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Ether and crown ether adduct complexes of sodium and potassium cyclopentadienide and methylcyclopentadienide—molecular structures of $[Na(dme)Cp]_{\infty}$, $[K(dme)_{0.5}Cp]_{\infty}$, [Na(15-crown-5)Cp], $[Na(18\text{-crown-}6)Cp^{Me}]$ and the "naked Cp^-" complex $[K(15\text{-crown-}5)_2][Cp]$

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The molecular structure, spectroscopy and mass spectrometry of the following compounds are described: $[Na(dme)Cp]_{\infty}$ (polymeric zigzag chain), $[K(dme)_{0.5}Cp]_{\infty}$ (2-dimensional polymeric zigzag), [Na(15-crown-5)Cp] (monomeric), $[Na(18\text{-crown-}6)Cp^{Me}]$ (monomeric) and $[K(15\text{-crown-}5)_2][Cp]$ $\{K(15\text{-crown-}5)_2$ cation/naked cyclopentadienide anion$\}$. The syntheses of the related species $[Na(dme)Cp^{Me}]$, $[K(dme)_{0.5}Cp^{Me}]$, $[Na(15\text{-crown-}5)Cp^{Me}]$, [Na(18-crown-6)Cp] and $[K(15\text{-crown-}5)_2][Cp^{Me}]$ are reported. The choice of coordination modes displayed by those species structurally characterised is discussed, particularly in terms of steric and electrostatic considerations.

1 Introduction

From its birth in the 1950s, the exponential growth of bis(cyclopentadienyl) transition metal chemistry encouraged the preparation of a plethora of alkali metal cyclopentadienide (Cp) salts to assist in metallocene preparation.[1] The alkali metal Cp salt has since become an indispensable precursor for the organometallic chemist, in particular sodium cyclopentadienide.

In spite of the development and expansion of cyclopentadienyl chemistry beyond the remit of purely carbon-based Cp rings and simple alkyl functionalisation,[2] data pertaining to the structure of these seminal cyclopentadienide transfer reagents remains surprisingly scarce.[3] This has resulted from the perceived lesser novelty of these reagents, which were established prior to the mainstream use of crystallography as a form of unequivocal chemical identification.

Among those that evaded study, the 'base-free' alkali metal salts proved the most capricious to solid-state structure determination. The low solubility of group 1 metal cyclopentadienides in non-donating solvents, and hence the paucity of single crystalline samples, was the predominant cause of this. However, recently, the use of high-resolution synchrotron radiation powder diffraction methodologies has overcome such impediments, permitting the structural characterisation of Li-, Na- and KCp.[4]

A development in the use of these species, first presented by Smart *et al.* in 1977, was to use the 1,2-dimethoxyethane (dme) adduct of NaCp, [Na(dme)Cp], because of its greater solubility in non-donating solvents.[5] During use, the amorphous nature of NaCp in tandem with its inherent low tolerance to minutely aerobic conditions results in a lack of absolute stoichiometry. The advent of a crystalline derivative of NaCp, heralded by [Na(dme)Cp], with improved aerobic and thermal stability[5,6] (conceived without diminishing reactivity) was a noteworthy advance taken up by many organometallic chemists.[7] As with the alkali metal Cp transfer reagents before it,[3] the solid-state nature of [Na(dme)Cp] was never reported. Instead, the composition of [Na(dme)Cp] was evaluated by equivalent weight determination, ^1H NMR (d_8-thf) and elemental analyses.[5,6] Herein, we report the spectroscopy, spectrometry [FTIR, ^1H, ^{13}C NMR (C_6D_6) and APCI MS] and solid-state structure determinations of $[Na(\eta^2\text{-dme})(\mu{:}\eta^5\text{-}C_5H_5)]_{\infty}$, **1**, and its potassium congener $[K_4(\mu{:}\eta^2{:}\eta^1\text{-dme})_2(\mu^4{:}\eta^5{:}\eta^1{:}\eta^1\text{-}C_5H_5)(\mu{:}\eta^5\text{-}C_5H_5)_3]_{\infty}$, **2**. The use of **1** in the synthesis of the crown ether species $[Na(\eta^5\text{-15-crown-5})(\eta^5\text{-}C_5H_5)]$, **5**, is also discussed, as well as analogous syntheses using **2** and the methylcyclopentadienide (Cp^{Me}) reagents $[Na(dme)Cp^{Me}]$, **3**, and $[K(dme)_{0.5}Cp^{Me}]$, **4**, to form the crown ether species $[Na(15\text{-crown-}5)Cp^{Me}]$, **6**, [Na(18-crown-6)Cp], **7**, $[Na(\eta^5\text{-18-crown-6})(\eta^5\text{-}Cp^{Me})]$, **8**, and the naked cyclopentadienide species $[K(\eta^5\text{-15-crown-5})_2][Cp]$, **9** and $[K(15\text{-crown-}5)_2][Cp^{Me}]$, **10**. The structure determinations of species **5**, **8** and **9** are included. Structures **8** and **9** are discussed in the context of host–guest size-fit conventions.

2 Results and discussion

2.1 dme adducts

Crystals of $[Na(dme)(\mu{:}\eta^5\text{-}C_5H_5)]_{\infty}$, **1**, of suitable quality for structure determination were grown from saturated dme solutions diffused with hexane. The crystallographic asymmetric unit of **1** consists of $Na_2(dme)_2Cp_2$; selected bond lengths and angles of the complex are listed in Table 1. The basic structure motif (Fig. 1) consists of sodium coordinated to a Cp ring; this unit repeats with set ring orientations to form infinite zigzag polymeric chains. The angles $Cp_{centroid}$–Na1–$Cp'_{centroid}$ (Cp = C1–C5, Cp′ = C6–C10) and $Cp'_{centroid}$–Na2–$Cp_{centroid}$ are 133.7 and 134.5° (average = 134.1°), respectively, these combine with the mean Na–Cp–Na angle of 175.7° to

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Table 1 Selected bond lengths [Å] and angles [°] for [Na(dme)Cp] (**1**)

Na(1)–O(1)	2.447(7)	Na(1)–centroid(1)[a]	2.54(2)
Na(1)–O(2)	2.457(8)	Na(1)–centroid(2)[b b]	2.54(2)
Na(2)–O(3)	2.463(9)	Na(2)–centroid(1)[a]	2.56(2)
Na(2)–O(4)	2.438(8)	Na(2)–centroid(2)[b]	2.55(2)
Na(1)–centroid(1)[a]–Na(2)	175.6(3)	centroid(1)[a]–Na(1)–centroid(2)[b]	133.7(3)
Na(1)–centroid(2)[b]–Na(2)	175.7(3)	centroid(1)[a]–Na(2)–centroid(2)[b]	134.5(3)
O(1)–Na(1)–O(2)	68.1(3)	O(4)–Na(2)–O(3)	68.1(3)

[a] Centroid(1) defined as the centroid of the C(1) to C(5) ring. [b] Centroid(2) defined as the centroid of C(6) to C(10) ring.

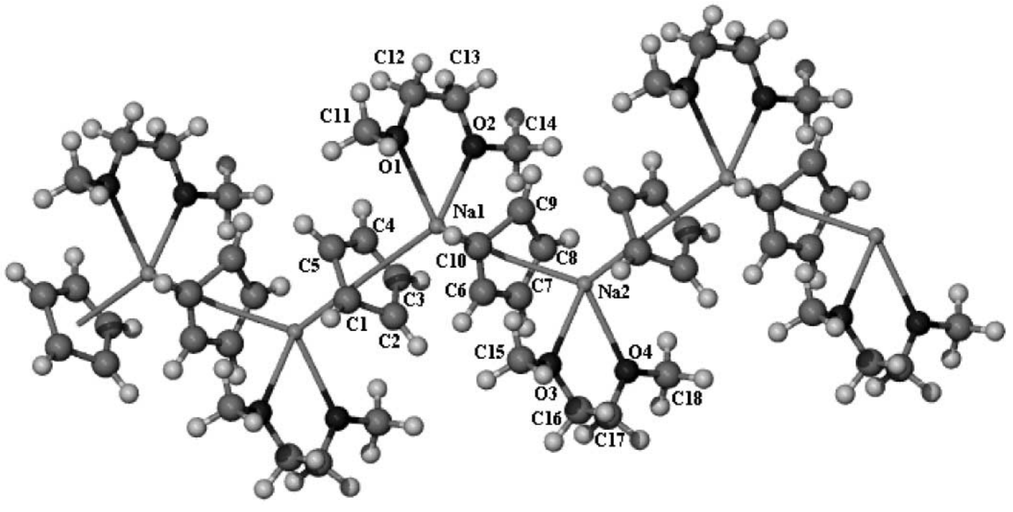

Fig. 1 Molecular structure of $[Na(\eta^2\text{-dme})(\mu\text{:}\eta^5\text{-}C_5H_5)]_\infty$ (**1**).

open the 'back' of the sodium cations to potential coordination; in this case, by a chelating 1,2-dimethoxyethane. Comparable examples of such coordination for other base-adducted unsubstituted sodium cyclopentadienides are limited to that of *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (tmeda) sodium cyclopentadienide,[6] which forms a comparable zigzag chain motif. The Cp chemistry of potassium displays numerous analogues where the Cp_2K sandwich subunit similarly allows supplementary donation *via* exposure of one side of the metal coordination sphere. Such examples include $[KCp]_\infty$,[4] $[K(Et_2O)Cp]_\infty$[8] and $[K(C_5H_4SiMe_3)]_\infty$,[9] where either an ethereal or interchain η^2-Cp donor augment the metal's two-fold bridging η^5-coordination.

The independent chains of **1** are packed without any neighbouring interactions as in $[Na(tmeda)Cp]_\infty$.[6] However, the observed Na–C bond lengths of 2.72–2.85 Å (mean average 2.76 Å), $Na\text{–}Cp_{centroid}$ bonds of 2.54–2.55 Å (mean average 2.55 Å) and the average cyclopentadienide C–C bond of 1.35 Å are considerably abated with respect to the analogous bonds of $[Na(tmeda)Cp]_\infty$ (Na–C average 2.924, $Na\text{–}Cp_{centroid}$ average 2.667, Cp C–C average 1.381 Å).[6] This can be rationalised by the steric strain imposed by tmeda over that of dme when coordinated, and the weaker donation of an O-donor to sodium with respect to amine donation. These influences manifest themselves in the form of greater sodium to η^5-Cp interactions, compounding the steric influence of the dme. This is indicated by the lesser centroid to sodium distance of **1** compared to $[Na(tmeda)Cp]_\infty$,[6] and the concomitantly shorter Cp C–C lengths mitigated by the constraints of the Cp geometry. Structural data based on solvate/base-free NaCp species, such as those for NaCp itself[4] and the sodocenes ($[Cp_2Na^-]$) from the groups of Mews and Harder[10] display Na–C distances in the ranges 2.631–2.671 and 2.584–2.670 Å, respectively. These values add credence to the rationale given above in that **1** represents an intermediary low in these competing influences, whereby the weaker donor nature of dme *versus* tmeda and greater Cp–Cp repulsion between adjacent rings ($Na\text{–}Cp_{centroid}$ distances) yields intermediate Na–C bonds for **1**, and correspondingly lower mean C–C Cp bond lengths. Finally, the C–C distances seen within the symmetrical Cp rings of the $[NaCp]_\infty$[4] and $[Cp_2Na^-]$[10] species are longer than those in **1** (1.381 and 1.423 Å, respectively), showing to a lesser extent that, as in $[Na(tmeda)Cp]_\infty$,[6] the strain of the ancillary ligands symptomatically constrict the Cp ring geometry with respect to base-free $[NaCp]_\infty$,[4] which can partake in greater sodium η^5-Cp overlap due to the absence of such ligands ($Na\text{–}Cp_{centroid}$ 2.357 Å).

Interestingly, the average Na–O bond length of 2.451 Å is almost exactly that of the mean average structurally characterised Na–O bond (2.450 Å),[11] whilst the d_6-benzene NMR spectra of **1** display ^1H resonances at δ 3.17, 3.30 and 6.07 (d_8-thf: δ 3.28, 3.42 and 5.60, respectively),[5] and ^{13}C resonances at δ 58.6, 71.8 and 103.4 (no reported d_8-thf spectrum).[12] Peaks in the APCI mass spectrum at *m*/*z* 113, 201 and 291 can be attributed to the $[Na(dme)]^+$ and $[Na_2(dme)_nCp]^+$ ($n = 1$ or 2) cationic subunits, indicating that **1** retains an oligomeric nature in solution. As an aside, the melting point of **1** was found to be 112 °C; this conflicts with the literature value of 92–95 °C reported by Aoyagi *et al.*;[6] decomposition was not observed below 180 °C in the solid state.

The potassium analogue of **1**, $[K(dme)_{0.5}Cp]_\infty$, **2** was prepared *via* the addition of cyclopentadiene monomer to a solution of potassium *tert*-butoxide in 1,2-dimethoxyethane. Crystals suitable for structure determination were grown from a concentrated dme solution of **2** at −30 °C, yielding large colourless extremely air-sensitive and solvent-dependent plates in high yield (87%). Compound **2** possesses good thermal stability, however, pronounced solvent loss at temperatures above 124 °C occurs to yield an amorphous powdered material that characterises as KCp (FTIR Nujol mull, elemental analysis).[4]

The structure of **2** represents only the third structurally characterised unsubstituted Cp potassium base adduct,[8,13] and is considerably different to that of the sodium homologue (Fig. 2). Akin to **1**, **2** forms a metal–η^5-bound Cp ring subunit that repeats with set ring orientations to form an infinite zigzag

Table 2 Selected bond lengths [Å] and angles [°] for $[K(dme)_{0.5}Cp]$ (**2**)

K(1)–O(1)	2.832(8)	K(1)–O(2)	2.932(9)
K(2)–O(3)	2.804(8)	K(3)–O(3)	2.897(9)
K(3)–O(4)	2.815(9)	K(4)–O(2)	2.824(9)
K(1)–centroid(1)[a]	2.98(2)	K(2)–centroid(3)[b]	2.779(18)
K(1)–centroid(2)[c]	2.84(2)	K(2)–centroid(4)[d]	2.80(4)
K(3)–centroid(1)[a]	2.86(3)	K(4)–centroid(2)[c]	2.779(18)
K(3)–centroid(2)[b]	2.850(18)	K(4)–centroid(2)[d]	2.80(3)
K(1)–centroid(1)[a]–K(3)	176.7(7)	K(2)–centroid(2)[b]–K(3)	174.8(7)
K(1)–centroid(1)[a]–K(4)	174.0(8)	K(2)–centroid(2)[d]–K(4)	176.7(7)
O(1)–K(1)–centroid(1)[a]	110.6(7)	O(3)–K(2)–centroid(2)[b]	139.4(8)
O(1)–K(1)–centroid(2)[c]	102.3(8)	O(3)–K(2)–centroid(2)[d]	106.8(8)
O(2)–K(1)–centroid(1)[a]	101.1(9)	centroid(2)[b]–K(2)–centroid(2)[d]	105.6(9)
O(2)–K(1)–centroid(2)[c]	131.3(7)	O(3)–K(3)–centroid(1)[a]	99.0(8)
centroid(1)[a]–K(1)–centroid(2)[c]	127.3(9)	O(3)–K(3)–centroid(3′)	132.2(8)
O(4)–K(3)–centroid(1)[a]	111.6(8)	O(2)–K(4)–centroid(2′)	106.3(8)
O(4)–K(3)–centroid(3′)	103.2(8)	O(2)–K(4)–centroid(4′)	103.8(8)
centroid(1)[a]–K(3)–centroid(3′)	128.2(9)	centroid(2′)–K(4)–centroid(4′)	142.6(9)

[a] Centroid(1) defined as the centroid of the C(1) to C(5) ring. [b] Centroid(3) defined as the centroid of the C(11) to C(15) ring. [c] Centroid(2) defined as the centroid of the C(6) to C(10) ring. [d] Centroid(4) defined as the centroid of the C(16) to C(20) ring.

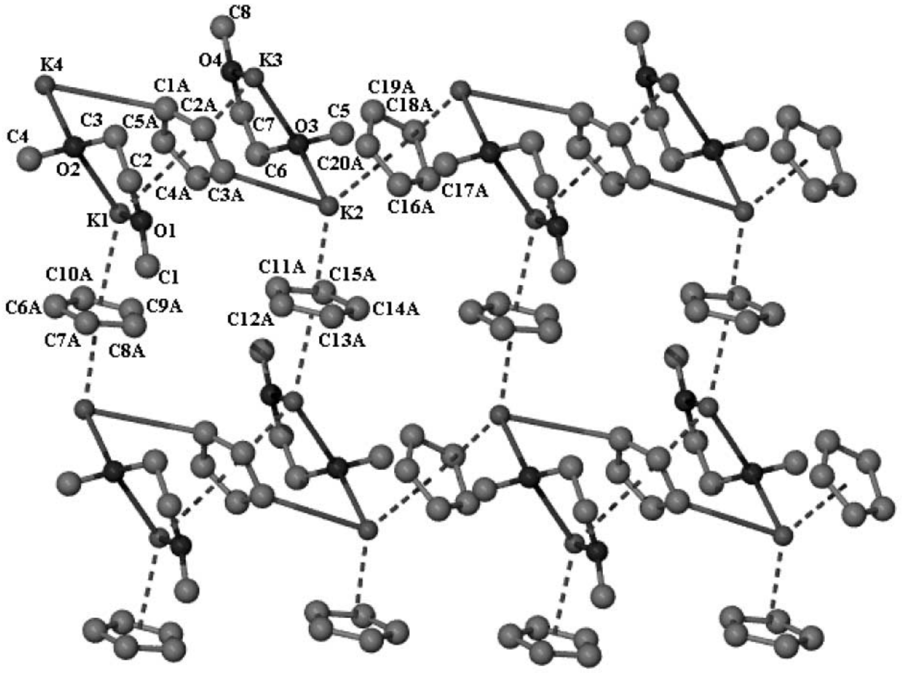

Fig. 2 Molecular structure of $[K_4(\mu{:}\eta^2{:}\eta^1\text{-dme})_2(\mu^4{:}\eta^5{:}\eta^1{:}\eta^1\text{-}C_5H_5)(\mu{:}\eta^5\text{-}C_5H_5)_3]_\infty$ (**2**). Hydrogen atoms have been omitted for clarity.

chain. The greater radius of K^+ ions (1.38 Å, Na^+ 0.99 Å)[14] induces a larger void between the two Cp rings (average $K\text{–}Cp_{centroid}$ 2.84 Å, **1** 2.55 Å) compared with **1**, which, as with other polymeric potassium Cp motifs,[4,9] allows interchain interactions to contribute to the potassium coordination sphere. Selected bond lengths and angles for complex **2** are listed in Table 2.

The crystallographic asymmetric unit of **2** is an extended $K_4(dme)_2Cp_4$ unit that presents both η^1-Cp and bridging methoxy interactions between adjacent chains in a single dimension roughly perpendicular to the direction of chain propagation. Species like $[KCp]_\infty$[4] and $[K(Et_2O)Cp]_\infty$[8] display similar interactions, *i.e.* η^2-Cp interchain bonding ($[KCp]_\infty$) and ethereal base donation to the exposed 'back-side' of the potassium coordination sphere ($[K(Et_2O)Cp]_\infty$). The average Cp–K–Cp′ angle in **2** is 134.3° (average K–Cp–K′ 175.6°) which is considerably smaller than that of either $[KCp]_\infty$[4] or $[K(Et_2O)Cp]_\infty$[8] (K–Cp–K′ 174.6, K–K′–K″ 138.0[4] and K–K′–K″ 145.3,[8] respectively) and is dwarfed by that of $[K(C_5H_4\text{-}SiMe_3)]_\infty$,[9] which possesses the greatest $Cp^x\text{–}K\text{–}Cp^x$ angle for a monosubstituted Cp–potassium zigzag chain motif (150.7°). It is therefore unsurprising that **2** presents several differing Cp and K environments. Of the four crystallographically different potassium centres, two exist between bridging η^5-Cps, with a chelating 1,2-dimethoxyethane completing a distorted tetrahedral geometry (K1 and K3), whilst the remaining pair (K2 and K4) sit between bridging η^5-Cps, with a single η^1-Cp and a bridging methoxy interaction (from a dme chelated to K3 or K1, respectively) yielding a similarly distended tetrahedral metal geometry. Consequently, there are four types of cyclopentadienide ring, of which just one participates in $\mu^4{:}\eta^1{:}\eta^1{:}\eta^5{:}\eta^5$-Cp coordination (C1–C5), the remaining three exist as simple $\mu{:}\eta^5{:}\eta^5$-bound moieties. Surprisingly, the geometry of Cp C1–C5 describes almost D_{5d} symmetry about the pentacarbon ring, bond lengths varying in the range 1.345–1.357 Å (mean 1.353 Å). Also, unlike the minute shortening of the K–C bonds of $[KCp]_\infty$, caused by $\eta^5{:}\eta^5{:}\eta^2{:}\eta^2$-Cp coordination (3.056 Å),[4] over those in [K(18-crown-6)Cp] (3.059 Å),[13] the average K–C bond length for the three solely η^5-bound Cps is 3.064 Å, almost 0.04 Å greater than for the C1–C5 ring; mean 3.026 Å. This finding is counter-intuitive, furthermore, the remaining three cyclopentadienides present more disparate C–C bond lengths in the range 1.31–1.47 Å (mean 1.415 Å), C16–C20 displaying by far the greatest ring deviation. This can be rationalised by consideration of the four Cp cavities within the two-dimensional polymer: Cp C16–C20 is compressed with respect to the two comparably free cyclopentadienides (C6–C10, C11–C15). Similarly, Cp C1–C5 exists in an analogous cavity to C16–C20 that is sterically favoured by the provision of η^1-Cp interactions.

Interestingly, the structure of the (+)-neomenthylcyclopentadienide (Cp^{neo}) complex $[K(dme)Cp^{neo}]_\infty$ exists with a stoichiometry of one dme to one KCp^{neo}.[15] The bulky neomenthyl substituent disrupts interactions between the zigzag polymer strands which otherwise permeate the structure, as in **2**. In doing this, interpolymer η^1/η^2-Cp–K contacts are frustrated and cannot saturate the metal coordination sphere. Thus, as in complex **1** and $[K(Et_2O)Cp]_\infty$[8] the coordination sphere of $[KCp^{neo}]_\infty$ is satisfied by Lewis base solvent-adduct formation, which demands a greater donor–acceptor stoichiometry than that of **2**.[15] The mean K–O bond distances displayed by **2** and $[K(dme)Cp^{neo}]_\infty$ (2.851 and 2.878 Å)[15] compare favourably to that of the mean structurally characterised K–O bond (2.819 Å),[11] whilst the K–$Cp_{centroid}$ distances are also remarkably similar (2.841 and 2.874 Å),[15] corroborating the supposition that the different solid-state motifs result solely from the inclusion of a neomenthyl substituent.

In solution, compound **2** displays just three proton NMR signals (*δ* 3.08, 3.21 and 5.78), as does **1**, and, similarly, three carbon resonances (*δ* 59.3, 70.4 and 104.0) that almost exactly coincide with those of **1**. Nothing tangible could be identified in the APCI mass spectrum, except two single peaks at *m*/*z* 39 (K^+) and 67 ($C_5H_7^+$).

In an effort to expand upon the methylcyclopentadienide structural archive of the group 1 elements, Cp^{Me} (C_5H_4Me) species analogous to **1** and **2** were prepared in high yield (94 and 83%, respectively) by addition of methylcyclopentadiene monomer to the appropriate metal *tert*-butoxide in dme. By ^1H NMR (C_6D_6), species **3** and **4**, $[Na(dme)Cp^{Me}]$ and $[K(dme)_{0.5}Cp^{Me}]$, respectively, possess identical adduct stoichiometries to their cyclopentadienide cousins. Unfortunately, the absolute architecture of their structures could not be compared due to unforeseen difficulties in crystallisation. The solvent dependency seen for compound **2** at elevated temperatures was heavily accentuated for both species. Successful crystallisation from dme yielded the products as exceptionally large colourless prisms that, as expected, melt at considerably lower temperatures than **1** or **2** [**3** 66 °C, **4** 85 °C (decomposition)]. Difficulties in the handling of both compounds were exacerbated relative to **1** and **2**, hence their proposed structural similarity to the non-substituted species could not be unequivocally defined. ^1H and ^{13}C NMR of compounds **1**–**4** (C_6D_6) are compiled in Table 3. Peaks in the APCI MS of species **3** and **4** are listed in the Experimental section. These have been tentatively assigned as the subunits $[M]^+$, $[M(dme)]^+$ and $[M_n(dme)_{n-1}Cp^{Me}_{n-1}]^+$ where $n = 2, 3$ (larger cations only seen for **3**).

Table 3 ^1H (300 MHz) and ^{13}C (75.5 MHz) C_6D_6 NMR data for compounds **1**–**4** (*δ* values in ppm)

	1	2	3	4
^1H NMR				
Cp-H (I)	6.07 (s)	5.78 (s)	5.72 (br s)	5.61 (br s)
Cp-H (II)	—	—	5.74 (br s)	5.66 (br s)
Cp–CH_3	—	—	2.42 (s)	2.41 (s)
OCH_3	3.17 (s)	3.08 (s)	2.99 (s)	3.07 (s)
OCH_2	3.30 (s)	3.21 (s)	3.04 (s)	3.24 (s)
^{13}C NMR				
Cp-C (I)	103.4	104.0	101.9	104.5
Cp-C (II)	—	—	103.6	105.5
Cp-C–CH_3	—	—	114.2	105.4
Cp–CH_3	—	—	15.3	15.6
OCH_3	58.6	59.3	58.7	58.8
OCH_2	71.8	70.4	71.4	72.1

2.2 Crown ether adducts

The structures reported for group 1 cyclopentadienides display an alarming lack of both Cp and Cp^{Me} contributions,[3] presumably as these have been superseded by the more novel catalogue of trimethylsilyl-substituted and other functionalised Cp ligands that are ubiquitous amongst the organometallic chemistry of the p-, d- and f-block elements.[2,16] In contrast to this, some crown ether adducts of alkali metal Cp complexes have been characterised by X-ray structure determination. These include the compounds [Li(12-crown-4)Cp],[17] [K(18-crown-6)Cp],[13] $[K(18\text{-crown-}6)_2(\text{indacene})]$[18] and [K(18-crown-6)(fluorenide)].[13] However, the complex [Na(15-crown-5)Cp], **5** the sodium size-fit analogue of the first two examples above has not been reported, nor have the questions posed by utilising non-complementary crowns been investigated. For archival value, **5** and the species $[Na(15\text{-crown-}5)Cp^{Me}]$, **6**, [Na(18-crown-6)Cp], **7**, $[Na(\eta^5\text{-}18\text{-crown-}6)(\eta^5\text{-}Cp^{Me})]$, **8**, and the naked Cp^- species $[K(\eta^5\text{-}15\text{-crown-}5)_2][Cp]$, **9**, and $[K(15\text{-crown-}5)_2][Cp^{Me}]$, **10**, were prepared employing species **1**–**4** as precursors.

Compound **5** was prepared *via* the addition of one equivalent of 15-crown-5 to a stirred solution of **1** in thf. Concentration of the sample and storage at 0 °C yielded large deep-red prismatic shards. The structure of **5** can be seen in Fig. 3. Further crops of crystalline **5** were obtained from the remaining mother liquor as colourless prisms. The cell parameters obtained for these subsequent crops matched those of **5**. We can only surmise that the presence of an unusually large quantity of intensely coloured aerobically-induced radical species caused the initial crop's observed colouration. Unfortunately, all efforts to identify and characterise this species, including EPR studies, proved fruitless.

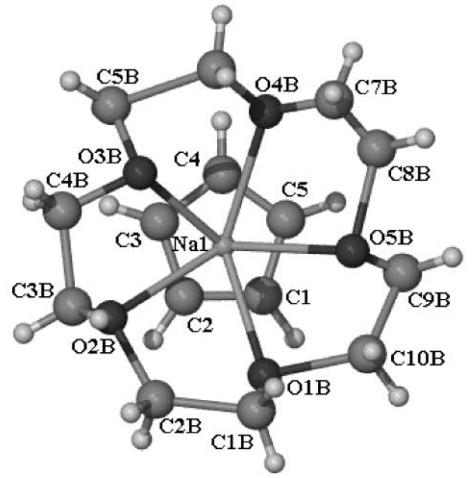

Fig. 3 Molecular structure of $[Na(\eta^5\text{-}15\text{-crown-}5)(\eta^5\text{-}C_5H_5)]$ (**5**), projected down the $\text{crown}_{(\text{centroid})}$–Na–$Cp_{(\text{centroid})}$ vector.

Complex **5** crystallises as discrete molecular units of sodium(15-crown-5) cyclopentadienide that are heavily disordered about the crown moiety to give two crown coordination motifs. The disorder of these was successfully modelled. The occupancy illustrated by Fig. 3 is that which has been listed as selected bond lengths and angles in Table 4, although both modelled occupancies are in essence structurally identical. The monomer describes a $Cp_{centroid}$–Na–$crown_{centroid}$ angle of 176.9°, the mean $Cp_{centroid}$–Na–O angle being 115.3°. Accordingly, the need or opportunity for supplementary coordination donors is successfully frustrated. This is as for the lithium[17] and potassium[13] crown species [Li(12-crown-4)Cp] and [K(18-crown-6)Cp]. The distance from the Na cation to the cyclopentadienide centroid is 2.563 Å, this compares well to the mean of **1** (2.55 Å) and that of Na(15-crown-5) isocyclopentadienide (2.519 Å).[19] However, although the crown species

Table 4 Selected bond lengths [Å] and angles [°] for [Na(15-crown-5)Cp] (**5**)

Na(1)–C(1)	2.865(4)	Na(1)–O(1A)	2.515(12)
Na(1)–C(2)	2.717(4)	Na(1)–O(2A)	2.471(8)
Na(1)–C(3)	2.703(5)	Na(1)–O(3A)	2.541(11)
Na(1)–C(4)	2.850(5)	Na(1)–O(4A)	2.447(13)
Na(1)–C(5)	2.948(4)	Na(1)–O(5A)	2.472(12)
Na(1)–centroid[a]	2.563(5)		
O(1A)–Na(1)–centroid[a]	109.6(5)	O(2A)–Na(1)–centroid[a]	133.1(5)
O(3A)–Na(1)–centroid[a]	106.2(4)	O(4A)–Na(1)–centroid[a]	111.4(7)
O(5A)–Na(1)–centroid[a]	117.5(5)		

[a] Centroid of the cyclopentadienyl ring.

listed do not ally the argument that the Na–$Cp_{centroid}$ distances of **1** are partly caused by steric strain, as in $[Na(tmeda)Cp]_\infty$[6] relative to **1**, they do promote the rationale that the smaller Na–C_{Cp} distances seen in **1** and **5** are caused by the relative donor qualities of the bis(amine) donor; *i.e.* that the contraction results from the weaker Na–O interactions of poly-O Lewis bases relative to N-donors. Similarly, this is observed for the K–O bond lengths of indenide potassium species adducted to *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (pmdeta) and 18-crown-6.[8,13] The average Na–O for **5**, at 2.488 Å, closely relates to that seen for **1** (**1** 2.451 Å), and is therefore extremely similar to the mean structurally reported Na–O bond (2.450 Å).[11]

Signals at *m*/*z* 23 and 243 were seen in the APCI mass spectrum of **5**. These were assigned as Na^+ and $[Na(15\text{-crown-}5)]^+$, respectively. The melting point of **5** bares close similarity to that of the reported benzo-15-crown-5 adduct of NaCp[6] (182 °C (**5**), compared to 175–176 °C).

The compound [Na(15-crown-5) methylcyclopentadienide], **6**, was made in a congruent manner to **5** employing **3** as a precursor. Samples of **6** suitable for X-ray structure determination could not be grown and, hence, its absolute solid-state nature can only be suggested to be akin to that of **5** due a slightly suppressed melting point, relative to **5**, of 165 °C and the presence of a signals no greater than *m*/*z* 243 ($[Na(15\text{-crown-}5)]^+$) in the APCI mass spectrum of **6**.

The use of 'non-complementary' crowns (*i.e.* crowns with an unsuitable size-fit metal receptor cavity) in the preparation of alkali metal Cp species asks questions of the metal in terms of preferred coordination motifs. For instance, would a larger crown be conformationally modified to allow a lower number of interactions to a smaller metal centre, or would a smaller crown be insufficient to satisfy the coordination sphere of a larger metal, and therefore perhaps allow the formation of bis(crown) metal Cp adducts (given excess crown)? In turn, would this increase the likelihood of 'naked' Cp species as in $[Li(12\text{-crown-}4)_2][1,2,4\text{-}(SiMe_3)_3C_5H_2]$?[17] What effect would a methyl substituent introduced by Cp^{Me} have on these findings? To answer these questions, compounds **1**–**4** were reacted with the crowns 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5 plus **2** and **4**) and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6 plus **1** and **3**) in tetrahydrofuran. The subsequent species, **7**–**10**, are all colourless solids that are highly sensitive to air and moisture, and decompose rapidly when removed from an inert atmosphere. They do not, however, appear to be solvent dependent, unlike the fluorenide potassium 18-crown-6 species recently reported by Olbrich *et al.*,[13] and species **3** and **4**.

2.3 [Na(18-crown-6)Cp] (7) and [Na(18-crown-6)Cp^{Me}] (8)

Reaction of **1** and **3** with 18-crown-6 in thf yields clear deep-brown solutions of **7** and **8** that can be crystallised to yield the products as large thick yellow/colourless plates that possess moderate melting points (123 and 108 °C, respectively) The quality of samples from **8** allowed a successful structure determination of [Na(18-crown-6)Cp^{Me}], which is illustrated in Fig. 4.

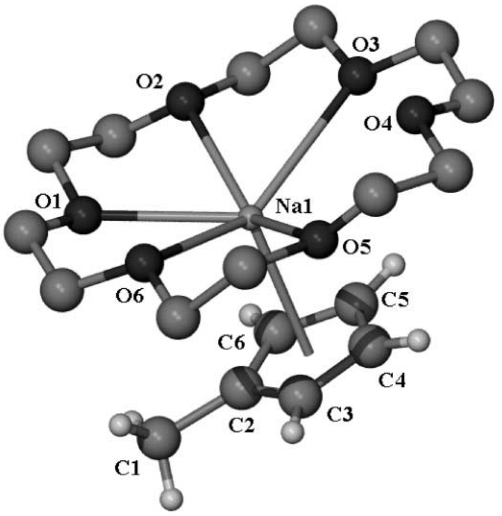

Fig. 4 Molecular structure of [Na(η^5-18-crown-6)(η^5-C_5H_4Me) (**8**). Hydrogen atoms on the crown ether have been omitted for clarity.

Adduct **8** crystallises as discrete monomeric units akin to the structure of **5** and is the second alkali metal Cp^{Me} complex characterised by XRD,[20] the first of sodium. Unlike **5** there is no disorder about the crown, this being a common feature of 18-crown-6 chemistry. Selected bond lengths and angles are listed in Table 5. Most interestingly, **8** displays two of the features that were proposed for a crown of greater size-fit cavity than the coordinated metal:

Firstly, the crown has been manipulated such that it assumes a *pseudo* 15-crown-5 pentaoxa- geometry. This can be seen in the disparity of Na–O distances and $Cp^{Me}{}_{centroid}$–Na–O angles within the crown, whereby five O-moieties display Na–O bond lengths in the range 2.602–3.038 Å (mean 2.806 Å), whilst a sixth assumes a position 3.316 Å from the central cation at an angle of 108.9° to the sodium–$Cp^{Me}{}_{centroid}$ bond. Meanwhile, the mean $Cp^{Me}{}_{centroid}$–Na–O angles of 107.0 and 115.3° (latter **5**) bare a great likeness. Compound **5** has an average Na–O length of 2.488 Å, far lower than that of **8**. This can be attributed to the large conformational strain involved in distorting the crown geometry.

Secondly, the 'ostracised' oxygen donor conveniently provides a cavity that the Cp ring can utilise to minimise steric strain between the crown and the C4 and C5 carbons. The cavity presented effects a virtual 'slip' of the crown and Cp^{Me} planes away from one another such that the Me group can nestle beneath C18 and C17 due to tilting of the Cp to minimise Me interactions (tilt permitted due to cavity). Compound **8** demonstrates the impact of non-complementary crowns upon a metal centre. The 'goodness-of-fit' of the Cp-methyl niche is exemplified by the minimal opening of the $Cp^{Me}{}_{centroid}$–Na–$crown_{centroid}$ angle. In the absence of such a 'cavity', this angle would intuitively be opened, *i.e.* a Cp-methyl substituent superimposed onto **5**, as in **6**. For **8**, the angle increases by 13.1° over that of **5** to 196.2° (**5** 183.1°). Finally, an interesting aspect of **8** is the average inter-Cp ring C–C distance (1.374 Å), which

Table 5 Selected bond lengths [Å] and angles [°] for [Na(18-crown-6)Cp^{Me}] (**8**)

Na(1)–C(2)	2.933(8)	Na(1)–O(1)	2.602(6)
Na(1)–C(3)	2.870(8)	Na(1)–O(2)	2.705(6)
Na(1)–C(4)	2.746(7)	Na(1)–O(3)	2.965(7)
Na(1)–C(5)	2.712(7)	Na(1)–O(4)	3.316(7)
Na(1)–C(6)	2.855(8)	Na(1)–O(5)	3.038(7)
Na(1)–centroid[a]	2.571(8)	Na(1)–O(6)	2.721(8)
O(1)–Na(1)–centroid[a]	106.8(5)	O(2)–Na(1)–centroid[a]	111.4(8)
O(3)–Na(1)–centroid[a]	103.1(5)	O(4)–Na(1)–centroid[a]	108.9(7)
O(5)–Na(1)–centroid[a]	102.9(5)	O(6)–Na(1)–centroid[a]	110.8(5)

[a] Centroid of the cyclopentadienyl ring.

is close to that of **5** (1.378 Å). Likewise, the Cp$_{centroid}$–Na distance of 2.571 Å mimics that of **5** (2.563 Å).

The solid-state nature of **7** could not be evaluated as suitable crystals for diffraction were not forthcoming from the thf mother liquor. However, the similarity of the melting points (**7** 123 °C, **8** 108 °C) and the common APCI MS signal of *m*/*z* 287 ([Na(18-crown-6)])$^+$ infer a likely solid-state motif which approximates that displayed by **8**.

2.4 [K(15-crown-5)$_2$][Cp] (9) and [K(15-crown-5)$_2$][Cp^{Me}] (10)

Reaction of **2** and **4** with a two-fold excess of 15-crown-5 (2.0 equivalents) in thf yielded clear light-brown solutions of compounds **9** and **10**, respectively. Both compounds could be recrystallised from the reaction mother liquor by concentration and storage at −30 °C overnight. This gave the two compounds as small colourless cubic prisms, of which **9** was suitable for structure determination studies. Both compounds display melting points that approach that of the conventional 18-crown-6 potassium cyclopentadienide species recently presented by Olbrich *et al.*; [K(18-crown-6)Cp][13] (m.p. 214 °C, **9** 187 °C, **10** 174 °C). The stoichiometry of species **9** and **10** was ascertained by ^{1}H NMR (C_6D_6), which indicated a ratio of two crowns to one Cp^x moiety, as well as the absence of coordinated thf.

The proposed effect of placing a larger cation into an unconventionally small crown cavity was to increase the possibility of additive donor interactions to an otherwise unsaturated metal centre. The stoichiometry of species **9** and **10** suggests that this vacancy could be satisfied by augmentative crown interactions and lower hapticity Cp interactions, as seen in many other KCp^x structural motifs.[8,13,15] The exact nature of these could not be evaluated without structure determination. To this end, the molecular structure of complex **9** was determined and is illustrated in Fig. 5, relevant bond lengths and angles are given in Table 6. The equivalency of the crown resonances in the ^{1}H NMR spectra of both **9** and **10** could result from either purely symmetrical K(15-crown-5)$_2$ cations or rapid exchange of inequivalent crowns in solution (both views are supported by the presence of a signal at *m*/*z* 479 in the APCI mass spectra).

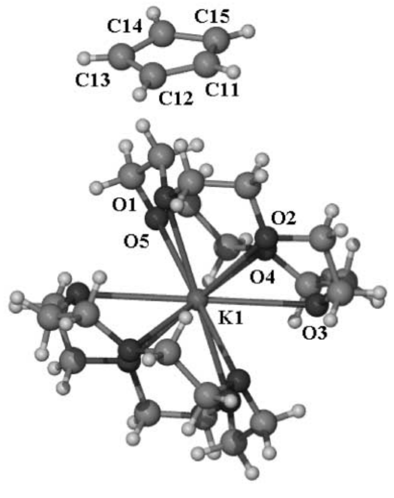

Fig. 5 Molecular structure of [K(η^5-15-crown-5)$_2$][C_5H_5] (**9**), showing the sandwiched potassium ion and the "naked" cyclopentadienide anion.

Table 6 Selected bond lengths [Å] and angles [°] for [K(15-crown-5)$_2$]-[Cp], (**9**)[a]

K(1)–O(1)	2.869(4)	K(1)–O(1)#1	2.869(4)
K(1)–O(2)	3.037(4)	K(1)–O(2)#1	3.037(4)
K(1)–O(3)	2.964(4)	K(1)–O(3)#1	2.964(4)
K(1)–O(4)	2.960(4)	K(1)–O(4)#1	2.960(4)
K(1)–O(5)	2.854(4)	K(1)–O(5)#1	2.854(4)
O(1)–K(1)–O(2)	57.19(11)	O(1)–K(1)–O(2)#1	122.81(11)
O(1)–K(1)–O(3)	108.32(11)	O(1)–K(1)–O(3)#1	71.68(11)
O(1)–K(1)–O(4)	92.74(12)	O(1)–K(1)–O(4)#1	87.26(12)
O(1)–K(1)–O(5)	60.69(12)	O(1)–K(1)–O(5)#1	119.31(12)
O(2)–K(1)–O(3)	57.46(11)	O(2)–K(1)–O(3)#1	122.54(11)
O(2)–K(1)–O(4)	85.95(12)	O(2)–K(1)–O(4)#1	94.05(12)
O(2)–K(1)–O(5)	104.03(12)	O(2)–K(1)–O(5)#1	75.97(12)
O(3)–K(1)–O(4)	56.93(10)	O(3)–K(1)–O(4)#1	123.07(10)
O(3)–K(1)–O(5)	112.83(12)	O(3)–K(1)–O(5)#1	67.17(11)
O(4)–K(1)–O(5)	57.92(11)	O(4)–K(1)–O(5)#1	122.08(11)
O(1)–K(1)–O(1)#1	180.0	O(2)–K(1)–O(2)#1	180.0
O(3)–K(1)–O(3)#1	180.0	O(4)–K(1)–O(4)#1	180.0
O(5)–K(1)–O(5)#1	180.0		

[a] Symmetry transformation used to generate equivalent atoms: #1 $-x + 2, -y, -z + 1$.

Complex **9** crystallises in the space group $P\bar{1}$, with the potassium atom and a 'naked' cyclopentadienide ion residing on an inversion centre. This necessitates disorder about the Cp anion that was successfully modelled and refined with 50% occupancies and idealised geometries. The [K(15-crown-5)$_2$]$^+$ unit is staggered crown to crown akin to the precedent for this type of cation.[21] The mean K–O distance for the D_{5d} 10-coordinate metal environment is 2.937 Å (range 2.854–3.037 Å). This compares well to other literature cations of this type, *e.g.* those of [K(15-crown-5)]$_2$[Ti(CO)$_6$SnMe$_3$],[21a] mean K–O distance 2.89 Å. These bonds are slightly distended with respect to the mean structurally characterised K–O bond (2.819 Å),[11] and akin to that of the (18-crown-6) adduct of KCp (mean K–O 2.901 Å).[13]

The sandwich-like cations and anions of **9** are well separated in the crystalline lattice. Unfortunately, the regular geometry of the Cp anion couldn't be successfully refined to further illustrate this. Instead, successful refinement necessitated use of an idealised geometry for the Cp anion of **9**. This bares similarity to the structural refinement employed for [(Me$_2$N)$_3$S}$_2$Cp][CpNaCp], synthesised by Mews *et al.* This complex contains one of the few structurally characterised unsubstituted naked cyclopentadienide anions without a transition metal-based counter ion. Similarly, heavy disorder about the Cp ring was seen, however, the quality of data in this case permitted a somewhat tenuous allocation of C–C$_{(cyclopentadienide)}$ bond lengths.[10a]

Interestingly, Mews *et al.* have reported the extreme reactivity of 'naked' Cp anions, *vis-à-vis* [Ph$_4$P][Cp], which can only be

Table 7 ^{1}H (300 MHz) and ^{13}C (75.5 MHz) C_6D_6 NMR data for compounds **5**–**10** (δ values in ppm)

	5	**6**	**7**	**8**	**9**	**10**
^{1}H NMR						
Cp-H (I)	6.73 (s)	6.31 (pseudo-d)	6.33 (s)	6.23 (br s)	6.64 (s)	6.33 (p-d)
Cp-H (II)	—	6.42 (pseudo-d)	—	6.31 (br s)	—	6.45 (p-d)
Cp–CH_3	—	2.69 (s)	—	2.82 (s)	—	2.73 (s)
OCH_2	3.19 (s)	3.26 (s)	3.14 (s)	3.29 (s)	3.41 (s)	3.40 (s)
^{13}C NMR						
Cp-C (I)	103.8	99.7	102.8	102.8	107.3	104.5
Cp-C (II)	—	102.3	—	104.2	—	105.5
Cp-*C*–CH_3	—	101.6	—	103.8	—	105.3
Cp–*C*H_3	—	17.3	—	17.6	—	16.9
OCH_2	69.0	67.7	70.3	70.2	72.3	71.0

isolated at low temperatures after low temperature preparation.[22] This situation is as found for many of the reported transition metal-based 'naked' Cp species.[23] Consequently, **9** presents one of, if not the, most thermally stable example(s) of a free Cp anion that has been fully characterised (only minor decomposition observed over temperatures of 150 °C). Attempts to form the 18-crown-6 analogue of **9** met with failure, addition of an excess of crown (2.0 eq.) to **2** simply gave the known complex [K(18-crown-6)Cp],[13] and not a crown sandwiched cation as in **9** (^{1}H NMR). As noted, the work of Power *et al.*[17] yielded the complex [Li(12-crown-4)$_2$][1,2,4-$(SiMe_3)_3C_5H_2$], however, attempts to form the Cp homologue by addition of excess 12-crown-4 to [Li(12-crown-4)Cp] also met with failure. Interestingly, a rationale presented by the authors to explain this concurs with our findings; *i.e.* that the Li–Cp ionic attraction displayed by [Li(12-crown-4)Cp] is too large to be disrupted by salt formation.[17] In the instance of **9**, the degree of ionic attraction between a potassium species would be significantly diminished with respect to a lithium analogue. Consequently, by this premise, it is unsurprising that **9** forms but surprising that the 18-crown-6 sandwich does not. Perhaps, in this instance, the second rationale presented by Power *et al.* becomes overriding, *i.e.* that the ion size matching is not close enough to present a lattice energy of adequate magnitude for salt formation.[17] This explanation would, however, promote the formation of [Li(12-crown-4)$_2$][Cp], given the formation of **9**. We would therefore like to add that, in our belief, the thermodynamic benefit of discrete monomer formation facilitated by correct size-fit crowns, as in [Li(12-crown-4)Cp], [K(18-crown-6)Cp] and now [Na(15-crown-5)Cp] (**5**), outweighs the energetic benefit of salt formation.

The exact solid-state nature of **10** could not be defined by XRD. All samples crystallised were highly disordered and, as such, refined to an insufficient standard for the indentification of the cation, or its proposed valency of 10. The assignment of a **9**-like molecular structure for **10** is made on the basis of ^{1}H and ^{13}C NMR, APCI MS and the similar magnitude of their melting points. The NMR data (^{1}H and ^{13}C) for species **5**–**10** are compiled in Table 7.

3 Experimental

3.1 General considerations

The 1,2-dimethoxyethane adduct of sodium cyclopentadienide was prepared as per the literature.[5] Cyclopentadiene and methylcyclopentadiene were prepared from their respective dimers after 'cracking' at ~43 and 65–72 °C, respectively. Sodium ingots, cyclopentadiene dimer and methylcyclopentadiene dimer[24] were obtained from Aldrich and used as received. Sodium and potassium *tert*-butoxide were purchased from Aldrich and sublimed prior to use. 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5) and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) were purchased from Aldrich and purified as per the literature.[25] Tetrahydrofuran, 1,2-dimethoxyethane and hexane were dried over sodium then freshly distilled from sodium–benzophenone ketyl. All manipulations were performed using conventional Schlenk or glovebox techniques under an atmosphere of high purity argon or dinitrogen in flame-dried glassware. Infrared spectra were recorded as Nujol mulls using sodium chloride plates on a Nicolet Nexus FTIR spectrophotometer. ^{1}H NMR spectra were recorded at 300.13 MHz and ^{13}C NMR spectra were recorded at 75.46 MHz using a Bruker BZH 300/52 spectrometer with a Varian console, chemical shifts were referenced to the residual ^{1}H or ^{13}C resonances of the solvent used (C_6D_6). Mass spectra were recorded on a VG Fisons Platform II instrument under APCI conditions. Melting points were determined in sealed glass capillaries under argon and are uncorrected. All compounds were exceedingly air- and moisture-sensitive and rapidly lost solvent (even under inert atmospheres). As such, repeated attempts to obtain meaningful microanalytical data were unsuccessful.

3.2 Data from characterisation of [Na(dme)Cp$_\infty$] (1)

M.p. 112 °C (decomp. 180 °C+). ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ 3.17 [s, 6H, OCH_3], 3.30 [s, 4H, OCH_2], 6.07 [s, 5H, CH]. ^{13}C NMR (75.5 MHz, C_6D_6, 300 K): δ 58.6 [s, OCH_3], 71.8 [s, OCH_2], 103.4 [s, CH]. MS APCI *m*/*z* (%): 113 ([Na(dme)]$^+$, 100), 201 ([Na$_2$Cp(dme)]$^+$, 32), 291 ([Na$_2$Cp(dme)$_2$]$^+$, 11). IR (Nujol) ν/cm^{-1}: 861 (m), 999 (m sh), 1127 (s br), 1240 (s sh), 1276 (m), 1522 (w), 1650 (w sh).

3.3 Synthesis of [K(dme)$_{0.5}$Cp]$_\infty$ (2)

Cyclopentadiene (8 cm^3, 96 mmol), prepared from commercial dicyclopentadiene by heating in a distillation apparatus at the boiling point of mono-Cp, ~43 °C, was added dropwise to a stirred solution of potassium *tert*-butoxide (5.40 g, 48.2 mmol) in dme (40 cm^3) at −30 °C. The stirred solution was then warmed to room temperature, with a concomitant colour change from colourless to light-brown. After stirring overnight, the volatiles were removed *in vacuo* and the resulting light-yellow solid extracted into dme (20 cm^3). Storage at −30 °C over 12 h yielded the title compound as large extremely air-sensitive, solvent-dependent plates (6.23 g, 87%), m.p. 124 °C (solvent loss, decomp.). ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ 3.08 [s, 6H, OCH_3], 3.21 [s, 4H, OCH_2], 5.78 [s, 5H, CH]. ^{13}C NMR (75.5 MHz, C_6D_6, 300 K): δ 59.3 [s, OCH_3], 70.4 [s, OCH_2], 104.0 [s, CH]. MS APCI *m*/*z* (%): 39 ([K]$^+$, 100), 67 ([C_5H_7]$^+$, 24). IR (Nujol) ν/cm^{-1}: 835 (m), 968 (m), 999 (m), 1071 (m), 1117 (s), 1189 (m sh), 1250 (m sh), 1296 (m sh), 1532 (w sh), 1670 (w sh).

3.4 Synthesis of [Na(dme)Cp^{Me}]$_\infty$ (3)

Methylcyclopentadiene (10 cm^3, 98.0 mmol), prepared from commercial methylcyclopentadiene dimer by heating in a distillation apparatus at the boiling point of mono-Cp^{Me}, ~65–72 °C, was added dropwise to a stirred solution of sodium *tert*-butoxide (4.60 g, 47.9 mmol) in dme (40 cm^3) at −30 °C. The stirred solution was then warmed to room temperature, with a concomitant colour change from colourless to light-pink/yellow. After stirring overnight, the solution was concentrated *in vacuo* and kept at −30 °C overnight to yield the title compound as large air-sensitive, solvent-dependent blocks (8.61 g, 94%), m.p. 66 °C. ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ 2.42 [s, 3H, CCH_3], 2.99 [s, 6H, OCH_3], 3.04 [s, 4H, OCH_2], 5.72 [br s, 2H, CH], 5.74 [br s, 2H, CH]. ^{13}C NMR (75.5 MHz, C_6D_6, 300 K): δ 15.3 [s, CCH_3], 58.7 [s, OCH_3], 71.4 [s, OCH_2], 101.9 [s, CH], 103.6 [s, CH], 114.2 [s, CCH_3]. MS APCI *m*/*z* (%): 23 ($[Na]^+$, 53), 113 ($[Na(dme)]^+$, 100), 215 ($[Na_2Cp^{Me}(dme)]^+$, 16), 305 ($[Na_2Cp^{Me}(dme)_2]^+$, 15), 407 ($[Na_3Cp^{Me}{}_2(dme)_2]^+$, 7). IR (Nujol) ν/cm^{-1}: 625 (m), 774 (m), 856 (m), 927 (w), 984 (w), 1025 (m), 1112 (s br), 1194 (s), 1245 (m sh), 1281 (m).

3.5 Synthesis of $[K(dme)_{0.5}Cp^{Me}]_\infty$ (4)

Methylcyclopentadiene (10 cm^3, 98.0 mmol), prepared from commercial methylcyclopentadiene dimer by heating in a distillation apparatus at the boiling point of mono-Cp^{Me}, ~65–72 °C, was added dropwise to a stirred solution of potassium *tert*-butoxide (4.60 g, 47.9 mmol) in dme (40 cm^3) at −30 °C. The stirred solution was then warmed to room temperature, with a concomitant colour change from colourless to deep red. After stirring overnight, the volatiles were removed *in vacuo* and the resultant light-pink solid extracted into dme (25 cm^3). Storage at −30 °C overnight yielded the title compound as large extremely air-sensitive, solvent-dependent two-dimensional plates (6.46 g, 83%), m.p. 85 °C (decomp.). ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ 2.41 [s, 3H, CCH_3], 3.07 [s, 6H, OCH_3], 3.24 [s, 4H, OCH_2], 5.61 [br s, 2H, CH], 5.66 [br s, 2H, CH]. ^{13}C NMR (75.5 MHz, C_6D_6, 300 K): δ 15.6 [s, CCH_3], 58.8 [s, OCH_3], 72.1 [s, OCH_2], 104.5 [s, CH], 105.4 [s, CCH_3], 105.5 [s, CH]. MS APCI *m*/*z* (%): 39 ($[K]^+$, 100), 129 ($[K(dme)]^+$, 29). IR (Nujol) ν/cm^{-1}: 769 (m), 860 (m), 926 (m), 979 (m sh), 1031 (m), 1121 (s br), 1589 (w sh), 1646 (w sh).

3.6 Synthesis of [Na(15-crown-5)Cp] (5)

15-Crown-5 (0.80 cm^3, 4.00 mmol) was added dropwise to a solution of **1** (0.71 g, 3.98 mmol) in thf (40 cm^3) at 0 °C. The resulting light-pink solution was then stirred for 2 h at room temperature, during which time the solution changed colour to a clear light-yellow. Concentration *in vacuo* (*ca.* 20 cm^3) gave a clear golden-brown solution. Storage at −30 °C overnight yielded the title compound as deep-red crystalline shards (0.29 g, 24%). Concentration of the mother liquor and cooling to −30 °C yielded more of the title compound (0.83 g, 68%; 92% total) as small colourless prisms, m.p. 182 °C. X-Ray structure determination of the two samples confirmed their congruent structure and composition. ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ 3.19 [br s, 20H, CH_2], 6.73 [s, 5H, CH]. ^{13}C NMR (75.5 MHz, C_6D_6, 300 K): δ 69.0 [s, CH_2], 103.8 [s, CH]. MS APCI *m*/*z* (%): 23 ($[Na]^+$, 65), 243 ($[Na(15\text{-crown-}5)]^+$, 100). IR (Nujol) ν/cm^{-1}: 697 (m), 830 (m), 937 (m), 999 (m), 1040 (m), 1132 (s br), 1230 (m sh), 1271 (m sh), 1296 (m sh).

3.7 Synthesis of [Na(15-crown-5)Cp^{Me}] (6)

15-Crown-5 (0.55 cm^3, 2.75 mmol) was added dropwise to a solution of **3** (0.53 g, 2.76 mmol) in thf (40 cm^3) at 0 °C. The resulting light-yellow solution was then stirred for 2 h at room temperature. Concentration *in vacuo* (*ca.* 25 cm^3) gave a clear golden brown solution. Placement at −30 °C overnight yielded the title compound as crystalline platelets (0.56 g, 63%), m.p. 165 °C. ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ 2.69 [s, 3H, CCH_3], 3.26 [br s, 20H, CH_2], 6.31 [pseudo-d, 2H, CH, $^3J_{HH}$ 2.3], 6.42 [pseudo-d, 2H, CH, $^3J_{HH}$ 2.3 Hz]. ^{13}C NMR (75.5 MHz, C_6D_6, 300 K): δ 17.3 [s, CCH_3], 67.7 [s. CH_2], 99.7 [s, CH], 101.6 [s, CCH_3], 102.3 [s, CH]. MS APCI *m*/*z* (%): 23 ($[Na]^+$, 65), 243 ($[Na(15\text{-crown-}5)]^+$, 100). IR (Nujol) ν/cm^{-1}: 825 (m), 1004 (m), 1105 (s br), 1277 (m), 1272 (m sh), 1306 (m).

3.8 Synthesis of [Na(18-crown-6)Cp] (7)

18-Crown-6 (0.52 g, 1.97 mmol) was added *via* solid addition apparatus to a solution of **1** (0.36 g, 2.02 mmol) in thf (40 cm^3) at room temperature. The solution initially sustained its clear pinky-brown appearance, no obvious reaction was observed. After stirring overnight, the solution had become more golden in colouration and was concentrated *in vacuo* (*ca.* 15 cm^3) and cooled to −30 °C to yield the title compound as large thick clear colourless plates (0.37 g, 53%), m.p. 123 °C. ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ 3.14 [s, 24H, CH_2], 6.33 [s, 5H, CH]. ^{13}C NMR (75.5 MHz, C_6D_6, 300 K): δ 70.3 [s, CH_2], 102.8 [s, CH]. MS APCI *m*/*z* (%): 23 ($[Na]^+$, 19), 287 ($[Na(18\text{-crown-}6)]^+$, 100). IR (Nujol) ν/cm^{-1}: 693 (m sh), 765 (m), 809 (m), 1134 (s), 1256(m sh), 1310(s sh), 1465 (w sh).

3.9 Synthesis of [Na(18-crown-6)Cp^{Me}] (8)

18-Crown-6 (0.75 g, 2.84 mmol) was added *via* solid addition apparatus to a solution of **3** (0.56 g, 2.91 mmol) in thf (40 cm^3) at room temperature. The solution sustained its clear dark brown appearance, no obvious reaction was observed. After stirring overnight, the solution was warmed to ~50 °C, concentrated *in vacuo* (*ca.* 10 cm^3) and cooled to room temperature to yield the title compound as large thick clear yellow plates (0.93 g, 89%), m.p. 108 °C. ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ 2.82 [s, 3H, CCH_3], 3.29 [s, 24H, CH_2], 6.23 [br s, 2H, CH], 6.31 [br s, 2H, CH]. ^{13}C NMR (75.5 MHz, C_6D_6, 300 K): δ 17.6 [s, CCH_3], 70.2 [s, CH_2], 102.8 [s, CH], 103.8 [s, CCH_3], 104.2 [s, CH]. MS APCI *m*/*z* (%): 23 ($[Na]^+$, 47), 287 ($[Na(18\text{-crown-}6)]^+$, 100). IR (Nujol) ν/cm^{-1}: 687 (m sh), 753 (m), 835 (m), 964 (s), 1015 (m), 1127 (s br), 1240 (m sh), 1281 (m sh), 1409 (w sh).

3.10 Synthesis of [K(15-crown-5)$_2$][Cp] (9)

15-Crown-5 (0.75 cm^3, 3.75 mmol) was added dropwise to a thf (60 cm^3) solution of **2** (0.33 g, 1.85 mmol) at room temperature. The light-brown solution was then stirred for 4 h, whereupon the volatiles were removed *in vacuo* to yield a highly air- and moisture-sensitive (browned upon exposure to air) light-coloured solid. Extraction into thf (20 cm^3), concentration (*ca.* 10 cm^3) and storage at −30 °C overnight yielded the title product as colourless cubic prisms (0.28g, 28%), m.p. 187 °C (mild decomp.) ^{1}H NMR (300 MHz, C_6D_6, 300K): δ 3.41 [s, 40H, CH_2], 6.64 [s, 5H, CH]. ^{13}C NMR (75.5 MHz, C_6D_6, 300K): δ 72.3 [s, CH_2], 107.3 [s, CH]. MS APCI *m*/*z* (%): 259 ($[K(15\text{-crown-}5)]^+$, 61), 479 ($[K(15\text{-crown-}5)_2]^+$, 100). IR (Nujol) ν/cm^{-1}: 671 (s), 743 (m), 845 (s), 937 (s br), 1194 (s), 1301 (s), 1455 (s br), 1593 (w sh).

3.11 Synthesis of [K (15-crown-5)$_2$][Cp^{Me}] (10)

15-Crown-5 (0.80 cm^3, 4.00 mmol) was added dropwise to a thf (60 cm^3) solution of **4** (0.33 g, 2.02 mmol) at room temperature. The light-brown solution was then stirred overnight, whereupon the volatiles were removed *in vacuo* to yield a highly air- and moisture-sensitive (browned upon exposure to air) light-yellow solid. Extraction into thf (25 cm^3), concentration (*ca.* 8 cm^3) and storage at −30 °C overnight yielded the title product as colourless cubic prisms (0.45g, 40%), m.p. 174 °C (mild decomp.) ^{1}H NMR (300 MHz, C_6D_6, 300K): δ 2.73 [s, 3H, CCH_3], 3.40 [s, 40H, CH_2], 6.33 [pseudo-d, 2H, CH, $^3J_{HH}$ 2.4], 6.45 [pseudo-d, 2H, CH, $^3J_{HH}$ 2.4 Hz]. ^{13}C NMR (75.5 MHz, C_6D_6, 300K): δ 16.9 [s, CH_3], 71.0 [s, CH_2], 104.5 [s, CH], 105.3 [s, CCH_3], 105.5 [s, CH]. MS APCI *m*/*z* (%): 479 ($[K(15\text{-crown-}5)_2]^+$, 100). IR (Nujol) ν/cm^{-1}: 678 (s), 743 (m), 825 (s), 1122 (s br), 1245 (s), 1352 (s), 1463(s br), 1593 (w sh).

3.12 Collection of X-ray diffraction data, solution and refinement of the structures

For compounds **1**, **2**, **5**, **8** and **9**, hemispheres of data were collected (capillary sealed specimens) at room temperature on

Table 8 Summary of crystal data[a] for compounds **1**, **2**, **5**, **8** and **9**

	$[Na(dme)Cp]_\infty$ (**1**)	$[K(dme)_{0.5}Cp]_\infty$ (**2**)	[Na(15-crown-5)Cp] (**5**)	$[Na(18\text{-crown-}6)Cp^{Me}]$ (**8**)	$[K(15\text{-crown-}5)_2][Cp]$ (**9**)
Mol. formula	$C_{18}H_{30}Na_2O_4$	$C_{28}H_{40}K_4O_4$	$C_{15}H_{25}NaO_5$	$C_{18}H_{31}NaO_6$	$C_{25}H_{45}KO_{10}$
Mol. weight	356.4	597.00	308.34	366.42	544.71
Space group	$Pna2_1$	$P\bar{1}$	$Pbca$	$Pna2_1$	$P\bar{1}$
a/Å	27.799(13)	8.972(3)	15.2065(16)	19.623(3)	8.793(3)
b/Å	8.149(3)	11.280(4)	14.8447(16)	9.8461(17)	9.119(3)
c/Å	9.379(4)	17.045(6)	15.5194(17)	10.8445(18)	9.377(3)
α/°	90	83.372(5)	90	90	84.667(6)
β/°	90	83.498(4)	90	90	89.760(5)
γ/°	90	82.935(7)	90	90	78.841(7)
Volume/Å^3	2277.7(17)	1692.0(10)	3503.3(7)	2095.2(6)	734.3(4)
Z	4	2	8	4	1
D_c/g cm^{-3}	1.039	1.172	1.169	1.162	1.232
μ/mm^{-1}	0.103	0.553	0.107	0.103	0.230
Reflections collected	10030	7399	15138	8839	3278
Unique reflections (R_{int})	3239 (0.167)	4528 (0.099)	2517 (0.076)	2639 (0.0783)	2079 (0.0678)
Parameters varied	221	464	327	227	187
Final R indices [$I > 2\sigma(I)$]: R_1, wR_2	0.069, 0.153	0.097, 0.253	0.069, 0.193	0.086, 0.2428	0.082, 0.214

[a] All datasets were measured at 296 K.

a Bruker SMART CCD diffractometer using the omega scan mode with total reflections and unique data listed in Table 8. Data sets were corrected for absorption using the program SADABS.[5] The structures were solved using direct methods and refined on F^2 using SHELXL97-2,[6] using X-SEED[7] as an interface. All non-hydrogen atoms were located and refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions (riding model) and were not refined. For compound **2**, the crystal was twinned and data were poor. Cyclopentadienyl carbon atoms were disordered, but were successfully refined with partial occupancies and two of the disordered Cp rings were refined isotropically. For compound **5**, the 15-crown-5 molecule was disordered, but was successfully refined over two sites of partial occupancy. For compound **9**, the cyclopentadienyl ring resides on an inversion centre and was therefore disordered equally over two sites. This disorder was successfully refined with an optimised geometry for the Cp ring. Crystal data and a summary of data collection appear in Table 8, while selected bond distances and angles appear in Tables 1, 2 and 4–6.

CCDC reference numbers 172086–172090.

See http://www.rsc.org/suppdata/dt/b1/b109124g/ for crystallographic data in CIF or other electronic format.

4 Conclusions

The paucity of structurally characterised cyclopentadienide and methylcyclopentadienide complexes of group 1 has been addressed by the addition of five examples to the archive. A further five new alkali metal complexes have been synthetically detailed and fully characterised. The potassium analogue of the known compound sodium(dme) cyclopentadiene exists in a 2 KCp : 1 dme stoichiometry. The 1,2-dimethoxyethane adducts of sodium and potassium methylcyclopentadienide are deleteriously solvent dependent; the added steric encumbrance of the methyl substituent apparently disrupting stabilising lattice interactions. The archival absence of the size-fit analogue of [Li(12-crown-4)Cp] and [K(18-crown-6)Cp]; [Na(15-crown-5)Cp], has been addressed. Finally, the marriage of non-size-fit crowns with sodium and potassium Cp^x species leads to predictable structural patterns. In the extreme, this negates cylcopentadienide donor interactions, as in $[K(15\text{-crown-}5)_2][Cp]$, whereby the two ions remain as discrete entities within a crystal lattice. $[K(15\text{-crown-}5)_2][Cp]$ is the only example of an s-block counter ion-stabilised naked cyclopentadienide anion. The need for trimethylsilyl groups on the Cp ring for steric and charge dissipation purposes (as in $[Li(12\text{-crown-}4)_2][1,2,4\text{-}(SiMe_3)_3C_5H_2]$) is obviated by the use of 'non-complementary' crowns. We believe our use of these crowns to induce novel solid-state motifs demands that the area of poly-O-macrocycle non-complementarity receive further attention.

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