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Preparation and Structure of Phenyldithioxophosphoranes Carrying *t*-Butyl and Dimethylaminomethyl or Dimethylaminoethyl Groups at the ortho-Positions

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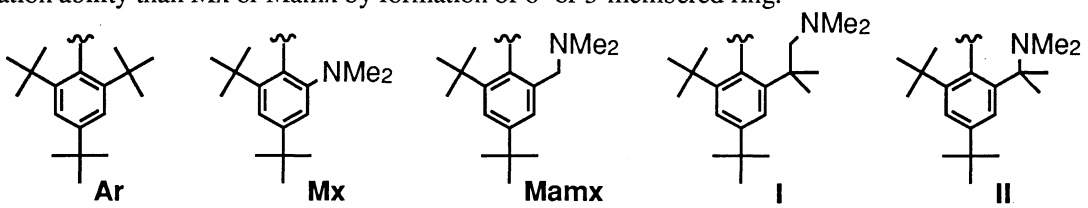
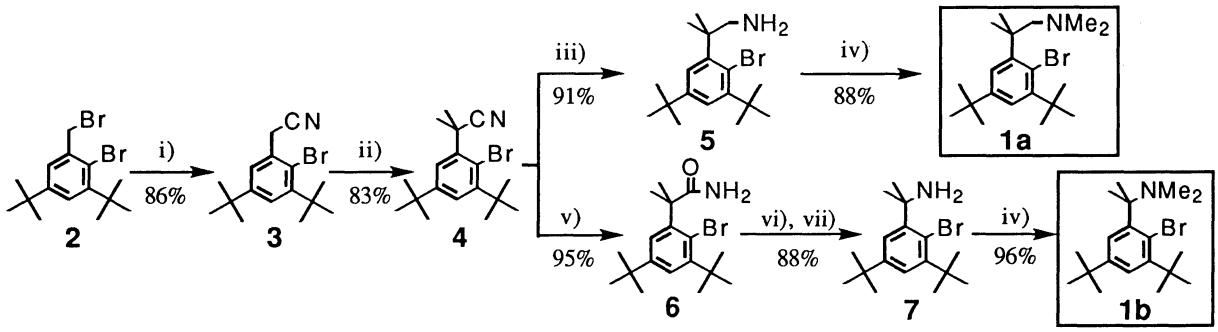
Dithioxophosphoranes and thioxophosphines carrying 2,4-di-*t*-butyl-6-(aminoalkyl)-phenyl groups were prepared and characterized. The intramolecular coordination of the nitrogen lone pair to the phosphorus atom was indicated by NMR and IR spectroscopy and was confirmed by X-ray crystallography.

Kinetic stabilization using bulky protecting groups is a useful method for investigation of low coordinated phosphorus compounds. Utilizing the extremely bulky 2,4,6-tri-*t*-butylphenyl (hereafter abbreviated to Ar group) as a sterically protecting auxiliary, we and others have successfully prepared various types of multiply bonded phosphorus compounds such as diphosphenes[1] and dithioxophosphorane.[2] However, thioxophosphines are too reactive to be isolated even if being sterically protected with the Ar group.[2c,3]

On the other hand, thermodynamic stabilization is an alternative method of stabilization of thioxophosphines. Recently, we have developed some novel stabilizing groups, such as 2,4-di-*t*-butyl-6-(dimethylamino)phenyl (Mx group)[4] and 2,4-di-*t*-butyl-6-(dimethylaminomethyl)phenyl (Mamx group),[5] having electron donating groups in their moieties. Using these substituents, dithioxophosphoranes as well as selenoxo- and thioxophosphines were prepared as stable compounds. In these compounds, the phosphorus-sulfur bonds are stabilized by both steric protection of the *o*-*t*-butyl group and thermodynamic stabilization caused by intramolecular coordination of the amino group of the substituents at ortho position. Now we developed novel stabilizing groups, 2,4-di-*t*-butyl-6-[1,1-dimethyl-2-(dimethylamino)ethyl]phenyl (**I**) and 2,4-di-*t*-butyl-6-[1-(dimethylamino)-1-methylethyl]phenyl (**II**), which are expected to have more protecting and coordination ability than Mx or Mamx by formation of 6- or 5-membered ring.



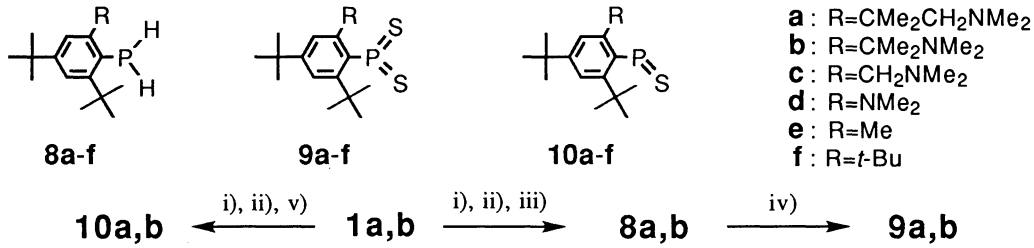
Sterically hindered bromobenzenes **1a**,**b**[6] were prepared from 2-bromo-1-(bromomethyl)-3,5-di-*t*-butylbenzene (**2**)[7] as shown in Scheme 1 via **3**, **4**, and **5** (57% overall yield of **1a**) or via **3**, **4**, **6**, and **7** (57% overall yield of **1b**) by the analogous method reported previously.[8] The bromobenzene **1a** (368 mg; 1.08 mmol) was lithiated with butyllithium (1.5 equiv) under argon in ether (20 mL) at 0 °C and the resulting solution was added to an ethereal (20 mL) solution of PCl_3·(1.5 equiv), then the product was treated with lithium



i) KCN, 18-crown-6 / CH_3CN, H_2O; ii) CH_3I, NaOH, 18-crown-6 / DMSO, H_2O; iii) $LiAlH_4$ / Et_2O; iv) HCHO (aq), $NaBH_3CN$, AcOH / CH_3CN; v) H_2SO_4, AcOH, H_2O; vi) NaOMe, Br_2 / MeOH; vii) KOH, 18-crown-6 / DMSO, H_2O.

Scheme 1.

aluminum hydride (2.0 equiv) to give the corresponding phosphine **8a**. The phosphine **8a** thus obtained was allowed to react with S_8 (5.4 mmol as S) in benzene (10 mL) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 0.3 equiv) at room temperature for 10 h to give the corresponding dithioxophosphorane **9a** (13% yield based on **1a**). Very similarly, **9b** was prepared from **1b** (3% yield based on **1b**). Formation of thioxophosphines **10a,b** was observed by ^{31}P NMR and MS spectroscopy by the successive reaction of **1a,b** with butyllithium (1.6 equiv), PCl_3 (1.6 equiv), and hexamethyldisilathiane (0.5 equiv) as shown in Scheme 2.



a: R=$CMe_2CH_2NMe_2$
b: R=CMe_2NMe_2
c: R=CH_2NMe_2
d: R=NMe_2
e: R=Me
f: R=*t*-Bu

i) *n*-BuLi / Et_2O; ii) PCl_3 / Et_2O; iii) $LiAlH_4$ / Et_2O; iv) S_8, DBU / C_6H_6; v) $(Me_3Si)_2S$, NEt_3 / Et_2O.

Scheme 2.

^{31}P NMR chemical shifts of the compounds **8a,b**, **9a,b**, **10a,b** and other related compounds are listed in Table 1. As for the phosphines **8a-f**, the effect of the amino group on the chemical shift are not apparent.[9] On the contrary, interaction of nitrogen to phosphorus in the dithioxophosphoranes **9a-d** is clearly shown by ^{31}P NMR spectroscopy. The signals due to the dithioxophosphoranes **9a-d** appear at higher field by ca. 150 ppm than that of **9e,f**. This up-field shift is ascribable to the coordination of the nitrogen lone pair to the phosphorus atom in **9a-d**. In the case of **9a**, such internal coordination is performed by forming 6-membered ring, while 5- or 4-membered ring is formed in the case of **9b,c** or **9d**, respectively. Thus, the degree of observed up-field shift corresponds to the size of coordination ring. The largest up-field shift in **9a** indicates that 6-membered ring is highly efficient for the coordination. Efficiency of coordination is also indicated by IR spectroscopy, thus the absorption due to phosphorus-sulfur double bond shifts to lower wavenumber as the ring increases in size.

The six-membered ring coordination in **9a** was established by X-ray crystallographic analysis.[10] Figure 1 depicts a molecular structure drawing of **9a** where *p*-*t*-butyl group is disordered and one with the higher occupancy factor is shown for clarity. The P=S bonds for **9a** (1.956(4), 1.946(4) Å) are longer than those for **9f** (1.90 Å)[2a] and slightly longer than those for **9c** (1.944(4), 1.936(4) Å).[5] This elongated bond length indicates that the multiplicity of P=S is decreased by the coordination. The P-N distance for **9a** (1.918(9) Å) is almost the same as that for **9c** (1.921(8) Å) and the most striking difference between **9a** and **9c** is the bond angles C1-P1-N1: 99.1(5)° for **9a** and 88.2(4)° for **9c**.

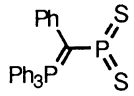
Table 1. $^{31}P\{^{1}H\}$ NMR and IR Data of **8**, **9**, and **10**

	8	9		10	
	δ_P[a)]	δ_P[a)]	ν (P=S) / cm^{-1}	δ_P[b)]	Ref.
a	−127.4	135.7	696 632	209.7	This work
b	−134.5	150.5	700 634	281.4	This work
c	−143.6	149.6	713 634	282.7	5
d	−141.6	170.6	725 653	388.5	4a,b
e	−143.0	285.2	—	—	11a,b
f	−129.9	298.2	792 660	—	11c,2c

a) Measured in $CDCl_3$ except for **9e** (in toluene); the reported value of **8e**: −149.9 (in C_6D_6).[11a] b) Measured in C_6D_6; the reported value of **10d**: 382.0 (in THF-d_8).[4a]

The ^{31}P NMR signals of thioxophosphines **10a-d** show a similar tendency observed in the case of dithioxophosphoranes **9a-d** and the degree of up-field shift due to the difference in the ring size is larger than that of the **9a-d**, thus **10a,b** resonate at δ_P= 209.7 and 281.4, higher than that for **10d** about 180 or 100 ppm, respectively. This fact also indicates that the coordination becomes more effective by the increased ring size. Although thioxophosphines **10a,b** did not decompose in $CDCl_3$ solution for one day, attempted isolation was not successful because of decomposition in the air.

The thermodynamically stabilized compounds **11** (δ_P= 243)[12a] and **12** (δ_P= 495.9)[12b] was reported by Schmidpeter et al. to resonate at lower field than **9a-d** and **10a-d**, respectively. This fact indicates the existence of the large electronic perturbation in **10a-d**.



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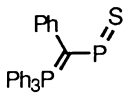

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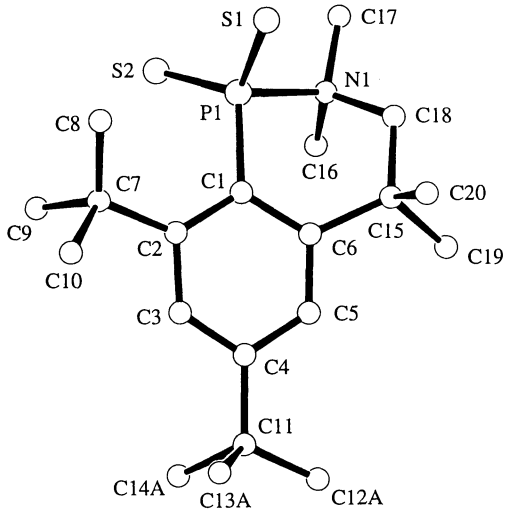

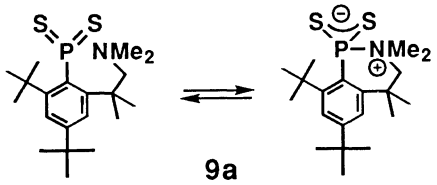

9a

Fig. 1. Molecular structure of **9a**. Some important bond lengths (Å) and bond angles(°): P1-S1, 1.956(4); P1-S2, 1.946(4); P1-C1, 1.83(1); P1-N1, 1.918(9); S1-P1-S2, 120.6(2); S1-P1-C1, 114.1(3); S2-P1-C1, 113.7(4); S1-P1-N1, 103.1(3); S2-P1-N1, 102.1(3); N1-P1-C1, 99.1(5); P1-C1-C2, 122.5(8); P1-C1-C6, 119.3(9); P1-N1-C18, 107.7(6); C1-C6-C15, 124(1); N1-C18-C15, 116.4(9); C6-C15-C18, 116.9(9).

In summary, preparations of thioxophosphines **10a,b** and dithioxophosphoranes **9a,b** were successful. ^{31}P NMR spectra and IR spectra indicated that ring size plays an important role in coordination structures. The new protecting groups **I**, **II** might be useful for stabilizing unstable molecules containing polarizable bonds.

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6) Selected spectroscopic data: **1a**: Colorless oil, ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.60 (6H, s, C$\underline{Me_2}CH_2$), 3.08 (6H, s, NMe_2), and 2.17 (2H, s, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 28.6 (C$\underline{Me_2}CH_2$), 47.6 (NMe_2), and 67.1 (CH_2); MS (70 eV, EI) *m/z* 366 (M^+–H). **1b**: Colorless crystals, mp 72.5–75.0 °C; ^{1}H NMR δ = 1.54 (6H, s, C$\underline{Me_2}NMe_2$) and 2.15 (6H, s, NMe_2); ^{13}C NMR δ = 22.8 (C$\underline{Me_2}NMe_2$) and 38.2 (NMe_2); MS *m/z* 353 (M^+). **3**: Colorless crystals, mp 79.0–80.0 °C; ^{1}H NMR δ = 3.90 (2H, s, CH_2CN); ^{13}C NMR δ = 37.5 ($\underline{C}H_2CN$); IR 2248 cm^{-1} (C≡N); MS *m/z* 307 (M^+). **4**: Colorless crystals, mp 157.5–159.0 °C; ^{1}H NMR δ = 1.93 (6H, s, CMe_2CN); ^{13}C NMR δ = 28.9 (C$\underline{Me_2}CN$); IR 2227 cm^{-1} (C≡N) ; MS *m/z* 335 (M^+). **5**: Colorless crystals, mp 176.0–178.0 °C; ^{1}H NMR δ = 1.11 (2H, br. s, NH_2), 1.41 (6H, s, C$\underline{Me_2}CH_2$), and 3.29 (2H, s, CH_2); ^{13}C NMR δ = 27.8 (C$\underline{Me_2}CH_2$) and 51.3 (CH_2NH_2); IR 3392 (N-H) and 3303 (N-H) cm^{-1}. **6**: Colorless crystals, mp 179.0–181.5 °C; ^{1}H NMR δ = 1.70 (6H, s, CMe_2C=O) and 5.26 (2H, br. s, NH_2); ^{13}C NMR δ = 50.5 ($\underline{C}Me_2C$=O); IR 3294 (br. N-H), 3153 (br. N-H), and 1691 (C=O) cm^{-1}. **7**: Colorless crystals, mp 174.5–176.0 °C; ^{1}H NMR δ = 1.73 (6H, s, C$\underline{Me_2}NH_2$) and 2.33 (2H, br. s, NH_2); ^{13}C NMR δ = 31.7 (C$\underline{Me_2}$N) and 55.5 ($\underline{C}Me_2$N); MS *m/z* 325 (M^+). **9a**: Colorless crystals, mp 278.0–280.0 °C; ^{1}H NMR δ = 1.59 (6H, s, C$\underline{Me_2}CH_2$), 3.05 (6H, d, J_{PH}= 7.7 Hz, NMe_2), and 4.00 (2H, br. s, C$\underline{H_2}NMe_2$); ^{13}C NMR δ = 45.4 (s, NMe_2) and 66.7 (s, CH_2); Found: *m/z* 383.1883. Calcd for $C_{20}H_{34}NPS_2$: M, 383.1870. **9b**: Colorless crystals, mp 264.0–265.0 °C; ^{1}H NMR δ = 1.97 (6H, s, C$\underline{Me_2}NMe_2$) and 3.01 (6H, d, J_{PH}= 8.4 Hz, NMe_2); ^{13}C NMR δ = 42.4 (d, J_{PC}= 2.51 Hz, NMe_2); Found: *m/z* 369.1693. Calcd for $C_{19}H_{32}NPS_2$: M, 369.1714. **10a** (not isolated): MS *m/z* (rel intensity) 351 (M^+; 4), 304 (M^+–Me–S; 32), and 58 ($CH_2NMe_2^+$; 100). **10b** (not isolated): MS *m/z* 337 (M^+; 54), 290 (M^+–Me–S; 95), and 57 (*t*-Bu^+; 100).

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9) Studies on the relationship between the structure and the chemical shift about **8** are in progress from the view point of both theoretical calculation and systematic modification of the substituent at ortho position.

10) Crystal data of **9a**: Recrystallized from $CHCl_3$. $C_{20}H_{34}NPS_2$, M_r = 383.59. Monoclinic, space group $P2_1/a$, a = 12.356(6), b = 10.07(1), c = 18.31(1) Å; β = 104.39(5)°; V= 2206(2) Å^3, Z = 4, ρ = 1.155 gcm^{-3}, μ = 3.16 cm^{-1}; 4137 independent reflections with $2\theta \leq 50.1°$ were recorded on a four-circle diffractometer (MoKα radiation, graphite monochrometer). Of these, 1557 with $I>3\sigma(I)$ were judged as observed. The structure was solved with SHELXS86. *p-t*-Butyl was disordered and they were solved into two positions of *t*-butyl groups from the difference maps, and their occupancy factor were refined to be 0.67 and 0.33. Hydrogen atoms were included at calculated position except for the *p-t*-butyl. All hydrogen atoms and the disordered carbon atoms were refined isotropically. R = 0.076, R_w= 0.080. Further details of the crystal structure investigation are available on request from Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK).

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