

Optimised Synthesis and Characterisation of 1-Adamantyltrimethylphosphonium Iodide

Riad Mansour,^{a,b} Phillip S. Nejman,^c Laurence J. Taylor,^c Brian A. Chalmers,^c Fernando Rey,^d Abdelkader Bengueddach,^a J. Derek Woollins,^c Alexandra M. Z. Slawin,^c Petr Kilian^{c*}

a) Laboratoire de Chimie des Matériaux, Département de Chimie, Faculté des Sciences, Université d'Oran 1 Ahmed Benbella, P.O. Box 1524 El-Menouer, 31000-Oran, Algeria

b) Centre Universitaire Salhi Ahme Naama, P.O. Box 66, 45000-Naama, Algeria

c) EaStChem School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, United Kingdom

d) Instituto de Tecnologia Química (CSIP-UPV), Avenida de los Naranjos s/n 46022, Valencia, Spain

Keywords: Organophosphorus, Phosphonium, Synthesis, Adamantyl group, Organic Structure-directing Agent

Abstract

A synthetic route to multigram quantities of 1-adamantyltrimethylphosphonium iodide is reported. The synthesis starts from the commercially available precursor 1-adamantyl bromide and was optimised with respect to yield and ease of purification. The title compound is of interest to zeolite chemists as a potent organic structure-directing agent. Full spectroscopic characterisation data of all isolated intermediates and single crystal X-ray diffraction data of $\text{AdP}(\text{O})\text{Cl}_2$, $[\text{AdPMe}_2\text{H}]\text{I}$ and $[\text{AdPMe}_3]\text{I}$ (Ad = 1-adamantyl) are reported.

Introduction

The adamantyl group occupies a rather special position amongst alkyl groups because of its cage structure, which confers 3D bulk, rigidity, and chemical inertness. These attributes led to adamantyl groups being exploited in the stabilisation of highly reactive species, such as the first isolable carbene.[1] In zeolite chemistry, an adamantyl group-containing tetraalkylammonium hydroxide, N,N,N-trimethyl-1-adamantylammonium hydroxide, TMAOH (Ad = 1-adamantyl), has been used as an organic structure-directing agent (OSDA). Several zeolite types have been synthesised using TMAOH as an OSDA, namely SSZ-13 (CHA), SSZ-23 (STT), and SSZ-24 (AFI).[2] The small-pore chabazite zeolite type SSZ-13 is the most significant of these, since it has proved to be a superior acid catalyst for the conversion of methanol to olefins,[3, 4] and a potential catalyst for reducing nitrogen oxide (NO_x) emissions.[5]

In contrast to tetraalkylammoniums,[6, 7] the use of structurally related tetraalkylphosphonium (TAP⁺) compounds as OSDAs is much less established in zeolite chemistry. Tetraalkylphosphoniums have been used as both OSDAs and modifying agents, in an effort to obtain more efficient P-modified zeolite catalysts and novel zeolite structures. Examples include zeolites ITQ-26 (IWS),[8] ITQ-27 (IWW),[9, 10] ITQ-34 (ITR),[11] ITQ-49 (IRN)[12] and ITQ-53.[13] Recently, tetraalkylphosphoniums have been used in the so-called

dual-template method for the synthesis of a P-modified chabazite zeolite. Here, N,N,N-trimethyl-1-adamantylammonium and tetraethylphosphonium cations were employed together in order to improve the thermal stability of chabazite zeolite catalysts.[14]

However, there are no reports of adamantyl group-containing phosphorus compounds as OSDAs in the literature. This is surprising, given the important role of its ammonium analogue TMAOH in chabazite synthesis. We believe this is because the synthesis of adamantylphosphoniums remains challenging, especially compared to their nitrogen congeners. The factors contributing to this are limited availability of potential precursors, such as adamantylphosphine and adamantyldihalophosphines, neither of which are commercially available. Moreover, the high reactivity of these intermediates towards air/moisture requires the use of rigorous inert atmosphere techniques during synthetic manipulations, adding an additional level of complexity.

The hydroxide $[\text{AdPMe}_3]\text{OH}$ is accessible via a standard anion-exchange resin procedure from $[\text{AdPMe}_3]\text{I}$. [15] Here we report an optimised synthetic sequence to 1-adamantyltrimethylphosphonium iodide $[\text{AdPMe}_3]\text{I}$, starting from commercially available 1-bromoadamantane. The sequence has been designed to cater for the needs of zeolite chemists; it is readily scalable to multigram scales, involves the minimum number of synthetic steps, and minimises (as far as possible) the requirement for strict inert atmosphere conditions. To facilitate monitoring of the reaction sequence progress by non-specialists, we provide full spectroscopic characterisation data of all the isolated intermediates. Single crystal X-ray diffraction data are also reported for completeness.

Results and Discussion

Syntheses

The synthetic pathway to $[\text{AdPMe}_3]\text{I}$ reported in this work is shown in Scheme 1. The pathway consists of four steps with three isolated intermediates.

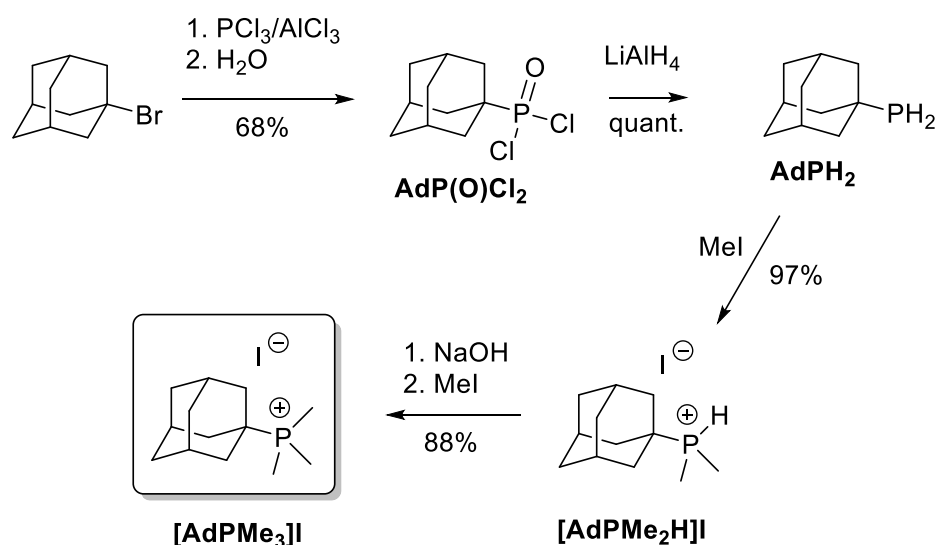
In the first step, Friedel-Crafts-like conditions were used to phosphorylate 1-bromoadamantane. This was followed by aqueous workup to yield crude $\text{AdP}(\text{O})\text{Cl}_2$. The crude product was purified by column chromatography on silica, to give pure $\text{AdP}(\text{O})\text{Cl}_2$ as an air stable colourless powder in 68% yield. Whilst the literature procedures use AlBr_3 , [16, 17] we have used the more readily available AlCl_3 to obtain comparable yields. The purity of the product was established chiefly by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy. For completeness, we also provide $^{13}\text{C}\{^1\text{H}\}$ NMR and IR spectroscopic data. Our data are in full agreement with those reported earlier. [17, 18]

The reduction of $\text{AdP}(\text{O})\text{Cl}_2$ with LiAlH_4 was performed as per the literature procedure, [16] and afforded AdPH_2 as colourless oil in a quantitative yield. No further purification of the oily product was needed providing pure starting material ($\text{AdP}(\text{O})\text{Cl}_2$) was used in the reaction. This is the preferred approach since AdPH_2 is air sensitive; its purification is hence rather more demanding (distillation under inert atmosphere) compared to the purification of the air stable $\text{AdP}(\text{O})\text{Cl}_2$ precursor. The purity of AdPH_2 was assessed by $^{31}\text{P}\{^1\text{H}\}$

and ^1H NMR spectroscopy, for completeness we also provide the $^{13}\text{C}\{^1\text{H}\}$ NMR data. Spectroscopic data are in full agreement with those reported earlier.[17] It should be noted that an alternative route to AdPH_2 via the use of Grignard chemistry has been reported by Imamoto.[19] However, this route proved less efficient in our hands, with the above synthesis via $\text{AdP}(\text{O})\text{Cl}_2$ proving significantly more reliable.

In the third step, AdPH_2 was treated with excess MeI using methanol as the solvent. The reaction affords the hydroiodide $[\text{AdPMe}_2\text{H}]\text{I}$ as the sole phosphorus containing product in a near quantitative yield. The exhaustive alkylation to the phosphonium iodide (according to the equation $\text{AdPH}_2 + 3 \text{MeI} \rightarrow [\text{AdPMe}_3]\text{I} + 2 \text{HI}$) did not proceed, even when a large excess of MeI was used coupled with both extended reaction times and heating. This is in agreement with the early work by Hays, who observed that the hydroiodides of trialkyl phosphines are exceptionally resistant to further alkylation due to being the adduct of a strong acid (HI) and a highly basic phosphine (PR_3).[20] Whilst alkylation of AdPH_2 with MeI has been reported in the literature, the experimental details and characterisation data are somewhat limited.[21] Moreover, the literature procedure suggests isolation of AdPMe_2 as an intermediate. This is obtained by in situ neutralisation of the initially formed hydroiodide $[\text{AdPMe}_2\text{H}]\text{I}$ with NaOH . We have found it more convenient to isolate the hydroiodide $[\text{AdPMe}_2\text{H}]\text{I}$, which is obtained as crystalline material and easily purified by washing with a non-polar solvent, such as hexane. The hydroiodide $[\text{AdPMe}_2\text{H}]\text{I}$ was fully characterised using ^1H , ^{31}P and ^{13}C NMR spectroscopy, HRMS, IR spectroscopy and elemental analysis.

Neutralisation of $[\text{AdPMe}_2\text{H}]\text{I}$ with NaOH and subsequent treatment of the formed AdPMe_2 with MeI afforded $[\text{AdPMe}_3]\text{I}$ as a white solid in a very good yield (88%). Analytically pure material was obtained with minimal purification (washing with hexane), and was fully characterised using ^1H , ^{31}P and ^{13}C NMR spectroscopy, HRMS, IR spectroscopy and elemental analysis. Our characterisation data is broadly in agreement with that reported earlier, which were obtained on $[\text{AdPMe}_3]\text{I}$ synthesised via a different route.[22]



Scheme 1 Synthetic pathway to $[\text{AdPMe}_3]\text{I}$ reported in this paper.

Crystallography

Crystal structures of AdP(O)Cl_2 , $[\text{AdPMe}_2\text{H}]\text{I}$ and $[\text{AdPMe}_3]\text{I}$ are shown in Figure 1, with selected data in Table 1 and Table 2. The AdP(O)Cl_2 is molecular, whilst the other two structures have ionic separated phosphonium cations and iodide anions. In each case the phosphorus atom adopts a slightly distorted tetrahedral geometry, indicating that attachment of the bulky adamantane group does not introduce substantial angular strain into the phosphorus environment. The P1-C1 bonds are crystallographically identical in all three structures and as expected for a normal P-C single bond.

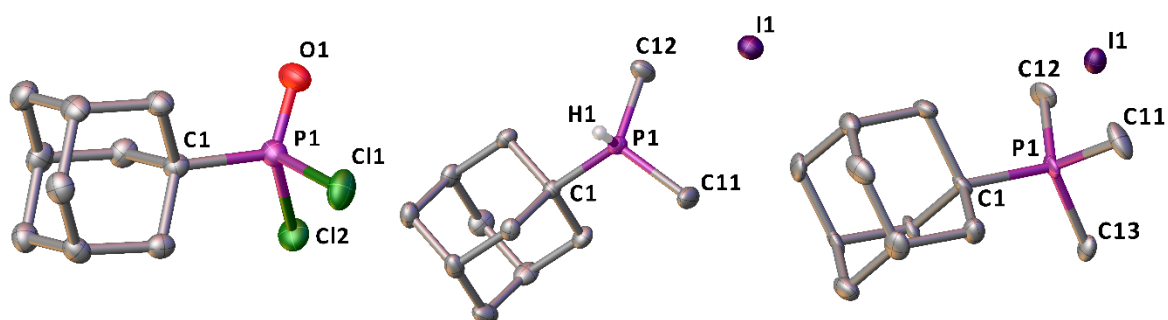


Figure 1 Left to right: The crystal structures of AdP(O)Cl_2 , $[\text{AdPMe}_2\text{H}]\text{I}$ and $[\text{AdPMe}_3]\text{I}$. Carbon-bound hydrogen atoms are omitted for clarity. Ellipsoids are plotted at the 40% level.

Table 1 Selected bond lengths (\AA) and angles ($^\circ$) for AdP(O)Cl_2 , $[\text{AdPMe}_2\text{H}]\text{I}$ and $[\text{AdPMe}_3]\text{I}$.

AdP(O)Cl_2			
P1-C1	1.816(3)	P1-Cl1	2.0250(12)
P1=O	1.455(2)	P1-Cl2	2.0259(10)
C1-P1-Cl1	106.38(9)	Cl1-P1-Cl2	101.32(5)
C1-P1-O1	116.69(12)	O1-P1-Cl1	112.57(10)
$[\text{AdPMe}_2\text{H}]\text{I}$			
P1-C1	1.8246(17)	P1-C11	1.7843(19)
		P1-C12	1.7759(19)
C1-P1-C11	111.34(8)	C1-P1-C12	112.67(9)
		C11-P1-C12	109.39(10)
$[\text{AdPMe}_3]\text{I}$			
P1-C1	1.817(11)	P1-C12	1.778(14)
P1-C11	1.786(14)	P1-C13	1.789(12)
C1-P1-C11	109.7(6)	C1-P1-C13	111.9(5)

Conclusion

An optimised synthetic sequence for multigram quantities of an adamantyl group containing phosphorus based OSDA [AdPMe₃]I is reported. The synthesis has been extensively tested and optimised for reproducibility. Particular attention has been paid to limiting the need for specialist procedures, and minimising laborious purification steps. Included in the sequence is column chromatography on (air stable) AdP(O)Cl₂. No purification was needed in the following two steps (producing AdPH₂ and [AdPMe₂H]I), providing the inert atmosphere conditions were maintained throughout the reaction and work-up. In the next step, extraction using an aqueous/organic biphasic system was required to remove salts from the in situ formation of AdPMe₂. This extraction was performed under an inert atmosphere using the cannulation technique, and is likely to be the most demanding purification procedure. Single crystal X-ray data revealed uncongested phosphorus centres in the three crystalline materials obtained, including the title compound, [AdPMe₃]I.

Experimental

General

Unless otherwise stated, all manipulations were performed under an oxygen-free nitrogen atmosphere using standard Schlenk techniques or under argon atmosphere using Saffron glove box. 1-Bromoadamantane was obtained from Sigma-Aldrich. Solvents were collected from an MBraun Solvent Purification System or dried and stored according to common procedures.[23] IR spectra were collected on a Perkin Elmer 2000 NIR/Raman Fourier Transform spectrometer. ¹H, ¹³C and ³¹P NMR spectra were obtained on either a Bruker Avance II 400, Bruker Avance III 500 or Jeol GSX Delta 270 spectrometer with δ_{H} and δ_{C} relative to TMS, residual solvent peaks (CDCl₃; δ_{H} 7.26, δ_{C} 77.2 ppm) were used for calibration. 85% H₃PO₄ was used as an external standard for ³¹P NMR. All measurements were performed at 25 °C with shifts reported in ppm. Mass spectra were acquired by the EPSRC UK National Mass Spectrometry Facility at Swansea University using nanospray ionisation (NSI). Elemental analyses were performed by Stephen Boyer at the London Metropolitan University.

AdP(O)Cl₂

An adapted literature procedure was used.[16, 17] AlCl₃ (20.20 g, 0.15 mol) and 1-bromoadamantane (21.73 g, 0.10 mol) were cooled in an ice bath and PCl₃ (150 mL, 2.0 mol) was added portionwise over 30 mins. Upon complete addition the reaction was heated to 90 °C for 24 h. The excess PCl₃ was removed *in vacuo* and the solid washed with hexane (200 mL). The remaining procedure was performed in air as the compounds are air stable. The solid was added to CH₂Cl₂ (500 mL) and the resulting suspension was cooled in an ice bath. Water (250 mL) was added dropwise until the vigorous reaction subsided. The organic layer was isolated and dried over magnesium sulfate. Removal of the solvent *in vacuo* afforded the crude product as a pale brown solid. Purification was performed by flash column

chromatography (silica/CH₂Cl₂). The product was obtained as a white powder (17.18 g, 0.067 mol, 68%). Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of a solution in CH₂Cl₂. ¹³C{¹H} and ³¹P{¹H} data was in good agreement with that previously reported.[18]

¹H NMR (500 MHz, CDCl₃): δ 2.21 – 2.15 (br m, 3 H, CH), 2.09 (dd, ³J_{HP} = 8.0 Hz, ³J_{HH} = 2.7 Hz, 6 H, CH₂), 1.84 – 1.74 (br m, 6 H, CH₂).

¹H{³¹P} NMR (500 MHz, CDCl₃): δ 2.18 (br s, 3 H, CH), 2.09 (br s, 6 H, CH₂), 1.84 – 1.74 (br m, 6 H, CH₂).

¹³C NMR (125 MHz, CDCl₃): δ 48.5 (d, ¹J_{CP} = 88.2 Hz, C_q), 35.8 (d, ⁴J_{CP} = 2.7 Hz, CH₂), 34.9 (d, ²J_{CP} = 4.2 Hz, CH₂), 27.5 (d, ³J_{CP} = 15.5 Hz, CH).

³¹P NMR (202 MHz, CDCl₃): δ 65.2 (br m (≈s)).

³¹P{¹H} NMR (109 MHz, CDCl₃): δ 65.2 (s).

IR (KBr): ν_{max}/cm⁻¹ 2924s (ν_{C-H}), 2857s (ν_{C-H}), 1453m, 1264s (ν_{P=O}), 542s.

AdPH₂

An adapted literature procedure was used.[16] To a cooled suspension (0 °C) of LiAlH₄ (5.00 g, 0.13 mol) in diethyl ether (150 mL) was added dropwise a solution of AdP(O)Cl₂ (17.00 g, 0.067 mol) in diethyl ether (120 mL). Upon complete addition, the reaction was heated to reflux for 1 h. The reaction was cooled in an ice bath and degassed water (100 mL) was added cautiously (vigorous reaction!). The organic layer was removed and the aqueous layer extracted with diethyl ether (2 x 50 mL), the combined organic fractions were dried over magnesium sulfate. Removal of the solvent afforded the product as a colourless oil (11.12 g, 0.066 mol, 99%). ¹³C{¹H} and ³¹P{¹H} data was in good agreement with that previously reported.[17]

¹H NMR (500 MHz, CDCl₃): δ 2.66 (d, ¹J_{HP} = 192.7 Hz, 2 H, PH₂), 1.93 (br s, 3 H, CH), 1.80 – 1.77 (m, 6 H, CH₂), 1.73 – 1.63 (m, 6 H, CH₂).

¹H{³¹P} NMR (500 MHz, CDCl₃): δ 3.06 – 2.34 (m, 2 H, PH₂), 1.93 (s, 3 H, CH), 1.79 (d, ³J_{HH} = 2.7 Hz, 6 H, CH₂), 1.73 – 1.63 (m, 6 H, CH₂).

¹³C NMR (125 MHz, CDCl₃): δ 44.7 (d, ²J_{CP} = 8.2 Hz, CH₂), 36.3 (s, CH₂), 28.9 (d, ³J_{CP} = 7.7 Hz, CH).

³¹P NMR (202 MHz, CDCl₃): δ -82.3 (t, ¹J_{PH} = 192.7 Hz).

³¹P{¹H} NMR (109 MHz, CDCl₃): δ -82.3 (s).

[AdPMe₂H]⁺ I⁻

To a MeOH (40 mL) solution of AdPH₂ (6.13 g, 0.036 mol) was added methyl iodide (20.44 g, 0.14 mol). The reaction was heated to 30°C under reflux conditions for 17 h. The remaining procedure was carried out in air, as the compounds are air stable. The volatiles were removed *in vacuo* and the resulting solid was washed with hexane (50 mL). Drying *in vacuo* afforded the product as a white solid (11.32 g, 0.035 mol, 97%). Crystals suitable for single crystal X-

ray diffraction were obtained by diffusion of diethyl ether into a CH₂Cl₂ solution of the product.

Anal. calcd. for C₁₂H₂₂IP (324.19 g mol⁻¹): C, 44.46; H, 6.84. Found: C, 44.37; H, 6.83.

¹H NMR (500 MHz, CDCl₃): δ 7.16 (d of septets, ¹J_{HP} = 489.0 Hz, ³J_{HH} = 5.4 Hz, 1 H, P-H), 2.16 (br s, 3 H, CH), 2.06 (dd, ²J_{HP} = 14.1 Hz, ³J_{HH} = 5.4 Hz, 6 H, P(CH₃)₂H), 1.97 (dd, ³J_{HP} = 6.7 Hz, ³J_{HH} = 2.4 Hz, 6 H, CH₂), 1.85 – 1.75 (m, 6 H, CH₂).

¹H{³¹P} NMR (500 MHz, CDCl₃): δ 7.16 (h, ³J_{HH} = 5.4 Hz, 1 H, P-H), 2.16 (br s, 3 H, CH), 2.06 (d, ³J_{HH} = 5.4 Hz, 6 H, P(CH₃)₂H), 1.97 (d, ³J_{HH} = 2.4 Hz, 6 H, CH₂), 1.85 – 1.75 (m, 6 H, CH₂).

¹³C NMR (125 MHz, CDCl₃): δ 36.1 (s, CH₂), 35.6 (s, CH₂), 29.9 (d, ¹J_{CP} = 47.8 Hz, C_q), 26.9 (d, ³J_{CP} = 10.6 Hz, CH), 1.3 (d, ¹J_{CP} = 50.4 Hz, P(CH₃)₂H).

³¹P NMR (109 MHz, CDCl₃): δ 12.5 (d, ¹J_{PH} = 489.0 Hz).

³¹P{¹H} NMR (109 MHz, CDCl₃): δ 12.5 (s).

HRMS (NSI⁺): *m/z* (%) 521.1949 (15) [C₂₄H₄₄P₂I]⁺ (M₂-I⁺), 425.2733 (20) [C₂₄H₄₃P₂O₂]⁺ ((M+O-HI)₂H⁺), 213.1399 (100) [C₁₂H₂₂PO]⁺ (M+O-I⁺), 197.1453 (50) [C₁₂H₂₂P]⁺ (M-I).

IR (KBr): *v*_{max}/cm⁻¹ 2957m (ν_{C-H}), 2913s (ν_{C-H}), 2849m (ν_{C-H}), 1298m, 973br s.

[AdPMe₃]⁺ I⁻

To a suspension of [AdPMe₂H]⁺ I⁻ (5.00 g, 0.015 mol) in hexane (50 mL) was added an aqueous solution of NaOH (6.50 g in 100 mL H₂O, 0.16 mol). The mixture was stirred vigorously for 15 mins, then the organic layer was removed and the aqueous layer extracted with hexane (2 x 50 mL). The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed *in vacuo*. MeOH (70 mL) was added, followed by methyl iodide (4.26 g, 0.030 mol) and the reaction mixture was stirred at room temperature for 5 h. The remaining procedure was carried out in air, as the compounds are air stable. The volatiles were removed *in vacuo* and the crude solid was washed with hexane (50 mL). Drying *in vacuo* gave product as a white solid (4.46 g, 0.013 mol, 88%). Crystals suitable for single crystal X-ray diffraction were obtained by diffusion of ether into a solution of the product in CH₂Cl₂.

Anal. calcd. for C₁₂H₂₂IP (338.20 g mol⁻¹): C, 46.16; H, 7.15. Found: C, 46.27; H, 7.08.

¹H NMR (400 MHz, CDCl₃): δ 2.15 – 2.09 (br m, 3 H, CH), 1.88 (dd, ³J_{HP} = 6.0 Hz, ³J_{HH} = 3.2 Hz, 6 H, CH₂), 1.84 – 1.80 (br m, 6 H, CH₂), 1.76 (d, ²J_{HP} = 13.5 Hz, 9 H, P(CH₃)₃).

¹H{³¹P} NMR (400 MHz, CDCl₃): δ 2.15 – 2.09 (br m, 3 H, CH), 1.88 (d, ³J_{HH} = 3.2 Hz, 6 H, CH₂), 1.84 – 1.80 (br m, 6 H, CH₂), 1.76 (d, ⁵J_{HH} = 0.9 Hz, 9 H, P(CH₃)₃).

¹³C NMR (100 MHz, CDCl₃): δ 35.2 (d, ⁴J_{CP} = 1.1 Hz, CH₂), 33.6 (d, ²J_{CP} = 1.3 Hz, CH₂), 27.0 (d, ³J_{CP} = 10.3 Hz, CH), 3.3 (d, ¹J_{CP} = 53.0 Hz, P(CH₃)₃).

³¹P NMR (109 MHz, CDCl₃): δ 33.7 (br s).

³¹P{¹H} NMR (109 MHz, CDCl₃): δ 33.7 (s).

HRMS (NSI⁺): *m/z* (%) 549.2246 (20) [C₂₆H₄₈P₂I]⁺ (M₂-I⁺), 331.2543 (10) [C₂₂H₃₆P]⁺ (Ad₂PMe₂⁺), 211.1602 (100) [C₁₃H₂₄P]⁺ (M-I).

IR (KBr): *v*_{max}/cm⁻¹ 2953m (ν_{C-H}), 2907s (ν_{C-H}), 2852m (ν_{C-H}), 1453m, 982s, 971s.

X-ray Diffraction.

CCDC 1544650-1544652 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Data for AdP(O)Cl₂ and [AdPMe₂H]I were collected using a Rigaku SCX-Mini (Mo–K α , graphite monochromator) at a temperature of –100°C to a maximum 2 θ value of 50.6°. Data for [AdPMe₃]I were collected on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Mo-K α radiation at a temperature of –180 ± 1°C to a maximum 2 θ value of 50.6°. Multiple data collections were conducted for [AdPMe₃]I, with crystals grown from a variety of solvents. The best quality data set was used for refinements. Although this crystal data set appears to be of lower quality upon first inspection, it is sufficient to demonstrate the connectivity for the purposes of this work. The large residual electronic density lies close to the iodine atom and may reflect some slight disorder in the position of this high Z atom. Attempts to refine this electron density as a partial weight iodine were unproductive. All data were corrected for Lorentz, polarisation and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections. Hydrogen atoms were refined using the riding model in all cases. The data for all compounds were collected and processed using *CrystalClear (Rigaku)*.^[24-26] The crystal structures were solved using direct methods and refined by heavy-atom Patterson methods and expanded using Fourier techniques.^[27-29] All calculations were performed using the *CrystalStructure* crystallographic software package except for refinement which was performed using *SHELXL-97/2013*.^[30-32] Table 2 lists the details of data collections and refinements. Images of crystal structures were obtained using *OLEX-2*^[33] with all other manipulations carried out using *Mercury 3.5*.^[34]

Table 2 Crystallographic data for AdP(O)Cl₂, [AdPMe₂H]I and [AdPMe₃]I.

	AdP(O)Cl ₂	[AdPMe ₂ H]I	[AdPMe ₃]I
Formula	C ₁₀ H ₁₅ Cl ₂ OP	C ₁₂ H ₂₂ IP	C ₁₃ H ₂₄ I P
M _r	253.09	324.18	338.21
Colour/Habit	colourless, prism	colourless, prism	colourless, platelet
Crystal Dimensions [mm]	0.260 × 0.110 × 0.090	0.440 × 0.270 × 0.180	0.100 × 0.100 × 0.010
Crystal System	monoclinic	monoclinic	triclinic
Space Group	P 1 21/n 1	P 1 21/n 1	P-1
a [Å]	7.0406(14)	7.5806(5)	6.6147(19)
b [Å]	10.702(3)	12.7807(8)	7.318(2)
c [Å]	15.181(4)	14.1507(9)	15.351(5)
α [°]	90	90	91.933(11)
β [°]	97.383(10)	104.460(4)	92.638(7)
γ [°]	90	90	90.395(9)
V [Å ³]	1134.4(5)	1327.57(15)	741.8(4)
Z	4	4	2
$\rho_{\text{calcd.}}$ [g cm ⁻³]	1.482	1.622	1.514
F ₀₀₀	528.0	648.0	340.0
μ [cm ⁻¹]	6.78	24.99	22.40

$2\theta_{\max}$	50.6	50.8	50.6
Measured refln.	9432	10668	10326
Unique refln.	2065	2319	2640
R_{int}	0.0756	0.0217	0.0957
$R [I > 2\sigma(I)]$	0.0407	0.0169	0.0804
wR (F^2 , all data)	0.1069	0.0419	0.2563
GOOF	1.063	1.063	1.190
Largest peak/hole [$e \text{ \AA}^{-3}$]	0.42/−0.32	0.36/−0.28	5.90/−1.12

Acknowledgements

This work was financially supported by the EPSRC (grant numbers EP/L505079/1 and EP/M506631/1) and COST action SM1302 SIPs. The authors thank the University of St Andrews NMR Service and the EPSRC UK National Mass Spectrometry Facility at Swansea University (NMSF).

References

- [1] A.J. Arduengo, R.L. Harlow, M. Kline, A stable crystalline carbene, *J. Am. Chem. Soc.*, 113 (1991) 361-363.
- [2] S.I. Zones, R.A. Van Nordstrand, D.S. Santilli, D.M. Wilson, L. Yuen, L.D. Scampavia, Sequence of High Silica Zeolites Found During Synthesis Experiments in The Presence of A Quaternary Adamantammonium Cation, *Stud. Surf. Sci. Catal.*, 49 (1989) 299-309.
- [3] L.-T. Yuen, S.I. Zones, T.V. Harris, E.J. Gallegos, A. Auroux, Product selectivity in methanol to hydrocarbon conversion for isostructural compositions of AFI and CHA molecular sieves, *Microporous Mater.*, 2 (1994) 105-117.
- [4] Q. Zhu, J.N. Kondo, T. Tatsumi, S. Inagaki, R. Ohnuma, Y. Kubota, Y. Shimodaira, H. Kobayashi, K. Domen, A Comparative Study of Methanol to Olefin over CHA and MTF Zeolites, *The Journal of Physical Chemistry C*, 111 (2007) 5409-5415.
- [5] J. Wang, H. Zhao, G. Haller, Y. Li, Recent advances in the selective catalytic reduction of NO_x with NH₃ on Cu-Chabazite catalysts, *Applied Catalysis B: Environmental*, 202 (2017) 346-354.
- [6] C.S. Cundy, P.A. Cox, The hydrothermal synthesis of zeolites: Precursors, intermediates and reaction mechanism, *Microporous Mesoporous Mater.*, 82 (2005) 1-78.
- [7] C.S. Gittleman, S.S. Lee, A.T. Bell, C.J. Radke, Zeolite synthesis from tetraalkylammonium silicate gels, *Microporous Mater.*, 3 (1995) 511-530.
- [8] D.L. Dorset, K.G. Strohmaier, C.E. Kliewer, A. Corma, M.J. Díaz-Cabañas, F. Rey, C.J. Gilmore, Crystal Structure of ITQ-26, a 3D Framework with Extra-Large Pores, *Chem. Mater.*, 20 (2008) 5325-5331.
- [9] A. Corma, M.J. Diaz, F. Rey, K. Strohmaier, D. Dorset, ITQ-27, new crystalline microporous material, in, Google Patents, 2006.
- [10] D.L. Dorset, G.J. Kennedy, K.G. Strohmaier, M.J. Diaz-Cabañas, F. Rey, A. Corma, P-Derived Organic Cations as Structure-Directing Agents: Synthesis of a High-Silica Zeolite (ITQ-27) with a Two-Dimensional 12-Ring Channel System, *J. Am. Chem. Soc.*, 128 (2006) 8862-8867.
- [11] A. Corma, M.J. Diaz-Cabanias, J.L. Jorda, F. Rey, G. Sastre, K.G. Strohmaier, A Zeolitic Structure (ITQ-34) with Connected 9- and 10-Ring Channels Obtained with Phosphonium Cations as Structure Directing Agents, *J. Am. Chem. Soc.*, 130 (2008) 16482-16483.
- [12] M. Hernández-Rodríguez, J.L. Jordá, F. Rey, A. Corma, Synthesis and Structure Determination of a New Microporous Zeolite with Large Cavities Connected by Small Pores, *J. Am. Chem. Soc.*, 134 (2012) 13232-13235.

- [13] Y. Yun, M. Hernandez, W. Wan, X. Zou, J.L. Jorda, A. Cantin, F. Rey, A. Corma, The first zeolite with a tri-directional extra-large 14-ring pore system derived using a phosphonium-based organic molecule, *Chem. Commun.*, 51 (2015) 7602-7605.
- [14] Y. Yamasaki, N. Tsunoji, Y. Takamitsu, M. Sadakane, T. Sano, Synthesis of phosphorus-modified small-pore zeolites utilizing tetraalkyl phosphonium cations as both structure-directing and phosphorous modification agents, *Microporous Mesoporous Mater.*, 223 (2016) 129-139.
- [15] R. Simancas, J.L. Jordá, F. Rey, A. Corma, A. Cantin, I. Peral, C. Popescu, A New Microporous Zeolitic Silicoborate (ITQ-52) with Interconnected Small and Medium Pores, *J. Am. Chem. Soc.*, 136 (2014) 3342-3345.
- [16] H. Stetter, W.-D. Last, Über Verbindungen mit Urotropin-Struktur, XLIV. Über Adamantanphosphonsäure-(1)-dichlorid, *Chem. Ber.*, 102 (1969) 3364-3366.
- [17] M. Gouygou, G. Etemad-Moghadam, M. Koenig, A Convenient Method for the Synthesis of 1-Adamantyl-dichlorophosphine, *Synthesis*, 1987 (1987) 508-509.
- [18] G.A. Olah, O. Farooq, Q. Wang, A.H. Wu, Synthetic methods and reactions. 147. Aluminum chloride-catalyzed dichlorophosphorylation of saturated hydrocarbons with phosphorus trichloride in methylene chloride solution, *The Journal of Organic Chemistry*, 55 (1990) 1224-1227.
- [19] A. Ohashi, S. Matsukawa, T. Imamoto, Improved synthesis of 1-adamantylphosphine and its use in the synthesis of cyclic phosphines containing 1-adamantyl group, *Heterocycles*, 52 (2000) 905-910.
- [20] H.R. Hays, The Controlled Alkylation of Mono-n-alkylphosphines, *The Journal of Organic Chemistry*, 31 (1966) 3817-3820.
- [21] R.Y. Yurchenko, E.E. Lavrova, A.G. Yurchenko, 1-Adamantylphosphine reactions, *Zh. Obshch. Khim.*, 56 (1986) 482-483.
- [22] J.R. Goerlich, C. Mueller, R. Schmutzler, Contributions to the chemistry of acylphosphines: 1-adamantylacyl-, di-1-adamantylacyl- and 1-adamantoylphosphines. Preparation and some reactions, *Phosphorus, Sulfur Silicon Relat. Elem.*, 85 (1993) 193-205.
- [23] W.L.F. Armarego, C.L.L. Chai, Purification of Laboratory Chemicals, 6th ed., Butterworth-Heinemann, Oxford, 2009.
- [24] CrystalClear 2.0, Rigaku Corporation, in, 2007.
- [25] CrystalClear Software User's Guide, Molecular Structure Corporation ©, in, 2007.
- [26] J.W. Pflugrath, MAD Data Collection, *Acta Crystallogr. Sect. D. Biol. Crystallogr.*, 55 (1999) 1718-1725.
- [27] A. Altomare, M.C. Burla, M. Camalli, G.L. Casciarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, SIR97: a new tool for crystal structure determination and refinement, *J. Appl. Crystallogr.*, 32 (1999) 115-119.
- [28] P. T. Beuerskens, G. Admiraal, G. Beuerskens, W. P. Bosman, R. de-Gelder, R. Israel, J. M. M. Smits, The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, in, 1999.
- [29] P.T. Beuerskens, G. Admiraal, H. Behm, G. Beuerskens, J.M.M. Smits, C. Smykalla, *Z. Kristallogr.*, (1991, Suppl 4) 99.
- [30] CrystalStructure 3.8.1: Crystal Structure Analysis Package, Rigaku and Rigaku/MS (2000-2006) 9009 New Trails Dr. The Woodlands, TX 77381 USA, in.
- [31] CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku Corporation (2000-2010). Tokyo 196-8666, Japan., in.
- [32] G.M. Sheldrick, A short history of SHELX, *Acta Crystallogr A*, 64 (2008) 112-122.
- [33] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.*, 42 (2009) 339-341.
- [34] C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, Mercury CSD 2.0– new features for the visualization and investigation of crystal structures, *J. Appl. Crystallogr.*, 41 (2008) 466-470.