

- spectrum obtained from the mass spectroscopic scan at nearly the center of each gas chromatographic peak for the total mixture. The following observation indicated the necessity of such a consideration (center of the peak), but the accuracy attained by this method is unknown for some compounds. When the gas chromatographic peak of deuterated **7b** was covered by three consecutive mass spectrometric scans, the first, the second, and the last spectra indicated the presence of **7c-d₂** and **7c-d₂** in 60–40, 47–53, and 40–60%, respectively. (a) A portion withdrawn for monitoring at an earlier reaction time (2 h) indicated a higher proportion of **4b-d₄** (75%). (b) The ratio of the intensities of the M⁺ peak (where all chlorine atoms are ³⁵Cl) of the indicated species and the peak at the (M – 1)⁺ position is approximately 92:8. (c) Values of 47–53%, subject to deviation from GC–mass run to run, obtained. (d) The spectrum is consistent with the structures. However, no peak apparently enables one to distinguish the two species.
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 (21) The expected decreasing stability of the radicals is **22** > **19** (> **21**), and definite stability differences seem to exist among them. If this is the case, the formation of comparable amounts of **19** and **22** is not understood unless one of the following conditions is satisfied: (1) Conversion of **2f** to **19** is reversible. (2) Direct conversion of **2f** to **22** occurs. (3) **21** and **22** (thus, **19** and **20**, too) are canonical forms of a resonance hybrid rather than equilibrating species. Condition 3 seems most probable.
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 (28) Where a structure containing chlorine is assigned, the existence of isotopic peaks in the relative intensities consistent with the number of chlorine atoms has been confirmed. In such cases, only the intensities of fragment (or parent) peaks where the chlorine atoms are all ³⁵Cl are indicated.

Studies on Organic Fluorine Compounds. 28.¹ Synthesis and Some Reactions of Tetrakis(trifluoromethyl)-1,4-diphospha-benzene

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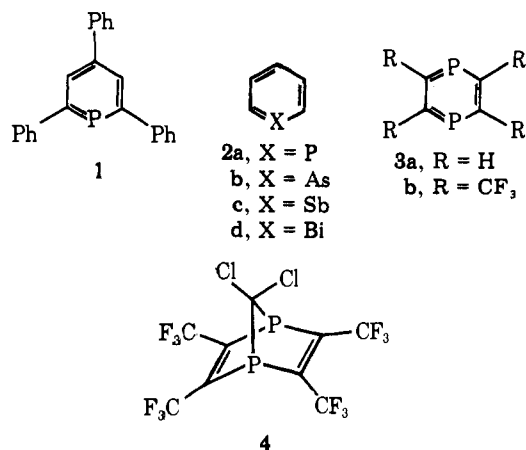
Abstract: Tetrakis(trifluoromethyl)-1,4-diphospha-benzene (**3b**), the first example of diphospha-benzenes, was synthesized by the thermolysis of 2,3,5,6,7,8-hexakis(trifluoromethyl)-7-methoxy-1,4-diphospha-bicyclo[2.2.2]octa-2,5-diene (**6**), which was obtained by addition of methanol to hexakis(trifluoromethyl)-1,4-diphospha-barrelene (**5**) in the presence of rhodium trichloride or some other catalysts. The compound **3b** seems to have some aromaticity since it shows a large absorption maximum at 282 nm. It is sensitive to air, but thermally stable and reacts with acetylenic compounds to give diphospha-barrelene compounds. Further, **3b** reacts with carbon tetrachloride to give a diphosphanorbornadiene compound (**4**). The air sensitivity and the formation of **4** suggests that the phosphorus atom of **3b** has some character of a trivalent phosphorus atom, while that of **5** hardly does.

Introduction

One of the heteroaromatic compounds containing group 5 elements, phosphabenzene, has been of much interest from the standpoints of its theoretical implication, structural property, and chemical reaction, since it is the first member of the series of compounds having an empty d orbital. The first synthesis of this type of compounds was achieved in 1967 by G. Märkl.² He synthesized 2,4,6-triphenylphosphabenzene (**1**) and reported that it was fairly stable. In 1971, A. J. Ashe reported the synthesis of unsubstituted phosphabenzene (**2a**).³ Further, he succeeded in the synthesis of arsabenzene³ (**2b**), stibabenzene⁴ (**2c**), and bismabenzene⁵ (**2d**) and reported the reactions and structural studies of these compounds.^{5,6} But the diphospha-benzene derivatives, which contain two phosphorus atoms in one ring, have not been synthesized yet. Particularly, unsubstituted diphospha-benzene (**3a**) is predicted to be very unstable because it has two trivalent phosphorus atoms.

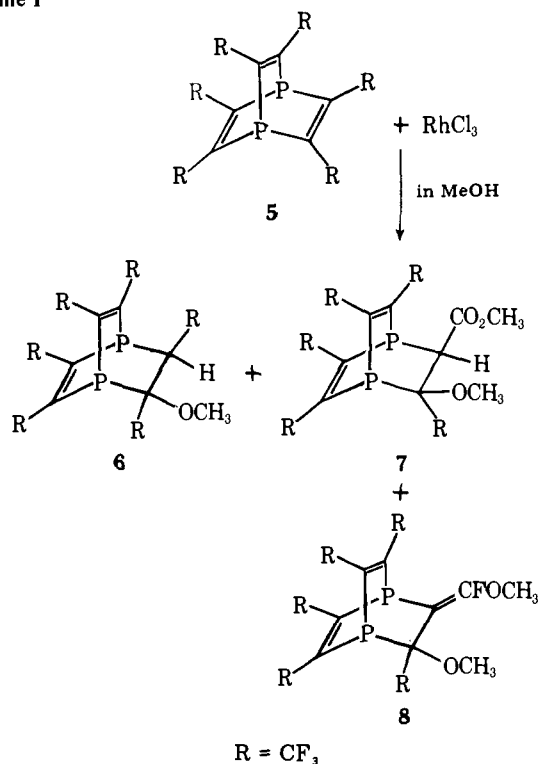
On the other hand, the perfluoroalkyl group is known to stabilize strained or labile compounds. This effect is often called "perfluoroalkyl effect".⁷ We expected that the intro-

Chart I

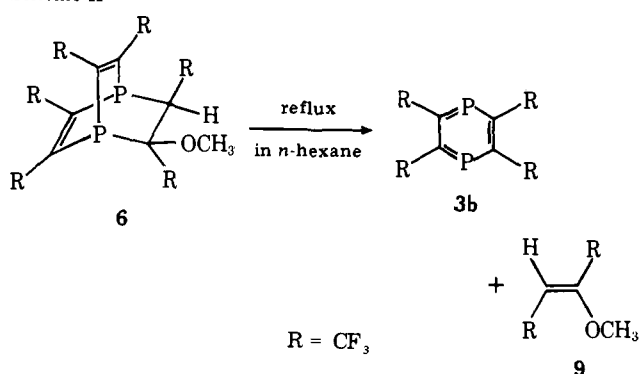


duction of perfluoroalkyl groups into the diphospha-benzene might allow the isolation of this new type of compound. From

Scheme I



Scheme II



this point of view, we chose 2,3,5,6,7,8-hexakis(trifluoromethyl)-1,4-diphosphabarrelene⁸ (**5**) as a starting material and succeeded in the synthesis of 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabenzene (**3b**). This paper deals with the synthesis of **3b** and some of its reactions involving a novel formation of 2,3,5,6-tetrakis(trifluoromethyl)-7,7-dichloro-1,4-diphosphabicyclo[2.2.1]hepta-2,5-diene (**4**).

1. Synthesis of 2,3,5,6-Tetrakis(trifluoromethyl)-1,4-diphosphabenzene (3b). It has been reported⁸ that 2,3,5,6,7,8-hexakis(trifluoromethyl)-1,4-diphosphabicyclo[2.2.2]octa-2,5,7-triene (**5**), a diphospha analogue of barrelene, has little character of the trivalent phosphorus atom: it is insoluble in concentrated sulfuric acid and inert to atmospheric oxygen, methyl iodide at room temperature, benzyl chloride at 100 °C, or bromine dissolved in chloroform, and the lack of reactivity is ascribed to the steric hindrance by the trifluoromethyl groups on the neighboring phosphorus atoms. We found that treatment of **5** with rhodium trichloride in methanol at room temperature for several days gave 2,3,5,6,7,8-hexakis(trifluoromethyl)-7-methoxy-1,4-diphosphabicyclo[2.2.2]octa-2,5-diene (**6**), 2,3,5,6,7-pentakis(trifluoromethyl)-7-methoxy-8-methoxycarbonyl-1,4-diphosphabicyclo[2.2.2]octa-2,5-diene (**7**), and 2,3,5,6,7-pentakis(trifluoromethyl)-7-methoxy-8-fluoromethoxymethylene-1,4-diphosphabicy-

Table I. ³¹P Chemical Shifts (ppm) of **3b** and Similar Compounds

3b	10	2	11
-287.1	-245.4	-178.2	-197.0

Table II. ¹³C Chemical Shifts of α Carbons to Heteroatoms

pyridine ⁶	phosphabenzene ⁶	10	3b
150.6	154.1	144.4	163.9

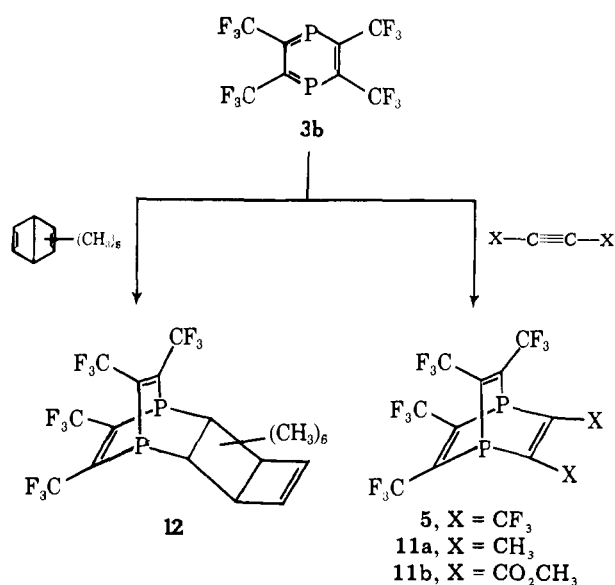
clo[2.2.2]octa-2,5-diene (**8**) in 55, 3.8, and 5.3% yields, respectively (Scheme I).

Metal ions other than those in rhodium trichloride, cuprous chloride, cupric chloride, and silver perchlorate also converted **5** into **6**, **7**, and **8**, while palladium chloride caused no reaction. Moreover, treatment of **5** with methanolic hydrogen chloride gave the same products, but in this case the reaction occurred much more slowly than the metal ion catalyzed reaction. From these facts, this reaction seemed to proceed via acid-catalyzed formation of a carbonium ion, and the metal ion is assumed to contribute to stabilization of the carbonium ion.

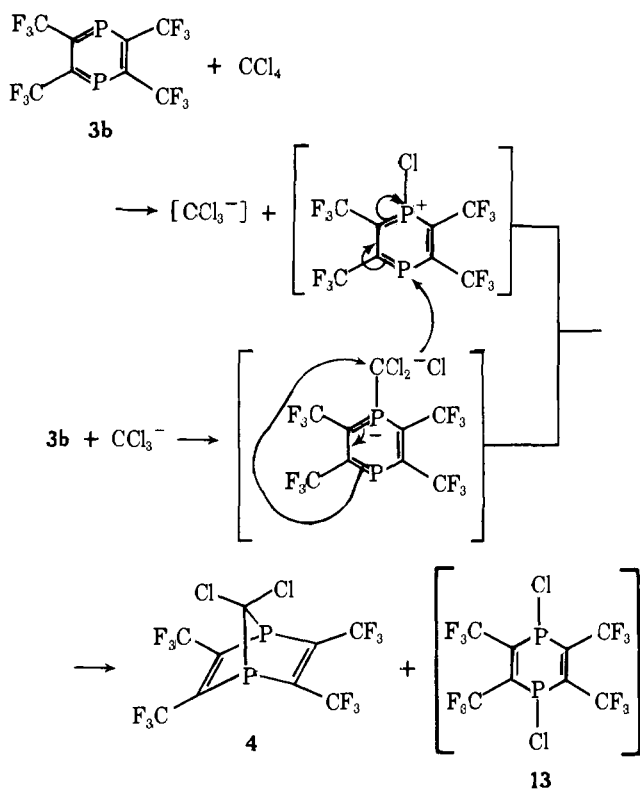
To our great interest, the mass spectrum of **6** shows no peak of a molecular ion but shows peaks of *m/e* 386 (corresponding to **3b**) and 194 (corresponding to 1,1,1,4,4,4-hexafluoro-2-methoxybutene-2 (**9**)). This fact suggests that **6** could be a precursor of **3b**. Actually, **3b** and **9** were obtained by refluxing **6** in *n*-hexane solution in a stream of oxygen-free argon (Scheme II). Compound **9** was collected in a trap connected to the top of a reflux condenser and cooled at -78 °C. Compound **3b** remained in the hexane solution in the reaction vessel. Because of the great sensitivity of **3b** toward oxygen, even a small amount of oxygen must be removed from argon. The structure of **9** was determined by comparison of ¹H and ¹⁹F NMR spectra with those of an authentic sample.⁹ A small coupling constant of the two trifluoromethyl groups shows that **9** is the trans isomer. The UV spectrum of **3b** shows a strong peak at 282 nm ($\epsilon > 4000$ –5000 in hexane in argon atmosphere). Although it was impossible to measure the accurate value for ϵ of **3b** because of its high sensitivity toward oxygen, it is evident from a comparison of this value of ϵ with those of **5** and **6** (**5**: 262 nm, ϵ 450; 330 nm, ϵ 640. **6**: 243 nm, ϵ 1650, 330 nm, ϵ 1010) that **3b** has a ring conjugation. The ¹⁹F NMR signal of the four equivalent trifluoromethyl groups of **3b** appears as a doublet at -11.6 ppm [$1/2(J_{PF} + J_{PF}) = 66$ Hz]. The ³¹P NMR of the two equivalent phosphorus atoms appears as a multiplet at -287.1 ppm. Irradiation at ¹⁹F frequency removed the fluorine coupling and the signal became singlet (See Table I). The ¹³C NMR under irradiation at ¹⁹F frequency shows a quartet at 163.9 ppm and a broad multiplet at 124.5–122.4 ppm. These ¹³C chemical shifts of **3b** correlated very closely with those of 2,3,5,6-tetrakis(trifluoromethyl)pyridazine (**10**) and those of heterobenzenes (Table II). The mass spectrum of **3b** after the removal of hexane in argon atmosphere shows a relatively weak molecular ion peak (*m/e* 386) and a strong peak [*m/e* 317 ($M^+ - CF_3$)]. These spectral data support the assumption that **3b** is 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabenzene.

2. Some Reactions of 2,3,5,6-Tetrakis(trifluoromethyl)-1,4-diphosphabenzene (3b). **2-1 Reaction with Acetylenic Compounds.** The compound **3b** is very sensitive toward oxygen and base, but is thermally stable (**3b** did not change on heating at 180 °C for 3 h). Next, we investigated the thermal reaction with acetylenic compounds. Treatment of the methanol adduct (**6**) with hexafluorobutene-2, dimethylacetylene, and di-

Scheme III



Scheme IV



methacetylenedicarboxylate in *n*-pentane at 90–95 °C in a sealed tube gave barrelene type 1:1 Diels–Alder adducts, **5**, **11a**, and **11b** in 52, 79 and 51% yields, respectively. These results are comparable to the reactions of **1**¹² and **2a**⁵ with hexafluorobutyne-2 in forming the corresponding 1-phospha-barrelene compounds. The difference is that the reaction of diphosphabenzene (**3b**) is much more rapid than those of phosphabenzenes (**1**, **2a**). This is perhaps due to the two unstable $\text{C}=\text{P}$ bonds and large polarizability of **3b**. This high reactivity of **3b** was more clearly demonstrated by the reaction with hexamethyl (Dewar benzene) to give a Diels–Alder adduct **12** (Scheme III).

2-2,3,5,6-Tetrakis(trifluoromethyl)-7,7-dichloro-1,4-diphospha[2.2.1]hepta-2,5-diene (Diphosphanorbornadiene 4) from 3b. Diphosphabarrelene (**5**) hardly shows the reactivity

as a trivalent phosphorus compound and is stable to oxygen. On the other hand, diphosphabenzene (**3b**) is very sensitive to oxygen and decomposed via monooxide compound. This fact suggests that diphosphabenzene (**3b**) had the reactivity as a trivalent phosphorus compound. Therefore we investigated the reaction of **3b** with carbon tetrachloride. Heating **3b** with carbon tetrachloride in a sealed NMR tube at 130 °C caused disappearance of the peak ascribed to **3b** and appearance of two new doublets (–8.0 and –10.2 ppm) of nearly the same intensities in ¹⁹F NMR spectrum, while no change was observed after heating **5** at 140 °C. Workup of the reaction mixture gave a diphosphanorbornadiene (**4**), to which the doublet at –8.0 ppm was assigned. The mechanism of formation of **4** is tentatively assumed by analogy with the reaction of triphenylphosphine with carbon tetrachloride¹³ as shown in Scheme IV. Then, the doublet at –10.2 ppm might be due to the compound **13**. Rapid disappearance of this peak on contact with atmosphere was in accordance with the expectation that a halophosphorus compound such as **13** should be unstable toward air and moisture. Although the precise mechanism is not clear, this reaction shows that **3b** has more character of a trivalent phosphorus compound than **5**. The compound **4** is a new ring system having two phosphorus atoms at the bridgeheads.

Experimental Section

General. ¹H and ¹⁹F NMR were obtained by an NEVA T-60 spectrometer. Benzotrifluoride was used as an internal or external standard for ¹⁹F NMR, upfield shifts being shown as positive. ³¹P and ¹³C NMR were obtained by a Varian XL-100-1z spectrometer and a Varian 620/L computer. A 50% solution of H₃PO₄ in D₂O and Me₄Si were used as an external standard for ³¹P and ¹³C NMR, upfield shifts being shown as positive for ³¹P and negative for ¹³C. JASCO-IR-AL diffraction grating spectrometer was used for IR spectra. A Hitachi 124 spectrometer was used for UV spectra.

Hexakis(trifluoromethyl)-1,4-diphosphabarrelene (**5**) was obtained according to Krespan's procedure⁸ from hexafluorobutyne-2, which was supplied by PCR Research Chemicals, Inc.

All the melting points were uncorrected.

2,3,5,6,7,8-Hexakis(trifluoromethyl)-7-methoxy-1,4-diphosphabicyclo[2.2.2]octa-2,5-diene (6). A suspension of **5** (1.72 g) and RhCl₃ (0.16 g) in MeOH (50 mL) was stirred at room temperature for 5 days. After evaporation of MeOH under vacuum, the residue was extracted with *n*-pentane. The extract was passed through a SiO₂ (100 g) column in *n*-pentane. The effluent was recrystallized from *n*-pentane to give colorless plates (0.994 g, 55%) (**6**): mp 68–70 °C (in a sealed tube); IR (KBr) $\nu_{\text{C}=\text{C}}$ 1600 cm⁻¹; UV $\lambda_{\text{max}}^{\text{MeOH}}$ 243 (log ϵ 3.29), 332 nm (3.00), ¹H NMR (CDCl₃) δ 3.37 (3 H, s, OCH₃), 2.80 (1 H, q, $J_{\text{HF}} = 9$ Hz, C–CH–CF₃); ¹⁹F NMR δ 3.36 (3 F, m, CF₃), –6.80 (15 F, m, CF₃); mass m/e 386 (M – 194, corresponding to compound **3b**), 194 (M – 386, corresponding to 1,1,1,4,4,4-hexafluoro-2-methoxybutene-2). High mass calcd for C₁₈F₁₂P₂: 385.928. Found: 385.926.

The next effluent was recrystallized from *n*-pentane to give colorless plates (**8**) (94 mg, 5.3%): mp 81–82 °C (in a sealed tube); IR (KBr) $\nu_{\text{C}=\text{C}}$ 1645, 1620; ¹H NMR (CDCl₃) δ 3.45 (3 H, s, OCH₃), 4.03 (3 H, s, COOCH₃); ¹⁹F NMR (CDCl₃) δ 2.20 (3 F, m, CF₃), –5.80 (13 F, m, 4 × CF₃ + C=CF(OCH₃)); mass m/e 572 (M⁺). High mass calcd for C₁₄H₆O₂F₁₆P₂ (M⁺): 571.959. Found: 571.959.

The third effluent was recrystallized from *n*-pentane to give colorless plates (**7**) (67 mg, 3.8%): mp 85–86 °C (in a sealed tube); IR (KBr) $\nu_{\text{C}=\text{O}}$ 1740, $\nu_{\text{C}=\text{C}}$ 1610; ¹H NMR δ 3.29 (1 H, d, $J_{\text{PH}} = 33$ Hz, >CH), 3.66 (3 H, s, OCH₃); ¹⁹F NMR (CDCl₃) δ 3.88 (3 F, m, CF₃), –6.40 (12 F, m, 4XCF₃); mass m/e 570 (M⁺); High mass calcd for C₁₄H₇F₁₅O₃P₂ (M⁺): 569.963. Found: 569.963.

Yields of methanol adduct (**6**) in the presence of catalyst other than RhCl₃ are as follows: 16.2 (CuCl), 8.6 (CuCl₂), 32.8 (AgClO₃), and 37.6% (CHCl₃).

2,3,5,6-Tetrakis(trifluoromethyl)-1,4-diphosphabenzene (3b). A solution of **6** (700 mg) in *n*-hexane (15 mL) was refluxed in a two-necked flask, equipped with an inlet tube for dry and deoxygenated argon gas. The top of the water-cooled reflux condenser was connected with a poly(vinyl chloride) tube to a trap cooled in an acetone–dry ice

bath and a buffer filled with liquid paraffin. Some of the hexane was carried by the argon through the reflux condenser into the cold trap. ^{19}F NMR showed that this hexane solution contained 2-methoxy-1,1,1,4,4,4-hexafluorobutene (**9**). After **9** was not detected in the hexane in the cold trap, reflux was continued further for 4 h. The total refluxing time was 40 h. ^{19}F NMR of this hexane solution showed one doublet at -11.6 ppm ($J_{\text{PF}} = 66$ Hz). UV spectrum was observed in a quartz cell with a stopcock: $\lambda_{\text{max}}^{n\text{-hexane}}$ 282 nm. Intensity was calculated by assuming complete conversion of **6** to **3b** ($\log \epsilon$ 3.60). Compound **3b** was sensitive to oxygen, and the intensity decreased gradually. Therefore, the value 3.60 means the minimum value of $\log \epsilon$. After evaporation of *n*-hexane with a vacuum pump, mass spectrum of the residue showed m/e 386 (M^+) ^{31}P NMR: δ -287.1 ppm (m, s, by irradiation of ^{19}F NMR); ^{13}C NMR (CDCl_3) (decoupled by ^{19}F) δ 163.9 (q, $J_{\text{PC}_2} = 80.5$ Hz, $J_{\text{PC}_3} = 5.0$ Hz, $-\text{C}=\text{P}-$), 123.5 ppm (b, m, CF_3).

Diels-Alder Reaction of 3b in Situ with Acetylenic Compounds. 2,3,5,6,7,8-Hexakis(trifluoromethyl)-1,4-diphosphabicyclo[2.2.2]octa-2,5,7-triene (5). A solution of **6** (294 mg) and hexafluorobutyne-2 (1 g) in *n*-pentane (16 mL) was heated at 90–95 °C for 14 h in a sealed stainless-steel tube. After evaporation of the solvent with a vacuum pump, the residue was sublimed under vacuum to give colorless needles (144 mg, 51.8%), which were identified by comparison of IR spectrum of an authentic sample of **5** and mixed melting point.

2,3-Dimethyl-5,6,7,8-tetrakis(trifluoromethyl)-1,4-diphosphabicyclo[2.2.2]octa-2,5,7-triene (11a). A solution of **6** (294 mg) and dimethylacetylene (0.5 mL) in *n*-pentane (16 mL) was treated in the same way as in the case of hexafluorobutyne-2. Colorless needles (**11a**) (175.5 mg, 78.7%) were obtained, mp 152.5–153 °C (in a sealed tube); IR $\nu_{\text{C}=\text{C}}$ 1600; UV $\lambda_{\text{max}}^{\text{MeOH}}$ 272 ($\log \epsilon$ 2.96), 326 nm (2.79); ^1H NMR [$(\text{CD}_3)_2\text{CO}$] δ 2.43 [6 H, d, $\frac{1}{2}(J_{\text{PH}} + J_{\text{PH}'}) = 43$ Hz]; ^{19}F NMR [$(\text{CD}_3)_2\text{CO}$] δ -6.30 ppm [12 F, d, $\frac{1}{2}(J_{\text{PF}} + J_{\text{PF}'}) = 37$ Hz, CF_3]; mass m/e 440 (M^+). High mass calcd for $\text{C}_{12}\text{H}_6\text{F}_{12}\text{P}_2$: 439.975. Found: 439.975. Anal. Calcd for $\text{C}_{12}\text{H}_6\text{F}_{12}\text{P}_2$: C, 32.75; H, 1.37. Found: C, 32.38; H, 1.79.

2,3-Bis(methoxycarbonyl)-5,6,7,8-tetrakis(trifluoromethyl)-1,4-diphosphabicyclo[2.2.2]octa-2,5,7-triene (11b). A solution of **6** (294 mg) and dimethylacetylenedicarboxylate (0.3 mL) in *n*-pentane (16 mL) was treated as above to give pale yellow plates (**11b**), (137 mg, 51.2%); mp 108–110 °C (in a sealed tube); IR $\nu_{\text{C}=\text{O}}$ 1740, $\nu_{\text{C}=\text{C}}$ 1600 cm^{-1} ; UV $\lambda_{\text{max}}^{\text{MeOH}}$ 317 (shoulder); ^1H NMR (CDCl_3) δ 3.90 (6 H, s, OCH_3); ^{19}F NMR (CDCl_3) δ -6.60 ppm [d, $\frac{1}{2}(J_{\text{PF}} + J_{\text{PF}'}) = 40$ Hz, CF_3]; mass spectrum m/e 528 (M^+); High mass calcd for $\text{C}_{14}\text{H}_6\text{F}_{12}\text{O}_4\text{P}_2$: 527.955. Found: 527.953. Anal. Calcd for $\text{C}_{14}\text{H}_6\text{F}_{12}\text{O}_4\text{P}_2$: C, 31.84; H, 1.15. Found: C, 32.27; H, 1.25.

2,3,4,5,6,7-Hexamethyl-9,10,11,12-tetrakis(trifluoromethyl)-1,8-diphosphatetracyclo[6.2.2.0^{2,7}.0^{3,6}]dodeca-4,9,11-triene (12). A so-

lution of **6** (52 mg) and hexamethyl (Dewar benzene) (32 mg) in CH_3CN (0.3 mL) was sealed in a Pyrex tube ($\phi = 3$ mm) under vacuum and heated at 80 °C for 1 h. The precipitate was filtered and recrystallized from acetone to give yellow plates (**12**) (27.4 mg, 56%); mp 182–184 °C (in a sealed tube); IR $\nu_{\text{C}-\text{H}}$ 2960, 2920, 2860, $\nu_{\text{C}=\text{C}}$ 1610, 1585 cm^{-1} ; ^1H NMR [$(\text{CD}_3)_2\text{C}=\text{O}$] δ 0.99 (6 H, s, CH_3), 1.40 [6 H, d, $\frac{1}{2}(J_{\text{PH}} + J_{\text{PH}'}) = 22$ Hz, CH_3], 1.72 (6 H, s, CH_3); ^{19}F NMR δ -5.76 [6 F, d, $\frac{1}{2}(J_{\text{PF}} + J_{\text{PF}'}) = 49.6$ Hz, CF_3], -6.36 [6 F, d, $\frac{1}{2}(J_{\text{PF}} + J_{\text{PF}'}) = 54.1$ Hz, CF_3]; mass m/e 548 (M^+). High mass calcd for $\text{C}_{20}\text{H}_{18}\text{F}_{12}\text{P}_2$: 548.069. Found: 548.070. Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{F}_{12}\text{P}_2$: C, 43.81; H, 3.31; F, 41.58. Found: C, 43.58; H, 3.48; F, 41.35.

2,3,5,6-Tetrakis(trifluoromethyl)-7,7-dichloro-1,4-diphosphabicyclo[2.2.1]hepta-2,5-diene (4). (a) A solution of **6** (60 mg) in CCl_4 (0.5 mL) was sealed under vacuum in a Pyrex tube ($\phi = 4$ mm) and heated at 130 °C. The reaction was followed by ^{19}F NMR. At first, signals of **6** gradually disappeared and those of **3b** and **9** appeared. On further heating, signals of **3b** decreased and two new doublets appeared at -8.0 ($J = 22.6$ Hz) and -10.2 ppm ($J_{\text{PF}} = 38.4$ Hz). The former peak was stable after opening of the tube but the latter disappeared on contact with air. Isolation of the former compound is shown in b.

(b) The solution of **6** (600 mg) in CCl_4 (5 mL) was sealed in a Pyrex tube ($\phi = 7$ mm) under vacuum and heated at 130 °C for 5 h. After evaporation of CCl_4 with a vacuum pump, the residue was dissolved in *n*-pentane and passed through a column of SiO_2 (60 g). The effluent was sublimed at 30 °C and 760 mmHg to give yellow needles (**4**) (136 mg, 54%); mp 39–39.5 °C (in a sealed tube); IR (KBr) $\nu_{\text{C}=\text{C}}$ 1600 cm^{-1} ; ^{19}F NMR δ -8.00 ppm [d, $\frac{1}{2}(J_{\text{PF}} + J_{\text{PF}'}) = 22.6$ Hz, CF_3]; mass m/e 468 (M^+). High mass calcd for $\text{C}_9\text{Cl}_2\text{F}_2\text{P}_2$ (M^+): 467.866. Found: 467.868.

References and Notes

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