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Hydrotris(mesitylpyrazol-1-yl)borate uranium(IV) compounds: synthesis, structure, and ligand isomerization

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Reaction of UCl_4 with one equivalent of the thallium salt of $[HB(3\text{-}Mspz)_3]^-$ (=Tp^{Ms}, Ms = mesityl) afforded UCl_3Tp^{Ms*} **1**, due to isomerization of the Tp^{Ms} ligand to give $[HB(3\text{-}Mspz)_2(5\text{-}Mspz)]^-$ (=Tp^{Ms*}). Crystals of UCl_3Tp^{Ms} **2** were obtained fortuitously in one particular instance, but a real synthetic route to this compound was not achieved. **1** adds THF to afford $UCl_3Tp^{Ms*}\cdot THF$ **3**. Derivatization of **1** allowed the synthesis of $UCl_2[N(SiMe_3)_2]Tp^{Ms*}$ **4** and $UCl_2[C_6H_4CH_2NMe_2\text{-}o]Tp^{Ms*}$ **5**. The X-ray analysis of **1**, **2** and **4** revealed that the uranium centre is in an octahedral configuration, while in **5** the uranium is seven-coordinated by an additional U–N donor bond due to the chelating nature of the hydrocarbyl ligand. Nitriles and isocyanides do not insert into the U–C bond of **5**, but reaction with acetone leads to formation of the uranium aldolate $UCl_2[\eta^2\text{-}OC(Me_2)_2CH_2C(O)Me]Tp^{Ms*}$ **6**.

Introduction

Since the synthesis of the $AnCp_3Cl$ complexes,[1] organometallic actinide (An) chemistry has been dominated by cyclopentadienyl ligands. In 1980 the introduction of the pentamethylcyclopentadienyl ligand system led to the preparation of the soluble bis-ligated complexes, $AnCp^*_2R_2$, which exhibited a remarkable reactivity.[2] Hence, it is not surprising that most of the work with early actinides has focused primarily on compounds based on Cp^*_2An and Cp_3An frameworks.[3] In contrast, reports of actinide compounds based on monocyclopentadienyl or mono(pentamethylcyclopentadienyl) ligand sets are scarce,[3,4] although increased reactivity should be expected for these compounds with a higher steric and electronic unsaturation.

As part of a study to assess the effect of the ancillary ligand system on the reactivity of uranium(IV) compounds, we have reported the synthesis and X-ray structural characterization of the compound $UCl_3Tp^*(THF)$[5] ($Tp^* = HB(3,5\text{-}Me_2pz)_3$), which is a versatile starting material for the synthesis of a series of uranium mono-ligated complexes,[6] including the hydrocarbyls $UCl_2(R)Tp^*$ (R = CH_2SiMe_3, $CH(SiMe_3)_2$, $C_6H_4NMe_2\text{-}o$ or $CH_2C_6H_4NMe_2\text{-}o$).[7,8] However, when R was Me, CH_2Ph or Ph stable U(IV) hydrocarbyl derivatives could not be isolated.[8]

The synthesis of a series of bulky hydrotris(pyrazolyl)borate ligands and their proven synthetic utility for transition metal, main group, and lanthanide derivatives[9] led us to study the behaviour of uranium(IV) compounds with such ligands, as it would be expected that a more constrained environment around the metal could provide an enhanced stability to the complexes, as compared with the Tp* ligand set. With this purpose we chose the hydrotris(3-mesitylpyrazolyl)borate ligand $[HB(3\text{-}Mspz)_3]^-$ (=Tp^{Ms}),[10] as the orthogonality between the plane of the mesityl substituent and that of the pyrazolyl ring leads to very efficient screening of the coordinated metal. We describe here the result of the reaction of UCl_4 with Tp^{Ms} that does not afford the expected UCl_3Tp^{Ms} but rather UCl_3Tp^{Ms*} ($Tp^{Ms*} = HB(3\text{-}Mspz)_2(5\text{-}Mspz)$), formed by way of isomerization of Tp^{Ms} to Tp^{Ms*}. The synthesis and X-ray structural characterization of the complexes $UCl_2[N(SiMe_3)_2]Tp^{Ms*}$ and $UCl_2(C_6H_4CH_2NMe_2\text{-}o)Tp^{Ms*}$ is also described.

Results and discussion

Synthesis and characterization of the complexes

UCl_3Tp^{Ms*} 1. Treatment of a thf solution of UCl_4 with 1 equivalent of the thallium salt of hydrotris(3-mesitylpyrazolyl)borate, at room temperature, resulted in precipitation of TlCl and formation of a green solution. Removal of the solvent gave a light green powder which still contained TlCl. The product could easily be separated from TlCl by extraction with toluene. The isolated compound was soluble in ether and halogenated solvents, and aromatic hydrocarbons, but insoluble in hexanes. With the ligand exhibiting C_{3v} symmetry, a fairly simple NMR spectrum was expected for the octahedral UCl_3Tp^{Ms} complex. Actually this was not the case, as the ^1H NMR spectrum of the compound isolated in the reaction displayed two resonances for each of the pyrazolyl 4 and 3(5) protons and for the 4′-methyl protons of the mesityl substituents with a 2 : 1 intensity ratio, consistent with C_s symmetry. The symmetry found in solution indicated that isomerization of the ligand to $HB(3\text{-}Mspz)_2(5\text{-}Mspz)$ (Tp^{Ms*}) may have occurred. If this was so the plane of symmetry passing through the 5-Mspz would separate the 2′,6′-methyls and the 3′,5′-protons of the 3-Mspz groups into inner and outer sets with respect to that plane. In fact, due to the paramagnetism of the uranium centre, 1 : 1 : 1 patterns for these methyls and for the protons were observed. Also, one resonance accounting for one single proton highly shifted to low field, as expected for a proton close to the paramagnetic centre, pointed to the presence of a proton in the 3 position of one pyrazolyl ring.

At room temperature, the resonances assigned to the 2′,6′-methyls and the 3′,5′-protons of the 3-mesitylpyrazolyl rings were broadened, probably due to a small degree of oscillatory freedom between the planes of the mesityl and the pyrazolyl rings, but on lowering the temperature they sharpened and shifted due to the temperature dependence of the magnetic susceptibility.

In the IR spectrum of the compound the B–H stretching vibration appeared at 2510 cm^{-1}, which is also consistent with the formation of a Tp^{Ms*} complex. As reported by Rheingold *et al.* the B–H stretching vibration appears at 2430 cm^{-1}

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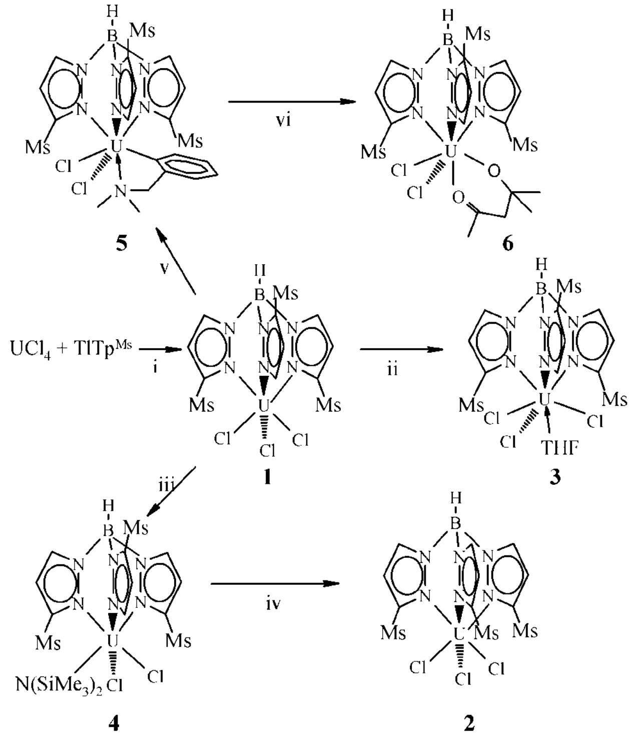
for $\mathrm{TlTp^{Ms}}$ and at 2492 $\mathrm{cm^{-1}}$ for $\mathrm{TlTp^{Ms*}}$.[10] The higher wavenumber for $\mathrm{Tp^{Ms*}}$ complexes, as compared with those for $\mathrm{Tp^{Ms}}$, was also observed for several $\mathrm{Tp^{Ms*}/Tp^{Ms}}$ derivatives with other elements.[10] Thus, the spectroscopic data were consistent with formation of $\mathrm{UCl_3Tp^{Ms*}}$ (**1**, Scheme 1). This conclusion was confirmed by running the reaction of $\mathrm{UCl_4}$ with one equivalent of the thallium salt of authentic $\mathrm{Tp^{Ms*}}$. The compound isolated displayed an NMR spectrum superimposable on that of the compound obtained in the reaction of $\mathrm{UCl_4}$ with $\mathrm{TlTp^{Ms}}$.



Scheme 1 (i) THF, extraction with toluene; (ii) THF; (iii) $\mathrm{KN(SiMe_3)_2}$, toluene; (iv) recrystallization from toluene; (v) $\mathrm{Li(C_6H_4CH_2NMe_2}$-*o*), toluene; (vi) acetone, n-hexane.

This rearrangement is unexpected since only the reverse isomerization, from $\mathrm{Tp^{Ms*}}$ to $\mathrm{Tp^{Ms}}$, has been reported to occur with $\mathrm{TlTp^{Ms*}}$, which was cleanly converted at the melting point into $\mathrm{TlTp^{Ms}}$,[10] although rearrangement of one of the pyrazolyl rings of a symmetrical ligand to yield an asymmetrical bound ligand is well documented for other hydrotris(pyrazolyl)borate ligands.[11] Isomerization of the related ligand system $\{\kappa^3\text{-HB(3-Pr}^i\text{pz)}_3\} \longrightarrow \{\kappa^3\text{-HB(3-Pr}^i\text{pz)}_2\text{(5-Pr}^i\text{pz)}\}$ has been observed during formation of the cobalt bis-ligand complex, resulting in conversion of one of the 3-isopropyl groups into a 5-isopropyl group, driven by relief of the strain imposed by six isopropyl rings in the equatorial belt of the octahedral complexes.[11a] In the uranium case, formation of the symmetrically bonded $\mathrm{UCl_3Tp^{Ms}}$ (**2**, Scheme 1) is not prevented by steric interactions of the three 3-mesityl groups, because this compound is accessible under different reaction conditions (see below). The actual mechanism of these rearrangements could involve either a 1,2-borotropic or 1,2-metallotropic shift, but at this stage we have no evidence of which type is operative in our system. Although a borotropic mechanism has often been invoked to explain the rearrangement of the ligands, recent work on the isolation of numerous 1,2-endobidentate pyrazolato complexes[9a] and the unusual side-on type interaction between uranium and one pyrazolyl ring of a Tp* ligand in the complex $\mathrm{UTp^*_2I}$[12] makes a metallotropic rearrangement mechanism plausible. The observation by some authors that rearrangement was significantly faster in THF than in non-coordinating solvents[11b,c] is consistent with either type of mechanism. The coordinating properties of the solvent can compete with the pyrazolyl ligands for the positions available in the coordination sphere of the metal ion, inducing pyrazole displacement and subsequent borotropic shift or favor the metallotropic rearrangement by stabilizing the trigonal boron transition state.[13]

In order to confirm the identity of compound **1**, to establish the precise coordination geometry and to obtain the metrical parameters, the solid state structure was determined by single crystal X-ray diffraction (see below).

$\mathrm{UCl_3Tp^{Ms*}(THF)}$ 3. Compound **1** readily forms the THF adduct $\mathrm{UCl_3Tp^{Ms*}{\cdot}THF}$ (**3**, Scheme 1) on addition of THF. This behaviour is similar to that found for the uranium compound with the Tp* ligand. Also in this case both compounds, $\mathrm{UCl_3Tp^*}$ and $\mathrm{UCl_3Tp^*{\cdot}THF}$, were isolated and structurally characterized.[5,14] At room temperature a complete assignment of the ^{1}H NMR spectrum could not be made, due to fortuitous overlap of some resonances, but on lowering the temperature the resonances shifted and a spectrum consistent with C_s symmetry could clearly be identified. In addition, the spectrum displayed two resonances accounting for the methylene groups of the coordinated THF.

$\mathrm{UCl_2[N(SiMe_3)_2]Tp^{Ms*}}$ 4. Slow addition of a stoichiometric amount of $\mathrm{K[N(SiMe_3)_2]}$ to a toluene solution of compound **1** led to immediate formation of a very intense green solution. Simple work-up followed by recrystallization from toluene yielded crystals of $\mathrm{UCl_2[N(SiMe_3)_2]Tp^{Ms*}}$ in moderate yield (**4**, Scheme 1). The room temperature ^{1}H NMR showed only one broad resonance for the 6 Me protons of the $\mathrm{N(SiMe_3)_2}$ group. This is in contrast with the NMR spectrum of the analogous $\mathrm{UCl_2[N(SiMe_3)_2]Tp^*}$ compound for which a 1 : 1 splitting of these protons was observed due to hindered rotation of the $\mathrm{[N(SiMe_3)_2]}$ group.[15] In addition the spectrum features five resonances for the Me groups of the mesityl substituents with an intensity ratio 2 : 2 : 2 : 2 : 1, consistent with C_s symmetry. Owing to the complexity of the spectrum and to the broadness of some resonances, two protons could not be assigned. The broadness of some resonances, especially those of the $\mathrm{N(SiMe_3)_2}$ ligand, suggested dynamic exchange processes taking place at room temperature. On lowering the temperature some of the resonances broadened into the baseline, but a limiting spectrum could not be reached in toluene, in accordance with the C_1 symmetry found in the solid (see below). The lower barrier associated with hindered rotation of the $\mathrm{[N(SiMe_3)_2]}$ group in **4** indicates a more open coordination sphere in this complex than in $\mathrm{UCl_2[N(SiMe_3)_2]Tp^*}$.

During one attempted recrystallization of compound **4** from a toluene solution green crystals suitable for X-ray diffraction analysis were obtained. The determination of the crystal and molecular structure showed that the compound obtained was the symmetrically bound $\mathrm{UCl_3Tp^{Ms}}$ **2**. Since the yield of the crystals was small it is possible that formation of the trichloride compound may be due to a side reaction, but this finding indicates that the uranium ion can accommodate three chloride ligands and the $\mathrm{Tp^{Ms}}$ ligand in its coordination sphere. It has been reported that, on heating above 220 °C, the lower-melting $\mathrm{TlTp^{Ms*}}$, $\mathrm{ZnClTp^{Ms*}}$, and $\mathrm{Zn(NCS)Tp^{Ms*}}$ rearranged to their $\mathrm{Tp^{Ms}}$ analogs, and it was assumed that $\mathrm{Tp^{Ms*}}$ was the kinetic product while $\mathrm{Tp^{Ms}}$ was the thermodynamically favored one. At this stage, it is tempting to consider that **1** is the kinetic product of reaction of uranium tetrachloride with the $\mathrm{Tp^{Ms}}$ ligand, but that reverse isomerization of $\mathrm{Tp^{Ms*}}$ to $\mathrm{Tp^{Ms}}$ is favored in non-coordinating solvents during a long period of time.

$\mathrm{UCl_2(C_6H_4CH_2NMe_2}$-*o*)$\mathrm{Tp^{Ms*}}$ 5. In contrast with $\mathrm{UCl_3Tp^*}$ from which several hydrocarbyl derivatives could be isolated, the reaction of $\mathrm{UCl_3Tp^{Ms*}}$ with the lithium salts of several

Table 1 Selected bond lengths (Å) and angles (°) for UCl_3Tp^{Ms*} **1**, $UCl_3Tp^{Ms}\cdot C_6H_5Me$ **2**$\cdot C_6H_5Me$, and $UCl_2[N(SiMe_3)_2]Tp^{Ms*}$ **4**

	1	**2**$\cdot C_6H_5Me$	**4**	
U–Cl(1)	2.535(4)	2.510(8)	U–Cl(1)	2.580(2)
U–Cl(2)	2.527(4)	2.546(9)	U–Cl(2)	2.545(2)
U–Cl(3)	2.534(4)	2.534(10)	U–N(4)	2.188(5)
U–N(1)	2.454(10)	2.43(2)	U–N(1)	2.474(5)
U–N(2)	2.495(10)	2.51(2)	U–N(2)	2.599(4)
U–N(3)	2.475(9)	2.51(3)	U–N(3)	2.541(4)
Cl(1)–U–Cl(2)	98.61(13)	93.7(3)	Cl(1)–U–Cl(2)	100.68(7)
Cl(1)–U–Cl(3)	91.8(2)	94.9(3)	Cl(1)–U–N(4)	92.37(14)
Cl(2)–U–Cl(3)	100.5(2)	93.7(3)	Cl(2)–U–N(4)	106.8(2)
N(1)–U–N(2)	75.4(3)	76.1(7)	N(1)–U–N(2)	70.0(2)
N(1)–U–N(3)	78.0(3)	77.8(9)	N(1)–U–N(3)	82.52(14)
N(2)–U–N(3)	77.2(3)	77.1(8)	N(2)–U–N(3)	73.16(13)

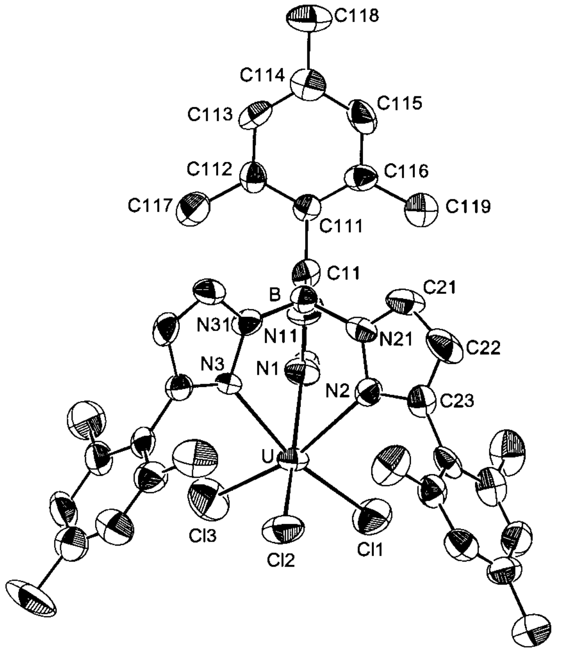


Fig. 1 An ORTEP[16] diagram of UCl_3Tp^{Ms*} **1**, using 50% probability ellipsoids.

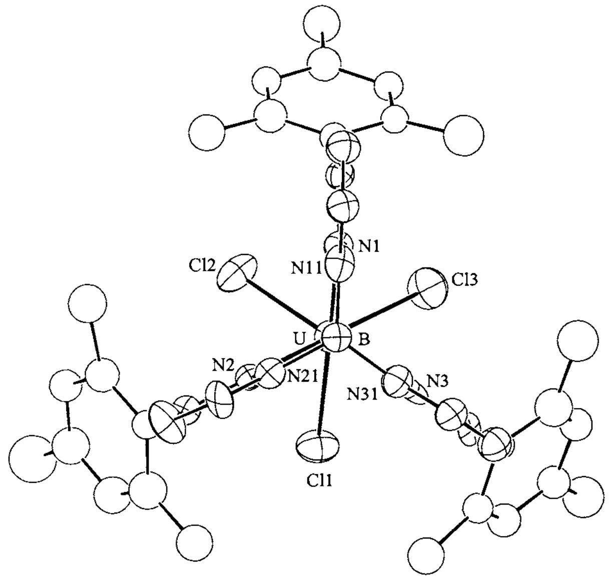


Fig. 2 An ORTEP diagram of UCl_3Tp^{Ms} **2**, using 40% probability ellipsoids.

hydrocarbyls yielded always complex product mixtures, but treatment of **1** with one equivalent of $Li(C_6H_4CH_2NMe_2$-*o*) in toluene solution led to immediate formation of a dark yellow solution which upon work-up, followed by extraction with n-hexane, gave a well defined product, $UCl_2(C_6H_4CH_2$-NMe_2-*o*)Tp^{Ms*} (**5**, Scheme 1). The ^1H NMR spectrum in C_6D_6 displays nine methyl resonances and twelve proton resonances for the mesitylpyrazolyl rings which is consistent with C_1 symmetry. In addition, the spectrum exhibits two resonances due to the NMe_2 groups and two due to the methylene hydrogens of the hydrocarbyl ligand. The diastereotopicity of the NMe_2 groups and of the methylene protons establishes that intramolecular U–N coordination is rigid on the NMR timescale. This is in contrast with the solution behaviour of the previously reported analog $UCl_2(C_6H_4CH_2NMe_2$-*o*)Tp*, for which a fast dynamic process involving breaking of the U–N donor bond was observed at room temperature.[8] These observations provide insight into the strength of this coordinative nitrogen–metal bond in both systems. The low activation energy associated with the fluxional process observed in $UCl_2(C_6H_4CH_2NMe_2$-*o*)Tp* indicates formation of a weaker U–N dative bond to the alkyl in this compound than in **4**. The difference in the donating properties between Tp* and Tp^{Ms*} ligands can be responsible for the difference in solution behaviour: if Tp* is a better donor than Tp^{Ms*}, the U–N donor bond to the alkyl group may become weaker, thus facilitating U–N bond breaking.

Hence, the solution behaviour of the compounds suggests that the uranium centre has a higher steric and electronic unsaturation when stabilized by Tp^{Ms*} than with Tp*, which would explain the impossibility of isolating those hydrocarbyl derivatives of **1** which were acessible with the "UTp*" ligand set.

X-Ray crystallographic studies

The X-ray diffraction determination of the molecular structures of compounds **1**, **2**, **4** and **5** was carried out. The structures confirm the expected κ^3-coordination mode of the ligand. In **1** and **2** the uranium atom is six-coordinated with three *fac* sites being occupied by the Tp^{Ms*} and Tp^{Ms} tridentate ligands, respectively, and the remainder being occupied by the three chlorine atoms. The ORTEP drawings are shown in Figs. 1 and 2 and important bond lengths and angles are listed in Table 1.

Complex **1** has C_s symmetry as found in solution and **2** has C_{3v} symmetry. The average U–N bond lengths are similar in **1** and **2** (2.475(10) and 2.48(3) Å, respectively) and slightly longer than in UCl_3Tp^* (2.43(1) Å),[14] due to the increase in spacial demand of the mesityl *versus* methyl group, or to the lesser electron donating properties of the Tp^{Ms*} ligand. The longer U–N bond lengths result in slightly shorter U–Cl bonds for **1** and **2** (2.532(4) and 2.53(1) Å, respectively) compared with the

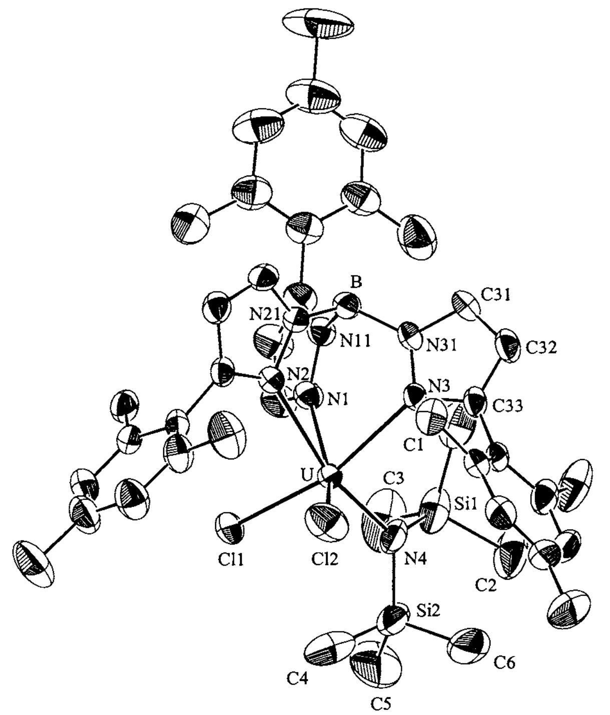


Fig. 3 An ORTEP diagram of $UCl_2[N(SiMe_3)_2]Tp^{Ms*}$ **4**, using 40% probability ellipsoids.

same bond in UCl_3Tp^* (2.56(1) Å).[14] The N–U–N bond angles average 76.9(3)° in **1** and 77(1)° in **2**, as compared with 77.3(2)° in UCl_3Tp^*. The most significant difference is found in Cl–U–Cl angles. In **2** these angles are similar, ranging from 93.7 to 94.9° (av. 94.1(3)°), and are smaller than those in UCl_3Tp^* which range from 95.0(2) to 99.6(2)° (av. 97.0°)[14] indicating a decrease in the area available in the coordination sphere of **2** in comparison with UCl_3Tp^*. In **1** these angles range from 91.8(2) to 100.5(2)° (av. 97.0(2)°), with the smaller angle associated with the two chlorides adjacent to the 5-mesitylpyrazolyl ring, and are in the range of the corresponding angles in UCl_3Tp^*. These results may indicate that, due to the isomerization reaction, the new ligand system does not lead to a more constrained coordination environment around the uranium ion. In **2** the mesityl groups are almost orthogonal to the pyrazolyl planes (88(1), 89 (1), 87(1)°), but in **1** the deviation from orthogonality of one of the mesityl groups reaches 7° (the angles are 89.1(4)° for the 5-mesitylpyrazolyl ring and 89.6(5) and 82.9(4)° for the 3-mesitylpyrazolyl rings).

The ORTEP diagram of compound **4** is shown in Fig. 3. In $UCl_2[N(SiMe_3)_2]Tp^{Ms*}$ the replacement of a chlorine atom in **1** by a bulky ligand such as $N(SiMe_3)_2$ results in a marked increase in the U–N bond lengths (av. 2.538(4) Å) compared to the 2.475(10) Å in **1**, and in an increase in the U–Cl bond lengths which average 2.563(2) Å (2.532(4) Å in **1**), as can be seen in Table 1. The angles at the metal atom from the pyrazolyl donor atoms (av. 75(1)°) are lower than in **1** (av. 76.9(3)°), allowing the Cl–U–Cl bond angle to increase to 100.68(7)° (the Cl–U–Cl bond angles average 97.0(2)° in **1**). These trends have previously been observed in $UCl_2(Cp)Tp^*$ as a result of replacement of a chloride ligand by the bulky cyclopentadienyl.[14] The deviations of the mesityl groups from orthogonality were 7.7, 9.8, and 17.6°, the highest deviation being observed for the 3-mesityl group adjacent to the silylamide group, and the lowest one for the 5-mesityl group. The U–N bond length to the $N(SiMe_3)_2$ group is 2.188(5). This value is slightly shorter than those previously found for terminal uranium–nitrogen bond lengths in $UCl_2[N(SiMe_3)_2](DME)$, $UH[N(SiMe_3)_2]_2$, $U(NEt_2)_4$, $U(NPh_2)_4$ and $[U(CH_3NCH_2CH_2NCH_3)_2]_3$ which are 2.235(8),[17] 2.24,[18] 2.22(1),[19] 2.27(2),[20] and 2.21 Å,[21] respectively.

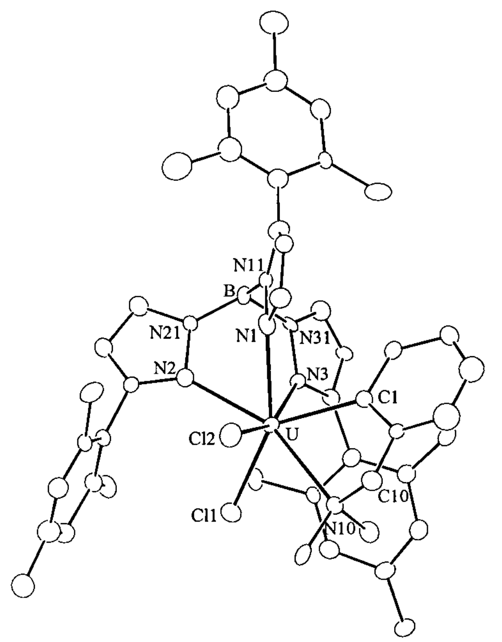


Fig. 4 An ORTEP diagram of $UCl_2(C_6H_4CH_2NMe_2\text{-}o)Tp^{Ms*}$ **5**.

For compound **5** the X-ray crystallographic analysis[22] on a poor quality crystal did not provide an adequate data set for accurate determination of the structure. It was not possible to refine the structure with acceptable *R* values and enough accuracy, worsened by the packing of two independent molecules per asymmetric unit. However, it was possible to define unambiguously the connectivity of the atoms around the metal. The uranium is seven-coordinate through the tridentate ligand, the two chlorine atoms, and the carbon and the nitrogen atoms of the chelating hydrocarbyl ligand, and displays pentagonal bipyramidal geometry, as can be seen in Fig. 4.

Reactivity of compound 5

Nitriles and isocyanides failed to react with compound **5**. Addition of stoichiometric amounts of acetonitrile, benzonitrile or cyclohexyl isocyanide to a toluene solution of **5** yielded after several hours only unchanged **5**. Nitrile or isocyanide coordination followed by insertion into the M–C σ bond is a general reaction for coordinatively and electronically unsaturated lanthanide and actinide compounds.[23] Probably, the chelating nature of the ligand $C_6H_4CH_2NMe_2\text{-}o$ hinders adduct formation with those molecules, preventing subsequent insertion reaction. This is corroborated by our previous observations that while $UCl_2(CH_2SiMe_3)Tp^*$ reacts with those substrates to yield the corresponding insertion products, $UCl_2(C_6H_4CH_2NMe_2\text{-}o)Tp^*$ and $UCl_2[CH(SiMe_3)_2]Tp^*$ do not.[24] Hence, **5** also does not insert acetone into the U–C bond, but instead forms $UCl_2[\eta^2\text{-}OC(Me)_2CH_2C(=O)Me]Tp^{Ms*}$ (**6**, Scheme 1). This result parallels those obtained for $UCl_2(C_6H_4CH_2NMe_2\text{-}o)(Tp^*)$ and $UCl_2[CH(SiMe_3)_2]Tp^*$ which failed to insert ketones into the U–C bond but yielded the aldolate $UCl_2[\eta^2\text{-}OC(Me)_2CH_2C(=O)Me]Tp^*$.[7] C–C coupling of two molecules of ketone in an aldol fashion on an actinide and lanthanide centre has also been observed by Marks[25] and Teuben and co-workers.[26] The IR spectrum of **6** showed the characteristic absorption band for the *v*(B–H) at 2480 cm^{-1} and a band at 1650 cm^{-1} for the carbonyl stretching vibration (this occurs at 1712 cm^{-1} for free acetone). The shift to low energy indicates that this group is coordinated to the uranium. The ^1H NMR spectrum features the required resonances for the protons of the pyrazolyl rings consistent with C_s symmetry and

Table 2 Selected bond lengths (Å) and angles (°) for $UCl_2[\eta^2\text{-}OC(Me)_2pz^{Ms}]Tp^{Ms*}\cdot C_6H_5Me$ **7**$\cdot C_6H_5Me$

U–Cl(1)	2.582(5)	U–N(1)	2.604(12)
U–Cl(2)	2.639(5)	U–N(2)	2.528(13)
U–O	2.082(10)	U–N(3)	2.542(12)
U–N(4)	2.547(13)		
Cl(1)–U–Cl(2)	92.4(2)	N(1)–U–N(2)	73.8(4)
O–U–N(4)	63.5(4)	N(1)–U–N(3)	70.5(4)
Cl(1)–U–O	90.2(3)	N(2)–U–N(3)	80.8(4)
Cl(1)–U–N(2)	164.5(3)	N(1)–U–O	81.1(4)
Cl(2)–U–N(4)	74.0(3)	N(3)–U–Cl(2)	72.4(4)
		U–O–C(1)	136.6(10)

for the protons of the $OC(Me)_2CH_2C(=O)Me$ ligand. However, several additional resonances were suggestive of a second species in solution. Attempts to recrystallize the complex did not decrease the amount of this minor side product. The symmetry found in solution indicates that the six-membered ring formed by coupling of the two ketone molecules and the uranium centre is planar and lies in the mirror plane of the molecule, or fluxional behaviour is taking place. The determination of the solid state structure of the compound could resolve this ambiguity but, unfortunately, crystallization of **6** from toluene did not yield crystals. Instead, crystals of $UCl_2[\eta^2\text{-}OC(Me)_2pz^{Ms}]Tp^{Ms*}$ **7** ($pz^{Ms} = NNC_{12}H_{13}$) were obtained after several weeks. We postulate that **7** is the minor product that caused the additional resonances detected in the ^1H NMR spectrum of $UCl_2[\eta^2\text{-}OC(Me)_2CH_2C(=O)Me]Tp^{Ms*}$. We have reported that the synthesis of $UCl_2[\eta^2\text{-}OC(Me)_2CH_2C(=O)Me]Tp^*$ was similarly accompanied by formation of $UCl_2[\eta^2\text{-}OC(Me)_2pz^*]Tp^*$ ($pz^* = NNC_5H_7$) in minor amounts, and this was also the compound obtained in crystalline form during recrystallization of $UCl_2[\eta^2\text{-}OC(Me)_2CH_2C(=O)Me]Tp^*$.[7] We have considered that in the formation of the aldolate a competitive mechanism involving deboronation of Tp* by acetone with release of pyrazolide or pyrazole groups is operative, based on the fact that $UCl_2[\eta^2\text{-}OC(Me)_2pz^*]Tp^*$ could quantitatively be obtained from the reaction of $UCl_2(\eta^2\text{-}C_5H_7N_2)Tp^*$ with acetone.[7] Fig. 5 shows an ORTEP drawing of **7**, selected bond lengths and angles are given in Table 2.

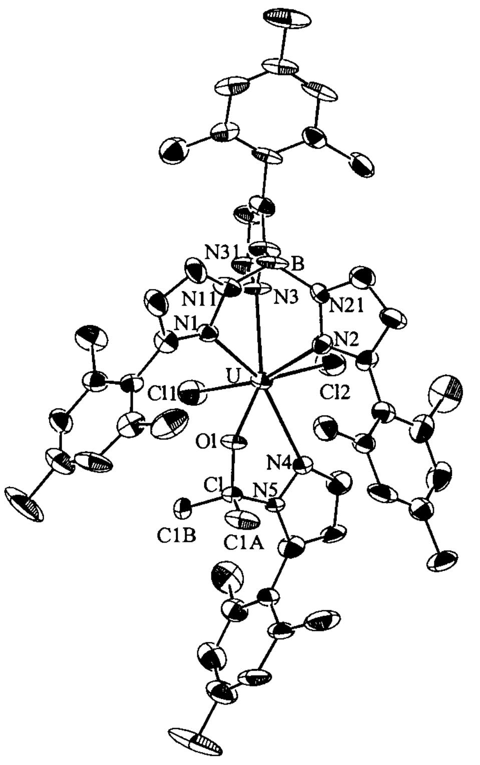


Fig. 5 An ORTEP diagram of $UCl_2[\eta^2\text{-}OC(Me)_2pz^{Ms}]Tp^{Ms*}$ **7**, using 40% probability ellipsoids.

The X-ray diffraction analysis revealed that N–C coupling had occurred between the carbonyl carbon of the acetone and a nitrogen of the pyrazolide group. The uranium centre is seven-coordinate through the tridentate ligand, the two chlorine atoms and the oxygen and nitrogen atoms of the five-membered metallacyclic ring. The coordination geometry can be described as a distorted pentagonal bipyramid with Cl(1) and N(2) occupying the axial sites and O(1), N(4), Cl(2), N(1), N(3) spanning the equatorial positions. The pyrazolyl U–N bond length averages 2.558(13) Å and is longer than the average values of this bond in **1**, **2**, and **4** reflecting the higher coordination number of the uranium. The U–O bond distance (2.082(10) Å) compares with the value 2.074(10) Å found in the similar compound $UCl_2[\eta^2\text{-}OC(Me)_2pz^*]Tp^*$[7] and is in the range for U–O bond lengths in poly(pyrazolyl)borate compounds with alkoxide and aryl oxide groups (2.03–2.12 Å).[24,27] The U–N(4) bond distance of 2.547(13) Å is in the range found for the corresponding distances in $UCl_2[\eta^2\text{-}OC(Me)_2pz^*]Tp^*$, $UCl_2[\eta^2\text{-}OC(H)(Me)pz^*]Tp^*$ and $UCl_2[\eta^2\text{-}OC(H)(Ph)pz^*]Tp^*$ which average 2.56(1), 2.56(1) and 2.61(1) Å, respectively.[7]

Conclusion

Reaction of UCl_4 with one equivalent of $TlTp^{Ms}$ affords UCl_3Tp^{Ms*} **1**, due to isomerization of Tp^{Ms} to give $[HB(3\text{-}Mspz)_2(5\text{-}Mspz)]^-$ ($=Tp^{Ms*}$). The ^1H NMR spectrum is consistent with the solid state structure. UCl_3Tp^{Ms*} **1** readily undergoes salt metathesis reactions to form new U–X and U–C bonds, similar to its Tp* analogs. This establishes that the ability of the hydrotris(pyrazolyl)borates to stabilize mono-ligated uranium compounds is quite general, although subtle differences in the reactivity of the compounds can be found on changing the pyrazolyl substituents. In fact, reactivity studies of **1** and NMR data of their derivatives suggest that the Tp^{Ms*} ligand is a poorer electron donor and provides a less sterically demanding environment for the metallic centre than the Tp* ligand. This last feature is due to the unexpected rearrangement of the Tp^{Ms} ligand. X-Ray data on crystals of the symmetrically bonded UCl_3Tp^{Ms} **2**, obtained fortuitously in one particular instance, show that the Tp^{Ms} ligand provides a more constrained coordination environment around the uranium ion than does the Tp* ligand.

Experimental

All manipulations were carried out under an atmosphere of dry nitrogen, using standard Schlenk and dry box techniques. Tetrahydrofuran, toluene and hexane were dried by refluxing, under nitrogen, with Na/K alloy and distilled prior to use. The solvents were degassed on a vacuum line before use. Deuteriated solvents were dried over Na (C_6D_6 and $C_6D_5CD_3$) and distilled. $TlTp^{Ms}$ and $TlTp^{Ms*}$ were synthesized as described previously.[10] $Li(C_6H_4CH_2NMe_2\text{-}o\text{-})$[28] was prepared as previously reported. Infrared (IR) spectra were recorded on a Perkin-Elmer 577 spectrometer, ^1H NMR spectra on a Varian 300 MHz spectrometer. Chemical shifts are reported in ppm relative to TMS. Elemental analyses were performed on a CE Instruments EA 1110 CHN analyser.

Preparations

UCl_3Tp^{Ms*}, 1. *Method 1.* To a solution of UCl_4 (0.380 g, 1 mmol) in THF (40 cm^3) was slowly added a stoichiometric amount of $TlTp^{Ms}$ (0.772 g, 1 mmol). After the mixture was stirred overnight the precipitate was separated and the solvent removed under reduced pressure giving a light green solid which was extracted with toluene (15 cm^3). Removal of the

Table 3 Summary of X-ray data for compounds **1**, **2**, **4** and **7**

	1	**2**·C_6H_5Me	**4**	**7**·C_6H_5Me
Chemical formula	$C_{36}H_{40}BCl_3N_6U$	$C_{36}H_{40}BCl_3N_6U\cdot C_7H_8$	$C_{42}H_{58}BCl_2N_7Si_2U$	$C_{51}H_{59}BCl_2N_8OU\cdot C_7H_8$
M	911.93	1004.06	1036.87	1211.94
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$
a/Å	12.132(2)	14.413(3)	12.538(2)	12.776(3)
b/Å	15.286(2)	15.748(1)	14.137(2)	28.661(5)
c/Å	21.327(3)	19.492(2)	16.016(3)	16.447(4)
α/°			112.53(1)	
β/°	100.04(1)		95.66(1)	109.31(1)
γ/°			92.70(1)	
V/Å^3	3894.5(10)	4424.2(11)	2598.2(7)	5684(2)
Z	4	4	2	4
μ/mm^{-1}	4.406	3.886	3.305	2.995
Measured reflections	6487	3445	9514	10338
Independent reflections [R(int)]	5857 (0.0454)	3445 (0.000)	9106 (0.0272)	9972 (0.0085)
Observed reflections [$I > 2\sigma(I)$]	3473	1949	7343	5760
$R1$	0.0514	0.0864	0.0402	0.0877
$wR2$	0.1137	0.1271	0.0811	0.1898

solvent afforded a green compound which was washed with n-hexane and vacuum dried. Yield: 71% (650 mg) (Found: C, 47.04; H, 4.44; N, 8.98. $C_{36}H_{40}BCl_3N_6U$ requires C, 47.41; H, 4.42; N, 9.23%). ν_{max}/cm^{-1} (BH) 2510 (Nujol). δ_H ($C_6D_5CD_3$, 25 °C, 300 MHz) 15.1 (1H, br, H(3)), 11.44 (2H, br, 3′,5′ (3-Mspz)), 10.72 (1H), 7.60 (2H, br, 3′,5′(3-Mspz)), 6.84 (2H, 3′,5′(5-Mspz)), 5.56 (2H, H(4) or H(5)), 3.57 (2H, H(5) or H(4)), 2.88 (6H, br, Me (3-Mspz)), 2.75 (3H, 4′-Me (5-Mspz)), 1.62 (6H, Me(5-Mspz)), 1.32 (6H, br, Me (3-Mspz) and −4.55 (6H, br, Me (3-Mspz)); (−20 °C) 15.30 (1H, H(3)), 12.20 (2H, 3′,5′ (3-Mspz)), 10.82 (1H), 7.73 (2H, 3′,5′ (3-Mspz)), 6.65 (2H, 3′,5′ (5-Mspz)), 5.48 (2H, H(4) or H(5)), 3.28 (2H, H(5) or H(4)), 3.07 (6H, 2′,6′-Me (3-Mspz)), 2.10 (3H, 4′-Me (5-Mspz)), 1.58 (6H, Me (5-Mspz)), 1.48 (6H, Me (3-Mspz)) and −5.13 (6H, Me (3-Mspz)).

Method 2. Reaction of UCl_4 (0.380 g, 1 mmol) in THF solution (40 cm^3) with $TlTp^{Ms*}$ (0.772 g, 1 mmol) followed by the procedure described above led to compound **1** in 70% yield.

UCl_3Tp^{Ms*}(THF), 3. 0.200 g (0.22 mmol) of compound **1** was dissolved in THF (10 cm^3). Removal of the solvent followed by washing with n-hexane afforded **3** (0.194 g, 90%) (Found: C, 48.27; H, 4.24; N, 7.95. $C_{40}H_{48}BCl_3N_6OU$ requires C, 48.82; H, 4.92; N, 8.54%). ν_{max}/cm^{-1} (BH) 2500 (Nujol). δ_H ($C_6D_5CD_3$, 25 °C, 300 MHz) 21 (1H, br, H(3)), 10.91 (1H), 9.68 (2H, br, 3′,5′ (3-Mspz)), 5.17 (2H), 3.74 (6H, br, 2′,6′-Me (3-Mspz)), 2.96 (2H), 2.34 (6H, Me (Mspz)), 1.26 (6H, Me (Mspz)), −1.28 (4H, THF), −3.48 (6H, br, 2′,6′ (3-Mspz)) and −5.52 (4H, THF); (−20 °C) 37.5 (1H, H(3)), 12.79 (1H), 9.69 (6H, 2′,6′-Me (3-Mspz)), 7.72 (2H, 3′,5′ (3-Mspz)), 6.02 (2H, 3′,5′ (3-Mspz)), 5.69 (2H), 4.13 (1H), 2.04 (2H), 1.74 (3H, 4′-Me (5-Mspz)), 1.06 (2H), 0.69 (6H, Me (Mspz)), 0.42 (6H, Me (Mspz)), −4.98 (4H, THF), −8.18 (6H, 2′,6′ (3-Mspz)) and −14.91 (4H, br, THF).

$UCl_2[N(SiMe_3)_2]Tp^{Ms*}$, 4. A suspension of $K[N(SiMe_3)_2]$ (0.037 g, 0.185 mmol) in toluene (10 cm^3) was slowly added to a solution of UCl_3Tp^{Ms*} (0.169 g, 0.185 mmol) in toluene (20 cm^3). After stirring for 6 hours the precipitate was separated from the supernatant. Concentration of the toluene solution under vacuum yielded in a few hours a bright green microcrystalline material (0.095 mg, 50%) (Found: C, 47.86, H, 5.01; N, 8.38. $C_{42}H_{58}BCl_2N_7Si_2U$ requires C, 48.65; H, 5.64; N, 9.46%). ν_{max}/cm^{-1} (BH) 2500 (Nujol). δ_H ($C_6D_5CD_3$, 25 °C, 300 MHz) 15.2 (1H, br), 13.8 (2H, br), 10.02 (6H, br, Me (Mspz)), 7.34 (24H, br, Me ($N(SiMe_3)_2$ + Me (Mspz)), 5.71 (2H), 4.56 (2H), 2.34 (1H), 1.41 (2H), 0.97 (3H, Me (Mspz)), −1.53 (6H, Me (Mspz)) and −3.53 (6H, br, Me (Mspz)).

$UCl_2(C_6H_4CH_2NMe_2$-*o*)Tp^{Ms*}, 5. To a toluene solution (20 cm^3) of UCl_3Tp^{Ms*} (0.360 g, 0.39 mmol) was slowly added $Li[C_6H_4CH_2NMe_2$-*o*] (0.056 mg, 0.39 mmol). During the reaction the solution changed from green to dark yellow. Stirring was continued for 3 hours. Separation of the precipitate and removal of the solvent under vacuum led to a solid which was further extracted with n-hexane. Concentration of the yellow solution afforded golden crystals of compound **5** (0.196 mg, 50%) (Found: C, 53.66; H, 5.71; N, 9.72. $C_{45}H_{52}BCl_2N_7U$ requires C, 53.48; H, 5.19; N, 9.70%). ν_{max}/cm^{-1} (BH) 2502 (Nujol). δ_H (C_6D_6, 20 °C, 300 MHz) 65.08 (1H), 34.02 (3H, Me (Mspz)), 33.39 (1H), 32.82 (1H), 27.76 (1H), 22.72 (1H), 22.03 (1H), 16.48 (1H), 7.60 (1H), 6.67 (1H), 5.81 (3H, Me (Mspz)), 5.68 (1H), 5.48 (1H), 3.99 (3H, Me (Mspz)), 3.64 (1H), 2.14 (1H), 2.01 (3H, Me (Mspz)), 1.26 (1H), 0.67 (3H, Me (Mspz)), 0.60 (1H), −0.82 (3H, Me (Mspz)), −2.04 (1H), −3.70 (3H, Me (Mspz)), −5.18 (1H), −6.07 (1H), −6.42 (3H, Me (Mspz)), −12.09 (3H, Me (Mspz)), −32.58 (3H, N*Me*Me) and −39.62 (3H, NMe*Me*).

$UCl_2[\eta^2$-$OC(Me)_2CH_2C(O)Me]Tp^{Ms*}$, 6. Two equivalents of acetone (0.042 g, 0.72 mmol) were stirred with a hexane solution (20 cm^3) of $UCl_2(C_6H_4CH_2NMe_2$-*o*)Tp^{Ms*} (0.360 g, 0.36 mmol), overnight. During the reaction a green yellowish precipitate was formed. This was separated from the supernatant, washed with hexane and vacuum dried (0.232 mg, 65%) (Found: C, 50.50; H, 5.18; N, 7.98. $C_{42}H_{51}BCl_2N_6O_2U$ requires C, 50.87; H, 5.18; N, 8.47%). ν_{max}/cm^{-1} (BH) 2480, (C=O) 1650 (Nujol). δ_H (C_6D_6, 20 °C, 300 MHz) 72.38 (6H), 45.54 (1H), 18.70 (2H), 17.61 (6H), 13.06 (2H), 11.90 (2H), 9.76 (3H), 7.02 (1H), 5.46 (6H), 4.70 (3H), 3.80 (6H), −8.35 (2H), −13.08 (2H) and −27.08 (6H).

X-Ray crystallographic analysis

Crystals were mounted in thin-walled glass capillaries in a nitrogen filled glove-box. Data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo-Kα radiation. A summary of the crystallographic data is given in Table 3. Data were corrected[29] for Lorentz-polarization effects, linear decay and absorption by empirical corrections based on ψ scans. The structures were solved by Patterson methods[30] and subsequent difference Fourier techniques and refined by full-matrix least-squares procedures on F^2 using SHELXL 93.[31] For compounds **2** and **7** a toluene solvent molecule was localized in the asymmetric unit. All the non-hydrogen atoms were refined anisotropically. For **2**, due to the weak diffraction, the mesityl and the toluene carbon atoms were refined isotropically; a few other atoms, which were non-positive definite when refined anisotropically, were restrained to isotropic behaviour. The contributions of the hydrogen atoms were included in calculated positions. Atomic scattering factors and anomalous disperson terms were taken from ref. 31. The illustrations were made with ORTEP II[16] and all calculations were performed on a Dec α 3000 computer.

CCDC reference number 186/2260.

See http://www.rsc.org/suppdata/dt/b0/b007505l/ for crystallographic files in .cif format.

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