Hydrotris(pyrazolyl)borate Chemistry of Uranium(III) and Uranium(IV). Synthesis of σ-Hydrocarbyl Derivatives of Uranium(IV) and Reactivity of UCl2R[HB(3,5-Me2pz)3] (R = CH2SiMe3, CH(SiMe3)2) and UCl2[HB(3,5-Me2pz)3] toward Ketones and Aldehydes

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The tetravalent uranium hydrocarbyl compounds UCl2[CH(SiMe3)2]L* (L* = HB(3,5-Me2-pz)3) and UCl3−x(CH2SiMe3)xL* (x = 1–3) have been prepared by salt metathesis from UCl3L* (THF) and the appropriate lithium alkyls. The reactivity of the carbyls UCl2[CH(SiMe3)2]L* (1) and UCl2(CH2SiMe3)L* (2) toward ketones has been studied. Compound 2 reacts with acetone and 3-pentanone in stoichiometric amount to yield the corresponding tertiary alkoxide compounds UCl2[OC(R)2CH2SiMe3]L* (R = Me, Et), as a result of insertion of the ketones into the U–C bond. Addition of excess acetone to 2 affords the uranium aldolate UCl2[OC(Me)2-CH2C(O)Me]L*, while excess 3-pentanone yields only the insertion compound. For compound 1 the corresponding insertion products are not formed, but addition of excess acetone yields the uranium aldolate. This compound is also obtained by reacting the U(III) compound (UCl2L*)x with excess acetone. Compound 2 reacts with aldehydes RCHO (R = Me, Ph) in a stoichiometric ratio, yielding the secondary alkoxides UCl2[OC(H)(R)CH2SiMe3]L* (R = Me, Ph), due to insertion of the aldehydes into the U–C bond. Similar reactions in 1:2 stoichiometric ratio yield the compounds UCl2[OC(H)(R)NNC5H7]L* (R = Me, Ph). The same compounds can be obtained by reacting carbyl 1 or (UCl2L*)x with aldehydes. The analogous compound UCl2[OC(Me)2-NNC5H7]L* was obtained during slow recrystallization of the uranium aldolate. The molecular structures of the following compounds were determined by single-crystal X-ray diffraction: UCl2[OC(Me)2CH2SiMe3]L*, orthorhombic, space group P2₁2₁2₁, a = 10.672(1) Å, b = 16.158(1) Å, c = 17.531(1) Å, V = 3023(1) Å³, Z = 4; UCl2[OC(H)(Me)NNC5H7]L*, monoclinic, space group P2₁/n, a = 9.662(2) Å, b = 16.093(2) Å, c = 18.527(3) Å, β = 93.28(1)°, V = 2876(1) Å³, Z = 4; UCl2[OC(H)(Ph)NNC5H 7]L*, monoclinic, space group P2₁/n, a = 11.588(3) Å, b = 19.376(4) Å, c = 14.707(4) Å, β = 101.90(2)°, V = 3231(3) Å³, Z = 4; UCl2[OC(Me)2NNC5H7]L*, orthorhombic, space group Pbca, a = 17.766(1) Å, b = 18.059(1) Å, c = 18.196(2) Å, V = 5838(1) Å³, Z = 8.

Introduction

The past several years have witnessed the appearance of a large number of organometallic compounds of uranium and thorium with unprecedented reactivity patterns.[1] Most of the chemistry has been carried out by Marks et al. and deals mainly with the bis(pentamethylcyclopentadienyl) type compounds Cp*2MR(Cl) and Cp*2MR2[2] or with compounds having two cyclopentadienyl rings bridged by an SiMe2 moiety,[3] bearing in mind that approaching the two rings will lead to an increase of the coordination space around the metal and consequently to enhanced reactivity. The pronounced effect that the steric hindrance around the metal atom seems to have on the reactivity of the compounds leads to the assumption that the chemistry of the mono(cyclopentadienyl) compounds will also present some interesting features. However, only a few studies have appeared dealing with this type of complex.

Most of the work carried out in our laboratories during the recent past concerns derivatives of MCl3L*(THF)[4] (L* = HB(3,5-Me2pz)3). The bulky hydrotris(pyrazolyl)-borate ligand, which some authors consider similar to the pentamethylcyclopentadienyl group, confers stability to a wide range of compounds of U(III) and U(IV) containing M–O, M–N, M–S, and M–C(π) bonds.[5] However, synthesis of σ-hydrocarbyl derivatives has hitherto not been re-

⊗ Abstract published in *Advance ACS Abstracts*, December 15, 1993.

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Table 1. Room-Temperature ^{1}H NMR^a and IR^b Data for UCl$_2$[CH(SiMe$_3$)$_2$]L* and UCl$_{3-x}$(CH$_2$SiMe$_3$)$_x$L*

complex	3,5-Me$_2$pz		H(4)	other		ν(B–H)	ν(U–Cl)
UCl$_2$[CH(SiMe$_3$)$_2$]L* (1)	21.7 (3H)	13.9 (3H)	31.8 (1H)	172.9 (1H)	10.7 (9H)	2550	275
	-3.1 (3H)	-3.3 (3H)	-4.9 (1H)		5.2 (9H)		
	-19.7 (3H)	-22.8 (3H)	-5.1 (1H)				
UCl$_2$(CH$_2$SiMe$_3$)L* (2)	23.4 (3H)	14.4 (3H)	36.7 (1H)	139.1 (2H)	18.1 (9H)	2543	272
	-19.8 (6H)	-3.6 (6H)	-5.7 (2H)				
UCl(CH$_2$SiMe$_3$)$_2$L* (3)	5.0 (6H)	2.0 (6H)	2.3 (2H)	4.3 (18H)	0.6 (2H, CHH)	2540	262
	-14.3 (3H)	-3.0 (3H)	-5.0 (1H)		-0.0 (2H, CHH)		
U(CH$_2$SiMe$_3$)$_3$L* (4)	2.4 (9H)	-2.3 (9H)	7.2 (3H)	0.7 (27H)	-32.8 (6H)	2540	

^{a} The shifts are in ppm from TMS; downfield shifts are positive. All spectra are in benzene-d_6. ^{b} In cm^{-1}.

ported. Here we report the synthesis and characterization of UCl$_2$[CH(SiMe$_3$)$_2$]L* and UCl$_{3-x}$(CH$_2$SiMe$_3$)$_x$L*[6] (x = 1–3) and the results of the reactivity studies of these compounds together with (UCl$_2$L*)$_x$ toward ketones and aldehydes.

Results and Discussion

Synthesis. UCl$_3$L*(THF) is a convenient starting material for the synthesis of σ-hydrocarbyl derivatives, via simple metathesis reactions (eq 1).

$$UCl_3L*(THF) + xLiR' \rightarrow UCl_{3-x}R'_xL* + xLiCl \quad (1)$$
$$1-4$$
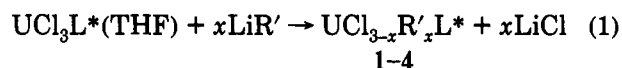
R' = CH(SiMe$_3$)$_2$, x = 1 (1);

R' = CH$_2$SiMe$_3$, x = 1 (2), 2 (3), 3 (4)

For the bulky CH(SiMe$_3$)$_2$ ligand only the mono(alkyl) derivative could be isolated. In this case the reaction proceeds smoothly at room temperature in toluene. For the other compounds the reactions were performed at -78 °C in THF. Workup procedures included extraction with toluene (compound 2) or n-hexane (3 and 4).

The compounds are crystalline and extremely air sensitive. The mono(alkyls) UCl$_2$R'L* (R' = CH(SiMe$_3$)$_2$, CH$_2$SiMe$_3$) are golden yellow, the bis(alkyl) UCl(CH$_2$SiMe$_3$)$_2$L* is yellowish green, and the tris(alkyl) U(CH$_2$SiMe$_3$)$_3$L* is green. The mono(alkyl) compounds have low solubility in aliphatic hydrocarbons but are very soluble in ethers and aromatic solvents. The other compounds are very soluble in all solvents.

IR Spectra. The IR spectra of the compounds show characteristic absorption bands for the ν(B–H) and ν(U–Cl) stretching vibrations (Table 1). The bands of medium intensity at about 400 cm^{-1} were assigned to the ν(U–C) stretching vibration. In the IR spectrum of compound 1 the band at 2700 cm^{-1} was assigned to a C–H stretching vibration. The low value of this vibration, compared with those found for normal C–H stretching vibrations, may be associated with an increase in the C–H length due to an agostic interaction between a hydrogen of the CH(SiMe$_3$)$_2$ ligand and the metal atom.[7]

^{1}H NMR Spectra. Proton NMR data are given in Table 1. All the uranium complexes exhibit substantial isotropic shifts, as is typical for uranium(IV) complexes. The spectrum of the tris(alkyl) complex 4 displays singlets for the 3-methyl and 5-methyl protons and 4-proton of the pyrazolyl rings, indicating that the three rings are equivalent, as previously observed for other compounds with C_{3v} symmetry.[4,5]

The resonances assigned to the poly(pyrazolyl)borate ligand in the spectra of compounds 2 and 3 indicate that only two of the three pyrazolyl rings are equivalent; this 2:1 pattern has already been found for other complexes with C_s symmetry.[5a,c,d] For complex 1 all the pyrazolyl rings are inequivalent, as well as the methyl protons of the two SiMe$_3$ groups. This lowering of the symmetry of the compound to C_1 is indicative of hindered rotation around the U–C bond, due to the bulkiness of the R' group or due to the U–H agostic interaction mentioned above.

Reactions with Ketones. Reaction of UCl$_2$(CH$_2$SiMe$_3$)L* with stoichiometric amounts of ketones gave tertiary alkoxide derivatives as a result of insertion of the ketone into the U–C bond (eq 2).

$$UCl_2(CH_2SiMe_3)L* + OCR_2 \rightarrow$$
$$UCl_2[OC(R)_2CH_2SiMe_3]L* \quad (2)$$
$$R = Me, 5$$
$$R = Et, 6$$
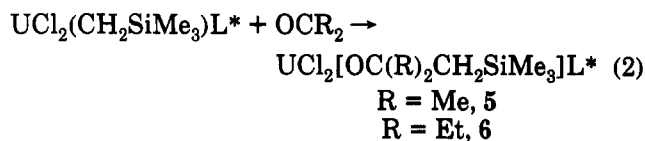
The compounds were obtained as green microcrystalline solids in reasonable yields. The chemical shifts of the resonances due to the pyrazolyl ring protons, as well as those of the OR groups, are in the range found for other tertiary alkoxides previously isolated[5c,d] (Table 2). In the IR spectra of the compounds the absorption due to the C=O stretch of the ketone, at about 1700 cm^{-1}, was absent. The absorption bands located at 905 cm^{-1} for compound 5 and 910 cm^{-1} for compound 6 were assigned to the ν(CO) stretching vibrations of the alkoxide groups. Compound 5 was further characterized by an X-ray diffraction study (vide infra).

When UCl$_2$(CH$_2$SiMe$_3$)L* reacted with excess 3-pentanone, only the insertion product 6 was obtained, but the reaction with excess acetone yielded a single compound together with quantitative liberation of the SiMe$_4$ (NMR experiment). IR and NMR data indicated that the complex was the uranium aldolate UCl$_2$[OC(Me)$_2$CH$_2$C(=O)Me]L* (eq 3).

The IR spectrum of 7 displays an absorption band at 1660 cm^{-1} for the carbonyl stretching vibration (this band

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Table 2. Room-Temperature ¹H NMR Data[a]

complex	3,5-Me₂pz		H(4)	CH₂SiMe₃	other
UCl₂(OC(Me)₂CH₂SiMe₃)L*[b] (5)	47.3 (3H) −8.3 (6H)	24.9 (3H) −33.3 (6H)	55.6 (1H) −16.9 (2H)	73.1 (2H), 14.6 (9H)	67.5 (6H)
UCl₂[OC(Et)₂CH₂SiMe₃]L*[b] (6)	50.2 (3H) −8.0 (6H)	25.8 (3H) −36.3 (6H)	57.5 (1H) −16.7 (2H)	75.3 (2H), 14.0 (9H)	73.0 (2H, q), 70.1 (2H, q), 29.3 (6H, t)
UCl₂[OC(Me)₂CH₂C(O)Me]L*[b] (7)	57.1 (3H) −9.6 (6H)	25.4 (3H) −27.1 (6H)	59.7 (1H) −18.5 (2H)		75.2 (6H), 61.9 (2H), −10.6 (3H)
UCl₂[OC(H)(Me)CH₂SiMe₃)]L*[b] (8)	53.4 (3H) −9.5 (6H) −28.1 (3H)	22.1 (3H) −28.2 (3H)	53.9 (1H) −15.9 (2H)	72.9 (1H), 65.6 (1H), 15.4 (9H)	165.1 (1H), 64.1 (3H)
UCl₂[OC(H)(Ph)CH₂SiMe₃)]L*[c] (9)	50.1 (3H) −8.6 (3H) −24.3 (3H)	22.0 (3H) −9.3 (3H) −32.0 (3H)	52.4 (1H) −15.3 (1H) −15.5 (1H)	68.9 (1H), 67.8 (1H), 15.0 (9H)	159.3 (1H), 46.6 (2H-o, d), 15.9 (2H-m, t), 13.1 (1 H-p, t)
U̅C̅l̅₂̅[̅O̅C̅(̅H̅)̅(̅M̅e̅)̅N̅N̅C̅₅̅H̅₇̅]L*[b] (10)	58.0 (3H) −9.4 (3H) 30.5 (3H)	20.7 (3H) −9.6 (3H) −49.4 (3H)	48.6 (1H) −12.9 (1H) −14.0 (1H)		153.6 (1H), 64.2 (3H), 17.4 (3H), −20.4 (3H), 2.9 (1H)
U̅C̅l̅₂̅[̅O̅C̅(̅H̅)̅(̅P̅h̅)̅N̅N̅C̅₅̅H̅₇̅]L*[b] (11)	57.5 (3H) −9.6 (6H) −26.3 (3H)	20.2 (3H) −46.7 (3H)	47.4 (1H) −12.7 (1H) −13.0 (1H)		145.2 (1H), 43.7 (1H-o, d), 17.7 (2H-m, t), 15.1 (1H-p, t), 16.5 (3H), 3.9 (1H), −19.6 (3H)

[a] The shifts are in ppm from TMS; downfield shifts are positive. [b] In benzene-d_6. [c] In toluene-d_8.

L'UCl₂(CH₂SiMe₃) + (excess) → L'Cl₂U + SiMe₄   (3)

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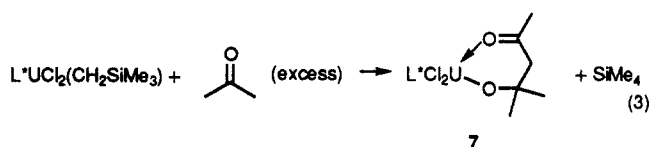
occurs at 1712 cm⁻¹ in free acetone). The shift to low energy indicates that this group is coordinated to the uranium center. The ¹H NMR spectrum showed a 1:2 pattern for the protons of the pyrazolyl rings, indicating C_s symmetry for the compound, which means that the six-membered ring formed by the coupling of the two ketone molecules and the uranium center is planar and lies in the mirror plane of the molecule.

Further evidence for the formation of the uranium aldolate was obtained by comparing the ¹H NMR spectrum with that of a sample prepared by reacting carbyl 2 with 4-hydroxy-4-methyl-2-pentanone (NMR-tube reaction, eq 4). The two spectra were identical.

L'UCl₂(CH₂SiMe₃) + → L'Cl₂U + SiMe₄   (4)

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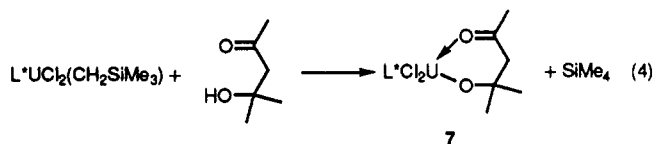
The more hindered carbyl UCl₂[CH(SiMe₃)₂]L* failed to insert ketones into the U–C bond but reacted with acetone to yield the aldolate together with elimination of H₂C(SiMe₃)₂ (by NMR). The same compound was also obtained by reacting (UCl₂L*)ₓ with excess acetone.

Although this result is in contrast to the ketone chemistry reported for carbyls of transition elements,[2a] C—C coupling of two molecules of ketones in an aldol fashion on a lanthanide or actinide center has some precedent in the literature. Marks and others[8] have found that the reaction of the complex Cp*₂Th(Cl)RuCp(CO)₂ with excess acetone yields the thorium aldolate Cp*₂Th-(Cl)OCMe₂CH₂C(=O)Me, and Teuben et al.[9] reported the formation of Cp*₂LnOCMe₂CH₂C(=O)Me (Ln = Ce,

La) by reacting the carbyls Cp*₂LnCH(SiMe₃)₂ with 2 equiv of acetone. In Marks' work a heterolytic C—H cleavage to produce a Th—C σ bond followed by C=O insertion into the Th—C bond is proposed to explain the aldolate formation. An alternative mechanism proposed by Teuben et al. involves the formation of an intermediary enolate and coordination of a second acetone molecule followed by C—C coupling to afford the aldol. Teuben has been able to isolate an enolate by reaction of Cp*₂-Ln[CH(SiMe₃)₂] with 3-pentanone. Due to the bulkiness of 3-pentanone, C—C coupling is not observed and an enolate with an additional coordinated molecule of 3-pentanone is obtained.

In this work no intermediates in the reactions have been detected. The tertiary alkoxide UCl₂[OC(Me)₂CH₂SiMe₃]-L* reacts very slowly with excess acetone, over several days, to yield a small amount of the aldol compound. This indicates that the alkoxide is not an intermediate in the aldolization reaction. We attempted also to synthesize the enolate UCl₂[OC(CH₂)CH₃]L* by treating UCl₃L*-(THF) with NaOC(CH₂)CH₃ and react it with acetone to test if the uranium aldolate was formed. However, the reaction of UCl₃L*(THF) with NaOC(CH₂)CH₃ gave the isopropoxide derivative UCl₂[OCH(Me)₂]L*.[5c] Due to the unstable character of the enolate, we tried to trap it by running the same reaction in the presence of acetone. Again, only formation of the isopropoxide was observed, which indicates that the enolate is not involved in the aldolization reaction.

One plausible mechanism involves prior coordination of acetone to the uranium through the oxygen lone pair, followed by a 1,3-alkyl shift from the metal to the ketone carbon atom, due to the slight polarization of the CO bond induced by the coordination of the ketone to the metallic center. This accounts for the formation of the insertion products when a single molecule of ketone is present (Scheme 1). However, if the alkyl is too bulky, preventing the insertion step (as for carbyl 1), or if there is a large excess of acetone, σ-bond metathesis between the acetone and the R' group followed by insertion of a second acetone molecule can account for the formation of the aldol product (Scheme 2).
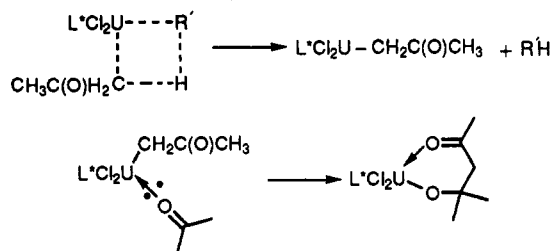
(8) Sternal, R. S.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7920.

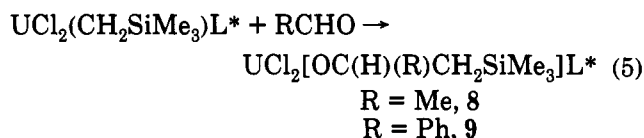(9) Heeres, H. J.; Maters, M.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1992**, *11*, 350.
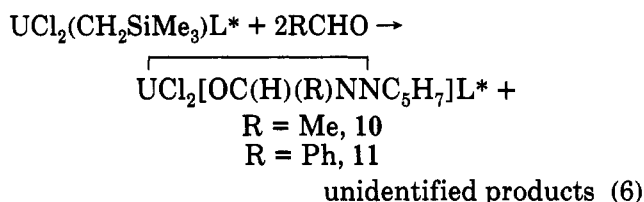
Scheme 1

Scheme 2

Scheme 3

$$\stackrel{\frown}{N-N} = 3,5\text{-Me}_2\text{pz}$$
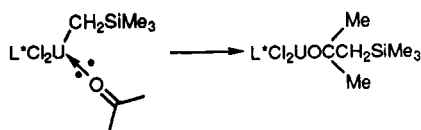
Reactions with Aldehydes. Insertion of acetaldehyde and benzaldehyde into the U–C bond of $UCl_2(CH_2SiMe_3)$-L* gave rise to the formation of compounds **8** and **9**, respectively (eq 5).

$$UCl_2(CH_2SiMe_3)L^* + RCHO \rightarrow$$
$$UCl_2[OC(H)(R)CH_2SiMe_3]L^* \quad (5)$$
$$R = Me, 8$$
$$R = Ph, 9$$

The microcrystalline green compounds were characterized by IR and ^{1}H NMR spectroscopy. In the IR spectra of compounds **8** and **9** the absorption bands located at 935 and 908 cm^{-1}, respectively, were assigned to the alkoxide RC–O stretching vibration. In both compounds, due to the chiral carbon atom of the alkoxides, the lack of symmetry of the molecules gives rise to inequivalent pyrazolyl rings and to diastereotopic methylenic protons of the CH$_2$SiMe$_3$ groups (Table 2).

When $UCl_2(CH_2SiMe_3)L^*$ reacted with aldehydes in a 1:2 stoichiometric ratio, or with excess aldehydes, the compounds **10** and **11** were formed (eq 6).
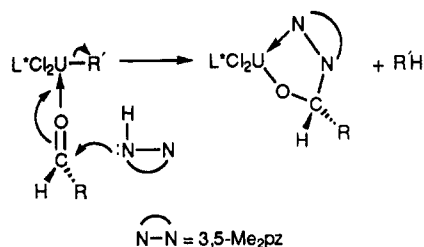
$$UCl_2(CH_2SiMe_3)L^* + 2RCHO \rightarrow$$
$$\overline{UCl_2[OC(H)(R)NNC_5H_7]L^*} +$$
$$R = Me, 10$$
$$R = Ph, 11$$
unidentified products (6)

The more hindered carbyl $UCl_2[CH(SiMe_3)_2]L^*$ failed to insert aldehydes into the U–C bond but reacted with acetaldehyde and benzaldehyde to yield the compounds **10** and **11**. These compounds were also obtained by reacting $(UCl_2L^*)_x$ with excess aldehydes.

These crystalline green compounds were identified on the basis of spectroscopic data and by X-ray diffraction studies, which have shown that N–C coupling had occurred between the α-carbon of the aldehyde and a nitrogen of the pyrazolide group. This group is also coordinated to the metal through the second nitrogen atom. The ^{1}H NMR spectra of both compounds (Table 2) show that all the pyrazolyl rings are inequivalent, which agrees with the C_1 symmetry found for the complexes by X-ray diffraction analysis.

Although the mechanism of these reactions is not well understood, release of pyrazolide[10] or pyrazole[11] groups from a HB(3,5-Me$_2$pz)$_3$ ligand has already been observed. McCleverty[12] found that L*Mo(NO)I$_2$ reacted with o-

catechol, yielding a molybdenium compound free of boron, $[Mo(NO)(O_2C_6H_4)(Me_2pz)(Me_2pzH)_2]I_3$. Due to the high affinity of boron for oxygen-containing ligands, it is conceivable that aldehydes are also responsible for deboronation reactions of this type.

As in the case of reaction with ketones, prior coordination of the aldehyde to the uranium center followed by a 1,3-alkyl shift from the metal to the α-carbon of the aldehyde can explain the formation of the insertion products. For the bulky carbyl **1** or in the presence of excess aldehyde, deboronation of the hydrotris(pyrazolyl)borate ligand with release of pyrazolide or pyrazole groups can occur. Nucleophilic attack of a nitrogen atom of the heterocyclic ring at the α-carbon of the aldehyde, followed by coordination of the second nitrogen to the metallic center with elimination of the R'H group, can compete with the insertion reaction, affording compounds **10** and **11** (Scheme 3).

Support of the role of the pyrazolide or the pyrazole rings was obtained when acetaldehyde was added to the previously reported $UCl_2(C_5H_7N_2)L^*$ or to $UCl_3L^*(C_5H_8-N_2)$.[10b] In both cases compound **10** was formed.

This type of mechanism accounts also for the formation of the compound $\overline{UCl_2[OC(Me)_2NNC_5H_7]L^*}$ (**12**). This compound could be quantitatively obtained from reaction of $UCl_2(C_5H_7N_2)L^*$ with acetone (NMR experiment). The ^{1}H NMR spectrum (Experimental Section) shows a 1:2 pattern for the resonances of the pyrazolyl rings, in accordance with the C_s symmetry found in the solid by X-ray diffraction analysis. In fact, in one attempt to grow crystals of the aldol **7** for X-ray diffraction analysis we have obtained crystals of the above compound **12**, which in some cases accompanied, in low yield, the formation of the products resulting from the reactions with ketones.

Molecular Structure of UCl$_2$[OC(Me)$_2$CH$_2$SiMe$_3$]-L* (5). Figure 1 shows an Ortep drawing of the molecule. The compound crystallizes in monomeric units with the uranium atom in a distorted-octahedral environment. Table 3 shows selected bond distances and bond angles; the positional parameters are given in Table 4. The U–O distance is 2.05(2) Å, which is in the range for U–O distances in poly(pyrazolyl)borate uranium compounds with an alkoxide ligand (2.03–2.11 Å).[13] The U–O–C angle is 160-(1)°, which is smaller than 164.5(4)° in UCl(OBu^t)(HB-(pz)$_3$)$_2$. The average U–Cl and U–N bond distances are

(10) (a) Bradley, D. C.; Hursthouse, M. B.; Newton, J.; Walker, N. P. C. *J. Chem. Soc., Chem. Commun.* **1984**, 188. (b) Marques, N.; Marçalo, J.; Pires de Matos, A.; Bagnall, K. W.; Takats, J. *Inorg. Chim. Acta* **1987**, *139*, 79. (c) Kime-Hunt, E.; Spartalian, K.; DeRusha, M.; Nunn, C. M.; Carrano, C. J. *Inorg. Chem.* **1989**, *28*, 4392.

(11) Apostolidis, C.; Kanellakopulos, B.; Maier, R.; Meyer, D.; Marques, N.; Rebizant, J. Unpublished results.

(12) Adams, H.; Bailey, N. A.; Drane, A. S.; McCleverty, J. A. *Polyhedron* **1983**, *2*, 465.

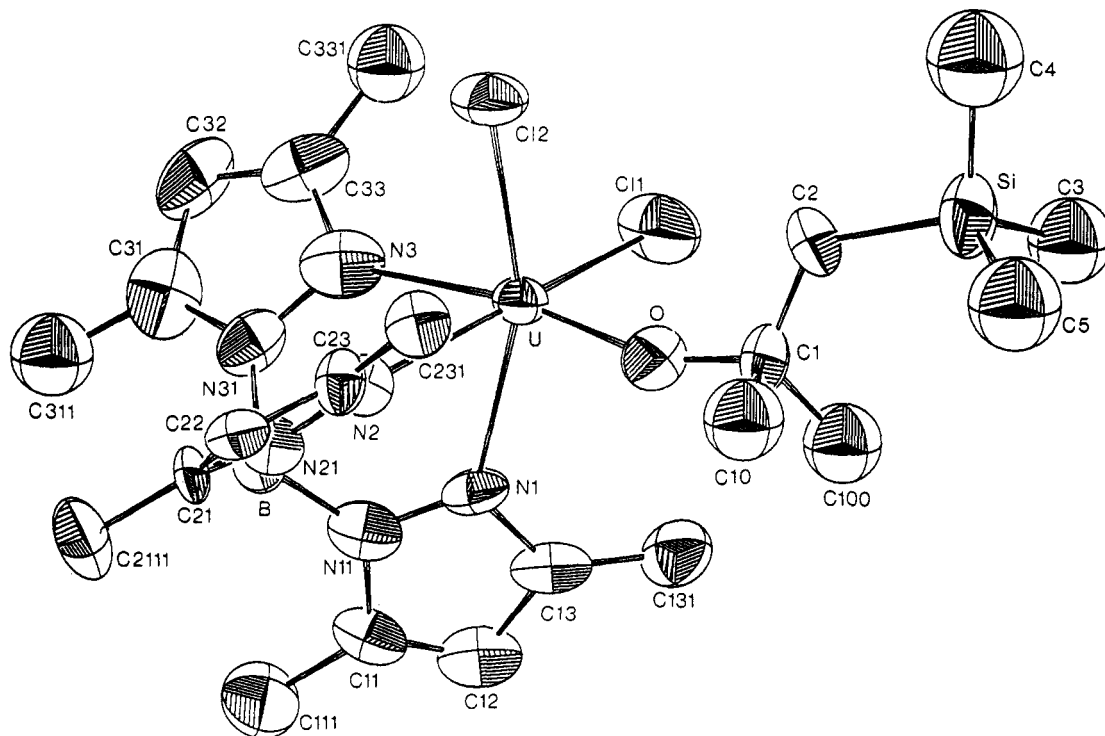(13) Domingos, A.; Pires de Matos, A.; Santos, I. *J. Less-Common Met.* **1989**, *149*, 279.

Figure 1. Ortep drawing of the uranium alkoxide compound 5.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 5

U–N(1)	2.51(2)	U–Cl(1)	2.603(8)
U–N(2)	2.46(2)	U–Cl(2)	2.617(8)
U–N(3)	2.49(2)	U–O	2.05(2)
O–C(1)	1.45(2)	C(1)–C(2)	1.46(3)
C(1)–C(10)	1.48(3)	C(1)–C(100)	1.56(3)
C(2)–Si	1.87(2)	Si–C(3)	1.82(3)
Si–C(4)	1.85(3)	Si–C(5)	1.86(3)
N–N^a	1.38(2)	C–C^a	1.37(4)
N–C^a	1.36(3)	C–CH$_3^a$	1.48(3)
N–B^a	1.54(1)		
Cl(1)–U–Cl(2)	98.2(3)	N(1)–U–N(2)	75.9(6)
Cl(1)–U–O	93.8(5)	N(2)–U–N(3)	76.5(7)
Cl(2)–U–O	95.9(5)	N(1)–U–N(3)	74.2(7)
U–O–C(1)	160(1)	O–C(1)–C(2)	113(2)
C(1)–C(2)–Si	124(2)	N–B–N^a	110(2)

^{a} The average N–N, N–C, B–N, C–C, C–CH$_3$, and N–B–N values of the ligand HB(3,5-Me$_2$pz)$_3$ are given.

2.61(1) and 2.48(2) Å and are in the range found for octahedral poly(pyrazolyl)borate uranium compounds.[4,5d-f]

Molecular Structures of ŪCl$_2$[OC(H)(Me)NNC$_5$-H$_7$]L* **(10),** ŪCl$_2$[OC(H)(Ph)NNC$_5$H$_7$]L* **(11), and** ŪCl$_2$[OC(Me)$_2$NNC$_5$H$_7$]L* **(12).** The structures consist of discrete molecules in which the uranium atom is seven-coordinate and displays capped-octahedral geometry. Figures 2–4 show views of the molecules. For compounds 10 and 11 the tridentate (pyrazolyl)borate ligand, the two chlorine atoms, and the oxygen atom define the two staggered triangular faces of the octahedron; the latter face is capped by a nitrogen of an additional 3,5-dimethylpyrazole ring. The planes of these two faces are inclined by 1.6 and 2.7° in compounds 10 and 11, respectively. A more irregular capped-octahedral poly-hedron is observed in compound 12, where one of the triangular faces is formed by the two chlorine atoms and the N(4) atom and is capped by the oxygen atom. Here the two staggered triangular faces are inclined by 10.8°.

Table 4. Positional Parameters for 5

atom	x	y	z	B$_{eq}$,^{a} Å^2
U	−0.09878(7)	0.02149(5)	−0.89363(4)	3.18(2)
Si	−0.3353(8)	0.3281(4)	−0.7918(5)	5.9(2)
Cl(1)	−0.3358(5)	−0.0129(5)	−0.8785(3)	6.8(2)
Cl(2)	−0.0407(5)	0.0304(4)	−0.7488(3)	5.2(2)
O	−0.1293(13)	0.1455(9)	−0.9080(8)	5.2(5)
N(1)	−0.0909(16)	−0.0187(11)	−1.0318(7)	3.6(4)
N(2)	0.1255(13)	0.0263(10)	−0.9255(8)	3.5(4)
N(3)	−0.0365(18)	−0.1266(12)	−0.8958(12)	5.6(6)
N(11)	−0.0016(18)	−0.0704(12)	−1.0602(9)	4.3(5)
N(21)	0.1804(14)	−0.0319(11)	−0.9741(8)	3.5(5)
N(31)	0.0503(18)	−0.1577(10)	−0.9470(10)	4.6(6)
C(11)	−0.0238(23)	−0.0805(15)	−1.1366(12)	4.2(7)
C(12)	−0.1291(23)	−0.0414(14)	−1.1535(12)	4.9(8)
C(13)	−0.1747(21)	−0.0007(12)	−1.0883(10)	4.1(7)
C(21)	0.3098(18)	−0.0167(15)	−0.9765(11)	3.9(6)
C(22)	0.3309(20)	0.0495(13)	−0.9319(11)	3.8(6)
C(23)	0.2203(18)	0.0748(12)	−0.9021(12)	3.6(5)
C(31)	0.0743(27)	−0.2355(15)	−0.9291(16)	6.2(9)
C(32)	0.0001(28)	−0.2622(14)	−0.8652(16)	6.4(9)
C(33)	−0.0663(22)	−0.1925(17)	−0.8489(14)	5.7(8)
C(111)	0.0564(24)	−0.1367(16)	−1.1844(13)	6.7(9)
C(131)	−0.2811(20)	0.0535(15)	−1.0780(12)	5.4(7)
C(211)	0.3934(21)	−0.0704(14)	−1.0230(13)	6.0(7)
C(231)	0.1981(20)	0.1427(13)	−0.8497(11)	4.2(5)
C(311)	0.1668(24)	−0.2856(17)	−0.9717(14)	7(1)*
C(331)	−0.1625(23)	−0.1811(16)	−0.7862(14)	7(1)*
C(1)	−0.1809(19)	0.2275(11)	−0.8957(14)	4.1(5)
C(10)	−0.0781(24)	0.2862(15)	−0.9118(14)	7(1)*
C(100)	−0.2784(24)	0.2381(17)	−0.9611(14)	7(1)*
C(2)	−0.2336(20)	0.2385(13)	−0.8192(13)	4.5(7)
C(3)	−0.4940(25)	0.3166(18)	−0.8288(16)	8(1)*
C(4)	−0.3430(31)	0.3281(21)	−0.6865(17)	10(1)*
C(5)	−0.2733(29)	0.4303(19)	−0.8221(17)	10(1)*
B	0.1067(24)	−0.1029(14)	−1.0097(12)	3.6(6)

^{a} The starred values denote atoms refined isotropically.

The presence of the two bulky methyl groups attached to the tetrahedral C(1) atom probably imposes steric constraints. In all three compounds the X-ray structures have revealed the presence of a planar five-membered metal-lacyclic ring, U–O–C(1)–N(41)–N(4). For compound 10, the plane of this ring (root-mean-square deviation of 0.079
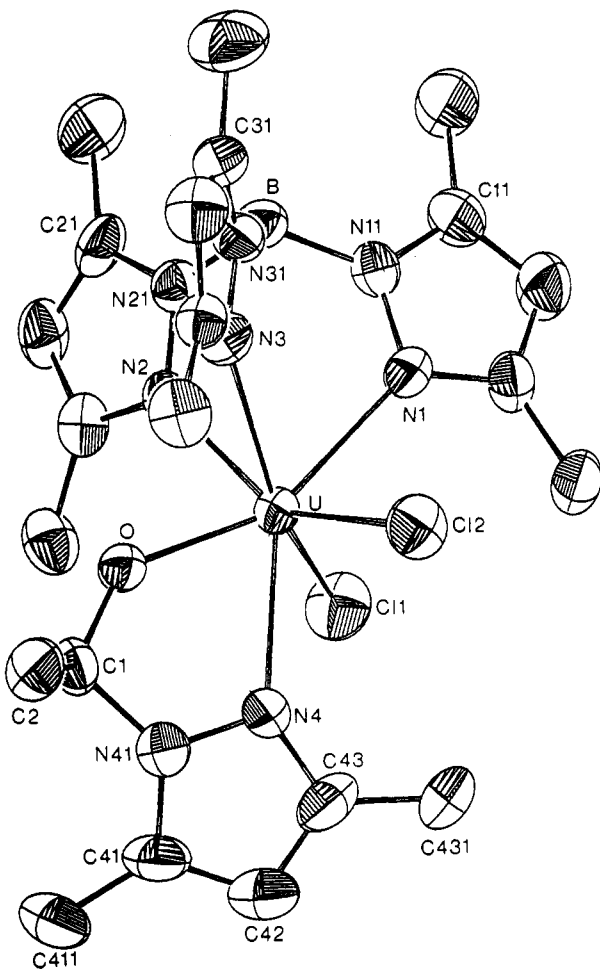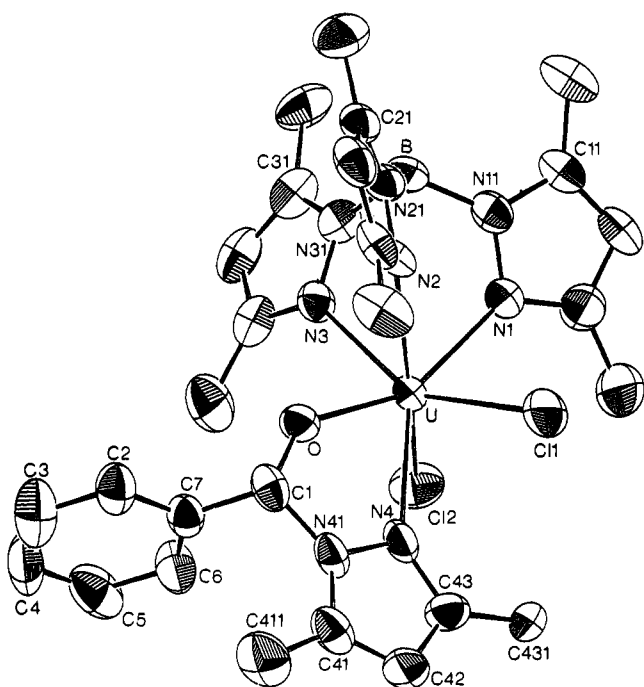
Figure 2. Ortep drawing of compound **10**.

Figure 3. Ortep drawing of compound **11**.

Å), with a maximum deviation from the least-squares plane of 0.1230 Å for N(41), makes a dihedral angle of 12.7° with the plane of the N(4) pyrazolyl ring (root-mean-square deviation of 0.032 Å). For compound **11**, the ring is more planar (root-mean-square deviation of 0.035 Å), with a maximum deviation from the least-squares plane of 0.050
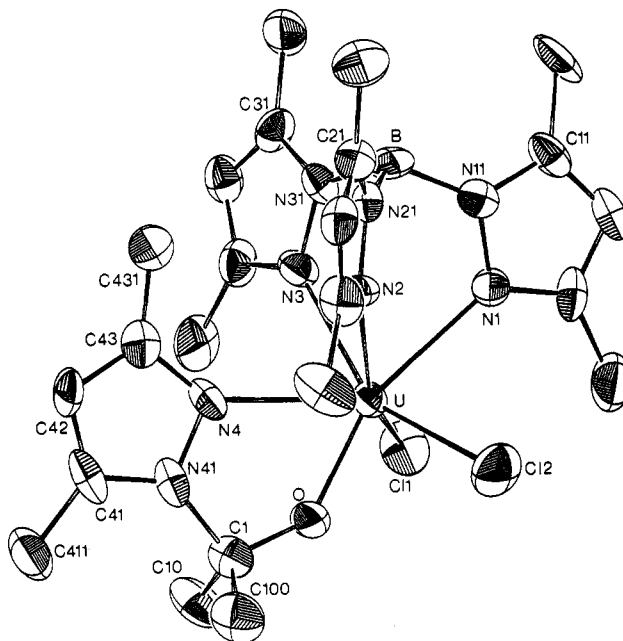

Figure 4. Ortep drawing of compound **12**.

Table 5. Selected Bond Distances (Å) and Angles (deg) for 10–12

	10	**11**	**12**
U–Cl(1)	2.627(5)	2.622(5)	2.630(6)
U–Cl(2)	2.630(5)	2.622(5)	2.616(6)
U–O	2.111(7)	2.108(7)	2.074(10)
U–N(1)	2.513(9)	2.512(10)	2.588(12)
U–N(2)	2.515(9)	2.503(10)	2.479(10)
U–N(3)	2.522(9)	2.517(10)	2.521(11)
U–N(4)	2.561(10)	2.558(10)	2.613(12)
O–C(1)	1.390(10)	1.381(10)	1.379(14)
C(1)–N(41)	1.501(12)	1.461(11)	1.502(15)
N(41)–N(4)	1.347(9)	1.358(10)	1.395(12)
Cl(1)–U–Cl(2)	114.1(2)	110.7(2)	102.9(2)
Cl(1)–U–O	109.6(3)	113.8(3)	86.1(3)
Cl(2)–U–O	111.8(3)	108.3(3)	85.0(3)
N(1)–U–N(2)	76.4(3)	77.2(3)	74.0(4)
N(2)–U–N(3)	72.3(3)	73.5(3)	75.8(4)
N(1)–U–N(3)	75.1(3)	74.0(3)	73.3(4)
N(4)–U–Cl(1)	76.3(3)	74.6(3)	117.9(3)
N(4)–U–Cl(2)	78.6(3)	78.8(3)	123.8(3)
N(4)–U–O	64.1(3)	63.3(3)	62.7(4)
N(4)–U–N(1)	140.8(2)	142.4(2)	138.2(3)
N(4)–U–N(2)	130.5(2)	127.2(3)	74.1(4)
N(4)–U–N(3)	134.6(2)	135.5(2)	73.3(4)
O–U–N(1)	155.0(2)	154.2(2)	159.0(3)
O–U–N(2)	82.3(3)	83.0(3)	119.6(4)
O–U–N(3)	86.1(3)	84.7(3)	123.7(4)
U–O–C(1)	137.4(5)	137.7(5)	142.2(7)
U–N(4)–N(41)	113.2(6)	114.6(6)	113.5(7)

Å for the oxygen atom, and makes a dihedral angle of 3.6° with the plane of the N(4) pyrazolyl ligand (root-mean-square deviation of 0.008 Å). For compound **12**, the two rings are coplanar (root-mean-square deviation of 0.024 Å) with a maximum deviation from the least-squares plane of 0.048 Å for the U atom. The molecule closely approximates C_s symmetry, with the mirror plane containing the N(1) and N(4) pyrazolyl rings and the U, O, C(1), and B atoms.

Bond distances and angles are given in Table 5; the positional parameters are given in Tables 6–8. The U–Cl and U–N distances observed in the compounds **10–12** (average U–Cl = 2.63(1), 2.62(1), and 2.62(1) Å and average U–N = 2.52(1), 2.51(1), and 2.53(1) Å, respectively) can be compared with the corresponding values of 2.60(1) and

Table 6. Positional Parameters for 10

atom	x	y	z	B_{eq}, Å²
U	0.04006(3)	0.11851(2)	0.31897(2)	2.75(1)
Cl(1)	−0.1338(2)	0.1161(2)	0.2047(1)	5.15(6)
Cl(2)	0.3027(2)	0.1201(2)	0.2887(1)	4.71(6)
O	−0.0047(5)	0.0192(3)	0.3883(3)	3.4(1)
N(1)	0.0538(7)	0.2687(4)	0.2829(3)	3.5(2)
N(11)	0.0079(6)	0.3316(4)	0.3254(4)	3.3(2)
N(2)	−0.1618(6)	0.1841(4)	0.3773(3)	3.0(2)
N(21)	−0.1561(6)	0.2618(4)	0.4080(3)	3.3(2)
N(3)	0.1334(7)	0.1927(4)	0.4314(3)	3.6(2)
N(31)	0.0965(7)	0.2728(4)	0.4462(3)	3.3(2)
N(4)	0.0689(7)	−0.0276(4)	0.2672(4)	3.8(2)
N(41)	0.0125(7)	−0.0874(4)	0.3071(4)	3.9(2)
C(11)	0.0075(10)	0.4029(5)	0.2895(5)	4.6(3)
C(12)	0.0519(9)	0.3878(6)	0.2225(5)	5.2(3)
C(13)	0.0792(9)	0.3042(6)	0.2194(5)	3.8(3)
C(21)	−0.2774(9)	0.2782(5)	0.4389(4)	4.2(3)
C(22)	−0.3628(9)	0.2109(6)	0.4263(5)	4.5(3)
C(23)	−0.2892(8)	0.1535(5)	0.3891(4)	3.7(2)
C(31)	0.1777(10)	0.3004(6)	0.5026(5)	4.5(3)
C(32)	0.2670(9)	0.2394(6)	0.5238(5)	4.5(3)
C(33)	0.2396(8)	0.1730(5)	0.4785(4)	3.4(2)
C(41)	−0.0037(11)	−0.1598(6)	0.2717(6)	5.6(4)
C(42)	0.0493(12)	−0.1466(7)	0.2047(6)	5.9(4)
C(43)	0.0900(10)	−0.0637(7)	0.2036(5)	5.1(4)
C(111)	−0.0386(12)	0.4843(6)	0.3214(5)	6.3(4)
C(131)	0.1342(9)	0.2559(6)	0.1578(4)	4.7(3)
C(211)	−0.3052(11)	0.3582(6)	0.4752(6)	6.8(4)
C(231)	−0.3347(9)	0.0687(5)	0.3611(5)	4.7(3)
C(311)	0.1620(11)	0.3865(6)	0.5318(5)	6.7(3)
C(331)	0.3061(9)	0.0887(5)	0.4790(5)	4.7(3)
C(411)	−0.0688(12)	−0.2354(6)	0.3004(6)	7.6(4)
C(431)	0.1462(12)	−0.0175(6)	0.1420(5)	6.6(3)
C(1)	−0.0125(9)	−0.0670(5)	0.3844(5)	3.9(3)
C(2)	0.0928(10)	−0.1075(6)	0.4355(4)	5.1(3)
B	−0.0266(11)	0.3159(6)	0.4053(5)	3.6(3)

Table 7. Positional Parameters for 11

atom	x	y	z	B_{eq}, Å²
U	0.23597(3)	0.20238(2)	0.44308(2)	2.88(1)
Cl(1)	0.0976(2)	0.2191(1)	0.5617(2)	5.9(1)
Cl(2)	0.1592(2)	0.2741(1)	0.2915(2)	5.1(1)
O	0.4129(5)	0.2301(3)	0.4962(4)	3.6(2)
N(1)	0.0741(6)	0.1203(4)	0.3732(5)	4.1(3)
N(2)	0.2965(6)	0.0928(4)	0.5301(5)	3.4(2)
N(3)	0.3209(6)	0.1256(4)	0.3354(5)	3.4(2)
N(4)	0.2731(6)	0.3258(4)	0.5038(5)	3.6(2)
N(11)	0.0957(6)	0.0502(4)	0.3804(5)	3.6(3)
N(21)	0.2933(6)	0.0308(4)	0.4868(5)	3.3(3)
N(31)	0.2819(6)	0.0587(4)	0.3194(5)	3.6(2)
N(41)	0.3870(6)	0.3397(4)	0.5444(5)	3.6(3)
C(11)	−0.0073(9)	0.0151(5)	0.3686(6)	3.7(3)
C(12)	−0.0967(9)	0.0623(5)	0.3505(7)	4.6(3)
C(13)	−0.0443(9)	0.1258(6)	0.3537(7)	4.9(4)
C(21)	0.3537(8)	−0.0161(5)	0.5458(7)	3.9(3)
C(22)	0.3966(8)	0.0179(6)	0.6270(7)	4.7(4)
C(23)	0.3587(8)	0.0848(5)	0.6164(7)	3.9(3)
C(31)	0.3137(9)	0.0350(6)	0.2438(7)	4.4(3)
C(32)	0.3741(9)	0.0853(6)	0.2091(7)	4.8(4)
C(33)	0.3781(8)	0.1408(6)	0.2671(7)	4.3(3)
C(41)	0.4016(9)	0.4026(5)	0.5832(7)	4.3(4)
C(42)	0.2913(9)	0.4327(5)	0.5658(7)	4.9(4)
C(43)	0.2145(8)	0.3839(5)	0.5191(6)	3.9(3)
C(111)	−0.0133(9)	−0.0615(5)	0.3754(7)	5.8(4)
C(131)	−0.1042(8)	0.1933(5)	0.3374(9)	7.2(4)
C(211)	0.3698(9)	−0.0892(5)	0.5199(7)	6.1(4)
C(231)	0.3798(9)	0.1407(5)	0.6858(6)	5.7(4)
C(311)	0.2855(10)	−0.0374(5)	0.2087(7)	6.1(4)
C(331)	0.4364(9)	0.2092(6)	0.2630(7)	5.9(4)
C(411)	0.5188(9)	0.4293(5)	0.6311(7)	6.3(4)
C(431)	0.0846(8)	0.3895(5)	0.4817(7)	5.4(4)
C(1)	0.4738(7)	0.2852(5)	0.5428(6)	3.8(3)
C(2)	0.6863(5)	0.2886(3)	0.5370(4)	4.7(3)
C(3)	0.7795(5)	0.3089(3)	0.4964(4)	6.7(4)
C(4)	0.7578(5)	0.3493(3)	0.4162(4)	6.4(5)
C(5)	0.6428(5)	0.3695(3)	0.3767(4)	6.1(5)
C(6)	0.5496(5)	0.3492(3)	0.4173(4)	4.9(3)
C(7)	0.5713(5)	0.3087(3)	0.4975(4)	3.5(3)
B	0.2198(9)	0.0210(6)	0.3890(8)	3.8(4)

2.49(2) Å in the seven-coordinate UCl₃L*(THF).[4] The U–O distances in the three compounds (2.111(7), 2.108(7), and 2.074(10) Å, respectively) are in the range for U–O distances in poly(pyrazolyl)borate uranium compounds with alkoxide and aryloxide groups (2.03–2.12 Å).[5d,13] The U–N(4) distances (2.56(1), 2.56(1), and 2.61(1) Å for compounds 10–12, respectively) are similar to the value found for the U–N bond in Cp*₂UCl₂pzH.[14]

Experimental Section

General Considerations. All manipulations were performed using glovebox and high-vacuum-line techniques. Tetrahydrofuran, toluene, and hexane were dried by refluxing, under argon, with Na/K alloy and distilled prior to use. Cyclohexane was washed with concentrated H₂SO₄, followed by water, 5% NaOH, and again water until neutral. It was then dried with CaCl₂ and then distilled from Na. The solvents were degassed on the vacuum line before use. Deuterated solvents (benzene-d₆ and toluene-d₈) were dried over Na and distilled. Acetone was dried with CaSO₄ and then distilled from CaSO₄. 3-Pentanone was dried with CaCl₂ and distilled from CaCl₂. Acetaldehyde was shaken with NaHCO₃, dried with CaSO₄, and fractionally distilled from CaSO₄; the middle fraction was collected. Benzaldehyde was washed with NaOH until no more CO₂ evolved and then with Na₂SO₃ and water, followed by drying with CaCl₂ and distilling at reduced pressure. UCl₃(THF)L*,[4] (UCl₂L*)ₓ,[5b] and LiCH(SiMe₃)₂[15] were prepared as previously reported. LiCH₂SiMe₃ was prepared by the procedure used for LiCH₂CMe₃.[16] IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer with samples mounted between CsI plates. The ¹H NMR spectra

were recorded using a Bruker SY80FT multinuclear spectrometer. Carbon, hydrogen, and nitrogen analyses were performed with a Perkin-Elmer automatic analyzer.[17]

Procedures. UCl₂[CH(SiMe₃)₂]L* (1). To a green slurry of UCl₃L*(THF) (200 mg, 0.28 mmol) in toluene (20 cm³) was added 47 mg of Li[CH(SiMe₃)₂] (0.28 mmol). After it was stirred for 16 h, the suspension was centrifuged and the supernatant liquid was decanted; after removal of the solvent the compound was obtained as a brown oil. Stirring with hexane for 2–3 h induces the formation of 197 mg of yellowish brown microcrystalline 1 (0.26 mmol, 92%). Anal. Calcd for UCl₂BSi₂C₂₂H₄₁N₆: C, 34.5; H, 5.4; N, 11.0. Found: C, 32.4; H, 5.2; N, 10.5.

UCl₂(CH₂SiMe₃)L* (2). A Schlenk tube was charged with UCl₃L*(THF) (200 mg, 0.28 mmol) and LiCH₂SiMe₃ (26 mg, 0.28 mmol). THF (40 cm³) was condensed into the flask in vacuo at −196 °C. The mixture was stirred at −78 °C, and after 2 h, the THF was removed in vacuo and the compound was extracted with toluene (5 cm³). The toluene was then evaporated on the vacuum line, and the resulting yellowish brown solid (116 mg) was washed with hexane and dried under vacuum (0.17 mmol, 62%). Anal. Calcd for UCl₂BSiC₁₉H₃₃N₆: C, 32.9; H, 4.8; N, 12.1. Found: C, 33.0; H, 4.6; N, 12.1.

UCl(CH₂SiMe₃)₂L* (3). THF (20 cm³) was condensed into a Schlenk tube in vacuo at −196 °C containing 110 mg (0.15 mmol) of UCl₃L*(THF) and 29 mg (0.31 mmol) of LiCH₂SiMe₃. After it was stirred for 2 h at −78 °C, the mixture was evaporated to dryness and the compound was isolated by extraction with hexane. Removal of the solvent in vacuo yielded 45 mg of the yellowish green compound 3 (0.06 mmol, 40%). Anal. Calcd for

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Table 8. Positional Parameters for 12

atom	x	y	z	B_{eq}, Å^2
U	0.04899(2)	0.26198(2)	0.69309(2)	2.58(1)
Cl(1)	0.1760(2)	0.2023(2)	0.6482(2)	4.8(1)
Cl(2)	−0.0070(2)	0.1600(2)	0.7793(2)	5.3(1)
O	−0.0016(5)	0.2026(4)	0.6090(4)	4.0(2)
N(1)	0.1253(5)	0.2874(4)	0.8116(5)	3.0(2)
N(2)	−0.0265(5)	0.3514(4)	0.7655(5)	3.0(3)
N(3)	0.1153(5)	0.3840(4)	0.6744(5)	3.1(3)
N(4)	−0.0304(5)	0.3365(5)	0.5976(5)	3.3(3)
N(11)	0.1301(5)	0.3574(5)	0.8421(5)	3.0(3)
N(21)	0.0036(5)	0.4108(4)	0.8032(6)	2.5(3)
N(31)	0.1232(5)	0.4365(5)	0.7285(5)	3.0(3)
N(41)	−0.0599(6)	0.2928(5)	0.5413(5)	3.4(3)
C(11)	0.1745(7)	0.3562(7)	0.9022(7)	3.7(4)
C(12)	0.1979(6)	0.2849(7)	0.9119(6)	3.8(4)
C(13)	0.1675(6)	0.2444(6)	0.8555(6)	3.6(3)
C(21)	−0.0512(8)	0.4512(5)	0.8346(6)	3.4(3)
C(22)	−0.1183(7)	0.4174(6)	0.8189(7)	3.5(3)
C(23)	−0.1018(6)	0.3569(7)	0.7762(7)	3.7(4)
C(31)	0.1663(6)	0.4927(5)	0.7028(7)	3.4(4)
C(32)	0.1854(7)	0.4766(6)	0.6323(7)	3.7(4)
C(33)	0.1525(7)	0.4110(6)	0.6161(7)	3.7(4)
C(41)	−0.0968(7)	0.3356(8)	0.4929(6)	4.1(4)
C(42)	−0.0932(7)	0.4060(6)	0.5162(7)	4.2(4)
C(43)	−0.0529(8)	0.4074(6)	0.5800(7)	4.1(4)
C(111)	0.1923(7)	0.4213(6)	0.9471(6)	5.4(4)
C(131)	0.1747(8)	0.1629(6)	0.8412(7)	5.8(5)
C(211)	−0.0385(7)	0.5184(5)	0.8797(7)	5.4(4)
C(231)	−0.1545(6)	0.3024(7)	0.7408(7)	5.3(4)
C(311)	0.1875(7)	0.5577(6)	0.7485(7)	5.0(4)
C(331)	0.1549(8)	0.3700(6)	0.5447(6)	5.4(5)
C(411)	−0.1360(8)	0.3061(7)	0.4261(6)	5.6(5)
C(431)	−0.0355(8)	0.4724(5)	0.6272(7)	5.3(5)
C(1)	−0.0423(8)	0.2115(6)	0.5450(7)	3.5(4)
C(10)	0.0040(7)	0.1895(7)	0.4792(6)	5.3(4)
C(100)	−0.1162(6)	0.1691(6)	0.5500(7)	4.9(4)
B	0.0898(8)	0.4244(6)	0.8064(9)	3.4(4)

UClBSi$_2$C$_{23}$H$_{44}$N$_6$: C, 37.1; H, 5.9; N, 11.3. Found: C, 36.4; H, 5.5; N, 11.4.

U(CH$_2$SiMe$_3$)$_3$L* (4). The compound was synthesized in a manner similar to that for the preparation of UCl(CH$_2$SiMe$_3$)$_2$L* by using 128 mg (0.18 mmol) of UCl$_3$L*(THF) and 51 mg (0.54 mmol) of LiCH$_2$SiMe$_3$. The bright green compound was obtained in a yield of 72% (104 mg, 0.13 mmol). Anal. Calcd for UBSi$_3$C$_{27}$H$_{55}$N$_6$: C, 40.7; H, 6.9; N, 10.6. Found: C, 39.6; H, 7.0; N, 11.1.

UCl$_2$[OC(Me)$_2$CH$_2$SiMe$_3$]L* (5). To a solution of UCl$_2$(CH$_2$-SiMe$_3$)L* (200 mg, 0.29 mmol) in THF (10 cm^3) was added 17 mg (0.29 mmol) of acetone. The brown solution of the alkyl turns almost immediately green after addition of the ketone. After being stirred for 3.5 h at room temperature, the clear green solution was evaporated to dryness, yielding 181 mg of 5 (0.24

mmol, 83%). Anal. Calcd for UCl$_2$BOSiC$_{22}$H$_{39}$N$_6$: C, 35.2; H, 5.2; N, 11.2. Found: C, 35.1; H, 5.7; N, 11.1.

UCl$_2$[OC(Et)$_2$CH$_2$SiMe$_3$]L* (6). 3-Pentanone (19 mg, 0.22 mmol) was added to a solution of UCl$_2$(CH$_2$SiMe$_3$)L* (150 mg, 0.22 mmol) in toluene (5 cm^3). After the mixture was stirred for 18 h, the green compound was isolated as described for 5 in a yield of 89% (150 mg, 0.20 mmol). Anal. Calcd for UCl$_2$BOSiC$_{24}$H$_{43}$N$_6$: C, 37.0; H, 5.5; N, 10.8. Found: C, 37.0; H, 5.5; N, 9.8.

UCl$_2$[OC(Me)$_2$CH$_2$C(O)Me]L* (7). (a) The compound was isolated in a manner similar to that described above for 5 by reacting UCl$_2$(CH$_2$SiMe$_3$)L* (150 mg, 0.22 mmol) with a large excess of acetone for 15 min. The green microcrystalline compound (150 mg, 0.21 mmol) was obtained in a yield of 95%. Anal. Calcd for UCl$_2$BO$_2$C$_{21}$H$_{33}$N$_6$: C, 35.0; H, 4.6; N, 11.7. Found: C, 34.9; H, 5.0; N, 10.8.

(b) The compound was isolated, in a manner similar to that described above, by using UCl$_2$[CH(SiMe$_3$)$_2$]L* (200 mg, 0.26 mmol) (yield 180 mg, 0.25 mmol, 96%) or (UCl$_2$L*)$_x$.

UCl$_2$[OC(H)(Me)CH$_2$SiMe$_3$]L* (8). The compound was obtained by reacting UCl$_2$(CH$_2$SiMe$_3$)L* (150 mg, 0.22 mmol) with acetaldehyde (10 mg, 0.23 mmol) in toluene (5 cm^3) for 4.5 h. The resulting clear solution was evaporated under vacuum, and the green microcrystalline compound (147 mg, 0.20 mmol) was obtained in a yield of 91%. Anal. Calcd for UCl$_2$BOSiC$_{21}$H$_{37}$N$_6$: C, 34.2; H, 5.0; N, 11.4. Found: C, 34.0; H, 4.9; N, 11.3.

UCl$_2$[OC(H)(Ph)CH$_2$SiMe$_3$]L* (9). The compound was obtained as described for 8 by using UCl$_2$(CH$_2$SiMe$_3$)L* (144 mg, 0.21 mmol) and benzaldehyde (22 mg, 0.21 mmol) in toluene (5 cm^3); yield 86% (144 mg, 0.18 mmol). Anal. Calcd for UCl$_2$BOSiC$_{26}$H$_{39}$N$_6$: C, 39.1; H, 4.9; N, 10.5. Found: C, 40.9; H, 5.1; N, 10.7.

UCl$_2$[OC(H)(Me)NNC$_5$H$_7$]L* (10). (a) The compound was obtained by reacting UCl$_2$(CH$_2$SiMe$_3$)L* (150 mg, 0.22 mmol) with acetaldehyde (19 mg, 0.44 mmol) in toluene (5 cm^3). After it was stirred for 3 h, the mixture was centrifuged and the green supernatant solution was evaporated to dryness; yield 73% (116 mg, 0.16 mmol). Anal. Calcd for UCl$_2$OBC$_{22}$H$_{33}$N$_8$: C, 35.4; H, 4.4; N, 15.7. Found: C, 34.9; H, 4.8, N, 14.0.

(b) The compound could also be obtained by reaction of UCl$_2$-[CH(SiMe$_3$)$_2$]L* (88 mg, 0.12 mmol) with 5 mg of acetaldehyde (0.12 mmol) in toluene (5 cm^3). The compound was isolated as described above.

(c) The reaction was carried out by using UCl$_2$[OC(H)(Me)CH$_2$-SiMe$_3$]L* (100 mg, 0.14 mmol) and 6 mg of acetaldehyde (0.14 mmol) in toluene, and the product was isolated as described above.

UCl$_2$[OC(H)(Ph)NNC$_5$H$_7$]L* (11). (a) The compound was obtained as described for 8 by using UCl$_2$(CH$_2$SiMe$_3$)L* (89 mg,

Table 9. Crystallographic Data

	5	10	11	12
formula	C$_{22}$H$_{39}$BN$_6$OCl$_2$SiU	C$_{22}$H$_{33}$BN$_8$OCl$_2$U	C$_{27}$H$_{35}$BN$_8$OCl$_2$U	C$_{23}$H$_{35}$BN$_8$OCl$_2$U
mol wt	751.42	745.80	807.37	759.33
cryst syst	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$Pbca$
a (Å)	10.672(1)	9.662(2)	11.588(3)	17.766(1)
b (Å)	16.158(1)	16.093(2)	19.376(4)	18.059(1)
c (Å)	17.531(1)	18.527(3)	14.707(4)	18.196(2)
β (deg)		93.28(1)	101.90(2)	
V (Å^3)	3023(1)	2876(1)	3231(3)	5838(1)
Z	4	4	4	8
D_{calcd} (g cm^{-3})	1.651	1.721	1.660	1.728
linear abs coeff (Mo Kα) (cm^{-1})	53.48	55.85	49.75	55.02
2θ range (deg)	3.0–46.00	3.0–52.0	3.0–50.0	3.0–48.0
no. of rflns	2286 ($F_o > 2\sigma(F_o)$)	3888 ($F_o > 3\sigma(F_o)$)	3285 ($F_o > 3\sigma(F_o)$)	2833 ($F_o > 3\sigma(F_o)$)
decay cor: min, max	1.000 19, 1.034 43	1.000 01, 1.032 73	1.000 01, 1.007 52	1.000 00, 1.009 70
range in abs cor factors	0.9063, 0.9996	0.7642, 0.9999	0.8623, 0.9997	0.7829, 0.9996
no. of params refined	275	319	352	328
weighting scheme used, $w = (\sigma^2(F_o) + gF_o^2)^{-1}$, g	0.001 758	0.000 08	0.0001	0.000 08
final R, R_w	0.051, 0.056	0.045, 0.034	0.042, 0.033	0.051, 0.034

0.13 mmol) and benzaldehyde (28 mg, 0.26 mmol) in THF (5 cm³); yield 72% (75 mg, 0.09 mmol). Anal. Calcd for $UCl_2BOC_{27}H_{35}N_8$: C, 40.2; H, 4.3; N, 13.9. Found: C, 42.0; H, 4.6; N, 12.7.

(b) The compound could also be obtained by reaction of UCl_2-$[CH(SiMe_3)_2]L^*$ (51 mg, 0.07 mmol) with 7 mg of benzaldehyde (0.07 mmol) in toluene (5 cm³). The compound (39 mg, 0.05 mmol, 69%) was isolated as described above.

NMR-Tube Reaction of $UCl_2(C_5H_7N_2)L^*$ with Acetone: $\overline{UCl_2[OC(Me)_2NNC_5H_7]L^*}$ (12). $UCl_2(C_5H_7N_2)L^*$ (30 mg, 0.043 mmol) was dissolved in benzene-d_6 (0.5 mL), and 4.0 μL (0.054 mmol) of acetone was added. ¹H NMR spectroscopy shows resonances for the poly(pyrazolyl)borate ligand at δ 63.1 (3H), 54.9 (1H), 21.7 (3H), -9.9 (6H), -16.0 (2H), and -31.3 (6H). The resonance due to the methyl groups of the ketone is at δ 71.0 (6H), and those of the two methyls of the pyrazole of the heterocyclic ring are located at δ 20.9 (3H) and -56.6 (6H). H(4) of the pyrazole ring could not be identified in the spectrum.

Crystallographic Analysis. Crystals of 5 and 10–12 were obtained by slow diffusion of *n*-hexane into saturated solutions of the compounds in toluene. They were mounted in quartz capillaries in an argon-filled glovebox and sealed under argon. The low quality of the crystal for compound 5 limited the accuracy of the X-ray structure analysis data but enabled satisfactory solution of the structure. Data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo Kα radiation using a ω–2θ scan mode. Crystal data, data collection, and refinement are presented in Table 9. Data were corrected for Lorentz–polarization, for decay,

and for absorption by empirical corrections based on ψ scans, using the Enraf-Nonius program. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares.[18] For 10–12 all non-hydrogen atoms were refined anisotropically, and the carbon atoms of the phenyl group in 11 were refined as a rigid group. For 5 all but some methyl carbon atoms were refined anisotropically. The contributions of the hydrogen atoms were included in calculated positions, constrained to ride on their carbon and boron atoms with group U_{iso} values assigned. For compound 5 the final model was refined to $R = 0.070$ and $R_w = 0.087$. Refinement of the other enantiomer converged to a model with $R = 0.051$ and $R_w = 0.056$, indicating this last choice of enantiomer was the correct one. Atomic scattering factors and anomalous dispersion terms were taken from ref 19.

Supplementary Material Available: Tables of thermal parameters, calculated hydrogen atom coordinates, bond distances, bond angles, and equations of mean least-squares planes for 5 and 10–12 (17 pages). Ordering information is given on any current masthead page.

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