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Synthesis and characterisation of complexes of the 2,6-diphenoxyphenyl ligand

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ABSTRACT

The use of the 2,6-diphenoxyphenyl ligand has facilitated the stabilisation of lithium, silane and stannane complexes. The *ortho*-metallation reaction between 1,3-$(PhO)_2C_6H_4$ and ^nBuLi yields 2,6-$(PhO)_2C_6H_3Li$ (**1**); the crystallographically characterised dimer [2,6-$(PhO)_2C_6H_3Li(OEt_2)]_2$ (**[1.Et$_2$O]$_2$**) can be obtained by the crystallisation of **1** from diethyl ether. The reaction between **1** and Me_3ECl gives rise to the structurally authenticated complexes 2,6-$(PhO)_2C_6H_3EMe_3$ [E = Si, **2**; E = Sn, **3**].

1. Introduction

The utilisation of ligands featuring intramolecular donors is an area of intense research interest [1]. In particular, aryl ligands featuring alkoxy substituents in the 2 and 6 positions have been used to great effect in the stabilisation of main group and transition metal compounds [2–6]. The rigid structure conferred by these ligands has given rise to unusual planar tetracoordinate carbon atoms in the tetrameric aggregate $[2,6\text{-}(MeO)_2C_6H_3Li]_4$ [2] and T-shaped oxygen coordination within the trimer $[2,6\text{-}(^tBuO)_2C_6H_3Li]_3$ [3]. The use of the lithium complexes of 2,6-dialkyloxyphenyl ligands has been instrumental in opening up new areas of transition metal chemistry, for example with the stabilisation of very short metal-metal bonding interactions in $[2,6\text{-}(MeO)_2C_6H_3M]_2$ (M = V, Cr, Mo) [4]. Moreover, 2,6-dialkyloxyphenyl ligands have been used to stabilise highly reactive main group centres, such as compounds containing Ca–C bonds $[(THF)_2Ca\{\mu\text{-}C_6H_3\text{-}2,6\text{-}(OMe)_2\}_3Ca(THF)I]$ [5] and the first germanium radical to exhibit near-planarity at the metal centre, $\bullet Ge[3,5\text{-}^tBu_2\text{-}2,6\text{-}(EtO)_2C_6H]$ [6].

The chemistry of the 2,6-substituted aryls of this type is dominated by these 2,6-dialkoxy species; as part of our ongoing investigations into the use of bulky ligands in the stabilisation of unusual coordination modes [7–9] we are investigating the synthesis of complexes of 2,6-diaryloxy substituted aryl ligands, in order to probe the effect of changing the electronic and steric features of 2,6-substituted aryl ligand systems on their coordination chemistry.

2. Experimental

2.1. General

All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk line or glove box techniques. Hexane, diethyl ether, THF and toluene were pre-dried over Na wire prior to passing through a column of alumina. Benzene-d_6 (Goss) was dried over potassium, while d_8-THF was dried over CaH_2; these NMR solvents were degassed with three freeze–pump–thaw cycles prior to use. $CDCl_3$ was used as received. ^1H, ^{13}C, ^7Li, ^{29}Si and ^{119}Sn NMR spectra for these complexes were collected on a Bruker DPX 400 spectrometer. Chemical shifts are quoted in ppm relative to TMS (^1H, ^{13}C and ^{29}Si), $LiCl/D_2O$ solution (^7Li) or $SnMe_4$ (^{119}Sn). The NMR spectra were assigned according to the ligand numbering scheme (Fig. 1). Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea, and by the departmental service at the School of Chemistry, University of Nottingham. Perfluorotributylamine was used as the standard for high-resolution EI mass spectra. Elemental analyses were performed by Stephen Boyer, London Metropolitan University.

2.2. Syntheses

2.2.1. Synthesis of 2,6-$(PhO)_2C_6H_3Li$ (1) and [2,6-$(PhO)_2C_6H_3Li(OEt_2)]_2$ (**[1.Et$_2$O]$_2$**)

To a solution of 1,3-$(PhO)_2C_6H_4$ (1.0 g, 3.81 mmol) in hexane (30 cm^3) was added ^nBuLi (1.51 cm^3, 3.81 mmol, 2.5 M in hexanes) and the resulting mixture heated to reflux with stirring for 16 h.

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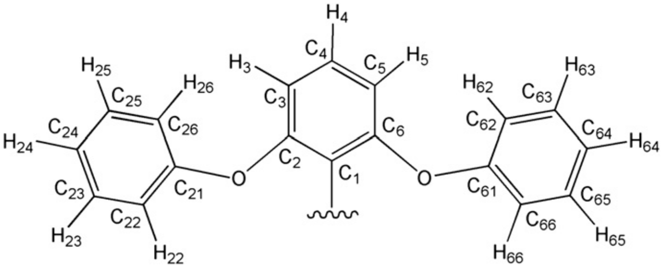

Fig. 1. Numbering scheme for the NMR spectra for the compounds in this investigation.

The reaction mixture was cooled to room temperature and a white precipitate of 2,6-$(PhO)_2C_6H_3Li$ (**1**) was collected by filtration. Yield: 0.78 g; 76%.

*2.2.1.1. Data for **1**.* ^1H NMR (d_8-THF, 298 K, 400.20 MHz): δ 6.43 (d, 2H, H3 + H5, $J = 7.6$ Hz), 6.74–6.79 (m, 2H, H24 + H64), 6.83 (t, 1H, H4, $J = 7.6$ Hz), 6.86–6.90 (m, 4H, H22 + H26 + H62 + H66), 7.10–7.15 (m, 4H, H23 + H25 + H63 + H65). $^{13}C\{^1H\}$ NMR (d_8-THF, 298 K, 100.64 MHz): δ 113.3 (C3 + C5), 117.4 (C24 + C64), 119.7 (C4), 125.6 (C22 + C26 + C62 + C66), 128.9 (C23 + C25 + C63 + C65), 161.8 (C21 + C61), 164.4 (C1), 168.0 (C2 + C6). ^7Li NMR (d_8-THF, 298 K, 155.53 MHz): δ −0.79. Elemental analysis: calcd for $C_{18}H_{13}LiO_2$: C 80.56, H 4.89; found C 80.59, H 4.89%. IR (nujol mull) ν/cm^{-1} 1592 md, 1565 md, 1490 st, 1412 st, 1262 w, 1213 st, 1162 st, 1086 md, 1023 md, 994 w, 948 st, 791 md, 761 md, 693 md, 585 w, 491 w.

Recrystallisation of **1** from diethyl ether solution at room temperature yielded $[2,6\text{-}(PhO)_2C_6H_3Li(OEt_2)]_2$ (**[1.Et₂O]₂**) as colourless crystals suitable for X-ray diffraction studies. Yield: 0.65 g; 66%.

*2.2.1.2. Data for **[1.Et₂O]₂**.* ^1H NMR (d_8-THF, 298 K, 400.20 MHz): δ 1.17 (t, 12H, OEt_2, $J = 7.0$ Hz), 3.43 (q, 8H, OEt_2, $J = 7.0$ Hz), 6.47 (d, 4H, H3 + H5, $J = 7.6$ Hz), 6.79–6.83 (m, 4H, H24 + H64), 6.87 (t, 2H, H4, $J = 7.6$ Hz), 6.90–6.94 (m, 8H, H22 + H26 + H62 + H66), 7.14–7.19 (m, 8H, H23 + H25 + H63 + H65). $^{13}C\{^1H\}$ NMR (d_8-THF, 298 K, 100.64 MHz): δ 15.4 (OEt_2), 66.0 (OEt_2), 113.2 (C3 + C5), 117.7 (C24 + C64), 119.6 (C4), 125.4 (C22 + C26 + C62 + C66), 129.1 (C23 + C25 + C63 + C65), 161.8 (C21 + C61), 164.4 (C1), 167.8 (C2 + C6). ^7Li NMR (d_8-THF, 298 K, 155.53 MHz): δ 1.04. Elemental analysis: calcd for $C_{44}H_{46}Li_2O_6$: C 77.15, H 6.77; found: C 77.23, H 6.65%. IR (nujol mull) ν/cm^{-1}: 1593 md, 1565 md, 1490 st, 1412 st, 1262 w, 1214 st, 1164 st, 1071 md, 1023 md, 994 w, 947 st, 911 w, 848 w, 815 w, 790 md, 762 md, 693 md, 585 w, 491 w.

2.2.2. Synthesis of 2,6-$(PhO)_2C_6H_3SiMe_3$ (**2**)

To a suspension of **1** (0.21 g, 0.78 mmol) in toluene (20 cm^3) and THF (1 cm^3) was added Me_3SiCl (0.15 cm^3, 1.18 mmol) *via* syringe and the resulting mixture was allowed to react with stirring for 72 h. Volatiles were removed *in vacuo* and the precipitate was extracted with hexane (30 cm^3). Cooling of the saturated hexane solution to −30 °C yielded 2,6-$(PhO)_2C_6H_3SiMe_3$ (**2**) as colourless crystals suitable for X-ray diffraction studies. Yield: 0.19 g, 73%. ^1H NMR ($CDCl_3$, 298 K, 400.20 MHz): δ 0.40 (s, 9H, $SiMe_3$), 6.66 (d, 2H, H3 + H5, $J = 8.2$ Hz), 7.05–7.09 (m, 4H, H22 + H26 + H62 + H66), 7.14–7.18 (m, 2H, H24 + H64), 7.26 (t, 1H, H4, $J = 8.0$ Hz), 7.39–7.44 (m, 4H, H23 + H25 + H63 + H65). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K, 100.64 MHz): δ 1.2 ($SiMe_3$), 113.5 (C3 + C5), 118.7 (C22 + C26 + C62 + C66), 123.0 (C24 + C64), 129.8 (C23 + C25 + C63 + C65), 131.3 (C4), 157.6 (C21 + C61), 162.9 (C2 + C6), (C1 not observed). $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 298 K, 79.51 MHz): δ −5.27. Elemental analysis: calcd for $C_{21}H_{22}O_2Si$: C 75.41, H 6.63; found: C 75.57, H 6.38%. IR (nujol mull) ν/cm^{-1} 2868 st, 1959 w, 1595 md, 1588 md, 1561 md, 1489 md, 1435 st, 1290 w, 1260 w, 1246 md, 1218 st, 1159 w, 1109 w, 1075 w, 1055 w, 1024 w, 984 w, 889 w, 843 md, 826 w, 753 w, 744 md, 691 md. Mass spec. (EI): *m*/*z* 334 ($[M]^+$, 85%), 319 ($[M - Me]^+$, 100%), 303 ($[M - 2Me]^+$, 15%), 261 ($[M - SiMe_3]^+$, 10%), 226 ($[M - OPh - Me]^+$, 15%), 211 ($[M - OPh - 2Me]^+$, 50%). Accurate mass: Calcd for $C_{21}H_{22}O_2Si$: 334.1389, measd 334.1389; Calcd for $C_{20}H_{19}O_2Si$ (*i.e.* M − Me): 319.1145, measd 319.1137.

2.2.3. Synthesis of 2,6-$(PhO)_2C_6H_3SnMe_3$ (**3**)

To a suspension of **1** (0.20 g, 0.75 mmol) in toluene (20 cm^3) was added a solution of Me_3SnCl (0.15 g, 0.75 mmol) in toluene (10 cm^3) and the resulting mixture was allowed to react with stirring overnight. Volatiles were removed *in vacuo* and the precipitate was extracted with hexane (30 cm^3). Cooling of the saturated hexane solution yielded 2,6-$(PhO)_2C_6H_3SnMe_3$ (**3**) as colourless crystals suitable for X-ray diffraction studies. Yield: 0.14 g, 45%. ^1H NMR (C_6D_6, 298 K, 300.13 MHz): δ 0.52 (s, 9H, $SnMe_3$, $^2J_{117SnH} = 54.9$ Hz, $^2J_{119SnH} = 57.6$ Hz), 6.66 (d, 2H, H3 + H5, $J = 7.8$ Hz), 6.98 (m, 3H, H4 + H24 + H64), 7.06 (m, 4H, H22 + H26 + H62 + H66), 7.17 (m, 4H, H23 + H25 + H63 + H65). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 100.64 MHz): δ −7.44 ($SnMe_3$, $^1J_{117SnC} = 352.4$ Hz, $^1J_{119SnC} = 369.1$ Hz), 113.3 (C3 + C5), 118.8 (C22 + C26 + C62 + C66), 123.0 (C24 + C64), 129.6 (C23 + C25 + C63 + C65), 131.3 (C4), 158.9 (C21 + C61), 163.5 (C2 + C6), (C1 not observed). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 298 K, 149.21 MHz): δ −37.9. Elemental analysis: calcd for $C_{21}H_{22}O_2Sn$: C 59.33, H 5.22; found: C 59.25, H 5.26%. IR (nujol mull) ν/cm^{-1} 2869 st, 1957 w, 1739 w br, 1598 w, 1569 md, 1490 md, 1436 st, 1261 md, 1218 st, 1173 w, 1098 w, 1076 w, 1024 md, 976 w, 799 w, 771 w, 750 w, 691 md. Mass spec. (EI): *m*/*z* 411 ($[M - Me]^+$, 100%), 396 ($[M - 2Me]^+$, 10%), 380 ($[M - 3Me]^+$, 20%), 302 ($[M - OPh - 2Me]^+$, 5%), 287 ($[M - OPh - 3Me]^+$, 20%), 261 ($[M - SnMe_3]^+$, 20%). Accurate mass: Calcd for $C_{20}H_{19}O_2{}^{112}Sn$, *i.e.* (M − Me): 403.0428, measd 403.0426.

2.3. Crystallography

Crystals of **[1.Et₂O]₂**, **2** and **3** were mounted on dual-stage glass fibres using YR-1800 perfluoropolyether oil (Lancaster) and cooled rapidly to 150 K in a stream of cold nitrogen using an Oxford Cryosystems low-temperature device [10]. Diffraction data were collected on a Bruker SMART APEX diffractometer equipped with a graphite-monochromated Mo-K_α radiation source ($\lambda = 0.71073$ Å). Absorption corrections were applied using a multi-scan method (SADABS) [11]. All non-H atoms were located using direct methods [12] and difference Fourier syntheses. All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained in calculated positions and refined with a riding model. For **[1.Et₂O]₂**, atoms C(19), C(20), C(21) and C(22) of the diethyl ether ligand exhibited disorder over two positions. The disorder was successfully modelled with 22:78 occupancy levels, in conjunction with distance restraints and anisotropic displacement parameter restraints and constraints. Crystal data for **[1.Et₂O]₂**, **2** and **3** can be found in Table 1.

3. Results and discussion

3.1. Syntheses

The *ortho*-metallation of 1,3-$(PhO)_2C_6H_4$ with ^nBuLi proceeds smoothly in hexane under reflux conditions over a period of 16 h to yield 2,6-$(PhO)_2C_6H_3Li$ (**1**) as a colourless powder (Eq. (1)):

$$1,3\text{-}(PhO)_2C_6H_4 + {}^nBuLi \rightarrow 2,6\text{-}(PhO)_2C_6H_3Li + {}^nBuH \qquad (1)$$

Recrystallisation of **1** from Et_2O affords $[2,6\text{-}(PhO)_2C_6H_3Li(OEt_2)]_2$ **[1.Et₂O]₂** as colourless crystals suitable for X-ray diffraction studies. Reaction of **1** with one equivalent of Me_3ECl yields

Table 1
Crystal data for **[1.Et$_2$O]$_2$**, **2** and **3**.

	[1.Et$_2$O]$_2$	**2**	**3**
Formula	$C_{44}H_{46}Li_2O_6$	$C_{21}H_{22}O_2Si$	$C_{21}H_{22}O_2Sn$
M_w	684.69	334.48	425.8
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\overline{1}$	$P2_1/n$	$P2_1/n$
a (Å)	9.2412(10)	11.5391(8)	19.8792(11)
b (Å)	9.7208(10)	8.0884(5)	8.1532(4)
c (Å)	11.7094(12)	19.4009(13)	11.5190(6)
α (°)	98.000(2)	90	90
β (°)	110.240(2)	99.667(1)	99.350(2)
γ (°)	98.723(2)	90	90
V (Å^3)	954.45(17)	1785.0(2)	1842.2(3)
T (K)	150(2)	150(2)	150(2)
D_{calc} (g cm^{-3})	1.191	1.245	1.533
F_{000}	364	712	856
Crystal size (mm)	0.47 × 0.21 × 0.14	0.52 × 0.48 × 0.17	0.84 × 0.16 × 0.06
μ (mm^{-1})	0.077	0.141	1.396
Z	1	4	4
Reflections measured	8391	11256	10308
Independent reflections	4294	4084	4146
R_{int}	0.059	0.0178	0.0384
Final GooF	1.058	1.071	1.079
R_1, wR_2	0.0584, 0.0784	0.0416, 0.107	0.0461, 0.107
Min. and max. electron densities (e Å^{-3})	−0.37, 0.64	−0.21, 0.42	−1.80, 1.55

$2,6\text{-}(PhO)_2C_6H_3EMe_3$ (E = Si, **2**; E = Sn, **3**) in good yields (Eq. (2)). Complexes **1**, **[1.Et$_2$O]$_2$**, **2** and **3** have been characterised by multinuclear NMR spectroscopy, elemental analysis and IR spectroscopy, and additionally in the case of **2** and **3**, mass spectrometry.

$$2,6\text{-}(PhO)_2C_6H_3Li + Me_3ECl \rightarrow 2,6\text{-}(PhO)_2C_6H_3EMe_3 + LiCl \qquad (2)$$

The NMR spectroscopy for **1** and **[1.Et$_2$O]$_2$** has been performed in d_8-THF solution, allowing the unambiguous assignment of ligand protons and carbons in the ^{1}H and ^{13}C{^{1}H} NMR spectra. In the case of both **1** and **[1.Et$_2$O]$_2$** one ligand environment is observed in solution; it is conceivable that the dissolution of these complexes in a coordinating solvent such as d_8-THF leads to the formation of monomers, or that the existence of oligomers in solution combined with fluxionality of the coordinated ligand oxygen (the coordination of one of the flanking phenoxy substituents to the lithium centres is observed in the solid state for **[1.Et$_2$O]$_2$**) leads to the observation of one ligand environment in the NMR spectra of these complexes. Due to the poor solubility of **1** and **[1.Et$_2$O]$_2$** it was not possible to obtain low-temperature NMR measurements on solutions of these compounds as has been performed for other aryllithium complexes [2,3,13,14]. The ^{7}Li NMR spectra of **1** and **[1.Et$_2$O]$_2$** display only one resonance each: at −0.79 and −1.04 ppm, respectively.

Table 2
Selected distances (Å) and angles (°) for **[1.Et$_2$O]$_2$**.

Li(1)–C(1)	2.159(4)	Li(1)···Li(1_2)	2.585(6)
Li(1_2)–C(1)	2.374(3)	C(1)–C(2)–O(1)	116.00(15)
Li(1)–C(2_2)	2.530(3)	C(1)–C(6)–O(2)	114.97(15)
Li(1)–O(1_2)	2.055(3)	Li(1)–C(1)–Li(1_2)	69.36(14)
Li(1)–O(3)	1.948(3)	C(1)–Li(1)–C(1_2)	110.64(14)
C(2)–O(1)	1.434(2)	C(2)–C(1)–C(6)	111.29(15)
C(6)–O(2)	1.418(2)	C(2)–O(1)–C(7)	117.46(13)
C(7)–O(1)	1.392(2)	C(6)–O(2)–C(13)	120.35(14)
C(13)–O(2)	1.378(2)	∠C(7) ring and central phenyl ring	76.97(6)
C(1)–C(2)	1.388(2)	∠C(13) ring and central phenyl ring	64.43(5)
C(1)–C(6)	1.393(2)	∠C(7) and C(13) rings	51.96(8)
Li(1)···O(2)	2.8976(35)	∠Li(1)–C(1)–Li(1_2)–C(1_2) and central phenyl ring	38.25(11)

Symmetry operation _2 = −x, −y + 1, −z + 1.

The ^{29}Si{^{1}H} NMR chemical shift for **2** (δ −5.27) is in good agreement with those values reported for related compounds; $\delta = -5.10$ for $2,6\text{-}(MeO)_2C_6H_3SiMe_3$ and $\delta = -6.6$ for $2,4,6\text{-}(MeO)_3C_6H_2SiMe_3$ [15,16]. The ^{119}Sn{^{1}H} NMR resonance for **3** (δ −37.9) is similar to those for related organostannanes $2,6\text{-}(MeO)_2C_6H_3SnMe_3$ (δ −43.7) and $2,4,6\text{-}(MeO)_3C_6H_2SnMe_3$ (δ −43.8) [17]. The ^{29}Si{^{1}H} chemical shift for **2** is very similar to that for the corresponding unsubstituted phenyl derivative $PhSiMe_3$ ($\delta_{29Si} = -4.1$ in $CDCl_3$) [18]; and indicates that there is likely no coordination of the phenoxy units to the silicon atom in solution. Similarly, the slight highfield shift of **3** compared to $PhSnMe_3$ ($\delta_{119Sn} = -24.1$ in C_6D_6) [19] indicates that there is likely no coordination of the phenoxy moieties to the tin atom in solution. These findings are in contrast to the highfield chemical shifts observed for the Si and Sn atoms in the hypercoordinate complexes $2,6\text{-}(Me_2NCH_2)_2C_6H_3EMe_3$ (E = Si, $\delta_{29Si} = -7.7$; E = Sn, $\delta_{119Sn} = -86.9$) [20].

3.2. Crystal structure analyses

Although it has not been possible to isolate single crystals of **1**, its diethyl ether adduct **[1.Et$_2$O]$_2$** forms single crystals suitable for X-ray diffraction from saturated solutions at ambient temperature. The crystal structure of **[1.Et$_2$O]$_2$** is shown in Fig. 2 and relevant bond lengths and angles can be found in Table 2. The solid state structure of **[1.Et$_2$O]$_2$** reveals a dimeric structure with the molecule lying across a crystallographic inversion centre, which requires the lithium-bonded aryl rings to be parallel. The lithium atoms bridge the phenyl groups and the primary interactions are with the *ipso* carbons of the central aryl rings. Additional coordination comes from diethyl ether and one of the ether linkages in the $2,6\text{-}(PhO)_2C_6H_3^-$ ligand. The

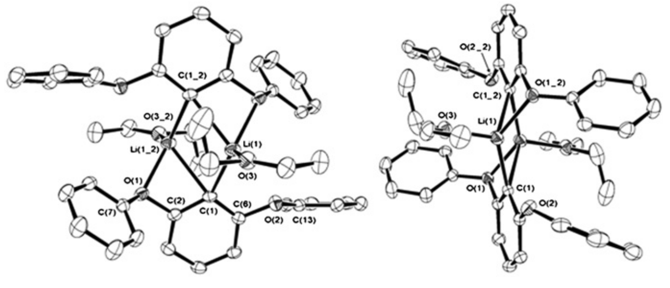

Fig. 2. Crystal structure of $[2,6\text{-}(PhO)_2C_6H_3Li(OEt_2)]_2$ (**[1.Et$_2$O]$_2$**) (right) and side view (left) with displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Symmetry operation _2 = −x, −y + 1, −z + 1.

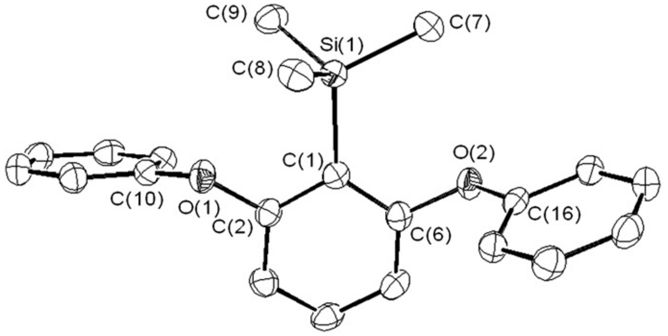

Fig. 3. Crystal structure of $2,6\text{-}(PhO)_2C_6H_3SiMe_3$ (**2**) with displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.

Table 3
Selected distances (Å) and angles (°) for **2**.

Si(1)–C(1)	1.9019(14)	C(2)–C(1)–C(6)	114.27(12)
Si(1)–C(7)	1.8636(15)	C(1)–C(2)–O(1)	116.75(11)
Si(1)–C(8)	1.8617(15)	C(1)–C(6)–O(2)	119.11(12)
Si(1)–C(9)	1.8682(15)	C(2)–O(1)–C(10)	117.89(10)
C(2)–O(1)	1.3969(16)	C(6)–O(2)–C(16)	117.56(10)
C(6)–O(2)	1.4028(16)	∠C(10) ring and central phenyl ring	76.69(4)
C(1)–C(2)	1.4015(18)	∠C(16) ring and central phenyl ring	86.96(4)
C(1)–C(6)	1.4009(18)	∠C(10) and C(16) rings	27.34(6)
Si(1)···O(1)	2.9764(11)		
Si(1)···O(2)	3.2419(10)		

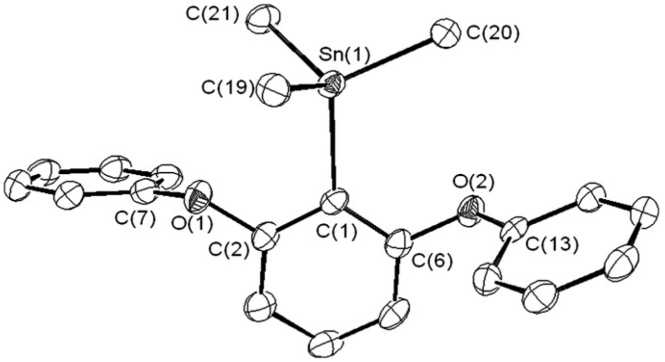

Fig. 4. Crystal structure of 2,6-$(PhO)_2C_6H_3SnMe_3$ (**3**) with displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.

twofold aggregation observed for **[1.Et$_2$O]$_2$** differs from that of the tetrameric aggregate [2,6-$(MeO)_2C_6H_3Li]_4$ [2] and the trimer [2,6-$(^tBuO)_2C_6H_3Li]_3$ [3].

The solid state structure of **[1.Et$_2$O]$_2$** features a planar Li(1)–C(1)–Li(1_2)–C(1_2) unit [Σ internal angles = 360° by symmetry; symmetry operation _2 = $(-x, -y+1, -z+1)$], akin to related *m*-terphenyl dimers [2,6-$(2,6\text{-}Me_2C_6H_3)_2C_6H_3Li]_2$ and [2,6-$(2,3,4,5,6\text{-}Me_5C_6)_2C_6H_3Li]_2$ [21]. The distance between the lithium centres in **[1.Et$_2$O]$_2$** [Li(1)···Li(1_2) = 2.585(6) Å] is similar to that found in dimeric complexes [2,4,6-$(CF_3)_3C_6H_2Li]_2$ and [2,6-$(Me_2PCH_2)_2$-$C_6H_3Li]_2$ [13,14]. Unlike these more symmetrical aryl bridged dimers, the Li(1)–C(1) and Li(1_2)–C(1) distances in **[1.Et$_2$O]$_2$** are very different [2.159(4) and 2.374(3) Å, respectively], which may be a reflection of the asymmetrical coordination of the flanking phenoxy groups (*vide infra*) in these complexes. The difference between the two Li–C distances in **[1.Et$_2$O]$_2$** is greater than that in [2,6-$(2,3,4,5,6\text{-}Me_5C_6)_2C_6H_3Li]_2$ [2.176(2) and 2.230(2) Å] [21]. The Li(1)–C(1)–Li(1_2) angle of 69.36(14)° is in the range of that reported for other dimeric lithium aryls [61.74(10)–73.82(18)°] [21-23]. Overall, the coordination environment around C(1) in the solid state structure of **[1.Et$_2$O]$_2$** is distorted tetrahedral.

A comparitively short Li(1)–O(1_2) distance [2.055(3) Å] indicates relatively strong coordination of one phenoxy unit to each lithium centre. The coordination environment around O(1_2) is pyramidal [Σ(angles) = 335.56(13)°], concomitant with this the Li(1)–O(1_2) distance in **[1.Et$_2$O]$_2$** is in the range of Li–O(pyramidal) distances reported by Brandsma and co-workers for [2,6-$(^tBuO)_2$-$C_6H_3Li]_3$ [2.043(6)–2.111(5) Å] [3]. The central ligand aryl rings sit at an angle of 38.25(11)° out of the best mean plane of the Li(1)–C(1)–Li(1_2)–C(1_2) moiety; this is in the range of that reported for dimeric *m*-terphenyl lithium complexes (32.4–43.5°) [21,24], but smaller than that for other pincer-type lithium dimers such as [2,6-$(Me_2PCH_2)_2C_6H_3Li]_2$ [14]. In **[1.Et$_2$O]$_2$** the Li(1)···O(2) distance [2.8976(35) Å] is significantly longer than that for Li(1)–O(1_2), but still significantly shorter than the sum of the van der Waals radii for these elements [3.75 Å] [25], indicating the possibility of a weak interaction between this oxygen and the lithium atom in the solid state. The formation of dimers and the intramolecular coordination of only one phenoxy moiety in **[1.Et$_2$O]$_2$** may be indicative of greater steric demands of the 2,6-$(PhO)_2C_6H_3^-$ ligand compared with 2,6-$(MeO)_2C_6H_3^-$ and 2,6-$(^tBuO)_2C_6H_3^-$. In **[1.Et$_2$O]$_2$** the two flanking phenyl rings form a dihedral angle of 51.96(8)°; the dihedral angles between these phenyls and the central aryl ring vary significantly [76.97(6)° and 64.43(5)°]; this difference is presumably in part due to the coordination of the phenoxy ring to the Li centre affecting the former angle.

Single crystals of **2** and **3** of quality suitable for X-ray diffraction were obtained by the storage of saturated hexane solutions at −30 °C. The crystal structure of **2** is shown in Fig. 3 and relevant bond lengths and angles can be found in Table 3. The comparison of selected crystallographic parameters of **2** and **3** with literature values can be found in Table 4. In **2**, the Si–C(aryl) distance [Si(1)–C(1) = 1.9019(14) Å] is similar to that found in 2,4,6-$(MeO)_3C_6H_2$-$SiMe_3$ [ave. = 1.904(3) Å] [16]. This distance is longer than the Si–C(alkyl) distances in **2**; ave. Si–C(alkyl) distance = 1.8645(26) Å. The two Si···O distances for **2** differ significantly [Si(1)···O(1) = 2.9764(11) Å, Si(1)···O(2) = 3.2419(10) Å], this difference in distances has also been seen in 2,4,6-$(MeO)_3C_6H_2Si(CH_2Cl)_3$ [Si···O = 2.8708(15) and 3.069(14) Å] [26] and 2,4,6-trimethoxysilanes [27]. These Si···O distances are smaller than the sum of the van der Waals radii for these elements [3.65 Å] [25], but are significantly longer than a typical Si–O bond for a four-coordinate Si atom [ave. 1.63 Å] [28].

In the case of **3**, the Sn–C(aryl) distance [Sn(1)–C(1) = 2.157(4) Å] is longer than that found in 2,5-$(C_8H_{17}O)_2C_6H_2(SnMe_3)_2$-1,4 [Sn–C(aryl) = 2.146(2) Å], presumably due to the greater degree of crowding around the Sn centre in **3** [29]. The crystal structure of **3** is shown in Fig. 4 and relevant bond lengths and angles can be found in Table 5. This distance in **3** is similar to those Sn–C(aryl) bond lengths found in the sterically crowded crown ether complex dimethylbis[(1,3-phenylene-16-crown-5)-2-yl]stannane [2.148(3), 2.152(2) Å] [30]. Analogous to the short Si···O distances in **2**, short Sn···O distances are observed in **3** [Sn(1)···O(1) = 3.101(3) Å, Sn(1)···O(2) = 3.395(3) Å], the shorter of these being similar to that found in 2,5-$(C_8H_{17}O)_2C_6H_2(SnMe_3)_2$-1,4 [Sn···O = 3.094 Å]. The Sn···O distances in **3** are smaller than the sum of the van der Waals radii for these elements [3.80 Å] [25], but are significantly longer than that of a typical Sn–O bond for a four-coordinate Sn atom [ave. 2.14 Å] [28].

The torsion angles between the two flanking phenyl rings in **2** and **3** [27.34(6)° and 29.09(19)°, respectively] are comparable to

Table 4
The comparison of selected crystallographic parameters (Å) of **2** and **3** with literature values.

	E–C(aryl)	E–C(alkyl)	E···O(1)	E···O(2)	Ref.
2	1.9019(14)	1.8645(3)	2.9764(11)	3.2419(10)	This work
2,4,6-$(MeO)_3C_6H_2SiMe_3$	1.904(3)	1.870(6)	2.926	3.129	[16]
2,4,6-$(MeO)_3C_6H_2Si(CH_2Cl)_3$	1.854(2)	1.869(3)	2.8768(15)	3.069(14)	[26]
3	2.157(4)	2.135(7)	3.101(3)	3.395(3)	This work
2,5-$(C_8H_{17}O)_2C_6H_2(SnMe_3)_2$-1,4	2.146(2)	2.143(5)	3.094	–	[29]
Dimethylbis[(1,3-phenylene-16-crown-5)-2-yl]stannane	2.150(4)	2.134(4)	3.075(3)	2.233(3)	[30]

Table 5
Selected distances (Å) and angles (°) for **3**.

Sn(1)–C(1)	2.157(4)	C(2)–C(1)–C(6)	115.4(4)
Sn(1)–C(19)	2.135(4)	C(1)–C(2)–O(1)	117.0(4)
Sn(1)–C(20)	2.128(4)	C(1)–C(6)–O(2)	118.7(4)
Sn(1)–C(21)	2.143(4)	C(2)–O(1)–C(7)	118.1(3)
C(2)–O(1)	1.403(5)	C(6)–O(2)–C(13)	117.5(3)
C(6)–O(2)	1.398(5)	∠C(7) ring and central phenyl ring	76.54(13)
C(1)–C(2)	1.389(6)	∠C(13) ring and central phenyl ring	86.38(12)
C(1)–C(6)	1.392(5)	∠C(7) and C(13) rings	29.09(19)
Sn(1)···O(1)	3.101(3)		
Sn(1)···O(2)	3.395(3)		

that found in 2,6-$(PhO)_2C_6H_3P(O)FH$ (29.41°) [31]. These differ significantly from the corresponding value in **[1.Et$_2$O]$_2$** [51.96(8)°] due to the differing coordination environments in these complexes. The torsion angles between the least-square mean planes of the flanking phenyl rings and the central aryl are similar for **2** and **3** [76.69(4)° and 86.96(4)° for **2**, 76.54(13)° and 86.38(12)° for **3**].

4. Conclusions

The *ortho*-metallation reaction between 1,3-$(PhO)_2C_6H_4$ and ^{n}BuLi forms 2,6-$(PhO)_2C_6H_3Li$ (**1**) in good yields. We have shown that **1** can be used as a precursor towards the formation of new aryl-element bonds (*e.g.* in compounds **2** and **3**) *via* methathesis chemistry. Long Si···O and Sn···O distances indicate that any interactions between these atoms in **2** and **3** are certainly very weak. Reactivity studies of these compounds are underway.

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Appendix A. Supplementary material

CCDC-778702, CCDC-778703, and CCDC-778704 (for **[1.Et$_2$O]$_2$**, **2** and **3**) contain the supplementary data for these compounds. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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