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Organoactinoid Chemistry with Phosphoylids[*]

JOHN W. GILJE[**], ROGER E. CRAMER[**], MICHAEL A. BRUCK, KELVIN T. HIGA and K. PANCHANETHESWARAN

Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822, U.S.A.

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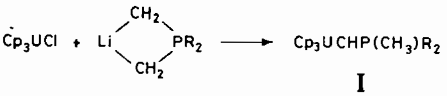
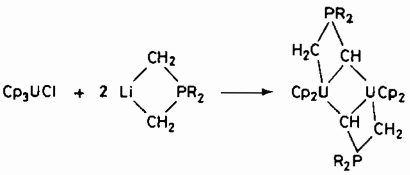
Phosphoylid complexes of metals from throughout the main group and d-block are well known [1, 2], and the ability of ylids to form complexes with the lanthanoids has been demonstrated [3]. As will be summarized in this paper, they are also versatile ligands towards the actinoid, U(IV), forming a number of structurally unique complexes which are beginning to show a varied chemistry.

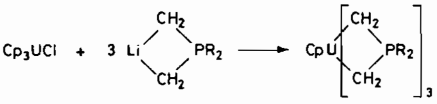
The first actinoid–ylid complexes were isolated [4–9] from the following reactions[†]:



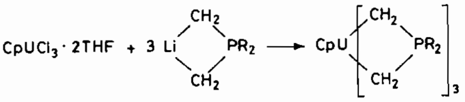
I



II



III

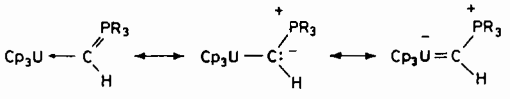


III

All of these compounds are stable if stored in the absence of air and moisture and have been well characterized by standard chemical and spectroscopic techniques as well as by X-ray crystallography.

Compound **III** demonstrates [6, 9] that ylids are capable of forming complexes which contain many actinoid–carbon sigma bonds. The ability of ylids to form structurally unique complexes is shown [4–6] by **II**. In this compound the mode of ylid attachment, in which a single ligand both chelates to one metal and, at the same time, bridges to a second metal, has not previously been observed and the diuranametalacylobutane unit is unusual.

Compound **I** is also a very interesting molecule [6–8]. We initially formulated it [10] as a substituted ylid, $Cp_3U{-}CH{=}P(CH_3)R_2$, **IA**. A tabulation of structural parameters for compounds **I**, **II**, **III**, and other compounds with uranium–carbon sigma bonds (Table I) shows all the ylid complexes to contain U–C(Cp) distances which are comparable to those in UCp_4, which is a very crowded molecule. Detailed inspection [4, 5, 7–9] of the structures of the ylid complexes reveals that they are also sterically congested, and it is probable that the separations of the uranium from the Cp groups reflect these crowdings. The U–C(σ) distances in **II** and **III** are also long [4, 5, 9], with the 2.66(3) Å distances in these molecules being the longest U–C sigma bonds yet reported. While electronic effects [9] may influence these bond lengths they also may reflect the steric crowding within the molecules. Thus, it is surprising when the shortest U–C distance yet observed, 2.29(3) Å, is encountered [7, 8] in **I**. These data combined with the relatively large U–C–P bond angle of 142(1)° suggests that the uranium–carbon bond in **I** is multiple. It can be described [8] in terms of the following resonance structures:



A hybrid of these structures:

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[**] Authors to whom correspondence should be addressed.

[†] The structure of $Li(CH_2)(CH_2)PPh_2$ has been determined [28]. When grown from a thf–dioxane mixture the compound exists as:

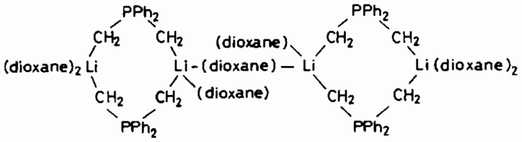

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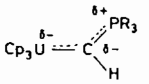
TABLE I. Uranium(IV)–Carbon Bond Distances in Organouranium Complexes (Å)·

Compound	U–C(Cp)	U–C (σ)	Ref.
$CpUCHP(CH_3)_2(C_6H_5)$, **I**	2.79(3)	2.29(3)	7, 8
$[Cp_2U]_2[\mu\text{-}CHP(C_6H_5)_2CH_2]_2$, **II**	2.78(1)	2.43(1), 2.53(2) 2.66(3)	4, 5
$CpU[(CH_2)(CH_2)P(C_6H_5)_2]_3$, **III**	2.79(1)	2.66(3)	9
$Cp_3U(n\text{-}C_4H_9)$	2.74(8)	2.43(2)	11
$Cp_3U(CH_2)\text{-}p\text{-}(CH_3C_6H_4)$	2.722(4)	2.54(2)	11
$Cp_3U[(CH_2)C(CH_3)(CH_2)]$	2.74(1)	2.48(3)	12
$Cp_3UC{\equiv}CH$	2.73(6)	2.36(3)	13
$Cp_3UC{\equiv}CC_6H_5$	2.68	2.33(2)	14
Cp_4U	2.81(2)		15



accounts for the abnormally short U–C bond in **I**.

EHMO calculations [16] support multiple bonding in **I**. Calculations were performed on both **I** and $Cp_3U{-}CH_3$ using U–C bond lengths of 2.40 Å for both compounds. The overlap population in the U–C (methyl) bond was 0.40 while for the U–C bond in **I** it was calculated to be 0.57. When the calculation was repeated at the observed U–C distance of 2.29 Å, the overlap population rose to 0.61, with a pi component of 0.19. These overlap populations strongly support the notion of a uranium–carbon multiple bond in **I**.

The electronic structure of **I** can be clarified by further comparisons with $Cp_3U{-}CH_3$. Depending upon the model chosen, the U–C bond in $Cp_3U{-}CH_3$ can be viewed as a polar covalent bond between the $[Cp_3U]^+$ ion and the methyl anion, or as a purely ionic interaction between these two ions. In any case, only two electrons are involved in the uranium–methyl bond. In contrast the bonding in **I** involves the interaction of $[Cp_3U]^+$ with the dicarbanion* $[:\overset{(2-)}{\underset{\cdot\cdot}{C}}H\overset{\oplus}{P}R_3]^-$. As in the case of $Cp_3U{-}CH_3$ the uranium–carbon bonding in **I** may be viewed as either ionic or polar covalent. However, in either case it is important to recognize that four electrons are involved in the uranium–carbon bond in **I**. It is well known that substantial chemical differences exist between two electron and four electron bonds, e.g. ethane and ethylene, and it should not be surprising that the chemistry of **I**, with a four electron uranium–carbon bond, should differ from that of $Cp_3U{-}CH_3$, and other compounds with two electron U–C bonds.

Compound **I** bears resemblance to Schrock type alkylidenes which can be formulated as complexes of a dicarbanion, $[\overset{\cdot}{:}CHR]^{2-}$. Although analogies with Shrock alkylidenes can be drawn, **I** and related compounds occupy a separate place within the framework of metal–carbon double bonding. In this respect a subdivision of compounds containing metal–carbon double bonds into three classes is convenient. The first class, often called Fischer carbene complexes, are compounds formed between an electron deficient ligand and an electron-rich metal, and are stabilized by an electron rich heteroatom attached to the alpha carbon atom. These complexes are 18-electron species involving group 6–8 transition metals in 0 or +1 oxidation states. Multiple metal–carbon bonding arises from σ donation from ligand to metal accompanied by back-donation of π electrons from the metal to the electron deficient carbene ligand. Even though the carbenoid center is further stabilized by π-electron donation from an electron rich substituent such as O or N, it remains electrophilic.

The second class are the alkylidene complexes, where no heteroatom substituents are attached to the α carbon atom. The metal involved in this class of bond either can be low valent, e.g. $(OC)_5WCPh_2$, in which case metal carbon bonding is similar to that in Fischer complexes, or can be in a higher oxidation state. In the latter case, a metal–carbon double bond formally results from the donation of both σ and π electrons from ligand to metal. Complexes of this

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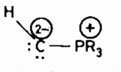
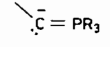
*The formulation of $[:\overset{(2-)}{\underset{\cdot\cdot}{C}}H\overset{\oplus}{P}R_3]^-$ as a dicarbanion is indicated by good quality *ab initio* molecular orbital calculations [29, 30] which show that there is little charge delocalization from the carbon to the phosphorus. The ylid resonance form:



clearly provides a better description of the bonding within the ligand than the ylene form:



type usually contain a group 5 or 6 transition metal in which there is a good match in energy and size between the appropriate metal and carbon sigma and pi orbitals. Consequently, considerable metal–carbon double bonding occurs, and no stabilizing groups are required on the α carbon atom.

The uranium–carbon double bond in I is a third class in which a negative charge on the α carbon is stabilized by an electron-withdrawing heteroatom substituent. Such bonds probably will be the most common type of metal–carbon double bonds in compounds of high valent, largely ionic metals, where extensive ligand to metal charge delocalization cannot occur.

With the recognition that I is the first example of a compound which contains a multiple bond between carbon and an f-block element, the nature of the chemistry of the molecule becomes an interesting question. In fact I is a reactive molecule. Consistent with the polar nature of the uranium–carbon bond the alpha carbon atom acts as a nucleophilic center. Reactions between both Lewis and Brønsted Acids have been studied [10, 17–19] and include:

$$Cp_3U{=}CHPR_3 + HNPh_2 \longrightarrow Cp_3UNPh_2 + CH_2{=}PR_3$$

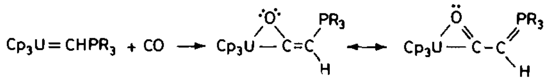
$$Cp_3U{=}CHPR_3 + HC{\equiv}CPh \longrightarrow Cp_3UC{\equiv}CPh + CH_2{=}PR_3$$

$$Cp_3U{=}CHPR_3 + CH_3I \longrightarrow Cp_3UI + \text{phosphonium salts}$$

These reactions allow I to be contrasted with the Cp_3U–alkyls. At least in our hands [20] Cp_3UCH_3 does not undergo analogous reactions with these species under the conditions used for their reactions with I.

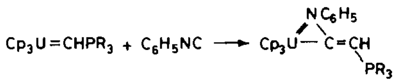
In contrast to both Fischer carbene complexes and Schrock alkylidene complexes which have important chemistries with unsaturated hydrocarbons, I does not react with internal monoalkenes and alkynes [19] over several months at room temperature. However, polar unsaturated molecules will react with I. The products arising from the reaction of I with CO [21], CH_3CN [22], and C_6H_5NC [23] have been characterized by X-ray crystallography and in each case addition occurs across the C–X multiple bond producing a product in which the nitrogen or oxygen is tightly bonded to the uranium. Some important metrical parameters for these products are summarized in Table II.

In the case of the reaction with CO insertion occurs into the four electron bond between uranium and carbon in I forming a complex whose structure can be described [21] as



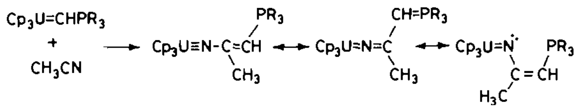
IVa **IVb**

Befitting the similarities which often exist between carbon monoxide and isonitrile chemistry, C_6H_5NC also reacts [23] with I



V

to form V in which the U–N bond appears [23] to contain significant multiple bond character. While the ability of U(IV) to tightly bind nitrogen and oxygen is evident in IV and V, this tendency is dramatically displayed in the reaction of I with acetonitrile



VIa **VIb** **VIc**

in which the shortest U(IV)–N bond yet recorded [22] is formed.

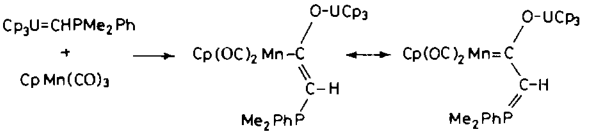
Uranium(IV) is a very electron deficient ion, and it has been pointed out [24] that organouranium compounds are sterically saturated but electronically unsaturated. As such uranium has a high affinity for small ligands with several available electron pairs. Oxygen ligands fall into this category, the well known affinity of uranium for oxygen is demonstrated in the structure of IV. The very short U–X bonds in I and VI also reflect the ability of U(IV),

TABLE II. Bond Distances (Å) in $Cp_3U(\eta^2\text{-}OC)CHPPh_2Me$, $Cp_3U[\eta^2\text{-}CN(C_6H_{11})]CHPPh_2Me$, and $Cp_3UNC(Me)CHPPh_2Me$.

	U–C(Cp)	U–O or U–N	U–C_α	C_α–C_β	C_α–O or C_α–N	C_β–P
$Cp_3U(\eta^2\text{-}OC)CHPPh_2Me$	2.81(3)	2.27(1)	2.37(2)	1.37(2)	1.27(3)	1.77(2)
$Cp_3U[(\eta^2\text{-}CN(C_6H_{11})]CHPPh_2Me$	2.83(3)	2.31(2)	2.44(3)	1.33(3)	1.39(4)	1.74(2)
$Cp_3UNC(Me)CHPPh_2Me$	2.81(3)	2.06(1)		1.39(2)		1.74(2)

and, presumably, other actinide ions to form multiple bonds with multiple electron pair donor ligands.

Not only does the uranium-carbon multiple bond in **I** react with small, polar unsaturated molecules, but also with coordinated carbon monoxide. We have observed [18] reactions between **I** and $CpMn(CO)_3$, $[CpFe(CO)_2]_2$, $Mo(CO)_6$, $CpCo(CO)_2$, $Ru_3(CO)_{12}$, and others. Most of these have proven to be complicated and are still under study. However, with $CpMn(CO)_3$ and $[CpFe(CO)_2]_2$ products are well characterized and illustrate some basic principles of this chemistry. At room temperature the following reaction takes place [25]



VIIa **VIIb**

in which a carbonyl group in $CpMn(CO)_3$ adds across the uranium-carbon bond in **I**. Two limiting resonance forms, **VIIa**, an enolate, and **VIIb**, a Fischer carbene complex, can be written to describe the bonding in this complex. The bond distances and angles are most consistent with **VIIa** or with a delocalized combination of the two.

The geometry about the uranium is normal. In accord with our observations [7, 8, 22] of multiple bond character in bonds between U(IV) and multiple electron pair donor atoms, the uranium–oxygen bond in **VII** appears to possess multiple bond character. The U–O distance is quite short, 2.13(1) Å, and the U–O–C angle is large, 160(1)°. Consistent with the tight bonding between oxygen and uranium, the C–O bond length has increased from the approximate 1.1 Å value seen in coordinated carbon monoxide to 1.37(4) Å.

The reaction can be viewed as an attack by the nucleophilic alpha carbon atom in **I** at the electrophilic carbon atom of a coordinated carbon monoxide, accompanied by the addition of **I** across the carbon–oxygen multiple bond. During this reaction the CO bond order decreases from 3 to less than 2 and uranium becomes tightly bonded to oxygen. Experiments with other metal carbonyls indicate this to be a general reaction of the uranium–carbon multiple bond which may provide a route by which coordinated carbon monoxide can be activated toward further reactions.

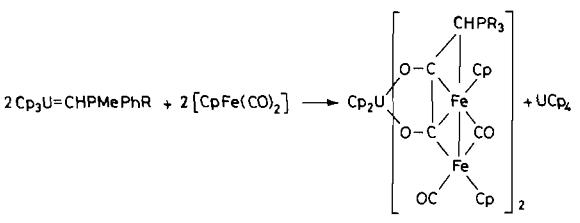
In fact, the carbon–oxygen bond in **VII** can be cleaved under fairly mild conditions [26]:

$$Cp(OC)_2MnC(OUCp_3)CHPMe_2Ph \longrightarrow Cp(OC)_2\overset{-}{Mn}\text{–}C{\equiv}C\overset{+}{P}Me_2Ph + Cp_3UOH$$

VIII

to form a complex, **VIII**, which contains a zwitterionic phosphonium acetylide ligand. The overall reaction is the deoxygenation of a terminal carbonyl to produce an acetylide complex. This clearly demonstrates that the attachment of an oxophilic uranium(IV) to a coordinated carbonyl oxygen can activate it toward C–O bond cleavage.

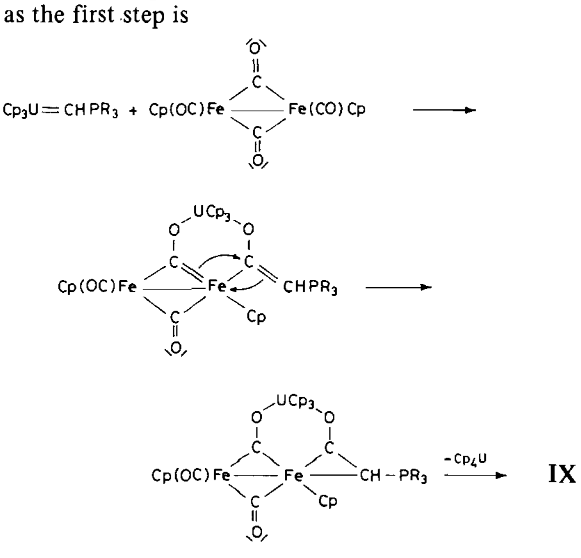
Addition of coordinated carbon monoxide across the U–C bond in **I** appears to occur frequently since peaks characteristic of a Metal–$C(OUCp_3){=}CHPR_3$ unit appear in NMR spectra taken during the reactions **I** with a variety of metal carbonyls [18]. While the more complex of these systems are still being studied an extension of this reaction pathway, found [27] in the case of $[CpFe(CO)_2]_2$, reveals that bridging carbonyls can also play an important role. In THF at room temperature



IX

In **IX** the ylid moiety, originally bonded to uranium in **I**, has become attached to a terminally coordinated CO and a second carbon–carbon bond has formed between this terminal CO and a bridging carbon monoxide. The new three carbon system is an allyl coordinated in a pi fashion to one iron atom and in a sigma fashion to the second.

While no detailed mechanistic information is available NMR peaks, which are characteristic of the addition of a terminal CO across the uranium–carbon bond in **I**, appear in the early stages of the reaction, and then disappear. A mechanism which involves this as the first step is



These reactions of **I** with metal carbonyls demonstrate its ability to activate coordinated carbon monoxide in several distinct fashions. Related systems are presently under study, but the initial results confirm that **I** can interact with a variety of unsaturated systems, and may presage the development of the actinoid-ylid complexes as reagents in synthetic chemistry.

Acknowledgement

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