solution in Et_2O) was slowly added, the color of the solution turned light red. The reaction mixture was warmed to $-15\,^\circ C$ and stirred for 1.5 h. At this temperature the Et_2O was pumped off and the residue was dissolved in a little *n*-pentane. With the help of a Teflon tube the solution was transferred into a 8-mL glass ampule. Upon cooling from $-20\,^\circ C$ to $-35\,^\circ C$ rubin red plates crystallized. Yield approximately 30%, losses were attributed to the filtration procedure and to the recrystallization. ^1H NMR (*n*-pentane, $-20\,^\circ C$): $\delta = 1.91$; ^{13}C NMR: $\delta = 60.20$ (broad), $^1J_{C,H} = 123.4$ Hz. Crystal structure analysis: A crystal ($0.5 \times 0.4 \times 0.1$ mm^3) was mounted under nitrogen with cooling on the CCD diffractometer and measured as described above. Solution and refinement were performed with the Shelx programs.[14,15] $a = 694.6(3)$, $b = 1278.50(14)$, $c = 1733.6(4)$ pm, $V = 1.5395(7)$ nm^3, $Z = 4$, space group $Pbc2_1$, 17322 measured, 4603 independent reflections, 222 parameters, $R' = 0.0323$, $wR_2 = 0.0778$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135548 ($[Mo(CH_3)_6]$) and CCDC-135549 ($[LiO(C_2H_5)_2]^+[Mo(CH_3)_7]^-$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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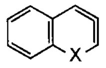
Synthesis of an Isolable Diphosphaisobenzene and a Stable Cyclic Allene with Six Ring Atoms[**]

Michael A. Hofmann, Uwe Bergsträßer, Guido J. Reiß, László Nyulászi, and Manfred Regitz[*]

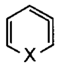
Dedicated to Professor Manfred Meisel
on the occasion of his 60th birthday

The synthesis of unusual, ring-strained isomers of benzene has been attracting increasing interest in the past few years. Besides cyclohexa-1,2,3-triene and cyclohexa-1-en-3-yne,[1] these species include cyclohexa-1,2,4-triene (**1**), an isobenzene that has been the subject of several theoretical studies.[2] In 1992, Christl et al. generated **1** for the first time using the Doering–Moore–Skattebøl method and confirmed its existence chemically by means of trapping reactions.[3] Compound **1** can also be formed by thermolysis of hexa-1,3-dien-5-yne.[4]

1



2a:X = CH_2
2b:X = CMe_2
2c:X = O



3a:X = S
3b:X = O

The benzo-condensed isobenzenes **2a**,[3] **2b**,[5] and the oxygen analogue **2c**[6] as well as the heteroatom-substituted isobenzene **3a**[7] have also been generated and trapped. Furthermore, substituted cyclohexa-1,2,4-trienes of the types **1** and **3b** have been discussed as nondetectable intermediates in the [4+2] cycloadditions of enynes and acylacetylenes, respectively, with alkynes.[8] We now report on the synthesis of the $1H$-$5\delta^2$-diphosphinine **8a**, which is stable at room temperature, and the cyclic allene **10** that can be prepared from it (see Scheme 2).

The starting material for the reactions described here is the previously unknown phosphatriafulvene **6** prepared from **4** and **5** (Scheme 1).[9] The structure of **6** was deduced from spectroscopic data as well as by comparison with the values reported for other known phosphatriafulvenes[9] and is not discussed in detail here. When **6** is allowed to react with the kinetically stabilized phosphaalkyne **7**[10] at 80 °C the isobenzene **8a** is obtained. This product is characterized by an

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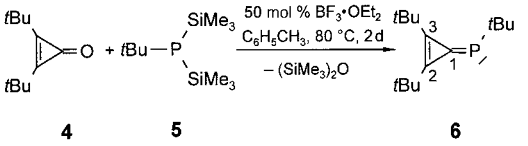
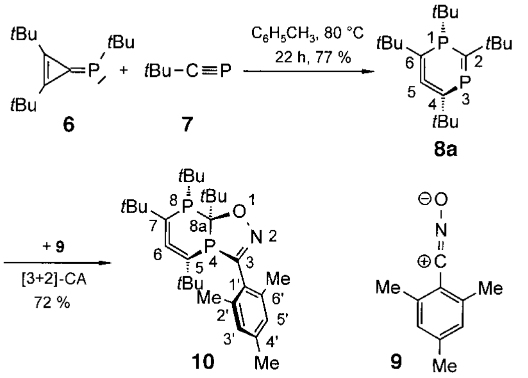


Scheme 1. Synthesis of **6**.

Table 1. Relative energies of **8**, **11**, and **12** [kcal mol^{-1}].

R	8	11	12
H	49.39	0.00	51.97
Me	43.61	0.00	45.86
*t*Bu	0.00	4.19	17.87



Scheme 2. Synthesis of **8a** and its further reaction to give **10**. CA cycloaddition.

unexpected thermal stability and was obtained as a red oil in 77% yield by bulb-to-bulb distillation.

The constitution of **8a** can be derived readily from its NMR data. The ^{31}P NMR spectrum contains two doublets at $\delta = 351.7$ (^2J(P,P) = 24.5 Hz; P3) and 52.3 (^2J(P,P) = 24.5 Hz; P1). The former is in the typical region for the signals of a P–C double bond, while the signal at higher field is split into a multiplet as a consequence of the direct adjacency of a *tert*-butyl group. The ^{13}C NMR spectrum provides decisive diagnostic information: the signal at $\delta = 208.1$, which is split into a double doublet by two ^1J(C,P) coupling constants, must be assigned to the carbon atom C2 of the P–C double bond. The two carbon atoms C4 and C6 give signals in the typical region for double bonds and are each in the immediate vicinity of a phosphorus atom. The position of the signal for C5 is typical for a central allene carbon atom.[11] The prominent IR bands at $\tilde{\nu} = 1865$ and 1846 cm^{-1} are also in accord with the structure deduced from the NMR spectral data. Two distinct allene bands in a similar region have been discussed for the short-lived cyclohexa-1,2-diene.[12] As shown by the NMR spectra, the diphosphaisobenzene **8a** is formed highly selectively as a single diastereomer.

For unequivocal confirmation of its isobenzene structure, **8a** was converted to the crystalline adduct **10** by treatment with 2,4,6-trimethylbenzonitrile oxide (**9**); this reaction proceeds chemo-, regio-, and stereoselectively.[13] Here again, the typical signal at $\delta = 207.1$ for C6 in the ^{13}C NMR spectrum and the conspicuous allene bands at $\tilde{\nu} = 1865$ and 1830 cm^{-1} in the IR spectrum are seen. A single-crystal X-ray structure analysis confirmed not only the constitution but also the relative configuration of the 5,7,8,8a-tetra-*tert*-butyl-3-(2,4,6-trimethylphenyl)-8a*H*-6δ^2-[1,3]diphosphinino[1,2-*d*][1,2,4]oxazaphosphole (**10**) and thus also those of **8a**.[14] To the best of our knowledge, compound **10** is the first stable cyclohexa-1,2-diene with only two heteroatoms in the six-membered ring.[15]

As expected, the allene unit is bent (155.8°; Figure 1). The C5–C6 and C6–C7 bond lengths of 1.327 and 1.302 Å, respectively, are in the typical range for cumulenes. The endocyclic dihedral angle as defined by the P4-C5-C6 and the C6-C7-P8 planes of 40.7° deviates widely from the ideal value (90°) and, together with the angle of the allene unit (155.8°), is considerably smaller than the corresponding angles in the first structurally characterized cyclohexa-1,2-diene (64.6° and 166.4°, respectively).[15] The P8–C8a bond length of 1.953 Å is markedly stretched.[16]

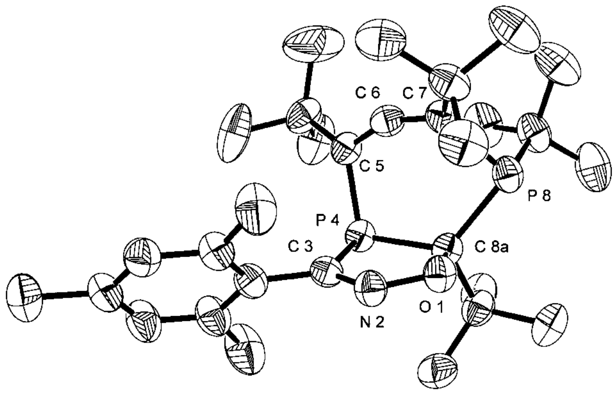
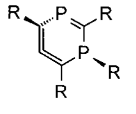


Figure 1. Structure of **10** in the crystal (thermal ellipsoids for 50% probability). Selected bond lengths [Å] and angles [°]: P4-C5 1.829(3), C5-C6 1.327(3), C6-C7 1.302(4), C7-P8 1.837(3), P8-C8a 1.953(3), C8a-O1 1.489(3), O1-N2 1.403(3), N2-C3 1.281(3), C3-P4 1.826(2), P4-C8a 1.901(3); P4-C5-C6 109.6(2), C5-C6-C7 155.8(3), C6-C7-P8 110.8(2), C7-P8-C8a 96.37(12), P8-C8a-P4 121.71(14), C8a-P4-C5 104.48(12), P4-C8a-O1 104.73(15), C8a-O1-N2 116.1(2), O1-N2-C3 114.0(2), N2-C3-P4 116.8(2), C3-P4-C8a 87.88(11).

Calculations on the relative energies[17] of the isomeric structures **8**, **11**, and **12** reveal that, for small substitutuents (R = H, Me), the diphosphabenzene **11** is, as expected, the most stable isomer (Table 1). When the *tert*-butyl groups are considered in the calculations it is found that the isobenzene **8** (≡**8a**) is more stable than the diphosphabenzene **11** by 4.19 kcal mol^{-1}. The latter is not planar on account of the enormous steric demands of the substituents; this leads to a loss of aromaticity. On the other hand, for **8a** the pyramidalization at P1 as well as the twisting of the six-membered ring through the 1,2-diene unit result in the best possible spatial arrangement of the large substituents. According to the calculations **12** is less stable than the diastereomer **8** and thus also cannot be detected experimentally.



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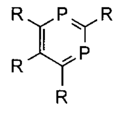

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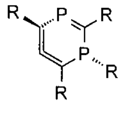

12

Experimental Section

All reactions were performed under an argon atmosphere in anhydrous solvents.

6: In a pressure Schlenk tube boron trifluoride etherate complex (0.63 mL, 0.71 g, 5 mmol) was added to **4** (3.17 g, 19 mmol)[18] and **5** (5.5 mL, 4.69 g, 20 mmol)[19] in toluene (15 mL) and the mixture was stirred at 80 °C for 24 h. After repeated addition of the same amount of boron trifluoride etherate, stirring at 80 °C was continued for further 20 h. The reaction mixture was then allowed to cool and volatile materials were removed at 25 °C/10^{-3} mbar. The resultant yellow solid was taken up in *n*-pentane and the solution filtered through celite. Yield: 3.57 g (79 %) pale yellow platelets (from *n*-pentane at −28 °C). M.p. 74 °C. Storage at −28 °C; ^{31}P NMR (C_6D_6): $\delta = 46.5$ (dec, ^3J(P,H) = 10.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 152.2$ (d, ^2J(C,P) = 31.4 Hz; C2), 154.6 (d, ^2J(C,P) = 11.0 Hz; C3), 158.5 (d, ^1J(C,P) = 89.0 Hz; C1); MS (EI, 70 eV): *m*/*z* (%): 238 (51) $[M]^+$.

8a: In a pressure Schlenk tube a solution of **6** (328 mg, 0.97 mmol) in toluene (5 mL) was treated with **7** (144 μL, (1 mmol)[20] and the mixture heated at 80 °C for 22 h. After the mixture was cooled to room temperature the volatile materials were removed at 25 °C/10^{-3} mbar and the crude product purified by bulb-to-bulb distillation (80 °C/10^{-3} mbar). Yield: 254 mg (77 %) red oil. ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 52.3$ (d, ^2J(P,P) = 24.5 Hz; P1), 351.7 (d, ^2J(P,P) = 24.5 Hz; P3); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 105.4$ (dd, ^1J(C,P) = 32.6 Hz, ^3J(C,P) = 3.0 Hz; C4/6), 113.3 (dd, ^1J(C,P) = 59.3 Hz, ^3J(C,P) = 2.5 Hz; C4/6), 202.4 (pseudo-t, ^2J(C,P) = ^2J(C,P) = 3.8 Hz; C5), 208.1 (dd, ^1J(C,P) = 69.5 Hz, ^1J(C,P) = 60.2 Hz; C2); MS (EI, 70 eV): *m*/*z* (%): 338 (19) $[M]^+$.

10: Compound **9** (42 mg, 0.26 mmol) in toluene (2 mL) was added by pipette at −78 °C to a solution of **8a** (88 mg, 0.26 mmol) in toluene (2 mL). The mixture was allowed to thaw and stirred for 14 h at room temperature. After removal of volatile materials at 25 °C/10^{-3} mbar, the residue was crystallized from *n*-pentane at −78 °C. Yield: 94 mg (72 %) yellowish crystals. M.p. 95 °C. ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 91.4$ (d, ^2J(P,P) = 13.5 Hz; P4), 122.5 (d, ^2J(P,P) = 13.5 Hz; P8); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 107.2$ (dd, ^1J(C,P) = 41.8 Hz, ^3J(C,P) = 2.4 Hz; C5/7), 110.3 (dd, ^1J(C,P) = 40.2 Hz, ^3J(C,P) = 2.4 Hz; C5/7), 127.8 (dd, ^1J(C,P) = 53.8 Hz, ^1J(C,P) = 52.2 Hz; C8a), 159.2 (d, ^1J(C,P) = 40.2 Hz; C3), 207.1 (pseudo-t, ^2J(C,P) = ^2J(C,P) = 6.6 Hz; C6); MS (CI, isobutene): *m*/*z*: 500 $[M+H]^+$.

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