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P-Stereogenic diamondoid phosphines

Despite diamondoid phosphines have found many synthetic applications and are even available commercially the chemistry of chiral diamondoid phosphines remains largely unexplored.

Aim. To develop the convenient preparative method for the preparation of sterically-congested *P*-stereogenic secondary diamodoidyl phosphines as potential organocatalysts and ligands in the asymmetric synthesis.

Results and discussion. A convenient method for the synthesis of *P*-stereogenic diamondoid phosphines with high yields through the phosphorylation of hydroxydiamondoids in trifluoroacetic acid followed by the reduction of the corresponding asymmetric chlorophosphonates has been proposed. The secondary phosphines obtained form stable complexes with borane that can be used to separate diamondoid phosphines into enantiomers.

Experimental part. The experimental procedures for the preparation of 1- and 4-diamantyl-1-adamantyl- and phenylphosphines were developed; the structures of new compounds were confirmed by NMR and HRMS spectral data.

Conclusions. A number of *P*-stereogenic mixed diamondoidylaryl phosphines and the secondary phosphines containing exclusively diamondoid substituents has been prepared. A degree of steric bulkiness is determined by the combination of diamondoid substituents around a phosphorus atom where 1-diamantyl derivatives are the most sterically-congested. The compounds obtained are potential ligands in asymmetric catalysis.

Key words: phosphine borane complexes; 1-adamantyldiamantylphosphine; 4-adamantyldiamantylphosphine; 1-phenyldiamantylphosphine; 4-phenyldiamantylphosphine; *P*-stereogenic phosphines

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P-стереогенні діамандоїдні фосфіни

Незважаючи на те, що діамандоїдні фосфіни широко використовуються в органічному синтезі і навіть доступні комерційно, хімія хіральних діамандоїдних фосфінів залишається не дослідженою.

Мета. Розробити зручний препаративний метод синтезу стереоускладнених *P*-стереогенних вторинних діамандоїдних фосфінів, які можуть бути використані як ліганди в асиметричному синтезі, а також як органокаталізатори.

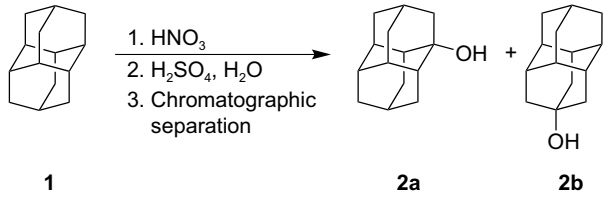
Результати та їх обговорення. Запропоновано зручний метод синтезу *P*-стереогенних діамандоїдних фосфінів шляхом фосфорилювання гідроксипохідних діамандоїдів у трифторацтовій кислоті з подальшим відновленням відповідних асиметричних хлорофосфонатів з високими виходами. Одержані таким чином фосфіни утворюють стійкі комплекси з бораном, які розглядаються як проміжні сполуки для подальшого розділення енантіомерів.

Експериментальна частина. Був розроблений препаративний метод синтезу 1- і 4-діамантил-, 1-адамантил- і фенілфосфінів, структури яких підтверджено мас-спектрометричними і ЯМР-спектральними даними.

Висновки. Одержано ряд *P*-стереогенних змішаних діамандоїларилфосфінів та вторинних фосфінів, які містять виключно діамандоїдні замісники. Ступінь стеричного навантаження сполук визначається комбінацією діамандоїдних замісників навколо атома фосфору, де похідні 1-діамантилу найбільш стерично ускладнені. Одержані сполуки є потенційними лігандами в асиметричному каталізі.

***Ключові слова*:** боранові комплекси фосфінів; 1-адамантилдіамантилфосфін; 4-адамантилдіамантилфосфін; 1-фенілдіамантилфосфін; 4-фенілдіамантилфосфін; *P*-стереогенні фосфіни

Organophosphorus compounds are among useful ligands in catalysts where further progress is largely associated with *P*-stereogenic phosphines as stated by W. Knowles in his Nobel Lecture: "*...if one wanted to get high values, the asymmetry would have to be directly on the phosphorus*" [1]. Accordingly, over the last decades many chiral tertiary phosphines trademarked as Quinox-P®, Benz-P®, Pincer-P®, and some others [2] become available commercially. These ligands allow obtaining high yields and enantiomeric



Scheme 1. The synthesis of 1- and 4-hydroxydiamantanes

excesses of products in various transformations involving hydroacylations [3, 4], catalytic asymmetric hydrogenations [5, 6] and many others [7].

Achiral bulky diadamantyl alkyl phosphines have been introduced as effective ligands where $Ad_2P(n\text{Bu})$ and Ad_2PBn are now commercially available as cataCXiumA and cataCXiumABn, respectively. The palladium complex with $Ad_2P(n\text{Bu})$ as a ligand acts as a highly efficient catalyst in Suzuki reactions for aryl chlorides [8], in the arylation reactions [9], in Buchwald–Hartwig coupling [10] and for the arylations of ketones [11]. The Na_2PdCl_4/Ad_2PBn system has been successfully applied for the Sonogashira coupling [12]. Extremely bulky Ad_3P in the presence of palladium acetate was recently used as a catalyst for the arylation of unsaturated cyclic ketoethers [13]. The chemistry of chiral diamondoid phosphines still remains almost unexplored. Only recently the rhodium complex of di-1-adamantylphosphino-(*tert*-butylmethylphosphino)methane (BulkyP®*) was prepared and tested as a ligand for Rh-promoted asymmetric hydrogenations of functionalized alkenes where effective transformations were achieved under very low catalyst loadings (< 0.001 mol%) [14].

All above makes important the preparation of *P*-stereogenic diamondoid phosphines since the incorporation of bulky substituents into phosphine may enhance the catalytic activity and selectivity of the catalyst. Previously, we prepared a number of *P*-stereogenic mixed diamondoidylaryl phosphines [15]. In this paper we present the preparation of the secondary diamondoid phosphines with the potential as ligands in asymmetric catalysis.

Results and discussion

The aim of this work was to develop a preparative method for the synthesis of chiral bulky phosphines containing phenyl, adamantyl, and diamantyl groups. The key starting compounds – 1-hydroxydiamantane **2a** and 4-hydroxydiamantane **2b** were prepared from diamantane **1** through the nitroxylation with the concentrated nitric acid and further acidic hydrolysis as previously described [16] (Scheme 1).

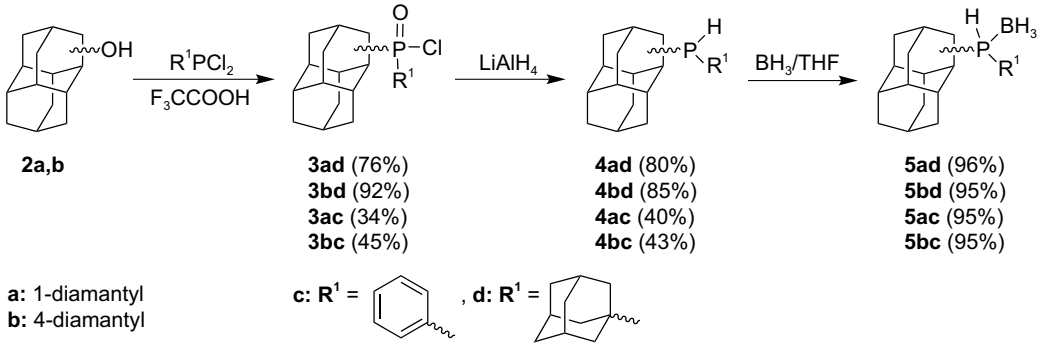
Hydroxydiamantanes **2a,b** were converted to the corresponding chlorophosphonates **3ad**, **3bd**, **3ac**, and **3bc** through the phosphorylation reaction in trifluoroacetic acid [17, 18] utilizing $PhPCl_2$ and $AdPCl_2$ as phosphorylating agents (Scheme 2). Chlorophosphonates **3ad, 3bd, 3ac,** and **3bc** were further reduced with $LiAlH_4$ in tetrahydrofuran to give phosphines **4ad, 4bd, 4ac**, and **4bc**. Stability towards oxygen is an important factor that determines the practical potential of phosphine ligands. In contrast to the primary diamondoid phosphines that were reactive towards oxygen, the secondary diamondoid phosphines even with one diamantyl group (**4ac** and **4bc)** were quite persistent towards oxidation. Nevertheless, for purifications *via* column chromatography phosphines **4ad, 4bd, 4ac**, and **4bc** were converted into boron complexes **5ad, 5bd, 5ac,** and **5bc** in the BH_3/THF system.

The structures of the phosphines obtained were proven by a number of spectral characteristics. The ^{13}C NMR DEPT 135 spectrum of 4-diamantyl-1-adamantylphosphine borane **5bd** contained four CH_2, four CH, and two C resonances. It agrees with the axial symmetry of diamondoid fragments. In contrast, the ^{13}C NMR spectrum of **5ad** contained ten resonances of the prochiral 1-diamantyl moiety due to the presence of the chiral *P*-center in the structure. The NMR spectra of complexes **5ac** and **5bc** displayed a dynamic behavior and were measured under cooling.

The borane protecting group can further be removed either by the treatment with excess of diethylamine [19] or, more conveniently, using pyrrolidine [20] under mild reaction conditions that retain the absolute configuration of the *P*-stereogenic center.

Experimental part

NMR spectra were recorded on a Bruker Avance III spectrometer at 400 and 600 MHz (for ^1H, the frequencies for ^{13}C and ^{31}P NMR are specified below)



Scheme 2. The synthesis of borane complexes of 1- and 4-diamantyl-1-adamantyl phosphines and 1- and 4-diamantylphenyl phosphines

with TMS (^{1}H and ^{13}C) and H_3PO_4 (^{31}P) as internal standards. High-resolution mass spectra (HRMS) were recorded using an ESI-MS Bruker Mikro-TOF spectrometer. Products were purified by chromatography on 100–160 mesh silica gel. Commercially available reagents (Aldrich) and solvents were used after standard purification procedures. Melting points were measured in sealed capillaries on Krüss KSP1N.

The synthesis of 1-adamantyl-*P,P*-dichlorophosphine. To the mixture of adamantane (100.0 g, 0.735 mol) and anhydrous $AlCl_3$ (120.3 g, 0.904 mol) in a 1000 mL Schlenk flask add 100 mL (1.14 mol) of PCl_3 *via* a syringe, and reflux the reaction mixture for 3.5 h at 75–80 °C. Add pyridine (116.0 g, 1.48 mol) dropwise, reflux the mixture for additional 0.5 h. Cool the mixture, add 200 mL of heptane, and reflux the suspension for 15 min, cool to the room temperature, decant the solvent (repeat the operation 3 times). Evaporate the combined heptane extracts under vacuum. Vacuum distillation ($5\cdot10^{-3}$ mbar, b.p. 75 °C) gave $AdPCl_2$ as a white solid. ^{31}P NMR (162 MHz, $CDCl_3$), δ, ppm: 192.1, (lit. 192.1 ppm [21]).

The general procedure for the preparation of chlorophosphonates 3. To the corresponding hydroxydiamantane (2.0 g, 9.8 mmol) and 85 mL of trifluoroacetic acid add $AdPCl_2$ (7.0 g, 30 mmol). Reflux the reaction mixture for 5 h, cool, pour onto ice (200 mL), and filter. Wash the precipitate with water and dry. Purify the crude product by column chromatography on silica (hexane–diethyl ether (2:1)) to give the corresponding diamantyl-1-adamantyl chlorophosphonate as colorless crystals. The NMR spectra of chlorophosphonates **3ac** and **3bc** were identical as previously described [18].

1-Diamantyl-1-adamantylchlorophosphonate 3ad. M. p. 265 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 1.49 (1H, d, *J* = 20 Hz), 1.52 (1H, d, *J* = 20 Hz), 1.63–1.81 (15H, m,), 1.85–2.01 (4H, m), 2.04–2.10 (3H, m), 2.13–2.27 (6H, m), 2.32–2.45 (2H, m), 2.93 (1H, d, *J* = 20 Hz), 3.04 (1H, d, *J* = 20 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ, ppm: 25.0 (CH), 25.8 (CH, d, *J*(C–P) = 12 Hz), 28.1 (CH, d, *J*(C–P) = 11 Hz), 33.0 (CH_2), 34.1 (CH_2), 36.3 (CH_2, d, *J*(C–P) = 1.7 Hz), 36.9 (CH_2, d, *J*(C–P) = 1.9 Hz), 37.1 (CH_2, d, *J*(C–P) = 2.6 Hz), 37.5 (CH, d, *J*(C–P) = 2 Hz), 37.6 (CH_2), 37.8 (CH, d, *J*(C–P) = 12 Hz), 38.6 (CH_2), 38.9 (CH_2), 39.1 (CH, d, *J*(C–P) = 10 Hz), 39.2 (CH, d, *J*(C–P) = 12 Hz), 39.5 (CH), 47.6 (C, d, *J*(C–P) = 56 Hz), 52.5 (C, d, *J*(C–P) = 51 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$), δ, ppm: 87.23. HRMS (EI), m/z: calcd. for $C_{24}H_{34}ClOP$ 404.2036; found 404.2030.

4-Diamantyl-1-adamantylchlorophosphonate 3bd. Yield – 92%. M. p. 285 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 1.69–1.85 (17H, m), 1.86–1.95 (3H, m), 2.05–2.10 (3H, m), 2.15–2.25 (11H, m). ^{13}C NMR (100 MHz, $CDCl_3$), δ, ppm: 25.4 (CH), 27.8 (CH, d, *J*(C–P) = 11 Hz), 36.3 (CH), 36.4 (CH_2), 36.9 (CH_2), 37.0 (CH), 37.5 (CH_2, d, *J*(C–P) = 1.6 Hz), 37.9 (CH_2, d, *J*(C–P) = 1.9 Hz), 43.8 (C, d, *J*(C–P) = 60 Hz), 45.7 (C, d, *J*(C–P) = 60 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$), δ, ppm: 87.0. HRMS (EI), m/z: calcd. for $C_{24}H_{34}ClOP$ 404.2036 [M$^+$]; found 404.2029.

The general procedure for the preparation of phosphine-borane complexes 5. Add the solution of chlorophosphonate **3** (9.6 mmol) in dry THF (20 mL) to $LiAlH_4$ (0.2 g, 5.26 mmol) stirred in dry THF (40 mL). Reflux the reaction mixture for 1–2 h, cool, then add 35% HCl (15 mL), and extract the mixture with chloroform (3×15 mL). Wash the combined extracts with water (10 mL) and dry over Na_2SO_4. After removing the solvent dissolve residue in 20 mL of THF; add slowly the BH_3–THF complex (25 mL, 1.01 M in THF, 25 mmol) at room temperature, and stir the resulting mixture for 2.5 h at this temperature. Remove the solvent in vacuum. Purify the residue by column chromatography on silica (CH_2Cl_2) to give phosphine-borane complex **5** as a colorless solid.

1-Diamantyl-1-adamantylphosphine-borane 5ad. Yield – 96%. M. p. 201–202 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm: 0.25–0.75 (3H, m), 1.12–1.18 (1H, m), 1.21–1.29 (1H, m), 1.50–1.60 (18H, m), 1.75–1.90 (10H, m), 2.00–2.25 (4H, m), 4.8 (1H, d, *J*(P–H) = 354 Hz). ^{13}C NMR (151 MHz, $CDCl_3$), δ, ppm: 25.3 (CH), 25.9 (CH, d, *J*(C–P) = 10 Hz), 28.2 (CH, d, *J*(C–P) = 9 Hz), 32.8 (CH_2), 33.4 (CH_2), 34.8 (C, d, *J*(C–P) = 28 Hz), 36.4 (CH_2), 37.0 (CH), 37.1 (CH_2), 37.6 (CH), 38.0 (CH_2), 38.2 (CH, d, *J*(C–P) = 9 Hz), 38.4 (CH, d, *J*(C–P) = 6 Hz), 38.6 (CH, d, *J*(C–P) = 8 Hz), 38.6 (CH_2), 40.3 (CH_2), 40.3 (CH_2), 41.3 (C, d, *J*(C–P) = 22 Hz). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ, ppm: 11.61 (d, *J*(P–H) = 354 Hz). HRMS (EI), m/z: calcd. for $C_{24}H_{38}BP$ 391.2702 [M+Na]$^+$; found 391.2704.

4-Diamantyl-1-adamantylphosphine-borane 5bd. Yield – 95%. M. p. 226–228 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 0.16–0.83 (3H, m), 1.85–1.70 (19H, m), 2.05–1.90 (15H, m), 3.76 (1H, d, *J*(H–P) = 370 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ, ppm: 25.4 (CH), 28.1 (CH, d, *J*(C–P) = 10 Hz), 32.6 (C, d, *J*(C–P) = 28 Hz), 34.6 (C, d, *J*(C–P) = 2 Hz), 36.4 (CH), 36.4 (CH_2), 37.3 (CH, d, *J*(C–P) = 10 Hz), 37.8 (CH_2, d, *J*(C–P) = 1.4 Hz), 40.0 (CH_2), 40.5 (CH_2). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$), δ, ppm: 39.6 (d, *J*(P–H) = 370 Hz). HRMS (EI), m/z: calcd. for $C_{24}H_{38}BP$ 391.2702 [M+Na]$^+$; found 391.2705.

4-Diamantylphenylphosphine-borane 5bc. Yield – 85%. M. p. 175 °C. ^{1}H NMR (600 MHz, 223 K, $CDCl_3$), δ, ppm: 0.75–1,25 (3H, m), 1.45–1.88 (19H, m), 4.95 (1H, d, *J*(H–P) = 390 Hz), 7.41–7.45 (2H, m), 7.46–7.48 (1H, m), 7.55–7.65 (2H, m). ^{13}C NMR (100 MHz, 248 K, $CDCl_3$, δ, ppm): 25.3 (CH), 29.4 (C, d, *J*(C–P) = 33 Hz), 36.6 (CH_2), 37.0 (CH_2, d, *J*(C–P) = 10 Hz), 37.5 (CH, d, *J*(C–P) < 1 Hz), 38.8 (CH), 123.8 (C, d, *J*(C–P) = 51 Hz), 128.4 (CH, d, *J*(C–P) = 9 Hz), 131.4 (C, d, *J*(C–P) = 8 Hz); 134.2 (CH, d, *J*(C–P) = 8 Hz). ^{31}P{^{1}H} NMR (243 MHz, 245K, $CDCl_3$), δ, ppm: 26.9. HRMS (EI), m/z: calcd. for $C_{20}H_{28}PB$ 310.2022 [M]$^+$; found 310.2025.

1-Diamantylphenylphosphine-borane 5ac. Yield – 75%. M. p. 147–148°C. ^{1}H NMR (400 MHz, 253 K, $CDCl_3$), δ, ppm: 0.20–1.20 (3H, m), 1.55–1.61 (1H, m), 1.70–1.75 (1H, m), 1.75–1.90 (12H, m), 1.91–2.20 (3H, m), 2.30–2.37 (1H, m), 2.49–2.62 (1H, m), 6.09 (1H, d, *J*(H–P) = 390 Hz), 7.45–7.48 (2H, m), 7.52–7.62 (1H, m), 7.85–7.91 (2H, m). ^{13}C NMR (100 MHz, 253 K, $CDCl_3$), δ, ppm: 25.7 (CH), 25.8 (CH, d, *J*(C–P) = 4 Hz), 32.8 (CH_2), 35.5 (CH_2, d, *J*(C–P) = = 10 Hz), 36.2 (CH, d, *J*(C–P) = 6 Hz), 36.6 (CH, d, *J*(C–P) = = 3 Hz), 36.9 (CH), 37.1 (CH_2), 37.4 (CH_2), 37.5 (C), 37.8 (CH, d, *J*(C–P) = 9 Hz), 38.0 (CH, d, *J*(C–P) = 7 Hz), 38.6 (CH_2, d, *J*(C–P) = 2 Hz), 123.9 (C, d, *J*(C–P) = 54 Hz), 128.6 (CH, d, *J*(C–P) = 9.5 Hz), 131.4 (CH, d, *J*(C–P) = 2.5 Hz), 134.6 (CH, d, *J*(C–P) = 7.3 Hz). ^{31}P{^{1}H} NMR (162 MHz, 293 K, $CDCl_3$), δ, ppm: –3.19 (d, *J*(P–H) = 390 Hz). HRMS (EI), m/z: calcd. for $C_{20}H_{28}PB$ 310.2022 $[M]^+$; found 310.2028.

Conclusions

Rigid diamondoidyl groups with controlled bulkiness are a promising building block in asymmetric catalysts. A convenient method for the synthesis of 1- and 4-diamantyl *P*-stereogenic phosphines with high yields from the corresponding chlorophosphonates has been proposed. These compounds with controlled topology are potential ligands for the asymmetric synthesis as organocatalysts. The borane complexes of the secondary diamondoid phosphines are subjected for further enantioseparation through diastereomeric derivatives that is currently underway in our laboratories.

Conflict of interests: authors have no conflict of interests to declare.

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