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Synthesis of crown ether complexes of alkali-metallated organophosphine oxides and insertion reactions with isonitriles

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Abstract

The synthesis and crystal structures of the alkali-metallated organophosphine oxides [$\{Ph_2P(O)CH_2\}K \cdot$ 18-crown-6] (**1**) and [$\{Ph_2P(O)CH_2\}Na \cdot$ 15-crown-5] (**2**) are reported. In addition the insertion reaction of an isonitrile into the C–Li bond of [$\{Ph_2P(O)CH_2\}Li$] is reported and the crystal structure of the resulting tetrameric complex $[Ph_2P(O)CH{=}CHN(Cy)Li]_4$ (**3**) (Cy = Cyclohexyl) described.

Keywords: Organophosphine oxide; Insertion reaction; Alkali metal complex; Wittig–Horner reaction

1. Introduction

Alkali-metallated derivatives of organophosphates and organophosphine oxides, are key intermediates in Wittig–Horner chemistry, widely used for the synthesis of alkenes [1,2]. The Wittig–Horner reaction employs metallated organophosphine oxides, with the original preparations involving metallation of benzyldiphenylphosphine oxide by potassium-*tert*-butoxide [2]. When lithium bases are used, the reaction yields an intermediate adduct in which the lithium counter ion binds strongly to the oxyanion formed in the process, preventing attack on the diphenylphosphoryl group [3]. Following acidification, β-hydroxyphosphine oxides are obtained, and these are stable and usually crystalline compounds at room temperature [3,4] (Fig. 1).

Despite such use, little was known about the lithium reagents in their own right until several solid-state structures of lithiated organophosphine oxides of the type $[LiR_2P(O)CH_2]_n$ and related compounds were determined, which showed that Li^+ ions are coordinated via the C and O atoms of $[R_2P(O)CH_2]^-$ and related bidentate ligands [5–9]. These results were followed by a study of the reactivity of the lithiated phosphine oxide nucleophiles with organic electrophiles but so far only reports of insertion reactions with nitriles exist [10,11]. In view of the advances made in the synthesis and structural characterisation of anionic lithium complexes with organophosphine oxide ligands, synthetic studies in this field are now extended to anionic organophosphine oxide complexes containing heavier alkali metals. The interest in heavier alkali metal derivatives was to assess the structural changes, in particular the influence on carbon–metal bonding as the size of the alkali metal ion changes. Furthermore the long-term aim of these investigations was to use variously metallated

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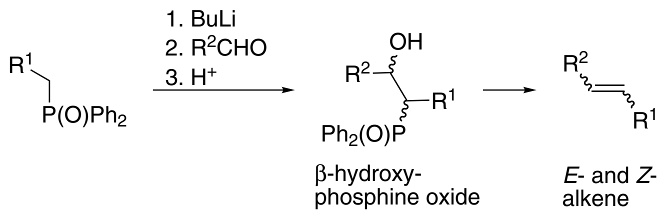

Fig. 1. The Wittig–Horner reaction (R^1, R^2 = alkyl, aryl).

organophosphine oxides in organic reactions with unsaturated compounds (e.g., nitriles, isonitriles, aldehydes, etc.).

2. Experimental

2.1. General remarks

All operations were carried out in an atmosphere of purified dinitrogen. Solvents were dried and freshly distilled prior to use. Benzylsodium (BzNa; Bz = CH_2Ph) and benzylpotassium (BzK) were prepared according to published procedures [12–14].

*[{$Ph_2P(O)CH_2$}K · 18-crown-6] (**1**).* A mixture of 0.53 g (2.00 mmol) of 18-crown-6, 0.26 g (2.00 mmol) of BzK and 0.43 g (2.00 mmol) of $Ph_2P(O)CH_3$ was suspended in 4 mL hexane. Addition of 15 mL thf to the reaction mixture and heating to reflux for 5 min afforded a brown solution. Storage of the solution at room temperature for 18 h, yielded brown crystals of **1**. Yield 0.51 g (49%). M.p. 138 °C; elemental analysis (calc. for $C_{25}H_{36}KO_7P$) C, 57.9; H, 7.0. Found: C, 56.2; H, 7.0%. ^1H NMR (27 °C, 250 MHz, [D_6]benzene): δ(ppm) = 8.7–6.9 (m., 10H, Ar–H), 3.4 (s., 24H, O–CH_2), 1.8, 1.7, 1.0 (d., $^2J_{HP}$ = 13.2 Hz, 2H, P(O)CH_2); ^{13}C NMR (27 °C, 100.62 MHz, [D_6]benzene): δ(ppm) = 148.2 (d., ^1JCP = 92.2 Hz, *ipso*-C), 133.2–127.1 (m., ar. C), 70.2 (s., OCH_2), 11.9 (d., $^1J_{CP}$ = 116 Hz, P(O)CH_2); ^{31}P NMR (27 °C, 161.975 MHz, [D_6]benzene): δ(ppm) = 36.1, 25.2,20.6, 14.2, 9.6 (s., $Ph_2P(O)CH_2$); IR (NaCl, nujol), $\tilde{\nu}(cm^{-1})$ = 1440 s (P–C ar.), 1302w (P–O) after hydrolysis. Variable-temperature ^{31}P NMR (0 °C, −25 °C, −50 °C, −75 °C, 161.975 MHz, [D_8]toluene) and ^1H NMR (0 °C, −25 °C, −50 °C, −75 °C, 400.16 MHz, [D_8]toluene) spectra did not show any significant difference from the spectra recorded at 25 °C. ^{39}K NMR (18.668 MHz, [D_8]toluene, saturated KBr solution in D_2O) spectroscopy did not give any observable signal. Cryoscopic experiments indicated a molecular mass of ca. 400 g mol^{-1} [15].

*[{$Ph_2P(O)CH_2$}Na · 15-crown-5] (**2**).* 0.23 g (2.00 mmol) of BzNa and 0.43 g (2.00 mmol) of $Ph_2P(O)CH_3$ were reacted together in a mixture of 7 mL of thf, 3.5 mL of hexane, and 0.41 mL (2.00 mmol) of 15-crown-5. Briefly heating to reflux followed by filtration afforded a brown solution. Storage at −20 °C for 18 h produced brown crystals of **2**. Yield 0.53 g (55%). M.p. 126 °C; elemental analysis (calc. for $C_{23}H_{32}NaO_6P$) C, 60.2; H, 7.0. Found: C, 59.5; H, 7.0%. ^1H NMR (27 °C, 400.16 MHz, [D_6]benzene): δ(ppm) = 8.6–7.1 (m., 10H, Ar–H), 3.4 (s., 20H, O–CH_2–O), 1.1 (d., $^2J_{HP}$ = 5.4 Hz, 2H; P(O)CH_2); ^{13}C NMR (27 °C, 100.62 MHz, [D_6]benzene): δ(ppm) = 146.2 (d., $^1J_{CP}$ = 92.3 Hz; *ipso*-C), 133.5–127.3 (m., ar. C), 69.7 (s., OCH_2), 10.5 (d., $^1J_{CP}$ = 107.6 Hz, P(O)CH_2); ^{31}P NMR (27 °C, 161.975 MHz, [D_6]benzene): δ(ppm) = 41.1, 25.8 (s., $Ph_2P(O)CH_2$); IR (NaCl, nujol), $\tilde{\nu}(cm^{-1})$ = 1441 s (P–C ar.), 1301w (P–O) after hydrolysis.

*[$Ph_2P(O)CH{=}CHN(Cy)Li]_4$ (**3**).* To a solution of 0.43 g (2.00 mmol) $Ph_2P(O)CH_3$ in 13 mL toluene was added ^{n}BuLi (1.33 mL, 2.00 mmol, 1.5 mol L^{-1} solution in hexanes). After 5 min a yellow precipitate formed and 0.25 mL of cyclohexylisonitrile (CyNC; Cy = cyclohexyl, C_6H_{11}) (2.00 mmol) was added. Stirring and short reflux afforded a deep orange-brown solution. Storage at room temperature for 2 days yielded yellow crystals of **3**. Yield 0.26 g (37%). M.p. 152 °C; elemental analysis (calc. for $C_{20}H_{23}LiNOP \cdot 0.25C_6H_5CH_3$) C, 73.7; H, 7.1; N, 4.0. Found: C, 73.9; H, 7.0; N, 4.1%. ^1H NMR (27 °C, 400.16 MHz, [D_8]THF), δ(ppm) = 7.8–7.2 (m., 10H, Ar–H), 2.7 (m., 1 H; C=CHN), 1.6 (m., $^2J_{PH}$ = 12 Hz, 1H, Ph_2PCH), 2.0–0.9 (m., 11H, Cy–H); ^{13}C NMR (27 °C, 100.62 MHz, [D_8]THF), δ(ppm) = 164.0 (s., C=NCy), 132.0–126.0 (m., ar. C), 69.8 (d., unresolved, $Ph_2P(O)C$), 34.8 (s., *ipso*-Cy), 24.0–22.0 (m., Cy); ^{31}P NMR (27 °C, 161.975 MHz, [D_8]THF), δ(ppm) = 35.5, 31.8, 25.2 (s., $Ph_2P(O)CH$); IR (NaCl, nujol), $\tilde{\nu}(cm^{-1})$ = 2260 s (NC), 1441s (P–C ar.); owing to the noxious smell of **3**, hydrolysis studies to identify a P–O stretching band were not carried out.

2.2. X-ray crystallographic study

Data were collected on a Rigaku diffractometer equipped with CCD detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (all data) using the SHELXTL program package [16]. Hydrogen atoms were placed in calculated positions, non-hydrogen atoms were assigned anisotropic thermal parameters. One molecule of lattice-bound toluene in **3** is disordered over two sites with poorly defined methyl carbon atom positions (H atoms were not refined for this toluene molecule). In Table 1 details of the refinement are listed.

3. Results and discussion

[{$Ph_2P(O)CH_2$}K · 18-crown-6] (**1**) and [{$Ph_2P(O)CH_2$}-Na · 15-crown-5] (**2**) were prepared in crystalline form via the reaction of $Ph_2P(O)CH_3$ with BzK or BzNa, respectively, in the presence of a crown ether of suitable size (Fig. 2). Despite repeated attempts we were unable to obtain crystalline material of the metallated phosphine oxides in the absence of crown ethers.

1 was initially characterised by NMR, IR spectroscopy and by elemental analysis. The high chemical shift of the deprotonated methyl group, observed as a doublet in the

Table 1
Details of the X-ray data collection and refinements

Compounds	1	2	3
Formula	$C_{25}H_{36}KO_7P$	$C_{23}H_{32}NaO_6P$	$C_{87}H_{100}Li_4N_4O_4P_4$
Formula weight	518.61	458.45	1417.35
T (K)	180(2)	180(2)	180(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.866(3)	10.2776(3)	13.8210(7)
b (Å)	19.854(6)	11.4077(3)	17.4460(9)
c (Å)	15.525(4)	11.9244(4)	17.4530(6)
α (°)	90	114.471(2)	92.702(3)
β (°)	100.96(2)	98.650(2)	97.744(3)
γ (°)	90	102.602(2)	96.836(2)
V (Å^3)	2683.0(14)	1195.33(6)	4131.7(3)
Z	4	2	2
ρ_{calc} (g cm^{-3})	1.284	1.274	1.139
μ (mm^{-1})	0.298	0.168	0.141
$F(000)$	1104	488	1508
2θ Range (°)	3.36–54.84	4.12–50.05	5.84–50.02
Reflections collected	10172	8038	23148
Unique data	6116	4211	14468
R_{int}	0.0308	0.0312	0.0338
Parameters	315	298	1020
wR_2 (all data)	0.1663	0.1901	0.2526
S (Goodness-of-fit)	1.054	1.084	0.940
R_1 [$I > 2\sigma(I)$]	0.0447	0.0567	0.0788
Peak, hole (e Å^{-3})	0.391, −0.496	0.866, −0.460	1.002, −0.539

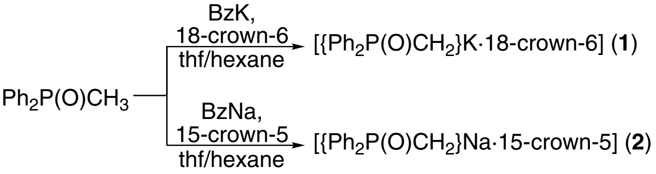

Fig. 2. Synthesis of the alkali-metallated organophosphine oxides **1** and **2**.

^{13}C NMR spectrum at δ 11.9 ppm, indicated that the successful synthesis of **1** had been achieved. The ^{1}H NMR spectrum shows the deprotonated methyl group resonances at δ 1.8, 1.7, 1.0 ppm. This, together with the presence of several resonances in the ^{31}P NMR spectrum, indicates that there are several different species present in solution. We believe these to be due, at least in part, to the formation of ion-separate species, as indicated by cryoscopic measurements which give an average aggregation number of less than 1 ($n = 0.8 \pm 0.2$ for $[\{Ph_2P(O)CH_2\}K \cdot 18\text{-crown-}6]_n$) in benzene solution. X-ray analysis of **1** reveals the monomeric unit $[\{Ph_2P(O)CH_2\}K \cdot 18\text{-crown-}6]$ to be a contact ion-pair (Fig. 3).

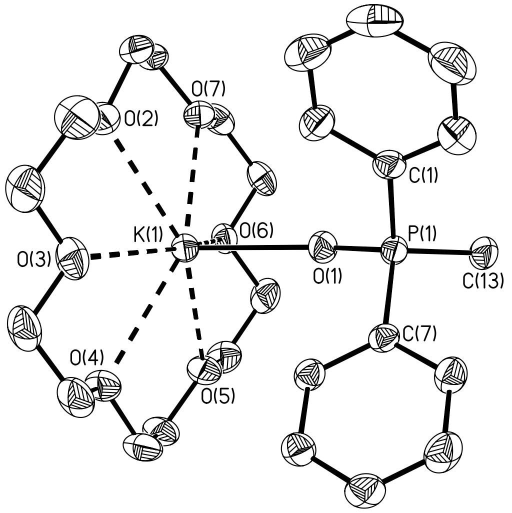

Fig. 3. Molecular structure of **1** (50% probability ellipsoids). Selected bond lengths (Å) and bond angles (°): K(1)–O(1) 2.563(2), K(1)–O(crown) 2.786(2)–2.932(2), P(1)–O(1) 1.516(2), P(1)–C(1) 1.829(3), P(1)–C(7) 1.836(2), P(1)–C(13) 1.687(3) and P(1)–O(1)–K(1) 155.26(11), O(1)–P(1)–C(7) 105.72(10), O(1)–P(1)–C(13) 126.58, C(7)–P(10)–C(13) 105.86(13).

The monoanionic ligand $[Ph_2P(O)CH_2]^-$ coordinates the potassium atom in the solid-state solely via its oxygen centre. The distance between the potassium and phosphoryl oxygen atom [2.563(2) Å] is shorter than those found in potassium complexes with neutral tertiary phosphine oxide ligands [cf. K···O(P) found in $Ph_3P(O)KX \cdot 18\text{-crown-}6$ (X = SCN, Br, I) = ca. 2.73 Å] [17]. The P–O bond distance in **1** [1.516(2) Å] is shorter than the P–O bond length observed in lithiated phosphine oxides [mean P–O 1.54 Å], although the P–C(H$_2$) bond distance in **1** [1.687(3) Å] is more comparable in length to the P–C(Li) bonds in these lithiates [mean 1.68 Å] [18]. The X-ray structure of **1** also shows that monomeric units of $[\{Ph_2P(O)CH_2\}K \cdot 18\text{-crown-}6]$ are closely packed in the solid-state forming a pseudo one-dimensional polymer with short distances between the potassium ions and an aromatic proton of a neighboring phenyl ring (Fig. 4).

The closest related compounds to **1** contain neutral organophosphine oxides as solubilizing additives for potassium salts [17,19–21].

Analogous to **1**, $[\{Ph_2P(O)CH_2\}Na \cdot 15\text{-crown-}5]$ (**2**) also contains both a crown ether and an anionic phosphine oxide ligand (Fig. 2). Previously sodium complexes with crown ether or phosphine oxide ligands had (like their potassium analogues) mainly been used as counter ions in transition metal complexes and cluster chemistry [17,19–21]. **2** was prepared according to Fig. 2 and characterised

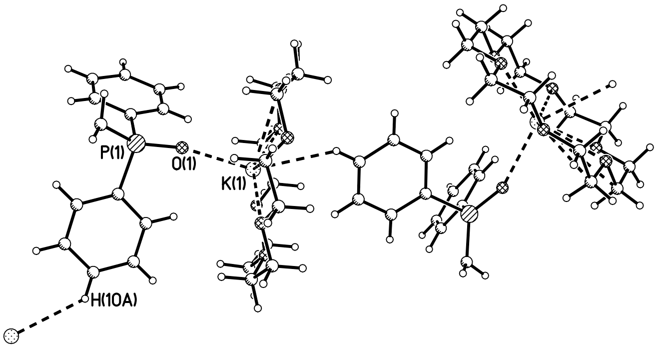

Fig. 4. Arrangement of **1** in the solid state (K···H ca. 2.85 Å).

by NMR, IR spectroscopy and elemental analysis. The deprotonated methyl group is observed as a doublet in the ^{13}C NMR spectrum at δ 10.5 ppm, indicative of the successful depronation of the parent phosphine oxide. The ^{1}H NMR spectrum shows the presence of the deprotonated methyl group at δ 1.1 ppm. The ^{31}P NMR spectrum shows resonances at δ 41.1 and 25.8 ppm, indicating the presence of two different aggregation states or bonding modes for **2** in solution. However, the low-temperature X-ray structure of **2** reveals it to be a monomer in the solid-state (Fig. 5).

The monoanionic phosphine oxide acts as a bidentate chelate ligand to the crown ether-solvated sodium cation. Unlike **1**, **2** does not show any intermolecular interactions. An explanation for this observation might be that the Na atom is sandwiched between the chelating phosphine oxide and crown ether and thus not available for close contacts in the solid-state with phenyl-protons from another molecule. In marked contrast to the potassium analogue **1**, in **2** the phosphine oxide chelates the alkali metal cation [Na(1)–C(1) 2.853(5) Å, Na(1)–O(1) 2.411(2) Å]. P–O and P–C(H) bond distances in **2** [P–O 1.511(2) Å and P(1)–C(1) 1.676(4) Å] are slightly shorter than those observed in **1**.

Recent studies have shown that nitriles insert into the C–Li bond of lithiated oganophosphine oxides such as [$Ph_2P(O)CH_2Li$] to give delocalised enamide species [11]. We have attempted similar insertion reactions of nitriles with **1** and **2**, although to date these have proved unsuccessful, resulting in the formation of amorphous polymeric compounds which could not be unambiguously identified. The synthetic potential of lithiated derivatives in reactions with organic unsaturated compounds, however, has not been fully investigated and a first result obtained from reactions with isonitriles is reported. **3** was synthesised by the reaction of [$Ph_2P(O)CH_2Li$] with cyclohexylisonitrile. Similarly to the syntheses of the intermediate lithium aldimines [11], it is also assumed that the first step of the reaction is the insertion of the isonitrile into the C–Li bond of [$Ph_2P(O)CH_2Li$] to give [$Ph_2P(O)CH_2C(Li){=}NCy$], which then rearranges via a 1,2 H-shift to form the lithiated organophosphorus imide **3** (Fig. 6).

Similar behaviour has been reported for reactions of arylisonitriles and organolithium reagents in the presence of tertiary amine donor solvents [10]. **3** was initially characterised by NMR and IR spectroscopy and by elemental analysis. The IR spectrum of the complex shows a strong N–C stretching band at 2260 cm^{-1}. The ^{1}H NMR spectrum shows the proton resonances within the OPCCN unit at δ 2.7 and 1.6 ppm, although these are not resolved and are partially obscured by the cyclohexyl protons. The ^{31}P NMR spectrum shows resonances at δ 35.5, 31.8 and

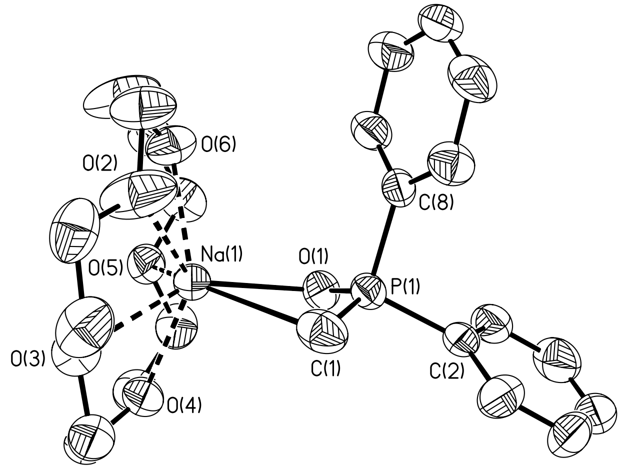

Fig. 5. Molecular structure of **2** (50% probability ellipsoids). Selected bond lengths (Å) and bond angles (°): P(1)–O(1) 1.511(2), P(1)–C(1) 1.676(4), P(1)–C(2) 1.833(3) and P(1)–C(8) 1.828(3), Na(1)–C(1) 2.853(5), Na(1)–O(1) 2.411(2), Na(1)–O(crown) 2.418(2)–2.566(3), P(1)–O(1)–Na(1) 97.00(11), O(1)–P(1)–C(1) 116.30(17), O(1)–P(1)–C(2) 106.05(13), P(1)–C(1)–Na(1) 78.14(16).

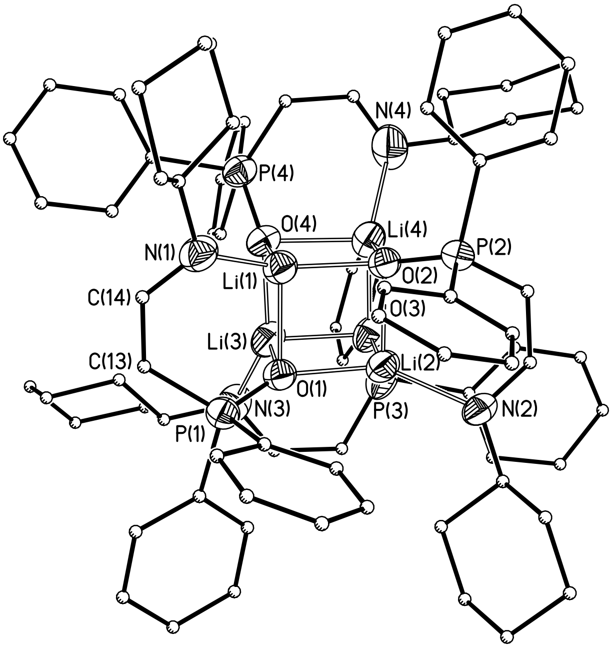

Fig. 7. Molecular structure of **3** (50% probability ellipsoids). Selected bond lengths (Å) and bond angles (°): P(1)–O(1) 1.533(3), P(1)–C(1) 1.804(4), P(1)–C(7) 1.814(4), P(1)–C(13) 1.716(4), Li(1)–O(1) 2.087(6), Li(1)–N(1) 2.049(7), N(1)–C(14) 1.307(5), C(13)–C(14) 1.393(6) and Li(1)–N(1)–C(14) 114.7(3), C(13)–C(14)–N(1) 127.1(4), O(1)–P(1)–C(13) 116.8(2).

$$Ph_2P(O)CH_3 \xrightarrow[\text{2. CyNC}]{\text{1. }^{n}\text{BuLi}} [Ph_2P(O)CH_2C(Li){=}NCy] \xrightarrow{\text{1,2 H-shift}} 1/4[\{Ph_2P(O)CH{=}CHNCy\}Li]_4\ (\mathbf{3})$$

Fig. 6. Synthesis of **3** (Cy = cyclohexyl).

25.2 ppm, suggesting that possibly more than one aggregation state is present in solution. The low solubility of **3** in benzene, however, prevented cryoscopic studies to verify this. X-ray structural characterisation of crystals of **3** reveals it to form a tetramer in the solid-state, based on a $(LiO)_4$ pseudo-cubane core (a CSD search revealed that more than 40 complexes containing $(LiO)_4$-cores have been reported [22,23]), with the N atoms internally donating to Li^+ cations of the core to form six-membered OPCCNLi chelate rings (Fig. 7). **3** is therefore structurally similar to the nitrile insertion product $[Ph_2P(O)CH{=}C(^tBu)N(H)Li]_4$ [11]. The long C–C and short N–C (C(14)–C(13) 1.393(6), N(1)–C(14) 1.307(5) Å) distances within these ring units indicate a similar degree of delocalisation as was found in $[Ph_2P(O)CH{=}C(^tBu)N(H)Li]_4$ [corresponding distances (PC=C) 1.399(5) and (C–N) 1.310(4) Å]. Also Li–N bonds found in the nitrile insertion product and **3** are almost identical [2.049(7) Å in **3**, cf. 1.958(6) Å in $[Ph_2P(O)CH{=}C(^tBu)N(H)Li]_4$].

4. Conclusion

The solid-state structures of **1** and **2** indicate that alkali metal complexes of a monoanionic tertiary phosphine oxide can be obtained by addition of crown ethers when attempts in non-donor media fail. In these complexes C–metal bonding is possibly less likely to occur in heavier alkali metal complexes (K, Rb and Cs) of organophosphine oxides when crown ether is present (so far the synthesis of a lithiated organophosphine oxide stabilised by 12-crown-4 did not produce single crystals). Future investigations of the reactivity of alkali-metallated organophosphine oxides could therefore possibly be related to the size of the alkali metal and ultimately the degree of C–metal bonding present in synthetic intermediates. Despite this potential, initial investigations of reactions of **1** and **2** with unsaturated compounds have not yielded any compounds that could be characterised unequivocally. The synthesis of **3** was achieved via the reaction of $[Ph_2P(O)CH_2Li]$ with cyclohexylisonitrile. Attempts to synthesise the heavier alkali metal derivatives of **3** are followed up in future investigations.

5. Supplementary material

CCDC Nos. 602310–602312 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

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