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Symmetrical and unsymmetrical diphosphanes with diversified alkyl, aryl, and amino substituents

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We present the comprehensive study of diphosphanes with diversified substituents regarding their syntheses, structures, and properties. To this end, we have synthesized a series of novel unsymmetrical alkyl, aryl and amino-substituted diphosphanes of the general formula $R_1R_2P\text{-}PR_3R_4$ (where R_1, R_2, R_3, R_4 = *t*Bu, Ph, Et_2N or *i*Pr_2N) *via* salt metathesis reactionof halophosphanes with metal phosphides in high yield. We vastly expanded this group of compounds by obtaining the first mono- and tri-amino-substituted systems. The structures of isolated compounds were characterized by NMR spectroscopy and X-ray diffraction. The isolated unsymmetrical diphosphanes have no tendency to rearrange to corresponding symmetrical species. Additionally, we proposed the general classification of diphosphanes based on the number of different groups attached to phosphorus atoms and their distribution within a molecule. To investigate the impact of substituents on the properties of P-centers and a molecule as a whole we conducted a DFT study on electronic and steric properties of obtained systems. The experimental and theoretical results can be very useful for designing P-P systems with desired properties.

Introduction

Diphosphanes are the simplest group of compounds containing the P-P bond.[1,2] These consisting of two PR_2 units systems are considered as organic derivatives of diphosphane P_2H_4[3] in which one or more hydrogen atoms were replaced with, *e.g.*, halogen,[4,5] silyl,[5–8] amine,[5,9–17] alkyl,[18–23] alkanoyl,[24] aryl,[18–20,22,24] boryl[25,26] or borazinyl[27] group giving diversified structures. Organo-substituted diphosphanes with P-C, P-Si, P-Li or P-Cl bonds are widely applicable in organometallic chemistry as precursors of diphosphorous or polyphosphorus ligands containing P-P bond[4,28–39] or precursors of bidentate PC···CP ligands.[18,19] Recently, Gudat *et al.* have developed a class of N-heterocyclic diphosphanes with P-N bonds and found that the systems with highly polarized P-P bond may serve as catalysts in the synthesis of disphosphanes.[10,11,40,41] The properties of diphosphanes strongly depend on the nature of substituents at P-atoms. In the case of unsymmetrical species, differences in electron-donating properties of substituents lead to the formation of more nucleophilic and electrophilic site of the P-P bond and, consequently, to an asymmetric distribution of electron density and polarization of the P-P bond.[41] While simple, symmetrical systems like $Ph_2P\text{-}PPh_2$ were found to be stable upon heating up to 200°C,[42] an asymmetric distribution of electron density over phosphorus atoms in unsymmetrical diphosphanes may affect their stability beside a steric hindrance.[43–45] The incorporation of sterically demanding and electron-withdrawing substituents on the P-atoms increases the tendency of the P-P bond to dissociate homolytically, and equilibrium between radical and dimer form is observed in the solution.[41,46,47] Type and size of substituents bound with phosphorus atoms determine their stereochemistry as well.[20,48–51] If two different groups are attached to one or both phosphorus atoms, symmetrical and unsymmetrical chiral structures may be obtained. Furthermore, the presence of two chiral centers allows the formation of the diastereomeric pairs. So far, several approaches to the synthesis of diphosphanes have been developed and applied. The first organo-substituted systems,[52–54] including unsymmetrical species,[55,56] were prepared *via* simple reaction of the secondary phosphine R_2PH with chlorophosphane R_2PCl (Scheme 1A). This method was further improved by the addition of tertiary amine capturing hydrochloride (Scheme 1B)[40,57] or replacing phosphine with its silyl derivative (Scheme 1C).[40] Symmetrical systems may be easily obtained by reductive coupling of two chlorophosphane molecules in the presence of active metals like lithium,[58] sodium,[42,59,60] potassium[42] or magnesium[61] (Scheme 1D) or by direct coupling reaction of phosphide R_2PLi and respective chlorophosphane R_2PCl (Scheme 1E).[18,62] Method E may also be applied for the synthesis of unsymmetrical diphosphanes[18,19], however, obtained products are significantly contaminated with symmetrical diphosphanes as in the case of method F where unsymmetrical systems are formed by mixing two different symmetrical species (Scheme 1F).[20,51,63] Furthermore, symmetrical diphosphanes can be obtained in dehydrocoupling reactions of secondary phosphines catalyzed by transition metal complexes (Scheme 1G)[64,65,66] or in P-P reductive coupling

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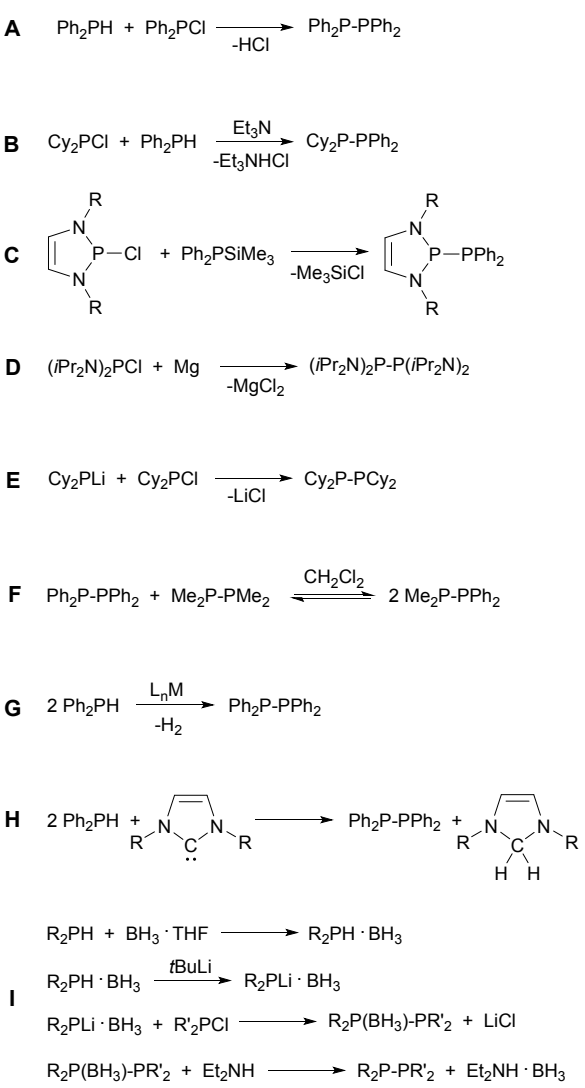
reactions mediated by N-heterocyclic carbenes (Scheme 1H).[67,68]



Scheme 1. Methods of diphosphanes synthesis

Pringle *et al.* proposed synthesis of unsymmetrical diphosphanes based on the formation of borane adduct of respective secondary phosphine at first step, then lithiation of intermediate complex, the coupling reaction with the appropriate chlorophosphane and finally removing the BH_3 group by an amine (Scheme 1I).[18,19] Given the anionic phosphorus center is more crowded by the presence of BH_3, the coupling of two bulky units, and consequently, the formation of the symmetrical system is less favored. Although this method enables us to obtain pure products, the yield of this processes is usually less than 50%. The low yield is mostly related to the last step – removal of the BH_3-protecting group and following isolation of a product.

The main aim of our study on diphosphanes was to obtain a range of new species with diversified nucleophilic properties of P-atoms to apply them as basic components in frustrated Lewis pairs (FLP). Hence, we synthesized of a series of novel symmetrical and unsymmetrical alkyl-, aryl- and amino-substituted diphosphanes of the general formula R_1R_2P-PR_3R_4 (where R_1, R_2, R_3, R_4 = *t*Bu, Ph, Et_2N or *i*Pr_2N; Chart 1, compounds **2**, **6**, **9**-**29**). Moreover, we found that there are no reports on mono- and triamino-substituted diphosphanes. To investigate the influence of substituents on the electronic and steric properties of diphosphanes and to determine the impact of selected groups, we conducted NMR, X-ray, and DFT study of obtained systems. Hence, previously synthesized systems including considered groups were also taken into account (Chart 1, compounds **1**,[18,69,70] **3**,[18] **4/5**,[71–73] **7**,[18,53,54] **8**,[5] **30**[5,9]). In general, we studied thirty compounds: alkyl-aryl-substituted systems (**1-7**), amino-substituted species with fragments (*i*$Pr_2N)_2P$ (**8-10**), ($Et_2N)_2P$ (**11-13**), (*i*Pr_2N)Ph (**14-20**), (*i*Pr_2N)*t*Bu (**21-27**) as well as systems with four different substituents **28/29** and tetra-amino-substituted one **30**. To arrange considered compounds **1-30**, we proposed a simple general classification of diphosphanes based on the number of different groups attached to phosphorus atoms and their distribution within a molecule, organized as follows (Chart 1).

Results and discussion

Syntheses and reactivity of diphosphanes

Searching for a simple and effective procedure to obtain the unsymmetrical P-P systems, firstly, we applied the approach presented by Pringle *et al.* However, it turned out that synthesis of unsymmetrical amino-substituted species is not achievable *via* this method.[18] To overcome this issue, we attempted to obtain these systems in direct coupling reaction between phosphide RR'PLi and chlorophosphane (*i*$Pr_2N)_2PCl$. It is worth mentioning that this method was previously used for the preparation of symmetrical diphosphanes (Scheme 1E).[18,62] Surprisingly, $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures (**8-10**) revealed a complete conversion of substrates into the products at low temperature and, what is the most important, no rearrangement products were observed. Pure diphosphanes were isolated in 80-98% yields, and X-ray quality crystals were grown from toluene solutions. Moreover, this method was also applied to the synthesis of alkyl-aryl-substituted systems. We obtained two new unsymmetrical systems of this kind – **2, 6** and repeated synthesis of previously described **3**.[18] In the latter case, we enhanced the yield of the reaction and isolated the product as colorless, X-ray quality crystals. Using respective chlorophosphane and phosphide fragments as shown in Figure 1 we obtained diphosphanes **2**, **3**, **6**, **8**-**17**, **21**-**24** and **28**/**29** (Scheme 2A). Although this method is a very efficient and effective way for the synthesis of diversified systems, it does have its limitations. At least one of the RR'P fragments building the P-P bond must be incorporated as a phosphide derivative RR'PLi. As we could not lithiate amino-substituted phosphanes RR'PH to yield respective RR'PLi, we were not able to obtain tri-amino-substituted species like **20** and **27** in this straightforward process. We have made a few attempts to obtain tri-amino-

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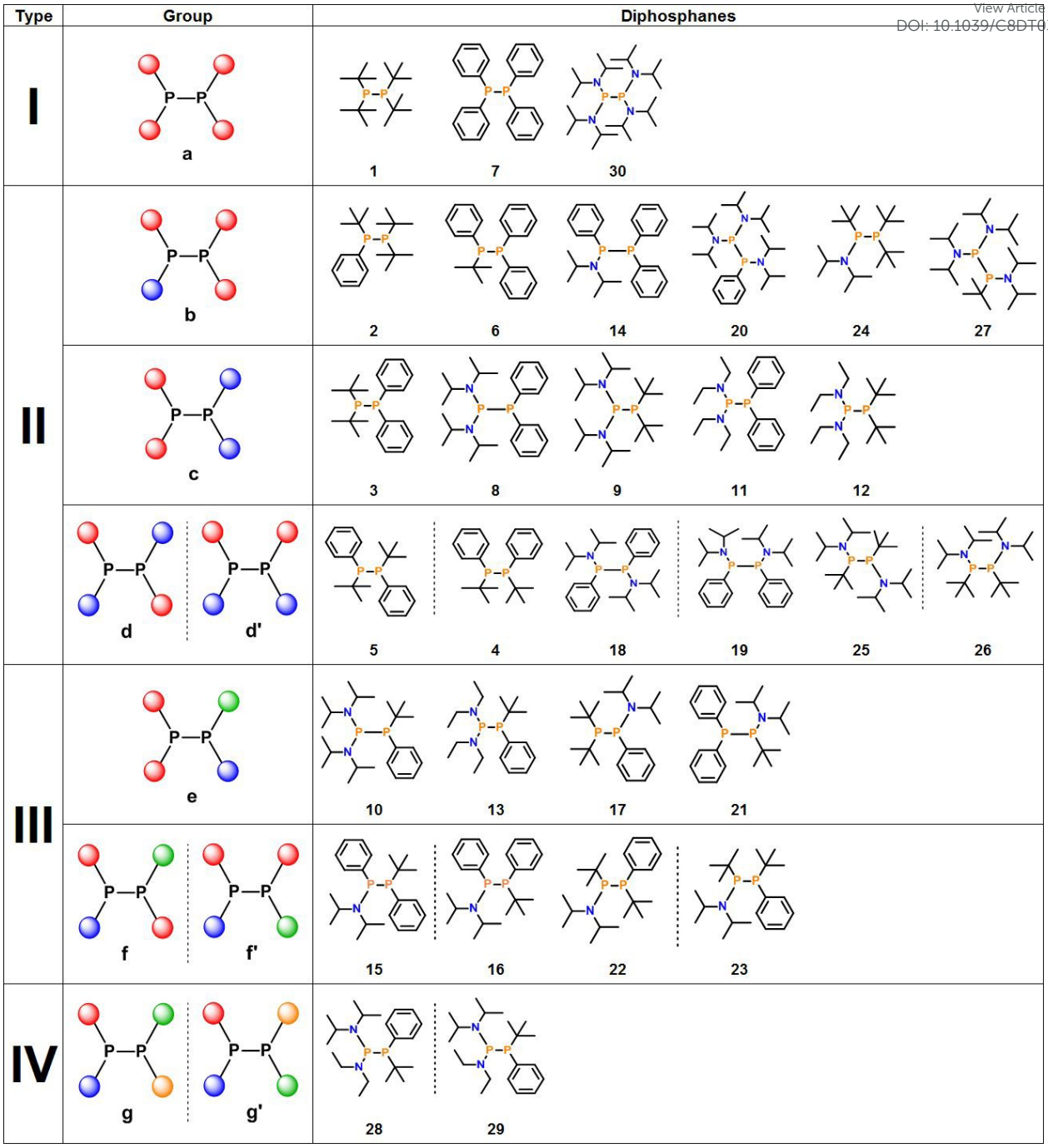


Chart 1. General classification of obtained diphosphanes into four types (**I-IV**) divided into seven groups (**a-g**) based on the number of different substituents and their arrangement within a molecule. All considered compound (**1-30**) were ordered into particular groups. The diphosphanes belonging to **d/d'**, **f/f,' g/g'** groups were isolated as pairs of diastereomers**.** The structures of diastereomers were taken into account in classification as their spectroscopic and computational properties differ essentially. Structures drawings ignore the pyramidal geometry of the P-atoms for simplicity. The previously obtained **1**,[18,69,70] **3**,[18] **4/5**,[71–73] **7**,[18,53,54] **8**[5] and **30**[5,9] are included in this classification.

substituted species *via* methods **A-E** (Scheme 1), however, in no case pure products were yielded. Some experimental, *e.g.*, spectroscopic data were collected when respective chlorophosphanes were mixed in 1:1 molar ratio in THF solution with magnesium turnings, giving **20** and **27** as one of three products in the reaction mixture (besides corresponding symmetrical species, see ESI Figure S34 and S35). By applying this approach, we synthesized and isolated symmetrical amino-substituted diphosphanes **18/19, 25/26** and **30** as analytically pure products (Scheme 2B). All isolated diphosphanes were obtained in high yields (65-98%) - for most syntheses the yield of the reaction was higher than 80%. The purity of the products was confirmed by means of ^{1}H, ^{13}C, ^{31}P NMR spectroscopy (Figures S15-S204 in ESI) and elemental analysis. The compounds **3**, **6**, **8-12**, **14**, **17**, **21**, **23**, **24** and **25/26** were isolated as colourless crystals, whereas, **2**, **11**, **13**, **28/29**

were obtained as colourless oils (**2**, **11**) or yellowish oils (**13,** diastereomers **28** and **29**).

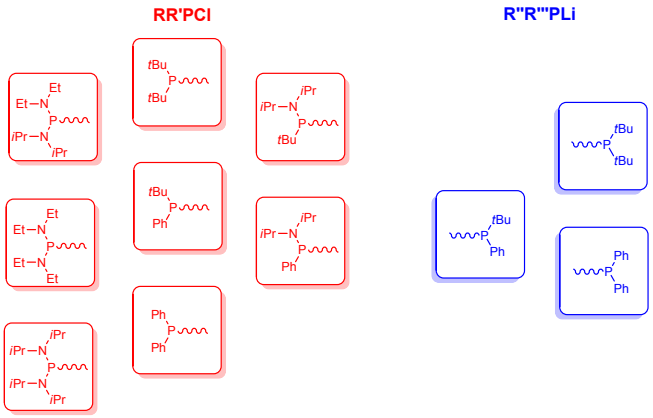
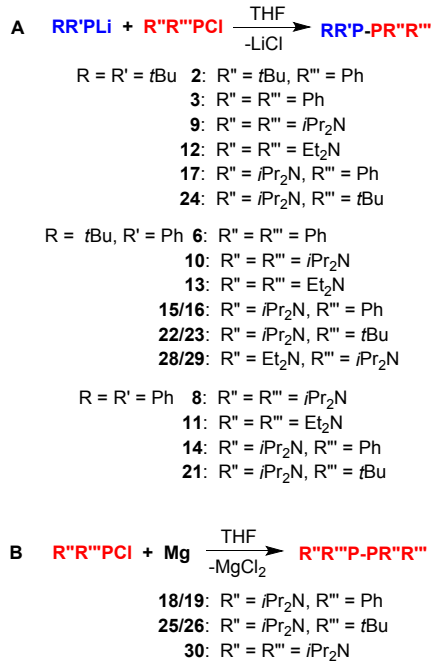


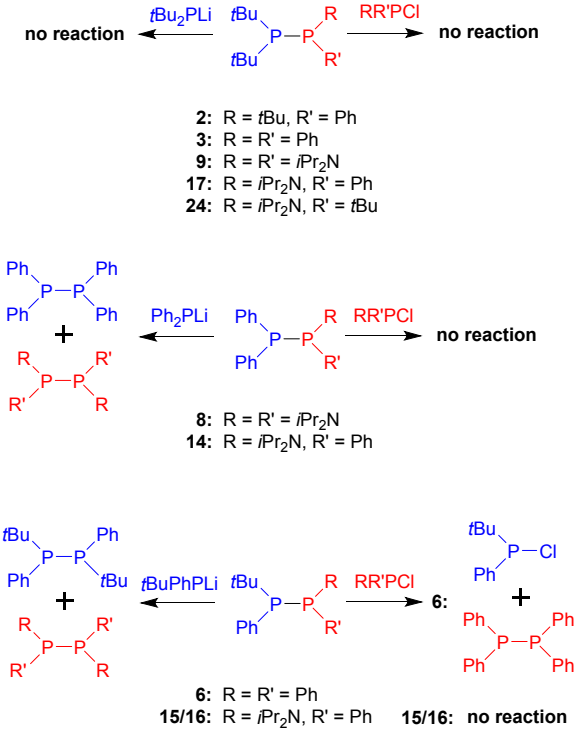
Figure 1. Fragments used to the synthesis of novel, unsymmetrical diphosphanes.



Scheme 2. Synthesis of unsymmetrical diphosphanes via direct coupling of RR'PLi and R"R'"PCl (A) and synthesis of symmetrical systems by reductive coupling of chlorophosphane with magnesium (B).

Furthermore, diphosphanes **15/16**, **18/19**, **22/23** were yielded as pairs of diastereomers forming white amorphic solids. The recrystallization of **22/23** and **28/29** gave a small number of crystals of diastereomers **23** and **28**. All isolated compounds are moisture and air sensitive, however, they can be handled using standard Schlenk technique. A long-term contact with air leads to the formation of oxidation products - the oxidation of **18/19** to (iPr_2N)PhP(O)-O-P(O)(iPr_2N)Ph (**ox18/19**) may serve as an example of such reaction (see Figure S14 for an X-ray structure **ox18/19**).

Our attempts to synthesize unsymmetrical diphosphanes revealed that under proper reaction conditions it is possible to obtain these compounds in good yield and high purity without the usage of the intermediate boron adducts (Scheme 1I). The crucial point is to isolate the diphosphanes immediately after the reaction is completed. The ^{31}P NMR analysis of reaction solutions indicates that generally, the complete conversion of substrates into products takes place after 30 minutes at low temperature. It is noteworthy that phosphides give coloured THF solutions which become colourless as the equimolar quantity of chlorophosphine is added and respective diphosphane is formed. Hence, the colourless or pale yellow reaction mixtures suggest the moment of complete conversion of substrates into products. We found that a prolonged keeping the reaction mixtures at room temperature promotes metathesis reactions, thus the formation of symmetrical species and other impurities. On the contrary, in toluene and/or petroleum ether solutions of isolated products metathesis did not proceed, even if they were stored over a few months at room temperature. Therefore, we decided to study the factors that may promote rearrangement at the group of nine selected systems (**2, 3, 6, 8, 9, 14, 15/16, 17** and **24**). We carried out a series of experiments to examine the impact of solvent (THF), an excess (≈10 mol%) of phosphide and chlorophosphane (≈30 mol%) used in the synthesis of these compounds on their stability (Scheme 3).



Scheme 3. Reactions of selected diphosphanes with 10mol% of corresponding phosphide and 30mol% of chlorophosphane in THF solution. Reaction progress was monitored for four days.

It turned out that diphosphane **6** reacts with corresponding Ph_2PCl yielding symmetrical **7** and *t*BuPhCl. This result was confirmed in the reaction with 150 mol% excess of Ph_2PCl in which **6** quantitatively converted into products after an hour of mixing. Reactivity towards phosphide components varies depending on substituents bonded with RR'PLi. In the case of

bulky *t*Bu$_2$PLi, no products of the P-P bond cleavage were formed. In reactions of Ph$_2$PLi with diphosphanes Ph$_2$P-PRR' (**8**, **14**) products of the P-P bond cleavage, symmetrical species (Ph$_2$P)$_2$ and (RR'P)$_2$ were identified in ^{31}P{^{1}H} NMR spectra of reaction mixtures. In case of a reaction involving **8** about 31 mol% of diphosphane undergoes the P-P bond cleavage that leads to the formation of respective symmetrical diphosphanes. This observation suggests that phosphides can catalyze the formation of symmetrical species. Similar results were obtained in the reactions of *t*BuPhPLi with *t*BuPhP-PRR' (**6**, **15/16**) that led to the formation of symmetrical diphosphanes (*t*BuPhP)$_2$ and (RR'P)$_2$. Therefore, during the synthesis of unsymmetrical diphosphanes, an excess of substrates should be avoided and products should be isolated immediately after the reaction is completed.

Structures of diphosphanes

Great majority of compounds was isolated in crystalline form (**3**, **6**, **8**, **9**, **10**, **12**, **14**, **17**, **21**, **23**, **24**, **25**, **28**) what allows us to discuss their structures in the solid state, including previously reported **3** and **8** for which X-ray structures were not determined before. Molecular structures representative for six groups of diphosphanes (**b-g**): **12**, **14**, **17**, **23**, **25** and **28** are presented in Chart 2 with their conformations in Newman projection. For X-ray structures of **3**, **6**, **8**, **9**, **10**, **21**, **24** see Figures S1-S5, S9, and S11 (ESI). The selected structural parameters of obtained diphosphanes are collected in Table S1 (ESI). It is noteworthy that crystal unit cell of compound **6** consists of two enantiomers whereas in the unit cell of **9** there are three different *eclipsed* conformers found that resulted from the rotation around the P-P bond (Figure S4). As expected, P-atoms in all analysed diphosphanes exhibit pyramidal geometry. In diphosphanes consisting of *i*Pr$_2$N or Et$_2$N groups geometry of N-atoms is almost planar. According to NBO analysis, this structural feature of amino-substituted compounds **8**, **9**, **10**, **12**, **14**, **23**-**25** and **28** may be explained by the interaction of molecular orbital associated to lone pair at N-atom with antibonding σ*(P-P) orbital.

The optimal conformations of diphosphanes vary depending on the substitution pattern and the bulkiness of the substituents bound with P-atoms. The idealized conformations of diphosphanes with diversified substituents are shown in Figure 2. *Anti* conformations are preferable for most systems in crystalline form (**3**, **6**, **8**, **10**, **12**, **14**, **21**, **23** and **28**). In the case of diphosphanes with bulky substituents, the most privileged conformation is determined by the size of these groups, rather than by the antiperiplanar alignment of lone pairs.[74]

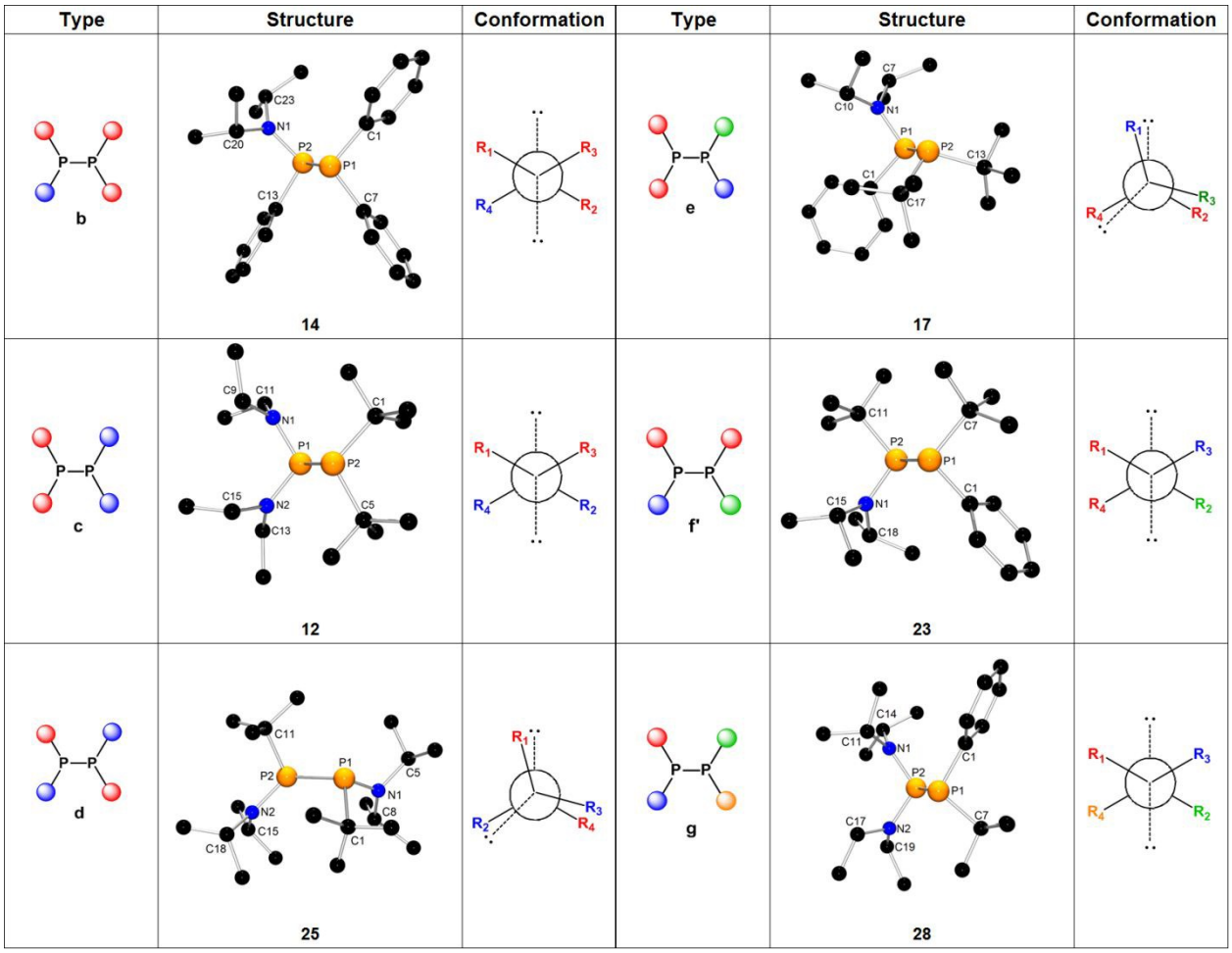


Chart 2. Selected X-ray structures of diphoshanes representative for groups **b**-**g** together with their conformations.

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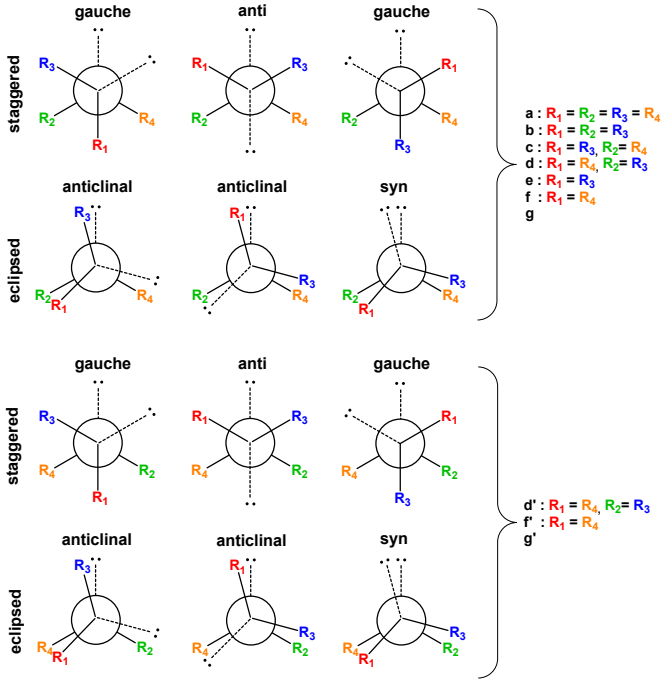

Figure 2. Possible, idealized conformations of diphosphanes belonging to groups **a**-**g** with distinction on two different diastereomeric forms.

A steric hindrance that is a consequence of intermolecular interactions between both RR'P fragments, may force adapting *eclipsed* conformations weakening σ-P orbitals overlapping and elongating the P-P bond. Indeed, diphosphanes **9**, **17**, **24** and **25/26** in which both P-atoms are substituted with bulky *t*Bu or/and *i*Pr$_2$N exhibit *anticlinal* conformations. The P-P bond distances of obtained compounds vary from 2.225(1) to 2.314(3) Å for **6** and **25**, respectively. The longest P-P bonds are observed in sterically crowded diphosphanes that adopt *eclipsed* conformations (**9**, **25**). DFT calculations of enthalpy ΔH_{diss} and free energy ΔG_{diss} of homolytic P-P bond dissociation (Table 1) revealed that these highly congested systems (**1**, **9**, **24/25** or **30)** have expectantly the least stable P-P bonds. Nevertheless, we cannot predict the stability of the P-P bond only on the basis of its length. It may be noted for the moderately congested systems that no strong correlation between the P-P bond lengthening and a decrease of ΔH_{diss} and ΔG_{diss} (compare, *e.g.* **1**, **3** and **28**, **17** and **21**) is visible. Calculations indicated that the most stable systems are those involving P*t*BuPh unit as the one site of the P-P bond: **4-6**, **13**, **15**,**16** or **28-29**. Structural and electronic features of P*t*BuPh moiety constitute an optimal compromise between a steric hindrance and electron-donating properties of substituents necessary for obtaining highly stable species.

To get a better insight into structural features of diphosphanes **1**-**30,** we performed conformational analysis using DFT methods, including obtained systems for which X-ray structures were not determined and known species **1**, **3**, **4**/**5**, **7**, **8** and **30**. The optimal conformations calculated for **1**-**30** are presented in Chart S1. Calculated molecular structures are in good agreement with those determined experimentally also for **1**, **2**, **9**, **17**, **23**, **24**, **25/26**, **27** and **30** where an antiperiplanar arrangement of lone pairs or adapting any staggered conformation is not attainable due to the presence of a few sterically demanding groups, *e.g.,* *t*Bu and *i*Pr$_2$N. It is worth mentioning that diastereomers **22** and **23** have different optimal conformations, (*anticlinal* and *anti,* respectively). Hence, isomer **22** has lower energy than isomer **23** which exhibits non-typical conformation for sterically crowded systems. Moreover, we observed a correlation between the spatial orientation of the lone pairs at P-atoms and the magnitude of $^1J_{P\text{-}P}$ coupling constants (Table 1). Unsymmetrical diphosphanes that adopt *eclipsed* conformations (**2**, **9**, **17**, **22**, **24**, **27**) which result in the proximity of lone pairs at P-atoms, display the largest magnitudes of $^1J_{P\text{-}P}$. For these species, $^1J_{P\text{-}P}$ values are in the range of 303.2-489.5 Hz. Unlike bulky species, less crowded unsymmetrical diphosphanes (**3**, **6**, **8**, **10-16**, **20**, **21**, **23**, **28/29**) exhibit smaller magnitudes of $^1J_{P\text{-}P}$ within the range of values 101.4 Hz and 283.4 Hz. It is caused by the antiperiplanar spatial orientation of lone pairs at P-atoms in the most energetically favoured conformers. Computational data confirmed the elongation of the P-P bond in **1**, **2**, **9**, **17**, **23**, **24, 25/26**, **27** and **30** compared to other systems. Additionally, conformational analysis of calculated structures revealed an interesting feature: the most stable conformer of bulky diphosphanes was the one with the shortest P-P bond. In the systems with smaller steric hindrance that may adopt staggered conformation with *anti*-lone pairs alignment, it is not the case (see ESI, Figures S205-S234, Table S6). In general, as the proximity of diphosphane lone pairs increases, the P-P bond shortens. As the spatial orientation of lone pairs changes from antiperiplanar to eclipsed, the energy of conformers increases for less sterically crowded systems and decreases for bulky ones. It is because of the London dispersion forces which play a crucial role in the stabilization of bulky systems.[45,75] Therefore, to understand the stability of different isomers we need to take into account not only the spatial orientation but also through-space interactions of substituents. By calculating the energy of the interaction $E_{F1\text{-}F2}$ between two RR'P fragments contained in Table 1, we confirmed that attractive dispersion interactions have a defining structural role and account for the increased stability of bulky systems. Since these interactions have additive character and increase with the number of interacting hydrogen atoms, the most sterically crowded systems (**1**,**2**, **9**,**17**, **22/23, 24, 25/26** and **30)** with a predominance of *i*Pr$_2$N and *t*Bu groups have the greatest values of $E_{F1\text{-}F2}$. As the size of substituents decreases, $E_{F1\text{-}F2}$ decreases (less negative) and diphosphanes adopt classical *gauche* or *anti*-lone-pairs conformations (see ESI, Chart S1). We noticed that $E_{F1\text{-}F2}$ decreases with the number of interacting H-atoms in neighbouring fragments in order (*i*Pr$_2$N)$_2$ > (*i*Pr$_2$N)*t*Bu > *t*Bu$_2$ > (*i*Pr$_2$N)Ph > *t*BuPh > Ph$_2$. For **4** and **7** *eclipsed* conformation is energetically favored due to π-π interactions of coplanar Ph groups of neighboring P-atoms.

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Table 1. Selected experimental (**a**) and calculated (**b**) properties of diphosphanes **1-30**: $^{31}P\{^{1}H\}$ NMR data, **P-P** bond length, ΔH_{diss} – enthalpy of the P-P bond dissociation, ΔG_{diss} – the free energy of the P-P bond dissociation, E_{F1-F2} – energy of dispersion interaction between two PR_2 units.

No.	Diphosphane	$^{1}J_{P-P}$[a] [Hz]	δP_1[a] [ppm]	δP_2[a] [ppm]	P-P[a] [Å]	P-P[b] [Å]	ΔH_{diss}[b] [kJ/mol]	ΔG_{diss}[b] [kJ/mol]	ΔE_{F1-F2}[b] [kJ/mol]
1	tBu$_2$P-PtBu$_2$	-	39.6	39.6	2.234(1)[70]	2.235	166.6	96.0	-34.5
2	tBu$_2$P-PtBuPh	370.3	30.8	1.4	-	2.244	201.3	131.0	-33.6
3	tBu$_2$P-PPh$_2$	254.3	33.0	-25.9	2.237(1)	2.264	200.1	137.9	-27.3
4	*rac*-tBuPhP-PtBuPh	-	1.9	1.9	-	2.257	223.2	153.2	-27.8
5	*meso*-tBuPhP-PtBuPh	-	-4.4	-4.4	2.229(1)[73]	2.252	226.2	156.9	-26.4
6	tBuPhP-PPh$_2$	158.5	9.7	-30.8	2.225(1)	2.252	210.3	152.2	-23.6
7	Ph$_2$P-PPh$_2$	-	-14.9	-14.9	2.2519(6)[53]	2.252	200.3	143.2	-30.1
8	(iPr$_2$N)$_2$P-PPh$_2$	119.3	71.8	-38.0	2.2444(6)	2.262	185.5	122.5	-38.0
9	(iPr$_2$N)$_2$P-PtBu$_2$	358.2	88.2	62.6	2.295(2)	2.296	145.8	66.6	-42.0
10	(iPr$_2$N)$_2$P-PtBuPh	155.3	72.2	-9.5	2.252(1)	2.271	183.2	107.8	-40.7
11	(Et$_2$N)$_2$P-PPh$_2$	135.0	108.4	-38.3	-	2.265	186.8	123.7	-21.3
12	(Et$_2$N)$_2$P-PtBu$_2$	193.7	111.1	11.8	2.2603(6)	2.275	174.8	103.5	-26.6
13	(Et$_2$N)$_2$P-PtBuPh	145.3	99.5	-15.7	-	2.250	202.0	130.7	-25.5
14	(iPr$_2$N)PhP-PPh$_2$	144.8	45.5	-36.0	2.229(1)	2.261	193.2	133.1	-27.5
15	p-*meso*-(iPr$_2$N)PhP-PtBuPh	138.0	28.3	-7.5	-	2.257	206.1	139.4	-30.0
16	p-*rac*-(iPr$_2$N)PhP-PtBuPh	145.3	27.6	-11.1	-	2.250	204.5	139.2	-26.2
17	(iPr$_2$N)PhP-PtBu$_2$	303.2	38.7	36.8	2.2445(5)	2.256	178.7	107.9	-37.4
18	*meso*-(iPr$_2$N)PhP-P(iPr$_2$N)Ph	-	23.6	23.6	-	2.246	181.5	115.9	-33.7
19	*rac*-(iPr$_2$N)PhP-P(iPr$_2$N)Ph	-	21.5	21.5	-	2.241	170.8	102.8	-29.1
20	(iPr$_2$N)PhP-P(iPr$_2$N)$_2$	101.7	63.3	16.1	-	2.259	162.8	88.6	-43.2
21	(iPr$_2$N)tBuP-PPh$_2$	185.8	68.5	-30.7	2.2432(9)	2.265	202.2	138.4	-32.8
22	p-*meso*-(iPr$_2$N)tBuP-PtBuPh	348.8	57.7	14.9	-	2.252	202.3	130.9	-37.6
23	p-*rac*-(iPr$_2$N)tBuP-PtBuPh	283.4	70.3	7.7	2.265(2)	2.282	186.8	109.5	-37.7
24	(iPr$_2$N)tBuP-PtBu$_2$	489.5	69.5	65.6	2.2508(6)	2.252	167.2	96.2	-39.0
25	*meso*-(iPr$_2$N)tBuP-P(iPr$_2$N)tBu	-	88.8	88.8	2.314(3)	2.294	154.4	80.4	-41.5
26	*rac*-(iPr$_2$N)tBuP-P(iPr$_2$N)tBu	-	82.0	82.0	-	2.252	157.4	76.8	-46.7
27	(iPr$_2$N)tBuP-P(iPr$_2$N)$_2$	327.0	92.1	88.7	-	2.299	155.8	74.4	-48.8
28	p-*meso*-(Et$_2$N)(iPr$_2$N)P-PtBuPh	143.1	79.5	-13.7	2.228(1)	2.264	205.1	133.2	-32.6
29	p-*rac*-(Et$_2$N)(iPr$_2$N)P-PtBuPh	140.4	79.3	-14.9	-	2.258	205.6	134.2	-29.7
30	(iPr$_2$N)$_2$P-P(iPr$_2$N)$_2$	-	83.5	83.5	2.2988(8)[9]	2.300	123.8	36.4	-54.3

Note: unambiguous attribution of signals in $^{31}P\{^{1}H\}$ NMR spectrum of **28/29** to isomers p-*meso* and p-*rac* is not possible. As signals in $^{31}P\{^{1}H\}$ NMR spectra of **17**, **24** and **25/26** recorded at room temperature are broad, low-temperature NMR experiments were applied to determine spectral data of these species.

Experimental part

Materials and methods

All manipulations were carried out under a dry argon atmosphere by using flame-dried Schlenk-type glassware on a vacuum line or in a glove-box. Solvents were dried *by standard procedures* over Na(K)/K/Na /benzophenone and distilled under argon. 1D (^{31}P, ^{13}C, and ^{1}H) and 2D NMR spectra in C_6D_6 solution were recorded on a Bruker AV400 MHz spectrometer (external standard TMS for ^{1}H and ^{13}C; 85% H_3PO_4 for ^{31}P) at ambient temperature. Low-temperature ^{31}P, $^{31}P\{^{1}H\}$ and ^{1}H NMR experiments were performed for toluene-d_8 solutions of **24** and **25/26** with data collected at 298 K, 273 K, 248 K and 223 K. Literature methods were used to synthesize tBu$_2$PLi, tBuPhPLi, Ph$_2$PLi,[76,77] tBu$_2$PCl,[77] iPr$_2$NPCl,[78] (iPr$_2$N)$_2$PCl[79] and (Et$_2$N)$_2$PCl.[79] Methods described for ^{t}BuPhPCl,[80] (iPr$_2$N)PhPCl[81] and (^{i}Pr$_2$N)^{t}BuPCl[82] were modified at the stage of purification of a crude product. tBuPhPCl and (iPr$_2$N)^{t}BuPCl were purified by distillation under reduced pressure, collecting pure chlorophosphanes at 62-57°C (2 mmHg) and 48-52°C (0.1 mmHg), respectively. (iPr$_2$N)PhPCl was dried under vacuum (0.01 mmHg) at ambient temperature for 1h giving greenish crystals. (Et$_2$N)(iPr$_2$N)PCl was synthesized via the method described in ESI (see Part A). PhPCl$_2$, Ph$_2$PCl, iPr$_2$NH Et$_2$NH were purchased from Aldrich. Commercial reagents were distilled

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prior to use. Reaction progress was monitored by $^{31}P\{^{1}H\}$ NMR spectra of reaction mixtures.

Diffraction data of compounds **3**, **6**, **8**, **9**, **10**, **12**, **14**, **17**, **ox18/19, 21**, **23**, **24**, **25**, **28** were collected on diffractometer equipped with a STOE image plate detector system IPDS2T using Mo*K*α (λ = 0.71073 Å) for **3**, **6**, **8**, **9**, **10**, **12**, **14**, **17**, **ox18/19, 21**, **24**, **25**, **28** and Cu*K*α *K*α (λ = 1.54178 Å) for **23** radiation with graphite monochromatization (λ = 0.71073 Å). Good quality single-crystal specimens were selected for the X-ray diffraction experiments at 120 K for **3, 6, 8, 9 10, 12, 14, ox18/19, 21, 25**, at 130 K for **17, 24, 28** and at 150 K for **23**. The structures were solved by direct methods and refined against F^2 using the Shelxs-97 and Shelxl-97[83] programs run under WinGX[84]. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were usually refined using the isotropic model with U_{iso}(H) values fixed to be 1.5 times U_{eq} of C atoms for $-CH_3$ or 1.2 times U_{eq} for –CH, $-CH_2$ groups and aromatic H. The crystallographic details for **3**, **6**, **8**, **9**, **10**, **12**, **14**, **17**, **ox18/19**, **21**, **23**, **24**, **25**, **28** are placed in ESI.

Crystallographic data for the structures of **3**, **6**, **8**, **9**, **10**, **12**, **14**, **17**, **ox18/18**, **21**, **23**, **24**, **25**, **28** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. 1560634-1560642, 1576833 – 1576836, 1585541. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk). For more crystallographic details see ESI.

Synthetic procedures

General procedure for preparation of 2, 3, 6, 8, 9, 10, 11, 12, 13, 14, 15/16, 17, 21, 22/23, 24, 28/29: To a solution of phosphide RR'PLi in 40 cm^3 of THF cooled to -50°C, a chlorophosphane R"R"'PCl was added dropwise. The reaction mixture was successively stirred at -50°C for 30 minutes and then allowed to warm up to room temperature for another 30 minutes. Then the solvent was evaporated and the residue was dried under vacuum (0.01 mmHg) for 30 minutes at 50°C to remove all volatiles. The crude product was dissolved in 15 cm^3 of petroleum ether and filtered. Removal of the solvent under vacuum resulted in the pure product as oil or solids. In the latter case, X-ray quality crystals were grown from petroleum ether or toluene solutions. A detailed description of syntheses including NMR data, elemental analyses, and crystallization conditions was presented in ESI (Part A).

General procedure for preparation of 18/19 and 25/26: To magnesium turnings in 40 cm^3 of Et_2O previously activated by iodine and a solution of chlorophosphane in 5 cm^3 of Et_2O was mixed at room temperature and vigorously stirred overnight. The solvent was removed in a vacuum, and the residue was extracted by 15 cm^3 of toluene/petroleum ether and filtered. The filtrate was evaporated to dryness giving the product. A detailed description of syntheses including NMR data, elemental analyses, and crystallization conditions was presented in ESI (Part A).

General procedure for preparation of 20 and 27: To magnesium turnings in 30 cm^3 of Et_2O previously activated by iodine solutions of chlorophosphanes A and B in 5 cm^3 of Et_2O were added simultaneously at room temperature and vigorously stirred overnight. $^{31}P\{^{1}H\}$ NMR spectra revealed that diphosphanes **20**/**27** were formed as one of three products with corresponding symmetrical diphosphanes. Diphosphanes **20**/**27** were obtained only in the reaction mixture, and pure compounds were not isolated. The approximate composition of the final reaction mixtures was estimated by ^{31}P NMR spectra. A detailed description of syntheses including NMR data and the composition of the reaction mixtures were presented in ESI (Part A).

General procedure for investigation of reactivity of diphosphanes towards RR'PLi phosphides: Diphosphane RR'P-PR"R"' (0.170 mmol) and respective RR'PLi phosphide (10%mol, 0.017 mmol,) were dissolved in 2 cm^3 of THF and mixed at room temperature. Reaction progress was controlled by $^{31}P\{^{1}H\}$ NMR spectra performed after 1 hour, 24 hours and 4 days. The approximate composition of the final reaction mixture was determined by means of ^{31}P NMR spectra analysis recorded after 4 days of mixing. A detailed description of reactions including NMR data and composition of the final reaction mixtures were presented in ESI (Part A).

General procedure for investigation of reactivity of diphosphanes towards R"R"'PCl chlorophosphanes: Diphosphane RR'P-PR"R"' (0.170 mmol) and respective R"R"'PCl chlorophosphane (30mol%, 0.051 mmol,) were dissolved in 2 cm^3 of THF and mixed at room temperature. Reaction progress was controlled by $^{31}P\{^{1}H\}$ NMR spectra performed after 1 hour, 24 hours and 4 days. The approximate composition of the final reaction mixture was determined by means of ^{31}P NMR spectra recorded after 4 days of mixing. A detailed description of reactions including NMR data and composition of the final reaction mixtures were presented in ESI (Part A).

Conclusions

We obtained and fully characterized a set of novel symmetrical and unsymmetrical diphosphanes with diversified substituents on the phosphorus atoms. We have found that synthesis of such systems in good yield and high purity is readily achievable by reaction of phosphides with chlorophosphanes. Our experiments showed that for obtaining unsymmetrical systems using boron protecting group is not necessary. The metathesis side-reactions during the syntheses of unsymmetrical diphosphanes can be eliminated by keeping reaction mixture at low temperature, using strictly stoichiometric amounts of reagents and isolation of the product directly after the reaction is completed. The obtained

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symmetrical and unsymmetrical diphosphanes with diversified substituents may be applied as P-donor ligands for transition metal complexes. Furthermore the unsymmetrical species with polarized P-P bond can be used as reagents in organophosphorus chemistry or in activation of small molecules. The studies of application of these highly nucleophilic systems in FLPs as basic components are in progress and will be published in due course.

Conflicts of interest

There are no conflicts to declare.

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Synthesis, classification, and analysis of structural, electronic and spectroscopic properties of series of novel diphosphanes with diversified substituents.

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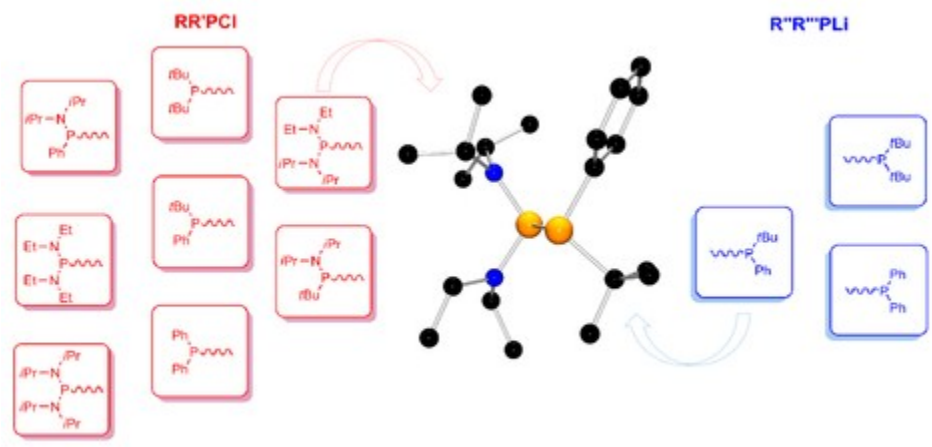

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