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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-PR_3R_4 (where R_1, R_2, R_3, R_4 = *t*Bu, Ph, Et_2N or iPr_2N) *via* a salt metathesis reaction of 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 the isolated compounds were characterized by NMR spectroscopy and X-ray diffraction. The isolated unsymmetrical diphosphanes have no tendency to rearrange to the 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 the electronic and steric properties of the 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 compounds consisting of two PR_2 units are considered as organic derivatives of diphosphane P_2H_4 [3] in which one or more hydrogen atoms were replaced with *e.g.*, a 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 the 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 systems with a highly polarized P–P bond may serve as catalysts in the synthesis of diphosphanes.[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 the electron-donating properties of substituents lead to the formation of more nucleophilic and electrophilic sites of the P–P bond and, consequently, to an asymmetric distribution of the electron density and polarization of the P–P bond.[41] While simple, symmetrical systems like Ph_2P-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 besides the 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 the radical and dimer form is observed in the solution.[41,46,47] The 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 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* a simple reaction of the secondary phosphine R_2PH with chlorophosphane R_2PCl (Scheme 1A). This method was further improved by the addition of a 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 the direct coupling reaction of phosphides R_2PLi and the respective chlorophosphanes R_2PCl (Scheme 1E).[18,62] Method

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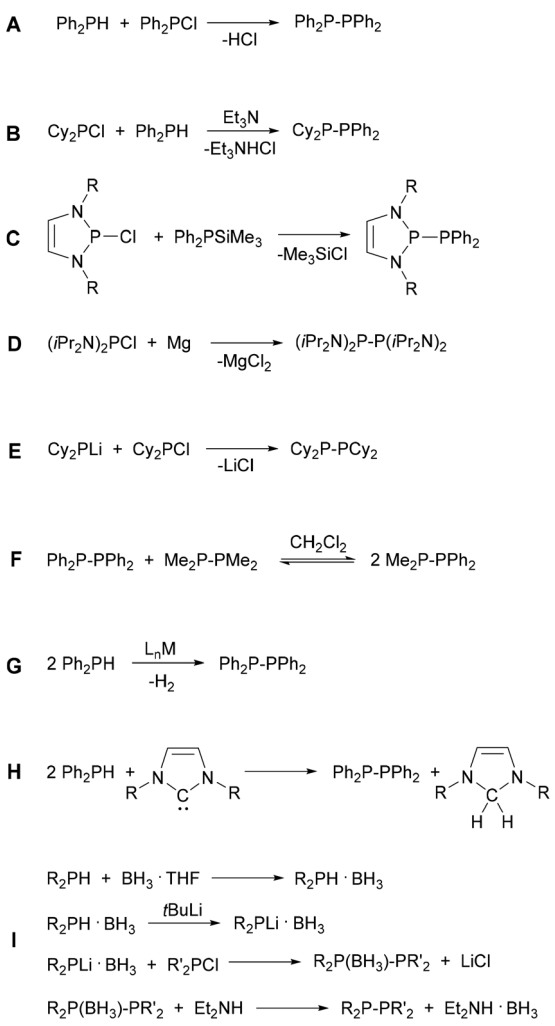


Scheme 1 Methods of diphosphane synthesis.

E may also be applied for the synthesis of unsymmetrical diphosphanes,[18,19] however the 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)[64–66] or in P–P reductive coupling reactions mediated by N-heterocyclic carbenes (Scheme 1H).[67,68]

Pringle *et al.* proposed the synthesis of unsymmetrical diphosphanes based on the formation of a borane adduct of the respective secondary phosphine in the first step, then lithiation of the intermediate complex, a coupling reaction with the appropriate chlorophosphane and finally the removal of the BH_3 group by an amine (Scheme 1I).[18,19] Given that 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 are less favored. Although this method enables us to obtain pure products, the yield of this process is usually less than 50%. The low yield is mostly related to the last step, removal of the BH_3-protecting group followed by the 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 (FLPs). Hence, we synthesized 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 iPr_2N; Chart 1, compounds **2**, **6**, and **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 studies of the obtained systems. Hence, the previously synthesized systems including the 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] and **30**[5,9]). In general, we studied thirty compounds: alkyl–aryl-substituted systems (**1–7**) and amino-substituted species with fragments $(iPr_2N)_2P$ (**8–10**), $(Et_2N)_2P$ (**11–13**), $(iPr_2N)Ph$ (**14–20**), and $(iPr_2N)t$Bu (**21–27**) as well as systems with four different substituents **28/29** and a tetra-amino-substituted one **30**. To arrange the 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

Synthesis and reactivity of diphosphanes

Searching for a simple and effective procedure to obtain unsymmetrical P–P systems, firstly, we applied the approach presented by Pringle *et al.* However, it turned out that the synthesis of unsymmetrical amino-substituted species is not achievable *via* this method.[18] To overcome this issue, we attempted to obtain these systems in a direct coupling reaction between phosphide RR′PLi and chlorophosphane $(iPr_2N)_2PCl$. It is worth mentioning that this method was previously used for the preparation of symmetrical diphosphanes (Scheme 1E).[18,62] Surprisingly, the $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures (**8–10**) revealed a complete conversion of substrates into the products at a 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** and **6** and repeated the 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 the respective chlorophosphane and phosphide fragments as shown in Fig. 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

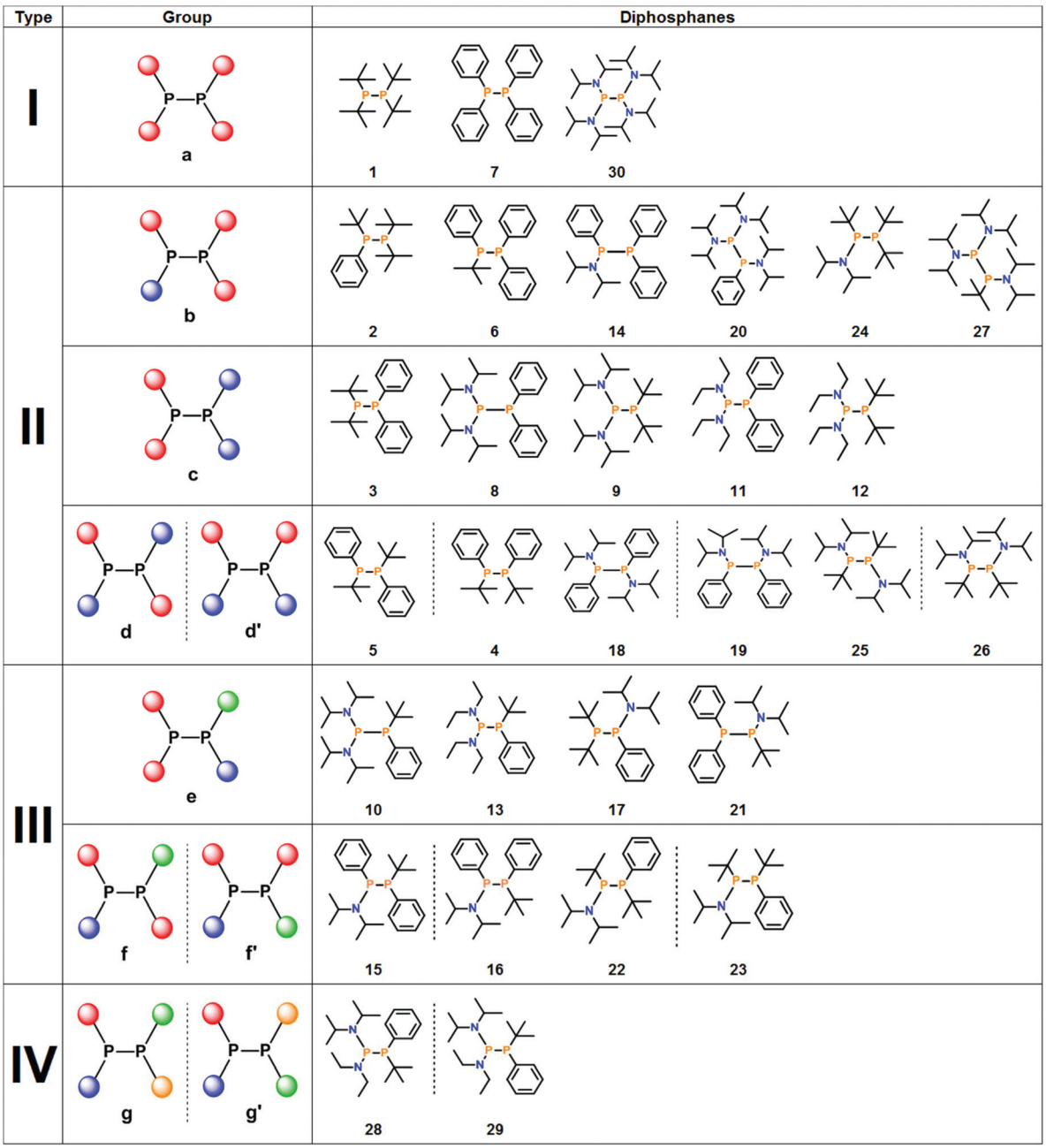


Chart 1 General classification of the obtained diphosphanes into four types (I–IV) divided into seven groups (a–g) based on the number of different substituents and their arrangement within a molecule. All considered compounds (**1–30**) were ordered into particular groups. The diphosphanes belonging to d/d′, f/f′, and g/g′ groups were isolated as pairs of diastereomers. The structures of diastereomers were taken into account in the classification as their spectroscopic and computational properties differ essentially. Structure 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.

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 the 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-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 the respective chlorophosphanes were mixed in a 1 : 1 molar ratio in THF solution with magnesium turnings, giving **20** and **27** as one of three products in the reaction mixture (besides the corresponding symmetrical species, see the ESI Fig. 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

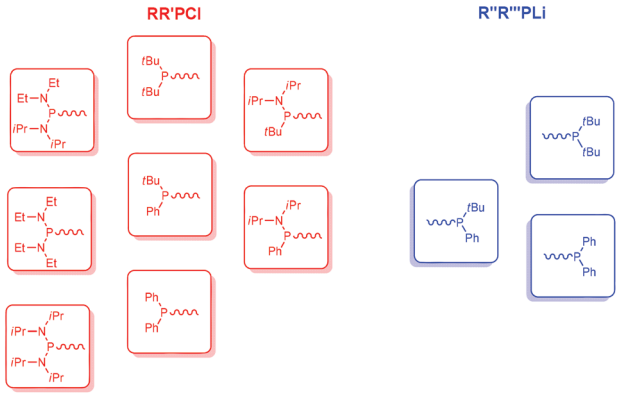


Fig. 1 Fragments used for the synthesis of novel, unsymmetrical diphosphanes.

A RR'PLi + R''R'''PCl $\xrightarrow[-LiCl]{THF}$ RR'P-PR''R'''

R = R' = *t*Bu **2**: R'' = *t*Bu, R''' = Ph
3: R'' = R''' = Ph
9: R'' = R''' = iPr_2N
12: R'' = R''' = Et_2N
17: R'' = iPr_2N, R''' = Ph
24: R'' = iPr_2N, R''' = *t*Bu

R = *t*Bu, R' = Ph **6**: R'' = R''' = Ph
10: R'' = R''' = iPr_2N
13: R'' = R''' = Et_2N
15/16: R'' = iPr_2N, R''' = Ph
22/23: R'' = iPr_2N, R''' = *t*Bu
28/29: R'' = Et_2N, R''' = iPr_2N

R = R' = Ph **8**: R'' = R''' = iPr_2N
11: R'' = R''' = Et_2N
14: R'' = iPr_2N, R''' = Ph
21: R'' = iPr_2N, R''' = *t*Bu

B R''R'''PCl + Mg $\xrightarrow[-MgCl_2]{THF}$ R''R'''P-PR''R'''

18/19: R'' = iPr_2N, R''' = Ph
25/26: R'' = iPr_2N, R''' = *t*Bu
30: R'' = R''' = iPr_2N

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).

(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, and ^{31}P NMR spectroscopy (Fig. S15–S204 in the 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**, and **28/29** were obtained as colourless oils (**2**, **11**) or yellowish oils (**13**, diastereomers **28** and **29**).

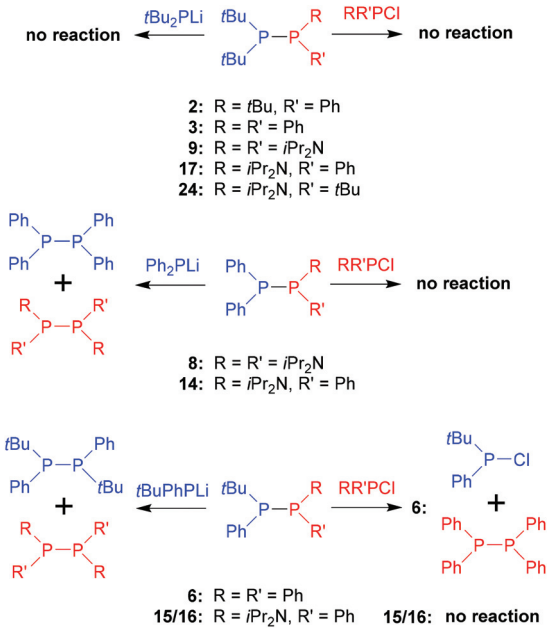
Furthermore, diphosphanes **15/16**, **18/19**, and **22/23** were yielded as pairs of diastereomers forming white amorphic solids. The recrystallization of **22/23** and **28/29** gave a small number of crystals of diastereomers **23** and **28**. All isolated compounds were moisture and air sensitive, however they can be handled using the standard Schlenk technique. 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 Fig. S14† for an X-ray structure **ox18/19**).

Our attempts to synthesize unsymmetrical diphosphanes revealed that under appropriate reaction conditions, it is possible to obtain these compounds in a 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 a low temperature. It is worth noting that phosphides give coloured THF solutions which become colourless as the equimolar quantity of chlorophosphine is added and the respective diphosphane is formed. Hence, the colourless or pale yellow reaction mixtures suggest the complete conversion of substrates into products. We found that keeping the reaction mixtures at room temperature for a prolonged time promotes the metathesis reactions, thus resulting in the formation of symmetrical species and other impurities. In contrast, in toluene and/or petroleum ether solutions of the 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 in 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 of phosphide (≈10 mol%) and chlorophosphane (≈30 mol%) used in the synthesis of these compounds on their stability (Scheme 3).

It turned out that diphosphane **6** reacts with the 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 the substituents bonded with RR'PLi. In the case of bulky tBu_2PLi, no products of the P–P bond cleavage were formed. In reactions of Ph_2PLi with diphosphanes Ph_2P-PRR' (**8**, **14**) products of the P–P bond cleavage, symmetrical species $(Ph_2P)_2$ and $(RR'P)_2$ were identified in the $^{31}P\{^{1}H\}$ NMR spectra of reaction mixtures. In the case of a reaction involving **8**, about 31 mol% of diphosphane undergoes the P–P bond cleavage that leads to the formation of the respective symmetrical diphosphanes. 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 $(tBuPhP)_2$ and $(RR'P)_2$. These observations suggest that phosphides can catalyze the formation of symmetrical species. 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

A great majority of compounds were isolated in the crystalline form (**3**, **6**, **8**, **9**, **10**, **12**, **14**, **17**, **21**, **23**, **24**, **25**, and **28**) which



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

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 of 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**, and **24**, see Fig. S1–S5, S9, and S11 (ESI†). The selected structural parameters of the obtained diphosphanes are collected in Table S1 (ESI†). It is worth noting that the 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 (Fig. S4†). As expected, the P-atoms in all analysed diphosphanes exhibit pyramidal geometry. In diphosphanes consisting of iPr_2N or Et_2N groups, the 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 the molecular orbital associated with the lone pair at the N-atom with the 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

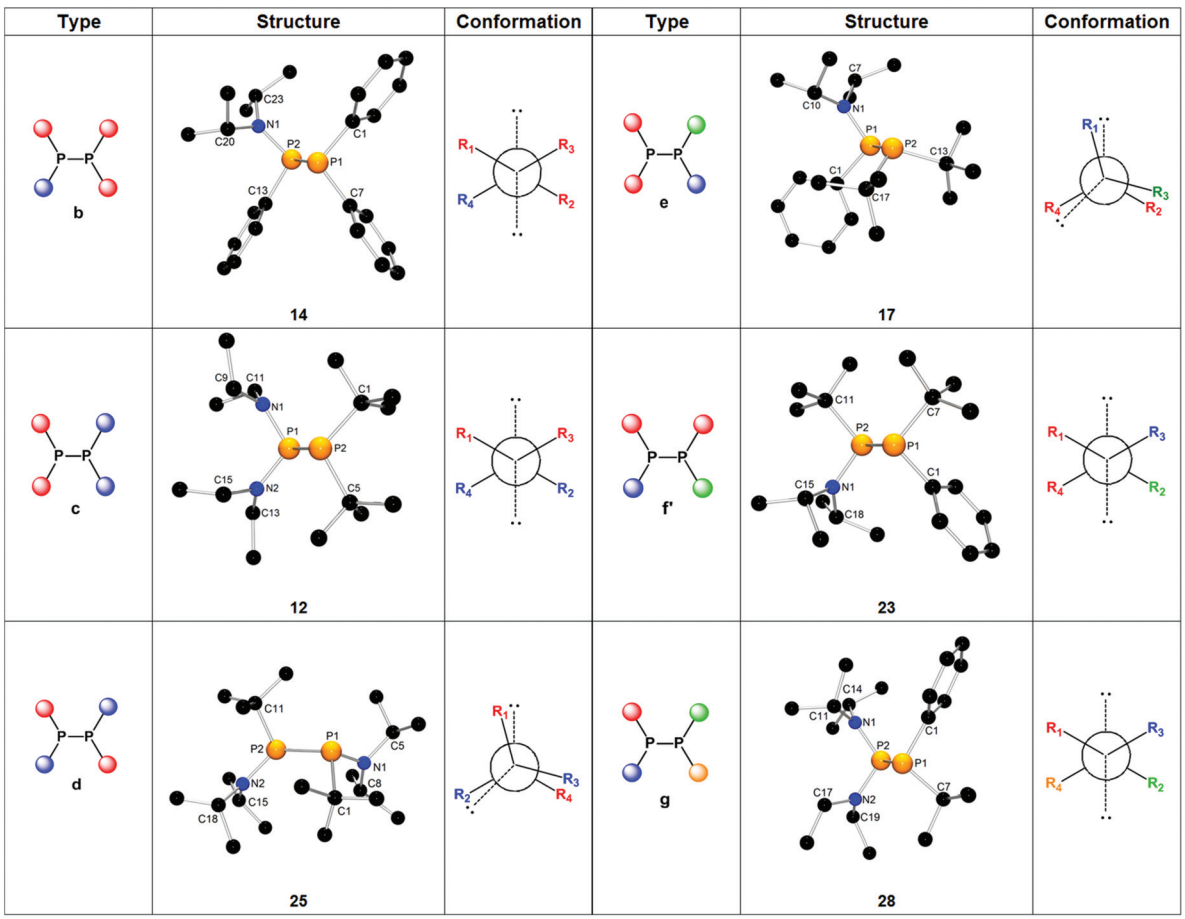


Chart 2 Selected X-ray structures of diphoshanes representative of groups b–g together with their conformations.

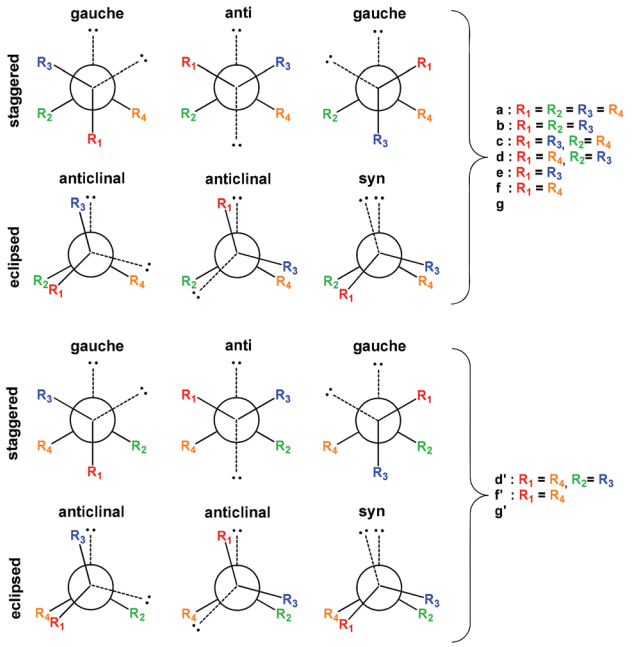


Fig. 2 Possible, idealized conformations of diphosphanes belonging to groups a–g with distinction in two different diastereomeric forms.

Fig. 2. *Anti* conformations are preferable for most systems in the 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]

Steric hindrance that is a consequence of intermolecular interactions between both RR′P fragments may force them to adapt *eclipsed* conformations weakening the overlapping of σ-P orbitals 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 iPr$_2$N exhibit *anticlinal* conformations. The P–P bond distances of the 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 the decrease of ΔH_{diss} and ΔG_{diss} (compare *e.g.* **1**, **3** and **28**, **17** and **21**) is visible.

Table 1 Selected experimental (a) and calculated (b) properties of diphosphanes **1–30**: $^{31}P\{^1H\}$ 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, and E_{F1-F2} – energy of dispersion interaction between two PR_2 units

No.	Diphosphane	$^1J_{P-P}$[a] [Hz]	δP_1[a] [ppm]	δP_2[a] [ppm]	P–P[a] [Å]	P–P[b] [Å]	ΔH_{diss}[b] [kJ mol^{-1}]	ΔG_{diss}[b] [kJ mol^{-1}]	ΔE_{F1-F2}[b] [kJ mol^{-1}]
1	*t*Bu$_2$P-P*t*Bu$_2$	—	39.6	39.6	2.234(1)[70]	2.235	166.6	96.0	−34.5
2	*t*Bu$_2$P-P*t*BuPh	370.3	30.8	1.4	—	2.244	201.3	131.0	−33.6
3	*t*Bu$_2$P-PPh$_2$	254.3	33.0	−25.9	2.237(1)	2.264	200.1	137.9	−27.3
4	*rac*-*t*BuPhP-P*t*BuPh	—	1.9	1.9	—	2.257	223.2	153.2	−27.8
5	*meso*-*t*BuPhP-P*t*BuPh	—	−4.4	−4.4	2.229(1)[73]	2.252	226.2	156.9	−26.4
6	*t*BuPhP-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-P*t*Bu$_2$	358.2	88.2	62.6	2.295(2)	2.296	145.8	66.6	−42.0
10	(iPr$_2$N)$_2$P-P*t*BuPh	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-P*t*Bu$_2$	193.7	111.1	11.8	2.2603(6)	2.275	174.8	103.5	−26.6
13	(Et$_2$N)$_2$P-P*t*BuPh	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-P*t*BuPh	138.0	28.3	−7.5	—	2.257	206.1	139.4	−30.0
16	*p-rac*-(iPr$_2$N)PhP-P*t*BuPh	145.3	27.6	−11.1	—	2.250	204.5	139.2	−26.2
17	(iPr$_2$N)PhP-P*t*Bu$_2$	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)*t*BuP-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)*t*BuP-P*t*BuPh	348.8	57.7	14.9	—	2.252	202.3	130.9	−37.6
23	*p-rac*-(iPr$_2$N)*t*BuP-P*t*BuPh	283.4	70.3	7.7	2.265(2)	2.282	186.8	109.5	−37.7
24	(iPr$_2$N)*t*BuP-P*t*Bu$_2$	489.5	69.5	65.6	2.2508(6)	2.252	167.2	96.2	−39.0
25	*meso*-(iPr$_2$N)*t*BuP-P(iPr$_2$N)*t*Bu	—	88.8	88.8	2.314(3)	2.294	154.4	80.4	−41.5
26	*rac*-(iPr$_2$N)*t*BuP-P(iPr$_2$N)*t*Bu	—	82.0	82.0	—	2.252	157.4	76.8	−46.7
27	(iPr$_2$N)*t*BuP-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-P*t*BuPh	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-P*t*BuPh	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

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

Calculations indicated that the most stable systems are those involving the P*t*BuPh unit as the one site of the P–P bond: **4–6**, **13**, **15**, **16** or **28–29**. The structural and electronic features of the P*t*BuPh moiety constitute an optimal compromise between the steric hindrance and electron-donating properties of substituents necessary for obtaining highly stable species.

To gain a better insight into the structural features of diphosphanes **1–30**, we performed conformational analysis using DFT methods, including the 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.† The 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 iPr_2N. 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 a 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 $^1J_{P-P}$ 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 $^1J_{P-P}$. For these species, $^1J_{P-P}$ 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 $^1J_{P-P}$ 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 the 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 a staggered conformation with *anti*-lone pair alignment, it is not the case (see ESI, Fig. S205–S234 and 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-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 iPr_2N and *t*Bu groups have the greatest values of E_{F1-F2}. As the size of substituents decreases, E_{F1-F2} decreases (less negative) and diphosphanes adopt classical *gauche* or *anti*-lone-pairs conformations (see ESI, Chart S1†). We noticed that E_{F1-F2} decreases with the number of interacting H-atoms in neighbouring fragments in the order $(iPr_2N)_2$ > $(iPr_2N)t$Bu > tBu$_2$ > (iPr_2N)Ph > *t*BuPh > Ph_2. For **4** and **7**, an *eclipsed* conformation is energetically favored due to the π–π interactions of coplanar Ph groups of neighboring P-atoms.

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, *t*BuPhPLi, Ph_2PLi,[76,77] tBu$_2$PCl,[77] iPr_2NPCl,[78] $(iPr_2N)_2PCl$[79] and $(Et_2N)_2PCl$.[79] Methods described for *t*BuPhPCl,[80] (iPr_2N)PhPCl[81] and (iPr_2N)BuPCl[82] were modified at the stage of purification of a crude product. *t*BuPhPCl and $(iPr_2N)t$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_2N)PhPCl was dried under vacuum (0.01 mmHg) at ambient temperature for 1 h giving greenish crystals. $(Et_2N)(iPr_2N)$PCl was synthesized *via* the method described in the ESI† (see Part A). $PhPCl_2$, Ph_2PCl, and iPr_2NH Et_2NH were purchased from Aldrich. Commercial reagents were distilled prior to use. Reaction progress was monitored by ^{31}P{^{1}H} NMR spectroscopy of the reaction mixtures.

Diffraction data of compounds **3**, **6**, **8**, **9**, **10**, **12**, **14**, **17**, **ox18/19**, **21**, **23**, **24**, **25**, and **28** were collected on a diffractometer equipped with a STOE image plate detector system IPDS2 T using MoKα radiation (λ = 0.71073 Å) for **3**, **6**, **8**, **9**, **10**, **12**, **14**, **17**, **ox18/19**, **21**, **24**, **25**, and **28** and CuKα Kα radiation (λ = 1.54178 Å) for **23** 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**, and **25**, at 130 K for **17**, **24**, and **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 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**, and **28** can be found in the ESI.†

Crystallographic data for the structures of **3**, **6**, **8**, **9**, **10**, **12**, **14**, **17**, **ox18/18**, **21**, **23**, **24**, **25**, and **28** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. 1560634–1560642, 1576833–1576836, and 1585541.†

Synthesis procedures

General procedure for preparation of 2, 3, 6, 8, 9, 10, 11, 12, 13, 14, 15/16, 17, 21, 22/23, 24, and 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 the syntheses including NMR data, elemental analyses, and crystallization conditions is presented in the ESI† (Part A).

General procedure for preparation of 18/19 and 25/26. 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 were mixed at room temperature and vigorously stirred overnight. The solvent was removed in a vacuum, and the residue was extracted with 15 cm^3 of toluene/petroleum ether and filtered. The filtrate was evaporated to dryness giving the product. A detailed description of the syntheses including NMR data, elemental analyses, and crystallization conditions is presented in the ESI† (Part A).

General procedure for preparation of 20 and 27. 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. The $^{31}P\{^1H\}$ NMR spectra revealed that diphosphanes **20/27** were formed as one of three products with the 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 spectroscopy. A detailed description of the syntheses including NMR data and the composition of the reaction mixtures is presented in the ESI† (Part A).

General procedure for investigation of reactivity of diphosphanes towards RR′PLi phosphides. A diphosphane RR′P-PR″R‴ (0.170 mmol) and the 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 monitored by $^{31}P\{^1H\}$ NMR spectroscopy 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 the reactions including the NMR data and composition of the final reaction mixtures is presented in the ESI† (Part A).

General procedure for investigation of reactivity of diphosphanes towards R″R‴PCl chlorophosphanes. A diphosphane RR′P-PR″R‴ (0.170 mmol) and the respective R″R‴PCl chlorophosphane (30 mol%, 0.051 mmol) were dissolved in 2 cm^3 of THF and mixed at room temperature. Reaction progress was monitored by $^{31}P\{^1H\}$ NMR spectroscopy 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 the reactions including the NMR data and composition of the final reaction mixtures is presented in the 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 the synthesis of such systems in a good yield and high purity is readily achievable by the reaction of phosphides with chlorophosphanes. Our experiments showed that for obtaining unsymmetrical systems, using a boron protecting group is not necessary. The metathesis side-reactions during the syntheses of unsymmetrical diphosphanes can be eliminated by keeping the reaction mixture at low temperature, using strictly stoichiometric amounts of reagents and isolation of the product directly after the reaction is completed. The obtained symmetrical and unsymmetrical diphosphanes with diversified substituents may be applied as P-donor ligands for transition metal complexes. Furthermore, the unsymmetrical species with a polarized P–P bond can be used as reagents in organophosphorus chemistry or in the 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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