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Preparation and Properties of Captodative 1-Amino-2-aryldiphosphenes Carrying Bis(trifluoromethyl)phenyl or Tris(trifluoromethyl)phenyl Group

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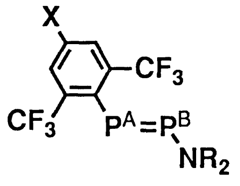
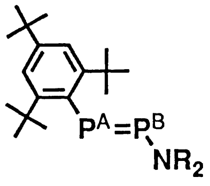
Novel 1-amino-2-aryldiphosphenes carrying 2,6-bis(trifluoromethyl)phenyl or 2,4,6-tris(trifluoromethyl)phenyl group as an aryl substituent were prepared and the push-pull substituent effect on -P=P- was demonstrated by ^{31}P NMR.

Compounds with multiple bonds involving the heavier main group elements are of current interest. There have been several reports on diphosphenes stabilized by bulky substituents.$^{1)}$ Diphosphenes substituted with electron donating groups such as 1-dialkylamino-2-aryldiphosphenes$^{2)}$ are known and those with electron withdrawing groups such as bis(trifluoromethyl)phenyl and tris(trifluoromethyl)phenyl$^{3)}$ are also known. However, to the best of our knowledge, diphosphenes bearing an electron donating group on one phosphorus and an electron withdrawing group on the other have not been reported yet. Such captodative diphosphenes would be interesting because each phosphorus atom is supposed to have an opposite electronic character. In such diphosphenes, the phosphorus-phosphorus double bonds are expected to be polarized to some extent. We now wish to report here the preparations and properties of several novel captodative diphosphenes such as 1-amino-2-aryldiphosphenes **1a–d** carrying 2,6-bis(trifluoromethyl)phenyl or 2,4,6-tris(trifluoromethyl)phenyl group as an electron withdrawing substituent and dialkylamino groups as an electron donating substituent.$^{4)}$



1a: X=H, R=c-C_6H_{11}
1b: X=H, NR_2=Tmp
1c: X=H, R=Me_3Si
1d: X=CF_3, R=c-C_6H_{11}

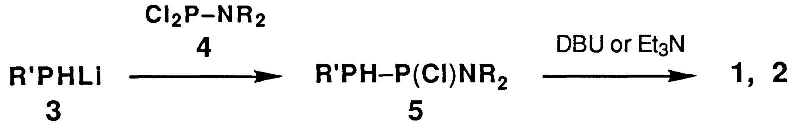


2a: R=c-C_6H_{11}
2b: NR_2=Tmp
2c: R=Me_3Si

Tmp: 2,2,6,6-tetramethylpiperidino

Diphosphenes **1** and **2a** were prepared as shown below. Lithium phosphide **3** was prepared by lithiation of the corresponding primary phosphine with butyllithium and was allowed to react with phosphoramidous dichloride **4**. Base induced dehydrochlorination of the resulting chlorodiphosphanes **5** afforded the diphosphenes. Typical procedure of the preparations of **1a-d** and **2a** is as follows: 2,6-Bis(trifluoromethyl)phenylphosphine$^{3a)}$ (241.2 mg, 0.98 mmol) was lithiated with 1.01 mmol of butyllithium (1.68 M in hexane) in tetrahydrofuran (THF; 3 ml) at –78 °C. This was added to a stirred solution of *N*,*N*-

dicyclohexylphosphoramidous dichloride[5] (200.0 mg, 0.71 mmol) in THF (3 ml) at –78 °C. The solution was allowed to warm to room temperature and treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 0.08 ml, 0.53 mmol). After stirring for 2 h, the solvent was removed under vacuum. Pentane (10 ml) was added to the residue and the insoluble material was removed by filtration. The filtrate was concentrated to afford **1a** (147.0 mg, 46% yield) as orange crystals: Mp 41 – 43 °C (decomp); ^1H NMR (200 MHz, $CDCl_3$) $\delta = 0.70 - 2.15$ (20H, m, CH_2), 3.79 (2H, bs, $NC\underline{H}$), and 7.35 – 8.05 (3H, m, arom.); UV (pentane) 265 (log ε 3.3), 327 (2.9), and 374 nm (2.9); MS (70 eV) *m/z* 455 (M^+). The diphosphenes **1** and **2** thus prepared were relatively stable under an inert atmosphere, however, they decomposed rapidly on exposure to air and/or moisture. Thus attempted purification of **1b-d** has been unsuccessful due to their facile decomposition.



$$\underset{\textbf{3}}{R'PHLi} \xrightarrow{\overset{Cl_2P{-}NR_2}{\textbf{4}}} \underset{\textbf{5}}{R'PH{-}P(Cl)NR_2} \xrightarrow{DBU\ or\ Et_3N} \textbf{1, 2}$$

R' = 2,6-$(CF_3)_2C_6H_3$, 2,4,6-$(CF_3)_3C_6H_2$, or 2,4,6-$Bu^t{}_3C_6H_2$
$NR_2 = N(c\text{-}C_6H_{11})_2$, Tmp, or $N(SiMe_3)_2$
DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene

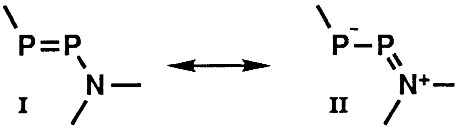
Table 1. ^{31}P NMR Data of the Diphosphenes **1** and **2**

Compds	$\delta_P(A)$	($^4J_{PF}$ / Hz)	$\delta_P(B)$	($^5J_{PF}$ / Hz)	$^1J_{PP}$ / Hz	Solvent[a]
1a	228.7	(26.7)	471.3	(17.2)	538.3	A
1b	287.8	(26.0)	482.3	(21.0)	570.6	A
1c	373.7	(23.7)	539.9	(17.2)	577.4	A
1d	224.5	(26.9)	470.2	(19.1)	538.9	A
(*E*)-**2a**[6]	270.2	—	448.8	—	543.5	A
(*Z*)-**2a**[6]	153.1	—	335.5	—	591.6	B
2b[2a]	336.1	—	460.7	—	579.9	THF
2c[2a]	409.3	—	501.5	—	584.2	hexane

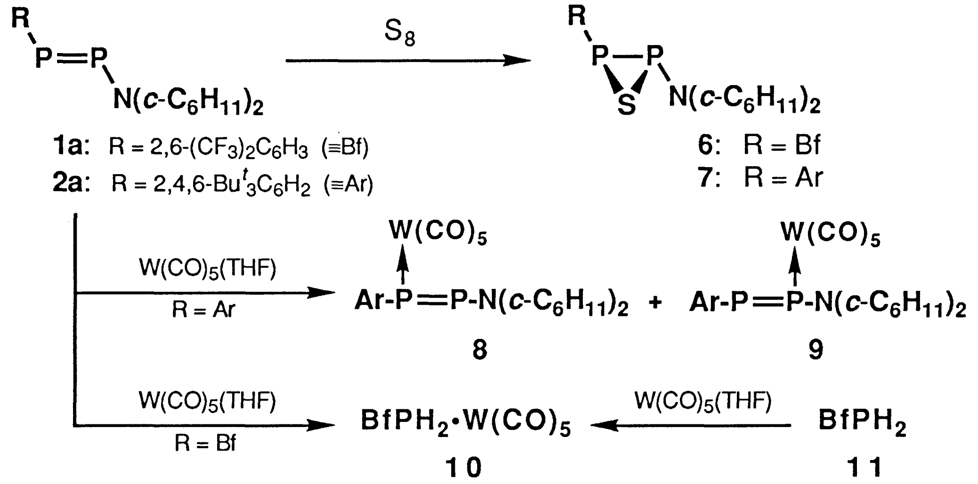
a) A: $CDCl_3$ / THF (1:3); B: $CDCl_3$ / Et_2O (1:3).

The ^{31}P NMR spectra of the diphosphenes **1a-d** showed ABX_6 pattern unequivocally characteristic of unsymmetrical diphosphenes and the peak assignment was made on the basis of the spin-coupling with the fluorine nuclei.[3] Table 1 shows that the aryl-substituted phosphorus atoms (P^A) are strongly shielded by 150 – 250 ppm compared with those of the amino-substituted phosphorus atoms (P^B). Furthermore, the substituent effect on the ^{31}P chemical shifts of the fluoroaryl substituents, 2,6-bis(trifluoromethyl)phenyl and 2,4,6-tris(trifluoromethyl)phenyl in **1a-d**, is demonstrated by comparing their ^{31}P chemical shifts with those of **2a-c** possessing 2,4,6-tri-*t*-butylphenyl group as an aryl moiety. The P^A atoms of diphosphenes **1a-d** exhibit the shifts to the higher field ($|\Delta\delta_P(A)| = 36 - 48$ ppm) compared with those of the corresponding **2a-c**, respectively, while the P^B atoms in **1a-d** exhibit the shifts to the lower field ($|\Delta\delta_P(B)| = 21 - 38$ ppm). This can be interpreted in terms of the increase in the polarization on phosphorus-phosphorus double bonds. Thus, in the resonance structures of PPN π-system[7] shown below, the contribution of the zwitter ionic form

(II) in **1** seems to play the more important role than **2**, due to the polarization caused by push-pull or captodative substituents on -P=P-.



Furthermore, we investigated some reactivities of polarized **1a** and **2a**. It is known that bis(2,4,6-tri-*t*-butylphenyl)diphosphene reacts with elemental sulfur in triethylamine to give thiadiphosphirane[8] via diphosphene sulfide.[9] The reaction of the diphosphene **1a** with elemental sulfur in toluene at room temperature overnight afforded the corresponding thiadiphosphirane **6**, which decomposed during column chromatography. **6**: ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$) δ = –25.0 ($^{5}J_{\mathrm{PF}}$ = 18.3 Hz) and –132.1 ($^{4}J_{\mathrm{PF}}$ = 41.4 Hz), ABX$_6$, $^{1}J_{\mathrm{PP}}$ = 250.0 Hz. Formation of the diphosphene sulfide has not been observed during the reaction monitored by ^{31}P NMR spectroscopy. The diphosphene **2a** also gave thiadiphosphirane **7** under the similar conditions. **7**: Colorless crystals; mp 176 – 178 °C; ^{1}H NMR (200 MHz, CDCl$_3$) δ = 0.9 – 1.9 (20H, m, CH$_2$), 1.24 (9H, s, *p*-Bu^{t}), 1.63 (18H, s, *o*-Bu^{t}), 2.72 (2H, bs, NCH), and 7.10 (2H, s, arom.); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$) δ = –4.7 and –113.7, ABq, $^{1}J_{\mathrm{PP}}$ = 251.1 Hz; IR (KBr) 1053 cm^{-1}; MS (70 eV) *m/z* 519 (M^{+}).



The reaction of **2a** with W(CO)$_5$(THF) in THF at 60 °C for 12 h gave a mixture of tungsten pentacarbonyl complexes **8** and **9** in 3:1 ratio. **8**: ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$) δ = 395.3 (satellite, $^{1}J_{\mathrm{P^{183}W}}$ = 272.7 Hz) and 451.6, ABq, $^{1}J_{\mathrm{PP}}$ = 559.9 Hz; **9**: ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$) δ = 149.9 and 296.0 (satellite, $^{1}J_{\mathrm{PW}}$ = 258.4 Hz), ABq, $^{1}J_{\mathrm{PP}}$ = 641.5 Hz. In the ^{31}P NMR spectra of **8**, the signal of the higher field was accompanied with doublet satellite signal due to ^{183}W of natural abundance, which indicated that the tungsten atom is bound to the aryl-substituted phosphorus atom. On the other hand, in the case of **9**, the signal of the lower field was associated with satellite signal.[10] A similar complex formation reaction of **1a** with W(CO)$_5$(THF) in THF at room temperature for 10 h resulted in the formation of phosphine complex **10**. **10**: ^{31}P NMR (81 MHz, CDCl$_3$) δ = –105.3 (t of sept, $^{1}J_{\mathrm{PH}}$ = 356.4 Hz and $^{4}J_{\mathrm{PF}}$ = 18.1 Hz; satellite, $^{1}J_{\mathrm{PW}}$ = 231.3 Hz). Although the attempted isolation of **10** by silica-gel column chromatography has not been successful, the structure of **10** was confirmed by a separate preparation of **10** from 2,6-bis(trifluoromethyl)phenylphosphine (**11**).[3a]

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6) The diphosphene (*E*)-**2a** was prepared by the method described in the text in 24% yield: Yellow prisms; mp 65 – 68 °C; ^{1}H NMR (200 MHz, C_6D_6) δ = 1.0–2.1 (20H, m, CH_2), 1.30 (9H, s, *p*-Bu^t), 1.69 (18H, s, *o*-Bu^t), 3.77 (2H, bs, NC$\underline{H}$), and 7.58 (2H, s, arom.); $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6) δ = 270.9 and 450.3, ABq, $^1J_{PP}$ = 543.7 Hz; UV (CH_2Cl_2) 247 (log ε 4.0), 360 (3.5), and 386 nm (3.6); IR (KBr) 1059 and 638 cm^{-1}; MS (70 eV) *m/z* 487 (M^+). The intermediate chlorodiphosphane (**5**: R=*c*-C_6H_{11}; R'=2,4,6-$Bu^t_3C_6H_2$) was observed by ^{31}P NMR as a diastereomeric mixture (3:2 ratio): Major: δ_P($CDCl_3$ / Et_2O) = –65.7 (d, $^1J_{PH}$ = 176.2 Hz) and 160.9 (s), ABq, $^1J_{PP}$ = 176.5 Hz; minor: δ_P = –38.2 (d, $^1J_{PH}$ = 221.7 Hz) and 166.4 (s), ABq, $^1J_{PP}$ = 248.9 Hz. As an alternate preparation, when lithium 2,4,6-tri-*t*-butylphenyl(trimethylsilyl)phosphide was allowed to react with *N,N*-dicyclohexylphosphoramidous dichloride in Et_2O, the formation of (*Z*)-**2a** was first observed as a major product by ^{31}P NMR and the (*Z*)-diphosphene gradually isomerized to (*E*)-form in Et_2O at room temperature.

7) Recently, Niecke *et al.* have reported the formation of several compounds of 4e-3c-PPN π-system: E. Niecke, B. Kramer, and M. Nieger, *Angew. Chem., Int. Ed. Engl.*, **28**, 215 (1989); E. Niecke, O. Altmeyer, and M. Nieger, *ibid.*, **30**, 1136 (1991).

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10) At present, we cannot assign the *E/Z* configuration of either **8** or **9**, since an attempted reaction of (*Z*)-**2a** with $W(CO)_5(THF)$ afforded the same reaction products, **8** and **9**.

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