Experimental Section

Catalytic additions of $Ph_2P(O)H$: Diphenylphosphane oxide (202 mg, 1.0 mmol), 1-octyne (110 mg, 1.0 mmol), diphenylphosphinic acid (11 mg, 5 mol%), and *cis*-$[PdMe_2(PPhMe_2)_2]$ (12 mg, 3 mol%) were dissolved in dry benzene (2 mL) under argon. The solution was heated at 70 °C for 4 h and evaporated in vacuo to leave a pale yellow oil, which was purified by column chromatography (SiO_2, EtOAc/hexane 1/1) to give the adducts as a colorless oil in 92% combined yield (287 mg, 0.92 mmol, **2a**:**1a** = 95:5). The two regioisomers (**2a** and **1a**) could be isolated by preparative thin layer chromatography (PTLC; silica gel, hexane/EtOAc 2/3; **2a**: 250 mg, 80% yield; **1a**: 11 mg, 4% yield).

2a: Colorless oil. ^{1}H NMR (300 MHz, C_6D_6): $\delta = 7.77-7.83$ (m, 4H), 7.05–7.16 (m, 6H), 5.60 (d, 1H, J(H,P) = 42.1 Hz), 5.55 (d, 1H, J(H,P) = 20.4 Hz), 2.30–2.38 (m, 2H), 1.39–1.49 (m, 2H), 1.01–1.21 (m, 6H), 0.80 (t, 3H, J = 6.8 Hz); ^{13}C NMR (C_6D_6, 75.5 MHz): $\delta = 145.8$ (J(C,P) = 90.8 Hz), 133.4 (J(C,P) = 99.8 Hz), 132.2 (J(C,P) = 9.3 Hz), 131.5 (J(C,P) = 2.7 Hz), 128.5 (J(C,P) = 11.6 Hz), 127.8 (J(C,P) = 9.6 Hz), 32.6 (J(C,P) = 15.0 Hz), 31.9, 29.2, 28.7 (J(C,P) = 4.9 Hz), 22.9, 14.2; ^{31}P NMR (C_6D_6, 121.5 MHz): $\delta = 27.9$; IR (neat/NaCl): $\tilde{\nu} = 3058$, 2930, 2860, 1437, 1191, 1120, 940, 727, 696 cm^{-1}. HRMS calcd for $C_{20}H_{25}OP$: 312.1642, found: 312.1624.

1a: White solid, m.p. 68–69 °C. ^{1}H NMR (300 MHz, C_6D_6): $\delta = 7.78-7.85$ (m, 4H), 7.05–7.08 (m, 6H), 6.87–7.01 (m, 1H), 6.11 (dd, 1H, J = 16.9, J(H,P) = 25.1 Hz), 1.87–1.91 (m, 2H), 1.09–1.21 (m, 8H), 0.82 (t, 3H, J = 6.8 Hz); ^{13}C NMR (C_6D_6, 75.5 MHz): $\delta = 152.2$ (J(C,P) = 1.7 Hz), 135.4 (J(C,P) = 92.9 Hz), 131.6 (J(C,P) = 9.5 Hz), 131.3 (J(C,P) = 2.7 Hz), 128.5 (J(C,P) = 11.7 Hz), 123.1 (J(C,P) = 101.8 Hz), 34.6 (J(C,P) = 16.6 Hz), 31.8, 29.1, 28.1, 22.9, 14.2; ^{31}P NMR (C_6D_6, 121.5 MHz): $\delta = 18.9$; IR (KBr): $\tilde{\nu} = 2962$, 2928, 2856, 1632, 1439, 1185, 1122, 1002, 814, 745 cm^{-1}. HRMS calcd for $C_{20}H_{25}OP$: 312.1642, found: 312.1603.

cis-[PdMe[OP(O)Ph_2](dmpe)]: To a solution of *cis*-$[PdMe_2(dmpe)]$ (17.2 mg, 0.06 mmol) in toluene/CH_2Cl_2 (1/1, 6 mL) was added $Ph_2P(O)OH$ (13 mg, 0.06 mmol) at room temperature under nitrogen. As the solid $Ph_2P(O)OH$ gradually dissolved, gas evolution from the solution was observed. A transparent colorless solution was obtained after 1 h at room temperature. Concentration of the solution to about half its volume in vacuo afforded a white precipitate of *cis*-[PdMe[OP(O)Ph_2](dmpe)] (28.6 mg, 0.058 mmol, 97% yield); m.p. 164 °C (decomp). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.26-7.94$ (m, 10H), 1.74 (br s, 2H), 1.48–1.55 (m, 14H), 0.55 (dd, 3H, J(H,P) = 2.2, 8.2 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): $\delta = 37.2$ (d, J(P,P) = 23.0 Hz), 22.6 (s), 21.4 (d, J(P,P) = 23.0 Hz); elemental analysis calcd for $C_{19}H_{29}O_2P_3Pd$: C 46.69, H 5.98; found: C 46.63, H 5.97.

3a: To a solution of *cis*-$[PdMe_2(dmpe)]$ (116.4 mg, 0.406 mmol) in benzene (4 mL) was added $Ph_2P(O)OH$ (88.6 mg, 0.406 mmol) at room temperature under nitrogen. Gas evolution was observed immediately. After the mixture was stirred for 6 h at room temperature, a solution of $Ph_2P(O)H$ (82.1 mg, 0.406 mmol) in benzene (3 mL) was slowly added. The reaction mixture was stirred overnight to afford analytically pure **3a** as a white solid (255.1 mg, 0.378 mmol, 93%); m.p. 198 °C (decomp). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.16-7.80$ (m, 20H), 1.80 (dd, 6H, J(H,P) = 1.8, 12.0 Hz), 1.71–1.83 (m, 4H), 1.56 (dd, 6H, J(H,P) = 3.5, 10.2 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): $\delta = 66.8$ (d, J(P,P) = 467.8 Hz), 42.7 (d, J(P,P) = 33.4 Hz), 26.1 (d, J(P,P) = 9.2 Hz), 20.6 (ddd, J(P,P) = 9.2, 33.4, 467.8 Hz); elemental analysis calcd for $C_{30}H_{36}O_3P_4Pd$: C 53.39, H 5.38; found: C 53.57, H 5.68.

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[5] The possibility of isomerization of **1a** to **2a** catalyzed by $Ph_2P(O)OH$ as the origin of the reversal is readily ruled out, since **1a** did not isomerize to **2a** when heated with $Ph_2P(O)OH$ (13 mol% relative to **1a**) in C_6D_6 at 70 °C for 4 h. Isomerization was also not observed when pure **1a** was added to the solution of the *cis*-$[PdMe_2(PPhMe_2)_2]$-catalyzed reaction of $Ph_2P(O)H$ with 1-octyne in the presence of 5 mol% of $Ph_2P(O)OH$ (Table 1) and reheated at 70 °C for 2 h.

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[10] Complex **3a** was similarly obtained when $Ph_2P(O)H$ was added first to $[PdMe_2(dmpe)]$ followed by treatment with $Ph_2P(O)OH$.

Molecular Aluminophosphonate: Model Compound for the Isoelectronic Double-Six-Ring (D6R) Secondary Building Unit of Zeolites[**]

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Herbert W. Roesky,[*] and Hans-Georg Schmidt

Dedicated to Professor Herbert D. Kaesz
on the occasion of his 65th birthday

One of the main thrusts in the area of advanced materials has been the synthesis of phosphate materials of Al and Ga,[1–5] which can potentially serve as highly organized matrices of tunable pore size and shape. Since the first successful synthesis of aluminophosphate materials in 1982,[1] several groups have synthesized alumino- and gallophosphate materials by hydrothermal routes in the presence of structure-directing agents.[2–5] To understand the local structures of these complex materials, a few soluble model compounds were prepared which can also serve as secondary building

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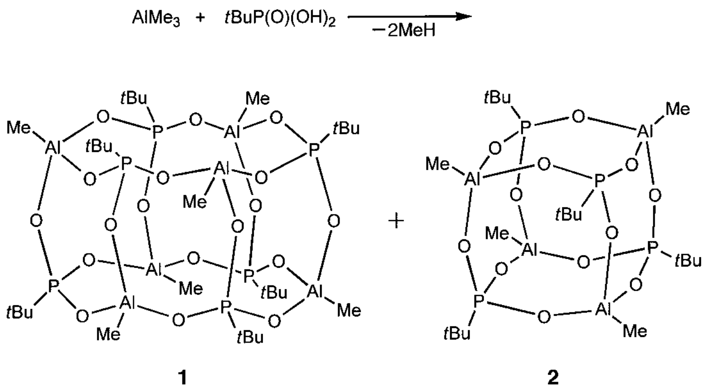
units (SBUs). In particular, we[6–8] and others[9–12] synthesized Group 13 phosphonates as soluble molecular compounds with a) a double-four-ring (D4R or 4–4) core structure with a $M_4O_{12}P_4$ central unit (M = Al, Ga) or b) stable eight-membered ring structures, which are conceived as intermediates during the formation of D4R structures. However, it has not yet been possible to obtain other larger assemblies which resemble the higher SBUs of zeolites. Here we report the first successful synthesis and molecular structure of an aluminophosphonate that is soluble in organic solvents and has an $Al_6O_{18}P_6$ central core which is identical to the double-six-ring (D6R or 6–6) building units found in zeolites.[13]

The reaction of *tert*-butylphosphonic acid[14] with equimolar quantities of $AlMe_3$ in THF/*n*-hexane yields a mixture of $[MeAlO_3PtBu]_6$ (**1**) and $[MeAlO_3PtBu]_4$ (**2**; Scheme 1).



Scheme 1. Synthesis of aluminophosphonates **1** and **2**.

Hexamer **1** is obtained as hexagonal single crystals from the reaction mixture by fractional crystallization at 4 °C. After removal of **1**, tetramer **2** was obtained from the mother liquor as an analytically pure solid. All our previous attempts to prepare aluminophosphonates from alkyl aluminum compounds containing bulky substituents invariably resulted in the tetrameric compound of the general formula [RAlO$_3$PR′].[6–8] In the present case, the smaller methyl substituent on aluminum allows isolation of hexameric **1** along with tetrameric **2**.

The constitution of **1** and **2** can be ascertained unequivocally from their elemental analyses, EI mass spectra, and NMR data. The base peaks observed in the EI mass spectra for **1** ($m/z = 1053$) and **2** ($m/z = 697$) each correspond to the loss of one methyl group. The chemical shift in the ^{31}P NMR spectrum of **2** ($\delta = 17.5$) is consistent with the value for the tetrameric aluminophosphonate $[iBuAlO_3PtBu]_4$ (**3**, $\delta = 16.9$), which could be characterized as a molecular tetramer by single-crystal structure analysis.[6] The ^{31}P NMR signal of **1** ($\delta = 13.4$) is shifted upfield by $\Delta\delta = 4.1$ with respect to that of **2**. Likewise, in the ^1H NMR spectra there are minor differences in the chemical shifts for the methyl and *tert*-butyl protons of **1** and **2**.

The X-ray structure analysis[15] showed that **1** crystallizes in the centrosymmetric triclinic space group with half of the hexamer in the asymmetric unit. The molecular structure (Figure 1) resembles the D6R building units found in phosphate materials such as $AlPO_4$-5, CoAPO-5, CrAPO-5, and SAPO-5.[19]

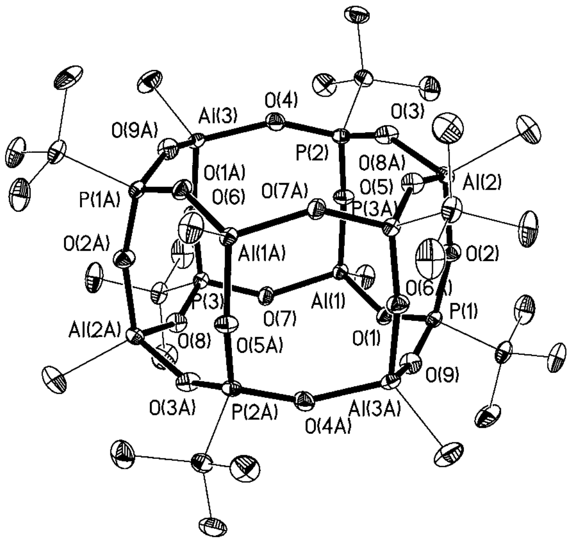


Figure 1. Molecular structure of **1** (thermal ellipsoids for the 20 % probability level). Selected bond lengths [Å] and angles [°]: Al–O 1.747(2)–1.757(2) (av 1.752), P–O 1.511(2)–1.519(2) (av 1.515); P(1)-O(1)-Al(1) 149.3(1), P(1)-O(9)-Al(3A) 151.9(1), P(2)-O(3)-Al(2) 148.9(1), P(2)-O(4)-Al(3) 148.8(1), P(3)-O(7)-Al(1) 148.4(1), P(3)-O(8)-Al(2A) 151.2(1), P(1)-O(2)-Al(2) 162.5(1), P(2)-O(5)-Al(1) 166.4, P(3)-O(6)-Al(3) 163.0(1).

The central core of the $Al_6O_{18}P_6$ polyhedron can be described as a cylindrical drum in the form of a hexagonal prism whose top and bottom faces are made up of twelve-membered $Al_3O_6P_3$ rings (including the oxygen atoms). The six remaining faces of this cylindrical drum are made up of $Al_2O_4P_2$ rings. All the twelve- and eight-membered rings exist in a crown conformation. The Al–O and P–O bonds within the molecule do not show any variation and are comparable to the corresponding values found for **3** (1.762 and 1.521 Å, respectively). All Al and P centers in the molecule largely have a tetrahedral geometry. The Al-O-P angles in the molecule fall into two different categories: The Al-O-P angles within the twelve-membered rings are much smaller (av 149.8°) than the six Al-O-P linkages that connect the two twelve-membered rings (av 164.0°).

Here we have shown that by tailoring the alkyl groups on aluminum and phosphorus, it is possible to generate bigger building units of aluminophosphate molecular sieves. By a proper balance of steric and electronic factors, it should be possible in the future to synthesize even larger SBUs such as D8R units. We plan to explore these possibilities.

Experimental Section

1 and **2**: A solution of *tert*-butylphosphonic acid (0.30 g, 2.17 mmol) in THF (20 mL) was added dropwise to an equimolar solution of $AlMe_3$ (2 M in hexane, 1.1 mL) in *n*-hexane (20 mL) at 0 °C. The reaction mixture was stirred at room temperature for 16 h and then concentrated to 20 mL in vacuo. The resulting solution was filtered and stored at 4 °C for two weeks to obtain hexagonal colorless crystals of **1** (0.041 g, 10.5 %). The crystals, which were suitable for X-ray diffraction studies, were separated from the mother liquor by decantation. The mother liquor contained predominately **2** (0.185 g, 48.1 %).

1: M.p. > 300 °C; IR (Nujol): $\tilde{\nu} = 1261, 1208, 1191, 1101, 1020, 974, 839, 800, 721, 686\ \text{cm}^{-1}$; ^{1}H NMR (400 MHz, C_6D_6): $\delta = -0.42$ (18H, s, $AlCH_3$), 1.08 (54H, d, $J = 17.4$ Hz, $C(CH_3)_3$); ^{31}P NMR (162 MHz, C_6D_6): $\delta = 13.4$; MS (EI, 70 eV): $m/z = 1053$ ($[M^+ - \text{Me}]$, 100%); elemental analysis calcd for $C_{30}H_{72}Al_6O_{18}P_6$ (1068.6): C 33.74, H 6.80, P 17.40; found: C 33.64, H 6.74, P 17.86.

2: M.p. 192–195 °C; IR (Nujol): $\tilde{\nu} = 1261, 1208, 1190, 1097, 1021, 870, 801, 722, 688\ \text{cm}^{-1}$; ^{1}H NMR (200 MHz, C_6D_6): $\delta = -0.31$ (12H, s, $AlCH_3$), 1.03 (36H, d, $J = 17.5$ Hz, $C(CH_3)_3$); ^{31}P NMR (101 MHz, C_6D_6): $\delta = 17.5$; MS (EI, 70 eV): $m/z = 697$ ($[M^+ - \text{Me}]$, 100%); elemental analysis calcd for $C_{20}H_{48}Al_4O_{12}P_4$ (712.4): C 33.74, H 6.80; found: C 33.42, H 6.88.

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The Mechanism for Hydrogen Abstraction by n,π* Excited Singlet States: Evidence for Thermal Activation and Deactivation through a Conical Intersection**

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Salem's correlation diagram for hydrogen abstraction by n,π* excited chromophores,[1] most often depicted for the reaction between formaldehyde and methane, has become the classic textbook example for a theoretical rationalization of photochemical reactivity and for the contrast between the reactivity of singlet and triplet states. According to this diagram the hydrogen abstraction by triplet states proceeds smoothly and with unit efficiency, whereas for singlet states the system is predicted to "pause" at an avoided crossing and then to proceed either to the products or back to the reactants; this reduces the efficiency to below unity.[1,2] While the triplet reaction has received considerable experimental and theoretical attention, the distinct singlet mechanism has not been examined in detail.[3–6]

The intermolecular hydrogen abstraction of the n,π* excited singlet states of ketones is difficult to examine owing to short lifetimes and efficient intersystem crossing. This limitation warrants the choice of an alternative n,π* chromophore. The azoalkane 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) appeared to be the predestined experimental test case, since excited singlet DBO is very long-lived (up to 1 μs) and undergoes neither intersystem crossing[7] nor efficient photodecomposition (only about 2%).[8] Moreover, excited singlet azoalkanes are efficiently quenched by C–H and O–H bonds of poor hydrogen donors such as chloroform or methanol.[9–11] This provides a fascinating case of a singlet hydrogen abstraction [Eq. (1)], which we have now elucidated in mechanistic detail. An unexpectedly low activation barrier and a large deuterium isotope effect are observed for chloroform as hydrogen donor. These findings are rationalized in terms of a thermally activated rather than a tunneling process.

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