ESI †

Optimised conditions: ^{n}BuLi (1.6M in hexanes, 0.61 ml, 0.98 mmol) was added dropwise to a solution of 1,2-$(PH_2)_2C_6H_4$ (70 mg, 0.49 mmol) in 3ml thf at 0°C. The orange solution was warmed to room temperature and stirred for 30 min. The reaction mixture was again cooled to 0°C and $Sb(NMe_2)_3$ (2M solution in toluene, 0.08 ml, 0.16 mmol) was added dropwise. The solution was then heated to reflux for 1h, during which time it had become a deep red colour. 12-Crown-4 (0.17 ml, 172 mg, 0.98 mmol) was added, and the reaction mixture allowed to cool slowly. After a period of 2d, orange-yellow crystals had formed. The supernatant liquid was removed *via* syringe and the crystals collected and allowed to dry on filter paper in a glovebox. Yield 61 mg [47%, based on 1,2-$(PH_2)_2C_6H_4$ supplied, assuming each $[C_6H_4P_3]^-$ anion formed requires 2 equiv. of 1,2-$(PH_2)_2C_6H_4$]. Prolonged standing of the reaction mixture (1 week) leads to the formation of black, block-shaped crystals of **2**, together with **1**. Characterisation of **1** (numbering scheme, Fig. 1): ^{1}H NMR (500.12MHz, +25°C, D_8-THF), δ= 8.43 [mult., 2H, C(27,28)-H, C_6H_4 group], 6.78 [mult., 2H, C(25,26)-H, C_6H_4 group], 3.48 [s., 24H, 12-crown-4]. ^{13}C NMR (125.74MHz, +25°C, D_8-THF), δ= 173.1 [mult., C(29,30)], 130.1 [mult., C(27,28)], 117.6 [mult., C(25,26)], 67.6 [s. 12-crown-4]. ^{31}P NMR (161.98MHz, +25°C, D_8-THF/acetone capillary), δ= 335.2 [dd., P(2)], 260.7 [dd., P(1,3)] ($|^1J_{P(1,3)-P(2)}|$ = ca. 500Hz, $|^2J_{P(1)-P(3)}|$ = ca. 10Hz). Found C 49.7, H 7.0, cald. for **1** C 50.0, H 6.9. **2** was characterized by X-ray crystallography alone.

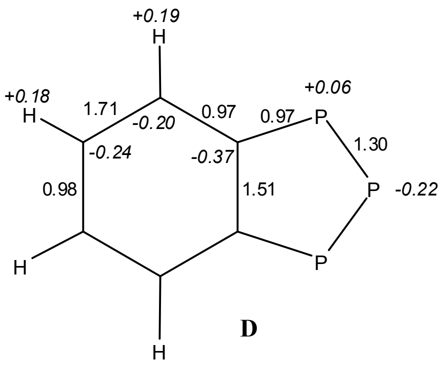
ESI ‡

Crystal data for **1**; $C_{22}H_{36}LiO_8P_3$, M= 528.36, crystal system Monoclinic, space group *P2*(1)/*n*, *Z*= 4, *a*= 11.8321(2), *b*= 8.36690(10), *c*= 26.5285(5)Å, β= 94.4390(10), *V*= 2618.39(7)Å^3, μ(Mo–Kα) = 0.270mm^{-1}, ρcalc= 1.340 Mg m^{-3}, *T*= 120(2)K. Total reflections 16782, unique 8021 (*R*int= 0.026). *R*1= 0.037 [I>2σ(I)] and *wR*2= 0.099 (all data). Crystal data for **2**; $C_{48}H_{96}Li_3O_{24}Sb_{11}$, M= 2417.32, crystal system Rhombohedral, space group *R*3, Z= 6, *a*= *b*= 21.138(3), γ= 32.330(7)Å, *V*= 12510(4)Å^3, μ(Mo–Kα) = 0.270mm^{-1}, ρcalc= 1.925 Mg m^{-3}, *T*= 180(2)K. Total reflections 2555, unique 2023 (Rint= 0.045). R1= 0.083 [I>2σ(I)] and *wR*2= 0.238 (all data). Due to shortage of data, caused by crystal decomposition, the 50:50 disordered 12-crown-4 ligands were assigned fixed geometries and refined with isotropic atomic displacement parameters. Running the cif through checkCIF suggested the higher symmetry space group *R*-3 is more appropriate. However, no solution could be found using this space group with the limited number of data available. Data were collected on a Nonius KappaCCD diffractometer and solved by direct methods and refined by full-matrix least squares on F^2 (G. M. Sheldrick, SHELX-97, Göttingen, Germany, 1997). CCDC 668766 and 668765 contain the supplementary crystallographic data for **1** and **2**, respectively. Data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; deposit@ccdc.cam.ac.uk).

ESI ¥
Summary of DFT Calculations

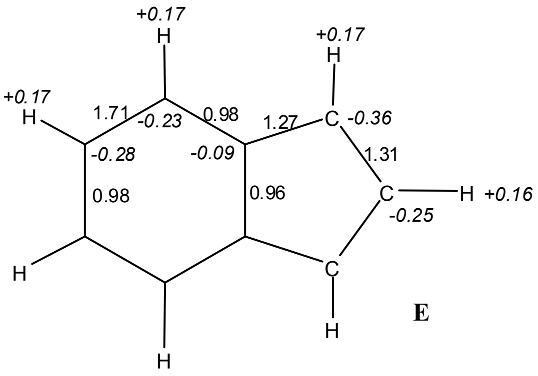
An NBO analysis based on DFT calculations at the B3LYP/6-311G* level on the triphosphinide anion reveal substantial delocalisation of the negative charge around both phenylene and C/P rings and significant π-bonding character in both the phenylene and heterocyclic C/P rings.

a)



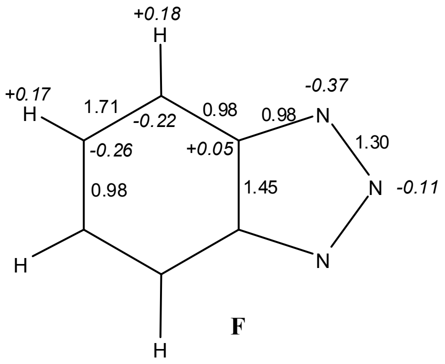
D

c)



E

c)



F

Fig. 3 DFT calculations at the B3LYP/6-311G* level on a) the $[C_6H_4P_3]^-$ anion (**D**), b) the $[C_6H_4(CH)_3]^-$ anion (**E**), c) $[C_6H_4N_3]^-$ anion (**F**). Values in plain text are bond orders, those in italics are charges.

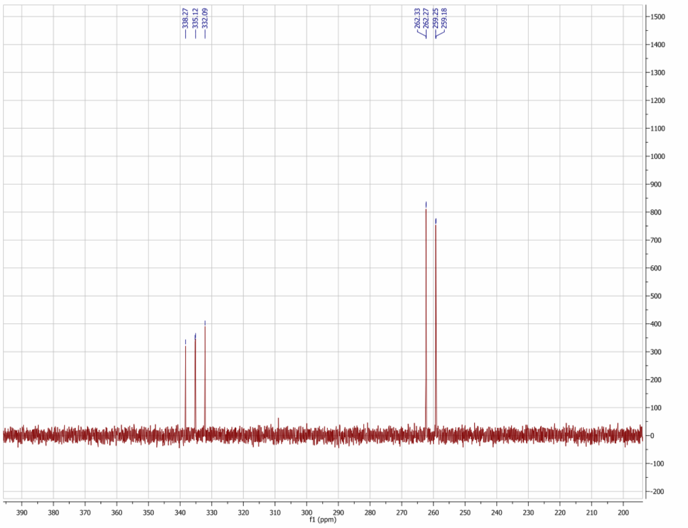
Calculated bond angles and lengths in the C_2P_3 ring are:

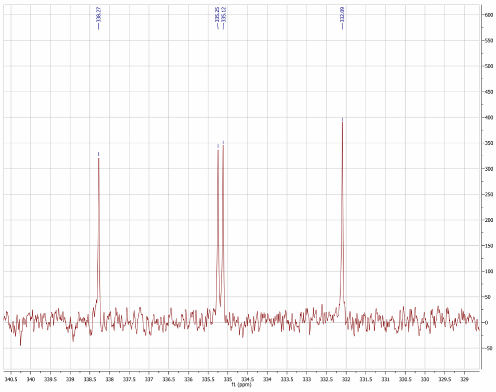
Parameter	B3LYP/6-31G	B3LYP/6-31G*	B3LYP/6-311G	B3LYP/6-311G*
C-C	1.432	1.435	1.428	1.432
C-P	1.837	1.802	1.834	1.802
P-P	2.208	2.121	2.217	2.123
CCP	121.9	120.6	122.2	120.7
CPP	98.0	98.9	97.9	98.8
PPP	100.0	101.0	99.6	101.0
E (au)	-1253.588025	-1255.189253	-1255.188187	-1255.324005

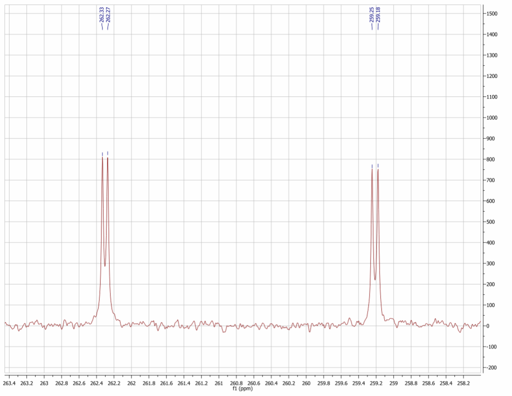
The energy converged as the basis set size was increased from double zeta 6-31G to triple zeta 6-311G*, although there is a small oscillation in bond distances and angles (ca. 0.01Å and ca. 1^o). The oscillations do not affect the NBO values significantly.

NMR Spectroscopy

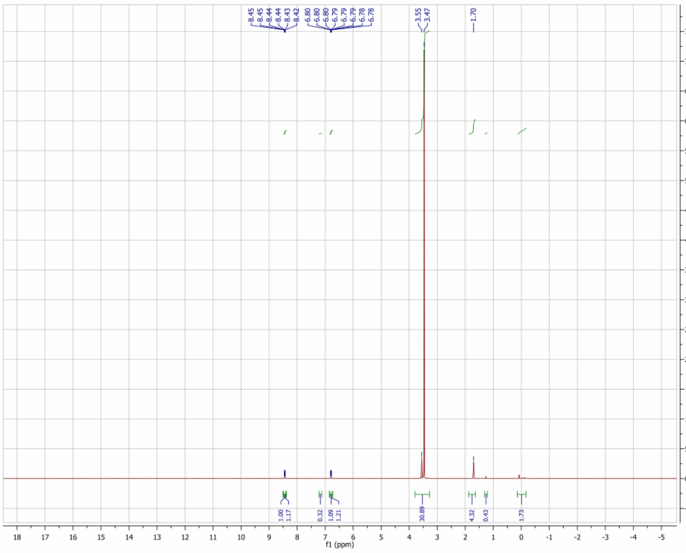
$^{31}P\{^1H\}$ NMR

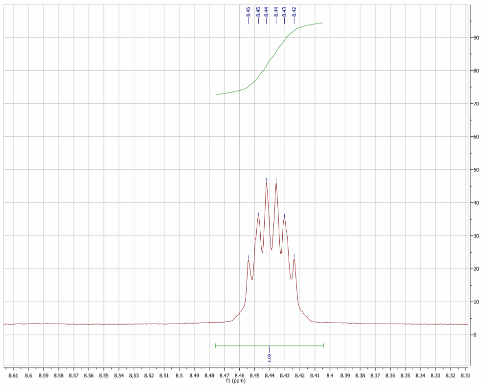


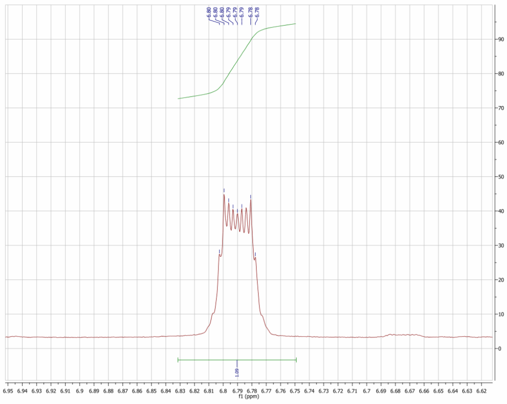




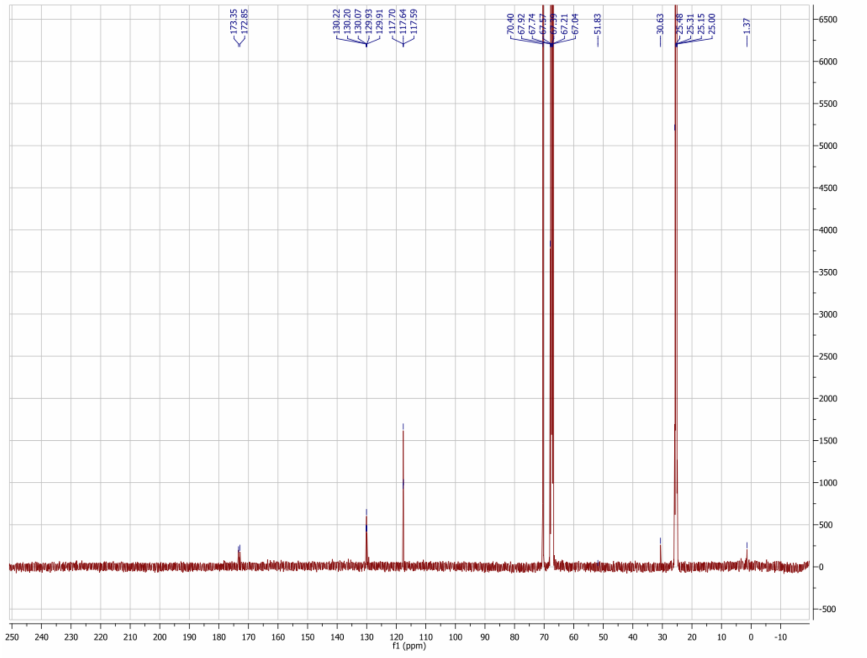
^{1}H NMR

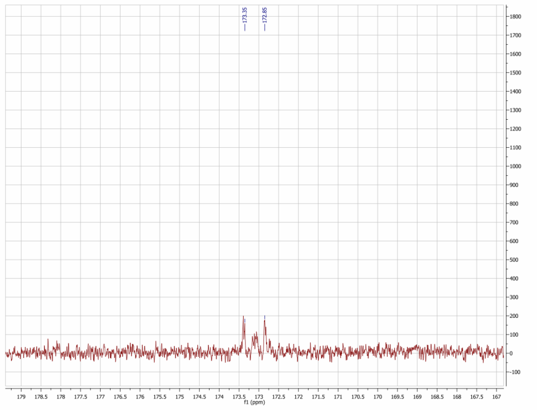

8.45
8.45
8.44
8.44
8.43
8.42
6.80
6.80
6.80
6.79
6.79
6.79
6.78
6.78
3.55
3.47
1.70
1.00
1.17
0.32
1.09
1.21
30.89
4.32
0.43
1.73
f1 (ppm)

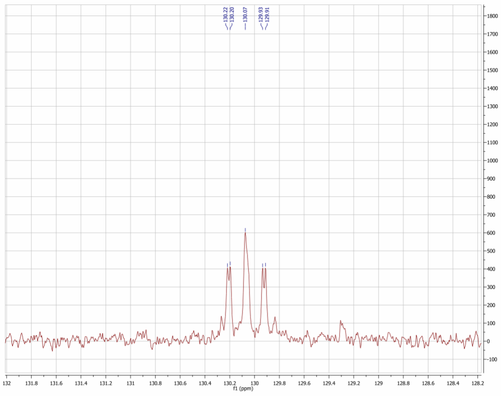

8.45
8.45
8.44
8.44
8.43
8.42
1.00
f1 (ppm)

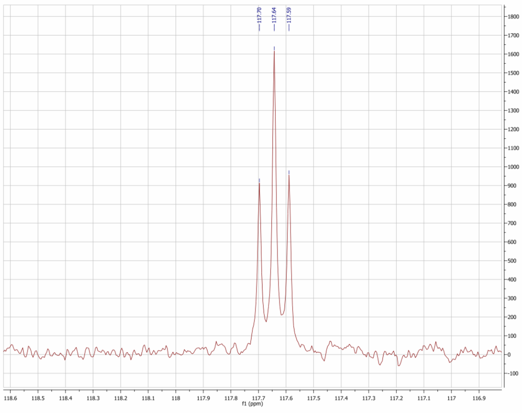

6.80
6.80
6.80
6.79
6.79
6.79
6.78
6.78
1.09
f1 (ppm)

^{13}C NMR


173.35
172.85
130.22
130.20
130.07
129.93
129.91
117.70
117.64
117.59
70.40
67.92
67.74
67.57
67.39
67.21
67.04
51.83
30.63
25.48
25.31
25.15
25.00
1.37
f1 (ppm)


173.35
172.85
f1 (ppm)


130.22
130.20
130.07
129.93
129.91
f1 (ppm)


117.70
117.64
117.59
f1 (ppm)