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Lithiated α-cyanophosphonates: self-assembly of two-dimensional molecular sheets composed of interconnected twenty-four membered rings †

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Reaction of the phosphonates $(RO)_2P(O)CH_2CN$ (R = Et **I** or Pr^i **II**) with one molar equivalent of $LiNPr^i_2$ in THF gave the metallated complexes $[(RO)_2P(O)CHCNLi\cdot THF]_\infty$ (R = Et **1** or Pr^i **2**). Crystallographic analyses of them reveal that they form dimeric $Li_2(O{=}P)_2$ units, which further aggregate through inter-dimer association *via* the nitrile of the phosphonate to form cross-linked, polymeric network structures. These sheets align in the crystals to form a 'patchwork' arrangement of molecular channels. The carbanionic centres of the phosphonates are devoid of Li–C contacts and almost perfectly planar. In solution, the dimeric units most likely remain intact but the nitrile is involved in chelation to a metal centre *via* intra-dimer association. Theoretical calculations show that chelation of the nitrile unit is a viable mode of bonding.

Introduction

Heteroatom-stabilised carbanions play a central role in the synthesis of new carbon–carbon bonds. Such reactions include Wittig-type olefinations, where a phosphorus functionality is present in the reagent.[1] These transformations can be classified into three general categories, depending on the nature of the phosphorus reagent: (i) Wittig reactions using phosphonium ylides,[2] (ii) Horner reactions using phosphine oxides[3] and (iii) Horner–Wadsworth–Emmons (HWE) reactions using phosphonates and other phosphonic acid derivatives (Fig. 1).[4]

Not surprisingly, the majority of research in this area has been directed towards the design of new reaction protocols or utilising developed methodologies in synthetic applications. Through careful selection of reagents and reaction conditions very high levels of chemo-, regio- stereo- and even enantio-selectivity can be achieved in a variety of olefination reactions.[1,5]

The wide applicability of Wittig-type reagents has also led to a keen interest in their solid- and solution-state structures.[6] Most notably, the groups of Snaith[7] and Denmark[8] have led the field in uncovering the structural patterns adopted by these compounds. Herein, we report the characterisation of a pair of lithiated α-cyanophosphonates, which are the first structurally characterised examples of HWE reagents utilising a α-functional group as a donor unit. The two reagents chosen, diethyl (cyanomethyl)phosphonate **I** and diisopropyl (cyanomethyl)phosphonate **II**, are known to undergo HWE reactions with differing stereoselectivities.[9–11] We therefore decided to investigate the properties of the lithiated derivatives of **I** and **II** in an attempt to discern any significant differences between the two complexes.[12]

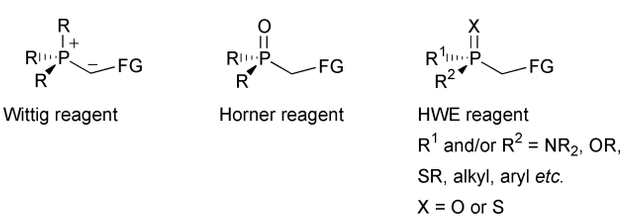


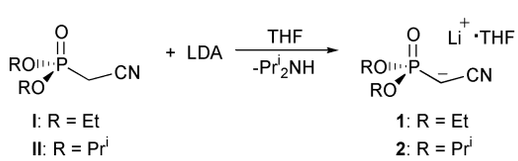
Fig. 1 Generalised Wittig-type reagents. FG = H, alkyl, aryl, or a functional group (*e.g.* CO_2R, OR, C≡N).

† Dedicated to the memory of Dr Ron Snaith, an inspiration in life as well as in science.

Results and discussion

Synthesis and spectroscopic characterisation

Reaction of either compound **I** or **II** with lithium diisopropylamide (LDA) in THF solution resulted in instantaneous precipitation of a solid (**1** or **2**), eqn. (1). Solid **1** proved difficult to



(1)

dissolve even on the introduction of additional THF or on extended heating of the mixture. In contrast, gentle heating of the mixture containing **2** resulted in complete dissolution. On isolation, **1** and **2** were initially analysed by infrared spectroscopy. Significantly, the C≡N signal of the lithiated complexes **1** and **2** was shifted down in wavenumber by >100 cm^{-1} compared to those of the parent ligands (Table 1). Furthermore, *both* the solid (Nujol mulls) and solution (THF) IR spectra gave similar frequency values for the nitriles. Such large shifts in frequency suggest a strong interaction between the metal and the nitrile.

NMR spectroscopic analysis of compounds **1** and **2** proved possible through use of d_5-pyridine as solvent media, and allowed the determination of their composition [eqn. (1)]. The significant features of the ^{1}H and ^{13}C NMR spectra of **1** and **2** are similar, and these are detailed in Table 1 along with comparative data for **I** and **II**. Both ^{1}H NMR spectra indicated the presence of mono-deprotonated phosphonate ligand, together with one mol equivalent of THF. In addition, the signal for the carbanionic (P–CH$^-$) proton shifts down in frequency (upfield) compared to those of the non-metallated ligands. Also of interest are the $^2J_{HP}$ values, which decrease on lithiation by 16.8 and

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Table 1 Comparative IR and NMR (d_5-pyridine) data for the "free" ligands and the complexes

Compound	$\tilde{\nu}$(C≡N)/cm^{-1}		δ_H(P–CH)	δ_C(P–C)	δ_C(C≡N)	$^2J_{HP}$/Hz	$^1J_{CP}$/Hz	$^2J_{CP}$ (CN)/Hz
	Nujol	THF						
I	2256	2254	3.78	18.33	116.65	21.0	141.0	11.2
II	2254	2253	3.72	18.04	115.68	20.8	140.6	11.2
1	2139	2143	1.72	4.69	133.30	4.2	241.7	11.6
2	2136	2145	1.68	5.93	133.62	4.9	239.4	11.1

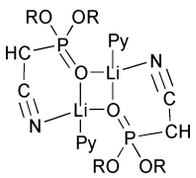

Fig. 2 Chelated dimeric solution structure for compounds **1** and **2** (where Py = pyridine and R = Et or Pr^i respectively).

15.9 Hz for **1** and **2** respectively. The large variance in the $^2J_{HP}$ coupling constants in similar systems has been shown to be related to the O=P–C–H torsion angle.[8b,13] These studies indicate that the values of 4.2 and 4.9 Hz found for **1** and **2** respectively are consistent with the O=P–C–H torsion angles lying between 120 and 180° (*anti*) for the ground state conformation of the complexes in solution.

The ^{13}C NMR spectroscopic data of compounds **1** and **2** gives some important insights into their solution structure. Most significantly, the $^1J_{CP}$ coupling constants of the carbanionic carbons (P–CH$^-$) are larger than for the parent phosphonate and this implies the formation of sp^2 centres with no Li–C contacts.[14] Also, lithiation of the phosphonates is accompanied by a downfield shift for the carbon of the nitrile, although there is essentially no accompanying change in the observed $^2J_{CP}$ coupling constants. It should also be noted that the THF present in both complexes is most likely displaced by d_5-pyridine molecules in solution. This is evidenced by the ^{1}H and ^{13}C chemical shift values of the donor ligand, which correspond to "free" THF.

In combination, the IR and NMR data suggest that *in solution* the nitriles are involved in chelation to the metals. This is consistent with the observed lowering of the C≡N frequencies in the solution spectra of compounds **1** and **2** compared to those of the non-metallated ligands. In addition, chelation of the nitrile would induce a O=P–C–H dihedral angle of ≈180° (antiperiplanar), which is consistent with the observed $^2J_{HP}$ coupling constants.[8b,13] Taking into account the spectroscopic data and by analogy with similar complexes,[8a–f,15] **1** and **2** are most likely to be chelated dimers in solution, which bridge through the P=O groups (Fig. 2).

There has been recent interest in the preparation of dilithiated derivatives of stabilised carbanions since in some instances these species have differing reactivities and selectivities compared to their monometallic analogues.[16] For example, Müller *et al.* have very recently prepared and characterised structurally an example of a dilithiated phosphonate, derived from dimethyl (trimethylsilylmethyl)phosphonate.[17] However, repeated attempts doubly to deprotonate **I** by reaction with two mol equivalents of LDA or even using the stronger base Bu^{t}Li resulted only in the formation of **1**.

X-Ray structural analysis

X-Ray quality crystals of compound **2** were readily prepared by slowly cooling a THF solution of it between 60 and 20 °C over a period of twelve hours. However, a similar approach for **1** only produced powders or microcrystalline materials. High quality crystals were eventually prepared by slow diffusion of the reactants in neat THF solution (see Experimental section).

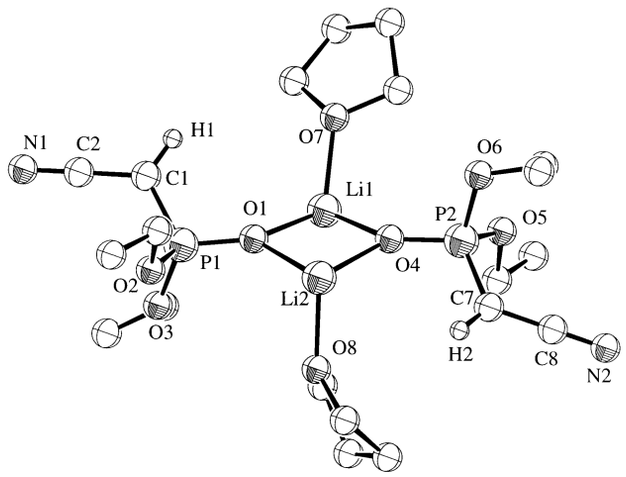

Fig. 3 Asymmetric unit of [(EtO)$_2$P(O)CHCNLi·THF] **1**. All hydrogens except that of the carbanion are removed for clarity, as are one of each pair of disordered atoms.

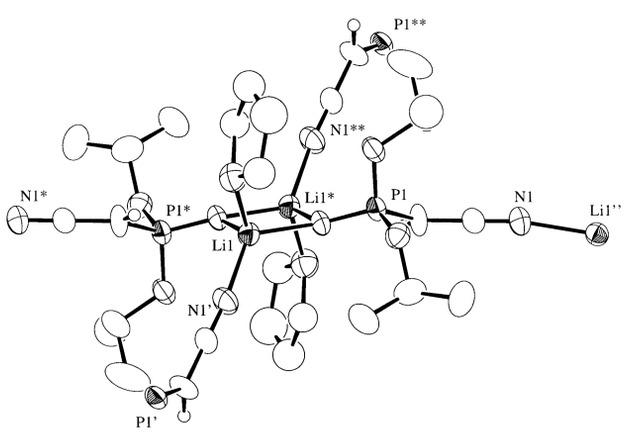

Fig. 4 Extended molecular structure of [(Pr^{i}O)$_2$P(O)CHCNLi·THF] **2** showing the dimeric Li_2O_2 unit and the linking nitrile groups. Other details as in Fig. 3.

Crystallographic analysis of **1** and **2** revealed that the extended solid-state structures of the two complexes are similar. The basic molecular units are dimeric Li_2O_2 rings, where the metals are bridged through the P=O groups (Figs. 3 and 4). Four-co-ordination of the metals is accomplished by binding to a single THF molecule and also to the nitrogen from a C≡N unit. The nitriles bond to the metals of neighbouring molecules (as opposed to chelation[18]) leading to the formation of one-dimensional polymeric chains.[19] These chains then interconnect *via* further Li···N≡C bonds to give the 'patchwork' two-dimensional sheet network shown in Fig. 5. The sheets are topologically equivalent to (4,4) nets and each twenty-four membered ring contains a Li_2O_2 dimeric unit at each of its four corners. Taking a view along a one-dimensional chain, it can be seen that neighbouring Li_2O_2 rings are rotated by approximately 90° in the plane of the network with respect to each other. Furthermore, each planar Li_2O_2 ring is tilted with respect to its neighbour by 75.8(2) and 88.7(2)° in **1** and **2** respectively.

The molecular sheets align in the crystal to form infinite pseudo-rectangular channels, which are partially filled by either the ethyl or isopropyl groups of the phosphonate (not shown).

Fig. 6 summarises the known solid-state molecular structures adopted by lithiated Wittig-type reagents.[7a,c,8a–g,15] Several features present in **1** and **2** have been previously noted for similar complexes: (i) the formation of Li_2O_2 rings, (ii) the lack of Li–C contacts, (iii) the *syn* orientation of the carbanionic hydrogen with respect to the P=O, and (iv) four-co-ordination of the metal centres. Only the new compounds **1** and **2**, as well as **8**, are polymeric, with the remaining complexes being monomeric, dimeric or tetrameric. Complex **8** adopts a polymeric network structure by utilising the bridging Lewis base DABCO ($N(CH_2CH_2)_3N$).[15] However, polymerisation of complexes **1** and **2** is achieved through the nitrile unit of the phosphonate. As such, they represent the only structurally characterised examples to date of Wittig-type reagents utilising an attached α-functional group as a Lewis base. This is most likely a consequence of the functional groups present in **3**–**12** being either alkyl or benzyl substituents, which display only limited abilities to act as donor units.

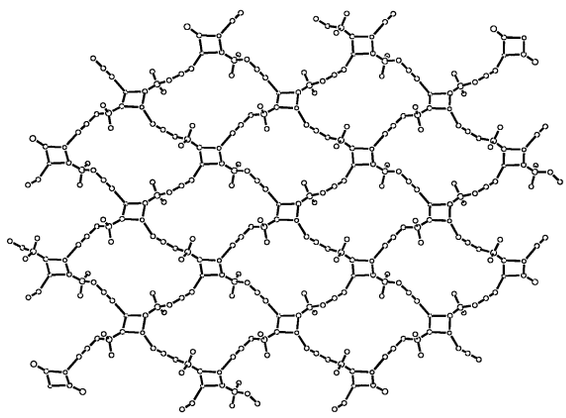

Fig. 5 Polymeric sheet network for compound **2** with all hydrogen atoms, THF molecules and carbons of the Pr^i groups removed for clarity.

The bond lengths in compounds **1** and **2** are similar to one another, and consistent with those found in the 'dimeric' complexes **3**–**8** (the key distances and angles for **1** and **2** are given in Tables 2 and 3). Each lithium lies in a distorted tetrahedral environment with the average of the angles being 109.6 and 109.2° for Li(1) and Li(2) in **1**, and 109.3° for the metals in **2**. Denmark *et al.*[8b] have previously used three indicators to assess the planarity of the carbanionic carbon: the sum of the angles around the carbanion (360.1 and 360.2° for C(1) and C(7) in **1**, and 360.0° in **2**); the deviation of the carbanion from the P–H–C(N) plane (0.02(3) and 0.04(2) Å for C(1) and C(7) in **1**, and 0.00(3) Å for **2**), and finally the angle (γ) between the C–H–C(N) plane and the C–P bond (2.6 and 5.2° using C(1) and C(7) in **1**, and 0.4° in **2**). From these data it is clear that

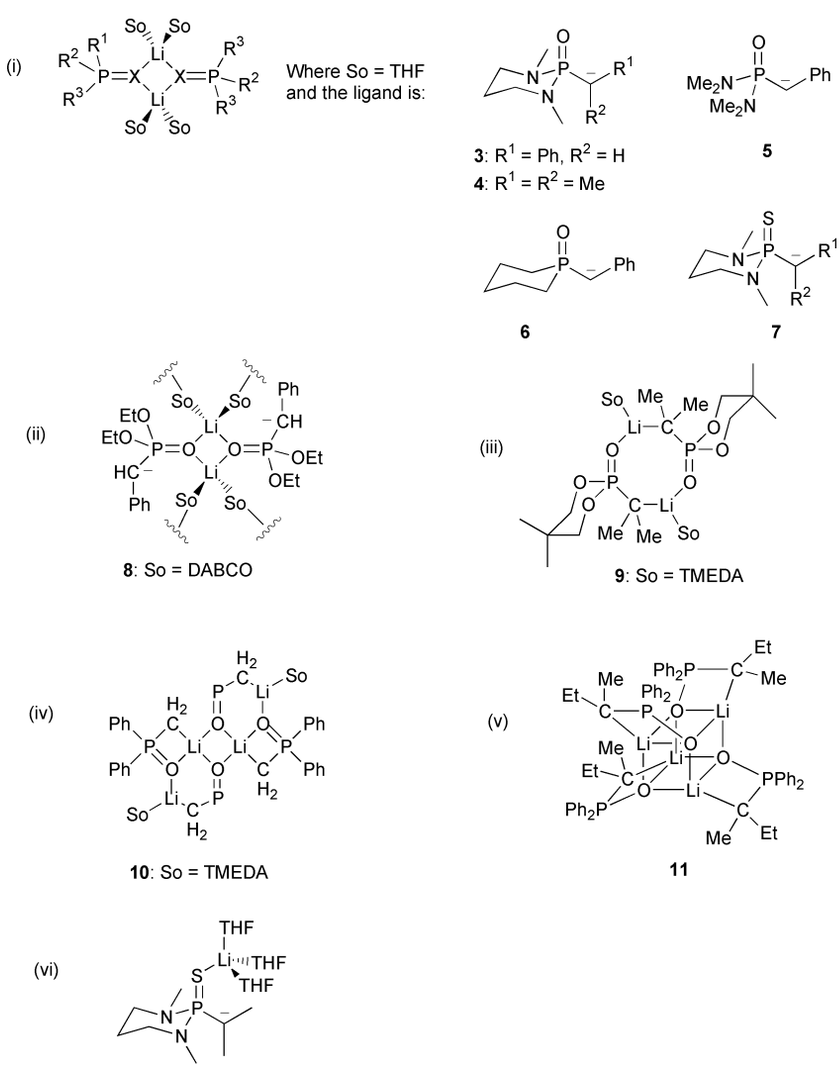

Fig. 6 Solid-state structures adopted by lithiated Wittig-type reagents.

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

P(1)–O(1)	1.502(2)	P(1)–O(2)	1.591(3)
P(1)–O(3)	1.583(3)	P(1)–C(1)	1.697(4)
P(2)–O(4)	1.492(2)	P(2)–O(5)	1.589(3)
P(2)–O(6)	1.589(3)	P(2)–C(7)	1.687(4)
Li(1)–O(1)	1.958(7)	Li(2)–O(1)	1.941(6)
Li(1)–O(4)	1.940(6)	Li(2)–O(4)	1.962(7)
Li(1)–O(7)	1.965(6)	Li(2)–O(8)	1.950(7)
N(1)–C(2)	1.160(5)	N(1)–Li(1)	2.009(7)
N(2)–C(8)	1.160(5)	Li(2)–N(2)	2.001(7)
C(1)–C(2)	1.391(5)	C(7)–C(8)	1.388(5)
N(1)–C(2)–C(1)	179.1(4)	N(2)–C(8)–C(7)	179.6(4)
O(1)–P(1)–O(2)	111.9(2)	O(1)–P(1)–O(3)	113.6(2)
O(1)–P(1)–C(1)	111.7(2)	P(1)–O(1)–Li(1)	137.3(2)
P(1)–O(1)–Li(2)	133.6(2)	Li(1)–O(1)–Li(2)	87.3(3)
P(2)–O(4)–Li(1)	141.5(2)	P(2)–O(4)–Li(2)	131.1(2)
Li(2)–O(4)–Li(2)	87.2(3)	Li(1)–N(1)–C(2)	152.8(4)
Li(2)–N(2)–C(8)	174.8(4)	P(1)–C(1)–C(2)	121.1(3)
P(2)–C(7)–C(8)	122.2(3)	O(1)–Li(1)–O(4)	92.3(3)
O(1)–Li(1)–O(7)	118.1(3)	O(1)–Li(1)–N(1)	114.8(3)
O(1)–Li(2)–O(4)	92.2(3)	O(1)–Li(2)–O(8)	105.4(5)
O(1)–Li(2)–N(2)	127.2(3)		
O(4)–P(2)–C(7)–C(8)	155.4(3)	O(1)–P(1)–C(1)–C(2)	177.9(3)
O(4)–P(2)–C(7)–H(2)	−25(3)	O(1)–P(1)–C(1)–H(1)	−2(3)
N(2)–C(8)–C(7)–H(2)	122(3)	N(1)–C(2)–C(1)–H(1)	−147(3)

Table 3 Selected bond lengths (Å) and angles (°) for compound **2**

P(1)–O(1)	1.585(4)	P(1)–O(2)	1.580(4)
P(1)–O(3)	1.488(4)	Li(1)–O(3)	1.925(9)
Li(1*)–O(3)	1.926(10)	Li(1)–O(4)	1.949(9)
Li(1)–N(1′)	1.957(10)	P(1)–C(1)	1.689(6)
N(1)–C(2)	1.160(7)	C(1)–C(2)	1.379(8)
N(1)–C(2)–C(1)	179.5(6)	O(1)–P(1)–O(2)	98.3(2)
O(1)–P(1)–O(3)	105.6(2)	O(3)–P(1)–C(1)	112.0(3)
P(1)–O(3)–Li(1)	148.0(4)	P(1)–O(3)–Li(1*)	122.6(3)
Li(1)–O(3)–Li(1*)	85.5(4)	C(2)–N(1)–Li(1″)	170.3(6)
P(1)–C(1)–C(2)	124.0(5)	O(3)–Li(1)–O(3*)	94.5(4)
O(3)–Li(1)–O(4)	106.3(4)	O(3)–Li(1)–N(1′)	108.0(4)
O(3)–P(1)–C(1)–C(2)	−166.1(5)	P(1)–C(1)–C(2)–N(1)	−143(77)
O(3)–P(1)–C(1)–H(1)	14(2)	N(1)–C(2)–C(1)–H(1)	35(2)

Symmetry relations: * $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$; ′ $x, -y, \frac{1}{2} + z$; ″ $x, -y, -\frac{1}{2} + z$.

the carbanions in **1** and **2** are essentially planar and sp^2 hybridised.

The bond lengths within the anionic phosphonate ligands of compounds **1** and **2** closely resemble those in **8** and the Li–N and N–C distances lie within the expected parameters for lithium salts complexed by a nitrile.[19,20]

In both complexes the hydrogen of the carbanion is oriented synperiplanar with respect to the P=O, and the key torsion angles in **1** and **2** are given in Tables 2 and 3 respectively. This clearly differs from the solution IR and NMR data for these complexes as discussed previously. To establish if chelation of the nitrile is feasible and to determine if this bonding mode would cause any distortion in the carbanion, an *ab initio* molecular orbital study of the model monomeric complex $[H_2P(O)CHCNLi]$ at the HF/6-31G* level of theory was undertaken. Two stationary points containing Li–O bonding were located using geometry optimisation procedures, with the cyano group in either chelated (H *anti*) or linear (H *syn*) arrangements (Fig. 7). Frequency analysis indicated that the chelated geometry is an energy minimum whereas the linear geometry is a transition state. Calculations using density functional theory (B3LYP/6-31G*) confirmed the chelated isomer as an energy minimum.[21]

The chelated isomer was found to be more stable by 26.9 kcal mol^{-1} than the linear arrangement, in accordance with the expected stabilisation induced by formation of a dative bond.[22]

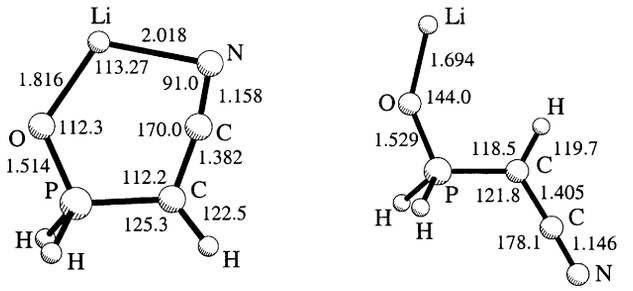

Fig. 7 Geometry optimised structures for the chelated and linear forms of the monomer $[H_2P(O)CHCNLi]$, with the key bond lengths (Å) and angles (°) shown.

Some distortions of the ligand occur on chelation, the most notable being the narrowing of the C–C≡N and the P–C–C angles and the lengthening the Li–O and C–N bonds, but the sum of the angles around the carbanion remains 360°. Overall, formation of a chelate appears to be a viable bonding option for the α-cyanophosphonate anion, with the predicted Li–N distance of 2.018 Å being reasonable for such an interaction.[19] The computed infrared wavenumbers for the nitrile of the chelated and linear isomers are 2134 and 2232 cm^{-1} respectively. These values further support ligation of the nitrile in both the solid state and in solution (Table 1). Furthermore, the O=P–C–H dihedral angle in the chelate is 180.0°, which is consistent with the observed $^2J_{HP}$ coupling constants for the complexes. It is pertinent that the $^2J_{HP}$ coupling constants of similar complexes are much larger than those for **1** and **2**.[8a–f,15] This suggests a *syn* arrangement for the O=P–C–H dihedral angles in these complexes as would be expected for non-chelating ligands.

Conclusion

The two newly characterised complexes **1** and **2** are mutually isostructural both in solution and in the solid state, and adopt a novel molecular architecture for Wittig-type reagents. The inter-dimer association of the nitriles found in the solid-state structures of **1** and **2** may be a consequence of a kinetic preference for precipitation of the polymeric networks. However, in solution chelation of the nitrile appears feasible with only limited distortion of the anionic ligand.

Lastly, from these studies it appears likely that the stereoselectivity differences between the phosphonates in HWE transformations[11] are due to subtle variances in the transition-state geometries adopted during their reactions, and not caused by gross aggregation effects.[1a,23]

Experimental

General preparative techniques

All experimental manipulations were performed under a purified argon atmosphere using standard Schlenk techniques or in an argon-filled glove box.[24] All solvents were distilled from sodium–benzophenone and used directly from the still. Diisopropylamine and the phosphonates **I** and **II** were purchased from Aldrich, distilled over CaH_2 and stored over 4A molecular sieves before use. *n*-Butyllithium was purchased from Aldrich as a 1.6 M solution in hexane and standardised before use.[25] The NMR spectroscopic data were recorded on a Bruker DPX 400 spectrometer at 298 K. Elemental analyses were carried out on a Perkin-Elmer 2400 elemental analyser. The IR data of compounds **1** and **2** were collected using a Nicolet Avatar 360 FTIR spectrophotometer as Nujol mulls or THF solutions prepared inside a glove box. Those of **I** and **II** were collected as neat liquid films.

Preparations and characterisations

$[(EtO)_2P(O)CHCNLi\cdot THF]_\infty$ 1. LDA was prepared by adding *n*-BuLi (5 mmol) to a solution of diisopropylamine (5 mmol) in 10 mL of THF at −78 °C. The solution was allowed to warm to ambient temperature before recooling to −78 °C. Dropwise addition of diethyl (cyanomethyl)phosphonate **I** immediately resulted in precipitation of a white solid, which only partially dissolved on warming the mixture. X-Ray quality crystals of **1** were obtained by layering a 15 mL THF solution of LDA (5 mmol) on top of a −78 °C cooled solution of phosphonate **I** (5 mmol) in 15 mL of THF. The reaction mixture was allowed to warm to ambient temperature and high quality crystals were produced at the interface of the two solutions over a period of 24 h. Yield 89% (Found: C, 45.5; H, 7.4; N, 5.8. $C_{10}H_{19}LiNO_4P$ requires C, 47.1; H, 7.4; N, 5.5%); $\tilde{\nu}_{max}/cm^{-1}$ (CN) 2139s (Nujol), 2143s (THF); δ_H (d_5-pyridine) 4.19 (4H, m, OCH_2, Et), 3.67 (4H, m, OCH_2, THF), 1.72 (1H, d, ^3J(HP) 4.2, PCH), 1.63 (4H, m, CH_2, THF) and 1.23 (6H, t, ^3J 7.1 Hz, CH_3, Et); δ_C (d_5-pyridine) 133.30 (d, ^2J(CP) 11.6, CN), 68.31 (s, OCH_2, THF), 61.06 (d, ^2J(CP) 5, OCH_2, Et), 26.28 (s, CH_2, THF), 17.18 (d, ^3J(CP) 7.5, CH_3, Et) and 4.69 (d, ^1J(CP) 241.7 Hz, PCH).

$[(Pr^iO)_2P(O)CHCNLi\cdot THF]_\infty$. LDA was prepared as above. Dropwise addition of diisopropyl (cyanomethyl)phosphonate **II** resulted in precipitation of a white solid after allowing the reaction mixture to warm to ambient temperature. X-Ray quality crystals of **2** were prepared by gently warming the mixture to dissolve the solid, followed by slow cooling of the solution to ambient temperature over 12 h. Yield 72% (Found: C, 50.1; H, 8.1; N, 5.0. $C_{12}H_{23}LiNO_4P$ requires C, 50.9; H, 8.1; N, 4.9%); $\tilde{\nu}_{max}/cm^{-1}$ (CN) 2136s (Nujol), 2145s (THF); δ_H (d_5-pyridine) 4.89 (2H, m, OCH, Pr^i), 3.67 (4H, m, OCH_2, THF), 1.68 (1H, d, ^2J(PH) 4.9, PCH), 1.63 (4H, m, CH_2, THF), 1.34 (6H, d, ^3J 6.18, CH_3, Pr^i) and 1.32 (6H, d, ^3J 6.18 Hz, CH_3, Pr^i); δ_C (d_5-pyridine) 133.62 (d, ^2J(CP) 11.1, CN), 68.63 (d, ^2J(CP) 5, OCH, Pr^i), 68.31 (s, OCH_2, THF), 26.28 (s, CH_2, THF), 24.98 (d, ^3J(CP) 4.0, CH_3, Pr^i), 24.85 (d, ^3J(CP) 5.0, CH_3, Pr^i) and 5.93 (d, ^1J(CP) 239.4 Hz, PCH).

X-Ray crystallography

Crystals of compounds **1** and **2** were taken directly from their crystallisation vessels and mounted using a protective oil blanket.[26]

Crystal data for compound 1. $C_{20}H_{38}Li_2N_2O_8P_2$, $M = 510.34$, −150 °C, monoclinic, space group $P2_1/n$, $a = 14.926(8)$, $b = 11.024(5)$, $c = 16.663(10)$ Å, $\beta = 97.83(5)°$, $V = 2716(2)$ Å^3, $Z = 4$, 4936 reflections collected, 4776 unique, $R_{int} = 0.067$, full-matrix least-squares refinement[27] on F^2 using 321 parameters and all unique reflections converged to $R1 = 0.065$ for 3534 observed reflections with $I > 2\sigma(I)$ and $wR2 = 0.1711$ for all data. C(6) was modelled as disordered over two sites. The H atoms were placed in calculated positions and allowed to ride on their parent atoms with the exception of HCCN, which was found in a difference synthesis and then refined isotropically.

Crystal data for compound 2. $C_{24}H_{46}Li_2N_2O_8P_2$, $M = 566.45$, −123 °C, monoclinic, space group $C2/c$, $a = 22.243(3)$, $b = 9.837(2)$, $c = 15.585(3)$ Å, $\beta = 107.131(8)°$, $V = 3258.8(10)$ Å^3, $Z = 4$, 4671 reflections collected, 2432 unique, $R_{int} = 0.0774$, full-matrix least-squares refinement[27] on F using 177 parameters and all unique reflections converged to $R1 = 0.0755$ for 1353 observed reflections and $wR2 = 0.2204$, for all reflections. C(4) and the THF molecule were modelled as disordered over two sites. The H atoms were treated as above.

CCDC reference number 186/2242.

See http://www.rsc.org/suppdata/dt/b0/b007038f/ for crystallographic files in .cif format.

Computational details

The GAUSSIAN 94 programm (revision E.2) run on a Silicon Graphics Origin 200 workstation was used for the calculations.[28] No symmetry constraints were imposed and all molecules allowed freely to optimise. Frequency analysis was used to determine if true minima or transition states were located. The quoted infrared frequencies were scaled by a factor of 0.8953.[29] All calculations used the general basis set 6-31G*,[30] which is known to be accurate for modelling lithium-based organometallics.[22,31] The HF/6-31G* absolute energies (Hartrees) of the complexes were −555.01452 and −554.97166 for the chelated and linear arrangements respectively.

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