

Inverse cycloheptatrienyl sandwich complexes of uranium and neodymium

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Reaction of UX_4 ($X = NEt_2$ or BH_4) with $K[C_7H_9]$ afforded the anionic complexes $K[X_3U(\mu-\eta^7:\eta^7-C_7H_7)UX_3]$ whereas treatment of $[Nd(BH_4)_3(thf)_2]$ ($thf =$ tetrahydrofuran) with $K[C_7H_9]$ gave the neutral compound $[(thf)(BH_4)_2Nd(\mu-\eta^7:\eta^7-C_7H_7)Nd(BH_4)(thf)_2]$. The formation of the cycloheptatrienyl ligand resulted from the disproportionation reaction $3 C_7H_9^- \longrightarrow C_7H_7^{3-} + 2 C_7H_{10}$. The crystal structure of $[(thf)(BH_4)_2Nd(\mu-\eta^7:\eta^7-C_7H_7)Nd(BH_4)(thf)_3]$, the first cycloheptatrienyl compound of a 4f element, has been determined.

The development of organometallic chemistry is coupled to the use of the aromatic hydrocarbon ligands, C_nH_m , and their substituted derivatives. The dominance of the η -cyclopentadienyl groups in this area is well established; this is particularly evident in organo-f-element chemistry since the synthesis of the first organo-lanthanide and -actinide complexes, $[An(\eta-C_5H_5)_3Cl]$ ($An = Th^1$ or U^2) and $[Ln(\eta-C_5H_5)_3]$ ($Ln = 4f$ element³). Whereas arene ligands have also played a major role in the chemistry of the d-transition metals, arene complexes of the f elements are relatively rare, even though it was recently demonstrated that the metal–ligand bond is very strong in the complexes $[Ln(\eta-C_6H_5Bu^1_{3-1,3,5})_2]$ ($Ln = Gd, Dy, Ho$ or Eu).⁴ The opposite situation is observed with η -cyclooctatetraene compounds; following the synthesis of $[An(\eta-C_8H_8)_2]$ ($An = U^5$ or Th^6) and $[Ln(\eta-C_8H_8)]$ ($Ln = Yb$ or Eu^7), the C_8H_8 group has become the second most important ligand in organo-f-element chemistry. In comparison with these C_nH_n ligands ($n = 5, 6$ or 8), the cycloheptatrienyl ligand has, for a long time, received little attention. Although the first η -cycloheptatrienyl compound $[Mo(\eta-C_7H_7)(CO)_3][BF_4]$ was isolated in 1958,⁸ shortly after the discovery of ferrocene, it is only during the last decade that the chemistry of the η - C_7H_7 compounds of the early transition metals has been considerably developed.⁹ These quite exciting novel results were certainly an incitement to our project for introducing the cycloheptatrienyl ligand into f-element chemistry. The first compounds that we isolated were found to possess an inverse-sandwich structure;¹⁰ this co-ordination mode of the η - C_7H_7 group was unprecedented. Here we report on the synthesis and characterization of the uranium compounds $K[X_3U(\mu-\eta^7:\eta^7-C_7H_7)UX_3]$ ($X = NEt_2$ or BH_4) and of the neodymium derivative $[(thf)(BH_4)_2Nd(\mu-\eta^7:\eta^7-C_7H_7)Nd(BH_4)(thf)_2]$ ($thf =$ tetrahydrofuran).

Results

The unique mention of f-element cycloheptatrienyl complexes appeared in a contribution by Miller and Dekock¹¹ who reported in 1981 that lithium cycloheptadienyl reacted with actinide and lanthanide chlorides to give the cycloheptatrienyl trianion co-ordinated to the metal ion. The complexes were not characterized but the presence of the trianionic C_7H_7 ligand was inferred from chemical reactivity and spectroscopy. We reexamined the reactions of UCl_4 and $K[C_7H_9]$ (1–3 equivalents) in tetrahydrofuran or toluene; we also observed the formation of a dark red solid, without being able to identify any uranium compound.

The products formed in the reactions of UX_4 and $K[C_7H_9]$ (1–2 equivalents) could be identified by replacing $X = Cl$ by the groups $X = NEt_2$ and BH_4 which are easily detected by NMR spectroscopy. Treatment of $[U(NEt_2)_4]$ with 1 equivalent of $K[C_7H_9]$ in toluene gave, after 3 d at 65 °C, an ochre precipitate in a brown solution. The precipitate was filtered off, extracted in thf and a brown powder of $K[(Et_2N)_3U(\mu-\eta^7:\eta^7-C_7H_7)U(NEt_2)_3]$ **1** was obtained after evaporation of the solvent. In the presence of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane), brown crystals of $[K(18-crown-6)][(Et_2N)_3U(\mu-\eta^7:\eta^7-C_7H_7)U(NEt_2)_3]$ **2** were isolated from thf -pentane. In the ¹H NMR spectra of **1** and **2** the triplet and quartet resonances at δ 1.5 and 6.1 respectively were attributed to the six equivalent NEt_2 groups and the C_7H_7 ligand was recognized by the singlet signal at δ –50.5. The yield of **1**, ca. 40%, was not increased by using 1.5 or 2 equivalents of $K[C_7H_9]$. The remaining $[U(NEt_2)_4]$ was transformed into unidentified uranium complexes, found in the toluene solution which also contained organic products, presumably polymers, among which traces of cycloheptadienes could be detected. Compound **1** was formed in poor yield (ca. 5%) when the reaction was performed in tetrahydrofuran; a complex mixture was thus obtained, in which $[U(NEt_2)_4]$ and $K[U(NEt_2)_3]$ ¹² were the major components.

Uranium tetrahydroborate reacted in thf with 1 equivalent of $K[C_7H_9]$ to give, after 1 h at 20 °C, a mixture of $[U(BH_4)_4(thf)_2]$ ¹³ (25%), $[U(BH_4)_3(thf)_3]$ ¹⁴ (30%) and the new compound $K[(BH_4)_3U(\mu-\eta^7:\eta^7-C_7H_7)U(BH_4)_3]$ **3** (45%). The latter was identified by its ¹H NMR spectrum which exhibited a singlet at δ –47.6 (7 H) and a quartet at δ 63.4 (24 H) corresponding respectively to the C_7H_7 and BH_4 ligands. Complete conversion of $[U(BH_4)_4(thf)_2]$ was achieved after further addition of 0.5 equivalent of $K[C_7H_9]$. The NMR analysis revealed that 2 mol of cycloheptadienes C_7H_{10} were formed per mol of complex **3**. The relative proportions of **3** and $[U(BH_4)_3(thf)_3]$ were ca. 60:40; this ratio was reversed in toluene. Despite many efforts, the cycloheptatrienyl complex **3** could not be obtained pure, free from $[U(BH_4)_3(thf)_3]$; these two uranium tetrahydroborates presented similar solubilities and **3** was not infinitely stable in solution. By considering that the phosphine adduct $[U(BH_4)_3(Me_2PCH_2CH_2PMe_2)]$ ¹⁵ would be more soluble and easier to eliminate than $[U(BH_4)_3(thf)_3]$, reaction of $[U(BH_4)_4]$ and $K[C_7H_9]$ was carried out in the presence of $Me_2PCH_2CH_2PMe_2$. During one of the attempts to isolate **3** by crystallization, a brown solution of the uranium(III) tris(tetrahydroborate) (60%) and **3** (40%) in thf -pentane deposited

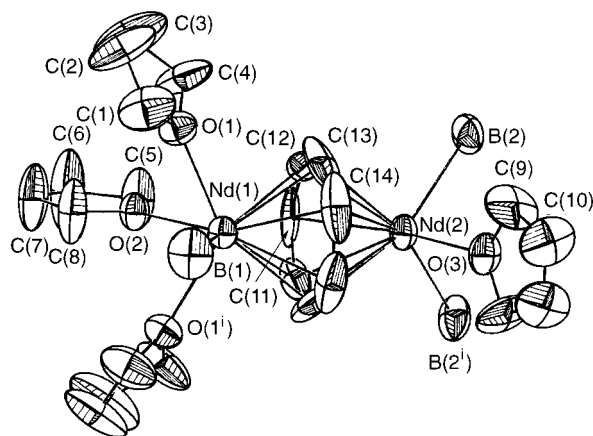


Fig. 1 Perspective view of $[(\text{thf})(\text{BH}_4)_2\text{Nd}(\mu\text{-}\eta^7\text{:}\eta^7\text{-C}_7\text{H}_7)\text{Nd}(\text{BH}_4)(\text{thf})_3]$ **6**; atoms labelled *i* are related by the plane of symmetry

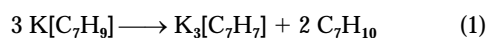
red crystals along with a beige powder. Crystal structure analysis revealed that these were in fact $[\text{U}(\text{BH}_4)_2(\text{thf})_5][(\text{BH}_4)_3\text{U}(\mu\text{-}\eta^7\text{:}\eta^7\text{-C}_7\text{H}_7)\text{U}(\text{BH}_4)_3]$ **4**; the inverse sandwich structure of the anion in **4** was described in our preliminary communication.¹⁰

The neodymium tetrahydroborate $[\text{Nd}(\text{BH}_4)_3(\text{thf})_2]$ cleanly reacted with 1.5 equivalents of $\text{K}[\text{C}_7\text{H}_9]$ in toluene to give a green precipitate in a clear yellow solution. After filtration, the solid was extracted in thf and green microcrystals were deposited upon addition of pentane; the product, $[(\text{thf})(\text{BH}_4)_2\text{Nd}(\mu\text{-}\eta^7\text{:}\eta^7\text{-C}_7\text{H}_7)\text{Nd}(\text{BH}_4)(\text{thf})_2]$ **5**, was isolated in 77% yield. Here again, 2 mol of cycloheptadienes C_7H_{10} (found in the toluene solution) were formed per mol of complex **5**. The ^1H NMR spectrum of **5** exhibited, at 30 °C, two signals at δ -29.4 and 70.5, with an intensity ratio 7:12, corresponding to the C_7H_7 and BH_4 ligands; at -90 °C, the low-field resonance, which was shifted to δ 91, was slightly broader ($\nu_2 = 700$ Hz) but it was not possible to make a distinction between the BH_4 groups. The co-ordination mode of these tetrahydroborate ligands is tridentate, according to the diagnostic IR vibrations,¹⁶ a sharp singlet at 2410 cm^{-1} and a broad band centred at 2220 cm^{-1} . Green crystals of $[(\text{thf})(\text{BH}_4)_2\text{Nd}(\mu\text{-}\eta^7\text{:}\eta^7\text{-C}_7\text{H}_7)\text{Nd}(\text{BH}_4)(\text{thf})_3]$ **6** were obtained by crystallization of **5** from thf-pentane. An ORTEP drawing¹⁷ of **6** is shown in Fig. 1; selected bond distances and angles are listed in Table 1.

Discussion

The compounds obtained by reaction of $[\text{U}(\text{NET}_2)_4]$, $[\text{U}(\text{BH}_4)_4]$ and $[\text{Nd}(\text{BH}_4)_3(\text{thf})_2]$ with the potassium salt of the cycloheptadienyl anion are the first metal complexes possessing an inverse cycloheptatrienyl sandwich structure. Such complexes in which two metals are bound on the opposite sides of an aromatic hydrocarbon ligand C_nH_m , although not familiar, are known for $n = 5, 6$ or 8 . In organo-*f*-element chemistry the crystal structures of $\{[\text{Th}_2(\eta\text{-C}_5\text{H}_5)(\text{OPr}^i)_7]_3\}$ ¹⁸ and $\{[\text{Eu}(\eta\text{-C}_5\text{Me}_5)(\text{thf})_2]_2(\mu\text{-C}_8\text{H}_8)\}$,¹⁹ which exhibit respectively a $\text{Th}(\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_5\text{H}_5)\text{Th}$ and a $\text{Eu}(\mu\text{-}\eta^8\text{:}\eta^8\text{-C}_8\text{H}_8)\text{Eu}$ unit, have been described recently but no compound with a $\text{M}(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_6)\text{M}$ fragment has been reported so far; however, this fragment was found in the triple-decker sandwich compound $[(\eta\text{-C}_5\text{H}_5)\text{V}(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_6)\text{V}(\eta\text{-C}_5\text{H}_5)]$.²⁰

Formation of the cycloheptatrienyl ligand in complexes **1**, **3** and **5** should result from the conversion of the cycloheptadienyl anion C_7H_9^- into the cycloheptatrienyl trianion $\text{C}_7\text{H}_7^{3-}$ with liberation of cycloheptadiene isomers, according to equation (1).



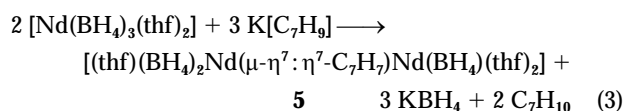
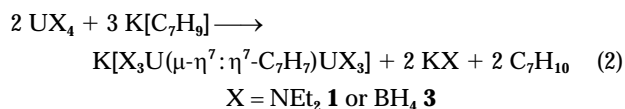
The NMR analysis showed that during the synthesis of **3** and **5** the ratio $\text{C}_7\text{H}_{10}:\text{C}_7\text{H}_7$ was effectively equal to 2:1; in the case

Table 1 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for compound **6**

$\text{C}(11)\text{--C}(12)$	1.41(3)	$\text{C}(12)\text{--C}(13)$	1.27(4)
$\text{C}(13)\text{--C}(14)$	1.36(4)	$\text{C}(14)\text{--C}(14^i)$	1.68(6)
$\text{Nd}(1)\text{--O}(1)$	2.54(1)	$\text{Nd}(1)\text{--O}(2)$	2.56(2)
$\text{Nd}(1)\text{--B}(1)$	2.74(3)	$\text{Nd}(1)\text{--C}(11)$	2.67(3)
$\text{Nd}(1)\text{--C}(12)$	2.67(4)	$\text{Nd}(1)\text{--C}(13)$	2.64(5)
$\text{Nd}(1)\text{--C}(14)$	2.64(3)	$\text{Nd}(1)\text{--Chp}$	2.12(3)
$\text{Nd}(2)\text{--O}(3)$	2.56(2)	$\text{Nd}(2)\text{--B}(2)$	2.68(2)
$\text{Nd}(2)\text{--C}(11)$	2.63(3)	$\text{Nd}(2)\text{--C}(12)$	2.63(3)
$\text{Nd}(2)\text{--C}(13)$	2.63(4)	$\text{Nd}(2)\text{--C}(14)$	2.67(2)
$\text{Nd}(2)\text{--Chp}^*$	2.10(3)		
$\text{C}(12^i)\text{--C}(11)\text{--C}(12)$	129(3)	$\text{C}(11)\text{--C}(12)\text{--C}(13)$	129(3)
$\text{C}(12)\text{--C}(13)\text{--C}(14)$	134(4)	$\text{C}(13)\text{--C}(14)\text{--C}(14^i)$	122(2)
$\text{Nd}(1)\text{--Chp--Nd}(2)$	177.2(8)	$\text{Chp--Nd}(1)\text{--O}(1)$	115.4(7)
$\text{Chp--Nd}(1)\text{--O}(2)$	117.0(7)	$\text{Chp--Nd}(1)\text{--B}(1)$	125.8(8)
$\text{Chp--Nd}(2)\text{--O}(3)$	116.2(7)	$\text{Chp--Nd}(2)\text{--B}(2)$	125.7(8)

* Chp is the centroid of the cycloheptatrienyl ring.

of **1**, only a trace of C_7H_{10} could be detected, because the diene was polymerized under the reaction conditions (65 °C, 5 d). Compounds **1**, **3** and **5** would be then formally seen as the products of the metathesis reaction of $\text{K}_3[\text{C}_7\text{H}_7]$ and 2 equivalents of $[\text{UX}_4]$ ($\text{X} = \text{NEt}_2$ or BH_4) or $[\text{Nd}(\text{BH}_4)_3(\text{thf})_2]$; their synthesis can be represented by equations (2) and (3).



The facile disproportionation of $\text{Li}[\text{C}_7\text{H}_9]$ in the presence of lanthanide and actinide chlorides was previously reported by Miller and Dekock.¹¹ This enhanced reactivity of the C_7H_9^- anion, which is otherwise stable in solution and is metallated with difficulty by very strong bases,²¹ was accounted for by its initial co-ordination to the metal; the methylene hydrogens would be thus rendered more acidic and the proton abstraction by another C_7H_9^- quite feasible. This hypothesis could not be verified; no intermediate was detected during the formation of the cycloheptatrienyl complexes **1**, **3** and **5** and the mechanism of reactions (2) and (3) was not further elucidated. Miller and Dekock concluded that the product resulting from reaction of UCl_4 and 3 equivalents of $\text{Li}[\text{C}_7\text{H}_9]$ was a cycloheptatrienyl-uranium compound in the +4 oxidation state. The ^1H NMR spectra of complexes **1–3** and **5**, which exhibit narrow and well resolved signals, are typical of uranium(IV) and neodymium(III) derivatives; this is consistent with the attribution of a formal charge of -3 to the C_7H_7 ligand.²²

Whereas reaction (3) afforded the neodymium compound **5** in good yield, the synthesis of **1** and **3** was impeded by the formation of side-products. Compound **3** could not be separated from $[\text{U}(\text{BH}_4)_3(\text{thf})_3]$ which resulted from the reduction of the uranium tetrahydroborate by the potassium reagent; this concomitant reduction of $[\text{U}(\text{BH}_4)_4]$ was also encountered during the preparation of $[\text{U}(\eta\text{-dienyl})(\text{BH}_4)_3]$ complexes.²³ Compound **1** was isolated pure, after elimination of the other products which were soluble and extracted in toluene.

In contrast to the uranium complexes **1** and **3** which are anionic and adopt a symmetrical structure with two UX_3 fragments linked by a C_7H_7 ligand, the neodymium compound **5** is neutral and not symmetrical. Complexes **1** and **3** showed no tendency to eliminate KX and attempts to extract the corresponding neutral derivatives in non-polar solvents were unsuccess-

cessful. The reasons for this difference, which are obviously not steric, are unclear.

The complexes $[\text{U}(\text{BH}_4)_2(\text{thf})_3][(\text{BH}_4)_3\text{U}(\mu\text{-}\eta^7\text{:}\eta^7\text{-C}_7\text{H}_7)\text{-U}(\text{BH}_4)_3]$ **4** and $[(\text{thf})(\text{BH}_4)_2\text{Nd}(\mu\text{-}\eta^7\text{:}\eta^7\text{-C}_7\text{H}_7)\text{Nd}(\text{BH}_4)(\text{thf})_3]$ **6** have been crystallographically characterized. In both the cycloheptatrienyl ligand is planar and perpendicular to the linear axis defined by the two metal centres and the ring centroid. The C_7H_7 ring in **6** is almost parallel to the plane defined by O(3), B(2) and B(2') and to the mean plane (± 0.1 Å) of O(1), O(1'), O(2) and B(1). The two neodymium–ring centroid distances are essentially identical, 2.12(3) and 2.10(3) Å, and the Nd–C bond lengths average 2.64(3) Å; the corresponding metal–ring centroid and –carbon distances average 2.13(3) and 2.68(3) Å in the uranium compound **4**.¹⁰ The short Nd–B distances, 2.68(2) and 2.74(3) Å, may be compared with that of 2.664(25) Å in $[\text{Nd}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OMe})_2(\text{BH}_4)]$ ²⁴ and indicate a tridentate ligation mode of the BH_4 ligands, consistent with the IR data. The Nd–O distances are unexceptional.²⁵

At this stage of the study it is not possible to give precise descriptions of the bonding between the metal and η^7 -cycloheptatrienyl ligand and in particular of the actual role of the *f* orbitals. Further spectroscopic and theoretical studies will give a better insight into the *f*-element– $\eta\text{-C}_7\text{H}_7$ bonding.

Experimental

All preparations and reactions were carried out under argon (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glove-box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. Deuteriated solvents were dried over Na–K alloy.

Elemental analyses were performed by Analytische Laboratorien at Gummersbach (Germany). The ¹H NMR spectra were recorded on a Bruker WP 60 (FT) or AC 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). The compounds UCl_4 ,²⁶ $[\text{U}(\text{NEt}_2)_4]$,²⁷ $[\text{U}(\text{BH}_4)_4]$,²⁸ $[\text{Nd}(\text{BH}_4)_3(\text{thf})_2]$ ²⁹ and $\text{K}[\text{C}_7\text{H}_9]$ ³⁰ were prepared by published methods.

Preparations

$[\text{K}(\text{Et}_2\text{N})_3\text{U}(\mu\text{-}\eta^7\text{:}\eta^7\text{-C}_7\text{H}_7)\text{U}(\text{NEt}_2)_3]$ 1. A round-bottom flask (50 cm³) was charged with $[\text{U}(\text{NEt}_2)_4]$ (453 mg, 0.86 mmol) and $\text{K}[\text{C}_7\text{H}_9]$ (115 mg, 0.87 mmol) and toluene (25 cm³) was condensed into it at -78 °C under vacuum. The mixture was stirred for 3 d at 65 °C. The brown precipitate was filtered off, washed with toluene (10 cm³) and extracted in thf (25 cm³). After decantation and filtration, the red-brown solution was evaporated to dryness, leaving a brown microcrystalline powder of complex **1** (193 mg, 43%). ¹H NMR (25 °C in $[\text{C}_6\text{D}_6]\text{thf}$): δ 6.04 (24 H, q, *J* 6, CH₂), 1.44 (36 H, t, *J* 6 Hz, Me) and -50.3 (7 H, s, *w*₁ 22 Hz, C₇H₇).

$[\text{K}(\text{18-crown-6})][(\text{Et}_2\text{N})_3\text{U}(\mu\text{-}\eta^7\text{:}\eta^7\text{-C}_7\text{H}_7)\text{U}(\text{NEt}_2)_3]$ 2. A round-bottom flask (50 cm³) was charged with complex **1** (158 mg, 0.15 mmol) and 18-crown-6 (40.2 mg, 0.15 mmol) and thf (20 cm³) was condensed into it at -78 °C under vacuum. The mixture was stirred at room temperature for 15 min. The solution was concentrated to 5 cm³ by evaporation and upon addition of pentane (15 cm³) deposited brown microcrystals of **2**; these were filtered off, washed with pentane (10 cm³) and dried under vacuum (150 mg, 76%) (Found: C, 39.3; H, 7.0; N, 6.25. C₄₈H₉₁KN₆O₆U₂ requires C, 39.6; H, 7.05; N, 6.45%). ¹H NMR (25 °C in $[\text{C}_6\text{D}_6]\text{thf}$): δ 6.12 (24 H, q, *J* 6, CH₂), 3.23 (24 H, s, 18-crown-6), 1.49 (36 H, t, *J* 6 Hz, Me) and -50.7 (7 H, s, *w*₁ 15 Hz, C₇H₇).

Reaction of $[\text{U}(\text{BH}_4)_4]$ with $\text{K}[\text{C}_7\text{H}_9]$. An NMR tube was charged with $[\text{U}(\text{BH}_4)_4]$ (13.6 mg, 0.045 mmol) and $\text{K}[\text{C}_7\text{H}_9]$ (9.0 mg, 0.067 mmol) in $[\text{C}_6\text{D}_6]\text{thf}$ (0.5 cm³). After 1 h at 20 °C the

spectrum showed that $[\text{U}(\text{BH}_4)_4]$ was totally converted into a mixture of $[\text{U}(\text{BH}_4)_3([\text{C}_7\text{H}_9]\text{thf})_3]$ (40%) and $\text{K}[(\text{BH}_4)_3\text{U}(\mu\text{-}\eta^7\text{:}\eta^7\text{-C}_7\text{H}_7)\text{U}(\text{BH}_4)_3]$ **3** (60%). ¹H NMR (25 °C in $[\text{C}_6\text{D}_6]\text{thf}$): δ 63.4 (24 H, q, *J* 85 Hz, BH₄) and -47.6 (7 H, s, *w*₁ 20 Hz, C₇H₇). The spectrum also indicated that 2 mol of C₇H₁₀ were formed per mol of complex **3**. The same reaction was performed in toluene or diethyl ether. After 15 d at 20 °C the solvent was evaporated off and the residue dissolved in $[\text{C}_6\text{D}_6]\text{thf}$; the ¹H NMR spectrum revealed the presence of $[\text{U}(\text{BH}_4)_3([\text{C}_7\text{H}_9]\text{thf})_3]$ and **3** in the proportions 60:40. These proportions did not change after prolonged reaction times. All attempts to obtain a pure sample of **3** by crystallization were unsuccessful.

Crystals of $[\text{U}(\text{BH}_4)_2(\text{thf})_3][(\text{BH}_4)_3\text{U}(\mu\text{-}\eta^7\text{:}\eta^7\text{-C}_7\text{H}_7)\text{U}(\text{BH}_4)_3]$ 4. The preparation of complex **4** was realized only once and we are not sure that it is reproducible. A round-bottom flask (50 cm³) was charged with $[\text{U}(\text{BH}_4)_4]$ (157 mg, 0.53 mmol) and Me₂PCH₂CH₂PMe₂ (160 mg, 1.06 mmol) and diethyl ether (25 cm³) was condensed into it at -78 °C under vacuum. The mixture was stirred for 12 h at 20 °C and upon addition of $\text{K}[\text{C}_7\text{H}_9]$ (76.9 mg, 0.58 mmol) a black precipitate was deposited from the green solution. After 2 h at 20 °C the solvent was evaporated off and the residue extracted in thf (25 cm³). The solution was filtered and evaporated to dryness, leaving a brown powder; the NMR spectrum in $[\text{C}_6\text{D}_6]\text{thf}$ revealed the presence of the inverse-sandwich compound (40%) and the uranium(III) tris(tetrahydroborate) (60%). The two components of this mixture could not be separated by selective extraction in toluene. A crystallization of the powder from thf–pentane afforded red crystals of **4** which were suitable for X-ray diffraction study.¹⁰

$[(\text{thf})(\text{BH}_4)_2\text{Nd}(\mu\text{-}\eta^7\text{:}\eta^7\text{-C}_7\text{H}_7)\text{Nd}(\text{BH}_4)(\text{thf})_2]$ 5. A round-bottom flask (50 cm³) was charged with $[\text{Nd}(\text{BH}_4)_3(\text{thf})_2]$ (190 mg, 0.57 mmol) and $\text{K}[\text{C}_7\text{H}_9]$ (129.5 mg, 0.98 mmol) and toluene (25 cm³) was condensed into it at -78 °C under vacuum. The mixture was stirred for 12 h at 20 °C, giving a green powder in a bright yellow solution. After filtration, the solid was dried under vacuum and extracted in thf (25 cm³), leaving an off-white precipitate in a green solution. The solution, which was filtered and concentrated to 10 cm³ by evaporation, deposited green microcrystals of complex **5** (140 mg, 77%) upon addition of pentane (10 cm³) (Found: C, 35.4; H, 6.65; B, 5.0. C₁₉H₄₃B₃Nd₂O₃ requires C, 35.65; H, 6.75; B, 5.05%). ¹H NMR (25 °C in $[\text{C}_6\text{D}_6]\text{thf}$): δ 70.5 (12 H, br, *w*₁ 300, BH₄) and -29.4 (7 H, s, *w*₁ 50 Hz, C₇H₇). IR (KBr): 2410 and 2220 (br) cm⁻¹

Crystallography

Crystals of complex **6** were obtained by crystallization of **5** from thf–pentane. A single crystal was introduced into a thin-walled Lindeman glass tube in a glove-box. Data were collected at 20 °C on an Enraf-Nonius diffractometer equipped with a graphite monochromator [$\lambda(\text{Mo-K}\alpha) = 0.71073$ Å]. The cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections with θ between 8 and 12°. Three standard reflections were measured after every hour; a decay was observed (4.3% in 18 h) and linearly corrected. The data were corrected for Lorentz-polarization and absorption.³¹ The structure was solved by the heavy-atom method and refined by full-matrix least squares on *F* with anisotropic thermal parameters. The hydrogen atoms were not introduced. The Nd(1), Nd(2), B(1), C(11), O(3) atoms and those of the thf molecule containing O(2) were found in the mirror plane. The planar geometry of this thf molecule is not realistic and the C(14)–C(14ⁱ) bond distance is obviously too long; however, attempts to solve this thf molecule by considering two positions for the carbon atoms C(5)–C(8) with an occupancy factor of 1/2 led to very close carbon positions which were replaced by one position having anisotropic parameters. All calculations were performed on a Vax 4000-200 computer with the MOLEN system.³² Analytical scattering factors for neutral atoms were

Table 2 Crystallographic data and experimental details for [(thf)(BH₄)₂Nd(μ-η⁷:η⁷-C₇H₇)Nd(BH₄)(thf)₃] **6**

Formula	C ₂₃ H ₅₁ B ₃ Nd ₂ O ₄
<i>M</i>	712.57
Crystal size/mm	0.50 × 0.40 × 0.12
Colour	Green
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
<i>a</i> /Å	22.232(11)
<i>b</i> /Å	12.024(5)
<i>c</i> /Å	11.782(2)
<i>U</i> /Å ³	3150(3)
<i>Z</i>	4
<i>D</i> _c /g cm ⁻³	1.503
μ(Mo-Kα)/cm ⁻¹	32.97
<i>F</i> (000)	1424
θ Limits/°	1–20
Scan type	ω–2θ
Scan width	0.8 + 0.35 tan θ
Range of absolute transmission	0.582–0.999
<i>hkl</i> Ranges	–11 to 0, 0–11, 0–21
Reflections collected	
total	1781
unique	1564
with <i>I</i> > 3σ(<i>I</i>)	1131
No. parameters	160
<i>R</i> = Σ <i>F</i> _o – <i>F</i> _c /Σ <i>F</i> _o	0.039
<i>R</i> ' = [Σ <i>w</i> <i>F</i> _o – <i>F</i> _c ² /Σ <i>w</i> (<i>F</i> _o) ²] ^{1/2}	0.046
Maximum residual electron density/e Å ⁻³	0.634

corrected for both Δ*f*' and Δ*f* components of the anomalous dispersion.³³ Crystallographic data are given in Table 2.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/546.

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