Supporting Information for:

"Exploring the reactivity of white phosphorus with electrophilic carbenes: synthesis of a P4 cage and P8 clusters"

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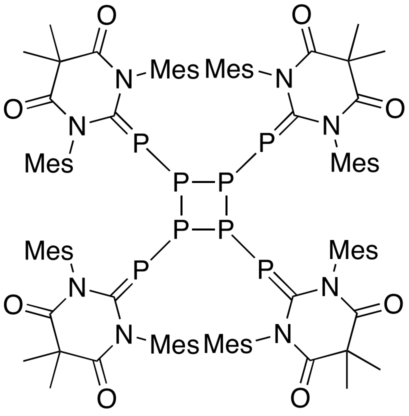
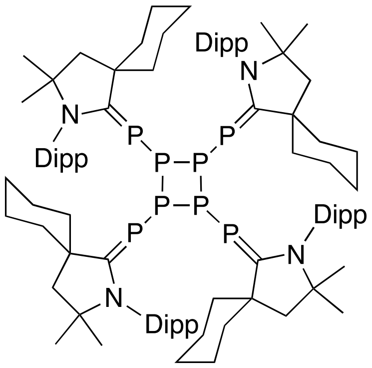
General Considerations:

All manipulations were performed under an inert atmosphere in an argon filled MBraun glove box or using standard Schlenk techniques. The carbenes **1c**, **1f** and **1g** were prepared via the literature procedures.[1-3] White phosphorus was sublimed and stored under argon in the dark. Toluene, benzene and hexane were freshly distilled over sodium metal. $CDCl_3$ used for ^1H NMR spectroscopy was purchased from Cambridge Isotope Laboratories and dried over CaH_2. Multinuclear NMR data are listed in ppm, relative to Me_4Si (^{13}C and ^1H) and H_3PO_4 (^{31}P), coupling constants are in Hertz and all NMR spectra were recorded on a Varian VX 500 MHz or JEOL 500 MHz spectrometer. Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo-K_α radiation ($\lambda = 0.71073$ Å). Crystals were selected under oil, mounted on nylon loops then immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL. Melting points were measured with a Büchi melting point apparatus.

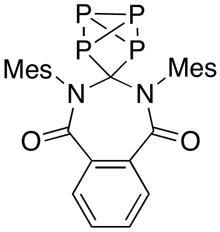
CAUTION: P_4 is extremely pyrophoric and the proper safety procedures should be followed when handling.



2: A solution of **1f** in benzene (0.500 g, 1.33 mmol; 40 mL) was cannula transferred dropwise to a solution of P_4 in toluene (0.330 g, 2.66 mmol; 20 mL) in the dark. The colorless solution immediately began acquiring an orange color, which then became red. After stirring for 2 hours, the solvent was removed *in vacuo*. The solids were washed with benzene (10 mL), then hexanes (2 × 15 mL) and dried *in vacuo* to give a red powder. Yield: 0.582 g, 66%; Single crystals of **2** for X-ray diffraction studies were grown by slow evaporation of a benzene solution. m.p. 160-162°C; $^{31}P\{^{1}H\}$ ($CDCl_3$) δ = 107.9 (4P, m), -37.9 (4P, m); ESI-MS *m/z* $C_{96}H_{112}O_8N_8P_8Na$ [MNa^+] Calc: 1775.6373 Found: 1775.6396.

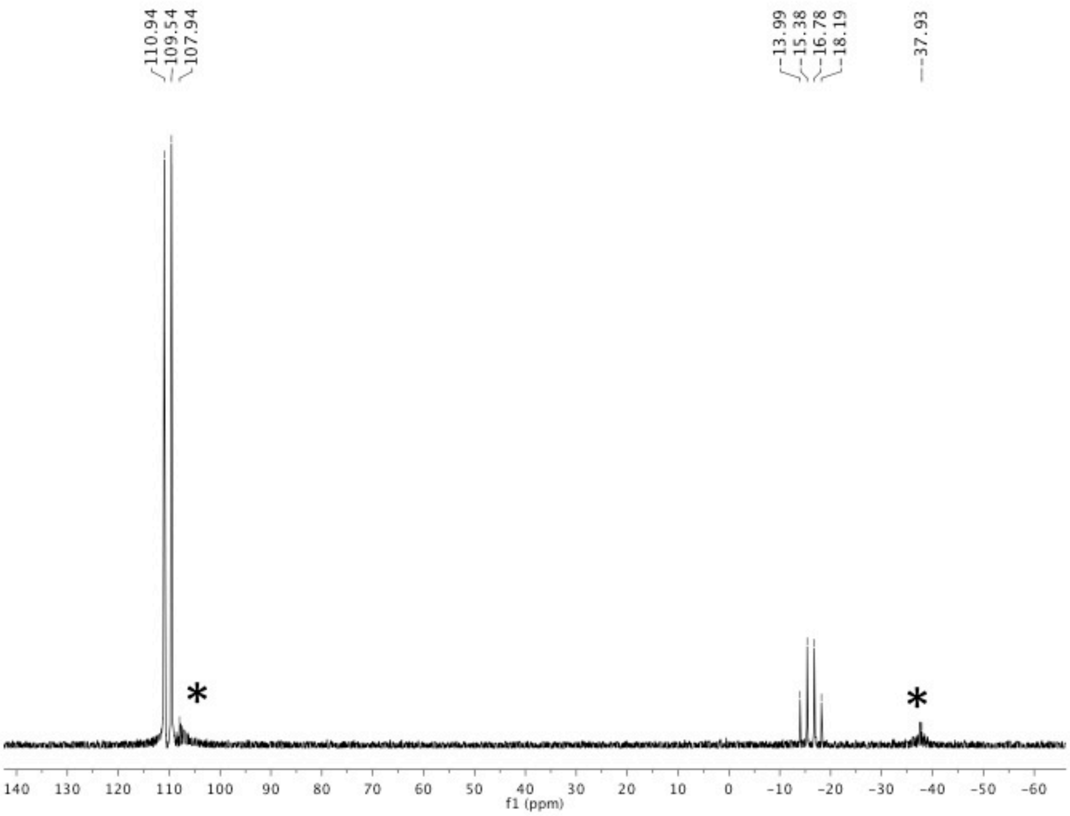


3: A solution of **1c** in benzene (0.500 g, 1.54 mmol; 40 mL) was cannula transferred dropwise to a solution of P_4 (0.382 g, 3.08 mmol; 25 mL) in toluene in the dark. The colorless solution immediately began acquiring a green color, which then became red. After stirring for 2 hours, the toluene was removed *in vacuo* to produce an orange powder. The product was extracted with THF and the solvent removed *in vacuo*. The solids were washed with cold pentane (2 × 15 mL) and dried *in vacuo* to give an orange powder. Yield 0.351 g, 40%; Single crystals of **3** for X-ray diffraction studies were grown by vapor diffusion of hexane into a saturated benzene solution. m.p. 204-206°C; ^{1}H NMR ($CDCl_3$) δ = 7.28 (4H, t, ^{3}J = 7.5 Hz), 7.14 (8H, d, ^{3}J = 7.5 Hz), 3.03-2.90 (8H, m), 2.80 (16H, sept, ^{3}J = 7.0 Hz), 2.01 (8H, s), 1.55-1.35 (32H, m), 1.29 (24H, d, ^{3}J = 7.0 Hz), 1.27-1.13 (8H, m), 1.18 (24H, d, ^{3}J = 7.0 Hz); $^{13}C\{^{1}H\}$ ($CDCl_3$) δ = 212.3 (br d, J = 84 Hz), 148.1 (d, J = 3 Hz), 134.6 (d, J = 3 Hz), 128.3, 124.9, 68.2 (d, J = 1 Hz), 56.1 (d, J = 11 Hz), 50.5, 29.7, 29.0, 27.7, 27.6, 25.1, 24.5, 23.5; $^{31}P\{^{1}H\}$ ($CDCl_3$) δ = 66.4 (4P, m), -44.5 (4P, m);. HRMS *m/z* calc 1549.9052, found 1549.9033 [MH^+].



4: Carbene **1g** (0.090 g, 0.220 mmol) was added to an NMR tube with P_4 (0.027 g, 0.220 mmol). C_6D_6 was then added to the mixture of solids. Upon dissolving of the solids, the solution turned a red-orange color and over time a yellow precipitate formed which was primarily **4** (See Fig S-4 for $^{31}P\{^1H\}$ NMR spectrum). Although we could not obtain a pure bulk sample, the reaction proceeded in >50% yield. Single crystals of **4** for X-ray diffraction studies were grown by vapor diffusion of hexane into a saturated $CDCl_3$ solution. $^{31}P\{^1H\}$ ($CDCl_3$) δ = -10.5 (1P, td, $^1J_{P\text{-}P}$ = 85 Hz and $^2J_{P\text{-}P}$ 19 Hz), -14.5 (1P, td, $^1J_{P\text{-}P}$ = 85 Hz and $^2J_{P\text{-}P}$ 19 Hz), -326 (2P, dd, $^1J_{P\text{-}P}$ = 89 Hz and $^2J_{P\text{-}P}$ 85 Hz).

Figure S-1: Crude $^{31}P\{^1H\}$ NMR spectrum for the reaction of **1f** with P_4.



Asterisks denote P_8 product.

Figure S-2: $^{31}P\{^{1}H\}$ NMR spectrum of **2**.

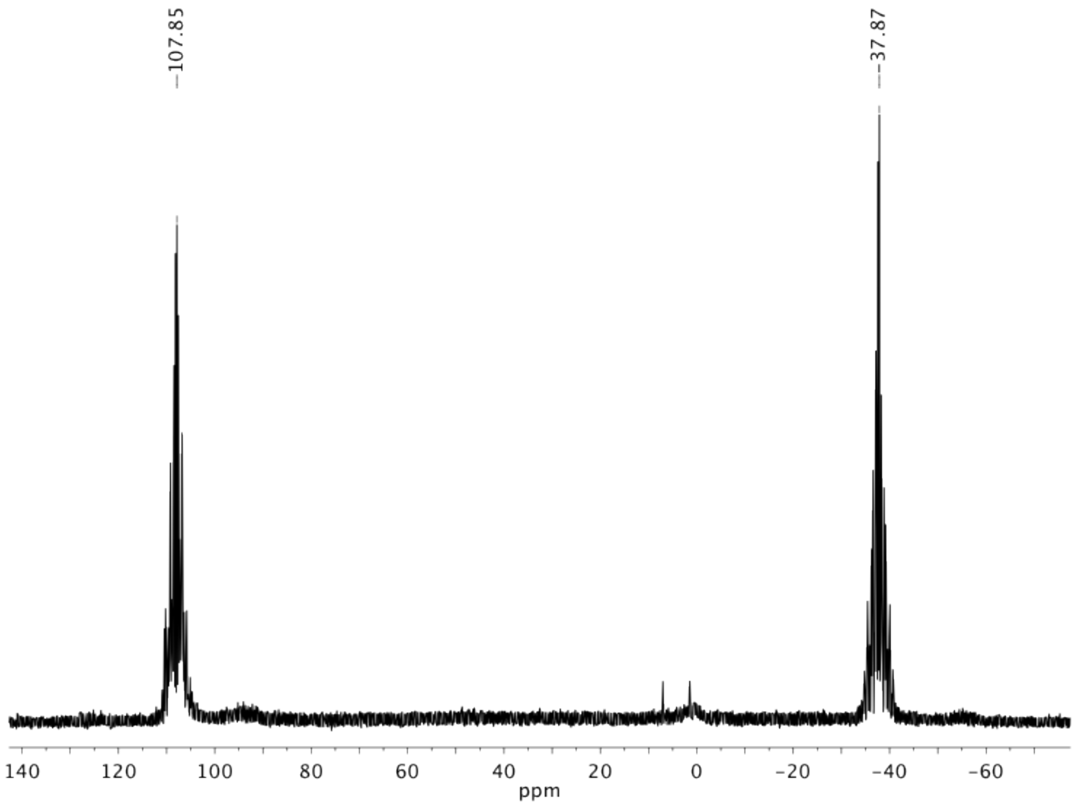


Figure S-3: $^{31}P\{^{1}H\}$ NMR spectrum of **3**.

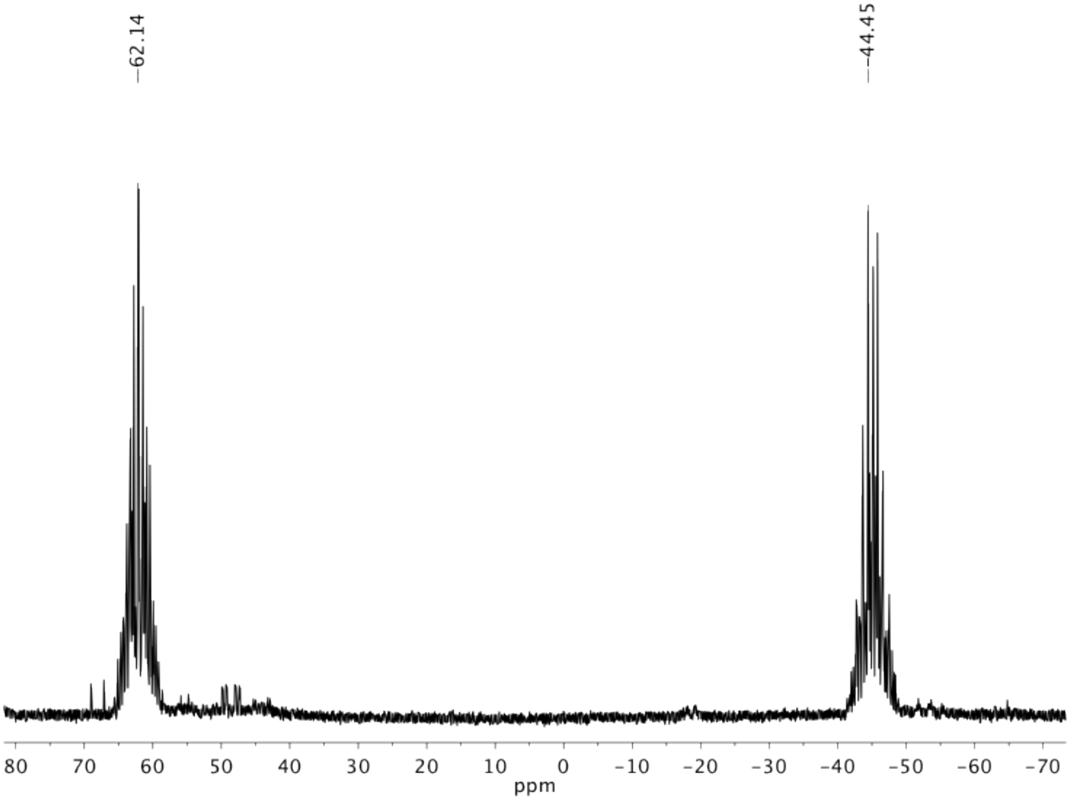


Figure S-4: $^{31}P\{^1H\}$ NMR spectrum of **4**.

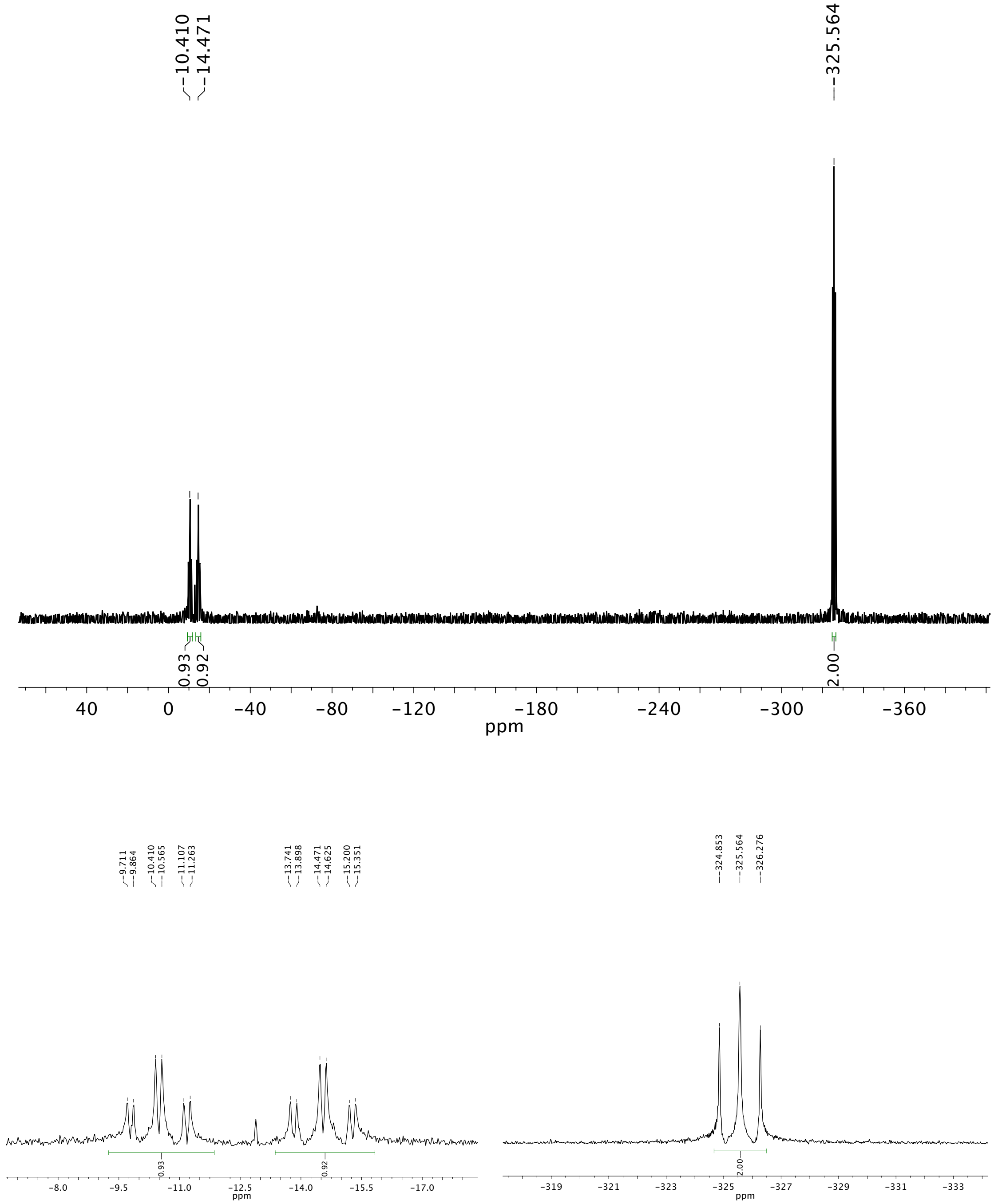


Table S1: X-ray details for **2-4**.

Compound	**2**	**3**	**4**
Empirical formula	$C_{120}H_{136}N_8O_8P_8$	$C_{98}H_{146}N_4P_8$	$C_{27.33}H_{26.33}ClN_2O_2P_4$
CCDC	930071	930072	930073
FW (g/mol)	2066.12	1628.0482	534.38
Crystal system	Monoclinic	Orthorhombic	Trigonal
Space group	*P*2/*c*	*Fddd*	*R*-3
a (Å)	12.600(4)	12.0923(12)	34.4341(10)
b (Å)	16.320(5)	29.578(3)	34.4341(10)
c (Å)	26.808(9)	53.934(5)	11.4555(4)
α (deg)	90	90	90
β (deg)	92.213(11)	90	90
γ (deg)	90	90	120
V (Å^3)	5508(3)	19290(3)	11763.1
Z	2	8	18
D_c (Mg m^{-3})	1.246	1.121	1.459
radiation, λ (Å)	.71073	.71073	.71073
temp (K)	100(2)	100(2)	100(2)
$R1[I>2\sigma I]$[a]	0.0625	0.0432	0.0645
$wR2(F^2)$[a]	0.1766	0.1067	0.1495
GOF (S)[a]	1.009	1.008	1.077

[a] $R1(F[I > 2(I)]) = \sum||F_o| - |F_c||/ \sum |F_o|$; $wR2(F^2 \text{ [all data]}) = [w(F_o^2 - F_c^2)^2]^{1/2}$; $S(\text{all data}) = [w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program.

References:

1. T. W. Hudnall, J. P. Moerdyk and C. W. Bielawski, *Chem. Commun.*, 2010, **46**, 4288.

2. R. Jazzar, R. D. Dewhurst, J.-B. Bourg, B. Donnadieu, Y. Canac and G. Bertrand, *Angew. Chem.*, *Int. Ed.*, 2007, **46**, 2899.

3. T. W. Hudnall, A. G. Tennyson and C. W. Bielawski, *Organometallics*, 2010, **29**, 4569.