

Invited review

Recent studies on metal and metalloid bis(trimethylsilyl) methyls and the transformation of the bis(trimethylsilyl) methyl into the azaallyl and β -diketiminato ligands

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Abstract

Recent results (post-1990) on the synthesis and structures of bis(trimethylsilyl)methyls $M(\text{CHR}_2)_m$ ($R = \text{SiMe}_3$) of metals and metalloids M are described, including those of the crystalline lipophilic $[\text{Na}(\mu\text{-CHR}_2)]_n$, $[\text{Rb}(\mu\text{-CHR}_2)(\text{PMDETA})]_2$, $\text{K}_4(\text{CHR}_2)_4(\text{PMDETA})_2$, $[\text{Mg}(\text{CHR}_2)(\mu\text{-CHR}_2)]_n$, $\text{P}(\text{CHR}_2)_2$ (gaseous) and $\text{P}_2(\text{CHR}_2)_4$, $[\text{Yb}(\text{CHR}_2)_2(\text{OEt}_2)_2]$ and $[\{\text{Yb}(\text{CR}_3)(\mu\text{-OEt})(\text{OEt}_2)\}_2]$; earlier information on other $M(\text{CHR}_2)_m$ complexes and some of their adducts is tabulated. Treatment of $M(\text{CHR}_2)$ ($M = \text{Li}$ or K) with four different nitriles gave the X-ray-characterized azaallyls or β -diketiminates $[\text{Li}(\text{LL}')]_2$, $[\text{Li}(\text{L}'\text{L}')]_2$ and $[\text{K}(\text{LL}'')(\text{NCAr})]_2$ ($\text{LL}' = \text{N}(\text{R})\text{C}(\text{tBu})\text{CHR}$, $\text{L}'\text{L}' = \text{N}(\text{R})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Ph})\text{NR}$, $\text{LL}'' = \text{N}(\text{R})\text{C}(\text{Ph})\text{NC}(\text{H})\text{C}(\text{Ph})\text{CHR}$, $\text{R} = \text{SiMe}_3$ and $\text{Ar} = \text{C}_6\text{H}_3\text{Me}_2$ -2,5). The two lithium reagents were convenient sources of other metal azaallyls or β -diketiminates, including those of K , $\text{Co}(\text{II})$, $\text{Zr}(\text{IV})$, $\text{Sn}(\text{IV})$, $\text{Yb}(\text{II})$, $\text{Hf}(\text{IV})$ and $\text{U}(\text{VI})/\text{U}(\text{III})$. Complexes having one or more of the bulky ligands $[\text{LL}']^-$, $[\text{L}'\text{L}']^-$, $[\text{LL}]^-$, $[\text{LL}'']^-$, $[\text{L}'\text{L}''']^-$, $[\text{LL}''']^-$ and $[\{\text{N}(\text{R})\text{C}(\text{tBu})\text{CH}\}_2\text{C}_6\text{H}_4\text{-2}\}^{2-}]^-$ are described and characterized ($\text{LL} = \text{N}(\text{H})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Ph})\text{NH}$, $\text{L}'\text{L}''' = \text{N}(\text{R})\text{C}(\text{tBu})\text{C}(\text{H})\text{C}(\text{Ph})\text{NR}$, $\text{LL}''' = \text{N}(\text{R})\text{C}(\text{tBu})\text{CHPh}$). Among the features of interest are (i) the contrasting tetrahedral or square-planar geometry for $[\text{Co}(\text{L}'\text{L}')_2]$ and $[\text{Co}(\text{LL})_2]$, respectively, and (ii) olefin-polymerization catalytic activity of some of the zirconium(IV) chlorides.

Keywords: Silicon; Alkali metals; Lanthanides; Bis(trimethylsilyl)methyls; Crystal structures; Azaallyls; β -Diketiminates

1. Introduction

We have a long-standing interest in the bis(trimethylsilyl)methyl ligand $\overline{\text{CHR}}_2$ ($R = \text{SiMe}_3$) [1], dating back to a patent 1969 [2] and our first paper in 1970 [3] relating to the then essentially new class of ligands of formula $\overline{\text{CH}}_{3-n}\text{R}_n$ ($n = 1, 2$ or 3). The features which we then considered to be significant were that (1) they constituted an interesting series of progressively increasing bulky ligands: $n = 3 > n = 2 > n = 1$; (ii) they were likely to confer lipophilicity on their metal or metalloid complexes; and (iii) they are free from β -hydrogen and hence the β -elimination pathway for their metal or metalloid complexes would be unavailable, giving rise to the possibility of preparing unusual kinetically stable metal complexes. (iv) Feature (iii) was further enhanced

by the ligands being free from β -carbon, so that even a β -methyl elimination pathway would be energetically unfavourable; and (v) the NMR spectra of metal complexes were likely to be simple; for example, a diamagnetic metal complex $M(\text{CHR}_2)_m$ was likely to show only two characteristic ^1H or ^{13}C signals and a single ^{29}Si resonance.

A good deal of our work concerning the $\overline{\text{CHR}}_2$ ligand has concentrated on the preparation, structure and reactivity of thermally stable homoleptic complexes, i.e. compounds of empirical formula $M(\text{CHR}_2)_m$ or their neutral ligand adducts. The terms ‘‘homoleptic’’ and ‘‘heteroleptic’’ were coined by us in 1974 to describe metal or metalloid complexes of empirical formula MX_m or $\text{MX}_{m-x}\text{Y}_x$, respectively [4]; the heteroleptic complexes include those in which there are more than two different ligands. The term ‘‘isoleptic’’ was used to designate two or more complexes having the same nature and number of ligands. For example,

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Table 1

Crystalline homoleptic main group metal bis(trimethylsilyl)methyls $M(\text{CHR}_2)_n$ and in some cases their neutral ligand adducts ($R = \text{SiMe}_3$)

Complex	State of aggregation	Metal coordination number	Comments	Ref.
LiCHR_2	∞	2	Dimer in gas at $\sim 100^\circ\text{C}/0.1$ Torr ($\mu\text{-CHR}_2$)	[5]
NaCHR_2	∞	2	Volatile at $\sim 100^\circ\text{C}/0.1$ Torr; ($\mu\text{-CHR}_2$)	[6]
$\text{K}_4(\text{CHR}_2)_4(\text{PMDETA})_2^a$	1	$2 \times 3\text{C}$, $2 \times 4 (2\text{C}, 2\text{N})$		[7]
$\text{Mg}(\text{CHR}_2)_2$	∞	3	Neutron diffraction; $\{[\text{Mg}(\text{CHR}_2)(\mu\text{-CHR}_2)]_\infty\}$; volatile at $\sim 100^\circ\text{C}/0.1$ Torr	[8]
$\text{Ca}(\text{CHR}_2)_2(\text{DIOX})_2^b$	1	$2 \times \text{C}$, $2 \times \text{O}$		[9]
$\text{B}(\text{CHR}_2)_2\text{Cl}$	1	3	$\text{B}(\text{CHR}_2)_3$ too bulky to be prepared, but $\text{B}(\text{CHR}_2)_2\text{Me}$ accessible [11]	[10]
$\text{Al}(\text{CHR}_2)_2$	2	3	Al–Al bond	[12]
$\text{Al}(\text{CHR}_2)_3$	1	3	Structure not determined	[13]
$\text{Ga}(\text{CHR}_2)_2$	2	3	Ga–Ga bond	[14]
$\text{Ga}(\text{CHR}_2)_3$	1	3	Structure not determined	[13]
$\text{In}(\text{CHR}_2)_2$	2	3	In–In bond	[15]
$\text{In}(\text{CHR}_2)_3$	1	3	D_{3h} Skeletal structure	[13]
$\text{Si}(\text{CHR}_2)_2$			Transient, postulated as intermediate	[16]
$\text{Si}(\text{CHR}_2)_3$	1	3	σ -Radical (ESR); half-life ca. 10 min at 25°C in PhMe	[16]
$\text{Ge}(\text{CHR}_2)_2$	2	3	GeGe “double” bond (pyramidal at Ge); monomer at $100^\circ\text{C}/0.1$ Torr or in dilute PhMe solution	[17]
$\text{Ge}(\text{CHR}_2)_3$	1	3	σ -Radical (ESR); half-life ∞ at 25°C in PhMe	[16]
$\text{Sn}(\text{CHR}_2)_2$	2	3	SnSn “double” bond (pyramidal at Sn); monomer at $100^\circ\text{C}/0.1$ Torr [19] or in dilute PhMe solution	[17]
$\text{Sn}(\text{CHR}_2)_3$	1	3	σ -Radical (ESR); half-life ∞ at 25°C in PhMe	[16]
$\text{Sn}(\text{CHR}_2)_3\text{Cl}$	1	4	$\text{Sn}(\text{CHR}_2)_4$ too bulky to be prepared	[18]
$\text{Pb}(\text{CHR}_2)_2$	1(?)	2	Structure not determined; m.p. 37°C ; volatile	[20]
$\text{P}(\text{CHR}_2)_2$	2	3	Very long P–P bond; readily dissociates to persistent monomer (π -radical) in PhMe or in gas phase (V-shaped; electron diffraction)	[21]

^a PMDETA = $\text{MeN}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2$.^b DIOX = $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$.

Table 2

Crystalline homoleptic *d*- and *f*-block bis(trimethylsilyl)methyls $M(\text{CHR}_2)_n$ and in some cases their adducts ($R = \text{SiMe}_3$)

Complex	State of aggregation	Metal coordination number	Comments	Ref.
$\text{Sc}(\text{CHR}_2)_3$	1	3	Structure not determined	[22]
$\text{Y}(\text{CHR}_2)_3$	1	3	Structure not determined	[23]
$\text{Ti}(\text{CHR}_2)_3$	1	3	Structure not determined	[23]
$[\text{Zr}(\text{CHR}_2)_3\text{Cl}]$	1	4	Structure not determined;	[23]
$\text{Hf}(\text{CHR}_2)_3\text{Cl}$			$\text{M}(\text{CHR}_2)_4$ too bulky to be accessible	
$\text{V}(\text{CHR}_2)_3$	1	3	Structure not determined	[23]
$[\text{Cr}(\text{CHR}_2)_3]$	1	3	CrC_3 : D_{3h}	[23]
$[\text{Mn}(\text{CHR}_2)_2]$	1	2	Electron diffraction (gas) at $\sim 100^\circ\text{C}/0.1$ Torr; CMnC linear	[24]
$[\text{Mn}(\text{CHR}_2)_2(\text{THF})]$	1	3		[25]
$[\text{Mn}(\text{CHR}_2)_2(\text{DMPE})]^a$	1	4		[25]
CuCH_2R	4	4	$\{[\text{Cu}(\mu\text{-CH}_2\text{R})]\}_4$; $(\text{CuC})_4$ planar	[26]
$[\text{La}(\text{CHR}_2)_3]$	1	3 + agostic	Pyramidal at La	[27]
$[\text{Sm}(\text{CHR}_2)_3]$	1	3 + agostic	Pyramidal at Sm	[27]
$[\text{Sm}(\text{CHR}_2)_3(\mu\text{-Me})\text{Li}(\text{PMDETA})]^b$	1	4	Sm–C(H ₃)–Li almost linear	[28]
$[\text{U}(\text{CHR}_2)_3]$	1	3	Pyramidal at U	[29]

^a DMPE = $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$.^b PMDETA = $\text{MeN}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2$.

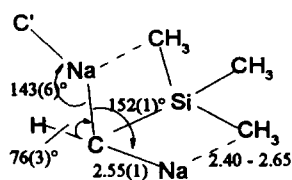


Fig. 1. A simplified bonding pattern showing key features of the X-ray molecular structure of $[\text{Na}(\mu\text{-CHR}_2)]_n$ (1) ($\text{R} = \text{SiMe}_3$) [6].

while each of $[\text{Ti}(\text{CH}_2\text{R})_4]$ and $\text{Ge}(\text{CH}_2\text{R})_4$ is homoleptic, they are an isoleptic pair, and $[\text{Ti}(\mu\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{R})_2]$ is a heteroleptic complex.

Tables 1 and 2 provide a summary of the homoleptic bis(trimethylsilyl)methyls which have been structurally characterized of both Main Group and transition (and also f-block) metals, with brief notes on the metal coordination number and other features of structural interest. Included is a small number of such complexes bearing a coligand and selected compounds for which structural data are at present not available.

2. Post-1990 studies of metal and metalloids bis(trimethylsilyl)methyls

The compounds considered in this section are (i) some alkali metal alkyls; (ii) a magnesium compound, (iii) a *p*-dioxane complex of the calcium compound, (iv) the phosphorus(II) alkyl and (v) the ytterbium(II) alkyls.

The synthesis of some alkyls 1–5 of the alkali metals is shown in Scheme 1. The lithium compound, which has long been known, was readily prepared from R_2CHCl and Li ($\text{R} = \text{SiMe}_3$) and was then converted into a heavier Group 1 congener by treatment with an appropriate metal alkoxide or aryloxy, chosen so as to facilitate the separation of the lithium alkoxide or aryloxy from the heavier Group 1 metal alkyl [6,7]. For

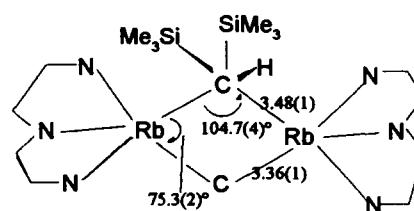
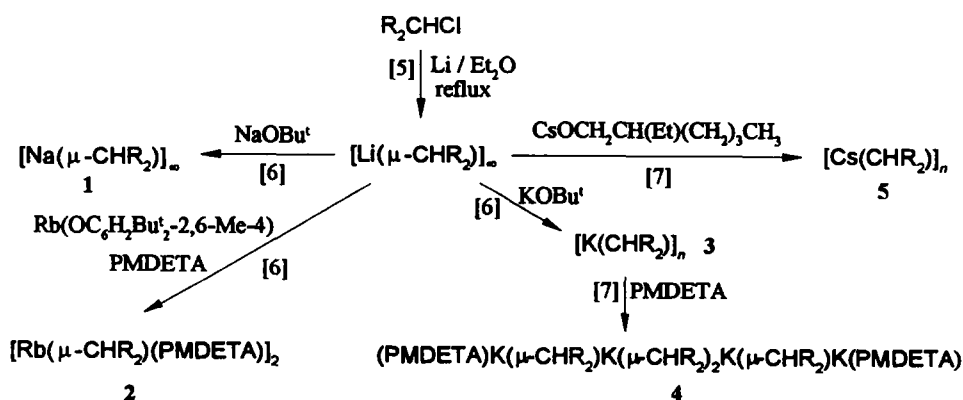


Fig. 2. A simplified bonding pattern showing key features of the X-ray molecular structure of $[\text{Rb}(\mu\text{-CHR}_2)(\text{PMDETA})]_2$ (2) [6].

compounds 1–3 or 5, the reactions were carried out in hexane, the lithium alkoxide or aryloxy being more soluble than 1 and 2 or the insoluble 3 or 5. The potassium alkyl 3 was readily converted into the PMDETA adduct 4; with that fact in mind, the rubidium complex 2 was prepared directly from $\text{Rb}(\text{OC}_6\text{H}_2^t\text{Bu}_2\text{-2,6-Me-4})$, LiCHR_2 and PMDETA. Each of the compounds 1, 2 and 4 was crystalline and lipophilic. Their X-ray crystal structures have been determined, as illustrated in Figs. 1, 2 and 3, respectively. The low coordination number of two for Na in 1 is noteworthy, as are the low metal coordination numbers in 2 and 4. Like LiCHR_2 [5], the sodium alkyl 1 is volatile and may be a monomer or dimer in the vapour [6], the gaseous lithium compound being a monomer (gas electron diffraction) [5]. The dimeric structure of the crystalline Rb compound 2 has some similarity in its bis(alkyl) bridging and five-coordinate carbon with the archetypal electron-deficient compound $[\text{AlMe}_2(\mu\text{-Me})]_2$. The presence in the potassium alkyl 4 [7] of both this type of bridging between the two internal potassium centres and of the single alkyl bridges between the outer metals (as in the Na compound 1 or its lithium analogue) is of interest.

The syntheses of the bis(trimethylsilyl)methyls of Mg (6–9) [8] and Ca (10) [9] are illustrated in Scheme 2. The coordination number of three for Mg in 7–9 is



Scheme 1. PMDETA = $\text{MeN}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2$.

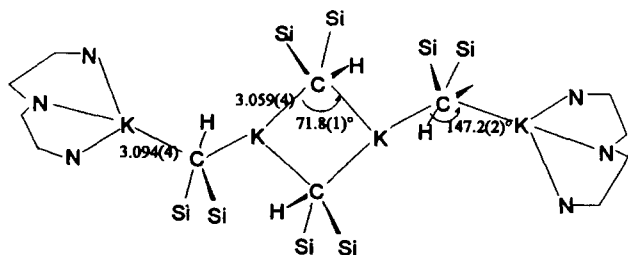


Fig. 3. A simplified bonding pattern showing key features of the X-ray molecular structure of $[K(PMDETA)(\mu-CHR_2)_2K(\mu-CHR_2)_2K(PMDETA)]$ (**4**) [7].

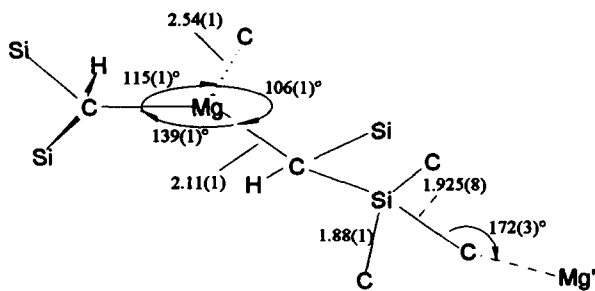


Fig. 4. A simplified bonding pattern showing key features of the low-temperature (15 K) neutron diffraction molecular structure of $[Mg(CHR_2)(\mu-CHR_2)]_n$ (**9**) [8].

unusual but has precedents. In crystalline $[Mg(CHR_2)(\mu-CHR_2)]_n$ (**9**), Fig. 4, this is achieved by virtue of intermolecular $C'H_3 \cdots Mg$ interaction involving one of the methyls of an $SiMe_3$ group with the Mg centre of a neighbouring molecule. The MgC_2C' unit is coplanar, the $Si'-C' \cdots Mg$ bond is almost linear and the $Si'-C'$

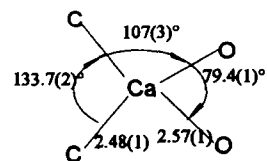
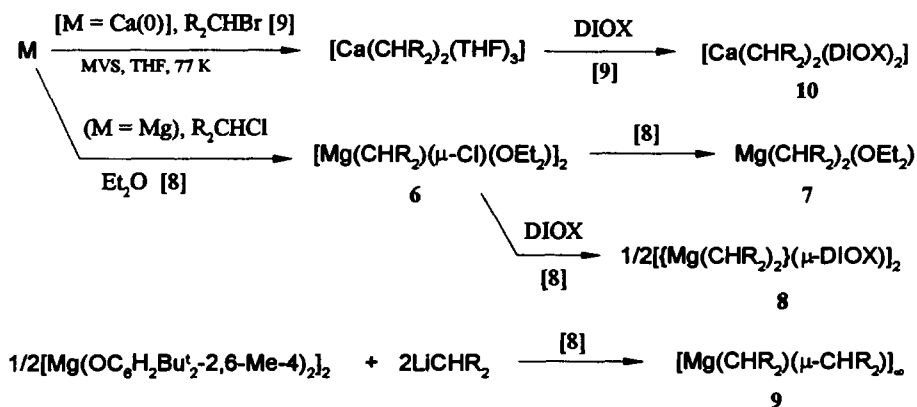


Fig. 5. A simplified bonding pattern showing key features of the X-ray molecular structure of $Ca(CHR_2)_2(DIOX)_2$ ($R = SiMe_3$, $DIOX = OCH_2CH_2OCH_2CH_2$) (**10**) [9].

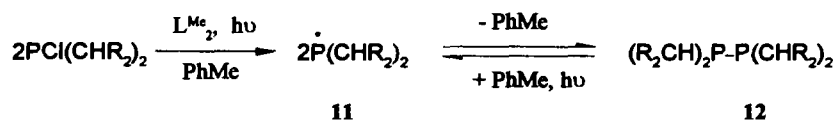
distance is significantly longer than the two remaining $Si'-C'$ bonds. A possible description of the bonding in the $Si'-C' \cdots Mg$ moiety is that of a linear three-centre, two-electron bond. The crystalline Grignard reagent **6** is unusual in that with less bulky alkyl groups, a mononuclear $[Mg(alkyl)(Cl)(OEt_2)_2]$ complex is the norm.

The crystalline alkyl $[Ca(CHR_2)_2(DIOX)_2]$ (**10**) proved to be particularly difficult to make [9]; unsuccessful attempts involved use of $CaCl_2/LiCHR_2$ or finely divided calcium with R_2CHBr . However, the metal vapour synthesis procedure using the latter reagents in THF and then replacing the THF by 1,4-dioxane yielded crystalline **10**. Four coordination for calcium is rare, and **10** is the first X-ray-characterized alkyl of calcium (Fig. 5).

The unusual persistent, red phosphorus-centred radical $P(CHR_2)_2$ (**11**) was made by us in 1980, as a toluene solution, as outlined in Scheme 3. The removal of toluene yielded the white crystalline diphosphine **12**, the X-ray structure of which showed it to be an extremely strained molecule with a long P-P bond [21]. When its solution in toluene was exposed to light,



Scheme 2.



Scheme 3. [21] $L^{Me} = CN(Me)CH_2CH_2NMe$.

compound **11** was re-formed; the red vapour was exclusively the V-shaped monomeric π -radical **11**.

Homoleptic alkyls of the f-block elements are exceedingly rare. For the greatly prevalent oxidation state of +3, the sole representatives are the La(III) and Sm(III) bis(trimethylsilyl)methyls $[\text{Ln}(\text{CHR}_2)_3]$ [27]. For the corresponding Ln(II) analogues, our efforts were centred on the f^{14} , diamagnetic ytterbium(II) alkyls [30], in part because ^{171}Yb ($I = 1/2$, 17% naturally abundant) NMR spectroscopy is a very powerful tool [31]. The alkyls $[\text{Yb}(\text{CHR}_2)(\text{X})\text{L}_m]$ ($\text{X} = \text{CHR}_2$ and $\text{L}_m = (\text{OEt}_2)_2$ (**13**) or DMPE (**14**) or $\text{X} = \text{OAr}$ and $\text{L}_m = (\text{THF})_3$ (**15**)) were prepared as shown in Scheme 4 (Ar = $\text{C}_6\text{H}_2^1\text{Bu}_2\text{-2,6-Me-4}$) and were analytically and spectroscopically characterized, the dialkyls showing a binomial triplet ^{171}Yb NMR spectral signal and the monoalkyl **15** a 1:1 doublet, the multiplicities being due to $^2J(^{171}\text{Yb-}^1\text{H}) = 30$ Hz. The dialkyl **13** was further converted into derivatives, the ytterbium *rac*-bis(1-azaallyl) **17** (see Fig. 10) and the bis(β -diketinate) **18**. Treatment of YbI_2 with 3NaCHR_2 yielded $[\text{Yb}(\text{CHR}_2)_3\text{Na}]$ (**16**), which may be isostructural with $[\text{Yb}(\text{NR}_2)(\mu\text{-NR}_2)_2\text{Na}]$ [32]. Because we were unable to obtain any of the Yb(II) bis(trimethylsilyl)methyls **13–16** in X-ray quality crystalline form, we investigated

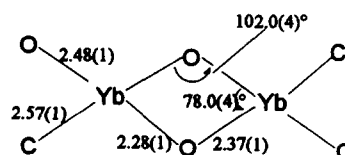
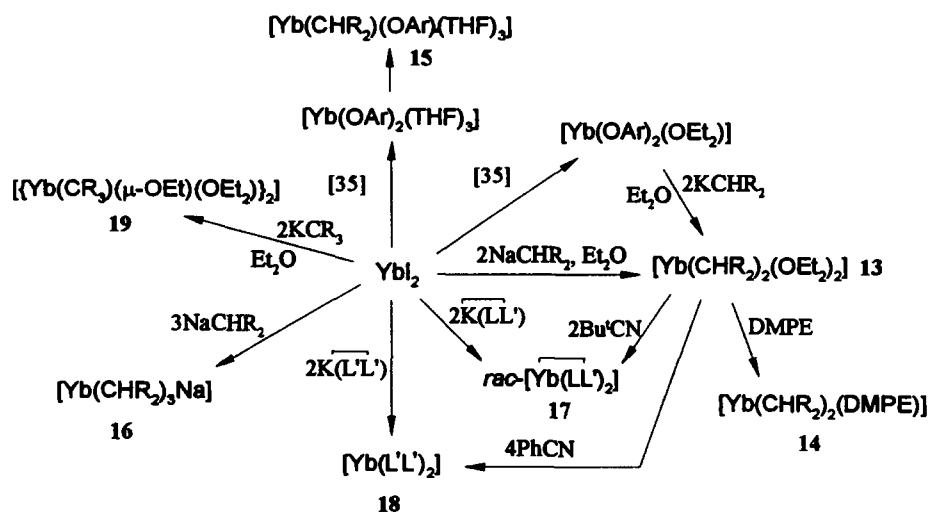


Fig. 6. A simplified bonding pattern showing key features of the X-ray molecular structure of $[\{\text{Yb}(\text{CR}_3)(\mu\text{-OEt})(\text{OEt}_2)\}_2]$ (**19**) [30].

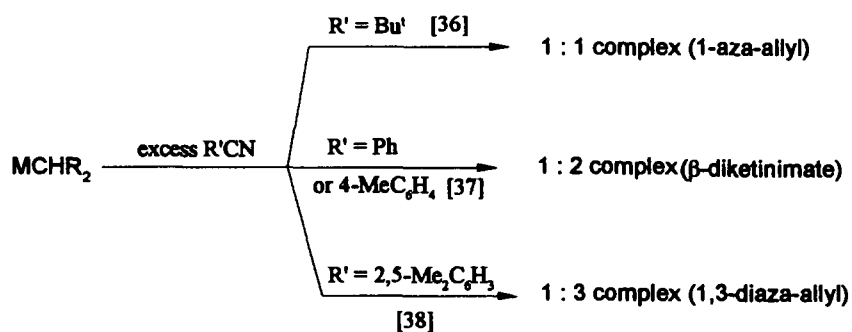
the reaction between YbI_2 and 2KCR_3 in dimethyl ether. Surprisingly, the product obtained was the alkyl-ytterbium(II) ethoxide **19** (Fig. 6) [30]. In an independent study, our Sussex colleagues showed that their X-ray-characterized $[\text{Yb}(\text{CR}_3)_2]$, obtained from $\text{YbI}_2 + 2\text{KCR}_3$ in C_6H_6 , reacted with diethyl ether to yield **19** [33]. Such facile C–O cleavage is unexpected, because previously such reactions were considered to be a property of a strong Lewis acid, such as BCl_3 [34].

3. Transformation of an alkali metal bis(trimethylsilyl)methyl into the corresponding metal 1-azaallyl, β -diketinate and 1,3-diazaallyl

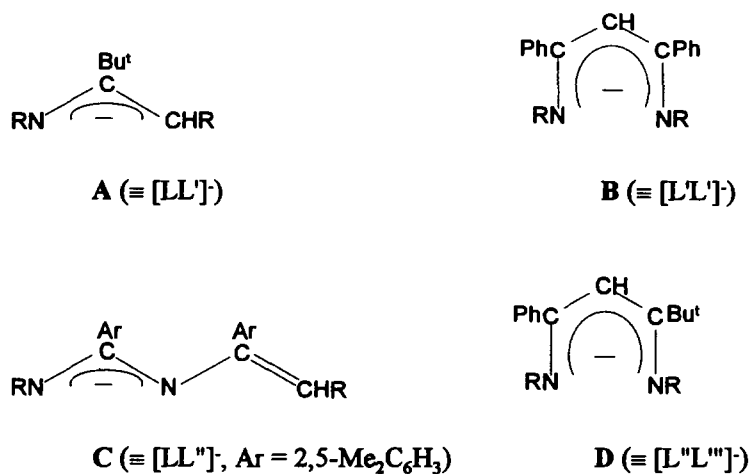
Irrespective of the stoichiometry of mixing, the reaction between the lithium or potassium bis(trimethyl-



Scheme 4. [30] Ar = $\text{C}_6\text{H}_2^1\text{Bu}_2\text{-2,6-Me-4}$.



Scheme 5.

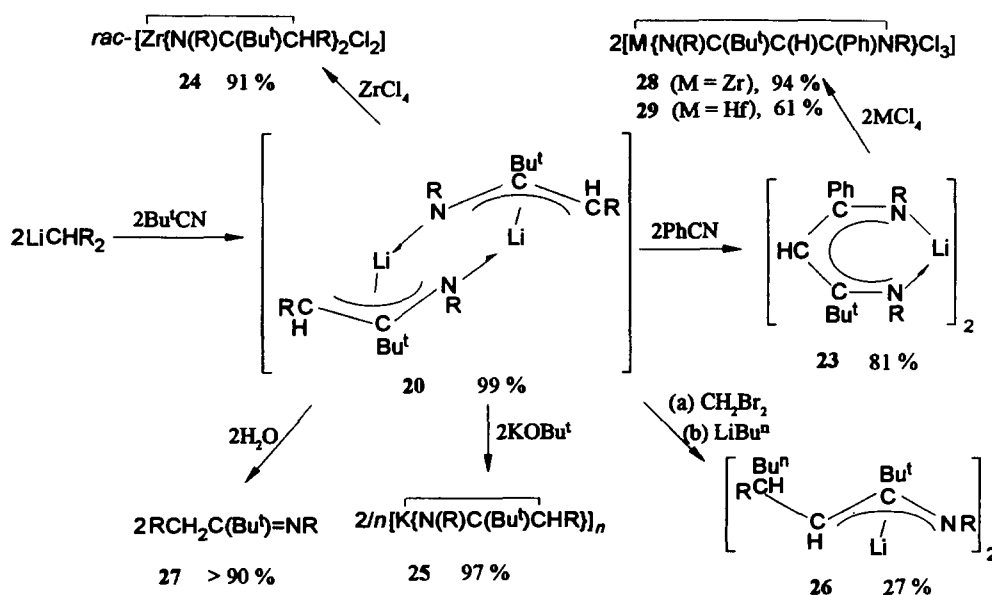


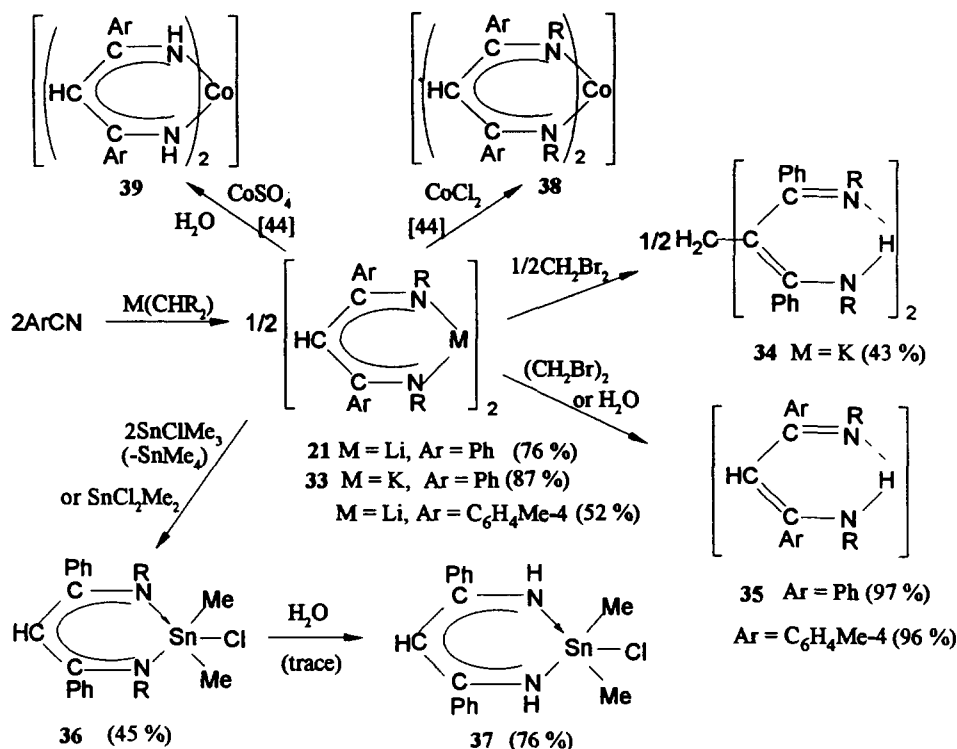
silyl)methyl MCHR₂ and excess of a nitrile R'CN free from α -hydrogen gave a 1:1 (R' = ^tBu) [36], 1:2 (R' = Ph or 4-MeC₆H₄) [37] or 1:3 (R' = 2,5-Me₂C₆H₃) [38] complex (Scheme 5). These were shown to be the alkali metal 1-azaallyl (**A**) [$\overline{M(LL')}$], β -diketiminato (**B**) (for R' = Ph) [$\overline{M(L'L')}$] or 1,3-diaza-allyl (**C**) [$\overline{M(LL'')}$], respectively. Although [$\overline{Li(LL')}$]₂ did not react with ^tBuCN, with PhCN it afforded the unsymmetrical β -diketiminato **D** of lithium [$\overline{Li(L''L''')}$]₂ (**23**) [36]. It is noteworthy that the ligands **B** and **C** are isomeric except for the nature of the aryl substituent.

The formation and some reactions (see Section 4) of the 1-azaallyllithium compound [$\overline{Li(N(R)C(Bu^t)CHR)}$]₂, i.e. [$\overline{Li(LL')}$]₂ (**20**), are shown in Scheme 6 (R = SiMe₃) [36]. Schemes 7 and 8 provide similar data on the β -diketiminatolithium compounds [$\overline{Li(N(R)C(Ph)C(H)C(Ph)NR)}$]₂, i.e. [$\overline{Li(L'L')}$]₂ (**21**) [37] and the 1,3-di-

azaallylpotassium compound [$\overline{K(N(R)C(Ar)NC(Ar)CHR)(NCAr)}$]₂, i.e. [$\overline{K(LL'')}(NCAr)$]₂ (**22**) [38], respectively.

The X-ray molecular structures of compounds **20**, **21** and **22** are illustrated schematically in Figs. 7, 8 and 9, respectively. Crystalline [$\overline{Li(LL')}$]₂ (**20**) has a central LiNLiN rhombus, Li–N–Li 73.0(4) and 74.2(4)°, N–Li–N 104.9(4) and 107.5(5)° the coordination environment for each Li atom is completed by the η^3 -1-azaallyl ligand and an agostic Li \cdots CH₃(SiMe₂CH–) contact; the Li atom is 1.44 Å out of the NCC azaallyl plane [36]. Crystalline [$\overline{Li(L'L')}$]₂ (**21**) has a fused tricyclic binuclear skeleton with a central LiNLiN rhombus; the small differences in each pair of the Li–N and N–C bond lengths within the [$\overline{L'L'}$][–] ligand **B** (those to the four-coordinate nitrogen being the slightly longer), and the virtual identity of the two CH = CPh bonds, sug-





Scheme 7. [37,44].

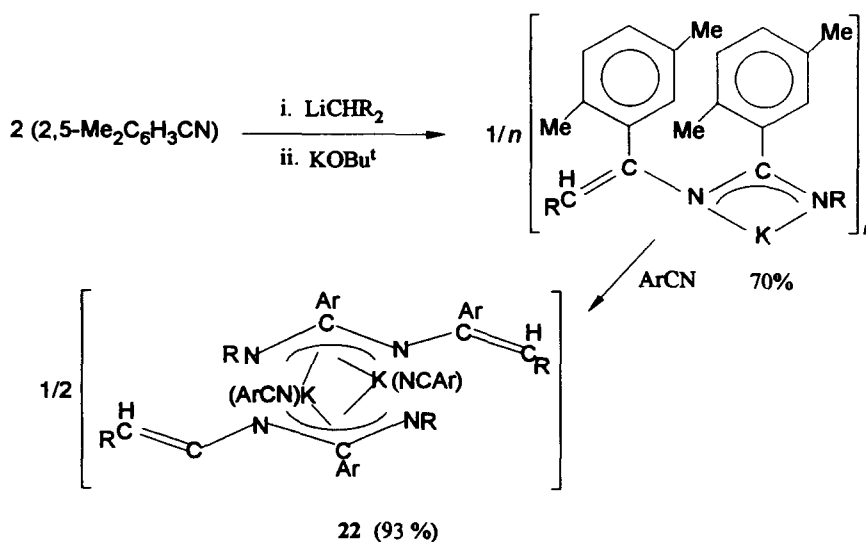
gests that the NCCCN fragment is substantially delocalized [37].

Crystalline $[\overline{\text{K}(\text{LL}')(\text{NCAr})}_2]$ (**22**) has each K coordinated to five nitrogens which form a square pyramid around the metal, with the two K–N(R) and K–N(CAr) bond lengths of the 1,3-diazaallyl moiety essentially identical and each of the N=C–N–C=C fragments coplanar [38].

Each of the ligands A–C is sterically demanding. The β -diketiminate ligand B in $[\overline{\text{Li}(\text{L}'\text{L}')}_2]$ (**21**) evi-

dently has some η^5 -character and among mono-anionic ligands is sterically comparable or even more (see Section 5) demanding than a highly substituted cyclopentadienyl or tris(pyrazolyl)borato ligand.

The proposed reaction pathway for the formation of these types of complexes from an alkali metal bis(trimethylsilyl)methyl MCHR_2 and a nitrile $\text{R}'\text{CN}$ free from α -hydrogen (see Scheme 5), i.e. the 1-azaallyl such as $[\overline{\text{Li}(\text{L}'\text{L}')}_2]$ (**20**), the β -diketiminate such as $[\overline{\text{Li}(\text{L}'\text{L}')}_2]$ (**21**) and the 1,3-diazaallyl such as



Scheme 8. [38].

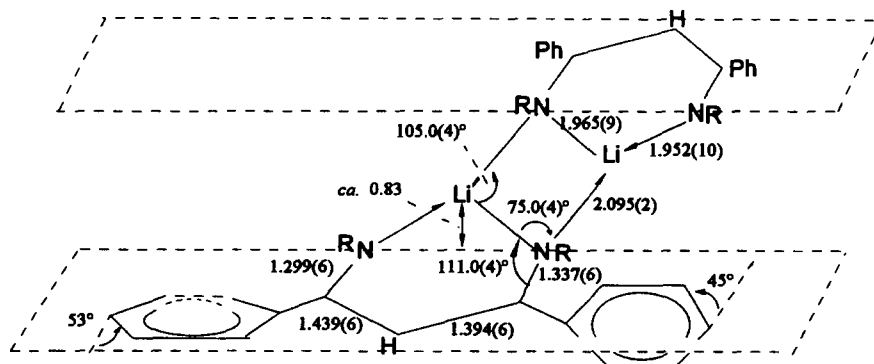


Fig. 7. A simplified bonding pattern showing key features of the X-ray molecular structure of $[\overline{\text{Li}}(\overline{\text{L}'\text{L}'})]_2$ (**21**) ($\text{L}'\text{L}' = \text{N}(\text{R})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Ph})\text{NR}$, $\text{R} = \text{SiMe}_3$) [37].

$[\overline{\text{K}}(\overline{\text{L}'\text{L}'})](\text{NCAR})_2$ (**22**), is shown in Scheme 9 [38]; for sake of simplicity, M is shown as Li . The initial step is an unexceptional attack of $\overline{\text{CHR}}_2$ on $\text{R}'\text{C}\equiv\text{N}$ to yield **I**. For $\text{R}' = 2,5\text{-Me}_2\text{C}_6\text{H}_3$, the N -centered nucleophile **I** or its rearrangement product **II** then attacks a second $\text{R}'\text{C}\equiv\text{N}$ molecule to give **III** or **IV**, respectively, each undergoing a further isomerization to give the final product **V**, $\text{Li}[\text{C}]$. For $\text{R}' = {}^t\text{Bu}$, the reaction stops at **II**, i.e. $\text{Li}[\text{A}]$, the latter proving unreactive with further ${}^t\text{BuCN}$ (although it does react with PhCN to give $\text{Li}[\text{D}]$). Finally, when $\text{R}' = \text{Ph}$ or $4\text{-MeC}_6\text{H}_4$, **II**, behaving as a C -centered nucleophile, attacks $\text{R}'\text{C}\equiv\text{N}$ to yield **VI**, which rearranges to the final product **VII**, i.e. $\text{Li}[\text{B}]$. The differences between the two cyanoarene systems leading to **V** or **VII** may lie in the relative rates of the isomerisation ($\text{I} \rightarrow \text{II}$) and insertion ($\text{I} \rightarrow \text{III}$) steps, the

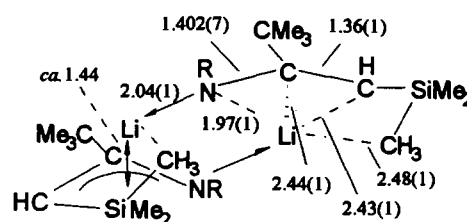
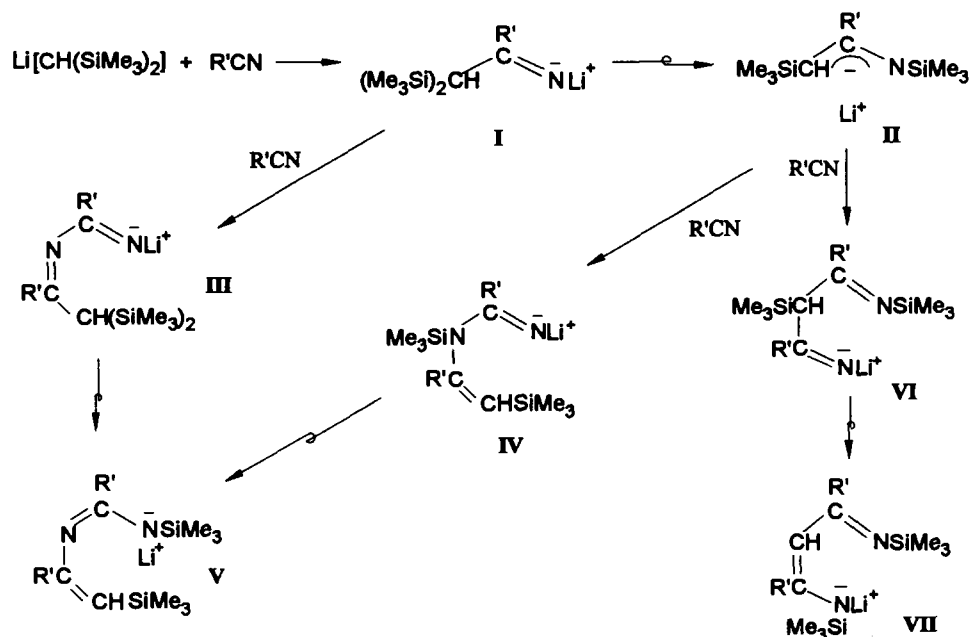


Fig. 8. A simplified bonding pattern showing key features of the X-ray molecular structure of $[\text{Li}(\overline{\text{L}'\text{L}'})]_2$ (**20**) ($\overline{\text{L}'\text{L}'} = \text{N}(\text{R})\text{C}({}^t\text{Bu})\text{CHR}$, $\text{R} = \text{SiMe}_3$) [36].

latter being favoured for the more hindered system. Anionic 1,3- SiMe_3 rearrangements are well known [39], although examples of such migrations from carbon to nitrogen are rare.



Scheme 9. [38].

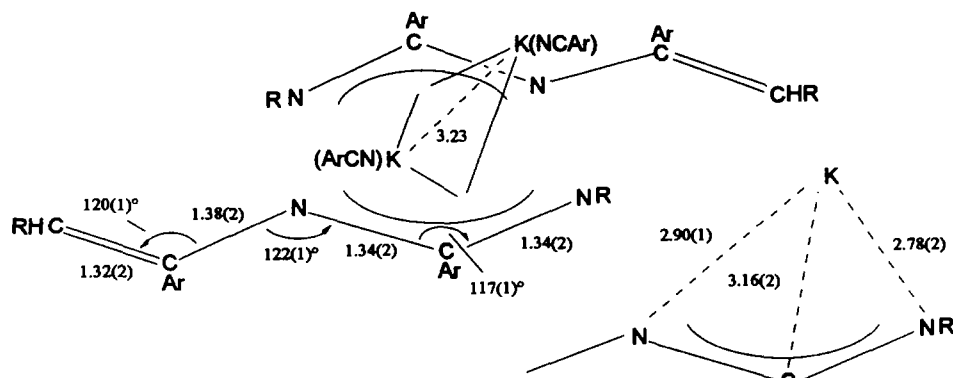


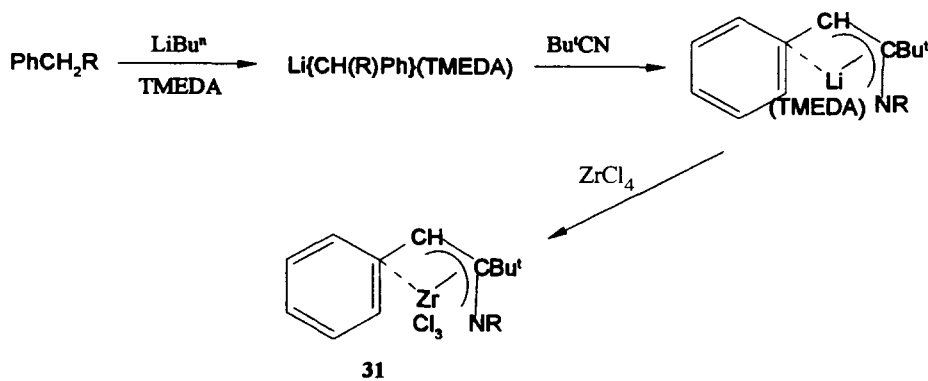
Fig. 9. A simplified bonding pattern showing key features of the X-ray molecular structure of $[\text{K}\{\text{N}(\text{R})\text{C}(\text{Ar})\text{NC}(\text{Ar})\text{CHR}\}(\text{NCAr})]_2$ (**22**) ($\text{Ar} = \text{C}_6\text{H}_3\text{Me}_2$ -2,5, $\text{R} = \text{SiMe}_3$) [38].

4. Synthesis, structures and reactions of various 1-azaallylmetal complexes

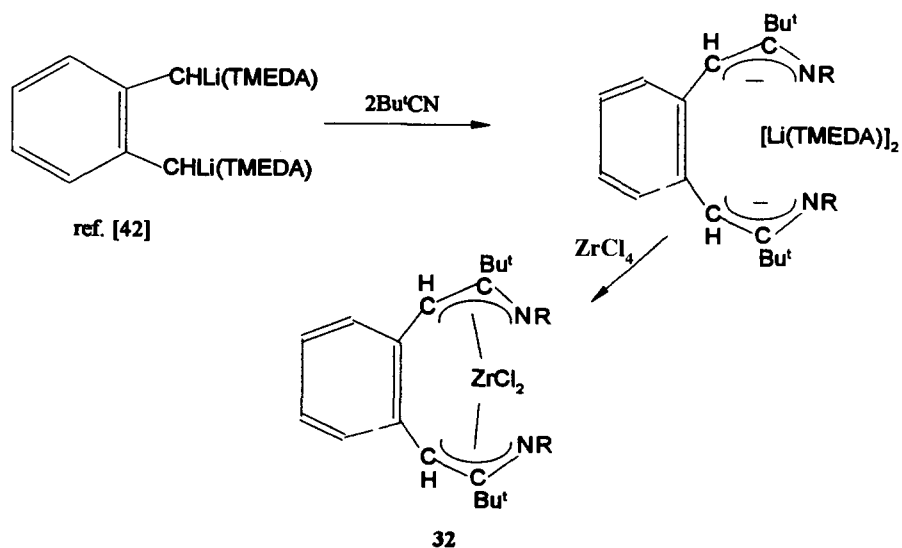
The synthesis and selected reactions of $[\text{Li}(\text{LL}')_2]$ (**20**) are outlined in Scheme 6 [36].

The conversion of **20** by PhCN into the unsymmetrical lithium β -diketiminato $[\text{Li}(\text{L}''\text{L}''')]_2$ (**23**) has already

been noted. This reaction, and also those of **20** with (i) an equimolar portion of ZrCl_4 , (ii) KO^tBu and (iii) successively CH_2Br_2 and Li^nBu , yielding **24**, **25** and **26**, respectively, demonstrate that these nucleophilic substitutions involve both the C- and N-centres of the 1-azaallyl ligand. By contrast, the hydrolysis of **20** giving the imine **27** shows **20** behaving as a C-centred



Scheme 10. [41].



Scheme 11. [43].

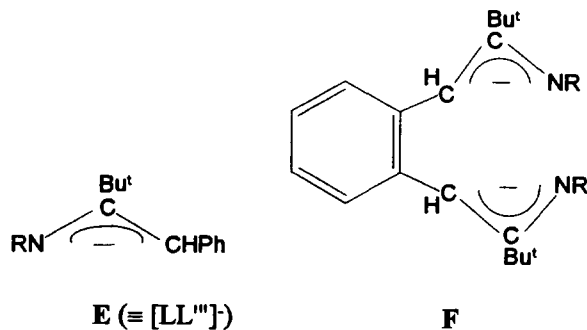
nucleophile. The β -diketiminatolithium compound **23** was readily converted into $[\overline{M(L''L''')}Cl_3]$ ($M = Zr$ (**28**) or Hf (**29**)).

The diastereoselective formation of $rac\text{-}[Zr\{\overline{N(R)C}(\text{}^t\text{Bu})CHR\}_2Cl_2]$ (**24**) rather than a mixture of rac - and $meso$ -isomers mirrors that for $rac\text{-}[Yb(LL')_2]$ (**17**), formed not only from $[Yb(CHR_2)_2(OEt)_2]_2$ (**13**) and 2^tBuCN but also from **20** + YbI_2 (Scheme 4) [30]. The isomerism arises because C-3 of the 1-azaallyl group is chiral, being attached to the metal, H, $SiMe_3$ and C.

The outcome of the reactions leading to the 1-azaallyllithium complex $[Li\{\overline{N(R)C}(\text{}^t\text{Bu})C(H)CH(R)^n\text{Bu}\}]_2$ (**26**) from $[Li(LL')]_2$ (**20**) was unexpected. The purpose of adding CH_2Br_2 to **20** was to generate a methylene-bridged bisazaallyl precursor. In the event, a crystalline product was not isolated and hence $2Li^n\text{Bu}$ was added to an in situ mixture of $CH_2Br_2 + 20$. The product was the higher homologue **26** rather than the isomer $Li\{\overline{N(R)C}(\text{}^t\text{Bu})C(R)CH_2\text{}^t\text{Bu}\}$. This apparent 1,2-H-R ($R = SiMe_3$) exchange represents an unusual dyotropic shift.

The rac -dichloride **24** and an equimolar portion of $ZrCl_4$ yielded the binuclear zirconium(IV) chloride $[[Zr(LL')Cl_2(\mu\text{-Cl})_2]$ (**30**) (Eq. (1)) [40]. The dimeric nature of this crystalline Zr(IV) trichloride complex **30**, contrasting with the monomeric **28**, shows that the 1-azaallyl ligand **A** is not as sterically demanding as the β -diketinate **B**.

Two other 1-azaallyl ligands **E** and **F**, have been investigated. Each was generated by a modification of the $LiCHR_2 + \text{}^t\text{BuCN}$ reaction (see Scheme 5), as shown in Schemes 10 [41] and 11 [43], respectively, for the synthesis of $[Zr\{\overline{N(R)C}(\text{}^t\text{Bu})CHPh\}Cl_3]$ (**31**) [41] and $[Zr\{\overline{N(R)C}(\text{}^t\text{Bu})CH\}_2C_6H_4-2)Cl_2]$ (**32**) [42,43].



The X-ray molecular structures of $rac\text{-}[Yb(LL')_2]$ (**17**) [30], $rac\text{-}[Zr(LL')_2Cl_2]$ (**24**) [36,40], $[[Zr(LL')Cl_2(\mu\text{-Cl})_2]$ (**30**) [40], $[Zr\{\overline{N(R)C}(\text{}^t\text{Bu})CHPh\}Cl_3]$ (**31**) [41] and $[Zr\{\overline{N(R)C}(\text{}^t\text{Bu})CH\}_2C_6H_4-2)Cl_2]$ (**32**) [43] are illustrated schematically in Figs. 10, 11, 12, 13 and 14, respectively.

Crystalline $rac\text{-}[Yb(LL')_2]$ (**17**) is mononuclear, the ytterbium atom being bound in an η^3 -fashion to the two

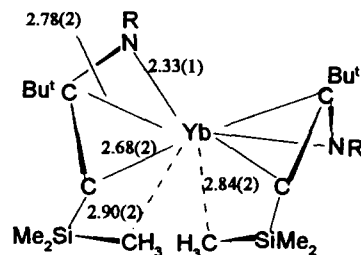


Fig. 10. A simplified bonding pattern showing key features of the X-ray molecular structure of $rac\text{-}[Yb(LL')_2]$ (**17**) ($LL' = N(R)C(\text{}^t\text{Bu})CHR$, $R = SiMe_3$) [30].

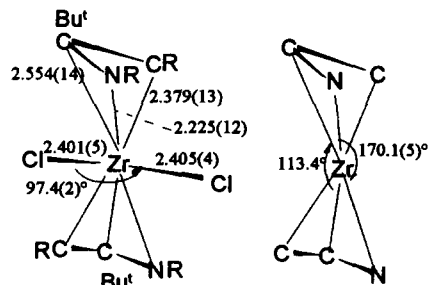


Fig. 11. A simplified bonding pattern showing key features of the X-ray molecular structure of $rac\text{-}[Zr(LL')_2Cl_2]$ (**24**) ($LL' = N(R)C(\text{}^t\text{Bu})CHR$, $R = SiMe_3$) [40].

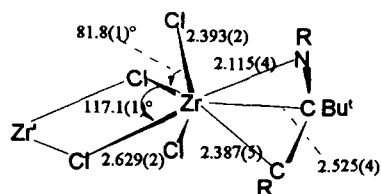


Fig. 12. A simplified bonding pattern showing key features of the X-ray molecular structure of $[[Zr(LL')Cl_2(\mu\text{-Cl})_2]$ (**30**) ($LL' = N(R)C(\text{}^t\text{Bu})CHR$, $R = SiMe_3$) [40].

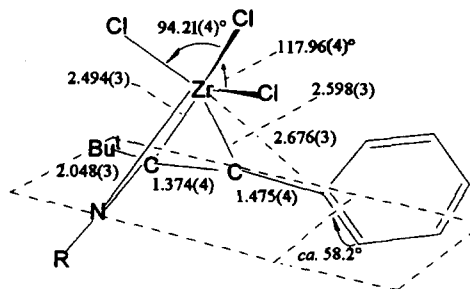


Fig. 13. A simplified bonding pattern showing key features of the X-ray molecular structure of $[Zr\{\overline{N(R)C}(\text{}^t\text{Bu})CHPh\}Cl_3]$ (**31**) ($R = SiMe_3$) [41].

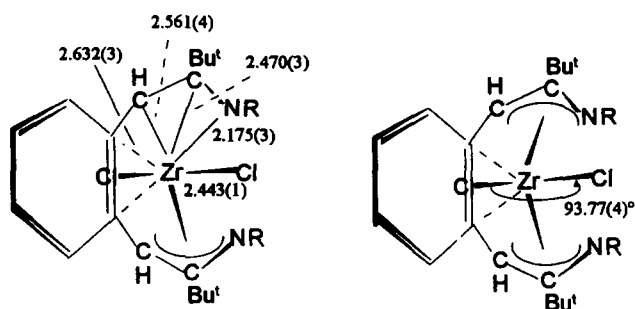


Fig. 14. A simplified bonding pattern showing key features of the X-ray molecular structure of $[\text{Zr}(\text{N}(\text{R})\text{C}(\text{tBu})\text{CH})_2\text{C}_6\text{H}_4-2]\text{Cl}_2$ (**32**) ($\text{R} = \text{SiMe}_3$) [43].

1-aza-allyl ligands **A** with an additional close agostic contact between Yb and one of the methyls of the SiMe_3 group (Fig. 10) [30]. In benzene solution, NMR spectra show the presence of two species, possibly the *rac*- and *meso*-diastereoisomers, C-3 of **A** being a chiral centre.

Crystalline *rac*- $[\text{Zr}(\text{LL}')_2\text{Cl}_2]$ (**24**) has the zirconium in a distorted tetrahedral environment, taking the η^3 -azaallyl ligand **A** as occupying a single coordination site (Fig. 11). A similar situation is found for $[\text{Zr}(\text{N}(\text{R})\text{C}(\text{tBu})\text{CH})_2\text{C}_6\text{H}_4-2]\text{Cl}_2$ (**32**), in which the two 1-azaallyl fragments are within the single bidentate ligand **F** (Fig. 14) [43].

The two crystalline 1-azaallylzirconium(IV) trichlorides $[\{\text{Zr}(\text{LL}')\text{Cl}_2(\mu\text{-Cl})\}_2]$ (**30**) [40] (Fig. 12) and $[\text{Zr}(\text{E})\text{Cl}_3]$ (**31**) [41] (Fig. 13) are interesting in that the former is binuclear whereas the latter is a monomer. Evidently, the η^3 - $[\text{N}(\text{R})\text{C}(\text{tBu})\text{CHPh}]^-$ ligand **E** ($\equiv [\text{LL}''']^-$) is sterically more demanding than $[\text{LL}']^-$ **A**.

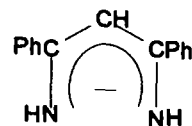
5. Synthesis, structures and reactions of various β -diketiminatometal complexes

The synthesis of $[\text{Li}(\text{L}'\text{L}')]_2$ (**21**) and the potassium analogue $[\text{K}(\text{L}'\text{L}')]_n$ (**33**) and a selection of their reac-

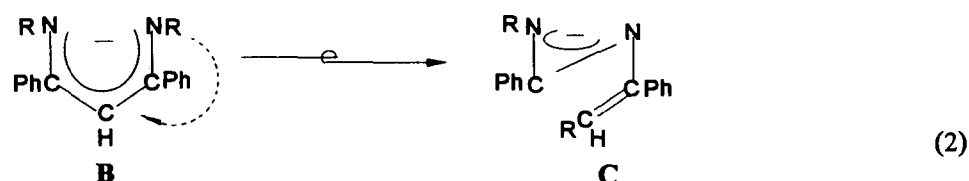
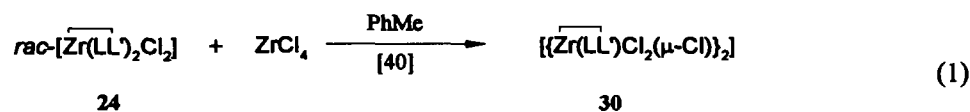
tions are outlined in Scheme 7 [$\text{L}'\text{L}' = \text{N}(\text{R})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Ph})\text{NR}$, $\text{R} = \text{SiMe}_3$] [37,44]. The conversion of $[\text{Li}(\text{N}(\text{R})\text{C}(\text{tBu})\text{C}(\text{H})\text{C}(\text{Ph})\text{NR})_2]$ (**23**), i.e. $[\text{Li}(\text{L}''\text{L}''')]_2$, into $[\text{M}(\text{L}''\text{L}''')\text{Cl}_3]$ ($\text{M} = \text{Zr}$ (**28**) or Hf (**29**)) has already been noted, as shown in Scheme 6 [36]. The reactions of **21** or **33** with CH_2Br_2 , H_2O , $(\text{CH}_2\text{Br})_2$, SnCl_2Me_2 , SnClMe_3 , or CoCl_2 (Scheme 7) yielding **34**, **35**, **35**, **36**, **36** or **38** demonstrate that the alkali metal β -diketiminates **21** and **33** may behave either as C- (\rightarrow **34** or **35**) or N- (\rightarrow **36** or **38**) centred nucleophiles; in this they resemble the β -diketonates.

It is interesting that $[\text{K}(\text{L}'\text{L}')]_n$ (**33**) and $(\text{CH}_2\text{Br})_2$ gave exclusively the elimination product $\text{L}'\text{L}'\text{H}$ **35** rather than also $\text{CH}_2(\text{L}'\text{L}')_2$. The $[\text{L}'\text{L}']^-$ ligand (**B**) transfer reactions to a $\text{Co}(\text{II})$ [44] or $\text{Sn}(\text{IV})$ [37] centre yielding **38** or **36**, respectively, are unexpected except in one particular. The formation of **36** from SnClMe_3 at first sight might be taken as indicating that Me^- was preferred over Cl^- as the leaving group; however, for each molecule of **21**, equimolar portions of **36** and SnMe_4 were formed; thus in this reaction $\text{SnMe}_3(\text{L}'\text{L}')$ was probably an intermediate which with SnClMe_3 gave **36** + SnMe_4 [37].

The formation of the *N,N'*-bis(desilylated)tin(IV) [37] or -cobalt(II) [44] complexes **37** and **39**, respectively, by controlled hydrolysis of their precursor complexes **36** and **38**, respectively, shows that the SiMe_3 substituents may play an additional useful role, as protecting groups, in the sequence: $4\text{PhCN} + 2\text{LiCHR}_2 \rightarrow [\text{Li}(\text{L}'\text{L}')]_2$ (**21**) $\rightarrow \text{Sn}(\text{L}'\text{L}')(\text{Cl})\text{Me}_2$ (**36**) or $[\text{Co}(\text{L}'\text{L}')_2]$ (**38**) $\rightarrow \text{Sn}(\text{LL}')(\text{Cl})\text{Me}_2$ (**37**) or $[\text{Co}(\text{LL}')_2]$ (**39**) [$\text{L}'\text{L}' = \text{B}$, $\text{LL}' = \text{N}(\text{H})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Ph})\text{NH}$ **G**].



G ($\equiv [\text{LL}']^-$)



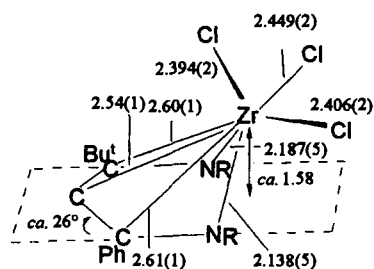


Fig. 15. A simplified bonding pattern showing key features of the X-ray molecular structure of $[\text{Zr}(\text{L}''\text{L}''')\text{Cl}_3]$ (**28**) ($\text{L}''\text{L}''' = \text{N}(\text{R})\text{C}(\text{tBu})\text{C}(\text{H})\text{C}(\text{Ph})\text{NR}$; $\text{R} = \text{SiMe}_3$) [36,45].

The X-ray molecular structures of $[\text{Zr}(\text{L}''\text{L}''')\text{Cl}_3]$ (**28**) [45], $\text{Sn}(\text{L}'\text{L}')(\text{Cl})\text{Me}_2$ (**36**) [37], $\text{Sn}(\text{LL})(\text{Cl})\text{Me}_2$ (**37**) [37], $[\text{Co}(\text{L}'\text{L}')_2]$ (**38**) [44] and $[\text{Co}(\text{LL})_2]$ (**39**) [44] are illustrated schematically in Figs. 15, 16(a), 16(b), 17(a) and 17(b), respectively ($\text{L}''\text{L}''' = \text{N}(\text{R})\text{C}(\text{tBu})\text{C}(\text{H})\text{C}(\text{Ph})\text{NR}$, $\text{R} = \text{SiMe}_3$).

It is interesting that $[\text{Zr}(\text{L}''\text{L}''')\text{Cl}_3]$ (**28**) should be a monomer (Fig. 15) [36,45]. It is most unusual to find that a zirconium(IV) trichloride is mononuclear. For example, $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2(\mu\text{-Cl})_k]$ [46] is polymeric in the crystal and even the pentamethyl analogue is a dimer, $[\text{Zr}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2(\mu\text{-Cl})_2]$ [47]. This shows that the β -diketiminato ligand $[\text{L}''\text{L}''']^-$ **D**, like $[\text{L}'\text{L}']^-$ **B**, is exceptionally sterically demanding.

Crystalline $\text{Sn}(\text{L}'\text{L}')(\text{Cl})\text{Me}_2$ (**36**) (Fig. 16(a)) and $\text{Sn}(\text{LL})(\text{Cl})\text{Me}_2$ (**37**) (Fig. 16(b)) have tin in a distorted trigonal bipyramidal environment, with the chloride and $\text{N}(2)$ axial (numbers in parentheses refer to **37**): Cl–Sn–N(2) 166.4(2) (163.2(1)), C–Sn–C 119.9(4) (122.7(1)), C–Sn–N(1) 111.1(4) and 129.0(4) (112.4(1) and 124.8(1)), C–Sn–N(2) 97.8(4) and 92.5(3) (97.5(1) and 94.1(1)), Cl–Sn–C 92.2(3) and 91.0(3) (92.7(1) and 91.7(1)), Cl–Sn–N(1) 85.4(2) (81.6(1)), N(1)–Sn–N(2)

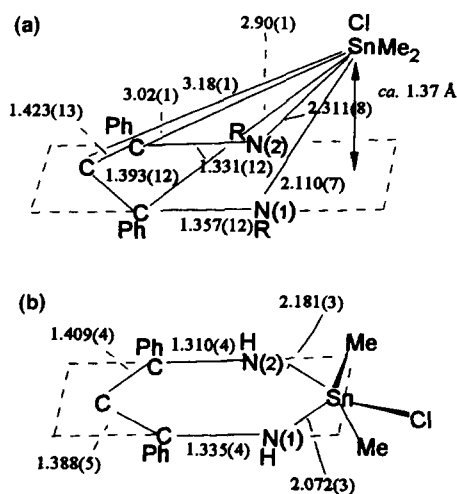


Fig. 16. Simplified bonding patterns showing key features of the X-ray molecular structures of (a) $\text{Sn}(\text{L}'\text{L}')(\text{Cl})\text{Me}_2$ (**36**) ($\text{L}'\text{L}' = \text{N}(\text{R})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Ph})\text{NR}$, $\text{R} = \text{SiMe}_3$) [37] and (b) $\text{Sn}(\text{LL})(\text{Cl})\text{Me}_2$ (**37**) ($\text{LL} = \text{N}(\text{H})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Ph})\text{NH}$, $\text{R} = \text{SiMe}_3$) [37].

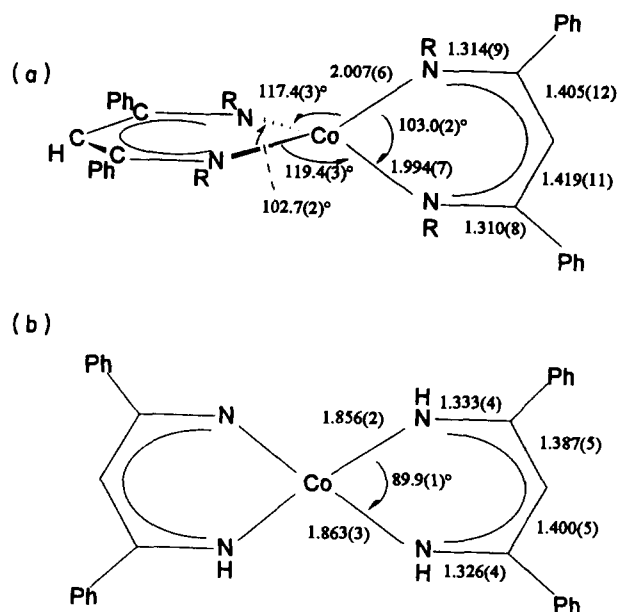


Fig. 17. Simplified bonding patterns showing key features of the X-ray molecular structures of $[\text{Co}(\text{L}'\text{L}')_2]$ (**38**) ($\text{L}'\text{L}' = \text{N}(\text{R})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Ph})\text{NR}$, $\text{R} = \text{SiMe}_3$) [44], and (b) $[\text{Co}(\text{LL})_2]$ (**39**) ($\text{LL} = \text{N}(\text{H})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Ph})\text{NH}$, $\text{R} = \text{SiMe}_3$) [44].

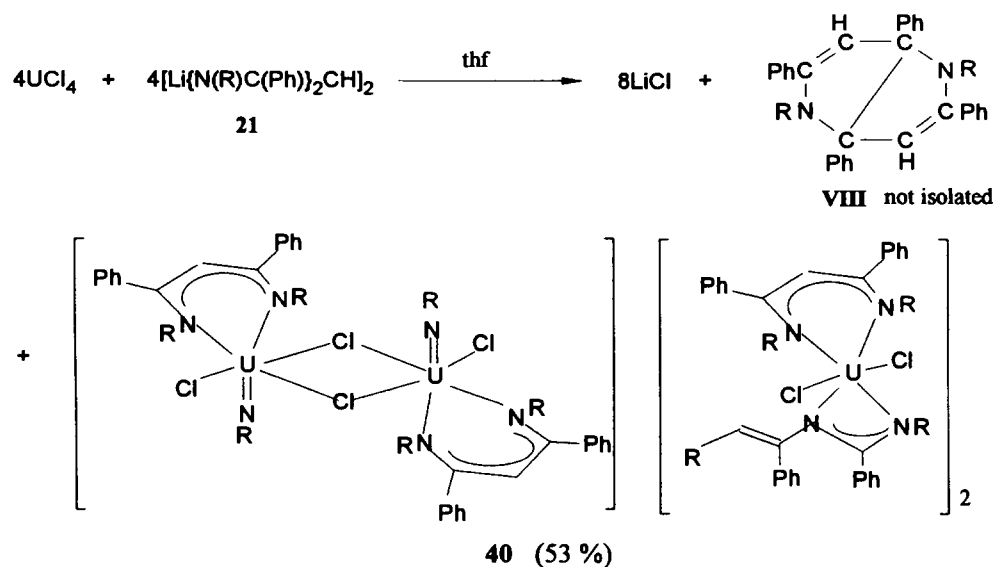
81.0(3) (82.1(1))° [37]. Compounds **36** and **37** differ in one important respect: the SnNC-C-CN skeleton in **37** is almost planar whereas the Sn atom in **36** is ca. 1.37 Å out of the NC–CN plane; the central C of $\text{L}'\text{L}'$ in **36** is 0.09 Å out of the NC–NC plane. The $[\text{L}'\text{L}']^-$ **B** arrangement around Sn in **36** is closely similar to that of $[\text{L}''\text{L}''']^-$ **D** around Zr in **28**.

The difference in relationship between the metal and either the $[\text{L}'\text{L}']^-$ or the $[\text{LL}]^-$ ligand for the tin complexes **36** and **37** clearly has a steric origin, which is even more obviously manifested by comparing the structures of $[\text{Co}(\text{L}'\text{L}')_2]$ (**38**) (Fig. 17(a)) and $[\text{Co}(\text{LL})_2]$ (**39**) (Fig. 17(b)). Both of these d^7 crystalline complexes are mononuclear, but whereas the former has a tetrahedral arrangement around the cobalt, the latter is square planar.

6. Synthesis and structure of a 1,3-diazaallyluranium complex

Treatment of UCl_4 with two equivalents of $[\text{Li}(\text{N}(\text{R})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Ph})\text{NR})_2]$, i.e. $[\text{Li}(\text{L}'\text{L}')_2]$ (**21**), yielded a pink product **40** composed of one $[\text{U}(\text{VI})]$ dication $[\{\text{UCl}_2(\mu\text{-Cl})(\text{L}'\text{L}')(\text{NR})_2\}]^{2+}$ and two $[\text{U}(\text{III})]$ anions $[\text{UCl}_2(\text{L}'\text{L}')(\text{LL}'')]^-$. The ligands $[\text{L}'\text{L}']^-$ **B** and $[\text{LL}''']^-$ **C** ($\text{Ar} = \text{Ph}$) [$\text{LL}'' = \text{N}(\text{R})\text{C}(\text{Ph})\text{NC}(\text{H})\text{C}(\text{Ph})\text{CHR}$, $\text{R} = \text{SiMe}_3$] are isomeric.

The organic coproduct was not isolated; if it is a single entity it should have the composition $[\text{N}(\text{R})]_2\text{-(CPh)}_4(\text{CH})_2$; a possible structure is shown in **VIII** (Scheme 12).



Scheme 12. [38].

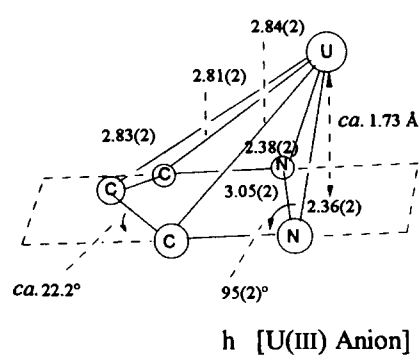
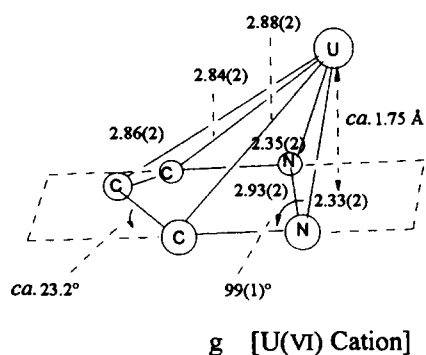
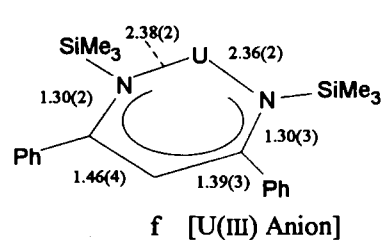
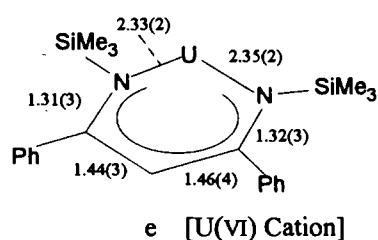
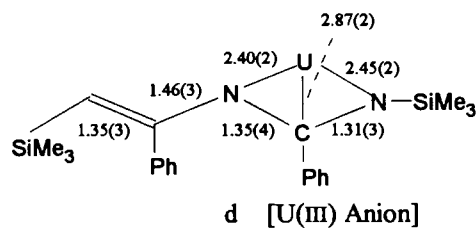
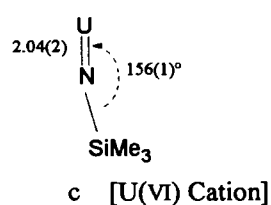
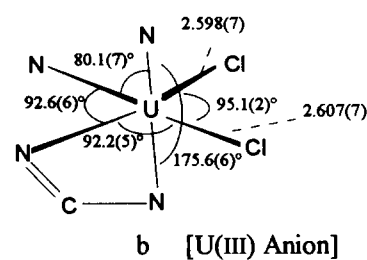
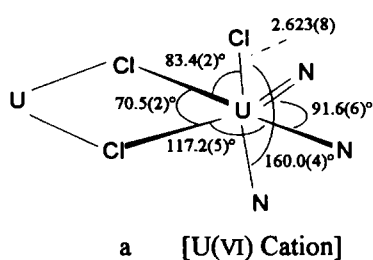


Fig. 18. Simplified bonding patterns showing key features of the X-ray molecular structure of $[\{\text{UCl}(\mu\text{-Cl})(\text{L}'\text{L}')\text{NR}\}]_2[\text{UCl}_2(\text{L}'\text{L}')(\text{LL}')_2]$ (**40**) ($\text{L}'\text{L}' = \text{N}(\text{R})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Ph})\text{NR}$, $\text{LL}' = \text{N}(\text{R})\text{C}(\text{Ph})\text{NC}(\text{Ph})\text{CHR}$, $\text{R} = \text{SiMe}_3$) [38].

The presence of the two U=N double bonds in the cation implies that a C–N bond in the [L'L']⁻ B β-diketiminato ligand must have been cleaved along the reaction pathway, in a reductive process.

The X-ray molecular structure of the salt **40** is shown schematically in Fig. 18(a–h) [38].

For both the cation (Fig. 18(a)) and anion (Fig. 18(b)), the central uranium is in a distorted octahedral site. The salt **40** has four different types of U–N bonds: U=N, U–N in [L'L']⁻ and [LL']⁻, illustrated in Fig. 18(c–f). The U=N bond distance (Fig. 18(c)) of 2.04 Å is the second shortest known for UN; this and the U=N–Si bond angle of 156(1)° suggest that there is UN triple-bond character. The delocalized five-membered β-diketiminato ligand (Fig. 18(e) and (f)) provides a stronger UN bond than the delocalized three-membered 1,3-diazaallyl ligand (Fig. 18(d)). The U atom in both the cation (Fig. 18(g)) and anion (Fig. 18(h)) is situated above the plane of the N=C–C=C–N fragment of [L'L']⁻, the central C atom being slightly out of plane (cf. the Sn(IV) and Co(II) complexes **36** and **38**).

The isomeric η⁵- and η³-ligands in the anion (Fig. 18(f)) and cation (Fig. 18(d)) may be related by the molecular rearrangement shown in Eq. (2); its occurrence may be sterically induced [38].

7. 1-Azaallyl and β-diketiminatozirconium(IV) chlorides as olefin polymerization catalysts

There is considerable current interest in the use of various Group 4 metal(IV) chlorides as polymerization catalysts [48], particularly those of zirconium. The majority of useful catalysts have been based on the zirconocene(IV) chlorides, of which the simplest is [Zr(η-C₅H₅)₂Cl₂], but *ansa*-bridged bis(cyclopentadienyl)s, especially those of C₂ symmetry, have been particularly important. Such a compound is used either with an excess of methylaluminoxane (MAO), or is converted into an appropriate alkylzirconium(IV) salt, as a single-site catalyst for the polymerization or oligomerization of ethylene, propylene or another α-olefin, or for the copolymerization of two olefins.

We have examined some of the zirconium(IV) chlorides described in Sections 4 and 5 as catalysts, with MAO as cocatalyst, for the polymerization of ethylene and propylene. Compounds [Zr{N(R)C('Bu)C(H)C(Ph)-NR}Cl₃] (**28**) [45], [Zr{N(R)C('Bu)CHPh}Cl₃] (**31**) [41] and [Zr{(N(R)C('Bu)CH)₂C₆H₄-2}Cl₂] (**32**) [43] showed significant activity for the polymerization of C₂H₄ in toluene under slight C₂H₄ pressure (6–10 bar) (**28** and **32**) or ambient conditions (**31**); **31** was also effective under ambient conditions for producing highly monodisperse atactic polypropylene.

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