DOI: 10.1002/adsc.200900774

Diamondoid Phosphines – Selective Phosphorylation of Nanodiamonds[1]

Hartmut Schwertfeger,[a,e] Mareike M. Machuy,[a,e] Christian Würtele,[b] Jeremy E. P. Dahl,[c] Robert M. K. Carlson,[d] and Peter R. Schreiner[a,*]

[a] Institut für Organische Chemie, Justus-Liebig University, Heinrich-Buff-Ring 58, 35392 Giessen, Germany
Fax: (+49)-641-34309; phone: (+49)-641-34301; e-mail: prs@org.chemie.uni-giessen.de
[b] Institut für Anorganische und Analytische Chemie, Justus-Liebig University, Heinrich-Buff-Ring 58, 35392 Giessen, Germany
[c] Geballe Laboratory for Advanced Materials, Stanford University, Stanford, California 94305, USA
[d] MolecularDiamond Technologies, Chevron Technology Ventures, 100 Chevron Way, Richmond, CA 94802, USA
[e] H. Schwertfeger and M. M. Machuy shall be considered as equal first authors.

Received: November 6, 2009; Published online: February 23, 2010

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.200900774.

Abstract: The diamondoids (nanodiamonds) diamantane and triamantane were selectively converted into diorganophosphinic acid chlorides by reacting them with phosphorus trichloride under Friedel–Crafts-like conditions. The di-diamondoid phosphinic acid chlorides were subsequently reduced with trichlorosilane to give the hitherto unknown corresponding di-diamondoid phosphines. These diamondoid phosphinic acid chlorides and phosphines are of great utility as starting materials in organo-element and coordination chemistry due to their extraordinary rigidity and steric bulk.

Keywords: diamondoids; nanodiamonds; phosphorylation; Sonogashira–Hagihara reaction; Suzuki–Miyaura reaction

An extraordinary class of hydrocarbon cage compounds, the so-called diamondoids are nanometer-sized, hydrogen-terminated diamond-like molecules consisting of fused adamantane units (Figure 1).[2] These nanodiamonds can be isolated from petroleum[3] and some smaller diamondoids can also be prepared synthetically.[2] While the so-called "lower diamondoids" [consisting of adamantane (**1**), diamantane (**2**), and triamantane (**3**)] have no structural isomers the "higher diamondoids" (tetra-, penta-, hexamantanes, etc.) have isomers, some of which are chiral.[4] Our recent reports on the selective functionalization[5] of these molecules led to the remarkable result that diamondoids exhibit some of the outstanding properties of macroscopic diamond, such as, for instance, negative electron affinity.[6] We were also able to show that diamondoids can be used as sterically demanding ligands in N-heterocyclic carbene reactions.[7]

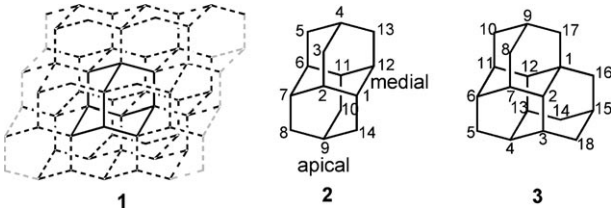
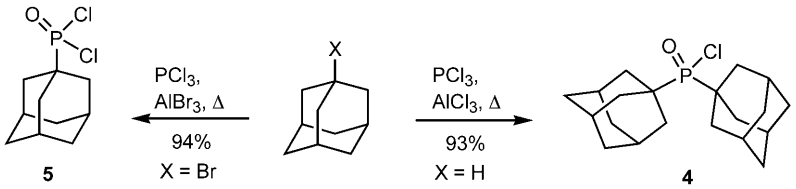


Figure 1. Adamantane (**1**) resembles the repeating unit of diamond and is the parent compound of all diamondoids like diamantane (**2**) and triamantane (**3**).

During our continuing studies of the selective functionalization of these saturated hydrocarbons we investigated their phosphorylation reactions. While numerous phosphorus adamantane derivatives have been prepared and studied, other phosphorylated diamondoids are virtually unknown. Since it is well known that adamantane serves as an excellent bulky moiety in phosphine ligands[8] we were interested if larger diamondoids than **1** can also be phosphorylated and potentially used as ligands in noble metal catalysis.

Adamantane (**1**) itself can be converted into di-1-adamantylphosphinic acid chloride (**4**) by refluxing **1** in PCl_3 with $AlCl_3$ (Scheme 1, *right*).[9,10] On the other hand, 1-bromoadamantane can be transformed into 1-adamantylphosphonic acid dichloride (**5**) by employing a $PCl_3/AlBr_3$ mixture (Scheme 1, *left*).[11]

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

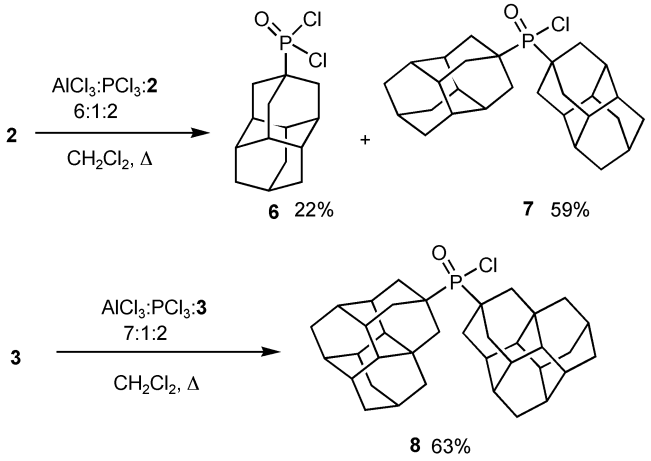


Scheme 1. Literature reported phosphorylation of adamantane[9,10] (**1**) leads to disubstituted phosphinic acid chloride **4** while 1-bromoadamantane[11] gives **5** exclusively.

Olah et al. found that the dichlorophosphorylation reaction also occurs with nearly equimolar amounts of PCl_3, $AlCl_3$, and **1** in CH_2Cl_2 as solvent.[12] This group also used **2** to give the medial substituted 1-diamantylphosphonic acid dichloride in 60% yield. We repeated the phosphorylation for **2** and found only apically but no medially substituted diamantane-phosphonic acid dichloride in contrast to the results described by Olah et al.[12] From the crude product mixture we also isolated an apical di-diamantane-phosphinic acid chloride derivative. By using a half equimolar amount of PCl_3 compared to **2** it was possible to isolate 4-diamantylphosphonic acid dichloride (**6**) in 22% yield and di-4-diamantylphosphinic acid chloride (**7**) in 59% yield (Scheme 2). These findings are in line with our earlier experimental and theoretical results that the use of Lewis acids leads to the formation of apically substituted diamondoid derivatives.[13] When **3** was treated under similar conditions with PCl_3 and $AlCl_3$ di-9-triamantylphosphinic acid chloride (**8**) was isolated in 63% yield. The selectivity of this reaction is remarkably high since **3** possesses four non-equivalent tertiary C–H bonds [adamantane (**1**) has only one and diamantane (**2**) has two non-equivalent tertiary C–H bonds]. These results are consistent with our previous reports that with the sizes of the diamondoids the reaction selectivities also increase.[14] Additionally, we were able to grow a single crystal of **8**. The crystal structure[15] reveals a co-crystal of **8** and one $CDCl_3$ solvent molecule (which has been omitted for clarity in Figure 2). The phosphinic acid structure shows nearly the same bond lengths and angles as the adamantane analogue **4**.[9]

Since **4** can readily be reduced to its corresponding phosphine by using $LiAlH_4$[10,16] we adapted this procedure to reduce **7**. Unfortunately, we were not able to isolate the desired phosphine by this method. Utilizing $NaBH_4$, DIBAL, and diphenylsilane was also unsuccessful. As $HSiCl_3$ is able to reduce phosphinic acid chlorides in one step,[17] this reaction was also used to reduce **4** to its phosphine but it required a reaction time of 11 days at room temperature.[16] By carrying out the $HSiCl_3$ reduction of **7** and **8** under reflux in toluene the reaction times were significantly reduced to 16 and 18 h, respectively, and we were able to obtain the corresponding phosphines in good yields (Scheme 3).

Both phosphines are colorless solids exhibiting the typical phosphine odor. While di-1-adamantylphosphine has been reported to be stable in air for hours[16] we observed that di-4-diamantylphosphine (**9**) oxidizes quickly in the solid state and in solution. Di-9-triamantylphosphine (**10**) is much less prone to oxidation. In order to prove that **9** and **10** are partially oxidized by moisture and air, both phosphine



Scheme 2. Phosphorylation of diamantane (**2**) and triamantane (**3**) by utilizing a 1:2 mixture of PCl_3 and the corresponding diamondoid in dry dichloromethane to give only apically substituted derivatives.

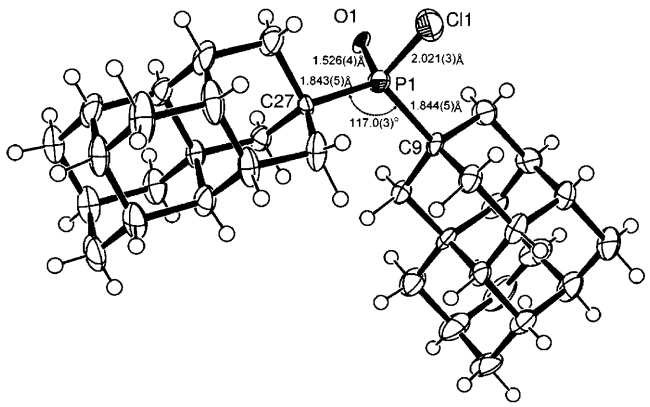
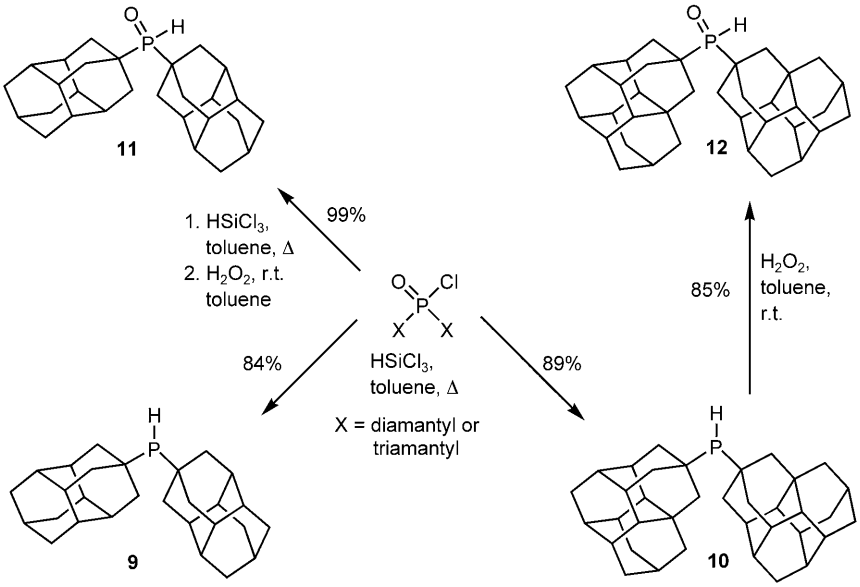


Figure 2. X-ray structure of di-9-triamantylphosphinic acid chloride (**8**) with selected bond lengths and angles. $CDCl_3$ as a solvent molecule has been omitted for clarity.

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

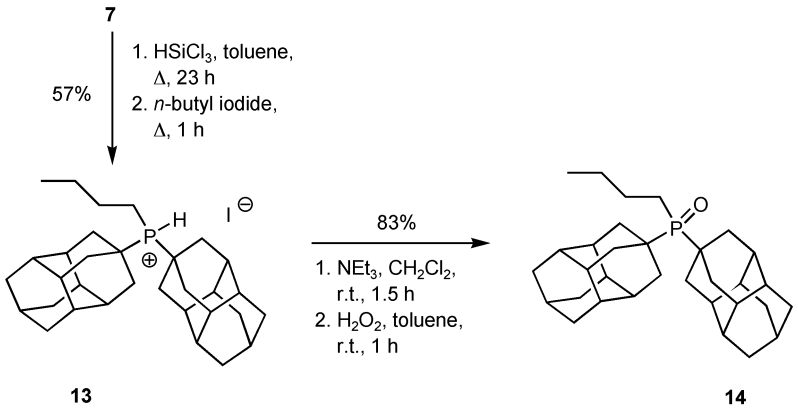


Scheme 3. Reduction of diamantane- and triamantane-phosphinic acid chlorides by using $HSiCl_3$ in boiling toluene. Resulting phosphines were oxidized by 30% H_2O_2 to give the corresponding phosphine oxides.

oxides were synthesized. Due to the oxygen sensitivity of **9**, **7** was reduced by $HSiCl_3$ and the crude product was treated directly with 30% H_2O_2. The oxide **11** was obtained in quantitative yield (Scheme 3). Triamantylphosphine **10** can be oxidized directly with 30% aqueous hydrogen peroxide.

As a next step we envisioned synthesizing a chlorinated di-diamondoid phosphine from secondary phosphines **9** and **10** in order to prepare tertiary phosphines *via* Grignard reactions. While in the literature procedures by Goerlich et al.[10,18] toxic phosgene in toluene is used, we looked for alternatives in order to avoid this reagent. Since di-1-adamantylphosphine can be chlorinated using water and oxygen-free CCl_4[19] we followed this procedure for **9** and **10** but were not able to isolate a diamondoid phosphine chloride. Instead, we mostly obtained mixtures containing phosphinic acid chloride. Other chlorinating agents like C_2Cl_6[20] and the reduction of **7** *via* alkylation with methyl triflate[21] were also not successful. It was also impossible to convert **7** into its thiol analogue using Lawesson's reagent. We hoped that the thiol derivative could be more readily reduced. In addition the treatment of **11** with PCl_3 (which is reported to work for adamantane[9]) did not give the desired chlorinated di-diamondoid phosphine.

While all these routes proved unsuccessful, we were attracted by the preparation of tertiary phosphines *via* phosphonium salts. For di-1-adamantylphosphine this reaction has been described by Goerlich et al.[16] and was extensively investigated by Tewari et al.[22] We tested this transformation and found that **9** reacts very well with *n*-butyl iodide. Unfortunately, the purification of the resulting diamantane-phosphonium



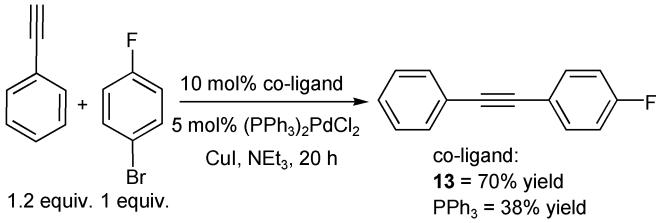
Scheme 4. Preparation of di-4-diamantyl-*n*-butylphosphonium iodide (**13**) and the following deprotonation/oxidation to obtain the tertiary phosphine oxide **14**.

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

salt *via* recrystallization, which has been described by Tewari et al. for adamantane analogues,[22] was not successful. The best results concerning purity were obtained when *n*-butyl iodide was added directly into the reaction mixture after the reduction of **7** with $HSiCl_3$ (Scheme 4). Thereby the crude product needs to be dissolved and filtered several times in order to remove the reaction products of $HSiCl_3$, which resulted in lower yield. While adamantylphosphonium salts can be deprotonated using NEt_3 as a base, this protocol failed for the isolation of a pure tertiary diamantane-phosphine and therefore the resulting crude product was oxidized directly with H_2O_2 into the tertiary phosphine oxide **14** that could be purified *via* column chromatography (Scheme 4). The hitherto unknown di-4-diamantylphosphinic acid iodide was isolated during one synthesis of **14** as a side product (see Experimental Section for spectroscopic data).

In order to briefly examine the catalytic potential of the phosphorylated diamondoid ligands we utilized the air- and moisture-stable phosphonium salt **13**. Adamantane phosphonium salts have been successfully used as co-ligands by Tewari et al.[22] As a first test reaction we used the Sonogashira–Hagihara[23] coupling of phenylacetylene with 4-bromofluorobenzene (Scheme 5). Thereby **13** was used as co-catalyst and 1-fluoro-4-(phenylethynyl)-benzene was isolated in 70% yield while the same reaction with standard co-ligand PPh_3 resulted in 38% isolated yield.

As a second test we used **13** as co-ligand in the Suzuki–Miyaura[24] coupling reaction of 4-bromotoluene with phenylboronic acid (Scheme 6). Thereby we were able to isolate 4-phenyltoluene in almost quantitative yield after 20 h. For comparison the same



Scheme 5. Sonogashira–Hagihara coupling of phenylacetylene with 4-bromofluorobenzene using phosphonium salt **13** and PPh_3 as co-ligands.

Scheme 6. Suzuki–Miyaura coupling reaction of phenylboronic acid with 4-bromotoluene utilizing $Pd(OAc)_2$ as catalyst and **13** as co-ligand.

reaction was carried out without **13** and was also terminated after 20 h. GC/MS analysis showed only partial conversion along with biphenyl as a side product. After preparative GC we were able to isolate the pure product in 18% yield.

In conclusion, we have synthesized the phosphinic acid chlorides of diamondoids **2** and **3**, which were reduced to the corresponding phosphines with $HSiCl_3$. The chlorination of the phosphines was not successful but can in principle be by-passed *via* the diamondoid phosphonium salts. The catalytic activity of the diamantane-phosphonium salt **13** as a co-ligand was shown in the Sonogashira–Hagihara and Suzuki–Miyaura coupling reactions. In our future work we will attempt to prepare a variety of diamondoid phosphines and phosphonium salts which will also be tested as sterically demanding ligands in noble metal catalysis.

Experimental Section

4-Diamantylphosphonic Acid Dichloride (6) and Di-4-diamantylphosphinic Acid Chloride (7)

Compound **2** (10 g, 53 mmol), $AlCl_3$ (21 g, 157 mmol), and PCl_3 (2.3 mL, 26 mmol) in dry CH_2Cl_2 (100 mL) were refluxed for 7 h, stirred at room temperature for 15 h and refluxed again for 9 h. Thereafter, the reaction mixture was quenched with 10% HCl solution (150 mL) and CH_2Cl_2 (30 mL). After phase separation the aqueous phase was extracted with CH_2Cl_2 (2×100 mL), combined organic phases were washed with distilled water (100 mL) and dried over Na_2SO_4. Purification by column chromatography on silica gel using CH_2Cl_2 (**2** and side products) and CH_2Cl_2:ether 95:5 (R_f: 0.61 for **6** and 0.27 for **7**). Yield of **6**: 1.78 g (5.82 mmol, 22%), yield of **7**: 7.12 g (15.6 mmol, 59%).

4-Diamantylphosphonic acid dichloride (6): mp 144–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=2.07$–2.02 (m, 6H, H-3,5,13), 1.99 (br s, 3H, H-2,6,12), 1.87–1.82 (m, 1H, H-9), 1.81–1.74 (m, 9H, H-1,7,8,10,11,14). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=47.1$ [d, $^1J(^{13}C,^{31}P)=89.5$ Hz, C-4], 37.2 [d, $^5J(^{13}C,^{31}P)=3.0$ Hz, C-8,10,14], 36.6 [d, $^3J(^{13}C,^{31}P)=17.1$ Hz, C-2,6,12], 36.0 [d, $^4J(^{13}C,^{31}P)=2.0$ Hz, C-1,7,11], 35.9 [d, $^2J(^{13}C,^{31}P)=4.0$ Hz, C-3,5,13], 25.1 (C-9); ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4 external standard): $\delta=66.67$; IR (KBr): $\nu=$ 2908, 2891, 2848, 1460, 1440, 1268, 1252, 1048, 945, 852 cm^{-1}; HR-MS: $m/z=304.0562$, calcd. for $C_{14}H_{19}Cl_2OP$: 304.0551; anal. calcd. for $C_{14}H_{19}Cl_2OP$ (305.18): C 55.10, H 6.28; found: C 55.22, H 6.21.

Di-4-diamantylphosphinic acid chloride (7): mp 340–343 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=2.18$–2.09 (m, 12H, H-3,5,13), 1.89 (br s, 6H, H-2,6,12), 1.83–1.68 (m, 20H, H-1,7,8,9,10,11,14); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=43.8$ [d, $^1J(^{13}C,^{31}P)=60.4$ Hz, C-4], 37.9 [d, $^2J(^{13}C,^{31}P)=1.0$ Hz, C-3,5,13], 37.5 [d, $^5J(^{13}C,^{31}P)=2.0$ Hz, C-8,10,14], 37.0 [d, $^3J(^{13}C,^{31}P)=12.1$ Hz, C-2,6,12], 36.4 [d, $^4J(^{13}C,^{31}P)=2.0$ Hz, C-1,7,11], 25.3 [C-9]; ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4 external standard): $\delta=88.50$; IR (KBr): $\nu=2906$, 2851, 1460, 1439, 1315, 1251, 1213, 1046, 948, 856 cm^{-1}; HR-MS: $m/z=$

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

456.2341, calcd. for $C_{28}H_{38}ClOP$: 456.2349; anal. calcd. for $C_{28}H_{38}ClOP$ (457.03): C 73.58, H 8.38; found: C 73.31, H 8.40.

Di-9-triamantylphosphinic Acid Chloride (8)

Compound **3** (1 g, 4.2 mmol), $AlCl_3$ (2 g, 15 mmol), and PCl_3 (0.18 mL, 2.1 mmol) in dry CH_2Cl_2 (20 mL) were refluxed for 4.5 h, stirred at room temperature for 15 h and refluxed again for 8.5 h. The reaction mixture was quenched with 10% HCl solution (100 mL) and CH_2Cl_2 (50 mL). After phase separation the aqueous phase was extracted with CH_2Cl_2 (2×50 mL), combined organic phases were washed with distilled water (100 mL) and dried over Na_2SO_4. Purification was achieved by column chromatography on silica gel (CH_2Cl_2:ether 9:1, R_f: 0.40); yield: 742 mg (1.32 mmol, 63%); mp 280–284 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18–2.04 (m, 8H, H-8,10), 1.88 (br s, 2H, H-15), 1.83 (br s, 4H, H-7,11), 1.77–1.63 (m, 24H, H-3,4,5,6,13,14,17,18), 1.51 (br s, 4H, H-2,12), 1.36–1.30 (m, 4H, H-16); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 45.8 (C-2,12), 45.6 [d, $^1J(^{13}C,^{31}P)$ = 58.9 Hz, C-9], 44.9 (C-16), 44.4 [d, $^5J(^{13}C,^{31}P)$ = 3.0 Hz, C-5], 37.9–37.75 (m, C-14,17,18), 37.68–37.48 (m, C-3,7,8,10,11,13), 34.7 (C-4), 34.1 (C-6), 33.6 [d, $^3J(^{13}C,^{31}P)$ = 10.6 Hz, C-1], 27.7 (C-15); ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4 external standard): δ = 86.33; IR (KBr): ν = 2909, 2869, 1445, 1336, 1306, 1223, 1057, 1001, 846, 755, 601, 546 cm^{-1}; HR-MS: m/z = 560.3001, calcd. for $C_{36}H_{46}ClOP$: 560.2975. anal. calcd. for $C_{36}H_{46}ClOP$ (561.18): C 77.05, H 8.26; found: C 77.01, H 8.30.

Di-9-diamantylphosphine (9)

Compound **7** (900 mg, 1.97 mmol) was refluxed in toluene (40 mL) for 18 h under argon with $HSiCl_3$ (0.9 mL, 8.9 mmol). The solution was cooled to room temperature and toluene (50 mL) followed by 20% NaOH solution (80 mL) were added. After phase separation the aqueous phase was extracted with toluene (80 mL); combined extracts were washed with distilled water (60 mL) and dried over Na_2SO_4. Purification was achieved by column chromatography on silica gel (CH_2Cl_2, R_f: 0.68); yield: 676 mg (1.66 mmol, 84%); mp 241–252 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.83 (d, J = 208.9 Hz, 1H, P-H), 1.94–1.80 (m, 12H, H-3,5,13), 1.76 (br s, 8H, H-2,6,9,12), 1.73–1.66 (m, 18H, H-1,7,8,10,11,14); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.3 [d, $^2J(^{13}C,^{31}P)$ = 10.1 Hz, C-3,5,13], 38.0 [d, $^3J(^{13}C,^{31}P)$ = 8.0 Hz, C-2,6,12], 37.9 (C-8,10,14), 36.7 (C-1,7,11), 31.7 [d, $^1J(^{13}C,^{31}P)$ = 14.1 Hz, C-4], 25.7 (C-9); ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4 external standard): δ = 13.37; IR (KBr): ν = 2899, 2882, 2845, 2267, 1453, 1435, 1312, 1246, 1047, 966, 850 cm^{-1}; HR-MS: m/z = 406.2790, calcd. for $C_{28}H_{39}P$: 406.2789; anal. calcd. for $C_{28}H_{39}P$ (406.58): C 82.71, H 9.67; found: C 82.38, H 9.93.

Di-9-triamantylphosphine (10)

Compound **8** (215 mg, 0.38 mmol) was refluxed in toluene (15 mL) for 16 h under argon with $HSiCl_3$ (0.3 mL, 3 mmol). The solution was cooled to room temperature and $CHCl_3$ (50 mL) followed by 20% NaOH solution (100 mL) were added. After phase separation the aqueous phase was extracted with $CHCl_3$ (2×50 mL); combined extracts were washed with distilled water (100 mL) and dried over Na_2SO_4. Purification was achieved by column chromatography on silica gel (CH_2Cl_2, R_f: 0.71); yield: 175 mg (0.34 mmol, 89%); mp 215–235 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.77 (d, J = 209.3 Hz, 1H, P-H), 1.93–1.73 (m, 10H, H-8,10,15), 1.72–1.56 (m, 24H, H-3,4,5,6,7,11,13,14,18), 1.46–1.31 (m, 8H, H-2,12,17), 1.26–1.21 (m, 4H, H-16); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.2 [d, $^2J(^{13}C,^{31}P)$ = 9.1 Hz, C-17], 46.0 (C-2,12), 45.2 (C-16), 44.0 [d, $^2J(^{13}C,^{31}P)$ = 10.1 Hz, C-8,10], 38.6 [d, $^3J(^{13}C,^{31}P)$ = 9.1 Hz, C-7,11], 38.1 (C-5), 38.0 (C-14,18), 37.8 (C-3,13), 35.0 (C-4), 34.3 (C-6), 34.2 [d, $^2J(^{13}C,^{31}P)$ = 8.0 Hz, C-1], 33.6 [d, $^1J(^{13}C,^{31}P)$ = 15.1 Hz, C-9], 27.8 (C-15); ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4 external standard): δ = 13.43; IR (KBr): ν = 2904, 2870, 2269, 1441, 1338, 1305, 1245, 1055, 1003, 845 cm^{-1}; HR-MS: m/z = 510.3402, calcd. for $C_{36}H_{47}P$: 510.3415; anal. calcd. for $C_{36}H_{47}P$ (510.73): C 84.66, H 9.28; found: C 84.51, H 9.20.

Di-4-diamantylphosphine oxide (11)

Compound **9** (1 g, 2.19 mmol) was refluxed in toluene (40 mL) for 24 h under argon with $HSiCl_3$ (1.5 mL, 14.8 mmol). The solution was cooled to room temperature and quenched with toluene (50 mL) and 20% NaOH solution (100 mL). The phases were separated and aqueous phase was extracted with toluene (40 mL). Combined organic extracts were washed with distilled water (80 mL) and stirred for 1 h with 30% H_2O_2 (15 mL). The reaction mixture was diluted with distilled water (60 mL) and CH_2Cl_2 (80 mL). After phase separation the aqueous phase was extracted with CH_2Cl_2 (60 mL) and the combined organic extracts were washed with distilled water (60 mL) and dried over Na_2SO_4. Purification was achieved by column chromatography on silica gel (CH_2Cl_2:MeOH 95:5, R_f: 0.44); yield: 921 mg (2.18 mmol, 99%); mp 320 °C (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.78 (d, J = 424.9 Hz, 1H, P-H), 2.04–1.90 (m, 12H, H-3,5,13), 1.87 (br s, 6H, H-2,6,12), 1.83–1.69 (m, 20H, H-1,7,8,9,10,11,14); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.7 (C-8,10,14), 37.6 (C-3,5,13), 36.7 [d, $^3J(^{13}C,^{31}P)$ = 11.1 Hz, C-2,6,12], 36.6 (C-1,7,11), 35.7 [d, $^1J(^{13}C,^{31}P)$ = 61.4 Hz, C-4]; ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4 external standard): δ = 60.53; IR (KBr): ν = 2880, 2846, 2262, 1458, 1439, 1314, 1258, 1176, 1048, 975, 909, 864 cm^{-1}; HR-MS: m/z = 422.2727, calcd. for $C_{28}H_{39}PO$: 422.2739; anal. calcd. for $C_{28}H_{39}PO$ (422.58): C 79.58, H 9.30; found: C 79.31, H 9.39.

Di-9-triamantyphosphine oxide (12)

Compound **10** (70 mg, 0.14 mmol) in toluene (4 mL) was mixed with 30% H_2O_2 (3 mL) and stirred at room temperature. After 1 h the reaction mixture was diluted with distilled water (50 mL) and CH_2Cl_2 (50 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2×50 mL). Combined organic extracts were washed with distilled water (50 mL) and dried over Na_2SO_4. Column chromatography on silica gel with CH_2Cl_2:MeOH 95:5 (R_f: 0.57) gave **12**; yield: 61 mg (0.12 mmol, 85%); mp >350 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.71 (d, J = 424.5 Hz, 1H, P-H), 2.04–1.84 (m, 10H, H-8,10,15), 1.81 (br s, 4H, H-7,11), 1.77–1.63 (m, 20H, H-3,4,5,6,13,14,18), 1.57–1.45 (m, 8H, H-2,12,17), 1.34–1.29 (m, 4H, H-16); ^{13}C NMR (100 MHz,

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

$CDCl_3$): $\delta = 46.0$ (C-2,12), 44.9 (C-16), 44.2 (C-17), 38.0 (C-5), 37.8 (C-14,18), 37.7 (C-3,13), 37.6 [d, $^1J(^{13}C,^{31}P) = 60.6$ Hz, C-9, from 600 MHz ^{13}C-APT C_q only experiment], 37.5–37.2 (m, C-7,8,10,11), 34.8 (C-4), 34.3 (C-6), 33.4 [d, $^3J(^{13}C,^{31}P) = 10.1$ Hz, C-1], 27.7 (C-15); ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4 external standard): $\delta = 58.97$; IR (KBr): $\nu =$ 2869, 2265, 1457, 1444, 1339, 1306, 1183, 1175, 1000, 911, 849 cm^{-1}; HR-MS: $m/z = 526.3370$, calcd. for $C_{36}H_{47}PO$: 526.3365; anal. calcd. for $C_{36}H_{47}PO$ (526.73): C 82.09, H 8.99; found: C 81.73, H 9.07.

Di-4-diamantyl-*n*-butylphosphonium Iodide (13)

Compound **7** (1 g, 2.19 mmol) was refluxed in toluene (40 mL) for 23 h under argon with $HSiCl_3$ (1.5 mL, 14.8 mmol). Then 1-iodobutane (5 mL) was added and the reaction mixture was stirred for 1 h at 120 °C. Thereby a colorless suspension formed which was filtered after cooling down to room temperature. The addition of $CHCl_3$ and several filtrations as well as removal of the solvent resulted in a colorless foam; yield: 738 mg (1.25 mmol, 57%); mp 313–314 °C; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.81$ (dt, $J = 472.9$ and 3.6 Hz, 1H, P-H), 2.23–2.10 (m, 12H, H-3,5,13), 2.09–2.01 (m, 2H, CH_2), 1.90 (br s, 6H, H-2,6,12), 1.85–1.73 (m, 10H, H-1,7,9,11,CH_2), 1.66 (br s, 12H, H-8,10,14), 1.47 (sext, $J = 7.2$ Hz, 2H, CH_2), 0.92 (t, $J = 7.2$ Hz, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 38.9$ [d, $^2J(^{13}C,^{31}P) = 1.5$ Hz, C-3,5,13], 37.2 (C-8,10,14), 36.4 [d, $^3J(^{13}C,^{31}P) = 10.6$ Hz, C-2,6,12], 35.9 [d, $^1J(^{13}C,^{31}P) = 34.7$ Hz, C-4], 35.8 (C-1,7,11), 28.3 [d, $^2J(^{13}C,^{31}P) = 4.5$ Hz, CH_2], 24.9 (C-9), 24.4 [d, $^2J(^{13}C,^{31}P) = 13.6$ Hz, CH_2], 13.4 (CH_3), 12.3 [d, $^1J(^{13}C,^{31}P) = 39.2$ Hz, CH_2]; ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4 external standard): $\delta = 20.55$; IR (KBr): $\nu = 2899$, 2848, 2262, 1460, 1440, 1316, 1252, 1048, 972, 750 cm^{-1}; HRMS: $m/z =$ 462.3440, calcd. for $C_{32}H_{47}P$ (−HI): 462.3415; anal. calcd. for $C_{32}H_{48}IP$ (590.60): C 65.08, H 8.19; found: C 64.90, H 8.35.

Di-4-diamantyl-*n*-butylphosphine Oxide (14)

Compound **13** (790 mg, 1.34 mmol) was dissolved in dry CH_2Cl_2 (30 mL) and NEt_3 (4 mL) was added. After 1.5 h at room temperature the solvent was removed under vacuum and toluene (20 mL) was added along with 30% H_2O_2 (6 mL). The mixture was stirred for 1 h at room temperature and was quenched with dist. water (60 mL) and toluene (30 mL). Phases were separated and the aqueous phase extracted with toluene (40 mL). Combined organic extracts were washed with distilled water (80 mL) and dried over Na_2SO_4. Column chromatography on silica gel with ether:MeOH 95:5 (R_f: 0.43) resulted in the pure product; yield: 529 mg (1.10 mmol, 83%); mp 259–260 °C; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 2.03$–1.97 (m, 12H, H-3,5,13), 1.84 (br s, 6H, H-2,6,12), 1.80–1.77 (m, 2H, H-9), 1.74 (br s, 6H, H-1,7,11), 1.70 (br s, 12H, H-8,10,14), 1.67–1.58 (m, 4H, 2× CH_2), 1.44–1.36 (m, 2H, CH_2), 0.93 (t, $J = 7.2$ Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 37.9$ [d, $^1J(^{13}C,^{31}P) = 60.4$ Hz, C-4], 37.7 (C-8,10,14), 37.6 [d, $^2J(^{13}C,^{31}P) = 2.0$ Hz, C-3,5,13], 36.9 [d, $^3J(^{13}C,^{31}P) = 10.1$ Hz, C-2,6,12], 36.6 (C-1,7,11), 25.5 (C-9), 25.3 [d, $^3J(^{13}C,^{31}P) = 4.0$ Hz, CH_2], 25.0 [d, $^2J(^{13}C,^{31}P) = 12.1$ Hz, CH_2], 20.0 [d, $^1J(^{13}C,^{31}P) = 57.3$ Hz, CH_2], 13.8 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4 external standard): $\delta = 51.71$; IR (KBr): $\nu = 2906$, 1460, 1440, 1376, 1315, 1148, 1049, 854, 747 cm^{-1}; HR-MS: $m/z =$ 478.3355, calcd. for $C_{32}H_{47}OP$: 478.3365; anal. calcd. for $C_{32}H_{47}OP$ (478.69): C 80.29, H 9.90; found: C 80.34, H 9.96.

Di-4-diamantylphosphinic iodide: mp 337–338 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.10$–2.03 (m, 12H, H-3,5,13), 1.82 (br s, 6H, H-2,6,12), 1.76–1.63 (m, 20H, H-1,7,8,9,10,11,14); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 47.2$ [d, $^1J(^{13}C,^{31}P) = 40.2$ Hz, C-4], 39.0 [d, $^2J(^{13}C,^{31}P) = 2.0$ Hz, C-3,5,13], 37.33 (C-8,10,14), 37.28 [d, $^3J(^{13}C,^{31}P) = 14.1$ Hz, C-2,6,12], 36.4 (C-1,7,11), 25.3 (C-9); ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4 external standard): $\delta = 107.96$; IR (KBr): $\nu =$ 2899, 2867, 2857, 2845, 1458, 1444, 1314, 1248, 1196, 1048, 945, 847 cm^{-1}; HR-MS: $m/z = 548.1709$, calcd. for $C_{28}H_{38}IOP$: 548.1705; anal. calcd. for $C_{28}H_{38}IOP$ (548.48): C 61.31, H 6.98; found: C 61.15, H 7.02.

1-Fluoro-4-(phenylethynyl)benzene

To a stirred mixture of 4-bromofluorobenzene (0.175 g, 1 mmol), $(PPh_3)_2PdCl_2$ (0.035 g, 0.05 mmol) CuI (0.01 g, 0.05 mmol) and a) **13** (0.059 g, 0.1 mmol) or b) PPh_3 (0.026 g, 0.1 mmol) under argon and dry conditions in NEt_3 (10 mL) was added phenylacetylene (0.123 g, 1.2 mmol). The solution was refluxed for 20 h. During this time the color turned from bright yellow to dark brown and a grey precipitate was formed. Aqueous NH_4Cl solution (70 mL) was added, the crude product was extracted with diethyl ether (3×50 mL) and subsequent purified by column chromatography on silica gel (hexane/CH_2Cl_2 9:1, R_f: 0.36); isolated yields for a): 136 mg (0.70 mmol, 70%) and for b): 75 mg (0.38 mmol, 38%). Identical spectral data as reported in the literature.[25]

4-Phenyltoluene

Phenylboronic acid (366 mg, 3 mmol), 4-bromotoluene (342 mg, 2 mmol), $Pd(OAc)_2$ (7 mg, 0.03 mmol), K_2CO_3 (1 g, 7 mmol), and a) **13** (16 mg, 0.03 mmol) or b) without coligand were mixed with toluene (10 mL) under dry conditions and argon. The solution was stirred for 20 h at 65 °C. After cooling to room temperature the mixture was diluted with CH_2Cl_2 (80 mL) washed with saturated $NaHCO_3$ solution (3×50 mL) and dried over $MgSO_4$. The so obtained crude product was purified by filtration over silica gel (pentane:CH_2Cl_2 95:5); isolated yields for a): 331 mg (1.97 mmol, 98%) and for b) after preparative GC: 60 mg (0.36 mmol, 18%). Identical spectral data as reported in the literature.[26]

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

References

[1] Functionalized nanodiamonds, part 26. For part 25, see: A. B. Lysenko, G. A. Senchyk, J. Lincke, D. Lässig, A. A. Fokin, P. R. Schreiner, H. Krautscheid, K. V. Domasevitch, *Dalton Trans.* **2010**, in press.

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[2] H. Schwertfeger, A. A. Fokin, P. R. Schreiner, *Angew. Chem.* **2008**, *120*, 1038–1053; *Angew. Chem. Int. Ed.* **2008**, *47*, 1022–1036.
[3] a) S. Landa, V. Macháček, *Collect. Czech. Chem. Commun.* **1933**, *5*, 1–5; b) S. Hála, S. Landa, V. Hanuš, *Angew. Chem.* **1966**, *78*, 1060–1061; *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 1045–1046; c) J. E. Dahl, S. G. Liu, R. M. K. Carlson, *Science* **2003**, *299*, 96–99.
[4] P. R. Schreiner, A. A. Fokin, H. P. Reisenauer, B. A. Tkachenko, E. Vass, M. M. Olmstead, D. Bläser, R. Boese, J. E. P. Dahl, R. M. K. Carlson, *J. Am. Chem. Soc.* **2009**, *131*, 11292–11293.
[5] a) A. A. Fokin, A. Merz, N. A. Fokina, H. Schwertfeger, S. L. Liu, J. E. P. Dahl, R. M. K. Carlson, P. R. Schreiner, *Synthesis* **2009**, 909–912; b) A. A. Fokin, B. A. Tkachenko, N. A. Fokina, H. Hausmann, M. Serafin, J. E. P. Dahl, R. M. K. Carlson, P. R. Schreiner, *Chem. Eur. J.* **2009**, *15*, 3851–3862; c) H. Schwertfeger, C. Würtele, M. Serafin, H. Hausmann, R. M. K. Carlson, J. E. P. Dahl, P. R. Schreiner, *J. Org. Chem.* **2008**, *73*, 7789–7792; d) H. Schwertfeger, C. Würtele, H. Hausmann, J. E. P. Dahl, R. M. K. Carlson, A. A. Fokin, P. R. Schreiner, *Adv. Synth. Catal.* **2009**, *351*, 1041–1054; e) B. A. Tkachenko, N. A. Fokina, L. V. Chernish, J. E. P. Dahl, S. Liu, R. M. K. Carlson, A. A. Fokin, P. R. Schreiner, *Org. Lett.* **2006**, *8*, 1767–1770.
[6] a) W. L. Yang, J. D. Fabbri, T. M. Willey, J. R. I. Lee, J. E. Dahl, R. M. K. Carlson, P. R. Schreiner, A. A. Fokin, B. A. Tkachenko, N. A. Fokina, W. Meevasana, N. Mannella, K. Tanaka, X. J. Zhou, T. van Buuren, M. A. Kelly, Z. Hussain, N. A. Melosh, Z.-X. Shen, *Science* **2007**, *316*, 1460–1462; b) W. A. Clay, Z. Liu, W. Yang, J. D. Fabbri, J. E. Dahl, R. M. K. Carlson, Y. Sun, P. R. Schreiner, A. A. Fokin, B. A. Tkachenko, N. A. Fokina, P. A. Pianetta, N. Melosh, Z.-X. Shen, *Nano Lett.* **2009**, *9*, 57–61.
[7] H. Richter, H. Schwertfeger, P. R. Schreiner, R. Fröhlich, F. Glorius, *Synlett* **2009**, 193–197.
[8] a) A. Zapf, A. Ehrentraut, M. Beller, *Angew. Chem.* **2000**, *112*, 4315–4317; *Angew. Chem. Int. Ed.* **2000**, *39*, 4153–4155; b) A. Aranyos, D. W. Old, A. Kiyomori, J. P. Wolfe, J. P. Sadighi, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 4369–4378; c) C. A. Fleckenstein, H. Plenio, *Chem. Soc. Rev.* **2010**, *39*, 694–711.
[9] J. R. Goerlich, A. Fischer, P. G. Jones, R. Schmutzler, *Z. Naturforsch.* **1994**, *49b*, 801–811.
[10] J. R. Goerlich, R. Schmutzler, *Phosphorus Sulfur Silicon Relat. Elem.* **1995**, *102*, 211–215.
[11] a) M. Gouygou, G. Etemad-Moghadam, M. Koenig, *Synthesis* **1987**, 508–509; b) H. Stetter, W.-D. Last, *Chem. Ber.* **1969**, *102*, 3364–3366.
[12] G. A. Olah, O. Farooq, Q. Wang, A. H. Wu, *J. Org. Chem.* **1990**, *55*, 1224–1227.
[13] A. A. Fokin, B. A. Tkachenko, P. A. Gunchenko, D. V. Gusev, P. R. Schreiner, *Chem. Eur. J.* **2005**, *11*, 7091–7101.
[14] P. R. Schreiner, N. A. Fokina, B. A. Tkachenko, H. Hausmann, M. Serafin, J. E. P. Dahl, S. Liu, R. M. K. Carlson, A. A. Fokin, *J. Org. Chem.* **2006**, *71*, 6709–6720.
[15] CCDC 753268 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.
[16] J. R. Goerlich, R. Schmutzler, *Phosphorus Sulfur Silicon Relat. Elem.* **1993**, *81*, 141–148.
[17] H. Fritzsche, U. Hasserodt, F. Korte, *Chem. Ber.* **1965**, *98*, 1681–1687.
[18] J. R. Goerlich, R. Schmutzler, *Phosphorus Sulfur Silicon Relat. Elem.* **1994**, *88*, 241–244.
[19] A. Köllhofer, H. Plenio, *Chem. Eur. J.* **2003**, *9*, 1416–1425.
[20] N. Weferling, *Z. Anorg. Allg. Chem.* **1987**, *548*, 55–62.
[21] J. Omelańczuk, *Heteroat. Chem.* **1992**, *3*, 403–405.
[22] A. Tewari, M. Hein, A. Zapf, M. Beller, *Synthesis* **2004**, 935–941.
[23] K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, *16*, 4467–4470.
[24] N. Miyaura, T. Yanagi, A. Suzuki, *Synth. Commun.* **1981**, *11*, 513–519.
[25] P. Li, L. Wang, M. Wang, F. You, *Eur. J. Org. Chem.* **2008**, 5946–5951.
[26] M. Cui, J. Li, A. Yu, J. Zhang, Y. Wu, *J. Mol. Catal. A: Chem.* **2008**, *290*, 67–71.

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim