Crystal and Molecular Structure of $(\eta^5\text{-}C_5H_5)_3U{=}CHP(CH_3)_2(C_6H_5)$. A Compound with a Uranium-Carbon Multiple Bond

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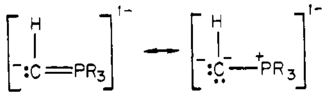
The structure of the complex $(\eta^5\text{-}C_5H_5)_3U{=}CHP(CH_3)_2(C_6H_5)$ has been determined by single-crystal X-ray methods. The compound crystallizes with four molecles in space group $P2_1/c$ of the monoclinic system in a cell with dimensions of a = 10.835 (2) Å, b = 8.481 (2) Å, c = 25.57 (1) Å, β = 111.77 (3)°, V = 2182 Å^3, and ρ_{calcd} = 1.78 g/cm^3. The structure has been refined by least-squares methods to a final R index on F of 0.071 for the 91 variables and 1985 data. The uranium is bound in a tetrahedral fashion to three cyclopentadienyl ligands and a $CHP(CH_3)_2(C_6H_5)$ ligand. The bond to the carbon atom of the phosphoylide ligand, 2.29 (3) Å, is the shortest U-C bond yet observed, and this is interpreted as indicating mutliple bonding in the U-C bond.

Introduction

Several compounds have been reported in which a phosphoylide is bound through a CHP linkage to a metal or metalloid atom. These include $(OC)_5MCHPR_3$ (M = Mn, Re),[1] $(CH_3)_3SiCHPR_3$,[2] $(CH_3)_3SbCHPR_3$,[3] $(\eta^5\text{-}C_5H_5)_2ClZrCHP(C_6H_5)_3$,[4] $(\eta^5\text{-}C_5H_5)_2ClZrCHP(CH_3)_3$,[5] $(\eta^5\text{-}C_5Me_5)ClTa(CHC_6H_5)(CHP(C_6H_5)_3)$,[6] $(\eta^5\text{-}C_5H_5)_2RZrCHP(CH_3)_3$ (R = $CH_2C(CH_3)_3$ and CH_3),[6] and $(\eta^5\text{-}C_5H_5)FeCHP(C_6H_5)_3$.[7] The closely related $(Ar)(OC)_2CrC(C_6H_5)P(CH_3)_3$ (Ar = C_6H_6, 1,4-$(CH_3)_2C_6H_4$, 1,3,5-$(CH_3)_3C_6H_3$),[8] $(\eta^5\text{-}C_5H_5)(OC)_2MC(C_6H_5)P(CH_3)_3$ (M = Mn, Re),[8,9] and $(\eta^5\text{-}C_5H_5)(OC)FeCRP(C_6H_5)_3$ (R = CH_3, $n\text{-}C_3H_7$)[7] are also known. Two resonance forms, A and B, can be written for the phosphoylide anions, which at least in a formal sense, are presesnt in each of the complexes.



A B

These indicate that more than one electron pair may be available for donation; consequently, these ligands may form multiple M-C bonds upon their coordination to metals. The structures of $(\eta^5\text{-}C_5H_5)_2ClZrCHP(C_6H_5)_3$ and $(\eta^5\text{-}C_5H_5)(OC)_2ReC(C_6H_5)P(CH_3)_3$ have been reported,[4,9] and we have published a preliminary account of the structure of $(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$,[10] hereafter $Cp_3U{=}CHPMe_2Ph$. In all three of these structures the bond between the metal ion and the carbon of the phosphoylide anion is short and is consistent with multiple bond character.[4,9,10] In this paper we report the details of the structure of $Cp_3U{=}CHPMe_2Ph$ and discuss the relationship between the metal $CHPR_3$ moiety and metal carbene complexes.

Table I. Summary of Crystal Data, Data Collection, and Refinement

space group	$P2_1/c$
a, Å	10.835 (2)
b, Å	8.481 (2)
c, Å	25.57 (1)
β, deg	111.77 (3)
V, Å^3	2182 (1)
Z	4
ρ(calcd), g/cm^3	1.78
abs grid	4 × 4 × 4
μ, cm^{-1}	71.31
transmissn coeff	0.2915-0.4457
cryst temp, °C	25
scan rate, deg/min	2-24
2θ range, deg	3.0-50.0
total no. of observns, m	4382
data with $I > 3\sigma(I)$	1985
P	0.02
R_1	0.071
R_w	0.078
goodness of fit	1.69
parameters	91
overdetermination ratio	21.8

Experimental Section

The complex $Cp_3U{=}CHPMe_2Ph$ was synthesized as previously described.[11] A dark green, orthorhombic-shaped crystal measuring 0.11 × 0.27 × 0.18 mm was inserted into a thin-walled glass capillary with Corning high vacuum grease as a lubricant and sealed under nitrogen.

A Syntex four-circle diffractometer with graphite-monochromatized Mo Kα radiation (Kα_1, λ = 0.709 30 Å, Kα_2, λ = 0.713 59 Å), and a scintillation counter with a pulse height analyzer was used for preliminary experiments and for the measurement of diffraction intensities. The cell constants and their standard deviations were determined by a least-squares treatment of the angular coordinates of 15 intense independent reflections with 2θ values between 4° and 23°. The space group was determined on the basis of systematic absences, l odd for $h0l$ and k odd for $0k0$ indicating the monoclinic space group $P2_1/c$.

Table I lists crystal data, data collection, and refinement parameters. The intensities of three check reflections, measured after every 100 reflections, did not vary beyond counting statistics. Standard deviations were assigned to the individual reflections according to the formula $\sigma(I) = [(\text{CT} + B_1 + B_2)\omega^2 + (pI)^2]^{1/2}$,

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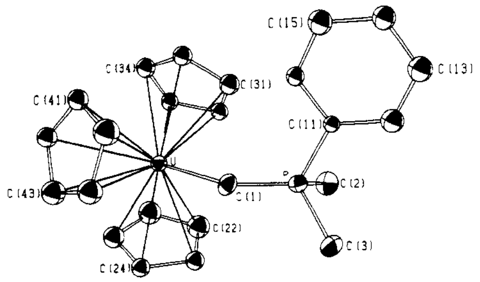

Figure 1. A labeled, perspective ORTEP view of (Cp)$_3$U=CHPMe$_2$Ph with 20% probability thermal ellipsoids. Hydrogen atoms are not shown.

where CT is the total integrated count, B_1 and B_2 are the background counts, and the intensity is $I = \omega(\mathrm{CT} - B_1 - B_2)$. To normalize for the variable scan rate, the counts are multiplied by the scan rate, ω. A value of 0.02 was assigned to the empirical parameter p to account for instrumental inaccuracies.[12] The weights (w) used in the least-squares refinement of the structural parameters were the reciprocal squares of $\sigma(F_o)$. Only intensities for which $F_o > 3\sigma(F_o)$ were used in subsequent calculations. The intensities were corrected for Lorentz and polarization effects.[13] Atomic scattering factors for U^0, P^0, O^0, C^0, and H^0 (bonded),[14] were used and anomalous dispersion corrections were included for the first three atoms.

The structure was solved by straightforward heavy-atom methods. The uranium atom was located from the Patterson function, and three cycles of Fourier synthesis revealed the positions of the remaining atoms. The details of an absorption correction that was applied to the data are set forth in Table I. Least-squares refinement[15] was carried out using a rigid-group model[16] for the cyclopentadienyl and phenyl groups. Bond distances in the cyclopentadienyl groups were fixed at 1.43 Å, and bond angles were set at 108° while for the phenyl group the corresponding parameters were set at 1.41 Å and 120°. Hydrogen atoms for the aromatic rings were placed in fixed, calculated positions with a C–H bond length of 0.95 Å. The hydrogen atoms of methyl group C(3) were located in a difference map and included at fixed positions. Hydrogen atom thermal parameters were fixed at the values reported in Table III.[17] Anisotropic thermal parameters were refined for U, P, C(1), C(2), and C(3) while isotropic thermal parameters were refined for the carbon atoms of the aromatic rings. When refinement was terminated, the maximum shift of any parameter was 13% of its estimated standard deviation.

A final electron density map with an estimated standard deviation of 0.306 e/Å^3 showed a maximum peak of 1.0 e/Å^3 near the cyclopentadienyl rings with the exception of ripples around the uranium with a maximum intensity of 2.0 e/Å^3.

The positional and thermal parameters from the last cycle of least-squares refinement have been published.[10] Group parameters appear in Table II.[17] The fixed positions of the hydrogen atoms are listed in Table III.[17] A listing of $10|F_o|$ vs. $10|F_c|$ is available as supplementary material. A view of the molecule as drawn by ORTEP is shown in Figure 1 while a stereoview of the contents of one unit cell is shown in Figure 2. Bond lengths and angles are summarized in Table IV.

Description of the Structure

The unit cell consists of four discrete molecules of Cp$_3$U=CHPMe$_2$Ph, as shown in Figure 2. Except for the interatomic contacts between C(16) and C(25) (x, 0.5 – y, 0.5 + z), 3.58 Å, and between C(11) and C(41) (–x, 0.5 + y, 0.5 – z), 3.63 Å, there are no nonbonded distances less than 3.7 Å, thus precluding any significant interaction between molecules.

The overall geometry (Cp)$_3$U=CHPMe$_2$Ph is not unlike those exhibited by other (Cp)$_3$UR species.[18-21] The co-

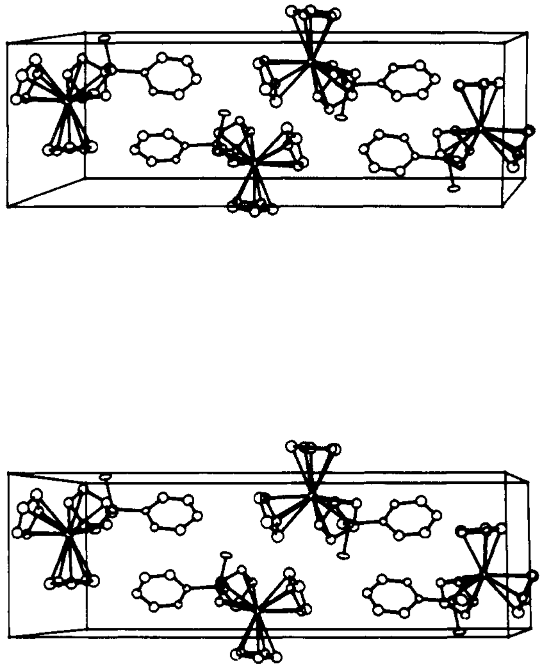

Figure 2. An ORTEP stereoview of the contents of the unit cell of (Cp)$_3$U=CHPMe$_2$Ph. The b axis is horizontal, the c axis is vertical, and the a axis extends upward out of the page. Thermal ellipsoids are 20% probability and hydrogen atoms are omitted.

Table IV. Bond Lengths (Å) and Selected Bond Angles (deg) for (Cp)$_3$U=CHPMe$_2$Ph

Bond Distances

U-C(1)	2.29 (3)	U-C(42)	2.84 (3)
U-C(21)	2.78 (3)	U-C(43)	2.84 (3)
U-C(22)	2.82 (2)	U-C(44)	2.82 (4)
U-C(23)	2.82 (2)	U-C(45)	2.80 (2)
U-C(24)	2.78 (2)	P-C(1)	1.69 (3)
U-C(25)	2.76 (2)	P-C(2)	1.83 (3)
U-C(31)	2.77 (2)	P-C(3)	1.83 (3)
U-C(32)	2.75 (2)	P-C(11)	1.80 (2)
U-C(33)	2.76 (2)	U-Cp(1)[a]	2.51 (2)
U-C(34)	2.78 (2)	U-Cp(2)[a]	2.49 (2)
U-C(35)	2.79 (2)	U-Cp(3)[a]	2.55 (3)
U-C(41)	2.81 (4)		

Bond Angles

U-C(1)-P	142 (1)		
C(1)-P-C(2)	114 (1)	C(1)-U-Cp(1)[a]	102 (1)
C(1)-P-C(3)	114 (1)	C(1)-U-Cp(2)[a]	105 (1)
C(2)-P-C(3)	104 (1)	C(1)-U-Cp(3)[a]	98 (1)
C(1)-P-C(11)	116 (1)	Cp(1)-U-Cp(2)[a]	115 (1)
C(2)-P-C(11)	104 (1)	Cp(1)-U-Cp(3)[a]	117 (1)
C(3)-P-C(11)	103 (1)	Cp(2)-U-Cp(3)[a]	116 (1)

[a] Cp(1) = Cp ring C(21)-C(25), Cp(2) = Cp ring C(31)-C(35), and Cp(3) = Cp ring C(41)-C(45). The distances are between the uranium atom and the cyclopentadienyl ring centroids.

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(17) Supplementary Material: Table II, parameters for the rigid groups of (Cp)$_3$U=CHPMe$_2$Ph, Table III, derived parameters for the rigid-group atoms, Table V, short nonbonded intramolecular contacts, and Table VII, listing of $10|F_o|$ vs. $10|F_c|$.

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Table VI. Uranium-Carbon Bond Distances in Organouranium Complexes (Å)

compd	U-C(σ)	ref
$(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$	2.29 (3)	this work
$(\eta^5\text{-}C_5H_5)_3U(OCCH)P(CH_3)(C_6H_5)_2$	2.37 (2)	36
$(\eta^5\text{-}C_5H_5)_3U(n\text{-}C_4H_9)$	2.43 (2)	19
$(\eta^5\text{-}C_5H_5)_3U(p\text{-}CH_3C_6H_4CH_2)$	2.54 (2)	19
$(\eta^5\text{-}C_5H_5)_3U[(CH_2)_2C(CH_3)]$	2.48 (3)	21
$(\eta^5\text{-}C_5H_5)_3UC{\equiv}CH$	2.36 (3)	20
$(\eta^5\text{-}C_5H_5)_3UC{\equiv}CC_6H_5$	2.33 (2)	18
$[\mu\text{-}CH(CH_2)P(C_6H_5)_2U(\eta^5\text{-}C_5H_5)_2]_2$	2.43 (1) 2.53 (2) 2.66 (3)	23
$(\eta^5\text{-}C_5H_5)U[(CH_2)(CH_2)P(C_6H_5)_2]_3$	2.66 (3)	24

ordination sphere about the uranium atom is roughly tetrahedral with three π-bonded η^5-cyclopentadienyl (Cp) ligands and a η^1-bonded $CHPMe_2Ph$ moiety giving approximate C_{3v} geometry. The average (center of ring)–U–(center of ring) angle of 116 (1)° is comparable to 117 (2)° reported for $(Cp)_3UC{\equiv}CC_6H_5$[18] and $(Cp)_3UCH_2C(CH_3)CH_2$[21] and 118 (3)° for $(Cp)_3UC{\equiv}CH$,[20] $(Cp)_3U(n\text{-}C_4H_9)$,[19] and $(Cp)_3UCH_2C_6H_4(p\text{-}CH_3)$.[19] The average C(1)–U–(center of ring) angle of 102 (3)° agrees reasonably well with those of other $(Cp)_3UR$ molecules, i.e., 100 (3)° for $(Cp)_3UC{\equiv}CC_6H_5$,[18] $(Cp)_3UCH_2C(CH_3)CH_2$,[21] $(Cp)_3U(n\text{-}C_4H_9)$,[19] and $(Cp)_3UCH_2C_6H_4(p\text{-}CH_3)$[19] and 98 (1)° for $(Cp)_3UC{\equiv}CH$.[20] This distortion from idealized tetrahedral geometry probably reflects the large size of the Cp ligands. A further indication of the bulk of the Cp groups is seen in the C(1)–P–C(2), C(1)–P–C(3), and C(1)–P–C(11) angles of 114 (1)°, 114 (1)°, and 117 (1)°, respectively, and the C(2)–P–C(3), C(2)–P–C(11), and C(3)–P–C(11) angles of 104 (1)°, 104 (1)°, and 103 (1)°, respectively. Here, the methyl and the phenyl groups are bent away from the area around the uranium atom apparently to relieve congestion. Steric crowding is also apparent in the numerous intramolecular contacts that are shorter than van der Waals (Table V).[17]

The U–C distances to the Cp rings range from 2.75 (2) Å for C(32) to 2.84 (4) Å for C(42) and C(43). The average values of the uranium–carbon distances for the three Cp rings are 2.79 (3) Å for Cp(1), 2.77 (2) Å for Cp(2), and 2.82 (2) Å for Cp(3). These are similar to those found for $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(Cp)_2]_2$ (2.78 (1) Å)[22,23] and $CpU[(CH_2)(CH_2)P(C_6H_5)_2]_3$ (2.79 (1) Å)[24] but are longer than the average U–C(Cp) bond distances in tricyclopentadienyluranium systems.[25] This is again consistent with a crowded molecule.

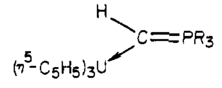
The most interesting feature of this structure is the U–C(1) bond whose length, 2.29 (3) Å, is shorter than any uranium–carbon bond yet reported (Table VI). In particular the U–C(1) bond is some 8σ shorter than the U–C σ bond in $(Cp)_3UCH_2C_6H_4(p\text{-}CH_3)$,[19] some 6$\sigma$ shorter than the similar bond in $(Cp)_3UCH_2C(CH_3)CH_2$[21] and more than 4σ shorter than that found in $(Cp)_3U(n\text{-}C_4H_9)$.[19] One may note that in all cases we have compared the U–C bond of $Cp_3U{=}CHPMe_2Ph$ in which the carbon is sp^2 hybridized to compounds in which the uranium is bonded to sp^3 carbons. Since sp^2 carbons are expected to form bonds about 0.03 Å shorter than those to sp^3 carbons,[26] it is necessary to apply this correction, which amounts to about 1σ. Even after correction the U–C(1) bond is significantly shorter than any known uranium–alkyl bond.

The shortest previously observed uranium–carbon bonds are those in $(Cp)_3UC{\equiv}CH$[20] and $(Cp)_3UC{\equiv}CC_6H_5$.[18] These bonds are only 2σ and 1σ, respectively, longer than the U–C(1) bond. However in these acetylides the carbon bound to the uranium is sp hybridized. Such a bond is expected to be 0.05 Å shorter than a bond to an sp^2 carbon.[26] Upon application of this correction, the U–C(1) bond is 4σ and 3σ shorter than the corresponding bonds in the acetylides.

The coordination about the phosphorus atom is roughly tetrahedral, as seen from the C–P–C bond angles. This is characteristic of phoshorus ylide ligands and has been observed in several transition-metal phosphoylide complexes.[4,8,24,27] The P–C(methyl) bond lengths, P–C(2) and P–C(3), are both 1.83 (3) Å and compare reasonably well to the P–C(methyl) bond lengths observed for $\mu\text{-}[(CH_2)(CH_2)P(CH_3)_2]_2Ni_2[(CH_2)(CH_2)P(CH_3)_2]_2$, 1.823 (4) Å for the bridging ylide and 1.816 (4) Å for the chelating ylide.[10] The P–C(phenyl) bond distance of 1.80 (2) Å is similar to those observed[22,23] for $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(Cp)_2]_2$ (1.83 (1) Å) and in typical ylide systems[27] as well as in phoshonium ions.[28] The P–C(1) (methine) bond length is 1.69 (3) Å, comparable to the P–C(methine) bond length of 1.74 (1) Å reported for $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(Cp)_2]_2$,[22] and is in the range of that found for the P=C bonds (1.64–1.74 Å) reported for several free ylides.[29]

Discussion

The Relationship of $Cp_3U{=}CHPMe_2Ph$ to Other Metal–Carbon Multiply Bonded Species. The important feature of this molecule is the nature of the U–C(1) bond. As discussed above the U–C(1) bond is significantly shorter than those observed for other uranium alkyls, which suggests multiple-bond character. Such multiple bonding can be rationalized after noting the contributing resonance forms of the free ylide anion, A and B. In resonance form B the carbon atom carries two pairs of electrons and has a double negative charge. Upon coordination to the electron-deficient $(Cp)_3U^+$ moiety, the resonance structures C–E may be written. A hybrid of these structures is F and accounts for the abnormally short uranium–C(1) bond. Furthermore, the metal atom acquires a formal partial negative charge that is consistent with the observed lengthening of the uranium–carbon (Cp) bond distances (vide supra).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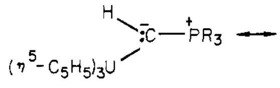
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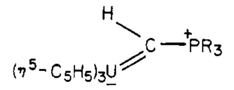
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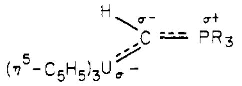
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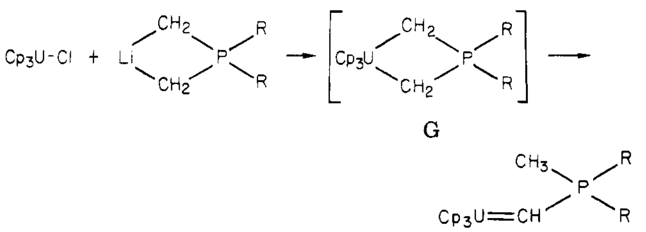
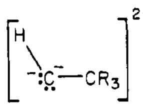
Scheme I



The concept of a multiple bond in $Cp_3U{=}CHPMe_2Ph$ is supported by extended Hückel molecular orbital calculations, which were performed on both Cp_3UCH_3 and $Cp_3U{=}CHPH_3$ using U–C bond lengths of 2.40 Å for both compounds.[30] The overlap population in the U–C(methyl) bond was 0.3967 while for the U–C bond in the phosphoylide complex the overlap population was calculated to be 0.5666. When the calculation was repeated at the observed U–C distance of 2.29 Å, the overlap population rose to 0.613 with a π-overlap population of 0.186. These overlap populations strongly support the notion of a uranium–carbon multiple bond in $Cp_3U{=}CHPMe_2Ph$.

A resonance form similar to B can describe the alkylidene ligand in the complexes reported by Schrock[31]



and suggests similarities between complexes of $CHPR_3{}^{1-}$ and $CHCR_3{}^{2-}$. The criteria, outlined by Schrock, which determine the formation of an alkylidene complex, are as follows.[32] (1) The complex must contain an electron-poor metal ion in a high oxidation state. (2) The complex must be sterically very crowded. (3) The precursor molecule, from which the alkylidene complex forms, must contain cis-alkyl groups. One of these alkyl groups is deprotonated by an α hydrogen transfer producing a metal bonded alkylidene ligand and free alkane. $Cp_3U{=}CHPMe_2Ph$, a sterically c rowded complex of U(IV), satisfies criteria 1 and 2 and a probable route to its formation can be postulated by using 3. Initial reaction could logically produce G of Scheme I, from which $Cp_3U{=}CHPMe_2Ph$ would form by an α-hydrogen transfer similar to those postulated by Schrock. One difference is that instead of producing a free alkane, a methyl group bound to phosphorus is produced in Scheme I.

Further structural and chemical similarities exist between $Cp_3U{=}CHPR_3$ and Schrock's alkylidene complexes. The large U–C(1)–P angle in $Cp_3U{=}CHPMe_2Ph$ is similar to the M–C–C angles in several of the alkylidenes.[33] As in Schrock's compounds, the α carbon in $Cp_3U{=}CHPR_3$ is a good nucleophile. Phosphonium salts and Cp_3UI result from its reaction with CH_3I,[34] and even with CF_2Cl_2, Cp_3UCl is produced.[35] A further similarity is the rich insertion chemistry of the uranium–carbon double bond. We have determined the structures of compounds that form from the insertion of CO,[36] $C_6H_{11}NC$,[37] CH_3CN,[35] and $[CpFe(CO)_2]_2$[38] into this bond. However, unlike complexes containing transition-metal–carbon double bonds,[31] $Cp_3U{=}CHPR_3$ does not react with simple alkenes[34] or alkynes.[34,35]

Although analogies can be drawn with the alkylidene complexes, $Cp_3U{=}CHPR_3$ 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 a heteroatom-stabilized, electron-deficient ligand and an electron-rich metal. These complexes are 18-electron species involving group 6–8 transition metals in 0 or +1 oxidation states, and 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., $(OC)_5WC(C_6H_5)_2$, 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 type usually contain a group 5 or 6 transition metal in which there is a good match in energy and size between appropriate metal and carbon σ and π 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 $Cp_3U{=}CHPR_3$ is of a third class in which an electron-*withdrawing* heteroatom substituent stabilizes a negative charge on the α carbon. 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. At present $Cp_2ClZr{=}CHPR_3$[4] and $Cp_3U{=}CHPR_3$ are the only structurally well-characterized members of this group. In contrast to the alkylidene and Fischer carbene complexes, this third class of compounds has received almost no attention.

Are There Other Uranium–Carbon Multiple Bonds? As mentioned in the results section, if hybridization differences are ignored, the U–C bonds in the acetylides $Cp_3UC{\equiv}CH$ and $Cp_3UC{\equiv}CPh$ are of similar length to the one in $Cp_3U{=}CHPMe_2Ph$. It has been suggested[21] that these bond distances reflect multiple metal–carbon bonding that can be rationalized by

$$\underset{\text{H}}{U^{-}{=}C^{+}{=}C{-}R} \leftrightarrow \underset{\text{I}}{U{-}C{\equiv}C{-}R}$$

In terms of H and I, U–C multiple bonding should be accompanied by a decrease in C–C bond order. Unfortunately the precision with which the acetylenic carbon atoms have been located in these structures[18,20] is too low

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(30) Tatsumi, K., Osaka University, private communication.

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(34) Cramer, R. E.; Gilje, J. W.; Higa, K. T., unpublished observations.

(35) Cramer, R. E.; Gilje, J. W.; Panchanatheswaran, K., unpublished observations.

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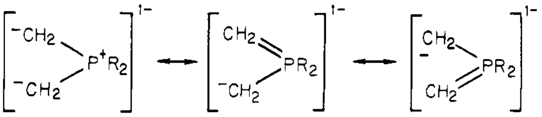
(38) Gilje, J. W.; Cramer, R. E.; Higa, K. T.; Pruskin, S. L. "Absatracts of Papers", 184th National Meeting of the American Chemical Society, Kansas City, Sept 1982; American Chemical Society, Washington, DC, 1982; INOR 216.

to permit a determination of whether lenghening of the C≡C bond occurs.

The idea of a multiple bond in $Cp_3UC{\equiv}CR$ is supported by the extended Hückel calculations of Tatsumi.[30] The calculated overlap population in this species is 0.5958, much higher than in the methyl compound and even a little higher than in $Cp_3U{=}CHPH_3$. In view of these structural and computational results, it will be interesting to see whether the uranium aceylides display any reactivity characteristic of metal–carbon multiple bonding.

The Nature of the Uranium–Carbon Bond. Structures of a number of Cp_3U–R complexes have been determined; U–C(R) bond distances in these compounds plus data for two ylide complexes are summarized in Table VI. Obviously uranium–carbon distances show a wide variation. The 0.37-Å range spanned by the compounds in Table VI corresponds to 8.7 σ and is, thus, statistically highly significant. At least qualitatively this variation can be inversely correlated with the formal negative charge on the carbon atom bound to uranium.

Comparing the ligands $[{<}C^-H{-}^+PR_3]^- \leftrightarrow [CH{=}PR_3]^{1-}$, $[CH_2CH_2CH_2CH_3]^{1-}$ and



the highest negative charge on the metal-bound carbon atom should occur in complexes of $[CHPR_3]^-$ and the smallest in those of $[(CH_2)(CH_2)PR_2]^-$, with $[C_4H_9]^-$ being intermediate. Correspondingly, the shortest U–C distance is found in $Cp_3U{=}CHPMe_2Ph$ and the longest in $CpU[(CH_2)(CH_2)PPh_2]_3$, with a middle value in $Cp_3U{-}C_4H_9$. Within the Cp_3U–R series, both 2-methylallyl and *p*-methylbenzyl ligands possess resonance structures that can delocalize negative charge from the carbon atom that binds to the metal, and their uranium carbon distances exceed the one in the *n*-butyl derivative.

Such a correlation of bond length with α-carbon charge is also consistent with another observation. We have attempted to prepare complexes in which a free ylide, rather than an anion, is bound to uranium. Thus in the reaction of Cp_3UCl and $H_2C{=}PPh_3$ we observe a color change indicating product formation. However, the product is very unstable and we have been unable to characterize it. In this neutral ylide, charge on the α-carbon would be less than in $[(CH_2)(CH_2)PPh_2]^-$ and the uranium–carbon bond should be even longer than the very long ones in $CpU[(CH_2)(CH_2)PPh_2]_3$. Presumably, this bond should be weak, probably leading to a marginally stable complex.

The variation in uranium–carbon distances with the negative charge on the α-carbon is consistent with an ionic component of the uranium carbon bond: as the charge on the carbon increases, electrostatic attraction increases and the bond shortens. In our view this correlation provides strong evidence that the uranium–carbon bond has an important ionic component.

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Registry No. $Cp_3U{=}CHPMe_2Ph$, 86584-33-0.

Supplementary Material Available: Table II, parameters for the rigid groups of $(Cp_3)U{=}CHPMe_2Ph$, Table III, derived parameters for the rigid group atoms, Table V, short nonbonded intramolecular contacts, and Table VII, listing of $10|F_o|$ vs. $10|F_c|$ (11 pages). Ordering information is given on any current masthead page.

A New Type of Triangular Tritungsten Cluster Compound from Reaction of 3-Hexyne with Hexa-*tert*-butoxyditungsten

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The reaction of $W_2(O\text{-}t\text{-}Bu)_6$ with EtC≡CEt at 75–80 °C for about 3 days affords moderate yields of a remarkable hexanuclear product, $[W_3(OCMe_3)_5(\mu\text{-}O)(\mu\text{-}CEt)O]_2$. The molecule consists of two trinuclear subunits joined by a pair of bridging oxygen atoms and related by a crystallographic center of inversion. In each moiety there is an isosceles triangle of W atoms (W–W distances: 2.420 (1), 2.895 (1), 2.899 (1) Å). One long edge is bridged by an EtC group and the other by an oxygen atom. The short W–W bond is not bridged. There are only six electrons available for metal–metal bonding within the W_3 moiety, and it is suggested that these may best be allocated to provide one double bond and a three-center–two-electron bond. The compound forms monoclinic crystals in space group $P2_1/n$ with unit-cell dimensions of a = 12.600 (3) Å, b = 14.415 (5) Å, c = 18.223 (4) Å, β = 97.02 (2)°, V = 3285 (3) Å^3, and Z = 2. The structure was refined to discrepancy indices of R = 0.0366 and R_w = 0.0448.

Introduction

Reactions between ditungsten hexaalkoxides and acetylenes have led to a remarkable variety of products, depending on the nature of the alkoxide, the acetylene, and the reaction conditions. The general case, which applies to most of the sterically nondemanding alkoxides, was extensively probed by Chisholm's group, yielding 1:1 adducts in an oxidative addition reaction.[1] Reactions of