C. R. Chimie 16 (2013) 391–405

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Uranium carbene compounds

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ARTICLE INFO

Article history:
Received 19 October 2012
Accepted after revision 3 December 2012
Available online 16 January 2013

Keywords:
Actinide
Carbene
Geminal dianion
DFT calculations

Mots clés :
Actinide
Carbène
Dianion germinal
Calculs DFT

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 methylidene compounds 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.

RÉSUMÉ

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 cyclooctatetraényle 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.

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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http://dx.doi.org/10.1016/j.crci.2012.12.001

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 f 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_α 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