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Reactions of organolithium complexes with elemental selenium: insertion producing $[\mathrm{PhC{\equiv}CSeLi \cdot TMEDA \cdot THF}]$ **1** and cyclisation producing $[\{\mathrm{PhC}\}_4\mathrm{Se}]$ **2** $(\mathrm{TMEDA} = [\mathrm{Me_2NCH_2}]_2)$[1]

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Abstract

The reaction of $[\mathrm{PhC{\equiv}CLi}]_n$ with Se metal (1:1 equivalents) in THF/TMEDA gives the insertion product $[\mathrm{PhC{\equiv}CSeLi \cdot TMEDA \cdot THF}]$ **1**, which is monomeric in the solid state. The reaction of $\mathrm{PhC{\equiv}CPh}$ with Li metal, generating dilithium tetraphenylbutadiene in situ, followed by the addition of elemental Se gives the selenophene $[\{\mathrm{PhC}\}_4\mathrm{Se}]$ **2**, as a result of insertion of Se followed by the elimination of $\mathrm{Li_2Se}$. The latter provides a clean and direct route to compounds of this type. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Organolithium; Organoselenides; Selenophene

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1. Introduction

Despite the fact that oligomeric alkali metal alkoxides and sulphides ($[\mathrm{REM}]_n$; M = Li–Cs, E = O, S) have been the focus for many synthetic and structural studies in the past twenty years [1,2], it is only recently that attention has turned to the related Se [3–8] and Te [9–13] complexes. Studies to date have concentrated on the structures of complexes produced by metallation of sterically encumbered organic acids REH (E = Se, Te) with organolithium reagents and the insertion reactions of elemental Se and Te into C–M or Si–M bonds. The latter route has significant advantages over metallation in that it avoids the synthesis of the intermediate organoselenides and tellurides and, in so doing, gives potentially easy access to species containing sterically undemanding organic groups (R). Prompted by the continued scarcity of structurally characterised alkali metal organo-selenides (containing C–Se–M grouping) [4–7] and particularly those containing less sterically demanding organic substituents, we report here the investigation of the insertion reactions of Se in two related organolithium systems, the lithium phenylacetylide, $[\mathrm{PhC{\equiv}CLi}]$, and dilithium tetraphenylbutadiene, $[\mathrm{PhC}\overset{\cdots}{-}\mathrm{C(Ph)}]_2\mathrm{Li}_2$ [15–18].

The reaction of $[\mathrm{PhC{\equiv}CLi}]$ with Se metal (1:1 equivalents) in THF followed by removal of the solvent and replacement with $\mathrm{Et_2O}$ and TMEDA $[= (\mathrm{Me_2NCH_2})_2]$ (1 equivalent) gives $[\mathrm{PhC{\equiv}CSeLi \cdot TMEDA \cdot THF}]$ (**1**), as a result of insertion of Se into the C–Li bond (Scheme 1). In contrast to the simple insertion reaction observed in the formation of **1**, the reaction of the dilithium complex $[\mathrm{PhC}\overset{\cdots}{-}\mathrm{C(Ph)}]_2\mathrm{Li}_2$ in $\mathrm{Et_2O}$ with Semetal (1:2 equivalents) gives tetraphenyl selenophene, $[\{\mathrm{PhC}\}_4\mathrm{Se}]$ (**2**), as a result of insertion followed by the elimination of $[\mathrm{Li_2Se}]$ (Scheme 2). Although the synthe-

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[1] Dedicated to Professor Brian Johnson on the occasion of his 60th birthday.

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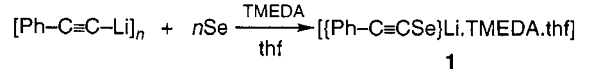


$$[Ph–C{\equiv}C–Li]_n + nSe \xrightarrow[thf]{TMEDA} [\{Ph–C{\equiv}CSe\}Li.TMEDA.thf]$$

1

Scheme 1.

sis of the same selenophene has been achieved using nucleophilic substitution of $SeCl_2$ with the $[PhC{\overset{...}{-}}C(Ph)]_2{}^{2-}$ dianion [17,18] direct reaction with Se provides a cleaner and more convenient pathway. However, as with the reaction involving $SeCl_2$ the yield of **2** is highly variable (ca. 20–40%) as a result of the inherent difficulty in generating the $[PhC{\overset{...}{-}}C(Ph)]_2{}^{2-}$ dianion from PhC≡CPh and Li without significant formation of the naphthylene byproduct [16–18]. In this regard, the reaction time, the nature of the Li metal used (powdered or chunks) and the nature and volume of solvent used in the reaction are critical. We have found that for a 15 mmol scale reaction the use of lithium powder in 50 ml of Et_2O with a reaction time of 2.5 h gives the most consistent yields of **2**.

Prior to their structural characterisation, **1** and **2** were fully characterised using analytical and spectroscopic means. These studies reveal that the THF ligand of **1** is highly labile and isolation of the crystalline complex under vacuum (10 min, 10^{-1} atm) leads to amorphous powder of formula [PhC≡CSe-Li · TMEDA]. Although **2** also contains a molecule of THF per molecular unit in the lattice, here too isolation under vacuum gives solvent-free material. Details of the subsequent structural refinements of **1** and **2** are given in Table 1 and Table 2 lists key bond lengths and angles in both complexes.

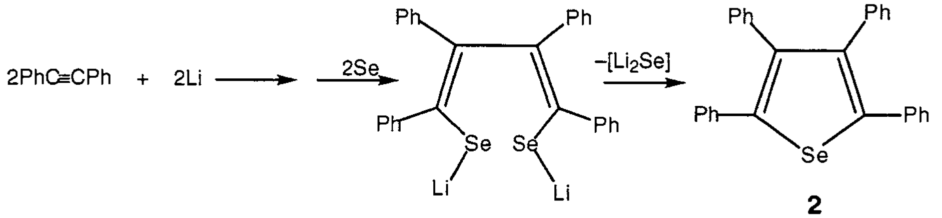
Table 1
Crystal data for **1** and **2**

Empirical formula	$C_9H_{14.5}Li_{0.5}N_{0.5}O_{0.5}Se_{0.5}$ **1**	$C_{24}H_{28}OSe$ **2**
Formula weight	187.67	411.36
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	Cc
Crystal size (mm^3)	0.50 × 0.50 × 0.40	0.20 × 0.20 × 0.30
Unit cell dimensions		
a (Å)	8.320(2)	13.349(3)
b (Å)	10.400(2)	14.966(3)
c (Å)	12.180(2)	12.807(3)
α (°)	109.70(3)	—
β (°)	98.57(3)	96.81(3)
γ (°)	93.31(3)	—
U ($Å^3$)	974.5(3)	2540(1)
Z	4	4
$D_{calc.}$ ($mg\ m^{-3}$)	1.279	1.055
θ range (°)	4.00–22.50	4.11–22.50
Refections collected	2767	2663
Independent reflections (R_{int})	2518 (0.120)	1669
R indices [$F > 4\sigma(F)$](reflections)	0.040; 0.097	0.069; 0.174
R indices (all data)	0.049; 0.103	0.092; 0.195
Largest difference peak and hole (e $Å^{-3}$)	0.493; −0.655	0.812; −0.634

Details in common: $\lambda = 0.71073$ Å, [$R_1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$, $w = 1/[\sigma^2(F_o^2) + (yP)^2 + xP]$, $P = F_o^2 + (2F_c^2/3)$].

The low-temperature (153 K) X-ray structural determination of **1** shows it to exist as monomers in the solid state in which the Li^+ cation is bonded to the anionic Se centre and coordinated by a TMEDA and THF ligand (Fig. 1). To our knowledge the only examples of alkali metal organoselenides to have been structurally characterised are the monomers [2,4,6-^{t}Bu$_3$C$_6$H$_2$SeLi · 3THF] [5] and [2,4,6-Me$_3$C$_6$H$_2$SeLi · 3THF] [6], the dimers [PhSeLi · 2,2′-bipy]$_2$ and [2-PyrSeLi · 2,2′-bipy]$_2$ (2,2′-bipy = 2,2′-bipyridine) [7], and the trimer [2,4,6-^{t}Bu$_3$C$_6$H$_2$SeLi · THF]$_3$ · toluene [4]. The overall structure of **1** is similar to that adopted in the previously characterised monomeric arylselenide complexes [5,6] and related monomeric tellurides, such as [(2-Me$_2$N)C$_6$H$_4$TeLi · DME] [DME = (MeOCH$_2$)$_2$] [12], in which the alkali metal centres are also pseudo-tetrahedral. However, **1** is the first example of an organo–selenide or telluride containing a non-aromatic organic substituent.

The Se–Li bond length in **1** [2.595(7) Å] is similar to those present in the other structurally characterised monomeric selenides [2,4,6-^{t}Bu$_3$C$_6$H$_2$SeLi · 3THF] [2.57(2) Å] [5] and [2,4,6-Me$_3$C$_6$H$_2$SeLi · 3THF] (2.56(1) and 2.58(1) Å in the two independent molecules) [6]. The more acute C–Se–Li angle in **1** [98.2(2)°] compared to those observed in the latter (range 101.4(3)–103.8(4)°) [5,6] is probably a consequence of the lesser steric demands of the essentially linear PhC≡C– group as compared to sterically encum-



2

Scheme 2.

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**

Compound **1**			
Bond lengths (Å)			
Se(1)–Li(1)	2.595(7)	N(1)–Li(1)	2.106(7)
Se(1)–C(11)	1.813(4)	N(2)–Li(2)	2.125(7)
C(11)–C(12)	1.219(6)	Li(1)–O(1)	1.937(7)
C(12)–C(13)	1.433(6)		
Bond angles (°)			
O(1)–Li(1)–N(1)	118.1(3)	Se(1)–Li(1)–N(2)	113.0(3)
O(1)–Li(1)–N(2)	110.0(3)	Li(1)–Se(1)–C(11)	98.2(2)
O(1)–Li(1)–Se(1)	108.2(3)	C(12)–C(11)–Se(1)	179.2(3)
Se(1)–Li(1)–N(1)	117.9(3)		
Compound **2**			
Bond lengths (Å)			
Se(1)–C(4)	1.82(3)	C(2)–C(3)	1.38(2)
Se(1)–C(1)	1.92(3)	C(3)–C(4)	1.46(5)
C(1)–C(2)	1.35(4)	Range C–Ph	1.31(4)–1.59(3)
Bond angles (°)			
C(1)–Se(1)–C(4)	88.7(7)	C(4)–C(3)–C(2)	114(4)
C(2)–C(1)–Se(1)	109(2)	C(3)–C(4)–Se(1)	110(2)
C(3)–C(2)–C(1)	119(4)		

bered aryl substituents. Comparison of the structural and IR spectroscopic data for **1** with that for the loosely-linked dimer [TMEDA · Cd(SeC≡CPh)$_2$]$_2$ [19] containing the same [PhC≡CSe]$^-$ ligand, provides some measure of the degree of charge dispersion from the anionic Se centre to the PhC≡C– substituent in **1**. Although there is no significant difference in the C≡C bond lengths in **1** and [TMEDA · Cd(SeC≡CPh)$_2$]$_2$, the C–Se bond [1.813(4) Å] in **1** is shorter than the terminal or μ-bridged PhC≡CSe groups (1.833(7) and 1.851(7) Å, respectively) in [TMEDA Cd(SeC≡CPh)$_2$]$_2$ [19]. In addition, there is a small decrease in the C≡C stretching frequency in the IR spectrum of **1** (2122 cm^{-1}) compared to that in [TMEDA · Cd(SeC≡CPh)$_2$]$_2$ (2130 cm^{-1}) [19] and PhC≡CH (2144 cm^{-1}). These structural and spectroscopic trends are consistent with the slightly greater charge separation for the Se–Li bond in **1**, anticipated on the grounds of the greater electronegativity of Li compared to Cd. The greater concentration of negative charge on the Se centre leads to a slightly greater dispersion of electron density towards the PhC≡C– group in **1** than in [TMEDA · Cd(SeC≡CPh)$_2$]$_2$ (although the extent of such delocalisation is clearly small in both complexes).

The low-temperature X-ray structure determination of **2** shows it to have the expected heterocyclic ring structure [{PhC}$_4$Se] (Fig. 2). In addition, there is one disordered THF molecule per formula unit in the lattice. In itself the structural characterisation of this compound is of lesser importance apart from confirming the outcome of the reaction between the $[\mathrm{PhC}{\cdots}\mathrm{C(Ph)}]_2{}^{2-}$ dianion and elemental Se unequivocally. The bond lengths and angles within **2** are as expected on the basis of the structures of other selenophenes, [20] with the presence of relatively long Se–C bonds (av. 1.87 Å; cf ca. 1.94 Å expected for a single C–Se bond) indicating that the extent of delocalisation in this system is low.

The work presented in this paper provides easy access to two useful ligand groups. Selenophenes have been employed as 6e ligands to low oxidation state transition metal centres (Scheme 3a) [21] and the [PhC≡CSe]$^-$ anion can potentially function as a σ/π ligand to transition metals (Scheme 3b).

2. Experimental section

2.1. General preparative techniques

All the reactions were undertaken under dry, O$_2$-free argon using a vacuum line and standard inert-atmosphere techniques. The THF and Et$_2$O were dried by distillation over Na/benzophenone. TMEDA was dried using molecular sieve (13X). Complexes **1** and **2** were isolated and characterised with the aid of an argon-filled glove box (Miller–Howe, fitted with a Belle internal circulation system). Melting points were determined using a conventional apparatus and sealing samples in capillaries under argon. Elemental analyses (C, H and N) were performed by firstly sealing samples in air-tight aluminium boats (1–2 mg) prior to analysis using a Perkin–Elmer 240 elemental analyser. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AP/DPX 250 MHz spectrometer, using the NMR solvent of DMSO as internal reference standards.

*2.2. Synthesis of **1***

To a solution of PhC≡CH (1.02 g, 10 mmol) in THF (20 ml) was added ^{n}BuLi (6.7 ml, 1.5 mol dm^{-3} in hexanes, 10 mmol) at 0°C. The tawny-brown solution produced after stirring briefly at 25°C was reacted with elemental Se (0.780 g, 10 mmol). The solution turned an orange-red colour and stirring was continued at 25°C (ca. 1 h) at which time no Se remained. The solution was filtered (celite, porosity 3) and the THF solvent removed and replaced with Et$_2$O (15 ml). TMEDA was added (1.51 ml, 10 mmol) and the yellow precipitate was dissolved by the addition of a minimum volume of THF (ca. 2 ml). Storage at -35°C gave large orange crystals of **1**. Isolation under vacuum prior to analysis (15 min, 10^{-1} atm) removes all the Li-

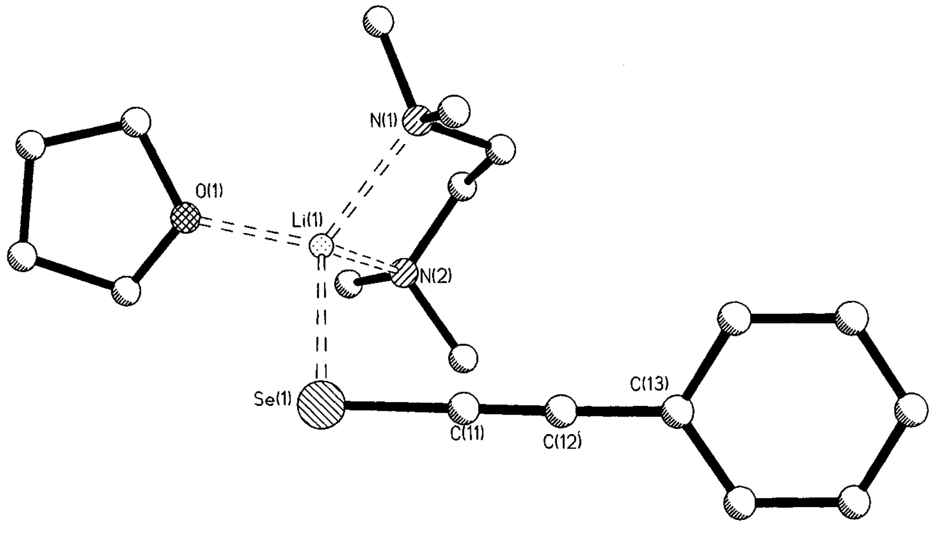


Fig. 1. Molecular structure of **1**. H atoms have been omitted for clarity.

bonded THF and gives an amorphous material of formula [PhC≡CSeLi · TMEDA]. The following data refers to this material; yield (0.69 g, 31%); m.p. 138°C; IR (Nujol), 3072(w) (C–H aryl str.), 2122(s) (C≡C str.), 1596(m) (aryl C$\overset{\cdots}{-}$C str.), other bands at 1290(m), 1180(w), 1160(w), 1128(w), 1098(w), 1066(m), 1034(s), 1019(s), 952(s), 792(s), 752(s), 691(s); ^{1}H-NMR (+25°C, 250 MHz, d_6-benzene), 7.63 (d.d., *o*-C–H), 7.15 (t.d., *p*-C–H), 7.09 (mult., *m*-C–H); ^{13}C-NMR (62.895 MHz, +25°C, D_6-DMSO), 131.7 [Ph, *p*-], 128.8 [Ph, C(α)], 128.5 [Ph, *m*-], 125.4 [Ph, *o*-], 85.2 [Ph–C≡C], 84.7 [Ph–C≡C], 56.8 [–CH$_2$, TMEDA], 46.4 [Me$_2$N, TMEDA]; Elemental Analysis; found, C 54.3, H 6.9, N 9.4; calc. for [PhC≡CSeLi · TMEDA]$_n$, C 55.4, H 6.9, N 9.2.

*2.3. Synthesis of **2***

To a suspension of Li powder (0.22 g, 31 mmol) in Et$_2$O (20 ml) was added a solution of PhC≡CPh (3.56 g, 30 mmol) in Et$_2$O (30 ml). The reaction changes to a deep red colour within ca. 5 min. Stirring at r.t. was continued for 2.5 h. Some orange solid is normally present at this stage and the Li metal has not reacted completely. The reaction was filtered and Se metal (2.34 g, 30 mmol) was added. The reaction was stirred for 12 h at r.t. Filtration gave an orange/yellow solution which was reduced to ca. 15 ml to give a yellow precipitate of **2**. Crystals are readily obtained by heating the precipitate into solution followed by storage of the resulting solution at 5°C; yields over several reactions 1.30–2.34 g (20–36%); m.p. 130–135°C; IR (Nujol), major bands at 1148(m), 1070(m), 1029(m), 913(m), 860(m), 791(m), 743(s), 694(s); ^{1}H-NMR (+25°C, 250 MHz, D_6-DMSO), 7.55 (mult.), 7.44 (mult.), 7.20 (mult.), 7.0 (mult.); Elemental Analysis; found, C 77.8, H 4.8; calc. for [{PhC}$_5$Se], C 77.4, H 4.6.

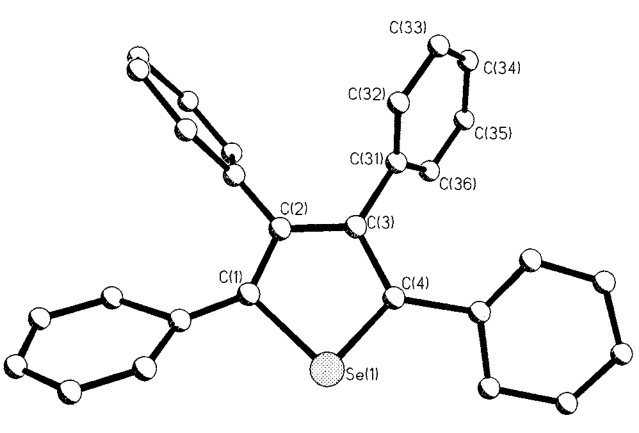
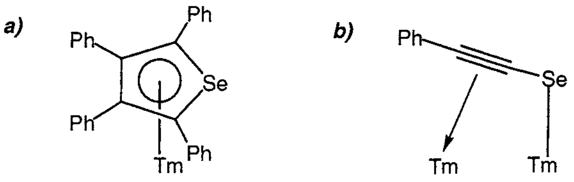


Fig. 2. Molecular structure of **2**. H atoms have been omitted for clarity.

2.4. X-ray structure determinations

Crystals were mounted directly from solution under argon using a perfluorocarbon oil which protects them from atmospheric O$_2$ and moisture. The oil freezes at reduced temperatures and holds the crystal static in the X-ray beam [22]. Data for **1** and **2** were collected on a Stoe–Siemens AED four circle diffractometer. The structures of both were solved by direct methods and



Scheme 3.

refined by full-matrix least squares on F^2 [23]. The disorder in the lattice-bound THF molecule was modelled with the four carbon atoms each being in two 50:50 sites. Details of the structure refinements for **1** and **2** are shown in Table 1. Atom coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge crystallography data centre.

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