Supplementary information

A neutral analogue of a phosphamethine cyanine

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General conditions

Unless otherwise stated, all manipulations were carried out under an inert atmosphere of purified argon or nitrogen, either using flame-dried glassware and standard Schlenk techniques, or in gloveboxes. *n*-Pentane and CH_3CN were distilled from NaK alloy and CaH_2, respectively, and stored in Schlenk-flasks under inert conditions. C_6D_6 was refluxed over NaK alloy for 72 h, followed by distillation and storage over molecular sieves in a glovebox. Reaction monitoring experiments were carried out using NMR-tubes with a PTFE screw. Imidazolio-phosphide **1** and borane **2** were prepared as described.[1,2]

NMR spectra were acquired on Bruker Avance 250 (^{1}H: 250.0 MHz, ^{11}B: 80.3 MHz, ^{13}C: 62.9 MHz, ^{31}P: 101.2 MHz) or Bruker Avance 400 (^{1}H: 400.1 MHz, ^{15}N 40.6: MHz) NMR spectrometers at 293 - 296 K if not stated otherwise. ^{1}H Chemical shifts were referenced to TMS using the signals of the residual protons of the deuterated solvent (δ^1H = 7.15 (C_6D_6)) as secondary reference. Spectra of heteronuclei were referenced using the Ξ-scale[3] using $BF_3{\cdot}OEt_2$ (Ξ = 32.083974 MHz, ^{11}B), TMS (Ξ = 25.145020 MHz, ^{13}C), $MeNO_2$ (Ξ = 10.136767 MHz, ^{15}N) and 85 % H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P) as secondary references. Coupling constants are generally given as absolute values. Assignments of ^{1}H, ^{13}C, and ^{15}N NMR signals were derived from ^{1}H,^{13}C and ^{1}H,^{15}N HMBC NMR spectra. FTIR-spectra were recorded on a Thermo Scientific Nicolet iS5 spectrometer equipped with an iD5 attenuated total reflectance (ATR) unit under nitrogen atmosphere. Elemental analyses were performed with an Elementar Micro Cube elemental analyser. Mass spectra were obtained using a Varian MAT 711 (EI at 70 eV) mass spectrometer.

Synthesis of 3

A 100 mL Schlenk flask equipped with a dropping funnel and a gas release tube was charged with **1** (1.00 g, 7.81 mmol, 1.0 equiv.), sodium hydride (190 mg, 9.37 mmol, 1.2 equiv.) and MeCN (10 mL). A solution of **2** (5.46 g, 11.7 mmol, 1.5 equiv.) in MeCN (10 mL) was slowly added to the constantly stirred suspension through the dropping funnel. Stirring was continued after the addition was complete until the gas evolution ceased and formation of an orange-coloured solution and a colourless precipitate had formed. Volatiles were then removed under reduced pressure and the residue extracted with n-pentane (15 mL). The resulting suspension was filtered over a G4-frit and the residual solid washed with pentane (2 x 5 mL). The combined filtrates were concentrated under reduced pressure to about half the original volume. Storage of the resulting solution at -30 °C afforded crystalline **3** (3.16 g, 6.14 mmol, yield 78%) as dark red needles.

^{1}H NMR (C_6D_6, 250 MHz): δ = 7.25 - 7.05 (m, 6 H, *m*/*p*-CH), 6.37 (d, $^4J_{PH}$ = 0.9 Hz, 2 H, NHB-CH), 5.49 (s, 2 H, imid-CH), 3.63 (sept, 4 H, $^3J_{HH}$ = 6.83 Hz, *i*Pr-CH), 3.03 (s, 6 H, NCH_3), 1.41 (d, 12 H, $^3J_{HH}$ = 6.83 Hz, CH_3), 1.25 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, CH_3). – ^{11}B (C_6D_6): δ = 32.3 (broad s, $w_{1/2} \approx 2.8{\cdot}10^2$ Hz). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 170.5 (d, $^1J_{CP}$ = 94 Hz, CP), 146.4 (s, *o*-C), 140.9 (s, *ipso*-C), 126.4 (s, *p*-C), 123.0 (s, *m*-C), 119.9 (d, $^4J_{PC}$ = 0.9 Hz, NHB-CH), 118.0 (d, $^3J_{PC}$ = 2.8 Hz, imid-CH), 36.4 (d, $^3J_{PC}$ = 7.8 Hz, NCH_3), 28.3 (d, $^4J_{PC}$ = 1.9 Hz, *i*Pr-CH), 25.8 (s, CH_3), 23.3 (d, $^5J_{PC}$ = 2.5 Hz, CH_3). – ^{15}N NMR (HMBC, C_6D_6, 400 MHz): δ = -215.2 (s, imid-N), -241.0 (s, NHB-N). – ^{31}P{^{1}H} NMR (C_6D_6): δ -176.6 (broad s, $w_{1/2} \approx 52$ Hz). – ATR-IR: $\tilde{\nu}$/cm^{-1} = 3066 (w), 3032 (w), 2959 (m), 2927 (w), 2868 (m), 1571 (w), 1457 (br), 1383 (br), 1361 (m), 1328 (w), 1296 (w), 1273 (w), 1254 (w), 1223 (s), 1178 (m), 1051 (m), 979 (w), 934 (w), 907 (w), 884 (w), 803 (m), 757 (vs), 708 (m), 691 (w). 654 (m), 619 (m). – HRMS (EI, 70 eV): m/e = 514.3396 ($M^{+\cdot}$, calcd. 514.3402 for $[C_{31}H_{44}BN_4P]^+$). – $C_{31}H_{44}BN_4P$ (516.7 g mol^{-1}): calcd. C 72.37 H 8.62 N 10.89, found C 71.81 H 8.62 N 10.52.

Crystallographic studies

X-ray diffraction data for **3** were collected on a Bruker diffractometer equipped with a Kappa Apex II Duo CCD-detector and a KRYO-FLEX cooling device with Mo-K_α radiation (λ = 0.71073 Å) at 135(2) K. The structure was solved with direct methods (SHELXS-2014[4]) and refined with a full-matrix least squares scheme on F^2 (SHELXL-2014[4]). A semi-empirical absorption correction was applied. One *i*Pr-moiety and the P-imidazole fragment were disordered. Constraints (EADP), restraints (SADI, FLAT), and a general RIGU restraint were used for the refinement. Occupancy factors were determined from free refinement at the isotropic stage and then fixed. Disordered C- and N-atoms were refined isotropically. All other non-hydrogen atoms were refined anisotropically and hydrogen atoms using a riding model. CCDC-2133603 (see Table S1 and cif-file for further details) contains the crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data for **3**.

	3
CSD	2133603
sum formula	$C_{31}H_{44}BN_4P$
M / g mol^{-1}	514.48
T	135(2)
radiation	Mo-K_α
wavelength	0.71073 Å
crystal system	Monoclinic
space group	$P2_1/c$
a / Å	13.1468(5)
b / Å	12.2571(5)
c / Å	19.3695(7)
α / °	90
β / °	101.993(2)
γ / °	90
V / Å^3	3053.1(2)
Z	4
ρ_{calcd} / g cm^{-3}	1.119
F(000)	1112
crystal size / mm^3	0.306 x 0.215 x 0.209
Θ-range / °	1.583 to 26.417
μ_{abs} / mm^{-1}	0.115
Refl. Collected	24668
Refl. Unique	6277
Refl. Obsd. (I > 2σ(I))	3686
$R_{int.}$	0.0495
Compl. to Θ = 25.242° [a)]	1.000
Absorp. corr.	Multi-scan
Max. / min. transm.	0.6233 / 0.3662
Data/restraints/parameters	6277 / 312 / 329
GoF (F^2)	1.026
R [I>2σ(I)]	0.0674
wR2 (all data)	0.1849
Largest diff. peak and hole/e Å^{-3}	0.550 / -0.424

a) Θ-full range according to the IUCr-rules.

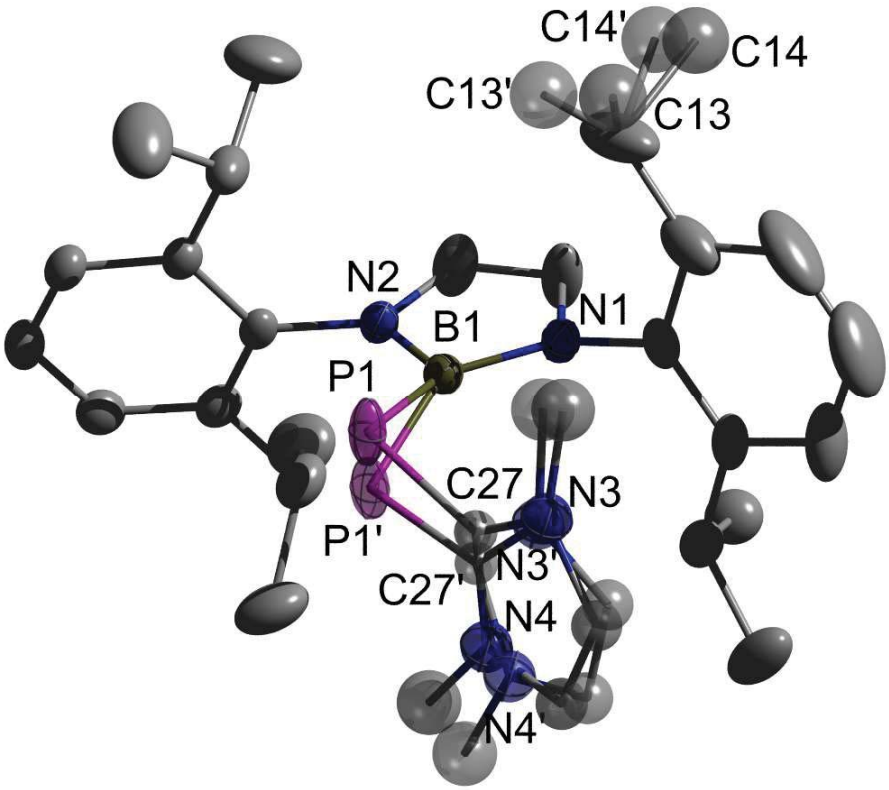


Figure S1. Representation of the molecular structure of **3** showing the positions of the disordered atoms. Occupancy factors are 0.56/0.44 for atoms labelled as X and X', respectively. Hydrogen atoms were omitted for clarity. Thermal ellipsoids were drawn at the 50% probability level.

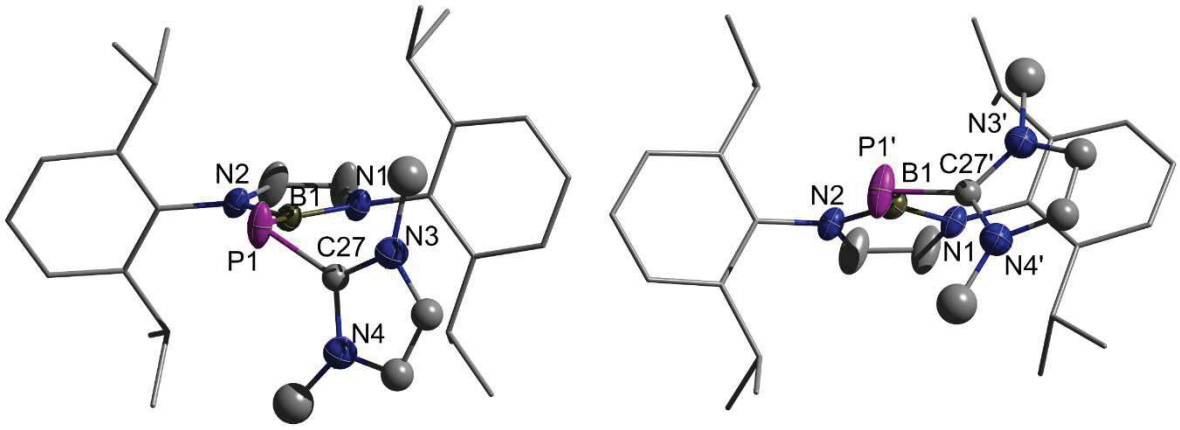


Figure S2. Separate representation of the major (left, occupancy 0.56) and minor (right, occupancy 0.44) conformer of **3** (occupancy factors 0.56/0.44). For clarity, hydrogen atoms were omitted and N-Dip substituents represented using a wire model. Thermal ellipsoids were drawn at the 50% probability level. Selected distances (Å) and angles (°): N1–B1 1.442(3), N2–B1 1.437(4), B1–P1 1.892(3), P1–C27 1.823(4), C27–N3 1.367(5), C27–N4 1.380(5), B1–P1' 1.892(4), P1'–C27' 1.776(5), C27'–N3' 1.360(6), C27'–N4' 1.370(6), N2–B1–N1 103.5(2), N2–B1–P1 120.9(2), N1–B1–P1 133.8(2), C27–P1–B1 100.78(19), N3–C27–N4 104.7(4), N3–C27–P1 127.9(3), N4–C27–P1 126.2(3), N2–B1–P1' 118.0(2), N1–B1–P1' 136.0(2), C27'–P1'–B1 108.7(2), N3'–C27'–N4' 101.0(4), N3'–C27'–P1' 127.9(4), N4'–C27'–P1' 130.7(4), N1–B1–P1–C27 -40.0(3), N1–B1–P1'–C27' 6.0(4).

NMR spectra

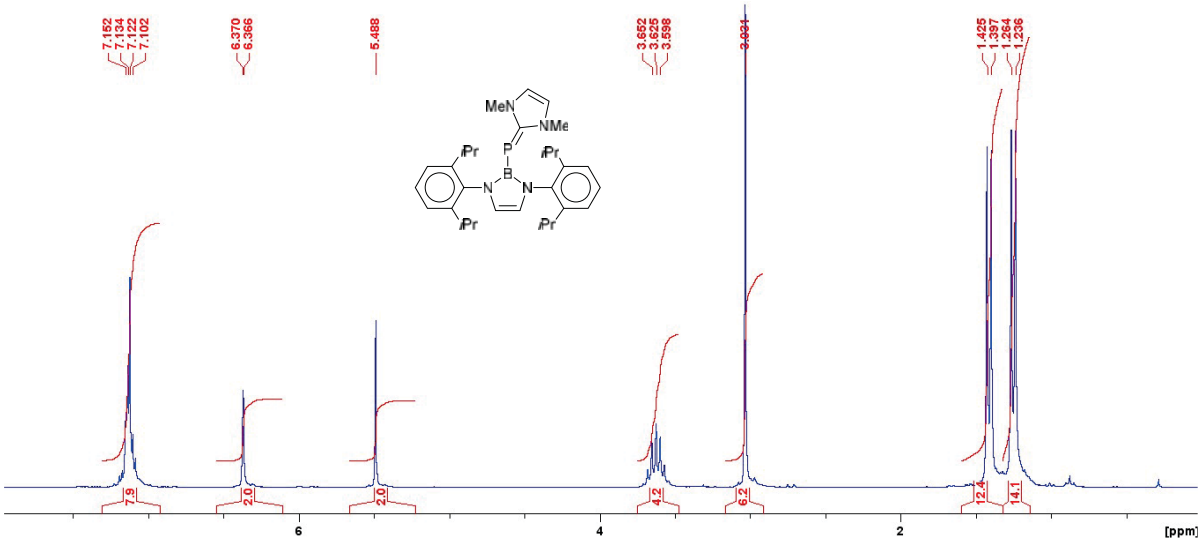


Figure S3. ^{1}H NMR spectrum (C_6D_6, 250 MHz, 296 K) of **3**.

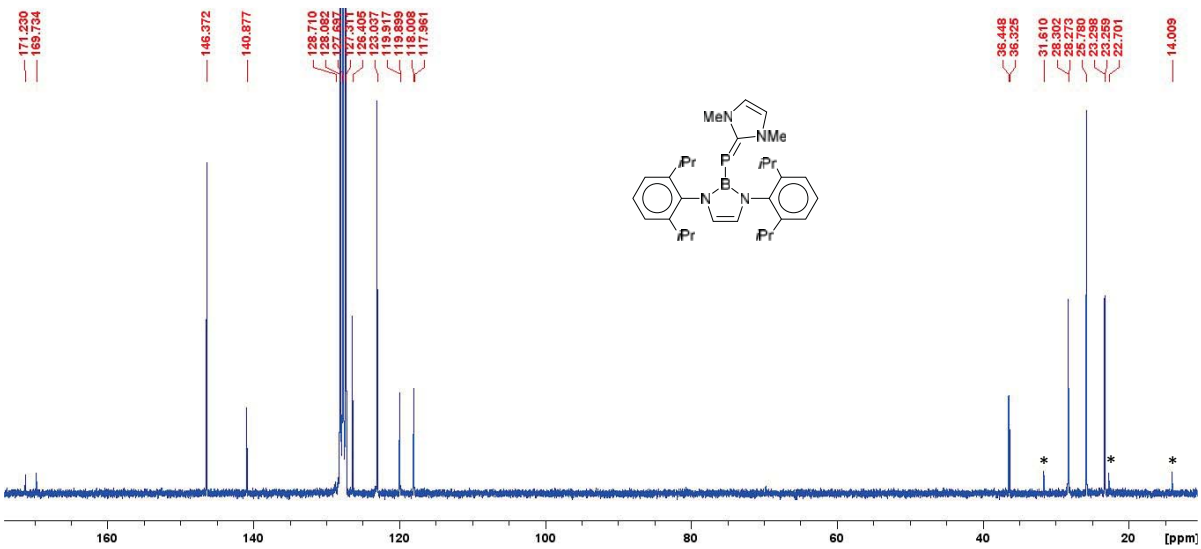


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 62.9 MHz, 296 K) of **3**. (* denotes residual solvent signals (pentane)).

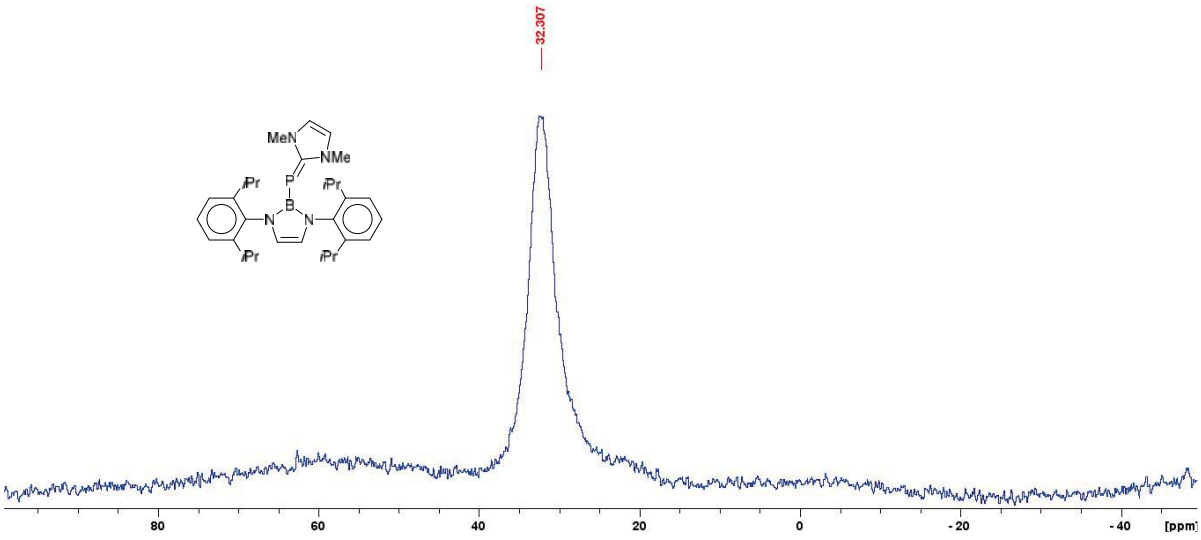


Figure S5. $^{11}B\{^{1}H\}$ NMR spectrum (C_6D_6, 80.9 MHz, 296 K) of **3** (uncorrected for probe background).

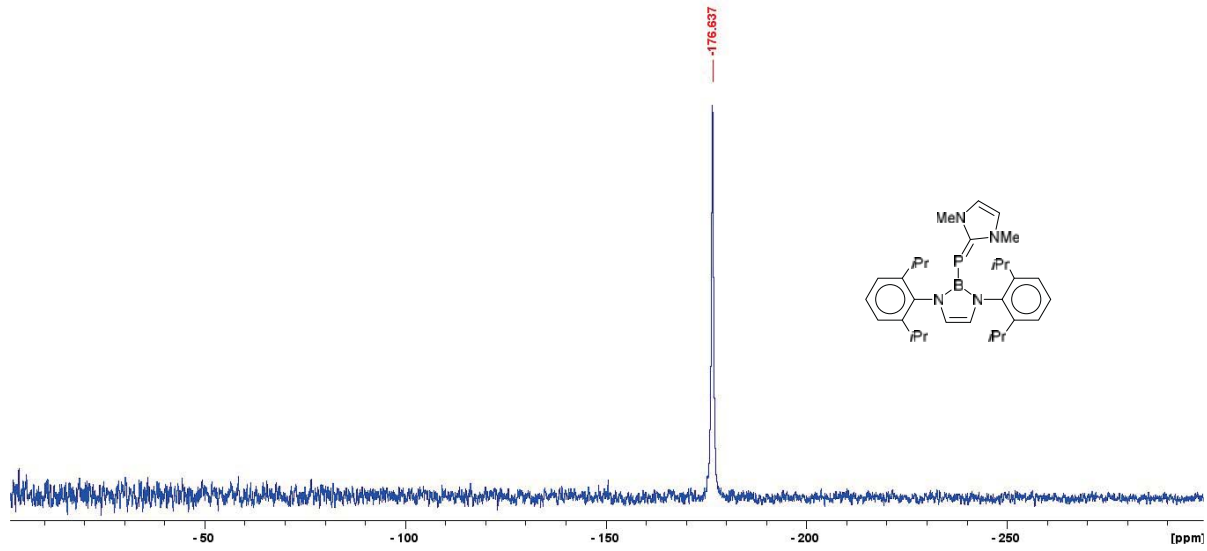


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 101.2 MHz, 296 K) of **3**.

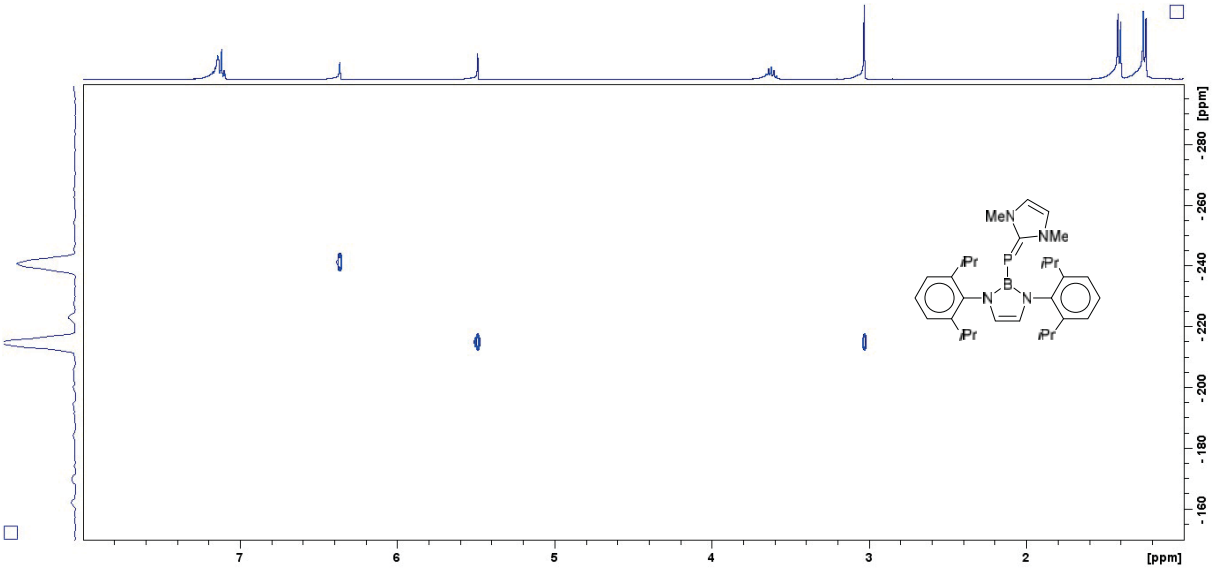


Figure S7. $^{1}H,^{15}N$ gsHMBC spectrum (C_6D_6, 400 MHz) of **3**.

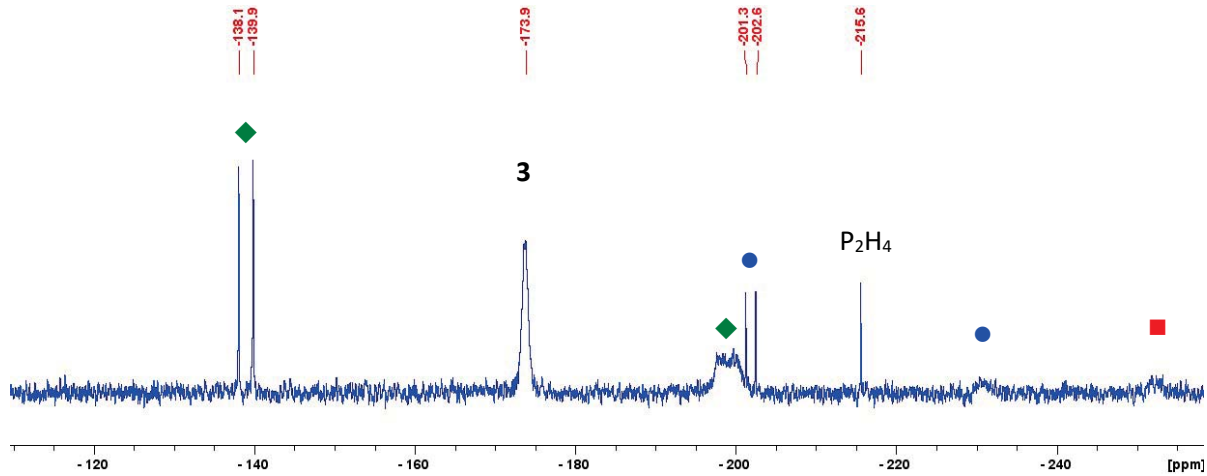


Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum (pentane, 162 MHz) of the product mixture resulting from reaction of **1** with **2** without additional base. Signal assignments: ■ = ^{Dip}NHB-PH_2, ● = ^{Dip}NHB-PH-PH_2, ◆ = ^{Dip}NHB-PH-P-Imid^{Me}.

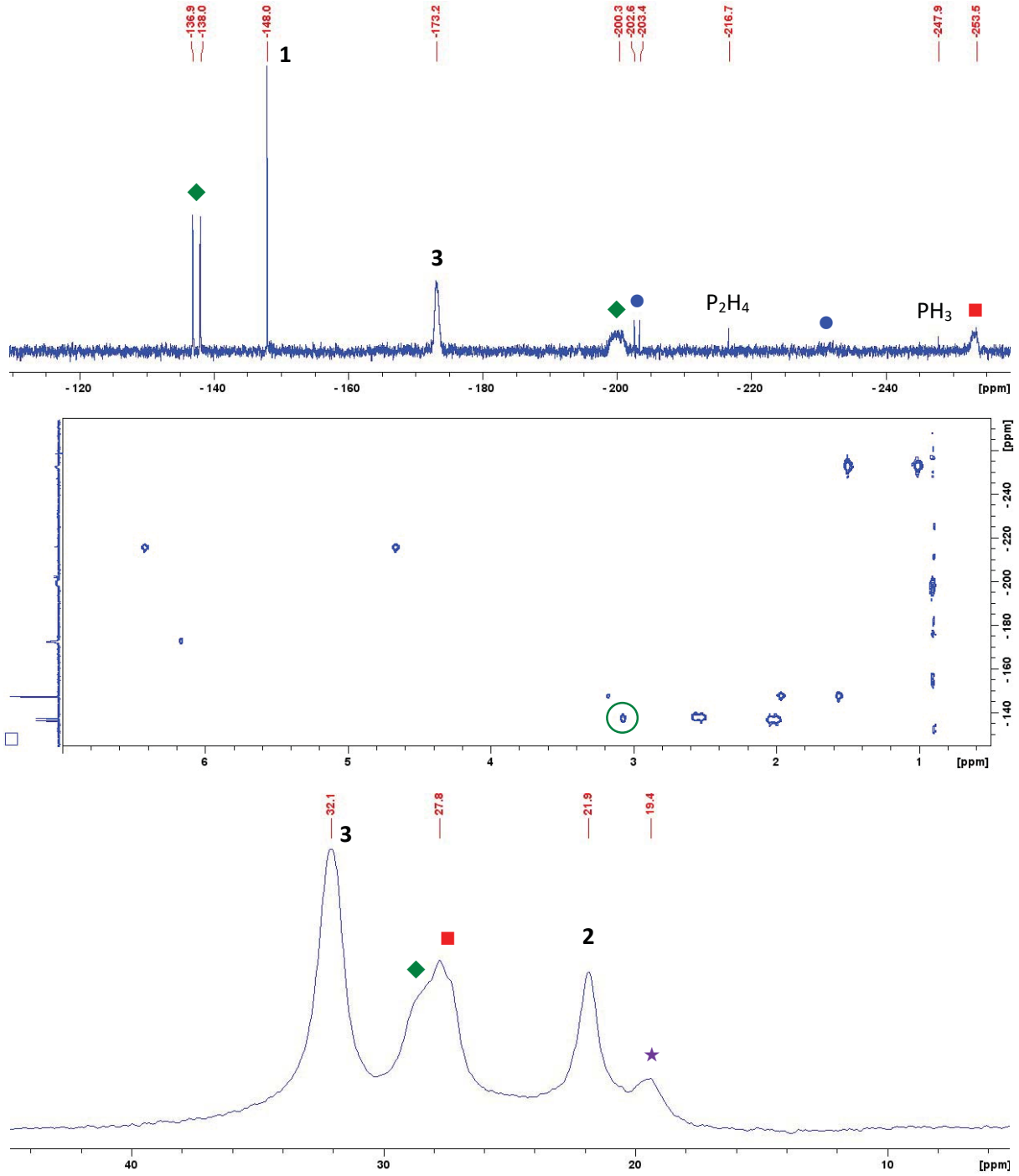


Figure S9. $^{31}P\{^{1}H\}$ (top), $^{1}H,^{31}P$ HMQC (middle) and $^{11}B\{^{1}H\}$ NMR spectra (pentane, 162 MHz) of the product mixture resulting from reaction of **1** with **2** (2 equivs.) in the presence of DABCO. Signal assignments: ■ = ^{Dip}NHB-PH_2, ● = ^{Dip}NHB-PH-PH_2, ◆ = ^{Dip}NHB-PH-P-Imid^{Me}, ★ = ^{Dip}NHB-H. Crucial for the assignment of ^{Dip}NHB-PH-P-Imid^{Me} is a correlation of one ^{31}P NMR signal with the signal of the NCH_3(imid) protons (green circle). The formation of this species can be explained as resulting from base induced condensation of a transient diphosphine ^{Me}Imid-$PHPH_2$ with **2** (see 5). The formation mechanism of ^{Dip}NHB-H is unknown.

Computational Studies

General remarks. DFT calculations were carried out with the Gaussian 16[6] program package using the B3LYP functional[7] with Weigend's and Ahlrichs' def2-SVP and def2-TZVP basis sets[8] on an ultrafine grid for numerical integration. Grimme's D3BJ formalism[9] was applied to include dispersion effects. The molecular structures were established by full energy optimization at the B3LYP-D3BJ/def2-SVP level. Harmonic vibrational frequency calculations were carried out at the same level to identify the resulting stationary points as local minima (only positive normal modes) or transition states (one imaginary normal mode). Electronic energies were recalculated at the final geometries at the B3LYP-D3BJ/def2-TZVP level. Standard Gibbs free energies ΔG^0 (for p=1 bar and T=298.13 K) of local minima and transition states were computed using these energies with the corrections obtained with the smaller basis sets. Relaxed potential energy scans (PES) were carried out at the B3LYP-D3BJ/def2-SVP level, using the optimized structures as starting points and one of the N-E-P-E (E = C, B) torsional angles as independent variable. The geometries obtained after convergence at each step were then used to evaluate the interplanar angles θ'(X) between the ring plane of a substituent X and the central EPE plane. For the graphic representation, the resulting angles (spanning a range between 0° and 90°) were projected on an interval 0° ≤θ ≤ 180° to represent a full torsional motion. NBO/NRT analyses of the B3LYP-D3BJ/def2-SVP densities were carried out with the NBO6.0 program.[10] MOLDEN[11] was used for visualization.

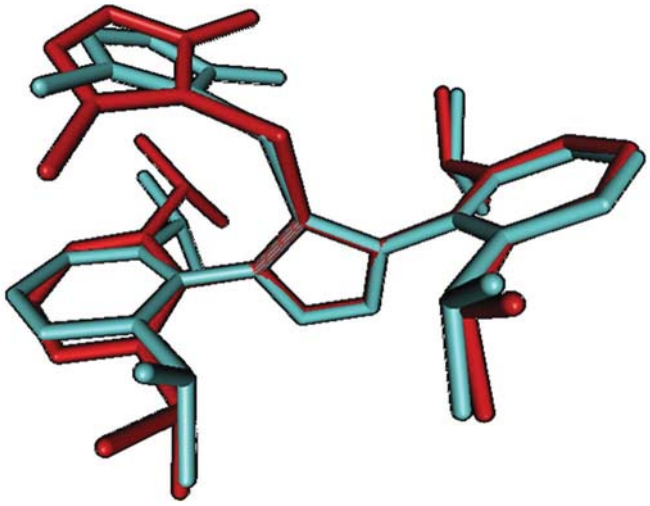


Figure S10. Wireframe representation of the overlay of the observed (red, major conformer) and computed (at the B3LYP-D3BJ/def2-SVP level) molecular structure of **3**. Hydrogen atoms were omitted for clarity.

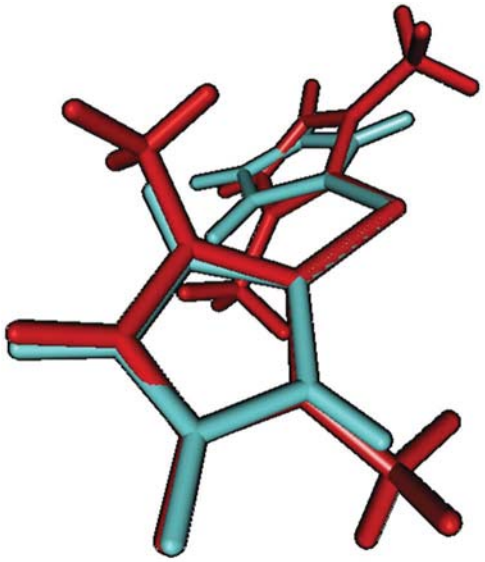


Figure S11. Wireframe representation of the overlay of the computed (at the B3LYP-D3BJ/def2-SVP level) molecular structures of $\mathbf{3^{Me}}$ (red) and $\mathbf{3^{H}}$ (blue) illustrating the shrinking skew in the helical conformation with decreasing steric demand of the N-substituents. Analogous trends for $(\mathbf{4^{R}})^{+}$ and $(\mathbf{5^{R}})^{-}$ can be derived from the θ-values in Table S2.

Table S2. Calculated E–P distances (at the B3LYP-D3BJ/def2-SVP level of theory, E = B, C), twist angles θ(X), Natural Bond Orders (from NRT analyses of the B3LYP-D3BJ/def2-SVP density) and Wiberg indexes (WBI) for **3**, $\mathbf{3^R}$ – $(\mathbf{5^R})^-$ (R = H, Me), ^{Me}imid-PH, $(^{Me}imid\text{-}PH_2)^+$, $(^{Me}NHB\text{-}PH)^-$ and $^{Me}NHB\text{-}PH_2$.

Compound	E	Θ [a]	E–P/Å	Natural bond order (NRT)	WBI
3	C	53.2	1.785		1.19
	B	42.7	1.902		1.20
^{Me}Imid-PH	C	0.0 [b]	1.760		1.38
^{H}Imid-PH	C	0.0 [b]	1.753	1.51	1.40
$(^{Me}Imid\text{-}PH_2)^+$ [c]	C	--	1.854		0.96
$(^{H}Imid\text{-}PH_2)^+$ [c]	C	--	1.856	1.00	0.96
$(^{Dip}NHB\text{-}PH)^-$	B	3.1 [b]	1.863		1.51
$(^{Me}NHB\text{-}PH)^-$	B	16.3 [b]	1.870		1.45
$(^{H}NHB\text{-}PH)^-$	B		1.872	1.85	1.48
$^{Dip}NHB\text{-}PH_2$	B	--	1.927		1.09
$^{Me}NHB\text{-}PH_2$ [c]	B	--	1.943		1.05
$^{H}NHB\text{-}PH_2$ [c]	B	--	1.943	1.02	1.05
$\mathbf{3^{Me}}$	C	27.8	1.773		1.30
	B	50.3	1.913		1.12
$\mathbf{3^{H*}}$ [d]	C	27.8	1.773	1.49	1.33
	B	50.3	1.913	1.04	1.13
$\mathbf{3^{H}}$	C	4.2	1.762	1.49	1.34
	B	37.6	1.911	1.15	1.14
$(\mathbf{4^{Me}})^+$	C	40.4	1.807		1.10
$(\mathbf{4^{H*}})^+$ [d]	C	40.4	1.807	1.22	1.12
$(\mathbf{4^{H}})^+$	C	27.5	1.798	1.26	1.14
$(\mathbf{5^{Me}})^-$	B	38.4	1.888		1.29
$(\mathbf{5^{H*}})^-$ [d]	B	38.4	1.888	1.35	1.31
$(\mathbf{5^{H}})^-$	B	16.3	1.883	1.39	1.33

a) interplanar angle between the central E1–P–E2 and the ring plane of the heterocyclic substituent containing E. b) angle between the plane of the N-heterocycle and the P–H bond. c) C_s-conformer in which the ring plane bisects the HPH angle and the heterocyclic π-system is orthogonal to the P-centred lone-pair. d) molecular geometry of the corresponding N-Me derivative with H-atom positions optimized.

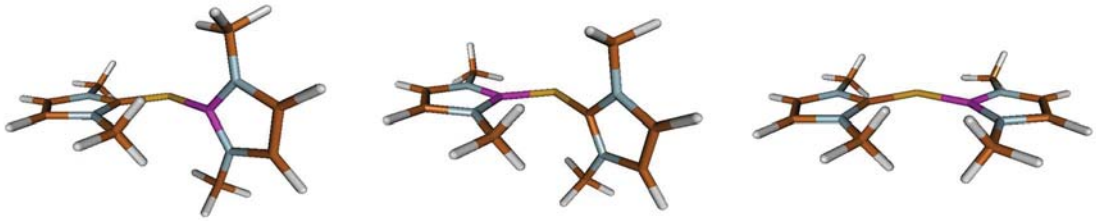


Figure S12. Wireframe representation of the molecular structures of rotational transition states for **3**^{Me} (at the B3LYP-D3BJ/def2-SVP level) showing (from left to right) 'orthogonal' transition states associated with rotation around the P–B and P–C bond, respectively, and the 'planar' transition state. Relative energies and Gibbs enthalpies are listed in Table S3.

Table S3. Computed electronic energies $\Delta E^{\neq}$ and standard Gibbs enthalpies $\Delta G^{0,\neq}$ (for T=298.13 K and p=1 bar) of transition states for P–C/B bond rotation processes in **3**^{R} – (**5**^{R})$^{-}$, ^{R}imid-PH and (^{R}NHB-PH)$^{-}$ calculated from B3LYP-D3BJ/def2-TZVP//B3LYP-D3BJ/def2-SVP energies and correction terms obtained from harmonic frequency analyses at the B3LYP-D3BJ/def2-SVP level of theory (R = H, Me).

Compound	Rotated bond	$\Delta E^{\neq}$	$\Delta G^{0,\neq}$	Compound	conformer	$\Delta E^{\neq}$	$\Delta G^{0,\neq}$
3^{Me}	P–B	0.9	1.7	**3**^{H}	P–C	1.2	1.5
	P–C	7.9	7.8		P–B	10.1	9.7
	planar TS	15.3	15.9		planar	4.1	3.6
(**4**^{Me})$^{+}$	P–C	4.0	4.2	(**4**^{H})$^{+}$	P–C	2.6	2.7
	planar TS [a]	22.9	25.3		planar	5.2	4.8
(**5**^{Me})$^{-}$	P–B	2.3	2.8	(**5**^{H})$^{-}$	P–B	3.6	3.6
	planar TS	12.3	13.5		planar	4.2	7.8
^{Me}Imid-PH	P–C	12.2	12.1	^{H}Imid-PH	P–C	11.9	11.9
(^{Me}NHB-PH)$^{-}$	P–B	5.3	6.1	(^{H}NHB-PH)$^{-}$	P–B	5.7	6.0

a) imidazole rings are coplanar but are twisted out of the CPC-plane (twist angle Θ 26.5°); the completely planar conformer is a higher order transition states with two imaginary modes at a relative energy of 5.4 kcal/mol.

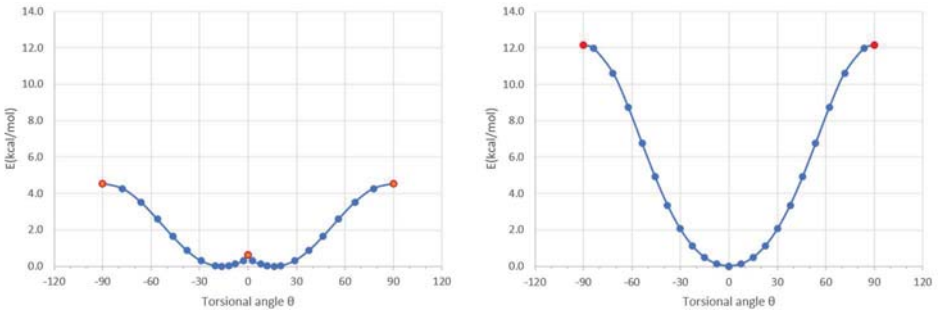


Figure S13. Energy profiles for rotation around the P–E bonds of (^{Me}NHB-PH)$^{-}$ (E = B, left) and ^{Me}Imid-PH (E = C, right). Θ denotes the torsional angle of the PH-bond vs. the NHB/imidazole ring plane. Blue data points were derived from relaxed potential energy scans (at the B3LYP-D3BJ/def2-SVP level) and red data points refer to transition states. Note that the equilibrium geometry of (^{Me}NHB-PH)$^{-}$ displays no planar but rather a slightly twisted (θ = ±16.3°) conformation; that the planar geometry (θ = 0°) corresponds to a rotational transition state.

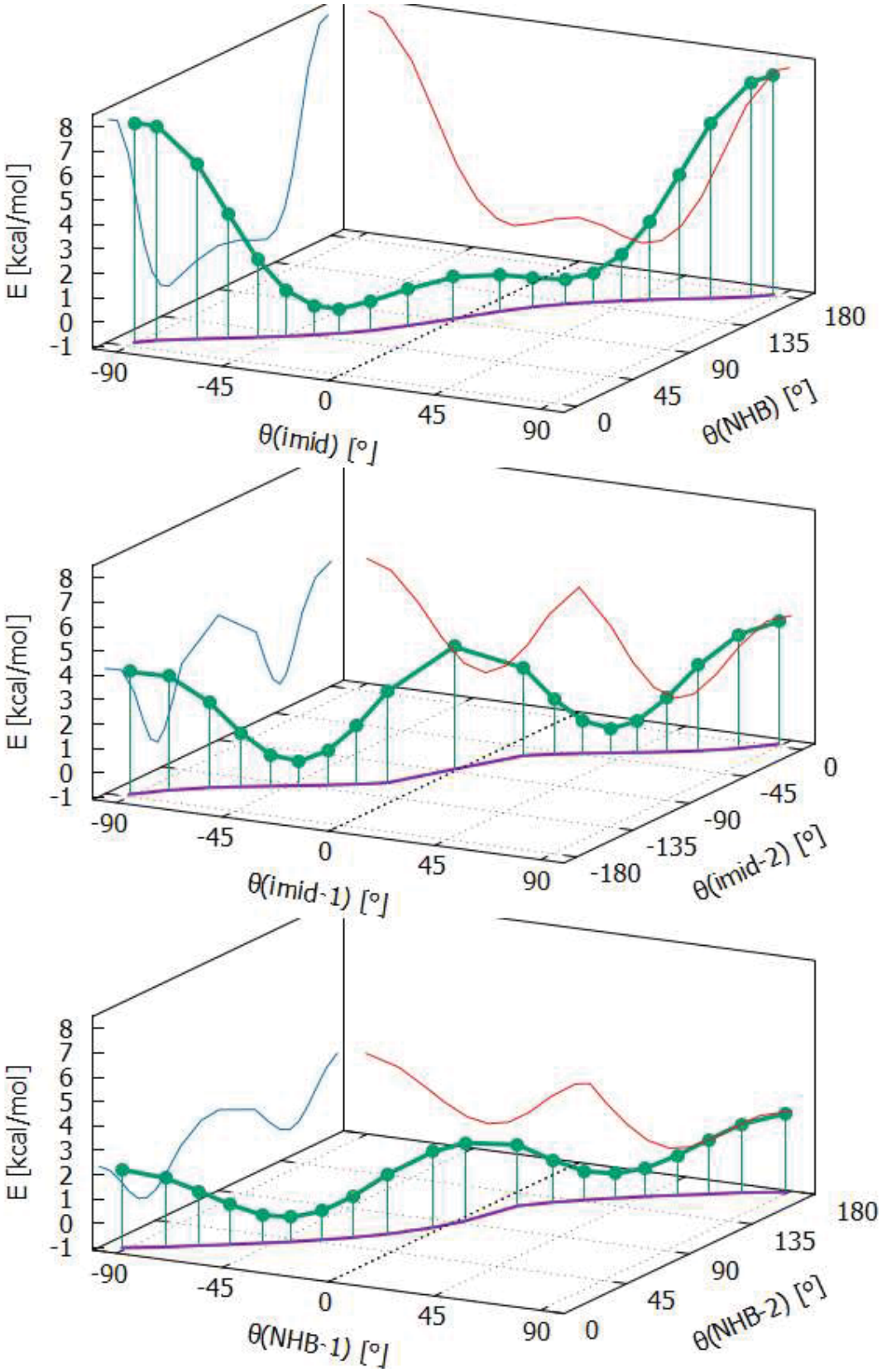
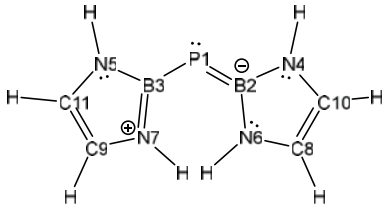


Figure S14. Energy profiles illustrating the concerted variation of the torsional angles θ(X) (X = imid, NHB; θ = angle between the ring plane of X and the central C/B–P–B/C plane) during rotations around the P–C/B bonds in **3**^{Me} (top), (**4**^{Me})$^{+}$ (middle) and (**5**^{Me})$^{-}$ (bottom). Energies and θ-values were derived from relaxed potential energy scans at the B3LYP-D3BJ/def2-SVP level using one of the N–E–P–E' (E, E' = B, C) dihedral angles as independent coordinate (key: purple trace – reaction path as defined by the angles θ(X1), θ(X2), green trace – energy on the reaction path, blue and red traces – projection of the energy on the two independent coordinates θ(X1), θ(X2).

Table S4. Results of the NRT analysis on 3H, 4H+ and (5H)-. The Lewis structure of the leading resonance structure (RS1) is shown on top. The further structures are encoded by listing incrementally any bonding (2-center NBOs) or non-bonding (1-center NBOs) electron pairs added to or removed from (in parentheses) RS 1.

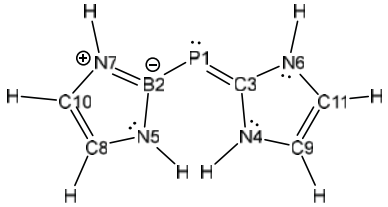


$(5^{H})^{-}$

Resonance

RS	Weight(%)	Added(Removed)
1*(2)	7.70	
2*(2)	7.70	(P 1- B 2), P 1- B 3, B 2- N 6, (B 3- N 7), (N 6), N 7
3*	7.60	B 3- N 5, (B 3- N 7), (N 5), N 7
4*	7.60	(P 1- B 2), P 1- B 3, B 2- N 4, (B 3- N 7), (N 4), N 7
5*	5.67	(P 1- B 2), B 2- N 6, P 1, (N 6)
6*(2)	5.54	(P 1- B 2), P 1- B 3, (B 3- N 7), N 7
7*(2)	5.54	(B 3- N 7), N 7
8*	5.31	(P 1- B 2), B 2- N 4, B 3- N 5, (B 3- N 7), P 1, (N 4), (N 5), N 7
9	4.99	(P 1- B 2), B 2- N 4, P 1, (N 4)
10	4.99	(P 1- B 2), B 2- N 6, B 3- N 5, (B 3- N 7), P 1, (N 5), (N 6), N 7
11	2.40	(P 1- B 2), P 1- B 3, B 2- N 4, (B 3- N 7), N 6- C 8, (C 8- C 10), (N 4), (N 6), N 7, C 10
12	2.40	(P 1- B 2), P 1- B 3, B 2- N 4, (B 3- N 7), N 7- C 9, (C 9- C 11), (N 4), C 11
13	2.40	B 3- N 5, (B 3- N 7), N 6- C 8, (C 8- C 10), (N 5), (N 6), N 7, C 10
14	2.40	B 3- N 5, (B 3- N 7), N 7- C 9, (C 9- C 11), (N 5), C 11
15	2.39	(P 1- B 2), P 1- B 3, B 2- N 4, (B 3- N 7), N 5- C 11, (C 9- C 11), (N 4), (N 5), N 7, C 9
16	2.39	B 3- N 5, (B 3- N 7), N 4- C 10, (C 8- C 10), (N 4), (N 5), N 7, C 8
17	2.27	(P 1- B 2), P 1- B 3, (B 3- N 7), N 4- C 10, (C 8- C 10), (N 4), N 7, C 8
18	2.27	(B 3- N 7), N 5- C 11, (C 9- C 11), (N 5), N 7, C 9
19	1.44	(P 1- B 2), B 2- N 6, N 4- C 10, (C 8- C 10), P 1, (N 4), (N 6), C 8
20	1.44	(P 1- B 2), B 2- N 6, N 5- C 11, (C 9- C 11), P 1, (N 5), (N 6), C 9
21	1.27	(P 1- B 2), N 6- C 8, (C 8- C 10), P 1, (N 6), C 10
22	1.27	(P 1- B 2), B 2- N 6, (B 3- N 7), N 7- C 9, (C 9- C 11), P 1, (N 6), C 11
23	0.98	N 4- C 10, (C 8- C 10), (N 4), C 8
24	0.98	(P 1- B 2), P 1- B 3, B 2- N 6, (B 3- N 7), N 5- C 11, (C 9- C 11), (N 5), (N 6), N 7, C 9
25	0.94	N 5- C 11, (C 9- C 11), (N 5), C 9
26	0.94	(P 1- B 2), P 1- B 3, B 2- N 6, (B 3- N 7), N 4- C 10, (C 8- C 10), (N 4), (N 6), N 7, C 8
27	0.89	N 6- C 8, (C 8- C 10), (N 6), C 10
28	0.89	(P 1- B 2), P 1- B 3, B 2- N 6, (B 3- N 7), N 7- C 9, (C 9- C 11), (N 6), C 11
29	0.89	(B 3- N 7), N 7- C 9, (C 9- C 11), C 11
30	0.89	(P 1- B 2), P 1- B 3, (B 3- N 7), N 6- C 8, (C 8- C 10), (N 6), N 7, C 10
31	0.65	P 1- B 3, B 2- N 4, (B 2- N 6), (B 3- N 7), (P 1), (N 4), N 6, N 7
32	0.65	P 1- B 3, B 3- N 5, (B 3- N 7), (B 3- N 7), (P 1), (N 5), N 7, N 7
33	0.64	(P 1- B 2), P 1- B 3, P 1- B 3, B 2- N 4, (B 3- N 7), (B 3- N 7), (P 1), (N 4), N 7, N 7
34	0.64	P 1- B 2, (B 2- N 6), B 3- N 5, (B 3- N 7), (P 1), (N 5), N 6, N 7
35	0.57	(P 1- B 2), (P 1- B 2), P 1- B 3, P 1- B 3, B 2- N 4, (B 3- N 5), (B 3- N 7), (N 4), N 5, N 7
36	0.57	P 1- B 2, (P 1- B 3), (B 2- N 4), B 3- N 5, (B 3- N 7), N 4, (N 5), N 7
37	0.50	P 1- B 3, (B 3- N 7), (P 1), N 7
38	0.25	P 1- B 2, (B 2- N 6), (P 1), N 6
39	0.25	(P 1- B 2), P 1- B 3, P 1- B 3, B 2- N 6, (B 3- N 7), (B 3- N 7), (P 1), (N 6), N 7, N 7
40	0.22	P 1- B 2, (P 1- B 3), (B 2- N 4), N 4
41	0.22	(P 1- B 2), (P 1- B 2), P 1- B 3, P 1- B 3, B 2- N 6, (B 3- N 5), (B 3- N 7), N 5, (N 6), N 7
42	0.22	(P 1- B 2), P 1- B 3, (B 3- N 5), N 5
43	0.22	(B 2- N 4), B 2- N 6, (B 3- N 7), N 4, (N 6), N 7
44-65	0.00	
	100.00	* Total *

Table S4 (continued).

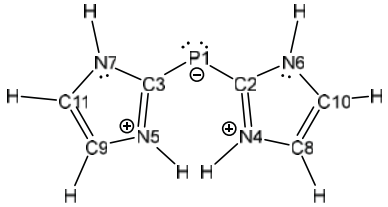


3^{H}

Resonance

RS	Weight(%)	Added(Removed)
1*	14.84	
2*	11.55	B 2- N 5, (B 2- N 7), (N 5), N 7
3*	8.53	(P 1- C 3), C 3- N 6, P 1, (N 6)
4*	7.88	(P 1- C 3), B 2- N 5, (B 2- N 7), C 3- N 4, P 1, (N 4), (N 5), N 7
5*	7.73	(P 1- C 3), C 3- N 4, P 1, (N 4)
6*	6.90	(P 1- C 3), B 2- N 5, (B 2- N 7), C 3- N 6, P 1, (N 5), (N 6), N 7
7*	4.33	(B 2- N 7), N 7
8*	3.93	P 1- B 2, (P 1- C 3), (B 2- N 7), C 3- N 6, (N 6), N 7
9*	3.15	P 1- B 2, (P 1- C 3), (B 2- N 7), C 3- N 4, (N 4), N 7
10*	2.68	P 1- B 2, (P 1- C 3), (B 2- N 7), N 7
11	2.39	(P 1- C 3), C 3- N 6, N 5- C 8, (C 8- C 10), P 1, (N 5), (N 6), C 10
12	2.35	(P 1- C 3), C 3- N 6, N 4- C 9, (C 9- C 11), P 1, (N 4), (N 6), C 11
13	1.92	(B 2- N 7), N 5- C 8, (C 8- C 10), (N 5), N 7, C 10
14	1.89	B 2- N 5, (B 2- N 7), N 7- C 10, (C 8- C 10), (N 5), C 8
15	1.87	B 2- N 5, (B 2- N 7), N 6- C 11, (C 9- C 11), (N 5), (N 6), N 7, C 9
16	1.85	B 2- N 5, (B 2- N 7), N 4- C 9, (C 9- C 11), (N 4), (N 5), N 7, C 11
17	1.45	P 1- B 2, (P 1- C 3), (B 2- N 7), C 3- N 4, N 7- C 10, (C 8- C 10), (N 4), C 8
18	1.44	(B 2- N 7), N 7- C 10, (C 8- C 10), C 8
19	1.36	N 6- C 11, (C 9- C 11), (N 6), C 9
20	1.33	N 4- C 9, (C 9- C 11), (N 4), C 11
21	1.32	P 1- B 2, (P 1- C 3), (B 2- N 7), C 3- N 4, N 6- C 11, (C 9- C 11), (N 4), (N 6), N 7, C 9
22	1.31	N 5- C 8, (C 8- C 10), (N 5), C 10
23	0.86	(P 1- C 3), B 2- N 5, (B 2- N 7), C 3- N 4, N 7- C 10, (C 8- C 10), P 1, (N 4), (N 5), C 8
24	0.85	P 1- B 2, (P 1- C 3), (B 2- N 7), C 3- N 4, N 5- C 8, (C 8- C 10), (N 4), (N 5), N 7, C 10
25	0.84	(P 1- C 3), B 2- N 5, (B 2- N 7), C 3- N 4, N 6- C 11, (C 9- C 11), P 1, (N 4), (N 5), (N 6), N 7, C 9
26	0.82	P 1- B 2, (P 1- C 3), (B 2- N 7), N 4- C 9, (C 9- C 11), (N 4), N 7, C 11
27	0.78	P 1- C 3, B 2- N 5, (B 2- N 7), (C 3- N 4), (P 1), N 4, (N 5), N 7
28	0.58	(P 1- B 2), P 1- C 3, B 2- N 5, (B 2- N 7), (C 3- N 6), (N 5), N 6, N 7
29	0.58	P 1- B 2, (P 1- C 3), (B 2- N 7), N 4- C 9, (C 9- C 11), C 3, (N 4), N 7
30	0.56	P 1- C 3, (C 3- N 4), (P 1), N 4
31	0.42	(P 1- B 2), P 1- C 3, (C 3- N 6), N 6
32	0.25	(P 1- C 3), B 2- N 5, (B 2- N 7), C 3- N 6, N 7- C 10, (C 8- C 10), P 1, (N 5), (N 6), C 8
33	0.24	(P 1- C 3), B 2- N 5, (B 2- N 7), C 3- N 6, N 4- C 9, (C 9- C 11), P 1, (N 4), (N 5), (N 6), N 7, C 11
34	0.23	(P 1- C 3), C 3- N 4, N 5- C 8, (C 8- C 10), P 1, (N 4), (N 5), C 10
35	0.23	(P 1- C 3), C 3- N 4, N 6- C 11, (C 9- C 11), P 1, (N 4), (N 6), C 9
36	0.21	P 1- B 2, (P 1- C 3), (B 2- N 7), C 3- N 6, N 7- C 10, (C 8- C 10), (N 6), C 8
37	0.19	P 1- B 2, (P 1- C 3), (B 2- N 7), C 3- N 6, N 4- C 9, (C 9- C 11), (N 4), (N 6), N 7, C 11
38	0.12	P 1- B 2, (P 1- C 3), (B 2- N 7), C 3- N 6, N 5- C 8, (C 8- C 10), (N 5), (N 6), N 7, C 10
39	0.12	P 1- B 2, (P 1- C 3), (B 2- N 7), N 6- C 11, (C 9- C 11), (N 6), N 7, C 9
40-49	0.08	
	100.00	* Total *

Table S4 (continued).



$(\mathbf{4}^{H})^{+}$

Resonance

RS	Weight(%)	Added(Removed)
1*	11.32	
2*	10.43	P 1- C 3, (C 2- N 4), C 2- N 6, (C 3- N 5), (P 1), N 4, N 5, (N 6)
3*	10.43	P 1- C 2, (C 2- N 4), (C 3- N 5), C 3- N 7, (P 1), N 4, N 5, (N 7)
4*	9.90	(C 3- N 5), C 3- N 7, N 5, (N 7)
5*	9.90	(C 2- N 4), C 2- N 6, N 4, (N 6)
6*	3.85	(C 2- N 4), C 2- N 6, (C 3- N 5), C 3- N 7, N 4, N 5, (N 6), (N 7)
7	3.53	P 1- C 2, (C 2- N 4), (C 3- N 5), (P 1), N 4, N 5
8	3.53	P 1- C 3, (C 2- N 4), (C 3- N 5), (P 1), N 4, N 5
9*	3.11	P 1- C 3, (C 3- N 5), (P 1), N 5
10*	3.11	P 1- C 2, (C 2- N 4), (P 1), N 4
11	2.60	(C 2- N 4), C 2- N 6, (C 3- N 5), C 3- N 7, N 4- C 8, (C 8- C 10), N 5, (N 6), (N 7), C 10
12	2.60	(C 2- N 4), C 2- N 6, (C 3- N 5), C 3- N 7, N 5- C 9, (C 9- C 11), N 4, (N 6), (N 7), C 11
13	2.13	P 1- C 3, (C 3- N 5), N 6- C 10, (C 8- C 10), (P 1), N 5, (N 6), C 8
14	2.13	P 1- C 2, (C 2- N 4), N 7- C 11, (C 9- C 11), (P 1), N 4, (N 7), C 9
15	1.96	P 1- C 3, (C 3- N 5), N 7- C 11, (C 9- C 11), (P 1), N 5, (N 7), C 9
16	1.96	P 1- C 2, (C 2- N 4), N 6- C 10, (C 8- C 10), (P 1), N 4, (N 6), C 8
17	1.89	P 1- C 3, (C 2- N 4), (C 3- N 5), N 4- C 8, (C 8- C 10), (P 1), C 2, N 5
18	1.89	P 1- C 2, (C 2- N 4), (C 3- N 5), N 5- C 9, (C 9- C 11), (P 1), C 3, N 4
19	1.81	(C 2- N 4), (C 3- N 5), C 3- N 7, N 6- C 10, (C 8- C 10), C 2, N 4, N 5, (N 6), (N 7)
20	1.81	(C 2- N 4), C 2- N 6, (C 3- N 5), N 7- C 11, (C 9- C 11), C 3, N 4, N 5, (N 6), (N 7)
21	1.55	P 1- C 3, (C 3- N 5), N 5- C 9, (C 9- C 11), (P 1), C 11
22	1.55	P 1- C 2, (C 2- N 4), N 4- C 8, (C 8- C 10), (P 1), C 10
23	1.33	P 1- C 3, (C 2- N 4), (C 3- N 5), N 4- C 8, (C 8- C 10), (P 1), N 5, C 10
24	1.33	P 1- C 2, (C 2- N 4), (C 3- N 5), N 5- C 9, (C 9- C 11), (P 1), N 4, C 11
25	1.29	(C 2- N 4), (C 3- N 5), C 3- N 7, N 6- C 10, (C 8- C 10), N 4, N 5, (N 6), (N 7), C 8
26	1.29	(C 2- N 4), C 2- N 6, (C 3- N 5), N 7- C 11, (C 9- C 11), N 4, N 5, (N 6), (N 7), C 9
27	0.22	(C 3- N 5), C 3- N 7, N 6- C 10, (C 8- C 10), N 5, (N 6), (N 7), C 8
28	0.22	(C 2- N 4), C 2- N 6, N 7- C 11, (C 9- C 11), N 4, (N 6), (N 7), C 9
29	0.20	(C 3- N 5), C 3- N 7, N 5- C 9, (C 9- C 11), (N 7), C 11
30	0.20	(C 2- N 4), C 2- N 6, N 4- C 8, (C 8- C 10), (N 6), C 10
31	0.18	(C 3- N 5), N 7- C 11, (C 9- C 11), C 3, N 5, (N 7)
32	0.18	(C 2- N 4), N 6- C 10, (C 8- C 10), C 2, N 4, (N 6)
33	0.14	(C 3- N 5), N 7- C 11, (C 9- C 11), N 5, (N 7), C 9
34	0.14	(C 2- N 4), N 6- C 10, (C 8- C 10), N 4, (N 6), C 8
35	0.13	(C 2- N 4), (C 3- N 5), C 3- N 7, N 4- C 8, (C 8- C 10), N 5, (N 7), C 10
36	0.13	(C 2- N 4), C 2- N 6, (C 3- N 5), N 5- C 9, (C 9- C 11), N 4, (N 6), C 11
37-50	0.00	
	100.00	* Total *

Table S5. Computed B3LYP-D3BJ/def2-SVP Cartesian atomic coordinates (in Å) and energies (in Hartree)

3 (E = -1792.15284854)

B	2.4783513885	12.7655804794	3.4394987701
N	3.145191299	14.0449208591	3.227290297
N	3.4796893326	11.9615707989	4.1051301958
P	0.8327284321	12.1576464925	2.7038673543
C	4.4592503439	13.9470973963	3.7061168692
C	2.7365000429	15.0403720268	2.2910257156
C	4.6539283096	12.7127930946	4.2361109378
C	3.3845737151	10.6122175298	4.5488656516
C	-0.1631453482	13.5931484602	3.0717582264
C	2.8584931469	14.7538189113	0.9111810444
C	2.1951068266	16.2658595092	2.7386036356
C	3.2239519226	10.3473494448	5.9244070321
C	3.4470383543	9.5664270846	3.5984184818
N	-1.0041546443	14.2423411828	2.2015663589
N	-0.421801984	14.1642381278	4.2982340859
C	3.5758478181	13.5045340077	0.4182255904
C	2.3726402896	15.6921288737	-0.008644909
C	1.7208287366	17.1740628638	1.7817720799
C	2.1876739799	16.6185450434	4.2185819658
C	3.1035922965	11.475711585	6.9378965186
C	3.1721636856	9.0112449804	6.3454754302
C	3.3792831089	8.2478667096	4.0642307473
C	3.6181601727	9.8726021398	2.1159386865
C	-1.0193719591	14.0201248072	0.7698028644
C	-1.7808623232	15.169966372	2.8752061923
C	0.1470561437	13.6831637399	5.5389586858
C	-1.4138564407	15.1239059169	4.1842277465
C	4.9804777326	13.8696679545	-0.0890656917
C	2.7820826598	12.7204463687	-0.6321678864
C	1.7943648577	16.8860253626	0.4194382174
C	3.5285479978	17.2496272196	4.6353356287
C	1.0369726906	17.5434010538	4.6311167273
C	1.8638382576	11.3192392475	7.8303231834
C	4.3791571224	11.6097397031	7.7836356442
C	3.2535347963	7.9689639164	5.4257915888
C	3.0065874081	8.8143395604	1.194285156
C	5.0962578703	10.1197775145	1.7715829401
H	5.1671435219	14.7663507796	3.6136975536
H	5.542897627	12.3015339886	4.7082735998
H	3.7077508576	12.838176254	1.2785924886
H	2.4551746859	15.4864028041	-1.0782594604
H	1.290709748	18.1231683952	2.1050351029
H	2.0864193495	15.6707003339	4.7672131553
H	2.9845509172	12.4084819044	6.3690814097
H	3.0566654069	8.7850906238	7.4080241186
H	3.4262256692	7.4222250231	3.352928569
H	3.078698148	10.8074741795	1.9138024473
H	-0.0120251076	13.7071372917	0.464637024
H	-1.2895545993	14.9560535207	0.2619060148
H	-1.7326320998	13.2278276233	0.4930106742
H	-2.5112590234	15.7920821311	2.3670079036
H	0.1997992555	12.584682658	5.488228065
H	-0.4863061086	14.0044388678	6.3765979266
H	1.1694726179	14.0596421234	5.6875983704
H	-1.7697500517	15.6916509948	5.0382672585
H	5.5330923599	12.9625692521	-0.3829219228
H	4.9295777972	14.5364616266	-0.9657126547
H	5.5614166347	14.3832743509	0.6922873052
H	3.3339260802	11.8115848858	-0.9216900502
H	1.8118831664	12.4070900916	-0.2194268033
H	2.6122776757	13.3066363707	-1.5502126023
H	1.4157064527	17.6046240812	-0.3120283318
H	3.5287241376	17.4879804113	5.7116641706
H	4.3747169357	16.5787329587	4.4396975164
H	3.701883032	18.1852099681	4.0789567091
H	0.9725024172	17.6025385488	5.7295175853
H	1.1922524281	18.5709206831	4.2644215235
H	0.0712936198	17.1913571203	4.2449253411
H	1.7312217578	12.2097019661	8.4665919236
H	0.9530788391	11.1860435607	7.2271373252
H	1.9485772098	10.4484962172	8.5000526514
H	5.2608727039	11.7857710268	7.149532866
H	4.2954607325	12.4511128679	8.4910459921
H	4.5644014708	10.693582773	8.3681213811
H	3.208338893	6.9320672902	5.7681751962
H	3.0383266888	9.1660182211	0.1511388831
H	3.5549100511	7.8588097715	1.2322958685
H	1.9549369528	8.6204204118	1.4542356046
H	5.2060520282	10.3855728547	0.7074274291
H	5.5149488356	10.942948854	2.3679647165
H	5.6989322457	9.2163879999	1.9622183922

Table S4. Continued

3^{Me} (E = -937.390033493)			
C	-1.5190279319	14.853577013	3.9279288475
N	-0.3756081227	14.0628678207	3.937486635
C	-0.1377861143	13.549468957	2.6746804207
N	-1.1740355251	14.0424126263	1.9031891311
C	-2.0189687999	14.8328526101	2.6662032666
P	1.0799330319	12.4208678979	2.0525638213
B	2.5360806778	12.8187094361	3.2281861919
N	3.3552014121	11.877124277	3.9539039439
C	3.2293315731	10.4409546675	4.0272778414
C	-1.3217370849	13.7605571264	0.4935825391
C	0.3233139313	13.6620513961	5.141570925
N	3.1253643523	14.1058303558	3.52924011
C	2.724795999	15.4097773012	3.0616293703
C	4.2015510026	13.9110045168	4.3945794063
C	4.3430211794	12.579295635	4.64031457
H	4.8042340981	14.7389279338	4.7648656618
H	5.0894099382	12.0775311722	5.2541733327
H	-0.3300763111	13.8076360149	0.0161482172
H	-1.9990946081	14.4997717938	0.0443462152
H	-1.7224788234	12.7473430023	0.3264064451
H	-2.892550284	15.3198354885	2.243089913
H	0.5377754073	12.5844680169	5.087392303
H	-0.3205176191	13.8680522337	6.0075553992
H	1.280445618	14.1882443426	5.2616629915
H	-1.8752031419	15.3594623852	4.8203894122
H	3.6036729352	16.037080658	2.8386080946
H	2.1341803894	15.2934922543	2.1416537573
H	2.1003567573	15.9508855601	3.7981641688
H	3.1836714117	10.0942366443	5.0749860687
H	2.3005724926	10.1398441846	3.5220107549
H	4.0742141593	9.9255746778	3.536565245

4^{Me} (E = -950.377864832)			
C	-1.4975453951	14.8916882721	3.9291939264
N	-0.4179246403	14.0277189395	4.03575407
C	-0.0923982293	13.536141893	2.8018318044
N	-0.9872975484	14.093000661	1.9346500158
C	-1.8610453754	14.9197359327	2.6181952588
P	1.0982888899	12.2641341934	2.3229053385
C	2.4885581367	12.7943422718	3.3481271312
N	3.3490056667	11.9260823432	3.9553199915
C	3.2046697664	10.4759704766	3.961677915
C	-1.0323801093	13.8337406429	0.5013269946
C	0.1848531161	13.6120580495	5.292053472
N	3.0065717613	14.0412199855	3.5653793993
C	2.4945015104	15.2757990143	2.992645229
C	4.1710715237	13.9443060681	4.3123073398
C	4.3912453983	12.6213300976	4.5422839319
H	4.7427757256	14.8192873832	4.6081952296
H	5.1953335606	12.1192157499	5.0726917811
H	-0.007278793	13.6829583291	0.1348737122
H	-1.4883047306	14.6942725888	-0.0042811053
H	-1.6209589399	12.9295712606	0.2856375466
H	-2.6612245273	15.4566643017	2.1167660587
H	0.3873252266	12.5329525032	5.2482558955
H	-0.5179285232	13.8199566853	6.1081905497
H	1.1277102327	14.1438503465	5.4854613344
H	-1.9156999819	15.4036664838	4.7911744584
H	3.3024975309	16.0172744775	2.9688889407
H	2.15020133	15.0755235089	1.9685813981
H	1.6551439751	15.677552661	3.5785364268
H	3.7123358881	10.0692758642	4.845352876
H	2.135148559	10.2251983745	3.9945982335
H	3.6427909956	10.0352486403	3.0537798456

5^{Me} (E = -924.253821079)			
C	-1.4911139016	14.9612171985	3.8983927017
N	-0.4498019237	14.0458121826	4.0244865732
B	-0.1769749672	13.4261873279	2.7201479474
N	-1.1817573809	14.0682384878	1.862329241
C	-1.9342151879	14.9694848932	2.6098893236
P	1.0584028412	12.0921957235	2.210335335
B	2.5320078304	12.6593819653	3.245956826
N	3.5100302115	11.8010174453	3.9274716931
C	3.4869347534	10.3692317785	4.0120902489
C	-1.3621503561	13.871585338	0.4528861143
C	0.1809886922	13.753771184	5.2820463465
N	3.0506660664	14.0029974837	3.5382022681
C	2.5405643539	15.2607394539	3.0664146616
C	4.1942461948	13.901471966	4.3256983683
C	4.4740074649	12.5872480311	4.5518884331
H	4.7432228618	14.7795003991	4.6683829076
H	5.2981515461	12.1573326381	5.1224438763
H	-0.5008963157	13.2936643007	0.0803489547
H	-1.4066210971	14.8340994762	-0.0955061334
H	-2.287222043	13.3095624206	0.208433274
H	-2.7375976967	15.5633839679	2.1723554439
H	0.6374499054	12.7541981254	5.2199813966
H	-0.5545660084	13.7627725724	6.1088390306
H	0.9905632089	14.4647176802	5.5385974623
H	-1.8570874832	15.5446732504	4.744197043
H	3.3640435162	15.9546911296	2.8114287678
H	1.9358994682	15.0766038997	2.1653990444
H	1.8834453596	15.7669223347	3.8002643574
H	3.6084095408	10.0157489123	5.0558579049
H	2.5101047865	10.0250982948	3.6353531304
H	4.2809077596	9.8861881388	3.4057424579

3^{Me} TS1 (θ(NHB) = 90°, E = -937.377203135)			
C	-2.660794	-0.232436	1.807482
N	-1.390039	-0.159998	1.244463
C	-1.480923	0.016089	-0.125916
N	-2.843680	0.048077	-0.373671
C	-3.561579	-0.103152	0.802504
P	-0.316136	0.186077	-1.446634
B	1.381221	0.070696	-0.552014
N	2.188781	-1.105303	-0.331996
C	1.879899	-2.480446	-0.645892
C	-3.401546	0.218687	-1.694122
C	-0.165775	-0.258356	2.010185
N	2.189573	1.153167	-0.043608
C	1.881570	2.563265	-0.001916
C	3.372540	0.626819	0.467292
C	3.372031	-0.725023	0.294736
H	4.144598	1.255222	0.908707
H	4.143575	-1.444729	0.564091
H	-3.061173	1.170580	-2.133549
H	-4.497444	0.210056	-1.625615
H	-3.061548	-0.590411	-2.361048
H	-4.647341	-0.105291	0.819303
H	0.442206	-1.111661	1.679416
H	-0.428723	-0.390764	3.067879
H	0.445079	0.648234	1.900405
H	-2.806677	-0.369769	2.874671
H	2.656366	3.162423	-0.510885
H	0.920748	2.725896	-0.510356
H	1.794902	2.933652	1.036209
H	1.791642	-3.099502	0.265921
H	0.919673	-2.509510	-1.179977
H	2.655073	-2.933330	-1.288034

Table S4. Continued

3^{Me} TS2 (θ(Imid) = 90°, E = -938.143193)			
C	-2.047816	13.275131	4.073787
N	-0.945442	14.085477	4.269844
C	-0.190123	14.164787	3.129268
N	-0.867027	13.400368	2.215681
C	-1.997853	12.843592	2.782251
P	1.271466	15.188911	2.840355
B	2.611440	13.913242	3.288683
N	2.589830	12.512243	3.682962
C	1.477122	11.618659	3.876079
C	-0.416126	13.171599	0.854496
C	-0.590514	14.721914	5.526054
N	4.021356	14.248775	3.269156
C	4.638276	15.499571	2.906791
C	4.760067	13.114912	3.605318
C	3.912561	12.084624	3.854966
H	5.847777	13.128093	3.655467
H	4.148592	11.066077	4.159373
H	-1.254333	13.304487	0.155533
H	-0.004322	12.155592	0.750346
H	0.380223	13.905521	0.656571
H	-2.671002	12.199232	2.224346
H	-0.252302	13.969700	6.255594
H	-1.456751	15.265622	5.929871
H	0.236333	15.414962	5.307491
H	-2.773005	13.079523	4.858298
H	5.011460	15.501177	1.865231
H	3.905024	16.314266	3.001389
H	5.488640	15.730956	3.571289
H	0.753849	12.007849	4.612020
H	0.920549	11.426744	2.941470
H	1.832093	10.646128	4.250374

4^{Me} TS (E = -951.147963)			
C	-1.784144	14.184346	4.006572
N	-0.417384	13.914829	3.953633
C	-0.045385	13.659133	2.660530
N	-1.192198	13.773578	1.921526
C	-2.262535	14.095650	2.741347
P	1.489391	13.244628	1.817141
C	2.672456	13.218540	3.216647
N	3.087096	12.123346	3.911567
C	2.509949	10.785747	3.809987
C	-1.255561	13.580659	0.482300
C	0.440353	13.916721	5.123627
N	3.489444	14.234074	3.611003
C	3.429825	15.609008	3.122592
C	4.384062	13.785327	4.558576
C	4.130793	12.456624	4.747770
H	5.128845	14.435411	5.009756
H	4.612961	11.729094	5.395141
H	-0.598814	14.301830	-0.028443
H	-2.288904	13.730446	0.147936
H	-0.931314	12.561822	0.219446
H	-3.266545	14.232398	2.350588
H	0.898342	12.931046	5.281629
H	-0.170373	14.158606	6.001677
H	1.232196	14.672516	5.034145
H	-2.286960	14.414035	4.941190
H	4.435636	15.935891	2.827067
H	2.758114	15.633132	2.255177
H	3.044612	16.273782	3.909841
H	1.949131	10.545137	4.725240
H	1.833446	10.771648	2.946083
H	3.313509	10.050734	3.669062

5^{Me} TS (E = -925.009747)			
C	-1.758802	14.230229	4.004725
N	-0.396803	13.941397	3.925153
B	-0.047990	13.606410	2.530991
N	-1.360951	13.685938	1.865098
C	-2.333088	14.077118	2.780722
P	1.547965	13.215806	1.616164
B	2.784040	13.168454	3.060407
N	3.206838	12.030197	3.877117
C	2.700240	10.687087	3.804226
C	-1.633012	13.490029	0.472211
C	0.476966	14.113039	5.053277
N	3.606141	14.251203	3.598828
C	3.570861	15.632080	3.202409
C	4.388346	13.776486	4.645094
C	4.151096	12.443320	4.811583
H	5.074786	14.417207	5.199783
H	4.603321	11.757912	5.529245
H	-0.797083	12.929546	0.025574
H	-1.732803	14.442643	-0.090739
H	-2.566406	12.913851	0.313703
H	-3.382459	14.188635	2.504138
H	1.278147	13.360916	5.042860
H	-0.084310	14.003606	5.999329
H	0.971563	15.105708	5.070694
H	-2.235340	14.498681	4.948716
H	4.575036	16.012988	2.929730
H	2.904090	15.703589	2.327781
H	3.168796	16.287382	4.001134
H	2.160050	10.391802	4.725826
H	1.994417	10.650835	2.958479
H	3.506390	9.945644	3.636095

3^{H} (E = -780.245147)			
P	-0.120099	1.669806	0.191117
B	1.373446	0.481486	0.098036
C	-1.390507	0.455022	0.074922
N	-1.338049	-0.905389	-0.131367
N	1.567970	-0.841889	0.670305
N	-2.743120	0.711740	0.134130
N	2.629400	0.726303	-0.561402
C	2.864493	-1.289613	0.386531
C	-2.608262	-1.458733	-0.222937
C	3.493292	-0.349817	-0.366054
C	-3.492884	-0.442712	-0.053572
H	-0.449025	-1.375551	-0.272408
H	1.023183	-1.272806	1.405223
H	2.888727	1.519954	-1.129973
H	-3.107120	1.645120	0.272657
H	3.241471	-2.251478	0.728173
H	-2.773508	-2.518591	-0.391120
H	4.495183	-0.381419	-0.789546
H	-4.578377	-0.443410	-0.042433

Table S4. Continued

4^H (E = -793.213973)			
P	0.000000	1.568406	-0.000000
C	1.353975	0.385802	0.006588
C	-1.353975	0.385802	-0.006588
N	1.471875	-0.865984	0.531390
N	-1.471875	-0.865984	-0.531390
N	2.598787	0.676709	-0.453236
N	-2.598787	0.676709	0.453236
C	2.774540	-1.336319	0.417686
C	-2.774540	-1.336319	-0.417686
C	3.486335	-0.358147	-0.202070
C	-3.486335	-0.358147	0.202070
H	0.738585	-1.312855	1.070505
H	-0.738585	-1.312855	-1.070505
H	2.822622	1.540729	-0.937968
H	-2.822622	1.540729	0.937968
H	3.074283	-2.315890	0.779007
H	-3.074283	-2.315890	-0.779007
H	4.531931	-0.315154	-0.492685
H	-4.531931	-0.315154	0.492685

5^H (E = -767.108306)			
P	0.000000	1.699554	0.000000
B	1.425242	0.469491	-0.041199
B	-1.425242	0.469491	0.041199
N	2.831572	0.738300	-0.368278
N	-2.831572	0.738300	0.368278
N	1.499220	-0.963689	0.289568
N	-1.499220	-0.963689	-0.289568
C	2.811333	-1.425595	0.208606
C	-2.811333	-1.425595	-0.208606
C	3.612107	-0.402512	-0.200415
C	-3.612107	-0.402512	0.200415
H	0.767519	-1.493780	0.741092
H	-0.767519	-1.493780	-0.741092
H	3.225384	1.616208	-0.671695
H	-3.225384	1.616208	0.671695
H	-4.683381	-0.424342	0.403581
H	4.683381	-0.424342	-0.403581
H	3.092737	-2.457690	0.421542
H	-3.092737	-2.457690	-0.421542

^{Me}Imid-PH (E = -646.948118)			
C	-1.743445	15.083698	3.834269
N	-0.811424	14.130842	4.238836
C	-0.165537	13.600077	3.139543
N	-0.724670	14.250691	2.057047
C	-1.688317	15.156682	2.481052
P	1.092540	12.378851	2.991875
H	1.186187	12.155938	4.398923
C	-0.325662	13.986433	0.696331
C	-0.545286	13.741350	5.601744
H	0.750065	14.192636	0.564924
H	-0.907117	14.621966	0.015813
H	-0.495310	12.925592	0.445676
H	-2.247610	15.771157	1.781892
H	-0.737707	12.665381	5.744192
H	-1.196879	14.316715	6.272388
H	0.507524	13.935620	5.864270
H	-2.360258	15.622550	4.547194

^{Me}Imid-PH TS (E = -646.928716)			
C	-1.783176	15.064481	3.851449
N	-0.804041	14.197889	4.293623
C	-0.092190	13.684738	3.241233
N	-0.654897	14.265660	2.135132
C	-1.689223	15.107176	2.491811
P	1.380438	12.608680	3.309299
H	0.562362	11.430849	3.216697
C	-0.225548	14.006049	0.771238
C	-0.564866	13.851965	5.684689
H	0.023236	14.951406	0.267033
H	-1.019911	13.487800	0.213132
H	0.666039	13.362019	0.847603
H	-2.266688	15.663994	1.759434
H	-1.426137	13.303483	6.095109
H	-0.391581	14.762980	6.276169
H	0.331465	13.210034	5.691460
H	-2.458187	15.576975	4.530859

$(MeNHB\text{-}PH)^-$ (E = -633.795426)			
C	-1.683226	15.078987	3.837626
N	-0.781243	14.118590	4.292488
B	-0.093261	13.495217	3.142072
N	-0.714291	14.208267	2.006374
C	-1.653362	15.121673	2.476473
P	1.178047	12.129855	3.012588
H	1.582856	12.184917	4.398172
C	-0.435221	14.002339	0.618503
C	-0.602833	13.810094	5.677792
H	0.576792	13.572739	0.523986
H	-0.467319	14.952679	0.048840
H	-1.139659	13.298592	0.123545
H	-2.234878	15.756291	1.805568
H	-0.198585	12.788370	5.762961
H	-1.561598	13.855420	6.232076
H	0.108570	14.489439	6.196792
H	-2.293693	15.672710	4.520114

$(MeNHB\text{-}PH)^-$ TS (E = -633.786960)			
C	-1.751408	15.054585	3.859984
N	-0.744620	14.230747	4.346945
B	0.000854	13.624986	3.235913
N	-0.686888	14.207976	2.076516
C	-1.716701	15.040896	2.495073
P	1.538041	12.490184	3.286415
H	0.743988	11.280272	3.278186
C	-0.376955	13.958231	0.696528
C	-0.505341	14.008882	5.745632
H	0.501496	13.287984	0.690180
H	-0.130374	14.888722	0.145493
H	-1.212398	13.465488	0.157993
H	-2.360428	15.576808	1.795746
H	0.371123	13.339096	5.810042
H	-1.367455	13.526917	6.250853
H	-0.286277	14.950317	6.289660
H	-2.429561	15.604089	4.514812

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