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Synthesis and crystal structures of alkali-metal (+)-neomenthylcyclopentadienyl complexes

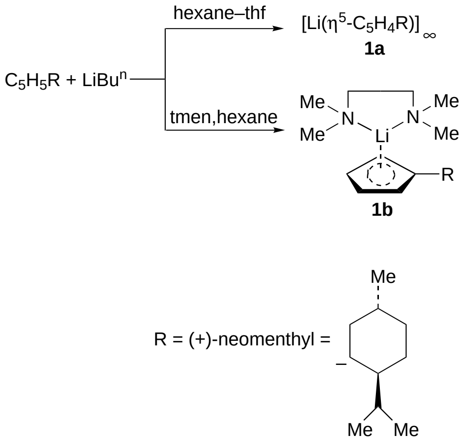
Wing-Por Leung,* Fu-Quan Song, Feng Xue and Thomas C. W. Mak

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

Polymeric alkali-metal (+)-neomenthylcyclopentadienyl complexes $[M(\eta^5\text{-}C_5H_4R)]_\infty$ (M = Li **1a**, Na **2a** or K **3a**) and $[M(\eta^5\text{-}C_5H_4R)L]_\infty$ [M = Na, L = tetrahydrofuran (thf) **2b**; M = K, L = thf **3b**, L = 1,2-dimethoxyethane (dme) **3c**] and monomeric neomenthylcyclopentadienyl(*N*,*N*,*N′*,*N′*-tetramethylethane-1,2-diamine)lithium **1b** have been synthesized and characterised by single-crystal X-ray analyses. Compounds **1a**, **2a**, **2b** and **3c** have multidecker polymeric chain structures with average M-Cp (centroid) (M = Li, Na or K) distances of 2.010 Å (Li), 2.437 and 2.503 Å (Na), and 2.874 Å (K). The average $Cp^R\text{–}M\text{–}Cp^R$ angles are 166.9 (Li), 170.2 and 135.1 (Na), and 135.5° (K), respectively. The (+)-neomenthyl groups on successive cyclopentadienyl rings are oriented along the polymeric zigzag chain with approximate twist angles of 116.2 (**1a**), 91.1 (**2a**), 179.9 (**2b**) and 165.8° (**3c**) respectively. In the monomeric half-sandwich compound **1b** the lithium atom is bonded to the pentahapto cyclopentadienyl ring at a metal-to-centre distance of 1.910 Å.

Alkali-metal cyclopentadienyl compounds are indispensable transfer reagents for the preparation of metallocene derivatives. Structural studies of this class of compounds have attracted attention and have been reviewed by Jutzi[1] and Weiss.[2] Among the alkali metals, lithium cyclopentadienyl compounds have been studied most extensively for their methods of synthesis, and their structure and bonding by theoreticians and experimentalists. In contrast, fewer structures of heavier alkali-metal cyclopentadienyl compounds have been reported. This is presumably due to the more ionic nature of these compounds and the formation of aggregates which causes difficulties in structural studies by X-ray crystallography. Recent work has shown that incorporation of lipophilic substituent groups such as $SiMe_3$ on the cyclopentadienyl ring and/or the use of coordinating bases such as tetramethylethane-1,2-diamine (tmen) have provided access to more soluble and crystallographically characterisable heavier alkali-metal cyclopentadienyl compounds. For example, the structures of $[K(\eta^5\text{-}C_5H_4SiMe_3)]_\infty$ and $[Na(\eta^5\text{-}C_5H_5)(tmen)]_\infty$ have been reported.[3,4] A recent review by Stalke[5] classifies alkali-metal cyclopentadienyls into four distinguishable structural forms: (*i*) monomeric half-sandwich metallocene, (*ii*) polymeric zigzag chain metallocene, (*iii*) metallocene cation and (*iv*) metallocene anion. Representative examples for (*i*) to (*iv*) are $[Li(\eta^5\text{-}C_5H_4R)(tmen)]$, (R = Me[6] or $SiMe_3$[7]), $[K(\eta^5\text{-}C_5Me_5)(py)_2]_\infty$ (py = pyridine),[6] $Li^+C_5H_5^-$[8] and $[Li(\eta^5\text{-}C_5H_5)_2]^-$,[9] respectively.

Lithium (−)/(+)-neomenthylcyclopentadienyl salts (neomenthyl = 2-isopropyl-5-methylcyclohexyl) have been prepared *in situ* for the synthesis of some early transition-metal compounds.[10,11] However, no structural evidence of these lithium salts has been reported. Alkali-metal (+)-neomenthylcyclopentadienyl compounds are particularly useful as more reactive transfer reagents for the preparation of some early-transition-metal and rare-earth-metal cyclopentadienyl compounds. In this paper, the synthesis and crystal structures of a series of (+)-neomenthylcyclopentadienyl (C_5H_4R) compounds of lithium, sodium and potassium are described. The effects of the coordinated solvent and the substituent group on the cyclopentadienyl ring are studied by comparing the structural data of these compounds.

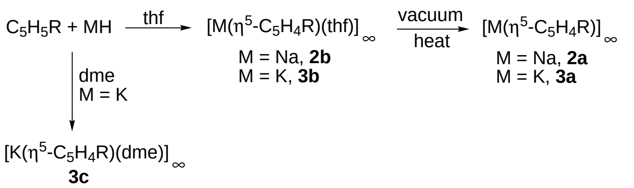


Scheme 1

Results and Discussion

Synthesis of the lithium compound $[Li(\eta^5\text{-}C_5H_4R)]_\infty$ **1a** was accomplished by the metallation of (+)-neomenthylcyclopentadiene with $LiBu^n$ in hexane (Scheme 1). The white solid obtained in 92% yield was recrystallised from a hexane–tetrahydrofuran (thf) solvent mixture to give a colourless crystalline solid. The structure of **1a** as determined by X-ray crystallography was found to be a polymeric zigzag chain of lithanocenes. However, the structural analysis results obtained were of low precision ($R = 0.1144$).

Treatment of (+)-neomenthylcyclopentadiene with the appropriate alkali-metal hydride MH (M = Na or K) in thf afforded white crystalline solids of $[Na(\eta^5\text{-}C_5H_4R)(thf)]_\infty$ **2b** and $[K(\eta^5\text{-}C_5H_4R)(thf)]_\infty$ **3b**, respectively (Scheme 2). The solubility of **3b** is comparatively the lowest among the three alkali-metal compounds due to the more ionic nature of potassium compounds. The unsolvated compounds $[M(\eta^5\text{-}C_5H_4R)]_\infty$ (M = Na **2a** or K **3a**) can be obtained by removal of thf *in vacuo* from their solvates **2b** and **3b** followed by recrystallisation from toluene. This was confirmed by the disappearance of peaks of coordinated thf in their ^1H NMR spectra. Using a more polar



Scheme 2 dme = 1,2-Dimethoxyethane

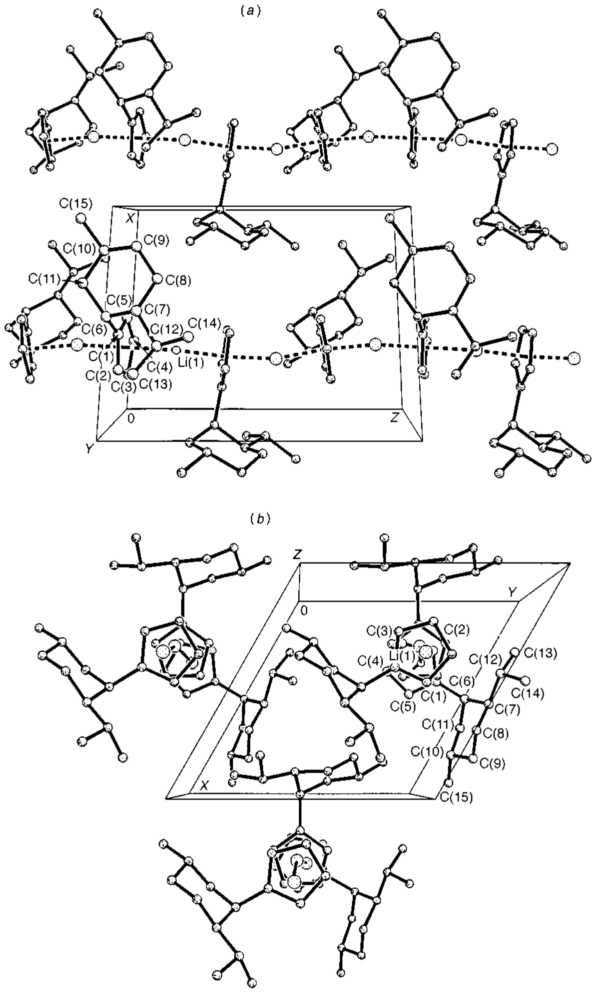


Fig. 1 Unit-cell contents of compound **1a** viewed along the *c* axis (*a*) and along the *b* axis (*b*)

solvent 1,2-dimethoxyethane (dme) for **3a**, better quality crystals of [K(η^5-C$_5$H$_4$R)(dme)]$_\infty$ **3c** have been obtained for X-ray analysis.

In contrast to the synthesis of compound **1a**, the metallation of (+)-neomenthylcyclopentadiene using LiBu^n in the presence of tmen afforded a hexane-soluble complex [Li(η^5-C$_5$H$_4$R)(tmen)] **1b** in high yield (91.4%) (Scheme 1). The use of a tertiary amine as a co-ordinating agent and to form more hydrocarbon-soluble monomeric lithium complexes is well documented. Single crystals of **1b** suitable for X-ray analysis were obtained by recrystallisation of the white solid from hexane.

The ^{1}H NMR spectra of the compounds prepared were consistent with pentahapto co-ordination of the cyclopentadienyl rings. The monosubstituted cyclopentadienyl protons exhibit two doublet signals in the region of δ 6.2 to 6.5 for compounds **1a**, **2a** and **2b** in C$_6$D$_6$–C$_5$D$_5$N (2:1). Owing to lower solubility in this solvent, the ^{1}H NMR spectra of **3a**–**3c** were recorded in (CD$_3$)$_2$SO which showed an upfield shift of the cyclopentadiene protons to δ 5.18 to 5.28.

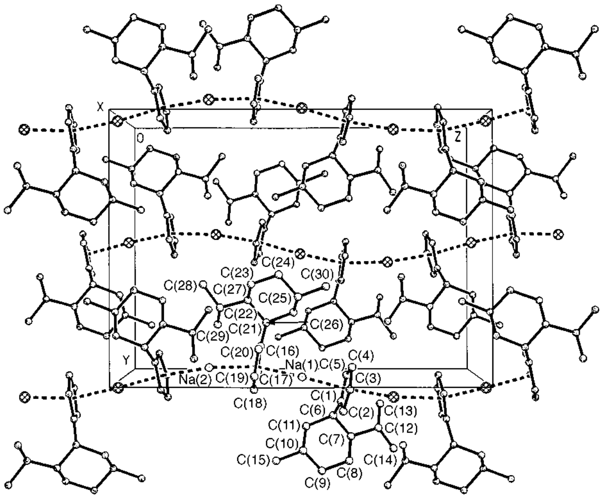


Fig. 2 Unit-cell contents of compound **2a** viewed along the *c* axis. Selected bond distances (Å) and angles (°): Na(1)–C(1) 2.761(3), Na(1)–C(2) 2.733(3), Na(1)–C(3) 2.634(3), Na(1)–C(4) 2.610(3), Na(1)–C(5) 2.668(3), Na(1)–C(16) 2.766(3), Na(1)–C(17) 2.673(3), Na(1)–C(18) 2.607(3), Na(1)–C(19) 2.645(3), Na(1)–C(20) 2.735(3), Na(2)–C(16) 2.931(3), Na(2)–C(17) 2.738(3), Na(2)–C(18) 2.575(3), Na(2)–C(19) 2.665(3) and Na(2)–C(20) 2.868(3); C(1)–Na(1)–C(2) 29.9(1), C(1)–Na(1)–C(3) 50.3(1), C(2)–Na(1)–C(3) 30.6(1), C(1)–Na(1)–C(4) 50.6(1), C(2)–Na(1)–C(4) 50.4(1), C(3)–Na(1)–C(4) 30.7(1), C(1)–Na(1)–C(5) 30.1(1), C(2)–Na(1)–C(5) 49.6(1), C(3)–Na(1)–C(5) 50.3(1) and C(4)–Na(1)–C(5) 30.9(1)

The structures of compounds **1a**, **2a**, **2b** and **3c** have been determined by X-ray analysis. They all comprise polymeric zig-zag chains of multi-decker metallocene complexes. The unit cells contain infinite chains parallel to the *c* (**1a** and **2a**) or *b* axis (**2b** and **3c**). Each polymeric chain contains repeated units of M(η^5-C$_5$H$_4$R) with adjacent cyclopentadienyl rings stacking at a dihedral angle θ. The neomenthyl groups (R*) and/or the solvent molecules are oriented along the chains at twist angles φ [defined as the torsion angle of C(1) (α)–C(1) (centroid)$\cdots$C(2) (centroid)–C(2) (α)] and ω [defined as the torsion angle of O(1) (solvent)–M(1)$\cdots$M(2)–O(2) (solvent)], respectively. For comparison, selected structural data of compounds from this work and the SiMe$_3$-substituted analogues [M(η^5-C$_5$H$_4$SiMe$_3$)]$_\infty$ [M = Li **4**[12] or K **5**[3]] are listed in Table 1. The separation between neighbouring strands of polymer chains among the compounds **1a**–**3c** is significantly larger than the similar distance in [K(η^5-C$_5$H$_4$SiMe$_3$)]$_n$,[3] thus ruling out the possibility of interaction between the polymer chains in these compounds.

The unit-cell contents of compound **1a** viewed in different axial directions are shown in Fig. 1(*a*) and 1(*b*). Within each chain, the Li–Cp^R (centroid) distances range from 2.038 to 1.981 Å which are comparatively longer than the range of 1.957 to 1.982 Å in the SiMe$_3$-substituted analogue [Li(η^5-C$_5$H$_4$SiMe$_3$)]$_\infty$ **4**. The Cp^R/Cp^R dihedral angle of 16.6° is significantly larger than the range of 5.1–8.1° in **4**. The Cp^R–Li–Cp^R and Li–Cp^R–Li angles in **1a** are 166.9 and 173.8°, respectively. They are smaller than the corresponding angles in **4** (see Table 1). The neomenthyl groups in the polymer of **1a** are oriented along the chain with a twist angle φ of 116.2°, which is different from the three torsion angles of 174.2, 90.7 and 95.0° found in **4**.[13]

The unit-cell contents showing the polymer chains of compound **2a** viewed along the *c* axis are shown in Fig. 2. The average Na–Cp (centroid) distance of 2.437 Å in **2a** is slightly longer than the corresponding distance of 2.40 Å in monomeric [Na(η^5-C$_5$Me$_5$)(py)$_3$][13] but significantly shorter than those bond distances in polymeric compounds [Na(η^5-C$_5$H$_5$)(tmen)]$_\infty$ (2.65 Å),[4] [Na(C$_5$H$_4$COMe)(thf)]$_\infty$ (2.53 Å)[14] and **2b** (2.503 Å). The Cp^R/Cp^R dihedral angles of 9.1° in **2a** is smaller than that of 16.6° in the lithium analogue **1a**.

Compound **2b** is a thf solvate of **2a**. The unit-cell contents of **2b** are shown in Fig. 3. Like **2a**, each structural repeat unit of **2b** is composed of a stacked sandwich metallocene unit. The steric effect caused by the co-ordination of a thf molecule is also

Table 1 Comparison of selected bond distances (Å), angles (°) and structural parameters of alkali-metal compounds

	1a	**2a**	**2b**	**3c**	**4**	**5**
M–C$_{C_5H_4}$ (average)	2.309	2.769	2.771	3.080	2.304	3.032
M–Cp$^{R}_{centroid}$ (average)	2.010	2.437	2.503	2.874	1.970	2.78
Cp^R–M–Cp^R (average)	166.9	170.2	135.1	135.5	174	—
M–Cp^R–M (average)	173.8	168.3	165.6	164.5	177.5	—
Cp^R/Cp^R dihedral angle θ	16.6	9.1	45.4	43.3	6.6	—
R*$_1$/R*$_2$ twist angle φ	116.2	91.1	179.9	165.8	174.2, 90.7, 95.0	—

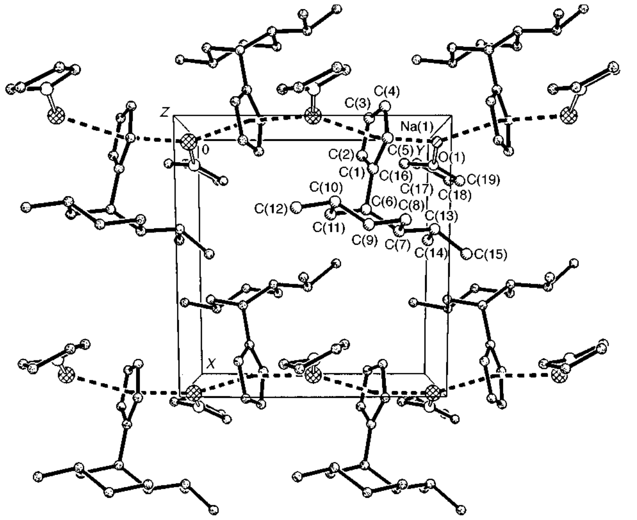


Fig. 3 Unit-cell contents of compound **2b** viewed along the *b* axis. Selected bond distances (Å) and angles (°): Na(1)–C(1) 2.918(1), Na(1)–C(2) 2.823(1), Na(1)–C(3) 2.657(1), Na(1)–C(4) 2.652(1), Na(1)–C(5) 2.803(1), Na(1)–O(1) 2.378(1), Na(1)–C(1a) 2.891(1), Na(1)–C(2a) 2.817(1), Na(1)–C(3a) 2.674(3), Na(1)–C(4a) 2.660(3), Na(1)–C(5a) 2.798(3), Na(1a)–C(1) 2.891(3), Na(1a)–C(2) 2.817(3), Na(1a)–C(3) 2.674(3), Na(1a)–C(4) 2.660(3) and Na(1a)–C(5) 2.798(3); C(1)–Na(1)–C(2) 28.2(1), C(1)–Na(1)–C(3) 47.7(1), C(2)–Na(1)–C(3) 29.4(1), C(1)–Na(1)–C(4) 47.9(1), C(2)–Na(1)–C(4) 48.8(1), C(3)–Na(1)–C(4) 30.6(1), C(1)–Na(1)–C(5) 28.2(1), C(2)–Na(1)–C(5) 47.3(1), C(3)–Na(1)–C(5) 48.8(1) and C(4)–Na(1)–C(5) 29.6(1)

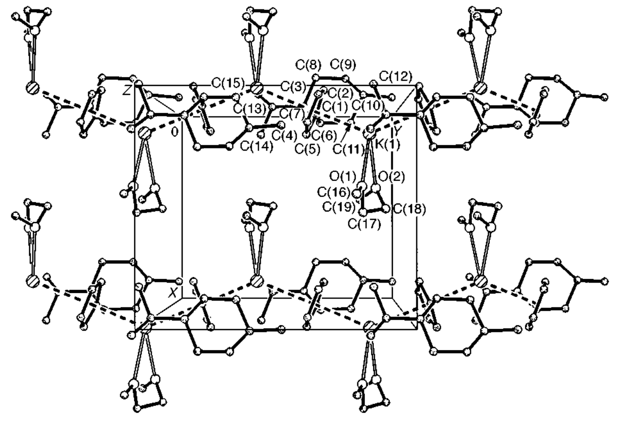


Fig. 4 Unit-cell contents of compound **3c** viewed along the *b* axis. Selected bond distances (Å) and angles (°): K(1)–C(1) 3.194(2), K(1)–C(2) 3.145(1), K(1)–C(3) 3.013(1), K(1)–C(4) 2.979(1), K(1)–C(5) 3.068(1), K(1)–O(1) 2.832(2), K(1)–O(2) 2.923(2), K(1)–C(1a) 3.343(2), K(1)–C(2a) 3.183(1), K(1)–C(3a) 2.980(1), K(1)–C(4a) 2.982(1) and K(1)–C(5a) 3.200(1); C(1)–K(1)–C(2) 25.7(1), C(1)–K(1)–C(3) 43.4(1), C(2)–K(1)–C(3) 26.4(1), C(1)–K(1)–C(4) 43.5(1), C(2)–K(1)–C(4) 43.1(1), C(3)–K(1)–C(4) 26.8(1), C(1)–K(1)–C(5) 25.9(1), C(2)–K(1)–C(5) 42.2(1), C(3)–K(1)–C(5) 43.3(1), C(4)–K(1)–C(5) 26.5(1) and O(1)–K(1)–O(2) 59.0(1)

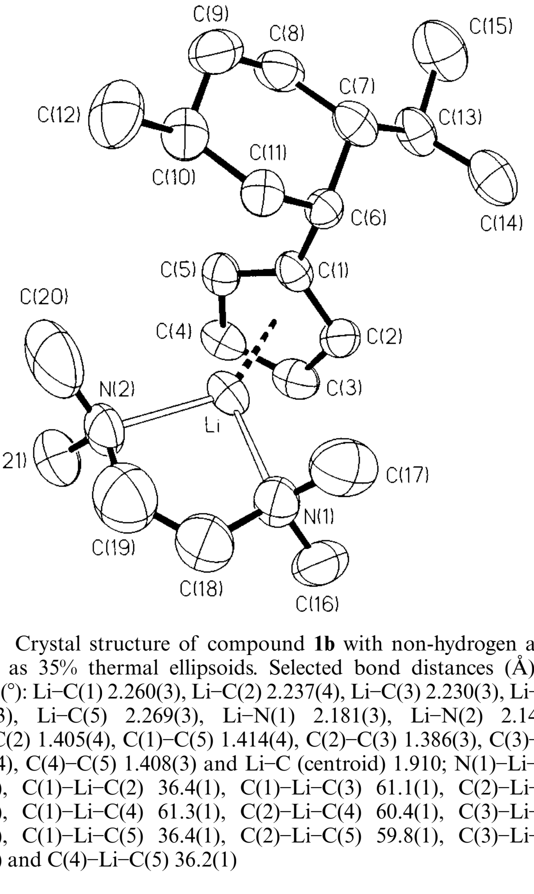


Fig. 5 Crystal structure of compound **1b** with non-hydrogen atoms shown as 35% thermal ellipsoids. Selected bond distances (Å) and angles (°): Li–C(1) 2.260(3), Li–C(2) 2.237(4), Li–C(3) 2.230(3), Li–C(4) 2.268(3), Li–C(5) 2.269(3), Li–N(1) 2.181(3), Li–N(2) 2.146(4), C(1)–C(2) 1.405(4), C(1)–C(5) 1.414(4), C(2)–C(3) 1.386(3), C(3)–C(4) 1.406(4), C(4)–C(5) 1.408(3) and Li–C (centroid) 1.910; N(1)–Li–N(2) 83.3(1), C(1)–Li–C(2) 36.4(1), C(1)–Li–C(3) 61.1(1), C(2)–Li–C(3) 36.2(1), C(1)–Li–C(4) 61.3(1), C(2)–Li–C(4) 60.4(1), C(3)–Li–C(4) 36.4(1), C(1)–Li–C(5) 36.4(1), C(2)–Li–C(5) 59.8(1), C(3)–Li–C(5) 60.2(1) and C(4)–Li–C(5) 36.2(1)

shown by the lengthening of the Na–Cp (centroid) distance of 2.506 Å (average) (*cf.* 2.437 Å in **2a**) and the smaller Cp^R–Na–Cp^R and Na–Cp^R–Na angles in **2b** (see Table 1). The dihedral angle of 45.4° for the cyclopentadienyl rings is surprisingly large when compared with **2a** and **3c**. The (+)-neomenthyl groups and the thf molecules are oriented alternatively and symmetrically along the polymeric chain of **2b** at approximate twist angles (φ and ω) of 179.9°.

The unit-cell contents of compound **3c** showing the polymer chains are shown in Fig. 4. The average K–Cp (centroid) distance of 2.874 Å in **3c** is significantly longer than that of 2.78 Å in the unsolvated compound [K(η^5-C$_5$H$_4$SiMe$_3$)]$_n$[3] and 2.79 Å in K[C$_5$(CH$_2$Ph)$_5$](thf)$_3$[15] although they have a more bulky SiMe$_3$ substituent and a very bulky pentabenzylcyclopentadienyl ligand. In **3c** co-ordination of the dme molecule to the metal contributes significantly to the increased K–Cp distance. Like **2b**, the (+)-neomenthyl group and dme in **3c** are oriented along the polymer chain with a twist angle close to 180°.

The structure analysis of compound **1b** is consistent with the formulation of Li(η^5-C$_5$H$_4$R)(tmen), in which the lithium atom in **1b** is bonded to the cyclopentadienyl ring in a pentahapto fashion forming a half-sandwich type lithanocene complex. The structure is comparable to that of the trimethylsilyl-substituted analogue Li(η^5-C$_5$H$_4$SiMe$_3$)(tmen).[7] The molecular structure of **1b** with the atom numbering scheme, selected bond distances and angles are shown in Fig. 5. The lithium–cyclopentadienyl (centroid) vector slightly deviates from being perpendicular to the cyclopentadienyl ring by 1.1°. The lithium to ring centroid distance is 1.910 Å which is slightly shorter than the corresponding distance of 1.928 Å in Li(η^5-C$_5$H$_4$SiMe$_3$)(tmen) and identical to that in Li(η^5-C$_5$H$_4$Me)(tmen).[6,7] The steric hindrance at the α-carbon of the neomenthyl group is presumably similar to that of a methyl group but smaller than that of the $SiMe_3$ group. The average C–C distance within the C_5H_4 ring is 1.404 Å which is very similar to that in Li(η^5-$C_5H_4SiMe_3$)(tmen). The N–Li–N angle of 83.3(1)° is very close to that of *ca.* 85° for (tmen)Li compounds.[16]

In conclusion, the M–Cp (centroid) distances of the alkali-metal compounds **1a**, **1b**, **2a**, **2b** and **3c** vary according to the size of the metal atoms. The distance of the solvated compound is comparatively longer due to the steric bulk of the ligand around the metal, for example in **2a** and **2b**. The Cp (centroid)–M–Cp (centroid), M–Cp (centroid)–M angles and the dihedral angle between the C_5H_4 rings are dependent on the occupancy and size of the ligand at the metal centre. It is obvious for steric reasons that co-ordination of the thf molecule enlarges the mutual tilt of the rings.

Experimental

All manipulations were carried out under an inert atmosphere of argon using standard Schlenk techniques or in a dinitrogen glove-box. Solvents were dried over and distilled from CaH_2 (hexane) and/or sodium–benzophenone (diethyl ether, thf, toluene) and degassed twice prior to use. Sodium hydride, KH and (+)-menthol were from Aldrich and used as received. (+)-Neomenthylcyclopentadiene was prepared according to literature methods.[12]

Proton NMR spectra were recorded at 250 MHz using a Brüker WM-250 spectrometer. Solvents used were C_6D_6–C_5D_5N (2 : 1) for compounds **1a**, **1b**, **2a** and **2b** and $(CD_3)_2SO$ for **3a**–**3c**, and the chemical shifts δ are relative internally to C_5D_5N and $(CD_3)_2SO$ respectively.

Preparations

(+)-Neomenthylcyclopentadienyllithium 1a. *n*-Butyllithium (0.11 mol, 68.8 cm^3, 1.6 M in hexane) was added slowly to a solution of (+)-neomenthylcyclopentadiene in hexane (50 cm^3) at 0 °C. After stirring the mixture at room temperature for 10 h, the solvent was removed *in vacuo* to afford a white solid. This was washed with cold hexane and yielded 15.0 g (92%) of the required compound, m.p. 253 °C. X-Ray quality crystals were obtained by recrystallising the compound from hexane–thf (10 : 1). ^{1}H NMR (C_6D_6–C_5D_5N, 250 MHz): δ 0.67–1.93 (menthyl), 3.51 (br s, 1 H), 6.22 (d, $^3J_{HH}$ = 5.2, 2 H) and 6.31 (d, $^3J_{HH}$ = 5.2 Hz, 2 H). ^{13}C NMR (C_6D_6–C_5D_5N, 125.75 MHz): δ 21.26, 22.34, 26.22, 27.55, 29.55, 30.55, 36.76, 39.17, 46.01, 49.81, 102.43, 106.36 and 122.56. α (589.3 nm, 25 °C, 0.05 M in thf) = 38.2°.

Neomenthylcyclopentadienyl(*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine)lithium 1b. To a solution of C_5H_5R (2.04 g, 0.01 mol) and tmen (1.5 cm^3) in hexane (30 cm^3) was slowly added $LiBu^n$ (6.3 cm^3, 1.6 M in hexane, 0.01 mol) at room temperature. The reaction mixture was stirred for 3 h and then concentrated to 10 cm^3, followed by cooling at −20 °C to afford a white crystalline solid. Recrystallisation from hexane yielded 2.98 g (91.4%) colourless crystals of the required compound, m.p. 85 °C. ^{1}H NMR (C_6D_6–C_5D_5N, 250 MHz): δ 0.78 (d, 6 H, *J* = 3.26), 1.02 (d, 3 H, *J* = 2.93), 0.78–2.20 (menthyl), 1.87 (s, 12 H), 1.89 (s, 4 H), 3.39 (s, 1 H), 6.05 (t, 2 H, *J* = 2.6) and 6.12 (t, 2 H, *J* = 2.5 Hz). ^{13}C NMR (C_6D_6–C_5D_5N, 125.75 MHz): δ 21.10, 22.49, 23.65, 25.83, 27.78, 30.41, 36.70, 39.06, 45.59, 49.85, 56.74, 102.11, 105.64 and 122.36.

(+)-Neomenthylcyclopentadienyl(tetrahydrofuran)sodium 2b. A solution of (+)-neomenthylcyclopentadiene in thf (30 cm^3) was added slowly to a stirring suspension of NaH (2.30 g, 0.10 mol) in thf (50 cm^3) at room temperature. After stirring at room temperature for 2 h the whole mixture was kept at 50 °C for 18 h. It was then cooled to room temperature and excess of NaH was filtered off. The solvent was removed from the filtrate under vacuum and the light brown solid residue was washed with hexane (2 × 20 cm^3) to afford 16.6 g (84%) of the required compound, m.p. 240 °C. ^{1}H NMR (C_6D_6–C_5D_5N, 250 MHz): δ 0.67–2.30 (menthyl), 3.55 (m, 4 H), 3.61 (br s, 1 H), 6.43 (d, $^3J_{HH}$ = 2.5, 2 H) and 6.48 (d, $^3J_{HH}$ = 2.5 Hz, 2 H). ^{13}C NMR (C_6D_6–C_5D_5N, 125.75 MHz): δ 21.28, 22.46, 23.59, 25.70, 26.13, 27.78, 30.56, 35.86, 36.95, 39.70, 46.00, 50.34, 67.73, 84.07, 102.19, 106.20 and 122.47. α (589.3 nm, 25 °C, 0.04 M in thf) = 34.76°.

(+)-Neomenthylcyclopentadienylsodium 2a. Compound **2a** was obtained by removal of thf from its solvate **2b** under vacuum. Good-quality crystals were obtained by recrystallisation from toluene, m.p. 287 °C. ^{1}H NMR (C_6D_6–C_5D_5N, 250 MHz): δ 0.71–2.21 (menthyl), 3.53 (br s, 1 H), 6.30 (d, $^3J_{HH}$ = 4.8, 2 H) and 6.33 (d, $^3J_{HH}$ = 4.8 Hz, 2 H). ^{13}C NMR (C_6D_6–C_5D_5N, 125.75 MHz): δ 21.64, 23.60, 26.19, 27.72, 30.56, 36.80, 39.45, 45.89, 50.29, 101.99, 106.23 and 122.76. α (589.3 nm, 25 °C) = 39.36 (0.05 M in thf), 79.01° (0.06 M in Me_2SO).

(+)-Neomenthylcyclopentadienyl(tetrahydrofuran)potassium 3b. The procedure was similar to that for compound **2b** except that KH was used, yielding 83% **3b**, m.p. 277 °C. ^{1}H NMR [$(CD_3)_2SO$, 250 MHz]: δ 0.70 − 1.98 (menthyl), 3.02 (br s, 1 H), 3.61 (m, 4 H), 5.19 (d, $^3J_{HH}$ = 2.4 Hz, 2 H) and 5.27 (br s, 2 H). ^{13}C NMR (C_6D_6–C_5D_5N, 125.75 MHz): δ 21.21, 21.92, 23.27, 25.11, 25.88, 26.38, 29.32, 39.00, 39.66, 40.00, 104.34 and 120.05. α (589.3 nm, 25 °C, 0.06 M in Me_2SO) = 59.64°.

(+)-Neomenthylcyclopentadienylpotassium 3a. Similar to **2a**, compound **3a** can be obtained by removal of co-ordinated thf under vacuum from **3b**, m.p. 277 °C. ^{1}H NMR [$(CD_3)_2SO$, 250 MHz]: δ 0.71–1.96 (menthyl), 3.03 (br s, 1 H), 5.21 (d, $^3J_{HH}$ = 2.2 Hz, 2 H) and 5.28 (br s, 2 H). Owing to the very low solubility of **3a**, the ^{13}C NMR spectrum has not been recorded. α (589.3 nm, 25 °C, 0.08 M in Me_2SO) = 61.88°.

(1,2-Dimethoxyethane)neomenthylcyclopentadienylpotassium 3c. A solution of (+)-neomenthylcyclopentadiene (2.00 g, 9.8 mmol) in thf (20 cm^3) was added slowly to a stirring suspension of KH (1.50 g, 37.5 mmol) in thf (30 cm^3) at room temperature. After the addition, the reaction mixture was stirred at ambient temperature for 10 h. The whole mixture was filtered, concentrated, and hexane (10 cm^3) was added to form a white precipitate. After recrystallisation from toluene, 2.98 g (91.6%) of colourless crystals of compound **3c** were obtained, m.p. 195 °C. ^{1}H NMR [$(CD_3)_2SO$]: δ 2.80 (t, 2 H, $^3J_{HH}$ = 2.5), 5.201 (t, 2 H, $^3J_{HH}$ = 2.5 Hz), 3.434 (s, 4 H), 3.244 (s, 6 H), 3.029 (s, 1 H) and 2.00–0.7 (18 H, neomenthyl). ^{13}C NMR [$(CD_3)_2SO$, 125.75 MHz]: δ 120.37, 104.79, 101.49, 71.04, 57.99, 49.44, 45.70, 36.11, 29.30, 26.39, 25.85, 23.21, 21.80 and 21.18.

X-Ray crystallography

Selected single crystals were sealed in Lindemann glass capillaries under dinitrogen. X-Ray intensities were measured at 294 K on an MSC/Rigaku AFC7R four-circle diffractometer for compounds **1a** and **1b**, on an MSC/Rigaku RAXIS IIc imaging-plate diffractometer for **2a**–**2c**, using Mo-Kα radiation (λ = 0.710 73 Å from a Rigaku RU-200 rotating-anode generator operating at 50 kV and 90 mA).[17–19] Empirical absorption corrections were applied by fitting a pseudo-ellipsoid to the ψ-scan data of selected strong reflections over a range of 2θ angles for **1a** and **1b**.[20] A self-consistent semiempirical absorption correction based on Fourier-coefficient fitting of symmetry-equivalent reflections was applied by using the ABSCOR program for **2a**, **2b** and **3c**.[21]

The crystal structures of compounds **1a**, **1b**, **2a**, **2b** and **3c** were determined by the direct method, which yielded the posi-

Table 2 Selected crystallographic and data collection parameters of compounds **1a**, **1b**, **2a**, **2b** and **3c**

	1a	**1b**	**2a**	**2b**	**3c**
Molecular formula	$C_{15}H_{23}Li$	$C_{21}H_{39}LiN_2$	$C_{30}H_{46}Na_2$	$C_{19}H_{31}NaO$	$C_{19}H_{33}KO_2$
M	210.3	326.5	452.6	298.4	332.6
Colour, habit	Yellow prism	Colourless plate	Colourless prism	Colourless needle	Colourless needle
Crystal size/mm	0.30 × 0.40 × 0.60	0.20 × 0.40 × 0.60	0.30 × 0.40 × 0.60	0.15 × 0.20 × 0.70	0.20 × 0.25 × 0.80
Crystal system	Trigonal	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P3_1$ (no. 144)	$P2_1$ (no. 4)	$P2_12_12_1$ (no. 19)	$P2_1$ (no. 19)	$P2_12_12_1$
a/Å	9.906(1)	8.477(2)	10.587(1)	9.650(1)	9.028(1)
b/Å	—	9.667(2)	13.737(1)	9.167(1)	10.526(1)
c/Å	11.925(1)	14.084(3)	19.086(1)	11.167(2)	22.201(1)
α/°	—	—	—	—	—
β/°	—	106.98(3)	—	103.79(1)	—
γ/°	—	—	—	—	—
U/Å^3	1013.4(5)	1103.8(6)	2776(1)	965.6(5)	2110(1)
Z	3	2	4	2	4
D_c/g cm^{-3}	1.034	0.982	1.083	1.026	1.047
μ/mm^{-1}	0.056	0.056	0.087	0.080	0.257
Scan type	ω	ω	Oscillation[a]	Oscillation[b]	Oscillation[c]
Scan rate/° min^{-1}	8.00–32.00	8.00–32.00	—	—	—
2θ Range/°	4–50	3–55	3–55	3–55	3–55
Unique data (R_{int})	1256 (0.0154)	2686 (0.0175)	5384 (0.0211)	3241 (0.0363)	3735 (0.0379)
Observed data, n	886 [$F > 10\sigma(F)$]	1109 [$F > 4\sigma(F)$]	4203 [$F > 6\sigma(F)$]	2295 [$F > 6\sigma(F)$]	2513 [$F > 6\sigma(F)$]
Transmission factors	0.969–1.000	0.967–1.000	0.856–1.000	0.758–1.000	0.852–1.000
No. variables, ρ	146	217	291	190	240
R_F[d]	0.1144	0.0746	0.0605	0.0722	0.0565
R'[e]	0.1593	0.0983	0.0531	0.0636	0.0586
Weighting scheme[f,g]	0.0003	0.0005	0.0000	0.0001	0.0000
S (goodness of fit)[g]	2.71	2.45	1.61	2.57	1.95
Large and mean Δ/σ	0.087, 0.015	0.064, 0.11	0.002, 0.000	0.021, 0.004	0.060, 0.009
$\Delta\rho_{max}$/e Å^{-3}	0.41, −0.45	0.39, −0.35	0.38, −0.34	0.41, −0.38	0.29, −0.32

[a] 36 Oscillation photos; φ = 0–180, $\Delta\varphi$ = 5°; 8 min per frame. [b] 24 Oscillation photos; φ = 0–180, $\Delta\varphi$ = 7.5°; 8 min per frame. [c] 36 Oscillation photos; φ = 0–180, $\Delta\varphi$ = 5°; 12 min per frame. [d] $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [e] $\Sigma w(F_o - F_c)/\Sigma w(F_o)$. [f] $w^{-1} = \sigma^2(F) + |g|F^2$. [g] $S = [\Sigma w(F_o - F_c)^2/(n - p)]^{\frac{1}{2}}$.

tions of all non-hydrogen atoms. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in the structure-factor calculation in the final stage of full-matrix least-squares refinement. All computations were performed on an IBM-compatible personal computer with the SHELXTL-PLUS program package.[22–24] Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[25] Crystallographic data collection and structure refinement of all compounds are summarised in Table 2.

CCDC reference number 186/718.

Acknowledgements

This research was supported by Hong Kong Research Grants Council Earmarked Grants CUHK 317/96P.

References

1 P. Jutzi, *J. Organomet. Chem.*, 1990, **400**, 1.
2 E. Weiss, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 1501.
3 P. Jutzi, W. Leffers, B. Hampel, S. Pohl and W. Saak, *Angew. Chem.*, *Int. Ed. Engl.*, 1987, **26**, 583.
4 T. Aoyagi, H. M. M. Shearer, K. Wade and G. Whitehead, *J. Organomet. Chem.*, 1979, **175**, 21.
5 D. Stalke, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 2168.
6 A. Hammel, W. Schwartz and J. Weidlein, *Acta Crystallogr.*, *Sect. C*, 1990, **46**, 2337.
7 M. F. Lappert, A. Singh, L. M. Engelhardt and A. H. White, *J. Organomet. Chem.*, 1979, **175**, 21.
8 H. Chen, P. Jutzi, W. Leffers, M. M. Olmstead and P. P. Power, *Organometallics*, 1991, **10**, 1282.
9 S. Harder and M. H. Prosenc, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 1744.
10 E. Cesarotti, H. B. Kagan, R. Goddard and C. Krüger, *J. Organomet. Chem.*, 1978, **162**, 297.
11 E. Cesarotti, R. Ugo and H. B. Kagan, *Angew. Chem.*, *Int. Ed. Engl.*, 1979, **18**, 779.
12 W. J. Evans, T. J. Boyle and J. W. Ziller, *Organometallics*, 1992, **11**, 3903.
13 G. Rabe, H. W. Roesky, D. Stalke, F. Pauer and G. M. Sheldrick, *J. Organomet. Chem.*, 1991, **403**, 11.
14 R. D. Rogers, J. L. Atwood, M. D. Rausch, D. W. Macomber and W. P. Hart, *J. Organomet. Chem.*, 1982, **238**, 79.
15 J. Lorberth, S.-H. Shin, S. Wocadlo, W. Massa, P. Jutzi, W. Leffers, B. Hampel, S. Pohl and W. Saak, *Angew. Chem.*, *Int. Ed. Engl.*, 1987, **28**, 735.
16 W. E. Rhine and G. Stucky, *J. Am. Chem. Soc.*, 1975, **97**, 737.
17 J. Tanner and K. Krause, *The Rigaku Journal*, 1994, **11**, 4; 1990, **7**, 28.
18 K. L. Krause and G. N. Phillips, jun., *J. Appl. Crystallogr.*, 1992, **25**, 146.
19 M. Sato, M. Yamamoto, K. Imada, Y. Katsube, N. Tanaka and T. Higashi, *J. Appl. Crystallogr.*, 1992, **25**, 348.
20 T. Higashi, ABSCOR, An Empirical Absorption Correction Based on Fourier Coefficient Fitting, Rigaku Corporation, Tokyo, 1995.
21 G. Kopfmann and R. Huber, *Acta Crystallogr.*, *Sect. A*, 1968, **24**, 348.
22 G. M. Sheldrick, *SHELXL PC Manual*, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.
23 G. M. Sheldrick, in *Computational Crystallography*, ed. D. Sayre, Oxford University Press, New York, 1982, p. 506.
24 G. M. Sheldrick, in *Crystallographic Computing 3*: *Data Collection*, *Structure Determination*, *Proteins*, *and Databases*, Oxford University Press, New York, 1985, p. 175.
25 J. A. Ibers and W. C. Hamilton, in *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 55, 99, 149; vol. 3, p. 278.

Received 18*th August* 1997; *Paper* 7/06073D