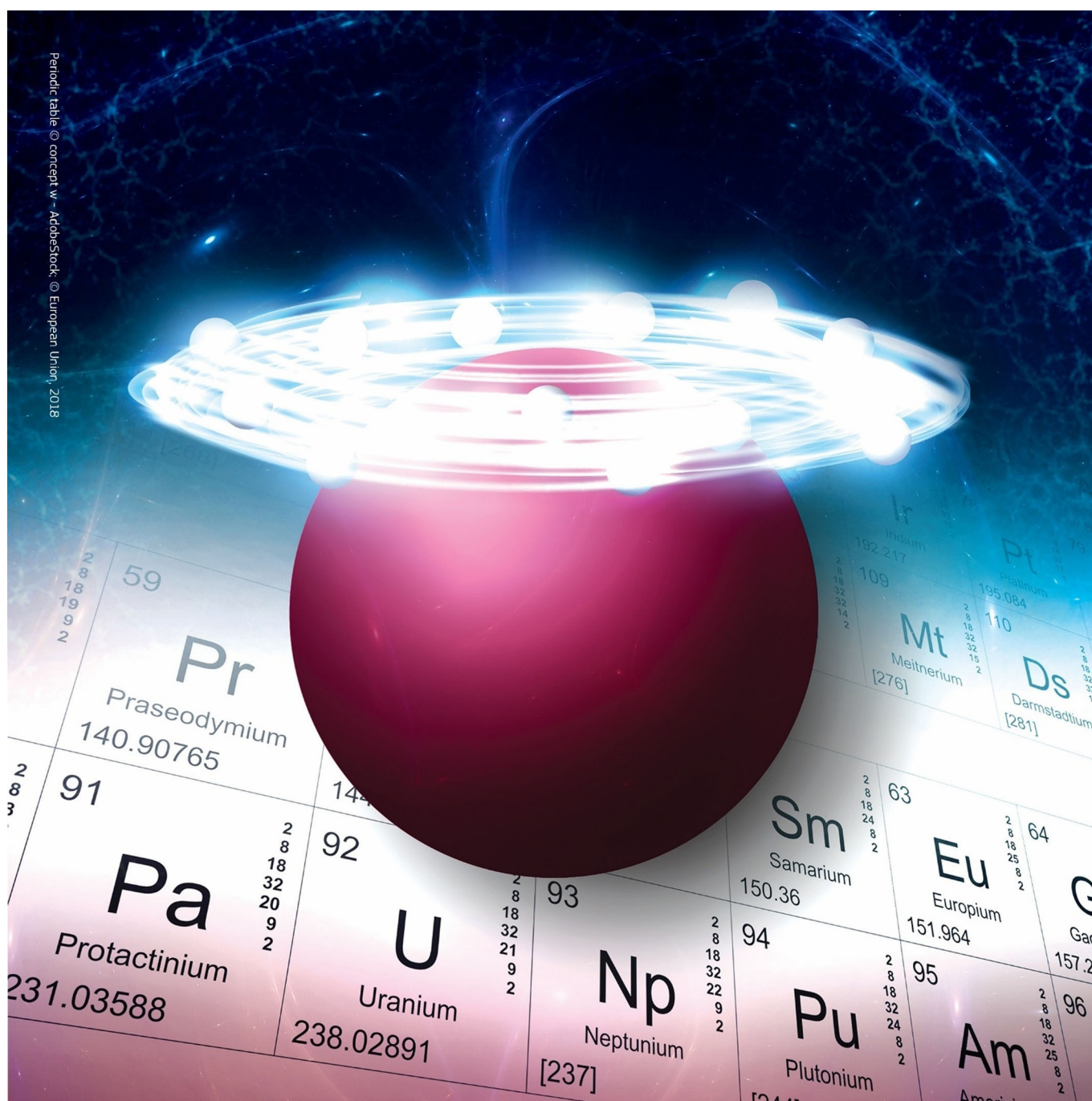


f-Block Elements

# Actinide Organometallic Complexes with $\pi$ -Ligands

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*Dedicated to Professor Bill Evans to the occasion of his 70th birthday*



**Abstract:** Recent developments and results from the organometallic chemistry of the actinides are reviewed. In the last one and a half years the structural data of about 15 organometallic complexes of transuranium actinides (Np or Pu) have been published, all involving  $\pi$ -ligands in the coordination sphere of the metal ion. On the basis of these data, a comparison of these molecules is presented. Depending on

the steric demands of the ligands, effects like the actinide contraction seem to be stronger or weaker in the structural features. This indicates that the interplay between the actinide ion and the  $\pi$ -ligand is rather flexible, enabling the formation of stable bonds over a broad range of actinide ion oxidation states.

## 1. Introduction

The organometallic chemistry of carbocyclic ligands with  $\pi$ -orbitals bonded to f-block elements developed soon after the discovery of Ferrocene in 1951. The milestone structural analysis of ferrocene in 1952 revealed the novel cyclopentadienyl ligand  $C_5H_5^-$ , or Cp, adopted a then novel but now typical  $\eta^5$ -coordination mode.<sup>[1]</sup> In the intervening years the Cp- ligand has been transferred to almost every metal in the periodic table resulting in a plethora of metal complexes.

In 1956 the first organometallic complex of an actinide was reported  $[U(Cp)_3Cl]$ ,<sup>[2]</sup> but then the chemistry was extended to the systems  $[An(Cp)_4]$ .<sup>[3]</sup> Structural characterization via single crystal X-ray diffraction followed later: the solid state structure of  $[U(Cp)_3Cl]$  was published in 1965.<sup>[4]</sup>

Of course over the last few decades several reviews have been published.<sup>[5]</sup> For example the annual survey on organometallic chemistry of lanthanides and actinides,<sup>[5a-e]</sup> and the book "Organometallic and Coordination Chemistry of the Actinides".<sup>[5f]</sup> Recently Evans summarized the lanthanide(II) and actinide(II) chemistry,<sup>[5g]</sup> N. Kaltsoyannis reviewed the theoretical approach to transuranic computational chemistry,<sup>[5h]</sup> M. Ephritikhine highlighted the rich uranium and thorium Cp-chemistry,<sup>[5i]</sup> and the organometallic neptunium chemistry was reviewed by P. Arnold.<sup>[5j]</sup>

Our aim for this present Minireview here is to focus more on the recent progress in structure determination of transuranium elements containing a Cp or the dianionic cyclooctatetradienide (COT) ligand in the An coordination sphere.

Actually about 1200 compounds containing a U–C interaction have been structurally characterized and deposited in the Cambridge Crystallographic Data Centre (CCDC)<sup>[6]</sup> compared to 15 compounds for Np<sup>[7]</sup> and 4 for Pu.<sup>[8]</sup> This disparate contrast is due to the limited access to radioactive elements because of

cost intensive radiation protection measures combined with the necessary licensing and safeguards control. Most of the structurally characterized Np organometallic complexes have been published since 2016;<sup>[7]</sup> for Pu all four solid structures based on single crystal data of organometallic compounds arise from 2017 and 2018.<sup>[8]</sup> The Np, Pu compounds will be analysed with their uranium or lanthanides analogues in order to identify trends in bonding which will then be discussed below.

In the following we will divide the discussion into two parts depending on the nature of the ligand: one part for Cp ligands and the 2<sup>nd</sup> for COT based systems.

## 2. Cyclopentadienide-Derived Ligands (Cp-ligands)


Uranium complexes with the Cp ligand in  $\pi$ - $\eta^5$ -coordination have been studied for more than 60 years. About 80 of these compounds containing the pure Cp ligand have been structurally characterized compared to more than 600 containing the bulkier Cp\* ligand (Cp\*: pentamethylcyclopentadienide). The difference here results from the fact that the larger Cp\* is able to shield the uranium more efficiently than the unsubstituted Cp leading to a higher selectivity in chemical transformations. Within this context refer to the M. Ephritikhine review from 2013;<sup>[5i]</sup> here the focus will be on recent progress in transuranium complexes.

One could consider the soft,  $\pi$ -electron aromatic carbocyclic anions, such as Cp or COT as versatile ligands engaging their  $\pi$ -orbitals with different metal f orbitals.


With the Cp ligands in the coordination sphere of a uranium atom it is possible to stabilise for example carbene complexes with M=C interactions of 227 to 239 pm.<sup>[9]</sup> This compares to U–C single bond lengths which are found to be longer in the range between 245 and 255 pm.<sup>[10]</sup> Due to conjugative effects the U–C bond lengths in complexes with terminal bound acetylene are found to be shorter in the range of 234 to 244 pm.<sup>[11]</sup> This reflects already the ability of actinide ions, in this case uranium, to establish U–C bonds with varying character in bond strength and nature. Over the next few years one can expect the extension of the above-mentioned examples of the U–C linkages to transuranic chemistry. This is inspired by the need of both: the comparative analyses of fundamental bonding interactions and their relevance in establishing physical models for extended lattice actinide materials, for example carbide-based nuclear fuel.

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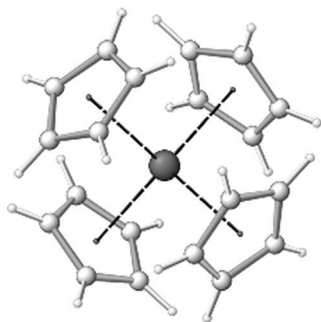
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## 2.1. [An(Cp)<sub>4</sub>]

At the beginning of the 1960's the complexes [An(Cp)<sub>4</sub>] have been reported<sup>[3]</sup> for the minor actinides from Th to Np. Upon to now the complexes [An(Cp)<sub>4</sub>] of Th, U, Np have been structurally characterised.<sup>[7a,12]</sup> In the solid state structures of these isostructural complexes all four Cp rings are equal in the tetragonal space group I4<sub>2</sub>m (Figure 1). This bonding scheme is unique to the large, relativistic actinide(IV) ions and the free Cp ligand and is unprecedented in any other region of the periodic table of elements.



**Figure 1.** Solid-state structure of [Np(Cp)<sub>4</sub>] with the four Cp rings in symmetrical  $\pi$ - $\eta^5$ -coordination.<sup>[7a]</sup>

Over the series [An(Cp)<sub>4</sub>] the actinide contraction is reflected in the reduction of the distances between metal and the centre of the Cp-rings (Table 1). The paramagnetism is nicely re-found in the <sup>1</sup>H NMR spectra where the [Th(Cp)<sub>4</sub>] acts as a diamagnetic reference signal.

Table 1. Selected data for the complexes [An(Cp) <sub>4</sub> ].			
	[Th(Cp) <sub>4</sub> ]	[U(Cp) <sub>4</sub> ]	[Np(Cp) <sub>4</sub> ]
M–Ct <sub>Cp</sub> (Å) <sup>[a]</sup>	2.606	2.588	2.551
a [Å] <sup>[b]</sup>	8.683(1)	8.635(2)	8.5980(1)
c [Å] <sup>[b]</sup>	10.644(3)	10.542(3)	10.5541(2)
<sup>1</sup> H NMR (ppm)	6.41	–12.79	–16.0

Standard deviations in parentheses. [a] Ct<sub>Cp</sub>: idealised position of centre of Cp ring. [b] Cell parameters.

In the literature the solid state structure of K[Np(Cp)<sub>4</sub>] is reported.<sup>[7a]</sup> Here the solid state the structure motif of [Np(Cp)<sub>4</sub>] with four Cp rings in  $\eta^5$ -coordination is established in a Np<sup>III</sup> complex. The mean centre of the Cp ring to Np distance in K[Np(Cp)<sub>4</sub>] is 2.635(1) Å and about 0.08 Å longer than found for the compound [Np(Cp)<sub>4</sub>] (Table 1). This is attributed to the change in the ionic radii from Np<sup>III</sup> to Np<sup>IV</sup> in an otherwise identical coordination environment as in this case for the four  $\pi$ - $\eta^5$ -coordinated Cp ligands.

There are only three comparable structure reports on complexes having four Cp rings in  $\eta^5$ -coordination: two ansa-Cp/indenyl complexes of Y(III) and Ce<sup>IV</sup>; and Evans reported on ([K(2.2.2-cryptand)]{La[Cp(TMS)]<sub>4</sub>})<sup>[13]</sup>

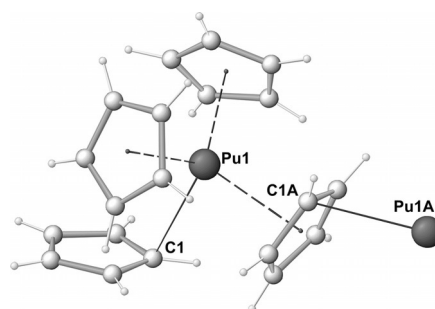
## 2.2. [An(Cp)<sub>3</sub>] and [Ln(Cp)<sub>3</sub>]

The complexes [An(Cp)<sub>3</sub>] started to be reported in the literature by the late 1960's covering a broad range of actinides from Th to Cf.<sup>[14]</sup> This is due to the fact that the oxidation state +III, even if it is not the most stable for the early actinides, exists for practically the entire actinide series.

There are only a few reports on [An(Cp)<sub>3</sub>] complexes for transuranium elements which include their structural data. Whereas Lewis base adducts of [U(Cp)<sub>3</sub>] are well known, only some examples exist for [Np(Cp)<sub>3</sub>].<sup>[7a]</sup> For [Pu(Cp)<sub>3</sub>] up to present only its Lewis base free solid state structure is published.<sup>[8c]</sup>

[Ln(Cp)<sub>3</sub>] (Ln: lanthanide) type complexes have been previously studied, not stabilized by Lewis base adduct formation.<sup>[15]</sup> A brief analysis of these has been done in<sup>[8c]</sup> coming to the conclusion that there are experimental indications for a stronger covalency in the system [An(Cp)<sub>3</sub>] compared with [Ln(Cp)<sub>3</sub>]. However, the need for more experimental data still exists here.

The complexes [Ln(Cp)<sub>3</sub>] exhibit in the solid a polymeric zig-zag structure motif.<sup>[15]</sup> The same is found for their An analogues [An(Cp)<sub>3</sub>] (Figure 2).<sup>[8c]</sup> In all structures all Cp rings show  $\eta^5$ -coordination. Due to the Lewis acidity of the metals an additional  $\eta^1$ -coordination of one Cp ring to a neighbored metal is formed ending in a  $\mu$ - $\eta^5, \eta^1$ -coordination of this ring (Figure 2). This leads to the polymeric zig-zag structure motif in the solid. For the solid state structure of [La(Cp)<sub>3</sub>] a  $\mu$ - $\eta^5, \eta^2$ -coordination was discussed.<sup>[15b]</sup> Whereas all other reported



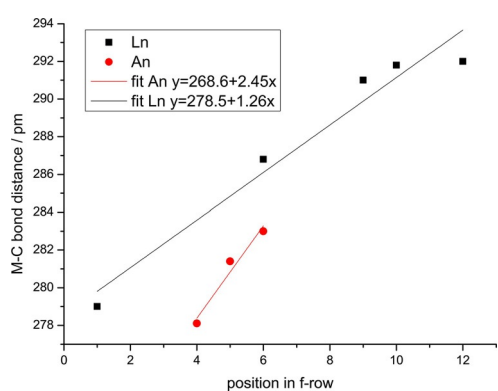
**Figure 2.** Solid-state structure of [An(Cp)<sub>3</sub>] with the three Cp rings in  $\pi$ - $\eta^5$ -coordination, one of them establishing  $\mu$ - $\eta^5, \eta^1$ -coordination leading to the polymeric solid state structure.<sup>[8c]</sup>

At the end of 1994 Olaf concluded his PhD at the University of Heidelberg with Prof. G. Huttner. Then he joined the Bertini group in Florence until March 1997. Afterwards he worked at the Forschungszentrum Karlsruhe (today: KIT) in the field of catalysis and process development. In 2011 he moved to the JRC-Karlsruhe (formerly: ITU) where since 2013 he is employed as research official in the field of syntheses and characterisation.



solid state structures for the complexes  $[M(\text{Cp})_3]$  ( $M$ : Ln, An) show the same polymeric zig-zag structure motif with one of the Cp rings in  $\mu\text{-}\eta^5, \eta^1$ -coordination.

Analysis of the data shows that besides a lot of common behaviour there are slight but possibly meaningful differences between lanthanides and actinides in their complexes  $[M(\text{Cp})_3]$ . Along the series from one element to the next heavier element the  $\pi\text{-}\eta^5$ -coordinated Cp rings move closer to the metal(III) ion centres by about  $0.018 \text{ \AA}$ .<sup>[8c]</sup> In parallel the  $\text{An-C}(\mu\text{-}\eta^1)$  bond length increases by  $0.05 \text{ \AA}$  from  $2.78(2) \text{ \AA}$  for  $[\text{U}(\text{Cp})_3]$  to  $2.83(2) \text{ \AA}$  for its Pu analogue (Figure 3).<sup>[8c]</sup> This elongation of  $0.05 \text{ \AA}$  seems to be about double the elongation effect that we see in the corresponding lanthanide complexes  $[\text{Ln}(\text{Cp})_3]$ . DFT calculations showed that the energy potential hyperface of the complexes  $[\text{An}(\text{Cp})_3]$  is very flat, so that small changes in energy could already influence significantly the solid state structures.<sup>[8c]</sup>



**Figure 3.**  $\eta^1$ -M-C distance for the  $\mu\text{-}\eta^5, \eta^1$ -coordinated C atom in the complexes  $[\text{M}(\text{Cp})_3]$  ( $M$ : Ln, An).<sup>[8c]</sup>

Finally, 50 years after the first reports our understanding of the bonding in the complexes  $[\text{An}(\text{Cp})_3]$  is still not complete. More data are necessary combined with powerful modelling.

### 2.3. Substituted Cp rings as ligands

Among all reported actinide complexes  $[\text{An}(\text{CpR})_n]$  stabilised by substituted Cp ligands about two third contain the Cp\* ligand. Again, within this context refer to the M. Ehtrikhine review from 2013,<sup>[5j]</sup> here we will focus more on a comparison with transuranium complexes.

### 2.4. Bis-trimethylsilylcyclopentadienide stabilised complexes, $[\text{An}(\text{Cp}^*)_3]$ and $[\text{An}(\text{Cp}^{\prime\prime})_3]^-$

Over the last five years, the mono- and bis-silylated cyclopentadienyl ligands (Cp':  $\text{C}_5\text{H}_4(\text{SiMe})_3^-$ , Cp'':  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2^-$ , or its congeners like  $\text{C}_5\text{H}_3(\text{SiMe}_2\text{R})_2^-$ ), have played a key role in extending the low-valence chemistry from the lanthanides to the 5f elements.<sup>[5g]</sup> They allowed the isolation and characterization of novel anionic actinide complexes, which stabilize the formal +II oxidation state of the actinide. These landmark molecules originated from previous research in the chemistry of lantha-

nides. It was highlighted recently by W. J. Evans.<sup>[5g]</sup> The main difference between Cp' and Cp'' anions is there is less steric hindrance for the mono-substituted Cp'. Accordingly  $[\text{U}(\text{Cp}')_3]$  adducts are described in the literature<sup>[16f]</sup> even involving bridging co-ligands like pyrazine.<sup>[16d,e]</sup> A metal-metal bond is established in  $[(\text{Cp}')_3\text{U-Ga}(\text{Cp})]$ .<sup>[16f]</sup> In contrast adducts on  $[\text{An}(\text{Cp}')_3]$  are described only for the larger Th.

In analogy to the lanthanides the first examples of actinide +II complexes were synthesized and characterized:  $[\text{U}(\text{Cp}')_3]\text{K}^*$ ,  $[\text{Th}(\text{Cp}'')_3]\text{K}^*$ ,  $[\text{Pu}(\text{Cp}'')_3]\text{K}^*$ , and only recently  $[\text{Np}(\text{Cp}'')_3]\text{K}^*$  ( $\text{K}^* = [\text{K}(18\text{-c-6})(\text{THF})_2]^+$  or  $[\text{K}(2.2.2\text{-cryptand})]^+$ ).<sup>[7b,8a,17]</sup> We had one crystal of the  $[\text{Np}(\text{Cp}')_3]\text{K}^*$  on our diffractometer but its diffractions properties were too poor to be analysed.<sup>[7a]</sup>

The solid states structures of the complexes  $[\text{Th}(\text{Cp}'')_3]^-$ ,  $[\text{U}(\text{Cp}'')_3]^-$ ,  $[\text{Np}(\text{Cp}'')_3]^-$ , and  $[\text{Pu}(\text{Cp}'')_3]^-$  will be compared to those of the  $\text{An}^{\text{III}}$  complexes  $[\text{An}(\text{Cp}(\text{SiMe}_3)_n)_3]$  before reduction<sup>[18]</sup> showing generally similar structural features (Table 2):

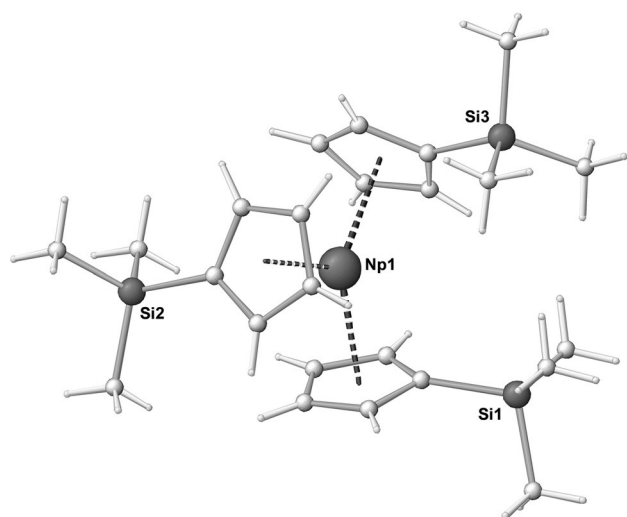
**Table 2.** selected distances and deviations from plane (Å) of complexes  $\text{An}(\text{CpR})_3$  and  $\{\text{An}(\text{CpR})_3\}^-$  (R = silyl substituents).

	M-Ct [Å] <sup>[a]</sup>	Deviation from plane M-Ct <sup>[b]</sup>	Ox. state
$\text{Th}(\text{Cp}^*)_3$	2.519(3)	< 0.003(1)	+III
$\text{Th}(\text{C}_5\text{H}_3(\text{SiMe}_2\text{Bu})_2)_3$	2.532(1)	0.004(1)	+III
$\text{U}(\text{Cp}')_3$	2.51(3)	0.05(3)	+III
$\text{U}(\text{Cp}'')_3$	2.54(2)	0.02(1)	+III
$\text{U}(\text{C}_5\text{Me}_4(\text{SiMe}_3))_3$	2.63(2)	0.03(2)	+III
$\text{Np}(\text{Cp}')_3$	2.481(2)	0.04(2)	+III
$\text{Pu}(\text{Cp}'')_3$	2.50(7)	0.05(1)	+III
$[\text{K}(2.2.2\text{-cryptand})][\text{Th}(\text{Cp}'')_3]$	2.52(1)	0.003(1)	+II
$[\text{K}(18\text{-c-6})(\text{THF})_2][\text{Th}(\text{Cp}'')_3]$	2.526(2)	0.008(4)	+II
$[\text{K}(2.2.2\text{-crypt})][\text{U}(\text{Cp}')_3]$	2.521(7)	0.012(7)	+II
$[\text{K}(2.2.2\text{-crypt})][\text{Np}(\text{Cp}'')_3]$	2.528(11)	0.017(7)	+II
$[\text{K}(2.2.2\text{-crypt})][\text{Pu}(\text{Cp}'')_3]$	2.52(1)	0.006(3)	+II

Cp':  $\text{C}_5\text{H}_4(\text{SiMe})_3$ , Cp'':  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ . Standard deviations based on statistic evaluation in parentheses. [a] Ct: idealised position of centre of Cp ring, mean value. [b] Average deviation for the four atoms forming the mean plane built by the three centres of the coordinated Cp rings and the central metal ion.

Whereas in the solid state for the pure Cp complexes  $[\text{AnCp}_3]$  a polymeric structure motif is expressed, this is not the case for the silyl-substituted Cp ligands. This might be due to the higher electron density of the substituted Cp ligands giving rise to a higher electron transfer to the Lewis acidic actinide ion or simply due to higher steric demands of the ligands. According to the  $\eta^5$ -coordination of the three Cp rings a trigonal planar arrangement of the Cp rings is established around the metal (Figure 4). This is reflected in the structural data of all the complexes  $\text{An}(\text{Cp}^{\text{R}})_3$  and  $[\text{An}(\text{Cp}^{\text{R}})_3]^-$  (R = silyl group) in their low deviation from the plane formed by the centroids of three Cp rings and the central metal atom (Table 2). This deviation for the complexes in Table 2 is maximal  $0.05 \text{ \AA}$  but in general lower.

The distances between the silylated Cp ligands and the central actinide atoms are most easily expressed in the distance between the centre of the Cp rings and the metal atom itself



**Figure 4.** View to the molecular structure of  $\text{Np}(\text{Cp}')_3$  in the crystal showing the trigonal planar arrangement of the three  $\text{Cp}'$  ligands around the  $\text{Np}^{\text{III}}$  centre ( $\text{Cp}'$ :  $\text{C}_5\text{H}_4(\text{SiMe}_3)_3^-$ ).<sup>[7a]</sup>

(Table 2). Looking at them no real trend can be observed (Table 2); they cover a range between 2.481(1) (in  $[\text{Np}(\text{Cp}')_3]$ ) and 2.567(6) Å (for  $[\text{U}(\text{Cp}')_3]\text{Na}$ ). One cannot really observe an effect dedicated to a change of the ionic radii from +III to +II. The steric influence on the distance between the actinide ion and the Cp ring is seen more clearly: the largest value with 2.63(2) Å is observed for the  $\text{U}^{\text{III}}$  complex  $\{\text{U}[\text{CpMe}_4(\text{SiMe}_3)_3]_3\}$  with three sterically demanding ligands in the coordination sphere of the metal ion.

In case of all lanthanides the complexes of type  $[\text{Ln}(\text{Cp}')_3]$  and  $[\text{Ln}(\text{Cp}')_3]\text{K}^*$  are known and their structural features have been summarized in Evans' review.<sup>[5g]</sup> Comparison of their data to the ones here for the actinides shows: for the actinides no real indication can be found for actinide contraction or change in ionic radii (both reflected in the An-Ct distance, Table 2). For the lanthanides this contraction of around 0.2 Å going from La to Lu is well observed for both  $[\text{Ln}(\text{Cp}')_3]$  and  $[\text{Ln}(\text{Cp}')_3]\text{K}^*$ .<sup>[5g]</sup> Additional analysis of the lanthanide data show that there is an increase of the ionic radius of about 0.03 Å on reduction of  $\text{Ln}^{\text{III}}$  in  $[\text{Ln}(\text{Cp}')_3]$  to its  $\text{Ln}^{\text{II}}$  homologue.

Analysis of the experimental data of the actinides summarised in Table 2 create the impression that there is a high flexibility in the bonding between the Cp ligands on one side and the actinide ions on the other side. Changes of ionic radii possibly due to actinide contraction or reduction seem to be less structure determining. To verify this statement and to understand in detail the differences between their lanthanide analogues, more experimental data are needed as well as supporting necessary theoretical models.

The low oxidation state compounds of the actinides show of course a high reactivity towards electrophiles.<sup>[19]</sup> So  $\text{Th}(\text{Cp}')_3$  is able to activate and to react with white phosphorous, transferring electrons to it; or it reacts with  $\text{CO}_2$  or  $\text{CS}_2$  as well under electron transfer, reducing the  $\text{CO}_2$  to oxalate in the coordination sphere of the metal. Electrons also can be transferred to

organic molecules such as 4,4'-bipyridine or to pyridine itself, the latter one then undergoing C–C coupling reaction.

Actually, these electron transfer reactions have not been applied to Np or Pu, respectively.

### 3. Cyclooctatetradienide-Derived Ligands (COT ligands)

COT (cyclooctatetradienide,  $\text{C}_8\text{H}_8^{2-}$ ) has been used in the actinide chemistry for 50 years. The chemistry of uranocene  $[\text{U}(\text{COT})_2]$  and thorocene  $[\text{Th}(\text{COT})_2]$  is under continuous development<sup>[20]</sup> whereas preparative experiments on plutonocene or neptunocene derivatives have been quasi discontinued since the 1980s due to the necessary radiation safety regulations.<sup>[20a]</sup>

Accordingly, up to the present about 200 compounds with at least one COT ligand in the coordination sphere of the actinide have been described including the determination of their solid-state structures via single crystal X-ray diffraction. Np and Pu contribute each one determined single crystal XRD structure.

These facts show clearly that with the COT ligands the situation is comparable to the one for the Cp ligands: a lot is known for Th and U but little for Np and Pu.

#### 3.1. Actinocene complexes

The pure actinocene complexes with the two COT ligands in the coordination sphere of the actinide central atom have been described at the end of the 1960's and the beginning of the 1970's.<sup>[21]</sup> Structures were determined for Th, U, Np on single crystal data whereas the protactinocene structure was verified by powder diffraction.<sup>[7d, 22]</sup> Anionic complexes of the type  $\text{K}[\text{An}(\text{COT})_2]$  ( $\text{An} = \text{Np}, \text{Pu}$ ) were reported,<sup>[21d,e]</sup> structure elucidation proceeded via powder diffraction and spectroscopic methods.

The series of the neutral bis-COT  $\text{An}^{\text{IV}}$  complexes was extended to ring-substituted derivatives as  $[\text{An}(\text{EtCOT})_2]$ ,  $[\text{An}(n\text{-BuCOT})_2]$ , and  $[\text{An}(\text{Me}_4\text{COT})_2]$ .<sup>[23]</sup> As well structural data were obtained on several alkyl-substituted thoro- and uranocenes<sup>[24]</sup> as well as for ansa-actinocenes.<sup>[20d]</sup> However, as for these examples only data for Th or U exist, here a more detailed discussion will not be presented.

The pure actinocene complexes  $[\text{An}(\text{COT})_2]$  crystallise isostructurally from Th to Np in the oxidation state +IV. Single crystal structure data are available for  $[\text{Th}(\text{COT})_2]$ ,  $[\text{Np}(\text{COT})_2]$ , and  $[\text{U}(\text{COT})_2]$  (Table 3) whereas for  $[\text{Pa}(\text{COT})_2]$  its isostructural behaviour was shown by powder diffraction.<sup>[22]</sup>

However for Pu there is actually reported only one single crystal structure determined on the substituted  $\text{Pu}^{\text{IV}}$  actinocene  $\{\text{Pu}[\text{COT}(\text{SiMe}_3)_2]_2\}$  (Table 3).<sup>[25a]</sup> The comparable actinide complexes of Th and U are listed in Table 3 as well.<sup>[25]</sup> One can expect the publication of the data for the corresponding neptunocene derivative  $\{\text{Np}[\text{COT}(\text{SiMe}_3)_2]_2\}$  in the near future.

All actinocene derivatives show common structural features: the two COT ligands form with the central metal atom a close to linear arrangement (Figure 5, Table 3). The distances of the

Table 3. Selected distances (Å) and angles in the actinocenes.		
	M–Ct [Å] <sup>[a]</sup>	∠Ct–M–Ct [°]
[Th(COT) <sub>2</sub> ]	2.003	180
{Th[COT(SiMe <sub>2</sub> <sup>t</sup> Bu) <sub>2</sub> ] <sub>2</sub> }	1.998	173.2
{Th[COT(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> }	198.6/202.1	173.9
	198.7/199.9	172.9
{Th[COT(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> }	2.012/2.010	174.3/175.3
[U(COT) <sub>2</sub> ]	1.923	180
{U[COT(SiPh <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> }	1.938	168.6
{U[COT(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> }	1.913/1.921	173.0
{U[COT(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> }	1.942/1.944	174.3
	1.938/1.945	174.9
{U[COT(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> }	1.922/1.923	173.5
[Np(COT) <sub>2</sub> ]	1.898/1.908	180
{Pu[COT(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> }	1.905/1.891	176.7

[a] Ct: idealised position of centre of COT ring. Some entries exist in more than one modification, therefore the number of entries may differ.

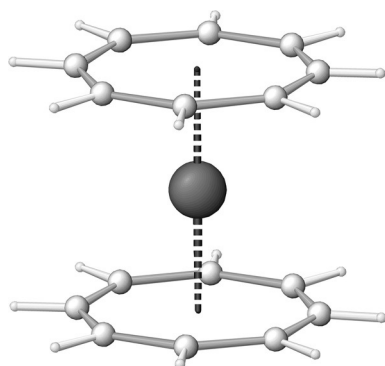


Figure 5. View to the molecular structure of [Np(COT)<sub>2</sub>] in the crystal showing the linear arrangement of the COT ligands around the metal.<sup>[7d]</sup>

COT rings to the metal are expressed in Table 3 by the distance between the geometrical centre of the COT ring and the actinide ion. As the COT ring is larger than the Cp ring, this distance is shorter for the COT than for the Cp. In contrast to the case of the already discussed {An[Cp(SiMe<sub>3</sub>)<sub>1,2</sub>]<sub>3</sub>} for the actinocenes some trends can be deduced: the distances Th–Ct (Table 3) are around 2.00 Å which is longer than those for the uranocenes with a mean value of around 1.935 Å. For Neptunocene the M–Ct distance is determined to 1.90 Å shorter again; which seems to be comparable to the plutonocene {Pu[COT(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>} with a higher steric demand. This approaching of the COT rings towards the An central ion can be attributed to the actinide contraction; a more detailed interpretation combining experimental data with computational comprehensive modelling like in<sup>[26]</sup> will contribute to our better understanding of the bonding in actinocenes. Recent progress on this was highlighted by Kaltsoyannis in 2018.<sup>[5h]</sup>

### 3.2. Actinocene chemistry

Like in the case for the An–Cp systems it is possible to reduce the An<sup>IV</sup> actinocene to their An<sup>III</sup> anionic analogues.<sup>[24c, 25f, 27]</sup> Again reduction proceeds more readily when electron-rich li-

gands such as silyl-substituted COT derivatives are present in the starting actinocene.

In the case of the actinocene complexes the actinide ions in the centre seem to be well shielded nevertheless Lewis base adducts are formed for Th (or U).<sup>[28]</sup> However, this chemistry needs to be developed further for Np or Pu.

### 3.3. Pentalene complexes

Some actinide pentalene complexes are reported always containing the pentalene ligand (C<sub>8</sub>H<sub>6</sub><sup>2-</sup>) in π-η<sup>8</sup>-coordination towards the actinide central atom.<sup>[29]</sup> However their role in actinide chemistry is not fully developed yet. For details of the coordination chemistry of the pentalene ligand please refer to a recent review by Cloke.<sup>[30]</sup>

### 3.4. Complexes containing COT-ligands and Cp\* ligands

Up to the present quite some complexes are described containing a Cp\* and a COT (or substituted COT) as π-ligands in the coordination sphere of the actinide, with other ligands or donors completing the coordination sphere. A rich actinide chemistry has been described involving the activation of small molecules like N<sub>2</sub>, CO<sub>2</sub>, CO, CS<sub>2</sub>, formation of azides and amides or oxides.<sup>[29b, 31]</sup> Some triple decker complexes with a COT ligand in a bridging mode between two [An(COT)(Cp\*)]-moieties have been isolated and characterised.<sup>[32]</sup> However, as this chemistry is actually limited to Th and U it will not be discussed in more detail here as comparable results for Np, Pu have not been determined yet.

## 4. Conclusions

Actinide chemistry involving π-ligands offers quite challenging possibilities. One could consider the π-ligands like Cp or COT as versatile; the relative large actinide ions also show flexibility, this is an ideal situation for a good interplay between them.

The actinide metal ion orbitals reach out far enough into space to establish excellent orbital overlapping with the π-orbitals of the ligands; it does not matter if the ligand is Cp or COT based. It seems that bonding interactions can be formed over a broad range of possible bond lengths.

The interplay between the actinide ions and the π-ligands, like Cp or COT, offers unique possibilities for studying in detail the nature of their bonding. The combination of experimental data with modern computational techniques will be the key for our understanding of the 5f/6d electron behaviour.

With the electron-rich silyl-substituted ligands, highly reactive actinide species in low oxidation states may be stabilised. These complexes have already shown their reactivity and unique reaction behaviour in many small-molecule activation reactions. It can be expected that this chemistry involving the π-ligands is further developed and extended now also for Np and Pu.

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## Conflict of interest

The authors declare no conflict of interest.

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