2-Trimethylsilylamidopyridine complexes of uranium(IV)

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Reaction of 2-trimethylsilylamidopyridine with n-butyl lithium or potassium hydride affords the alkali metal ligand transfer reagents \([\text{Li}(\text{C}_5\text{H}_4\text{N}-2-\text{NSiMe}_3)\text{(THF)}]_2\) (1) and \([\text{K}(\text{C}_5\text{H}_4\text{N}-2-\text{NSiMe}_3)\text{(THF)}]_{0.25}\) (2), respectively. The solid state structure of complex 1 was determined revealing a dimeric structure in the solid state constructed around a centrosymmetric trans-\(\mu\)-amide-lithium \(\text{Li}_3\text{N}_2\) core. The synthetic utility of 1 and 2 was demonstrated by their reactions with \(\text{UCl}_4\) and \(\text{UI}_4\) to give the corresponding uranium(IV) complexes \([\text{U}(\text{Cl})(\text{C}_5\text{H}_4\text{N}-2\text{-NSiMe}_3)\text{]}_3\) (3) and \([\text{U}(\text{I})(\text{C}_5\text{H}_4\text{N}-2\text{-NSiMe}_3)\text{]}_3\) (4), respectively. Crystallographic analyses of 3 and 4 revealed heteroleptic monomeric complexes where all three trimethylsilyl groups are ‘up’ with respect to the halide co-ligand. The three 2-trimethylsilylamidopyridine ligands in 3 and 4 are arranged in a twist-propeller orientation around each uranium centre giving approximate \(C_3\) symmetry down the uranium-halide bond vector but crystals of 3 and 4 are racemic. Attempts to reduce 4 to give the hypothetical uranium(III) complex \([\text{U}(\text{C}_5\text{H}_4\text{N}-2\text{-NSiMe}_3)\text{]}_2\) were unsuccessful and instead the only product that could be isolated from a variety of reactions was the homoleptic uranium(IV) complex \([\text{U}(\text{C}_5\text{H}_4\text{N}-2\text{-NSiMe}_3)\text{]}_4\) (5). Complex 5 exhibits fluxionality in solution which was studied by variable-temperature \(^1\text{H}\) NMR spectroscopy revealing decoalescence at low temperature which is consistent with the presence of a structure in solution that is analogous to the solid state structure. Complexes 1–5 have been characterised by NMR and FTIR spectroscopy, Evans method magnetic moment determinations, CHN microanalyses, and X-ray crystallography for 1 and 3–5.

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1. Introduction

2-Amidopyridine ligands have found extensive utility in transition metal chemistry in recent years because they combine an anionic amide with a neutral pyridine in a chelate ring and offer a wide range of substitution patterns [1]. A substantial number of rare earth derivatives are also now known [1], but surprisingly only two closely related examples with uranyl have been reported for the actinide series [2]. Given the longstanding interest that one would complicate the preparation of uranium derivatives. Therefore, we investigated the preparation of alkali metal complexes of 2-trimethylsilylamidopyridine in the presence of the co-ligand THF since this is a typical solvent for uranium complexes. Accordingly, we treated 2-trimethylsilylamidopyridine, prepared as

Here, we report the synthesis of two new alkali metal 2-amidopyridine ligand transfer reagents and demonstrate their utility in the preparation of two heteroleptic uranium(IV) \(L_3UX\) complexes. Attempts to reduce these \(L_3UX\) complexes to homoleptic uranium(III) \(L_3U\) complexes were, however, unsuccessful and only the homoleptic uranium(IV) \(L_4U\) complex could be isolated from reaction mixtures. We selected the 2-trimethylsilylamidopyridine ligand because of its close relationship to the exemplar bis(trimethylsilyl)amide ligand that has found extensive use in f-element chemistry [8].

2. Results and discussion

2.1. Alkali metal ligand transfer reagents

Prior work by some of us [3–7] resulted in the synthesis of alkali metal complexes of 2-trimethylsilylamidopyridine that incorporated crown ethers. The object of that study was to elucidate structural changes brought about in the solid state by variation of the crown or alkali metal. However, we anticipated that crown ethers would complicate the preparation of uranium derivatives. Therefore, we investigated the preparation of alkali metal complexes of 2-trimethylsilylamidopyridine in the presence of the co-ligand THF since this is a typical solvent for uranium complexes. Accordingly, we treated 2-trimethylsilylamidopyridine, prepared as
plex is best formulated as \([K(C_5H_4N-2-NSiMe_3)(THF)]_{0.25}\). NMR spectroscopy and CHN microanalyses suggest that this complex crystallises in the crystallographic asymmetric unit but their metrical parameters are very similar so we focus our discussion on one of the molecules only. The Li(1)–N(1) and Li(1)–N(3) bond lengths are 2.053(6), 2.114(6) Å, respectively, and these compare well to previous Li–N bond distances in related systems [49]. The Li(1)–O(1) bond length of 1.940(6) Å is unremarkable.

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Although lithium amides are excellent ligand transfer reagents, reactions with electropositive metals such as f-block elements often result in the formation of ‘ate’ salt occlusion complexes because of the small size of lithium [50]. However, the corresponding potassium salts rarely give occlusion complexes due to the large radius of potassium it is likely that the structure of 2 involves a complex aggregate [52]. However, crystalline material suitable for X-ray diffraction has not been obtained so the structure of 2 remains unclear. However, 2 is analytically pure, rendering it suitable for use as a ligand transfer reagent.

### 2.2. Uranium derivatives

Since one objective of this work was to isolate homoleptic uranium(III) \(\text{L}_2\text{U}\) complexes we investigated the synthesis of the corresponding heteroleptic \(\text{L}_3\text{UX}\) precursor complexes. Treatment of UCl\(_4\) with three equivalents of 1 in cold (−78 °C) THF afforded, after filtration and work-up, green crystals of the heteroleptic uranium(IV) complex formulated as \([\text{U}(\text{Cl})(\text{C}_5\text{H}_4\text{N}-2-\text{NSiMe}_3)]_2(\text{THF})\) (3) in 63% isolated yield, Scheme 2. The \(^1\text{H}\) NMR spectrum of 3 spans the relatively narrow range of +12 to 0 ppm, which suggests a relatively symmetrical environment at uranium in 3. The magnetic moment of 3 in benzene solution at 298 K was found to be 2.54 \(\mu_\text{B}\) which is consistent with the uranium(IV) formulation of 3 since molecular uranium(IV) complexes tend to exhibit magnetic
moments in the range 2.5–3.0 $\mu_B$ per uranium centre [53]. To confirm the structure of 3 we determined the crystal structure of crystals grown from a saturated solution in hexane.

Complex 3 is mononuclear in the solid state and the structure is shown in Fig. 2 with selected bond lengths given in Table 1. The uranium centre adopts an irregular 7-coordinate geometry which is constrained by the acute bite angles of the three chelating 2-amidopyridine ligands [55.74(11)$^\circ$ av.]. The three amide centres are co-planar with respect to the uranium centre, and each other, and the sum of the three $\text{Namide–U–Namide}$ angles is 359.89(12)$^\circ$. The U(1)–N(2), U(1)–N(4), and U(1)–N(6) bond lengths of 2.358(3), 2.342(3), and 2.328(3)$\AA$, respectively, are characteristic of uranium(IV)–amide bond lengths [8] and as expected are shorter than the dative U(1)–N(1), U(1)–N(3), and U(1)–N(5) bond distances of 2.487(3), 2.483(4), and 2.478(3)$\AA$, respectively. The U(1)–Cl(1) bond length of 2.6494(9)$\AA$ is in the range of previously reported uranium–chloride distances [49]. The three 2-amidopyridine ligands arrange around a given uranium centre in a twist-propeller orientation. This results in an approximate $C_3$ rotation axis aligned along the uranium–chloride vector and is reminiscent of tris(amidinate)uranium halide complexes [9,14]. This imparts chirality to individual uranium centres, but crystals of 3 are racemic overall since there is no chiral induction in the formation of 3. Furthermore, this twist-propeller arrangement results in all the trimethylsilyl groups pointing ‘up’ with respect to the chloride co-ligand.

Having established that the heteroleptic complex 3 could be isolated, we targeted the iodide congener since we anticipated this to be a better reagent for reduction chemistry. Analogously to the preparation of 3, we repeated the synthesis but substituted UCl$_4$ with Ul$_4$(OEt)$_2$ and 2 for 1. Following filtration and work-up a brown solid was isolated from which brown [Ul(1)(C$_5$H$_4$N-2-NSiMe$_3$)$_3$] (4) was obtained in 82% crystalline yield, Scheme 3. The $^1$H NMR spectrum of 4 spans the range +19 to –17 ppm, which is over twice the range of 3. The magnetic moment of 4 in benzene solution at 298 K was found to be 2.80 $\mu_B$, and although this magnetic moment is higher than 3 it falls well within the range of reported magnetic moments for trimidoamine uranium(IV) complexes [53]. It is germane to note that we have previously observed magnetic moments for trimidoamine uranium(IV) complexes with soft pseudo-halide ligands that are lower than the analogous chloride complexes [26], but a thorough understanding of the factors which determine uranium orbital magnetism is still an ongoing challenge.

We determined the structure of complex 4 and this is depicted in Fig. 3 and selected bond lengths are tabulated in Table 1. Complex 4 is essentially isostructural to 3 except for the obvious replacement of chloride by iodide. As in 3, the three amide atoms in 4 are co-planar with respect to uranium and each other [av. bite angle = 55.76(16)$^\circ$] and the sum of the three $\text{Namide–U–Namide}$ angles is 359.93(16)$^\circ$. The U(1)–N(2), U(1)–N(4), and U(1)–N(6) bond lengths of 2.352(5), 2.337(4), and 2.338(5)$\AA$, respectively, and the longer, dative U(1)–N(1), U(1)–N(3), and U(1)–N(5) bond distances of 2.503(4), 2.474(5), and 2.478(3)$\AA$, respectively are statistically indistinguishable to the corresponding values observed in 3 and demonstrate that the replacement of chloride by iodide [U(1)–$l$(1) = 3.0888(5)$\AA$] has no structural impact on the coordination of the three 2-amidopyridine ligands which, like 3, are all aligned ‘up’ with respect to the halide.

With the synthesis of 4 accomplished, we investigated its reduction in an attempt to prepare a homoleptic uranium(III) [U(C$_5$H$_4$N-2-NSiMe$_3$)$_3$] derivative, Scheme 4. We investigated the reduction of 4 with potassium graphite, potassium naphthalenide, or potassium mirror in THF and toluene but in all cases yellow crystals, indicative of uranium(IV), were isolated from hexane in an average yield of 32%. Since potassium iodide was eliminated, and purple solutions were observed, we reasoned that reduction to uranium(III) was proceeding, but subsequent disproportionation and ligand redistribution were occurring during work-up. In an attempt to prevent disproportionation and ligand scrambling we conducted reduction reactions in 1,2-dimethoxyethane reasoning that this may block coordination sites that would enable dimerisation and the aforementioned disproportionation/ligand redistribution to occur. However, this method also generated yellow crystals characteristic of uranium(IV), which is supported by the observed solution magnetic moment of 2.87 $\mu_B$. Given that the closely related uranium(III) complex [UN$_3$] [$N^\equiv = N(SiMe_3)_2$] [54] may be routinely prepared and isolated we posit that the pyridyl group destabilises the trivalent state of uranium. This destabilisation promotes disproportionation and ligand redistribution. Thus, the tetravalent state of uranium is stabilised even though the pyridyl groups may in principle saturate the coordination sphere of uranium and suppress

![Fig. 2. Molecular structure of 3 with selected labelling. Displacement ellipsoids set to 30% and hydrogen atoms are omitted for clarity.](image)

![Scheme 2. Synthesis of 3.](image)

![Scheme 3. Synthesis of 4.](image)
disproportionation and ligand scrambling. Although pyridine can be considered a ‘softer’ donor than ‘hard’ alkoxides it is a strong donor ligand and it would appear that its strong donor nature is sufficient to push the U(III)/(IV) redox couple of uranium, which is already favourable, in these 2-amidopyridine systems past the cusp of stability. This presumably outweighs any stabilisation effects gained by saturating the coordination sphere of uranium such that the trivalent system is destabilised with respect to the tetravalent state.

The yellow crystals isolated from the reduction reactions were all determined to be the homoleptic uranium(IV) complex $\text{[U(C}_5\text{H}_4\text{N-2-NSiMe}_3)_4]}$ (5), Scheme 5, and the structure is illustrated in Fig. 4 and selected bond lengths are given in Table 1. The uranium centre in 5 adopts an irregular 8-coordinate geometry and the four 2-amidopyridine ligands are geared such that the trimethylsilyl groups mesh efficiently. The U–Namide and U–Namine distances average 2.429(12) and 2.514(12) Å, respectively, which are substantially longer than observed in 3 and 4, reflecting the higher steric congestion and higher coordination number at uranium in 5. This is reflected in the more narrow bite angle of the 2-amidopyridine ligands in 5 [av. 54.68(4)] compared to 3 and 4.

At room temperature the $^1$H NMR spectrum of 5, Fig. 5, exhibits one major broad resonance (fwhm $\sim$ 2700 Hz) along with two minor resonances but apart from a small quantity of sharp diamagnetic impurity resonances it is otherwise apparently featureless which suggests one or more fluxional processes are operating in solution for 5. Upon cooling a sample of 5 in toluene-$d_8$, the major and minor resonances collapse into two broad features centred at $-5$ and $-20$ ppm. At 263–253 K four broad features in the range $+20$ to $-15$ ppm are evident and as the temperature is lowered further these resonances become sharper and other resonances become apparent until at the low temperature limit of 213 K a spectrum exhibiting four trimethylsilyl resonances and 16 pyridyl C–H resonances is observed. This suggests that at low temperature a structure analogous to the solid state structure is present in solution, where the interlocked nature of the trimethylsilyl groups renders the ligand environments magnetically inequivalent, whereas at higher temperatures this species undergoes fluxional exchange behaviour which renders all four of the 2-amidopyridyl ligands equivalent on the NMR timescale. The overlapping nature of the resonances results in this process being somewhat underdetermined, which prevents precise thermodynamic parameters from being extracted, but line-shape analysis yields an estimated $\Delta G^\ddagger$ value of $\sim$50 kJ mol$^{-1}$ in the coalescence regime.

3. Summary and conclusions

To conclude, we have prepared two new 2-trimethylsilylamido-pyridine alkali metal ligand transfer reagents and demonstrated their utility in the synthesis of two heteroleptic uranium(IV) L$_3$UX (X = Cl, I) complexes which are stable. Attempts to isolate the hypothetical homoleptic uranium(III) L$_3$U complex under a variety of conditions resulted in disproportionation and ligand redistribution affording the corresponding homoleptic uranium(IV) L$_4$U complex. This instability may be rationalised on the basis that the strong donor pyridyl group destabilises the trivalent state of uranium and
promotes disproportionation and ligand redistribution to access the tetravalent state of uranium. On the one hand it was anticipated that the pyridyl donors would saturate the coordination sphere of uranium suppressing disproportionation and ligand scrambling, but this is apparently outweighed by the destabilising effect that this strongly donating group has on the U(III)/(IV) redox couple which already favours the tetravalent state.

4. Experimental

4.1. General

All manipulations were carried out using standard Schlenk techniques, or an MBraun UniLab glovebox, under an atmosphere of dry nitrogen. Solvents were dried by passage through activated alumina towers and degassed before use. All solvents were stored over potassium mirrors, with the exception of ethers which were stored over activated 4 Å molecular sieves. Deuterated solvents were distilled from potassium, degassed by three freeze-pump-thaw cycles and stored under nitrogen. The compounds C₅H₄N-2-N(H)SiMe₃ [3], UCl₄ [55], and UI₄(OEt)₂ [56] were prepared according to published procedures.

¹H NMR spectra were recorded on a Bruker 400 spectrometer operating at 400.2 MHz; chemical shifts are quoted in ppm and are relative to TMS. FTIR spectra were recorded on a Bruker Tensor 27 spectrometer. Elemental microanalyses were carried out by Tong Liu at the University of Nottingham.

4.2. Synthesis of [{Li(C₅H₄N-2-NSiMe₃)(THF)}₂] (1)

C₅H₄N-2-N(H)SiMe₃ (3.43 g, 20.60 mmol) was dissolved in THF and cooled to –78 °C. Bu³Li (8.24 ml, 20.60 mmol) was added dropwise and the solution allowed to warm slowly to room temperature with stirring over 16 h. Volatiles were removed in vacuo and the resulting solid was washed with hexanes (2 × 20 ml). The product was dried in vacuo to yield 1 as an off-white solid. Colourless crystals were grown from a saturated solution of 1 in hexanes at –30 °C. Yield: 4.03 g, 80%. Anal. Calc. for C₂₅H₄₂Li₂N₄O₂Si₂: C, 58.99; H, 8.66; N, 11.47. Found: C, 58.81; H, 8.63; N, 11.32%. ¹H NMR (CD₂NO, 298 K): δ 0.52 (s, 18H, SiCH₃), 1.28 (m, 8H, OCH₂CH₂), 3.45 (m, 8H, OCH₂CH₂), 6.30 (m, 2H, Py-H), 6.72 (m, 2H, Py-H), 7.20 (m, 2H, Py-H), 8.05 (m, 2H, Py-H). ¹³C{H} (CD₂NO, 298 K): δ 1.71 (SiCH₃), 25.05 (OCH₂CH₂), 67.93 (OCH₂CH₂), 108.05 (Py-CH), 115.36 (Py-CH), 136.95 (Py-CH), 147.41 (Py-CH), 171.67 (Py-C).

4.3. Synthesis of [{K(C₅H₄N-2-NSiMe₃)(THF)₀.₂₅}] (2)

THF (40 ml) was added slowly to a stirring mixture of C₅H₄N-2-N(H)SiMe₃ (4.16 g, 25.00 mmol) and KH (1.00 g, 25.00 mmol) at –78 °C. The mixture was allowed to warm to room temperature with stirring over 16 h. The volatiles were removed in vacuo and the resulting solid was washed with hexanes (2 × 20 ml). The product was dried in vacuo to yield 2 as an off-white solid. Yield: 5.39 g, 97%. Anal. Calc. for C₉H₁₅N₂O₀.₂₅KSi: C, 48.60; H, 6.80; N, 12.60. Found: C, 48.51; H, 6.68; N, 12.51%. ¹H NMR (CD₂NO, 298 K): δ 0.50 (s, 9H, SiCH₃), 1.52 (m, 1H, OCH₂CH₂), 3.63 (m, 1H, OCH₂CH₂), 6.29 (m, 1H, Py-H), 6.59 (m, 1H, Py-H), 7.23 (m, 1H, Py-H), 8.06 (m, 1H, Py-H). ¹³C{H} (CD₂NO, 298 K): δ 2.41 (SiCH₃), 25.48 (OCH₂CH₂), 67.47 (OCH₂CH₂), 105.52 (Py-CH), 115.49 (Py-CH), 136.53 (Py-CH), 149.23 (Py-CH), 168.99 (Py-C). ²⁹Si NMR (CD₂NO, 298 K): δ –8.52. FTIR cm⁻¹ (Nujol): 2954 (vs), 2924 (vs), 2854 (vs), 1601 (w), 1461 (s), 1377 (m), 1318 (w), 1261 (m), 1091 (m), 1020 (m), 901 (w), 843 (w), 801 (m).

4.4. Synthesis of [{U(Cl)(C₅H₄N-2-NSiMe₃)₃}] (3)

THF (40 ml) was added slowly to a stirring mixture of 1 (1.47 g, 3.00 mmol) and UCl₄ (0.38 g, 1.00 mmol) at –78 °C. The mixture was allowed to warm to room temperature with stirring over 16 h. Volatiles were removed in vacuo and the product was extracted into hot toluene (30 ml). The mixture was filtered to remove the LiCl.
precipitate and volatiles were removed in vacuo to yield 3 as a brown solid. Green crystals were grown from a saturated solution of hexanes at 0 °C. Yield: 0.48 g, 63%. Anal. Calc. for C24H24N2Si3UCl: C, 37.47; H, 5.11; N, 10.92. Found: C, 38.92; H, 5.49; N, 10.87%. 1H NMR (C6D6, 298 K): 2.87 (s, 1H, py-H), 10.09 (s, 3H, py-H), 4.84 (s, 27H, SiC3) (29Si NMR (C6D6, 298 K): δ = –40.79. FTIR ν/cm−1 (Nujol): 2955 (vs), 2924 (vs), 1595 (s), 1541 (w), 1495 (s), 1433 (m), 1377 (m), 1319 (m), 1289 (m), 1259 (m), 1246 (w), 1153 (w), 1094 (m), 1019 (m), 936 (m), 843 (s), 800 (s), 774 (m), 732 (w). µeff (Evans method, C6D6 solution, 298 K): 2.54 μα.

### 4.5. Synthesis of [U(I)(C6H4N-2-NSiMe3)3] (4)

THF (40 ml) was added slowly to a stirring mixture of 2 (4.00 g, 18.00 mmol) and U4(OEt2)2 (5.36 g, 6.00 mmol) at –78 °C. The mixture was allowed to warm to room temperature with stirring over 16 h. Volatiles were removed in vacuo and the product was extracted into hot toluene (30 ml). The mixture was filtered to remove the LiCl precipitate and volatiles were removed in vacuo to yield 4 as a brown solid. Green crystals were grown from a saturated solution of hexanes at 0 °C. Yield: 4.23 g, 82%. Anal. Calc. for C24H24N2Si3U: C, 33.49; H, 4.57; N, 9.76. Found: C, 34.77; H, 4.79; N, 10.06%. 1H NMR (C6D6, 298 K): δ = 18.90 (s, 3H, py-H), 11.06 (s, 3H, py-H), 9.47 (s, 27H, SiC3), –1.55 (s, 3H, py-H), –16.70 (d, 3H, py-H). 29Si NMR (C6D6, 298 K): δ = –10.62 ppm (s). FTIR ν/cm−1 (Nujol): 2956 (vs), 2925 (vs), 1597 (m), 1456 (s), 1377 (m), 1334 (w), 1318 (w), 1260 (m), 1094 (s), 1020 (s), 841 (m), 800 (s). µeff (Evans method, C6D6 solution, 298 K): 2.80 μα.

### 4.6. Attempted synthesis of [U(C6H4N-2-NSiMe3)3] and isolation of [U(C6H4N-2-NSiMe3)3] (5)

**Method A:** THF (20 ml) was added slowly to a stirring mixture of 4 (0.86 g, 1.00 mmol) and KC8 (0.18 g, 1.30 mmol) at –78 °C. The mixture was allowed to warm to room temperature with stirring over 16 h. The solution was filtered to remove the KI and C8 precipitate. Volatiles were removed in vacuo and the product was extracted into hexanes. Yellow crystals were grown from a saturated solution of hexanes. **Method B:** Toluene (20 ml) was added slowly to a stirring mixture of 4 (0.86 g, 1.00 mmol) and KC8 (0.18 g, 1.30 mmol) at –78 °C. The mixture was allowed to warm to room temperature with stirring over 16 h. The solution was filtered to remove the KI and C8 precipitate. Volatiles were removed in vacuo and the product extracted into hexanes. Yellow crystals were grown from a saturated solution of hexanes. **Method C:** DME (20 ml) was added slowly to a stirring mixture of 4 (0.86 g, 1.00 mmol) and KC8 (0.18 g, 1.30 mmol) at –78 °C. The mixture was allowed to warm to room temperature with stirring over 16 h. The solution was filtered to remove the KI and C8 precipitate. Volatiles were removed in vacuo and the product extracted into hexanes. Yellow crystals were grown from a saturated solution of hexanes. **Method D:** A solution of potassium naphthalenide (0.17 g, 1.90 mmol) in THF (10 ml) was added to a stirring solution of 4 (0.86 g, 1.00 mmol) in THF (10 ml) at –78 °C. The mixture was allowed to warm to room temperature with stirring over 16 h. The solution was filtered to remove the KI and C8 precipitate. Volatiles were removed in vacuo and the product extracted into hexanes. Yellow crystals were grown from a saturated solution of hexanes. **Method E:** A solution of 4 (0.86 g, 1.00 mmol) in toluene (20 ml) was vigorously stirred over a potassium mirror (20 fold excess) for 2 days. The mixture was filtered and volatiles removed in vacuo. Yellow crystals were grown from a saturated solution of hexanes.

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Table 2

|   | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Formula | C24H24LiN2O2Si2 | C24H24CN3Si3U | C24H24Ni2Si3U | C24H24U4Si3 | C24H24U6 |
| Formula weight | 488.68 | 769.36 | 860.81 | 899.21 | 870.37 |
| Crystal size (mm) | 0.12 × 0.11 × 0.10 | 0.24 × 0.08 × 0.06 | 0.11 × 0.04 × 0.03 | 0.25 × 0.09 × 0.02 | 0.25 × 0.09 × 0.02 |
| Crystal system | triclinic | triclinic | monoclinic | monoclinic | monoclinic |
| Space group | P1 | P1 | P2_1/n | P2_1/n | P2_1/n |
| a (Å) | 8.58(2) | 8.28(5) | 17.21(5) | 82.85(4) | 83.58(4) |
| b (Å) | 10.19(3) | 9.17(2) | 11.36(26) | 83.58(4) | 83.58(4) |
| c (Å) | 17.21(5) | 12.04(2) | 18.84(17) | 94.40(2) | 95.31(3) |
| α (°) | 90 | 90 | 90 | 90 | 90 |
| γ (°) | 90 | 90 | 90 | 90 | 90 |

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Method A: THF (20 ml) was added slowly to a stirring mixture of 4 (0.86 g, 1.00 mmol) and KC8 (0.18 g, 1.30 mmol) at –78 °C. The mixture was allowed to warm to room temperature with stirring over 16 h. The solution was filtered to remove the KI and C8 precipitate. Volatiles were removed in vacuo and the product was extracted into hexanes.
4.7. X-ray crystallography

Crystal data for compounds 1 and 3–5 are given in Table 2 and bond lengths and angles are listed in Table 1. Crystals were examined variously on a Bruker APEX CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), or on an Oxford Diffraction SuperNova Atlas CCD diffractometer using mirror-monochromated CuKα radiation (λ = 1.5418 Å). Intensities were integrated from data recorded on 0.3° (APEX) or 1° (SuperNova) frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. Semi-empirical absorption correction based on symmetry-equivalent and repeat reflections (APEX) or Gaussian grid face-indexed absorption correction with a beam profile correction (Supernova) were applied. The structures were solved variously by direct and heavy atom methods and were refined by full-matrix least-squares on all unique F² values, with anisotropic displacement parameters for all non-hydrogen atoms, and with constrained riding hydrogen geometries; Uiso(H) was set at 1.2 (1.5 for methyl groups) times Ueq of the parent atom. The largest features in final difference syntheses were close to heavy atoms and were of no chemical significance. Programs were Bruker AXS SMART [57] and CrysAlisPro [58] (control), Bruker AXS SAINT [57] and CrysAlisPro [58] (integration), and SHELXTL [59] and Olex2 [60] were employed for structure solution and refinement and for molecular graphics.

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Appendix A. Supplementary material

CCDC 832296–832299 contain the supplementary crystallographic data for complexes 1 and 3–5, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.09.005.

References

[1] R. Kempe, Eur. J. Inorg. Chem. (2003) 791, and references therein.
[2] K.T. Potts, J.J. O'Brien, F.S. Tham, Inorg. Chem. Acta 177 (1990) 13.
[3] S.T. Liddle, W. Clegg, J. Chem. Soc., Dalton Trans. (2001) 402.
[4] S.T. Liddle, W. Clegg, J. Chem. Soc., Dalton Trans. (2001) 3549.
[5] S.T. Liddle, W. Clegg, Polyhedron 21 (2002) 2451.
[6] S.T. Liddle, W. Clegg, Polyhedron 22 (2003) 3507.
[7] S.T. Liddle, W. Clegg, C.A. Morrison, Dalton Trans. (2004) 2514.
[8] J.C. Berthet, M. Ephritikhine, Coord. Chem. Rev. 178–180 (1998) 83.
[9] M. Wedler, F. Knosel, M. Noltemeyer, F.T. Edelmann, U. Behrens, J. Organomet. Chem. 5802.
[10] M.J. Sarsfield, M. Helliwell, J. Am. Chem. Soc. 126 (2004) 1036.
[11] M.J. Sarsfield, M. Helliwell, J. Raftery, Inorg. Chem. 43 (2004) 3170.
[12] C. Villers, P. Thuery, M. Ephritikhine, Eur. J. Inorg. Chem. (2004) 4624.
[13] C. Villers, P. Thuery, M. Ephritikhine, Chem. Commun. (2006) 392.
[14] C. Villers, P. Thuery, M. Ephritikhine, Chem. Commun. (2007) 2832.
[15] W.J. Evans, C.A. Traina, J.W. Ziller, J. Am. Chem. Soc. 131 (2009) 17473.
[16] W.J. Evans, J.R. Walensky, J.W. Ziller, A.L. Rheingold, Organometallics 28 (2009) 5802.
[17] W.J. Evans, M.K. Takase, J.W. Ziller, A.L. Rheingold, Organometallics 28 (2009) 5851.
[18] W.J. Evans, J.R. Walensky, J.W. Ziller, Chem. Commun. (2009) 7342.
[19] W.J. Evans, J.R. Walensky, J.W. Ziller, Chem. Eur. J. 15 (2009) 12204.
[20] W.J. Evans, J.R. Walensky, J.W. Ziller, Organometallics 29 (2010) 101.
[21] E. Montalvo, J.W. Ziller, A.G. DiPasquale, A.L. Rheingold, W.J. Evans, Organometallics 29 (2010) 2104.
[22] W.J. Evans, E. Montalvo, J.W. Ziller, A.G. DiPasquale, A.L. Rheingold, Inorg. Chem. 49 (2010) 222.
[23] W.J. Evans, J.R. Walensky, J.W. Ziller, Inorg. Chem. 49 (2010) 1743.
[24] S.T. Liddle, J. McMaster, D.P. Mills, A.J. Blake, C. Jones, W.D. Woodul, Angew. Chem. Int. Edit. 48 (2009) 1077.
[25] B.M. Gardner, J. McMaster, W. Lewis, S.T. Liddle, Chem. Commun. (2009) 2851.
[26] B.M. Gardner, J. McMaster, W. Lewis, A.J. Blake, S.T. Liddle, J. Am. Chem. Soc. 131 (2009) 10388.
[27] D. Patel, W. Lewis, A.J. Blake, S.T. Liddle, Dalton Trans. 39 (2010) 6638.
[28] D. Patel, D.M. King et al. / Inorganica Chimica Acta 380 (2012) 167–173
[29] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[30] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[31] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[32] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[33] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[34] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[35] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[36] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[37] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[38] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[39] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[40] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[41] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[42] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[43] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[44] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[45] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[46] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[47] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[48] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[49] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[50] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[51] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[52] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[53] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[54] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[55] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[56] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[57] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[58] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[59] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173
[60] D.M. King et al. / Inorganica Chimica Acta 380 (2012) 173