LANTHANIDES AND ACTINIDES

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I. Organometallic derivatives of lanthanides

Considerable progress towards the characterisation of lanthanide σ-bonds to carbon has been made with the preparation of the aryllutetium derivative $[Lu\{C_6H_3(CH_3)_2\}_4]^-$, isolated [1] as its lithium derivative. The compound was prepared by the reaction of 2,6-dimethylphenyllithium with anhydrous lutetium trichloride in tetrahydrofuran (THF) at -78°C:

$$LuCl_3 + 4\ LiC_6H_3(CH_3)_2 + 4\ C_4H_8O \xrightarrow[-78^\circ C]{THF}$$

$$[Li(C_4H_8O)_4]\,[Lu\{C_6H_3(CH_3)_2\}_4] + 3\ LiCl \qquad (1)$$

The X-ray structure of the lithium derivative has shown that the aryl groups are tetrahedrally arranged around the central metal atom, thus establishing the first example of coordination number four for a lanthanide element. Of particular interest are the lutetium—carbon lengths. These distances are 2.425, 2.439, 2.442 and 2.501 Å. According to Pauling [2], the lutetium ionic radius is 0.93 Å. It is interesting to compare the lutetium—carbon bond lengths with the similar distances for a 3*d* transition element. The average chromium—carbon bond length in the cationic arylchromium(III) derivative *cis*-bis(2-methoxyphenyl)bis(2,2'-dipyridyl)iodide [3] is 2.10 Å. Considering that the ionic radius of trivalent chromium is 0.69 Å, the longer lutetium—carbon distance experimentally found can be justified simply on the basis of the increased size of the central metal atom. The X-ray structure of the aryllutetium(III) derivative definitely established the existence of σ-bonds to aryl groups for lanthanide elements. Whether these bonds are predominantly ionic or covalent is probably a question which will not be settled soon. The present writer feels that it is important for preparative chemists to make new contributions in this field of organometallic chemistry.

The ^1H NMR and IR spectra of cyclohexylisocyanide adducts of tricyclopentadienyl derivatives of all the lanthanide elements from lanthanum to lutetium have been measured [4]. The complexes have the general formula $Ln(C_5H_5)_3CNC_6H_{11}$. The cerium, samarium, europium, gadolinium, dysprosium, erbium, thulium and lutetium derivatives were reported for the first time. In agreement with the relatively high oxidation state of the central metal atom, an increase of the CN stretching frequency with respect to the uncoordinated isonitrile was observed in all the complexes. However, the observed CN stretching frequency depends on the atomic number of the central metal atom and, more specifically, on its electron configuration.

The Lewis acidity of the lanthanide elements in their tricyclopentadienyl derivatives has been evidenced [5] by the formation of adducts with some carbonyl and nitrosyl complexes of *d* transition elements. Tris(methylcyclopentadienyl)samarium and $[Fe(C_5H_5)(CO)_2]_2$ form a 1/2 adduct in benzene at room temperature: the infrared spectrum (nujol mulls) shows bands at 2024, 1980 and 1700 cm^{-1}, the latter being attributed to the bridging CO groups coordinated to samarium through the oxygen atom. Evidence of oxygen-bonded adducts with other metal carbonyl derivatives and metal nitrosyl complexes was gathered in CH_2Cl_2 solutions. This choice of the solvent may, however, appear somewhat unfortunate since it had been shown [6] earlier that halogenated solvents react with $[FeC_5H_5(CO)_2]_2$.

Of particular interest is the molecular structure [7] of the anionic dicyclooctatetraene complex of cerium(III) whose isolation as its potassium diglyme derivative, $[K(diglyme)][Ce(C_8H_8)_2]$, had been reported earlier by Streitwieser and coworkers [8]. As shown in Fig. 1, the anion is of the sandwich type, similar to dicyclooctatetraeneuranium(IV): contrary to the uranium analogue having D_{8h} symmetry, however, in this case the two eight-membered rings are staggered thus leading to the D_{8d} symmetry for the anion. A further interesting feature of the structure is that the potassium cation is coordinated not only to the oxygen atoms of diglyme, but also to one of the eight-membered rings.

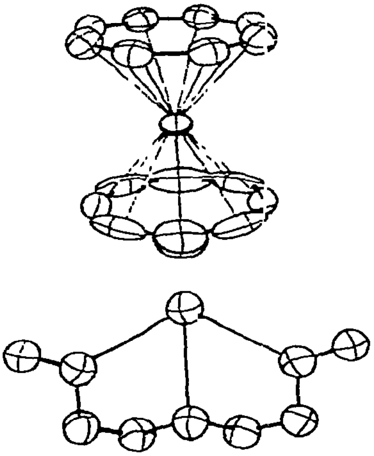


Fig 1 Structure of the $[Ce(C_8H_8)_2]^-$ anion forming ion pair with $[K(diglyme)]^+$ (K.O Hodgson and K.N. Raymond, Inorg. Chem., 11 (1972) 3030).

The molecular structure of another cyclooctatetraene complex of cerium(III), $[Ce(C_8H_8)Cl(THF)_2]_2$ has been investigated [9]. The complex was prepared [10] by the reaction of cerium(III) chloride with $K_2C_8H_8$ (1/1) in tetrahydrofuran (THF). The X-ray investigation has established that the compound is a chlorine-bridged dimer. The coordination of each of the cerium atoms consists of two chlorine atoms, two oxygens of the THF units and a planar cyclooctatetraene ligand.

The preparation of anhydrous cyanides of europium(II) and ytterbium(II) from the metals and NH_4CN in liquid ammonia was reported [11]:

$$\mathrm{Eu(Yb)} \xrightarrow[\mathrm{NH_4CN}]{\mathrm{liq.\,NH_3}} \mathrm{Eu(Yb)(CN)_2} \tag{2}$$

The compounds were probably contaminated with the cyanides of Eu^{III} and Yb^{III}. The relatively high wavenumber value of the CN stretching vibration of the solids led to the suggestion of some covalent character in the metal—carbon bond.

II. Organometallic derivatives of actinides

Thermally stable alkyl and aryl derivatives of uranium(IV) of formula $U(C_5H_5)_3R$ have been reported by three groups of workers [12—15]. The compounds were synthesized by the classical alkylation reactions of $U(C_5H_5)_3Cl$ by either alkyl- and aryllithiums or Grignard reagents:

$$\mathrm{U(C_5H_5)_3Cl + LiR} \longrightarrow \mathrm{LiCl + U(C_5H_5)_3R} \tag{3}$$

$$\mathrm{U(C_5H_5)_3Cl + RMgX} \longrightarrow \mathrm{MgXCl + U(C_5H_5)_3R} \tag{4}$$

The compounds with the following R ligands were reported: CH_3 [13, 14], n-C_4H_9 [13, 14], $(CH_3)_3CCH_2$ [14], allyl [14], $C_6H_5CH_2$ [13], p-$CH_3C_6H_4CH_2$ [13], i-C_3F_7 [14], $C_6H_5C{\equiv}C$ [15], C_6H_5 [12, 13, 15], p-$CH_3C_6H_4$ [15], C_6F_5 [14]. It is interesting noting that the reaction of phenyllithium with $U(C_5H_5)_3Cl$ had been carried out earlier [16] but had not resulted in the formation of a pure product. The alkyl and aryl derivatives of uranium(IV) are remarkably stable thermally. The n-butyl compound was reported [14] to be completely decomposed at 100°C only after 15 h in toluene solution; the phenyl, methyl and benzyl derivatives are not decomposed upon heating at 150°C [13]. This high thermal stability contrasts with the very high sensitivity to both oxygen and water. Hydrolysis of the phenyl derivatives yields benzene [15]. Reaction with methanol gives cleavage of the uranium—carbon bond with formation of the methoxy derivative [15] and the hydrocarbon in substantially quantitative yields [13]:

$$\mathrm{U(C_5H_5)_3R + ROH} \longrightarrow \mathrm{RH + U(C_5H_5)_3OR} \tag{5}$$

It has been observed [13], however, that the attack by methanol can also take place at the uranium—cyclopentadienyl bond with formation of cyclopentadiene

$$\mathrm{U(C_5H_5)_3OR} \xrightarrow{\mathrm{ROH}} \mathrm{U(OR)_4 + C_5H_6} \tag{6}$$

Cyclopentadiene is also an important fragment in the mass spectrum of the phenyl derivative [13]. The corresponding deuterated compound $U(C_5H_5)_3C_6D_5$ gives the same fragment, thus showing that an intramolecular hydrogen shift between two cyclopentadienyl groups is occurring.

These alkyl and aryl derivatives are paramagnetic with μ_{eff} in the neighbourhood of 2.8 BM, which is typical of several uranium(IV) compounds of f^2 configuration. The proton resonance spectra can be observed and the presence of the paramagnetic center gives rise to very remarkable and unique upfield shifts.

The borohydrido derivative of uranium(IV), $U(BH_4)_4$, has a polymeric structure in the solid state [17] with four intermolecular bridging and two terminal BH_4 per uranium atom; this investigation by X-ray diffraction could not locate the hydrogen atoms. The uranium—boron building unit of the solid state structure is shown in Fig. 2

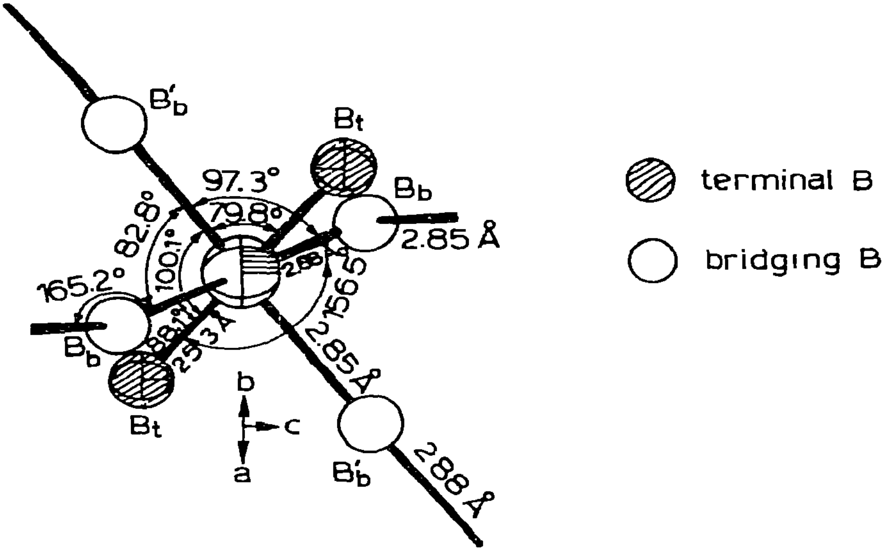
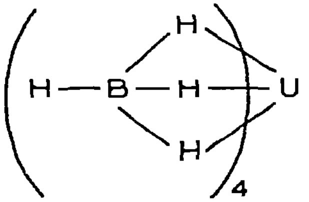


Fig. 2. The arrangement of terminal and intermolecular bridging BH_4 units around uranium in $U(BH_4)_4$ (E.R. Bernstein, T.A. Keiderling, S.J. Lippard and J.J Mayerle, J. Amer. Chem. Soc., 94 (1972) 2552)

The vapour phase infrared spectrum of $U(BH_4)_4$ suggests that the compound is monomeric [18]. The mass spectrum yielded the parent peak at *m/e* 298 and the infrared spectrum is rather simple thus suggesting a highly symmetrical molecule, probably with four terminal BH_4 groups. In the gas phase the uranium atom was suggested to be bonded to the BH_4 units via a triple intramolecular hydrogen bridge of the type indicated below, thus resulting in a twelve-coordinate uranium atom.



Some of the recent work with carbocyclic derivatives of uranium and heavier actinide elements has been reviewed [19].

Mössbauer spectra of $Np(C_5H_5)_4$, $Np(C_5H_5)_3Cl$ and $Np(C_5H_5)_3 \cdot THF$ have been measured [20]. From the isomer shift data obtained, which were found to be considerably different from those of typical ionic compounds of neptunium(IV), it was concluded that in $Np(C_5H_5)_4$ and $Np(C_5H_5)_3Cl$ a considerable contribution from covalency is operating in the formation of the bonds. On the other hand, in $Np(C_5H_5)_3 \cdot 3THF$, the ionic contribution to bonding was suggested to be predominant.

Three new alkoxytricyclopentadienyl derivatives of uranium(IV) were prepared and their proton magnetic resonance spectra measured [21]. The new compounds were $U(C_5H_5)_3OR$ (R = n-hexyl, cyclohexyl and cholesteryl). The large chemical shifts induced by the paramagnetic center were used to establish conformational details of the R groups.

The complex $U(C_5H_5)Cl_3 \cdot$ dimethoxyethane was prepared [22] by the reaction of anhydrous UCl_4 with cyclopentadienylthallium in dimethoxyethane as solvent:

$$UCl_4 + TlC_5H_5 \longrightarrow TlCl + U(C_5H_5)Cl_3 \qquad (7)$$

The compound crystallized out as the dimethoxyethane adduct and has a μ_{eff} 2.59 BM.

Substitution reactions at the eight-membered rings of "uranocene" systems were reported [23]. Treatment of 1,1′-dimethoxyuranocene with excess n-butyllithium yielded $U(C_8H_7\text{-}n\text{-}C_4H_9)_2$ in good yields. A similar reaction was observed starting with $U[C_8H_7N(CH_3)_3^{+}I^{-}]_2$.

The complete details of the X-ray investigation on $U(C_8H_8)_2$ have appeared [24]. The molecular structure is that of a sandwich type of complex with eclipsed planar cyclooctatetraene rings. The corresponding thorium derivative is isomorphous and isostructural. The mean metal—carbon distances are: 2.647 (uranium) Å; 2.701 (thorium) Å.

A molecular orbital treatment of "uranocene", $U(C_8H_8)_2$ has been published [25], together with similar calculations for the corresponding neptunium and plutonium derivatives. Better agreement with the observed magnetic susceptibility data for $U(C_8H_8)_2$ and $Np(C_8H_8)_2$ were found with this molecular orbital treatment than with earlier predictions made by using a weak field model.

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