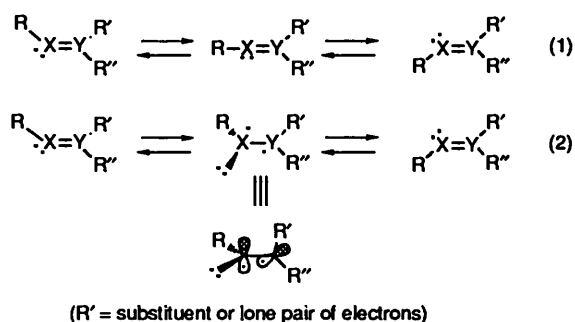


## Synthesis, Photochemical Behaviour and *cis/trans* Isomerisation of 1-(2,4,6-Triisopropylphenyl)-2-(2,4,6-tri-*tert*-butylphenyl)diphosphene

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Irradiation of (*E*)-1-(2,4,6-triisopropylphenyl)-2-(2,4,6-tri-*tert*-butylphenyl)diphosphene (**1a**) yields its thermally unstable *cis*-isomer **1b**, the diastereoisomeric cyclisation products **4a** and **4b** and the cleavage product **5**. A mechanism for the formation of these products is proposed. The activation parameters for the thermal isomerisation reaction **1b**  $\rightarrow$  **1a** are experimentally determined as  $\Delta H^\ddagger = 29.5 \pm 1.4$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger = 38 \pm 6$  cal mol<sup>-1</sup> K<sup>-1</sup> (1 kcal = 4.18 kJ);  $\Delta H^\ddagger$  is the first experimentally determined measure for the strength of the  $\pi$ -component of a phosphorus-phosphorus double bond.

An interesting feature of (hetero)alkenes is *cis/trans* isomerisation. It has been studied for many representatives containing C=C,<sup>1</sup> N=N,<sup>2</sup> P=C,<sup>3</sup> Si=Si<sup>4</sup> and N=C<sup>5</sup> double bonds; in this paper, we wish to address the case of the P=P bond of diphosphenes.<sup>6</sup> In diphosphenes, as in other heteroalkenes involving one or two group 15 elements, the *cis/trans* isomerisation can in principle occur by two mechanisms: inversion *via* a planar transition state [eqn. (1)] or rotation involving a perpendicular orientation of R-X towards the X-YR'R'' plane [eqn. (2)].

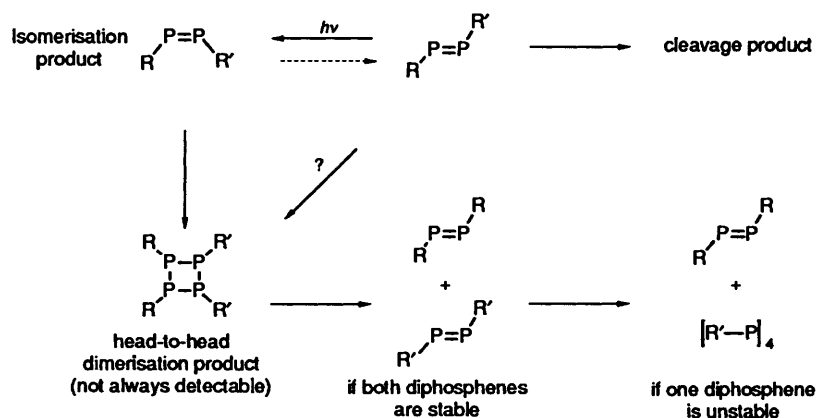


It is likely that the *cis/trans* isomerisation of a diphosphene occurs *via* a rotation mechanism rather than an inversion mechanism in line with the general observation that for tertiary phosphines, contrary to amines, inversion is a difficult process; this will, *a fortiori*, be true for two-coordinate phosphorus. Indeed, the computed energy barriers for HP=PH are 34 kcal mol<sup>-1</sup> (1 kcal = 4.18 kJ) for rotation and 66 kcal mol<sup>-1</sup> for inversion.<sup>7</sup> If the *cis/trans* isomerisation proceeds by a rotation

mechanism, the p-orbitals of the two phosphorus atoms will be orthogonal in the transition state, and, as a consequence, their overlap will be zero [eqn. (2)]. This implies that the height of the activation barrier ( $\Delta H^\ddagger$ ) is approximately equivalent to the  $\pi$ -bond strength of the phosphorus-phosphorus double bond.<sup>8,9</sup> Recently, Warren *et al.*<sup>10</sup> calculated a  $\pi$ -increment for a phosphorus-phosphorus double bond of 29 kcal mol<sup>-1</sup>.

Previous irradiation studies on *E*-diphosphenes (sterically hindered diphosphenes are normally stable in the *E*-form) have shown that dimerisation,<sup>11,12</sup> cleavage<sup>13</sup> and *cis/trans* isomerisation<sup>13-15</sup> may occur depending on the substituents and irradiation conditions (Scheme 1).

Only two kinetic studies of *cis*  $\rightarrow$  *trans* isomerisation of diphosphenes have been published. Caminade *et al.*<sup>15</sup> performed an experimental study by laser irradiation of Mes\*<sub>2</sub>P=P-Mes\* (**2**) (Mes\* = supermesityl: 2,4,6-tri-*tert*-butylphenyl) and found that the free activation energy ( $\Delta G^\ddagger$ ) for the *cis*  $\rightarrow$  *trans* conversion is 20.3 kcal mol<sup>-1</sup> at 273 K. Niecke *et al.* isolated the first stable *cis*-diphosphenes.<sup>16</sup> For the diphosphene (Me<sub>3</sub>Si)<sub>2</sub>N(Me<sub>3</sub>Si)N-P=P-Mes\* (**6**), they measured the free energy for the *cis*  $\rightarrow$  *trans* conversion ( $\Delta G^\ddagger = 25.5$  kcal mol<sup>-1</sup>) as well as for the *trans*  $\rightarrow$  *cis* conversion ( $\Delta G^\ddagger = 25.4$  kcal mol<sup>-1</sup>) at 293 K.<sup>17</sup> These isolated *cis*-diphosphenes are stable in the solid state under an inert atmosphere, but in solution at room temperature, they form, most likely *via* their (head-to-head) dimers, the symmetrical substituted diphosphenes of which the less bulky unstable ones form cyclotetraphosphanes ([R-P]<sub>4</sub>), depending on the substituents R (Scheme 1).<sup>16,17</sup> It should be pointed out that dimerisation of *trans*-diphosphenes without irradiation does not occur, and secondly, that of the two processes, *i.e.*, dimerisation or *trans*  $\rightarrow$  *cis* isomerisation, only one has been



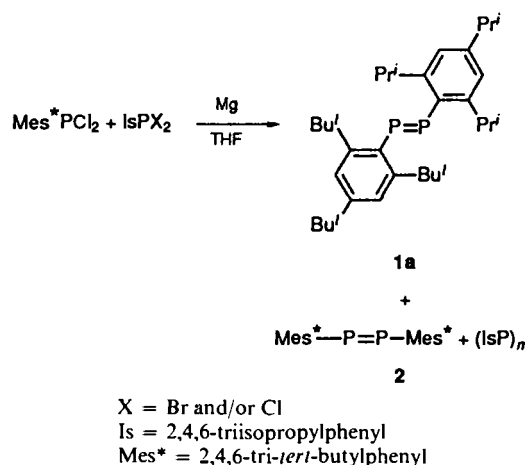
Scheme 1

observed for any particular diphosphene system. These data, suggest that the head-to-head dimerisation is not a direct result of irradiation (see Scheme 1) but occurs *via* dimerisation of the initially formed, unstable (and undetectable) *cis*-isomers.

We have chosen  $\text{Is-P=P-Mes}^*$  (**1a**; Is = isityl: 2,4,6-triisopropylphenyl) to investigate the photochemical behaviour of diphosphenes in continuation of our earlier work on less hindered and unsymmetrical diphosphenes.<sup>18</sup>

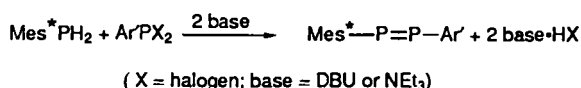
## Results and Discussion

**Synthesis.**—After the synthesis of very bulky and symmetrical diphosphenes had been reported,<sup>10,19,20</sup> we investigated the synthesis of less hindered and unsymmetrically substituted diphosphenes.<sup>18</sup> The first unsymmetrical diphosphene **1a** was observed on reductive cross-coupling of the corresponding dihalophosphines with magnesium; besides **1a**, the already known symmetrical diphosphene **2** and some cyclooligophosphines ( $[\text{IsP}]_n$ ) were formed (Scheme 2).



Scheme 2

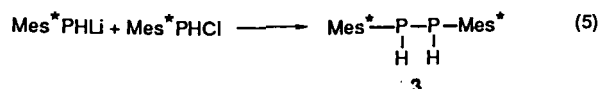
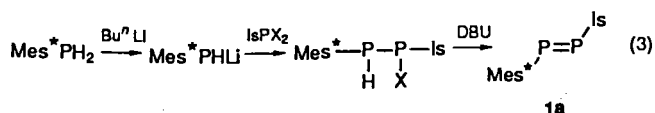
Because of these side products, this approach is not attractive as a preparative route to unsymmetrical diphosphenes. A better synthesis of unsymmetrical diphosphenes has been reported by Yoshifuji *et al.*<sup>21</sup> (Scheme 3). This method did not work in the



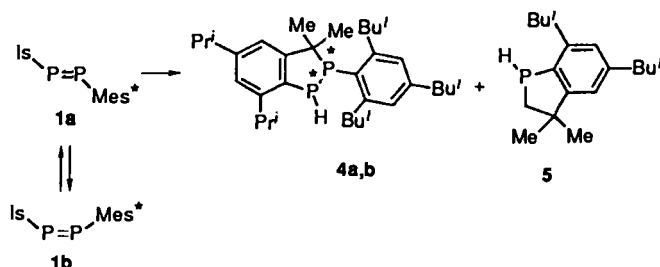
Scheme 3

case of **1a**;  $\text{Mes}^*\text{PH}_2$  was left unchanged while  $\text{IsPX}_2$  (X = Cl and/or Br, because  $\text{IsMgBr}$  and  $\text{PCl}_3$ ) disappeared, probably because it reacts rapidly with DBU to form a salt-like adduct.<sup>22</sup> However, by a slight variation, we prepared **1a** by coupling of  $\text{Mes}^*\text{PHLi}$  with  $\text{IsPX}_2$  followed by HX elimination with DBU [eqn. (3)]. Although this method gives **1a** as the main product, diphosphene **3** was formed, too, presumably *via* the side reactions depicted in eqns. (4) and (5). The diphosphane **3** had already been obtained as a side product in the synthesis of  $\text{Mes}^*\text{-P=P-Mes}^*$  from  $\text{Mes}^*\text{PCl}_2$  and magnesium;<sup>6,19</sup> Cowley *et al.*<sup>19</sup> reported the formation of **3** from  $\text{Mes}^*\text{PHLi}$  and several chlorinated compounds, *e.g.*,  $\text{CCl}_4$ ,  $\text{Mes}^*\text{PCl}_2$ ,  $\text{Bu}^*\text{PCl}_2$  and  $\text{PCl}_3$ .

**Irradiation of 1a.**—After irradiation ( $\lambda = 300 \text{ nm}$ ,  $T = 193 \text{ K}$ , Pyrex NMR-tube) of a solution of **1a** in THF, the thermally unstable *cis*-isomer **1b**, the rearrangement products **4a** and **4b**, and the cleavage product **5** were observed by  $^{31}\text{P}$  NMR spectroscopy (Scheme 4). Dimerisation products or symmetrical



diphosphenes were not observed, in line with the results of the previous irradiation studies (see the introduction).<sup>11-15</sup>



Scheme 4

Irradiation of **1a** over a short period (approximately 1 h) lead almost exclusively to the formation of the *cis*-isomer **1b** (20%); at that stage, the irradiation products **4a** and **4b** were detectable in minor amounts (1%) only. After a longer period of irradiation (approximately 1 day), almost 50% of **1** had rearranged to **4a** and **4b**. This time, the cleavage product **5** was also detected by  $^{31}\text{P}$  NMR spectroscopy. Complete conversion of **1a** took approximately one week. At this stage, high field signals ( $\delta_{\text{P}} = -113$  and  $-118$ ) of some unidentified products **X** appeared. These are probably decomposition products of **4a** and **4b**; **X** is not identical with  $(\text{IsP})_3$  ( $\delta_{\text{P}} = -99.3; -133$ ).<sup>18</sup> When all of the diphosphene had disappeared, the ratio of the irradiation products was approximately 4:5:**X** = 75:10:15.

**Identification of the Irradiation Products.**—The irradiation products were characterised by NMR techniques. The *cis*-isomer **1b** was identified, besides by its quantitative thermal reconversion into its *trans*-isomer **1a**, by its typical low-field  $^{31}\text{P}$  NMR signals, two doublets ( $\delta_{\text{P}} 429.2, 391.5$ ) with a large coupling constant of  $^1J(\text{PP}) = 584 \text{ Hz}$ . It appears to be a general trend that the  $^{31}\text{P}$  nuclei of the *cis*-isomer are more shielded than those of the *trans*-isomer; this is illustrated in Table 1 for **1**, **2**,<sup>15</sup> **6**<sup>17</sup> and  $\text{Mes}^*\text{-P=P-NHMe}^*$  (**7**).<sup>23</sup>

The assignment of the chemical shifts to the two different phosphorus nuclei is only tentative at the moment. In **1a**, the assignment of the signal at  $\delta 473.4$  to  $\text{P}(2)\text{-Mes}^*$  occurs with a high degree of confidence. A range of  $\delta = 456\text{--}492$  for this type of phosphorus follows from the results of Smit<sup>18,24</sup> and Yoshifuji,<sup>21</sup> while the less heavily substituted second phosphorus nuclei [ $\text{P}(1)$ ] in these diphosphenes are less shielded and fall in the range  $\delta = 512\text{--}540$ . Furthermore, Yoshifuji *et al.* succeeded in identifying the mesityl-substituted phosphorus [ $\text{P}(1)$ ] in  $\text{Mes-P=P-Mes}^*$  (Mes = mesityl: 2,4,6-trimethylphenyl) at  $\delta = 540$  by the  $^4J(\text{PH})$  coupling of the *ortho*-methyl protons. Applying this relation from the *trans*-diphosphenes to **1b**, we assign the doublet centred at 429.2 ppm to  $\text{P}(1)\text{-Is}$  and the one at 391.5 ppm to (the more shielded)  $\text{P}(2)\text{-Mes}^*$ .

When we compare the chemical shifts of all bisaryl substituted *trans*-diphosphenes, we find certain trends<sup>24</sup> in the chemical shifts of  $\text{P}(1)$  and  $\text{P}(2)$ .

(1) As the substituent at  $\text{P}(1)$  becomes less bulky,  $\text{P}(1)$

**Table 1**  $^{31}\text{P}$  NMR parameters for some diphosphenes

P=P	$\delta_{cis}$	$\delta_{trans}$	$\Delta\delta^a$	$^1J(\text{PP})_{cis}/\text{Hz}$	$^1J(\text{PP})_{trans}/\text{Hz}$	Ref.
1	429.2 391.5	535.1 473.4	106 82	584	574	This work
2	368	492	124	—	—	6, 15
6	358	481	123	516	554	17, 23
7	190 387 206	311 450 316	121 63 110	522	532	23

$$^a \Delta\delta = \delta[\text{P}(n)]_{trans} - \delta[\text{P}(n)]_{cis}$$

becomes increasingly less shielded and P(2) more shielded, relative to the reference value of **2** ( $\delta_{\text{P}} = 492$ ).

(2) The difference  $\delta_{\text{P}}[\text{P}(1)] - \delta_{\text{P}}[\text{P}(2)]$  increases with increasing difference in size between the *ortho* substituents of the aryl groups on P(1) and P(2).

(3) The mean value of  $\delta_{\text{P}}[\text{P}(1)]$  and  $\delta_{\text{P}}[\text{P}(2)]$  falls into the rather narrow range of 491 and 509 ppm.

While for *trans*-diphosphenes these trends are consistent, this is only true in part for the *cis*-diphosphene **1b**: while P(1) is less shielded than P(2), P(2) of **1b** is *less* shielded ( $\delta_{\text{P}} = 391.5$ ) than its counterpart in *cis*-**2** ( $\delta_{\text{P}} = 368$ ).

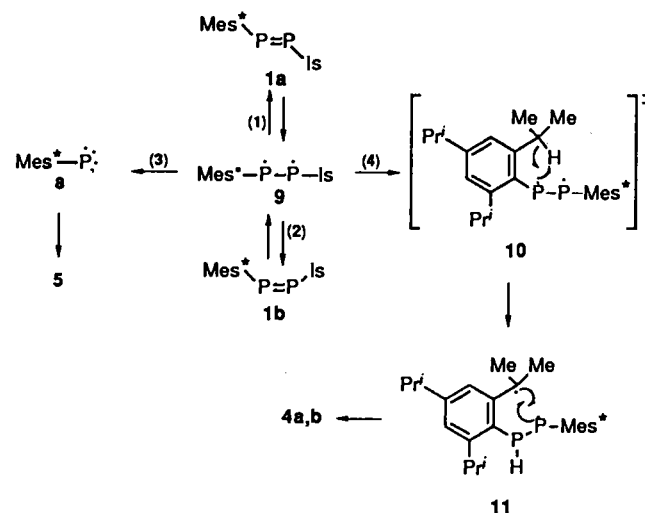
The situation concerning trend (2) is less straightforward. While the difference  $\delta_{\text{P}}[\text{P}(1)] - \delta_{\text{P}}[\text{P}(2)]$  is almost equal for *trans*- and *cis*-**6** (170 and 168 ppm, respectively) there is a considerable difference for **1a** and **1b** (62 and 38 ppm, respectively) and also for *trans*- and *cis*-**7** (134 and 181, respectively), even though they have the same substituents. The chemical shift differences of the two phosphorus nuclei in **1a** and **1b** ( $\Delta\delta = 106$  and 82; Table 1) are of the same order as for **7**<sup>23</sup> [ $\Delta\delta = 110$  (PN) and 63 (PC)], but are somewhat smaller compared with those of the other known *cis/trans* diphosphene systems [ $\Delta\delta = 124$  for **2**<sup>15</sup> and  $\Delta\delta = 123$  (PN) and 121 (PC) for **6**].<sup>17</sup>

Finally there appears to be no clear correlation between the configuration, the  $^1J(\text{PP})$  and the hybridisation of diphosphenes. The  $^1J(\text{PP})$  coupling constant of the *cis*-isomer **1a** (584 Hz) is very large and similar to that of the *trans*-isomer **1b** (574 Hz; Table 1). This might be rationalised as a result of steric repulsion between the bulky *cis*-substituents which opens the P-P-C angle and, as a consequence, imports more s-character to the P-P  $\sigma$  bond for the *cis*-isomer. However, the experimental support for this hypothesis is not straightforward. On the one hand, the trend of  $^1J(\text{PP})_{cis} > ^1J(\text{PP})_{trans}$  holds for **1**, for metal complexes of bisaryl-substituted diphosphenes<sup>14</sup> and of bispentamethylcyclopentadienyl-substituted diphosphenes;<sup>25</sup> the expected concomitant geometrical changes are indeed observed in *cis*- and *trans*-**6**.<sup>17</sup> On the other hand, the coupling constants of the nitrogen-substituted diphosphenes **6** and **7** are  $^1J(\text{PP})_{cis} < ^1J(\text{PP})_{trans}$ ; (Table 1),<sup>17,23</sup> demonstrating the shaky basis for the abovementioned rule. Further research on this topic is clearly required.

The rearrangement products **4a** and **4b** have chemical shifts in the high-field region: two pairs of double doublets in the proton-decoupled spectrum [**4a**, -18.9, -90.7 ppm,  $^1J(\text{PP}) = 188$  Hz; **4b**, -14.0, -78.8 ppm,  $^1J(\text{PP}) = 209$  Hz]. The high-field chemical shifts and the magnitude of the  $^1J(\text{PP})$  coupling constants indicate that a tertiary and a secondary phosphine phosphorus are separated by a single bond, implying that only the  $\text{p}\pi\text{-p}\pi$  bond in the original phosphorus-phosphorus double bond has been broken. The multiplicity and magnitudes of the observed proton couplings give further structural information [**4a**,  $^1J[\text{P}(1)\text{H}] = 212$ ,  $^2J[\text{P}(2)\text{H}] = 15$ ; **4b**  $^1J[\text{P}(1)\text{H}] = 199$ ,  $^2J[\text{P}(2)\text{H}] = 7$ ]. With this information, we propose structure **4** for the rearrangement products as indicated in Scheme 4. Because of the two chiral phosphorus atoms, **4** can, and does, occur as a pair of diastereoisomers **4a** and **4b**.

An additional product with a signal in the high-field region [-78.8 ppm; d,  $^1J(\text{PH}) = 176$ ] was identified as the cleavage product **5**, which is identical with a product obtained previously by different routes, e.g., by irradiation of **2**.<sup>13</sup>

**Mechanism.**—The formation of the photoreaction products is tentatively rationalised as shown in Scheme 5. First, the phosphorus-phosphorus bond is excited to form the intermediate diradical **9**. This intermediate can react by four different routes.

**Scheme 5**

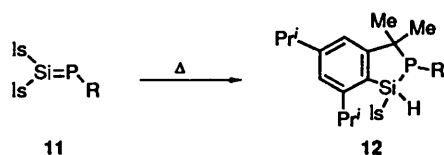
Routes (1) and (2) involve the formation of the phosphorus-phosphorus double bond which leads from **9** to the *cis*-isomer **1b** or back to the *trans*-isomer **1a**. As has already been discussed in the introduction, it is most likely that *cis/trans* isomerisation of diphosphenes is a rotation process. 'Metathesis' via a bimolecular process is excluded, because, in that case, the symmetrical diphosphene  $\text{Mes}^*\text{-P=P-Mes}^*$  (**2**) is expected as one of the products;<sup>12</sup> this is not observed. The mechanism of the photochemical *cis/trans* isomerisation by rotation is probably analogous to that of alkenes, which has been thoroughly studied. The singlet state is excited to the diradical state. After this ( $\pi \rightarrow \pi^*$ ) excitation, the (phosphorus-phosphorus) double bond is twisted to the more stable perpendicular structure [see eqn. (2)]. The interconversion of **1a** and **1b** is photoreversible and may establish a photodynamic equilibrium. In addition, the conversion **1b**  $\rightarrow$  **1a** occurs thermally; this irreversible process will be discussed in the section *cis/trans Isomerisation*. The main irreversible reaction of **9** [route (4)] is the abstraction of a benzylic hydrogen from an *ortho*-isopropyl group via a five-membered ring transition state **10** to give **11**. This diradical recombines to form the diastereomeric mixture of **4a** and **4b** (which are involved in a photodynamic equilibrium; see the subsection *Isomerisation of the Rearrangement Products* 4). Route (3) involves the cleavage of the phosphorus-phosphorus single bond, by which the phosphinidene **8** is

Table 2 Kinetic data of the *cis*→*trans* isomerisation of **1**

T/K	k/s <sup>-1</sup>	ΔG <sup>‡</sup> /kcal mol <sup>-1</sup>
258	1.27·10 <sup>-4</sup>	19.63
253	3.57·10 <sup>-5</sup>	19.88
246	7.32·10 <sup>-6</sup>	20.09

formed; the latter gives **5** on C–H insertion into an *ortho-tert*-butyl group. Several examples of this type of ring closure are known for supermesitylphosphorus<sup>13,26–29</sup> and supermesityl-arsenic<sup>24,30</sup> compounds. For isityl compounds, analogous ring closure has so far not been reported. We attempted the thermal ring closure with IsPX<sub>2</sub> in analogy to that described for Mes\*PCl<sub>2</sub>,<sup>26</sup> but IsPX<sub>2</sub> was stable under these conditions. Obviously, extreme steric hindrance as caused by the supermesityl group is required for this unusual type of reactivity to occur. At present, the fate of IsP, the formally expected counterpart of **8**, is not known.

Very recently, a conversion analogous to that of **1a**→**4** was observed by Driess *et al.*<sup>31</sup> however, in this case the transformation of the phosphasilene **12** into its isomer **13** is a thermal process (Scheme 6). In contrast, heating a solution of Is–P=P–Mes\* did not give **4** but resulted in decomposition to unidentified products.



**Isomerisation of the Rearrangement Products 4.**—The isomeric rearrangement products **4a** and **4b** are involved in a photodynamic and thermal equilibrium. Shortly after irradiation of **1a** at low temperature, one observes by <sup>31</sup>P NMR spectroscopy both isomers with **4a** in excess; the ratio may be as high as **4a**:**4b** = 2:1, depending on the length of irradiation. When the irradiation is interrupted, the equilibrium shifts slowly towards isomer **4b**; this isomerisation process (**4a**→**4b**) can be accelerated by raising the temperature from 193 K to room temperature, but stops when the ratio **4a**:**4b** is approximately 1:2, even at higher temperatures. Subsequent irradiation of the equilibrium mixture leads to partial conversion of **4b** into **4a**; this sequence can be repeated.

**cis/trans Isomerisation.**—Irradiation (λ = 300 nm, T = 193 K, 1 h) of the *trans*-isomer (**1a**) induces the formation of approximately 20% of the thermally unstable *cis*-isomer (**1b**). The thermal back reaction (**1b**→**1a**) was followed by <sup>31</sup>P NMR spectroscopy at different temperatures (Fig. 1 and Table 2); the rearrangement was first order in **1b** which excludes dimer formation (Scheme 1) as the mechanism.

From these data, the activation parameters ΔH<sup>‡</sup> = 29.5 ± 1.4 kcal mol<sup>-1</sup> and ΔS<sup>‡</sup> = 38 ± 6 cal mol<sup>-1</sup> K<sup>-1</sup> were obtained. The large entropy of activation may be explained by steric factors: the overcrowding in the *cis*-isomer is reduced on rotation about the double bond, releasing frozen degrees of motion; transition state **9** (and the *trans*-isomer **1a**) has less steric hindrance and consequently more degrees of freedom. Of great interest is the enthalpy of activation which is in fact the first experimentally obtained rotational barrier for a phosphorus–phosphorus double bond. The computed rotational barrier for a phosphorus–phosphorus double bond is 34.0 kcal mol<sup>-1</sup>.<sup>7</sup> Recently,<sup>10</sup> a π-increment for a phosphorus–phosphorus double bond of 29 kcal mol<sup>-1</sup> has been presented (the

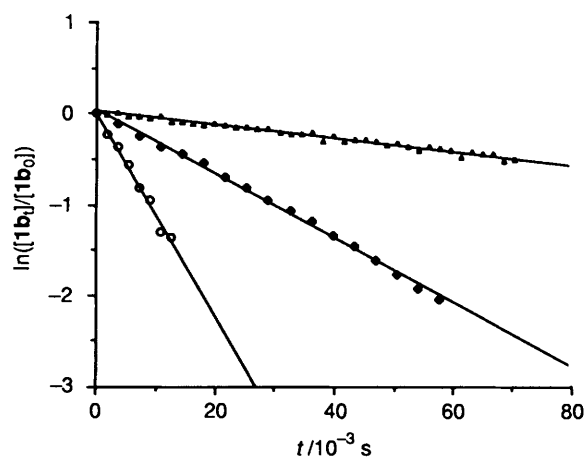


Fig. 1 Plots of ln ([**1b**]/[**1b**]<sub>0</sub>) versus time at three different temperatures: ○, 258 K; ◆, 253 K; ▲, 246 K.

estimated energy of an average phosphorus–phosphorus double bond, 84 kcal mol<sup>-1</sup> minus the estimated energy for the phosphorus–phosphorus single bond, 55 kcal mol<sup>-1</sup>). These theoretically calculated values for the rotational barrier are in good agreement with the activation enthalpy for the *cis*→*trans* isomerisation of **1**, ΔH<sup>‡</sup> = 29.5 ± 1.4 kcal mol<sup>-1</sup>. It should be pointed out, however, that the temperature range for measuring the isomerisation **1b**→**1a** is relatively small (12 K).

The result of Caminade *et al.*,<sup>15</sup> ΔG<sup>‡</sup> = 20.3 kcal mol<sup>-1</sup> (at 273 K) for the *cis*→*trans* isomerisation of **2** is in surprisingly good agreement with our ΔG<sup>‡</sup> values (20 kcal mol<sup>-1</sup>). If one assumes the same entropy factor because the steric situation is expected to be similar, the enthalpy of activation for the *cis*→*trans* isomerisation of **2** will be 30.7 kcal mol<sup>-1</sup>. Niecke *et al.*<sup>17</sup> reported a free energy ΔG<sup>‡</sup> = 25.5 kcal mol<sup>-1</sup> (at 293 K) for the *cis*→*trans* isomerisation of **6**. A direct comparison between the kinetic data of the *cis*→*trans* isomerisation of **1** and **6** is problematic without dissection for the latter into ΔH<sup>‡</sup> and ΔS<sup>‡</sup>. Assuming a similar entropy factor (which is risky because the diphosphene systems differ considerably), the enthalpy of activation for **6** is found to be larger (about 37 kcal mol<sup>-1</sup>). Apparently, this effect is due to the nitrogen atom directly attached to the pπ–pπ phosphorus–phosphorus bond.

## Conclusions

Irradiation of diphosphenes, depending upon the substituents and irradiation conditions, gives not only dimerisation, cleavage and *cis/trans* isomerisation, but also rearrangement reactions *via* the excited biradical.

The activation parameters for the thermal *cis/trans* isomerisation reaction of **1** were experimentally determined as ΔH<sup>‡</sup> = 29.5 ± 1.4 kcal mol<sup>-1</sup> and ΔS<sup>‡</sup> = 38 ± 6 cal mol<sup>-1</sup> K<sup>-1</sup>.

## Experimental

**General.**—The irradiation experiments and the crystallisation of **1a** were carried out in sealed, evacuated systems.<sup>32</sup> The synthesis of **1a** was performed under a nitrogen atmosphere. All solvents were dried before use: THF was distilled from sodium–benzophenone, pentane was distilled from lithium aluminium hydride and toluene was distilled from sodium. NMR spectra were recorded on a Bruker WM250, a Bruker AC200 or a Bruker MSL400 spectrometer. *J* values are given in Hz. <sup>1</sup>H NMR spectra were recorded with tetramethylsilane as an external standard, <sup>31</sup>P NMR spectra with 85% H<sub>3</sub>PO<sub>4</sub> as an

external standard. The temperature in the NMR probe was determined by measuring the  $^1\text{H}$  chemical shift difference of methanol which is related to the temperature.<sup>33</sup> The error limits for the activation parameters of the conversion  $1\text{b} \rightarrow 1\text{a}$  include both the error in measurement of temperature ( $\pm 1$  K) and the standard deviation of the rate constant  $k$ . Irradiation experiments were performed with a rayonet (Srinivasan-Griffin, photochemical reactor), equipped with 16 lamps ( $\lambda = 300$  nm), in a Pyrex NMR tube in THF at 193 K. Low temperature was maintained by the use of a quartz Dewar vessel equipped with a liquid nitrogen blow-off system and temperature controller.

**Preparation of 1a.**—(E)-1-(2,4,6-Triisopropylphenyl)-2-(2,4,6-tri-*tert*-butylphenyl)diphosphene (**1a**) was synthesised from 2,4,6-tri-*tert*-butylphenylphosphine ( $\text{Mes}^*\text{PH}_2$ )<sup>19</sup> and dihalo-(2,4,6-triisopropylphenyl)phosphine ( $\text{IsPX}_2$ ).<sup>34</sup> To a solution of  $\text{Mes}^*\text{PH}_2$  (1.7 g, 6.1 mmol) in THF (100 cm<sup>3</sup>), a solution of *n*-butyllithium (4.5 cm<sup>3</sup> 1.5 mol dm<sup>-3</sup>, 6.8 mmol) was added at  $-60^\circ\text{C}$ . After being stirred for 30 min at  $-60^\circ\text{C}$ , the reaction mixture was stirred at room temperature for 2 h [ $^{31}\text{P}$  NMR spectroscopy of the crude reaction mixture:  $-107.4$  ppm,  $^1J(\text{PH}) = 174$  Hz;  $\text{Mes}^*\text{PHLi}$ ]. The reaction mixture was slowly added to a cooled ( $-60^\circ\text{C}$ ) solution of  $\text{IsPX}_2$  (1.9 g, 6.2 mmol) in THF (50 cm<sup>3</sup>). Afterwards the reaction mixture was stirred for 1.5 h at room temperature. To this crude reaction mixture, freshly distilled DBU (0.9 cm<sup>3</sup>, 6.1 mmol) was added at  $0^\circ\text{C}$ ; the resulting reaction mixture was stirred overnight and then warmed to room temperature. The solvent of the supernatant was evaporated off under vacuum. The residue was extracted twice with pentane. The pentane extracts were partly evaporated and placed in a closed glass vessel for crystallisation. First the side product **3** crystallised; pure diphosphene **1** was obtained after several recrystallisations.

**Identification.** **1a**:  $\delta_{\text{P}}$ (250 MHz; [ $^2\text{H}_8$ ]THF; 258 K) 535.1 [1 P, d,  $J(\text{PP})$  574, P-Is] and 473.4 [1 P, d,  $J(\text{PP})$  574, P-Mes\*];  $\delta_{\text{H}}$ (200 MHz; [ $^2\text{H}_8$ ]THF) 1.10 [12 H, d,  $J$  6.7, *ortho*-CH(CH<sub>3</sub>)<sub>2</sub>], 1.16 [6 H, d,  $J$  7.0, *para*-CH(CH<sub>3</sub>)<sub>2</sub>], 1.26 [9 H, s, *para*-C(CH<sub>3</sub>)<sub>3</sub>], 1.41 [18 H, s, *ortho*-C(CH<sub>3</sub>)<sub>3</sub>], 2.79 [1 H, septet,  $J$  7.0, *para*-CH(CH<sub>3</sub>)<sub>2</sub>], 3.19 [2 H, br septet,  $J$  6.7, *ortho*-CH(CH<sub>3</sub>)<sub>2</sub>], 6.98 (2 H, s, Is) and 7.40 (2 H, s, Mes\*);  $\delta_{\text{C}}$ (200 MHz; [ $^2\text{H}_8$ ]THF) 24.28 [2 C, s, *para*-CH(CH<sub>3</sub>)<sub>2</sub>], 24.32 [4 C, s, *ortho*-CH(CH<sub>3</sub>)<sub>2</sub>], 31.60 [3 C, s, *para*-C(CH<sub>3</sub>)<sub>3</sub>], 34.3 [2 C, d,  $^3J(\text{CP})$  7.4, *ortho*-CH(CH<sub>3</sub>)<sub>2</sub>], 34.4 [6 C, d,  $^4J(\text{CP})$  6.1, *ortho*-C(CH<sub>3</sub>)<sub>3</sub>], 35.19 [1 C, s, *para*-CH(CH<sub>3</sub>)<sub>2</sub>], 35.40 [1 C, s, *para*-C(CH<sub>3</sub>)<sub>3</sub>], 39.08 [2 C, s, *ortho*-C(CH<sub>3</sub>)<sub>3</sub>], 122.27 [2 C, s, C(3), C(5), Is], 123.00 [2 C, s, C(3), C(5), Mes\*], 137.12 and 139.40 [1 C, dd,  $^1J(\text{CP})$  51.8,  $^2J(\text{CP})$  13.6 and 1 C, dd,  $^1J(\text{CP})$  67.4,  $^2J(\text{CP})$  10.6, C(1'); C(1')], 150.31 and 150.76 [1 C, d,  $^4J(\text{CP})$  1.7 and 1 C, d,  $^4J(\text{CP}) \leq 1$  C(4) and C(4')] and 151.43 and 154.21 [2 C, dd,  $^1J(\text{CP})$  8.1,  $^2J(\text{CP})$  5.0 and 2 C, d,  $^1J(\text{CP})$  9.1, C(2), C(6) and C(2'), C(6')];  $m/z$  510 ( $\text{M}^+$ , 48%) (Found: 510.355. Calc. for  $\text{C}_{33}\text{H}_{52}\text{P}_2$ :  $M$ , 510.3544).

**3**:  $\delta_{\text{P}}$ (250 MHz;  $\text{C}_6\text{D}_6$ )  $-60.41$ ;  $-60.23$  (two isomers 2:9);  $\delta_{\text{H}}$ (200 MHz;  $\text{C}_6\text{D}_6$ ) 1.3 (18 H, s, *para*-Bu<sup>t</sup>), 1.5 (36 H, s, *ortho*-Bu<sup>t</sup>), 4.5–5.8 (2 H, m, P-H) and 7.45 (4 H, s, *meta*-CH);  $^{19}\text{F}$   $m/z$  554 ( $\text{M}^+$ , 8%) (Found: 554.417. Calc. for  $\text{C}_{36}\text{H}_{60}\text{P}_2$ :  $M$ , 554.4171).

**Thermal Behaviour of Dihalo(2,4,6-triisopropylphenyl)phosphine and Dichloro-(2,4,6-tri-*tert*-butylphenyl)phosphine.**—A solution of  $\text{IsPX}_2$  (0.6 g, 2 mmol) in toluene (20 cm<sup>3</sup>) and pyridine (0.2 cm<sup>3</sup>) was heated under reflux for several days. No reaction could be observed ( $^{31}\text{P}$  NMR). In a control experiment, a solution of  $\text{Mes}^*\text{PCl}_2$  (0.35 g, 1 mmol) in toluene (10 cm<sup>3</sup>) and pyridine (0.1 cm<sup>3</sup>) was heated under reflux; after a few days, phosphaindane **5** was formed quantitatively [ $^{31}\text{P}$  NMR:  $\delta = 108.1$  (crude reaction mixture)],  $\delta = 111.5$  in  $\text{CDCl}_3$ .<sup>26</sup>

**Thermal Behaviour of (E)-1-(2,4,6-Triisopropylphenyl)-2-(2,4,6-tri-*tert*-butylphenyl)diphosphene (1a).**—A sample of **1a** was dissolved in toluene in a sealed NMR tube. The NMR tube was heated in an oven. No reaction occurred after 3 days at  $80$ – $100^\circ\text{C}$ , but after 1 day at  $120^\circ\text{C}$ , **1a** decomposed; several unidentified high-field signals were observed.

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