Reductive Rearrangement of a 1-Phospha-2-azanorbornene

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In memory of François Mathey

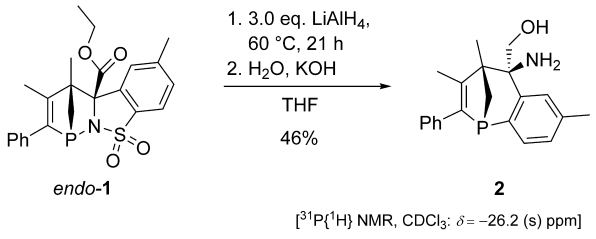
Abstract: The reduction of the 1-phospha-2-azanorbornene derivate *endo*-**1** with lithium aluminium hydride leads to an unprecedented 1-phosphabicyclo[3.2.1]octa-2,5-diene, while a phospholide anion is formed with lithium. The latter can be protonated resulting in formation of an unusual 2*H*-phosphole dimer. Furthermore, 3*H*-phospholes, previously assumed to have no synthetic relevance as intermediates, were proposed to act as dienophile in the dimerisation of 3,4-dimethyl-1-phenylphosphole at elevated temperatures based on theoretical calculations.

Introduction

Phospholes, five-membered unsaturated phosphorus heterocycles, exhibit properties of both pyrrols[1] and cyclopentadienes.[2] Tautomerisation in the phosphole ring can lead to a dramatic change in properties. Thus, poorly aromatic 1*H*-phospholes[3,4] form 2*H*-phospholes *in situ* by a [1,5]-sigmatropic shift;[2,5] the latter are powerful dienes and undergo Diels-Alder reactions with a variety of dienophiles resulting in 1-phosphanorbornenes or 1-phosphanorbornadienes.[2] Recently, we reported the first phospha-aza-Diels-Alder reaction between 2*H*-phospholes and an electron-poor *N*-sulfonyl-α-iminoester, resulting in 1-phospha-2-azanorbornenes (PANs).[6] The phosphorus-nitrogen bond in PANs is highly reactive, and we could already show that 2,3-dihydrophospholes can readily be obtained with nucleophiles by P–N bond cleavage.[6] In the present work, we have extended the synthetic potential of PANs further. With reducing agents, cleavage of the P–N bond also occurs, but the presence and reduction of additional functional groups results in unexpected rearrangements, depending on the reducing agent used. Thus, reduction of *endo*-5-phenyl-1-phospha-2-azanorbornene (*endo*-**1**) with $LiAlH_4$ results in formation of an unprecedented seven-membered phosphorus heterocycle, while a phospholide anion is formed with elemental lithium.

Results and Discussion

Only a few synthetic pathways to bridged seven-membered phosphorus heterocycles have been reported until now.[7–10] The reduction of *endo*-5-phenyl-1-phospha-2-azanorbornene (*endo*-**1**) with lithium aluminium hydride in THF at 60 °C, followed by aqueous work up, chemoselectively leads to 1-phosphabicyclo-[3.2.1]octa-2,5-diene **2** (Scheme 1, Figure 1).



Scheme 1. Synthesis of 1-phosphabicyclo[3.2.1]octa-2,5-diene **2**. All chiral compounds presented here are racemic mixtures. For clarity, always only one enantiomer of each compound is shown.

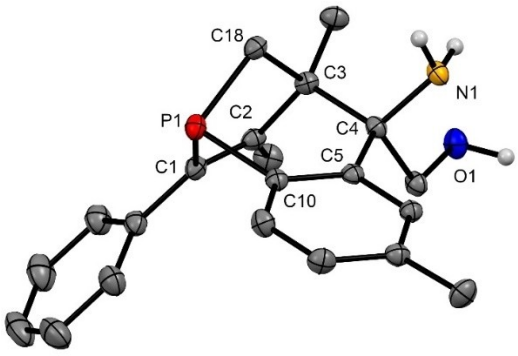


Figure 1. Molecular structure of **2**. Ellipsoids at 50% probability. Co-crystallised toluene and hydrogen atoms other than NH and OH have been omitted for clarity. Selected bond lengths [pm] and angles [°]: P1–C1 184.7(2), P1–C10 182.8(2), P1–C18 183.0(2), C1–C2 134.0(2), C3–C18 153.6(2), N1–C4 148.4(2); C1–P1–C10 100.10(7), C1–P1–C18 88.62(7), C10–P1–C18 94.05(7), P1–C18–C3 105.5(1), C10–C5–C4 124.7(1).

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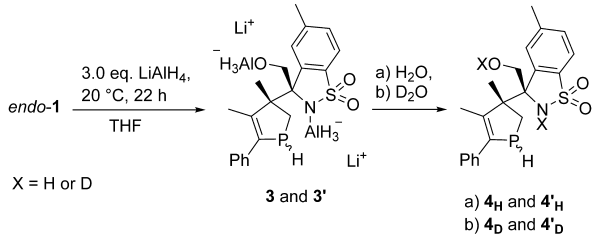
To probe the mechanism for formation of **2**, the reaction was conducted at room temperature to prevent a rapid further reduction of the intermediates. One part of the reaction mixture was quenched with H_2O, the other with D_2O, to trap the proposed intermediate 2,3-dihydrophospholes **3** or **3′** before full conversion to **2** was reached (Scheme 2). The ^{31}P NMR spectra of both hydrolysed mixtures are very similar and show a singlet at −26.2 ppm for the product **2** and two broad doublets at −50.5 (d, $^1J_{P-H}$ = 181.6 Hz) ppm ($\mathbf{4}_H$ and $\mathbf{4}_D$) and −55.2 (d, $^1J_{P-H}$ = approx. 170 Hz) ppm ($\mathbf{4'}_H$ and $\mathbf{4'}_D$).

This observation clearly indicates that $LiAlH_4$ and not H_2O (or D_2O) is the source of the hydrogen atom on phosphorus. High-resolution mass spectra (ESI, pos., THF) further corroborate the formation of $\mathbf{4}_H$ and $\mathbf{4'}_H$ (*m/z* calcd for $C_{21}H_{24}NO_3PS + {}^7Li^+$: 408.1369 $[M+{}^7Li]^+$, found: 408.1378 (H_2O)) and of $\mathbf{4}_D$ and $\mathbf{4'}_D$ (*m/z* calcd for $C_{21}H_{22}D_2NO_3PS + {}^7Li^+$: 410.1495 $[M+{}^7Li]^+$, found: 410.1490 (D_2O)), which could, however, not be isolated. Thus, the structural differences between **3** and **3′** or **4** and **4′** are unknown; presumably, diastereomers were formed resulting from different configurations at the phosphorus atom (*R* or *S*).

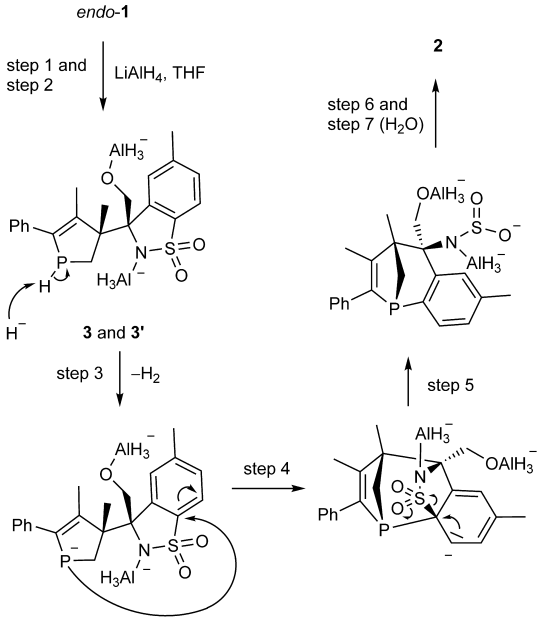


Scheme 2. Formation of the proposed intermediate 2,3-dihydrophospholes **3** and **3′**, and hydrolysis products **4** and **4′**.

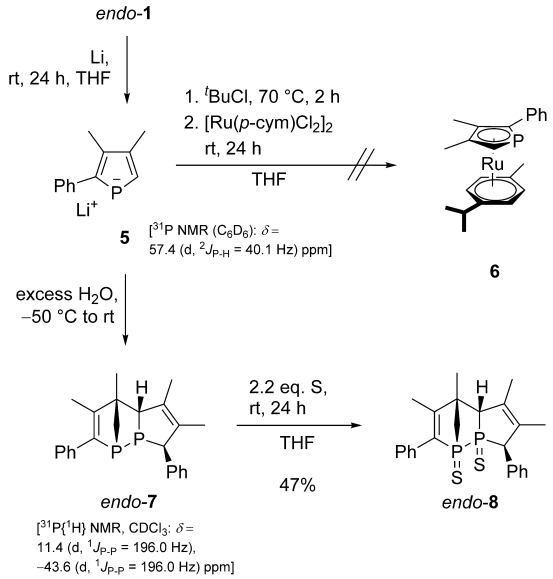
Reductive P–N bond cleavage reactions are known,[11] and we have already reported that PANs can be converted to 2,3-dihydrophospholes by reaction with nucleophiles.[6] A proposed mechanism for the formation of **2** is shown in Scheme 3. Apparently, the ester group has been reduced besides the expected cleavage of the P–N bond via nucleophilic attack of a hydride anion in the first two steps. The formation of the $P-C_{aryl}$ bond in **2** from **3**/**3′** can be rationalised as an intramolecular nucleophilic attack of a phosphanide moiety (steps 4 and 5), formed by deprotonation of the secondary 2,3-dihydrophosphole with $LiAlH_4$ (step 3), at the *ipso*-carbon atom bearing the sulfonyl group. Such nucleophilic aromatic substitutions at arylsulfonates with alkali metal phosphanides have been reported.[12] The leaving group is a formal amidosulfinate, which is further reduced by $LiAlH_4$ to the amino group and a sulfide anion (step 6). Finally, **2** is formed on work up with water (step 7). Alternative mechanisms, such as the "double reduction" of cyclic aromatic sulfonamides[13] under Birch conditions with a single electron transfer can be excluded.

A different product was formed in the reaction of *endo*-**1** with excess of lithium shavings as reducing agent in THF at room temperature, namely lithium phospholide **5** (Scheme 4), which could not be obtained as a pure compound. The mechanism of the reduction and the fate of the aryl sulfonamide group are unknown. The corresponding potassium salt had been reported by Mathey *et al.*,[14] but was synthesised by a completely different route. Mathey *et al.* successfully isolated the phospholide as the corresponding phospharuthenocene complex **6**;[15] however, this reaction failed with **5**. The reaction of **5** with excess oxygen-free water resulted in formation of the dimer *endo*-**7** as main product.

Sulfurisation of *endo*-**7** gave 2*H*-phosphole sulfide dimer *endo*-**8** (Scheme 4). Vapour diffusion of hexane into a dichloro-



Scheme 3. Proposed mechanism of the formation of **2** from *endo*-**1**. Counterions (Li^+) are omitted for clarity.



Scheme 4. Formation of lithium phospholide **5** followed by hydrolysis to give the dimer *endo*-**7** and formation of 2*H*-phosphole sulfide dimer *endo*-**8** by sulfurisation.

methane solution of *endo*-**8** gave colourless crystals suitable for X-ray crystallography. The molecular structure (Figure 2) allowed an indirect determination of the relative configuration of *endo*-**7**.

A possible mechanism for the formation of *endo*-**7** from **5** (Scheme 5) was supported by theoretical calculations (DSD-PBEP86-D3BJ/def2-TZVP;[16,17] solvent effects (THF) were included by C–PCM,[18] at 273 K).

Protonation of **5** results in 1*H*-phosphole **10**, which is in equilibrium with the 2*H*-phospholes **11** and **12**. The interconversion between **10**, **11** and **12** occurs via a [1,5]-sigmatropic proton shift. Such proton rearrangements have a low activation barrier (approx. 80 kJ·mol^{-1}) and are possible under the chosen reaction conditions, in contrast to [1,5]-sigmatropic phenyl shifts, which require higher temperatures.[2,5] The differences in relative Gibbs free energy of the intermediates are low; **10** (1.21 kJ·mol^{-1}) and **12** (0 kJ·mol^{-1}) have similar energies, while **11** (11.48 kJ·mol^{-1}) is less stable than **12**. This indicates that the formation of **11** (2*R*-2*H*-phosphole) from **10** is slightly less favoured than the formation of **12** (5*R*-2*H*-phosphole). At low temperatures (−50 °C to 0 °C), mainly **12** acts as diene and **11** as dienophile in the phospha-Diels-Alder reaction. The absence of *endo*-**9** (Scheme 5) as a product indicates that the dimerisation of **12** is not favoured, even though the concentration of **12** is probably higher than that of **11**. One possible reason could be the steric hindrance of the phenyl moiety, located at the geminal position of P2 in *endo*-**9** (see Supporting Information).

Beside the theoretical consideration, we were able to verify the formation of 1*H*-phosphole **10** by low temperature ^{31}P NMR spectroscopy in THF-*d*8 (Scheme 6). The solution which was obtained by reaction of *endo*-**1** with Li (Scheme 4) was treated with trifluoroacetic acid at −70 °C, and a ^{31}P NMR spectrum was measured at −60 °C. The chemical shift ($\delta = -50.9$ ppm) and the $^{1}J_{P-H}$ coupling constant ($^{1}J_{P-H} = 218.2$ Hz) are in the same range as comparable 1*H*-phospholes, reported by Mathey *et al.*[19] Other phosphorus-containing compounds were not observed. The further reactions of **10** (Scheme 5) require higher temperatures.

A different kind of dimerisation, which leads mainly to *exo*-**15**, was reported by Mathey *et al.* for 3,4-dimethyl-1-phenyl-phosphole (**13**) at elevated temperatures (>120 °C) (Scheme 7).[20] The same compound was formed when *endo*-**7** was heated to 140 °C. The formation of *exo*-**15** was explained by dimerisation of 2*H*-phosphole **12**,[20] which, based on our observations, seems less feasible. We have, therefore, repeated this reaction and were able to confirm the structure assigned to the proposed product *exo*-**15** (based on NMR spectroscopic data) via synthesis and X-ray structure analysis of its sulfurisation product, phosphole sulfide dimer *exo*-**16**, in which carbon

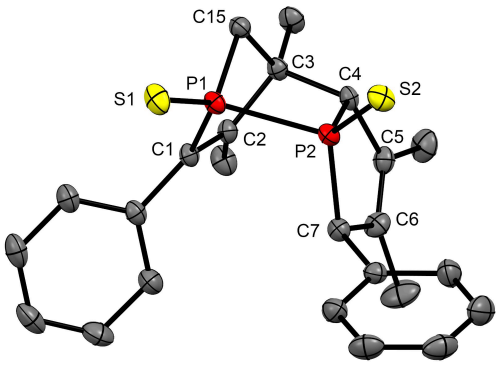
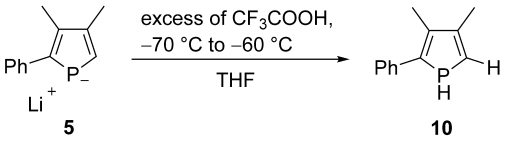
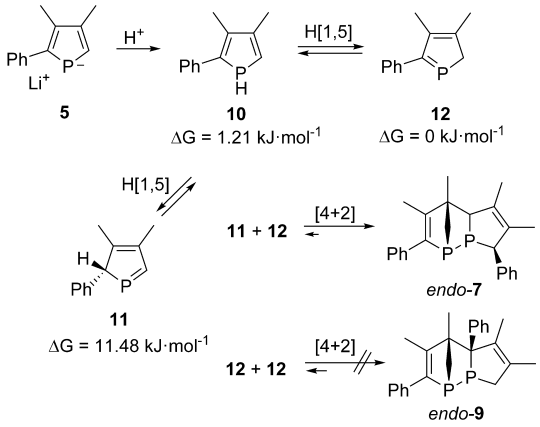


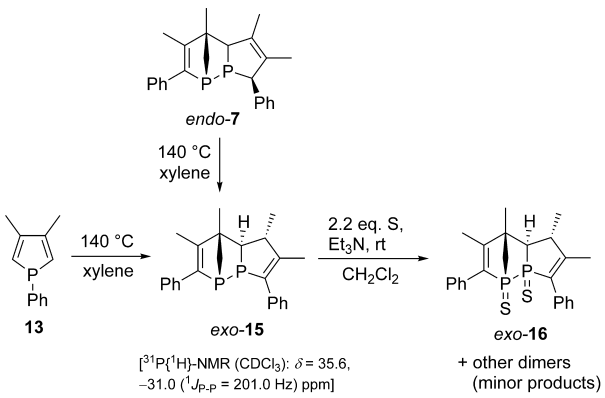
Figure 2. Molecular structure of *endo*-**8**. Ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: P1–P2 222.80(7), P1–C1 180.1(2), P1–C15 181.0(2), P2–C4 184.1(2), P2–C7 185.2(2), C1–C2 134.4(3), C5–C6 134.0(3); C1–P1–C15 92.44(9), C1–P1–P2 98.90(6), C15–P1–P2 89.43(7), P1–C15–C3 98.2(1).



Scheme 6. Protonation of phospholide anion **5** at −70 °C and verification of 1*H*-phosphole **10** by ^{31}P NMR spectroscopy at −60 °C.



Scheme 5. The fate of the phospholide anion in **5** after protonation (at 0 °C). The calculated relative Gibbs free energy of **10**, **11**, and **12** is given.



Scheme 7. Synthesis of *exo*-**15**[20] and conversion to phosphole sulfide dimer *exo*-**16**.

atom C5 is clearly sp^3-hybridised (Figure 3). Thus, it can be assumed that the formation of *exo*-**15** most likely can be explained by the intermediate occurrence of 3*H*-phosphole **14**, as was also corroborated by theoretical calculations (Scheme 8).

All thermochemistry calculations were carried out at 413 K, but otherwise using the same computational methods.[16,17] **12** is energetically slightly favoured over **14** (21.77 kJ·mol^{-1}). A graphic representation of the transition state (TS) for the interconversion of **12** and **14** is shown in the Supporting Information. The Gibbs free energy of activation ($\Delta G^{\neq}$) for the TS relative to **12** was estimated at 116.95 kJ·mol^{-1}. This value is in good agreement with previous results from Sastry *et al.* for related systems.[5] The activation energy for the [1,5]-sigmatropic proton shift [**12** (2*H*-phosphole) and **14** (3*H*-phosphole)] is in the order of magnitude of the [1,5]-sigmatropic phenyl shift between **13** (1*H*-phosphole) and **11** (2*H*-phosphole).[2] This also explains why the formation of **14** (and respectively *exo*-**15**) only occurs at higher temperatures and is not observed in the reaction shown in Scheme 5. Interestingly, so far it has been assumed that 3*H*-phospholes as intermediates have no synthetic relevance.[2] However, our studies indicate that the formation of **14** is possible under the given reaction conditions from a theoretical point of view.

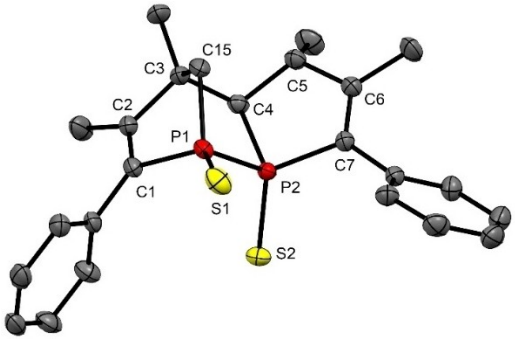
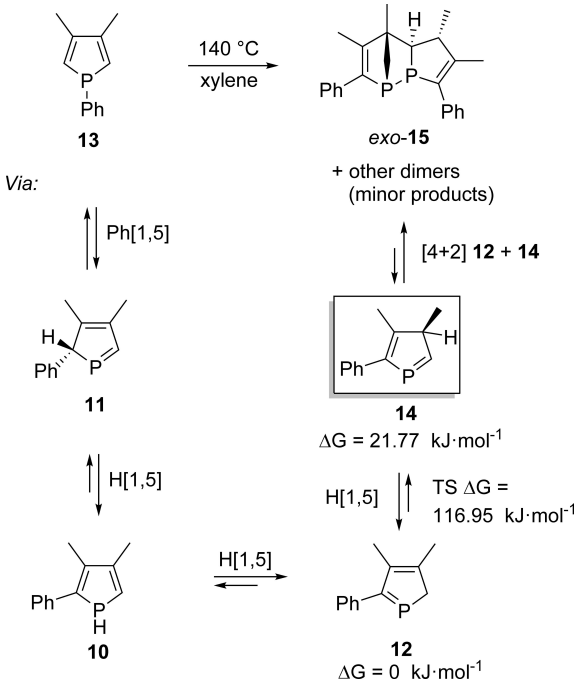


Figure 3. Molecular structure of *exo*-**16**. Ellipsoids at 50% probability. Hydrogen atoms and disordered CH_2Cl_2 molecules are omitted for clarity. Selected bond lengths [pm] and angles [°]: P1–P2 222.83(7), P1–C1 180.8(2), P1–C15 181.2(2), P2–C4 184.7(2), P2–C7 179.1(2), C1–C2 134.2(3), C4–C5 155.2(3), C5–C6 150.7(3), C6–C7 134.6(3); C1–P1–P2 93.37(7), C15–P1–P2 91.87(7).



Scheme 8. Proposed mechanism for the formation of *exo*-**15** involving 3*H*-phosphole **14**.

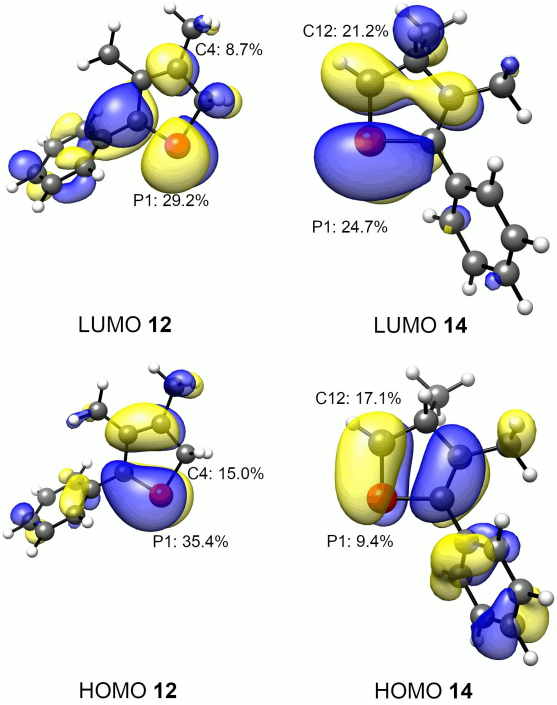


Figure 4. Frontier molecular orbitals of **12** (left) and **14** (right). The percentage of the largest contributions of p_z basis functions are also shown.

The chemoselectivity of the phospha-Diels-Alder reaction leading to *exo*-**15** can by explained with the frontier molecular orbital theory (Figure 4). The HOMO of **12** has π(P–C) and π(C–C) character, while the LUMO of **14** has mainly π*(P–C) character. The largest HOMO-LUMO overlap would arise between P1 of **12** and P1 of **14**, followed by C4 of **12** and C12 of **14**, thus enabling the formation of *exo*-**15**.

Conclusion

In summary, the reaction of *endo*-5-phenyl-1-phospha-2-azanorbornene (*endo*-**1**) with lithium aluminium hydride leads to 1-phosphabicyclo[3.2.1]octa-2,5-diene **2**, which is a rare example for a bridged 7-membered phosphorus heterocycle. With elemental lithium, lithium phospholide **5** is formed. Protonation of **5** at low temperature results in a phospha-Diels-Alder reaction, yielding the novel 2*H*-phosphole dimer *endo*-**7**, isolated as its sulfurisation product *endo*-**8**. The previously reported thermal dimerisation of 3,4-dimethyl-1-phenylphosphole (**13**) at high temperatures resulting in formation of the

dimer *exo*-**15** was rationalised as a [4 + 2] cycloaddition reaction between 2*H*-phosphole **12** and an intermediate 3*H*-phosphole **14** on the basis of theoretical calculations.

Experimental Section

General: All reactions were carried out under dry high purity nitrogen using standard Schlenk techniques. Experiments including elemental lithium were carried out under dry high purity argon. THF was degassed and distilled from potassium. Xylene (mixture of isomeres) was degassed and distilled from sodium. Diethyl ether, toluene, hexane (mixture of isomers) and dichloromethane were dried and degassed with a solvent purification system SPS-800 series from MBRAUN. The NMR spectra were recorded with a Bruker Avance DRX 400 spectrometer (^{1}H NMR 400.13 MHz, ^{13}C NMR 100.63 MHz, ^{31}P NMR 161.98 MHz) or a Bruker Ascend 400 spectrometer (^{1}H NMR 400.16 MHz, ^{13}C NMR 100.63 MHz, ^{31}P NMR 161.99 MHz). For ^{1}H NMR and ^{13}C NMR spectra, $SiMe_4$ (TMS) was used as internal standard. The ^{31}P NMR spectra were referenced to TMS using the Ξ scale.[21] Assignment of the configurations and chemical shifts was done using HSQC, HMQC, HMBC, COSY and NOESY techniques. High-resolution mass spectra (HRMS; ESI) were measured with a Bruker Daltonics Impact II ESI-TOF spectrometer. IR spectra were obtained with an FTIR spectrometer PerkinElmer Spektrum 2000 in the range of 400–4000 cm^{-1} in KBr. Elemental analyses were obtained with a Hereaus Vario EL oven. The melting points were determined in glass capillaries sealed under vacuum using a Gallenkamp apparatus and are uncorrected. $LiAlH_4$, lithium (under paraffin oil), deuterium oxide and sulfur (powder) are commercially available; *endo*-**1**[6] and phosphole **13**[22] were prepared according to literature procedures.

1-Phosphabicyclo[3.2.1]octa-2,5-diene (2): A solution of 2.95 g (6.7 mmol, 1.0 eq.) *endo*-**1** in 48 mL THF was added with stirring at 0 °C to 0.76 g (20.0 mmol, 3.0 eq.) lithium aluminium hydride (powder). The cooling bath was removed after 5 min and the supension stirred at 60 °C for 21 h. The reaction mixture was hydrolysed carefully at 0 °C by adding a solution of potassium hydroxide in degassed water (1.4 mL, 2 M). The slurry was heated to 60 °C for 15 min to convert the aluminium salts to a precipitate that could be removed by using a Schlenk frit. The solid was washed four times with 5 mL THF each. The solvent of the combined filtrates was removed under reduced pressure, and the obtained yellowish residue was dissolved in 4 mL boiling toluene. 12 mL *n*-octane was added and the mixture was stored over night at −20 °C. The formed crystals were separated from the mother liquor by using a filter cannula and washed two times with 7 mL hexane each. Solvent residues were removed at 60 °C under high vacuum. 1.04 g (3.1 mmol, 46 %) of **2** was obtained as dirty white crystals. Single crystals suitable for X-ray analysis were obtained by vapour diffusion of hexane into a solution of **2** in THF at room temperature. Mp: 158 °C. EA: calcd for $C_{21}H_{24}NOP$: C = 74.76, H = 7.17, N = 4.15; found: C = 74.47, H = 6.92, N = 4.17. HRMS (ESI, THF, pos. mode): *m/z* calcd for $C_{21}H_{24}NOP + H^+$: 338.1668 $[M+H]^+$; found: 338.1674. IR (KBr): $\tilde{\nu}$ = 3287 (m), 3148 (s), 3079 (m), 3052 (m), 3019 (m), 2990 (m), 2956 (s, νC–H), 2939 (m, νC–H), 2893 (m, νC–H), 2863 (s, νC–H), 1584 (s, νC=C), 1470 (s), 1441 (m), 1415 (m), 1378 (m), 1362 (m), 1088 (m), 1052 (s), 1036 (s), 929 (m), 913 (m), 756 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.52 (bs, 1H; Ar–H), 7.36–7.24 (m, 3H; Ar–H), 7.21–7.14 (m, 3H; Ar–H), 6.95 (d, $^{3}J_{H-H}$ = 7.5 Hz, 1H; Ar–H), 3.90–3.73 (m, 2H; CH_2), 2.63–2.56 (m, 1H; OH), 2.32 (s, 3H; CH_3), 2.19 (dd, $^{2}J_{H-H}$ = 13.1 Hz, $^{2}J_{H-P}$ = 6.4 Hz, 1H; PCH_2), 2.03 (dd, $^{2}J_{H-H}$ = 13.1 Hz, $^{2}J_{H-P}$ = 9.9 Hz, 1H; PCH_2), 1.91 (s, 3H; CH_3), 1.68 (bs, 2H; NH_2), 1.49 (s, 3H; CH_3) ppm. ^{13}C APT NMR ($CDCl_3$): δ = 150.3 (s; C = CCH_3), 145.4 (d, $^{2}J_{C-P}$ = 3.8 Hz; Ar–C), 144.0 (d, J_{C-P} = 11.0 Hz; Ar–C or C = CCH_3), 140.0 (s; Ar–C), 138.7 (d, J_{C-P} = 21.8 Hz; Ar–C or C=CCH_3), 134.1 (d, $^{2}J_{C-P}$ = 42.3 Hz; Ar–C), 133.0 (d, $^{1}J_{C-P}$ = 13.9 Hz; Ar–C), 130.1 (s; Ar–C), 128.5 (d, J_{C-P} = 6.8 Hz; Ar–C), 128.0 (s; Ar–C), 127.2 (d, $^{3}J_{C-P}$ = 13.5 Hz; Ar–C), 126.4 (d, J_{C-P} = 1.6 Hz; Ar–C), 68.5 (s; CH_2OH), 57.9 (d, J_{C-P} = 4.0 Hz; quart. C), 57.8 (s; quart. C), 39.6 (d, $^{1}J_{C-P}$ = 2.0 Hz; PCH_2C), 23.7 (d, $^{3}J_{C-P}$ = 2.9 Hz; CH_3), 21.7 (s; CH_3), 15.6 (d, $^{3}J_{C-P}$ = 1.9 Hz; CH_3) ppm. ^{31}P NMR ($CDCl_3$): δ = −26.1 to −26.3 (m) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −26.2 (s) ppm.

2*H*-Phosphole dimer (*endo*-7): 10 mL of a 0.092 molar solution (0.92 mmol, 2.0 eq.) of *endo*-**1** in THF and an excess of lithium shavings were stirred for 24 h at room temperature. The resulting dark brownish solution was separated from the solids with a filter cannula. The solution was then treated with 0.6 mL (33 mmol, 72 eq.) degassed water at −50 °C. The solvent was removed under reduced pressure. 5 mL water was added to the remaining solid. The mixture was extracted three times with 5 mL hexane each. The combined hexane phases were dried over $MgSO_4$. After filtration and removal of the solvent under reduced pressure, 162 mg of a yellowish solid were obtained. The solid contains *endo*-**7** and also other dimers. The content of *endo*-**7** (approx. 80 mol %) was determined by inverse gated proton decoupled ^{31}P NMR spectroscopy. HRMS (ESI, MeCN/DCM, pos. mode): *m/z* calcd for $C_{24}H_{26}P_2 + Na^+$: 399.1402 $[M+Na]^+$; found: 399.1417. ^{1}H NMR ($CDCl_3$): δ = 7.39–7.35 (m, 3H; Ar–H), 7.29–7.22 (m, 2H; Ar–H), 7.21–7.15 (m, 2H; Ar–H), 7.13–7.07 (m, 1H; Ar–H), 6.94–6.89 (m, 2H; Ar–H), 3.59 (s, 1H; Ar-CH), 3.09 (d, $^{2}J_{H-P}$ = 27.6 Hz, 1H; C_3CH), 1.95 (s, 3H; CH_3), 1.93 (s, 3H; CH_3) 1.67 (s, 3H; CH_3), 1.59–1.51 (m, 1H; PCH_2), 1.42–1.34 (m, 1H; PCH_2), 1.29 (s, 3H; CH_3) ppm. ^{31}P NMR ($CDCl_3$): δ = 11.4 (dt, $^{1}J_{P-P}$ = 196.0 Hz, $^{2}J_{P-H}$ = 27.6 Hz), −43.6 (dm, $^{1}J_{P-P}$ = 196.0 Hz) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$) δ = 11.4 (d, $^{1}J_{P-P}$ = 196.0 Hz), −43.6 (d, $^{1}J_{P-P}$ = 196.0 Hz) ppm.

2*H*-Phosphole Sulfide dimer (*endo*-8): A solution of 1.34 g (3.04 mmol, 2.0 eq.) *endo*-**1** in 40 mL THF and an excess of lithium shavings were stirred for 24 h at room temperature. The resulting dark brownish solution was separated from the solid with a filter cannula. The solution was then treated with 3.2 mL (178 mmol, 117 eq.) degassed water at −50 °C. The solvent was removed under reduced pressure. 40 mL water was added to the remaining solid. The mixture was extracted three times with 25 mL hexane each. The combined hexane phases were dried over $MgSO_4$. After filtration and removal of the solvent, 15 mL THF and 130 mg (4.05 mmol, 2.6 eq.) sulfur were added and the mixture was stirred for 24 h at rt. The solvent was removed under reduced pressure, and the resulting yellowish solid was dissolved in 10 mL dichloromethane. Vapour diffusion of hexane into the dichloromethane solution gave colourless crystals of *endo*-**8** suitable for X-ray analysis. Yield: 380 mg (0.86 mmol, 57 %). Mp: 159 °C. EA: calcd for $C_{24}H_{26}P_2S_2$: C = 65.43, H = 5.95; found: C = 63.82, H = 5.72. HRMS (ESI, MeCN/DCM, pos. mode): *m/z* calcd for $C_{24}H_{26}P_2S_2 + H^+$: 441.1024 $[M+H]^+$; found: 441.1048; calcd for $C_{24}H_{26}P_2S_2 + Na^+$: 463.0843 $[M+Na]^+$; found: 463.0884. IR (KBr): $\tilde{\nu}$ = 3437 (m), 2963 (m, νC–H), 1606 (m), 1489 (m, νC=C), 1073 (s), 805 (s), 775 (s), 699 (s), 665 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.55–7.39 (m, 5H; Ar–H), 7.33–7.21 (m, 3H; Ar–H), 6.96–6.91 (m, 2H; Ar–H), 4.19 (s, 1H; Ar-CH), 3.10 (d, $^{2}J_{H-P}$ = 11.3 Hz, 1H; C_3CH), 2.95 (dd, $^{2}J_{H-P}$ = 12.7 Hz, J = 4.4 Hz, 1H; PCH_2), 2.52 (dt, J = 18.9, 12.2 Hz, 1H; PCH_2), 2.03 (s, 3H; CH_3), 1.97 (t, J = 3.2 Hz, 3H; CH_3), 1.68 (t, J = 2.3 Hz, 3H; CH_3), 1.57 (s, 3H; CH_3) ppm. ^{13}C{^{1}H,^{31}P} NMR ($CDCl_3$): δ = 158.1 (C=CCH_3), 136.6 (C=CCH_3), 133.4 (C_2C=C), 133.2 (C_2C=C), 131.7 (Ar–C), 131.5 (Ar–C), 130.4 (Ar–C), 129.8 (Ar–C), 128.7 (Ar–C), 128.6 (Ar–C), 128.3 (Ar–C), 127.7 (Ar–C), 65.6 (C_3CH), 54.6 (Ph-CC_2H), 54.0 (PCH_2C), 50.3 (quart. C), 24.1 (CH_3), 18.7 (CH_3), 16.4 (CH_3), 16.0 (CH_3) ppm. ^{31}P NMR ($CDCl_3$): δ = 66.9 (dt, $^{1}J_{P-P}$ = 69.5 Hz, $^{2}J_{P-H}$ = 12.7 Hz), 47.2 (dd, $^{1}J_{P-P}$ = 69.5 Hz, $^{2}J_{P-H}$ = 10.3 Hz) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 66.9 (d, $^{1}J_{P-P}$ = 69.5 Hz), 47.2 (d, $^{1}J_{P-P}$ = 69.5 Hz,) ppm.

Phosphole Sulfide dimer (*exo*-16): A solution of 200 mg (1.06 mmol, 2.0 eq.) 3,4-dimethyl-1-phenylphosphole (**13**) in 4 mL xylene was stirred for 8 h at 140 °C. After removal of the solvent, 4 mL dichloromethane and 40 mg (1.25 mmol, 2.2 eq.) sulfur were added and the mixture was stirred for 24 h at rt. The solvent was removed under reduced pressure and the yellowish solid was dissolved in 2 mL dichloromethane. Vapour diffusion of hexane into the dichloromethane solution gave colourless crystals of *exo*-**16** suitable for X-ray analysis. Yield: 138 mg (0.31 mmol, 59%). The product contains small amounts of dichloromethane and two other unidentified phosphole sulfide dimers. EA: calcd for $C_{24}H_{26}P_2S_2$: C = 65.43, H = 5.95, found: C = 64.34, H = 5.67. HRMS (ESI, CH_3CN/DCM, pos. mode): *m/z* calcd for $C_{24}H_{26}P_2S_2 + H^+$: 441.1024 $[M+H]^+$; found: 441.1113; *m/z* calcd for $C_{24}H_{26}P_2S_2 + Na^+$: 463.0843 $[M+Na]^+$; found: 463.0935. IR (KBr): $\tilde{\nu}$ = 2963 (w, νC–H), 1489 (m, νC=C), 1452 (m), 1037 (m), 945 (m), 874 (m), 780 (m), 760 (m), 750 (m), 737 (m), 698 (s), 685 (s), 672 (s), 649 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.64–7.60 (m, 2H; Ar–H), 7.55–7.50 (m, 2H; Ar–H), 7.44–7.26 (m, 6H; Ar–H), 2.81–2.70 (m, 1H; C_3CH), 2.27–2.15 (m, 2H; PCH_2), 2.10–2.03 (m, 7H; C_3CH, CH_3), 1.50 (bs, 3H; CH_3), 1.44 (d, $^3J_{H-H}$ = 7.2 Hz, 3H; CH_3) ppm. ^{13}C APT NMR ($CDCl_3$): δ = 159.1 (dd, J_{C-P} = 25.8, 7.0 Hz; $C_2C=CCH_3$), 155.7 (dd, J_{C-P} = 18.5, 4.9 Hz; $C_2C=CCH_3$), 134.3 (dd, $^1J_{C-P}$ = 58.8, $^2J_{C-P}$ = 6.2 Hz; $C_2C=C$), 132.4 (dd, $^1J_{C-P}$ = 58.9, $^2J_{C-P}$ = 9.7 Hz; $C_2C=C$), 131.8 (d, J_{C-P} = 12.9 Hz; Ar–C), 131.2 (d, J_{C-P} = 9.3 Hz; Ar–C), 130.5–130.2 (m; Ar–C), 128.5–128.3 (m; Ar–C), 128.1–127.8 (m; Ar–C), 55.5 (dd, $^2J_{C-P}$ = 43.8, 11.2 Hz; quart. C), 48.3 (d, $^2J_{C-P}$ = 13.8 Hz; quart. C), 45.8–45.0 (m; PCH_2 and C_3CH), 23.1 (d, $^3J_{C-P}$ = 4.2 Hz; CH_3), 21.4 (dd, $^3J_{C-P}$ = 10.9, 5.6 Hz; CH_3), 17.9 (d, $^3J_{C-P}$ = 13.1 Hz; CH_3), 14.9 (d, $^3J_{C-P}$ = 12.8 Hz; CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 74.6 (d, $^1J_{P-P}$ = 50.5 Hz), 54.5 (d, $^1J_{P-P}$ = 50.5 Hz) ppm.

Verification of 1*H*-phosphole 10: Under an argon atmosphere, 50 mg (0.11 mmol) of PAN *endo*-**1** were dissolved in 2 mL of THF-*d*8 and an excess of lithium shavings was added. After stirring for three hours at room temperature, the dark brown solution was filtered off and 0.6 mL of this solution were transferred to an NMR tube. The NMR tube was cooled to −70 °C and 50 μL (0.65 mmol) of trifluoroacetic acid were slowly added dropwise and a slightly brown solution was obtained. After rapid homogenisation, the ^{31}P NMR spectrum was measured at −60 °C. ^{31}P NMR (THF-*d*8): δ = −50.9 (dd, $^1J_{P-H}$ = 218.2 Hz, $^2J_{P-H}$ = 40.0 Hz) ppm.

Crystallographic data: Deposition numbers 2027161, 2027162, and 2027163 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

The authors declare no conflict of interest.

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[1] G. Keglevich, Z. Böcskei, G. M. Keserü, K. Újszászy, L. D. Quin, *J. Am. Chem. Soc.* **1997**, *119*, 5095–5099.
[2] F. Mathey, *Acc. Chem. Res.* **2004**, *37*, 954–960.
[3] A. Dransfeld, L. Nyulászi, P. von Ragué Schleyer, *Inorg. Chem.* **1998**, *37*, 4413–4420.
[4] E. Mattmann, F. Mathey, A. Sevin, G. Frison, *J. Org. Chem.* **2002**, *67*, 1208–1213.
[5] T. C. Dinadayalane, K. Geetha, G. Narahari Sastry, *J. Phys. Chem. A* **2003**, *107*, 5479–5487.
[6] P. Wonneberger, N. König, F. B. Kraft, M. B. Sárosi, E. Hey-Hawkins, *Angew. Chem. Int. Ed.* **2019**, *58*, 3208–3211; *Angew. Chem.* **2019**, *131*, 3240–3244.
[7] J. E. MacDiarmid, L. D. Quin, *J. Org. Chem.* **1981**, *46*, 1451–1456.
[8] L. D. Quin, S. C. Spence, *Tetrahedron Lett.* **1982**, *23*, 2529–2532.
[9] D. G. Gilheany, B. J. Walker, *Phosphorus Sulfur Relat. Elem.* **1983**, *18*, 183–186.
[10] B. Krauss, C. Mügge, B. Ziemer, A. Zschunke, F. Krech, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1542–1552.
[11] F. Gol, G. Hasselkuß, P. C. Knüppel, O. Stelzer, *Z. Naturforsch.* **1988**, *43b*, 31–44.
[12] H. Zorn, H. Schindlbauer, H. Hagen, *Chem. Ber.* **1965**, *98*, 2431–2437.
[13] P. Evans, T. McCabe, B. S. Morgan, S. Reau, *Org. Lett.* **2005**, *7*, 43–46.
[14] S. Holand, M. Jeanjean, F. Mathey, *Angew. Chem. Int. Ed.* **1997**, *36*, 98–100; *Angew. Chem.* **1997**, *109*, 117–119.
[15] D. Carmichael, F. Mathey, L. Ricard, N. Seeboth, *Chem. Commun.* **2002**, 2976–2977.
[16] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
[17] S. Kozuch, J. M. L. Martin, *J. Comput. Chem.* **2013**, *34*, 2327–2344.
[18] V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995–2001.
[19] C. Charrier, H. Bonnard, G. de Lauzon, F. Mathey, *J. Am. Chem. Soc.* **1983**, *105*, 6871–6877.
[20] F. Mercier, F. Mathey, *J. Organomet. Chem.* **1984**, *263*, 55–66.
[21] R. K. Harris, E. D. Becker, S. M. Cabral De Menezes, R. Goodfellow, P. Granger, *Concepts Magn. Reson.* **2002**, *14*, 326–346.
[22] A. Breque, F. Mathey, P. Savignac, *Synthesis* **1981**, *1981*, 983–985.

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