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Transformation of the bis(trimethylsilyl)methyl into a 1,3-diaza-allyl ligand. Synthesis and crystal structures of $[K\{N(R)C(Ar)NC(Ar)CHR\}(NCAr)]_2$ and $[\{UCl(\mu\text{-}Cl)(L)(NR)\}_2][UCl_2(L)(L')]_2[R = SiMe_3; Ar = C_6H_3Me_2\text{-}2,5; L = N(R)C(Ph)C(H)C(Ph)NR; L' = N(R)C(Ph)NC(Ph)CHR]$ ☆

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Abstract

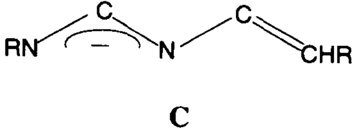
Treatment of $LiCHR_2$ ($R = SiMe_3$) with an excess of ArCN ($Ar = C_6H_3Me\text{-}2,5$) yields the 1,3-diaza-allylpotassium compound $[K\{N(R)C(Ar)NC(Ar)CHR\}(NCAr)]_2$, **2**, whereas use of only two equivalents of ArCN affords the sparingly hydrocarbon-soluble $[K\{N(R)C(Ar)NC(Ar)CHR\}]_n$, **1**. The reaction of uranium(IV) chloride with the β-diketinimatolithium compound $(LiL)_2$ (**A**) leads to the mixed valence $[\{U(VI)\}_2][U(III)]_2$ salt $[\{UCl(\mu\text{-}Cl)(L)(NR)\}_2][UCl_2(L)(L')]_2$, **3**, containing not only the $[N(R)C(Ph)C(H)C(Ph)NR]^-$ ($\equiv L^-$) but also the isomeric 1,3-diaza-allyl $[N(R)C(Ph)NC(Ph)CHR]^-$ ($\equiv L'^-$) ligand. Compounds **1**–**3** have been identified by microanalysis, ^1H NMR spectra, and in the case of **2** and **3**, by single crystal X-ray diffraction studies.

Keywords: 1,3-Diaza-allylpotassium; Uranium; β-Diketinimates; Crystal structure; Silicon

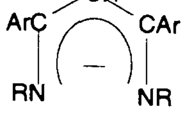
1. Introduction

We recently showed that, irrespective of the stoichiometry of mixing, the reaction of bis(trimethylsilyl)methyllithium $LiCHR_2$ ($R = SiMe_3$) with a nitrile R′CN free from α-hydrogen gave a 1 : 2 (R′ = Ph or $C_6H_4Me\text{-}4$) [1] or a 1 : 1 complex ($R' = {}^tBu$) [2]. These were shown to be the β-diketinimate **A** or the 1-aza-allyl **B**, (Scheme 1).

We now report that, by use of an excess of the slightly more bulky aromatic nitrile ArCN ($Ar = C_6H_3Me_2\text{-}2,5$), a 1:3-complex $Li(CHR_2)(NCAr)_3$ is obtained; this contained the 1,3-diaza-allyl ligand **C**, an isomer of the β-diketinimate ligand **D**. Although we have not yet explored reactions of $Li(CHR_2)(NCAr)_3$ as a *C*-ligand transfer reagent, we also report herein a reaction of Li(**D**) with uranium(IV) chloride, which yields a uranium salt containing ligated **C**.



C



D

There has been a recent upsurge in interest in the 1,3-diaza-allyls (or amidates), especially the *N*,*N*′-bis(trimethylsilyl)benzamidates, e.g. **E**, which have their origin in a reaction reported from these laboratories in 1973, eqn. (1) ($R = SiMe_3$) [3]; the structure of the lithium benzamidate was inferred [4] to be that shown in eqn. (1), and this was eventually confirmed by X-ray crystallography [5].

☆ Dedicated to Prof. F. Calderazzo, as a mark of esteem and friendship on the occasion of his 65th birthday.

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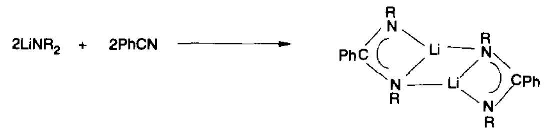
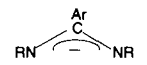


(1)



E

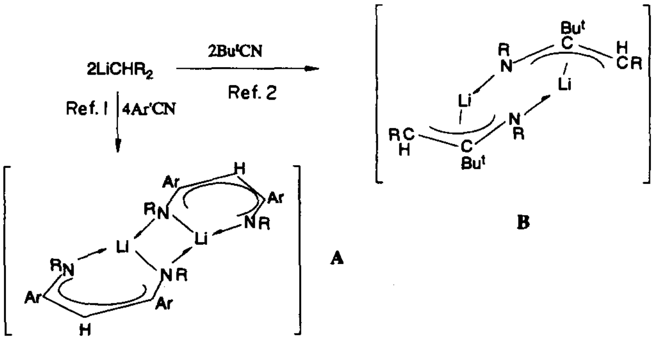
The lithium benzamidates have been used as ligand transfer reagents, e.g. 2Li{N(R)C(Ar')NR} + UCl$_4$, afforded the X-ray-characterised complex [U{N(R)C(Ar')NR}$_2$Cl$_2$] [Ar' = C$_6$H$_2$(CF$_3$)$_3$-2,4,6] [6].

The oxidation state +5 for uranium in its organic compounds is very rare, except for alkoxides U(OR')$_5$ [7], which are accessible from UCl$_4$ from U(OR')$_4$ and O$_2$. Crystallographically characterised complexes include [U(η-C$_5$H$_4$Me)$_3$(NPh)] [8] and [U{N(R)C(Ar')NR}$_2$Cl$_3$] [9] (Ar' = C$_6$H$_4$Me-4). A mixed valence U(IV)/U(VI) organouranium salt (containing coordinated buta-1,3-diene) has been described, namely [U(η-C$_5$H$_5$)$_3$(NCMe)$_2$]$_2$[U(O)$_2$Cl$_4$](C$_4$H$_6$)$_2$ [10].

2. Experimental details

2.1. Materials and procedures

All manipulations were carried out under vacuum or argon by Schlenk techniques. Solvents were dried and distilled over potassium-sodium alloy under argon prior to use. The compounds LiCHR$_2$ [11] and UCl$_4$ [12] were prepared by known procedures. Others were purchased, and purified by standard procedures. Microanalyses were carried out by Medac Ltd (Brunel University). NMR Spectra were recorded with Bruker WM250, WM360 or WM 500 instruments.



Scheme 1.

2.2. Synthesis of [K{N(R)C(Ar)NC(Ar)CHR}]$_n$ (Ar = C$_6$H$_3$Me$_2$-2,5, R = SiMe$_3$) (1)

The nitrile 2,5-Me$_2$C$_6$H$_3$CN (2.08 ml, 15.22 mmol) was added dropwise to a cooled (−78°C) and stirred solution of LiCHR$_2$ (1.26 g, 7.59 mmol) in diethyl ether (ca. 40 ml). There was an immediate colour change from colourless to orange, and a yellow precipitate was formed. The mixture was allowed to warm slowly to room temperature, and then was stirred for a further 4 h, the precipitate redissolving. The solvent was removed in vacuo, and the residue was dried at 75–80°C/10^{-2} mm Hg for 1 h, then dissolved in hexane (ca. 30 ml), and the solution added to KO^{t}Bu (0.77 g, 6.88 mmol) at room temperature. The mixture was stirred overnight. The pale-yellow precipitate that had separated was filtered off, and washed with hexane (ca. 30 ml) to give the pale-yellow solid compound **1** (2.45 g, 70%). Anal. Found: C, 66.6; H, 8.52; N, 6.21. C$_{25}$H$_{37}$KN$_2$Si$_2$ Calc. C, 65.1; H, 8.11; N, 6.08%. M.p. 145–148°C. NMR: ^{1}H (C$_6$D$_6$, 25°C): δ −0.49 and 0.00 (s, 9H, SiMe$_3$); 4.64 (s, 1H, CH); 6.04 and 6.81 (b, 2H, phenyl), 6.90–6.96 (m, 2H, phenyl); 2.08, 2.11, 2.15 and 2.25 (s, 3H, Me). ^{13}C (C$_6$D$_6$, 25°C): δ 0.85 and 3.25 (SiMe$_3$); 126.96 (CH); 166.37, 144.90, 144.88, 133.48, 133.28, 131.35 (phenyl); 20.33, 20.62, 20.82 and 29.36 (Me).

2.3. Synthesis of [K{N(R)C(Ar)NC(Ar)CHR}(NCAr)]$_2$ (Ar = C$_6$H$_3$Me$_2$-2,5; R = SiMe$_3$) (2)

A suspension of compound **1** (0.26 g, 0.56 mmol) in hexane was stirred with an approximately equimolar amount of 2,5-Me$_2$C$_6$H$_3$CN (0.08 ml, 0.61 mmol). Yellow crystals of compound **2** (0.31 g, 93%) were formed, and were used for the single crystal X-ray diffraction study. Anal. Found: C, 69.4; H, 7.78; N, 7.16. C$_{68}$H$_{92}$K$_2$N$_6$Si$_4$ Calc. C, 70.0; H, 7.83; N, 7.10%. M.p. 50–54°C. NMR: ^{1}H (C$_6$D$_6$, 25°C): δ −0.15 and 0.00 (s, 9H, SiMe$_3$); 4.75 (s, 1H, CH); 6.07 and 6.80 (b, 2H, phenyl), 6.92–6.96 (m, 2H, phenyl); 1.76, 2.07, 2.12 and 2.32 (s, 3H, Me); signals attributed to coordinated 2,5-Me$_2$C$_6$H$_3$CN: 6.56 and 6.67 (d, 1H, phenyl), 6.87 (s, 1H, phenyl); 2.17 and 2.15 (s, 3H, Me).

2.4. Synthesis of the salt 3

A solution of [Li{N(R)C(Ph)}$_2$CH]$_2$ (A) (1.57 g, 2.11 mmol) in diethyl ether (ca. 15 ml) was added dropwise to a cooled (−20°C), stirred solution of UCl$_4$ (0.8 g, 2.11 mmol) in tetrahydrofuran (ca. 15 ml). The mixture was allowed to warm to room temperature, and was stirred for a further 28 h; there was a change in colour from green to red. The solvent was removed and the residue was dried in vacuo at 50–60°C/10^{-2} mm Hg for 2 h and extracted into dichloromethane (ca. 25 ml),

Table 1
X-ray crystal structure details

	[$\overline{\mathrm{K\{N(R)C(Ar)N}}$C(Ar)CHR}(NCAr)]$_2$ (**2**)	[{UCl(μ-Cl)(L)(NR)}$_2$][UCl$_2$(L)(L′)]$_2$ (**3**)
Formula	$C_{68}H_{92}K_2N_6Si_4$	$C_{132}H_{192}N_{14}Si_{14}U_4$
M	1184.1	3604.0
Crystal system, space group	triclinic, $P\bar{1}$ (No. 2)	triclinic $P\bar{1}$ (No. 2)
a, b, c (Å)	9.915(14), 12.964(8), 16.079(6)	11.651(2), 12.470(2), 31.618(5)
α, β, γ (°)	99.85(4), 107.65(6), 110.54(8)	89.74(1), 98.65(1), 117.43(1)
U (Å^3), Z, D_c (g cm^{-1})	1752.9, 1, 1.12	4019.9, 1, 1.49
T (K)	173	298
F(000)	636	1782
μ(Mo–Kα) (cm^{-1})	2.4	40.9
Crystal size (mm^3)	0.3 × 0.2 × 0.05	0.2 × 0.2 × 0.02
Total unique reflections ($2 < \theta < 22°$)	4292	7444
Significant reflections [$\|F^2\| > n\sigma(F^2)$]	1297 ($n = 3$)	4225 ($n = 2$)
R, R'	0.088, 0.109	0.071, 0.078
Structural solution	direct methods	heavy atom methods

[a] $R = \Sigma(|F_0| - |F_c|)/\Sigma(|F_0|)$; $R' = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w(|F_0|)^2]^{1/2}$

Table 2
Fractional atomic coordinates ($\times 10^{-4}$) and equivalent isotropic thermal parameters (Å$^2 \times 10^{-3}$) for [$\overline{\mathrm{K\{N(R)C(Ar)N}}$C(Ar)CHR}(NCAr)]$_2$ (**2**)

Atom	x	y	z	U_{eq} [a]
K	1707(5)	6083(3)	5253(2)	35(1)
Si(1)	2334(6)	3416(4)	8178(3)	33(2)
Si(2)	−1696(6)	6977(4)	5552(3)	31(2)
N(1)	540(14)	5195(9)	6588(7)	27(4)
N(2)	−650(14)	6177(9)	5819(7)	25(4)
N(3)	3141(18)	7938(12)	4719(10)	64(5)
C(1)	1274(17)	4978(11)	7374(9)	21(4)
C(2)	1146(17)	3917(12)	7334(9)	24(5)
C(3)	−74(18)	5969(12)	6610(10)	29(5)
C(4)	2335(17)	5939(12)	8267(9)	23(4)
C(5)	3768(19)	6804(13)	8330(10)	38(5)
C(6)	4683(18)	7646(13)	9186(10)	35(5)
C(7)	4250(19)	7664(13)	9926(10)	37(5)
C(8)	2879(19)	6805(13)	9856(10)	34(5)
C(9)	1936(18)	5935(12)	9019(10)	27(5)
C(10)	4315(20)	6819(13)	7533(10)	43(6)
C(11)	2327(21)	6801(14)	10671(1)	50(6)
C(12)	−203(18)	6529(12)	7454(9)	27(5)
C(13)	−1361(19)	5936(13)	7749(10)	35(5)
C(14)	−1484(20)	6536(14)	8504(11)	41(5)
C(15)	−435(19)	7696(13)	8966(10)	39(5)
C(16)	734(19)	8296(13)	8702(11)	42(5)
C(17)	794(19)	7673(13)	7896(10)	37(5)
C(18)	−2396(19)	4655(13)	7280(10)	40(5)
C(19)	1891(21)	9559(14)	9235(11)	55(6)
C(20)	4440(21)	4423(14)	8686(11)	52(6)
C(21)	2167(21)	2008(14)	7540(11)	49(6)
C(22)	1625(20)	3165(14)	9123(11)	49(6)
C(23)	−304(24)	8411(16)	5605(13)	75(7)
C(24)	−3143(21)	6162(14)	4334(11)	44(6)
C(25)	−2777(23)	7223(16)	6209(13)	70(7)
C(26)	5259(20)	9338(13)	3589(11)	44(6)
C(27)	3801(18)	8989(13)	3557(10)	37(5)
C(28)	2652(21)	9195(14)	2973(11)	51(6)
C(29)	2972(20)	9763(13)	2341(11)	43(5)
C(30)	4393(20)	10059(14)	2332(11)	46(6)
C(31)	5614(21)	9903(14)	2945(11)	51(6)
C(32)	6626(22)	9194(15)	4270(12)	63(7)
C(33)	1645(22)	9980(15)	1684(12)	66(7)
C(34)	3384(21)	8404(14)	4212(12)	53(6)

[a] U_{eq} is defined as one third of the trace of the orthogonal U_{ij} tensor.

and the extract was filtered from the residual lithium chloride. Slow evaporation of the solvent from the filtrate gave pink crystals of *the salt* **3** (1.21 g, 58%) which were washed with hexane (ca. 10 ml). Anal. Found: C, 48.4; H, 5.58; N, 5.38. $C_{66}H_{96}N_7Si_7U_2$ Calc. C, 44.0; H, 5.37; N, 5.44%. M.p. 215–222°C.

2.5. *An attempt to separate the cationic and anionic parts of the salt 3 by reaction with Na[BPh$_4$]*

Tetrahydrofuran (ca. 20 ml) was added to a mixture of Na[BPh$_4$] (0.23 g, 0.67 mmol) and **3** (0.62 g, 0.33 mmol) at room temperature. The mixture was stirred overnight, and the solvent then removed in vacuo. The residue was extracted into dichloromethane and the extract filtered to remove a white solid. Concentration of the filtrate in vacuo produced dark-pink crystals (0.48 g), which were identified as the starting material **3**.

2.6. *X-Ray structure determination for the potassium diaza-allyl 2 and the uranium salt 3*

In each case, unique data sets were collected from a crystal sealed in a capillary under argon on an Enraf-Nonius CAD4 diffractometer in the θ–2θ mode with monochromated Mo–Kα radiation ($\lambda = 0.71069$ Å). Two standard reflections monitored every hour showed no significant change. Data were corrected for Lorentz and polarisation effects (Lp) and also for absorption using DIFABS [13] after isotropic refinement. Reflections with $|F^2| > n\sigma(F^2)$] ($n = 3$ for **2**, $n = 2$ for **3**), where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/\mathrm{Lp}$, were considered observed.

Each structure was solved using the heavy atom routines of SHELXS-86 [14]. Non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares using programs from the Enraf-Nonius MOLEN package. The hydrogen atoms were held

Table 3
Fractional atomic coordinates (×10^{-4}) and equivalent isotropic thermal parameters (Å^2 ×10^{-3}) for [{UCl(μ-Cl)(L)(NR)}$_2$][UCl$_2$(L)(L′)]$_2$ (**3**)

Atom	*x*	*y*	*z*	U_{eq} [a]
U(1)	4424.0(10)	55.5(8)	1698.4(3)	37.1(3)
U(2)	4076.4(10)	4359.9(8)	5611.1(3)	34.0(3)
Cl(1)	2330(8)	−769(7)	1117(2)	73(4)
Cl(2)	3743(8)	−1976(6)	2066(2)	73(4)
Cl(3)	1837(7)	4178(6)	5233(2)	63(4)
Cl(4)	5784(7)	6347(5)	5231(2)	52(3)
Si(1)	1875(8)	158(7)	2314(3)	62(4)
Si(2)	6937(9)	620(7)	2712(3)	61(4)
Si(3)	5347(9)	−2039(6)	1086(3)	58(4)
Si(4)	8412(10)	4658(7)	811(3)	74(4)
Si(5)	1998(8)	2792(7)	6456(3)	59(4)
Si(6)	7150(8)	4520(7)	6320(3)	57(4)
Si(7)	4684(10)	7047(7)	6249(3)	75(4)
N(1)	3294(18)	814(14)	2075(6)	32(5)
N(2)	6061(19)	1088(15)	2299(6)	42(6)
N(3)	5639(18)	−586(14)	1278(6)	34(5)
N(4)	5783(19)	1274(16)	1206(6)	46(6)
N(5)	2870(18)	2823(15)	6036(6)	39(6)
N(6)	5626(17)	3796(14)	5943(5)	29(5)
N(7)	4409(15)	5678(12)	6065(5)	15(5)
C(1)	3995(22)	1937(17)	2000(7)	31(7)
C(2)	5338(24)	2499(20)	1990(8)	48(8)
C(3)	6329(23)	2187(18)	2204(7)	37(7)
C(4)	3414(24)	2780(20)	1896(8)	47(8)
C(5)	4000(22)	3933(18)	2094(7)	33(7)
C(6)	3452(27)	4690(22)	1945(9)	61(9)
C(7)	2367(31)	4340(26)	1651(10)	92(12)
C(8)	1821(31)	3208(26)	1450(10)	87(11)
C(9)	2313(27)	2362(22)	1576(9)	63(9)
C(10)	7777(25)	3238(20)	2262(8)	48(8)
C(11)	8743(30)	2947(25)	2164(10)	81(11)
C(12)	10040(31)	3936(25)	2205(10)	82(11)
C(13)	10233(32)	5023(27)	2347(11)	94(12)
C(14)	9330(34)	5360(28)	2442(11)	101(13)
C(15)	7982(28)	4361(22)	2384(9)	64(9)
C(16)	1612(28)	1301(23)	2607(9)	66(9)
C(17)	2181(36)	−760(30)	2744(12)	115(14)
C(18)	438(37)	−799(31)	1900(12)	123(15)
C(19)	5770(30)	−290(25)	3043(10)	80(11)
C(20)	7611(31)	−236(26)	2427(10)	86(11)
C(21)	8330(31)	1885(25)	3080(10)	83(11)
C(22)	6119(24)	426(20)	1090(8)	47(8)
C(23)	6258(25)	2486(20)	1050(8)	48(8)
C(24)	7555(24)	3235(20)	1075(8)	47(8)
C(25)	7130(26)	739(21)	756(8)	56(9)
C(26)	8334(30)	623(25)	905(10)	79(10)
C(27)	9069(32)	822(27)	577(11)	97(12)
C(28)	8774(34)	1130(28)	206(11)	101(12)
C(29)	7619(30)	1149(25)	65(10)	83(11)
C(30)	6759(24)	1022(20)	362(8)	48(8)
C(31)	5195(24)	2743(20)	864(8)	47(8)
C(32)	5269(30)	3880(24)	960(10)	78(10)
C(33)	4266(28)	4140(23)	763(9)	70(10)
C(34)	3223(34)	3313(29)	511(11)	106(13)
C(35)	3058(30)	2168(25)	423(10)	83(11)
C(36)	4046(27)	1879(23)	616(9)	66(9)
C(37)	3568(29)	−3042(24)	969(10)	76(10)
C(38)	6102(33)	−2632(28)	1516(11)	103(13)
C(39)	5935(34)	−2142(28)	588(11)	102(13)
C(40)	7523(33)	4742(27)	299(11)	96(12)
C(41)	9834(41)	4562(35)	697(13)	140(17)
C(42)	8917(40)	6020(34)	1141(13)	139(16)
C(43)	2754(23)	1875(18)	5813(7)	36(7)
C(44)	3811(22)	1967(18)	5597(7)	35(7)
C(45)	5198(24)	2764(19)	5717(8)	42(7)
C(46)	1588(21)	703(17)	5722(7)	26(6)
C(47)	1644(25)	−359(20)	5745(8)	50(8)
C(48)	531(28)	−1465(23)	5652(9)	69(10)
C(49)	−652(28)	−1481(24)	5530(9)	72(10)
C(50)	−758(27)	−425(22)	5489(9)	63(9)
C(51)	397(24)	689(20)	5591(9)	47(8)
C(52)	6081(26)	2313(22)	5545(8)	60(9)
C(53)	7100(27)	3196(22)	5384(9)	61(9)
C(54)	7903(28)	2761(23)	5228(9)	66(9)
C(55)	7737(27)	1642(23)	5247(9)	64(9)
C(56)	6700(34)	803(29)	5399(11)	105(13)
C(57)	5859(28)	1134(23)	5577(9)	69(10)
C(58)	3282(31)	3508(26)	6940(10)	85(11)
C(59)	867(31)	1262(26)	6602(10)	88(11)
C(60)	1082(31)	3671(26)	6315(10)	85(11)
C(61)	7564(36)	3362(30)	6558(12)	114(14)
C(62)	8501(44)	5610(38)	6065(15)	165(19)
C(63)	6895(39)	5270(33)	6754(13)	131(16)
C(64)	4509(29)	6991(24)	6824(9)	78(11)
C(65)	3558(40)	7462(34)	5932(13)	139(16)
C(66)	6344(35)	8209(30)	6189(12)	115(14)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

fixed at calculated positions with $U_{iso} = 1.3U_{eq}$ for the parent atom.

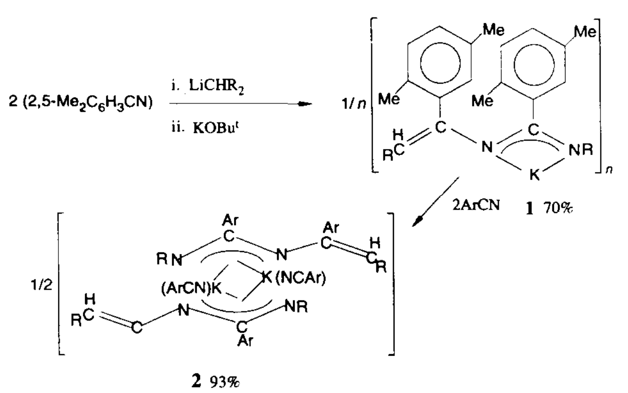
Further details are given in Table 1, atom positions are listed in Tables 2 and 3 and selected bond lengths and angles in Tables 4 and 5. Complete lists of bond lengths and angles, and tables of H atom positions and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. *The potassium 1,3-diaza-allyls **1** and **2**: syntheses and reaction pathway*

The reaction between 2,5-$Me_2C_6H_3CN$ (ArCN) and $LiCH(SiMe_3)_2$ and subsequent treatment with KO^tBu gave the diaza-allylpotassium complex **1** (Scheme 2) rather than a 1-aza-allyl complex or a β-diketinimate (Scheme 1).

Compound **1** was almost insoluble in hexane; but when an equimolar amount of 2-5-$Me_2C_6H_3CN$ was added to a hexane suspension of **1**, the latter readily dissolved to give the complex **2**, which was shown by a single crystal X-ray diffraction study to be dimeric in the solid state, with each potassium bonded to a 1,3-diaza-allyl ligand as well as a coordinated nitrile, Fig. 1.



Scheme 2.

It is interesting to compare the reaction of $LiCHR_2$ (1 mol) with an excess of the nitrile R′CN. For $R' = {}^tBu$, the product was a 1 : 1 complex (the 1-aza-allyl **B**) [2], and for R′ = Ph or C_6H_4Me-4 it was the 1 : 2 adduct (the β-diketinimate **A**) [1]. In contrast, we now find that for $R' = C_6H_3Me_2$-2,5, the 1 : 3 adduct **2** (a 1,3-di-aza-allyl) is formed.

The proposed reaction pathway to these three types of product is shown in Scheme 3. The initial step is an unexceptional attack of the *C*-centred nucleophile on $R'C\equiv N$ to yield **F**. For $R' = C_6H_3Me_2$-2,5, the *N*-centred nucleophile **F** or its rearrangement product **G** then attacks a second $R'C\equiv N$ molecule to give **H** or **I**, respectively, each undergoing a further isomerisation to give the final product **J**. For $R' = {}^tBu$, the reaction stops at **G**, the latter proving to be unreactive with respect to further reaction with ^tBuCN. In contrast, for R′ = Ph or C_6H_4Me-4, **G** behaves as a *C*-centred nucleophile to yield **K**, which rearranges to give the final product **L**. The difference between the systems with $R' = C_6H_3Me_2$-2,5 and those with R′ = Ph or C_6H_4Me-4 may lie in the relative rates of the isomerisation (**F** **G**) and insertion (**F** → **H**) steps, the latter being favoured for the more hindered system. Anionic 1,3-$SiMe_3$ rearrangements are well known [15], although examples of such migrations from carbon to nitrogen are rare.

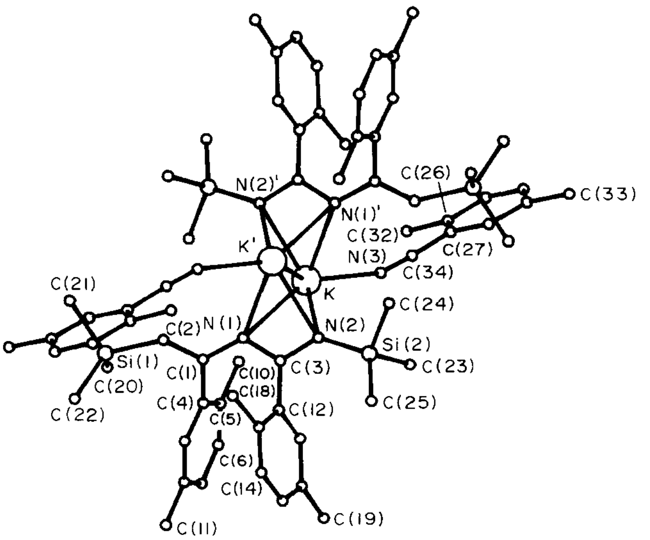


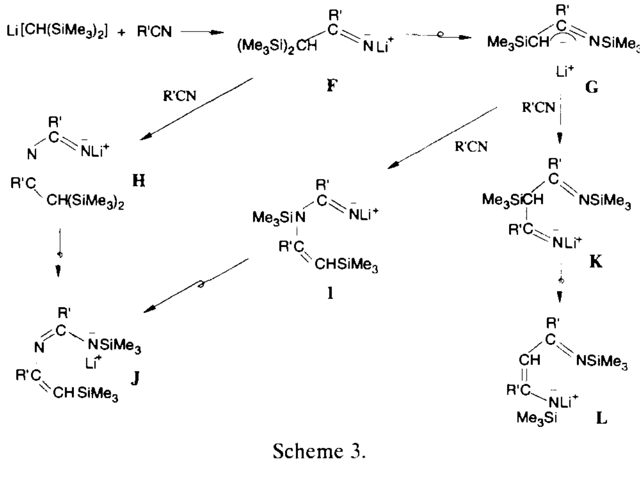
Fig. 1. X-ray molecular structure and atom labelling scheme for $[\overline{K\{N(R)C(Ar)N}C(Ar)CHR\}(NCAr)]_2$ (R = $SiMe_3$, Ar = $C_6H_3Me_2$-2,5) (**2**).

Table 4
Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for $[\overline{K\{N(R)C(Ar)N}C(Ar)CHR\}(NCAr)]_2$ (**2**)

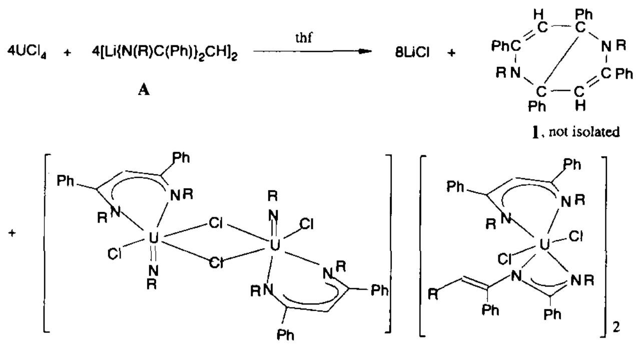
Bonds			
K–K′	3.299(5)	N(2)–C(3)	1.34(2)
K–N(1)	2.95(1)	N(3)–C(34)	1.13(3)
K′–N(1)	2.84(1)	C(1)–C(2)	1.32(2)
K–N(2)	2.79(2)	C(1)–C(4)	1.51(2)
K′–N(2)	2.77(1)	C(3)–C(12)	1.49(2)
K–N(3)	2.75(2)	C(4)–C(5)	1.43(2)
K–C(3)	3.19(2)	C(4)–C(9)	1.38(2)
K′–C(3)	3.16(1)	C(5)–C(6)	1.39(2)
Si(2)–N(2)	1.72(2)	C(5)–C(10)	1.54(3)
Si(1)–C(2)	1.88(2)	C(6)–C(7)	1.38(3)
N(1)–C(1)	1.38(2)	C(7)–C(8)	1.38(2)
N(1)–C(3)	1.34(2)	C(8)–C(9)	1.39(2)
		C(8)–C(11)	1.56(3)
Angles			
K′–K–N(1)	54.2(2)	N(1)–K–N(2)	47.0(4)
K′–K–N(2)	53.4(2)	N(1)–K–N(2)′	89.4(4)
K′–K–N(3)	142.6(3)	N(1)–K–N(3)	91.7(4)
K–N(1)–C(1)	131(1)	N(2)–K–N(2)′	107.1(4)
K–N(1)–C(3)	88(1)	N(2)–K–N(3)	115.1(5)
K–N(2)–C(3)	95(1)	N(1)–C(1)–C(2)	120(1)
K–N(3)–C(34)	155(1)	N(1)–C(1)–C(4)	122(1)
K–N(2)–Si(2)	121.3(5)	N(1)–C(3)–N(2)	117(1)
		C(1)–N(1)–C(3)	122(1)

3.2. *The uranium(VI / III) salt 3*

Treatment of UCl_4 with two equivalents of $[\overline{Li\{N}(R)C(Ph)\}_2CH]_2$ (**A**) in tetrahydrofuran yielded a pink product, **3**, composed of one [U(VI)] dication



Scheme 3.



3, 58 %

Scheme 4.

$[\{UCl(\mu-Cl)(L)(NR)\}_2]^{2+}$ and two [U(III)] anions $[UCl_2(L)(L')]^-$. The ligands L^- and $L^{-\prime}$ are isomeric, and have the formulae **D** and **C**, respectively. The organic coproduct was not isolated, but if it is a single entity it would have the composition $[N(R)]_2(CPh)_4(CH)_2$; a possible structure is shown in **4**, Scheme 4.

The formation of the two U=N double bonds in the cation implies that a C–N bond in the β-diketinimato ligand must have been cleaved at some point along the reaction pathway, in a reductive process.

The uranium salt **3**, which was not very air-sensitive, was soluble in polar solvents such as CH_2Cl_2 and $CHCl_3$, and slightly soluble in toluene, but not in aliphatic hydrocarbons. When the pink crystals were exposed to the atmosphere, no perceptible change was observed after several hours.

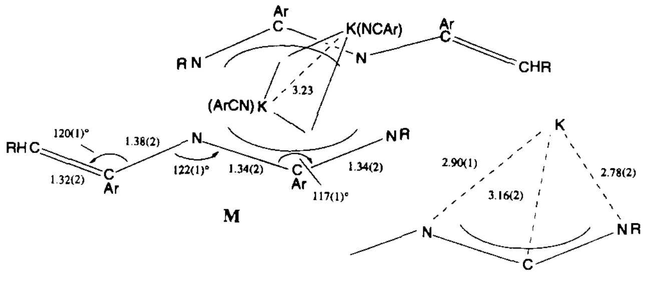
An attempt to displace the cation or anion by reaction with $Na[BPh_4]$ in tetrahydrofuran was not successful; only the starting materials were recovered.

The pink crystalline salt **3** was obtained in substantial yield (58%). The analytical data were satisfactory, except for carbon (the low figure may have been a result of formation of uranium carbide upon incomplete combustion). The ^1H NMR spectrum is shown in Fig. 2. The paramagnetic **3** showed a substantial peak-broadening effect, not usually observed for a uranium(IV) compound; there were three broad peaks at δ 13.9, 1.89, and −7.68.

3.3. The crystal X-ray structure of the potassium 1,3-diaza-allyl 2

The molecular structure and atom numbering scheme for **2** are shown in Fig. 1. Selected bond distances and angles are presented in Table 4, and a simplified bonding pattern for **2**, with selected bond lengths (Å) and angles (°) is shown in **M** and **M′**.

The molecular structure of the crystalline **2** shows it to be a dimer. Each potassium atom is coordinated to five nitrogen atoms, which form a square pyramid around the metal; interestingly, there is a close **K**...**K** distance of 3.23 Å. Equivalent bond distances of N(1)–C(3) and N(2)–C(3) [1.34(2) Å] provide firm evidence for η^3-p_π bonding, **M**. Each of the fragments N=C–N–C=C is coplanar. However, the dimethylphenyl groups are twisted away from the plane [for example, the dihedral angle N(1)–C(3)–C(12)–C(13) is 76°] and therefore, the conjugation cannot efficiently extend to the aryl groups.



M′

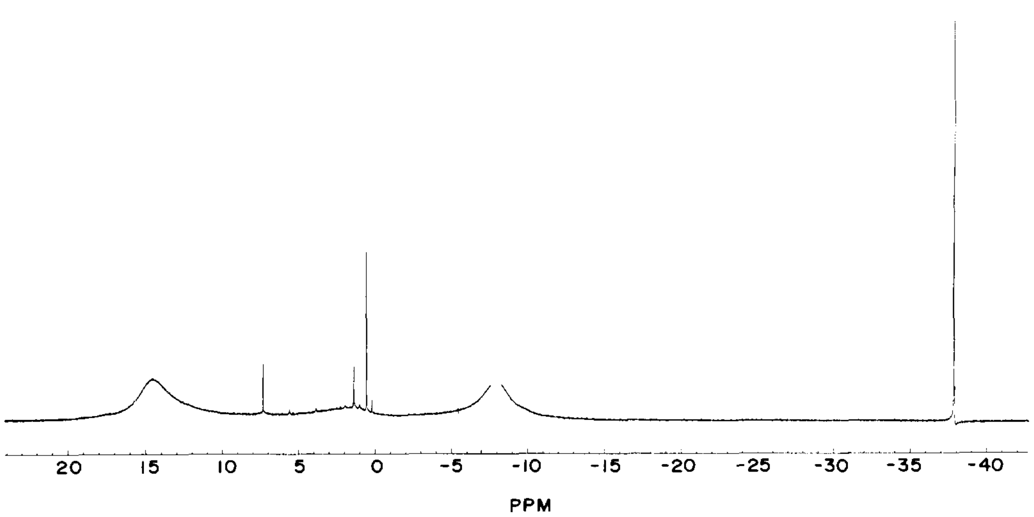


Fig. 2. The ^1H NMR spectrum of $[\{UCl(\mu-Cl)(L)(NR)\}_2][UCl_2(L)(L')]_2$ (3) in $CDCl_3$.

3.4. The crystal X-ray structure of the salt 3

The structure and atom numbering scheme of the cation and anion of **3** are shown in Figs. 3(a) and 3(b), respectively. Selected bond distances and angles are presented in Table 4, and the simplified geometry about (i) uranium and (ii) U–N for both the cation and anion of **3**, with selected bond lengths (Å) and angles (°) are in **N**–**S**, respectively.

The structure of **3** shows that the salt consists of a binuclear U(VI) cation and two U(III) monoanions. For each, there is a distorted octahedral geometry about uranium as illustrated in **N** and **O**.

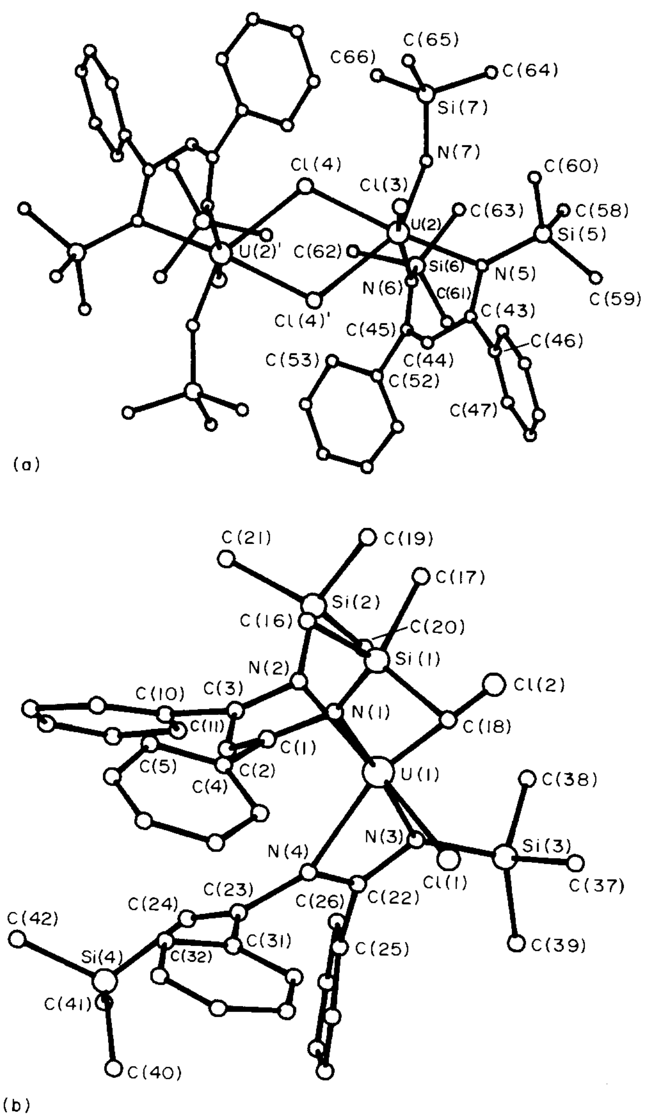
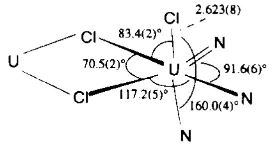


Fig. 3. (a) X-ray molecular structure and atom labelling scheme for the cation $[\{UCl(\mu\text{-}Cl)(L)(NR)\}_2]^{2+}$ of **3**. (b) X-ray molecular structure and atom labelling scheme for the anion $[UCl_2(L)(L')]^-$ of **3**.

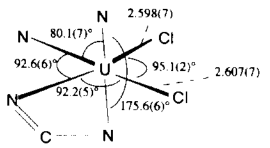
Table 5
Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for $[\{UCl(\mu\text{-}Cl)(L)(NR)\}_2][UCl_2(L)(L')]_2$ (**3**)

Bonds			
U(1)–Cl(1)	2.598(7)	N(3)–C(22)	1.31(3)
U(1)–Cl(2)	2.607(7)	N(4)–C(22)	1.35(4)
U(2)–Cl(3)	2.623(8)	N(4)–C(23)	1.46(3)
U(2)–Cl(4)	2.793(6)	N(5)–C(43)	1.32(3)
U(2)–Cl(4)′	2.870(7)	N(6)–C(45)	1.31(3)
U(1)–N(1)	2.38(2)	C(1)–C(2)	1.39(3)
U(1)–N(2)	2.36(2)	C(2)–C(3)	1.46(4)
U(1)–N(3)	2.45(2)	C(23)–C(24)	1.35(3)
U(1)–N(4)	2.40(2)	C(43)–C(44)	1.46(4)
U(2)–N(5)	2.35(2)	C(44)–C(45)	1.44(3)
U(2)–N(6)	2.33(2)	Si(1)–N(1)	1.76(2)
U(2)–N(7)	2.04(2)	Si(3)–N(3)	1.77(2)
N(1)–C(1)	1.30(2)	Si(5)–N(5)	1.78(2)
N(2)–C(3)	1.30(3)	Si(6)–N(6)	1.81(2)
		Si(7)–N(7)	1.67(2)
Angles			
Cl(1)–U(1)–Cl(2)	95.1(2)	N(7)–U(2)–Cl(3)	94.8(5)
Cl(3)–U(2)–Cl(4)	99.8(2)	U(1)–N(1)–C(1)	95(2)
Cl(3)–U(2)–Cl(4)′	83.4(2)	U(2)–N(5)–C(43)	99(1)
N(1)–U(1)–N(2)	80.1(7)	U(2)–N(6)–C(45)	98(2)
N(1)–U(1)–N(3)	175.6(6)	U(2)–N(7)–Si(7)	156(1)
N(1)–U(1)–N(4)	120.1(7)	C(22)–N(4)–C(23)	125(2)
N(2)–U(1)–N(3)	100.2(7)	N(4)–C(23)–C(24)	121(3)
N(1)–U(1)–Cl(2)	89.9(5)	N(6)–C(45)–C(44)	121(3)
N(5)–U(2)–Cl(3)	86.5(5)	C(1)–C(2)–C(3)	129(2)
N(6)–U(2)–Cl(3)	160.0(4)	C(43)–C(44)–C(45)	128(2)

Symmetry element ′ is 1-*x*, 1-*y*, 1-*z*.

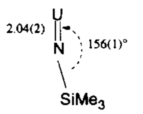


N [U(VI) Cation]

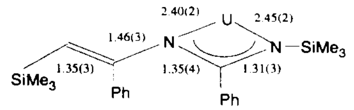


O [U(III) Anion]

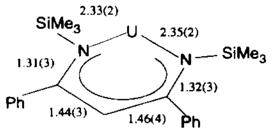
Another interesting feature of the X-ray data is that the salt **3** has three different types of U–N bonds: U=NR, U–N in the 1,3-diaza-allyl and the β-diketinimate, cf. **P**–**S**.



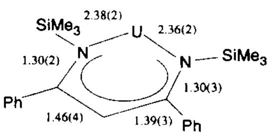
P [U(VI) Cation]



Q [U(III) Anion]

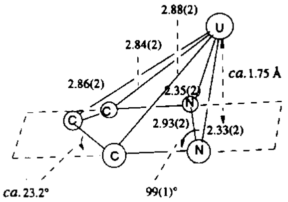


R [U(VI) Cation]

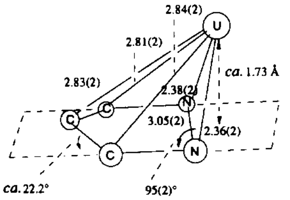


S [U(III) Anion]

The U=NR bond distance of 2.04 Å is the second shortest known for uranium–nitrogen; this and the bond angle U(2)–N(7)–Si(7) of 156(1)° suggest that there is UN triple-bond character, a formally lone-pair of electrons from the N atom contributing to a second π-bond. A comparison between U–N bonds in the fragments **Q**, **R** and **S** is instructive. The delocalised five-membered β-diketinimato ligand, structure **R** or **S**, provides a stronger UN bond than the delocalised three-membered diaza-allyl ligand, structure **Q**. The uranium ion in both the cationic and anionic parts of the salt **3** is situated above the plane of the N=C–C=C–N fragment (the central C atom is situated slightly above the plane with a dihedral angle of ca. 9.85° or 12.83°); the U–N–C bond angles of 95(2)° or 99(1)° and the U^{VI}–C_{av} bond distance of 2.83 Å are comparable with those in uranium cyclopentadienyls [16]. A simplified η^5-bonding pattern is shown in **T** and **U**.

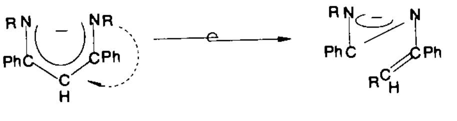


T [U(VI) Cation]



U [U(III) Anion]

The η^5- and η^3-ligands in the anion (**S** and **Q**, respectively) are isomers, which are related by the molecular rearrangement shown in eqn. (2); its occurrence may be sterically induced.



(2)

Although the salt **3** has been formulated as comprising a U(VI) cation and two U(III) counteranions, an alternative could in principle be that in which the charges are reversed, $[\{U^{IV}Cl(\mu\text{-}Cl)(L)(NR)\}_2][U^{V}Cl_2(L)(L')]_2$. The former assignment (**N** and **O**) is preferred largely because a U=NSiMe$_3$ fragment is much more plausible for a U(VI) than a U(IV) complex. The terminal U–Cl bond distances in the two fragments could, however, indicate the reverse, although the β-diketinimato U–N bond lengths are rather similar.

Acknowledgements

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