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Preparation, Structure, and Reaction of a Sterically Encumbered 1-Phosphaallene Containing a Cyclopropylidene Moiety

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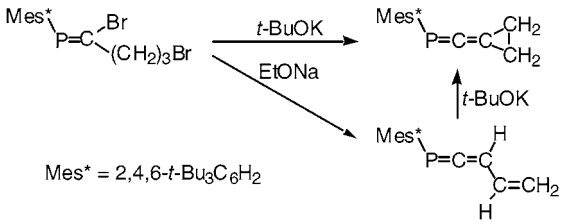
ABSTRACT



Sterically protected (*Z*)-1-(2,4,6-tri-*tert*-butylphenyl)-2,5-dibromo-1-phosphapent-1-ene was allowed to react with potassium *tert*-butoxide to afford a cyclopropylidenephosphaethene, which was characterized spectroscopically and by X-ray crystallography. Construction of the cycloalkyl groups and isomerization of 1-phosphapenta-1,2,4-trienes to cyclopropylidenephosphaethenes are also described.

Kinetic stabilization with bulky substituents has been widely utilized for the preparation of various unstable chemical species such as the unsaturated bonds of heavier main-group elements and the chemistry of multiple-bonded phosphorus compounds.[1] Since we reported the first example of a stable phosphorus−phosphorus double-bonded species (diphosphene),[2] we have now synthesized a number of low-coordinated phosphorus compounds bearing the 2,4,6-tri-*tert*-butylphenyl (abbreviated to Mes*) group.[3] In the course of research on low-coordinated phosphorus compounds, several 1-phosphaallene derivatives[4] have been prepared as "phosphacumulenes". Since allene derivatives have been widely used in organic synthesis due to their high reactivities,[5] 1-phosphaallenes might be of interest as novel synthons for unusual organophosphorus compounds.[1,3a] However, studies on 1-phosphaallenes have not been performed so extensively and only a few 1-phosphaallenes have been prepared.[1] On the other hand, cyclopropane derivatives as a group are one of the most attractive organic counterparts due to their ring distortion and unique electronic properties.[6] Additionally, cyclopropanes bearing unsaturated bonds as in methylenecyclopropane have shown extensive utility and versatility in reactions.[6,7] We now report the preparation, structure, and a

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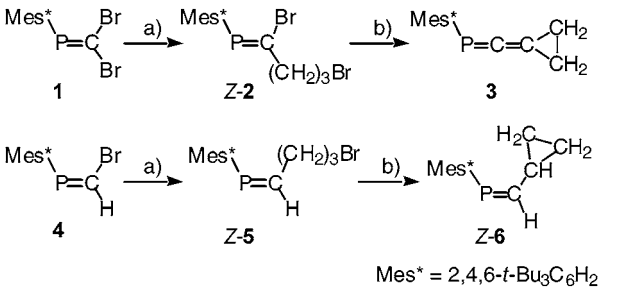
selection of reactions of a bulky cyclopropylidenephosphaethene stabilized by the Mes* group, as exemplified by the construction of the cyclopropyl moiety. Moreover, the preparation of a cyclobutylidenephosphaethene is also described.

The sterically encumbered 2,2-dibromo-1-phosphaethene (**1**)[8] bearing the Mes* group was allowed to react with butyllithium[3a,9] and then with 1,3-dibromopropane to afford (*Z*)-2,5-dibromo-1-phosphapent-1-ene *Z*-**2** in excellent yield (>90%).[10] Phosphapentene *Z*-**2** was treated with potassium *tert*-butoxide to afford a novel cyclopropylidenephosphaethene derivative **3**, which was first characterized by spectroscopic methods.[11] In the ^{31}P NMR spectrum, the signal of **3** was observed at a lower field than that reported for 3-methyl-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphabuta-1,2-diene (Mes*P═C═CMe$_2$; δ_P 60), whereas in the ^{13}C NMR spectrum the signals due to the two sp^2 carbon atoms of **3** appeared at a higher field than those reported for Mes*P═C═CMe$_2$ ($\delta_{P=C}$ 235.0; $\delta_{C=C}$ 117.0).[12] The UV spectrum of **3** displayed a bathochromic shift compared with that of 1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaallene [λ_{max} 275 nm (sh, log ϵ 3.18)],[13] probably due to a hyperconjugation effect enhanced by the cyclopropyl group.[6,14] On the other hand, the (*Z*)-5-bromo-1-phosphapent-1-ene *Z*-**5**, prepared from 2-bromo-1-phosphaethene **4**,[8a] was allowed to react with potassium *tert*-butoxide to afford the (*Z*)-2-cyclopropyl-1-phosphaethene *Z*-**6**.[10] The formation of *Z*-**6** under these

Scheme 1[a]

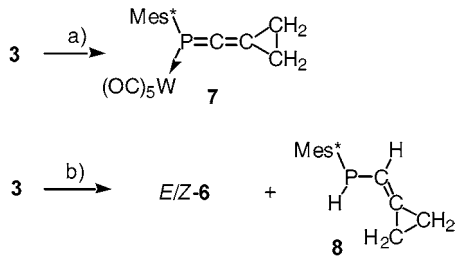


[a] Reagents and conditions: (a) (i) *n*-BuLi, THF, −78 °C; (ii) 1,3-dibromopropane, −78 °C to room temperature. (b) *t*-BuOK, THF, 0 °C.

conditions indicated that, in the reaction of *Z*-**2** with potassium *tert*-butoxide, the cyclopropyl ring was first formed by γ-elimination before the 1-phosphaallene skeleton was constructed. No β-elimination took place to afford either 1-phosphapenta-1,2,4-triene or 1-phosphapenta-1,4-diene derivative from *Z*-**2** or *Z*-**5** with potassium *tert*-butoxide, probably indicating that the acidity of the protons at the 3-position is sufficiently high to generate the requisite anion.[15]

Next, the cyclopropylidenephosphaethene **3** was allowed to react with W(CO)$_5$(thf) to afford the corresponding complex **7** in 70% yield (Scheme 2).[16] The structure of **7**

Scheme 2[a]



[a] Reagents and conditions: (a) W(CO)$_5$(thf), rt. (b) LiAlH$_4$, THF, 0 °C.

was confirmed by X-ray crystallographic analysis as shown in Figure 1.[17] The C1−C2 distance is shorter whereas the P−C1 distance is slightly longer than the corresponding data for [Mes*P═C═CPh$_2$][W(CO)$_5$] [C═C 1.311(10), P═C 1.632(7) Å].[18] On the other hand, the C2−C3 and C3−C4 distances in **7** are elongated compared to the proximal bonds

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(10) *Z*-**2**: Colorless crystals, mp 108−109 °C dec; ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ 250; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.50 (t, 2H, $^3J_{HH}$ = 7 Hz, CH$_2$Br), 3.05 (dt, 2H, $^3J_{PH}$ = 21 Hz, $^3J_{HH}$ = 7 Hz, P═CCH$_2$), 2.24 (quin, 2H, $^3J_{HH}$ = 7 Hz, CH$_2$). *Z*-**5**: ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ 250; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.12 (dd, 1H, $^2J_{PH}$ = 39 Hz, $^3J_{HH}$ = 8 Hz, P═CH), 3.21 (t, 2H, $^3J_{HH}$ = 7 Hz, CH$_2$Br), 1.76 (m, 2H, CH$_2$), 1.66 (m, 2H, P═CCH$_2$). *Z*-**6**: ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ 232; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.57 (dd, 1H, $^2J_{PH}$ = 38 Hz, $^3J_{HH}$ = 11 Hz, P═CH), 0.85 (m, 1H, CH), 0.69 (m, 2H, C*H*H), 0.48 (m, 2H, CH*H*); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 177.7 (d, $^1J_{PC}$ = 43 Hz, P═C), 18.3 (d, $^2J_{PC}$ = 21 Hz, CH), 10.6 (d, $^3J_{PC}$ = 7 Hz, CH$_2$). *Z*-**10**: ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ 247; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.48 (t, 2H, $^3J_{HH}$ = 7 Hz, CH$_2$Br), 2.91 (dt, 2H, $^3J_{PH}$ = 21 Hz, $^3J_{HH}$ = 7 Hz, P═CCH$_2$), 1.99 (quin, 2H, $^3J_{HH}$ = 7 Hz, CH$_2$), 1.85 (quin, 2H, $^3J_{HH}$ = 7 Hz, CH$_2$). **11**: ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ 76; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.03 (m, 2H, CH$_2$), 2.96 (m, 2H, CH$_2$), 1.92 (m, 2H, CH$_2$); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 229.4 (d, $^1J_{PC}$ = 24 Hz, P═C), 122.1 (d, $^2J_{PC}$ = 14 Hz, P═C═*C*), 31.2 (d, $^3J_{PC}$ = 15 Hz, CH$_2$), 17.4 (s, CH$_2$). **12**: ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ 66; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.68 (dt, 1H, $^2J_{PH}$ = 27 Hz, $^3J_{HH}$ = 8 Hz, ═CH), 3.35 (t, 2H, $^3J_{HH}$ = 7 Hz, CH$_2$Br), 1.99 (m, 2H, P═CCH$_2$), 1.96 (quin, 2H, $^3J_{HH}$ = 7 Hz, CH$_2$); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 239.3 (d, $^1J_{PC}$ = 27 Hz, P═C), 109.2 (d, $^2J_{PC}$ = 13 Hz, P═C═*C*), 33.1 (s, CH$_2$Br), 32.7 (d, $^4J_{PC}$ = 2 Hz, CH$_2$), 27.8 (d, $^3J_{PC}$ = 13 Hz, P═C*C*H$_2$).

(11) **3**: Colorless crystals, mp 85−86 °C dec; ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ 70; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.74 (m, 2H, C*H*H), 1.69 (m, 2H, CH*H*); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 221.9 (d, $^1J_{PC}$ = 26 Hz, P═*C*═C), 94.5 (d, $^2J_{PC}$ = 14 Hz, P═C═*C*), 11.0 (d, $^3J_{PC}$ = 7 Hz, CH$_2$); UV (hexanes) λ_{max} (log ϵ) 210 (4.71), 224 (4.63), 263 (3.95), 308 (sh, 3.34).

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(16) **7**: Orange crystals, mp 122−124 °C.; ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ 40 ($^1J_{PW}$ = 265 Hz); ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.96 (m, 2H, C*H*H), 1.85 (m, 2H, CH*H*); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 223.2 (d, $^1J_{PC}$ = 94 Hz, P═*C*═C), 200.5 (d, $^2J_{PC}$ = 34 Hz, CO$_{ax}$), 197.5 (d, $^2J_{PC}$ = 10 Hz, CO$_{eq}$), 95.2 (d, $^2J_{PC}$ = 11 Hz, P═C═*C*), 12.0 (d, $^3J_{PC}$ = 15 Hz, CH$_2$); IR (KBr) ν 2071, 1955, 1930 cm^{-1}. Anal. Calcd for C$_{27}$H$_{33}$O$_5$PW: C, 49.71; H, 5.10. Found: C, 49.73; H, 5.04.

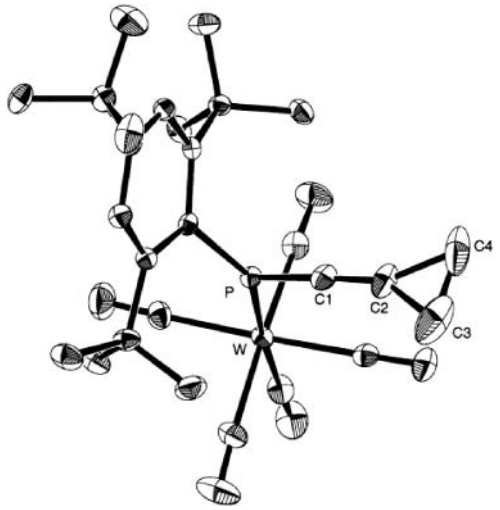


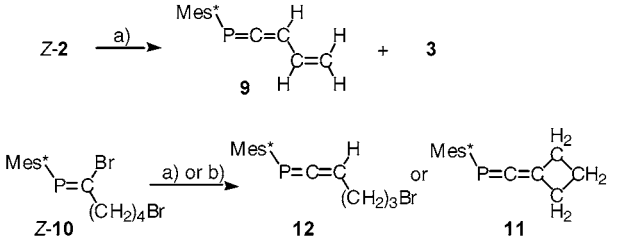
Figure 1. An ORTEP drawing of the molecular structure for **7** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P−W 2.5311(8), P−C1 1.637(4), P1−C_{Mes*} 1.847(4), C1−C2 1.269(5), C2−C3 1.481(6), C2−C4 1.480(7), C3−C4 1.53(1), W−P−C1 115.4(1), W−P−C_{Mes*} 141.8(1), C1−P1−C_{Mes*} 102.6(2), P1−C1−C2 171.7(3), C1−C2−C3 148.8(6), C1−C2−C4 149.0(5), C3−C2−C4 62.2(5), C2−C3−C4 58.9(4), C2−C4−C3 58.9(4).

in methylenecyclopropane [1.457(14) Å] and the C3−C4 distance is close to the distal bond [1.5415(3) Å].[19] It is suggested that the high-energy HOMO of the cyclopropyl group can interact with the P═C═C skeleton, especially, to raise the bond order of the C═C part.[6,14]

Taking into account the existence of the phosphaallene group and the cyclopropyl ring in the same molecule, the reactivity of **3**, especially the transformation of the cyclopropylidenephosphaethene skeleton, is of great interest and the reaction of **3** with a hydride reagent was carried out. Compound **3** was thus reacted with lithium aluminum hydride to mainly afford a geometric mixture of phosphaethenes *E*/*Z*-**6** (*E*/*Z* = 4:1) together with the phosphinomethylenecyclopropane **8**.[20,21] Interestingly **8** isomerized to *E*/*Z*-**6** (*E*/*Z* = 5:1) upon heating in the presence of a base such as triethylamine.[22] Although it is not obvious whether the P═C or C═C moiety displays higher reactivity,[23] it should be noted that the cyclopropyl ring remained unchanged under similar reaction conditions that were employed for vinylidenecyclopropane (Scheme 2).[24] Neither thermolysis (80 °C in toluene) nor photolysis (λ >300 nm in benzene-d_6) of **3** afforded any skeletal isomerization product probably due to the bulky Mes* group,[25] even though several isomerizations of ethenylidenephosphiranes giving the corresponding phospha[3]radialenes have been reported.[26]

Since the γ-elimination by potassium *tert*-butoxide was established, we then examined the reaction of *Z*-**2** with another base and an alkoxide was selected. Compound *Z*-**2** was thus allowed to react with sodium ethoxide to afford 1-phosphapenta-1,2,4-triene **9** in 11% isolated yield together with **3** (Scheme 3).[27] It is suggested that the weaker basicity

Scheme 3[a]



[a] Reagents and conditions: (a) NaOEt, THF, reflux. (b) *t*-BuOK, THF, rt.

of the ethoxide might facilitate the formation of the 1-phosphaallene skeleton rather than the formation of the cyclopropylidene group. Interestingly, compound **9** isomerized to

(17) Crystal data for **7**: $C_{27}H_{33}O_5PW$: *M* 652.38, red prisms crystallized from dichloromethane at 0 °C, crystal dimensions 0.30 × 0.30 × 0.25 mm^3, monoclinic, space group $P2_1/c$ (no. 14), a = 13.2761(4) Å, b = 10.1614(3) Å, c = 20.8686(8) Å, β = 101.7659(9)°, V = 2756.1(2) Å^3, Z = 4, ρ_{calcd} = 1.572 g cm^{-3}, F(000) = 1296.00, μ = 4.287 mm^{-1}, T = 150 K, 21968 reflections measured ($2\theta_{max}$ = 55.0°), 6225 were observed (R_{int} = 0.044), $R1$ = 0.031 [$I > 2.0\sigma(I)$], R_w = 0.042 (all data), S = 1.23 (439 parameters). CCDC-200284.

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(20) To a solution of **3** (123 mg, 0.38 mmol) in THF was added a THF solution of $LiAlH_4$ (0.75 mmol) at 0 °C. The reaction mixture was warmed to room temperature and then refluxed for 1 h. After cooling to room temperature, the mixture was treated with ethyl acetate at 0 °C. The solvent was removed in vacuo and the residue was extracted with hexane. In the ^{31}P NMR spectrum *E*/*Z*-**6** (*E*/*Z* 4:1) and **8** were observed in a 2:1 ratio together with trace amounts of unidentified products. *E*-**6**: $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 234; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (dd, 1H, $^2J_{PH}$ = 25 Hz, $^3J_{HH}$ = 11 Hz, P═CH), 2.10 (m, 1H, CH), 0.96 (m, 2H, C*H*H), 0.57 (m, 2H, CH*H*). **8**: ^{31}P NMR (162 MHz, $CDCl_3$) δ −70 (dd, $^1J_{PH}$ = 230 Hz, $^2J_{PH}$ = 22 Hz); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (d, 1H, $^1J_{PH}$ = 230 Hz, PH), 6.03 (m, 1H, CH). Phosphaethene *E*-**6** was alternatively obtained in a similar manner for *Z*-**6**.

(21) The reaction of 1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaallene (Mes*P═C═CH_2)[13] with lithium aluminum hydride gave Mes*P(H)CH═CH_2 (δ_P −66) and (*E*)-Mes*P═$CHCH_3$ (δ_P 250) in a 1:4 ratio. As for the preparation of (*E*)-Mes*P═$CHCH_3$: (a) Märkl, G.; Bauer, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1695. (b) Ito, S.; Toyota, K.; Yoshifuji, M. *Chem. Commun.* **1997**, 1637.

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(27) **9**: Colorless crystals, mp 82−84 °C dec; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 68; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (m, 1H, ═CH), 6.37, (m, 1H, ═CH), 5.25 (m, 1H, ═CH), 5.06 (m, 1H, ═CH); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 242.5 (d, $^1J_{PC}$ = 25 Hz, P═*C*═C), 131.7 (d, $^2J_{PC}$ = 13 Hz, P═C═*C*), 118.1 (d, $^5J_{PC}$ = 3 Hz, CH_2), 112.9 (d, $^3J_{PC}$ = 11 Hz, CH).

3 in the presence of potassium *tert*-butoxide probably through cyclization involving the [1,2]-migration of the allenic proton.[28]

Second, we applied the above procedure to a cyclobutylidene derivative. The 6-bromo-1-phosphahex-1-ene *Z*-**10,** prepared by a similar method for *Z*-**2** with 1,4-dibromobutane, was allowed to react with potassium *tert*-butoxide to afford the cyclobutylidenephosphaethene **11** in only 15% isolated yield.[10,29] On the other hand, the reaction of *Z*-**10** with sodium ethoxide afforded 6-bromo-1-phosphahexa-1,2-diene **12**,[10] which was converted to **11** in the presence of potassium *tert*-butoxide (Scheme 3).

In conclusion, we have demonstrated that it is possible to prepare a novel 1-phosphaallene derivative **3** containing the cyclopropylidene moiety and the carbonyltungsten(0) complex **7**. Reaction of **3** with a hydride reagent afforded **6** and **8** without cleavage of the cyclopropyl rings. The cyclopropylidenephosphaethene skeleton remained unchanged by heat and by light. Potassium *tert*-butoxide promoted not only γ-elimination but also isomerization of **9** to **3**. The phosphaethenes carrying the cycloalkyl group are expected to be utilized as a synthon for a variety of organophosphorus compounds to reveal several unique properties that are enhanced by the electronic effects of the cyclopropane ring.

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Supporting Information Available: Full spectroscopic data for *Z*-**2**, **3**, *Z*-**5**, *Z*/*E*-**6**, **7**, **9**, *Z*-**10**, **11**, and **12**, experimental details for the preparation of **3**, **7**, and **9**, and X-ray crystallographic data (CIF) for **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) We obtained 1,7-bis(2,4,6-tri-*tert*-butylphenyl)-1,7-diphosphacyclododeca-2,8-diyne [$\delta_P = -50$; $\nu_{C\equiv C}$ 2189 cm^{-1}; *m*/*z* 684 (M^+)] as a byproduct in the reaction of *Z*-**10** under condition b in Scheme 3.