Cyclopentadienylactinoid(IV) Poly(pyrazol-1-yl)borates

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The bis(cyclopentadienyl) complexes $[U(cp)_2Cl_{2-x}\{HB(pz)_3\}_x]$ (cp = η-C_5H_5, pz = $C_3H_3N_2$, $x = 1$ or 2) have been prepared and are stable with respect to disproportionation, whereas the corresponding complexes with the $H_2B(pz)_2$ ligand are not. The complexes $[M(cp)Cl_{3-x}\{HB(pz)_3\}_xL_y]$ [M = Th, $x = 1$, $y = 1$, L = $Me_3CCONMe_2$ (dmpva) or $y = 1.5$, L = $MeCONMe_2$(dma); M = U, $x = y = 1$, L = PPh_3O and $x = 2$, $y = 0$], $[U(mcp)Cl_2\{HB(pz)_3\}]$ (mcp = η-methylcyclopentadienyl), $[Th(cp)Cl_2\{H_2B(pz)_2\}(dma)_{1.5}]$, $[Th(cp)Br_2\{HB(pz)_3\}(dmpva)_{1.5}]$, $[U(cp)Cl_2\{H_2B(pz)_2\}L_y]$ ($y = 2$, L = PPh_3O; and $y = 0$), $[U(cp)Cl\{H_2B(pz)_2\}_2(PPh_3O)_2]$, and $[Th(cp)Cl_2\{B(pz)_4\}]$ have also been prepared. Infrared, u.v.–visible (solution and reflectance, uranium complexes), and ^1H n.m.r. spectra are reported.

BIS(CYCLOPENTADIENYL)URANIUM(IV) complexes are unstable with respect to disproportionation to $[U(cp)_3Cl]$ and solvated $[U(cp)Cl_3]$ [1] or UCl_4,[2] but the disproportionation is inhibited when the uranium atoms are held apart in dimeric molecules, as in the complexes with ligands of the type [3] C_5H_4–$[CH_2]_n$–C_5H_4 and with a bis(phosphine oxide) ligand,[1] or when substituted cyclopentadienes are used, such as (C_5Me_4Et) [4] or (C_5Me_5),[5] which are too bulky to permit formation of the tris(cyclopentadienyl) complex. In the complex $[U(cp)Cl_2\{HB(pz)_3\}]$ (pz = pyrazolyl), reported earlier from this laboratory,[6] the $HB(pz)_3$ ligand is tridentate, so that it was of interest to attempt the preparation of complexes of the type $[U(cp)_2Cl_{2-x}\{HB(pz)_3\}_x]$ in the expectation that the need to break the three U–N bonds for the ligand rearrangement would provide a kinetic barrier to the disproportionation; the analogous complexes with the potentially bidentate $H_2B(pz)_2$ would also be of interest in this respect.

TABLE 1

Infrared spectra (cm^{-1}) of the complexes

Complex	ν(X=O) [a]	$\Delta\nu$(X=O) [a]	ν(M–Cl) [b]	ν(M–C_5H_5) [b]
$[Th(cp)Cl_2\{HB(pz)_3\}(dma)_{1.5}]$	1 605vs	42		
$[Th(cp)Cl_2\{HB(pz)_3\}(dmpva)]$	1 565vs	67	240s	255s
$[Th(cp)Br_2\{HB(pz)_3\}(dmpva)_{1.5}]$	1 565vs, 1 621m	67, 11		250m
$[Th(cp)Cl_2\{H_2B(pz)_2\}(dma)_{1.5}]$ [c]	1 605vs, 1 635 (sh)	42, 12		
$[U(mcp)Cl_2\{HB(pz)_3\}]$			240s	265s
$[U(cp)Cl_2\{HB(pz)_3\}(PPh_3O)]$	1 065s	125	230s	260m
$[U(cp)Cl_2\{H_2B(pz)_2\}]$			235m	260m
$[U(cp)Cl_2\{H_2B(pz)_2\}(PPh_3O)_2]$	1 060s	130	235m	260m
$[U(cp)Cl\{HB(pz)_3\}_2]$			245s	260—270br
$[U(cp)Cl\{H_2B(pz)_2\}_2(PPh_3O)_2]$	1 055s	135	235s	260m
$[U(cp)_2Cl\{HB(pz)_3\}]$			238s	260s
$[U(cp)_2\{HB(pz)_3\}_2]$				250s

br = Broad; m = medium; s = strong; v = very. [a] X=C(amide) or P(phosphine oxide). [b] Assignments are tentative. [c] Solution in CH_2Cl_2.

RESULTS AND DISCUSSION

Complexes of $[M(cp)X_2\{HB(pz)_3\}]$(M = Th *or* U, X = Cl *or* Br).—Amide [$MeCONMe_2$ (dma) or $Me_3CCONMe_2$ (dmpva)] complexes of $[Th(cp)Cl_2\{HB(pz)_3\}]$ were obtained by reaction of the corresponding amide complexes of [7] $[Th(cp)Cl_3]$ with the stoicheiometric quantity of $K[HB(pz)_3]$ in tetrahydrofuran (thf), a procedure used also for the preparation of $[Th(cp)Br_2\{HB(pz)_3\}(dmpva)_{1.5}]$ from the $[Th(cp)Br_3]$ complex. The attempted preparation of $[Th(cp)Cl_2\{HB(pz)_3\}]$ itself by the analogous reaction with $[Th(cp)Cl_3(thf)_{2.5}]$ did not yield an identifiable compound; when the product was heated at 220 °C (10^{-5} Torr),† a white sublimate of $[Th(cp)Cl_2\{B(pz)_4\}]$ was obtained, in marked contrast to the behaviour of $[U(cp)Cl_2\{HB(pz)_3\}]$ [6] and $[U(mcp)Cl_2\{HB(pz)_3\}]$ (mcp = methylcyclopentadienyl), prepared in the same way as the cp complex, which sublimed at 220 °C (10^{-3} Torr) (cp) and 180 °C (10^{-3} Torr) (mcp). In the i.r. spectra of the amide complexes, the shifts, $\Delta\nu$(CO), on complexation of the amide ligand (Table 1) in the complexes containing chloride are of the same order (solid mulls) as those observed for the corresponding amide complexes of $[Th(cp)Cl_3]$;[7] the i.r. spectrum of a chloroform solution of the complex $[Th(cp)Cl_2\{HB(pz)_3\}(dma)_{1.5}]$ exhibited two carbonyl features [ν(CO) at 1 605s and 1 635(sh) cm^{-1}] indicating the presence of both strongly and weakly bonded dma. However, the ^1H n.m.r. spectrum (see below) showed no resonances attributable to free or weakly bonded ligand at room temperature. In contrast, the i.r. spectrum of $[Th(cp)Br_2\{HB(pz)_3\}(dmpva)_{1.5}]$ indicates the presence of both strongly and weakly bonded dmpva in the solid

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† Throughout this paper: 1 Torr = (101 325/760) Pa.

state, and the ^{1}H n.m.r. spectrum of this complex (see below) suggests fluxional behaviour of the dmpva ligand.

The analogous reaction of $[U(cp)Cl_3(PPh_3O)_2]$ with the stoicheiometric quantity of $K[HB(pz)_3]$ in thf yielded a product the i.r. spectrum of which indicated that both free [ν(PO) at 1 190 cm^{-1}] and bonded [ν(PO) at 1 065 cm^{-1}] PPh_3O were present, although the situation was complicated by features due to the $HB(pz)_3$ ligand in this region of the i.r. spectrum. For this reason the i.r. spectra of 1 : 1 and 1 : 2 mol ratios of $[U(cp)Cl_2\{HB(pz)_3\}]$: PPh_3O were examined. The u.v.–visible spectra (Table 2) were the same for both mixtures, but the i.r. spectrum of the 1 : 1 mixture in dichloromethane showed only bonded PPh_3O, whereas features assignable to both bonded and free ligand were observed for the 1 : 2 mixture. The free ligand sublimed from these products at 190 °C (10^{-3} Torr) leaving $[U(cp)Cl_2\{HB(pz)_3\}(PPh_3O)]$. The shift, Δν(PO), on complexation is 125 cm^{-1} (Table 1), somewhat less than the values reported[1] for $[UCl_4(PPh_3O)_2]$ (150 cm^{-1}) and $[U(cp)Cl_3(PPh_3O)_2]$ (130 cm^{-1}).

TABLE 2

Principal features (1 000—1 300 nm) of the u.v.–visible spectra of the uranium(IV) complexes

Complex	Solution in thf	Solid reflectance
$[U(cp)Cl_2\{HB(pz)_3\}]$	1 157m (sh), 1 177s	1 174s
$[U(cp)Cl_2\{HB(pz)_3\}(PPh_3O)]$	1 025w, 1 112m, 1 172s	1 065w, 1 103m, 1 153s
$[U(cp)Cl_2\{H_2B(pz)_2\}]$	1 159s (sh), 1 183m	1 126s, 1 169(sh)
$[U(cp)Cl_2\{H_2B(pz)_2\}(PPh_3O)_2]$	1 112s, 1 149m, 1 183w	1 102s, 1 197(sh)
$[U(cp)Cl\{HB(pz)_3\}_2]$	1 077s, 1 123m, 1 172w	1 070s, 1 134(sh)
$[U(cp)Cl\{H_2B(pz)_2\}_2(PPh_3O)_2]$	1 128s, 1 159s	1 140s
$[U(cp)_2Cl\{HB(pz)_3\}]$	1 171s	1 164s
$[U(cp)_2\{HB(pz)_3\}_2]$	1 175s	1 146s

m = Medium, s = strong, sh = shoulder, w = weak.

TABLE 3

Hydrogen-1 and ^{13}C n.m.r. spectra of $[Th(cp)Cl_2\{HB(pz)_3\}(dma)_{1.5}]$

^{1}H (CD_2Cl_2) τ [a]				^{13}C $[CH_2Cl_2–CD_2Cl_2$ (3 : 1)] Chemical shifts (p.p.m.) [b]		
3.90(t)	(1)	H(4)U		20.2	$(N)CH_3$	dma
3.80(t)	(2)	H(4)B		38.5	$(N)CH_3$	
2.50	(1)	H(5)U		36.1	$(C)CH_3$	
2.38	(1)	H(3)U		104.46	C_5H_5	
				104.86		
2.29(d)	(2)	H(5)B		118.4	C(4)U	
1.95(d)	(2)	H(3)B		119.2	C(4)B	
9.10	(1)	BH		133.7	C(3)U	
7.99(s)	(4.5)	$(C)CH_3$	dma	133.8	C(3)B	
7.10(d)	(9)	$(N)CH_3$		143.8	C(5)U	
				145.0	C(5)B	
3.58(s)	(5)	C_5H_5				
3.38(s)						

d = Doublet; s = singlet; t = triplet. B indicates pyrazole ring which is bonded, and U unbonded, to the metal atom.

[a] Proton integrations are given in parentheses. [b] Chemical shifts downfield from $SiMe_4$, assuming that for CH_2Cl_2 is 54 p.p.m.

TABLE 4

Hydrogen-1 and ^{13}C n.m.r. spectra of $[Th(cp)Cl_2\{HB(pz)_3\}(dmpva)]$

^{1}H (CD_2Cl_2) τ [a]			^{13}C $[CH_2Cl_2–CD_2Cl_2$ (3 : 1)] Chemical shifts (p.p.m.) [b]	
3.80(3)	H(4)		27.8	$(C)CH_3$
2.38(3)	H(5)		38.9	$(N)CH_3$
2.00(3)	H(3)		104.9	C_5H_5
8.60(1)	B–H		105.3	
			120.0	C(4)
8.90(9)	$C–CH_3$	(dmpva)	136.6	C(3)
7.12(2)	$N–CH_3$		145.0	C(5)
3.63 (5)	C_5H_5			
3.40				

[a] Proton integrations are given in parentheses. [b] Chemical shifts downfield from $SiMe_4$, assuming that for CH_2Cl_2 is 54 p.p.m.

The ^{1}H n.m.r. spectrum of $[Th(cp)Cl_2\{HB(pz)_3\}(dma)_{1.5}]$ (Table 3) can be assigned on the basis that the $HB(pz)_3$ group is behaving as a bidentate ligand in this complex, in contrast to its tridentate behaviour in $[U(cp)Cl_2\{HB(pz)_3\}]$.[6] An interesting feature of the spectrum is the appearance of two sharp singlets at τ 3.58 and 3.38 (integration ratio, 2 : 1) arising from the η-C_5H_5 ring. This may be due to the presence of configurational isomers of the complex in the solution, as has been observed[8] for the complex $[Co(cp)\{HB(pz)_3\}(C_2F_5)]$. A similar splitting has been recorded[6] for $[U(cp)Cl_2\{HB(pz)_3\}]$, in the ^{1}H n.m.r. spectrum of which the two singlets at τ 3.44 and 3.34 are in the same ratio. The ^{13}C n.m.r. spectrum of the thorium complex (Table 3) confirms that the $HB(pz)_3$ group is bidentate and that the η-C_5H_5 ring is present in two different environments.

The ^{1}H and ^{13}C n.m.r. spectra of $[Th(cp)Cl_2\{HB(pz)_3\}(dmpva)]$ (Table 4) indicate that the $HB(pz)_3$ group is tridentate in this complex and that the η-C_5H_5 ring is again present in two different environments. This last feature is also evident from the ^{1}H n.m.r. spectrum of $[Th(cp)Br_2\{HB(pz)_3\}(dmpva)_{1.5}]$, but the remainder of the spectrum (Table 5) is more complicated than that of the chloro-complex. At room temperature it can be

TABLE 5

Hydrogen-1 n.m.r. spectra (τ) of $[Th(cp)Br_2\{HB(pz)_3\}(dmpva)_{1.5}]$ (1) and $[U(mcp)Cl_2\{HB(pz)_3\}]$ (2) in CD_2Cl_2 solution

(1) *				(2) *		
3.69(t)	(1)	H(4)U	bidentate $HB(pz)_3$	7.5(1)	B–H	
2.38(d)	(1)	H(5)U		6.6(3)	H(5) of pz or mcp ring CH_3	
2.35(d)	(1)	H(3)U		5.6(3)		
3.80	(2)	H(4)B		3.0(3)	H(4) of pz	
2.20	(2)	H(5)B		−5.9(2)	H(2) + H(5)	mcp ring
2.15	(2)	H(3)B		−7.7(2)	H(3) + H(4)	
3.66	(3)	H(4)	tridentate $HB(pz)_3$	−10.8(3)	H(3) of pz	
2.28	(3)	H(5)				
1.85	(3)	H(3)				
8.72	(27)	$(C)CH_3$	dmpva			
6.98	(18)	$(N)CH_3$				
3.46	(5)	C_5H_5				
3.25	(5)					

d = Doublet, t = triplet.

* Proton integrations are given in parentheses.

interpreted on the basis of a binuclear species with two bromine atoms bridging the two thorium atoms, one of which is co-ordinated to a bidentate, and the other to a tridentate, $HB(pz)_3$ group. Presumably, the co-ordination sphere about the first thorium atom is then completed by the extra dmpva molecule, giving rise to the non-integral stoicheiometry. The signal expected for the BH proton could not be identified in the spectrum. At <-45 °C, however, both $HB(pz)_3$ groups became identical and tridentate, and signals assignable to free dmpva were observed; thus, additional resonances at τ 6.88 and 7.14 (−90 °C) were assigned to the protons of the two non-equivalent $N-CH_3$ groups of free dmpva, together with a sharp singlet at τ 8.76 assigned to the $C-CH_3$ protons of the free ligand. Proton integration gave a ratio of 2 : 1 for non-bonded : bonded dmpva at this temperature, which suggests that there is an equilibrium of the form:

$$[\{Th(cp)Br_2[HB(pz)_3](dmpva)_{1.5}\}_2] \rightleftharpoons [\{Th(cp)Br_2[HB(pz)_3](dmpva)_{0.5}\}_2] + 2dmpva$$

The ^1H n.m.r. spectrum of $[U(mcp)Cl_2\{HB(pz)_3\}]$ exhibits a large chemical shift (τ—10.8) for H(3) of the pyrazole rings of the tridentate $HB(pz)_3$ group, as in the spectrum of $[U(cp)Cl_2\{HB(pz)_3\}]$,[6] and for two resonances (τ −5.9 and −7.7) which are each equivalent to two protons. These are presumably attributable to H(2),-H(5) and H(3),H(4) (or *vice versa*) of the mcp ring protons; if this assignment is correct, the chemical shifts are far larger than would be expected for mcp ring protons.

Complexes of $[M(cp)Cl_2\{H_2B(pz)_2\}]$.—The complex $[Th(cp)Cl_2\{H_2B(pz)_2\}(dma)_{1.5}]$ was obtained in the same way as the $HB(pz)_3$ analogue; as with the latter, the i.r. spectrum in chloroform exhibited two carbonyl stretching features (Table 1), at 1 605vs and 1 635(sh) cm^{-1}. indicative of the presence of both strongly and weakly bonded dma. However, the room-temperature ^1H n.m.r. spectrum (Table 6) showed no resonances attributable to the free or weakly bonded ligand. This spectrum also indicates that both the η-C_5H_5 rings and bidentate $H_2B(pz)_2$ ligands are bonded to the thorium atom in two different environments, both in the ratio 2 : 1. One possible interpretation could be that the species is ionic, of the form: $[Th(cp)\{H_2B(pz)_2\}(dma)_x]^+$-$[Th(cp)\{H_2B(pz)_2\}_2(dma)_{4.5-x}]^+[ThCl_6]^{2-}$. The problem can only be resolved by an *X*-ray structure determination; unfortunately, the complex is not well crystalline.

TABLE 6

Hydrogen-1 n.m.r. spectra (τ) of $[Th(cp)Cl_2\{H_2B(pz)_2\}$-$(dma)_{1.5}]$ (1), $[U(cp)_2Cl\{HB(pz)_3\}]$ (2), and $[U(cp)_2$-$\{HB(pz)_3\}_2]$ (3)

(1) ($CDCl_3$ solution) *			(2), (3) (CD_2Cl_2 solution) *	
2.31(4)	H(3)	$H_2B(pz)_2$		(2)
2.35(4)	H(5)		2.62	C_5H_5
3.70(4)	H(4)		3.58	H(5)
8.70(4)	BH_2		−2.0	H(4)
2.40(2)	H(3)	$H_2B(pz)_2$	−14.0	H(3)
2.42(2)	H(5)			(3)
3.80(2)	H(4)		3.03(10)	C_5H_5
9.11(2)	BH_2		3.22(6)	H(4)
3.36(5)		C_5H_5	1.92(12)	H(3), H(5)
3.54(10)			−0.02(2)	B–H
6.92(13.5)	(C)–CH_3	dma		
7.78(27)	(N)–CH_3			

* Proton integrations are given in parentheses.

The complex $[U(cp)Cl_2\{H_2B(pz)_2\}]$, prepared by reaction of $[U(cp)Cl_3(thf)_2]$ with the stoicheiometric quantity of $K[H_2B(pz)_2]$ in thf, is extremely air- and moisture-sensitive, being immediately oxidised to a dioxouranium(VI) species on exposure to the atmosphere; this reactivity led to poor analyses. Its u.v.-visible spectrum in thf is very similar to that of $[U(cp)Cl_2$-$\{HB(pz)_3\}]$, presumably because of solvation by thf. When heated at 200 °C (10^{-3} Torr) a green sublimate of approximate composition $U(cp)Cl_2\{H_2B(pz)_2\}(C_3H_4N_2)_3$ was obtained once in poor yield, but this result was irreproducible. Reaction of $[U(cp)Cl_2\{H_2B(pz)_2\}]$ with the stoicheiometric amount of Tl(cp) in thf led to immediate formation of $[U(cp)_3Cl]$, identified spectrophotometrically, indicating that the bidentate $H_2B(pz)_2$ ligand did not stabilise the expected bis(cyclopentadienyl)uranium(IV) complex, $[U(cp)_2Cl\{H_2B(pz)_2\}]$.

The complex $[U(cp)Cl_2\{H_2B(pz)_2\}(PPh_3O)_2]$, obtained by both of the methods used to prepare $[U(cp)Cl_2$-$\{HB(pz)_3\}(PPh_3O)]$, is much more stable towards air and moisture than $[U(cp)Cl_2\{H_2B(pz)_2\}]$ probably because of co-ordinative saturation; both molecules of PPh_3O are bonded to the metal atom [ν(PO) at 1 060 cm^{-1}].

Complexes $[U(cp)Cl\{H_nB(pz)_{4-n}\}_2]$ ($n = 1$ *or* 2).—The reaction of $[UCl_2\{HB(pz)_3\}_2]$ with Tl(cp) in thf is slow, ultimately yielding $[U(cp)Cl\{HB(pz)_3\}_2]$; the u.v.–visible spectrum of the complex (Table 2) is markedly different from that of the starting material and the complex does not sublime but decomposes at 200 °C (10^{-3} Torr). The complex $[U(cp)Cl\{H_2B(pz)_2\}_2(PPh_3O)_2]$ was obtained by the procedures used for $[U(cp)Cl_2\{H_2B$-$(pz)_2\}(PPh_3O)]$; its i.r. spectrum (Table 1) indicates that both molecules of PPh_3O are bonded to the metal atom and its u.v.–visible spectrum (Table 2) suggests a uranium(IV) species of high (>8) co-ordination number. No reaction occurred between $[UCl_2\{HB(3,5Me_2$-$pz)_3\}_2]$ ($3,5Me_2$-pz = 3,5-dimethylpyrazolyl) and Na(cp) in thf, and the reaction of $[U(cp)Cl_3(thf)_2]$ with $K[B(pz)_4]$ (1 : 1, 1 : 2, and 1 : 3 mol ratios) in thf gave involatile products of variable and inconclusive compositions.

The Complexes $[U(cp)_2Cl_n\{HB(pz)_3\}_{2-n}]$ ($n = 0$ *or* 1).—$[U(cp)_2Cl\{HB(pz)_3\}]$, obtained by reaction of $[U(cp)Cl_2$-$\{HB(pz)_3\}]$ or its PPh_3O complex with the stoicheiometric quantity of Tl(cp) in thf, is not volatile and does not decompose at 210 °C (10^{-3} Torr); it does not form a complex with PPh_3O when stirred overnight with the ligand in thf. Its ^1H n.m.r. spectrum indicates that the $HB(pz)_3$ group is tridentate, but the solubility of the compound in CD_2Cl_2 is low and the spectrum (Table 6) was not well defined. There was no evidence for σ-bonded cp at 175 K. Reaction of this compound with the stoicheiometric quantity of $K[HB(pz)_3]$ in thf yielded $[U(cp)_2\{HB(pz)_3\}_2]$; the u.v.–visible spectrum of this compound (Table 2) is very similar to that of $[U(cp)_2$-

$Cl\{HB(pz)_3\}]$, both being consistent with that expected for uranium(IV) species of high (>8) co-ordination number. Its ^1H n.m.r. spectrum (Table 6) indicates that the $HB(pz)_3$ groups are tridentate; the chemical shifts for H(3) and H(4) of the pyrazole rings are much smaller than those observed in the spectrum of $[U(cp)_2Cl\{HB(pz)_3\}]$, probably because of steric crowding in the bis $HB(pz)_3$ complex.

The attempted preparation of $[U(cp)_3\{HB(pz)_3\}]$ by reaction of $[U(cp)_3Cl]$ with the stoicheiometric quantity of $K[HB(pz)_3]$ yielded a product from which a small quantity of $[U(cp)_2\{HB(pz)_3\}_2]$ sublimed at 150 °C (10^{-3} Torr); the yield of the latter increased when the quantity of $K[HB(pz)_3]$ was doubled, confirming that the $HB(pz)_3$ group was replacing the C_5H_5 ring. In other experiments of this type a product of composition $[U(cp)\{HB(pz)_3\}_3]$ was occasionally obtained as a sublimate at 200 °C (10^{-3} Torr), but this result was not reproducible.

TABLE 7

Analytical results (%) [a]

Complex	Colour	M [b]	C	H	Halogen	N
$[Th(cp)Cl_2\{HB(pz)_3\}(dma)_{1.5}]$	White	32.5 (32.6)	32.9 (33.7)	4.1 (4.0)	10.2 (10.0)	14.3 (14.8)
$[Th(cp)Cl_2\{HB(pz)_3\}(dmpva)]$	White	33.2 (32.7)	35.0 (35.5)	4.6 (4.3)	9.4 (10.0)	12.5(13.8)
$[Th(cp)Br_2\{HB(pz)_3\}(dmpva)_{1.5}]$	White	26.7 (26.9)	33.6 (34.0)	4.6 (4.3)	18.6 (18.5)	11.6 (12.2)
$[Th(cp)Cl_2\{B(pz)_4\}]$	White	35.8 (35.9)	31.3 (31.5)	3.0 (2.8)	11.0 (10.1)	16.9 (17.3)
$[Th(cp)Cl_2\{H_2B(pz)_2\}(dma)_{1.5}]$ [c]	White	35.4 (35.9)	30.1 (31.6)	4.0 (4.1)	11.3 (11.9)	10.6 (10.9)
$[U(mcp)Cl_2\{HB(pz)_3\}]$	Bright green	36.6 (39.7)	29.7 (30.0)	2.8 (2.8)	11.0 (11.8)	14.9 (14.0)
$[U(cp)Cl_2\{HB(pz)_3\}(PPh_3O)]$	Green	26.9 (26.4)	43.5 (44.4)	3.8 (3.5)	8.2 (7.5)	8.5 (9.7)
$[U(cp)Cl_2\{H_2B(pz)_2\}]$	Green	45.0 (45.7)	26.8 (25.9)	3.1 (2.6)	12.8 (13.6)	9.8 (10.7)
$[U(cp)Cl_2\{H_2B(pz)_2\}(PPh_3O)_2]$	Green	21.4 (22.1)	52.9 (52.4)	4.4 (4.0)	5.9 (6.6)	5.4 (5.2)
$[U(cp)Cl\{HB(pz)_3\}_2]$	Green	29.9 (31.1)	34.9 (36.1)	3.6 (3.5)	5.7 (4.6)	21.3 (22.0)
$[U(cp)Cl\{H_2B(pz)_2\}_2(PPh_3O)_2]$	Green	19.5 (20.0)	52.7 (53.7)	4.6 (4.3)	2.6 (2.9)	9.6 (9.4)
$[U(cp)_2Cl\{HB(pz)_3\}]$	Dark green	37.9 (38.6)	35.3 (37.0)	3.5 (3.2)	5.6 (5.8)	13.2 (13.6)
$[U(cp)_2\{HB(pz)_3\}_2]$	Dark green-brown	30.3 (29.9)	42.0 (42.3)	4.0 (3.8)		21.5 (21.2)

[a] Calculated values are given in parentheses. [b] Th or U. [c] Calc. for $[Th(cp)_2\{H_2B(pz)_2\}(dma)_2]^+[Th(cp)\{H_2B(pz)_2\}_2(dma)_2]^+[ThCl_6]^{2-}$: C, 31.1; H, 4.0; Cl, 11.2; N, 11.8; Th, 36.8%.

Infrared Spectra.—In addition to the specific details given in Table 1, ν(BH) appeared at 2 400—2 490 cm^{-1} and C_5H_5 ring modes at 1 010—1 025 and 780—795 cm^{-1} in the spectra of the complexes.

EXPERIMENTAL

All the experimental work, including the drying of solvents and physical measurements, was carried out as described previously.[6,9,10] The compounds Tl(cp),[11] $K[HB(pz)_3]$, $K[H_2B(pz)_2]$,[12] $[Th(cp)X_3L_{2.5}]$ (X = Cl or Br; L = thf, dma, or dmpva),[7] $[UCl_2\{HB(pz)_3\}_2]$,[10] $[U(cp)Cl_3(thf)_2]$,[6] $[U(cp)Cl_2\{HB(pz)_3\}]$,[6] $[U(cp)Cl_3(PPh_3O)_2]$,[1] and $[U(mcp)Cl_3(thf)_2]$ [1] were prepared by published methods.

Preparations.— *Dichloro(η-cyclopentadienyl)(dimethylpivalamide)[hydrotris(pyrazol-1-yl)borato]thorium*(IV). The compound $K[HB(pz)_3]$ (0.335 0 g, 1.329 mmol) was added to a solution of $[Th(cp)Cl_3(dmpva)_{2.5}]$ (0.832 3 g, 1.329 mmol) dissolved in thf (40 cm^3); after stirring for 12 h the supernatant was evaporated to dryness *in vacuo*, leaving the white *complex* which was washed with n-pentane (3 × 2 cm^3) and vacuum dried (yield 74%). The complexes $[Th(cp)Cl_2\{HB(pz)_3\}(dma)_{1.5}]$ (yield 68%), $[Th(cp)Cl_2\{H_2B(pz)_2\}(dma)_{1.5}]$ (yield 65%), and $[Th(cp)Br_2\{HB(pz)_3\}(dmpva)_{1.5}]$ (yield 70%) were similarly prepared from $[Th(cp)Cl_3(dma)_{2.5}]$ and $[Th(cp)Br_2\{HB(pz)_3\}(dmpva)_{1.5}]$.

Dichloro(η-cyclopentadienyl)[tetrakis(pyrazol-1-yl)borato]thorium(IV). The compound $K[HB(pz)_4]$ (0.542 5 g, 2.153 mmol) was added to a solution of $[Th(cp)Cl_3(thf)_{2.5}]$ (1.256 3 g, 2.153 mmol) in thf (40 cm^3); the residue remaining after vacuum evaporation of the supernatant was heated at 220 °C (10^{-5} Torr), whereupon the *complex* sublimed in poor yield.

Dichloro[hydrotris(pyrazol-1-yl)borato](η-methylcyclopentadienyl)uranium(IV) was prepared from $[U(mcp)Cl_3(thf)_2]$ in the same way as $[U(cp)Cl_2\{HB(pz)_3\}]$;[6] the bright green *complex* sublimed at 180 °C (10^{-3} Torr) (yield 40%).

Dichloro(η-cyclopentadienyl)[hydrotris(pyrazol-1-yl)borato](triphenylphosphine oxide)uranium(IV). The compound PPh_3O (0.259 g, 0.932 mmol) in thf (30 cm^3) was added to a stirred solution of $[U(cp)Cl_2\{HB(pz)_3\}]$ (0.540 g, 0.919 mmol) in thf (20 cm^3). Vacuum evaporation of the solution left a green oily residue which yielded the solid *complex* when washed with n-pentane (2 × 5 cm^3) and vacuum dried (4 h) (yield 80%). The complex was also obtained by reaction of $[U(cp)Cl_3(PPh_3O)_2]$ with the calculated quantity of $K[HB(pz)_3]$; in this procedure the liberated PPh_3O was removed from the product by vacuum sublimation at 190 °C (10^{-3} Torr). The complexes $[U(cp)Cl_2\{H_2B(pz)_2\}(PPh_3O)_2]$ and $[U(cp)Cl\{H_2B(pz)_2\}_2(PPh_3O)_2]$ were similarly prepared from $[U(cp)Cl_3(PPh_3O)_2]$ (yields 65 and 60% respectively); the former was also prepared from $[U(cp)Cl_2\{H_2B(pz)_2\}]$ and PPh_3O in a similar manner to the above (yield 80%).

Dichloro(η-cyclopentadienyl)[dihydrobis(pyrazol-1-yl)borato]uranium(IV). The compound $K[H_2B(pz)_2]$ (0.361 g, 1.930 mmol) in thf (10 cm^3) was added to $[U(cp)Cl_3(thf)_2]$ (1.055 g, 1.908 mmol) in thf (20 cm^3); after stirring overnight, the green supernatant was evaporated to dryness *in vacuo* leaving a green oily residue which solidified on trituration with n-pentane to the very air- and moisture-sensitive complex. This was vacuum dried (4 h) (yield 65%).

Chloro(η-cyclopentadienyl)bis[hydrotris(pyrazol-1-yl)borato]uranium(IV). The compound Tl(cp) (0.381 g, 1.416 mmol) was added to a solution of $[UCl_2\{HB(pz)_3\}_2]$ (1.036 g, 1.409 mmol) in CH_2Cl_2 (25 cm^3). The mixture was stirred for 5 d, after which the supernatant was evaporated to dryness *in vacuo*; the *complex* was extracted into thf (10 cm^3) to separate it from any unchanged $[UCl_2\{HB(pz)_3\}_2]$. Vacuum evaporation of the extract yielded a green oily product which solidified on standing under n-pentane. This was vacuum dried (4 h) (yield 45%). The complex

$[U(cp)_2Cl\{HB(pz)_3\}]$ was prepared similarly from $[U(cp)Cl_2\{HB(pz)_3\}]$ (yield 60—75%). It did not sublime at 210 °C (10^{-3} Torr).

Bis(η-cyclopentadienyl)bis[hydrotris(pyrazol-1-yl)borato]-uranium(IV). A solution of $K[HB(pz)_3]$ (0.478 g, 1.889 mmol) in thf (10 cm^3) was added to a solution of $[U(cp)_2Cl\{HB(pz)_3\}]$ (1.157 g, 1.878 mmol) in thf (30 cm^3). After stirring overnight the green supernatant was treated in the same way as described for $[U(cp)Cl\{HB(pz)_3\}_2]$ to yield the dark greenish brown complex (yield 50%).

Analyses (Table 7) were obtained as described previously.[10]

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