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Uranium carbene compounds

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ABSTRACT

This article gives an overview of the development of uranium carbene complexes. The first example of these compounds was reported in 1981 with the phosphoylide complex $Cp_3U=CHPMe_2Ph$ but nearly three decades passed before the area witnessed spectacular advances. During this time, actinide methylenes were detected in solid argon, carbenoid uranium species were evidenced in McMurry type reactions, and a series of uranium complexes with *N*-heterocyclic carbene ligands was isolated. The recent developments in uranium carbene chemistry have to be related to the use of bis-phosphorus stabilized geminal carbon dianions as ligands. Homoleptic complexes and a series of mixed chloro-, tetrahydroborato-, amido-, cyclopentadienyl- and cyclooctatetraenyl-carbene complexes of thorium(IV) and uranium in the +4, +5 and +6 oxidation states have been isolated and characterized. DFT calculations led to a good description of the U=C double bond that demonstrates a double σ and π donation toward the metal atom with the involvement of the 5f orbitals.

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R É S U M É

Cet article présente une revue sur le développement des complexes carbéniques de l'uranium. Le premier exemple de ces composés apparut en 1981 avec le complexe phosphoylide $Cp_3U=CHPMe_2Ph$ mais ce n'est que presque trente ans plus tard que ce domaine connut de spectaculaires avancées. Entre-temps, des composés méthylidènes des actinides furent détectés dans des matrices d'argon, des espèces carbénoïdes de l'uranium furent mises en évidence au cours de réactions du type McMurry, et une série de complexes de l'uranium comportant des carbènes *N*-hétérocycliques fut isolée. Les progrès récents dans la chimie des complexes carbéniques de l'uranium doivent être reliés à l'utilisation des dianions géminaux carbonés stabilisés par des groupes phosphorés. Des complexes homoleptiques et une famille de composés carbéniques portant des ligands chlorure, borohydrure, amidure, cyclopentadiényle et cyclooctatétraynyle du thorium(IV) et de l'uranium aux degrés d'oxydation +4, +5 et +6 ont été isolés et caractérisés. Les calculs en DFT conduisent à une bonne description de la double liaison U=C qui présente une double donation σ et π vers le métal avec l'implication des orbitales 5f.

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1. Introduction

The history of actinide chemistry has been greatly influenced by the nuclear industry and many research programs were supervised in specialized laboratories

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having the necessary equipment in an interdisciplinary framework. This development was however much uneven, in terms of times, space and scope, because rapid answers must be given to the most urgent problems. Major attention was first turned to the synthesis of volatile compounds of uranium, for isotopic enrichment and fabrication of the atomic bomb, while recent efforts were devoted to the separation and elimination of wastes coming from nuclear power plants and destruction of weapons. These works obviously induced significant advances in actinide chemistry but large domains of this discipline had been neglected and were much less explored than those of other metals. It is clear today that this underdevelopment was not only the result of a chemical necessity but reflected a disfavored historical background. This situation is well illustrated with the advances in organometallic chemistry of actinides, in particular uranium.

The first organouranium compound, Cp_3UCl ($Cp = \eta-C_5H_5$), was synthesized by Reynolds and Wilkinson in 1956, a few years after the discovery of ferrocene [1]. Fisher and Hristidu prepared the tetracyclopentadienyl complexes Cp_4An ($An = U, Th$) in 1962 [2]. The German workers extended the series of cyclopentadienyl compounds to transuranium elements [3] and isolated the first organometallic complex of uranium(III), Cp_3U , in 1970 [4]. A milestone in organometallic chemistry was the preparation in 1968 by Streitwieser and Mueller-Westerhoff of the so-called uranocene $(COT)_2U$ ($COT = \eta-C_8H_8$), the first representative of a new class of π -bonded cyclooctatetraenyl sandwich complexes [5]. Lugli et al. reported in 1974 on the stereospecific polymerization of butadiene catalyzed by uranium allyl complexes [6]. These initial results revealed the unique properties of uranium compounds, the novelty of their structures determined by the size of the ions and the participation of the orbitals in metal-ligand bonding, and their remarkable performances in catalysis. But following a period of relative stagnation, it is only in the 1980's that organoactinide chemistry received a more regular and sustained attention and since the beginning of the 21st century, this discipline is witnessing a speeding up of its historical process which can be measured quantitatively by the increasing number of publications and characterized compounds and, very importantly, by the emergence of a new generation of young enthusiastic chemists [7]. In addition to the wish to find applications and give solutions to the topical problems of environmental remediation, these advances were clearly motivated by the revealed existence of fundamental and fascinating aspects of f elements chemistry. Organouranium complexes became much more attractive in view of their structures which were unsuspected or reputed non accessible, the multiplicity of their oxidation states exploited in redox reactions, their efficiency in the activation of small molecules and their peculiar magnetic properties. The remarkable improvements in computational investigations now permit to support an increasing number of experimental structural and thermodynamic data by a detailed theoretical analysis, giving a clear description of the bonding and the role of the f electrons.

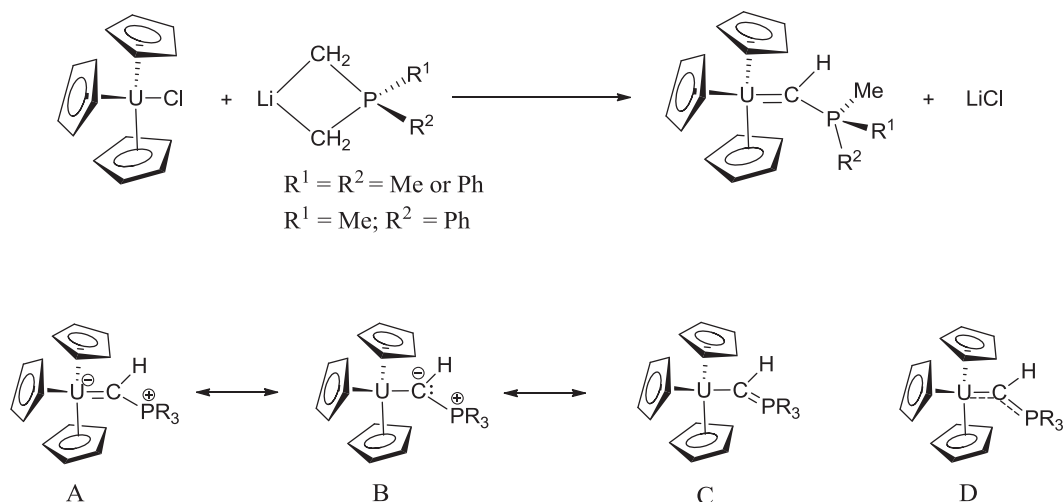
This history of organoactinide chemistry, with its initial exciting discoveries followed by a rather long period of stagnation and its recent blooming, is well illustrated by the development of the uranium carbene complexes. By comparison with the considerable amount of work devoted to the carbene complexes of d transition metals due to their fundamental aspects and their extensive applications in organic synthesis and catalysis [8], the chemistry of such compounds with f elements remains largely unexplored. This was related to the strong ionic character of the metal-ligand bonding and the weak stabilization of the carbenic centre by π -back-donation from the metal fragment. The phosphoylide uranium compounds $Cp_3U=CHP(Me)RR'$, reported by Gilje et al. in 1981, were the first actinide carbenes with significant metal-carbon multiple bond character to be structurally characterized. However, nearly three decades passed before such new compounds came out again with the use of bis-phosphorus(V) stabilized carbon dianions as ligands. Meanwhile, uranium carbenoid species were detected in matrix isolation experiments and evidenced in McMurry type reactions; the only isolated carbene complexes were N-heterocyclic carbene (NHC) compounds which are in fact simple Lewis base adducts without significant M-C double bond character. Here we give a complete description of these successive steps in the development of uranium carbene complexes, in which we have been involved since 1997.

2. The first uranium carbene complexes

The uranium complexes $Cp_3U=CHPMeRR'$ ($R = R' = Me, Ph$; $R = Me$ and $R' = Ph$) were synthesized by reaction of Cp_3UCl with the lithium salt of the phosphoylide anion $Li(CH_2)(CH_2)RR'$ (Scheme 1) [9]. The crystal structures of $Cp_3U=CHPMe_2Ph$ and $Cp_3U=CHPMe_3$ determined by X-ray or neutron diffraction analysis [9,10], showed that the uranium-carbon bond is the shortest yet observed, with a distance very close to 2.29 Å, and the U-C-P angle is slightly larger than 140°. These geometrical parameters clearly revealed the multiple bond character of the U-C bond. The concept of multiple bond in $Cp_3U=CHPR_3$ was supported by extended Hückel molecular orbital calculations which show covalency with a significant π component for the U-C $_{\alpha}$ bond [11]. The multiple uranium-carbon bonding can be formulated in terms of several resonance structures (A-C) with the hybrid D of these structures, as given in Scheme 1.

Cramer, Gilje et al. outlined that these complexes represent, after the so called Fisher carbene compounds and the Shrock alkylidene derivatives, a third class of complexes with a metal carbon double bond in which a negative charge on the α carbon is stabilized by an electron withdrawing heteroatom substituent [12]. These authors also predicted that such bonds probably will be the most common type of metal-carbon double bonds in compounds of high-valent, largely ionic metals, where effective ligand to metal charge delocalization cannot occur.

In contrast to both Fisher carbene complexes and Shrock alkylidene complexes, the uranium phosphoylides were inert in the presence of internal monoalkenes and



Scheme 1. Synthesis and resonance forms of the phosphoylide complexes $(\text{C}_5\text{H}_5)_3\text{U}=\text{CHPR}_3$.

alkynes. However, consistent with the polar nature of the U–C bond and the nucleophilic character of the α carbon, they react with the electrophile MeI, the weak acids Ph_2NH and $\text{PhC}\equiv\text{CH}$, and the polar unsaturated molecules CO, MeCN, $\text{C}_6\text{H}_{11}\text{NC}$ and PhNCO [13], according to Scheme 2. Thus, products from the insertion of small molecules into a metal–carbon multiple bond were structurally characterized for the first time.

The carbene complexes $\text{Cp}_3\text{U}=\text{CHPMePhR}$ also react with coordinated CO in carbonyl compounds $[\text{M}](\text{CO})$ [$\text{M} = \text{CpMn}(\text{CO})_2, \text{W}(\text{CO})_5, \text{CpCo}(\text{CO})$] to give bimetallic derivatives of general formula $\text{M}-\text{C}(\text{OUCp}_3)=\text{CHPMePhR}$ (Scheme 2) [13c,e]. The last paper on these series of uranium carbenes was published in 1990, which described the neutron diffraction crystal structure of $\text{Cp}_3\text{U}=\text{CHPMe}_3$ [10], and no study on such compounds was reported until 2009, with the use of geminal dianions (see chapter 5).

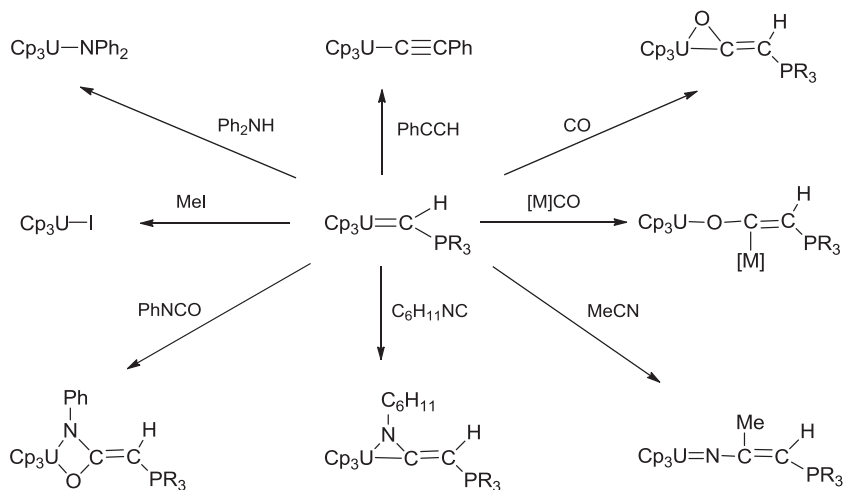
It should be noted here that a novel route to a uranium phosphoylide complex was designed in 2011 by the group of Hayton (Scheme 3). Treatment of $\text{U}(\text{NR}_2)_3$ ($\text{R} = \text{SiMe}_3$)

with 1 equivalent of the Wittig reagent $\text{Ph}_3\text{P}=\text{CH}_2$ gave the U(III)-ylide adduct $\text{U}(\text{CH}_2\text{PPh}_3)(\text{NR}_2)_3$ which underwent in diethyl ether a one-electron oxidation concomitant with formal loss of H radical from the coordinated Wittig ligand to give the uranium(IV) carbene $\text{U}(\text{CHPPh}_3)(\text{NR}_2)_3$. This latter was found to be in equilibrium with the metallacycle $\text{U}(\text{CH}_2\text{SiMe}_2\text{NR})(\text{NR}_2)_2$ and the free Wittig reagent, an equilibrium which is shifted toward the formation of the carbene in diethyl ether at low temperature, thus permitting its synthesis under these conditions [14].

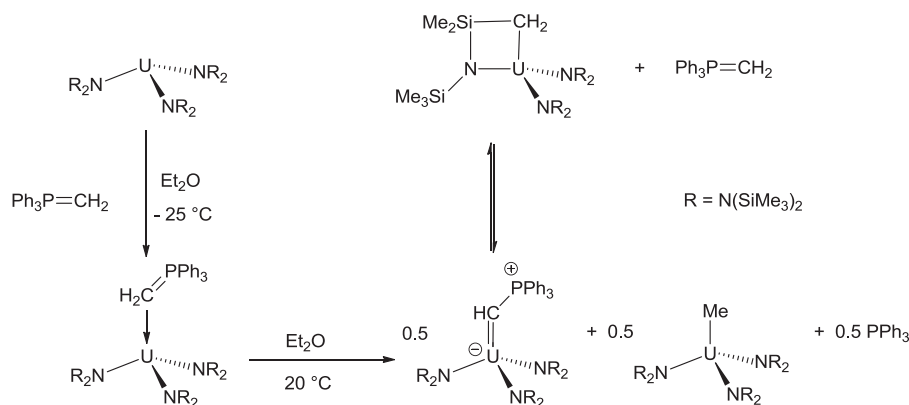
3. Matrix preparation of actinide methyldene complexes and evidence for uranium carbenoid species in McMurry type reactions

3.1. Actinide methyldene complexes

The methyldene complexes $\text{H}_2\text{C}=\text{AnHX}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) and $\text{H}_2\text{C}=\text{AnH}_2$ ($\text{An} = \text{Th}, \text{U}$) have been prepared in 2006 by Andrews et al. by reactions of excited thorium and



Scheme 2. Reactions of the phosphoylide complexes $(\text{C}_5\text{H}_5)_3\text{U}=\text{CHPR}_3$.



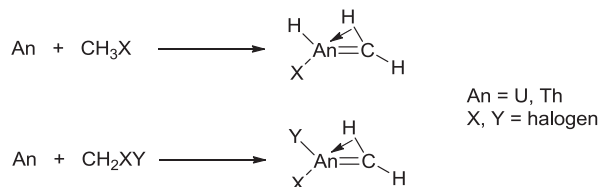
Scheme 3. Synthesis of the phosphoylide complex $U(CHPPh_3)(NR_2)_3$ ($R = SiMe_3$).

uranium atoms with methyl halides and methane in solid argon at 7 K (Scheme 4) [15].

These simple organometallic complexes were identified by matrix infrared spectra through isotopic substitution and by comparison with vibrational characteristics calculated by DFT. Similar reactions of laser-ablated uranium atoms with methylene halides CH_2XY ($XY = F_2, FCl$ and Cl_2) gave the methyldene molecules $H_2C=UF_2$, $H_2C=UFCl$, and $H_2C=UCl_2$ as the major products [16]. These complexes exhibit highly distorted agostic structures with agostic $H-C-U$ angles of ca 89° , in contrast with those of analogous transition-metal complexes such as $H_2C=WF_2$, where a nonagostic ethylene-like symmetric structure is computed. Electronic structure calculations reveal that these U(IV) molecules all have strong $U=C$ double bonds in the triplet ground states with $5f^2$ configurations. The calculated bond lengths and bond energies indicate that the $C=U$ double bonds are slightly weaker in the fluoride species (2.066 \AA , $109 \text{ kcal.mol}^{-1}$) than in the chloride species (2.049 \AA , $113 \text{ kcal.mol}^{-1}$) because of the radial contraction of the U (6d) orbitals by the inductive effect of the fluorine substituent.

3.2. Uranium carbenoid species in McMurry type reactions

Our first encounter with uranium carbenes occurred in 1997 during our studies on the mechanism of the McMurry reaction, which is the reductive coupling of carbonyl compounds into alkenes upon treatment with low-valent titanium reagents [17]. Uranium and titanium complexes exhibit strong similarities in structure and reactivity, and uranium metal powder is effective in the reductive coupling of aromatic ketones. Moreover, uranium

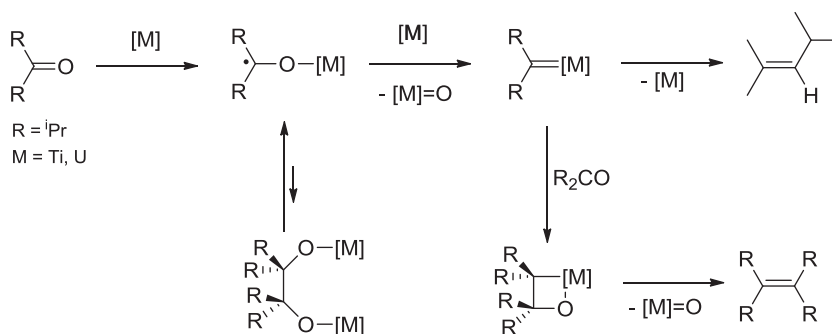


Scheme 4. Synthesis of actinide methyldene complexes.

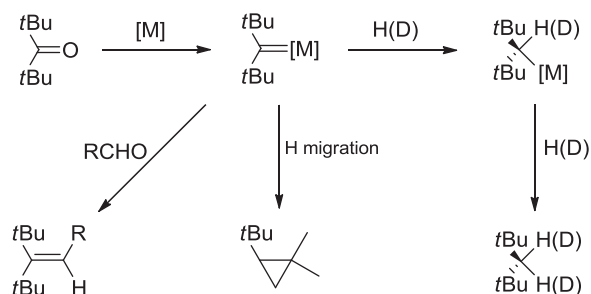
compounds have some advantages over their titanium counterparts: they can be easily detected by their highly shifted paramagnetic NMR signals and they often crystallize with less difficulty. Therefore, the chances of isolating and characterizing intermediates are greater. Indeed, the first metallopinacolate complexes isolated in a McMurry reaction were obtained at 25°C by treating benzophenone or acetone with the $UCl_4\text{-Na(Hg)}$ system, and were transformed into the corresponding pinacol upon hydrolysis or the tetrasubstituted alkenes $Ph_2C=CPh_2$ and $Me_2C=CMe_2$ after further treatment with sodium amalgam at higher temperature [18,19]. These results were in agreement with the generally accepted mechanism of the McMurry reaction which involves the intermediacy of a metallopinacolate resulting from dimerization of two ketyl radicals.

Reaction of diisopropyl ketone was found to be quite different from that of acetone since the only coupling product, formed at 25°C , was tetraisopropylethylene. In fact, formation of the corresponding pinacol was never observed in any McMurry reaction of diisopropyl ketone. Moreover, it was demonstrated that $iPr_2C=CiPr_2$ could not be obtained by deoxygenation of the pinacolate $Cl_3M-OCiPr_2CiPr_2O-MCl_3$ which, in the case of $M=Ti$, was not stable towards rupture of the pinacolic $C-C$ bond and was readily transformed into $TiCl_3$ and iPr_2CO . The facile cleavage of the pinacolates and the absence of pinacol in the product mixtures indicated that reductive coupling of $iPr_2C=O$ would not proceed by dimerization of ketyl radicals. A more careful analysis of the products showed that the McMurry reactions of iPr_2CO afforded an important quantity of 2,4-dimethyl-2-pentene resulting from deoxygenation of the ketone. This observation, which was overlooked so far, revealed that carbenoid species were likely intermediates. These latter would be formed by reduction and deoxygenation of the ketyl radicals; their reaction with another molecule of ketone would give $iPr_2C=CiPr_2$, presumably via a metallaoxetane complex, and their rearrangement by H migration would afford $Me_2C=C(H)iPr$ (Scheme 5) [20].

These results revealed the dual nature of the mechanism of the McMurry type reactions. Contrary to the generally accepted mechanism, metallopinacols



Scheme 5. Involvement of carbenoid species in the reductive coupling of diisopropyl ketone with the $\text{MCl}_4\text{-Li}(\text{Hg})$ system ($\text{M} = \text{Ti, U}$).



$\text{R} = \text{Me, } t\text{Bu}$

Scheme 6. Involvement of carbenoid species in the reaction of ditertibutyl ketone with the $\text{MCl}_4\text{-Li}(\text{Hg})$ system ($\text{M} = \text{Ti, U}$).

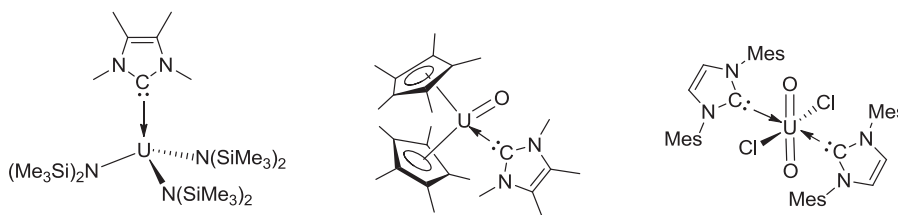
are not the only precursors to the alkene; if the ketyl radicals can be effectively coupled into pinacolate intermediates, they can also be reduced and deoxygenated into carbenoid species which provide the alkene after further reaction with the ketone. The course of the reaction, via the metalpinacol or the carbenoid intermediates, is largely determined by the steric hindrance of the ketone; the most hindered ketones would follow the carbenoid route because of the difficult coupling of the ketyl radicals and the reversible cleavage of the pinacolic C–C bond [21]. The involvement of carbenoid species in the McMurry reaction of sterically hindered ketones was further demonstrated by analysis of the products resulting from the reduction of ditertibutyl ketone. In that case, H migration within the carbenoid species $[\text{M}]=\text{CtBu}_2$ gave the expected cyclopropane compound in 2% yield with $\text{M} = \text{Ti}$. The major product was $t\text{Bu}_2\text{CH}_2$ (40 and 50% yield for $\text{M} = \text{Ti}$ and U , respectively) which was liberated after hydrolysis

of the reaction mixture; deuterolysis experiments confirmed that this alkane was formed by successive addition of H(D) atoms to the carbenoid species $[\text{M}]=\text{CtBu}_2$. The latter were thus much more stable than $[\text{M}]=\text{CiPr}_2$ and could also be trapped with aldehydes RCHO to give the cross-coupling products $t\text{Bu}_2\text{C}=\text{C(R)H}$ ($\text{R} = \text{Me, } t\text{Bu}$) (Scheme 6) [21].

4. Uranium complexes with N-heterocyclic carbene ligands

N-heterocyclic carbene (NHC) ligands are most well-known as soft, two-electron σ -donors and are used widely as strongly basic phosphine analogues, to support late transition metal complexes [22]. In contrast to alkyl phosphines, NHC are effective ligands for high-valent metal complexes [23]. The first NHC compounds of an f element, $\text{Cp}^*_2\text{Sm}(\text{C}\{\text{NMeCMe}\}_2)_2$ and $(t\text{Bu}_2\text{acac})_3\text{Eu}(\text{C}\{\text{NHCMe}\}_2)$ ($t\text{Bu}_2\text{acac} = t\text{BuC}(\text{O})\text{CHC}(\text{O})t\text{Bu}$) were isolated by Arduengo et al. in 1994 [24], and such carbenes were coordinated to uranium after 2000 [25]. To the best of our knowledge, no NHC complex of thorium was structurally characterized. Monodentate NHC adducts have been reported for tri-, tetra- and hexavalent uranium, as illustrated by $(\{\text{Me}_3\text{Si}\}_2\text{N})_3\text{U}(\text{C}\{\text{NMeCMe}\}_2)$ [26], $\text{Cp}^*_2\text{UO}(\text{C}\{\text{NMeCMe}\}_2)$ [27] and $\text{UO}_2\text{Cl}_2(\text{C}\{\text{NMesCH}\}_2)_2$ ($\text{Mes} = \text{mesityl}$) [28], represented in Scheme 7.

Functionalized NHC ligands were designed to stabilize electropositive metal cations. Reaction of UCl_4 with the pincer dicarbene ligand CNC gave the adduct $(\text{CNC})\text{UCl}_4$ [$\text{CNC} = 2,6\text{-bis}(\text{arylimidazol-2-ylidene})\text{pyridine}$ with $\text{aryl} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$] [29]. The UO_2^{2+} ion was complexed by the alkoxide- and amido-NHC ligands $\text{OCMe}_2\text{CH}_2[1\text{-C}(\text{NCHCHNiPr})]$ (L^0) [30] and $t\text{BuNCH}_2\text{CH}_2[1\text{-C}(\text{NCHCHN}t\text{Bu})]$ [31]. The alkoxide-NHC ligand L^0 was also attached to the U^{4+} ion in the complexes $\text{U}(\text{L}^0)_3$ and



Scheme 7. NHC complexes of uranium in the +3, +4 and +6 oxidation states.

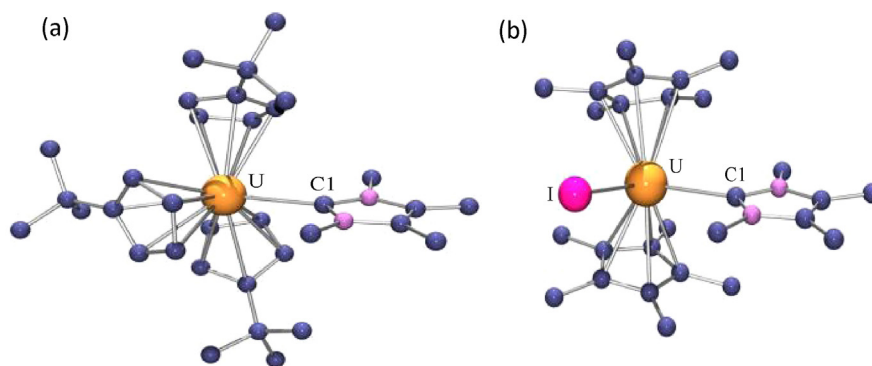


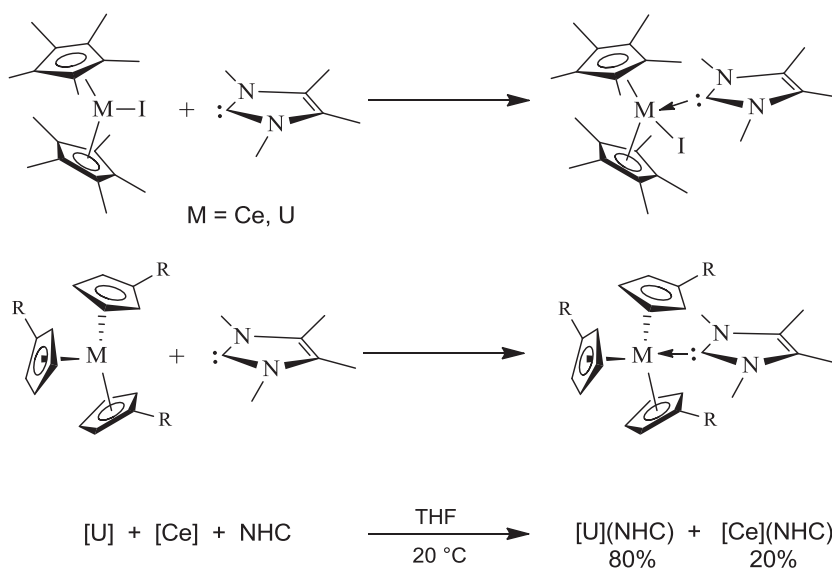
Fig. 1. X-ray crystal structures of $(C_5H_4tBu)_3U(C\{NMeCMe\}_2)$ (a) and $Cp^*_2UI(C\{NMeCMe\}_2)$ (b).

$U(L^O)_4$; in this latter, one of the four carbene groups remains uncoordinated, being in fast exchange in solution with the other bound NHC ligands, and was trapped by BH_3 and a range of 16-valence-electron metal carbonyl fragments [32].

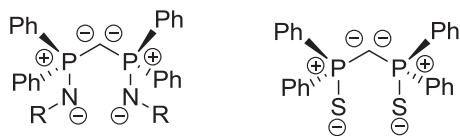
We have found a novel aspect of the NHC ligand's chemistry, which is their high capacity to discriminate between trivalent lanthanide (Ln) and actinide (An) ions. This separation, which is a difficult task in view of the similar properties of the ions, represents a challenging problem in both its fundamental aspects and potential applications, especially the reprocessing of spent nuclear fuels. Selective complexation of An^{3+} over Ln^{3+} ions reflects the slightly less hard character of the former, leading to a better affinity towards soft nitrogen donors and to the formation of bonds with a larger degree of covalency. A usual way to probe the extent of covalent interactions in actinide complexes is to compare bond distances in analogous uranium(III) and lanthanide(III) compounds [33]. The crystal structures of the two pairs of isomorphous U(III) and Ce(III) complexes $(C_5H_4tBu)_3M(C\{NMeCMe\}_2)$ and $Cp^*_2MI(C\{NMeCMe\}_2)$ ($M=U, Ce$) (Fig. 1) show that

the uranium-carbene distances are shorter by ca 0.03 \AA than the cerium-carbene distances while the ionic radius of uranium(III) is 0.02 \AA longer than that of cerium(III) [34]. Such shortening of the uranium-ligand distances from a purely ionic bonding model is accounted for by the presence of a stronger, more covalent interaction between the actinide and the soft ligand.

The much stronger affinity of the NHC molecule for the 5f than the 4f ion was confirmed by competition reactions (Scheme 8). Addition of the NHC molecule to 1 mol equivalent of both the analogous trivalent uranium and cerium complexes in THF gave the uranium and cerium carbene complexes in a molar ratio of 80:20 at $23 \text{ }^\circ\text{C}$, and 90:10 at $-60 \text{ }^\circ\text{C}$. By comparison with the other molecules which have been considered for the differentiation of the $(C_5H_4R)_3U$ and $(C_5H_4R)_3Ce$ complexes (i.e. phosphine, phosphite, isonitrile and azine ligands), the NHC is by far the most efficient, presenting the best affinity and the best selectivity for the U(III) compound [34]. The selective complexation of the uranium over the cerium metallocenes by $C_3Me_4N_2$ in THF can only be compared with that of UX_3 over CeX_3 ($X=I, OTf$) by



Scheme 8. Efficiency of NHC in cerium(III)/uranium(III) differentiation.



Scheme 9. Most accurate Lewis structures to describe the electronic structures of the geminal dianions $(^R\text{NCN})^{2-}$ and $(\text{SCS})^{2-}$.

2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine (Rbtp) molecules in pyridine [33a]. Currently, these terdentate nitrogen ligands are among the most promising extractants available for the hydrometallurgical reprocessing of nuclear waste.

5. Bis-phosphorus stabilized actinide carbene complexes

5.1. Synthesis and crystal structures of the actinide(IV) complexes

A novel synthetic route to carbene complexes was opened with the design and use of geminal carbon dianions stabilized by phosphorous(V) substituents [35]. The real beginning of this new development dates back from 1999, when the groups of Stephan and Cavell reported independently the high yield preparation of the bis(iminophosphoranyl) methanediide ligand $[\text{Ph}_2\text{P}(=\text{NR})]_2\text{C}^{2-}$ ($\text{R} = \text{SiMe}_3$) [36,37]. Other such bis(iminophosphorane) derivatives with various R substituents, named $(^R\text{NCN})^{2-}$ thereafter, were synthesized during the 2000–2006 period, while Le Floch et al. reported in 2004 the quantitative preparation of the bis(thiophosphinoyl) methanediide $[\text{Ph}_2\text{P}(=\text{S})]_2\text{C}^{2-}$, named $(\text{SCS})^{2-}$ thereafter [38]. The most accurate Lewis structures to describe the electronic structure of the geminal dianions $(^R\text{NCN})^{2-}$ and $(\text{SCS})^{2-}$ are presented in Scheme 9.

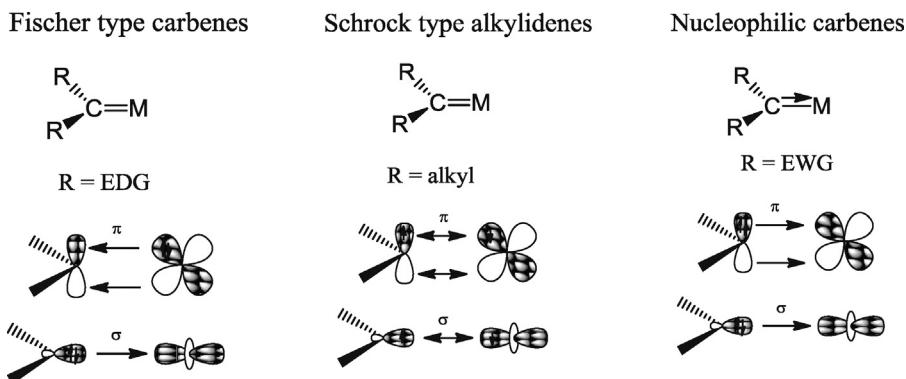
In the new class of ^RNCN and SCS complexes, and like in the phosphoylide complexes isolated by Gilje et al., the four electrons of the formal $\text{M}=\text{C}$ double bond are provided by the sole ligand, in contrast to the Fischer and Schrock type carbenes, where both the carbenic and metal fragments bring two electrons to the $\text{M}=\text{C}$ interaction (Scheme 10). The bis-phosphorus stabilized carbene

compounds could therefore be constructed from any electron deficient metal center and, most notably, from oxidized f-element ions, where stabilization of the carbenic centre by π -back donation from the metal fragment is very unlikely. Similarly to Schrock alkylidenes, these carbene complexes exhibit a nucleophilic character.

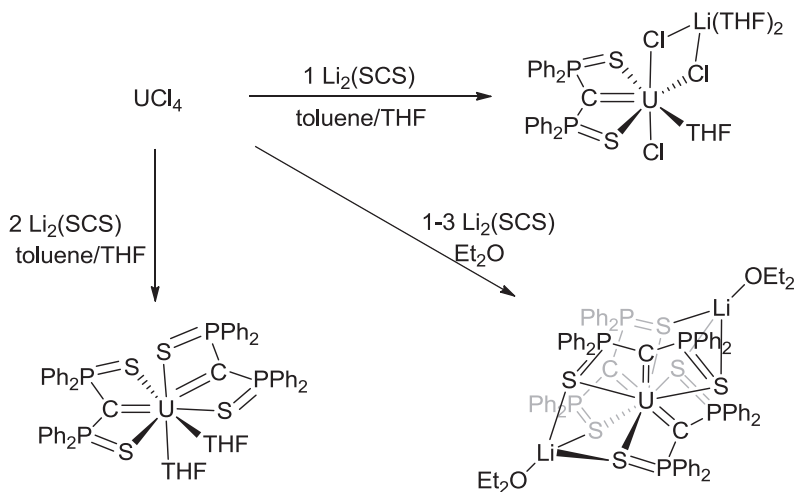
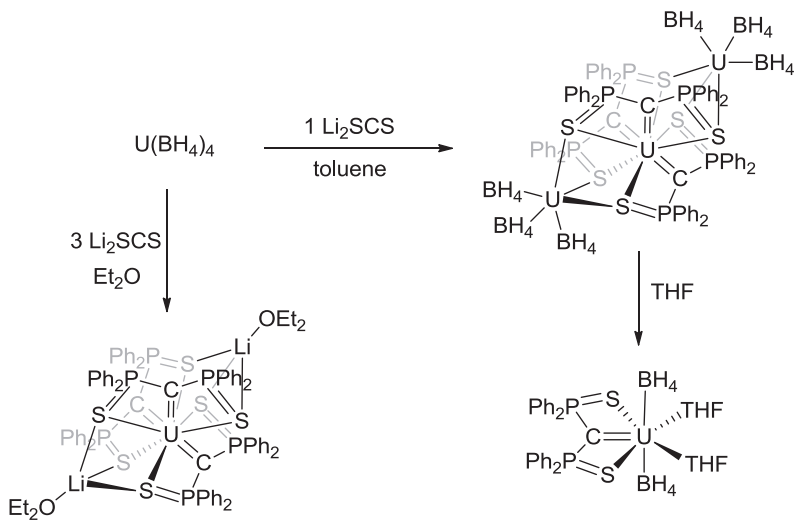
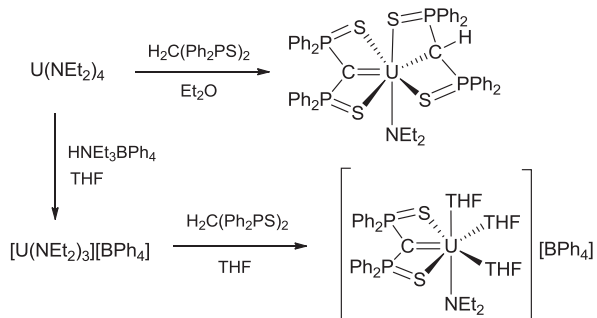
We introduced the SCS ligand in 5f element chemistry with the reactions of the lithium salt of the geminal dianion and uranium tetrachloride [39,40] or uranium tetraborohydride [41]. Treatment of UCl_4 with 1, 2 or 3 molar equivalents of Li_2SCS gave respectively the mono-carbene “ate” complex $\text{Li}(\text{THF})_2\text{U}(\text{SCS})\text{Cl}_3(\text{THF})$, the bis-carbene complex $\text{U}(\text{SCS})_2(\text{THF})_2$ and the unique example of a homoleptic tris-carbene complex, $\text{Li}_2(\text{OEt})_2\text{U}(\text{SCS})_3$, in very good yields (Scheme 11). Without going into details of experimental conditions, it is necessary to note the importance of the nature of the solvent and the order of introduction of the reagents, in particular for avoiding the detrimental protonation of the $(\text{SCS})^{2-}$ dianion into the $(\text{SCHS})^-$ monoanion in protic solvents. The thorium analogues $\text{Th}(\text{SCS})_2(\text{DME})$ and $[\text{Li}_2(\text{DME})\text{Th}(\text{SCS})_3]_n$ were synthesized by Fang et al. from $\text{ThCl}_4(\text{DME})_2$ [42]. The uranium bis-carbene complex was also obtained in almost quantitative yield from a 1:2 mixture of uranium tetrachloride and the tris-carbene in THF. Under the same conditions, the comproportionation reaction between uranium chloride and the bis-carbene in a 1:1 molar ratio led to the quantitative formation of the neutral mono-carbene compound $\text{U}(\text{SCS})\text{Cl}_2(\text{THF})_2$ [39,40].

The tris-carbene complex was also obtained by using the uranium tetraborohydride as precursor. Reaction of $\text{U}(\text{BH}_4)_4$ with 1 equivalent of Li_2SCS in toluene afforded the trinuclear complex $\text{U}(\mu\text{-SCS})_3[\text{U}(\text{BH}_4)_3]_2$ which was transformed in THF into the mononuclear derivative $\text{U}(\text{SCS})(\text{BH}_4)_2(\text{THF})_2$ (Scheme 12) [41].

The uranium amides $\text{U}(\text{NET}_2)_4$ and $[\text{U}(\text{NET}_2)_3][\text{BPh}_4]$ were found to be also good precursors of carbene complexes by protonolysis reactions with the neutral molecule $[\text{Ph}_2\text{P}(=\text{S})]_2\text{CH}_2$ (SCH_2S). Thus were obtained $\text{U}(\text{SCS})(\text{SCHS})(\text{NET}_2)$, the first mixed alkyl-carbene compound of an actinide with both methanide and methanediide ligands, and $[\text{U}(\text{SCS})(\text{NET}_2)(\text{THF})_3][\text{BPh}_4]$, the first example of a cationic uranium carbene complex (Scheme



Scheme 10. Bonding modes in the different types of metal carbene complexes.

Scheme 11. Synthesis of uranium carbene complexes from UCl_4 .Scheme 12. Synthesis of uranium carbene complexes from $\text{U}(\text{BH}_4)_4$.Scheme 13. Synthesis of uranium carbene complexes from $\text{U}(\text{NEt}_2)_4$.

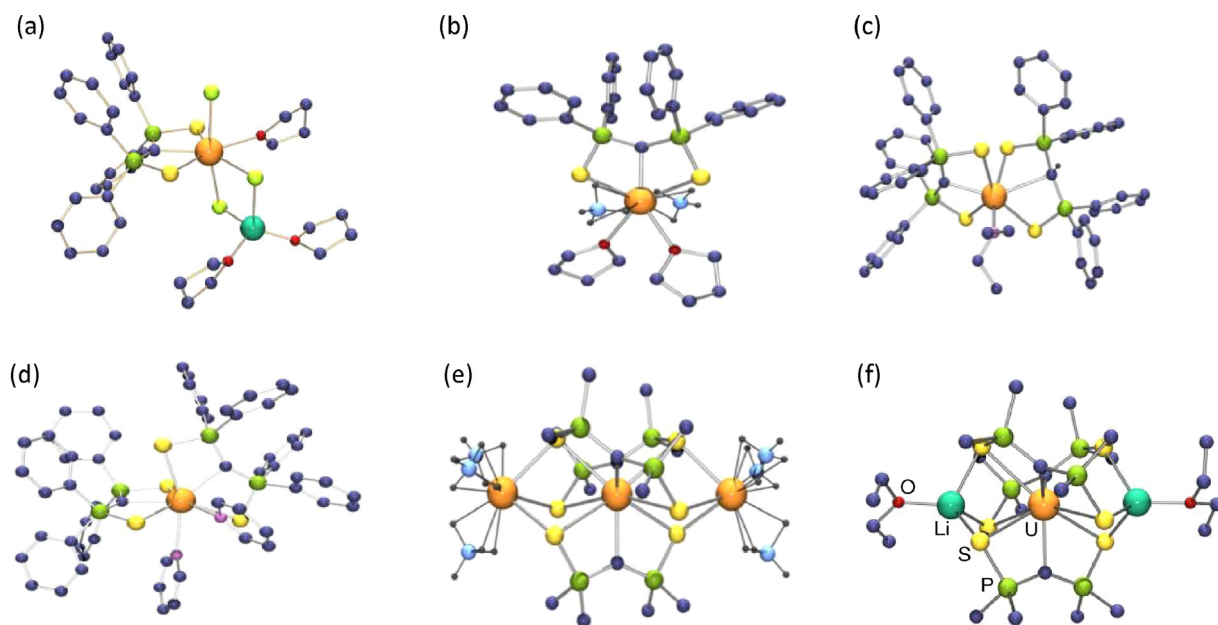


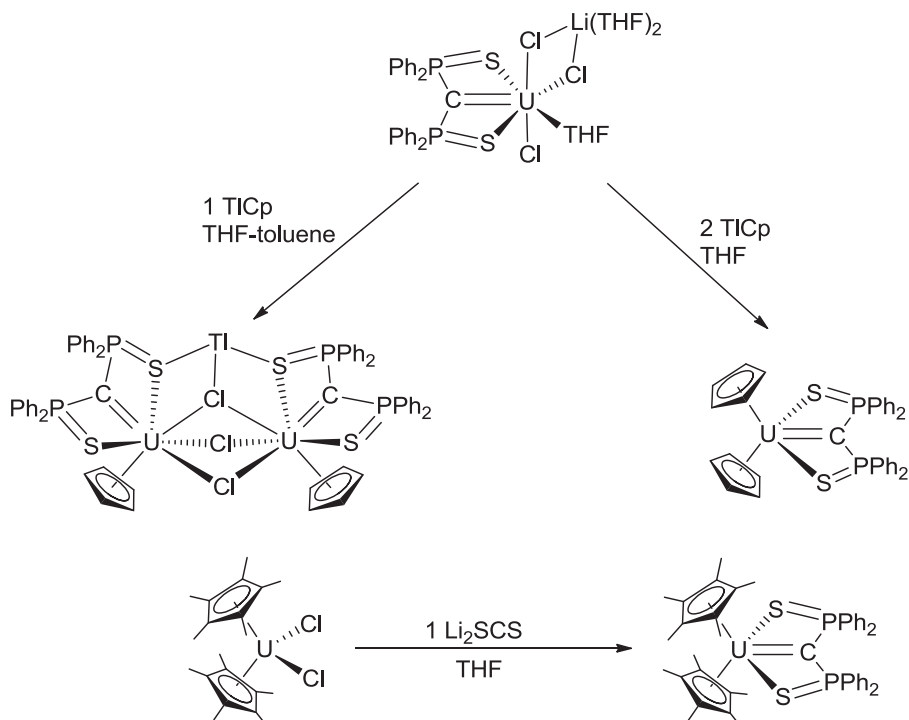
Fig. 2. X-ray crystal structures of Li(THF)₂U(SCS)Cl₃(THF) (a), U(SCS)(BH₄)₂(THF)₂ (b), U(SCS)(SCHS)(NEt₂) (c), U(SCS)₂(py)₂ (d), U(SCS)₃[U(BH₄)₃]₂ (e), Li₂(OEt₂)₂U(SCS)₃ (f).

13) [40]. The crystal structures of the chloro-, tetrahydroborato and amido-carbene complexes are shown in Fig. 2.

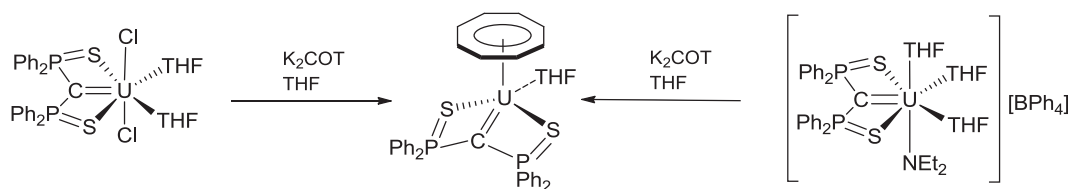
Liddle et al. have used the $(^{\text{Mes}}\text{NCN})^{2-}$ ligand to prepare the homoleptic bis-carbene complex U($^{\text{Mes}}\text{NCN}$)₂ [43] while Cavell et al. synthesized the mono-carbenes An($^{\text{TMS}}\text{NCN}$)Cl₂

(An = U, Th) which were transformed into the cyclopentadienyl and the pyrazolyl borate derivatives Cp₂An($^{\text{TMS}}\text{NCN}$) and TpAn($^{\text{TMS}}\text{NCN}$)Cl [44].

The series of mixed uranium SCS carbene complexes was extended to π -organometallic compounds. The anionic, neutral and cationic mono-carbenes were used



Scheme 14. Synthesis of cyclopentadienyl uranium carbene complexes.



Scheme 15. Synthesis of the cyclooctatetraenyl uranium carbene complex (COT)U(SCS)(THF).

as precursors for the synthesis of cyclopentadienyl and cyclooctatetraenyl derivatives (Schemes 14 and 15) [40]. Treatment of the “ate” complex with 1 molar equivalent of freshly sublimed TICp in THF gave the trinuclear compound $\text{Ti}[\text{CpU}(\text{SCS})_2(\mu\text{-Cl})_3]$ which can be seen as the assemblage of the expected monocyclopentadienyl uranium carbene $\text{CpU}(\text{SCS})\text{Cl}$ with half the quantity of the by-product thallium chloride. Such compounds where thallium(I) coordinates to metal-bound halide ions to form soluble coordination compounds are quite uncommon and have been obtained by serendipity. The same reaction with 2 molar equivalents of TICp gave the biscyclopentadienyl complex $\text{Cp}_2\text{U}(\text{SCS})$. In contrast, the bis(pentamethylcyclopentadienyl) analogue could not be obtained from the “ate” complex and was synthesized by reaction of Cp^*UCl_2 and Li_2SCS in diethyl ether (Scheme 14).

Although the chemistry of the monocyclooctatetraenyl uranium compounds has been significantly developed during the last years, such complexes with uranium-carbon bonds remain very rare. The monocyclooctatetraenyl uranium carbene (COT)U(SCS)(THF) was synthesized by metathesis reaction of $\text{U}(\text{SCS})\text{Cl}_2(\text{THF})_2$ and K_2COT in THF. This complex was alternatively prepared in almost quantitative yield from the cationic precursor $[\text{U}(\text{SCS})(\text{NEt}_2)(\text{THF})_3][\text{BPh}_4]$ (Scheme 15) [40]. The crystal structures of the cyclopentadienyl and cyclooctatetraenyl carbene complexes are shown in Fig. 3.

The crystal structures of the uranium SCS compounds show that, with the exception of the trinuclear compounds $\text{M}_2\text{U}(\text{SCS})_3$ [$\text{M} = \text{U}(\text{BH}_4)_3$ or $\text{Li}(\text{OEt}_2)$] where the central uranium atom is sterically encumbered and very electron rich, the U–C bond distances vary from of 2.327(3) Å in $\text{U}(\text{SCS})(\text{BH}_4)_2(\text{THF})_2$ to 2.396(4) Å in $\text{Cp}^*\text{U}(\text{SCS})$ derivative. These short distances are similar to those measured in the phosphoylide complexes isolated by Gilje et al. They are smaller than the σ U–C bond lengths of uranium(IV) alkyl compounds, which are comprised between 2.4 and 2.6 Å,

and significantly smaller than those found in uranium(IV) complexes with *N*-heterocyclic carbene ligands, by more than 0.2 Å. In all the complexes, the P–C distances with an average value of 1.676 Å are short, suggesting that the two lone pairs at the carbon atom are stabilized by negative hyperconjugation into the Ph_2PS arms. The U–S–P–S cores are planar, except in the monocyclooctatetraenyl compound which adopts a classical four legged piano stool configuration. The short U–C distances and the planarity at the carbene carbon atoms show the donation of both lone pairs from the dianionic fragment to the metal centre and the likely formation of a U=C double bond.

Similar short U–C distances were found in the uranium R^{NCN} complexes, as shown by the values of 2.336(6) and 2.351(2) Å for $\text{Cp}_2\text{U}(\text{SCS})$ [40] and $\text{Cp}_2\text{U}(\text{TM}^{\text{S}}\text{NCN})$ [44], respectively. However, the R^{NCN} ligands generally adopt an “open book” conformation, in contrast to the planar SCS ligands. This difference likely reflects the much greater steric constraints due to U–N and P–N bonds much shorter than U–S and P–S bonds and to the presence of bulky substituents on the coordinated nitrogen atoms.

Comparison of the crystal structures of analogous uranium and thorium carbene complexes $\text{Cp}_2\text{An}(\text{TM}^{\text{S}}\text{NCN})$ ($\text{An} = \text{U}, \text{Th}$) [44], $\text{TpAn}(\text{TM}^{\text{S}}\text{NCN})\text{Cl}$ ($\text{An} = \text{U}, \text{Th}$) [44], $\text{U}(\text{SCS})_2(\text{py})_2$ [40] and $\text{Th}(\text{SCS})_2(\text{DME})$ [42], $\text{Li}_2(\text{OEt}_2)_2\text{U}(\text{SCS})_3$ [40] and $[\text{Li}_2(\text{DME})\text{Th}(\text{SCS})_3]_n$ [42] indicates that the differences of 0.07–0.09 Å between the Th–C and U–C distances are larger than the value of 0.05 Å expected from the variation in the radii of the Th^{4+} and U^{4+} ions [45]. These features suggest that the double bond character of the M–C bond is less pronounced for $\text{M} = \text{Th}$ than for $\text{M} = \text{U}$.

5.2. Electronic structures of the actinide(IV) complexes

The electronic structure of the actinide carbenes has been investigated using DFT approaches. The optimized structure of the model complex $\text{U}(\text{C}(\text{PH}_2(=\text{S}))_2)(\text{BH}_4)_2$

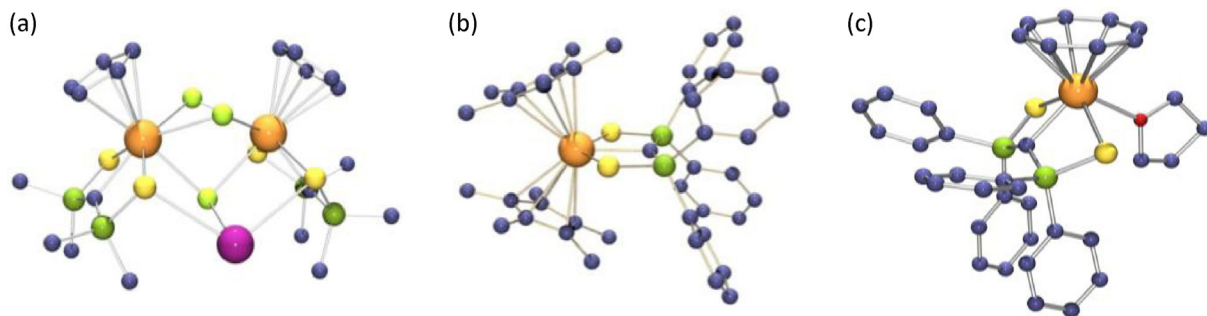


Fig. 3. X-ray crystal structures of $\text{Ti}[\text{CpU}(\text{SCS})_2(\mu\text{-Cl})_3]$ (a), $\text{Cp}^*\text{U}(\text{SCS})$ (b) and $(\text{COT})\text{U}(\text{SCS})(\text{THF})$ (c).

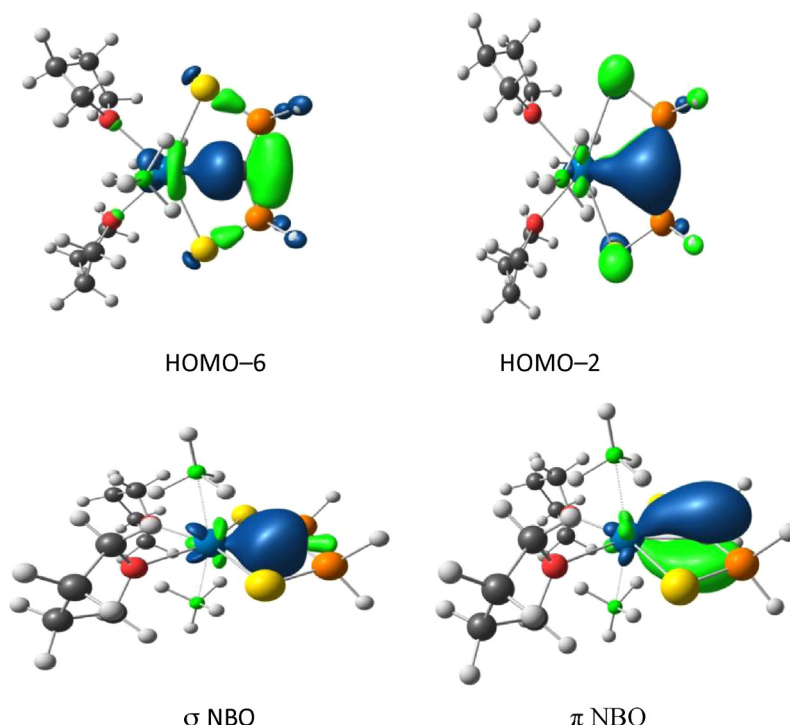


Fig. 4. Plots of the HOMO and NBO for $U(C(PH_2(=S))_2)(BH_4)_2(THF)_2$ describing the U=C double bond.

(THF)₂ is in perfect agreement with the X-ray diffraction data obtained for $U(SCS)(BH_4)_2(THF)_2$. The interaction between the uranium(IV) ion and the dianionic ligand is described by the HOMOs (Fig. 4). In particular, the HOMO-6 clearly describes the U–C σ -bond which results from the donation of the carbon sp^2 lone pair to a vacant hybrid orbital on U while the HOMO-2 mainly corresponds to a U–C π -bond, polarized on the C atom [41].

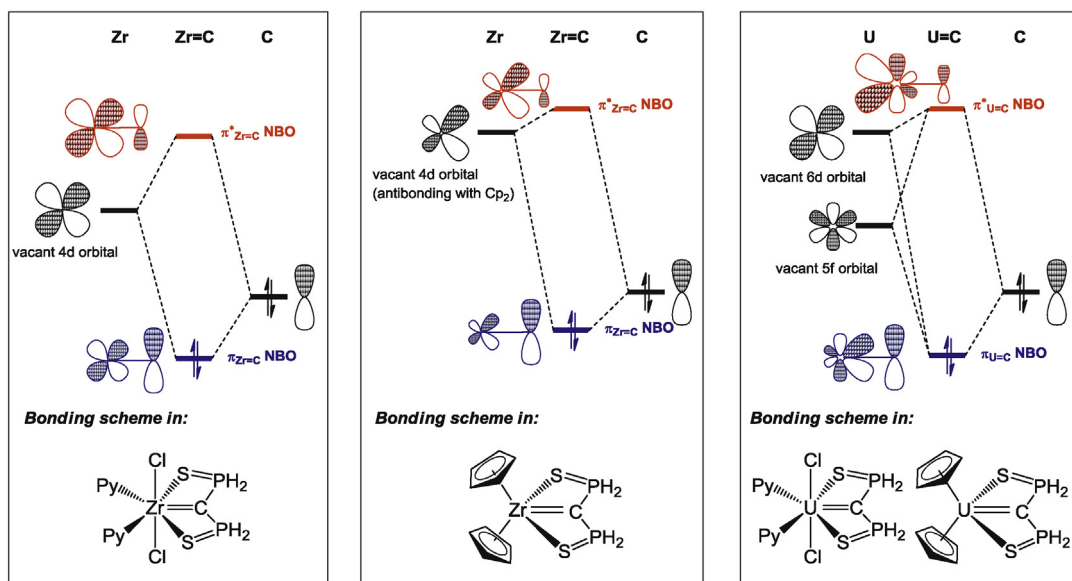
The Natural Bond Orbital analysis gives a more localized and chemically relevant picture of the U=C interaction. The NBO describing the two U–C σ and π -bonds are represented in Fig. 4. The U–C σ -bond comes from the interaction of the C sp^2 lone pair (80.7%) with a uranium hybrid orbital (19.3%) of 52.6% 5f and 37.0% 6d character. The U–C π -bond is made of a carbon 2p pure lone pair (82.9%) and a metal hybrid orbital (17.1%) of 59.0% 5f and 40.9% 6d character. This bonding scheme shows that the U=C double bond is polarized towards the carbon atom, in agreement with the Mulliken analysis. The polarization is not only due to the greater electronegativity of carbon compared to uranium but also to the presence of two thiophosphinoyl groups attached to the carbene centre. The two lone pairs on the carbon atom are indeed stabilized by negative hyperconjugation in the free SCS^{2-} ligand. The same occurs also, but to a lower extent, in the complex. Upon coordination to the metal fragment, the charge of the carbon atom drops from -1.90 in the free ligand to -1.52 in the complex. This is diagnostic of a significant electron transfer from the two carbon lone pairs to the U(IV) metal centre that establishes the U=C double bond. The NBO analysis also confirms the important involvement of the uranium 5f orbitals in stabilizing the

U=C double bond. Overall, the contribution of the uranium 5f orbitals is somewhat higher than that of the 6d orbitals in the U=C interaction. Though the 5f orbitals are more radially contracted than the 6d AOs, the 5f AOs are indeed lower in energy in uranium and can lead to greater angular overlaps where symmetry constraints are high (such as in HOMO-2) [41].

DFT calculations on the whole molecule of $U(MesNCN)_2$ [43] and parent models of $Cp_2An(^{TM}SCN)$ and $TpAn(^{TM}SCN)Cl$ ($An=U, Th$) [44] also showed that the components of the M=C double bond involve the 5f and 6d orbitals of the actinide metal and the carbene 2p orbitals, as both σ bond and π bond components. The formation of the formal M=C double bonds is not disfavoured by the ‘open book’ conformation of the RNCN carbene ligands. Wiberg bond indices indicated that the U=C bond is stronger than the Th=C bond, which is consistent with the relative U–C and Th–C distances in $Cp_2An(^{TM}SCN)$. The double $\sigma+\pi$ donation toward the metal atom was demonstrated in the thorium complexes $Th(SCS)_2(DME)$ and $[Li_2(DME)Th(SCS)_3]_n$ where the Th=C double bonds were described as single bonds with a lone pair localized on the carbene carbon atom [42].

Theoretical calculations revealed that the bonding scheme in uranium(IV) phosphoylides $U(CHPhP_3)(NR_2)_3$ and $Cp_3U=CHPMe_2Ph$ is quite identical to that determined in SCS and RNCN carbene compounds, the U–C interaction being highly polarized with modest π character [14].

For comparing the electronic structure of the uranium(IV) carbene complexes with transition metal analogues and explaining the distinct influence of the coordination environment around the M^{4+} ion ($M=Zr, U$) on the M=C



Scheme 16. Representation of the metal–carbon double bond in zirconium and uranium carbene complexes.

double bond, the electronic structure of parent models of the complexes $M(\text{SCS})\text{Cl}_2(\text{py})_2$ and $\text{Cp}_2\text{M}(\text{SCS})$ ($M = \text{Zr}, \text{U}$) has been investigated [40]. Together with crystal data, theoretical calculations show that the $\text{U}=\text{C}$ multiple bond presents a covalent character similar to the bonding situation in transition metal complexes. In addition, the vacant 5f atomic orbitals on the actinide ion engage in covalent interactions with the carbene centre, so as to better stabilize the carbene valence orbitals. This effect is noticeable in the $\text{Cp}_2\text{M}(\text{SCS})$ complexes for which the repulsive interaction between the SCS dianion and the Cp anions is observed for $M = \text{Zr}$ while the 5f orbitals play a “buffer” role in the uranium compound, leading to a metal–carbon bond elongation in the zirconium complex only (Scheme 16). As a result, and in contrast with transition metal complexes, changes in the coordination sphere of the uranium(IV) centre have little influence on the $\text{U}=\text{C}$ bond.

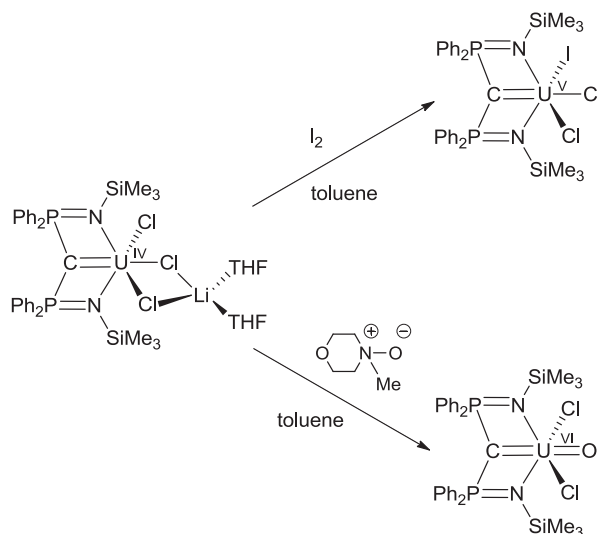
5.3. Uranium carbene complexes in the +5 and +6 oxidation states

The SCS and $^{\text{R}}\text{NCN}$ ligands were found to also stabilize uranium compounds in their highest oxidation states. The group of Liddle recently reported on the oxidation of the uranium(IV) “ate” complex $\text{Li}(\text{THF})_2\text{U}(\text{TM}^{\text{S}}\text{NCN})\text{Cl}_3(\text{THF})$ with iodine and 4-morpholine *N*-oxide which led to the formation of the uranium(V) compound $\text{U}(\text{TM}^{\text{S}}\text{NCN})\text{Cl}_2\text{I}$ [46] and the uranium(VI) oxo derivative $\text{U}(\text{TM}^{\text{S}}\text{NCN})\text{Cl}_2(\text{O})$ [47], respectively (Scheme 17). The $\text{U}-\text{C}$ distances decrease with increasing oxidation state, with values of 2.310(4), 2.268(10) and 2.183(4) Å.

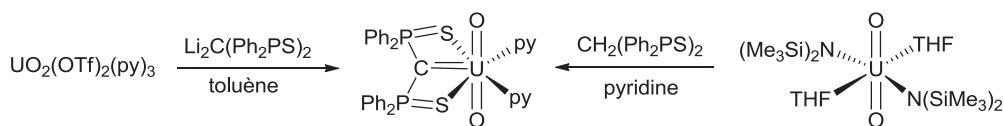
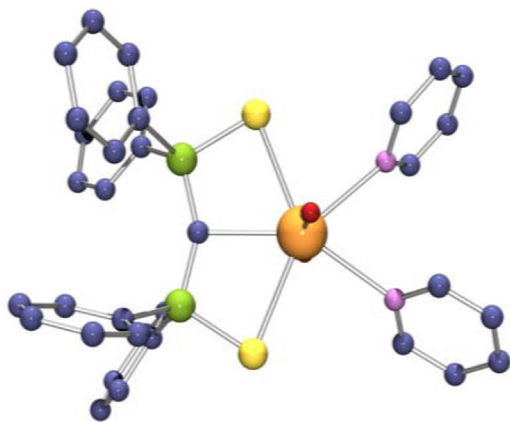
Natural Bond Order analyses indicate that upon oxidation from uranium(IV) to (V) to (VI) the uranium contribution to the $\text{U}-\text{C}$ σ -bond can increase from ca. 18 to 32%, while for the corresponding $\text{U}=\text{C}$ π -components, the uranium contribution increases from ca. 18 to 26% but then

decreases to ca. 24%. The calculations suggest that as a function of increasing oxidation state of uranium, the radial contraction of the valence 5f and 6d orbitals may outweigh the increased polarizing power of uranium in $\text{U}(\text{TM}^{\text{S}}\text{NCN})\text{Cl}_2(\text{O})$ compared to $\text{U}(\text{TM}^{\text{S}}\text{NCN})\text{Cl}_2\text{I}$ [47].

The synthesis of uranyl compounds with metal–carbon bonds remains a challenging goal because of the reduction of $\text{U}(\text{VI})$ to $\text{U}(\text{V})$ by the alkyl ligand. As such, only two uranyl complexes with alkyl or π -organometallic ligands have been observed to date: the cyclopentadienyl compound $[\text{NEt}_4]_2[\text{UO}_2(\text{Cp}^*)(\text{CN})_3]$ [48] and the bis-iminophosphoranyl complex $[\text{UO}_2(\text{TM}^{\text{S}}\text{NCHN})\text{Cl}]_2$ and its derivatives [49]. Interestingly, the cyclopentadienyl uranyl complex was not synthesized by treatment of a UO_2X_2 precursor



Scheme 17. Synthesis of $\text{U}(\text{V})$ and $\text{U}(\text{VI})$ carbene complexes.

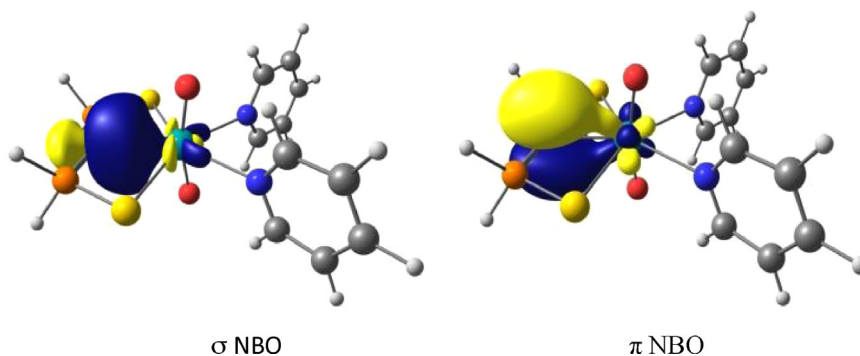
Scheme 18. Synthesis of the uranyl carbene complex $\text{UO}_2(\text{SCS})(\text{py})_2$.Fig. 5. X-ray crystal structure of $\text{UO}_2(\text{SCS})(\text{py})_2$.

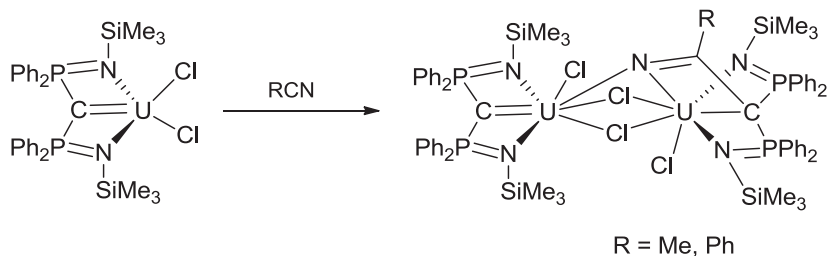
with the $[\text{C}_5\text{Me}_5]^-$ anion, a reaction which provides in fact a convenient route to the corresponding pentavalent UO_2X derivative [50], but was isolated from the reaction of the linear metallocene $[\text{NEt}_4]_3[\text{U}(\text{Cp}^*)_2(\text{CN})_5]$ and pyridine *N*-oxide. The uranyl carbene complex $\text{UO}_2(\text{SCS})$ was synthesized in 95% yield by treatment of uranyl triflate with Li_2SCS in pyridine or by protonolysis of uranyl triflate with $\text{UO}_2(\text{N}\{\text{SiMe}_3\}_2)_2(\text{THF})_2$ with SCH_2S (Scheme 18) [51]. The crystal structure shows the planar carbene ligand (Fig. 5). The U–C distance of 2.430(6) is 0.2 Å smaller than those measured in the uranyl methanide complexes $\text{UO}_2(\text{SCHS})(\text{OTf})(\text{Et}_2\text{O})$ and $\text{UO}_2(\text{SCHS})_2$, which were isolated from reactions of $\text{UO}_2(\text{OTf})_2$ with LiSCHS [51]. However, this distance is 0.1 Å larger than those found in mononuclear uranium(IV) carbenes, while the radius of the UO_2^{2+} ion is 0.2 Å smaller than that of U^{4+} . These features suggest that the multiple bond character of the U–C bond is less pronounced in the uranyl than in the uranium(IV) compounds.

DFT calculations showed that the U=C interaction in the uranyl carbene is properly described by two distinct NBO, as previously found for uranium(IV) and zirconium(IV) complexes (Fig. 6). The formation of the U=C double bond upon conversion of the methanide to carbene complex is clearly reflected by the change in the uranium–carbon bond Wiberg bond order which increases from 0.43 in the alkyl complex to 0.91 in the carbene. However, the bond polarization is more marked than in uranium(IV) complexes. This result is surprising considering the greater electrophilicity of U(VI) compared to U(IV) which was expected to maximize the U=C interaction and therefore electron donation from the ligand to uranium. However, inspection of the U=O Wiberg bond indexes and q_{O} charges in the alkyl and carbene complexes show that the uranium–oxo interactions are only slightly perturbed by the formation of the U=C double bond. In other words, among the three double bonds present in the uranium coordination sphere, the metal ion preferentially accommodates the oxo ligands, leaving a nucleophilic carbene center.

5.4. Reactions of the actinide carbene complexes

While reactions of the complexes $\text{Cp}_3\text{U}=\text{CHPR}_3$ were much explored by Gilje et al. (Scheme 2), limited studies were devoted to the more recently synthesized SCS and $^{\text{R}}\text{NCN}$ compounds. The nucleophilic character of the U(IV), Th(IV), U(V) and U(VI) carbene complexes was illustrated by metallo–Wittig reactivity with 9-anthracene carboxaldehyde, benzaldehyde or benzophenone to afford the alkene $(\text{Ph}_2\text{P}=\text{NR})_2\text{C}=\text{CR}^1\text{R}^2$ or $(\text{Ph}_2\text{P}=\text{S})_2\text{C}=\text{CR}^1\text{R}^2$ ($\text{R}^1 = 9$ -anthracene or Ph and $\text{R}^2 = \text{H}$; $\text{R}^1 = \text{R}^2 = \text{Ph}$) [40–42,47]. A novel behaviour of the U=C double bond was revealed by the reaction of $\text{U}(\text{TMS}^{\text{N}}\text{NCN})\text{Cl}_2$ with MeCN or PhCN in which the C≡N triple bond of the nitrile suffered a 1,2-cycloaddition to the carbon–metal bond to form a new

Fig. 6. Plots of the NBO for $\text{UO}_2(\text{C}\{\text{PH}_2(=\text{S})\}_2)(\text{py})_2$ describing the U=C double bond.

Scheme 19. Reaction of $U^{(TM5)N(CN)Cl_2}$ with RCN.

C–C bond and build a tetradentate ligand with three imine centers which coordinate to the uranium atom while maintaining a single U–C bond. The newly formed complex dimerizes with one equivalent of unconverted $U^{(TM5)N(CN)Cl_2}$ using two chlorides and the imine group derived from the nitrile as three connecting bridges (Scheme 19) [44].

6. Conclusion

After the initial discovery of the phosphoylide complexes $Cp_3U=CHPR_3$, the detection of actinide methylenide compounds in solid argon and the evidence for carbenoid uranium species in McMurry type reactions, the spectacular recent advances in uranium carbene chemistry have to be related to the use of geminal carbon dianions stabilized by phosphorous(V) substituents. A variety of uranium compounds in the +4, +5 and +6 oxidation states were thus isolated and fully characterized. At the same time, the progress of theoretical calculations led to a good description of the U=C double bond that demonstrates a double σ and π donation toward the metal atom with the involvement of the 5f orbitals. Reactions of these complexes were not much developed, being limited to reactions with aldehydes and ketones, and confirmed the polarization of the U=C bond toward the nucleophilic carbene carbon atom. Further attention should be paid to the characterization of thorium carbene complexes, which remain very rare, and their reactions, for comparison with those of the uranium analogues, in order to determine the influence of the f electrons on their structure and reactivity.

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