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Cation size dependent reactivity of lanthanide trihalides with bulky alkylcyclopentadienyl anions

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Reactions of $NdCl_3$ and $PrCl_3$ with two equivalents of sodium tri-*tert*-butylcyclopentadienide furnished base- and salt-free [Cp'_2NdCl] and [Cp'_2PrCl] ($Cp' = 1,2,4\text{-}(Me_3C)_3C_5H_2$) in good yield. Trimethylaluminium has been added to the neodymium complex to form [$Cp'_2NdClAlMe_3$]. With $LaCl_3$ or $CeCl_3$ base-free bis(ring) complexes were not obtained, but in the latter case the salt adduct [$(^4Cp_2Ce)(\mu\text{-}Cl)_2Na(tmeda)_2]_\infty$ ($^4Cp = (Me_2CH)_4C_5H$) could be extracted from the product mixture with tetramethylethylenediamine and crystallized as a zigzag chain polymer. [$^4Cp_2SmCl_2Na(dme)_2$] retained the coordinated sodium chloride even when dissolved in non-polar solvents. Attempted preparation of [Cp'_2YbCl] gave the mono(ring) complex [$Cp'YbCl(\mu\text{-}OCH_2CH_2OCH_3)]_2$ from cleavage of the dimethoxyethane solvent and with lutetium trichloride the hexanuclear complex [$(^4CpLu)_5LuCl_{13}(OEt_2)_5$] was prepared in low yield. For lanthanum and thulium use of the triiodide as a starting compound enabled synthesis of the corresponding bis(tetraisopropylcyclopentadienyl)metal iodide, bis{tri-*tert*-butylcyclopentadienyl}lanthanum iodide was also prepared from LnI_3. [$^4Cp_2TmI$] shows a unique conformation of one of the tetraisopropylcyclopentadienyl ligands with two isopropyl neighbours rotated towards each other indicating extreme steric congestion. Oxidation of [Cp'_2Sm] with copper(I) iodide gave [Cp'_2SmI] in high yield. Mono(ring) complexes are readily available from trichlorides of thulium, ytterbium, and lutetium. Apart from the donor solvent adducts [$^4CpTmCl_2(dme)$], [$Cp'YbCl_2(thf)_2$], and [$^4CpLuCl_2(dme)$], which were isolated from solutions in the corresponding donor solvent, the salt- and donor-free dihalides [$Cp'TmCl_2]_n$ and [$Cp'YbCl_2]_n$ were obtained as oligomers from pentane or petroleum ether extracts. The thulium compound gave [$Cp'Tm\{N(SiMe_3)_2\}_2$] with two equivalents of $Na[N(SiMe_3)_2]$ and the ytterbium complex underwent ring exchange with lithium *tert*-butylcyclopentadienide and formation of the bis(*tert*-butylcyclopentadienyl)ytterbium complex [$(Me_3CC_5H_4)_2Yb(\mu\text{-}Cl)]_2$.

Introduction

Cyclopentadienyl complexes of the lanthanides are known for their versatility as catalyst precursors in homogeneous reactions such as hydrogenation,[1] stereospecific polymerization of acrylates,[2] hydroamination/cyclization,[3,4] hydroboration,[5] hydrophosphination,[6] hydrosilylation,[7,8] hydrostannylation,[9] C–F activation,[10–13] and other catalytic transformations. For a detailed account of these transformations, see the literature.[14–18]

Although there have been recent approaches towards lanthanide complexes with ligands exhibiting O- or N-donor sites and certainly promising exciting developments in catalysis,[19–22] cyclopentadienyl complexes of the lanthanides are still very important and their catalytic potential has not yet been fully explored. Therefore research projects on lanthanide complexes with extremely bulky alkylcyclopentadienyl ligands have been started recently,[12,13,23–28] and they give access to unusual molecules such as base-free thulocene [Cp'_2Tm][27] and monomeric metallocene hydride complexes, [Cp'_2CeH] ($Cp' = \eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2$), which show unprecedented reactivity toward C–F bonds.[12,13] In our laboratory, bulky tetraisopropylcyclopentadienide has been able to stabilize monomeric, salt and base-free biscyclopentadienyl lanthanide complexes of the type [$^4Cp_2LnCl$] ($^4Cp = \eta^5\text{-}(Me_2CH)_4C_5H$; Ln = La, Pr, Nd.[25] The extension of this work to mono- and dicyclopentadienyl lanthanide complexes with bulky substituents from various metal halide precursors and subsequent derivatization reactions are the subject of this paper.

Results and discussion

Strategy

The monomeric [$^4Cp_2LnCl$] ($^4Cp = \eta^5\text{-}(Me_2CH)_4C_5H$; Ln = La, Pr, Nd) (**1**, Scheme 1) complexes can conveniently be prepared from Na^4Cp and $LnCl_3$ in good yield. Salt incorporation is inhibited if the solvent polarity is reduced by the addition of toluene to the tetrahydrofuran solution during the reaction and if the work-up procedure is performed in *n*-pentane or toluene as solvent.[25] A similar procedure has

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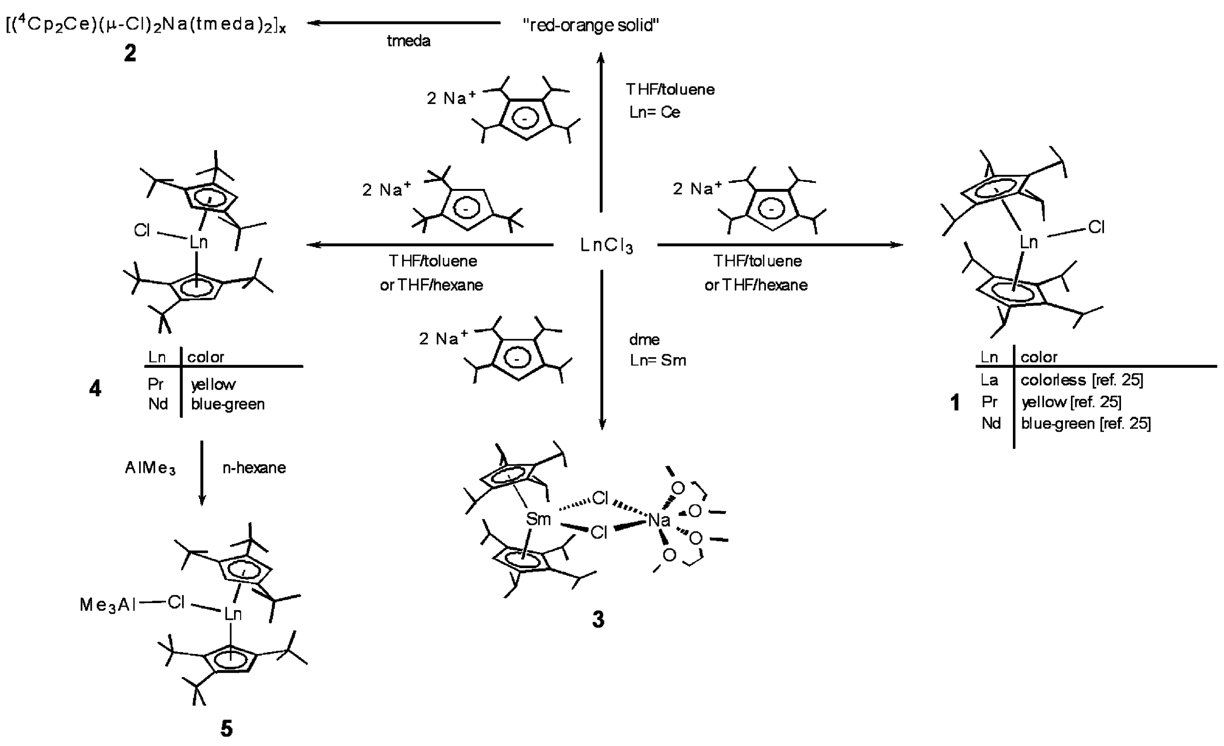

Scheme 1

recently been reported for the synthesis of [Cp′$_2$CeOTf] (Cp′ = η^5-1,2,4-(Me$_3$C)$_3$C$_5$H$_2$) from Ce(OTf)$_3$ and MgCp′$_2$.[12] The extension and the limitations of salt metathesis for the generation of base-free lanthanide halo complexes with bulky alkylcyclopentadienides are described.

Reactivity of LnCl$_3$ salts

^{4}Cp$_2$LnCl. Although the outlined procedure works very well for the early lanthanides lanthanum, praseodymium and neodymium,[25] it proved to be unsuccessful with cerium, samarium and the late lanthanides. With decreasing ionic radius while approaching the late lanthanides a minimum size requirement to form chlorobis(tetraisopropylcyclopentadienyl) complexes was to be expected and the samarium trication seems to be the first member of the series that is too small to easily fit into this particular ligand environment. This does not mean that [^{4}Cp$_2$SmCl] will never be made nor can the size argument be used to explain the failure of cerium trichloride to form such a complex with sodium tetraisopropylcyclopentadienide under the conditions reported. In our hands CeCl$_3$ and SmCl$_3$ both yielded only mixtures of compounds from which the base- and salt-free complexes could not be isolated. Only solvent-coordinated sodium chloride adducts crystallized after addition of coordinating solvents like dimethoxyethane (dme) or tetramethylethylenediamine (tmeda) (Scheme 1). LnCl$_3$ derivatives of the late lanthanides (Ln = Tm, Yb, Lu) gave mono(cyclopentadienyl) complexes as the only isolable products (Scheme 2).

The tetrahydrofuran adduct of cerium trichloride, CeCl$_3$(thf)$_{1.5}$, reacts with two equivalents of Na^{4}Cp at ambient temperature to yield a yellow solution. Evaporation of the solvent and repeated toluene extraction gives a red-orange, solid mixture of compounds. But crystallization from a saturated tmeda solution gives very air sensitive, yellow crystals of [(^{4}Cp$_2$Ce)(μ-Cl)$_2$Na(tmeda)$_2$]$_\infty$ (**2-Ce**).[29] **2-Ce** is only moderately soluble in coordinating solvents, in which it forms yellow solutions, less soluble in aromatic solvents and nearly insoluble in aliphatic hydrocarbons to form orange-red solutions. Due to the low solubility in C$_6$D$_6$ and the air sensitivity the ^{1}H NMR spectra were uninformative. EI mass spectra show the [^{4}Cp$_2$CeCl]$^+$ fragment as the highest mass peak with low intensity. The origin of the poor solubility can be traced to the crystal structure of **2-Ce** (Table 1): the [^{4}Cp$_2$CeCl]-centers are bridged by [NaCl(tmeda)$_2$] units to form zigzag chains with a Cl–Ce–Cl angle of 92.68(4)°. The Ce–Cl distances (2.7719(9)/2.7720(9) Å) are smaller than the Na–Cl distance of 3.014(3) Å. The two ^{4}Cp rings are planar with a Cp(centroid)–Ce–Cp(centroid) angle of 137°, which is close to the value of 136° found in [Cp*$_2$Ce(μ-Cl)$_2$Li(OEt$_2$)$_2$].[30] To the best of our knowledge this structural motif of a one-dimensional zigzag chain with bridging [NaCl(tmeda)$_2$] units has not been observed in lanthanide chemistry before (Fig. 1a and b).

The reaction of SmCl$_3$(thf)$_2$ with two equivalents of sodium tetraisopropylcyclopentadienide in tetrahydrofuran or a tetrahydrofuran–toluene mixture did not proceed smoothly and a mixture of compounds was obtained. However, in dimethoxy ethane with subsequent solvent evaporation an orange solid was formed, from which [^{4}Cp$_2$SmCl$_2$Na(dme)$_2$] (**3-Sm**) was isolated in good yield. In this respect, samarium behaves quite differently from cerium.[29] **3-Sm** is soluble in toluene or *n*-hexane and does not eliminate the coordinated sodium chloride in these solvents. Single crystals suitable for X-ray diffraction (Table 1) were grown from a saturated

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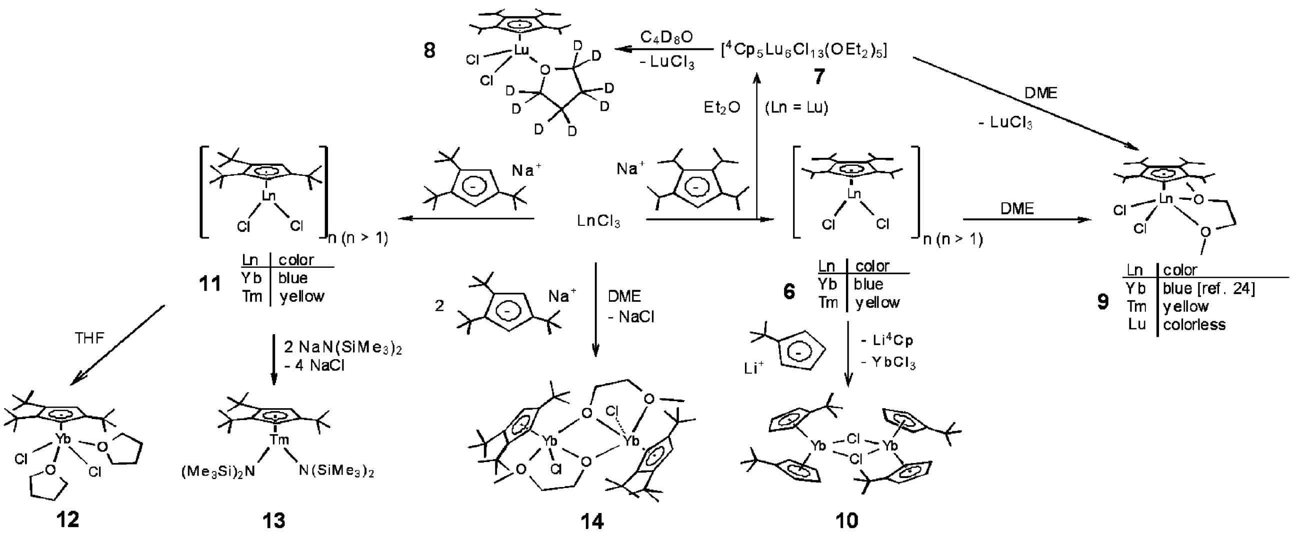

Scheme 2

dimethoxyethane solution at room temperature and show an almost planar $SmCl_2Na$ four-membered ring with a fold angle of 178.3° along the Cl1···Cl2 axis (Fig. 2).

Cp′$_2$LnCl. The sterically more demanding Cp′ ligand was employed for the synthesis of monomeric, base-free [Cp′$_2$CeX] (X = H, F, Cl, I, OTf) compounds.[12,31] This spurred our interest in analogous [Cp′$_2$LnCl] (**5**) complexes along the lanthanide series. The neodymium and praseodymium complexes, **5-Nd** and **5-Pr**, were synthesized from corresponding $LnCl_3$ and two equivalents of NaCp′ in a solvent mixture of tetrahydrofuran–toluene or *n*-hexane over a period of several days and the extraction of the product was carried out with apolar solvents (Scheme 1). Interestingly, only traces of [Cp′$_2$LaCl] were obtained from $LaCl_3$ under similar conditions. **5-Nd** and **5-Pr** crystallize from toluene or *n*-hexane to yield blue-green (**5-Nd**) and yellow crystals (**5-Pr**), which melt without decomposition at 180–181 °C and 189–192 °C, respectively. Both molecules give molecular ions in their EI mass spectra and **5-Nd** sublimes at 140 °C in a glass tube at 10^{-2} mbar. They are readily soluble in ethers (THF, Et_2O), less soluble in aromatic hydrocarbons and moderately soluble in aliphatic solvents (such as *n*-pentane and *n*-hexane). The ^1H NMR spectra of **5-Nd/5-Pr** show paramagnetic chemical shifts corresponding to the two types of Me_3C groups $-5.4/-7.9$ and $-18.3/-35.1$ ppm in a 36 : 18 intensity ratio, and a single Cp′ ring CH resonance at -9.0 and -7.9 ppm, respectively. This pattern is consistent with metallocenes that have idealized C_{2v} symmetry in solution. They are most likely monomeric in the solid state like the closely related **1-Nd**, which was characterized by an X-ray crystal structure.[25] Unfortunately, no single crystals of **5** suitable for X-ray crystallography were obtained under various conditions (neither by sublimation nor crystallization from solution). Similar problems have been encountered with [Cp′$_2$M] (M = Ca, Sr, Ba, Yb, Sm), whose almost spherical molecules produce crystals which suffer from poor ordering. An additional ligand (THF or xylyl isocyanide) helped to improve ordering of the molecules within the crystal and enhanced the quality of diffraction data.[26]

From titanium chemistry it is known that [Cp_2TiCl_2] does react with an excess of $AlMe_3$ to yield the μ-methylene compound [$Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$].[32] A $Nd(\mu\text{-}R)(\mu\text{-}Cl)AlR_2$ structural motif has been mentioned in the literature as a possible active center in Nd-based polymerization.[33] For an analogous reaction of [$(C_5Me_5)_2YbCl_2Na(OEt_2)$] with $AlMe_3$ the formation of a 1 : 2 adduct has been observed and its stoichiometry has been confirmed by ^1H NMR and elemental analysis.[34] Its structure is thought to be analogous to [$(C_5Me_5)_2Yb(ER)(AlMe_3)_2$]$_2$ (ER = SPh, SePh, SC_6H_4-*p*-Me).[35] However, **5-Nd** reacts with an excess of $AlMe_3$ in *n*-hexane to form a light green solution from which grass-green single crystals of the $AlMe_3$ adduct [Cp′$_2$NdCl($AlMe_3$)] (**6-Nd**) can be isolated. The 1 : 1 stoichiometry is established by ^1H NMR spectroscopy, elemental analysis and X-ray crystallography (Table 1). In the ^1H NMR spectrum of **6-Nd** two broad resonances corresponding to the CMe_3 groups at -6.1 and -17.5 ppm (ratio 36 : 18), one signal at -4.4 ppm for the $AlMe_3$ group and a ring proton signal at -9.8 ppm are observed. Trimethylaluminium is loosely coordinated to the [Cp′$_2$NdCl]-fragment and is exchanging rapidly on the NMR time scale, which has been demonstrated by addition of free $AlMe_3$ to an NMR sample. The trimethylaluminium proton signal was shifted to the resonance frequency of the free Lewis acid at -0.4 ppm. The EI mass spectrum shows the [M–$AlMe_3$]$^+$ fragment as the highest mass peak, besides smaller Nd-containing fragments and $AlMe_3$. The crystal structure confirms that the [Cp′$_2$NdCl] acts as a Lewis base coordinating to the hard Lewis acid, $AlMe_3$, to form a simple 1 : 1 adduct (Fig. 3). The averaged Nd–C distances are 2.759(6) Å and the two ring planes form an angle of 147°, which is significantly larger than in the [$^4Cp_2NdCl$] complex with 134°.[25] This reflects the enhanced steric bulk of the Cp′ ligand compared to its ^{4}Cp analogue. In agreement with a weak interaction the Nd–Cl bond distance of 2.7106(17) Å is nearly unperturbed upon coordination to $AlMe_3$ compared to 2.713(4) Å in [$^4Cp_2NdCl$].[25] The Al–Cl bond is 2.403(2) Å. While the database available for this kind of adducts is limited, it can be compared to 2.35 Å in {[(dibenzo-

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Table 1 X-Ray crystal structure determination of **2-Ce**, **3-Sm**, **6-Nd**, **9-Tm**, **12-Yb**, **14**, **15-Tm**

Complex	**2-Ce**	**3-Sm**	**6-Nd**	**9-Tm**	**12-Yb**	**14**	**15-Tm**
Formula	$C_{46}H_{90}CeCl_2N_2Na$	$C_{42}H_{78}Cl_2NaO_4Sm$	$C_{37}H_{67}AlClNd$	$C_{21}H_{39}Cl_2O_2Tm$	$C_{25}H_{45}Cl_2O_2Yb$	$C_{40}H_{72}Cl_2O_4Yb_2$	$C_{34}H_{58}ITm$
FW/g mol^{-1}	933.24	891.28	718.58	563.35	621.55	1033.96	762.63
Crystal size/mm	0.59 × 0.48 × 0.35	0.55 × 0.32 × 0.18	0.52 × 0.48 × 0.24	0.32 × 0.23 × 0.12	0.35 × 0.25 × 0.22	0.56 × 0.44 × 0.36	0.32 × 0.27 × 0.07
Space group	*I*4(1)/*a*	*P*2(1)/*n*	*Pbca*	*P*2(1)/*c*	*P*2(1)/*c*	$R\bar{3}$	*P*2(1)/*n*
Lattice parameters							
a/Å	18.7950(9)	12.6251(13)	12.6235(7)	8.8947(6)	13.2826(8)	16.2836(11)	11.7891(6)
b/Å	18.7950(9)	15.9950(13)	18.0143(10)	13.8338(7)	11.7557(5)	16.2836(11)	15.4829(8)
c/Å	29.9286(19)	24.079(4)	35.025(3)	10.3037(8)	34.576(3)	16.2836(11)	18.5865(10)
α/°	90.00	90.00	90.00	90.00	90.00	109.604(7)	90.00
β/°	90.00	100.451(16)	90.00	105.603(8)	97.344(8)	109.604(7)	95.586(6)
γ/°	90.00	90.00	90.00	90.00	90.00	109.604(7)	90.00
V/Å^3	10572.3(10)	4781.8(10)	7964.9(9)	1221.12(14)	5354.6(6)	3307.3(4)	3376.5(3)
Z	8	4	8	2	8	3	4
T/K	293(2)	293(2)	293(2)	293(2)	173(2)	293(2)	193(2)
D_{calc}/g cm^{-3}	1.173	1.238	1.198	1.532	1.542	1.557	1.500
μ/cm^{-1}	10.02	13.83	14.14	38.63	37.11	43.71	35.61
Transmission factors	0.573–0.693	0.506–0.813	0.53052–0.72046	0.364–0.717	0.3567–0.4957	0.2216–0.3909	0.3648–0.7717
Theta limits (°)	2.72–25.68	2.80–25.68	2.83–24.08	2.69–25.68	2.32–28.07	3.06–25.68	2.63–26.73
Total reflections	70 575	45 300	56 112	17 167	50 981	46 593	36 088
Unique reflections	5027	8813	6231	4553	12 895	4177	7156
Structure solution	Direct methods	Direct methods	Direct methods	Direct methods	Direct methods	Direct methods	Direct methods
Program used	SIR97	SIR97	SHELXS-97		SHELXS-97	SHELXS-97	SHELXS-97
Refinement	SHELXL97	SHELXL-97	SHELXL-97		SHELXL-97	SHELXL-97	SHELXL-97
Data/Restraints/Parameters	3416/7/282	5204/0/471	4141/0/382	3573/1/245	10137/0/559	3674/0/227	5553/0/341
$R1$	0.0333 ($I > 2\sigma(I)$)	0.0373 ($I > 2\sigma(I)$)	0.0412 ($I > 2\sigma(I)$)	0.0367 ($I > 2\sigma(I)$)	0.0400 ($I > 2\sigma(I)$)	0.0411 ($I > 2\sigma(I)$)	0.0244 ($I > 2\sigma(I)$)
$wR2$ (all data)	0.0798	0.0735	0.1068	0.0745	0.0825	0.1048	0.0502
GooF (all data)	0.914	0.820	1.038	0.901	0.984	1.041	0.885
Max./min difference peak/e Å^{-3}	−0.284–0.333	−0.444–0.498	−0.464–0.580	−0.823–1.243	−1.359–1.592	−0.466–0.579	−1.008–0.091

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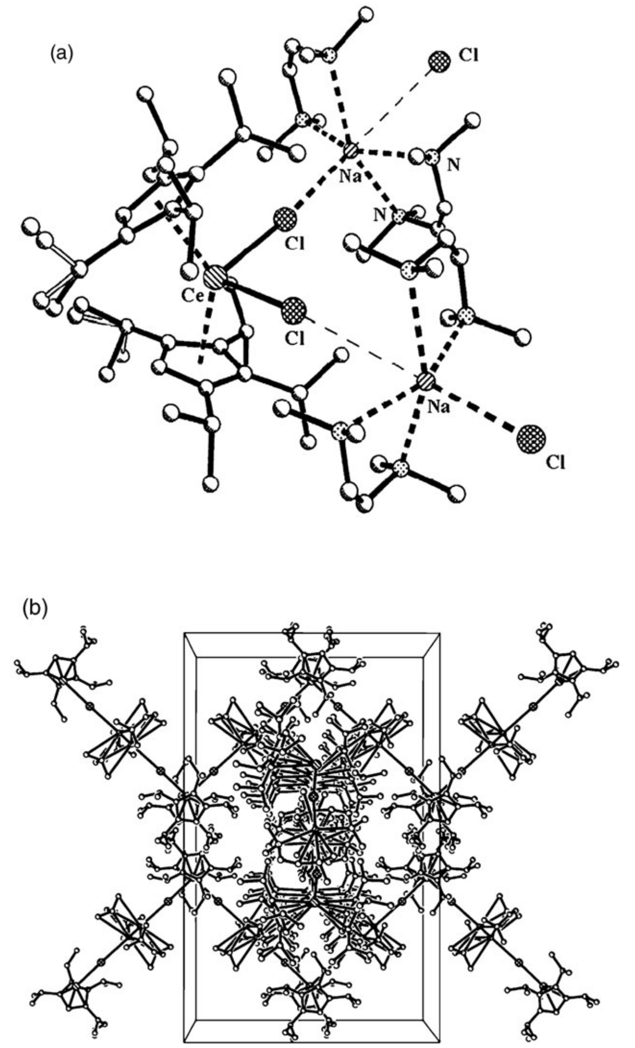

Fig. 1 (a) Ball and stick diagram of **2-Ce**. (b) Structure of the one-dimensional chain of **2-Ce** running parallel to the *c*-axis.†

18-crown-6)K][Me$_3$Al–Cl–AlMe$_3$]}[36] and well as 2.3482(16) and 2.3130(12) Å in {[2,6-(i-Pr)PhN=C(Me)]$_2$(C$_5$H$_3$N)}Cr(μ-ClAlMe$_3$)$_2$(toluene).[37] Two very short contacts to the methyl groups of the ring substituents C44 and C63 of 3.15 and 3.33 Å stabilize the central atom with its low coordination number. Similar contacts have been observed in [^{4}Cp$_2$NdCl][25] and in 1,1′,3,3′-tetra-*tert*-butylytterbocene.[38]

Cp^{x}LnCl$_2$ (Cp^x = ^{4}Cp, Cp′). In the case of the late and smaller lanthanides, such as thulium, ytterbium and lutetium we have not been able to introduce more than one bulky alkylcyclopentadienyl ligand under all conditions examined and regardless of the sodium cyclopentadienide to lanthanide trichloride ratio (1 : 1 or 2 : 1) (Scheme 2). This contrasts with the reactivity of the also sterically encumbered pentamethylcyclopentadienyl ligand.[39]

The reaction of LnCl$_3$ (Ln = Tm, Yb or Lu) in tetrahydrofuran with one equivalent of sodium tri-*tert*-butylcyclopentadienide or tetraisopropylcyclopentadienide proceeds smoothly within 1–3 days at ambient temperature to afford the monosubstitution products **6**[24] and **11** after extraction with petroleum ether or a 3 : 1 mixture of diethyl ether and

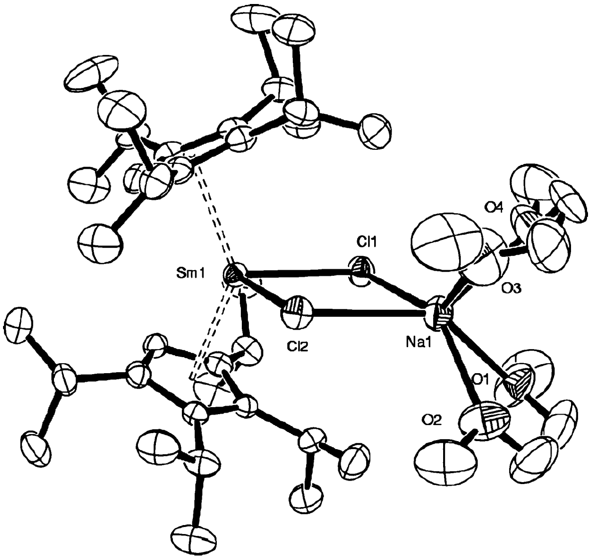

Fig. 2 ORTEP diagram of **3-Sm** with 30% thermal ellipsoids. Selected bond distances [Å] and angles [°]: Sm1–Cl1 2.6873(14), Sm1–Cl2 2.6827(14), Na1–Cl1 2.840(3), Na1–Cl2 2.853(3), Cl1–Sm1–Cl2 84.45(4), Sm1–Cl1–Na1 98.53(6), Sm1–Cl2–Na1 98.31(6), Cl1–Na1–Cl2 78.69(5), ^{4}Cp$_{\text{centroid}}$–Sm1 2.52, ^{4}Cp$_{\text{centroid}}$–Sm1–^{4}Cp$_{\text{centroid}}$ 137°.

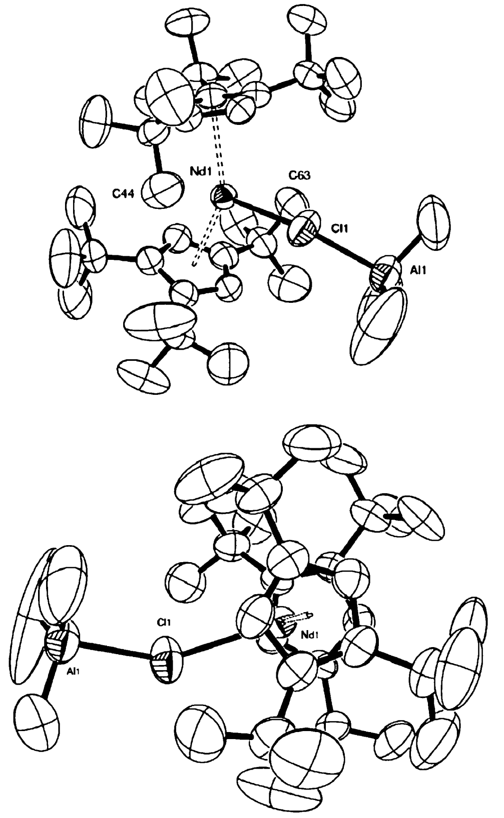

Fig. 3 ORTEP diagrams of **6-Nd** with 50% thermal ellipsoids.

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† CCDC reference numbers 604031–604036 and 604428. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603701a

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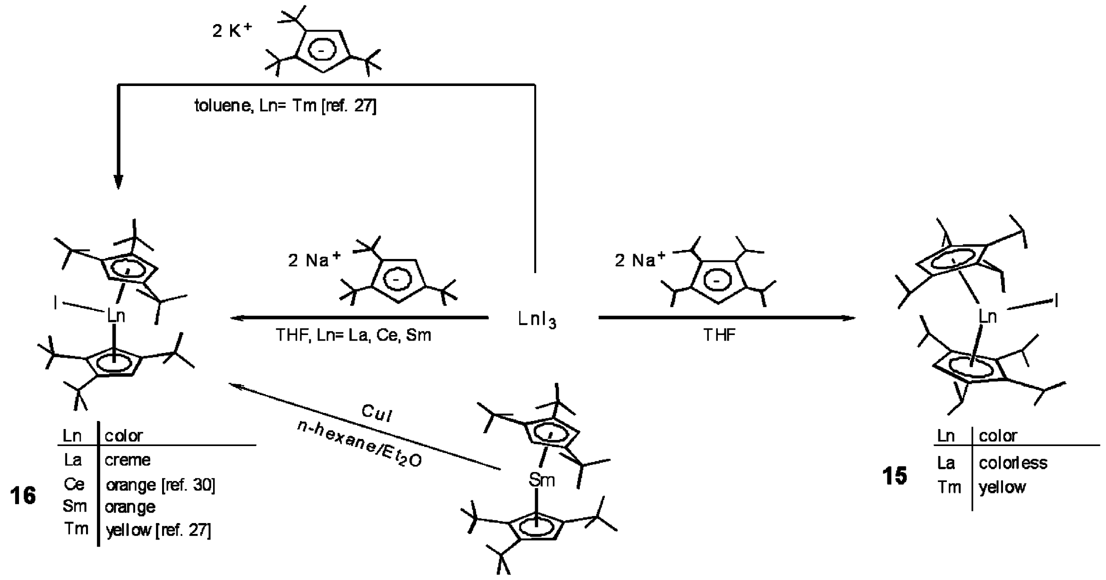

Scheme 3

n-pentane in good yield. Compounds **6** and **11** are moderately soluble in apolar solvents (such as pentane or petroleum ether) from which they are obtained as analytically pure powders which precluded X-ray structure analysis. Although they are soluble in benzene, their ^{1}H NMR spectra obtained in C_6D_6 were rather complicated and this behavior might be due to dynamic processes or an oligomeric structure in solution. No metal-containing ions are detected in the EI-mass spectra of compound **6-Tm/Yb**. However, complexes **6** and **11** have been characterized by follow-up reactions (Scheme 2).

6-Tm readily adds dimethoxyethane to form the bright yellow, monomeric half sandwich complex [^{4}CpTmCl$_2$(dme)] (**9-Tm**) (Fig. 4), whose ytterbium analogue [^{4}CpYbCl$_2$(dme)] (**9-Yb**) is dark blue.[24] Both compounds were obtained as single crystals suitable for X-ray diffraction (Table 1). **9-Tm** displays a four-legged piano-stool geometry with a 2.35 Å distance between Tm and the ^{4}Cp ring plane, one O donor atom situated underneath the only ring-CH for steric reasons, the other O donor atom between two isopropyl groups rotated away from each other, an almost rectangular Cl–Tm–Cl (92.1°) moiety, and an acute DME bite angle of 66.6°.

Interestingly, when pure diethyl ether is used for product extraction after the reaction of LuCl$_3$ with one equivalent of Na^{4}Cp in tetrahydrofuran, the lutetium complex **7** was obtained in low yield as colorless crystals, which did not produce diffraction data of good quality, but could be characterized as a hexanuclear lutetium complex containing five [^{4}CpLuCl$_2$] fragments, one LuCl$_3$ moiety and coordinated solvent, [^{4}Cp$_5$Lu$_6$Cl$_{13}$(OEt$_2$)$_5$] (**7-Lu**) (Fig. 5). According to the diffraction data the atom inside the cavity is a chloro ligand (compare for example the interstitial chloro ligand in the hexanuclear anion of [(CpYb)$_3$(μ^3-Cl)$_2$(μ-Cl)$_3$(THF)$_3$]$^+$ [(CpYb)$_6$(μ^6-Cl)(μ-Cl)$_{12}$]$^-\cdot$2C$_7$H$_8$,[40] but the electron density maxima corresponding to the outer ligand of Lu6 could not be assigned to a specific donor molecule.

This complex is soluble in octadeuterotetrahydrofuran with formation of the mononuclear donor adduct [^{4}CpLuCl$_2$(OC$_4$D$_8$)$_x$] (**8-Lu**), which was characterized by NMR spectroscopy. **7-Lu** also adds dimethoxethane to yield colorless plates of **9-Lu** losing coordinated solvent more easily than **9-Tm** or **9-Yb**. The identity of the compounds was established by ^{1}H NMR spectroscopy and elemental analysis. **9-Lu** shows one set of resonances for the tetraisopropylcyclopentadienyl ring with its diastereotopic CHMe$_2$ groups (*cf.* ref. 41 for the signal pattern of C$_5$H(CHMe$_2$)$_4$).

6-Tm/Yb do not react with a second equivalent of Na^{4}Cp in tetrahydrofuran at room temperature and the starting materials are recovered. In an attempt to synthesize a mixed-ligand bis(cyclopentadienyl) complex, the reaction of **6-Yb** with less sterically demanding Li(C$_5$H$_4$CMe$_3$) has been investigated. From this reaction mixture in Et$_2$O the known dimeric [(Me$_3$CC$_5$H$_4$)$_2$Yb(μ-Cl)]$_2$ (**10-Yb**) is obtained in moderate yield as the only isolable product (Scheme 3).[42] The identity of **10-Yb** was established by ^{1}H NMR spectroscopy and X-ray

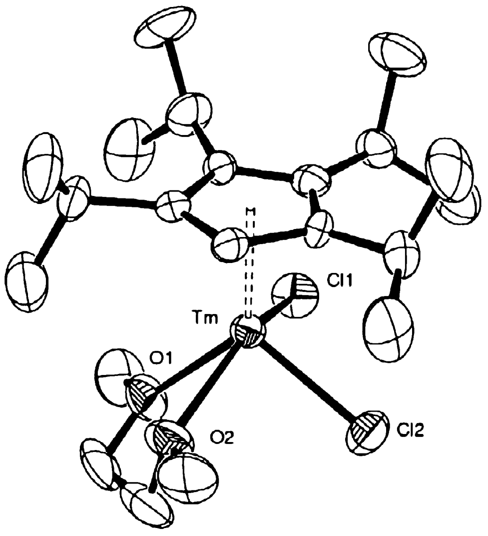

Fig. 4 ORTEP diagram of **9-Tm** (50% probability ellipsoids).

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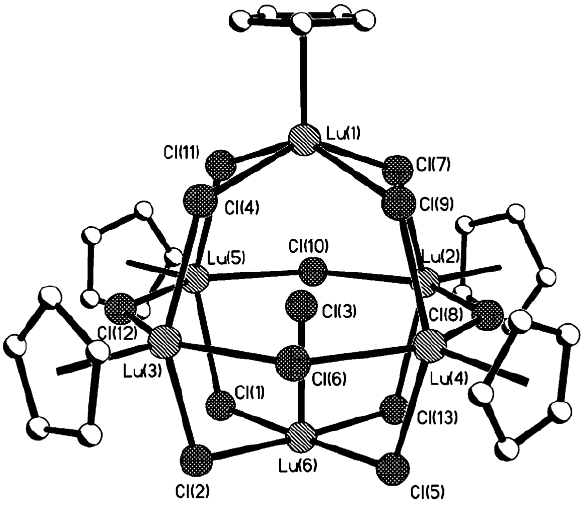

Fig. 5 Ball and stick diagram of **7-Lu**. $CHMe_2$ groups have been omitted for clarity.

crystal structure determination. Obviously, one chloro and one tetraisopropylcyclopentadienyl ligand have been replaced by two *tert*-butylcyclopentadienide anions. The ^{4}Cp ligand acting as a leaving group in organolanthanide chemistry has been observed before under similar conditions.[25]

11-Yb readily adds tetrahydrofuran to form the blue bis (tetrahydrofuran) adduct **12-Yb** as deep blue cubes (for details regarding the crystal structure determination see Table 1), which lose coordinated tetrahydrofuran at 80–150 °C and turn light blue, but do not melt upon heating to 240 °C. The coordination sphere around the Yb center (Fig. 6) can be described as a four-legged piano stool geometry. Due to the steric bulk of the Cp′ ring the two tetrahydrofuran ligands are pushed towards the chloro ligands, Cl1 and Cl2, resulting in an O1–Yb1–O2 angle of 147.65(10)°. The Yb–Cp′$_{centroid}$ distance is 2.34 Å, and from the structural point of view, complex **12-Yb** is closely related to the known [{1,3-$(Me_3C)_2H_2C_4N$}$YbCl_2(thf)_2$].[43]

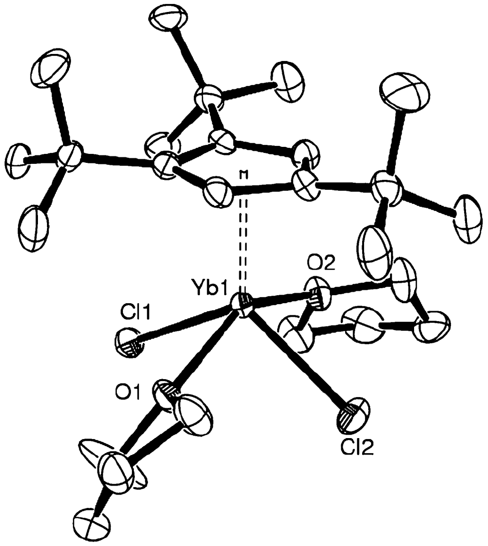

Fig. 6 ORTEP diagram of **12-Yb** (50% probability ellipsoids). Selected bond distances [Å] and angles [°]: Yb1–Cl1 2.5124(9), Yb1–Cl2 2.5409(10), Yb1–O1 2.362(3), Yb1–O2 2.344(3), Yb1–Cp$_{centroid}$ 2.34, O1–Yb1–O2 147.65(10), Cl1–Yb1–Cl2 117.59(3).

11-Tm reacts with two equivalents of Na[$N(SiMe_3)_2$] in toluene to give the light yellow-green thulium bis{bis(trimethylsilyl)amide} complex, [Cp′Tm{$N(SiMe_3)_2$}$_2$] (**13-Tm**), in high yield. The compound is readily soluble in aliphatic hydrocarbons and the ^{1}H NMR spectrum shows four broad resonances at δ 202.6 and 18.8 ppm for the *tert*-butyl groups (intensity ratio 18 : 9), one signal corresponding to 36 protons of four $SiMe_3$ groups at −0.5 ppm and the signal for the two ring protons at −218 ppm. The EI mass spectra show the molecular ion of low intensity and other metal-containing fragments. With respect to the steric bulk of the three anionic ligands and to its solubility a monomeric structure is reasonable, that has been observed in the related [(C_5Me_5)Ce{$N(SiMe_3)_2$}$_2$] complex.[44] Unfortunately, the diffraction data of **13** were not of high quality due to disorder and twinning problems, and the quality of the crystals was not improved by crystallization from different solvents (pentane or toluene), but the location of the heavy atoms agrees with a monomeric structure.

The attempted preparation of [Cp′$_2$YbCl] by the reaction of two equivalents of NaCp′ with ytterbium trichloride has been unsuccessful and from the reaction mixture formed in dimethoxyethane only the alkoxide [Cp′YbCl(μ-OC_2H_4OMe)]$_2$ (**14**) could be isolated in low yield (Scheme 2). The compound is very sparingly soluble in aromatic hydrocarbons and a ^{1}H NMR spectrum was not obtained in C_6D_6. The reluctance of **11-Yb** towards replacement of a second chloro ligand with another bulky alkylcyclopentadienyl ligand obviously leads to solvent cleavage. As an intermediate the solvent complex [Cp′$YbCl_2$(dme)] may be assumed, whose DME ligand is activated by coordination to the Lewis acid Yb^{3+} and can therefore act as alkylating agent. The bridging methoxyethanolate ligand ensues most likely from transfer of a methyl cation to the Cp′ anion yielding the corresponding alkoxide. The X-ray crystal structure of **14** (Table 1) shows a dimer with crystallographically imposed inversion center (Fig. 7).

The alkoxo function of each methoxyethanolate ligand bridges the two Yb centers symmetrically (2.194(3) Å) whereas each metal center is coordinated by one ether function with longer Yb–O distance of 2.362(3) Å. The non-bonding distance between the two metal atoms is 3.59 Å and the distance metal–ring plane is 2.35 Å. Ether cleavage reactions in lanthanide chemistry have been well documented for tetrahydrofuran,[45–49] but are rare for dimethoxyethane where the formation of methoxide bridges is common,[50] and only recently an example of methoxyethanolate formation has been observed.[51]

Reactivity of LnI_3 salts

$^4Cp_2LnI$. Since it was impossible to introduce a second bulky alkylcyclopentadienyl ligand into compounds **6** or **11** in tetrahydrofuran or dimethoxyethane at ambient temperature, the question arises whether this problem is due to steric effects or to leaving group properties of the lanthanide halides. Experimentally, it was shown that the Ln–I bond is roughly

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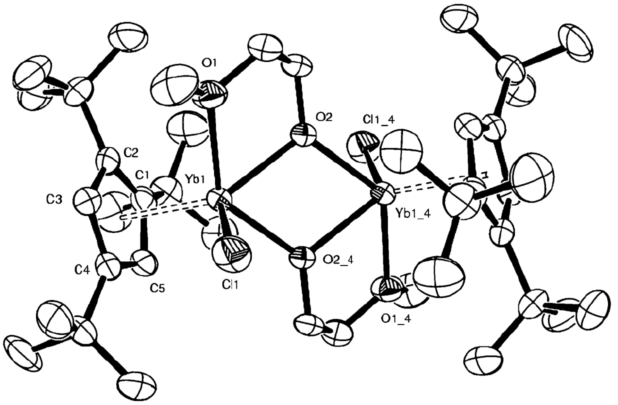

Fig. 7 ORTEP diagram of **14** (50% probability ellipsoids). Atom labels bearing _4 are symmetry related positions. Selected bond distances [Å] and angles [°]: Yb1–O2 2.198(3), Yb1–O2_4 2.191(3), Yb1–O1 2.362(3), Yb1–Cl1 2.5145(13), Yb1···Yb1_4 3.5874(8), O2–Yb1_4 2.191(3), Yb1–$Cp_{centroid}$ 2.36, Yb1–O1–Yb1_4 109.64(12), O1–Yb1–O1_2 70.36(12).

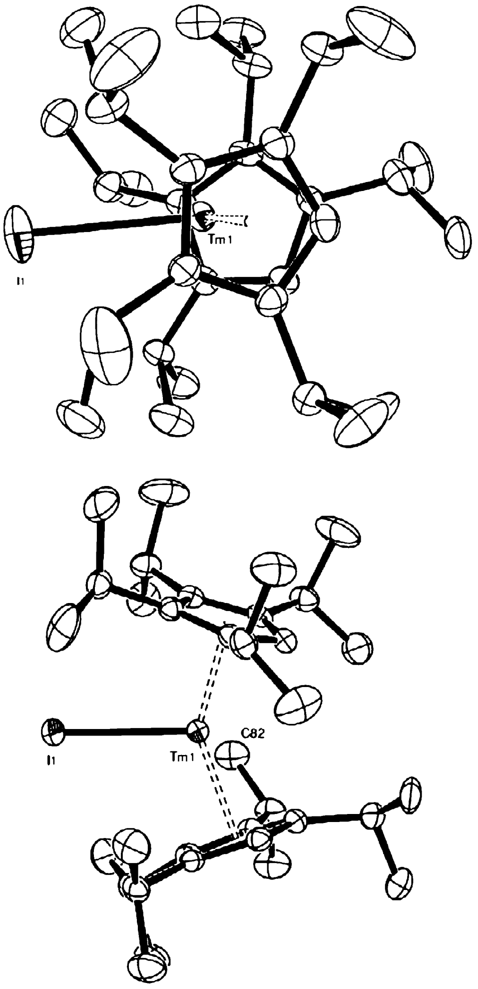

Fig. 8 ORTEP diagram of **15-Tm** (50% probability ellipsoids).

30% weaker than the Ln–Cl bond,[52] and recently the successful synthesis of [Cp'_2TmI] (**16-Tm**) from KCp′ and TmI_3 in boiling toluene has been reported.[27]

Two equivalents of sodium tetraisopropylcyclopentadienide react with TmI_3 in tetrahydrofuran at ambient temperature and after extraction with *n*-hexane a yellow-brown solid is obtained, from which **15-Tm** is isolated by sublimation in oil-pump vacuum at 80–90 °C as yellow crystals (Scheme 3). **15-Tm** is another example of a solvent free bis(cyclopentadienyl) halo complex [$^4Cp_2LnX$], of which the neodymium complex [$^4Cp_2LnCl$] was characterized by X-ray diffraction.[25] The crystal structure of **15-Tm** (Table 1) has some similarities to the [$^4Cp_2NdCl$] complex (Fig. 8): the Tm–C distances are within a narrow range 2.57 to 2.68 Å and the $Cp_{centroid}$–Tm–$Cp_{centroid}$ angle is 144°, which is smaller than in the sterically even more encumbered [Cp'_2TmI] complex of 148°.[27] A short contact between the Tm center and a methyl group of the ring substituents (Tm···C82 distance of 3.43 Å) serves to increase the low coordination number of the central atom. Seven of eight isopropyl α-carbon atoms are bent out of the ring plane away from the metal center by 0.06–0.42 Å, but the α-carbon atom C81 carrying the methyl C82 atom is bent towards the central atom by 0.12 Å. The isopropyl substituents at C8 of the cyclopentadienyl ring in **15-Tm** seem to adopt the role of a side chain capable of an additional stabilizing interaction. Similar intramolecular Ln···CH_3 interactions have been found for 1,1′,3,3′-tetra-*tert*-butylytterbocene.[38]

The Tm–I distance of 2.8866(3) Å is close to the value of 2.8999(5) Å observed in the related [Cp'_2TmI] complex.[27] More interesting is the $CHMe_2$ orientation in the ^4Cp ligand that has a rich array of possible conformations. Only three of them (**a**, **e**, and **f**) do not posses destabilizing close methyl–methyl contacts (Fig. 9).[53] Sitzmann *et al.* observed in [$^4Cp_2NdCl_2Na(OEt_2)$]$_2$ and [$^4Cp_2NdCl$] conformer **f** for both ^4Cp rings,[24] and in [$^4Cp_2LnCl\{Na(N(SiMe_3)_2\}$]$_2$ (Ln = La, Nd, Pr) **a** and **f**.[25] However, in [$^4Cp_2TmI$] conformer **a** is accompanied by the energetically unfavorable conformation **c**. To the best of our knowledge this is the first time that conformation **c** has ever been observed in any ^4Cp compound. Most likely the steric bulk of the iodide anion is the reason for this unexpected conformation. Not only are the four isopropyl groups adjacent to the iodo ligand on the open front of the bent metallocene forced to bend away from the bulky halide, but congestion is also severe in the rear part of the molecule, where one isopropyl group has to rotate into a rather unfamiliar position. This finding may be compared to the attempted synthesis of [$^4Cp_2BiCl$], where obviously the eighth isopropyl substituent created so much strain that the desired molecule was not formed, but only the propene elimination product [$^4Cp^3CpBiCl$] could be isolated and isotope labeling experiments have been used to demonstrate that the second incoming tetraisopropylcyclopentadienyl ligand eliminates propene.[54]

The reactivity pattern observed upon introduction of alkylcyclopentadienyl anions into halides of the lanthanides suggests that a weak Ln–X bond for facile substitution is increasingly important in the case of bulky alkylcyclopentadienyl ligands. A controlled synthesis of mono- and dicyclopentadienyl complexes of the late and therefore smaller lanthanides can be easily achieved by the choice of an appropriate leaving group.

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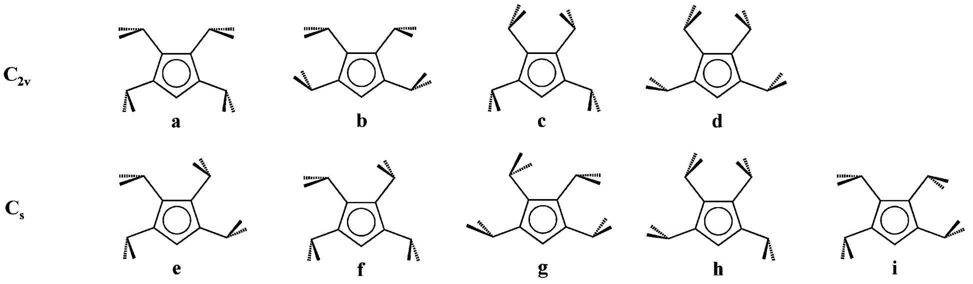

Fig. 9 Possible conformers of the ^{4}Cp ligand.

To anchor this study with respect to early lanthanides the reactivity of $LaI_3 \cdot 3.75THF$ towards two equivalents of sodium tetraisopropylcyclopentadienide in tetrahydrofuran has been investigated. After *n*-hexane extraction [$^4Cp_2LaI$] (**15-La**) is obtained in 66% yield as an ivory powder that is very soluble in apolar solvents such as *n*-hexane, melts with decomposition at 98 °C, and gives a molecular ion of low intensity in the EI-MS spectrum. NMR spectra of [$^4Cp_2LaI$] are well resolved and show one set of resonances for the tetraisopropylcyclopentadienyl ring. The ^{1}H NMR spectra of [$^4Cp_2LaI$] (**15-La**) and [$^4Cp_2LaCl$] (**1-La**) are nearly identical, except that the resonance of the ring proton is shifted low-field by 0.13 ppm upon iodide *vs*. chloride substitution. This trend is also reflected in the ^{13}C NMR spectrum.

Cp'_2LnI. LaI_3 is also a suitable starting material for the synthesis of [Cp'_2LaI] (**16-La**), whereas $LaCl_3$ only gives traces of [Cp'_2LaCl]. $LaI_3 \cdot 3.75THF$ reacts with two equivalents of sodium tri-*tert*-butylcyclopentadienide in tetrahydrofuran to give the ivory **16-La** in moderate yield. **16-La** is very soluble in apolar solvents such as *n*-hexane, melts with decomposition at 93 °C, and shows a molecular ion with low intensity in the EI-MS spectrum. The room temperature ^{1}H NMR spectra of **16-La** show the two types of Me_3C groups in a 36 : 18 intensity ratio, but no Cp′ ring CH resonance. This pattern can be explained with rotation about the pseudo C_5 axes of the Cp rings so that the complex idealized C_{2v} symmetry in solution. However due to the steric bulk of the Cp′ ring and the iodo ligand the ring rotation might be restricted as indicated by the absence of the Cp′ ring CH resonance. At 370 K in C_7D_8 the Cp′ ring CH resonance is recorded at 6.64 ppm in the correct intensity ratio. Lowering the temperature of a C_7D_8 solution results in decoalescence of the Me_3C resonance of area 36, so that at low temperature the Me_3C resonances appear as three separate resonances of equal intensity. The Cp′ CH resonances however, do not show decoalescence at temperatures as low as 193 K. This behavior is consistent with slowing the rotation or oscillation of the cyclopentadienyl rings and generating a molecule with C_2 (eclipsed) cyclopentadienyl rings. Based on the coalescence temperature of 219 K, $\Delta G^{\ddagger}$ for this equal population two site exchange process is 45 ± 1 kJ mol^{-1}.[55] This type of fluxional behavior has been observed in cerium and uranium metallocene complexes with the same cyclopentadienyl ligand.[12,13,56,57] Interestingly, in ref. 27 failure of the synthesis of **16-Tm** in tetrahydrofuran was observed, but a clean procedure was developed using boiling toluene.

Synthesis of [Cp'_2LnI] complexes *via* oxidation of Ln(II) compounds. Of the lanthanide series Eu, Sm, Tm and Yb have a divalent oxidation state available. Therefore trivalent lanthanide complexes are accessible by controlled oxidation of a suitable divalent precursor. This methodology has been extensively demonstrated in the case of $(C_5Me_5)_2Sm$[58,59] and $(C_5Me_5)_2Yb(OEt_2)$,[10,60–63] and more recently for [Cp'_2Tm].[27] [Cp'_2Sm] is another interesting starting material for various oxidation reactions,[26] one of which is reported in this paper. It reacts with CuI in diethyl ether to form the dark orange [Cp'_2SmI] (**16-Sm**) in high yield (Scheme 3). This synthesis is superior to the traditional salt metathesis as the only side product is copper, which can be easily removed from the oxidation product. Like its La analogue, **16-Sm** is very soluble in common organic solvents; and it decomposes at 146 °C to form a brown oil. EI mass spectra show the molecular ion with correct isotope pattern, and consistent with this observation the compound can be sublimed at 120 °C at 10^{-2} mbar in a glass tube. Crystals grown by slow sublimation did not produce diffraction data of good quality; however the monomeric nature was established,[64] in contrast to the dimeric [$(\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3)_2Sm(\mu\text{-}I)]_2$.[65] The room temperature ^{1}H NMR spectrum shows three inequivalent CMe_3 and two inequivalent Cp′ CH resonances consistent with a C_2 symmetry in solution and it agrees with an increased rotational barrier due to the smaller ionic radius of Sm(III) compared to La(III).[66]

Conclusions

The introduction of bulky alkylcyclopentadienyl ligands allows a controlled synthesis of mono- and dicyclopentadienyl lanthanide halo complexes as well as oligomeric clusters. The proper choice of solvent, starting materials and reaction conditions determines the formation of alkylcyclopentadienyl lanthanide derivatives as well as the product distribution. The dicyclopentadienyl halo complexes are obtained as their base-free, monomeric representatives exhibiting relatively low sublimation temperatures. The smaller lanthanides (Tm, Yb, Lu) form the mono-ring complexes, if $LnCl_3$ (Ln = Tm, Yb, Lu) is used as starting material. These mono-ring species have been shown to be suitable for synthetic transformations. Although bis(ring) complexes of the late lanthanides are not accessible by the $LnCl_3$ route, they can be prepared as sterically extremely congested species employing LnI_3 as starting materials which was confirmed in the case of TmI_3. This synthetic pathway can also be applied to early lanthanides to yield

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$[Cp'_2LaI]$, whose chloro derivative is not easily accessible from $LaCl_3$. The steric bulk of the two $C_{17}H_{29}^-$ isomers employed as ligands in this study (tetraisopropylcyclopentadienide and 1,2,4-tri-*tert*-butylcyclopentadienide) is quite large in both cases. The tetraisopropylcyclopentadienyl ligand is more flexible due to the different conformations available, which allow for closer contact between two adjacent rings in bent sandwich molecules with two tetraisopropylcyclopentadienyl ligands, compared to the corresponding tri-*tert*-butylcyclopentadienyl derivatives. The conformation with two adjacent isopropyl substituents rotated towards each other found in the respective bis(ring)thulium iodo complex illustrates this behavior, which could be described as "soft bulk", compared to the "hard bulk" of the tri(*tert*-butylcyclopentadienyl ligand. The latter ligand appears to be more bulky mostly because of its larger rigidity.

Experimental

General procedures

All synthetic operations were performed under a dry argon atmosphere using a drybox from MBraun company, Garching, or by using standard Schlenk techniques. Tetrahydrofuran and *n*-hexane were distilled from potassium metal, toluene from sodium metal. NMR spectra were taken on a Bruker DPX 400 NMR spectrometer. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents, which are internal standards, for proton chemical shifts. Mass spectra were taken on a Finnigan MAT 90 mass spectrometer and elemental analyses were performed with Perkin Elmer Elemental Analyzer 240. Tri-*tert*-butylcyclopentadiene,[67,68] sodium tetraisopropylcyclopentadienide,[41] $[CeCl_3(THF)_{1.5}]$,[69] $[SmCl_3(THF)_2]$,[69] $[Cp'_2Sm]$,[26] LnI_3 (Ln = La and Tm)[70] and YbI_2 [71] were prepared as previously reported. Anhydrous trichlorides of praseodymium, neodymium, thulium, ytterbium, and lutetium were purchased from Strem Chemicals and used as received. In some cases the results of the elemental analyses were not satisfactory and the best results from repeated runs were given. The low carbon values are probably a combination of their increased air sensitivity, partial loss of coordinated solvents during sample preparation, and incomplete combustion. The halide content was determined by volumetric precipitation analysis.

Synthesis of $[\{\eta^5\text{-}(Me_2CH)_4C_5H\}_2CeCl_2Na(tmeda)_2]_\infty$ (2-Ce). A solution of sodium tetraisopropylcyclopentadienide (2.28 g, 8.90 mmol) was added to a suspension of $[CeCl_3(THF)_{1.5}]$ (1.42 g, 4.45 mmol) in tetrahydrofuran (50 mL) and the mixture was stirred for 5 h at room temperature, then sonicated for 12 h. Removal of the solvent under dynamic vacuum, extraction with toluene (5 × 10 mL), centrifugation and evaporation of the toluene solvent afforded a light red solid, which was recrystallized from a saturated tetramethyl ethylenediamine solution at room temperature to yield yellow crystals suitable for X-ray diffraction (1.45 g, 1.55 mmol, 35%). The compound was insoluble in pentane and only sparingly soluble in toluene. Mp 125 °C (dec.). Anal. calcd. for $C_{46}H_{90}CeCl_2N_4Na$ (933.26): C, 59.2; H, 9.72; N, 6.00; Cl, 7.60. Found: C, 56.4; H, 9.20; N, 5.67; Cl, 7.16%. The low solubility of the product prevented the acquisition of a ^1H NMR spectrum in C_6D_6.

Synthesis of $[\{\eta^5\text{-}(Me_2CH)_4C_5H\}_2SmCl_2Na(dme)_2]$ (3-Sm). To a suspension of $[SmCl_3(THF)_2]$ (0.80 g, 2.0 mmol) in dimethoxyethane (20 mL) solid sodium tetraisopropylcyclopentadienide (1.03 g, 4 mmol) was added. The reaction mixture was stirred at room temperature for 12 h, then the solvent was removed under dynamic vacuum. The solid residue was extracted with *n*-pentane, insoluble solids were separated by centrifugation. The *n*-pentane solution was concentrated until the deposition of crystalline material was observed and the solution was then placed in a freezer at −20 °C to yield crystalline product (1.05 g, 1.18 mmol, 59%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated dimethoxyethane solution at room temperature. Mp 115 °C (dec.). Anal. calcd. for $C_{42}H_{78}Cl_2NaO_4Sm$ (891.28): C, 56.6; H, 8.82; Cl, 7.96. Found C, 52.5; H, 7.95; Cl, 7.42%.

Synthesis of $[\{\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2\}_2NdCl]$ (4-Nd). A mixture of solid $NdCl_3$ (0.75 g, 3.00 mmol) and sodium tri-*tert*-butylcyclopentadienide (1.54 g, 6.00 mmol) was suspended in a 1 : 1 mixture of toluene and tetrahydrofuran (50 mL) and stirred at room temperature. The color changed to blue-green within a few minutes and the reaction mixture was stirred for 4 d, then the solvents were removed under dynamic vacuum and the dark green residue was extracted with toluene (5 × 10 mL). Centrifugation and evaporation of the intense blue-green extracts to a residual volume of *ca.* 30 mL and crystallization at −20 °C yielded blue-green crystals (1.62 g, 2.50 mmol, 83%), which could be sublimed at 130 °C in a glass tube sealed at 10^{-3} mbar. Mp 180–181 °C (reversible). Anal. calcd. for $C_{34}H_{58}ClNd$ (646.53): C, 63.2; H, 9.04. Found C, 62.8; H, 8.95%. ^1H NMR (400.13 MHz, 298 K, C_6D_6): δ −5.4 (36H, CMe_3, $\nu_{1/2}$ = 135 Hz), −9.0 (4H, ring-H, $\nu_{1/2}$ = 150 Hz), −18.3 (18H, CMe_3, $\nu_{1/2}$ = 100 Hz). MS (70 eV, EI): m/z (%) = 644.9 (12) M^+, 610 (3) $M^+ - Cl$, 411.9 (100) $M^+ - C_5H_2(CMe_3)_3$, 234.1 (26), $HC_5H_2(CMe_3)_3$, 178.1 (54) $NdCl^+$, 57 (99) $CMe_3{}^+$.

Synthesis of $[\{\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2\}_2PrCl]$ (4-Pr). $PrCl_3$ (0.56 g, 2.25 mmol) and sodium tri-*tert*-butylcyclopentadienide (1.16 g, 4.50 mmol) were suspended in a 2 : 5 mixture of *n*-hexane and tetrahydrofuran (50 mL) and stirred at room temperature for 4 d. The yellow solution was separated from a white precipitate by centrifugation, the solvent was removed under dynamic vacuum, and the remaining solid was extracted with toluene (5 × 10 mL). Centrifugation of the intense yellow extracts and evaporation of the solvent gave a yellow powder, which was recrystallized from hexane at −20 °C to yield yellow crystals (1.02 g, 1.59 mmol, 70%). Mp 189–192 °C (reversible). Anal. calcd. for $C_{34}H_{58}ClPr$ (643.20): C, 63.5; H, 9.09. Found C, 63.7; H, 8.95%. ^1H NMR (400.13 MHz, 298 K, C_6D_6): δ −7.9 (40H, CMe_3 and ring-H, $\nu_{1/2}$ = 600 Hz), −35.1 (18H, CMe_3, $\nu_{1/2}$ = 110 Hz). MS (70 eV, EI): m/z (%) = 641.9 (7) M^+, 607 (2) $M^+ - Cl$, 408.9 (100) $M^+ - C_5H_2(CMe_3)_3$, 234.1 (4), $HC_5H_2(CMe_3)_3$, 57 (63) $CMe_3{}^+$.

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Synthesis of $[\{\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2\}_2NdCl(AlMe_3)]$ (5-Nd). A solution of trimethylaluminium (0.20 g, 2.77 mmol) in *n*-hexane (2 mL) was slowly added to a solution of **4-Nd** (0.32 g, 0.50 mmol) in *n*-hexane (10 mL) at room temperature. The color changed from blue-green to light green and the reaction mixture was stirred for 1 day at ambient temperature. Small amounts of insoluble material were removed by centrifugation and the solvent was evaporated to a residual volume of 2 mL. Crystallization readily occurred at room temperature and grass-green single crystals suitable for X-ray diffraction were obtained (0.20 g, 0.28 mmol, 56%), which upon heating to 110 °C decomposed to a green, oily solid. Anal. calcd. for $C_{37}H_{67}AlClNd$ (718.62): C, 61.8; H, 9.40. Found: C, 57.3; H, 8.95%. ^{1}H NMR (400.13 MHz, 298 K, C_6D_6): δ −4.4 (9H, $AlMe_3$ $\nu_{1/2}$ = 350 Hz), −6.1 (36H, CMe_3, $\nu_{1/2}$ = 790 Hz), −9.8 (4H, ring-H, $\nu_{1/2}$ = 200 Hz). −17.5 (18H, CMe_3, $\nu_{1/2}$ = 180 Hz); MS (70 eV, EI): *m*/*z* (%) = 641.9 (5) $M^+ - AlMe_3$, 607 (3) $M^+ - AlMe_3 - Cl$, 408.9 (100) $M^+ - AlMe_3 - C_5H_2(CMe_3)_3$, 234.1 (3), $HC_5H_2(CMe_3)_3$, 72.0 (7) $AlMe_3^+$, 57 (71) CMe_3^+.

Synthesis of $[\{\eta^5\text{-}(Me_2CH)_4C_5H\}TmCl_2]$ (6-Tm). A solution of sodium tetraisopropylcyclopentadienide (3.08 g, 12.0 mmol) in tetrahydrofuran (15 mL) was slowly added to a suspension of $TmCl_3$ (3.25 g, 11.8 mmol) in tetrahydrofuran (10 mL). The mixture turned yellow-green immediately and was stirred for 2 d at ambient temperature, then evaporated to dryness under dynamic vacuum and the light-yellow residue was extracted with a solvent mixture of diethyl ether and pentane (3 : 1, 3 × 10 mL). Centrifugation of the combined extracts and evaporation of the solution yielded a light-yellow, microcrystalline powder (4.59 g, 9.67 mmol, 82%). Anal. calcd. for $C_{17}H_{29}Cl_2Tm$ (473.27): C, 43.2; H, 6.18. Found C, 44.7; H, 6.19%.

Synthesis of $[\{\eta^5\text{-}(Me_2CH)_4C_5H\}_5Lu_6Cl_{13}(OEt_2)]$ (7-Lu). To a magnetically stirred suspension of $LuCl_3$ (1.09 g, 3.8 mmol) in tetrahydrofuran (50 mL) a solution of sodium tetraisopropylcyclopentadienide (1.05 g, 4.1 mmol) in tetrahydrofuran (30 mL) was added slowly. During the addition the suspended solid dissolved and the clear solution was heated to reflux for 3 h. A white precipitate formed and the suspension was stirred for 12 h at room temperature. The solvent was evaporated and the solid residue was stirred with diethyl ether (40 mL) for 12 h. Centrifugation of the extract, extraction of the solid residue with diethyl ether (2 × 10 mL), followed by centrifugation and concentration of the combined extracts under dynamic vacuum gave a concentrated diethyl ether solution, which was allowed to slowly evaporate in a glove box equipped with a charcoal filter to afford colorless crystals of the Lu_6 complex containing five equivalents of coordinated diethyl ether (0.36 g, 0.12 mmol, 19%). Anal. calcd. for $C_{105}H_{195}Cl_{13}Lu_6O_5$ (3024.37): C, 41.8; H, 6.50. Found: C, 40.9; H, 6.44%. In d_8-THF this complex dissolved to form a solution of $[(Me_2CH)_4C_5H)LuCl_2(OC_4D_8)_x]$ **(8-Lu)**; ^{1}H NMR (400.13 MHz, 298 K, d_8-THF): δ 5.81 (s, 1H, ring-H), 3.28 (m, 2H, C*H*Me$_2$), 3.08 (m, 2H, C*H*Me$_2$), 1.54 (d, 6H, C*H*$_3$, *J* = 7.2 Hz), 1.35 (d, 6H, C*H*$_3$, *J* = 6.9 Hz), 1.18 (d, 6H, C*H*$_3$, *J* = 6.9 Hz), 1.05 (d, 6H, C*H*$_3$, *J* not determined because of superimposition with the triplet signal of diethyl ether present in the solution). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, d_8-THF): δ 134.3 (2C, *C*CHMe$_2$), 129.1 (2C, *C*CHMe$_2$), 104.8 (1C, ring-*C*H), 28.4 (2C, *C*HMe$_2$), 28.3 (2C, *C*H$_3$), 27.9 (2C, *C*HMe$_2$), 26.0 (2C, *C*H$_3$), 23.7 (2C, *C*H$_3$), 23.4 (2C, *C*H$_3$); diethyl ether signals: 66.3 (O*C*H$_2$), 15.8 (OCH$_2$*C*H$_3$).

Synthesis of $[\{\eta^5\text{-}(Me_2CH)_4C_5H\}TmCl_2(dme)]$ (9-Tm). Single crystals of the dimethoxyethane adduct were grown from a concentrated DME solution of **6-Tm** at room temperature in 72% yield. Anal. calcd. for $C_{21}H_{39}Cl_2O_2Tm$ (563.39): C, 44.8; H, 6.98. Found C, 44.7; H, 6.91%.

Synthesis of $[\{\eta^5\text{-}(Me_2CH)_4C_5H\}LuCl_2(dme)]$ (9-Lu). Dissolving complex **7-Lu** in dimethoxyethane, centrifugation and slow cooling to −35 °C yielded colorless crystalline plates losing coordinated solvent rapidly in an inert gas atmosphere. Alternatively, crystallization at −35 °C from a saturated toluene–dimethoxyethane (10 : 1) solution gave colorless blocks (56% yield) subjected to elemental and ^{1}H NMR analysis. Anal. calcd. for $C_{21}H_{39}O_2Cl_2Lu$ (569.41): C, 44.3; H, 6.9. Found C, 45.0; H, 7.0%. ^{1}H NMR (400.13 MHz, 298 K, C_6D_6): δ 6.44 (s, 1H, ring-H), 3.41 (m, 2H, C*H*Me$_2$), 3.32 (8H, C*H*Me$_2$ and (C*H*$_2$OCH$_3$)$_2$ superimposed), 3.14 (s, 6H, (C*H*$_2$OC*H*$_3$)$_2$), 1.70 (d, 6H, C*H*$_3$, *J* = 7.25 Hz), 1.59 (d, 6H, C*H*$_3$, *J* = 6.53 Hz), 1.38 (d, 6H, C*H*$_3$, *J* = 7.05 Hz), 1.19 (d, 6H, C*H*$_3$, *J* = 6.62 Hz).

Synthesis of $[\{\eta^5\text{-}Me_3CC_5H_4\}_2Yb(\mu\text{-}Cl)]_2$ (10-Yb). To a solution of **6-Yb** (0.72 g, 1.51 mmol) in diethyl ether (20 ml) lithium *tert*-butylcyclopentadienide (0.19 g, 1.51 mmol) was added. The color changed to red-brown immediately and the reaction mixture was stirred for 2 d at ambient temperature. The solvent was evaporated and the residue extracted with pentane (2 × 15 ml). Centrifugation, concentration of the combined pentane extracts and crystallization at −15 °C resulted in big, red-brown hexagonal crystals (0.2 g, 0.22 mmol, 58%). The compound was identified by X-ray diffraction as 1,1′-bis((*tert*-butylcyclopentadienyl)ytterbium chloride. ^{1}H NMR (400.13 MHz, 298 K, C_6D_6): δ 55.6 (18H, $\nu_{1/2}$ = 280 Hz, CMe$_3$), −60.2 (4 H, $\nu_{1/2}$ = 560 Hz, ring-CH).

Synthesis of $[\{\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2\}TmCl_2]$ (11-Tm). A suspension of $TmCl_3$ (0.55 g, 2.03 mmol) in THF (15 mL) was stirred at ambient temperature for 3 d with sodium tri-*tert*-butylcyclopentadienide (0.52 g, 2.03 mmol). The solvent was removed under dynamic vacuum and the remaining solid was extracted with two 15 mL portions of petroleum ether. After centrifugation the yellow extracts were combined and evaporated to dryness to yield 0.75 g (1.58 mmol, 79%) bright yellow powder. Mp 200 °C (dec.). Anal. calcd. for $C_{17}H_{29}Cl_2Tm$ (473.27): C, 43.2; H, 6.18. Found C, 42.8; H, 6.33%.

Synthesis of $[\{\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2\}YbCl_2]$ (11-Yb). $YbCl_3$ (0.56 g, 2.00 mmol) and potassium tri-*tert*-butylcyclopentadienide (0.55 g, 2.02 mmol) were stirred in tetrahydrofuran (50 mL) for 3 d at ambient temperature before the purple mixture was evaporated to dryness *in vacuo*. The blue residue was extracted with three 15 mL portions of petroleum ether and the filtered extracts were combined and evaporated to *ca.* 20

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mL. After 2 d at −40 °C dark blue, microcrystalline product could be collected in 0.40 g (0.84 mmol, 43%) yield. Mp 250 °C (dec.). Anal. calcd. for $C_{17}H_{29}Cl_2Yb$ (477.36): C, 42.8; H, 6.12. Found C, 43.1; H, 6.64%.

Synthesis of [{η^5-1,2,4-$(Me_3C)_3C_5H_2$}$YbCl_2(thf)_2$] (12-Yb). Crystallization of **11-Yb** at −15 °C from a saturated tetrahydrofuran solution gave deep-blue cubes in 75% yield. Coordinated solvent was lost on heating, above 80 °C the color of the crystals turned lighter blue and tetrahydrofuran was found in the head space of the sealed capillary, Mp >240 °C. Anal. calcd. for $C_{25}H_{45}Cl_2O_2Yb$ (621.58): C, 48.3; H, 7.30. Found C, 48.1; H, 7.09%.

Synthesis of [{η^5-1,2,4-$(Me_3C)_3C_5H_2$}$Tm\{N(SiMe_3)_2\}_2$] (13-Tm). A solution of sodium bis(trimethylsilyl)amide (0.28 g, 1.52 mmol) in toluene (5 mL) was added to a solution of **11-Tm** (0.36 g, 0.76 mmol) in toluene (10 mL) and stirred at ambient temperature for 2 h. The solvent was removed under dynamic vacuum and the yellow residue was extracted with pentane (2 × 10 mL). After centrifugation the volume of the combined extracts was reduced to *ca.* 5 mL and cooled to 3 °C. Seven days later light yellow-green crystals could be harvested (0.48 g, 0.73 mmol, 87%). Anal. calcd. for $C_{29}H_{65}N_2Si_4Tm$ (723.13): C, 48.2; H, 9.06; N, 3.87. Found C, 48.0; H, 8.86; N, 3.85%. ^1H NMR (400.13 MHz, 298 K, C_6D_6): δ 202.6 (18H, $\nu_{1/2}$ = 1550 Hz), 18.8 (9H, $\nu_{1/2}$ = 1140 Hz), −0.5 (36H, $\nu_{1/2}$ = 425 Hz), −218 (2H, $\nu_{1/2}$ = 4500 Hz); MS (70 eV, EI): *m*/*z* (%) = 722.1 (<1) M^+, 707.1 (<1) $M^+ - CH_3$, 635.1 (<1) $M^+ - SiMe_4$, 562.2 (<1) $M^+ - N(SiMe_3)_2$, 489.2 (28) $M^+ - C_5H_2(CMe_3)_3$, 234.1 (12) $HC_5H_4(CMe_3)_3{}^+$, 161.2 (3) $HN(SiMe_3)_2{}^+$, 146.2 (75) $Me_3Si\text{-}SiMe_3{}^+$, 57.1 (62) $CMe_3{}^+$.

Synthesis of [{η^5-1,2,4-$(Me_3C)_3C_5H_2$}$Yb(Cl)(\mu\text{-}OCH_2CH_2OMe)$]$_2$ (14-Yb). To a suspension of $YbCl_3$ (0.21 g, 0.75 mmol) in dimethoxyethane (6 mL) a solution of sodium tri-*tert*-butylcyclopentadienide (0.39 g, 1.5 mmol) in dimethoxyethane (5 mL) was added slowly at room temperature. Within a few minutes the suspended solid was dissolved and a purple-red color was observed. Stirring was continued for 2 d, then *n*-pentane (5 mL) was added and the precipitate formed was removed by centrifugation. Evaporation of the solution afforded a purple-red oil, which was dissolved in *n*-hexane (5 mL) and stirred at room temperature for 20 min. The green precipitate formed during this period was removed by centrifugation and the solution was evaporated under dynamic vacuum. The red-brown, oily solid was recrystallized by slow cooling of a saturated *n*-hexane solution to −10 °C to yield the dark red, crystalline product (0.11 g, 0.11 mmol, 28%). Anal. calcd. for $C_{20}H_{36}O_2ClYb$ (517.00): C, 46.5; H, 7.02. Found C, 45.5; H, 6.94%. The low solubility of the product prevented the acquisition of an ^1H NMR spectrum in C_6D_6.

Synthesis of [{η^5-$(Me_2CH)_4C_5H$}$_2TmI$] (15-Tm). A solution of sodium tetraisopropylcyclopentadienide (1.02 g, 4 mmol) was added to a suspension of TmI_3 (1.1 g, 2 mmol) in tetrahydrofuran (10 mL) and the mixture was stirred for 2 d at room temperature. Solvent removal under dynamic vacuum, extraction with *n*-hexane (5 × 10 mL), centrifugation and evaporation of the *n*-hexane solvent in dynamic vacuum afforded a yellow-brown solid. **15-Tm** was obtained as yellow crystals by sublimation in oil pump vacuum at 80–90 °C (0.96 g, 1.26 mmol, 63%). Single crystals for X-ray diffraction were grown by sublimation in an ampoule sealed under oil pump vacuum and stored at 70 °C for a couple of days. Anal. calcd. for $C_{34}H_{58}TmI$ (762.63): C, 53.6; H, 7.67. Found C, 54.3; H, 7.02%; MS (70 eV, EI): *m*/*z* (%) = 762 (7) M^+, 635 (2) $M^+ - I$, 529 (100) $M^+ - C_5H(CHMe_2)_4$, 496 (1) $M^+ - I - C_5H(CHMe_2)_4$, 149 (5) $C_{11}H_{17}{}^+$, 107 (14) $C_8H_{11}{}^+$.

Synthesis of [{η^5-$(Me_2CH)_4C_5H$}$_2LaI$] (15-La). $LaI_3 \cdot 3.75THF$ (0.34 g, 0.5 mmol) was stirred with tetrahydrofuran (20 mL) and solid sodium tetraisopropylcyclopentadienide (0.26 g, 1.0 mmol) was added in small portions. The brown suspension was stirred for 2 d at room temperature. During this time the suspension turned clear and a light yellow solution was formed. Evaporation of the solvent, followed by extraction with *n*-hexane and evaporation yielded the product as an ivory solid (0.24 g, 0.33 mmol, 66%). Mp 98 °C (dec.). Anal. calcd. for $C_{34}H_{58}ILa$ (732.64): C, 55.7; H, 7.98. Found: C, 54.8; H, 7.94%. ^1H NMR (400.13 MHz, 300 K, C_6D_6): δ 6.31 (s, 2H, ring-H), 3.52 (m, 4H, C*H*Me$_2$), 3.04 (m, 4H, C*H*Me$_2$), 1.51 (d, 12H, C*H*$_3$, *J* = 7.04 Hz), 1.39 (d, 12H, C*H*$_3$, *J* = 6.66 Hz), 1.24 (d, 12H, C*H*$_3$, *J* = 7.04 Hz), 1.07 (d, 12H, C*H*$_3$, *J* = 6.65 Hz). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298 K, C_6D_6): δ 136.0 (4C, ring-*C*CHMe$_2$), 135.5 (4C, ring-*C*CHMe$_2$), 106.7 (2C, ring-*C*H), 27.7 (4C, *C*HMe$_2$), 27.5 (4C, *C*HMe$_2$), 26.6 (4C, *C*H$_3$), 25.2 (4C, *C*H$_3$), 24.1 (4C, *C*H$_3$), 23.5 (4C, *C*H$_3$). MS (70 eV, EI): *m*/*z* (%) = 731 (2) M^+, 604 (2) $M^+ - I$, 498 (15) M^+ C $_5H(CHMe_2)_4$, 234 (84) $C_{17}H_{30}{}^+$, 219 (100) $C_{16}H_{27}{}^+$, 149 (56) $C_{11}H_{17}{}^+$, 107 (75) $C_8H_{11}{}^+$.

Synthesis of [{η^5-1,2,4-$(Me_3C)_3C_5H_2$}$_2LaI$] (16-La). $LaI_3 \cdot 3.75THF$ (5.80 g, 6.43 mmol) was stirred with tetrahydrofuran (60 mL) and solid sodium tri-*tert*-butylcyclopentadienide (3.3 g, 12.87 mmol) was added in small portions. Within a few minutes a clear, light yellow solution was formed, which was stirred at room temperature for 2 d. Evaporation of the solvent, followed by extraction with *n*-hexane and evaporation yielded the product as a cream-colored solid (1.91 g, 2.61 mmol, 41%). Mp 93 °C (dec.). Anal. calcd. for $C_{34}H_{58}ILa$ (732.64): C, 55.7; H, 7.98. Found: C, 53.6; H, 8.01%. ^1H NMR (400.13 MHz, 300 K, C_6D_6): δ 1.51 (s, 36H, C(C*H*$_3$)$_3$), 1.20 (s, 18H, C(C*H*$_3$)$_3$), no other resonances were detected. ^1H NMR (400.13 MHz, 370 K, C_7D_8): δ 6.64 (s, 4H, ring-*H*), 1.49 (s, 36H, C(C*H*$_3$)$_3$), 1.22 (s, 18H, C(C*H*$_3$)$_3$). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298 K, C_6D_6): δ = 138.0 (2C, ring-*C*(CMe$_3$)), 126.7 (4C, ring-*C*(CMe$_3$)), 114.0 (2C, ring-*C*H), 34.2 (12C, C(*C*H$_3$)$_3$), 33.2 (4C, *C*(CH$_3$)$_3$), 32.4 (6C, C(*C*H$_3$)$_3$), 31.8 (2C, *C*(CH$_3$)$_3$). MS (70 eV, EI): *m*/*z* (%) = 732.0 (<1) M^+, 605.1 (<1) $M^+ - I$, 499.0 (2) $M^+ - C_5H_2(CMe_3)_3$, 179.2 (24) $C_{13}H_{23}{}^+$, 57.1 (71) $C_4H_9{}^+$, 28.0 (100) $C_2H_4{}^+$.

Synthesis of [{η^5-1,2,4-$(Me_3C)_3C_5H_2$}$_2SmI$] (16-Sm). A solution of hexa-*tert*-butylsamarocene (0.31 mg, 0.5 mmol) in a 2 : 1 mixture of hexane and diethyl ether (30 mL) was stirred with copper(I)iodide (0.1 g, 0.5 mmol) at room temperature for 12 h. The suspension was evaporated to a remaining volume of 20 mL and subjected to centrifugation. The bright orange

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solution was evaporated to yield the product as a dark orange powder (0.32 g, 0.42 mmol, 85%). Mp. 146 °C (dec.). Anal. calcd. for $C_{34}H_{58}ISm$ (744.10): C, 54.9; H, 7.86. Found: C, 54.6; H, 7.84%. ^1H NMR (400.13 MHz, 300 K, C_6D_6): δ = 24.5 (s, 2H, ring-H, $\nu_{1/2}$ = 172 Hz), 16.6 (s, 2H, ring-H, $\nu_{1/2}$ = 155 Hz), 1.36 (s, 18H, CMe_3, $\nu_{1/2}$ = 220 Hz), 0.45 (s, 18H, CMe_3, $\nu_{1/2}$ = 220 Hz), −6.9 (s, 18H, CMe_3, $\nu_{1/2}$ = 15 Hz). MS (70 eV, EI): m/z (%) = 744.6 (11) M^+, 617.9 (24) $M^+ - I$, 511.7 (95) $M^+ - C_5H_2(CMe_3)_3$, 496.7 (21) $M^+ - C_5H_2(CMe_3)_3 - CH_3$, 368.9 (34) $M^+ - C_5H_2(CMe_3)_3 - CH_3 - I$, 57.1 (100) $C_4H_9^+$.

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