

Synthesis and structural characterisation of lithium and sodium 2,6-dibenzylphenolate complexes

Marcus L. Cole,^{a,b} Peter C. Junk,^{a,*} Kathryn M. Proctor,^{a,c} Janet L. Scott^c and Christopher R. Strauss^c

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The stoichiometric treatment of 2,6-dibenzylphenol (HODbp) or 2',2''-dimethoxy-2,6-dibenzylphenol (HODbpOMe) with *n*-butyllithium or sodium bis(trimethylsilyl)amide (the latter as a solution in THF) in Et₂O or DME affords the dimeric alkali metal phenolates [$\{M(\text{Odbp})(L)\}_2$] ($M = \text{Li}$; $L = \text{Et}_2\text{O}$ (1), $L = \text{DME}$ (2), $M = \text{Na}$; $L = \text{Et}_2\text{O}$ (5), $L = \text{DME}$ (6)), [$\{\text{Li}(\text{OdbpOMe})\}_2$] (3) and [$\{M(\text{OdbpOMe})(L)\}_2$] ($M = \text{Li}$; $L = \text{DME}$ (4), $M = \text{Na}$; $L = \text{THF}$ (7), $L = \text{DME}$ (8)). Complexes 3 and 7 exhibit π -OdbpOMe methoxy coordination and all four sodium complexes (5–8) display π -aryl contacts from one phenolate radial arm to each sodium centre. The attempted synthesis of $\{\text{Na}(\text{odbp})\}_n$ by direct sodiation of HODbp yields a small quantity of the 2-benzylphenolate [$\{\text{Na}(\text{Ombp})(\text{DME})\}_4$] (9) ($\text{Ombp} = ^-\text{OC}_6\text{H}_4\text{-2-CH}_2\text{Ph}$), providing a rare example of benzyl C–C bond scission.

Introduction

Alkali metal phenolates^{1–4} have recently attracted interest beyond their use as precursors to other metal aryloxides.⁵ This, primarily structural, interest has partly focused on the broad variety of binding modes displayed when phenolates are coordinated to highly electropositive metal centres deprived of conventional Lewis base donors. Here, the breadth of coordination possible is typified by the complexes [$\{M(\mu_2:\eta^1:\eta^6\text{-OC}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2)(\text{OC}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2)_2\}_2$], where $M = \text{La}$, Nd , Sm and U ,^{6–8} and [$\{\text{RbTi}(\mu_2:\eta^1:\eta^4\text{-OC}_6\text{H}_3\text{-2,6-Me}_2)(\mu_2:\eta^1:\eta^3\text{-OC}_6\text{H}_3\text{-2,6-Me}_2)(\mu_2:\eta^1:\eta^4\text{-OC}_6\text{H}_3\text{-2,6-Me}_2)(\mu_2:\eta^1:\eta^3\text{-OC}_6\text{H}_3\text{-2,6-Me}_2)(\text{OC}_6\text{H}_3\text{-2,6-Me}_2)\}_n$],⁹ which display phenolate ligands that bridge metal centres by oxygen and π -aryl coordination. This type of phenolate bridging is prevalent amongst the heavier alkali metal containing heterobimetallic phenolates,^{10–14} particularly those of potassium. By contrast, lithium and sodium phenolates tend to bridge using the phenolate oxygen only.^{15–18} This leads to the formation of “–M–[O–M]_n–O–” oligomeric chains, cages, boxes and ladders.^{1–3,19}

Alkali metal phenolates can be prepared by two paths,⁵ namely direct oxidation of the metal by a phenol accompanied by the evolution of dihydrogen,^{20,21} or reaction of a phenol with a suitable transfer reagent, *e.g.* an alkali metal hydride, organoamide or alkyl.^{1,2} These reactions are typically performed in coordinating solvents like diethyl ether or tetrahydrofuran due to the insolubility of phenolates in apolar solvents. Such insolubility usually arises from a high molecular weight poly- or oligomeric composition^{21a,22} wherein the use of a donor solvent breaks down the aggregate by coordination to the metal in preference to bridging phenolates.^{23,24} This explanation is borne out by the reduced nuclearity of sterically hindered phenolates^{2,20,25} and the diminished reactivity of highly

aggregated alkali metal species relative to known monomeric alternatives.^{26–28}

Lithium phenolates are the most widely investigated subclass of alkali metal aryloxide.⁵ The reported lithium phenolates, excluding calixarenes and donor atom substituted examples, vary from unsubstituted or low bulk species, *e.g.* 2-methyl^{25b} or 4-ethylphenolate,¹ to more bulky variants like 2,6-di-*tert*-butylphenolate²⁵ and 3,5-di-*tert*-butyl-2,6-diphenylphenolate.²⁹ There are no examples of lithium phenolates bearing benzyl substituents.³⁰

The known donor free or O-donor supported lithium phenolates with or without alkyl/aryl substituents on the aryl group can be separated into four broad classes based on their nuclearity (see Fig. 1). The most common composition is the cubic- or ‘daisy-chain’ Li₄O₄ tetramer (Fig. 1; A and B, respectively).^{1,19,25b,31–33}

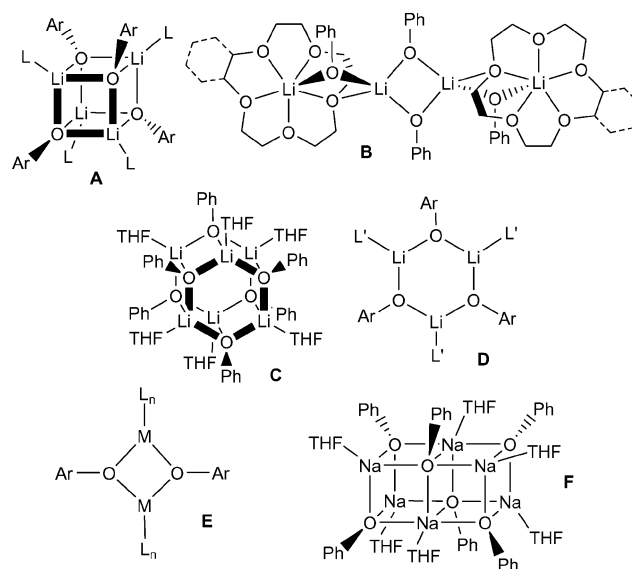


Fig. 1 Typical structural subclasses for O-donor supported lithium and sodium phenolates. A; $L = \text{THF}$ or 1,4-dioxane, D; $L' = \text{THF}$ or no ligand, E; $M = \text{Li}$, $L_n = \text{Et}_2\text{O}$, THF or 2 THF, $M = \text{Na}$, $L_n = 2 \text{ THF}$ or no ligand.

^aSchool of Chemistry, Monash University, Victoria, 3800, Australia E-mail: peter.junk@sci.monash.edu.au; Fax: +61 (0)3 9905 4597

^bSchool of Chemistry and Physics, University of Adelaide, Adelaide, South Australia, 5005, Australia

^cSpecial Research Centre for Green Chemistry, Monash University, Victoria, 3800, Australia

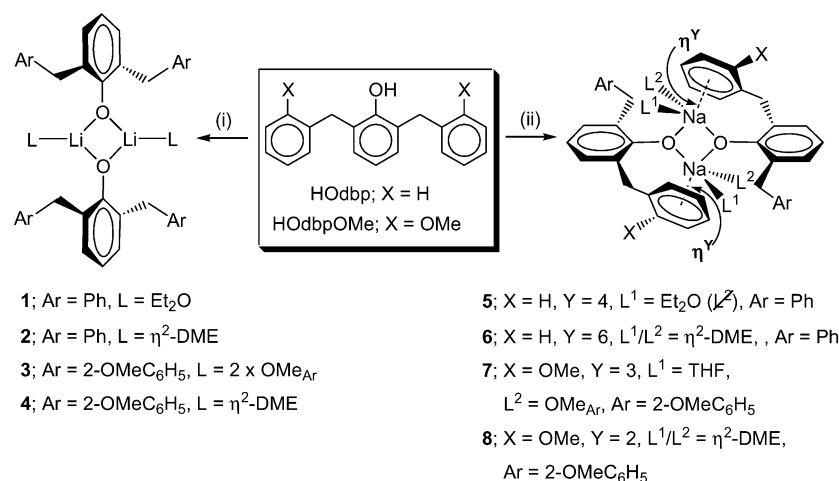
These architectures are exemplified by the unsubstituted lithium phenolates $[\{\text{Li}(\text{OC}_6\text{H}_5)(\text{THF})\}_4]^{25b}$ and $[\text{Li}_4(\text{OC}_6\text{H}_5)_4(15\text{-crown-5})_2]^{19}$ respectively. The coordination requirements of a 15-crown-5 donor, exhibited by all reported 'daisy-chain' tetramers, restrict the μ_3 phenolate oxygen bridging necessary for cubic species (**A**) to μ_2 -bridging interactions (**B**). Besides classes **A** and **B**, the only non-polymeric²² lithium phenolate with a nuclearity of four or above is the unsubstituted, THF solvated, hexamer $[\{\text{Li}(\text{OC}_6\text{H}_5)(\text{THF})\}_6]$ (Fig. 1; **C**),³⁴ which possesses a 'drum' type structure much like that of related hexameric lithium enolates,^{35,36} amides^{37,38} and alkoxides.³⁹⁻⁴¹ The phenolate oxygen atoms of this species bridge three lithium centres as per the cubic tetramer **A**, however, in this instance two lithium centres engage in one puckered six-membered Li_3O_3 ring, which alleviates the bond strain inherent in the μ_3 -bridging of **A**, and the remaining lithium is incorporated into a similar ring that stacks above and eclipses the former. The puckering of these rings, which approaches a chair conformation, contrasts with the two cyclic trimers $[\{\text{Li}(\text{OC}_6\text{H}_3-3,5\text{-}^i\text{Bu}_2-2,6\text{-Ph}_2)\}_3]^{29}$ and $[\{\text{Li}(\text{OC}_6\text{H}_3-2,6\text{-}^i\text{Pr}_2)(\text{THF})\}_3]^{25b}$ (see Fig. 1; **D**). These compounds display near planar Li_3O_3 rings due to steric buttressing that also frustrates ring-stacking like that in **C**. The remaining crystallographically characterised lithium phenolates are dimeric with a four-membered central Li_2O_2 metallacycle akin to the central unit of **B** or one face of **A** (Fig. 1; **E**, **M** = Li). Without exception these complexes incorporate a *tert*-butyl group at the 2- and/or 6-aryl position,^{20,25,42-44} Dipp groups at the 2- and 6-position (Dipp = 2,6-diisopropylphenyl)² or are constrained by complexation of both lithium atoms within the cavity of an 18-crown-6 macrocycle.²⁴

Sodium phenolates, like their lithium relatives, are useful reagents for salt elimination syntheses.⁵ They have also been applied extensively as reactants in the large scale 2-carboxylation of phenols, otherwise known as the Kolbe–Schmitt synthesis, from which a variety of pigments, fertilisers and pharmaceuticals are derived.^{45,46} The most noted example of these is, of-course, the industrial preparation of aspirin. Despite this, few *simple* sodium phenolate complexes, *i.e.* phenolates without additional donor atoms on the aryl group, have been crystallographically characterised.³⁰ Of the thirteen sodium species studied by X-

ray methods, three exhibit 2,6-dialkyl/aryl substitution of the aromatic ring.^{2,47,48} The remaining nine complexes, all containing $^-\text{OC}_6\text{H}_5$ or $^-\text{OC}_6\text{H}_4\text{-4-Me/Et}$, are either polymeric or of high nuclearity,^{21,32,49-51} *e.g.* compound **F**, the Na analogue of **C**, consisting of two face fused cubic tetramers reminiscent of **A** (Fig. 1),^{21a} or contain sodium phenolate constrained within an 18-crown-6 donor with⁵² or without²³ extended contacts to 18-crown-6 *free* sodium phenolate in the lattice.

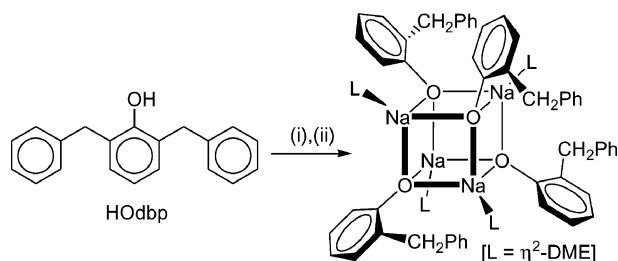
The three 2,6-dialkyl/aryl substituted sodium phenolates are dimeric in composition (Fig. 1; **E**, **M** = Na) and display solvent coordination consistent with aryl substituent bulk. For instance, the compound $[\{\text{Na}(\text{OC}_6\text{H}_3-2,6\text{-Tripp})_2\}_2]$ (Tripp = 2,4,6-triisopropylphenyl),² isolated from diethyl ether, is a non-solvated dimer that exhibits low hapticity π -aryl to metal contacts. This contrasts the related 2,4,6-tris(trifluoromethyl)phenolate⁴⁸ and 2,6-di-*tert*-butylphenolate⁴⁷ compounds, both prepared in THF, which contain two coordinated solvent donors per sodium. It is noteworthy that the "2,6-Tripp" phenolate is one of two reported sodium phenolates that exhibit sodium to aryl–carbon contacts, the other being a polymeric unsubstituted sodium phenolate ($^-\text{OC}_6\text{H}_5$) incorporating unreacted phenol.⁵⁰ Similarly, the only lithium phenolates to exhibit lithium to π -aryl contacts are the aforementioned "solvent-free" complexes $[\{\text{Li}(\text{OC}_6\text{H}_3-2,6\text{-Dipp})_2\}_2]^2$ and $[\{\text{Li}(\text{OC}_6\text{H}_3-3,5\text{-}^i\text{Bu}_2-2,6\text{-Ph}_2)\}_3]^{29}$ which display η^3 - (*ipso* and *ortho* carbon atoms) and η^1 -contacts (*ipso* or *ortho* carbon atoms), respectively from *one* 2/6-aryl group to each lithium centre (*cf.* η^1 -contacts from *ipso* carbon of *both* 2- and 6-Tripp substituents for $[\{\text{Na}(\text{OC}_6\text{H}_3-2,6\text{-Tripp})_2\}_2]^2$).

Herein we report the syntheses of the first lithium and sodium phenolates with benzyl groups at the 2- and 6-aryl position, *e.g.* 2,6-dibenzylphenolate or " $^-\text{Odbp}$ " (see Scheme 1).⁵³⁻⁵⁵ These include complexes of the ether donor functionalised 2',2''-dimethoxy-2,6-dibenzylphenolate, " $^-\text{OdbpOMe}$ ", which we have previously employed in related potassium studies.⁵⁴ All complexes have been prepared by reaction of the parent phenol^{53,54} with *n*-butyllithium or sodium bis(trimethylsilyl)amide in diethyl ether or 1,2-dimethoxyethane (DME). This approach was taken to allow direct competition of the pendant methoxy donors of $^-\text{OdbpOMe}$ with the solvent, using the $^-\text{Odbp}$ compounds as



Scheme 1 Reagents and conditions: (i) 1.0 eq. *n*-BuLi in hexane, Et₂O (**1** and **3**) or DME (**2** and **4**), room temperature, -1.0 eq. *n*-BuH. (ii) 2.0 eq. Na{N(SiMe₃)₂} in THF, Et₂O (**5** and **7**) or DME (**6** and **8**), room temperature, -1.0 eq. HN(SiMe₃)₂.

a control. Furthermore, as the flexibility of the benzyl radial arms of both ligands can enable metal to π -aryl contacts, direct competition of aryl coordination with solvent donation and, in the case of $^-OdbpOMe$, pendant methoxy coordination has also been observed. We also report the structure of the phenol $HOdbpOMe$ ⁵⁴ and the preparation of the sodium 2-benzylphenolate cubic tetramer; $[Na(Ombp)(DME)]_4$ ($Ombp$ = 2-monobenzylphenolate), isolated in low yield after direct reaction of sodium metal with $HOdbp$ (Scheme 2). This outcome for direct sodiation suggests the preparation of future alkali metal *o*-benzyl substituted phenolates by metallation of *ortho*-benzylphenols may be flawed by benzyl C–C bond scission.



Scheme 2 Reagents and conditions: (i) > 1.0 eq. Na (s), 2 mbar, 150 °C, C–C bond scission, – “CH₂Ph”. (ii) DME.

Results and discussion

The 1 : 1 stoichiometric treatment of diethyl ether or DME solutions of 2,6-dibenzylphenol ($HOdbp$) or 2,6-di(2'-methoxy)benzylphenol ($HOdbpOMe$) with *n*-butyllithium (1.6 M in hexane) or sodium bis(trimethylsilyl)amide (1.0 M in THF) results in clean deprotonation of the phenol (no O–H stretch or ¹H NMR resonance by FTIR and ¹H NMR spectroscopy; liquid film $HOdbp$ 3560 cm^{−1} (s br)/4.61 ppm in CDCl₃, Nujol mull $HOdbpOMe$ 3417 cm^{−1} (s br)/7.10 ppm CDCl₃)⁵⁴ to yield air- and moisture-sensitive species that crystallise directly from the reaction mother-liquor upon concentration (see Scheme 1). According to ¹H NMR spectra (C₆D₆), the isolated compounds possess the empirical formulae $Li(Odbp)(Et_2O)$ (**1**), $Li(Odbp)(DME)$ (**2**), $Li(OdbpOMe)$ (**3**), $Li(OdbpOMe)(DME)$ (**4**), $Na(Odbp)(Et_2O)$ (**5**), $Na(Odbp)(DME)$ (**6**), $Na(OdbpOMe)(THF)$ (**7**) and $Na(OdbpOMe)(DME)$ (**8**). The anomalous inclusion of THF in compound **7** results from use of commercial sodium bis(trimethylsilyl)amide supplied as a 1.0 M solution in THF. Attempts to isolate the diethyl etherate repeatedly gave **7** in moderate yield without isolation of the Et₂O adduct. All complexes were fully characterised by FTIR, ¹H and ¹³C{¹H} NMR spectroscopy (¹³C{¹H} NMR spectra of compounds **1** and **5** could not be obtained due to low solubility in C₆D₆), melting point and, for DME coordinated $^-OdbpOMe$ compounds **4** and **8**; C,H,N elemental analyses. Meaningful elemental analyses for compounds **1–3** and **5–7** were repeatedly prevented by solvent loss, poor combustion and/or enhanced air-sensitivity relative to **4** and **8**.

The empirical formula of compound **3** suggests saturation of the metal coordination sphere by either radial arm pendant methoxy or π -aryl coordination instead of solvent donation. In either instance, the interaction responsible appears to be overcome by the introduction of DME to give compound **4**, although this may

result from inclusion of lattice DME in **4**. Perhaps the best evidence for *intramolecular* ether or aryl coordination within **3** (and not **4**) comes in the form of the unusual thermal stability of the former. Compound **3** neither decomposes nor melts prior to 360 °C (limit of instrument employed, **1**; 123 °C, **2**; 112 °C), while compound **4** melts at 82 °C. It is noteworthy that the other solvent or ether crown free lithium phenolates, $[Li(OC_6H_3-3,5-Bu_2-2,6-Ph_2)]_3$ ²⁹ and $[Li(OC_6H_3-2,6-Dipp_2)]_2$,² exhibit several lithium to aryl–carbon contacts.

Further to spectroscopic characterisation, the isolation of **1–8** as crystalline materials permitted single-crystal X-ray structure determinations of all eight compounds. As can be seen in Fig. 2–4 and 6–10 (POV-RAY illustrations, thermal ellipsoids 40%) the bonding interactions present and aggregation of these compounds can be described fully. The structure of the previously reported parent ligand $HOdbpOMe$ is also included (see Fig. 5) to complement the molecular structures of $^-OdbpOMe$ compounds **3**, **4**, **7** and **8**. Tables 1 and 3 contain a summary of crystallographic refinement data for the lithium compounds and $HOdbpOMe$, and sodium compounds, respectively, while Tables 2 and 4 provide selected distances (Å) and angles (°) for compounds **1–4** and **5–8** (and **9** *vide infra*), respectively.

Structural studies

The four lithium phenolate complexes **1–4** are dimeric and crystallise in the centrosymmetric space group $P\bar{1}$ (see Tables 1 and 2). Compound **1** (Fig. 2), like **4** (see below), crystallises with one half of the molecule comprising the asymmetric unit. The dinuclear complex comprises two three-coordinate near trigonal planar lithium centres bridged by two phenolate oxygen atoms, which generate a M₂O₂ metallacycle (Li(1)–O(1)–Li(1)# 83.7(4)°, O(1)–Li(1)–O(1)# 96.3(4)°) that is commonplace in alkali metal phenolate structures,³⁰ and each coordinated by a terminal

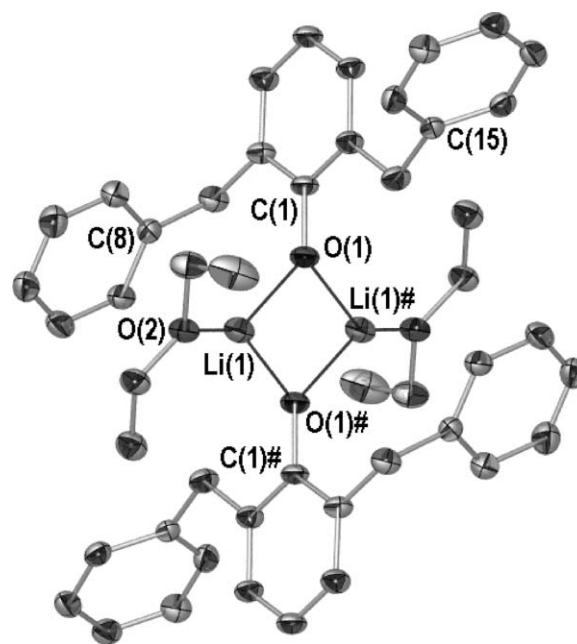


Fig. 2 Molecular structure of $[Li(\mu_2-Odbp)(Et_2O)]_2$ (**1**). All hydrogen atoms omitted for clarity. Symmetry transformation used to generate equivalent (#) atoms: $-x, -y, -z$.

Table 1 Summary of crystallographic data for compounds **1–4** and HOdbpOMe

	[Li(μ ₂ -Odbp)(Et ₂ O)] ₂ (1)	[Li(μ ₂ -Odbp)(DME)] ₂ (2)	[{Li(μ ₂ -O ³ -O ³ -O ³ -O ³ -OdbpOMe)(DME)] ₂ (3)	[{Li(μ ₂ -OdbpOMe)(DME)] ₂ (4)	HOdbpOMe
Formula	C ₄₈ H ₅₄ Li ₂ O ₄	C ₄₈ H ₅₄ Li ₂ O ₆	C ₄₄ H ₄₂ Li ₂ O ₆	C ₅₂ H ₆₂ Li ₂ O ₁₀	C ₂₂ H ₂₂ O ₃
<i>M_r</i>	708.80	740.79	680.66	860.90	334.20
<i>T</i> /K	123(2)	123(2)	123(2)	123(2)	123(2)
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	9.4436(19)	11.5653(2)	11.015(3)	9.6584(13)	6.7898(2)
<i>b</i> /Å	10.290(2)	13.4617(2)	11.345(2)	10.738(2)	10.4137(3)
<i>c</i> /Å	11.684(2)	14.4056(3)	15.006(2)	12.246(2)	24.7155(6)
<i>a</i> /°	77.75(3)	91.8320(10)	90.582(8)	97.659(9)	90
<i>b</i> /°	89.93(3)	112.2690(10)	105.252(9)	112.495(9)	90
<i>γ</i> /°	68.08(3)	92.0970(10)	95.986(11)	94.353(13)	90
<i>V</i> /Å ³	1025.5(4)	2071.57(6)	1797.9(6)	1151.7(4)	1747.56(8)
<i>Z</i>	1	2	2	1	4
<i>D_c</i> /g cm ⁻³	1.148	1.188	1.257	1.241	1.271
<i>μ</i> /mm ⁻¹	0.070	0.076	0.081	0.084	0.083
Reflections collected	13933	24711	27121	16328	13157
Unique reflections	4652	9853	8400	5327	4184
Parameters varied	246	509	473	293	314
<i>R</i> _{int}	0.2431	0.0769	0.1266	0.2389	0.0593
<i>R</i> ₁	0.0780	0.0506	0.0574	0.0965	0.0405
<i>wR</i> ₂	0.1770	0.1288	0.1348	0.1970	0.0760

Table 2 Selected bond lengths, out-of-plane (oop) distances (Å), angles and interplanar angles (°) for compounds **1–4**

	1 ^f	2	3	4 ^h
Li(1)–O(1)	1.851(8)	1.869(2)	1.850(4)	1.857(9)
Li(1)–O(2)	1.842(9)	1.872(2)	1.855(4) ^g	1.897(8)
Li(2)–O(1)	1.842(9)	1.938(2)	1.844(4)	1.897(8)
Li(2)–O(2)	1.851(8)	1.872(2)	1.847(4) ^g	1.857(9)
Li(1)–O _{Et₂O} /DME	1.935(9)	1.965(3)	—	2.117(9)
Li(1)–O _{DME} ^a	—	2.301(3)	—	2.026(9)
Li(1)–O _{OMe}	—	—	1.911(5)	—
Li(1)–O _{OMe} ^a	—	—	2.023(5)	—
Li(2)–O _{Et₂O} /DME	1.935(9)	2.130(3)	—	2.117(9)
Li(2)–O _{DME} ^a	—	2.107(3)	—	2.026(9)
Li(2)–O _{OMe}	—	—	2.060(5)	—
Li(2)–O _{OMe} ^a	—	—	1.962(5)	—
Li(1)–O(1)–Li(2)	83.7(4)	83.79(10)	82.68(19)	84.5(4)
Li(1)–O(2)–Li(2)	83.7(4)	85.44(11)	82.44(19) ^g	84.5(4)
O(1)–Li(1)–O(2)	96.3(4)	96.13(12)	97.2(2) ^g	95.5(4)
O(1)–Li(2)–O(2)	96.3(4)	93.96(11)	97.6(2) ^g	95.5(4)
O(1)–Li(1)–O _{Et₂O} /DME	119.5(4)	110.27(12)	—	138.2(4)
O(1)–Li(1)–O _{DME} ^a	—	143.99(14)	—	117.0(4)
O(1)–Li(1)–O _{OMe}	—	—	113.0(2)	—
O(1)–Li(1)–O _{OMe} ^a	—	—	110.4(2)	—
O(2)–Li(1)–O _{Et₂O} /DME	128.0(4)	128.11(14)	—	110.6(4)
O(2)–Li(1)–O _{DME} ^a	—	104.59(11)	—	114.8(4)
O(2)–Li(1)–O _{OMe}	—	—	109.3(2) ^g	—
O(2)–Li(1)–O _{OMe} ^a	—	—	117.4(2) ^g	—
O(1)–Li(2)–O _{Et₂O} /DME	128.0(4)	143.70(14)	—	110.6(4)
O(1)–Li(2)–O _{DME} ^a	—	104.62(11)	—	114.8(4)
O(1)–Li(2)–O _{OMe}	—	—	111.4(2)	—
O(1)–Li(2)–O _{OMe} ^a	—	—	108.1(2)	—
O(2)–Li(2)–O _{Et₂O} /DME	119.5(4)	103.70(11)	—	138.2(4)
O(2)–Li(2)–O _{DME} ^a	—	142.15(15)	—	117.0(4)
O(2)–Li(2)–O _{OMe}	—	—	117.6(2) ^g	—
O(2)–Li(2)–O _{OMe} ^a	—	—	111.2(2) ^g	—
O _{Et₂O} oop Li ₂ O ₂	0.636(9)	—	—	—
O _{Et₂O} oop Li ₂ O ₂ ^b	0.636(9)	—	—	—
C _{ipso} oop Li ₂ O ₂ ^c	0.562(5)	0.098(2)	0.006(3)	0.284(7)
C _{ipso} oop Li ₂ O ₂ ^c	0.562(5)	0.174(2)	0.794(16)	0.284(7)
C ₆ : Li ₂ O ₂ ^d	87.85(11)	44.50(9)	61.01(9)	84.03(29)
C ₆ : Li ₂ O ₂ ^d	87.85(11)	72.69(7)	50.72(10)	84.03(29)
Ar ₁ –CH ₂ –C ₆ ^{d,e}	115.3(4)	111.64(11)	113.9(2)	115.3(4)
Ar ₂ –CH ₂ –C ₆ ^{d,e}	114.9(4)	111.93(12)	114.9(2)	116.1(4)
Ar ₁ ′–CH ₂ –C ₆ ^{d,e}	—	116.79(11)	113.4(2)	—
Ar ₂ ′–CH ₂ –C ₆ ^{d,e}	—	115.29(12)	115.0(2)	—

^a O_{DME} and O_{DME}^a and O_{OMe} and O_{OMe}^a refer to the lowest and highest numbered DME or [−]OdbpOMe methoxy oxygen atoms, respectively.

^b O_{Et₂O} refers to the symmetry generated O_{Et₂O} oxygen atom O(2)#. ^c C_{ipso} and C_{ipso} refer to the *ipso* carbons of C₆ and C₆. ^d C₆ and C₆ refer to phenol phenyl rings of the lowest and highest numbered (or symmetry generated) [−]Odbp or [−]OdbpOMe ligands, respectively. ^e Ar and Ar′ refer to lowest and highest numbered benzyl phenyl rings on a particular [−]Odbp or [−]OdbpOMe ligand. The subscripts refer to the lowest and highest numbered ligands, respectively. ^f Li(2), O(2) and O_{Et₂O} are symmetry generated equivalents (#) of Li(1), O(1) and O(2), respectively. Symmetry transformation used to generate equivalent atoms: $-x, -y, -z$. ^g For the purposes of 3; O(2) = O(4). ^h Li(2), O(2), O_{DME} and O_{DME}^a are symmetry generated equivalents (#) of Li(1), O(1), O(2) and O(3), respectively. Symmetry transformation used to generate equivalent atoms: $-x, -y, -z$.

diethyl ether oxygen. The Li–O_{phenolate} bond distances (Li(1)–O(1) 1.851(8) Å, Li(1)–O(1)# 1.842(9) Å) are consistent with Li–O_{phenolate} bond lengths for other dimeric diethyl ether solvated three-coordinate lithium phenolates, e.g. [Li(OC₆H₂-2,6-^tBu₂-4-Me)(Et₂O)]₂ (1.849(11) and 1.867(10) Å).²⁰ The Li–O_{Et₂O} bond

distance of 1.9635(9) Å is also typical of this structural type ($[\{\text{Li}(\text{OC}_6\text{H}_2\text{-}2,6\text{-}^i\text{Bu}_2\text{-}4\text{-Me})(\text{Et}_2\text{O})_2\}_2]$; 1.961(11) Å)²⁰ and, likewise, suggests a weaker interaction compared with the bridging anionic donors. A characteristic nuance of dimeric lithium phenolates is placement of the phenolate aryl ring near orthogonal to the Li_2O_2 metallacycle.^{20,25,42–44} This usually occurs with the *ipso*-carbon in the metallacyclic plane, however, in **1** the *ipso*-carbon atoms sit well out of the Li_2O_2 plane (0.562(5) Å). Likewise, the solvent donor, also typically maintained within the metallacycle plane for three-coordinate lithium, deviates significantly from coplanarity (0.636(9) Å). These data, and the pyramidalisation of the lithium coordination geometry that they accompany (Li(1) sits 0.373(7) Å out of the O(1)–O(1)#–O(2) plane, $\Sigma\text{O–Li(1)–O}$ 343.8(12)°), are suggestive of a four-coordinate lithium centre. However, the closest non-oxygen contact to Li(1) is that of the *ipso* carbon of the benzyl group associated with C(8) (see Fig. 1, Li(1)⋯C(8) 2.969(7) Å) that projects toward the lithium centre. This contact is well outside accepted neutral arene Li–C contacts, such as those in $[\text{Sn}(2,6\text{-Tripp}_2\text{C}_6\text{H}_3)(\text{CH}_3)_2\text{Sn}(2,6\text{-Tripp}_2\text{C}_6\text{H}_3)(\text{Li})]$ (2.367(9)–2.707(9) Å)⁵⁶ and $[\{\text{Li}(\mu\text{-S}\{2,6\text{-Mes}_2\text{C}_6\text{H}_3\})_3\}]$ (2.38(2)–2.77(2) Å, Mes = 2,4,6-Me₃C₆H₂),⁵⁷ or those in $[\{\text{Li}(\text{OC}_6\text{H}_3\text{-}3,5\text{-}^i\text{Bu}_2\text{-}2,6\text{-Ph}_2)\}_3]$ ²⁹ and $[\{\text{Li}(\text{OC}_6\text{H}_3\text{-}2,6\text{-Dipp}_2)\}_2]^2$ (2.478(8)–2.689(8) Å and 2.390(3)–2.647(3) Å, respectively), inferring the distorted LiO_3 geometry of **1** may simply result from steric influences and/or crystal packing effects.

Dimeric compounds **2** and **4** (Fig. 3 and 4, Table 2 for selected bond lengths and angles), both exhibit lithium centres chelated by DME and crystallise with a half and a full molecular unit in the asymmetric unit, respectively. Both complexes display near tetrahedral lithium ions that, like **1**, participate in a central Li_2O_2 unit. For compound **2**, one phenolate ring (that of O(1)) significantly deviates from the expected orthogonal arrangement relative to the Li_2O_2 ring (see Table 2; interplanar angle 44.50(9)°). This does not occur for the other phenolate ligand nor do those of compounds **1** and **4** which remain near orthogonal (**2**; O(2)

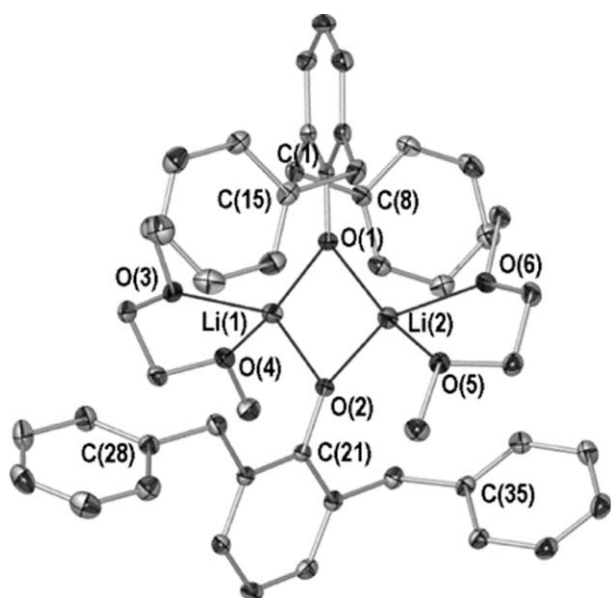


Fig. 3 Molecular structure of $[\{\text{Li}(\mu_2\text{-Odbp})(\text{DME})\}_2]$ (**2**). All hydrogen atoms omitted for clarity.

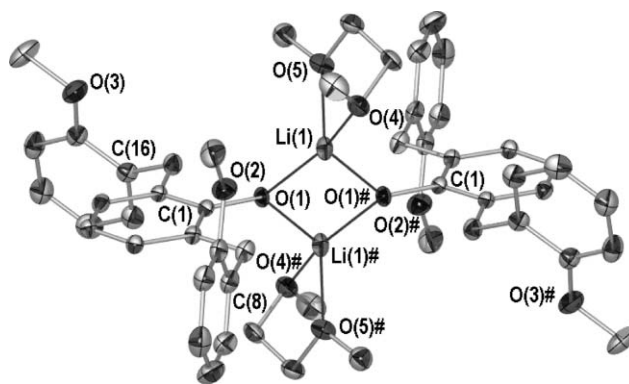


Fig. 4 Molecular structure of $[\{\text{Li}(\mu_2\text{-OdbpOMe})(\text{DME})\}_2]$ (**4**). All hydrogen atoms omitted for clarity. Symmetry transformation used to generate equivalent (#) atoms: $-x, -y, -z$.

phenolate 72.69(7)°, **1**; 87.85(11)°, **4**; 84.03(29)°). This results in extension of one Li–O_{phenolate} contact for **2** (Li(2)–O(1)) while the others are consistent with related contacts in **1** and **4** (1.938(2) Å vs. (1.87 Å, **1**; (1.85 Å, **4**; (1.88 Å)) and extension of one Li(1)–O_{DME} contact (Li(1)–O(3) 1.965(3) Å, Li(1)–O(4) 2.301(5) Å, Li(2)–O(5) 2.130(3) Å, Li(2)–O(6) 2.017(3) Å, **4**; Li(1)–O(4) 2.117(9) Å, Li(1)–O(5) 2.026(9) Å). The benzyl groups of both **2** and **4** project away from the Li_2O_2 core unlike the aforementioned single benzyl of **1** (see above) as is consistent with increased coordination of the lithium centres and the steric imposition of the bidentate DME ligands.

At the outset of this study it was anticipated that the introduction of methoxy groups at the benzyl 2-aryl position of Odbp to give OdbpOMe would result in alkali metal phenolates with reduced solvent donor inclusion. In addition, we viewed the preparation of such complexes in donor solvents as a means of evaluating the strength of methoxy, or perhaps π -aryl, coordination relative to the donor solvent. This interest in the coordinative capacity of the radial arms of OdbpOMe meant a crystal structure of the phenol would be useful when comparing conformational strain within complexes bearing “ Odbp ” type ligands. Accordingly, HOdbpOMe ⁵⁴ was recrystallised from acetone solution and a structure determination undertaken (Fig. 5, POV-Ray

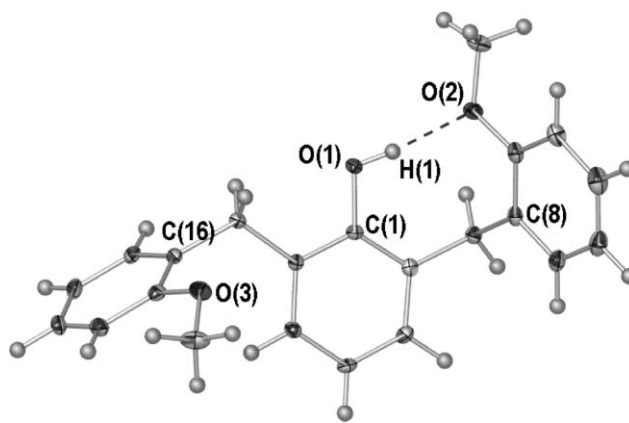


Fig. 5 Molecular structure of HOdbpOMe . Selected distances (Å) and angles (°): C(1)–O(1) 1.3724(17), O(1)–H(1) 0.86(2), H(1)⋯O(2) 1.90(2), O(1)⋯O(2) 2.737(2); O(1)–H(1)⋯O(2) 165(2), aryl : aryl (benzyl phenyl : phenol phenyl) 61.97(5) and 77.73(4).

illustration, 40% thermal ellipsoids, refinement parameters are listed in Table 1).

The phenol HOdbpOMe crystallises in the orthorhombic space group $P2_12_12_1$ with one phenol in the asymmetric unit. The hydrogen atoms of HOdbpOMe were located from difference maps and refined isotropically permitting full assessment of hydrogen bonding and intermolecular interactions. The phenolic proton of HOdbpOMe (H(1)) interacts with one methoxy oxygen (O(2)) resulting in the following hydrogen bonding parameters; O–H...O 165(2)°, H(1)...O(2) 1.90(2) Å, O(1)–H(1) 0.86(2) Å and O(1)...O(2) 2.737(2) Å. This interaction necessitates slight opening (*ca.* 0.5°, see Fig. 5 caption) of the benzyl methylene bridge C–C–C angle relative to the non hydrogen bonding benzyl group. No other bonding contacts, hydrogen bonding or otherwise, can be identified about the molecular unit of HOdbpOMe. Other salient structural parameters are the phenol C–O bond length and aryl: aryl (benzyl phenyl: phenol phenyl) interplanar angles of 1.3724(17) Å, 61.97(5)° and 77.73(4)°. The former compares well to the analogous C–O length of the bulky phenol HOC₆H₃-2,6-Tripp₂ (1.381(2) Å), which does not participate in any hydrogen bonding due to the sheer steric bulk of its aryl substituents.²

Compound **3**, prepared in diethyl ether, crystallises as a $\mu_2:\kappa^3$ -OdbpOMe bridged solvent free dimer, with one $[\{\text{Li}(\text{OdbpOMe})\}_2]$ comprising the asymmetric unit (Fig. 6, see Table 2 for selected distances and angles). All four pendant ether donors (two on each phenolate) coordinate the two lithium centres providing near tetrahedral lithium coordination. The Li–O_{OMe} contacts vary from 1.911(5) to 2.060(5) Å and are therefore shorter than the mean Li–O_{DME} contacts of four-coordinate lithium compounds **2** and **4** (2.10 Å) and (2.07 Å), respectively) and flank the Li–O_{Et₂O} contact of three-coordinate lithium complex **1** (1.935(8) Å). This coordination results in twisting of the phenolate aryl rings away from orthogonal to the central Li₂O₂ metallacycle (Table 2; 61.01(9) and 50.72(10)°). Surprisingly, twisting occurs without significant reduction of the benzyl methylene linker C–C–C angle from that of the parent phenol, HOdbpOMe, or the analogous angles for the non-coordinating benzyl groups of **1**, **2**

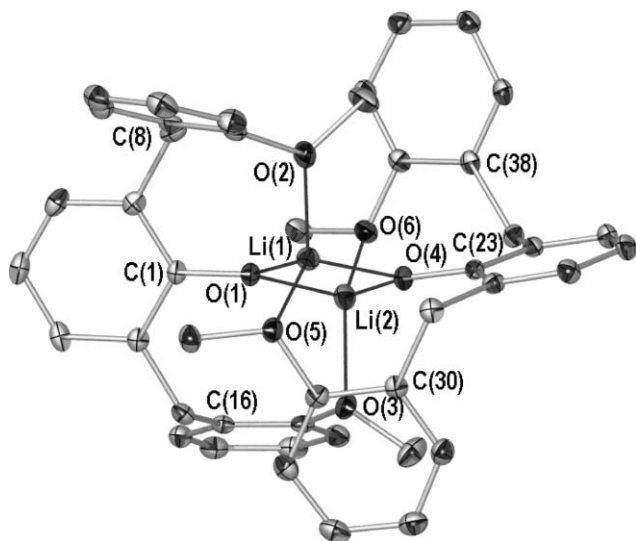


Fig. 6 Molecular structure of $[\{\text{Li}(\mu_2:\kappa^3\text{-OdbpOMe})\}_2]$ (**3**). All hydrogen atoms omitted for clarity.

and **4** (angles of HOdbpOMe; 115.35(12)°_{H-bonded} and 114.83(12)°, **1**; (115.1°), **2**; (113.9), **3**; (114.3), **4**; (115.7)). Further to related potassium studies,⁵⁴ compound **3** represents the first alkali metal OdbpOMe complex where the coordination of the pendant ether groups has been observed. Thus, the isolation of **3** from diethyl ether and **4** from DME suggests that the pendant methoxy groups of OdbpOMe are of intermediate donor character to these ligands.

Like their lithium counterparts, the sodium phenolates **5–8** (see Fig. 7–10) exist as dimers in the solid state (see Tables 3 and 4). The asymmetric unit of all four compounds comprise either one half (**5** and **7**) or two unique halves (**6** and **8**) of a dimeric unit with compounds **5** and **7** crystallising in the monoclinic space group $P2_1/c$ and **6** and **8** crystallising in the triclinic space group $P\bar{1}$. Due to the similar metrical parameters of the two unique halves of compounds **6** and **8**, only the first (Na(1) containing) unit of each compound will be discussed here.

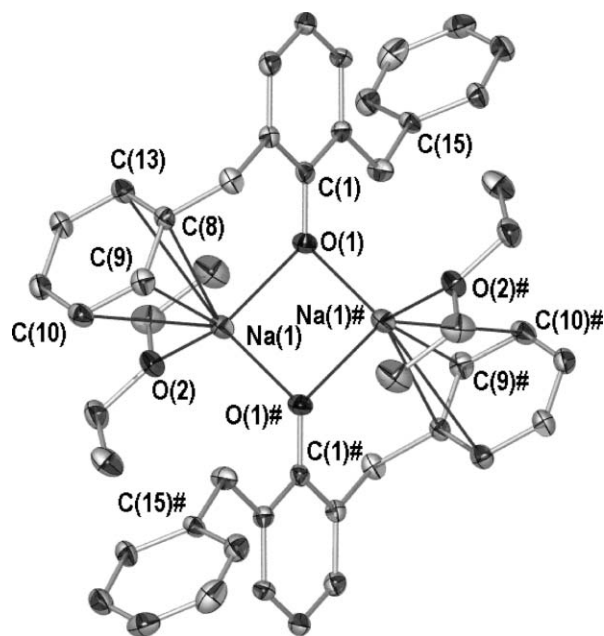
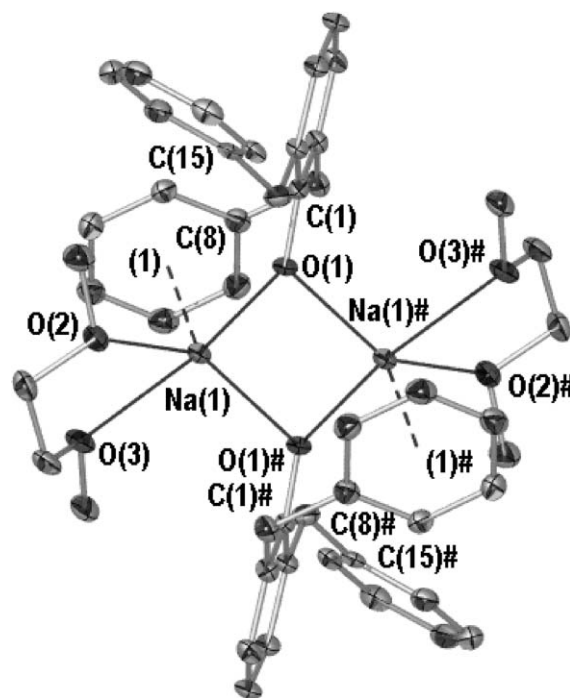
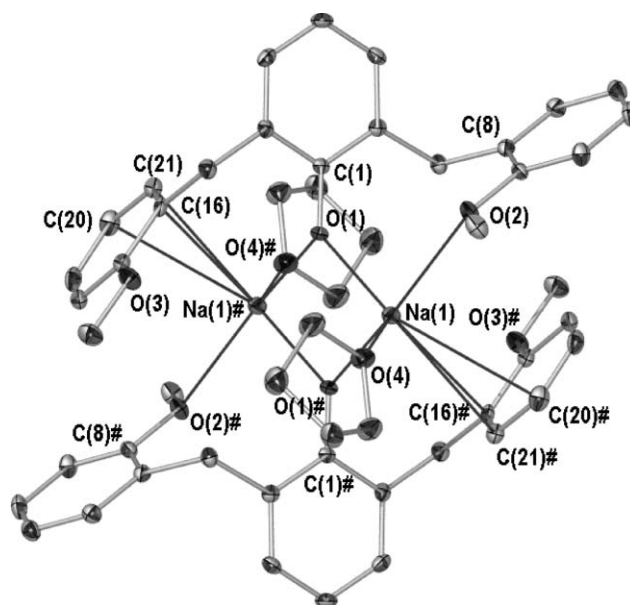


Fig. 7 Molecular structure of $[\{\text{Na}(\mu_2:\eta^1:\eta^1\text{-Odbp})(\text{Et}_2\text{O})\}_2]$ (**5**). All hydrogen atoms omitted for clarity. Symmetry transformation used to generate equivalent (#) atoms: $-x, -y, 2 - z$.

Despite their similar Na₂O₂ units, the non-Na₂O₂ sodium coordination of compounds **5–8** differ considerably. For example, phenolate oxygen coordination is supplemented by ether coordination to provide phenolate and solvent coordination numbers of either three or four for **5** and **7**, and **6** and **8**, respectively. For compound **7** (see Fig. 9) this coordination is joined by OdbpOMe methoxy donation. However, contrary to **3**, where both methoxy donors coordinate the dilithium unit, just one methoxy per phenolate coordinates in **7**. Thus, the oxygen-only coordination number of compound **5** is three while compounds **6–8** possess oxygen-only coordination numbers of four. Further to this, the sodium geometries of **5–8** are far from ideal polyhedra (*e.g.* **5**; $\Sigma\text{O}(\text{Na}(1))\text{O}$ angles 334.8(4)°, **8**; mean deviation of $\text{O}(\text{Na}(1))\text{O}$ from 109.5° = 32.0°) and are suggestive of further

Table 3 Summary of crystallographic data for compounds **5–9**

	$[\{\text{Na}(\mu_2:\eta^1:\eta^1\text{-}O,Ar\text{-}Odbp)(\text{DME})\}_2]$ (5)	$[\{\text{Na}(\mu_2:\eta^1:\eta^1\text{-}O,Ar\text{-}Odbp)(\text{DME})\}_2]$ (6)	$[\{\text{Na}(\mu_2:\eta^1:\eta^1\text{-}O,Ar\text{-}Odbp\text{OMe})(\text{THF})\}_2]$ (7)	$[\{\text{Na}(\mu_2:\eta^1:\eta^1\text{-}O,Ar\text{-}Odbp\text{OMe})(\text{DME})\}_2]$ (8)	$[\{\text{Na}(\mu_2:\eta^1:\eta^1\text{-}Ombp)(\text{DME})\}_4]$ (9)
Formula	$\text{C}_{48}\text{H}_{54}\text{Na}_2\text{O}_4$	$\text{C}_{48}\text{H}_{54}\text{Na}_2\text{O}_6$	$\text{C}_{52}\text{H}_{58}\text{Na}_2\text{O}_8$	$\text{C}_{52}\text{H}_{62}\text{Na}_2\text{O}_{10}$	$\text{C}_{68}\text{H}_{84}\text{Na}_4\text{O}_{12}$
M_r	740.90	772.89	856.96	893.00	1185.32
T/K	123(2)	123(2)	123(2)	123(2)	123(2)
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$Pbcn$
$a/\text{\AA}$	8.9157(5)	9.2892(4)	9.5356(19)	10.4333(2)	20.2800(5)
$b/\text{\AA}$	25.073(2)	10.1342(5)	10.974(2)	11.0954(3)	15.0904(3)
$c/\text{\AA}$	10.1182(9)	23.5197(13)	21.326(4)	20.7892(5)	21.4779(6)
$\alpha/^\circ$	90	81.467(2)	90	89.254(2)	90
$\beta/^\circ$	111.526(4)	87.774(2)	90.24(3)	80.838(2)	90
$\gamma/^\circ$	90	72.651(2)	90	83.6230(10)	90
$V/\text{\AA}^3$	2104.1(3)	2089.96(18)	2231.6(8)	2361.16(10)	6573.0(3)
Z	2	2	2	2	4
$D_c/\text{g cm}^{-3}$	1.169	1.228	1.275	1.256	1.198
μ/mm^{-1}	0.090	0.097	0.101	0.101	0.103
Reflections collected	26204	22270	12461	21328	34697
Unique reflections	4777	9528	5151	9822	8106
Parameters varied	246	509	282	585	383
R_{int}	0.2829	0.0665	0.0860	0.0273	0.0828
R_1	0.0928	0.0745	0.0628	0.0622	0.0514
wR_2	0.1507	0.1905	0.1249	0.1541	0.1160

**Fig. 8** Molecular structure of $[\{\text{Na}(\mu_2:\eta^1:\eta^1\text{-}O,Ar\text{-}Odbp)(\text{DME})\}_2]$ (**6**). All hydrogen atoms omitted for clarity. Arene centroid represented as “(1)”. Symmetry transformation used to generate equivalent (#) atoms and centroid: $2 - x, 2 - y, -z$.**Fig. 9** Molecular structure of $[\{\text{Na}(\mu_2:\eta^1:\eta^1\text{-}O,Ar\text{-}Odbp\text{OMe})(\text{THF})\}_2]$ (**7**). All hydrogen atoms omitted for clarity. Symmetry transformation used to generate equivalent (#) atoms and centroid: $-x, 1 - y, 1 - z$.

non-O coordination. This is borne out by the close placement of one benzyl aryl ring relative to the sodium atoms of **5–8** (see Table 4). Contrary to **1**, where the lithium to carbon contacts are beyond the limit of accepted Li–C contacts, the $\text{Na} \cdots \text{C}_{(\text{aryl})}$ approaches of **5–8** are similar to those proposed for Robinson's

Table 4 Selected bond lengths, out-of-plane (oop) distances (Å), angles and interplanar angles (°) for compounds **5–9**

	5^f	6^g	7^h	8ⁱ	9^j
Na(1)–O(1)	2.226(3)	2.3723(19)	2.2139(18)	2.2016(17)	⟨2.33⟩
Na(1)–O(1)#	2.198(3)	2.2493(18)	2.2450(18)	2.2252(17)	—
Na(1)–O _{Et₂O/DME/THF}	2.306(3)	2.355(2)	2.3312(18)	2.3361(18)	⟨2.47⟩
Na(1)–O _{DME} ^a	—	2.499(2)	2.6415(19)	2.399(2)	—
Na(1)–O _{OMe}	—	—	—	—	—
Na(1)–C _{Ar1} ^b	2.906(5)	2.912(3)	3.102(2)	3.341(3)	—
Na(1)–C _{Ar2} ^b	2.908(4)	2.953(3)	3.347(3)	3.037(3)	—
Na(1)–C _{Ar3} ^b	3.306(4)	3.148(3)	3.064(3)	—	—
Na(1)–C _{Ar4} ^b	3.253(5)	3.295(3)	—	—	—
Na(1)–C _{Ar5} ^b	—	3.247(3)	—	—	—
Na(1)–C _{Ar5} ^b	—	3.053(3)	—	—	—
Na(1)–Ar _{cent} ^b	—	2.776(6)	—	—	—
Na(1)–O(1)–Na(1)#	90.40(12)	90.86(6)	93.33(6)	88.57(6)	⟨91.5⟩
O(1)–Na(1)–O(1)#	89.60(12)	89.14(6)	86.67(6)	91.43(6)	⟨88.4⟩
O(1)–Na(1)–O _{Et₂O/DME/THF}	130.01(13)	94.36(7)	112.05(7)	171.52(8)	⟨100.9⟩
O(1)–Na(1)–O _{DME} ^a	—	162.32(8)	—	99.98(7)	⟨164.6⟩
O(1)–Na(1)–O _{OMe}	—	—	84.68(6)	—	—
O(1)#–Na(1)–O _{Et₂O/DME/THF}	115.19(13)	128.58(8)	99.26(7)	95.77(6)	⟨135.1⟩
O(1)#–Na(1)–O _{DME} ^a	—	100.06(7)	—	152.08(9)	⟨92.1⟩
O(1)#–Na(1)–O _{OMe}	—	—	163.25(6)	—	—
O _{Et₂O/THF} oop Na ₂ O ₂	1.474(4)	—	2.135(2)	—	—
C _{ipso} oop Na ₂ O ₂ ^c	0.345(6)	0.426(4)	0.243(3)	0.389(4)	—
C ₆ :Na ₂ O ₂ ^d (interplanar)	71.73(10)	84.44(6)	63.90(7)	80.29(7)	—
Ar–CH ₂ –C ₆ ^{d,e}	114.7(3)	115.5(2)	113.25(18)	115.70(18)	⟨115.7⟩
Ar'–CH ₂ –C ₆ ^{d,e}	113.9(4)	115.5(2)	116.06(19)	115.08(19)	—

^a O_{DME} And O_{DME} refer to the lowest and highest numbered DME methoxy oxygen atoms, respectively. ^b C_{Ar#} Refer to the aryl carbons that possess Na...C bonding contacts in numerical order. ^c C_{ipso} Refers to *ipso* carbon of phenol phenyl ring. ^d C₆ Refers to phenol phenyl ring. ^e Ar And Ar' refer to lowest and highest numbered benzyl phenyl rings on a [−]Odbp or [−]OdbpOMe ligand, respectively. ^f Symmetry transformation used to generate equivalent (#) atoms: $-x, -y, 2-z$. ^g Values refer to a one (Na(1)) of two half molecular units in the asymmetric unit. Symmetry transformation used to generate equivalent (#) atoms: $2-x, 2-y, -z$. ^h Symmetry transformation used to generate equivalent (#) atoms: $-x, 1-y, 1-z$. ⁱ Values refer to a one (Na(1)) of two half molecular units in the asymmetric unit. Symmetry transformation used to generate equivalent (#) atoms: $1-x, 1-y, -z$. ^j Mean values given for comparison with **5–8**. O(1) Taken as oxygen atoms in Na₄O₄ heterocube. Symmetry transformation used to generate equivalent atoms: $-x, y, 1/2-z$.

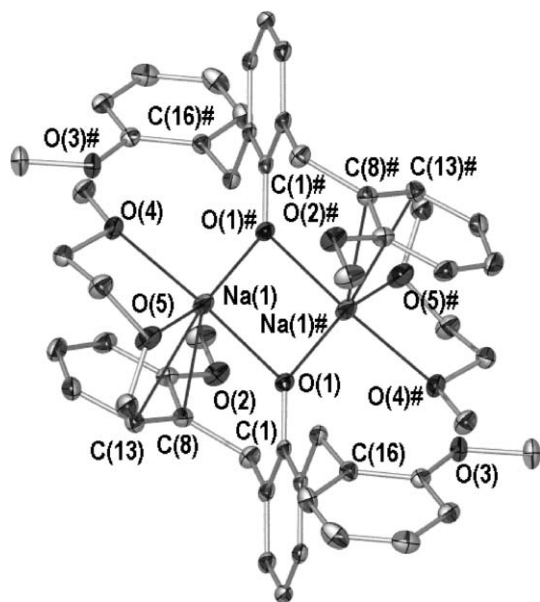


Fig. 10 Molecular structure of $[\{Na(\mu_2\eta^1\eta^2\text{-OdbpOMe})(\text{DME})\}_2]$ (**8**). All hydrogen atoms omitted for clarity. Symmetry transformation used to generate equivalent (#) atoms: $1-x, 1-y, -z$.

'Gallyne'; Na₂[Ga₂(2,6-Tripp₂C₆H₂)₂] (Na–C 2.87(2)–3.13(2) Å)⁵⁸ and are well within the range proposed for Ruhlandt-Senge's toluene coordinated sodium thiolate $[\{Na(\text{SSiPh}_3)\}_6(\text{tol})_2]$ (Na–C 2.852(6)–3.664(3) Å).⁵⁹ With the exception of compound **7**, where the remaining benzyl coordinates to sodium by a methoxy oxygen in preference to solvent donation, the phenolates of **5–8** possess one non-coordinating benzyl group. This does not generate a disparity between the observed C–C–C angles of the non-coordinated benzyl arms and those that are coordinated (see Table 4). In all four instances, these angles compare well to the analogous angles of HOdbpOMe (see Fig. 5). The Na–C_(aryl) hapticities for compounds **5–8** (see Fig. 7–10) are η^4 , η^6 , η^3 and η^2 , respectively. The increased hapticity of **6** relative to **5** despite lower oxygen-coordination is consistent with the longer Na–O_{phenolate} and Na–O_{ether} contacts of the former (**5**; Na–O_{phenolate} 2.198(3)–2.226(3) Å, Na–O_{Et₂O} 2.306(3) Å, **6**; Na–O_{phenolate} 2.2493(18)–2.2723(19) Å, Na–O_{DME} 2.355(2)–2.499(2) Å). Overall, the Na–C distances of the four compounds (Table 4) are close to those of $[\{Na(\text{OC}_6\text{H}_3\text{-2,6-Tripp}_2)\}_2]$ (2.995(3)–3.076(3) Å),² as are the Na–O_{phenolate} bond lengths (2.226(2)–2.237(2) Å, **5**; (2.21 Å), **6**; (2.26 Å), **7**; (2.23 Å), **8**; (2.21 Å)), which are expectedly shorter than those of the cubic tetramer $[\{Na(\text{OC}_6\text{H}_4\text{-4-Me})(\text{DME})\}_4]$ ((2.31 Å)).⁴⁹ Lastly, the O–Na–O and Na–O–Na angles of the Na₂O₂ metallacycles of **5–8** approach 90° (see Table 4) in a similar

manner to the aforementioned “Tripp” sodium phenolate (O–Na–O (85.8°), Na–O–Na (94.2°)).²

Sodiation of HOdbp

In instances where the pK_a of a protonated anionic ligand precursor is favourable, direct metallation of the precursor is often preferred to the use of a metal alkyl or amide, as in the syntheses of **1–8**, due to simpler work-up and decreased overall cost.⁵ Several sodium and potassium phenolates, *e.g.* $\text{Na}(\text{OC}_6\text{H}_2-2,6\text{-i-Bu}_2-4\text{-Me})(\text{Et}_2\text{O})^{20}$ and $\{\text{K}(\text{OC}_6\text{H}_3)\}_n$,²¹ have been prepared using direct metallation of a parent phenol. As an accompaniment to the transamination syntheses of **5–8**, the direct sodiation of HOdbp was attempted using a method employed extensively by us⁶⁰ for the solvent-free syntheses of homoleptic alkaline earth⁶¹ and lanthanoid metal aryloxides,⁶² including $^-$ Odbp complexes of lanthanum, europium and ytterbium.⁵⁵ This method circumvents the low solubility of halides and relative scarcity of commercially available alkyls and related transfer reagents for f- and heavy group 2 elements. The absence of solvent also provides scope for self-saturation of the metal coordination sphere by pendant functions on the ligand such as those possessed by $^-$ Odbp and $^-$ OdbpOMe.^{55,61,62}

Our standard protocol for solvent free direct metallation involves the high-temperature reaction (up to 300 °C) of a chosen ligand with the desired metal in a Carius glass tube under reduced pressure.⁶⁰ Staged cooling gives the homoleptic complex, in some cases of suitable quality for X-ray structure determination. This can be accompanied by the inclusion of protonated ligand either in the lattice or as a neutral donor.⁶⁰ Under those circumstances, and when crystalline compounds are not forthcoming, one can resort to the use of a suitable solvent to extract the metal complex and hinder neutral ligand inclusion.

The reduced pressure reaction of excess HOdbp with sodium metal at 150 °C over several days results in the low quantity isolation of an intractable low melting colourless solid⁶³ containing unreacted sodium. Recrystallisation of this material from DME followed by cooling to –30 °C provided several colourless prismatic crystals.⁶⁴ Analysis of these by single-crystal X-ray diffraction unit cell collection indicated a compound (**9**) of different morphology to the anticipated **6** (see Table 3; compound **6** triclinic $P\bar{1}$, compound **9** orthorhombic $Pbcn$). Full data collection and refinement reveals the source of this difference to be the mono-, and not di-, benzyl substituted sodium phenolate cubic tetramer $[\{\text{Na}(\mu_3\text{-Ombp})(\text{DME})\}_4]$, **9**, where $^-$ Ombp = $^-$ OC₆H₄-2-CH₂Ph (see Fig. 11, POV-RAY illustration 40% thermal ellipsoids, Table 3 and Figure caption for relevant collection data and bond lengths and angles, respectively). Compound **9** bears a close structural resemblance to the aforementioned $[\{\text{Na}(\mu_3\text{-OC}_6\text{H}_4\text{-4-CH}_3)(\text{DME})\}_4]$.⁴⁹ This compound represents the only other O-donor supported cubic sodium phenolate³⁰ and also includes 1,2-dimethoxyethane (DME) (**9**; Na–O_{phenolate} (2.35 Å), Na–O_{DME} (2.47 Å), O_{phenolate}–Na–O_{phenolate} (88.0°), Na–O_{phenolate}–Na < 91.8°, $[\{\text{Na}(\mu_3\text{-OC}_6\text{H}_4\text{-4-CH}_3)(\text{DME})\}_4]$; Na–O_{phenolate} (2.31 Å), Na–O_{DME} (2.42 Å), O_{phenolate}–Na–O_{phenolate} (90.4°)).⁴⁹

The HOdbp used in this study was prepared by high temperature palladium-charcoal catalysed isomerisation of 2,6-dibenzalcylohexanone.⁵³ Accordingly, the formation of **9** using our synthetic protocol must result from phenolate *o*-benzyl C–

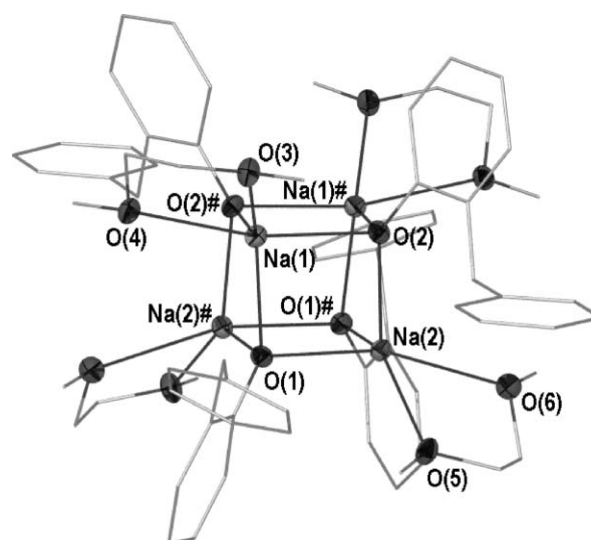


Fig. 11 Molecular structure of $[\{\text{Na}(\mu_3\text{-Ombp})(\text{DME})\}_4]$ (**9**). All hydrogen atoms omitted and hydrocarbons of ligands depicted as wire frames for clarity. Symmetry transformation used to generate equivalent (#) atoms: $-x, y, 1/2 - z$. Selected bond lengths (Å) and angles (°): Na(1)–O(1) 2.2959(14), Na(1)–O(2) 2.3535(14), Na(1)–O(2)# 2.3291(14), Na(1)–O(3) 2.3785(15), Na(1)–O(4) 2.5032(15), Na(2)–O(1) 2.3523(14), Na(2)–O(1)# 2.3483(14), Na(2)–O(2) 2.3057(14), Na(2)–O(5) 2.3689(14), Na(2)–O(6) 2.6188(15), O(1)–Na(1)–O(2) 86.95(5), O(1)–Na(1)–O(2)# 93.99(5), O(2)–Na(1)–O(2)# 88.77(5), O(3)–Na(1)–O(4) 68.37(5), O(1)–Na(2)–O(2) 86.75(5), O(2)–Na(1)–O(1)# 93.23(5), O(1)–Na(1)–O(1)# 89.65(5), O(5)–Na(2)–O(6) 66.99(5).

C bond scission during high temperature/low pressure reaction with elemental sodium metal. To our knowledge, the loss of a benzyl substituent from a diphenylmethane compound bearing an *ortho*-heteroatom, *e.g.* O, N, S or P, as per the conversion of $^-$ Odbp to $^-$ Ombp ($= \text{OC}_6\text{H}_4\text{-2-CH}_2\text{Ph}$), has been reported once before.⁶⁵ This bond scission was observed during the catalysed hydroprocessing of HOmbp over sulfided $\text{CoOMoO}_3/\gamma\text{-Al}_2\text{O}_3$ at 300–330 °C, a process studied as part of a modelling analysis for the catalytic hydrodeoxygenation of lignin. Aside from this report, we are unaware of any similar reactions catalysed by either alkali metals or metal containing species in general.

Conclusion

We have reported the syntheses of the first lithium and sodium complexes of the phenolates “ $^-$ Odbp” and “ $^-$ OdbpOMe” in both monodentate and bidentate ether solvents. All compounds are dimeric in the solid state and, aside from compound **3**, contain coordinated solvent. Use of monodentate ether solvents like Et₂O and THF results in coordination of either two or one pendant methoxy donor when using $^-$ OdbpOMe for lithium (**3**) and sodium, respectively (**7**). In the case of the latter, THF and methoxy coordination occur concurrently, perhaps indicating similar coordination strengths. Phenolate methoxy coordination is frustrated in the presence of DME (*cf.* **4** and **8**), indicating that the use of 18-crown-6 in prior potassium-OdbpOMe studies may have stifled similar methoxy donation.⁵⁴ All four sodium complexes exhibit pendant benzyl π -aryl coordination to the metal centre with greater hapticities exhibited for the $^-$ Odbp species. The high-temperature low-pressure reaction of elemental sodium with

HOdbp results in a small quantity of the sodium monobenzyl phenolate [$\{\text{Na}(\mu_3\text{-Ombp})(\text{DME})\}_4\}$ (**9**) by the unusual scission of a benzyl C–C bond. These compounds represent a sizeable contribution to the phenolate structural catalogue, particularly that of sodium, and emphasise the significant structural diversity possible.

The study of substituted phenolates, in particular when coordinated to highly reactive heavy alkaline earth and lanthanoid metals, is ongoing in our respective laboratories.

Experimental

2,6-Dibenzylphenol (HOdbp) and 2,6-di(2'-methoxy)benzylphenol (HOdbpOMe) were prepared by a modified literature procedure.^{53,54} 1.6 M *n*-Butyllithium in hexane, and 1.0 M sodium bis(trimethylsilyl)amide in THF and sodium were purchased from Aldrich and used as is. Diethyl ether and 1,2-dimethoxyethane were dried over sodium and freshly distilled from sodium benzophenone ketyl (Et_2O) or sodium wire (DME) before freeze-thaw degassing prior to use. All manipulations were performed using conventional Schlenk or glovebox techniques under an atmosphere of high purity dinitrogen in flame-dried glassware. Infrared spectra were recorded as Nujol mulls using sodium chloride plates on a Nicolet Nexus FTIR spectrophotometer. ^1H NMR spectra were recorded at 300.13 MHz and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at 75.46 MHz using a Bruker DPX 300 spectrometer with chemical shifts referenced to the residual ^1H or ^{13}C resonances of the deuterobenzene solvent (δ 7.16 and 128.39 ppm, respectively). Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. All microanalyses were conducted by the Campbell Microanalytical Laboratory, Chemistry Department, University of Otago, P.O. Box 56, Dunedin, New Zealand.

General procedure (1–8)

n -Butyllithium (0.50 cm³, 0.80 mmol) or sodium bis(trimethylsilyl)amide (0.80 cm³, 0.80 mmol) was added drop wise to a stirred colourless solution of HOdbp (0.22 g, 0.80 mmol) or HOdbpOMe (0.27 g, 0.81 mmol) in Et_2O or DME at ambient temperature. The resulting solution, which was either pale yellow or yellow in appearance, was then stirred overnight prior to work-up as described below. For compounds **1**, **3** and **5**, the colour change from colourless to pale yellow/yellow was accompanied by the formation of a colourless precipitate that was discarded during work-up. All isolated compounds were devoid of FTIR absorbances and ^1H NMR resonances attributable to the parent phenol. Relevant details for each compound are as follows:

$\{\{\text{Li}(\mu_2\text{-Odbp})(\text{Et}_2\text{O})\}_2\}$ (**1**). The yellow solution was filtered, concentrated *in vacuo* and cooled to 5 °C to give colourless square plates (0.12 g, 42%), mp 123 °C. ^1H NMR (298 K): δ 7.09–6.92 (m, 20H, Ar-*H*), 6.88 (m, 4H, Ar-*H*), 6.76 (m, 2H, Ar-*H*), 4.72 (s, 8H, CH_2Ph), 3.25 (q, 8H, OCH_2 , Et_2O , $^3J_{\text{HH}}$ 7.0 Hz), 1.12 (t, 12H, CH_3 , Et_2O , $^3J_{\text{HH}}$ 7.0 Hz). IR (Nujol)/cm⁻¹: 1594 (s), 1455 (s), 1305 (w), 1261 (s), 1155 (w), 1089 (s), 1027 (s), 866 (w), 800 (s), 755 (w), 733 (w), 700 (s).

$\{\{\text{Li}(\mu_2\text{-Odbp})(\text{DME})\}_2\}$ (**2**). The yellow solution was filtered, concentrated *in vacuo* and left at ambient temperature to give colourless rectangular prisms of **2** (0.14 g, 47%), mp 112 °C. ^1H NMR (298 K): δ 7.32 (m, 8H, Ar-*H*), 7.23–7.13 (m, 8H, Ar-*H*), 7.09–7.01 (m, 8H, Ar-*H*), 6.73 (m, 2H, Ar-*H*), 4.40 (s, 8H, CH_2Ph), 2.83 (s, 20H, OCH_3 and OCH_2 , DME). $^{13}\text{C}\{^1\text{H}\}$ NMR (298 K): δ 151.6, 130.0, 129.7, 129.0, 128.8, 128.7, 126.5, 126.2 (s, Ar-*C*), 70.9 (s, OCH_2 , DME), 59.1 (s, OCH_3 , DME), 37.6 (s, CH_2Ph). IR (Nujol)/cm⁻¹: 1601 (m), 1344 (w), 1305 (m), 1250 (s), 1194 (m), 1111 (s), 1083 (s), 1027 (s), 983 (s), 855 (m), 794 (s), 744 (w), 700 (m).

$\{\{\text{Li}(\mu_2\text{-}\kappa^3\text{-O},\text{O}',\text{O}'\text{-OdbpOMe})\}_2\}$ (**3**). For compound **3**, a white precipitate appeared approximately 30 minutes after addition of *n*-butyllithium. The resulting slurry was filtered and cooled to 5 °C. Cubic colourless crystals, which were isolated by filtration, appeared after standing for two days (0.20 g, 73%), mp > 360 °C. ^1H NMR (298 K): δ 7.44–7.38 (m, 8H, Ar-*H*), 6.85–6.71 (m, 10H, Ar-*H*), 6.53–6.48 (m, 4H, Ar-*H*), 3.83 (s, 8H, CH_2Ph), 2.61 (s, 12H, OCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (298 K): δ 155.3, 153.2, 132.3, 130.3, 128.6, 128.5, 125.4, 122.1, 114.0, 112.6 (s, Ar-*C*), 57.2 (s, OCH_3), 29.8 (s, CH_2Ph). IR (Nujol)/cm⁻¹: 1600 (m), 1583 (m), 1461 (s), 1389 (m), 1325 (w), 1230 (s), 1179 (m), 1101 (s), 1044 (w), 1012 (m), 917 (w), 856 (m), 828 (w), 792 (w), 749 (s), 698 (m).

$\{\{\text{Li}(\mu_2\text{-OdbpOMe})(\text{DME})\}_2\}$ (**4**). The pale yellow solution was filtered, concentrated *in vacuo* (ca. 5 cm³) and placed at 5 °C. Colourless rectangular prisms formed after three days (0.19 g, 55%), mp 82 °C. Found: C 72.28, H 7.42; $\text{C}_{52}\text{H}_{62}\text{Li}_2\text{O}_{10}$ requires C 72.54, H 7.26%. ^1H NMR (298 K): δ 7.45 (m, 6H, Ar-*H*), 6.95–6.78 (m, 12H, Ar-*H*), 6.53 (m, 4H, Ar-*H*), 3.87 (s, 8H, CH_2Ph), 3.31 (s, 8H, OCH_2 , DME), 3.11 (s, 12H, OCH_3 , DME), 2.66 (s, 12H, OCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (298 K): δ 155.6, 151.8, 130.4, 129.7, 128.2, 127.9, 126.3, 120.2, 119.2, 109.4 (s, Ar-*C*), 71.0 (s, OCH_2 , DME), 58.6, 53.7 (s, OCH_3 , -OdbpOMe and DME), 29.7 (s, CH_2Ph). IR (Nujol)/cm⁻¹: 1585 (m), 1492 (m), 1480 (s), 1436 (m), 1330 (m), 1239 (s), 1179 (w), 1137 (w), 1107 (s), 1014 (m), 859 (w), 826 (w), 748 (s).

$\{\{\text{Na}(\mu_2\text{-}\eta^1\text{-}\eta^4\text{-O},\text{Ar-Odbp})(\text{Et}_2\text{O})\}_2\}$ (**5**). For compound **5**, a white precipitate formed immediately upon addition of sodium bis(trimethylsilyl)amide. The resulting pale yellow slurry was left stirring overnight, prior to filtration. Cooling of the filtrate (5 °C) for three days provided **5** as colourless rectangular prisms that were isolated by further filtration (0.11 g, 37%), mp 321 °C. ^1H NMR (298 K): δ 7.42 (br s, 2H, Ar-*H*), 7.02 (m, 8H, Ar-*H*), 6.90 (m, 10H, Ar-*H*), 6.79–6.63 (m, 6H, Ar-*H*), 3.72 (s, 8H, CH_2Ph), 3.21 (q, 8H, OCH_2 , Et_2O , $^3J_{\text{HH}}$ 7.0 Hz), 1.09 (t, 12H, CH_3 , Et_2O , $^3J_{\text{HH}}$ 7.0 Hz). IR (Nujol)/cm⁻¹: 1600 (s), 1582 (s), 1450 (s), 1389 (s), 1366 (m), 1314 (w), 1264 (w), 1229 (s), 1154 (w), 1122 (w), 1081 (m), 1028 (m), 950 (w), 929 (m), 886 (w), 856 (w), 829 (w), 748 (s), 700 (s).

$\{\{\text{Na}(\mu_2\text{-}\eta^1\text{-}\eta^6\text{-O},\text{Ar-Odbp})(\text{DME})\}_2\}$ (**6**). The yellow solution stirred overnight, filtered, concentrated *in vacuo* and cooled to 0 °C to give large colourless square plates of **6** (0.09 g, 29%), mp 293 °C. ^1H NMR (298 K): δ 7.21 (m, 12H, Ar-*H*), 7.00 (m, 8H, Ar-*H*), 6.88 (m, 4H, Ar-*H*), 6.69 (m, 2H, Ar-*H*), 3.85 (s, 8H, CH_2Ph), 2.99 (s, 8H, OCH_2 , DME), 2.86 (s, 12H, OCH_3 , DME). $^{13}\text{C}\{^1\text{H}\}$ NMR (298 K): δ 153.2, 130.7, 128.6, 125.3, 124.8, 124.1, 122.3, 116.6 (s, Ar-*C*), 72.5 (s, OCH_2 , DME), 67.3 (s, OCH_3 , DME), 37.1 (s,

CH₂Ph). IR (Nujol)/cm⁻¹: 1601 (s), 1451 (s), 1366 (s), 1261 (m), 1229 (s), 1089 (m), 1028 (m), 950 (w), 923 (w), 761 (m), 755 (s), 698 (s), 668 (m).

[Na(μ₂:η¹:η³:η¹-O,Ar,O'-OdbpOMe)(THF)]₂ (7). The yellow solution was filtered and left to stand at 0 °C for four days. This yielded pale yellow cubic crystals of **7** in one crop (0.19 g, 55%), mp 123 °C. ¹H NMR (298 K): δ 6.78 (m, 4H, Ar-H), 6.72–6.59 (m, 8H, Ar-H), 6.42 (m, 4H, Ar-H), 6.17 (m, 6H, Ar-H), 3.54 (s, 8H, CH₂Ph), 3.34 (m, 8H, OCH₂, THF), 2.78 (s, 12H, OCH₃), 1.13 (m, 8H, CH₂, THF). ¹³C{¹H} NMR: (298 K): δ 157.2, 151.3, 130.9, 130.6, 128.8, 127.4, 127.2, 121.5, 119.4, 112.4 (s, Ar-C), 67.7 (s, OCH₂, THF), 56.1 (s, OCH₃), 31.2 (s, CH₂, THF), 25.6 (s, CH₂Ph). IR (Nujol)/cm⁻¹: 1594 (s), 1452 (s), 1383 (s), 1327 (m), 1294 (w), 1238 (s), 1166 (w), 1105 (m), 1077 (w), 1050 (m), 1022 (w), 905 (w), 866 (w), 805 (w), 766 (m), 744 (s), 727 (m).

[Na(μ₂:η¹:η²-O,Ar-OdbpOMe)(DME)]₂ (8). The pale yellow solution was filtered and the filtrate (concentrated to ca. 3 cm³) cooled to 0 °C to give **8** as colourless square plates (0.16 g, 45%), mp 114 °C. Found: C 69.87, H 7.17; C₅₂H₆₂Na₂O₁₀ requires C 69.94, H 7.00%. ¹H NMR (298 K): δ 7.02–6.95 (m, 10H, Ar-H), 6.83–6.76 (m, 4H, Ar-H), 6.58–6.51 (m, 8H, Ar-H), 3.91 (s, 8H, CH₂Ph), 3.29 (s, 8H, OCH₂, DME), 3.15 (s, 12H, OCH₃, DME), 3.06 (s, 12H, CH₃). ¹³C{¹H} NMR (298 K): δ 164.5, 156.2, 130.3, 129.8, 127.7, 127.1, 125.9, 120.3, 111.2, 110.9 (s, Ar-C), 70.7 (s, OCH₂, DME), 57.5, 54.9 (s, OCH₃, -OdbpOMe and DME), 30.1 (s, CH₂Ph). IR (Nujol)/cm⁻¹: 1601 (m), 1452 (s), 1366 (s), 1260 (w), 1229 (s), 1105 (w), 1028 (w), 949 (w), 923 (w), 829 (w), 797 (w), 755 (s), 698 (s), 668 (w).

[Na(μ₃-Ombp)(DME)]₄ (9). A thick walled Carius tube was charged with freshly cut sodium pieces (0.05 g, 2.17 mmol) and HOdbp (0.30 g, 1.10 mmol). The tube was evacuated to 2 mbar, sealed and heated to 150 °C. The tube was cooled to ambient temperature over 6 h after 3 days heating to give an amorphous colourless solid intermixed with unreacted sodium. Extraction with DME (20 cm³), concentration *in vacuo* (ca. 5 cm³) and placement at -5 °C gave **9** as several colourless trapezoidal prisms. No characterisation, other than X-ray structure determination and unit cell analyses⁶⁴ was undertaken due to the quantity of **9** isolated.

X-Ray crystal structure determination

Crystalline samples of compounds **1–9** were mounted on glass fibres in silicone oil at -150(2) °C (123 (2) K). A summary of crystallographic data can be found in Table 1 (**1–4** and HOdbpOMe) and **2 (5–9)**. Hydrogen atoms were refined in calculated positions (riding model) for compounds **1–9**. For HOdbpOMe, hydrogen atoms were located from difference maps and refined isotropically. Data were collected on an Enraf-Nonius Kappa CCD diffractometer using graphite-monochromated Mo-Kα X-ray radiation (λ = 0.71073 Å). Data were corrected for absorption by the DENZO-SMN package.⁶⁶ Lorentz polarization and absorption corrections were applied. Structural solution and refinement was carried out using the SHELX suite of programs⁶⁷ with the graphical interface X-seed.⁶⁸

CCDC reference numbers 299151–299160.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602706g

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