

Clear-Cut Lanthanide(III)/Actinide(III) Differentiation in Coordination of Pyrazine to Tris(cyclopentadienyl) Complexes of Cerium and Uranium, Involving Reversible $U^{III} \rightarrow U^{IV}$ Oxidation

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Keywords: Actinides / Lanthanides / Nitrogen ligands / Selective complexation

In contrast to the $[Ce(C_5H_4R)_3]$ complexes (where $R = tBu$, $SiMe_3$), which react with pyrazine to give the Lewis base adducts $[Ce(C_5H_4R)_3(pyz)]$ (where $R = tBu$ **1**, $SiMe_3$ **2**), the uranium analogues are oxidized by the azine molecule to the dinuclear U^{IV} complexes $[U(C_5H_4R)_3]_2(\mu-pyz)$ ($R = tBu$ **3**, $SiMe_3$ **4**). The U–N distances of approximately 2.32 Å in the crystal structures of **3** and **4** are characteristic of U^{IV} –N bond

lengths of terminally-coordinated amide groups. The formation constants of **1** and **3** in THF at 23 °C are 0.28(6) and $8(1) \times 10^3$, respectively, permitting the clear differentiation between the two metallocenes by means of the nitrogen ligand.

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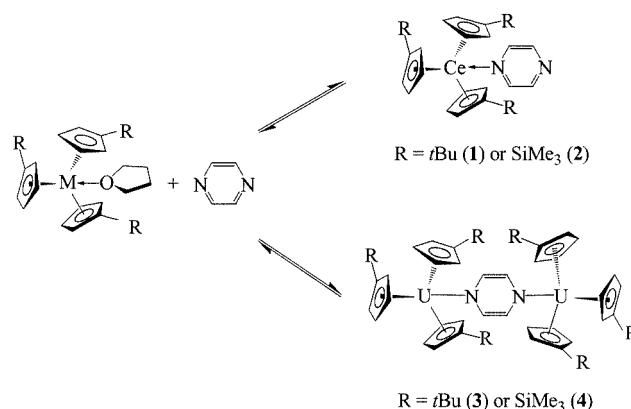
Introduction

The separation of trivalent minor actinides (An) from trivalent lanthanides (Ln) is a challenging goal in the management of nuclear waste; this key step in the advanced reprocessing of spent nuclear fuels would permit the subsequent transmutation of the long-lived americium and curium radionuclides into short-lived isotopes, by neutron bombardment.^[1] A number of extractant molecules have been designed and tested for the selective complexation of An^{III} ions in solution; polydentate aromatic amines proved to be the most promising.^[2] The better affinity of these molecules for An^{III} rather than Ln^{III} ions is generally explained by the stronger interaction between the softer (or less hard) 5f ion and the nitrogen atom. The greater stability of the An–N bond, in relation to its more covalent character, would result from π back donation of the f orbitals into the π^* orbitals of the aromatic ligand, which is less likely in the lanthanide counterpart.^[3] This assumption was consolidated after our recent studies on the complexation of the organometallic compounds $[M(C_5H_4R)_3]$ (where $M = Ce, U$; $R = tBu, SiMe_3$) with various azines, which revealed that the selectivity of the nitrogen ligand in favour of U^{III} is proportional to its π -accepting ability, measured by its reduction potential.^[4] Since extensive π back donation would eventually lead to metal oxidation and formation of an An^{IV} –N bond, a conceptual question arising from these results then concerned the possibility of clearly differen-

tiating the trivalent actinide from the lanthanide ions by a reversible oxido-reduction reaction between the An^{III} compound and the extractant molecule. This scenario, which would open new routes to the selective complexation of An^{III} over Ln^{III} ions and the discrimination of minor actinides (americium and curium), should turn out to be successful as the formation of the An^{IV} complex is thermodynamically favoured over that of the simple An^{III} and Ln^{III} Lewis base adducts. Here we demonstrate the feasibility of such a process by presenting the distinct behaviour of the uranium and cerium compounds $[M(C_5H_4R)_3]$ ($M = Ce, U$; $R = tBu, SiMe_3$) in the presence of pyrazine.

Results and Discussion

Addition of pyrazine (pyz) to a solution of $[Ce(C_5H_4R)_3]$ in THF led to an equilibrium between $[Ce(C_5H_4R)_3(THF)]$



Scheme 1. The distinct reactions of $[M(C_5H_4R)_3]$ ($M = Ce, U$) with pyrazine

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and $[\text{Ce}(\text{C}_5\text{H}_4\text{R})_3(\text{pyz})]$ (see Scheme 1). The formation constants K_{CeL} of the pyrazine adducts were calculated by using Equation (1), where C_0 is the initial concentration of $[\text{Ce}(\text{C}_5\text{H}_4\text{R})_3(\text{THF})]$, n the number of molar equivalents of pyrazine added to the solution, and x_{CeL} the molar fraction of $[\text{Ce}(\text{C}_5\text{H}_4\text{R})_3(\text{pyz})]$, which was determined from the ^1H NMR spectra of the mixtures.

$$K_{\text{CeL}} = [\text{Ce}(\text{C}_5\text{H}_4\text{R})_3(\text{pyz})]/[\text{Ce}(\text{C}_5\text{H}_4\text{R})_3(\text{THF})][\text{pyz}] = x_{\text{CeL}}/C_0(1 - x_{\text{CeL}})(n - x_{\text{CeL}}) \quad (1)$$

The formation constants at 23 °C of $[\text{Ce}(\text{C}_5\text{H}_4t\text{Bu})_3(\text{pyz})]$ (**1**) and $[\text{Ce}(\text{C}_5\text{H}_4\text{SiMe}_3)_3(\text{pyz})]$ (**2**) in THF are equal to 0.28(6) and 0.23(2), respectively. These constants are smaller than those measured for the equilibrating formation of **1** and **2** from $[\text{Ce}(\text{C}_5\text{H}_4\text{R})_3]$ and pyrazine in toluene [0.44(3) and $1.4(1) \times 10^2$],^[4] because of the competing coordination of THF to the Lewis acidic metal centre. The formation constants of **1** and **2** in toluene are quite similar to those of $[\text{Ce}(\text{C}_5\text{H}_4\text{R})_3(3,5\text{-Me}_2\text{pyz})]$ [0.33(3) and $1.6(1) \times 10^2$ for $\text{R} = t\text{Bu}$ and SiMe_3 , respectively] which are themselves lower than those of the uranium analogues [$1.5(1)$ and $1.5(2) \times 10^3$]. The slightly greater stability of the U^{III} compounds was explained by the presence of a π back-bonding interaction between the uranium atom and the 3,5-dimethylpyrazine ligand.^[4]

In striking contrast with dimethylpyrazine, pyrazine reacted with two molar equivalents of $[\text{U}(\text{C}_5\text{H}_4\text{R})_3]$ in toluene to give the dinuclear compounds $[\{\text{U}(\text{C}_5\text{H}_4\text{R})_3\}_2(\mu\text{-pyz})]$ ($\text{R} = t\text{Bu}$ **3**; $\text{R} = \text{SiMe}_3$ **4**) in quantitative yields. The mononuclear species $[\text{U}(\text{C}_5\text{H}_4\text{R})_3(\text{pyz})]$ could not be detected, even after further addition of free pyrazine. The ^1H NMR spectra of **3** and **4** exhibit three signals, of relative intensities 54:12:12, corresponding to the six equivalent $\text{C}_5\text{H}_4\text{R}$ groups and a single resonance attributed to the four equivalent protons of the nitrogen ligand. These uranium complexes were stable in the toluene or pentane solutions from which they were isolated as black powders after evap-

oration. It is noteworthy that the complexes $[\{\text{U}(\text{C}_5\text{H}_4\text{R})_3\}_2(\mu\text{-pyz})]$ ($\text{R} = \text{H}$ or Me) were synthesized in a similar way from $[\text{U}(\text{C}_5\text{H}_4\text{R})_3(\text{THF})]$ and pyrazine and, in the absence of structural information, were considered as π -bridged dimers of U^{III} .^[5]

Black crystals of $[\{\text{U}(\text{C}_5\text{H}_4t\text{Bu})_3\}_2(\mu\text{-pyz})] \cdot 0.5\text{pyz}$ (**3**·0.5pyz) and $[\{\text{U}(\text{C}_5\text{H}_4\text{SiMe}_3)_3\}_2(\mu\text{-pyz})] \cdot 2\text{pyz}$ (**4**·2pyz) were obtained by cooling concentrated solutions of $[\text{U}(\text{C}_5\text{H}_4\text{R})_3]$ and excess pyrazine in pentane. The crystal structures of **3** and **4** are very similar; **3** is shown in Figure 1 with selected bond lengths and angles. The two $\text{U}(\text{C}_5\text{H}_4\text{R})_3$ fragments are bridged by a pyrazine ring, coordinated through its nitrogen atoms; the middle of the U–U' segment in **4** is an inversion centre. The pyrazine rings are planar within $\pm 0.019(6)$ and $\pm 0.001(3)$ Å in **3** and **4**, respectively. The U(1) and U(2) atoms in **3** are located out of the plane, on the same side, at a distance of 0.075(13) and 0.257(12) Å, respectively; because of the imposed symmetry, U and U' in **4** are on either side of the plane, at a distance of 0.071(9) Å. The U–N distances of 2.323(6) and 2.325(6) Å in **3**, and 2.318(4) Å in **4**, are much shorter than those measured in the series of trivalent $[\text{U}(\text{C}_5\text{H}_4\text{R})_3(\text{azine})]$ complexes, which vary from 2.646(4) Å in $[\text{U}(\text{C}_5\text{H}_4\text{SiMe}_3)_3(\text{lutidine})]$ to 2.688(7) Å in $[\text{U}(\text{C}_5\text{H}_4\text{SiMe}_3)_3(\text{pyrimidine})]$,^[4] they are also 0.34 Å shorter than the average U–N(pyrazine) distance in $[\text{UI}_3(\text{tpza})(\text{MeCN})]$ {tpza = tris[(2-pyrazinyl)methyl]amine}.^[3a] In fact, the U–N distances in **3** and **4** are in the range of U^{IV} –N bond lengths of terminally-coordinated amide groups^[6] and are, in particular, similar to that of 2.29(2) Å in $[\text{U}(\text{C}_5\text{H}_5)_3(\text{NPh}_2)]$.^[7] Concomitantly with the oxidation of the metal centre, the pyrazine ligand in **3** and **4** appears to be reduced to its dianionic form, since the average C–N and C–C distances of 1.405(5) and 1.340(5) Å are, respectively, longer and shorter than those in the free or coordinated neutral molecule, which are typically equal to 1.34 and 1.38 Å. These distances are equal to 1.33(2) and 1.37(2) Å in the Yb^{III} complex $[\{\text{Yb}(\text{C}_5\text{H}_5)_3\}_2(\mu\text{-pyz})]$,^[8] and to 1.339(1) and 1.378(6) Å in $[\text{Ce}(\text{C}_5\text{H}_4t\text{Bu})_3(\text{pyz})]$.^[4]

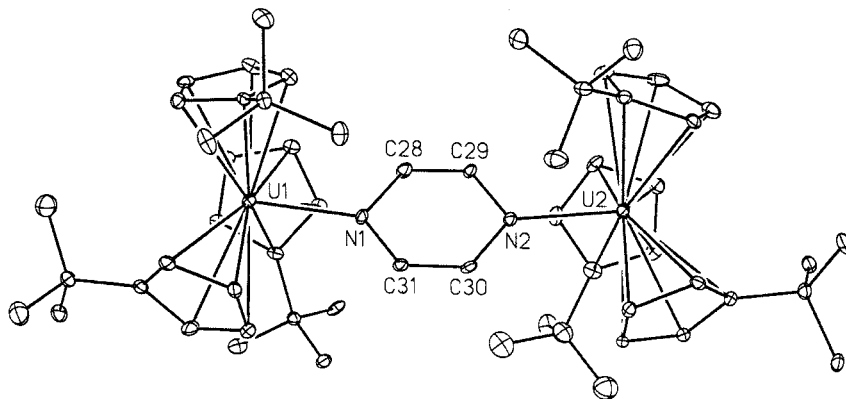


Figure 1. View of $[\{\text{U}(\text{C}_5\text{H}_4t\text{Bu})_3\}_2(\mu\text{-pyz})]$; hydrogen atoms are omitted for clarity; only one position of the disordered $\text{C}_5\text{H}_4t\text{Bu}$ group is represented; the displacement ellipsoids are drawn at the 10 % probability level; selected bond lengths (Å) and angles (°), the corresponding values for $[\{\text{U}(\text{C}_5\text{H}_4\text{SiMe}_3)_3\}_2(\mu\text{-pyz})]$ are given in brackets: U(1)–N(1) 2.323(6) [2.318(4)], U(2)–N(2) 2.325(6), N(1)–C(28) 1.406(11) [1.410(6)], N(1)–C(31) 1.399(9) [1.411(6)], N(2)–C(29) 1.399(10), N(2)–C(30) 1.404(10), C(28)–C(29) 1.335(12) [1.342(7)], C(30)–C(31) 1.344(11); Cp–U(1)–Cp 110.6–124.3 [114.9–118.0], Cp–U(2)–Cp 115.7–117.1, Cp–U(1)–N(1) 94.4–107.7 [98.6–102.3], Cp–U(2)–N(2) 99.2–103.8; Cp is the centroid of the $\text{C}_5\text{H}_4\text{R}$ rings

The crystal structures of **3** and **4** clearly revealed that the remarkable difference between the reactions of $[\text{U}(\text{C}_5\text{H}_4\text{R})_3]$ and $[\text{Ce}(\text{C}_5\text{H}_4\text{R})_3]$ with pyrazine is related to the actual $\text{U}^{\text{III}} \rightarrow \text{U}^{\text{IV}}$ oxidation; this process is clearly favoured by the electron richness of the trivalent metallocenes. Reduction of pyrazine with the divalent lanthanide compounds $[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)]^{[9]}$ and $[\text{Sm}\{\text{HB}(3,5\text{-Me}_2\text{-pyrazolyl})_3\}_2]^{[10]}$ has also been reported, but the products have not been identified. The distinct reactions of pyrazine and dimethylpyrazine with $[\text{U}(\text{C}_5\text{H}_4\text{R})_3]$ should be related to their reduction potentials $E_{1/2}$ which are equal to -2.17 and -2.28 V vs. Ag/AgCl , respectively.^[11] Thus, azine molecules with $E_{1/2}$ values higher than about -2.2 V vs. Ag/AgCl should be reduced by the trivalent metallocenes, while the less reducible ones should give the simple U^{III} Lewis base adducts.

Most notably, compounds **3** and **4** were found to undergo reversible reductive elimination of pyrazine in coordinating solvents, like THF and pyridine. The equilibrium between $[\text{U}(\text{C}_5\text{H}_4\text{R})_3(\text{THF})]$, free pyrazine and $[\{\text{U}(\text{C}_5\text{H}_4\text{R})_3\}_2(\mu\text{-pyz})]$ in THF (Scheme 1) was studied by ^1H NMR spectroscopy, and the formation constants $K_{\text{U}2\text{L}}$ of the dinuclear compounds were determined from Equation (2), where C_0 is the initial concentration of $[\text{U}(\text{C}_5\text{H}_4\text{R})_3(\text{THF})]$, n the number of molar equivalents of pyrazine and $x_{\text{U}2\text{L}}$ the molar fraction of **3** or **4**. This expression is simplified to Equation (3) for $n = 0.5$ (stoichiometric ratio).

$$K_{\text{U}2\text{L}} = [\{\text{U}(\text{C}_5\text{H}_4\text{R})_3\}_2(\mu\text{-pyz})]/[\text{U}(\text{C}_5\text{H}_4\text{R})_3(\text{THF})]^2[\text{pyz}] \quad (2)$$

$$K_{\text{U}2\text{L}} = x_{\text{U}2\text{L}}(1 + x_{\text{U}2\text{L}})^2/C_0^2(1 - x_{\text{U}2\text{L}})^2[n(1 + x_{\text{U}2\text{L}}) - x_{\text{U}2\text{L}}]$$

$$K_{\text{U}2\text{L}} = 2x_{\text{U}2\text{L}}(1 + x_{\text{U}2\text{L}})^2/C_0^2(1 - x_{\text{U}2\text{L}})^3 \quad (n = 0.5) \quad (3)$$

The values of $K_{\text{U}2\text{L}}$ at 23°C are $8(1) \times 10^3$ and $1.5(1) \times 10^2$ for **3** and **4**, respectively. The difference between these constants reflects the more important electron richness of the $[\text{U}(\text{C}_5\text{H}_4\text{tBu})_3]$ fragment, with respect to $[\text{U}(\text{C}_5\text{H}_4\text{SiMe}_3)_3]$,^[4] which has a double beneficial effect on the reaction: it impedes the competitive coordination of THF and favours the oxidation of the U^{III} centre. The $K_{\text{U}2\text{L}}/K_{\text{CeL}}$ ratios of 2.8×10^4 and 6.5×10^2 , for $\text{R} = \text{tBu}$ and SiMe_3 , respectively, are considerably higher than those found in the case of the complexation of $[\text{M}(\text{C}_5\text{H}_4\text{R})_3]$ ($\text{M} = \text{Ce}$ or U) with various azines in toluene, which do not exceed the value of nine for the reactions of $[\text{M}(\text{C}_5\text{H}_4\text{SiMe}_3)_3]$ with 3,5-dimethylpyrazine.^[4] The distinct nature of the reactions of $[\text{Ce}(\text{C}_5\text{H}_4\text{R})_3]$ and $[\text{U}(\text{C}_5\text{H}_4\text{R})_3]$ with pyrazine is also re-

flected in the thermodynamic parameters ΔH and ΔS corresponding to the formation of $[\text{Ce}(\text{C}_5\text{H}_4\text{R})_3(\text{pyz})]$ and $[\{\text{U}(\text{C}_5\text{H}_4\text{R})_3\}_2(\mu\text{-pyz})]$ in THF, which were determined from the van't Hoff diagrams (see Table 1). The difference between the enthalpies of formation of **1** and **3** is as high as $54 \text{ kJ}\cdot\text{mol}^{-1}$, whereas the corresponding $\Delta(\Delta H)$ values for the $[\text{M}(\text{C}_5\text{H}_4\text{R})_3(\text{azine})]$ adducts ($\text{M} = \text{Ce}, \text{U}$) range from 3 to $17 \text{ kJ}\cdot\text{mol}^{-1}$.^[4]

As expected from the thermodynamic parameters, the competition reactions of $[\text{Ce}(\text{C}_5\text{H}_4\text{R})_3]$ and $[\text{U}(\text{C}_5\text{H}_4\text{R})_3]$ with pyrazine in THF favoured the formation of the dinuclear uranium compounds **3** and **4**. Thus, the ^1H NMR spectrum of an equimolar mixture of the two trivalent metallocenes $[\text{M}(\text{C}_5\text{H}_4\text{tBu})_3]$ ($C_0 = 0.049 \text{ M}$) in the presence of 0.5 molar equivalent of pyrazine {which is identical to that of a 2:1 mixture of $[\text{Ce}(\text{C}_5\text{H}_4\text{tBu})_3]$ and **3**} showed that 45 % of the U^{III} complex was transformed into **3**, while the quantity of **1** was too small to be measured; the molar fraction of **1** should be less than 5×10^{-3} , from Equation (1). In the presence of 9 molar equivalents of pyrazine, 90 % of $[\text{U}(\text{C}_5\text{H}_4\text{tBu})_3]$ and 17 % of $[\text{Ce}(\text{C}_5\text{H}_4\text{tBu})_3]$ were converted into **3** and **1**, respectively. Similar experiments with $[\text{U}(\text{C}_5\text{H}_4\text{-SiMe}_3)_3]$ and $[\text{Ce}(\text{C}_5\text{H}_4\text{SiMe}_3)_3]$ showed that pyrazine is less efficient in the differentiation of these metallocenes, since 18 molar equivalents of the nitrogen ligand were necessary for a 45 % conversion of the U^{III} complex into **4**, and 12 % of **2** were also formed.

Conclusion

The reactions of $[\text{Ce}(\text{C}_5\text{H}_4\text{R})_3]$ and $[\text{U}(\text{C}_5\text{H}_4\text{R})_3]$ with pyrazine are very different because the former is a Lewis acid–Lewis base reaction whereas the latter is a redox reaction. These two reactions led to the equilibrium between $[\text{M}(\text{C}_5\text{H}_4\text{R})_3(\text{THF})]$ ($\text{M} = \text{Ce}$ and U), $[\text{Ce}(\text{C}_5\text{H}_4\text{R})_3(\text{pyz})]$ ($\text{R} = \text{tBu}$ **1**; $\text{R} = \text{SiMe}_3$ **2**) and $[\{\text{U}(\text{C}_5\text{H}_4\text{R})_3\}_2(\mu\text{-pyz})]$ ($\text{R} = \text{tBu}$ **3**; $\text{R} = \text{SiMe}_3$ **4**) in THF solution. The greater stability of the dinuclear U^{IV} compounds **3** and **4** with respect to the Ce^{III} complexes **1** and **2** permits a clear differentiation of the two metallocenes by means of the nitrogen ligand. As expected from an oxidation process, the selectivity in favour of uranium(III) is backed by an increased electron density on the metal centre. Oxidation of U^{III} can be seen as the ultimate result of extensive π back donation of the metal orbitals into the π^* orbitals of the aromatic ring, which is thought to play a major role in the selective complexation of An^{III} over Ln^{III} ions by nitrogen ligands. It is, however, important to note that Am^{III} and Cm^{III} are less easily oxidized than U^{III} ; their extraction based on a redox process would be rendered possible if their oxidation potentials were lowered by using anionic and/or neutral donor ligands, or by operating in specific media, like ionic liquids.

Experimental Section

General: All reactions were carried out under argon (< 5 ppm oxygen or water) using standard Schlenk-vessel and vacuum line tech-

Table 1. Values of K , $-\Delta H$ ($\text{kJ}\cdot\text{mol}^{-1}$) and $-\Delta S$ ($\text{J}\cdot\text{mol}^{-1} \text{ K}^{-1}$) for the formation of the complexes in THF

Compound	K	$-\Delta H$	$-\Delta S$
$[\text{Ce}(\text{C}_5\text{H}_4\text{tBu})_3(\text{pyz})]$ (1)	0.28(6)	0(3)	12(7)
$[\text{Ce}(\text{C}_5\text{H}_4\text{SiMe}_3)_3(\text{pyz})]$ (2)	0.23(2)	19(2)	79(5)
$[\{\text{U}(\text{C}_5\text{H}_4\text{tBu})_3\}_2(\mu\text{-pyz})]$ (3)	$8(1) \times 10^3$	54(5)	109(20)
$[\{\text{U}(\text{C}_5\text{H}_4\text{SiMe}_3)_3\}_2(\mu\text{-pyz})]$ (4)	$1.5(1) \times 10^2$	35(3)	76(15)

niques or in a glove box. Solvents were dried by standard methods and distilled immediately before use; deuterated toluene and THF (Eurisotop) were distilled from over Na/K alloy and stored over 3 Å molecular sieves. Pyrazine (Aldrich) was used as received; the metallocenes $[M(C_5H_4tBu)_3]$ ($M = Ce^{[12]}$, $U^{[13]}$) and $[M(C_5H_4SiMe_3)_3]$ ($M = Ce^{[12]}$, $U^{[14]}$) and the pyrazine adducts **1** and **2**^[4] were prepared by published methods. The 1H NMR spectra were recorded on a Bruker DPX 200 instrument and referenced internally using the residual protio-solvent resonances relative to tetramethylsilane ($\delta = 0$ ppm). Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany).

Synthesis of 3 and 4: A flask was charged with $[U(C_5H_4tBu)_3]$ (200 mg, 0.33 mmol) and pyrazine (26.6 mg, 0.33 mmol) in pentane (15 mL). After 3 h at 20 °C, the dark blue solution deposited a black powder of **3**; a greater quantity of precipitate was obtained after cooling at -78 °C for 3 h. The product was then filtered off and dried under vacuum. Yield: 134 mg (63 %). 1H NMR (200 MHz, $[D_8]$ toluene): $\delta = -70.26$ (4 H, pyz), -13.67 (12 H, C_5H_4R), -12.91 (12 H, C_5H_4R), 0.85 (54 H, C_5H_4R) ppm. $C_{58}H_{82}N_2U_2$ (1283): calcd. C 54.29, H 6.40, N 2.18; found C 54.44, H 6.25, N 2.31. The same reaction with $[U(C_5H_4SiMe_3)_3]$ gave **4** in 65 % yield. 1H NMR (200 MHz, $[D_8]$ toluene): $\delta = -69.79$ (4 H, pyz), -15.24 (12 H, C_5H_4R), -10.68 (12 H, C_5H_4R), 0.24 (54 H, C_5H_4R).

Determination of the Formation Constants K_{CeL} : An NMR tube was charged with a 0.1 M solution of $[Ce(C_5H_4R)_3]$ in $[D_8]THF$. Under fast exchange conditions, successive addition of pyrazine lead to the displacement of the three resonances of the metallocene towards the limit positions corresponding to the complete formation of $[Ce(C_5H_4R)_3(pyz)]$. The observed chemical shifts for the C_5H_4R ligands, δ_{obs} , are a weighted average of the chemical shifts of these cyclopentadienyl groups in $[Ce(C_5H_4R)_3(THF)]$ and $[Ce(C_5H_4R)_3(pyz)]$, δ_{Ce} and δ_{CeL} , proportional to their relative concentrations, according to $\delta_{obs} = (1 - x_{CeL})\delta_{Ce} + x_{CeL}\delta_{CeL}$, in which x_{CeL} is the molar fraction of $[Ce(C_5H_4R)_3(pyz)]$; the values of x_{CeL} were thus obtained by $x_{CeL} = (\delta_{obs} - \delta_{Ce})/(\delta_{CeL} - \delta_{Ce})$.^[4] After each addition of pyrazine, the complexation reactions were monitored by recording the 1H NMR spectra from $+23$ to -30 °C with intervals of 5 °C. For a 0.146 M solution of $[Ce(C_5H_4tBu)_3(THF)]$ at 23 °C, 1H NMR (200 MHz, $[D_8]THF$): $\delta_{Ce} = -3.29$ (27 H), 11.22 (6 H), 11.72 (6 H) ppm; $\delta_{CeL} = -3.17$ (27 H), 10.17 (6 H), 12.39 (6 H) ppm; δ_{obs} ($n = 11.5$) = -3.23 (27 H), 10.83 (6 H), 11.91 (6 H) ppm. For a 0.100 M solution of $[Ce(C_5H_4SiMe_3)_3(THF)]$ at 23 °C, 1H NMR (200 MHz, $[D_8]THF$): $\delta_{Ce} = -0.97$ (27 H), 6.75 (6 H), 10.03 (6 H) ppm; $\delta_{CeL} = -1.52$ (27 H), 6.88 (6 H), 10.95 (6 H) ppm; δ_{obs} ($n = 14.5$) = -1.10 (27 H), 6.76 (6 H), 10.25 (6 H) ppm. The K_{CeL} constants and the corresponding ΔH and ΔS values are given in Table 1.

Determination of the Formation Constants K_{U2L} : In a typical experiment, an NMR tube was charged with a 0.037 M solution of $[U(C_5H_4tBu)_3]$ in $[D_8]THF$. 1H NMR (200 MHz, $[D_8]THF$): $\delta = -23.16$ (6 H), -7.76 (27 H), -2.85 (6 H) ppm. After addition of pyrazine, new signals corresponding to **3** appeared. 1H NMR (200 MHz, $[D_8]THF$): $\delta = -72.95$ (4 H, pyz), -14.93 (12 H, C_5H_4R), -12.97 (12 H, C_5H_4R), 0.76 (54 H, C_5H_4R) ppm. In the presence of 0.5 molar equivalent of pyrazine, the spectrum was identical to that obtained by dissolving **3** in $[D_8]THF$, showing the presence of $[U(C_5H_4tBu)_3(THF)]$ and **3** in relative proportions of 55:45. Similarly, an NMR tube was charged with a 0.025 M solution of $[U(C_5H_4SiMe_3)_3]$ in $[D_8]THF$. 1H NMR (200 MHz, $[D_8]THF$): $\delta = -17.61$ (6 H), -5.97 (6 H), -4.03 (27 H) ppm. Addition of 0.5 molar equivalent of pyrazine had practically no influence on

these signals, in agreement with the fact that **4** is almost totally dissociated into $[U(C_5H_4SiMe_3)_3(THF)]$ and pyrazine in THF. After addition of 8.8 molar equivalents of pyrazine, new signals corresponding to **4** appeared. 1H NMR (200 MHz, $[D_8]THF$): $\delta = -73.73$ (4 H, pyz), -16.25 (12 H, C_5H_4R), -10.84 (12 H, C_5H_4R), -0.16 (54 H, C_5H_4R) ppm. The two complexes $[U(C_5H_4SiMe_3)_3(THF)]$ and **4** were in relative proportions of 70:30. The K_{U2L} constants and the corresponding ΔH and ΔS values are given in Table 1.

X-ray Crystallography: The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer^[15] using graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073$ Å). The crystals were introduced in glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from ten frames, then refined on all data. A 180° ϕ -range was scanned with 2° steps during data collection, with a crystal-to-detector distance fixed to 28 mm. The data were processed with DENZO-SMN.^[16] The structures were solved by direct methods (**3**) or Patterson map interpretation (**4**) with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.^[17] Absorption effects were corrected empirically with the program DELABS from PLATON.^[18] One C_5H_4tBu group in compound **3** was found to be disordered over two positions sharing two aromatic and one terminal methyl carbon atom, which were refined with occupancy parameters constrained to sum to unity and with some restraints on bond lengths and displacement parameters. Some short intramolecular C...C contacts result from the imperfect location of the disordered parts. The solvent pyrazine molecule in **3** is disordered around a symmetry centre and the position of the nitrogen atom was not determined. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced at calculated positions (except in the disordered parts when present) and were treated as riding atoms with a displacement parameter equal to 1.2 (CH) or 1.5 (CH₃) times that of the parent atom. The molecular plot was drawn with SHELXTL.^[19] CCDC-231705 (**3**·0.5pyz) and -231706 (**4**·2pyz) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Crystal Data for 3·0.5pyz: $C_{60}H_{84}N_3U_2$, $M = 1323.36$ g mol⁻¹, monoclinic, $P2_1/c$, $a = 15.9661(6)$, $b = 10.6364(4)$, $c = 31.6769(11)$ Å, $\beta = 94.115(2)^\circ$, $U = 5365.6(3)$ Å³, $Z = 4$, $\mu(Mo-K_\alpha) = 6.068$ mm⁻¹, 35622 reflections measured, 10137 unique ($R_{int} = 0.086$) which were used in all calculations. Final R values: $R_1 = 0.047$, $wR_2 = 0.105$ (all data).

Crystal Data for 4·2pyz: $C_{60}H_{90}N_6Si_6U_2$, $M = 1539.98$ g mol⁻¹, triclinic, $P\bar{1}$, $a = 11.0619(7)$, $b = 11.1804(6)$, $c = 15.1358(10)$ Å, $\alpha = 105.831(3)$, $\beta = 105.869(3)$, $\gamma = 103.017(4)^\circ$, $U = 1638.86(19)$ Å³, $Z = 1$, $\mu(Mo-K_\alpha) = 5.084$ mm⁻¹, 11306 reflections measured, 5732 unique ($R_{int} = 0.038$) which were used in all calculations. Final R values: $R_1 = 0.030$, $wR_2 = 0.073$ (all data).

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Received February 18, 2004