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endo and *exo* Ring fusion in the Diels–Alder reaction of 1-(2,4,6-trialkylphenyl-)3-methylphospholes with maleic acid derivatives

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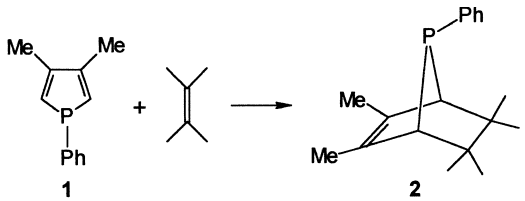
Abstract—Diels–Alder reaction of the title phospholes and *N*-phenylmaleimide afforded, surprisingly, a mixture of *endo* and *exo* fused cycloadducts with the P-aryl substituent *anti* to the double bond giving, after oxidation the corresponding P-oxides. The P-center of the *exo* ring fused P-oxides was found to be inverted under the conditions of the oxidation. The cycloaddition of triisopropylphenylphosphole with *N*-methylmaleimide or with maleic acid anhydride gave the corresponding *endo* fused phosphanorbornenes affording stable products after oxidation. Relative stability of the possible isomers was evaluated experimentally and by quantum chemical calculations.

1. Introduction

Phospholes, perhaps the most representative class of P-heterocycles, are of current interest.[1,2] Their application as P-ligands in transient metal complexes has been investigated, and their reactivity studied in detail.[3] Surprisingly, not much is known on the [π4s+π2s] cycloaddition of phospholes with dienophiles. Only the Diels–Alder reaction of 3,4-dimethyl-1-phenylphosphole (Mathey phosphole) with *N*-phenylmaleimide (NPMI)[4] and fumaronitrile[5] has been investigated resulting in the corresponding 7-phosphanorbornene with the phenyl substituent *anti* to the double bond (Scheme 1).



1 2

Scheme 1.

In stark contrast, the cycloaddition of phosphole oxides with a variety of dienophiles, including another molecule of the starting material, affords the 7-phosphanorbornene oxide with the P-substituent *syn* to the double bond.[6]

Recently, a special class of phospholes bearing a sterically demanding 2,4,6-trialkylphenyl substituent on the phosphorus atom has been introduced by us.[7,8] These phospholes have some aromatic character, due to the flattening of the P-pyramid allowing electron delocalization.[7,8] Hence, the arylphospholes undergo aromatic electrophilic substitutions,[9] and they also demonstrate dienic reactivity.[10] In this paper, the stereostructure of the arylphosphole–NPMI cycloadducts is evaluated by means of NMR spectroscopy and quantum chemical calculations.

2. Results and discussion

2,4,6-Triisopropylphenylphosphole **3a** and 2,4-di-*tert*-butyl-6-methylphenyl derivative **3b** available from earlier studies[7,8] were reacted with NPMI at 110°C. The ^{31}P NMR spectrum of the crude mixtures obtained after evaporation of the solvent revealed the presence of two components, one at around δ_P 73, while the other at ~δ_P 2. In the case of triisopropylphenyl substituent, the species with the downfield shift (δ_P 73) was the major component (90%), while with di-*tert*-butyl-methylphenyl substituent, the proportion

Keywords: phospholes; Diels–Alder reactions; stereochemistry; theoretical studies.

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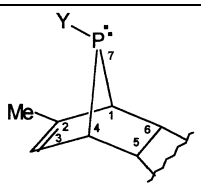
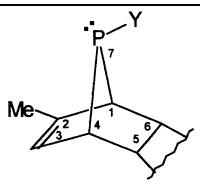
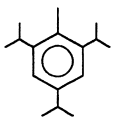
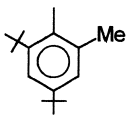
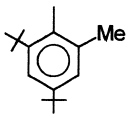
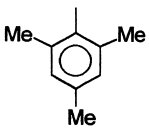
Table 1. Control of $^2J_{PC}$ by lone pair orientation in phosphanorbornene derivatives with phosphine function



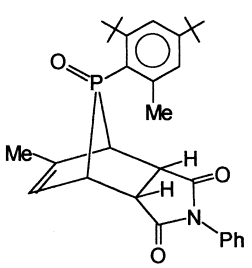


Y	$^2J_{PC}$[Hz] C_2	C_3	C_5	C_6	C_2	C_3	C_5	C_6	Ref./comp
Literature									
Me	4.9	*	*	28.3	20.5	*	*	3.9	11
Ph					26.4	23.0	3.8	3.3	12
Present cases									
					21.4	20.8	2.4	2.3	*anti-endo*-**4a**
					22.5	*	~2	~2	*anti-endo*-**4b**
					22.9	*	~2	~2	*anti-exo*-**6b**
					23.2	22.5	3.2	2.7	*anti-endo*-**4d**

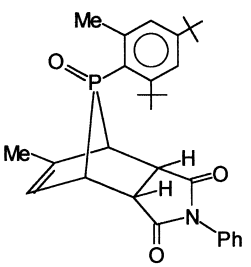
* —Not available.

of the two components was found to be comparable (42–58%). According to the stereospecific $^2J_{PC}$ couplings obtained from the ^{13}C NMR spectra of the crude mixtures, the configuration of the phosphorus atom must be the same in the two kinds of phosphanorbornenes (*anti-endo*-**4** and *anti-exo*-**6**). Extensive data support that the coupling is large when the lone pair is close and it is quite small when remote. This relationship is also valid for rigid bicyclic structures, such as phosphanorbornenes.[11] Based on analogies (Table 1),[11,12] the $^2J_{PC}$ couplings of 21–23 Hz measured on C_2 and C_3 of phosphines *anti-endo*-**4** and *anti-exo*-**6** together with the $^2J_{PC}$ values of ca. 2 Hz detected on C_5 and C_6 of the same compounds (*anti-endo*-**4** and *anti-exo*-**6**) suggested the *anti* relation of the aryl group to the double bond. The only difference between the stereostructure of the two species formed may be in the fusion of the five-membered hetero ring. The isomer at the downfield shift must have the five-membered ring in the usual *endo* fusion as represented in cycloadducts *anti-endo*-**4a** and *anti-endo*-**4b** (Scheme 2). In the other isomer with the unusual upfield shift (δ_P ~2), the rings may join in the *exo* fusion, as can been seen in structure *anti-exo*-**6** (Scheme 2). Phosphanorbornene with this kinds of stereostructure (e.g. *anti-exo*-**6** with *anti* P-substituent and with *exo* ring fusion) has only been observed once[13] and these kinds of species are probably of higher energy content than the *endo* fused counterparts (e.g. *anti-endo*-**4**). For this, it may be reasonable to assume that the less crowded *syn* form (*syn-exo*-**5**) is formed initially, giving the *anti* isomer (*anti-exo*-**6**) by inversion at the phosphorus atom. At the same time, the immediate formation of cycloadduct *anti-exo*-**6** cannot be excluded either. The selective formation of the cycloadducts (*anti-endo*-**4** and *anti-exo*-**6**) with *anti* P-aryl group to the double bond may be the consequence of secondary orbital interaction of the HOMO(diene) with the π system of the imide moiety of the dienophile.

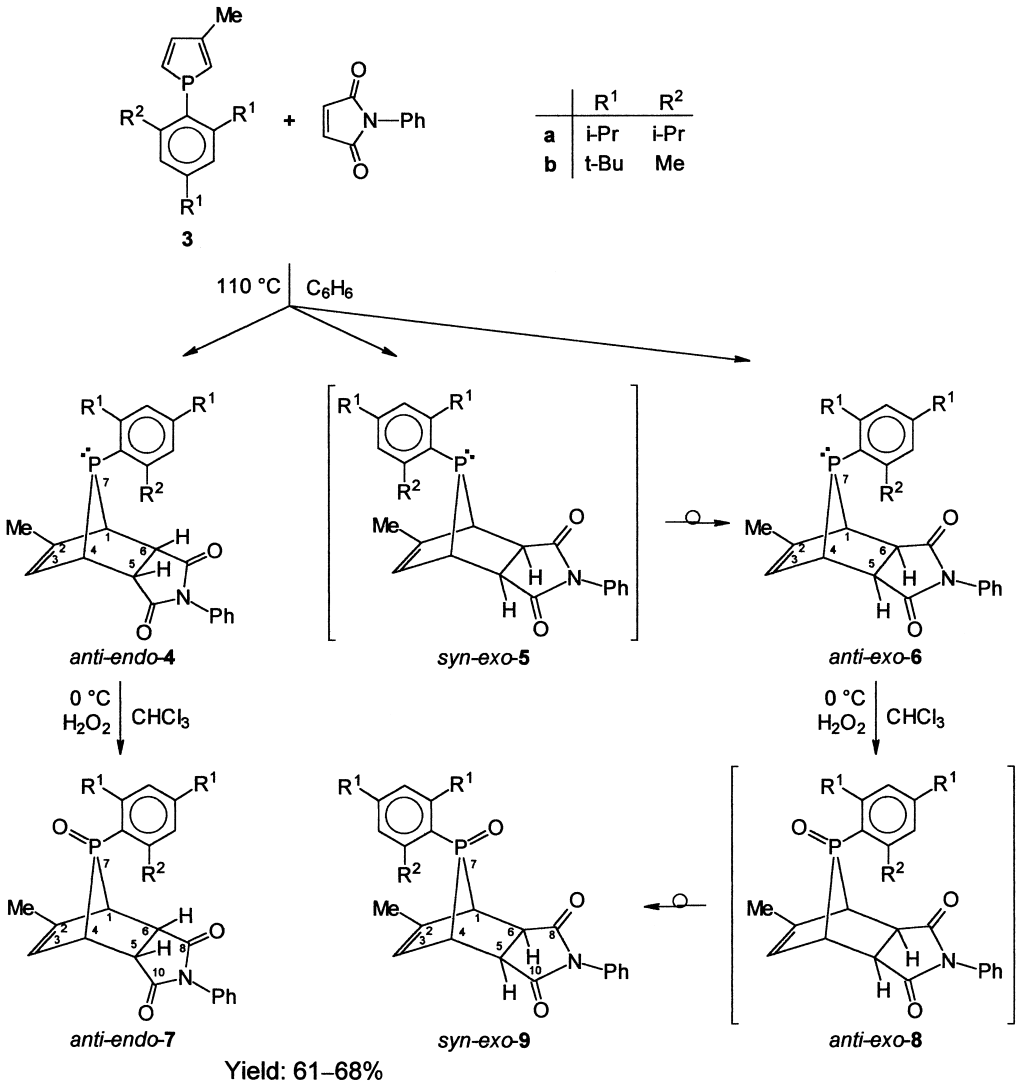
To obtain stable products, the phosphines (*anti-endo*-**4** and *anti-exo*-**6**) were converted to the corresponding phosphine oxides *anti-endo*-**7** and *anti-exo*-**8**, respectively. Isomer *anti-endo*-**7b** was formed as the mixture of two rotamers (*anti-endo*-**7b$_1$** and *anti-endo*-**7b$_2$**, Fig. 1) due to the two possible positions of the di-*tert*-butyl-methylphenyl ring. The stereospecific $^2J_{PC}$ couplings[11] obtained from the ^{13}C NMR spectra of the isomeric mixtures (purified by chromatography) suggested that the configuration of the phosphorus atom was different in the two 7-phosphanorbornene 7-oxides. In one form, ~2–5 and ~19–23 Hz was found for C_2/C_3 and C_5/C_6, respectively, while in the



7b$_1$



7b$_2$



Scheme 2.

other species, ~10 and ~15 Hz was detected for C_2/C_3 and C_5/C_6, respectively. Hence, it had to be assumed that *anti-exo*-**8** was only an intermediate to furnish epimer *syn-exo*-**9** by inversion at the P-center (Scheme 2).

On the basis of earlier examples,[12] the inversion may involve an intermediate with a pentavalent pentacoordinated phosphorus atom formed by the addition of water on the P=O group of compound *anti-exo*-**8**. The values of the stereospecific $^2J_{PC}$ couplings were in full agreement with structure *anti-endo*-**7** and *syn-exo*-**9** suggested (Table 2).[12] The orientation of the oxygen atom on the phosphorus controls the value of $^2J_{PC}$ in phosphanorbornenes.[11]

Regardless of the P-function, inversion at the phosphorus atom of *syn* phosphanorbornenes is not unprecedented.[12,14] We wished to test the stability of the *syn* P-aryl phosphanorbornenes. For this, the arylphosphole oxide–NPMI cycloadduct *syn-endo*-**10** prepared by our earlier procedure[9] was deoxygenated using only 0.5 equiv. of trichlorosilane at 26°C (to leave unreacted starting material in the reaction mixture as a reference) and then the reaction mixture was treated with 30% hydrogen peroxide at 0°C. ^{31}P NMR analysis of the mixture obtained by flash chromatography showed the presence of two P-oxides (at δ_P 90.1 (55%) and 90.3 (45%)) indicating that the *syn* phosphine (*syn-endo*-**11**) was converted to the *anti* isomer (*anti-endo*-**4a**) (Scheme 3). Only phosphine *anti-endo*-**4a** could be detected by ^{31}P NMR prior to the oxidation (δ_P 72.8).

While the Diels–Alder reaction of arylphospholes **3a** and **3b** afforded the corresponding cycloadducts as two isomers (*anti-endo*-**4a**/*anti-exo*-**6a** and *anti-endo*-**4b**/*anti-exo*-**6b**, respectively), the reaction of 1-(2,4,6-trimethylphenyl-) and 1-(2,4,6-tri-*tert*-butylphenyl)phospholes (**3c** and **3d**) with NPMI resulted in the phosphanorbornene as a single isomer, with *anti* aryl group to the double bond (*anti-endo*-**4c** and *anti-endo*-**4d**, respectively, Table 1). Oxidation of the phosphines (*anti-endo*-**4c** and *anti-endo*-**4d**) led to phosphine oxides *anti-endo*-**7c** and *anti-endo*-**7d**, respectively (Table 2, Scheme 4).

The reaction of phosphole **3a** with *N*-methylmaleimide (NMMI) or with maleic acid anhydride (MAA) also led to a single isomer (*anti-endo*-**12** or *anti-endo*-**14**, respectively) with an *anti* configuration (Scheme 4).

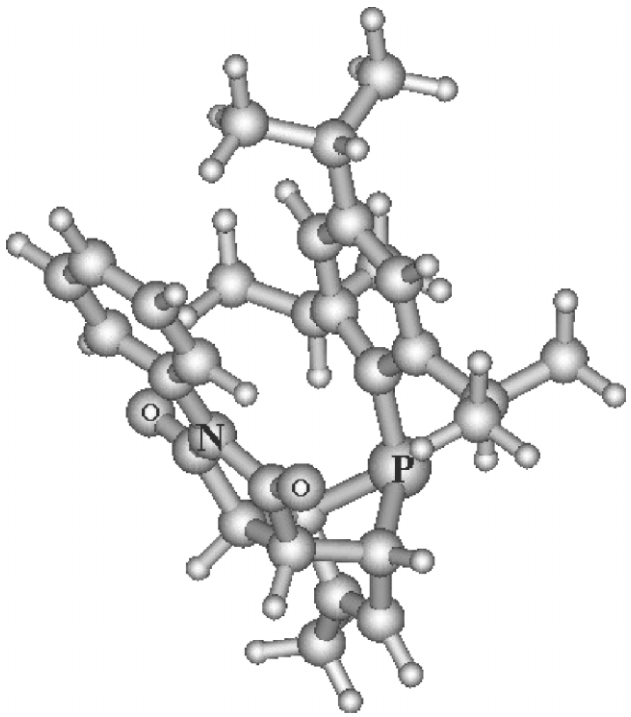


Figure 1. Stereostructure of phosphanorbornene *anti-exo*-**6a** obtained at the B3LYP/3-21G* level of theory.

It is noteworthy that the cycloaddition with MAA was rather reluctant to proceed at 100°C; a prolonged reaction time of 10 days was necessary to assure quantitative conversion. Elevation of the temperature to 130°C led to the formation of an unidentified by-product with δ_P 24.8 (after oxidation). The air-sensitive phosphines (*anti-endo*-**12** and *anti-endo*-**14**) were converted to the stable oxides (*anti-endo*-**13** and *anti-endo*-**15**, respectively) that were purified by column chromatography (Scheme 4).

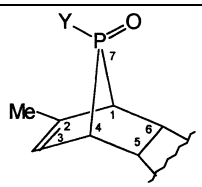
It is noted that above 110°C, the efficiency of the cycloadditions was somewhat decreased by the fragmentation involving the loss of the bridging P–Ar moiety. It is known that the phosphanorbornenes may lose the bridging P unit on heating to give a dihydrophosphindole and a reactive P-species that is polymerised under the conditions of the thermolysis.[15]

The phosphine oxide derivatives of the cycloadducts (*anti-endo*-**7**, *syn-exo*-**9** and *anti-endo*-**13**) proved to be stable on standing at room temperature. No *exo*→*endo* or *endo*→*exo* conversions could be observed.

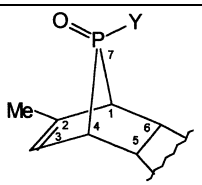
2.1. Computational studies

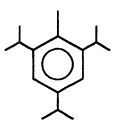
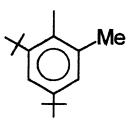
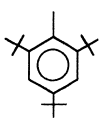
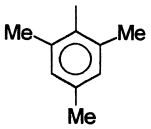
The stability of the possible arylphosphole–maleimide cycloadducts (**A**, **B**, **C** and **D**, Table 3) was characterised

Table 2. Control of $^2J_{PC}$ by the configuration of the P-function in phosphanorbornene 7-oxides

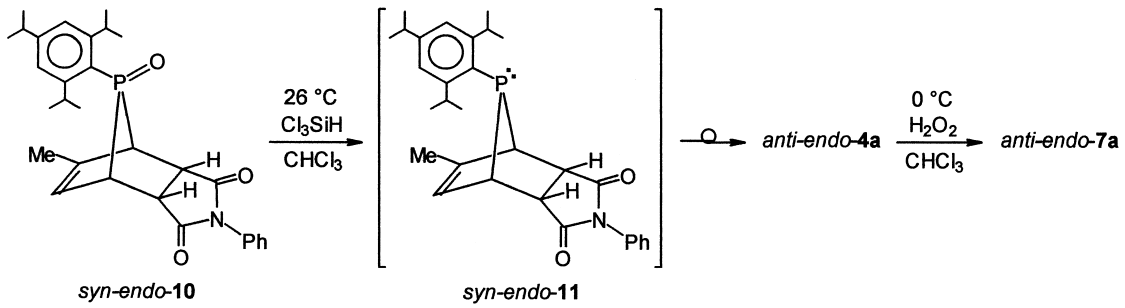


$^2J_{PC}$[Hz]



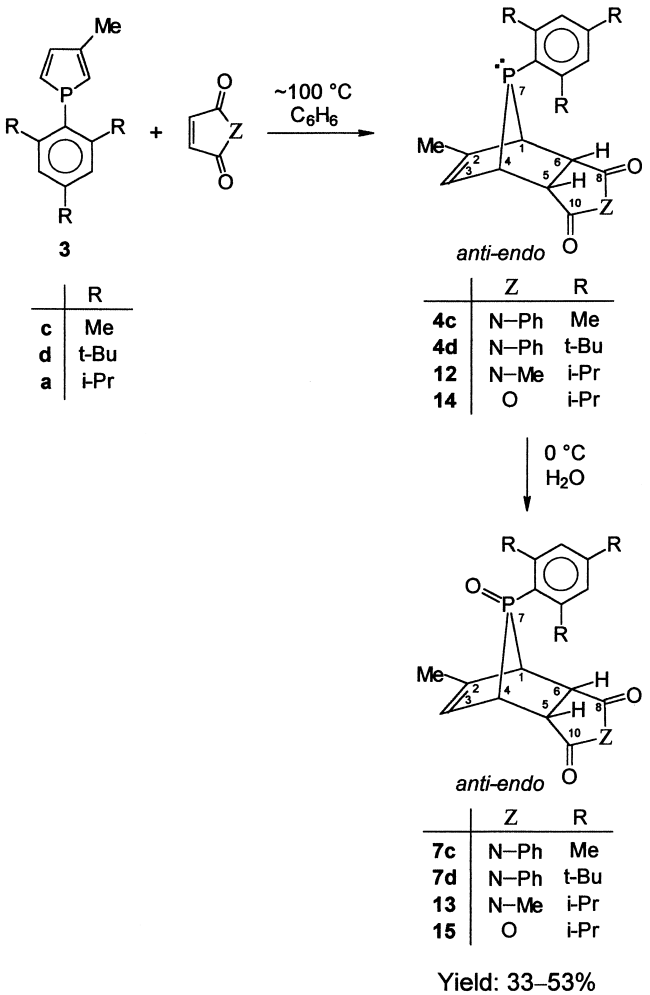
Y	C_2	C_3	C_5	C_6		C_2	C_3	C_5	C_6	Ref./comp
Literature										
Ph	12.1	8.4	10.4	13.2		4.4	4.3	16.5	13.2	12
Present cases										
						5.4	0	22.5	20.8	*anti-endo*-**7a**
	*	9.7	16.3	14.6	*syn-exo*-**9b**	2.0	0	21.9	19.0	*anti-endo*-**7b$_1$**
						6.5	3.5	20.8	19.2	*anti-endo*-**7d**
						4.9	0	22.9	21.0	*anti-endo*-**7c**

* —Not available.



Scheme 3.

by relative energies obtained by quantum chemical calculations including B3LYP/3-21G* and B3LYP/6-31+G* ab initio calculations.[16] In order to simplify the cycloadducts, the phenyl group at the nitrogen atom and the 4′-alkyl substituent of the P-aryl moiety were first neglected due to the length of time which would be required for the calculations. As it was suggested by the density functional calculations, the **A** form with *endo* ring fusion and with *anti* aryl substituent was found to be the most favourable species (0 kcal/mol on the relative scale) in all cases, while the *endo* fused *syn* isomer (**B**), as well as forms **C** and **D** with *exo* ring fusion proved to be somewhat unfavoured (0.7–5.8 kcal/mol). The relative stability of isomers **C** and **D** does not seem to be unambiguous on the basis of quantum chemical calculations. It turned out that species **C** is the preferred structure when using the small 3-21G* basis set, at the same time, the relative stability of **C** and **D** was switched with the increase in the basis to 6-31+G*, no matter if there is a skeletal methyl group or not (entries 1 and 2 vs entries 4 and 5, respectively). Changing the 2,6-diisopropylphenyl to a phenyl group caused the difference in the relative stability of isomers **C** and **D** to decrease (entries 4 and 3). Due to the significant steric compression between the *exo*cycle and the aryl group, the analogue of **C** with tri-*tert*-butylphenyl substituent becomes unfavourable by 8.7 kcal/mol as compared to **A** at the B3LYP/6-31+G*//B3LYP/3-21G* level. Experimentally, this isomer was not formed.



	R
c	Me
d	t-Bu
a	i-Pr

	Z	R
4c	N–Ph	Me
4d	N–Ph	t-Bu
12	N–Me	i-Pr
14	O	i-Pr

	Z	R
7c	N–Ph	Me
7d	N–Ph	t-Bu
13	N–Me	i-Pr
15	O	i-Pr

Scheme 4.

In agreement with the results of the B3LYP/3-21+G* calculations, the experimental data including our own experiences (e.g. the *syn-endo*-**11**→*anti-endo*-**4a** transformation) suggests that the phosphanorbornenes with *anti* aryl substituent to the double bond (e.g. *anti-exo*-**6**) are more stable than the corresponding *syn* isomer (e.g. *syn-exo*-**5**).[14] Hence, species *syn-exo*-**5** is possibly the result of kinetic control and may be an intermediate of phosphanorbornene *anti-exo*-**6**.

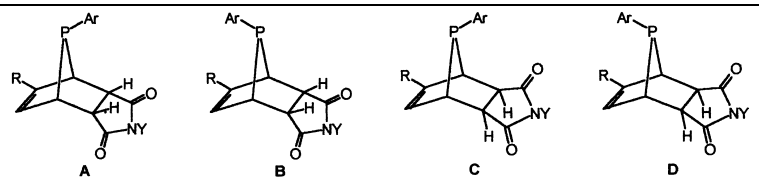
From the above data, it can be seen that the energy content of isomers *syn-exo*-**5a** and *anti-exo*-**6a** cannot be too far from each other. It may be assumed that cycloadduct *anti-exo*-**6** is formed immediately from phosphole **3** and NPMI, without the intermediacy of isomer *syn-exo*-**5**.

Especially noteworthy is the structure of *anti-exo*-**6a**, which is shown in Fig. 1. The most important B3LYP/3-21G* optimised structural data are compiled in Table 4. The two aryl rings (one at the phosphorus, the other at the nitrogen of the maleinimide unit) are nearly parallel forming a 3.5–4 Å diameter cavity, which seems suitable for the inclusion of some transition metals (Ni, Cr, Rh), provided that the phosphorus lone pair is blocked. The exploration of this possibility will be the subject of a subsequent study.

The special geometry of the *exo* fused cycloadducts (e.g. *anti-exo*-**6**) may be stabilised by a favourable interaction between the electron rich trialkylphenyl ring and the electron deficient imide π system.

It can be concluded that the [4+2] cycloaddition reaction of trialkylphenylphospholes (**3**) and NPMI gives an entry to phosphanorbornenes with unusual configuration at P and with both possible fusions of the other hetero ring to afford

Table 3. Relative energies of the possible phenylphosphole-maleimide cycloadducts (**A**–**D**) with respect to the most stable structure (0.0)



Ar	Y	R	Method	Relative energies (kcal/mol)				Entry
2,6-di $^{i}PrC_6H_3$	H	H	B3LYP/3-21G*	0	3.8	0.7	3.8	1
2,6-di $^{i}PrC_6H_3$	H	Me	B3LYP/3-21G*	0	–	2.0	5.3	2
Ph	H	H	B3LYP/6-31+G*	0	2.9	4.1	4.2	3
2,6-di $^{i}PrC_6H_3$	H	H	B3LYP/6-31+G*	0	2.7	5.7	3.9	4
2,6-di $^{i}PrC_6H_3$	H	Me	B3LYP/6-31+G*	0	4.3	5.8	4.6	5

Table 4. Selected geometrical parameters for *anti-exo*-**6a** obtained at the B3LYP/3-21G* level of theory

P–C_1	1.918 Å	C_1–P–C_4	77.7°
P–C_4	1.918 Å	P–C_1–C_6–C(O)	79.8°
C_1–C_2	1.542 Å	P–C_4–C_5–C(O)	78.9°
C_2–C_3	1.345 Å		
C_3–C_4	1.534 Å		
C_4–C_5	1.567 Å		
C_5–C_6	1.537 Å		

phosphines *anti-endo*-**4** and *anti-exo*-**6**. The cycloadducts with *exo* ring fusion (*anti-exo*-**6**) are of special importance, as they form a less studied class of P-heterocycles. After oxidation, the P-center of the *exo* fused isomer (*anti-exo*-**8**) was inverted to furnish product *syn-exo*-**9**.

3. Experimental

3.1. General

The ^{31}P, ^{13}C and ^{1}H NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 125.7 and 500 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4 or TMS. The couplings are given in Hertz. Mass spectrometry was performed on a ZAB-2SEQ instrument at 70 eV.

3.2. General procedure for the synthesis of the arylphosphole–NPMI cycloadducts

A solution of 0.45 g (1.50 mmol) of phosphole **3a**[8] or **3b**[7] and 0.26 g (1.50 mmol) of NPMI in 6 mL of benzene was degassed by nitrogen and placed into a tube. The sealed tube was kept at 110°C for 2 days. The solvent was evaporated to give the mixture of phosphines *anti-endo*-**4** and *anti-exo*-**6**, or phosphine *anti-endo*-**4** alone almost quantitatively, in a purity of ca. 95%. High sensitivity of the phosphines (*anti-endo*-**4** and *anti-exo*-**6**) toward air prevented further purification, they could, however, be purified as the P-oxides (*anti-endo*-**7** and *syn-exo*-**9**, respectively, see below).

The following compounds were thus synthesized.

3.2.1. 8-Methyl-4-phenyl-10-(2′,4′,6′-tri-*i*-propylphenyl-)-4-aza-10-phosphabicyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dion (*anti-endo*-4a and *anti-exo*-6a).[17] Yield: 0.71 g (~100%) airsensitive oil as a mixture of *anti-endo*-**4a** (90%) and *anti-exo*-**6a** (10%) isomers in a purity of 94%. MS, *m/z* (rel. int.) 473 (M^+, 44), 234 (P–Ar, 94), 43 (100); M^+ found 473.2464. $C_{30}H_{36}NO_2P$ requires 473.2484.

anti-endo-**4a**. δ_P 72.8 ($CDCl_3$); δ_C 47.4 (J=2.4 Hz, C_5),[a] 47.5 (J=15.1 Hz, C_4),[b] 48.7 (J=2.3 Hz, C_6),[a] 51.9 (J=16.8 Hz, C_1),[b] 124.9 (J=20.8 Hz, C_3), 144.0 (J=21.4 Hz, C_2), 175.7 (C_8),[c] 175.9 (C_{10}),[c] [a–c]may be reversed.

anti-exo-**6a**. δ_P 2.1 ($CDCl_3$)—minor component.

3.2.2. 8-Methyl-4-phenyl-10-(2′,4′-di-*tert*-butyl-6′-methylphenyl-)4-aza-10-phosphabicyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dion (*anti-endo*-4b and *anti-exo*-6b).[17] Yield: 0.70 g (~100%) airsensitive oil as a mixture of *anti-endo*-**4b** (42%) and *anti-exo*-**6b** (58%) isomers in a purity of 96%. MS, *m/z* (rel. int.) 473 (M^+, 4), 234 (P–Ar, 42), 57 (100); M^+ found 473.2468. $C_{30}H_{36}NO_2P$ requires 473.2484.

anti-endo-**4b**. δ_P 72.9 ($CDCl_3$); δ_C 46.9 (J~2 Hz, C_5),[a] 47.4 (J=18.1 Hz, C_4),[b] 48.3 (J~2 Hz, C_6),[a] 51.8 (J=19.5 Hz, C_1),[b] 144.2 (J=22.5 Hz, C_2), 175.9 (C_8),[c] 176.0 (C_{10}).[c]

anti-exo-**6b**. δ_P 2.2 ($CDCl_3$); δ_C 46.6 (J~2 Hz, C_5),[d] 48.0 (J~2 Hz, C_6),[g] 49.3 (J=15.3 Hz, C_4),[e] 53.8 (J=16.7 Hz, C_1),[e] 143.4 (J=22.9 Hz, C_2), 175.6 (C_8),[f] 175.7 (C_{10}),[f] [a–f]may be reversed.

3.2.3. 8-Methyl-4-phenyl-10-(2′,4′,6′-tri-*tert*-butylphenyl)-4-aza-10-phosphabicyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dion (*anti-endo*-4d).[17] The title compound was prepared using 0.51 g (1.50 mmol) of phosphole **3** as the starting material. Yield: 0.77 g (~100%) airsensitive oil in a purity of 94%. δ_P 72.2 ($CDCl_3$); δ_C 46.7 (J=3.2 Hz, C_5),[a] 48.0 (J=2.7 Hz, C_6),[a] 50.9 (J=18.9 Hz, C_4),[b] 55.3 (J=20.3 Hz, C_1),[b] 124.8 (J=22.5 Hz, C_3), 144.0 (J=23.2 Hz, C_2), 176.7 (C_8),[c] 177.0 (C_{10}),[c] [a–c] may be reversed; MS, *m/z* 516 $(M+H)^+$; $(M+H)^+$ found 516.2909. $C_{33}H_{43}NO_2P$ requires 516.3031.

3.3. General procedure for the oxidation of phosphines to phosphine oxides

The mixture of the phosphines (*anti-endo*-**4** and *anti-exo*-**6**) was dissolved in 25 mL of chloroform and 0.34 mL (3.0 mmol) of 30% hydrogen peroxide was added dropwise at 0°C. After stirring the contents of the flask for 1 h, the

organic phase was extracted with 3×12 mL of water and dried (Na_2SO_4). The crude product obtained after filtration and evaporation was purified by column chromatography (silica gel, 3% methanol in chloroform) to give the mixture of phosphine oxides *anti-endo*-**7** and *syn-exo*-**9**, or phosphine oxide *anti-endo*-**7** alone.

The following compounds were thus prepared.

3.3.1. 8-Methyl-4-phenyl-10-(2′,4′,6′-tri-*i*-propylphenyl)-4-aza-10-phosphabicyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dion 10-oxide (*anti-endo*-7a and *syn-exo*-9a).[17] Yield: 0.50 g (68%) thick oil as a mixture of *anti-endo*-**7a** (88%) and *syn-exo*-**9a** (12%) isomers; IR ν_{max} (film) 2960, 1716, 1334, 1192 cm^{-1}; MS, *m/z* (rel. int.) 489 (M^+, 40), 251 (P(O)Ar+H, 89), 43 (100); M^+ found 489.2411. $C_{30}H_{36}NO_3P$ requires 489.2433.

anti-endo-**7a**. δ_P 87.6 ($CDCl_3$); δ_C 19.4 (J=2.3 Hz, C_2–CH_3), 23.1 (J=5.0 Hz, $CH(CH_3)_2$), 23.2 ($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$), 32.4 (J=7.2 Hz, $CHMe_2$), 32.4 ($CHMe_2$), 34.2 ($CHMe_2$) 41.1 (J=20.8 Hz, C_6),[a] 42.5 (J=22.5 Hz, C_5),[a] 47.7 (J=64.7 Hz, C_4),[b] 51.2 (J=64.6 Hz, C_1),[b] 122.2 (C_3), 122.8 (J=10.8 Hz, $C_{3'}$),[c] 122.9 (J=11.3 Hz, $C_{5'}$),[c] 124.1 (J=80.8 Hz, $C_{1'}$), 126.3 ($C_{2''}$),[d] 129.1 ($C_{4''}$), 129.2 ($C_{3''}$)[d] 131.6 ($C_{1''}$), 141.7 (J=5.4 Hz, C_2), 152.0 (J=9.5 Hz, $C_{2'}$, $C_{6'}$), 153.7 ($C_{4'}$), 174.6 (J=14.9 Hz, C_8),[e] 175.0 (J=15.7 Hz, C_{10}),[e] [a–e]may be reversed; δ_H 1.26 (d, J=6.1 Hz, 6H, $CH(CH_3)_2$), 1.29 (d, J=7.0 Hz, 6H, $CH(CH_3)_2$), 1.54 (d, J=6.4 Hz, 6H, $CH(CH_3)_2$), 1.84 (s, C_2–CH_3), 5.89 (d, J=6.0 Hz, 1H, C_3-H).

syn-exo-**9a**. δ_P 85.6 ($CDCl_3$)—minor component.

3.3.2. 8-Methyl-4-phenyl-10-(2′,4′-di-*tert*-butyl-6′-methylphenyl-)4-aza-10-phosphabicyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dion 10-oxide (*anti-endo*-7b and *syn-exo*-9b).[17] Yield: 0.45 g (61%) thick oil as a mixture of *anti-endo*-**7b$_1$** (26%), *anti-endo*-**7b$_2$** (20%) and *syn-exo*-**9b** (54%) isomers; IR ν_{max} (film) 2968, 1712, 1334, 1192 cm^{-1}; MS, *m/z* (rel. int.) 489 (M^+, 6), 251 (P(O)Ar+H, 100), 57 (74); M^+ found 489.2401. $C_{30}H_{36}NO_3P$ requires 489.2433.

anti-endo-**7b$_1$**. δ_P 89.43 ($CDCl_3$); δ_C 19.4 (J=2.3 Hz, C_2–CH_3), 23.1 (J=6.5 Hz, CH_3), 31.0 ($C(CH_3)_3$), 33.3 ($C(CH_3)_3$), 34.7 (CMe_3), 38.2 (J=1.5 Hz, CMe_3), 40.0 (J=19.0 Hz, C_6),[a] 41.2 (J=21.9 Hz, C_5),[a] 47.8 (J=67.7 Hz, C_4),[b] 51.3 (J=68.3 Hz, C_1),[b] 122.0 (C_3), 141.3 (J=2.0 Hz, C_2), 174.6 (J=15.3 Hz, C_8),[c] 175.0 (J=14.5 Hz, C_{10});[c] δ_H 1.28 (s, 9H, $C(CH_3)_3$), 1.56 (s, 9H, $C(CH_3)_3$), 1.75 (s, 3H, C_2–CH_3), 2.0 (s, 3H, $C_{6'}$–CH_3), 5.80 (d, J=6.0 Hz, 1H, C_3-H).

anti-endo-**7b$_2$**. δ_P 89.19 ($CDCl_3$); δ_C 19.5 (J=2.0 Hz, C_2–CH_3), 23.1 (J=6.5 Hz, CH_3), 31.0 ($C(CH_3)_3$), 33.3 ($C(CH_3)$), 34.7 (CMe_3), 38.3 (J=1.5 Hz, CMe_3), 41.3 (J=20.7 Hz, C_6),[d] 42.6 (J=23.9 Hz, C_5),[d] 48.3 (J=63.4 Hz, C_4),[e] 51.7 (J=63.6 Hz, C_1),[e] 122.0 (C_3), 141.3 (J=2.0 Hz, C_2), 175.0 (J=15.8 Hz, C_8),[f] 175.4 (J=15.0 Hz, C_{10});[f] δ_H 1.28 (s, 9H, $C(CH_3)_3$), 1.55 (s, 9H, $C(CH_3)_3$), 1.75 (s, 3H, C_2–CH_3), 2.0 (s, 3H, $C_{6'}$–CH_3), 5.80 (d, J=6.0 Hz, 1H, C_3–H).

syn-exo-**9b**. δ_P 89.37 ($CDCl_3$); δ_C 18.8 (J=1.9 Hz, C_2–CH_3), 24.4 (J=7.5 Hz, CH_3), 30.9 ($C(CH_3)_3$), 32.9 ($C(CH_3)_3$), 34.6 (CMe_3), 37.6 (J=1.5 Hz, CMe_3), 43.3 (J=14.6 Hz, C_6),[g] 44.5 (J=16.3 Hz, C_5),[g] 49.4 (J=63.7 Hz, C_4),[h] 50.9 (J=66.6 Hz, C_1),[h] 120.4 (J=9.7 Hz, C_3), 121.2 (J=91.7 Hz, $C_{1'}$), 123.2 (J=11.8 Hz, $C_{3'}$),[i] 125.5 (J=10.6 Hz, $C_{5'}$),[i] 126.4 ($C_{2''}$),[j] 129.1 ($C_{3''}$),[j] 129.1 ($C_{4''}$), 131.7 ($C_{1''}$), 140.8 (J=10.5 Hz, $C_{6'}$), 141.6 (J=9.2 Hz, C_2), 153.4 (J=1.7 Hz, $C_{4'}$), 155.4 (J=7.4 Hz, $C_{2'}$), 175.6 (J=14.0 Hz, C_8),[k] 176.0 (J=11.8 Hz, C_{10});[k] δ_H 1.24 (s, 9H, $C(CH_3)_3$), 1.47 (s, 9H, $C(CH_3)_3$), 1.75 (s, 3H, C_2–CH_3), 2.0 (s, 3H, $C_{6'}$–CH_3), 5.80 (d, J=6.0 Hz, 1H, C_3–H), [a–k]may be reversed.

3.3.3. 8-Methyl-4-phenyl-10-(2′,4′,6′-tri-*tert*-butylphenyl)-4-aza-10-phosphabicyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dion 10-oxide (*anti-endo*-7d).[17] Yield: 0.34 g (43%) thick oil; δ_P 86.0 ($CDCl_3$); δ_C 19.5 (J=2.1 Hz, C_2–Me), 31.0 ($C(CH_3)_3$), 33.3 (J=7.8 Hz, $C(CH_3)_3$), 34.7 (CMe_3), 39.8 (J=2.8 Hz, CMe_3), 40.5 (J=19.2 Hz, C_6),[a] 41.8 (J=20.8 Hz, C_5),[a] 49.3 (J=67.9 Hz, C_4),[b] 52.7 (J=67.7 Hz, C_1),[b] 120.7 (J=83.2 Hz, $C_{1'}$), 123.0 (J=3.5 Hz, C_3), 124.6 (J=11.0 Hz, $C_{3'}$),[c] 124.7 (J=11.2 Hz, $C_{5'}$),[c] 126.2 ($C_{2''}$),[d] 129.0 ($C_{3''}$),[d] 142.5 (J=6.5 Hz, C_2), 153.7 (J=2.6 Hz, $C_{4'}$), 156.6 (J=9.1 Hz, $C_{2'}$),[e] 156.7 (J=9.1 Hz, $C_{6'}$),[e] 174.9 (J=14.3 Hz, C_8),[f] 175.3 (J=15.6 Hz, C_{10}),[f] [a–f]may be reversed; δ_H 1.35 (s, 9H, $C(CH_3)_3$), 1.58 (s, 18H, $C(CH_3)_3$), 1.85 (s, 3H, C_2–CH_3), 6.14 (d, J=5.5 Hz, 1H, C_3–H); MS, *m/z* 532 $(M+H)^+$; $(M+H)^+$ found 532.2849. $C_{33}H_{43}NO_3P$ requires 532.2981.

3.3.4. 8-Methyl-4-phenyl-10-(2′,4′,6′-trimethylphenyl-)4-aza-10-phosphabicyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dion 10-oxide (*anti-endo*-7c).[17] The title compound was prepared from phosphine *anti-endo*-**4c** (δ_P 69.9 ($CDCl_3$); $(M+H)^+$ found 390.1538 $C_{24}H_{25}NO_2P$ requires 390.1623) obtained from phosphole **3c** and NPMI according to the general procedure. Yield: 0.33 g (52%) thick oil; IR ν_{max} (film) 2968, 1708, 1376, 1200 cm^{-1}; δ_P 88.8 ($CDCl_3$); δ_C 19.3 (J=2.5 Hz, C_2-Me), 21.0 (Me), 21.1 (Me), 21.8 (J=11.2 Hz, Me), 40.6 (J=21.0 Hz, C_6),[a] 42.0 (J=22.9 Hz, C_5),[a] 46.5 (J=64.4 Hz, C_4),[b] 50.0 (J=64.5 Hz, C_1),[b] 122.1 (C_3), 126.3 ($C_{2''}$),[c] 129.0 ($C_{4''}$), 129.1 ($C_{3''}$),[c] 130.4 (J=9.8 Hz, $C_{3'}$),[d] 130.5 (J=9.9 Hz, $C_{5'}$),[d] 131.6 ($C_{1''}$), 140.2 (J=9.6 Hz, $C_{2'}$),[e] 140.3 (J=10.0 Hz, $C_{6'}$),[e] 141.4 (J=4.9 Hz, C_2), 142.6 ($C_{4'}$), 174.7 (J=15.7 Hz, C_8),[f] 175.1 (J=16.0 Hz, C_{10}),[f] [a–f]may be reversed; δ_H 1.77 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 6.17 (d, J=5.8 Hz, 1H, C_3–H); MS, *m/z* 406 $(M+H)^+$; $(M+H)^+$ found 406.1503. $C_{24}H_{25}NO_3P$ requires 406.1572.

3.3.5. 8,4-Dimethyl-10-(2′,4′,6′-tri-*i*-propylphenyl-)4-aza-10-phosphabicyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dion 10-oxide (*anti-endo*-13). The title compound was prepared from phosphine *anti-endo*-**12** (δ_P 73.7 ($CDCl_3$); δ_C 18.5 (C_2–CH_3), 46.8 (J=15.1 Hz, C_4),[a] 47.6 (J=3.0 Hz, C_5),[b] 48.7 (J=2.3 Hz, C_6),[b] 51.3 (J=16.6 Hz, C_1),[a] 124.6 (J=20.7 Hz, C_3), 143.9 (J=21.7 Hz, C_2), 176.6 (C_8),[c] 176.8 (C_{10}),[c] [a–c]may be reversed; $(M+H)^+$ found 412.2315, $C_{25}H_{35}NO_2P$ requires 412.2405) obtained from phosphole **3a** and NMMI according to the general procedure. Yield: 0.34 g (53%) thick oil; IR ν_{max} (film) 2967, 1704, 1350, 1196 cm^{-1}; δ_P 88.0 ($CDCl_3$); δ_C 19.2 (C_2–CH_3), 23.0 (J=4.7 Hz, $CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$),

32.3 (J=7.3 Hz, $CHMe_2$), 34.2 ($CHMe_2$), 41.2 (J=21.3 Hz, C_6),[a] 42.3 (J=23.8 Hz, C_5),[a] 47.2 (J=66.0 Hz, C_4),[b] 50.8 (J=66.6 Hz, C_1),[b] 121.9 (C_3), 122.6 (J=11.7 Hz, $C_{3'}$),[c] 122.7 (J=10.4 Hz, $C_{5'}$),[c] 124.2 (J=84.5 Hz, $C_{1'}$), 141.6 (J=5.2 Hz, C_2), 151.9 (J=13.0 Hz, $C_{2'}$),[d] 152.0 (J=13.0 Hz, $C_{6'}$),[d] 153.6 ($C_{4'}$), 175.5 (J=15.6 Hz, C_8),[e] 175.9 (J=15.6 Hz, C_{10}),[e] [a–e]may be reversed; δ_H 1.23 (d, J=6.7 Hz, 6H, $CH(CH_3)_2$), 1.25 (d, J=6.7 Hz, 6H, $CH(CH_3)_2$), 1.50 (d, J=6.7 Hz, 6H, $CH(CH_3)_2$), 1.98 (s, 3H, C_2-CH_3), 2.83 (s, 3H, $N-CH_3$), 6.07 (d, J=6.0 Hz, 1H, C_3-H); MS, m/z 428 $(M+H)^+$; $(M+H)^+$ found 428.2272. $C_{25}H_{35}NO_3P$ requires 428.2355.

3.3.6. 8-Methyl-10-(2′,4′,6′-tri-*i*-propylphenyl-)4-oxa-10-phosphabicyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dion 10-oxide (*anti-endo*-15). The title compound was prepared from phosphine *anti-endo*-**14** (δ_P 78.7 ($CDCl_3$); (M+H) 399) obtained from phosphole **3a** and MAA (100°C/10 days) according to the general procedure. Yield: 0.22 g (33%) thick oil with a purity of 93% (the product partly decomposed during the chromatography) IR ν_{max} (film) 2966, 1734, 1348, 1194 cm^{-1}; δ_P 89.0 ($CDCl_3$); δ_C 19.7 (J=10.5 Hz, C_2-CH_3), 23.0 ($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$), 23.9 (J=5.0 Hz, $CH(CH_3)_2$), 32.0 (J=12.3 Hz, $CHMe_2$), 33.9 ($CHMe_2$), 42.5 (J=23.7 Hz, C_6),[a] 43.4 (J=27.9 Hz, C_5),[a] 47.2 (J=64.8 Hz, C_4),[b] 52.7 (J=65.1 Hz, C_1),[b] 122.1 (J=11.0 Hz, $C_{3'}$, $C_{5'}$), 122.4 (C_3), 141.6 (J=5.0 Hz, C_2), 151.5 (J=11.6 Hz, $C_{2'}$, $C_{5'}$), 152.1 ($C_{4'}$), 174.7 (J=15.0 Hz, C_8, C_{10}), [a,b]tentative assignment; MS, m/z 415 $(M+H)^+$; $(M+H)^+$ found 415.1963. $C_{24}H_{32}O_4P$ requires 415.2038.

3.4. Calculations

Quantum chemical calculations were carried out by using the GAUSSIAN 98 suite of programs (REF). Preliminary geometry optimizations were carried out at the PM3 semiempirical level, followed by calculation of the second derivatives. Further geometry optimizations were performed at the B3LYP/3-21G* level of the density functional theory. For the model compounds (but not for the systems with the real substituents) second derivatives were calculated at this level of the theory. The nature of the stationary point has been established from these calculations. For minima, all the second derivatives were positive, while for saddle points a single imaginary frequency has been obtained. In case of the transition structures, the imaginary vibrational mode has clearly shown the expected movement in the concerted cycloaddition reaction pathway. In case of the transition structures, the wavefunction has been tested for UHF stability. Further geometry optimization has been carried out for the model systems at the B3LYP/6-31+G* level, using the B3LYP/3-21G* second derivatives. For the system with the real substituents, no further optimization has been carried out, but single point calculations were performed using larger basis sets. For the smallest model systems single point MP2/6-31G*//B3LYP/6-31+G* calculations were also carried out.

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17. According to the IUPAC nomenclature, the following numbering was used for naming products *anti-endo*-**4**, *anti-exo*-**6**, *anti-endo*-**7**, *syn-exo*-**9**, *anti-endo*-**12**–**15**.