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The Role of Neutral Coligands on the Stabilization of Mono-$Tp^{{}^iPr_2}$ U(III) Complexes

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The reaction of $[UI_3(THF)_4]$ with 1 equiv of $KTp^{{}^iPr_2}$ in toluene in the presence of several neutral coligands allowed the synthesis of a novel family of mono-$Tp^{{}^iPr_2}$ complexes, $[UI_2Tp^{{}^iPr_2}(L)_x]$ [L = $OPPh_3$, $x = 1$ (**3**); L = C_5H_5N, $x = 2$ (**4**); L = $Hpz^{{}^tBu,Me}$, $x = 2$ (**5**); and L = bipy, $x = 1$ (**6**)]. The adduct with THF, $[UI_2Tp^{{}^iPr_2}(THF)_{2-3}]$ (**1**), could also be isolated by reacting $[UI_3(THF)_4]$ with 1 equiv of $KTp^{{}^iPr_2}$ in tetrahydrofuran. However, complex **1** is not a good starting material to enter into the mono-$Tp^{{}^iPr_2}$ U(III) complexes as it decomposes in solution, leading to mixtures of U(III) species coordinated with $Hpz^{{}^iPr_2}$. The solid-state structures of **3**, **4**, and **6** were determined by single-crystal X-ray diffraction and revealed that this family of mono-$Tp^{{}^iPr_2}$ complexes can be six- (**3**) or seven-coordinated (**4** and **6**), depending on the nature of the neutral coligand. Complex **3** displays distorted octahedral coordination geometry, while **4** and **6** display distorted pentagonal bipyramid and capped octahedral geometries, respectively. Complexes **3** and **6** are static in solution, and the patterns of the ^1H NMR spectra are consistent with the C_s symmetry found in the solid state. The other complexes (**1**, **4**, and **5**) are fluxional, but the dynamic processes involved can be slowed by decreasing the temperature.

Introduction

Scorpionates are flexible and versatile polydentate ligands used as complexation agents for a wide range of metal ions, including lanthanides and actinides.[1−3] When the number of pyrazolyl rings attached to the boron atom and/or the size of the substituent on the pyrazolyl rings is changed, especially those at the 3-position, it is possible to tune the electronic and steric properties of these ligands. In our laboratory, uranium(III) complexes with different heteroscorpionates ($Bp^{R,R'}$) have been isolated, and we found that the nature of the compound formed is strongly affected by the bulkiness of the groups introduced in the 3-position of the pyrazolyl rings. The use of Bp^{Me_2} allowed the synthesis of the homoleptic compound $[U\{\kappa^3\text{-}Bp^{Me_2}\}_3]$,[4] while heteroleptic complexes $[UI_2\{\kappa^3\text{-}Bp^{{}^tBu,Me}\}(L)_2]$ (L = THF or Ph_3PO) are formed with the sterically hindered $Bp^{{}^tBu,Me}$.[5] The utility of asymmetric heteroscorpionates was also demonstrated by the synthesis of bisubstituted complexes, namely, $[UI\{\kappa^3\text{-}H_2B(pz^{{}^tBu,Me})(pz^{Me,{}^tBu})\}_2]$ and $[UI\{\kappa^3\text{-}H_2B(pz^{{}^tBu,Me})(pz^{Me_2})\}_2]$.[6] Interestingly, we have also found that the $Bp^{{}^iPr_2}$ ligand, despite presenting a steric hindrance between Bp^{Me_2} and $Bp^{{}^tBu,Me}$, reacts with $[UI_3(THF)_4]$, leading to the homoleptic $[U\{\kappa^3\text{-}Bp^{{}^iPr_2}\}_3]$ complex.[7] The synthesis of this compound clearly indicated the importance of the symmetry of the substituents at the 3-position of the pyrazolyl rings. The significant difference found for symmetric and asymmetric 3-R substituents, such as ^{t}Bu and ^{i}Pr, prompted us to evaluate the possibility of preparing U(III) compounds anchored by the homoscorpionate $Tp^{{}^iPr_2}$. To the best of our knowledge, there are no U(III) complexes anchored by only one homoscorpionate of the second generation.[1,3] In fact, in our hands, reactions of $[UI_3(THF)_4]$ with $Tp^{{}^tBu,Me}$ did not succeed in preparing these types of compounds.[3] With this in mind,

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we studied the reaction of [$\mathrm{UI_3(THF)_4}$] with 1 equiv of $\mathrm{KTp}^{i\mathrm{Pr}_2}$ in tetrahydrofuran. The mono-Tp$^{i\mathrm{Pr}_2}$ complex [$\mathrm{UI_2Tp}^{i\mathrm{Pr}_2}\mathrm{(THF)_{2-3}}$] (**1**) was isolated and characterized, but we found that **1** was not a good starting material to enter into the chemistry of the mono-Tp$^{i\mathrm{Pr}_2}$ U(III) complexes due to instability problems. The identification of one of the decomposition products, [$\mathrm{UI_2}(\kappa^4\text{-}\mathrm{Tp}^{i\mathrm{Pr}_2})(\kappa^1\text{-}\mathrm{pz}^{i\mathrm{Pr}_2}\mathrm{H})$] (**2**), prompted us to explore the reaction of [$\mathrm{UI_3(THF)_4}$] with $\mathrm{KTp}^{i\mathrm{Pr}_2}$ in a noncoordinating solvent and in the presence of neutral coligands with different denticities and donor atoms and with a higher affinity for U(III) than THF. Here, we report these reactions and the compounds that were isolated, which were formulated as [$\mathrm{UI_2Tp}^{i\mathrm{Pr}_2}\mathrm{(L)}_x$] [L = THF, $x = 2-3$ (**1**); L = $\mathrm{OPPh_3}$, $x = 1$ (**3**); L = $\mathrm{C_5H_5N}$, $x = 2$ (**4**); L = $\mathrm{Hpz}^{t\mathrm{Bu,Me}}$, $x = 2$ (**5**); and L = bipy, $x = 1$ (**6**)].

2. Experimental Section

2.1. General Procedures. All of the reactions were carried out under an inert atmosphere using standard Schlenk and vacuum-line techniques or in an argon-filled glovebox. Tetrahydrofuran, toluene, and hexane were distilled from a Na alloy under nitrogen immediately prior to use and deoxygenated. Tetrahydrofuran-d_8, benzene-d_6, and toluene-d_8 were dried over sodium benzophenone. Pyridine and pyridine-d_5 were distilled from Na under nitrogen and maintained in contact with molecular sieves for several days before use. Triphenylphosphine oxide was recrystallized from ethyl acetate and vacuum-dried. [$\mathrm{UI_3(THF)_4}$] and $\mathrm{KTp}^{i\mathrm{Pr}_2}$ were prepared as previously reported.[8,9]

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

Synthetic Procedures. Synthesis of [$\mathbf{UI_2Tp}^{i\mathbf{Pr}_2}\mathbf{(THF)_3}$] (1). To a solution of [$\mathrm{UI_3(THF)_4}$] (432 mg, 0.476 mmol) in THF was slowly added a solution of $\mathrm{KTp}^{i\mathrm{Pr}_2}$ (240 mg, 0.476 mmol) in the same solvent. After the solution was stirred overnight at room temperature, the reaction mixture was filtered. The solvent was removed under vacuum to yield a blue solid. Yield: 78.4% (438 mg, 0.373 mmol). IR [Nujol, ν (cm^{-1})]: 2550 (B−H), 855 [$\mathrm{(C{-}O{-}C)_{sym}}$]. UV−vis (THF) λ_{max}, nm (ϵ): 913 (s), 1014 (s), 1076 (w), 1095 (vs), 1194 (s). ^{1}H NMR (toluene-d_8, 20 °C, δ ppm): −19.24 [3H, br, 3-CH(^{i}Pr)], −4.94 [18H, br, 3-Me(^{i}Pr)], 2.40 (12H, H_β-THF), 3.49 [18H, 5-Me(^{i}Pr)], 5.06 (12H, H_α-THF), 8.18 [3H, 5-CH(^{i}Pr)], 8.52 (3H, s, 4-H), 16.0 (1H, br, B−H). ^{1}H NMR (THF-d_8, 20 °C, δ ppm): 8.40 (3H, s, 4-H), 7.60 [3H, br, 5-CH(^{i}Pr)], 3.33 [18H, s, 5-Me(^{i}Pr)], −5.26 [18H, s, 3-Me(^{i}Pr)]. ^{1}H NMR (THF-d_8, −50 °C, δ ppm): 29.30 [1H, br, 5-CH(^{i}Pr)], 13.63 [2H, s, 5-CH(^{i}Pr)], 9.81 (2H, s, 4-H), 8.33 (1H, s, 4-H), 5.89 [12H, 5-Me(^{i}Pr)], 3.07 [6H, 5-Me(^{i}Pr)], −7.00 [6H, 3-Me(^{i}Pr)], −10.07 [12H, 3-Me(^{i}Pr)], −25.14 [1H, br, 3-CH(^{i}Pr)], −42.23 [2H, br, 3-CH(^{i}Pr)].

Synthesis of [$\mathbf{UI_2Tp}^{i\mathbf{Pr}_2}\mathbf{(OPPh_3)}$] (3). A solution of $\mathrm{OPPh_3}$ (138 mg, 0.496 mmol) in toluene was added to a slurry of [$\mathrm{UI_3(THF)_4}$] (450 mg, 0.496 mmol) in toluene and followed by the addition of a solution of $\mathrm{KTp}^{i\mathrm{Pr}_2}$ (250 mg, 0.496 mmol) in the same solvent. The mixture was stirred for 7 h at room temperature. After centrifugation, the supernatant was decanted off and the solvent removed under reduced pressure. The blue solid obtained was washed with *n*-hexane and vacuum-dried. Yield: 64% (392 mg, 0.496 mmol). Single dark-blue prismatic crystals suitable for X-ray analysis were obtained by the slow diffusion of *n*-hexane into a toluene solution of **3**. Anal. Calcd for $\mathrm{C_{45}H_{61}B_{I2}N_6OPU}$: C, 43.74; H, 4.98; N, 6.80. Found: C, 43.83; H, 5.16; N, 6.80. IR [Nujol, ν (cm^{-1})]: 2500 (B−H), 1580 (C═C), 1120 (P═O). UV−vis (toluene) λ_{max}, nm (ϵ): 861 (m), 913 (s), 958 (w), 1003 (m), 1036 (w), 1053 (w), 1081 (m), 1190 (m), 1209 (w), 1233 (m). ^{1}H NMR ($\mathrm{C_6D_6}$, 21 °C, δ ppm): 26.11 (1H, s, 4-H), 21.16 (6H, *o*−OPPh$_3$), 19.94 (1H, br, B−H), 16.20 [1H, 5-CH(^{i}Pr)], 9.88 [6H, 5-Me(^{i}Pr)], 9.39 (6H, *m*-OPPh$_3$), 9.08 (3H, *p*-OPPh$_3$), 6.57 [2H, 5-CH(^{i}Pr)], 2.99 [6H, 5-Me(^{i}Pr)], 2.81 [6H, 3-Me(^{i}Pr)], −0.17 (2H, s, 4-H), −0.59 [6H, 5-Me(^{i}Pr)], −3.68 [1H, br, 3-CH(^{i}Pr)], −7.52 [6H, 3-Me(^{i}Pr)], −14.56 [6H, 3-Me(^{i}Pr)], −32.32 [2H, br, 3-CH(^{i}Pr)].

Synthesis of [$\mathbf{UI_2Tp}^{i\mathbf{Pr}_2}\mathbf{(C_5H_5N)_2}$] (4). Pyridine (3 mL) was added to a slurry of [$\mathrm{UI_3(THF)_4}$] (360 mg, 0.397 mmol) in toluene and followed by the addition of a solution of $\mathrm{KTp}^{i\mathrm{Pr}_2}$ (200 mg, 0.397 mmol) in the same solvent. After an overnight reaction occurred, **4** was isolated following a procedure analogous to the one describe for **3**. Yield: 74.5% (330 mg, 0.296 mmol). Diffusion of *n*-hexane into a toluene/pyridine solution of the complex afforded dark crystals suitable for X-ray diffraction. Anal. Calcd for $\mathrm{C_{37}H_{56}N_8BI_2U{\cdot}C_7H_8}$: C, 43.76; H, 5.34; N, 9.28. Found: C, 43.19; H, 5.34; N, 9.20. IR [Nujol, ν (cm^{-1})]: 2540 (B−H), 1600 (C═C and C═N). UV−vis (toluene) λ_{max}, nm (ϵ): 917 (s), 1022 (w), 1088 (w), 1213 (w), 1245 (w). ^{1}H NMR ($\mathrm{C_7D_8}$, 21 °C, δ ppm): 12.55 (4H, br, H-*o*-py), 9.17 (2H, H-*p*-py), 8.19 (3H, s, 4-H), 7.79 [3H, br, 5-CH(^{i}Pr)], 6.11 (4H, H-*m*-py), 3.55 [18H, s, 5-Me(^{i}Pr)], −5.26 [18H, s, 3-Me(^{i}Pr)], −18.68 [3H, br, 3-CH(^{i}Pr)]. ^{1}H NMR ($\mathrm{C_7D_8}$, −75 °C, δ ppm): 31.24 (1H, br, B−H), 16.61 (4H, H-*m*-py), 15.10 [1H, 5-CH(^{i}Pr)], 12.29 [2H, 5-CH(^{i}Pr)], 11.50 (1H, s, 4-H), 8.77 (2H, H-*p*-py), 8.06 (2H, s, 4-H), 7.45 [6H, 5-Me(^{i}Pr)], 7.00 [6H, 5-Me(^{i}Pr), accidentally overlapping with the aromatic toluene-d_8 resonance], 5.83 [6H, 5-Me(^{i}Pr)], −11.09 [6H, 3-Me(^{i}Pr)], −11.73 [6H, 3-Me(^{i}Pr)], −13.23 [6H, 3-Me(^{i}Pr)], −48.07 [3H, br, 3-CH(^{i}Pr)].

Synthesis of [$\mathbf{UI_2Tp}^{i\mathbf{Pr}_2}\mathbf{(Hpz}^{t\mathbf{Bu,Me}}\mathbf{)_2}$] (5). Compound **5** was prepared as described for **4**, using 360 mg (0.4 mmol) of [$\mathrm{UI_3(THF)_4}$], 200 mg (0.4 mmol) of $\mathrm{KTp}^{i\mathrm{Pr}_2}$, and 111 mg (0.8 mmol) of $\mathrm{Hpz}^{t\mathrm{Bu,Me}}$. Compound **5** was obtained as a blue solid after the extraction of the crude product with *n*-hexane and the removal of the solvent under vacuum. Yield: 72% (355 mg, 0.288 mmol). Anal. Calcd for $\mathrm{C_{43}H_{74}N_{10}BI_2U}$: C, 41.86; H, 6.05; N, 11.35. Found: C, 41.8; H, 5.95; N, 10.67. IR [Nujol, ν (cm^{-1})]: 2560 (B−H), 3220 (N−H). UV−vis (toluene) λ_{max}, nm (ϵ): 920 (s), 1023 (m), 1050 (s), 1099 (s), 1238 (m). ^{1}H NMR (toluene-d_8, −50 °C, δ ppm): 24.38 (1H, 4-H), 21.61 (1H, br, 4-H), 17.76 [1H, 5-CH(^{i}Pr)], 11.05 [6H, s, 5-Me(^{i}Pr)], 7.82 (6H, Me), 6.93 [2H, 5-CH(^{i}Pr)], 4.78 [6H, s, 5-Me(^{i}Pr)], 1.52, 1.39 [4H, 4-H + 4-H(Hpz*)], −0.34 [6H, s, 5-Me(^{i}Pr)], −2.20 (18H, s, ^{t}Bu), −4.80 (2H, N−H), −5.55 [6H, 3-Me(^{i}Pr)], −9.34 [6H, 3-Me(^{i}Pr)], −11.35 [6H, 3-Me(^{i}Pr)], −29.27 [2H, br, 3-CH(^{i}Pr)], −42.23 [1H, br, 3-CH(^{i}Pr)].

Synthesis of [$\mathbf{UI_2Tp}^{i\mathbf{Pr}_2}\mathbf{(bipy)_2}$] (6). A solution of bipyridine (66 mg, 0.400 mmol) in toluene was added to a slurry of [$\mathrm{UI_3(THF)_4}$] (361 mg, 0.400 mmol) in toluene and followed by the addition of a solution of $\mathrm{KTp}^{i\mathrm{Pr}_2}$ (200 mg, 0.400 mmol) in the same solvent. After an overnight reaction, the resultant dark-blue precipitate was isolated by centrifugation. The complex was extracted with a mixture of toluene/pyridine (1:1) to separate the KI that was formed, and the solvent was pumped to dryness. The solid obtained was

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Table 1. Crystallographic Data for **3**·C_7H_8, **4**·C_7H_8, and **6**

	3·C_7H_8	**4**·C_7H_8	**6**
formula	$C_{45}H_{69}BI_2N_6OPU·C_7H_8$	$C_{44}H_{64}BI_2N_8U$	$C_{37}H_{48}BI_2N_8U$
fw	1327.74	1207.67	1107.47
crystal system	orthorhombic	orthorhombic	hexagonal
space group	*Pbca*	$P2_12_12_1$	$P3_1$
a (Å)	14.1812(14)	15.4762(13)	11.809(2)
b (Å)	20.028(2)	15.7291(8)	11.809(2)
c (Å)	39.809(9)	20.6915(14)	27.411(4)
α (deg)			90
β (deg)	90	90	90
γ (deg)			120
V (Å^3)	11307(3)	5036.9(6)	3310.5(9)
Z	8	4	3
ρ_{calcd} (g cm^{-3})	1.560	1.593	1.667
μ (mm^{-1})	4.031	4.484	5.109
no. of measured reflns	5255	10483	7625
no. of unique reflns	5255	9843	4858
R1[a]	0.0482	0.0538	0.0623
wR2[b]	0.1198	0.0828	0.0907

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

washed with *n*-hexane and vacuum-dried. Yield: 72% (320 mg, 0.287 mmol). Anal. Calcd for $C_{37}H_{54}N_8BI_2U$: C, 39.91; H, 4.89; N, 10.06. Found: C, 39.79; H, 4.82; N, 9.84. IR [Nujol, ν (cm^{-1})]: 2540 (B−H), 1590 (C═C and C═N). UV−vis (pyridine) λ_{max}, nm (ϵ): 926 (s), 1029 (m), 1105 (w), 1210 (m), 1227 (m), 1245 (m). ^{1}H NMR (C_6D_6, 21 °C, δ ppm): 58.21 (1H, br, CH-bipy), 25.49 (1H, s, CH-bipy), 22.86 (1H, br, B−H), 19.08 (1H, s, CH-bipy), 17.46 (1H, s, CH-bipy), 16.99 (1H, s, 4-H), 15.21 (1H, CH-bipy), 13.92 [1H, 5-CH(^{i}Pr)], 11.50 (1H, d, CH-bipy), 8.75 [2H, 5-CH(^{i}Pr)], 7.56 [6H, d, 5-Me(^{i}Pr)], 4.00 [6H, d, 5-Me(^{i}Pr)], 3.70 (2H, s, 4-H), 2.00 [6H, d, 5-Me(^{i}Pr)], −1.00 (1H, CH-bipy), −2.19 [6H, s, 3-Me(^{i}Pr)], −5.95 (1H, CH-bipy), −8.65 [6H, s, 3-Me(^{i}Pr)], −10.19 [6H, s, 3-Me(^{i}Pr)], −18.77 [1H, br, 3-CH(^{i}Pr)], −36.04 [2H, br, 3-CH(^{i}Pr)].

X-ray Crystallographic Analysis. Black crystals of **3** and **4** were grown by the slow diffusion of *n*-hexane into a toluene solution of the complex, and crystals of **6** were grown by the slow diffusion of *n*-hexane into a toluene/pyridine mixture. All of the crystals were mounted under Nujol in thin-walled glass capillaries in a nitrogen-filled glovebox (crystals of **3** were mounted with a solvent atmosphere). Data were collected at −30 °C for **3** and at room temperature for **4** and **6** on an Enraf-Nonius CAD4 diffractometer with graphite monochromatized Mo Kα radiation, using the $\omega-2\theta$ scan mode. A summary of the crystallographic data is given in Table 1. Data were corrected for Lorentz polarization effects, for linear decay, and for absorption by empirical corrections based on Ψ scans.[10] The heavy atom positions were located by Patterson methods.[11] The remaining atoms were located by successive difference Fourier maps and refined by least-squares refinements on F^2 using SHELXL-93 and SHELXL-97.[12] For **3** and **4**, one toluene molecule of crystallization was located in the Fourier difference map. All of the non-hydrogen atoms were refined with anisotropic thermal motion parameters (except the phenyl carbons in **3** and the solvent carbon atoms in **3** and **4**), and the contribution of the hydrogen atoms were included in calculated positions. For **3**, the data used in the refinement resulted from the measuring of two separated data sets. This was done in order to eliminate the ice formation in the capillary. Due to the abnormal sensitivity of the crystals of **3**, data collection was limited to $\theta_{max} \leq 20°$. Atomic scattering factors and anomalous dispersion terms were taken as described in ref 12. The drawings were made with the ORTEP-3 program.[13]

Results and Discussion

As briefly described, $[UI_3(THF)_4]$ reacts with $KTp^{^iPr_2}$ in a 1:1 molar ratio in THF, yielding the monosubstituted complex $[UI_2Tp^{^iPr_2}(THF)_x]$ (x = 2−3) (**1**).[7] The ^{1}H NMR pattern obtained for **1** (one set of resonances for the protons of the pyrazolyl rings in a 1:6:6:1:1 ratio, one resonance for the B−H proton, and two resonances for the THF integrating of two or three molecules, depending on the workup) indicated a fluxional behavior for this compound, thus making it structurally uninformative. Complex **1** dissolves easily in *n*-hexane, toluene, and THF, but after some time in these solvents, it decomposes. All of the attempts made to obtain crystals of **1** were not successful, and mixtures of compounds were always obtained. By ^{1}H NMR spectroscopy, the identification of these compounds was impossible. However, the presence in the ^{1}H NMR spectra of resonances assigned to methyl groups, other than the ones corresponding to the $Tp^{^iPr_2}$ ligand, and the observation in the IR spectra of stretching bands in the region where N−H stretches usually appear led us to consider that some of the species that formed could have coordinated $Hpz^{^iPr_2}$. The complexity of the NMR pattern was certainly due to intermolecular dynamic processes involving these species and complex **1**. From the several attempts at obtaining single crystals that were adequate for crystallographic analysis, it was possible to identify $[UI_2(\kappa^4\text{-}Tp^{^iPr_2})(\kappa^1\text{-}pz^{^iPr_2}H)]$ (**2**) as the main decomposition product. As indicated by X-ray crystallographic analysis, in complex **2**, the U(III) is seven-coordinated by the three nitrogen atoms of the $Tp^{^iPr_2}$ ligand, by two iodide ions, by one nitrogen atom of the $\kappa^1\text{-}Hpz^{^iPr_2}$, and by a U···H[^{i}Pr(3)] agostic interaction.[7] This is the first f element anchored by a scorpionate ligand presenting an agostic interaction between the metal and one hydrogen of the alkyl group of the pyrazolyl rings. For d-transition elements, the examples are also rare and the only case known is $[Ru\{k^4\text{-}Tp^{^iPr_2}\}(dppe)]OTf$.[14] We think that the instability of **1** and its unsuitability to enter into the chemistry of the mono-$Tp^{^iPr_2}$ U(III) complexes is related to the lability of the THF molecules in **1** and the coordinative unsaturation of the resulting species. This unsaturation probably promotes additional interactions with hydrogen atoms of the 3-R groups since these interactions are responsible for the partial decomposition of the $Tp^{^iPr_2}$ ligand. Variable-temperature ^{1}H NMR studies for **1** in toluene-d_8 and in tetrahydrofuran-d_8 were undertaken to see whether it was possible to get a better

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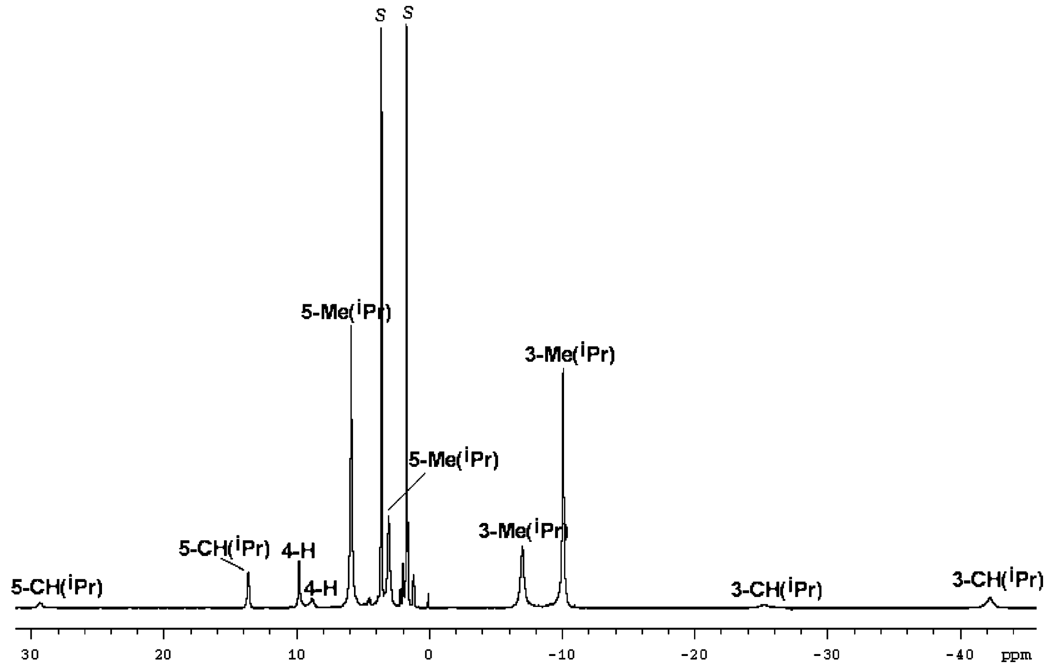
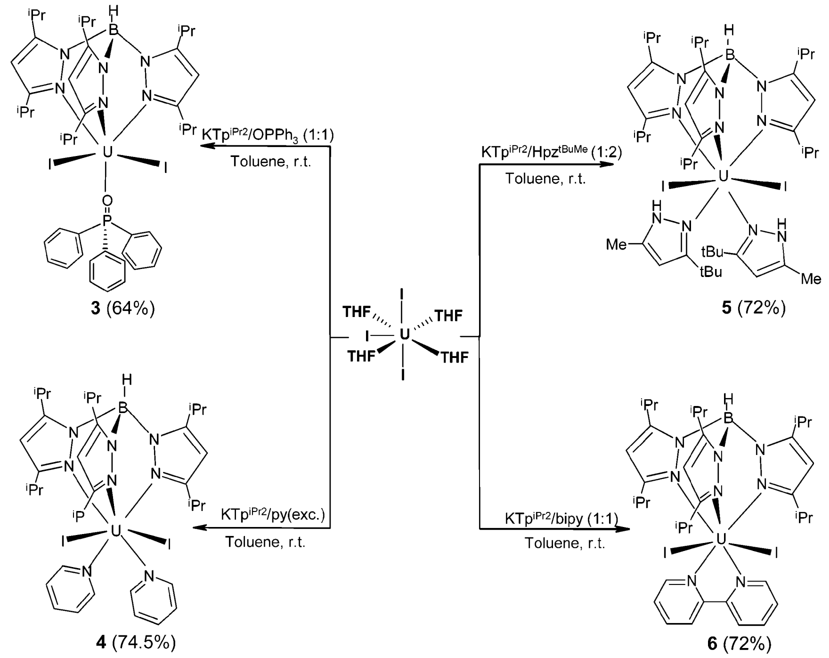


Figure 1. ^{1}H NMR spectrum of [UI$_2${κ^3-Tp^{iPr_2}}(THF)$_x$] (**1**) recorded in THF-d_8 at −50 °C.

Scheme 1



insight on the solution behavior and structure of this compound. In toluene-d_8, by lowering the temperature, the resonances of the protons of the pyrazolyl rings and of the coordinated THF shifted and became broader, but no structurally informative pattern could be obtained in this solvent. In THF-d_8, the spectrum obtained at room temperature did not show the resonances due to the B−H and 3-CH(^{i}Pr) protons, but for the methyl groups, the pattern was similar to the one obtained in toluene-d_8. At −50 °C, the spectrum obtained had a pattern consistent with a C_s symmetry (Figure 1) (two sets of resonances due to the Tp^{iPr_2} ligand in the intensity ratio of 2:1). The fluxional behavior found for **1** seems to be mainly of the intermolecular type. This conclusion was based on the variable amounts of THF coordinated to the metal, depending on the workup of **1**, and also on the great lability of the THF, which could be easily and quantitatively replaced by pyridine, OPPh$_3$, and bipyridine.

In fact, ^{1}H NMR studies in benzene-d_6 indicated that the THF in [UI$_2$Tp^{iPr_2}(THF)$_x$] (**1**) is readily displaced by OPPh$_3$ or C$_5$H$_5$N, yielding the stable complexes [UI$_2$Tp^{iPr_2}(L)$_x$] (L = OPPh$_3$, $x = 1$ for **3**; L = C$_5$H$_5$N, $x = 2$ for **4**). The stability in solution of **3** and **4** and the instability of **1**, as well as the difficulty on obtaining **1** in a pure form, led us to consider a different synthetic strategy for preparing mono-Tp^{iPr_2} U(III) complexes. As can be seen in Scheme 1, this process

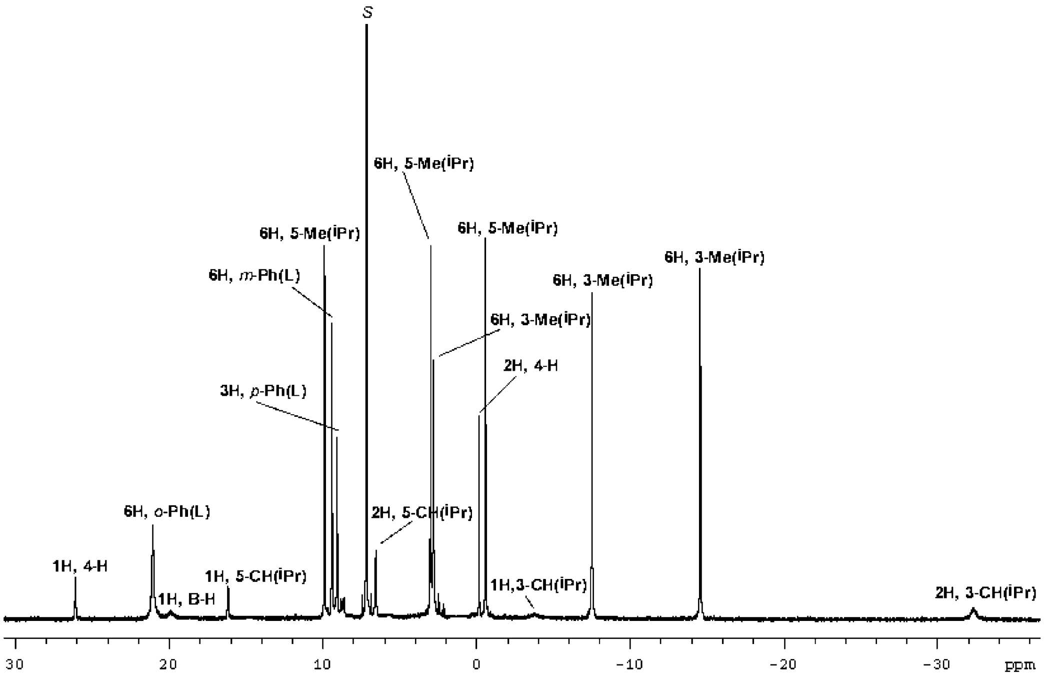


Figure 2. ^{1}H NMR spectrum of [$UI_2\{\kappa^3\text{-}Tp^{^iPr_2}\}(OPPh_3)$] (**3**) recorded in benzene-d_6 at 20 °C.

Table 2. Most Relevant Stretching Bands for Complexes **3**−**6**

complex	coligand L	ν(B−H) (cm^{-1})	stretching vibrations of L (cm^{-1})
3	$OPPh_3$	2500	1580 (ν(C=C)); 1120 (ν(P=O))
4	C_5H_5N	2540	1600 (ν(C=C); ν(C=N))
5	$Hpz^{^tBu,Me}$	2560	3220 (ν(N−H))
6	bipy	2535	1590 (ν(C=C); ν(C=N))

consisted of reacting [$UI_3(THF)_4$] in a 1:1 molar ratio with $KTp^{^iPr_2}$ in the presence of different Lewis bases, using toluene as the solvent. The mono-$Tp^{^iPr_2}$ complexes [$UI_2Tp^{^iPr_2}(OPPh_3)$] (**3**), [$UI_2Tp^{^iPr_2}(C_5H_5N)_2$] (**4**), [$UI_2Tp^{^iPr_2}(Hpz^{^tBu,Me})_2$] (**5**), and [$UI_2Tp^{^iPr_2}(bipy)$] (**6**) were obtained as blue microcrystalline solids in moderate to high yield (64−75%).

Complexes **3** and **4** are soluble in toluene, benzene, and sparingly soluble in hexane. Complex **6** is not very soluble in toluene and has to be extracted with a pyridine/toluene (1:1) solution to remove the KI that was formed during the reaction. In contrast, complex **5** is very soluble in aromatic and aliphatic solvents, which makes the growing of crystals difficult.

In the IR spectra of compounds **3**−**6**, the bands due to the $Tp^{^iPr_2}$ ligand are observed, as well as the stretching bands that are characteristic of the neutral coligands. In Table 2, some of the complexes are shown. The ν(B−H) stretching vibration appears in the range of 2500−2560 cm^{-1}, confirming a tridentate coordination mode for the $Tp^{^iPr_2}$ ligand.[15] The presence of $OPPh_3$ in the spectrum of **3** and of $Hpz^{^tBu,Me}$ in the spectrum of **5** is confirmed by strong absorption bands which appear at 1120 [$\Delta\nu(P{=}O) = 75$ cm^{-1}] and 3220 cm^{-1} [$\Delta\nu(N{-}H) = 150$ cm^{-1}], respectively. In complex [$UI_2Tp^{^iPr_2}(bipy)$] (**6**), the presence of a strong band at 1580 cm^{-1} and the absence of bands in the 900−1000 cm^{-1} range is consistent with the coordination of the bipyridyl ligand as neutral.[16]

The ^{1}H NMR spectra of **3** and **6** at room temperature exhibit two sets of resonances assigned to the $Tp^{^iPr_2}$ ligand in the intensity ratio of 2:1 and three or eight resonances assigned to the $OPPh_3$ or bipyridyl ligands, respectively. This pattern is consistent with the apparent C_s molecular symmetry found in the solid state by X-ray crystallographic analysis. As a representative, the ^{1}H NMR spectrum of adduct **3** is shown in Figure 2. The assignment of all of the resonances was done by COSY experiments considering that the broader resonances were due to the isopropyl protons in the 3-position of the pyrazolyl rings.

In contrast to **3** and **6**, the room temperature ^{1}H NMR spectrum of [$UI_2\{\kappa^3\text{-}Tp^{^iPr_2}\}(C_5H_5N)_2$] (**4**) in toluene-$d_8$ presents only one set of resonances for the 3-^{i}Pr, 5-^{i}Pr, and H(4) protons of the scorpionate ligand, also showing three resonances due to the pyridine ligands (Figure 3a). This pattern was not in accordance with the approximate C_s symmetry found in the solid state, indicating a fluxional behavior for the complex. When the samples were cooled, the resonances that were assigned to the H(4) pyrazolyl protons and the ^{i}Pr groups (Me and C−H) shifted, became broad, collapsed, and finally separated into new resonances. At −75 °C, the ^{1}H NMR spectrum (Figure 3b) exhibited two singlets in a 1:2 ratio assigned to the H(4) protons [11.50 (1H), 8.06 (2H)], six singlets for the ^{i}Pr methyl protons (6:6:6:6:6:6), and two signals in a 1:2 ratio assigned to the 5-^{i}Pr methine protons [15.10 (1H), 12.29 (2H)]. The remaining methine protons [3-CH(^{i}Pr)] were accidentally overlapped and appear at −48.07 (2H) ppm. The 1:2 pattern observed for the protons of the $Tp^{^iPr_2}$ ligand (at −75 °C) was in

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(15) Akita, M.; Otha, K.; Takahashi, Y.; Hikichi, S.; Moro-Oka, Y. *Organometallics* **1997**, *16*, 4121−4128.

(16) Saito, Y.; Takemoto, J.; Hutchinson, B.; Nakamoto, K. *Inorg. Chem.* **1972**, *11*, 2003.

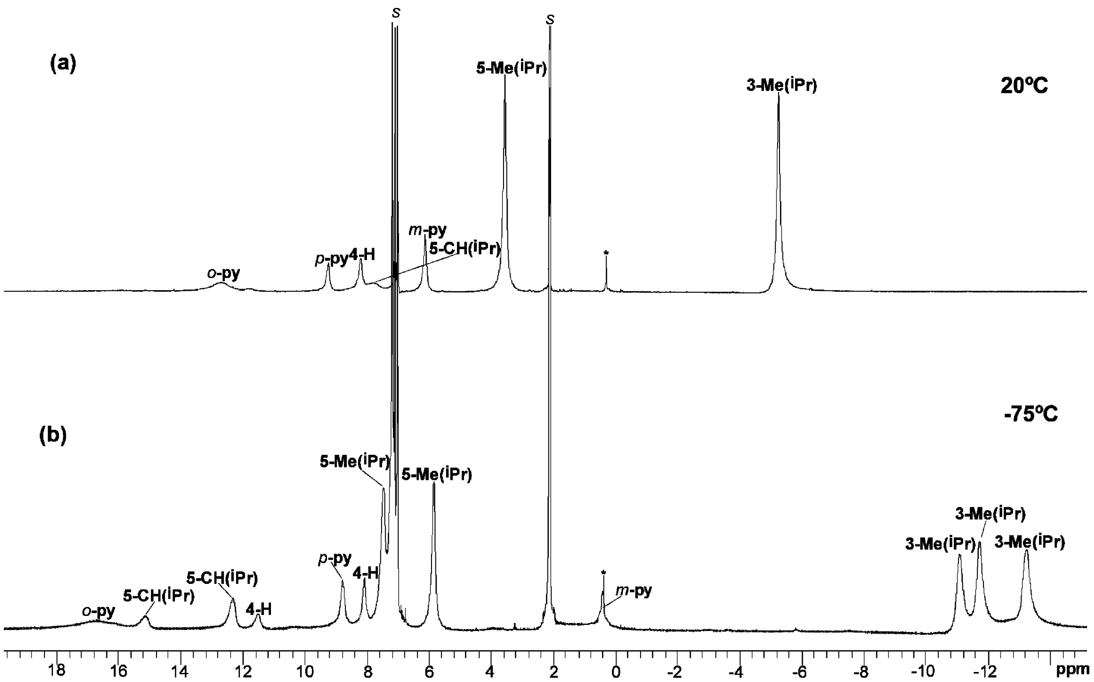

Figure 3. Temperature-dependent ^{1}H NMR spectra (toluene-d_8) of **4** ($* =$ grease).

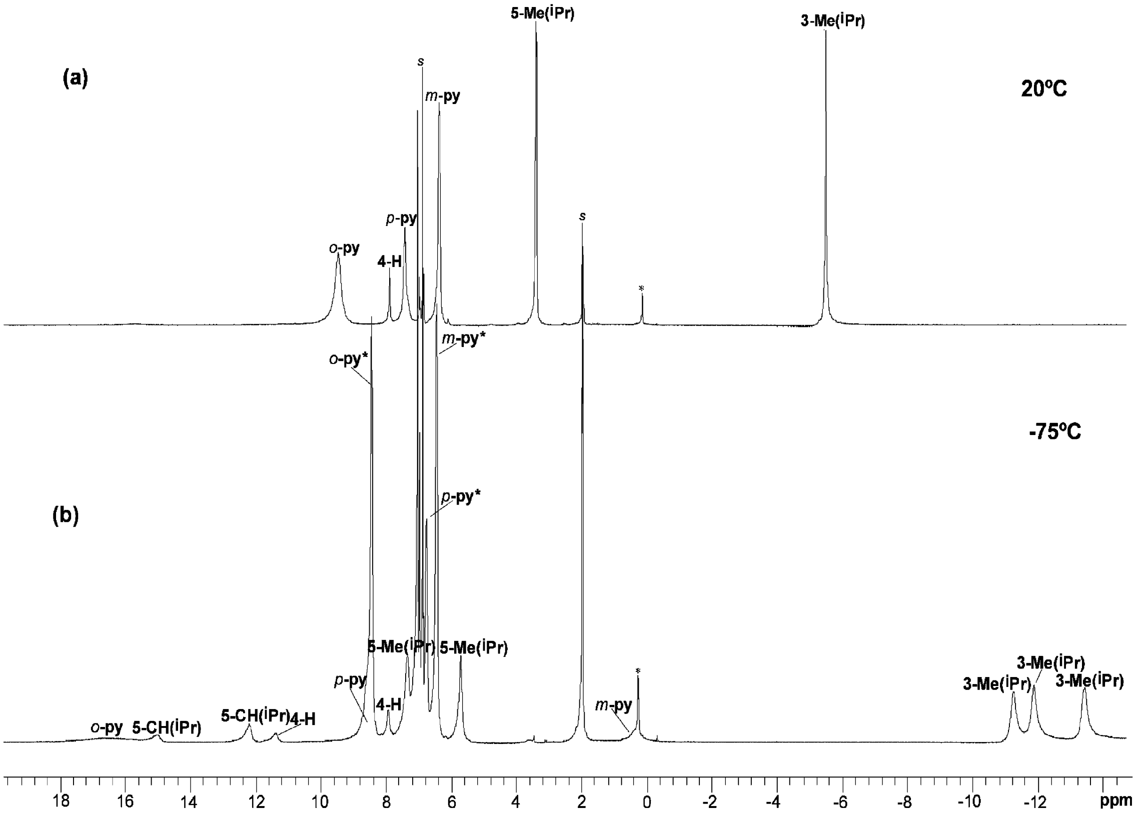

Figure 4. Temperature-dependent ^{1}H NMR spectra (toluene-d_8) of **4** with added pyridine (py*-free pyridine; $* =$ grease).

agreement with the apparent mirror-symmetrical structure determined by X-ray crystallography.

To get a better insight on the dynamic process involved in solution, an excess of free pyridine was added to a solution of **4** in toluene-d_8. The ^{1}H NMR spectrum recorded at room temperature showed three average resonances for the pyridine protons that were shifted toward the values of the free pyridine (Figure 4a). When the temperature was lowered to −75 °C, the resonances assigned to the pyridine protons broadened and separated into two sets of signals (Figure 4b). One set corresponded to the protons of the free pyridine, and the other three resonances were assigned to the coordinated pyridine. These observations are consistent with the existence of a dissociative mechanism, involving an

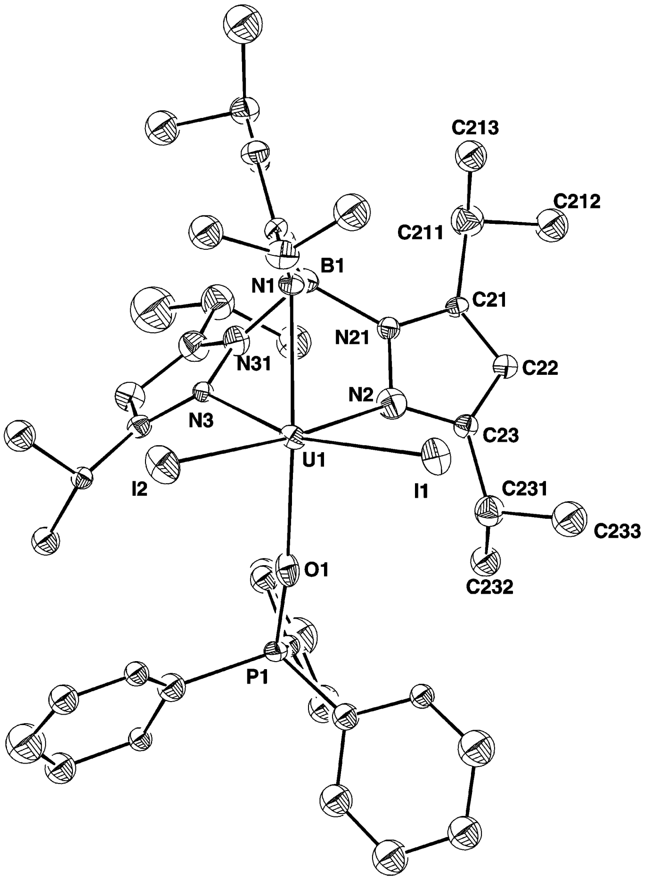

Figure 5. ORTEP view of $[UI_2\{\kappa^3\text{-}Tp^{^iPr_2}\}(OPPh_3)]$ (**3**). Vibrational ellipsoids are drawn at the 30% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[UI_2\{\kappa^4\text{-}Tp^{^iPr_2}\}(pz^{^iPr_2}H)]$ (**2**)[7] and $[UI_2\{\kappa^3\text{-}Tp^{^iPr_2}\}(OPPh_3)]$ (**3**) [X = N(4) for **2**; X = O for **3**]

	2	**3**$\cdot C_7H_8$
	Distances (Å)	
U−N(1)	2.484(10)	2.553(13)
U−N(2)	2.588(11)	2.612(14)
U−N(3)	2.581(11)	2.561(12)
U−I(1)	3.0723(14)	3.1094(13)
U−I(2)	3.0734(14)	3.1216(14)
U−X	2.552(12)	2.350(11)
	Angles (deg)	
N(1)−U−N(2)	75.1(4)	78.0(4)
N(1)−U−N(3)	72.9(3)	72.5(4)
N(2)−U−N(3)	76.0(3)	75.1(4)
I(1)−U−I(2)	91.14(14)	94.41(4)
N(1)−U−X	140.0(4)	160.3(4)
N(2)−U−I(2)	174.0(2)	174.2(3)
N(3)−U−I(1)	170.2(2)	163.1(3)
N(1)−U−I(1)	103.9(2)	96.4(3)
N(1)−U−I(2)	106.0(3)	98.1(3)
N(2)−U−I(1)	94.3(2)	90.3(3)
N(3)−U−I(2)	98.6(2)	99.7(3)
N(2)−U−X	74.0(4)	88.7(5)
N(3)−U−X	75.5(4)	90.2(4)
I(1)−U−X	103.1(3)	98.1(3)
I(2)−U−X	102.3(3)	94.0(3)
	Torsion Angles (deg)	
U−N(1)−N(11)−B	5.65	22.63
U−N(2)−N(21)−B	8.36	30.88
U−N(3)−N(31)−B	3.68	30.03
$(U-N-N-B)_{av}$	5.9	27.8

exchange between the free and the coordinated pyridine molecules.

The room-temperature ^1H NMR spectrum of **5** in toluene-d_8 displayed several broad resonances, from which the resonances at −5.72 and 0.70 ppm have been assigned to the three ^{i}Pr methyl protons of the $Tp^{^iPr_2}$ and to the ^{t}Bu protons of $Hpz^{^tBu,Me}$, respectively. Variable-temperature NMR studies led to a static spectrum at −50 °C, showing a pattern analogous to the ones obtained for **3** and **6**. In this spectrum, we could assign six resonances due to the ^{i}Pr methyl protons (6:6:6:6:6:6), four due the ^{i}Pr methine protons (1:2:2:1), and two due to the pyrazolyl ring protons (1:2), which is in agreement with the expected C_s symmetry. The resonances due to the $Hpz^{^tBu,Me}$ coligands appeared at 7.82, 1.52, −2.20, and −4.80 ppm with an intensity ratio of 6:2:18:2. The assignment of all of the resonances was based on the intensity and shape of the resonances and by using COSY experiments.

Crystallographic Studies. Molecular Structure of $[UI_2\{\kappa^3\text{-}Tp^{^iPr_2}\}(OPPh_3)]$ (3). X-ray quality crystals of **3** were grown by the slow diffusion of *n*-hexane into a toluene solution of the complex. The compound crystallized with one molecule of toluene in the lattice. The molecular structure is shown in Figure 5, and selected bond distances and angles are given in Table 3. The structure consists of monomeric molecular units in which the uranium is six-coordinated by a tridentate $Tp^{^iPr_2}$ ligand, two bound iodide ions, and one oxygen of the $OPPh_3$ ligand. The arrangement around the metal center is better described as a distorted octahedron; the axial positions are occupied by the N(1) atom of the $Tp^{^iPr_2}$ ligand and by the oxygen of the $OPPh_3$ [angle N(1)−U−O of 160.3(4)°]. The remaining nitrogen and iodide atoms define the equatorial plane.

The average U−N($Tp^{^iPr_2}$) bond distance [2.58(2)Å] compares with the one in $[UI_2\{\kappa^4\text{-}Tp^{^iPr_2}\}(Hpz^{^iPr_2})]$ (**2**) [2.55(1) Å],[7] but the average U−I bond length in **3** [3.116(1) Å] is slightly longer than the corresponding distance in **2** [3.073(1) Å]. This may reflect the greater steric demand of the $OPPh_3$ compared to that of $Hpz^{^iPr_2}$. The bulkiness of the $OPPh_3$ is also probably responsible for higher B−N−N−U torsion angles in **3** (average of 27.8°) than in **2** (average of 5.9°). In complex **3**, the U−O bond distance [2.35(1) Å] is comparable with the average bond distances described for the previously reported seven-coordinate complexes $[UI_2\{\kappa^3\text{-}(Bp^{^tBu,Me})_2\}(OPPh_3)_2]$[5] and $[U(OTf)_2(OPPh_3)_4][OTf]$ [2.36(2) Å][17] but is slightly shorter than the U−O bond distance found in $[U\{MeC_5H_4\}_3(OPPh_3)]$ [2.389(6) Å].[18]

Molecular Structure of $[UI_2\{\kappa^3\text{-}Tp^{^iPr_2}\}(C_5H_5N)_2]$ (4) and $[UI_2\{\kappa^3\text{-}Tp^{^iPr_2}\}(bipy)]$ (6). X-ray quality crystals of **4** and **5** were grown by the slow diffusion of *n*-hexane into a toluene or a toluene/pyridine solution, respectively. Compound **4** crystallized with one molecule of toluene in the lattice. The crystal structures of complexes **4** and **6** are shown in Figures 6 and 7, respectively. Selected interatomic distances and angles are given in Table 4.

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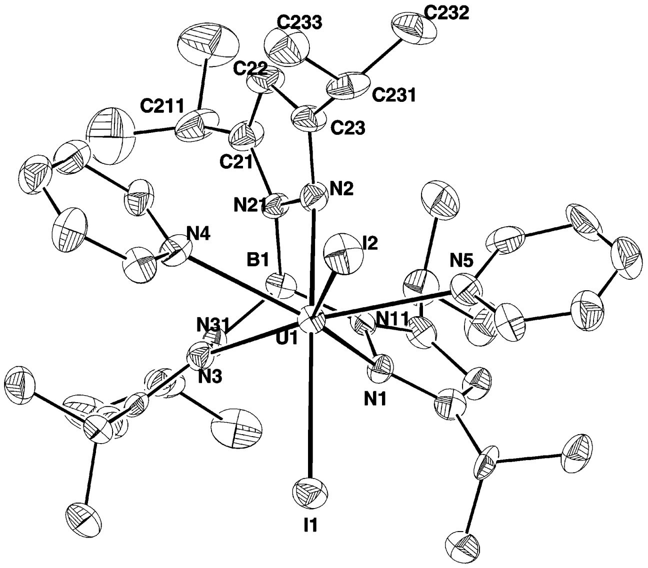

Figure 6. ORTEP view of [UI$_2${κ^3-Tp^{iPr_2}}(C$_5$H$_5$N)] (**4**). Vibrational ellipsoids are drawn at the 30% probability level.

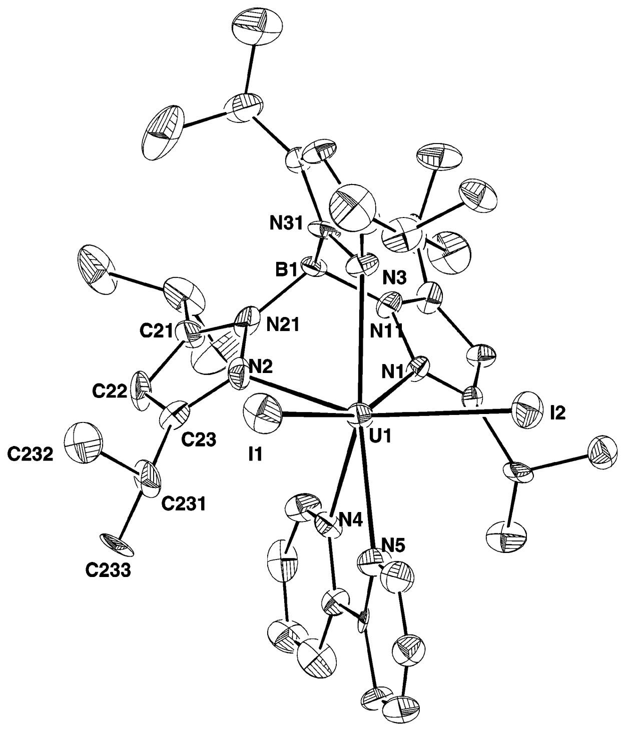

Figure 7. ORTEP view of [UI$_2${κ^3-Tp^{iPr_2}}(bipy)] (**6**). Vibrational ellipsoids are drawn at the 30% probability level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [UI$_2$Tp^{iPr_2}(C$_5$H$_5$N)$_2$] (**4**) and [UI$_2$Tp^{iPr_2}(bipy)] (**6**)

	4·C$_7$H$_8$	**6**
	Distances (Å)	
U−N(1)	2.622(8)	2.600(15)
U−N(2)	2.570(9)	2.564(17)
U−N(3)	2.610(9)	2.613(15)
U−I(1)	3.1034(9)	3.1429(18)
U−I(2)	3.2100(8)	3.1464(18)
U−N(4)	2.655(9)	2.663(16)
U−N(5)	2.653(9)	2.645(18)
	Angles (deg)	
N(1)−U−N(2)	75.4(3)	77.3(5)
N(1)−U−N(3)	71.7(3)	71.6(5)
N(2)−U−N(3)	79.2(3)	74.4(5)
I(1)−U−I(2)	91.02(3)	99.30(5)
N(2)−U−I(1)	163.07(18)	89.7(4)
N(2)−U−I(2)	105.55(19)	159.5(4)
N(1)−U−I(1)	89.52(19)	159.3(3)
N(3)−U−I(1)	89.52(19)	89.6(3)
N(4)−U−I(1)	108.7(2)	117.9(4)
N(5)−U−I(1)	99.8(2)	80.7(4)
N(2)−U−I(2)	105.55(19)	159.5(4)
N(1)−U−N(4)	137.6(3)	73.4(5)
N(3)−U−N(5)	141.1(3)	162.9(5)
	Torsion Angles (deg)	
U−N(1)−N(11)−B	34.89	9.21
U−N(2)−N(21)−B	39.10	26.97
U−N(3)−N(31)−B	17.29	27.89
(U−N−N−B)$_{av}$	30.4	21.4

In **4** and **6**, the uranium atom is seven-coordinated by the three pyrazolyl nitrogen atoms, two iodides, and two nitrogens of the neutral coligands. The coordination geometry for the two compounds is not regular, and assignment to one of the basic polytopal forms, normally assigned to the seven-coordination (capped octahedron, monocapped trigonal prism, and pentagonal bipyramid), is difficult.[19] For complex **4**, the polyhedron which best describes the coordination geometry around the metal is a distorted pentagonal bipyramid, while for **6**, it is a distorted capped octahedron. In complex **4**, the apical positions of the bipyramid are occupied by one iodide and one nitrogen atom of the Tp^{iPr_2} ligand [I1−U−N2 = 163.07(18) Å]. The second iodide atom (I2) lies in the equatorial plane together with the other two nitrogen atoms of the Tp^{iPr_2} and the two nitrogen atoms of the pyridine ligands. The angles in the equatorial plane range between 70.5(3) and 75.44(19)°, and the sum of the five angles within the equatorial plane is 362.4°. The average N2−U−L$_{eq}$ and I1−U−L$_{eq}$ angles are 84.3 and 95.6°, respectively.

In complex **6**, the two iodide atoms and one of the nitrogen atoms (N3) of the Tp^{iPr_2} ligand define one of the triangular faces of the capped octahedron, while the other two nitrogen atoms of Tp^{iPr_2} and N5 of the bipy ligand form the staggered triangular face. The N4 atom of the bipyridine ligand is capping the latter face of the octahedron. The two staggered triangular faces are inclined by an angle of 9.74°.

The stereochemistry of a homoleptic ML$_7$ complex with capped octahedral geometry can be defined by the two spherical angles formed by the metal−ligand vectors and the capping ligand lying on the 3-fold axis.[20] In **6**, the angles are N4−U−N2, N4−U−N1, N4−U−N5, N4−U−I1, N4−U−I2, and N4−U−N3 with observed values of 72.2(5), 73.7(5), 61.1(6), 117.9(4), 118.2(4), and 135.9(5)°, respectively. The average angles of 69 and 124° differ and are lower than those corresponding to the theoretical values of 74.6 and 130.3° obtained for an ideal polyhedron ML$_7$ complex.[20]

In complex **6**, the distortion from the regular capped octahedral geometry is higher than those found previously for other U(III) complexes anchored by scorpionates, such as [UI$_2${κ^3-Tp^{Me_2}}(THF)$_2$] (82.1°, 134.8°), [UI$_2${κ^3-Bp^{tBu,Me}}-

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(THF)$_2$] (77.3°, 131.2°), and [UI$_2${κ^3-Bp$^{t\mathrm{Bu,Me}}$}(OPPh$_3$)$_2$] (82.7°, 133.7°).[5,21] This can certainly be explained by the restrictions imposed by the bidentate bipy ligand.

The average U−N(Tp$^{i\mathrm{Pr}_2}$) bond distances in **4** and **6** are comparable [2.60(2) Å for **4** and 2.59(2) Å for **6**] but are slightly longer than those reported for the seven-coordinated complexes [UI$_2$Tp$^{\mathrm{Me}_2}$(THF)$_2$] [2.53(3) Å] and [U{Tp$^{\mathrm{Me}_2}$}$_2$-(THF)][BPh$_4$] [2.54(4) Å],[21] confirming the highest steric hindrance of Tp$^{i\mathrm{Pr}_2}$ compared to that of Tp$^{\mathrm{Me}_2}$. In **4** and **6**, the pyrazolyl rings are considerably twisted about their B−N bonds, with B−N−N−U torsion angles of 34.89−39.10−17.29° and 9.21−26.97−27.89° for **4** and **6**, respectively. In compound **4**, there are two types of U−I bond distances: 3.103(1) Å for the axial iodide and 3.210(1) Å to the equatorial one. The U−I$_{\mathrm{ax}}$ bond distance found for **4** is comparable to the corresponding U−I$_{\mathrm{ax}}$ bond lengths in [UI$_3$(THF)$_4$] [3.103(2) and 3.119(2) Å].[8] For **6**, both iodide atoms occupy equatorial positions, with the two U−I bond distances being comparable [average 3.144(2) Å] and similar to the average U−I$_{\mathrm{eq}}$ bond distance described for the capped octahedron [UI$_2$Tp$^{\mathrm{Me}_2}$(THF)$_2$] [3.145(2) Å].[21]

In **4**, the average U−N bond distances of the pyridine ligands [2.654(9) Å] compare with those in [UI$_3$(bipy)$_2$-(C$_5$H$_5$N)] [2.679(9) Å] and [UI$_2${C$_5$Me$_5$}(C$_5$H$_5$N)$_3$] [2.72(3) Å].[22,23]

The U−N bond distances of the bipyridine ligand in **6** are comparable and are in the range reported for the corresponding distances in [UI$_3$(bipy)$_2$(py)] [2.611(9)−2.694(9) Å][22] and higher than those in [U{C$_5$Me$_5$}(COT)-(Me$_2$bipy)] [2.429(11) and 2.423(11) Å].[24] The pyridyl rings are twisted with respect to each other, with a torsion angle of 5.79°.

Concluding Remarks

We have shown that is possible to isolate mono-Tp$^{i\mathrm{Pr}_2}$ U(III) complexes due to the symmetry of the ^{i}Pr substituent introduced in the 3-position of the pyrazolyl rings. To the best of our knowledge, these are the first examples of mono-Tp$^{\mathrm{R,R}}$ 5f complexes anchored by one homoscorpionate of the second generation. We also have shown that the adduct with tetrahydrofuran, [UI$_2${κ^3-Tp$^{i\mathrm{Pr}_2}$}(THF)$_2$] (**1**), although being obtained by a metathesis reaction, is not stable enough to be considered a good starting material to enter into the mono-Tp$^{i\mathrm{Pr}_2}$ U(III) chemistry. The lability of the THF coordinated and/or additional agostic interactions between the U(III) and the ^{i}Pr(3) groups of the pyrazolyl may promote partial decomposition of the Tp$^{i\mathrm{Pr}_2}$ and liberation of Hpz$^{i\mathrm{Pr}_2}$. The lability of the THF in **1**, observed by ^{1}H NMR spectroscopy studies, led us to devise a new strategy to enter into the chemistry of the mono-Tp$^{i\mathrm{Pr}_2}$ complexes. This strategy consisted of reacting [UI$_3$(THF)$_4$] with Tp$^{i\mathrm{Pr}_2}$ in toluene in the presence of mono- or bidentate neutral coligands with a higher affinity for U(III) than THF. Depending on the bulkiness of the neutral ligand, it was possible to isolate six-(**3**) or seven-coordinated (**4** and **6**) complexes. The solution behavior of these complexes was strongly dependent on the steric hindrance, denticity, and donor atoms of the neutral coligands. So, to enter into the mono-Tp$^{i\mathrm{Pr}_2}$ U(III) chemistry will be determinant upon choosing an adequate neutral coligand to achieve stable but still reactive starting materials. These are not common complexes and constitute a new entry into organouranium(III) chemistry. Our findings indicated that the adduct with pyridine is the more promising, with some derivative chemistry underway.

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