Uranium–Ligand Bond-dissociation Enthalpies of Uranium(IV) Poly(pyrazolyl)borate Complexes†

João Paulo Leal[a] **and José A. Martinho Simões***[,b]
[a] *Departamento de Química, ICEN/INETI, 2686 Sacavém Codex, Portugal*
[b] *Departamento de Química, Faculdade de Ciências, Universidade de Lisboa, 1700 Lisboa, Portugal*

Solution calorimetry measurements involving the complexes $[UCl_2L\{HB(dmpz)_3\}]$ (L = $OCMe_2CH_2COMe$ or dmpz; dmpz = 3,5-dimethylpyrazol-1-yl) led to *D*(U–$OCMe_2CH_2COMe$) and *D*(U–dmpz) bond-dissociation enthalpies of 484.2 ± 8.6 and 393 ± 16 kJ mol^{-1} in solution. The fact that the uranium–ligand bond-dissociation enthalpy in the L = $OCMe_2CH_2COMe$ complex is about 20 kJ mol^{-1} higher than *D*(U–O) values observed for other complexes of the same type is consistent with a bidentate co-ordination of the ligand to the metal centre. This conclusion relies on literature data and on equilibrium studies in solution involving the complex $[UCl_3\{HB(dmpz)_3\}]\cdot OC_4H_8$, which afforded the U–$OC_4H_8$ bond-dissociation enthalpy, 21.5 ± 2.9 kJ mol^{-1}.

Previous thermochemical studies involving uranium(IV) organometallic compounds afforded several uranium–ligand bond-dissociation enthalpies, *D*(U–L). The results, displayed in Table 1, rely on solution alcoholytic or iodolytic titration calorimetry studies, on static bomb-combustion calorimetry determinations, or on gas-phase equilibrium experiments.[1–16] Despite this recent wealth of information on the energetics of uranium–ligand bonds, data for multihapto bonds are still scarce: only *D*(U–cp) (cp = η^5-C_5H_5) = 362 ± 12[16] and $\bar{D}$(U–O_2CMe) = 517 ± 7 kJ mol^{-1} (Table 1) are available. The present paper describes the thermochemical studies that led to the uranium–ligand bond-dissociation enthalpies in the compounds $[UCl_2L\{HB(dmpz)_3\}]$ (L = $OCMe_2CH_2COMe$ or dmpz; dmpz = 3,5-dimethylpyrazol-1-yl). Solution NMR spectra of the L = dmpz complex show that the fourth pyrazolyl ligand is η^2-bonded to the metal centre[17] and our results for the L = $OCMe_2CH_2COMe$ complex are in keeping with a bidentate co-ordination of the aldol ligand.

Experimental

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. $[^2H_8]$Toluene, $[^2H]$chloroform and Bu^tOH were dried over sodium, P_2O_5 and calcium hydride, respectively, and distilled. All solvents were degassed before use.

Physical Measurements.—Infrared spectra were obtained with a Perkin-Elmer 577 spectrophotometer with samples mounted as Nujol mulls between CsI plates. Proton NMR spectra were recorded with a Bruker SY80-FT spectrometer and were referenced to $SiMe_4$. Elemental analyses were made with a Perkin-Elmer automatic analyser for carbon, hydrogen and nitrogen. Uranium and chlorine were analysed gravimetrically as U_3O_8 and AgCl.

Synthesis of the Uranium Compounds.—All organoactinide compounds were handled in a glove-box equipped with an atmosphere purification system, maintained under argon (Air Liquide), or in Schlenk-type glassware in a vacuum line. The complexes $[UCl_3\{HB(dmpz)_3\}]$, $[UCl_3\{HB(dmpz)_3\}]\cdot$thf and $[UCl_2L\{HB(dmpz)_3\}]$ (L = $OCMe_2CH_2COMe$ or dmpz) were synthesised and purified as described in the literature.[16–19]

Calorimetry.—The reaction-solution calorimeter and the experimental procedure have been described elsewhere.[20] The enthalpy change measured for the hydrolysis of tris(hydroxymethyl)methylamine in a 0.1 mol dm^{-3} HCl aqueous solution, −29.89 ± 0.29 kJ mol^{-1}, agrees with the literature value for this test reaction.[21] A solution of Bu^tOH in toluene (0.0385 mol dm^{-3}) or of 4-hydroxy-4-methylpentan-2-one in toluene (0.0308 mol dm^{-3}) were used and these concentrations ensured a large stoichiometric excess of the alcohol or the aldol relative to the amount 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.

Variable-temperature NMR Spectroscopy.—The variable-temperature spectra were performed on a Bruker SY80-FT spectrometer, and the temperature was controlled (precision ±0.5 K, stability ±0.1 K) by a Bruker B-VT1000 unit.

The chemical shifts observed can be affected by exchange phenomena or by chemical association [see equation (6)], where thf exchanges between the solution and the $[UCl_3\{HB(dmpz)_3\}]$ complex. Let $1/\tau_{U'}$ and $1/\tau_U$ be the rates of the direct and reverse reactions, respectively, τ being the residence times of the thf co-ordinated to the uranium compound or in solution. If these rates are similar to the NMR time-scale (10^{-1}–10^{-5} s^{-1}) the exchange effect can be observed in the spectra, both as a broadening of the peaks or as changes in the values of the chemical shifts. The mathematical treatment to calculate the shape of the peaks is quite elaborate[22] and will not be given here. It will be sufficient to stress that for low temperatures [$1/\tau_{U'}$, $1/\tau_U \ll (\omega_{U'} - \omega_U)$, where $\omega_{U'}$ and ω_U are the precession frequencies of the nuclei in the two species], the thf molecule will be in a slow exchange and the spectrum obtained will be the sum of the spectra of the two compounds. At high enough temperatures, so that $1/\tau_{U'}$ and $1/\tau_U \gg (\omega_{U'} - \omega_U)$, a rapid exchange is achieved and the chemical shifts in the spectrum are a weighted average of the values observed in the individual

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† *Supplementary data available* (No. SUP 57023, 12 pp.): observed and calculated NMR shifts for $[UCl_3\{HB(dmpz)_3\}]$, $[UCl_3\{HB(dmpz)_3\}]\cdot$thf and solutions A and B and calculated equilibrium constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

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

Complex	L	D(U–L)/ kJ mol^{-1}	Reference
$[U(\eta^5\text{-}C_5Me_5)_2L_2]$	Me	300 ± 11[b,c]	1
	CH_2Ph	244 ± 8[b,c]	1
	CH_2SiMe_3	307 ± 8[b,c]	1
$[U(\eta^5\text{-}C_5Me_5)_2Cl(L)]$	Me	312 ± 8[c]	1
	CH_2Ph	263 ± 12[c]	1
	Ph	358 ± 11[c]	1
$[U(\eta^5\text{-}C_5Me_5)_2(OSiBu^tMe_2)L]$	Me	317 ± 6[c]	1
	H	342 ± 5[c]	1
$[U\{\eta^5\text{-}C_5H_4(SiMe_3)\}_3L]$	Me	185 ± 2	2
	Bu	152 ± 8	2
	CH_2SiMe_3	168 ± 8	2
	CH_2Ph	149 ± 8	2
	$CHCH_2$	223 ± 10	2
	C≡CPh	363	2
	I	262 ± 1	2
		265.6 ± 4.3	3
	H	253.7 ± 5.1	3
$[U(\eta^5\text{-}C_5H_4Bu^t)_3L]$	H	251.6 ± 5.7	3
	I	246.3 ± 5.3	3
$[U(C_9H_7)_3L]$	Me	195 ± 5	4
	OCH_2CF_3	301 ± 9	4,5
	I	267 ± 3	4
$[U(C_9H_6Et)_3L]$	Me	187 ± 6	4,5
$[U(cp)_3L]$	$SiPh_3$	156 ± 18	6
	$GePh_3$	163 ± 19	6
	$SnPh_3$	156 ± 17	6
	$Fe(CO)_2(cp)$	129 ± 13	6
	$Ru(CO)_2(cp)$	169 ± 17	6
	cp	299 ± 10[b,d]	7
	Bu^i	D[(cp)$_3$U–cp] − (70 ± 35)[d]	8
	OBu	D[(cp)$_3$U–cp] + (247 ± 28)[d]	8
	Cl	D[(cp)$_3$U–cp] + (73 ± 31)[d]	8
$[UL_2]$	C_8H_8	344 ± 7[b,d]	7
		442 ± 16[b,d]	9
		190 ± 27[e,f]	10
	C_8H_7Bu	417 ± 13[b,d]	11
$[UL_4]$	$MeCO_2$	517 ± 7[b,d,g]	12
	Cl	422.6[f]	15
$[UCl_2L\{HB(dmpz)_3\}]$	OBu^t	460.5 ± 5.0	16
	$N(SiMe_3)_2$	334 ± 10[h]	16
	$CH(SiMe_3)_2$	295 ± 11[h]	16
	cp	362 ± 12[h]	16

[a] Determined using reaction-solution calorimetry unless indicated otherwise. [b] Mean bond-dissociation enthalpy. [c] Relies on D(U–O) = 481.2 kJ mol^{-1}. [d] Static bomb-combustion calorimetry. [e] $D_1(U\text{–}C_8H_8)$. [f] Gas-phase equilibrium. [g] Obtained using the estimate $\Delta H_{sub} = 130 \pm 20$ kJ mol^{-1}, together with $\Delta H_f^\circ = -2493 \pm 5$ kJ mol^{-1} (ref. 12) and auxiliary data.[13,14] [h] Relies on D(U–O) = 460.5 ± 5.0 kJ mol^{-1}.

spectra. The precession frequency of the mixture is given by equation (1), where $p_{U'}$ and p_U are the population weights of

$$\omega = p_{U'}\omega_{U'} + p_U\omega_U \qquad (1)$$

$[UCl_3\{HB(dmpz)_3\}]\cdot thf$ and $[UCl_3\{HB(dmpz)_3\}]$, respectively. If $\omega_{U'}$, ω_U and ω are known at each temperature, the populations $p_{U'}$ and p_U can be calculated, as well as the solution concentrations of the two species.

The NMR spectra of the complexes $[UCl_3\{HB(dmpz)_3\}]\cdot thf$ and $[UCl_3\{HB(dmpz)_3\}]$ were recorded at various temperatures (SUP 57023). The former were obtained in [$^2H_8$]thf, to be sure that one thf or [$^2H_8$]thf molecule was always co-ordinated, and the latter in deuteriated chloroform.

Results and Discussion

The enthalpy of reaction (2) ($\Delta H_r = -54.1 \pm 3.0$ kJ mol^{-1}),

$$[UCl_3\{HB(dmpz)_3\}]\,(cr) + HOCMe_2CH_2COMe\,(soln) \longrightarrow [UCl_2(OCMe_2CH_2COMe)\{HB(dmpz)_3\}]\,(soln) + HCl\,(soln) \qquad (2)$$

which was found to be rapid and quantitative, together with the enthalpy of solution of $[UCl_3\{HB(dmpz)_3\}]$ ($\Delta H_{soln} = -0.51 \pm 0.54$ kJ mol^{-1}), enabled $D(U\text{–}OCMe_2CH_2COMe) - D(U\text{–}Cl) = 61.6 \pm 8.6$ kJ mol^{-1} [equation (3)] to be

$$D(U\text{–}OCMe_2CH_2COMe) - D(U\text{–}Cl) = -\Delta H_r + \Delta H_{soln} + D(O\text{–}H) - D(H\text{–}Cl) \qquad (3)$$

determined. This difference relies also on the gas-phase value of D(H–Cl) (431.95 kJ mol^{-1})[13] and on D(O–H) [≈ D(Bu^{t}O–H) = 440 ± 8 kJ mol^{-1} [14]]. Although an experimental value of D(U–Cl) is not available for $[UCl_3\{HB(dmpz)_3\}]$, it can be estimated (based on that for UCl_4) as 422.6 kJ mol^{-1},[16] leading to $D(U\text{–}OCMe_2CH_2COMe) = 484.2 \pm 8.6$ kJ mol^{-1}.

The measurement of the enthalpy of reaction (4) (−50.9 ±

$$[UCl_2(dmpz)\{HB(dmpz)_3\}]\,(cr) + Bu^tOH\,(soln) \longrightarrow [UCl_2(OBu^t)\{HB(dmpz)_3\}]\,(soln) + Hdmpz\,(soln) \qquad (4)$$

2.2 kJ mol^{-1}), which was also found to be rapid and quantitative, together with the enthalpy of solution of $[UCl_2(dmpz)\{HB(dmpz)_3\}]$ [estimated as −4 ± 1 kJ mol^{-1}, on the basis of experimental data obtained for similar uranium(IV) complexes],[16] yielded the quantity D(U–OBu^t) – D(U–dmpz) = 67.9 ± 15.7 kJ mol^{-1} [equation (5)], taking

$$D(\text{U–OBu}^t) - D(\text{U–dmpz}) = -\Delta H_r + \Delta H_{\text{soln}} + D(\text{O–H}) - D(\text{dmpz–H}) \quad (5)$$

D(O–H) as 440 ± 4 kJ mol^{-1} [14] and D(dmpz–H), identified with D(N–H) in pyrrole, as 419 ± 15 kJ mol^{-1}.[23] By using D(U–OBu^t) = 460.5 ± 5.0 kJ mol^{-1},[16] which relies on the same anchor as above [*i.e.* D(U–Cl) = 422.6 kJ mol^{-1}], D(U–dmpz) = 393 ± 16 kJ mol^{-1} is finally obtained.

The U–OCMe$_2$CH$_2$COMe bond-dissociation enthalpy is some 24 kJ mol^{-1} higher than D(U–OBu^t). It is stressed that this conclusion does *not* depend on the value chosen for the anchor [422.6 kJ mol^{-1} for D(U–Cl)]. Therefore, despite the error that affects the difference, D(U–OCMe$_2$CH$_2$COMe) – D(U–OBu^t) = 23.7 ± 9.9 kJ mol^{-1}, it seems safe to conclude that the uranium–aldol bond-dissociation enthalpy is *at least* 14 kJ mol^{-1} higher than the uranium–Bu^{t}OH bond-dissociation enthalpy. This trend may be explained by assuming a bidentate co-ordination of the aldol ligand, in which the oxygen of the carbonyl group forms a dative bond to the metal centre. The different stretching frequencies of the carbonyl group of the aldol in the free and in the co-ordinated ligand, 1712 and 1660 cm^{-1},[19] respectively, are in line with that assumption. In order to find further support for the aldol bidentate co-ordination, we have decided to probe the energetics of another dative uranium–oxygen bond and check whether this information would be consistent with the above difference. The model compound used for this study was the complex [UCl$_3${HB(dmpz)$_3$}]·thf. It has been shown that in chloroform solution this adduct is in equilibrium with [UCl$_3${HB(dmpz)$_3$}].[17a] The U–thf bond-dissociation enthalpy was therefore obtained by determining the equilibrium constant of reaction (6) in deuteriated

$$[\text{UCl}_3\{\text{HB(dmpz)}_3\}]\cdot\text{thf (soln)} \rightleftharpoons [\text{UCl}_3\{\text{HB(dmpz)}_3\}]\text{ (soln)} + \text{thf (soln)} \quad (6)$$

chloroform, at several temperatures. NMR spectroscopy was used to evaluate the equilibrium concentrations of the two uranium species in solution.

The chemical shifts of the methyl groups in positions 3 and 5 and of the protons in position 4 for the pure compounds are presented in Fig. 1 and are fitted by linear correlations. To study the equilibrium concentrations, two solutions (A and B) with known initial quantities of [UCl$_3${HB(dmpz)$_3$}] (11.875 × 10^{-3}, A and 26.235 × 10^{-3} mol dm^{-3}, B) and thf (587.12 × 10^{-3}, A and 122.07 × 10^{-3} mol dm^{-3}, B) in deuteriated chloroform were prepared and their spectra recorded at various temperatures [260–325, A and 260–330 K, B] (SUP 57023). The chemical shifts observed, illustrated for solution A in Fig. 1, show that the concentration of the complex with co-ordinated thf increases with decreasing temperature. The population of each species was calculated as follows. The chemical shifts for the complexes with (δ′) and without (δ) thf as a function of T^{-1} are given by equations (7)–(9) and (10)–(12), respectively (r = the correlation

$$\delta'_{\text{Me}^3} = 4.943 - 2167.29\,T^{-1} \qquad r = 0.9997 \quad (7)$$

$$\delta'_{\text{H}^4} = 6.146 + 588.61\,T^{-1} \qquad r = 0.9948 \quad (8)$$

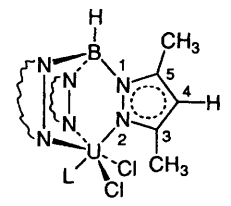
$$\delta'_{\text{Me}^5} = 0.538 + 180.67\,T^{-1} \qquad r = 0.9713 \quad (9)$$

$$\delta_{\text{Me}^3} = -0.929 - 1243.50\,T^{-1} \qquad r = 0.9994 \quad (10)$$

$$\delta_{\text{H}^4} = 7.907 - 76.75\,T^{-1} \qquad r = 0.9991 \quad (11)$$

$$\delta_{\text{Me}^5} = 2.524 + 269.55\,T^{-1} \qquad r = 0.9992 \quad (12)$$

coefficient). Using these linear regressions and the chemical shifts observed for solutions A and B, the ratios (ρ) between the populations of the two species were calculated for each peak under observation (SUP 57023). The values of ρ = (δ$_{eq}$ – δ′)/(δ$_{eq}$ – δ) (where δ$_{eq}$ = observed shift of the solution in equilibrium), together with the initial concentrations, enabled the calculation of the equilibrium concentrations and the equilibrium constant, K = [UCl$_3${HB(dmpz)$_3$}][thf]/[UCl$_3${HB(dmpz)$_3$}·thf], for each temperature (SUP 57023). The slopes and intercepts of the five van't Hoff plots relying on solutions A and B and on the data relative to each of the monitored peaks are presented in Table 2, together with the calculated values of ΔH and ΔS for the equilibrium (6). It must be stressed that the van't Hoff plots do not include all the determined values of K and although the molar concentrations of the solutions will vary with temperature, modifying ΔH and ΔS by *ca.* 1 kJ mol^{-1} and 5 J K^{-1} mol^{-1}, respectively, these changes are small compared with the experimental errors. As observed in Fig. 2, deviations from linearity occur at the lower temperature range, probably because the assumption of fast exchange of the thf molecule between the complex and the solution does not hold.



[UCl$_2$L{HB(dmpz)$_3$}]

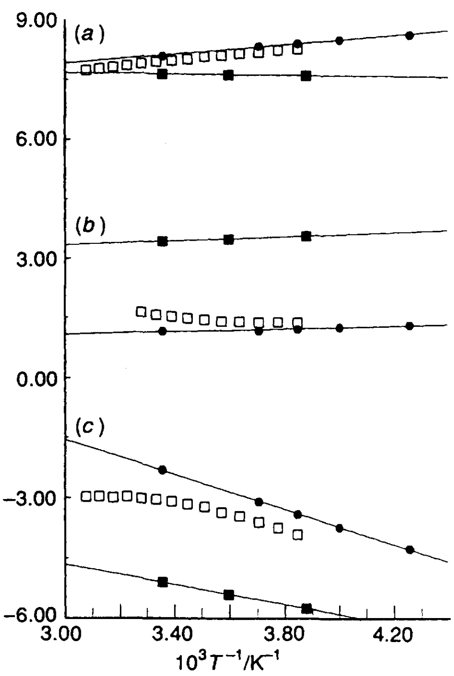


Fig. 1 Chemical shifts for (*a*) H^4, (*b*) Me^5 and (*c*) Me^3 *versus* T^{-1}; ●, [UCl$_3${HB(dmpz)$_3$}]·thf, ■, [UCl$_3${HB(dmpz)$_3$}] and □, solution A

The ΔH and ΔS values obtained from Me^3 and Me^5 peaks are in fair agreement, despite the fact that the initial concentration ratios [thf]$_0$/[UCl$_3${HB(dmpz)$_3$}]$_0$ in solutions A (49.4) and B (4.6) vary by a factor of ten. However, a large discrepancy between these data and the results derived from the H^4 chemical shifts is apparent. A problem that affects only the results relying on the H^4 chemical shifts is that the difference between the chemical shifts for the species with and without co-ordinated thf

Table 2 Entropy and enthalpy values for the equilibrium (6)

Solution	Peak	Intercept	Slope	r	ΔS/J K^{-1} mol^{-1}	ΔH/kJ mol^{-1}
A	Me^3	6.10 ± 0.26	−2282 ± 79	0.996	50.7 ± 2.2	18.97 ± 0.66
B	Me^3	5.91 ± 0.21	−2587 ± 63	0.998	49.1 ± 1.7	21.51 ± 0.52
A	H^4	21.8 ± 2.1	−6959 ± 671	0.982	182 ± 17	57.9 ± 5.6
B	H^4	17.8 ± 1.5	−6129 ± 468	0.983	148 ± 12	51.0 ± 3.9
A	Me^5	7.68 ± 0.39	−2895 ± 113	0.995	63.8 ± 3.2	24.07 ± 0.94

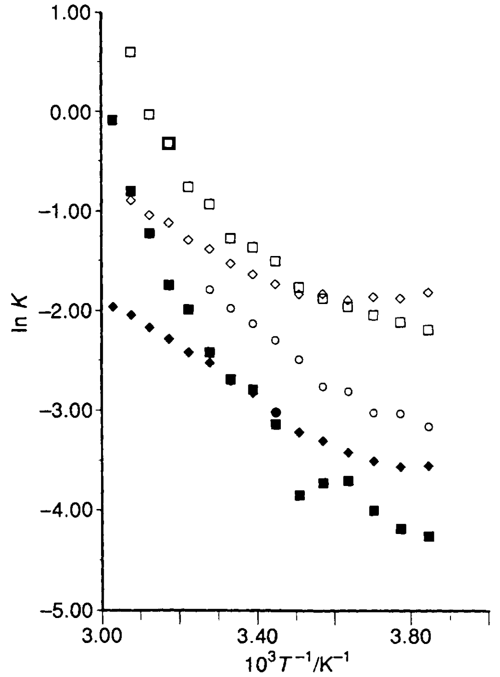


Fig. 2 van't Hoff plots of the equilibrium (6). Solution A: □, H^4, ◇, Me^3, ○, Me^5. Solution B: ■, H^4, ◆, Me^3

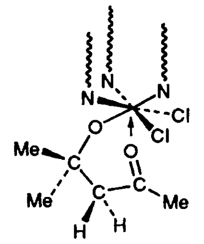
are very small. This can lead to larger errors when calculating the concentration ratio between the two species. For example, since the ratio $[thf]_0/[UCl_3\{HB(dmpz)_3\}]_0$ in solution A was ten times larger than in solution B, the ratio $[UCl_3\{HB(dmpz)_3\}\cdot thf]/[UCl_3\{HB(dmpz)_3\}]$ should be, for each temperature, larger in A. This is true for the values obtained from the Me^3 peak but not for the ones calculated from H^4. The data derived from the Me^3 and Me^5 chemical shifts are thus considered more reliable and lead to the average values ΔH = 21.5 ± 2.9 kJ mol^{-1} and ΔS = 54.5 ± 9.3 J K^{-1} mol^{-1}.

Another possible source of error in the equilibrium results is that the NMR spectra of $[UCl_3\{HB(dmpz)_3\}]\cdot thf$ were recorded in $[^2H_8]$thf (to be sure that one molecule of thf or $[^2H_8]$thf is always co-ordinated to the uranium centre), whereas all the other spectra were recorded in deuteriated chloroform. Can this change of solvent significantly affect the results? Knowing the susceptibilities of the two solvents it is possible to gauge their influence on the experimental values of the chemical shifts. The literature values for the molar magnetic susceptibility of chloroform are in the range $-(58.79\text{–}59.52) \times 10^{-6}$.[24] We are not aware of data for thf but, assuming that the difference in the molar magnetic susceptibilities of cyclopentane $[-(58.8\text{–}59.2) \times 10^{-6}$, ref. 24] and cyclopentadiene $[-(44.5\text{–}44.9) \times 10^{-6}$, ref. 24] is similar to that of furan $[-(43.1\text{–}44.8) \times 10^{-6}$, ref. 24] and thf, an estimate can be made at $-(57\text{–}58) \times 10^{-6}$. This small difference in the magnetic susceptibilities should not affect the values of the chemical shifts.

The uranium–ligand bond-dissociation enthalpies derived in the present study are summarized in Table 3. It is noted that the uranium–nitrogen bond-dissociation enthalpy in the complex $[UCl_2(dmpz)\{HB(dmpz)_3\}]$ is 60 kJ mol^{-1} higher than D(U–N) in $[UCl_2\{N(SiMe_3)_2\}\{HB(dmpz)_3\}]$ (Table 1), which is consistent with different bonding arrangements of the pyrazolyl and the amino groups. As mentioned above, there is solution NMR evidence that the pyrazolyl ligand is η^2-co-ordinated to the metal centre.[17] This type of bonding was also found, for example, in the complex $[U(cp)_3(C_3H_3N_2)]$.[25] Interestingly, the 60 kJ mol^{-1} difference in the above bond-dissociation enthalpies is close to the one found when comparing D(U–cp) (362 ± 12 kJ mol^{-1}, ref. 16) in $[UCl_2(cp)\{HB(dmpz)_3\}]$ with D(U–C) (295 ± 11 kJ mol^{-1}, ref. 16) in $[UCl_2\{CH(SiMe_3)_2\}\{HB(dmpz)_3\}]$.

Table 3 Uranium–ligand bond dissociation enthalpies in solution

Complex	L	D(U–L)/ kJ mol^{-1}
$[UCl_2L\{HB(dmpz)_3\}]$	$OCMe_2CH_2COMe$	484.2 ± 8.6
$[UCl_2L\{HB(dmpz)_3\}]$	dmpz	393 ± 16
$[UCl_3\{HB(dmpz)_3\}]\cdot L$	thf	21.5 ± 2.9



$[UCl_2(OCMe_2CH_2COMe)\{HB(dmpz)_3\}]$

As remarked above, the U–$OCMe_2CH_2COMe$ bond-dissociation enthalpy is some 24 kJ mol^{-1} higher than D(U–OBu^t). This difference is very close to the uranium–oxygen bond-dissociation enthalpy in the complex $[UCl_3\{HB(dmpz)_3\}]\cdot thf$, which is consistent with the bidentate co-ordination of the aldol ligand and in keeping with the suggestion by Domingos *et al.*,[19] based on IR and NMR spectra, that the ligand will form a regular σ bond through the alcohol function and a dative bond, using the carbonyl group. Other U–thf bond-dissociation enthalpies have been reported by Schock *et al.*[2] and Jemine *et al.*,[26] but they refer to uranium(III) complexes and fall in a higher range, *ca.* 40–70 kJ mol^{-1}.

With regard to the weak bond between the carbonyl group and the uranium centre, it is interesting that similar interactions have been found in lithium compounds.[27–29] For example, Klumpp[27] reported that the enthalpy of alcoholysis of $Li(C_6H_4OMe\text{-}p)$ is about 15 kJ mol^{-1} more exothermic than the alcoholysis of the *ortho* analogue. The difference was attributed to the intramolecular interaction between the electropositive lithium and the methoxy oxygen in the *ortho* compound.

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