Unique molecular distortion in the 2,4,6-tri-*t*-butylphenyl group

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This article is dedicated to Professor Anthony J. Arduengo, III on the occasion of his 60th birthday

DOI: http://dx.doi.org/10.3998/ark.5550190.0013.202

Abstract

X-ray structure of a stable chlorophosphine and a secondary phosphine both bearing one or more sterically bulky 2,4,6-tri-*t*-butylphenyl (Mes*) group(s) are discussed in terms of molecular distortion. Steric encumbrance of the bulky aromatic ring induces a boat-type structure of the six-membered aromatic ring, and the degree of distortion depends on a substituent in the *ipso* position.

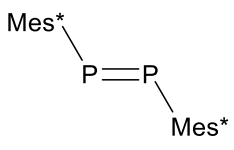
Keywords: Molecular distortion, steric effect, conformation, X-ray structure

Introduction

Kinetic stabilization techniques with sterically encumbered substituents have been utilized for isolation of inherently unstable chemical species including multiple bonds of heavier main group elements. Since successful characterization of a stable P=P double bond, named as diphosphene,

a number of congeners of alkenes and alkynes have been synthesized by use of steric protecting groups. The following Scheme 1 shows formula of the first isolable diphosphene reported in 1981 bearing 2,4,6-tri-*t*-butylphenyl groups (**1**).[1] This bulky aryl group, hereafter abbreviated as Mes*, has played an important role in development of main group chemistry for connecting various π-conjugated systems. Indeed a number of low-coordinated organophosphorus compounds bearing the Mes* group(s) have been synthesized and characterized.[2,3]

On the other hand, we have found that several normal organic compounds bearing the Mes* group(s) show remarkable molecular distortion of the aromatic skeleton. We reported that an extremely crowded phosphinic chloride **2**[4] exhibits boat-shaped aromatic rings according to its X-ray structure.[5,6] Also we found a similar distortion of the aromatic ring in **3**[7] and tri(carbonyl)chromium π-complexes of diphosphene **1**.[8]



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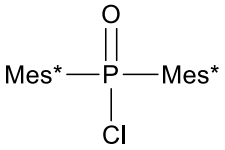

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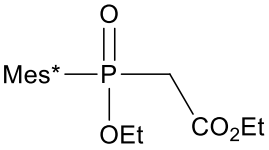

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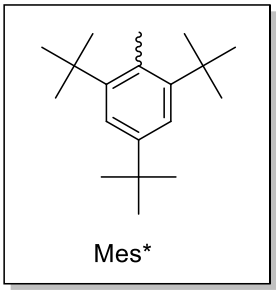


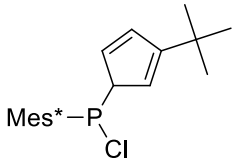
In this paper we discuss two typical structural characteristics of normal $\lambda^3\sigma^3$-phosphines bearing the Mes* group(s). An air-tolerant tertiary chlorophosphine exhibits remarkable distortion of the aromatic ring as well as sterically congested conformation. A secondary ethynylphosphine bearing two Mes* groups shows high stability in air and the structure in the solid state is discussed.

Results and Discussion

Air-stable chlorophosphine bearing the Mes* group

Whereas chlorophosphines are normally decomposed in air, (3-*t*-butylcyclo-penta-2,4-dienyl)chloro(2,4,6-tri-*t*-butylphenyl)phosphine (**4**) can be handled in the ordinary atmosphere and recrystallized from dichloromethane, and the structural properties were discussed in our previous report.[9] Figure 1 shows a representation of the molecular structure of **4**

[(*R*,*S*)-isomer]. The PCl moiety is effectively protected by the steric encumbrance of the Mes* sphere to reduce reactivity of the phosphorus center. On the other hand, steric hindrance around the phosphorus atom causes remarkable distortion of the aromatic 6-membered ring to a boat-type conformation [Θ(P–C_{ipso}–C_{ortho}–$C_{t\mathrm{Bu}}$) = –56.07, 44.09°. Θ(P–C_{ipso}–C_{ortho}–C_{meta}) = 130.97, –109.28°. Θ(C_{ipso}–C_{ortho}–C_{meta}–C_{para})] = –4.35, 4.20°], and correspondingly the *ipso* carbon atom in the Mes* group exhibits slight pyramidalization [Σ(angles) = 354.1°], where $C_{t\mathrm{Bu}}$ stands for the base carbon of the *t*-butyl group attached to C_{ortho}. As for the conformational characteristics of **4**, despite the considerable steric repulsion, the *t*-butyl group on the cyclopentadienyl ring is not far from the Mes* moiety. Molecular mechanics calculations of the most stable conformer for the (*R*,*S*) isomer suggests an optimum structure with the dihedral angle of 120° around the P–C1 bond [Θ(C_{ipso}–P–C1–C2)]. This sterically congested form of **4** might be affected by the CH-π interaction between the Mes* and cyclopentadienyl groups[10] which might also be suggested from the higher field chemical shifts of the proton on the C2 position (δ_H = 4.47 ppm) compared with those on the C4 and C5 positions (6.43 and 6.27 ppm). Additionally, the P–C_{ipso}–C_{ortho} angles of 128.6(2) and 107.2(2)° indicate the conformational property of the P(Cl)(C_5H_4*t*Bu) moiety to induce different steric effects of the *o*-*t*Bu groups, as observed also in **2**[6] and a sterically crowded dichlorophosphine Mes*PCl_2.[9]



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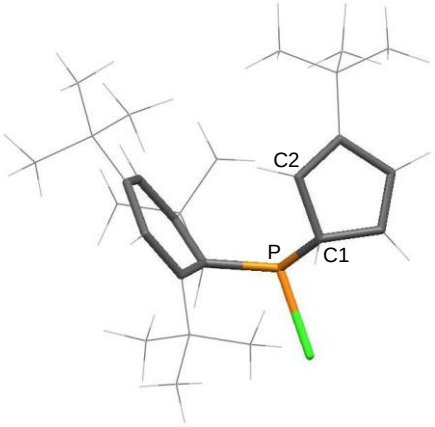
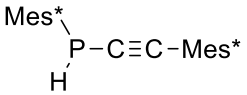


Figure 1. Molecular structure of **4**.[9]

Characterization of a stable secondary ethynylphosphine

Phosphines bearing both P–H bond and acetylene structure are of interest from the views of synthesis of particular organophosphorus compounds as well as coordination chemistry. For example, we have utilized some (2,4,6-tri-*t*-butylphenyl)(ethynyl)phosphines for preparation of the corresponding 3,4-diphosphinidenecyclobutenes (DPCB) which have recently been studied in terms of unique and efficient catalysts.[11] However, there has not been a detailed discussion of characteristics of the secondary ethynylphosphines so far. Previously, we reported unique trimerization reaction of a sterically encumbered phosphanylidene carbenoid [Mes*P=C(Br)Li][3a] affording the corresponding 1,3,6-triphosphafulvene.[12] At the same time, we observed formation of a secondary ethynylphosphine **5** as one of the byproducts. We succeeded in isolation, crystallization, and X-ray structural analysis of **5**.



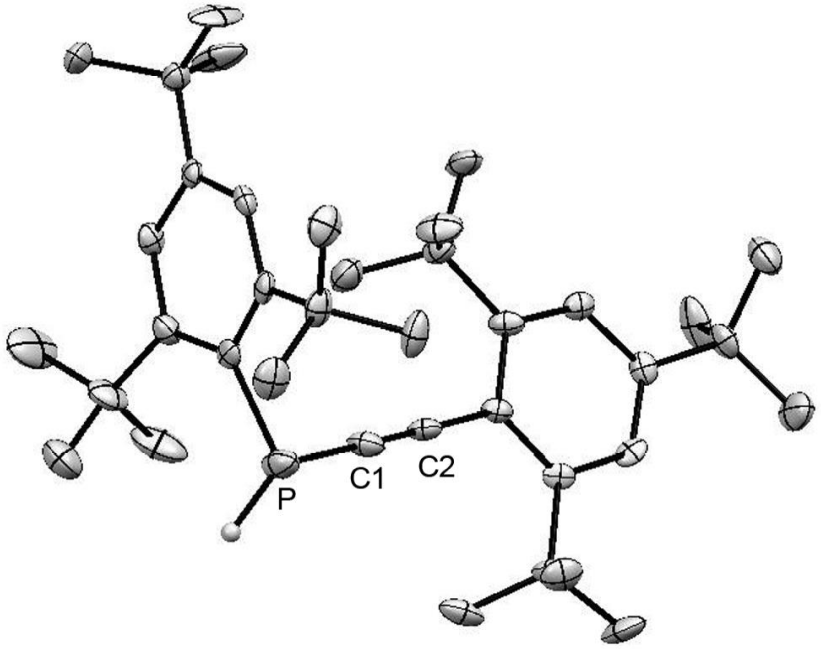
5

Figure 2a displays an ORTEP drawing of **5** (50% probability ellipsoids). The aromatic ring in the Mes*P moiety shows smaller distortion compared with **4** [Θ(P–C_{ipso}–C_{ortho}–$C_{t\mathrm{Bu}}$) = 26.49, –24.94°.a Θ(P–C_{ipso}–C_{ortho}–C_{meta}) = 159.10, –159.18°. Θ(C_{ipso}–C_{ortho}–C_{meta}–C_{para})] = –1.37, 0.90°], and smaller pyramidalization of the C_{ipso} atom [Σ(angles) = 358.8°]. This boat-like structure, though indicating somewhat of an envelope-type distortion, is comparable to the aryl groups in **1**.[1] On the other hand, the six-membered ring in the Mes*C group shows almost planar structure [Θ(C2–C_{ipso}–C_{ortho}–$C_{t\mathrm{Bu}}$) = 3.75, –2.55°. Θ(P–C_{ipso}–C_{ortho}–C_{meta}) = 175.98, –175.06°. Θ(C_{ipso}–C_{ortho}–C_{meta}–C_{para})] = 0.80, 1.15°]. Thus, the distortion of aromatic rings depend on steric encumbrance around the *ipso* carbon atom of the Mes* group. The P1–C1 and C1–C2 distances and the P1–C1–C2 angle are comparable to ethynylphosphine (**6**) [H_2PC≡CH] (P–C 1.774 Å, C≡C 1.208 Å, P–C≡C 173°).[13] The Mes*C≡C moiety shows similar geometrical parameters to **7**.[14] Crystal structure of **5** (Figure 2b) indicates effective steric encumbrance around the inherently unstable PH–C≡C moiety to prevent interaction by small molecules.

As discussed above, the magnitude of the benzene ring distortion of **5** depends on steric encumbrance around the *ipso* substituent. Similarly to **5**, highly stabilized 1,3-diphosphacyclobutane-2,4-diyls **8** and **9** also exhibit the ring distortion, and the distortion

parameters around the Mes* groups depend on the substituents at the phosphorus atoms. The average torsion angles Θ($C_{skeletal}$–C_{ipso}–C_{ortho}–$C_{t\mathrm{Bu}}$) and Θ($C_{skeletal}$–C_{ipso}–C_{ortho}–C_{meta}) for **8** are 26.10° and 155.84°,[15] respectively, whereas **9** shows smaller degree of distortion [Θ($C_{skeletal}$–C_{ipso}–C_{ortho}–$C_{t\mathrm{Bu}}$) = 15.5°, 9.5°. Θ($C_{skeletal}$–C_{ipso}–C_{ortho}–C_{meta}) = 163.7°, 173.5°].[16] Also, the magnitude of the benzene distortion might be responsible for the air-stability; **8** did not change under air, whereas **9** decomposed completely under ambient conditions within a day. The distortion of the Mes* group appears to be crucial for stabilizing unstable molecular structure.

a)



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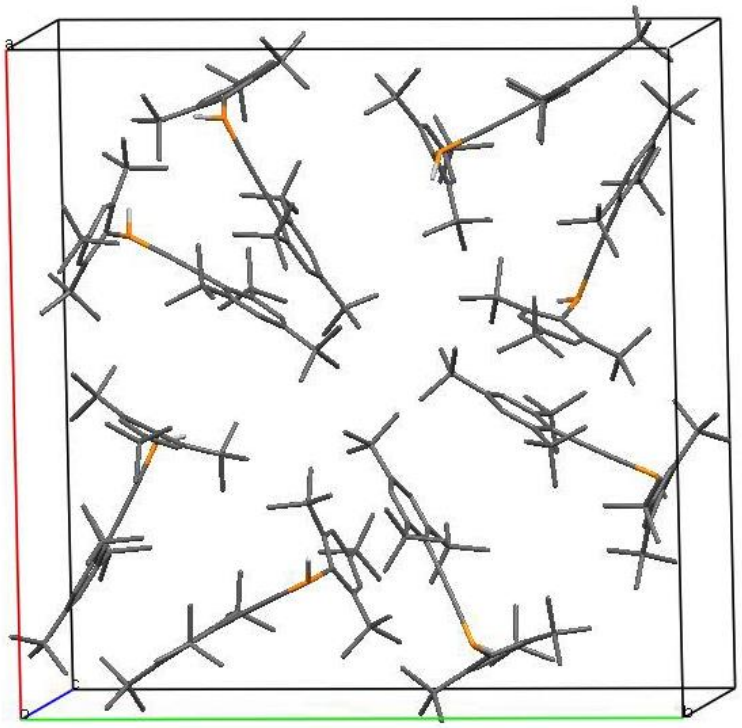
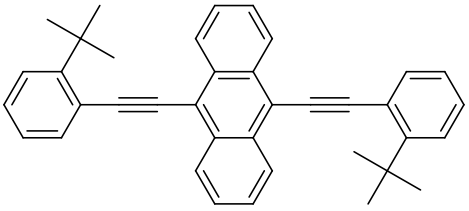


Figure 2. a) molecular structure of **5** (50% probability ellipsoids). The *p*-*t*-butyl group of Mes* at P is disordered, and the atoms with predominant occupancy factor (0.84) are displayed. Hydrogen atoms except for one attached to the phosphorus atom are omitted for clarity. Selected bond lengths (Å) and angles (°): P–C1 1.770(5), P–C_{Mes*} 1.855(4), C1–C2 1.190(7), C2–C_{Mes*} 1.456(7). C1–P–C_{Mes*} 99.8(2), P–C1–C2 178.3(4), C1–C2–C_{Mes*} 179.0(5). b) Crystal structure of **5** along the *c* axis.



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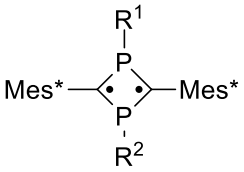


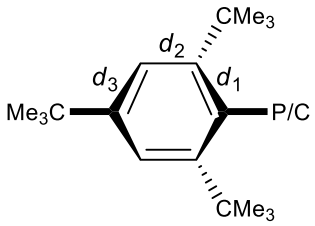
8: R^1 = *t*Bu, R^2 = CH_2Ph
9: R^1 = R^2 = Me

Comparison of the aromatic C–C distances of (4 and 5)

As demonstrated in the research on cyclophanes, distortion of benzene ring causes alteration of the aromatic C–C bond distances.[17,18] Thus, similar phenomenon is plausible in the cases of **4** and **5**. Table 1 displays the aromatic C–C distances of **4** and **5**.

Due to the steric repulsion between the Mes* group and the *ipso*-substituents, parameters d_1 of both **4** and **5** exhibit remarkable elongation from the normal C–C distance of benzene (1.394 Å). This finding indicates that the elongated C–C distances do not necessarily correspond to the distorted aromatic ring because the elongation is observed even in the almost planar Mes*C moiety of **5**. On the other hand, d_2 and d_3 are close to the normal aromatic C–C bond, indicating smaller steric encumbrance in comparison with those around the *ipso* position, and the intrinsic aromatic stabilizing tendency.

Table 1. C–C Bond distances of the aromatic rings in **4** and **5**



	d_1 / Å	d_2 / Å	d_3 / Å
4	1.432(4)	1.385(5)	1.403(4)
	1.422(4)	1.406(5)	1.386(4)
5: Mes*P	1.424(7)	1.406(5)	1.386(7)
	1.429(7)	1.390(5)	1.393(7)
5: Mes*C	1.428(5)	1.379(7)	1.395(7)
	1.414(6)	1.401(6)	1.386(7)

Conclusions

Steric encumbrance of the 2,4,6-tri-*t*-butylphenyl (Mes*) group shows remarkable distortion to a boat-type structure indicating preferable characters for stabilization of unstable chemical species.

According to the X-ray structural determination of chlorophosphine **4** and secondary phosphine bearing two Mes* groups **5**, the molecular distortion is a result of steric encumbrance around the *ipso* position. On the other hand, degree of the boat-type distortion depends on the substituent at the *ipso* aromatic carbon. Thus, steric encumbrance of the Mes* group, which is essential for protecting unstable organophosphorus structures, gives rise to corresponding distortions around the aromatic skeleton, and proper molecular distortion might be a parameter for design of stabilization of reactive intermediates.

Experimental Section

Crystallographic data for 4 [9]

$C_{27}H_{42}ClP$: M = 433.06, monoclinic, $P2_1/n$ (#14), a = 8.9814(3), b = 17.6217(5), c = 16.5341(5) Å, β = 93.331(1)°, V = 2612.4(1) Å^3, Z = 4 (CCDC-667900).

X-ray crystallography for (2,4,6-tri-t-butylphenyl)((2,4,6-tri-t-butylphenyl)ethynyl) phosphine (5)[12]

Diffractometer: Rigaku RAXIS-IV imaging plate detector, $C_{38}H_{59}P$, colorless prisms (CH_2Cl_2), M = 546.86, crystal dimensions = 0.20 × 0.20 × 0.15 mm^3, tetragonal, space group $P4_22_12$ (#94), a = 25.6257(3), b = 25.6257(3), c = 10.7101(1) Å, V = 7033.1(1) Å^3, Z = 8, λ = 0.7107 Å, T = 133 K, ρ_{calcd} = 1.033 g cm^{-3}, μ(MoKα) = 0.100 mm^{-1}, 66622 total reflections ($2\theta_{max}$ = 51.0°), 45480 unique reflections (R_{int} = 0.087), $R1$ = 0.0448 ($I > 2\sigma(I)$), Rw = 0.0496 (all data), GOF = 0.933 (366 parameters) (CCDC-818921).

Acknowledgements

This work was supported in part by Grant-in-Aid for Scientific Research (Nos. 13304049, 14044012, 20750098, and 22350058) from the Ministry of Education, Culture, Sports, Science and Technology, Japan; the Program Research, Center for Interdisciplinary Research, and the Support for Young Researchers, Graduate School of Science, Tohoku University; Casio Science Promotion Foundation; and Nissan Chemical Industries, Ltd.

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