

Synthetic, structural and theoretical studies on new aromatic 1,2,4-azadiphosphole ring systems: crystal and molecular structure of $P_2C_2Bu^t_2NPh$

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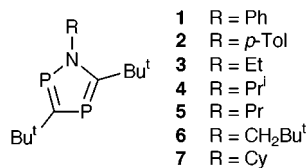
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Two different synthetic routes to the new aromatic 1,2,4-azadiphosphole ring system $P_2C_2Bu^t_2NR$ ($R = Pr^i, Pr, Ph, MeC_6H_4, Bu^tCH_2$ and cyclohexyl) are presented and the planar structure of $P_2C_2Bu^t_2NPh$, established by a single crystal X-ray diffraction study, is in good agreement with theoretical calculations at the B3LYP/6-311G* level on the parent $P_2C_2H_2NH$ ring.

We recently described reactions of vanadium(v), titanium(IV) and zirconium(IV) imides with phosphalkynes ($RC\equiv P$).^{1,2} Thus, $Bu^tC\equiv P$ reacts with $VCl_3=NBu^t$ or its DME adduct to afford 2,4,6-tri-*tert*-butyl-1,3,5-triphospha-benzene or 3-aza-1,2,4,6-tetraphosphaquadricyclane, respectively.¹ Likewise one- and two-step [2 + 2] cycloaddition reactions of $Bu^tC\equiv P$ with $[Zr(\eta^5-C_5H_5)_2(NC_6H_3-2,6-Me_2)]$ and $[TiCl_2(NBu^t)(py)_3]$ gave the structurally characterised complexes $[Zr(\eta^5-C_5H_5)_2(PCBu^tNC_6H_3-2,6-Me_2)]$ and $[TiCl_2(P_2C_2Bu^t_2NBu^t)(py)]$.²

We now report that minor modification of the reactions described above leads to the formation of the first examples of the previously unknown aromatic 1,2,4-azadiphosphole ring systems $P_2C_2Bu^t_2NR$. Thus heating $[TiCl_2(NPh)(py)_3]$ with $Bu^tC\equiv P$ at 60 °C for 56 h gave $P_2C_2Bu^t_2NPh$ **1** (31%) as a white solid after sublimation.† The analogous $P_2C_2Bu^t_2N(p\text{-tolyl})$ **2** (30%), $P_2C_2Bu^t_2NEt$ **3** (15%) and $P_2C_2Bu^t_2NPr^i$ **4** (20%) were also made by a similar route using the appropriate titanium imide precursor.

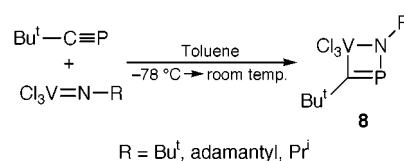


In a related series of reactions, **4** was also obtained (67%) from the reaction of the vanadium imido complex $[VCl_3=NR]$ ($R = Pr^i$) with $Bu^tC\equiv P$ on warming the mixture from -78 °C to room temperature.‡

This route also afforded $P_2C_2Bu^t_2NPr$ **5** (55%), $P_2C_2Bu^t_2NCH_2Bu^t$ **6** (87%) and $P_2C_2Bu^t_2N(cyclohexyl)$ **7** (61%). The $^{31}P\{^1H\}$ NMR spectra of all the 1,2,4-azadiphospholes **1–7** exhibited the characteristic AX pattern of lines whose chemical shifts, as expected, both lay in the unsaturated region.

The reaction mechanism of the vanadium imide reaction most likely involves the four-membered ring intermediate $[VCl_3(NR)P=CBu^t]$ (Scheme 1), which was characterised spectroscopically ($R = Bu^t$).§

The molecular structure of the phenyl-substituted 1,2,4-azadiphosphole **1** has been determined by a single crystal X-ray diffraction study (Fig. 1).¶ The ring is completely planar (Σ



Scheme 1

internal angles = 539.9° ; Σ angles at N = 359.9° and the P(2)–N [1.715(6) Å], P(2)–C(1) [1.697(8) Å], P(1)–C(1) [1.746(8) Å], P(1)–C(2) [1.740(9) Å] and C(2)–N [1.366(10) Å] bond distances are all fully consistent with significant electron delocalisation.

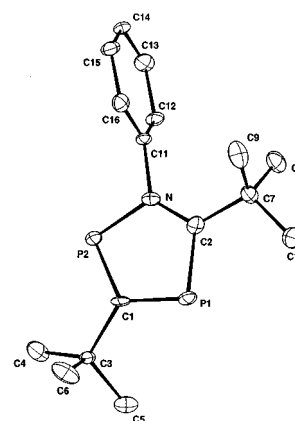
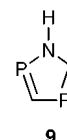


Fig. 1 Molecular structure of **1**.

The parent hydrogen-substituted derivative $P_2C_2H_2NH$ **9** has been calculated at the B3LYP/6-3111G* level of the theory.³ The free azadiphosphole was a real minima on the potential



energy surface and the five-membered ring is perfectly planar. The calculated bond lengths and bond angles, which are in good agreement with those obtained from the X-ray diffraction study on **1**, are collected in Table 1. To characterise the aromaticity of the system several criteria were investigated. According to geometric BDSHRT⁴ and Bird⁵ indices (BI) and NICS⁶ data the 1,2,4-aza-, 1,2,4-oxa- and 1,2,4-thia-diphosphole ring systems are somewhat less aromatic than the analogous organic rings furan, pyrrole and thiophene (see Table 2).

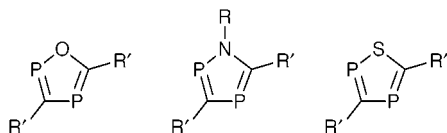
Table 1 Theoretical and observed bond length data and bond angles of azadiphospholes **9** and **1** (ring numbering as in Fig. 1)

	Calculated bond lengths for 9 /Å	Observed bond lengths for 1 /Å	Calculated bond angles for 9 (°)	Observed bond angles for 1 (°)
N–P2	1.725	1.715(6)	P2NC2 119.4	119.6(5)
P2–C1	1.709	1.697(8)	NC2P1 117.1	113.7(6)
C1–P1	1.764	1.746(8)	C2P1C1 92.2	95.8(4)
P1–C2	1.734	1.740(9)	P1C1P2 118.8	115.8(5)
C2–N	1.354	1.366(10)	C1P2N 92.5	95.0(4)

Table 2 BDSHRT, BI and NICS data for several unsaturated rings systems

Ring	BDSHRT	BI	NICS
1,2,4-Oxadiphosphole	46	37	−11.0
1,2,4-Azadiphosphole	48	52	−12.8
1,2,4-Thiadiphosphole	53	56	−12.4
Furan	51	49	−12.3
Pyrrole	55	73	−14.7
Thiophene	57	68	−13.2

It is also interesting to compare NMR data for the 1,2,4-azadiphosphole rings with the isoelectronic series of 1,2,4-oxa-⁷ and 1,2,4-thia-diphosphole⁸ ring systems, P₂C₂R'₂E, (R' = Bu^t, Mes; E = O, S).



As the electronegativity of the heteroatom becomes smaller, the *difference* in chemical shifts of the two unsaturated P centres decreases significantly (161, 99 and 11 ppm respectively for E = O, NR and S). The magnitude of the ²J_(PP') cross-ring coupling constants are also dependent on the nature of the heteroatom [17.5, (E = O) 34.9 (E = NR) and 49.9 Hz (E = S)].

We anticipate that, by analogy with other unsaturated polyphosphorus ring systems,⁹ the new 1,2,4-azadiphosphole ring systems will have an interesting coordination chemistry, behaving as 2e, 4e or 6e donors towards suitable transition metal centres, and this aspect is currently under investigation.¹⁰

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Notes and references

† *Synthesis of 1*: A high pressure ampoule was loaded with [Ti(NC₆H₅)Cl₂(py)₃], (0.400 g, 0.89 mmol), P=C₆H₅ (0.027 g, 2.70 mmol) and toluene (25 ml). The reaction vessel was stoppered (Teflon stopcock) and heated with stirring at 60 °C for 56 h. The volatiles were removed *in vacuo* and the resulting brown residue was extracted with light petroleum (bp 40–60 °C) (20 ml). Volatiles were removed from the filtrate and the residue sublimed (70 °C, 10^{−5} mbar), yielding **1** as an off-white powder (0.08 g, 31%). Crystals suitable for X-ray analysis were grown by careful sublimation under static vacuum (10^{−2} mbar, 70 °C) (Found: C, 65.88; H, 8.20; N, 5.32. C₁₆H₂₃NP₂ requires: C, 65.97; H, 7.96; N, 4.81%). *Selected data* for δ_H(benzene-*d*₆, 295 K, 300.13 MHz) 7.1, 6.98 (m, 5H, C₆H₅), 1.64 [d, 9H, PC(C(CH₃)₃)P, ⁴J_(PH) 1.3], 1.29 [d, 9H, PC(C(CH₃)₃)N, ⁴J_(PH) 1.93; δ_P(benzene-*d*₆, 295 K, 121.52 MHz) 262.6 (d, NPC, ²J_(PP) 30.4, 156.3 (d, PCP, ²J_(PP) 30.4; *m/z* (EI) 291 ([M]⁺, 70%), 276 (M − Me)⁺, 55). For δ_H(benzene-*d*₆, 295 K, 300.13 MHz) 7.34, 7.22 [(AB)₂, 4H, C₆H₄, ³J_(HH)

7.88], 2.47 (s, 3H, CCH₃), 1.56 [d, 9H, PC(C(CH₃)₃)P, ⁴J_(HP) 1.19], 1.37 [d, 9H, PC(C(CH₃)₃)N, ⁴J_(HP) 1.92]; δ_C(benzene-*d*₆, 295 K, 75.48 Hz) 204.3 (dd, PCP, *J*_(CP) 57.9 Hz, *J*_(CP) 62.7), 196.8 [dd, br, NCP, *J*_(PC) 60.7, ²*J*_(PC) unresolved], 140.5 [dd, *ipso*-NC₆H₄(CH₃), ²*J*_(CP) 16.1], 138.7 [d, *p*-NC₆H₄(CH₃), ⁵*J*_(CP) 2.1], 129.54 [d, *o*-NC₆H₄(CH₃), ³*J*_(PC) 5.2], 128.83 [d, *m*-NC₆H₄(CH₃), ⁴*J*_(PC) 1.2], 39.91 [dd, NCC(CH₃), ²*J*_(PC) 14.95, ⁴*J*_(PC) 3.1], 37.5 [dd, PC(C(CH₃)₃), ²*J*_(PC) 16.77], 35.59 [dd, PC(C(CH₃)₃)P, ³*J*_(PC) 8.12, 11.13], 33.41 [d, NCC(CH₃), ³*J*_(CP) 13.14], 21.5 [C₆H₄(CH₃)]]; δ_P(benzene-*d*₆, 295 K, 121.52 MHz) 262.5 [d, NP, ²*J*_(PP) 29.2], 153.5 [d, NCP, ²*J*_(PP) 29.2 *m/z* (EI) 305 ([−M]⁺, 90%), 290 [M − Me]⁺, 35), 234 ([M − Me − Bu]⁺, 30).

‡ *Synthesis of 4*: To a solution of [VCl₃=NPrⁱ] (0.14 g, 0.63 mmol) in toluene (5 ml) was added, with stirring, BuC≡P (0.06 g, 0.63 mmol) at −78 °C and the solution was warmed to room temperature. After 24 h the solvent was removed *in vacuo* and the residue dissolved in *n*-pentane and filtered through Celite. The product **4** was obtained (by distillation at 130 °C, 10^{−2} mbar) as a white solid (0.055 g, 67%); δ_H(benzene-*d*₆, 295 K, 300.13 MHz) 1.63 [dd, 9H, PC(C(CH₃)₃)P, ⁴*J*_(HP) 1.8, 0.7], 1.39 [d, 9H, PC(C(CH₃)₃)N, ⁴*J*_(HP) 2.2], 1.38 [d, 6H, ³*J*_(HH) 6.6], 4.69 [dsep, 1H, ³*J*_(HH) 6.6, ³*J*_(HP) 2.7]; δ_C(benzene-*d*₆, 295 K, 75.48 MHz) 202.2 [dd, PCP, *J*_(CP) 62.3, *J*_(CP) 52.5], 193.8 (dd, NCP, *J*_(PC) 59.8, ²*J*_(PC) 3.7), 53.2 [dd, (CH) ²*J*_(PC) 17.1, ³*J*_(PC) 2.5], 38.2 [dd, NCC(CH₃), ²*J*_(PC) 19.1, ³*J*_(PC) 2.5], 37.4 [dd, PC(C(CH₃)₃), ²*J*_(PC) 28.1, 17.3], 35.4 [dd, PC(C(CH₃)₃)P, ³*J*_(PC) 8.6, 11.0], 32.0 [d, NCC(CH₃), ³*J*_(CP) 13.4], 27.6 [d, (CH₃)₂, ³*J*_(CP) 12.1]; δ_P(benzene-*d*₆, 295 K, 121.52 MHz) 247.3 (d, NP, ²*J*_(PP) 34.9), 148.1 (d, NCP, ²*J*_(PP) 34.9); *m/z* (EI) 275 ([M]⁺, 29%), 242 ([M − Me]⁺, 6), 200 ([M − PrⁱN]⁺, 12), 186 (M − Prⁱ − Me)⁺, 7), 57 (Bu⁺, 20), 43 (Pr⁺, 11).

§ *Selected data* for δ_P(benzene-*d*₆, 81 MHz) −73.0 (²*J*_(PV) 30.3); δ_V 310.

¶ *Crystal data* for **1**: C₁₆H₂₃NP₂, *M* = 291.3, orthorhombic space group *Pna*2₁ (No. 33), *a* = 26.960(5), *b* = 5.916(2), *c* = 10.299(3) Å, *U* = 1642.6(8) Å³, *Z* = 4, *D*_c = 1.18 Mg m^{−3}, crystal dimensions 0.1 × 0.1 × 0.05 mm, *F*(000) = 624, *T* = 173(2) K, Mo-Kα, radiation λ = 0.71073 Å. Data were collected on an Enraf-Nonius CAD4 diffractometer. A total 1071 reflections were measured. *R*₁ = 0.044 for 859 reflections with *I* > 2σ(*I*), *wR*₂ = 0.106 for all data. All non-H atoms were anisotropic. H atoms were included in riding mode with *U*_{iso}(H) equal to 1.2eq(C) or 1.5eq(C) for methyl groups. CCDC 182/1447. See <http://www.rsc.org/suppdata/cc/1999/2363/> for crystallographic data in .cif format.

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