A Comparison of Analogous 4f- and 5f-Element Compounds: Syntheses, X-ray Crystal Structures and Catalytic Activity of the Homoleptic Amidinate Complexes [M{MeC(NCy)$_2$}$_3$] (M = La, Nd or U)

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Reaction of UCl$_4$ with [Li{RC(NCy)$_2$}(THF)]$_2$ (R = Me, **1a**; R = *n*Bu, **1b**) in THF gave the tris(amidinate) compounds [U{RC(NCy)$_2$}$_3$Cl] (R = Me, **2a**; R = *n*Bu, **2b**) which were reduced with lithium powder in THF to the homoleptic complexes [U{RC(NCy)$_2$}$_3$] (R = Me, **3a**; R = *n*Bu, **3b**). Complexes **1a**, **1b**, **2a** and **3a** have been crystallographically characterized. Comparison of the crystal structure of **3a** with those of the lanthanide analogues [Ln{MeC(NCy)$_2$}$_3$] (Ln = La, **4**; Ln = Nd, **5**; Ln = Yb, **6**) shows that the average U–N distance is shorter than expected from a purely ionic bonding model. The uranium complex **3a** is much less efficient than its lanthanide counterparts in the catalytic polymerization of ε-caprolactone because of its rapid oxidation into U^{IV} species.

Introduction

Amidinate complexes of main group and d-block transition metals are currently receiving a great deal of interest, especially for use in the catalytic polymerization of alkenes and lactides.[1] Homoleptic metal amidinates were also recently found to be useful precursors for atomic layer deposition of thin films.[2] A major advantage of the bidentate [RC{NR′}$_2$]$^-$ anions, which are considered as alternatives to the ubiquitous cyclopentadienyl-based ligands, is the easy modification of both their steric bulk and electronic properties through changes to the R and R′ substituents. In this context, special attention has been paid during the last decade to the bis(benzamidinate) complexes of group 3 metals and lanthanides as they exhibit catalytic activities similar to those of the corresponding metallocenes.[3] More recently, homoleptic tris(amidinate) lanthanide complexes have proved to be efficient catalysts for the ring-opening polymerization of ε-caprolactone.[4]

The amidinate ligand was introduced into 5f-element chemistry by Edelmann et al. who synthesized a series of bis- and tris(benzamidinate) compounds of thorium(IV) and uranium(IV), [M{ArC(NSiMe$_3$)$_2$}$_3$Cl] and [M{ArC(NSiMe$_3$)$_2$}$_2$Cl$_2$] (M = Th, U) and their derivatives,[5] the uranium(V) complex [U{(C$_6$H$_4$Me)C(NSiMe$_3$)$_2$}$_2$Cl$_3$][6] and the uranyl compound [UO$_2${PhC(NSiMe$_3$)$_2$}$_2$].[7] Another complex, [{UCl(μ-Cl)(L)(NSiMe$_3$)}$_2$][UCl$_2$(L)(L′)]$_2$, in which L is a β-diketiminate and L′ a benzamidinate ligand, can be considered either as a [{U^{VI}}$_2$][U^{III}]$_2$ or a [{U^{IV}}$_2$][U^{V}]$_2$ mixed-valence salt.[8] Here we report on the first well-characterized uranium(III) amidinate complexes, [U{RC(NCy)$_2$}$_3$] (R = Me, *n*Bu), which were prepared by reduction of the chloride precursors [U{RC(NCy)$_2$}$_3$Cl]. We describe the crystal structures of these U^{III} and U^{IV} compounds, as well as those of the lithium amidinates [Li{RC(NCy)$_2$}(THF)]$_2$, and finally we present the activity of the homoleptic complexes in ε-caprolactone polymerization, and we compare the structural features and catalytic properties of [U{MeC(NCy)$_2$}$_3$] with those of the lanthanide analogues.

Results and Discussion

The Lithium Amidinate Complexes [Li{RC(NCy)$_2$}(THF)]$_2$ (R = Me, *n*Bu)

Addition of MeLi or *n*BuLi to *N*,*N*′-dicyclohexylcarbodiimide in THF, according to Equation (1), led to the formation of the lithium amidinates [Li{RC(NCy)$_2$}(THF)]$_2$ (R = Me, **1a**; R = *n*Bu, **1b**) which were isolated as colorless crystals in almost quantitative yield.

$$\text{Cy–N=C=N–Cy} + \text{RLi} \xrightarrow{\text{THF}} 0.5\,[\text{Li}\{\text{RC(NCy)}_2\}(\text{THF})]_2 \qquad (1)$$

R = Me, **1a**; R = *n*Bu, **1b**

The two compounds were characterized by ^{1}H NMR spectroscopy (Table 1) and an X-ray crystal structure. A

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Table 1. ^{1}H NMR spectra of the amidinate complexes[a]

Compound	R group (Me or *n*Bu)	Cyclohexyl group
[Li{MeC(NCy)$_2$}(THF)]$_2$ (**1a**)	2.89 (s, 3 H)	1.47−1.07 (m, 22 H)
[Li{*n*BuC(NCy)$_2$}(THF)]$_2$ (**1b**)	2.91, 2.15 and 1.47 (m, 3 × 2 H), 0.82 (t, 3 H)	1.56−1.08 (m, 22 H)
[U{MeC(NCy)$_2$}$_3$Cl] (**2a**)	3.32 (3 H)	1.47−1.07 (m, 16 H), −0.51 (m, 2 H), −2.6 (br., $w_{1/2}$ = 250 Hz, 4 H)
[U{*n*BuC(NCy)$_2$}$_3$Cl] (**2b**)	5.69, 4.19 and 2.72 (m, 3 × 2 H), 1.70 (t, 3 H)	1.50−1.00 (m, 16 H), −0.50 (m, 2 H), −2.0 (br., $w_{1/2}$ = 300 Hz, 4 H)
[U{MeC(NCy)$_2$}$_3$] (**3a**)	11.79 (3 H)	25.10 (2 H), −0.82 (6 H), −1.29 (4 H), −2.22 (4 H), −3.61 (2 H), −11.20 (4 H)
[U{*n*BuC(NCy)$_2$}$_3$] (**3b**)	14.82, 8.00 and 4.90 (m, 3 × 2 H), 2.98 (t, 3 H)	27.48 (2 H), 0.80 (6 H), 0.90 (4 H), −1.17 (4 H), −4.50 (2 H), −12.50 (4 H)
[La{MeC(NCy)$_2$}$_3$] (**4**)	3.22 (3 H)	2.12−1.24 (m, 22 H)
[Nd{MeC(NCy)$_2$}$_3$] (**5**)	12.64 (3 H)	20.25 (2 H), 0.31 (6 H), −0.38 (4 H), −1.26 (4 H), −3.22 (2 H), −10.93 (4 H)

[a] At 23 °C in [D$_8$]THF; when not specified, the signals are singlets with a half-height width between 10 and 50 Hz.

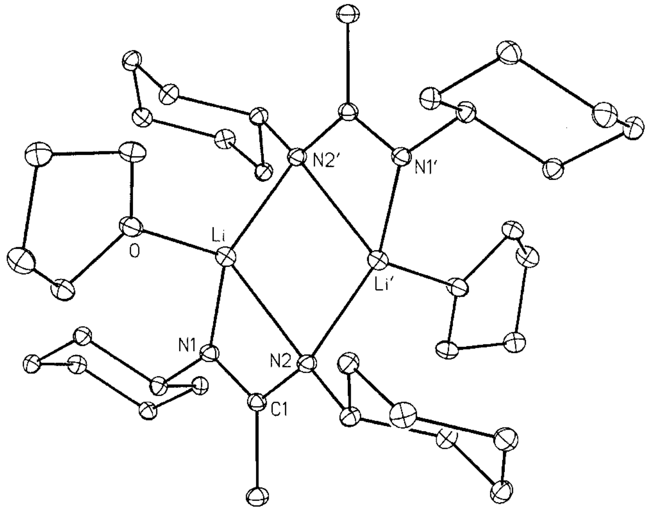


Figure 1. View of the complex [Li{MeC(NCy)$_2$}(THF)]$_2$ (**1a**) with displacement ellipsoids drawn at the 20% probability level; hydrogen atoms have been omitted for clarity; primed atoms are related to the unprimed ones by the symmetry centre

Table 2. Selected distances [Å] and angles [°] in the lithium amidinate complexes

	[Li{MeC(NCy)$_2$}(THF)]$_2$ (**1a**)	[Li{*n*BuC(NCy)$_2$}(THF)]$_2$ (**1b**)[a]
Li−N(1)	2.008(3)	1.987(6); 1.992(8)
Li−N(2)	2.143(3)	2.251(6); 2.201(9)
Li−N(2′)	2.066(3)	2.093(6); 2.085(8)
Li−O	1.936(3)	1.947(6); 1.950(9)
Li···C(1)	2.417(3)	2.459(6); 2.423(8)
N(1)−Li−N(2)	66.14(10)	64.59(19); 65.0(3)
N(2)−Li−N(2′)	110.01(14)	112.1(3); 112.7(4)
Li−N(2)−Li′	69.99(14)	67.9(3); 67.3(4)
N(1)−C(1)	1.322(2)	1.328(4); 1.316(5)
N(2)−C(1)	1.347(2)	1.350(4); 1.344(4)
<N−C(1)>	1.335(18)	1.335(15)
N(1)−C(1)−N(2)	116.35(14)	116.4(3); 116.4(3)

[a] Individual values are given for the two independent complex molecules, mean values include both of them. Primed atoms are related to the unprimed ones by the symmetry centre.

view of **1a** is shown in Figure 1; selected bond lengths and angles are listed in Table 2. Both **1a** and **1b** are centrosymmetric dimers which adopt a ladder-type structure similar to that determined for several lithium amidinate complexes.[9] The lithium atoms are bound to the two nitrogen atoms of one amidinate ligand, one nitrogen atom of the other ligand and the oxygen atom of a THF molecule. The two nearly planar four-membered Li−N(1)−C(1)−N(2) rings [maximum deviations: 0.102(1) Å in **1a** and 0.121(2) and 0.135(3) Å in **1b**] are connected on either side of the planar central Li$_2$N$_2$ ring. These central and side planes form dihedral angles of 59.99(17)° and 56.3(4)° in **1a** and **1b**, respectively, with the usual *transoid* arrangement. The Li−N bond lengths, which range from 1.987(6) to 2.251(6) Å, indicate some asymmetry in the bonding of the bidentate ligand, with Li−N(1) shorter than Li−N(2) by 0.135 Å in **1a** and 0.209−0.264 Å in **1b**; the third bond length, Li−N(2′), is intermediate but closer to the former. The N(1)−C(1) and N(2)−C(1) bond lengths in both compounds are similar, with mean values of 1.322(6) and 1.347(3) Å, indicating uniform π delocalisation throughout the amidine moiety. The environment of the lithium atom is tetrahedral, but strongly distorted owing to the small bite angle of the bidentate amidinate. The Li···C(1) contacts, with a mean value of 2.43(2) Å, are larger than the usual values in such compounds, which are in the range 2.30−2.42 Å.[9b] The Li−O(THF) bond lengths are in perfect agreement with the mean value of 1.94(6) Å from the Cambridge Structural Database.[10]

The Uranium(IV) Amidinate Complexes [U{RC(NCy)$_2$}$_3$Cl] (R = Me, *n*Bu)

Treatment of UCl$_4$ with **1a** in THF gave the tris(amidinato)uranium chloride [U{MeC(NCy)$_2$}$_3$Cl] (**2a**), according to Equation (2); extraction in toluene and crystallization from this solvent afforded pale-green crystals of **2a** in 85% yield. A similar reaction with **1b** led to the quantitative formation of **2b** (NMR-tube experiment). The ^{1}H NMR signals corresponding to the R and Cy substituents of the amidinate ligands are visible at lower and higher field, respectively (Table 1), as previously observed for the resonances of the R and R′ groups in the series of $[U\{RC(NR')_2\}_3Cl]$ complexes (R = C_6H_4X with X = H, Me, OMe, CF_3; R′ = $SiMe_3$).[5b]

$$UCl_4 + 1.5\,[Li\{RC(NCy)_2\}(THF)]_2 \xrightarrow{THF} [U\{RC(NCy)_2\}_3Cl] + 3\,LiCl \quad (2)$$

1

R = Me, **2a**; R = *n*Bu, **2b**

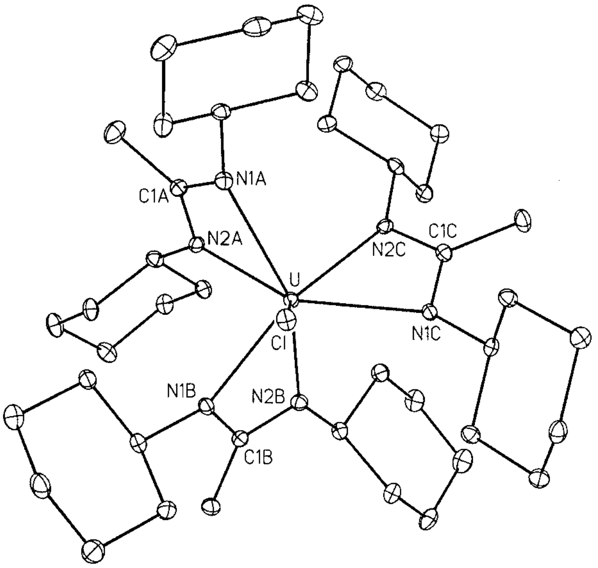


Figure 2. View of the complex $[U\{MeC(NCy)_2\}_3Cl]$ (**2a**) with displacement ellipsoids drawn at the 20% probability level; hydrogen atoms have been omitted for clarity

The molecular structure of **2a**, represented in Figure 2, is devoid of any imposed crystallographic symmetry, but possesses a pseudo C_3 axis defined by the U and Cl atoms; the three amidinate ligands are arranged in a propeller shape around this axis (the position of some cyclohexyl rings does not match this pseudo-trigonal symmetry). The structure of **2a** resembles that of the two tris(benzamidinate) compounds $[U\{ArC(NSiMe_3)_2\}_3Cl]$ (Ar = Ph, $C_6H_4CF_3$) which have been crystallographically characterized.[5b] The mean U−N bond length [2.43(4) Å] matches that in the above-mentioned complexes [2.44(5) Å], and for each of the three ligands (denoted A, B and C), the U−N(1) distance is shorter than the U−N(2) distance by 0.032−0.097 Å (Table 3). The atoms N(1A), N(1B) and N(1C), which are on the side of the complex on which the chlorine atom is located, are farther apart from each other than N(2A), N(2B) and N(2C); the steric strain between the cyclohexyl rings bound to the latter may explain the larger U−N(2) bond lengths. The three four-membered U−N(1)−C(1)−N(2) rings are planar, with a maximum deviation of 0.07 Å, the carbon atom always being the more displaced one. The mean U···C(1) distance [2.870(10) Å] is somewhat larger than its counterpart in the tris(benzamidinate) derivatives [2.84(2) Å], which is in agreement with smaller N(1)−C(1)−N(2) angles [mean value 114.3(8)° compared with 117(1)° in the latter]. Electronic delocalisation throughout the amidinate ligands is reflected by the identical N−C(1) bond lengths in the range 1.330(5)−1.337(5) Å. The uranium atom is displaced by 0.707(2) Å from the plane defined by the three atoms C(1A), C(1B) and C(1C) (on the same side as the chlorine atom), and the C(1A)···U···C(1B), C(1A)···U···C(1C) and C(1B)···U···C(1C) angles are 107.29(11)°, 114.50(12)° and 120.46(11)°, respectively; the C(1)···U−Cl angles vary from 102.14(8)° to 106.18(8)°. These values are similar to those of the ring centroid−U−ring centroid and ring centroid−U−Cl angles in the series of tris(cyclopentadienyl)[11] and tris(indenyl)uranium(IV)[12] complexes, which adopt a pseudo-tetrahedral configuration.

Interestingly, complex **2a** has the second longest U−Cl bond [2.6783(10) Å] in the series of 13 uranium(IV) complexes $[UL_3Cl]$ which have been crystallographically characterized and which include five cyclopentadienyl,[11a−11d,13] three indenyl,[12] three amidinate,[5b] including **2a**, one phospholyl,[14] and one imidophosphinate[15] derivatives (Table 4). The U−Cl bond lengths in this series lie in the range 2.559−2.90 Å. The shortest bond belongs to the first known organometallic uranium compound $[U(C_5H_5)_3Cl]$[11a] while the longest one, 2.90 Å, appears as a peculiar case since it corresponds to a chlorine atom disordered over two positions in $[U(C_5Me_5)_3Cl]$;[13] apart from this case, the twelve other U−Cl bond lengths define a relatively narrow range (0.12 Å). The lengthening of the U−Cl bond in each of the cyclopentadienyl, indenyl and amidinate families can be related to the increasing steric bulk and electron-donating capacity of the substituted ligands. Substitution of the cyclopentadienyl ring by methyl groups gives rise to an amazing gap in the variation of the U−Cl bond lengths, with a major influence of the fifth methyl group on the lengthening of the bond. In reference to $[U(C_5H_5)_3Cl]$,[11a] the complexes $[U(C_5Me_4H)_3Cl]$[11d] and $[U(C_5Me_5)_3Cl]$[13] exhibit variations in their U−Cl bond lengths of 0.08 Å and 0.26 Å, respectively, and, in contrast to the other tris(cyclopentadienyl)uranium chlorides, $[U(C_5Me_5)_3Cl]$ does not adopt a pseudo-tetrahedral structure; the ring centroid−U−ring centroid angles are equal to 120°. The long U−Cl bond in **2a** is in agreement with the electron richness of the $[U\{RC(NCy)_2\}_3]$ moiety, which is manifest in its redox reactions (vide infra).

The Uranium(III) and Lanthanide(III) Amidinate Complexes $[U\{RC(NCy)_2\}_3]$ (R = Me, nBu) and $[Ln\{MeC(NCy)_2\}_3]$ (Ln = La, Nd)

In contrast to $[U(C_5H_5)_3Cl]$, which is reduced with Na/Hg in THF to give $[U(C_5H_5)_3(THF)]$,[16] complexes **2** do not react with sodium amalgam. The synthesis of the uranium(III) amidinate $[U\{MeC(NCy)_2\}_3]$ (**3a**) therefore required a stronger reducing agent. Treatment of **2a** with lithium powder in THF cleanly afforded **3a** which, after extraction

Table 3. Selected distances [Å] and angles [°] in the uranium, lanthanum and neodymium amidinate complexes

	[U$\{MeC(NCy)_2\}_3$Cl] **(2a)**	[U$\{MeC(NCy)_2\}_3$] **(3a)**	[La$\{MeC(NCy)_2\}_3$] **(4)**	[Nd$\{MeC(NCy)_2\}_3$] **(5)**[a]
M−N(1A)	2.388(3)	2.493(4)	2.531(6)	2.459(3); 2.464(2)
M−N(2A)	2.485(3)	2.501(4)	2.521(6)	2.471(2); 2.471(3)
M−N(1B)	2.380(3)	2.487(4)	2.538(6)	2.458(3); 2.480(3)
M−N(2B)	2.436(3)	2.497(4)	2.545(6)	2.473(3); 2.454(2)
M−N(1C)	2.418(3)	2.481(4)	2.512(6)	2.468(3); 2.455(3)
M−N(2C)	2.450(3)	2.477(4)	2.521(6)	2.445(3); 2.469(3)
<M−N>	2.43(4)	2.489(9)	2.528(12)	2.464(10)
M−Cl	2.6783(10)			
M···C(1A)	2.881(4)	2.939(5)	2.979(7)	2.899(3); 2.908(3)
M···C(1B)	2.865(4)	2.942(5)	2.971(8)	2.900(3); 2.907(3)
M···C(1C)	2.863(4)	2.940(5)	2.989(7)	2.897(3); 2.904(3)
<M···C(1)>	2.870(10)	2.9403(15)	2.980(9)	2.903(5)
N(1A)−M−N(2A)	54.70(11)	53.85(14)	53.2(2)	54.59(8); 54.45(9)
N(1B)−M−N(2B)	55.12(11)	53.23(14)	53.0(2)	54.56(9); 54.44(9)
N(1C)−M−N(2C)	55.08(10)	53.99(14)	53.3(2)	54.61(9); 54.53(9)
<N(1)−M−N(2)>	55.0(2)	53.7(4)	53.1(2)	54.5(7)
<N−C(1)>	1.333(3)	1.335(11)	1.341(16)	1.335(4)
<N(1)−C(1)−N(2)>	114.3(8)	114.8(8)	115.1(17)	115.4(2)

[a] Individual values are given for the two independent complex molecules, mean values include both of them; the second values correspond to amidinate groups D, E and F in place of A, B and C, respectively.

with pentane and crystallization from this solvent, was isolated as dark-green crystals in 80% yield [Equation (3)]. Similarly, **2b** was quantitatively transformed into **3b** (NMR-tube experiment). The paramagnetic ^{1}H NMR resonances corresponding to the cyclohexyl substituents of **3** are more shifted than those of **2**, with one signal at high field and the others at low field (Table 1).

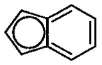
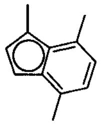
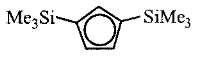
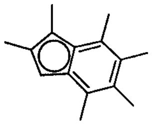
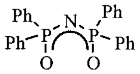
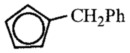
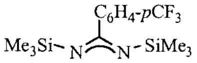
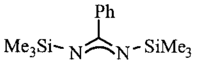
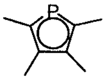
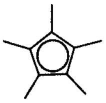
$$\underset{\textbf{2}}{[U\{RC(NCy)_2\}_3Cl]} + Li \xrightarrow{THF} \underset{R = Me,\ \textbf{3a};\ R = n\text{Bu},\ \textbf{3b}}{[U\{RC(NCy)_2\}_3] + LiCl} \qquad (3)$$

Monitoring of the **2** → **3** transformation by NMR spectroscopy showed that the signals of the two complexes were distinct and not shifted during the reduction process, indicating the absence of electron-transfer or ligand-exchange reactions similar to those occurring during the reduction of [U$(C_5H_5)_3$Cl], where the intermediate formation of the bridged species $[\{U(C_5H_5)_3\}_2(\mu\text{-}Cl)]^{n-}$ (n = 0 or 1) was observed.[16] These results, with the more difficult reduction of **2**, can be explained by the greater electron density on the metal atom.

In order to compare their crystal structures and reactions with those of **3a**, the lanthanum and neodymium analogues [Ln$\{MeC(NCy)_2\}_3$] [Ln = La (**4**) or Nd (**5**)] were prepared by treatment of LaI_3 or $NdCl_3$ with **1a** in THF; colorless (**4**) or pale blue-purple (**5**) crystals were obtained from a pentane solution. Contrary to previous reports[4] the ^{1}H NMR spectrum of **5** is well resolved; it is similar to that of **3a** (Table 1). The crystal structure of the ytterbium counterpart [Yb$\{MeC(NCy)_2\}_3$] (**6**) has been reported previously.[4]

Complexes **3a**, **4** and **6** are isomorphous. The crystal structure of **3a** is shown in Figure 3; selected bond lengths and angles are listed in Table 3. The complex possesses a pseudo-trigonal symmetry axis, with the three ligands in a propeller-like arrangement. As usual with six-coordinate compounds with three identical small-bite bidentate ligands, the environment of the central metal atom is intermediate between octahedral and trigonal prismatic.[17] The uranium atom is located at 1.013(3) and 0.979(2) Å from the planes defined by N(1A), N(1B), N(1C) and N(2A), N(2B), N(2C), respectively, which form a dihedral angle of 0.77(15)°. In contrast with what has been observed in **2a**, these two sets of nitrogen atoms are not located differently with respect to the metal atom and, as a consequence, the U−N distances span a relatively narrow range [2.477(4)−2.501(4) Å]. The average U−N distance of 2.489(9) Å is larger than that in **2a** by about 0.06 Å, in fair agreement with a difference of about 0.075 Å in ionic radii between seven-coordinate U^{IV} and six-coordinate U^{III};[18] this distance is longer than that of 2.320(4) Å in the homoleptic tris(amide) uranium(III) compound [U$(N\{SiMe_3\}_2)_3$].[19] The three U−N(1)−C(1)−N(2) rings in **3a** define mean planes with a maximum deviation of 0.020(3) Å at most, the carbon atom being the farthest from the plane. The U···C(1) distances, with a mean value of 2.9403(15) Å, follow the same trend as the U−N bond lengths when passing from U^{IV} to U^{III}, since the N(1)−C(1)−N(2) angle remains approximately constant. The N−C(1) bond lengths span the range 1.317(7)−1.348(7) Å, wider than in **2a** and equivalent to that in the lithium complexes, the mean value being constant in all cases. The metal atom is displaced by 0.030(3) Å from the mean plane defined by atoms C(1A), C(1B) and C(1C) and the three angles C(1A)···U···C(1B), C(1A)···U···C(1C) and C(1B)···U···C(1C) are 123.25(14)°, 117.75(14)° and 118.96(14)°, respectively, with a sum equal

Table 4. Variation of the U−Cl bond length among the [UL_3Cl] complexes

Ligand L		U–Cl [Å]	Ref.
Cyclopentadienyl		2.559(16)	[11a]
Indenyl		2.593(3)	[12a]
1,4,7-Trimethylindenyl		2.601(3)	[12b]
1,3-Bis(trimethylsilyl)cyclopentadienyl		2.614(2)	[11b]
1,2,4,5,6,7-Hexamethylindenyl		2.621(1)	[12c]
Tetraphenylimidophosphinato		2.624(3)	[15]
Benzylcyclopentadienyl		2.627(2)	[11c]
N,*N'*-Bis(trimethysilyl)-4-trifluoromethylbenzamidinato		2.634(2)	[5b]
Tetramethycyclopentadienyl		2.637	[11d]
N,*N'*-Bis(trimethysilyl)benzamidinato		2.660(9)	[5b]
Tetramethylphospholyl		2.67(1)	[14]
N,*N'*-Bis(cyclohexyl)methylamidinato		2.6783(10)	this work
Pentamethylcyclopentadienyl		2.90(1)	[13]

to 359.96°. The geometry around the metal atom can thus be described as trigonal-planar if each bidentate amidinate ligand is considered to occupy a single coordination site. This arrangement is reminiscent of that adopted by the three cyclopentadienyl ligands in sterically encumbered trivalent metallocenes such as [$U(C_5H_5SiMe_3)_3$],[20] [$U(C_5Me_5H)_3$][21] and [$U(C_5Me_5)_3$],[22] and reinforces the analogy which has been established between the amidinate and cyclopentadienyl ligands.

Complexes **3a**, **4**, **5** and **6** are isostructural but not isomorphous since the neodymium derivative **5** crystallizes in a different system and space group, with two independent molecules in the asymmetric unit (corresponding to ligands A, B, C and D, E, F; Figure 4). The Nd−N bond lengths are in the range 2.445(3)−2.480(3) Å, with a mean value of 2.464(10) Å, which is identical to that found in the homoleptic guanidinate compounds [$Nd\{i\mathrm{Pr}_2NC(NR)_2\}_3$] (R = Cy or *i*Pr),[23a] and is slightly shorter than that of 2.49(3) Å determined in the other neodymium amidinates.[23b,23c] The Nd−N(1)−C(1)−N(2) four-membered rings define mean planes with maximum deviations of 0.032(2) Å for the carbon atoms, the latter being at a mean distance of 2.903(5) Å from the metal centres. The N−C(1) bond lengths are in the range 1.330(4)−1.340(4) Å, the mean value being identical to that in the other complexes. The two independent neodymium atoms are displaced by 0.021(2) and 0.034(2) Å from the mean planes defined by the atoms C(1) of the three ligands in each molecule, and the angles defined by the atoms C(1) around Nd are in the range 117.80(9)−121.76(9)°, nearly identical to those in **3a**, **4** and **6**.

The plot of the average Ln−N distances versus the ionic radii $r(\mathrm{Ln^{III}})$ of the six-coordinate $\mathrm{Yb^{III}}$, $\mathrm{Nd^{III}}$ and $\mathrm{La^{III}}$ ions (Figure 5) shows the usual almost perfect linear relationship, with a correlation coefficient of 0.998. However, the average U−N distance is shorter by 0.025 Å than that expected from a purely ionic bonding model; the same trend is observed when considering the U···C(1) distances. Although this difference is smaller than three times the value of the standard deviation for the measured distances (0.01 Å), it seems significant, as the average distances are calculated from six M−N distances and the values are

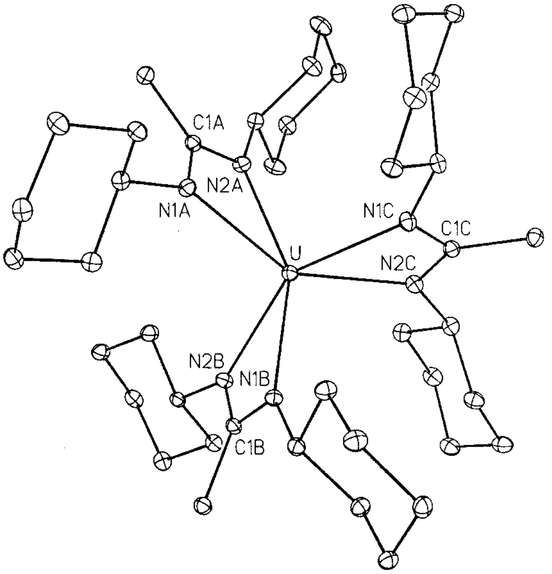


Figure 3. View of the complex [U{MeC(NCy)$_2$}$_3$] (**3a**) with displacement ellipsoids drawn at the 10% probability level; hydrogen atoms have been omitted for clarity

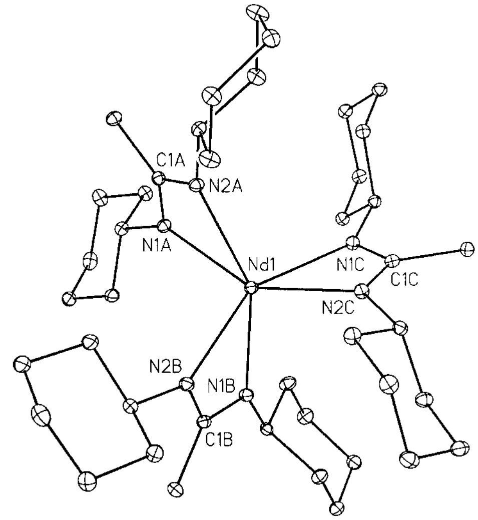


Figure 4. View of one molecular unit in the complex [Nd{MeC(NCy)$_2$}$_3$] (**5**) with displacement ellipsoids drawn at the 10% probability level; hydrogen atoms have been omitted for clarity

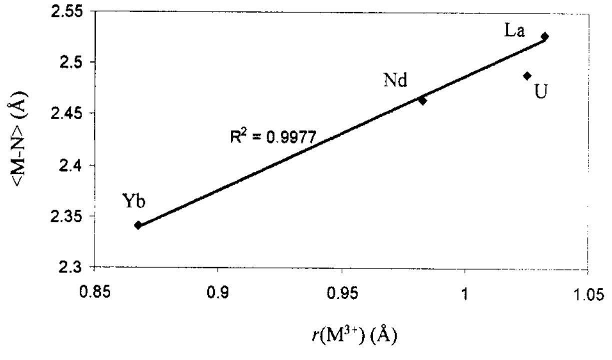


Figure 5. Average M−N distances as a function of the metal ionic radii in the complexes [M{MeC(NCy)$_2$}$_3$]

identical for each of the two independent [Nd{MeC(NCy)$_2$}$_3$] molecules. The shortening of the U−N distances with respect to the Ln−N distances in the series of isostructural compounds **3a**, **4**, **5** and **6** could reflect a stronger interaction between the actinide and the amidinate ligand, in relation with the more covalent character of the bond. The better affinity of neutral nitrogen, phosphorous and sulfur ligands or anionic cyclopentadienyl and iodide groups for U^{III} than for Ln^{III} ions has been similarly assessed from the crystal structures of analogous complexes, by measuring the deviations, Δ, between the differences [<U−X> − <Ln−X>] and [r(U^{III}) − r(Ln^{III})].[24] These deviations are generally equal to 0.02−0.05 Å, as found, for example, in [MI$_3$(bipy)(C$_5$H$_5$N)] (M = Ce or U; bipy = 2,2′-bipyridine),[24a] [M(C$_5$H$_4$R)$_3$(L)] (M = Ce or U; R = *t*Bu or SiMe$_3$; L = pyridine, picoline, lutidine, pyrimidine and 3,5-dimethylpyrazine),[24b] [MI$_2$(OPPh$_3$)$_4$]I (M = Nd, Ce, La, U),[24c] [M(terpy)$_3$]I$_3$ (M = La, Ce, Nd or U; terpy = 2,2′:6′,2′′-terpyridine)[24d] and [MI$_3$(1,4,7-trithiacyclononane)(MeCN)$_2$] (M = La or U).[24e] In the phosphorus-containing complexes [M(C$_5$H$_4$Me)$_3$(L)] [M = Ce or U; L = PMe$_3$ or P(OCH$_2$)$_3$CEt][24f] and in the tris(btp) compounds [M(btp)$_3$]I$_3$ [M = La, Ce, Sm or U; btp = 2,6-dialkyl-1,2,4-triazin-3-yl)pyridine],[24d] Δ is equal to 0.1 Å; this deviation has been explained by the softer character and better π-accepting ability of the phosphane, phosphite and btp ligands. In agreement with these arguments, the low value of Δ for the series of compounds **3a**, **4**, **5** and **6**, if significant, would result from the lower softness of the nitrogen atoms and the energetically less accessible π* orbitals of the amidinate ligand.[25]

Polymerization of ε-Caprolactone

Homoleptic amidinate lanthanide complexes show extremely high activity in the ring-opening polymerization of ε-caprolactone (CL) at room temperature.[4] Thus, in the presence of 0.5% mol-equiv. of the neodymium complex **5** in toluene, polymerization of CL was achieved in less than 2 min, giving a viscous gel of poly(ε-caprolactone), which was characterized by its ^{1}H NMR spectrum.[26] It is likely that the mechanism of this reaction is similar to that proposed for the polymerization of CL catalyzed by guanidino-[23a] or amidolanthanide[27] compounds, in which the initial step is the nucleophilic attack of a nitrogen atom at the carbonyl carbon atom of the lactone, followed by acyl-bond cleavage and formation of an alkoxide complex. Under the same conditions, when using the uranium(III) counterpart **3a** in place of **5**, polymerization of CL was very much slower, requiring 5 d to go to completion. In view of the poor catalytic activity of **3a**, the properties of the polyester obtained were not analyzed further. However, the ^{1}H NMR spectra showed that **3a** reacts immediately with 0.5 mol-equiv. of CL to give a mixture of unidentified compounds, while the colour of the solution turned from green to yellow; these observations suggest that **3a** is oxidized to U^{IV} derivatives by CL. The ability of CL to oxidize low-valent f-element complexes was previously noted during its polymerization by means of a variety of Sm^{II} initiators, like $[Sm(OAr)_2(THF)_3]$ (Ar = $C_6H_2tBu_2$-2,6-Me-4),[28a] $[Sm\{N(SiMe_3)_2\}_2(THF)_2]$ and $[Sm(C_5Me_5)_2(THF)_x]$,[28b] which were initially transformed into the true, uncharacterized Sm^{III} catalysts. It is possible that one of the products resulting from oxidation of **3a** is the dinuclear species [U]−$O(CH_2)_5CO$−[U] ([U] = $\{MeC(NCy)_2\}_3$), by analogy with the compound $[U(C_5H_5)_3{-}O(CH_2)_5CO{-}U(C_5H_5)_3]$ (**7**), which is readily obtained by treating $[U(C_5H_5)_3(THF)]$ with CL in toluene.[29] Complex **7** exhibits the same activity as the oxidation product(s) of **3a** in the catalytic polymerization of CL. The much lower performances of these compounds, by comparison with those of the lanthanide amidinates, can be explained by the more difficult insertion of the lactone monomer into a U^{IV}−O bond than into an Ln^{III}−N or Ln^{III}−O bond; this difference can be compared with that previously noted between titanium(IV)[30] and lanthanide(III)[26a] alkoxides in their reactions with CL.

Conclusion

After the benzamidinate compounds $[U\{ArC(NSiMe_3)_2\}_3Cl]$ (Ar = C_6H_5 or 4-$CF_3C_6H_4$), the complexes $[U\{RC(NCy)_2\}_3Cl]$ (R = Me or *n*Bu) are new examples of tris(amidinato)uranium chlorides. Their reduction with lithium metal affords the first homoleptic tris(amidinate) compounds of uranium(III). Comparison of the crystal structure of $[U\{MeC(NCy)_2\}_3]$ with those of the lanthanide analogues shows that the average U−N distance is shorter than expected from a purely ionic bonding model. This U^{III} complex was found to be much less efficient than the lanthanide counterparts in the catalytic polymerization of ε-caprolactone because of its rapid oxidation into poorly active U^{IV} species.

Experimental Section

General: All preparations and experiments were carried out under argon (< 5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques, or in a glove box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use; deuterated toluene and THF (Eurisotop) were distilled from Na/K alloy and stored over molecular sieves (3 Å). UCl_4 was prepared by a published method.[31] LaI_3, $NdCl_3$, *N*,*N′*-dicyclohexylcarbodiimide, ε-caprolactone, MeLi (1.6 M in diethyl ether) and *n*BuLi (2.0 M in hexanes) were purchased from Aldrich and used without further purification. The ^1H NMR spectra were recorded with a Bruker DPX 200 instrument and referenced internally using the residual protonated solvent resonances relative to tetramethylsilane ($\delta = 0$ ppm); the spectra of the amidinate complexes are reported in Table 1. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany).

Synthesis of $[Li\{MeC(NCy)_2\}(THF)]_2$ (1a): A flask was charged with *N*,*N′*-dicyclohexylcarbodiimide (330 mg, 1.6 mmol) and THF (10 mL) was condensed into it under vacuum at −78 °C. MeLi (1.0 mL of a 1.6 M solution in diethyl ether, 1.6 mmol) was added with a syringe at room temperature. After 2 h, evaporation of the solvent gave colorless crystals which were dried under vacuum (447 mg, 93%).

Synthesis of $[Li\{nBuC(NCy)_2\}(THF)]_2$ (1b): This compound was prepared by using the same procedure as for **1a**, from *N*,*N′*-dicyclohexylcarbodiimide (330 mg, 1.6 mmol) and *n*BuLi (0.8 mL of a 2.0 M solution in hexanes, 1.6 mmol). Colorless crystals were obtained after drying (498 mg, 91%).

Synthesis of $[U\{MeC(NCy)_2\}_3Cl]$ (2a): A flask was charged with UCl_4 (152 mg, 0.4 mmol) and **1a** (360 mg, 0.6 mmol), and THF (10 mL) was condensed into it under vacuum at −78 °C. The reaction mixture was stirred at room temperature for 2 h. The solvent was evaporated and the residue extracted with toluene (10 mL). The solution was filtered and concentrated to dryness, leaving pale-green crystals of **2a** (318 mg, 85%). $C_{42}H_{75}ClN_6U$ (937): calcd. C 53.80, H 8.06, N 8.96; found C 53.92, H 8.15, N 9.08.

Synthesis of $[U\{nBuC(NCy)_2\}_3Cl]$ (2b): An NMR tube was charged with UCl_4 (11.4 mg, 0.030 mmol) and **1b** (30.9 mg, 0.045 mmol) in $[D_8]$THF (0.3 mL). The NMR spectrum showed the immediate and almost quantitative formation of **2b**.

Synthesis of $[U\{MeC(NCy)_2\}_3]$ (3a): A flask was charged with **2a** (281 mg, 0.29 mmol) and Li powder (2.1 mg, 0.29 mmol), and THF (10 mL) was condensed into it under vacuum at −78 °C. The reaction mixture was stirred at room temperature for 2 h. The solvent was evaporated to dryness and the residue extracted with pentane (10 mL). The solution was filtered and concentrated to dryness, leaving dark-green crystals of **3a** (219 mg, 80%). $C_{42}H_{75}N_6U$ (902): calcd. C 55.92, H 8.38, N 9.32; found C 55.68, H 8.44, N 9.22.

Synthesis of $[U\{nBuC(NCy)_2\}_3Cl]$ (3b): An NMR tube was charged with **2b** (29.7 mg, 0.030 mmol) and Li powder (0.2 mg, 0.030 mmol) in $[D_8]$THF (0.3 mL). The pale-green solution progressively turned dark blue, and after 2 h at room temperature the NMR spectrum showed the quantitative formation of **3b**.

Synthesis of $[Ln\{MeC(NCy)_2\}_3]$ [Ln = La (4) or Nd (5)]: These complexes were prepared by modifying a published procedure.[4] A flask was charged with LaI_3 (51.9 mg, 0.1 mmol) and **1a** (90 mg, 0.15 mmol) and THF (5 mL) was condensed into it under vacuum at −78 °C. The reaction mixture was stirred at room temperature for 24 h. The solvent was evaporated and the residue extracted with pentane (5 mL). The solution was filtered and concentrated to dryness, leaving colorless crystals of **4** (60 mg, 75%). Compound **5** was similarly prepared from $NdCl_3$ (100.2 mg, 0.4 mmol) and **1a** (360 mg, 0.6 mmol) and isolated as pale blue-purple crystals (298 mg, 92%).

Polymerization of ε-Caprolactone (CL). a) With $[Nd\{MeC(NCy)_2\}_3]$ (5): An NMR tube was charged with **5** (0.80 mg, 0.0010 mmol) in $[D_8]$toluene (0.6 mL) and CL (22 μL, 0.20 mmol) was introduced with a microsyringe. After 2 min at 20 °C, a viscous gel was obtained and the spectrum showed that CL had completely polymerized. ^1H NMR: $\delta = 1.29$ (m, 2 H, γ-CH_2), 1.54 (m, 4 H, β- and δ-CH_2), 2.20 (t, $J = 7$ Hz, 2 H, ε-CH_2), 3.94 (t, $J = 7$ Hz, 2 H, α-CH_2) ppm; α, β, γ, δ and ε are the positions of the carbon atoms of the polyester chain with respect to the oxygen atom. **b) With $[U\{MeC(NCy)_2\}_3]$ (3a) or $[U(C_5H_5)_3(THF)]$:** An NMR tube was charged with **3a** (0.9 mg, 0.0010 mmol) in $[D_8]$toluene (0.6 mL) and CL (22 μL, 0.20 mmol) was introduced with a microsyringe. The NMR spectra showed the slow formation of the polyester, which required 5 d at 20 °C to go to completion. The same observations were made upon replacing **3a** with $[U(C_5H_5)_3(THF)]$.

Table 5. Crystal data and structure refinement details

	1a	**1b**	**2a**	**3a**	**4**	**5**
Empirical formula	$C_{36}H_{66}Li_2N_4O_2$	$C_{42}H_{78}Li_2N_4O_2$	$C_{42}H_{75}ClN_6U$	$C_{42}H_{75}N_6U$	$C_{42}H_{75}LaN_6$	$C_{42}H_{75}N_6Nd$
M [g mol^{-1}]	600.81	684.96	937.56	902.11	802.99	808.32
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a [Å]	9.8074(5)	21.6623(12)	12.1285(3)	11.6077(10)	11.6688(12)	11.5709(3)
b [Å]	10.9431(7)	17.5871(15)	17.3182(7)	12.8671(10)	12.8558(18)	32.5180(10)
c [Å]	17.3307(11)	11.1983(9)	21.5602(9)	16.2289(10)	16.278(2)	22.4268(8)
α [°]	90	90	90	104.222(5)	104.358(7)	90
β [°]	105.731(3)	95.137(5)	105.398(3)	90.740(5)	90.650(9)	90.727(2)
γ [°]	90	90	90	115.175(4)	115.035(8)	90
V [Å^3]	1790.32(19)	4249.2(6)	4366.0(3)	2107.3(3)	2124.5(5)	8437.7(5)
Z	2	4	4	2	2	8
$\rho_{calcd.}$ [g cm^{-3}]	1.115	1.071	1.426	1.422	1.255	1.273
μ(Mo-K_α) [mm^{-1}]	0.067	0.064	3.814	3.886	1.040	1.266
F(000)	664	1520	1912	922	852	3432
No. of data collected	13809	32315	29703	14463	13811	57209
No. of unique data	3322	7810	8113	7357	7262	15852
Observed data [$I > 2\sigma(I)$]	2493	5114	6547	6183	5794	11905
R_{int}	0.060	0.096	0.066	0.040	0.076	0.055
Parameters	200	493	454	445	445	889
R_1	0.049	0.088	0.030	0.037	0.074	0.033
wR_2	0.120	0.263	0.063	0.088	0.198	0.082
S	1.048	1.065	1.031	1.014	1.024	1.017
$\Delta\rho_{min}$ [e Å^{-3}]	−0.23	−0.61	−0.52	−1.03	−0.82	−0.62
$\Delta\rho_{max}$ [e Å^{-3}]	0.19	0.91	0.45	1.23	1.58	1.35

X-ray Crystallography of 1a, 1b, 2a, 3a, 4 and 5: Data collections were carried out at 100(2) K with a Nonius Kappa-CCD area-detector diffractometer[32] using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The crystals were introduced into 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 at 28 mm. The data were processed with DENZO-SMN.[33] The structures were solved by direct methods or Patterson map interpretation with SHELXS-97 and subsequent Fourier difference synthesis and refined by full-matrix least squares on F^2 with SHELXL-97.[34] Absorption effects of the uranium and neodymium complexes were corrected empirically with the program DELABS from PLATON.[35] In one of the two independent molecules in compound **1b** (unit B), the terminal carbon atom of the *n*-butyl chain and three carbon atoms of the tetrahydrofuran molecule were found disordered over two positions, which were refined with occupancy parameters constrained to sum to unity and some restraints on bond lengths and displacement parameters for the atoms of the tetrahydrofuran molecule. The 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, CH_2) or 1.5-times (CH_3) that of the parent atom. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data and structure refinement parameters are given in Table 5. The molecular plots were drawn with SHELXTL.[36] CCDC-240952 to -240957 (for **1a**, **1b**, **2a**, **3a**, **4** and **5**, respectively) 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: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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