Synthesis and Structure of Bis[hydrotris(3,5-dimethylpyrazolyl)borato]iodouranium(III), $U[HB(3,5\text{-}Me_2pz)_3]_2I$: Unprecedented Side-On Interaction Involving a Hydrotris(pyrazolyl)borate Ligand

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Received January 28, 1994

Interest in the chemistry of complexes based on the hydrotris(pyrazolyl)borate ligands ($Tp^{R,R'}$) continues unabated.[1] Indeed, with the advent of the sterically-demanding, so called "second generation Trofimenko's ligands", there is a resurgence of interest in this field. It has been demonstrated that the complexes participate in unique chemical transformations, such as C—H activation[2] and that the ligands are eminently suited for building bioinorganic models[3] and for stabilizing monomeric hydrocarbyl and hydrido main group compounds.[4]

The versatility of the $Tp^{R,R'}$ ligands resides in the facility by which the substituents on the 3- and 5-positions of the pyrazolyl rings can be modified, the attendant changes in the size of the ligands allow for steric fine-tuning the coordination environment of metal centers.[1] Another feature is the variable hapticity exhibited by the ligands. A feature which may be of crucial importance in metal-mediated processes. However, despite the numerous well documented cases of η^3-,η^2-coordination,[1] the recently identified η^1-bonding in *trans*-$[Ni(p\text{-}MeC_6H_4)(Tp^{t\text{-}Bu})(PMe_3)_2]$[5] and even complexes containing strong M—N and weaker M---N bonds,[6] side-on type interaction between a metal and the pyrazolyl ring of a $Tp^{R,R'}$ ligand has not been reported. Here we wish to describe a uranium complex which is representative of this, hitherto unprecedented, type of interaction.

Reaction of uranium triiodide with two equivalents of potassium hydrotris(3,5-dimethylpyrazolyl)borate (KTp^{Me_2}) proceeds readily and gives, after simple workup, $(Tp^{Me_2})_2UI$ (**1**) as

$$UI_3(THF)_4 + 2KTp^{Me_2} \xrightarrow[3\ h]{THF/room\ temp} \underset{\mathbf{1}\ (82\%)}{(Tp^{Me_2})_2UI} + 2KI$$

a dark-blue, air-sensitive crystalline powder in good yield.[7] The elemental analysis and the spectroscopic data are in full accord with the molecular formulation. The ^1H NMR spectrum of the complex is deceptively simple. It displays only a single set of signals (ratio 3:3:1) for *all six* pyrazolyl groups. The shape of the resonances remains unchanged down to −100 °C. The absence of signals due to coordinated THF is to be contrasted with the nature of $(C_5Me_5)_2U(Cl)L$ (L = THF, pyridine, PMe_3) complexes,[8] which contain an additional Lewis base, but is not surprising in view of the sterically more demanding nature of the Tp^{Me_2} ligand. Unfortunately, the simple spectrum is singularly uninformative as to the coordination mode of the Tp^{Me_2} ligands and the structure of the complex.

To resolve this ambiguity the solid state structure of **1** was determined by single-crystal X-ray diffraction.[9] A view of the molecule is shown in Figure 1 and reveals several interesting features. It is immediately evident that the coordination modes of the two Tp^{Me_2} ligands are different, and therefore the simple ^1H NMR spectrum of **1** is clearly not the result of high molecular symmetry but is due to very facile interchange between the coordination modes of the two pyrazolylborate ligands and the resulting time-averaged environments of the pyrazolyl rings.

One of the Tp^{Me_2} ligands is bonded to uranium in an η^3-fashion, via N41, N51, and N61. However the second ligand is unusual and does not fit into any previously described categories. Two of the pyrazolyl nitrogens, N11 and N21, are at normal U—N separation, 2.559(6) and 2.591(5) Å, respectively. The orientation of the third pyrazolyl ring of this ligand is such that the lone pair of the potential donor atom, N31, is not pointing at the metal but, instead, it is the N—N bond of the pyrazolyl ring which is brought into side-on bonding interaction. Indeed, the U—N31 (2.807(5) Å) and U—N32 (2.833(5) Å) distances are nearly identical and are only 0.2−0.3 Å longer than the conventional U—N bond lengths. It may be somewhat bold to postulate a secondary, π-type interaction

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(1) (a) Trofimenko, S. *Prog. Inorg. Chem.* **1986,** *34,* 115. (b) Trofimenko, S. *Chem. Rev.* **1993,** *93,* 943. (c) Ligand nomenclature follows the method described by Trofimenko in ref 1b; Tp is the hydrotris(pyrazolyl)borate, and R and R′ identify the substituents on the 3- and 5-positions of the pyrazolyl rings, respectively.

(2) (a) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987,** *109,* 4726. (b) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989,** *111,* 375. (c) Ghosh, C. K.; Hoyano, J. K.; Krentz, R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989,** *111,* 5480.

(3) See for instance: (a) Ruggiero, C. E.; Carrier, S. M.; Antholine, W. E.; Whittaker, J. W.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **1993,** *115,* 11285. (b) Kitajima, N.; Hikichi, S.; Tanaka, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1993,** *115,* 5496. (c) Kitajima, N. *Adv. Inorg. Chem.* **1992,** *39,* 1. (d) Looney, A.; Parkin, G.; Alsfasser, R.; Ruf, M.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 92.

(4) (a) Han, R.; Parkin, G. *Inorg. Chem.* **1993,** *32,* 4968. (b) Reger, D. L.; Mason, S. S. *J. Am. Chem. Soc.* **1993,** *115,* 10406.

(5) Gutierrez, E.; Hudson, S. A.; Monge, A.; Nicasio, M. C.; Paneque, M.; Carmona, E. *J. Chem. Soc., Dalton Trans.* **1992,** 2651.

(6) (a) Canty, A. J.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1987,** *40,* 1609. (b) Bruce, M. I.; Walsh, J. D.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981,** 956.

(7) A THF solution (20 mL) of KTp^{Me_2} (285 mg, 0.846 mmol) is added dropwise, at room temperature, to a slurry of $UI_3(THF)_4$ (384 mg, 0.423 mmol) in the same solvent (15 mL). The mixture is stirred for 3 h and then inverse filtered. The solvent is removed under vacuum to give **1** as dark-blue, crystalline powder in quantitative yield. Analytically pure sample can be obtained (82% yield) by crystallization from THF. Data for **1** are as follows. IR (KBr, cm^{-1}); 2484 (ν_{B-H}). ^1H NMR (benzene-d_6, 25 °C), δ (ppm): 0.33 (s, Me), −11.71 (s, Me), 7.44 (s, 4-H). ^{11}B NMR (benzene-d_6, 25 °C), δ (ppm): 2.99. MS (EI, 70 eV, 200 °C): *m/z* 959 (M^+), 832 ($(M - I)^+$). Anal. Calcd for $C_{30}H_{44}B_2N_{12}IU$: C, 37.56; H, 4.62; N, 17.52; I, 13.23. Found: C, 37.40; H, 4.78; N, 16.66; I, 12.95.

(8) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W. *Organometallics* **1982,** *1,* 170.

(9) Crystal data for **1** ($C_{30}H_{44}B_2N_{12}IU$, fw = 959.32) at 23 °C are as follows: triclinic space group $P\bar{1}$ (No. 2), with $a = 11.866(2)$ Å, $b = 15.062(2)$ Å, $c = 11.423(2)$ Å, $\alpha = 93.12(1)°$, $\beta = 115.32(1)°$, $\gamma = 82.84(1)°$, $V = 1831.1$ Å^3, and $Z = 2$; $d_{calcd} = 1.740$ g cm^{-3}; μ(Mo Kα) = 50.74 cm^{-1}. A total of 6411 independent reflections having 2θ (MoKα < 50.0°) were collected on an Enraf-Nonius CAD4 automated diffractometer. Least-squares refinement of 415 parameters on 5068 absorption corrected reflections having $I > 3\sigma(I)$ converged at $R(R_w) = 0.043$ (0.053).

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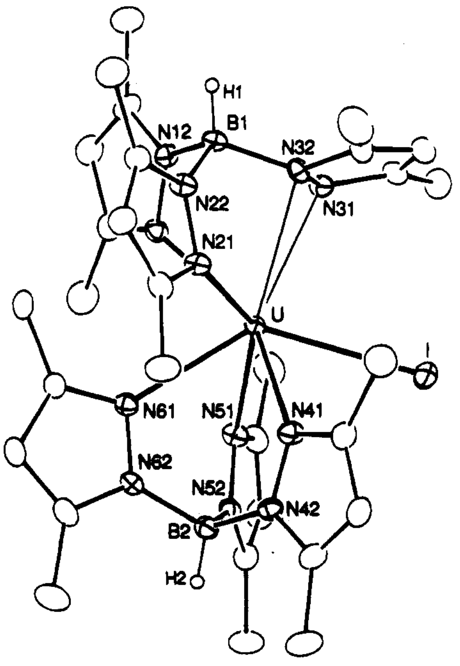

Figure 1. Perspective view of the molecule showing the atom-labeling scheme. Atoms are represented by Gaussian ellipsoids at the 20% probability level. Selected bond distances: U—N11 2.559(5), U—N21 2.591(5), U—N41 2.509, U—N51 2.510(6), U—N61 2.657(5), U- -N31 2.807(5), U- -N32 2.833(5) and U—I 3.220(1) Å.

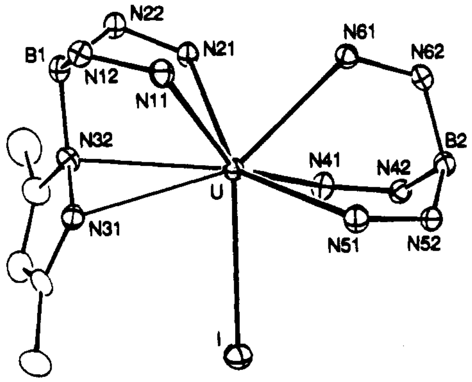

Figure 2. View of compound **1** showing the capped-octahedral molecular geometry, some atoms have been removed for clarity.

when the bonding in f-element complexes is commonly thought as being largely ionic.[10] However, Andersen[11] has clearly shown that the U(III) compounds, $(C_5H_4R)_3U$ (R = Me, $SiMe_3$), prefer soft donor ligands and form complexes with classical π-acceptor ligands, such as CNR′ and CO. That is, U(III) is capable of displaying characteristic covalent and π-type bonding interactions. The strength of the interaction in the present case may not rival that observed with $(C_5H_4R)_3U$. The N31—N32 distance is not different from the other N—N bond distances; however, a slight increase in the B—N bond length to the "dangling" pyrazolyl ring[12] and, more significantly, the "pyramidalization" of N32 in the complex[13] are further corroborative evidences for the presence of an attractive interaction between uranium and the pyrazolyl ring. Changes in hybridization and the attendant out-of-plane bending of the substituents is one of the typical consequences of metal coordination to unsaturated ligands.[14] It is interesting to note that, in the 16-electron complex $(\eta^2\text{-Tp}^{Me_2})Rh(CNCH_2CMe_3)_2$,[15] the orientation of the third pyrazolyl group is similar to that in **1**. However in that case no secondary interactions between Rh and the pyrazolyl ligand were detected, the calculated Rh---N distances are 3.92 and 3.30 Å, more than 1.2 Å longer than the normal Rh—N σ bonds.

The arrangements of the ligands around the U(III) center also supports the unusual interaction. A simplified diagram, focusing on the coordination environment, is shown in Figure 2. The coordination geometry is best described as a capped octahedron. One triangular face is formed by N11, N21, and N61 while the other comprises N41, N51, and the midpoint of N31—N32, with the iodide capping the latter face of the octahedron. The two triangular faces are almost parallel, the angle between the planes is 6.2°. The U—I bond length is 3.220(1) Å, which is almost 0.1 Å longer than the corresponding distances in $UI_3(THF)_4$.[16] The congested nature of the uranium center is manifested in the flattening of the octahedron; the *trans*-N—U—N angles range between 141 and 150°. It is also noteworthy that the U—N61 bond distance (2.657(5) Å), the one trans to the weakly interacting pyrazolyl ring, is significantly longer than the other two U—N bond lengths of the $\eta^3\text{-Tp}^{Me_2}$ ligand (U—N41 2.509(5) and U—N51 2.510(5) Å, respectively). It is as if the solid state structure represents a snap shot in the trajectory of the solution fluxional process. As one pyrazolyl group becomes fully coordinated, another changes its bonding mode and the exchange process is initiated. The presence of subtly different U—pyrazolyl interactions is consistent with the highly fluxional structure of **1**.

In summary we have presented evidence for a unique type interaction between a $Tp^{R,R'}$ ligand and a metal center. The observed bonding arrangement in complex **1** is undoubtedly due to a delicate balance between electronic demand of and steric congestion around the U(III) center; slight disturbances have potentially profound effect on coordination number and geometry.[17] Work is continuing to assess the influence that the substituents on the pyrazolyl ring and the ancillary ligands on uranium have on the nature of the bonding between U(III) and $Tp^{R,R'}$ type ligands. The chemistry of $(Tp^{Me_2})_2UI$ and the related $(Tp^{Me_2})UI_2(THF)_2$ is also under active investigation.

Acknowledgment. We thank Drs. D. L. Clark and A. P. Sattelberger for an initial gift of $UI_3(THF)_4$. Financial support from the University of Alberta and the NSERC (Canada) is gratefully acknowledged.

Supplementary Material Available: Text giving a detailed crystal structure analysis report for **1** including figures showing perspective views of the molecule and tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, rms amplitudes of thermal vibrations, hydrogen atom parameters, bond lengths and angles, and torsional angles (19 pages). Ordering information is given on any current masthead page.

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(11) Brennan, J. G.; Andersen, R. A.; Robbins, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 335.

(12) The B—N32 distance is 1.561(7) Å, compared to 1.537(7) Å, the average value of the other B—N bonds.

(13) A measure of this can be gauged from the displacement of N32 from the plane formed by B1, N31, and C34 and from the value of the sum of the angles around N32. N32 is out of the plane by 0.23 Å and the sum of the angles is 352.4° instead of 360°. The other N(B) nitrogens are strictly planar.

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(16) Clark, D. L.; Sattelberger, A. P.; Bott, S. G.; Vrtis, R. N. *Inorg. Chem.* **1989**, *28*, 1771.

(17) Indeed, iodide abstraction from **1** proceeds readily and gives $[(\eta^3\text{-Tp}^{Me_2})_2U(THF)]^+$. The presence of two $\eta^3\text{-Tp}^{Me_2}$ ligands and a coordinated THF molecule was corroborated by single-crystal X-ray determination. Sun, Y. M.; McDonald, R.; Takats, J. Manuscript in preparation.