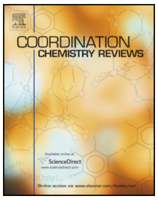
Coordination Chemistry Reviews 293–294 (2015) 211–227

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Inverted sandwich arene complexes of uranium

Stephen T. Liddle*

School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK

Contents

ARTICLE INFO

Article history:
Received 18 July 2014
Received in revised form 1 September 2014
Accepted 10 September 2014
Available online 28 September 2014

Keywords:
Uranium
Cyclobutadienyl
Cyclopentadienyl
Arene
Cycloheptatrienyl
Cyclooctatetraenyl

ABSTRACT

The chemistry of arene complexes of uranium has for over half a century been an important facet of organoactinide chemistry. Within this extensive and burgeoning field, in the past two decades inverted sandwich complexes have emerged incorporating cyclobutadienyl, arene, cycloheptatrienyl, and cyclooctatetraenyl ligands. Herein, the field is reviewed with an emphasis on well-defined molecular species that have been unambiguously characterised by X-ray crystallography.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Since the report of the synthesis of $[U(\eta^5\text{-}C_5H_5)_3Cl]$ in 1956 [1], and its structural characterisation in 1965 [2], the chemistry of arene-derived complexes of uranium (where arene is defined as a cyclic hydrocarbon with alternating single and double bonds which includes heteroarenes as a sub-class), and more broadly speaking of the actinides, has developed over the last half a century to become an important facet of non-aqueous uranium chemistry [3]. Such organometallics are of interest not only from a fundamental perspective of understanding the bonding of uranium to organometallic ligands, but also because of the potentially novel

---

* Tel.: +0044 1158467167.
E-mail address: stephen.liddle@nottingham.ac.uk

http://dx.doi.org/10.1016/j.ccr.2014.09.011
0010-8545/© 2014 Elsevier B.V. All rights reserved.

reactivity that such complexes might underpin [4–12]. Regarding the bonding aspects, the nature (5f vs 6d orbital participation; σ, π, or δ-bonding) and extent of any covalency in uranium–ligand linkage bonding is still widely debated and seems to vary depending on the nature of the ligand and oxidation state of uranium so studies of the bonding of varying sizes of arene ligands to uranium can be very instructive. Cyclopentadienyl/metallocene derivatives of uranium are legion, and sandwich molecules such as uranocene, $[U(\eta^8\text{-}C_8H_8)_2]$ [13–15], represent major milestones in organoactinide chemistry because of the profound implications the bonding schemes of such molecules have had on our understanding of chemical bonding. An interesting and burgeoning category of arene complexes of uranium is that of inverted sandwich complexes where the arene bridges two uranium centres. Examples of these complexes now include cyclobutadienyl, benzene-derivatives, cycloheptatrienyl, and cyclooctatetraenyl derivatives. Herein, the field is reviewed with an emphasis on well-defined molecular species that have been unambiguously characterised by X-ray crystallography. In reaction schemes specific conditions of reactions are not given unless they are of major significance and the reader is referred to the individual references for further experimental details. In discussions of uranium–ring distances the ranges of U—C bond lengths are given rather than U-centroid distances; not all U–ring interactions are symmetrical so U-centroid distances can be skewed whereas the range of U–C distances arguably gives a more representative picture of the U–C interactions. This Review is structured by increasing size of the bridging arene, and within each class of arene in chronological order so the reader may appreciate the historical development of each area.

Before the various classes of inverted sandwich arene complexes of uranium are described, it is instructive to overview the nature of arene ligands and the character of their potential interactions with uranium, Fig. 1. In all instances, from the formal perspective of complex construction, a neutral arene can be combined with neutral uranium fragments with a net sharing of some valence electrons to construct bonding interactions. For transition metals, the bonding is often quite covalent so considerations of any electron transfer are to some extent formal. However, although uranium does engage in some covalent bonding these interactions are predominantly electrostatic so it is convenient to consider formal electron transfer from uranium to arene fragments to generate formal anionic ligand species bonded to a cationic metal fragment. This is in much the same way that sodium cyclopentadienyl is intuitively considered to be a sodium cation paired with a 6π-electron cyclopentadienyl anion rather than a neutral sodium paired with a 5π-electron radical cyclopentadiene species. An important aspect to appreciate is that arenes usually principally donate electron density to transition metal centres with some backbonding, and hence they are usually, but not always, bound to only one metal. For uranium, a formal electron transfer from metal to ligand usually occurs, and thus the arene becomes an electron rich, predominantly electron acceptor moiety and so bridging coordination modes, the subject of this review, are much more common than in the d-block.

1.1. C_4-Ligands

The D_{4h} cyclobutadiene presents a π molecular orbital manifold of ψ orbitals 1–4 of a, e, and b symmetry, respectively. The a-orbital is suited to σ-type bonding, the e-set to π-bonding, and the b-orbital to δ-bonding. Square butadiene is a diradical according to Hund's rule, and in the absence of metal-stabilisation would be expected to distort to the rectangular singlet form. Alternatively, two-electron reduction to cyclobutadienyl affords a 6π-electron aromatic system. Although δ-bonding of cyclobutadienyl is in principle possible from a symmetry perspective, in practice the vacant ψ_4 orbital is usually energetically too high-lying to effectively engage in δ-bonding and the small ring size may result in poor δ-orbital overlap with metal-based frontier orbitals so σ- and π-bonding would be expected to dominate for this system, as is the case with transition metals.

1.2. C_5-Ligands

Cyclopentadiene, C_5, exhibits a π molecular orbital manifold of ψ orbitals 1–5 of a and two pairs of e symmetry, respectively. As for C_4, these are suitable for σ, π, and δ-type bonding interactions. Cyclopentadiene, a 5π-electron radical readily accepts an electron to become an 6π-electron aromatic cyclopentadienyl system that has an extensive literature regarding bonding to uranium. However, the D_{5h} cyclopentadienyl monoanion is not particularly electron rich, and so there are few precedents of inverted sandwich complexes of cyclopentadienyl in the f-block. Like C_4, σ- and π-bonding modes are anticipated to dominate and although δ-bonding is more favourable than for C_4, angular constraints often result in weak δ-bonding of the empty ψ_4 and ψ_5 orbitals to metal centres.

1.3. C_6-Ligands

The D_{6h} C_6-arene scaffold, is a neutral 6π-electron manifold of ψ orbitals 1–6 of a, two e pairs, and b symmetry. These frontier orbitals may be classified as being suitable for σ (ψ_1), π (ψ_2 and ψ_3), and δ (ψ_4 and ψ_5) bonding combinations, with in principle the ψ_6 being suited to ϕ bonding, the latter of which is a bonding mode unique to actinides and invoked for uranium in the bonding scheme of uranocene [13]. Although in principle C_6 aromatics do not require the addition of any electrons to satisfy Huckel's $4n+2\pi$-electron rule, the strongly reducing nature of uranium(III) combined with the relatively low-lying ψ_4 and ψ_5 orbitals often results in the generation of arene rings with variable levels of reduction—for diuranium derivatives formal two-electron reduction is now relatively common, and formal four-electron reduction, which generates a 10π-electron system that satisfies Huckel's $4n+2\pi$-electron rule, is also now known. However, it is germane to reiterate that these situations are accompanied by extensive δ-bonding, which tends to dominate over σ and π interactions because of better spatial overlap and energetically matched frontier orbitals (cf. bonding schemes of metallocenes versus bis-benzene metal complexes), so classifying formal charges and electron sharing/transfer becomes something of a nebulous endeavour.

1.4. C_7-Ligands

The cycloheptatriene C_7 framework is an interesting carbocycle-removal of hydride from the parent C_7H_8 molecule generates a 6π-electron monocation, whereas removal of a proton generates a 8π-electron monoanion, which if reduced by two electrons generates a cycloheptatrienyl 10π-electron trianion that meets Huckel's $4n+2$ π-electron rule. In the context of uranium chemistry, cycloheptatrienyl is best regarded as a 10π-electron trianion. The π molecular orbital manifold of D_{7h} cycloheptatrienyl follows a familiar pattern of ψ orbitals 1–7, of a (σ), and three pairs of e symmetry (π then δ), with the first five orbitals being most important from symmetry and energetic considerations with respect to bonding to metal centres.

1.5. C_8-Ligands

The C_8 cyclooctatetraene exhibits a π molecular orbital manifold of ψ orbitals 1–8 of a, three e pairs, then b symmetry orbitals. Analogously to C_7 the top three ψ orbital combinations can be essentially ignored in the treatment of the bonding of C_8, with the remaining

Download English Version:

https://daneshyari.com/en/article/1299366

Download Persian Version:

https://daneshyari.com/article/1299366

Daneshyari.com