Synthesis of mono- and di-potassium salts and methoxy adducts of sulfur-bridged biphenols by selective deprotonation †

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Treatment of the sulfur-bridged biphenol $[1,1'-S(2-HOC_6H_2Bu^t-3-Me-5)_2]$ with potassium hydride in diethyl ether results in the selective deprotonation of one phenol group to yield $[1,1'-S(2-KO)(2'-HO)(C_6H_2Bu^t-3-Me-5)_2(Et_2O)]$, whereas an excess of potassium hydride in thf is required to generate the dianion $[1,1'-S(2-KOC_6H_2Bu^t-3-Me-5)_2-(thf)_2]$; the same selective deprotonation is observed for the binaphthol $[1,1'-S(2-HOC_{10}H_4Bu^t_2-3,6)_2]$, suggesting that intramolecular H-bonding stabilises the second, remaining hydroxyl group, allowing new, simple routes to tuneable, mono- or di-anionic aryloxide-based ligands.
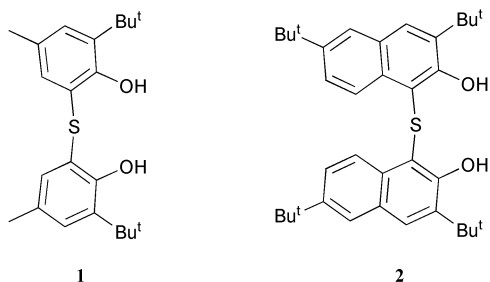
The d-block chemistry of sulfur bridged biphenolates based on **1** has been studied in depth in recent years. It has already been show that lithiation of the biphenol allows easy access to $[Ti[1,1'-S(2-OC_6H_2Bu^t-3-Me-5)_2](Cl)_2]$, an excellent precatalyst for the polymerisation and copolymerisation of alkenes in conjunction with a cocatalyst methylalumoxane (MAO).[1] In the course of our investigations on new f-block adducts of 2,2'-thiobis-(2,4-di-*tert*-butylphenol) $[1,1'-S(2-HOC_6H_2Bu^t-3-Me-5)_2]$, **1** and its naphthyl analogue, 2,2'-thiobis-(2,4-di-*tert*-butylnaphthol) $[1,1'-S(2-HOC_{10}H_4Bu^t_2-3,6)_2]$ **2**, we found that tris(aryloxide)lanthanide(III) complexes react cleanly with dilithiated **1** – $[S(LiOC_6H_2Bu^tMe)_2]$ to give pentane-insoluble lithium aryloxide as a byproduct.[2] However, it is now widely accepted that the use of potassium salts gives cleaner metathesis chemistry for the f-block elements, and reduces salt incorporation. Since it is desirable to use metathetical routes to access many new f- as well as new d-block systems of the sulfur-bridged biphenolates, we have studied the Group 1 chemistry of **1** and **2**. Traditionally, phenols are cleanly deprotonated by treatment with one equivalent of potassium hydride in any ethereal solvent in which the phenol is soluble. A macrocyclic analogue of **1**, *p-tert*-butyltetrathiacalix[4]arene has been reported; only the monopotassium salt is reported to be accessible.[3]

Herein, we show that stabilisation of the monoanion of **1** or **2** allows either mono- or di-anionic biphenolate and binaph-

tholates to be synthesised cleanly. This provides potentially tridentate ligands that have a tuneable balance between electric charge and donor functional group type and strength.

Addition of an ethereal solution of **1** to a stirred suspension of stoichiometric KH in diethyl ether affords an analytically pure pale yellow precipitate characterised as the monopotassium salt, $[1,1'-S(2-KO)(2'-HO)(C_6H_2Bu^t-3-Me-5)_2-(Et_2O)]$ **3**, isolated in 82% yield,‡ Scheme 1. ^{1}H NMR spectroscopic analysis of a d_6-benzene solution of **3** reveals the remaining OH resonates at 14.9 ppm (fwhm 50 Hz), compared with 6.6 ppm in **1**. This contrasts with the synthesis of the lithiated derivatives that afford only the doubly deprotonated material. To confirm the composition, flame photometry (K content) analysis and a crystal X-ray structural determination, Fig. 1 have been carried out.

Scheme 1

The structure of **3** is dimeric and diethyl ether solvated. The anionic O of each ligand bridges the two potassium centres, and in an unprecedented binding mode for this ligand, the neutral phenol of each bridges the two potassium ions. The K–phenoxide distance is 2.6778(11) Å, much shorter than the mean K–O distance measured for a range of terminal K phenoxides (2.765 Å).[4] Although the two rings are dissimilar in the solid state, solution characterisation shows them to be equivalent at room temperature; the molecule of diethyl ether remaining bound to each metal. Of the few reported potassium complexes which are stabilised by thioether interactions, structural data show K · · · S distances that range from 3.222 to 3.496 Å.[5] In this complex, only the closest S atom is deemed to interact. The K–S distance of 3.3145(7) Å is only 0.112 Å longer than other examples of K–S single bonds,[6] implying a significant K–S interaction in the solid state.[7]
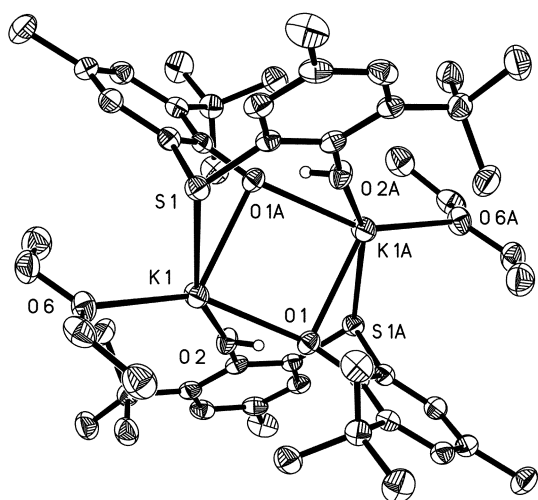
Fig. 1 Ellipsoid drawing (50%) of the molecular structure of **3**. Selected distances (Å) and angles (°): K(1)–O(1) 2.6778(11), K(1)–O(1A) 2.7012(12), K(1)–O(6) 2.7064(12), K(1)–O(2) 2.7428(12), K(1)–S(1) 3.3145(7), K(1)–K(1A) 3.9412(9); O(1)–K(1)–O(1A) 85.78(4), O(1)–K(1)–O(6) 148.17(4) O(1)–K(1A)–O(2) 53.74(3).

Repetition of this reaction in thf, using two equivalents or an excess of KH, affords the dipotassium [1,1′-S(2-KOC$_6$H$_2$Bu^t-3-Me-5)$_2$(thf)$_2$] **4**.

The binaphthol **2** can also be converted cleanly into a mono- or a di-potassium salt, **5** and **6** in Scheme 2. The selectivity is still quantitative (as measured spectroscopically) for the products.
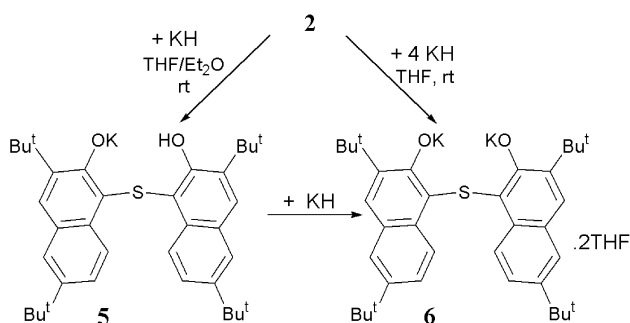
Scheme 2

Crystals of **5** suitable for single crystal X-ray diffraction were grown under identical conditions to **3**,§ but show a mono-nuclear structure, Fig. 2. The triangle of [OSO] donor atoms facially caps only one K ion rather than capping a K$_2$ fragment of the dimeric **3**. The hydroxyl H was not located, even though K–O(2) is significantly longer than K–O(1). Here, a longer K–S interaction of 3.436(3) Å is measured.

The monopotassium salt of *p-tert*-butyltetrathiacalix[4]arene forms K-sandwiched calixarene dimers with K–O distances of 2.796 Å,[3] longer than all the ionic K–O bond distances in **3** and **5**, with OH ··· O and K interactions complicated by disorder, and K–S distances 3.335(1) and 3.348(1) Å – intermediate between the structures described above. No π-stacking inter-actions or close K–H contacts are observed in either structure.

Interestingly, although the solid state structures of **3** and **5** are very different, in each the K–O–C angles are close to linear, and the O(H)–K–O angle is particularly acute – 53.7 and 52.1° respectively – significantly narrower than the C–S–C angle that would normally determine this parameter (105.61(8) and 107.3(3)° for **3** and **5** respectively). It is possible that a sym-metrical disposition of the remaining hydroxyl H between the two O atoms renders the rings approximately equivalent even in a non-fluxional system as is observed in the ¹H NMR spectra,
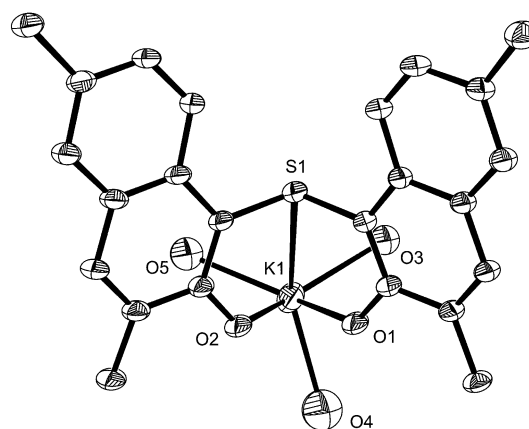
and this interaction favours the first deprotonation over the second in the reaction solution.

Thus a monophenolic alternative to **1**, with potentially hemi-labile O and S donor groups, is now a viable alternative ligand with a reduced electrical requirement. Both the mono- and di-potassium salts may be quenched with methyl iodide to afford **7** and **8** respectively in quantitative yield, Scheme 1. Compound **8** has been reported previously.[8]

The tetrathiacalixarene *p-tert*-butylthiacalix[4]arene has recently been proposed as an alternative to non-sulfur-containing calixarenes in the coordination of Group 1 metals, producing different structural types for different members of the series, with the metal ions and remaining hydroxyl protons often disordered over the phenolic sites.[3] The non-macrocyclic ligands described above show selective deproto-nation chemistry, creating new, simple routes to tuneable, mono- or di-anionic aryloxide-based ligands.

Fig. 2 Ellipsoid drawing (50%) of the molecular structure of **5**, Bu^t methyl groups and solvent Et groups omitted for clarity. Selected distances (Å) and angles (°): K(1)–S(1) 3.436(3), K(1)–O(1) 2.776(6), K(1)–O(2) 2.697(7), K(1)–O$_{ether}$ range 2.666(7)–2.80(2); O(1)–K(1)–O(2) 52.1(2), O(1)–K(1)–O(3) 96.3(3), O1–K1–S1 55.89(11).

Notes and references

‡ Data for **3**: 82%. δ_H (C$_6$D$_6$): 14.9 (br s, 1H, O*H*), 7.65 (s, 2H, aryl *H*), 2.19, (s, 6H, methyl C*H$_3$*), 1.46 (s, 18H, Bu^t), 3.24, 1.13 (q, t, 4H, 3H, (CH$_3$C*H$_2$*)$_2$O). ν/cm⁻¹: 3426.5. Calc.(found) C$_{22}$H$_{29}$O$_2$SK·Et$_2$O: C 66.34 (66.28), H 8.35 (8.29%). Flame photometry – Calc. (found): K 8.31 (8.50%). C$_{44}$H$_{58}$O$_4$S$_2$K$_2$·(C$_4$H$_{10}$O)$_2$, *M* = 941.46, monoclinic, *a* = 12.065(2), *b* = 17.968(3), *c* = 12.609(3) Å, *a* = 90, *β* = 99.857(4), *γ* = 90°, *U* = 2693.1(9) Å³, *T* = 150(2) K, *P*2₁/*c*, *Z* = 2, *D$_c$* = 1.161 g cm⁻³, *μ*(Mo-K*α*) = 0.297 mm⁻¹, 6310 unique reflections (*R*$_{int}$ 0.0579). *R*$_1$ [4477 *F* > 4σ(*F*)] = 0.0405, w*R*(all *F*²) 0.0952. For **4**: 63%. δ_H (C$_6$D$_6$): 7.47, 7.00 (s, 1H, aryl *H*), 1.96 (s, 3H, C*H$_3$*), 1.62 (s, 9H, Bu^t). Calc.(found) C$_{22}$H$_{28}$O$_2$SK$_2$: C 60.78 (60.51), H 6.41 (6.69%). Flame photometry – Calc.(found) [M·2thf] 13.51 (13.78%). For **5**: 58%. δ_H (C$_6$D$_6$): 1.31 (s, 9H, 6-Bu^t). 1. 58 (s, 9H, 3-Bu^t), 7.76 (s, 2H, 4-H, 5-H), 7.73 (s, 1H, 7-H), 9.40 (d, 1H, 8-H, ³*J*$_{HH}$ 8.73 Hz). ν/cm⁻¹: 3338.39. Calc.(found) C$_{36}$H$_{45}$O$_2$SK: C 74.48 (74.64), H 7.76 (7.89%). C$_{36}$H$_{45}$O$_2$SK·(C$_4$H$_{10}$O)$_{3.5}$, *M* = 840.30, monoclinic, *a* = 12.9794(15), *b* = 23.913(3), *c* = 17.896(2) Å, *V* = 5216.5(11) Å³, *T* = 150(2) K, *P*2₁/*c* (no. 14), *Z* = 4, *D$_c$* = 1.070 g cm⁻³, *μ*(Mo-K*α*) = 0.717 mm⁻¹, 12542 unique reflections (*R*$_{int}$ 0.047). *R*$_1$ [5471 *F* > 4σ(*F*)] = 0.124, w*R*(all *F*²) 0.328. CCDC reference numbers 202297 and 202298. See http://www.rsc.org/suppdata/dt/b3/b301015e/ for crystallographic data in CIF or other electronic format. For **6**: 89%. NMR/C$_6$D$_6$ δ_H: 14.2 (s, fwhm 561 Hz, 1H, O*H*), 1.29 (br s, 9H, 6-Bu^t), 1. 47(br s, 9H, 3-Bu^t), 7.65 (br, 4H, 4-H, 5-H, 7-H, 8-H), 3.52 (br m, 2H, thf), 1.39 (br m, 2H, thf). Calc.(found) C$_{36}$H$_{44}$O$_2$SK$_2$: C 69.85 (67.87), H 7.16 (7.69%). HRMS Calc.(found) [MH]⁺ 618.2336 (619.2345).

§ Dietherate: 10⁻³mbar/20 °C/8 h. Solvent-free: 10⁻³mbar/50 °C/16 h.

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