Supplementary Information

1,2-Diphosphinobenzene as a Synthon for the 1,2,3-Triphospha- and 2-Arsa-1,3-Diphosphaindenyl Anions and a Stable Organo Derivative of the P_8 unit of Hittorf's Phosphorus

Craig P. Butts,[a] Michael Green,*[,a] Thomas N. Hooper,[a] Richard J. Kilby,[a] John E. McGrady,[b] Dimitrios A. Pantazis[b] and Christopher A. Russell*[,a]

[a] *School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS (UK) Fax: +44 (0)117 929 0509; Tel: +44 (0)117 928 7599; E-mail: Chris.Russell@bris.ac.uk*

[b] *WestCHEM, University of Glasgow, Joseph Black Building, Glasgow, G12 8QQ (UK).*

Computational Analysis of the 1,2,3-triphosphaindenyl Anion

We have used density functional theory to compare the electronic structure of the all-carbon analogue, the indenyl anion $[C_9H_9]^-$, with the so far hypothetical $[1,2,3\text{-}C_6H_4P_3]^-$ anion, and then to go on to compare the ligating properties of these two systems. A comparison (Figure S1) of the frontier orbitals of the two anions, $[C_9H_7]^-$ and $[1,2,3\text{-}C_6H_4P_3]^-$, reveals significant differences that may influence their coordination chemistry.

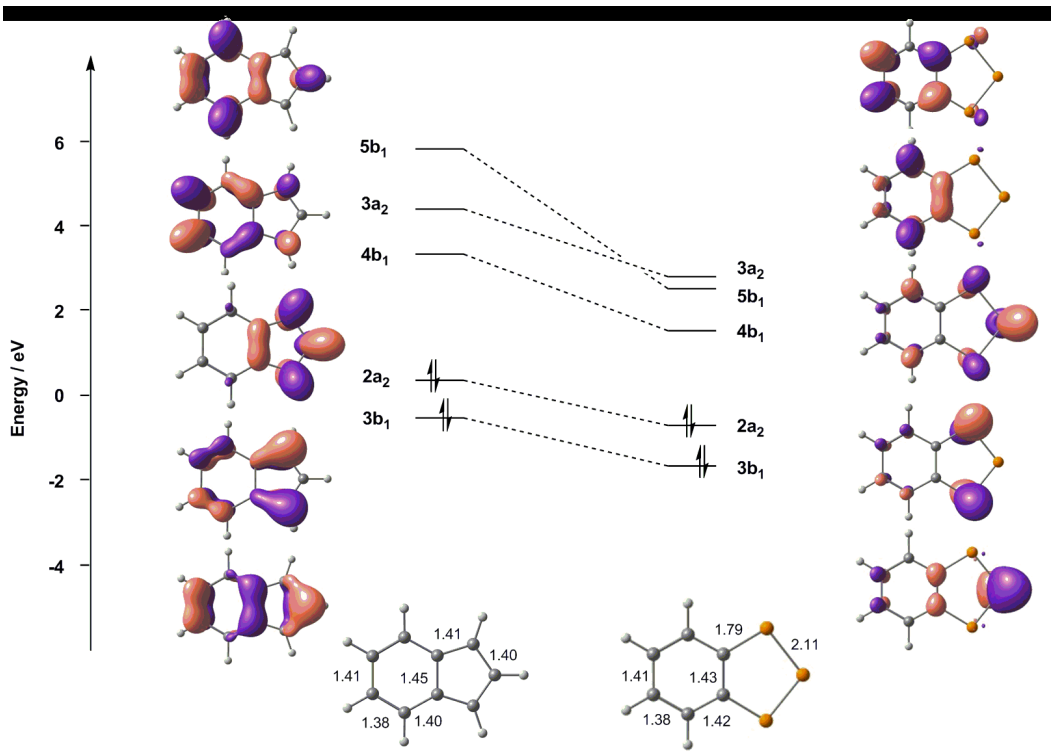

Fig. S1 Optimised geometries and frontier π orbitals of $[C_9H_7]^-$ and $[1,2,3\text{-}C_6H_4P_3]^-$.

The presence of three phosphorus centres in the latter substantially stabilises the π manifold, but the effect is most dramatic in the vacant orbitals. The frontier orbitals ($3b_1$, $2a_2$, $4b_1$) are strongly localised on the P_3 unit in $[1,2,3\text{-}C_6H_4P_3]^-$, while the remaining six π orbitals (only two of which are shown in the Figure) are strongly localised on the benzene ring. In the indenyl anion, in contrast, the frontier orbitals are delocalised over the entire C_9 framework. The separation of the π manifolds of the C_6 and P_3 units in $[1,2,3\text{-}C_6H_4P_3]^-$ is consistent with the relative instability of P=P π bonds compared to their C=C analogues, and should lead to a reduction in the aromaticity of the C_2P_3 ring. Nucleus-independent chemical shift values (NICS),[1] confirm this expectation: the computed NICS values at the centre of the 5-membered ring in $[1,2,3\text{-}C_6H_4P_3]^-$ is -11.7 ppm compared to -13.7 ppm for the all-carbon analogue.

The stabilisation of the π* LUMO of $[1,2,3\text{-}C_6H_4P_3]^-$ ($4b_1$) relative to its counterpart on the indenyl anion would be expected to enhance the backbonding when coordinated to a metal centre.

To provide a quantitative estimate of the difference between the two ligands in this regard, we have followed the methodology used by J. C. Green and co-workers in their study of 1,2,4-triphosphorus-substituted cyclopentadienyl analogues.[2, 3] We have optimised the structure of a putative ferrocene analogue containing both ligands, [Fe(C_9H_7)(1,2,3-$C_6H_4P_3$)] (C_s symmetry, staggered conformation) and then performed a fragment calculation where the electron density is converged from distinct Fe^{2+}, $[C_9H_7]^-$ and $[1,2,3\text{-}C_6H_4P_3]^-$ components (rather than the separated atoms). In this way, the extent to which the vacant orbitals on the indenyl and 1,2,3-triphosphaindenyl anions interact with the metal centre can be estimated from the population of these two orbitals in the converged solution. The populations of the $4b_1$, $3a_2$ and $5b_1$ orbitals of the fragments (all of which are vacant in the isolated anions) are summarised in Table S1, and confirm the stronger back-bonding to the phosphorus-substituted ring, most notably in the $4b_1$ orbital.

	$4b_1$	$3a_2$	$5b_1$
$[C_9H_7]^-$	0.07	0.07	0.09
$[C_6H_4P_3]^-$	0.23	0.12	0.07

Table S1 Populations of the fragment orbitals of $[C_9H_7]^-$ and $[1,2,3\text{-}C_6H_4P_3]^-$ in [Fe(C_9H_7)(1,2,3-$C_6H_4P_3$)] (in units of electrons).

 Calculations on the free anions, including the NICS values,[1] were performed using the Gaussian 03 package.[4] The structure were optimised using the B3LYP functional[5] in conjunction with the 6-311+G(2df,p) basis set on all atoms. NICS values were computed using the GIAO approach.[6] Calculations on the iron complexes, including the fragment calculations, were done with the Amsterdam Density Functional package (ADF2005.01).[7-9] A double-ζ Slater-type basis set, extended with a single polarization function, was used to describe the main group atoms, while iron was modeled with a triple-ζ basis set. Electrons in orbitals up to and including 1s {C}, 2p {P} and 3p {Fe} were considered part of the core and treated in accordance with the frozen core approximation. The local density approximation[10] was employed for the optimizations, along with the local exchange-correlation potential of Vosko, Wilk and Nusair[11] and gradient corrections to exchange and correlation proposed by Becke and Perdew (BP86).[12, 13] All structures were optimized using the gradient algorithm of Versluis and Ziegler.[14] The structures of the isolated anions, $[1,2,3\text{-}C_6H_4P_3]^-$ and $[C_9H_7]^-$, were constrained to C_{2v} point symmetry, while the complex [Fe(C_9H_7)(1,2,3-$C_6H_4P_3$)] was optimized in C_s symmetry, with a staggered arrangement of the ligands.

Synthesis of 1, 2 and 3

To a THF (20 mL) solution of 1,2-diphosphinobenzene (1 mL, 1 M solution in *n*-hexane, 1 mmol) was added four equivalents of $LiBu^n$ (2.5 mL, 1.6 M in hexanes, 4 mmol) at -78 °C. The orange solution was allowed to warm to room temperature and stirred for 20 minutes before being recooled back to -78 °C whereupon PCl_3 (1 mL, 1 M solution in *n*-hexane, 1 mmol) was added giving a dark red solution. Crystals of **3** are produced by concentrating the solution *in vacuo* to *ca.* 1 mL and layering with *n*-hexane; storage at 20 °C for 16 h yielded a small crop of yellow rectangular prismatic crystals which were suitable for an X-ray diffraction study. Compound **1** was purified by addition of extra THF (80 mL) and 12-crown-4 (1.29 mL, 8 mmol) to the orange solution which gives an orange-yellow coloured precipitate. The precipitate was removed by filtation (porosity 3 sinter with Celite); storage of the solution for 16 h at 5 °C gave 260 mg (49 %) of **1**.

Data for **1**: m.p.: the sample loses a colourless oily liquid (presumably 12-crown-4) at 169 °C resulting in an orange solid - no further change was seen up to 200 °C; $^{31}P\{^1H\}$ NMR (121.45 MHz, 21 °C, C_4D_8O): δ = 260.3 (d, J_{PP} 486 Hz), 260.3 (d, J_{PP} 514 Hz), 334.8 (dd, J_{PP} 486, 514 Hz) ppm; ^1H NMR (270.16 MHz, 21 °C, C_4D_8O): δ = 8.46 (m, 2H), 6.81 (m, 2H), 3.50 (s, 32H, 12-c-4). Anal. Calcd. for $C_{22}H_{36}P_3O_8Li$ C 50.00 %, H 6.82 %; found C 49.54 %, H 7.29 %;

Data for **2**: Isolation was carried out as described above to give 40 mg of **2**. (7 %) m.p.: the sample decomposes to a black solid at ca. 198 °C; $^{31}P\{^1H\}$ NMR (121.45 MHz, 21 °C, C_4D_8O): δ = 302.9 (s) ppm; ^1H NMR (270.16 MHz, 21 °C, C_4D_8O): δ = 8.52 (m, 2H), 6.79 (m, 2H), 3.50 (s, 32H, 12-c-4). Despite repeated attempts we were unable to obtain a satisfactory elemental analysis for **2**.

X-ray Data on 1-3

Single crystals of **1** and **2** were grown from thf solutions stored at 5 °C for 16 h. Single crystals of **3** (polymorph *a*) were grown from a saturated thf solution layered with *n*-hexane stored at 20 °C for 16 h. Single crystals of polymorph *b* were grown from a 1,2-dimethoxyethane solution stored at 20 °C for 72 h. Crystals of **1-3** were mounted in an inert oil and transferred to the cold gas stream of the diffractometer. X-ray measurements were made for **1, 3a** and **3b** using a Bruker PROTEUM CCD three circle diffractometer with Cu-K_α radiation (λ = 1.54178 Å); the corresponding measurements for **2** were made on a Bruker SMART CCD area-detector diffractometer with Mo-K_α radiation (λ = 0.71073 Å).

Crystal data for **1**: $C_{22}H_{36}LiO_8P_3$, M = 528.36, monoclinic space group $P(2)1/n$, a = 11.7697(2), b =

8.3447(2), c = 26.3675(5) Å, β = 94.255(1)°, U = 2582.54(9) Å^3, T = 100(2) K, Z = 4, μ(Cu-K$_\alpha$) = 2.490 mm^{-1}, 16147 reflections measued, 3782 unique (R_{int} = 0.0709) which were used in all calculations. The final R_1 [I>2σ(I)] was 0.0435.

Crystal data for **2**: $C_{22}H_{36}AsLiO_8P_2$, M = 572.31, monoclinic space group $P2(1)/n$, a = 11.796(2), b = 8.344(2), c = 26.460(5) Å, β = 94.13(3)°, U = 2597.8(9) Å^3, T = 100(2) K, Z = 4, μ(Mo-K$_\alpha$) = 1.475 mm^{-1}, 28216 reflections measured, 5012 unique (R_{int} = 0.0775) which were used in all calculations. The final R_1 [I>2σ(I)] was 0.0709.

Crystal data for **3** (polymorph *a*): $C_{12}H_8P_8$, M = 399.94, triclinic, space group P-1, a = 6.6704(1), b = 10.8568(2), c = 10.9239(2) Å, α = 92.738(1)°, β = 92.683(1)°, γ = 107.170(1)°, U = 753.44(2) Å^3, T = 100(2) K, Z = 2, μ(Cu-K$_\alpha$) = 8.527 mm^{-1}, 5874 reflections measued, 2570 unique (R_{int} = 0.0367) which were used in all calculations. The final R_1 [I>2σ(I)] was 0.0372.

Crystal data for **3** (polymorph *b*): $C_{12}H_8P_8$, M = 399.94, triclinic, space group P-1, a = 7.7205(5), b = 10.0155(7), c = 10.5675(7) Å, α = 87.305(3)°, β = 76.293(4)°, γ = 80.703(4)°, U = 783.40(9) Å^3, T = 100(2) K, Z = 2, μ(Cu-K$_\alpha$) = 8.201 mm^{-1}, 5822 reflections measued, 2658 unique (R_{int} = 0.0376) which were used in all calculations. The final R_1 [I>2σ(I)] was 0.0422.

Table S2 Comparison of selected bond lengths (Å) and angles (°) for the two polymorphs of **3**

	Polymorph *a*	**Polymorph *b***
P(1)-P(3)	2.222(1)	2.227(1)
P(1)-P(5)	2.224(1)	2.228(1)
P(1)-P(2)	2.243(1)	2.241(1)
P(2)-P(6)	2.231(1)	2.222(1)
P(2)-P(4)	2.234(1)	2.235(1)
P(3)-P(7)	2.218(1)	2.221(1)
P(4)-P(7)	2.220(1)	2.216(1)
P(5)-P(8)	2.216(1)	2.213(1)
P(6)-P(8)	2.218(1)	2.221(1)
P(7)-P(8)	2.220(1)	2.216(1)
P(3)-C(1)	1.832(3)	1.828(3)
P(4)-C(6)	1.842(3)	1.831(3)
P(5)-C(7)	1.832(3)	1.834(3)
P(6)-C(12)	1.843(3)	1.835(3)
P(3)-P(1)-P(5)	86.36(3)	86.70(3)
P(3)-P(1)-P(2)	102.36(3)	102.79(3)
P(5)-P(1)-P(2)	102.24(3)	103.58(4)
P(6)-P(2)-P(4)	88.13(3)	87.83(3)
P(6)-P(2)-P(1)	103.14(3)	101.81(4)
P(4)-P(2)-P(1)	102.69(3)	102.00(3)
C(1)-P(3)-P(7)	92.65(9)	92.71(9)
C(1)-P(3)-P(1)	100.66(8)	100.77(9)
P(7)-P(3)-P(1)	100.17(3)	99.37(3)
C(6)-P(4)-P(7)	92.30(8)	92.63(9)
C(6)-P(4)-P(2)	100.50(8)	101.05(9)
P(7)-P(4)-P(2)	99.09(3)	100.05(3)
C(7)-P(5)-P(8)	92.93(9)	92.14(9)
C(7)-P(5)-P(1)	98.99(8)	99.66(9)

P(8)-P(5)-P(1)	99.93(3)	99.25(3)
C(12)-P(6)-P(8)	92.63(8)	92.13(9)
C(12)-P(6)-P(2)	99.04(8)	100.77(9)
P(8)-P(6)-P(2)	98.90(3)	99.63(3)
P(3)-P(7)-P(8)	100.56(3)	100.59(3)
P(3)-P(7)-P(4)	92.64(3)	101.47(3)
P(8)-P(7)-P(4)	101.43(3)	92.29(4)
P(5)-P(8)-P(6)	93.20(3)	100.41(4)
P(5)-P(8)-P(7)	100.82(3)	93.14(3)
P(6)-P(8)-P(7)	101.58(3)	102.17(4)

References

1. P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. J. Jiao and N. Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317
2. F. G. N. Cloke, J. C. Green, J. R. Hanks, J. F. Nixon and J. L. Suter, *J. Chem. Soc., Dalton Trans.*, 2000, 3534
3. R. Bartsch, F. G. N. Cloke, J. C. Green, R. M. Matos, J. F. Nixon, R. J. Suffolk, J. L. Suter and D. W. Wilson, *J. Chem. Soc., Dalton Trans.*, 2001, 1013
4. Gaussian 03, Revision D.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
5. (a) A. D. Becke, *J. Chem. Phys.* **1993**, ***98***, 5648. (b) P. J. Stevens, J. F. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623. (c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
6. K. Wolinski, J. F. Hilton and P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251
7. *ADF2005.01: SCM, Theoretical Chemistry*, Vrije Universiteit, Amsterdam, The Netherlands.
8. G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders and T. Ziegler, *J. Comput. Chem.*, 2001, **22**, 931
9. C. Fonseca Guerra, J. G. Snijders, G. te Velde and E. J. Baerends, *Theor. Chem. Acc.*, 1998, **99**, 391
10. R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989.

11. S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200
12. J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822
13. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098
14. L. Versluis and T. Ziegler, *J. Chem. Phys.*, 1988, **88**, 322