Lithium Alkyl Anions of Uranium(IV) and Uranium(V). Addition Compounds of Uranium(VI) Hexaisopropoxide with Lithium, Magnesium, and Aluminium Alkyls †

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Organouranium compounds with six or eight uranium-to-carbon σ-bonds have been synthesized for the first time. The interaction of uranium tetrachloride with lithium alkyls in diethyl ether leads to the isolation of unstable lithium alkyluranate(IV) compounds of stoicheiometry $Li_2UR_6·8Et_2O$ (R = Me, CH_2SiMe_3, Ph, and o-$Me_2NCH_2C_6H_4$). These lithium salts can also be obtained with other donor solvents, such as tetrahydrofuran or *NNN'N'*-tetramethylethylenediamine. From uranium pentaethoxide similar lithium salts of stoicheiometry $Li_3UR_8·3$ dioxan (R = Me, CH_2CMe_3, and CH_2SiMe_3) can be obtained. The interaction of uranium(VI) hexaisopropoxide with lithium, magnesium, or aluminium alkyls does not give compounds containing U–C bonds, but green oils, *e.g.*, $U(Pr)_6(MgMe_2)_3$, that appear to be adducts in which the oxygen atom of the isopropoxide group bound to uranium is acting as a donor.

I.r. and n.m.r. spectroscopy and analytical data for the new compounds are presented.

EARLY efforts to prepare binary alkyls and aryls of uranium date back to the search for volatile derivatives to be used in uranium isotope separation. Attempts to synthesize compounds such as tetramethyl- and tetraethyl-uranium were unsuccessful and, to date, the only isolated peralkyl of an actinoid element is tetrabenzylthorium.[1] Following the recognition that, by use of elimination-stabilized alkyl groups such as trimethylsilylmethyl, transition-metal peralkyls may be thermally stable, a uranium complex from UCl_4 was obtained [2a] in petroleum solution; subsequent attempts to isolate this compound were unsuccessful. Similarly, the species generated *in situ* by the interaction of four equivalents of an alkyl-lithium reagent with uranium tetrachloride in diethyl ether or hydrocarbon solvents are very thermally unstable and reactive.[2b] These species were assumed to be ' UR_4 ' and ' a discrete four-connected geometry involving uranium ' was proposed; this formulation is suspect (see later).

In view of the high co-ordination numbers normally found in lanthanoid and actinoid compounds, coupled with the repeated failure to isolate binary uranium alkyls from alkyl-lithium and magnesium reagents (even norbornyl-lithium) we concluded that only highly congested uranium (or other actinoid) alkyls would be kinetically stable, and that the stability should be improved by maximizing the co-ordination number through complex anion formation. This view was supported by the isolation of some thermally stable anionic aryl lanthanoid complexes, notably $[LnPh_4]^-$ (Ln = La or Pr) [3] and $[Ln(2,6\text{-}Me_2C_6H_3)_4]^-$ (Ln = Yb or Lu).[4]

Uranium(IV) tetrachloride and uranium(V) pentaethoxide react with an excess of lithium alkyls to afford the thermally unstable hexa-alkyluranate(IV) and reasonably stable octa-alkyluranate(V) complexes respectively. These are, so far, the only uranium compounds containing more than one uranium-to-carbon σ-bond. However, treatment of uranium(VI) isopropoxide with methyl-lithium, dialkylmagnesium, or trimethylaluminium reagents, affords thermally stable addition complexes having the formulae $(MeLi)_3·U(OPr^i)_6$, $(R_2Mg)_3·U(OPr^i)_6$, and $(Me_3Al)_6·U(OPr^i)_6$ respectively.

Synthesis and Properties of Hexa-alkyluranate(IV) *Complexes.*—Uranium tetrachloride reacts with an excess of alkyl- or aryl-lithium reagents in diethyl ether or a diethyl ether–tetrahydrofuran (thf) mixture to afford thermally unstable hexa-alkyl- or -aryluranate(IV) complexes of stoicheiometry $Li_2UR_6·8Et_2O$ and $Li_2UR_6·8thf$ respectively. Addition of *NNN'N'*-tetramethylethylenediamine (tmed) to diethyl ether solutions of the complexes precipitates the dianion as the adduct, $Li_2UR_6·7tmed$. Details are given in the Experimental section. The compounds and some of their properties are listed in Table 1. It seems likely that the species studied by Marks [2b] were in fact these anionic complexes rather than the neutral ' UR_4 ' species.

TABLE 1

Properties of lithium peralkyluranates

Compound	Colour	Decomp. point (θ_c/°C)	μ_{eff} [a]
Uranium(IV)			
$Li_2UMe_6·8Et_2O$	Olive green	−20	
$Li_2UMe_6·8thf$	Olive green	−15	2.9 (−30)
$Li_2UMe_6·7tmed$	Dark green	−5	2.9 (−30)
$Li_2U(CH_2SiMe_3)_6·8Et_2O$	Light green	30	
$Li_2U(CH_2SiMe_3)_6·8thf$	Light green	30	2.7 (0)
$Li_2U(CH_2SiMe_3)_6·7tmed$	Dark green	35	2.8 (0)
$Li_2UPh_6·8Et_2O$	Red	5	2.7 (−10)
$Li_2U(o\text{-}PhCH_2NMe_2)_6·8Et_2O$	Red	0	
$Li_2U(o\text{-}PhCH_2NMe_2)_6·7tmed$	Red	10	2.7 (−10)
Uranium(V)			
$Li_3UMe_8·3$ dioxan	Pale green	265—268	
$Li_3U(CH_2CMe_3)_8·3$ dioxan	Olive green	120—122	
$Li_3U(CH_2SiMe_3)_8·3$ dioxan	Olive green	150—154	

[a] By Evans' n.m.r. method measured at temperature specified (°C).

The methyl compounds are the least stable, decomposing with gas evolution above −20 °C. The green

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† No reprints available.

[1] E. Kohler, W. Brüser, and K.-H. Thiele, *J. Organometallic Chem.*, 1974, **76**, 235.

[2] (*a*) G. Yagupsky, W. Mowat, A. Shortland, and G. Wilkinson, *Chem. Comm.*, 1970, 1309; (*b*) T. J. Marks and A. M. Seyam, *J. Organometallic Chem.*, 1974, **67**, 61.

[3] F. A. Hart, A. G. Massey, and M. S. Saran, *J. Organometallic Chem.*, 1970, **21**, 147.

[4] S. A. Cotton, F. A. Hart, M. B. Hursthouse, and A. J. Welch, *J.C.S. Chem. Comm.*, 1972, 1225.

trimethylsilylmethyl and red phenyl and 2-(dimethylaminomethyl)phenyl compounds decompose rapidly in solution at room temperature. The solids can be handled for very short periods of time at that temperature without substantial decomposition. They inflame in air and should be handled with great care. (*Note:* we have, on one occasion, experienced a violent explosion when handling the solid at room temperature.) The solids are soluble in polar solvents such as diethyl ether, tetrahydrofuran, and pyridine, slightly soluble in toluene, and insoluble in light petroleum. They are decomposed by trace amounts of oxygen in solvents and by water, dilute acids, and bases. They do not sublime. The solution magnetic moments are very close to the spin-only moment of 2.83 B.M. for two unpaired electrons and consistent with that expected for an ion with a $5f^2$ ground-state configuration.[5]

TABLE 2

N.m.r. spectra of lithium peralkyluranate compounds in pyridine or [$^2H_5$]pyridine

		R				Lewis base			
Compound	θ_c/°C	τ	Multiplicity	Intensity	Assignment	τ	Multiplicity	Intensity	Assignment
Uranium(IV)									
$Li_2UMe_6{\cdot}8Et_2O$	−40	10.51	br s	9	CH_3	6.64	q	16	OCH_2
						8.84	t	24	CH_3
$Li_2UMe_6{\cdot}8thf$	−40	10.44	br s	9	CH_3	6.32	br s	16	OCH_2
						8.22	br s	16	CH_2
$Li_2UMe_6{\cdot}7tmed$	−40	11.20	br s	9	CH_3	7.71	s	14	NCH_2
						7.91	s	42	NCH_3
$Li_2U(CH_2SiMe_3)_6{\cdot}8Et_2O$	0	10.80	s	27	$SiCH_3$	6.64	q	16	OCH_2
		17.82	br s	6	$SiCH_2$	8.98	t	24	CH_3
$Li_2U(CH_2SiMe_3)_6{\cdot}8thf$	0	11.22	s	27	$SiCH_3$	6.51	s	16	OCH_2
		19.63	br s	6	$SiCH_2$	8.25	s	6	CH_2
$Li_2U(CH_2SiMe_3)_6{\cdot}7tmed$	0	10.50	s	27	$SiCH_3$	7.53	s	14	NCH_2
		17.56	br s	6	$SiCH_2$	7.75	s	42	NCH_3
$Li_2UPh_6{\cdot}8Et_2O$	−10	2.90	m	15	CH	6.80	q	16	OCH_2
						9.03	t	24	CH_3
$Li_2U(o\text{-}Me_2NCH_2C_6H_4)_6{\cdot}Et_2O$	−10	3.05	m	24	CH	6.64	q	32	OCH_2
		7.13	s	12	NCH_2	8.95	t	48	CH_3
		8.12	s	36	NCH_3				
$Li_2U(o\text{-}Me_2NCH_2C_6H_4)_6{\cdot}7tmed$	0	2.98	m	24	CH	7.48	s	28	NCH_2
		7.10	s	12	NCH_2	7.70	s	84	NCH_3
		8.20	s	36	NCH_3				
Uranium(V)									
$Li_3UMe_8{\cdot}3$ dioxan	35	8.70	br s	1	CH_3	6.66	s	1	OCH_2
$Li_3U(CH_2Bu^t)_8{\cdot}3$ dioxan	35	7.85	br s	2	CH_2	6.68	s	3	OCH_2
		9.32	s	9	CH_3				
$Li_3U(CH_2SiMe_3)_8{\cdot}3$ dioxan	35	8.56	br s	2	CH_2	6.66	s	3	OCH_2
		10.2	s	9	CH_3				
$U_2(OEt)_{10}$ [a]	35	−4.54	br s	2	CH_2				
		7.99	br s	3	CH_3				

[a] In benzene.

The compounds react with acetic acid (containing a little acetic anhydride) at −70 °C giving alkane and uranium(IV) acetate. Lithium hexamethyluranate(IV) reacts with carbon dioxide at −70 °C and 1 atm affording a small amount of uranium(IV) acetate although substantial decomposition, as evidenced by gas evolution and concomitant metal deposition, occurs. The anions also react with protic solvents such as methanol, diethylamine, and acetylacetone giving uranium(IV) methoxide,[6] diethylamide,[6] and acetylacetonate [7] respectively. The complexes are not oxidized to neutral hexa-alkyluranium(VI) by air, hydrogen peroxide, benzoyl peroxide, t-butyl peroxide, chlorine, bromine, or iodine. Lithium hexamethyluranate(IV) reacts with carbon monoxide, nitric oxide, nitrosyl chloride, ethylene, and tetramethylphosphonium chloride affording brown or black intractable solids from which no isolable uranium complexes could be characterized.

The n.m.r. spectra (Table 2) were recorded at low temperature in pyridine or [$^2H_5$]pyridine. In general the signals assigned to protons on the α-carbon of the alkyl groups are shifted upfield and broadened substantially (width at half peak height 10—20 Hz) while protons further removed from the paramagnetic centre exhibit very small isotropic shifts and very little broadening. The spectra do not change on cooling or heating (to just below the decomposition temperature of the compound).

The i.r. spectrum of the hexakis(trimethylsilylmethyl)uranate(IV) complexes (the others were too unstable to be studied) have the expected bands due to solvent and trimethylsilylmethyl vibrations. Significantly, the region between 2 600 and 2 850 cm^{-1}, where low C–H stretches indicative of Li–H_3C interactions occur, was clear, suggesting that the complexes exist as discrete ions in the solid and that they may be formulated as

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[6] R. G. Jones, G. Karmas, G. A. Martin, jun., and H. Gilman, *J. Amer. Chem. Soc.*, 1956, **78**, 4285.

[7] H. Gilman, R. G. Jones, E. Bindschadler, D. Blume, G. Karmas, G. A. Martin jun., J. F. Nobis, J. R. Thirtle, H. L. Yale, and F. A. Yoeman, *J. Amer. Chem. Soc.*, 1956, **78**, 2790.

$[LiS_4]_2[UR_6]$, where S is a solvent molecule. It is useful to compare these complexes with the anionic complexes $[Li(thf)_4][Lu(2,6\text{-}Me_2C_6H_3)_6]$,[4] and $[Li(thf)_4]_2[U(C_2B_9H_{11})_2Cl_2]$.[8] Single-crystal *X*-ray studies of these complexes show that the cation and anion exist as discrete ions with no interaction between the lithium atom, which is tetrahedrally co-ordinated by the oxygen atoms of the tetrahydrofuran, and the ligands bound to the 4 or 5*f* metal ion. For the complexes $Li_2UR_6\cdot 8S$ (S = Et_2O or thf), it seems reasonable to propose that they may be formulated as $[LiS_4]_2[UR_6]$.

Unless *NNN'N'*-tetramethylethylenediamine acts as a unidentate ligand, the complexes of stoicheiometry $Li_2UR_6\cdot 7$tmed would require a formulation $[Li(tmed)_2]_2[UR_6(tmed)_3]$, thus invoking a complex anion with twelve-co-ordinate uranium. High co-ordination numbers for uranium(IV) are not unusual and the metal appears to have a higher affinity towards nitrogen donors, forming $UCl_4\cdot 8NH_3$, $UCl_4\cdot 4$pip, and $UCl_4\cdot 4$en, whereas oxygen donors give complexes such as $UCl_4\cdot 3$thf.[9] However, the bond between the amine and the complex anion must be quite labile as the thermal stability of the tmed complexes is not significantly greater than that of the ether complexes.

Synthesis and Properties of Octa-alkyluranate(V) *Complexes*.—The interaction of uranium(V) pentaethoxide, $U_2(OEt)_{10}$, with an excess of alkyl-lithium reagents in light petroleum or light petroleum–diethyl ether mixtures affords, on addition of dioxan, the thermally stable green octa-alkyluranate(V) complexes, $Li_3UR_8\cdot 3$dioxan [R = Me, CH_2CMe, and CH_2SiMe_3 (Table 1)]. The thermal stability decreases in the order methyl > trimethylsilylmethyl > neopentyl, which reflects the increasing steric crowding around the metal and implies that the uranium atom is co-ordinatively saturated. In saturated compounds the reverse trend is generally observed, with the neopentyl and trimethylsilylmethyl complexes being significantly more stable than the corresponding methyl derivative.

Despite the larger effective ionic radius of uranium(IV) compared with uranium(V), we were unable to prepare the analogous octa-alkyluranate(IV), $[UR_8]^{4-}$. This may be explained by assuming that addition of a seventh alkyl group to $[UR_6]^{2-}$ will reduce the effective nuclear charge experienced by each ligand and hence reduce the U–C bond energy. The energy gained by forming a seventh or eighth U–C bond must be less than the energy lost in breaking the methyl-lithium bonds. Other factors, such as geometry and bond lengths, undoubtedly contribute to this trend.

The uranium(V) compounds do not sublime and cannot be chromatographed. They are readily soluble in polar solvents such as diethyl ether, tetrahydrofuran, and pyridine, but are insoluble in toluene and light petroleum. Trace amounts of oxygen in the solvents decompose the compounds and the solids are slowly turned red by the small amount of oxygen in ordinary 'oxygen-free' nitrogen. They inflame in air and are decomposed by water, alcohol, dilute acids, and bases.

The compounds react with acetic acid (containing a little acetic anhydride) giving an insoluble green solid the analysis for which corresponds to its formulation as $UO(CO_2Me)_3$; it is probably an equimolar mixture of $U(CO_2Me)_4$ and $UO_2(CO_2Me)_2$. The same material is produced from the reaction between uranium(V) pentaethoxide and acetic acid, and between octamethyluranate(V) and carbon dioxide. Carbon disulphide also inserts into the uranium–methyl bond, but the product could not be purified. The anions also react with ethanol affording lithium hexaethoxyuranate(V),[10] and with acetylacetone yielding, upon hydrolysis, uranyl(VI) acetylacetonate.[11] The reaction of the anions with hydrogen peroxide, benzoyl peroxide, di-t-butyl peroxide, carbon monoxide, nitric oxide, sulphur dioxide, ethylene, ethanethiol, diethylamine, 1,1,1,3,3,3-hexamethyldisilazane, and tetramethylphosphonium chloride affords brown or black intractable solids from which no isolable uranium complexes could be isolated.

The i.r. spectra (Table 3) of the solid octa-alkyluranate complexes contain the expected bands due to alkyl and dioxan vibrations. In addition, two weak absorptions are present in each case at *ca*. 2 700 and 2 600 cm^{-1}. These are the low C–H stretches indicative of Li–H_3C interactions.[12] A molecular structure with eight alkyl groups surrounding the uranium atom in a dodecahedral or bicapped trigonal prism or antiprism geometry with each lithium atom complexed by one dioxan and bridging a face is consistent with these facts.

TABLE 3

Infrared spectra of uranium(V) compounds

$[Li(dioxan)]_3$ $[UMe_8]$	$[Li(dioxan)]_3$ $[U(CH_2Bu^t)_8]$	$[Li(dioxan)]_3$ $[U(CH_2SiMe_3)_8]$	$U_2(OEt)_{10}$ [a]
			2 960s
2 710w	2 705w	2 695w	2 884s
2 598w	2 600w	2 600w	1 438w
1 852w	1 355s	1 246s	1 367m
1 155sh	1 238vs	1 103s	1 348m
1 095s	1 105s	1 055s	1 120sh
1 050s	1 052s	884m	1 088s
965w	930m	875sh	1 045s
880m	882m	858m	1 018m
825w	753s	836m	898s
718m		719m	872m
		691m	624w

[a] Film of pure liquid.

As with the uranium(IV) complexes, substantial broadening of the α-protons of the alkyl group is observed in the n.m.r. spectra (Table 2) although the dioxan resonance is quite sharp. The isotropic shift for the uranium(V) complexes is downfield.

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[11] H. I. Schlesinger, H. C. Brown, J. J. Katz, S. Archer, and R. A. Lad, *J. Amer. Chem. Soc.*, 1953, **75**, 2446.

[12] R. A. Andersen, E. Carmona Guzman, J. F. Gibson, and G. Wilkinson, *J.C.S. Dalton*, 1976, 2204.

Synthesis and Properties of Some Uranium(VI) *Addition Complexes*.—Uranium hexachloride is an unsuitable starting material for the preparation of uranium(VI) alkyls, being readily reduced to uranium metal at low temperatures by trimethylaluminium in light petroleum,[13] and reacting vigorously with solvents such as diethyl ether. The only other practical uranium(VI) starting materials are the alkoxides.[14]

TABLE 4

N.m.r. spectra of uranium(VI) compounds in benzene

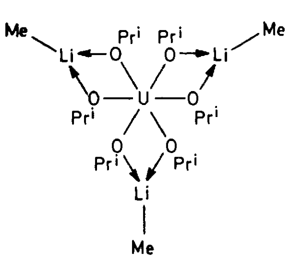
	OPr^i				R			
Compound	τ	Multiplicity [a]	Intensity	Assignment	τ	Multiplicity	Intensity	Assignment
U(OPr^i)$_6$	1.98	h	1	CH				
		J = 10 Hz						
	8.33	d	6	CH$_3$				
U(OPr^i)$_6$(MeLi)$_3$	5.94	h	2	CH	10.9	s	3	CH$_3$
		J = 9 Hz						
	8.48	d	12	CH$_3$				
U(OPr^i)$_6$(Me$_3$Mg)$_3$	6.26	h	1	CH	10.7	s	3	CH$_3$
		J = 10 Hz						
	8.74	d	6	CH$_3$				
U(OPr^i)$_6${(CH$_2$Bu^t)$_2$Mg}$_3$	6.38	h	1	CH	9.65	s	2	CH$_2$
		J = 10 Hz						
	8.65	d	6	CH$_3$	8.60	s	9	CH$_3$
U(OPr^i)$_6${(CH$_2$SiMe$_3$)$_2$Mg}$_3$	6.24	h	1	CH	10.1	s	2	CH$_2$
		J = 10 Hz						
	8.45	d	6	CH$_3$	9.75	s	9	CH$_3$
U(OPr^i)$_6$(Me$_3$Al)$_6$	6.74	h	1	CH	10.4	s	9	CH$_3$
		J = 10 Hz						
	8.91	d	6	CH$_3$				

[a] h = heptet

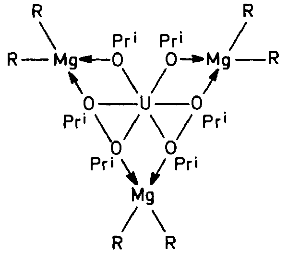
Uranium(VI) isopropoxide does not react with alkyllithium reagents to form complex alkyl anions. Solid, ether-free methyl-lithium readily dissolves in a light petroleum solution of uranium(VI) isopropoxide and forms the 3 : 1 addition complex, (LiMe)$_3$·U(OPr^i)$_6$. Addition of three equivalents of trimethylsilylmethyl- or neopentyl-lithium to uranium(VI) isopropoxide affords similar green oils, which do not react with an excess of alkyl-lithium, as is shown by the appearance of free RLi in the n.m.r. spectrum. Similarly, dimethyl-, dineopentyl-, and bis(trimethylsilylmethyl)-magnesium react with uranium isopropoxide to form (MgR$_2$)$_3$·U(OPr^i)$_6$, while trimethylaluminium forms a 6 : 1 adduct (AlMe$_3$)$_6$·U(OPr^i)$_6$. The compounds are thermally stable oils which cannot be chromatographed or sublimed. They are very soluble in common organic solvents such as light petroleum, benzene, and diethyl ether and do not react with Lewis bases. While not pyrophoric, they decompose in air and react rapidly with water, alcohol, dilute acids, and bases.

Very few mixed alkyl-alkoxide bimetallic complexes appear to be known. The reaction of sodium t-butoxide with diethylberyllium yields the dimeric {NaBeEt$_2$(OBu^t)}$_2$ [15] while beryllium t-butoxide reacts [16] with tiimethylaluminium giving (AlMe$_3$)·{Be(OBu^t)$_2$}$_3$ which is monomeric in benzene. Complexes of this type are not known for the lanthanoids and actinoids but some covalent bimetallic alkoxides, La{Al(OPr^i)$_4$}$_3$,[17] Pr{Al(OPr^i)$_4$}$_3$,[17] Ca{U(OEt)$_6$}$_2$,[10] and Al{U(OEt)$_6$}$_3$,[10] and bimetallic alkyls, Ln(C$_5$H$_5$)$_2$(AlMe$_4$),[18] have been reported. These complexes are covalent, highly soluble, often sublimable solids containing bridging alkyl- or alkoxy-groups.

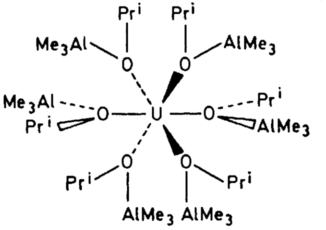
The n.m.r. spectrum (Table 4) of the methyl-lithium complex exhibits a single sharp methyl resonance at 10.9 and the heptet and doublet of the isopropyl group at 5.94 and 8.48 respectively. The position of the methyl resonance is only slightly downfield from the resonance position of methyl-lithium in diethyl ether, which suggests that a structure (I) in which lithium is solvated by oxygen donors is reasonable.



(I)



(II)



(III)

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[15] R. A. Andersen and G. E. Coates, *J.C.S. Dalton*, 1974, 1729.

[16] R. A. Andersen and G. E. Coates, *J.C.S. Dalton*, 1972, 2153.

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[18] J. Holton, M. P. Lappert, G. R. Scollary, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter, *J.C.S. Chem. Comm.*, 1976, 425.

The alkyl resonances of the dialkylmagnesium complexes, $(\text{MgR}_2)_3\cdot\text{U(OPr}^i)_6$, are also just downfield from the position of the corresponding dialkylmagnesium in diethyl ether, indicating that the alkyl groups are probably bound to a magnesium atom which is solvated by two oxygen donors. The structure (II) seems likely for these compounds.

The fact that uranium(VI) isopropoxide requires six equivalents of trimethylaluminium for complete reaction reflects the tendency of aluminium to achieve four-co-ordination. We suggest that each trimethylaluminium group is bound by an oxygen lone pair of the isopropoxy-groups. Free trimethylaluminium is not formed even when the oil is heated to 200 °C *in vacuo*. Since the n.m.r. spectrum shows only one methyl resonance, it is unlikely that any of the methyl groups had transferred to uranium, and we propose structure (III).

EXPERIMENTAL

Spectroscopic Instruments.—N.m.r. spectra were recorded on a Perkin-Elmer R12A (60 MHz) spectrometer. Signal positions are reported on the τ scale using hexamethyldisiloxane or benzene as the internal standard. I.r. spectra were obtained on Perkin-Elmer model 257 to 457 spectrometers.

TABLE 5

Analytical data [Found (required) %]

Compound	Li, Mg, or Al	U	Alkyl : Base [a]
$\text{Li}_2\text{UMe}_6\cdot8\text{Et}_2\text{O}$			2.08(Li) : 1(U) : 5.83(CH_3)
$\text{Li}_2\text{UMe}_6\cdot8\text{thf}$			2.02(Li) : 1(U) : 5.93(CH_3)
$\text{Li}_2\text{UMe}_6\cdot7\text{tmed}$			2.03(Li) : 1(U) : 5.99(CH_3)
$\text{Li}_2\text{U(CH}_2\text{SiMe}_3)_6\cdot8\text{Et}_2\text{O}$	0.98 (1.02)	17.6 (17.4)	6 : 8
$\text{Li}_2\text{U(CH}_2\text{SiMe}_3)_6\cdot8\text{thf}$	0.99 (1.04)	17.9 (17.6)	6 : 8
$\text{Li}_2\text{U(CH}_2\text{SiMe}_3)_6\cdot7\text{tmed}$	0.81 (0.87)	14.5 (15.0)	6 : 7
$\text{Li}_2\text{UPh}_6\cdot8\text{Et}_2\text{O}$	0.95 (1.07)	18.3 (18.2)	6 : 8
$\text{Li}_2\text{U(}o\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_6\cdot8\text{Et}_2\text{O}$	0.81 (0.85)	13.8 (14.4)	6 : 8
$\text{Li}_2\text{U(}o\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_6\cdot7\text{tmed}$	0.81 (0.87)	14.4 (14.9)	6 : 7
$\text{Li}_3\text{UMe}_8\cdot3$ dioxan	3.3 (3.3)	37.4 (37.0)	8 : 3
$\text{Li}_3\text{U(CH}_2\text{Bu}^t)_8\cdot3$ dioxan	1.2 (1.3)	21.6 (22.0)	8 : 3
$\text{Li}_3\text{U(CH}_2\text{SiMe}_3)_8\cdot3$ dioxan	1.6 (1.7)	19.3 (19.5)	8 : 3
$\text{U(OPr}^i)_6(\text{MeLi})_3$	3.3 (3.2)	36.4 (36.2)	
$\text{U(OPr}^i)_6(\text{Me}_2\text{Mg})_3$	10.3 (9.7)	30.0 (31.5)	
$\text{U(OPr}^i)_6\{(\text{Me}_3\text{CCH}_2)_2\text{Mg}\}_3$	7.0 (6.7)	22.0 (21.8)	
$\text{U(OPr}^i)_6\{(\text{Me}_3\text{SiCH}_2)_2\text{Mg}\}_3$	6.2 (6.1)	19.8 (20.1)	
$\text{U(OPr}^i)_6(\text{Me}_3\text{Al})_6$	10.4 (10.0)	25.8 (25.5)	

[a] CH_3 determined as CH_4 on hydrolysis. Other alkyls (as RH on hydrolysis) to base ratio by n.m.r.

Preparations.—All preparations and other operations were carried out under oxygen-free nitrogen or argon, or in a vacuum unless otherwise stated. Solvents were dried, distilled, and degassed prior to use. Light petroleum used had b.p. 40—60 °C.

Uranium tetrachloride was obtained from the U.K.A.E.A , Harwell, or was made by refluxing UO_3 with hexachloropropene; uranium(V) ethoxide [19] and uranium(VI) isopropoxide [20] were prepared by literature methods; uranyl chloride was prepared by treating uranium tetrachloride with oxygen at 300 °C or by heating the monohydrate to 250—280 °C under a stream of dry hydrogen chloride for 36 h.

Methyl- [21] and phenyl-lithium [22] were prepared in diethyl ether as *ca.* 1M-solutions; neopentyl- and trimethylsilylmethyl-lithium were prepared by the same method in hexane; [23] 2-[(dimethylamino)methyl]phenyl-lithium was prepared by the metallation of *NN*-dimethylbenzylamine with n-butyl-lithium.[24] The synthesis of the dialkylmagnesium reagents, dimethyl-, bisneopentyl- and bis(trimethylsilylmethyl)-magnesium, has been described.[25] Trimethylaluminium was from the Ethyl Corporation.

CAUTION. The lithium alkyluranate(IV) complexes particularly should be handled with great care since they may explode unpredictably.

Analyses.—Analytical data for the compounds are collected in Table 5.

Analyses of the compounds for C and H by standard microanalytical techniques were consistently low by 10—25% due to incomplete combustion. This phenomenon has been observed for other organo-actinoids [1] and lanthanoids [4] and appears to be due to carbide formation.

The low thermal stability of hexamethyluranate(IV) complexes precluded weighing so that we could only determine the ratio Li : U : CH_3. The CH_3 was determined by alcoholysis with isopropyl alcohol and measurement of CH_4 with a gas burette; the Li and U were determined on the same sample.

The other uranium compounds were analysed for Li and U and for the ratio of the alkyl group to the Lewis base; the latter was done by adding one drop of water to deuteriotoluene solutions in an n.m.r. tube and then integrating the alkane *vs.* donor resonances. Metal analyses were made using a plasma emission spectrometer by the Trace Analysis Laboratory, Imperial College. Metal and conventional microanalyses were by Butterworth Microanalytical Consultancy Ltd.

Dilithium Hexaphenyluranate(IV)*-Diethyl Ether* (1/8).—Phenyl-lithium (35 ml of a 0.97M-solution, 34 mmol) was added dropwise to a suspension of UCl_4 (2.2 g, 5.8 mmol) in diethyl ether (20 ml) at −70 °C. The mixture was warmed

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to and stirred at −5 °C for 4 h. After filtration the volume was reduced to *ca.* 15 ml and the solution was stored at −70 °C for 24—48 h to precipitate unchanged phenyl-lithium. Addition of chilled, light petroleum to the ether filtrate yielded a red *solid*, which was washed with chilled, light petroleum and dried *in vacuo* at −20 °C (yield *ca.* 45%).

Dilithium Hexamethyluranate(IV)*–Diethyl Ether* (1/8).—(*a*) Methyl-lithium (6.7 ml of a 0.90M-solution, 6.0 mmol) was added dropwise to a suspension of UCl_4 (0.38 g, 1.0 mmol) in diethyl ether (7 ml) at −70 °C. The mixture was warmed to −25 °C and stirred for 2 h. After filtration the green solution was reduced to *ca.* 10 ml and cooled to −70 °C for 24—48 h to precipitate unchanged MeLi. Chilled, light petroleum was added to the solution at −30 °C yielding a green *powder*. The product was washed with cold, light petroleum (2 × 5 ml) and dried *in vacuo* at −70 °C (yield *ca.* 70%).

(*b*) The reaction between methyl-lithium (4.5 ml of a 0.90M-solution, 4.0 mmol) and UCl_4 (0.38 g, 1.0 mmol) afforded, after filtration to remove unchanged UCl_4 (*ca.* 50%) and precipitation, a green *powder* (yield *ca.* 45%). These were the conditions used by Marks[2b] and it is clear that he was dealing with the lithium salt.

Dilithium Hexamethyluranate(IV)*–Tetrahydrofuran* (1/8). Methyl-lithium (6.7 ml of a 0.90M-solution, 6.0 mmol) was added dropwise to a solution of UCl_4 (0.38 g, 1.0 mmol) in tetrahydrofuran (7 ml) at −70 °C. After being warmed to −25 °C and stirred for 1 h the solution was filtered and the green filtrate evaporated at −20 °C. After extraction with chilled Et_2O (3 × 10 ml), the ether solution was reduced to 10 ml and cooled to −70 °C for 24—48 h. The small amount of MeLi which separated was removed and chilled, light petroleum added to the green solution at −30 °C. The green *solid* was collected, washed with cold diethyl ether (1 × 2 ml) and light petroleum (2 × 5 ml), and dried *in vacuo* at −70 °C (yield *ca.* 65%).

Dilithium Hexamethyluranate(IV)*–tmed* (1/7).—(a) *NN-N'N'*-Tetramethylethylenediamine was added to an ethereal solution of dilithium hexamethyluranate(IV) at −70 °C. The green solution was warmed slowly to −20 °C and stirred for 2 h. Concentration of the solution, filtration at −70 °C (to remove most of the unchanged tmed), and slow addition to the filtrate of chilled, light petroleum yielded a dark green *powder*. The solid was washed with cold, light petroleum and dried *in vacuo* at −70 °C.

(*b*) An ether solution of methyl-lithium (2.9 ml of a 0.90M-solution, 26 mmol) was evaporated to dryness and heated *in vacuo* at 100 °C for 16 h. The solid was suspended in light petroleum (40 ml) and tmed (4 ml) at −70 °C and UCl_4 (0.25 g, 6.6 mmol) were added. As the mixture was warmed to −20 °C a black oil formed. The oil was washed with chilled, light petroleum (2 × 10 ml) and was then extracted by chilled diethyl ether. Addition of chilled, light petroleum to the ether extracts at −40 °C gave the dark green *powder* (yield *ca.* 40% based on UCl_4).

Dilithium Hexakis(*trimethylsilylmethyl*)*uranate*(IV)*–Diethyl Ether* (1/8).—Trimethylsilylmethyl-lithium (40 ml of a 0.93M-solution, 37 mmol) was added dropwise to a suspension of UCl_4 (2.31 g, 6.10 mmol) in diethyl ether (40 ml) at −70 °C. After being warmed to 0 °C and stirred for 1 h, the solution was cooled to −70 °C and filtered. The solvent was removed *in vacuo* at −10 °C and the product extracted with a minimum amount of diethyl ether. Addition of chilled, light petroleum gave a green *solid* which was washed thoroughly with chilled, light petroleum and dried *in vacuo* at −20 °C (yield *ca.* 80%).

Dilithium Hexakis(*trimethylsilylmethyl*)*uranate*(IV)*–Tetrahydrofuran* (1/8).—Trimethylsilylmethyl-lithium (15 ml of a 0.95M-solution, 14 mmol) was added dropwise to a solution of UCl_4 (0.55 g, 1.45 mmol) in thf (15 ml) at −70 °C. With rapid stirring, the mixture was warmed to 0 °C and stirred for 1 h. The solvent was removed *in vacuo* at 0 °C and the residue extracted with a minimum of chilled diethyl ether. Addition of chilled, light petroleum to the green solution at −70 °C yielded a dark green *solid* which was washed with chilled, light petroleum and dried *in vacuo* at 0 °C (yield *ca.* 65%). I.r. (Nujol): 1 250s, 1 235sh, 1 078w, 1 070sh, 1 020s, 860s, 740w, 730m, and 668w cm^{-1}. The magnetic moment of the solid, as determined by the Gouy method, was μ_{eff} (296 K) 2.72 B.M.

Dilithium Hexakis(*trimethylsilylmethyl*)*uranate*(IV)*–tmed* (1/7).—(*a*) An ethereal solution of hexakis(trimethylsilylmethyl)uranate(IV) was prepared as above, from UCl_4 (1.37 g, 3.60 mmol) and Me_3SiCH_2Li (24 ml of a 0.95M-solution, 22 mmol). The solution was cooled to −70 °C and tmed (4 ml) was added slowly. The solution was warmed to 0 °C and the volume reduced to *ca.* 10 ml. Addition of chilled, light petroleum produced a dark-green *solid* which was washed with chilled, light petroleum and dried *in vacuo* at 0 °C.

(*b*) Trimethylsilylmethyl-lithium (4.2 ml of a 0.95M-solution, 4.0 mmol) was added slowly to a rapidly stirred suspension of UCl_4 (0.38 g, 1.0 mmol) and tmed (1 ml) in light petroleum (20 ml) at −70 °C. The suspension was warmed to 0 °C and stirred for 1 h to yield a heavy black oil. The solvent was decanted, and the oil was washed with chilled, light petroleum (4 × 10 ml); the resulting green product was extracted with chilled ether. Some unchanged UCl_4 remained. Addition of chilled, light petroleum to the ether extracts at 0 °C precipitated the dark green *solid* (yield *ca.* 55%). I.r. (Nujol): 1 270sh, 1 248s, 1 045w, 1 030s, 845s, and 735w cm^{-1}. Magnetic moment (Gouy method) μ_{eff} (296 K), 2.77 B.M.

Dilithium Hexakis{*2-*[(*dimethylamino*)*methyl*]*phenyl*}*uranate*(IV)*–Diethyl Ether* (1/8).—n-Butyl-lithium (3.85 ml of a 2.6M-solution, 10 mmol) was added to a solution of benzyldimethylamine (1.35 g, 10 mmol) in diethyl ether (20 ml). After being stirred overnight, the product was filtered off and the lithium reagent suspended in diethyl ether (30 ml). Uranium tetrachloride (0.62 g, 1.6 mmol) was added slowly to the rapidly stirred suspension at −70 °C. The mixture was warmed to 0 °C and stirred for 4 h. The solution was filtered, the volume reduced to *ca.* 10 ml, and chilled, light petroleum was added. The red *solid* was filtered off, washed with chilled, light petroleum, and dried *in vacuo* at 0 °C (yield *ca.* 65%).

Dilithium Hexakis{*2-*[(*dimethylamino*)*methyl*]*phenyl*}*uranate*(IV)*–tmed* (1/7).—A solution of hexakis{2-[(dimethylamino)methylphenyl}uranate(IV) in diethyl ether at −70 °C was treated with an excess of tmed. The solution was warmed to 0 °C and the volume was reduced. Addition of chilled, light petroleum precipitated a red *solid* which was washed with chilled, light petroleum and dried *in vacuo* at 0 °C (yield *ca.* 70%).

Trilithium Octamethyluranate(V)*–Dioxan* (1/3).—Methyl-lithium (30 ml of a 0.98M-solution, 30 mmol) was added dropwise to a light petroleum (30 ml) solution of uranium pentaethoxide (0.54 ml, 2.0 mmol) at −70 °C. The mixture was warmed to room temperature and stirred for 1 h. Dioxan (5 ml) was added dropwise to the green solution, precipitating a light green solid which was filtered off, washed with light petroleum (2 × 20 ml), and extracted with diethyl ether (2 × 20 ml). The combined extracts were concentrated to *ca.* 10 ml and cooled to −70 °C. The light green *crystals* were collected, washed with cold diethyl ether (2 × 5 ml), and dried *in vacuo* (yield 0.52 g, 81%).

Trilithium Octakis(trimethylsilylmethyl)uranate(v)*-Dioxan* (1/3).—Trimethylsilylmethyl-lithium (21 ml of a 0.75M-solution, 16 mmol) was added slowly to a solution of $U_2(OEt)_{10}$ (0.54 ml, 2.0 mmol) in light petroleum (30 ml) at −70 °C. The reaction was warmed to room temperature and stirred for 16 h. Dioxan (6 ml) was added to the brown solution at room temperature, precipitating a green solid. After filtration, the solid was extracted with thf (2 × 20 ml) and the combined extracts were reduced in volume to *ca.* 5 ml; the solid was precipitated by addition of light petroleum (20 ml). The light green *solid* was washed with diethyl ether (10 ml) and light petroleum (2 × 10 ml) and dried *in vacuo* (yield 1.8 g, 74%).

Trilithium Octaneopentyluranate(v)*-Dioxan* (1/3).—Neopentyl-lithium (19 ml of a 0.84M-solution, 16 mmol) was added slowly to a light petroleum (30 ml) solution of uranium pentaethoxide (0.54 ml, 2.0 mmol) at −70 °C. After warming to room temperature the solution was stirred for 24 h. The reaction was filtered and addition of dioxan (3 ml) precipitated a green solid which was filtered off, washed with light petroleum (2 × 10 ml), and dried *in vacuo*. Recrystallization from tetrahydrofuran–light petroleum afforded a light green *solid* (yield 1.4 g, 65%).

Uranium(vi) *Hexa(isopropoxide)-Methyl-lithium* (1/3).—(*a*) Methyl-lithium (2.8 ml of a 0.90M-solution, 2.5 mmol) was evaporated to dryness and heated to 150 °C *in vacuo* for 24 h to remove the co-ordinated diethyl ether. The unsolvated methyl-lithium was suspended in light petroleum (5 ml) at −70 °C and a light petroleum (5 ml) solution of uranium(vi) isopropoxide (0.50 g, 0.85 mmol) was added dropwise. The reaction was warmed to room temperature and stirred overnight to afford a green solution and a white solid. (The solid was identified by n.m.r. spectroscopy in diethyl ether as unchanged methyl-lithium.) The solution was filtered and the solvent removed to yield a green *oil*.

(*b*) A large excess of methyl-lithium in diethyl ether was added to an ethereal solution of uranium(vi) isopropoxide. After careful drying to remove all diethyl ether the same product was isolated by extracting the residue with light petroleum.

Uranium(vi) *Hexa(isopropoxide)-Dimethylmagnesium* (1/3).—(*a*) Dimethylmagnesium (1.1 ml of a 0.75M-solution, 0.82 mmol) was added dropwise to a solution of uranium(vi) isopropoxide (0.16 g, 0.27 mmol) in light petroleum (10 ml) at −70 °C. The reaction was warmed to room temperature and stirred for 1 h to afford a clear green solution and no precipitate. Removal of the solvent *in vacuo* for 5—6 h afforded a green oil free of diethyl ether. The product was extracted with light petroleum (2 × 5 ml) and the combined extracts were evaporated to yield a green *oil*.

(*b*) An identical product was obtained when the addition was reversed, *i.e.* when a diethyl ether solution of uranium(vi) isopropoxide was added to a diethyl ether solution of dimethylmagnesium at −70 °C.

(*c*) Solid dimethylmagnesium was heated to 150 °C under high vacuum for 16 h and suspended in light petroleum at −70 °C. Addition of a light petroleum solution of uranium(vi) isopropoxide afforded the same product described in (*a*).

Uranium(vi) *Hexa(isopropoxide)-Bis(trimethylsilylmethyl)-magnesium* (1/3).—(*a*) Bis(trimethylsilylmethyl)magnesium (1.0 ml of a 1.2M solution, 1.2 mmol) was added slowly to a light petroleum solution of uranium(vi) isopropoxide (0.23 g, 0.39 mmol). The reaction was warmed to room temperature and stirred overnight. Removal of solvent and extraction with light petroleum gave a green *oil*.

(*b*) Unsolvated bis(trimethylsilylmethyl)magnesium was prepared by heating the diethyl ether solvate *in vacuo* at 140 °C. The white solid was suspended in light petroleum at −70 °C and a light petroleum solution of uranium(vi) isopropoxide was added slowly. Warming to room temperature afforded the same product described in (*a*).

(*c*) Reverse addition of the same reactants in diethyl ether also afforded the green oil described in (*a*).

Uranium(vi) *Hexa(isopropoxide)-Bis(neopentyl)magnesium* (1/3).—(*a*) Bis(neopentyl)magnesium (2.3 ml of a 1.1M-solution, 2.5 mmol) was added slowly to a light petroleum (50 ml) solution of uranium(vi) isopropoxide (0.50 g, 0.85 mmol) at −70 °C. The reaction was warmed slowly to room temperature and stirred for 16 h. The solvent was evaporated and the green oil dried at room temperature *in vacuo* for 5—6 h. The product was extracted into light petroleum. Removal of solvent afforded a green *oil*.

(*b*) Addition of a diethyl ether solution of uranium(vi) isopropoxide to bis(neopentyl)magnesium at −70 °C afforded the green oil as above.

(*c*) Unsolvated bis(neopentyl)magnesium in light petroleum was cooled to −70 °C and a light petroleum solution of uranium(vi) isopropoxide was added. The reaction was warmed to room temperature to give the same green oil.

Uranium(vi) *Hexa(isopropoxide)-Trimethylaluminium* (1/6).—Trimethylaluminium (5.4 ml of a 0.50M-solution in light petroleum, 2.7 mmol) was added slowly to a light petroleum (20 ml) solution of uranium(vi) isopropoxide (0.25 g, 0.42 mmol) at −70 °C. No visible reaction occurred at −70 °C but warming to room temperature afforded a clear green solution. The solvent was removed and the product heated to 50 °C under high vacuum for 4—5 h to yield a green *oil*.

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