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P-Rich Ylides

Phosphanylphosphinidene-Phosphoranes: A Study on Building and Decomposition of Phosphorus-Rich Chains with Two Ylidic Moieties

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Abstract: The reactions of tBu$_2$P–P=P(tBu$_2$)CH$_2$Li at low temperature with dichlorophosphanes RPCl$_2$ (R = Ph, Me, NEt$_2$, tBu) lead to "P-7-chains" as primary products wherein two ylidic moieties are linked by a CH$_2$–PR–CH$_2$ unit. However, if R = tBu the long chain is only a by-product in addition to tBu$_2$P–P=P(tBu$_2$)Me. The thermal decomposition of "P-7-chains" as monitored by ^{31}P NMR spectroscopy results in tBu$_2$P–CH$_2$–PR–CH$_2$–PtBu$_2$ ("P-3-chains") and the phosphanylphosphanylidene {tBu$_2$P–P} which is observed as its cyclic trimer or tetramer. In the reactions of tBu(Me$_3$Si)P–P=P(tBu$_2$)CH$_2$Li with RPCl$_2$ the corresponding "P-7-chains" and the P$_4$CH$_2$-rings are formed. The substituent R strongly determines the ratio of chain to ring as well as the thermal stability of the products. The solid-state structures of one representative of both "P-7-chains", and of the oxidized derivative of the P$_4$CH$_2$-ring with R = tBu were determined by single-crystal X-ray diffraction analysis.

Introduction

Phosphinidene-σ^4-phosphoranes (XP=PR$_3$) can be interpreted as phosphinidenes protected by phosphanes PR$_3$. Most phosphinidenes are too reactive to be isolated and can only be observed as trapped products.[1] Only recently Bertrand et al. reported on the first isolated phosphinidene, which is stable for weeks in the solid state at room temperature.[2] Since the first example of a neutral phosphinidene-phosphorane, CF$_3$P=PMe$_3$, was reported by Burg and Mahler,[3] further types of this class of low-coordinated linear phosphorus compounds have been synthesized, such as the phosphanyl-substituted P-rich ylides, R$_2$P–P=PR$_3$ discovered by the group of Fritz[4] and later the thermally stable ArP=PR$_3$ (Ar are sterically demanding aryl groups) observed by Protasiewicz et al.[5] It has been shown that the latter representatives can react with electrophiles[6] and can be used for phospha-Wittig syntheses.[7]

Our research interests are focused on the chemistry of ylides of type R$_2$P–P=PR$_3$ with a pure phosphorus chain. We have synthesized numerous representatives of this class of materials[4,8] and studied extensively how their formation and properties depend on their substituents,[9] and some of these compounds were also structurally characterized.[10] These ylides possess a remarkable synthetic potential as phosphanylphosphinidene transfer reagents in the chemistry of transition metal complexes.[11] A number of other phosphanylphosphinidene-phosphoranes are accessible by phosphane-exchange reactions. The extent of these equilibrium reactions depends on the substituents in the phosphanes.[12]

Linear oligophosphanes of type R$_2$P–(PR)$_n$–PR$_2$ (R = alkyl, aryl, SiMe$_3$) with a chain length n > 4 are unstable.[13] Attempts to access such long P-chains resulted in cyclophosphanes and diphosphanes as a consequence of disproportionation and rearrangement reactions. The synthesis of tBu(Me$_3$Si)P–P=P(tBu$_2$)Me[8b] with the functional SiMe$_3$ group at the terminal P-atom offered the chance to study the influence of a phosphinidene-phosphorane unit on the formation of longer P-chains. Furthermore, the question arises whether the inclusion of a second phosphinidene-phosphorane unit in the same molecule might be possible. Schmidpeter et al. reported earlier on the preparation of tetraphosphenes and cyclotetraphosphanes with two R$_3$P=C ylidyl substituents which stabilize a low coordination environment of phosphorus.[14] The bis- and tris(alkylidene-phosphoranyl)phosphanes observed by Karsch represent a new type of ylide–phosphane chelating ligands.[15] Protasiewicz et al. developed a diphospha-Wittig reagent containing two Me$_3$P=P ylidyl units that was successfully used for the synthesis of phosphaalkene polymers.[16]

In order to obtain a P-rich phosphinidene-phosphorane the cleavage of the Si–P bond in tBu(Me$_3$Si)P–P=P(tBu$_2$)Me with nBuLi in THF was attempted. However, the PMe group was lithiated resulting in the ylide tBu(Me$_3$Si)P–P=P(tBu$_2$)CH$_2$Li; this sur-

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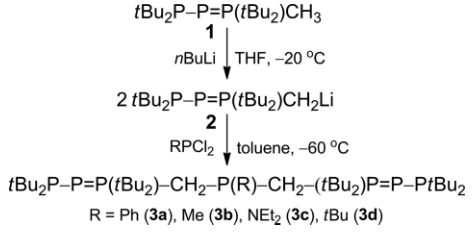
prising reactivity is similar to that previously reported for tBu$_2$P–P=P(tBu$_2$)Me.[17] In the present work, we describe the reactions of these functionalized ylides with various dichlorophosphanes RPCl$_2$, which result in neutral P-rich chains and rings, and the effect of the group R on the thermal stability of these new ylides. The decomposition processes could be monitored by ^{31}P NMR spectroscopy. All compounds were investigated by NMR spectroscopy in solution, and by single-crystal X-ray structural determination when appropriate.

Results and Discussion

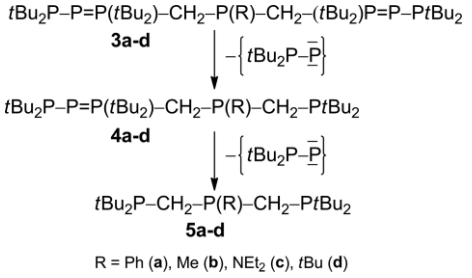
Reactions of tBu$_2$P–P=P(tBu$_2$)CH$_2$Li (2) with RPCl$_2$

Generated via lithiation of the parent ylide **1**, compound **2** reacts with dichlorophosphanes RPCl$_2$ with R = Ph, Me, NEt$_2$, and tBu (molar ratio 2:1) at low temperature to afford the new P-rich compounds **3a**–**d** which contain two ylidic moieties linked by a CH$_2$–P–CH$_2$ unit, which we will refer to here as "P-7-chains" (Scheme 1).



Scheme 1. Formation of "P-7-chains" **3a**–**d**.

The stability of **3a**–**d** formed as primary products in all reactions depends strongly on the substituent R. Dichlorophosphanes RPCl$_2$ (R = Ph, Me, or NEt$_2$) react with **2** to give almost exclusively the "P-7-chains" **3a**–**c**. Only small amounts of tBu$_2$P–P=P(tBu$_2$)Me (**1**) were observed as by-product, which is formed by protonation of the starting THF-containing compound **2**. This back-protonation occurred already during the synthesis of **2**. In contrast, the reaction of tBuPCl$_2$ with **2** gives the "P-7-chain" **3d** only in low yield, with the major product the starting material tBu$_2$P–P=P(tBu$_2$)Me **1**. The formation of the protonated ylide corresponds to the general behavior of compounds with sterically strained tBu groups, which readily eliminate Me$_2$C=CH$_2$.[18] During the reaction, the shorter chain **4d** was already being formed by decomposition of **3d** (Scheme 2), with the molar ratio of compounds **1**:**3d**:**4d** estimated as 4:1:1 by integration of the ^{31}P{^{1}H} NMR spectra. Compound **3d** could not be isolated, however **3a**–**c** were obtained as colorless solids and investigated by ^{1}H and ^{31}P NMR spectroscopy in solution.



Scheme 2. Decomposition of **3a**–**d**.

At room temperature, compounds **3a**–**c** can be stored for days in the solid state under dry nitrogen with little decomposition, whereas in solution the long "P-7-chains" decompose much more rapidly, forming successively the shorter chains **4a**–**d** and then **5a**–**d** by loss of the phosphinidene unit {tBu$_2$P–P} (Scheme 2). The latter oligomerizes, forming the cyclophosphanes [tBu$_2$PP]$_4$ and [tBu$_2$PP]$_3$. These decomposition processes could be monitored by ^{31}P NMR spectroscopy (Figure 1). A similar decomposition was also observed in the case of the previously investigated compounds of type R$_2$P–P=PR$_3$ containing only one ylidic unit.[4] The PPh-bridged compound **3a** proved to be the most stable of these "P-7-chains" in solution, and both **3a** and its decomposition product **4a** could also be characterized by ^{13}C NMR spectroscopy.

Reactions of tBu(Me$_3$Si)P–P=P(tBu$_2$)CH$_2$Li (7) with RPCl$_2$

Analogously to the formation of **2** from **1**, the lithiated tBu(Me$_3$Si)P–P=P(tBu$_2$)CH$_2$Li (**7**) can be generated from the ylide

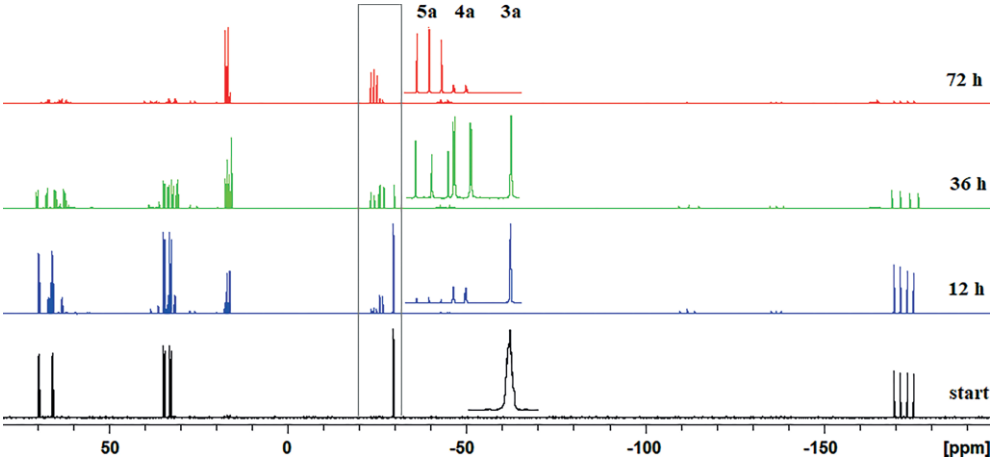


Figure 1. 31P{^{1}H} NMR spectra of the decomposition of **3a** in C$_6$D$_6$ at 25 °C. Bottom trace: pure **3a**; second trace: decomposition beginning (**3a** > **4a** > **5a**); third trace: further decomposition; top trace: **5a** >> **4a**, no **3a** remains.

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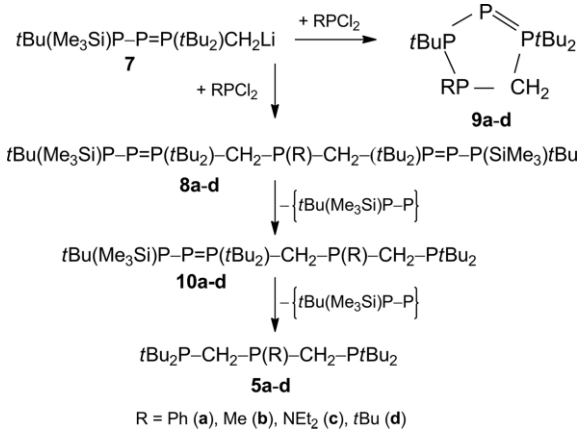
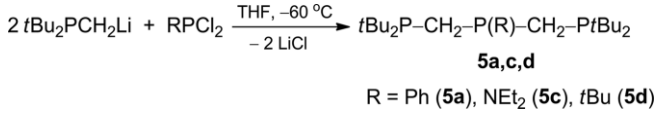
*t*Bu(Me$_3$Si)P–P=P(*t*Bu$_2$)Me (**6**). In contrast to **2**, compound **7** now has two functional groups and can therefore react with RPCl$_2$ to form either the "P-7-chains" **8a**–**d** or P$_4$CH$_2$-rings **9a**–**d** (Scheme 3). Which reaction branch prevails depends strongly on the substituent R and less on the molar ratio of the reactants. In the case of R = Me or Ph, "P-7-chain" formation is favored at low temperature (–60 °C), independent of the stoichiometry. In the ^{31}P NMR spectra of the reaction solutions, signals of rings could only be observed with low intensity. For R = *t*Bu or NEt$_2$ the formation of both ring and chain was observed. However, when R = *t*Bu a molar ratio of **7:**RPCl$_2$ = 1:1 favors the ring formation, whereas ring and chain are formed in comparable amounts with a molar ratio of **7:**RPCl$_2$ = 2:1. If the reaction was carried out at a slightly higher temperature (–30 °C), the amount of chains increased compared to that of the rings. In addition, the back-protonation of **7** to the starting compound *t*Bu(Me$_3$Si)P–P=P(*t*Bu$_2$)Me (**6**) was also observed. Furthermore, all reactions were accompanied by the formation of *t*Bu(Me$_3$Si)P–P=P(*t*Bu$_2$)–CH$_2$–SiMe$_3$ (**11**) as a by-product.



Scheme 3. Formation and decomposition of "P-7-chains" **8a**–**d** and rings **9a**–**d**.

Due to the rather low thermal stability of these "P-7-chains" in solution at room temperature, they decompose rapidly, first to the "P-5-chains" **10a**–**d**, and then the "P-3-chains" **5a**–**d.** The formation of these compounds results from the loss of the phosphinidene {*t*Bu(Me$_3$Si)P–P}, similar to the decomposition of the chains **3a**–**d**. However the analogous subsequent reaction, the formation of cyclophosphanes by tri- or tetramerization of {*t*Bu(Me$_3$Si)P–P}, could not be detected; only signals from monophosphanes [e.g. *t*BuP(SiMe$_3$)$_2$] and higher phosphanes could be observed in the ^{31}P NMR spectra. These decomposition products can be formed by breaking of all P–P bonds in the chains.

Compounds **5a,c,d** could be synthesized and isolated by a different procedure (Scheme 4) and characterized by ^{1}H, ^{13}C, ^{31}P NMR spectroscopy, as well as by mass spectrometry. These



Scheme 4. Synthesis of "P-3-chains" **5a**,**c**,**d**.

results have greatly facilitated the identification of the decomposition products and the assignment of the signals in the NMR spectra, as only compound **5b** had been previously reported.[19]

^{31}P{^{1}H} NMR Investigations

The ^{31}P{^{1}H} NMR spectra of the chains **3a**–**d** show four signal groups (Table 1); the (P^1–P^2–P^3–CH$_2$–) and (–CH$_2$–P^5–P^6–P^7) moieties give identical spectra by symmetry. (The notation of the P atoms is consistent with that of the molecular structures.) The ^{31}P NMR signals of the phosphanyl atoms P^1, P^7 appear in the range of 30.9 to 33.5 ppm as dd multiplet, similar to those in *t*Bu$_2$P–P=P(*t*Bu$_2$)Me (**1**), while those for the phosphinidene atoms P^2, P^6 are in the range of –167.4 to –173.7 ppm. The latter are strongly shifted downfield compared to **1** (δP^2 = –200.6 ppm), and show ddd splitting owing to the atoms P^1, P^7, and P^3, P^5, and P^4, respectively. The ^{31}P NMR signals of the phosphorane atoms P^3, P^5 (in the range of 62.0 to 67.6 ppm) are observed slightly downfield relative to the corresponding signal in **1** and show ddd splitting. The ^{31}P chemical shifts of P^4 depend on the substituents (Table 1). The coupling constants $^1J_{P1,P2}$, $^1J_{P6,P7}$ with values of about 290 Hz and $^1J_{P2,P3}$, $^1J_{P5,P6}$ of about 600 Hz, respectively, indicate a strongly different bonding situation in the molecules. The large absolute values of $^1J_{P2,P3}$ indicate a partial double bond between P^2 and P^3, as was also shown for **1**.[10b] The molecular structure of **3a** from single-crystal X-ray diffraction is in accordance with the NMR results (see later).

Table 1. ^{31}P NMR data of *t*Bu$_2$P^1–P^2=P^3(*t*Bu$_2$)Me (**1**), *t*Bu$_2$P^1–P^2=P^3(*t*Bu$_2$)CH$_2$Li (**2**), and *t*Bu$_2$P^1–P^2=P^3(*t*Bu$_2$)–CH$_2$–P^4(R)–CH$_2$–(*t*Bu$_2$)P^5=P^6–P^7*t*Bu$_2$ (**3a**–**d**).[a]

	3a	**3b**	**3c**	**3d**	**1**	**2**
δP^1/P^7	33.5	30.9	33.1	30.9	33.6	39.9
δP^2/P^6	–172.5	–173.7	–172.2	–167.4	–200.6	–176.2
δP^3/P^5	67.5	63.2	67.6	62.0	58.0	78.8
δP^4	–29.8	–38.6	53.3	–1.0		
$^1J_{P1,P2}$	289.1	288.5	290.8	291.7	275.2	324.3
$^1J_{P2,P3}$	608.1	616.4	605.1	618.8	604.4	494.2
$^2J_{P1,P3}$	53.6	54.3	54.3	52.8	64.3	34.9
$^2J_{P3,P4}$	5.6	14.1	9.6	18.9		
$^3J_{P2,P4}$	0	21.1	4.3	22.9		

[a] 298 K, C_6D_6, δ [ppm], J [Hz], $^1J_{P1,P2} = {}^1J_{P6,P7}$, $^1J_{P2,P3} = {}^1J_{P5,P6}$, $^2J_{P1,P3} = {}^2J_{P5,P6}$, $^2J_{P3,P4} = {}^2J_{P4,P5}$, $^2J_{P2,P4} = {}^2J_{P4,P6}$.

The "P-7-chains" **8a**–**d** contain two asymmetric centers with the same constitution: P^1 and P^7. If these atoms possess opposite configuration, then P^4 is a pseudocenter, i.e. a stereogenic atom. Accordingly, four stereoisomeric chains exist in the same quantity: P^1*R*,P^7*R*, P^1*R*,P^7*S*, P^1*S*,P^7*R*, and P^1*S*,P^7*S* (Figure S9 in the SI). Since P^1*R*,P^7*R* and P^1*S*,P^7*S* are an enantiomeric pair, only three diastereomers can be observed in the ^{31}P NMR spectra in the molar ratio of 1:1:2. Using the optimized coupling constants as obtained by iterations to simulate the superimposed multiplet regions, the ^{31}P NMR spectra of the "P-7-chains" with terminal *t*Bu(Me$_3$Si)P groups can be assigned in the same way as those with *t*Bu$_2$P groups.[20] An example is given in SI (Figure S15). As expected, the ^{31}P NMR signals appear in the following three ranges for the *t*Bu(Me$_3$Si)P–P=P*t*Bu$_2$ moiety successively: –73.9 to –77.0 ppm (P^1, P^7), –178.5 to –182.7 ppm (P^2, P^6), and

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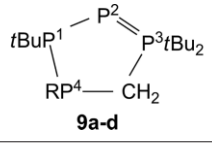
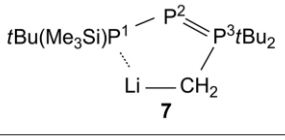
60.1–66.2 (P^3, P^5). Similarly to compounds **3a**–**d**, the ^{31}P NMR signals of P^2, P^6 lie significantly downfield with respect to those in *t*Bu(Me$_3$Si)P–P=P(Me)*t*Bu$_2$ (**6**), whereas the signals of P^3, P^5 are only slightly downfield shifted (**6**: δP^2: –207.2 ppm; P^3: 57.8 ppm).[10b] The large difference between the coupling constants $^1J_{P1,P2}$, $^1J_{P6,P7}$ (about 250 Hz) and $^1J_{P2,P3}$, $^1J_{P5,6}$ (about 625 Hz) shows that a bond system typical for ylides as **1** and **6** is present also in these "P-7-chains".

The ^{31}P NMR investigations of **9a**–**d** confirmed the formation of rings (Table 2). As a result of the elimination of the SiMe$_3$ group from P^1 during the formation of the rings the nuclei P^1 are strongly deshielded compared to the parent lithium compound **7** as expected, whereas the phosphinidene nuclei P^2 in **9a**–**d** are strongly shielded, the chemical shifts for P^3 show no significant change relative to those of **7**. The coupling constants $^1J_{P1,P2}$ and $^1J_{P1,P4}$ with values between 196 Hz and 287 Hz are typical for P–P single bonds, while the $^1J_{P2,P3}$ above 500 Hz are much higher and indicate a partial double bond between P^2 and P^3. However, the differentiation between the P–P bonds in these rings does not reach that in the chain-like ylides, but shows more similarity to compound **7**, in which lithium easily coordinates P^1 forming a ring.[17]

Table 2. ^{31}P NMR data of **9a**–**d** and **7**.[a]



9a-d



7

	9a	9b	9c	9d	7
$\delta P^1/P^7$	43.3	49.7	4.0	31.9	–67.1
$\delta P^2/P^6$	–224.7	–222.4	–258.7	–225.0	–186.0
$\delta P^3/P^5$	82.5	87.0	64.0	87.9	79.8
δP^4	–30.8	–43.4	54.2	16.9	
$^1J_{P1,P2}$	251.4	255.2	249.7	287.1	294.3
$^1J_{P2,P3}$	522.8	532.2	506.8	543.8	505.1
$^1J_{P1,P4}$	206.5	196.2	226.3	240.7	
$^2J_{P3,P4}$	16.5	10.9	21.4	3.5	
$^2J_{P2,P4}$	6.4	4.5	10.3	0	
$^2J_{P1,P3}$	0	0	2.8	7.6	25.6

[a] 298 K, C_6D_6, δ [ppm], J [Hz].

Crystal Structure Investigations

Crystal structures of one representative of each set of "P-7 chains" (**3a**, **8b**) were determined. Colorless crystals suitable for X-ray structure investigations were obtained from toluene/pentane solution. Compound **3a** crystallizes in the monoclinic space group $P2_1/n$ (Figure 2). The P1–P2 and P6–P7 distances are located at the lower limit of the range of 2.17–2.24 Å given by Corbridge for P–P single bonds.[21] In contrast to these, the P2–P3 and P5–P6 distances are shorter by 0.0519 Å and 0.0453 Å, respectively, and point to a small partial double bond character. These data are similar to those in the parent compound *t*Bu$_2$P–P=P(*t*Bu$_2$)Me (**1**) (P1–P2 2.1791 Å, P2–P3 2.1263 Å),[10b] consequently the linkage of two ylidic moieties by a CH$_2$–P–CH$_2$ unit does not severely influence the bonding system. The sum of the angles around P4 in **3a** is 297.6°, thus P4 has a pyramidal coordination geometry.

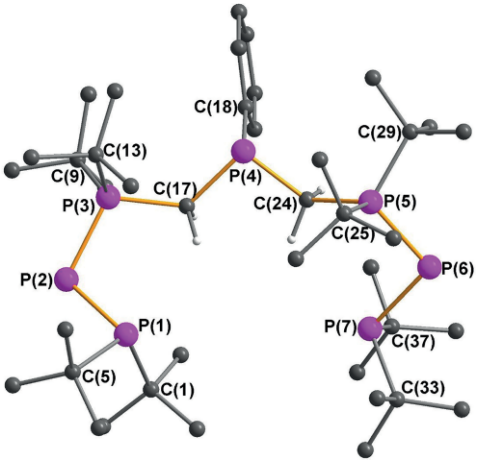


Figure 2. Molecular structure of **3a**. H atoms [except for those of the methylene groups C(17) and C(24)] are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: P1–P2 2.1851(9), P2–P3 2.1332(8), P3–C17 1.835(2), P4–C17 1.869(2), P4–C24 1.872(2), P4–C18 1.835(2), P5–C24 1.824(2), P5–P6 2.1320(9), P6–P7 2.1773(10), P1–P2–P3 102.83(4), C17–P3–P2 110.25(8), C17–P4–C24 96.04(11), C17–P4–C18 102.07(11), C18–P4–C24 99.45(11), C24–P5–P6 110.87(8), P5–P6–P7 100.63(4), P3–C17–P4 126.51(13), P5–C24–P4 123.36(13).

Compound **8b** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ (Figure 3). The central P4 is slightly (P4A 92 %; P4B 8 %) disordered to either side of the C16–C17–C18 triangle, while the *t*Bu and SiMe$_3$ substituents on P7 are also mutually disordered (major component A 78 %, minor component B 22 %). Thus, in the molecule shown in Figure 3, P1 has an *R*-configuration, while in 78 % of the molecules in the crystal P7 is also *R*, but in the other 22 % it is *S*. The second molecule in the centrosymmetric unit cell then shows the opposite enantiomeric configurations to these. Thus in the crystal the chiral diastereomer (*RR* and *SS*) dominates over the *meso* form (*RS* or *SR*). The P–P bond lengths and differences between the P1–P2 and

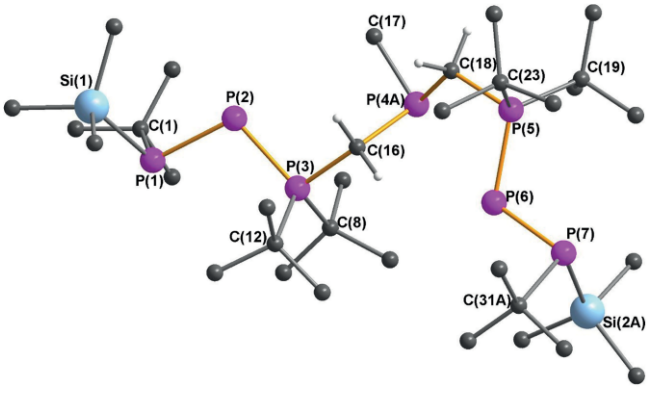


Figure 3. Molecular structure of **8b**. H-atoms [except for methylene groups C(16) and C(18)] and the minor disordered component are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: P1–P2 2.1947(9), P2–P3 2.1342(9), P3–C16 1.831(2), P4A–C16 1.848(3), P4A–C17 1.854(3), P4A–C18 1.852(2), P5–C18 1.830(2), P5–P6 2.1378(8), P6–P7 2.1867(9), P1–P2–P3 107.43(3), C16–P3–P2 101.17(8), C16–P4A–C18 97.32(11), C16–P4A–C17 100.38(13), C18–P4A–C17 95.54(12), C18–P5–P6 104.54(8), P5–P6–P7 107.25(4), P3–C16–P4A 124.32(13), P5–C18–P4A 120.87(13).

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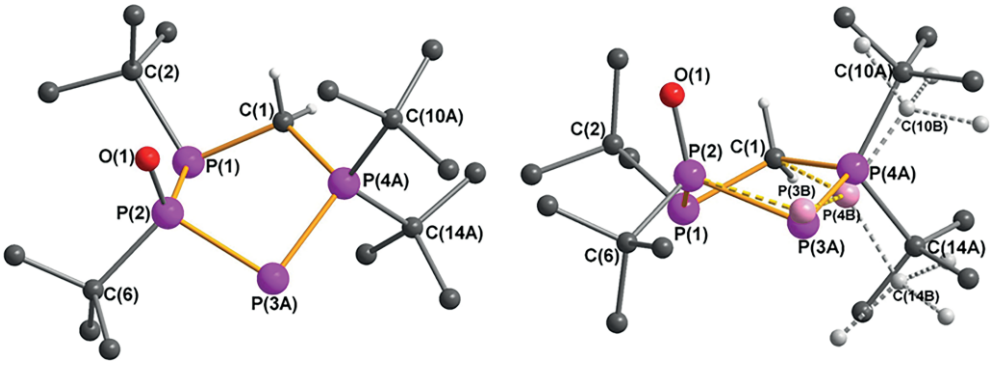

Figure 4. (a) Molecular structure of **9d-O** (major disorder component), (b) the twisting disorder of the P_4C ring in **9d-O** (minor component drawn with smaller and paler spheres and dashed bonds). All H-atoms except those of the methylene group C(1), have been omitted for clarity. Selected bond lengths [Å] and bond angles [°] for the major component: P1–P4 2.273(2), P1–P2A 2.189(7), P2A–P3A 2.178(9), P4–C1 1.882(6), P3A–C1 1.846(9), P2A–P1–P4 95.9(4), P1–P2A–P3A 94.1(4), C1–P4–P1 93.37(18), C1–P3A–P2A 106.1(6).

P2–P3 distances (Δ = 0.0605 Å), and the P5–P6 and P6–P7 distances (Δ = 0.0489 Å) show a close similarity to **3a**. A comparison of these data with those of *t*Bu(Me$_3$Si)P1–P2=P3(*t*Bu$_2$)Me (**6**) (P2–P3 2.1358 Å; P1–P2 2.1826 Å; difference 0.0468 Å)[10b] shows that the bonding system is not substantially affected by the concatenation of the two ylides by a P-link. It is clear from Figure 2 and Figure 3 that molecules of **3a** and **8b** pack in their respective crystals with very different conformations. While the backbone of **3a** adopts a structure with an idealized twofold axis through P4, that of **8d** is highly unsymmetrical.

After several attempts to obtain crystals of **9d** suitable for X-ray structure investigations, a few crystals could be obtained from lengthy storage of a toluene solution overlaid with hexane/CH_2Cl_2. The X-ray crystallographic study (trigonal $R\bar{3}$ with Z = 18) revealed that these crystals contained were not of **9d**, but its oxidation product, **9d-O**, which contained the expected P_4C ring, but with an O atom now bonded to P1 (Figure 4a), in contrast to the results of ^{31}P NMR and HRMS measurements. Unfortunately, insufficient **9d-O** could be isolated to be characterized spectroscopically.

In the structure of **9d-O**, the P_4C ring system showed a twisting disorder in which the atoms of the *t*Bu$_2$P–P moiety were disordered (56:44 %, Figure 4b). The P1–P2 and P2–P3 distances are closely similar and lie just at the lower limit of P–P single bonds, slightly shorter than those in the P_3CLi ring of **2**.[17] In contrast, the P1–P4 distance with 2.273(2) Å is significantly longer and comparable with the P–P bond lengths in the five-membered ring $(PPh)_4CH_2S_2$ (2.233–2.253 Å).[22]

Conclusions

The functionalized ylides *t*Bu$_2$P–P=P(*t*Bu$_2$)CH$_2$Li (**2**) and *t*Bu(Me$_3$Si)P–P=P(*t*Bu$_2$)CH$_2$Li (**7**) opened a way to form linear P-rich chains. **2** reacted with dichlorophosphanes $RPCl_2$ (R = Ph, Me, NEt_2) in molar ratio 2:1 at –60 °C to afford the new "P-7-chains" (**3a**–**c**) almost quantitatively; these contain two ylidic moieties linked by a CH_2–P–CH_2 unit. In contrast, the reaction of *t*BuPCl$_2$ with **2** resulted in *t*Bu$_2$P–P=P(*t*Bu$_2$)Me as main product; the "P-7-chain" (**3d**) was here only a by-product. In the solid state **3a**–**c** can be stored under dry nitrogen for days at room temperature, and for long periods at –30 °C, without noticeable decomposition, whereas in solution the "P-7-chains" decompose successively within a few days to "P-5-" and "P-3-chains" by elimination of the phosphinidene {*t*Bu$_2$P–P}. The decomposition processes could be monitored by ^{31}P NMR spectroscopy.

*t*Bu(Me$_3$Si)P–P=P(*t*Bu$_2$)CH$_2$Li (**7**) reacts with $RPCl_2$ forming either the corresponding "P-7-chains" by elimination of LiCl, or P_4CH_2-rings by elimination of Me$_3$SiCl. The substituent R strongly determines the ratio of chain to ring, whereas the stoichiometry has less influence on the reaction.

The molecular structures of the "P-7-chains" **3a** and **8b** show a similar bonding situation as it was observed in the parent ylides **1** and **6**. The P–P bond lengths differ only slightly, the terminal P–P distances are near the border between single and double bonding, while the ylidic P–P distances suggest a small partial double bond character.

Experimental Section

General

All manipulations were performed under a dry nitrogen atmosphere with exclusion of air and moisture using standard Schlenk techniques. All solvents were dried by using standard procedures (toluene, THF, C_6D_6, and [D_8]toluene over sodium/benzophenone; hexane, and pentane over $LiAlH_4$) and freshly distilled prior to use. CD_2Cl_2 was dried with activated molecular sieves. *n*BuLi (1.6 M in hexane), $PhPCl_2$, and $MePCl_2$ were purchased from Sigma-Aldrich, and *n*BuLi was used as received, the dichlorophosphane was freshly distilled under dry nitrogen atmosphere. *t*Bu$_2$P–P=P(*t*Bu$_2$)Me (**1**),[10] *t*Bu(Me$_3$Si)P–P=P(*t*Bu$_2$)Me (**6**),[8a] *t*Bu$_2$P–P=P(*t*Bu$_2$)CH$_2$Li (**2**),[17] *t*Bu(Me$_3$Si)P–P=P(*t*Bu$_2$)CH$_2$Li (**7**),[17] *t*Bu$_2$PCH$_2$Li,[23] *t*Bu$_2$PMe,[24] *t*BuPCl$_2$,[25] and Et_2NPCl_2[26] were prepared according to literature procedures.

The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AMX 300, Av 400, and DRX 500 spectrometers, using the deuterated solvents (C_6D_6, CD_2Cl_2, or [D_8]toluene for low temperature experiments) as internal lock, and TMS (^{1}H, ^{13}C), and 85 % H_3PO_4 (^{31}P) as external standards. Two-dimensional ^{1}H–^{13}C HSQC, HMBC, and ^{1}H–^{31}P HMBC spectra were recorded using standard Bruker pulse sequences. Temperature calibration of the NMR measurements was carried out using Bruker standard samples. ^{1}H NMR spectra of

higher order and $^{31}P\{^1H\}$ NMR spectra (for an exact assignment of the signals) were analyzed using Daisy iterations.[20] High resolution mass spectra were measured on a Varian MAT 8200 mass spectrometer. The MS investigations for "P-7-" and "P-5-chains" were unsuccessful, no M^+-Ion could be observed, only the decomposition products could be detected. Elemental analyses were performed with an Elementar vario EL analyser.

Data for **3a** and **8b** were collected at 200(2) K on a Stoe IPDS II diffractometer, data for **9d**-**O** at 100(2) K on a Bruker SMART Apex diffractometer, in all cases using graphite-monochromated Mo-K_α radiation. Structure solution was by direct methods (SHELXS-97[27]), followed by full-matrix least-squares refinement against F^2_{obs} using SHELXL-2018[28] within the Olex2 platform.[29] Anisotropic thermal parameters were assigned to all non-H atoms, apart from C-atoms of minor disorder components; H-atoms were placed in calculated positions. Further details of the structural refinements and a table of crystallographic parameters (Table S1) can be found in the Supporting Information.

CCDC 1848034 (for **3a**), 1848035 (for **8b**), and 1848036 (for **9d**-**O**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Synthesis of Compounds 3a–d

A solution of the corresponding $RPCl_2$ (0.75 mmol) in toluene (5 mL) was added dropwise to a solution of tBu$_2$P–P=P(tBu$_2$)CH$_2$Li•2.5THF (**2**) (0.78 g, 1.50 mmol) in toluene (10 mL) at –60 °C. After 4 hours stirring at the same temperature the formed precipitate was removed by filtration. During the filtration the filtrate was kept at –60 °C. Then, two thirds of the solvent were removed under reduced pressure, and a little pentane was layered on the remaining residue. Colorless crystals grew from this solution at –40 °C. In the case of **3a** single crystals suitable for X-ray structure determinations could be obtained.

3a (R = Ph): Yield: 0.47 g (81 %), m.p. 103 °C (dec.). ^1H NMR (400.13 MHz, C_6D_6, 25 °C): δ = 1.09 (d, $^3J_{HP3}$ = 14.0 Hz, 18H, C(CH$_3$)$_3$), 1.56 (d, $^3J_{HP1}$ = 11.0 Hz, 18H, C(CH$_3$)$_3$), 1.57 (d, $^3J_{HP3}$ = 14.5 Hz, 18H, C(CH$_3$)$_3$), 1.60 (d, $^3J_{HP1}$ = 11.5 Hz, 18H, C(CH$_3$)$_3$), 3.18 (J_{AB} = 15.5 Hz, $^2J_{HP}$ = 9.8 Hz, $^2J_{HP}$ = 2.0 Hz, 2H, CH$_2$(A)), 3.33 (J_{AB} = 15.5 Hz, $^2J_{HP}$ = 14.2 Hz, $^2J_{HP}$ = 5.6 Hz, 2H, CH$_2$(B)), 6.96–7.06 (m, 3H, Ph), 7.69–7.75 (m, 2H, Ph) ppm. $^{13}C\{^1H\}$ NMR (201.11 MHz, C_6D_6, 25 °C): δ = 29.7 (dd, $^2J_{CP3}$ = 5.9 Hz, $^3J_{CP2}$ = 2.5 Hz, (*C*H$_3$)$_3$CP^3), 30.3 (dd, $^2J_{CP3}$ = 6.4 Hz, $^3J_{CP2}$ = 3.6 Hz, (*C*H$_3$)$_3$CP^3), 30.6 (dddd, $^1J_{CP3}$ = 46.2 Hz, $^1J_{CP4}$ = 24.7 Hz, $^2J_{CP2}$ = 17.8 Hz, $^3J_{CP1}$ = 6.7 Hz, CH$_2$), 32.6 (dd, $^2J_{CP1}$ = 13.6 Hz, $^3J_{CP2}$ = 4.8 Hz, (*C*H$_3$)$_3$CP^1), 33.1 (dd, $^2J_{CP1}$ = 13.1 Hz, $^3J_{CP2}$ = 5.0 Hz, (*C*H$_3$)$_3$CP^1), 35.5 (ddd, $^1J_{CP1}$ = 27.6 Hz, $^2J_{CP2}$ = 11.3 Hz, $^3J_{CP3}$ = 7.6 Hz, (CH$_3$)$_3$CP^1), 35.7 (ddd, $^1J_{CP1}$ = 26.2 Hz, $^2J_{CP2}$ = 11.5 Hz, $^3J_{CP3}$ = 8.3 Hz, (CH$_3$)$_3$CP^1), 38.4 (dd, $^1J_{CP3}$ = 30.2 Hz, $^2J_{CP2}$ = 9.8 Hz, (CH$_3$)$_3$CP^3), 39.7 (ddd, $^1J_{CP3}$ = 26.2 Hz, $^2J_{CP2}$ = 6.0 Hz, $^3J_{CP1}$ = 2.0 Hz, (CH$_3$)$_3$CP^3), 129.6 (d, J_{CP} = 8.7 Hz, Ph), 131.2 (d, J_{CP} = 1.2, Ph), 135.0 (d, J_{CP} = 22.2 Hz, Ph), 140.5 (d, J_{CP} = 19.9 Hz, Ph) ppm. $^{31}P\{^1H\}$ NMR (161.97 MHz, C_6D_6, 25 °C): δ = –172.5 (dd, $^1J_{P2P3}$ = 608.1 Hz, $^1J_{P1P2}$ = 289.1 Hz, P^2, P^6), –29.8 (unresolved multiplet, P^4), 33.5 (dd, $^1J_{P1P2}$ = 289.1 Hz, $^2J_{P1P3}$ = 53.6 Hz, P^1, P^7), 67.5 (ddd, $^1J_{P2P3}$ = 608.1 Hz, $^2J_{P1P3}$ = 53.6 Hz, $^2J_{P3P4}$ = 5.6 Hz, P^3, P^5) ppm. Elemental analysis calcd. for $C_{40}H_{81}P_7$: C 61.68, H 10.48, found C 61.01, H 10.50.

3b (R = Me): Yield: 0.38 g (71 %), m.p. 79 °C (dec.). ^1H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ = 1.29 (d, $^3J_{HP1}$ = 10.9 Hz, 18H, C(CH$_3$)$_3$), 1.30 (d, $^3J_{HP1}$ = 11.0 Hz, 18H, C(CH$_3$)$_3$), 1.53 (d, $^3J_{HP3}$ = 14.0 Hz, 18H, C(CH$_3$)$_3$), 1.54 (d, $^3J_{HP1}$ = 13.9 Hz, 18H, C(CH$_3$)$_3$), 1.68 (d, $^2J_{HP4}$ = 5.9 Hz, 3H, PCH$_3$), 2.24 (J_{AB} = 14.6 Hz, $^2J_{HP}$ = 10.4 Hz, $^2J_{HP}$ = 3.8 Hz, 2H, CH$_2$(A)), 2.63 (J_{AB} = 14.6 Hz, $^2J_{HP}$ = 13.1 Hz, $^2J_{HP}$ = 3.1 Hz, J_{HP} = 1.6 Hz, 2H, CH$_2$(B)) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 25 °C): δ = –173.7 (ddd, $^1J_{P2P3}$ = 616.4 Hz, $^1J_{P1P2}$ = 288.5 Hz, $^3J_{P2P4}$ = 21.1 Hz, P^2,P^6), –38.6 (tt, $^2J_{P3P4}$ = 14.1 Hz, $^3J_{P2P4}$ = 21.1 Hz, P^4), 30.9 (dd, $^1J_{P1P2}$ = 288.5 Hz, $^2J_{P1P3}$ = 54.3 Hz, P^1, P^7), 63.2 (ddd, $^1J_{P2P3}$ = 616.4 Hz, $^2J_{P1P3}$ = 54.3 Hz, $^2J_{P3P4}$ = 14.1 Hz, P^3, P^5) ppm. Elemental analysis calcd. for $C_{35}H_{79}P_7$: C 58.64, H 11.11, found C 58.74, H 11.13.

3c (R = NEt$_2$): Yield: 0.37 g (64 %), m.p. 84 °C (dec.). ^1H NMR (400.13 MHz, C_6D_6, 25 °C): δ = 1.03 (hidden by NCH$_2$*C*H$_3$), 1.45 (d, $^3J_{HP3}$ = 13.9 Hz, 18H, C(CH$_3$)$_3$), 1.51 (d, $^3J_{HP3}$ = 14.0 Hz, 18H, C(CH$_3$)$_3$), 1.54 (d, $^3J_{HP1}$ = 10.4 Hz, 18H, C(CH$_3$)$_3$), 1.54 (d, $^3J_{HP1}$ = 10.9 Hz, 18H, C(CH$_3$)$_3$), 2.64 (J_{AB} = 15.7 Hz, $^2J_{HP}$ = 12.6 Hz, $^2J_{HP}$ = 3.4 Hz, 2H, CH$_2$(A)), 2.99 (J_{AB} = 15.7 Hz, 2H, CH$_2$(B)), 3.0 (unresolved, NC*H*$_2$CH$_3$) ppm. $^{31}P\{^1H\}$ NMR (161.97 MHz, C_6D_6, 25 °C): δ = –172.2 (ddd, $^1J_{P2P3}$ = 605.1 Hz, $^1J_{P1P2}$ = 290.8 Hz, $^3J_{P2P4}$ = 4.3 Hz, P^2,P^6), 33.1 (dd, $^1J_{P1P2}$ = 290.8 Hz, $^2J_{P1P3}$ = 54.3 Hz, P^1, P^7), 53.3 (tt, $^2J_{P3P4}$ = 9.6 Hz, $^3J_{P2P4}$ = 4.3 Hz, P^4), 67.6 (ddd, $^1J_{P2P3}$ = 605.1 Hz, $^2J_{P1P3}$ = 54.3 Hz, $^2J_{P3P4}$ = 9.6 Hz, P^3, P^5), ppm. Elemental analysis calcd. for $C_{38}H_{86}NP_7$: calcd. C 58.97, H 11.20, N 1.81, found C 58.68, H 11.43, N 1.60.

3d (R = *t*Bu): Yield: 16 % (estimated by integration of the $^{31}P\{^1H\}$ NMR spectra). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 25 °C): δ = –167.4 (ddd, $^1J_{P2P3}$ = 618.8 Hz, $^1J_{P1P2}$ = 291.7 Hz, $^3J_{P2P4}$ = 22.9 Hz, P^2,P^6), –1.0 (tt, $^2J_{P3P4}$ = 18.9 Hz, $^3J_{P2P4}$ = 22.9 Hz, P^4), 30.9 (dd, $^1J_{P1P2}$ = 291.7 Hz, $^2J_{P1P3}$ = 52.8 Hz, P^1, P^7), 62.0 (ddd, $^1J_{P2P3}$ = 618.8 Hz, $^2J_{P1P3}$ = 52.8 Hz, $^2J_{P3P4}$ = 18.9 Hz, P^3, P^5) ppm.

Synthesis of Compounds 5a,c,d

10 mL of THF was added to 0.60 g (3.60 mmol) tBu$_2$PCH$_2$Li and the resulting mixture was cooled to –40 °C. To this solution the corresponding $RPCl_2$ (1.80 mmol) in 5 mL of THF was added dropwise. The reaction mixture was warmed slowly to room temperature and stirred for another 3 h. The solvent was removed under reduced pressure, 10 mL of toluene was added to the residue and the formed precipitate was removed by filtration. All volatile compounds were removed from the filtrate in high-vacuum, and the residue was sublimated (100 °C oil bath/10^{-3} mbar).

5a (R = Ph): ^1H NMR (500.13 MHz, C_6D_6, 25 °C): δ = 1.04 (d, $^3J_{HP1}$ = 10.6 Hz, 18H, C(CH$_3$)$_3$), 1.24 (d, $^3J_{HP1}$ = 10.8 Hz, 18H, C(CH$_3$)$_3$), 1.73 (J_{AB} = 13.8 Hz, J_{HP} = 2.6 Hz, J_{HP} = 1.3 Hz, J_{HP} = 0.8 Hz, 2H, CH$_2$(A)), 2.23 (J_{AB} = 13.8 Hz, J_{HP} = 3.8 Hz, J_{HP} = 1.5 Hz, 2H, CH$_2$(B)), 7.11–7.24 (m, 3H, Ph), 7.82–7.87 (m, 2H, Ph) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 25 °C): δ = 22.5 (ddd, $^1J_{CP}$ = 34.0 Hz, $^1J_{CP}$ = 22.5 Hz, $^3J_{CP}$ = 9.9 Hz, P^{1}CH$_2$P^2), 29.4 (dd, $^2J_{CP1}$ = 14.1 Hz, $^4J_{CP2}$ = 1.8 Hz, (CH$_3$)$_3$CP^1), 29.7 (dd, $^2J_{CP1}$ = 14.2 Hz, $^4J_{CP2}$ = 1.9 Hz, (CH$_3$)$_3$CP^1), 31.4 (dd, $^1J_{CP1}$ = 25.0 Hz, $^3J_{CP2}$ = 6.7 Hz, (CH$_3$)$_3$CP^1), 31.9 (dd, $^1J_{CP1}$ = 24.9 Hz, $^3J_{CP2}$ = 6.2 Hz, (CH$_3$)$_3$CP^1), 128.0 (s, *m*Ph), 128.8 (s, *p*Ph), 133.0 (d, $^2J_{CP2}$ = 19.8 Hz, *o*Ph), 140.8 (dt, $^1J_{CP2}$ = 21.5 Hz, $^3J_{CP1}$ = 6.1 Hz, *i*Ph) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 25 °C): δ = –24.0 ("t", $^2J_{P1P2}$ = 133.1 Hz, P^2), 17.2 (d, $^2J_{P1P2}$ = 133.1 Hz, P^1) ppm. HRMS (EI) *m/z* (%): 369.2007 (56.3) (calcd. for $C_{20}H_{36}P_3$ 369.2030) [M – *t*Bu]$^+$, 313.1371 (16.9) (calcd. for $C_{16}H_{28}P_3$ 313.1404) [M–2 × *t*Bu + H]$^+$.

5c (R = NEt$_2$): ^1H NMR (300.13 MHz, C_6D_6, 25 °C): δ = 1.13 (t, $^3J_{HH}$ = 7.1 Hz, 6H, NCH$_2$*C*H$_3$), 1.18 (d, $^3J_{HP1}$ = 10.7 Hz, 18H, C(CH$_3$)$_3$), 1.23 (d, $^3J_{HP1}$ = 10.7 Hz, 18H, C(CH$_3$)$_3$), 1.67 (J_{AB} = 14.0 Hz, J_{HP} = 4.0 Hz, J_{HP} = 2.0 Hz, 2H, CH$_2$(A)), 1.97 (J_{AB} = 14.0 Hz, J_{HP} = 8.0 Hz, J_{HP} = 2.2 Hz, 2H, CH$_2$(B)), 3.04 (dq, $^3J_{HP2}$ = 9.1 Hz, $^3J_{HH}$ = 7.1 Hz, 4H, NC*H*$_2$CH$_3$) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 25 °C): δ = 16.5 (dt, $^3J_{CP2}$ = 2.8 Hz, $^5J_{CP1}$ = 1.4 Hz, NCH$_2$CH$_3$) 24.7 (ddd, $^1J_{CP}$ = 35.4 Hz, $^1J_{CP}$ = 28.7 Hz, $^3J_{CP}$ = 8.6 Hz, P^{1}CH$_2$P^2), 30.8 (dd, $^2J_{CP1}$ = 14.2 Hz, $^4J_{CP2}$ = 1.2 Hz, (*C*H$_3$)$_3$CP^1), 31.0 (dd, $^2J_{CP1}$ = 14.1 Hz, $^4J_{CP2}$ = 2.8 Hz, (CH$_3$)$_3$CP^1), 32.5 (dd, $^1J_{CP1}$ = 25.1 Hz, $^3J_{CP2}$ = 6.2 Hz, (CH$_3$)$_3$CP^1), 32.8 (dd, $^1J_{CP1}$ = 25.2 Hz, $^3J_{CP2}$ = 5.6 Hz, (CH$_3$)$_3$*C*P^1), 43.9 (d, $^2J_{CP1}$ =

14.2 Hz, NCH_2CH_3) ppm. $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 25 °C): δ = 17.3 (d, $^2J_{P1P2}$ = 130.1 Hz, P^1), 53.8 ("t", $^2J_{P1P2}$ = 130.1 Hz, P^2) ppm. MS (FI): *m/z* (%) = 421.3 (63.5) $[M]^+$; HRMS (EI): *m/z* (%) = 364.2443 (17.5) (calcd. for $C_{18}H_{41}NP_3$ 364.2452) $[M - t\text{Bu}]^+$, 293.1736 (15.0) (calcd. for $C_{14}H_{32}P_3$ 313.1404) $[M–t\text{Bu–NEt}_2]^+$.

5d (R = *t*Bu): ^{1}H NMR (500.13 MHz, C_6D_6, 25 °C): δ = 1.19 (d, $^3J_{HP1}$ = 10.5 Hz, 18H, $C(CH_3)_3$), 1.22 (d, $^3J_{HP2}$ = 11.7 Hz, 9H, $C(CH_3)_3$), 1.25 (d, $^3J_{HP1}$ = 10.9 Hz, 18H, $C(CH_3)_3$), 1.53 (J_{AB} = 14.0 Hz, J_{HP} = 4.0 Hz, J_{HP} = 1.5 Hz, 2H, CH_2(A)), 1.78 (J_{AB} = 14.0 Hz, J_{HP} = 1.8 Hz, J_{HP} = 1.6 Hz, 2H, CH_2(B)) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 25 °C): δ = 18.4 (ddd, $^1J_{CP}$ = 34.6 Hz, $^1J_{CP}$ = 31.1 Hz, $^3J_{CP}$ = 8.0 Hz, $P^1CH_2P^2$), 28.6 (dt, $^2J_{CP2}$ = 13.2 Hz, $^4J_{CP1}$ = 2.5 Hz, $(CH_3)_3CP^2$), 30.6 (dt, $^1J_{CP2}$ = 19.6 Hz, $^3J_{CP1}$ = 4.6 Hz, $(CH_3)_3CP^2$), 30.9 (dd, $^2J_{CP1}$ = 13.5 Hz, $^4J_{CP2}$ = 2.2 Hz, $(CH_3)_3CP^1$), 31.1 (dd, $^2J_{CP1}$ = 13.7 Hz, $^4J_{CP2}$ = 2.8 Hz, $(CH_3)_3CP^1$), 33.1 (dd, $^1J_{CP1}$ = 25.1 Hz, $^3J_{CP2}$ = 5.1 Hz, $(CH_3)_3CP^1$), 33.2 (dd, $^1J_{CP1}$ = 25.3 Hz, $^3J_{CP2}$ = 4.6 Hz, $(CH_3)_3CP^1$) ppm. $^{31}P\{^1H\}$ NMR (202.46 MHz, C_6D_6, 25 °C): δ = –5.6 ("t", $^2J_{P1P2}$ = 101.5 Hz, P^2), 17.6 (d, $^2J_{P1P2}$ = 101.5 Hz, P^1) ppm. HRMS (EI): *m/z* (%) = 349.2323 (21.8) (calcd. for $C_{18}H_{40}P_3$ 349.2343) $[M–t\text{Bu}]^+$, 293.1697 (15.6) (calcd. for $C_{14}H_{32}P_3$ 293.1717) $[M–2\ t\text{Bu} + H]^+$.

Reaction of *t*Bu(Me_3Si)P–P=P(*t*Bu_2)CH_2Li (7) with $RPCl_2$ in a molar ratio of 2:1 and 1:1.

2:1: A solution of the corresponding $RPCl_2$ (0.66 mmol) in toluene (5 mL) was added dropwise to a solution of *t*Bu(Me_3Si)P–P=P(*t*Bu_2)CH_2Li•2.4THF (**7**) (0.70 g, 1.32 mmol) in toluene (10 mL) at –60 °C. The reaction mixture was stirred for further 4 hours at the same temperature, then the formed precipitate was removed by filtration. During the filtration the filtrate was kept at –60 °C. The filtrate was concentrated under reduced pressure, then a little pentane was layered on the remaining residue. A colorless crystal mass precipitated from this solution at –40 °C. Only in the case of **8b** single crystals suitable for X-ray structure determinations could be obtained.

Molar distribution of products determined by ^{31}P NMR spectra (mol-%): **8a**/**9a** = 90:10; **8b**/**9b** = 95:5; **8c**/**9c** = 60:40; **8d**/**9d** = 50:50.

1:1: A solution of *t*Bu(Me_3Si)P–P=P(*t*Bu_2)CH_2Li•2.4THF (**7**) (0.72 g, 1.36 mmol) in toluene (10 mL) was added dropwise to a solution of the corresponding $RPCl_2$ (1.36 mmol) in toluene (5 mL) at –60 °C. Then the reaction was carried out as written above. In the case of R = *t*Bu single crystals suitable for X-ray structure determinations could be obtained (**9d-O**).

Molar distribution of products determined by ^{31}P NMR spectra (mol-%): **8a**/**9a** = 95:5; **8b**/**9b** = 100:0; **8c**/**9c** = 45:55; **8d**/**9d** = 30:70.

8a (R = Ph): $^{31}P\{^1H\}$ NMR (161.97 MHz, $[D_8]$toluene, 25 °C): *R,S/S,R*: δ = –180.5 (dd, $^1J_{P2P3}$ = 624.9 Hz, $^1J_{P1P2}$ = 250.6 Hz, P^2,P^6), –75.1 (dd, $^1J_{P1P2}$ = 250.6 Hz, $^2J_{P1P3}$ = 45.5 Hz, P^1,P^7), –30.7 (t, $^2J_{P3P4}$ = 5.6 Hz, P^4), 65.0 (ddd, $^1J_{P2P3}$ = 624.9 Hz, $^2J_{P1P3}$ = 45.5 Hz, $^2J_{P3P4}$ = 5.6 Hz, P^3, P^5) ppm. *R,S/S,R*: δ = –179.9 (ddd, $^1J_{P2P3}$ = 625.4 Hz, $^1J_{P1P2}$ = 250.5 Hz, $^3J_{P2P4}$ = 6.1 Hz, P^2,P^6), –74.9 (dd, $^1J_{P1P2}$ = 250.5 Hz, $^2J_{P1P3}$ = 45.0 Hz, P^1,P^7), –32.6 (tt, $^2J_{P3P4}$ = 7.7 Hz, $^3J_{P2P4}$ = 6.1 Hz, P^4), 65.0 (ddd, $^1J_{P2P3}$ = 625.4 Hz, $^2J_{P1P3}$ = 45.0 Hz, $^2J_{P3P4}$ = 7.7 Hz, P^3, P^5) ppm. *R,R/S,S*: δ = –179.5 (dd, $^1J_{P5P6}$ = 623.8 Hz, $^1J_{P6P7}$ = 255.1 Hz, P^6), –178.5 (dd, $^1J_{P2P3}$ = 624.5 Hz, $^1J_{P1P2}$ = 252.1 Hz, P^2) –74.5 (dd, $^1J_{P6P7}$ = 255.1 Hz, $^2J_{P5P7}$ = 45.2 Hz, P^7), –74.1 (dd, $^1J_{P1P2}$ = 252.1 Hz, $^2J_{P1P3}$ = 44.6 Hz, P^1),–28.9 (dd, $^2J_{P4P5}$ = 4.2 Hz, $^2J_{P3P4}$ = 3.1 Hz, P^4), 66.1 (ddd, $^1J_{P5P6}$ = 623.8 Hz, $^2J_{P4P5}$ = 4.2 Hz, $^2J_{P5P7}$ = 45.2 Hz, P^5), 66.2 (ddd, $^1J_{P2P3}$ = 624.5 Hz, $^2J_{P1P3}$ = 44.6 Hz, $^2J_{P3P4}$ = 3.1 Hz, P^3) ppm.

8b (R = Me): $^{31}P\{^1H\}$ NMR (161.97 MHz, $[D_8]$toluene, 25 °C): *R,S/S,R*: δ = –181.7 (ddd, $^1J_{P2P3}$ = 632.5 Hz, $^1J_{P1P2}$ = 252.3 Hz, $^3J_{P2P4}$ = 22.4 Hz, P^2,P^6), –74.6 (dd, $^1J_{P1P2}$ = 253.3 Hz, $^2J_{P1P3}$ = 47.8 Hz, P^1,P^7), –37.6 (tt, $^2J_{P3P4}$ = 14.6 Hz, $^3J_{P2P4}$ = 22.4 Hz, P^4), 60.7 (ddd, $^1J_{P2P3}$ = 632.5 Hz, $^2J_{P1P3}$ = 47.8 Hz, $^2J_{P3P4}$ = 14.6 Hz, P^3, P^5) ppm. *R,S/S,R*: δ = –181.7 (ddd, $^1J_{P2P3}$ = 632.2 Hz, $^1J_{P1P2}$ = 251.1 Hz, $^3J_{P2P4}$ = 34.3 Hz, P^2,P^6), –75.1 (dd, $^1J_{P1P2}$ = 251.1 Hz, $^2J_{P1P3}$ = 48.6 Hz, P^1,P^7), –39.5 (tt, $^2J_{P3P4}$ = 14.8 Hz, $^3J_{P2P4}$ = 34.3 Hz, P^4), 60.1 (ddd, $^1J_{P2P3}$ = 632.2 Hz, $^2J_{P1P3}$ = 48.6 Hz, $^2J_{P3P4}$ = 14.8 Hz, P^3, P^5) ppm. *R,R/S,S*: δ = –182.7 (ddd, $^1J_{P2P3}$ = 631.4 Hz, $^1J_{P1P2}$ = 252.5 Hz, $^3J_{P2P4}$ = 37.6 Hz, P^2), –180.7 (ddd, $^1J_{P5P6}$ = 631.8 Hz, $^1J_{P6P7}$ = 250.7 Hz, $^2J_{P4P6}$ = 17.6 Hz, P^6), –74.9 (dd, $^1J_{P6P7}$ = 250.7 Hz, $^2J_{P5P7}$ = 48.9 Hz, P^7),–74.9 (dd, $^1J_{P1P2}$ = 252.5 Hz, $^2J_{P1P3}$ = 47.8 Hz, P^1), –38.5 (dddd, $^2J_{P4P5}$ = 15.6 Hz, $^2J_{P3P4}$ = 13.5 Hz, $^3J_{P2P4}$ = 37.6 Hz, $^3J_{P4P6}$ = 17.6 Hz, P^4), 60.3 (ddd, $^1J_{P5P6}$ = 631.8 Hz, $^2J_{P5P7}$ = 48.9 Hz, $^2J_{P4P5}$ = 15.6 Hz, P^5), 61.2 (ddd, $^1J_{P2P3}$ = 631.4 Hz, $^2J_{P1P3}$ = 47.8 Hz, $^2J_{P3P4}$ = 13.5 Hz, P^3) ppm.

8c (R = NEt_2): $^{31}P\{^1H\}$ NMR (161.97 MHz, $[D_8]$toluene, 25 °C): *R,S/S,R*: δ = –180.2 (ddd, $^1J_{P2P3}$ = 624.7 Hz, $^1J_{P1P2}$ = 252.3 Hz, $^3J_{P2P4}$ = 12.0 Hz, P^2,P^6), –75.0 (dd, $^1J_{P1P2}$ = 252.3 Hz, $^2J_{P1P3}$ = 47.0 Hz, P^1,P^7), 50.3 (tt, $^2J_{P3P4}$ = 12.5 Hz, $^3J_{P2P4}$ = 12.0 Hz, P^4), 62.8 (ddd, $^1J_{P2P3}$ = 624.7 Hz, $^2J_{P1P3}$ = 47.0 Hz, $^2J_{P3P4}$ = 12.5 Hz, P^3, P^5) ppm. *R,S/S,R*: δ = –180.0 (ddd, $^1J_{P2P3}$ = 624.0 Hz, $^1J_{P1P2}$ = 254.3 Hz, $^3J_{P2P4}$ = 8.4 Hz, P^2,P^6), –74.5 (dd, $^1J_{P1P2}$ = 254.3 Hz, $^2J_{P1P3}$ = 46.7 Hz, P^1,P^7), 50.6 (tt, $^2J_{P3P4}$ = 12.4 Hz, $^3J_{P2P4}$ = 8.4 Hz, P^4), 63.3 (ddd, $^1J_{P2P3}$ = 624.0 Hz, $^2J_{P1P3}$ = 46.7 Hz, $^2J_{P3P4}$ = 12.4 Hz, P^3, P^5) ppm. *R,R/S,S*: δ = –181.1 (ddd, $^1J_{P5P6}$ = 624.2 Hz, $^1J_{P6P7}$ = 250.4 Hz, $^2J_{P4P6}$ = 15.5 Hz, P^6), –180.7 (ddd, $^1J_{P2P3}$ = 624.4 Hz, $^1J_{P1P2}$ = 252.1 Hz, $^3J_{P2P4}$ = 16.1 Hz, P^2), –77.0 (dd, $^1J_{P6P7}$ = 250.4 Hz, $^2J_{P5P7}$ = 46.2 Hz, P^7), –75.3 (dd, $^1J_{P1P2}$ = 252.1 Hz, $^2J_{P1P3}$ = 47.8 Hz, P^1), 50.7 (ddd, $^2J_{P4P5}$ = 15.4 Hz, $^3J_{P2P4}$ = 16.1 Hz, $^3J_{P4P6}$ = 15.5 Hz, $^2J_{P3P4}$ = 0, P^4), 63.2 (dd, $^1J_{P2P3}$ = 624.4 Hz, $^2J_{P1P3}$ = 47.8 Hz, P^3), 60.3 (ddd, $^1J_{P5P6}$ = 624.2 Hz, $^2J_{P5P7}$ = 46.2 Hz, $^2J_{P4P5}$ = 15.4 Hz, $^2J_{P3P4}$ = 0, P^5), ppm.

9a (R = Ph): $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 25 °C): δ = –224.7 (ddd, $^1J_{P2P3}$ = 522.8 Hz, $^1J_{P1P2}$ = 251.4 Hz, $^2J_{P2P4}$ = 16.5 Hz, P^2), –30.8 (ddd, $^1J_{P1P4}$ = 206.5 Hz, $^2J_{P3P4}$ = 16.5 Hz, $^2J_{P2P4}$ = 6.4 Hz, P^4), 43.3 (dd, $^1J_{P1P2}$ = 251.4 Hz, $^1J_{P1P4}$ = 206.5 Hz, P^1), 82.5 (dd, $^1J_{P2P3}$ = 522.8 Hz, $^2J_{P3P4}$ = 16.5 Hz, P^3) ppm. HRMS (EI): *m/z* (%) = 386.1593 (2.0) (calcd. for $C_{14}H_{36}P_4Si_2$ 386.1611) $[M^+]$.

9b (R = Me): $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 25 °C): δ = –222.4 (ddd, $^1J_{P2P3}$ = 532.2 Hz, $^1J_{P1P2}$ = 255.2 Hz, $^2J_{P2P4}$ = 4.5 Hz, P^2), –43.4 (ddd, $^1J_{P1P4}$ = 196.2 Hz, $^2J_{P3P4}$ = 10.9 Hz, $^2J_{P2P4}$ = 4.5 Hz, P^4), 49.7 (dd, $^1J_{P1P2}$ = 255.2 Hz, $^1J_{P1P4}$ = 196.2 Hz, P^1), 87.0 (dd, $^1J_{P2P3}$ = 532.2 Hz, $^2J_{P3P4}$ = 10.9 Hz, P^3) ppm.

9c (R = NEt_2): $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 25 °C): δ = –258.7 (ddd, $^1J_{P2P3}$ = 506.8 Hz, $^1J_{P1P2}$ = 249.7 Hz, $^2J_{P2P4}$ = 10.3 Hz, P^2), 4.0 (ddd, $^1J_{P1P2}$ = 249.7 Hz, $^1J_{P1P4}$ = 226.3 Hz, $^2J_{P1P3}$ = 2.8 Hz, P^1), 54.2 (ddd, $^1J_{P1P4}$ = 226.3 Hz, $^2J_{P3P4}$ = 21.4 Hz, $^2J_{P2P4}$ = 10.3 Hz, P^4), 64.0 (ddd, $^1J_{P2P3}$ = 506.8 Hz, $^2J_{P3P4}$ = 21.4 Hz, $^2J_{P1P3}$ = 2.8 Hz, P^3) ppm. HRMS (EI): *m/z* (%) = 381.2004 (12.1) (calcd. for $C_{17}H_{39}P_4N$ 381. 2033) $[M^+]$.

9d (R = *t*Bu):[17] ^{1}H NMR (300.13 MHz, C_6D_6, 25 °C): δ = 1.16 (d, $^3J_{HP3}$ = 14.5 Hz, 9H, $C(CH_3)_3$), 1.18 (d, $^3J_{HP3}$ = 14.5 Hz, 9H, $C(CH_3)_3$), 1.22 (d, $^3J_{HP4}$ = 10.6 Hz, 9H, $C(CH_3)_3$), 1.53 (d, $^3J_{HP1}$ = 11.0 Hz, 9H, $C(CH_3)_3$), 2.13 (J_{AB} = 13.8 Hz, J_{HP} = 20.2 Hz, J_{HP} = 12.6 Hz, J_{HP} = 9.9 Hz, J_{HP} = 1.9 Hz, 1H, CH_2(A)), 2.36 (J_{AB} = 13.8 Hz, J_{HP} = 11.0 Hz, J_{HP} = 2.9 Hz, 1H, CH_2(B)) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 25 °C): δ = 20.1 (m, CH_2), 27.5, 28.5 (unresolved, $P^3C(CH_3)_3$), 29.6 (d, $^2J_{P4,C}$ = 13.5 Hz, $P^4C(CH_3)_3$), 30.6 (d, $^2J_{P1,C}$ = 14.4 Hz, $P^1C(CH_3)_3$), 30.7, 32.1, 35.8, 38.0 (unresolved, $PC(CH_3)_3$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 25 °C): δ = –225.0 (dd, $^1J_{P2P3}$ = 543.8 Hz, $^1J_{P1P2}$ = 287.1 Hz, P^2), 16.9 (dd, $^1J_{P1P4}$ = 240.7 Hz, $^2J_{P3P4}$ = 3.5 Hz, P^4), 31.9 (ddd, $^1J_{P1P2}$ = 287.1 Hz, $^1J_{P1P4}$ = 240.7 Hz, $^2J_{P1P3}$ = 7.6 Hz, P^1), 87.9 (ddd, $^1J_{P2P3}$ = 543.8 Hz, $^2J_{P1P3}$ = 7.6 Hz, $^2J_{P3P4}$ = 3.5 Hz, P^3) ppm. HRMS (EI): *m/z*

(%) = 366.1885 (29.8) (calcd. for $C_{17}H_{38}P_4$ 366.1924) [M^+], 310.1406 (26.5).

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