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Defying Stereotypes with Nanodiamonds: Stable Primary Diamondoid Phosphines

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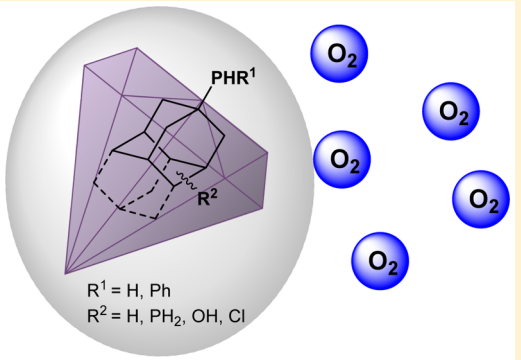
Supporting Information

ABSTRACT: Direct unequal C−H bond difunctionalization of phosphorylated diamantane was achieved in high yield from the corresponding phosphonates. Reduction of the functionalized phosphonates provides access to novel primary and secondary alkyl/aryl diamantane phosphines. The prepared primary diamantyl phosphines are quite air stable compared to their adamantyl and especially alkyl or aryl analogues. This finding is corroborated by comparing the singly occupied molecular orbital energy levels of the corresponding phosphine radical cations obtained by density functional theory computations.



INTRODUCTION

Naturally occurring diamondoids[1] are nanometer-sized hydrocarbons (i.e., nanodiamonds) with structures resembling the diamond crystal lattice.[2] Higher diamondoids bridge the gap between simple organic molecules and diamond, possessing some properties of bulk diamond. Further progress in material applications of diamondoids requires synthesis of functionalized derivatives by introducing strategically placed substituents into their skeleton.[3] For instance, self-assembled monolayers (SAMs) of [121]tetramantane-6-thiol deposited on Ag and Au surfaces display unusually high negative electron affinities (NEAs).[4] However, the metal−sulfur bond breaks at elevated temperatures,[5] and the thiol moiety is therefore not ideal as a surface attachment group. One of the ways to solve this problem is to create additional attachment points on the diamondoid (e.g., adamantane tripods bearing several anchoring thiol groups).[6−8] Alternatively, the thiol group may be replaced with a phosphonate moiety providing thermally stable multivalent surface bonding.[9]

Phosphonic acid dichlorides are also ideal starting materials for the preparation of phosphines that are viable building blocks for new materials[3,10] and as ligands in catalysis.[11,12] Phosphines bearing bulky alkyl moieties such as adamantyl (Figure 1) have shown excellent ligand properties and have provided many advances in terms of scope and efficiency for C−C and C−N bond formation reactions.[13−23]

Preparation of diadamantyl phosphines (e.g., *CataCXium* (**7**), *Mor-DalPhos* (**8**), Figure 1b) was achieved by reacting halophosphorus compounds with organometallic reagents.[14,24−28] Synthesis of higher diamondoid phosphines was accomplished after reduction of di-4-diamantyl and di-9-triamantyl phosphonic acid chlorides using $HSiCl_3$ with a Lewis acid. The corresponding secondary phosphines **4a** and **4b** as well as salt **5a** were obtained in good yields.[29] Preliminary studies using phosphonium salt **5a** as a ligand in C−C bond formation reactions showed promising results.[29] Recently, triadamantyl phosphine metal complexes were synthesized, and their application in cross coupling reactions involving aryl chlorides and boronic acids was reported.[30]

Although primary phosphines have been used as starting materials in asymmetric catalysis,[31,32] their applications are limited due to their air sensitivity.[33] Low molecular weight, lack of steric hindrance, and the absence of a heteroatom in the backbone can even result in pyrophoricity of such compounds.[33] The air stability of some primary phosphines (e.g.,

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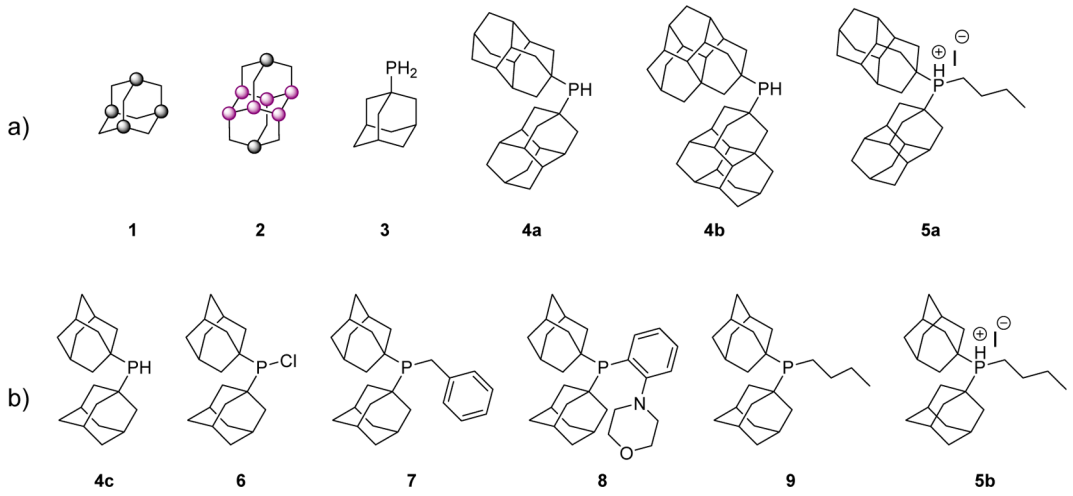
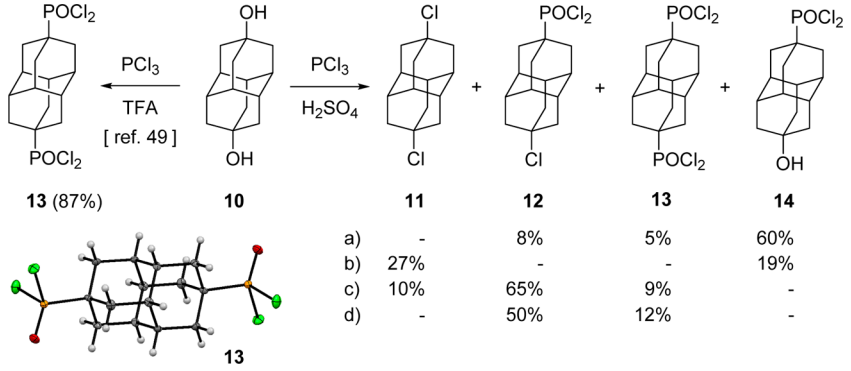


Figure 1. (a) Adamantane (**1**), diamantane (**2**), adamantylphosphine (**3**), diamondoid phosphines (**4a** and **4b**) and phosphonium salt **5a**. (b) commercially available diadamantyl phosphines (**4c** and **6**–**9**) and phosphonium salt **5b**.

Scheme 1. Phosphorylation of Diamantane Diol 10 with Yields Dependent upon the Reaction Conditions[a]



[a](a) 1 equiv of PCl_3, 98% H_2SO_4 at −15 °C for 1 h, 3.5 h at rt. (b) 1 equiv of PCl_3, 98% H_2SO_4 at 0 °C for 1 h, 6 h at rt. (c) 2.5 equiv of PCl_3, 98% H_2SO_4 at −15 °C for 1 h, 3.5 h at rt. (d) 10 equiv of PCl_3, 98% H_2SO_4 at −15 °C for 1 h, 3.5 h at rt. Inset: X-ray crystal structure of **13** (color code: C, gray; H, white; P, orange; O, red; Cl, green). The X-ray crystal structure of **13** was also obtained, and we found bond lengths somewhat shorter than those typical for C−P and O−P bonds (C_{apical}−P = 1.813(3) Å, and O−P = 1.463(2) Å).

binaphthyl MOP phosphines) that are neither hindered nor include a heteroatom in their structures[34−36] is due to a high degree of π-conjugation. Bulky substituents also inhibit the reaction with dioxygen, thereby making primary phosphines more "user friendly".[33] The primary adamantane phosphine **3** (Figure 1), prepared through the reduction of the corresponding phosphonic dichloride **16**,[37] is very air-sensitive, making its application as a ligand in catalysis challenging. We envisioned that larger diamondoid groups (e.g., diamantane) would substantially increase the air stability of the corresponding primary phosphines. Diamondoid cage substitution changes the electronic properties significantly.[38] We also studied the influence of additional functional groups on the stability of primary diamondoid phosphines. This requires the preparation of novel phosphorylated diamondoid derivatives via the C−H bond substitution, which is described in the present work.

RESULTS AND DISCUSSION

Diamondoid Phosphorylations. In contrast to **1**,[39,40] **2** displays two types of tertiary carbons, apical and medial, thus making its selective functionalization by cationic activation challenging.[2,3,10] Therefore, use of protection/deprotection sequences[41−43] is necessary to obtain unequally difunctionalized diamantyl derivatives. Diamondoid phosphonic dichloride derivatives are typically obtained via Lewis acid catalysis,[37,44] but the direct monophosphorylation of diamantane in the $AlCl_3/PCl_3/CH_2Cl_2$ system[45] results in mixtures[29] and low yields compared to that of adamantane. We found that employing a Brønsted acid[46−48] gives rise to higher yields and, most importantly, that it is applicable to cages larger than adamantane.[49] However, this procedure does not allow for the preparation of unequally disubstituted diamondoids, and in trifluoroacetic acid, the reaction of **10** resulted only in product **13** (Scheme 1).[49] This can be understood readily because **10** and all monosubstituted intermediates are soluble in TFA, while **13** precipitates from this media. As **10** is only poorly soluble in H_2SO_4, a variety of products can form. We first tested the phosphorylation of **10** with PCl_3 in concd H_2SO_4, which gave monophosphorylated derivative **14** in up to 60% yield (with method a, Scheme 1) depending on the reaction conditions.

It has been shown that PCl_3 decomposes rapidly in H_2SO_4.[47] Because the reaction proceeds slowly in sulfuric acid due to the low solubility of the substrate, the carbocation can be attacked by either nucleophile, resulting in chlorination and phosphor-

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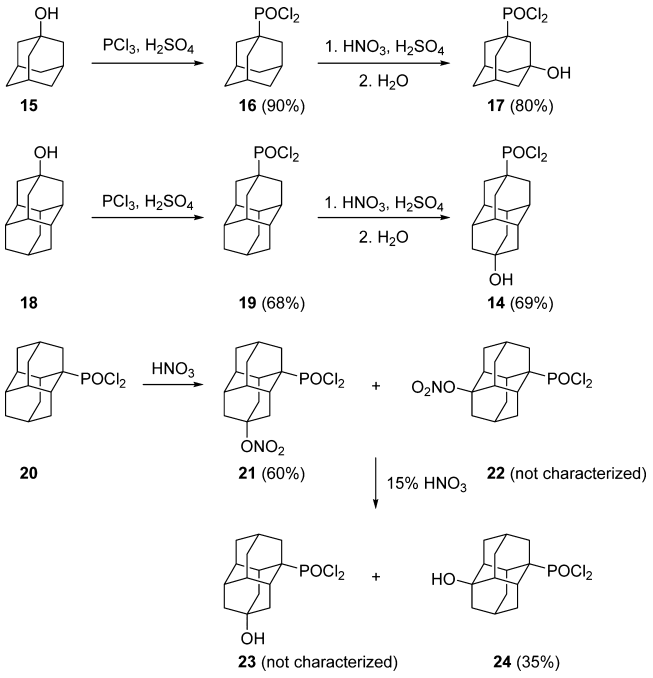
ylation products. Therefore, we chose a different approach based on C−H bond functionalization (Scheme 2).

Scheme 2. C−H Bond Functionalization of Diamondoid Phosphonic Acid Dichlorides

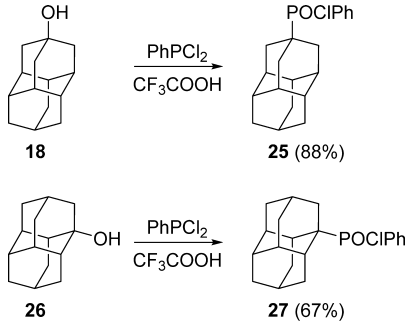


We showed previously that oxidation of diamondoids with 100% nitric acid affects only tertiary positions and can be performed in a kinetically controlled way.[50] While the question of regioselectivity does not arise for **16**, diamantane derivative **19** displays three different tertiary C−H positions. Moreover, the electron withdrawing group (EWG) deactivates the medial positions, and only the remaining apical position reacts. Consequently, with HNO_3, C−H bond functionalization of **19** occurs regioselectively in position 9 (apical) of the diamantane cage. For the medially substituted diamantane phosphonic dichloride **20**, C−H bond functionalization occurs at the position farthest from the $POCl_2$ group, resulting in a mixture of 1,6- and 1,4- derivatives (**24** and **23**, respectively).

We also attempted the Brønsted acid catalyzed phosphorylation with two different substituents (alkyl and aryl) present on phosphorus.[46] We chose trifluoroacetic acid to avoid the formation of chlorinated products. The phosphorylation of 4-hydroxydiamantane **18** with $PhPCl_2$ gave the corresponding phenyl-4-diamantylphosphonic acid chloride (**25**) in high yield (Scheme 3). Although medially substituted diamantane derivatives are sterically hindered,[50] the phosphorylation of 1-hydroxydiamantane (**26**) also proceeded smoothly to give phenyl-1-diamantylphosphonic acid chloride (**27**). The phosphonic dichlorides and chlorides described above were used as precursors for primary and secondary diamondoid phosphines.

Primary Diamondoid Phosphines. Commonly used metal catalyzed hydrogenation methods or reducing agents cannot be applied to the reduction of diamondoid phosphonic dichlorides; conversely, use of $LiAlH_4$ has been reported.[51] Starting from diamantane phosphonic dichlorides **19** and **20**, the corresponding primary phosphines **29** and **31** were obtained. They have different topologies, **29** being less hindered than **31**, as the medial position is known to be much more crowded than the apical one.[10] The two primary phosphines **29** and **31** were characterized only by NMR and show the following characteristic signals in the ^{31}P NMR: $\delta_P(\mathbf{29}) = -85.2$ ppm, $^1J_{PH}(\mathbf{29}) = 145$ Hz, $\delta_P(\mathbf{31}) = -97.4$ ppm, and $^1J_{PH}(\mathbf{31}) = 194$ Hz, respectively. They were fully characterized via the corresponding Staudinger iminophosphorane derivatives **30** and **32** (Scheme 4). The ^1H and ^{31}P NMR spectra of primary phosphines **29** and **31** show broadening of the signals at room temperature in chloroform-d. To clarify this observation, we undertook further NMR investigation using **31** in various solvents with different additives and at various temperatures (Supporting Information, pages S101−S105). When THF-d^8 was used as the solvent, the broadening phenomenon was not observed, but upon addition of acid, broadening occurred again. Therefore, we concluded that the observed behavior was solely caused by proton exchange at the phosphine.

Scheme 3. Synthesis of Diamantyl Phosphonic Chlorides



The primary diphosphine **33** prepared by reduction of diphosphorylated derivative **13** could be fully characterized because it appears to be stable for several minutes in air unlike monophosphine **29**. In compound **29**, the donor effect of the cage is proposed to influence only one phosphorus atom, thus making it more electron-rich, which is not the case for **33**. Therefore, the monosubstituted phosphine should react with oxygen more readily. Primary diphosphine **33** also showed the same signal broadening in ^1H and ^{31}P NMR spectra like monophosphines **29** and **31** at room temperature, a consequence of phosphine proton exchange.

Reduction of unequally substituted diamondoids **12**, **14**, and **17** with $LiAlH_4$ readily led to primary phosphines **37**, **36**, and **34**, respectively (Scheme 5), similar to the reduction of monophosphorylated and diphosphorylated compounds **19**, **20**, and **13**. Compound **34** is air-sensitive and quantitatively converts to oxide **35**. This result is consistent with the reported high air sensitivity of other 1-adamantyl phosphines substituted in position 3.[52]

An increase in the $^1J_{PH}$ coupling constant is noticeable when comparing compounds **29** and **36** ($\Delta J = 45$ Hz). Despite the large spatial separation along the cage framework between the hydroxy group and the phosphorus, the electron-withdrawing effect is enhanced by hyperconjugation.[53−56] It is know that primary phosphines attached to a backbone containing a heteroatom are more likely to be air stable compared to their homologues without heteroatoms.[33] This is also the case for compounds **36** and **37** because we found that in solution they were stable for at least 1 h in air. Such stability was not observed for the adamantane homologues despite the presence of an EWG. Two EWGs (OH or Cl) seem to provide additional air stability (e.g., compare compounds **3** and **29** with

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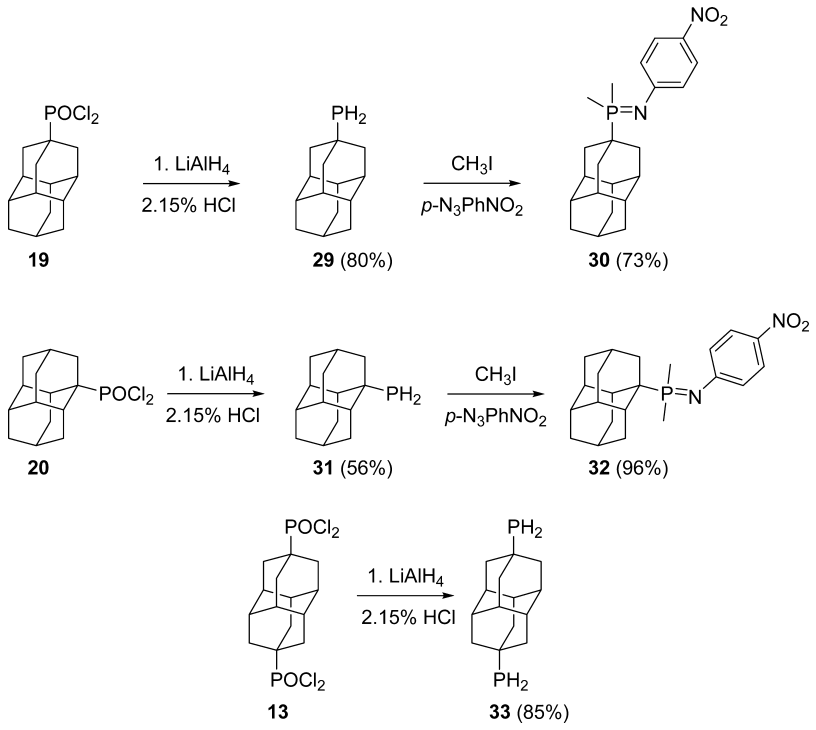
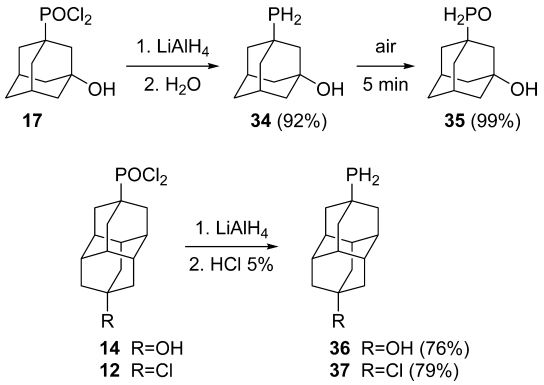
Scheme 4. Synthesis of Primary Diamantyl Phosphines



Scheme 5. Synthesis of Unequally Substituted Primary Diamondoid Phosphines



34 and **36**, respectively). The mechanism of phosphine oxidation by O_2 has not been fully elucidated, but the formation of the radical cation of primary phosphine is a postulated pathway.[34−36] Primary phosphines with extended π-electron structural motifs (such as naphthyl, binaphthyl, and triptycenyl) do not have a significant phosphorus contribution to their HOMO and are stable to air oxidation.[35] Even though in our case there is no such conjugated motif, we propose that an increase of bulkiness by the diamantane cage surrounding the phosphorus atom can induce a significant resistance toward air oxidation (compare **34** with **36**).

It was suggested that the SOMO level and geometry of the corresponding phosphine radical cation is key for understanding the air stability of the related primary phosphine.[35] An empirically derived value of −10.0 eV was proposed to be a threshold, and phosphines with radical cation SOMO energies below this value are expected to be easily oxidized in air.[35] This agrees in part with our computed SOMO energies of the radical cations derived from phosphines **3**, **29**, **33**, **34**, **36**, and **49** (Figure 2), where these values for relatively air stable $\mathbf{33}^{\bullet+}$ (−9.9 eV) and $\mathbf{36}^{\bullet+}$ (−10.3 eV) approach the above threshold. Note that the SOMO of $\mathbf{36}^{\bullet+}$ is located predominantly on the oxygen atom of the hydroxy group, which is a complementary explanation for the stability of **36** toward oxidation. As experimentally observed, primary diphosphine **33** also is more stable than primary monophosphine **29**. This finding is in agreement with the computed SOMO energies of the radical cations derived from **33** and **29** (−9.9 and −11.0 eV, respectively). We also performed an NBO analysis of spin densities for radical cations derived from primary diamondoid phosphines and found that the spin density on phosphorus is generally smaller for more air stable derivatives (Table S1). These findings are in agreement with the proposed radical mechanism of phosphine oxidation because radical cations of stable diamondoid phosphines have spin densities distributed in other parts of the molecule, implying that the spin is not solely localized on the phosphorus atom, resulting in higher resistance to oxidation.

Secondary Diamondoid Phosphines. Secondary diamantane phosphines were also prepared using a $LiAlH_4$/ethereal system (Scheme 6). In contrast to primary phosphines **29** and **31**, only the apical secondary phosphine **38** forms a phosphazo derivative. The medial phosphine **39** is unreactive, probably due to steric hindrance caused by the cage in the medial position.[57] The ^{31}P NMR characterization of **38** at room temperature in $CDCl_3$ was surprising because no signal was observed. At around 240 K, the expected doublet appears at −9.5 ppm ($^1J_{PH}$(**38**) = 178 Hz) as well as the corresponding doublet at 3.82 ppm in the ^1H NMR. Fluxional behavior was also observed in the ^{31}P and ^1H NMR spectra of 1-diamantylphenylphosphine (**39**), which is only slightly different from those of secondary phosphine **38** because at 273 K the spectrum of **39** indicates a broad singlet at −23.1 ppm. Upon cooling, decoalescence occurs at around 255 K, and at 240 K, the expected doublet is observed at −23.9 ppm ($^1J_{PH}$(**39**) = 178

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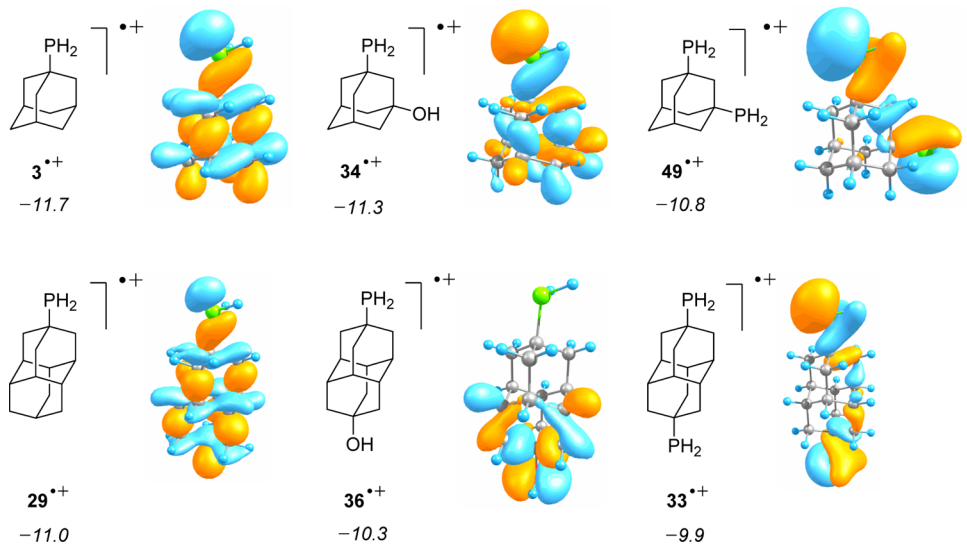
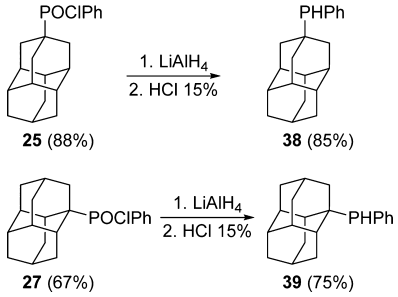
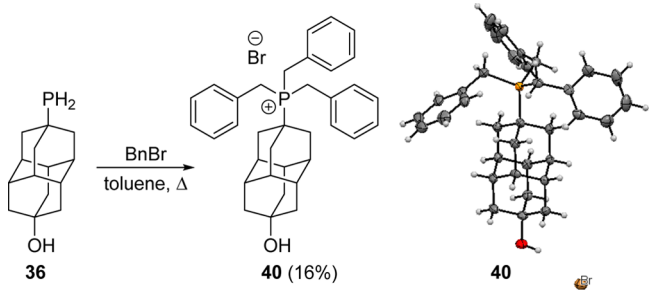


Figure 2. Shapes and energies (eV) of the SOMOs for the B3LYP/6-311+G(d,p) optimized structures of the radical cations derived from primary phosphines **3**, **29**, **33**, **34**, **36**, and **49**.

Scheme 6. Synthesis of Unequally Substituted Secondary Diamantyl Phosphines



Scheme 7. Benzylation of Unequally Substituted Primary Diamantane Phosphine 36 and the X-ray Single Crystal Diffraction Structure of Phosphonium Salt 40[a]



[a]Color code: C, gray; H, white; P, orange; O, red; Br, dark red.

Hz). As was the case for primary diamantyl phosphines, proton exchange is responsible for the observed NMR behavior of secondary diamantyl phosphines. For further understanding of phosphines **38** and **39**, we performed computational studies and identified their stationary structures for the rotation around the C−P bonds (Figures S1 and S2, pages S111−S112). The results indicate that a planar inversion around phosphorus is not an energetically favorable pathway and that the conformers interconvert through a rotation of the diamantane cage or the phenyl group.

Diamondoid Phosphine Postfunctionalization. Conversion of primary diamantane phosphines was explored as a direct synthetic pathway toward functionalized higher analogues. We aimed at exploring whether the direct functionalization of primary diamondoid phosphines would be a feasible method. By refluxing hydroxyphosphine **36** with benzyl bromide, the expected alkylation reaction occurred, but we mainly isolated the phosphonium salt **40** in modest yield (16%, Scheme 7). A characteristic ^{31}P NMR signal at 27.5 ppm was observed for **40**, and its X-ray structure indicates a weak hydrogen bond between the hydroxy group and the bromide O−H···Br (d(O−Br) = 3.4239(15); angle O−H−Br = 162.6°). The observed bond length values for C4−P = 1.835(2) Å and C9−O = 1.429(2) Å were expected and correspond to typical C−P and C−O bonds.

As the direct approach for phosphine functionalization was low-yielding, an indirect strategy was envisioned that would lead to pentacoordinated phosphorus derivatives that could further be reduced.[58,59] We first arylated diamondoid phosphonic dichlorides to obtain the mixed phosphorylated oxides **41**−**44** (Scheme 8). In the X-ray crystal structures of **41**−**44**, typical C−P and O−P bond lengths were observed (e.g., C_{apical}−P = 1.833(2) Å and O−P = 1.500(2) Å for **43**). Their reduction was expected to give access to mixed aryl/alkyl diamondoid phosphines.

Unfortunately, adamantyl derivative **41** (δ_P = 34.3 ppm, in agreement with the literature[60]) could not be reduced with $LiAlH_4$ in THF or dioxane[51] to the corresponding phosphine, and we did not pursue this line of investigation further with the diamantyl homologues. Instead, we prepared the parent sulfide **46** and selenide **47** that could be readily reduced to the target phosphine **48** in 60% yield (Scheme 9). In the X-ray crystal structure of sulfide **46**, we found somewhat longer bond lengths: C_{medial}−P = 1.859(2) Å and P−S = 1.9717(7) Å.

The $^1J_{P=Se}$ (**47**) = 712 Hz coupling constant is lower than the value for triphenylphosphine selenide ($^1J_{P=Se}$ = 730 Hz), which is consistent with an electron-donating effect of the adamantyl group toward phosphorus. Thus, we expect a higher basicity of **48** compared to that of PPh_3, rendering this phosphine potentially useful in the catalytic steps of cross-coupling reactions.[61−63] The pathway to **48** using sulfide **46** is the most efficient synthetically (Scheme 9) with an overall yield

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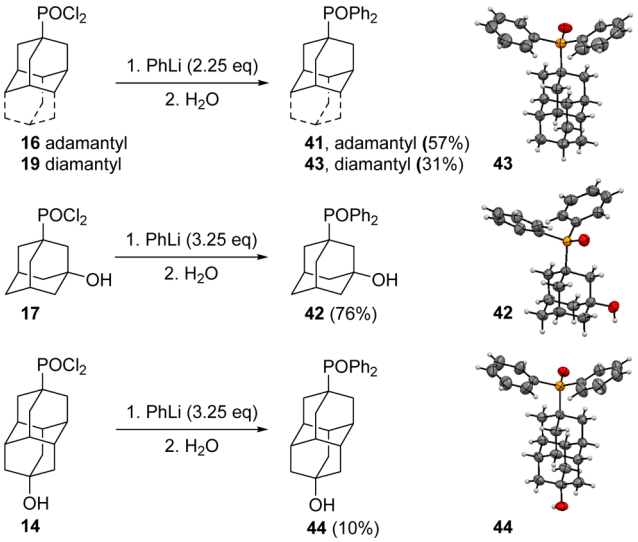
Scheme 8. Arylation of Diamondoid Phosphonic Acid Dichlorides and the X-ray Single Crystal Diffraction Structures of 42, 43, and 44[a]



[a]Color code: C, gray; H, white; P, orange; O, red.

from bromide **45** of 27%. Compound **48** has previously been reported as a side-product formed in the photochemical reaction of 1,3-dichloroadamantane with the $[Ph_2P^-]$ anion in liquid ammonia but had not been isolated (because oxide **41** forms instead).[59]

CONCLUSIONS

Direct unequal difunctionalization of phosphorylated diamondoid derivatives avoiding protection/deprotection sequences has now been made possible by C−H bond functionalization without affecting the existing $POCl_2$ group. Using Brønsted acid catalysis, we prepared unequally substituted diamantyl phosphonic chlorides, which are excellent precursors for the corresponding phosphines. The reduction of phosphonic chlorides described herein provided access to novel primary and alkyl/aryl secondary diamantane phosphines. Primary diamantyl phosphines were found to be surprisingly air stable compared to their adamantyl homologues. We computed diamantyl and adamantyl phosphine radical cation energies and found that the corresponding SOMO levels were close to the air stability threshold of −10 eV. These functionalized diamondoid phosphines are currently being explored in material science and catalytic applications.

EXPERIMENTAL SECTION

General Information. Synthesis of sensitive products was done using Schlenk techniques. Glassware was dried in an oven at 110 °C before use. THF and diethyl ether were prepared by distillation under argon using sodium and benzophenone; dichloromethane (DCM) was purified by distillation under argon using CaH_2. 1,4-Dioxane was purified by stirring with $LiAlH_4$ under argon overnight and was then distilled under argon (bp = 101 °C). $CDCl_3$ was dried over activated 4 Å molecular sieves under argon. The other solvents were obtained directly from the manufacturer or distilled from technical grade. Commercially available reagents were used without further purification. TLC was done on 0.2 mm silica gel with fluorescent indicator (precoated polyester sheets UV_{254} or TLC silica gel 60 F_{254} on aluminum sheets). Column chromatography was done on silica gel (70−230/100−160/230−400mesh ASTM). NMR spectra were recorded at 300, 400, 500, and 600 MHz spectrometers in chloroform ($CDCl_3$) unless stated otherwise with/without TMS as an internal standard. ^1H and ^{13}C NMR assignments were confirmed by DEPT-135/JMOD and sometimes with two-dimensional $^1H-^{13}C$ NMR experiments. High-resolution mass spectra (HRMS) were recorded using electron impact ionization on a focusing sector field-type mass spectrometer.

*Phosphorylation of 4,9-Dihydroxydiamantane (**10**) in Sulfuric Acid to Prepare Compounds **11**, **12**, **13**, and **14**.* Concentrated sulfuric acid (98%, 8.5 mL, freshly prepared from oleum 20% and H_2SO_4 94%) was cooled to 0 °C or −15 °C. At the respective temperature, 4,9-dihydroxydiamantane (**10**) (0.880 g, 4 mmol) was added followed by PCl_3 (PCl_3 was varied according to Scheme 1). The reaction mixture was stirred for 1 h at the corresponding temperature and 3.5 or 6 h at rt. The reaction mixture was slowly poured onto crushed ice. The white precipitate that formed was filtered with a Büchner funnel and rinsed with distilled water until reaching a neutral pH; the remaining solid was dried in air. Purification by column chromatography on silica gel with pentane:diethyl ether (3:1) afforded 4,9-dichlorodiamantane (**11**) (R_f = 0.88) and (9-chloro-diamant-4-yl)phosphonic dichloride (**12**) (R_f = 0.28). Changing the eluent to DCM:diethyl ether (3:1) gave (4,9-diamantyl)diphosphonic dichloride (**13**) (R_f = 0.76). Changing the ratio of the same eluent to 1:1 afforded (9-hydroxydiamant-4-yl)phosphonic dichloride (**14**) (R_f = 0.22) as a white solid. Yields are specified in Scheme 1 as a function of the reaction conditions.

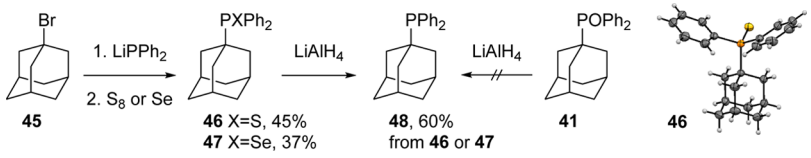
*4,9-Dichlorodiamantane (**11**).* Spectral data were identical to those previously reported.[64]

*(9-Chlorodiamant-4-yl)phosphonic Dichloride (**12**).* The X-ray structure is available in the Supporting Information, page S124. ^1H NMR (600 MHz, 291 K, $CDCl_3$): δ 2.17 (d, J = 3.4 Hz, 6H), 2.11−2.06 (m, 6H), 2.06−2.01 (m, 3H), 2.01−1.06 (m, 3H) ppm. ^{13}C NMR (150 MHz, 291 K, $CDCl_3$): δ 65.7 (s, C_q), 47.1 (d, J(C,P) = 3.1 Hz, CH_2), 46.5 (d, J(C,P) = 92.8 Hz, C_q), 39.1 (d, J(C,P) = 2.6 Hz, CH), 35.2 (d, J(C,P) = 16.7 Hz, CH), 35.0 (d, J(C,P) = 3.3 Hz, CH_2) ppm. $^{31}P\{^1H\}$ NMR (243 MHz, 291 K, $CDCl_3$): δ 64.85 ppm.

*(4,9-Diamantyl)diphosphonic Dichloride (**13**).* **13** was identical to the material previously obtained through the phosphorylation of **10** in trifluoroacetic acid.[49] The X-ray structure is available in the Supporting Information, page S128.

*(9-Hydroxydiamant-4-yl)phosphonic Dichloride (**14**).* Mp 204−205 °C. ^1H NMR (600 MHz, 298 K, $CDCl_3$): δ 2.14−2.02 (m, 6H), 1.98 (br s, 6H), 1.82−1.68 (m, 6H; CH_2), 1.51 (br s, 1H, OH) ppm. ^{13}C NMR (151 MHz, 298 K, $CDCl_3$): δ 66.8 (s, C_q), 46.8 (d, J(C,P) = 91.6 Hz, C_q), 44.8 (d, J(C,P) = 3.2 Hz, CH_2), 38.5 (d, J(C,P) = 2.3

Scheme 9. Reduction of Adamantyl Phosphine Sulfide or Selenide to 1-Adamantyl Diphenyl Phosphine (48) and the X-ray Single Crystal Diffraction Structure of 46[a]



[a]Color code: C, gray; H, white; P, orange; S, yellow.

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Hz, CH), 35.6 (d, J(C,P) = 16.6 Hz, CH), 35.0 (d, J(C,P) = 3.1 Hz, CH_2) ppm. $^{31}P\{^1H\}$ NMR (243 MHz, 300 K, $CDCl_3$): δ 65.29 ppm. HRMS (EI): m/z [M] $^+$ calcd for $C_{14}H_{19}Cl_2O_2P$ 320.0500; found 320.0468.

*(4-Diamantyl)phosphonic Dichloride (**19**).* **19** was identical to the material previously obtained through the phosphorylation of **18** in sulfuric acid.[49] The X-ray structure is available in the Supporting Information, page S139.

*Another Method for Preparing (9-Hydroxydiamant-4-yl)-phosphonic Dichloride (**14**) from **19**.* Concentrated sulfuric acid (96%, 2.5 mL) was placed in a 5 mL round-bottom flask and cooled to −15 °C with an ice-salt bath. 4-Diamantylphosphonic acid dichloride (**19**) (0.332 g, 1.1 mmol) was added followed by HNO_3 100% (0.4 mL, 9.8 mmol, 9 equiv). The reaction mixture was stirred for 1 h at −15 °C and for 7 h at 18 °C. The reaction mixture was poured slowly onto 40 g of crushed ice. DCM (40 mL) was added followed by solid $NaHCO_3$ in portions until a neutral pH was reached and the aqueous phase turned clear yellow. It was extracted with DCM (3 × 30 mL) and dried over $MgSO_4$. The solvent was evaporated to yield 0.325 g of crude product. It was purified by column chromatography on silica gel using DCM:diethyl ether (1:1) to afford (9-hydroxydiamant-4-yl)phosphonic dichloride (**14**) (0.242 g, 69% yield) as a white solid.

*(3-Hydroxyadamant-1-yl)phosphonic Dichloride (**17**).* In a 10 mL round-bottom flask, 3 mL of H_2SO_4 94% was cooled with an ice-salt bath to −13 °C. 1-Adamantylphosphonic dichloride (**16**) (1.66 g, 6.6 mmol) was added and stirred until completely dissolved. Then, HNO_3 100% (3 mL, 72 mmol, 11 equiv) was slowly added. The solution was stirred for 1 h at −13 °C and for 22 h at rt. The colorless solution was slowly poured onto 15 g of crushed ice. DCM (100 mL) was added, and the mixture was stirred at rt. Solid $NaHCO_3$ was added in small portions until no more gas evolution was observed. The aqueous phase was extracted with DCM (3 × 30 mL) and diethyl ether (4 × 40 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated and gave a yellow sticky compound. Purification by column chromatography on silica gel in diethyl ether 100% (R_f = 0.3) gave pure (3-hydroxyadamant-1-yl)phosphonic dichloride (**17**) (1.42 g, 80%). The X-ray structure is available in the Supporting Information, page S132. ^1H NMR (400 MHz, 300 K, $CDCl_3$): δ 2.50−2.36 (m, 2H), 2.04−1.94 (m, 6H), 1.78−1.69 (m, 5H), 1.69−1.57 (m, 2H) ppm. ^{13}C NMR (100 MHz, 300 K, $CDCl_3$): δ 68.1 (d, J(C,P) = 19.4 Hz, C_q), 51.0 (d, J(C,P)= 91.3 Hz, C_q), 43.9 (d, J(C,P) = 2.5 Hz, CH_2), 42.6 (d, J(C,P) = 4.6 Hz, CH_2), 34.5 (d, J(C,P) = 2.8 Hz, CH_2), 34.0 (d, J(C,P) = 3.8 Hz, CH_2), 30.1 (d, J(C,P) = 17.6 Hz, CH) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, 300 K, $CDCl_3$, H_3PO_4 external standard): δ 62.21 ppm. HRMS (EI): m/z [M] $^+$ calcd for $C_{10}H_{15}Cl_2O_2P$: 268.0187; found: 268.0169. Anal. calcd for $C_{10}H_{15}Cl_2O_2P$: C, 44.63; H, 5.62, found: C, 44.15; H, 5.59.

*4-Nitroxydiamantyl-1-dichlorophosphonate (**21**).* Diamantyl-1-dichlorophosphonate (**20**) (1.22 g, 4 mmol) was added to 20 mL of 100% HNO_3 under intense stirring at 10 °C. The reaction mixture was stirred for 20 h at 20 °C, poured onto ice (200 g), and extracted with $CHCl_3$ (3 × 20 mL). The combined organic extracts were washed with water, saturated aq $NaHCO_3$, brine, and dried over Na_2SO_4 to give 1.45 g of a mixture of 4-nitroxydiamantyl-1-dichlorophosphonate (**21**) and 6-nitroxydiamant-1-yldichlorophosphonate (**22**) after solvent removal. The mixture (0.725 g) was separated by column chromatography on silica gel (9:1 hexane:ether) to give 4-nitroxydiamantyl-1-dichlorophosphonate (**21**) as a colorless solid (0.439 g, 60%). Mp 120−121 °C. The X-ray structure is available in the Supporting Information, page S144. ^1H NMR (400 MHz, $CDCl_3$): δ 2.97 (d, 2H, J = 12 Hz), 2.55−2.43 (bs, 2H), 2.21−2.15 (bs, 2H), 2.06−1.95 (m, 8H), 1.80−1.62 (bs, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 87.0 (C), 54.0 (C, d, J = 78 Hz), 38.8 (CH_2, d, J = 9.5 Hz), 39.1 (CH, d, J = 3 Hz), 38.7 (CH, d, J = 3 Hz), 37.5 (CH, d, J = 15 Hz), 37.45 (d, CH_2, J = 1.3 Hz), 36.4 (CH_2), 35.5 (CH_2, d, J = 3 Hz), 25.4 (d, CH, J = 15 Hz) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, H_3PO_4): δ = 63.1 ppm.

*6-Hydroxydiamantyl-1-dichlorophosphonate (**24**).* The above-described mixture (0.725 g) was refluxed with 3 mL of 15% HNO_3 under intense stirring, cooled, and extracted with $CHCl_3$. The combined organic extracts were washed with water, saturated aq $NaHCO_3$, brine, and dried over Na_2SO_4. After concentration under reduced pressure, the mixture was separated by column chromatography on silica gel (4:1 hexane:ether). 6-Hydroxydiamant-1-yldichlorophosphonate (**24**) was obtained (0.225 g, 35%) as a colorless solid. Mp 168−170 °C. The X-ray structure is available in the Supporting Information, page S129. ^1H NMR (400 MHz, $CDCl_3$): δ 2.65 (AB, 2H, J_{AB} = 8 Hz), 2.42 (d, 2H, J = 1.5 Hz), 2.21 (m, 2H), 2.17 (bs, 1H), 1.98−1.88 (m, 3H), 1.77 (d, 2H, J = 1.5 Hz), 1.65 (s, 2H), 1.48 (m, 3H), 1.40 (AB, 2H, J_{AB} = 8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.6 (C), 55.0 (d, C, J = 75 Hz), 46.7 (CH_2), 44.1 (d, CH, J = 17.5 Hz), 38.4 (d, CH_2, J = 2 Hz), 39.2 (CH), 33.4 (CH_2), 30.9 (d, CH_2, J = 2.6 Hz), 29.2 (CH), 25.3 (d, CH, J = 15 Hz) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, H_3PO_4): δ 65.4 ppm. HRMS (EI): m/z [M] $^+$ calcd for $C_{14}H_{19}Cl_2O_2P$: 320.0500; found: 320.0503.

*4-Diamantylphenylchlorophosphonate (**25**).* To a mixture of 3.00 g (14.7 mmol) of 4-hydroxydiamantane (**18**) and 50 mL of trifluoroacetic acid was added 7 mL (80 mmol) of dichlorophenyl phosphine, and the reaction mixture was refluxed for 3.5 h, cooled, and then poured onto ice. The reaction mixture was filtered, and the precipitate was washed with water and dried. The crude product was purified by column chromatography on silica (3:1 hexane:ether) to give 4-diamantylphenylchlorophosphonate (**25**) as colorless crystals (4.49 g, 88%). Mp 190−192 °C (hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.85−7.70 (m, 2H), 7.65−7.59 (m, 1H), 7.58−7.44 (m, 2H), 2.01−1.83 (m, 9H), 1.79 (bs, 1H), 1.75−1.61 (m, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.8 (d, CH, J = 3 Hz), 132.7 (d, CH, J = 10 Hz), 129.0 (d, C, J = 103 Hz), 128.3 (d, CH, J = 14 Hz), 39.8 (d, C, J = 80 Hz), 37.5 (d, CH_2, J = 2 Hz), 36.4 (d, CH, J = 13 Hz), 36.1 (d, CH, J = 1.3 Hz), 35.7 (d, CH_2, J = 6.3 Hz), 25.3 (CH) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, H_3PO_4): δ 68.8 ppm. HRMS (EI): m/z [M] $^+$ calcd for $C_{20}H_{24}ClOP$: 346.1253; found: 346.1249.

*1-Diamantylphenylchlorophosphonate (**27**).* **27** was prepared from 1-hydroxydiamantane (**26**) as described above with 67% yield (3.42 g) as a colorless solid. Mp 257−259 °C (hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.82−7.70 (m, 2H), 7.58−7.51 (m, 1H), 7.50−7.39 (m, 2H), 3.05−2.90 (m, 2H), 1.95−1.89 (m, 3H), 2.41−2.30 (m, 1H), 1.88−1.86 (m, 1H), 1.85−1.62 (m, 8H), 1.61−1.45 (m, 2H), 1.40−1.25 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.6 (d, CH, J = 10 Hz), 131.0 (d, C, J = 100 Hz) 132.5 (d, CH, J = 3 Hz), 128.2 (d, CH, J = 12 Hz), 47.9 (d, C, J = 70 Hz), 38.8 (CH_2), 38.7 (CH), 38.5 (d, CH, J = 5 Hz), 38.2 (CH_2), 37.3 (d, CH, J = 2.5 Hz), 37.06 (d, CH_2, J = 3 Hz), 37.03 (d, CH_2, J = 3 Hz), 36.7 (CH), 36.5 (d, CH, J = 4 Hz), 34.3 (CH_2), 33.9 (CH_2), 25.6 (d, CH, J = 13 Hz), 25.1 (CH) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, H_3PO_4): δ 71.3 ppm. HRMS (EI): m/z [M] $^+$ calcd for $C_{20}H_{24}ClOP$: 346.1253; found: 346.1248.

General Procedure for the Preparation of Diamondoid Phosphines in Benzene/Ether. A solution of the respective diamantylphosphonic acid chloride (1.64 mmol) in dry benzene (8 mL) was added to a mixture of $LiAlH_4$ (16.4 mmol, 10 equiv) in dry ether (3.5 mL). The reaction mixture was refluxed for 1−2 h, cooled to 0 °C, and 15 mL of 15% HCl was added dropwise. The aqueous phase was extracted with benzene (3 × 15 mL). Combined organic phases were washed with water (10 mL) and dried over Na_2SO_4. Evaporation of solvents in vacuo yielded respective phosphine in 70−96% yield.

*4-Diamantylphosphine (**29**).* **29** was isolated after 2 h of reflux in 80% (0.288 g) yield as a colorless air-sensitive solid. ^1H NMR (600 MHz, $CDCl_3$): δ 2.83 (bs, 1H), 2.51 (bs, 1H), 1.79−1.73 (m, 10H), 1.72−1.70 (bs, 6H), 1.69−1.64 (bs, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 45.6 (d, CH_2, J = 21 Hz), 38.2 (d, CH, J = 22 Hz), 37.8 (CH_2), 36.3 (CH), 26.9 (d, C, J = 8 Hz), 25.6 (CH) ppm. ^{31}P NMR (243 MHz, $CDCl_3$, H_3PO_4): δ= −85.2 (t, J = 145 Hz) ppm.

*4-Diamantyldimethylphosphazo-p-nitrobenzene (**30**).* To a solution of phosphine **29** (0.34 g, 1.54 mmol) in dry benzene (3 mL) was added 1 mL of methyl iodide, and the mixture was stirred for 3 h under reflux. After being cooled to rt and filtered, the precipitate (0.25 g) was dissolved in ethanol (6 mL), and NaOH (0.4 g, 10 mmol) was added. The mixture was stirred for 1 h at rt; the solvent was removed by distillation, and 3 mL of water was added. The residue was extracted with benzene (2 × 10 mL), and combined organic extracts

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were washed with water and dried over Na_2SO_4. Solvent evaporation gave 0.242 g of a white solid which was dissolved in dry benzene (10 mL); 0.254 g (1.55 mmol) of *p*-nitrobenzene azide was added, and the solution was heated at 36 °C for 5 min. After completion of the gas evolution (N_2) and cooling, the yellow precipitate was filtered and washed with benzene to give 4-diamantyldimethylphenylphosphazo-*p*-nitrobenzene (**30**) as yellow solid (0.320 g, 73%). Mp 285−287 °C (ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.0−7.8 (m, 2H), 7.70−7.48 (m, 5H), 6.45 (bs, 2H), 2.00−1.80 (m, 9H), 1.83 (s, 3H), 1.75−1.70 (bs, 10H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5 (C), 137.2 (CH), 132.2 (d, CH, J = 9.0 Hz), 128.9 (d, CH, J = 10 Hz), 125.7 (CH), 121.8 (bd, CH, J = 23 Hz), 37.5 (CH_2), 36.5 (d, CH, J = 14 Hz), 36.3 (CH), 35.2 (CH_2), 31.3 (d, C, J = 90 Hz), 25.3 (CH), 5.30 (d, CH_3, J = 55 Hz), ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, H_3PO_4): δ 21.2 ppm. HRMS (EI): m/z [M] $^+$ calcd for $C_{22}H_{29}N_2O_2P$: 384.1967; found: 384.1957.

*1-Diamantylphosphine (**31**).* **31** was prepared after 1 h of reflux in 56% yield as a colorless air-sensitive solid. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): 2.80−2.24 (bs, 2H), 2.24 (AB, 2H, J_{AB} = 16 Hz), 1.86−1.78 (m, 4H), 1.74−1.66 (m, 11H), δ 1.56 (AB, 2H, J_{AB} = 16 Hz) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 48.5 (d, CH_2, J = 6 Hz), 42.2 (d, CH, J = 7 Hz), 38.7 (d, CH_2, J = 1 Hz), 38.5 (d, CH, J = 5 Hz), 38.3 (CH_2), 38.2 (CH_2), 37.6 (CH), 37.0 (d, C, J = 8 Hz), 34.7 (d, CH, J = 6 Hz), 27.9 (d, CH, J = 6 Hz) ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, H_3PO_4): δ= −97.4 (t, J = 194 Hz) ppm.

*1-Diamantyldimethylphosphazo-p-nitrobenzene (**32**).* **32** was prepared as described above (procedure for **30**) from **31** in 96% yield (0.357 g) as yellow solid. Mp 162−164 °C (cyclohexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.0 (d, 2H, J = 8 Hz), 6.52 (d, 2H, J = 8 Hz), 2.63 (AB, 2H, J_{AB} = 16 Hz), 2.15 (bs, 2H), 2.0 (bs, 1H), 1.9 (bs, 2H), 1.81−1.62 (m, 16H), 1.50 (AB, 2H, J_{AB} = 16 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2 (C), 128.3 (CH), 125.9 (d, CH, J = 1 Hz), 121.1 (d, CH, J = 18 Hz), 43.4 (d, C, J = 63 Hz), 39.0 (CH_2), 38.6 (d, CH, J = 9 Hz), 38.5 (CH_2), 37.5 (d, CH, J = 11 Hz), 37.3 (d, CH_2, J = 13 Hz), 37.0 (d, CH, J = 2 Hz), 33.8 (CH_2), 26.1 (d, CH, J = 10 Hz), 24.9 (CH), 12.1 (d, CH_3, J = 61 Hz) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, H_3PO_4): δ 26.0 ppm. HRMS (EI): m/z [M]$^+$ calcd for $C_{22}H_{29}N_2O_2P$: 384.1967; found: 384.1957.

*4,9-Diamantyldiphosphine (**33**).* 4,9-Bis(dichlorophosphoryl)-diamantane (**13**) (0.051 g, 0.12 mmol) was placed in a 5 mL flask under argon and dissolved in 0.5 mL dry THF. The obtained solution was cooled to −60 °C, and 0.30 mL $LiAlH_4$ (1 M in THF, 2.5 equiv) was added dropwise for 15 min. The mixture was stirred at −20 °C for 1 h and at −10 °C for 4 h. The reaction was quenched with HCl 15% (0.1 mL) followed by extraction with cold dichloromethane (3 × 3 mL) and drying over $MgSO_4$ under argon. The solvent was removed in vacuo, affording 4,9-diphosphinodiamantan (0.029 g, 85%) as a white powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.72 (d, 2H, J_{P-H} = 195 Hz), 1.77 (s, 12H), 1.72 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 45.2 (s, CH_2), 37.0 (s, CH), 26.9 (s, C) ppm. ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ= −85.4 ppm. HRMS (EI): m/z [M + H] $^+$ calcd for $C_{14}H_{23}P_2$ 253.1270; found: 253.1259.

*3-Phosphinoadamantan-1-ol (**34**) and (3-Hydroxyadamant-1-yl)phosphine Oxide (**35**).* (3-Hydroxyadamant-1-yl)phosphonic dichloride (**17**) (0.054 g, 0.2 mmol) was placed in a 5 mL flask under argon. Thereafter, dry THF (1 mL) was added. The solution was cooled to −78 °C, and $LiAlH_4$ solution (1 mL, 1 M in THF, 1 mmol, 5 equiv) was slowly added at −78 °C. The colorless solution was stirred for 4 h at −78 °C and for 1 h at rt. Distilled water (1 mL) was added followed by extraction with DCM (total 10 mL) and drying over $MgSO_4$. The solvent was evaporated to yield white air-sensitive solid compound **34** (0.034 g, 92%) that was stored under argon. When put in contact with air for 5 min, the product was quantitatively oxidized into (3-hydroxyadamant-1-yl)phosphine oxide **35**.

*3-Phosphinoadamantan-1-ol (**34**).* ^{1}H NMR (600 MHz, 300 K, C_6D_6): δ 2.70 (d, J(H,P) = 188 Hz, 2H), 1.91−1.83 (m, 2H), 1.59 (d, J = 4.2 Hz, 2H), 1.53−1.4 (m, 8H), 1.32−1.23 (m, 2H), 1.16 (s, 1H, OH) ppm. ^{13}C NMR (150 MHz, 300 K, C_6D_6): δ 67.8 (d, J(C,P) = 8.7 Hz, C_q), 52.8 (d, J(C,P) = 7.8 Hz, CH_2), 44.3 (s, CH_2), 43.6 (d, J(C,P) = 8.8 Hz, CH_2), 35.0 (s, CH_2), 31.6 (d, J(C,P) = 8.4 Hz, CH), 31.5 (d, J(C,P) = 4.8 Hz, C_q) ppm. ^{31}P NMR (243 MHz, 300 K, C_6D_6): δ= −85.97 (t, ^1J(P,H) = 188.5 Hz) ppm.

*(3-Hydroxyadamant-1-yl)phosphine Oxide (**35**).* ^{1}H NMR (600 MHz, 300 K, $CDCl_3$): δ 7.15 (d, J(H,P) = 452.8 Hz, 2H), 2.40−2.34 (m, 2H), 1.95−1.67 (m, 13H) ppm. ^{13}C NMR (150 MHz, 303 K, $CDCl_3$): δ 67.7 (d, J(C,P) = 15.7 Hz, C_q), 44.5 (s, CH_2), 42.1 (s, CH_2), 36.8 (d, J(C,P) = 72.7 Hz, C_q), 35.1 (d, J(C,P) = 2.2 Hz, CH_2), 33.6 (s, CH_2), 30.0 (d, J(C,P) = 13.4 Hz, CH) ppm. ^{31}P NMR (243 MHz, 303 K, $CDCl_3$): δ 25.71 (t, ^1J(P,H) = 452.8 Hz) ppm.

*9-Phosphinodiamantan-4-ol (**36**).* 9-Hydroxydiamant-4-yl phosphonic dichloride (**14**) (0.050 g, 0.16 mmol) was placed in a 5 mL two-neck flask under argon and cooled to a temperature between −78 and −60 °C while 0.5 mL dry THF was added. The $LiAlH_4$ solution (0.19 mL, 1 M in THF, 0.2 mmol, 1.3 equiv) was added dropwise for 10 min. The mixture was stirred at −10 °C for 5 h. The reaction was quenched with HCl (5%, 0.5 mL) followed by extraction with cold dichloromethane (3 × 3 mL) and drying over $MgSO_4$. The solvent was removed in vacuo, affording 9-phosphinodiamantan-4-ol (**36**) (0.028 g, 76%) as a white powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.68 (d, 2H, J_{P-H} = 192.85 Hz), 1.93−1.86 (m, 3H), 1.82−1.78 (m, 6H), 1.77−1.71 (m, 3H), 1.71−1.67 (m, 6H), 1.52 (br, 1H, OH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 67.3 (s, C), 45.3 (s, CH_2), 44.6 (d, CH_2, J = 8.75 Hz), 38.7 (s, CH), 37.1 (d, CH, J = 8.75 Hz), 26.9 (d, C, J = 2.5 Hz) ppm. ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ= −85.7 ppm. HRMS (EI): m/z [M] $^+$ calcd for $C_{14}H_{21}OP$ 236.1330; found: 236.1340.

*(9-Chlorodiamant-4-yl)phosphine (**37**).* (9-Chlorodiamant-4-yl)-phosphonic dichloride (**12**) (0.051 g, 0.15 mmol) was placed in a 5 mL flask under argon and dissolved in 0.5 mL of dry THF. The obtained clear solution was cooled to −40 °C, and 0.15 mL $LiAlH_4$ (1 M in THF, 1.2 equiv) was added dropwise for 10 min. The mixture was stirred at −10 °C for 4.5 h. The reaction was quenched with HCl (5%, 0.5 mL) followed by extraction with cold dichloromethane (3 × 3 mL) and drying over $MgSO_4$. The solvent was removed in vacuo, affording (9-chlorodiamant-4-yl)phosphine (**37**) (0.030 g, 79%) as a white powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.70 (d, 2H, J_{P-H} = 192 Hz), 2.12−2.11 (m, 6H), 1.89 (br s, 3H), 1.82 (br s, 3H), 1.80−1.78 (m, 6H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 67.3 (s, C), 47.7 (s, CH_2), 44.4 (d, CH_2, J = 9 Hz), 39.5 (s, CH), 36.6 (d, CH, J = 7.5 Hz), 26.6 (s, C) ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): −85.9 ppm. HRMS (EI): m/z [M + O + Na] $^+$ calcd for $C_{14}H_{20}ClNaOP$ 293.0833; found: 293.0832.

*4-Diamantylphenylphosphine (**38**).* **38** was isolated in 85% yield as a white solid using the general procedure for the preparations of diamondoid phosphines in benzene/ether. Mp 96−98 °C. ^{1}H NMR (600 MHz, 223 K, $CDCl_3$): δ 7.50−7.40 (m, 2H), 7.30−7.23 (bs, 3H), 3.87 (d, 1H, J_{P-H} = 218 Hz), 1.80−1.71 (bs, 5H), 1.70−1.56 (m, 14H) ppm. ^{13}C NMR (150 MHz, 248 K, $CDCl_3$): δ 135.5 (d, CH, J = 14 Hz), 132.2 (d, C, J = 12 Hz), 128.1 (CH), 127.8 (d, CH, J = 6 Hz), 42.2 (d, CH_2, J = 9 Hz), 38.2 (d, CH, J = 8 Hz), 37.7 (CH_2), 36.2 (CH), 25.4 (CH) ppm. ^{31}P NMR (243 MHz, $CDCl_3$, H_3PO_4): δ= −8.6 (bs, 293 K, d, J = 216.6 Hz, 243 K) ppm. HRMS (EI): m/z [M] $^+$ calcd for $C_{20}H_{25}P$: 296.1694; found: 296.1692.

*1-Diamantylphenylphosphine (**39**).* **39** was isolated in 75% yield as a colorless solid using the general procedure for the preparations of diamondoid phosphines in benzene/ether. Mp 147−148 °C. ^{1}H NMR (400 MHz, 253 K, $CDCl_3$): δ 7.42 (m, 2H), 7.31 (m, 3H), 4.10 (d, 1H, J_{P-H} = 144 Hz), 2.62 (AB, 2H, J_{AB} = 12 Hz), 1.82−1.71 (m, 4H), 1.70−1.43 (m 17H), ppm. ^{13}C NMR (100 MHz, 253 K, $CDCl_3$): δ 135.8 (d, CH, J = 10 Hz), 133.1 (d, C, J = 11.5 Hz), 128.1 (CH), 127.9 (d, CH, J = 4.8 Hz), 43.8 (d, CH_2, J = 1.8 Hz), 39.7 (d, CH, J = 3 Hz), 39.3 (d, C, J = 9 Hz), 38.9 (d, CH_2, J = 1.8 Hz), 38.8 (d, CH, J = 9 Hz), 38.6 (d, CH, J = 2 Hz), 38.3 (CH_2), 38.2 (d, CH, J = 5 Hz), 37.9 (CH_2), 37.7 (CH_2), 37.2 (d, CH, J = 4 Hz), 33.9 (d, CH_2, J = 5.5 Hz), 33.6 (d, CH_2, J = 5.5 Hz), 27.3 (d, CH, J = 3 Hz), 26.3 (CH) ppm. ^{31}P NMR (162 MHz, 253 K, $CDCl_3$, H_3PO_4, 235 K): δ= −24.0 (d, J = 144 Hz) ppm. HRMS (EI): m/z [M]$^+$ calcd for $C_{20}H_{25}P$: 296.1694; found: 296.1702.

*Tribenzyl(9-hydroxydiamantan-4-yl)phosphonium Bromide (**40**).* 9-Phosphinodiamantan-4-ol (**36**) (0.050 g, 0.21 mmol) and dry

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toluene (2 mL) were placed under argon in a 5 mL flask equipped with a reflux system. Benzyl bromide (0.06 mL, 0.50 mmol, 2.4 equiv) was slowly added at rt. The resulting colorless solution was heated at 100 °C for 16 h; a white precipitate formed, which was filtered and rinsed with toluene and diethyl ether and dried in air. Purification by column chromatography on silica gel with eluent diethyl ether:-methanol (3:1) gave tribenzyl(9-hydroxydiamantan-4-yl)phosphonium bromide (**40**). The crystals were grown in ethanol (0.020 g, 16%); the X-ray structure is available in the Supporting Information, page S165. ^{1}H NMR (600 MHz, 300 K, CD_3OD) δ 7.43−7.37 (m, 9H), 7.22−7.17 (m, 6H), 3.84 (d, J = 13.3 Hz, 6H), 1.99−1.94 (m, 6H), 1.94−1.90 (m, 3H), 1.88−1.83 (m, 3H), 1.69 (d, J = 2.7 Hz, 6H) ppm. ^{13}C NMR (150 MHz, 300 K, CD_3OD): δ 132.1 (d, J(C,P) = 4.8 Hz, CH), 130.7 (d, J(C,P) = 2.3 Hz, CH), 129.8 (d, J(C,P) = 3.1 Hz, CH), 129.7 (d, J(C,P) = 8.2 Hz, Cq), 66.9 (s, Cq), 45.3 (s, CH_2), 39.4 (s, CH), 36.8 (d, J(C,P) = 10.3 Hz, CH), 35.5 (s, CH_2), 25.1 (d, J(C,P) = 41.3 Hz, CH_2) ppm. ^{31}P{^{1}H} NMR (243 MHz, 300 K, CD_3OD): δ 27.51 ppm.

*1-Adamantyldiphenylphosphine Oxide (**41**).* 1-Adamantylphosphonic dichloride (**16**) (1.01 g, 4 mmol) and 15 mL of freshly distilled dry THF were placed under argon in a 50 mL flask equipped with a reflux system. The mixture was cooled to −78 °C; phenyllithium (5.0 mL, 1.8 M in dibutyl ether, 9 mmol, 2.25 equiv) was slowly added with a syringe, and the solution was stirred for 30 min at the same temperature, for 40 min at rt, and for 24 h at 60 °C. Distilled water (10 mL) was added, and the water phase was extracted with diethyl ether (3 × 20 mL) and DCM (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was evaporated to yield the crude product. Purification by column chromatography on silica gel was performed first with pentane as the eluent and then with diethyl ether:ethanol (9:1). A second column chromatography on silica gel was done with diethyl ether:methanol (9:1) but failed to remove all of the impurities. The fractions containing the product were then recrystallized from warm methanol (60 °C) to give pure 1-adamantyldiphenylphosphine oxide (**41**) (0.772 g, 57%). The X-ray structure is available in the Supporting Information, page S170. ^{1}H NMR (400 MHz, 296 K, $CDCl_3$): δ 8.06−7.91 (m, 4H), 7.63−7.43 (m, 6H), 2.03−1.88 (m, 9H), 1.80−1.60 (m, 6H) ppm. ^{13}C NMR (100 MHz, 300 K, $CDCl_3$): δ 132.4 (d, J(C,P) = 7.9 Hz, CH), 131.5 (d, J(C,P) = 2.6 Hz, CH), 130.8 (d, J(C,P) = 90.0 Hz, C_q), 128.4 (d, J(C,P) = 10.9 Hz, CH), 37.2 (d, J(C,P) = 72.5 Hz, C_q), 36.6 (d, J(C,P) = 1.3 Hz, CH_2), 35.5 (d, J(C,P) = 1.8 Hz, CH_2), 27.7 (d, J(C,P) = 10.3 Hz, CH) ppm. ^{31}P{^{1}H} NMR (162 MHz, 296 K, $CDCl_3$, H_3PO_4 external standard): δ 34.30 ppm. HRMS (EI): m/z [M] $^{+}$ calcd for $C_{22}H_{25}PO$: 336.1643; found: 336.1640. Anal. calcd for $C_{22}H_{25}PO$: C, 78.55; H, 7.49, found: C, 78.44; H, 7.58.

*(3-Hydroxyadamant-1-yl)diphenylphosphine Oxide (**42**).* (3-Hydroxyadamant-1-yl) phosphonic dichloride (**17**) (0.269 g, 1 mmol) and fresh distilled dry THF (9 mL) were placed under argon in a two-neck 25 mL flask cooled to −78 °C. Phenyllithium (1.8 mL, 1.8 M in dibutylether, 3.3 mmol, 3.25 equiv) was slowly added with a syringe. The mixture was stirred for 1 h at −78 °C and further for 18 h at rt. Distilled water (4.5 mL) was added, and the water phase was extracted with diethyl ether (30 mL) and DCM (30 mL). The combined organic phases were dried over $MgSO_4$; the solvent was evaporated, and the crude compound (0.302 g) was obtained. It was recrystallized from DCM/hexane to obtain crystals of **42** (0.269 g, 76%). The X-ray structure is available in the Supporting Information, page S174. ^{1}H NMR (600 MHz, 294 K, $CDCl_3$): δ 7.98−7.93 (m, 4H), 7.56−7.51 (m, 2H), 7.51−7.45 (m, 4H), 2.28−2.21 (m, 2H), 1.96 (s, 1H, OH), 1.89 (d, J = 5.4 Hz, 2H), 1.87−1.75 (m, 4H), 1.66 (AB_q, $\Delta\delta_{AB}$ = 0.03, J_{AB} = 12 Hz, 4H), 1.55 (s, 2H) ppm. ^{13}C NMR (150 MHz, 294 K, $CDCl_3$): δ 132.4 (d, J(C,P) = 8.4 Hz, CH), 131.7 (d, J(C,P) = 2.9 Hz, CH), 130.3 (d, J(C,P) = 91.1 Hz, C_q), 128.5 (d, J(C,P) = 11.1 Hz, CH), 68.1 (d, J(C,P) = 12.5 Hz, C_q), 44.4 (s, CH_2), 43.1 (s, CH_2), 40.4 (d, J(C,P) = 72.0 Hz, C_q), 35.1 (s, CH_2), 34.3 (s, CH_2), 30.3 (d, J(C,P) = 11.3 Hz, CH) ppm. ^{31}P{^{1}H} NMR (243 MHz,294 K, $CDCl_3$): δ 32.38 ppm.

*4-Diamantyldiphenylphosphine Oxide (**43**).* 4-Diamantylphosphonic dichloride (**19**) (0.122 g, 0.4 mmol) and 1.5 mL of fresh distilled dry THF were placed under argon in a 5 mL flask. The mixture was cooled to −78 °C, and phenyllithium (0.5 mL, 1.8 M in dibutyl ether, 0.9 mmol, 2.25 equiv) was slowly added with a syringe. The mixture was stirred for 4 h at the same temperature and for 42 h at rt. Distilled water (1 mL) was added followed by saturated NH_4Cl (3 mL) and diethyl ether (10 mL). The water phase was extracted with diethyl ether (2 × 10 mL) and dichloromethane (3 × 10 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was evaporated. It was recrystallized from warm methanol (60 °C) to yield pure 4-diamantyldiphenylphosphine oxide (**43**) (0.042 g, 31%). The X-ray structure is available in the Supporting Information, page S180. ^{1}H NMR (400 MHz, 295 K, $CDCl_3$): δ 8.03−7.91 (m, 4H), 7.58−7.42 (m, 6H), 2.00−1.85 (m, 6H), 1.80 (br s, 3H), 1.75 (m, 1H), 1.72−1.55 (m, 9H) ppm. ^{13}C NMR (100 MHz, 296 K, $CDCl_3$): δ 132.4 (d, J(C,P) = 8.1 Hz, CH), 131.6 (d, J(C,P) = 2.6 Hz, CH), 130.7 (d, J(C,P) = 73.1 Hz, C_q), 128.4 (d, J(C,P) = 10.8 Hz, CH), 37.7 (d, J(C,P) = 1.5 Hz, CH_2), 36.8 (d, J(C,P) = 11.3 Hz, CH), 36.4 (s, CH_2), 35.2 (d, J(C,P) = 72.8 Hz, C_q), 25.48 (s, CH) ppm. ^{31}P{^{1}H} NMR (162 MHz, 296 K, $CDCl_3$, H_3PO_4 external standard): δ 35.02 ppm. HRMS (EI): m/z: [M]$^{+}$ calcd for $C_{26}H_{29}OP$: 388.1956; found: 388.1949.

*(9-Hydroxydiamant-4-yl)diphenylphosphine Oxide (**44**).* (9-Hydroxydiamant-4-yl) phosphonic dichloride (**14**) (0.161 g, 0.5 mmol) and 4.5 mL of freshly distilled dry THF were placed under argon in a 50 mL two-neck flask. It was cooled to −78 °C, and phenyllithium (0.9 mL, 1.8 M in dibutyl ether, 1.6 mmol, 3.25 equiv) was slowly added with a syringe. The mixture was stirred for 1 h at the same temperature and for 18.5 h at rt. Distilled water (4 mL) was added, and the water phase was extracted with diethyl ether (40 mL) and DCM (40 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was evaporated. Recrystallization from warm MeOH at 60 °C yielded crystals that were rinsed with cold MeOH to obtain pure colorless crystals of **44** (0.019 g, 10%). The X-ray structure is available in the Supporting Information, page S186. ^{1}H NMR (400 MHz, 270 K, $CDCl_3$): δ 8.20−7.86 (m, 4H), 7.71−7.42 (m, 6H), 2.05 (br s, OH), 2.01−1.92 (m, 6H), 1.88 (br s, 3H), 1.81 (br s, 3H), 1.77−1.59 (m, 6H) ppm. ^{13}C NMR (100 MHz, 270 K, $CDCl_3$): δ 132.4 (d, J(C,P) = 8.1 Hz, CH), 131.9 (d, J(C,P) = 2.5 Hz, CH), 128.5 (d, J(C,P) = 11.0 Hz, CH), 67.1(s, C_q), 45.1 (s, CH_2), 38.8 (s, CH), 35.7(d, J(C,P) = 11.2 Hz, CH), 35.4 (s, CH_2) ppm. ^{31}P{^{1}H} NMR (162 MHz, 270 K, $CDCl_3$): δ 35.96 ppm. HRMS (EI): m/z [M] $^{+}$ calcd for $C_{26}H_{29}O_2P$: 404.1905; found: 404.1901.

*1-Adamantyldiphenylphosphine Sulfide (**46**).* First step: In a two-neck flask containing 20 mL of dry THF and lithium (0.240 g), distilled chlorodiphenylphosphine (0.9 mL, 5 mmol) was added under argon, and the mixture was stirred at rt for 19 h. The remaining Li was removed with forceps. Second step:1-Bromoadamantane (**45**) (1.08 g, 5 mmol, 1 equiv) in dry THF (10 mL) was added into the reaction mixture over 20 min at −78 °C and stirred for 2 h at the same temperature and for 5 days at rt. Third step: Sulfur powder (0.160 g, 5 mmol, 1 equiv) was added at rt, and the solution was stirred under argon for 3 h. The solvent was evaporated, and diethyl ether (60 mL) was added followed by distilled water. The mixture was extracted three times with DCM and dried over $MgSO_4$ and, after solvent evaporation, yielded white crystals (0.793 g, 45%). Note: using sodium (first step lasting 2.5 days) yielded 18% (0.317 g) of **46**. The X-ray structure is available in the Supporting Information, page S191. ^{1}H NMR (300 MHz, 300 K, $CDCl_3$): δ 8.12−7.99 (m, 4H), 7.55−7.39 (m, 6H), 2.08−1.95 (m, 9H), 1.76−1.59 (m, 6H) ppm. ^{13}C NMR (75 MHz, 300 K, $CDCl_3$): δ 133.5 (d, J(C,P) = 8.9 Hz, CH), 131.3 (d, J(C,P) = 2.9 Hz, CH), 130.4 (d, J(C,P) = 73.1 Hz, C_q), 128.2 (d, J(C,P) = 11.2 Hz, CH), 39.2 (d, J(C,P) = 50.2 Hz, C_q), 36.4 (s, CH_2), 28.2 (d, J(C,P) = 10.6 Hz, CH) ppm. ^{31}P NMR (121 MHz, 300 K, $CDCl_3$, H_3PO_4 external standard): δ 56.33 (t, ^{1}J(P,C) = 35.7 Hz) ppm. HRMS (EI): m/z [M] $^{+}$ calcd for $C_{22}H_{25}PS$: 352.1415; found: 352.1410. Anal. calcd for $C_{22}H_{25}PS$: C, 74.97; H, 7.15. found: C, 74.89; H, 7.06.

*1-Adamantyldiphenylphosphine Selenide (**47**).* First step: In a two-neck flask containing dry THF (20 mL) and lithium (0.090 g), distilled chlorodiphenylphosphine (0.9 mL, 5 mmol) was added under argon, and the mixture was stirred at rt for 17 h. The remaining Li was

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removed with forceps. Second step: 1-Bromoadamantane (**45**) (5 mmol, 1.08 g, 1 equiv) in 20 mL of dry THF was added into the reaction mixture over 20 min at −78 °C and stirred for 1 h at the same temperature and for 7 days at rt. Third step: Selenium powder (0.395 g, 5 mmol) was added at rt, and the mixture was stirred under argon for 3 h. The solvent was evaporated; distilled water was added, and it was then extracted with DCM, dried over $MgSO_4$, and filtered. The solvent was evaporated to afford 1.95 g of yellow oil. Diethyl ether (5 mL) was added, and the resulting white solid was separated, rinsed with pentane, and dried in air (0.679 g, 34%). ^{1}H NMR (300 MHz, 297 K, $CDCl_3$): δ 8.10−7.96 (m, 4H), 7.55−7.38 (m, 6H), 2.09−1.96 (m, 9H), 1.76−1.59 (m, 6H) ppm. ^{13}C NMR (75 MHz, 297 K, $CDCl_3$): δ 134.1 (d, J(C,P) = 8.9 Hz, CH), 131.3 (d, J(C,P) = 2.9 Hz, CH), 129.3 (d, J(C,P) = 65.7 Hz, C_q), 128.2 (d, J(C,P) = 11.3 Hz, CH), 38.7 (d, J(C,P) = 40.6 Hz, C_q), 36.9 (s, CH_2), 36.4 (s, CH_2), 28.3 (d, J(C,P) = 10.4 Hz, CH) ppm. ^{31}P NMR (121 MHz, 297 K, $CDCl_3$, H_3PO_4 external standard): δ 53.66 (t, ^1J(P,Se) = 712.3 Hz) ppm.

*1-Adamantyldiphenylphosphine (**48**).* Method A: 1-Adamantyldiphenylphosphine sulfide (**46**) (0.053 g, 0.15 mmol), $LiAlH_4$ (0.017 g, 0.45 mmol, 3 equiv), and dry 1,4-dioxane (6 mL) were placed under argon in a Schlenk tube equipped with a reflux system, and the mixture was refluxed for 24 h. The reaction mixture was cooled and filtered under argon and rinsed with dry 1,4-dioxane (3 mL), and the solvent was evaporated. A very air-sensitive white solid was obtained (0.029 g, 60%). Any contact with air oxidizes **48** to 1-adamantyldiphenylphosphine oxide (**41**). Method B: 1-Adamantyldiphenylphosphine selenide (**47**) (0.060 g, 0.15 mmol), $LiAlH_4$ (0.017 g, 0.45 mmol, 3 equiv), and dry 1,4-dioxane (6 mL) were placed under argon in a Schlenk tube equipped with a reflux system, and the mixture was refluxed for 24 h. The reaction mixture was cooled, filtered under argon, rinsed with dry 1,4-dioxane (3 mL), and the solvent was evaporated. A very air-sensitive white solid **48** was obtained (0.029 g, 60%). Any contact with air oxidizes **48** to 1-adamantyldiphenylphosphine oxide (**41**). ^{1}H NMR (400 MHz, 270 K, $CDCl_3$): δ 7.66−7.57 (m, 4H), 7.39−7.30 (m, 6H), 1.99−1.91 (m, 3H), 1.88−1.79 (t, 6H), 1.75−1.61 (m, 6H) ppm. ^{13}C NMR (100 MHz, 270 K, $CDCl_3$): δ 135.7 (d, J(C,P) = 17.5 Hz, C_q), 135.1 (d, J(C,P) = 20.0 Hz, CH), 128.6 (s, CH), 128.1 (d, J(C,P) = 7.2 Hz, CH), 39.9 (d, J(C,P) = 11.3 Hz, CH_2), 36.9 (s, CH_2), 34.6 (d, J(C,P) = 14.2 Hz, C_q), 28.8 (d, J(C,P) = 9.0 Hz, CH) ppm. ^{31}P NMR (162 MHz, 270 K, $CDCl_3$): δ 16.25 ppm.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01219.

Copies of NMR spectra and VT-NMR data, X-ray crystallographic data, and optimized geometries given in Carthesian coordinates (PDF)

CIF files of the compounds (ZIP)

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Notes

The authors declare no competing financial interest.

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