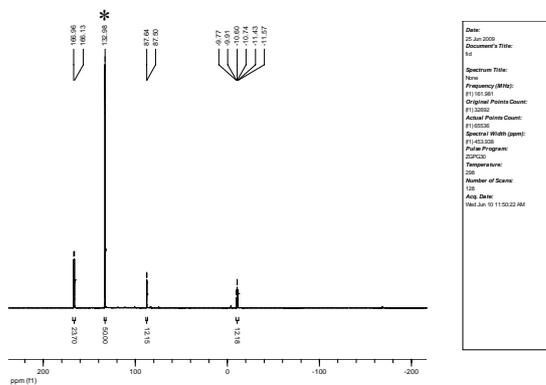


ESI

Selected NMR Spectroscopic Data

a)



b)

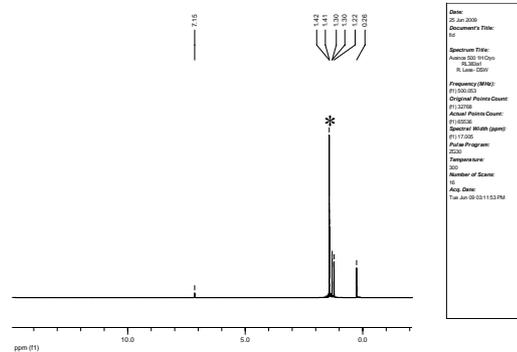


Fig. S1 a) *In situ*  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the reaction of  $[\text{CIP}(\mu\text{-N}^i\text{Bu})_2]$  with Mg after reflux (16h in THF) (using an internal  $d_6$ -acetone capillary to obtain the lock); b)  $^1\text{H}$  NMR spectrum of the same mixture (the resonances mark \* are those of  $1\alpha$ ).

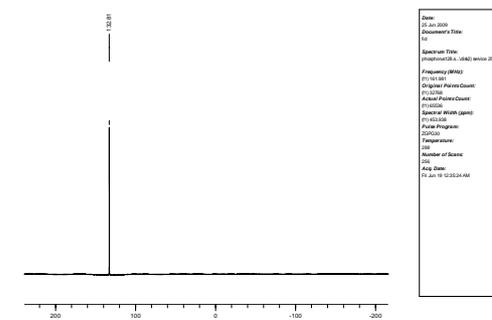


Fig. S2  $^{31}\text{P}\{^1\text{H}\}$ -NMR of isomer  $1\alpha$ .

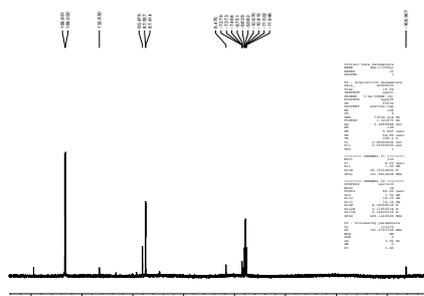


Fig. S3  $^{31}\text{P}\{^1\text{H}\}$ -NMR of  $1\alpha$  after irradiation with UV light (600W, 72h).

*Crystallographic data for 1β*, were collected on a Nonius Kappa CCD at  $T = 180(2)$  K using monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å),  $\text{C}_{16}\text{H}_{36}\text{N}_4\text{P}_4$ ,  $M_r = 408.37$ , monoclinic, spacegroup  $Cc$ ,  $a = 15.8849(2)$ ,  $b = 69.0550(10)$ ,  $c = 15.7466(3)$  Å,  $\beta = 106.4990(10)^\circ$ ,  $V = 16561.7(4)$  Å<sup>3</sup>,  $Z = 28$ ,  $\rho = 1.146$  g cm<sup>-3</sup>,  $2\theta_{\text{max}} = 45^\circ$ , data/parameter = 15249/1633,  $R1$  ( $I > 2\sigma(I)$ ) = 0.112,  $wR2$  (all data) = 0.315. The crystal structure was refined by full-matrix least squares against  $F^2$  using all data (SHELXTL, G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112-122). The crystal structure exhibits seven crystallographically unique molecules, all of which are disordered. Fig. S4 illustrates the disorder, which projects the entire molecule across a virtual (non-crystallographic) mirror plane that cuts through the centre of the molecule. The seven occupancy factors refined to 0.751, 0.731, 0.718, 0.698, 0.550, 0.534 and 0.519. were split on two positions and refined using one occupancy factor per independent molecule. The P atoms were refined with anisotropic displacement parameters, while the C and N atoms were refined isotropically. H-atoms were fixed as rigid methyl groups. The disorder was treated with the help of *similar U* and *similar distance restraints* (in accordance to the molecular  $C_s$  symmetry of **1**, P3 and P4 as well as the *t*BuN fragments of N3 and N4 were treated as topologically equivalent units). The high  $R$ -values reflect the extensive disorder (anisotropic refinement of C and N atoms brings the  $R1$  value to 0.095 but with a low data/parameter ratio and strong correlations of ADPs). The crystals diffracted only weakly, thus the data were truncated at  $2\theta = 45^\circ$ . The diffraction pattern did not exhibit additional reflections that would indicate twinning.

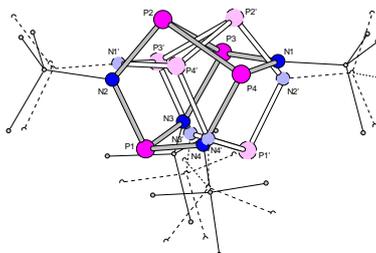


Fig. S4.

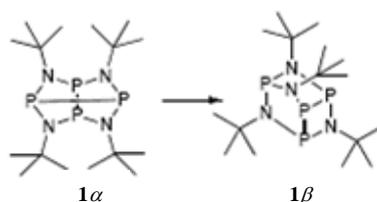
**Table S1** Selected bond lengths (Å)<sup>a</sup> and angles (°)<sup>a</sup> of **1β**:

	average	range
P2-P3	2.26	2.243(5) - 2.275(5)
P1-N2	1.71	1.696(8) - 1.725(8)
P2-N2	1.68	1.664(9) - 1.696(8)
P1-N3	1.74	1.723(9) - 1.750(9)
P3-N1	1.73	1.711(9) - 1.749(8)
P3-N3	1.71	1.692(8) - 1.723(9)
P3-P2-P4	76.0	75.8(2) - 76.2(2)

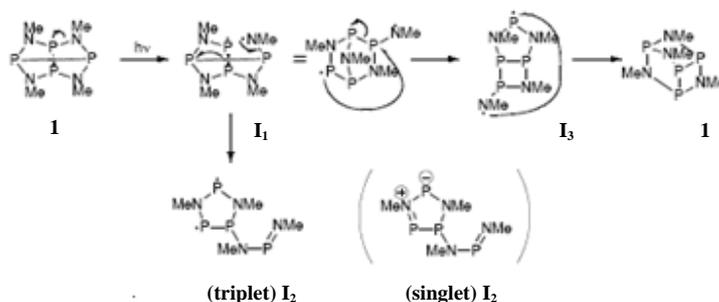
<sup>a</sup> These are based on average values of the major domains of four independent molecules, all of which show occupancy factors larger than 0.68 and the topological equivalence of P3, P4 and N3, N4, respectively. It should be added that, due to the extensive disorder, these values should be treated with some caution.

**DFT calculations:** The calculations were run using Jaguar [Jaguar 7.0 (Schrodinger LLC: New York, 2007)], the 6-31G\*\* basis set and B3LYP [Becke, A. D. *J. Chem. Phys.* 1993, 98, 5648–5652. Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* 1988, 37, 785–789.].

The reaction is thermodynamically favourable, with the product 20 kJ/mol lower in energy than the starting material. The analogues for which all the tertiary-butyl groups were replaced with methyl groups shows a similar preference, and so further calculations were run on these systems. The process resembles a type-I dyotropic rearrangement. The process may be thermally allowed for phosphorus, although it is not for first row elements. A photochemical dyotropic rearrangement may well be more favourable. However, the geometry looks impossible for the ring system here, and it has not been possible to locate transition states on this pathway.



A multi-step radical reaction seems more likely, beginning with a P-N bond cleavage. All of the P-N bonds are equivalent, so there is no selectivity at this stage. The initial diradical **I**<sub>2</sub> could rearrange to form a new diradical **I**<sub>3</sub> that could form **1β** after conversion to a singlet state. Structures corresponding to **I**<sub>1</sub> and **I**<sub>3</sub> were found as triplets. However, attempts to find similar structures as singlets were unsuccessful, as **I**<sub>3</sub>-like structures all collapsed to **1β** and **I**<sub>1</sub>-like structures all changed to **I**<sub>2</sub>, to a conformation with energy 127.67 kJ/mol relative to **1α**. The global minimum conformation of singlet **I**<sub>2</sub> is at 116.38 kJ/mol. This intermediate **I**<sub>2</sub> is the lowest energy of all the triplet states that were found as minima. The P-N bond is the highest occupied orbital which does not correspond to a phosphorus or nitrogen lone pair (MO 56; E=-0.284119).

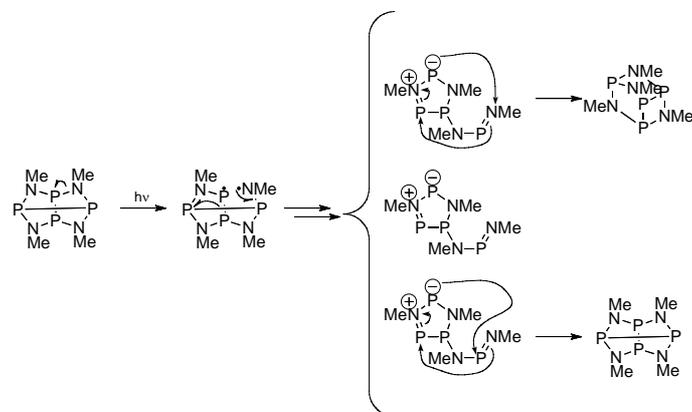


**Table S2**

	<b>I</b> <sub>1</sub>	<b>I</b> <sub>3</sub>	<b>I</b> <sub>2</sub>
singlet	127.67 (→ <b>I</b> <sub>2</sub> )	-21.15 (→ <b>1β</b> )	116.38
triplet	215.81	226.20	206.00

Energies in kJ/mol, relative to structure **1α**. A singlet state for a structure resembling **I**<sub>3</sub> could not be found, and all conformations became **1β** after minimisation.

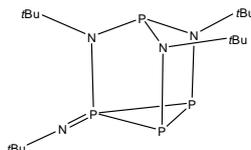
The singlet intermediate **I**<sub>2</sub> can do two different 3 + 2 cycloadditions between the P=N bond and the P=N-P system (below). One regiochemistry gives the starting material **3** and the other gives the product **1β**. Transition states have been found for both processes. The barrier to the reaction forming the product **1β** is 33.8 kJ/mol, and the barrier for the reverse process to the starting material **1α** is 38.2 kJ/mol.



<sup>31</sup>P NMR Chemical Shift calculations of **1α** and **1β**

Isomer	Experimental (ppm)	Calculated (ppm)
<b>1α</b>	132.9	155.0 (mean)
<b>1β</b>	-10, 87.5, 166.5 (1:1:2) <b>Relative to 1α<sub>(exp)</sub> 33.6, -45.4, -142.9</b>	40.5, 107.5, 186 (1:1:2) <b>Relative to 1α<sub>(calc)</sub> 31.0, -47.5, -115.0</b>

NB One of the referees noted that the NMR data could potentially be interpreted in terms of the structure shown below (bearing in mind the disorder present in the X-ray structure).



We calculate that this structure is at least 100 kJ mol<sup>-1</sup> higher in energy than that proposed by us for **1β** and that the chemical shifts for this species relative to **1α**(calc) = -177.8, -99.8, -280.4 (1:1:2, where the first resonance is that for the P<sup>V</sup> centre), i.e., inconsistent with the structure of **1α**.

See *Assigning the Stereochemistry of Pairs of Diastereoisomers Using GIAO NMR Shift Calculation*, S. G. Smith and J. M. Goodman *J. Org. Chem.* 2009, **74**, 4597, where it is shown using comparative values of chemical shifts (in the manner used in the above table) is a better method of assigning structures than using chemical shifts directly.