

Synthesis and characterization of trimethylsilylmethyl-, bis(trimethylsilyl)methyl- and silyl-substituted cyclopentadienes and their alkali metal complexes¹

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Abstract

A series of new $\text{Me}_3\text{SiCH}_2-$, $(\text{Me}_3\text{Si})_2\text{CH}-$, $\text{Me}_2\text{Bu}^t\text{Si}-$ or $\text{Me}_3\text{Si}-$ substituted cyclopentadienes and some of their alkali metal complexes has been prepared. Alkylation or silylation of NaC_5H_5 with $(\text{Me}_3\text{Si})_2\text{CHBr}$ or $\text{Bu}^t\text{Me}_2\text{SiCl}$ in tetrahydrofuran yielded $\text{C}_5\text{H}_5\{\text{CH}(\text{SiMe}_3)_2\}$ **1** ($\equiv\text{Cp}^{\text{R}}\text{H}$) or $\text{C}_5\text{H}_5(\text{SiMe}_2\text{Bu}^t)$ **2** ($\equiv\text{Cp}^t\text{H}$) and $\text{C}_5\text{H}_4(\text{SiMe}_2\text{Bu}^t)_2$ **3** ($\equiv\text{Cp}^{\text{H}}\text{H}$), respectively. Metallation of **1**, **2** or **3** with LiBu^n , NaNH_2 or KH gave MCp^{R} ($\text{M} = \text{Li}$ **4**, Na **5** or K **6**), NaCp^t **7** or MCp^{H} ($\text{M} = \text{Li}$ **8** or K **9**). Treatment of **6** with $(\text{Me}_3\text{Si})_2\text{CHBr}$ produced $\text{C}_5\text{H}_4[\text{CH}(\text{SiMe}_3)_2]_2$ **10** ($\equiv\text{Cp}^{\text{RR}}\text{H}$). Addition of $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ (TMEDA) to **4** or **8** afforded $[\text{LiCp}^{\text{R}}(\text{TMEDA})]$ **11** or $[\text{LiCp}^{\text{H}}(\text{TMEDA})]$ **12**. From **6** and Me_2SiCl_2 $\text{Me}_2\text{Si}[\text{C}_5\text{H}_4\text{CH}(\text{SiMe}_3)_2]_2$ **13** [$\equiv\text{Me}_2\text{Si}(\text{Cp}^{\text{R}}\text{H})_2$] was obtained and converted into its potassium salt $\text{Me}_2\text{Si}(\text{Cp}^{\text{R}}\text{K})_2$ **14**. Metallation of $\text{C}_5\text{H}_3(\text{SiMe}_3)_3$ ($\equiv\text{Cp}^{\text{H}}\text{H}$) with LiBu^n , NaNH_2 or KH in tetrahydrofuran yielded $[\text{LiCp}^{\text{H}}(\text{THF})_3]$ **15**, NaCp^{H} **16** or KCp^{H} **17**, respectively. Addition of $\text{MeN}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2$ (PMDETA) to **16** afforded $[\text{NaCp}^{\text{H}}(\text{PMDETA})]$ **18**. Treatment of **6** with Me_3SiCl gave $\text{C}_5\text{H}_4(\text{SiMe}_3)\{\text{CH}(\text{SiMe}_3)_2\}$ ($\equiv\text{Cp}^{\text{R}}\text{H}$) **19** which, with KH , underwent a dyotropic transformation in yielding $[\text{KC}_5\text{H}_2(\text{SiMe}_3)_2\text{-2,4-CH}_2\text{SiMe}_3\text{-1}]$ **20**. Each of the new compounds **1–20** was characterized by multinuclear NMR spectroscopy (^1H , ^{13}C , ^{29}Si or ^7Li) and C, H, N elemental analysis (not **1**), and in the case of the neutral cyclopentadienes, by GC/MS. The molecular structure of the crystalline complex **18** was also established by X-ray crystallography, as was that of $[\text{LiC}_5\text{H}_3\text{Bu}_2\text{-1,3}](\text{TMEDA})$ **21**. © 1998 Elsevier Science S.A.

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1. Introduction

Cyclopentadiene is one of the most important and extensively used ligand precursors in organometallic chemistry. Many organometallic complexes of the transition metals contain a cyclopentadienyl ($\bar{\text{Cp}}$) ligand or a derivative thereof [1]. Cyclopentadienyl- or substituted cyclopentadienyl-metal (M) complexes (π or σ bonded to M) are now known for most main group [2,3] and

transition metals [4], as well as for the lanthanide and the accessible parts of the actinide series [5]; The $\bar{\text{Cp}}$ ligand can be modified by introducing substituents on the cyclopentadienyl ring and then employed to stabilize complexes of unusual geometry or metal oxidation states [4]. Numerous alkyl- and silyl-substituted cyclopentadienyl ligands feature in organometallic chemistry, e.g., $\bar{\text{C}}_5\text{Me}_5$, $\bar{\text{C}}_5\text{H}_{5-n}(\text{CMe}_3)_n$ ($n = 1$ or 2), or $\bar{\text{C}}_5\text{H}_{5-m}(\text{SiMe}_3)_m$ ($m = 1$ or 2 , abbreviated as $\bar{\text{Cp}}'$ and $\bar{\text{Cp}}''$, respectively). We have extensively used the $\bar{\text{Cp}}'$ and $\bar{\text{Cp}}''$ ligands in the chemistry of early transition metals [6–12] and f-elements [13–25]. The steric bulk exerted by the electron-withdrawing SiMe_3 group(s) are important effects. The solubility in non-polar solvents and the crystallinity of their complexes is also enhanced. In order to further increase the bulk of the ligand, we have modified the $\bar{\text{C}}_5\text{H}_{5-m}(\text{SiMe}_3)_m$ ligands by replacing the SiMe_3 group by SiMe_2Bu^t , and now

Abbreviations: Cp^{R} $\eta^5\text{-C}_5\text{H}_4\text{CH}(\text{SiMe}_3)_2$; Cp^{RR} $\eta^5\text{-C}_5\text{H}_3\{\text{CH}(\text{SiMe}_3)_2\}_2\text{-1,3}$; Cp^t $\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Bu}^t)$; Cp^{H} $\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{Bu}^t)_2\text{-1,3}$; Cp^{R^t} $\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)\{\text{CH}(\text{SiMe}_3)_2\}_2\text{-1,3}$; $\text{Cp}^{\text{R}^{\text{H}}}$ $\eta^5\text{-C}_5\text{H}_2(\text{SiMe}_3)_2\text{-2,4-}(\text{CH}_2\text{SiMe}_3)\text{-1}$; $\text{Me}_2\text{Si}(\text{Cp}^{\text{R}})_2$ $\text{Me}_2\text{Si}\{\eta^5\text{-C}_5\text{H}_3\text{CH}(\text{SiMe}_3)_2\}_2$; Cp' $\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$; Cp'' $\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}$; Cp''' $\eta^5\text{-C}_5\text{H}_2(\text{SiMe}_3)_3\text{-1,2,4}$

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¹ Dedicated to Professor Ken Wade, as a mark of friendship and as a recognition of his many contributions to chemistry.

report the synthesis of the alkali metal cyclopentadienyls $\text{MC}_5\text{H}_{5-m}(\text{SiMe}_2\text{Bu}^t)_m$ ($m = 1$ or 2 , abbreviated as MCp^t and MCp^u , respectively). Although $\text{C}_5\text{H}_2(\text{SiMe}_3)_{3-1,2,4}$ ($\equiv \text{Cp}^m$) has been reported previously, we present some new data on $\text{LiCp}^m(\text{THF})_3$ and $\text{NaCp}^m(\text{PMDETA})$ [$\text{THF} = \text{tetrahydrofuran}$, $\text{PMDETA} = \text{MeN}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2$].

The role of the $\text{CH}(\text{SiMe}_3)_2$ ligand in organometallic chemistry is well recognized [26]. We have synthesized a large series of metal and metalloid bis(trimethylsilyl) methyls and transformed the alkali metal bis(trimethylsilyl) methyls into η^3 -1-aza-allyl and β -diketiminates [27]. To extend our study on both cyclopentadienyls and bis(trimethylsilyl) methyls, we now report the preparation of $\text{C}_5\text{H}_5\{\text{CH}(\text{SiMe}_3)_2\}$ ($\equiv \text{Cp}^R\text{H}$), $\text{Me}_2\text{Si}[\text{C}_5\text{H}_4\{\text{CH}(\text{SiMe}_3)_2\}]_2$ [$\equiv \text{Me}_2\text{Si}(\text{Cp}^R\text{H})_2$] and $\text{C}_5\text{H}_4(\text{SiMe}_3)\{\text{CH}(\text{SiMe}_3)_2\}$ ($\equiv \text{Cp}^R\text{H}$) and some derived alkali metal complexes.

We have previously described the preparation of NaCp' [22], NaCp'' [23], KCp'' [22], $[\text{LiCp}^m(\text{thf})_3]$ [25], and NaCp^m [25], mainly in the context of their use to make Cp' , Cp'' or Cp^m complexes of lanthanides, uranium or thorium. We now report two further compounds KCp^m and $[\text{NaCp}^m(\text{PMDETA})]$, including the crystal structure of the latter, as well as that of $[\text{LiC}_5\text{H}_3\text{Bu}_2^{1,3}(\text{TMEDA})]$ [$\text{TMEDA} = (\text{Me}_2\text{NCH}_2)_2$] [28].

X-Ray structural data on several monomeric trimethylsilyl-substituted cyclopentadienyl lithium complexes have been published, including $[\text{LiCp}'(\text{TMEDA})]$ [29], $[\text{LiCp}^m(\text{THF})]$ [28], $[\text{LiCp}^m(\text{TMEDA})]$ [28], $[\text{LiCp}^m(\text{quinuclidine})]$ [30], $[\text{LiCp}^m(\text{PMDETA})]$ [31] and $[\text{Li}(12\text{-crown-4})_2][\text{Cp}^m]$ [32]. However, the corresponding crystallographically characterized monomeric sodium analogues are rare and the only such data for a monomeric trimethylsilyl-substituted cyclopentadienyl sodium complex is for $[\text{Na}(\eta^5\text{-C}_5\text{Me}_5)(\text{pyridine})_3]$ [33].

2. Experimental details

2.1. Materials and procedures

All manipulations were carried out under vacuum or argon by Schlenk techniques. Solvents were dried and distilled over potassium–sodium alloy under argon prior to use. The following compounds were prepared by known procedures: $(\text{Me}_3\text{Si})_2\text{CHBr}$ [34], $\text{Cp}'\text{H}$ [35], $\text{Cp}''\text{H}$ [36], Cp^mH [36] and $\text{Li}(\text{C}_5\text{H}_3\text{Bu}_2^{1,3})(\text{TMEDA})$ [28]. Others were purchased and purified by standard procedures. Microanalyses were carried out by Medac (Brunel University). NMR Spectra were recorded with Bruker WM250, WM360 or WM500 instruments. GC/MS data were obtained using a HP 5995 Gas Chromatography/Mass Spectrometer.

2.2. Synthesis of Cp^RHI

Cyclopentadiene dimer was thermally cracked and distilled directly into a reaction vessel containing sodium wire (6.8 g, 295 mmol) in tetrahydrofuran (500 ml) at 0°C until all the sodium metal had disappeared. The resultant colorless solution was warmed to room temperature with stirring for 3 h. Dropwise addition of bis(trimethylsilyl)methyl bromide (52.2 g, 217 mmol) into this solution caused it to become orange and cloudy after stirring at ca. 20°C for 12 h. The mixture was refluxed for three days, yielding a red brown solution and a white precipitate. The solvent was removed in vacuo and diethyl ether (200 ml) was added. The mixture was then hydrolyzed at 0°C with aqueous HCl (200 ml of a 0.05 mol dm^{-3} solution). The two layers were separated and the aqueous layer was extracted with diethyl ether ($3 \times 75 \text{ ml}$). The combined ether extracts were dried over anhydrous MgSO_4 and filtered. The solvent was evaporated from the filtrate using a rotary evaporator. Vacuum distillation of the red brown residual oil yielded the colorless liquid **1** (34.8 g, 65%), b.p. $68\text{--}70^\circ\text{C}/0.5 \text{ mm Hg}$ or $38\text{--}40^\circ\text{C}/0.01 \text{ mm Hg}$; GC/MS: $m/z = 224$.

2.3. Synthesis of $\text{Cp}'\text{H}_2$ and $\text{Cp}''\text{H}_3$

A solution of $\text{Bu}^t\text{Me}_2\text{SiCl}$ (23.0 g, 150 mmol) in tetrahydrofuran (200 ml) was added slowly to a stirred solution of NaCp (80 ml of a 2.45 mol dm^{-3} solution in tetrahydrofuran, 180 mmol). The mixture was stirred at ca. 20°C for 2 days and was refluxed for 12 h. The solvent was removed in vacuo and diethyl ether (150 ml) was added. The mixture was hydrolyzed with H_2O (100 ml). The aqueous solution was extracted with diethyl ether ($3 \times 40 \text{ ml}$). The extract was dried over anhydrous CaCl_2 overnight. After filtration, solvent was removed from the filtrate under reduced pressure. Vacuum distillation of the residue gave two fractions: (i), $\text{Cp}'\text{H}$ **2** (14.5 g, 54%), b.p. $30\text{--}35^\circ\text{C}/0.01 \text{ mm Hg}$, GC/MS: $m/z = 180$; and (ii), $\text{Cp}''\text{H}$ **3** (8.7 g, 39%), b.p. $65\text{--}70^\circ\text{C}/0.01 \text{ mm Hg}$, GC/MS: $m/z = 294$.

2.4. Synthesis of LiCp^R **4**

LiBu^n (100 ml of a 1.6 mol dm^{-3} solution in hexane, 160 mmol) was added to a stirred solution of **1** (35.0 g, 160 mmol) in diethyl ether (350 ml) at 0°C . The clear solution was stirred at ca. 20°C for 20 h. Volatiles were removed in vacuo, leaving a white powder which was washed with pentane ($3 \times 20 \text{ ml}$) and dried in vacuo to yield **4** (31.4 g, 85%), as a free-flowing white powder.

2.5. Synthesis of NaCp^R 5

An excess of solid NaNH₂ (5.0 g, 130 mmol) was added to a stirred solution of **1** (12.8 g, 60 mmol) in tetrahydrofuran (200 ml). The mixture was stirred at 20°C for 6 h and refluxed for 12 h. Unreacted NaNH₂ was removed by filtration. Tetrahydrofuran was removed in vacuo from the filtrate to yield a pale brown solid, which was washed with hexane (3 × 50 ml) and dried in vacuo to yield **5** (7.15 g, 51%), as a free-flowing white powder.

2.6. Synthesis of KCp^R 6

A solution of **1** (66.7 g, 298 mmol) in diethyl ether (100 ml) was added to a stirred suspension of KH (15.2 g, 380 mmol) in diethyl ether (300 ml) at 0°C. The mixture was allowed to warm to room temperature to permit the evolution of H₂ and was stirred for two days. Unreacted KH was filtered off and solvent was removed from the filtrate in vacuo to yield a pale yellow solid, which was washed with hexane (3 × 40 ml) and dried in vacuo, yielding **6** (72.0 g, 92%), as free-flowing white powder.

2.7. Synthesis of NaCp^I 7

An excess of solid NaNH₂ (2.12 g, 50.5 mmol) was added to a stirred solution of **2** (3.2 g, 17.8 mmol) in tetrahydrofuran (100 ml). The mixture was stirred at ca. 20°C for 2 h, then refluxed for 10 h and filtered. Tetrahydrofuran was removed in vacuo from the filtrate to yield a white solid, which was washed with hexane (2 × 50 ml) and dried under vacuum to yield **7** (2.6 g, 73%), as a free-flowing white powder.

2.8. Synthesis of Cp^{II}H **3** by reaction of NaCp^I **7** with Bu^IMe₂SiCl

A solution of Bu^IMe₂SiCl (21.0 g, 140 mmol) in tetrahydrofuran (100 ml) was added to a stirred solution of **7** (25.0 g, 124 mmol) in tetrahydrofuran (150 ml). The mixture was refluxed for three days. The solvent was removed in vacuo and diethyl ether (200 ml) was added. The mixture was hydrolyzed with H₂O (150 ml). The aqueous layer was extracted with diethyl ether (3 × 40 ml) and the extract was dried over anhydrous CaCl₂. After filtration, solvent was evaporated from the filtrate using a rotary evaporator. Vacuum distillation of the residue gave the colorless liquid **3** (23.0 g, 63%), b.p. 65–70°C/0.01 mm Hg, GC/MS: *m/z* = 294.

2.9. Synthesis of LiCp^{II} **8**

A hexane solution of LiBuⁿ (8.7 ml of a 1.6 mol dm⁻³ solution, 14.0 mmol) was added dropwise to a

stirred solution of **3** (4.1 g, 14.0 mmol) in diethyl ether (200 ml). The resultant clear solution was stirred at ca. 20°C for 12 h. Volatiles were removed in vacuo to yield a white solid, which was washed with hexane (2 × 50 ml) and dried under vacuum to yield **8** (3.0 g, 71%), as a free-flowing white powder.

2.10. Synthesis of KCp^{II} **9**

A solution of **3** (62.0 g, 210 mmol) in tetrahydrofuran (100 cm³) was added to a stirred suspension of KH (11.8 g, 295 mmol) in tetrahydrofuran (300 ml) at 0°C. The mixture was stirred at ca. 20°C for 24 h, and was filtered. Tetrahydrofuran was removed from the filtrate in vacuo to yield a white solid, which was washed with hexane (3 × 20 ml) and dried in vacuo to yield **9** (62 g, 89%), as a free-flowing white powder.

2.11. Synthesis of [LiCp^R(TMEDA)] **11**

TMEDA (0.2 ml, 1.3 mmol) was added by a syringe to a solution of **4** (0.3 g, 1.3 mmol) in diethyl ether (30 ml). The clear yellow solution was stirred at ca. 20°C for 2 h. The solvent was removed in vacuo, leaving a pale yellow powder. Recrystallization from pentane at –30°C afforded yellow crystals of **11** (0.28 g, 62%).

2.12. Synthesis of [LiCp^{II}(TMEDA)] **12**

TMEDA (0.65 ml, 4.5 mmol) was added to a stirred solution of **8** (1.36 g, 4.5 mmol) in diethyl ether (100 ml). The mixture was stirred at ca. 20°C for 4 h. The solvent was removed in vacuo to yield a pale yellow solid, which was extracted into hexane and filtered. The volume of the filtrate was reduced to ca. 10 ml under vacuum. Cooling to –30°C yielded colorless needles of **12** (1.65 g, 88%).

2.13. Synthesis of Me₂Si(Cp^RH)₂ **13**

Dichlorodimethylsilane (4 ml, 32.6 mmol) was syringed into a stirred solution of excess of **6** (19.0 g, 72.5 mmol) in tetrahydrofuran (200 ml) at 0°C. The solution was stirred at ca. 20°C for 12 h and then refluxed for four days, yielding a red brown solution and a white precipitate. Tetrahydrofuran was removed from the mixture in vacuo and diethyl ether (100 ml) was added. The mixture was hydrolyzed with aqueous HCl solution (100 ml of a 0.1 mol dm⁻³ solution) and separated. The aqueous layer was extracted with diethyl ether (3 × 30 ml). The extract was dried over anhydrous CaCl₂ and filtered. The solvent was evaporated from the filtrate using a rotary evaporator. Vacuum distillation of the residual oil yielded the pale yellow, viscous liquid **13** (12.64 g, 77%), b.p. 60–70°C/10⁻⁴ mm Hg, GC/MS: *m/z* = 504.

2.14. Synthesis of $\text{Me}_2\text{Si}(\text{Cp}^R\text{K})_2$ **14**

A solution of **13** (12.64 g, 25.0 mmol) in diethyl ether (50 ml) was added to a stirred suspension of KH (3.74 g, 96 mmol) in diethyl ether (100 ml). The mixture was stirred at ca. 20°C for 3 h and then refluxed for 12 h. Unreacted KH was filtered off and solvent was removed from the filtrate in vacuo to yield a brown foam. Pentane (50 ml) was added to give a slightly brown solution which was concentrated to ca. 15 ml and cooled at -30°C for one week to yield a white precipitate and a brown solution. After filtration, the white solid was washed with pentane (2×10 ml) and dried in vacuo, yielding the free-flowing white powder **14** (6.1 g, 42%).

2.15. Synthesis of $[\text{LiCp}^m(\text{THF})_3]$ **15** [25]

A 5% excess of LiBu^n (1.6 mol dm^{-3} solution in hexane, 23.27 ml, 37.23 mmol) was added to a cooled (0°C), stirred solution of Cp^mH (10.0 g, 35.36 mmol) in tetrahydrofuran (100 ml). Stirring was continued at ca. 20°C for 12 h. The tetrahydrofuran was removed in vacuo to yield a white solid which was washed with cold (0°C) hexane (2×50 ml) and was dried in vacuo to yield the free-flowing, white powder **15** (13.4 g, 75%).

2.16. Synthesis of $[\text{NaCp}^m]$ **16** [22]

A several fold excess of NaNH_2 (5.67 g, 145.38 mmol) was added to a stirred solution of Cp^mH (5.84 g, 20.71 mmol) in tetrahydrofuran (100 ml). The mixture was stirred at ca. 20°C for 24 h, then filtered. The tetrahydrofuran was removed from the filtrate in vacuo to yield the free-flowing, white powder **16** (5.68 g, 90%).

2.17. Synthesis of KCp^m **17**

Tris(trimethylsilyl)cyclopentadiene (3.37 g, 11.9 mmol) was added to a cooled (ca. -50°C), stirred suspension of KH (1.37 g, 34.2 mmol) in tetrahydrofuran. The mixture was stirred at 20°C for 12 h and refluxed for another 3 h. The resulting suspension was filtered and the solvent removed from the filtrate in vacuo to give a white solid which was washed with hexane (2×100 ml) and dried under vacuum to yield the free-flowing, white powder **17** (2.73 g, 71%).

2.18. Synthesis of $[\text{NaCp}^m(\text{PMDETA})]$ **18**

PMDETA (0.75 ml, 3.46 mmol) was added to a cooled (ca. -30°C) suspension of **15** in diethyl ether (50 ml). The solid immediately dissolved to yield a clear-colorless solution, which was stirred at ca. 20°C for 1 h. The diethyl ether was removed in vacuo to yield a white solid which was extracted into toluene (40 ml) and the extract was filtered. The volume of the filtrate was reduced to ca. 20 ml. Cooling to -30°C yielded clear, colorless crystals of **18** (1.13 g, 68%).

2.19. Synthesis of Cp^RH **19**

Chlorotrimethylsilane (7.6 ml, 60.0 mmol) was added to a stirred solution of KCp^R **6** (11.8 g, 45.0 mmol) in tetrahydrofuran (150 ml), which immediately became cloudy. The mixture was stirred for 12 h and was then refluxed for 24 h, yielding an orange solution and a white precipitate. The latter was removed by filtration and tetrahydrofuran and excess of Me_3SiCl were removed in vacuo. Distillation afforded a pale yellow oil (8.8 g), b.p. $50\text{--}60^\circ\text{C}/0.01$ mmHg. Redistillation gave the colorless liquid **19** (7.5 g, 55.6%), b.p. $40\text{--}45^\circ\text{C}/0.05$ mmHg, GC/MS: $m/z = 296$.

Table 1

X-ray crystal structure details for $[\text{NaCp}^m(\text{PMDETA})]$ **18** and $[\text{Li}(\text{C}_5\text{H}_3\text{Bu}_2-1,3)(\text{TMEDA})]$ **21**

Formula	$\text{C}_{23}\text{H}_{52}\text{N}_3\text{NaSi}_3$	$\text{C}_{19}\text{H}_{37}\text{LiN}_2$
<i>M</i>	477.9	300.5
Crystal system, space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/c$
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.710(5), 17.597(30), 15.678(4)	8.570(8), 27.486(4), 9.821(2)
β (°)	95.37(3)	115.09(4)
$U(\text{Å}^3)$, <i>Z</i> , <i>D_c</i> (g cm^{-3})	3216.3, 4, 0.99	2095.1, 4, 0.95
<i>F</i> (000)	528	672
$\mu(\text{Mo-K}\alpha)(\text{cm}^{-1})$	1.69	0.5
Crystal size (mm^3)	$1.0 \times 0.25 \times 0.15$	$0.5 \times 0.25 \times 0.15$
Total unique reflections ($2 < \theta < \alpha^\circ$)	3322 ($\alpha = 20$)	3790 ($\alpha = 25$)
Significant reflections [$ F^2 > 3\sigma(F^2)$]	1735	1275
<i>R</i> , <i>R</i> ^a	0.051, 0.063	0.067, 0.078

$$^a R = \frac{\sum(|F_o| - |F_c|)}{\sum(|F_o|)}$$

$$R' = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2}$$

Table 2

Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for [NaCp^m(PMDETA)] **18**

Bonds			
Na–N(1)	2.533(5)	Na–N(2)	2.560(5)
Na–N(3)	2.645(5)	Na–C(1)	2.787(5)
Na–C(2)	2.711(5)	Na–C(3)	2.739(5)
Na–C(4)	2.803(5)	Na–C(5)	2.851(5)
Na–Cent(Cp)	2.501		
Angles			
Cent (Cp)–Na–N(1)	121.4	Cent (Cp)–Na–N(2)	143.3
Cent (Cp)–Na–N(3)	125.9	N(1)–Na–N(2)	72.7(2)
N(1)–Na–N(3)	105.6(2)	N(2)–Na–N(3)	72.4(2)

2.20. Synthesis of KCp^m **20**

A solution of **19** (6.0 g, 20.3 mmol) in diethyl ether (50 ml) was added to a stirred suspension of KH (1.0 g, 25.0 mmol) in diethyl ether (150 ml). Stirring was continued at ca. 20°C for two days and the mixture was then refluxed for 4 h. Unreacted KH was removed by filtration and solvent was removed in vacuo from the filtrate. The resultant solid was washed with hexane

Table 3

Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses for [NaCp^m(PMDETA)] **18**

	x	y	z
Si(1)	5136.4(15)	783.1(9)	8259.0(11)
Si(2)	6967.7(15)	1051.3(10)	4990.0(10)
Si(3)	9315.0(15)	1620.0(10)	6836.3(12)
Na	5991.3(19)	2501.1(2)	6817.0(4)
N(1)	6593(4)	3504(3)	7925(3)
N(2)	6104(5)	3765(3)	6023(3)
N(3)	3884(4)	2879(3)	6204(3)
C(1)	6917(4)	1188(3)	6157(3)
C(2)	5926(4)	977(3)	6563(3)
C(3)	6109(4)	1051(3)	7456(3)
C(4)	7270(5)	1303(3)	7614(3)
C(5)	7777(4)	1391(3)	6839(3)
C(6)	4580(7)	–201(4)	8077(5)
C(7)	5861(7)	853(6)	9348(5)
C(8)	3852(7)	1391(6)	8234(6)
C(9)	7928(7)	1719(5)	4458(5)
C(10)	7387(6)	48(4)	727(4)
C(11)	5515(6)	1202(5)	4415(4)
C(12)	10115(6)	899(4)	6235(5)
C(13)	9981(6)	1622(5)	7962(5)
C(14)	9628(6)	2578(4)	6367(5)
C(15)	6424(8)	4260(4)	7497(5)
C(16)	6728(8)	4313(4)	6646(5)
C(17)	4939(7)	4017(4)	5751(5)
C(18)	4126(7)	3377(5)	5495(5)
C(19)	7777(7)	3389(5)	8250(5)
C(20)	5879(7)	3458(5)	8617(5)
C(21)	6742(8)	3680(5)	5276(5)
C(22)	3251(7)	2218(5)	5821(5)
C(23)	3169(7)	3250(5)	6775(5)

Table 4

Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for [Li(C₅H₃Bu₂^t-1,3)(TMEDA)] **21**

Bonds			
Li–N(1)	2.173(10)	Li–N(2)	2.221(9)
Li–C(2)	2.287(10)	Li–C(1)	2.298(8)
Li–C(4)	2.285(10)	Li–C(3)	2.295(11)
Li–Cent (Cp)	1.952	Li–C(5)	2.292(8)
Angles			
Cent (Cp)–Li–N(1)	134.5	Cent (Cp)–Li–N(2)	143.1
N(1)–Li–N(3)	82.3(3)		

(3 × 30 ml) and dried in vacuo to yield **20**, as a free-flowing white powder.

2.21. X-ray structure determination for [NaCp^m(PMDETA)] **18** and [LiC₅H₃Bu₂^t-1,3)(TMEDA)] **21** [28]

Data sets were collected from a crystal sealed in a capillary under argon on an Enraf-Nonius CAD4 diffractometer in the θ – 2θ mode with monochromated Mo–K α radiation ($\lambda = 0.71069$ Å). Data were corrected for Lorentz and polarization effects (Lp). Reflections with $|F^2| > 3\sigma(F^2)$, where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/Lp$, were considered observed. The structure was solved by the direct method using MULTAN [37]. Non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares on F

Table 5

Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses for [Li(C₅H₃Bu₂^t-1,3)(TMEDA)] **21**

	x	y	z
Li	1759(9)	6093(3)	2358(9)
N(1)	3230(4)	5528(2)	1882(4)
N(2)	4117(5)	6526(2)	2817(5)
C(1)	–989(5)	6404(2)	1336(4)
C(2)	–208(5)	6520(2)	2886(4)
C(3)	174(5)	6086(2)	3744(4)
C(4)	–401(5)	5701(2)	2696(4)
C(5)	–1109(5)	5896(2)	1232(5)
C(6)	–1688(5)	6752(2)	2(5)
C(7)	–1352(9)	7278(2)	500(7)
C(8)	–877(8)	6643(3)	–1083(6)
C(9)	–3648(7)	6684(3)	–873(7)
C(10)	918(5)	6030(2)	5433(5)
C(11)	2470(6)	5697(2)	6006(5)
C(12)	1443(7)	6518(2)	6241(5)
C(13)	–468(6)	5796(2)	5869(5)
C(14)	4967(7)	5691(3)	2508(8)
C(15)	5139(6)	6198(3)	2259(7)
C(16)	2449(7)	5455(2)	249(6)
C(17)	3197(8)	5051(2)	2587(7)
C(18)	4974(8)	6601(3)	4434(8)
C(19)	3855(9)	6993(3)	2035(10)

using programs from the Enraf–Nonius MOLEN package. The hydrogen atoms were held fixed at calculated positions with $U_{\text{iso}} = 1.3 U_{\text{eq}}$ for the parent atom.

Further details are given in Table 1, selected bond lengths and angles are listed in Tables 2 and 3 and atom positions in Tables 4 and 5. Complete lists of bond lengths and angles, and Tables of H atom positions and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

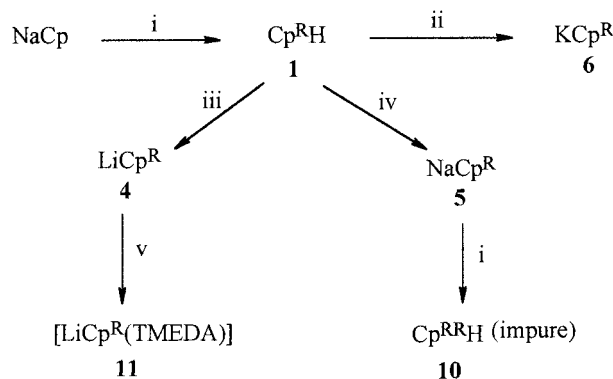
3. Results and discussion

3.1. Synthesis and characterization of $\text{Cp}^{\text{R}}\text{H}$ **1**, LiCp^{R} **4**, $[\text{LiCp}^{\text{R}}(\text{TMEDA})]$ **11**, NaCp^{R} **5**, KCp^{R} **6** and $\text{Cp}^{\text{RR}}\text{H}$ **10** [$\text{Cp}^{\text{R}} = \eta^5\text{-C}_5\text{H}_4\text{CH}(\text{SiMe}_3)_2$, $\text{Cp}^{\text{RR}} = \eta^5\text{-C}_5\text{H}_3\{\text{CH}(\text{SiMe}_3)_2\}_{2-1,3}$]

The synthesis of compounds **1**, **4**, **5**, **6**, **10** and **11** is illustrated in Scheme 1. Yields and analytical data (not **10**) for the cyclopentadienyl-alkali metal complexes are summarized in Table 6, and mass spectra of the neutral cyclopentadienes **1** and **10** in Table 7, which shows the parent molecular ions and appropriate fragments.

Bis(trimethylsilyl)methylcyclopentadiene $\text{Cp}^{\text{R}}\text{H}$ **1** was obtained from an excess of sodium cyclopentadienide (prepared in situ from freshly cracked monomeric cyclopentadiene and sodium in tetrahydrofuran solution) and bis(trimethylsilyl)bromomethane, (i) in Scheme 1.

The lithium derivative LiCp^{R} **4** was prepared from **1** and LiBu^{n} , (iii) in Scheme 1. Addition of TMEDA yielded (v in Scheme 1) yellow crystals of $[\text{LiCp}^{\text{R}}(\text{TMEDA})]$ **11**. Treatment of **1** with an excess of NaNH_2 gave (iv in Scheme 1) NaCp^{R} **5**, while KCp^{R} **6**



Scheme 1.

was obtained from **1** and an excess of KH , (ii) in Scheme 1.

The reaction of **5** with $(\text{Me}_3\text{Si})_2\text{CHBr}$ was monitored by GC/MS analysis; formation of bis[bis(trimethylsilyl)methyl]cyclopentadiene $\text{Cp}^{\text{RR}}\text{H}$ **10** did not proceed to completion and the yield of **10** was low even after refluxing for several days. After work-up procedures similar to that for **1**, unreacted $(\text{Me}_3\text{Si})_2\text{CHBr}$ and **1** were removed from the red brown residue under high vacuum (ca. 10^{-4} – 10^{-5} mmHg), leaving a viscous dark brown oil; GC/MS showed it to contain ca. 70% of **10** and unidentified impurities. Attempts to isolate pure $\text{Cp}^{\text{RR}}\text{H}$ **10** by further distillation were unsuccessful; **10** decomposed when heated in vacuo above 120°C .

It is noteworthy that complexes LiCp^{R} **4** and KCp^{R} **6** were extremely soluble in diethyl ether unlike, for example, MC_5H_5 , MC_5Me_5 , $\text{MC}_5\text{H}_{5-n}(\text{CMe}_3)_n$, $\text{MC}_5\text{H}_{5-n}(\text{SiMe}_3)_n$ ($\text{M} = \text{Li}, \text{Na}$ or K , $n = 1$ or 2); KC_5Me_5 was even insoluble in tetrahydrofuran [38,39].

Table 6

Yields and elemental analytical data for the new cyclopentadienyl alkali metal complexes

Compound	C(%) Found (Calcd.)	H(%) Found (Calcd.)	N(%) Found (Calcd.)	Yield (%)
LiCp^{R} 4	60.8 (62.6)	10.50 (10.1)	—	85
NaCp^{R} 5	58.2 (58.5)	9.38 (9.40)	—	51
KCp^{R} 6	55.9 (54.9)	9.00 (9.83)	—	92
NaCp^{I} 7	64.2 (65.3)	9.41 (9.47)	—	73
LiCp^{II} 8	65.0 (67.9)	10.9 (11.10)	—	71
KCp^{II} 9	62.5 (63.4)	10.5 (10.0)	—	89
$[\text{LiCp}^{\text{R}}(\text{TMEDA})]$ 11	61.2 (62.4)	11.2 (11.34)	7.51 (8.08)	62
$[\text{LiCp}^{\text{II}}(\text{TMEDA})]$ 12	68.2 (66.3)	12.3 (11.9)	7.07 (6.22)	88
$\text{Me}_2\text{Si}(\text{Cp}^{\text{R}}\text{K})_2$ 14	53.02 (53.7)	8.72 (8.67)	—	42
$[\text{LiCp}^{\text{III}}(\text{THF})_3]$ 15	^a	^a	—	75
NaCp^{IV} 16	59.4 (60.0)	7.83 (8.10)	—	—
NaCp^{III} 16	53.6 (56.9)	9.04 (9.10)	—	90
KCp^{IV} 17	53.5 (53.2)	8.43 (8.50)	—	—
KCp^{III} 17	56.5 (52.5)	10.15 (9.90)	—	71
$[\text{NaCp}^{\text{IV}}(\text{PMDTA})]$ 18	55.2 (57.9)	11.12 (10.90)	8.48 (8.81)	68
KCp^{III} 20	52.4 (53.8)	9.10 (9.33)	—	33

^aNot recorded.

Table 7
Mass spectral data for the new cyclopentadienes **1**, **2**, **3**, **10** and **13** with assignments

Cyclopentadiene	Fragments and m/z (relative intensity, %)
Cp ^R H 1	[M] ⁺ , 224 (5.4); [M-Me] ⁺ , 209 (1.6); [M-SiMe ₄] ⁺ , 136 (42.7); [SiMe ₃] ⁺ , 73 (100); [SiMe ₂] ⁺ , 58 (25.3).
Cp ^H H 2	[M] ⁺ , 180 (21.1); [M-Bu ^t] ⁺ , 123 (100); [SiMe ₃] ⁺ , 73 (42.3).
Cp ^H H 3	[M] ⁺ , 294 (2.7); [M-Bu ^t] ⁺ , 237 (36.5); [M-Bu ^t SiMe ₃ -1] ⁺ , 163 (83.2); [SiMe ₃] ⁺ , 73 (100).
Cp ^{RR} H 10	[M] ⁺ , 382 (50.1); [M-Me] ⁺ , 367 (5.9); [M-SiMe ₃] ⁺ , 309 (9.9); [Cp ^R -2] ⁺ , 221 (35.6); [SiMe ₃] ⁺ , 73 (100).
Me ₂ Si(Cp ^R H) ₂ 13	[M] ⁺ , 504 (10.3); [M-Me] ⁺ , 489 (6.6); [M-Cp ^R] ⁺ , 281 (54.8); [SiMe ₃] ⁺ , 73 (100).
Cp ^R H 19	[M] ⁺ , 296 (7.4); [M-Me] ⁺ , 281 (1.7); [M-SiMe ₃] ⁺ , 208 (7.5); [SiMe ₃] ⁺ , 73 (100).

The ¹H NMR spectrum of the bis(trimethylsilyl)methylcyclopentadiene Cp^RH **1** showed it to contain the two isomers shown in Table 8.

The alkali metal cyclopentadienes **4**, **5**, **6** and **11** were characterized by multinuclear (¹H, ¹³C{¹H}, ²⁹Si{¹H} and ⁷Li{¹H}) NMR spectra, Tables 9–11, respectively.

3.2. Synthesis and characterization of Cp^HH **2**, Cp^HH **3**, NaCp^t **7**, LiCp^{tt} **8**, KCp^{tt} **9** and [LiCp^{tt}(TMEDA)] **12** [Cp^t = η⁵-C₅H₄(SiMe₂Bu^t), Cp^{tt} = η⁵-C₅H₃-(SiMe₂Bu^t)₂-1,3]

The synthesis of compounds **2**, **3**, **7**, **8**, **9** and **12** is presented in Scheme 2. Yields and analytical data are summarized in Table 6 and mass spectra (parent molecular ions) of **1** and **3** in Table 7.

From NaC₅H₅ (ca. 20–30% excess) and Bu^tMe₂SiCl in tetrahydrofuran under reflux a mixture of approximately of Cp^HH **2** (2 parts) and Cp^HH **3** (1 part) was obtained (i in Scheme 1). The large difference in the boiling points of **2** and **3** facilitated their ready separation by distillation.

From **2** and an excess of NaNH₂, NaCp^t **7** was obtained, (ii in Scheme 2), which with Bu^tMe₂SiCl

afforded (i in Scheme 2) Cp^HH **3**. Lithiation of **3** gave (iii in Scheme 2) LiCp^{tt} **8**. Like **4** and **6**, compound **8** was very soluble in diethyl ether. [LiCp^{tt}(TMEDA)] **12** was obtained from **8** and TMEDA, (v in Scheme 2), while KCp^{tt} **9** was synthesised from **3** and an excess of KH, (iv in Scheme 2).

The alkali metal cyclopentadienides **7**, **8**, **9** and **12** were characterized by multinuclear (¹H, ¹³C{¹H}, ²⁹Si{¹H} and ⁷Li{¹H}) NMR spectra (Tables 9–11, respectively). The ¹H and ¹³C{¹H} NMR spectra of **12** were unusual in that the two Me groups in Me₂Si were magnetically inequivalent so as to give two signals in both the ¹H and ¹³C NMR spectra; this would be consistent with **12** having the structure **12a** having diastereotopic methyl groups. Complexes **7**, **8** and **9**, however, only gave one ¹H or ¹³C{¹H} NMR signal for the Me₂Si group.

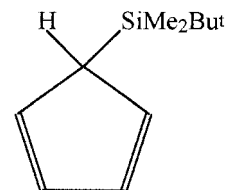


Table 8
¹H NMR spectral chemical shift (δ) data and assignments for **1** (in C₆D₆, at 293 K)

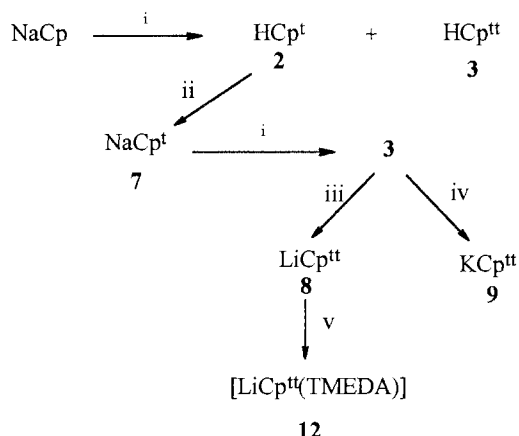
	60%	40%
δ[¹ H NMR] (360 MHz)	0.02 (s, 18H, Me ₃ Si) 1.28 (s, 1H, CH(SiMe ₃) ₂) 2.76 (t, 2H, H _d) 6.22 (m, 1H, H _a) 6.18 (m, 1H, H _b) 5.61 (t, 1H, H _c)	-0.03 (s, 18H, Me ₃ Si) 1.20 (s, 1H, CH(SiMe ₃) ₂) 2.60 (d, 2H, H _h) 6.40 (m, 1H, H _e) 6.01 (m, 1H, H _f) 5.85 (m, 1H, H _g)

Table 9
¹H NMR Spectral chemical shifts (δ) and assignments for the new cyclopentadienyl alkali metal complexes (360 MHz, 293 K)

Compound	(CH ₃) ₃ Si	CH(SiMe ₃) ₂	(CH ₃) ₃ C	(CH ₃) ₂ Si	Cp ring	-bases-TMEDA, PMDETA, THF	Solvent
LiCp ^R 4	0.22 (s, 18H)	1.71 (s, 1H)			6.23 (t, 2H), 5.59 (t, 2H)		C ₅ D ₂ N
NaCp ^R 5	-0.04 (s, 18H)	1.39 (s, 1H)			5.39 (t, 2H), 5.54 (t, 2H)		C ₄ D ₈ O
KCp ^R 6	0.25 (s, 18H)	1.74 (s, 1H)			5.97 (t, 2H), 6.24 (t, 2H)		C ₅ D ₂ N
NaCp ^I 7			1.06 (s, 9H)	0.29 (s, 6H)	6.04 (t, 2H), 6.15 (t, 2H)		C ₄ D ₈ O
LiCp ^{II} 8			1.05 (s, 18H)	0.27 (s, 12H)	6.70 (d, 2H), 6.81 (s, 1H)		C ₅ D ₂ N
KCp ^{II} 9			1.10 (s, 18H)	0.34 (s, 12H)	6.76 (d, 2H), 6.87 (t, 1H)		C ₅ D ₂ N
[LiCp ^R (TMEDA)] 11	0.27 (s, 18H)	1.61 (s, 1H)			5.77 (t, 2H), 6.04 (t, 2H)	1.67 (s, 12H, Me) 1.45 (s, 4H, CH ₂)	C ₆ D ₆
[LiCp ^{II} (TMEDA)] 12			1.14 (s, 18H)	0.35 (s, 6H) 0.41 (s, 6H)	6.46 (t, 2H), 6.53 (t, 1H)	1.36 (s, 4H, CH ₂) 1.64 (s, 12H, Me)	C ₆ D ₆
Me ₂ Si(Cp ^R K) ₂ 14		1.67 (s, 2H)		0.26 (s, 6H)	6.02 (t, 2H), 6.16 (t, 2H), 6.39 (t, 2H)		C ₅ D ₂ N
NaCp ^I	0.81 (s, 36H)				6.83 (d, 2H), 6.76 (d, 2H)		C ₅ D ₂ N
NaCp ^{II}	0.35 (s, 9H)				7.02 (t, 1H), 6.93 (d, 2H)		C ₅ D ₂ N
NaCp ^{III}	0.30 (s, 18H)				7.02 (t, 1H), 6.93 (d, 2H)		C ₅ D ₂ N
KCp ^I	0.30 (s, 18H)				7.02 (t, 1H), 6.93 (d, 2H)		C ₅ D ₂ N

Table 10
¹³C{¹H} NMR Spectral chemical shifts (δ) and assignments for the new cyclopentadienyl alkali metal complexes (62.9 MHz, 293 K)

Compound	(CH ₃) ₃ Si	CH(SiMe ₃) ₂	(CH ₃) ₃ C	(CH ₃) ₂ Si	(CH ₃) ₃ C	(CH ₃) ₃ C	Cp ring	PMDETA or TMEDA	Solvent
LiCp ^R 4	1.55	21.27					103.63, 106.24, 116.28		C ₅ D ₂ N
NaCp ^R 5	1.09	21.67					101.39, 104.95, 115.35		C ₄ D ₈ O
KCp ^R 6	1.37	21.26					103.63, 106.25, 116.32		C ₅ D ₂ N
NaCp ^I 7				-3.44	17.81	27.65	106.10, 113.27, 108.60		C ₄ D ₈ O
LiCp ^{II} 8				-3.65	17.94	27.50	110.75, 116.00, 122.26		C ₅ D ₂ N
KCp ^{II} 9				3.07	18.14	27.83	111.62, 111.98, 123.72		C ₅ D ₂ N
[LiCp ^R (TMEDA)] 11	1.27	20.85		-4.18	17.99	27.26	102.09, 104.15, 116.91	46.86 55.86	C ₆ D ₆
[LiCp ^{II} (TMEDA)] 12				-3.55			110.61, 115.28, 121.35	45.55 55.73	C ₆ D ₆
NaCp ^I	2.08						112.58, 107.53, 104.43		C ₅ D ₂ N
NaCp ^{II}	2.02						120.76, 107.53, 104.43		C ₅ D ₂ N
KCp ^I	1.89						121.15, 116.06, 115.20		C ₅ D ₂ N
KCp ^{II} 17	3.23 1.94						128.25, 121.17, 115.95		C ₅ D ₂ N
[NaCp ^{II} (PMDETA)] 18								44.26 46.09 (Me) 54.46, 57.44 (C H ₂)	C ₆ D ₅ C D ₃
KCp ^{III} 20	-0.03, 2.02 2.55	20.28 (C H ₂ SiMe ₃)					113.10, 113.26, 115.67, 121.50		C ₅ D ₂ N
[LiCp ^{II} (THF)] 15	0.40 (s, 18H), 0.31 (s, 9H)						6.77 (s, 2H)	3.34 (m, 12H, α-CH ₂) 1.32 (m, 12H, β-CH ₂)	C ₅ D ₂ N
NaCp ^{III} 16	0.21 (s, 18H), -0.10 (s, 9H)						not observed		C ₅ D ₂ N
KCp ^{III} 17	0.38 (s, 18H), 0.49 (s, 9H)						6.76 (s, 2H)		C ₅ D ₂ N
[NaCp ^{II} (PMDETA)] 18	0.45 (s, 18H), 0.34 (s, 9H)						6.65 (br, 2H)	1.89 (s, 12H, Me) 1.86 (s, 3H, Me) 1.68 (s, 8H, CH ₂)	C ₆ D ₅ CD ₃
KCp ^{III} 20	0.23 (s, 9H), 0.24 (s, 9H) 0.40 (s, 9H) 1.67 (s, 2H) (CH ₂ SiMe ₃)						6.37 (s, 1H), 6.64 (s, 1H)		C ₅ D ₂ N



Scheme 2.

3.3. Synthesis and characterization of $\text{Me}_2\text{Si}(\text{Cp}^R\text{H})_2$ **13** and $\text{Me}_2\text{Si}(\text{Cp}^R\text{K})_2$ **14** [$\text{Me}_2\text{Si}(\text{Cp}^R)_2 = \text{Me}_2\text{Si}\{\text{C}_5\text{H}_3\text{-CH}(\text{SiMe}_3)_2\}_2$]

The synthesis of compounds **13** and **14** is illustrated in Scheme 3. The dicyclopentadiene $\text{Me}_2\text{Si}(\text{Cp}^R\text{H})_2$ **13** was obtained from Me_2SiCl_2 and an excess of KCp^R **6**, (i in Scheme 3). Treatment of **13** with KH yielded (ii in Scheme 3) $\text{Me}_2\text{Si}(\text{Cp}^R\text{K})_2$ **14**, which was very soluble in diethyl ether and even sparingly soluble in pentane.

Compound **13** was characterized by GC/MS, showing its molecular weight to be 504; a peak at $m/z = 281$ is attributed to the $[\text{M-Cp}^R]^+$ fragment (Table 7). The dipotassium salt **14** was identified by its ^1H NMR spectrum (Table 9), and C, H elemental analysis (Table 6).

3.4. Synthesis and characterization of $[\text{LiCp}^m(\text{THF})_3]$ **15**, NaCp^m **16**, KCp^m **17** and $[\text{NaCp}^m(\text{PMDETA})]$ **18**

The synthesis of NaCp^m , NaCp^m and KCp^m was described in our previous publications [22,23], but some ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectral (Tables 9–11,

Table 11
 $^{29}\text{Si}\{^1\text{H}\}$ (49.7 MHz) and $^7\text{Li}\{^1\text{H}\}$ (97.2 MHz) NMR spectral chemical shifts (δ) for the new cyclopentadienyl alkali metal complexes (at 293 K)

Compound	$^{29}\text{Si}\{^1\text{H}\}$	$^7\text{Li}\{^1\text{H}\}$	Solvent
LiCp^R 4	0.1	−6.4	$\text{C}_5\text{D}_5\text{N}$
KCp^R 6	0.6	−6.4	$\text{C}_5\text{D}_5\text{N}$
LiCp^t 8	−4.1	−3.6	$\text{C}_5\text{D}_5\text{N}$
KCp^t 9	−3.6	−3.6	$\text{C}_5\text{D}_5\text{N}$
$[\text{LiCp}^R(\text{TMEDA})]$ 11	−0.2	−7.8	C_6D_6
$[\text{LiCp}^t(\text{TMEDA})]$ 12	−5.0	−8.0	C_6D_6
NaCp^m	−13.7		$\text{C}_5\text{D}_5\text{N}$
NaCp^m	−14.1		$\text{C}_5\text{D}_5\text{N}$
KCp^m	−13.9		$\text{C}_5\text{D}_5\text{N}$
$[\text{LiCp}^m(\text{THF})_3]$ 15		−7.4	C_6D_6
NaCp^m 16			$\text{C}_5\text{D}_5\text{N}$
KCp^m 17	−14.2, −13.9		$\text{C}_5\text{D}_5\text{N}$
$[\text{NaCp}^m(\text{PMDETA})]$ 18			$\text{C}_6\text{D}_5\text{CD}_3$
KCp^m 20	−15.0, −14.9, −1.1		$\text{C}_5\text{D}_5\text{N}$

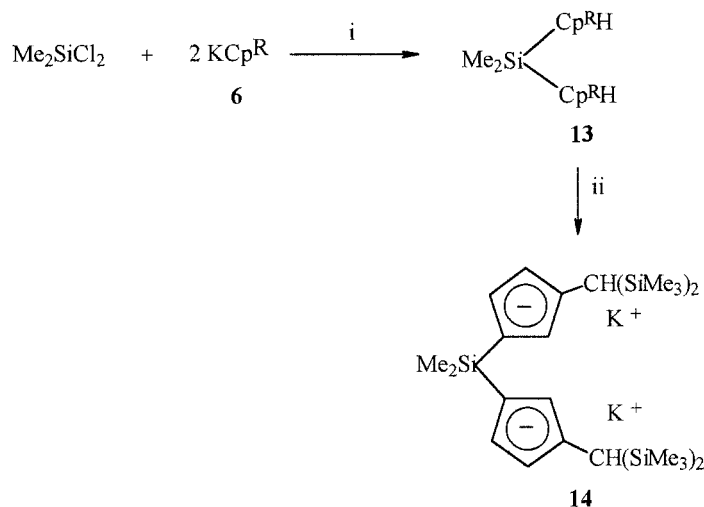
respectively) and microanalytical (Table 6) data are now presented.

Metallation of Cp^mH with LiBu , NaNH_2 or KH provided $[\text{LiCp}^m(\text{THF})_3]$ **15**, NaCp^m **16** or KCp^m **17**, respectively, and **16** with PMDETA afforded $[\text{NaCp}^m(\text{PMDETA})]$ **18** as illustrated in Scheme 4.

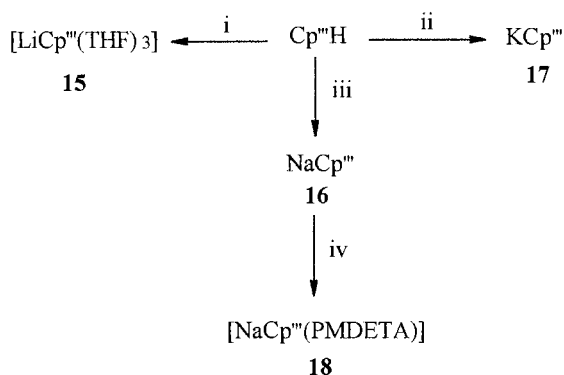
Complexes **15–18** were characterized by microanalysis (Table 6) and ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{29}\text{Si}\{^1\text{H}\}$ and $^7\text{Li}\{^1\text{H}\}$ NMR spectra, Tables 9–11, respectively.

3.5. Synthesis and characterization of Cp^RH **19** and KCp^R **20** [$\text{Cp}^R = \text{C}_5\text{H}_3(\text{SiMe}_3)\{\text{CH}(\text{SiMe}_3)_2\}$, $\text{Cp}^R = \{\text{C}_5\text{H}_2(\text{SiMe}_3)_2\text{-2,4-CH}_2\text{SiMe}_3\}$]

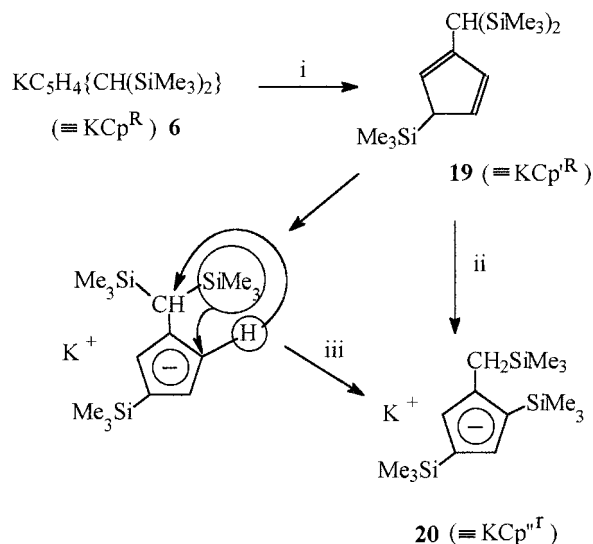
The formation of compounds **19** and **20** is illustrated in Scheme 5. Compound **19**, prepared from KCp^R and Me_3SiCl , (i in Scheme 5), was obtained (56%) as a



Scheme 3.



Scheme 4.

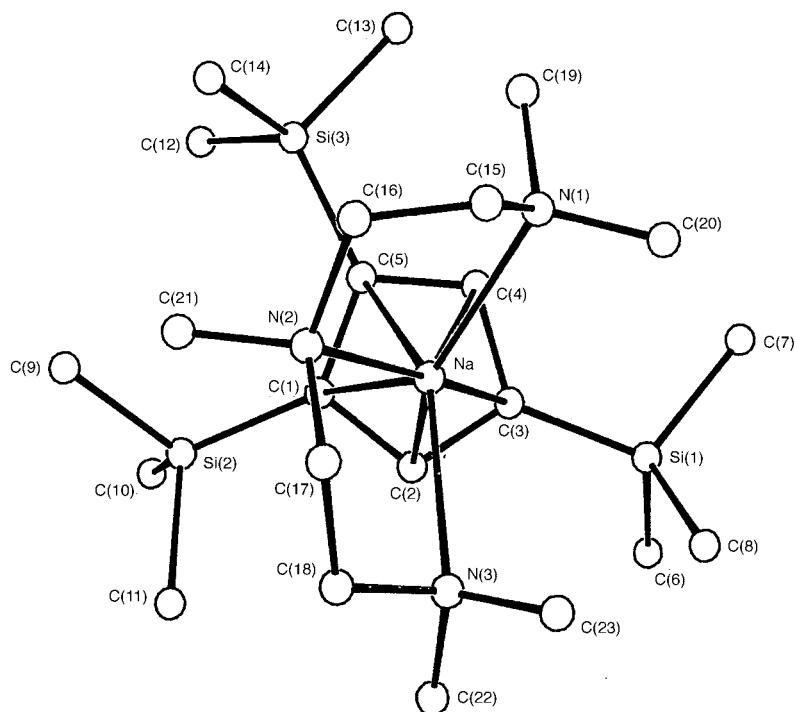


Scheme 5.

colorless, volatile liquid, identified by GC/MS (which showed the parent molecular ion, see also Table 6) and its ^1H NMR spectrum (Table 9). Treatment of **19** with KH unexpectedly yielded **20**, the potassium salt of an isomerised cyclopentadienide, (ii in Scheme 5). The rearrangement involved a 1,3-migration of a SiMe_3 group from the methine carbon of the $\text{CH}(\text{SiMe}_3)_2$ substituent to a carbon on the C_5 ring and the reverse migration of a hydrogen, (iii in Scheme 5). Anionic SiMe_3 migrations are well documented [40]; the present example may be regarded as a dyotropic rearrangement,

a term used to describe an uncatalysed process in which two σ bonds are broken so that the two groups migrate intramolecularly and exchange position in a concerted fashion [41]. We have previously made a brief reference to the sequence $\text{KCp}^{\text{R}} \rightarrow \mathbf{19} \rightarrow \mathbf{20}$ [42].

Microanalytical and ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectral data are shown in Tables 6, 9–11, respectively.

Fig. 1. Molecular structure and atom numbering scheme for $[\text{NaCp}^{\text{M}}(\text{PMDETA})]$ **18**.

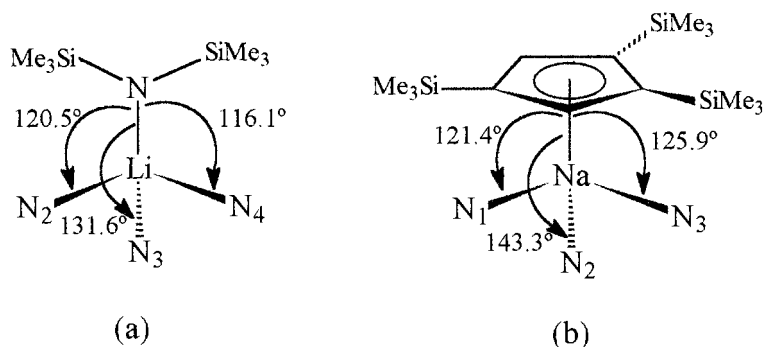


Fig. 2. Comparison of the steric strain in (a) $[\text{LiN}(\text{SiMe}_3)_2(\text{PMDETA})]$ [45] and (b) **18**.

3.6. The single crystal X-ray structure of $[\text{NaCp}''(\text{PMDETA})]$ **18**

The molecular structure and atom numbering scheme for compound **18** are shown in Fig. 1, selected bond distances and angles and atomic coordinates are in Tables 2 and 3, respectively.

The sodium is η^5 -bound to the planar cyclopentadienyl ring. A tridentate PMDETA ligand chelates the sodium atom, which occupies a strained tetrahedral environment, taking the ligand as occupying a single coordination site. The Na–Cp(centroid) distance is 2.501 Å, which is shorter than the 2.65 Å in $[\{\text{Na}(\eta^5\text{-C}_5\text{H}_5)(\text{TMEDA})\}_2]$ [43] or the 2.53 Å in $[\{\text{Na}(\eta^5\text{-C}_5\text{H}_4\text{COMe})\}_2]$ [44], but longer than the 2.399 Å in $[\text{Na}(\eta^5\text{-C}_5\text{Me}_5)(\text{pyridine})_3]$ [33]. $[\text{NaCp}''(\text{PMDETA})]$ **18** may be compared with $[\text{LiCp}''(\text{PMDETA})]$ [31] and

$[\text{LiN}(\text{SiMe}_3)_2(\text{PMDETA})]$ [45]. A notable difference between **18** and $[\text{LiCp}''(\text{PMDETA})]$ is that in the latter, only two of the three potentially chelating nitrogens bind to the lithium. This can be attributed to the greater ionic radius of sodium than lithium, which allows sodium to form complexes with higher co-ordination number. The angles describing the tetrahedral environment around the lithium atom in $[\text{LiN}(\text{SiMe}_3)_2(\text{PMDETA})]$ are not as strained as those in **18** because the steric constraints placed on the alkali metal by $\overline{\text{N}}(\text{SiMe}_3)_2$ are not as great as those imposed by the $\overline{\text{Cp}}''$ ligand, Fig. 2.

3.7. The single crystal X-ray structure of $[\text{LiC}_5\text{H}_3\text{Bu}^t\text{-1,3}](\text{TMEDA})$ **21**

Single crystals of **21** were obtained by recrystallizing a specimen [28] from hexane. The molecular structure is shown in Fig. 3 and selected bond lengths and angles and atomic coordinates in Tables 3 and 5, respectively. The molecular structure is very similar to those of $[\text{LiCp}'(\text{TMEDA})]$ [29] and $[\text{LiCp}''(\text{TMEDA})]$ [31]. In the former, the Li–C bonds range from 2.257(10) to 2.286(10) Å (the carbon bearing the SiMe_3 substituent), the cyclopentadienyl C–C bonds from 1.38(1) (the two bonds furthest from the C– SiMe_3) to 1.42(8) Å and the Li–N bonds are somewhat shorter at 2.119(10) and 2.142(8) Å than the 2.173(10) and 2.221(9) Å in **21**.

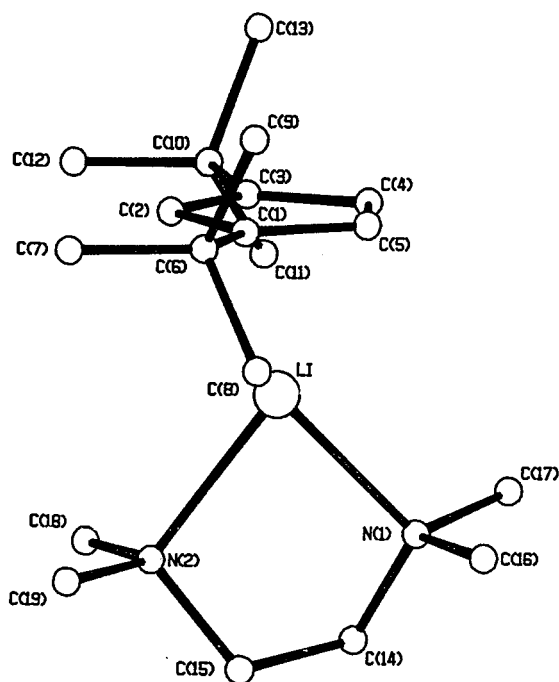


Fig. 3. Molecular structure and atom numbering scheme for $[\text{Li}(\text{C}_5\text{H}_3\text{Bu}^t\text{-1,3})(\text{TMEDA})]$ **21**.

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