Alkoxide and Aryloxide Derivatives of Actinide(IV) Polypyrazolylborates. Part II. Uranium(IV) Bis[hydrotris(pyrazol-1-yl)borate] Complexes*

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Abstract

The complexes $U(HBpz_3)_2(OR)_xCl_{2-x}$ (pz = pyrazol-1-yl; $x = 1$, 2; R = Bu^t, Pr^i, and C_6H_2-2,4,6-Me_3) have been prepared from the reaction of $U(HBpz_3)_2Cl_2$ with sodium alkoxides and aryloxides in the ratio 1:1 and 1:2. The temperature dependence of the ^1H NMR of the complexes has been studied. Fluxional behaviour was observed for the poly(pyrazol-1-yl)borate ligands and the barrier to rotation about the U–B axis was estimated for the complexes $U(HBpz_3)_2(OBu^t)_2$ ($\Delta G^{\ddagger} = 53 \pm 4$ kJ mol^{-1}) and $U(HBpz_3)_2(OC_6H_2$-2,4,6-$Me_3)Cl$ ($\Delta G^{\ddagger} = 39 \pm 3$ kJ mol^{-1}). ^1H NMR studies also indicated restricted rotation about the U–O–R bonds in the complexes $U(HBpz_3)_2(OR)Cl$ ($\Delta G^{\ddagger} = 62 \pm 5$ kJ mol^{-1}) and $U(HBpz_3)_2(OR)_2$ ($\Delta G^{\ddagger} = 62 \pm 4$ kJ mol^{-1}) with R = C_6H_2-2,4,6-Me_3.

Introduction

Since the discovery in 1966 of the hydridotris(pyrazol-1-yl)borate ligand by Trofimenko [1] an extensive d-transition metal chemistry based on this ligand has emerged. Most of the studies have been with first-row transition metals and molybdenum [2]. The temperature dependence of the ^1H NMR spectra of some complexes was also studied and important information was obtained about the fluxional behaviour of this ligand [3–5]. Fewer complexes have been prepared with lanthanides [6] and actinides [7] and only a few reactivity studies have been made [7].

In this work the reactions of the compound $U(HBpz_3)_2Cl_2$ [8] with sodium t-butoxide, sodium isopropoxide, and sodium 2,4,6-trimethylphenoxide were studied. Special attention was given to the ^1H NMR studies; the spectra obtained for the complexes in several solvents and the variable temperature measurements made gave important information about the stereochemical non-rigidity of the complexes. The dynamic behaviour of the '$(HBpz_3)_2$' moiety and of the other ligands attached to the central atom was ascertained.

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Experimental

All experimental details concerning physical and analytical measurements and materials and methods were as described in the accompanying paper (Part I). $U(HBpz_3)_2Cl_2$ was prepared by the published method [8].

Synthesis

$U(HBpz_3)_2(OBu^t)Cl$ (1)

178 mg (0.24 mmol) of $U(HBpz_3)_2Cl_2$ and 23.2 mg (0.24 mmol) of $NaOBu^t$ in toluene (10 ml) were stirred overnight at room temperature. The suspension was centrifuged and the supernatant was vacuum dried. The pale green solid obtained was washed with n-pentane and vacuum dried.

$U(HBpz_3)_2(OBu^t)_2$ (2)

288 mg (0.39 mmol) of $U(HBpz_3)_2Cl_2$ and 75.3 mg (0.78 mmol) of $NaOBu^t$ in THF (10 ml) were stirred overnight at room temperature. The suspension was centrifuged and the solution was vacuum dried. The solid obtained was washed with a small amount of n-pentane and then extracted into 10 ml of n-pentane. The n-pentane solution was filtrated and vacuum dried, giving a green solid.

$U(HBpz_3)_2(OPr^i)Cl$ (3)

The pale green solid was obtained as described for **1** using 325 mg (0.44 mmol) of $U(HBpz_3)_2Cl_2$ and 36.3 mg (0.44 mmol) of $NaOPr^i$ in THF (15 ml).

$U(HBpz_3)_2(OPr^i)_2$ (4)

The dark green solid was prepared as described for **2** starting from 180 mg (0.24 mmol) of $U(HBpz_3)_2Cl_2$ and 40 mg (0.48 mmol) of $NaOPr^i$ in toluene (10 ml).

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TABLE I. Analytical and Physical Data for the $U(HBpz_3)_2Cl_2$ Derivatives

Complex	Yield (%)	Analysis[a] (%)			IR (cm^{-1})		Electronic spectrum (nm)
		C	H	N	ν(B–H)	ν(U–Cl)	
$U(HBpz_3)_2(OBu^t)Cl$ (1)	60	35.4 (34.2)	4.0 (3.8)	21.5 (21.8)	2450	235	602sh, 618w, 642m, 730w,br, 958sh, 1011s, 1026s, 1043s, 1076s, 1129sh, 1271s, 1383s, 1469s[b, c]
$U(HBpz_3)_2(OBu^t)_2$ (2)	70	38.3 (38.5)	5.1 (4.7)	19.9 (20.8)	2440		616w, 648w, 667w, 776w,br, 969m, 1027s, 1100s, 1255s, 1393s[b, c, d]
$U(HBpz_3)_2(OPr^i)Cl$ (3)	52	33.0 (33.2)	3.6 (3.6)	21.9 (22.2)	2470	240	605sh, 619w, 644m, 733w,br, 764sh, 962sh, 1026s, 1071sh, 1269s, 1383s, 1460sh, 1474s[c]
$U(HBpz_3)_2(OPr^i)_2$ (4)	58	37.0 (36.9)	4.6 (4.4)	20.8 (21.4)	2440		615w, 648w, 658sh, 776w,br, 1025vs, 1074vs, 1261s, 1389s[b]
$U(HBpz_3)_2(OC_6H_2\text{-}2,4,6\text{-}Me_3)Cl$ (5)	60	38.7 (38.8)	3.8 (3.7)	20.2 (20.1)	2470	232	659s, 671sh, 768w, 790sh, 996s, 1055s, 1082s, 1145s, 1340m, 1465m, 1514sh[c]
$U(HBpz_3)_2(OC_6H_2\text{-}2,4,6\text{-}Me_3)_2$ (6)	75	46.1 (46.3)	4.7 (4.5)	17.6 (17.9)	2450		664s, 1005sh, 1076s, 1145m, 1340m,br[c]

[a]Required values in parentheses. [b]In toluene. [c]In THF. [d]In n-pentane.

TABLE II. ^1H NMR Spectroscopic Data for the $U(HBpz_3)_2Cl_2$ Derivatives[a, b]

Complex	$HBpz_3$[c]				Other resonances
	H(3)	H(4)	H(5)	BH	
$U(HBpz_3)_2(OBu^t)Cl$ (1)	27.38(6H)	6.41(6H)	−0.43(6H)	−18.28(2H)	71.94(9H,CH_3)
$U(HBpz_3)_2(OBu^t)_2$[d] (2)				−13.37(2H)	15.45(18H,CH_3)
$U(HBpz_3)_2(OPr^i)Cl$ (3)	29.16(6H)	6.39(6H)	−0.59(6H)	−18.59(2H)	188.97(1H,CH), 71.89(6H,CH_3)
$U(HBpz_3)_2(OPr^i)_2$ (4)	26.15(6H)	6.31(6H)	1.35(6H)	−13.79(2H)	53.27(2H,CH), 14.52(12H,CH_3)
$U(HBpz_3)_2(OC_6H_2\text{-}2,4,6\text{-}Me_3)Cl$[e] (5)		5.62(6H)	−1.76(6H)	−20.26(2H)	44.94,26.14(3H,3H; *o*-CH_3) 41.23,37.94(1H,1H; *m*-H) 23.24(3H, *p*-CH_3)
$U(HBpz_3)_2(OC_6H_2\text{-}2,4,6\text{-}Me_3)_2$ (6)	28.66(6H)	6.54(6H)	−0.05(6H)	−17.22(2H)	16.30,14.69(2H,2H; *m*-H) 14.96,4.20(6H,6H; *o*-CH_3) 7.71(6H, *p*-CH_3)

[a]All the chemical shifts are reported in ppm from TMS; downfield shifts are positive; T = 300 K. [b]All spectra were recorded in toluene-d_8 except for complex **6** which was recorded in chloroform-d_1. [c]The assignments are based on the ^1H NMR spectrum of $U(HBpz_3)_2Cl_2$ in CD_2Cl_2. [d]At 300 K no signals could be observed for the protons of the polypyrazolyl ligands; see Fig. 1 for low temperature spectrum. [e]At 300 K no H(3) signal could be observed; see Fig. 3 for low temperature spectrum.

$U(HBpz_3)_2(OC_6H_2\text{-}2,4,6\text{-}Me_3)Cl$ (5)

The yellow–green solid was prepared by the same procedure as reported for **1** using 186 mg (0.25 mmol) of $U(HBpz_3)_2Cl_2$ and 40 mg (0.25 mmol) of $NaOC_6H_2$-2,4,6-Me_3 in THF (15 ml).

$U(HBpz_3)_2(OC_6H_2\text{-}2,4,6\text{-}Me_3)_2$ (6)

The beige solid was obtained in the same way, using 116 mg (0.16 mmol) of $U(HBpz_3)_2Cl_2$ and 50 mg (0.32 mmol) of $NaOC_6H_2$-2,4,6-Me_3 in THF (15 ml).

The results of the physical and analytical measurements are summarized in Table I (analytical and physical data) and Table II (^1H NMR data).

Results and Discussion

Tetrahydrofuran or toluene suspensions of $U(HBpz_3)_2Cl_2$ react rapidly with sodium alkoxides and aryloxides according to eqn. (1):

$$U(HBpz_3)_2Cl_2 + xNaOR \xrightarrow[RT]{THF/tol} U(HBpz_3)_2(OR)_xCl_{2-x} + xNaCl \quad (1)$$

R = Bu^t, Pr^i and C_6H_2-2,4,6-Me_3

All the complexes are soluble in aromatic solvents except complex **6**, which is only soluble in ethers

and halogenated solvents. The complexes **2** and **4** are also soluble in aliphatic hydrocarbons.

The ^1H NMR of the starting material $U(HBpz_3)_2Cl_2$ in CD_2Cl_2* presents four bands centered at 21.63 [6H, doublet, H(3)], 7.36 [6H, triplet, H(4)], 3.58 [6H, doublet, H(5)], and −10.36 ppm (2H, broad, B–H). This pattern clearly shows that the ligands are tridentate and that all pyrazol-1-yl rings are equivalent. This equivalence can be explained in terms of the fluxional behaviour of these ligands which has already been described for several transition metal compounds on the basis of a non-dissociative trigonal twist mechanism (rotation of the polypyrazol-1-yl ligands about the U–B axis) [4, 5].

The ^1H NMR spectra at 300 K for the mono-substituted t-butoxide derivative **1**, for the mono- and di-substituted isopropoxide derivatives **3**, **4**, and for the disubstituted aryloxide derivative **6** (Table II) display a pattern for the protons of the polypyrazol-1-yl ligands quite similar to the one obtained for the starting material $U(HBpz_3)_2Cl_2$. However, the complexes **2** and **5** present spectra at room temperature (Table II) where all or some of the resonances of the pyrazol-1-yl ring protons have collapsed. This suggests that exchange processes are occurring. In fact, variable temperature ^1H NMR studies gave important information on the structural dynamics of these complexes.

*Variable Temperature ^1H NMR Studies***

The ^1H NMR spectrum of complex **2** at 320 K shows that the H(4), H(5) and B–H protons of the two polypyrazol-1-yl ligands are equivalent. No signal for the H(3) protons was observed. On lowering the temperature to 280 K, three resonances in the ratio 1:1:1 appear for the H(3) protons (58.00, 33.74, 18.60 ppm) and two different signals in the ratio 2:1 appear for the H(4) (7.97, 3.40 ppm) and also for the H(5) (−8.81, −16.90 ppm) protons. The B–H continue to display only one signal (−14.25 ppm). At 260 K further splitting for the H(4) and H(5) protons is observed and three signals in the ratio 1:1:1 appear for each of them. The three resonances for the H(4) protons are at 10.33, 8.04 and 2.79 ppm, whereas the resonances for the H(5) protons are at −9.10, −9.99 and −18.21 ppm. Further lowering of the temperature does not cause any more splitting and the slow exchange limiting spectrum at 190 K (Fig. 1) presents nine signals for the protons H(3), H(4), and H(5) and one signal for the B–H protons. This pattern clearly indicates that the three pyrazol-1-yl rings of each ligand are non-

*The shifts are in ppm from TMS; downfield shifts are positive; T = 300 K.

**In all studies, spectral changes were found to be independent of concentration and were completely reversible.

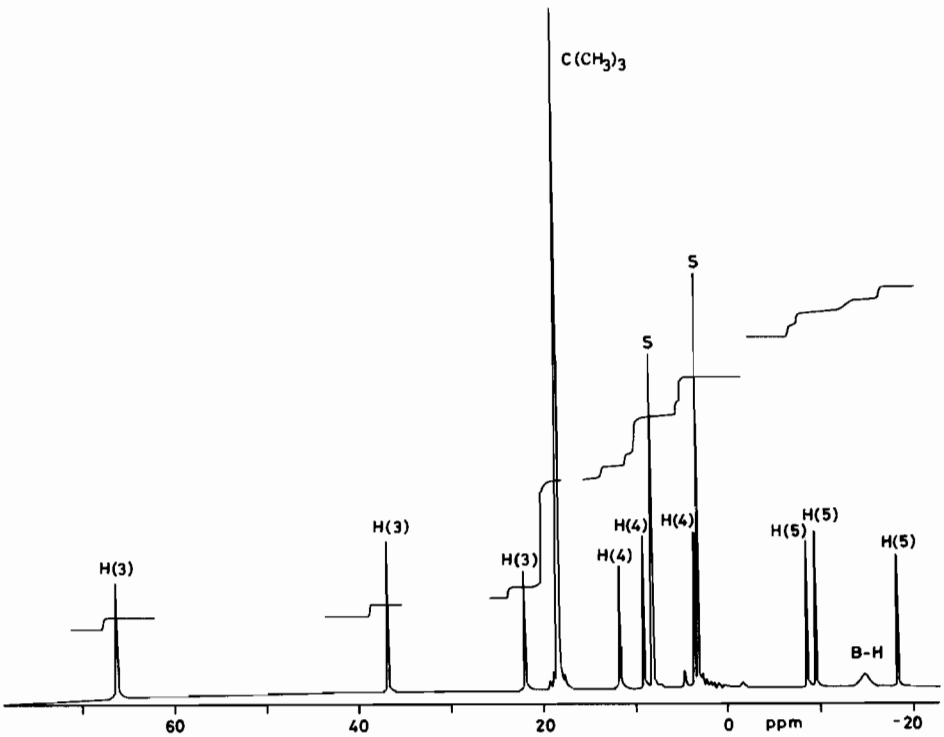

Fig. 1. ^1H NMR spectrum of $U(HBpz_3)_2(OBu^t)_2$ (**2**) as a solution in toluene-d_8 at 190 K. The resonances labelled S are due to the solvent.

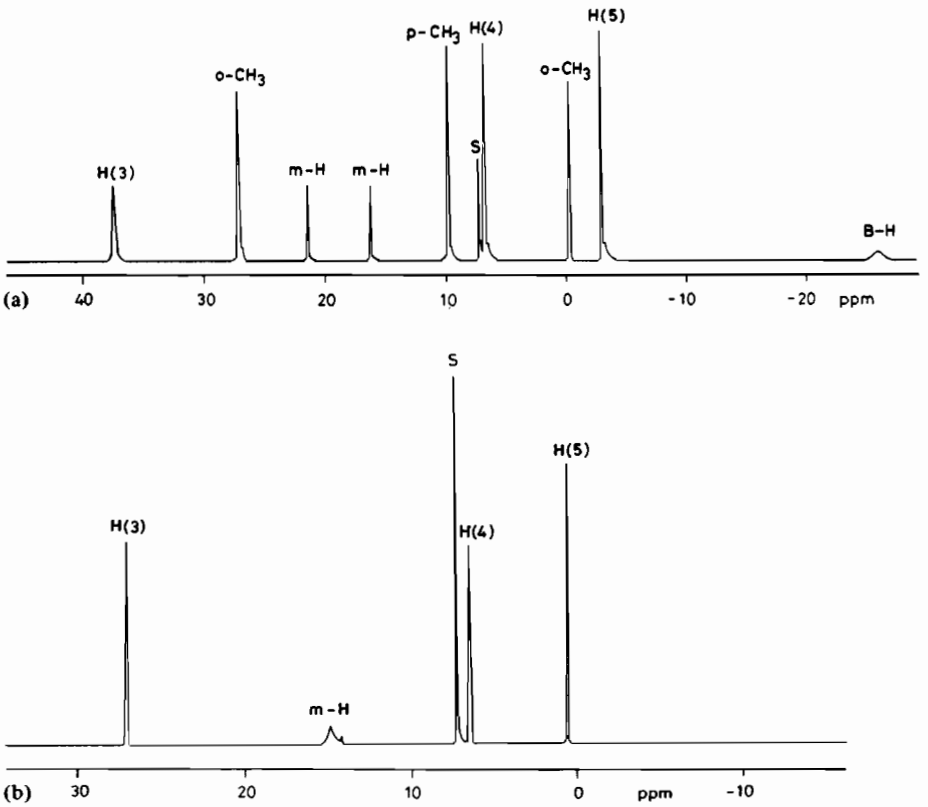

Fig. 2. ^{1}H NMR spectra of U(HBpz$_3$)$_2$(OC$_6$H$_2$-2,4,6-Me$_3$)$_2$ (6) as a solution in chloroform-d$_1$. The resonances labelled S are due to the solvent: (a) T = 215 K; (b) T = 325 K.

equivalent and this is indicative of restricted rotation of these ligands about the U–B axis.

The barrier to rotation can be estimated from the standard coalescence point formalism, provided the frequency separation of the exchanging sites in the absence of exchange can be estimated at the coalescence temperature [9]. The chemical shifts of the H(4) resonances were found to obey an approximate Curie relationship (a plot of δ *versus* T^{-1} was linear) below the coalescence temperature (270 K) and an extrapolation of a least-squares fit of these data ($\delta_1 = 9.0 + 0.4 \times 10^3\ T^{-1}$; $\delta_2 = 9.6 - 0.4 \times 10^3\ T^{-1}$) yields $\Delta\nu$ = 173 Hz at this temperature. The $\Delta G^{\ddagger}$ for rotation about the U–B axis in complex 2 was estimated to be 53 ± 4 kJ mol^{-1}. The same $\Delta G^{\ddagger}$ value was obtained by using the values for the absorption resonances of the H(5) protons ($\delta_1 = -3.9 - 1.4 \times 10^3\ T^{-1}$; $\delta_2 = -4.2 - 1.5 \times 10^3\ T^{-1}$; $\Delta\nu$ = 54 Hz at T_c = 265 K).

The line shape of the absorption resonance for the protons of the two OBu^t ligands is temperature independent and the chemical shift was found to obey an approximate Curie relationship ($\delta = 8.6 + 2.1 \times 10^3\ T^{-1}$).

The ^{1}H NMR spectra at 300 K for complexes 1, 3 and 4 (Table II) indicate a fluxional behaviour for the tridentate polypyrazol-1-yl borate ligands. Upon lowering the temperature to 190 K, the absorption resonances for the protons of the polypyrazol-1-yl ligands broaden and collapse for complex 1 but no splitting is observed; for complexes 3 and 4 the resonances, especially the one assigned to the H(3) protons, broaden but no collapse is observed. This is indicative that the rotation about the U–B axis is being hindered as we decrease the temperature; the coalescence temperature could not be reached, so $\Delta G^{\ddagger}$ could not be calculated. Large chemical shifts are observed for the OBu^t ligand in complex 1 and for the OPr^i ligand in complexes 3 and 4 and variable temperature ^{1}H NMR studies indicate that the line shapes are essentially temperature independent and all the chemical shifts were found to obey approximate Curie relationships.

The observed ^{1}H NMR spectra for complex 6 are shown in Fig. 2 at 325 and 215 K. The pattern obtained at 300 K (Table II) for the protons of the polypyrazol-1-yl ligands is maintained in all the temperature range studied (325–215 K) and no special broadening was observed. However, the pattern obtained at 300 K for the protons of the aryloxide groups (Table II) is not maintained and upon raising the temperature the absorption resonances of the *m*-H and *o*-CH$_3$ protons collapse and at 325 K only one signal appears for the *m*-H protons,

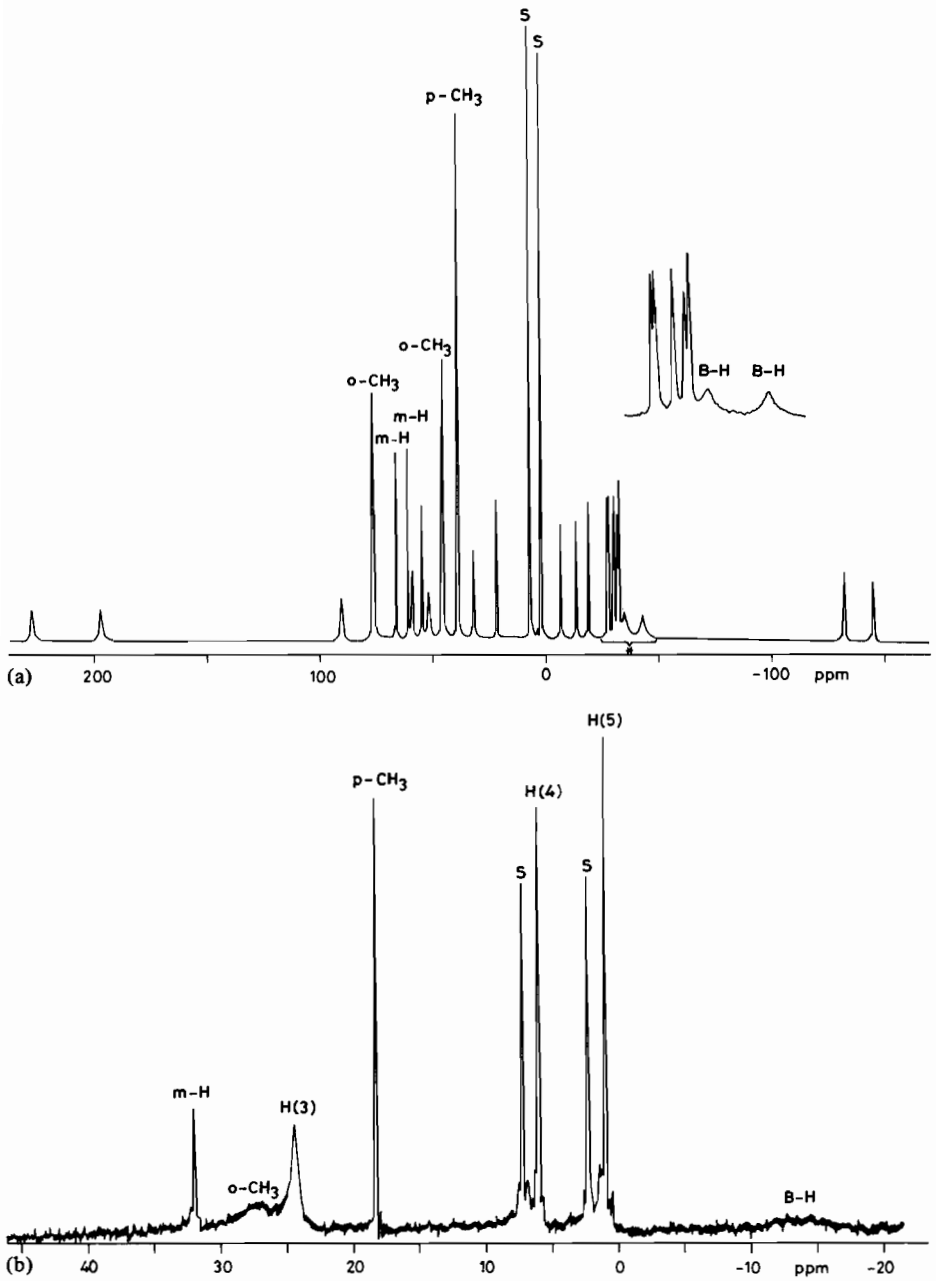

Fig. 3. ^{1}H NMR spectra of U(HBpz$_3$)$_2$(OC$_6$H$_2$-2,4,6-Me$_3$)Cl (**5**) as a solution in toluene-d$_8$. The resonances labelled S are due to the solvent; the resonances labelled with an asterisk are expanded in the insert: (a) T = 190 K; (b) T = 375 K.

at δ = 14.96 ppm (Fig. 2b). In the low temperature limiting spectrum (Fig. 2a) two non-equivalent signals in a 1:1 intensity ratio appear for the *o*-CH_3 protons at δ_1 = 27.21 and δ_2 = −0.33 ppm and also two non-equivalent signals in a 1:1 intensity ratio appear for the *m*-H protons at δ_1 = 21.47 and δ_2 = 16.27 ppm. For the *p*-CH_3 protons at δ_1 = 21.47 and δ_2 = 16.27 ppm. For the *p*-CH_3 protons of the aryloxide groups only one signal is observed in all the temperature range studied and its chemical shift was found to obey an approximate Curie relationship (δ = 2.3 + $1.6 \times 10^3\ T^{-1}$). The behaviour observed for the absorption resonance of the *p*-CH_3 protons is indicative of the equivalence of the two aryloxide groups, and so the splitting observed for the *o*-CH_3 and *m*-H protons is indicative of restricted rotation about the U–O–R bonds. The barrier to rotation was estimated from the temperature dependence of the chemical shifts of the *m*-H protons below the coalescence temperature ($\delta_1 = 4.1 + 3.7 \times 10^3\ T^{-1}$; $\delta_2 = 10.7 + 1.2 \times 10^3\ T^{-1}$); this yields by extrapolation $\Delta\nu$ = 113 Hz at T_c = 312 K and $\Delta G^{\ddagger}$ = 62 ± 4 kJ mol^{-1}.

The ^1H NMR spectra at several temperatures obtained for complex **5** are presented in Fig. 3. At 375 K (Fig. 3b) the H(3), H(4), H(5) and B–H protons of the polypyrazol-1-yl ligands are equivalent and this indicates that the ligands are tridentate and fluxional. Upon lowering the temperature the proton resonances broaden and collapse and the slow exchange limiting spectrum at 190 K (Fig. 3a) consists of twenty resonances for the protons of the polypyrazol-1-yl ligands (18 from the pyrazol-1-yl rings and 2 from the B–H protons) with the same intensity. Due to the complexity of this spectrum the assignments for the H(3), H(4) and H(5) protons were not made. Nevertheless, the $\Delta G^{\ddagger}$ for rotation about the U–B axis could be estimated from the behaviour of the B–H protons resonance with temperature. On lowering the temperature this resonance broadens and at 210 K two non-equivalent resonances in a 1:1 intensity ratio are observed at $\delta_1 = -30.10$ and $\delta_2 = -37.21$ ppm. The chemical shifts of the B–H resonances were found to obey an approximate Curie relationship below the coalescence temperature ($T_c = 215$ K; $\delta_1 = 18.7 - 11.8 \times 10^3\ T^{-1}$; $\delta_2 = 18.6 - 10.3 \times 10^3\ T^{-1}$) and an extrapolation of these data yields $\Delta\nu = 551$ Hz and $\Delta G^{\ddagger} = 39 \pm 3$ kJ mol^{-1}. The pattern observed for the aryloxide group at room temperature (Table II) is indicative of restricted rotation about the U–O–R bonds. Upon raising the temperature until 375 K the *o*-CH_3 protons become equivalent and only one signal appears at $\delta = 27.00$ ppm. The same behaviour is observed for the *m*-H protons ($\delta = 31.44$ ppm). The barrier to rotation about the U–O–R bonds was evaluated from the temperature dependence of the chemical shifts of the *o*-CH_3 below the coalescence temperature ($\delta_1 = -8.6 + 16.1 \times 10^3\ T^{-1}$; $\delta_2 = -6.1 + 9.8 \times 10^3\ T^{-1}$). This yields by extrapolation $\Delta\nu = 1254$ Hz and $\Delta G^{\ddagger} = 62 \pm 5$ kJ mol^{-1}, at $T_c = 347$ K. The same value was obtained from the *m*-H protons of the aryloxide rings ($\delta_1 = -1.5 + 12.9 \times 10^3\ T^{-1}$; $\delta_2 = 0.4 + 11.4 \times 10^3\ T^{-1}$; $\Delta\nu = 218$ Hz at $T_c = 325$ K).

Hindered rotation of aryloxide groups has also been observed in the complexes $U[HB(3,5\text{-}Me_2pz)_3](OC_6H_2\text{-}2,4,6\text{-}Me_3)_xCl_{3-x}$ ($x = 1$, $\Delta G^{\ddagger} = 49 \pm 4$ kJ mol^{-1}; $x = 2$, $\Delta G^{\ddagger} = 41 \pm 3$ kJ mol^{-1}) [10].

Conclusions

The complex $U(HBpz_3)_2Cl_2$ is fairly reactive and stable derivatives with alkoxide and aryloxide could be prepared. Variable temperature ^1H NMR studies on $U(HBpz_3)_2Cl_2$ showed fluxional behaviour for the $HBpz_3^-$ ligands in all the temperature range studied. However, substitution of the chloride ligand by bulkier ligands decreases the rate of the exchange process for the $HBpz_3^-$ ligands in complexes **1**, **2**, **3**, **4** and **5**, and it was possible to record the limiting static spectra for complexes **2** and **5**. The patterns obtained for the static spectra depend on the symmetry of the complexes.

The degree of substitution of the chloride ligands allied to the structural nature of the new ligands seem to determine the rate of the dynamic processes. This is shown by the variable temperature ^1H NMR spectra obtained for the monosubstituted **5** and disubstituted **6** aryloxide complexes. Complex **5**, at room temperature, seems to be reasonably sterically congested because the rotation of the aryloxide about the U–O–R bonds is hindered and the $HBpz_3^-$ ligands rotate slowly about the U–B axis (H(3) resonance is collapsed). For complex **6**, in the temperature range studied, the $HBpz_3^-$ ligands rotate freely about the U–B axis. However, as was observed, the rotation of the aryloxides around the U–O–R bonds is hindered and their conformation should be such that there is no interaction with the $HBpz_3^-$ ligands as with the monosubstituted complex **5**.

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