Small Molecule Activation at the Uranium Carbon Multiple Bond*

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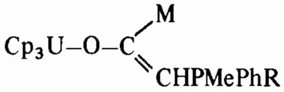
Abstract

One strategy for the activation of CO involves the formation of bimetallic compounds where one metal is bonded to a carbonyl carbon atom while the second coordinates oxygen. Insertion of CO, coordinated to transition metals, into the uranium–carbon multiple bond in $Cp_3U{=}CHPMeRPh$ produces such complexes.

$$M{-}CO + Cp_3U{=}CHPMePhR \longrightarrow$$



$$Cp_3U{-}O{-}C(M){=}CHPMePhR$$

The resulting phosphonium-metallaenolate complexes have been shown to undergo further reactions which include CO coupling to produce an allyl moiety, a novel isomerization, and carbon–oxygen bond cleavage to form phosphonium acetylide zwitterions.

Introduction

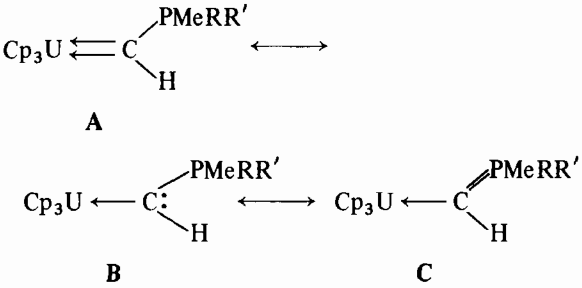
While transition metal–carbon multiple bonds are known to play key roles in catalytic processes, very little attention has been paid to catalysis or small molecule activation by f-element–carbon multiple bonds [1]. This probably reflects both the rarity of systems which contain actinide– or lanthanide–carbon multiple bonds and the overall nascent state of f-element catalysis.

Results and Discussion

The only well characterized f-element multiple bonds occur in $Cp_3U{=}CHPMeRR'$, **Ia**: $R = R' = Ph$; **Ib**: $R = Me$, $R' = Ph$; **Ic**: $R = R' = Me$, which we prepared [2] by the reaction:

$$Cp_3UCl + Li(CH_2)(CH_2)PPRR' \longrightarrow Cp_3U{=}CHPMeRR'$$

$Cp_3U{=}CHPMe_2Ph$ [3, 4] and $Cp_3U{=}CHPMe_3$ [5] have been structurally characterized and multiple bond character has been assigned to the uranium–carbon bond on the basis of the short metal–carbon bond distances, large M–C–P bond angles, and small $^{13}C{-}H$ coupling constants at the alpha carbon atom [3–5]. The assignment has been further supported by EHMO calculations on $Cp_3U{=}CHPH_3$, which show a large overlap population and a significant pi component to the uranium–carbon bond [6]. Consistent with a bonding model in which the $CHPR_3^-$ serves as a four electron donor, high quality *ab initio* MO calculations indicate that $CHPH_3^-$ is best formulated as a phosphonium-dicarbanion $[\ddot{:}CH{-}PH_3]^-$ [7]. Several resonance structures describe the metal carbon bond in **I** [4]:



Metal–carbon multiple bonding is emphasized by **A** while **B** and **C** reflect the ability of a ylidic phosphorus moiety to stabilize negative charge on an adjacent carbon atom [4].

The alpha carbon atom in $Cp_3U{=}CHPMeRR'$ is nucleophilic, as illustrated by some reactions with electrophiles and weak acids [8–10]:

$$Cp_3U{=}CHPMePhR + MeI \longrightarrow$$

$$\text{`}[Cp_3U{-}CH(Me){-}PMePhR]^+I^-\text{'} \longrightarrow Cp_3UI + \text{phosphonium salts}$$

$$Cp_3U{=}CHPMePh_2 + H{-}C{\equiv}C{-}Ph \longrightarrow Cp_3U{-}C{\equiv}C{-}Ph + CH_2PMePh_2$$

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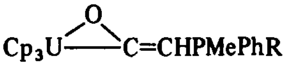
$$\mathrm{Cp_3U{=}CHPMePh_2 + HNPh_2 \longrightarrow Cp_3UNPh_2 + CH_2PMePh_2}$$

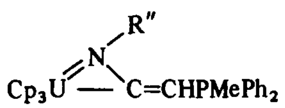
In this respect, I resembles the Schrock-type alkylidene complexes [11]. Since the alkylidenes are well known olefin metathesis catalysts [1,12], we examined the reactivity of I with unsaturated systems. With simple internal alkenes and alkynes no reactions are noted over long periods of time [8,9].

On the other hand, polar unsaturated molecules readily insert into the U=C bond [13–15]:

$$\mathrm{Cp_3U{=}CHPMePhR + CO \longrightarrow}$$



$$\mathrm{Cp_3U{=}CHPMePh_2 + R''NC \longrightarrow}$$



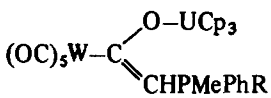
$$\mathrm{Cp_3U{=}CHPMePh_2 + MeCN \longrightarrow Cp_3U{\equiv}N{-}C(Me){=}CHPMePh_2}$$

Structures have been determined for each of these products and metrical parameters are consistent with the structures drawn above [13–15]. There are only a few other reports of insertion reactions involving metal carbon multiple bonds [11,16] and to our knowledge our results represent the first systematic investigation and the first structural characterization of products from the insertion of small molecules into any metal–carbon multiple bond. Notably, and in contrast to insertion reactions into metal–carbon single bonds which form carbon–carbon single bonds, the products of all of these reactions utilize all four electrons from the U=C bond to form carbon–carbon multiple bonds.

Because its organo-complexes are nearly always sterically crowded but electronically unsaturated, uranium has an affinity for small donor ligands [17]. As a consequence of the electron deficiency of the metal, ligands which can donate more than a single electron pair tend to form multiple bonds with uranium, often with a concomitant decrease in the order of other bonds within the ligand [15]. The formation of I, itself, demonstrates this tendency, as does the tight coordination of oxygen or nitrogen to the uranium in the insertion products mentioned above.

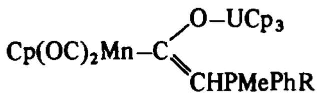
Reactions of I with coordinated carbon monoxide also reflect the features described in the previous paragraph. The prototypic reaction of a terminal carbonyl is illustrated in the following [18–20]:

$$\mathrm{Cp_3U{=}CHPMePhR + W(CO)_6 \longrightarrow}$$



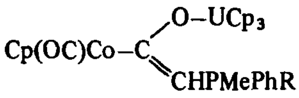
$$\mathrm{(OC)_5W{-}C(O{-}UCp_3){=}CHPMePhR}$$

$$\mathrm{Cp_3U{=}CHPMePhR + CpMn(CO)_3 \longrightarrow}$$



$$\mathrm{Cp(OC)_2Mn{-}C(O{-}UCp_3){=}CHPMePhR}$$

$$\mathrm{Cp_3U{=}CHPMePhR + CpCo(CO)_2 \longrightarrow}$$



$$\mathrm{Cp(OC)Co{-}C(O{-}UCp_3){=}CHPMePhR}$$

Metrical parameters for these three products are summarized in Table I. Within experimental uncertainty all of the $\mathrm{-C(OUCp_3)CHPMePhR}$ ligands are identical and can be formulated as phosphonium-metallaenolates. In each complex the uranium is tightly bonded to oxygen; correlations based on EHMO calculations indicate between a double and triple U–O bond [21]. As a consequence the C–O distance is considerably longer than the 1.15 Å typical of a terminal carbonyl.

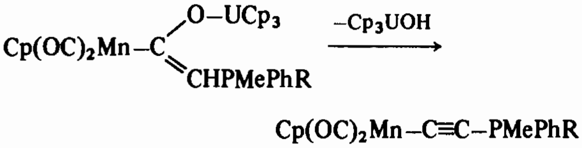
In a formal sense, the $\mathrm{M{-}C(OUCp_3){=}CHPMePhR}$ unit is an (O,C)-coordinated carbon monoxide which

TABLE I. Selected Bond Distances and Angles within $\mathrm{M{-}C(OUCp_3){=}CHPPhRMeR}$ Moieties[a]

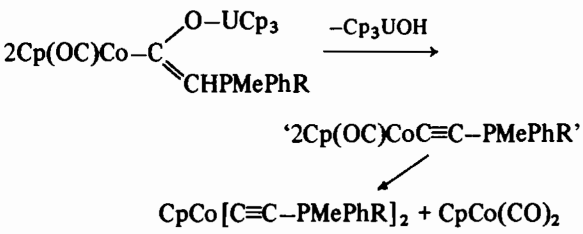
	M = $\mathrm{Cp(OC)_2Mn}$ R = Me [b]	M = $\mathrm{(OC)_5W}$ R = Ph [c]	M = $\mathrm{Cp(OC)Co}$ R = Me [d]
Distances (Å)			
U–O	2.14(2)	2.15(1)	2.11(2)
C–O	1.37(4)	1.33(3)	1.36(4)
C=C	1.41(5)	1.36(3)	1.36(4)
C–P	1.75(3)	1.79(2)	1.77(3)
M–C	2.00(4)	2.27(2)	1.87(3)
Angles (°)			
U–O–C	161(2)	158(1)	171(2)
M–C–O	113(2)	116(1)	111(3)
M–C–C	138(3)	134(2)	131(2)
O–C–C	110(3)	110(2)	117(2)
P–C–C	123(3)	128(2)	124(2)

[a] Average values given for the two independent molecules of $\mathrm{Cp(OC)_2Mn{-}C(OUCp_3){=}CHP(CH_3)_2(C_6H_5)}$ and $\mathrm{Cp(OC)Co{-}C(OUCp_3){=}CHP(CH_3)_2(C_6H_5)}$. [b] Taken from ref. 19. [c] Taken from ref. 18. [d] Taken from ref. 20.

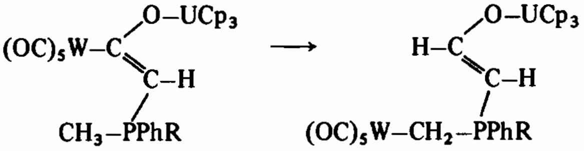
has been attacked by a four-electron donating nucleophile. From this perspective the M–C(OUCp$_3$)=CHPMePhR group represents an intermediate of CO activation. In fact, the compounds which contain this unit all undergo further reactions. In view of the strong U–O interaction, rupture of the C–O bond might be expected, and, in fact, occurs nearly quantitatively when Cp(OC)$_2$Mn–C(OUCp$_3$)=CHPMePhR is heated to about 90 °C [22]:



Similarly, a Co–C≡C–PMePhR moiety is formed when Cp(OC)Co–C(OUCp$_3$)=CHPMePhR is heated. However, rather than forming Cp(OC)CoC≡C–PMePhR, disproportionation occurs to produce CpCo[C≡C–PMePhR]$_2$ and CpCo(CO)$_2$ [20]:



This is not the only reaction of the M–C(OUCp$_3$)=CHPMePhR unit. Over about a year at room temperature (OC)$_5$W–C(OUCp$_3$)=CHPMePhR isomerizes nearly quantitatively [18]:



At about 90 °C C–O bond cleavage is also an important process and ^{1}H and ^{31}P NMR spectra indicate that Cp$_3$UOCH=CHP(Ph)(R)CH$_2$W(CO)$_5$ and (OC)$_5$W–C≡C–PMePhR form in nearly equal quantities [18, 20]. Some ^{31}P data, summarized in Table II, reveal that isomerization and phosphonium-acetylide formation are competing processes during the thermolysis of most of the complexes which contain a M–C(OUCp$_3$)=CHPMePhR unit. Based on the admittedly limited data in Table I, phosphonium-acetylide formation appears to predominate in derivatives of first transition series metals and is most favored when R = Ph.

To determine whether (OC)$_5$W dissociation occurs during the isomerization, reactions were run in the presence of PPh$_3$. As judged by NMR spectra [19], neither the rate of reaction nor the yield of the isomerization product was affected by the presence of phosphine, and, consequently, we feel that dissociation of the transition metal carbonyl fragment is unlikely during the reaction. The isomerization is accelerated with increased methyl substitution on phosphorus. In NMR spectra taken during the course of the isomerization at 90 °C the peaks due to

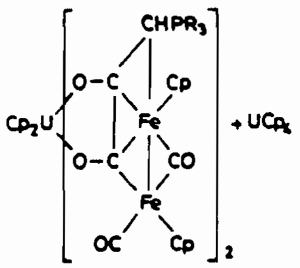
TABLE II. Some ^{31}P NMR Data for the Products of the 90 °C Thermolysis of M–C(OUCp$_3$)=CHPMeRPh Compounds

Compound thermalized		^{31}P Chemical shifts of products (ppm)	Intensity of ^{31}P resonance (%)	Assignment
M	R			
(OC)$_5$W	Me	23	10	(OC)$_5$W–C≡CMe$_2$Ph
		27	80	(OC)$_5$WCH$_2$PMePhCH=CHOUCp$_3$
		34	10	(OC)$_4$W[C≡CMe$_2$Ph]$_2$
(OC)$_5$Mo	Me	23	15	(OC)$_5$Mo–C≡CMe$_2$Ph
		27	70	(OC)$_5$MoCH$_2$PMePhCH=CHOUCp$_3$
		33	15	(OC)$_4$Mo[C≡CMe$_2$Ph]$_2$
(OC)$_5$Cr	Me	23	45	(OC)$_5$Cr–C≡CMe$_2$Ph
		27	20	(OC)$_5$CrCH$_2$PMePhCH=CHOUCp$_3$
		35	35	(OC)$_4$Cr[C≡CMe$_2$Ph]$_2$
(OC)$_5$W	Ph	23	50	(OC)$_5$W–C≡CMePh$_2$
		27	50	(OC)$_5$WCH$_2$PPh$_2$CH=CHOUCp$_3$
(OC)$_5$Cr	Ph	22	40	(OC)$_5$Cr–C≡CMePh$_2$
		35	60	(OC)$_4$Cr[C≡CMePh$_2$]$_2$
Cp(OC)$_2$Mn	Me	23	100	Cp(OC)$_2$Mn–C≡CPMe$_2$Ph
Cp(OC)Co	Me	34	100	CpCo[C≡CMePh$_2$]$_2$

$(OC)_5W{-}C(OUCp_3){=}CHPMePhR$ disappear in less than an hour and are replaced by a series of broad resonances which undergo complex changes to finally produce the characteristic spectrum of $Cp_3UOCH{=}CHP(Ph)(R)CH_2W(CO)_5$. While the mechanism is not yet well understood, the reaction is obviously complex and goes through several intermediates.

With bimetallic carbonyls the $M{-}C(OUCp_3){=}CHPMePhR$ unit can exhibit other behavior. The most interesting which we have uncovered to date [23] is the reaction of $[CpFe(CO)_2]_2$ with **I**:

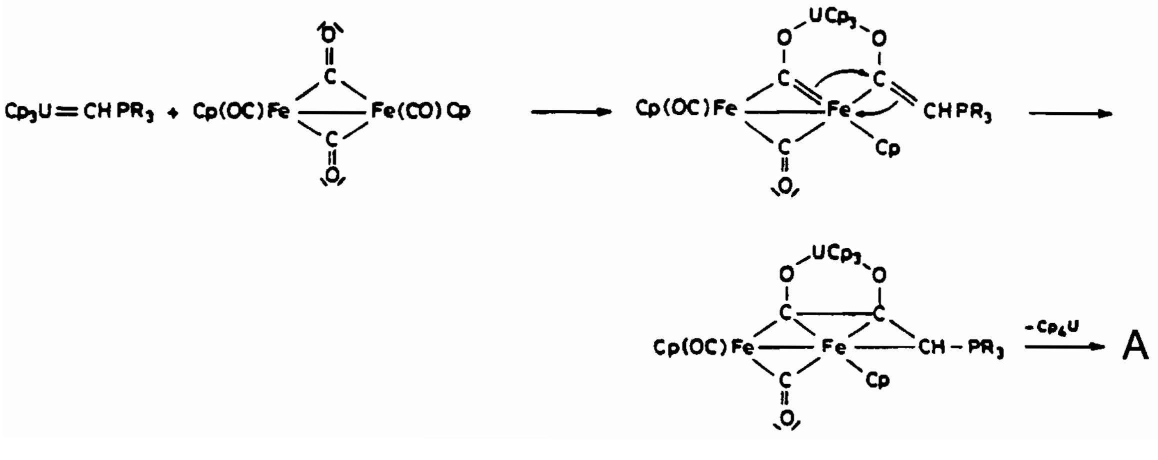
$$Cp_3U{=}CHPMePhR + [CpFe(CO)_2]_2 \longrightarrow$$



A

The complex, which forms in good yield, contains an allyl group which has been formed from a bridging and a terminal carbonyl originally present in $[CpFe(CO)_2]_2$ and a carbon atom from the ylide moiety of **I**. The allyl is pi bonded to one iron and sigma bonded to the other.

Shortly after $[CpFe(CO)_2]_2$ and **I** are mixed, peaks which are characteristic of the $M{-}C(OUCp_3){=}CHPMePhR$ unit appear in the NMR spectrum, but ultimately disappear as the reaction goes to completion [9]. Based on these data and analogies to known metallaacetylacetonate chemistry [24], we suggested the following reaction sequence.



In these reactions it is reasonable that the association of the oxophilic Cp_3U^+ to a carbonyl oxygen reduces carbon–oxygen bond order while the alpha carbon atom of **I** is able to utilize all four electrons from the U=C multiple bond to supply charge at electrophilic centers. As a consequence **I** and metal carbonyls produce uranium–transition metal complexes in which carbon monoxide has been activated with respect to C–O bond cleavage, isomerization and carbonyl coupling reactions.

In contrast to carbon–carbon single bond forming reactions of metal–carbon single bonds, these reactions result in the formation of new carbon–carbon multiple bonds. It is important to note this difference for it demonstrates that metal–carbon multiple bonds are potential synthons for carbon–carbon multiple bonds. With the exception of olefin metathesis [12] and a few other studies [25], this aspect of metal–carbon multiple bond chemistry is yet to be exploited.

Acknowledgements

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