(1*SR*,2*SR*,4*RS*,6*SR*)-2,4-Dineopentyl-1-methoxy-6-(trimethylsilyl)-1,3,3-triphenyl-1,3-disilacyclohexane (11b): ^{1}H NMR δ −0.08 (s, 9 H, $Si(CH_3)_3$), 0.70 and 0.76 (s, 9 H, $C(CH_3)_3$), 2.44 (ddd, *J* = 2.2, 7.6, 9.8 Hz), 3.62 (s, 3 H, OCH_3), 7.14–7.70 (m, 15 H, aryl H), other protons were overlapped with those of **11c** as mentioned below; ^{13}C NMR δ 0.26 (s, $Si(C\mathrm{H}_3)_3$), 6.69 (CH), 14.13 (CH), 15.45 ($C\mathrm{H}_2$), 22.66 (CH), 29.34 and 29.79 ($C(C\mathrm{H}_3)_3$), 31.48 and 32.45 ($C(\mathrm{CH}_3)_3$), 36.74 and 44.89 ($C\mathrm{H}_2\mathrm{C}(\mathrm{CH}_3)_3$), 51.67 ($OCH_3$), aryl carbons were overlapped with those of **11c** as mentioned below.

(1*RS*,2*SR*,4*SR*,6*SR*)-2,4-Dineopentyl-1-methoxy-6-(trimethylsilyl)-1,3,3-triphenyl-1,3-disilacyclohexane (11c): ^{1}H NMR δ 0.02 (s, 9 H, $Si(CH_3)_3$), 0.63 and 0.74 (s, 9 H, $Si(CH_3)_3$), 0.89 (dd, *J* = 2.7, 16.4 Hz, 1 H) (CH), 0.96–1.03 (m, 1 H) and 1.12 (t, *J* = 4.5 Hz, 1 H) (CH_2), 1.19–1.35 (m, 2 H) (CH), 1.51 (dd, *J* = 8.3, 13.3 Hz, 1 H), 1.64 (dd, *J* = 4.5, 13.8 Hz, 1 H) (CH_2), 1.75 (t, *J* = 13.0 Hz, 1 H) (CH_2), 2.04 (ddd, *J* = 2.7, 5.1, 14.1 Hz, 1 H) (ring CH_2), 3.41 (s, 3 H, OCH_3), 7.14–7.70 (m, 15 H, aryl H); ^{13}C NMR δ 0.09 ($Si(C\mathrm{H}_3)_3$), 4.58 (CH), 9.90 (CH), 15.92 ($C\mathrm{H}_2$), 21.84 (CH), 29.39 and 30.00 ($C(C\mathrm{H}_3)_3$), 31.60 and 32.45 ($C(\mathrm{CH}_3)_3$), 37.82 and 44.89 ($C\mathrm{H}_2\mathrm{C}(\mathrm{CH}_3)_3$), 51.20 ($OCH_3$), 127.16, 127.27, 127.39, 127.68, 127.90, 128.83, 129.07, 129.23, 129.50, 134.33, 134.91, 134.99, 135.08, 135.24, 135.83, 135.95, 136.04, 136.10, 136.40, 136.78, 137.07 (aryl carbons were overlapped with those of **11b**); HRMS *m/e* calcd for $Si_3C_{36}H_{54}O$ 586.3468, found 586.3459.

Photolysis of 1 (93% 1c) in the Presence of Methoxytrimethylsilane. This experiment was carried out in the same manner as experiment 4, except that a mixture of **1a** (2.2%), **1b** (5.1%), and **1c** (92.7%) (28.4 mg, 0.059 mmol) was irradiated. Yields of products were as follows: **2a**, 20.0%; **2b**, 11.1%; **3a**, 5.6%; **3b**, 2.1%; **9**, 18.0%; **10**, 15.5%; **11a–c**, 2.7%. The ratio of the two diastereomers D_1:D_2 in **9** was 40:60.

Photolysis of 1a,b in the Presence of 1,3-Dimethylbutadiene. A solution of a mixture of **1a** (30%) and **1b** (70%) (13.0 mg, 0.027 mmol) in 0.54 mL of cyclohexane was photolyzed for 4 h. **1** (83.0%) had decomposed to give a mixture of products including **2a** (20.0%), **2b** (4.7%), **3a** (6.9%), and **3b** (trace). GC/MS analysis of the reaction mixture was not observed for trapped silene products.

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Uranium–Ligand Bond Dissociation Enthalpies in Uranium(IV) Polypyrazolylborate Complexes

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Reaction-solution calorimetry measurements of the enthalpies of alcoholysis of a series of complexes of the type $[HB(3,5\text{-}Me_2Pz)_3]UCl_2L$, where Pz = pyrazolyl and L = O-*t*-Bu, $OCH(CMe_3)_2$, $N(SiMe_3)_2$, $CH(SiMe_3)_2$, and C_5H_5 led to the following uranium–ligand bond dissociation enthalpies, *D*(U–L), kJ/mol: 460.5 ± 5.0 (O-*t*-Bu), 334 ± 10 ($N(SiMe_3)_2$), 295 ± 11 ($CH(SiMe_3)_2$), 362 ± 12 (C_5H_5). These results, which are anchored on *D*(U–Cl) = 422.6 kJ/mol, were compared with early literature data for other uranium systems. Together with extended Hückel molecular orbital calculations, they provided some ground to address the discrepancy between the uranium–ligand bond dissociation enthalpies obtained from iodinolysis and alcoholysis reactions.

Introduction

There has been a considerable interest in the thermochemistry of uranium organometallic compounds. Most of the available data have recently been reported by three groups. Marks and co-workers made reaction-solution calorimetry studies involving the complexes $U(Cp')_3L$ (L = Me, Bu, CH_2SiMe_3, CH_2Ph, $CHCH_2$, CCPh, CO, I),[1] $U(C_5H_4Me)_3thf$,[1] $U(Cp^*)_2L_2$ (L = Me, CH_2Ph, CH_2SiMe_3),[2] $U(Cp^*)_2(Cl)L$ (L = Me, Ph, CH_2Ph),[2] and $U(Cp^*)_2[OSi(t\text{-}Bu)Me_2]L$ (L = H, Me),[2] where $Cp' = \eta^5\text{-}Me_3SiC_5H_4$ and $Cp^* = \eta^5\text{-}C_5Me_5$. Bettonville, Goffart, and Fuger have also used reaction-solution calorimetry to examine the complexes $U(C_9H_7)_3L$ (L = Me, I)[3,4] and $U(1\text{-}EtC_9H_6)_3Me$,[3] where C_9H_7 = indenyl. Finally, the enthalpies of formation of the compounds $U(Cp)_3L$ (L = $i\text{-}C_4H_9$, OC_4H_9, Cp, Cl)[5,6] and $U(C_8H_8)_2$,[5] where $Cp = \eta^5\text{-}C_5H_5$, have been determined by Telnoy and co-workers, by using static-bomb combustion calorimetry. A very large discrepancy between Telnoy's value for $\Delta H_f^\circ[U(C_8H_8)_2,cr]$, 326.4 ± 12.6 kJ/mol, and the one obtained by Kuznetsov et al.,[7] 131 ± 15 kJ/mol, by using the same technique, suggests that static-bomb combustion calorimetry is probably not the best option to study these systems (see also discussion below). Kuznetsov et al. have also reported the enthalpy of formation of $U(C_8H_7Bu)_2$ and derived uranium–butylcyclooctatetraene mean bond dissociation enthalpy.[8] A gas-

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phase study of the equilibrium $U(C_8H_8)_2 = U(C_8H_8) + C_8H_8$, leading to uranium–cyclooctatetraene bond dissociation enthalpy,[9] 190 ± 27 kJ/mol, is finally mentioned.

There is a discrepancy between the values of uranium–ligand bond dissociation enthalpies in the (trimethylsilyl)cyclopentadienyl and the indenyl systems. This discrepancy, which does not question the reliability of the experimental results (enthalpies of reaction) but rather is centered on the use of these data to derive the bond dissociation enthalpies, can be summarized by using the results for the indenyl complexes.[3,4] Absolute values of D(U–I) and D(U–Me), 267 ± 3 and 195 ± 5 kJ/mol, respectively, were derived from the enthalpies of reactions 1 and 2, as shown in eqs 3 and 4. Note that the only

$$U(C_9H_7)_3(\text{sln}) + \tfrac{1}{2}I_2(\text{sln}) \rightarrow U(C_9H_7)_3I(\text{sln}) \quad (1)$$

$$U(C_9H_7)_3Me(\text{sln}) + I_2(\text{sln}) \rightarrow U(C_9H_7)_3I(\text{sln}) + MeI(\text{sln}) \quad (2)$$

$$D(\text{U–I}) = -\Delta H_r^\circ(1) + 0.5D(\text{I–I}) \quad (3)$$

$$D(\text{U–Me}) = \Delta H_r^\circ(2) + D(\text{U–I}) - D(\text{I–I}) + D(\text{Me–I}) \quad (4)$$

assumption involved in the calculation of D(U–I) and D(U–Me) is the cancellation of solvation enthalpies in reactions 1 and 2, which is needed if the bond dissociation enthalpies are to be referred to the gas phase.

The energetics of the uranium–methyl bond were also examined by measuring the enthalpy of reaction 5, from which the difference D(U–Me) − D(U–O) can be derived

$$U(C_9H_7)_3Me(\text{sln}) + CF_3CH_2OH(\text{sln}) \rightarrow U(C_9H_7)_3OCH_2CF_3(\text{sln}) + CH_4(\text{g/sln}) \quad (5)$$

$$D(\text{U–Me}) = \Delta H_r^\circ(5) + D(\text{U–O}) - D(\text{O–H}) + D(\text{Me–H}) \quad (6)$$

(eq 6). The evaluation of D(U–Me) requires, therefore, an estimate of D(U–O), the so-called *anchor*. Marks and co-workers used D(U–O) = 481 kJ/mol,[2] a value that relies on an empirical—and approximate—relationship between metal–oxygen and metal–halogen bond enthalpies in M(IV) molecules, to derive D(U–L) in the above mentioned pentamethylcyclopentadienyl complexes. When the same value is introduced in eq 6, one obtains D(U–Me) = 375 ± 8 kJ/mol, which is 180 kJ/mol higher than the *absolute* result derived from eq 4. In other words, the anchor chosen is a very high upper limit *in the case of the indenyl complex* $U(C_9H_7)_3OCH_2CF_3$. While this conclusion is very likely correct, it does not necessarily challenge the reliability of D(U–O) = 481 kJ/mol in the case of the Cp* systems.

The aim of the present paper is to report some uranium–ligand bond dissociation enthalpies in compounds of the type $[HB(3,5\text{-}Me_2Pz)_3]UCl_2L$, where Pz = pyrazolyl and L = O-*t*-Bu, $OCH(CMe_3)_2$, $N(SiMe_3)_2$, $CH(SiMe_3)_2$, and Cp. These data were compared with uranium–ligand bond dissociation enthalpies in the other uranium systems in an attempt to clarify the question raised above on the transferability of D(U–O). The problem was also addressed semiquantitatively by using extended Hückel molecular orbital calculations.

Experimental Section

Materials. Tetrahydrofuran 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. Toluene-d_8 was dried over sodium and distilled. *tert*-Butanol was dried over calcium hydride and distilled. All solvents were degassed before use.

Table I. Experimental Enthalpies of Alcoholysis, ΔH_r,[a] and Solution Enthalpies, ΔH_{d1}, of the Complexes (Values in kJ/mol)

complex	ΔH_r	ΔH_{d1}
$[HB(3,5\text{-}Me_2Pz)_3]UCl_3$	−29.7 ± 2.2 −23.7 ± 1.1[b]	0.2 ± 2.0
$[HB(3,5\text{-}Me_2Pz)_3]UCl_2[N(SiMe_3)_2]$	−93.0 ± 2.2	−4.62 ± 0.57
$[HB(3,5\text{-}Me_2Pz)_3]UCl_2[CH(SiMe_3)_2]$	−135.4 ± 4.1	−4.84 ± 0.42
$[HB(3,5\text{-}Me_2Pz)_3]UCl_2Cp$	−7.0 ± 1.1	−1.30 ± 0.76

[a] With *t*-BuOH, unless indicated otherwise. [b] With (*t*-Bu)$_2$CHOH.

Physical Measurements. Infrared spectra were obtained with a Perkin-Elmer 577 spectrophotometer with samples mounted as Nujol mulls between CsI plates. ^{1}H NMR spectra were recorded with a Bruker SY80-FT spectrometer and were referenced to TMS. C, H, and N elemental analyses were made with a Perkin-Elmer automatic analyzer. Uranium and chlorine were analyzed as U_3O_8 and AgCl, respectively, by gravimetric techniques.

***t*-Bu$_2$CHOH (bitox-H) Synthesis.** Rather than using the method described by Syper[10] we have used a general path to make secondary alcohols from ketones. 2,2,4,4-Tetramethylpentanone-3 (4.8 g, 33.74 mmol) and 326 mg (8.59 mmol) of $LiAlH_4$ were added, inside an inert-atmosphere glovebox (water and oxygen contents lower than 5 ppm) to ca. 40 mL of thf at room temperature, and the mixture was stirred for several hours. The solution was taken out of the glovebox and centrifuged after a few drops of distilled water were added to hydrolyze the product. The supernatant solution was then evaporated to dryness, yielding a very hygroscopic white product identified with the title product. Melting point 48.5 °C (lit. 50.0 °C).[10] Elemental Anal. Calcd for $C_9H_{20}O$: C, 75.00; H, 13.89. Found: C, 73.21; H, 13.12.

Uranium Compound Syntheses. The complexes were handled in Schlenk-type glassware in a vacuum line or in the inert-atmosphere glovebox.

$[HB(3,5\text{-}Me_2Pz)_3]UCl_2(O\text{-}t\text{-}Bu)$, $[HB(3,5\text{-}Me_2Pz)_3]UCl_2[N(SiMe_3)_2]$, $[HB(3,5\text{-}Me_2Pz)_3]UCl_2[CH(SiMe_3)_2]$, $[HB(3,5\text{-}Me_2Pz)_3]UCl_2Cp$, and $[HB(3,5\text{-}Me_2Pz)_3]UCl_3\cdot thf$ were synthesized and purified as described in the literature.[11-15]

$[HB(3,5\text{-}Me_2Pz)_3]UCl_3$. $[HB(3,5\text{-}Me_2Pz)_3]UCl_3\cdot thf$ (300 mg, 0.468 mmol) was washed twice with ca. 5 mL of pentane and then dried in vacuum (10^{-5} Torr) for several hours. Elemental analysis and ^{1}H NMR spectrometry agreed with the existing literature values.[12]

$[HB(3,5\text{-}Me_2Pz)_3]UCl_2[OCH(t\text{-}Bu)_2]$. $[HB(3,5\text{-}Me_2Pz)_3]UCl_3\cdot thf$ (54 mg, 0.076 mmol) was added to ca. 20 mL of toluene at room temperature. After stirring for 10 min, 17 mg (0.118 mmol) of HOCH(*t*-Bu)$_2$ was added and the solution was stirred for about 3 h. The solution was centrifuged and then evaporated to dryness. A pale green powder was obtained. ^{1}H NMR (C_7H_8): δ 160.80 (1 H), 54.69 (3 H), 52.35 (1 H), 32.07 (18 H), 20.60 (3 H), −9.52 (6 H), −15.14 (2 H), −34.12 (6 H). Anal. Calcd for $C_{24}H_{41}N_6UOCl_2B$: C, 38.47; H, 5.51; N, 11.21. Found: C, 38.30; H, 5.20; N, 11.47.

Calorimeter. The reaction-solution calorimeter and the experimental procedure used were described elsewhere.[16a] The enthalpy change measured for the hydrolysis of TRIS (tris(hydroxymethyl)aminomethane) in a 0.1 M HCl aqueous solution, −29.89 ± 0.29 kJ/mol, agrees with the literature value for this test

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Table II. Auxiliary Data (kJ/mol)[a]

LX(g)	L	D(L–X)
t-BuOH	t-BuO	440 ± 4[b]
$(SiMe_3)_2NH$	$(SiMe_3)_2N$	(401 ± 8)
$(SiMe_3)_2CH_2$	$(SiMe_3)_2CH$	(405 ± 8)
CpH	Cp	347 ± 10[c]
HCl	Cl	432.0[d]
UCl_4	UCl_3	422.6[e]

[a] Estimated values in parentheses. [b] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. [c] DeFrees, D. J.; McIver, R. T., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 3334. [d] Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, S. M.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. No. 2. [e] Reference 17.

Table III. Bond Dissociation Enthalpies in Solution (kJ/mol)

complex	L	D(U–L)
$[HB(3,5\text{-}Me_2Pz)_3]UCl_3$	Cl	422.6[a]
$[HB(3,5\text{-}Me_2Pz)_3]UCl_2(O\text{-}t\text{-}Bu)$	O-t-Bu	460.5 ± 5.0
$[HB(3,5\text{-}Me_2Pz)_3]UCl_2[N(SiMe_3)_2]$	$N(SiMe_3)_2$	334 ± 10
$[HB(3,5\text{-}Me_2Pz)_3]UCl_2[CH(SiMe_3)_2]$	$CH(SiMe_3)_2$	295 ± 11
$[HB(3,5\text{-}Me_2Pz)_3]UCl_2Cp$	Cp	362 ± 12

[a] Anchor. See text.

reaction.[16b] The alcoholysis reactions were studied either with a 0.0385 M solution of *tert*-butanol in toluene or a 0.0198 M solution of bitox-H in toluene. These concentrations ensured a large stoichiometric excess of the alcohol relative to the amounts of complexes used in each calorimetric experiment. All measurements were made at 298 K, and the results are averages of at least four runs. The errors presented are twice the standard deviation of the mean in each case.

Results and Discussion

The measurement of the enthalpy of reaction 7, which was found to be rapid and quantitative, together with the enthalpy of solution of the trichloride complex, $\Delta H_{d1}°$

$$U[HB(3,5\text{-}Me_2Pz)_3]Cl_3(cr) + t\text{-}BuOH(sln) \rightarrow U[HB(3,5\text{-}Me_2Pz)_3]Cl_2(O\text{-}t\text{-}Bu)(sln) + HCl(sln) \tag{7}$$

$$D(U\text{–}O) - D(U\text{–}Cl) = -\Delta H_r°(7) + \Delta H_{d1}° + D(O\text{–}H) - D(H\text{–}Cl) \tag{8}$$

(Table I), led to the difference between uranium–oxygen and uranium–chloride bond dissociation enthalpies (eq 8). The obtained value, 37.9 ± 5.0 kJ/mol, relies on the auxiliary data given in Table II. While D(U–Cl) is not available, it can be estimated with reasonable confidence by identifying the energetics of processes 9 and 10, i.e.

$$U[HB(3,5\text{-}Me_2Pz)_3]Cl_3(g) \rightarrow U[HB(3,5\text{-}Me_2Pz)_3]Cl_2(g) + Cl(g) \tag{9}$$

$$UCl_4(g) \rightarrow UCl_3(g) + Cl(g) \tag{10}$$

$\Delta H(9) \cong \Delta H(10)$. The enthalpy of reaction 10 has been determined by Lau and Hildenbrand as 422.6 kJ/mol[17] and yields D(U–O) = 460.5 kJ/mol.

The enthalpy of a reaction similar to (7) but where the t-BuOH is replaced by bitox-H (Table I) led to D(U–O) – D(U–Cl) = 31.9 ± 4.6 kJ/mol, in good agreement with the above value. The O–H bond dissociation enthalpy in bitox-H is not known, but it should not be much different from D(O–H) in t-BuOH.

Table IV. Bond Dissociation Enthalpies for Selected Uranium Compounds[a] (Values in kJ/mol)

compd	L	D(U–L)	method[b]	ref
$U(Cp^*)_2(Me)_2$	Me	300 ± 11[c,d]	RSC	2
$U(Cp^*)_2[CH_2Si(Me)_3]_2$	$CH_2Si(Me)_3$	307 ± 8[c,d]	RSC	2
$U(Cp^*)_2(Cl)Me$	Me	312 ± 8[d]	RSC	2
$U(Cp^*)_2[OSi(t\text{-}Bu)Me_2]Me$	Me	317 ± 6[d]	RSC	2
$U(Cp')_3Me$	Me	185 ± 2	RSC	1
$U(Cp')_3Bu$	Bu	152 ± 8	RSC	1
$U(Cp')_3CH_2Si(Me)_3$	$CH_2Si(Me)_3$	168 ± 8	RSC	1
$U(Cp')_3I$	I	262 ± 1	RSC	1
$U(C_9H_7)_3(Me)$	Me	195 ± 5	RSC	4
$U(C_9H_7)_3OCH_2CF_3$	OCH_2CF_3	301 ± 9	RSC	3, 4
$U(C_9H_7)_3I$	I	267 ± 3	RSC	4
$U(Cp)_4$	Cp	Z[e]		
$U(Cp)_3(i\text{-}Bu)$	i-Bu	Z – (70 ± 35)[e]	SB	6
$U(Cp)_3OBu$	OBu	Z + (247 ± 28)[e]	SB	6
$U(Cp)_3Cl$	Cl	Z + (73 ± 31)[e]	SB	6

[a] Solution data, unless indicated otherwise (see text). Cp* = η^5-$C_5(Me)_5$, Cp′ = η^5-$(Me_3SiC_5H_4)$, C_9H_7 = indenyl, and Cp = η^5-C_5H_5. Most bond dissociation enthalpies have been recalculated in: Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629. [b] RSC = reaction-solution calorimetry; SB = static-bomb combustion calorimetry. [c] Mean bond dissociation enthalpy. [d] Value anchored on D(U–O) = 481 kJ/mol. [e] Z = $D(Cp_3U\text{–}Cp)$.

The alcoholyses of the complexes $U[HB(3,5\text{-}Me_2Pz)_3]Cl_2L$ (L = $N(SiMe_3)_2$, $CH(SiMe_3)_2$, Cp), reactions 11–13, are rapid and quantitative under the calorimetric conditions and led to the reaction enthalpies displayed in Table I.

$$U[HB(3,5\text{-}Me_2Pz)_3]Cl[N(SiMe_3)_2](cr) + t\text{-}BuOH(sln) \rightarrow U[HB(3,5\text{-}Me_2Pz)_3]Cl_2(O\text{-}t\text{-}Bu)(sln) + (SiMe_3)_2NH(sln) \tag{11}$$

$$U[HB(3,5\text{-}Me_2Pz)_3]Cl_2[CH(SiMe_3)_2](cr) + t\text{-}BuOH(sln) \rightarrow U[HB(3,5\text{-}Me_2Pz)_3]Cl_2(O\text{-}t\text{-}Bu)(sln) + (SiMe_3)_2CH_2(sln) \tag{12}$$

$$U[HB(3,5\text{-}Me_2Pz)_3]Cl_2Cp(cr) + t\text{-}BuOH(sln) \rightarrow U[HB(3,5\text{-}Me_2Pz)_3]Cl_2(O\text{-}t\text{-}Bu)(sln) + CpH(sln) \tag{13}$$

$$D(U\text{–}L) = \Delta H_r° - \Delta H_{d1}° + D(U\text{–}O) - D(O\text{–}H) + D(L\text{–}H) \tag{14}$$

These values and the enthalpies of solution of the complexes in toluene, ΔH_{d1}, were introduced in eq 14, from which the uranium–ligand bond dissociation enthalpies (Table III) were derived. The auxiliary data are shown in Table II and D(U–O) = 460.5 kJ/mol, as calculated above. It is stressed that the values of D(L–H) for L = $N(SiMe_3)_2$ and $CH(SiMe_3)_2$ have not been measured and so the corresponding results of D(U–L) in Table III rely on the estimates given in Table II.

The D(U–L) results in Table III are in the expected order, i.e. D(U–O) > D(U–Cl) > D(U–N) > D(U–σ–C). The difference D(U–O-t-Bu) – $D[U\text{–}CH(SiMe_3)_2]$ = 166 kJ/mol compares with 174 kJ/mol obtained by Marks and co-workers for the complexes $U(Cp^*)_2(O\text{-}t\text{-}Bu)_2$ and $U(Cp^*)_2(CH_2SiMe_3)$[2] and contrasts with the static-bomb combustion results in Table IV, which lead to D(U–OBu) – D(U–i-Bu) = 317 kJ/mol. This discrepancy seems to be mainly due to a high result for the uranium–oxygen bond dissociation in $U(Cp)_3OBu$, as suggested by the fact that the static-bomb combustion result for the difference D(U–Cl) – D(U–i-Bu), 143 kJ/mol, is in the range of D(U–Cl) – $D[U\text{–}CH(SiMe_3)_2]$ = 128 kJ/mol found for the complexes in Table III. The remark is also in keeping with the similar differences D(U–Cl) – D(U–Cp), 61 and 73 kJ/mol, found for the complexes $U[HB(3,5\text{-}Me_2Pz)_3]Cl_2L$

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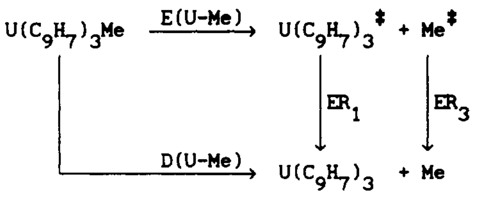
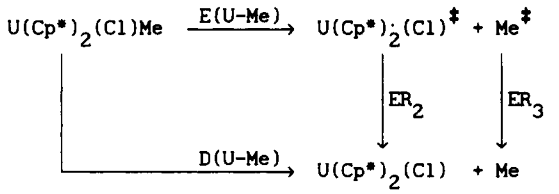
Scheme I



Scheme II

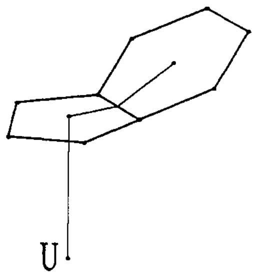


and $U(Cp)_3L$, respectively (Tables III and IV).

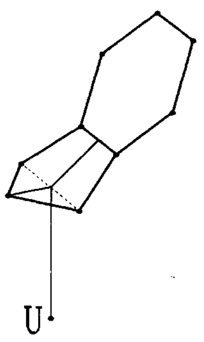
The method used to estimate the anchor in the present work, $D(U–Cl) = 422.6$ kJ/mol (eq 10), which led to $D(U–O) = 460.5$ kJ/mol, is clearly more reliable than the one used by Marks and co-workers to estimate $D(U–O) = 481$ kJ/mol.[2] Nevertheless, it is noted that both estimates are similar. Although this agreement does not provide a confirmation of the *absolute* value for uranium–oxygen bond dissociation enthalpies in the pentamethylcyclopentadienyl complexes and in $U[HB(3,5\text{-}Me_2Pz)_3]Cl_2(O\text{-}t\text{-}Bu)$ (Table III), it strongly supports a value in the above range. However, as stated in the Introduction, these anchors were found to be inadequate for the systems $U(C_7H_9)_3L$, where $D(U–OCH_2CF_3)$ was calculated as 301 kJ/mol.

As evidenced in Table IV, the uranium–ligand bond dissociation enthalpies in the indenyl and the (trimethylsilyl)cyclopentadienyl (Cp′) complexes, in both cases determined through the iodinolysis method (see Introduction), are ca. 120 kJ/mol lower than the values obtained for the Cp* complexes (and also for those in Table III). This difference has been attributed to steric and electronic factors in the case of the Cp′ complexes.[1] A more detailed discussion can be made by using extended Hückel molecular orbital calculations to derive the reorganization energies involved in Schemes I and II. Here, $E(U–Me)$ and $D(U–Me)$ are uranium–methyl bond enthalpy terms and bond dissociation enthalpies, respectively. The differences $D(U–Me) - E(U–Me)$ reflect the relaxation or reorganization energies (ER) of the fragments after the bond cleavage (the superscript ‡ indicates that the fragment retains the structure of the parent complex). As the reorganization energies are not included in the uranium–methyl bond enthalpy terms, these quantities are likely to yield a better correlation with other structural parameters, such as bond lengths, than bond dissociation enthalpies. Although there are no structural data available, it can be assumed, as a first approximation, that $E(U–Me)$ values are identical in Schemes I and II. On the other hand, it is likely that the methyl moieties have similar structures in both complexes, implying equal values of ER_3 in Schemes I and II. The problem will then be how to determine ER_1 and ER_2.

The molecular structure of $U(C_9H_7)_3$ is known,[18] but as that of $U(C_9H_7)_3Me$ has not to our knowledge been reported, the complexes $U(C_9H_7)_3X$ (X = Cl, Br, I) have been used as model compounds. In these three complexes, the coordination around uranium is approximately tetrahedral, if one considers as a ligand the center of the five-membered ring in the indenyl ligand. The angles $X–U–C_9H_7$ vary from 99.3° (I) to 100.8° (Br), while $C_9H_7–U–C_9H_7$ is 117.5° (I) or 116.6° (Cl, Br).[19-21] On the other hand, the U–C(five-membered ring) distances are not all equal. In most cases, but not all, two are slightly longer (ca. 10–20 pm) and some authors have considered these to define an η^3-coordinated indenyl.[20,21] The folding pattern **1** across the central C–C bond is not the one expected from an η^3-indenyl, **2**. In this case, the six carbon atoms of the benzene should be planar (sp^2 hybridized) in order to preserve aromaticity, while the allylic moiety binds to the metal. The distance from the metal to two central carbons should be much longer than to the three bonded carbons. The situation found in $U(C_9H_7)_3X$ is different: the folding is such that not all the benzene carbons have a planar environment, and it arises from steric repulsions between adjacent bulky ligands. A small tilting and slipping of the indenyl takes place, but the final U–C(five-membered ring) distances are not very different.

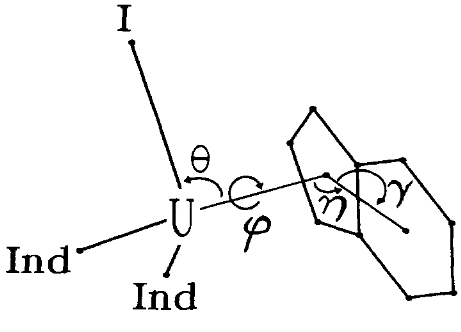


1



2

In order to look for an optimized geometry of $U(C_9H_7)_3{}^‡$ that is as it occurs in $U(C_9H_7)_3X$ complexes, we started from $U(C_9H_7)_3I$ using the experimental data taken from its crystal structure.[21] A C_{3v} geometry was kept, and the four parameters to be optimized are shown in **3**. The angle θ represents the deviation from the regular tetrahedral coordination, φ is the rotation of the indenyl group about the normal to the cyclopentadienyl ring, γ represents the folding angle of the indenyl system across the central C–C bond, and η reflects an $\eta^5 \rightarrow \eta^3$ geometry change through a tilt of the indenyl group, **4**.



3

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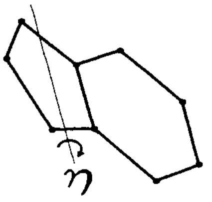
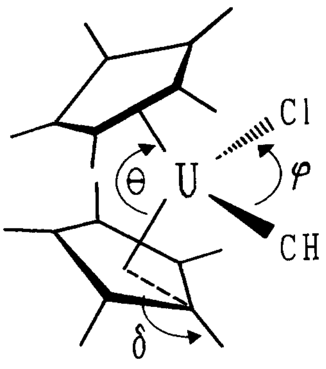


4

Extended Hückel calculations were done and the optimized geometry was found to be very similar to the experimental one, as shown in Table V. The reorganized $U(C_9H_7)_3$ fragment was also studied, and its geometry obtained from extended Hückel calculations is also given in Table V. Its energy is 0.29 eV lower than that of the initial fragment. It should be added that even though an X-ray-determined structure exists, as mentioned earlier, the data are probably not very reliable.[18] The agreement between experimental and calculated structures is not as good as for the previous example.

Suitable parent structures to obtain the geometries of $U(Cp^*)_2Cl^\ddagger$ in $U(Cp^*)_2(Cl)Me$ and in the reorganized form are not available. The relaxation of $U(Cp^*)_2Cl^\ddagger$ to $U(Cp^*)_2Cl$ was calculated as 0.08 eV by using an approach similar to the one described for the indenyl system: the geometry of the nonreorganized fragment was obtained by optimization of the model compound $U(Cp^*)_2(Cl)Me$. The ligands were kept in an approximate tetrahedral environment at fixed distances from the uranium. The optimized angles are shown in **5** (θ is the angle between normals to the Cp* rings, φ is the angle between the other two ligands, and δ describes the bending of the methyl groups away from the ring plane) and their values displayed in Table VI.



5

The extended Hückel calculations predict that ER_1 is 0.21 eV (20 kJ/mol) more exothermic than ER_2, confirming that, at least in part, the weaker uranium–ligand bonds in the indenyl complexes are related to a larger reorganization of the $U(C_9H_7)_3^\ddagger$ fragment. As stated above, the bond dissociation enthalpy differences are, however, substantially larger than 20 kJ/mol, suggesting, despite the semiquantitative nature of the Hückel calculations, that E(U–Me) in Scheme I is actually smaller than in Scheme II. In principle, this should be reflected by a shorter U–Me bond length in the case of the polypyrazolylborate and the pentamethylcyclopentadienyl complexes, relative to the indenyl and the (trimethylsilyl)cyclopentadienyl complexes. These structures are not available, but a comparison can be made involving some of the chlorine analogues. The U–Cl bond length in $U(C_9H_7)_3Cl$, 2.593 (3) Å,[19] is 0.034 Å longer than the average U–Cl bond length in $[HB(3,5\text{-}Me_2Pz)_3]UCl_3$, 2.559 (10) Å.[22] We are not able to predict the effect of this bond length difference on E(U–Cl). It is just noted that bond enthalpy terms/bond length correlations involving, e.g., the bonds C–C, C–H, C–O, O–H, etc.[23] indicate that 0.034 Å bond length changes may lead to differences up to ca. 50 kJ/mol.

Table V. Optimized and Experimental[a] Structural Parameters for $U(C_9H_7)_3I$ and Optimized Values for $U(C_9H_7)_3$

angle	$U(C_9H_7)_3I$ X-ray	$U(C_9H_7)_3I$ EHMO	$U(C_9H_7)_3$ EHMO
θ	99 ± 1	95	90
φ	100	120	165
γ	7	8	4
η	7	8	2

[a] Reference 21.

Table VI. Optimized Structural Parameters for $U(Cp^*)_2(Cl)^\ddagger$ and $U(Cp^*)_2(Cl)$

angle	$U(Cp^*)_2(Cl)^\ddagger$	$U(Cp^*)_2(Cl)$
θ	140	144
$\varphi/2$	44	24
δ	9	9

Throughout the above discussion we have neglected the existence of a metal–metal bond in the U(III) compounds, which would tend to reconcile the two sets of data. No evidence of this bond has, however, been reported.

While the previous analysis supports the view that uranium–ligand bond enthalpy terms and bond dissociation enthalpies in the indenyl and the (trimethylsilyl)cyclopentadienyl complexes are in fact smaller than in the pentamethylcyclopentadienyl and in the polypyrazolylborate complexes (i.e. the anchors chosen for these latter families are probably not overestimated), a problem remains to be solved. The anchor chosen for the polypyrazolylborate complexes (eq 10) relies on $D(Cl_3U\text{–}Cl)$ = 422.6 kJ/mol. On this basis, one could expect that the uranium–iodine bond dissociation enthalpy in these complexes would be close to $D(I_3U\text{–}I)$. Unfortunately, this value has not been measured and its estimate is subject to some controversy. Morss recommends 274.8 kJ/mol,[24] but a value of ca. 240 kJ/mol is obtained if the enthalpies of formation of gaseous UI_4 and UI_3 are estimated by using a method described elsewhere.[25] The difference is however irrelevant for the point to be made, which is as follows. If the uranium–iodine bond dissociation enthalpy in the polypyrazolylborate complex fell in the above range, then one would predict that D(U–I) in $U(C_9H_7)_3I$ and in $U(Cp')_3I$ should be ca. 120 kJ/mol smaller. However, this is not confirmed by the results in Table IV, where D(U–I) $\simeq$ 260 kJ/mol. We are unable to solve this apparent discrepancy. It would be worthwhile to measure D(U–Cl) in those complexes by reaction of $U(C_9H_7)_3$ and $U(Cp')_3$ with Cl_2 in toluene and compare them with the much more reliable value of $D(Cl_3U\text{–}Cl)$, or alternatively, to measure D(U–I) in the polypyrazolylborate complex. Efforts in this

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Table VII. Exponents and Parameters for Uranium[26c]

orbital	$-H_{ii}$/eV	ζ_1	ζ_2	C_1	C_2
U 7s	5.5	1.914			
U 7p	5.5	1.914			
U 6p	30.03	4.033			
U 6d	9.19	2.581	1.207	0.7608	0.4126
U 5f	10.62	4.943	2.106	0.7844	0.3908

direction are presently being made.

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Appendix

All the calculations were of the extended Hückel[26] type with modified H_{ij}'s.[27] The basis set for the metal atoms consisted of *ns*, *np*, $(n-1)$p, $(n-1)$d, and $(n-2)$f orbitals. The s and p orbitals were described by single Slater type wave functions, and d and f orbitals were taken as contracted linear combinations of two Slater type wave functions.

The geometries of $U(C_9H_7)_3$, $U(C_9H_7)_3I$, $U(Cp^*)_2(Cl)Me$, and $U(Cp^*)_2(Cl)$ were modeled as described above. The distances (pm) used were as follows: U-Cp* or U-C_9H_7 = 253.4, U-I = 304, U-Cl = 265, U-Me = 245; C-C(Cp* or C_9H_7) = 140; C(Cp*)-Me(Cp*) = 150; C-H = 108. The five- and six-membered rings were taken as regular pentagons and hexagons. All the other parameters were optimized.

Standard parameters were used for C, H, Cl, and I, while those for the uranium atom were obtained by using a semirelativistic approach (Table VII).[26c]

Registry No. $[HB(3,5\text{-}Me_2Pz)_3]UCl_2(O\text{-}t\text{-}Bu)$, 112812-84-7; $[HB(3,5\text{-}Me_2Pz)_3]UCl_2(OCH(CH_3)_2)$, 112786-13-7; $[HB(3,5\text{-}Me_2Pz)_3]UCl_2(N(SiMe_3)_2)$, 106354-63-6; $[HB(3,5\text{-}Me_2Pz)_3]UCl_2(CH(SiMe_3)_2)$, 139461-22-6; $[HB(3,5\text{-}Me_2Pz)_3]UCl_2(C_5H_5)$, 106354-62-5; $[HB(3,5\text{-}Me_2Pz)_3]UCl_3$, 106354-68-1; U, 7440-61-1.

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Gas-Phase Chemistry of Bare Transition-Metal Ions in Comparison. 2.[1] Reactions of Ti^+ to Zn^+ with 2-Ethylbutanenitrile

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The reactions of the first-row transition-metal ions from Ti^+ to Zn^+ with 2-ethylbutanenitrile (**23**) are studied using a Fourier transform ion cyclotron resonance (FTICR) spectrometer. The general behavior of the ions is compared and is found to be in line with previous studies. While the early-transition-metal ions Ti^+ and V^+ mainly give rise to C-H activation products, Cr^+, Mn^+, and Zn^+ are unreactive without collisional activation and form only adduct complexes. For Fe^+-Cu^+ three processes are operative whose relative importance varies: an ion/dipole mechanism which leads to $MHCN^+$ ions and loss of HCN, remote functionalization forming H_2 and C_2H_4 from the chain termini, and an allylic mechanism which generates CH_4 by initial C-CN insertion. The results are further compared with those of the lower homologue, 2-methylbutanenitrile, studied in part 1, and are found to be in very good agreement. Finally, an instrumental comparison is provided between ion/molecule reactions of Fe^+ with **23** under FTICR conditions and metastable-ion decompositions of $Fe(\mathbf{23})^+$ adduct complexes in a sector mass spectrometer showing that the two approaches provide the same results within previously formulated restrictions.

Introduction

Gas-phase organometallic chemistry[2] renders much of its current interest from the fact that intrinsic properties of bare ions may be studied without any interferences from solvents or counterions. These studies can be performed with either bare metal ions M^+ or ligated metal ions L_nM^+ so that the influence of the ligands may be exploited as well. Most of the studies have so far focused on reactions of M^+ with various substrates. Despite the knowledge accumulated in recent years,[2] one important point is still not very well understood, the role of the substrate itself. The general properties of the metal ions are reasonably well-known, but the products that are formed from a particular substrate are more or less unpredictable. For example, early-transition-metal ions like Sc^+, Ti^+, or V^+ often give rise to C-H activation with losses of up to three molecules of hydrogen or hydrogen together with other small neutrals being observed. Cr^+, Mn^+, Cu^+, and Zn^+ are often unreactive and second- or third-row ions behave similar to the early-transition-metal ions. But especially for Fe^+, Co^+, and Ni^+, a versatile chemistry is encountered which can vary significantly from substrate to substrate.

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