ELSEVIER

Coordination Chemistry Reviews 178–180
(1998) 83–116

COORDINATION
CHEMISTRY
REVIEWS

New advances in the chemistry of uranium amide compounds

J.C. Berthet, M. Ephritikhine *

CEA Saclay, DSM/DRECAM/Service de Chimie Moléculaire, CNRS URA 331,
91191 Gif sur Yvette cédex, France

Received 3 November 1997; accepted 5 January 1998

Contents

---

* Corresponding author.

PII S0010-8545(98)00061-7

Abstract

The chloroamide complexes $U(NEt_2)_{4-x}Cl_x$ ($x=1, 2$) were obtained by comproportionation of UCl_4 and $U(NEt_2)_4$. The novel protonolysis reaction of a metal–amide bond with an acidic ammonium salt proved to be an efficient and convenient synthesis of cationic compounds. Thus were synthesized a series of metallo-organic and organometallic uranium cations in the oxidation states +3, +4, +5. The cationic amide compounds were valuable precursors of new derivatives, as they reacted with anionic reagents, acidic substrates and unsaturated molecules to give the addition, substitution and insertion products; in particular, such reactions were useful for the synthesis of monocyclooctatetraene uranium compounds. The dialkyl amide ligand was found able to stabilize the +5 oxidation state of uranium; neutral and cationic uranium(V) complexes were obtained by oxidation of their corresponding anionic and neutral U(IV) precursors. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Amide; Uranium; Uranium(V); Titanium; Zirconium; Hafnium; Cation; Monocyclooctatetraene; Pentamethylcyclopentadienyl

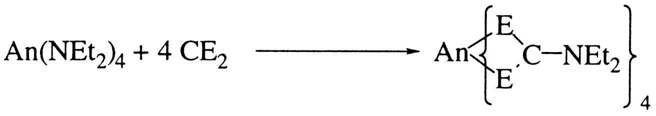
---

1. Introduction

The first metal amide, $Zn(NEt_2)_2$, was prepared by Frankland in 1856 [1], but it is only 100 years after that most of the transition metal amides were discovered [2]. $U(NEt_2)_4$ was isolated in 1956 by Gilman and coworkers in their search of volatile uranium compounds under the Manhattan project [3]. Initial studies revealed the great reactivity of the U–NR_2 bond towards proton acidic molecules like alcohols and thiols; $U(NEt_2)_4$ served to prepare the first alkoxide and thiolate complexes of uranium (Eq. (1)) [3].

$$\begin{gathered} An(NR_2)_4 + 4\ REH \rightarrow An(ER)_4 + 4\ NHR_2 \\ E=O, S \end{gathered} \tag{1}$$

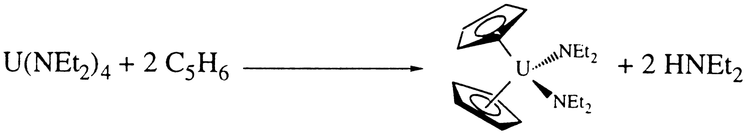
Following a period of relative stagnation, uranium chemistry has enjoyed a spectacular development since the late 1970s, and amide complexes have played an important role in this renewal. In 1974, Bagnall and Yanir reported the synthesis of carbamate and thiocarbamate derivatives, by insertion of CO_2 and CS_2 into the An–N bonds of $An(NEt_2)_4$ (An = U, Th) (Eq. (2)) [4].



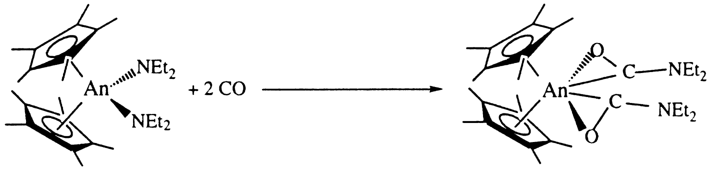
(2)

E=O, S

That same year, Jamerson and Takats prepared the first organoactinide amide complexes, by treatment of $U(NEt_2)_4$ with cyclopentadiene (Eq. (3)) [5], whereas Marks and coworkers described in 1981 the first insertion of carbon monoxide into an [M]–NR_2 bond (Eq. (4)) [6].



(3)



(4)

An = U, Th

Actinide amide complexes are now well considered, generally used, and they occupy a central place in synthetic chemistry. Most of the work concerns the homoleptic amides $An(NEt_2)_4$ which are valuable precursors of new complexes in the +4 oxidation state. However, Andersen and coworkers [7–10] and Sattelberger and coworkers [11–13] exploited the particular properties of the bistrimethylsilylamide ligand $N\{SiMe_3\}_2$ and of some bulky arylamide groups for the preparation of very rare uranium compounds in the oxidation states +3 [7,11,12,8], +5 [9] and +6 [10,13]. All of these results demonstrated that the actinide amides, like their d transition metal counterparts, are very reactive towards proton acidic substrates and small unsaturated dipolar molecules, and are very useful for the synthesis of a large array of coordination compounds [2].

In this review, we wish to report our contribution to the development of uranium amide chemistry. After the synthesis of new chloroamide compounds, we found a novel protonolysis reaction of the amide ligand which constitutes an efficient method of preparation of cationic complexes. These exhibited an interesting reactivity and proved to be valuable precursors of a series of organometallic derivatives. We also found that the dialkylamide group was quite useful for the stabilization of unique uranium complexes in the +5 oxidation state.

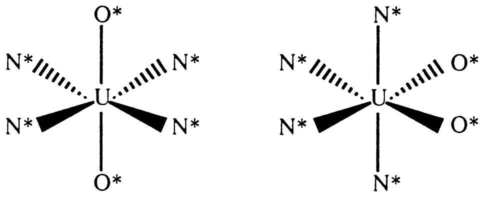
2. Synthesis of new homoleptic amide and chloroamide complexes of uranium(IV)

2.1. *Synthesis and structure of* $[U(NMe_2)_4]_3$

The structure and reactivity of metal amides depend markedly on the steric hindrance of the NR_2 ligands. In the series of the uranium tetra-amides, $U(NEt_2)_4$ is a doubly bridged dimer in the solid state and in benzene solution [14,15] whereas $U(NPh_2)_4$ is monomeric [16]. We have prepared the dimethylamide derivative $U(NMe_2)_4$ since we suspected it to exhibit a peculiar behaviour, owing to the small size of the NMe_2 group [17]. Although $U(NEt_2)_4$ was easily synthesized in diethyl ether by adding 4 equiv. or a slight excess of $LiNEt_2$ to UCl_4 [14,15], similar reaction of UCl_4 and $LiNMe_2$ was not straightforward; the anionic complex

[Li][U$(NMe_2)_4$Cl] was first formed and several extractions in diethyl ether were necessary to eliminate LiCl. The complex is a centrosymmetric linear trimer in its crystalline form (Fig. 1), the metal centres being bridged by three amide ligands; such a geometry was previously found in the compound $U_3(MeNCH_2CH_2NMe)_6$ [18]. The central uranium atom is in an octahedral environment and the other two have a trigonal prismatic coordination. The U–N distances are equal to 2.39 and 2.67 Å for the bridging ligands and 2.25 Å for the terminal groups. It is interesting to note the distinct structures of the analogous complexes $[M(NMe_2)_4]_n$ ($n=1$, 2 and 3 for M = Mo [19], Zr [20] and U respectively) which reflect the increasing radius of the metal centres.

The trimeric structure of $U(NMe_2)_4$ can be broken by coordination of Lewis bases having a high affinity for uranium. For example, addition of two molecules of $(Me_2N)_3PO$ (hexamethylphosphorotriamide, HMPA) led to the monomeric adduct $U(NMe_2)_4(HMPA)_2$ which exists in the form of the cis and trans isomers, observed by nuclear magnetic resonance (NMR) in OC_4H_8 (tetrahydrofuran, THF) at −80 °C.



trans *cis*

N* = NMe_2

O* = HMPA

Interestingly, the cis isomer is predominant (cis/trans = 83/17), whereas only the trans isomer could be detected in the analogous complexes $UX_4(HMPA)_2$ (X = Cl,

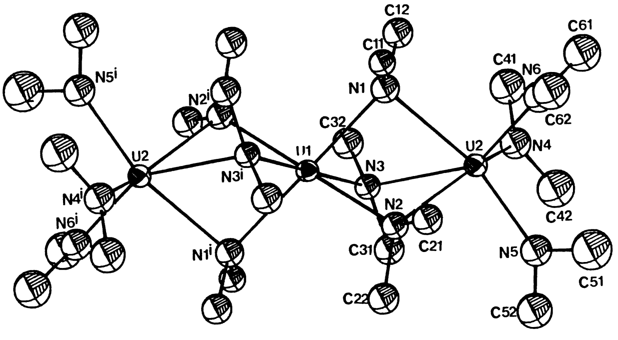


Fig. 1. X-ray structure of $[U(NMe_2)_4]_3$ reprinted from Ref. [17].

Br [21], BH_4 [22], S^iPr [23,24]). This feature is in accordance with the strong trans influence of the dialkylamide ligand.

2.2. Synthesis of $[Li(THF)][U(NEt_2)_5]$ and $[Li(THF)]_2[U(NMe_2)_6]$

It was noted that the amides $U(NR_2)_4$, like the other UX_4 compounds (X = Cl, BH_4, SR), were able to coordinate anionic ligands [14,15,25]. We were interested in the anionic complexes of uranium(IV) since these could be oxidized into the corresponding neutral U(V) derivatives (Section 5.1).

The complexes $[Li(THF)][U(NEt_2)_5]$ and $[Li(THF)]_2[U(NMe_2)_6]$ were easily obtained by addition of $LiNEt_2$ (1 equiv.) or $LiNMe_2$ (2 equiv.) to the corresponding amide $U(NR_2)_4$ [17,26]; however, these compounds were best prepared directly from UCl_4, by treatment with $LiNR_2$ in THF (Eq. (5)).

$$[Li(THF)][U(NEt_2)_5] \xleftarrow[\text{THF}]{5LiNEt_2} UCl_4 \xrightarrow[\text{THF}]{6LiNMe_2} [Li(THF)]_2[U(NMe_2)_6] \qquad (5)$$

In contrast to the dianion $[Mo(NMe_2)_6]^{2-}$ which releases two NMe_2 ligands in toluene [27], these uranium(IV) amide anions are soluble and stable in non-polar solvents.

2.3. Synthesis of the chloroamide complexes

We wished to have at our disposal the chloroamide complexes $U(NEt_2)_{4-x}Cl_x$ as we initially planned to prepare some new uranium amide derivatives by using the metathesis reaction

$$Cl\{U\}NR_2 + MA \longrightarrow A\{U\}NR_2 + MCl \qquad (6)$$

Halogenoamide compounds of the d transition metals, which contain two distinctly reactive functionalities, are of major interest in inorganic and organometallic synthesis, but similar complexes of the f elements were very rare, being limited to the derivatives $M(N\{SiMe_3\}_2)_2Cl_2$ and $M(N\{SiMe_3\}_2)_3Cl$ (M = Th, U) [28,29]. Such silylamide derivatives generally exhibit a peculiar chemistry, different from that of the dialkylamide analogues, owing to the distinct electronic and steric effects of the $N\{SiMe_3\}_2$ ligand [2].

Our attempts to isolate the chloroamide complexes $U(NEt_2)_{4-x}Cl_x$ ($x = 1$, 2, 3) from metathesis reactions between UCl_4 and $LiNEt_2$ were unsuccessful; only anionic products were observed, with retention of lithium chloride on the metal centre. For example, $Li[U(NEt_2)_2Cl_3]$ was obtained in 91% yield by treating UCl_4 with 2 equiv. of $LiNEt_2$ in Et_2O and proved to be stable in alkane and aromatic solvents [30]. This easy formation of anionic "ate" products is a pervasive problem in the chemistry of the f elements [31]. The most straightforward route to the chloroamide complexes was the comproportionation reaction between UCl_4 and $U(NEt_2)_4$ in THF (Eqs. (7) and (8)). These reactions were rapid and the analytically pure complexes $U(NEt_2)_2Cl_2$ and $U(NEt_2)Cl_3(THF)$ were obtained in almost quantitative yields [30].

$$UCl_4 + U(NEt_2)_4 \xrightarrow{THF} 2\ U(NEt_2)_2Cl_2 \qquad (7)$$

$$3UCl_4 + U(NEt_2)_4 \xrightarrow{THF} 4\ U(NEt_2)_2Cl_3(THF) \qquad (8)$$

The tris diethylamide compound $U(NEt_2)_3Cl$ was found to be in equilibrium with $U(NEt_2)_2Cl_2$ and $U(NEt_2)_4$ (Eq. (9)), these complexes being obtained in the same proportions (60:20:20 in THF) when $U(NEt_2)_4$ was mixed with UCl_4 (0.33 equiv.) or $U(NEt_2)_2Cl_2$ (1 equiv.) or when it was treated with 1 equiv. of $HNEt_3Cl$.

$$2\ U(NEt_2)_3Cl \rightleftharpoons U(NEt_2)_4 + U(NEt_2)_2Cl_2 \qquad (9)$$

This behaviour is in contrast to that of the stable silylamide analogue $U(N\{SiMe_3\}_2)_3Cl$ [29]. The chloroamide derivatives $U(NEt_2)_{4-x}Cl_x$ are poorly soluble in aromatic solvents, suggesting that they have an oligomeric or polymeric structure ensured by bridging amide ligands, as observed in the complexes $[U(NR_2)_4]_n$ (R = Et, $n = 2$ [14,15]; R = Me, $n = 3$ [17]), and/or bridging chloride groups, as found in the titanium analogues $Ti(NR_2)Cl_3$ (R = Et, Me) [32,33]. The HMPA adduct $U(NMe_2)_3Cl(HMPA)_2$ was prepared from $U(NMe_2)_4(HMPA)_2$ either by protonation with $NHEt_3Cl$ or substitution reaction with 1 equiv. of LiCl in toluene. Such a displacement of an NMe_2 group by a chloride ion was not so surprising, since it has recently been found that Cl^- was able to displace a cyclopentadienyl ligand from $U(Cp)_4$ ($Cp = \eta^5\text{-}C_5H_5$, cyclopentadienyl) [34]. The NMR spectra at −80 °C in toluene showed that $U(NMe_2)_3Cl(HMPA)_2$ exists in the form of cis and trans isomers, in the proportions 63:37. The crystal structure of the cis isomer

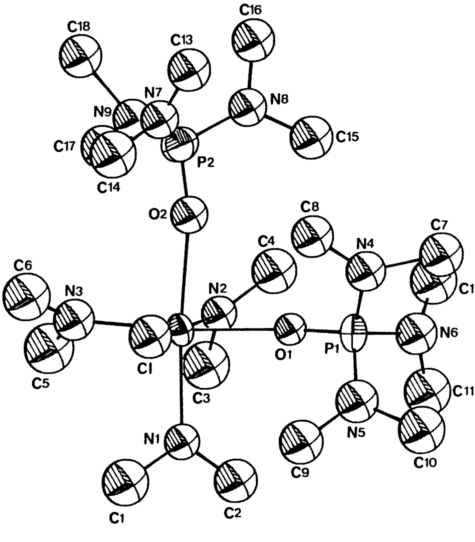
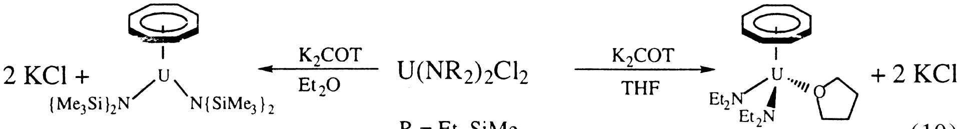


Fig. 2. X-ray structure of $U(NMe_2)_3Cl(HMPA)_2$ reprinted from Ref. [17].

could not be determined with good accuracy because of the disorder of the HMPA ligands; the model is shown in Fig. 2 [17].

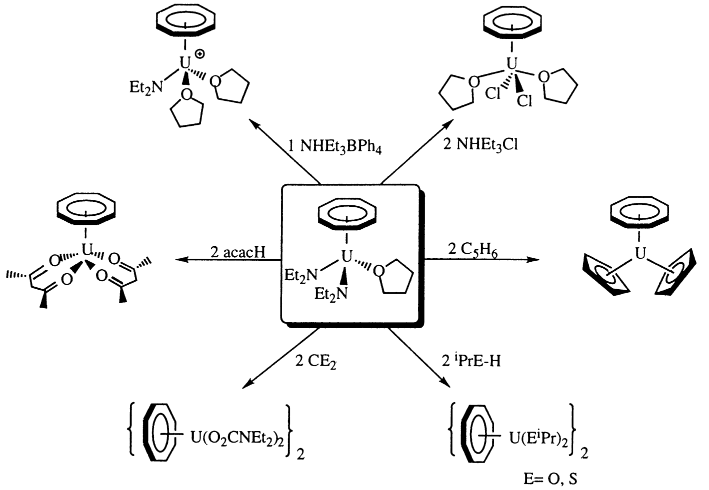
2.3.1. Synthesis of monocyclooctatetraene uranium compounds from $U(NR_2)_2Cl_2$

The chloroamide complexes $U(NEt_2)_{4-x}Cl_x$ can serve as precursors for the synthesis of new derivatives. For example, treatment of $U(NEt_2)_2Cl_2$ with the potassium salt of the cyclooctatetraene anion gave $U(COT)(NEt_2)_2(THF)$ ($COT = \eta^8\text{-}C_8H_8$, cyclooctatetraene) in almost quantitative yield; the same reaction starting from $U(N\{SiMe_3\}_2)_2Cl_2$ led to the known complex $U(COT)(N\{SiMe_3\}_2)_2$ (Eq. (10)) [35,36].



(10)

This bis amide complex proved to be useful for the synthesis of monocyclooctatetraene uranium derivatives, as illustrated in Scheme 1. In particular, reactions with ^{i}PrOH and ^{i}PrSH constitute the best routes to the alkoxide and thiolate complexes $[U(COT)(E^iPr)_2]_2$ ($E = O$, S), which were previously prepared from the borohydride compound $[U(COT)(BH_4)_2]$ [37,38].



Scheme 1. Synthesis of monocyclooctatetraene complexes from $U(COT)(NEt_2)_2(THF)$.

3. Synthesis of cationic uranium and Group IVb metal complexes by protonolysis of amide precursors

It appeared that the metathesis reaction of Eq. (6) could be impeded, here again, by the easy formation of anionic complexes, with retention of the alkali metal in the product. Moreover, elimination of LiCl or NaCl from the reaction mixture is not always straightforward. In order to circumvent these difficulties, which are quite common in actinide chemistry, we have devised a new route, represented by Eq. (11), which consists of the addition of an anionic ligand to a cationic amide species.

$$[\{U\}][BPh_4]+MA \longrightarrow \{U\}\text{–}A+MBPh_4 \tag{11}$$

In addition to these aspects, and from a more general point of view, we were incited to prepare new cationic complexes of uranium, which were rather uncommon, for their potential in stoichiometric and catalytic reactions. In particular, cationic amide complexes of the f and d elements, which had thus far been very scarce and restricted to a few $[\{M\}\text{–}NHR]^+$ and $[\{M\}(N\{SiMe_3\}_2)]^+$ derivatives [39–42], were expected to be quite reactive. In this context, the interest of some organozirconium cations with heteroatom ligands has recently been pointed out [43–45].

Cationic metal complexes are most generally prepared by protonolysis of a metal–carbon or metal–hydrogen bond [46,47], heterolytic cleavage of a metal–halogen or metal–alkyl bond [48,49], and oxidation of a low-valent compound with $AgBPh_4$ [50,51]. Our attempts to abstract chloride ions from the above chloro-amide complexes were unsuccessful. Unexpectedly, treatment of $U(NEt_2)_2Cl_2$ with $AgBPh_4$ led to the formation of the cation $[U(NEt_2)Cl_2]^+$; this reaction is likely to proceed via the oxidation of the uranium(IV) precursor into the corresponding U(V) cation, followed by homolytic cleavage of a $U\text{–}NEt_2$ bond (Section 5.2). By analogy with the protonation of alkyl compounds, we considered the protonolysis of a $[U]\text{–}NR_2$ bond by means of an acidic trialkylammonium salt of the weakly associating counter ion BPh_4^- and we found that this method constitutes an efficient route to cationic metal complexes (Eq. (12)) [26,30].

$$\{U\}\text{–}NR_2+NHR'_3BPh_4 \xrightarrow{THF} [\{U\}][BPh_4]+NHR_2+NR'_3 \tag{12}$$

This reaction is rapid, giving the products in good yields; the volatile amines NHR_2 and NR_3 are easily eliminated from the reaction mixture by evaporation. Whereas the reactivity of the $[M]\text{–}NR_2$ bond towards acidic substrates was well established, the protonolysis reaction in Eq. (12) was unprecedented. We have demonstrated the efficiency and general applicability of this reaction (Eq. (12)) with the preparation of some cations of transition metals (Ti, Zr, Hf) [52] and of a large array of cationic uranium compounds in the oxidation states +3 [53], +4 [30,54] and +5 [26,35,36,55].

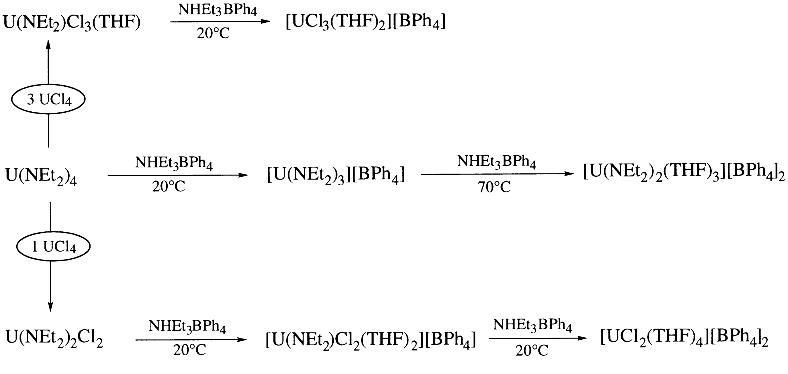
3.1. Uranium and Group IVb metal cations in the oxidation state +4

In Schemes 2–4 are noted the metallo-organic and organometallic complexes of U, Ti, Zr and Hf in the oxidation state +4 that have been isolated by using the protonolysis reaction (Eq. (12)).

3.1.1. Metallo-organic U(IV) cations

Treatment of the amide and chloroamide compounds $U(NEt_2)_4$, $U(NEt_2)_2Cl_2$ and $U(NEt_2)Cl_3(THF)$ with 1 equiv. of the ammonium salt $NHEt_3BPh_4$ readily afforded the cationic derivatives $[U(NEt_2)_3][BPh_4]$, $[U(NEt_2)Cl_2(THF)_2][BPh_4]$ and $[UCl_3(THF)_2][BPh_4]$ in good yields. These reactions were performed in THF at 0–20 °C and it was possible to obtain the dicationic species $[U(NEt_2)_2(THF)_3]^{2+}$ and $[UCl_2(THF)_4]^{2+}$ by further protonation in the refluxing solvent or at room temperature respectively (Scheme 2) [30]. Dark green crystals of $[U(NEt_2)_3(THF)_3][BPh_4]$ were obtained by crystallization from THF–pentane of the pale green powder of $[U(NEt_2)_3][BPh_4]$ and were transformed back into this THF-free compound by drying *in vacuo*. The NMR spectra revealed that $[U(NEt_2)_3][BPh_4]$ adopts a zwitterionic structure in the solid state or in non-coordinating solvents, with two phenyl groups of BPh_4 coordinated to the metal centre. Such a structure has already been observed in the lanthanum complex $(\{Me_3Si\}_2CH)(C_5Me_5)La(\eta^6\text{-}Ph)_2BPh_2$ [56] and a variety of complexes of the transition metals [57].

The crystal structures of the cations $[U(NEt_2)_3(THF)_3]^+$ and $[U(NEt_2)_2(py)_5]^{2+}$ (py = NC_5H_5, pyridine) are represented in Figs. 3 and 4 [30]. The uranium–nitrogen bond distances in these octahedral and pentagonal bipyramidal complexes are quite similar and average 2.18 Å (Table 1). These values are at the lower limit of the range of U–N bond distances for terminally coordinated amide groups (Tables 1 and 2). As previously reported for transition metal and uranium terminal amides, each nitrogen atom lies in the plane (within ±0.02 Å) defined by the metal and the two α carbons; these structural parameters suggest the presence of a π interaction between uranium and nitrogen atoms.



Scheme 2. Synthesis of metallo-organic uranium(IV) cations. All reactions in THF.

3.1.2. Organouranium(IV) cations

The protonolysis reaction (Eq. (12)) served to prepare a variety of cationic organouranium(IV) compounds, as illustrated in Scheme 3 [54]; the yields varied

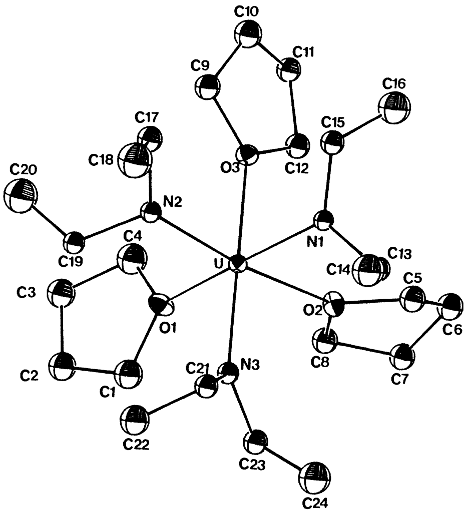


Fig. 3. X-ray structure of $[U(NEt_2)_3(THF)_3]^+$. Reprinted with permission from Ref. [30]. Copyright 1995, The Royal Society of Chemistry.

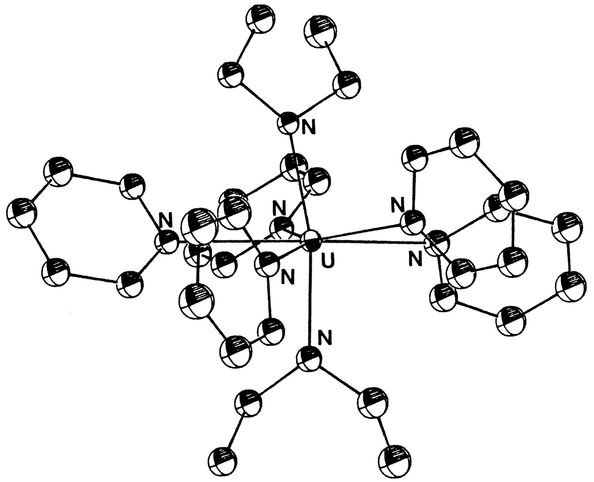


Fig. 4. X-ray structure of $[U(NEt_2)_2(py)_5]^{2+}$.

from 50 to 87%. These are the first examples of cationic monocyclopentadienyl, biscyclopentadienyl, cyclooctatetraene and mixed ring complexes of uranium(IV). However, in contrast to the metallo-organic compounds, no dicationic organouranium complex could be isolated, even in refluxing THF or by using the more acidic and less encumbered ammonium salt NH_4BPh_4 (Section 3.3); such organoactinide dications remain unknown at this time.

The crystal structure of $[U(Cp)_2(NEt_2)(THF)_2]^+$ could not be solved with good accuracy because of the poor quality of the crystals; however, the model (Fig. 5)

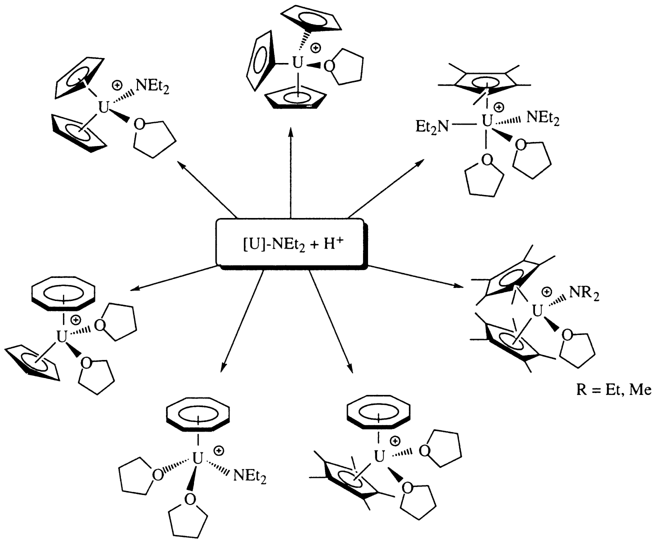
Table 1
Metal–nitrogen bond lengths in uranium metallo-organic complexes

Compound	Average U–N bond lengths[a] (Å)	Reference
Oxidation state +3		
$[\mathrm{U(N\{SiMe_3\}_2)_2(\mu\text{-}NH\{mesityl\})}]_2$	t: 2.339(8) b: 2.55(10)	[8]
$\mathrm{U(N\{SiMe_3\}_2)_3}$	t: 2.320(4)	[11] and references cited therein
$[\mathrm{K(THF)_2}]_2[\mathrm{U(NH\text{–}2,6\text{-}{}^iPr_2C_6H_3)_5}]$	t: 2.34(4)	[11]
Mixed valence +3, +4		
$[\mathrm{U(L)_3}]_2\{\mu\text{-}\mathrm{Cl}\}$ $\mathrm{L = N(CH_2CH_2NSiMe_2{}^tBu)_3}$	t: 2.241(11)	[58]
Oxidation state +4		
$\mathrm{U(NEt_2)(}O\mathrm{\text{–}2,6\text{-}{}^tBu_2C_6H_3)_3}$	t: 2.16(1)	[59]
$[\mathrm{U(NEt_2)_3(THF)_3}]^+$	t: 2.18(2)	[30]
$[\mathrm{U(NEt_2)_2(py)_5}]^{2+}$	t: 2.20(1)	[30]
$\mathrm{U_3(MeNCH_2CH_2NMe)_6}$	t: 2.21(3) b: 2.37(1)	[18]
$[\mathrm{U(NEt_2)_4}]_2$	t: 2.22(2) b: 2.51(6)	[14,15]
$\mathrm{U(N\{SiMe_3\}_2)_2Cl_2(DME)}$	t:2.23(1)	[28]
$\mathrm{U(N\{SiMe_3\}_2)_3H}$	t:2.237(9)	[60]
$\mathrm{U(N\{SiMe_3\}_2)_3(S\text{–}2,6\text{-}Me_2C_6H_3)}$	t:2.24(1)	[61]
$\mathrm{(Me_2N)_3U^1(\mu\text{-}NMe_2)_3U^2(\mu\text{-}NMe_2)_3U^1(NMe_2)_3}$	t: 2.25(1) b: $\mathrm{U^1}$–N: 2.67(2) and $\mathrm{U^2}$–N: 2.39(2)	[17]
$[\mathrm{UCl_2(N\{CH_2CH_2PEt_2\}_2)_2}]_2$	t: 2.25(3)	[62]
$\mathrm{U(N\{CH_2CH_2NSiMe_3\}_3)(BH_4)(THF)}$	t: 2.25(2)	[63]
$[\mathrm{U(N\{CH_2CH_2NSiMe_3\}_3)Cl}]_2$	t: 2.25(2)	[64]
$\mathrm{U(N\{CH_2CH_2NSiMe_3\}_3)(Cp^*)}$	t: 2.26(2)	[63]
$\mathrm{U_4(MeNCH_2CH_2NMe)_8}$	t: 2.27(5) b: 2.50(6)	[65]
$\mathrm{U(NPh_2)_4}$	t: 2.27(8)	[16]
$[\mathrm{U(N\{SiMe_3\}_2)_2(\mu\text{-}N\{}p\mathrm{\text{-}tolyl\})}]_2$	t: 2.28(1)	[8]
$\mathrm{U(N\{SiMe_3\}_2)_3(}O\mathrm{\text{–}2,6\text{-}{}^tBu_2C_6H_3)}$	t: 2.285(2)	[66]
$\mathrm{U(Cp)_3(NPh_2)}$	t: 2.29(2)	[67]
$[\mathrm{Li(OEt_2)}][\mathrm{U(NPh_2)_3(O)}]$	t: 2.37(7)	[16]
Oxidation state +5		
$\mathrm{U(N\{CH_2CH_2P^iPr_2\}_2)_3Cl_2}$	t: 2.156(4)	[68]
$\mathrm{U(N\{SiMe_3\}_2)_3(NSiMe_3)}$	t: 2.295(10)	[9]
Oxidation state +6		
$\mathrm{U(N\{SiMe_3\}_2)_3(NPh)F}$	t: 2.22(2)	[13]
$\mathrm{U(N\{SiMe_3\}_2)_3(NSiMe_3)F}$	t: 2.23(2)	[13]

[a] Terminal (t) and bridging (b).

Table 2
Metal–nitrogen and metal–carbon bond lengths in organouranium amide compounds and some of their cationic derivatives

Compound	Average U–C (Å)	Average U–N (Å)	Reference
Oxidation state +3			
$[U(Cp^*)_2(THF)_2]^+$	2.72(4)		[53]
Oxidation state +4			
$[U(COT)(S_2CNEt_2)(THF)_2]^+$	2.64(4)		[69]
$[U(COT)(NEt_2)(THF)_3]^+$	2.71(7)	2.18(4)	[69]
$[U(COT)(Cp^*)(THF)_2]^+$	2.65(3) U–C(COT) 2.74(1) U–C(Cp*)		[54]
$Na[U(COT)(NEt_2)_3]$ by EXAFS	2.77	2.26	[70]
$[U(Cp^*)(NEt_2)_2(THF)_2]^+$	2.77(5)	2.17(1)	[54]
$[U(Cp^*)_2(O\{CH_2\}_4)_2NMe_2]^+$	2.77(4)		[71]
$U(Cp^*)_2(NH\{C_6H_3Me_2\text{-}2,6\})_2$	2.78(4)	2.267(6)	[72]
$[U(Cp^*)_2(NMe_2)(CN^tBu)_2]^+$	2.77(3)	2.22(1)	[73]
Oxidation state +5			
$[U(COT)(NEt_2)_2(THF)]^+$	2.68(3)	2.116(6)	[35]
and by EXAFS	2.66	2.13	[70]
$[U(COT)(NEt_2)_3]$ by EXAFS	2.73	2.19	[70]
$[U(Cp^*)_2(NEt_2)_2]^+$	2.76(4)	2.164(3)	[55]
$[U(Cp^*)(NMe_2)_3(THF)]^+$	2.76(1)	2.30(5)	[55]



Scheme 3. Synthesis of organometallic cations of uranium(IV).

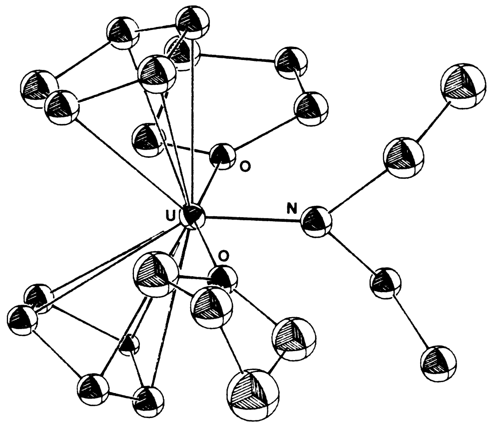


Fig. 5. X-ray structure of $[U(Cp)_2(NEt_2)(THF)_2]^+$.

clearly shows that the amide and two THF ligands lie in a symmetrical arrangement in the equatorial girdle of the bent sandwich, in contrast to that observed in the thorium alkyl compound $[Th(Cp^*)_2(Me)(THF)_2]^+$ ($Cp^* = \eta^5$-C_5Me_5, pentamethylcyclopentadienyl) [46]. The compound $[U(COT)(Cp^*)(THF)_2]^+$ is the second mixed ring complex of uranium to have been crystallographically characterized (Fig. 6), after the trivalent species U(COT)(Cp*)(dmbipy) (dmbipy = $Me_2C_{10}H_6N_2$, 4,4′-dimethyl-2,2′-bipyridine) [74].

The average U–C(COT) and U–C(Cp*) distances of 2.65(2) and 2.74(1) Å are slightly shorter than those reported in the above U(III) complex (respectively 2.703 Å and 2.752 Å) and compare well with those determined in other cyclooctatet-

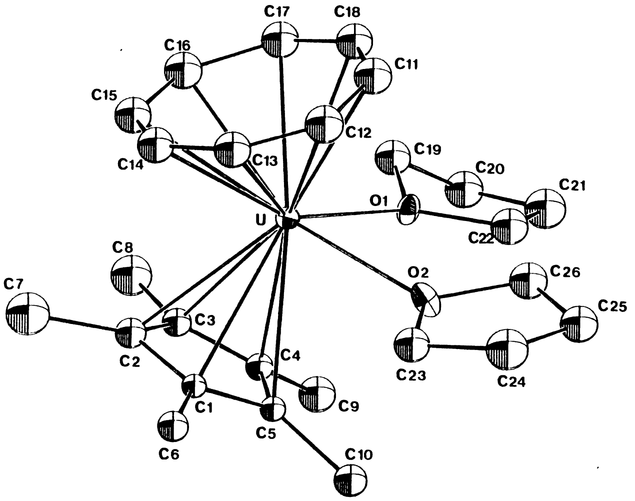


Fig. 6. X-ray structure of $[U(COT)(Cp^*)(THF)_2]^+$. Reprinted with permission from Ref. [54]. Copyright 1995, The Royal Society of Chemistry.

raene and pentamethylcyclopentadienyl uranium(IV) compounds (Table 2). In the amide cations $[U(COT)(NEt_2)(THF)_3]^+$ and $[U(Cp^*)(NEt_2)_2(THF)_2]^+$, (Figs. 7 and 8), the uranium–nitrogen bond distances, which are typically equal to 2.18 Å, are similar to those found in $[U(NEt_2)_3(THF)_3]^+$ and $[U(NEt_2)_2(py)_5]^{2+}$.

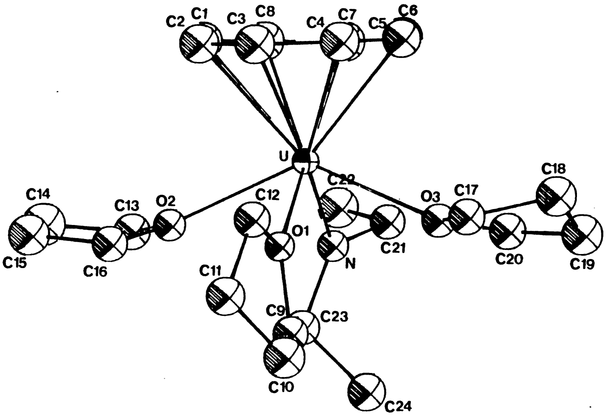


Fig. 7. X-ray structure of $[U(COT)(NEt_2)(THF)_3]^+$. Reprinted with permission from Ref. [69]. Copyright 1996, Elsevier Science.

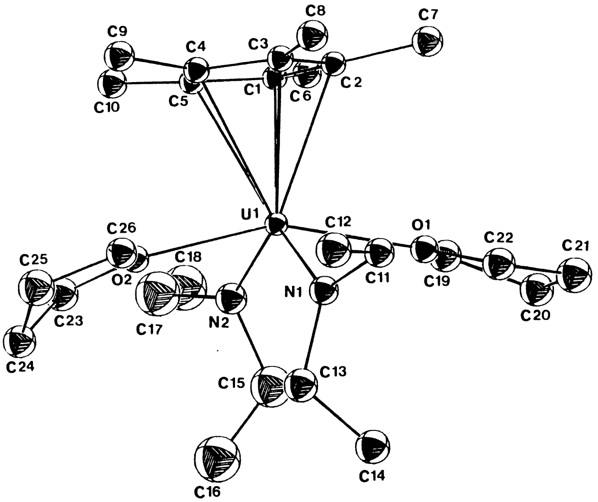


Fig. 8. X-ray structure of $[U(Cp^*)(NEt_2)_2(THF)_2]^+$. Reprinted with permission from Ref. [54]. Copyright 1995, The Royal Society of Chemistry.

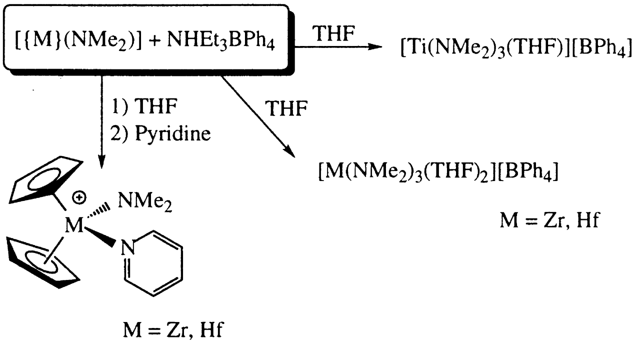
3.1.3. Cationic Group IVb metal compounds

For testing the potential of the protonolysis reaction (Eq. (12)) in the synthesis of cationic complexes of the d transition metals, we considered its application to some representative amide derivatives of the Group IVb elements. Thus, the cations

$[Ti(NMe_2)_3(THF)]^+$ and $[M(NMe_2)_3(THF)_2]^+$ (M = Zr, Hf), the first tris dialkylamido complexes of zirconium and hafnium, and the metallocenes $[M(Cp)_2(NMe_2)(py)]^+$ (M = Zr, Hf) were easily obtained in good yields from the corresponding $M(NMe_2)_4$ and $M(Cp)_2(NMe_2)_2$ compounds (Scheme 4) [52].

In order to displace completely the amine ligand $NHMe_2$ which was in competition with THF in its coordination to the metal centre, pyridine was added to give the stable adducts $[Ti(NMe_2)_3(py)_2]^+$ and $[M(Cp)_2(NMe_2)(py)]^+$ (M = Zr, Hf).

The crystal structure of $[Ti(NMe_2)_3(py)_2]^+$ (Fig. 9) shows the titanium atom in a quite perfect trigonal bipyramidal environment. The Ti–NMe_2 bond distances



Scheme 4. Synthesis of cationic Group IVb metal complexes.

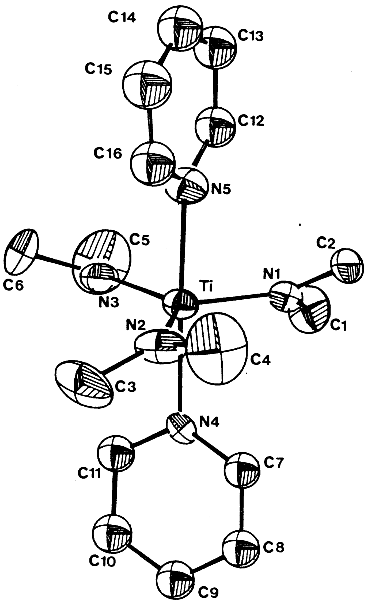


Fig. 9. X-ray structure of $[Ti(NMe_2)_3(py)_2]^+$. Reprinted with permission from Ref. [52]. Copyright 1997, Elsevier Science.

average 1.87(1) Å; as noticed for the uranium analogue $[U(NEt_2)_3(THF)_3]^+$, this value is at the lower limit of the average metal–nitrogen bond distances for terminally coordinated amide groups [52].

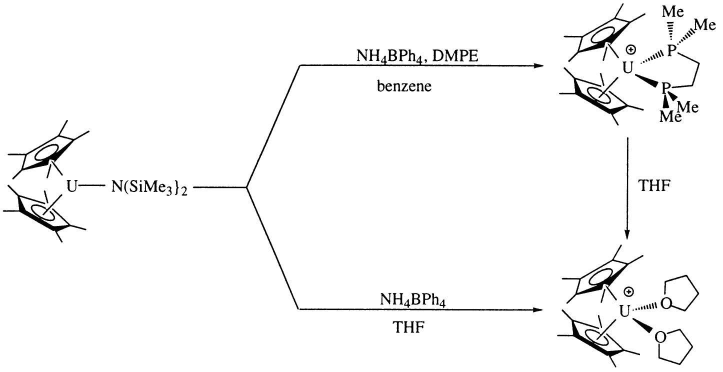
3.2. Selectivity of the protonation of the [U]–X bonds ($X = NR_2$, $N\{SiMe_3\}_2$, alkyl)

We found that $NHEt_3BPh_4$ reacted in THF with the complexes $U(COT)(NEt_2)(N\{SiMe_3\}_2)$ and $U(NEt_2)_2(N\{SiMe_3\}_2)_2$ (the latter being prepared by transamination reaction between $U(NEt_2)_4$ and excess $NH\{SiMe_3\}_2$) to give immediately the cations $[U(COT)(N\{SiMe_3\}_2)(THF)_x]^+$ [69] and $[U(NEt_2)(N\{SiMe_3\}_2)_2(THF)_x]^+$ [53] in quantitative yields, with liberation of $NHEt_2$ and NEt_3 (1 equiv. each). This remarkable selectivity can be explained by the steric and electronic effects of the $SiMe_3$ group; the steric hindrance of the $SiMe_3$ fragment would hinder the approach of the ammonium salt, whereas the delocalization of the nitrogen lone pair on the silicon atoms would decrease the basic character of the $N\{SiMe_3\}_2$ amido group versus its diethylamide analogue.

It was also of interest to compare the protonolysis of a [U]–NR_2 bond with that of a [U]–R bond. This latter reaction has not been used in uranium chemistry, although numerous d transition metal, lanthanide and some organothorium cations have been synthesized by treating the corresponding alkyl precursors with acidic ammonium salts. The cation $[U(Cp)_3(THF)]^+$ was obtained by protonolysis of $U(Cp)_3{}^nBu$ with $NHEt_3BPh_4$, but this transformation was much slower, requiring 10 h instead of 1 h when starting from $U(Cp)_3(NEt_2)$ [26]. Moreover, $U(Cp^*)_2Me_2$ did not react with $NHEt_3BPh_4$, whereas $U(Cp^*)_2(NR_2)_2$ (R = Me, Et) was rapidly transformed into the cation $[U(Cp^*)_2(NR_2)(THF)]^+$. However, by replacing $NHEt_3BPh_4$ with $NHMe_3BPh_4$, it was possible to convert $U(Cp^*)_2Me_2$ into $[U(Cp^*)_2Me(THF)]^+$, which is the first uranium alkyl cation [34]. The same cation was best prepared in quantitative yield following Jordan's method, by reacting the neutral dimethyl complex with $AgBPh_4$ in THF. In contrast, $U(Cp^*)_2Me_2$ was quantitatively transformed into the stable cation $[U(Cp^*)_2(NH_2)(THF)]^+$ when treated with 1 equiv. of NH_4BPh_4 [34]. These results underline the importance of the nature of the ammonium salt in the protonolysis reactions. The reaction in Eq. (12) is much more efficient than protonolysis of alkyl analogues which are less reactive or inert towards the ammonium salts and shows the advantage of amide compounds as precursors to cationic species. These two routes, protonolysis of an M–NR_2 bond with an ammonium salt or cleavage of an M–R bond with $AgBPh_4$ or NHR_3^+, must be considered as important and complementary methods for the synthesis of cations, depending on whether the alkyl or amide precursors are available or not.

3.3. Synthesis of a organouranium(III) cation

Neutral uranium amide complexes in the oxidation state +3 are scarce, being limited to the bistrimethylsilylamide derivatives $[U(N\{SiMe_3\}_2)_2(\mu\text{-}NH\{mesityl\})]_2$ [8], $U(N\{SiMe_3\}_2)_3$ [7] and $U(Cp^*)_2(N\{SiMe_3\}_2)$ [75]. These two latter compounds were found to be inert towards $NHEt_3BPh_4$. However, by using the more acidic and less sterically hindered NH_4BPh_4 salt, the cation $[U(Cp^*)_2(THF)_2]^+$ could be obtained (Scheme 5) [53]. This complex is a very rare example of an organouranium(III) cation [76,77]. The DMPE adduct $[U(Cp^*)_2(DMPE)][BPh_4]$ was prepared by treating $U(Cp^*)_2(N\{SiMe_3\}_2)$ with NH_4BPh_4 in refluxing benzene in the presence of 1 equiv. of DMPE. However, owing to the low solubility of the ammonium salt, the reaction was slow and required about 4 days to afford the cation in 78% yield. $[U(Cp^*)_2(THF)_2]^+$ is the second organouranium(III) cation to have been structurally characterized, after $[U_3(\eta^6\text{-}C_6Me_6)_3(AlCl_4)_3Cl_5]^+$ [76]; it is isostructural with its samarium analogue (Fig. 10) [50]. It is noteworthy that the geometry of the $U(Cp^*)_2$ fragment is quite similar to that found in the complexes



Scheme 5. Synthesis of the trivalent uranium metallocenes

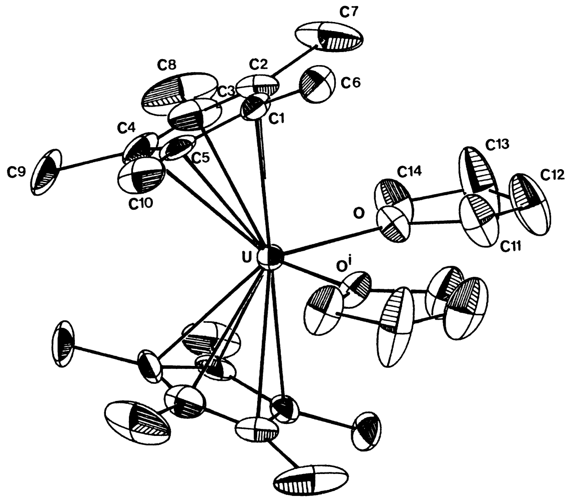
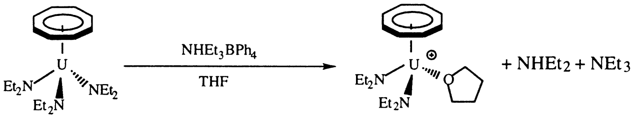


Fig. 10. X-ray structure of $[U(Cp^*)_2(THF)_2]^+$. Reprinted with permission from Ref. [53]. Copyright 1997, Elsevier Science.

$U(Cp^*)_2(BH_4)_2$ [78] and $[U(Cp^*)_2(NEt_2)_2][BPh_4]$ [55], which are respectively in the +4 and +5 oxidation states.

3.4. Synthesis of a organouranium(V) cation

Protonolysis of the U(V) complex $U(COT)(NEt_2)_3$ (Eq. (13)) is the best route to the cation $[U(COT)(NEt_2)_2(THF)]^+$ (Section 5.2).



(13)

4. Reactions of the cationic uranium complexes

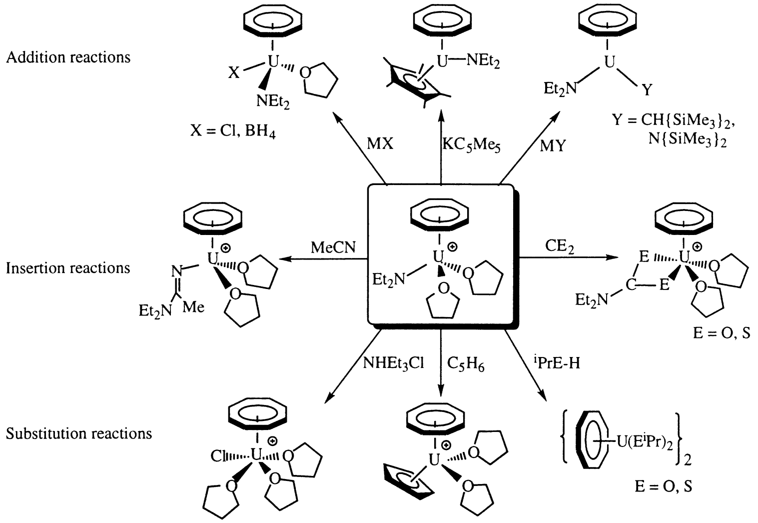
As mentioned above, cationic metal compounds are of major interest in the synthesis of neutral derivatives by reactions with anionic reagents (Eq. (11)) and offer many advantages over the corresponding chloride compounds (Eq. (6)). The weak coordination of the BPh_4 anion [79–81] and the poor solubility of the alkali metal tetraphenylborate $MBPh_4$ (M = Li, Na, K) avoids the formation of "ate" complexes and/or the tedious elimination of salts. In some cases, the cationic complex is the sole useful precursor because the chloride counterpart is not reactive [82] or because the classical metathesis exchange of the chloride is impeded by the reverse reaction of the desired product with the alkali metal chloride, leading to an equilibrium mixture [83,84]. The utility of the cationic complex is even more evident when the corresponding chloride is not stable. In particular, $[U(NEt_2)_3][BPh_4]$ was prepared in grams quantities, whereas $U(NEt_2)_3Cl$ was readily disproportionated into $U(NEt_2)_2Cl_2$ and $U(NEt_2)_4$. The monocyclooctatetraene cation $[U(COT)(NEt_2)(THF)_2]^+$ was also quite stable in contrast to the neutral derivatives $[U(COT)(NEt_2)X(THF)_n]$ (X = Cl, BH_4) which could not be isolated and were transformed into $U(COT)_2$ [69].

Besides the addition reactions giving neutral products, the amide cations can undergo classical reactions of the NR_2 ligand, i.e. substitution with proton acidic substrates and insertion of unsaturated molecules into the metal–nitrogen bond, leading to the formation of new cationic derivatives.

We studied in more detail the reactivity of the cations $[U(COT)(NEt_2)(THF)_2]^+$ and $[U(Cp^*)_2(NMe_2)(THF)]^+$ [69,73] and compared it with that of their neutral precursors $U(COT)(NEt_2)_2(THF)$ and $U(Cp^*)_2(NMe_2)_2$.

4.1. Reactions of $[U(COT)(NEt_2)(THF)_2]^+$

These reactions are summarized in Scheme 6. In the presence of a nucleophile X^-, $[U(COT)(NEt_2)(THF)_2]^+$ was transformed into the neutral complexes



Scheme 6. Reactions of the amide cation $[U(COT)(NEt_2)(THF)_2]^+$.

$U(COT)(NEt_2)X$ (X = Cp, Cp*, $CH\{SiMe_3\}_2$, $N\{SiMe_3\}_2$). The chloride and tetraborohydride complexes $U(COT)(NEt_2)(X)(THF)_x$ (X = Cl, BH_4), readily prepared by addition of LiCl or KBH_4, were stable in THF but decomposed into uranocene and other unidentified products by desolvation. These results underline the advantage of such addition reactions over the classical substitution reactions of halide ligands [82–84].

Like the neutral compound $U(COT)(NEt_2)_2(THF)$, the cation $[U(COT)(NEt_2)(THF)_2]^+$ reacted with the heteroallene molecules CO_2 and CS_2 to give the insertion products, the cationic carbamates $[U(COT)(E_2CNEt_2)(THF)_2]^+$ (E = O, S). In this first crystallographically characterized uranium(IV) dithiocarbamate (Fig. 11) [69], the S_2CNEt_2 ligand is bidentate with an average U–S distance of 2.8(1) Å, similar to that found in the uranyl compound $[UO_2(S_2CNEt_2)_3]^-$ (2.83 Å) [85].

The amide cation was inert towards CO in CH_2Cl_2 but reacted in THF with acetonitrile to give the cationic amidino derivative $[U(COT)(NC\{Me\}\{NEt_2\})(THF)_2]^+$ resulting from insertion of MeCN into the U–NEt_2 bond. In contrast, treatment of $U(COT)(NEt_2)_2(THF)$ with MeCN gave the substitution product, with liberation of $NHEt_2$. It is known that acetonitrile can, in fact, react with metal amides as an unsaturated molecule, giving the insertion amidino product [86,87] or/and as a protic species, giving the cyanoalkyl derivative [88,89]. These results revealed that the cation $[U(COT)(NEt_2)(THF)_2]^+$ was less sensitive to acids than its neutral precursor. Treatment of $[U(COT)(NEt_2)(THF)_2]^+$ with $NHEt_3Cl$ afforded the cation $[U(COT)Cl(THF)_3]^+$. This reaction probably proceeded by the intermediacy of the neutral chloroamide $U(COT)(NEt_2)Cl(THF)_x$, which was further protonated with $NHEt_3BPh_4$; the cation $[U(COT)(NEt_2)(THF)_2]^+$ was found

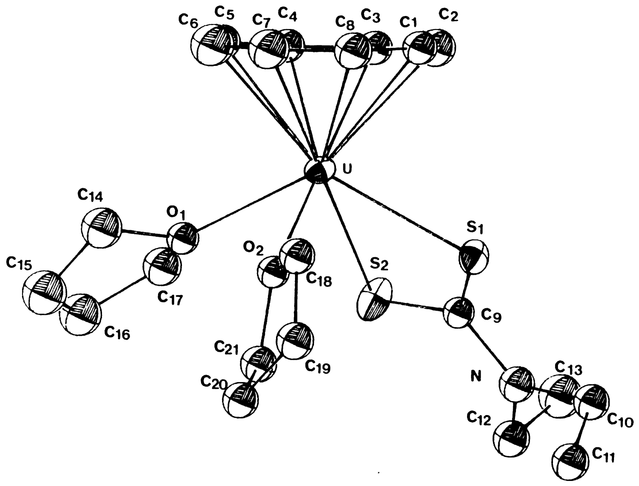


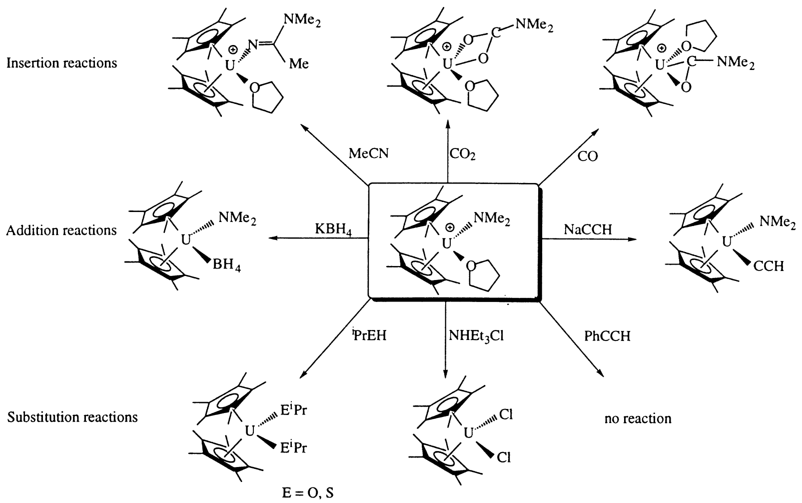
Fig. 11. X-ray structure of $[U(COT)(S_2CNEt_2)(THF)_2]^+$. Reprinted with permission from Ref. [69]. Copyright 1996, Elsevier Science.

to be totally inert towards the acidic ammonium salts $NHEt_3BPh_4$ and NH_4BPh_4. Synthesis of the mixed ring cation $[U(COT)(Cp)(THF)_2]^+$ by treating $[U(COT)(NEt_2)(THF)_2]^+$ with cyclopentadiene required 60 h to go to completion, whereas formation of $U(COT)(Cp)(NEt_2)$ from $U(COT)(NEt_2)_2(THF)$ and C_5H_6 was achieved after only 24 h at 20°C. The cation was inert towards the less acidic phenylacetylene, in contrast to the neutral bis amide which was readily transformed into $U(COT)(NEt_2)(CCPh)$. Reactions of $[U(COT)(NEt_2)(THF)_2]^+$ with isopropanol or isopropanethiol afforded the neutral derivatives $[U(COT)(E^iPr)_2]_2$ ($E=O$, S). The distinct reactivity of the amide cation towards ^iPrOH and PhCCH, which have similar acidities, can be accounted for by initial coordination of the alcohol to the cation, giving $[U(COT)(NEt_2)(HO^iPr)(THF)_x]^+$ followed by proton transfer and elimination of $NHEt_2$. The intermediate $[U(COT)(O^iPr)(THF)_x]^+$ was observed by NMR but could not be isolated as it further coordinated a second ^iPrOH molecule to give the cationic adduct $[U(COT)(O^iPr)(HO^iPr)(THF)_x]^+$ which was then deprotonated into the neutral bisalkoxide by $NHEt_2$ [69].

4.2. Reactions of $[U(Cp^*)_2(NMe_2)(THF)]^+$

The reactions are summarized in Scheme 7. Addition of KBH_4 or NaCCH to the cation gave the neutral derivatives $U(Cp^*)_2(NMe_2)X$ ($X=BH_4$, CCH) [73].

Like the monocyclooctatetraene amide cation $[U(COT)(NEt_2)(THF)_2]^+$, $[U(Cp^*)_2(NMe_2)(THF)]^+$ was rather inert towards proton acidic molecules unless these could be activated by prior coordination to the metal centre. Thus, $[U(Cp^*)_2(NMe_2)(THF)]^+$ did not react with cyclopentadiene, phenylacetylene or



Scheme 7. Reactions of the amide cation $[U(Cp^*)_2(NMe_2)(THF)]^+$.

$NHEt_3BPh_4$ but was transformed in the presence of 2-propanol or 2-propanethiol into the neutral derivatives $[U(Cp^*)_2(E^iPr)_2]_2$ (E=O, S); the cationic intermediate $[U(Cp^*)_2(O^iPr)(THF)]^+$ was observed by NMR. It should not be concluded from these results that alcoholysis of amide cations would not be a suitable route to cationic alkoxide species or that $[\{U\}–OR]^+$ compounds would be inherently unstable. This route was efficient for the synthesis of the first uranium alkoxide cation $[U(Cp^*)(OEt)_2(THF)_2]^+$, isolated in 82% yield from $[U(Cp^*)(NEt_2)_2(THF)]^+$; another way of preparation will be mentioned in Section 5.3. In contrast to its monocyclooctatetraene analogue, the cation $[U(Cp^*)_2Cl(THF)]^+$ could not be obtained by treating $[U(Cp^*)_2(NMe_2)(THF)]^+$ with $NHEt_3Cl$; only the presence of the neutral complex $U(Cp^*)_2Cl_2$ was detected in solution.

The cation $[U(Cp^*)_2(NMe_2)(THF)]^+$ was cleanly transformed into the cationic amidino and carbamate derivatives $[U(Cp^*)_2(NC\{Me\}\{NMe_2\})(THF)]^+$ and $[U(Cp^*)_2(O_2CNMe_2)(THF)]^+$ by insertion of acetonitrile and carbon dioxide into the uranium–nitrogen bond. In contrast to $[U(COT)(NEt_2)(THF)_2]^+$, the bis(pentamethylcyclopentadienyl) cation reacted with carbon monoxide to afford the carbamoyl cation $[U(Cp^*)_2(OCNMe_2)(THF)]^+$; the strong CO stretching vibration band at 1566 cm^{-1} in the infra-red spectrum is characteristic of an η^2 carbamoyl ligand. Such insertion of CO into an $M–NR_2$ bond, which occurred readily in the coordinating solvent THF, is unusual [6]. Insertion of tertiobutyl isocyanide was not observed and only the stable adduct $[U(Cp^*)_2(NMe_2)(CN^tBu)_2]^+$ could be isolated. Its infra-red spectrum exhibits a strong band at 2181 cm^{-1} corresponding to the CN stretching vibration (2136 cm^{-1} in free ^tBuNC) and is in accordance with the crystal structure (Fig. 12) which shows the linear arrangement of the isocyanide groups and the short $C–N(^tBu)$ bond distances (1.14(1) and 1.16(1) Å) [73].

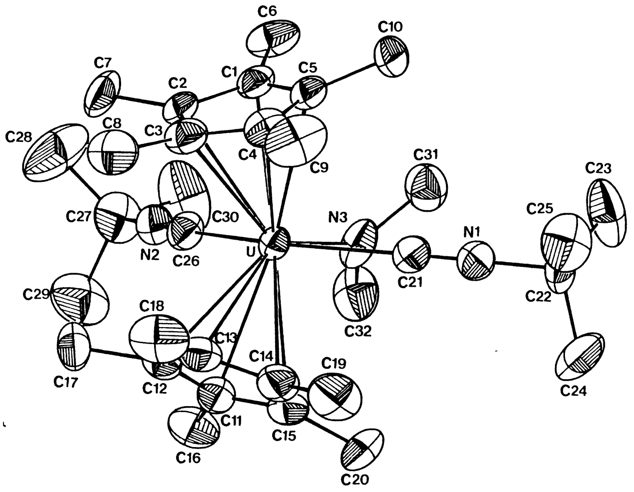


Fig. 12. X-ray structure of $[U(Cp^*)_2(NMe_2)(CN^tBu)_2]^+$. Reprinted with permission from Ref. [73]. Copyright 1997, Elsevier Science.

Another characteristic of cationic complexes is their Lewis acidity which is often evidenced by their ability to promote the ring opening reaction of THF. The complex $[U(Cp^*)_2(NMe_2)(THF)][BPh_4]$ was readily prepared in this solvent and was isolated in very good yield. However, by keeping the reaction mixture for a longer period at room temperature, this compound was slowly transformed into the metallacycle $[(Cp^*)_2\overline{U(O(CH_2)_4NMe_2(CH_2)_4O})][BPh_4]$ which was characterized by its crystal structure (Fig. 13) [71]. This complex is a unique example of a heterocyclic metallacycle

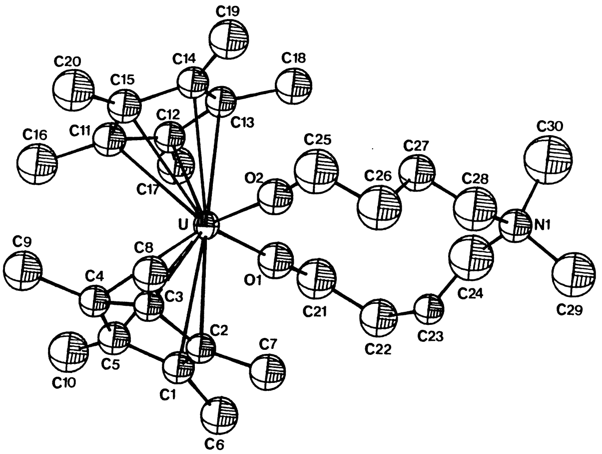
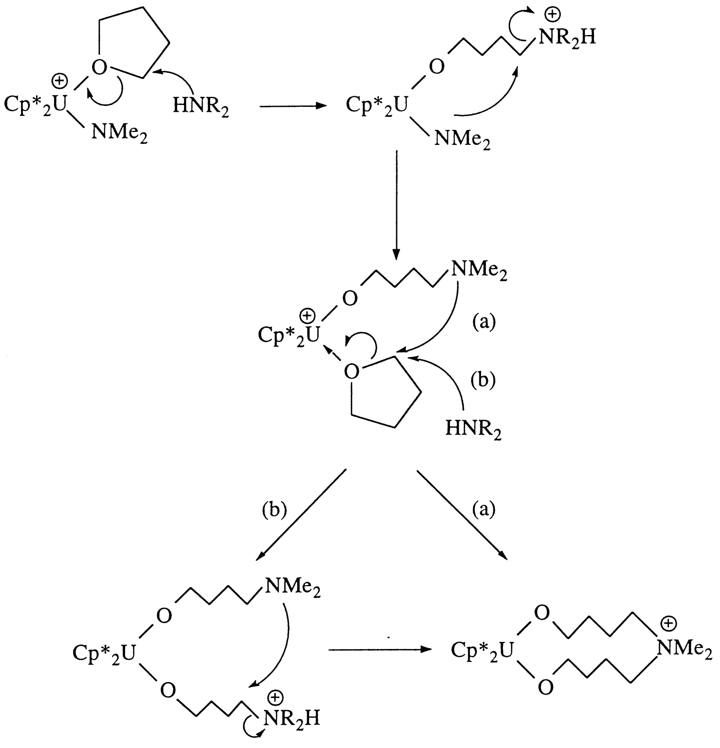


Fig. 13. X-ray structure of $[(Cp^*)_2\overline{U(O(CH_2)_4NMe_2(CH_2)_4O})]^+$. Reprinted with permission from Ref. [71]. Copyright 1996, The Royal Society of Chemistry.

containing both oxygen and nitrogen atoms. A mechanism for its formation is proposed in Scheme 8; the free amine plays a catalytic role in the reaction. While nucleophilic ring opening reactions of THF are well documented [90–93], this synthesis provides the first example of such a transformation where two molecules are opened on a single metal centre to give a heterocyclic metallacycle.



Scheme 8. Proposed mechanism for the formation of $[(Cp^*)_2\overline{U(O(CH_2)_4NMe_2(CH_2)_4O})]^+$.

4.3. *Attempted reductions of the cationic uranium(IV) amide complexes*

Reduction of amide cations seemed to us a possible route to the corresponding neutral U(III) complexes. Our attempts to isolate such species, which have not been reported so far, were unsuccessful; only tetravalent uranium products could be identified. Treatment of $[U(NEt_2)_3]^+$ with Na(Hg) afforded $U(NEt_2)_4$ with total recovery of the NEt_2 ligands, suggesting that the putative $U(NEt_2)_3$ species would readily disproportionate into the tetra-amide and uranium metal [53]. Uranocene and $U(COT)(NEt_2)_2(THF)$ were formed by similar reduction of $[U(COT)(NEt_2)(THF)_2]^+$, whereas $[U(Cp^*)_2(NMe_2)(THF)]^+$ was transformed into $U(Cp^*)_2(NMe_2)_2$.

5. Synthesis and reactions of uranium(V) complexes

At the beginning of this work, uranium (V) compounds were uncommon (Table 3), being limited to some bistrimethylsilyl amide and alkoxide derivatives in the metallo-organic series and a few cyclopentadienyl imido or oxo complexes in the organometallic series; these latter were synthesized by oxidation of their U(III) precursors with organic azides or pyridine oxide.

If not helpful for the preparation of U(III) species, the dialkylamide group was attractive for the synthesis of new high-valent uranium compounds, since this relatively hard ligand proved to be efficient for stabilizing a number of d transition metal complexes in their highest oxidation states. We have synthesised the first homoleptic dialkylamide complexes of uranium(V) and (VI), and unique examples of neutral and cationic organouranium(V) compounds in the monocyclooctatetraene, mono and bis(pentamethylcyclopentadienyl) series.

Table 3
Compounds of uranium in the oxidation state +5

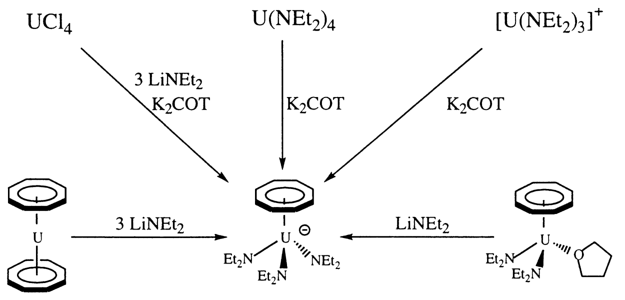
Compound	Reference
$U(\eta^5\text{-}C_5H_4Me)_3(=NR)$ ($R=SiMe_3$, Ph)	[94]
$(L)_3U=NC_6H_4N=U(L)_3$ ($L=\eta^5\text{-}C_5H_4Me$)	[95]
$U(\eta^5\text{-}C_5H_3\{SiMe_3\}_2)_2(=NSiMe_3)Cl$	[96]
$U(N\{SiMe_3\}_2)_3(=O)$	[7]
$U(N\{SiMe_3\}_2)_3(=NR)$ ($R=SiMe_3$, Ph)	[9,97]
$U(OR)_5$, $U(OR)_4Br$,...	[98]
$U(OSiR_3)_5$ ($R=Me$, Et)	[99]
$[Li(dioxane)]_3[UR_8]$($R=Me$, CH_2CMe_3, $SiMe_3$)	[100]

5.1. Synthesis and oxidation of anionic uranium(IV) complexes

Our initial strategy for obtaining uranium(V) amide compounds was the oxidation of anionic tetravalent precursors, according to Eq. (14) [55,101].

$$[\{U^{IV}\}\text{–}(NR_2)_n]^- + M^+ \xrightarrow{THF} [\{U^V\}\text{–}(NR_2)_n] + \underset{M=Tl,\ Ag}{M(0)} \qquad (14)$$

The synthesis of the homoleptic anions $[U(NEt_2)_5]^-$ and $[U(NMe_2)_6]^{2-}$ has been described in Section 2.2. The anion $[U(COT)(NEt_2)_3]^-$ was prepared by different reactions, represented in Scheme 9. The best route was the addition of K_2COT to the cation $[U(NEt_2)_3]^+$, giving the product in 80% yield; the COT bridged compound $(Et_2N)_3U(COT)U(NEt_2)_3$ was an intermediate in this reaction. Treatment of $U(COT)_2$ with $LiNEt_2$ or NaO^iPr afforded the anions $[U(COT)X_3]^-$ ($X=NEt_2$, O^iPr). Such displacement of a COT ligand from uranocene leading to the formation of a monocyclooctatetraene derivative was unprecedented; this did not occur for the preparation of the chloride and borohydride



Scheme 9. Syntheses of the anion $[U(COT)(NEt_2)_3]^-$. All reactions in THF.

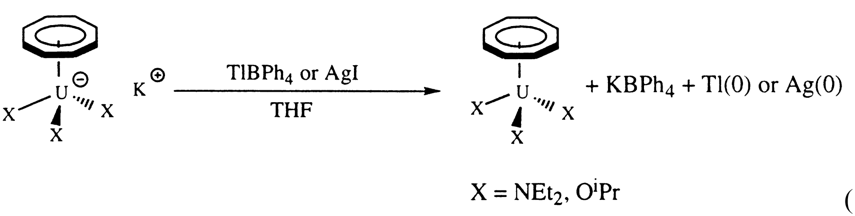
analogues. This difference is probably related to the greater steric hindrance and/or better electron-donating ability of the amide and alkoxide ligands.

Treatment of $[U(NEt_2)_5]^-$ and $[U(NMe_2)_6]^{2-}$ with $TlBPh_4$ or AgI gave immediately the U(V) derivatives $U(NEt_2)_5$ and $[U(NMe_2)_6]^-$ in quantitative yields (Eqs (15) and (16)) [17,26]. Osmometric measurements showed that $U(NEt_2)_5$ is monomeric in benzene, like the other known penta-amide complexes of niobium and tantalum [102,103]. Further oxidation of $[U(NMe_2)_6]^-$, a rare example of a molecular U(V) anionic species, led to the formation of $U(NMe_2)_6$, the first uranium(VI) dialkylamide compound. This latter was moderately stable in solution and progressively decomposed into $U(NMe_2)_5$ and other unidentified products; it was characterized only by its NMR spectrum.

$$[U(NEt_2)_5]^- \xrightarrow{TlBPh_4 \text{ or } AgI} U(NEt_2)_5 \qquad (15)$$

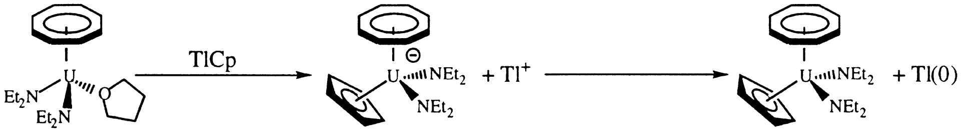
$$[U(NMe_2)_6]^{2-} \xrightarrow{AgI} [U(NMe_2)_6]^- \xrightarrow{AgI} U(NMe_2)_6 \qquad (16)$$

The first uranium(V) monocyclooctatetraene compounds $U(COT)X_3$ ($X = NEt_2$, O^iPr) were obtained in quantitative yield by treatment of the corresponding anions with $TlBPh_4$ or AgI (Eq. (17)). No U(V) compound could be isolated with the softer ligands X = I, BH_4, SR or alkyl [35].



(17)

The neutral complex $U(COT)(NEt_2)_2(THF)$ was inert towards $TlBPh_4$, but in the presence of TlCp it was readily transformed into the U(V) mixed ring compound $U(COT)(Cp)(NEt_2)_2$ with precipitation of metallic thallium (Eq. (18)). It is likely that this reaction proceeded by initial coordination of the cyclopentadienyl ligand, giving the anion $[U(COT)(Cp)(NEt_2)_2]^-$, followed by oxidation with Tl(I). In agreement with this mechanism, the anion was prepared by adding NaCp to $U(COT)(NEt_2)_2(THF)$ and was oxidized by $TlBPh_4$ into the U(V) complex [35].



(18)

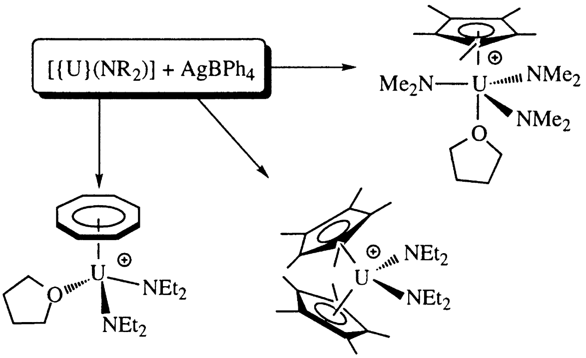
Electrochemical studies indicated that reversible oxidation of $[U(COT)X_3]^-$ ($X=NEt_2$, NMe_2, O^iPr) and $[U(COT)(Cp)(NEt_2)_2]^-$ occurred at a potential which varied from −1.6 to −1.75 V (vs ferrocene–ferrocinium) [104].

5.2. Oxidation of neutral uranium(IV) amide complexes

The neutral uranium(IV) amide compounds were inert towards $TlBPh_4$, but in the presence of the more oxidizing silver salt $AgBPh_4$ some of these could be transformed into the corresponding U(V) cationic complexes, according to Eq. (19).

$$\{U^{IV}\}(NR_2)_n + AgBPh_4 \xrightarrow{THF} [\{U^V\}(NR_2)_n][BPh_4] + Ag(0) \qquad (19)$$

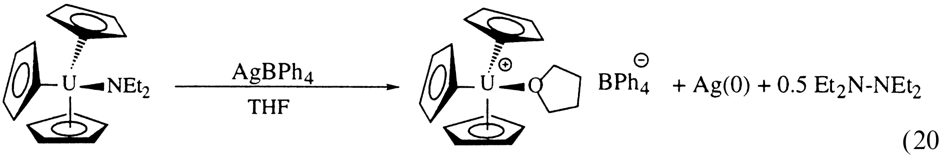
Thus were isolated $[U(COT)(NEt_2)_2(THF)]^+$, $[U(Cp^*)(NMe_2)_3(THF)]^+$ and $[U(Cp^*)_2(NEt_2)_2]^+$ which are the first cationic complexes of uranium(V) (Scheme 10). Electrochemical oxidation of the pentamethylcyclopentadienyl U(IV) precursors was observed at ca −0.7 V (vs ferrocene–ferrocinium).



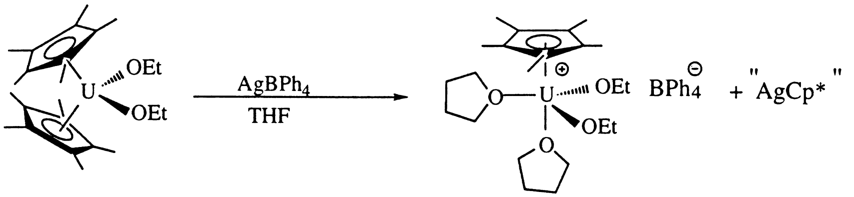
Scheme 10. Synthesis of the cationic organouranium(V) complexes.

5.3. Stability of the uranium(V) compounds

The factors, steric and electronic, which determine the stability of the uranium(V) complexes are not well understood. The cations $[U(Cp^*)(NMe_2)_3(THF)]^+$ and $[U(Cp^*)_2(NEt_2)_2]^+$ and the neutral compound $U(COT)(NEt_2)_3$ were stable in THF solution at 60 °C, but in these conditions $U(COT)(Cp)(NEt_2)_2$ and $[U(COT)(NEt_2)_2(THF)]^+$ were reduced into the U(IV) complexes $U(COT)(Cp)(NEt_2)$ and $[U(COT)(NEt_2)(THF)_2]^+$, following homolytic cleavage of a U–NEt_2 bond. Treatment of the neutral compounds $U(Cp)_3(NEt_2)$ and $U(Cp^*)_2(OEt)_2$ with $AgBPh_4$ in THF afforded the U(IV) cations $[U(Cp)_3(THF)]^+$ and $[U(Cp^*)(OEt)_2(THF)_2]^+$ (Eqs. (20) and (21)).



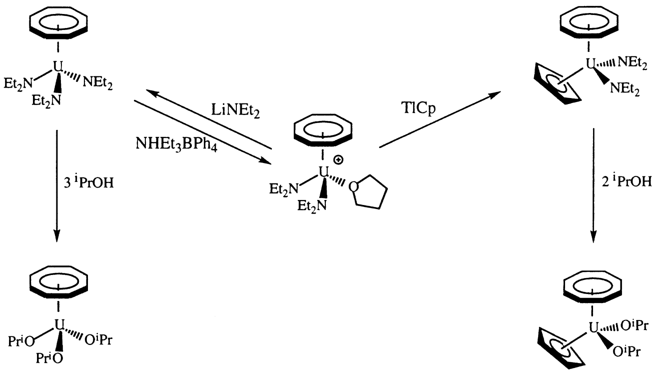
(20)



(21)

Electrochemical studies on a series of complexes $U(Cp)_3X$ ($X=Cl$, BH_4, OR, SR, NEt_2) and $U(Cp^*)_2X_2$ ($X=Me$, BH_4, OEt) have shown that their oxidation gave an unstable U(V) complex and was followed by a chemical reaction, the mechanism of which was not determined [105,106].

Our attempts to use the uranium(V) amide compounds as precursors for the synthesis of new derivatives in this oxidation state were not very successful since, in most cases, uranium(IV) compounds were, here again, the major products. Thus, addition of $LiNEt_2$ or TlCp to $[U(COT)(NEt_2)_2(THF)]^+$ gave the complexes $U(COT)(NEt_2)_3$ and $U(COT)(Cp)(NEt_2)_2$ in ca 40% yield, but $U(COT)(NEt_2)_2(THF)$, $U(Cp)_2(NEt_2)_2$ and other U(IV) species were also present. In the presence of $LiNMe_2$, $[U(Cp^*)(NMe_2)_3]^+$ was transformed into a complex mixture containing $U(Cp^*)(NMe_2)_3$ and $[U(NMe_2)_5]^-$. The uranium(IV) compounds $U(COT)X_2$ were formed when $U(COT)(NEt_2)_3$ was treated with CO_2 or with most of the proton acidic substrates; none of the complexes $U(COT)(NEt_2)_{3-n}X_n$ ($X=O_2CNEt_2$, acac, S^iPr) (acac = $MeC(O)CHC(O)Me^-$, acetylacetonate) could be detected by NMR spectroscopy. The penta-amide $U(NEt_2)_5$ reacted with cyclopentadiene or $NHEt_3BPh_4$ to give $U(Cp)_4$ or $[U(NEt_2)_3]^+$ respectively. The only unequivocal syntheses of uranium(V) derivatives from U(V) precursors were provided by the protonolysis of $U(COT)(NEt_2)_3$ with $NHEt_3BPh_4$, leading to the cation $[U(COT)(NEt_2)_2(THF)]^+$ (Section 3.4) and the alcoholysis of $U(COT)(NEt_2)_3$ and $U(COT)(Cp)(NEt_2)_2$ with ^iPrOH which afforded the corresponding alkoxide compounds (Scheme 11). The mixed alkoxo–amide complexes $U(COT)(NEt_2)_{3-n}(O^iPr)_n$ were not detected during the reaction with 1 or 2 equiv. of isopropanol. The tris alkoxide $U(COT)(O^iPr)_3$ was particularly stable, since a benzene solution did not show any sign of decomposition after 20 h at 70 °C.



Scheme 11. Synthesis of uranium(V) complexes from [U(COT)$(NEt_2)_2$(THF)]$^+$.

5.4. *Structure of the uranium(V) complexes*

The cationic uranium(V) complexes have been characterized by their X-ray crystal structures (Table 2 and Figs. 14–16) [35,55]. Whereas [U(COT)$(NEt_2)_2$(THF)]$^+$ and [U(Cp*)$_2$$(NEt_2)_2$]$^+$ adopt a classical pseudo tetrahedral geometry, the trigonal bipyramidal coordination of [U(Cp*)$(NMe_2)_3$(THF)]$^+$ is rare for actinide complexes. The U–N bond distances vary from 2.11 Å in the cyclooctatetraene cation to 2.35 Å in the monopentamethylcyclopentadienyl cation; this latter distance is surprisingly larger than those found in the cationic U(IV) analogues. The U–N and U–C bond distances in the cation [U(COT)$(NEt_2)_2$(THF)]$^+$ were also determined

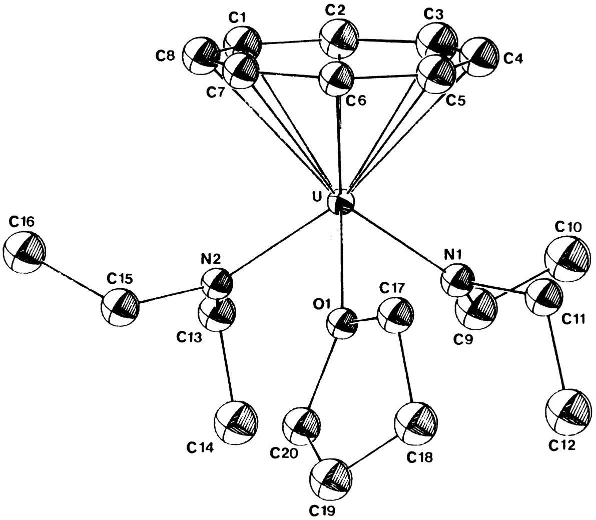


Fig. 14. X-ray structure of [U(COT)$(NEt_2)_2$(THF)]$^+$. Reprinted with permission from Ref. [35]. Copyright 1996, The Royal Society of Chemistry.

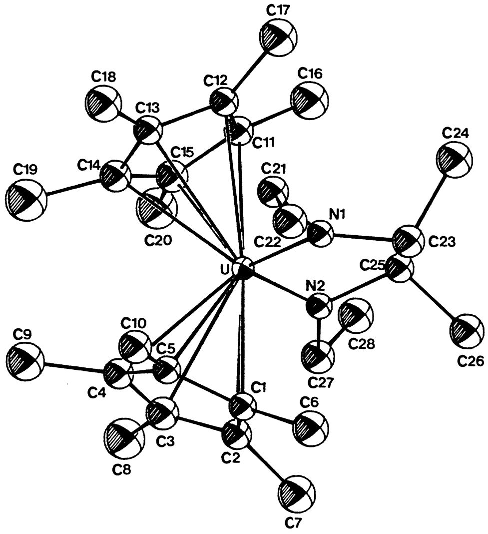


Fig. 15. X-ray structure of $[U(Cp^*)_2(NEt_2)_2]^+$. Reprinted with permission from Ref. [55]. Copyright 1995, The Royal Society of Chemistry.

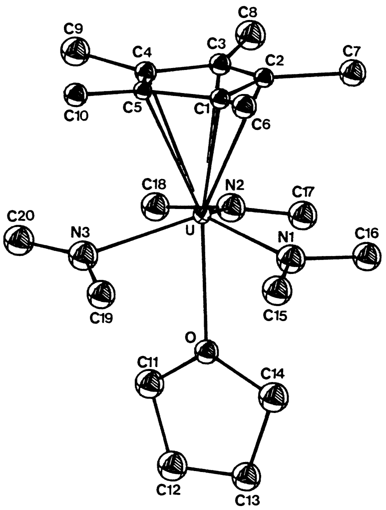


Fig. 16. X-ray structure of $[U(Cp^*)(NMe_2)_3(THF)]^+$. Reprinted with permission from Ref. [55]. Copyright 1995, The Royal Society of Chemistry.

by EXAFS; the values of 2.13 and 2.66 Å are quite identical to those found by X-ray crystallography. The corresponding distances in the geometrically similar compounds $U(COT)(NEt_2)_3$ (2.19 and 2.73 Å) and $[U(COT)(NEt_2)_3]^-$ (2.26 and 2.77 Å) are longer and reflect the increasing electronic charge of these complexes. These extended X-ray absorption fine structure (EXAFS) and X-ray crystal data showed that the metal–ligand distances in the uranium(V) complexes are not significantly different from those determined in U(IV) compounds [70]; these results confirmed that these structural parameters cannot be used with confidence for predicting the metal oxidation state.

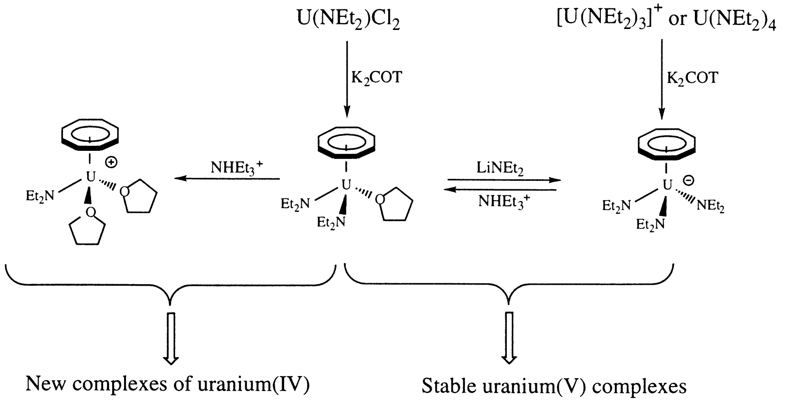
The uranium(V) compounds were further characterized by their X-ray absorption near edge structure (XANES) and electron spin resonance (ESR) spectra. XANES at the L_3 and M_5 edges showed the screening effect of the additional 5f electron when the metal oxidation varied from +5 to +4. At the L_3 edge, the overall energy shift from $U(COT)(NEt_2)_2(THF)$ to $[U(COT)(NEt_2)_2(THF)]^+$ was equal to 1.6 eV; this value, which may be compared with that of 2.2 eV for UF_4 and UF_5 complexes [107], suggested that the cyclooctatetraene compounds have a more covalent character [70]. The ESR spectra of the U(V) compounds revealed that the interaction of 5f orbitals with the COT, Cp, Cp*, NEt_2 and THF ligands are sufficiently small to conserve the ground state quantum number $J=5/2$ of the free U(V) ion as a good quantum number for the complex. The contribution of the 5f orbitals to the electronic structure is essentially non-bonding and the metal–ligand bonding should involve mainly 6d orbitals. The experimental ***g*** tensors were quantitatively interpreted within the weak field approximation. Replacement of the NR_2 groups by OR ligands has a dramatic effect on the electronic ground state of the complex. The 5f–OR interaction is strong, J is no longer a good quantum number and the weak field approximation is no longer valid [108].

6. Conclusions and perspectives

Two major points emerge from these studies on uranium amide compounds. We found that the dialkylamide ligand is able to stabilize the +5 oxidation state of the metal. Treatment of anionic uranium(IV) amides with Tl(I) or Ag(I) salts gave the corresponding neutral derivatives, in particular $U(NEt_2)_5$, the first penta-amide of a 5f element. The first cationic complexes of uranium(V) were synthesized by oxidizing the neutral U(IV) precursors with $AgBPh_4$. Despite their frequent instability towards reductive processes, we are trying to use such complexes as precursors of new uranium(V) derivatives, taking advantage of the remarkable reactivity of the $U–NR_2$ bond.

The other contribution to the chemistry of metal amide complexes is the development of the novel protonolysis reaction of the amide group with the ammonium salt NHR_3BPh_4, which proved to be an efficient route to cationic complexes. Thus were synthesized a series of metallo-organic and organometallic cations of uranium in the oxidation states +3, +4 and +5. This protonolysis reaction has a general applicability and should be useful for the preparation of new cationic species of the f elements and d transition metals, as shown with the synthesis of some representative derivatives of the Group IVb metals.

Cationic amide complexes of the type $[\{M\}(NEt_2)_n]^+$, as well as the corresponding neutral chloroamide $Cl–\{M\}(NEt_2)_n$ and amide $\{M\}(NEt_2)_{n+1}$, are useful precursors for the synthesis of new derivatives. The complementary advantages of these



Scheme 12. Development of monocyclooctatetraene uranium chemistry from amide and chloroamide precursors.

complexes must be considered, each one exhibiting distinct stability and chemical behaviour. As an illustration, reaction of $U(NEt_2)_4$, $U(NEt_2)_2Cl_2$, and $[U(NEt_2)_3]^+$ with K_2COT provided a convenient entry into the chemistry of the monocyclooctatetraene uranium compounds, which has been significantly developed during recent years (Scheme 12)

The first studies on the amide cations $[U(COT)(NEt_2)(THF)]^+$ and $[U(Cp^*)_2(NMe_2)(THF)]^+$ demonstrated that such species are very reactive, giving a number of addition, substitution and insertion products. These cationic complexes were found to be less sensitive towards acidic substrates than their neutral amide precursors. The potential of similar amide cations in homogeneous catalysis are currently being evaluated. We are convinced that the present craze for amide chemistry will continue, particularly in the field of 4f elements which has been much less explored. Thus we plan to extend these studies to lanthanide dialkylamide complexes, which are actually very rare, with special attention being paid to the development of the cerium(IV) chemistry.

7. Abbreviations

THF	OC_4H_8 (tetrahydrofuran)
HMPA	$(Me_2N)_3PO$ (hexamethylphosphorotriamide)
DMPE	$Me_2PCH_2CH_2PMe_2$ (dimethylphosphinoethane)
DME	$MeOCH_2CH_2OMe$ (dimethoxyethane)
COT	η^8-C_8H_8 (cyclooctatetraene)
Cp*	η^5-C_5Me_5 (pentamethylcyclopentadienyl)
Cp	η^5-C_5H_5 (cyclopentadienyl)
acacH	$MeC(O)CH_2C(O)Me$ (acetylacetone)
acac	$MeC(O)CHC(O)Me$- (acetylacetonate)

py	NC_5H_5 (pyridine)
dmbipy	$Me_2C_{10}H_6N_2$ (4,4′-dimethyl-2,2′-bipyridine)
EXAFS	extended X-ray absorption fine structure
XANES	X-ray absorption near edge structure
ESR	electron spin spectroscopy
NMR	nuclear magnetic resonance

References

[1] E. Frankland, Proc. R. Soc. 8 (1856) 502.
[2] M.F. Lappert, P.P. Power, A.R. Sanger, R.C. Srivastava, Metal and Metalloid Amides: Syntheses, Structures and Physical and Chemical Properties, Ellis Horwood/Wiley, Chichester/New York, 1980.
[3] R.G. Jones, G. Karmas, G.A. Martin Jr.,, H. Gilman, J. Am. Chem. Soc. 78 (1956) 4285.
[4] K.W. Bagnall, E. Yanir, J. Inorg. Nucl. Chem. 36 (1974) 777.
[5] J.J. Jamerson, J. Takats, J. Organomet. Chem. 78 (1974) C23.
[6] P.J. Fagan, J.M. Manriquez, S.H. Vollmer, C.S. Day, V.W. Day, T.J. Marks, J. Am. Chem. Soc. 103 (1981) 2206.
[7] R.A. Andersen, Inorg. Chem. 18 (1979) 1507.
[8] J.L. Stewart, R.A. Andersen, New J. Chem. 19 (1995) 587.
[9] A. Zalkin, J.G. Brennan, R.A. Andersen, Acta Crystallogr. Sect. C: 44 (1988) 1553.
[10] R.A. Andersen, Inorg. Chem. 18 (1979) 209.
[11] J.E. Nelson, D.L. Clark, C.J. Burns, A.P. Sattelberger, Inorg. Chem. 31 (1992) 1976.
[12] L.R. Avens, S.G. Bott, D.L. Clark, A.P. Sattelberger, J.G. Watkin, B.D. Zwick, Inorg. Chem. 33 (1994) 2248.
[13] C.J. Burns, W.H. Smith, J.C. Huffman, A.P. Sattelberger, J. Am. Chem. Soc. 112 (1990) 3237.
[14] J.G. Reynolds, A. Zalkin, D.H. Templeton, N.M. Edelstein, L.K. Templeton, Inorg. Chem. 15 (1976) 2498.
[15] P.J. Fagan, Ph.D. Thesis, Northwestern University, Illinois, 1981.
[16] J.G. Reynolds, A. Zalkin, D.H. Templeton, N.M. Edelstein, Inorg. Chem. 16 (1977) 1090.
[17] C. Boisson, Ph.D. Thesis, University of Orsay, Paris XI, 1996.
[18] J.G. Reynolds, A. Zalkin, D.H. Templeton, N.M. Edelstein, Inorg. Chem. 16 (1977) 599.
[19] M.H. Chisholm, A. Cotton, M.W. Extine, Inorg. Chem. 17 (1978) 1329.
[20] M.H. Chisholm, C.E. Hammond, J.C. Huffman, Polyhedron 7 (1988) 2515.
[21] J.G.H. Du Preez, B.J. Gellatly, G. Jackson, L.R. Nassimbleni, Inorg. Chem. 17 (1978) 181.
[22] D. Baudry, M. Ephritikhine, J. Organomet. Chem. 349 (1988) 123.
[23] P.C. Leverd, T. Arliguie, M. Ephritikhine, M. Nierlich, M. Lance, J. Vigner, New J. Chem. 17 (1993) 769.
[24] P.C. Leverd, M. Lance, J. Vigner, M. Nierlich, M. Ephritikhine, J. Chem. Soc. Dalton Trans. (1995) 237.
[25] S.E. Turman, W.G. Van der Sluys, Polyhedron 11 (1992) 3139.
[26] J.C. Berthet, M. Ephritikhine, J. Chem. Soc. Chem. Commun. (1993) 1566.
[27] M.H. Chisholm, C.E. Hammond, J.C. Huffman, Polyhedron 7 (1988) 399.
[28] L.G. McCullough, H.W. Turner, R.A. Andersen, A. Zalkin, D.H. Templeton, Inorg. Chem. 20 (1981) 2869.
[29] H.W. Turner, R.A. Andersen, A. Zalkin, D.H. Templeton, Inorg. Chem. 18 (1979) 1221.
[30] J.C. Berthet, C. Boisson, M. Lance, J. Vigner, M. Nierlich, M. Ephritikhine, J. Chem. Soc. Dalton Trans. (1995) 3019.
[31] H. Schumann, J.A. Meese-Marktscheffel, L. Esser, Chem. Rev. 95 (1995) 865.
[32] V.H. Bürger, H.J. Neese, Z. Anorg. Allg. Chem. 365 (1969) 243.

[33] V.H. Bürger, K. Wiegel, Z. Anorg. Allg. Chem. 398 (1973) 257.
[34] J.C. Berthet, M. Ephritikhine, unpublished results.
[35] C. Boisson, J.C. Berthet, M. Lance, J. Vigner, M. Nierlich, M. Ephritikhine, J. Chem. Soc. Dalton Trans. (1996) 947.
[36] T.M. Gilbert, R.R. Ryan, A.P. Sattelberger, Organometallics 7 (1988) 2514.
[37] T. Arliguie, D. Baudry, M. Ephritikhine, M. Nierlich, M. Lance, J. Vigner, J. Chem. Soc. Dalton Trans. (1992) 1019.
[38] P. Leverd, T. Arliguie, M. Lance, M. Nierlich, J. Vigner, M. Ephritikhine, J. Chem. Soc. Dalton Trans. (1994) 501.
[39] J. Feldman, J.C. Calabrese, J. Chem. Soc. Chem. Commun. (1991) 134
[40] G.C. Martin, G.J. Palenik, J.M. Boncella, Inorg. Chem. 29 (1990) 2027.
[41] A.L. Casalnuovo, J.C. Calabrese, D. Milstein, J. Am. Chem. Soc. 110 (1988) 110.
[42] A.D. Horton, J. de With, J. Chem. Soc. Chem. Commun. (1996) 1375.
[43] S. Collins, B.E. Koene, R. Ramachandran, N.J. Taylor, Organometallics 10 (1991) 2092.
[44] Y. Hong, B.A. Kuntz, S. Collins, Organometallics 12 (1993) 964.
[45] D. Röttger, G. Erker, M. Grehl, R. Fröhlich, Organometallics 13 (1994) 3897.
[46] Z. Lin, J.F. Le Maréchal, M. Sabat, T.J. Marks, J. Am. Chem. Soc. 109 (1987) 4127.
[47] J.C. Berthet, J.F. Le Maréchal, M. Lance, M. Nierlich, J. Vigner, M. Ephritikhine, J. Chem. Soc. Dalton Trans. (1992) 1573.
[48] R. McDonald, Y. Sun, J. Takats, V.W. Day, T.A. Eberspracher, J. Alloys Compd. 213–214 (1994) 8.
[49] R.A. Jordan, Adv. Organomet. Chem. 32 (1991) 325.
[50] W.J. Evans, T.A. Ulibarri, L.R. Chamberlain, J. Ziller, D. Alvarez Jr., Organometallics 9 (1990) 2124.
[51] F. Yuan, Q. Shen, J. Sun, J. Organomet. Chem. 538 (1997) 241.
[52] C. Boisson, J.C. Berthet, M. Ephritikhine, M. Lance, M. Nierlich, J. Organomet. Chem. 531 (1997) 115.
[53] C. Boisson, J.C. Berthet, M. Ephritikhine, M. Lance, M. Nierlich, J. Organomet. Chem. 533 (1997) 7.
[54] J.C. Berthet, C. Boisson, M. Lance, J. Vigner, M. Nierlich, M. Ephritikhine, J. Chem. Soc. Dalton Trans. (1995) 3027.
[55] C. Boisson, J.C. Berthet, M. Lance, M. Nierlich, J. Vigner, M. Ephritikhine, J. Chem. Soc. Chem. Commun. (1995) 543.
[56] C.J. Schaverien, Organometallics 11 (1992) 3476.
[57] K. Seppelt, Angew. Chem. Int. Ed. Engl. 32 (1993) 1025.
[58] P. Roussel, P.B. Hitchcock, N. Tinker, P. Scott, J. Chem. Soc. Chem. Commun. (1996) 2053.
[59] P.B. Hitchcock, M.F. Lappert, A. Singh, R.G. Taylor, D. Brown, J. Chem. Soc. Chem. Commun. (1983) 56.
[60] R.A. Andersen, A. Zalkin, D.H. Templeton, Inorg. Chem. 20 (1981) 622.
[61] D.L. Clark, M.M. Miller, J.G. Watkin, Inorg. Chem. 32 (1993) 772.
[62] S.J. Coles, A.A. Damopoulos, P.G. Edwards, M.B. Hursthouse, P.W. Read, J. Chem. Soc. Dalton Trans. (1995) 3401.
[63] P. Scott, P.B. Hitchcock, J. Chem. Soc. Dalton Trans. (1995) 603.
[64] P. Scott, P.B. Hitchcock, Polyhedron 13 (1994) 1651.
[65] J.G. Reynolds, A. Zalkin, D.H. Templeton, N.M. Edelstein, Inorg. Chem. 16 (1977) 1858.
[66] J.M. Berg, D.L. Clark, J.C. Huffman, D.E. Morris, A.P. Sattelberger, W.E. Streib, W.G. Van der Sluys, J.G. Watkin, J. Am. Chem. Soc. 114 (1992) 10811.
[67] R.E. Cramer, U. Engelhardt, K. Higa, J.W. Gilge, Organometallics 6 (1987) 41.
[68] S.J. Coles, P.G. Edwards, M.B. Hursthouse, P.W. Read, J. Chem. Soc. Chem. Commun. (1994) 1967.
[69] C. Boisson, J.C. Berthet, M. Lance, M. Nierlich, M. Ephritikhine, J. Organomet. Chem. 522 (1996) 249.
[70] C. Den Auwer, C. Madic, J.C. Berthet, M. Ephritikhine, J.J. Rehr, R. Guillaumont, RadioChim. Acta 76 (1997) 211.

[71] C. Boisson, J.C. Berthet, M. Lance, M. Nierlich, M. Ephritikhine, J. Chem. Soc. Chem. Commun. (1996) 2129.
[72] T. Straub, W. Frank, G.J. Reiss, M. Eisen, J. Chem. Soc. Dalton Trans. (1996) 2451.
[73] C. Boisson, J.C. Berthet, M. Lance, M. Nierlich, M. Ephritikhine, J. Organomet. Chem. 548 (1997) 9.
[74] A.R. Schake, L.R. Avens, C.J. Burns, D.L. Clark, A.P. Sattelberger, W.H. Smith, Organometallics 12 (1993) 1497.
[75] J.M. Manriquez, P.J. Fagan, T.J. Marks, S.H. Vollmer, C.S. Day, V.W. Day, J. Am. Chem. Soc. 101 (1979) 5075.
[76] A. Cotton, W. Schwotzer, SimpsonC.Q., II, Angew. Chem. Int. Ed. Engl. 25 (1986) 637.
[77] D. Baudry, E. Bulot, M. Ephritikhine, J. Chem. Soc. Chem. Commun. (1989) 1316.
[78] P. Gradoz, D. Baudry, M. Ephritikhine, M. Lance, M. Nierlich, J. Vigner, J. Organomet. Chem. 466 (1994) 107.
[79] S.H. Strauss, Chem. Rev. 93 (1993) 927.
[80] W. Beck, K. Sünkel, Chem. Rev. 88 (1988) 1405.
[81] M. Bochmann, Angew. Chem. Int. Ed. Engl. 31 (1992) 1181.
[82] J.C. Berthet, M. Lance, M. Nierlich, J. Vigner, M. Ephritikhine, J. Organomet. Chem. 420 (1991) C9.
[83] S.M. Cendrowski-Guillaume, M. Ephritikhine, J. Chem. Soc. Dalton Trans. (1996) 1487.
[84] C.D. Sofield, R.A. Andersen, J. Organomet. Chem. 501 (1995) 271.
[85] K. Bowman, Z. Dori, J. Chem. Soc. Chem. Commun. (1968) 636.
[86] G. Chandra, A.D. Jenkins, M.F. Lappert, R.C. Srivastava, J. Chem. Soc. A: (1970) 2550
[87] D.C. Bradley, M.C. Ganorkar, Chem. Ind. (1968) 1521.
[88] K. Jones, M.F. Lappert, J. Organomet. Chem. 3 (1965) 295.
[89] M. Rivière-Baudet, P. Rivière, J. Organomet. Chem. 116 (1976) C49.
[90] L.R. Avens, D.M. Barnhart, C.J. Burns, S.D. McKee, Inorg. Chem. 35 (1996) 537.
[91] J. Collin, A. Pires de Matos, I. Santos, J. Organomet. Chem. 463 (1993) 103.
[92] S.L. Borkowsky, R.F. Jordan, G.D. Hinch, Organometallics 10 (1991) 1268.
[93] W.J. Evans, T.A. Ulibarri, L.R. Chamberlain, J.W. Ziller, D. Alvarez Jr., Organometallics 9 (1990) 2124.
[94] J.G. Brennan, R.A. Andersen, J. Am. Chem. Soc. 107 (1985) 514.
[95] R.K. Rosen, R.A. Andersen, N.M. Edelstein, J. Am. Chem. Soc. 112 (1990) 4588.
[96] P.C. Blake, M.F. Lappert, R.C. Taylor, J.L. Atwood, H. Zhong, Inorg. Chim. Acta 139 (1987) 13.
[97] J.G. Brennan, Ph.D. Thesis, University of Berkeley, California, 1985.
[98] W.G. Van der Sluys, A.P. Sattelberger, Chem. Rev. 90 (1990) 1027.
[99] D.C. Bradley, R.N. Kapoor, B.C. Smith, J. Chem. Soc. (1963) 204.
[100] E.R. Sigurdson, G. Wilkinson, J. Chem. Soc. Dalton Trans. (1977) 812.
[101] M. Ephritikhine, J. Alloys Compd. 213–214 (1994) 1519.
[102] D.C. Bradley, I.M. Thomas, Can. J. Chem. 4 (1962) 449.
[103] D.C. Bradley, I.M. Thomas, Can. J. Chem. 4 (1962) 1355.
[104] D. Auchard, C. Clappe, J.C. Berthet, C. Boisson, M. Ephritikhine, unpublished results.
[105] C. Clappe, Ph.D. Thesis, University Pierre et Marie Curie, Paris VI, 1997
[106] F. Ossola, P. Zanella, P. Vigo, R. Seeber, Inorg. Chim. Acta 147 (1988) 123.
[107] G. Kalkowski, G. Kaindl, W.D. Brewer, W. Krone, Phys. Rev. B 35 (1987) 2667.
[108] D. Gourier, D. Caurant, J.C. Berthet, C. Boisson, M. Ephritikhine, Inorg. Chem. 36 (1997) 5931.