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CHARACTERIZATION OF A 3,4-DIHYDRO-1,3,4-TRIPHOSPHACYCLOPENTA[*a*]INDENE AS AN ISOMER OF A Mes*-SUBSTITUTED 1,3,6-TRIPHOSPHAFULVENE (Mes* = 2,4,6-*t*-$\mathrm{Bu_3C_6H_2}$)

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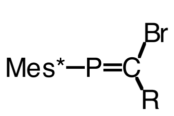
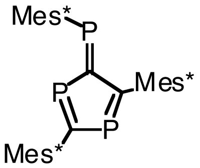
Abstract – Reaction of 2,2-dibromo-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene and *t*-butyllithium gave a 3,4-dihydro-1,3,4-triphosphacyclopenta[*a*]indene as an isomer of a bulky 1,3,6-triphosphafulvene, which was isolated as a major product in this reaction, and the structure was confirmed by X-Ray analysis. Spectroscopic and redox properties of the 3,4-dihydro-1,3,4-triphosphacyclopenta[*a*]indene have been studied.

INTRODUCTION

We have demonstrated reaction diversity of kinetically stabilized phosphanylidene carbenoids such as **1**,[1] generated from dibromophosphaethene (**2**), affording considerably unique unsaturated compounds containing low-coordinated phosphorus atoms.[2,3] We previously reported a formal trimerization of phosphanylidene carbenoid affording bulky 1,3,6-triphosphafulvene (**3**).[4] Although the real reason why the phosphanylidene carbenoid (**1**) displays the trimerization toward **3** has been unclear so far, **3** is a promising compound for developing novel chemistry of phosphorus-containing aryl molecules.[2,3,5] The curious reaction affording **3** has led us to isolate novel products from **1** as well as to understand further properties of phosphanylidene carbenoid. Actually we have made efforts not only to improve the yield of **3** but also to isolate other novel compounds in the reaction mixture and have recently succeeded in characterization of a novel compound from the reaction of **1**. In this paper we describe the structure of another novel formal trimer of [Mes*P=C:] as well as its several physical properties.


$\mathrm{Mes^*{-}P{=}C(Br)R}$

1: R = Li
2: R = Br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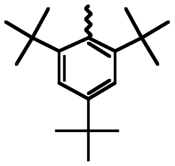
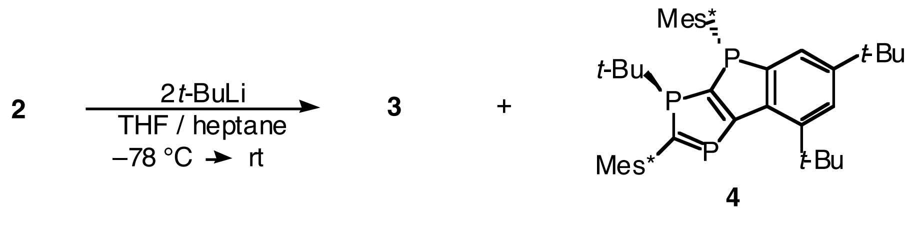

Mes*

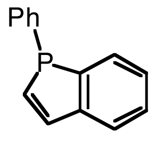
RESULTS AND DISCUSSION

Dibromophosphaethene (**2**), prepared according to the procedure reported in ref. 6, was allowed to react with *t*-butyllithium at –78 °C in a mixture of THF and heptane (1:1) and the reaction mixture was allowed to warm to room temperature. The solution turned deep red and was concentrated to dryness. Silica gel column chromatography (hexane/toluene) of the residue afforded compound (**4**) as an air- and moisture stable yellow solid together with **3** (Scheme 1).[2] In the ^{31}P NMR spectrum, **4** displayed an ABX system, which contained two phosphino groups and a P=C moiety, indicating a trimer of **1** along with the elimination of LiBr.

Crystallization of **4** was successful and a single crystal was selected for X-Ray crystallography. Figure 1 displays an ORTEP drawing of the molecular structure of **4**. Compound (**4**) bears a tricyclic structure containing three phosphorus atoms and one of the three Mes* aromatic rings is included to form a 3,4-dihydro-1,3,4-triphosphacyclopenta[*a*]indene skeleton. Indeed, the composition of **4** is the same as **1**, and one *o*-*t*-butyl group in the C2–Mes* group appeared to have migrated to P2. The tricyclic dihydrotriphosphacyclopenta[*a*]indene skeleton is almost planar [the largest torsion angle in the triphosphacyclopenta[*a*]indene skeleton is P2–C3–P3–C1: Θ 14.2(3)°] and the Mes* group on P2 is located in the *trans* position relative to the *t*-butyl group on P3, probably due to steric hindrance. The two Mes* groups are not co-planar with the tricyclic system due to the steric bulkiness. Indeed the structure of **4** indicates a combination of benzophosphole[7] and 1*H*-[1,3]diphosphole.[8] The sum of the bond angles around P2 (320.8°) is larger than the corresponding value for **5** (296.34°),[5] which might represent the effect of the bulky substituents.[9,10] On the other hand, the sum of the bond angles around P3 is 327.0°, which is comparable to that of the 1,1'-phosphorus atoms in 3,3'-diphospha-1,1'-biphospholyl (**6**) (320.0°).[6] Theoretical investigations of 1*H*-[1,3]diphosphole indicated the phosphorus effect widens the sum of bond angles around the $\lambda^3\sigma^3$ phosphorus atoms.[10,11] The P1–C1 distance and the C1–P1–C2 angle indicate the –P=C< group, which is comparable to those for the 3,3'-P atoms in **6** [1.673(5) Å, 99.7(2)°].[6]



Scheme 1



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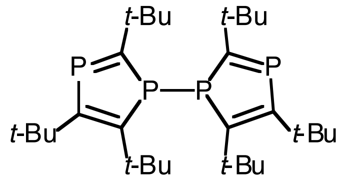
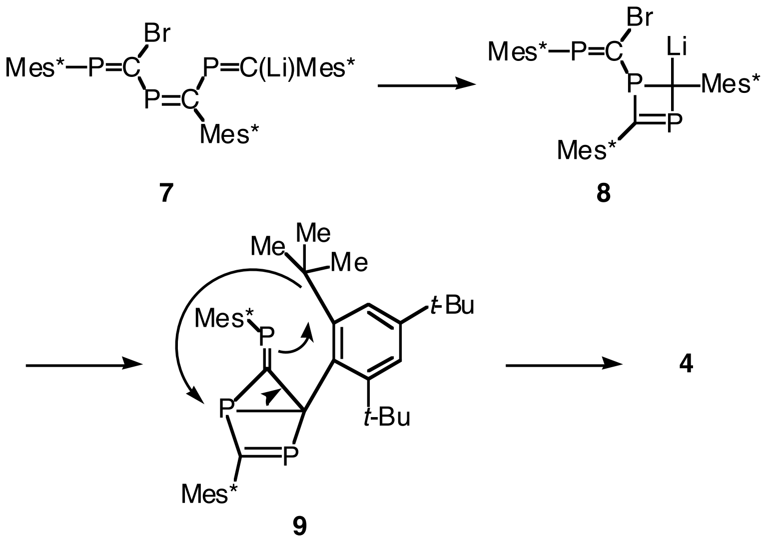


6

Compound (**4**) was formed in the reaction of **2** and *t*-butyllithium in THF, THF/pentane, or THF/hexane in *ca*. 5% yield together with **3**.[12] In the reaction in DME, **4** was isolated in a small amount (1% yield), whereas no **3** was observed in the reaction mixture. Compound (**4**) was not observed in the reaction mixture of **3** with *t*-butyllithium, indicating that the *t*-Bu group at position 3 of compound (**4**) was not derived from the employed *t*-butyllithium. Generation of **4** might include an insertion (or addition) of the $C_{t\text{-Bu}}$–C_{ortho} bond into the 1,3,6-triphospha-1,3,5-triene system.[13] We have tried to obtain **4** from the reactions of **3**, but no formation of **4** from **3** has been observed by heating, irradiation, or treatment with Lewis acids or bases so far. An intermediate before formation of the 1,3,6-triphophafulvene might produce **4** and a plausible formation mechanism of **4** is shown in Scheme 2. Compound (**7**), which has been proposed as an intermediate for the formation of **3**,[4] may take an alternative process to form **8**,[14] leading to the formation of a bicyclic intermediate (**9**). A successive migration of an *o*-*t*-butyl group may afford **4**. Studies to clarify the formation mechanism for **4** as well as **3** are in progress.



Scheme 2

The yellow **4** might suggest a different conjugated system from that for the red **3** as indicated by the UV-spectrum. Moreover, we investigated redox properties of **4** by cyclic voltammetry. Compound (**4**) displayed an irreversible reduction peak at –0.78 V (*vs*. Ag/AgCl), whereas **3** showed a reversible ($E_{1/2}$) peak at –0.68 V under the same conditions. On the other hand, **4** displayed irreversible oxidation peaks at +0.98 and +1.17 V (Figure 2), which shows the character of the phosphino group in both the 1*H*-

[1,3]diphosphole and the phosphole moieties.

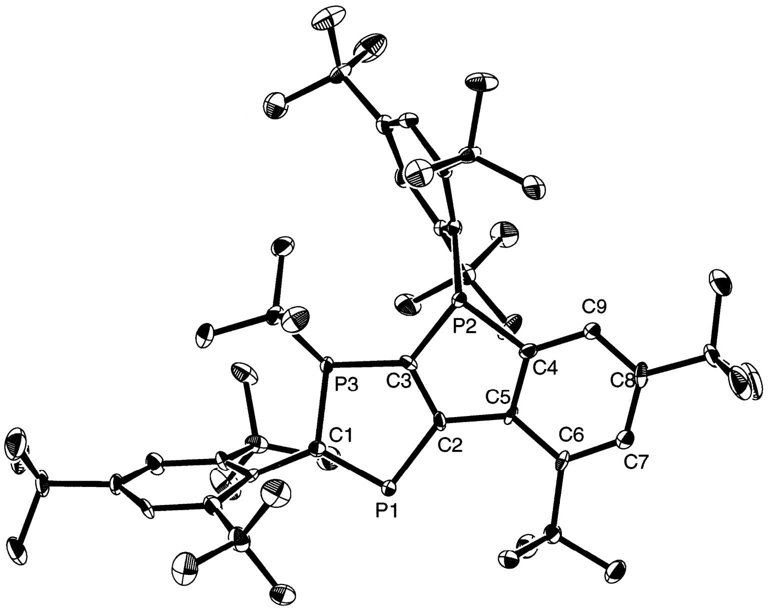


Figure 1. Molecular structure of **4** (with 50% probability ellipsoids). Hydrogen atoms and the solvent molecule (dichloromethane) are omitted for clarity. Numbering system is sequential by element. Selected bond lengths (Å) and angles (°): P1–C1 1.709(5), P1–C2 1.818(5), P2–C3 1.792(5), P2–C4 1.850(5), P2–C$_{\text{Mes*}}$ 1.862(5), P3–C1 1.778(5), P3–C3 1.770(5), P3–C$_{t\text{-Bu}}$ 1.887(5), C1–C$_{\text{Mes*}}$ 1.520(6), C2–C3 1.385(7), C2–C5 1.506(6), C4–C5 1.415(6), C1–P1–C2 98.2(2), C3–P2–C4 90.2(2), C3–P2–C$_{\text{Mes*}}$ 112.4(2), C4–P2–C$_{\text{Mes*}}$ 118.2(2), C1–P3–C3 97.8(2), C1–P3–C$_{t\text{-Bu}}$ 117.7(2), C3–P3– C$_{t\text{-Bu}}$ 111.5(2), P1–C1–P3 112.5(3), P1–C1–C$_{\text{Mes*}}$ 127.8(3), P3–C1–C$_{\text{Mes*}}$ 118.4(3), P1–C2–C3 114.5(3), P1–C2–C5 132.2(4), C3–C2–C5 113.2(3), P2–C3–P3 132.7(4), P2–C3–C2 111.9(3), P3–C3–C2 115.3(3), P2–C4–C5 112.0(3), P2–C4–C9 124.7(3).

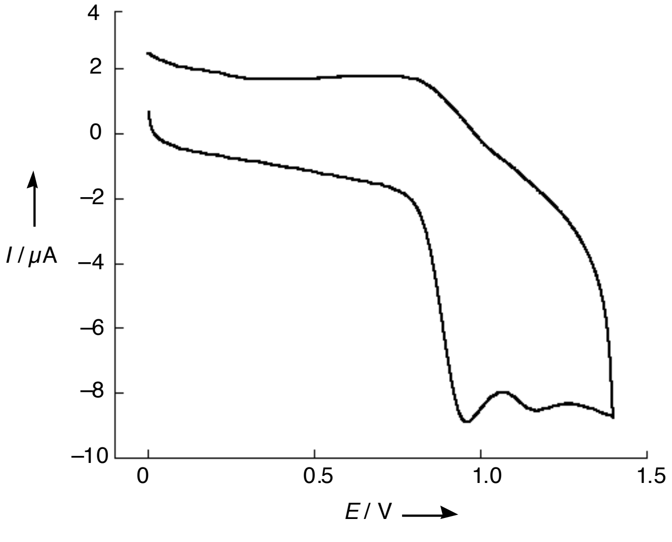


Figure 2. Cyclic voltammogram of **4**. *Conditions:* 1 mM in dichloromethane; supporting electrolyte: 0.1 M n-Bu$_4$NClO$_4$ (TBAP); working electrode: grassy carbon; counter electrode: platinum wire; reference electrode: Ag/AgCl at 20 °C; scan rate: 50 mV s^{-1}; E = potential, I = current.

In conclusion, we succeeded in isolation and characterization of 3,4-dihydro-1,3,4-triphosphacyclopenta[*a*]indene (**4**) together with 1,3,6-triphosphafulvene (**3**), suggesting the versatile reactivity of phosphanylidene carbenoid. Compound (**4**) is a formal trimer of the phosphanylidene carbenoid showing the same molecular formula as **1**. Structural analyses of **4** have been accomplished and the generation of **4** as well as **3** may proceed via unusual mechanisms. Properties of both benzophosphole and 1*H*-[1,3]diphosphole were shown by the X-Ray structure and the redox properties of **4**.

EXPERIMENTAL

Reaction of 2 with *t*-butyllithium: To a solution of **2** (500 mg, 1.12 mmol) in a 1:1 mixture of THF and heptane (26 mL) was added *t*-butyllithium (2.23 mmol, 1.4 M solution in pentane) at –78 °C and the whole was stirred for 5 min. The reaction mixture was allowed to warm to rt and stirred for an additional 3 h. The solvent was removed in vacuo and the residue was extracted with hexane. The solvent was removed in vacuo and silica gel column chromatography of the residue (hexane) afforded 28.1 mg of **4** (9% isolated yield) together with 42.3 mg of **3** (13% isolated yield). Data of **4**: Yellow prisms (CH_2Cl_2), mp 244–246 °C (decomp); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 245 (dd, $^2J_{PP}$ = 44 Hz, $^3J_{PP}$ = 24 Hz, P1), 84 (dd, $^2J_{PP}$ = 54 Hz, $^2J_{PP}$ = 44 Hz, P3), –7 (dd, $^2J_{PP}$ = 54 Hz, $^3J_{PP}$ = 24 Hz, P4); ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (1H, d, $^3J_{PH}$ = 7 Hz, H7), 7.59 (1H, brs, H5), 7.51 (2H, d, $^4J_{PH}$ = 5 Hz, PMes*), 7.40 (2H, s, CMes*), 1.82 (9H, s, *t*-Bu), 1.42 (18H, s, *t*-Bu), 1.42 (9H, s, *t*-Bu), 1.37 (18H, s, *t*-Bu), 1.32 (9H, s, *t*-Bu), 1.32 (9H, s, *t*-Bu), 0.62 (9H, d, $^3J_{PH}$ = 16 Hz, *t*-BuP); UV (hexanes) λ_{max} (log ε) 407 (3.75), 319 (4.23). Anal. Calcd for $C_{57}H_{87}P_3 \cdot 0.5CH_2Cl_2$: C, 76.09; H, 9.77%. Found: C, 76.51; H, 9.97%.

X-Ray data of 4: $C_{57}H_{87}P_3 \cdot CH_2Cl_2$, M = 950.17, monoclinic $P2_1/n$ (#14), a = 9.7896(3), b = 20.3478(5), c = 28.4293(5) Å, β = 96.0502(9)°, V = 5631.5(2) Å^3, Z = 4, $2\theta_{max}$ = 55.0°, T = 173 K, ρ = 1.121 g cm^{-1}, μ = 0.235 mm^{-1}, 43487 collected reflections, 12747 unique reflections (R_{int} = 0.094), $R1$ = 0.094 ($I > 2\sigma(I)$), R_W = 0.121 (all data), S = 1.99 (568 parameters), CCDC-243192.

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