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Accounts

Recent Progress in the Chemistry of Rare Earth Metal Alkyl and Hydrido Complexes Bearing Mono(cyclopentadienyl) Ligands

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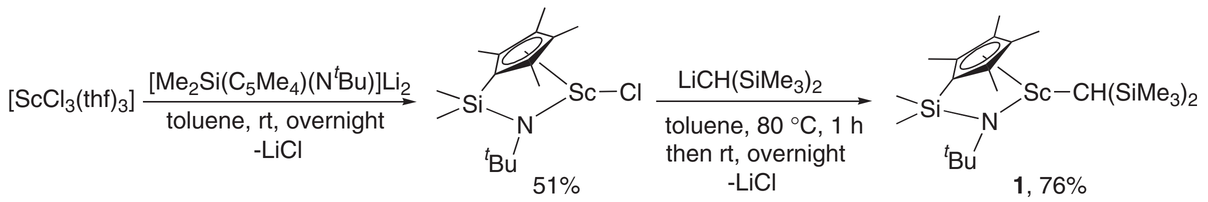
The acid–base reactions between rare earth tris(alkyl) complexes and silylene-linked cyclopentadiene–amines and –phosphines afford straightforwardly the corresponding cyclopentadienyl–amido and –phosphido rare earth alkyl complexes, respectively. This method can also be utilized for the synthesis of rare earth bis(alkyl) complexes bearing mono(cyclopentadienyl) ligands such as $C_5Me_4SiMe_3$. The reaction of the alkyl complexes with H_2 or $PhSiH_3$ readily gives the corresponding hydrido complexes; in the case of the bis(alkyl) complexes bearing the $C_5Me_4SiMe_3$ ligand, a novel type of rare earth polyhydrido cluster has been isolated and structurally characterized. The silylene-linked cyclopentadienyl–arylamido and –phosphido rare earth alkyl complexes act as excellent catalyst precursors for the dimerization of terminal alkynes and hydrosilylation of olefins, respectively. The rare earth polyhydrido clusters exhibit unique reactivities toward unsaturated organic substrates such as lactones, nitriles, and olefins.

Organo rare earth alkyl and hydrido complexes are among the most important organometallic compounds, because of their novel activity in various catalytic processes.[1] These complexes have long been dominated by the so-called metallocene complexes which bear two cyclopentadienyl ancillary ligands. Recently, considerable attention has been directed to rare earth half-metallocene complexes which are supported by only one cyclopentadienyl ancillary ligand, because such complexes are expected to provide a sterically and electronically more unsaturated metal center and thus to show unique reactivities that differ from those of the metallocenes. This account is intended to give an overview on recent developments in this area, with a focus on the mono(cyclopentadienyl)-supported rare earth alkyl and hydrido complexes, including those of the bis(alkyl) and dihydrido complexes. Emphases are placed on complexes which can certainly or potentially serve as catalysts for useful transformations. Divalent lanthanide half-metallocenes have been recently reviewed[2] and will not be described here. A more comprehensive review on mono(cyclopentadienyl) complexes of the rare earth elements has also appeared.[3]

1. Rare Earth Metal Alkyl and Hydrido Complexes Bearing Silylene-Linked Cyclopentadienyl–Amido Ligands

The first silylene-linked cyclopentadienyl–amido rare earth alkyl complex was prepared by the metathetical reaction between a rare earth metal chloride complex and $LiCH(SiMe_3)_2$, as shown in Scheme 1.[4] It was later found that the acid–base reactions between the rare earth tris{(trimethylsilyl)methyl} complexes $[Ln(CH_2SiMe_3)_3(thf)_2]$ (Ln = Sc, Y, Yb, Lu) and an amine ligand offer an excellent salt-free route to the corresponding cyclopentadienyl–amido/alkyl complexes (Schemes 2–5).[5–10] The similar reactions between the bulkier alkyl complexes $[Ln\{CH(SiMe_3)_2\}_3]$ (Ln = Yb, Lu) or the silylamido complexes $[Ln\{N(SiMe_3)_2\}_3]$ (Ln = Nd, Sm, Lu) with the amine ligand $(C_5Me_4H)SiMe_2(NH^tBu)$ also afforded the corresponding alkyl (**12**, **13**) or silylamido (**14**–**16**) complexes, respectively, but a slightly harsh condition (reflux in toluene) was required (Scheme 6).[11]

The yttrium alkyl complex **2** underwent σ-bond metathesis reactions with furan and thiophene to give the binuclear 2-furyl



Scheme 1.

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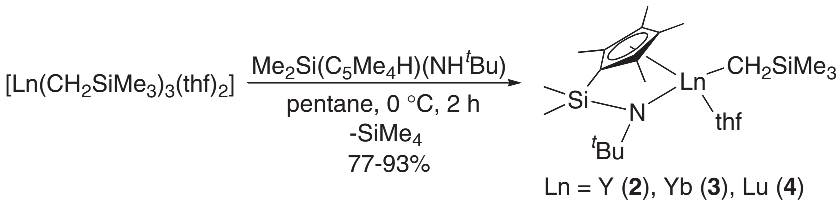
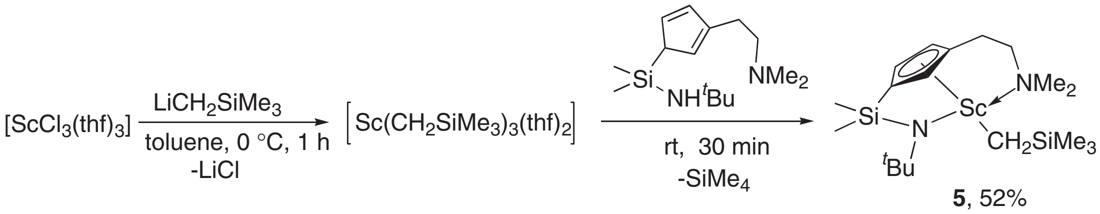
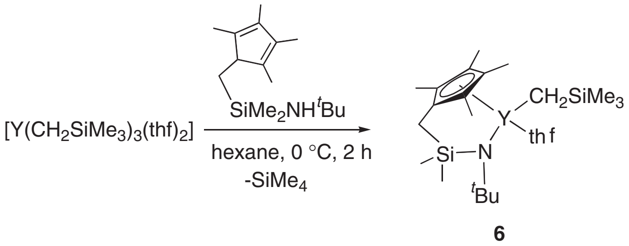


Scheme 2.

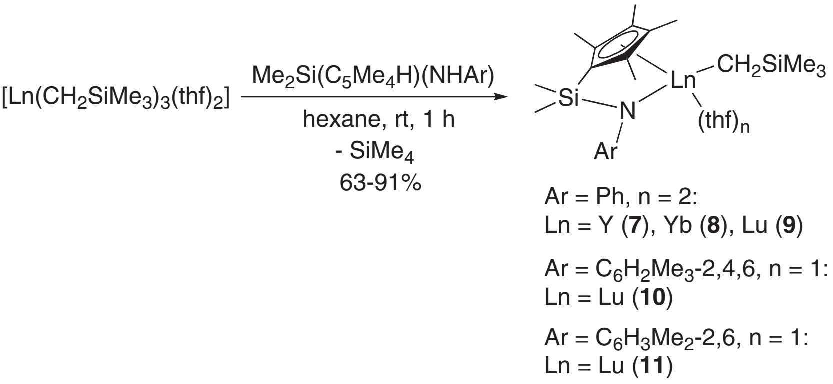


Scheme 3.

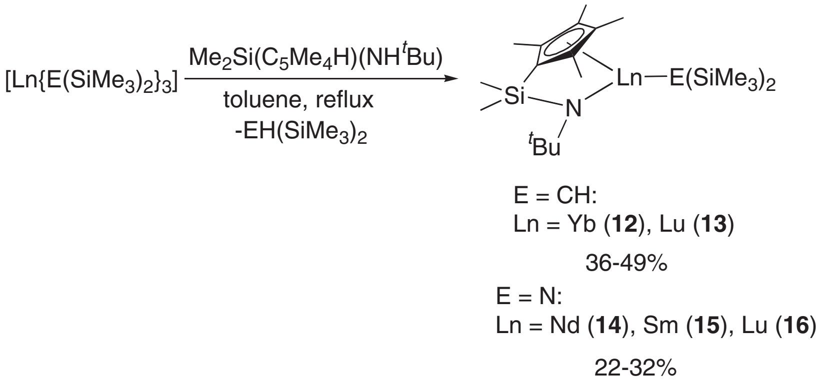


Scheme 4.

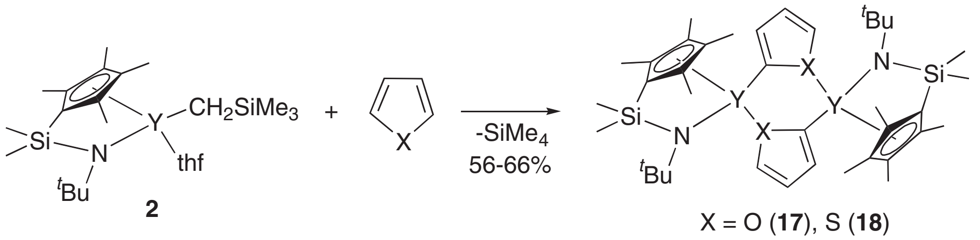
and 2-thienyl complexes **17** and **18**, respectively (Scheme 7).[12] The reactions of the lutetium arylamido/alkyl complexes such as **7**, **10**, and **11** with terminal alkynes at room temperature afforded the corresponding dimeric alkynide complexes (**19**–**22**) (Scheme 8).[10] In contrast with the analogous metallocene or Cp-free alkynide complexes,[13] the alkynide-bridges in these half-metallocene complexes are rather strong, so the complexes remained unchanged even in the presence of THF at high temperatures (80–150 °C), As described below, these novel characteristics of the half-metallocene alkynide complexes enable them to serve as a unique catalyst system for the dimerization



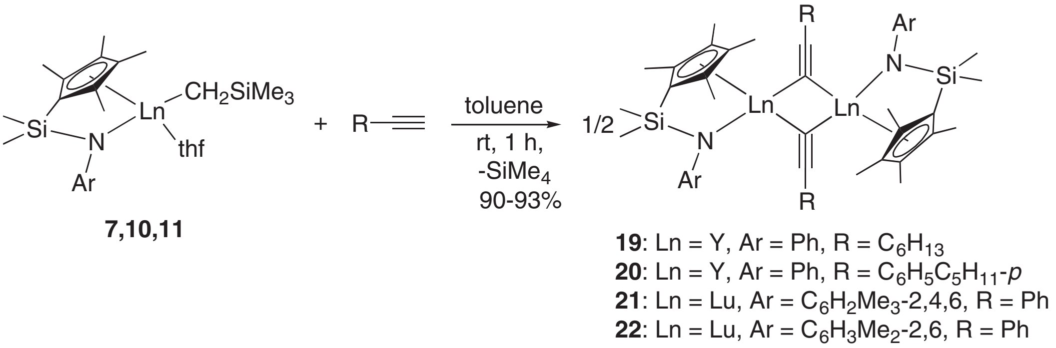
Scheme 5.



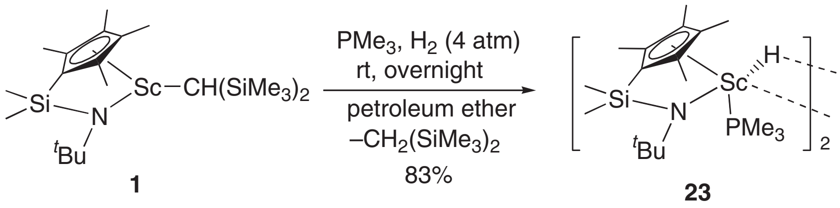
Scheme 6.



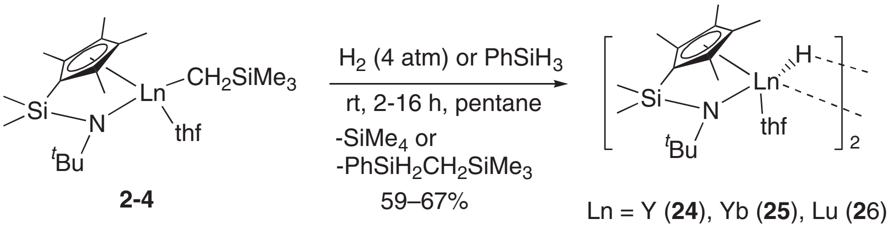
Scheme 7.



Scheme 8.



Scheme 9.



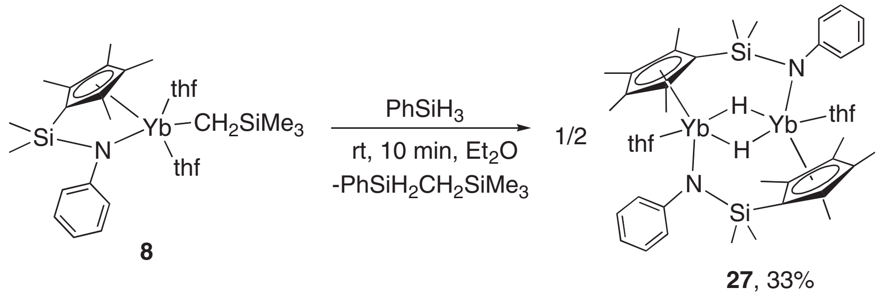
Scheme 10.

of terminal alkynes.

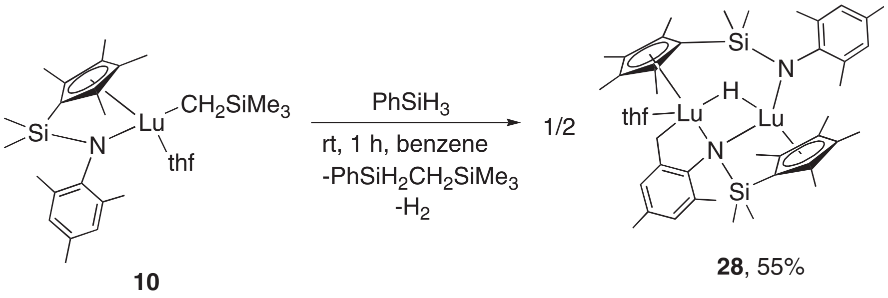
Hydrogenolysis of the scandium alkyl complex **1** in the presence of PMe_3 in petroleum ether yielded the corresponding PMe_3-coordinated hydrido complex **23**, which adopts a dimeric structure via μ-H-bridges (Scheme 9).[4] Similarly, the reactions of **2–4** with H_2 or $PhSiH_3$ in pentane easily afforded the hydrido complexes **24–26** (Scheme 10).[5–7] The reaction of the ytterbium phenylamido/alkyl complex **8** with $PhSiH_3$ in Et_2O gave the hydrido compound **27**, in which the Cp′–amido ligand spans two metal centers rather than chelates one metal as in **23–26** or its alkyl precursor **8** (Scheme 11).[14] In contrast with the analogous alkylamido/hydrido complexes **23–26**, which were stable in THF, the arylamido/hydrido complex **27** decomposed gradually into unidentified products in THF. The reaction of the 2,4,6-trimethylphenylamido complex **10** with $PhSiH_3$ in benzene yielded **28**, in which one of the *ortho*-methyl groups was metallated via σ-bond metathesis with a Lu–H bond (Scheme 12).[14] These results indicate that the nature of the substituents on the N atom in such half-metallocene complexes could strongly influence the structure and reactivity of the whole molecule. An arylamido-supported hydrido species seemed to be more reactive (less stable) than an alkylamido-supported analogue.

2. Rare Earth Metal Alkyl and Hydrido Complexes Bearing Silylene-Linked Cyclopentadienyl–Phosphido Ligands

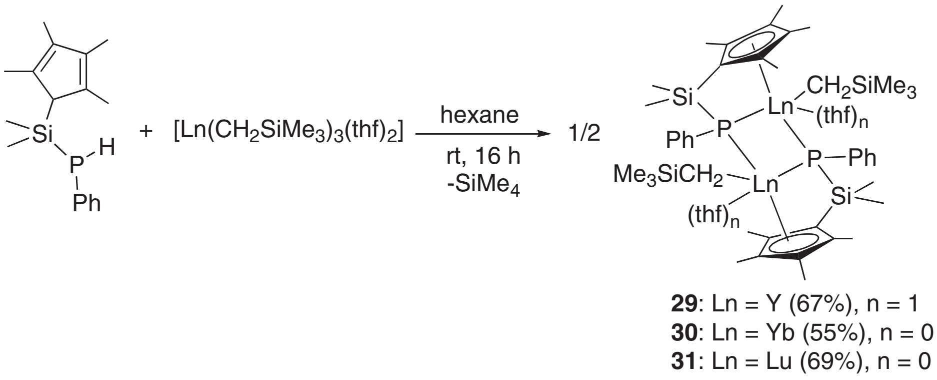
Analogously to the salt-free synthesis of the silylene-linked cyclopentadienyl–amido/alkyl complexes, the acid–base reactions between $[Ln(CH_2SiMe_3)_3(thf)_2]$ ($Ln = Y, Yb, Lu$) and the phosphine ligands $Me_2Si(C_5Me_4H)(PHR)$ ($R = Ph, Cy$) also



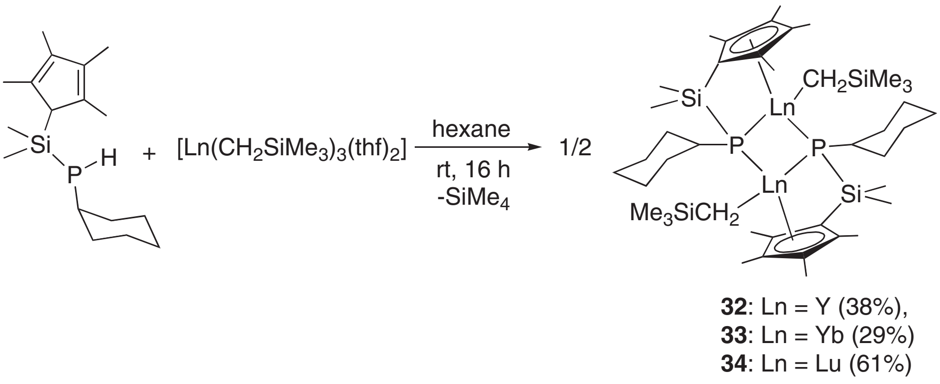
Scheme 11.



Scheme 12.



Scheme 13.

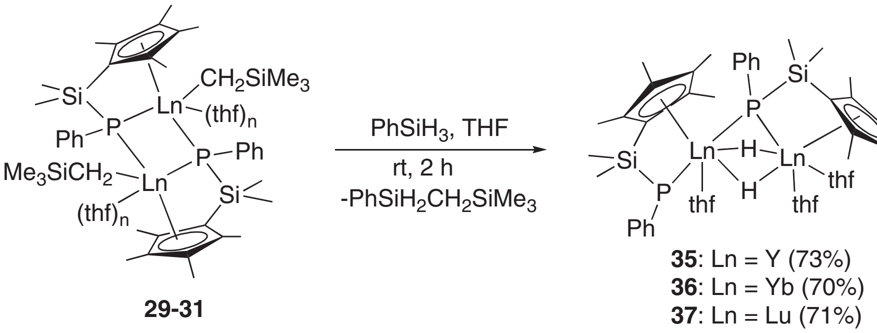


Scheme 14.

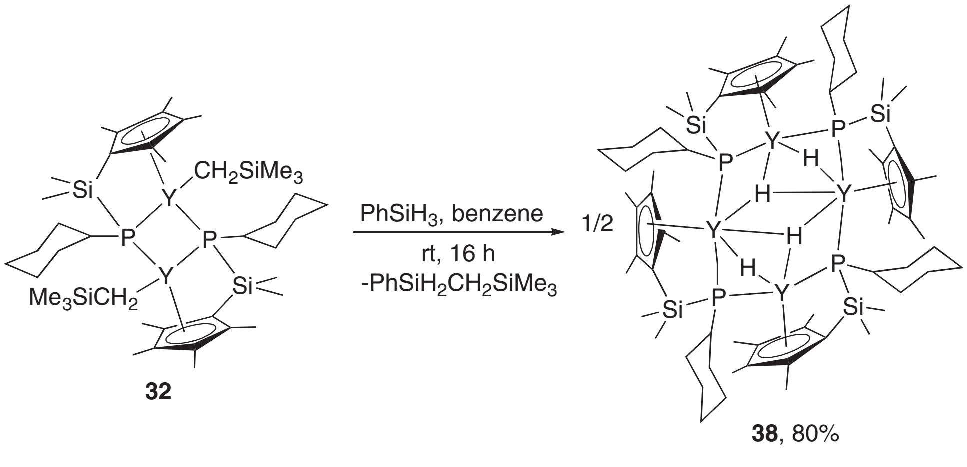
afforded straightforwardly the corresponding cyclopentadienyl–phosphido/alkyl complexes **29–34** (Schemes 13 and 14).[15] In contrast with the analogous cyclopentadienyl–amido complexes **1–16** that adopt a monomeric structure, however, the phosphido complexes **29–34** form a dimeric structure through phosphido-bridging, while the alkyl ligand is placed in a terminal position. X-ray analyses have shown that the phosphido bridges in these complexes are asymmetric, with the "intermolecular” Ln–P bridging bond distances being significantly shorter than those of the “intramolecular” chelating Ln–P bonds.[15]

It should be pointed out that the metathetical reactions between $LnCl_3$ and the alkali metal salts of a ligand seemed not suitable for the synthesis of the corresponding silylene-linked cyclopentadienyl–phosphido rare earth complexes because of the preferred cleavage of the P–Si bond,[16,17] although divalent rare earth complexes $[Me_2Si(C_5Me_4)(PAr)Ln]$ (Ln = Sm, Yb; Ar = $C_6H_2{}^tBu_3$-2,4,6) could be prepared by the reactions of LnI_2 with $K_2[Me_2Si(C_5Me_4)(PAr)]$.[16]

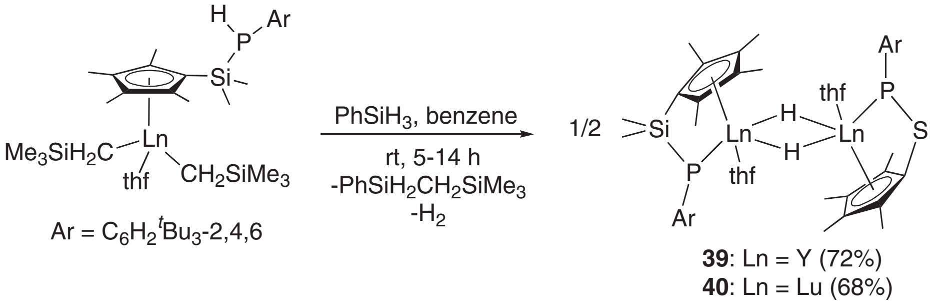
The reactions of the alkyl complexes **29**–**31** with $PhSiH_3$ in THF easily afforded the corresponding hydrido compounds **35**–**37**, which also adopt a dimeric structure but the two metal centers are bridged by two hydrido ligands and one phosphido ligand (Scheme 15).[15] The hydrido-bridges in these complexes are rather strong and could survive in THF solution, as shown by the NMR spectra. When the alkyl complex **32** was treated in benzene with 2 equiv of $PhSiH_3$, the tetranuclear hydrido complex **38** was obtained (Scheme 16). Complex **38** was insoluble in almost all common organic solvents such as benzene, THF, pyridine, or HMPA (hexamethylphosphoric triamide), demonstrating that the tetranuclear core structure is unusually robust. The similar reaction of the PH-functionalized-cyclopentadienyl/bis(alkyl) complexes $[C_5Me_4(SiMe_2PHAr)Ln(CH_2SiMe_3)_2(thf)]$ (Ln = Y, Lu; Ar = $C_6H_2{}^tBu_3$-2,4,6) with $PhSiH_3$ in benzene yielded the corresponding cyclopentadienyl–phosphido-ligated hydrido complexes **39**, **40**, probably via dehydrogenation of the PHAr group by the in situ generated dihydrido species “$C_5Me_4(SiMe_2PHAr)LnH_2$” (Scheme 17).[15] In contrast with the phosphido-bridging in the phenylphosphido and cyclohexylphosphido complexes **35**–**38**, the “Cp′–PAr” li-



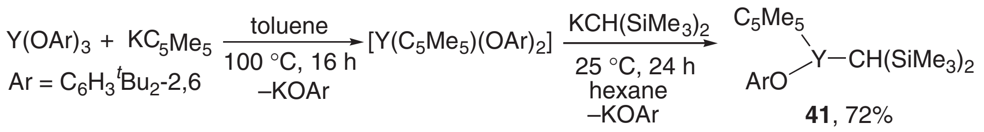
Scheme 15.



Scheme 16.



Scheme 17.



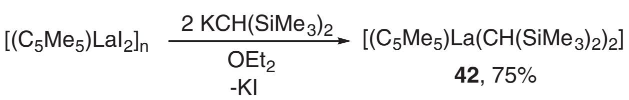
Scheme 18.

gand in **39**, **40** is bonded to one metal center in a chelating fashion and a phosphido bridge is not formed, obviously owing to the bulkiness of the sterically demanding substituent $C_6H_2{}^tBu_3$-2,4,6 on the P atom.

3. Rare Earth Metal Alkyl and Hydrido Complexes Bearing Unlinked Mono(cyclopentadienyl) Ligands

The isolation of a rare earth metal alkyl or hydrido complex bearing unlinked mono(cyclopentadienyl) ligands is generally more difficult than that with the linked ones, because of ligand redistribution problems. An appropriate metal/ligand combination seemed to be rather critical.

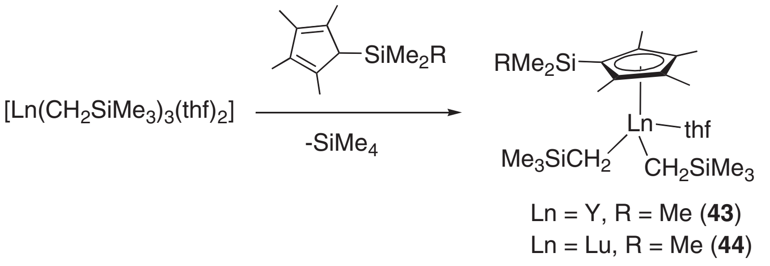
The C_5Me_5/OAr-ligated yttrium alkyl complex **41** (Ar = $C_6H_3{}^tBu_2$-2,6) was synthesized by the reaction of $[(C_5Me_5)Y(OAr)_2]$ with 1 equiv of $[KCH(SiMe_3)_2]$ in hexane (Scheme 18).[18] The reaction of $YCl_3(thf)_{3.5}$ with KC_5Me_5 followed by $Li(OEt_2)[PhC(NSiMe_3)_2]$ in THF gave the yttrium cyclopentadienyl/benzamidinate chloride complex $[(C_5Me_5)Y(PhC(NSiMe_3)_2)(\mu\text{-Cl})]_2$, which upon reaction with 2 equiv of MeLi in the presence of TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) afforded the structurally characterizable Me-bridged Y/Li heterobimetallic complex $[(C_5Me_5)Y(PhC(NSiMe_3)_2)(\mu\text{-Me})_2Li(tmeda)]$.[19] The reaction of LaI_3 with 1 equiv of KC_5Me_5 in THF gave the mono(pentamethylcyclopentadienyl)lanthanum diiodide complex $[(C_5Me_5)LaI_2(thf)_3]$,[20] which on treatment with Me_3SiI yielded the unsolvated analogue $[(C_5Me_5)LaI_2]_n$.[21] The metathetical reaction of $[(C_5Me_5)LaI_2]_n$ with 2 equiv of $KCH(SiMe_3)_2$ gave straightforwardly the dialkyl complex $[(C_5Me_5)La\{CH(SiMe_3)_2\}_2]$ (**42**) (Scheme 19).[21] Similarly, the reaction of $[(C_5Me_5)Ce(OAr)_2]$ (Ar = $C_6H_3{}^tBu_2$-2,6) with 2 equiv of $LiCH(SiMe_3)_2$ afforded the cerium dialkyl complex $[(C_5Me_5)Ce\{CH(SiMe_3)_2\}_2]$[22] A mixed dialkyl complex $[(C_5Me_5)Lu(CH_2SiMe_3)\{CH(SiMe_3)_2\}(thf)]$ was obtained by sequential reactions of $[Na(thf{\cdot}OEt_2)][Lu(C_5Me_5)Cl_3]$ with $LiCH(SiMe_3)_2$ and $LiCH_2SiMe_3$.[23]



Scheme 19.

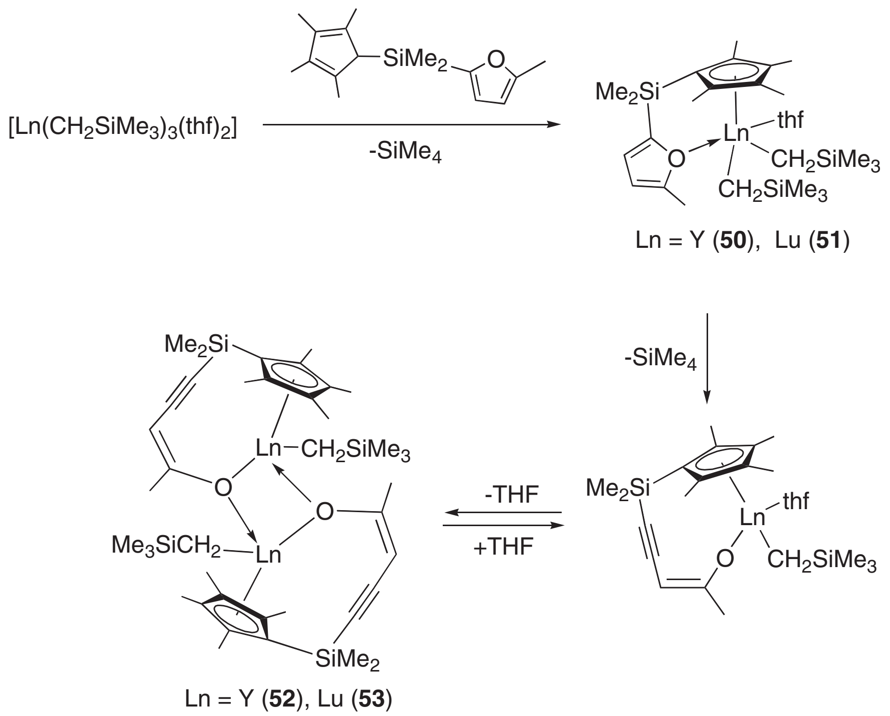
As a convenient salt-free route, the acid–base reactions between $[Ln(CH_2SiMe_3)_3(thf)_2]$ (Ln = Y, Lu) and $(C_5Me_4H)SiMe_2R$ (R = Me,[24,25] Ph,[24] 2-furyl,[26] $PHC_6H_2{}^tBu_3$-2,4,6[15]) afforded straightforwardly the mono(cyclopentadienyl)/bis(alkyl) complexes $[\{C_5Me_4(SiMe_2R)\}Ln(CH_2SiMe_3)_2(thf)]$ (**43**–**49**) (Scheme 20).[15,24–26] The reactions of $[Ln(CH_2SiMe_3)_3(thf)_2]$ (Ln = Y, Lu) with the 5-methylfuryl-functionalized tetramethylcyclopentadiene $(C_5Me_4H)SiMe_2\{(C_4H_2MeO\text{-}5)\text{-}2\}$, however, resulted in formation of the furyl-ring-opening products (**52**, **53**) as the final isolable products, whereas the bis(alkyl) species **50**, **51** were observed only as intermediates by ^{1}H NMR (Scheme 21).[26] The cationic mono(alkyl) complexes **54** and **55** were obtained by the reactions of the bis(alkyl) complexes **46** and **47** with BPh_3 in THF, respectively (Scheme 22).[26]

Hydrogenolysis of **41** with H_2 afforded the C_5Me_5/OAr-ligated yttrium hydrido complex **56** (Scheme 23).[18] The reactions of the bis(alkyl) complexes **43** and **44** with 1 equiv of $PhSiH_3$ in hexane at −30 °C gave selectively the mixed alkyl/hydrido complexes **57** and **58**, respectively (Scheme 24).[25,27] The hydrogenolysis reaction of the mixed alkyl/hydrido yttrium complex **57** with H_2 in THF yielded the tetranuclear polyhydrido complex **59**, which consists formally of two "$(C_5Me_4SiMe_3)YH_2$" units and two "$(C_5Me_4SiMe_3)YH_2(thf)$" units (Scheme 25).[25,27] The similar reaction of the lutetium analogue **58** with H_2 in THF produced **60**, in which only one of the four Lu atoms is coordinated to a thf ligand, probably owing to the ion size of Lu^{3+} being smaller than that of Y^{3+}.[25] Complex **59** could also be obtained by hydrogenolysis of the bis(alkyl) complex **43** in THF (Scheme 26).[25,27,28] When the

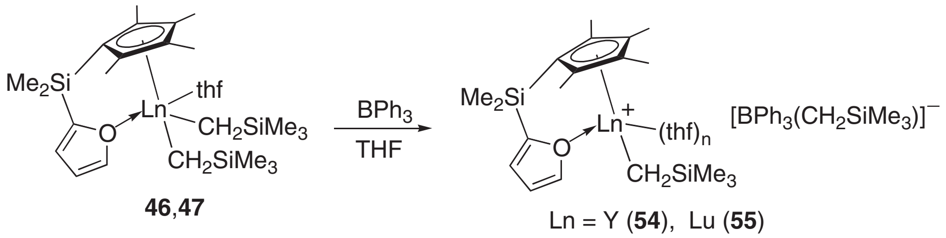


Ln = Y, R = Me (**43**)
Ln = Lu, R = Me (**44**)
Ln = Y, R = Ph (**45**)
Ln = Y, R = 2-furyl (**46**)
Ln = Lu, R = 2-furyl (**47**)
Ln = Y, R = $PHC_6H_2{}^tBu_3$-2,4,6 (**48**)
Ln = Lu, R = $PHC_6H_2{}^tBu_3$-2,4,6 (**49**)

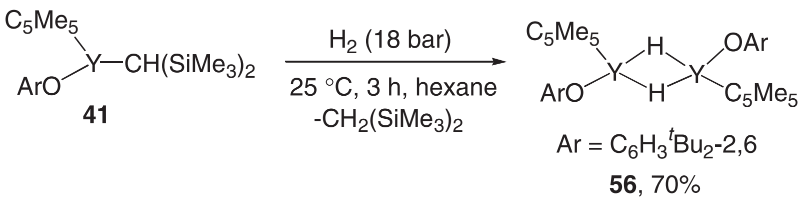
Scheme 20.



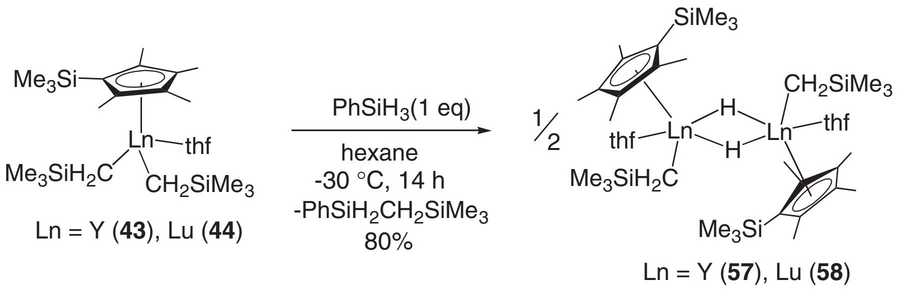
Scheme 21.



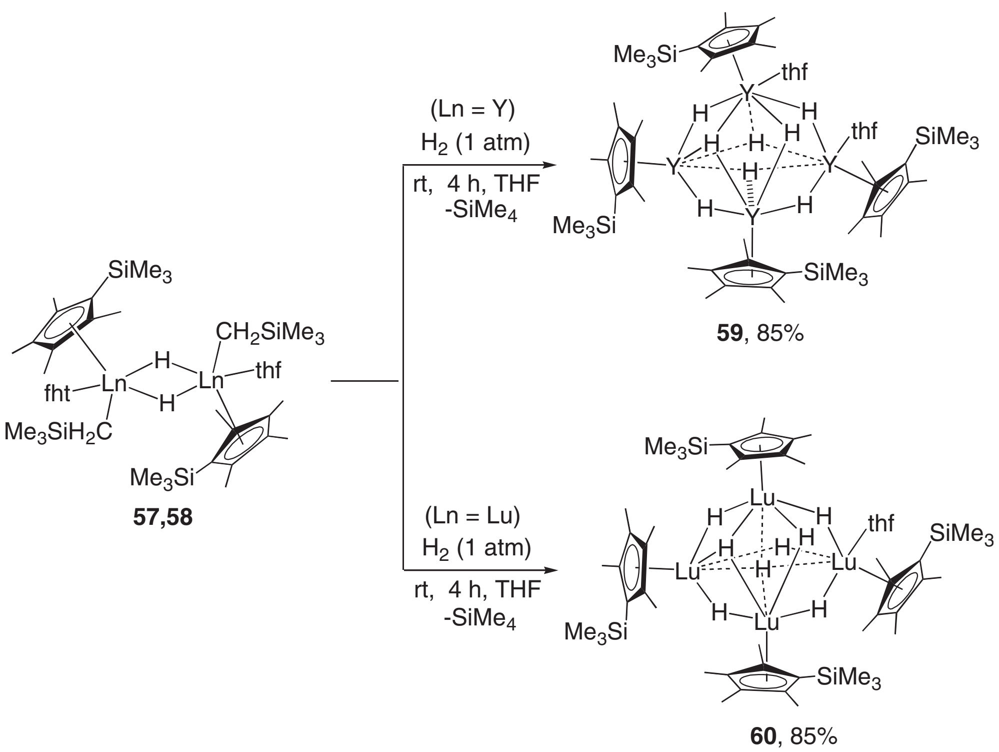
Scheme 22.



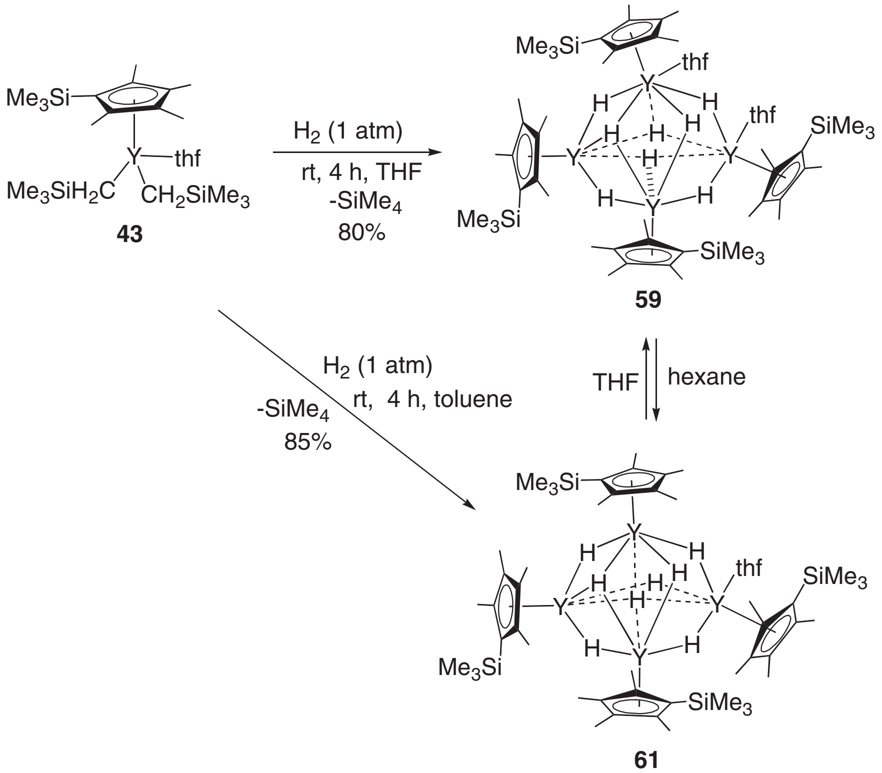
Scheme 23.



Scheme 24.



Scheme 25.



Scheme 26.

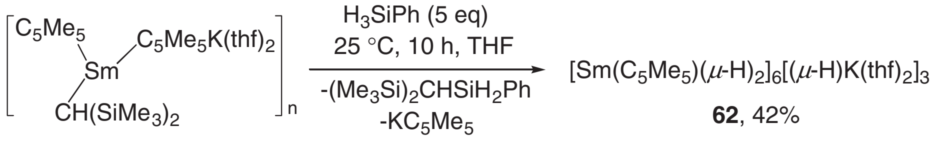
reaction was carried out in toluene at room temperature, however, the mono(thf)-coordinated complex **61** was obtained (Scheme 26).[25,27] Complexes **59** and **61** could be easily converted into each other by recrystallization from different solvents, as shown in Scheme 26.[25,27]

In sharp contrast to the easy formation of the structurally characterizable $C_5Me_4SiMe_3$-supported polyhydrido complexes **59–61**, the similar hydrogenolysis of the C_5Me_5-ligated bis(alkyl) complexes such as $[(C_5Me_5)Lu(CH_2CMe_3)_2(thf)]$ or $[(C_5Me_5)Lu(CH_2SiMe_3)\{CH(SiMe_3)_2\}(thf)]$ did not afford an isolable hydrido species,[23] showing that the nature of the substituents on the cyclopentadienyl ring play a critically important role in the stabilization of a dihydrido species. A structurally characterized C_5Me_5-ligated Sm(III) dihydrido species (**62**) was isolated in a heteropolymetallic form through combination with the "$KH(thf)_2$" unit by the reaction (σ-bond metathesis and subsequent oxidation) of the Sm(II) alkyl complex $[(C_5Me_5)SmCH(SiMe_3)_2\{(C_5Me_5)K(thf)_2\}]_n$ with an excess amount of $PhSiH_3$ in THF (Scheme 27).[29] Mono(cyclopentadienyl)/bis(tetrahydroborato) complexes $[(C_5H^iPr_4)Ln(BH_4)_2(thf)]$ (Ln = Nd, Sm) could be prepared by the reaction of $Ln(BH_4)_3(thf)_3$ with 1 equiv of $NaC_5H^iPr_4$.[30]

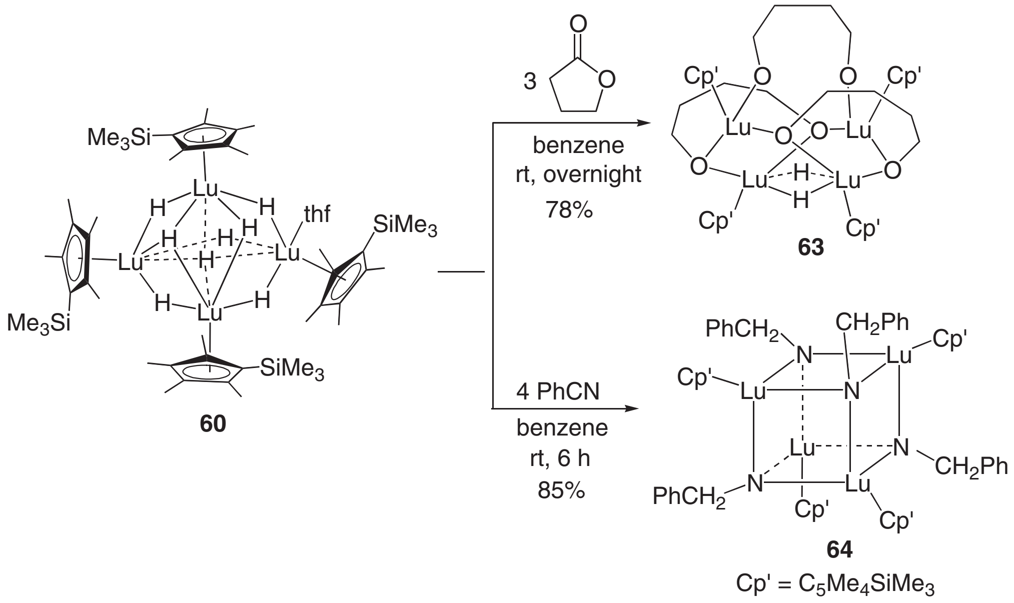
The polyhydrido clusters **59**–**61** are soluble and thermally stable in common organic solvents such as hexane, toluene, and THF. No decomposition or ligand redistribution was observed in THF-d_8 or toluene-d_8, as monitored by ^1H NMR. Preliminary studies demonstrated that this new type of rare earth hydrido compound could show rich and unique reaction chemistry toward a variety of unsaturated substrates. For example, γ-butyrolactone, a stable five-membered cyclic ester, was completely reduced to the linear diolate unit $[^-O(CH_2)_4O^-]$ by the lutetium polyhydrido complex **60** at room temperature to give the corresponding mixed alkoxo/hydrido tetranuclear complex **63** (Scheme 28).[31] The C–N triple bond of benzonitrile could be easily reduced into the C–N single bond via double Ln–H addition, to afford the cubane imido cluster complex **64**. The reactions of the yttrium hydrido cluster **61** with styrene yielded the benzylic allyl complex **65**, in which the allyl part is bonded to one Y atom in a η^3-fashion, while the phenyl part is bonded to another Y atom in a η^2-form (Scheme 29). The similar reaction of **61** with 1,3-hexadiene afforded **66**, in which the allyl unit interacts with two Y atoms via the two terminal carbon atoms, each bonding to one metal center in a η^1-fashion. In all these cases, the tetranuclear metal skeleton was retained.

4. Polymerization of Olefins

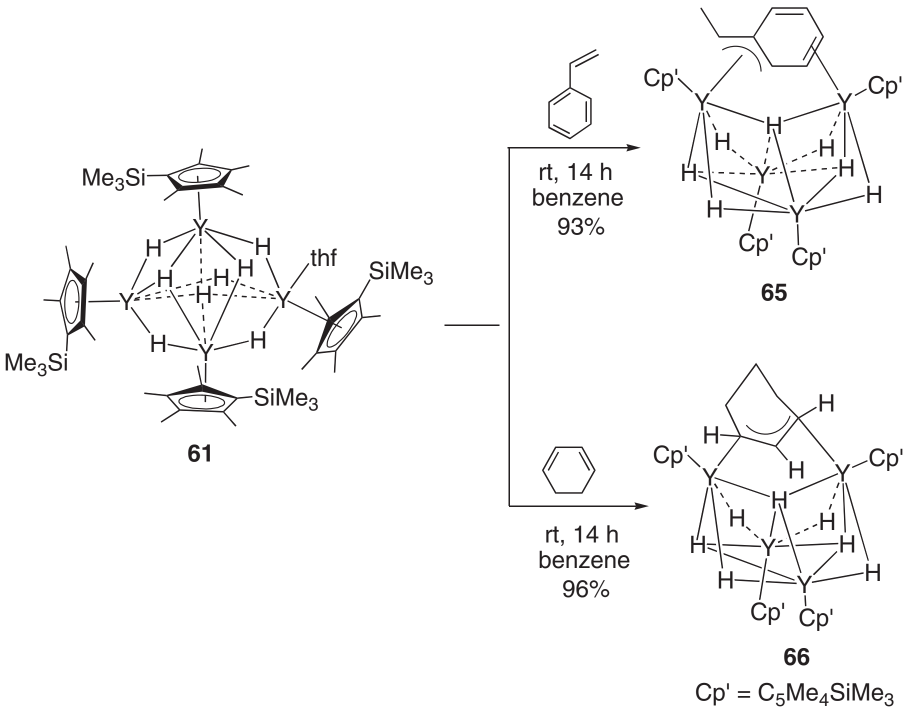
The silylene-linked cyclopentadienyl–phosphido alkyl complexes were active for the polymerization of ethylene, with the activity being dependent on the ion size of the central metals and on the substituent on the P atom.[15] The largest Y complexes (**29**, **32**) showed the highest activity (79–183 g (mmol $Y)^{-1}$ h^{-1} atm^{-1}), whereas the smallest lutetium complexes (**31**, **34**) were almost inert under the same conditions. The phenylphosphido complexes **29** and **30** showed a higher activity than the corresponding cyclohexylphosphido analogues **32** and **33**, respectively. The silylene-linked cyclopentadienyl–phosphido/hydrido complexes **35**–**40** were almost inactive for the polymerization of ethylene under the same conditions (25 °C, 1 atm), probably owing to the strong hydrido-bridges. The silylene-linked cyclopentadienyl–amido yttrium(III) alkyl (**2**) or hydrido (**24**) complexes were reported to show a very low activity for the polymerization of ethylene (**2**: 0.21 g $mmol^{-1}$ h^{-1} atm^{-1}, **24**: 0.08 g $mmol^{-1}$ h^{-1} atm^{-1}), probably owing to the presence of the strongly coordinating thf



Scheme 27.



Scheme 28.



Scheme 29.

ligand.[6] The activity of the C_5Me_5/OAr-supported Y(III) hydrido complex **36** for ethylene polymerization was also very low because of the strong μ-H-bridges.[18] The mono(cyclopentadienyl) lanthanum dialkyl complex [$(C_5Me_5)La(CH(SiMe_3)_2)_2(thf)$] showed a moderate activity at 25 °C (ca. 20 $g\,mmol^{-1}\,h^{-1}\,atm^{-1}$), yielding linear polyethylene with M_n up to 1.5×10^6 and $M_w/M_n = 1.28$–1.79.[32]

The silylene-linked cyclopentadienyl–amido scandium or yttrium hydrido complexes **23** or **24** did not polymerize styrene because of formation of stable η^3-allyl type complexes.[4,6] After treatment with an 1-alkene compound such as 1-hexene, however, the yttrium complex **24** became active for the polymerization of styrene.[6,33] This reaction was thought to be initiated by a monomeric, thf-coordinated *n*-alkyl complex such as [$Me_2Si(C_5Me_4)(N^tBu)Y(\mu\text{-}C_6H_{13})(thf)$], which could be generated in situ by insertion of 1-hexene into the Y–H bond.[33] The presence of the thf ligand and the *n*-alkyl group seemed to be critical for initiation of the polymerization. Neither the unsolvated dimeric alkyl complex [$Me_2Si(C_5Me_4)(N^tBu)Y(\mu\text{-}C_6H_{13})$]$_2$ nor the DME adduct [$Me_2Si(C_5Me_4)(N^tBu)Y(\mu\text{-}C_6H_{13})(dme)$] nor the (trimethylsilyl)methyl complex [$Me_2Si(C_5Me_4)(N^tBu)Y(CH_2SiMe_3)(thf)$] initiated the polymerization of styrene.[33] The mono(cyclopentadienyl) lanthanum dialkyl complex [$(C_5Me_5)La(CH(SiMe_3)_2)_2(thf)$] was reported to show an activity for styrene polymerization at 50 °C.[32]

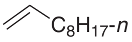
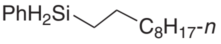
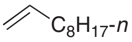
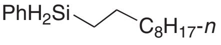
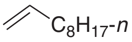
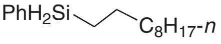
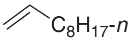
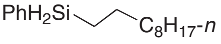
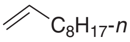
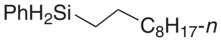
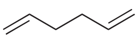
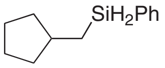
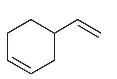
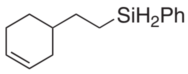
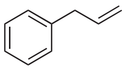
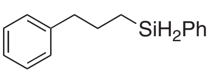
1-Alkenes such as propene, 1-pentene, and 1-hexene could be oligomerized by the silylene-linked cyclopentadienyl–amido scandium hydride complex **23**[4] and the C_5Me_5/OAr-ligated yttrium hydride complex **41**,[18] albeit with low activity. The silylene-linked cyclopentadienyl–amido yttrium hydride complex **24** or the phosphido complexes **29–40** showed no activity for the polymerization or oligomerization of 1-alkenes.[6,7,15]

5. Hydrosilylation of Olefins

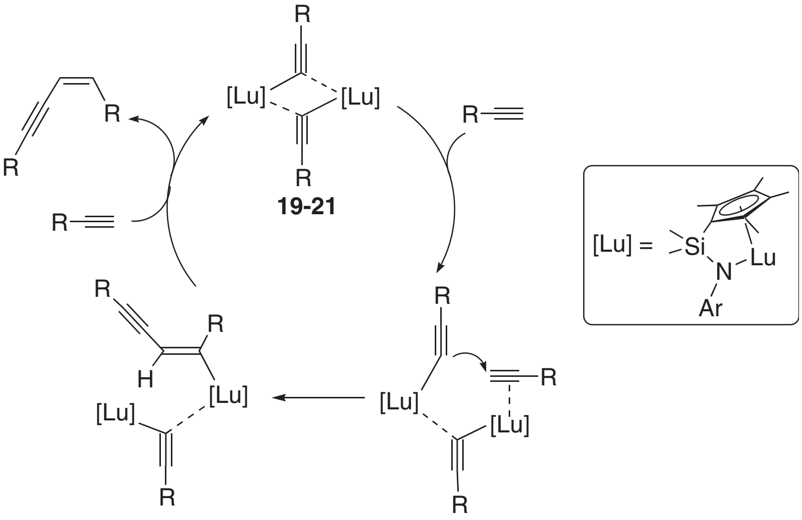
The silylene-linked cyclopentadienyl–phosphido rare earth metal alkyl complexes, in particular the cyclohexylphosphido lutetium complex **34**, acted as an excellent catalyst precursor for the hydrosilylation of olefins (Table 1).[15] Complex **34** is perhaps the most active and regioselective rare earth catalyst (or catalyst precursor) ever reported for the hydrosilylation of 1-alkenes.[1c,34] At room temperature 1-decene was quantitatively hydrosilylized within 10 min by $PhSiH_3$ in the presence of 2.5 mol% of **34**, yielding selectively the linear silylation product 1-(phenylsilyl)decane (Table 1). 1,5-Hexadiene was converted quantitatively into the cyclization/silylation product (phenylsilylmethyl)cyclopentane within 45 min. The hydrosilylation of 4-vinyl-1-cyclohexene occurred selectively at the terminal C–C double bond, affording quantitatively the terminal silane product 4-[2-(phenylsilyl)ethyl]cyclohex-1-ene in less than 30 min. The reaction of 3-phenylpropene was completed in 15 min to give cleanly the linear silane product 1-phenyl-3-(phenylsilyl)propane. These reactions might proceed via a terminal hydride species which was generated in situ by σ-bond metathesis between the Lu–CH_2SiMe_3 bond and $PhSiH_3$. The isolated dimeric hydride complex **8b** showed a much lower activity and the tetrameric complex **38** was completely inactive under the same conditions owing to the strong hydrido-bridges. The hydrosilylation of styrene by **34** yielded a mixture of terminal and internal regioisomers.

The silylene-linked cyclopentadienyl–amido yttrium alkyl complexes **2**, **6** and the Sm(III)/K heterometallic polyhydride cluster **62** also effected the hydrosilylation of olefins, but with lower activity.[9,29] The silylene-linked cyclopentadienyl–amido samarium complex **15** showed a higher activity for the hydroamination/cyclization of aminoalkenes[11,35] and the hydrophos-

Table 1. Catalytic Hydrosilylation of Olefins by Silylene-Linked Cyclopentadienyl–Phosphido Rare Earth Alkyl Complexes[a)]

Cat	Substrate	Time/min	Product	Yield /%
29		60		95
31		180		100
32		45		100
33		45		100
34		10		100
34		45		100
34		30		100
34		15		100

a) Conditions: substrate (0.4 mmol), H_3SiPh (0.5 mmol), cat. (0.01 mmol), in C_6D_6 at rt.



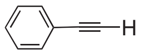
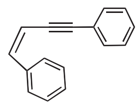
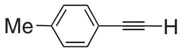
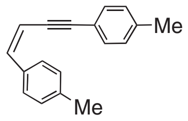
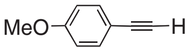
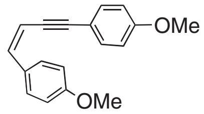
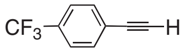
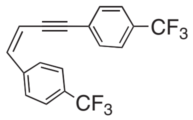
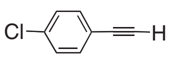
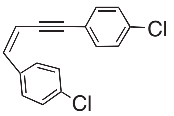
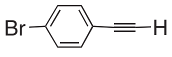
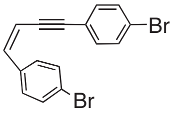
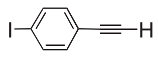
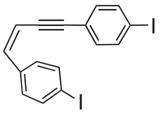
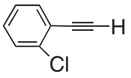
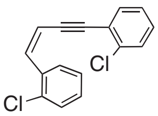
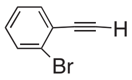
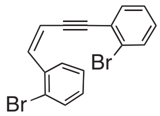
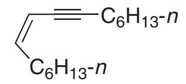
Scheme 30.

phination/cyclization of aminoalkynes[36] compared to its metallocene analogues.

6. Dimerization of 1-Alkynes and Polymerization of Diynes

The silylene-linked cyclopentadienyl–arylamido lutetium alkyl complexes such as **9–11** could serve as excellent catalyst precursors for the regio- and stereoselective head-to-head (*Z*)-dimerization of 1-alkynes.[10] As shown in Table 2, various terminal alkynes can be cleanly dimerized into the corresponding (*Z*)-1,3-enynes. Aromatic C–Cl, C–Br, and C–I bonds, which are known to be extremely susceptible to reductive cleavage by transition metals, survived in these reactions. The corresponding dimeric alkynide species such as **19–22** were confirmed to be the true catalysts. The (*Z*)-selective dimerization was thus achieved by "intermolecular" alkynide addition at the two adjacent, alkynide-bridged metal centers (Scheme 30).[10] This is in sharp contrast with the analogous reactions catalyzed by the rare earth metallocene or benzamidinate-ligated catalysts, in which the reaction took place in a "intramolecular" fashion at a monomeric alkynide/alkyne intermediate and thus always led to formation of the (*E*)-enyne products whenever a head-to-head reaction occurred.[13] It is also noteworthy that the dimeric alkynide catalyst species such as **21** and **22** were thermally stable and soluble at the reaction temperatures (80–110

Table 2. Catalytic Dimerization of Terminal Alkynes by Silylene-Linked Cyclopentadienyl–Arylamido Lutetium Alkyl Complex **10**[a]

Substrate	Product	Solvent[b]	Temp /°C	Time /h	Conversion /%	Selectivity /%
		C_6D_6	80	5	>99	>99
		Toluene-d_8	110	2	>99	>99
		Toluene-d_8 + THF[c]	110	2	>99	>99
		Toluene-d_8	110	2	97	95[d]
		C_6D_6	80	2	>99	>99
		C_6D_6	80	2	>99	>99
		C_6D_6	80	2	>99	>99
		C_6D_6	80	3	>99	>99
		C_6D_6	80	3	>99	>99
n-C_6H_{13}—≡—H		THF-d_8	100	14	>99	95[e]

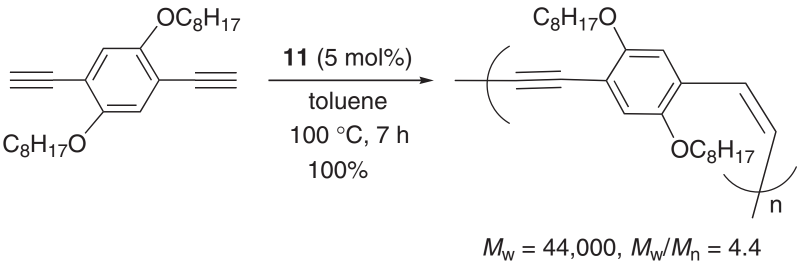
a) Conditions: substrate (1 mmol), **10** (0.02–0.05 mmol). b) 0.45 mL. c) THF: 5 equiv per **10**. d) 1,4,6-Tris[4-(trifluoromethyl)phenyl]hexa-3,5-dien-1-yne (5%) was also formed. e) 2-Hexyldec-1-en-3-yne (5%, head-to-tail dimer) was also formed.

°C), but precipitated upon cooling to room temperature after completion of the reaction. Therefore, this catalyst system worked homogeneously but could be easily separated and reused, thus constituting the first example of a recyclable catalyst system for the dimerization of terminal alkynes.

Aromatic diynes such as 1,4-diethynyl-2,5-alkoxybenzene could be polymerized regio- and stereoselectively to give the corresponding π-conjugated (Z)-polyenynes (Scheme 31).[37]

7. Conclusion and Outlook

By use of appropriate ligand/metal combinations, several types of rare earth metal alkyl and hydrido complexes bearing mono(cyclopentadienyl) ligands have been isolated and structurally characterized. In the silylene-linked cyclopentadienyl–amido and –phosphido complexes, the interplay of the two different ancillary ligands offers an stereically and electronical-



Scheme 31.

ly unique environment for the metal center, which behaves differently than those of the metallocene and Cp-free analogues, as demonstrated in the dimerization of terminal alkynes and hydrosilylation of olefins. The susceptibility of the structure and reactivity of these complexes to the variation of the heteroatoms (N, P) and the substituents attached to them would allow more sophisticated modification and further expansion in the design and construction of more selective, more efficient catalyst systems in future. The mono(cyclopentadienyl)-supported rare earth polyhydrido clusters represent a new type of metal hydrido compound. Its exciting chemistry awaits to be explored.

Although synthetic and reactivity studies of rare earth complexes bearing mono(cyclopentadienyl) ligands are still in their infancy, it is now evident that these complexes can indeed show unprecedented behaviors in catalytic and stoichiometric processes. A prosperous future in this area can confidently be predicted.

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