

Organouranium(IV) pseudo-salts containing the tricyclopentadienyluranium moiety and one loosely coordinated tetraphenylborate or triphenylmethylborate unit *

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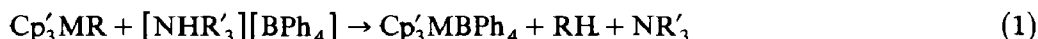
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Abstract

The complexes $\text{Cp}'_3\text{UBPh}_4$ (type A) and $\text{Cp}'_3\text{UCH}_3 \cdot \text{BPh}_3$ (type B) ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$ or $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$) have been respectively prepared by dehydration of the corresponding new salts $[\text{Cp}'_3\text{U}(\text{OH}_2)_2][\text{BPh}_4] \cdot x\text{H}_2\text{O}$ and addition of BPh_3 to $\text{Cp}'_3\text{UCH}_3$. Several spectroscopic and chemical properties of these compounds are indicative of some loose coordination of the BPh_4 and BPh_3CH_3 units to the uranium centre, making their formulation as genuine salts, $[\text{Cp}'_3\text{U}]^+[\text{BPh}_3\text{R}]^-$, rather doubtful. While the type A systems are reluctant to add Lewis bases L (to form cations of the previously described class $[\text{Cp}'_3\text{UL}_2]^+$), the type B complex with $\text{Cp} = \text{C}_5\text{H}_5$ reacts with acetonitrile to afford a pseudo-salt of the unexpected composition $\text{Cp}_3\text{U}(\text{NCCH}_3)\text{CH}_3\text{BPh}_3$, with a trigonal bipyramidal (tbp) configuration. This latter compound, which is not accessible from the corresponding new tbp-system " $\text{Cp}_3\text{UCH}_3(\text{NCCH}_3)$ ", does give true salts of the type $[\text{Cp}_3\text{U}(\text{CNR})(\text{NCR}')][\text{BPh}_3\text{CH}_3]$.

Introduction

Organoactinoid(IV) compounds of the general composition $\text{Cp}'_3\text{MBPh}_4$ ($\text{M} = \text{U}$ or Th ; $\text{Ph} = \text{C}_6\text{H}_5$) have been obtained either via protonolysis of one M-R bond by use of suitable ammonium tetraphenylborates,

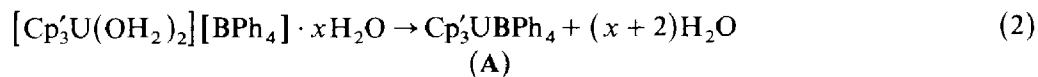


(a) $\text{M} = \text{U}$, $\text{R} = \text{Cp}' = \text{C}_5\text{H}_5$, $\text{R}' = \text{H}$ [1];

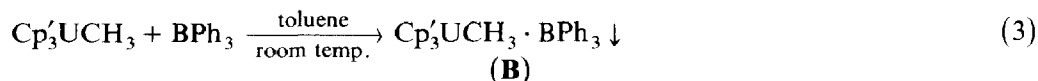
(b) $\text{M} = \text{Th}$, $\text{R} = \text{CH}_3$, $\text{R}' = \text{C}_2\text{H}_5$ [2a]

* Dedicated to Professor Dr.Dr.h.c.mult. E.O. Fischer on the occasion of his seventieth birthday.

or by exhaustive dehydration of the salts $[\text{Cp}'_3\text{U}(\text{OH}_2)_2][\text{BPh}_4] \cdot n\text{H}_2\text{O}$ [3]:

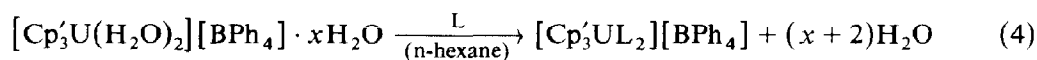


In view of the current interest in cationic organoactinoid complexes [2a*,4,5], we describe here some examples of the pseudo-salts **A** as obtained by the second route (eq. 2), along with their hydrated salt-like precursors. Two related pseudo-salts $\text{Cp}'_3\text{UCH}_3\text{BPh}_3$ (type **B**) are also described; they were obtained when the insertion of BH_3 into $\text{Cp}'_3\text{UCH}_3$ [6] was tentatively repeated with BPh_3 :



Complexes of type A: preparation, spectroscopy, and reactivity

The salt-like precursors $[\text{Cp}'_3\text{U}(\text{OH}_2)_2][\text{BPh}_4] \cdot n\text{H}_2\text{O}$ of the type **A** systems $\text{Cp}'_3\text{UBPh}_4$ separate in good yields from the green aqueous solutions of $\text{Cp}'_3\text{UCl}$ upon addition of NaBPh_4 . Cautious drying at the oil pump gave light-green, air-sensitive powders of the composition $[(\text{C}_5\text{H}_5)_3\text{U}(\text{OH}_2)_2][\text{BPh}_4] \cdot 10\text{H}_2\text{O}$ (**1**) and $[(\text{C}_5\text{H}_5)_2(\text{C}_5\text{H}_4\text{CH}_3)\text{U}(\text{OH}_2)_2][\text{BPh}_4] \cdot \text{H}_2\text{O}$ (**2**), respectively, which can be stored at -25°C for weeks without decomposition. Unlike **1** and **2**, the initially dark green precipitate **3**, obtained in substantially lower yields from $(\text{C}_5\text{H}_4\text{CH}_3)_3\text{UCl}$ and NaBPh_4 , turns dark brown overnight (at -25°C). Spontaneous loss of water is indicated by the appearance of small drops of water on the glass walls of the Schlenk tube. Partial loss of H_2O molecules from **1** and **2** imbedded in KBr pellets is indicated by the absence of the two characteristic $\nu(\text{OH})$ bands above 3500 cm^{-1} that are always present in the infrared spectra of samples in Nujol mulls. The electronic NIR/VIS transmission spectra of KBr-pellets of **1** and **2** remain, nevertheless, typical of $\text{Cp}'_3\text{U}$ derivatives of trigonal bipyramidal (tbp) configuration, suggesting that at least the two axially coordinated H_2O molecules have not been absorbed by the KBr. Hence, by analogy with the structurally well defined compound $[\text{UO}_2(\text{OH}_2)_2(\text{NO}_3)_2] \cdot 4\text{H}_2\text{O}$ [7], two different types of H_2O molecules may also be present in **1** and **2**. Evidently the ability of the $\text{Cp}'_3\text{U}$ moiety to accommodate H_2O molecules depends strongly on the number of CH_3 substituents on the cyclopentadienyl ring. Along with the previously reported salt $[\text{Cp}_3\text{U}(\text{H}_2\text{O})_2]\text{NO}_3$ [8], compounds **1** and **2** appear to be the only solids in which the spectroscopically long-known Cp_3U -aqua cation has been stabilized. A valuable preparative route is based on the ready substitution of all the H_2O molecules by, e.g., two isocyanide [4] or nitrile [9] molecules:



Complete conversion of **1** and **2** into their dehydrated derivatives $\text{Cp}'_3\text{UBPh}_4$, **4** and **5**, takes place within 30 minutes at 30°C and a pressure of ca. 10^{-3} bar. To

* Reference number with asterisk indicates a note in the list of references.

date simultaneous liberation of BPh_3 has led to failure of potential alternative routes starting from other salts $[\text{Cp}'_3\text{UL}_2][\text{BPh}_4]$. The quick colour change of the solids from green to beige-brown is accompanied by the disappearance of all the $\nu(\text{OH})$ and $\delta(\text{OH})$ absorptions in the infrared (IR) spectrum. Moreover, the absorption spectra in the near infrared and visible ranges (NIR/VIS) of solids **4** and **5** (Teflon pellets) are devoid of the intense absorptions characteristic of *tbp* configuration at ca. 6400 ± 200 and $16500 \pm 200 \text{ cm}^{-1}$.

Compounds **4** and **5**, which are somewhat more thermally stable than their green precursors **1** and **2**, do not behave like coordinatively unsaturated systems, as would be expected for genuine salts $[\text{Cp}'_3\text{U}]^+[\text{BPh}_4]^-$. In particular, they do not immediately react with H_2O or CH_3CN to give green, *tbp*-configured complexes. After longer treatment with CH_3CN , only brown solutions together with a large brown residue are obtained. Similar results are obtained when **4** or **5** is treated with THF, CH_2Cl_2 , or even toluene. Although a clear brown solution is first obtained in THF, partial decomposition, indicated by the formation of a dark brown precipitate, takes place reproducibly within less than one minute. From the solutions, which are still coloured, significant amounts of triphenylboron (BPh_3) can be isolated, suggesting that THF, and probably other solvents, stimulate metal phenylation by the coordinated BPh_4 anions [10]. The high sensitivity of **4** and **5** towards THF casts some doubt on the formation of pure **4** from Cp_4U and $[\text{NH}_4][\text{BPh}_4]$ after extraction with THF [1]. In contrast to the apparently less sensitive thorium(IV) analogues of type A, $(\text{C}_5\text{H}_4\text{R})_3\text{ThBPh}_4$ ($\text{R} = \text{CH}_3$ and $\text{Si}(\text{CH}_3)_3$ [2a*]), **4** and **5** are unstable in most solvents, and this prevented successful ^1H NMR studies.

Thermolysis of **4** and **5** under high vacuum leads to quantitative elimination of BPh_3 . While, e.g., $\text{Na}[\text{BPh}_4]$ and $[\text{NH}_4][\text{BPh}_4]$ lose BPh_3 above 220 and 100 °C, respectively, the optimal decomposition temperatures of **4** and **5** are as low as 100 and 60 °C. The BPh_3 from **5** even sublimes out at the same temperature as pure BPh_3 . The rather facile liberation of BPh_3 both from solid and dissolved type A systems is strongly indicative of a uranium-assisted activation of one B–C(Ph) bond. While there are precedents for *d*-transition and main group metal assisted B–C(Ph) bond cleavage [11], a corresponding activity of *f*-transition metal ions has not previously been reported. Interestingly, detailed variable-temperature solution NMR studies in non-coordinating solvents suggest that the recently described pseudo-salt “ $\{\text{C}_5(\text{CH}_3)_5\}_2\text{ThCH}_3\text{BPh}_4$ ” has a “tightly ion-paired or nonrigid η^1 -arene structure” [2a*].

Complete elimination of BPh_3 (by sublimation) from **4** requires about 3 h at temperatures between 100 and 140 °C. The elemental analysis of the air sensitive brown-red residue **6** agrees satisfactorily with that for the expected composition “ $(\text{C}_5\text{H}_5)_3\text{UC}_6\text{H}_5$ ”; however, **6** is much less soluble in common solvents than authentic Cp_3UPh [12,13*], and this has so far prevented its NMR spectroscopic characterization. Most of the expected *f*–*f*-transitions are almost completely buried under the extremely broad low-frequency wing of an intense charge transfer band (Fig. 1), and the vibrational IR spectrum differs somewhat from the corresponding spectrum of authentic Cp_3UPh in that the reported [12] bands at 723, 707 and 230 cm^{-1} are missing [26*].

Unlike **6**, the initially dark brown residue resulting from **5** after incomplete elimination of BPh_3 between 60 and 80 °C is converted above 95 °C into a black decomposition product. The extremely facile liberation of BPh_3 from **5** (i.e. at

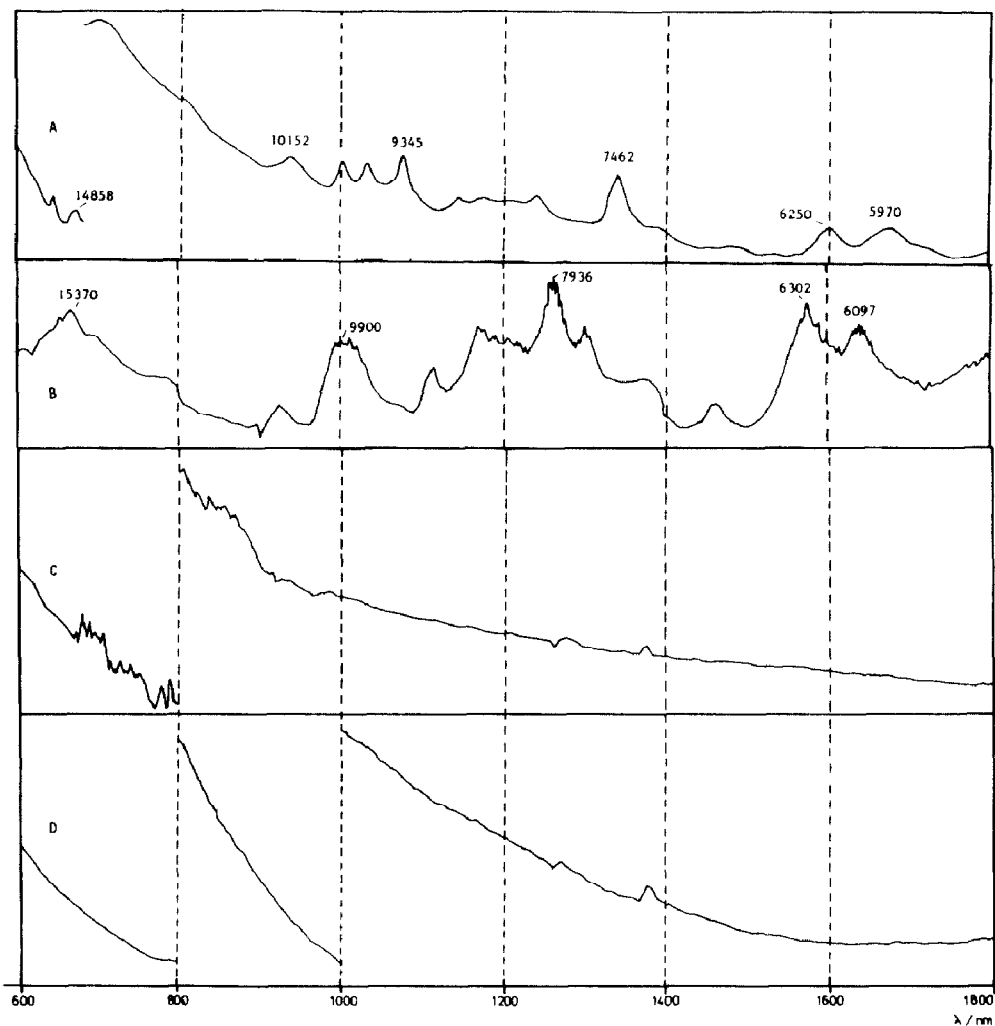


Fig. 1. NIR/VIS absorption spectra of A: solid $(C_5H_5)_3UCH_3$ (**8**) (KBr pellet); B: solid $(C_5H_5)_3UCH_3BPh_3$ (**10**) (Teflon pellet); C: solid $C_5H_4CH_3(C_5H_5)_2UBPh_4$ (**5**) (Teflon pellet) and D: solid " $C_5H_4CH_3(C_5H_5)_2UPh$ " (**6'**) (KBr pellet).

$\sim 60^\circ C$) could involve a modified mechanism involving the ring methyl group as a proton donor to one of the phenyl groups of the BPh_4 anion.

Complexes of type B: preparation, spectroscopy and reactivity

In contrast to its thorium analogue $[2a^*]$, the alkyluranium(IV) complex $(C_5H_4CH_3)_3UCH_3$ (**7**) cannot be converted into the corresponding pseudo-salt Cp'_3UBPh_4 by treatment with $[HN(C_2H_5)_3][BPh_4]$ (cf. eq. 1; solvent: toluene). The beige material obtained is, according to its 1H NMR spectrum in toluene- d_8 , free from starting material, but contains substantial amounts of free BPh_3 , which again suggests a pronounced sensitivity of the expected pseudo-salt towards common solvents.

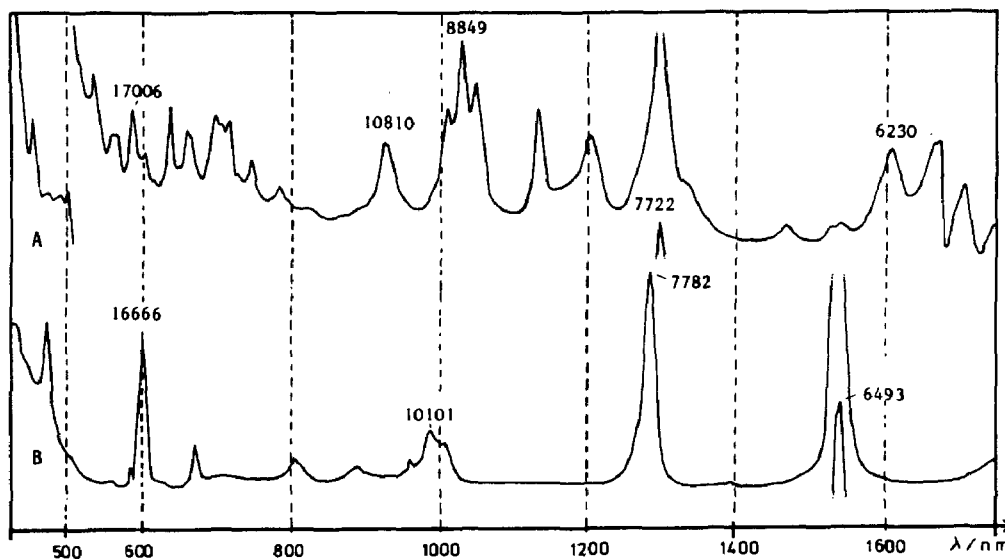


Fig. 2. NIR/VIS absorption spectra of A: dissolved $(C_5H_5)_3UCl$ (in $NCCH_3$), and B: $(C_5H_5)_3UCH_3BPh_3(NCCH_3)$ (**11**) (in $NCCH_3$).

On the other hand, both **7** and its non ring-methylated homologue $(C_5H_5)_3UCH_3$, **8**, react with BPh_3 in toluene solution to give the brown precipitates **9** and **10**, respectively, the elemental analyses of which suggest the uptake of one molecule of BPh_3 per metal complex.

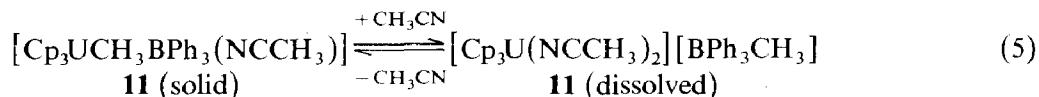
The IR spectra of **9** and **10** resemble those obtained by superposition of the spectra of the free components except that most of the bands of pure BPh_3 have been shifted by $5\text{--}10\text{ cm}^{-1}$. Interestingly, the bands of pure **7** or **8** at 400 cm^{-1} , which have been assigned to the $\nu(UC(CH_3))$ vibration [12], are absent in the spectra of **9** and **10**. While the NIR/VIS spectrum of solid **10** (Fig. 1) may be attributed to a Cp'_3UX system of pseudotetrahedral symmetry, the spectrum of **9** (like that of product **6**) shows almost no sharp $f\text{--}f$ transitions. In common solvents, both **9** and **10** are either sparingly soluble (hexane, toluene) or undergo partial decomposition (THF, CH_2Cl_2 , H_2O), preventing NMR spectroscopic studies (except in CD_3CN , vide infra).

Under vacuum (ca. 10^{-3} bar), and at temperatures as low as 60°C , compound **10** (like product **5**, vide supra) evolves pure BPh_3 . The mass spectrum of **10** displays the individual fragmentation patterns of BPh_3 and Cp_3UCH_3 , but no signal for the molecular ion.

From the initially clear, green solutions of **9** in CH_3CN a grey decomposition product separates rapidly, but the novel green adduct $Cp_3UCH_3BPh_3(NCCH_3)$ (**11**) can be isolated from the similarly green solution of **10** in CH_3CN . The IR spectrum of the extremely air sensitive adduct displays the two absorptions characteristic of coordinated $NCCH_3$ at 2275 ($\nu(CN)$) and 3005 cm^{-1} (Fermi resonance), while the NIR/VIS spectrum of both solid and dissolved **11** (in $NCCH_3$) shows the two intense absorptions characteristic of tbp -coordination at ca. 6500 and 15000 cm^{-1} . The 1H NMR spectrum of **11** in CD_3CN solution is consistent with:

(a) a tbp -configuration, as the Cp proton resonance lies close to $\delta = 0$ ($\delta -0.41$, s, 15H); (b) the presence of only one CH_3CN ligand per metal ion, in view of the

appearance of an appropriate signal (δ 1.54, 3H) alongside the multiplet of the solvent, which is absent for a solution of **10** in CD_3CN ; and (c) the transfer of the initially uranium-bonded CH_3 group to the boron atom (δ 0.13, q, $^2J(^1\text{H}-^{11}\text{B})$ 3.8 Hz, 3 H). The value of the coupling constant $^2J(^1\text{H}-^{11}\text{B})$ agrees well with that of the long-known "pseudo-salt" $[\text{LiB}(\text{CH}_3)_4]_4$ (3.5 Hz [14]). The striking contradiction between the actual composition of solid **11** and its ^1H NMR spectroscopic behaviour which indicates apparent migration of the methyl group, can best be explained in terms of the following equilibrium:



Thus the $\{\text{CH}_3\text{BPh}_3\}^-$ moiety may serve either (e.g., in the presence of an excess of NCCH_3) as the familiar triphenylmethylborate anion or as a genuine ligand that coordinates to the uranium centre by formation of a "linear methyl bridge". Recently a number of new examples of systems involving linear, or almost linear, CH_3 -bridges between particularly Lewis-acidic metal ions has been found [15,16]. Although the latest examples involve, e.g., the combinations $\text{Zr}^{\text{IV}}-(\mu\text{-CH}_3)\text{-Zr}^{\text{IV}}$ [18], $\text{Ln}^{\text{III}}-(\mu\text{-CH}_3)\text{-Ln}^{\text{III}}$, $\text{Ln}^{\text{III}}-(\mu\text{-CH}_3)\text{-Al}^{\text{III}}$, and $\text{Ln}^{\text{II}}-(\mu\text{-CH}_3)\text{-Be}^{\text{II}}$, it should be recalled that both bent and linear $\text{Li}^{\text{I}}-(\mu\text{-CH}_3)\text{-B}^{\text{III}}$ units are present in the long-known structure of $[\text{LiB}(\text{CH}_3)_4]_4$ [14].

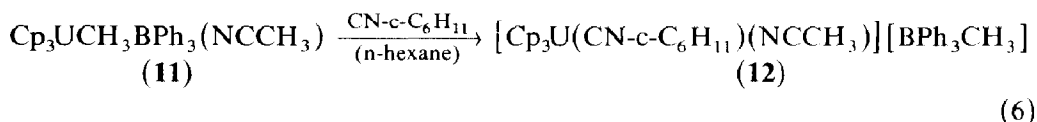
Our experimental findings seems to justify the view that in the new compounds **9-11** there is also a linear $\text{U}^{\text{IV}}-(\mu\text{-CH}_3)\text{-B}^{\text{III}}$ arrangement. Alternative formulations for **9** and **10**, e.g. in terms of the coordinatively unsaturated salt $[\text{Cp}'_3\text{U}]^+[\text{BPh}_3\text{CH}_3]^-$, the "insertion product" $\text{Cp}'_3\text{U-C}_6\text{H}_4\text{-BPh}_2\text{CH}_3$, or its sterically more crowded precursor $\text{Cp}'_3\text{U}(\mu\text{-C}_6\text{H}_5)\text{BPh}_2\text{CH}_3$, can probably be ruled out. The anionic ligand $\{\text{CH}_3\text{BPh}_3\}^-$ may thus tentatively be compared with the BH_3 -coordinated BH_3CN anion, which has been shown also to be present in tbp -systems such as solid $[\text{Cp}_3\text{UNCBH}_3]_\infty$ [17]:



Interestingly, Cp_3UCH_3 does not react with $\text{B}(\text{c-C}_6\text{H}_{11})_3$ and $\text{B}(\text{OCH}_3)_3$ [6], whereas reaction of AlR'_3 with Cp_3UR ($\text{R}, \text{R}' = \text{alkyl}$) results in exchange of R and R' via non-isolable intermediates involving two alkyl bridges [18].

Complexes derived from type B systems

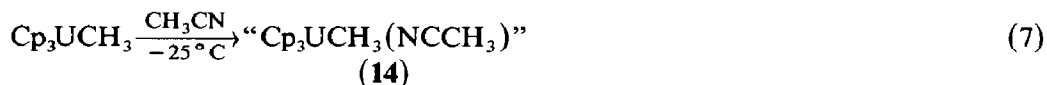
Unlike its BPh_3 -free precursors **8** [19,20*], the adduct $\text{Cp}_3\text{UCH}_3\text{BPh}_3$ (**10**) does not insert (or add) cyclohexylisocyanide, but its acetonitrile adduct **11** reacts readily with an equimolar amount of $\text{CN-c-C}_6\text{H}_{11}$ when suspended in n -hexane:



According to its IR spectrum in the $\nu(\text{CN})$ range ($\nu(\text{CN})$ of nitrile: 2275 cm^{-1} , $\nu(\text{CN})$ of isocyanide: 2190 cm^{-1} , Fermi resonance of nitrile: 3005 cm^{-1}), the light

green product **12** probably contains the previously described [5] cation $[\text{Cp}_3\text{U}(\text{NC-c-C}_6\text{H}_{11})(\text{NCCH}_3)]^+$. When suspended in *n*-hexane, the new salt **12** reacts further with various nitriles. The IR spectrum in the $\nu(\text{CN})$ range of the green product from *n*-butyronitrile, **13**, still displays the $\nu(\text{CN})$ band of coordinated $\text{CN-c-C}_6\text{H}_{11}$ at 2190 cm^{-1} , while the two bands indicative (in the spectrum of **12**) of NCCH_3 are replaced by the single $\nu(\text{CN})$ band of coordinated $\text{NC-c-C}_3\text{H}_7$ (2270 cm^{-1}). An explanation for the selective substitution of only the NCCH_3 ligand is not quite straightforward. In control the previously described mixed-ligand systems $[\text{Cp}_3\text{U}(\text{NCR})(\text{CNR}')][\text{BPh}_4]$ selectively exchange the isocyanide ligand when treated with another nitrile (1/1) in *n*-hexane [5].

Attempts to prepare the pseudo-salt **11** by treating the methyl complex **8** first with acetonitrile and then with BPh_3 gave the light green adduct “ $\text{Cp}_3\text{UCH}_3(\text{NCCH}_3)$ ” (**14**) (eq. 7), which is probably again *tbp*-configured,



but reluctant to react further with BPh_3 . While compound **14** is insoluble in toluene and acetonitrile, its solubility in methylene chloride allows a study of the ^1H NMR spectrum in CD_2Cl_2 . The appearance of three singlets at $\delta -0.02$ (15H), $\delta -13.75$ (3H) and $\delta 1.26$ (3H) agrees well with the analytically determined composition. The NIR/VIS spectrum displays absorptions typical of *tbp*-configured Cp_3U derivatives, but the $\nu(\text{CN})$ range of the IR spectrum shows only one band at a notably lower frequency (2110 cm^{-1}) than for non-coordinated NCCH_3 . The latter feature probably rules out both an insertion of the nitrile (into the U-CH_3 bond) and its isomerization (to CNCH_3), but would be consistent with the formation of a CN-bridge between two metal centres [21*].

Experimental

All manipulations were carried out under nitrogen by the Schlenk tube technique. Infrared spectra were recorded on Perkin–Elmer PE 577 and PE 325 spectrometers, NIR/VIS spectra on a CARY 17 (Varian) spectrometer, and ^1H NMR spectra on Bruker WP 80 or AM 360 spectrometers. All elemental analyses (theoretical values in parentheses) were performed by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim/Ruhr (F.R.G.). The complex $(\text{C}_5\text{H}_4\text{CH}_3)(\text{C}_5\text{H}_5)_2\text{UCl}$ was prepared from $\text{C}_5\text{H}_4\text{CH}_3\text{UCl}_3(\text{THF})_2$ [22] by adaptation of a procedure described by Dormond [23].

$[(\text{C}_5\text{H}_5)_3\text{U}(\text{H}_2\text{O})_2][\text{B}(\text{C}_6\text{H}_5)_4] \cdot 10\text{H}_2\text{O}$ (**1**). Preparation: 2.35 g (5.0 mmol) of $(\text{C}_5\text{H}_5)_3\text{UCl}$ is dissolved with stirring in ca. 250 ml O_2 -free H_2O . The dark green solution is filtered and a concentrated aqueous solution of 1.71 g (5.0 mmol) of $\text{NaB}(\text{C}_6\text{H}_5)_4$ is added slowly. The precipitate (green voluminous flakes) is filtered off from the colourless solution and cautiously dried at room temperature under an oil pump vacuum. The final dry powder (yield: 2.1 g $\hat{=}$ 43.3%) is stored at -25°C . Analysis for $\text{C}_{39}\text{H}_{59}\text{O}_{12}\text{BU}$: C, 47.26 (48.39); H, 6.12 (6.10); U, 25.96 (24.61); B, 1.18 (1.11)%. IR absorptions of H_2O : 3580 s, 3515 s, 3465 s, 1608 s (Nujol mull); 3460 br, 3392 br, 1603 m, 1590 m, 1579 m cm^{-1} (KBr). ^1H NMR (CD_3CN): δ 6.8 to 7.3, broad, 20 H, C_6H_5 ; δ 0.66, s, 24 H, H_2O ; $\delta -0.22$, s, 15H, C_5H_5 . NIR/VIS spectrum: 6439 and 16 502 cm^{-1} (most intense).

$[\text{C}_5\text{H}_4\text{CH}_3(\text{C}_5\text{H}_5)_2\text{U}(\text{H}_2\text{O})_2][\text{B}(\text{C}_6\text{H}_5)_4] \cdot \text{H}_2\text{O}$ (**2**). A procedure similar to that described for **1** was used, starting from 0.40 g (0.83 mmol) of $\text{C}_5\text{H}_4\text{CH}_3(\text{C}_5\text{H}_5)_2\text{UCl}$ dissolved in 50 ml H_2O and 0.283 g (0.83 mmol) of $\text{NaB}(\text{C}_6\text{H}_5)_4$ in 10 ml H_2O . Yield: 359.7 mg $\hat{=}$ 54.4%. Analysis for $\text{C}_{40}\text{H}_{43}\text{O}_3\text{BU}$: C, 58.7 (58.55); H, 6.42 (5.24); B, 1.20 (1.32)%. IR absorptions of H_2O : 3580, s, 3510 m, 3470 m, 1608 m (Nujol mull); 3500 vw, 3460 m, 1603 m, (KBr). ^1H NMR (CD_3CN): δ 6.8 to 7.3, broad, 20H, C_6H_5 ; δ 5.5 s, 2H, C_5H_4 ; δ 1.63 s, 6H, H_2O ; δ -0.04, 2H, C_5H_4 ; δ -0.43 s, 5H, C_5H_5 ; δ -0.96 s, 5H, C_5H_5 (CH_3 of $\text{C}_5\text{H}_4\text{CH}_3$ undetectable [24*]). NIR/VIS spectrum: 6451 and 16666 cm^{-1} (most intense).

$(\text{C}_5\text{H}_5)_3\text{UB}(\text{C}_6\text{H}_5)_4$ (**4**). This was prepared by keeping a sample of **1** for 3 h under high vacuum at 30–40 °C. Analysis for $\text{C}_{39}\text{H}_{35}\text{BU}$: C, 61.00 (62.31); H, 4.56 (4.66); U, 32.26 (31.69)%. NIR/VIS spectrum: 7741 s, 9688 m cm^{-1} (most intense bands).

$(\text{C}_5\text{H}_5)_3\text{UC}_6\text{H}_5$ (**6**). This was prepared by keeping compound **4** for ca. 5 h under high vacuum at 130–140 °C. Analysis for $\text{C}_{21}\text{H}_{20}\text{U}$: C, 49.30 (49.41); H, 3.97 (3.92); U, 46.55 (46.66)%.

$(\text{C}_5\text{H}_4\text{CH}_3)_3\text{UCH}_3$ (**7** [25*]). Preparation: 1.25 ml of a fresh solution of LiCH_3 in $(\text{C}_2\text{H}_5)_2\text{O}$ (1.6 M; 44.0 mg $\hat{=}$ 2.00 mmol) are added with stirring to a cooled (-80 °C) solution of 1022 mg (2.01 mmol) of $(\text{C}_5\text{H}_4\text{CH}_3)_3\text{UCl}$ in 200 ml of toluene. After ca. 3 h evaporation of the solvent at room temperature and recrystallization of the residue from hexane gives 765.0 mg of green **7** (yield: 78%). Analysis for $\text{C}_{19}\text{H}_{24}\text{U}$: C, 46.47 (46.53); H, 4.66 (4.93); U, 48.51 (48.54)%. NIR/VIS spectrum (Teflon pellet): Very similar to that of $(\text{C}_5\text{H}_5)_3\text{UCH}_3$.

$(\text{C}_5\text{H}_5)_3\text{UCH}_3\text{B}(\text{C}_6\text{H}_5)_3$ (**10**). A solution of 277 mg (1.15 mmol) of BPh_3 in 20 ml toluene is added with stirring to a filtered solution of 513 mg (1.45 mmol) of $(\text{C}_5\text{H}_5)_3\text{UCH}_3$ in 40 ml toluene. After a few minutes the colour of the solution changes from deep brown to light brown, and the brown product is allowed to separate out overnight and then filtered off, washed with n-hexane (2 \times 30 ml), and dried under oil pump vacuum to give 474 mg (yield: 60%) of **9**. Analysis for $\text{C}_{34}\text{H}_{33}\text{UB}$: C, 59.36 (59.14); H, 4.82 (4.78)%.

$(\text{C}_5\text{H}_4\text{CH}_3)_3\text{UCH}_3\text{B}(\text{C}_6\text{H}_5)_3$ (**9**). The procedure used for **9** is used but starting from saturated solutions of **7** (313.1 mg $\hat{=}$ 0.64 mmol) and 157.0 mg (0.64 mmol) of BPh_3 in toluene. Isolation of the brown precipitate after two days (ca. 2 °C) gives 365.7 mg (yield: 78%) of pure **10**. Analysis for $\text{C}_{37}\text{H}_{39}\text{UB}$: C, 60.29 (60.42); H, 5.36 (5.34); U, 32.26 (32.36)%.

$(\text{C}_5\text{H}_5)_3\text{UCH}_3\text{B}(\text{C}_6\text{H}_5)_3(\text{NCCH}_3)$ (**11**). Preparation: 200 mg (0.29 mmol) of **10** are dissolved in 30 ml of NCCH_3 . The clear green solution is separated from the precipitate, and evaporation of the solvent leaves 150 mg (yield: 71%) of **11**. Analysis for $\text{C}_{36}\text{H}_{36}\text{NBU}$: C, 59.08 (59.11); H, 4.94 (4.92); N, 2.06 (1.91); U, 32.44 (32.56)%. Except for that attributed to CH_3CN , the positions of all the ^1H NMR signals remain practically unchanged over the temperature range of 300–240 K.

$[(\text{C}_5\text{H}_5)_3\text{U}(\text{CNC}_6\text{H}_{11})(\text{NCCH}_3)][\text{U}(\text{C}_6\text{H}_5)_3\text{CH}_3]$ (**12**). Preparation: 1.5 ml (2.4 mmol) of $\text{CNC}_6\text{H}_{11}$ are added with stirring to a suspension of 100 mg (0.137 mmol) of **11** in 25 ml n-hexane. The green precipitate is filtered off, washed with fresh n-hexane (3 \times 30 ml), and dried under oil pump vacuum to give 110 mg of pure **12** (yield: 96%). Analysis for $\text{C}_{43}\text{H}_{47}\text{N}_2\text{BU}$: C, 61.39 (61.44); H, 5.62 (5.59); N, 3.40 (3.33); U, 28.40 (28.33)%.

$[(\text{C}_5\text{H}_5)_3\text{U}(\text{CNC}_6\text{H}_{11})(\text{NCC}_3\text{H}_7)][\text{B}(\text{C}_6\text{H}_5)_3\text{CH}_3]$ (**13**). The procedure described

for **12** but starting from 300 mg (0.357 mmol) of **12** suspended in 50 ml n-hexane and 2 ml NCC_3H_7 gives 305 mg (98%) of pure **13**. Analysis for $\text{C}_{45}\text{H}_{51}\text{N}_2\text{BU}$: C, 62.02 (62.22); H, 5.80 (5.87); N, 3.26 (3.22); B, 1.12 (1.24)%.

" $(\text{C}_5\text{H}_5)_3\text{UCH}_3(\text{NCCH}_3)$ " (**14**). Preparation: 600 mg (1.34 mmol) of $(\text{C}_5\text{H}_5)_3\text{UCH}_3$ are dissolved in 60 ml of CH_3CN . The brownish green solution is filtered, then kept for ca. 15 h at -25°C , and the green precipitate is filtered off, washed with 10 ml of n-hexane, and dried under oil pump vacuum to give a yellowish green, air sensitive powder. Yield: 100 mg (15%). Analysis for $\text{C}_{12}\text{H}_{21}\text{NU}$: C, 44.08 (44.17); H, 4.40 (4.29); N, 2.90 (2.86)%.

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