# Multinuclear Magnetic Resonance Investigation of the Fluxionality of $\mathrm{CH(SiMe_3)_2}$ Groups in Organolanthanide Complexes

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A series of related complexes, $[\mathrm{La(C_5Me_5)\{CH(SiMe_3)_2\}_2}]$ **1**, $[\mathrm{M(C_5Me_5)_2\{CH(SiMe_3)_2\}}]$ [M = La **2** or Lu **3**], $[\mathrm{Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K}]$ **4** and the homoleptic tris-alkyls $[\mathrm{M\{CH(SiMe_3)_2\}_3}]$ (M = Lu **5**, La **6** or Al **7**), have been prepared to investigate the factors influencing the fluxionality of their $\mathrm{CH(SiMe_3)_2}$ groups. Complexes **1**–**7** have been studied by the complementary techniques of variable-temperature solution- and solid-state $^{13}$C NMR spectroscopy. Differences are observed that can only be metal dependent. Variable-temperature very fast magic-angle spinning solid-state $^{1}$H NMR spectra of complexes **2**, **3** and **5–7** have also been recorded. Sequences of relative mobility of the $\mathrm{CH(SiMe_3)_2}$ groups in the solid state can be formulated: complex **2** > **1** > **3** and complex **5** > **6** > **7**. In complex **4** a preferential orientation of the $\mathrm{CH(SiMe_3)_2}$ ligands is caused by KCl co-ordination. Collation of $\mathrm{M\text{-}C_\gamma}$ and $\mathrm{M\text{-}Si_\beta}$ distances for the structurally characterized $\mathrm{M\text{-}CH(SiMe_3)_2}$ and $\mathrm{M\text{-}N(SiMe_3)_2}$ complexes results in the mean distances falling in a narrow range, $\mathrm{M\text{-}CH(SiMe_3)_2}$ $\mathrm{M\text{-}C_\gamma}$ 1.867(0.11), $\mathrm{M'\text{-}Si_\beta}$ 2.244(0.085) Å, $\mathrm{M\text{-}N(SiMe_3)_2}$ $\mathrm{M'\text{-}C_\gamma}$ 1.973(0.11), $\mathrm{M'\text{-}Si_\beta}$ 2.205(0.056) Å. Co-ordination of a β-Si–C σ bond would lead to just such a consistency of data, given the absence of other geometric constraints. It is suggested that in electrophilic complexes, containing a $\mathrm{CH(SiMe_3)_2}$ or $\mathrm{N(SiMe_3)_2}$ ligand, the metal may be stabilized by a β-Si–Me–M rather than a γ-C–H–M interaction.

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One of us recently reported the synthesis and X-ray structure determination of $[\mathrm{La(C_5Me_5)\{CH(SiMe_3)_2\}_2}]$ **1** and its tetrahydrofuran (thf) adduct.[1] As well as the expected α-C–H–La interactions, these species are stabilized by the co-ordination of one Si–Me σ bond of each $\mathrm{CH(SiMe_3)_2}$ group to the lanthanum centre. Although close intramolecular contacts between a methyl group of a $\mathrm{CH(SiMe_3)_2}$ ligand and an electrophilic lanthanide centre have been structurally characterized,[1–12] there is a paucity of conclusive evidence as to the exact nature of this interaction; the crystal structures of $[\mathrm{Ln(C_5Me_5)_2\{CH(SiMe_3)_2\}}]$ (Ln = Nd,[2] Y[3] or Ce[4]) and $[\mathrm{Ln\{CH(SiMe_3)_2\}_3}]$ (Ln = La or Sm)[5] suffered from disorder problems, so that unequivocable differentiation between either a γ-C–H–Ln[2–9] or a β-Si–Me–Ln[1,10–12] interaction has not been possible.

In order to investigate more fully these relationships, an alternative method of analysis was sought which would complement the crystallographic data. For this purpose, NMR measurements, in both the solution and solid state, are known to be extremely useful. By studying a related series of organolanthanide complexes containing $\mathrm{CH(SiMe_3)_2}$ ligands, evidence might be obtained to determine the co-ordination of the β-Si–Me σ bond. For this reason mono- and homoleptic tris-alkyl organolanthanide species were synthesised as a comparison with compound **1** for which good crystallographic evidence for the co-ordination of the β-Si–Me bond exists.[1] The size[13] of the metal is also of importance in determining the energetics of the accessible intramolecular interactions, so analogous lutetium and lanthanum complexes were studied.

The NMR experiment is sensitive to both the structural and dynamic properties of nuclei of diamagnetic complexes in the solution and solid state,[14] and can provide insight into the local 'short-range' order present in a structure, even where 'long-range' order, necessary for resolved crystallographic analysis, is absent.[15] In principle, $^{1}$H, $^{13}$C and $^{29}$Si nuclei represent potential NMR probes which would be sensitive to interactions with a metal centre.

High-resolution $^{13}$C cross-polarization[16] magic-angle-spinning[17] (CP MAS) NMR spectroscopy, in conjunction with high-power proton decoupling,[18] combines pulsed NMR spectroscopy with high-speed sample rotation, and can, under favourable circumstances, produce 'liquid-like' NMR spectra of solids.[19] Moreover, structural information is retained which would otherwise be lost as the result of the inherent isotropic averaging which occurs in the solution state. In combination with variable-temperature techniques to study these fluxional molecules, a powerful tool complementary to both crystal structure analysis and solution NMR spectroscopy is realised which can be used to study conformational behaviour and motion in complex structures,[20–23] and which is currently finding increasing use in organometallic systems.[24]

In this manner we reasoned that the combination of variable-temperature solution- and solid-state $^{1}$H, $^{13}$C and $^{29}$Si NMR spectroscopic studies would provide new information where crystallographic data are not available, and might also allow the differentiation of β-Si–Me–Ln from γ-C–H–Ln interactions. Thus $[\mathrm{La(C_5Me_5)\{CH(SiMe_3)_2\}_2}]$, **1**,[1] $[\mathrm{M(C_5Me_5)_2\{CH(SiMe_3)_2\}}]$ [M = La **2**[2] or Lu **3**[2]], $[\mathrm{Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K}]$, **4** and $[\mathrm{La\{CH(SiMe_3)_2\}_3}]$ **5**,[5] together with the new homoleptic trialkyl complexes $[\mathrm{Lu\{CH(SiMe_3)_2\}_3}]$ **6** and $[\mathrm{Al\{CH(SiMe_3)_2\}_3}]$ **7** were studied by these complementary techniques.

## Results and Discussion

*Possible Mechanisms of Methyl Group Equilibration.*—The following dynamic processes are possible for a single $\mathrm{CH(SiMe_3)_2}$ ligand (the arguments presented here modify those previously proposed[3]): (A) rotation around $\mathrm{Ln\text{-}C_\alpha}$ (sometimes)†

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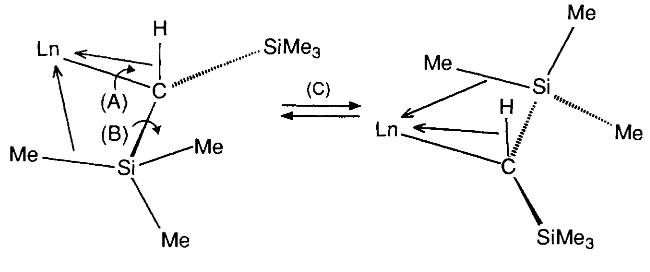
† This is valid for $[\mathrm{Ln(C_5Me_5)_2\{CH(SiMe_3)_2\}}]$, but not for compound **1** because of the different possible (*endo* and *exo*) orientations of the two $\mathrm{CH(SiMe_3)_2}$ groups.

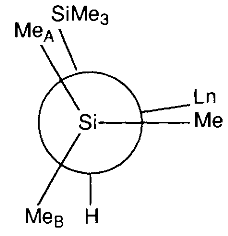
**Table 1** Partial summary of solution- and solid-state $^{13}C$ NMR spectral data[a]

| | Solution state | | | | | Solid state (at 25 °C) | | | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | $T$/°C | $C_5Me_5$ | $C_5\mathit{Me}_5$ | CH | $SiMe_3$ | $C_5Me_5$ | $C_5\mathit{Me}_5$ | CH | $Si\mathit{Me}_3$ |
| **1** | 25 | 120.85 | 10.1 | 58.35 | 3.62 | 121.7(40) | 11.6(15) | 60(900) | 7.5[6] |
| | | | | | | | | | 5.7[3] |
| | | | | | | | | | 4.6[3] |
| | −90 | 120.40[4] | | 59.3 | | | | | |
| | | 120.12[9] | | 54.3 | | | | | |
| **2**[b] | | 121.1 | 11.49 | 44.64 | 4.50 | 121.8(40) | 12.1(30) | 40 | 5.46(55) |
| | | 120.6 | 11.29 | | | | | | |
| | | | | | | 121.1(40) | | | |
| | | | | | | 120.6(40) | | | |
| **3** | | | | | | 119.6 | 13.3 | 25.8 | 12.7[1] |
| | | | | | | 119.15 | 12.7 | | 7.1[3] |
| | | | | | | | | | 5.0[2] |
| **4** | −80 | | | 52.4 | 3.74 | | | 60.2 | 7.75 |
| | | | | | | | | 53.3 | 6.66 |
| | | | | | | | | | 5.97 |
| | | | | | | | | | 5.4 |
| **5** | 25 | | | 57.35 | 3.69 | | | 58.4(100) | 6.23 |
| **6**[c] | −30 | | | 75.2 | 5.20 | | | 77.0(900) | 6.3[1] |
| | | | | | | | | | 5.4[1] |
| **7** | −80 | | | 10.07 | 3.35 | | | 11.9 | 6.9 |
| | | | | | | | | | 6.1 |
| | | | | | | | | | 5.8 |
| | | | | | | | | | 5.4 |

[a] Values of the full width at half maximum are given in parentheses and the relative intensities of the peaks in square brackets. [b] Solution data taken from ref. 26. [c] Solution data taken from ref. 5.



exchanging $SiMe_3$ groups, (B) rotation around $C_\alpha$–$Si_\beta$ exchanging methyl groups within the same $SiMe_3$ group; and (C) wagging of the Ln–$C_\alpha$ bond exchanging $SiMe_3$ groups. A relative order of activation energies for these processes has been proposed,[3] $E_A \gg E_C > E_B$. An α-agostic C–H ⋯ Ln interaction also favours a rigid Ln–$C_\alpha$ bond, although this probably accounts for only *ca.* 20 kJ $mol^{-1}$.[25] In a static structure, methyl resonances in a 1 : 1 : 1 : 3 ratio should be observed as a Newman projection along the $Si_\beta$–$C_\alpha$ bond shows an eclipsed conformation with the two unco-ordinated methyls ($Me_A$ and $Me_B$) chemically inequivalent. Their chemical-shift difference, however, is likely to be small and unobservable.



To facilitate the comparison of solution- and solid-state results, the $^{13}C$ NMR data for compounds **1**–**7** are summarized in Table 1. Some small differences between the solution- and solid-state chemical shifts can be seen, when the resonances are not associated with coalescence phenomena. No attempt is made here to assign significance to this, although it may be explained by a small change in the local environment of a nucleus as it accommodates the constraints of a rigid lattice imposed by the solid state.

*Characterisation of Complexes* **1**–**7** *by NMR Spectroscopy*.—$[La(C_5Me_5)\{CH(SiMe_3)_2\}_2]$ **1**. Variable-temperature solution $^{13}C$ NMR spectra of complex **1** were recorded between 25 and −90 °C in $C_7D_8$. At 25 °C the spectrum exhibits sharp Lorentzian lineshapes for all resonances. The methyne and trimethylsilyl carbons of the $CH(SiMe_3)_2$ groups are observed at δ 58.35 and 3.62 respectively, while the $C_5Me_5$ and $C_5\mathit{Me}_5$ resonances occur at δ 120.85 and 10.1. These data are indicative of a symmetrical time-averaged trigonal-planar structure with equivalent trimethylsilyl groups.

The low-temperature measurements are shown in Fig. 1, where at −90 °C two different $C_5Me_5$ resonances are observed at δ 120.40 and 120.12 in a 4 : 9 ratio. Although $^{13}C$-$\{^1H\}$ NMR spectra are not quantitative, hence the intensities of the resonances are not necessarily proportional to the number of atoms giving rise to the signals, it is, however, a reasonable assumption that the relative intensities of identical atom types in similar local environments, *e.g.* $C_5Me_5$, $C_5\mathit{Me}_5$, $SiMe_3$ in the *exo*/*endo* isomer are comparable with those of their respective counterparts in the *endo*/*endo* isomer. Two methyne resonances are also observed, at δ 59.3 and 54.3, in *ca.* 1 : 2 ratio respectively, together with three separate $SiMe_3$ resonances. By comparison, solution $^1H$ NMR spectroscopic studies indicate that the $SiMe_3$ methyl groups are magnetically equivalent at −80 °C. The $^{13}C$-$\{^1H\}$ NMR spectral data are consistent with the presence of two isomers, one of which is *exo–endo* [*] as was determined by X-ray crystallography.[1] The second isomer is presumably *endo*/*endo*

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[*] Here *endo* and *exo* are used to describe the orientation of the α-CH groups with respect to the $C_5Me_5$ ring. Although not completely accurate, this representation conveniently differentiates between the two orientations of the $CH(SiMe_3)_2$ ligands in complex **1**.

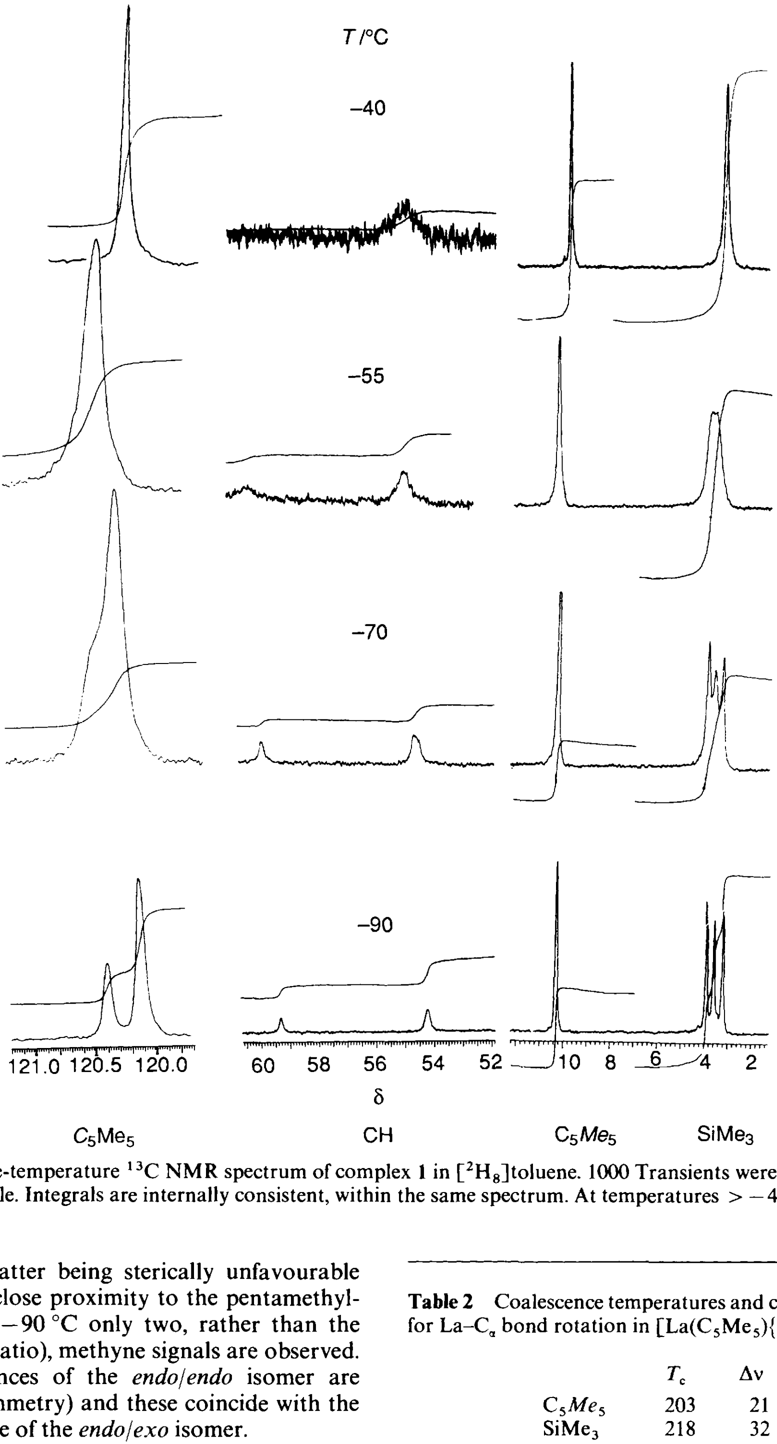

**Fig. 1** Regions of the variable-temperature $^{13}$C NMR spectrum of complex **1** in [$^2H_8$]toluene. 1000 Transients were accumulated at each denoted temperature on the same sample. Integrals are internally consistent, within the same spectrum. At temperatures > −40 °C all resonances are sharp

rather than *exo*/*exo*, the latter being sterically unfavourable with the SiMe$_3$ groups in close proximity to the pentamethylcyclopentadienyl ring. At −90 °C only two, rather than the expected three (in a 8:9:9 ratio), methyne signals are observed. Both *C*H(SiMe$_3$)$_2$ resonances of the *endo*/*endo* isomer are equivalent (pseudo $C_{2v}$ symmetry) and these coincide with the *endo* *C*H(SiMe$_3$)$_2$ resonance of the *endo*/*exo* isomer.

At −70, −55 and −40 °C coalescence of the $C_5$Me$_5$, SiMe$_3$ and methyne† resonances, respectively, was observed. The coalescence is due to just one dynamic process, *i.e.* rotation around the La–C$_\alpha$ bonds, since the calculated activation free energies are identical as given in Table 2. This compares with [Ln(C$_5$Me$_5$)$_2${CH(SiMe$_3$)$_2$}] where Ln = Y (88.4), La (78.9) or Ce (79.2 kJ mol$^{-1}$).[26] These higher barriers are presumably steric in origin.

**Table 2** Coalescence temperatures and calculated activation energies* for La–C$_\alpha$ bond rotation in [La(C$_5$Me$_5$){CH(SiMe$_3$)$_2$}$_2$] in C$_7$D$_8$

| | $T_c$ | Δν | $\Delta G^{\ddagger}$ kJ mol$^{-1}$ |
|---|---|---|---|
| C$_5$$Me_5$ | 203 | 21 | 42.6 |
| SiMe$_3$ | 218 | 32 | 45.1 |
| Methyne | 233 | 385 | 43.5 |

* At $T_c$, based on the coalescence ($^{13}$C NMR, 75.4 MHz) for a simple two-site exchange model.

The variable-temperature solid-state $^{13}$C CPMAS NMR spectra of complex **1** between 25 and −90 °C are shown in Fig. 2. Throughout the studied temperature range, the linewidths and isotropic chemical shift of the $C_5$Me$_5$ and C$_5$$Me_5$ resonances remain constant, showing no evidence of the isomers observed in the solution spectra over the same temperature range. There is also no evidence of La–C coupling in the $C_5$Me$_5$ peaks, indicating that the co-ordination is π in character.

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† The coalescence of the methyne resonance should be accompanied by a change in chemical shift representative of the isotropically averaged environment of the isomers. That this does not appear to be the case can be explained by a chemical shift dependence of the methyne group. Although it could be argued that rather than coalescence one methyne peak appears to be missing at −40 °C, the relative intensity of the observed resonance corresponds to that of the two peaks observed at lower temperatures.

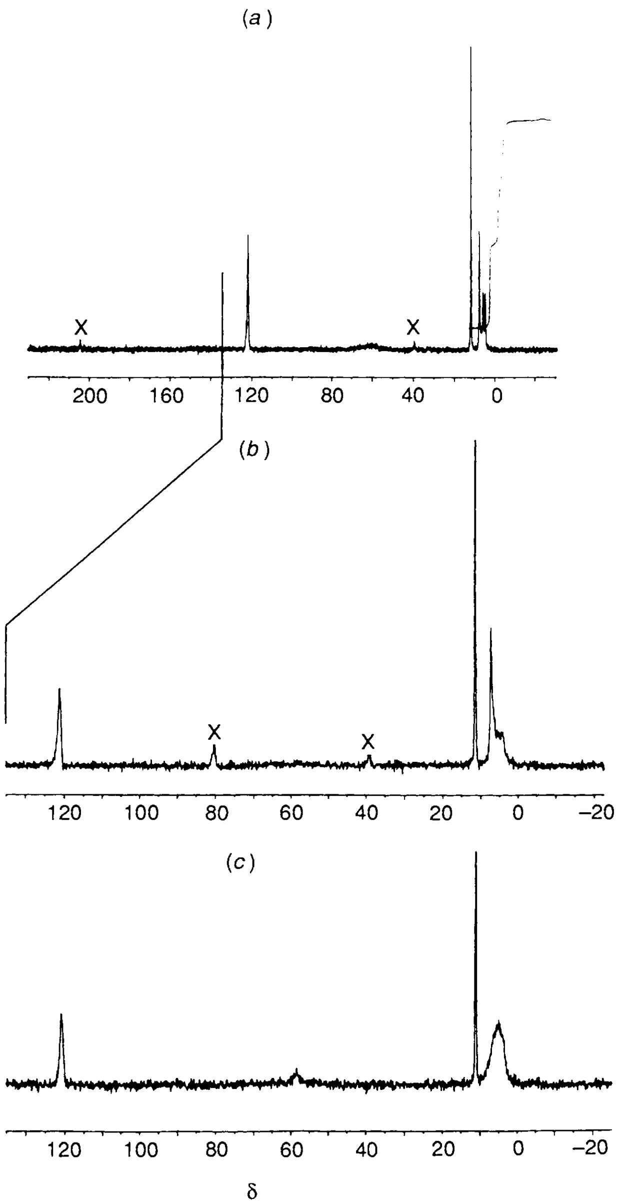

**Fig. 2** Variable-temperature solid-state $^{13}$C CPMAS NMR spectrum of [La(C$_5$Me$_5$){CH(SiMe$_3$)$_2$}$_2$] **1** at (*a*) 25, (*b*) –40 (624) and (*c*) –90 °C (200 scans). X = spinning side bands

Throughout this discussion we assume that the solid-state structure of complex **1** as determined by single crystal X-ray diffraction[1] (*i.e.* the *exo*/*endo* isomer) is that observed by solid-state NMR spectroscopy, crystal-packing effects being unimportant in determining the geometry of the CH(SiMe$_3$)$_2$ groups. The number of resonances anticipated for the $^{13}$C MAS NMR spectrum of a microcrystalline powder is, however, determined by the space group of the crystal unit cell ($P6_3$ in complex **1**) rather than the point group of the molecule. Hence accidental isochronies may reduce the number of resonances actually observed.

At room temperature the trimethylsilyl groups give three peaks at δ 7.5, 5.7 and 4.6 in a 6:3:3 ratio respectively, which bear some similarity to the three peaks observed in the solution state at –90 °C. Rapid rotation, on an NMR time-scale, around the C$_\alpha$–Si$_\beta$ bond would make the methyl resonances in each SiMe$_3$ group equivalent giving rise to a 3:3:3:3 ratio. A simultaneous wagging process would afford a 6:6 ratio, if rapid for both *exo* and *endo* CH(SiMe$_3$)$_2$ ligands. An advantage of solid- over solution-state NMR spectroscopy is that the former is not complicated by a temperature-dependent interconversion of *endo*/*exo* and *endo*/*endo* isomers.

The methyne resonance is very broad and centred around δ 60 [full width at half maximum (f.w.h.m.) = *ca.* 1000 Hz]. This linewidth may be explained by several contributing mechanisms, all arising from the proximity of the methyne carbon to the quadrupolar La ($I = \frac{7}{2}$, $Q = 0.21e \times 10^{-24}$ cm$^2$) centre. Broadening (or splitting) arises when the energy of the quadrupolar interaction is comparable in magnitude to the Zeeman interaction. Then, the quadrupolar interaction tilts the axis of quantization away from the static field direction, so that residual dipolar coupling to $^{13}$C is not removed by MAS. Values for $e^2qQ/h$ of 11 and 21.5 MHz have been reported[27] from the solid-state $^{139}$La NMR spectra of [La(acac)$_3$] (acac = acetylacetonate) and La(NO$_3$)$_3$•6H$_2$O respectively.

Relaxation of the methyne carbon with the quadrupolar moment of the metal, if significant, should be greater at lower temperatures. However, the methyne peak is sharpest at low temperature. It is the SiMe$_3$ resonances which sharpen at higher temperatures, consistent with coalescence phenomena. The lack of information about the magnitude of the nuclear quadrupolar coupling constants and relaxation times of lanthanide nuclei makes it difficult to estimate the expected broadening, but its maximum value is likely to be comparable to the dipolar coupling constant.

The integrated intensity of the methyne resonances is enhanced, and that for the SiMe$_3$ resonances diminished, based on the number of carbon atoms in each environment. The spectra were recorded using the cross-polarization technique which is known to be sensitive to molecular motion. Specifically, the sensitivity enhancement for any particular carbon nucleus will depend upon the $T_{1\rho}$ of attached protons or, if spin diffusion is active, of the 'proton domain' with which thermal contact is made through the CP experiment. Longer $T_{1\rho}$(H) values are associated with immobile protons and these exhibit greater enhancement.[18,28] For this reason $^{13}$C CPMAS NMR spectra were also measured with cross-polarization times of 1.0, 3.0, 5.0, 10.0 and 20.0 ms. The relative signal intensities of the SiMe$_3$, *C*$_5$Me$_5$ and C$_5$*Me*$_5$ resonances did not vary significantly between spectra, indicating that spin diffusion is sufficient to average the effective $T_{1\rho}$(H) for both groups, or that the motional processes that serve to average C–H dipolar interactions do not differ greatly.

The intensities of the *C*$_5$Me$_5$ and C$_5$*Me*$_5$ (isotropic plus side-bands) resonances are equivalent, and remain so over a wide range of contact times. This is surprising since, in principle, the CP rate* should be quite different for non-protonated and protonated carbons.[30] Other factors being equal, the greatest enhancement should be obtained from those carbons associated with a proton reservoir which has the longest $T_{1\rho}$.[31] It is clear that the $r_{CH}^{-6}$ distance dependence, or the number of directly bonded protons, is not determining the relative enhancement here. Two possible explanations present themselves: the *C*$_5$Me$_5$ resonance obtains enhancement through intermolecular mechanisms [the closest intermolecular contact to a *C*$_5$Me$_5$ carbon is 2.95 Å, from a C$_5$*Me*$_5$ group of an adjacent molecule, see Fig. 3, which is probably an underestimate (by $\leqslant$0.14 Å) due to the systematic errors inherent in the H-atom positions determined by X-ray diffraction (C–H distance set at 0.96 Å, true distance *ca.* 1.10 Å)] or spin diffusion[29] modulates the $^{13}$C–$^1$H relationship and removes any unique pathways. In addition, the effects of motional averaging of the C–H dipolar coupling due to methyl-group rotation (and

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* Carbon atoms that have no directly bonded protons will generally cross-polarize more slowly, the CP rate being the reciprocal of the cross-relaxation rate between the $^1$H and $^{13}$C spin reservoirs. Cross-relaxation is dependent on $r_{CH}^{-6}$, where $r_{CH}$ is the distance between the carbon nucleus in question and its adjacent (but not necessarily attached) protons, assuming spin diffusion is not significant.[29]

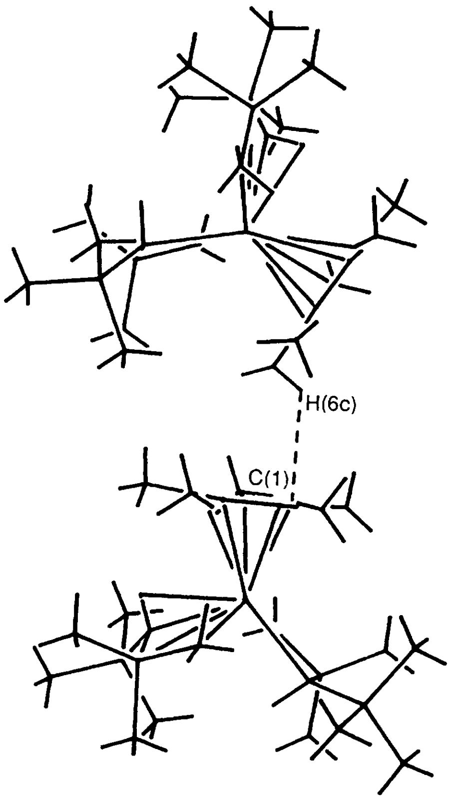

**Fig. 3** Selected region of the packing diagram for complex **1** showing the close intermolecular $C_5Me_5$–$C_5\mathit{Me}_5$ interaction

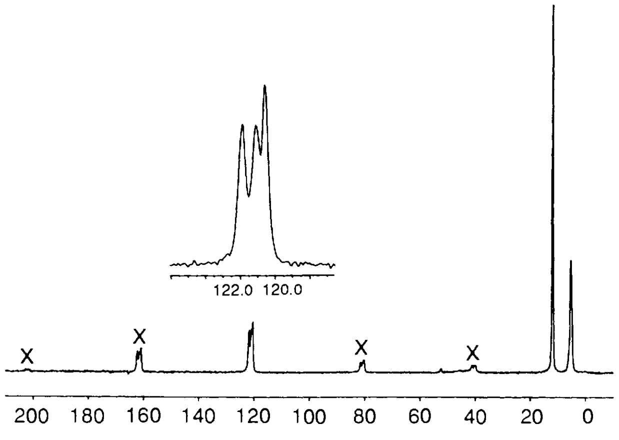

**Fig. 4** Solid-state $^{13}$C CPMAS NMR spectrum (10 376 scans) of complex **2**. X = spinning side bands

$C_5Me_5$ ring rotation) need to be considered for all orientations.

The $^{29}$Si NMR spectrum (−40 °C, $C_7D_8$) is a singlet at δ −14.62 (f.w.h.m. = 5 Hz). At −80 °C three peaks at δ −14.45, −14.62 and −15.21 (f.w.h.m. = 2–3 Hz) are observed in a 5:5:6 ratio, respectively. The number as well as the intensities of the peaks is consistent with assignments made from the solution $^{13}$C NMR spectrum at −90 °C. Similarly, the $^{29}$Si CPMAS NMR spectrum of complex **1** displayed a sharp singlet at δ −4.0 as well as two broader singlets at δ −12.4 and −13.0.

$[La(C_5Me_5)_2\{CH(SiMe_3)_2\}]$ **2**. To gain insight into the steric influence on the solid-state dynamics of the $CH(SiMe_3)_2$ groups, whilst keeping the metal constant, the solid-state NMR spectrum of $[La(C_5Me_5)_2\{CH(SiMe_3)_2\}]$ **2** was determined and is shown in Fig. 4. A broad, slightly asymmetric lineshape, at δ 5.46 (f.w.h.m. = 50–60 Hz), can be assigned to the $SiMe_3$ groups. The chemical shift and equivalence of all methyl groups indicates that interaction with La is weaker than in complex **1**, reflecting the decreased electrophilicity. Although rotation about the La–$C_\alpha$ bond is inhibited, processes B and C occur. The $CH(SiMe_3)_2$ ligand in complex **2** is more fluxional than those found in **1**. This appears to be contrary to the calculated free-energy barriers for the solution state, where rotation around the La–$C_\alpha$ bond leads to the observed fluxionality. In the solid state the relative ease of processes B and C in complexes **1** and **2** are compared.

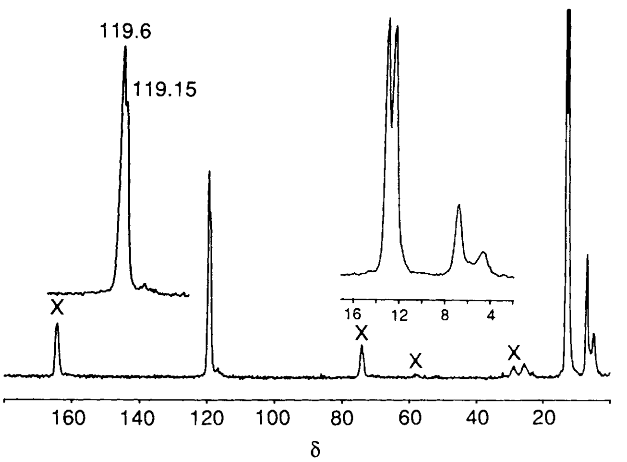

**Fig. 5** Solid-state $^{13}$C CPMAS NMR spectrum (7304 scans) of complex **3**. X = spinning side bands

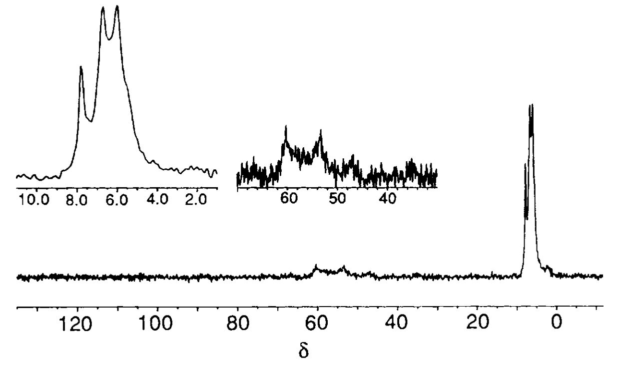

**Fig. 6** Solid-state $^{13}$C CPMAS NMR spectrum (6811 scans) of complex **4**

A single, symmetrical peak at δ 12.1 (f.w.h.m. = 30 Hz) is observed for all $C_5\mathit{Me}_5$ groups (see Table 1). However, three peaks are observed for the $\mathit{C}_5Me_5$ carbons which also exhibit residual anisotropy, in the form of spinning sidebands, which has not been averaged by MAS at 5 kHz. Given the single isotropic peak observed for the $C_5Me_5$ methyl groups it is difficult to explain this pattern simply as inequivalent ring environments. For $[Y(C_5Me_5)_2\{CH(SiMe_3)_2\}]$, three $\mathit{C}_5Me_5$ resonances were also observed, apparently in a 4:4:2 ratio.[3] No explanation was given.

$[Lu(C_5Me_5)_2\{CH(SiMe_3)_2\}]$ **3**. To determine the influence, if any, of the size,[13] or nature of the metal on the dynamics of alkyl group co-ordination, the solid-state NMR spectrum of $[Lu(C_5Me_5)_2\{CH(SiMe_3)_2\}]$ was determined (Fig. 5). Trimethylsilyl methyl resonances in a 3:2 ratio are observed, the other methyl resonance apparently being hidden by the $C_5\mathit{Me}_5$ resonances; a similar result was reported for the yttrium congener.[3] These data are consistent with a static, α-carbon atom geometry, and of a static $CH(SiMe_3)_2$ group. This is confirmed by the observation of two $\mathit{C}_5Me_5$ and two $C_5\mathit{Me}_5$ resonances for the two inequivalent $C_5Me_5$ rings.

$[Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K]$ **4**. The $^{13}$C NMR spectrum of

$[Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K]$ **4**[32] at −80 °C in $C_7D_8$ shows chemically equivalent methynes at δ 52.4 and $SiMe_3$ groups at δ 3.74, the co-ordinated KCl apparently not inducing time-averaged asymmetry in this complex in solution. In the solid state two separate broad methyne resonances are observed at δ 60.2 and 53.3 (Fig. 6). A static structure, with the potassium atom interacting with just one of the $CH(SiMe_3)_2$ ligands, would be expected to display methyne resonances in a 2:1 ratio. In the related complexes, $[La\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)Li(pmdien)]$[33] and $[Sm\{CH(SiMe_3)_2\}_3(\mu\text{-}Me)Li(pmdien)]$[34] (pmdien = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine) the pyramidal $Ln\{CH(SiMe_3)_2\}_3$ fragments have a geometry that is not significantly perturbed from that found in $[Ln\{CH(SiMe_3)_2\}_3]$ (Ln = La or Sm).[5] The much simpler spectrum of complex **5** (see below) is indicative of a preferred orientation of the $CH(SiMe_3)_2$ groups about the co-ordinated KCl in the solid state.

$[Lu\{CH(SiMe_3)_2\}_3]$ **5**. $[Lu\{CH(SiMe_3)_2\}_3]$ was prepared analogously to $[La\{CH(SiMe_3)_2\}_3]$.[5] The $^{13}C$ CPMAS NMR spectrum of complex **5** (Fig. 7) acts as a reference for that of complex **4**. It shows a comparatively sharp methyne resonance at δ 58.4 (f.w.h.m. = *ca.* 100 Hz) and equivalent trimethylsilyl groups at δ 6.23. Although rotation about the Lu–$C_\alpha$ bonds is restricted, dynamic processes **B** and **C** operate, making the methyl groups equivalent.

$[La\{CH(SiMe_3)_2\}_3]$ **6**. In contrast to complex **5**, the $^{13}C$ CPMAS spectrum (Fig. 8) of complex **6**[5] shows two peaks for the trimethylsilyl groups in a 1:1 ratio at δ 6.3 and 5.4. This is caused by rotation around the $C_\alpha$–Si bonds (process **B**). In complex **5** process **C** also operates, implying that the larger ionic radius of lanthanum ($La^{3+}$ 1.16, $Lu^{3+}$ 0.977 Å)[13] has more influence, relative to the increased Lewis-acid character of lutetium, in constraining the $SiMe_3$ groups. The methyne resonance is much broader at δ 77 (f.w.h.m. = 800–1000 Hz) than for $[Lu\{CH(SiMe_3)_2\}_3]$. This may be an inherent

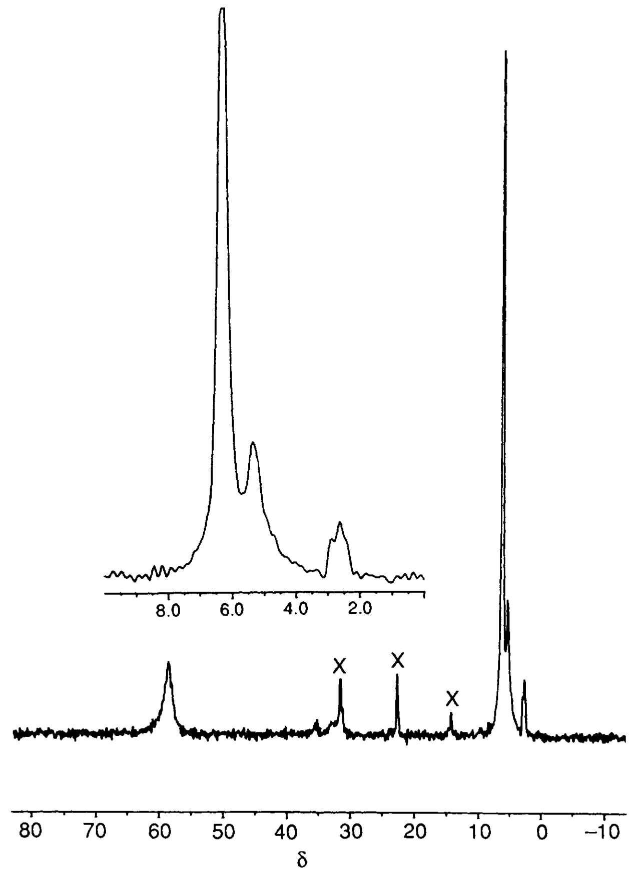

**Fig. 7** Solid-state $^{13}C$ CPMAS NMR spectrum (4670 scans) of complex **5**. X = hexane

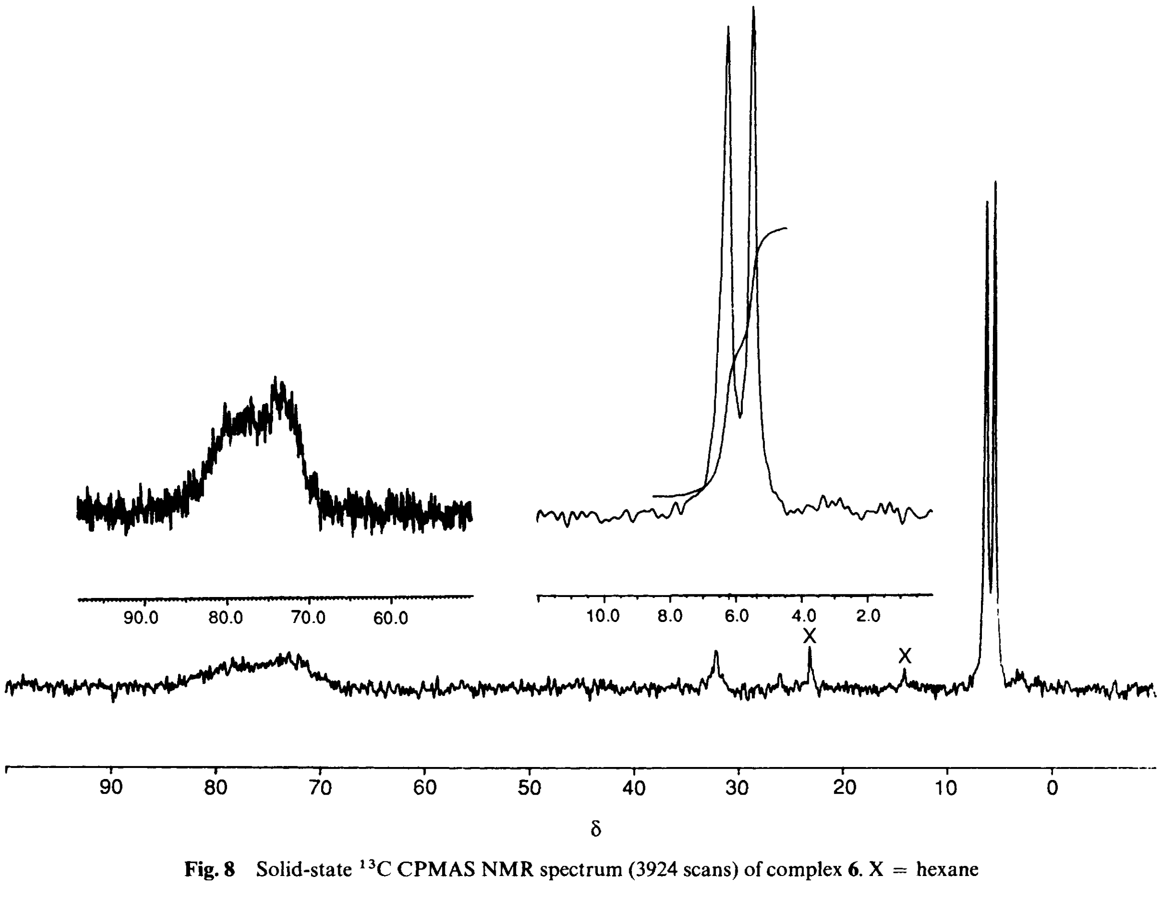

**Fig. 8** Solid-state $^{13}C$ CPMAS NMR spectrum (3924 scans) of complex **6**. X = hexane

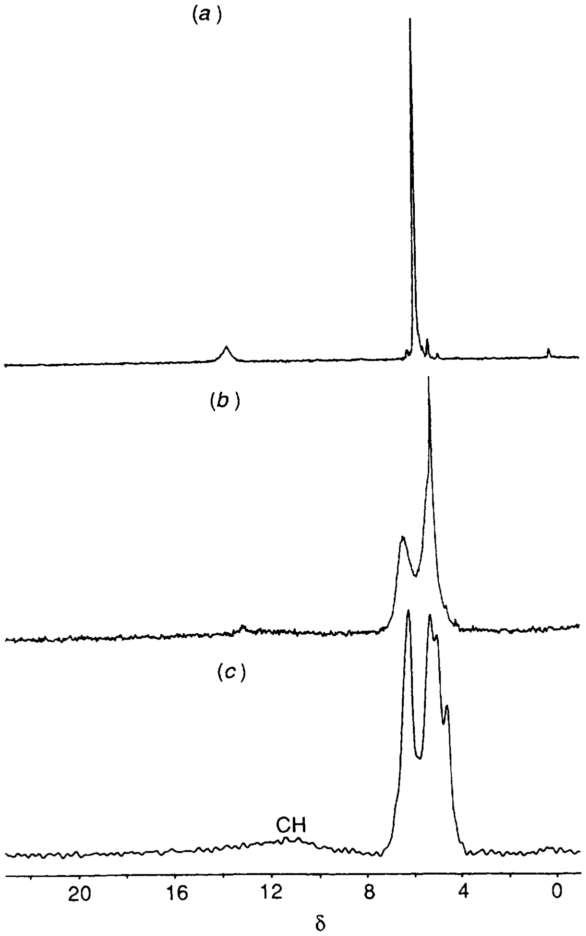

**Fig. 9** Variable-temperature solid-state $^{13}C$ CPMAS NMR spectrum of complex 7 at (*a*) 105 (304), (*b*) 60 (120) and (*c*) 25 °C (1624 scans)

property of a carbon directly bound to the quadrupolar half-integral spin lanthanide ($^{139}La$: $I = \frac{7}{2}$, $Q = 0.21e \times 10^{-24}$ cm$^2$; $^{175}Lu$: $I = \frac{7}{2}$, $Q = 5.68e \times 10^{-24}$ cm$^2$). The fast relaxation of these quadrupolar nuclei (X), typical (solution) $T_1$ values are $10^{-3}$ (La) and $< 10^{-6}$ s (Lu), can lead to scalar relaxation of the second kind for the directly bonded carbon if $1/T_{2X} \gg J_{CX}$. This is expressed as a broad absorption line. Thus, rather than having its origin in the relative molecular dynamics of complexes 5–7, the methyne group bonded to Lu may have an inherently narrower linewidth in complex 5, than in its lanthanum or aluminium congeners (see below). In contrast to the plethora of literature on the magnitude of $^{27}Al$–$^{13}C$ quadrupolar coupling constants (see below) no $^{139}La$- or $^{175}Lu$–$^{13}C$ dipolar couplings have been reported. This absence of information makes it difficult to predict the relative[35] magnitude of the expected MAS NMR broadening.

$[Al\{CH(SiMe_3)_2\}_3]$ 7. The new homoleptic alkyl complex $[Al\{CH(SiMe_3)_2\}_3]$ was prepared (see Experimental section) to ascertain whether effects due to the small aluminium ionic radius (0.535 Å)[13] manifested themselves in the solid state. Complex 7 is assumed to be monomeric,[36] as is $[In\{CH(SiMe_3)_2\}_3]$[37] which has a trigonal-planar geometry. The stereochemistry of the alkyl group co-ordination in these main-group complexes is in contrast to their pyramidal lanthanide congeners $[Ln\{CH(SiMe_3)_2\}_3]$ (Ln = La or Sm).[5]

The $^{13}C$ NMR spectrum of complex 7 in $C_7D_8$ at −80 °C (Table 1) is indicative of a symmetrical, time-averaged, trigonal-planar structure with equivalent $SiMe_3$ groups. The variable-temperature $^{13}C$ CPMAS NMR spectrum is shown in Fig. 9. At 25 °C the methyne group gives rise to a broad peak, centred around δ 11.9. The trimethylsilyl groups give a complex pattern which is difficult to assign. Increasing temperature leads to a simplification of the $SiMe_3$ resonances, and virtual disappearance of the methyne resonance, until at 105 °C just one sharp $SiMe_3$ resonance is observed at δ 6.0 with a sharp methyne resonance at δ 13.8. A very small temperature-dependent chemical-shift effect was observed. The complex pattern observed at 25 °C may arise from the small size of the Al not allowing three sterically demanding $CH(SiMe_3)_2$ groups to pack, or mesh properly, thus rendering their $SiMe_3$ groups inequivalent.

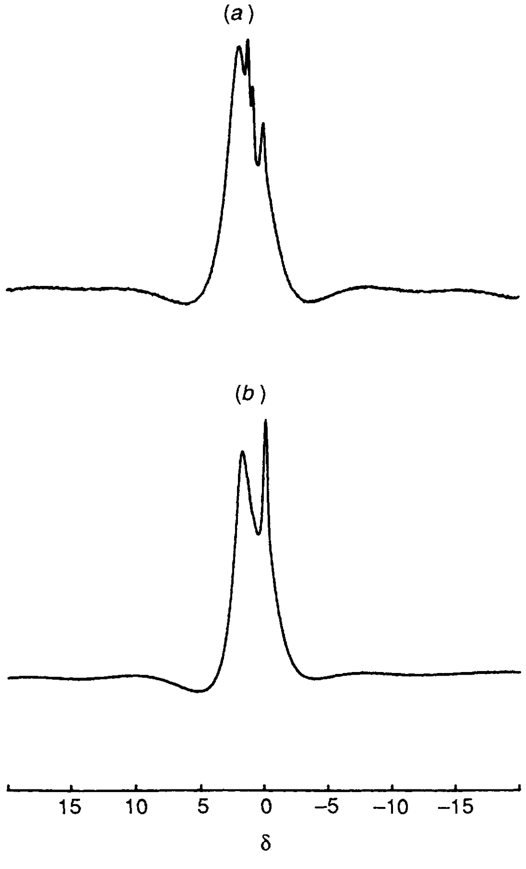

**Fig. 10** Very fast MAS-only solid-state $^1H$ NMR spectrum at 22 °C of complexes 3(*a*) and 2(*b*)

As mentioned previously, a contribution to line broadening or line-shape perturbation, due to relaxation of the quadrupolar $^{27}Al$ ($I = \frac{5}{2}$, $Q = 0.149e \times 10^{-24}$ cm$^2$) nucleus, may be possible. However, at this field strength (78.16 MHz for $^{27}Al$) the residual $^{27}Al$–$^{13}C$ dipolar coupling is largely removed by MAS, making any contributions from Zeeman[38] splitting negligible. Reported $^{27}Al$ $e^2qQ/h$ (the nuclear quadrupolar coupling constant) values usually fall in the range 7–38 MHz, while $^{27}Al$–$^{13}C$ interactions can be > 750 Hz at 15 MHz.[24a,39]

The compound $[Al\{CH(SiMe_3)_2\}_3]$ is very unreactive. No β-Me elimination (or any other reaction!) was observed on heating (sealed tube) in $C_6D_6$ (210 °C, 4 h) or in the presence of $PMe_3$ (30 mol equivalents, 170 °C, 3 h), in contrast to the reversible β-Me elimination/olefin insertion seen for $[Al(CH_2CMe_3)_3]$,[40] presumably due to the kinetic unfavourability of concomitant formation of the silene $Me_3SiCH{=}SiMe_2$. We note, however, that silene formation is kinetically, rather than thermodynamically, unfavourable.[41]

*Solid-state* $^1H$ *NMR.* Solid-state $^1H$ NMR MAS[42] spectra were measured at MAS speeds of 10–11 kHz* between −100 °C

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* Control experiments were also performed at MAS speeds of 7–8 kHz. No further line narrowing was observable at the faster MAS speeds used, indicating that proton–proton dipolar interactions in these compounds are rather weak and have been selectively averaged.

and ambient probe temperature for complexes **2**, **3**, **5**, **6** and **7**. In all cases rapid MAS was sufficient substantially to eliminate broadening from $^1H$–$^1H$ dipolar coupling or any anisotropic contributions to the chemical-shift tensor, giving spectra which show largely isotropic proton chemical shifts. Unlike $^{13}C$ CP MAS NMR spectra, the peak intensity obtained from single-pulse solid-state proton NMR spectra is quantitative.

The solid-state proton NMR spectra of complexes **5** and **6** show a differentiation between the $SiMe_3$ groups, although the fine structure remains unresolved due to the poor chemical-shift dispersion. However, clear differences between the solid-state $^1H$ NMR MAS spectrum of complexes **2** and **3** could be observed (Fig. 10). The peak arising from the $C_5Me_5$ protons is clearly resolved from the $SiMe_3$ resonance; the different linewidths reflect the different relative mobility of the two environments. Over the temperature range employed no significant spectral changes were observed, and unfortunately the α-CH resonance could not be resolved.

γ-C–H–Ln versus β-Si–Me–Ln *Interactions*.—It is pertinent within the context of this paper to discuss the subtle structural differences between γ-C–H–Ln and β-Si–Me–Ln interactions. At this juncture, it is important to note that although the terminology 'γ-C–H–Ln' and 'β-Si–Me–Ln' has been used, the observed[1–12] secondary co-ordination of a $CH(SiMe_3)_2$ group to an electron-deficient metal centre may not fall into two distinct and separate categories, experimental methodology being unable to distinguish unequivocably between these very similar interactions.

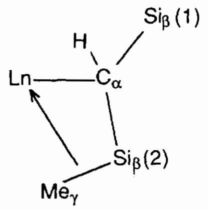
Although β-methyl migration[43] is now accepted as an analogous decomposition pathway to β-hydrogen transfer for metal-alkyl complexes, the related activation of a β-Si–C bond in β-silaalkyl complexes has few precedents.[44]

There has been little definitive evidence to support conclusively γ-C–H–Ln[2–9] interactions, as opposed to a β-Si–Me–Ln[1,10–12] interaction. Little consideration as to the role of the polarised, high energy, spatially diffuse Si–Me σ bond has been given, although this would be of a more appropriate energy to donate effectively into a low-lying lanthanide lowest unoccupied molecular orbital particularly as, in all cases,[1–12] the silicon atom lies within the sum of the van der Waals radii. The most reliable method of determining the nature of this attractive interaction is the geometry of the interacting γ-Me group, and the elongation, if any, of that β-Si–C σ bond. Although these parameters are most precisely determined by neutron diffraction, no such study has yet been performed. The hydrogen atoms on the interacting γ-carbon have been reliably located by X-ray diffraction studies only in a few cases.[1,3,6,10,11] In complex **1**,[1] its isostructural cerium congener,[10] $[Yb\{N(SiMe_3)_2\}_2(Me_2PCH_2CH_2PMe_2)]$[6] and $[Nd\{(C_5Me_4)_2SiMe_2\}\{CH(SiMe_3)_2\}]$[11] the γ-methyl group appears to adopt an energetically favourable[45] staggered conformation, thereby maximizing all $Ln\cdots H_\gamma$ distances that are inevitably associated with the close $Ln\cdots C_\gamma$ distance. This is in contrast to the orientation observed in C–H–M agostic interactions.[25] That a static structure could not be obtained by low-temperature solid-state $^{13}C$ or $^{29}Si$ NMR spectroscopy could support a β-Si–Me–Ln interaction, as a γ-C–H–Ln interaction might be expected to be frozen out by analogy with the observed behaviour of α-, β- and transannular-C–H agostic interactions.[25]

A β-Si–Me–Ln interaction will manifest itself by having $Ln–C_\alpha–Si(2)–Me_\gamma$ essentially coplanar and with a distorted geometry around the α-carbon atom, such that typically $Ln–C_\alpha–Si_\beta(1)$ 120–135° and $Ln–C_\alpha–Si_\beta(2)$ 95–105°, as has been observed crystallographically.

The consequence of this distortion allows the γ-Me group to interact with the electrophilic lanthanide centre ($Ln\cdots C_\gamma = Ln–C_\alpha + 0.4 - 0.5$ Å; see Table 3). The $Ln–Si_\beta(2)$ distance falls well within the sum of the van der Waals radii; thus the β-Si–Me bond can participate in an agostic interaction.

*Ab initio* calculations[45] on $[Ti(C_5H_5)_2(CMePh)(SiMe_3)][AlCl_4]$[5] also suggest that the β-Si–C σ bond is the major donor to the metal centre. A staggered γ-Me group conformation occupies a local minimum, whilst an eclipsed conformation, in which one γ-C–H bond is orientationally disposed to interact with the titanium centre, is destabilized by *ca.* 17 kJ mol$^{-1}$. The magnitude of a β-Si–C σ-bond interaction is difficult to estimate. We note that a $La(C_5Me_5)$ dialkyl moiety has four available acceptor orbitals of mainly 5d character, so although two α-C–H and two β-C–Si interactions are possible in complex **1**, in $[La(C_5Me_5)\{CH(SiMe_3)_2\}_2(thf)]$ **8**[1] one of these orbitals is occupied by thf. Thus a β-Si–C σ-bond interaction may be energetically more favourable than a α-C–H–La interaction, where the limited number of acceptor orbitals in complex **8** forces discrimination by the lanthanum both β-Si–C σ bonds being clearly co-ordinated in **8**.



To place this study in a wider context, relevant structural parameters have been collated (Table 3) of all lanthanide species containing $CH(SiMe_3)_2$ or $N(SiMe_3)_2$ groups, together with the compounds $[Ti(C_5H_5)_2(CMePh)(SiMe_3)][AlCl_4]$[12] and $[Th(C_5Me_5)\{N(SiMe_3)_2\}_2]$.[8]

The orientation of the β-Si–C σ bond, with respect to the metal centre, can be defined by the parameters $M–C_\gamma$ and $M–Si_\beta$. In order to compare distances between different lanthanides, subtraction of the effective eight-co-ordinate ionic radius[13] (*I*) affords comparable $M'–C_\gamma$ and $M'–Si_\beta$ distances. These fall in a narrow range. For the $CH(SiMe_3)_2$ groups average (standard deviations $\sigma_n$ in parentheses) $M'–C_\gamma$ and $M'–Si_\beta$ distances are 1.867(0.11) and 2.244(0.085) Å respectively. For the $N(SiMe_3)_2$ groups average $M'–C_\gamma$ and $M'–Si_\beta$ distances are 1.973(0.11) and 2.205(0.056) Å respectively. The longer $M–C_\gamma$ distances consistently seen in the amides are partially a consequence of $N \longrightarrow M$ π donation reducing the electrophilicity of the metal. Co-ordination of a β-Si–C σ bond to an electrophilic metal centre would lead to just such a consistency of data, given the absence of other geometric constraints on these rather flexible alkyl groups.

## Conclusion

These experiments have given insight into new structural information, especially in the case of the highly symmetrical complexes $[M\{CH(SiMe_3)_2\}_3]$ (M = La, Lu or Al) where their effective molecular symmetry* is reduced through preferred orientations in the solid state, thus making the $SiMe_3$ groups inequivalent. In general, the $CH(SiMe_3)_2$ groups remain rather mobile in the solid state. In the homoleptic tris-alkyl complexes $M\{CH(SiMe_3)_2\}_3$ (M = Al, Lu or La) clear differences are observed which can only be metal dependent.

Solution studies at −80 °C indicate that facile dynamic

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* A referee has suggested that the inequivalences observed may arise from site inequivalences in the crystal rather than in the molecule. Although accidental isochronies may reduce the number of resonances actually observed, we note that in the variable-temperature solid-state $^{13}C$ CPMAS NMR spectrum of $[Al\{CH(SiMe_3)_2\}_3]$ a temperature-dependence simplification of the resonance is observed. For example, the solid-state $^{13}C$ NMR spectrum of $[Cr(C_6Et_6)(CO)_2(PPh_3)]$ shows six $C_6Et_6$ resonances, a site inequivalence that was attributed to the asymmetric location of the molecule in the crystal, with the observed equivalence of the methyl and methylene carbons being due to accidental isochrony.[46]

**Table 3** Structural data (in Å) for neutral $CH(SiMe_3)_2$ and $N(SiMe_3)_2$ complexes

| $CH(SiMe_3)_2$ | M–$C_\alpha$ | M–$C_\gamma$ | M–$Si_\beta$[a] | $I$[b] | M–$C_\alpha$ – M–$C_\gamma$ | M–$Si_\beta$ – $I$ | M–$C_\gamma$ – $I$ | Ref. |
|---|---|---|---|---|---|---|---|---|
| $[Nd(C_5Me_5)_2\{CH(SiMe_3)_2\}]$ | 2.517 | 2.895 | 3.311 | 1.109 | 0.378 | 2.202 | 1.786 | 2 |
| $[Y(C_5Me_5)_2\{CH(SiMe_3)_2\}]$ | 2.468 | 2.878 | 3.257 | 1.019 | 0.410 | 2.238 | 1.858 | 3 |
| $[Ce(C_5Me_5)_2\{CH(SiMe_3)_2\}]$ | 2.535 | 2.917 | 3.406 | 1.143 | 0.382 | 2.263 | 1.774 | 4 |
| $[Nd\{(C_5Me_4)_2SiMe_2\}\{CH(SiMe_3)_2\}]$ | 2.506 | 2.862 | 3.269 | 1.109 | 0.356 | 2.160 | 1.867 | 11 |
| $[Ti(C_5H_5)_2(CMePh)(SiMe_3)]^+$ | — | 2.52 | 2.82 | 0.74 | — | 2.08 | 1.78 | 12 |
| $[La(C_5Me_5)\{CH(SiMe_3)_2\}_2(thf)]$ | 2.651 | 3.265 | 3.561 | 1.16 | 0.602 | 2.400 | 2.105 | 1 |
| | 2.627 | 3.241 | 3.545 | | 0.626 | 2.385 | 2.081 | |
| $[La(C_5Me_5)\{CH(SiMe_3)_2\}_2]$ | 2.537 | 2.978 | 3.353 | 1.16 | 0.446 | 2.193 | 1.818 | 1 |
| | 2.588 | 2.988 | 3.400 | | 0.395 | 2.240 | 1.828 | |
| $[Ce(C_5Me_5)\{CH(SiMe_3)_2\}_2]$ | 2.508 | 2.959 | 3.332 | 1.143 | 0.451 | 2.189 | 1.817 | 10 |
| | 2.556 | 2.973 | 3.378 | | 0.416 | 2.235 | 1.830 | |
| $[La\{CH(SiMe_3)_2\}_3]$ | 2.515 | 3.12 | 3.42 | 1.16 | 0.605 | 2.26 | 1.96 | 5 |
| $[Sm\{CH(SiMe_3)_2\}_3]$ | 2.33 | 2.85 | 3.41 | 1.079 | 0.520 | 2.33 | 1.771 | 5 |
| $N(SiMe_3)_2$ | M–$N_\alpha$ | M–$C_\gamma$ | M–$Si_\beta$ | $I$ | | M–$Si_\beta$ – $I$ | M–$C_\gamma$ – $I$ | Ref. |
| $[Y(C_5Me_5)_2\{N(SiMe_3)_2\}]$ | 2.274 | 2.970 | 3.218 | 1.019 | | 2.199 | 1.951 | 3 |
| $[Ce(C_5Me_5)\{(SiMe_3)_2\}_2]$ | 2.357 | 2.972 | 3.277 | 1.143 | | 2.134 | 1.829 | 10 |
| | 2.349 | 2.952 | 3.268 | | | 2.125 | 1.809 | |
| $[Yb\{N(SiMe_3)_2\}_2(dmpe)]$[c] | 2.331 | 3.04 | 3.285 | 1.14 | | 2.145 | 1.900 | 6 |
| $[Yb\{N(SiMe_3)_2\}_2(AlMe_3)_2]$ | 2.510 | 3.067 | | 1.14 | | | 1.927 | 7 |
| | 2.573 | 3.039 | | | | | 1.899 | |
| $[Th(C_5Me_5)\{N(SiMe_3)_2\}_2]$ | 2.35 | 3.041 | 3.292 | 1.05 | | 2.242 | 1.991 | 8 |
| | 2.32 | 3.147 | 3.35 | | | 2.300 | 2.097 | |
| $[Sm\{N(SiMe_3)_2\}_2(thf)_2]$[d] | 2.442 | 3.32 | 3.501 | 1.27 | | 2.231 | 2.05 | 9 |
| | 2.424 | 3.42 | 3.489 | | | 2.219 | 2.15 | |
| $[\{Sm[N(SiMe_3)_2](I)(dme)(thf)\}_2]$[d,e] | 2.455 | 3.54 | 3.522 | 1.27 | | 2.252 | 2.10 | 9 |
| | | 3.37 | | | | | | |

[a] Typical 'non-co-ordinated' M–$Si_\beta$ distances are $\geqslant 4$ Å using representative data, *e.g.* M–$C_\alpha$ 2.70 and $C_\alpha$–$Si_\beta$ 1.85 Å, M–$C_\alpha$–$Si_\beta$ 125°. [b] $I$ = Effective eight-co-ordinate ionic radius. [c] dmpe = $Me_2PCH_2CH_2PMe_2$. [d] The Ni–$Si_\beta$ bond length was not reported, so was estimated at 1.70 Å and the M–$Si_\beta$ distance calculated accordingly. [e] dme = $MeOCH_2CH_2OMe$.

processes equivalence the $CH(SiMe_3)_2$ groups. In comparison, as a result of the variable-temperature $^{13}C$ CPMAS NMR spectral data, sequences of relative mobility of the $CH(SiMe_3)_2$ groups in the solid state can be formulated as **2** > **1** > **3** and **5** > **6** > **7**. In complex **4** a preferential orientation of the $CH(SiMe_3)_2$ ligands is caused by KCl co-ordination.

An attempt has been made to differentiate between the secondary interactions, γ-C–H–M or β-Si–C–M, available to alkyl groups to facilitate stabilization of electrophilic metal centres. The dynamic nature of the $CH(SiMe_3)_2$ group, even at −90 °C in the solid state, has prevented unequivocable differentiation between γ-C–H–M or β-Si–C–M interactions. We suggest that a viable alternative to the attractive secondary interactions available to the $N(SiMe_3)_2$ and $CH(SiMe_3)_2$ groups could be β-Si–Me–Ln, rather than γ-C–H–Ln, interactions.

## Experimental

Compound **1** was prepared as described,[1] **2** and **3** as in ref. 2, and **6** as in ref. 5. The synthesis of **4** has been reported separately.[32] The synthesis of compounds **5** and **7** and their solution NMR spectra and analytical data are given below.

All experiments were performed under an argon atmosphere using Schlenk techniques or in a Braun single station dry-box equipped with a −40 °C fridge under nitrogen. Solvents were P. A. grade and were distilled from the appropriate drying reagent (sodium diphenylketyl for diethyl ether and thf, sodium for hexane and toluene) under argon prior to use. Elemental analyses were performed at the Analytische Laboratorien, Engelskirchen, West Germany. Solution NMR spectra were recorded on Varian XL-200 ($^1H$) or Varian VXR-300 ($^{13}C$, $^{29}Si$) spectrometers. Chemical shifts are reported in ppm and the residual protons in the deuteriated solvents used as a secondary reference with respect to tetramethylsilane. Coupling constants are reported in Hertz. Deuteriated solvents were dried over 4 Å molecular sieves.

*High Resolution Solid-state $^{13}C$ NMR Spectroscopy.*—Carbon 13 CPMAS NMR spectra were measured at 75.468 MHz on a Bruker MSL-300 spectrometer equipped with Bruker temperature-control hardware. All solid-state $^{13}C$ NMR spectra were externally referenced to liquid $SiMe_4$ based on the substitution of adamantane as a secondary reference. High-power $^1H$ decoupling (> 40 kHz, *ca.* 10 mT field strength) and magic angle spinning were employed. Sample rotors of 4 mm external diameter, machined from zirconia, were measured at spinning speeds of 3.8–6.2 kHz using dry nitrogen as the spinning gas. Approximately 100 mg of finely ground sample were packed into a rotor using specially designed Kel-f inserts. The rotors were dried thoroughly in a vacuum oven at 100 °C overnight before being taken into the dry-box. Since the samples are extremely air- and moisture-sensitive the rotors were packed inside the dry-box. Careful handling techniques ensured that no decomposition of the samples was observed. On deliberately exposing the organolanthanide sample to air by removal of the cap, the exposed sample surface immediately changed colour from white to brown. Additionally, after each $^{13}C$ CPMAS NMR experiment, a sample from the rotor was removed in the dry-box and a solution-state $^1H$ NMR spectrum measured. Hence we are confident that the integrity of the samples was retained during spectral acquisition. For low- and high-temperature experiments a boron nitride cap was used.

Cross-polarization contact times were 3 ms and the 90° proton pulse was 4.7 μs with a recycle delay of 6–12 s between pulses. The cross-polarization pulse sequence incorporated flipback[47] and spin-temperature inversion.[48] A check for $T_1$ was made so that saturation did not occur. Between 1000 and 7000 transients were normally accumulated.

*Solid-state $^1H$ NMR Spectroscopy.*—Variable-temperature solid-state proton MAS spectra were recorded at 300 MHz, using the decoupler channel of the same dual-channel probe, and spinning at speeds of up to 14 kHz. The probe was checked to be free of any proton background signal. Single-pulse acquisition was used with a 90° pulse of 3.0 μs and recycle delays of between 10 and 15 s. No saturation effects were observed under these conditions. All spectra were referenced externally to the proton absorption of $SiMe_4$ at δ 0.0.

*Syntheses.*—$[Lu\{N(SiMe_3)_2\}_3]$. To a stirred solution of $[Li\{N(SiMe_3)_2\}]$ (6.8 g, 40.72 mmol) in thf (300 $cm^3$) was added $LuCl_3$ (3.8 g, 13.6 mmol) and the stirring continued at 25 °C for 16 h. Tetrahydrofuran was removed under vacuum to afford a white solid that was transferred to a sublimer and sublimed at 140–155 °C, $10^{-2}$ mmHg (*ka.* 1.33 Pa) to give an involatile residue (2.1 g) and $[Lu\{N(SiMe_3)_2\}_3]$ (7.7 g, 87%) as a fine white powder (Found: C, 29.20; H, 7.25; Cl, 0.60; Li, 0.00; Lu, 34.85. $C_{18}H_{54}LuN_3Si_6$ requires C, 32.95; H, 8.25; Lu, 26.65%. These analysis data fit '$[Lu\{N(SiMe_3)_2\}_2]$', presumably formed by decomposition of $[Lu\{N(SiMe_3)_2\}_3]$ by combustion. $C_{12}H_{36}LuN_2Si_4$ requires C, 29.05; H, 7.30; Lu, 35.30%). $^1H$ NMR ($C_6D_6$): δ 0.349.

$[Lu(OC_6H_3Bu^t_2\text{-}2,6)_3]$. (*a*) *From* $[LuCl_3(thf)_3]$. Solid $[LuCl_3(thf)_3]$ (4.0 g, 8.04 mmol) was added to $[Li(OC_6H_3Bu^t_2\text{-}2,6)]$ (5.10 g, 24.05 mmol) in thf (200 $cm^3$) and the resulting suspension was refluxed for 15 h. The thf was removed in vacuum and the white solid washed with hexane (50 $cm^3$) to remove any free phenol formed by decomposition during the reaction. The white solid was transferred to a sublimer in the dry-box and heated at 80 °C for 6 h under vacuum to remove co-ordinated thf. Raising the temperature to 240–250 °C, $10^{-2}$ mmHg allowed the sublimation of $[Lu(OC_6H_3Bu^t_2\text{-}2,6)_3]$ accompanied by decomposition and melting of the residue. Yield 2.1 g, 33% (Found: C, 63.70; H, 7.85; Lu, 22.30. $C_{42}H_{63}O_3Lu$ requires C, 63.80; H, 8.05; Lu, 22.10%). $^1H$ NMR ($C_6D_6$): δ 7.30 (d, 6 H, $H_m$), 6.85 (t, 3 H, $H_p$) and 1.54 (s, 54 H, $Bu^t$).

(*b*) *From* $[Lu\{N(SiMe_3)_2\}_3]$. A higher yield method was to add $HOC_6H_3Bu^t_2\text{-}2,6$ (7.26 g, 35.24 mmol) in hexane (20 $cm^3$) slowly to $[Lu\{N(SiMe_3)_2\}_3]$ (7.7 g, 11.75 mmol) dissolved in hexane (250 $cm^3$) at 25 °C. The solution was refluxed gently for 16 h, filtered, and the hexane removed under vacuum to afford $[Lu(OC_6H_3Bu^t_2\text{-}2,6)_3]$ (8.02 g, 86%).

$[Lu\{CH(SiMe_3)_2\}_3]$ **5**. Solid $[Li\{CH(SiMe_3)_2\}]$ (1.34 g, 8.07 mmol) was added slowly to a colourless solution of $[Lu(OC_6H_3Bu^t_2\text{-}2,6)_3]$ (2.1 g, 2.66 mmol) in hexane (100 $cm^3$) at 25 °C. A white suspension rapidly formed, which was stirred for 30 min at 25 °C then filtered to remove $[Li(OC_6H_3Bu^t_2)]$. The volume of the colourless filtrate was reduced and crystallisation at −40 °C afforded $[Lu\{CH(SiMe_3)_2\}_3]$ as white fluffy needles (0.92 g, 53%) {Found: C, 41.2; H, 9.2; Lu, 24.55. $[Lu\{CH(SiMe_3)_2\}_3]\cdot 0.5\ C_6H_{14}$ ($C_{24}H_{64}LuSi_6$) requires C, 41.40; H, 9.25; Lu, 25.15%}. NMR: $^1H$ ($C_6D_6$), δ 0.308 ($SiMe_3$) and − 0.82 (CH); $^{13}C$ ($C_7D_8$, 25 °C), δ 57.35 (d, *J* 90, CH) and 3.69 (q, *J* 116 Hz, $SiMe_3$).

$[Al\{CH(SiMe_3)_2\}_3]$ **7**. Freshly sublimed $AlCl_3$ (0.84 g, 6.3 mmol) was added in small portions to diethyl ether (60 $cm^3$) in the dry-box at 25 °C to give an ethereal solution of $AlCl_3(OEt_2)_x$. Solid $[Li\{CH(SiMe_3)_2\}]$ (3.17 g, 19.1 mmol) was then added slowly. An immediate reaction ensued and the ether suspension was stirred for 16 h at 25 °C to ensure complete reaction. The ether was removed under vacuum and the residue extracted with hexane (100 $cm^3$). Filtration and evaporation of the hexane afforded a slightly sticky, almost crystalline, white solid which was purified by sublimation at 140 °C, $10^{-2}$ mmHg to afford compound **7** as a white powder (Found: C, 49.40; H, 11.10; Al, 5.15; Cl, 0.3. $C_{21}H_{57}AlSi_6$ requires C, 49.95; H, 11.35; Al, 5.35%). NMR: $^1H$ ($C_6D_6$, 25 °C), δ 0.292 ($SiMe_3$) and −0.35 (CH); $^{13}C$ ($C_7D_8$, −80 °C), δ 10.07 (d, *J* 93, CH) and 3.35 (q, *J* 118 Hz, $SiMe_3$).

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## References

1 H. van der Heijden, C. J. Schaverien and A. G. Orpen, *Organometallics*, 1989, **8**, 255.
2 G. Jeske, H. Lauke, H. Mauermann, P. N. Swepston, H. Schumann and T. J. Marks, *J. Am. Chem. Soc.*, 1985, **107**, 8091; H. Mauermann, P. N. Swepston and T. J. Marks, *Organometallics*, 1985, **4**, 200.
3 K. H. den Haan, J. L. de Boer, J. H. Teuben, A. L. Spek, B. Kojic-Prodic, G. R. Hays and R. Huis, *Organometallics*, 1986, **5**, 1726.
4 H. J. Heeres, J. Renkema, M. Booij, A. Meetsma and J. H. Teuben, *Organometallics*, 1988, **7**, 2495.
5 P. B. Hitchcock, M. F. Lappert, R. G. Smith, R. A. Barlett and P. P. Power, *J. Chem. Soc., Chem. Commun.*, 1988, 1007.
6 T. D. Tilley, R. A. Andersen and A. Zalkin, *J. Am. Chem. Soc.*, 1982, **104**, 3725.
7 J. M. Boncella and R. A. Andersen, *Organometallics*, 1985, **4**, 205.
8 T. M. Gilbert, R. R. Ryan and A. P. Sattelberger, *Organometallics*, 1988, **7**, 2514.
9 W. J. Evans, D. K. Drummond, H. Zhang and J. L. Atwood, *Inorg. Chem.*, 1988, **27**, 575.
10 H. J. Heeres, A. Meetsma, J. H. Teuben and R. D. Rogers, *Organometallics*, 1989, **8**, 2637.
11 G. Jeske, L. E. Schock, P. N. Swepston, H. Schumann and T. J. Marks, *J. Am. Chem. Soc.*, 1985, **107**, 8103.
12 J. J. Eisch, A. M. Pitrowski, S. K. Brownstein, E. J. Gabe and F. L. Lee, *J. Am. Chem. Soc.*, 1985, **107**, 7219.
13 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
14 R. R. Ernst and A. Wokaun, *Principles of NMR in One and Two Dimensions*, Clarendon Press, Oxford, 1987; A. Abragam, *Principles of Nuclear Magnetism*, Clarendon Press, Oxford, 1961.
15 R. E. Wasylishen and C. A. Fyfe, *Annu. Rep. N.M.R. Spectrosc.*, 1982, **12**, 1.
16 A. Pines, M. G. Gibby and J. S. Waugh, *J. Chem. Phys.*, 1973, **59**, 569; *Chem. Phys. Lett.*, 1972, **15**, 373; C. S. Yannoni, *Acc. Chem. Res.*, 1982, **15**, 201.
17 E. R. Andrew, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1971, **8**, 1.
18 F. Bloch, *Phys. Rev.*, 1958, **111**, 841.
19 J. Schaeffer, E. O. Stejskal and R. Buchdahl, *Macromolecules*, 1975, **8**, 291.
20 J. R. Lyerla, C. S. Yannoni and C. A. Fyfe, *Acc. Chem. Res.*, 1982, **15**, 209.
21 G. E. Maciel, *Science*, 1984, **226**, 282; C. A. Fyfe, *Solid-State NMR for Chemists*, C.F.C. Press, Ontario, 1983.
22 M. Mehring, *Principles of High Resolution NMR in Solids*, 2nd edn., Springer, Berlin, 1983.
23 G. E. Balimann, C. J. Groombridge, R. K. Harris, K. J. Packer, B. J. Say and S. F. Tanner, *Philos. Trans. R. Soc. London, Ser. A*, 1981, **299**, 643.
24 (*a*) P. J. Toscano and T. J. Marks, *J. Am. Chem. Soc.*, 1985, **107**, 653; (*b*) M.-Y. He, G. Xiong, P. J. Toscano, R. L. Burwell, jun. and T. J. Marks, *J. Am. Chem. Soc.*, 1985, **107**, 641; (*c*) R. Benn, H. Grondey, R. Nolte and G. Erker, *Organometallics*, 1988, **7**, 777; (*d*) P. L. Watson, *J. Am. Chem. Soc.*, 1983, **105**, 6491; (*e*) J. W. Bruno, G. M. Smith, T. J. Marks, C. K. Fair, A. J. Schultz and J. M. Williams, *J. Am. Chem. Soc.*, 1986, **108**, 40; (*f*) P. A. Downton, B. Mailvaganam, C. S. Frampton, B. G. Sayer and M. J. McGlinchey, *J. Am. Chem. Soc.*, 1990, **112**, 27; (*g*) R. Benn, H. Grondey, G. Erker, R. Aul and R. Nolte, *Organometallics*, 1990, **9**, 2493; (*h*) G. Erker, F. Sosna, J. L. Petersen, R. Benn and H. Grondey, *Organometallics*, 1990, **9**, 2462; (*i*) W. C. Finch, R. D. Gillespie, D. Hedden and T. J. Marks, *J. Am. Chem. Soc.*, 1990, **112**, 6221.
25 M. Brockhart, M. L. H. Green and L.-L. Wong, *Prog. Inorg. Chem.*, 1988, **36**, 1.
26 M. Booij, Ph.D. Thesis, University of Groningen, 1989.
27 A. R. Thompson and E. Oldfield, *J. Chem. Soc., Chem. Commun.*, 1987, 27.
28 G. E. Maciel, J. F. Haw, I.-S. Chuang, B. L. Hawkins, T. A. Early, D. R. McKay and L. Petrakis, *J. Am. Chem. Soc.*, 1983, **105**, 5529.
29 I. D. Campbell, C. M. Dobson, R. Ratcliffe and R. J. P. Williams, *J. Magn. Reson.*, 1978, **29**, 397; H. H. Limbach, B. Wehrle, M. Schabach, R. Kendrick and C. S. Yannoni, *J. Magn. Reson.*, 1988, **77**, 84.

30 J. Schaeffer, E. O. Stejskal and R. Buchdahl, *Macromolecules*, 1977, **10**, 384.

31 H. W. Bernard, J. E. Tanner and J. G. Aston, *J. Chem. Phys.*, 1969, **50**, 5016; L. B. Alemany, D. M. Grant, R. J. Pugmire, T. D. Alger and K. W. Zilm, *J. Am. Chem. Soc.*, 1983, **105**, 2142; L. B. Alemany, D. M. Grant, T. D. Alger and R. J. Pugmire, *J. Am. Chem. Soc.*, 1983, **105**, 6697.

32 C. J. Schaverien and J. B. van Mechelen, *Organometallics*, 1991, **10**, 1704.

33 J. L. Atwood, M. F. Lappert, R. G. Smith and H. Zhang, *J. Chem. Soc., Chem. Commun.*, 1988, 1308.

34 P. B. Hitchcock, M. F. Lappert and R. G. Smith, *J. Chem. Soc., Chem. Commun.*, 1989, 369.

35 R. Dupree, M. H. Lewis and M. E. Smith, *J. Am. Chem. Soc.*, 1989, **111**, 5125.

36 J. Z. Nyathi, J. M. Ressner and J. D. Smith, *J. Organomet. Chem.*, 1974, **70**, 35; E. G. Hofmann, *Liebigs Ann. Chem.*, 1960, **629**, 104; H. Lehmkuhl, *Liebigs Ann. Chem.*, 1968, **719**, 41.

37 A. J. Carty, M. J. S. Gynane, M. F. Lappert, S. J. Miles, A. Singh and N. J. Taylor, *Inorg. Chem.*, 1980, **19**, 3637.

38 E. Kundla and M. Alla, *Magn. Reson. Relat. Phenom.*, 1979, **20**, 92; J. G. Hexam, M. H. Frey and S. J. Opella, *J. Am. Chem. Soc.*, 1981, **103**, 224; S. J. Opella, J. G. Hexam, M. H. Frey and T. A. Cross, *Philos. Trans. R. Soc. London, Ser. A*, 1981, **299**, 665; J. Böhm, D. Fenzke and H. Pfeifer, *J. Magn. Reson.*, 1983, **55**, 197.

39 M. J. S. Dewar, D. B. Patterson and W. I. Simpson, *J. Am. Chem. Soc.*, 1971, **93**, 1030; *J. Chem. Soc., Dalton Trans.*, 1973, 2381.

40 K. Ziegler, *Angew. Chem.*, 1956, **68**, 721; W. Pfohl, *Liebigs Ann. Chem.*, 1960, **629**, 207; K. Ziegler, K. Nagel and W. Pfohl, *Liebigs Ann. Chem.*, 1960, **629**, 210.

41 C. E. Allison and T. B. McMahon, *J. Am. Chem. Soc.*, 1990, **112**, 1672.

42 J. S. Waugh, L. M. Huber and U. Haeberlen, *Phys. Rev. Lett.*, 1968, **20**, 180; U. Haeberlen and J. S. Waugh, *Phys. Rev.*, 1968, **175**, 453; U. Haeberlen, *High Resolution NMR in Solids. Selective Averaging*, Academic Press, New York, 1976.

43 P. L. Watson and D. C. Roe, *J. Am. Chem. Soc.*, 1982, **104**, 6471; T. C. Flood and J. A. Statler, *Organometallics*, 1984, **3**, 1795 and refs. therein, T. C. Flood and S. P. Bitler, *J. Am. Chem. Soc.*, 1984, **106**, 6076.

44 S. K. Thomson and G. B. Young, *Organometallics*, 1989, **8**, 2068; K. Itoh and T. Fukahori, *J. Organomet. Chem.*, 1988, **349**, 227; S. Karrass and H. Schwarz, *Organometallics*, 1990, **9**, 2409.

45 N. Koga and K. Morokuma, *J. Am. Chem. Soc.*, 1988, **110**, 108.

46 D. J. Iverson, G. Hunter, J. F. Blunt, J. R. Damewood, jun., and K. Mislow, *J. Am. Chem. Soc.*, 1981, **103**, 6073.

47 E. O. Stejskal and J. Schaefer, *J. Magn. Reson.*, 1975, **18**, 560.

48 U. Haeberlen and J. Tegenfeldt, *J. Magn. Reson.*, 1979, **36**, 453.

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