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Synthesis and reactivity of hydrotris(pyrazolyl)borate σ-hydrocarbyl uranium(IV) complexes

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Abstract

Stable σ-hydrocarbyl uranium (IV) compounds could not be obtained by simple metathesis reactions of [$UCl_3L^\star$(THF)] ($L^\star = HB(3,5\text{-}Me_2pz)_3$) with LiMe, LiC_6H_5, or $LiCH_2C_6H_5 \cdot$ THF. The reactions with LiMe resulted in uncharacterizable mixtures of products and the reactions with $LiCH_2C_6H_5 \cdot$ THF or LiC_6H_5 yielded a known reduced uranium compound, $\{UCl_2L^\star\}_x$. Decomposition pathways could be prevented by using a second ancillary ligand such as Cp or by introducing a bulky substituent on the aromatic ring of the benzyl or phenyl. Reactions of [$UCl_2CpL^\star$] with LiMe gave [$UCl_{2-x}CpMe_xL^\star$] ($x = 1$ (**1**) or 2 (**2**)) depending of the stoichiometric ratio of the reagents and the reactions of [$UCl_3L^\star$(THF)] with Li-2-$CH_2C_6H_4NMe_2$ or Li-2-$C_6H_4CH_2NMe_2$ yielded the compounds [UCl_2(2-$CH_2C_6H_4NMe_2$)$L^\star$] (**3**) and [UCl_2(2-$C_6H_4CH_2NMe_2$)$L^\star$] (**4**), respectively. Compounds **3** and **4** are fluxional in solution at room temperature, but static spectra were obtained at low temperature. The observed dynamic behaviour can be explained by breaking and making the U–N coordinate bond of the chelating (2-$CH_2C_6H_4NMe_2$) or (2-$C_6H_4CH_2NMe_2$).

Keywords: Uranium; Hydrocarbyl complexes; Pyrazolylborate complexes; Synthesis; Reactivity

1. Introduction

The syntheses of σ-hydrocarbyl uranium(IV) complexes of general formula [$UCl_{3-x}R_xL^\star$] [$L^\star = HB(3,5\text{-}Me_2Pz)_3$) ($x = 1$, $R = CH(SiMe_3)_2$ or CH_2SiMe_3; $x = 2$ or 3 $R = CH_2SiMe_3$) have been reported recently [1]. The reactivity of the U–C bond of these compounds towards several substrates has been investigated [1,2], and it was found that the reactivity were dependent on the bulk of the R group. This prompted us to extend these studies to other hydrocarbyl derivatives with smaller R ligands (Me, C_6H_5, or $CH_2C_6H_5$). However, in all cases the complexes formed were unstable and only increasing the steric crowding around the uranium centre allowed the synthesis of stable uranium(IV) hydrocarbyls.

2. Experimental details

2.1. General considerations

All manipulations were performed with an inert atmosphere glovebox and high-vacuum-line techniques. Tetrahydrofuran, toluene and hexane were dried by refluxing under argon with Na–K alloy, and were distilled prior to use. Cyclohexane was washed with concentrated H_2SO_4, followed by water, 5% NaOH, and water again until neutral. It was next dried with $CaCl_2$ and then distilled from Na. The solvents were degassed on the vacuum line before use. Deuterated solvents were dried over Na (C_6D_6, C_6D_{12}, and C_7D_8) or P_2O_5 ($CDCl_3$) and distilled. LiC_6H_5 (Aldrich) was used without further purification. [$UCl_3L^\star$(THF)] [3], [$UCl_2CpL^\star$] [4], $LiCH_2C_6H_5 \cdot$ THF [5], $KCH_2C_6H_5$ [6], Li(2-$CH_2C_6H_4NMe_2$) [7], and Li(2-$C_6H_4CH_2NMe_2$) [8] were prepared as previously reported. IR spectra were recorded using a Perkin Elmer 577 spectrophotometer with samples mounted as Nujol mulls between CsI plates. The ^1H NMR spectra were recorded using a Bruker SY80FT spectrometer. Carbon, hydrogen and nitrogen analyses were performed with a Perkin Elmer automatic analyser [9].

2.2. Procedures

2.2.1. [$UClCpMeL^\star$] 1

To a solution of [$UCl_2CpL^\star$] (200 mg, 0.30 mmol) in toluene (25 cm^3) at -78°C was added slowly a 5%

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solution of LiMe in diethylether (131 mg, 0.30 mmol). The reaction mixture was stirred for 1 h at −78°C, and was then allowed to warm to room temperature. After 2 h the suspension was centrifuged and the solvent was removed in vacuum to yield a yellow compound. Yield 77% (147 mg, 0.23 mmol). IR Nujol (cm^{-1}): ν(B–H) 2555, ν(U–Cl) 245.

2.2.2. [UCpMe$_2$L*] 2

The green compound was obtained as described for **1** by reaction of [$UCl_2CpL^\star$] (200 mg, 0.30 mmol) with LiMe (263 mg, 0.60 mmol). Yield 90% (168 mg, 0.27 mmol). IR Nujol (cm^{-1}): ν(B–H) 2545.

2.2.3. [UCl$_2$(2-CH$_2$C$_6$H$_4$NMe$_2$)L*] 3

To a green slurry of [$UCl_3L^\star$(THF)] (121 mg, 0.17 mmol) in cyclohexane (20 cm^3) was added 24 mg (0.17 mmol) of Li(2-$CH_2C_6H_4NMe_2$). After stirring for 18 h, the suspension was centrifuged to remove LiCl, the supernatant liquid was decanted and the solvent was removed from it on the vacuum-line. The brownish-red compound was obtained in a yield of 88% (111 mg, 0.15 mmol). IR Nujol (cm^{-1}): ν(B–H) 2560, ν(U–Cl) 260.

2.2.4. [UCl$_2$(2-C$_6$H$_4$CH$_2$NMe$_2$)L*] 4

The compound was synthesized in a manner similar to that described for **3** by using 200 mg of [$UCl_3L^\star$(THF)] (0.28 mmol) and 40 mg of Li(2-$C_6H_4CH_2NMe_2$ (0.28 mmol). The greenish-yellow solid was washed with hexane and dried in vacuum. Yield: 61% (126 mg, 0.17 mmol). IR Nujol (cm^{-1}): ν(B–H) 2545, ν(U–Cl) 270.

3. Results and discussion

Treatment of [$UCl_3L^\star$(THF)] with stoichiometric amounts of LiMe in THF or toluene solutions at low temperature always yielded mixtures of uncharacterizable products. Similarly, the benzyl or the phenyl derivatives could not be isolated from the reactions of [$UCl_3L^\star$(THF)] with the corresponding lithium alkyl or aryl. Instead, a uranium(III) species, identified by ^1H NMR spectroscopy as previously reported {$UCl_2L^\star$}$_x$ [10], was formed.

Reduction of uranium(IV) complexes by lithium alkyls or lithium phosphides has already been observed by others [11], but there is some controversy concerning the mechanism of the reduction process. It has been reported that a stable U(IV) phosphide complex was isolated if the potassium salt of the phosphide was used instead of the lithium salt [11(e)], but the attempted preparation of the benzyl–uranium compound by reaction of the stoichiometric amount of [$UCl_3L^\star$(THF)] with $KCH_2C_6H_5$ again yielded {$UCl_2L^\star$}$_x$. Following this reaction, ^1H NMR spectroscopy showed that some minutes after adding the potassium salt of the benzyl to the uranium compound, the resonances of {$UCl_2L^\star$}$_x$ were present, together with the resonances from another species. The splitting and the chemical shifts of these resonances were similar to those found in the ^1H NMR spectrum of the analogous compound [UCl_2(2-$CH_2C_6H_4NMe_2$)$L^\star$] described below, indicating that the intermediate is probably the compound [UCl_2(CH_2-C_6H_5)$L^\star$]. As the reaction progressed, a steady increase in the proportion of the U(III) compound and a consequent decrease in the proportion of the benzyl derivative was observed. From these observations it seems that the reduced species arises from decomposition of the benzyl derivative, and not from competitive reduction of the starting uranium IV compound by the lithium alkyl.

In order to confirm the existence of the intermediate [$UCl_2(CH_2C_6H_5)L^\star$], the reaction of $KCH_2C_6H_5$ with a THF solution containing [$UCl_3L^\star$(THF)] and acetone in the stoichiometric ratio 1 : 1 : 1 was carried out. ^1H NMR monitoring of this reaction showed the formation of the tertiary alkoxide [$UCl_2\{OC(Me)_2CH_2C_6H_5\}L^\star$], which we explain by the insertion of acetone into the U–C bond of the benzyl uranium derivative. Together with the resonances of the alkoxide, there were other resonances that we assign to the aldol compound [$UCl_2\{OC(Me)_2CH_2C(O)Me\}L^\star$] [1]. This compound may arise from the reaction of acetone with a small amount of the UIII compound formed by competition between the reduction reaction of the benzyl derivative and the insertion reaction. In fact, {$UCl_2L^\star$}$_x$ reacts with acetone to yield [$UCl_2\{OC(Me)_2CH_2C(O)Me\}L^\star$], as previously reported [1].

As pointed out by Blake et al. [11(d)], steric effects play a role in competing reactions of ligand-transfer and reduction. We therefore tested the possibility of preventing reduction by increasing the crowding around the uranium by using a second ancillary ligand such as Cp (eqn. 1) or by replacing an *ortho*-hydrogen of the aromatic ring of the benzyl or phenyl ligands (eqns. 2 and 3).

In fact, we observed that the second ancillary ligand prevents reduction of the uranium, but the UIV benzyl derivatives could not be obtained analytically pure. Treatment of [$UCl_2CpL^\star$] with one equivalent of $LiCH_2C_6H_5 \cdot$THF in toluene solution at −78°C gave a mixture of [$UCp(CH_2C_6H_5)_2L^\star$] (13%), [$UClCp(CH_2$-$C_6H_5)L^\star$] (74%) and [$UCl_2CpL^\star$] (13%), as judged by NMR spectroscopy. The similar solubilities of these compounds impeded their separation. The analogous reaction in the stoichiometric ratio 1 : 2 yielded a mixture of [$UCp(CH_2C_6H_5)_2L^\star$] (80%), and [$UClCp(CH_2$-$C_6H_5)L^\star$] (20%).

However, metathesis of [$UCl_2CpL^\star$] with LiMe in various stoichiometric ratios gave the hydrotris(pyrazolyl)borate methyl derivatives of uraniumIV (eqn. 1).

$$[\mathrm{UCl_2CpL^\star}] + x\mathrm{LiMe} \rightarrow [\mathrm{UCl}_{2-x}\mathrm{CpMe}_x\mathrm{L^\star}] + x\mathrm{LiCl} \qquad \begin{array}{l} x = 1\ \mathbf{1} \\ x = 2\ \mathbf{2} \end{array} \qquad (1)$$

The yellow compound **1** and the green compound **2** are soluble in ethereal and aromatic solvents. Compound **2** is also soluble in aliphatic hydrocarbons.

The resonances assigned to the poly(pyrazolyl)borate in the ^{1}H NMR spectrum of **1** indicate that the three pyrazolyl rings are inequivalent, while for compound **2** the ^{1}H NMR spectrum indicates that two of the pyrazolyl rings are equivalent. These are the expected patterns for compounds with a C_1 and C_s symmetries, respectively.

Simple metathesis reactions of $[\mathrm{UCl_3L^\star(THF)}]$ with $\mathrm{Li(2\text{-}CH_2C_6H_4NMe_2)}$ and $\mathrm{Li(2\text{-}C_6H_4CH_2NMe_2)}$ yielded stable UIV hydrocarbyls (eqns. 2 and 3).

$$[\mathrm{UCl_3L^\star(THF)}] + \mathrm{Li(2\text{-}CH_2C_6H_4NMe_2)} \rightarrow [\mathrm{UCl_2(2\text{-}CH_2C_6H_4NMe_2)L^\star}] + \mathrm{LiCl} \qquad (2)$$

$$[\mathrm{UCl_3L^\star(THF)}] + \mathrm{Li(2\text{-}C_6H_4CH_2NMe_2)} \rightarrow [\mathrm{UCl_2(2\text{-}C_6H_4CH_2NMe_2)L^\star}] + \mathrm{LiCl} \qquad (3)$$

Compound **3** is synthesized by the slow, ambient-temperature addition of an equivalent of $\mathrm{Li(2\text{-}CH_2C_6H_4NMe_2)}$ to a magnetically stirred suspension of $[\mathrm{UCl_3L^\star(THF)}]$ in cyclohexane. Compound **4** was obtained by a similar procedure by reaction of the stoichiometric amounts of $[\mathrm{UCl_3L^\star(THF)}]$ and $\mathrm{Li(2\text{-}C_6H_4CH_2NMe_2)}$ in toluene or cyclohexane. When the reactions were carried in the stoichiometric ratio 2 : 1, the same compounds were obtained. In fact, the $[\mathrm{2\text{-}CH_2C_6H_4NMe_2}]^-$ [12,13] and $[\mathrm{2\text{-}C_6H_4CH_2NMe_2}]^-$ [7(a)] can chelate with formation of five-membered rings, and it is not unexpected that these sterically demanding ligands prevent the replacement of a second chlorine.

The brownish-red microcrystalline compound **3** and the greenish-yellow compound **4** are soluble in ethereal, chlorinated, and aromatic solvents. We were not able to obtain crystals suitable for X-ray diffraction analysis, because the compounds are not very stable in solution; compound **3** decomposes in a few hours.

The ^{1}H NMR spectrum at room temperature of compound **3** (Table 1) displays two sets of resonances for the protons of the pyrazolyl rings, one resonance for the two methyls of the $\mathrm{NMe_2}$ group and one single resonance for the two methylene protons, compatible with a C_s symmetry for the complex in solution. The resonance for the protons of the methyls of the $\mathrm{NMe_2}$ group is already very broad at room temperature, which suggests a fluxional process. On lowering the temperature to 275 K this resonance collapses and gives rise to two signals in a 1 : 1 intensity ratio. This also happens with the two methylene protons of the benzyl group and the protons of the two equivalent pyrazolyl rings. The $\Delta G^\#$ calculated by the standard coalescence point formalism [14] from the coalescence of the methyl groups of $\mathrm{NMe_2}$, of the methylene protons or of the protons of the pyrazolyl rings are similar (44.5 ± 4.0 kJ mol^{-1}), suggesting that the same process is responsible for the equivalence observed at room temperature for the protons of all these groups. The lowering of the symmetry of the complex from C_s to C_1 indicates restricted rotation around the U–C bond, because of ligand bulk or because of an interaction between the lone pair of the nitrogens of the $\mathrm{NMe_2}$ group of the potentially chelating ligand and the uranium atom. This interaction is compatible with the C_s symmetry observed at room temperature if the dynamic behaviour involves breaking of the U–N donor bond, followed by rotation around the C(Ar)–$\mathrm{NMe_2}$ bond, inversion of configuration at nitrogen, and finally recoordination of the amine [13].

The ^{1}H NMR spectrum of compound **4** at room temperature displays a spectrum similar to that of **3** (Table 1). The variable temperature measurements show

Table 1
Room-temperature ^{1}H NMR data [a]

Complex	δ(ppm)			
	(3,5-$\mathrm{Me_2}$pz)		H(4)	R, R′
$[\mathrm{UClCpMeL^\star}]$**1** [b]	28.6(3H)	10.1(3H)	30.1(1H)	118.7(3H)
	−4.8(3H)	−6.0(3H)	−2.0(1H)	−19.5(5H)
	−7.3(3H)	−11.4(3H)	−15.6(1H)	
$[\mathrm{UCpMe_2L^\star}]$**2** [b]	17.8(6H)	3.2(6H)	14.4(2H)	8.4(6H)
	−7.1(3H)	−15.6(3H)	−7.5(1H)	−30.8(5H)
$[\mathrm{UCl_2(2\text{-}CH_2C_6H_4NMe_2)L^\star}]$**3** [c]	45.1(3H)	3.1(3H)	26.4(1H)	28.2(1H,d), 14.8(1H,t)
	−6.3(6H)	−14.6(6H)	−2.0(2H)	6.9(1H,d), 3.3(1H,t)
				105.1(2H), −17.4(6H)
$[\mathrm{UCl_2(2\text{-}C_6H_4CH_2NMe_2)L^\star}]$**4** [b]	34.5(3H)	9.6(3H)	31.4(1H)	37.8(1H,d), 25.8(1H,t)
	−5.7(6H)	−15.4(6H)	−4.6(2H)	23.7(1H,t), 21.0(1H,d)
				20.9(2H), −9.8(6H)

[a] The shifts are in ppm from TMS; downfield shifts are positive; d = doublet; t = triplet; $T = 301$ K. [b] In benzene-d$_6$. [c] In cyclohexane-d$_{12}$.

a similar behaviour to compound **3**. In the limiting static spectrum at 210 K, two resonances for the methylene protons and two resonances for the methyl protons were observed, as well as three sets of resonances for the inequivalent pyrazolyl groups. The activation energy $\Delta G^{\#}$ associated with the fluxional process was determined from the coalescence of the methylene, of the methyl and of the pyrazolyl protons (46.8 ± 4.0 kJ mol^{-1}), and similar to that determined for complex **3**, which probably indicates that the process responsible for the fluxional behaviour of both compounds is the same.

When $[UCl_2(2\text{-}CH_2C_6H_4NMe_2)L^{\star}]$ reacted with acetone, the tertiary alkoxide $[UCl_2\{OC(Me)_2CH_2C(O)Me\}L^{\star}]$ was formed, because of insertion of the acetone into the U–C bond. Compound $[UCl_2(2\text{-}C_6H_4CH_2NMe_2)L^{\star}]$ failed to react with acetone stoichiometrically but it reacts with an excess of acetone to yield the previously reported uranium aldolate $[UCl_2\{OC(Me)_2CH_2C(O)Me\}L^{\star}]$ [1]. There is also quantitative liberation of $C_6H_5CH_2NMe_2$ (NMR experiment). In this case α-CH activation rather than insertion is observed.

These results parallel our previous observations on the reactivity towards ketones of other uranium hydrocarbyls [1]. We had found that the reactivities were critically dependent upon the size of R. $[UCl_2(CH_2SiMe_3)L^{\star}]$ reacted with ketones to yield the corresponding tertiary alkoxides, but $[UCl_2\{CH(SiMe_3)_2\}L^{\star}]$ failed to insert ketones, and C–C coupling of two molecules of acetone in an aldol fashion on the actinide was observed [1]. From the present results, it seems that $[2\text{-}C_6H_4CH_2NMe_2]^-$ is sterically demanding, yielding a more congested σ-hydrocarbyl uranium compound than the $[2\text{-}CH_2C_6H_4NMe_2]^-$.

The activation energies found for the fluxional process observed for compounds **3** and **4** were similar. If the dynamic process observed in solution was because of hindered rotation around the U–C bond, the activation energies found for both compounds would depend on the bulkiness of the ligands R. As the $\Delta G^{\#}$ values are similar, we conclude that $[2\text{-}CH_2C_6H_4NMe_2]^-$ and $[2\text{-}C_6H_4CH_2NMe_2]^-$ are of similar size, which is not consistent with the difference in the reactivity pattern observed for both complexes. The dynamic process occurring in solution is therefore probably related to the breaking and remaking of the U–N donor bond of the chelating ligands, and not with hindered rotation around the U–C bonds.

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