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Photochemical Reactions of Diphosphenes Carrying 2,4,6-Tris(trifluoromethyl)phenyl Group

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Synopsis. Photoreactions of 1,2-bis[2,4,6-tris(trifluoromethyl)phenyl]diphosphene and 1-(2,4,6-tri-*t*-butylphenyl)-2-[2,4,6-tris(trifluoromethyl)phenyl]diphosphene were studied. The latter diphosphene gave formally an intramolecular cyclization product by photoirradiation, whereas the former diphosphene showed no change on irradiation.

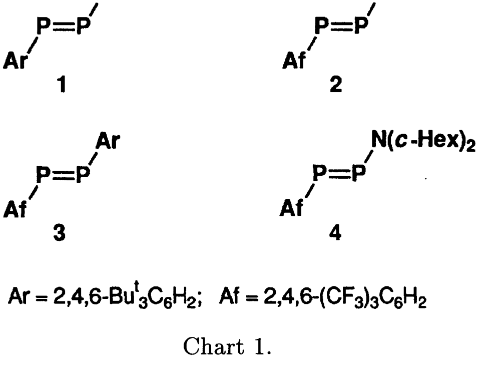
Compounds with multiple bonds involving the heavier main-group elements in low coordination states are of interest. Diphosphenes[1,2)] are typical examples in this category of coordination number 2.

There have been many studies on preparation, physical properties, and reactivities of diphosphenes, but it remains intriguing to study their photochemical properties. The reported study on photoreactions of diphosphenes so far involves *E*/*Z* isomerization for 1,2-bis(2,4,6-tri-*t*-butylphenyl)diphosphene (**1**),[3,4)] bond cleavage,[4)] and dimerization.[5,6)] The courses of photoreactions seem to depend on the substituents on the phosphorus atom(s). For example, the [2+2] cycloaddition is preferable to *E*/*Z* isomerization if the substituents are less bulky. Scholz et al. and we have reported the preparations of diphosphenes carrying the 2,4,6-tris(trifluoromethyl)phenyl group (abbreviated here to Af), **2**[7)] and **3**,[8)] and we have very recently reported the preparation of captodative diphosphenes such as **4**.[9)] The properties of these diphosphenes are interesting because the Af group is expected to have some effect on the phosphorus–phosphorus double bond both sterically and electronically (Chart 1).

Here we describe the photoreaction of **3**, which caused formally an intramolecular cyclization reaction.

Results and Discussion

1-(2,4,6-Tri-*t*-butylphenyl)-2-[2,4,6-tris(trifluoromethyl)phenyl]diphosphene (**3**) has been prepared by the base-induced coupling reaction[2)] of [2,4,6-tris(trifluoromethyl)phenyl]phosphine (**5**)[7)] with 2,4,6-tri-*t*-butylphenylphosphonous dichloride using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base.[8)] Irradiation experiments of **2** and **3** were carried out in C_6D_6/C_6H_6 at 5 °C using a medium-pressure mercury lamp (100 W). First, irradiation of the diphosphene **2** in the presence of 2,3-dimethyl-1,3-butadiene showed no change (3-h irradiation), thus an attempted trapping experiment during the photoreaction of **2** using the 1,3-butadiene as a trapping reagent of phosphinidene intermediate[10)] has failed so far.[11)] On the other hand, irradiation of the unsymmetrical diphosphene **3** gave diphosphane **6** (a mixture of diastereomers, ratio 4 : 1) as a major product together with the symmetrical diphosphene **2**, diphosphanes **7** (a mixture of diastereomers, ratio 2 : 1) and **8** (single isomer), phosphaindan **9**.[4,12)] and the phosphine **5** (Scheme 1). Figure 1 shows the ^{31}P NMR (81 MHz) spectrum of the reaction mixture after 46-h irradiation, when the starting diphosphene **3** had been almost consumed. Since these products were sensitive to air and/or moisture, the identifications were mainly made by ^{31}P NMR spectroscopy. Furthermore, the structures of the products, **6**, **7**, and **8**, were confirmed by alternative preparations (Scheme 2) as follows. The phosphine **5** was lithiated with butyllithium and the resulting



Ar = 2,4,6-$Bu^t_3C_6H_2$; Af = 2,4,6-$(CF_3)_3C_6H_2$

Chart 1.

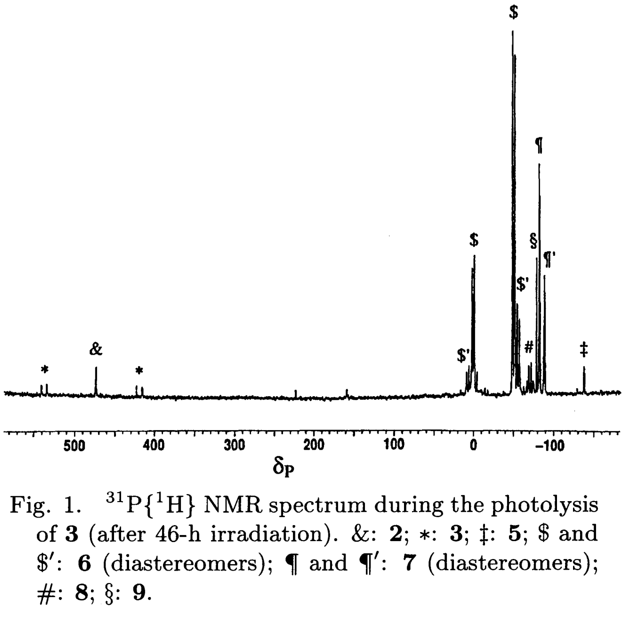
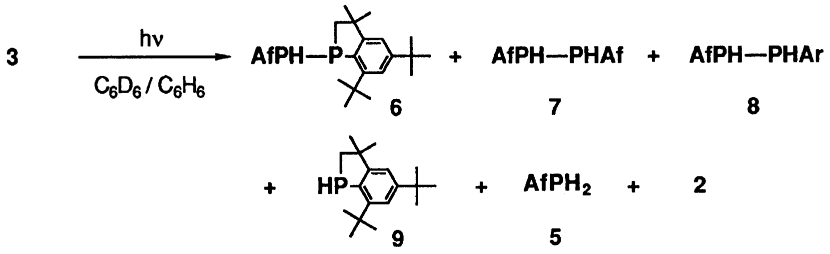
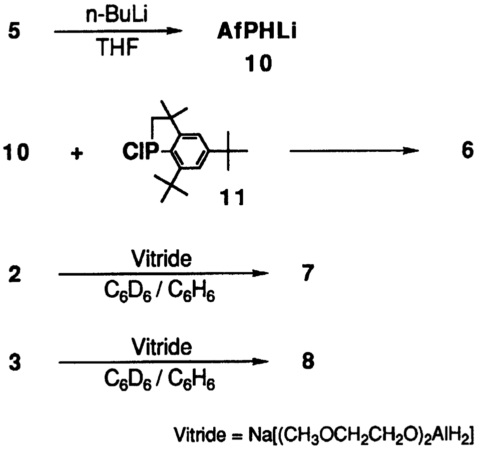


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum during the photolysis of **3** (after 46-h irradiation). &: **2**; *: **3**; ‡: **5**; $ and $': **6** (diastereomers); ¶ and ¶': **7** (diastereomers); #: **8**; §: **9**.



Scheme 1.



Scheme 2.

lithium phosphide **10**[13] was allowed to react with chlorophosphaindan **11**[14] to give **6**. The ^{31}P NMR signal was identical with that observed for the product during the photolysis of **3**. We have previously reported the reduction of diphosphenes using sodium bis(2-methoxyethoxy)aluminum hydride (Vitride),[15] and this method was used to prepare the diphosphanes **7** and **8**. Thus the diphosphenes **2** and **3** were reduced with Vitride to give **7** and **8**, respectively. The ^{31}P NMR spectra of them were identical with those observed for the photoreaction products, respectively. Furthermore it should be mentioned that both the ratios of diastereoisomers of **6** and **7** thus obtained were almost the same as those observed for the photolysis products of **3**, respectively.

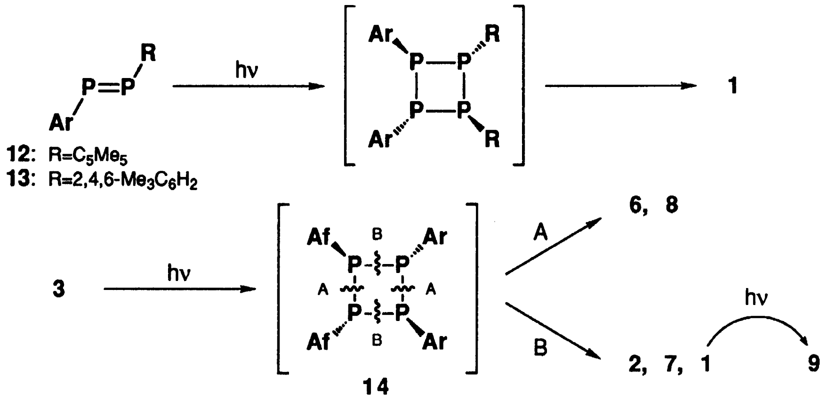
Jutzi et al. and we have reported the photolysis of unsymmetrical diphosphenes, 1-(pentamethylcyclopentadienyl)-2-(2,4,6-tri-*t*-butylphenyl)diphosphene (**12**) and 1-mesityl-2-(2,4,6-tri-*t*-butylphenyl) diphosphene (**13**), through a Pyrex filter leading to the formation of symmetrical diphosphene **1** and both of the reactions suggested the intermediacy of cyclotetraphosphanes formed by head-to-head dimerization of diphosphenes.[5,6] The results of the photolysis of **3** seem to be explicable by a reaction mechanism shown in Scheme 3. The diphosphene **3** dimerizes in a head-to-head manner to form an intermediary cyclotetraphosphane **14** followed by two types of homolytic P–P bond cleavages (A and B). The cleavage of the type A leads to the formation of **6** and **8** after intramolecular and intermolecular H-abstractions, respectively, whereas the cleavage of the type B leads to the formation of **2** and **7** after H-abstraction. The symmetrical diphosphene **1**,[1a] which may be formed along with **2** (cleavage B), is supposed to afford phosphaindan **9** in almost quantitative yield[4] during the photoirradiation. The formation of a small amount of phosphine **5** can be explained by H-abstraction of a phosphinidene intermediate [AfP:] generated through either path A or path B.[4]

Experimental

All experiments were carried out under argon atmosphere using anhydrous solvents unless specified otherwise. NMR spectra were recorded on a Bruker AC-200P spectrometer. MS spectra were taken on either JEOL HX-110 or Hitachi M-2500 spectrometer. The diphosphenes **2**[7] and **3**,[8] the phosphine **5**,[7] and the chlorophosphaindan **11**[14] were prepared as described previously. The diphosphene **3** was purified by silica-gel column chromatography, although **2** decomposed during the column-chromatographic treatment.

Photolysis of 1-(2,4,6-Tri-*t*-butylphenyl)-2-[2,4,6-tris(trifluoromethyl)phenyl]diphosphene (3). A solution of **3** (151.4 mg, 0.257 mmol) in 0.4 ml of C_6D_6/C_6H_6 (1 : 5) in a sealed Pyrex NMR tube (5 mmϕ) was irradiated with a medium-pressure mercury lamp (100 W) at 5 °C. The reaction was monitored by ^{31}P NMR spectroscopy. After 51-h irradiation, the signal due to **3** disappeared and the ^{31}P NMR of the resulting solution showed the formation of **2** (δ_P=474), **5** (δ_P=−138), **6** (mixture of diastereomers), **7** (mixture of diastereomers), **8**, and **9** (δ_P=−79).

Preparation of 5,7-Di-*t*-butyl-3,3-dimethyl-1-[2,4,6-tris(trifluoromethyl)phenylphosphino]-1-phosphaindan (6). The phosphine **5** (697.8 mg, 2.22 mmol) in THF (7 ml) was lithiated with 2.36 mmol of butyllithium (1.63 M in hexane, 1M=1 mol dm^{-3}) at −78 °C. This solution containing phosphide **10**[13] was added to a stirred solution of 5,7-di-*t*-butyl-1-chloro-3,3-dimethyl-1-phosphaindan **11**[14] (714.2 mg, 0.230 mmol) in THF–xylene (3 : 1 v/v) at −78 °C. The reaction mixture was warmed up to room temperature and stirred for 1.5 h. The volatile components were removed in vacuo and the residue was dissolved in hexane (7 ml). Insoluble material was filtered off and the filtrate was concentrated in vacuo to give **6** (553.2 mg, 0.941 mmol) in 42% yield. **6** (mixture of diastereomers, isomer ratio, 4 : 1): orange viscous oil; ^{31}P{^{1}H} NMR (81 MHz, C_6D_6/C_6H_6): major isomer: δ=−50.7 (d of sept, $^{1}J_{PP}$=221.7 Hz and $^{4}J_{PF}$=30.1 Hz, AfPH, and $^{1}J_{PH}$=229.3 Hz from ^{1}H non-decoupled NMR spectrum) and 0.0 (d of sept, $^{1}J_{PP}$=221.7 Hz, $^{5}J_{PF}$=25.9 Hz, CH_2P); minor isomer: δ=−56.5 (d of sept,



Scheme 3.

$^1J_{PP}$=224.0 Hz, $^4J_{PF}$=27.3 Hz, AfPH, and $^1J_{PH}$=212.5 Hz from ^{1}H non-decoupled NMR spectrum) and 6.9 (d of sept, $^1J_{PP}$=224.0 Hz, $^5J_{PF}$=23.6 Hz, CH$_2$P); ^{1}H NMR (200 MHz, C$_6$D$_6$) (major isomer) δ=1.30 (9H, s, *p*-Bu^t), 1.40 (6H, s, 3-CH$_3$), 1.41 (9H, s, *o*-Bu^t), 2.35—2.45 (2H, m, 2-CH$_2$), 4.91 (1H, d of m, $^1J_{PH}$=229.3 Hz, $^5J_{FH}$=6.2 Hz, PH), 7.18—7.47 (2H, m, Ar), and 7.84 (2H, s, Af); MS (70 eV) *m/z* (rel intensity) 588 (M$^+$; 16), 312 (AfP; 21), 275 (M$^+$−AfPH; 92), and 250 (M$^+$−Af−Bu^t; 100). Found: *m/z* 588.1749. Calcd for C$_{27}$H$_{31}$F$_9$P$_2$: M, 588.1757.

Preparation of 1,2-Bis[2,4,6-tris(trifluoromethyl)phenyl]diphosphane (7). To a stirred solution of **2** (641.3 mg, 1.03 mmol) in THF (7 ml) was added 1.21 mmol of Vitride (3.4 M in toluene) at room temperature and the mixture was stirred for 3 h. The solution was diluted with hexane (15 ml) and stirred for 5 min. The volatile components were removed in vacuo and the residue was dissolved in hexane (8 ml). Insoluble material was removed by filtration and the filtrate was concentrated in vacuo to give **7** (215.1 mg, 0.344 mmol) in 33% yield. **7** (mixture of diastereomers, isomer ratio, 2 : 1): pale yellow viscous oil; ^{31}P{^{1}H} NMR (81 MHz, C$_6$D$_6$/C$_6$H$_6$): major isomer: δ=−82.7 (m, $^1J_{PH}$=217.8 Hz and $^4J_{PF}$=24.5 Hz); minor isomer: δ=−88.9 (m, $^1J_{PH}$=197.6 Hz, $^4J_{PF}$=24.4 Hz); ^{1}H NMR (200 MHz, C$_6$D$_6$) (major isomer) δ=3.33 (2H, d of m, $^1J_{PH}$=217.8 Hz, PH) and 7.75 (4H, s, Af); MS (70 eV) *m/z* (rel intensity) 626 (M$^+$; 43), 312 (AfP; 28), 307 (M$^+$−Af−2F, 45), 262 (Af−F, 25), 212 (Af−CF$_3$, 27), and 193 (Af−CF$_3$−F, 100). Found: *m/z* 625.9702. Calcd for C$_{18}$H$_6$F$_{18}$P$_2$: M, 625.9657.

Preparation of 1-(2,4,6-Tri-*t*-butylphenyl)-2-[2,4,6-tris(trifluoromethyl)phenyl]diphosphane (8). To a solution of **3** (1.137 g, 1.93 mmol) in THF (7 ml) was added 1.00 mmol of Vitride (3.4 M in toluene) at room temperature and the mixture was stirred for 2 h. The solution was diluted with hexane (12 ml) and stirred for 5 min. The volatile materials were removed in vacuo and the residue was dissolved in hexane (8 ml). Insoluble material was removed by filtration and the filtrate was concentrated in vacuo to give **8** (445.3 mg, 0.755 mmol) in 39% yield. **8**: pale yellow viscous oil; ^{31}P{^{1}H} NMR (C$_6$D$_6$/C$_6$H$_6$) δ=−73.7 (d of sept, $^1J_{PP}$=184.7 Hz, $^5J_{PF}$=21.3 Hz, ArP) and −68.3 (d of sept, $^1J_{PP}$=184.7 Hz, $^4J_{PF}$=29.3 Hz, AfP); ^{1}H NMR (200 MHz, C$_6$D$_6$) δ=1.24 (9H, s, *p*-Bu^t), 1.35 (18H, s, *o*-Bu^t), 4.33 (1H, d of m, $^1J_{FH}$=5.2 Hz, AfP$\underline{H}$), 5.48 (1H, d of m, $^1J_{PH}$=236.4 Hz, ArP$\underline{H}$), 7.56 (2H, s, Ar), and 7.85 (2H, s, Af); MS (70 eV) *m/z* (rel intensity) 590 (M$^+$; 1), 589 (M$^+$−1; 1), 309 (M$^+$−Af; 5), 277 (ArPH; 24), 245 (Ar; 8), 231 (Ar−Me+1; 100), and 57 (Bu^t; 40). Found: *m/z* 590.1909. Calcd for C$_{27}$H$_{33}$F$_9$P$_2$: M, 590.1914.

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butadiene showed no change, either.[8] Similarly, attempted photoreactions of 1-dicyclohexylamino-2-(2,4,6-tri-*t*-butylphenyl)diphosphene and 1-[2,6-bis(trifluoromethyl)phenyl]-2-dicyclohexylaminodiphosphene resulted in the recovery of the starting diphosphenes, respectively.

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13) The formation of the lithium phosphide **10** was alternatively confirmed by alkylation reaction with MeI which gave AfPHMe almost quantitatively as follows. The phosphine **5** (87.6 mg, 0.279 mmol) was lithiated with an equimolar amount of butyllithium (1.44 M in hexane) in THF (1.5 ml) at −78 °C. To this solution was added 2.5 mmol of iodomethane and the reaction mixture was warmed to room temperature. The ^{31}P NMR spectrum of the resulting solution showed the formation of AfPHMe as a sole product: ^{31}P NMR (C_6D_6/THF) $\delta=-82.3$ (d of sept, $^1J_{PH}=225.7$ Hz and $^4J_{PF}=28.0$ Hz); MS (25 eV) m/z (rel intensity) 327 (M^+-1; 100).

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