Synthesis, spectroscopy, and crystal structure of a new stable biscyclopentadienyl uranium(IV) dichloride containing two C_5H_4-rings interlinked by a metal-coordinated 2,6-bis(methylene)pyridyl unit *

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Abstract

Reaction of the new disodium salt: $Na_2[2,6-C_5H_3N(CH_2C_5H_4)_2$ (**2**; $2,6-C_5H_3N = 2,6$-pyridyl) with UCl_4 in THF affords the reddish-green, mononuclear $Cp_2U^{IV}Cl_2$-derivative ($Cp = \eta^5-C_5H_5$): $\mu-\{2,6-CH_2C_5H_3NCH_2\}(\eta^5-C_5H_4)_2U^{IV}Cl_2$ (**1**). According to a single-crystal X-ray study, **1** involves a notably strong U–N bond (U–N_{av}: 2.62(1) Å) along with two nonequivalent Cl ligands (U–Cl: 2.615(3) and 2.636(3) Å).

The low-temperature ^1H NMR spectrum of the paramagnetic complex is in full accord with the solid state structure **1**. Up to room temperature, the dissolved molecules of **1** show no fluxionality on the NMR time scale, although the two CH_2 proton resonances appear to undergo coalescence.

Introduction

While mononuclear complexes of the type $(\eta^5-Cp)_2M^{IV}Cl_2$ (M=Ti, Zr and Hf) are readily accessible for ($Cp=C_5H_5$) [1], their U- and Th-congeners, in spite of a few contradictory reports [2], undergo facile ligand redistribution owing to the large size of the coordinatively unsaturated, U^{IV}- and Th^{IV}-ions [3]. To our knowledge, only with much bulkier cyclic ligands Cp′ like C_5Me_4R (R = Me or Et) [4] and $C_5(Me_3Si)_nH_{5-n}$ ($n = 2$ [5] and 3 [6]), or in the presence of ancillary ligands such as

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(unchelated) $Ph_2P(O)CH_2CH_2P(O)Ph_2$ [7] and 2,2'-bipyridine (bipy) [8], respectively, have stable $Cp_2'UCl_2$ systems been isolated. In the latter case [8], the chelating $C_5H_4CH_2C_5H_4$ ligand replaces two isolated C_5H_5 rings.

Tsutsui et al. [9] have shown first that the mononuclear $(C_5H_5)_2Ln^{III}Cl$ unit, which is similarly prone to ligand redistribution when Ln is one of the earlier lanthanoid metals, may be stabilized as a suitable metallocenophane derivative μ-$\{(CH_2)_n(\eta^5$-$C_5H_4)_2\}LnCl \cdot L$ ($n = 3$; Ln = La, Ce) [9]. More recently, some related metallocenophanes involving a bridging $(CH_2)_2O(CH_2)_2$ chain with a potentially metal-coordinating oxygen atom have been reported [10,19].

Following the strategy of making optimal use of the metallocenophane effect, we introduced the use of the notably more rigid, but likewise coordinatively active, 2,6-dimethylenepyridine group:
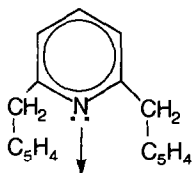
as a novel link of two C_5H_4 ligands coordinating a lanthanoid or actinoid ion [11–13]. In the present contribution, we describe the new uranium(IV) complex: μ-$\{2,6$-$CH_2C_5H_3NCH_2\}(\eta^5$-$C_5H_4)_2U^{IV}Cl_2$ (**1**), which is the first Cp_2UCl_2 system to be stable in the absence of ring peralkylation or any separate ancillary ligand.

Results

Synthetic procedures

The title complex, μ-$\{2,6$-$CH_2C_5H_3NCH_2\}(\eta^5$-$C_5H_4)_2U^{IV}Cl_2$ (**1**), was prepared at room temperature in yields of 70% by treating the disodium salt $Na_2[2,6$-$C_5H_3N(CH_2C_5H_4)_2]$ (**2**) with anhydrous UCl_4 (1:1) in tetrahydrofuran (THF). **2** was obtained by treating 2,6-bis(chloromethyl)pyridine (**3**) with $Na(C_5H_5)$ (1:4) in THF. Use of an excess of $Na(C_5H_5)$ is essential to bring about the sequence of reactions depicted on the next page.

Reaction of **3** with $Na(C_5H_5)$ in a 1:2 ratio gave only a rubber-like polymer still containing some chlorine. The synthesis of **3**, based on the replacement of the OH group of 2,6-bis(hydroxymethyl)pyridine by treatment with $SOCl_2$ was carried out by slight modification of the literature method [14] (cf. Experimental Section). It is noteworthy that **2** is more sensitive towards protolysis and traces of oxygen than, e.g., $Na(C_5H_5)$.

The ^1H NMR spectrum of the diamagnetic disodium salt **2** in THF-d_8 consists of one triplet (δ 7.54, $J = 7.5$ Hz, 1H) and one doublet (δ 7.01, $J = 7.5$ Hz, 2H) for the 2,6-pyridyl group, one singlet (δ 4.06, 4H) for the methylene groups, and two multiplets (centered at δ 5.62 and δ 5.44, respectively, 4H each) for the two C_5H_4 units. In contrast to the low-temperature ^1H NMR spectrum of the corresponding uranium(IV) salt (*vide infra*) that of **2** shows that the two $CH_2C_5H_4$ groups are virtually symmetrical with respect to mirror planes perpendicular to the plane spanned by all six carbon atoms of a $CH_2C_5H_4$ unit. The dark reddish-green colour of **1** contrasts significantly with the orange-brown colour reported for $[(Me_3Si)_2C_5H_3]UCl_2$ [5].

Na(C₅H₅) THF, RT   Na(C₅H₅) -C₅H₆   **(3)**

Na(C₅H₅) -NaCl   Na(C₅H₅) -C₅H₆   **(2)**
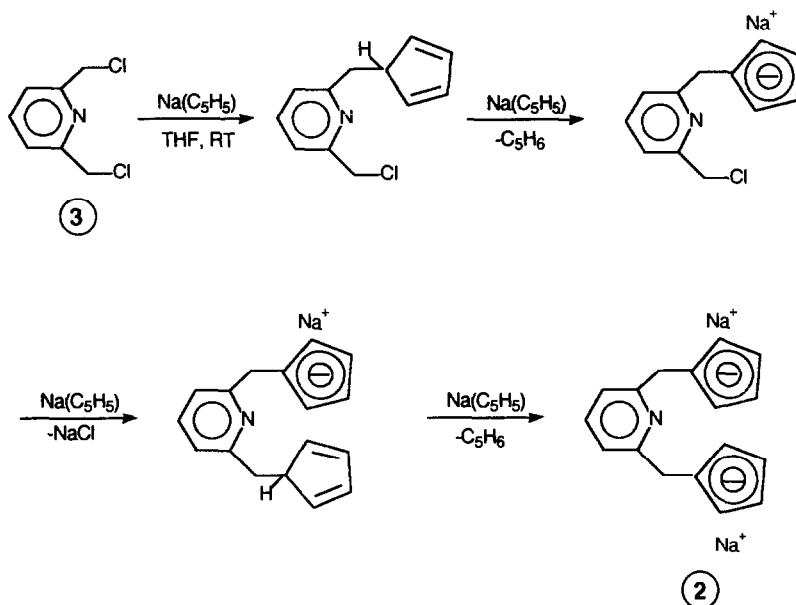
Spectroscopic properties of 1

^1H NMR. Owing to the (expected) paramagnetism of **1**, its ^{1}H NMR spectrum displays a series of widely separated resonances, partially devoid of multiplet splittings, whose shifts vary strongly with temperature. Up to room temperature, the total number of resonances is consistent with a rigid molecular structure involving two equivalent $CH_2C_5H_4$ units. Alongside one doublet and one triplet due to the pyridyl protons (-60 °C, δ 21.3, d, $J = 8$ Hz, 2H; δ 19.9, t, $J = 8$ Hz, 1H), and two doublets of the CH_2 protons (-60 °C: δ 5.7, d, $J = 17.5$ Hz, 2H; δ 11.2, d, $J = 17.5$ Hz, 2H), the rigidly fixed (*vide infra*) C_5H_4 units give rise to four equally intense singlets (-60 °C, d, -10.0, -25.4, -29.6 and -92.1, 2H each). Thus, the two ring H atoms in the α- and β-positions relative to the CH_2-group experience notably different magnetic environments. The anisotropy of the paramagnetic susceptibility of the non-axially symmetric complex **1** must be described in terms of *three* different principal tensor components, χ_x, χ_y and χ_z. Another organouranium(IV) system in which two C_5H_4 units are efficiently tied together is the complex μ-$\{CH_2CH_2CHMe\}(\eta^5$-$C_5H_4)_2U(\eta^5$-$C_5H_5)Cl$. The room temperature ^{1}H NMR shifts of its likewise spatially-fixed C_5H_4 groups (of all possible isomers) have been reported to lie between $+19$ and -35 ppm [15].

The strongly negative average of the four C_5H_4 proton resonances of **1** (-60 °C, δ_{av} -39.2) in keeping with those for the corresponding resonances of the rapidly rotating η^5-C_5H_5 ligands of the phosphoylide complex $[(\eta^5$-$C_5H_5)_2U(\mu$-$CHPCH_2Ph_2)]_2$ (ca -90 °C, δ_{av} -37.6) and $(C_5H_5)^a_2(C_5H_5)^bU\{\eta^2$-$N(2,6$-$Me_2C_6$-$H_4)C(^nC_4H_9)\}$ (-70 °C, $\delta(C_5H_5)^a$ -41.4), but less so with the resonances of $(C_5H_5)_2UX_2$ systems with X = BH_4, $^tC_4H_9$, and $N(C_2H_5)_2$ (room temperature, 5.8, -9.8 and -14.1 ppm, respectively) [16].

As the NMR spectrum of **1** in total indicates the presence of C_5H_4 ring and CH_2 substituent protons in both *cisoid* and *transoid* positions with respect to the halide
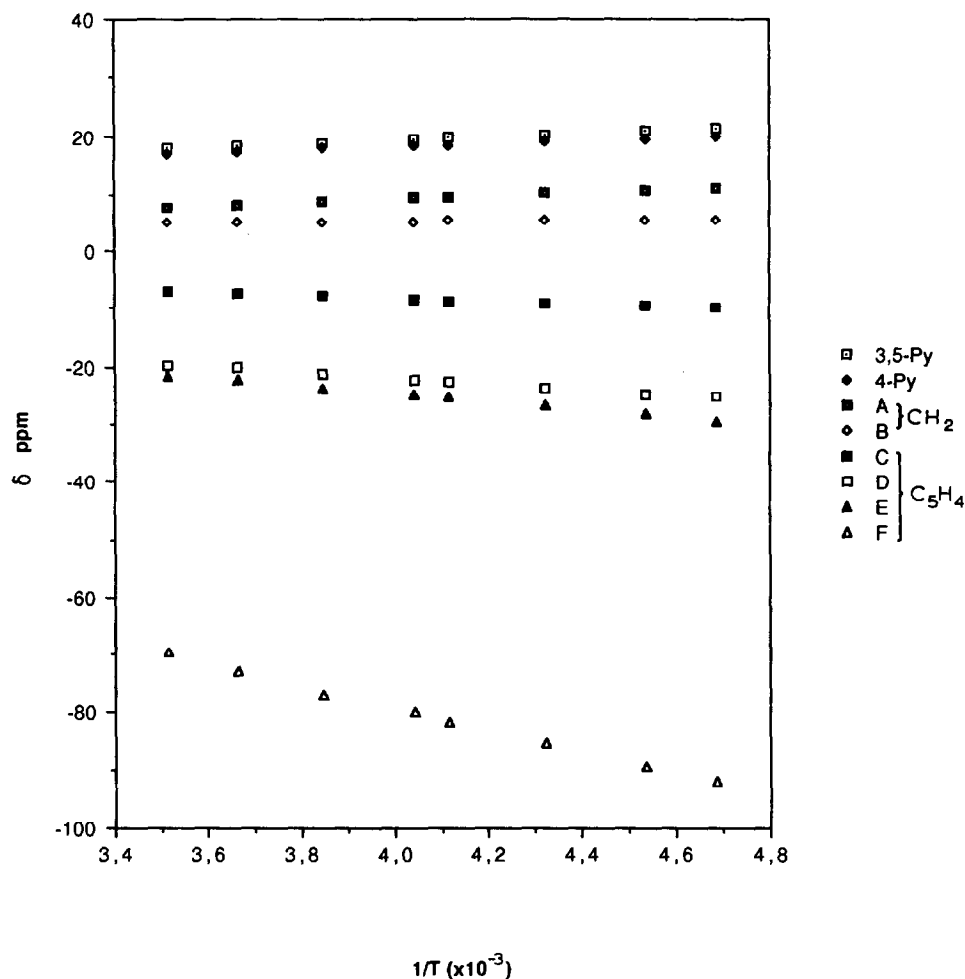
Fig. 1. Temperature-dependent NMR shifts of protons of compound 1.

ligands (cf. Figs. 3 and 4), it is reasonable to ascribe the most negative $\delta(C_5H_4)$ value to a *transoid* position. Assignment of all CH_2 and C_5H_4 resonances is, however, somewhat uncertain in view of the very low molecular symmetry of 1.

Figure 1 illustrates that up to room temperature all the ^1H NMR shifts for 1 vary inversely with temperature. Around 300 K only the two plots for the methylene resonances display slight deviations from linearity, suggesting, when considered along with the non-constancy of $J(^1H-^1H)$, that at more elevated temperatures full coalescence might be observed.

The mass spectrum of 1 is in excellent accord with the assumed composition $C_{17}H_{15}NCl_2U$, and hence with a mononuclear formulation. As revealed by extensive B/E linked-scan studies, the readily observable molecular ion $M^{+\cdot}$ strongly prefers to lose one Cl atom rather than direct loss of two Cl atoms and of the full organic ligand. The $C_{17}H_{15}NClU^+$ ion may fragment further by to six different pathways, three of which involve the liberation of the simple molecular moieties C_5H_5N, C_6H_6Cl and C_6H_6, respectively (Scheme 1). The loss of C_6H_6, C_5H_5N and $C_5H_5^\cdot$ is

-233 $[C_{17}H_{15}NUCl_2]^{+\cdot}$ $-\ 2Cl^-$ $[C_{17}H_{15}NU]^{+\cdot}$

M$^{+\cdot}$, m/z 541   m/z 471

$[UCl_2]^{+\cdot}$
m/z 308 $-\ Cl^-$ $-\ Cl^-$ $-\ Cl^-$

$[UCl]^+$ -233 $[C_{17}H_{15}NUCl]^+$ $-C_5H_5$ $[C_{12}H_{10}NUCl]^+$
m/z 273   m/z 506   m/z 441

$-C_6H_6Cl^\cdot$ $-C_6H_6$ $-C_5H_5N$

$[C_{11}H_9NU]^{+\cdot}$ $-\ Cl^-$ $[C_{11}H_9NUCl]^+$ $[C_{12}H_{10}UCl]^+$
m/z 393   m/z 428   m/z 427

Scheme 1

reminiscent of the previously reported fragmentations of organolanthanoid complexes containing substituted cyclopentadienyl ligands [17]. Moreover, several new lanthanoid complexes $[\mu\text{-}\{2,6\text{-}CH_2C_5H_3NCH_2\}(\eta^5\text{-}C_5H_4)_2Ln^{III}Cl]_n$ display mass spectra with fragmentation pathways very similar to those of **1** [11]. The relative abundances of the most important fragments of **1** are listed in Table 1.

The infrared spectrum of **1** (Nujol mull between KBr disks, 4000–400 cm^{-1}) is indicative of the coordination mode of the ligand. Thus a strong band at 1628 cm^{-1} (in the disodium salt **2** of the ligand this band occurs at 1591 cm^{-1}) can be assigned to $\nu(C{=}N)$ vibration, which is shifted to higher wavenumbers due to its coordination to the uranium ion. Moreover, coordination of the pyridine N-atom is strongly indicated by the well-documented shift of the ring-breathing vibration of the pyridine skeleton to higher wavenumbers (i.e. from 997 cm^{-1} for **2** to 1009 cm^{-1} for **1**).

Crystal and molecular structure of 1

The unit cell of **1** (Fig. 2) consists of two pairs of non-identical, mononuclear $\mu\text{-}\{2,6\text{-}CH_2C_5H_3NCH_2\}(\eta^5\text{-}C_5H_4)_2U^{IV}Cl_2$ molecules. Each pair is related by a center of symmetry, as the compound crystallizes in a triclinic cell, with two

Table 1

Mass spectrometric data of **1** (EI, 70 eV, T_{probe} 100 °C)

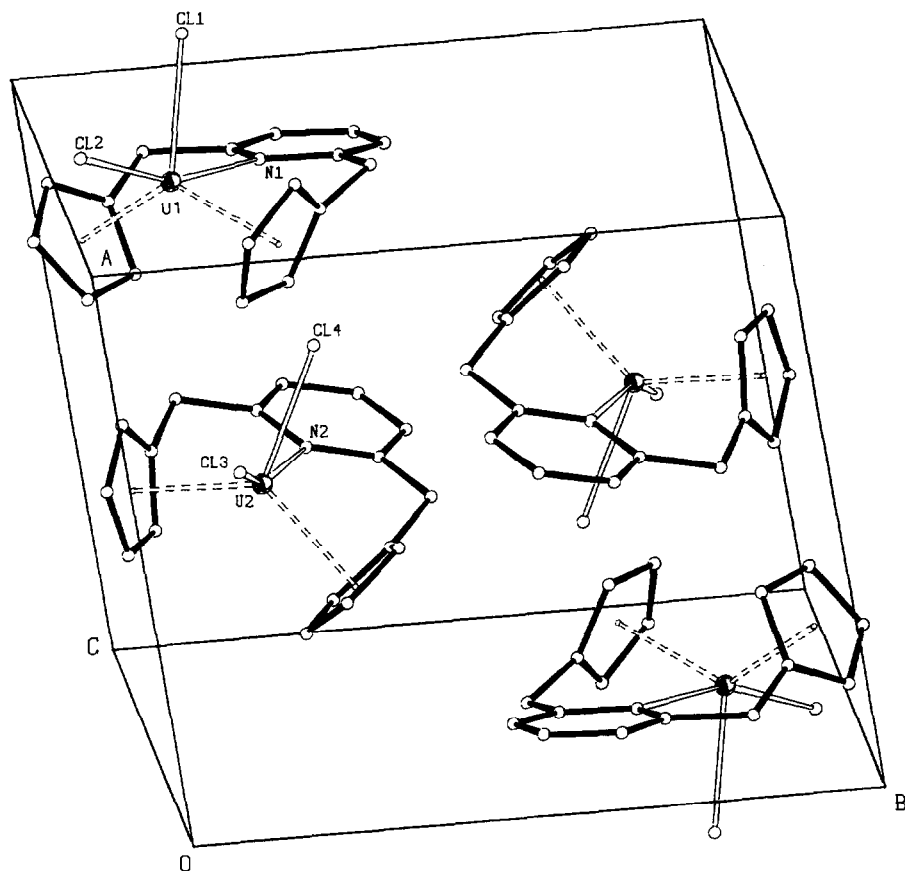| Fragment	m/z	Relative abundance (%)
$[C_{17}H_{15}NUCl_2]^{+\cdot}$	541	40
$[C_{17}H_{15}NUCl]^+$	506	62
$[C_{17}H_{15}NU]^{+\cdot}$	471	10
$[C_{12}H_{10}NUCl]^+$	441	5
$[C_{12}H_{10}UCl]^+$	427	10
$[C_{11}H_9NUCl]^+$	428	6
$[C_{11}H_9NU]^{+\cdot}$	393	1
$[C_5H_5UCl_2]^+$	373	100
$[UCl_2]^{+\cdot}$	308	30
$[UCl]^+$	273	11
$[C_{17}H_{15}N]^+$	233	19
$[C_5H_3N]^+$	77	30

Fig. 2. Unit cell of **1**.

molecules in the asymmetric unit. ORTEP plots of the two independent molecules, along with the atom numbering schemes, are given in Figs. 3 and 4, and individual interatomic distances and angles in Table 2.

The two non-equivalent molecules differ mainly in their conformations, as can be seen by comparing the torsion angles spanned by the two CH_2 bridges and the C_5H_4 and C_5H_3N units, respectively (cf. Table 2). In both molecules a plane containing the two Cl atoms together with the N- and the U-atom is almost symmetrically inserted between the two centers of the C_5H_4-rings. Among the possible coordination modes for 5-coordinated complexes, the moleculear configuration seems to be intermediate between the common structure of $Cp_2ML^1L^2_2$ systems [18] with perpendicular planes containing cent1, cent2, M and L^1, L^2, L^2, respectively, and trigonal bipyramidal (tbp) Cp_3ML_2 complexes [19], the latter being somewhat more realistic.

In this tbp-configuration, the pairs of atoms N(1)/Cl(2) and N(2)/Cl(3) would occupy axial positions, while the two C_5H_4 ring centroids and Cl(1) (or Cl(4) would lie at the equatorial sites. Comparison of the angles around the uranium ions reveals that the N–U–Cl axial systems are bent to different extents towards the equatorial chlorine. The departure from linearity is shown by the widening of the angle
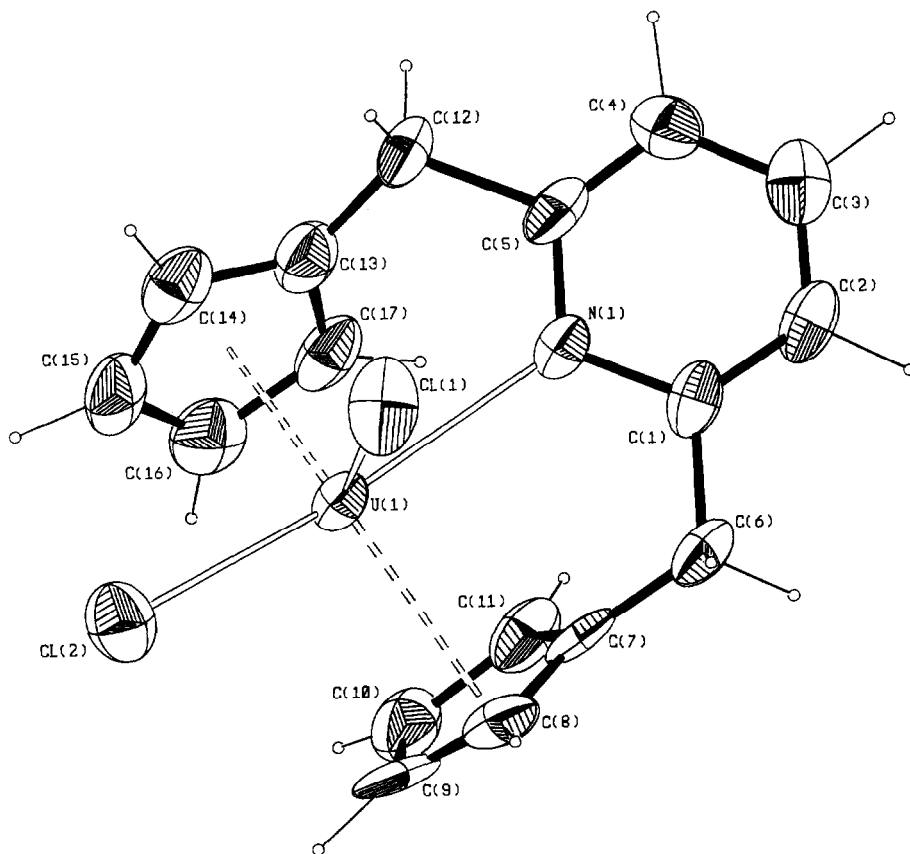
Fig. 3. ORTEP plot of one (A) of the two independent molecules in the asymmetric unit.

between the two Cp centroids (125.4(6)°) compared with that (120°) in the UCp_3 derivatives mentioned below. A view of the unit cell is shown in Fig. 2. There are no unusually short intermolecular nonbonding distances. In particular there is no evidence of stacking of the pyridine rings. A remarkable feature is that the mean U–N distance of 2.62(1) Å is shorter than the U–N distances in $(C_5H_5)_3U(NCS)$ $(NCCH_3)$ (U–NCC = 2.66(1) Å [20]), μ-$CH_2(C_5H_4)_2UCl_2$(bipy) (2.68(2) Å [8], $(C_5H_5)_3U(NCBH_3)(NCCH_3)$ (U–NCC = 2.699(12) Å [21]) and $U(H_3BCH_3)_4 \cdot L$ (L = $Me_2N(CH_2)_2NMe_2$; U–N_{av} = 2.73 Å [22]). However if we consider the individual U–N distances in the two independent molecules (A and B), they are significantly different: U(1)–N(1) is 2.635(9) Å and U(2)–N(2) is 2.597(9) Å (all the remaining bond distances in the uranium coordination spheres are equal within the experimental error). This difference is related to the conformational difference between the two ligand molecules as noted above (different torsional angles to the methylene bridges (see Table 2) and angles to the side chains: CMet–C–N(1) averages 114.5(5)° in molecule A and 117.5(5)° in molecule B). This suggests a possible reaction pathway to the complex formation: first coordination of the Cp rings takes place with the consequent rearrangement of the ligand, and this is followed by the pyridine nitrogen coordination. This behaviour is likely in view of
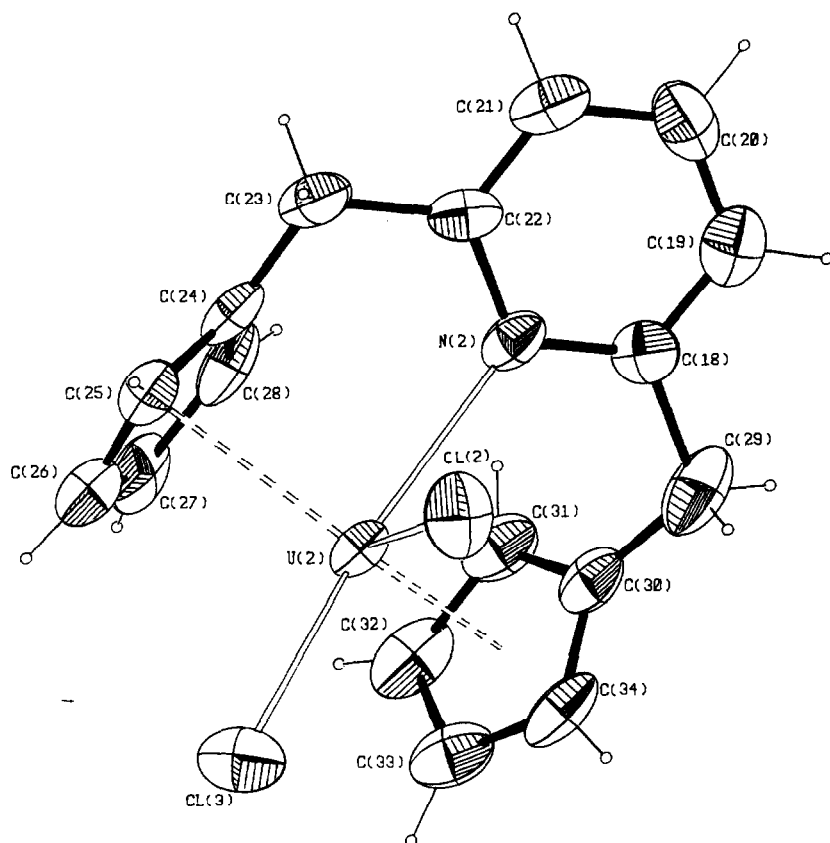
Fig. 4. ORTEP plot of the second (B) independent molecule in the asymmetric unit.

the ease with which the methylene groups can assume different conformations, which in all cases must be energetically rather similar. They are comparable to the values U–N(1) 2.639(5) Å, U–N(2) 2.644(6) Å found for the coordinated pyridine molecules in $(C_8H_8)UCl_2(NC_5H_5)_2$ [23]. The comparatively short U–N distance in 1 leaves no doubt that there is substantial chemical bonding between the pyridine nitrogen atom and the central uranium ion and accounts for the rigidity of the rather low-symmetry molecules in solution, as reflected by the low-temperature ^{1}H NMR spectra of 1 (*vide supra*).

As noted above, the two U–Cl distances in 1 differ slightly, but significantly (U–Cl$_{eq}^{av}$: 2.615(3) Å; U–Cl$_{ax}^{av}$: 2.636(3) Å. Thus as usual the pseudoequatorial ligand lies closer to the central metal ion than the pseudo-axial one. Both values exceed the U–Cl distances in $[(Me_3Si)_2C_5H_3]_2UCl_2$ (2.579(2) Å [24]), but are notably shorter than the distances in $CH_2(C_5H_4)_2UCl_2(bipy)$ (2.706(5) Å [8]) and in the anion $[\{(Me_3Si)_2C_5H_3\}_2UCl]^-$ (2.667(8) Å [25]), but are comparable with the distances U–Cl(1) 2.638(2) Å, U–Cl(2) 2.649(2) Å in the pentacoordinated complex (C_8H_8)-$UCl_2(NC_5H_5)_2$ [23]. Thus it seems that the N → U donor bond in 1 is less effective in lengthening the U–Cl distance than, e.g., the N → U bonds in $CH_2(C_5H_4)_2UCl_2$ (bipy). The distances of the two ring centers of 1 from the metal ion are practically equal, their average of 2.42(1) Å being slightly shorter than corresponding distances

Table 2

Selected bond distances (Å) and angles (°) with esd's in parentheses

Molecule A		Molecule B	
Coordination sphere			
U(1)–Cl(1)$_{eq}$	2.610(3)	U(2)–Cl(4)$_{eq}$	2.620(3)
U(1)–Cl(2)$_{ax}$	2.634(5)	U(2)–Cl(4)$_{ax}$	2.640(5)
U(1)–N(1)	2.635(12)	U(2)–N(2)	2.597(12)
U(1)–CE(7)	2.43(1)	U(2)–CE(24)	2.42(1)
U(1)–CE(13)	2.41(1)	U(2)–CE(30)	2.43(1)
U(1)–C$_{av}$	2.70(1)	U(2)–C$_{av}$	2.70(1)
Cl(2)–U(1)–N(1)	162.1(2)	Cl(3)–U(2)–N(2)	158.6(3)
Cl(1)–U(1)–Cl(2)	85.9(2)	Cl(3)–U(2)–Cl(4)	84.5(1)
N(1)–U(1)–Cl(1)	76.3(2)	N(2)–U(2)–Cl(4)	74.2(2)
N(1)–U(1)–CE(7)	87.9(4)	N(2)–U(2)–CE(24)	88.8(4)
N(1)–U(1)–CE(13)	87.1(4)	N(2)–U(2)–CE(30)	86.((5)
CE(7)–U(1)–CE(13)	125.8(6)	CE(24)–U(2)–CE(3)	124.9(6)
CE(7)–U(1)–Cl(1)	114.6(4)	CE(24)–U(2)–Cl(3)	113.5(4)
CE(13)–U(1)–Cl(1)	116.4(3)	CE(30)–U(2)–Cl(4)	117.5(3)
Ligand geometry			
N(1)–C(1)	1.39(1)	N(2)–C(18)	1.34(2)
N(1)–C(5)	1.36(2)	N(2)–C(22)	1.37(1)
C(1)–C(2)	1.35(2)	C(18)–C(19)	1.38(2)
C(1)–C(6)	1.52(2)	C(18)–C(29)	1.51(2)
C(2)–C(3)	1.36(2)	C(19)–C(20)	1.37(2)
C(3)–C(4)	1.38(2)	C(20)–C(21)	1.38(2)
C(4)–C(5)	1.35(2)	C(21)–C(22)	1.38(2)
C(5)–C(12)	1.56(2)	C(22)–C(23)	1.52(2)
C(6)–C(7)	1.51(2)	C(23)–C(24)	1.49(2)
C(7)–C(8)	1.40(2)	C(24)–C(25)	1.41(2)
C(7)–C(11)	1.42(2)	C(24)–C(28)	1.42(2)
C(8)–C(9)	1.43(2)	C(25)–C(26)	1.44(2)
C(9)–C(10)	1.39(3)	C(26)–C(27)	1.42(3)
C(10)–C(11)	1.44(2)	C(27)–C(28)	1.41(2)
C(12)–C(13)	1.49(2)	C(29)–C(30)	1.49(2)
C(13)–C(14)	1.38(2)	C(30)–C(31)	1.41(2)
C(13)–C(17)	1.42(2)	C(30)–C(34)	1.40(2)
C(14)–C(15)	1.39(2)	C(31)–C(32)	1.42(2)
C(15)–C(16)	1.41(2)	C(32)–C(33)	1.37(2)
C(16)–C(17)	1.42(2)	C(33)–C(34)	1.41(2)
C(1)–N(1)–C(5)	115(1)	C(18)—N(2)–C(22)	117(1)
N(1)–C(1)–C(6)	115(1)	N(2)–C(18)–C(29)	117(1)
N(1)–C(1)–C(2)	123(1)	N(2)–C(18)–C(19)	123(1)
C(2)–C(1)–C(6)	122(1)	C(19)–C(18)–C(29)	120(1)
C(1)–C(2)–C(3)	120(1)	C(18)–C(19)–C(20)	120(1)
C(2)–C(3)–C(4)	119(1)	C(19)–C(20)–C(21)	118(1)
C(3)–C(4)–C(5)	119(1)	C(20)–C(21)–C(22)	120(1)
N(1)–C(5)–C(4)	124(1)	N(2)–C(22)–C(21)	121(1)
C(4)–C(5)–C(12)	122(1)	C(21)–C(22)–C(23)	121(1)
N(1)–C(5)–C(12)	114(1)	N(2)–C(22)–C(23)	118(1)
C(1)–C(6)–C(7)	115(1)	C(22)–C(23)–C(24)	114(1)
C(6)–C(7)–C(11)	125(1)	C(23)–C(24)–C(28)	127(1)
C(6)–C(7)–C(8)	125(1)	C(23)–C(24)–C(25)	124(1)
C(8)–C(7)–C(11)	110(1)	C(25)–C(24)–C(28)	109(1)
C(7)–C(8)–C(9)	105(1)	C(24)–C(25)–C(26)	107(1)
C(8)–C(9)–C(10)	112(1)	C(25)–C(26)–C(27)	108(1)

Table 2 (continued)

Molecule A		Molecule B	
C(9)–C(10)–C(11)	106(1)	C(26)–C(27)–C(28)	108(1)
C(7)–C(11)–C(10)	107(1)	C(24)–C(28)–C(27)	108(1)
C(5)–C(12)–C(13)	113(1)	C(18)–C(29)–C(30)	113(1)
C(12)–C(13)–C(17)	127(1)	C(29)–C(30)–C(34)	126(1)
C(12)–C(13)–C(14)	126(1)	C(29)–C(30)–C(31)	126(1)
C(14)–C(13)–C(17)	107(1)	C(31)–C(30)–C(34)	108(1)
C(13)–C(14)–C(15)	110(1)	C(30)–C(31)–C(32)	108(1)
C(14)–C(15)–C(16)	107(1)	C(31)–C(32)–C(33)	108(1)
C(15)–C(16)–C(17)	107(1)	C(32)–C(33)–C(34)	110(1)
C(13)–C(17)–C(16)	108(1)	C(30)–C(34)–C(33)	107(1)
Torsion angles			
C(1)–C(6)–C(7)–C(8)	– 126(1)	C(22)–C(23)–C(24)–C(25)	– 122(1)
C(5)–C(12)–C(13)–C(14)	133(1)	C(18)–C(29)–C(30)–C(34)	130(1)
C(2)–C(1)–C(6)–C(7)	– 155(1)	C(21)–C(22)–C(23)–C(24)	– 162(1)
C(4)–C(5)–C(12)–C(13)	153(1)	C(19)–C(18)–C(29)–C(30)	157(1)
Significant angles among the ring planes of the organic ligand			
pCE(7)–pCE(13)	54.0(5)	pCE(24)–pCE(30)	54.9(5)
pPy(1)–pCE(7)	66.2(5)	pPy(2)–PCE(24)	65.5(5)
pPy(1)–PCE(13)	60.7(5)	pPy(2)–PCE(30)	59.8(4)
pPy(1)–pPy(2)	23.1(4)		

in the sterically more congested $(C_5H_5)_3U$-derivatives of genuine tbp-configuration (2.48(1) Å [20,21]).

Experimental

All reactions and handling of the complexes were carried out in a nitrogen-filled glove box (< 10 ppm of oxygen).

Materials

For all syntheses and further reactions, the reagent grade solvents used were rigorously freed from water and oxygen. Tetrahydrofuran (THF) was dried first by reflux over and distillation over $LiAlH_4$, and then by reflux over and distillation from potassium benzophenone. n-Hexane was dried by distillation over $LiAlH_4$ and then over potassium benzophenone solubilized with tetraglyme. Either Linde 4Å molecular sieve, activated by heating with a cool flame under high vacuum, or calcium hydride, was used to dry other organic solvents. THF-d_8 was dried over potassium benzophenone and degassed and transferred under high vacuum. CD_2Cl_2 was dried over CaD_2 and degassed and transferred under high vacuum. Anhydrous UCl_4 was prepared from uranium(IV) oxide and hexacloropropene [26]. Cyclopentadienyl sodium was prepared by treating the freshly distilled monomer with sodium dispersion in tetrahydrofuran.

Infrared spectra were recorded on a BIORAD FTS-40 interferometer. Samples were prepared in the glove-box as mulls in previously dried and degassed Nujol. Mulls were sandwiched between polished KBr plates contained in a O-ring sealed, airtight holder.

Elemental analyses were performed by Dornis and Kolbe Mikroanalytisches Laboratorium, Mühlheim/Ruhr, West Germany.

^{1}H NMR spectra were recorded on Varian FT-80 spectrometer equipped with a variable temperature accessory (Stelar VTC-87). Chemical shifts are reported relative to external $SiMe_4$.

All mass spectrometric data were obtained with a V.G. ZAB 2F instrument, interfaced with a V.G. 11/250 data system and operating under electron impact (EI) conditions (70 eV, 200 μA). Samples were prepared in glove-box in capillary glass tubes and introduced through a direct probe inlet at temperatures between 100 and 150°C. The ion source temperature was 200°C. Exact mass measurements were made only for uranium-containing ions by adopting the peak-matching technique at 10000 resolving power (10% valley definition). Metastable transitions were detected by B/E-linked scans [27].

2,6-Bis(chloromethyl)pyridine

2,6-Bis(hydroxymethyl)pyridine (Aldrich) (10 g, 7.18×10^{-2} mol) was dissolved in thionyl chloride (Aldrich) (50 mL) at 0°C and the solution gently warmed to 60°C under magnetic stirring during 3 h. Two thirds of the remaining thionyl chloride was distilled off and the mixture was added to 1 L of water-ice. The solution was made neutral with aqueous ammonia (25% NH_3), and the white precipitate was filtered off, washed several times with water, and dried under vacuum. Recrystallization from absolute ethanol/water (2:1, v:v) gave white needles (11.120 g, 88%yield), m.p. 74°C Anal Found: C, 47.55; H, 3.95; N, 7.90; Cl, 40.5. $C_7H_7NCl_2$ calcd.: C, 47.73; H, 3.98; N, 7.95; Cl, 40.34%. The major infrared (KBr pellets) peaks occurred at 1593, 1578, 1460, 1260, 1095, 998, 978, 752, 690, 680, 618, 565, 298 cm^{-1}.

2,6-Bis(methylenecyclopentadienyl)pyridine disodium salt [2]

To a magnetically-stirred solution of sodium cyclopentadienide (0.1436 mol) in 100 mL of THF was added during 2 h a solution of 2,6-bis(chloromethyl)pyridine (6.318 g, 3.59×10^{-2} mol) in THF (150 mL). The mixture was stirred overnight and the NaCl then filtered off. The volume of the light-brown solution was reduced under vacuum to 80 mL then n-hexane (100 mL) was added. The solution was set aside overnight and the white needles formed were filtered, washed with several portions of n-hexane, and dried under vacuum (8.57 g, 85% yield). Anal. Found: C, 73.05; H, 5.45; N, 5.25. $C_{17}H_{15}NNa_2$ calcd.: C, 73.12, H, 5.37; N, 5.02%. The major infrared (Nujol mull between KBr disks) peaks occurred at 1591, 1572, 1452, 1447, 1415, 1377, 1365, 1155, 1055, 1036, 1022, 997, 899, 796, 714, 661, 548 cm^{-1}. ^{1}H NMR (THF-d_8): δ 7.54 (t, 1H, py-H4, $J = 7.5$ Hz); 7.01 (d, 2H, py-H3,5, $J = 7.5$ Hz); 5.56 (m, 8H, Cp protons); 4.06 (s, 4H, CH_2).

$C_{17}H_{15}NUCl_2$ [1]

A solution of UCl_4 (2.084 g, 5.4×10^{-3} mol) in THF (50 mL) was slowly added at room temperature to a magnetically-stirred solution of 2,6-bis(methylenecyclopentadienyl)pyridine disodium salt (1.5 g, 5.35×10^{-3} mol) in THF (80 mL). During the addition the solution colour changed from light-brown to red-violet to green. When the addion was complete, the mixture was set aside overnight and the NaCl formed was then filtered of and the solution evaporated to dryness. The green

Table 3

Crystallographic details

Formula	$UCl_2NC_{17}H_{15}$
M	542.25
Space group	$P\bar{1}$
$a/\text{Å}$	13.611(3)
$b/\text{Å}$	12.935(3)
$c/\text{Å}$	10.210(2)
$\alpha/°$	78.01(3)
$\beta/°$	110.34(4)
$\gamma/°$	106.21(4)
$V/\text{Å}^3$	1607.1(9)
Z	4
$\rho/\text{calcd (g cm}^{-3})$	2.24
Radiation $(\lambda/\text{Å})$	0.71069
$\mu(\text{Mo-}K_\alpha)/\text{cm}^{-1}$	99.62
Reflections measured	6100
Reflections $I \geqslant 3\sigma(I)$	3514
$F(000)$	1000
$R = \Sigma[F_o| - |F_c|]/\Sigma|F_o|$	0.0341
$R_w = [\Sigma(F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$	0.0335
Weighting scheme w	$[\sigma^2(F_o) + 0.000515(F_o^2)]^{-1}$
Goodness of fit, S	1.15

crude product (2.037 g, 70% yield), was recrystallized from THF/n-hexane (2 : 1; v : v) to give dark red-green crystals suitable for an X-ray study. Anal. Found: C, 37.45; H, 2.90; N, 2.45; Cl, 13.15 $C_{17}H_{15}NUCl_2$ calcd.: C, 37.64; H, 2.77; N, 2.58; Cl, 13.10; U, 43.91%. The major infrared (Nujol mull on KBr disks) peaks occurred at 1628, 1611, 1572, 1462, 1377, 1365, 1167, 1063, 1051, 1036, 1009, 800, 797, 791, 650 cm^{-1}.

X-Ray measurements and structure determination

The crystal and refinement data for [(C$_5$H$_3$N)-2,6-(CH$_2$C$_5$H$_5$)$_2$]UCl$_2$ (dark-red transparent prism) are summarized in Table 3. A prismatic air sensitive crystal of dimension 0.14 × 0.12 × 0.008 mm was lodged in a Lindemann glass capillary and centred on a four-circle Philips PW 1100 diffractometer with graphite-monochromated Mo-K_α radiation. The orientation matrix and preliminary unit cell dimension were determined from 25 reflections found by mounting the crystal at random and varying each of the orientation angles χ and ϕ over a range of 120°, with $5 \leqslant \theta \leqslant 7°$. For the determination of precise lattice parameters, 25 strong reflections with $10 \leqslant Q \leqslant 13°$ were used. Integrated intensities for *hkl* reflections in the interval $h \pm 14$; $k \pm 14$; $l\ 0 \rightarrow 12$ were measured and two standard reflections, $-2,3,1$ and $2,2,2$ were examined every 180 min. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorentz-polarization effects and absorption as described by North et al. [28]. No correction was made for extinction. The structure was solved by use of three-dimensional Patterson Fourier techniques and refined with a full-matrix least-squares, with anisotropic thermal parameters assigned to all the non-hydrogen atoms. Hydrogen atoms were introduced at calculated positions and

Table 4

Fractional coordinates ($\times 10^4$) for non-hydrogen atoms and equivalent isotropic thermal parameters ($\mathring{A}^2 \times 10^3$) with esd's in parentheses

Atom	x	y	z	U_{eq}
U(1)	−1059.6(3)	1849.1(3)	7352.6(5)	32.7(2)
Cl(1)	877(3)	2482(3)	9042(4)	60(1)
Cl(2)	−236(3)	565(3)	6549(4)	55(2)
N(1)	−1276(7)	3250(7)	8716(10)	36(4)
C(1)	−1158(8)	4347(9)	8231(13)	38(5)
C(2)	−1268(9)	5074(10)	8914(14)	44(6)
C(3)	−1471(10)	474(10)	10163(15)	50(6)
C(4)	−1577(10)	3662(11)	10701(14)	49(6)
C(5)	−1502(10)	2960(10)	9952(13)	44(5)
C(6)	−885(10)	4685(9)	6856(12)	43(5)
C(7)	−1252(9)	3800(10)	5918(12)	40(5)
C(8)	−588(11)	3474(11)	5373(13)	48(6)
C(9)	−1272(15)	2612(13)	4584(15)	72(8)
C(10)	−2309(13)	2377(11)	4661(14)	60(7)
C(11)	−2313(10)	3139(10)	5512(13)	47(5)
C(12)	−1611(13)	1726(10)	10497(14)	59(7)
C(13)	−2006(10)	1038(10)	9337(14)	48(6)
C(14)	−1575(10)	210(10)	9262(15)	50(6)
C(15)	−2123(11)	−223(10)	7997(16)	55(7)
C(16)	−2939(11)	345(11)	7237(15)	55(7)
C(17)	−2851(9)	1147(10)	8060(14)	47(6)
U(2)	3878.8(3)	2319.7(3)	6489.4(5)	32.8(2)
Cl(3)	4727(3)	1917(3)	4736(4)	60(2)
Cl(4)	5812(2)	3474(3)	7587(4)	54(2)
N(2)	3758(7)	3168(8)	8505(10)	38(4)
C(18)	3547(9)	4157(10)	8283(13)	42(5)
C(19)	3602(10)	4685(11)	9353(15)	53(6)
C(20)	3824(11)	4180(11)	10703(17)	59(7)
C(21)	4008(11)	3152(11)	10955(14)	53(6)
C(22)	3979(9)	2658(10)	9859(12)	41(5)
C(23)	4210(10)	1534(10)	10122(13)	47(6)
C(24)	3810(10)	973(10)	8840(13)	42(5)
C(25)	4464(10)	597(9)	8325(13)	42(5)
C(26)	3788(13)	131(11)	7059(15)	63(7)
C(27)	2729(13)	251(10)	6813(15)	61(6)
C(28)	2740(9)	770(9)	7902(14)	47(5)
C(29)	3294(13)	4702(12)	6784(15)	68(8)
C(30)	2853(9)	3921(10)	5726(13)	41(5)
C(31)	2029(10)	2975(10)	5732(14)	49(5)
C(32)	1899(9)	2436(11)	4587(14)	54(5)
C(33)	2604(10)	3047(12)	3892(14)	55(6)
C(34)	3218(10)	3963(10)	4585(14)	50(6)

allowed to ride on associated carbon atoms during the least-squares refinement (d(C–H) = 0.95 $\mathring{A}$ and U = 0.07 $\mathring{A}^2$). The function minimized was $\Sigma w \Delta^2$ with $\Delta = (|F_o| - |F_c|)$. The final Fourier difference map showed only a residual of about 1 e $\mathring{A}^3$ near each uranium position.

The anomalous dispersion terms [29] for U and Cl were taken into account in the refinement. Atomic scattering factors were taken from ref. 29. Data processing and

computation were carried out by using the SHELX76 program package [30]; the program for the ORTEP drawing was from ref. 31. Table 4 shows the fractional coordinates of the non hydrogen atoms with equivalent isotropic U values. Tables of hydrogen atom coordinates, thermal parameters, a complete list of bond lengths and angles, and lists of calculated and observed structure factors are available from the authors.

Discussion

Complex **1** is the first structurally and spectroscopically well-characterized example of a bis(cyclopentadienyl)uranium(IV) dichloride, $Cp''_2U^{IV}Cl_2 \cdot L_n$ involving two monosubstituted cyclopentadienyl ligands and $n \leqslant 1$ (Table 5). Unlike the other complexes with $n > 0$, the ancillary ligand L of **1** is part of the bridge connecting the two cyclopentadienyl rings and may thus be considered as virtually masked. Both the relatively short U–N distances found crystallographically and the ^1H NMR spectra suggest that the U–N bond remains intact even in the presence of an excess of a donor species such as THF. Thus the strong similarity of the ^1H NMR spectra of **1** in CD_2Cl_2 and THF-d_8 solutions rules out the formation of any adduct of the type $\mathbf{1} \cdot (THF)_n$. The notably large isotropic shifts of the pyridyl protons, which probably reflect a considerable transfer of the free electron spin density from the metal ion into the pyridyl unit, still give a linear δ vs T^{-1} plot (cf. Fig. 1) at temperatures at which the methylene protons as well as two C_5H_4 ring protons (D and E) resonances start displaying coalescence. This feature could be due to an intramolecular inversion of **1** during which the equatorial and axial Cl atoms are mutually interchanged.

Metallocenophane complexes of transition metals poor in d-electrons (such as the rare earths Zr, Hf, Th, U etc.) and carrying two cyclopentadienyl ligands which are

Table 5

Survey of all stable $Cp''_2U^{IV}Cl_2 \cdot L_n$ ssytems reported to date

Cp ligands	Ancillary ligands n	Comments	X-ray study reported
C_5H_5	$(CH_2)_2\{P(Ph_2)O\}_2$ 1	binuclear complex	–
$(C_5H_4)_2CH_2$	bipy 2		[8]
μ-$\{2,6$-$CH_2C_5H_3NCH_2\}$ $(\eta^5$-$C_5H_4)_2$	C_5H_3N 1	ancillary ligand "masked"	this paper
$C_5H_3(SiMe_3)_2$ $(2\times)$	– 0		[5]
$C_5H_2(SiMe_3)_3$ $(2\times)$	– 0	incomplete description of the molecular structure	[6]
C_5Me_5 $(2\times)$	– 0		[8b]
C_5Me_5 $(2\times)$	$HNS(C_6H_5)_2$ 1		[22]
C_5Me_4Et $(2\times)$	– 0		–

chemically interlinked by a suitable group X have been of particular interest as potential precursors of homogeneous catalysts. The presence of the bridging group X is essential for several reasons: (a) the chelation of a Cp–X–Cp′ ligand efficiently prevents the complex from undergoing an otherwise facile stepwise loss of the cyclic ligands or, in cases of insufficient coordinative saturation, from undergoing inter-molecular ligand rearrangements; (b) the non-parallel arrangement of the two Cp ring planes enforced by most bridging groups X favours the availability of coordination sites for additional ligands and intermediately coordinated substrates; (c) when one of the cyclic ligands (Cp) differs from the other (Cp′), the resulting species $[(Cp–X–Cp')M]^{n+}$ will become intrinsically dissymmetric, a condition highly desirable in potential enantioselective catalysts; (d) recently, somewhat more sophisticated Cp–X′–Cp ligands have been introduced, in which the bridging groups X′ contains one sufficiently Lewis-basic atom which is, at least in the absence of likewise basic substrate molecules, able to coordinate loosely to the central metal atom [19].

In complex 1, the three conditions (a), (b), and (d), at least are fulfilled, making this complex a promising species for catalysis studies. In view of the rather strong U–N bond, 1 is, moreover, likely to form a cationic derivative in which the positive charge could be stabilized by delocalization over the fragment. There is increasing evidence that cationic biscyclopentadienyl zirconium(IV) complexes are of considerable importance as catalysts of homogeneous olefin polymerization [32].
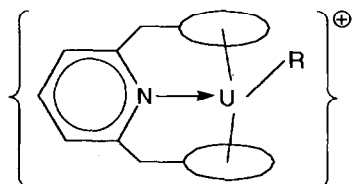
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