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Synthesis and Structural Characterization of Unprecedented Bis-Asymmetric Heteroscorpionate U(III) Complexes: $[U\{\kappa^3\text{-}H_2B(pz^{tBu,Me})(pz^{Me,tBu})\}_2I]$ and $[U\{\kappa^3\text{-}H_2B(pz^{tBu,Me})(pz^{Me2})\}_2I]$

Leonor Maria, Ângela Domingos, and Isabel Santos*

Departamento de Química, ITN, Estrada Nacional 10, 2686-953 Sacavém Codex, Portugal

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$[UI_3(THF)_4]$ reacts at room temperature with 2 equiv of $KBp^{tBu,Me}$, in toluene, yielding $[U\{\kappa^3\text{-}H(\mu\text{-}H)B(pz^{tBu,Me})(pz^{Me,tBu})\}_2I]$ (**1**). This unprecedented complex, stabilized by two asymmetric heteroscorpionate ligands, is formed due to an isomerization process promoted in situ by the metal center. To find a general method for preparing this type of compound, we synthesized the novel asymmetric $K[H_2B(pz^{tBu,Me})(pz^{Me2})]$, and by a straightforward salt metathesis with $[UI_3(THF)_4]$ the novel bis-asymmetric complex $[U\{\kappa^3\text{-}H(\mu\text{-}H)B(pz^{tBu,Me})(pz^{Me2})\}_2I]$ (**2**) was isolated and characterized in the solid state and in solution. As indicated by X-ray crystallographic analysis, the U(III) in **1** and **2** is seven-coordinated by two tridentate asymmetric dihydrobis(pyrazoly)borates and by an iodide. In both cases, the coordination geometry around the metal is very distorted, the pentagonal bipyramid being the one which better describes the arrangement of the atoms around the U(III). An approximate C_2 axis can be defined in the solid state, and is maintained in solution as indicated by the ^1H NMR spectrum of **1** and **2**. In the course of attempting to crystallize some of the compounds, monocrystals of the dimer $[U\{\kappa^3\text{-}Bp^{tBu,Me}\}(Hpz^{tBu,Me})I(\mu\text{-}I)]_2$ (**3**) were isolated. In this compound each U(III) atom is seven-coordinated by one $\kappa^3\text{-}Bp^{tBu,Me}$, by one terminal and by two bridging iodide ligands, and by a monodentate $Hpz^{tBu,Me}$, exhibiting a distorted 4:3 tetragonal base-trigonal geometry.

Introduction

The interest in poly(pyrazolyl)borates, as complexation agents for a broad range of metal ions, has advanced considerably over the past few years, specially for larger metal ions, such as lanthanides and actinides.[1−3] From all the scorpionate ligands, homoscorpionates (Tp) have been the more extensively studied.[1−3] For f elements this choice was mainly determined by the large size of the metal ions and by the extreme steric crowding which can be achieved with $Tp^{R,R'}$ ligands. The easy manipulation of the 3- or 5-substituents of the pyrazolyl rings (R, R′) allows a fine-tuning of the steric and/or electronic properties of this class of ligands, and mono-, bis-, or even tris-Tp type f complexes have been the subjects of extensive study.[2,3] Despite the plethora of Tp-based f complexes, very little work has been carried out with the heteroscorpionates $Bp^{R,R'}$ ($R = R'$ or $R \neq R'$) and none with asymmetric scorpionates.[1−7] The main reason is the regioselectivity of the reaction between MBH_4 and the 3,5-disubstituted pyrazoles, a limitation for the synthesis of asymmetric scorpionates. During the synthesis of this class of ligands, the boron−nitrogen bond formation and the concerted loss of hydrogen proceeds through the less sterically encumbered transition state.[1]

In the course of our systematic synthetic study of U(III) complexes with dihydrobis(pyrazolyl) ($Bp^{tBu,Me}$, Bp^{Me2}, Bp^{iPr2}) and bis(mercaptoimidazolyl)borates ($M[R(H)B(tim^{Me})_2] \equiv Bm^{Me}$) we have found that the nature of the compounds and their structures are not only affected by the bulkiness of the 3-R substituents, and by the size of the chelate rings around the metal, but also by the symmetry of the 3-R groups.[4,6−8]

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* Author to whom correspondence should be addressed. E-mail: isantos@itn.pt.

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As a result, tris- or mono-Bp and bis-Bm^{Me} type U(III) complexes have been characterized.[4,6-8]

Here we wish to report the first examples of bis-asymmetric heteroscorpionate type f complexes: $[U\{\kappa^3\text{-}H(\mu\text{-}H)B(pz^{tBu,Me})(pz^{Me,tBu})\}_2I]$ (**1**) and $[U\{\kappa^3\text{-}H(\mu\text{-}H)B(pz^{tBu,Me})(pz^{Me2})\}_2I]$ (**2**). Complex **1** has been obtained due to an isomerization rearrangement of the $Bp^{tBu,Me}$ at the U(III) center, while complex **2** has been prepared by a metathesis reaction of $[UI_3(THF)_4]$ with the novel asymmetric heteroscorpionate $K[H_2B(pz^{tBu,Me})(pz^{Me2})]$. The solid-state and solution structures of these compounds have been studied by X-ray crystallography and by ^1H NMR spectroscopy. During the attempts to crystallize some of our compounds, monocrystals suitable for X-ray crystallography of the dimeric complex $[U\{\kappa^3\text{-}Bp^{tBu,Me}\}(Hpz^{tBu,Me})I(\mu\text{-}I)]_2$ (**3**) were obtained. The structure of **3** will also be reported herein.

Experimental Section

General Procedures. All preparations and manipulations were carried out under inert atmosphere, using standard Schlenk techniques and a dry nitrogen filled glovebox. Toluene, tetrahydrofuran, and *n*-hexane were distilled from Na under nitrogen, immediately prior to use, and deoxygenated. Acetonitrile-d_3 was distilled from P_2O_5 and stored under molecular sieves; benzene-d_6 and toluene-d_8 were dried over sodium−benzophenone. $[UI_3(THF)_4]$ was prepared as previously reported.[9] The asymmetric $M[H_2B(pz^{tBu,Me})(pz^{Me2})]$ (M = Li, K) ligands were synthesized by a slightly modification of the procedure described by Parkin et al.[10]

^1H NMR spectra were recorded on a Varian Unity 300 MHz spectrometer.^1H chemical shifts were referenced with the residual solvent resonances relative to tetramethylsilane. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 577 spectrophotometer. Absorption electronic spectra in toluene solutions were recorded on a Cary 2390 Varian spectrometer. Carbon, hydrogen, and nitrogen elemental analyses were performed on EA110 CE Instruments automatic analyzer.

Synthesis of $Li[H_2B(pz^{tBu,Me})(pz^{Me2})]$. A solution of $LiBH_4$ (600 mg, 27.3 mmol) in THF/toluene (14/16 cm^3) was added to a mixture of Hpz^{Me2} (2.62 g, 27.3 mmol) and $Hpz^{tBu,Me}$ (3.95 g, 28.6 mmol). The mixture was stirred overnight at room temperature. The solvent was removed in a vacuum; toluene (20 cm^3) was added, and the resulting mixture was refluxed for 1 day. After evaporation of the solvent, the crude product was purified by three sucessive recrystallizations using toluene/*n*-hexane. The solid obtained was vacuum dried and analyzed (2.06 g, 8.19 mmol, 30% yield). IR (Nujol, $\nu(cm^{-1})$): 2440, 2250 (ν(B−H)). ^1H NMR (CD_3CN, 21 °C): 5.69 (1H, s, CH-pz), 5.59 (1H, s, CH-pz), 2.23 (3H, s, Me), 2.22 (3H, s, Me), 2.15 (3H, s, Me),1.25 (9H, s, ^tBu).

Synthesis of $K[H_2B(pz^{tBu,Me})(pz^{Me2})]$. A mixture of $Li[H_2B(pz^{Me2})(pz^{tBu,Me})]$ (746 mg, 2.96 mmol) and KOAc (581 mg, 2.96 mmol) in CH_3CN (20 cm^3) was stirred overnight at 50 °C. The mixture was centrifuged to separate the solid residues, and the solvent was removed under a vacuum. The product obtained was washed with *n*-hexane and dried in a vacuum. The potassium salt of the asymmetric ligand was obtained as a white solid in 62% yield (520 mg, 1.83 mmol). Anal. Calcd for $C_{13}H_{22}BN_4K$: C, 54.93; H, 7.80; N, 19.71. Found: C, 54.09; H, 7.16; N, 19.15. IR (Nujol, $\nu(cm^{-1})$): 2440, 2265 (ν(B−H)). ^1H NMR (CD_3CN, 21 °C): 5.64 (1H, s, CH-pz); 5.54 (1H, s, CH-pz); 2.25 (3H, s, Me); 2.20 (3H, s, Me); 2.07 (3H, s, Me); 1.19 (9H, s, ^tBu).

Synthesis of $[U\{\kappa^3\text{-}H_2B(pz^{tBu,Me})(pz^{Me,tBu})\}_2I]$ (1). To a slurry of $[UI_3(THF)_4]$ (454 mg, 0.5 mmol) in toluene (10 cm^3) was slowly added a suspension of $K[H_2B(pz^{tBu,Me})_2] \equiv Bp^{tBu,Me}$ (326 mg, 1 mmol) in the same solvent (10 cm^3). After stirring overnight, at room temperature, the reaction mixture was centrifuged, the supernatant solution separated, and the solvent was removed under reduced pressure. The resultant violet solid was washed several times with *n*-hexane and vacuum dried, yielding a dark-violet solid. Yield: 34% (160 mg, 0.17 mmol). Anal. Calcd for $C_{32}H_{56}B_2N_8IU$: C, 40.91; H, 6.01; N, 11.93. Found: C, 39.94; H, 5.83; N, 11.33. IR (Nujol, $\nu(cm^{-1})$): 2440, 2270, 2240, 2190, 2080 (ν(B−H)). UV−vis (toluene, λ_{max}/nm): 859 (m), 893 (s), 899 (s), 985 (m), 1043 (m), 1067 (m), 1103 (w), 1183 (m), 1213 (s), 1255 (w). ^1H NMR (benzene-d_6, 21 °C): 36.39 (2H, s, CH-pz); 15.55 (6H, s, Me); 14.30 (4H, br, B−H); 0.91 (18H, br, ^tBu); −0.63 (18H, br, tBu); −1.39 (6H, s, Me); −5.27 (2H, s, CH-pz).

Synthesis of $[U\{\kappa^3\text{-}H_2B(pz^{Me2})(pz^{tBu,Me})\}_2I]$ (2). To a slurry of $[UI_3(THF)_4]$ (239 mg, 0.264 mmol) in toluene (10 cm^3) was slowly added a suspension of $K[H_2B(pz^{tBu,Me})(pz^{Me2})]$ (150 mg, 0.528 mmol) in the same solvent (5 cm^3). After stirring overnight, at room temperature, a white precipitate was observed in the gray-blue solution. The reaction mixture was centrifuged, the supernatant was separated, and the solvent was removed in a vacuum. The resulting blue-green solid was washed with *n*-hexane and vacuum dried, yielding a gray-blue solid. Yield: 68% (154 mg, 0.180 mmol). Anal. Calcd for $C_{26}H_{44}N_8B_2IU$: C, 36.51; H, 5.19; N, 13.10. Found: C, 36.83; H, 5.04; N, 12.4. IR (Nujol, $\nu(cm^{-1})$): 2450, 2250, 2220, 2190, 2080 (ν(B−H)). UV−vis (toluene, $\lambda_{max/}$nm): 909 (s), 930 (s), 984 (m), 997 (m),1023 (m), 1054 (m), 1064 (m), 1161 (m), 1184 (m), 1207 (m), 1221 (s), 1257 (m). ^1H NMR (benzene-d_6, 20 °C): 35.51 (2H, s, CH-pz); 14.33 (6H, s, Me); 8.88 (4H, br, B−H); −0.79 (18H, br, ^tBu); −3.69 (6H, br, Me); −4.90 (2H, s, CH-pz); −7.08 (6H, s, Me).

X-ray Crystallographic Analysis. Black crystals of **1** were grown from *n*-hexane and of **2** and **3** from toluene/hexane. The crystals were immersed in Nujol and mounted in thin-walled glass capillaries, with solvent atmosphere, in a nitrogen-filled glovebox. Data were collected, at room temperature on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation and the $\omega-2\theta$ scan technique. Data were corrected[11] for Lorentz and polarization effects, for linear decay, and for absorption by empirical corrections based on Ψ scans. A summary of the crystallographic data is given in Table 1. The structures were solved by Patterson methods using SHELXS-86 for **1** and **3** and SHELXS-97 for **2**[12] and successive difference Fourier techniques and refined by full-matrix least squares refinements on F^2 using SHELXL-93 (**1** and **3)** and SHELXL-97 (**2**).[13,14] For **1** the six strongest peaks in the difference Fourier map were introduced as carbon atoms, presenting considerable thermal motion, and so they were assumed as atoms of a severely disordered hexane molecule of crystallization. For **3** there is one toluene solvent molecule per formula unit, much

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Table 1. Crystallographic Data for **1**, **2** and **3**

	1·C_6H_{14}	**2**	**3**·$2C_7H_8$
formula	$C_{32}H_{56}B_2IN_8U{\cdot}C_6H_{14}$	$C_{26}H_{44}B_2IN_8U$	$C_{48}H_{84}B_2I_4N_{12}U_2{\cdot}2C_7H_8$
M	1025.57	855.24	2018.82
T/K	293	293	293
crystal size, mm	0.63 × 0.45 × 0.36	0.42 × 0.40 × 0.22	0.50 × 0.31 × 0.27
space system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/a$	$P2_1/c$
a, Å	12.010(1)	17.762(2)	11.050(1)
b, Å	14.103(2)	10.2865(10)	20.460(4)
c, Å	14.137(2)	19.579(3)	17.361(2)
α, deg	84.07(1)	90	90
β, deg	85.50(1)	110.810(10)	93.42(1)
γ, deg	76.96(1)	90	90
V, Å^3	2316.5(5)	3343.9(7)	3918.0(10)
Z	2	4	2
ρ_{calc}, gcm^{-3}	1.470	1.699	1.711
μ(Mo Kα), mm^{-1}	4.203	5.805	5.745
no. of reflns measd	6567	7081	6376
no. of unique reflns	6288	6878	6148
R1[a]	0.0585	0.0559	0.0988
wR2[a]	0.1217	0.0907	0.1834

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$. The values were calculated for data with $I > 2\sigma(I)$.

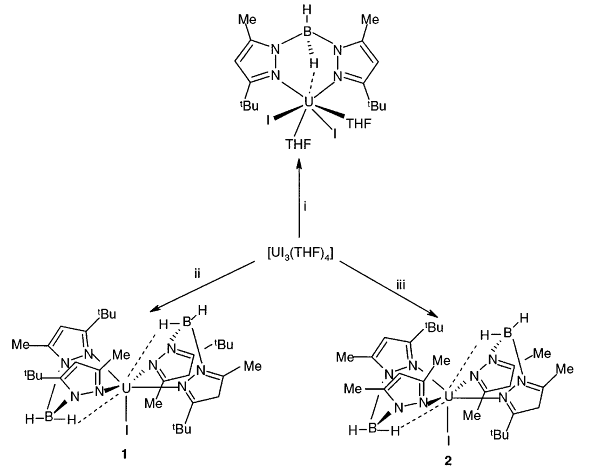
disordered, and so geometrical restraints were imposed to bond distances. All the non-hydrogen atoms were refined with anisotropic thermal motion parameters (except the solvent atoms in **1**), and the contributions of the hydrogen atoms were included in calculated positions (except for the solvent in **1**). Atomic scattering factors and anomalous dispersion terms were taken as in refs 13 and 14. The drawings were made with ORTEP-3.[13]

Results and Discussion

As we have previously described, $[UI_3(THF)_4]$ reacts with 1 equiv of $K[H_2B(pz^{tBu,Me})_2]$ (≡$Bp^{tBu,Me}$) in THF yielding, in relatively high yield, a black crystalline material, which has been identified as the mono-$Bp^{tBu,Me}$ complex $[U\{\kappa^3\text{-}Bp^{tBu,Me}\}I_2(THF)_2]$.[6] The unprecedented stabilization of a mono-$Bp^{R,R'}$ type f complex indicated clearly the steric demand of $Bp^{tBu,Me}$. Chemical studies on this system have shown that it was possible to replace the two THF molecules by other bulky ligands, such as Ph_3PO, bipyridine, or $Hpz^{tBu,Me}$.[6,15] The molecular structure of these "half-sandwich" compounds and their dynamic behavior in solution indicated a metal center relatively unprotected from incoming ligands. Therefore, we tried to see whether two $Bp^{tBu,Me}$ could coordinate to the U(III), studying the reaction of $K[H_2B(pz^{tBu,Me})_2]$ with $[UI_3(THF)_4]$ in THF, in the molar ratio 2:1. The analysis of the products, by NMR spectroscopy and X-ray crystallography, showed the presence of free ligand together with the previously described mono-Bp complex $[UI_2\{\kappa^3\text{-}Bp^{tBu,Me}\}(THF)_2]$ (Scheme 1).[6]

However, when $Bp^{tBu,Me}$ was reacted with $[UI_3(THF)_4]$ in toluene in the 2:1 stoichiometric ratio, a different behavior was observed. The initial dark blue color of the solution gradually disappeared, yielding a dark violet solution and a white precipitate of KI. Separation of the supernatant, evaporation of the solvent, and washing of the crude with *n*-hexane led to a dark-violet solid, which was analyzed by NMR, elemental analysis, and IR spectroscopy. The ^1H NMR spectrum of this compound in toluene-d_8 or in benzene-d_6 exhibits two sets of broad resonances for the protons of the pyrazolyl rings in a 1:3:9 ratio (benzene-d_6: 36.39 (1H), 15.55 (3H), 0.91 (9H), −0.63 (9H), −1.39 (3H), −5.27 (1H) ppm), one resonance for the B−H protons (14.3 ppm), and no THF coordinated to the U(III) center. This pattern was clearly different from the one obtained for the mono-$Bp^{tBu,Me}$ complex,[6] and the analytical data were consistent with the presence of two $Bp^{R,R'}$ ligands (Scheme 1). By X-ray crystallographic analysis we confirmed the formation of the bis-$Bp^{R,R'*}$ complex $[U\{\kappa^3\text{-}H(\mu\text{-}H)B(pz^{tBu,Me})(pz^{Me,tBu})\}_2I]$ (**1**) (vide infra), which is the first *f*-element complex stabilized by two asymmetric heteroscorpionates.[1−3]

Scheme 1. Synthesis of U(III) Complexes with Heteroscorpionates[a]



[a] (i) 1 equiv of $Bp^{tBu,Me}$, rt, THF;[6] (ii) 2 equiv of $Bp^{tBu,Me}$, rt, toluene; (iii) 2 equiv of $K[H_2B(pz^{tBu,Me})(pz^{Me2})]$, rt, toluene.

In the ^1H NMR spectrum of **1**, the splitting of the protons from the pyrazolyl rings agrees with the solid state structure (vide infra), which indicates an approximate C_2 molecular symmetry. However, the presence of only one resonance for the $B{-}H_2$ protons cannot be explained by this symmetry and indicates the existence of a dynamic process which equilibrates the two B−H hydrogens in each ligand. The mech-

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anism proposed for this type of equilibrium involves breaking of the three-center interactions, flipping of the boat-shaped six-membered UN_4B rings, and re-forming of the three-center interactions on the other adjacent face.[1,7] This dynamic process was not slowed by lowering the temperature, as the shape of all the signals remains temperature invariant down to 193 K.

To generate a more general class of asymmetric $(Bp^{R,R'})_2$ U(III) compounds, it was desirable to find a direct synthetic process for this class of complexes, such as salt metathesis. However, as we referred to above, the synthesis of $K[H_2B(pz^{tBu,Me})(pz^{MetBu})]$ is not possible due to the regioselectivity of the reaction between MBH_4 and $Hpz^{tBu,Me}$. To overcome this problem we decided to synthesize an asymmetric ligand with analogous steric demands in the 3-position of the pyrazolyl rings. Our choice was the novel synthetically available $M[H_2B(pz^{tBu,Me})(pz^{Me2})]$ (M = Li, K). The lithium salt was obtained by reacting $LiBH_4$ with equimolar amounts of $Hpz^{tBu,Me}$ and Hpz^{Me2} in THF/toluene. The conversion to the potassium salt was made by reaction with KOAc in acetonitrile. The use of the potassium salt is quite convenient because the desired complex can be separated easily from KI and salt incorporation is more easily avoided.[16] In fact, by reacting $[UI_3(THF)_4]$ with 2 equiv of $K[H_2B(pz^{tBu,Me})(pz^{Me2})]$, in toluene, a white precipitate of KI is formed and a gray-blue solution results. Removal of the solvent and washing with *n*-hexane yields the novel complex $[U\{\kappa^3\text{-}H(\mu\text{-}H)B(pz^{tBu,Me})(pz^{Me2})\}_2I]$ (**2**) in 68% yield (Scheme 1). Monocrystals suitable for X-ray crystallographic analysis were obtained by recrystallization of the crude product from toluene/hexane. The ^1H NMR spectrum of **2** presents six resonances for the protons of the pyrazolyl rings in the ratio 1:3:9:3:1:3 and one for the B−H protons (35.51 (2H, H(4)), 14.33 (6H; Me), 8.88 (broad, B−H), −0.79 (18H, ^{t}Bu), −3.69 (6H, Me), −4.90 (2H, H(4)), −7.08 (6H, Me)). This pattern is analogous to the one obtained for **1**, being consistent with the approximated C_2 symmetry found in the solid state (vide infra) and also with a dynamic process which makes the two hydrogen atoms of each ligand magnetically equivalent.[1,7]

Complexes $[U\{\kappa^3\text{-}H(\mu\text{-}H)B(pz^{tBu,Me})(pz^{Me,tBu})\}_2I]$ (**1**) and $[U\{\kappa^3\text{-}H(\mu\text{-}H)B(pz^{tBu,Me})(pz^{Me2})\}_2I]$ (**2**) are quite soluble in common organic solvents such as THF, toluene, and benzene and slightly soluble in *n*-hexane.

The IR spectra of **1** and **2** indicated the presence of agostic B−H···U interactions, later confirmed by the solid state structure of these compounds. For **1**, one strong and sharp band at 2440 cm^{-1} and a complex group of medium bands between 2080 and 2280 cm^{-1} were found, while for **2** there were a strong broad band at 2450 cm^{-1} and a complex group of bands between 2080 and 2220 cm^{-1}. The higher frequency stretching bands, due to the $\nu(B-H)_{term}$, compare well with the values of 2420 and 2440 cm^{-1} found for $\nu(B-H)_{term}$ in the complexes $[UI_2\{\kappa^3\text{-}Bp^{tBu,Me}(L)_2]$, L = THF and $OPPh_3$, respectively.[6] However, the group of bands due to the bridging ν(B−H)···U in **1** and **2** are slightly shifted to lower frequencies relative to the corresponding bands in the previously described mono-Bp complexes (2200−2280 cm^{-1}).[6]

Trying to see whether it was possible to stabilize a Lewis base adduct free mono Bp complex, we studied the reaction of $UI_3(THF)_4$ with 1 equiv of $KBp^{tBu,Me}$ in toluene. The NMR and IR data of the crude product of this reaction indicate a mixture of species, which could not be identified. Recrystallization of this material from *n*-hexane/toluene led to some monocrystals which have been identified, only by X-ray crystallography, as the dimer $[U\{\kappa^3\text{-}H(\mu\text{-}H)B(pz^{tBu,Me})_2\}(Hpz^{tBu,Me})I(\mu\text{-}I)]_2$ (**3**).

Coming back to compound **1**, the unexpected formation of this asymmetric complex can only be explained by a rearrangement of the $Bp^{tBu,Me}$ ligand during the course of the reaction. Several examples of $Tp^{R,R'}$ ligands undergoing rearrangement to $Tp^{R,R'*}$ during the preparation of d-transition complexes are known,[17] and an asymmetric f complex, $[Yb(Tp^{Ms*})I(THF)_2]$, has also been recently described.[2] The isomerization of Bp ligands is much more rare, and, to the best of our knowledge, the aluminum complex $[\{\kappa^2\text{-}H_2B(pz^{tBu,H})(pz^{H,tBu})\}Al(CH_3)_2]$ is the only example known.[18] While a more systematic study of these complexes would be required to clearly identify the factors favoring such rearrangements, it is likely that they are mainly driven by the tendency to reduce intramolecular van der Waals type repulsions. It is well accepted that this is a sterically driven process favored, in some cases, by coordinating solvents and temperature.[1]

As described above, we obtained **1** in toluene and at room temperature. However, this compound was also obtained, in very low yield, during our attempts for replacing the THF in $[U\{\kappa^3\text{-}Bp^{tBu,Me}\}I_2(THF)_2]$ by 1,2-dimethoxyethane (DME). Several neutral ligands were able to replace THF, namely, $Hpz^{R,R'}$, $OPPh_3$, pyridine, or bipyridine, leading to seven-coordinated complexes with two monodentate or one bidentate neutral ligand.[6,15] By contrast, the DME derivative was never isolated and the workup of the crude material with *n*-hexane allowed the identification of **1** in the *n*-hexane solution. The formation of **1** during these studies can only be explained by a redistribution process followed by an isomerization. In the synthesis of **1** described in Scheme 1,

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(16) The preparation of **2** in THF using $Li[H_2B(pz^{tBu,Me})(pz^{Me2})]$ led to a solid, which was extracted with toluene and recrystallized from toluene/hexane. The analysis of this material, by NMR spectroscopy and elemental analysis, indicated the presence of Li and THF. The pattern for the protons of the pyrazolyl rings is analogous to the one obtained for **1**, with two more resonances due to THF coordinated, which could not be removed either by recrystallization or by washing with *n*-hexane (^1H NMR (toluene-d_8, ppm): 35.1 (2H), 14.1 (6H), 8.5 (broad, B−H), 3.8 (12H, THF), 1.37 (12H; THF), −0.91 (18H, ^{t}Bu), −3.26 (6H, Me), −4.65 (2H, H(4)), −7.03 (6H, Me)).

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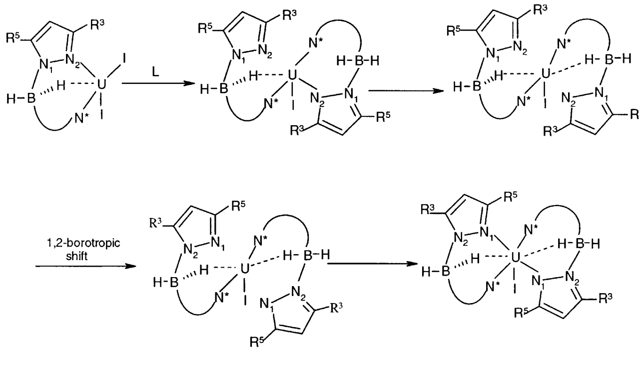
Scheme 2. Possible Pathway for the Isomerization of the Bp Ligands by a 1,2-Borotropic Shift



the formation of this complex involves only the isomerization process. The most popular mechanism to explain the isomerization process has been the 1,2-borotropic shift.[1,17,18] This mechanism consists of the detachment of one pyrazolyl ring from the metal, migration of the boron from N1 to N2, and re-coordination of the pz* to the metal.[1,17,18] More recently, another mechanism, the 1,2-metallotropic shift, has also been considered and consists of the breaking of one boron−nitrogen bond, the formation of an η^2-pyrazolato intermediate, an N2 to N1 metallotropic rearrangement, and the re-coordination of the boron to the N2 atom of the pz* ring.[1] Such a hypothesis was considered when it was found that the formation of η^2-pyrazolato d complexes was not that uncommon and also when an unusual interaction between the U and one pyrazolyl ring in the complex $[U(Tp^{Me2})_2I]$ was described.[1,19a] This complex has been considered as a possible intermediate in the breaking of the B−N bond, an important issue in the 1,2-metallotropic shift mechanism. However, more recent work on Sm(III) poly(pyrazolyl)borates[20] has shown that crystal packing forces can probably explain the unusual bonding mode found in $[U(Tp^{Me2})_2I]$.[19a] Although not having definitive experimental data for the assignment of the mechanism responsible for the formation of **1**, we consider that the Sm(III) results and the well-known haptotropism of poly(pyrazolyl)borates indicate that the 1,2-borotropic shift is the most probable mechanism. As indicated in Scheme 2, in a first step the previously described mono-κ^3-Bp U(III) complex is formed.[6] In this complex the κ^3-Bp ligand becomes κ^2-coordinate in order to facilitate the coordination of a second κ^2-Bp. Finally, the "$[UI(\kappa^2\text{-Bp})_2]$" intermediate is transformed in **1**, by a migration of the boron atom from N1 to N2 of the uncoordinated $pz^{tBu,Me}$ rings and by a re-coordination of the two $pz^{Me,tBu}$ rings to the metal center (Scheme 2).

Crystallographic Studies. Complexes 1 and 2. Complexes **1** and **2** crystallize from *n*-hexane and toluene/*n*-hexane in the space groups $P\bar{1}$ and $P2_1/a$, respectively, **1** having a molecule of hexane included in the lattice. The molecular structures are shown in Figures 1 and 2. Selected bond distances and angles are given in Table 2.

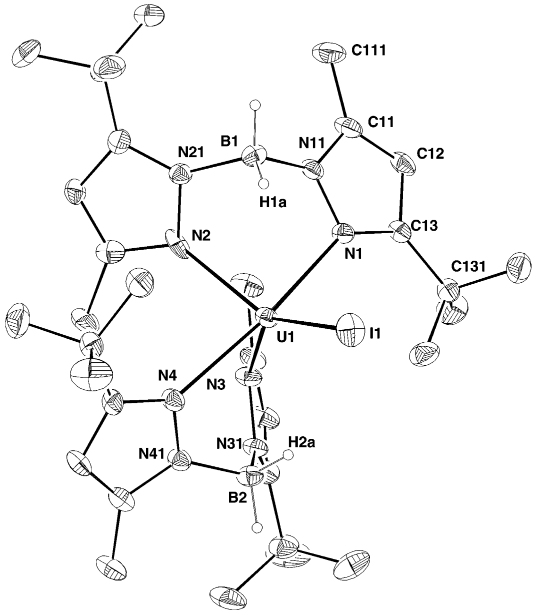


Figure 1. ORTEP view of $[U\{\kappa^3\text{-H}(\mu\text{-H})B(pz^{tBu,Me})(pz^{Me,tBu})\}_2I]$ (**1**). Vibrational ellipsoids are drawn at the 20% probability level.

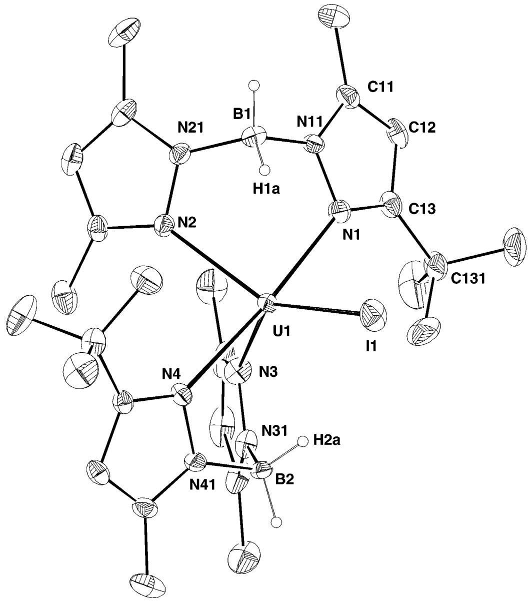


Figure 2. ORTEP view of $[U\{\kappa^3\text{-H}(\mu\text{-H})B(pz^{Me,tBu})(pz^{Me2})\}_2I]$ (**2**). Vibrational ellipsoids are drawn at the 20% probability level.

For both compounds the crystal structure consists of monomeric molecules with no unusual intermolecular contacts. The central U(III) ion is seven-coordinate by the two tridentate asymmetric Bp ligands and an iodide. Among all the polyhedral forms considered ideal for this coordination number,[21] the distorted pentagonal bipyramid is the one which better describes the coordination geometry about the U(III) atom in both complexes. The apical sites are occupied by N(1) and N(4), and the equatorial plane is defined by the [H(1A), N(2), N(3), H(2A), I(1)] atoms. The distortion from the ideal polyhedron can be seen by the bent axial N(4)−U−N(1) angles (**1**, 165.5(3); **2**, 169.9° (3)), by the deviation

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Table 2. Selected Bond Lengths and Angles for $[\mathrm{U}\{\kappa^3\text{-H}(\mu\text{-H})\mathrm{B}(\mathrm{pz}^{\mathrm{tBu,Me}})(\mathrm{pz}^{\mathrm{Me,tBu}})\}_2\mathrm{I}]\cdot\mathrm{C}_6\mathrm{H}_{14}$ (**1**) and $[\mathrm{U}\{\kappa^3\text{-H}(\mu\text{-H})\mathrm{B}(\mathrm{pz}^{\mathrm{tBu,Me}})(\mathrm{pz}^{\mathrm{Me2}})\}_2\mathrm{I}]$ (**2**)

	1	**2**
Distances (Å)		
U−I(1)	3.1027(11)	3.0989(9)
U−N(1)	2.498(8)	2.504(8)
U−N(2)	2.466(11)	2.527(8)
U−N(3)	2.547(9)	2.516(8)
U−N(4)	2.497(9)	2.519(8)
U···B(1)	3.136(14)	3.141(11)
U···B(2)	3.162(14)	3.111(12)
U···H(1a)	2.66[a]	2.66[a]
U···H(2a)	2.69[a]	2.62[a]
Angles (deg)		
N(1)−U−N(2)	80.4(3)	80.4(3)
N(4)−U−N(3)	81.1(3)	82.3(3)
N(4)−U−N(1)	165.5(3)	169.9(3)
N(2)−U−N(3)	77.2(3)	82.6(3)
N(2)−U−N(4)	88.6(3)	91.5(3)
N(1)−U−N(3)	87.2(3)	90.7(3)
I(1)−U−N(1)	98.5(2)	94.13(18)
I(1)−U−N(2)	141.0(2)	138.4(2)
I(1)−U−N(3)	141.8(2)	138.94(18)
I(1)−U−N(4)	96.0(2)	96.0(2)
N(11)−B(1)−N(21)	113.0(9)	111.5(8)
N(31)−B(2)−N(41)	112.9(10)	110.9(8)
B(1)−U−B(2)	160.6(3)	168.9(3)
Torsion Angles (deg)		
U−N(1)−N(11)−B(1)	19.3	5.40
U−N(2)−N(21)−B(1)	21.3	7.34
U−N(3)−N(31)−B(2)	17.6	6.94
U−N(4)−N(41)−B(2)	19.24	1.06
U−N−N−B_{av}	19.24	5.19

[a] This parameter was calculated using a B−H bond distance of 1.01 Å.

Table 3. Comparative Selected Parameters for Pentagonal Bipyramidal (BP) U(III) and Related Complexes

complex	CN	coord geom	X_{ax}−M−X_{ax} (deg)	equatorial plane: sum angles (deg) (planarity)	ref
1	7	BP	165.5(3)	368.2 (0.377)	*a*
2	7	BP	169.9(3)	366.6 (0.353)	*a*
$[\mathrm{UI}_3(\mathrm{THF})_4]$	7	BP	171.3()	360.5 (0.08)	9
$[\mathrm{Sm}(\mathrm{Tp}^{\mathrm{Me2}})_2\mathrm{F}]$	7	BP	156.9(3)	362.5 (0.215)	22
$[\mathrm{Sm}(\mathrm{Tp}^{\mathrm{Me2}})_2\mathrm{Cl}]$	7	BP	156.7(3)	361.2 (0.155)	22

[a] This work.

from planarity of the equatorial plane (**1**, 0.377 Å; **2**, 0.353 Å), and by the sum of the five angles within this plane (**1**, 368.17°; **2**, 366.55°) (Table 3). The analysis of these parameters indicates for **1** a greater distortion than for **2**, certainly due to the highest steric congestion found in **1**, by the presence of $^{\mathrm{t}}$Bu groups in the 5-position of the pyrazolyl rings.

There are no suitable bis-Bp type U(III) complexes for direct comparison, the only related seven-coordinate U(III) compounds being $[\mathrm{U}\{\kappa^3\text{-Bp}^{\mathrm{tBu,Me}}\}\mathrm{I}_2\mathrm{L}_2]$ (L = THF, OPPh_3, $\mathrm{Hpz}^{\mathrm{tBu,Me}}$),[6,15] $[\mathrm{U}\{\kappa^3\text{-Tp}^{\mathrm{iPr2}}\}\mathrm{I}_2\mathrm{L}_2]$ (L = $\mathrm{C}_5\mathrm{H}_5\mathrm{N}$, OPPh_3, bipy),[23] $[\mathrm{UI}_2\{\kappa^3\text{-Tp}^{\mathrm{Me2}}\}(\mathrm{THF})_2]$,[19b] $[\mathrm{UI}\{\mathrm{Tp}^{\mathrm{Me2}}\}_2]$,[19a] and $[\mathrm{UI}_3(\mathrm{THF})_4]$.[9] For the mono-Bp or bis-Tp complexes the coordination geometry about the central uranium was described as distorted capped octahedron (CO), the triiodide being the only one displaying a pentagonal bipyramidal (BP) geometry. Other, somehow related, seven-coordinate compounds also displaying a pentagonal bipyramidal coordination geometry are $[\mathrm{Sm}\{\kappa^3\text{-Tp}^{\mathrm{Me2}}\}_2\mathrm{X}]$ (X = F, Cl).[22] On the basis of the parameters shown in Table 3, it is easy to conclude that **1** and **2** present a distortion from the ideal polyhedron higher than $[\mathrm{UI}_3(\mathrm{THF})_4]$, but this is not so clear relative to the Sm complexes. However, the geometrical requirements imposed by the two κ^3-Bp* ligands, comparatively to the ones imposed by the two κ^3-Tp ligands (C_{3v} symmetry) or by identical and monodentate ligands, like iodides and THF, are certainly responsible for the high distortion observed for **1** and **2**.

In **1** and **2** the approximate C_2 symmetry axis is formed by I, U, and the midpoint of N(2) and N(3). The two κ^3-Bp* ligands are staggered with respect to each other and are bent away from the iodide, as indicated by the B−U−B angles of 160.6 (3)° and 168.9 (3)° for **1** and **2**, respectively. These angles are larger than the corresponding B−M−B bond angles found in the seven-coordinate complexes $[\mathrm{U}\{\mathrm{Tp}^{\mathrm{Me2}}\}_2\mathrm{I}]$ (147.9°)[19a] and $[\mathrm{Sm}\{\kappa^3\text{-Tp}^{\mathrm{Me2}}\}_2\mathrm{X}]$ (X = F, 144.4°; Cl, 145.7°).[22] These differences are easily explained by the geometrical restrictions imposed by the two κ^3-heteroscorpionates, which coordinate through the two nitrogen atoms of the pyrazolyl rings and through one of the hydrogen atoms attached to the boron atoms forming agostic B−H···U interactions. The five-membered chelate rings resulting from this type of coordination, compared with the six-membered chelate rings found in κ^3-Tp, impose, obviously, much more linear B−U−B bond angles. However, the angles subtended by the pyrazolyl groups and hydrogen atoms at boron are essentially tetrahedral (X−B−X_{av} bond angles: **1**, 109.5°; **2**, 109.5°), being comparable with the average values of 109.96(8)°, 111.4(9)°, and 110.8(8)° found for $\mathrm{Tl}[\kappa^3\text{-Bp}^{\mathrm{tBu,Me}}]$, $[\mathrm{Sm}\{\kappa^3\text{-Tp}^{\mathrm{Me2}}\}_2\mathrm{F}]$, and $[\mathrm{Sm}\{\kappa^3\text{-Tp}^{\mathrm{Me2}}\}_2\mathrm{Cl}]$, respectively.[22,24] The adjustment of the pyrazolyl borates in the coordination sphere of the metal can be analyzed on the basis of their slippage (B−M−B angle) but also on the twisting of the pyrazolyl rings about the B−N bond (M−N−N−B angle). In fact, the steric restrictions imposed by the tridentate coordination mode of Bp* and most probably the presence of the bulkier $^{\mathrm{t}}$Bu substituent at the 5-position of the pyrazolyl rings are responsible for a smaller B−M−B bond angle in **1** than in **2** but also for higher B−N−N−U torsional angles in **1** than in **2** (average: **1**, 19.4°; **2**, 5.2°).

In **1** the U−N bond distances and the N−U−N angles are similar and average 2.50(3) Å and 80.8(3)°, respectively. In **2**, the U−N distances and the N−U−N bond angles are also similar, averaging 2.516(10) Å and 81.4(3)°, respectively. These bond distances are similar to those observed in the related seven-coordinate $[\mathrm{UI}_2\{\kappa^3\text{-Bp}^{\mathrm{tBu,Me}}\}(\mathrm{THF})_2]$ (2.53(2) Å)[6] and $[\mathrm{UI}_2\{\kappa^3\text{-Bp}^{\mathrm{tBu,Me}}\}(\mathrm{Hpz}^{\mathrm{tBu,Me}})_2]$ (2.54(2) Å),[15] but are shorter than the 2.60(2) Å value found in the complex

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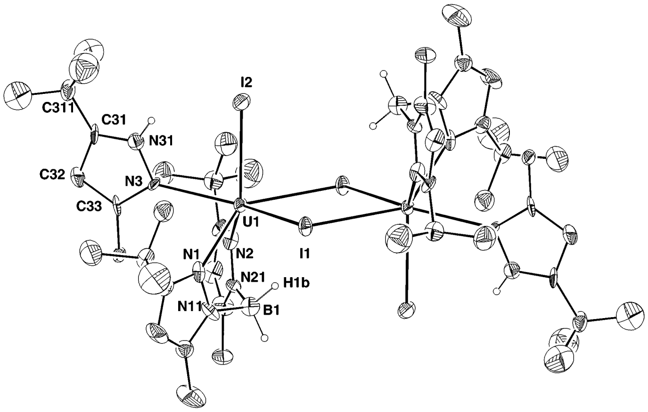

Figure 3. ORTEP view of [U{κ^3-H(μ-H)B(pz^{tBu,Me})$_2$}(Hpz^{tBu,Me})I(μ-I)]$_2$ (**3**). Vibrational ellipsoids are drawn at the 20% probability level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [U{κ^3-H(μ-H)B(pz^{tBu,Me})$_2$}(Hpz^{tBu,Me})I(μ-I)]$_2$·2C$_7$H$_8$ (**3**·2C$_7$H$_8$)

Distances (Å)			
U−I(1)	3.215(2)	U−N(2)	2.49(2)
U−I(2)	3.117(2)	U−N(3)	2.61(2)
U−I(1)[a]	3.238(2)	U−B(1)	3.07(4)
U−N(1)	2.45(3)	U···H(1b)	2.58[b]
Angles (deg)			
N(1)−U−N(2)	87.4(8)	N(3)−U−I(2)	81.8(4)
N(1)−U−N(3)	78.3(7)	N(2)−U−I(2)	132.0(6)
N(2)−U−N(3)	78.1(7)	N(1)−U−I(2)	130.2(6)
N(1)−U−I(1)	80.8(5)	N(2)−U−I(1)	134.5(5)
N(3)−U−I(1)	140.0(6)	I(1)−U−I(1)[a]	79.19(6)
I(1)[a]−U−I(2)	87.07(7)	I(1)−U−I(2)	86.22(6)
Torsion Angles (deg)			
U−N(1)−N(11)−B(1)	9.6		
U−N(2)−N(21)−B(1)	9.6		
U−N−N−B$_{av}$	9.6		

[a] Atoms related by the symmetry operation −*x*, −*y*, −*z*. [b] This parameter was calculated using a B−H bond distance of 1.01 Å.

[UI$_2${κ^3-Bp^{tBu,Me})$_2$}(OPPh$_3$)$_2$],[6] containing two bulky OPPh$_3$ ligands. The U−I bond distances in **1** and **2**, respectively 3.103(1) and 3.099(1) Å, are similar but are shorter than the average distances in [UI$_3$(THF)$_4$][9] (3.13 (3) Å) and in [UI$_2${κ^3-Bp^{tBu,Me}}L$_2$] (L = THF, 3.118(2) Å; OPPh$_3$, 3.182(2) Å; Hpz^{tBu,Me}, 3.139(1) Å).[6,15]

The B−H···U agostic interactions observed in **1** and **2** are manifested in the short U···B distances and also in the folding of the two six-membered UN$_4$B rings into a twisted boat conformation. The U···B distances in **1** and **2** average 3.15 and 3.13 Å, respectively. The folding of the rings is pronounced, the dihedral angles [UN(1)N(2)]/[B(1)N(11)N(21)] and [UN(3)N(4)]/[B(2)N(41)N(31)] being 73.9° and 75.5° (av 74.7°) for **1**, 72.5° and 71.8° (av 72.1°) for **2**. The smaller dihedral angles in **2** indicate a greater bending of the rings enabling slightly shorter U···B distances and consequently stronger B−H···U interactions in **2** (av U−H, 2.64 Å) than in **1** (av U−H, 2.68 Å). Other U(III) complexes with Bp ligands and B−H···U agostic interactions are the tris-Bp complexes [U(κ^3-Bp)$_3$(THF)] (ten-coordinate; av U···B distance, 3.42 Å) and [U(κ^3-Bp^{Me2})$_3$] (nine-coordinate; av U···B distance, 3.20 Å) and the mono-Bp complexes [UI$_2$(κ^3-Bp^{tBu,Me})(L)$_2$] (L = THF, Ph$_3$PO, Hpz^{tBu,Me}) (seven-coordinate; U···B distance in the range 3.11−3.19 Å).[4−6,15] As expected, the U···B distances found for **1** and **2** are in the range found for the mono-Bp complexes, but are smaller than the values found for the tris-Bp complexes, which have higher coordination numbers.

Complex 3. Complex **3** is a centrosymmetric dimer and crystallizes from toluene/*n*-hexane in the monoclinic space group *P*2$_1$/*c*, with two molecules of toluene in the lattice. The molecular structure is shown in Figure 3, and selected bond distances and angles are given in Table 4.

There is approximately a plane of symmetry passing through the uranium, the terminal iodides, and the boron atoms and containing the neutral pyrazolyl rings. Each U(III) atom is seven-coordinate by one tridentate Bp^{tBu,Me} ligand, one terminal and two bridging iodide ligands, and a nitrogen atom of a Hpz^{tBu,Me}. The coordination geometry is very irregular, and the assignment to one of the most common seven-coordinate polyhedrons was difficult, the 4:3 tetragonal base-trigonal geometry being the one chosen for a better description.[19] The tetragonal base, defined by the [N(2)N(1)N(3)H(1B)] atoms, has a deviation from planarity of 0.2446 Å and makes an angle of 11.8° with the [I(2)I(1)I(−1)] plane.

In **3,** the Bp^{tBu,Me} ligand has an average U−N bond distance of 2.47(2) Å and the N(1)−U−N(2) angle is 87.4(8)°, shorter and larger than the values found in **1** and **2**, probably due to the steric congestion around the U(III) imposed by two κ^3-Bp* ligands in **1** and **2**. The less congested complex **3** also presents a shorter U···B distance (3.07 Å) and a stronger B−H···U agostic interaction (U−H, 2.58 Å) than **1** and **2**. The agostic interaction found for **3** is stronger and out of the range, 2.62−2.79 Å, previously found in other seven-coordinate monomeric mono-Bp complexes [UI$_2${κ^3-Bp^{tBu,Me}}L$_2$] (L = THF, OPPh$_3$, Hpz^{tBu,Me}).[6,15]

The terminal U−I distance (3.116(2) Å) of **3** can be compared to that in **1** and **2**. The two U−I bridging bond distances of 3.216(2) and 3.238(2) Å are comparable but, as expected, substantially longer than the terminal U−I bond distances in all the complexes isolated with the Bp^{tBu,Me} ligand. The U−N bond distance of the neutral pyrazole molecule (2.61(2) Å) is comparable with the average found in [UI$_2${κ^3-Bp^{tBu,Me}}(Hpz^{tBu,Me})$_2$] (2.65(1) Å).[15] There are no unusual short intermolecular contacts in the structure of **3**. The intramolecular N(31)−I(2) distance is at 3.49 Å, a distance less than the sum of the iodine and nitrogen van der Waals radii (3.70 Å), indicating an eventual intramolecular hydrogen bonding (H31···I(2) 2.79 Å; N(31)−H31−I(2) 140.1°).

So far, the coordination number seven seems to be the most favorable for all the mono- or bis-U(III) complexes stabilized with Bp^{tBu,Me}, Tp^{Me2}, or Tp^{iPr2}.[6,7,19,23,25] During the formation of **3** the Hpz^{tBu,Me} can only result from the partial degradation of the Bp^{tBu,Me} ligand within the coordination sphere of the U(III), during the long recrystallization process. The hydrolysis of the ligand by adventitious water is the

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(25) Maria, L.; Domingos, A.; Galvão, A.; Santos, I. Personal communication at *4th* International Conference on f elements, Madrid, Spain, 2000.

most probable process for its degradation, and such reactions have been described both for d and f elements.[1−3]

Concluding Remarks

The first bis-asymmetric heteroscorpionate U(III) complexes, [U{κ^3-H(μ-H)B($pz^{tBu,Me}$)($pz^{Me,tBu}$)}$_2$I] (**1**) and [U{κ^3-H(μ-H)B($pz^{tBu,Me}$)(pz^{Me2})}$_2$I] (**2**), have been isolated and characterized in the solid state and in solution. Complex **1** was obtained due to an unprecedented isomerization of $Bp^{tBu,Me}$ at an f-element center, during the reaction of [UI_3(THF)$_4$] with 2 equiv of $Bp^{tBu,Me}$ in toluene. This serendipitous result gave us a better insight on the steric and/or electronic demands of U(III) toward Bp ligands. Based on this, the novel heteroscorpionate K[H_2B($pz^{tBu,Me}$)(pz^{Me2})] was prepared and by salt metathesis, the most simple and straightforward synthetic method, the asymmetric complex [U{κ^3-H(μ-H)B($pz^{tBu,Me}$)(pz^{Me2})}$_2$I] (**2**) was synthesized and fully characterized.

So far, most of the U(III) chemistry involves cyclopentadienyls, and complexes of the type “[UL_2I]” have been described with the bulky ligands L = 1,3-$(SiMe_3)_2C_5H_3$ or Cp*.[26,27] With poly(pyrazolyl)borates the only complex of this type structurally characterized was [U(Tp^{Me2})$_2$I],[19a] stabilized by two ligands which have been compared to cyclopentadienyls.[1,28] The almost unexplored heteroscorpionates, although presenting normally a κ^3-coordination mode, have never been compared to cyclopentadienyls.[1] Complexes **1** and **2** may open a new avenue for heteroscorpionates as ancillary ligands, allowing an interesting comparison of their chemistry with the cyclopentadienyls.

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Supporting Information Available: Crystallographic data for the structures of **1**−**3**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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