New Phosphorus Heterocycles by Rearrangement of a [1,4-Bis(trimethylsilyl)-η^8-cyclooctatetraene]-1,3,5-triphospha-7-hafnanorbornadiene Complex☆

Paul Binger*, Stefan Leininger, Klaus Günther, and Uwe Bergsträßer[+]

Fachbereich Chemie der Universität Kaiserslautern,
Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany
Fax: (internat.) +49(0)631/205-3921

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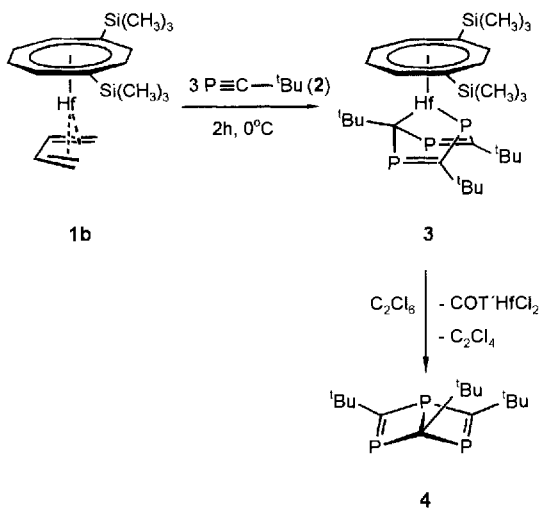
[1,4-Bis(trimethylsilyl)-η^8-cyclooctatetraene]-2,4,6-tri-*tert*-butyl-1,3,5-triphospha-7-hafnanorbornadiene (**3**) rearranges nearly quantitatively to the corresponding 3,5,6-tri-*tert*-butyl-1,2,4-triphospha-7-hafnanorbornadiene complex **5** upon heating at 70 °C. Treatment of complex **5** with trimethylphosphane at 50 °C induces the displacement of di-*tert*-butylacetylene to give the new (η^4-triphosphacyclobutadiene)hafnium complex **7**, the crystal structure of which has been determined by X-ray analysis. From complex **5**, 3,5,6-tri-*tert*-butyl-1,2,4-triphospha Dewar benzene (**6**) can be synthesized by a redox reaction with hexachloroethane.

It is now well-established that kinetically stabilized phosphaalkynes, e.g. *tert*-butylphosphaacetylene **2**, behave like acetylenes, i.e. they are easily cyclooligomerized under the influence of appropriate transition-metal complexes[1]. However, unlike acetylenes, which are catalytically transformed by a wide range of transition-metal complexes into benzene derivatives[2], phosphaalkynes most frequently form metal complexes in which the phosphaalkyne is bound to the metal center as a cyclodimer[3]. Until recently, only one unambiguous example was known in which **2** is cyclotrimerized to give a stable 1,3,5-triphospha Dewar benzene derivative, this being a complex of vanadium[4a]. In 1996, a scandium triple-decker complex incorporating a 1,3,5-triphosphabenzene moiety as the middle deck was described[4b].

In the meantime, we have discovered that (η^8-cyclooctatetraene)(η^4-cyclooctatetraene)zirconium and (η^8-cyclooctatetraene)(η^4-1,3-butadiene) complexes of zirconium and hafnium (**1a**), as well as the corresponding [η^8-1,4-bis(trimethylsilyl)cyclooctatetraene]hafnium complex **1b**, readily cyclotetramerize **2** by displacement of the η^4-bonded unsaturated hydrocarbons to produce the corresponding (1,3,5,7-tetraphosphabarrelene)zirconium and -hafnium complexes in high yields[5][6]. The only products of the reactions of in situ generated "Cp_2Zr" and "Cp_2Hf" with **2** are 1,3-diphosphabicyclo[1.1.0]butanediyl complexes of these metallocenes[7]. Moreover, it was found that the degree of cyclooligomerization of **2**, especially with the (η^8-cyclooctatetraene)hafnium complexes **1a** and **1b**, depends on the reaction temperature[6]. The tetramers are formed at 20–60 °C, while at 140 °C only the dimers are produced. On the other hand, lowering of the reaction temperature to −78 (**1a**) or 0 °C (**1b**) resulted in the formation of two different cyclotrimer complexes of **2** with hafnium, the structures of which have yet to be fully characterized. From these low-temperature products, metal-free 1,3,5-triphosphabenzene and 1,3,5-triphospha Dewar benzene were liberated upon treatment with hexachloroethane[6]. Thus, overall, starting with **1b** and **2** the reaction sequence of eq. 1 can be realized.



In order to fully elucidate the structure of complex **3**, we recorded its NMR spectra at various temperatures. In the course of these investigations it became apparent that the complex is unstable in solution. Even at room temperature, a slow rearrangement takes place, leading to the formation of the new, unsymmetrical 1,2,4-triphospha-7-hafnanorbornadiene complex **5**. At 70 °C, this rearrangement is com-

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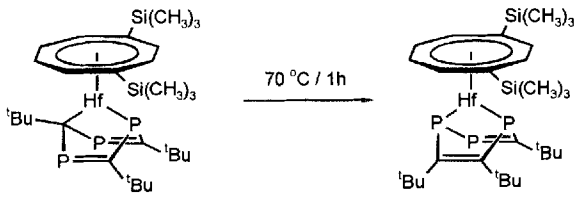
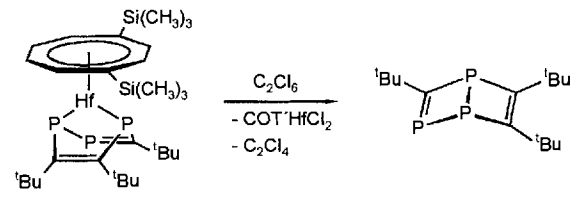
plete after 1 h and complex **5** can be isolated as reddish-brown microcrystals in 88 % yield.



3 **5**

Complex **5** is stable at room temperature as a solid as well as in solution. Moreover, in contrast to complex **3**[6], **5** shows no dynamic behavior in solution. Therefore, its structure can be elucidated by NMR spectroscopy. In its ^{31}P-NMR spectrum, three signals are found for the three phosphorus atoms at δ = 234.3 ($J_{P,P}$ = 354 and 62 Hz, P-2), δ = 156.8 ($J_{P,P}$ = 62 Hz, P-4) and δ = 108.2 ($J_{P,P}$ = 354 Hz, P-1). Consequently, in the ^{1}H-NMR spectrum, three singlets for the *tert*-butyl groups are observed, while in the ^{13}C-NMR spectrum the three ring carbon atoms C-3, C-5 and C-6 give rise to sharp, distinct signals in the region typical of sp^2-carbon atoms, each having its own characteristic $J_{C,P}$ coupling pattern (see Experimental Section). The C_1 symmetry of complex **5** is reflected in the observation that distinct signals are observed for all eight carbon atoms of the cyclooctatetraene ligand.

Further strong evidence to support the structure of **5** determined by NMR spectroscopy is provided by the product formed upon reaction of the complex with hexachloroethane. As found earlier with complex **3**, this mild chlorinating agent readily displaces the triphospha heterocycle from complex **5** at room temperature in a redox reaction to give the new triphospha Dewar benzene **6** in an isolated yield of 49 % as a pale-yellow powder. No other phosphorus-containing products can be detected by ^{31}P NMR.



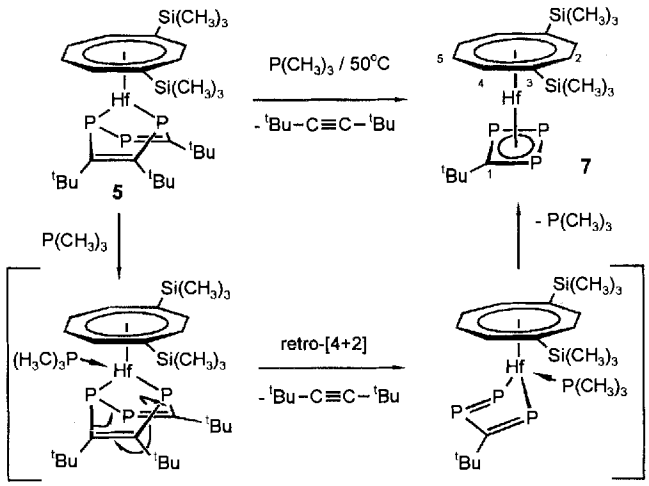
5 **6**

The 1,2,4-triphospha Dewar benzene **6** is an air-sensitive solid, which is indefinitely stable in an inert atmosphere, at least at room temperature. The unsymmetrical structure of **6** is unequivocally established by a combination of mass spectrometry and NMR spectroscopy. The mass spectrum of **6** exhibits a molecular ion peak at *m/z* = 300, and the intensities and patterns of the fragment ion signals are quite different from those found in the mass spectrum of 1,3,5-triphospha Dewar benzene **4**.

The ^{31}P-NMR spectrum of **6** exhibits three signals as double doublets at δ = 350.4 (P-2), δ = −28.4 (P-4) and δ = −154.9 (P-1), with characteristic coupling constants ($J_{P\text{-}1,P\text{-}2}$ = 191.8; $J_{P\text{-}1,P\text{-}4}$ = 4.2; $J_{P\text{-}2,P\text{-}4}$ = 87.2 Hz). In the ^{1}H-NMR spectrum, two singlets in the ratio 2:1 are found for the three *tert*-butyl groups, while three distinct signals for ring sp^2-carbon atoms are observed in the ^{13}C-NMR spectrum (see Experimental Section).

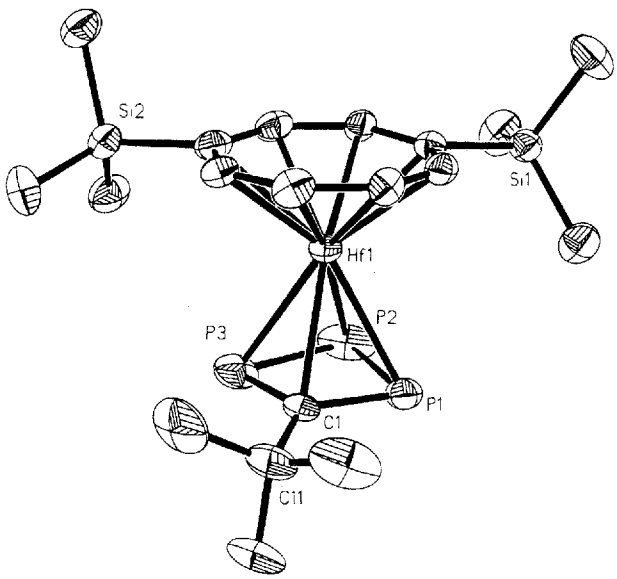
An unexpected displacement of di-*tert*-butylacetylene was observed when complex **5** was heated to 50 °C in the presence of trimethylphosphane. The new hafnium complex thus obtained was identified as the η^4-triphosphacyclobutadiene (triphosphete) derivative **7**. Complex **7** could be isolated in 55% yield as yellow needles, which allowed the unambiguous determination of its structure by X-ray analysis.

Scheme 1. Proposed mechanism of the formation of **7**



The X-ray analysis revealed compound **7** to be a hafnium sandwich complex, with the two ligands almost parallel to one another. Whereas the triphosphete moiety is completely planar, the eight-membered ring is slightly bent towards the

Figure 1. Molecular structure of **7**[a]



[a] Selected bond lengths [Å] and angles [°]: Hf−C1 2.540(6), Hf−P1 2.668(2), Hf−P2 2.637(2), Hf−P3 2.672(2), C1−P1 1.754(6), C1−P3 1.771(9), P1−P2 2.173(2), P2−P3 2.173(4); P1−C1−P3 107.8(5), P1−P2−P3 81.9(11), P2−C3−C1 84.9(3), C1−P1−P2 85.3(3).

metal along the C4–C8 axis (2.2°). At 2.173 Å, the two P–P bond lengths in the triphosphete are only slightly shorter than the P–P distance in 3,4-di-*tert*-butyl-1,2-dihydro-1,2-diiododiphosphete [2.192(4) Å][8], but are perceptibly longer than P=P bonds [2.019–2.045 Å][9]. The same P–P distance has been found in an (η^4-1,2-diphosphete)-titanium complex[10]. The two P–C distances P1–C1 and P3–C1 [1.754(6) Å and 1.771(9) Å] are similar and fall in a region intermediate between P–C single and P=C double bond lengths[11]. Since the angles at the phosphorus atoms are considerably smaller than 90° (81.9–85.3°) and the P–C–P angle is greater than 90° (107.8°), the triphosphete ring is deformed towards a rhombic arrangement. The same phenomenon was observed in the first triphosphete complex, prepared by the reaction of tricarbonyl(toluene)molybdenum with the phosphaalkyne **2**[12].

In agreement with the single-crystal structure, the three phosphorus atoms give rise to two signals in the ratio 2:1 in the ^{31}P-NMR spectrum of complex **7**, at δ = 246 (d, $J_{P,P}$ = 239 Hz) and δ = 53 (t, $J_{P,P}$ = 239 Hz). The ^{13}C-NMR spectrum of **7** features one signal for the triphosphete C atom at δ = 194.2 [$J_{C,P}$ = 74.6 (t) and 15.2 Hz (d)].

Whereas the mechanistic pathway for the transformation of complex **5** into complex **7** can most likely be formulated as a retro Diels-Alder reaction (see Scheme 1), this is not as obvious for the isomerization of complex **3** into complex **5**. As shown in Scheme 2 (path A) a retro [4+2] cycloaddition would liberate one phosphaalkyne unit, which may dissociate from the complex or stay bonded to the hafnium center during the whole rearrangement procedure as a π-complex. Substitution experiments using a second phosphaalkyne or some disubstituted alkynes (e.g. tolane) show that the isomerization is an intramolecular process, since no trace of the new dienophile is incorporated into the rearranged complex. Hence, path B also needs to be considered as a possible mechanism. Here, the rearrangement would begin with an isomerization into a prismane-like hafnium complex. Opening of the newly formed three-membered rings and rearrangement of the thus obtained 1,2,5-triphospha Dewar benzene complex via a 1,2,4-triphosphabenzene complex would also lead to the synthesized complex **5**. As yet, we are unable to decide which of these two mechanisms is in operation.

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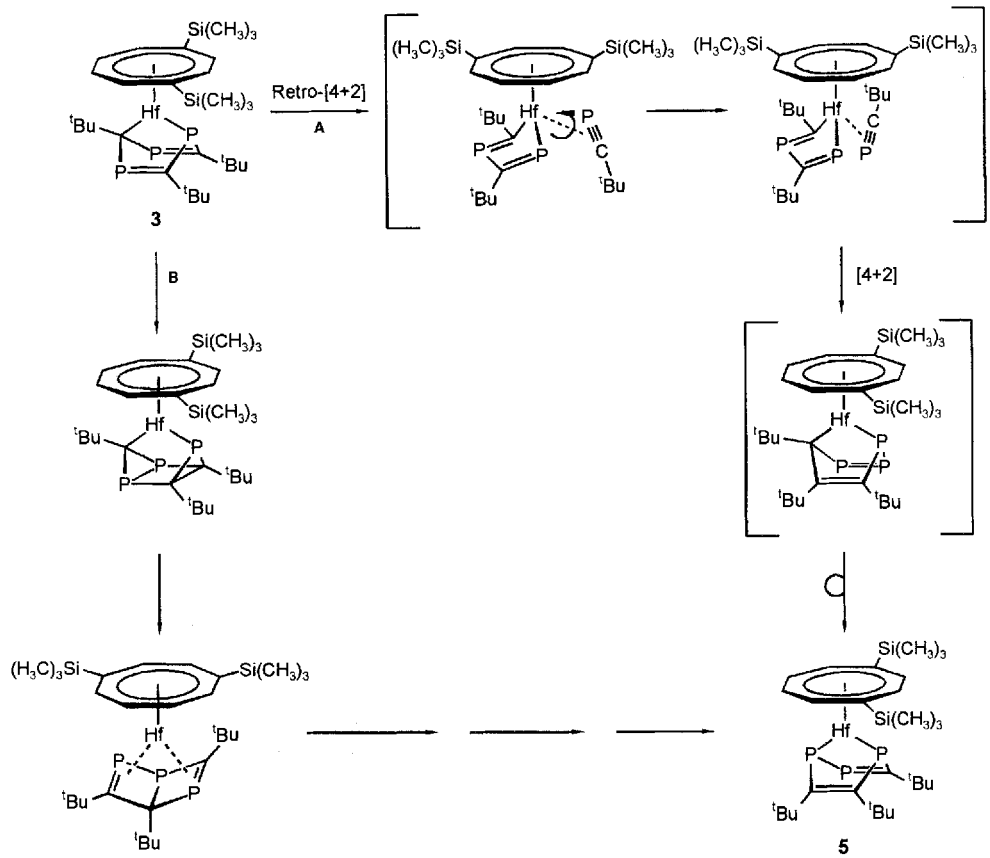
Experimental Section

All experiments were carried out under argon in anhydrous solvents. – MS: Finnigan MAT 90. – ^{1}H and ^{13}C NMR: Bruker AC 200 and AMX 400; chemical shifts relative to the solvent signals, calibrated to TMS. – ^{31}P NMR: Bruker AC 200, external standard H_3PO_4. – Elemental analysis: Perkin-Elmer EA 240. – [1,4-Bis(trimethylsilyl)-η^8-cyclooctatetraene]-2,4,6-tri-*tert*-butyl-1,3,5-triphospha-7-hafnanorbornadiene (**3**)[6] was prepared according to a published procedure.

Scheme 2. Proposed mechanisms for the rarrangement of **3** to **5**



[Bis(trimethylsilyl)cyclooctatetraene]-3,5,6-tri(tert-butyl)-1,2,4-triphospha-7-hafnanorborna-2,5-diene (**5**): A solution of **3** (430 mg, 0.592 mmol) in toluene (20 ml) was heated to 70°C for 1 h under stirring. The toluene was then removed in vacuo and the residue was taken up in pentane. The solution was filtered through Celite and the filtrate was concentrated to one third of its original volume. At −30°C, red-brown microcrystals of **5** were obtained; yield 380 mg (88 %), m. p. 184°C (dec.). − ^{1}H NMR (C_6D_6, 200 MHz): δ = 0.61 (s, 18 H, $SiMe_3$); 1.48 (s, 9 H), 1.54 (s, 9 H), 1.70 (s, 9 H) (*t*Bu); 6.1−6.9 (m, 6 H, COT). − ^{13}C{^{1}H} NMR (C_6D_6, 50 MHz): δ = 213.3 (ddd, $^1J_{C,P}$ = 112 and 100 Hz, $^2J_{C,P}$ = 3.4 Hz, C-3); 164.9 (dd, $^1J_{C,P}$ = 61.1, $^2J_{C,P}$ = 11.9 Hz, C-6); 153.1 (d, $^1J_{C,P}$ = 57.6 Hz, C-5); 45.1 [ddd, $^2J_{C,P}$ = 20.4 and 12.1 Hz, $^3J_{C,P}$ = 3.4 Hz, $C(CH_3)_3$ at C-3]; 36.7 [pseudo t, $^3J_{C,P}$ = 9.2 Hz, $C(CH_3)_3$ at C-3]; 41.0 [d, $^2J_{C,P}$ = 28.9 Hz, $C(CH_3)_3$ at C-5]; 34.6 [d, $^3J_{C,P}$ = 9.0 Hz, $C(CH_3)_3$ at C-5]; 41.3 [d, $^2J_{C,P}$ = 32.7 Hz, $C(CH_3)_3$ at C-6]; 34.3 [d, $^3J_{C,P}$ = 9.5 Hz, $C(CH_3)_3$ at C-6]; 100.5, 100.3, 99.9, 99.7, 96.1, 95.9, 95.8, 95.5 (8 s, COT); 0.78, 0.71 (2 s, $SiMe_3$ at COT). − ^{31}P NMR (C_6D_6, 80.8 MHz): δ = 234.3 (dd, $^1J_{P,P}$ = 354 Hz, $^2J_{P,P}$ = 62 Hz, P-2), 156.8 (d, $^2J_{P,P}$ = 62 Hz, P-4), 108.2 (d, $^1J_{P,P}$ = 354 Hz, P-1). − MS (70 eV); *m/z* (%): 728 (1) [M^+], 589 (6) [M^+ − $C_{10}H_{18}$], 301 (84) [$(t$BuCP$)_3H^+$], 175 (90) [$COT(SiMe_3)^+$], 131 (71) [$C_5H_9P_2^+$], 73 (100) [$SiMe_3^+$]. − $C_{29}H_{51}HfP_3Si_2$ (727.3): calcd. C 47.86, H 7.01, P 13.20; found C 47.31, H 6.94, P 13.08.

3,5,6-Tri(tert-butyl)-1,2,4-triphospha Dewar Benzene (**6**): To a solution of complex **5** (820 mg, 1.13 mmol) in toluene (10 ml) at 20°C was added hexachloroethane (270 mg, 1.13 mmol). After stirring for 2 h, the color of the solution had changed from brown to yellow. The toluene was evaporated at 0.5 bar and the residue was taken up in pentane (10 ml). The deposited $(COT)HfCl_2$ was removed by filtration through Celite; the remaining $(COT)HfCl_2$ could be removed by cooling to −20°C and filtering once more. After evaporation of the solvent, **6** was obtained as a pale-yellow oil; yield 160 mg (46.9%). − ^{1}H NMR (C_6D_6, 200 MHz): δ = 1.29 (s, 18 H, *t*Bu), 1.37 (s, 9 H, *t*Bu). − ^{13}C{^{1}H} NMR (C_6D_6, 50 MHz): δ = 251.0 (ddd, $^1J_{C,P}$ = 76.1, 57.0 Hz, $^2J_{C,P}$ = 7.8 Hz, C-3); 165.3 (ddd, $^1J_{C,P}$ = 32.6 Hz, $^2J_{C,P}$ = 11.4 Hz, $^3J_{C,P}$ = 8.1 Hz), 160.3 (ddd, $^1J_{C,P}$ = 33.5 Hz, $^2J_{C,P}$ = 25.0 Hz, $^3J_{C,P}$ = 12.7 Hz) (C-5 and C-6); 44.8 [ddd, $J_{C,P}$ = 11.4, 7.2 and 2.1 Hz, $C(CH_3)_3$ at C-3], 31.6 [dd, $J_{C,P}$ = 9.3 and 5.1 Hz, $C(CH_3)_3$], 37.7 [d, $J_{C,P}$ = 16.1 Hz, $C(CH_3)_3$], 32.2 [d, $J_{C,P}$ = 8.5 Hz, $C(CH_3)_3$], 37.1 [d, $J_{C,P}$ = 13.6 Hz, $C(CH_3)_3$], 30.3 [d, $J_{C,P}$ = 7.6 Hz, $C(CH_3)_3$]. − ^{31}P NMR (C_6D_6, 80.8 MHz): δ = 350.4 (dd, $^1J_{P,P}$ = 191.8 Hz, $^2J_{P,P}$ = 4.2 Hz, P-2), −28.4 (dd, $^1J_{P,P}$ = 87.2 Hz, $^2J_{P,P}$ = 4.2 Hz, P-4), −154.9 (dd, $^1J_{P,P}$ = 191.8 and 87.2 Hz, P-1). − MS (70 eV); *m/z* (%): 300 (100) [M^+], 169 (28) [$PC_2tBu_2^+$], 162 (35) [P_3CtBuH^+], 147 (44). − $C_{15}H_{27}P_3$ (300.3): calcd. C 59.99, H 9.06; found C 59.70, H 8.79.

[η⁸-1,4-Bis(trimethylsilyl)cyclooctatetraene][η⁴-1,2,3-triphosphacyclobutadiene]hafnium (**7**): To a solution of complex **5** (860 mg, 1.18 mmol) in toluene (20 ml) was added trimethylphosphane (1 ml) and the mixture was warmed to 50°C for 2 h in a pressure vessel. The solvent was then removed (0.5 bar) and the residue was redissolved in diethyl ether (20 ml). After filtration of some insoluble particles, the filtrate was concentrated to a volume of ca. 10 ml and cooled to −30°C. The yellow needles thus obtained were collected by filtration and dried at 0.5 bar; yield 380 mg (55%), m.p. >230°C (dec.). − ^{1}H NMR (C_6D_6, 400.1 MHz): δ = 1.22 (s, 9 H, *t*Bu), 0.50 [s, 18 H, $Si(CH_3)_3$], 6.88 (s, 2 H, 2-H), 6.39 (AA'BB' spin system, $^3J_{AB}$ = 11.5 Hz, $^3J_{AA}$ = 11.2 Hz, $^4J_{A'B}$ = 1.1 Hz, calcd. by simulation, 2 H, 4-H), 6.87 (AA'BB' spin system, 2 H, 5-H) (for numbering see Scheme 1). − ^{13}C{^{1}H} NMR (C_6D_6, 100.8 MHz): δ = 194.2 (td, $^1J_{C,P}$ = 74.6 Hz, $^2J_{C,P}$ = 15.2 Hz, C-1), 42.6 [pseudo q, $^2J_{C,P}$ = $^3J_{C,P}$ = 7.3 Hz, $C(CH_3)_3$ at C-1], 32.4 [t, $^3J_{C,P}$ = 6.4 Hz, $C(CH_3)_3$ at C-1], 99.8 (s, C-4), 99.7 (s, C-5), 94.4 (s, C-3), 94.2 (s, C-2), 0.27 [s, $Si(CH_3)_3$] (for numbering see Scheme 1). − ^{31}P NMR (C_6D_6, 80.8 MHz): δ = 246 (d, $^1J_{P,P}$ = 239 Hz), 53 (t, $^1J_{P,P}$ = 239 Hz). − MS (CI-POS, isobutane, 120 eV); *m/z* (%): 589 (100) [M^+ + H], 488 (29) [M^+ − $PCtBu$], 250 (33) [$COT(SiMe_3)_2H^+$], 176 (31) [$COT(SiMe_3)_2H^+$], 162 (33) [P_3CtBu^+], 147 (36) [$P_3CtBuMe^+$], 73 (100) [$SiMe_3^+$].

X-ray Crystal Structural Analysis of **7**[13]: Single crystal from Et_2O: 0.5 × 0.2 × 0.2 mm, Siemens P4 diffractometer, Mo-K_α radiation (graphite monochromator, λ = 0.71073 Å); empirical formula $C_{19}H_{33}HfP_3Si_2$, space group $P2_12_12_1$ [Flack parameter: −0.016(12)]; unit cell dimensions: a = 7.606(2), b = 16.274(3), c = 20.037(4) Å; $d_{calcd.}$ = 1.577 g·cm^{-3}, V = 2480.2(9) Å^3, μ (Mo-K_α) = 44.98 cm^{-1}, Z = 4; range for data collection: 1.61 to 24.98°; index ranges: $-9 \le h \le 8$, $-5 \le k \le 19$, $-6 \le l \le 23$; reflections collected 3251; independent reflections 3040 (R_{int} = 0.0288), parameters 235; absorption correction: DIFABS. Structure solution (SHELXS-86[14]): Patterson method, structure refinement (SHELXL-93[15]): full-matrix least squares on F^2, $R1$ = 0.0276, $wR2$ = 0.0653 (all data: $R1$ = 0.0351, $wR2$ = 0.0885).

☆ Dedicated to Professor *C. G. Kreiter* on the occasion of his 60th birthday.

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[13] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-406797, the names of the authors, and the journal citation.

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