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Synthesis and structural characterization of uranium *ansa*-metallocene complexes containing organoimido functional groups; electronic effects of ancillary ligands

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Abstract

Complexes of U(IV) employing the chelating bis(cyclopentadienyl) ligand sets $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]^{2-}$ and $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]^{2-}$ have been prepared to examine their utility in generating organoimido complexes of uranium. The chloride complexes $[Me_2Si(C_5Me_4)_2]UCl_2{\cdot}2LiCl{\cdot}4(Et_2O)$ (**1**) and $[Me_2Si(C_5Me_4)(C_5H_4)]\text{-}UCl_2{\cdot}2LiCl{\cdot}4(THF)$ (**2**) may be generated at room temperature by reaction of UCl_4 with the corresponding bis(cyclopentadienyl) dilithio salt in diethyl ether and tetrahydrofuran, respectively. Complex **1** may be recrystallized from toluene in the presence of TMEDA to yield the complex $[Me_2Si(C_5Me_4)_2]U(\mu\text{-}Cl_4)\{Li(TMEDA)\}_2$ (**1**·TMEDA). The molecular structure of this complex has been determined by single-crystal X-ray diffraction. Compounds **1** and **2** may be alkylated by Grignard reagents. While the dimethyl complex $[Me_2Si(C_5Me_4)_2]UMe_2$ (**3**) may be isolated, the analogous complex and $[Me_2Si(C_5Me_4)(C_5H_4)]UMe_2$ appears to be thermally unstable. Benzyl derivatives employing both ligand sets (**4**, **5**) have been prepared. These alkyl complexes are protonated by *N*,*N*′-diphenylhydrazine to yield phenylimido-containing products. Surprisingly, while reaction of compounds **3** or **4** with *N*,*N*′-diphenylhydrazine yields the expected U(VI) complex $[Me_2Si(C_5Me_4)_2]U(NC_6H_5)_2$, reactions employing **5** generate only the U(IV) monoimido dimer $[Me_2Si(C_5Me_4)(C_5H_4)]U\text{-}(NC_6H_5)]_2$ (**8**). The molecular structure of **8** has been determined; the compound exists as a dimer with asymmetric organoimido bridging ligands. Electrochemical investigations of the chloride compounds **1** and **2** suggest that the ancillary ligands have the capacity to significantly alter the redox activity of the metal center. The use of electron-rich ancillary ligands appears to be important in the isolation of high-valent organouranium complexes. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Uranium; Organoimido; *ansa*-Metallocene

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1. Introduction

Complexes of the actinides containing terminal metal–ligand multiple bonds are becoming increasingly common [1] as researchers seek to compare the reactivity of these species with those of their early transition metal cogeners. Although in some cases these functional groups have been implicated as the active sites in processes catalyzed by organoactinide complexes [2], isolated uranium or thorium oxo or imido ligands are not generally found to be as reactive as titanium or zirconium species toward electrophilic reagents. We have investigated the preparation of oxo and imido complexes of uranium(IV), (V), and (VI) utilizing the bis(pentamethylcyclopentadienyl) supporting ligand framework ($(\eta^5\text{-}C_5Me_5)_2An$, An = Th, U) [3]. Although the complexes $(\eta^5\text{-}C_5Me_5)_2U(NR)_2$ (R = aryl, 1-adamantyl) are reduced slowly by dihydrogen or silanes [3,4], neither these species nor the related uranium(IV) monoimido complexes react with alkenes or alkynes by cycloaddition, as is commonly observed in the chemistry of Group 4 complexes containing organoimido ligands [5]. Similarly, although C–H bond activation of benzene is commonly observed in reactions of Group 4 imido complexes [6], this reaction has not been observed in thermolyses of uranium imido complexes [7].

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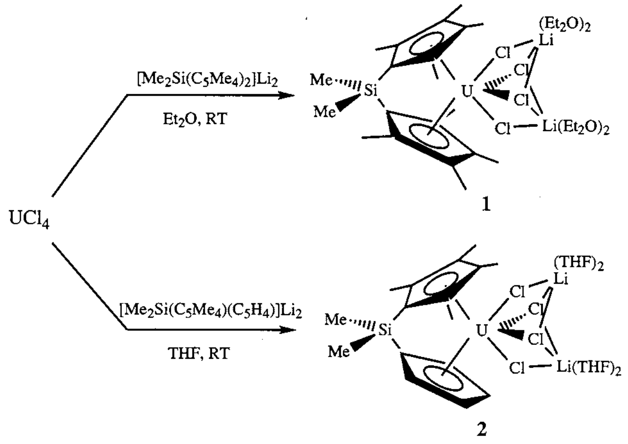
The lack of reactivity could be attributed to a number of factors, including the greater polarity of actinide-element bonds, the potential for enhanced metal–ligand multiple bonding employing actinide 5f-orbitals, or the steric congestion accompanying the use of the bulky bis(pentamethylcyclopentadienyl) ligand set. In an effort to clarify the steric role of the ancillary ligands, we have attempted to prepare uranium(VI) organoimido complexes employing the 'tied-back' bis(cyclopentadienyl) ligand sets. The silyl-bridged ligands $[Me_2Si(\eta^5\text{-}Me_4C_5)_2]^{2-}$ and $[Me_2Si(\eta^5\text{-}Me_4C_5)(\eta^5\text{-}C_5H_4)]^{2-}$ were chosen to improve the solubility of the resulting complexes. The precursor halide complexes of U(IV) have been synthesized; these may be alkylated by Grignard reagents to yield the corresponding dialkyl derivatives $[Me_2SiCpCp']UR_2$. Reactions of the dialkyl compounds with N,N′-diphenylhydrazine were examined, with the expectation that the products would be bis(phenylimido)uranium(VI) complexes in all cases, by analogy with known chemistry of complexes $(\eta^5\text{-}C_5Me_5)_2UR_2$ [3]. It was envisioned that these more constrained ligand sets would primarily alter the reactivity of the organoimido products by relieving steric congestion around the metal center. We have determined instead that the electronic nature of the ligand set has a more profound impact on the course of reactions; the more electron-rich permethylated ligand sets are required to stabilize uranium(VI) products. In their absence, only uranium(IV) imido complexes are isolated.

2. Results and discussion

2.1. Synthesis and properties of organouranium halide complexes

Chelating bis(cyclopentadienyl) metallocene complexes of both actinides and lanthanides have been previously reported [8]. Metallocene halide complexes of the f-elements using these ligands are generally prepared by reaction of the metal tetrachloride with the dilithio salts of the bis(cyclopentadienyl) ligands. We have examined the comparable reactions of UCl_4 with the lithium salts. We have found that these reactions provide an effective high yield of the desired U(IV) halogen complexes, $[Me_2Si(C_5Me_4)_2]UCl_2\cdot 2LiCl\cdot 4(Et_2O)$ (**1**) and $[Me_2Si(C_5Me_4)(C_5H_4)]UCl_2\cdot 2LiCl\cdot 4(THF)$ (**2**) (Eq. (1)). The complexes **1** and **2** are isolated as dark-red, air-sensitive solids. As has been observed for the thorium analog $[Me_2Si(C_5Me_4)_2]ThCl_2\cdot 2LiCl\cdot 2(DME)$ [8], the reduced steric bulk of the chelating bis(cyclopentadienyl) ligand set results in the isolation of lithium chloride adducts from metathesis reactions. This results in somewhat lower solubility than observed for the precursor halide complex $(C_5Me_5)_2UCl_2$ [9]; both are soluble in aromatic hydrocarbons but insoluble in hexane. The complexes are static at room temperature in aromatic solvents. The ^{1}H-NMR spectrum of complex **2** consists of two discrete sets of isotropically shifted, narrow resonances for the (C_5Me_4), (C_5H_4), and Me_2Si groups, suggesting C_s symmetry for the molecule comparable to the known lanthanide complex $[Me_2Si(C_5Me_4)(C_5H_4)]LuCl_2\cdot Li(Et_2O)_2$ [8b] Complex **1** exhibits C_2 symmetry; the resonances are fairly broad, as has been previously observed for $(\eta^5\text{-}C_5Me_5)_2UCl_2$.



(1)

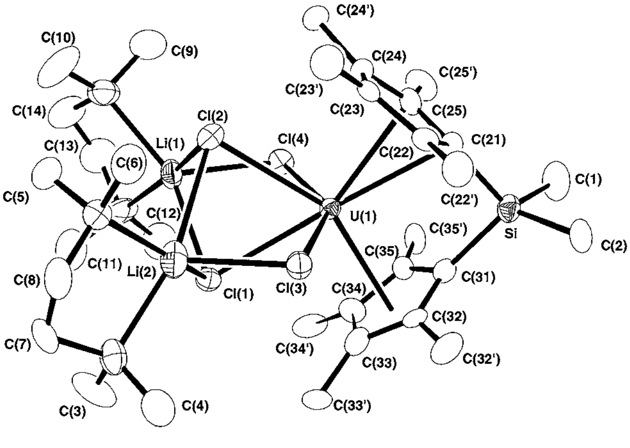


Fig. 1. Thermal ellipsoid plot of $[Me_2Si(C_5Me_4)_2]UCl_2\cdot 2LiCl\cdot (TMEDA)_2$ (**1**·TMEDA) with atomic numbering scheme.

2.2. Molecular structure of $[Me_2Si(C_5Me_4)_2]U(\mu\text{-}Cl_4)\{Li(TMEDA)\}_2$ (**1**·TMEDA)

Recrystallization of complex **1** from toluene containing tetramethylethylenediamine (TMEDA) generates a TMEDA adduct that is more suitable for characterization by single crystal X-ray diffraction (Fig. 1, Tables 1 and 2). The molecular structure of the complex reveals a typical bent metallocene complex. The ring centroid–U–centroid angle (114.1°) is considerably smaller than

Table 1
Crystallographic parameters for the compounds $[Me_2Si(C_5Me_4)_2]U(\mu\text{-}Cl_4)\{Li(TMEDA)\}_2$ (**1**·TMEDA) and $\{[Me_2Si(C_5Me_4)(C_5H_4)]U(NPh)\}_2$ (**8**)

	(1)·TMEDA	**(8)·toluene**
Empirical formula	$C_{32}H_{62}Cl_4Li_2N_4SiU$	$C_{51}H_{58}N_2Si_2U_2$
Space group	$P2_1/n$	$P2/n$
Temperature (°K)	173	178
a (Å)	13.085(2)	13.251(1)
b (Å)	22.723(2)	10.104(2)
c (Å)	14.111(3)	17.251(2)
β (°)	106.62	100.85
V (Å^3)	4020.3(11)	2268.4(5)
Z	4	2
ρ_{calc} (Mg m^{-3})	1.528	1.803
Radiation (λ (Å))	Mo–K$_\alpha$ (0.71069)	Mo–K$_\alpha$ (0.71069)
F_w (g mol^{-1})	924.66	1231.23
Absorption coefficient (mm^{-1})	4.359	7.219
Absorption correction	Empirical	Empirical
Min./max. trans.	0.17/0.59	0.31/0.75
Range (°)	1.75–22.50	2.55–20.00
R (%) [a]	4.78	3.96
R_w (%) [a]	9.46	8.37

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o^2)+(0.0595*P)^2]$, with $P=(F_o^2+2F_c^2)/3$.

Table 2
Selected bond lengths (Å) and angles (°) for $[Me_2Si(C_5Me_4)_2]U(\mu\text{-}Cl_4)\{Li(TMEDA)\}_2$ (**1**·TMEDA)

Bond lengths			
U–C(21)	2.732(10)	Si–C(1)	1.880(11)
U–C(22)	2.799(10)	Si–C(31)	1.867(10)
U–C(23)	2.899 (10)	Si–C(2)	1.868(11)
U–C(24)	2.864 (10)	Si–C(21)	1.863(10)
U–C(25)	2.785 (10)	Li(1)–N(3)	2.26 (2)
U–C(31)	2.764 (9)	Li(1)–N(4)	2.13(2)
U–C(32)	2.792(10)	Li(2)–N(1)	2.12(2)
U–C(33)	2.845 (11)	Li(2)–N(2)	2.17(2)
U–C(34)	2.852(10)	Li(1)–Cl(1)	2.49(2)
U–C(35)	2.781(9)	Li(1)–Cl(2)	2.43(2)
U–Cl(1)	2.885(3)	Li(1)–Cl(4)	2.50(2)
U–Cl(2)	2.853(3)	Li(2)–Cl(1)	2.45(2)
U–Cl(3)	2.760(2)	Li(2)–Cl(2)	2.68 (2)
U–Cl(4)	2.746 (3)	Li(2)–Cl(3)	2.42(2)
Bond angles			
Cp–U–Cp	114.1	C(1)–Si–C(2)	101.2(5)
Cl(1)–U–Cl(2)	67.24(8)	Cl(1)–U–Cl(3)	76.78(8)
Cl(1)–U–Cl(4)	74.96(8)	Cl(2)–U–Cl(3)	75.55(8)
Cl(2)–U–Cl(4)	76.41(8)	Cl(3)–U–Cl(4)	145.98(8)

that observed in unconstrained bis(cyclopentadienyl)uranium complexes (133–138°) [10], and is comparable to the angle determined for the thorium dialkyl complex $[Me_2Si(C_5Me_4)_2]Th(CH_2Si(CH_3)_3)_2$ (118.4°) [8a]. The average U–C (Cp) distance is 2.80(1) Å, although there is a wide range of distances (2.73(1)–2.90(1) Å). The longest U–C distances are those between the metal and the carbons farthest in the ring from the silyl bridge. This dispersion of U–C bond distances has been reported in other chelating metallocene complexes, and is thought to be due to the strain implemented by the Me_2Si bridge. The uranium is coordinated to four bridging chloride ligands. Two of the uranium chloride bond distances are longer than the others: U(1)–Cl(1) = 2.885(3) Å, U(1)–Cl(2) = 2.853(3) Å; U(1)–Cl(3) = 2.760(3) Å, U(1)–Cl(4) = 2.746(3) Å. The longer U–Cl distances correspond to those chlorides that are in three-fold bridging positions, coordinated to both lithium ions. Those chloride ligands that are more closely associated with the uranium center only bridge to one lithium ion. The U–Cl distances are longer than typical terminal U–Cl distances (e.g. U–Cl(avg) = 2.696(2) Å in $(C_5Me_5)_2UCl_2(N_2C_3H_3))$ [11], as might be expected for a bridging chloride. The average Li–Cl distance is 2.49(2) Å and the average Li–N distance is 2.17(2) Å; these are typical distances seen for other anionic uranium complexes such as $(C_5Me_5)_2U(NPh)(\mu\text{-}Cl)Li(TMEDA)$ [3c].

2.3. Preparation of alkyl derivatives

The uranium center in complex **1**·TMEDA is formally ten coordinate in the solid state, and yet complex **1** efffectively behaves in solution as an eight-coordinate $[Me_2Si(C_5Me_4)_2]UCl_2$ fragment useful as a precursor to a number of complexes. Alkylation of the halo-precursors **1** and **2** with Grignard reagents in most cases (in the presence of excess 1,4-dioxane) proceeds smoothly to give the dialkyl complexes as crystalline solids which are exceedingly air and moisture sensitive (Eqs. (2) and (3)).

$$\underset{\mathbf{1}}{[Me_2Si(C_5Me_4)_2]UCl_2{\cdot}2LiCl{\cdot}4(Et_2O)} \xrightarrow[Et_2O,\ dioxane]{2RMgCl} \underset{\substack{\mathbf{3},\ R = Me \\ \mathbf{4},\ R = CH_2C_6H_5}}{[Me_2Si(C_5Me_4)_2]UR_2} \quad (2)$$

$$\underset{\mathbf{2}}{[Me_2Si(C_5Me_4)(C_5H_4)]UCl_2{\cdot}2LiCl{\cdot}4(THF)} \xrightarrow[Et_2O,\ dioxane]{2RMgCl} \underset{\mathbf{5},\ R = CH_2C_6H_5}{[Me_2Si(C_5Me_4)(C_5H_4)]UR_2} \quad (3)$$

In contrast to the reported instability of the analogous thorium dimethyl derivative [8a], the dimethyl complex **3** is quite stable and can be isolated. The dimethyl derivative could not be generated from complex **2**, however; alkylation with methyl Grignards gave rise to insoluble precipitates accompanied by gas generation. The use of bulkier alkyl groups drastically improves the isolated yield of the dialkyl products. The dibenzyl complexes **4** and **5** were obtained in 80–90% yield as green–black microcrystalline solids. Attempts to make the alkyl-chloride complexes via conproportionation of complex **1** with **3** or **4** or complex **2** with **5** did not yield the desired products. The mixed alkyl-chloride complex $[Me_2Si(C_5Me_4)_2]UCl(CH_2C_6H_5)$ (**7**) may be obtained in good yield, however, by protonation of the bis(alkyl) **4** with $[HNMe_3]Cl$ (Eq. (4)).

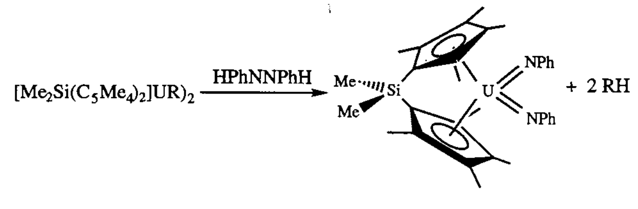
$$[Me_2Si(C_5Me_4)_2]U(CH_2C_6H_5)_2 \xrightarrow[\text{toluene}]{[HNMe_3]Cl} \underset{\mathbf{6}}{[Me_2Si(C_5Me_4)_2]U(CH_2C_6H_5)Cl} \quad (4)$$

2.4. Synthesis and characterization of organoimido complexes

Protonation of metallocene dialkyl complexes by substituted anilines has been employed as a route for the generation of mono(arylimido) complexes of U(IV) [3c]. In the case of the bis(pentamethylcyclopentadienyl)uranium framework, the success in forming mono(arylimido) complexes is controlled the steric bulk of the aryl substituent. The reaction of $(C_5Me_5)_2UMe_2$ with one equivalent of a bulky aniline in toluene at elevated temperatures produces the corresponding terminal imido compound $(C_5Me_5)_2U(NAr)$ (Ar = 2,6-di-*iso*-propyl-C_6H_3 or 2,4,6-tri-*tert*-butyl-C_6H_2). However, reaction of $(C_5Me_5)_2UMe_2$ with one equivalent of a less sterically demanding ligand, such as aniline, yields an equimolar mixture of $(C_5Me_5)_2UMe_2$ and $(C_5Me_5)_2U(NHPh)_2$.

The comparable reaction of the uranium dialkyl complexes incorporating chelating bis(cyclopentadienyl) ancillary ligands with anilines was investigated to determine if the steric bulk of the metal complex had an effect on the course of the reaction. The reactions of compounds **3**, **4**, and **5** with with bulkier anilines such as 2,4,6-tri-*tert*-butylaniline and 2,6-di-*iso*-propylaniline was monitored in situ by ^{1}H-NMR spectrometry. No reaction was observed with any aniline at room temperature over the course of 48 h. At elevated temperatures, decomposition of the bis(alkyl) is observed before protonation of the metal bound alkyl via the aniline occurs. Total decomposition of **3**, **4**, and **5** occurs when these complexes are heated to 80°C in benzene for a period of 12 h.

The lack of success in obtaining U(IV) mono(imido) complexes through protonation routes prevented their use as reagents in generating U(VI) bis(imido) compounds by reaction with organoazides [3]. Another route commonly employed to prepare the uranium(VI) involves reaction of metallocene dialkyl complexes with *N*,*N*′-diphenylhydrazine. In this reaction, two organoimido ligands are formed at uranium by reductive cleavage of the hydrazine. The reaction of complexes **3** or **4** with *N*,*N*′-diphenylhydrazine proceeds analogously, yielding the U(VI) bis(phenylimido) complex $[Me_2Si(C_5Me_4)_2]U(NPh)_2$ (**7**) as a black microcrystalline solid in near quantitative yield (Eq. (5)). The ^{1}H-NMR of complex **7** reveals chemical shifts in a range similar to that previously observed for $(C_5Me_5)_2U(NPh)_2$ [3a], consistent with the formulation of **7** as a U(VI) bis(phenylimido) complex. Two resonances are observed for the inequivalent methyl pairs on the (C_5Me_4) moieties ($\delta = 3.67, 5.67$ ppm), and a single resonance is observed for the methyl groups on the dimethylsilyl backbone ($\delta = 1.03$ ppm). X-ray data collected for **7** were of poor quality and did not permit adequate refinement of a structural model; full structural details will not be presented. The atom connectivity was identified, however, and the identity of the complex as a monomeric bis(phenylimido)uranium(VI) complex confirmed.



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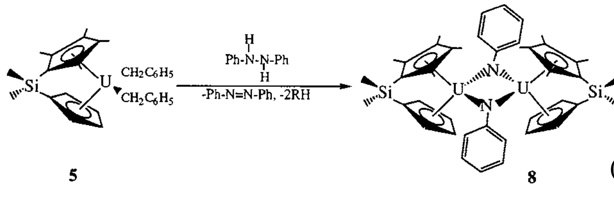
(5)

Attempts to produce the analogous mixed ring U(VI) bis(imido) complex by oxidation of **5** yielded an unexpected product. The reaction of the bis(benzyl) complex **5** with *N*,*N*′-diphenylhydrazine generates the dimeric uranium(IV) complex $\{[Me_2Si(C_5Me_4)(C_5H_4)]U(\mu\text{-}NPh)]\}_2$ (**8**) (Eq. (6)). This compound is very similar to previously reported examples of bridging organoimido species [12], although there are no examples of this class with the chelating bis(cyclopentadienyl) ligand set. The ^{1}H-NMR spectrum of compound **8** suggests that the molecule exists as a symmetric dimer in solution; one set of phenyl resonances and one set of resonances for the chelating $[Me_2Si(C_5Me_4)(C_5H_4)]$ ligand may be identified. If the reaction is monitored by ^{1}H-NMR, the only products detected when the bis(benzyl) complex **5** is reacted with one equivalent of *N*,*N*′-diphenylhydrazine in C_6D_6 at room temperature are the dimeric U(IV) complex **8**, two equivalents of toluene, and one equivalent of azobenzene. The generation of both oxidized (azobenzene) and reduced (organoimido ligands generated from hydrazine cleavage) products from hydrazine activation has been reported previously in the catalytic disproportionation of *N*,*N*′-diphenylhydrazine to azobenzene and aniline [2b]. The lack of an observable hexavalent bis(imido) complex suggests either that the metal center is less susceptible to oxidation in this complex, or that the hexavalent species reacts much more quickly than the corresponding complexes **7** or $(C_5Me_5)_2U(NPh)_2$ with reductants in solution (e.g. unreacted *N*,*N*′-diphenylhydrazine).



5 **8** (6)

2.5. Molecular structure of $\{[Me_2Si(C_5Me_4)(C_5H_4)]U(\mu\text{-}NPh)\}_2$ (*8*)

The molecular structure of **8** was determined by single-crystal X-ray diffraction (Fig. 2, Tables 1 and 3). The complex is composed of dimeric $[Me_2Si(C_5Me_4)(C_5H_4)]U(NPh)$ units with a crystallographic two-fold axis located in the middle of the U_2N_2 unit. This mandates that both of the larger (C_5Me_4) rings lie on the same side of the U_2N_2 plane. The average U–C(C_5H_4) and U–C(C_5Me_4) distances are both 2.75(1) Å, again with some dispersion in the U–C bond lengths (range 2.72(1)–2.80(1) Å), and the centroid–uranium–centroid angle is 115.5°. The geometry of the central U_2N_2 core is similar to that reported for the closely related complex $[(MeC_5H_4)_2U(\mu\text{-}NPh)]_2$ [12a]. The phenylimido groups bridge the two uranium centers in an asymmetric fashion in both complexes. The U_2N_2 unit is nearly planar, with a maximum deviation from the plane of 0.02 Å. The U–N bond distances in compound **8** are 2.31(1) and 2.19(1) Å; these distances in $[(MeC_5H_4)_2U(\mu\text{-}NPh)]_2$ are 2.315(4) and 2.156(4) Å. The phenyl groups of the phenylimido ligands are neither parallel nor perpendicular to the U_2N_2 ring plane. The phenyl ring is bent significantly toward one uranium center (U–N–C(11) = 100.3(8)°), resulting in a short contact distance of 2.89(1) Å for U...C(11). This distance is shorter than that found in the complex $[(MeC_5H_4)_2U(\mu\text{-}NPh)]_2$ (3.09(1) Å), longer than that found for the uranium–aryl distance in $Cp_3U(CH_2Ph\text{-}p\text{-}Me)$ (2.51(2) Å) [13] and comparable to other metal–aryl contact distances found either in benzyl complexes [14] or in η^6-arene complexes [15] of the actinides. As has been postulated for the complex $[(MeC_5H_4)_2U(\mu\text{-}NPh)]_2$, the unsymmetrical U–N–C bond angles and U–N bond lengths in **8** are likely the consequence of the complex having one resonance form in which the bridging phenylimido ligands act as η^3-azo-benzyl groups.

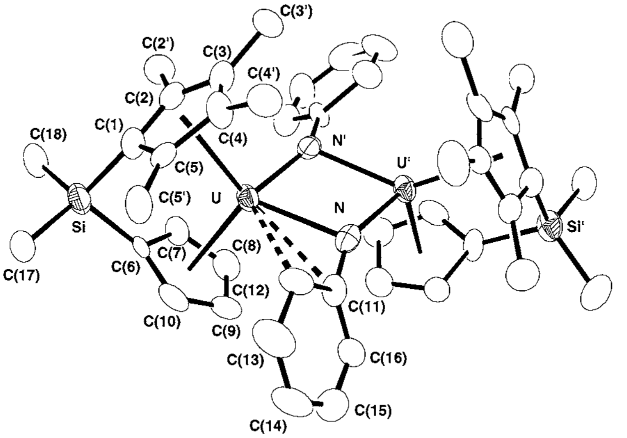


Fig. 2. Thermal ellipsoid plot of $\{[Me_2Si(C_5Me_4)(C_5H_4)]U(\mu\text{-}NPh)\}_2$ (**8**) with atomic numbering scheme.

Table 3
Selected bond lengths (Å) and angles (°) for $\{[Me_2Si(C_5Me_4)(C_5H_4)](\mu\text{-}NPh)\}_2$ (**8**)

Bond lengths			
U–C(1)	2.750 (13)	Si–C(18)	1.855(15)
U–C(2)	2.718(14)	Si–C(17)	1.843(13)
U–C(3)	2.757(15)	N–C(11)	1.371(16)
U–C(4)	2.792(14)	U–N′	2.189(11)
U–C(5)	2.750(13)	U–N	2.311(10)
U–C(6)	2.726(13)		
U–C(7)	2.748(14)		
U–C(8)	2.796(14)		
U–C(9)	2.765(14)		
U–C(10)	2.731(13)		
Bond angles			
N–U–N(0a)	75.4(4)	C(17)–Si–C(18)	109.4(7)
U–N–U(0a)	104.6(4)	Cp′–U–Cp	115.5
U–N–C(11)	100.3(8)	U(0a)–N–C(11)	153.2(9)

2.6. Electrochemistry of $[Me_2Si(C_5Me_4)_2]UCl_2\cdot 2LiCl\cdot 4(Et_2O)$ (*1*) and $[Me_2Si(C_5Me_4)(C_5H_4)]UCl_2\cdot 2LiCl\cdot 4(THF)$ (*2*)

Although clearly the relatively open coordination environment promoted by the $[Me_2Si(C_5Me_4)(C_5H_4)]$ ligand may play a role in the tendency to form a tetravalent product (reduction reactions enhanced by reduced steric constraints), it is also possible that this ligand alters the relative stability of the +4 and +6 formal oxidation states for the uranium center. This is supported by the observation that compound **8** is stable with respect to further oxidation to yield a U(VI) bis(imido) compound; the compound does not react with organoazides. It has previously been reported that introduction of chelating bis(cyclopentadienyl) ligand sets can have a significant impact on the reactivity of a transition metal center. In particular, it has been reported that the silyl (Me_2Si) linked chelating bis(cyclopentadienyl) ligand set can generate more electrophilic metal centers in some complexes, and promote C–H bond activation at metals in other species [16]. In the present study, however, differences in chemistry are observed between two uranium complexes which both contain chelating bis(cyclopentadienyl) ligands. This suggests that the key electronic difference is not the introduction of a bridge between the two Cp ligands, but rather the extent of alkylation of these rings. In order to examine the effect of the substitution pattern of the chelating bis(cyclopentadienyl) ligands on the redox characteristics of the metal center, we have undertaken investigations of the electrochemistry of the parent complexes **1** and **2**. Cyclic voltammetry experiments conducted in THF solution demonstrate a

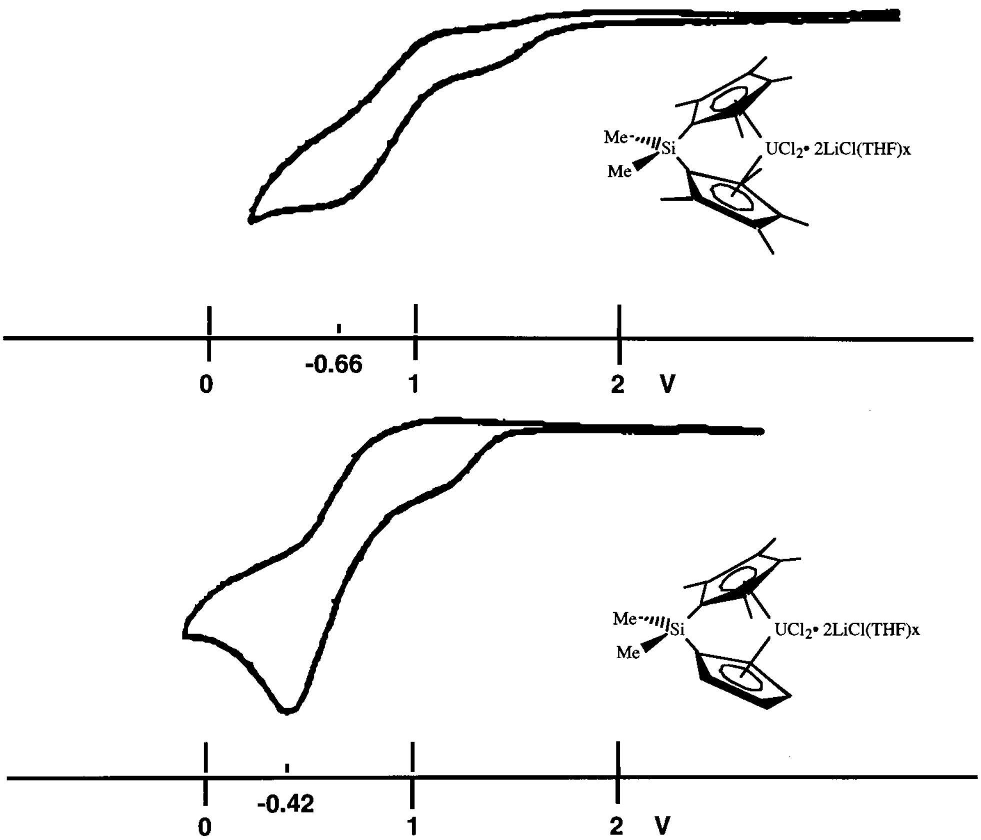


Fig. 3. Cyclic voltammagrams of $[Me_2Si(C_5Me_4)_2]UCl_2{\cdot}2LiCl{\cdot}4(Et_2O)$ (**1**) and $[Me_2Si(C_5Me_4)(C_5H_4)]UCl_2{\cdot}2LiCl{\cdot}4(THF)$ (**2**) (0.10 M $[Bu_4N][BPh_4]$ solution in THF) vs. $FeCp_2/FeCp_2^+$.

substantial difference in the redox potentials of compounds. Both compounds display quasi-reversible oxidation waves at scan rates of approximately 0.20 V s^{-1} (Fig. 3); compound **2** is more difficult to oxidize by approximately 0.24 V(**1**: $E_{1/2} = -0.66$ V; **2**: $E_{1/2} = -0.42$ V versus $FeCp_2/FeCp_2^+$ added as an internal standard). The difference in redox potential of the metal center induced by the different ligands sets of compounds **1** and **2** is greater than that between $(C_5Me_5)_2Ru$ ($E_{1/2} = 0.42$ V) and $(C_5H_5)(C_5Me_5)Ru$ ($E_{1/2} = 0.54$) [17].

3. Conclusions

The chelating bis(cyclopentadienyl) ligand sets $[Me_2Si(\eta^5\text{-}Me_4C_5)_2]^{2-}$ and $[Me_2Si(\eta^5\text{-}Me_4C_5)(\eta^5\text{-}C_5H_4)]^{2-}$ have been introduced to complexes of uranium(IV) in hopes of providing more 'open' and more reactive coordination environments to promote the reactivity of organoimido functional groups bound to the metal center. While structural evidence supports the contention that these ligands generate less steric bulk at the uranium center, their use is not conducive to the isolation of certain classes of compounds, such as U(IV) monoimido compounds produced by protonation of the metallocene dialkyl complexes with substituted anilines. In some cases the chelating ligand sets support the formation higher valent organouranium complexes analogous to species which have been previously isolated using the more traditional $(C_5Me_5)_2U$ ligand framework. The electronic characteristics of the ancillary ligands appear to play a more important role than has previously been identified, however, in the stability of these complexes. Paradoxically, the more electron-rich ancillary ligand sets are required to support uranium complexes in higher formal oxidation states. This is demonstrated by the failure to isolate a U(VI) bis(imido) complex using the less highly alkylated ligand set and $[Me_2Si(\eta^5\text{-}Me_4C_5)(\eta^5\text{-}C_5H_4)]^{2-}$. It is still anticipated that within a class of uranium(VI) compounds, the 'tied-back' ligand set will generate a more reactive complex; with this in mind, we are now examining the reactivity of $[Me_2Si(C_5Me_4)_2]U(NC_6H_5)_2$ to determine if it will be more reactive than its counterpart $(C_5Me_5)_2U(NC_6H_5)_2$.

4. Experimental

All operations were performed using standard Schlenk techniques under UHP-grade argon, or under helium in a Vacuum Atmospheres HE-553-2 drybox with a MO-40-2 Dri-Train. Tetrahydrofuran (THF), diethyl ether (Et_2O), hexane, TMEDA, and toluene were dried and distilled under nitrogen from sodium benzophenone. Benzene-d_6, toluene-d_6, and THF-d_8 were degassed and passed down a short column (5–6 cm) of activated alumina prior to use. Nuclear magnetic resonance (NMR) spectra were recorded on an Bruker 300 MHz spectrometer. Chemical shifts were referenced to protio solvent impurities (δ 7.15, C_6D_6; 1.73, THF-d_8; 2.09, toluene-d_8), and are reported in ppm downfield of Me_4Si. Infrared spectra were obtained in Nujol mulls between KBr plates on a Bio-Rad Digilab FTS 40 spectrophotometer. Elemental analyses were performed on a Perkin–Elmer 2400 CHN analyzer utilizing sealed aluminum capsules for delivery. UCl_4 [18], $[Me_2Si(C_5Me_4)_2]Li_2(THF)_4$ [8d] and $[Me_2Si(C_5Me_4)(C_5H_4)]Li_2(THF)_4$ [8b] were made following published procedures. Grignard reagents and *N*,*N*′-diphenylhydrazine were obtained from Aldrich and used as received.

4.1. *Electrochemistry*

Cyclic voltammetry experiments were carried out in an inert-atmosphere drybox with a PAR/EG&G model 270 electrochemical analysis system. All measurements were conducted in THF solution utilizing 0.10 M $[Bu_4N][BPh_4]$ ($Ph = C_6H_5$) as the supporting electrolyte. The working electrode was a gold disk, and the counter electrode was a platinum wire. A silver wire, separated from the bulk solution by a fine-porosity fritted glass disk, was used as a pseudo-reference electrode. Solution resistance was compensated by electronic positive feedback. Potentials are referenced to the ferrocene/ferrocenium couple used as an internal standard. The measured half-wave potential ($E_{1/2}$) for the ferrocene/ferrocenium internal standard is +0.705 V versus the pseudo-reference electrode at a scan rate of 0.20 V s^{-1}.

4.2. *$[Me_2Si(C_5Me_4)_2]UCl_2\cdot 2LiCl\cdot 4(Et_2O)$ (**1**)*

In the drybox, a 250 ml Erlenmeyer flask equipped with a magnetic stir bar was charged with 2.05 g (5.32 mmol) of UCl_4 and 3.19 g (5.32 mmol) of $[Me_2Si(C_5Me_4)_2]Li_2(THF)_4$. The solids were dissolved in 120 ml of Et_2O and the reaction mixture was allowed to stir at room temperature (r.t.) for 48 h. The mixture was filtered through Celite; removal of the solvent under reduced pressure yielded a dark red–brown solid. The solid was washed with hexane, filtered, and dried under vacuum. Yield 3.92 g (70%). ^{1}H-NMR (300 MHz, C_6D_6): δ −27.3 (bs, $\nu_{1/2} = 2400$ Hz, 12H, (C_5Me_4)), −18.8 (bs, $\nu_{1/2} = 570$ Hz, 6H, Me_2Si), 1.04 (bt, $J = 7.6$ Hz, 24H, Et_2O), 3.14, (bq, $J = 7.6$ Hz, 16H, Et_2O), 52.3 (bs, $\nu_{1/2} = 2400$ Hz, 12H, (C_5Me_4)). IR (cm^{-1}): 1300 m, 1259 m, 1200 w, 1095 w, 1042, w, 890 w, 813 m, 757 m, 721 m. Anal. Calc. for complex (**1**·TMEDA) $C_{32}H_{62}SiUCl_4Li_2N_4$: C, 41.57; H, 6.76; N, 6.06. Found: C, 41.40; H, 6.75; N, 6.03.

4.3. *$[Me_2Si(C_5Me_4)(C_5H_4)]UCl_2\cdot 2LiCl\cdot 4(THF)$ (**2**)*

In the drybox, a 250 ml Erlenmeyer flask equipped with a magnetic stir bar was charged with 2.72 g (7.16 mmol) of UCl_4 and 3.81 g (7.16 mmol) of $[Me_2Si(C_5Me_4)(C_5H_4)]Li_2(THF)_4$. The solids were dissolved in 120 ml of THF and the reaction mixture was allowed to stir at r.t. for 12 h. The mixture was filtered through Celite; removal of the solvent under reduced pressure yielded 5.98 g (90%) of a dark red micro-crystalline solid. ^{1}H-NMR (300 MHz, tol-d_8): δ −60.6 (s, 1H, (C_5H_4)), −52.0 (s, 1H, (C_5H_4)), −41.2 (s, 3H, (C_5Me_4)), −29.4 (s, 3H, (C_5Me_4)), −16.5 (s, 3H, Me_2Si), −14.9 (s, 3H, Me_2Si), −11.48 (s, 16 H, THF), −5.99 (s, 16H, THF), 63.7 (s, 3H, (C_5Me_4)), 65.8 (s, 3H, (C_5Me_4)), 90.7 (s, 1H, (C_5H_4)), 96.2 (s, 1H, (C_5H_4)). IR (cm^{-1}): 1299 m, 1269 m, 1110 w, 1075 w, 1052, w, 990 w, 813 m, 727 m, 701 m. Anal. Calc. for $C_{32}H_{54}SiUCl_4Li_2O_4$: C, 41.57; H, 5.89. Found: C, 41.40; H, 5.88.

4.4. *$[Me_2Si(C_5Me_4)_2]U(CH_3)_2$ (**3**)*

In a drybox, a 250 ml Erlenmeyer flask was charged with 1.09 g (1.10 mmol) of **1,** 120 ml Et_2O, and 1 ml dioxane. At room temperature 0.85 ml (2.3 equivalents, 2.53 mmol) of $ClMgCH_3$ (3M, in THF) was added dropwise, resulting in the formation of a orange solution. Stirring was continued for 2 h, during which time a white suspension formed. The solution was filtered through Celite and the volatiles were removed under reduced pressure to yield a bright orange powder. Recrystallization at −35°C in pentane afforded 0.425 g (68%) of orange needles. ^{1}H-NMR (300 MHz, C_6H_6): δ −49.7 (s, 6H, UMe_2), −7.18 (s, 12H, (C_5Me_4)), −4.37 (s, 6H, Me_2Si), 11.0 (s, 12H, (C_5Me_4)). IR (cm^{-1}): 1312 w, 1250 w, 1022 w, 935 w, 877 w, 833 m, 764 m, 673 m. Anal. Calc. for $C_{22}H_{36}SiU$: C, 46.63; H, 6.40. Found: C, 46.30; H, 6.56.

4.5. *$[Me_2Si(C_5Me_4)_2]U(CH_2C_6H_5)_2$ (**4**)*

In a drybox, a 250 ml Erlenmeyer flask was charged with 2.02 g (2.04 mmol) of **1,** 120 ml toluene, and 1 ml dioxane. At r.t., 4.6 ml (2.3 equivalents, 4.69 mmol) of $ClMgCH_2C_6H_5$ (1 M, in Et_2O) was added dropwise, resulting in the formation of a dark green solution. Stirring was continued for 2 h, during which time a white suspension formed. The solution was filtered through Celite and the volatiles were removed under reduced pressure to yield a dark black–green powder. The solid was washed with a minimum amount of hexane, filtered, and dried in vacuo. Yield: 1.22 g (84%). ^{1}H-NMR (300 MHz, C_6D_6): δ −10.33 (d, $J=$ 6.3 Hz, 4H, *ortho*), −8.00 (s, 6H, Me_2Si), −2.40 (s, 12H, (C_5Me_4)), 1.74 (t, $J=7.6$ Hz, 2H, *para*), 7.38 (t, $J=6.3$ Hz, 4H, *meta*), 15.8 (s, 12H, (C_5Me_4)), 22.63 (bs, 4H, $CH_2C_6H_5$). IR (cm^{-1}): 1576 w, 1320 w, 1250 m, 1109 m, 1077 m, 874 m, 831 m, 803 m, 769 m, 665 w. Anal. Calc. for $C_{34}H_{44}SiU$ C, 56.81; H, 6.17. Found: C, 56.83; H, 6.38.

4.6. [$Me_2Si(C_5Me_4)(C_5H_4)]U(CH_2C_6H_5)_2$ (**5**)

In a drybox, a 250 ml Erlenmeyer flask was charged with 2.02 g (2.18 mmol) of **2**, 120 ml toluene, and 1 ml dioxane. At r.t., 5.0 ml (2.3 equivalents, 5.03 mmol) of $ClMgCH_2C_6H_5$ (1 M, in Et_2O) was added dropwise resulting in the formation of a dark green solution. Stirring was continued for 2 h, during which time a white suspension formed. The solution was filtered through Celite and the volatiles were removed under reduced pressure to yield a dark black–green powder. The solid was washed with a minimum volumn of cold hexane, filtered, and dried in vacuo. Yield: 1.22 g (83%). ^{1}H-NMR (300 MHz, C_6D_6): δ −21.6 (d, $J=7.5$ Hz, 4H, *ortho*), −19.4 (s, 2H, (C_5H_4)), −4.66 (s, 6H, Me_2Si), −3.33 (t, $J=7.6$ Hz, 2H, *para*), −0.63 (s, 6H, (C_5Me_4)), 2.32 (t, $J=7.6$ Hz, 4H, meta), 4.84 (s, 6H, (C_5Me_4)), 9.94 (s, 2H, (C_5H_4)), 29.5, 24.7 (s, 4H, $CH_2C_6H_5$). IR (cm^{-1}): 1676 w, 1333 w, 1252 m, 1006 m, 1037 m, 974 w, 854 m, 813 m, 709 m, 625 m. Anal. Calc. for $C_{34}H_{36}SiU$: C, 57.46; H, 5.11. Found: C, 57.40; H, 5.15.

4.7. [$Me_2Si(C_5Me_4)_2]U(CH_2C_6H_5)Cl$ (**6**)

In a drybox, a scintillation vial was charged with 0.502 g (0.698 mmol) of **4** and 0.067 g (0. 698 mmol) of [$HNMe_3$]Cl; the solids were dissolved in 12 ml of toluene. The reaction was allowed to stir at r.t. for 12 h. The solution was filtered through Celite and the volatiles removed under reduced pressure. The resultant green powder was recrystallized from toluene to give **6** as dark green needles. Yield 0.412 g (89%). ^{1}H-NMR (300 MHz, C_6D_6): δ −35.2 (d, $J=7.6$ Hz, 2H, *ortho*), −13.8 (bs, $CH_2C_6H_5$), −12.2 (s, 3H, $SiMe_2$), −10.3 (t, $J=7.6$ Hz, 1H, *para*), −9.02 (s, 3H, $SiMe_2$), −3.10 (t, $J=7.6$ Hz, 2H, *meta*), 1.78 (s, 6H, (C_5Me_4)), 7.74 (s, 6H, (C_5Me_4)), 11.6 (s, 6H, (C_5Me_4)), 14.8 (s, 6H, (C_5Me_4)). IR (cm^{-1}): 1506 w, 1344 w, 1266 m, 1001 m, 977 m, 884 m, 832 m, 799 m, 769 m, 644 w. Anal. Calc. for $C_{27}H_{37}SiUCl$: C, 48.90; H, 5.62. Found: C, 50.01; H, 5.66.

4.8. [$Me_2Si(C_5Me_4)_2]U(NC_6H_5)_2$ (**7**)

In a drybox, a scintillation vial was charged with 0.502 g (0.886 mmol) of **3** and 0.163 g (0.886 mmol) of $C_6H_5NHNHC_6H_5$; the solids were dissolved in 12 ml of toluene. The reaction was allowed to stir at r.t. for 2 days during which time the color changed from deep black–green to black. The solution was filtered through Celite and the volatiles removed under reduced pressure. The resultant black oil was triturated several times with hexane to give a black powder. Yield 0.588 g (92%). ^{1}H-NMR (300 MHz, C_6D_6): δ 1.03 (s, 6H, Me_2Si), 1.77 (t, $J=7.3$ Hz, 2H, *para*), 3.60 (d, $J=8.3$ Hz, 4H, *ortho*), 3.67 (s, 12H, (C_5Me_4)), 4.67 (s, 12H, (C_5Me_4)), 8.90 (t, $J=7.3$ Hz, 4H, *meta*). IR (cm^{-1}): 1916 w, 1583 s, 1251 s, 1170 m, 1080 w, 1022 w, 987 w, 876 m, 836 m, 756 s, 696 m. Anal. Calc. for $C_{32}H_{40}SiUN_2$: C, 53.47; H, 5.61; N, 3.90. Found: C, 53.26; H, 5.72; N, 3.62.

4.9. [$Me_2Si(C_5Me_4)(C_5H_4)]U(NC_6H_5)]_2$ (**8**)

In a drybox, a scintillation vial was charged with 0.502 g (0.706 mmol) of **5** and 0.130 (0.706 mmol) of $C_6H_5NHNHC_6H_5$; the solids were dissolved in 12 ml of toluene. The reaction was allowed to stir at r.t. for 2 days during which time the color changed from deep black–green to black. The solution was filtered through Celite and the volume of the filtrate was reduced under reduced pressure to 2 ml. Cooling the solution to −34°C for 2 days afforded 0.521 g (65%) of black crystals. ^{1}H-NMR (300 MHz, C_6D_6): δ −57.8 (s, 2H, (C_5H_4)), −22.6 (s, 6H, (C_5Me_4)), −12.4 (t, $J=7.5$ Hz, *para*), −9.92 (bs, 2H, *ortho*), 2.13 (s, 6H, Me_2Si), 7.02 (t, $J=7.5$ Hz, 2H, *meta*), 13.08 (s, 6H, (C_5Me_4)), 29.81 (s, 2H, (C_5H_4)). IR (cm^{-1}): 1923 w, 1251 m, 1175 w, 1109 m, 1076 m, 1043 m, 1021 m, 875 w, 831 m, 806 w, 775 m, 690 w. Anal. Calc. for $C_{22}H_{27}SiNU$: C, 46.23; H, 4.76; N, 2.45. Found: C, 46.29, H, 4.56, N, 2.24.

5. Structural determinations

5.1. [$Me_2Si(C_5Me_4)_2]U(\mu\text{-}Cl_4)\{Li(TMEDA)\}_2$ (**1**·TMEDA)

Complex **1** was dissolved in a minimum amount of toluene, excess TMEDA was added, and the solution was placed in a −40°C refrigerator. After several days, large red plates of complex **1**·TMEDA were obtained. A dark red rectangular plate was attached to a thin glass fiber using silicone grease. The crystal was them immediately placed under a liquid N_2 stream on a Siemens P4/PC diffractometer. Data were collected with graphite monochromatized Mo–K$_\alpha$ radiation ($\lambda=$ 0.71069 Å). The lattice parameters were optimized from a least-squares calculation on 32 carefully centered reflections of high Bragg angles. Three check reflections monitored every 97 reflections showed no systematic variation of intensities. Lattice determination and data collection were carried out using XSCANS Version 2.10b software. All data reduction, including Lorentz and polarization corrections and structure solution and graphics were performed using SHELXTL PC Version 4.2/360 software. The structure refinement was performed using SHELX 93 software [19]. Absorption corrections were performed using the laminar option in the XEMP facility of SHELXTL PC. Data collection parameters are given in Table 1.

5.2. Structure solution and refinement

The space group $P2_1/n$ was uniquely determined by the systematic absences. Patterson techniques were used to locate the uranium and chlorine atom positions. The remaining atoms appeared in subsequent Fourier synthesis. All hydrogen atoms were fixed in positions corresponding to a C–H distance of 0.96 using the HFIX facility in SHELXL 93. The final refinement included anisotropic thermal parameters on all non-hydrogen atoms. Hydrogen atoms had their isotropic temperature factors fixed at 1.2 (ethyl) or 1.5 (methyl) times the equivalent isotropic U of the carbon atom to which they were bonded. The final refinement included anisotropic thermal parameters on all non-hydrogen atoms and converged to $R_1 = 0.0478$ and $wR_2 = 0.0946$.

5.3. $\{[Me_2Si(C_5Me_4)(C_5H_4)]U(NC_6H_5)\}_2$ (**8**)

A black, elongated hexagonal plate was attached to a thin glass fiber using silicone grease. The crystal, which was mounted from a crystallizing dish bathed in argon, was then immediately placed under a liquid N_2 stream on a Siemens P4/PC diffractometer. Data were collected with graphite monochromatized Mo–K_α radiation ($\lambda = 0.71069$ Å). The lattice parameters were optimized from a least-squares calculation on 32 carefully centered reflections of high Bragg angles. Three check reflections monitored every 97 reflections showed no systematic variation of intensities. Lattice determination and data collection were carried out using XSCANS Version 2.10b software. All data reduction, including Lorentz and polarization corrections and structure solution and graphics were performed using SHELXTL PC Version 4.2/360 software. The structure refinement was performed using SHELX 93 software [19]. Absorption corrections were performed using the laminar option in the XEMP facility of SHELXTL PC. Data collection parameters are given in Table 1.

5.4. Structure solution and refinement

The structure was solved in space group $P2/n$ using Patterson techniques, which revealed the uranium and silicon atom positions. The carbon and nitrogen atoms appeared in subsequent Fourier synthesis. All hydrogen atoms were refined using the riding model in the HFIX facility in SHELXL 93. Hydrogen atoms had their isotropic temperature factors fixed at 1.2 (phenyl) or 1.5 (methyl) times the equivalent isotropic U of the carbon atom they were bonded to. One toluene molecule per dimer was found in the lattice and refined with isotropic temperature factors and no hydrogen atoms. The final refinement included anisotropic thermal parameters on all non-hydrogen atoms (except the toluene) and converged to $R_1 = 0.0396$ and $wR_2 = 0.0837$.

6. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 127518 and 127519 for **1**·TMEDA and **8**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ [fax: +44-1223-336-033 or e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk].

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