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Bond dissociation enthalpies of U(IV) complexes. An integrated view

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Dedicated to Professor A.R. Dias on the occasion of his 60th birthday

Abstract

A brief overview of the bond dissociation enthalpies in U(IV) organometallic compounds published earlier is made. Some new results of the bond dissociation enthalpies on U(IV) compounds (kJ mol^{-1}), D(U–I) = 260 ± 11, D(U–O) = 307 ± 13, D(U–Cl) = 369 ± 14 and D(U–Cl) = 341 ± 19, are presented and used to discuss the literature data critically. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Bond dissociation enthalpy; Uranium compounds

1. Introduction

Metal–ligand bond energy data provide an unique insight into the reaction pathways of organometallic chemical transformations. Therefore, knowledge of the energetics of metal–ligand bonds is essential in understanding the chemical reactivity. For the past three decades, a major effort has been focused on determining the energetics of organometallic compounds from the first-row transition metals to lanthanide and to actinide elements [1–19].

Previous thermochemical studies involving uranium(IV) organometallic compounds gave a large number of uranium–ligand bond dissociation enthalpies, D(U–L) (Table 1). The values displayed in that table are based on solution alcoholytic or iodolytic titration calorimetric studies, static bomb-combustion calorimetry, and gas phase and solution equilibrium experiments [4–19]. Despite the amount of data and their good quality, there exist some apparent discrepancies. As an example, the U–Me bond enthalpies can be considered. The six values (kJ mol^{-1}) reported are 300 ± 11 [4], 312 ± 8 [4], 317 ± 6 [4], 185 ± 2 [5], 195 ± 5 [8], and 187 ± 6 [8,9]. The data fall into two distinct groups. We note that two different research groups obtained the values from six different compounds. In Ref. [5] Marks and co-workers state that the origin of the disparity 'resides in several difficult quantifiable steric and electronic factors', but the steric repulsion is thought to be more important. However, there is a common feature between the results in each group. The first three values are anchored on an estimate of the U–O bond dissociation enthalpy [4], while the remaining three are based on experiments involving oxidative addition to U(III) organometallic compounds and the estimate of the U–I bond enthalpy. Marks and co-workers has already commented on the potential problems associated with the transferability of M–OR bond enthalpy data and suggested that halogen is a more reliable anchor ligand.

Here we wish to provide more data, access this problem critically and suggest an integrated bond dissociation enthalpy scale for uranium(IV) compounds.

2. Results and discussion

The reactions examined in this work (Eqs. (1)–(4)) (Tp^{Me_2} = $HB(3,5\text{-}Me_2Pz)_3$; Pz = pyrazolyl; $C_5H_{11}Cl$ = 1-chloropentane) were found to be rapid and quantitative (see Section 3).

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Table 1
Bond dissociation enthalpies in U(IV) compounds [a]

Compound	L	D(U–L) (kJ mol^{-1})	Reference
U(η^5-C$_5$Me$_5$)$_2$L$_2$	Me	300 ± 11 [b,c]	[4]
	CH$_2$Ph	244 ± 8 [b,c]	[4]
	CH$_2$SiMe$_3$	307 ± 8 [b,c]	[4]
U(η^5-C$_5$Me$_5$)$_2$Cl(L)	Me	312 ± 8 [c]	[4]
	CH$_2$Ph	263 ± 12 [c]	[4]
	Ph	358 ± 11 [c]	[4]
U(η^5-C$_5$Me$_5$)$_2$(OSi^{t}BuMe$_2$)(L)	Me	317 ± 6 [c]	[4]
	H	342 ± 5 [c]	[4]
U{η^5-C$_5$H$_4$(SiMe$_3$)}$_3$L	Me	185 ± 2	[5]
	Bu	152 ± 8	[5]
	CH$_2$SiMe$_3$	168 ± 8	[5]
	CH$_2$Ph	149 ± 8	[5]
	CHCH$_2$	223 ± 10	[5]
	C≡CPh	363	[5]
	I	262 ± 1	[5]
		265.6 ± 4.3	[6]
	SEt	266 ± 9	[7]
	S^{t}Bu	158 ± 8	[7]
	H	253.7 ± 5.1	[6]
U(η^5-C$_5$H$_4^t$Bu)$_3$L	H	251.6 ± 5.7	[6]
	I	246.3 ± 5.3	[6]
	SEt	252 ± 8	[7]
U(C$_9$H$_7$)$_3$L	Me	195 ± 5	[8]
	OCH$_2$CF$_3$	301 ± 9	[8,9]
	I	267 ± 3	[8]
U(C$_9$H$_6$Et)$_3$L	Me	187 ± 6	[8,9]
U(C$_9$H$_6$SiMe$_3$)$_3$L	SEt	158 ± 8	[7]
U(η^5-C$_5$H$_5$)$_3$L	SiPh$_3$	156 ± 18	[10]
	GePh$_3$	163 ± 19	[10]
	SnPh$_3$	156 ± 17	[10]
	Fe(CO)$_2$(cp)	129 ± 13	[10]
	Ru(CO)$_2$(cp)	169 ± 17	[10]
	Cp	299 ± 10 [b,d]	[11]
	Bu^i	D[(cp)$_3$U-cp] −(70 ± 35) [d,e]	[12]
	OBu	D[(cp)$_3$U-cp] +(247 ± 28) [d,e]	[12]
	Cl	D[(cp)$_3$U-cp] +(73 ± 31) [d,e]	[12]
UL$_2$	C$_8$H$_8$	344 ± 7 [b,d]	[11]
		442 ± 16 [b,d]	[13]
		190 ± 27 [f,g]	[14]
	C$_8$H$_7$Bu	417 ± 13 [b,d]	[15]
UL$_4$	MeCO$_2$	517 ± 7 [b,d,h]	[16]
	Cl	422.6 [g]	[17]
UCl$_2$L(Tp^{Me_2})$_3$	CH(SiMe$_3$)$_2$	295 ± 11 [i]	[18]
	Cp	362 ± 12 [i]	[18]
	O^{t}Bu	460.5 ± 5.0 [i]	[18]
	OCMe$_2$CH$_2$COMe	484.2 ± 8.6 [i]	[19]
	N(SiMe$_3$)$_2$	334 ± 10 [i]	[18]
	(3,5-Me$_2$pz)	393 ± 16 [i]	[19]
UCl$_3$L(Tp^{Me_2})$_3$·thf	Thf	21.5 ± 2.9	[19]

[a] Determined using reaction-solution calorimetry unless otherwise indicated.

[b] Mean bond-dissociation enthalpy.

[c] Relies on $D(\text{U–O}) = 481$ kJ mol^{-1}.

[d] Static bomb combustion calorimetry.

[e] This notation mean that the bond is the stated amount stronger or weaker than the first bond dissociation enthalpy in U(cp)$_4$.

[f] D_1(U–C$_8$H$_8$).

[g] Gas-phase equilibrium.

[h] Obtained using the estimate $\Delta_{sub}H = 130 \pm 20$ kJ mol^{-1}, together with $\Delta_f H° = -2493 \pm 5$ kJ mol^{-1} [12] and auxiliary data.

[i] Based on $D(\text{U–Cl}) = 422.6$ kJ mol^{-1}.

$$\underset{\mathbf{1}}{\mathrm{UTp^{Me_2}I_2{\cdot}thf_2}}\,(\mathrm{cr}) + \tfrac{1}{2}\mathrm{I_2}\,(\mathrm{soln}) \rightarrow \underset{\mathbf{2}}{\mathrm{UTp_2^{Me_2}I_3}}\,(\mathrm{soln}) + 2\mathrm{thf}\,(\mathrm{soln}) \tag{1}$$

$$\mathrm{UTp^{Me_2}I_2{\cdot}thf_2}\,(\mathrm{cr}) + \tfrac{1}{2}{}^t\mathrm{BuO\text{–}O\text{–}}{}^t\mathrm{Bu}\,(\mathrm{soln}) \rightarrow \underset{\mathbf{3}}{\mathrm{UTp^{Me_2}I_2(O\text{–}{}^tBu)}}\,(\mathrm{soln}) + 2\mathrm{thf}\,(\mathrm{soln}) \tag{2}$$

$$\mathrm{UTp^{Me_2}I_2{\cdot}thf_2}\,(\mathrm{cr}) + \mathrm{C_5H_{11}Cl}\,(\mathrm{soln}) \rightarrow \underset{\mathbf{4}}{\mathrm{UTp^{Me_2}I_2(Cl)}}\,(\mathrm{soln}) + \tfrac{1}{2}\underset{\mathbf{5}}{\mathrm{(C_5H_{11})_2}}\,(\mathrm{soln}) + 2\mathrm{thf}\,(\mathrm{soln}) \tag{3}$$

$$\mathrm{UTp^{Me_2}I_2{\cdot}thf_2}\,(\mathrm{cr}) + \tfrac{3}{2}\mathrm{Cl_2}\,(\mathrm{soln}) \rightarrow \underset{\mathbf{6}}{\mathrm{UTp^{Me_2}Cl_3}}\,(\mathrm{soln}) + \mathrm{I_2}\,(\mathrm{soln}) + 2\mathrm{thf}\,(\mathrm{soln}) \tag{4}$$

Reactions (1)–(4) lead to Eqs. (5)–(8), where $\Delta_{\mathrm{soln}}H$ is the dissolution enthalpy of $\mathrm{UTp^{Me_2}I_2{\cdot}thf_2}$ and $D(\mathrm{X–Y})$ is the bond dissociation enthalpy for the X–Y bond. The value of $\Delta_{\mathrm{soln}}H$ was not measured but can be estimated as -4 ± 1 kJ mol^{-1}, based on similar uranium compounds [18]. Eqs. (5)–(7) were deduced easily as shown for Eq. (5) (Scheme 1). For the deduction of Eq. (8), Scheme 2 was used. According to the scheme, three $D(\mathrm{U–Cl})$ and two different $D(\mathrm{U–I})$ should be considered, but experimental results (see e.g. [4]) indicate that the values can be assumed to be equal, leading to Eq. (8) (in Eqs. (5)–(8) $D(\mathrm{U–L})$ is used instead of $D_1(\mathrm{U–L})$ for simplicity).

$$D(\mathrm{U–I}) - 2D(\mathrm{U–thf}) = -\Delta_r H(1) + \tfrac{1}{2}D(\mathrm{I–I}) + \Delta_{\mathrm{soln}}H \tag{5}$$

$$D(\mathrm{U–O}) - 2D(\mathrm{U–thf}) = -\Delta_r H(2) + \tfrac{1}{2}D(\mathrm{O–O}) + \Delta_{\mathrm{soln}}H \tag{6}$$

$$D(\mathrm{U–Cl}) - 2D(\mathrm{U–thf}) = -\Delta_r H(3) + D(\mathrm{C–Cl}) - \tfrac{1}{2}D(\mathrm{C–C}) + \Delta_{\mathrm{soln}}H \tag{7}$$

$$3D(\mathrm{U–Cl}) - 2D(\mathrm{U–thf}) = -\Delta_r H(4) + 2D(\mathrm{U–I}) - D(\mathrm{I–I}) + \tfrac{3}{2}D(\mathrm{Cl–Cl}) + \Delta_{\mathrm{soln}}H \tag{8}$$

The experimental enthalpies of reaction and the bond dissociation enthalpies, not corrected by the U–thf bond dissociation enthalpy, are presented in Table 2. To arrive at the values some auxiliary data shown in Table 3 were used [3,20–23]. From the values listed in Table 2 it is possible to calculate the differences between the bond dissociation enthalpies of $\mathrm{UTp^{Me_2}I_2L}$ compounds (Eqs. (9)–(11)). It should be stressed that these differences are independent of the values of $D(\mathrm{U–thf})$ and $\Delta_{\mathrm{soln}}H$.

$$D(\mathrm{U–O}) - D(\mathrm{U–I}) = 47.4 \pm 7.5\ \mathrm{kJ\ mol^{-1}} \tag{9}$$

$$D(\mathrm{U–Cl}) - D(\mathrm{U–I}) = 109.2 \pm 8.7\ \mathrm{kJ\ mol^{-1}} \tag{10}$$

$$D(\mathrm{U–Cl}) - D(\mathrm{U–O}) = 62 \pm 11\ \mathrm{kJ\ mol^{-1}} \tag{11}$$

To determine the absolute values for the bond dissociation enthalpies in the U(IV) compounds studied, the value of $D(\mathrm{U–thf})$ in compound **1** is needed. The measurement of such a value is not easy, but can be estimated with reasonable precision. Zachariasen proposed a relationship between the bond length and the bond strength in compounds of transition metals and f Group metals [24] (Eq. (12)), where d is the bond-length and s the intrinsic strength. Application of Eq. (12) requires some tabulated parameters that depend on the metal and oxidation state ($d(\mathbf{1})$ and B)). Looking for compounds for which both the bond dissociation enthalpy, $D(\mathrm{M–thf})$, and the M–O(thf) distance are known, three such f-element compounds could be found [5,19,25–28] (Table 4).

$$\begin{array}{ll}
\mathrm{UTp^{Me_2}I_2.thf_2 \rightarrow UTp^{Me_2}I_2 + 2\ thf} & \mathrm{2D(U\text{-}thf)} \\
\mathrm{UTp^{Me_2}I_2 + I \rightarrow UTp^{Me_2}I_3} & \mathrm{–D(U\text{-}I)} \\
\mathrm{½\ I_2 \rightarrow I} & \mathrm{½\ D(I\text{-}I)} \\
\hline
\mathrm{UTp^{Me_2}I_2.thf_2 + ½\ I_2 \rightarrow UTp^{Me_2}I_3 + 2\ thf} & \mathrm{2D(U\text{-}thf) – D(U\text{-}I) + ½\ D(I\text{-}I)}
\end{array}$$

Scheme 1.

$$\begin{array}{ll}
\mathrm{UTp^{Me_2}I_2.thf_2 \rightarrow UTp^{Me_2}I_2 + 2\ thf} & \mathrm{2D(U\text{-}thf)} \\
\mathrm{UTp^{Me_2}I_2 + Cl \rightarrow UTp^{Me_2}I_2Cl} & \mathrm{–D_1^A(U\text{-}Cl)} \\
\mathrm{UTp^{Me_2}I_2Cl + Cl \rightarrow UTp^{Me_2}ICl_2 + I} & \mathrm{–D_1^B(U\text{-}Cl) + D_1^A(U\text{-}I)} \\
\mathrm{UTp^{Me_2}ICl_2 + Cl \rightarrow UTp^{Me_2}Cl_3 + I} & \mathrm{–D_1^C(U\text{-}Cl) + D_1^B(U\text{-}I)} \\
\mathrm{I + I \rightarrow I_2} & \mathrm{–D(I\text{-}I)} \\
\mathrm{3/2\ Cl_2 \rightarrow 3\ Cl} & \mathrm{3/2\ D(Cl\text{-}Cl)} \\
\hline
\mathrm{UTp^{Me_2}I_2.thf_2 + 3/2\ Cl_2 \rightarrow UTp^{Me_2}Cl_3 + I_2 + 2\ thf} & \\
& \mathrm{2D(U\text{-}thf) – 3D_1(U\text{-}Cl) + 2D_1(U\text{-}I) – D(I\text{-}I) + 3/2\ D(Cl\text{-}Cl)}
\end{array}$$

$$\mathrm{(assuming\ D_1^A(U\text{-}Cl) = D_1^B(U\text{-}Cl) = D_1^C(U\text{-}Cl)\ and\ D_1^A(U\text{-}I) = D_1^B(U\text{-}I))}$$

Scheme 2.

Table 2
Experimental reaction enthalpies and relative bond dissociation enthalpies

Reaction	$\Delta_r H$	L	$D(\mathrm{U–L}) - 2D(\mathrm{U–thf})$
1	-136.7 ± 2.5	I	208.4 ± 2.7
2	-173.6 ± 2.1	O	255.8 ± 7.0
3	-150.0 ± 8.0	Cl	317.6 ± 8.3
4	-240.5 ± 2.5		–

Table 3
Auxiliary bond enthalpy data

Bond	$D(\mathrm{X–Y})$ (kJ mol^{-1})	Reference
I–I	151.3	[3]
^{t}BuO–O^{t}Bu	172.5 ± 6.6	[20a]
	172.3 ± 10.2	[20b]
$\mathrm{C_5H_{11}–C_5H_{11}}$	361.7 ± 2.0	[21,22]
$\mathrm{C_5H_{11}–Cl}$	352.5 ± 1.6	[22]
Cl–Cl	243.36	[23]

Table 4
Estimation of D(U–thf) bond dissociation enthalpy

Compound	D(M–thf) (kJ mol^{-1})	d(U–O) (pm)	Estimated D(U–thf) in compound 1 (kJ mol^{-1}) [a]
Cp*Sm(thf)2	25.5 ± 4.5 [b,c]	263.5 [d,e]	24.5 ± 4.3
$UTp^{Me_2}Cl_3$·thf	21.5 ± 2.9 [f]	254.6 [g]	18.7 ± 2.5
$(C_5H_4Me)_3U$·thf	41.0 ± 0.8 [h]	255.1 [i]	34.2 ± 0.7
Average			25.8 ± 7.8

[a] Calculated using Eq. (12).
[b] Average value of D_1 and D_2.
[c] Data from Ref. [25].
[d] Average value of d(U–O).
[e] Data from Ref. [26].
[f] Data from Ref. [19].
[g] Data from Ref. [27].
[h] Data from Ref. [5].
[i] Data for d(U–O) in $(C_5H_5)_3U$·thf [28].

$$d = d(\mathbf{1}) - B \ln s \qquad (12)$$

The bond dissociation enthalpy of the U–thf bond of $UTp^{Me_2}I_2$·thf_2 was then estimated from each of the three compounds and are shown in Table 4. As no preference can be given to any of the calculated values, their average (25.8 ± 7.8 kJ mol^{-1}) will be used as the average value of the bond dissociation enthalpy of both the U–thf bonds in compound **1**. In Table 5 the absolute values of D(U–L) (L = I, O^tBu and Cl) were calculated considering the average D(U–thf) calculated in Table 4.

First, we draw attention to the small errors associated with the experimental measurements and the relative bond dissociation enthalpies (Eqs. (9)–(11)) compared with the larger errors on the absolute D values. This is not only because of the error associated with the D(U–thf) value, but also, as in the case of D(U–Cl) derived from reaction (4), because of the error in the absolute D(U–I) that has to be included in the calculation. Despite the large errors affecting the absolute values, it can be seen that D(U–Cl) is clearly higher than D(U–O) which in turn is higher than D(U–I).

The value obtained for D(U–O) is in excellent agreement with a previously measured value using oxidative addition, Table 1 [8,9]. In addition, the D(U–I) value is also in good agreement with the values reported in Refs. [5,6,8]. Both these results suggest that the estimated value for D(U–thf) is acceptable.

Some selected literature values of bond enthalpy data together with the values determined in the present work are plotted in Fig. 1. It appears that the estimated value of 481 ± 42 kJ mol^{-1} [4] for the U–O bond dissociation enthalpy is too high. In addition, the use, as a reference, of the gas-phase value for D_1(U–Cl) in UCl_4 in Refs. [18,19] may not be appropriate.

It is suggested that the values anchored on the estimated D(U–O) be lowered by about 120 kJ mol^{-1}. This would bring the average D(U–Me) values anchored on D(U–O) [4] to a value similar to the ones measured by oxidative addition [5,8,9]. It is also suggested that the value of D(U–Cl) in UCl_4 be abandoned as an anchor and the values previously anchored on it be lowered by about 100 kJ mol^{-1} in order to have a D(U–O) value similar to the above-referred value (360 kJ mol^{-1}). Although this change of anchors is arbitrary, a good consistency of bond dissociation enthalpy is obtained, despite some scattering that can be attributed to the influence of ancillary ligands (Fig. 2).

However, to have a definitive absolute scale of bond dissociation enthalpies in U(IV) compounds a complete study on a system like $UL'X_2L$ (with L′ = stabilizing

Table 5
Absolute bond dissociation enthalpies in $UTp^{Me_2}I_2L$

Bond	D (kJ mol^{-1})
U–I	260 ± 11
U–O	307 ± 13
U–Cl (reaction (3))	369 ± 14
U–Cl (reaction (4))	341 ± 19

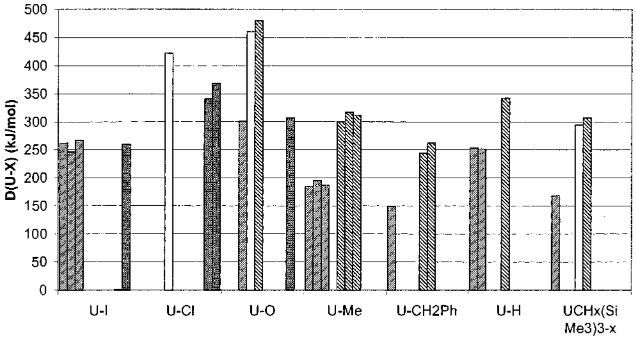

Fig. 1. Bond dissociation enthalpies, uncorrected (thin stripes — oxidative addition [5,6,8], white — anchored on D(U–Cl) [18], thick stripes — anchored on estimated D(U–O) [4], squares — values measured in this paper).

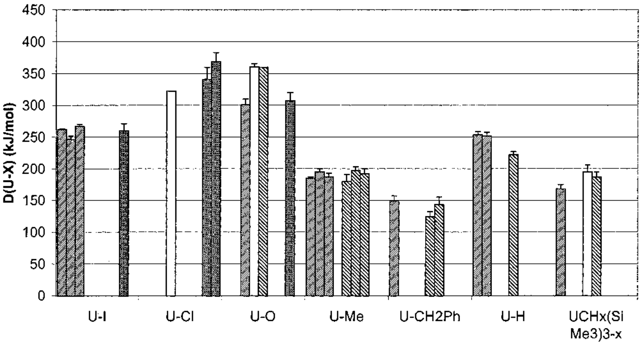

Fig. 2. Bond dissociation enthalpies modified according to the proposed correction (thin stripes — oxidative addition, white — previously anchored on *D*(U–Cl), thick stripes — previously anchored on estimated *D*(U–O), squares — values measured in this paper). Associated error bars are also shown.

ligand, X = halogen and L = I, Cl, OR, NRR′, R, SR, etc.) should be carried out, both by ligand exchange and oxidative addition to U(III) species (preferably without solvent adducts). It will be difficult to prepare such a system, but it may not be impossible to find closer and closer approximations to it.

3. Experimental

3.1. Materials

Tetrahydrofuran (thf) and toluene were predried over 4 Å molecular sieves and distilled from sodium, potassium and benzophenone. Pentane was dried over P_2O_5, fractionally distilled and kept over 4 Å molecular sieves.

All solvents were degassed before use.

Compound **1** was prepared as described earlier in Ref. [29].

3.2. Physical measurements

Infrared spectra were obtained with a Perkin–Elmer 577 spectrophotometer with samples mounted as Nujol mulls between KBr plates. Proton NMR spectra were recorded with a Bruker SY80-FT spectrometer and referenced to $SiMe_4$. The FTICR mass spectra were done by electron impact (EI) with a Finnigan 2001-DT Instrument equipped with a 3.0 T superconducting magnet.

3.3. Calorimeter

The calorimeter used was specially built for the study of oxygen and water sensitive compounds, and the experimental procedure was described in Ref. [30]. After each calorimetric measurement, the cell was again transferred to the glove-box and a sample was taken from the final solution for identifying the final products. The enthalpy change measured for the hydrolysis of tris(hydroxymethyl)methylamine in a 0.1 mol dm^{-3} aq. HCl, -29.89 ± 0.29 kJ mol^{-1}, agrees with literature value for this reaction [31]. All measurements were made at 298 K, and the results are the average of at least four runs. The errors presented are twice the standard deviation of the mean in each case.

3.4. Final states of calorimetric reactions

The final solutions were taken to dryness, and the ^{1}H-NMR spectrum recorded in toluene-d_8.

Compounds **2** and **6** were identified easily by comparing the obtained spectra with the literature values (**2** [32], **6** [33]).

Compound **3** has not been described in the literature but the spectra of the product obtained displayed the expected 2:1 pattern and compares with the one obtained for $UTp_2^{Me_2}I_2(O(CH_2)_4I)$ [32]. ^{1}H-NMR (C_7D_8): δ -31.9 (6H, Me(pz)), -17.5 (2H, H(4)(pz)), -9.5 (6H, Me(pz)), 24.2 (3H, Me(pz)), 48.3 (3H, Me(pz)), 55.3 (1H, H(4)(pz)), 73.5 (9H, ^{t}Bu).

The ^{1}H-NMR of **4** displayed a 2:1 pattern that agrees with the proposed formulation but there is no data in the literature to compare with. ^{1}H-NMR (C_7D_8): δ -13.5 (3H, Me(pz)), -1.9 (1H, H(4)(pz)), -1.3 (6H, Me(pz)), 7.5 (3H, Me(pz)), 10.9 (2H, H(4)(pz), 12.3 (3H, Me(pz)). In this case, as an additional confirmation, the solution was also injected trough a leak valve in an FT-ICR mass spectrometer and a positive ion spectra of the volatile part was made using EI as the ionization mean. Uranium species were not detected probably because of its low vapor pressure, but a peak at $m/z = 143$ corresponding to the protonated **5** species was identified clearly.

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References

[1] (a) G. Pilcher, H.A. Skinner, in: F.R. Hartley, S. Patai (Eds.), The Chemistry of the Metal–Carbon, Wiley, New York, 1982, pp. 43–90;
(b) A.R. Dias, M.S. Salema, J.A. Martinho Simões, J. Organomet. Chem. 222 (1981) 69;
(c) J.A. Connor, Top. Curr. Chem. 71 (1977) 71;
(d) H.A. Skinner, J.A. Connor, Pure Appl. Chem. 57 (1985) 79.

[2] (a) J.W. Bruno, T.J. Marks, L.R. Morss, J. Am. Chem. Soc. 105 (1983) 6824;
(b) D.C. Sonnenberger, L.R. Morss, T.J. Marks, Organometallics 4 (1985) 352;
(c) X. Jemine, J. Goffart, M. Ephritikhine, J. Fuger, J. Organomet. Chem. 448 (1993) 95;

(d) S.P. Nolan, D. Stern, D. Hedden, T.J. Marks, in: T.J. Marks (Ed.), Bonding Energetics in Organometallic Compounds, American Chemical Society, Washington, DC, 1990, pp. 159–174;
(e) W.A. King, T.J. Marks, J. Am. Chem. Soc. 114 (1992) 9221;
(f) W.A. King, S. Di Bella, G. Lanza, K. Khan, D.J. Duncalf, F.G.N. Cloke, I.L. Fragala, T.J. Marks, J. Am. Chem. Soc. 118 (1996) 627;
(g) T.J. Marks (Ed.), Bonding Energetics in Organometallic Compounds, ACS Symposium Series, American Chemical Society, Washington, DC, 1990;
(h) J.A. Martinho Simões (Ed.), Energetics of Organometallic Species, NATO ASI Series, Kluwer Academic, Dordrecht, 1992;
(i) M.E. Minas da Piedade (Ed.), Energetics of Stable Molecules and Reactive Intermediates, NATO ASI Series, Kluwer Academic, Dordrecht, 1999.

[3] J.A. Martinho Simões, J.L. Beauchamp, Chem. Rev. 90 (1990) 629 (and references cited therein).

[4] J.W. Bruno, H.A. Stecher, L.R. Morss, D.C. Sonnenberger, T.J. Marks, J. Am. Chem. Soc. 108 (1986) 7275.

[5] L.E. Schock, A.M. Seyam, M. Sabat, T.J. Marks, Polyhedron 7 (1988) 1517.

[6] X. Jemine, J. Goffart, J.-C. Berthet, M. Ephritikhine, J. Chem. Soc. Dalton Trans. (1992) 2439.

[7] X. Jemine, J. Goffart, P.C. Leverd, M. Ephritikhine, J. Organomet. Chem. 469 (1994) 55.

[8] S. Bettonville, J. Goffart, J. Fuger, J. Organomet. Chem. 393 (1990) 205.

[9] S. Bettonville, J. Goffart, J. Fuger, J. Organomet. Chem. 377 (1989) 59.

[10] S.P. Nolan, M. Porchia, T.J. Marks, Organometallics 10 (1991) 1450.

[11] V.I. Telnoy, I.B. Rabinovich, M.R. Leonov, G.V. Solov'yova, N.I. Gramoteeva, Dokl. Akad. Nauk. SSSR 245 (1979) 1430.

[12] V.I. Telnoy, I.B. Rabinovich, V.M. Larina, M.R. Leonov, G.V. Solov'yova, Radiokhimiya 31 (1989) 38.

[13] N.T. Kuznetsov, K.V. Kir'yanov, V.A. Mitin, V.G. Sevast'yanov, V.A. Bogdanov, Radiokhimiya 28 (1986) 709.

[14] R.G. Bedford, J. Phys. Chem. 81 (1977) 1284.

[15] N.T. Kuznetsov, V.A. Mitin, K.V. Kir'yanov, V.G. Sevast'yanov, V.A. Bogdanov, Radiokhimiya 29 (1987) 109.

[16] (a) L. Thakur, R. Prasad, A.K. Thakur, Md.F. Ahmad, Indian J. Chem. A 18 (1979) 258;
(b) L. Thakur, A.K. Thakur, Md.F. Ahmad, Indian J. Chem. A 19 (1980) 793.

[17] K.H. Lau, D.L. Hildenbrand, J. Chem. Phys. 80 (1984) 1312.

[18] J.P. Leal, N. Marques, A. Pires de Matos, M.J. Calhorda, A.M. Galvão, J.A. Martinho Simões, Organometallics 11 (1992) 1632.

[19] J.P. Leal, J.A. Martinho Simões, J. Chem. Soc. Dalton Trans. (1994) 2687.

[20] (a) V.F. DeTuri, K.M. Ervin, J. Phys. Chem. A 103 (1999) 6911;
(b) R.M. Borges dos Santos, V.S.F. Muralha, C.F. Correia, J.A. Martinho Simões, submitted for publication.

[21] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (Suppl. 1) (1988) 0.

[22] http://www.webbook.gov/chemistry/

[23] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney, R.L. Nutall, J. Phys. Chem. Ref. Data 11 (Suppl. 2) (1982) 00.

[24] W.H. Zachariasen, J. Less-Common Met. 62 (1978) 1.

[25] S.P. Nolan, D. Stern, T.J. Marks, J. Am. Chem. Soc. 111 (1989) 7844.

[26] W.J. Evans, J.W. Grate, H.W. Choi, I. Bloom, W.E. Hunter, J.L. Atwood, J. Am. Chem. Soc. 107 (1985) 941.

[27] R.G. Ball, F. Edelmann, J.G. Matisons, J. Takats, N. Marques, J. Marçalo, A. Pires de Matos, K.W. Bagnall, Inorg. Chim. Acta 132 (1987) 137.

[28] H.J. Wasserman, A.J. Zozulin, D.C. Moody, R.R. Ryan, K.V. Salazar, J. Organomet. Chem. 254 (1983) 305.

[29] Yimin Sun, PhD Thesis, University of Alberta, Edmonton, Alberta, 1995.

[30] J.P. Leal, A. Pires de Matos, J.A. Martinho Simões, J. Organomet. Chem. 403 (1991) 1.

[31] C.E. Vanderzee, D.H. Vaugh, N.C. Hass, J. Chem. Thermodyn. 13 (1981) 1.

[32] J. Collin, A. Pires de Matos, I. Santos, J. Organomet. Chem. 463 (1993) 103.

[33] A. Domingos, N. Marques, A. Pires de Matos, Polyhedron 9 (1990) 69.