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U(IV) and Th(IV) Hydrotris(3,5-dimethylpyrazolyl)borate Complexes with Asymmetric Metal Centres*

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The syntheses of $MCl_3[HB(3,5\text{-}Me_2pz_3)](thf)$ (where pz = pyrazolyl and thf = tetrahydrofuran) and their derivatives have been recently reported [1, 2]. It was shown that the ligand $[HB(3,5\text{-}Me_2pz_3)]^-$ was quite sensitive to the arrangement of the other ligands around the metal centre.

In this work we have studied the syntheses of complexes with asymmetric metal centres obtained from the above trischloro complexes by replacing two Cl^- ligands by Cp^- (Cp = cyclopentadienide) and OR^-. The chiral characteristics of the complexes $MCl(Cp)[HB(3,5\text{-}Me_2pz_3)](OR)$ could be detected by their ^1H NMR spectra.

Experimental

All preparative work was carried out in a nitrogen-filled glove-box or using Schlenk and vacuum line techniques. NaOR, NaCp, $MCl_2(Cp)[HB(3,5\text{-}Me_2pz)_3]$ and $UCl_2[HB(3,5\text{-}Me_2pz)_3](OR)$ were prepared as previously reported [2, 3].

Solution electronic absorption spectra were recorded using a Perkin-Elmer 577 spectrophotometer with samples mounted as Nujol mulls between CsI plates. ^1H NMR spectra were recorded using a Bruker SY80FT multinuclear spectrometer. C, H, and N analyses were obtained using a Perkin-Elmer automatic analyser.

Syntheses

All the compounds were prepared in a similar way, exemplified by the procedure (a) below. For the uranium complexes procedure (b) was also applied.

(a) To 202 mg (0.30 mmol) of $UCl_2(Cp)[HB(3,5\text{-}Me_2pz)_3]$ in 10 cm^3 of thf were added 28.9 mg (0.30 mmol) of $NaOBu^t$. After stirring for 24 h, the solution was centrifuged and the resulting green supernatant was evaporated to dryness, washed with a small volume of n-pentane (2 ml) and vacuum dried. The green solid could be sublimed onto a cold finger at 200 °C (10^{-2} mm Hg).

(b) A solution of 204 mg (0.30 mmol) of $UCl_2[HB(3,5\text{-}Me_2pz)_3](OBu^t)$ in 10 cm^3 of toluene was stirred with 26.4 mg (0.30 mmol) of sodium cyclopentadienide for 20 h. The solution, after being centrifuged, was evaporated to dryness, and the resulting green solid washed with n-pentane and vacuum dried.

The analytical and physical data of the complexes are collected in Table I.

Results and Discussion

The mixed complexes $MCl(Cp)[HB(3,5\text{-}Me_2pz)_3](OR)$ were obtained by reaction of the previously reported $MCl_2(Cp)[HB(3,5\text{-}Me_2pz)_3]$ [2], with the appropriate sodium alkoxide or aryloxide as shown in eqn. (1):

$$MCl_2(Cp)[HB(3,5\text{-}Me_2pz)_3] + NaOR \xrightarrow[RT]{thf} MCl(Cp)[HB(3,5\text{-}Me_2pz)_3](OR) + NaCl \qquad (1)$$

(M = U(IV), Th(IV); R = Bu^t, Pr^i, $C_6H_2\text{-}2,4,6\text{-}Me_3$)

In the uranium case the same compounds could be obtained by reaction of the previously reported $UCl_2[HB(3,5\text{-}Me_2pz)_3](OR)$ [2] with sodium cyclopentadienide in toluene (eqn. (2)):

$$UCl_2[HB(3,5\text{-}Me_2pz)_3](OR) + NaCp \longrightarrow UCl(Cp)[HB(3,5\text{-}Me_2pz)_3](OR) + NaCl \qquad (2)$$

(R = Bu^t, Pr^i, $C_6H_2\text{-}2,4,6\text{-}Me_3$)

This second procedure could not be applied to thorium because the analogous starting material could not be isolated.

The compounds are oxygen and moisture sensitive but can be stored at room temperature under nitrogen without noticeable decomposition. They are thermally stable and sublime in vacuum (10^{-2} mm Hg) at temperatures around 200 °C. They are soluble in aromatic solvents and moderately soluble in aliphatic solvents.

The ^1H NMR data (Table II) indicate that the three pyrazolyl rings are magnetically non-equivalent, giving rise to three distinct resonances for hydrogen-4 and five or six signals for the hydrogen atoms of methyl-3 and methyl-5.

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TABLE I. Analytical and Physical Data

Complex	Analysis (%)[a]			IR ν(B–H) (cm^{-1})	Electronic spectra[b] (nm)
	C	H	N		
$UCl(Cp)[HB(3,5\text{-}Me_2pz)_3](OBu^t)$ (1)	41.0 (40.7)	5.0 (5.0)	11.9 (11.9)	2553	646(m), 674(sh), 679(m), 694(sh), 900(w), 945(w), 1007(sh), 1036-(sh), 1071(sh), 1140(s), 1288(w,br)
$ThCl(Cp)[HB(3,5\text{-}Me_2pz)_3](OBu^t)$ (2)	39.5 (41.0)	4.8 (5.1)	11.3 (12.0)	2561	
$UCl(Cp)[HB(3,5\text{-}Me_2pz)_3](OPr^i)$ (3)	39.4 (39.7)	5.0 (4.9)	11.0 (12.1)	2553	640(m), 669(m), 695(sh), 900(w), 940(w), 1010(sh), 1030(sh), 1060-(sh), 1145(s), 1280(w,br)
$ThCl(Cp)[HB(3,5\text{-}Me_2pz)_3](OPr^i)$ (4)	38.3 (40.1)	5.1 (5.0)	11.4 (12.2)	2552	
$UCl(Cp)[HB(3,5\text{-}Me_2pz)_3](OC_6H_2\text{-}2,4,6\text{-}Me_3)$ (5)	43.3 (45.2)	4.9 (4.9)	10.4 (10.9)	2548	657(m), 669(w), 680(s), 690(sh), 940(w), 1014(sh), 1027(sh), 1054-(sh), 1071(sh), 1133(m), 1169(s)
$ThCl(Cp)[HB(3,5\text{-}Me_2pz)_3](OC_6H_2\text{-}2,4,6\text{-}Me_3)$ (6)	45.7 (45.5)	5.3 (5.0)	10.9 (11.0)	2565	

[a] Calc. values are in parentheses. [b] In toluene.

TABLE II. Room temperature ^{1}H NMR Data[a]

Complex	$HB(3,5\text{-}Me_2pz)_3$		Other resonances	
	(3,5-Mepz)	H(4)	Cp	OR
$UCl(Cp)[HB(3,5\text{-}Me_2pz)_3]$-$(OBu^t)$ (1)	50.61(3H), 18.07(3H) −10.36(3H),−11.15(3H) −17.51(3H),−18.00(3H)	49.33(1H) −13.61(1H) −16.07(1H)	−41.68(5H)	65.78(9H)
$ThCl(Cp)[HB(3,5\text{-}Me_2pz)_3]$-$(OBu^t)$ (2)	2.75(3H), 2.07(6H) 2.62(3H), 1.86(3H) 2.42(3H)	5.59(1H) 5.49(1H) 5.32(1H)	6.57(5H)	1.36(9H)
$UCl(Cp)[HB(3,5\text{-}Me_2pz)_3]$-$(OPr^i)$ (3)	55.76(3H), 16.51(3H) −11.64(3H),−11.79(6H) −16.17(3H)	48.87(1H) −13.12(1H) −15.71(1H)	−41.34(5H)	172.23(1H, m, CH) 65.81(3H, d, 6Hz, CH_3) 64.96(3H, d, 6Hz, CH_3)
$ThCl(Cp)[HB(3,5\text{-}Me_2pz)_3]$-$(OPr^i)$ (4)	2.69(3H), 2.07(6H) 2.60(3H), 1.88(3H) 2.36(3H)	5.59(1H) 5.50(1H) 5.31(1H)	6.58(5H)	4.37(1H, s, 6Hz) 1.20(6H, d, 6Hz)
$UCl(Cp)[HB(3,5\text{-}Me_2pz)_3]$-$(OC_6H_2\text{-}2,4,6\text{-}Me_3)$ (5)	46.80(3H), 9.48(3H) 3.23(3H), −9.72(3H) −11.97(3H),−19.35(3H)	37.51(1H) −4.14(1H) −12.07(1H)	−26.81(5H)	27.88(3H,o-CH_3), 24.28(3H,o-CH_3) 30.89(1H,m-H), 30.53(1H,m-H) 17.15(3H,p-CH_3)
$ThCl(Cp)[HB(3,5\text{-}Me_2pz)_3]$-$(OC_6H_2\text{-}2,4,6\text{-}Me_3)$ (6)	2.60(3H), 2.05(6H) 2.38(3H), 1.84(3H) 2.22(3H)	5.58(1H) 5.50(1H) 5.23(1H)	6.63(5H)	2.00(3H,o-CH_3), 1.98(3H,p-CH_3) 6.76(2H,m-H, br) 2.16(3H,p-CH_3)

[a] The shifts are in ppm from TMS; downfield shifts are positive; temperature = 300 K; d = doublet, s = septet, m = multiplet, br = broad; in benzene d_6.

In $UCl(Cp)[HB(3,5\text{-}Me_2pz)_3](OPr^i)$, (3), the isopropyl methyl groups are diastereotopic, giving rise to two doublets in the ^{1}H NMR spectrum.

The spectra of the aryloxide derivatives (5 and 6) display two resonances for the o-CH_3 protons of the aryl ring. For complex 5 two resonances are also observed for the m-H protons, while for the complex 6 only a broad resonance appears. This is indicative of hindered rotation of the aryloxide group that has already been observed for the complexes $UCl_2[HB(3,5\text{-}Me_2pz)_3](OC_6H_2\text{-}2,4,6\text{-}Me_3)$ and $UCl[HB(3,5\text{-}Me_2pz_3](OC_6H_2\text{-}2,4,6\text{-}Me_3)_2$ [3], but only below room temperature.

However, the most striking feature with the uranium complexes is the highfield shift experienced by the resonance of the protons of the cyclopentadienyl ring. The resonance of the Cp protons in $UCl_2(Cp)[HB(3,5\text{-}Me_2pz)_3]$ is at 15.3 ppm. After replacement of one of the Cl^- ligands by OR^- the value is shifted by +56.98 and +56.66 ppm for $R = Bu^t$ and Pr^i respectively. On the other hand, the resonance positions of the protons of OR^- groups and of the pyrazolyl ring which is *trans* to the OR^- group do not change when Cl^- is replaced by Cp^- in the parent compounds $UCl_2[HB(3,5\text{-}Me_2pz)_3](OR)$. When Cl^- is substituted by an aryloxide ligand a smaller highfield shift is observed for the Cp protons (+42.99 ppm) and even much smaller (+8.2 ppm) if a thiolate substitutes the Cl^-, as in the complex $UCl(Cp)[HB(3,5\text{-}Me_2pz)_3](SBu^t)$ [4]. These differences may be due to the different metal–Cp strengths of the various complexes according to the type of ligands involved and the attendant changes in magnetic susceptibility.

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