Supporting Information

Synthesis and structure of the extended phosphazane ligand [(1,4-C6H4){N(µ-PNtBu)2NtBu}2] ⁴⁻

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Figure S1. ^{31}P NMR (298 K, C_6D_6, 161.97 MHz) spectrum of $(1,4\text{-}C_6H_4)[N(\mu\text{-}PNH^tBu)_2N^tBu]_2$ (**1**H_4).
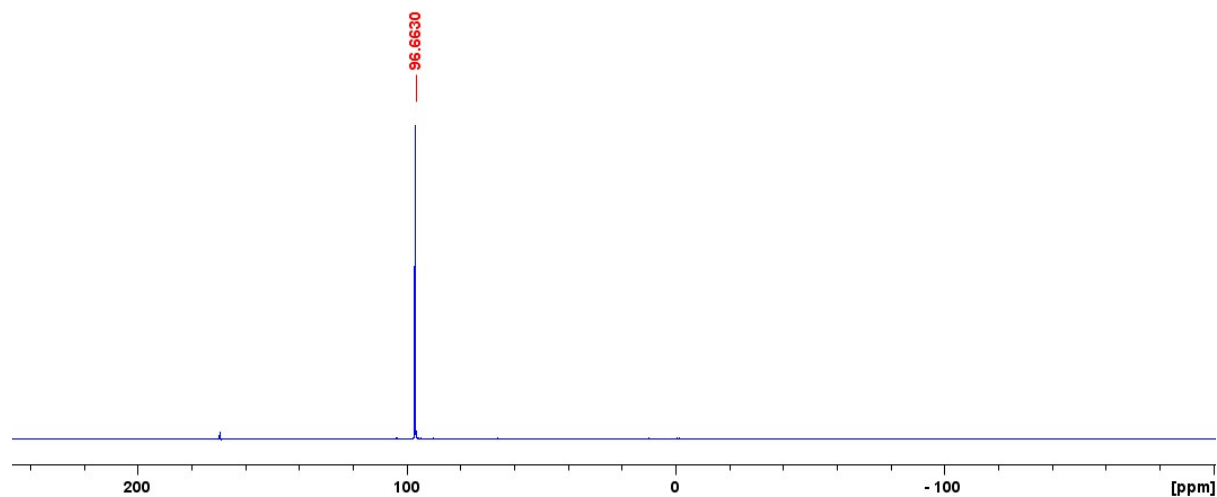
Figure S2. ^{1}H NMR (298 K, C_6D_6, 400 MHz) spectrum of $(1,4\text{-}C_6H_4)[N(\mu\text{-}PNH^tBu)_2N^tBu]_2$ (**1**H_4); (*)residual benzene-d6, (**) silicone grease.
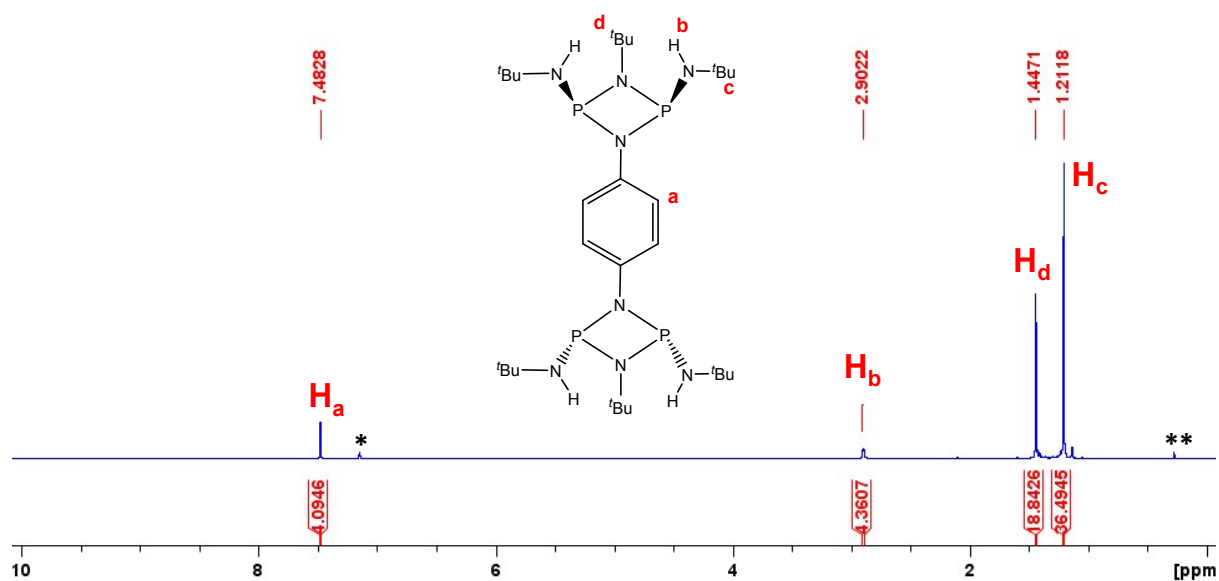
Figure S3. $^{13}C\{^1H\}$ NMR (298 K, C_6D_6, 100.62 MHz) spectrum of $(1,4-C_6H_4)[N(\mu-PNH^tBu)_2N^tBu]_2$ (**1**H_4); (*)residual benzene-d6, (**) silicone grease.
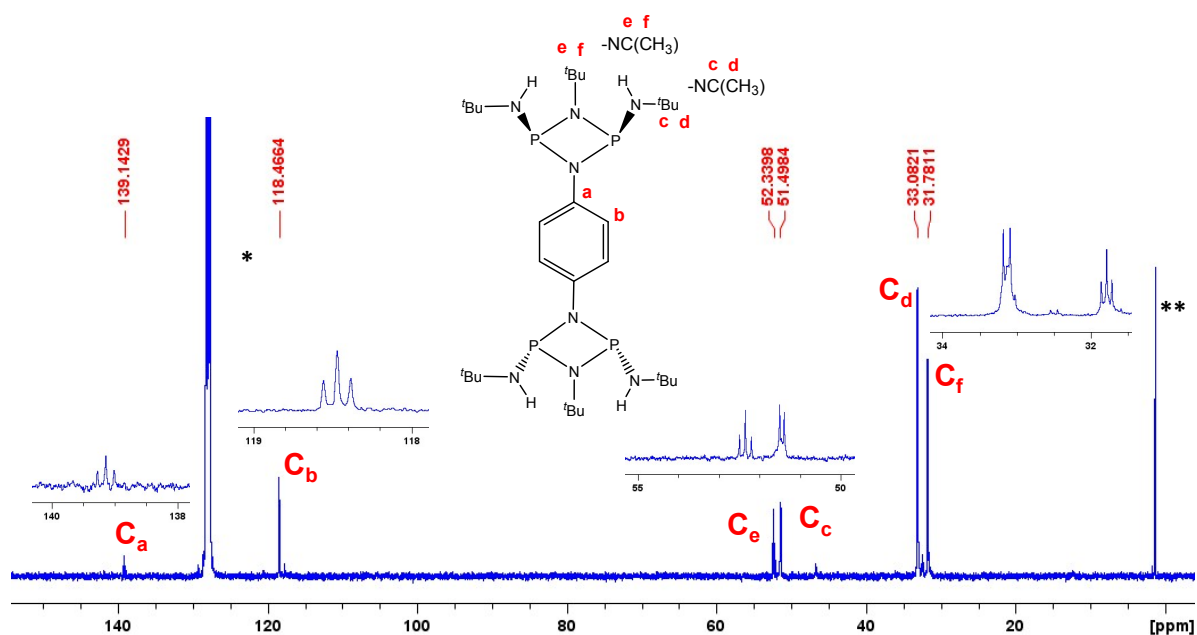
Figure S4. ^{31}P NMR (298 K, THF-d8, 202.48 MHz) spectrum of $(1,4-C_6H_4)[N(\mu-(PN^tBu)_2Mg\cdot(THF)_2)N^tBu]_2$ [**1**{Mg·(THF)$_2$}$_2$].
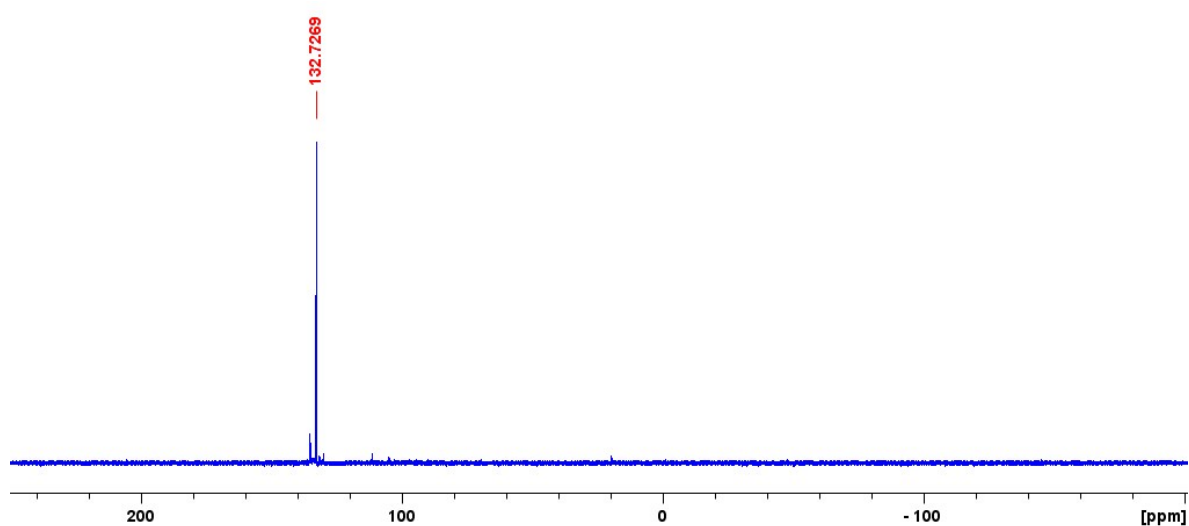
Figure S5. ^{1}H NMR (298 K, d8-THF, 500 MHz) spectrum of (1,4-C$_6$H$_4$)[N(μ-(PN^{t}Bu)$_2$Mg·(THF)$_2$)N^{t}Bu]$_2$ [**1**{Mg·(THF)$_2$}$_2$]; (*)residual d8-THF, (**) silicone grease. Note: a small amount of H-grease and heptane (from the Bu$_2$Mg solution) was also present (δ 0.85-0.92).
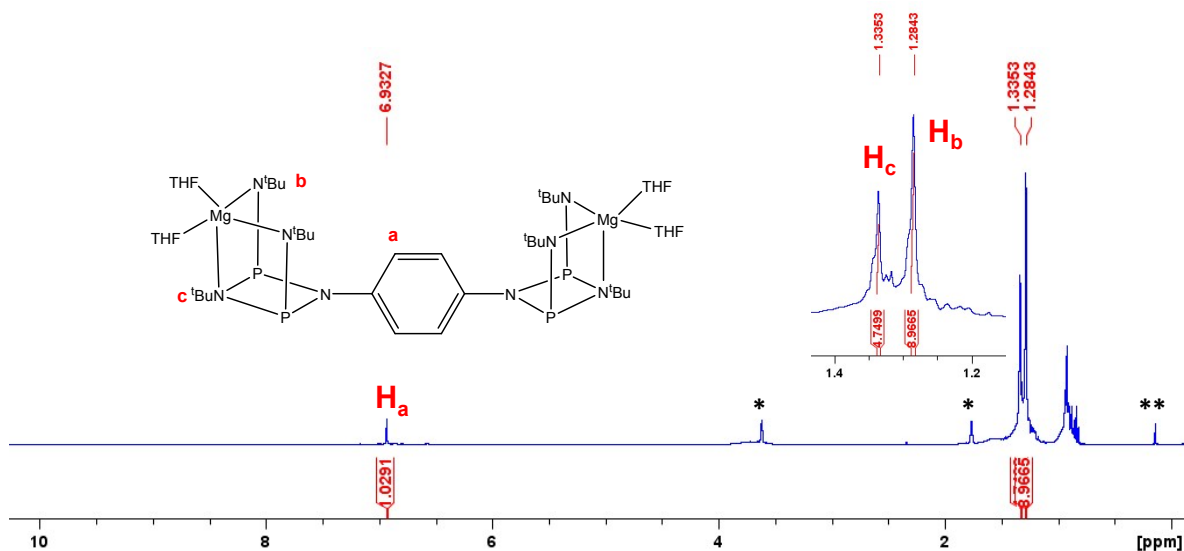

Figure S6. ^{1}H-^{31}P HMBC (298 K, d8-THF, 500 MHz) spectrum of (1,4-C$_6$H$_4$)[N(μ-(PN^{t}Bu)$_2$Mg·(THF)$_2$)N^{t}Bu]$_2$ [**1**{Mg·(THF)$_2$}$_2$].
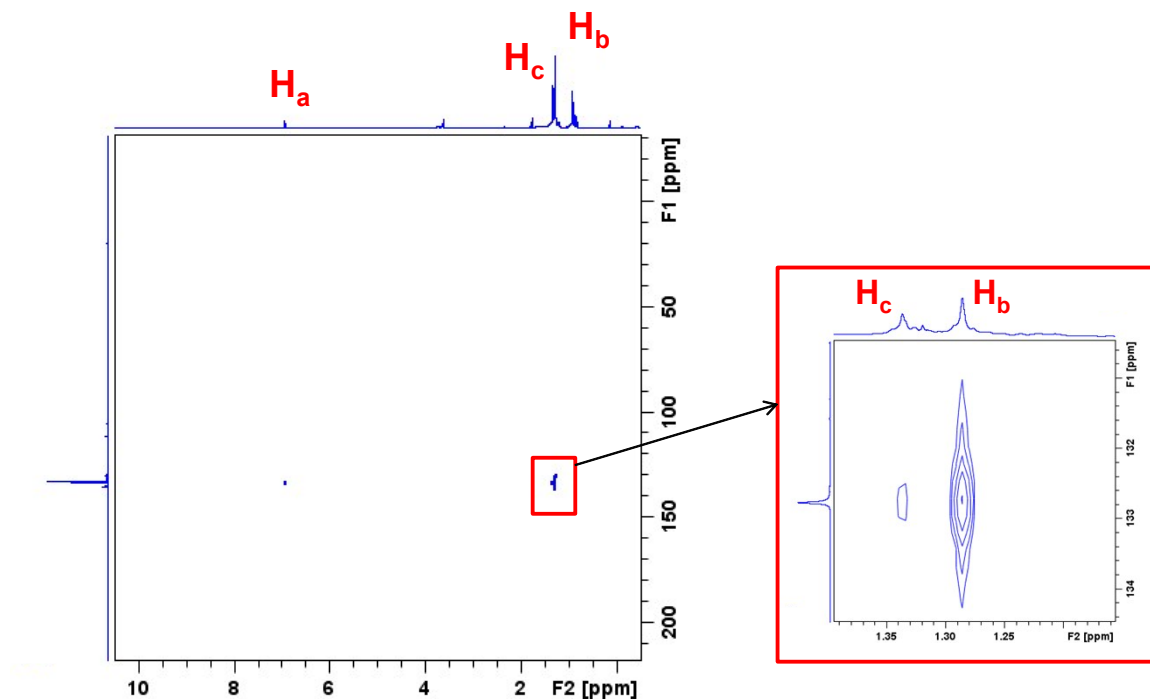
Figure S7. ^{1}H-^{1}H NOESY (298 K, d8-THF, 500 MHz, mixing time 600 ms) spectrum of (1,4-C$_6$H$_4$)[N(μ-(PN^{t}Bu)$_2$Mg·(THF)$_2$)N^{t}Bu]$_2$ [**1**{Mg·(THF)$_2$}$_2$] showing the crosspeak between H^b and the protons of the aromatic ring arising from intramolecular cross-relaxation of protons that are close to each other in space.
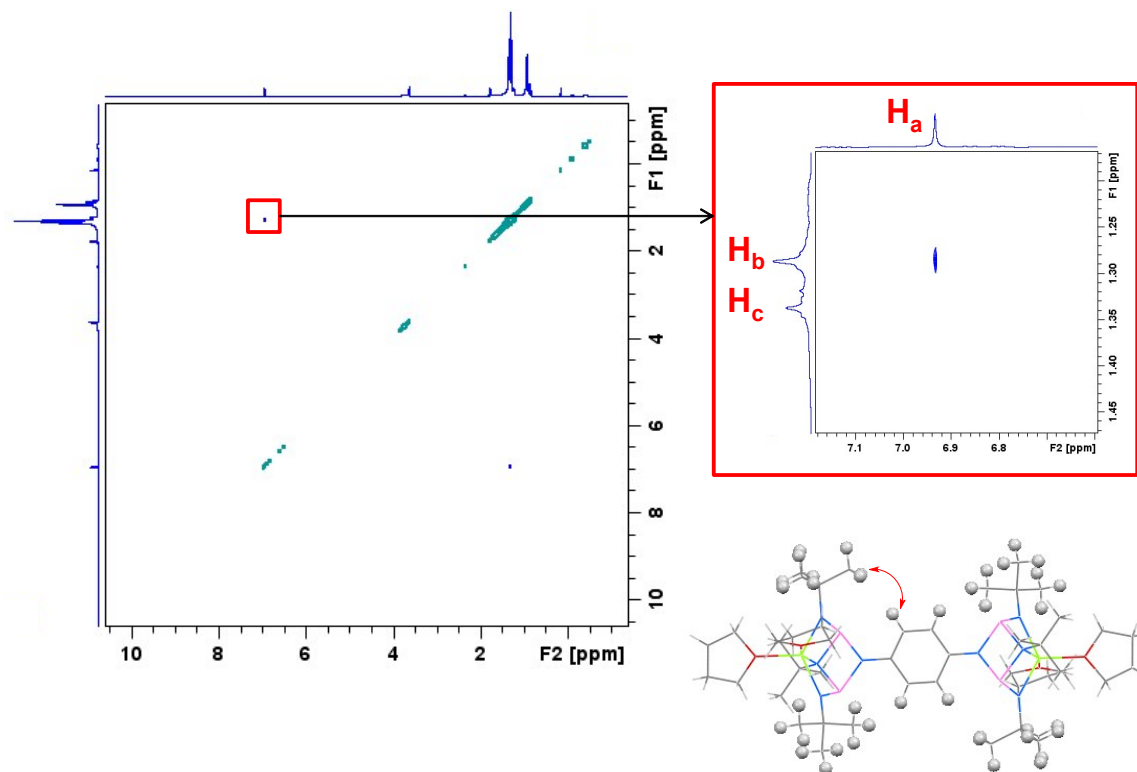
Figure S8. (Bottom, blue) ^{1}H NMR (298 K, d8-THF, 500 MHz) spectrum of (1,4-C$_6$H$_4$)[N(μ-PNH^{t}Bu)$_2$N^{t}Bu]$_2$ (**1**H$_4$); (top, red) ^{1}H NMR (298 K, d8-THF, 500 MHz) spectrum of (1,4-C$_6$H$_4$)[N(μ-(PN^{t}Bu)$_2$Mg·(THF)$_2$)N^{t}Bu]$_2$ [**1**{Mg·(THF)$_2$}$_2$]. Complete deprotonation is observed (disappearance of signal corresponding to the N*H* protons at 3.91).

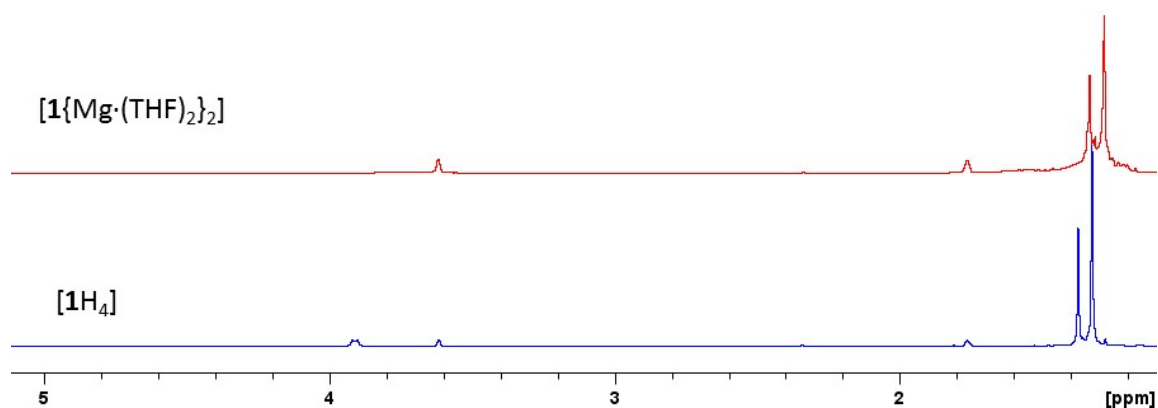**Figure S9.** $^{13}C\{^1H\}$ NMR (298 K, d8-THF, 100.62 MHz) spectrum of $(1,4-C_6H_4)[N(\mu-(PN^tBu)_2Mg\cdot(THF)_2)N^tBu]_2$ [**1**$\{Mg\cdot(THF)_2\}_2$]. Although the quarternary carbon C^b is easily observed through ^1H-^{13}C HMBC experiment (see insert), its direct observation in the $^{13}C\{^1H\}$ spectrum was challenging. Note: resonances at 67.21 and 25.10 arise from d_8-THF. Note 2: resonance for H-grease and heptane present (observed in the ^1H NMR as well).
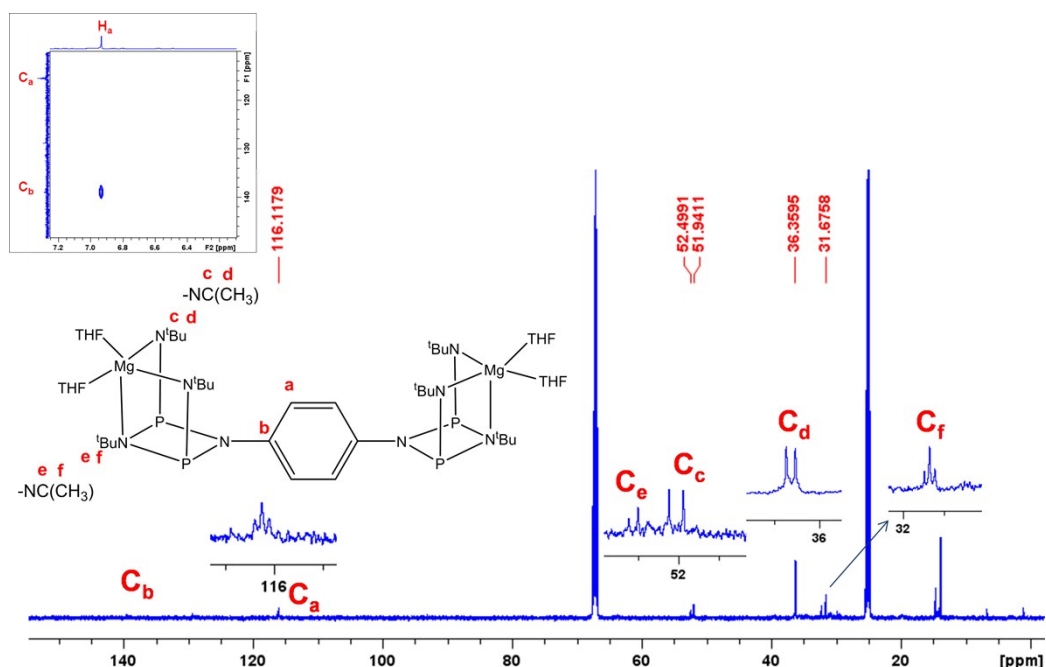
Figure S10. ^1H-^{13}C HMQC (298 K, d8-THF, 500 MHz) spectrum of $(1,4-C_6H_4)[N(\mu-(PN^tBu)_2Mg\cdot(THF)_2)N^tBu]_2$ [**1**$\{Mg\cdot(THF)_2\}_2$].
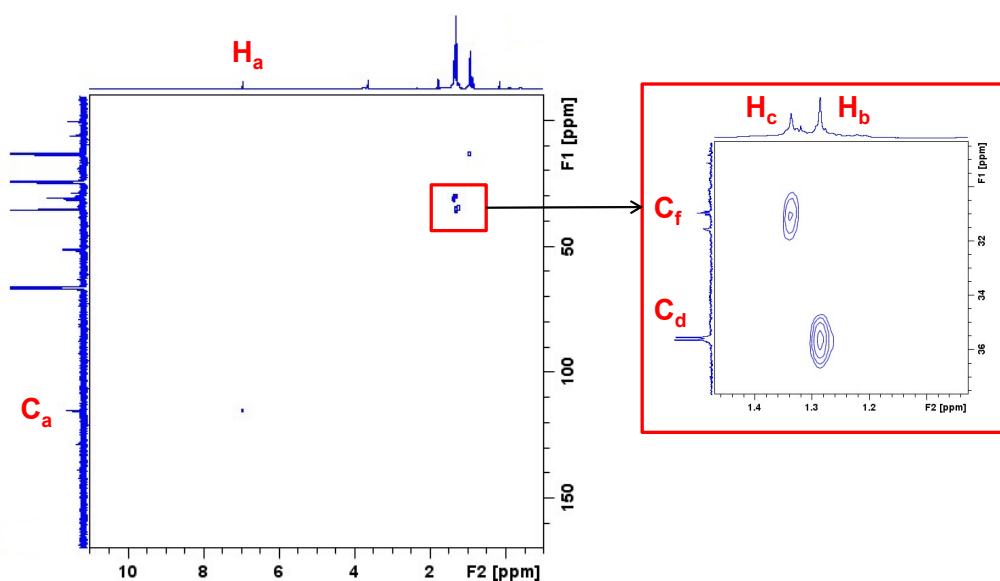
Elemental analysis found for the solid isolated upon removal of the reaction solvent of [**1**$\{Mg\cdot(THF)_2\}_2$]: C, 39.19; H, 7.86; N 2.76; P 6.87. Anal. Calcd for [**1**$\{Mg\cdot(THF)_2\}_2$] C, 55.94; H, 8.78; N 11.34; P 12.54. Anal. Calcd for **1**Mg_2 (THF-desolvation) C, 51.23; H, 8.31; N 15.93; P 17.61.

Figure S11. *In situ* ^{31}P NMR (298 K, CDCl$_3$ capillary, 161.97 MHz) spectrum from reaction of **1**H$_4$ with 2,6-diisopropylaniline.
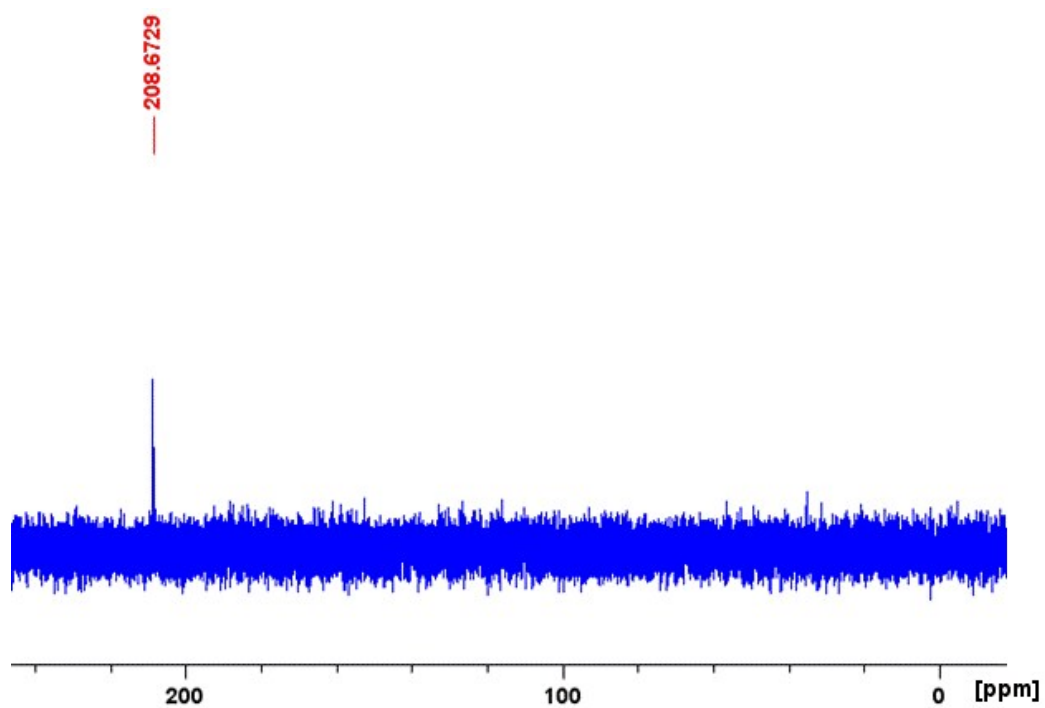
X-ray Crystallographic Studies

Table S1. Crystal, measurement and refinement data for the compounds studied by X-ray diffraction.

|	$1H_4$[a]	$1H_4\cdot$cyclohexane[b]	$1\{Mg\cdot(THF)_2\}_2$
CCDC number	1435095	1435096	1435098
Chemical formula	$C_{30}H_{62}N_8P_4$	$C_{30}H_{62}N_8P_4\cdot2(C_6H_{12})$	$C_{46}H_{90}Mg_2N_8O_4P_4$
Formula mass	658.8	827.1	991.8
Crystal system	triclinic		monoclinic
a/Å	6.0734(9)	6.1188(3)	10.4939(4)
b/Å	12.3908(14)	14.0514(6)	17.4459(6)
c/Å	14.032(2)	15.4022(7)	16.1229(7)
α/°	106.920(4)	88.944(3)	90
β/°	98.179(6)	89.034(3)	96.9488(16)
γ/°	100.308(10)	81.094(2)	90
Unit cell volume/Å³	972.5(2)	1307.9(1)	2930.0(2)
Temperature/K	180(2)	220(2)	180(2)
Space group	P−1	P−1	P2$_1$/n
Z	1	1	2
Radiation type	MoKα	CuKα	MoKα
Absorption coefficient, μ/mm^{-1}	0.224	1.585	0.194
No. of reflections measured	4947	14919	17185
No. of independent reflections	2396	4576	5034
R$_{int}$	0.054	0.063	0.056
Final R1 values (I > 2σ(I))	0.083	0.099	0.068
Final wR(F^2) values (I > 2σ(I))	0.188	0.281	0.143
Final R1 values (all data)	0.096	0.140	0.101
Final wR(F^2) values (all data)	0.194	0.320	0.160
Goodness of fit on F^2	1.28	1.06	1.07

[a] Refined as a non-merohedral twin.

[b] The version of this structure with SQUEEZE applied is deposited as CCDC-1435097.

Data were collected for $1H_4$ and $1\{Mg\cdot(THF)_2\}_2$ at 180(2) K on a Nonius KappaCCD diffractometer, using graphite-monochromated MoKα radiation (λ = 0.7107 Å). Data for $1H_4\cdot$cyclohexane were collected at 220(2) K on a Bruker D8-QUEST diffractometer using an Incoatec IμS Cu microsource (λ = 1.5418 Å). Structures were solved using SHELXT (Sheldrick, 2015) and refined using SHELXL-2014 (Sheldrick, 2015). Data for $1H_4$ were identified to be subject to non-merohedral twinning corresponding to a 2-fold rotation around the a axis using the TWINROTMAT procedure in PLATON (Spek, 2009). The structure was refined using an HKLF-5 file generated by TWINROTMAT. The structure of $1H_4\cdot$cyclohexane contains cyclohexane molecules that exhibit rotational disorder. Modelling of these as two molecular components with restrained geometries, a refined site occupancy factor constrained to sum to unity for the two components, and a common isotropic displacement parameter produced the result indicated in Table S1. Confirmation that the relatively high R-factors stem from inadequate modelling of the solvent molecules was provided by application

of the SQUEEZE procedure (Spek, 2015), which produces R1 = 0.071, wR2 = 0.214. The procedure indicates masking of 84 electrons per void, corresponding to one cyclohexane molecule (with two voids per unit cell). The CIF after application of SQUEEZE is provided. For $1H_4$, the H atoms of the NH groups were refined with isotropic displacement parameters and with the N–H bond length restrained to be 0.88(1) Å. For $1H_4$·cyclohexane, the corresponding atoms were placed geometrically with N–H = 0.87 Å and $U_{iso}(H) = 1.2U_{iso}(N)$. The structures of $1H_4$ and $1H_4$·cyclohexane contain essentially identical 2-dimensional sections (parallel to the *ac* planes in $1H_4$ and *ab* planes in $1H_4$·cyclohexane; compare the unit-cell parameters in Table S1). Thus, the structure of $1H_4$·cyclohexane is derived from that of $1H_4$ by insertion of the cyclohexane solvent molecules.

Overlay of the structures of $1H_4$ (red) and $1H_4$·cyclohexane (blue) showing the consistent 2-D sections (horizontal). The upper layer in the diagram is overlaid exactly. The cyclohexane molecules are omitted from $1H_4$·cyclohexane.
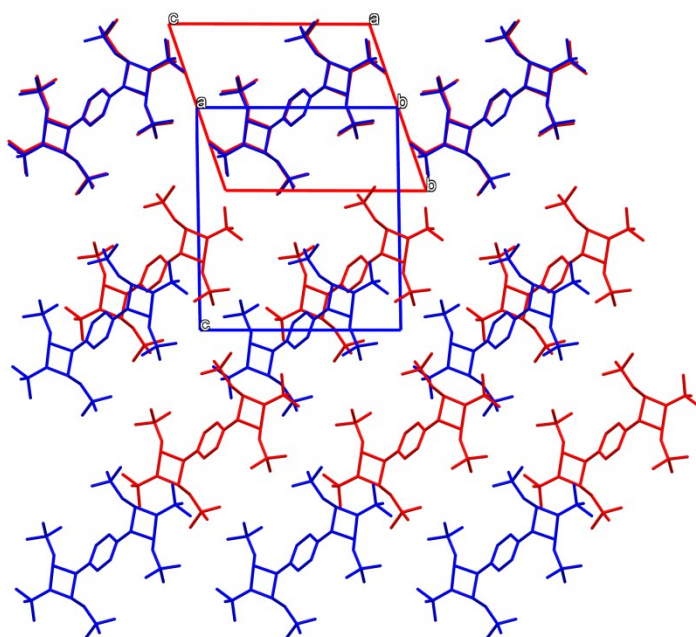
SHELXT: G. M. Sheldrick, Acta Cryst. Sect. A, 2015, 71, 3–8.

SHELXL: G. M. Sheldrick, Acta Cryst. Sect. C, 2015, 71, 3–8.

PLATON: A. L. Spek, Acta Cryst. Sect. D, 2009, 65, 148–155.

SQUEEZE: A. L. Spek, Acta Cryst. Sect. C, 2015, 71, 9–18.