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Revisiting the Schlenk dimerisation reaction of 1,1-diphenylethene

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ABSTRACT

The reaction between 1,1-diphenylethene and two equivalents of lithium in THF gave the complex [($Ph_2CCH_2CH_2CPh_2$)Li_2(THF)$_4$] (**3**), which crystallised from Et_2O/THF as the dialkyllithate salt [Li(THF)$_4$][($Ph_2CCH_2CH_2CPh_2$)Li(THF)] (**3a**). A similar reaction between 1,1-diphenylethene and sodium metal in THF gave [($Ph_2CCH_2CH_2CPh_2$)Na_2(THF)$_{1.5}$] (**4**), which crystallised from THF as the polymer [($Ph_2CCH_2CH_2CPh_2$)Na_2(THF)$_3$]$_\infty$ (**4a**). In contrast, reactions between 1,1-diphenylethene and potassium under the same conditions gave intractable mixtures of products. However, treatment of **3** with two equivalents of KO*t*Bu in THF yielded the complex [($Ph_2CCH_2CH_2CPh_2$)K_2(THF)$_{0.5}$] (**5**) as a deep red powder; treatment of **5** with two equivalents of 12-crown-4, followed by crystallisation from methylcyclohexane/THF, gave the adduct [($Ph_2CCH_2CH_2CPh_2$)K_2(THF)$_2$(12-crown-4)$_2$] (**5a**). A similar reaction between **3** and 12-crown-4 gave the separated ion pair [Li(THF)(12-crown-4)][Li(THF)$_{0.5}$(OEt_2)$_{0.5}$(12-crown-4)]($Ph_2CCH_2CH_2CPh_2$) (**3b**), which contains the free 1,1,4,4-tetraphenyl-1,4-butanediide dicarbanion. X-ray crystallography revealed that the C_3C centres of the ligands adopt a near planar geometry, irrespective of whether a metal cation is in close contact.

1. Introduction

The reaction of 1,1-diphenylethene with lithium was first investigated by Wilhelm Schlenk in the early 20th century and was shown to yield dilithio-1,1,4,4-tetraphenyl-1,4-butanediide via a radical coupling reaction, which has become known as the Schlenk dimerisation reaction (Scheme 1) [1]. The 1,1,4,4-tetraphenyl-1,4-butanediide dicarbanion has subsequently been shown to initiate the living anionic polymerisation of alkene and diene monomers, most notably in the polymerisation of 1,3-butadiene to give 1,4-*cis*-poly(butadiene) [2].

Subsequently, J. J. Eisch and co-workers showed that this dimerisation reaction could also be applied to silicon-substituted alkenes [3] and later M. Kira, H. Sakurai and co-workers extended this to include 1,1-bis(trimethylsilyl)ethene [4]; the 1,4-dicarbanion derived from this latter precursor has been employed extensively for the synthesis of numerous ground-breaking heavier main group element compounds [5]. A similar Schlenk dimerisation reaction between alkali metals and phosphine- or phosphine-borane-substituted alkenes was shown to yield the correspondingly substituted 1,4-dicarbanions [6]. The common thread that links the precursors for these reactions is the presence of charge-delocalising groups which stabilise both the intermediate radical anion species and the resulting 1,4-dicarbanion.

While the silyl- and phosphine/phosphine-borane-substituted 1,4-dicarbanions described above have been the subject of extensive structural and solution-state NMR investigations [3,4,6], there is only a single report relating to the solid-state structures of complexes of the 1,1,4,4-tetraphenyl-1,4-butanediide dianion itself: in 1991 H. Bock and co-workers reported the synthesis and solid-state structures of [($Ph_2CCH_2CH_2CPh_2$)Li_2(OEt_2)$_4$] (**1**) and [($Ph_2CCH_2CH_2CPh_2$)Na_2(OEt_2)$_2$]$_\infty$ (**2**) [7]. Both **1** and **2** were synthesised via the Schlenk dimerisation of 1,1-diphenylethene with the respective alkali metal in diethyl ether. While **1** adopts a monomeric structure, in which each carbanion centre is associated with a single lithium cation, compound **2** crystallises with a complex one-dimensional polymeric structure containing two distinct types of sodium cation: one coordinated by two carbanion centres from adjacent ligands and the second coordinated by the phenyl rings of a single ligand, to give what might be described as a polymeric sodium dialkylsodate (Chart 1).

Since the structural motif adopted by organo-alkali metal compounds is highly dependant on the nature of the metal and the presence of co-ligands, we were interested to observe the structural impact of replacing diethyl ether with the stronger donor ligand THF in the Schlenk dimerisation of 1,1-diphenylethene. We report here the structures of several complexes of the resulting 1,4-dicarbanion, including

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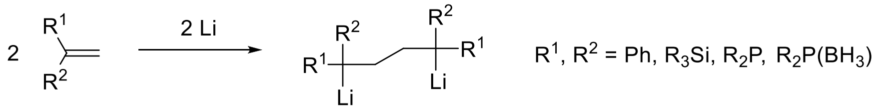
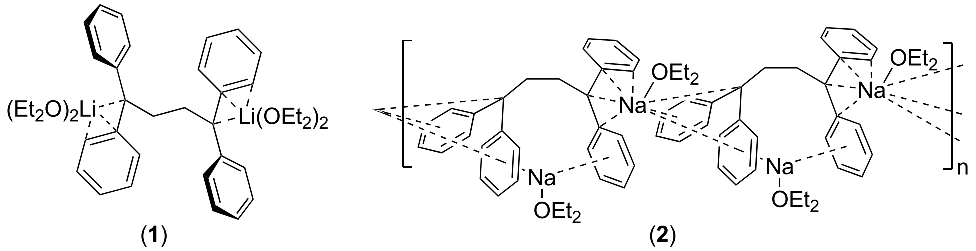
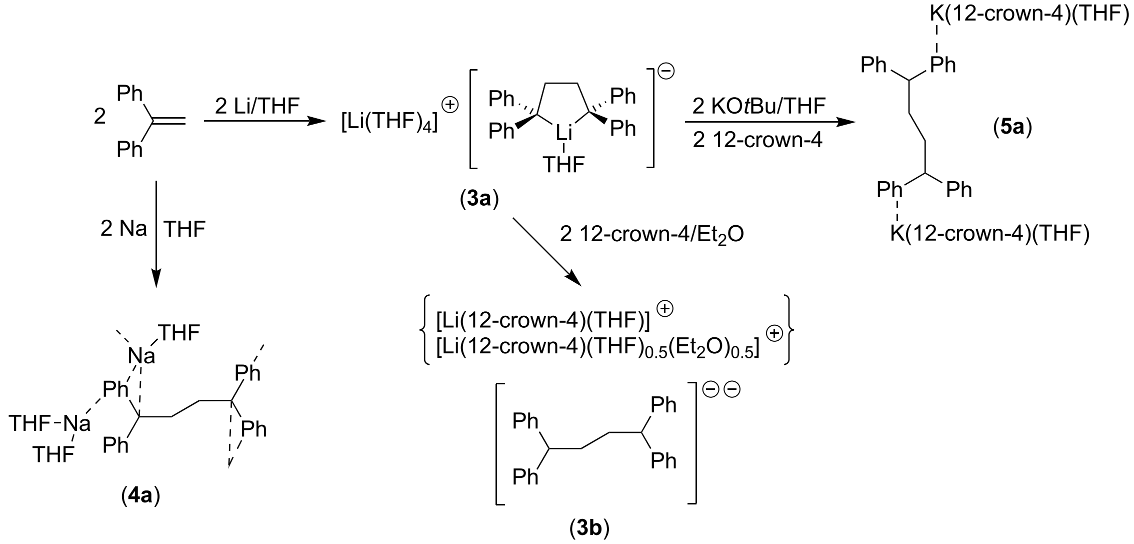


Scheme 1. The Schlenk dimerisation of activated alkenes.



(**1**) (**2**)

Chart 1. .



Scheme 2. Products of the Schlenk dimerisation of 1,1-diphenylethene in THF.

the first potassium derivative, and demonstrate the effect of co-ligands on the structural motif adopted.

2. Results and discussion

The reaction between 1,1-diphenylethene and lithium pieces in THF proceeded rapidly to give the corresponding 1,4-butanediide complex, $[(Ph_2CCH_2CH_2CPh_2)Li_2(THF)_4]$ (**3**) as an air-sensitive deep red powder; single crystals suitable for X-ray crystallography of the alternative solvate $[Li(THF)_4][(Ph_2CCH_2CH_2CPh_2)Li(THF)]$ (**3a**) were isolated from cold diethyl ether containing a few drops of THF (Scheme 2). Exposure of crystalline **3a** to vacuum led to a loss of crystallinity, with concomitant loss of one molecule of coordinated THF to regenerate **3**. We note that the composition of **3a** is identical to that of Kira and Sakurai's silicon-substituted analogue $[(Me_3Si)_2CCH_2CH_2C(SiMe_3)_2]Li_2(THF)_5$, although the structure of this latter species is as yet unknown [4,5f]. A similar reaction between 1,1-diphenylethene and a sodium mirror in THF gave the corresponding sodium complex $[(Ph_2CCH_2CH_2CPh_2)Na_2(THF)_{1.5}]$ (**4**), which was obtained as single crystals of the alternative solvate $[(Ph_2CCH_2CH_2CPh_2)Na_2(THF)_3]_\infty$ (**4a**) after crystallisation from cold diethyl ether. Compound **4a** loses coordinated solvent on exposure to vacuum, eventually yielding **4**, according to ^{1}H NMR spectroscopy.

While **3** and **4** are easily obtained via this route, the corresponding reaction between **1** and a potassium mirror led to a complex mixture of products, possibly due to competing potassium-mediated Ph-C cleavage reactions or Birch-type reduction of the aromatic rings. However, a metathesis reaction between in situ-prepared **3** and two equivalents of KO*t*Bu in THF gave $[(Ph_2CCH_2CH_2CPh_2)K_2(THF)_{0.5}]$ (**5**) as a deep red powder. Unfortunately, we were unable to crystallise **5** in a form suitable for X-ray crystallography. However, treatment of **5** with two equivalents of 12-crown-4, followed by crystallisation from a THF solution layered with methylcyclohexane, gave the adduct $[(Ph_2CCH_2CH_2CPh_2)K_2(THF)_2(12\text{-crown-}4)_2]$ (**5a**). A similar reaction between **3** and 12-crown-4 gave the separated ion pair $[Li(THF)(12\text{-crown-}4)][Li(THF)_{0.5}(OEt_2)_{0.5}(12\text{-crown-}4)](Ph_2CCH_2CH_2CPh_2)$ (**3b**), containing the free 1,4-dicarbanion, after crystallisation from THF/Et_2O; this compound loses coordinated solvent on exposure to vacuum to give a compound of formula $[(Ph_2CCH_2CH_2CPh_2)Li_2(12\text{-crown-}4)_2(THF)(OEt_2)_{0.5}]$ (**3c**), according to ^{1}H NMR spectroscopy.

The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **3, 3c, 4**, and **5** are as expected; compound **5a** has limited solubility in organic solvents, including benzene, toluene and THF and so was not amenable to analysis by NMR spectroscopy. In each case the ^{1}H and $^{13}C\{^1H\}$ NMR signals corresponding to the 1,1,4,4-tetraphenylbutane-1,4-diide ligand are almost identical, despite the different structures adopted by these compounds in the solid state (see below); for example, in the $^{13}C\{^1H\}$ NMR spectra the carbanion centres give rise to peaks at 82.0 (**3**), 85.9 (**3c**), 80.3 (**4**) and

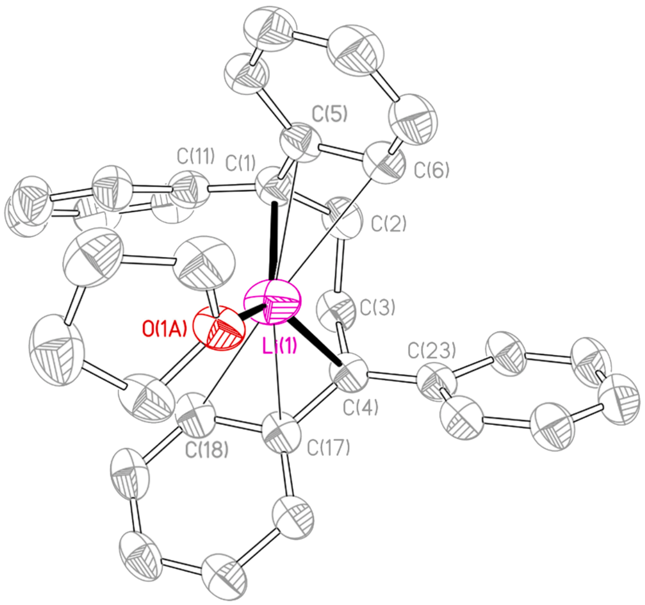


Fig. 1. Structure of one of the two crystallographically independent anions of **3a** with 40% probability ellipsoids and with H atoms omitted for clarity. Selected bond lengths and angles [values for the second anion in the asymmetric unit in square brackets]: Li(1)-C(1) 2.264(4) [Li(3)-C(49) 2.235(4)], Li(1)-C(4) 2.251(4) [Li(3)-C(52) 2.211(4)], Li(1)-O(1A) 1.909(8) [Li(3)-O(6A) 1.892(9)], C(1)-C(5) 1.452(3) [C(49)-C(53) 1.451(3)], C(1)-C(11) 1.440(3) [C(49)-C(59) 1.444(3)], C(4)-C(17) 1.444(3) [C(52)-C(65) 1.445(3)], C(4)-C(23) 1.445(3) [C(52)-C(71) 1.450(3)], C(1)-Li(1)-C(4) 88.28(16) [C(49)-Li(3)-C(52) 90.31(16)], C(5)-C(1)-C(2) 118.83(19), C(5)-C(1)-C(11) 123.00(19), C(2)-C(1)-C(11) 117.80(19), C(3)-C(4)-C(17) 118.56(19), C(3)-C(4)-C(23) 116.56(18), C(17)-C(4)-C(23) 123.34(19) [C(50)-C(49)-C(53) 118.49(18), C(50)-C(49)-C(59) 117.71(17), C(53)-C(49)-C(59) 123.27(18), C(51)-C(52)-C(65) 116.88(17), C(51)-C(52)-C(71) 117.81(19), C(65)-C(52)-C(71) 123.64(18)].

84.9 ppm (**5**). This clearly suggests that these compounds adopt similar structures in the strong donor solvent THF.

Attempts to obtain variable-temperature ^{7}Li NMR spectra of **3** in d_8-toluene were frustrated by its poor solubility in this solvent, which led to significant amounts of crystalline material being deposited in the NMR tube and very poor signal quality. Despite the two lithium environments observed in the solid state structure of **3a**, only a single signal was observed in the ^{7}Li NMR spectrum of this compound in d_8-THF, in which this compound has much greater solubility, and no change in the spectrum was observed down to 213 K. This suggests either the formation of a species containing a single lithium environment (*e.g.* a separated ion triple such as $[Li(THF)_4]_2[Ph_2CCH_2CH_2CPh_2]$), or else rapid dynamic equilibrium between species on the NMR time scale in this solvent. Nonetheless, in the variable-temperature ^{1}H NMR spectra of **3**, significant line-broadening of the signals due to the *ortho-* and *meta*-protons of the phenyl rings at low temperatures suggests restricted rotation about the C-C(Ph) bonds in this compound (see the Supporting Information).

Compound **3a** crystallises as a separated ion pair with two crystallographically independent cations and anions in the asymmetric unit. The cation consists of a typical $[Li(THF)_4]^+$ ion, while the anion comprises a cyclic dialkyllithate ion. This is significantly different to the diethyl ether adduct **1** reported by Bock and co-workers [7], which crystallises as a molecular species in which each end of the dicarbanion coordinates a separate lithium ion.

In spite of the wide structural variety of organolithium compounds, few diorganolithate salts, containing a $[R_2Li]^-$ anion, have been isolated. Structurally characterised examples are limited to complexes of cyclic and acyclic silicon-stabilised (di)carbanions [8], a small number of phosphorus-stabilised carbanion complexes [9], and a single example of a benzylic carbanion system free from additional stabilisation by a silicon substituent [10]. In this regard, the reaction between (*Z*)−1,2-bis(trimethylsilyl)−1-phenylethene and lithium metal in THF has been shown to generate a mixture of the doubly reduced species $[(Me_3Si)PhCCH(SiMe_3)]Li_2$ and the Schlenk dimerisation product $[(Me_3Si)PhCCH(SiMe_3)CH(SiMe_3)CPh(SiMe_3)]Li_2$ (**6**), according to ^{1}H, $^{13}C\{^1H\}$ and ^{6}Li NMR spectroscopy [11]. A dialkyllithate structure was proposed for the latter, based on the observation of two ^{6}Li NMR signals at 0.37 and −1.20 ppm in solution, which were attributed to the dialkyllithate anion and the lithium cation, respectively. However, no data on the solid state structure of **6** are available.

The structure of one of the crystallographically independent anions of **3a** is shown in Fig. 1, along with selected bond lengths and angles; the structure of the $[Li(THF)_4]^+$ cation is unremarkable. The lithium ion in the anionic component of **3a** is coordinated by the two carbanion centres of the 1,1,4,4-tetraphenyl-1,4-butanediide ligand to give a five-membered chelate ring (C-Li-C bite angles 88.28(16)° and 90.31(16)° for the two independent molecules in the asymmetric unit) and by a molecule of THF. Additionally, the lithium ions in the anionic components have short contacts to the *ipso* and *ortho* carbons of a phenyl ring at each end of the ligand. The Li-C(carbanion) distances in **3a** range from 2.211(4) to 2.264(4) Å and are similar to the Li-C distances in other dialkyllithate anions; for example, the Li-C distances in $[Li(TMEDA)_2][(TMEDA)Li(CH_2C_6H_3\text{–}3,5\text{-}Me_2)_2]$ are 2.257(7) and 2.325(7) Å [10], while the Li-C distances in the contact ion dialkyllithate complex $[(THF)_3Li\{(Me_3Si)_2CPMe_2(BH_3)\}_2Li]$ are 2.249(8) and 2.252(8) Å [9b]. However, these distances are somewhat longer than the Li-C(carbanion) distances in the closely related phenyl-substituted dialkyllithate complexes $[Li(THF)_4][Li\{CRPh_2\}_2]$ (R = $SiMe_3$ 2.141(4) Å; R = $SiMe_2Ph$ 2.124(3) Å) [8e], possibly reflecting the lower coordination number of the lithium ion in the latter compounds.

Compound **3b** crystallises as a separated ion triple containing an isolated 1,1,4,4-tetraphenyl-1,4-butandiide anion, along with two $[Li(12\text{-crown-}4)(L)]^+$ cations, in one of which the lithium ion is coordinated by a molecule of THF and in the other of which the lithium ion is coordinated by a disordered mixture of THF and diethyl ether, each with 50% occupancy (Fig. 2). The asymmetric unit contains one of each cation and one half of each of two crystallographically independent anions, each half of which is related by a centre of inversion.

Perhaps surprisingly, the skeletal structure of the carbanion centres in **3b** is very similar to those in the cyclic dialkyllithate anion in **3a**; neither the two Li-C(carbanion) contacts nor the significantly different ligand conformation (*i.e.* chelating *versus* linear) appears to have any significant impact. The C(carbanion)-C(Ph) distances in **3b** [1.439(3) and 1.429(3) Å (1.434(3) and 1.429(3) Å in the second dicarbanion in the asymmetric unit)] are slightly shorter than the corresponding distances in **3a** [range 1.440(3) to 1.452(3) Å]; however, the sum of C—C-C angles at the carbanion centres is essentially 360° in both compounds (see below).

Compound **4a** crystallises with a complex structure containing two types of sodium ion and two distinct ligand environments; the solid-state structure of **4a** is shown in Fig. 3, along with selected bond lengths and angles. The two sodium cations lie in quite different coordination environments: Na(1) has short contacts to the carbanion centre and the *ipso-* and *ortho*-carbon atoms of one phenyl ring from dicarbanion 1, the O atom of a molecule of THF, and an η^6-phenyl ring from dicarbanion 2; in addition, this sodium ion has a short contact to one of the methylene carbon atoms in ligand 1. In contrast, Na(2) is coordinated by an η^4-phenyl ring from ligand 1, such that this ring forms an η^2:η^4 bridge between Na(1) and Na(2). This ion is further coordinated by two molecules of THF and an η^6-phenyl ring from ligand 2, such that this phenyl ring forms an η^6:η^6 bridge between Na(2) and its symmetry equivalent. Somewhat surprisingly, there are no short contacts between either Na(1) or Na(2) and the carbanion centres of ligand 2, nor any contacts between Na(2) and the carbanion centres in ligand 1; only Na(1)-C(carbanion, ligand 1) contacts are evident. The numerous multihapto interactions

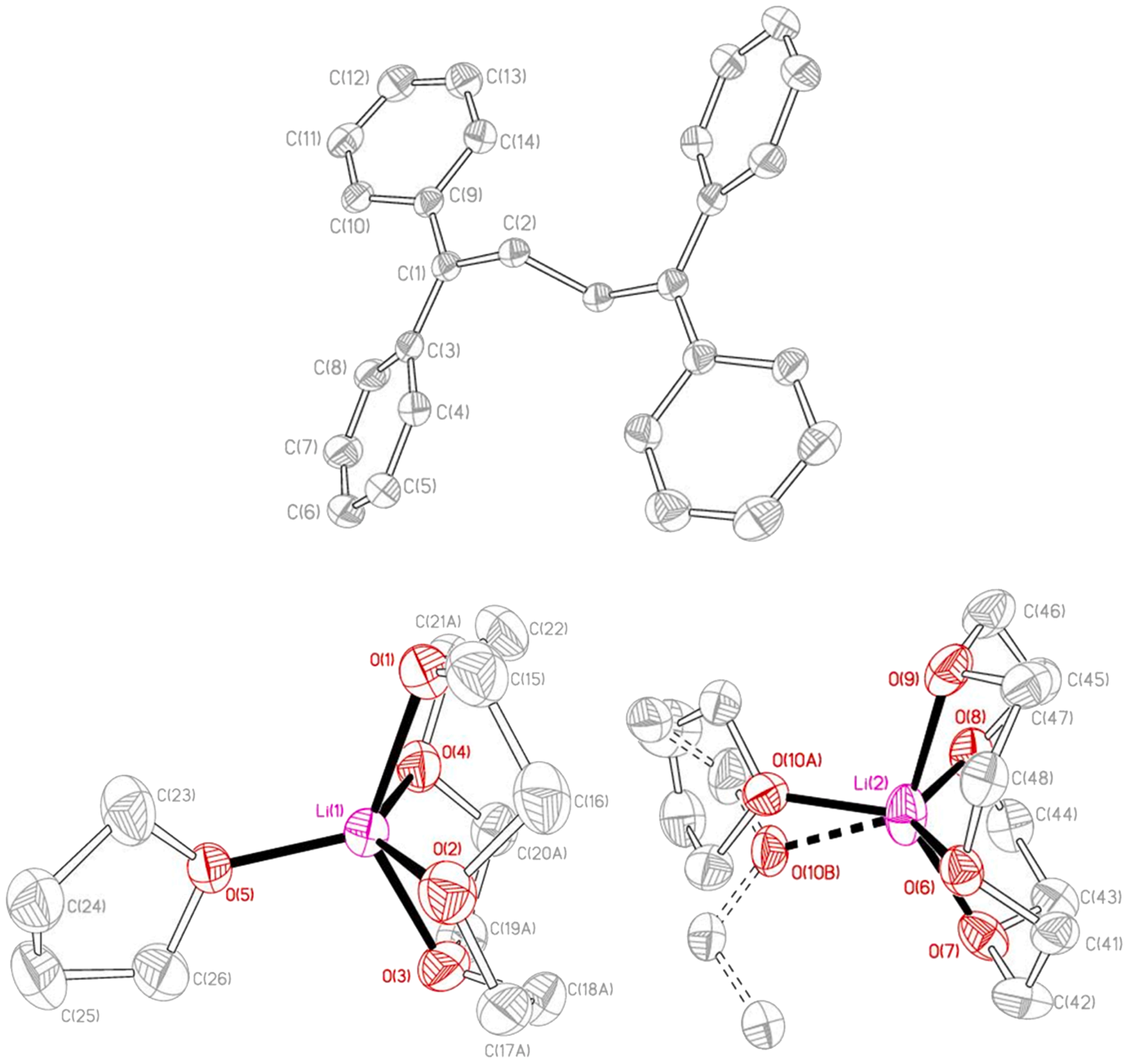


Fig. 2. Solid-state structure of **3b** with 40% probability ellipsoids and with H atoms omitted for clarity (only one of the two crystallographically independent anions is shown). Selected bond lengths (Å) and angles (°) [values for the second independent anion in the asymmetric unit in square brackets]: Li(1)-O(1) 2.068(4), Li(1)-O(2) 2.085(4), Li(1)-O(3) 2.024(4), Li(1)-O(4) 2.080(4), Li(1)-O(5) 1.895(4), Li(2)-O(6) 2.067(4), Li(2)-O(7) 2.098(5), Li(2)-O(8) 2.051(4), Li(2)-O(9) 2.141(5), Li(2)-O(10A) 1.922(5), Li(2)-O(10B) 2.024(6), C(1)-C(2) 1.518(3) [C(27)-C(28) 1.520(3)], C(1)-C(3) 1.439(3) [C(17)-C(29) 1.434(3)], C(1)-C(9) 1.429(3) [C(27)-C(35) 1.429(3)], C(2)-C(1)-C(3) 116.76(16) [C(28)-C(27)-C(29) 117.71(16)], C(2)-C(1)-C(9) 118.75(15) [C(28)-C(27)-C(35) 118.09(15)], C(3)-C(1)-C(9) 124.44(17) [C(29)-C(27)-C(35) 124.06(16)].

between the sodium ions and the dicarbanion ligands result in the formation of a complex sheet polymer.

Once again, the structure of **4a** is substantially different to that of **2** reported by Bock and co-workers, in which the dicarbanion ligand sandwiches one sodium ion between two of its phenyl rings, while the second sodium ion has short contacts to the carbanion centres of two adjacent ligands [7]. However, multihapto Ph···Na interactions are prevalent in both structures. The Na(1)-C(carbanion) distance in **4a** [2.8025(15) Å] is somewhat shorter than the Na-C(carbanion) distance in **2** (3.03 Å), but is typical of contacts between a sodium ion and a delocalised η^3 carbanion system (typical range 2.63–3.00 Å) [12].

Compound **5a** represents the first time that the solid-state structure of a potassium complex of the 1,1,4,4-tetraphenyl-1,4-butanediide ligand has been determined; this compound crystallises as a molecular species with a centre of symmetry midway along the C(2)-C(2A) vector. The molecular structure of **5a** is shown in Fig. 4, along with selected bond lengths and angles. Each potassium cation is coordinated by the four oxygen atoms of a 12-crown-4 ligand, a molecule of THF and an η^6-phenyl ring from the dicarbanion ligand, along with short C···K contacts to two of the methylene carbons of the 12-crown-4 ligand. There are no short contacts between the potassium cations and the carbanion centres. This is consistent with the noted preference for the heavier alkali metals to engage in multihapto M···arene interactions rather than M-C(carbanion) contacts [12]. For example, in the series of complexes (Me_6TREN)M($CH_2C_6H_3$–3,5-Me_2) (M = Li, Na, K) the solid-state structures of the lithium and sodium complexes exhibit M-CH_2 contacts, but no M… arene contacts, whereas, the solid-state structure of the potassium complex exhibits solely K…arene contacts [Me_6TREN = N($CH_2CH_2NMe_2$)$_3$] [13]. The K···C distances (3.1016(12)−3.4200(15) Å) are similar to those previously reported for the K···(η^6-arene) distances in polymeric [{PhC($SiMe_3$)$_2$}K]$_n$ (3.093(2)−3.522(2) Å) [14].

In all of the compounds **3a, 3b, 4a** and **5a** the C_3C skeletons of the carbanion centres are essentially planar, irrespective of whether a metal is formally coordinated to the carbanion centre itself [sum of C—C(carbanion)-C angles for **3a**: 359.63, 358.46, 359.47, 358.33; **3b**: 359.95; **4a**: 359.70; **5a**: 359.99°]. The C(phenyl)-C(carbanion) distances also show very little variation amongst these compounds [C(phenyl)-C(carbanion) distances for **3a**: 1.440(3)−1.452(3) Å; **3b**: 1.429(3), 1.439(3) Å; **4a**: 1.408(2), 1.456(2) Å; **5a**: 1.4431(17), 1.4232(18) Å].

In summary, we have shown that the Schlenk dimerisation of 1,1-

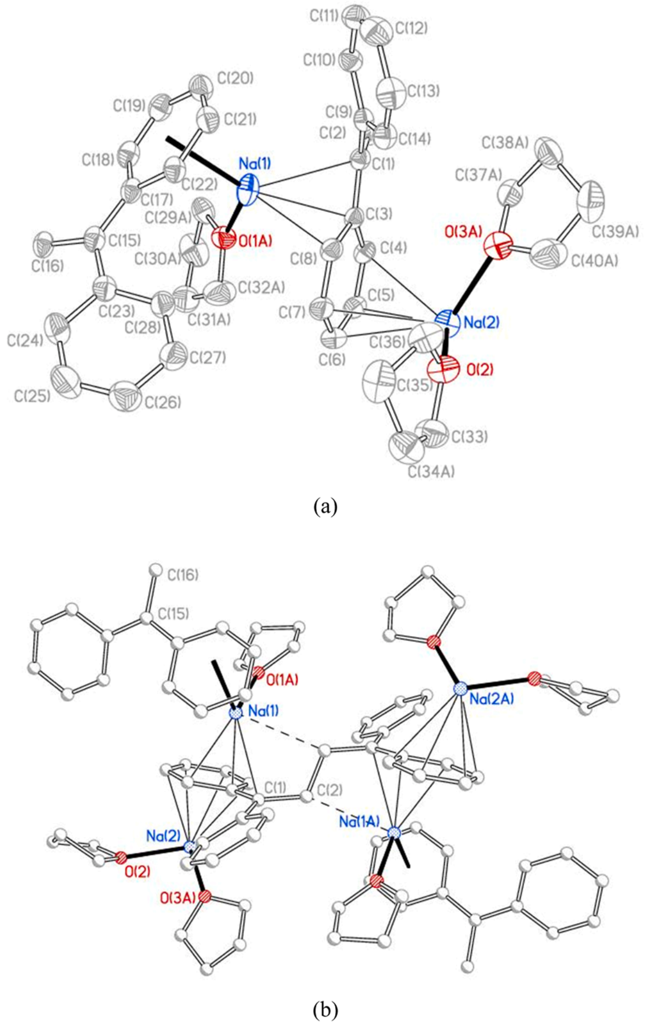


Fig. 3. (a) Asymmetric unit and (b) extended solid-state structure of **4a**, with 40% probability ellipsoids and with H atoms and disorder components omitted for clarity. Selected bond lengths (Å): Na(1)-C(1) 2.8025(15), Na(1)-C(3) 2.6553(14), Na(1)-C(8) 2.8495(15), Na(1)-O(1A) 2.272(4), Na(1)-Cent 2.479(9), Na(2)-C(4) 3.0828(15), Na(2)-C(5) 28,225(17), Na(2)-C(6) 2.7694(19), Na(2)-C(7) 2.9827(17), Na(2)-Cent 2.6133(9), Na(2)-O(2) 2.3219(12), Na(2)-O(3A) 2.2891(14), C(1)-C(2) 1.5232(19), C(1)-C(3) 1.416(2), C(1)-C(9) 1.456(2), C(15)-C(16) 1.521(2), C(15)-C(17) 1.408(2), C(15)-C(23) 1.454(2), C(2)-C(1)-C(3) 118.26(12), C(2)-C(1)-C(9) 117.40(12), C(3)-C(1)-C(9) 124.04(12), C(16)-C(15)-C(17) 118.87(14), C(17)-C(15)-C(23) 124.08(13), C(16)-C(15)-C(23) 116.96(13) [Cent: centroid of the ring containing C(17)-C(22)].

diphenylethene in THF yields structurally diverse products, where the structure adopted depends on a subtle interplay between the nature of the metal centre and the donor properties and denticity of the co-ligands.

3. Experimental procedure

General: All manipulations were carried out using standard Schlenk and dry-box techniques under an atmosphere of dry nitrogen or argon. THF, diethyl ether, methylcyclohexane and light petroleum (b.p. 40–60 °C) were dried prior to use by distillation under nitrogen from sodium, potassium, or sodium/potassium alloy, as appropriate. THF was stored over activated 4A molecular sieves; all other solvents were stored over a potassium film. Deuterated toluene and THF were distilled from potassium under argon; all NMR solvents were deoxygenated by three freeze-pump-thaw cycles and were stored over activated 4A molecular sieves.

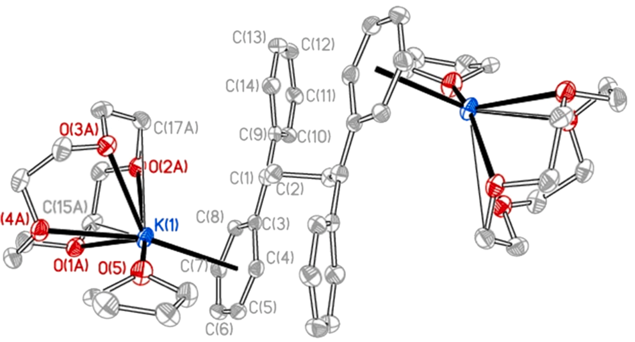


Fig. 4. Molecular structure of **5a** with 40% probability ellipsoids and with H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): K(1)-Cent 2.9472(6), K(1)-O(1A) 2.7751(12), K(1)-O(2A) 2.7667(11), K(1)-O(3A) 2.7556(11), K(1)-O(4A) 2.8593(12), K(1)-O(5) 2.7441(10), C(1)-C(2) 1.5161(17), C(1)-C(3) 1.4232(18), C(1)-C(9) 1.4431(17), C(2)-C(1)-C(3) 118.32(10), C(2)-C(1)-C(9) 117.53(13), C(3)-C(1)-C(9) 124.14(11) [Cent: centroid of the ring containing C(3)-C(8)].

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AvanceIII 500 spectrometer operating at 500.16 and 125.65 MHz, respectively, or a Bruker AvanceIII 300 spectrometer operating at 300.15 and 75.47 MHz, respectively; chemical shifts are quoted in ppm relative to tetramethylsilane. ^{7}Li NMR spectra were recorded on a Bruker AvanceIII 500 spectrometer operating at 194.38 MHz; chemical shifts are quoted in ppm relative to external 0.1 M LiCl. All NMR data were acquired at 298 K. Consistent elemental analyses could not be obtained due to the air- and moisture sensitivity of the reported compounds.

Synthesis of [$(Ph_2CCH_2CH_2CPh_2)Li_2(THF)_4$] (3): A solution of 1,1-diphenylethene (2.05 g, 11.4 mmol) in THF (25 ml) was added to lithium pieces (0.09 g, 13.0 mmol) and this mixture was stirred for 24 h, during which the mixture gradually became deep red. The solution was filtered to remove excess lithium, the solvent was removed *in vacuo* from the filtrate and the product was washed with diethyl ether (10 ml). Residual solvent was removed *in vacuo* from the solid to give **3** as a red powder. Single crystals of the alternative solvate [$Li(THF)_4$][$(Ph_2CCH_2CH_2CPh_2)Li(THF)$] (**3a**) suitable for X-ray crystallography were obtained by storing a solution of **3** in diethyl ether containing a few drops of THF at 3 °C overnight. Exposure of these crystals to vacuum resulted in loss of one coordinated THF molecule to give a species with composition corresponding to **3**; all NMR data refer to this modification. Yield 2.46 g, 65%. ^{1}H NMR (d_8-THF): δ 1.77 (m, 16H, THF), 2.42 (s, 4H, CH_2CH_2), 3.61 (m, 16H, THF), 5.63 (m, 4H, Ph), 6.48 (m, 8H, Ph), 7.04 (m, 8H, Ph). ^{13}C{^{1}H} NMR (d_8-THF): δ 26.4 (THF), 31.4 (CH_2CH_2), 68.5 (THF), 82.0 (Ph_2C), 107.7, 117.8, 128.3, 147.1 (Ph). ^{7}Li NMR (d_8-THF): δ 0.7 (s).

Synthesis of [Li(12-crown-4)(THF)] [$Li(THF)_{0.5}(Et_2O)_{0.5}$(12-crown-4)] ($Ph_2CCH_2CH_2CPh_2$) (3b): Compound **3** (1.00 g, 1.5 mmol) was dissolved in THF (10 ml) and to this solution was added 12-crown-4 (0.53 g, 0.49 ml, 3.0 mmol) via syringe. The reaction mixture was stirred for 1 min. and then concentrated *in vacuo* until incipient crystallisation. The small amount of solid was re-dissolved by heating, diethyl ether (0.5 ml) was added, and the solution was stored at 3 °C overnight to afford **3b** as maroon crystals. Once crystallised **3b** exhibited limited solubility in common organic solvents. The coordinated solvent is partially lost under vacuum, giving a compound of formula [$(Ph_2CCH_2CH_2CPh_2)Li_2$(12-crown-4)$_2$(THF)(Et_2O)$_{0.5}$] (**3c**); all data refer to this modification. Yield 1.04 g, 83%. ^{1}H NMR (d_8-THF): δ 1.12 (t, 3H, Et_2O), 1.78 (m, 4H, THF), 2.49 (s, 4H, CH_2CH_2), 3.39 (q, 2H, Et_2O), 3.56 (s, 32H, 12-crown-4), 3.62 (m, 4H, THF), 5.60 (m, 4H, Ph), 6.51 (m, 8H, Ph), 7.18 (m, 8H, Ph). ^{13}C{^{1}H} NMR (d_8-THF): δ 15.7 (Et_2O), 26.4 (THF), 32.8 (CH_2CH_2), 66.4 (Et_2O), 68.3 (THF), 69.0 (12-crown-4), 85.9 (Ph_2C). 106.7, 117.6, 128.3, 147.1 (Ph).

Synthesis of [$(Ph_2CCH_2CH_2CPh_2)Na_2(THF)_{1.5}$] (4): A solution of

1,1-diphenylethene (3.61 g, 20.0 mmol) in THF (50 ml) was added to a sodium mirror (0.51 g, 22.0 mmol) and this mixture was stirred for 24 h. The solvent was removed *in vacuo* and the product was extracted into diethyl ether (100 ml) and filtered. The solution was concentrated to incipient crystallisation and stored at 3 °C overnight to afford the alternative solvate $[(Ph_2CCH_2CH_2CPh_2)Na_2(THF)_3]_\infty$ (**4a**) as red cubic crystals. The mother liquor was decanted and residual solvent was removed from the crystals *in vacuo*, leading to loss of coordinated solvent and regeneration of **4**. Yield: 3.32 g, 76%. ^{1}H NMR (d_8-THF): δ 1.77 (m, 6H, THF), 2.42 (s, 4H, CH_2CH_2), 3.61 (m, 6H, THF), 5.74 (m, 4H, Ph), 6.61 (m, 8H, Ph), 7.19 (m, 8H, Ph). ^{13}C{^{1}H} NMR (d_8-THF): δ 26.5 (THF), 31.3 (CH_2CH_2), 68.4 (THF), 80.3 (Ph_2*C*), 108.7, 117.3, 129.1, 146.7 (Ph).

Synthesis of $[(Ph_2CCH_2CH_2CPh_2)K_2(THF)_{0.5}]$ (5): A solution of 1,1-diphenylethene (2.05 g, 11.4 mmol) in THF (20 ml) was added to lithium pieces (0.09 g, 13.0 mmol) and this mixture was stirred at room temperature for 24 h. The red solution was filtered to remove excess lithium, a solution of KO*t*Bu (1.27 g, 11.4 mmol) in THF (20 ml) was added to the filtrate and the resulting mixture was stirred for 1 h. The solvent was removed *in vacuo* and the resulting solid was washed with light petroleum (3 × 30 ml). Residual solvent was removed *in vacuo* to give **5** as a deep red powder. Yield 2.06 g, 62%. ^{1}H NMR (d_8-THF): δ 1.78 (m, 2H, THF), 2.46 (s, 4H, CH_2CH_2), 3.62 (m, 2H, THF), 5.67 (m, 4H, ArH), 6.54 (m, 8H, ArH), 7.05 (m, 8H, ArH). ^{13}C{^{1}H} (d_8-THF): 26.4 (THF), 31.1 (CH_2CH_2), 68.3 (THF), 84.9 (Ph_2*C*), 107.8. 117.1, 128.8, 146.5 (Ph).

Synthesis of $[(Ph_2CCH_2CH_2CPh_2)K_2(THF)_2(12\text{-crown-}4)_2]$ (5a): To a solution of **5** (0.87 g, 1.5 mmol) in THF (10 ml) was added 12-crown-4 (0.52 g, 0.5 ml, 3.0 mmol). The reaction mixture was stirred for 5 min. and the solution was concentrated *in vacuo* to *ca*. 5 ml. Methylcyclohexane (5 ml) was carefully layered on top of this solution and this mixture was cooled to 3 °C for four weeks to give **5a** as dark red-brown needles. Once isolated **5a** has very limited solubility in organic solvents, preventing its characterisation by NMR spectroscopy.

X-ray crystallography: Crystal structure datasets for all compounds were collected on an Xcalibur, Atlas, Gemini Ultra diffractometer using an Enhance Ultra X-ray Source ($\lambda_{CuK\alpha} = 1.54184$ Å). Using an Oxford Cryosystems CryostreamPlus open-flow N_2 cooling device, data for all structures were collected at 150 K. Cell refinement, data collection and data reduction were undertaken using CrysAlisPro [15]. For **3a** an analytical numeric absorption correction was applied using a multifaceted crystal model based on expressions derived by R. C. Clark and J. S. Reid [16]; for **3b, 4a** and **5a** intensities were corrected for absorption empirically using spherical harmonics. The structures were solved using XT [17] and refined by XL [18] through the Olex2 interface [19]. Hydrogen atoms were positioned with idealised geometry and their displacement parameters were constrained using a riding model.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters in CIF format. ^{1}H and ^{13}C{^{1}H} NMR spectra for all compounds and ^{7}Li NMR spectra for **3**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 2,257,449–2,257,452 contain the supplementary crystallographic data for **3a, 3b, 4a**, and **5a**, respectively, in this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336,033. Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2023.122865.

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