Neodymium and uranium borohydride complexes, precursors to cationic derivatives: comparison of 4f and 5f element complexes

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Abstract – $Nd(BH_4)_3(THF)_3$, **1**, reacted with KCp*, KP* and K_2COT (Cp* = η-C_5Me_5, P* = η-PC_4Me_4, COT = η-C_8H_8) to form (Cp*)$Nd(BH_4)_2(THF)_2$, **2**, [K(THF)][(P*)$_2Nd(BH_4)_2$], **3** and (COT)$Nd(BH_4)(THF)_2$, **4a**, respectively. The mixed ring complexes (COT)Nd(Cp*)(THF), **6**, and [(COT)Nd(P*)(THF)], **7a**, the alkoxide [(COT)Nd(OEt)(THF)]$_2$, **8**, and the thiolates [Na][(COT)Nd-(S^{t}Bu)$_2$], **11**, and [Na(THF)$_2$][{(COT)Nd}$_2$(S^{t}Bu)$_3$], **12**, were similarly synthesised from **4a** by reaction with the alkali metal salt of the respective ligand. Protonolysis of the metal–borohydride bonds in **4a** or (COT)$U(BH_4)_2(THF)$, with NEt_3HBPh_4 in THF afforded the cations [(COT)$Nd(THF)_4$][BPh$_4$], **5**, [(COT)U(BH$_4$)(THF)$_2$][BPh$_4$], **13**, and [(COT)U(HMPA)$_3$][BPh$_4$]$_2$, **14**. These cations allowed the preparation of (COT)U(P*)(HMPA)$_2$, **15**, [(COT)U(P*)(HMPA)$_2$][BPh$_4$], **16**, and [(COT)U(HMPA)$_3$][BPh$_4$], **17**. The X-ray crystal structures of [(COT)M(HMPA)$_3$][BPh$_4$], M = Nd, **18**, U, **17**, have been determined, allowing comparison of Nd(III) and U(III) derivatives. *To cite this article: S.M. Cendrowski-Guillaume et al., C. R. Chimie 5 (2002) 73–80* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

lanthanide / actinide / neodymium / uranium / borohydride / cation / cyclooctatetraenyl

Résumé – **Complexes borohydrures du néodyme et de l'uranium, précurseurs de dérivés cationiques : comparaison de complexes des éléments 4f et 5f.** Le borohydrure de néodyme $Nd(BH_4)_3(THF)_3$, **1**, est le précurseur de nouveaux dérivés organométalliques, notamment les premiers bisborohydrures organométalliques de lanthanide (Cp*)$Nd(BH_4)_2(THF)_2$, **2**, [K(THF)][(P*)$_2Nd(BH_4)_2$], **3a**, et le premier complexe borohydrure de lanthanide en série cyclooctatétraényle (COT)$Nd(BH_4)(THF)_2$, **4a** (Cp* = η-C_5Me_5, P* = η-PC_4Me_4, COT = η-C_8H_8). Ces complexes sont facilement isolés par substitution du ligand (BH$_4$) de **1** au moyen du sel alcalin de l'anion correspondant. De même, les complexes sandwiches mixtes, (COT)Nd(Cp*)(THF), **6**, et [(COT)Nd(P*)(THF)], **7a**, l'alcoolate [(COT)Nd(OEt)(THF)]$_2$, **8**, et les thiolates [Na][(COT)Nd-(S^{t}Bu)$_2$], **11**, et [Na(THF)$_2$][{(COT)Nd}$_2$(S^{t}Bu)$_3$], **12**, sont synthétisés à partir de **4a**. D'importance plus notoire, la protonolyse de la liaison métal–BH$_4$ par le sel d'ammonium acide NEt_3HBPh_4 permet d'accéder aux complexes cationiques. Les premiers cations organométalliques du néodyme et de l'uranium en série cyclooctatétraényle [(COT)$Nd(THF)_4$][BPh$_4$], **5**, [(COT)U(BH$_4$)(THF)$_2$][BPh$_4$], **13**, et l'unique dication organométallique d'un élément f [(COT)U(HMPA)$_3$][BPh$_4$]$_2$, **14**, sont ainsi isolés à partir de **4a** et de (COT)$U(BH_4)_2(THF)$, respectivement ; ils permettent de synthétiser des composés jusqu'alors inaccessibles, tels que le premier complexe de l'uranium trivalent en série cyclooctatétraényle [(COT)U(HMPA)$_3$][BPh$_4$], **17**. Les structures cristallines des composés analogues [(COT)M(HMPA)$_3$][BPh$_4$], avec M = Nd, **18**, U, **17**, et [(COT)U(HMPA)$_3$][BPh$_4$]$_2$ sont comparées. *Pour citer cet article : S.M. Cendrowski-Guillaume et al., C. R. Chimie 5 (2002) 73–80* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

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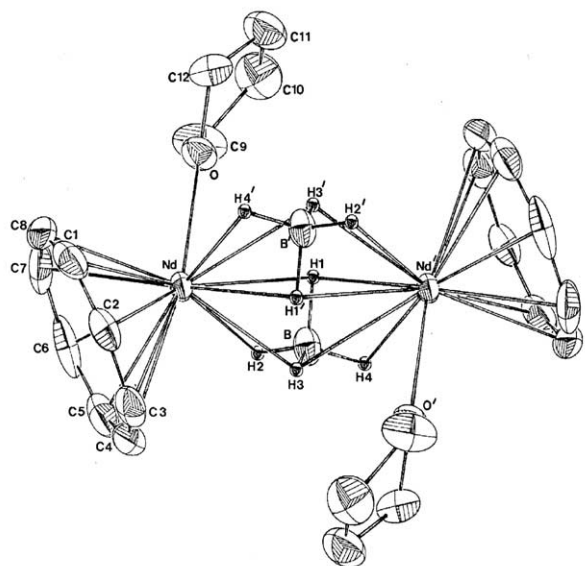
1. Introduction

Although their chemistry has long remained unexplored, trivalent lanthanide borohydrides $Ln(BH_4)_3(THF)_x$ (Ln = lanthanide, THF = tetrahydrofuran), as opposed to the commercially available lanthanides triflates and chlorides, are valuable starting reagents in 4f-elements chemistry. Indeed, several advantages are inherent to the use of a (BH_4) ligand [1–9]. First, it imparts quite some stability to the compounds and thus allows the preparation of products otherwise inaccessible. Although it is isosteric to the chloride anion, it behaves as a greater electron donor entity. Thus, sterically unsaturated complexes can be obtained and dimers, Lewis base adducts or "ate" species are not as readily observed as with chloride groups [8].

In contrast to the chloride and triflate ions, it can be clearly identified by ^1H NMR spectroscopy. Its coordination mode through bridging hydrogen atoms in a bidentate or tridentate fashion can be determined by infrared analyses and eventually further confirmed by X-ray diffraction studies [1–2]. While the borohydride ligand greatly promoted the actinide (especially uranium) chemistry over several decades (see for instance [3–9]), its impact on the lanthanide congeners remains negligible. We thus investigated the chemistry of neodymium(III) borohydride derivatives, because this lanthanide element has an ionic radius (0.983 Å) close to that of uranium (1.025 Å) [10]. We then used these new borohydride complexes as precursors to organometallic derivatives, especially f-elements cationic species. The reactivity of all these newly made compounds was studied in an effort to establish homologous series of neodymium and uranium products so as to set the bases for the comparison of lanthanide–actinide organometallic complexes.

2. Results and discussion

2.1. Neodymium borohydride complexes

Substitution of the borohydride groups in $Nd(BH_4)_3(THF)_3$, **1**, by several anionic reagents allowed the preparation of various organoneodymium derivatives. Upon reaction with cyclic ligands, such as the cyclopentadienyl and phospholyl potassium salts, KCp* (Cp* = η-C_5Me_5) and KP* (P* = η-PC_4Me_4), respectively, the first organometallic bisborohydride complexes of a trivalent lanthanide $(Cp*)Nd(BH_4)_2(THF)_2$, **2**, and $[K(THF)][(P*)_2Nd(BH_4)_2]$, **3a**, were quantitatively isolated, as illustrated in Fig. 1 [11]. While a neutral mono-(pentamethylcyclopentadienyl) compound, **2**, was obtained with the Cp* ligand, an anionic bis(tetramethylphospholyl) product, **3a**, was isolated when the P* group was used. Although both ligands are isosteric, formation of this 'ate' derivative **3a** is easily rationalised by the weaker electron donating ability of P* over Cp*. This feature of the phospholyl ligand has been previously highlighted in uranium coordination chemistry [12–14]. Addition of a crown-ether to **3a** allowed the preparation of $[K(18-C-6)(THF)_2][(P*)_2Nd(BH_4)_2]$, **3b**, the monomeric structure of which has been determined by X-ray crystallography [15]. Infrared spectra of **2** (strong: 2361, 2337, 2291, 2216 cm^{-1}) and **3b** (strong: 2415, 2363, 2332, 2198, 2130) are quite complex and suggest the presence of both bidentate and tridentate BH_4 units, supporting a monomeric structure in the solid state [1]. Complex **2** can be desolvated upon gentle heating under reduced pressure to form $(Cp*)Nd(BH_4)_2$, whose unique IR absorption at 2291 cm^{-1}, typical of bridging borohydride groups, is indicative of a polymeric structure in the solid state [1,16]. Complexes **3a** and **3b** are the latest addition to the series of bis(phospholyl) lanthanide(III) derivatives consisting of $[P*_2LnCl_2]^-$ (Ln = Y, Nd, Sm,

Fig. 1. Syntheses of neodymium borohydrides.

Fig. 2. Molecular structure of [(COT)Nd(BH$_4$)(THF)]$_2$, **4b**, with thermal ellipsoids drawn at the 30% probability level. Atoms labelled with primes are related to the non-primed atoms by the centre of symmetry. Reprinted with permission from Ref. [19]. Copyright The American Chemical Society.

Lu), (P*)$_2$Ln(CH{SiMe$_3$}$_2$) (Ln = Nd, Sm) and (P*)$_2$NdH [17,18].

Two borohydride groups in **1** can be simultaneously exchanged upon reaction with K$_2$COT (COT = η-C$_8$H$_8$) to afford the unique cyclooctatetraenyl borohydride compound of a lanthanide, (COT)Nd(BH$_4$)(THF)$_2$, **4a**, in 98% yield (Fig. 1) [11,19]. Again, the binding mode of the BH$_4$ unit was determined from the IR spectrum, which showed it to be tridentate non-bridging (sharp: 2424; broad: 2000 cm^{-1}) in a monomeric structure. During the crystallization of **4a** in benzene, one THF ligand dissociated upon dimerisation into [(COT)Nd(BH$_4$)(THF)]$_2$, **4b**, the crystal structure of which (Fig. 2) has been previously described in details [19]. The most distinctive feature of this structure is the unusual coordination mode of the bridging BH$_4$ ligands in a (μ$_3$-H)$_2$B(μ$_2$-H)$_2$ fashion, only once encountered in [(C$_5$H$_3$^{t}Bu$_2$)$_2$Ce(BH$_4$)]$_2$ [16] and further confirmed by the IR data (a unique broad strong band at 2255 cm^{-1}). Indeed, in f-element chemistry, bridging borohydride ligands are rather rare and usually coordinate the metallic centres in a (μ$_2$-H)$_2$B(μ$_2$-H)$_2$ mode [4, 20, 21].

2.2. Neodymium cyclooctatetraenyl complexes

The most important reactivity of these new neodymium borohydride complexes **2–4** has been unveiled by the protonolysis reaction of (COT)Nd(BH$_4$)(THF)$_2$, **4a**, with the acidic ammonium salt NEt$_3$HBPh$_4$ which afforded [(COT)Nd(THF)$_4$][BPh$_4$], **5**, in 75% yield (Fig. 1). The X-ray structure of this neodymium cation has been previously reported [19]. Direct syntheses of complexes **4a** or **5** from the triflate or chloride congeners of **1** were less selective than those involving borohydride ligands as a consequence of the greater solubility of triflate or chloride salts. Compound **5** could neither be prepared via cleavage of the Nd–BH$_4$ bond in **4a** by TlBPh$_4$ or AgBPh$_4$, a previously established route to cationic species from halide precursors [22–24]. The cationic derivative **5** was transformed back into **4a** by addition of a borohydride ligand (Fig. 1). The formation of [(COT)Nd(THF)$_4$][BPh$_4$], **5**, the sole example of a cationic (cyclooctatetraenyl)lanthanide complex, from the borohydride reagent **4a** clearly revealed the superiority of the borohydride ligand in 4f-element chemistry.

The mixed cyclooctatetraenyl–cyclopentadienyl or –phospholyl complexes (COT)Nd(Cp*)(THF), **6**, and [(COT)Nd(P*)(THF)], **7a**, were formed either by metathesis reaction of **2** with K$_2$COT or **4a** with KCp*, and **4a** with KP*, respectively, or by addition of these latter two potassium salts to **5** (Fig. 1). The phospholyl product **7a** lost the one THF molecule upon drying under vacuum and was thus isolated as a dimer [(COT)Nd(P*)]$_2$, **7b** (Fig. 1) [25]. This result is in agreement with the weaker electron-donating power of the P* group relative to the isosteric Cp*; desolvation of **7a** renders the neodymium centre electron-deficient, which consequently couples to another [(COT)Nd(P*)] fragment to form **7b**. These two compounds **6–7** represent the only mixed sandwich (cyclooctatetraenyl)neodymium complexes reported to date.

The first cyclooctatetraenyl neodymium complexes incorporating alkoxide and thiolate ligands [(COT)Nd(OEt)(THF)]$_2$, **8**, [Na][(COT)Nd(BH$_4$)(S^{t}Bu)], **9**, (COT)Nd(S^{t}Bu)(THF)$_x$, **10**, [Na][(COT)Nd(S^{t}Bu)$_2$], **11**, and [Na(THF)$_2$][{(COT)Nd}$_2$(S^{t}Bu)$_3$], **12**, were similarly obtained upon treatment of **4a** or **5** with NaOEt or NaS^{t}Bu (Fig. 3) [11]. While the dimeric alkoxide **8** could be isolated via both ways, the anionic **9** and neutral **10** monothiolate complexes were observed as intermediate during the formation of **11** from **4a** or **5**, respectively. The greater electron-donating ability of the alkoxide group compared to the thiolate ligand accounts for the anionic nature of **11** in contrast to **8**. The above two different routes to the neodymium alkoxide **8** represent alternative pathways to the previously established metathetical exchange between (COT)LnCl(THF)$_x$ and alkoxide anions [26–27]. The only three crystallographically characterised monocyclooctatetraenyl lanthanide alkoxides, [(COT)Ln(OR)(THF)]$_2$ (Ln = Nd, R = Et, **8**, previously presented [11]; Ln = Dy, R = (CH$_2$)$_3$CH=CH$_2$)
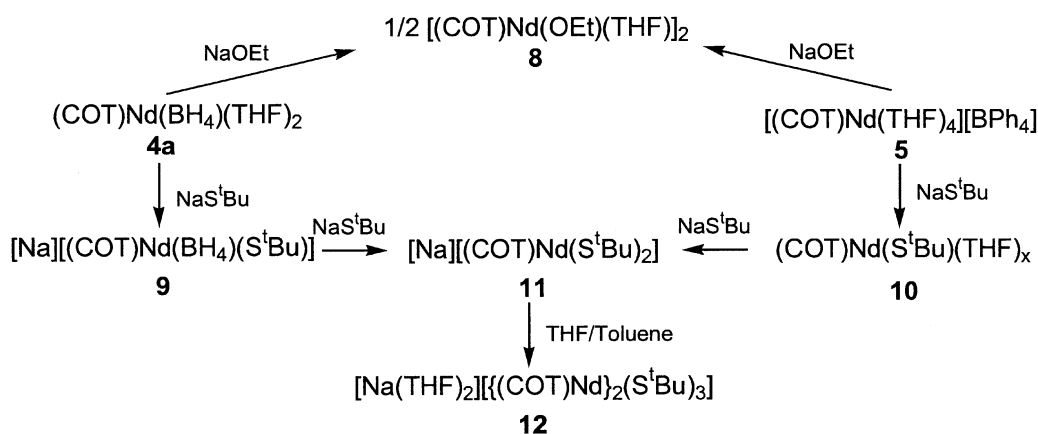
Fig. 3. Syntheses of cyclooctatetraenyl neodymium alkoxides and thiolates complexes.

and Ln = Y, R = Ph [13]); all exhibit a dimeric structure with two bridging alkoxide ligands. The sole organometallic neodymium thiolate complex **11** looses one S^tBu group and dimerises upon THF/toluene crystallisation to afford $[Na(THF)_2][\{(COT)Nd\}_2(S^tBu)_3]$, **12**, the X-ray structure of which is illustrated in Fig. 4 [11]. The particularity lies in the presence of three S^tBu groups bridging the two neodymium centres, of which two S^tBu are coordinated to the $[Na(THF)_2]$ moiety. The sodium salt in **12** remained firmly bound, compound **12** not evolving toward the formation of **10**.

Reactions of the cationic complex $[(COT)Nd(THF)_4][BPh_4]$, **5**, with these various substrates (NaCp*, KP*, NaOEt, NaS^tBu) gave high yields and were generally more selective than those involving the borohydride **4a**. Such an observation on
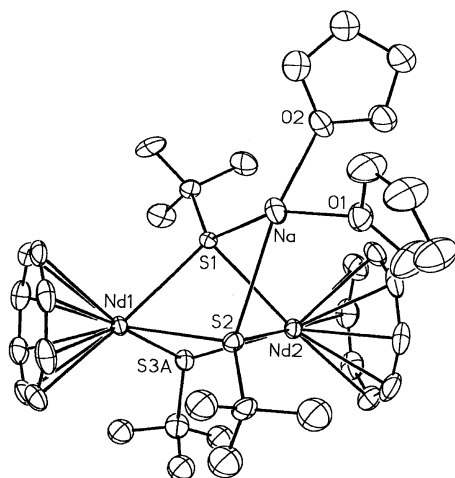

Fig. 4. Molecular structure of $[Na(THF)_2][\{(COT)Nd\}_2(S^tBu)_3]$, **12**, with thermal ellipsoids drawn at the 20% probability level. Only one of the two disordered ^tBu and S^tBu groups is represented. Reprinted with permission from Ref. [11]. Copyright The American Chemical Society.
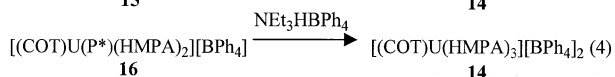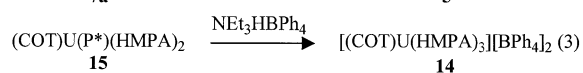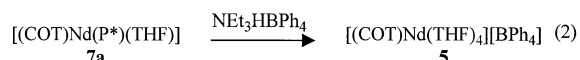
the superiority of cationic reagents has already been made in uranium chemistry [28–29]. Complex **5** thus appears as a versatile precursor to organometallic derivatives. Hence, it seemed important to further develop cationic derivatives of f-element in general. Besides, cationic species are now well recognised as key intermediates in many catalytic and polymerisation processes (see for instance [30–33]).

### 2.3. Neodymium and uranium cationic complexes

While organo-f-element cations have so far been most commonly formed by oxidation of divalent products, heterolytic rupture of a metal–halide or metal–carbon bond or protonolysis of a metal–carbon or metal–nitrogen bond [22–24,34–43], most uranium cations have been prepared following this latter approach [44–47]. The inorganic $[U(NEt_2)_3][BPh_4]$ and $[U(NEt_2)_2(THF)_3][BPh_4]_2$ and the organometallic $[(Cp*_2)U(NMe_2)(THF)][BPh_4]$ and $[(COT)U(NEt_2)(THF)_2][BPh_4]$ cationic amide compounds were thus obtained by protonolysis of the $U–NEt_2$ bond [44–47]. As mentioned above, protonolysis of the metal–borohydride bound in $(COT)Nd(BH_4)(THF)_2$, **4a**, by the ammonium salt NEt_3HBPh_4, afforded the unique example of a $[(COT)Ln]^+$ complex, $[(COT)Nd(THF)_4][BPh_4]$, **5**. In order to generalise this method to the synthesis of 4f- and 5f-element cations, we similarly transformed uranium borohydride precursors by protonolytic cleavage of the $U–BH_4$ bond.

Using $(COT)U(BH_4)_2(THF)$ [48] as starting reagent, we successfully isolated, upon treatment with NEt_3HBPh_4 in THF, the cyclooctatetraenyl uranium cations $[(COT)U(BH_4)(THF)_2][BPh_4]$, **13**, and $[(COT)U(HMPA)_3][BPh_4]_2$, **14** (HMPA = hexamethylphosphoramide) in 87% and 75% yield, respectively (Fig. 5) [49]. The monoprotonolysis experiment of $(COT)U(BH_4)_2(THF)$ to make the monocation **13** had to be performed at reflux temperature to speed up the
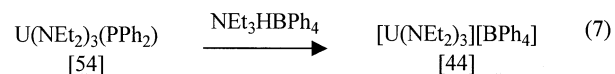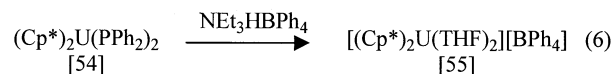
Fig. 5. Syntheses of cyclooctatetraenyl uranium compounds.

reaction, which only reached completion after three weeks at ambient temperature. Yet, a default of the ammonium reactant had to be used to ensure that the protonolysis would not proceed any further towards the formation of the dication **14**. Reaction times were lowered upon addition of a stronger Lewis base (L = OPPh$_3$, OP(NMe$_2$)$_3$) to the reaction mixture and the compounds analogues to **13**, [(COT)U(BH$_4$)(L)$_3$][BPh$_4$] (L = OPPh$_3$, HMPA), were observed as monitored by NMR spectroscopy. However, the selectivity was greatly affected by this modification: an inseparable mixture of the monocation and dication species was commonly observed in NMR spectra. Thus, only the THF adduct [(COT)U(BH$_4$)(THF)$_2$][BPh$_4$], **13**, could be isolated [49]. The IR spectrum of **13** displayed a strong absorption band centred at 2462 cm^{-1}, which is diagnostic of a bidentate BH$_4$ ligand [1]. Further reaction of the monocations [(COT)U(BH$_4$)(L)$_x$][BPh$_4$] ((L)$_x$ = (THF)$_2$, (OPPh$_3$)$_3$, (HMPA)$_3$), with an excess of NEt$_3$HBPh$_4$ in refluxing THF afforded the corresponding dications [(COT)U(L)$_x$][BPh$_4$]$_2$. As mentioned for the preparation of the monocations [(COT)U(BH$_4$)(L)$_x$][BPh$_4$] ((L)$_x$ = (THF)$_2$, (OPPh$_3$)$_3$, (HMPA)$_3$), the formation of the dication was faster with HMPA than with OPPh$_3$ or THF. For similar solubility properties, the dications could not be obtained pure from the corresponding monocations, themselves never fully consumed, except for the HMPA-solvated product [(COT)U(HMPA)$_3$][BPh$_4$]$_2$, **14**, for this latter precipitates in THF. Complex **14** could also be directly and cleanly prepared by protonolysis of both U-BH$_4$ bonds in the bisborohydride precursor (COT)U(BH$_4$)$_2$(THF) (Fig. 5) [49]. The crystal structure of this dication **14** was successfully resolved, as illustrated in Fig. 6, and has already been discussed [49].

The mixed ring compound (COT)(Cp)U(BH$_4$)(THF) [48] was also found to be easily and quantitatively transformed into the cation [(COT)(Cp)U(THF)$_2$] [BPh$_4$] (Cp = η-C$_5$H$_5$, [47]) (equation (1)) [50]. All these protonolysis reactions occurred with gas evolution,

$$(COT)U(Cp)(BH_4)(THF) \xrightarrow{NEt_3HBPh_4} [(COT)U(Cp)(THF)_2][BPh_4] \qquad (1)$$
[48] \qquad\qquad\qquad\qquad [47]

presumably hydrogen, along with the formation of the borane BH$_3$·NEt$_3$. In contrast, protonolysis of the uranium–amide bond in (COT)U(NEt$_2$)$_2$(THF) by NEt$_3$HBPh$_4$ only occurred once, precluding the formation of the dication [(COT)U]$^{+2}$ in this manner, and further highlighting the great potential of borohydride precursors in the synthesis of organometallic complexes. Besides these thorough investigations on the preparation of the organometallic cations [(COT)Nd(THF)$_4$][BPh$_4$], **5**, [(COT)U(BH$_4$)(THF)$_2$][BPh$_4$], **13**, and [(COT)U(HMPA)$_3$][BPh$_4$]$_2$, **14**, by protonolysis of the metal–borohydride bond [11,19,49], the inorganic [U(BH$_4$)$_2$(THF)$_5$][(BPh$_4$)] product was similarly prepared [51]. Compounds [(COT)U(BH$_4$)(THF)$_2$][BPh$_4$], **13**, and [(COT)U(HMPA)$_3$][BPh$_4$]$_2$, **14**, represent the sole example of a cationic organometallic borohydride and the unique organometallic dication of an f-element, respectively. Both cations **13** and **14** are valuable reagents for obtaining new neodymium and uranium derivatives (see below) [25,49,52,53].

Fig. 6. Molecular structure of one of the two independent dications [(COT)U(HMPA)$_3$]$^{+2}$, **14**, with thermal ellipsoids drawn at the 30% probability level. Reprinted with permission from Ref. [49]. Copyright The American Chemical Society.

Still using the same ammonium salt NEt_3HBPh_4, the metal-P* and metal-PPh$_2$ bonds were successfully cleaved in THF to make cationic derivatives [50]. Thereby, [(COT)Nd(P*)(THF)], **7a**, and its uranium analogue (COT)U(P*)(HMPA)$_2$, **15**, as well as the cationic congener [(COT)U(P*)(HMPA)$_2$][BPh$_4$], **16**, (see thereafter) easily gave, at room temperature, the corresponding cation, [(COT)Nd(THF)$_4$][BPh$_4$], **5**, and [(COT)U(HMPA)$_3$][BPh$_4$]$_2$, **14**, respectively, as observed from NMR analyses (equations (2)–(4)). In the case of the neutral phospholyl precursor **15**, the monocation **16**, initially formed,

$$[(COT)Nd(P*)(THF)] \xrightarrow{NEt_3HBPh_4} [(COT)Nd(THF)_4][BPh_4] \quad (2)$$
$$\textbf{7a} \qquad\qquad\qquad\qquad\qquad \textbf{5}$$

$$(COT)U(P*)(HMPA)_2 \xrightarrow{NEt_3HBPh_4} [(COT)U(HMPA)_3][BPh_4]_2 \quad (3)$$
$$\textbf{15} \qquad\qquad\qquad\qquad\qquad \textbf{14}$$

$$[(COT)U(P*)(HMPA)_2][BPh_4] \xrightarrow{NEt_3HBPh_4} [(COT)U(HMPA)_3][BPh_4]_2 \quad (4)$$
$$\textbf{16} \qquad\qquad\qquad\qquad\qquad \textbf{14}$$

further reacted with the acidic reactant to finally give the dication **14**. Protonolysis of the mixed borohydride-phospholyl complex (COT)U(BH$_4$)(P*)(THF) (equation (5)) [52], showed the uranium–phospholyl bond to be protonated more easily than the uranium-borohydride one,

$$(COT)U(BH_4)(P*)(THF) \xrightarrow{NEt_3HBPh_4} [(COT)U(BH_4)(THF)_2][BPh_4] \quad (5)$$
$$[52] \qquad\qquad\qquad\qquad\qquad \textbf{13}$$
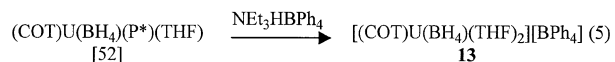
as the cationic borohydride complex **13** was formed selectively [50]. This trend should certainly be further confirmed on more complexes before any generalisation is driven. Finally, the uranium–phosphide bonds in complexes (Cp*)$_2$U(PPh$_2$)$_2$ and U(NEt$_2$)$_3$(PPh$_2$) [54] were also successfully protonated by NEt_3HBPh_4 to give the known compounds [(Cp*)$_2$U(THF)$_2$][BPh$_4$] [55] and [U(NEt$_2$)$_3$][BPh$_4$] [44], as monitored by NMR spectroscopy (equations (6) and (7)) [50]. Formation of [(Cp*)$_2$U(THF)$_2$]$^+$ proceeds through the initial

$$(Cp*)_2U(PPh_2)_2 \xrightarrow{NEt_3HBPh_4} [(Cp*)_2U(THF)_2][BPh_4] \quad (6)$$
$$[54] \qquad\qquad\qquad\qquad\qquad [55]$$

$$U(NEt_2)_3(PPh_2) \xrightarrow{NEt_3HBPh_4} [U(NEt_2)_3][BPh_4] \quad (7)$$
$$[54] \qquad\qquad\qquad\qquad\qquad [44]$$

uranium(IV) phosphido cation [(Cp*)$_2$U(PPh$_2$)(THF)$_x$][BPh$_4$], which undergoes a reductive elimination of Ph$_2$P–PPh$_2$. Protonolysis of f element–borohydride–phospholyl or –phosphide bond by NEt_3HBPh_4 has been shown to allow the access to a wide variety of cationic species, as illustrated with neodymium and uranium complexes in Figs 1 and 5 and equations (1)–(7).

2.4. Reactivity of the uranium dicationic complex

Besides checking the effectiveness of the protonolysis reaction of the metal–borohydride in making

cations, the U(IV) dication, [(COT)U(HMPA)$_3$][BPh$_4$]$_2$, **14**, was also prepared with the hope to access the previously never observed (cyclooctatetraenyl)U(III) derivatives. Reduction of the orange dication **14**, by sodium amalgam in THF smoothly afforded at 20 °C the monocation [(COT)U(HMPA)$_3$][BPh$_4$], **17**, as a green product in 88% yield [53]. This is the first cationic cyclooctatetraenyl trivalent uranium complex, the only other two [(COT)U(III)] derivatives being either anionic [K(diglyme)][U(η-C$_8$H$_7$Me)$_2$] [56], or neutral (COT)U(Cp*)(L) (L = HMPA, THF, 4,4'-dimethyl-2,2'-bipyridine) [25,57]. To date, the other cationic organometallic uranium(III) examples are limited to [(Cp*)$_2$U(THF)$_2$][BPh$_4$] [55], [U(η-2,4-Me$_2$-C$_5$H$_3$)$_2$][BPh$_4$] [58] and the trinuclear [U$_3$(η-C$_6$Me$_6$)$_3$(AlCl$_4$)$_3$Cl$_5$][AlCl$_4$] [59]. The crystal structure of the monocation **17** is presented in Fig. 7 (vide infra) [53]. Addition in THF of KP* to the dicationic uranium compound [(COT)U(HMPA)$_3$][BPh$_4$]$_2$, **14**, readily allowed the preparation of the sole cationic phospholyl uranium species [(COT)U(P*)(HMPA)$_2$][BPh$_4$], **16**, in 81% yield (Fig. 5) [52]. The similar reduction of **16** by Na/Hg amalgam in THF gave the first example of cyclooctatetraenyl uranium(III) phospholyl complex (COT)U(P*)(HMPA)$_2$, **15**, in 57 % yield [25,52].

2.5. Comparison of neodymium and uranium complexes

In an effort to compare structural and chemical properties of homologous 4f and 5f compounds, we prepared additional products to complete the series of [(COT)M(HMPA)$_3$]$^{+n}$ cations ($n = 1$, M = Nd, **18**, U, **17**; $n = 2$, M = U, **14**) [49, 53]. The neodymium compound **18** was synthesised by substitution of the THF ligands in [(COT)Nd(THF)$_4$][BPh$_4$] [11,19] and crystallised as a THF solvate **18**·THF [53]. All three complexes **14**, **17**, **18**·THF have been characterized by their crystal structures, which are very similar, as illustrated in Figs 6, 7 and 8, respectively. This allowed the direct comparison of the Nd(III) and U(III) compounds as well as that of U(III) and U(IV) derivatives [49, 53]. The most significant averaged parameters are reported in Table 1. All three cations adopt a three-legged piano-stool configuration, in which the angles do not greatly differ from one structure to another, with an average O–M–O angle of 85° and COT–M–O angle of 128° (COT = centroid of the C$_8$H$_8$ ring). The average metal–COT, metal–carbon and metal–oxygen bond distances are all shorter for Nd(III) compared to U(III) as well as for the U(IV) and U(III) couple, respectively. Comparison of the structures of the U(IV), **14**, and U(III), **17**, cations, whose metals display a 0.14 Å difference in their ionic radius, shows a significant difference in the bond lengths, from 0.1 to 0.2 Å. Note that this same
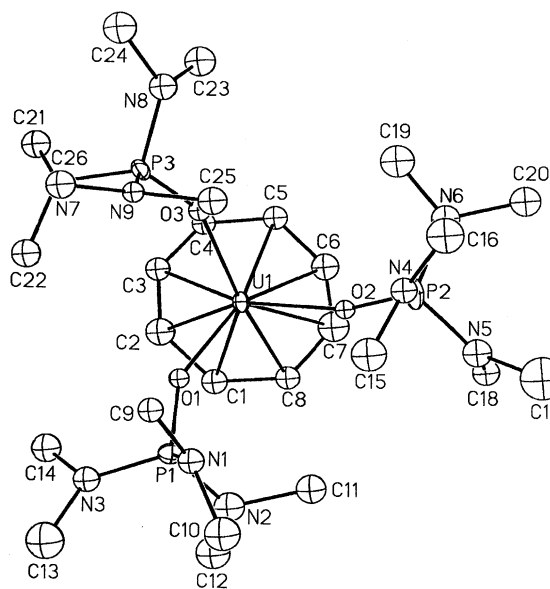
Fig. 7. Molecular structure of one of the two independent cations [(COT)U(HMPA)$_3$]$^+$, **17**, with thermal ellipsoids drawn at the 30% probability level. Reprinted with permission from Ref. [53]. Copyright Wiley-VCH.
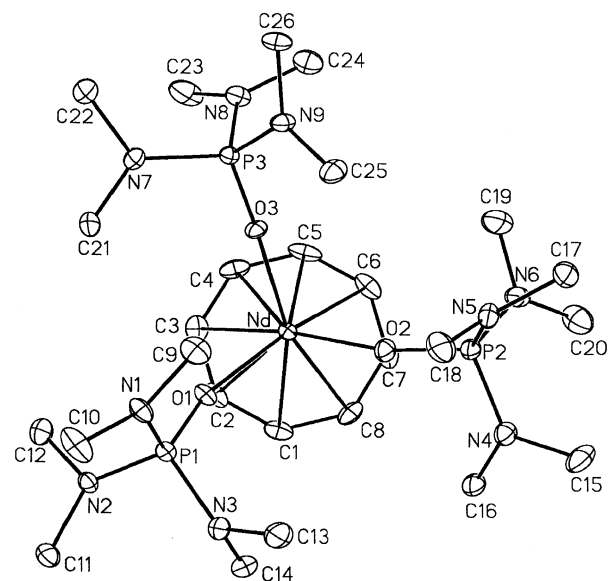

Fig. 8. Molecular structure of [(COT)Nd(HMPA)$_3$]$^+$, **18**·THF, with thermal ellipsoids drawn at the 30% probability level [53].

difference between the Nd(III), **18**·THF, and the U(III), **17**, complexes is of only 0.05 Å with a similar value for the difference in the ionic radii (0.04 Å). These trends follow the variation in the ionic radii of the metals Nd(III) (0.983 Å), U(III) (1.025 Å) and U(IV) (0.89 Å) [10]. Such comparative studies have previously been performed on a limited number of isostructural derivatives [60–63]. A better assessment of the differences in the nature of the chemical bonds in lanthanide and actinide compounds will require much more results. Also, a comparison of [(COT)M(Cp*)(HMPA)] and [(COT)M(P*)(HMPA)] complexes (M = Nd, U) will be presented in a forthcoming paper [25].

3. Conclusion

The borohydride ligand has been very valuable in developing organometallic complexes of neodymium(III). Substitution of the BH$_4$ ligand with alkali

metal salts of various anionic reagents allowed the isolation of several pentamethylcyclopentadienyl, tetramethylphospholyl and cyclooctatetraenyl products, **2–12**. Both (COT)Nd(BH$_4$)(THF)$_2$, **4a** and [(COT)Nd(THF)$_4$][BPh$_4$], **5**, were largely employed to extend the chemistry of mono(COT) neodymium compounds. The main advantage in using borohydride reagents was revealed by their protonolysis, which allowed access to highly valuable cationic species, such as the borohydride [(COT)U(BH$_4$)(THF)$_2$][BPh$_4$], **13**, the dication [(COT)U(HMPA)$_3$][BPh$_4$]$_2$, **14**, and trivalent uranium complex [(COT)U(HMPA)$_3$][BPh$_4$], **17**. This new method for preparing cations by protonolysis of a metal–BH$_4$ bond by the ammonium salt NEt$_3$HBPh$_4$, was further extended to the protonolysis of metal–P* and metal–PPh$_2$ bonds. The first cyclooctatetraenyl–uranium (III) derivatives, [(COT)U(HMPA)$_3$][BPh$_4$], **17**, and (COT)U(P*)(HMPA)$_2$, **15**, were formed by reduction of parent tetravalent uranium precursors **14** and [(COT)U(P*)(HMPA)$_2$][BPh$_4$], **16**. All the new products **2–18** were fully characterised, especially by IR, ^{1}H and ^{31}P NMR, elemental analyses and also by determination of the X-ray structure in many cases (**3b**, **4a**, **5**, **6**, **8**, **12**,

Table 1. Geometrical parameters of the cations [(COT)Nd(HMPA)$_3$]$^+$, **18**, [(COT)U(HMPA)$_3$]$^+$, **17**, and [(COT)U(HMPA)$_3$]$^{+2}$, **14** (COT = centroid of the C$_8$H$_8$ ring; M–C = metal–C$_8$H$_8$ ring carbon distance).

	[(COT)Nd(HMPA)$_3$]$^+$	[(COT)U(HMPA)$_3$]$^+$	[(COT)U(HMPA)$_3$]$^{+2}$
M–COT (Å)	1.98(1)	2.00(1)	1.92(2)
<M–C> (Å)	2.70(2)	2.71(4)	2.65(2)
<M–O> (Å)	2.36(3)	2.41(4)	2.22(1)
<O–M–O> (°)	85(1)	85(2)	87(1)
<COT–M–O> (°)	129(3)	129(3)	127(1)

14, **17**, **18**·THF [11,15,19,25,49,53]). Finally, homologous organometallic complexes (**14**, **17**, **18**) allowed the direct evaluation of chemical and structural differences between a 4f and a 5f element, an ongoing research [25].

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