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X-Ray Analysis of a Captodative Diphosphene, 1-(*N*-Mesityl-9-fluorenylamino)-2-[2,4,6-tris(trifluoromethyl)phenyl]diphosphene

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Synopsis. The *N*-mesityl-9-fluorenylamino group was utilized as an electron-donating new sterically protecting group for stabilizing low coordinate organophosphorus compounds. A push-pull substituent effect on the P–P double bond was demonstrated by the X-ray analysis of a captodative diphosphene, 1-(*N*-mesityl-9-fluorenylamino)-2-[2,4,6-tris(trifluoromethyl)phenyl]diphosphene.

Compounds with multiple bonds involving phosphorus1) have attracted considerable attention because of their unusual bonding nature. Utilizing an extremely bulky 2,4,6-tri-*t*-butylphenyl moiety as a sterically protecting group, we were successful in preparation of diphosphene **1** as a stable compound.2) We have recently reported the preparation and properties of some push-pull diphosphenes such as 1-(*N*-mesityl-9-fluorenylamino)-2-[2,4,6-tris(trifluoromethyl)phenyl]-diphosphene **2** [abbreviated to (Flu)(Mes)NP=PAf, where Flu=9-fluorenyl; Mes=mesityl; Af=2,4,6-tris(trifluoromethyl)phenyl] carrying both an electron-withdrawing fluoroaromatic group and an electron-donating dialkylamino group.3,4) Such captodative diphosphene is of interest because each phosphorus atom is supposed to have an opposite electronic character. We report here the X-ray structure of **2** and MO calculations of a captodative push–pull model compound, 1-dimethylamino-2-[2,4,6-tris(trifluoromethyl)phenyl]diphosphene, **3** (Scheme 1).

Results and Discussion

The $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectrum of the diphosphene **2** showed an ABX$_6$ pattern. The peak due to the phosphorus atom (P$^{\mathrm{A}}$), β to the nitrogen atom, appears at higher field than the peak due to the nitrogen-substituted phosphorus atom (P$^{\mathrm{B}}$).5,6) The observed phosphorus-fluorine spin-spin couplings ($^{4}J_{\mathrm{PF}}$ and $^{5}J_{\mathrm{PF}}$) in **2** were consistent with the above assignments.4) Thus, among the resonance structures of P–P–N π-system,5) the contribution of the zwitter ionic form (III) in Scheme 2 seems to be important, due to the polarization caused by push–pull substitution on the phosphorus–phosphorus double bond.

Figure 1 depicts an ORTEP drawing7) of the molecular structure of diphosphene **2** with the atom labeling scheme. The atoms P1, P2, N3, C4, C17, and C26 are almost coplanar within 0.061(4) Å, indicating that the nitrogen atom is of an sp^2 configuration in the 4e-3c P–P–N π-system as in the case of **4**, reported by Niecke et al.5) The Af group, the Mes group, and the Flu group make angles of 84.7(3)°, 81.6(3)°, and 62.3(2)° to this P–P–N π plane, respectively. Therefore, the P–P double bond is protected effectively by the Af, Flu, and Mes groups as is shown in Fig. 1. *o*-Trifluoromethyl groups of the Af group and *o*-methyl groups of the Mes group sandwich the P–P–N π-system from above and below. The Flu group covers the P$^{\mathrm{B}}$ part from the side of the P–P–N π-plane due to an sp^3 configuration at C4.

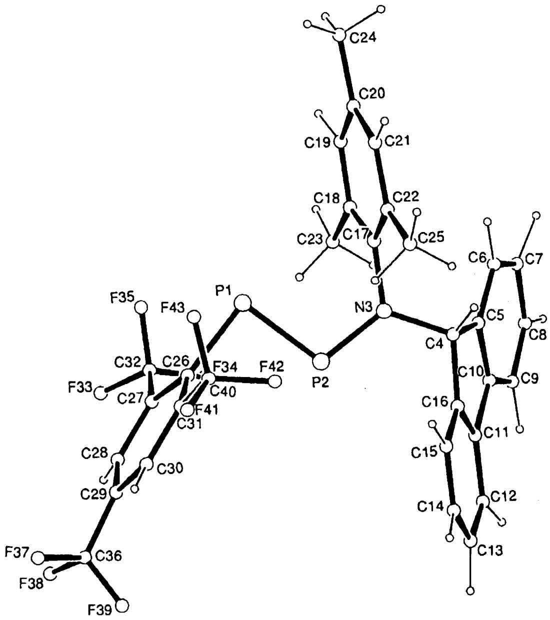
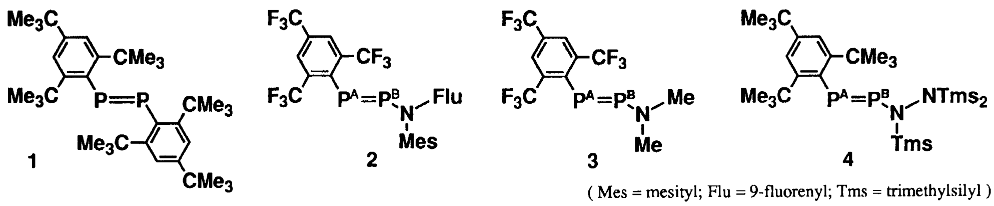


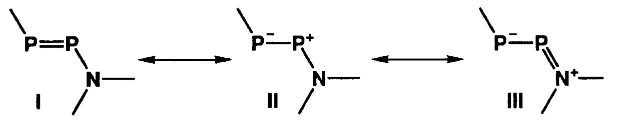
Fig. 1. Molecular structure of diphosphene **2** with the atom labeling scheme. *p*-Trifluoromethyl group on C29 is disordered and one with the higher occupancy factor is shown for clarity.

Some important bond lengths and angles, and dihedral angles are listed in Table 1 for diphosphenes **2**, **4**,5) and **1**.2) The bond angle ∠P–P–N is larger than ∠P–P–C for both **2** and **4**. Although the bond length of P–P for **2** is almost the same as that for **1** or **4**, the bond length of P–N for **2** is significantly shorter than that for **4** or the P–N bond length of 1.77(2) Å for sodium hydrogenphosphoramidate, NaPO$_3$NH$_3$,8) suggesting again that the contribution of III (Scheme 2) is important in **2**. Furthermore, the bond angle ∠P2–P1–C26 is almost at right angle for **2**, suggesting the increased s-character in the P=P system of **2**. Thus the coupling constant $^{1}J_{\mathrm{PP}}$ observed for **2** (531.7 Hz) is larger than that reported for **4** ($^{1}J_{\mathrm{PP}}$=516 Hz).5)



(Mes = mesityl; Flu = 9-fluorenyl; Tms = trimethylsilyl)

Scheme 1.



Scheme 2.

Table 1. Some Important Bond Lengths and Bond and Dihedral Angles for **2**, **4**, and **1**[a)]

Bond distance and bond and dihedral angles	**2**	**4**[b)]	**1**[c)]
P–P/Å	2.040(2)	2.037(2)	2.034(2)
P–C/Å	1.871(6)	1.864(4)	1.862(2)
P–N/Å	1.668(5)	1.700(3)	—
P–P–C/°	90.4(2)	97.6(1)	102.8(1)
P–P–N/°	104.5(2)	106.1(1)	—
C–P–P–N/°	176.9(2)	179.4(3)	172.2(1)[d)]

a) Standard deviations of the least significant figures are given in parentheses. b) Data taken from Ref. 5. c) Data taken from Ref. 2. d) The dihedral angle of CPPC for **1**.

Computer calculations for AfP=PNMe$_2$ **3** as a model of push–pull diphosphene were carried out using the CAChe-MOPAC program.[9)] Figure 2 shows its HOMO and LUMO orbitals calculated by the semiempirical PM3 SCF-MO method[10)] for the energy-optimized conformation. The calculated Mulliken partial charges of the P–P–N system in **3** show that P^A (−0.0904 a.u.) is far electronegative than P^B (+0.2523 a.u.) affecting the ^{31}P NMR chemical shifts for **2**, δ_{PA} 254.0 and δ_{PB} 478.4, respectively. Another amino-substituted diphosphene **4**,[5)] shows similar chemical-shift difference indicating slightly less important contribution of II or III, taking δ_P 311 for P^A and δ_P 481 for P^B into account. Furthermore, the captodative substitution effect was also demonstrated in the reaction of **2** with nucleophiles such as butyllithium to give diphosphane AfP(H)–P(*n*-Bu)–N(Mes)(9-Flu).[4)] In this reaction, the nucleophile attacked the relatively positive phosphorus atom P^B, or rather the nucleophilic reaction occurred in a LUMO-controlled manner.

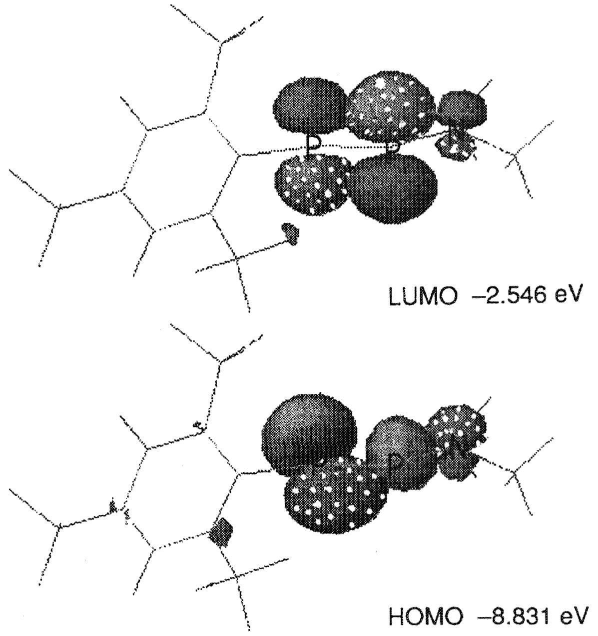


Fig. 2. Calculated HOMO and LUMO orbitals for a push–pull diphosphene **3**.

Experimental

1-(*N*-Mesityl-9-fluorenylamino)-2-[2,4,6-tris(trifluoromethyl)phenyl]diphosphene (2). Starting from 2,4,6-tris(trifluoromethyl)phenylphosphine, **2** was prepared according to the method reported previously.[4)] Pale yellow crystals; mp 167—169 °C (hexane); ^{31}P {^{1}H} NMR δ=254.0 (d of sept, $^1J_{PP}$=531.7 Hz, $^4J_{PF}$=25.8 Hz, P^A) and 478.4 (d of sept, $^1J_{PP}$=531.7 Hz, $^5J_{PF}$=18.7 Hz, P^B).

X-Ray Crystal Structure Determination of 1-(*N*-Mesityl-9-fluorenylamino)-2-[2,4,6-tris(trifluoromethyl)phenyl]diphosphene (2). The diphosphene **2** was recrystallized from hexane. $C_{31}H_{22}F_9NP_2$, M_r=641.454. Orthorhombic, space group $P2_12_12_1$, a=21.682(3), b=17.016(3), c=8.144(1) Å, U=3004.3(8) Å^3, Z=4, D_c=1.418 g cm^{-3}, μ=2.16 cm^{-1}. 3016 Reflections with $2\theta \leq 50.0°$ were recorded on a four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Of these, 2520 with $I>3\sigma(I)$ were judged as observed. The structure was solved using SHELX86.[11)] The disordered *p*-trifluoromethyl group was resolved into two positions of CF$_3$ groups from the difference maps. Their occupancy factors were refined to be 0.70 and 0.30. H-atoms and the disordered atoms were refined isotropically. Full-matrix least-squares refinement with anisotropic temperature factors for nonhydrogen atoms converged to R=0.081 and R_w=0.117.[12)] Atomic coordinates and thermal parameters and bond lengths and angles have been deposited as Document No. 66057 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Molecular Orbital Calculation of 1-Dimethylamino-2-[2,4,6-tris(trifluoromethyl)phenyl]diphosphene (3). Computer calculations were carried out by the CAChe–MOPAC program (Release 6.1).[9)] Semiempirical

PM3 SCF-MO calculations[10] were executed to search an energy-optimized conformation for **3**. Some important bond lengths and angles and a dihedral angle for the energy-minimum conformation for **3** with the heat of formation of -397.943 kcal mol^{-1} were as follows: P–N, 1.747 Å; P–P 2.011 Å; C–P, 1.888 Å $\angle$CPP, 112.5°; $\angle$NPP, 107.3°; $\angle$CPPN, $-173.2°$; the tilt angle of the Af plane to the NPPC plane is 72.2°. The HOMO and LUMO orbital energies were -8.831 eV and -2.546 eV, respectively.

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