5\text{-}C_5Me_5)\{\eta^2\text{-}PhC(NSiMe_3)_2\}(\mu\text{-}Me)_2Li(TMEDA)]$		I	X-ray	49
$[Y(\eta^5\text{-}C_5Me_5)\{\eta^2\text{-}PhC(NSiMe_3)_2\}(\mu\text{-}C{\equiv}C^tBu)_2Li(TMEDA)]$		III	^1H, ^{13}C NMR, IR	49
$[Ln(\eta^5\text{-}C_5Me_5)(H_4C_6\text{-}C_6H_4\text{-}2,2')(TMEDA)]$, Ln = Sm, Yb, Lu	**J**	I	^1H NMR, IR	83
$[Li(DME)_3]^+[Nd(\eta^5\text{-}C_5H_4Me)^tBu_3]^-$		I	IR	84
$[Y(\eta^5\text{-}C_5Me_4SiMe_2X)(CH_2SiMe_3)_2(THF)]$, X = Me, Ph, C_6F_5	**I**	III	^1H, ^{13}C, ^{19}F, ^{29}Si NMR	81
$[Y(\eta^5\text{-}C_5Me_4H)\{N(SiMe_2CH_2SiMe_3)X\}(CH_2SiMe_3)(THF)]$, X = CH_2CH_2OMe, $CH_2CH_2NMe_2$, $CH_2CH_2CH_2OMe$, CMe_2CH_2OMe	**J**	III	^1H, ^{13}C, ^{29}Si NMR	92
$[Y\{\eta^5{:}\eta^1\text{-}C_5H_4CH_2CR_2O\}\{CH(SiMe_3)_2\}(THF)_2]$, R = $C_6H_3(CF_3)_2$-3,5	**J**	I	^1H, ^{19}F, ^{29}Si NMR	132
$[Y\{\eta^5{:}\eta^1\text{-}C_5H_4CH_2CR_2O\}\{\mu\text{-}CH(SiMe_3)_2\}_2Li(THF)_2]$, R = $C_6H_3(CF_3)_2$-3,5		V	^1H, ^{13}C, ^{19}F, ^{29}Si NMR	132
$[Y(\eta^5\text{-}C_5Me_4SiMe_2CH_2CHCH_2)(CH_2SiMe_3)_2(THF)_2]$	**J**	III	^1H, ^{13}C NMR	133

Table 6. Mono(cyclopentadienyl) Allyl and Allenyl/Propargyl Rare-Earth Metal Complexes

compound	type	methods of preparation	characterization	ref
Trivalent Complexes				
$[La(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_3H_5)_2]$, R = H, Me	**J**		^{139}La NMR	85
$[Li(C_4H_8O_2)]^+[La(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_3H_5)_3]^-$, $C_5R_5 = C_5H_5$, C_5Me_5, indenyl, fluorenyl		II	^1H, ^{13}C NMR	86
$[Li(C_4H_8O_2)_2]^+[La(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_3H_5)_3]^-$, R = H, Me			^{139}La NMR	85
$[Li(C_4H_8O_2)_2]^+[Nd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)_3]^-$		I	^1H NMR, IR	87
$[Li(DME)_3]^+[Nd(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_3H_5)_3]^-$		II	X-ray, ^1H NMR, IR	87
$[Y\{(\eta^5{:}\eta^1)(\mu\text{-}\eta^3)\text{-}C_5Me_4SiMe_2(C_3H_3)\}L]_2$, L = THF, DME	**N**, **O**	III	X-ray, IR	133
$[Sm\{\eta^5{:}\eta^3\text{-}C_5H_2(SiMe_3)_2\text{-}2,4\text{-}SiMe_2(C_3H)SiMe_3\}Cl_3Li_2(TMEDA)_2]$		I	(X-ray), ^1H NMR	135
$[Sm\{\eta^5{:}\eta^1\text{-}C_5H_2(SiMe_3)_2\text{-}2,4\text{-}SiMe_2CHCCSiPh_3\}(TMEDA)Cl_2Li(TMEDA)]$		I	(X-ray)	135
$[Sm\{\eta^5{:}\eta^3\text{-}C_5H_2(SiMe_3)_2\text{-}2,4\text{-}SiMe_2(C_3H)SiPh_3\}I_2Li(TMEDA)]$		V	X-ray	135
$[Sm\{\eta^5{:}\eta^3\text{-}C_5H_2(SiMe_3)_2\text{-}2,4\text{-}SiMe_2(C_3H)SiPh_3\}CH(SiMe_3)_2Cl][Li(TMEDA)_2]$		I	X-ray, ^1H NMR	135

VI. Hydrocarbyl and Silyl Complexes

A. General

No mono(cyclopentadienyl) hydrocarbyl complexes of divalent lanthanides $[Ln(\eta^5\text{-}C_5R_5)R']$ are known so far. Despite the paramount importance of lanthanide hydrocarbyl complexes, e.g., as precatalysts in olefin polymerization reactions, the number of bis(hydrocarbyl) complexes of the simple type $[Ln(\eta^5\text{-}C_5R_5)R'_2]$ is surprisingly limited, also for the trivalent lanthanide (Table 5). The in-depth characterization of the alkyl ligands in these formally 10-electron complexes is limited to the previously published remarkable complex $[La(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}_2]$,[80] and its extension remains a challenge. Complexes containing allyl, butadiene, and related aromatic ligands are listed in Tables 6, 7, and 8, respectively. The use of functionalized cyclopentadienyl ligands such as the linked amido−cyclopentadienyl ligands allowed more systematic studies of a series of hydrocarbyl complexes (Table 10). A series of metallacarbaboranes featuring the novel *ansa*-type ligand $(C_5R_4ZC_2B_{10}H_{11})$ also became known (Table 9).[18,24,35−37,73−75]

B. Divalent Complexes

1. Metallacarbaboranes

Xie et al. reported the X-ray crystallographically characterized *ansa*-indenyl complex $[Yb(\eta^5{:}\eta^1\text{-}C_9H_6\text{-}SiMe_2C_2B_{10}H_{10})(THF)_3]$ with a σ-bonded (monoanionic, *closo*-type) carbaboranyl group which was obtained by the reaction of YbI_2 with 1 equiv of the disodium salt of the ligand in THF.[24] A related compound with an isopropylidene group bridging the indenyl and the carbaboryl unit $[Yb\{\eta^5{:}\eta^1\text{-}C_9H_6\text{-}CMe_2C_2B_{10}H_{10}\}(DME)_2]$ was obtained by a similar procedure.[75] Samarium and ytterbium *ansa*-cyclopentadienyl complexes $[K(THF)_2][Ln(\mu_2\text{-}\eta^5{:}\eta^6\text{-}C_5H_4\text{-}SiMe_2C_2B_{10}H_{11})(THF)_2]$ (Ln = Sm, Yb) with η^6-bonded (dianionic, *nido*-type) carbaboranyl function were obtained by reaction between the lanthanide trichloride and the tripotassium salt of the ligand.[35] By X-ray crystallography of the samarium complex, the cyclopentadienyl ligand was shown to act as a neutral ligand at the lanthanide center due to an additional potassium coordination.

Table 7. Mono(cyclopentadienyl) Rare-Earth Metal Complexes Containing a Butadiene Ligand

compound	type	methods of preparation	characterization	ref
Trivalent Complexes				
[Er(η^5-C_5H_5)(C_4H_6)($MgCl_2$)($THF)_2$]		I	^1H, ^{13}C NMR, MS, IR	61
[Nd(η^5-1,3-$^tBu_2C_5H_3$)(C_4H_6)($MgCl_2$)($THF)_2$]		I	^1H, ^{13}C NMR, MS, IR	61
[Lu(η^5-1,3-$^tBu_2C_5H_3$)(C_4H_6)($MgCl_2$)($THF)_2$]		I	^1H, ^{13}C NMR, MS, IR	61
[La(η^5-C_5Me_5)(1,4-$Ph_2C_4H_4$)(DME)]	**J**	I	^1H, ^{13}C NMR, MS, IR	88
[La(η^5-C_5Me_5){1,4-(*o*-MeO-$C_6H_4)_2C_4H_4$}($DME)_2$]	**L**	I	^1H, ^{13}C NMR, MS, IR	88
[La(η^5-C_5Me_5)(C_4H_6)(MgI_2)($THF)_3$]		I	^1H, ^{13}C NMR, MS, IR	61
[Ce(η^5-C_5Me_5)(C_4H_6)($MgBr_2$)($THF)_2$]		I	^1H, ^{13}C NMR, MS, IR	61
[Nd(η^5-C_5Me_5)(C_4H_6)($MgCl_2$)($THF)_2$]		I	^1H, ^{13}C NMR, MS, IR	61

Table 8. Mono(cyclopentadienyl) Rare-Earth Metal Complexes Containing an Aromatic Ligand

compound	type	methods of preparation	characterization	ref
Divalent Complexes				
[{Ln(η^5-C_5H_5)(THF)$_2$}$_2$(μ-$C_{10}H_8$)], Ln = Sm, Yb	**G**		IR	76
[Eu(μ_2-η^5:η^5-C_5H_5)(THF)(μ_2-$C_{10}H_8$)V(η^5-C_5H_5)]$_x$		V	X-ray, IR	77
[Sm(η^5-C_5H_5)($C_{10}H_8$)(THF)V(η^5-C_5H_5)]$_x$		V	IR	77
[Yb(η^5-$C_{13}H_8SiMe_3$){η^6-$C_{13}H_8$($SiMe_3$)($AlMe_3$)}]			X-ray, ^1H NMR, MS	101
Trivalent Complexes				
[Ln(η^5-C_5H_5)(η^1:η^1:η^2-$C_{10}H_8$)(DME)], Ln = Y, Gd, Er, Tm	**K**	I	X-ray (Ln = Y), IR	76
[Lu(η^5-C_5H_5)(C_{60})(DME)]	**J**	III	ESR	90
[Lu(η^5-C_5Me_5)($C_{10}H_8$)(DME)]	**K**	I	IR	89
[Lu(η^5-C_5Me_5)($C_{10}H_8)_2$Na($THF)_x$]		I	IR	89
[Lu(η^5-C_5Me_5)(C_{60})(DME)](PhMe)	**J**	III	ESR	90

Table 9. Rare-Earth Metal Complexes Containing a Carboranyl-Functionalized Cyclopentadienyl Ligand

compound	type	methods of preparation	characterization	ref
Divalent Complexes				
[K($THF)_2$][Ln(μ_2-η^5:η^6-$C_5H_4SiMe_2C_2B_{10}H_{11}$)($THF)_2$], Ln = Sm, Yb		VII	X-ray (Ln = Sm), ^1H, ^{11}B NMR, IR	35
[Yb(η^5:η^1-$C_9H_6CMe_2C_2B_{10}H_{10}$)($DME)_2$]	**D**	I	^1H, ^{13}C, ^{11}B NMR, IR	75
[Yb(η^5:η^1-$C_9H_6SiMe_2C_2B_{10}H_{10}$)($THF)_3$]	**C**	I	X-ray, ^1H, ^{13}C, ^{11}B NMR, IR	24
Trivalent Complexes				
[Sm(η^5:η^6-$C_5H_4CMe_2C_2B_{10}H_{11}$)($THF)_2$]	**J**	VI	X-ray, ^1H, ^{13}C, ^{11}B NMR, IR	36
[Er(η^5:η^6-$C_5H_4CMe_2C_2B_{10}H_{11}$)($THF)_2$]	**J**	I	X-ray, ^1H, ^{13}C, ^{11}B NMR, IR	36,37
[{Er(η^5:η^7-$C_5H_4CMe_2C_2B_{10}H_{11}$)}$_2${$Na_4$($THF)_9$}]$_x$		VII	X-ray, ^1H, ^{13}C, ^{11}B NMR, IR	36,37
[Er_2(η^5:η^7-$C_5H_4CMe_2C_2B_{10}H_{11}$)($THF)_3$($\mu$-Cl)]$_2$		I	X-ray, ^1H, ^{13}C, ^{11}B NMR, IR	36,37
[Sm(η^5:η^6-$C_5H_4SiMe_2C_2B_{10}H_{11}$)($THF)_2$]	**J**	VI	X-ray, ^1H, ^{13}C, ^{11}B NMR, IR	18,35,73
[Nd(η^5:η^6-$C_5H_4SiMe_2C_2B_{10}H_{11}$)($THF)_2$]	**J**	I	^1H, ^{11}B NMR, IR	35
[Er(η^5:η^6-$C_9H_6SiMe_2C_2B_{10}H_{11}$)($THF)_2$]	**J**	I	^1H, ^{11}B NMR, IR	74
[Sm(η^5:η^6-$C_9H_6SiMe_2C_2B_{10}H_{11}$)($THF)_2$]	**J**	VI	X-ray, ^1H, ^{13}C, ^{11}B NMR, IR	24

2. Bimetallic Naphthalene Complexes

Reaction between sodium naphthalenide and [Ln(η^5-C_5H_5)Cl_2($THF)_3$] in THF gave the naphthalene-bridged homobimetallic samarium and ytterbium naphthalene complexes [Ln(η^5-C_5H_5)(THF)]$_2$(μ_2-$C_{10}H_8$) (Ln = Sm, Yb).[76] Related heterobimetallic complexes [Ln(μ_2-η^5:η^5-C_5H_5)(μ_2-$C_{10}H_8$)V(η^5-C_5H_5)(THF)]$_x$ (Ln = Eu, Sm) were formed by the reactions of LnI_2($DME)_3$ with K(C_5H_5) and K[V(η^5-C_5H_5)($C_{10}H_8$)]. X-ray crystallography of the europium derivative showed a one-dimensional polymeric structure consisting of [Eu(η^5-C_5H_5)(THF)] fragments η^2-coordinated to the vanadium sandwich unit.[77]

3. Silyl Complexes

The divalent ytterbium silyl complex [Yb(η^5-C_5Me_5){Si($SiMe_3)_3$}($THF)_2$] was obtained by the reaction of the decamethylytterbocene complex [Yb(η^5-$C_5Me_5)_2$(OEt_2)] with the lithium silyl salt Li{Si($SiMe_3)_3$} in toluene and was characterized by X-ray crystallography as well as ^{171}Yb and ^{29}Si NMR spectroscopy.[78]

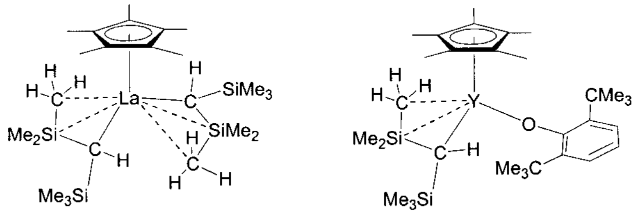
C. Bis(Hydrocarbyls)

1. Bis(alkyl), Bis(aryl), and Anionic Tris(alkyl) Complexes

A neutron diffraction study of the base-free complex [La(η^5-C_5Me_5){CH($SiMe_3)_2$}$_2$] as well as density-functional calculations of the model compound [La(η^5-C_5H_5){CH($SiMe_3)_2$}$_2$] unequivocally showed that the β-SiC agostic interaction predominates over α-CH, α-CSi, and γ-CH interactions in stabilizing the 10-electron metal center (Scheme 4).[79,80]

Low-melting bis(alkyl) yttrium complexes [Y(η^5-$C_5Me_4SiMe_2X$)($CH_2SiMe_3)_2$(THF)] (X = Me, Ph, C_6F_5) can be synthesized by alkane elimination (synthetic method III) starting from [Y($CH_2SiMe_3)_3$($THF)_2$] and the corresponding cyclopentadienes (C_5Me_4H)$SiMe_2X$ in pentane.[81] They were found to catalyze the polymerization of ethylene and polar monomers such as *tert*-butyl acrylate and acrylonitrile. The related

Scheme 4



yttrium complex with an allyl function at the silicon atom $[Y(\eta^5\text{-}C_5Me_4SiMe_2CH_2CHCH_2)(CH_2SiMe_3)_2(THF)_2]$ was formed by alkane elimination and isolated as an oily product. NMR spectroscopic studies did not indicate an interaction of the allyl function with the metal center.[133] The yellow dibenzyl gadolinium complex $[Gd(\eta^5\text{-}C_5Me_5)(CH_2Ph)_2(THF)]$ was obtained by salt metathesis of $GdBr_3$ with $K(C_5Me_5)$ and benzyl potassium in THF and characterized by X-ray crystallography as type **I**. The *ipso*-carbon atoms of the benzyl ligands interact with the gadolinium center, with rather small angles at the α-carbon atoms (92.1(4)° and 96.4(4)°).[82]

The synthesis of lanthanafluorene complexes $[Ln(\eta^5\text{-}C_5Me_5)(C_6H_4C_6H_4)(TMEDA)]$ (Ln = Sm, Yb, Lu) by the reactions of lanthanide trichlorides with $Na(C_5Me_5)$ and 2,2′-dilithiobiphenyl TMEDA in THF was reported.[83]

The anionic neodymium complex $[Li(DME)_3]^+[Nd(\eta^5\text{-}C_5H_4Me)^tBu_3]^-$ was obtained by salt metathesis and was reported to polymerize styrene, giving atactic polystyrene.[84]

2. Allyl and Anionic Tris(allyl) Complexes

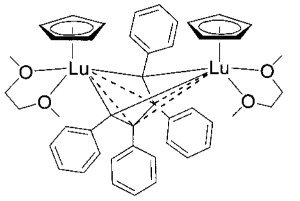
Taube et al. reported ^{139}La NMR spectroscopic investigations of the lanthanum complexes $[La(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_3H_5)_2]$ (R = H, Me).[85] A series of anionic neodymium and lanthanum allyl complexes $[Ln(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_3H_5)_3]^-$ (Ln = La, Nd; R = H, Me) were reported to be catalytically active in the stereospecific butadiene polymerization.[85−87] The neodymium complex $[Li(DME)_3]^+[Nd(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_3H_5)_3]^-$, prepared by the reaction of anionic tetrakis(allyl) neodymium with C_5Me_5H, was shown by X-ray crystallography to adopt a piano-stool configuration.[87] If one regards an allyl ligand as equivalent to an LX-type ligand, the structure is isoelectronically related to the pentagonal bipyramidal structure of type **L** with 18 electrons ($[Ln(\eta^5\text{-}C_5R_5)L_3X_3]^-$ instead of $[Ln(\eta^5\text{-}C_5R_5)L_4X_2]$).

Thermal decomposition of the bis(alkyl) complex $[Y(\eta^5\text{-}C_5Me_4SiMe_2CH_2CHCH_2)(CH_2SiMe_3)_2(THF)_2]$ gave, by multiple alkane elimination reactions, the bimetallic complexes $[Y\{\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2(\mu\text{-}\eta^3\text{-}C_3H_3)\}L]_2$, which were isolated as DME and THF adducts. X-ray diffraction studies showed that the novel trianionic ligand bridges the two yttrium atoms by coordinating $\eta^5{:}\eta^1$ to one and η^3 to the other metal.[133]

3. Metallacyclopentenes

Butadiene Complexes. A series of lanthanide 1,3-butadiene complexes incorporating magnesium halides $[Ln(\eta^5\text{-}C_5R_2R'_3)(C_4H_6)(MgX_2)(THF)_n]$ (Ln = Er, Nd, Lu, Ce, La; R = R′ = H or R = R′ = Me or R = ^{t}Bu and R′ = H; X = Cl, Br, I; n = 2 or 3) was reported by Kretschmer et al.[61] These complexes were characterized by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and mass spectroscopy, but structural details are not available, as crystallographic studies were not carried out. They were obtained from the mono(cyclopentadienyl)lanthanide dihalides and magnesium butadienide in THF solutions.

Scheme 5



Lanthanide butadienides $[La(\eta^5\text{-}C_5Me_5)\{1,4\text{-}(o\text{-}MeOC_6H_4)_2C_4H_4\}(DME)_2]$ and $[La(\eta^5\text{-}C_5Me_5)(1,4\text{-}Ph_2C_4H_4)(DME)]$ free of magnesium halides are accessible by the reaction between 1,4-diaryl-substituted butadienes and (pentamethylcyclopentadienyl)lanthanum dihalides in the presence of alkali metals in DME.[88]

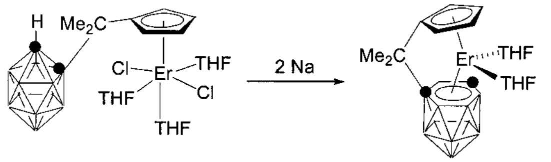
Reactions of $[Lu(\eta^5\text{-}C_5H_5)(\eta^1{:}\eta^1{:}\eta^2\text{-}C_{10}H_8)(THF)_2]$ with diphenylacetylene gave $[\{Lu(\eta^5\text{-}C_5H_5)(DME)\}_2\{\mu\text{-}1,1,4,4\text{-}(Ph)C(Ph)C{=}C(Ph)C(Ph)\}]$, which contains a tetraanionic bridging ligand $(C_4Ph_4)^{4-}$, resulting from a reductive C−C coupling reaction. According to the crystallographically determined structure of the benzene solvate, two $Lu(\eta^5\text{-}C_5H_5)$ units are connected by a C_4Ph_4 ligand. The shortest Lu−C distances of 2.280(7) and 2.336(7) Å are for the terminal carbon atoms of the $(C_4Ph_4)^{4-}$ ligand (Scheme 5). The structural data together with the diamagnetism suggest a bridging dialkylidene ligand in this complex.[68]

Naphthalene Complexes. The yttrium complex $[Y(\eta^5\text{-}C_5H_5)(\eta^1{:}\eta^1{:}\eta^2\text{-}C_{10}H_8)(DME)]$ was obtained from the reaction of $[Y(\eta^5\text{-}C_5H_5)Cl_2(THF)_3]$ and sodium naphthalenide in DME solution. The structure of the complex was determined by X-ray diffraction and revealed a nonplanar coordination mode of the naphthalene ring with two short and two long yttrium−carbon distances. The data suggest that this naphthalene complex can be regarded as a metallacyclopentene with the double bond weakly coordinated to the trivalent metal center (σ^2,π-coordination). Analogous complexes with gadolinium, erbium, and thulium were also reported.[76] The reaction of $[Lu(\eta^5\text{-}C_5Me_5)Cl_2(THF)_3]$ and sodium naphthalenide in DME solution gave the analogous pentamethylcyclopentadienyl complex $[Lu(\eta^5\text{-}C_5Me_5)(\eta^1{:}\eta^1{:}\eta^2\text{-}C_{10}H_8)(DME)]$. When the reaction was carried out in THF, a compound of the formula $[Lu(\eta^5\text{-}C_5Me_5)(C_{10}H_8)_2][Na(THF)_x]$ was isolated.[89]

4. Metallacarbaboranes

An extensive series of trivalent lanthanide complexes with cyclopentadienyl or indenyl ligands attached to the carbaboranyl fragment via dimethylsilylene or isopropylidene bridges was published by Xie et al. (Table 9). In contrast to the divalent lanthanide carbaboranyl compounds with the 1,2-

Scheme 6



$C_5R_4ZC_2B_{10}H_{11}$ ligand moiety, the rearranged $C_2B_{10}H_{11}$ unit is invariably coordinated in an η^6-fashion. The samarium complexes $[Sm(\eta^5{:}\eta^6\text{-}C_5H_4SiMe_2C_2B_{10}H_{11})(THF)_2]$[18,35,73] and $[Sm(\eta^5{:}\eta^6\text{-}C_9H_6SiMe_2C_2B_{10}H_{11})(THF)_2]$[24] were obtained from THF solutions of SmI_2 and the monosodium salt of the ligand and were characterized by X-ray diffraction. The reaction of $NdCl_3$ with the tripotassium salt of the ligand in THF gave the analogous complex $[Nd(\eta^5{:}\eta^6\text{-}C_5H_4SiMe_2C_2B_{10}H_{11})(THF)_2]$.[35] By an analogous procedure, $ErCl_3$ and the tripotassium salt of the corresponding ligand gave $[Er(\eta^5{:}\eta^6\text{-}C_9H_6SiMe_2C_2B_{10}H_{11})(THF)_2]$, which can also be obtained by reaction of $[Er(\eta^5\text{-}C_9H_6SiMe_2C_2B_{10}H_{11})Cl_2(THF)_3]$ with potassium metal in THF (Scheme 6).[74] The isopropylidene-bridged erbium complex $[Er(\eta^5{:}\eta^6\text{-}C_5H_4CMe_2C_2B_{10}H_{11})(THF)_2]$ was obtained by the reduction method and characterized by X-ray crystallography. Excess sodium in THF afforded $[\{Er(\eta^5{:}\eta^7\text{-}C_5H_4CMe_2C_2B_{10}H_{11})\}_2\{Na_4(THF)_9\}]_x$, which contains an η^7-bonded *arachno*-type $[C_2B_{10}H_{11}]^{4-}$ and which underwent substitution with $ErCl_3$ to give an unusual tetranuclear cluster $[Er_2(\eta^5{:}\eta^7\text{-}C_5H_4CMe_2C_2B_{10}H_{11})(THF)_3(\mu\text{-}Cl)]_2$.[36,37] The crystallographically characterized analogous samarium complex $[Sm(\eta^5{:}\eta^6\text{-}C_5H_4CMe_2C_2B_{10}H_{11})(THF)_2]$ was obtained in THF from SmI_2 and the mono(sodium) salt of the ligand.[36]

5. Fullerides

The paramagnetic lutetium fullerides $[Lu(\eta^5\text{-}C_5H_5)(C_{60})(DME)]$ and $[Lu(\eta^5\text{-}C_5Me_5)(C_{60})(DME)](PhMe)$ were prepared by the reactions of the DME adducts of the mono(cyclopentadienyl) naphthalene lutetium complexes with fullerene C_{60} in toluene and characterized by ESR spectroscopy.[90]

D. Hydrocarbyl Complexes with Rare-Earth Metal to Chlorine, Oxygen, and Nitrogen Bonds

1. Aryloxo, Silylamido, and Amidinato Complexes

Schaverien et al. reported a series of monomeric and dimeric mono(pentamethylcyclopentadienyl) alkyl yttrium complexes supported by the bulky 2,6-di-*tert*-butylphenoxy ligand. The reaction of $[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)_2]$ with $M\{CH(SiMe_3)_2\}$ (M = Li, K) gave base-free $[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)\{CH(SiMe_3\}_2]$.[91] The presence of a β Si−C agostic interaction of the $CH(SiMe_3)_2$ group was detected by X-ray crystallography and, more recently, confirmed by neutron diffraction experiments (Scheme 4).[79,80] This alkyl complex reacted with excess trimethylsilylacetylene to give the terminal acetylide $[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)(C{\equiv}CSiMe_3)]$.[91] The analogous bis(THF) adduct was reported to form from the hydride $[Y_2(\eta^5\text{-}C_5Me_5)_2(OC_6H_3{}^tBu_2\text{-}2,6)_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CSiMe_3)]$ in the presence of excess trimethylsilylacetylene.[91] The dimeric methyl-bridged complex $[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)(\mu\text{-}Me)]_2$ was obtained by the reaction of the bis(aryloxide) $[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)_2]$ with methyllithium. In the presence of THF, the monomeric bis(THF) adduct $[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)(Me)(THF)_2]$ was formed.[91]

Fryzuk et al. reported the phosphine-functionalized silylamides $[Sc(\eta^5\text{-}C_5H_5)\{N(SiMe_2CH_2P^iPr_2)_2\}Me]$ and $[Sc(\eta^5\text{-}C_5H_5)\{N(SiMe_2CH_2P^iPr_2)_2\}Ph]$ which were obtained from the parent scandium chloro complex $[Sc(\eta^5\text{-}C_5H_5)\{N(SiMe_2CH_2P^iPr_2)_2\}Cl]$ and the corresponding lithium hydrocarbyl in toluene and characterized by ^1H and ^{31}P NMR spectroscopy.[65]

The X-ray crystallographically characterized benzamidinato methyl complex $[Y(\eta^5\text{-}C_5Me_5)\{\eta^2\text{-}PhC(NSiMe_3)_2\}(\mu\text{-}Me)_2Li(TMEDA)]$ was synthesized by the reaction of the chloro complex $[Y(\eta^5\text{-}C_5Me_5)\{\eta^2\text{-}PhC(NSiMe_3)_2\}(\mu\text{-}Cl)]_2$ with methyllithium in the presence of TMEDA. Protonolysis of the methyl complex with *tert*-butylacetylene gave the acetylide ate complex $[Y(\eta^5\text{-}C_5Me_5)\{\eta^2\text{-}PhC(NSiMe_3)_2\}(\mu\text{-}C{\equiv}C^tBu)_2Li(TMEDA)]$.[49]

A series of ether- and amino-functionalized silylamides $[Y(\eta^5\text{-}C_5Me_4H)\{N(SiMe_2CH_2SiMe_3)(CH_2CH_2X)\}(CH_2SiMe_3)(THF)]$ (X = OMe, NMe_2, CH_2OMe) and $[Y(\eta^5\text{-}C_5Me_4H)\{N(SiMe_2CH_2SiMe_3)(CMe_2CH_2OMe)\}(CH_2SiMe_3)(THF)]$ were obtained unexpectedly from the reaction of $[Y(CH_2SiMe_3)_3(THF)_2]$ with $(C_5Me_4H)SiMe_2NCH_2CH_2X$ and characterized by NMR spectroscopy. The products were thought to have formed by cleavage of the carbon−silicon bonds of the amino−cyclopentadienes as a result of $SiMe_4$ elimination.[92]

The linked alkoxo−cyclopentadienyl complex $[Y\{\eta^5{:}\eta^1\text{-}C_5H_4CH_2CR_2O\}Cl(THF)_2]$, R = $C_6H_3(CF_3)_2\text{-}3,5$, underwent a salt metathesis reaction with $LiCH(SiMe_3)_2$ to give the NMR spectroscopically characterized amido complexes $[Y\{\eta^5{:}\eta^1\text{-}C_5H_4CH_2CR_2O\}\{CH(SiMe_3)_2\}(THF)_2]$. In the presence of a second equivalent of $LiCH(SiMe_3)_2$, the heterobimetallic complex $[Y\{\eta^5{:}\eta^1\text{-}C_5H_4CH_2CR_2O\}\{\mu\text{-}CH(SiMe_3)_2\}_2Li(THF)_2]$ formed.[132]

2. Linked Pnicogenido Cyclopentadienyl Complexes

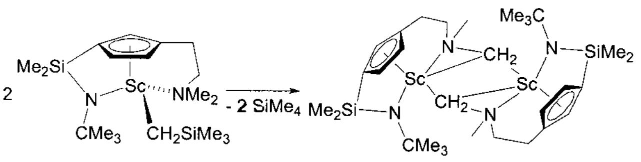
Alkyl Complexes. Bercaw et al. obtained the Lewis base-free scandium alkyl complex $[Sc(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)\{CH(SiMe_3)_2\}]$ by salt metathesis between the scandium chloro complex $[Sc(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)Cl]_x$ and $Li\{CH(SiMe_3)_2\}$ in toluene.[93,94] Analogous lutetium and ytterbium complexes $[Ln(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)\{CH(SiMe_3)_2\}]$ (Ln = Lu, Yb) were synthesized by the alkane elimination route starting from lanthanide tris(alkyl) $[Ln\{CH(SiMe_3)_2\}_3]$ and the linked amino−cyclopentadiene. The single-crystal X-ray diffraction study of the ytterbium complex $[Yb(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)\{CH(SiMe_3)_2\}]$ revealed a pseudotrigonal configuration of type **H** similar to that of $[Ln(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)\{N(SiMe_3)_2\}]$.[58]

The scandium complex $[Sc\{\eta^5{:}\eta^1{:}\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)(SiMe_2N^tBu)\}(CH_2SiMe_3)]$ with an intramolecular donor function was obtained by alkane elimination during the reaction of $[Sc(CH_2SiMe_3)_3(THF)_2]$ with the functionalized cyclopentadiene in hexane.

Table 10. Hydrocarbyl Rare-Earth Metal Complexes Containing a Linked Pnicogenido Cyclopentadienyl Ligand

compound	type	methods of preparation	characterization	ref
Trivalent Complexes				
$[Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(PMe_3)]_2(\mu\text{-}\eta^2:\eta^2\text{-}C_2H_4)$	**N**	III	X-ray, ^1H, ^{13}C, ^{31}P NMR	94
$[Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)\{CH(SiMe_3)_2\}]$	**H**	I	^1H NMR, IR	94
$[Ln(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)\{CH(SiMe_3)_2\}]$, Ln = Yb, Lu	**H**	III	X-ray (Ln = Yb), ^1H, ^{13}C NMR (Ln = Lu), MS	58
$[Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(\mu\text{-}(CH_2)_nCH_3)]_2$, $n = 2,3$	**M**	IV	X-ray ($n = 2$), ^1H, ^{13}C NMR, IR	94
$[Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu(PMe_3)\{CH_2CHMe(CH_2)_2Me\}]$	**I**	IV	^1H, ^{13}C, ^{31}P NMR, IR	94
$[Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu(PMe_3)\{^{13}CH_2CH(^{13}CH_3)_2\}]$	**I**	IV	^1H, ^{13}C NMR	94
$[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)\{\mu\text{-}(CH_2)_5CH_3\}(THF)]_2$	**N**	IV	^1H, ^{13}C, ^{29}Si, NMR	92
$[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)\{CH_2CH(CH_2)_4\}(THF)]$	**I**	IV	^1H, ^{13}C, ^{29}Si NMR	92
$[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NR)CH_2SiMe_3(THF)]$, R = ^tBu, ^tPe	**I**	III	X-ray (R = ^tPe), ^1H, ^{13}C, ^{29}Si NMR	81,92
$[Ln(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(CH_2SiMe_3)(THF)]$, Ln = Yb, Lu	**I**	III	^1H, ^{13}C, ^{29}Si NMR (Ln = Lu)	72
$[Y(\eta^5:\eta^1\text{-}C_9H_6SiMe_2N^tBu)(CH_2SiMe_3)(THF)]$	**I**	III	^1H, ^{13}C, ^{29}Si NMR,	92
$[Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu(PMe_3)\{CHPh(CH_2)_3Ph\}]$	**I**	IV	^1H, ^{13}C, ^{31}P NMR, IR	94
$[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NR)\{CHMePh)\}(THF)]$, R = ^tBu, ^tPe	**I**	IV	^1H, ^{13}C, ^{29}Si NMR	92
$[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tPe)\{CHMe(C_6H_4{}^tBu\text{-}4)\}(THF)]$	**I**	IV	X-ray, ^1H, ^{13}C, ^{29}Si NMR	92
$[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)\{CH(Me)(C_6H_4OMe\text{-}4)\}(THF)]$	**I**	IV	^1H, ^{13}C, ^{29}Si NMR	92
$[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)\{CH(Me)(C_6H_3Me_2\text{-}2,4)\}(THF)]$	**I**	IV	^1H, ^{13}C, ^{29}Si NMR	92
$[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(\mu\text{-}C_4H_3S)]_2$		III	X-ray, ^1H, ^{13}C, ^{29}Si NMR	59,60
$[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(\mu\text{-}C_4H_3O)]_2$		III	^1H, ^{13}C, ^{29}Si NMR	60
$[Y(\eta^5:\eta^1\text{-}C_5Me_4CH_2SiMe_2N^tBu)(C_4H_3S)(THF)]$	**I**	III	X-ray, ^1H, ^{13}C, ^{89}Y NMR	59
$[Y(\eta^5:\eta^1\text{-}C_5Me_4CH_2SiMe_2N^tBu(\mu\text{-}C_4H_3O)]_2$		III	^1H, ^{13}C, ^{89}Y NMR	59
$[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)\{\mu\text{-}2\text{-}(OC_4H_2Me\text{-}5)\}]_2$		III	^1H, ^{13}C NMR	59
$[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(2\text{-}C_4H_3O)(DME)]$	**J**	III	X-ray, ^1H, ^{13}C NMR	59
$[Y(\eta^5:\eta^1\text{-}C_5Me_4CH_2SiMe_2N^tBu(CH_2SiMe_3)(THF)]$	**I**	III	X-ray, ^1H, ^{13}C, ^{89}Y NMR	95
$[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu(CH_2SiMe_3)(DME)]$	**J**	V	^1H, ^{13}C NMR	59
$[Y(\eta^5:\eta^1\text{-}C_5Me_4CH_2SiMe_2N^tBu)\{CHMePh\}(THF)]$	**I**	IV	X-ray, ^1H, ^{13}C, ^{89}Y NMR	95
$[Sc\{\eta^5:\eta^1:\eta^1\text{-}C_5H_3(SiMe_2N^tBu)(CH_2CH_2NMe_2)\}(CH_2SiMe_3)]$	**I**	III	^1H, ^{13}C NMR	97
$[Li(THF)][Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2X)(o\text{-}C_6H_4CH_2NMe_2)(\mu\text{-}Cl)]$, X = NMe_2, OMe, CH_2OMe		I	X-ray (X = OMe), ^1H, ^{13}C, ^{29}Si NMR	96
$[Sm_2\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2P(C_6H_2{}^tBu_3\text{-}2,4,6)\}_2(THF)_2(\mu\text{-}OCPh_2)]$	**N**	VI	X-ray, ^1H NMR	134
$[Sm\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2P(C_6H_2{}^tBu_3\text{-}2,4,6)\}(THF)(\mu\text{-}I)]_2$	**N**	VI	X-ray, ^1H NMR	134

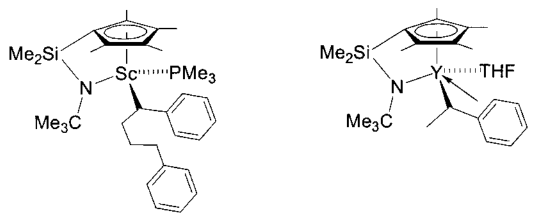
Scheme 7



The synthesis 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 center and the enantiotopic faces of the ligand). The molecular structure of the metalated thermolysis product $[Sc\{\eta^5:\eta^1\text{-}C_5H_3(SiMe_2N\text{-}{}^tBu)\{CH_2CH_2NMe(\mu\text{-}CH_2)\}\}]_2$ formed by σ-bond metathesis involving one amino methyl group was determined by X-ray diffraction (Scheme 7).

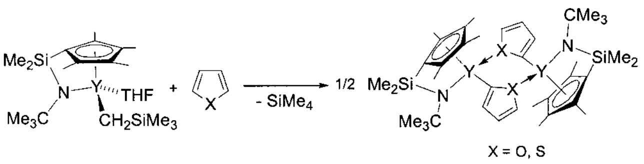
Alkyl yttrium, ytterbium, and lutetium complexes $[Ln(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(CH_2SiMe_3)(THF)]$ (Ln = Y, Lu, Yb) can be obtained by alkane elimination starting from $[Ln(CH_2SiMe_3)_3(THF)_2]$.[72,81,92] The yttrium complex was reported to be a precatalyst for the polymerization of ethylene, *tert*-butyl acrylate, and acrylonitrile. The THF ligand is labile on the NMR time scale, more so for the yttrium than for the lutetium complex. The yttrium complex reacts with DME to give the 16-electron complex $[Y(\eta^5:\eta^1\text{-}C_5Me_4\text{-}SiMe_2N^tBu)(CH_2SiMe_3)(DME)]$.[59] By the alkane elimination method, the indenyl complex $[Y(\eta^5:\eta^1\text{-}C_9H_6\text{-}SiMe_2N^tBu)(CH_2SiMe_3)(THF)]$ and the crystallographically characterized complex $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\text{-}{}^tPe)(CH_2SiMe_3)(THF)]$ were obtained.[92] The reaction of the related amino–cyclopentadiene $(C_5Me_4H)CH_2\text{-}SiMe_2NH^tBu$ with $[Y(CH_2SiMe_3)_3(THF)_2]$ in hexane gives the crystallographically characterized alkyl complex of type **I** $[Y(\eta^5:\eta^1\text{-}C_5Me_4CH_2SiMe_2N^tBu)(CH_2\text{-}SiMe_3)(THF)]$.[95]

Scheme 8



A significant number of alkyl complexes are obtained from insertion reactions of α-olefins with hydrido complexes (synthetic method IV). The reaction of the dimeric hydride $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\text{-}{}^tBu)(THF)(\mu\text{-}H)]_2$ with 1,5-hexadiene gave under cyclization the cyclopentylmethyl complex $[Y(\eta^5:\eta^1\text{-}C_5\text{-}Me_4SiMe_2N^tBu)\{CH_2CH(CH_2)_4\}(THF)]$.[92] Styrene reacted with the scandium hydride $[Sc(\eta^5:\eta^1\text{-}C_5Me_4\text{-}SiMe_2N^tBu)(PMe_3)(\mu\text{-}H)]$ to form orange $[Sc(\eta^5:\eta^1\text{-}C_5\text{-}Me_4SiMe_2N^tBu)(PMe_3)\{CHPh(CH_2)_3Ph\}]$ as the result of a primary(1,2) insertion followed by a secondary-(2,1) insertion of styrene.[94] Contrary to this finding, the related yttrium hydrido complexes $[Y(\eta^5:\eta^1\text{-}C_5\text{-}Me_4SiMe_2N^tBu)(THF)(\mu\text{-}H)]_2$ regioselectively underwent secondary insertion with styrenes with not more than one *ortho*-substituent to give the bright yellow mono(insertion) products (Scheme 8). An X-ray diffractionstudyof$[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tPe)(CHMeC_6H_4\text{-}{}^tBu\text{-}4)(THF)]$ confirmed that the insertion occurred

Scheme 9



in a Markovnikov(2,1)-fashion and that the phenyl ring is η^3-coordinated. Variable-temperature NMR spectroscopy further revealed fluxional behavior including THF dissociation, phenyl ring coordination, and rotation about the *ipso*- and α-carbon atom.[92] Such an interaction is not present in the crystallographically characterized complex [Y(η^5:η^1-C_5Me_4-$CH_2SiMe_2N^tBu$){CH(CH_3)(C_6H_5)}(THF)].[95]

The reaction of the scandium hydride [Sc(η^5:η^1-$C_5Me_4SiMe_2N^tBu$)(PMe_3)(μ-H)]$_2$ with 2 equiv of ethylene generated the unusual ethylene-bridged dimer [Sc(η^5:η^1-$C_5Me_4SiMe_2N^tBu$)(PMe_3)]$_2$(μ-η^2:η^2-C_2H_4) besides 1 equiv of ethane. A single-crystal diffraction study showed a completely symmetrical ethylene ligand bridging two [Sc(η^5:η^1-$C_5Me_4SiMe_2N^tBu$)(PMe_3)] fragments in a centrosymmetrical fashion. The above-mentioned scandium hydride regioselectively reacted with propene to give the base-free alkyl-bridged dimer [Sc(η^5:η^1-$C_5Me_4SiMe_2N^tBu$)(μ-$CH_2CH_2CH_3$)]$_2$, which was crystallographically characterized to show a structure of type *trans*-**M** and was employed as a precatalyst for the polymerization of olefins.[93,94] The yttrium hydride [Y(η^5:η^1-$C_5Me_4SiMe_2N$-^tBu)(THF)(μ-H)]$_2$ exhibited a similar reactivity toward 1-hexene, yielding the *n*-hexyl-bridged dimer [Y(η^5:η^1-$C_5Me_4SiMe_2N^tBu$){μ-(CH_2)$_5CH_3$}]$_2$, which features a monomer−dimer equilibrium in the presence of THF.[92]

Oxidation of the divalent samarium complex [Sm{η^5:η^1-$C_5Me_4SiMe_2P(C_6H_2{}^tBu_3$-2,4,6)}(THF)$_3$] with benzophenone gave the bimetallic cyclopentadienyl phosphido complex [Sm_2{η^5:η^1-$C_5Me_4SiMe_2P(C_6H_2{}^tBu_3$-2,4,6)}$_2(THF)_2$($\mu$-$OCPh_2$)], which was studied by X-ray diffraction.[134]

Aryl Complexes. The trimethylsilylmethyl yttrium complex containing the linked amido−cyclopentadienyl [Y(η^5:η^1-$C_5Me_4SiMe_2N^tBu$)(CH_2SiMe_3)(THF)] underwent σ-bond metathesis reactions with the five-membered heterocycles furan and thiophene (Scheme 9). It reacted with excess thiophene in pentane to give the sparingly soluble dinuclear 2-thienyl complex [Y(η^5:η^1-$C_5Me_4SiMe_2N^tBu$)(μ-C_4H_3S)]$_2$, which is soluble only in bases such as THF and pyridine. The crystal structure determination confirmed a centrosymmetric dimeric structure of type **M** with the ancillary ligands arranged in a transoidal fashion. The two "metallocene-like" [Y(η^5:η^1-$C_5Me_4SiMe_2N^tBu$)] fragments are connected by two bridging 2-thienyl ligands forming a puckered six-membered ring core.[59,60] The related 2-furyl compounds [Y(η^5:η^1-$C_5Me_4SiMe_2N^tBu$)(μ-C_4H_3O)]$_2$ and [Y(η^5:η^1-$C_5Me_4SiMe_2N^tBu$){μ-2-(OC_4H_2Me-5)}]$_2$ were obtained by the same method and NMR spectroscopically characterized.[59,60] When the alkyl complex containing the CH_2SiMe_2 link [Y(η^5:η^1-$C_5Me_4CH_2$-$SiMe_2N^tBu$)(CH_2SiMe_3)(THF)] was reacted with furan, a triplet at 201.7 ppm with $^1J_{YC} = 24.7$ Hz was detected in the ^{13}C NMR spectrum; this indicates a dimeric structure [Yη^5:η^1-$C_5Me_4CH_2SiMe_2N^tBu$)(μ-C_4H_3O)]$_2$ in which not only the oxygen, but the 2-carbon of the furyl group is interacting with both yttrium atoms.[59] The monomeric yttrium complex [Y(η^5:η^1-$C_5Me_4SiMe_2N^tBu$)(μ-C_4H_3O)(DME)] was crystallographically characterized.[59] In contrast to the analogous compound with the shorter bridge, the crystallographically characterized 2-thienyl complex [Y(η^5:η^1-$C_5Me_4CH_2SiMe_2N^tBu$)(C_4H_3S)(THF)] was successfully isolated as a monomeric THF adduct.[59]

The ate complex [Li(THF)][Y(η^5:η^1-$C_5Me_4SiMe_2$-NCH_2CH_2OMe)(o-$C_6H_4CH_2NMe_2$)Cl] was synthesized by salt metathesis in THF and characterized by X-ray diffraction. The related compounds [Li(THF)][Y-(η^5:η^1-$C_5Me_4SiMe_2NCH_2CH_2X$)(o-$C_6H_4CH_2NMe_2$)(μ-Cl)] (X = NMe_2, CH_2OMe) were obtained by the same route.[96]

Propargyl/Allenyl Complexes. Reacting the dilithium salt of the new propargyl-functionalized cyclopentadienyl ligand $C_5H_3(SiMe_3)_2SiMe_2CH_2C{\equiv}C$-$SiMe_3$ with $SmCl_3$ in the presence of TMEDA gave the NMR spectroscopically characterized heterobimetallic complex [Sm{η^5:η^3-$C_5H_2(SiMe_3)_2$-2,4-$SiMe_2$-(C_3H)$SiMe_3$}Cl_3Li_2(TMEDA)$_2$]. When the bulkier ligand $C_5H_3(SiMe_3)_2SiMe_2CH_2C{\equiv}CSiPh_3$ was used instead, the samarium center in [Sm{η^5:η^1-C_5H_2-($SiMe_3$)$_2$-2,4-$SiMe_2CHCCSiPh_3$}(TMEDA)Cl_2Li-(TMEDA)] was coordinated by an additional molecule of TMEDA and the dianionic ligand adopted an η^5:η^1-coordination mode. This complex underwent reaction with LiCH($SiMe_3$)$_2$ to give the crystallographically studied anionic samarium alkyl complex [Li(TMEDA)$_2$][Sm{η^5:η^3-$C_5H_2(SiMe_3)_2$-2,4-$SiMe_2$(C_3H)-$SiPh_3$}CH($SiMe_3$)$_2$Cl]. The TMEDA ligand at the samarium center in [Sm{η^5:η^1-$C_5H_2(SiMe_3)_2$-2,4-$SiMe_2$-$CHC{\equiv}CSiPh_3$}(TMEDA)Cl_2Li(TMEDA)] can be removed when the chloro is exchanged against an iodo ligand. Reaction with a mixture of LiCH($SiMe_3$)$_2$ and LiI gave the crystallographically characterized bimetallic complex [Sm{η^5:η^3-$C_5H_2(SiMe_3)_2$-2,4-$SiMe_2$-(C_3H)$SiPh_3$}I_2Li(TMEDA)] with an η^5:η^3-coordinating cyclopentadienyl allenyl/propargyl ligand.[135]

VII. Hydrido Complexes

A. General

The area of mono(cyclopentadienyl) hydrido lanthanide complexes is restricted to trivalent mono(hydrido) complexes, and the known complexes are summarized in Table 11.[72,81,91−94,97,98] The hydrido complexes are obtained from σ-bond metathesis reactions of monomeric alkyl complexes with phenylsilane or dihydrogen (method III). All of the crystallographically characterized compounds show a dimeric structure with a [Ln(μ-H)]$_2$ core in the solid state.[72,92,94,97] By scrambling, insertion, and C−H bond activation reactions, dimeric hydrides with a mixed [Ln(μ-H)-(μ-X)] core can be generated.[72,91] The linked amido−cyclopentadienyl complexes can only be isolated as THF or PMe_3 adducts.[72,81,92−94] Complexes derived from the related ligand $C_5H_3(CH_2CH_2NMe_2)(SiMe_2N^t$-Bu) contain an intramolecular donor.[97] In contrast, aryloxides stabilize mono(cyclopentadienyl) hydrido

Table 11. Mono(cyclopentadienyl) Hydrido and Tetrahydridoborato Rare-Earth Metal Complexes

compound	type	methods of preparation	characterization	ref
		Trivalent Complexes		
$[Y(\eta^5-C_5Me_5)(OC_6H_3{}^tBu_2-2,6)(\mu-H)]_2$	**M**	III	^1H NMR	91,98
$[Y_2(\eta^5-C_5Me_5)_2(OC_6H_3{}^tBu_2-2,6)_2(\mu-H)\{\mu-(CH_2)_nCH_3\}]$, $n = 1, 2, 3, 5$	**M**	IV	^1H, ^{13}C NMR	91
$[Y_2(\eta^5-C_5Me_5)_2(OC_6H_3{}^tBu_2-2,6)_2(\mu-H)(\mu-CCSiMe_3)]$	**M**	III	^1H, ^{13}C NMR	91
$[Sc(\eta^5-C_5H_5)\{N(SiMe_2CH_2P^iPr_2)_2\}H]$	**J**	V	^1H, ^{31}P NMR	65
$[Sc\{\eta^5:\eta^1:\eta^1-C_5H_3(SiMe_2N^tBu)(CH_2CH_2NMe_2)\}(\mu-H)]_2$	**N**	III	X-ray, ^1H, ^{13}C NMR	97
$[Sc(\eta^5:\eta^1-C_5Me_4SiMe_2N^tBu)(PMe_3)(\mu-H)]_2$	**N**	III	X-ray, ^1H, ^{13}C, ^{31}P NMR, IR	94
$[Lu(\eta^5:\eta^1-C_5Me_4SiMe_2N^tBu)(PMe_3)(\mu-H)]_2$	**N**	V (and III)	X-ray, ^1H, ^{13}C, ^{29}Si, ^{31}P NMR	72
$[Y(\eta^5:\eta^1-C_5Me_4SiMe_2N^tBu)(PMe_3)(\mu-H)]_2$	**N**	V	X-ray, ^1H, ^{13}C, ^{31}P NMR	72
$[Lu(\eta^5:\eta^1-C_5Me_4SiMe_2NR)(THF)(\mu-H)]_2$, $R = {}^tBu$, ${}^tPe$	**N**	III	^1H, ^{13}C, ^{29}Si NMR	72
$[Yb(\eta^5:\eta^1-C_5Me_4SiMe_2NR)(THF)(\mu-H)]_2$, $R = {}^tBu$, ${}^tPe$	**N**	III	X-ray ($R = {}^tPe$), ^1H NMR	72
$[Y(\eta^5:\eta^1-C_5Me_4SiMe_2NR)(\mu-H)(THF)]_2$, $R = {}^tBu$, ${}^tPe$	**N**	III	X-ray ($R = {}^tBu$), ^1H, ^{13}C, ^{29}Si, ^{89}Y ($R = {}^tBu$) NMR	81,92
$[Y(\eta^5:\eta^1-C_5Me_4SiMe_2N^tBu)(\mu-D)(THF)]_2$	**N**	III	^2H NMR	92
$[Y_2(\eta^5:\eta^1-C_5Me_4SiMe_2NR)_2(THF)_2(\mu-H)(\mu-Cl)]$, $R = {}^tBu$, ${}^tPe$	**N**		^1H, ^{13}C, ^{29}Si, ^{89}Y NMR ($R = {}^tBu$)	72
$[Ln(\eta^5-C_5Me_5)(BH_4)_2]$, Ln = Sm, Dy, Yb	**H**	I	^1H, ^{11}B NMR (Ln = Sm, Yb), MS, IR	100
$[Ln(\eta^5-C_5{}^iPr_4H)(BH_4)_2(THF)]$, Ln = Nd, Sm	**I**	I	X-ray, ^1H NMR, IR	99
$[Sc(\eta^5-C_5H_5)\{N(SiMe_2CH_2P^iPr_2)_2\}BH_4]$	**J**	I	^1H, ^{31}P, ^{11}B NMR, IR	65

complexes without additional donor ligands.[91] The mono(cyclopentadienyl) hydrido complexes are reported to be catalytically active in polymerizations of both polar and nonpolar monomers.[81,91–94] In addition, a few examples of borohydrides have been described in the recent literature.[65,99,100] The dialkyl complexes $[Y(\eta^5-C_5Me_4SiMe_2X)(CH_2SiMe_3)_2(THF)]$ (X = Me, Ph) were reported to undergo hydrogenolysis to give the tetranuclear dihydrido complexes $[Y(\eta^5-C_5Me_4SiMe_2X)H_2]_4(THF)_2$.[81]

B. Complexes with a $[Ln(\mu\text{-}H)]_2$ Core

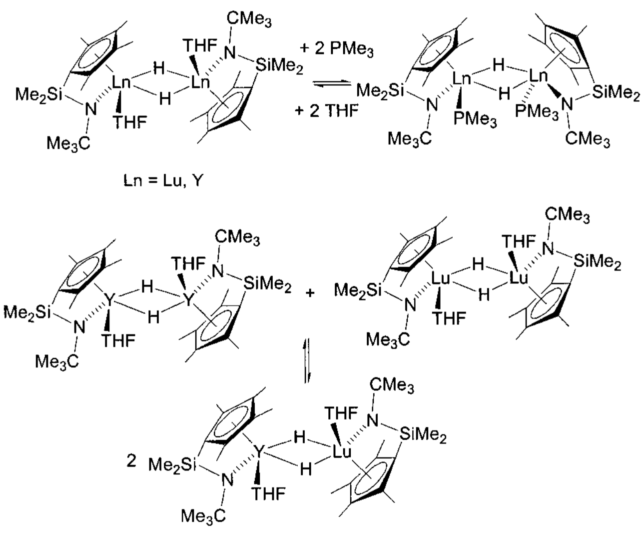
The Lewis base-free hydride $[Y(\eta^5-C_5Me_5)(OC_6H_3{}^tBu_2-2,6)(\mu-H)]_2$, reported by Schaverien, was obtained by hydrogenolysis of the alkyl complex $[Y(\eta^5-C_5Me_5)(OC_6H_3{}^tBu_2-2,6)\{CH(SiMe_3)_2\}]$ at 20 bar H_2 and 25 °C.[91] The dimeric nature of the hydride in solution gives rise to a triplet at 5.64 ppm ($^1J_{YH} = 35.2$ Hz) in the ^1H NMR spectrum. In the absence of crystal structure determinations, the arrangement of the cyclopentadienyl ligands in the structure of type **M** (which can be bound to the $[Ln(\mu-H)]_2$ core in a cis or trans fashion) has not been determined. The hydrido complex $[Y(\eta^5-C_5Me_5)(OC_6H_3{}^tBu_2-2,6)(\mu-H)]_2$ was reported to polymerize ethylene and to be a single-component catalyst for the polymerization of α-olefins and nonconjugated dienes.

Bercaw et al. reported the scandium hydride $[Sc(\eta^5:\eta^1-C_5Me_4SiMe_2N^tBu)(PMe_3)(\mu-H)]_2$ containing the linked amido–cyclopentadienyl ligand.[93,94] In contrast to the aryloxide-supported yttrium complex $[Y(\eta^5-C_5Me_5)(OC_6H_3{}^tBu_2-2,6)(\mu-H)]_2$,[91] this dimeric scandium compound is not accessible without the presence of a coordinating Lewis base. The complex was formed by hydrogenolysis of $[Sc(\eta^5:\eta^1-C_5Me_4SiMe_2N^tBu)\{CH(SiMe_3)_2\}]$ in the presence of trimethylphosphine. X-ray crystal structure determination revealed the hydride to be a homochiral molecule of C_2 symmetry with *cis*-arranged cyclopentadienyl ligands (*homo*-cis-**N**). The ^1H NMR spectra are consistent with the presence of a single species over the temperature range of −80 to 25 °C, although at −66 °C two signals in a 4:1 ratio are present in the ^{31}P NMR spectrum. The hydride complex is a catalyst precursor for the polymerization of α-olefins.

Analogous lutetium and yttrium hydrides were isolated by displacement of THF by PMe_3 in $[Ln(\eta^5:\eta^1-C_5Me_4SiMe_2N^tBu)(THF)(\mu-H)]_2$ (Ln = Lu, Y) and are isostructural (*homo*-*cis*-**N**) with the scandium complex $[Sc(\eta^5:\eta^1-C_5Me_4SiMe_2N^tBu)(PMe_3)(\mu-H)]_2$.[72] For the lutetium complex, hydrogenolysis of the alkyl $[Lu(\eta^5:\eta^1-C_5Me_4SiMe_2N^tBu)(CH_2SiMe_3)(THF)]$ in the presence of PMe_3 is also feasible. In the ^1H NMR spectrum, the hydride resonance appears as a singlet at 10.44 ppm at −60 °C for the lutetium complex. The corresponding resonance for the yttrium compound is observed at 5.59 ppm as a higher-order spin pattern. In the ^{31}P NMR spectrum at −60 °C the lutetium complex gave rise to a signal at −28.1 ppm, whereas two doublets in a 2:3 ratio at −42.5 ($^1J_{YP} = 85.2$ Hz) and −42.4 ppm ($^1J_{YP} = 64.3$ Hz) were recorded for the yttrium complex, consistent with the presence of two diastereomers at lower temperatures.

THF-stabilized rare-earth hydrido complexes $[Ln(\eta^5:\eta^1-C_5Me_4SiMe_2NR)(THF)(\mu-H)]_2$ (Ln = Lu, Y, R = ${}^tBu$, ${}^tPe$) were obtained by reaction of pentane solutions of the alkyls $[Ln(\eta^5:\eta^1-C_5Me_4SiMe_2NR)(CH_2SiMe_3)(THF)]$ (Ln = Lu, Y, R = ${}^tBu$, ${}^tPe$) with dihydrogen (4 bar) or phenylsilane at 25 °C.[72,81,92] In contrast to the related PMe_3 adducts, the THF complexes were shown to be C_2-symmetric homochiral molecules with trans-configured ancillary ligands by X-ray structural analysis (*homo*-*trans*-**N**). It seems that at least within the series containing the metals scandium, lutetium, and yttrium it is the nature of the Lewis base rather than the size of the metal center that determines the configuration.[72] ^1H NMR spectroscopic investigations of the lutetium and yttrium complexes revealed dynamic behavior as a result of fast dissociation of THF ligands. Furthermore, the dissociation into monomers was indicated by the formation of the heterobimetallic complex $[LuY(\eta^5:\eta^1-C_5Me_4SiMe_2N^tBu)_2(THF)_2(\mu-H)_2]$ within 5 min of equimolar amounts of the lutetium and yttrium hydrides being mixed in C_6D_6 (Scheme 10).[72,92]

Scheme 10



With a CH_2 group added to the bridge between the amido and the tetramethylcyclopentadienyl moieties, hydrogenolysis of the alkyl $[Y(\eta^5:\eta^1\text{-}C_5Me_4CH_2SiMe_2N^tBu)(CH_2SiMe_3)(THF)]$ resulted in clean formation of the X-ray crystallographically characterized homochiral dimer $[Y(\eta^5:\eta^1\text{-}C_5Me_4CH_2SiMe_2N^tBu)(THF)(\mu\text{-}H)]_2$. The dimeric structure is intermediate between a cis and a trans arrangement of the ancillary ligands. This hydrido complex polymerized ethylene and efficiently catalyzed the hydrosilylation of olefins.[95]

Piers et al. reported scandium hydrides bearing the tridentate ligand $C_5H_3(CH_2CH_2NMe_2)(SiMe_2N^tBu)$ that contains both a pendant amine-donor group and an amido ligand.[97] The hydrido complex $[Sc\{\eta^5:\eta^1:\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)(SiMe_2N^tBu)\}(\mu\text{-}H)]_2$ was obtained upon hydrogenolysis of the alkyl $[Sc\{\eta^5:\eta^1:\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)(SiMe_2N^tBu)\}(CH_2SiMe_3)]$ in benzene at 70 °C under elevated pressure. Due to the enantiotopic faces of the cyclopentadienyl ligand, complexation to the chiral metal center 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 a heterochiral C_i-symmetric dimer with trans-arranged cyclopentadienyl units. The two isomers interconvert slowly, indicating a monomeric hydride in equilibrium with the dimers. Sluggish reaction with α-olefins suggests a slow dissociation process.

C. Complexes with a $[Ln_2(\mu\text{-}H)(\mu\text{-}X)]$ Core

When the aryloxide-supported hydride $[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)(\mu\text{-}H)]_2$ was treated with terminal olefins, μ-hydrido μ-alkyl-bridged complexes $[Y_2(\eta^5\text{-}C_5Me_5)_2(OC_6H_3{}^tBu_2\text{-}2,6)_2(\mu\text{-}H)\{\mu\text{-}(CH_2)_nMe\}]$ ($n = 1$, 2, 3, 5) were regiospecifically formed by 1,2-insertion.[91] ^1H NMR spectroscopy revealed diastereotopic α-CH_2 resonances, indicating mutually trans geometry of the cyclopentadienyl and aryloxide ligands (structure type *trans*-**M**). These complexes were reported to be single-component catalysts for the polymerization of α-olefins and nonconjugated dienes. $[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)(\mu\text{-}H)]_2$ reacted with the trimethylsilylacetylene to give $[Y_2(\eta^5\text{-}C_5Me_5)_2(OC_6H_3{}^tBu_2\text{-}2,6)_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CSiMe_3)]$. Scrambling reactions of the chloro complexes $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NR)(THF)(\mu\text{-}Cl)]_2$ (R = ^{t}Bu, ^{t}Pe) and the hydrido complexes $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NR)(THF)(\mu\text{-}H)]_2$ resulted in the formation of the mixed μ-hydrido μ-chloro complexes $[Y_2(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NR)_2(THF)_2(\mu\text{-}H)(\mu\text{-}Cl)]$ with *homo-trans*-**N** structure.[72]

D. Tetrahydridoborato Complexes

The synthesis of tetrahydridoborato rare-earth complexes is being pursued with the aim of obtaining precursors for reactive hydrido complexes. Samarium and neodymium complexes $[Ln(\eta^5\text{-}C_5{}^iPr_4H)(BH_4)_2(THF)]$ (Ln = Sm, Nd) that contain a sterically demanding tetra(isopropyl)cyclopentadienyl ligand can be prepared by salt metathesis of $[Ln(BH_4)_3(THF)_3]$ (Ln = Sm, Nd) with $Na(C_5{}^iPr_4H)$ in toluene or THF.[99] X-ray crystallography of both complexes revealed monomeric structures of type **I** and tridentate coordination modes of the borohydride ligands. Similar complexes were obtained by reacting $[LnCl(BH_4)_2]$ with $K(C_5Me_4)$ to give $[Ln(\eta^5\text{-}C_5Me_5)(BH_4)_2]$ (Ln = Sm, Dy, Yb).[100] Fryzuk et al. synthesized a scandium borohydride complex $[Sc(\eta^5\text{-}C_5H_5)\{N(SiMe_2CH_2P^iPr_2)_2\}(BH_4)]$ by salt metathesis of $[Sc(\eta^5\text{-}C_5H_5)\{N(SiMe_2CH_2P^iPr_2)_2\}Cl]$ with MBH_4 (M = Li, Na) in toluene or THF.[65] NMR spectroscopic data are consistent with the formation of the hydrido complex $[Sc(\eta^5\text{-}C_5H_5)\{N(SiMe_2CH_2P^iPr_2)_2\}H]$ when 100-fold excess of PMe_3 was present.

VIII. Complexes without Any Additional Anionic Ligands

Very few cationic mono(cyclopentadienyl) complexes of the divalent rare-earth metals are known (Table 12). The unsymmetric bis(trimethylsilylfluorenyl) ytterbium complex $[Yb(\eta^5\text{-}C_{13}H_8SiMe_3)\{\eta^6\text{-}C_{13}H_8(SiMe_3)(AlMe_3)\}]$ was reported to give with excess THF the crystallographically characterized ion pair $[Yb(\eta^5\text{-}C_{13}H_8)(THF)_4]^+[AlMe_4]^-$ in low yield. Although the reaction pathway is not completely understood, experiments with deuterated THF indicated that elimination of the $SiMe_3$ group from the indenyl ligand involves THF.[101] The crown ether 18-crown-6 displaced one of the two cyclopentadienyl ligands in divalent lanthanocenes $[Ln\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2]$ (Ln = Sm, Yb) in benzene to form crystallographically characterized ion pairs. Depending on the lanthanide ion, the cations $[Ln\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}([18]\text{-crown-}6)]^+$ (Ln = Sm, Yb) were accompanied by the counterions $[Sm\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]^-$ or $[C_5H_3(SiMe_3)_2\text{-}1,3]^-$ (Ln = Yb) (Scheme 11).[102,103]

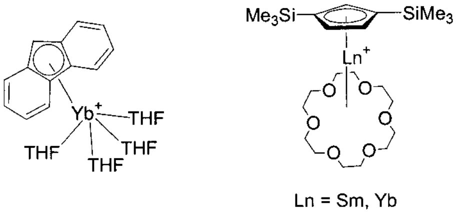
IX. Applications

The number of applications of lanthanide half-sandwich complexes stands in no relation to the plethora of lanthanocene-catalyzed homogeneous reactions.[9] This clearly results from the difficulty to rationally and efficiently synthesize half-sandwich complexes of rare-earth metals. Nonetheless, simply for steric reasons, the reactivity of lanthanide half-sandwich complexes can be expected to be signifi-

Table 12. Divalent Mono(cyclopentadienyl) Rare-Earth Metal Complexes without Any Additional Anionic Ligands

compound	type	methods of preparation	characterization	ref
$[Yb(\eta^5\text{-}C_{13}H_8)(THF)_4]^+[AlMe_4]^-$		V	X-ray, ^{1}H NMR	101
$[Yb\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}([18]\text{-crown-6})]^+[C_5H_3(SiMe_3)_2\text{-}1,3\}]^-(C_6H_6)_3$		V	X-ray, ^{1}H, ^{29}Si, ^{171}Yb NMR, IR	102, 103
$[Sm\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}([18]\text{-crown-6})]^+[Sm\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]^-(C_6H_6)_{0.5}$		V	X-ray, ^{29}Si NMR, IR	102, 103

Scheme 11



cantly higher than that of the metallocene analogues. In fact, a few examples that confirm this assumption have recently become known and many more can be expected.

A. C–X Bond Forming Reactions (X = H, B, Si, N, P)

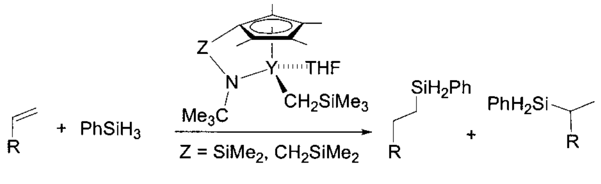
1. Hydrogenation of Alkenes

Although one of the most intensely studied areas of lanthanocene-catalyzed homogeneous reactions,[9] the hydrogenation of olefins by half-sandwich complexes of the rare-earth metals have not yet found wide application. One report describes the hydrogenation of cyclohexene using the bis(methanesulfonato) complexes $[Ln(\eta^5\text{-}C_5H_5)(O_3SMe)_2(THF)_x]$, ($x$ = 1, Ln = La; x = 2, Ln = Pr, Nd, Eu; X = 0, Ln = Yb) and $[Ln(\eta^5\text{-}C_5H_5)(O_3SMe)_2(PPh_3)]$ (Ln = La, Pr, Nd, Eu, Yb).[104] Due to the scarcity of systematic studies, no reports on mechanistic studies or on stereoselective hydrogenation have been found. To improve the chemoselectivity of acrolein hydrogenation to give allyl alcohol, $[Sm(\eta^5\text{-}C_5H_5)Cl_2(THF)_3]$ was added to the hydrogenation catalyst system $NaBH_4$/CuBr in methanol.[105]

2. Hydroboration and Hydrosilylation of Alkenes

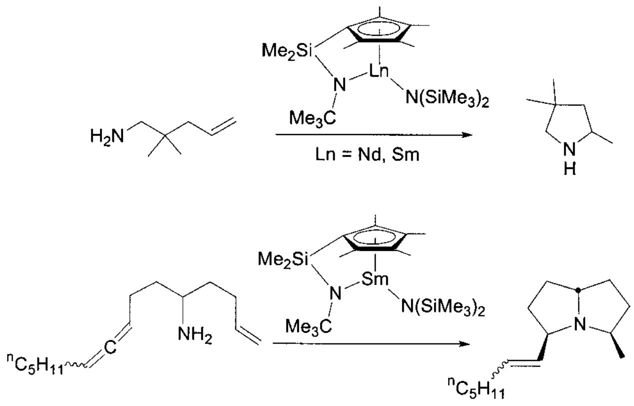
Catalytic hydroboration of α-alkenes using divalent samarium complexes $[Sm(\eta^5\text{-}C_5Me_5)(\mu\text{-}OC_6H_2{}^tBu_2\text{-}2,6\text{-}Me\text{-}4)]_2$ and $[Sm(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(OC_6H_2{}^tBu_2\text{-}2,6\text{-}Me\text{-}4)\{K(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(THF)_2\}]$ has been mentioned.[106] α-Alkenes such as 1-decene can be efficiently hydrosilylated with $PhSiH_3$ by catalytic amounts of the hydride $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4ZN^tBu)(\mu\text{-}H)(THF)]_2$ (Z = $SiMe_2$, CH_2SiMe_2), conveniently generated in situ from the alkyl complexes $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4ZN^tBu)(CH_2SiMe_3)(THF)]$ (Scheme 12). The silane $^nC_{10}H_{23}SiPhH_2$ 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 toward 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.[95]

Scheme 12



$[Sm(\eta^5\text{-}C_5Me_5)(\mu\text{-}H)_2]_6[K(THF)_2(\mu\text{-}H)]_3$, a novel type of hydrido cluster, generated by the hydrogenolysis of polymeric alkyl $[Sm(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}\text{-}\{K(\mu_2\text{-}\eta^5{:}\eta^5\text{-}C_5Me_5)(THF)_2\}]_x$, was reported to exhibit high activity in the hydrosilylation of α-alkenes.[131]

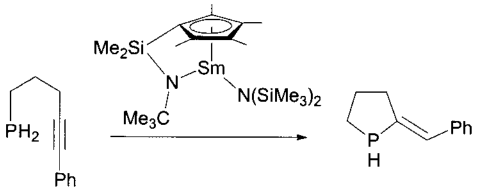
Scheme 13



3. Hydroamination/Cyclization

A series of lanthanide alkyl and amide complexes bearing a linked amido–cyclopentadienyl ligand $[Ln(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)\{E(SiMe_3)_2\}]$ (Ln = Sm, Nd, Lu; E = N; Yb, Lu, E = CH) was introduced as efficient hydroamination/cyclization catalysts for α,ω-aminoolefins (Scheme 13). These catalysts exhibited significantly higher activity than the typical lanthanocene derivatives $[Ln(\eta^5\text{-}C_5Me_5)_2\{E(SiMe_3)_2\}]$ (E = CH, N). The use of these half-sandwich complexes in the total synthesis of the natural products pyrrolidine alkaloid (+)-197B and pyrrolizidine alkaloid (+)-xenovenine was reported. The aminoallene (5*S*,8*S*)-5-amino-trideca-8,9-diene and the aminoallene–alkene (5*S*)-5-amino-pentadeca-1,8,9-triene underwent intramolecular regio- and diastereoselective hydroamination/cyclization catalyzed by $[Ln(\eta^5{:}\eta^1\text{-}C_5Me_4\text{-}SiMe_2N^tBu)\{N(SiMe_3)_2\}]$. 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.[58,107]

Scheme 14



4. Hydrophosphination/Cyclization

Precatalysts of the type [Sm(η^5:η^1-$\mathrm{C_5Me_4SiMe_2N}$-^{t}Bu){N($\mathrm{SiMe_3}$)$_2$}] catalyzed the intramolecular hydrophosphination/cyclization of phosphinoalkenes and phosphinoalkynes (Scheme 14). Substrates such as $\mathrm{H_2P(CH_2)_3C{\equiv}CPh}$ were converted into cyclized products, such as 2-methylenephospholane. Higher turnover frequencies resulted when the lanthanide coordination sphere was opened with the (η^5:η^1-$\mathrm{C_5Me_4}$-$\mathrm{SiMe_2N}^t$Bu) ancillary ligand. Thus, the turnover number at 40 °C for [Sm(η^5:η^1-$\mathrm{C_5Me_4SiMe_2N}^t$Bu)-{N($\mathrm{SiMe_3}$)$_2$}] was 13 $\mathrm{h^{-1}}$, compared to 2 $\mathrm{h^{-1}}$ for [Sm-(η^5-$\mathrm{C_5Me_5}$)$_2${CH($\mathrm{SiMe_3}$)$_2$}] at 22 °C.[108]

B. C–C Bond-Forming Reaction

1. Aldol Condensation

Mono(cyclopentadienyl) dichloro complexes [Ln(η^5-$\mathrm{C_5R_5}$)$\mathrm{Cl_2}$] ($\mathrm{C_5R_5}$ = $\mathrm{C_5H_4}{}^t$Bu, Ln = Yb, Nd; $\mathrm{C_5R_5}$ = $\mathrm{C_5H_4Me}$, Ln = Yb) along with lanthanocene complexes [Ln(η^5-$\mathrm{C_5R_5}$)$_2$Cl] ($\mathrm{C_5R_5}$ = $\mathrm{C_5H_4}{}^t$Bu, Ln = Yb, Er; $\mathrm{C_5R_5}$ = $\mathrm{C_5H_4Me}$, Ln = Yb) were reported to catalyze the selective dimerization of butanal to butyl butyrate in moderate yields under mild conditions when activated with *n*-butyllithium.[109]

2. Diels–Alder Reactions

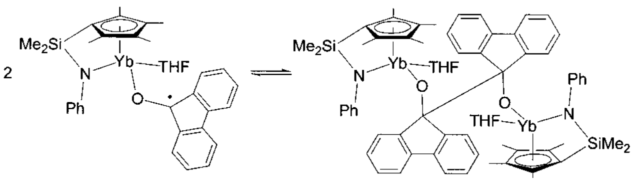
The fluxional mono(cyclopentadienyl) iodo complexes [Ln{(S)-η^5-$\mathrm{C_5H_4CH_2CHMeOCH_2Ph}$)}$\mathrm{I_2}(THF)_n$] (Ln = Sm, n = 3; Ln = La, n = 2), containing a cyclopentadienyl ligand with a chiral alkoxy-functionalized side chain, were reported to catalyze the Diels−Alder reaction of cyclopentadiene with methacrolein to give 90% of the *exo* isomer with low enantioselectivity (13% ee).[34]

3. Reductive Coupling

The reaction of [Lu(η^5-$\mathrm{C_5H_5}$)($\mathrm{C_{10}H_8}$)(THF)$_2$] with diphenylacetylene gave dinuclear [{Lu(η^5-$\mathrm{C_5H_5}$)-(DME)}$_2${μ-1,1,4,4-(Ph)C(Ph)C=C(Ph)C(Ph)}] with a ligand that resulted from C−C coupling, giving rise to a tetraanionic bridging $(\mathrm{C_4Ph_4})^{4-}$ ligand (see section VI.C.3, Butadiene Complexes).[68]

Reactions of fluorenone with [Sm(η^5-$\mathrm{C_5Me_5}$)($\mathrm{OC_6H_2}$-^{t}Bu$_2$-2,6-Me-4)(HMPA)$_2$] in THF gave the structurally characterized dark-brown ketyl complex [Sm(η^5-$\mathrm{C_5}$-$\mathrm{Me_5}$)($\mathrm{OC_6H_2}{}^t$Bu$_2$-2,6-Me-4)($\mathrm{OC_{13}H_8}$)(HMPA)] ($\mathrm{OC_{13}H_8}$ = biphenyl-2,2′-diyl ketyl) in 91% yield by one-electron reduction of fluorenone. This chiral complex was stable toward ligand distribution, although complexes of the type [Ln(η^5-$\mathrm{C_5Me_5}$)$_2$(HMPA)(ketyl)] and [Sm($\mathrm{OC_6H_2}{}^t$Bu$_2$-2,6-Me-4)$_2$(ketyl)(HMPA)$_2$] were isolable. No formation of μ-pinacolate complexes was observed.[110] Reversible formation of μ-pinacolate complex was observed for the ketyl complex [Yb-(η^5:η^1-$\mathrm{C_5Me_4SiMe_2NPh}$)(THF)($\mathrm{OC_{13}H_8}$)] to give [Yb-($\eta^5$:$\eta^1$-$\mathrm{C_5Me_4SiMe_2NPh}$)(THF)]$_2$($\mu$-$\mathrm{O_2C_{26}H_{16}}$) with a gauche conformation of the pinacolate ligand (Scheme 15).[129]

Scheme 15



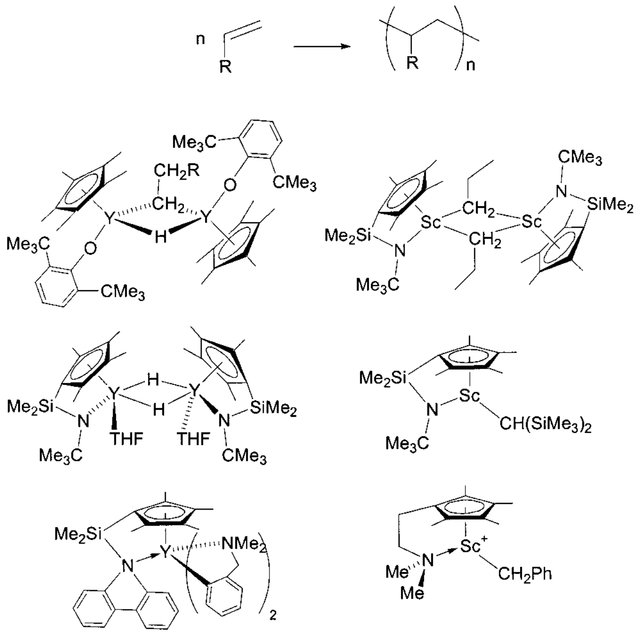
C. Polymerization

1. Polymerization of Ethylene and of α-Olefins

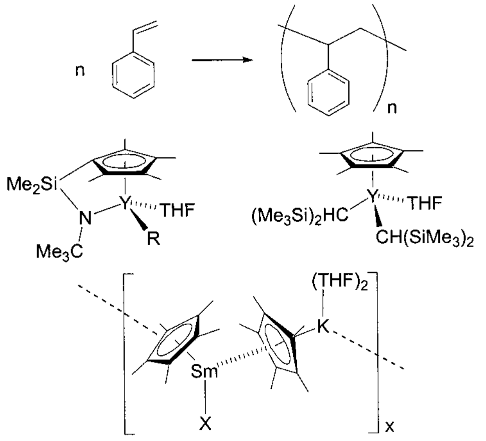
Terminal olefins $\mathrm{CH_2{=}CHR}$ (R = H, Me, Et, ^{n}Bu) reacted regiospecifically and irreversibly with the hydride dimer [Y(η^5-$\mathrm{C_5Me_5}$)($\mathrm{OC_6H_3}{}^t$Bu$_2$-2,6)(μ-H)]$_2$ to give the alkyl hydride complex *trans*-[Y(η^5-$\mathrm{C_5Me_5}$)-($\mathrm{OC_6H_3}{}^t$Bu$_2$-2,6)]$_2$(μ-$\mathrm{CH_2CH_2R}$)(μ-H). Reaction of [Y(η^5-$\mathrm{C_5Me_5}$)($\mathrm{OC_6H_3}{}^t$Bu$_2$-2,6)(μ-D)]$_2$ with propene selectively yielded only *trans*-[Y(η^5-$\mathrm{C_5Me_5}$)($\mathrm{OC_6H_3}{}^t$Bu$_2$-2,6)]$_2$(μ-$\mathrm{CH_2CHDMe}$)(μ-D), confirming the nonreversibility of olefin insertion. The alkyl complexes polymerized ethylene and were single-component catalysts for the polymerization of α-olefins and nonconjugated dienes. Dissolution of [Y(η^5-$\mathrm{C_5Me_5}$)($\mathrm{OC_6H_3}{}^t$Bu$_2$-2,6)-(μ-H)]$_2$ in neat 1-hexene (to give [Y(η^5-$\mathrm{C_5Me_5}$)($\mathrm{OC_6H_3}$-^{t}Bu$_2$-2,6)(μ-$\mathrm{CH_2CH_2}{}^n$Bu)]$_2$ in situ) resulted in slow polymerization to yield poly(1-hexene) with M_w = 15 700 and $M_\mathrm{w}/M_\mathrm{n}$ = 1.67. [Y(η^5-$\mathrm{C_5Me_5}$)($\mathrm{OC_6H_3}{}^t$Bu$_2$-2,6)(μ-H)]$_2$ cyclopolymerized neat 1,5-hexadiene to poly(methylene-1,3-cyclopentanediyl) rather than promoting cyclization to methylenecyclopentane.[91,98]

Propene, 1-butene, and 1-pentene were cleanly, albeit slowly, polymerized by [Sc(η^5:η^1-$\mathrm{C_5Me_4SiMe_2N}$-^{t}Bu)($\mathrm{PMe_3}$)(μ-H)]$_2$ with >99% “head-to-tail” coupling to produce linear, atactic poly(α-olefins). Chain transfer was relatively slow and appears to occur by β-H elimination. The hydride complex was a precatalyst for the polymerization of α-olefins, yielding atactic products of low molecular weight (M_n = 3000−7000). GC/MS analysis of volatile, oligomeric products revealed that all scandium centers were active during the polymerization. Selectivity for head-to-tail insertion was high (>99%), and for the tetramer, pentamer, and hexamer formed during propene polymerization, the maximum theoretical numbers of head-to-tail stereoisomers were observed by GC. The stoichiometric reaction between [Sc(η^5:η^1-$\mathrm{C_5Me_4}$-$\mathrm{SiMe_2N}^t$Bu)($\mathrm{PMe_3}$)(μ-H)]$_2$ and 2 equiv of ethylene produced the unusual ethylene-bridged dimer [Sc-(η^5:η^1-$\mathrm{C_5Me_4SiMe_2N}^t$Bu)($\mathrm{PMe_3}$)]$_2$($\mu$-$\eta^2$:$\eta^2$-$\mathrm{C_2H_4}$) and 1 equiv of ethane, whereas the same reaction with propene afforded the phosphine-free, alkyl-bridged scandium dimer [Sc(η^5:η^1-$\mathrm{C_5Me_4SiMe_2N}^t$Bu)($\mu$-$\mathrm{CH_2}$-$\mathrm{CH_2CH}$)]$_2$ which functioned as a more active olefin polymerization catalyst precursor. The structure of the catalytic intermediate was determined by low-temperature ^{13}C NMR spectroscopic studies of the model complexes [Sc(η^5:η^1-$\mathrm{C_5Me_4SiMe_2N}^t$Bu){P-($^{13}\mathrm{CH_3}$)$_3$}$\mathrm{CH_2CH(CH_3)CH_2CH_2CH_3}$] and [Sc($\eta^5$:$\eta^1$-$\mathrm{C_5}$-$\mathrm{Me_4SiMe_2N}^t$Bu)($\mathrm{PMe_3}$)$^{13}\mathrm{CH_2CH}$($^{13}\mathrm{CH_3}$)$_2$] to be a mon-

Scheme 16



Scheme 17



omeric, 12-electron, scandium alkyl complex $[Sc(\eta^5{:}\eta^1-C_5Me_4SiMe_2N^tBu)X]$ (X = H, alkyl) of the type **H**.[94] The base-free alkyl complex $[Sc(\eta^5{:}\eta^1-C_5Me_4SiMe_2N^tBu)\{CH(SiMe_3)_2\}]$ was also claimed to be an ethylene polymerization catalyst in the patent literature.[111]

Ethylene underwent slow sequential insertion at low temperatures (<−30 °C) with the hydrido complex $[Y(\eta^5{:}\eta^1-C_5Me_4SiMe_2N^tBu)(THF)(\mu-H)]_2$ to give a mixture of *n*-alkyl complexes $[Y(\eta^5{:}\eta^1-C_5Me_4SiMe_2N^tBu)\{\mu-(CH_2CH_2)_nH\}]_2$. The *n*-alkyl complexes could be synthesized independently by 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 $[Y(\eta^5{:}\eta^1-C_5Me_4SiMe_2N^tBu)\{(CH_2)_nCH_3\}(THF)]$. 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.[92] Ethylene oligomerization was claimed for $[Y(\eta^5{:}\eta^1-C_5Me_4SiMe_2NC_{12}H_8)(o-C_6H_4CH_2NMe_2)_2]$, which contain a *N*-carbazolyl-functionalized tetramethylcyclopentadienyl ligand.[112] A cationic alkyl complex $[Sc(\eta^5{:}\eta^1-C_5Me_4CH_2CH_2NMe_2(CH_2Ph)]^+$ was also introduced as an ethylene polymerization catalyst.[113] Divalent samarium complexes $[Sm(\eta^5{:}\eta^1-C_5Me_4SiMe_2NPh)(THF)_n]$ were capable of polymerizing ethylene to give linear polyethylene with M_n = 726 000 and $M_w/M_n = 1.58$.[129] Catalytsts are summarized in Scheme 16. The divalent samarium complex $[Sm(\mu_2-\eta^5{:}\eta^5-C_5Me_5)(OC_6H_2{}^tBu_2-2,6-Me-4)\{K(\mu_2-\eta^5{:}\eta^5-C_5Me_5)(THF)_2\}]_x$ is reported to polymerize ethylene. The less reducing Yb(II) complex or the silylene-linked cyclopentadienyl Sm(II) complex $[Sm(OC_6H_2{}^tBu_2-2,6-R-4)\{(\mu_2-\eta^5{:}\eta^5)_2-C_5Me_4SiMe_2C_5Me_4\}\{K(THF)_n\}]_x$ does not polymerize ethylene under the same conditions, suggesting that the polymerization reaction in the present systems is initiated by dissociation of the neutral "$M(C_5Me_5)$" ligand (M = K or Na) from the Sm(II) center, followed by a one-electron transfer from the resultant C_5Me_5/X-ligated Sm(II) species to an incoming monomer. As a leaving group, "$K(C_5Me_5)$" seemed to be more suitable than "$Na(C_5Me_5)$".[41]

2. Polymerization of Styrene

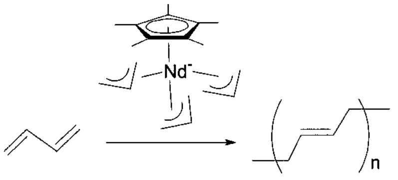
The divalent samarium complexes $[Ln(\mu_2-\eta^5{:}\eta^5-C_5Me_5)(X)(THF)_m\{K(\mu_2-\eta^5{:}\eta^5-C_5Me_5)(THF)_n\}]_x$, in particular $[Sm(\mu_2-\eta^5{:}\eta^5-C_5Me_5)(OC_6H_2{}^tBu_2-2,6-Me-4)\{K(\mu_2-\eta^5{:}\eta^5-C_5Me_5)(THF)_2\}]_x$, are capable of homopolymerizing styrene and copolymerizing styrene with ethylene to give ethylene−styrene block copolymers. Among the X-type ligands, the thiolate $SC_6H_2{}^iPr_3$-2,4,6 showed the highest selectivity for the block copolymerization of ethylene with styrene while the aryloxide X = $OC_6H_2{}^tBu_2$-2,6-Me-4 and the silylamide X = $N(SiMe_3)_2$ gave the highest activities for the polymerization of styrene, respectively.[41] Possible mechanisms for the polymerization and copolymerization reactions involve the intermediate formation of a hydride complex as the active species.[106] The dimeric samarium complex $[Sm(\eta^5-C_5Me_5)(\mu-OC_6H_2-{}^tBu_2-2,6-Me-4)]_2$ was evaluated in the high-pressure polymerization of styrene.[114]

Styrenes reacted with the hydride $[Y(\eta^5{:}\eta^1-C_5Me_4SiMe_2N^tBu)(THF)(\mu-H)]_2$ to give isolable 1-phenethyl complexes which failed to react further with styrene. However, the monomeric *n*-alkyl complex $[Y(\eta^5{:}\eta^1-C_5Me_4SiMe_2NCMe_3)\{(CH_2CH_2)_nH\}(THF)]$ polymerized styrene in a controlled manner to give atactic polystyrene with low polydispersity. Thus, 50 equiv of styrene gave polystyrene with M_n = 24 100 and $M_w/M_n = 1.10$, *rr* = 70%.[92] Atactic polystyrene was formed with $[Li(DME)_3]^+[Nd(\eta^5-C_5H_4Me)({}^tBu)_3]^-$, possibly by anionic polymerization.[84] $[La(\eta^5-C_5Me_5)\{CH(SiMe_3)_2\}_2(THF)]$ was claimed to polymerize both ethylene and styrene (Scheme 17).[115]

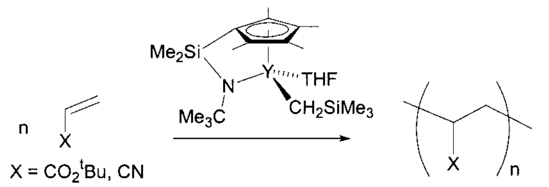
3. Polymerization of Butadiene

The mono(cyclopentadienyl)tris(allyl)lanthanate(III) complexes $[Li(THF)]^+[La(\eta^5-C_5R_5)(\eta^3-C_3H_5)_3]^-$ ($C_5R_5 = C_5H_5$, C_5Me_5, indenyl) catalyzed butadiene polymerization in toluene under standard conditions with moderate activity and high trans selectivity (Scheme 18).[86] The ate complexes $[Li(THF)_2]^+[Nd(\eta^5-C_5H_5)(\eta^3-C_3H_5)_3]^-$ and $[Li(DME)_3]^+[Nd(\eta^5-C_5Me_5)(\eta^3-C_3H_5)_3]^-$ catalyzed the polymerization of butadiene in toluene with a preference for the trans microstruc-

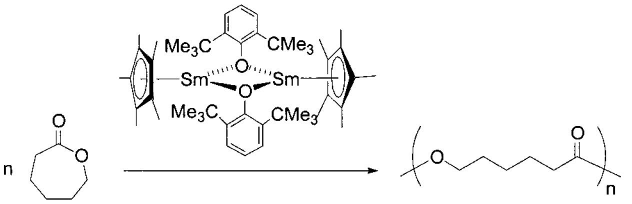
Scheme 18



Scheme 19



Scheme 20



ture. In THF the formation of polybutadiene with 80% 1,2-microstructure was observed. The catalytic activity depends on the degree of $Li(C_3H_5)$ dissociation from the complexes under the reaction conditions. However, in contrast to the anionic homoleptic tetraallyl complexes $[Ln(\eta^3\text{-}C_3H_5)_4]^-$, the activity was suppressed upon addition of Lewis acids such as BEt_3 or Et_2AlCl. [87]

4. Polymerization of Alkyl Acrylate and Acrylonitrile

The alkyl complexes $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(CH_2SiMe_3)(THF)]$ and $[Y(\eta^5\text{-}C_5Me_4SiMe_2X)(CH_2SiMe_3)_2(THF)]$ ($X = Me, Ph, C_6F_5$) as well as the yttrium–hydrido complex $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(THF)(\mu\text{-}H)]_2$ were found to polymerize the polar monomers *tert*-butyl acrylate and acrylonitrile (Scheme 19). *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 $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(THF)(\mu\text{-}H)]_2$, 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.[81,116]

5. Ring-Opening Polymerization of Lactones

The aryloxo samarium(II) complex $[Sm(\eta^5\text{-}C_5Me_5)(\mu\text{-}OC_6H_2{}^tBu_2\text{-}2,6\text{-}Me\text{-}4)]_2$ showed high activity for the ring-opening polymerization of ϵ-caprolactone (Scheme 20): 500 equiv of monomer was polymerized in 99% yield with $M_n = 120\,000$ and $M_w/M_n = 1.40$.[117] The samarium complexes $[Sm_2(\eta^5\text{-}C_5Me_5)(\mu\text{-}OSi(O^tBu)_3)_3]$ and $[Sm(III)\{OSi(O^tBu)_3\}_3(\mu\text{-}C_5Me_5)Sm(II)_2\{\mu\text{-}OSi(O^tBu)_3\}]$,[43] $[Sm(\eta^5\text{-}C_5{}^iPr_4H)(O^tBu)I(THF)]$[118] as well as the alkyl yttrium complexes $[Y(\eta^5\text{-}C_5Me_4SiMe_3)(CH_2SiMe_3)_2(THF)]$ and $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)CH_2SiMe_3(THF)]$[130] were also reported to show high catalytic activity for the ring-opening polymerization of ϵ-caprolactone.

X. Conclusion

It is still too early to assess the full potential of half-sandwich lanthanide complexes in the context of homogeneously catalyzed reactions. The underrepresentation compared to the metallocenes is clearly due to synthetic difficulties and the seemingly bewildering number of structural types. The introduction of the pentamethylcyclopentadienyl ligand followed by the linked amido–cyclopentadienyl ligand as well as sterically demanding 2,6-disubstituted phenolato ligands have undoubtedly allowed a more rapid and systematic development of the chemistry involving half-sandwich lanthanide complexes. With more practical synthetic pathways becoming available, the near future will clearly see a further expansion of the applications of these type of complexes exhibiting high, yet flexible, electronic and steric unsaturation.

XI. Acknowledgment

We thank the Deutsche Forschungsgemeinschaft, the Bundesministerium für Bildung und Forschung, BASF AG, and the Fonds der Chemischen Industrie for generous financial support of our research. Dr. Kai C. Hultzsch, Erlangen, is gratefully acknowledged for originally initiating organolanthanide chemistry in our group.

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