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Synthesis and structures of some silylallyl-lithium or -potassium complexes

Peter B. Hitchcock,[a] Michael F. Lappert,*[a] Wing-Por Leung,[b] Dian-Sheng Liu,[b] Thomas C. W. Mak[b] and Zhong-Xia Wang[a]

[a] *The Chemistry Laboratory, University of Sussex, Brighton, UK BN1 9QJ. E-mail: M.F.Lappert@sussex.ac.uk*
[b] *Department of Chemistry, The Chinese University of Hong Kong, Shatin, NT, Hong Kong*

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The η[3]-1,3-bis(silyl)allyllithium [Li{η^3-CH(CHSiMe$_2$Bu^t)(CHSiMe$_2$R)}(tmen)] (R = Bu^t or Me) and 1,3-bis(trimethylsilyl)cyclohexenyllithium [Li{C(SiMe$_3$)CHC(SiMe$_3$)(CH$_2$)$_2$CH$_2$}(tmen)] complexes were obtained by lithiation of the appropriate 1,3-bis(silyl)propene or 1,3-bis(trimethylsilyl)cyclohexene. The lithium complexes were transformed into the potassium complexes [K{CH(CHSiMe$_2$Bu^t)$_2$}] or [K{C(SiMe$_3$)CHC(SiMe$_3$)(CH$_2$)$_2$CH$_2$}] by reaction with KOBu^t. A dimethylsilyl *ansa*-bridged bis(cyclohexenyl)dipotassium complex [{K$_2${(η^3-C$_6$H$_4$SiMe$_3$-6)$_2$SiMe$_2$}(thf)$_3$}$_\infty$] was obtained by a similar route. Single crystal structures of three complexes have been determined.

Allyls and substituted allyls of alkali metals have been the subject of extensive investigations of their chemistry,[1–6] molecular structures by X-ray crystallography,[7–13] solution structures by NMR spectroscopy[14–18] and by calculation.[19–24] These compounds display an astonishing variety of properties that vary with substituents, temperature and especially the nature of coligands.

The allyl ion is one of the simplest π-electron systems. Structural studies of allylalkali metal compounds showed interesting features,[7–13] which were recently reviewed by Weiss.[13]

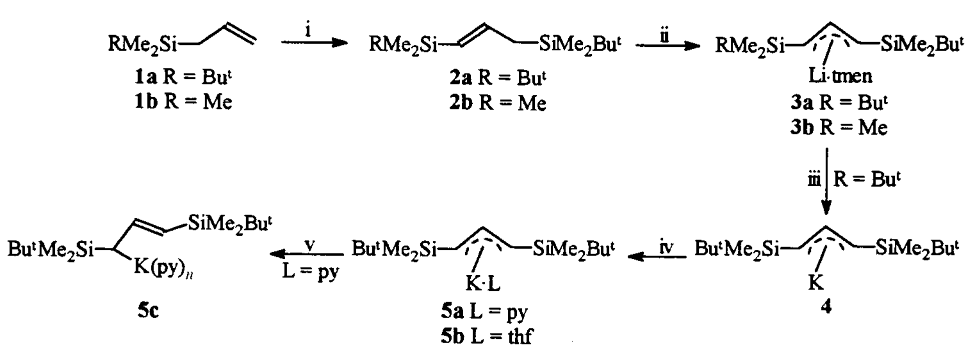
The structures of α-silylallyl anions in solution have been extensively studied by Fraenkel and co-workers[17,18,25] using NMR spectroscopy. The (trimethylsilyl)allyl anion seemed to adopt exclusively an *exo* orientation. This is to be contrasted with simple alkylallyl anions, which tend to exist as a mixture of *exo* and *endo* isomers, with the latter generally predominating.[26,27] A neutral ligand, such as tmen or pmdeta [(Me$_2$NCH$_2$CH$_2$)$_2$NMe], when co-ordinated to 1,3-bis(trimethylsilyl)allyllithium or 1,1,3-tris(trimethylsilyl)allyllithium also adopted an *exo* orientation in solution. The crystal structure of crystalline [Li{C$_3$H$_3$(SiMe$_3$)$_2$-1,3}(tmen)] showed that it has the *exo*,*exo* orientation.[11]

In a preliminary publication[28] we have briefly described an exploration of the synthesis and reactions of 1,3-bis(silyl)allyllithium or -potassium compounds. We now provide: (i) details on these compounds, (ii) the synthesis of related compounds and (iii) structures of crystalline complexes.

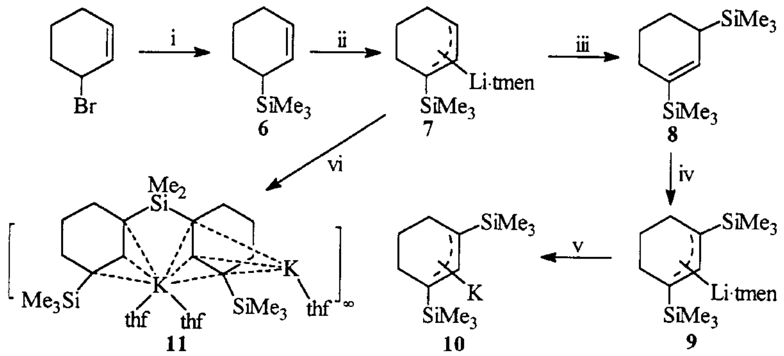
Results and discussion

The two 1,3-bis(silyl) propenes RMe$_2$SiC(H)=CHCH$_2$SiMe$_2$Bu^t (R = Bu^t **2a** or Me **2b**) were prepared from the appropriate 3-silylpropene C$_3$H$_5$SiMe$_2$R (R = Bu^t **1a** or Me **1b**) (i in Scheme 1) by successive lithiation and quenching with Bu^{t}Me$_2$SiF. Although **1a** was a known compound, having been synthesized by the reaction of Bu^{t}Me$_3$SiCl with CH$_2$=CHCH$_2$MgBr,[29] no physical or analytical data had been reported. We obtained **1a** from Bu^{t}Me$_2$SiF and CH$_2$=CHCH$_2$MgBr. Each propene **1a** or **1b** was lithiated by the addition of LiBu^n to a stirred solution in the presence of tmen in hexane, and then treated *in situ* with Bu^{t}Me$_2$SiF to form the appropriate 1,3-bis(silyl)propene **2a** or **2b**. 1,3-Bis(trimethylsilyl)cyclohexene **8** was prepared similarly (i–iii in Scheme 2). Thus, 3-bromocyclohexene was converted into 3-trimethylsilylcyclohexene **6** by successive treatment with magnesium and quenching with Me$_3$SiCl; and **6** upon lithiation and then addition of Me$_3$SiCl afforded **8**.

The silylallyllithium compound [Li{η^3-C$_6$H$_8$(SiMe$_3$)}(tmen)] **7** and the 1,3-bis(silyl)allyllithium complexes [Li{η^3-CH(SiMe$_2$Bu^t)CHCH(SiMe$_2$R)}(tmen)] (R = Bu^t **3a** or Me **3b**) and [Li{C$_6$H$_7$(SiMe$_3$)$_2$-1,3}(tmen)] **9** were prepared from the appropriate silyl- or bis(silyl)-alkene. *n*-Butyllithium was added to a stirred solution of the silyl-substituted alkenes **2a**, **2b**, **6** or **8** and tmen in hexane at room temperature and the mixture was stirred overnight (and refluxed for 2 h for the case of **2a**) to yield the silylallyllithium–tmen complexes **3a**, **3b** (ii in Scheme 1), **7**



Scheme 1 i, LiBu^n, tmen, hexane, 0 °C to room temperature, 12 h, then Bu^{t}Me$_2$SiF, room temperature 1 h and reflux 6 h; ii, LiBu^n, tmen, hexane, −78 °C to room temperature, 12 h; iii, KOBu^t, hexane, room temperature, 4 h; iv, pyridine or thf, hexane; v, pyridine.



Scheme 2 i, Mg, Et_2O, Me_3SiCl, 0 °C, 12 h; ii, $LiBu^n$, tmen, hexane, room temperature, 12 h; iii, Me_3SiCl, hexane, −78 °C to room temperature, 4 h; iv, $LiBu^n$, tmen, hexane, room temperature, 12 h; v, $KOBu^t$, hexane, room temperature, 12 h; vi, Me_2SiCl_2, hexane, −78 °C to room temperature, 12 h then $LiBu^n$, tmen, room temperature, 12 h and then $KOBu^t$, 12 h, recrystallisation in thf–hexane.

or **9** (ii or iv in Scheme 2). Upon treatment of **3a** or **9** with an equimolar amount of $KOBu^t$ in hexane at room temperature the corresponding tmen-free potassium complex **4** (iii in Scheme 1) or **10** (v in Scheme 2) was precipitated. From **3b** and $KOBu^t$ under the same conditions only an unidentified brown solution was obtained.

Crystallisation of complex **4** from hexane in the presence of pyridine (py) or thf yielded (iv in Scheme 1) the adducts $[K\{\eta^3\text{-}CH(CHSiMe_2Bu^t)_2\}L]$ (L = py **5a** or thf **5b**). The crystalline dimethylsilyl *ansa*-bis(silylcyclohexenyl)dipotassium complex $[K_2[(\eta^3\text{-}C_6H_4SiMe_3\text{-}6)_2SiMe_2](thf)_3\}_\infty]$ **11** was obtained from **7** by several steps in a one-pot reaction sequence. A dimethylsilyl-bridged bis(cyclohexene), presumably formed from **7** and Me_2SiCl_2, was lithiated by $LiBu^n$ and tmen; the product was further treated with $KOBu^t$ and crystallisation in the presence of thf gave **11**.

The identity of each of the air-stable silyl-substituted alkenes **1a**, **2a**, **2b**, **6** and **8** was established by their ^1H NMR, IR and (for **1a**, **2a** and **2b**) GC-MS spectra, as well as (for **2a** and **2b**) elemental analysis. The lithium complexes **3a**, **3b**, **7** and **9** were obtained as air-sensitive, colourless crystals, soluble in hexane or pentane and purified by crystallisation from hexane or pentane. They were characterised by elemental analyses (**3a** and **3b**) and ^1H (**3a**, **3b**, **7** and **9**) and (for **3a** and **3b**) $^{13}C\text{-}\{^1H\}$, $^7Li\text{-}\{^1H\}$ and $^{29}Si\text{-}\{^1H\}$ NMR spectra. These data were consistent with the formulae shown in Schemes 1 and 2. Thus, the ^1H NMR spectra in C_6D_6 showed the η^3 co-ordination mode of each allylic ligand; in addition, complex **3a** (but not the less hindered **3b**) showed the presence of magnetically inequivalent methyls attached to the same silicon atom. This is attributed to the greater restriction to rotation about the silicon–allyl–carbon bond in the more hindered of the two compounds. The same distinction between **3a** and **3b** was also observed in the ^{13}C NMR spectrum. It may be that at a lower temperature the $SiMe_2Bu^t$ methyls in **3b** would also have shown inequivalence.

The solid white (**4**) or yellow (**10**) potassium complexes were insoluble in pentane or hexane. Their pyridine (**5a**) or thf (**5b** or **11**) adducts were hydrocarbon-soluble, crystalline solids. They were characterised by elemental analyses (**4**, **5a** and **5b**) and ^1H (**4**, **5a**, **5b**, **10** and **11**), $^{13}C\text{-}\{^1H\}$ (**4**, **5a** and **5b**) and $^{29}Si\text{-}\{^1H\}$ (**5a**) NMR spectra. The ^1H NMR spectrum of each neutral donor adduct **5a** and **5b** was consistent with the η^3-allylic co-ordination mode in the non-co-ordinating C_6D_6 or $C_6D_5CD_3$. However, when the ^1H NMR spectrum of the allylpotassium complex **4** was recorded in $[^2H_5]$pyridine it showed three sets of different allyl proton signals. This is attributed to the co-ordination of pyridine to potassium (v in Scheme 1) to yield the σ-allylmetal complex $[K\{C(H)(SiMe_2Bu^t)C(H)CHSiMe_2Bu^t\}\text{-}(py)_n]$ (**5c** $n \geq 2$), due to steric repulsion between the co-ordinated pyridines and the $SiMe_2Bu^t$ group. Attempts to crystallise the adduct **5c** by adding pyridine to **4** in hexane failed. The ^1H NMR spectrum of complex **10** in C_6D_6 (2 parts) and C_5D_5N (1 part) was somewhat similar to that of **4**, but a little more complicated. It showed two sets of trimethylsilyl signals and two sets of allyl proton signals, respectively, in a ratio of 1 to 3. This may have been due to the formation of a mixture of σ-allylmetal complexes **10a** [**10**·*n*py] (1 part) and **10b** (**10**·*m*py) (3 parts) ($n \neq m$).

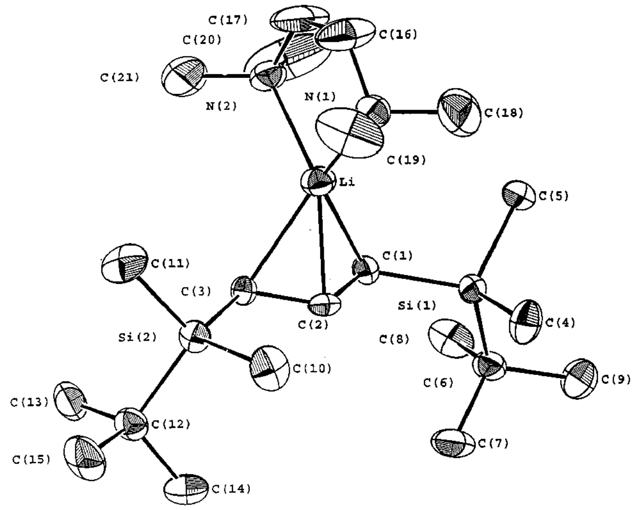
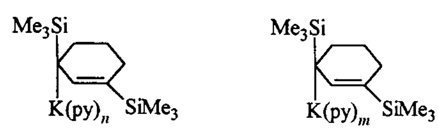


Fig. 1 An ORTEP[30] representation of the molecular structure of crystalline complex **3a**.



10a **10b**

An interesting difference between the lithium compound $[Li\{\eta^3\text{-}CH(CHSiMe_2Bu^t)_2\}(tmen)]$ **3a** and the related potassium compounds **4**, **5a** and **5b** is that each of the latter showed singlets, rather than the two singlets for **3a**, in their ^1H NMR spectra (see Experimental section). This may be because the potassium complexes are loose ion pairs, with weak potassium–ligand contacts.

Crystal structures of the bis(silyl)allyllithium complexes 3a and 9

The molecular structures with the atom numbering schemes of the crystalline complexes **3a** and **9** are shown in Figs. 1 and 2, respectively. Selected bond distances and angles are listed in Tables 1 and 2.

Crystalline complex **3a** is a monomer with an η^3-co-ordination mode of ligand to metal and *exo,exo* orientation of the *tert*-butyldimethylsilyls. The lithium atom lies almost symmetrically above the allyl group, the Li–C(2) distance of 2.11(2) Å being slightly shorter than the Li–C(1) and Li–C(3)

Table 1 Selected intramolecular distances (Å) and angles (°) for complex **3a**

Li–N(1)	2.13(2)	Li–N(2)	2.09(2)
Li–C(1)	2.23(2)	Li–C(2)	2.11(2)
Li–C(3)	2.22(2)	Si(1)–C(1)	1.844(7)
C(1)–C(2)	1.415(10)	Si(2)–C(3)	1.848(8)
C(2)–C(3)	1.408(9)		
N(1)–Li–N(2)	86.2(6)	N(1)–Li–C(1)	133.0(6)
N(1)–Li–C(2)	130.4(7)	N(1)–Li–C(3)	134.6(8)
N(2)–Li–C(1)	119.9(7)	N(2)–Li–C(2)	143.4(8)
N(2)–Li–C(3)	119.1(6)	C(1)–Li–C(2)	38.0(4)
C(1)–Li–C(3)	69.0(5)	C(2)–Li–C(3)	37.8(4)
Li–N(1)–C(16)	103.1(7)	Li–N(2)–C(17)	104.0(7)
Li–C(1)–Si(1)	124.9(5)	Li–C(1)–C(2)	66.6(6)
Li–C(2)–C(1)	75.4(6)	Li–C(2)–C(3)	75.4(6)
Li–C(3)–C(2)	66.8(5)	Li–C(3)–Si(2)	126.4(5)
C(1)–C(2)–C(3)	126.5(6)		

Table 2 Selected intramolecular distances (Å) and angles (°) for complex **9**

Li(1)–N(2)	2.145(7)	Li(1)–C(2)	2.395(7)
Li(1)–C(6)	2.428(7)	C(2)–C(3)	1.541(5)
C(1)–Li(1)	2.140(6)	Li(1)–N(1)	2.116(7)
C(2)–Si(2)	1.305(4)	C(6)–Si(1)	1.792(4)
C(1)–C(6)	1.379(5)	C(1)–C(2)	1.412(4)
C(3)–C(4)	1.460(6)	C(4)–C(5)	1.490(5)
C(5)–C(6)	1.537(6)		
N(1)–Li(1)–C(1)	152.2(4)	N(1)–Li(1)–N(2)	86.0(2)
C(1)–Li(1)–N(2)	121.5(3)	N(1)–Li(1)–C(2)	129.3(3)
N(2)–Li(1)–C(2)	130.6(3)	N(1)–Li(1)–C(6)	126.6(4)
N(2)–Li(1)–C(6)	127.3(3)	C(2)–Li(1)–C(6)	63.20(17)
C(1)–C(2)–C(3)	112.8(3)	C(6)–C(1)–C(2)	129.8(3)
C(1)–C(2)–Si(2)	125.4(3)	C(3)–C(2)–Si(2)	121.1(2)
Si(2)–C(2)–Li(1)	118.2(2)	C(4)–C(3)–C(2)	114.9(3)
C(3)–C(4)–C(5)	114.8(4)	C(4)–C(5)–C(6)	113.6(4)
C(1)–C(6)–C(5)	115.2(3)	C(1)–C(6)–Si(1)	126.6(3)
C(5)–C(6)–Si(1)	116.6(3)	Si(1)–C(6)–Li(1)	121.3(2)

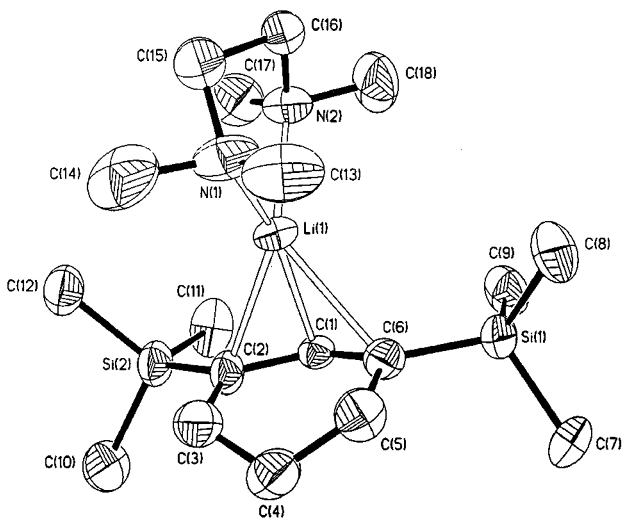


Fig. 2 An ORTEP representation of the molecular structure of crystalline complex **9**.

distances, average 2.22(3) Å; this corresponds to the situation found in other allyllithium compounds[7–13] and most allyltransition metal complexes.[31] The C(1)–C(2) and C(2)–C(3) bond lengths are closely similar, average 1.41(2) Å. Comparison with the structure of $[Li\{C_3H_3(SiMe_3)_2\text{-}1,3\}(tmen)]$[11] reveals that complex **3a** has the more symmetrical structure.

The molecular structure of crystalline complex **9** shows it also to be monomeric. Compared with **3a**, the structure of **9** has somewhat longer Li–C distances, the central Li–C [C(1)] bond of 2.140(6) Å being shorter than the Li–C(Si) [C(2) and C(6)] bonds, average 2.412(7) Å. Noteworthy features are the very different bond distances for C(1)–C(2) [1.412(4) Å] and C(1)–C(6) [1.379(5) Å] in complex **9**, corresponding to a formal double and single bond, respectively. The C(2)–C(1)–C(6) angle of 129.8(3)° is almost the same as that subtended at the central carbon of $[Li\{\eta^3\text{-}CH(CHSiMe_3)_2\}(tmen)]$ [129.4(4)°],[11] but is bigger than that in **3a** [126.5(6)°]. Perhaps **9** is better formulated as a σ- (or η^1)-allyllithium, rather than an η^3-allyllithium compound.

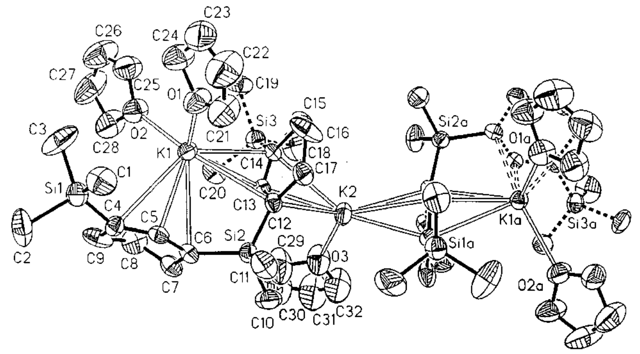


Fig. 3 An ORTEP representation of the structure of crystalline complex **11**.

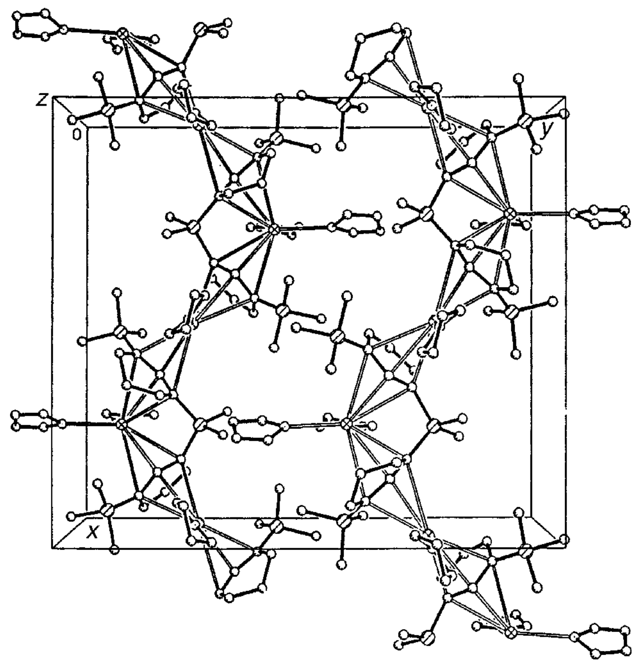


Fig. 4 The unit cell of crystalline complex **11**.

Crystal structure of the dimethylsilyl-*ansa*-bis(cyclohexenyl)-potassium complex 11

The molecular structure of the crystalline complex **11**, with the atom numbering scheme, is shown in Fig. 3, the unit cell in Fig. 4 and selected bond distances and angles in Table 3. The crystalline complex **11** is a polymer with different co-ordination environments for successive potassium atoms, one co-ordinated by the *ansa*-bridged bis(cyclohexenyl) and the other between two such ligands. The three disordered thf molecules in an asymmetric unit of the cell have a half occupancy. The potassium atoms make contact with the allyl units of the cyclohexenyls in an asymmetric manner, the K–C distances ranging from 2.932(6) to 3.350(7) Å, which are comparable to those in $[K\{\eta^4\text{-}N(SiMe_2Bu^t)C(Bu^t)(CH)_3SiMe_2Bu^t\}]_\infty$[28] or $[\{K[C(SiMe_3)_3]\}_\infty]$.[32] The various C–C distances of the allyl units of the cyclohexenyls are in the narrow range 1.374(8) to 1.386(9) Å.

Table 3 Selected intramolecular distances (Å) and angles (°) for complex **11**

K(1)–O(2)	2.726(7)	K(1)–O(1)	2.734(8)
K(1)–C(13)	2.932(6)	K(1)–C(5)	2.942(6)
K(1)–C(12)	3.141(7)	K(1)–C(6)	3.201(7)
K(1)–C(4)	3.329(7)	K(1)–C(14)	3.350(7)
K(1)–Si(2)	3.727(3)	K(2)–O(3)	2.706(9)
K(2)–C(13)	2.951(6)	K(2)–C(14)	3.084(7)
K(2)–C(12)	3.184(7)	K(2)–C(15)	3.412(11)
K(2)–C(17)	3.484(10)	C(4)–C(5)	1.386(9)
C(4)–C(9)	1.520(10)	C(5)–C(6)	1.380(9)
C(6)–C(7)	1.510(9)	C(7)–C(8)	1.493(12)
C(8)–C(9)	1.533(13)	C(12)–C(13)	1.374(8)
C(12)–C(17)	1.498(9)	C(13)–C(14)	1.381(9)
C(14)–C(15)	1.536(10)	C(14)–Si(3)	1.799(8)
C(15)–C(16)	1.476(12)	C(16)–C(17)	1.453(12)
O(2)–K(1)–O(1)	109.2(2)	O(2)–K(1)–C(13)	116.1(2)
O(1)–K(1)–C(13)	118.4(2)	O(2)–K(1)–C(5)	119.0(2)
O(1)–K(1)–C(5)	99.1(2)	C(13)–K(1)–C(5)	93.48(19)
O(2)–K(1)–C(12)	142.0(2)	O(1)–K(1)–C(12)	99.8(2)
C(13)–K(1)–C(12)	25.86(16)	C(5)–K(1)–C(12)	78.53(17)
O(2)–K(1)–C(6)	124.1(2)	O(1)–K(1)–C(6)	115.6(2)
C(13)–K(1)–C(6)	68.68(17)	C(5)–K(1)–C(6)	25.52(17)
C(12)–K(1)–C(6)	58.20(18)	O(2)–K(1)–C(4)	95.9(2)
O(1)–K(1)–C(4)	101.0(2)	C(13)–K(1)–C(4)	113.00(17)
C(5)–K(1)–C(4)	24.56(16)	C(12)–K(1)–C(4)	102.29(17)
C(6)–K(1)–C(4)	45.22(16)	O(2)–K(1)–C(14)	99.6(2)
O(1)–K(1)–C(14)	112.7(2)	C(13)–K(1)–C(14)	24.25(16)
C(5)–K(1)–C(14)	117.64(17)	C(12)–K(1)–C(14)	45.23(17)
C(6)–K(1)–C(14)	92.53(17)	C(4)–K(1)–C(14)	135.31(17)
O(2)–K(1)–Si(2)	146.48(19)	O(1)–K(1)–Si(2)	103.91(18)
C(13)–K(1)–Si(2)	47.99(12)	C(12)–K(1)–Si(2)	29.90(12)
C(13)–K(2)–C(14)	26.34(16)	C(13)–K(2)–C(12)	25.52(16)
C(14)–K(2)–C(12)	47.05(18)	C(13)–K(2)–C(15)	44.93(19)
C(14)–K(2)–C(15)	26.74(18)	C(12)–K(2)–C(15)	53.1(2)
O(3)–K(2)–C(17)	137.6(2)	C(13)–K(2)–C(17)	43.29(17)
C(14)–K(2)–C(17)	52.46(19)	C(12)–K(2)–C(17)	25.46(16)
C(15)–K(2)–C(17)	43.2(2)	C(5)–C(4)–K(1)	61.9(4)
C(9)–C(4)–K(1)	100.8(4)	Si(1)–C(4)–K(1)	101.0(3)
C(6)–C(5)–C(4)	130.6(7)	C(6)–C(5)–K(1)	87.8(4)
C(4)–C(5)–K(1)	93.5(4)	C(5)–C(6)–K(1)	66.7(4)
C(7)–C(6)–K(1)	101.9(5)	Si(2)–C(6)–K(1)	91.2(2)
C(8)–C(7)–C(6)	113.4(7)	C(7)–C(8)–C(9)	115.3(8)
C(4)–C(9)–C(8)	110.5(7)	C(6)–Si(2)–K(1)	59.2(2)
C(13)–C(12)–K(1)	68.5(4)	C(17)–C(12)–K(1)	101.2(5)
C(13)–C(12)–K(2)	67.7(4)	C(17)–C(12)–K(2)	88.5(4)
K(1)–C(12)–K(2)	135.1(2)	C(12)–C(13)–C(14)	130.6(6)
C(12)–C(13)–K(1)	85.6(4)	C(14)–C(13)–K(1)	95.1(4)
K(1)–C(13)–K(2)	167.2(2)	K(2)–C(14)–K(1)	130.6(2)

Experimental

All reactions were performed under argon using standard Schlenk techniques. The thf and diethyl ether were dried using sodium–benzophenone, hexane and pentane using sodium–potassium alloy. The compound Bu^tMe_2SiF was prepared according to a published procedure.[32] Allyltrimethylsilane was purchased from Aldrich. The NMR spectra were recorded on AC-P250, WM-360 and AMX-500 instruments, and the solvent resonances were used as the internal references for ^{1}H and ^{13}C spectra; LiCl (1 mol dm^{-3} aqueous solution) was the external reference for ^{7}Li NMR spectra. The IR spectra were recorded on a Perkin-Elmer 1720 FT spectrometer as liquid films or Nujol mulls using KBr windows. The GC-MS data were recorded on a MD800 apparatus: EI, 70 eV. Elemental analyses were carried out by Medac Ltd., Brunel University. Melting points were determined under argon in sealed capillaries on an electrothermal apparatus and were uncorrected.

Preparations

$Bu^tMe_2SiCH_2CH=CH_2$ 1a. Allylmagnesium bromide (0.25 mol), prepared from $CH_2=CHCH_2Br$ (30.25 g, 0.25 mol) and magnesium turnings (6.5 g, 0.27 mol) in diethyl ether (150 cm^3), was mixed with *tert*-butyldimethylsilyl fluoride (25 g, 0.187 mol) and the mixture refluxed for 15 h. After cooling, water (100 cm^3) was added. The organic layer was separated and dried ($CaCl_2$); diethyl ether was then removed *in vacuo* and the residue distilled to give the colourless oil **1a** (26.0 g, 90%), bp 150–155 °C. ^{1}H NMR (298 K, $CDCl_3$): δ −0.03 (s, 6 H, $SiMe_2$), 0.91 (s, 9 H, $SiBu^t$), 1.56 (d, 2 H, J = 8.3 Hz), 4.82–4.90 (m, 2 H) and 5.76–5.88 (m, 1 H). GC-MS: m/z = 156 (M^+). IR (liquid film): $\tilde{\nu}_{max}$/cm^{-1} 3079w, 2955vs, 2930vs, 2884s, 2858s, 1632m, 1471m, 1392w, 1363w, 1253s, 1155m, 1039w, 1008w, 992w, 893s, 838s, 750w and 658m.

$RMe_2SiCH=CHCH_2SiMe_2Bu^t$ (R = Bu^t 2a or Me 2b). *n*-Butyllithium (26.5 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 42.4 mmol) was added dropwise at 0 °C with stirring to a solution of *tert*-butyldimethylsilylpropene (6.5 g, 41.7 mmol) and tmen (6.3 cm^3, 41.8 mmol) in hexane (50 cm^3), and stirred overnight at room temperature. *tert*-Butyldimethylsilyl fluoride (5.6 g, 41.8 mmol) was added at room temperature. The mixture was stirred for 1 h and then heated at 75–80 °C for 6 h. The tmen was removed by column chromatography and the eluent distilled under vacuum to obtain colourless crystals of compound **2a** (11.3 g, 91%) (Found: C, 66.2; H, 12.7. $C_{15}H_{34}Si_2$ requires C, 66.6; H, 12.7%), mp 52.5–54 °C. ^{1}H NMR (298 K, C_6D_6): δ −0.04 (s, 6 H, $SiMe_2$), 0.10 (s, 6 H, $SiMe_2$), 0.88 (s, 9 H, $SiBu^t$), 0.99 (s, 9 H, $SiBu^t$), 1.65 (d, 2 H, J = 7.9, CH_2), 5.54 (d, 1 H, J = 17.6 Hz, CH) and 6.08–6.18 (m, 1 H, CH). ^{13}C NMR (298 K, $CDCl_3$): δ −6.46, −5.92, 16.61, 16.81, 24.69, 26.50, 26.58, 125.06 and 145.43. IR (Nujol): $\tilde{\nu}_{max}$/cm^{-1} 2953vs, 2926vs, 2855vs, 1604m, 1463m, 1377w, 1251w, 1143w, 1007w, 989w, 938w, 840w, 823w, 806w, 752vw and 723vw.

Compound **2b** was prepared similarly. Trimethylsilylallyllithium [prepared from trimethylsilylpropene (3.6 g, 31.6 mmol), tmen (4.8 cm^3, 31.8 mmol) and $LiBu^n$ (20 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 32 mmol)] was treated with *tert*-butyldimethylsilyl fluoride (4.3 g, 32.1 mmol). The resultant solution was distilled, after removing tmen by column chromatography, to produce the colourless oil **2b** (5.84 g, 81%) (Found: C, 62.1; H, 12.0. $C_6H_{14}Si$ requires C, 63.1; H, 12.4%), bp 50–52 °C (0.5 Torr). NMR (298 K, $CDCl_3$): ^{1}H, δ −0.02 (s, 6 H, $SiMe_2$), 0.07 (s, 9 H, $SiMe_3$), 0.93 (s, 9 H, $SiBu^t$), 1.68 (d, 2 H, J = 6.8, CH_2), 5.47 (d, 1 H, J = 18.4 Hz, CH) and 6.01–6.11 (m, 1 H, CH); ^{13}C, δ −6.45, −0.97, 16.90, 24.56, 26.63, 128.11 and 144.11. GC-MS: m/z = 228 (M^+). IR (liquid film): $\tilde{\nu}_{max}$/cm^{-1} 2954vs, 2929vs, 2897vs, 2858vs, 1605s, 1471s, 1464s, 1402w, 1363w, 1251vs, 1143s, 1005w, 987w, 938vw, 873vs, 840vs, 766w, 749m, 720w, 692s, 667w and 633w.

[Li{CH(CHSiMe$_2$Bu^t)$_2$}(tmen)] 3a. *n*-Butyllithium (5 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 8 mmol) was added dropwise with stirring to a solution of 1,3-bis(*tert*-butyldimethylsilyl)-propene (2.1 g, 7.78 mmol) and tmen (1.2 cm^3, 7.96 mmol) in hexane (25 cm^3) at −78 °C. The mixture was allowed to warm to room temperature, stirred overnight and then filtered. The filtrate was concentrated to *ca.* 3 cm^3 to yield colourless crystals of complex **3a** (2.8 g, 92%) (Found: C, 66.6; H, 13.0; N, 6.67. $C_{21}H_{49}LiN_2Si_2$ requires C, 64.2; H, 12.6; N, 7.13%), mp 83–85 °C. NMR (298 K, C_6D_6): ^{1}H, δ 0.14 (s, 6 H, $SiMe_2$), 0.29 (s, 6 H, $SiMe_2$), 1.22 (s, 18 H, $SiBu^t$), 1.59 (s, 4 H, tmen), 1.81 (s, 12 H, tmen), 2.83 (d, 2 H, J = 16, CH) and 7.04 (t, 1 H, J = 16 Hz, CH); ^{13}C, δ −4.21, −2.58, 18.62, 27.46, 46.15, 56.56, 64.53 and 156.52; ^{7}Li, δ −0.22; ^{29}Si, δ −3.20.

[Li{CH(CHSiMe$_2$Bu^t)(CHSiMe$_3$)}(tmen)] 3b. Complex **3b** was synthesized using a similar method as that for **3a**. A mixture of 3-*tert*-butyldimethylsilyl-1-trimethylsilylpropene (3.3 g, 14.5 mmol) and tmen (2.2 cm^3, 14.6 mmol) in pentane (30 cm^3) was treated with $LiBu^n$ (9 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 14.4 mmol). After work-up the colourless crystalline complex **3b** (4.0 g, 79%) was obtained (Found: C, 61.1; H, 12.8; N, 7.66. $C_{18}H_{43}LiN_2Si_2$ requires C, 61.7; H, 12.4; N, 7.99%), mp 70–

72 °C. NMR (298 K, C_6D_6): ^{1}H, δ 0.13 (s, 6 H, $SiMe_2$), 0.28 (s, 9 H, $SiMe_3$), 1.17 (s, 9 H, $SiBu^t$), 1.64 (s, 4 H, tmen), 1.82 (s, 12 H, tmen), 2.77 (d, 1 H, $J = 15.7$, CH), 2.90 (d, 1 H, $J = 15.7$, CH) and 7.03 (t, 1 H, $J = 15.7$ Hz, CH); ^{13}C, δ −4.04, −2.49, 2.29, 18.57, 27.53, 46.19, 56.52, 63.76, 69.24 and 155.22; ^{7}Li, δ −0.22; ^{29}Si, δ −9.98 and −1.25.

[{K[CH(CHSiMe$_2$Bu^t)$_2$]}$_\infty$] 4. Potassium *tert*-butoxide (0.83 g, 7.41 mmol) was added at room temperature with stirring to a hexane (30 cm^3) solution of complex **3a** [prepared from **2a** (1.98 g, 7.33 mmol), tmen (1.1 cm^3, 7.3 mmol) and $LiBu^n$ (4.6 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 7.36 mmol)]. After several minutes a white precipitate appeared. Stirring was continued for 4 h. The mixture was filtered and the precipitate washed with hexane (2 × 15 cm^3) and dried *in vacuo* to afford the white solid **4** (1.95 g, 86%) (Found: C, 56.7; H, 10.7. $C_{15}H_{33}KSi_2$ requires C, 58.4; H, 10.8%), mp 271–275 °C. NMR (298 K, C_5D_5N): ^{1}H, δ 0.10 (s, 6 H, $SiMe_2$), 0.19 (s, 6 H, $SiMe_2$), 0.91 (s, 9 H, $SiBu^t$), 1.05 (s, 9 H, $SiBu^t$), 5.38 (d, 1 H, $J = 17.6$, CH), 6.08 (d, 1 H, $J = 10.8$, CH) and 6.97 (dd, 1 H, $J = 10.8$, 17.6 Hz, CH); ^{13}C, δ −5.20, −4.04, 17.22, 19.17, 26.89, 27.30, 113.08, 117.86 and 149.75.

[K{CH(CHSiMe$_2$Bu^t)$_2$}(py)] 5a. Pyridine (0.5 cm^3) was added to a suspension of complex **4** (0.5 g, 1.62 mmol) in hexane (*ca.* 10 cm^3). The complex slowly dissolved and a red-brown mixture was formed. After filtration all volatiles were removed from the filtrate *in vacuo*. The resultant solid was redissolved in hexane (*ca.* 10 cm^3) and concentrated *in vacuo*. Crystallisation at room temperature yielded the yellow crystalline complex **5a** (0.5 g, 80%) (Found: C, 61.3; H, 9.89; N, 3.54. $C_{18}H_{43}LiN_2Si_2$ requires C, 62.0; H, 9.88; N, 3.61%), mp 85–88 °C. NMR (298 K, toluene-d^8): ^{1}H, δ 0.11 (s, 12 H, $SiMe_2$), 1.00 (s, 18 H, $SiBu^t$), 2.92 (d, 2 H, $J = 16$, CH), 6.89 (t, 1 H, $J = 16$ Hz, CH), 6.67–6.71 (m, 2 H, py), 6.94–6.96 (m, 1 H, py) and 8.43–8.45 (m, 2 H, py); ^{13}C, δ −2.51, 18.38, 28.03, 67.30, 123.81, 137.46, 149.96 and 157.28; ^{29}Si, δ −4.21.

[K{CH(CHSiMe$_2$Bu^t)$_2$}(thf)] 5b. Tetrahydrofuran (*ca.* 0.5 cm^3) was added to a suspension of complex **4** (0.9 g, 2.92 mmol) in hexane (*ca.* 10 cm^3). The solid slowly dissolved and a colourless solution was formed. After filtering off a small precipitate the filtrate was concentrated *in vacuo*. Crystallisation at room temperature yielded colourless crystals of complex **5b** (0.93 g, 84%) [Found: C, 58.5; H, 10.6. $C_{15}H_{33}KSi_2$ (the co-ordinated thf was lost during elemental analysis) requires C, 58.4; H, 10.8%], mp 138–140 °C. NMR (298 K, C_6D_6): ^{1}H, δ 0.19 (s, 12 H, $SiMe_2$), 1.08 (s, 18 H, $SiBu^t$), 1.39 (m, 4 H, thf), 2.75 (d, 2 H, $J = 16.4$, CH), 3.55 (m, 4 H, thf) and 6.89 (t, 1 H, $J = 16.4$ Hz, CH); ^{13}C, δ −2.24, 18.87, 28.37, 25.76, 67.95, 66.30 and 157.57.

CH=CHCH(SiMe$_3$)(CH$_2$)$_2$CH$_2$ 6. Magnesium (2.8 g, 0.117 mol) in Et_2O (*ca.* 15 cm^3) was treated with a few particles of I_2 until the brown colour was discharged. The compound Me_3SiCl (13 cm^3, 0.103 mol) was added. A solution of 3-bromocyclohexene (15 g, 0.093 mol) in Et_2O (*ca.* 60 cm^3) was slowly added into the stirred mixture during 12 h at ice-bath temperature. The mixture was carefully hydrolysed with crushed ice. The organic phase was collected and dried ($CaCl_2$). Distillation under reduced pressure gave **6** (8.7 g, 61%), bp 64–66 °C (20 Torr). ^{1}H NMR (298 K, $CDCl_3$): δ 0.01 (s, 9 H, $SiMe_3$), 1.55 (m, 3 H), 1.73 (m, 2 H), 1.96 (m, 2 H) and 5.64 (s, 2 H).

[Li{C(SiMe$_3$)(CH)$_2$(CH$_2$)$_2$CH$_2$}(tmen)] 7. The compound tmen (3 cm^3, 20.31 mmol) and $LiBu^n$ (10 cm^3 of a 2 mol dm^{-3} solution in hexane, 20 mmol) were added to a solution of **6** (3.1 g, 20.31 mmol) in hexane (*ca.* 30 cm^3) at room temperature. The mixture was stirred for 12 h and then concentrated and crystallised at −78 °C to give white crystals of **7** (5.0 g, 90%). ^{1}H NMR (298 K, C_6D_6): δ 0.37 (s, 9 H, $SiMe_3$), 1.66 (s, 4 H, tmen), 1.81 (s, 12 H, tmen), 2.01 (br, 3 H), 2.43 (br, 1 H), 2.85 (br, 2 H), 3.94 (m, 1 H) and 6.62 (d, 1 H).

Table 4 Crystallographic data for complexes **3a**, **9** and **11**[c]

	3a	**9**	**11**
Empirical formula	$C_{21}H_{49}LiN_2Si_2$	$C_{18}H_{41}Li_2Si_2$	$C_{32}H_{62}K_2O_3Si_3$
Formula weight	392.8	348.65	657.3
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$ (no. 14)	$Pna2_1$ (no. 33)	$Pna2_1$ (no. 33)
a/Å	11.295(3)	19.325(4)	17.298(1)
b/Å	21.365(3)	8.660(2)	20.032(1)
c/Å	12.254(4)	14.750(3)	11.727(1)
β/°	103.33(2)	—	—
V/Å^3	2877(1)	2468.5(9)	4064(2)
Z	4	4	4
D_c/g cm^{-3}	0.910	0.938	1.074
μ/mm^{-1}	0.13	0.145	0.348
Reflections collected	5478	4366	5680
Independent, n (R_{int})	5217 (0.02)	2263 (0.17)	5680 (0.06)
Observed, n [$I > 2\sigma(I)$]	1780	614	5179
No. parameters, p	235	203	362
$R1$ [$I > 2\sigma(I)$]	0.094	0.0482	0.0989
$wR2$[a] or wR[b]	0.083	0.1019	0.2606

[a] For $I > 2\sigma(I)$ (complexes **9** and **11**). [b] For complex **3a**. [c] All data were collected at 293 K.

C(SiMe$_3$)CHC(SiMe$_3$)(CH$_2$)$_2$CH$_2$ 8. A solution of complex **7** in hexane (*ca.* 20 cm^3) [prepared from tmen (2.25 cm^3, 14.94 mmol), $LiBu^n$ (9.7 cm^3 of a 1.4 mol dm^{-3} solution in hexane, 13.58 mmol) and **6** (2.3 g, 14.94 mmol)] was added dropwise to a solution containing an equimolar portion of Me_3SiCl in hexane (*ca.* 10 cm^3) at −78 °C. The mixture was warmed to room temperature and stirred for 4 h, then hydrolysed and the organic phase separated. After drying ($CaCl_2$) it was distilled to give **8** (2.6 g, 77%), bp 49–50 °C (1 Torr). ^{1}H NMR (298 K, $CDCl_3$): δ −0.01 (s, 9 H, $SiMe_3$), 0.03 (s, 9 H, $SiMe_3$), 1.40 (m, 2 H), 1.54 (m, 1 H), 1.69 (m, 2 H), 1.93 (m, 2 H) and 5.91 (m, 1 H).

[Li{C(SiMe$_3$)CHC(SiMe$_3$)(CH$_2$)$_2$CH$_2$}(tmen)] 9. Employing a procedure similar to that for complex **7**, **8** (1.9 g, 8.39 mmol), tmen (1.26 cm^3, 8.39 mmol) and $LiBu^n$ (5.43 cm^3 of a 1.54 mol dm^{-3} solution in hexane, 8.36 mmol) in pentane (*ca.* 20 cm^3) gave white crystals of **9** (2.6 g, 89%). ^{1}H NMR (298 K, C_6D_6): δ 0.31 (s, 18 H, $SiMe_3$), 1.52 (s, 4 H, tmen), 1.77 (s, 12 H, tmen), 2.05 (m, 4 H), 2.78 (m, 2 H) and 6.82 (s, 1 H).

[K{C(SiMe$_3$)CHC(SiMe$_3$)(CH$_2$)$_2$CH$_2$}] 10. The compound tmen (0.86 cm^3, 5.7 mmol) and $LiBu^n$ (3.7 cm^3 of a 1.54 mol dm^{-3} solution in hexane, 5.7 mmol) were added to a solution of **8** (1.30 g, 5.7 mmol) in hexane (*ca.* 30 cm^3) at room temperature. The mixture was stirred for 12 h and then $KOBu^t$ (0.64 g, 5.71 mmol) was added. An additional 12 h of stirring yielded a yellow precipitate of complex **10** (0.90 g, 60%). ^{1}H NMR (298 K, C_6D_6–pyridine-d^5 2:1): δ −0.05, 0.05 (s, 6 H, $SiMe_3$), 0.94, 0.20 (s, 12 H, $SiMe_3$), 1.70 (m, 3 H), 2.05, 2.15, 2.37, 2.56 (m, 3 H), 6.05 (m, 1/3 H) and 6.58 (s, 2/3 H).

[{K$_2$[(η^3-C$_6$H$_4$SiMe$_3$-6)$_2$SiMe$_2$](thf)$_3$}$_\infty$] 11. A solution of complex **7** (3.00 g, 10.87 mmol) in hexane (*ca.* 40 cm^3) was added dropwise to the solution of Me_2SiCl_2 (0.66 cm^3, 5.44 mmol) in hexane (*ca.* 10 cm^3) at −78 °C. The mixture was warmed to room temperature stirred for 12 h and then filtered. The compound tmen (1.63 cm^3, 10.87 mmol) and $LiBu^n$ (5.4 cm^3 of a 2.0 mol dm^{-3} solution in hexane, 10.8 mmol) were added to the filtrate. The mixture was stirred for 12 h and

KOBu^t (1.22 g, 10.89 mmol) added. After 12 h of stirring the yellow precipitate **11** (2.4 g, 99%) was filtered off and crystallised from thf. NMR (298 K, C_6D_6): ^{1}H, δ 0.28 (s, 18 H, $SiMe_3$), 0.35 (s, 6 H), 1.84 (br, 4 H), 2.56 (br, 8 H), 6.46 (s, 2 H), 1.39 (m, 6 H, thf) and 3.56 (m, 6 H); ^{13}C, δ 0.82, 0.89, 15.31, 26.54, 30.12, 25.76, 28.56, 67.96, 70.60, 77.54, 143.52 and 176.48.

Crystallography

Details are given in Table 4. Single crystals of each of the complexes **3a**, **9** and **11** were mounted in Lindemann capillaries under argon. Data were collected on Enraf-Nonius CAD4 (for **3a**), Rigaku AFC7R (for **9**) or Rigaku Raxis IIc (for **11**) diffractometers in the θ–2θ mode with monochromated Mo-Kα radiation. The structure was solved by direct methods (SHELXS 86[34] or Siemens SHELXSTL plus) and refined by full-matrix least squares on F for **3a** or on F^2 for **9** and **11**. All non-H atoms were anisotropic. The diffraction for the crystal of **9** was rather weak resulting in a limited data set.

CCDC reference number 186/1314.

See http://www.rsc.org/suppdata/dt/1999/1257/ for crystallographic files in .cif format.

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