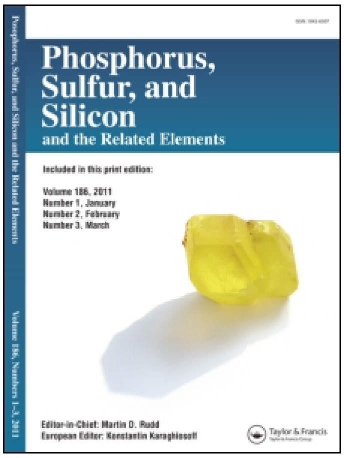

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SYNTHESIS OF TWO STABLE DIPHOSPHENES WITH A NEW STABILIZING SUBSTITUENT

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Two new diphosphenes **7** and **10** have been synthesized by action of DBU on trichlorogermylphosphines **4** and **8**; this route involves the intermediate formation of chlorophosphines **5** and **9**. Diphosphenes **7** and **10** are stabilized by the 2,6-bis(trifluoromethyl)phenyl group which presents both steric and electronic effects and is used for the first time in phosphorus chemistry.

INTRODUCTION

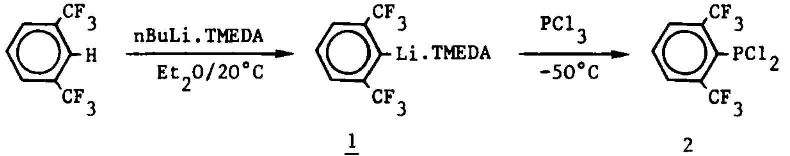
Since the isolation of the first stable diphosphene by Yoshifuji *et al.* in 1981,[1] some other diphosphenes have been synthesized;[2-9] all these derivatives are stabilized by bulky substituents such as aromatic groups,[2,3] tris(trimethylsilyl)methyl,[2,4] bis(trimethylsilyl) methyl,[2,5] bis(silyl)amino,[2] piperidyl,[6,7] transition metal,[8] and other bulky groups.[9] It seems quite evident that the steric hindrance is the most important stabilizing factor. The influence of electronic effects has not yet been clearly demonstrated.

The 2,6-bis(trifluoromethyl)phenyl group which can present both steric and electronic effects has been successfully used in the stabilization of a stannylene.[10] It was reasonable to think that such a substituent could also stabilize dicoordinated phosphorus species RP=Y (Y: C<, N—, P—, Si<, Ge<, . . .).

We describe in this paper the use of this substituent for the first time in diphosphene chemistry. We have prepared the bis[2,6-bis(trifluoromethyl)phenyl]-diphosphene **7**, and, to determine the influence of electronic effects on the phosphorus-phosphorus double bond, we have then synthesized the diphosphene **10** with two substituents having an opposite electronic effect.

RESULTS AND DISCUSSION

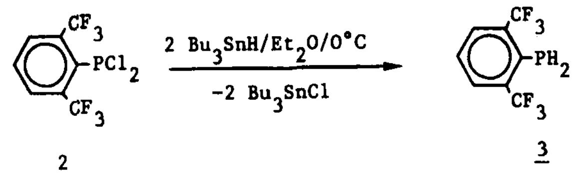
All the routes to diphosphenes need the previously synthesis of dichlorophosphines $RPCl_2$ or primary phosphines RPH_2.[2] Dichlorophosphine **2** has been obtained by addition of lithio compound **1**[10] to phosphorus trichloride:



1 2

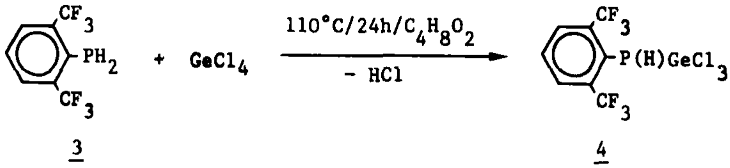
2: NMR,[11] ^1H: δ 7.26–7.99 (m, arom. H), $^{31}P\{^1H\}$: 146.6 (sept, $^4J_{PF}$: 61.0 Hz), ^{19}F: +25.4 (d, $^4J_{PF}$: 61 Hz). The unusual high value of the coupling constant $^4J_{PF}$ is due to the proximity of P and F atoms.[12]

Reduction of **2** by tri-*n*-butyltinhydride led to the primary phosphine **3** (attempts to reduce **2** by lithium aluminium hydride failed because of a cleavage of the CF_3—C bond):



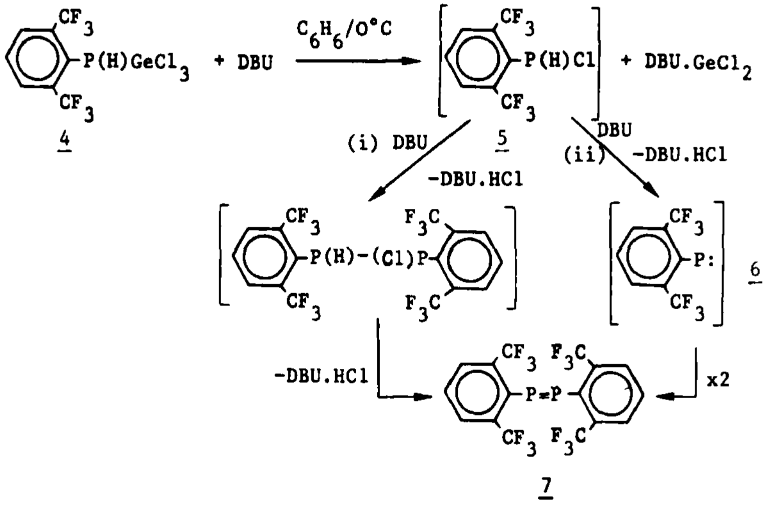
3: NMR: ^1H: δ 3.90 (sept d, PH, $^1J_{PH}$ 214 Hz, $^5J_{FH}$ 5 Hz), 6.90–7.60 (m, arom H). $^{31}P\{^1H\}$: δ −142.7 (sept, $^4J_{PF}$ 29.4 Hz), ^{19}F: +17.0 (dt, $^4J_{PF}$ 29.4 Hz, $^5J_{HF}$ 5.0 Hz); IR (neat): ν_{PH}: 2370 cm^{-1}.

As classical routes to diphosphenes (reaction of dichlorophosphines with magnesium, lithio compounds, etc. . .)[2] were unsuccessful, we have used the organogermanium way previously described for the synthesis of the dibisyldiphosphene.[5] This method needs the preparation of the trichlorogermylphosphine **4** which has been obtained in nearly quantitative yield from **3** and $GeCl_4$:



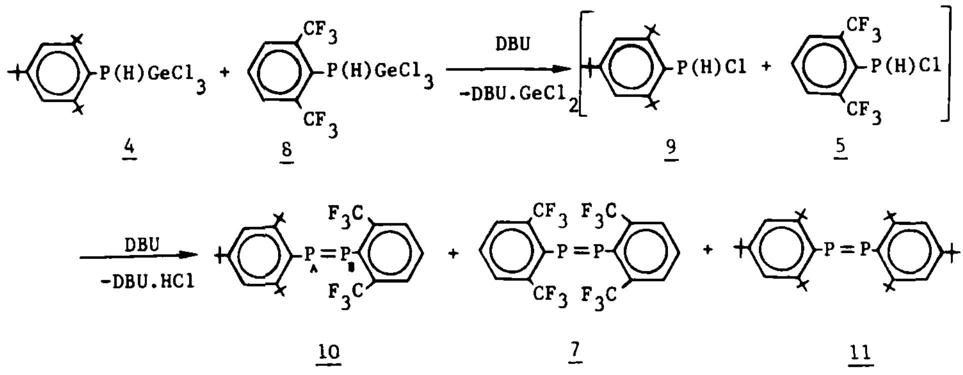
4: NMR, ^1H: δ 4.40 (sept d, PH, $^1J_{PH}$ 218 Hz, $^5J_{FH}$ 4.5 Hz), 6.90–7.43 (m, arom. H). $^{31}P\{^1H\}$: −77.8 (sept, $^4J_{PF}$ 29.2 Hz), ^{19}F: δ +21.4 (dd, $^4J_{PF}$: 29.2 Hz, $^5J_{HF}$ 4.5 Hz); IR (nujol): ν(PH): 2350 cm^{-1}.

Addition of **4** to a twofold excess of DBU led to the new diphosphene **7**. As previously demonstrated,[5,13] the first step of this reaction is the formation of the complex DBU·$GeCl_2$ and of the chlorophosphine **5**. We postulate two competitive reactions with the excess of DBU (i) intermolecular dehydrochlorination and (ii) intramolecular dehydrochlorination via a phosphinidene intermediate **6**:



After filtration and elimination of the solvent in vacuo, crude **7** was obtained in 60% yield and recrystallized from pentane as very pale yellow crystals; NMR ^{1}H: δ 6.46–7.48 (m, arom. H). $^{31}P\{^{1}H\}$: δ +477.1, $X_6AA'X'_6$ type spectrum but, as $|^{1}J_{AA'}| \gg |^{4}J_{AX} - {}^{5}J_{AX'}|$, this system becomes approximately an X_2A_{12} spectrum: 13 peaks separated by 23.0 Hz. This extremely low field chemical shift in ^{31}P NMR is characteristic of a diphosphene structure.[2–9] ^{19}F: δ +22.8 (pseudo-triplet, $^{4}J_{FP} + {}^{5}J_{FP}$: 46.0 Hz). U.V. (cyclohexane): 394 nm (ε: 197), $n \rightarrow \pi^*$; 277 nm (ε: 11640), $\pi \rightarrow \pi^*$. In U.V., it is interesting to note the very important differences of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions (about 70 nm) between diphosphene **7** and other diphosphenes;[2] this ipsochromic shift is due to the great electronic effect of 2,6-bis(trifluoromethyl)phenyl group which strongly decreases the availability of *n* and π electrons.

Another purpose of this work was the synthesis of the unsymmetric diphosphene **10**. Using the same method as for **7**, we prepared **10** from an equimolar mixture of trichlorogermylphosphines **4** and **8**:[13]



The three expected diphosphenes were formed in the relative proportions **7** (30%), **10** (60%), **11** (10%), and separated by column chromatography on silica. **10** NMR ^{1}H: δ 1.33 (s, *p*-*t*-Bu), 1.61 (s, *o*-*t*-Bu), 6.35–7.63 (m, arom. $C_6H_3(CF_3)_2$), 7.66 (dd, $^{4}J_{HP}$: 1.6 Hz, $^{5}J_{HP}$: 1.0 Hz, arom. C_6H_2 (tBu)$_3$). $^{31}P\{^{1}H\}$: δ P_A: 533.0 (sept., d, $^{5}J_{PF}$: 17.9 Hz), $^{1}J_{PP}$: 574.3 Hz (see Figure 1) P_B: 422.1 (sept., d, $^{4}J_{PF}$: 23.5 Hz) ^{19}F: δ +22.6 (dd, $^{4}J_{PF}$: 23.5, $^{5}J_{PF}$: 17.9 Hz) U.V. (cyclohexane) 437 nm (ε: 880), $n \rightarrow \pi^*$; 298 nm (ε: 23950), $\pi \rightarrow \pi^*$; 246 nm (ε: 21000):

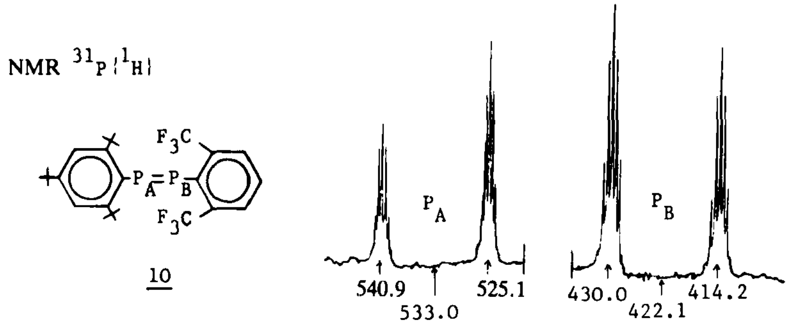


FIGURE 1

These results show that the 2,6-bis(trifluoromethyl)phenyl group is very effective in stabilizing low-coordinated phosphorus species. Moreover, the study of the reactivity of diphosphenes **7** and **10**, now in progress, should allow us to determine the electronic influence of this group on the phosphorus-phosphorus double bond.

EXPERIMENTAL

All syntheses were performed under an atmosphere of dry nitrogen. Solvents were dried by distillation from benzophenone ketyl immediately prior to use. Commercial 1,3-bis(trifluoromethyl)benzene was purchased from Alfa. ^{1}H NMR spectra were recorded at 60 MHz on a Varian EM 360 A. ^{31}P and ^{19}F NMR spectra were recorded at 36.4 MHz (Bruker WH 90) and 84.6 MHz (Perkin Elmer) respectively.[11]

Melting points are uncorrected. Elemental analyses were performed at the "Service Central de Microanalyse du CNRS" à Vernaison (France).

Synthesis of the [2,6-bis(trifluoromethyl)phenyl]dichlorophosphine **2**

A solution of the *n*-butyllithium-TMEDA complex (prepared from TMEDA (5.69 g, 49 mmoles), 29.2 ml of a solution of *n*-butyllithium 1.6 M in diethylether (46.7 mmoles) and 10 ml of diethylether) was added to 10.0 g (46.7 mmoles) of 1,3-bis(trifluoromethyl)benzene in 30 ml of the same solvent at 0°C. The reaction mixture becomes dark brown; after stirring overnight at room temperature it is slowly added to a solution of phosphorus trichloride (12.85 g, 93.4 mmoles) in 30 ml of diethylether at −78°C. The reaction mixture is then allowed to warm to room temperature, and 50 ml of pentane are added. After centrifugation and elimination of solvents in vacuo, distillation afforded 4.5 g of dichlorophosphine **2** (b.p. 80°C/10^{-1} mm, 30% yield).

Anal. $C_8H_3Cl_2F_6P$, Calc. C 30.50, H 0.97; Found C 30.71, H 1.06

Synthesis of the 2,6-bis(trifluoromethyl)phenylphosphine **3**

To 3 g of **2** (9.52 mmoles) in solution of 20 ml of diethylether are added at 0°C two equivalents of tributyltinhydride (5.53 g, 19.04 mmoles). The reaction mixture is then stirred two hours at room temperature and distilled to give 1.9 g of **3** (b.p. 70°C/20 mm, 80% yield).

Anal. $C_8H_5F_6P$, Calc. C 39.04, H 2.05 Found C 38.87, H 2.07

Synthesis of [2,6-bis(trifluoromethyl)phenyl]trichlorogermylphosphine **4**

A mixture of **3** (1.9 g, 7.72 mmoles), germanium tetrachloride (6.63 g, 30.90 mmoles) and 10 ml of dioxane was heated at 110°C for 24 h. After elimination of the excess of $GeCl_4$, we obtained a white product identified to **4** (2.88 g, 88% yield). **4** can also be prepared by heating a mixture of **2** (1.50 g, 4.76

mmoles) and $GeCl_2$. Dioxane complex (1.1 g, 4.76 mmoles) in refluxing dioxane for 3 hours in about 50% yield (1.07 g). **4** is only slightly soluble in C_6H_6.

Synthesis of bis[2,6-bis(trifluoromethyl)phenyl]diphosphene **7**

To a solution of **4** (2.25 g, 5.30 mmoles) in 15 ml of benzene were added two equivalents of DBU in the same solvent. The reaction is slightly exothermic. After elimination of the precipitate of DBU·HCl and DBU·$GeCl_2$, the resulting crude **7** was purified by column chromatography on silica (eluent: diethylether), and recrystallized in pentane to give 0.62 g of light yellow crystals (mp 167–170°C (dec.), 60% yield).

Anal. $C_{16}H_6F_{12}P_2$, Calc. C 39.37, H 1.24; Found C 39.48, H 1.42

Synthesis of the dissymetrical diphosphene **10**

To a mixture of **4** (obtained from 1.16 g, (4.70 mmoles) of **3**) and **8** (prepared according to the same experimental process than **4** from 1.30 g (4.70 mmoles) of (2,4,6-tri-tert-butylphenylphosphine) in 20 ml C_6H_6 was added an excess of DBU (2.88 g, 19.00 mmoles). After filtration of the precipitate of DBU·HCl and DBU·$GeCl_2$, chromatography on silica allowed the separation of the three diphosphenes (elution with pentane for **10** and **11** and diethylether for **7**). **10** was recrystallized from pentane to give light yellow crystals (0.85 g, 35% yield, mp 136–139°C).

Anal. $C_{26}H_{32}F_6P_2$, Calc. C 60.00, H 6.20; Found C 59.87, H 6.26

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