

Oxidation of Tetraphosphacubane by Bis(trimethylsilyl) Peroxide, Sulfur, and Selenium [1]

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ABSTRACT

*Although the nucleophilicity/basicity at the phosphorus atom of the tetraphosphacubane **2** is reduced, apparently owing to the participation of the lone pairs of electrons in the P/C σ bonds, stepwise oxidation of the phosphorus atoms with bis(trimethylsilyl) peroxide or sulfur (in the presence of triethylamine) can be realized until all four phosphorus atoms have reacted to give products **10–17**. When **2** was treated with a large excess of selenium at 110°C, only the triselenide **18** was obtained.*

INTRODUCTION

Tetra-*tert*-butyltetraphosphacubane **2** was first obtained by Regitz and co-workers [2,3] from the cyclooligomerization of *tert*-butylphosphaacetylene, *t*Bu-C \equiv P, **1** [4] upon heating in the absence of a solvent at 130°C. Recently, the same authors [5] found that chlorination of the tricyclic zirconium complex **3**, obtained from treatment of bis(η^5 -cyclopentadienyl)zirconium dichloride with *n*-butyllithium or metallic magnesium in the presence of the phosphalkyne, led to a high yield of **2**; this method is also applicable to other derivatives of the same type bearing bulky substituents [5]. The

development of this convenient method, which is currently the best route for the preparation of tetra-*tert*-butyltetraphosphacubane **2** on a laboratory scale, made further investigations on the reactivity of this novel pentacyclic phosphorus compound possible [6].

The ^{31}P and ^{13}C NMR spectra [2], as well as photoelectron (PE) spectroscopic studies [7] of **2**, strongly suggest that the lone pairs of electrons at the phosphorus atoms have participated in the P/C cage σ bonds, leading to an overall electron density shift from P to C and thus reduced basicity/nucleophilicity at the phosphorus atoms of **2**. Similar conclusions can be drawn from the predictions of MO calculations on **2** [7].

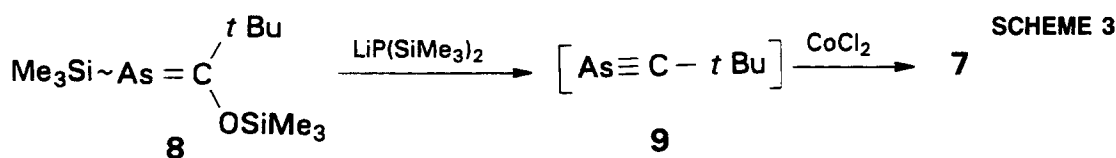
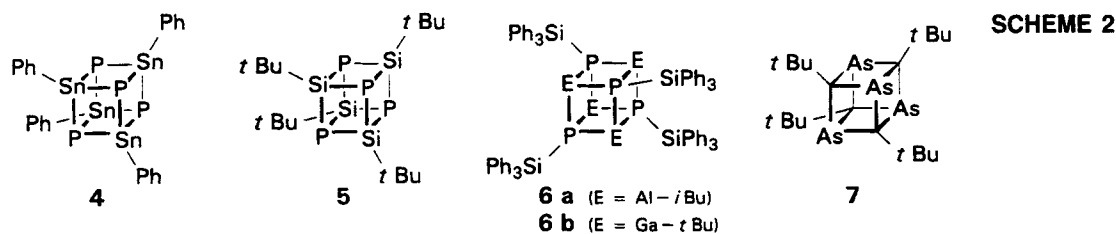
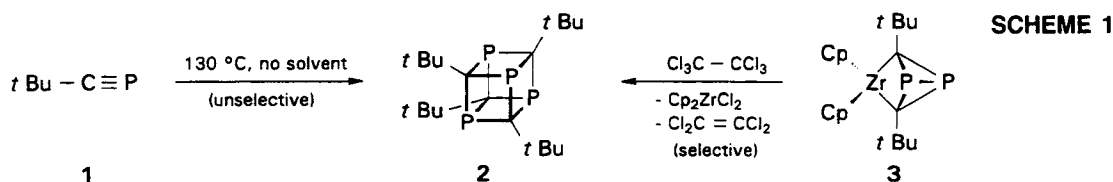
The experimental results are also in agreement with the preceding conclusions. In fact, functionalization reactions of **2** at phosphorus require rather drastic conditions [8]. It was found that alkylation with methyl triflate and complex formation with diiron nonacarbonyl only take place at one phosphorus atom even when an excess of the respective reagent is employed. Mono- and diprotonations of **2** were achieved with fluorosulfonic acid in liquid sulfur dioxide at low temperature [8].

A twofold [4 + 1]-cycloaddition, however, was observed when electron-poor reagents such as tetrachloro-*o*-benzoquinone and diethyl azodicarboxylate were used. In addition, the Staudinger reaction of **2** with one or two equivalents of an azide results in the 1:1 or 1:2 stoichiometric formation of iminophosphoranes via cleavage of nitrogen [6].

With regard to other heterocubanes, Schumann and Benda [9] and Baudler et al. [10] synthesized the stanna- and silaphosphacubanes **4** and

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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5 from phenyltrichlorostannane and *tert*-butyltrichlorosilane in 1968 and 1989, respectively. Furthermore, Cowley et al. [11] obtained the aluminum- and gallium-containing, cubelike tetramers **6a–b** in 1990. To the best of our knowledge, however, no functionalization reactions of any of these heterocubanes have so far been observed. In 1990, Nixon's group [12] reported the synthesis of the tetraarsacubane **7** from the reaction of the arsaalkene **8** with lithium bis(trimethylsilyl)phosphide to form the *tert*-butylarsaacetylene intermediate **9** and subsequent treatment of the latter with cobalt(II) chloride. As a result of the similarity between phosphorus and arsenic, it is not surprising that a monocomplexation reaction between this tetraarsacubane and diiron nonacarbonyl diiron was observed [12].

As an extension of the P-functionalization studies on **2**, we report in this article on the mono-, di-, tri-, and tetraoxidation of **2** with bis(trimethylsilyl) peroxide, sulfur, and selenium and the structural characterization of the corresponding products.

RESULTS AND DISCUSSION

Monooxidation of **2** with Bis(trimethylsilyl) Peroxide or Sulfur

The monoxide **10** or monosulfide **14** were obtained when **2** was stirred at room temperature for 2 days with equimolar amounts of bis(trimethylsilyl) peroxide or sulfur, respectively. The reaction with sulfur is advantageously performed under triethylamine catalysis. As shown in Table 1, the yield for

the reaction with sulfur is much lower than that with bis(trimethylsilyl) peroxide. More surprisingly, no reaction was observed when **2** was stirred at 110°C for 5 days with 1 equivalent of elemental selenium in the presence of triethylamine.

As shown in Table 2, the ^{31}P NMR spectrum of **10** shows two phosphorus signals at $\delta = 124.7$ and 66.6 in a 3:1 relative ratio. Also, the ^{13}C NMR spectrum exhibits two types of cage carbon atoms at $\delta = 41.1$ [$^1J(\text{P},\text{C}) = 41.3$ Hz] as a doublet and $\delta = -24.2$ as an unresolved multiplet. The more upfield phosphorus signal at $\delta = +66.6$ (P=O) and the more deshielded cage carbon signal at $\delta = 41.1$ (C1) are assigned to the C–P=O units, whereas the signals at $\delta = 124.7$ (P) and -24.2 (C2) are assigned to the C–P units. The observed shielding at phosphorus (P=O) and the accompanying deshielding of the three cage carbons (C1) are strongly indicative of electron density delocalization from C1 to P=O. Moreover, the deshielded phosphorus (P) and the upfield cage carbon (C2) signals are in agreement with an electron density shift from P to C2. Similar results can be obtained from an analysis of the NMR spectra of compound **14**.

Dioxidation of **2** with Bis(trimethylsilyl) Peroxide or Sulfur

Dioxidation or sulfidation of **2** were achieved by reaction with 2 equivalents of bis(trimethylsilyl) peroxide or sulfur, respectively. The dioxide **11** was isolated in high yield when **2** was reacted with bis(trimethylsilyl) peroxide at room temperature for 2 days, but for the reaction with sulfur, only 30% of the disulfide **15** was obtained even after

TABLE 1 Analytical and Physical Properties of the Compounds 10–18

Number	Mp (°C)	Formula	C% ^a	H% ^a	IR (cm ⁻¹) <i>ν</i>
10	264	C ₂₀ H ₃₆ OP ₄	57.4 (57.68)	8.5 (8.71)	1460, 1360, 1230, 790, 750
11	307–308	C ₂₀ H ₃₆ O ₂ P ₄	53.8 (55.55)	8.2 (8.39)	1465, 1394, 1364, 1240, 1210, 1050, 814, 800, 662
12	267	C ₂₀ H ₃₆ O ₃ P ₄	53.2 (53.57)	7.9 (8.09)	1472, 1394, 1366, 1238, 1212, 1048, 810
13	220	C ₂₀ H ₃₆ O ₄ P ₄	51.6 (51.72)	7.8 (7.81)	1470, 1395, 1370, 1240, 1210, 1040, 815, 785
14	243	C ₂₀ H ₃₆ P ₄ S	55.5 (55.54)	8.5 (8.35)	1460, 1390, 1360, 1230, 1030, 810, 780, 760
15	228	C ₂₀ H ₃₆ P ₄ S ₂	50.0 (51.71)	7.71 (7.81)	1470, 1400, 1370, 1240, 1110, 1045, 820, 810, 780, 685
16	263	C ₂₀ H ₃₆ P ₄ S ₃	48.6 (48.37)	7.2 (7.25)	1460, 1395, 1360, 1220, 1030, 800, 770, 660
17	230	C ₂₀ H ₃₆ P ₄ S ₄	45.5 (45.43)	6.8 (6.81)	1480, 1410, 1380, 1230, 1045, 940, 810, 680
18	286	C ₂₀ H ₃₆ P ₄ Se ₃	37.6 (37.69)	5.6 (5.64)	1470, 1395, 1220, 790, 750

^aThe figures in parentheses are calculated values.

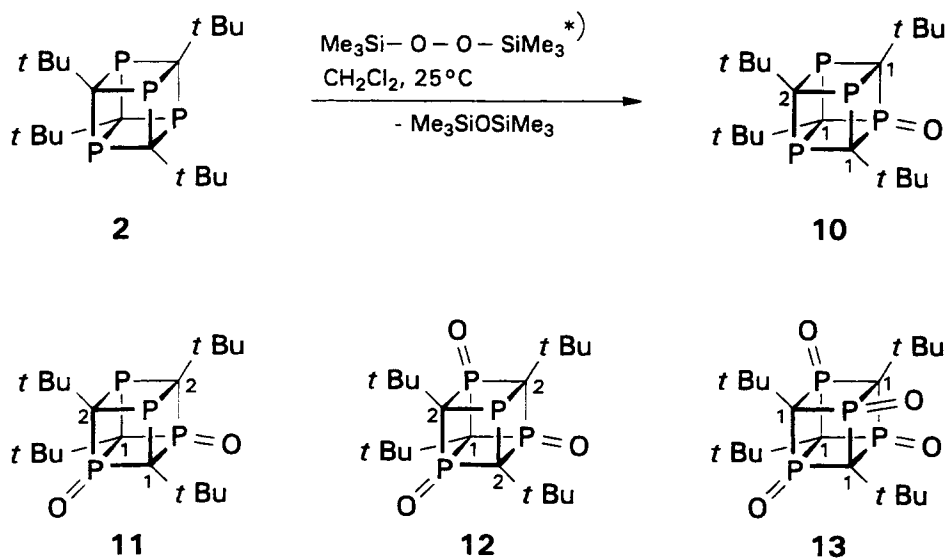
stirring in the presence of triethylamine at room temperature for 4 days. No similar dioxidative addition product was detected when a mixture of **2** and selenium (2.0 equiv) was kept at 110°C for 5 days.

Similar assignments can be made for the structures of compounds **11** and **15**. Thus, the more deshielded ³¹P NMR signal of **11** at $\delta = 31.96$ and the upfield ¹³C NMR signal at $\delta = 45.06$ are assigned to the C–P units and the other signals at $\delta = -14.25$ (P) and at $\delta = 86.93$ (C2) to the C–P=O units, which also agrees with the electron density transfer from C1 to P (P=O) and from P to C2. It should be noted, however, that this delocalization

from P to C2 is much weaker than that in **10** owing to the introduction of the second P=O group.

Trioxidation of 2 with Bis(trimethylsilyl) Peroxide, Sulfur, or Selenium

Similarly, the trioxide **12** was isolated in high yield from the reaction of **2** with 3 equivalents of bis(trimethylsilyl) peroxide at room temperature for 2 days, while the corresponding reaction with sulfur needed about 1 week and only a 50% yield of the trisulfide **16** was obtained. In contrast, a high yield (90%) of the triselenide **18** was obtained when **2** was stirred at 110°C for 4 days with 6 equivalents of elemental selenium.



SCHEME 4 *The product formation depends on the molar ratio of **2** to the peroxide

TABLE 2 NMR Data of the Compounds 10–18 [δ , J (Hz)]

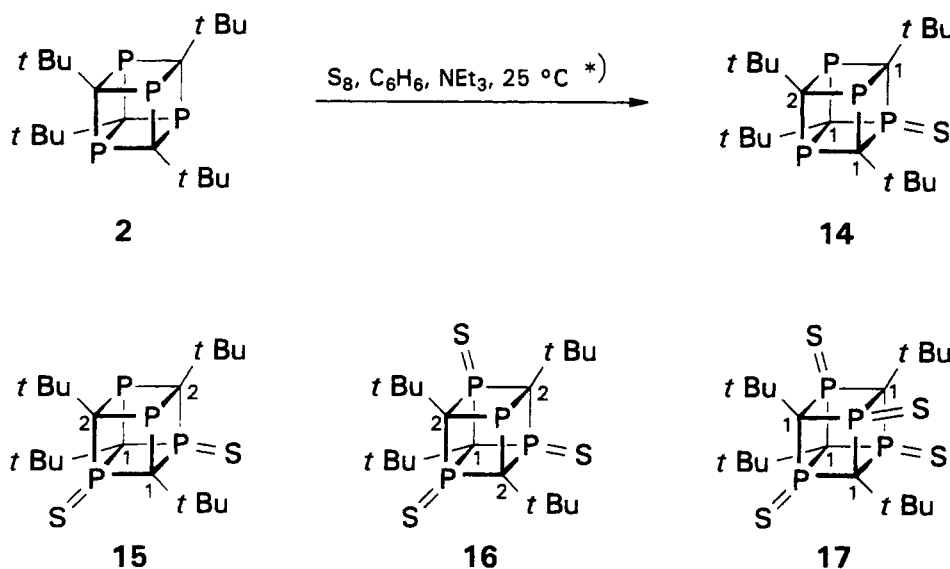
Number	^1H NMR (CDCl_3)	^{13}C NMR (CDCl_3)	^{31}P NMR $\text{P}=\text{X}^a$	(CDCl_3) $\text{P}-\text{C}$
10	1.13 (s, 27H, <i>t</i> Bu), 1.02 (s, 9H, <i>t</i> Bu)	41.1 (d, $^1J(\text{P}, \text{C}) = 41.3$, $3 \times \text{C1}$), 32.1 (m, $3 \times \text{C}(\text{CH}_3)_3$), 30.9 (m, $1 \times \text{C}(\text{CH}_3)_3$), 26.2 (s, $3 \times \text{C}(\text{CH}_3)_3$), 20.8 (s, $1 \times \text{C}(\text{CH}_3)_3$), -24.2 (m, $1 \times \text{C2}$)	66.6 (1P)	124.7 (3P)
11	1.20 (s, 18H, <i>t</i> Bu), 1.09 (s, 18H, <i>t</i> Bu)	86.9 (m, $2 \times \text{C1}$), 45.1 (m, $2 \times \text{C2}$), 35.2 (t, $^2J(\text{P}, \text{C}) = 8.8$, $2 \times \text{C}(\text{CH}_3)_3$), 33.3 (t, $^2J(\text{P}, \text{C}) = 10.4$, $2 \times \text{C}(\text{CH}_3)_3$), 29.0 (s, $2 \times \text{C}(\text{CH}_3)_3$), 25.8 (s, $2 \times \text{C}(\text{CH}_3)_3$)	-14.3 (2P)	32.0 (2P)
12	1.57 (s, 9H, <i>t</i> Bu), 1.16 (s, 27H, <i>t</i> Bu)	111.4 (qd, $^1J(\text{P}, \text{C}) = 24.1$ Hz, $^3J(\text{P}, \text{C}) = 4.8$, $1 \times \text{C1}$), 91.3 (qd, $^1J(\text{P}, \text{C}) = 42.6$, $^3J(\text{P}, \text{C}) = 11.2$, $3 \times \text{C2}$), 41.3 (s, $1 \times \text{C}(\text{CH}_3)_3$), 36.9 (d, $^2J(\text{P}, \text{C}) = 10.5$, $3 \times \text{C}(\text{CH}_3)_3$), 31.0 (q, $^3J(\text{P}, \text{C}) = 6.4$, $1 \times \text{C}(\text{CH}_3)_3$), 28.7 (s, $1 \times \text{C}(\text{CH}_3)_3$)	4.3 (3P)	-194.2 (1P)
13	1.48 (s, 36 H, <i>t</i> Bu)	111.2 (m, $4 \times \text{C1}$), 45.5 (m, $4 \times \text{C}(\text{CH}_3)_3$), 29.5 (m, $4 \times \text{C}(\text{CH}_3)_3$)	-8.6 (4P)	—
14	1.20 (s, 27H, <i>t</i> Bu), 1.05 (s, 9H, <i>t</i> Bu)	32.3 (m, $3 \times \text{C}(\text{CH}_3)_3$), 31.5 (m, $1 \times \text{C}(\text{CH}_3)_3$), 25.3 (s, $3 \times \text{C}(\text{CH}_3)_3$), 24.7 (d, $^1J(\text{P}, \text{C}) = 29.6$, $3 \times \text{C1}$), 21.4 (q, $^3J(\text{P}, \text{C}) = 5.8$, $1 \times \text{C}(\text{CH}_3)_3$), -25.3 (m, $1 \times \text{C2}$)	120.1 (1P)	157.8 (3P)
15	1.24 (s, 18H, <i>t</i> Bu), 1.03 (s, 18H, <i>t</i> Bu)	64.4 (m, $2 \times \text{C1}$), 35.4 (m, $2 \times \text{C}(\text{CH}_3)_3$), 33.6 (t, $^2J(\text{P}, \text{C}) = 10.9$, $2 \times \text{C}(\text{CH}_3)_3$), 28.8 (t, $^1J(\text{P}, \text{C}) = 40.0$, $2 \times \text{C2}$), 27.7 (m, $2 \times \text{C}(\text{CH}_3)_3$), 25.5 (m, $2 \times \text{C}(\text{CH}_3)_3$)	47.1 (2P)	80.8 (2P)
16	1.73 (s, 9H, <i>t</i> Bu), 1.31 (s, 27H, <i>t</i> Bu)	89.7 (qd, $^1J(\text{P}, \text{C}) = 16.8$, $^3J(\text{P}, \text{C}) = 6.1$, $1 \times \text{C1}$), 68.5 (pseudo-q, d, $^1J(\text{P}, \text{C}) = 35.1$, $^3J(\text{P}, \text{C}) = 6.2$, $3 \times \text{C2}$), 40.2 (s, $1 \times \text{C}(\text{CH}_3)_3$), 36.4 (d, $^2J(\text{P}, \text{C}) = 10.7$, $3 \times \text{C}(\text{CH}_3)_3$), 28.9 (q, $^3J(\text{P}, \text{C}) = 6.1$, $1 \times \text{C}(\text{CH}_3)_3$), 27.3 (s, $1 \times \text{C}(\text{CH}_3)_3$)	48.2 (3P)	-82.1 (1P)
17	1.60 (s, 36 H, <i>t</i> Bu)	91.3 (m, $4 \times \text{C1}$), 42.2 (m, $4 \times \text{C}(\text{CH}_3)_3$), 28.5 (m, $4 \times \text{C}(\text{CH}_3)_3$)	19.0 (4P)	—
18	1.72 (s, 9H, <i>t</i> Bu), 1.31 (s, 27H, <i>t</i> Bu)	75.2 (qd, $^1J(\text{P}, \text{C}) = 12.1$, $^3J(\text{P}, \text{C}) = 3.0$, $1 \times \text{C1}$), 56.1 (pseudo-q, d, $^1J(\text{P}, \text{C}) = 29.0$, $^3J(\text{P}, \text{C}) = 4.6$, $3 \times \text{C2}$), 40.9 (s, $1 \times \text{C}(\text{CH}_3)_3$), 36.3 (d, $^2J(\text{P}, \text{C}) = 10.7$, $3 \times \text{C}(\text{CH}_3)_3$), 28.2 (q, $^3J(\text{P}, \text{C}) = 6.9$, $1 \times \text{C}(\text{CH}_3)_3$), 26.6 (d, $^3J(\text{P}, \text{C}) = 5.3$, $3 \times \text{C}(\text{CH}_3)_3$)	41.1 (3P) [$^1J(\text{P}, \text{Se}) = 866$ Hz]	-45.2 (1P)

^aX = O, S, Se

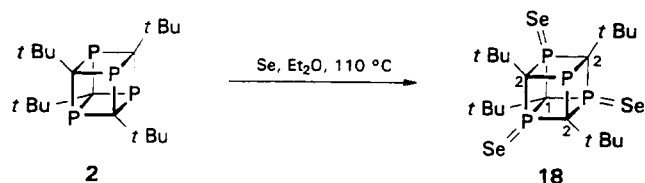
As expected, the ^{13}C NMR spectrum of **12** exhibits two types of cage carbons. The signal at $\delta = 91.28$ can be assigned to the three cage carbon atoms (C2) directly bonded to one $\lambda^3\sigma^5$ -phosphorus (P) and two $\lambda^5\sigma^4$ -phosphorus atoms (P=O). The other at $\delta = 111.4$ is due to the cage carbon (C1) directly bonded to three $\lambda^5\sigma^4$ -phosphorus atoms (P=O), which is deshielded by ca. 24 ppm compared to C1 of compound **11**. Similarly, in the ^{13}C NMR spectrum of **16**, the signal at $\delta = 89.7$ assigned to C1 of compound **16** is deshielded by ca. 25 ppm com-

pared to C1 of compound **15**. Accordingly, the carbons C1 of **12** and **16** are deshielded by almost the same δ value as a result of the introduction of a third P=O or P=S functionality.

With the introduction of more P=O groups on going from **10** to **12** and of more P=S groups on going from **14** to **16**, the corresponding cage carbon atoms C1 are more and more deshielded. On the other hand, as shown by the ^{13}C NMR spectra of compounds **12**, **16**, and **18**, this deshielding decreases in the order **12**, **16**, and **18**. It is thus ob-



SCHEME 5 *The product formation depends on the molar ratio of **2** to sulfur



SCHEME 6

vious that the electron-withdrawing capacity of the $P=O$, $P=S$, and $P=Se$ groups decreases in this order.

In the ^{31}P NMR spectra of **12**, **16**, and **18**, the signals for the oxidized phosphorus atoms are observed in the region from $\delta = 4.3$ to $\delta = 41.1$ (3P), whereas those for the $\lambda^3\sigma^3$ phosphorus atoms of the same molecules, as expected, experience large shifts to high field ($\delta = -194.2$ to -45.2 , 1P, see Table 2).

Tetraoxidation of **2** with Bis(trimethylsilyl) Peroxide or Sulfur

An approximately 90% yield of the tetraoxide **13** was obtained when **2** was stirred at room temperature for 2 days with 4 equivalents or more of bis(trimethylsilyl) peroxide. However, at least 6.25 equivalents of sulfur and a reaction time as long as 1 week were required in order to obtain a 90% yield of the tetrasulfide **17**. The corresponding tetraselenide could not be obtained even with a large excess of elemental selenium at $110\text{ }^\circ\text{C}$. The reaction stopped at the stage of the triselenide **18** as a consequence of the distortion geometry of the product with small exocyclic $P-C-C$ bond angles at the nonoxidized phosphorus atom [8].

Owing to their high symmetry, the ^{13}C NMR spectra of the tetraoxide **13** and the tetrasulfide **17** show only single signals at $\delta = 111.2$ and $\delta = 91.3$, respectively. Similarly to the case of **12**, the cage carbons C1 of **13** are also bonded directly to three $P=O$ groups. This is the reason why the carbon atoms C1 of **12** and **13** possess almost the same ^{13}C NMR chemical shift values. A similar phenomenon is also observed for compounds **16** and **17**.

CONCLUSIONS

Following the monofunctionalization of tetraphosphacubanes **2** via complexation with diiron nonacarbonyl and via alkylation with methyl triflate and the double functionalization with tetrachloro-*o*-benzoquinone and with alkyl azides, we have now demonstrated the stepwise additions to **2** of oxygen [using bis(trimethylsilyl) peroxide], sulfur (in the presence of triethylamine), and selenium. Mono-, bi-, tri-, and tetraoxidative addition reactions of **2** with bis(trimethylsilyl) peroxide or sulfur can be realized at room temperature. A similar reaction with selenium to give rise to the triselenide was only observed when **2** was treated with a large excess of selenium at $110\text{ }^\circ\text{C}$. The experimental results and the ^1H , ^{13}C , and ^{31}P NMR analyses for the products are strongly indicative of the acceptor character of the $P=O$, $P=S$, and $P=Se$ groups and the electron density shift from $\lambda^3\sigma^3$ -phosphorus to the adjacent cage carbon. This conclusion is consistent with those based on the ^1H , ^{13}C , and ^{31}P NMR data, photoelectron spectroscopy, and MO calculations of **2** [6–8].

EXPERIMENTAL

Tetra-*tert*-butyltetraphosphacubane **2** [5] and bis(trimethylsilyl) peroxide [13] were synthesized

according to published procedures. All reactions were performed under an argon atmosphere (Schlenk tube technique); reaction vessels were evacuated, baked out, and flushed with argon before use. The solvents used were anhydrous and were distilled and stored under argon prior to use. Melting points (uncorrected): Mettler FP 61 apparatus (heating rate: 3°C/min). Microanalyses: Perkin-Elmer Analyzer 240. IR spectra: Perkin-Elmer 397 and Beckman IR 20A spectrophotometers. ¹H NMR spectra: Varian EM 390 (90 MHz), Bruker WP 200, and Bruker AMX 400 spectrometers (TMS as internal standard). ¹³C NMR spectra: Bruker AMX 400 spectrometer (100.61 MHz, TMS as internal standard). ³¹P NMR spectra: Bruker WP 200 (80.82 MHz) and Bruker AMX 400 (161.98 MHz) spectrometers (85% orthophosphoric acid as external standard). Mass spectra: Finnigan MAT90 instrument (70 eV; reported as percent relative intensity to the base peak after the corresponding *m/e* values). Silica gel for flash column chromatography (0.063–0.2 mm) was dried at 210°C in vacuo for 3 days, and then 3% water was added.

Monooxidation Reactions

Preparation of 2,4,6,8-Tetra-tert-butyl-1,3,5,7-tetraphosphapentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane Monoxide (10). To a solution of tetraphosphacubane **2** (0.18 g, 0.45 mmol) in dichloromethane (8 mL) was added bis(trimethylsilyl) peroxide (0.08 g, 0.45 mmol) at room temperature. The yellow solution was stirred for 2 days until it became colorless. The product was isolated by column chromatography (pentane). Yield: 0.16 g (86%), white crystals.

Preparation of 2,4,6,8-Tetra-tert-butyl-1,3,5,7-tetraphosphapentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane Monosulfide (14). To a solution of tetraphosphacubane **2** (0.40 g, 1.0 mmol) in benzene (15 mL) was added sulfur (0.032 g, 1.0 mmol) and triethylamine (0.2 mL). The reaction was monitored by ³¹P NMR spectroscopy. The reaction mixture was stirred at room temperature for 2 days until the signals of the tetraphosphacubane had disappeared, and the solvent was subsequently removed under vacuum. The resulting white powder was dissolved in THF (10 mL). The solution was kept at –30°C for crystallization. Yield: 0.22 g (50%), white crystals.

Dioxidation Reactions

Preparation of 2,4,6,8-Tetra-tert-butyl-1,3,5,7-tetraphosphapentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane Dioxide (11). To a solution of tetraphosphacubane **2** (0.24 g, 0.6 mmol) in dichloromethane (10 mL) was added bis(trimethylsilyl) peroxide (0.21 g, 1.2 mmol). The yellow solution was stirred at room temperature for 2 days until it became colorless. The product was isolated by column chromatog-

raphy (diethyl ether/pentane, 1:4). Yield: 0.22 g (85%), white crystals.

Preparation of 2,4,6,8-Tetra-tert-butyl-1,3,5,7-tetraphosphapentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane Disulfide (15). To a solution of tetraphosphacubane **2** (0.40 g, 1.0 mmol) in benzene (15 mL) was added sulfur (0.064 g, 2.0 mmol) and triethylamine (0.2 mL). After the mixture had been stirred at room temperature for 4 days, the solvent was removed under vacuum. The resulting white powder was purified by column chromatography (diethyl ether/petroleum ether, 1:10). Yield: 0.14 g (30%), white crystals.

Trioxidation Reactions

Preparation of 2,4,6,8-Tetra-tert-butyl-1,3,5,7-tetraphosphapentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane Trioxide (12). To a solution of tetraphosphacubane **2** (0.24 g, 0.6 mmol) in dichloromethane (10 mL) was added bis(trimethylsilyl) peroxide (0.32 g, 1.8 mmol). The yellow solution was stirred at room temperature for 2 days until it became colorless. The product was isolated by column chromatography (diethyl ether/pentane, 1:4). Yield: 0.22 g (89%), white crystals.

Preparation of 2,4,6,8-Tetra-tert-butyl-1,3,5,7-tetraphosphapentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane Trisulfide (16). To a solution of tetraphosphacubane **2** (0.40 g, 1.0 mmol) in benzene (15 mL) was added sulfur (0.096 g, 3.0 mmol) and triethylamine (0.2 mL). After the mixture had been stirred at room temperature for 1 week, until the ³¹P NMR signals of the tetraphosphacubane **2** had disappeared, the solvent was subsequently removed under vacuum. The resulting white powder was dissolved in diethyl ether (10 mL) and the solution was kept at –30°C for crystallization. Yield: 0.25 g (50%), white crystals.

Preparation of 2,4,6,8-Tetra-tert-butyl-1,3,5,7-tetraphosphapentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane Triselenide (18). To a solution of tetraphosphacubane **2** (0.40 g, 1.0 mmol) in diethyl ether (10 mL) was added selenium (0.47 g, 6.0 mmol). After having been stirred at 110°C for 4 days, until the ³¹P NMR signal of tetraphosphacubane **2** had disappeared, the mixture was filtered to remove the insoluble materials. The filtrate was kept at –78°C for crystallization (24 hours). Yield: 0.58 g (90%), pale yellow crystals.

Tetraoxidation Reactions

Preparation of 2,4,6,8-Tetra-tert-butyl-1,3,5,7-tetraphosphapentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane Tetraoxide (13). To a solution of tetraphosphacubane **2**

(0.40 g, 1.0 mmol) in dichloromethane (20 mL) was added bis(trimethylsilyl) peroxide (1.07 g, 6.0 mmol). The yellow solution was stirred at room temperature for 2 days until it became colorless. The solvent was subsequently removed under vacuum. The resulting white powder was dissolved in diethyl ether (10 mL) and the solution kept at -30°C for crystallization. Yield: 0.21 g (90%), white crystals.

Preparation of 2,4,6,8-Tetra-tert-butyl-1,3,5,7-tetrakis(trimethylsilyl)peroxyoctane Tetrasulfide (17). To a solution of tetraphosphacubane **2** (0.40 g, 1.0 mmol) in benzene (20 mL) was added sulfur (0.20 g, 6.2 mmol) and triethylamine (0.5 mL). The reaction was monitored by ^{31}P NMR spectroscopy. After having been stirred at room temperature for 3 weeks, until the signal of tetraphosphacubane **2** had disappeared, the reaction mixture was filtered to remove the insoluble solid. The solvent was subsequently removed under vacuum. The resulting white powder was dissolved in ether (10 mL) and kept at -30°C for crystallization. Yield: 0.48 g (90%), white crystals.

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