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Preparation and reaction of sterically crowded *N*-(2,4-di-*t*-butylphenyl)-*N*-methylaminodichlorophosphine

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Abstract—One of the *o*-*t*-butyl groups was eliminated from 2,4,6-tri-*t*-butyl-*N*-methylaniline by reaction with phosphorus trichloride in DME to afford sterically crowded *N*-(2,4-di-*t*-butylphenyl)-*N*-methylaminodichlorophosphine, which was utilized for preparation of a novel unsymmetrical diphosphene.

Since the first example of kinetically stabilized diphosphene **1** (Fig. 1) was reported,[1] many efforts have been made to synthesize low-coordinated phosphorus compounds with bulky substituents.[2–4] The 2,4,6-tri-*t*-butylphenyl (hereafter abbreviated to the Mes*) group is a most useful protecting substituent for various low-coordinated organophosphorus compounds. On the other hand, thermodynamic stabilization by electronic effects has also been applied for stabilization of unusual phosphorus compounds.[2,3] In the last decade, we have investigated such stabilizing groups as to have both kinetic and thermodynamic stabilizing abilities, and they have been utilized for stabilization of unusual and/or unstable compounds bearing such as phosphorus–chalcogen double bonds.[5,6] In the course of these investigations, the Mes* framework has acted as a prototype of novel protecting groups.[7] The 2,4,6-tri-*t*-butylphenoxy group is one substituent providing both kinetic and thermodynamic stabilizations, and has been utilized for diphosphene **2**[8] (Fig. 1) as well as many inorganic compounds as a catalyst.[9] On the other hand,

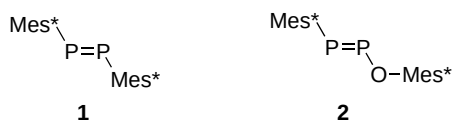

Figure 1.

the 2,4,6-tri-*t*-butylanilino moiety has hardly been utilized for low-coordinated organophosphorus compounds until now, although it has been applied for some monomeric organogallium compounds.[10] In this paper we report preparation of a bulky aminodichlorophosphine starting from *N*-methyl-2,4,6-tri-*t*-butylaniline, and its application for preparation of a diphosphene. In the course of this study, we observed an interesting elimination reaction of one of the *o*-*t*-butyl groups from the Mes*N(Me) moiety.

N-Methyl-*N*-(2,4,6-tri-*t*-butylphenyl)aminodichlorophosphine (**3**) was selected as the target compound. At first, *N*-methylaniline **4** (Mes*NHMe)[11] was lithiated to derive Mes*NMeLi, and was allowed to react with PCl_3. However, the desired compound **3** was not formed and Mes*NHMe was recovered almost quantitatively, while Mes*NHLi reacted with PCl_3 to afford *N*-(2,4,6-tri-*t*-butylphenyl)aminodichlorophosphine (Mes*NHPCl_2).[12] Steric bulkiness within the Mes*N(Me) moiety might weaken the nucleophilicity, and indeed the reaction of Mes*NHMe with PCl_3 did not proceed in the presence of a base such as triethylamine or potassium *t*-butoxide. Next, we investigated the reaction of **4** with PCl_3 in DME at 100°C as described in Scheme 1, and observed an aminodichlorophosphine in the reaction mixture by monitoring ^{31}P NMR spectroscopy. The major product was not the target product **3**, but *N*-(2,4-di-*t*-butylphenyl)-*N*-methylaminodichlorophosphine (**5**) was obtained in 80% yield.[13] Compound **5** might be formed by elimination of a *t*-butyl group. A possible intermediate would be **6**, indicating the Lewis acid character of PCl_3. Although we did not confirm the generation of 2-methylpropene (isobutene), we found that the reac-

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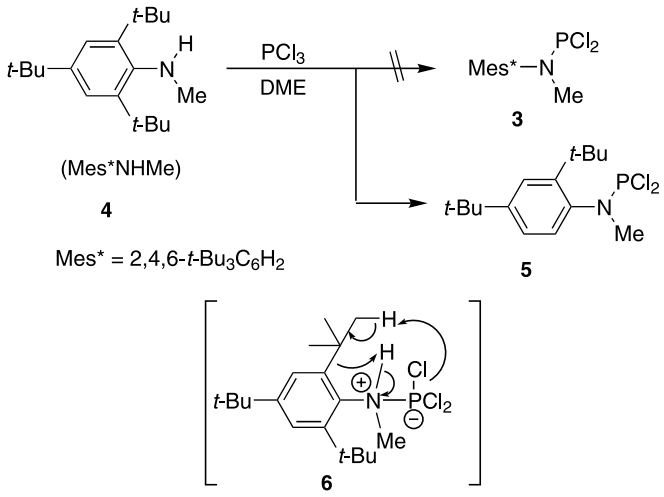


Scheme 1.

tion of deuterated Mes*NDMe with PCl_3 gave *N*-(2,4-di-*t*-butyl-6-deuteriophenyl)-*N*-methylaminodichlorophosphine of ca. 50% D/H ratio determined by the ^1H NMR spectroscopy indicating that intramolecular rearrangement might be involved to some extent. Alternatively, an electron transfer mechanism might operate during the reaction to give **5**. A similar de-*t*-butylation of Mes*NHMe **4** was reported in the reaction with iodomethane under high pressure affording 2,4-di-*t*-butyl-*N*,*N*-dimethylanilinium iodide.[14] Although a Lewis acid would play an important role in giving the de-*t*-butylated compound, the reaction of **4** with PCl_3 in the presence of aluminum trichloride did not give **5**.[15,16]

We investigated some reactions of aminodichlorophosphine **5** as shown in Scheme 2. Methanolysis of **5** yielded the phosphoric acid derivative **7** (δ_P 14), which was easily hydrolyzed to afford *N*-methyl-2,4-di-*t*-butylaniline (**8**). Aniline **8** was allowed to react with HCl to afford the corresponding ammonium chloride **9**, which was analyzed by X-ray crystallography to reveal elimination of a *t*-butyl group, but the quality of the analytical result was not satisfactory (Fig. 2).[17] The reaction of **5** with lithium 2,4,6-tri-*t*-butylphenylphosphide (**10**) and DBU gave the corresponding diphosphene **11** in 47% yield after purification by column chromatography (SiO_2, hexane) and GPC.[18,19] In the ^{31}P NMR spectrum

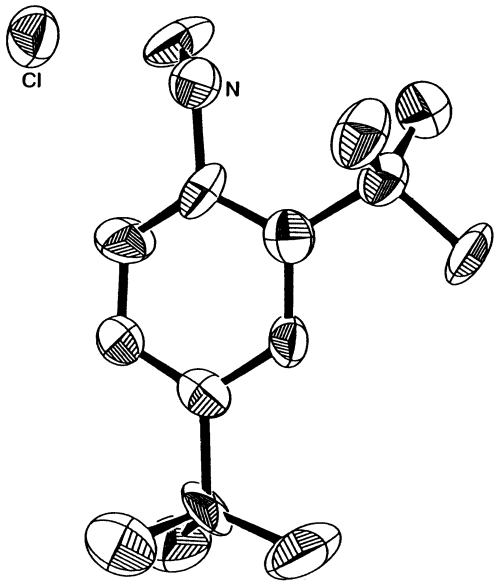
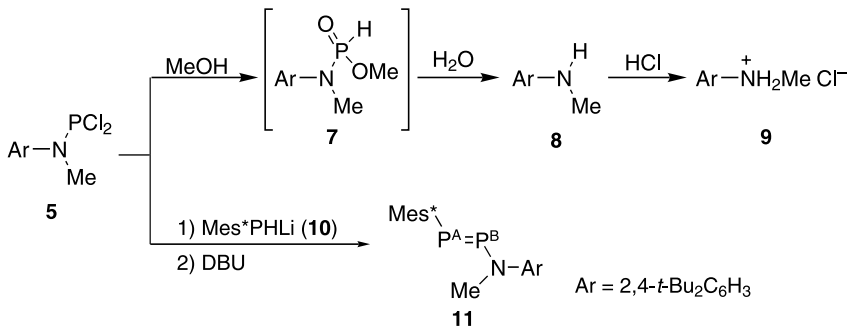


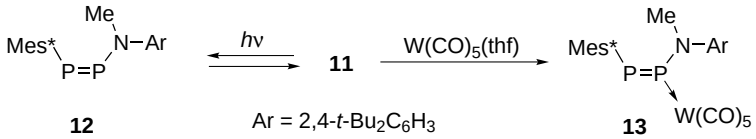
Figure 2. An ORTEP drawing of **9** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

of diphosphene **11**, an AB signal was observed, and the chemical shifts indicated the *trans* configuration.[20–22] The phosphorus atom P^A shows higher chemical shift (δ_P 308) due to the resonance effect by the nitrogen atom [>N–P=P–↔>N^+=P–P^-–], which is similar to the case of **2**.[8] Although diphosphene **11** slowly decomposed at room temperature, suggesting that **11** is slightly less stable than **2**, it is obvious that the *N*-(2,4-di-*t*-butylphenyl)-*N*-methylamino group is applicable to construct the P=P skeleton.

Compound **11** was irradiated with a medium-pressure mercury lamp through a Pyrex filter in dichloromethane for 5 h to afford a mixture of *E*/*Z* isomers in a ratio of 3:1.[23] The ^{31}P chemical shift of **12** was observed in a higher field (δ_P 351, 187, $^1J_{PP}$ 539 Hz) than that of **11** (δ_P 458, 308, $^1J_{PP}$ 543 Hz). Complex formation of **11** with $W(CO)_5$(thf) afforded the corresponding product **13** in 23% yield. The ^{31}P chemical shift indicated the coordination of tungsten at P^B with *Z*-configuration [δ_P 300 ($^1J_{PW}$ 203 Hz), 160, $^1J_{PP}$ 550 Hz] (Scheme 3), suggesting that the *E*/*Z* isomerization took place during the reaction.[24] Further investigation on **11** is in progress.



Scheme 2.



Scheme 3.

Acknowledgements

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13. NMR data of **5**: $^{31}P\{^1H\}$ NMR (81 MHz, CD_2Cl_2): δ 163; ^1H NMR (200 MHz, CD_2Cl_2) δ 1.09 (9H, *p*-*t*-Bu), 1.25 (9H, *o*-*t*-Bu), 2.91 (3H, d, $^3J_{PH}$ 7 Hz, NMe), 6.98 (1H, ddd, $^5J_{PH}$ 0.8 Hz, $^3J_{HH}$ 8 Hz, $^5J_{HH}$ 2 Hz, H^6), 7.13 (1H, dd, $^3J_{HH}$ 8 Hz, $^4J_{HH}$ 2 Hz, H^5), 7.48 (1H, dd, $^4J_{HH}$ 2 Hz, $^5J_{HH}$ 2 Hz, H^3); $^{13}C\{^1H\}$ NMR (50 MHz, CD_2Cl_2): δ 30.1 (*p*-C*Me*$_3$), 31.4 (*o*-C*Me*$_3$), 33.7 (*p*-*C*Me$_3$), 34.9 (*o*-*C*Me$_3$), 35.9 (NMe), 124.8 (C^6), 125.4 (C^5), 130.9 (C^3), 140.2 (d, $^1J_{PC}$ 26 Hz, *ipso*), 147.8 (C^2), 151.5 (C^4).
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17. Crystal data of **9**: $C_{15}H_{26}ClNP$, $M=255.83$; triclinic, $P\bar{1}$ (#2), $a=10.924(6)$, $b=14.92(1)$, $c=10.40(2)$ Å, $\alpha=107.1(1)$, $\beta=91.7(1)$, $\gamma=99.75(6)°$, $V=1591(4)$ Å^3, $Z=4$, $D_{calcd}=1.067$ g cm^{-1}; $R=0.218$ [$I=3.0\sigma(I)$] (CCDC 169417).
18. NMR data of **11**: $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 458 (N*P*=P), 308 (NP=*P*), $^1J_{PP}$ 543 Hz; ^1H NMR (200 MHz, $CDCl_3$): δ 1.28 (9H, *p*-*t*-Bu), 1.29 (9H, *p*-*t*-Bu), 1.34 (9H, *o*-*t*-Bu), 1.53 (18H, *o*-*t*-Bu), 3.59 (3H, d, $^3J_{PH}$ 6 Hz, NMe), 6.90 (1H, d, $^3J_{HH}$ 8 Hz, *p*-anilino), 7.16 (1H, dd, $^3J_{HH}$ 8 Hz, $^4J_{HH}$ 2 Hz, *m*-anilino), 7.37 (2H, *m*-Mes*), 7.42 (1H, d, J_{HH} 2 Hz, *m*′-anilino).
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