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 tBu2P–P=P(tBu2)CH2Li at low temperature with dichlorophosphanes RPCl2 (R = Ph, Me, NEt2, tBu) lead to "P-7-chains" as primary products wherein two ylidic moieties are linked by a CH2–PR–CH2 unit. However, if R = tBu the long chain is only a by-product in addition to tBu2P–P=P(tBu2)Me. The thermal decomposition of "P-7-chains" as monitored by 31P NMR spectroscopy results in tBu2P–CH2–PR–CH2–P(tBu2) ("P-3-chains") and the phosphorylphosphanylidylened (tBu2P–P) which is observed as its cyclic trimer or tetramer. In the reactions of tBu(Me3Si)P–P=P(tBu2)CH2Li with RPCl2 the corresponding "P-7-chains" and the P4CH2-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 P4CH2-ring with R = tBu were determined by single-crystal X-ray diffraction analysis.

Introduction

Phosphinidene-σ4-phosphoranes (XP=PR3) can be interpreted as phosphinidenes protected by phosphanes PR3. 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 phosphinidine, which is stable for weeks in the solid state at room temperature.[2] Since the first example of a neutral phosphinidene-phosphorane, CF3P=PMe3Me, 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, R2P–P=PR3 discovered by the group of Fritz[4] and later the thermally stable ArP=PAr (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 R2P–P=PR3 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 phosphorylphosphinidene transfer reagents in the chemistry of transition metal complexes.[11] A number of other phosphorylphosphinidene-phosphoranes are accessible by phosphane-exchange reactions. The extent of these equilibrium reactions depends on the substituents in the phosphoranes.[12]

Linear oligophosphanes of type R2P–(PR)n–P=PR (R = alkyl, aryl, SiMe3) with a chain length n > 4 are unstable.[13] Attempts to access such long P-chains resulted in cyclophosphanes and diphasphanes as a consequence of disproportionation and rearrangement reactions. The synthesis of tBu(Me3Si)P–P=P(tBu2)Me[14] with the functional SiMe3 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 tetraphosphanes and cyclooctaphosphanes with two R2P=C ylidyl substituents which stabilize a low coordination environment of phosphorus.[14] The bis- and tris(alkylidene-phosphoranyl)phosphoranes observed by Karsch represent a new type of ylide–phosphane chelating ligands.[15] Protasiewicz et al. developed a diphospha-Wittig reagent containing two Me3P=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(Me3Si)P–P=P(tBu2)Me with nBuLi in THF was attempted. However, the PMe group was lithiated resulting in the ylide tBu(Me3Si)P–P=P(tBu2)CH2Li; this sur-
prising reactivity is similar to that previously reported for \( \text{tBu}_2\text{P-P=P(tBu)}_2\text{Me} \). In the present work, we describe the reactions of these functionalized ylides with various dichlorophosphanes \( \text{RPCl}_2 \), 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 \( ^{31}\text{P} \) 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 \( \text{tBu}_2\text{P-P=P(tBu)}_2\text{CH}_2\text{Li} \) (2) with \( \text{RPCl}_2 \)**

Generated via lithiation of the parent ylide 1, compound 2 reacts with dichlorophosphanes \( \text{RPCl}_2 \) with \( R = \text{Ph}, \text{Me}, \text{NEt}_2 \), and \( \text{tBu} \) (molar ratio 2:1) at low temperature to afford the new P-rich compounds 3a–d which contain two ylidic moieties linked by a \( \text{CH}_2\text{P-CH}_2 \) 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 \( \text{RPCl}_2 \) (\( R = \text{Ph}, \text{Me}, \text{orNEt}_2 \)) react with 2 to give almost exclusively the “P-7-chains” 3a–c. Only small amounts of \( \text{tBu}_2\text{P-P=P(tBu)}_2\text{Me} \) (1) were observed as by-product, which is formed by protonation of the starting THF-containing compound 2. In contrast, the reaction of \( \text{tBuPCl}_2 \) with 2 gives the “P-7-chain” 3d only in low yield, with the major product the starting material \( \text{tBu}_2\text{P-P=P(tBu)}_2\text{Me} \) 1. The formation of the protonated ylide corresponds to the general behavior of compounds with sterically strained \( \text{tBu} \) groups, which readily eliminate \( \text{Me}_2\text{C=CH}_2 \). During the reaction, the shorter chain 4d was already being formed by decomposition of 3d (Scheme 2), with the molar ratio of compounds 13d:4d estimated as 4:1:1 by integration of the \( ^{31}\text{P}[^{1}\text{H}] \) NMR spectra. Compound 3d could not be isolated, however 3a–c were obtained as colorless solids and investigated by \( ^{1}\text{H} \) and \( ^{31}\text{P} \) NMR spectroscopy in solution.

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 \( \text{tBu}_2\text{P-P=P(tBu)}_2\) (Scheme 2). The latter oligomerizes, forming the cyclophosphanes \( \text{[tBu}_2\text{PP]}_4 \) and \( \text{[tBu}_2\text{PP]}_3 \). These decomposition processes could be monitored by \( ^{31}\text{P} \) NMR spectroscopy (Figure 1). A similar decomposition was also observed in the case of the previously investigated compounds of type \( R_2\text{P-P=PR}_3 \) containing only one ylidic unit. 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 \( ^{13}\text{C} \) NMR spectroscopy.

**Reactions of \( \text{tBu(Me}_3\text{Si)}\text{P-P=P(tBu)}_2\text{CH}_2\text{Li} \) (7) with \( \text{RPCl}_2 \)**

Analogously to the formation of 2 from 1, the lithiated \( \text{tBu(Me}_3\text{Si)}\text{P-P=P(tBu)}_2\text{CH}_2\text{Li} \) (7) can be generated from the ylide.
tBu(Me3Si)P–P=P(tBu2)Me (6). In contrast to 2, compound 7 now has two functional groups and can therefore react with RPCl2 to form either the "P-7-chains" 8a–d or P4Ch2-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 31P NMR spectra of the reaction solutions, signals of rings could only be observed with low intensity. For R = tBu or NEt2 the formation of both ring and chain was observed. However, when R = tBu a molar ratio of 7:RPCl2 = 1:1 favors the ring formation, whereas ring and chain are formed in comparable amounts with a molar ratio of 7:RPCl2 = 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 "P-5-chains" in solution at room temperature, they decompose rapidly, first to the "P-3-chains" 3a and 5a,c,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 phosphiniene (tBu(Me3Si)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 (tBu(Me3Si)P–P), could not be detected; only signals from monophosphines [e.g. tBuP(SiMe3)2] and higher phosphines could be observed in the 31P 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 1H, 13C, 31P NMR spectroscopy, as well as by mass spectrometry. These 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]

**31P[1H] NMR Investigations**

The 31P[1H] NMR spectra of the chains 3a–d show four signal groups (Table 1); the (P1–P2–P3–CH2–) and (–CH2–P5–P6–P7) moieties give identical spectra by symmetry. (The notation of the P atoms is consistent with that of the molecular structures.) The 31P NMR signals of the phosphanyl atoms P1, P7 appear in the range of 30.9 to 33.5 ppm as dd multiplet, similar to those in tBu2–P–P=tBu(Me3Si)Me (1), while those for the phosphinide atoms P3, P6 are in the range of –167.4 to –173.7 ppm. The latter are strongly shifted downfield compared to 1 (δP3 = –200.6 ppm), and show ddd splitting owing to the atoms P1, P3, and P6, respectively. The 31P NMR signals of the phosphorane atoms P2, P5 (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 31P chemical shifts of P4 depend on the substituents (Table 1). The coupling constants J1,P1,P2, J2,P2,P3, J3,P3,P5 of about 600 Hz, respectively, indicate a strongly different bonding situation in the molecules. The large absolute values of J1,P2,P3 indicate a partial double bond between P2 and P3, 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).

![Scheme 3. Formation and decomposition of "P-7-chains" 8a–d and rings 9a–d.](image)

![Scheme 4. Synthesis of "P-3-chains" 5a,c,d.](image)
0.1–66.2 (P², P³). Similarly to compounds 3a–d, the ³¹P NMR signals of P², P⁴ lie significantly downfield with respect to those in fBu(Me₃Si)P=P(PtBu₂) (6), whereas the signals of P³, P⁵ are only slightly downfield shifted (6: δP²: −207.2 ppm; P³: 57.8 ppm).[10b] The large difference between the coupling constants 1J₁₂,P₃, 1J₆₇,P₇ (about 250 Hz) and 1J₂₃,P₆, 1J₅₆ (about 625 Hz) shows that a bond system typical for ylides as 1 and 6 is present also in these “P-7-chains”.

The ³¹P NMR investigations of 9a–d confirmed the formation of rings (Table 2). As a result of the elimination of the SiMe₃ group from P¹ during the formation of the rings the nuclei P¹ are strongly deshielded compared to the parent lithium compound 3a as expected, whereas the phosphinidene nuclei P² in 9a–d are strongly shielded, the chemical shifts for P³ show no significant change relative to those of 3a. The coupling constants 1J₁₂,P₃ above 500 Hz are much higher and indicate a partial double bond between P² and P³. 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 P¹ forming a ring.[17]

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

|     | 9a       | 9b       | 9c       | 9d       | 7        |
|-----|----------|----------|----------|----------|----------|
| δP¹/P⁷ | 43.3     | 49.7     | 4.0      | 4.0      | −67.1    |
| δP²/P⁶ | −224.7   | −222.4   | −258.7   | −225.0   | −186.0   |
| δP³/P⁵ | 82.5     | 87.0     | 64.0     | 87.9     | 79.8     |
| δP⁴   | −30.8    | −43.4    | 54.2     | 16.9     |          |
| 1J₁₂,P₃ | 251.4    | 255.2    | 249.7    | 287.1    | 294.3    |
| 1J₁₂,P₆ | 522.8    | 532.2    | 506.8    | 543.8    | 505.1    |
| 1J₁₂,P₇ | 206.5    | 196.2    | 226.3    | 240.7    |          |
| 1J₂₃,P₆ | 16.5     | 10.9     | 21.4     | 3.5      |          |
| 1J₂₃,P₇ | 1.4      | 4.5      | 10.3     | 0        |          |
| 1J₃₄,P₆ | 0        | 0        | 2.8      | 7.6      | 25.6     |

[a] 298 K, C₁₂D₁₀, 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 P2₁/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 fBu₂P=P(PtBu₂)Me (1) (P₁–P₂ 2.1791 Å, P₂–P₃ 2.1263 Å),[10b] consequently the linkage of two ylidic moieties by a CH₂–P–CH₂ 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 94.95(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 P1 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 fBu and SiMe₃ 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
P2–P3 distances ($\Delta = 0.0605$ Å), and the P5–P6 and P6–P7 distances ($\Delta = 0.0489$ Å) show a close similarity to 3a. A comparison of these data with those of $t$Bu(Me3Si)P–P=PtBu3Li (6) (P2–P3 2.1358 Å; P1–P2 2.1826 Å; difference 0.0468 Å)\[10\] 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/CH2Cl2. The X-ray crystallographic study (trigonal Z = 18) revealed that these crystals contained were not of 9d, but its oxidation product, (minor component drawn with smaller 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).

Conclusions

The functionalized ylides $t$Bu2P–P=P(tBu3)CH2Li (2) and $t$Bu(Me3Si)P–P=P(tBu3)CH2Li (7) opened a way to form linear P-rich chains. 2 reacted with dichlorophosphanes RPCI2 (R = Ph, Me, NEt2) in molar ratio 2:1 at –60 °C to form the new “P-7-chains” (3a–c) almost quantitatively; these contain two ylidic moieties linked by a CH2–P–CH2 unit. In contrast, the reaction of $t$BuPCl2 with 2 resulted in $t$Bu2P–P=P(tBu3)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 ($t$Bu3P–P). The decomposition processes could be monitored by 31P NMR spectroscopy.

$t$Bu(Me3Si)P–P=P(tBu3)CH2Li (7) reacts with RPCI2 forming either the corresponding “P-7-chains” by elimination of LiCl, or P4CH2-rings by elimination of Me3SiCl. 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, C6D6, [D8]toluene over sodium/benzophenone; hexane, and pentane over LiAlH4 and freshly distilled prior to use. CD2Cl2 was dried with activated molecular sieves. nBuLi (1.6 M in hexane), PhPCl2, and MePCl2 were purchased from Sigma-Aldrich, and nBuLi was used as received, the dichlorophosphane was freshly distilled under dry nitrogen atmosphere. $t$Bu2P–P=P(tBu3)Me (1),[10] $t$Bu(Me3Si)P–P=P(tBu3)Me (6),[8a] $t$Bu2P–P=P(tBu3)CH2Li (2),[17] $t$Bu(Me3Si)P–P=P(tBu3)CH2Li (7),[17] $t$Bu4PCH2Li,[23] $t$Bu4PMe,[24] $t$BuPCl2,[25] and Et3NPCl,[26] were prepared according to literature procedures.

The 1H, 13C, and 31P NMR spectra were recorded on Bruker AMX 300, Av 400, and DRX 500 spectrometers, using the deuterated solvents (CDCl3, CD2Cl2, or [D8]toluene for low temperature experiments) as internal lock, and TMS (1H, 13C), and 85 % H3PO4 (31P) as external standards. Two-dimensional 1H–13C HSQC, HMBC, and 1H–31P HMBC spectra were recorded using standard Bruker pulse sequences. Temperature calibration of the NMR measurements was carried out using Bruker standard samples. 1H NMR spectra of
higher order and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (for an exact assignment of the signals) were analyzed using Daisey iterations.\textsuperscript{20} High resolution mass spectra were measured on a Varian MAT 8200 mass spectrometer. The MS investigations for "P-7" and "P-chains" were unsuccessful, no $^{31}$P$^{-}\text{ion}$ could be observed, only the decomosition 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-$\text{K}_{\alpha}$ radiation. Structure solution was by direct methods (SHELXS-97\textsuperscript{[22]}) followed by full-matrix least-squares refinement against $F^2$ using SHELXL-2018\textsuperscript{[28]} within the Olex2 platform.\textsuperscript{[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 RPC$_2$(0.75 mmol) in toluene (5 mL) was added dropwise to a solution of Bu$_2$P=P(Bu$_2$CH$_2$Li)2.5THF (2) (0.78 g, 15 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 stirring at the same temperature the formed precipitate was removed by filtration. The filtrate was kept at –60 °C. Then, two thirds of the solvent were removed under reduced pressure in high-vacuum, and the resulting mixture was cooled to –40 °C. To this solution the resulting mixture was cooled to –40 °C. To this solution 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).

**Synthesis of Compounds 5a-c,d**

10 mL of THF was added to 0.60 g (3.60 mmol) Bu$_2$P=CH$_2$Li and the resulting mixture was cooled to –40 °C. To this solution the corresponding RPC$_1$(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).

**3c (R = NEt$_2$)** Yield: 0.37 g (64 %), m.p. 84 °C (dec.). $^{1}$H NMR (400.13 MHz, CD$_2$$_2$, 25 °C): $\delta$ = 1.03 (b, $^{31}$P$^\text{H}$) ppm. $^{31}$P$\{^1\text{H}\}$ NMR (121.49 MHz, CD$_2$$_2$, 25 °C): $\delta$ = –172.2 (dd, $^{31}$P$^{\text{H}}$ = 260.1, $^{1}$J$_{\text{HP1}}$ = 13.9 Hz, $^{1}$J$_{\text{HP2}}$ = 2.9 Hz, Ph).
14.2 Hz, N(CH3)2 ppm. 31P{1H} NMR (121.49 MHz, CD2O, 25 °C): δ = 17.3 (dd, 2Jp1P2 = 130.1 Hz, P1), 53.8 (t, 2Jp2P3 = 130.1 Hz, P1) ppm. MS (EI): m/z (%): 421.3 (63.5) [M+]; HRMS (EI); m/z (%) = 364.2443 (17.5) (calcd. for C18H41NP3 364.2452) [M~Bu–NEt]+.

5d (R = tBu): 1H NMR (500.13 MHz, CD2O, 25 °C): δ = 1.19 (d, 3Jp1P1 = 10.5 Hz, 1H, C(CH3)3), 1.22 (d, 3Jp2P2 = 11.7 Hz, 9H, C(CH3)3), 1.25 (d, 3Jp3P3 = 10.9 Hz, 1H, C(CH3)3), 1.53 (d, 3Jp4P4 = 14.0 Hz, 3H, J4P4 = 14.0 Hz, J4P3 = 1.5 Hz, 2H, CH2(HP)), 1.78 (d, 3Jp5P5 = 14.0 Hz, 3H, J5P5 = 1.5 Hz, 2H, CH2(HP)), 1.8 (d, 3Jp6P6 = 14.0 Hz, 3H, J6P6 = 1.5 Hz, 2H, CH2(HP)). 13C{1H} NMR (100.61 MHz, CD2O, 25 °C): δ = 18.4 (d, 2Jcp = 34.6 Hz, 3Cp), 31.1 (dd, 2Jcp = 13.7 Hz, 3Cp, 2Jcp = 2.8 Hz, (CH3)2CP), 31.3 (dd, 2Jcp = 25.1 Hz, 3Cp, 2Jcp = 5.1 Hz, (CH3)2CP), 33.2 (dd, 2Jcp = 25.3 Hz, 3Cp, 2Jcp = 4.6 Hz, (CH3)2CP). ppm. HRMS (EL): m/z (%) = 349.2323 (21.8) (calcd. for C18H41NP3 349.2343) [M~Bu–NEt]+, 293.1697 (15.6) (calcd. for C11H24P2 293.1717) [M–2Bu+].

Reaction of RBU(Me)SiP=P(PhBu)CH2Li (7) with RPCl2 in a molar ratio of 2:1 and 1:1.

2:1: A solution of the corresponding RPCl2 (0.66 mmol) in toluene (5 mL) was added dropwise to a solution of RBU(Me)SiP=P(PhBu)CH2Li 1.4THF (7) (0.70 g, 1.36 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 31P NMR spectra (mol-%): 8a/9a = 90:10; 8b/9b = 95:5; 8c/9c = 60:40; 8d/9d = 50:50.

1:1: A solution of RBU(Me)SiP=P(PhBu)CH2Li 1.4THF (7) (0.72 g, 1.36 mmol) in toluene (10 mL) was added dropwise to a solution of the corresponding RPCl3 (1.36 mmol) in toluene (5 mL) at −60 °C. Then the reaction was carried out as written above. In the case of R = tBu single crystals suitable for X-ray structure determinations could be obtained (9d-O).

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

8a (R = Ph): 31P{1H} NMR (161.97 MHz, D6O/toluene, 25 °C): R/S/S:R: δ = −180.5 (dd, 2Jp1P2 = 624.9 Hz, 2Jp2P3 = 250.6 Hz, P1, P1), −75.1 (dd, 2Jp1P2 = 250.6 Hz, 2Jp2P3 = 45.5 Hz, P1, P1), −30.7 (t, 2Jp2P3 = 5.6 Hz, P1), 65.0 (dd, 2Jp2P3 = 624.9 Hz, 2Jp3P4 = 45.5 Hz, 2Jp3P4 = 5.6 Hz, P1), P1) ppm. R/S:R/S:R: δ = −179.9 (dd, 2Jp2P3 = 625.4 Hz, 2Jp3P4 = 250.5 Hz, 2Jp3P4 = 61.2 Hz, P1, P1), −74.9 (dd, 2Jp1P2 = 250.5 Hz, 2Jp2P3 = 45.0 Hz, P1, P1), −32.6 (tt, 2Jp2P3 = 7.7 Hz, 2Jp2P3 = 61.2 Hz, P1, P1), 65.0 (dd, 2Jp2P3 = 625.4 Hz, 2Jp3P4 = 45.0 Hz, 2Jp3P4 = 7.7 Hz, P1, P1) ppm. R/S/R:S:R: δ = −179.5 (dd, 2Jp2P3 = 623.8 Hz, 2Jp3P4 = 255.1 Hz, P1, P1), −178.5 (dd, 2Jp2P3 = 624.5 Hz, 2Jp2P3 = 252.1 Hz, P1, P1), −74.5 (dd, 2Jp2P3 = 255.1 Hz, 2Jp3P4 = 45.2 Hz, P1), −74.1 (dd, 2Jp2P3 = 252.1 Hz, 2Jp2P3 = 44.6 Hz, P1), −28.9 (dd, 2Jp2P3 = 4.2 Hz, 2Jp2P3 = 3.1 Hz, P1), 66.1 (dd, 2Jp2P3 = 623.8 Hz, 2Jp3P4 = 45.2 Hz, 2Jp3P4 = 45.2 Hz, P1), 66.2 (dd, 2Jp2P3 = 624.5 Hz, 2Jp2P3 = 44.6 Hz, 2Jp2P3 = 3.1 Hz, P1) ppm.

8b (R = Me): 31P{1H} NMR (161.97 MHz, D6O/toluene, 25 °C): R/S/S:R: δ = −181.7 (dd, 2Jp3P4 = 632.5 Hz, 2Jp1P2 = 252.3 Hz, 2Jp1P2 = 242.2 Hz, P2, P2), −74.6 (dd, 2Jp1P2 = 253.3 Hz, 2Jp1P2 = 47.8 Hz, P1, P1), −37.6 (tt, 2Jp3P4 = 14.6 Hz, 2Jp3P4 = 22.4 Hz, P3, P3), 60.7 (dd, 2Jp3P4 = 632.5 Hz, 2Jp1P2 = 47.8 Hz, 2Jp3P4 = 14.6 Hz, P3, P3) ppm. R/S/S/R: δ = −181.7 (dd, 2Jp1P2 = 632.2 Hz, 2Jp1P2 = 251.1 Hz, 2Jp1P2 = 34.3 Hz, P1, P1), −75.1 (dd, 2Jp1P2 = 251.1 Hz, 2Jp3P4 = 48.6 Hz, P1, P1), −39.5 (tt, 2Jp3P4 = 14.8 Hz, 2Jp3P4 = 34.3 Hz, P3, P3), 60.1 (dd, 2Jp3P4 = 632.2 Hz, 2Jp1P2 = 48.6 Hz, 2Jp3P4 = 14.8 Hz, P3, P3) ppm. R/R:S:S:R: δ = −182.7 (dd, 2Jp3P4 = 631.4 Hz, 2Jp1P2 = 252.5 Hz, 2Jp3P4 = 37.6 Hz, P3, P3), −180.7 (dd, 2Jp3P4 = 631.8 Hz, 2Jp1P2 = 250.7 Hz, 2Jp3P4 = 17.6 Hz, P3, P3), −74.9 (dd, 2Jp3P4 = 250.7 Hz, 2Jp3P4 = 48.9 Hz, P3, P3) ppm. (17.5) (calcd. for C18H41NP3 364.2452) [M – H3] (17.5) (calcd. for C11H24P2 293.1717) [M–2Bu+].
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