Substituted Cyclooctatetraenes as Ligands in *f*-Metal Chemistry

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Dedicated to Professor Dr. Dr. h.c. Oskar Glemser on the occasion of his 90th birthday

Keywords: Actinides / Cyclooctatetraenes / Lanthanides / Sandwich complexes

The use of substituted cyclooctatetraenes confers various desired properties on the resulting metal complexes such as a higher thermal and kinetic stability as well as higher solubility relative to the nonsubstituted systems. Furthermore, the formation of polymeric structures is inhibited because intermolecular interactions are reduced. Alkyl- and aryl-substituted cyclooctatetraenes were mainly used as ligands in the 1970s and 1980s. The vast majority of known complexes containing these ligands in the coordination sphere are uranium compounds. Since then the alkyl- and aryl-substituted cyclooctatetraenes have been replaced almost exclusively in synthesis by silyl-substituted ones. Complexes with silyl-substituted cyclooctatetraenes are known for both 4f and 5f elements.

1. Introduction

The replacement of the classic cyclopentadienyl ligand (C_5H_5 = Cp) with bulkier analogues such as C_5Me_5 (Cp*) and $C_5H_3(SiMe_3)_2$ (Cp′′) in main group and transition metal chemistry has led to complexes with more convenient properties.[1,2] Due to the steric shielding of the metal centers with Cp* and Cp′′ ligands, the resulting compounds are thermally and kinetically more stable. They are more soluble, crystallize more readily, and the formation of polymeric structures is inhibited because intermolecular interactions are reduced. These advantages led to the isolation and structural characterization of a number of main group and transition metal complexes which are difficult to obtain with the unsubstituted Cp ligand.[1,3−7] In particular, in *f*-element chemistry the use of bulky cyclopentadienyl ligands has paved the way for the exploration of their organometallic chemistry.[2,6]

In contrast to the rich chemistry of complexes with substituted cyclopentadienyl ligands, the number of complexes with η^8-coordinated substituted cyclooctatetraenes in the ligand sphere is virtually underdeveloped. Part of the reason for this stems from the fact that the 10-π-aromatic cyclooctatetraene dianion $C_8H_8^{2-}$ can be η^8-coordinated to a limited number of elements only (groups 3 and 4, the lanthanides and the actinides). Furthermore, there is no relevant industrial application for cyclooctatetraene complexes of the *f*-elements.

Since the cyclooctatetraene dianion is one of the most important ligands in organo-f-element chemistry,[8−12] this account presents the conceptual foundations for metal complexes with η^8-coordinated substituted cyclooctatetraenes in the ligand sphere.

2. Discussion

2.1. Alkyl-, Aryl-, Amino-, and Alkoxy-Substituted Cyclooctatetraenes

Most of the alkyl-, aryl-, amino-, and alkoxy-substituted cyclooctatetraenes C_8H_7-R which have been used as ligands in *f*-metal chemistry were first prepared in the 1950s by A. C. Cope et al.[13−17] The synthesis of these compounds

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MICROREVIEWS: This feature introduces the readers to the authors′ research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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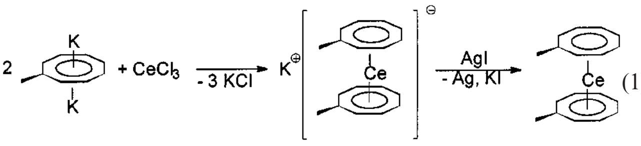
has been reviewed.[18,19] Therefore, only the most common routes leading to C_8H_7-R will be discussed here. Alkyl cyclooctatetraenes can be obtained either by the reaction of C_8H_8 with alkyllithium reagents,[13,14] by the reaction of C_8H_7-Br with the corresponding dialkylcuprates,[20,21] or by a modified Reppe synthesis (the cyclization of ethyne with the corresponding substituted alkyne).[15,16] Many functionalized cyclooctatetraenes such as C_8H_7-$(CH_2)_3NMe_2$ were prepared starting from C_8H_7-$(CH_2)_3OH$, which itself was obtained by copolymerization of ethyne with $HC{\equiv}C$-$(CH_2)_3OH$.[16,17]Alkoxy cyclooctatetraenes, C_8H_7-OR, are obtained by the Williamson reaction of bromocyclooctatetraene, C_8H_7-Br, and the corresponding sodium alkoxides.[22]

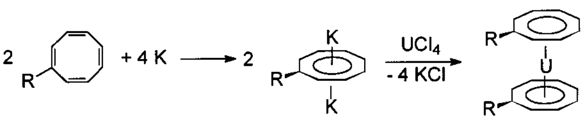
Very few lanthanide complexes have been prepared with C_8H_7-R as a ligand. The substituents on the eight-membered ring in these compounds were alkyl groups such as Me, *n*Bu or *t*Bu. Using these ligands the chloride $[(nBuC_8H_7)LuCl(THF)_2]$,[23] the amide $Li[(nBuC_8H_7)Lu\{NMeCH_2CH_2NMe_2\}_2]$,[23] and the sandwich complex $[K(diglyme)][Yb(tBuC_8H_7)_2]$[24] were made. The synthesis of these compounds begins with the reaction of C_8H_7-R with potassium which leads to $K_2C_8H_7$-R. The dipotassium salt is then further reacted with the corresponding lanthanide chlorides. Since only $[K(diglyme)][Yb(tBuC_8H_7)_2]$ has been characterized by X-ray diffraction, the influence of the substituents on the eight-membered ring is hard to judge. The cerocene $[Ce(MeC_8H_7)_2]$ was reported by a two step procedure. In the first step, $K_2(MeC_8H_7)$ was reacted with $CeCl_3$ which led to $K[Ce(MeC_8H_7)_2]$. The anion was then oxidized with AgI to yield $[Ce(MeC_8H_7)_2]$ [Equation (1)].[25] The sandwich complex $[Ce(C_8H_8)_2]$ has conclusively shown to be a Ce^{3+} ($4f^1$) complex by theoretical as well as experimental investigations. Cerocene is best formulated as a sandwich complex containing two coordinated $(C_8H_8)^{1.5-}$ ions. This topic was recently reviewed and therefore will not be discussed further here.[26]



(1)

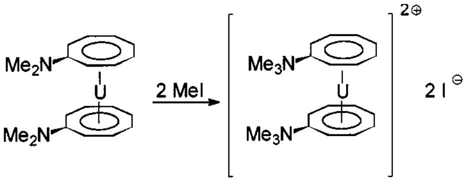
Table 1. Monosubstituted actinocenes (IV) $[(C_8H_7\text{-}R)_2An]$

An	R	Ref.
Th	Me	42
	*n*Bu	42
	*t*Bu	42, 43
	C_6H_5	42
	o-tolyl	43
	mesityl	43
U	Me	29, 31
	Et	22, 30, 44
	$CH{=}CH_2$	30
	*c*Pr	30
	*n*Bu	22, 29, 30, 31, 44
	*t*Bu	22, 29, 33
	$(CH_2)_4CH_3$	22
	C_6H_5	29, 35
	o-tolyl	39
	mesityl	38, 39
	C_8H_7	37, 40
	COOEt	36
	COO*t*Bu	36
	$COOCH_2C_6H_5$	36
	OMe	22
	OEt	22, 29
	O*t*Bu	22
	$OCH_2CH{=}CH_2$	22
	NMe_2	22
	CH_2NMe_2	22
	$(CH_2)_3NMe_2$	22
	$N^+Me_3\ I^-$	22, 29
	$CH_2N^+Me_3\ I^-$	22
	PR_2 (R= Et, *t*Bu, Ph)	37
Np	Et	44
	*n*Bu	44
Pu	Et	44
	*n*Bu	44



(2)

In contrast to the few reported 4*f*-metal complexes a large number of substituted uranocenes were reported mainly by A. Streitwieser et al. Most of this work was reviewed in 1979[27] and 1985.[28] The majority of the known substituted uranocenes can be prepared by three types of methods: 1) Reaction of $(C_8H_7\text{-}R)^{2-}$ with UCl_4;[22,29,30] 2) Reaction of C_8H_7-R with finely divided uranium powder;[28] 3) Functional group reactions of substituted uranocenes.[22] By using these methods 1,1′ substituted uranocenes, $[U(C_8H_7\text{-}R)_2]$ were prepared (Table 1).[22,27–37] The first of these methods is also the most common. $K_2C_8H_7$-R, which is obtained from C_8H_7-R and potassium, is reacted with UCl_4 [Equation (2)]. The second method leads more or less to the same products. Functional groups that are not stable in the presence of elemental potassium or uranium can be attached to the eight-membered ring by performing functional group reactions of substituted uranocenes (third method). With this method, amino groups can be transformed into ammonium ions, for example [Equation (3)]. Whereas uranocene itself has low solubility many substituted uranocenes have greater solubility and thus are easier to purify. Strong intramolecular interactions are observed only for very large substituents on the eight membered ring. For R = mesityl, the two groups are markedly bent away from the opposite ring in solution. The ^1H NMR spectrum shows the mesityl groups in a locked position with *exo*- and



(3)

endo-methyl groups.[27,38,39] A striking example in this series is bis(bicyclooctatetraenyl)diuranium (biuranocenylene) in which two U^{4+} ions are bridged by two $(C_8H_7-C_8H_7)^{4-}$ units (Figure 1).[40,41] Substituted thorocenes,[42,43] plutocenes[44] and neptunocenes[44] are also known, but their number in comparison to uranocenes is more limited. With the exception of the uranocenes, only aryl and alkyl-substituted actinocenes are known (Table 1).

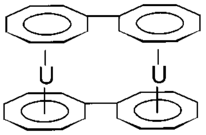


Figure 1. Bis(bicyclooctatetraenyl)diuranium (biuranocenylene)

Similar synthetic routes to those outlined above have been used to prepare di- and multiple ring substituted bis(cyclooctatetraene)actinocenes $[An(C_8H_{8-n}\text{-}R_n)_2]$ (Table 2).[45−51] Most common in this series are the octamethyl compounds $[An(1,3,5,7\text{-}Me_4C_8H_4)_2]$.[27,48,49] The structure of $[U(1,3,5,7\text{-}Me_4C_8H_4)_2]$ was established by single crystal X-ray diffraction (Figure 2).[50] This complex crystallizes as molecules in two rotameric configurations. In one form the methyl groups are essentially eclipsed whereas in the other form the methyl groups are essentially staggered. A truly remarkable species is the highly substituted 1,3,5,7,1′,3′,5′,7′-octaphenyluranocene.[27,51] In contrast to pyrophoric $[U(C_8H_8)_2]$, this material is completely air stable due to the effective shielding of the metal center by eight phenyl groups. Another interesting example in this series is an uranocene in which two (1,6)cyclooctatetraenyl(1,4)cyclophanes were used as ligands (Figure 3).[52]

Table 2. Di- and tetrasubstituted actinocenes(IV) $[(C_8H_{8-n}\text{-}R_n)_2An]$

An	R	Ref.
Th	$1,3,5,7\text{-}Me_4$	48
Pa	$1,3,5,7\text{-}Me_4$	49
U	$1,4\text{-}t\text{Bu}_2$	47
	$1,5\text{-}t\text{Bu}_2$	46
	$1,3,5,7\text{-}Me_4$	27, 50
	$1,3,5,7\text{-}Ph_4$	51
Np	$1,3,5,7\text{-}Me_4$	49
Pu	$1,3,5,7\text{-}Me_4$	49

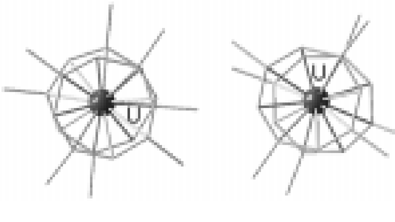


Figure 2. Crystal structure of $[U(1,3,5,7\text{-}Me_4C_8H_4)_2]$

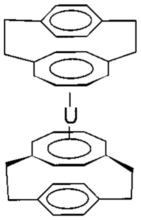
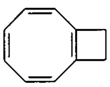
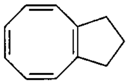
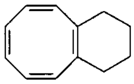
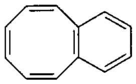


Figure 3. A uranocene containing two (1,6)cyclooctatetraenyl(1,4)-cyclophanes as ligands

Ring fused cyclooctatetraens, which are shown in Table 3, have also been used as ligands for thorocenes and also for uranocenes.[53−56] The structures of dicyclobutenouranocene (Figure 4) and dicyclopentenouranocene were characterized by X-ray diffraction. It was shown that the two annulated four- or five-membered rings are located in *trans* positions. Thus the molecule had approximate C_2 symmetry.[53,54]

Table 3. Ring-fused actinocenes (IV)

Ligand	An	Ref.
	U	53
	U	54
	U	56
	Th, U	56

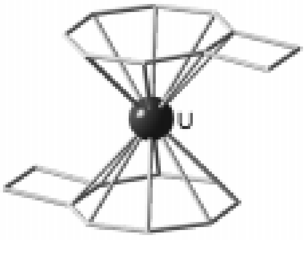


Figure 4. Crystal structure of dicyclobutenouranocene

Besides substituted actinocenes, in which the metal centers are formally in oxidation state +4, there are also some substituted actinocenes(III), $K[An(C_8H_7\text{-}R)_2]$. These compounds can be compared with the lanthanidocenes which are usually found in the same oxidation state. The uranocene(III) $[K(diglyme)][U(MeC_8H_7)_2]$ was obtained by potassium reduction of the corresponding uranocene (Figure 5).[25] The structure shows that the uranium(III) and potassium ions are bridged by a MeC_8H_7 ligand to give a nearly linear $(MeC_8H_7)U(\mu\text{-}MeC_8H_7)K$ arrangement. The neptunium and plutonium compounds $K[An(tBuC_8H_7)_2]$ (An = Np, Pu) were prepared from the corresponding hexachloride salts, $(Et_4N)_2[AnCl_6]$, and $tBuC_8H_7$. A mixture of $K[An(tBuC_8H_7)_2]$ and $[An(tBuC_8H_7)_2]$ shows rapid electron exchange.[57]

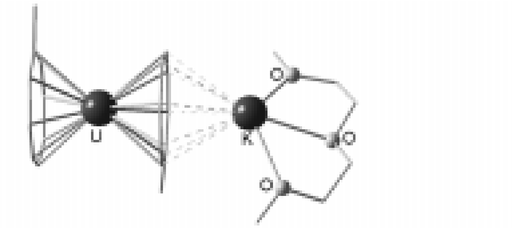


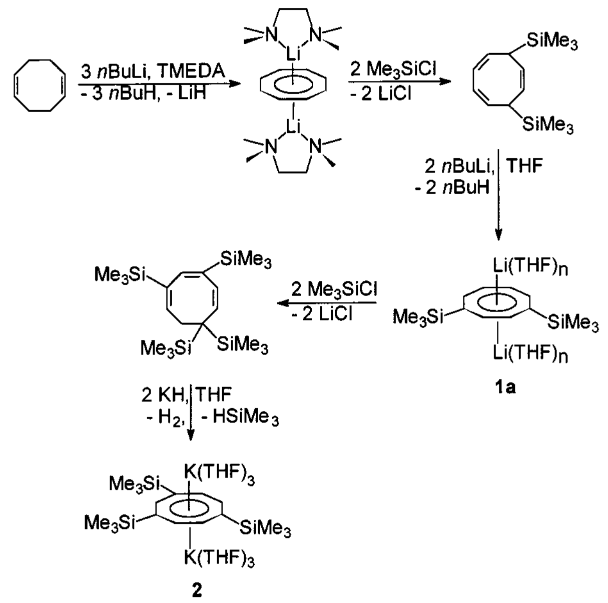
Figure 5. Crystal structure of $[K(diglyme)][U(MeC_8H_7)_2]$

Only a few substituted cyclooctatetraene half-sandwich complexes of the actinides are known. Their synthesis proved to be significantly more difficult than the synthesis of the corresponding sandwich complexes. The thorium complexes $[(C_8H_7\text{-}R)ThCl_2]$ and $[(1,3,5,7\text{-}Me_4C_8H_4)ThCl_2]$ were obtained by a ligand redistribution between the corresponding thorocene and $ThCl_4$.[58] $[(nBuC_8H_7)Th(BH_4)_2]$ can be prepared in a similar reaction of $[(nBuC_8H_7)_2Th]$ and $Th(BH_4)_4$ or by reaction of $[Th(BH_4)_4(THF)_2]$ with $K_2(nBuC_8H_7)$.

2.1. Silyl-Substituted Cyclooctatetraenes

The disadvantage of multiple alkyl-substituted cyclooctatetraenes such as $1,4\text{-}tBu_2C_8H_6$ [47] or $1,3,5,7\text{-}Me_4C_8H_4$ [59] is their lengthy preparation and the resulting low yields. Moreover, C_8H_8 which is used as a starting material for a number of substituted cyclooctatetraenes is getting more and more expensive. This has recently limited the use of alkyl-substituted cyclooctatetraenes as ligands for metal complexes. In 1993, F. G. N. Cloke et al. developed a cheap and convenient one pot synthesis of the silyl-substituted cyclooctatriene $1,4\text{-}(Me_3Si)_2C_8H_8$ which can easily be deprotonated with *n*-butyllithium to yield $[Li_2(THF)_n][1,4\text{-}(Me_3Si)_2C_8H_6]$ (**1a**) (Scheme 1).[60,61] By analogy, the *t*Bu-substituted salt $[Li_2(THF)_n][1,4\text{-}(Me_2tBuSi)_2C_8H_6]$ (**1b**) was also obtained.[62] Further treatment of **1a** with Me_3SiCl and subsequent reaction with KH gave the tris(trimethylsilyl)-substituted compound $[K_2(THF)_3][1,3,6\text{-}(Me_3Si)_3C_8H_5]$ (**2**) (Scheme 1).[63] The easy accessibility of **1a,b** and **2** paved the way to a number of new actinide and lanthanide complexes.

The treatment of various anhydrous lanthanide trichlorides with two equivalents of **1a** gave the ionic sandwich complexes $[Li(THF)_4][Ln\{1,4\text{-}(Me_3Si)_2C_8H_6\}_2]$ (Ln = Y, Ce, Pr, Nd, Sm) [Equation (4)]. Ion exchange of $[Li(THF)_4][Sm\{1,4\text{-}(Me_3Si)_2C_8H_6\}_2]$ with [PPN]Cl afforded $[PPN][Sm\{1,4\text{-}(Me_3Si)_2C_8H_6\}_2]$ (Table 4).[64] The derivatives of **2**, $[K(THF)_3][Ln\{1,3,6\text{-}(Me_3Si)_3C_8H_5\}_2]$ (Ln = Ce, Tb), were obtained in a similar manner (Table 4). Both



Scheme 1

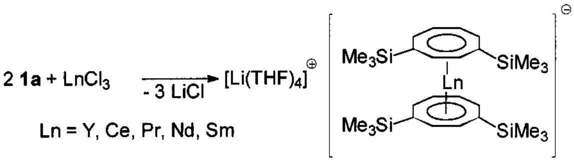
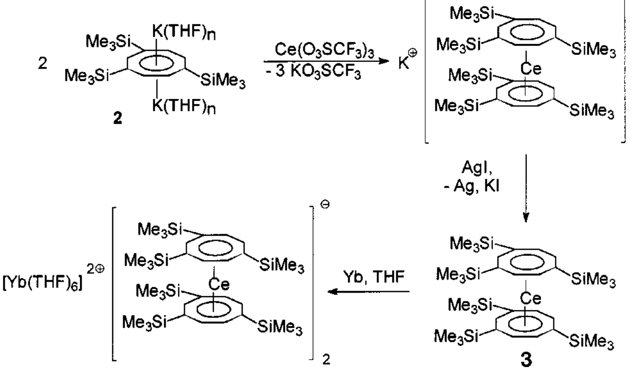
 (4)

Table 4. Silyl-substituted lanthanocenes

Ln	Complex	Ref.
Y, Ce, Pr, Nd, Sm	$[Li(THF)_4][Ln\{1,4\text{-}(Me_3Si)_2C_8H_6\}_2]$	64
Sm	$[PPN][Ln\{1,4\text{-}(Me_3Si)_2C_8H_6\}_2]$	64
Ce, Tb	$[K(THF)_3][Ln\{1,3,6\text{-}(Me_3Si)_3C_8H_5\}_2]$	63
Ce	$[Yb(THF)_6][Ln\{1,3,6\text{-}(Me_3Si)_3C_8H_5\}_2]_2$	66
Ce	$[CoCp_2][Ln\{1,3,6\text{-}(Me_3Si)_3C_8H_5\}_2]_2$	63
Ce (**3**)	$[Ln\{1,3,6\text{-}(Me_3Si)_3C_8H_5\}_2]$	63
Ce, Nd, Sm	$[Ln_2\{1,4\text{-}(Me_3Si)_2C_8H_6\}_3]$	67
Nd, Sm	$[Li(diglyme)_2][Ln(1,4\text{-}R_2C_8H_6)_2]$[a]	72

[a] R = *ortho*-(Dimethylsilyl)-*N*,*N*-dimethylaniline.



Scheme 2

cerium complexes could be oxidized with AgI to the corresponding neutral sandwich complexes [Ce{1,4-$(Me_3Si)_2C_8H_6\}_2$] and [Ce{1,3,6-$(Me_3Si)_3C_8H_5\}_2$] (**3**) (Scheme 2).[63] In contrast to the nonsubstituted complex [$Ce(C_8H_8)_2$] both compounds have good solubility in organic solvents and can be handled in air for a short time. Complex **3** was also characterized by X-ray diffraction (Figure 6). It was shown that the complex crystallizes in a staggered-like conformation.[63] XANES spectra give the assignment of the oxidation state of the cerium ion of **3** as trivalent.[65] In a few investigations **3** was used as an oxidizing reagent. Thus the redox reaction of **3** with ytterbium metal gave the first heterobimetallic organolanthanide complex [$Yb(THF)_6$][Ce{1,3,6-$(Me_3Si)_3C_8H_5\}_2]_2$ (Scheme 2),[66] whereas the redox reaction of **3** and cobaltocene yielded [$CoCp_2$][Ce{1,3,6-$(Me_3Si)_3C_8H_5\}_2]_2$.[63]

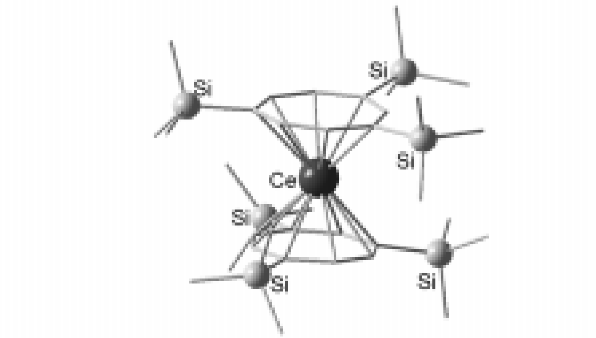
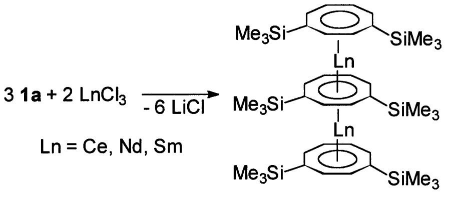


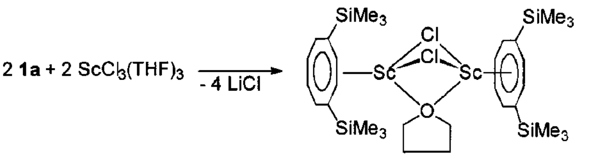
Figure 6. Crystal structure of [Ce{1,3,6-$(Me_3Si)_3C_8H_5\}_2$] (**3**)

Treatment of anhydrous lanthanide trichlorides with **1a** in a 2:3 molar ratio afforded the first well defined organolanthanide triple-decker sandwich complexes of composition [Ln_2\{1,4-$(Me_3Si)_2C_8H_6\}_3$] (Ln = Ce, Nd, Sm) [Equation (5)].[67] Due to the presence of six trimethylsilyl substituents in the molecules, the intensely colored complexes are readily soluble in most common organic solvents.



(5)

Cyclooctatetraene half-sandwich complexes of yttrium and scandium were the first complexes with silyl substituents on the eight-membered ring. Reaction of **1a** with [$LnCl_3(THF)_3$] (Ln = Sc, Y) gave the half-sandwich complexes [{{1,4-$(Me_3Si)_2C_8H_6\}Sc(\mu\text{-}Cl)\}_2(\mu\text{-}THF)$] and [{1,4-$(Me_3Si)_2C_8H_6\}Y(THF)(\mu\text{-}Cl)]_2$, respectively [Equation (6) and (7)].[68] The structure of the scandium compound was determined by single crystal X-ray diffraction (Figure 7). The most interesting feature of the dimeric structure concerns the THF ligand, which is in a bridging position. This structure has no parent C_8H_8 analogue.



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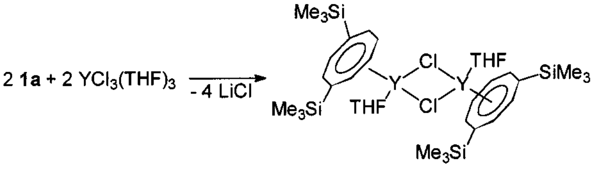

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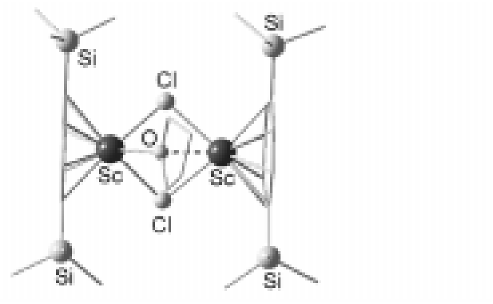


Figure 7. Crystal structure of [{{1,4-$(Me_3Si)_2C_8H_6\}Sc(\mu\text{-}Cl)\}_2(\mu\text{-}THF)$]

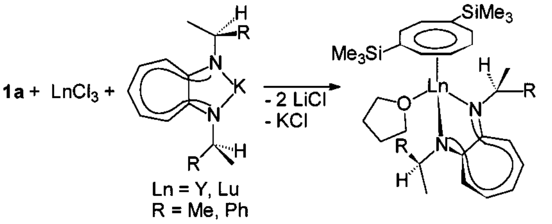
Derivatives of the cyclooctatetraene half-sandwich halides were usually made in a one-pot reaction starting from $LnCl_3$ and **1a** without isolation of the halogen intermediate (Table 5). Thus, the polysilylated complexes of composition [{1,4-$(Me_3Si)_2C_8H_6\}Ln\{1,3\text{-}(Me_3Si)_2C_5H_3\}$] (Ln = Pr, Sm, Tb) were prepared by treatment of $LnCl_3$ simultaneously with equivalent amounts of **1a** and Li{1,3-$(Me_3Si)_2C_5H_3$}.[69] The isopropyl-aminotroponimate complexes [{1,4-$(Me_3Si)_2C_8H_6$}Ln{(iPr)$_2$ATI}(THF)] [Ln = Y, Lu; (iPr)$_2$ATI = *N*-isopropyl-2-(isopropylamino)troponiminate] and the enantiomerically pure (*S*)-phenylethyl-aminotroponimate complex [{1,4-$(Me_3Si)_2C_8H_6$}Y{((*S*)-$PhCHCH_3)_2$ATI}(THF)] were obtained by the consecutive treatment of $LnCl_3$ with **1a** and {$(R)_2$ATI}K [Equation (8)].[70] The structure of [{1,4-$(Me_3Si)_2$-C_8H_6}Y{(iPr)$_2$ATI}(THF)] was confirmed by single crystal X-ray diffraction. In contrast, the 1,4-diazadiene (DAD) complexes [{1,4-$(Me_3Si)_2C_8H_6$}Ln(DAD)(THF)] (Ln =

Table 5. Monomeric half-sandwich complexes of the general formula [{1,4-$(Me_3Si)_2C_8H_6$}Ln-R]

Ln	R	Ref.
Pr, Sm, Tb	1,3-$(Me_3Si)_2C_5H_3$	69
Y, Lu	{(iPr)$_2$ATI}(THF)[a]	70
Y	{((*S*)-$PhCHCH_3)_2$ATI}(THF)	70
Sm, Yb	(DAD)(THF)[b]	71

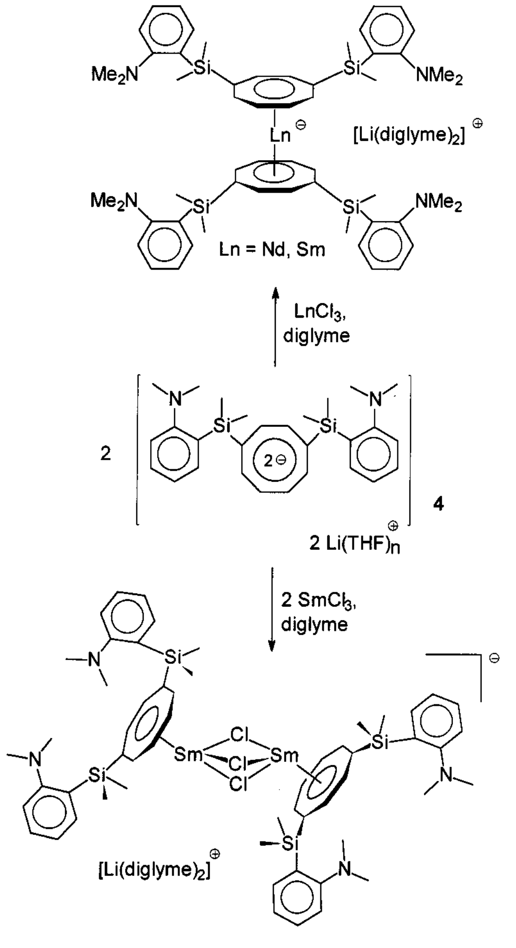
[a] (iPr)$_2$ATI = *N*-isopropyl-2-(isopropylamino)troponiminate. − [b] 1,4-Diazadiene.

Sm, Yb) have been prepared by reacting the cyclooctatriene 1,4-$(Me_3Si)_2C_8H_8$ with the elemental lanthanides and 1,4-diazadienes. As shown by NMR techniques, the interesting feature of these complexes is that by using the same reaction pathway the samarium complex is in the oxidation state +3, whereas the corresponding ytterbium compound is only divalent.[71] The silylated and thus very bulky cyclooctatetraene dianion provides higher solubility and often better crystallinity to organolanthanide derivatives relative to the parent C_8H_8 complexes.



(8)

Recently, by using $[Li_2(THF)_n][1,4\text{-}(o\text{-}Me_2N\text{-}C_6H_4Me_2Si)_2\text{-}C_8H_6]$ (**4**) the first donor-functionalized lanthanide cyclooctatetraene complexes were prepared. Transmetallation of **4** with anhydrous $NdCl_3$ or $SmCl_3$ in a 2:1 stoichiometric ratio gave the sandwich complexes $[Li(diglyme)_2][Ln(1,4\text{-}R_2C_8H_6)_2]$ [Ln = Nd, Sm; R = *ortho*-(dimethylsilyl)-*N,N*-dimethylaniline] (Scheme 3).[72] The single crystal X-ray structures of both complexes show that the dimethylamino group of the aniline ring is turned away from the metal center (Figure 8). Obviously the metal atom is shielded by the two eight-membered rings of the ligand. Thus, neither intra- nor intermolecular coordination is observed in the solid state. The dimeric ionic half-sandwich complex $[Li(diglyme)_2][\{1,4\text{-}R_2C_8H_6\}_2Sm_2(\mu\text{-}Cl)_3]$ was synthesized by the reaction of **4** with $SmCl_3$ in a 1:1 stoichiometric ratio (Scheme 3).[73] The anion of the new complex is a unique example of a dimeric organolanthanide complex that is bridged by three chlorine atoms. In the solid state the donor functionality does not coordinate to the samarium center. As shown by spin lattice relaxation experiments there is a coordination of one amino group to the samarium atom in solution. Density Functional Theory (DFT) calculations show that this coordination might in principle be in an intramolecular fashion.[73]



Scheme 3

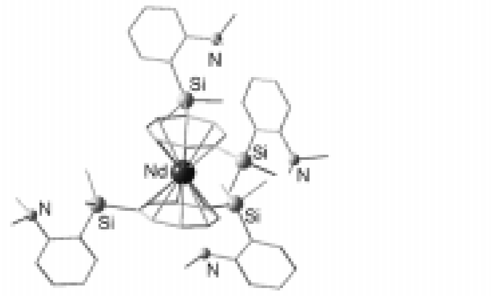
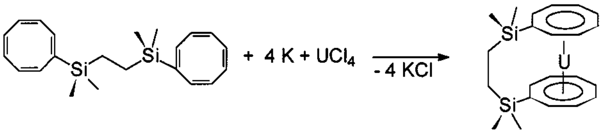


Figure 8. Crystal structure of the anion of $[Li(diglyme)_2][Nd(1,4\text{-}R_2C_8H_6)_2]$ [R = *ortho*-(dimethylsilyl)-*N,N*-dimethylaniline]

In contrast to the large number of alkyl-substituted actinocenes only a few silyl-substituted actinocenes are known. Complexes of composition $[An\{1,4\text{-}(Me_3Si)_2C_8H_6\}_2]$ (An = Th, U),[68] $[An\{1,4\text{-}(Me_2tBuSi)_2C_8H_6\}_2]$ (An = Th, U),[62] and $[An\{1,3,6\text{-}(Me_3Si)_3C_8H_5\}_2]_2$ (An = Th, U, Np)[63,74] were obtained by reaction of $AnCl_4$ with **1a,b** and **2**, respectively. Reduction of $[An\{1,4\text{-}(Me_2tBuSi)_2C_8H_6\}_2]$ by potassium in DME yielded the anionic compounds $[K(DME_2)][An\{1,4\text{-}(Me_2tBuSi)_2C_8H_6\}_2]$, which were crystallographically characterized.[62] The thorium complex was the first Th^{III} sandwich to be discovered. EPR spectroscopic studies indicated that the molecule possesses a $6d^1$ ground state.

The first bridged uranocene is also a silyl-substituted complex. The ligand 1,2-bis(cyclooctatetraenyldimethylsilyl)ethane, $C_8H_7\text{-}Si(Me_2)\text{-}CH_2CH_2\text{-}Si(Me_2)\text{-}C_8H_7$, was prepared by the reaction of LiC_8H_7 and 1,2-bis(chlorodimethylsilyl)ethane. Further reaction of the ligand with potassium and UCl_4 gave the corresponding bridged uranocene [Equation (9)].[75] The only known half-sandwich complex of the actinides with silyl-substituted cyclooctatetraenes is $[\{1,4\text{-}(Me_3Si)_2C_8H_6\}U(BH_4)_2]$ which was obtained from **1a** and $[UCl_2(BH_4)_2]$.[68]



(9)

3. Conclusion

The recent developments in the chemistry of substituted cyclooctatetraenes has shown that silyl-substituted cyclooctatetraenes are becoming more and more popular in *f*-metal chemistry. There are several reasons for this development. In contrast to alkyl-substituted cyclooctatetraenes the silylated ligands are easily accessible from cheap starting materials. As observed for highly substituted alkyl complexes, the silyl groups are bulky enough to shield the highly reactive metal centers. Thus, more stable complexes are available. Furthermore, due to the silyl groups the solubility of the resulting metal complexes is increased. This facilitates the purification of some of the complexes such as half-sandwich lanthanide halides. Additionally, in some cases the steric bulk of the substituents on the eight-membered ring led to new coordination modes on the center metal. Finally, the introduction of the silicon atom facilitates the attachment of functional groups on to the ligand. Due to these advantages all recent publications on substituted cyclooctatetraenes deal exclusively with the silyl-substituted form.

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