JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

Selective Preparation of Diamondoid Phosphonates

Andrey A. Fokin,*[,#,‡] Raisa I. Yurchenko,[#] Boryslav A. Tkachenko,[‡] Natalie A. Fokina,[‡] Maria A. Gunawan,[‡,§] Didier Poinsot,[§] Jeremy E. P. Dahl,[∥] Robert M. K. Carlson,[∥] Michael Serafin,[⊥] Hélène Cattey,[§] Jean-Cyrille Hierso,*[,§] and Peter R. Schreiner*[,‡]

[#]Department of Organic Chemistry, Kiev Polytechnic Institute, pr. Pobedy 37, 03056 Kiev, Ukraine

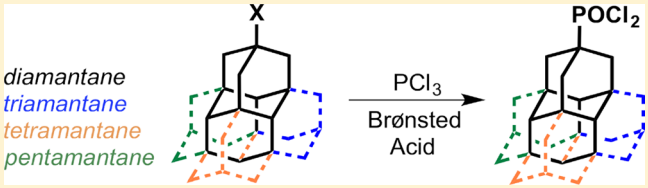
[‡]Institute of Organic Chemistry and [⊥]Institute of Inorganic Chemistry, Justus-Liebig University, Heinrich-Buff-Ring 58, 35392 Giessen, Germany

[§]Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), UMR CNRS 6302, Université de Bourgogne, 9 avenue Alain Savary, 21078 cedex, Dijon, France

[∥]Stanford Institute for Materials & Energy Science, Stanford University, 476 Lomita Mall, Stanford, California 94305, United States

Supporting Information

ABSTRACT: We present an effective sequence for the preparation of phosphonic acid derivatives of the diamondoids diamantane, triamantane, [121]tetramantane, and [1(2,3)4]-pentamantane. The reactions of the corresponding diamondoid hydroxy derivatives with PCl_3 in sulfuric or trifluoroacetic acid give mono- as well as didichlorophosphorylated diamondoids in high preparative yields.



The family of naturally occurring diamondoids, which are nanometer-sized hydrocarbons resembling subunits of the cubic diamond lattice,[1−3] have been shown to be highly useful in a variety of applications[4−7] by mimicking many properties of natural H-terminated diamond. For example, diamondoid thiol self-assembled monolayers (SAMs) on metal surfaces reproduce the negative electron affinity (NEA) of bulk diamond.[8] While such SAMs with extraordinary monochromatic photoemission properties are useful for the construction of novel cathodes, their long-term stability is low as a result of the weakness of the metal−sulfur bonds. Even though cesium bromide can be added as a protective layer to increase overall device stability,[9] the weak linkage problem remains unsolved. Very recently[10] we demonstrated that covalent attachment of phosphonic acid dichloride of diamantane (**1**, Figure 1) to tungsten (oxide) surfaces displays a characteristic monochromatic NEA peak and provides a material that exhibits remarkable thermal stability (>300 °C). Considering that the photoemission efficiency increases with an increase of the diamondoid cage size,[8] it is important to note that higher diamondoids[11] are effective dispersion energy donors (DEDs), a property that also increases the stability of SAMs.[12] This is crucial for the construction of nanometer-scale devices,[13] whose properties are strongly affected by intermolecular van der Waals interactions.[14]

Preparative methods for the functionalizations of triamantane (**2**),[15] [121]tetramantane (**3**),[15] and [1(2,3)4]pentamantane (**4**)[16] with radical and oxidative reagents allow their selective C−H-bond functionalizations. However, direct phosphorylation of **1** and **2**,[17] in contrast to parent adamantane,[18,19] gives mixtures and is low-yielding; the monophosphorylation of **1** in the $AlCl_3/PCl_3/CH_2Cl_2$ system[20] was difficult to reproduce[17] as didiamantane-phosphinic acid chloride derivatives form as the main products. Ditriamantane-phosphinic acid chloride was the only product of the reaction of **2** with $AlCl_3/PCl_3/CH_2Cl_2$.[17] Hence, this makes the selective C−H-bond phosphorylation of diamondoids problematic in the presence of strong Lewis acids. The phosphorylation of haloadamantanes with $AlBr_3/PCl_3$ is the well-known Clay−Kinnear−Perren reaction[21] that, however, requires large amounts of reagents and strongly depends on the quality of the employed $AlBr_3$.[22]

Diamondoidyl cations can easily be generated from the corresponding halogen or hydroxy derivatives in the presence of strong Brønsted acids. Previously one of us discovered the dichlorophosphorylation of 1-bromoadamantane with PCl_3 in concentrated sulfuric acid with >95% preparative yield,[22−24] revealing effective trapping of the 1-adamantyl cation with nucleophilic PCl_3 in *protic* solvents. Trifluoroacetic acid (TFA) can also be used and provides adamantyl phosphonic dichloride in 69% preparative yield from 1-hydroxy adamantane with PCl_3.[25] We have recently found that both methods are applicable to the preparation of diamantane 1-phosphonic dichloride (**5**) from the 1-bromo derivative (**6**).[10] As we found substantial discrepancies between our and previously published spectral data,[20] the structure of **5** was additionally confirmed by an X-ray crystal structure analysis (Figure 2).

The fact that 4-phosphonic dichloride (**8**) did not form in this reaction is somewhat surprising as the 1- and 4-diamantyl cations equilibrate in H_2SO_4.[26] Presumably PCl_3 rapidly traps the 1-diamantyl cation, thus preventing isomerization (Figure

Received: April 8, 2014
Published: May 9, 2014

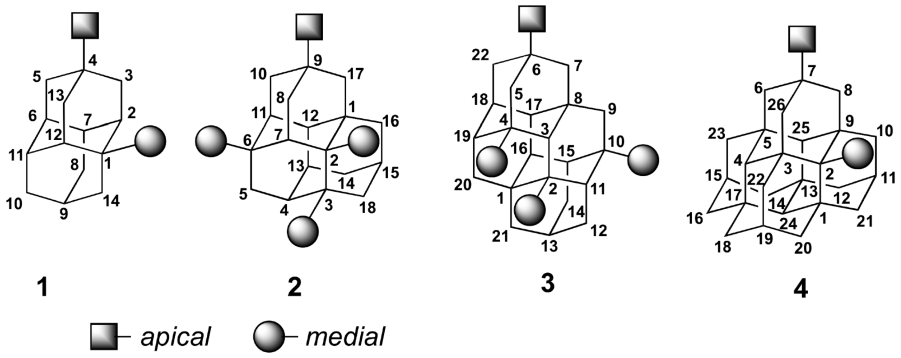


Figure 1. Diamantane (**1**), triamantane (**2**), [121]tetramantane (**3**), and [1(2,3)4]pentamantane (**4**), with numbering of carbon atoms and their apically as well as medially substituted derivatives.

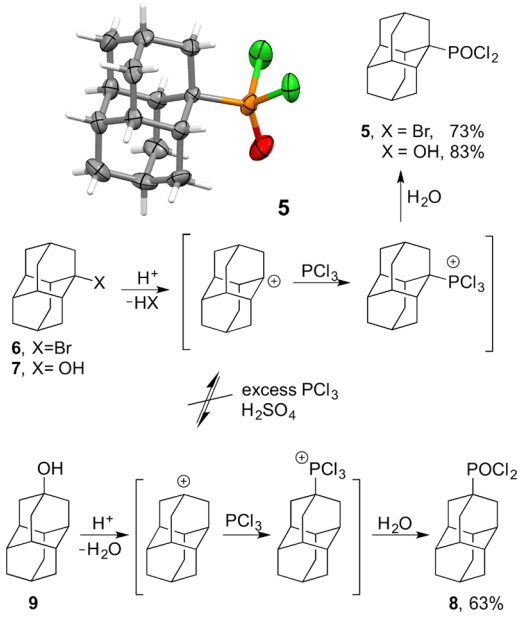


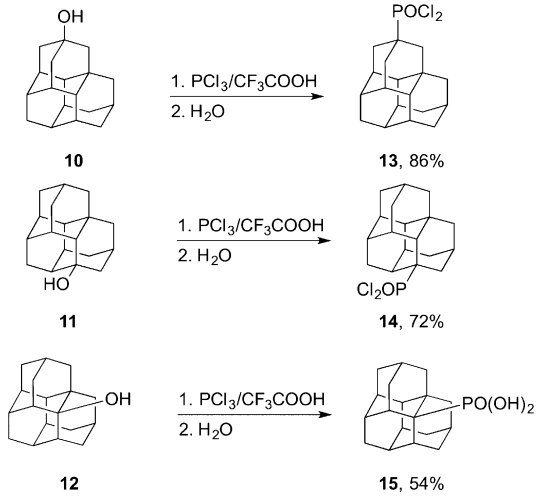
Figure 2. Phosphorylations of diamantane derivatives in sulfuric acid (yields are preparative) and the X-ray crystal structure of dichlorophosphonate **5**.

2). This was confirmed by a separate experiment in the PCl_3/H_2SO_4 system where 4-hydroxydiamantane (**9**) gave **8**[17] exclusively with a 5 equiv excess of PCl_3 (Figure 2). In contrast, with only 1 equiv of PCl_3 already ca. 10% of isomerized dichloride **5** forms, together with **8** as the main product.

We also found that the preparative yield slightly increases for 1-hydroxydiamantane (**7**) when TFA is used for the phosphorylation.[10] The 4-hydroxy derivative **9** gave **8** in 75% preparative yield under these conditions. Thus, for the phosphorylations of larger diamondoids we employed the PCl_3/TFA system, which additionally provides higher solubility of the starting material. We first tested various triamantane hydroxy derivatives **10**–**12** that are available through the nitroxylation/hydrolysis of **2**.[15]

The phosphorylation of alcohols **10** and **11** in the PCl_3/TFA system provides the phosphoryl derivatives **13** and **14** in high preparative yields (Scheme 1). In contrast, the sterically congested alcohol **12** gave a complex mixture under these conditions, from which we were able to isolate phosphonic acid **15** in only moderate yield due to its low solubility in organic solvents. The behavior of **12** is in line with the low selectivities

Scheme 1. Phosphorylation of Triamantane Derivatives in Trifluoroacetic Acid (Yields Are Preparative)



of the functional group transformations of 2-triamantyl derivatives in electrophilic media.[27]

As higher diamondoid derivatives larger than **2** demonstrate enhanced potential in the construction of electron-emitting devices,[8] we extended our phosphorylation protocol to the apical derivatives of [121]tetramantane (**16**) and [1(2,3)4]-pentamantane (**18**). The apical dichloro phosphoryl derivatives **17** and **19** were isolated in high preparative yields, and their structures were confirmed by X-ray crystal structure analyses (Figure 3).

In contrast to other alkanes, whose already poor electron conductivity exponentially decreases with chain length,[28] diamondoids are superior semiconductors as their band gap narrows with increasing molecule size.[29] As we have shown that the $POCl_2$ group provides strong attachment to metal-oxide surfaces,[10] double-phosphorylated diamondoids are potentially useful as saturated spacers in molecule/metal oxide molecular electronic junctions.[30−33] Previous attempts to attach two phosphoryl groups to 1,3-adamantane derivatives in sulfuric acid gave mixtures of monophosphorylated products only. This is due to the presence of the highly electron-withdrawing trichlorophosphonium group in the positively charged intermediates.[34] More distant substituents in the diamantane cage allow for double phosphorylation. The readily available dihydroxy diamantanes **20**[35] and **21**[36] that are typically poorly soluble in polar media are highly soluble in the TFA/PCl_3 system and give the desired dichloro phosphonates **22** and **23**

dx.doi.org/10.1021/jo500793m | J. Org. Chem. 2014, 79, 5369−5373

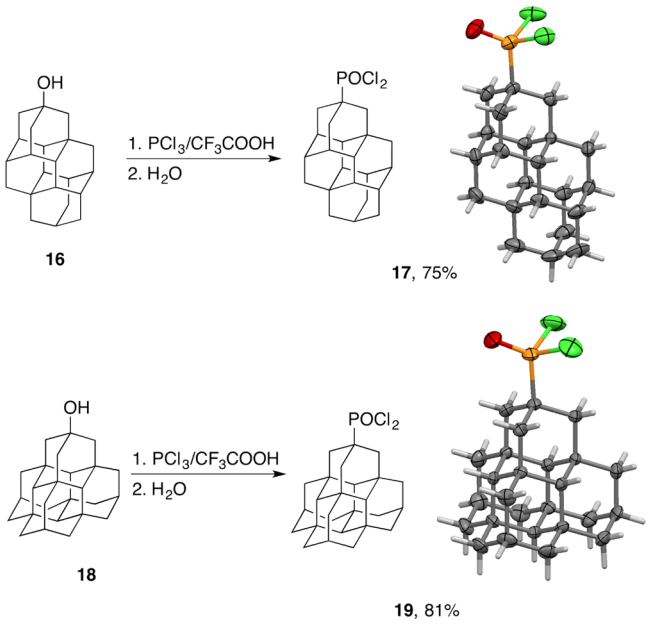
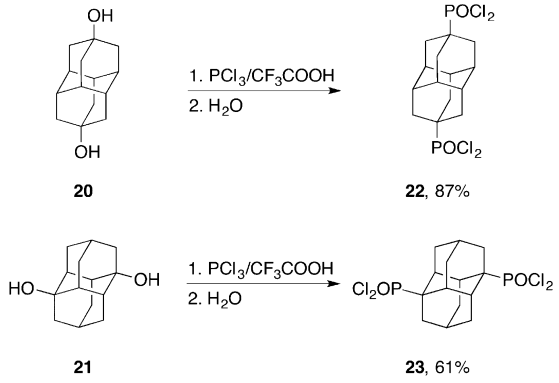


Figure 3. Phosphorylations of the apical [121]tetramantane (**16**) and [1(2,3)4]pentamantane (**18**) derivatives (yields are preparative) and the X-ray crystal structures of dichlorophosphonates **17** and **19**.

in high preparative yields (Scheme 2). These compounds are characterized by exceptionally high thermal stabilities and high

Scheme 2. Double Phosphorylations of Diamantane Derivatives in Trifluoroacetic Acid (Yields Are Preparative)



melting points. For instance, dichloro phosphonate **23** melts without decomposition at 360 °C and may be useful for high-temperature deposition on metal oxide surfaces.

In summary, we have developed a Brønsted acid catalyzed protocol for the phosphorylation of diamondoids with PCl_3. Highly nucleophilic PCl_3 effectively traps the intermediate cations, thereby avoiding the rearrangements that usually complicate transformations of diamondoids. Thus, this method is superior to previously reported Lewis acid catalyzed phosphorylations. The resulting dichlorophosphoryl diamondoid derivatives have high potential not only in nanoelectronics for surface oxide modifications[10] but also for the preparation of highly sterically demanding building blocks for catalysis.

EXPERIMENTAL SECTION

General Information. NMR spectra were recorded on 400 and 600 MHz (^{1}H) spectrometers with TMS as internal standard. High-resolution mass spectra (HRMS) were recorded using electron impact ionization on a focusing sector-type mass spectrometer. Products were purified by chromatography on 100−160 mesh silica gel. All melting points were determined without correction. Commercially available reagents and solvents were used without further purification.

General Procedure for the Phosphorylation of Diamondoid Derivatives in Sulfuric Acid. The diamondoid derivative (bromo or hydroxy, 0.0024 mol) was added to a cooled mixture (ice bath) of 100 mL of 96% sulfuric acid and 30 mL of 20% oleum (0.0024 mol), followed by addition of 1.4 mL (0.017 mol) of phosphorus trichloride at 7−10 °C. The reaction mixture was stirred for 1.5 h at room temperature and 0.5 h at 45−55 °C, cooled, and then poured onto ice. The reaction mixture was filtered, and the precipitate was washed with water and dried over sodium sulfate. The crude product was purified by column chromatography on silica gel (pentane/ether = 5:1).

General Procedure for the Phosphorylation of Diamondoid Derivatives in Trifluoroacetic Acid. To a mixture of 3 g (0.015 mol) of the corresponding hydroxy diamondoid and 50 mL of trifluoroacetic acid was added 7 mL (0.08 mol) of phosphorus trichloride, and the reaction mixture was refluxed for 3.5 h and then poured onto ice. The reaction mixture was extracted three times with CH_2Cl_2, washed with brine, and dried over sodium sulfate. The resulting crude product was purified as above.

1-Dichlorophosphoryldiamantane (5). Obtained from 150 mg (0.73 mmol) of 1-hydroxydiamantane (**7**) as a colorless solid through the phosphorylation in trifluoroacetic acid, yield 186 mg (83%). Mp = 98−100 °C. ^{1}H NMR (δ, 400 MHz, $CDCl_3$): 1.58 (d, J = 12 Hz, 2H), 1.70−1.80 (m, 7H), 1.92 (bs, 1H), 1.90−2.10 (m, 5H), 2.30 (d, J = 8 Hz, 2H), 2.74 (d, J = 12 Hz, 2H). ^{13}C NMR (δ, 100 MHz, $CDCl_3$): 24.7 (CH), 26.1 (CH, d, J_{CP} = 15 Hz), 34.0 (CH_2), 36.7 (CH, d, J_{CP} = 2 Hz), 36.8 (CH_2, d, J_{CP} = 3 Hz), 37.0 (CH, d, J_{CP} = 2 Hz), 38.4 (CH_2), 38.8 (CH_2, d, J_{CP} < 1 Hz), 38.9 (CH, d, J_{CP} = 16 Hz), 56.3 (C, d, J_{CP} = 73 Hz). ^{31}P NMR (δ, 162 MHz, $CDCl_3$): 66.1. EI-HRMS (m/z): found 304.0564, calcd for $C_{14}H_{19}Cl_2OP$ 304.0551. Anal. Calcd for $C_{14}H_{19}Cl_2OP$ C 55.10, H 6.28. Found C 55.34, H 6.26.

9-Dichlorophosphoryltriamantane (13). Obtained from 150 mg (0.58 mmol) of 9-hydroxytriamantane (**10**) as a colorless solid through the phosphorylation in trifluoroacetic acid, yield 179 mg (86%). Mp = 142−143 °C. ^{1}H NMR (δ, 400 MHz, $CDCl_3$): 1.36 (d, J = 2.9 Hz, 2H), 1.51 (bs, 2 H), 1.60 (d, J = 8 Hz, 2 H), 1.64−1.80 (m, 10 H), 1.86−1.96 (m, 3 H), 1.96−2.11 (m, 4 H). ^{13}C NMR (δ, 100 MHz, $CDCl_3$): 27.5 (CH), 33.5 (C), 33.7 (d, J_{CP} = 2.2 Hz, CH), 34.4 (CH), 35.6 (d, J_{CP} = 3.8 Hz, CH_2), 37.2 (d, J_{CP} = 16 Hz, CH), 37.4 (d, J_{CP} = 2.2 Hz, CH), 37.5 (d, J_{CP} = 2.7 Hz, CH_2), 37.6 (CH_2), 42.1 (d, J_{CP} = 4.4 Hz, CH_2), 44.6 (CH_2), 45.3 (d, J_{CP} = 2.2 Hz, CH), 48.5 (d, J_{CP} = 88 Hz, C). ^{31}P NMR (δ, 162 MHz, $CDCl_3$): 65.1. MS (m/z): 356 (<1), 239 (100), 183 (2), 157 (4), 143 (8), 129 (5). EI-HRMS (m/z): found 356.0846, calcd for $C_{18}H_{23}Cl_2OP$ 356.0864.

3-Dichlorophosphoryltriamantane (14). Obtained from 150 mg (0.58 mmol) of 3-hydroxytriamantane (**11**) through the phosphorylation in trifluoroacetic acid as a colorless solid, yield 150 mg (72%). Mp = 135−136 °C. ^{1}H NMR (δ, 600 MHz, $CDCl_3$): 1.26−1.35 (m, 2 H), 1.40 (s, 2 H), 1.47−1.55 (m, 2 H), 1.65−1.81 (m, 8 H), 1.82−1.91 (m, 2 H), 1.96−2.09 (m, 4 H), 2.18−2.25 (m, 1 H), 2.67−2.76 (m, 2 H). ^{13}C NMR (δ, 151 MHz, $CDCl_3$): 26.9 (CH), 27.4 (d, J_{CP} = 16 Hz, CH), 33.2 (CH), 33.9 (CH), 34.4 (d, J_{CP} = 15 Hz, C), 34.7 (CH_2), 34.74 (d, J_{CP} = 2.2 Hz, CH), 36.6 (d, J_{CP} = 3 Hz, CH_2), 37.3 (CH_2), 37.4 (CH), 37.5 (CH_2), 38.99 (d, J_{CP} = 0.9 Hz, CH_2), 39.0 (d, J_{CP} = 17 Hz, CH), 44.2 (d, J_{CP} = 3 Hz, CH_2), 45.3 (d, J_{CP} = 3 Hz, CH_2), 45.9 (d, J_{CP} = 2.3 Hz, CH), 46.2 (d, J_{CP} = 3 Hz, CH), 57.4 (d, J_{CP} = 72 Hz, C). ^{31}P NMR (δ, 162 MHz, $CDCl_3$): 65.7. MS (m/z): 358 (<1), 356 (<1), 239 (100), 167 (16), 143 (9), 129 (7). EI-HRMS (m/z): found 356.0851, calcd for $C_{18}H_{23}Cl_2OP$ 356.0864.

2-Triamantane Phosphonic Acid (15). Obtained from 150 mg (0.58 mmol) of 2-hydroxytriamantane (**12**) through the phosphorylation in trifluoroacetic acid. The reaction mixture was filtered, and the precipitate was washed with water, ether, chloroform and dried in vacuum, yield 101 mg (54%) of white solid (mp = 342−343 °C). ^{1}H NMR (δ, 400 MHz, DMSO-d_6): 0.93 (d, J = 12 Hz, 2 H), 1.24 (d, J = 13 Hz, 2 H), 1.37 (bs, 1 H), 1.53−1.71 (m, 10 H), 1.77 (bs, 2 H), 1.90 (bs, 2 H), 2.35 (d, J = 12 Hz, 2 H), 3.08 (d, J = 12 Hz, 2 H). ^{13}C NMR

dx.doi.org/10.1021/jo500793m | J. Org. Chem. 2014, 79, 5369−5373

(δ, 100 MHz, DMSO-d_6): 27.1 (CH), 34.1 (CH_2), 35.5 (C), 36.6 (d, J_{CP} = 11 Hz, CH), 37.5 (CH), 37.9 (CH_2), 38.4 (CH), 39.1 (CH_2), 40.4 (CH_2), 47.9 (d, J_{CP} = 129 Hz, C), 49.9 (d, J_{CP} = 12 Hz, CH). ^{31}P NMR (δ, 162 MHz, DMSO-d_6): 30.2. MS (m/z): 320 (2), 239 (100), 197 (2), 183 (1), 143(9), 129 (12). EI-HRMS (m/z): found 320.1524, calcd for $C_{18}H_{25}O_3P$ 320.1541.

6-Dichlorophosphoryl[121]tetramantane (17). Obtained from 80 mg of 9-hydroxytriamantane (0.26 mmol) (**16**) as a colorless solid through the phosphorylation in trifluoroacetic acid, yield 80 mg (75%). Mp = 175−176 °C. ^{1}H NMR (δ, 600 MHz, $CDCl_3$): 1.30 (d, J = 3 Hz, 2 H), 1.32 (d, J = 2.9 Hz, 2 H), 1.34 (d, J = 3 Hz, 2 H), 1.44 (bs, 2 H), 1.47 (bs, 2 H), 1.64 (d, J = 8 Hz, 2 H), 1.67−1.72 (m, 6 H), 1.72−1.77 (m, 2 H), 1.86−1.90 (m, 1 H), 1.90−1.95 (m, 2 H), 2.00−2.05 (m, 4 H). ^{13}C NMR (δ, 151 MHz, $CDCl_3$): 27.6 (CH), 30.9 (C), 31.6 (d, J_{CP} = 16 Hz, C), 35.43 (d, J_{CP} = 3.7 Hz, CH_2), 35.45 (CH), 36.6 (d, J_{CP} = 1.3 Hz, CH), 37.26 (d, J_{CP} = 16 Hz, CH), 37.6 (CH_2), 37.8 (CH), 41.3 (d, J_{CP} = 4.4 Hz, CH_2), 43.9 (CH_2), 44.7 (d, J_{CP} = 2.5 Hz, CH_2), 45.0 (CH_2), 45.8 (d, J_{CP} = 2.3 Hz, CH), 46.5 (d, J_{CP} = 1.9 Hz, CH), 48.6 (d, J_{CP} = 88 Hz, C). ^{31}P NMR (δ, 243 MHz, $CDCl_3$): 65.1. MS (m/z, %): 408 (1), 404 (1), 325 (1), 305 (2), 292 (100), 155 (11), 141 (8). EI-HRMS (m/z): found 408.1174, calcd for $C_{22}H_{27}Cl_2OP$ 408.1177.

7-Dichlorophosphoryl[1(2,3)4]pentamantane (19). Obtained from 50 mg of 7-hydroxy[1(2,3)4]pentamantane (0.14 mmol) (**18**) as a colorless solid through the phosphorylation in trifluoroacetic acid, yield 52 mg (81%). Mp = 330−331 °C. ^{1}H NMR (δ, 600 MHz, $CDCl_3$): 1.00 (s, 4 H), 1.28−1.38 (m, 12 H), 1.38−1.43 (m, 6 H), 1.63 (d, J = 8 Hz, 6 H), 1.87−1.98 (m, 3 H). ^{13}C NMR (δ, 151 MHz, $CDCl_3$): 28.2 (CH), 32.8 (C), 33.4 (d, J_{CP} = 15 Hz, C), 41.7 (d, J_{CP} = 5 Hz, CH_2), 44.2 (CH_2), 44.4 (CH_2), 49.1 (d, J_{CP} = 85 Hz, C), 52.2 (d, J_{CP} = 2 Hz, CH), 52.9 (CH).^{31}P NMR (δ, 243 MHz, $CDCl_3$): 64.1. MS (m/z, %): 461 (<1%), 343 (100), 230 ((2), 181 (2), 171 (5), 141 (1) ESI-HRMS (m/z + Na): found 483.1378, calcd for $C_{26}H_{31}Cl_2OPNa$ 483.1387.

4,9-Bis(dichlorophosphoryl)diamantane (22). Obtained from 120 mg (0.54 mmol) of 4,9-dihydroxydiamantane (**20**) as a colorless solid through the phosphorylation in trifluoroacetic acid, yield 200 mg (87%). Mp = 340−341 °C. ^{1}H NMR (δ, 400 MHz, $CDCl_3$): 2.05 (bs, 6 H), 2.08−2.16 (m, 12 H). ^{13}C NMR (δ, 100 MHz, $CDCl_3$): 35.03 (CH), 35.07 (dd; J_{CP} = 17, 3 Hz; CH_2), 46.0 (d, J_{CP} = 93 Hz, C). ^{31}P NMR (δ, 162 MHz, $CDCl_3$): 64.0. MS (m/z, %): 305 (70), 303 (100), 185 (38), 157 (2), 143 (4), 129 (12). Anal. Calcd for $C_{14}H_{18}Cl_4O_2P_2$ C 39.84, H 4.30. Found C 39.49, H 4.32.

1,6-Bis(dichlorophosphoryl)diamantane (23). Obtained from 110 mg (0.50 mmol) of 1,6-dihydroxydiamantane (**21**) as a colorless solid through the phosphorylation in trifluoroacetic acid, yield 128 mg (61%). Mp = 360−361 °C. ^{1}H NMR (δ, 400 MHz, $CDCl_3$): 1.61 (d, J = 13.5 Hz, 4 H), 2.09 (bs, 4 H), 2.14−2.23 (m, 2 H), 2.47 (bs, 4 H), 2.85 (d, J = 13.3 Hz, 4 H). ^{13}C NMR (δ, 100 MHz, $CDCl_3$): 24.8 (t, J_{CP} = 7 Hz, CH), 32.8 (CH_2), 38.5 (t, J_{CP} = 8 Hz, CH), 39.3 (CH_2), 55.4 (d, J_{CP} = 76 Hz, C). ^{31}P NMR (δ, 162 MHz, $CDCl_3$): 63.5. MS (m/z, %): 305 (50), 303 (62), 185 (100), 143 (10), 129 (30). Anal. Calcd for $C_{14}H_{18}Cl_4O_2P_2$ C 39.84, H 4.30. Found C 40.05, H 4.27.

■ ASSOCIATED CONTENT

Supporting Information

Copies of NMR spectra and selected X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: aaf@xtf.kpi.ua.
*E-mail: Jean-Cyrille.Hierso@u-bourgogne.fr.
*E-mail: prs@uni-giessen.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Ukrainian Basic Research Foundation, Ministry of Science and Education of Ukraine and in part by the Department of Energy, Office of Basic Energy Sciences, Division of Materials, Science and Engineering under Contract DE-AC-76SF00515.

■ REFERENCES

(1) Dahl, J. E.; Moldowan, J. M.; Peters, K. E.; Claypool, G. E.; Rooney, M. A.; Michael, G. E.; Mello, M. R.; Kohnen, M. L. *Nature* **1999**, *399*, 54−57.

(2) Dahl, J. E. P.; Moldowan, J. M.; Peakman, T. M.; Clardy, J. C.; Lobkovsky, E.; Olmstead, M. M.; May, P. W.; Davis, T. J.; Steeds, J. W.; Peters, K. E.; Pepper, A.; Ekuan, A.; Carlson, R. M. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2040−2044.

(3) Dahl, J. E.; Liu, S. G.; Carlson, R. M. K. *Science* **2003**, *299*, 96−99.

(4) Ishiwata, H.; Acremann, Y.; Scholl, A.; Rotenberg, E.; Hellwig, O.; Dobisz, E.; Doran, A.; Tkachenko, B. A.; Fokin, A. A.; Schreiner, P. R.; Dahl, J. E. P.; Carlson, R. M. K.; Melosh, N.; Shen, Z. X.; Ohldag, H. *Appl. Phys. Lett.* **2012**, *101*, 163101.

(5) Schwertfeger, H.; Fokin, A. A.; Schreiner, P. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 1022−1036.

(6) Lysenko, A. B.; Senchyk, G. A.; Lincke, J.; Lassig, D.; Fokin, A. A.; Butova, E. D.; Schreiner, P. R.; Krautscheid, H.; Domasevitch, K. V. *J. Chem. Soc., Dalton Trans.* **2010**, *39*, 4223−4231.

(7) Sinkel, C.; Agarwal, S.; Fokina, N. A.; Schreiner, P. R. *J. Appl. Polym. Sci.* **2009**, *114*, 2109−2115.

(8) Yang, W. L.; Fabbri, J. D.; Willey, T. M.; Lee, J. R. I.; Dahl, J. E.; Carlson, R. M. K.; Schreiner, P. R.; Fokin, A. A.; Tkachenko, B. A.; Fokina, N. A.; Meevasana, W.; Mannella, N.; Tanaka, K.; Zhou, X. J.; van Buuren, T.; Kelly, M. A.; Hussain, Z.; Melosh, N. A.; Shen, Z. X. *Science* **2007**, *316*, 1460−1462.

(9) Clay, W. A.; Maldonado, J. R.; Pianetta, P.; Dahl, J. E. P.; Carlson, R. M. K.; Schreiner, P. R.; Fokin, A. A.; Tkachenko, B. A.; Melosh, N. A.; Shen, Z. X. *Appl. Phys. Lett.* **2012**, *101*, 241605.

(10) Li, F. H.; Fabbri, J. D.; Yurchenko, R. I.; Mileshkin, A. N.; Hohman, J. N.; Yan, H.; Yuan, H.; Tran, I. C.; Willey, T. M.; Bagge-Hansen, M.; Dahl, J. E. P.; Carlson, R. M. K.; Fokin, A. A.; Schreiner, P. R.; Shen, Z.-X.; Melosh, N. A. *Langmuir* **2013**, *29*, 9790−9797.

(11) Schreiner, P. R.; Chernish, L. V.; Gunchenko, P. A.; Tikhonchuk, E. Y.; Hausmann, H.; Serafin, M.; Schlecht, S.; Dahl, J. E. P.; Carlson, R. M. K.; Fokin, A. A. *Nature* **2011**, *477*, 308−311.

(12) Grimme, S.; Huenerbein, R.; Ehrlich, S. *ChemPhysChem* **2011**, *12*, 1258−1261.

(13) Kergueris, C.; Bourgoin, J. P.; Palacin, S.; Esteve, D.; Urbina, C.; Magoga, M.; Joachim, C. *Phys. Rev. B* **1999**, *59*, 12505−12513.

(14) Nerngchamnong, N.; Yuan, L.; Qi, D. C.; Li, J.; Thompson, D.; Nijhuis, C. A. *Nat. Nanotechnol.* **2013**, *8*, 113−118.

(15) Schreiner, P. R.; Fokina, N. A.; Tkachenko, B. A.; Hausmann, H.; Serafin, M.; Dahl, J. E. P.; Liu, S. G.; Carlson, R. M. K.; Fokin, A. A. *J. Org. Chem.* **2006**, *71*, 6709−6720.

(16) Fokin, A. A.; Schreiner, P. R.; Fokina, N. A.; Tkachenko, B. A.; Hausmann, H.; Serafin, M.; Dahl, J. E. P.; Liu, S. G.; Carlson, R. M. K. *J. Org. Chem.* **2006**, *71*, 8532−8540.

(17) Schwertfeger, H.; Machuy, M. M.; Wurtele, C.; Dahl, J. E. P.; Carlson, R. M. K.; Schreiner, P. R. *Adv. Synth. Catal.* **2010**, *352*, 609−615.

(18) Goerlich, J. R.; Fischer, A.; Jones, P. G.; Schmutzler, R. *Z. Naturforsch. B* **1994**, *49*, 801−811.

(19) No, B. I.; Zotov, Y. L.; Karev, V. N. *Zh. Obshch. Khim.* **1982**, *52*, 933−934.

(20) Olah, G. A.; Farooq, O.; Wang, Q.; Wu, A. H. *J. Org. Chem.* **1990**, *55*, 1224−1227.

(21) Stetter, H.; Last, W. D. *Chem. Ber. Recl.* **1969**, *102*, 3364−3366.

(22) Yurchenko, R. I.; Peresypkina, L. P. *Zh. Obshch. Khim.* **1991**, *61*, 1019−1019.

(23) Yurchenko, R. I.; Peresypkina, L. P. *Zh. Obshch. Khim.* **1994**, *64*, 1564−1564.

(24) Yurchenko, R. I.; Peresypkina, L. P.; Miroshnichenko, V. V.; Yurchenko, A. G. *Zh. Obshch. Khim.* **1993**, *63*, 1534−1539.
(25) Erokhina, E. V.; Shokova, E. A.; Luzikov, Y. N.; Kovalev, V. V. *Synthesis (Stuttgart)* **1995**, 851−854.
(26) Gund, T. M.; Nomura, M.; Schleyer, P. v. R. *J. Org. Chem.* **1974**, *39*, 2987−2994.
(27) Fokina, N. A.; Tkachenko, B. A.; Dahl, J. E. P.; Carlson, R. M. K.; Fokin, A. A.; Schreiner, P. R. *Synthesis (Stuttgart)* **2012**, *44*, 259−264.
(28) Wold, D. J.; Frisbie, C. D. *J. Am. Chem. Soc.* **2001**, *123*, 5549−5556.
(29) Fokin, A. A.; Schreiner, P. R. *Mol. Phys.* **2009**, *107*, 823−830.
(30) Kalakodimi, R. P.; Nowak, A. M.; McCreery, R. L. *Chem. Mater.* **2005**, *17*, 4939−4948.
(31) Kolipaka, S.; Aithal, R. K.; Kuila, D. *Appl. Phys. Lett.* **2006**, *88*, 233104.
(32) Lenfant, S.; Krzeminski, C.; Delerue, C.; Allan, G.; Vuillaume, D. *Nano Lett.* **2003**, *3*, 741−746.
(33) Selzer, Y.; Salomon, A.; Cahen, D. *J. Phys. Chem. B* **2002**, *106*, 10432−10439.
(34) Yurchenko, R. I.; Voitsekhovskaya, O. M.; Verpovskaya, I. N.; Kudryavtsev, A. A. *Zh. Obshch. Khim.* **1992**, *62*, 589−592.
(35) Fokina, N. A.; Tkachenko, B. A.; Merz, A.; Serafin, M.; Dahl, J. E. P.; Carlson, R. M. K.; Fokin, A. A.; Schreiner, P. R. *Eur. J. Org. Chem.* **2007**, 4738−4745.
(36) Burns, W.; McKervey, M. A.; Mitchell, T. R. B.; Rooney, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 906−911.