Dppm-derived phosphonium salts and ylides as ligand precursors for s-block organometallics

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Dedicated to Professor Rainer Beckert on the Occasion of his 60th Birthday

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Abstract

The addition reaction of 1,1-bis(diphenylphosphino)methane (dppm) and haloalkanes R-X yields the corresponding phosphonium salts [Ph₂PCH₂PPh₂]X (1a: R = Me, X = I; 1b: R = Et, X = Br; 1c: R = iPr, X = I; 1d: R = CH₂Mes, X = Br; 1e: R = tBu, X = Br). In case of the synthesis of 1e, [Ph₂MePH]Br (3) was identified as a by-product. Deprotonation of 1 by KOrBu offers access to the corresponding phosphonium ylides [Ph₂PCHPPh₂R] (2a: R = Me; 2b: R = Et; 2c: R = iPr; 2d: R = CH₂Mes) in good yields. Further deprotonation of 2a using n-butyllithium allows the isolation of the lithium complex [Li(Ph₂PCHPPh₂CH₂)]ₙ (4) and its monomeric tmeda adduct [(tmeda)Li(Ph₂PCHPPh₂CH₂)] (4a). All compounds were characterized by NMR measurements and, except of 4, by X-ray diffraction experiments.

Keywords: Phosphonium salt, phosphonium ylide, lithium, lithium phosphorus coupling

Introduction

Phosphonium ylides gained tremendous importance in organic chemistry, since Wittig and co-workers developed their alkene synthesis in the early 50’s.¹ Nowadays, the Wittig reaction is textbook chemistry² and numerous applications and variations of this reaction are known.³ Beside their impact on synthetic organic chemistry, the bonding situation of phosphonium ylides is a subject of considerable interest; for instance the (non-existing) d-orbital participation and hypervalence have been studied intensively.⁴

In inorganic chemistry, neutral phosphonium ylides and their deprotonated anions are interesting ligands for s-block and d-block metals.⁵ Especially ylides derived from bidentate
diphosphanes proved to be useful in early studies due to the additional chelate effect.\textsuperscript{6} So far predominately keto stabilized ylides were used as neutral ligands\textsuperscript{7} and a variety of coordination modes of these derivatives with different d-block metals was observed.

In contrast, the s-block organometallic chemistry of this type of chelating ylide ligands and their anions is still underdeveloped. Continuing our previous investigation of the coordination chemistry of anionic ligands derived from 1,1-bis(diphenylphosphino)methane (dppm),\textsuperscript{8} the synthesis of a series of phosphonium salts and their phosphonium ylides is presented.

**Results and Discussion**

Chelating ylidic ligands are easily obtainable from 1,1-bis(diphenylphosphino)methane (dppm) by well known synthetic protocols. The stepwise deprotonation of phosphonium salts obtained from dppm and simple alkyl halides have been previously used by e.g. the groups of Issleib\textsuperscript{9} and Schmidbaur.\textsuperscript{10}

![Scheme 1. Synthesis of 1 and 2.](image)

Applying this approach, a series of phosphonium salts was synthesized in order to test its limitations (see scheme 1). Table 1 summarizes the reaction conditions and yields.

**Table 1. Synthesis of 1a-e**

| Compound | R-X | Equivalents | R-X | T [°C] | Reaction time [d] | Isolated Yield [%] | Reference |
|----------|-----|-------------|-----|--------|------------------|-------------------|-----------|
| 1a       | MeI | 1           | 80  | 0.17   | 97.5             | [10b]             |
| 1b       | EtBr| 6.1         | 50  | 7      | 51               | -                 |
| 1c       | iPrI| 4.1         | 80  | 7      | 37               | -                 |
| 1d       | MesCH\textsubscript{2}Br | 1 | 80 | 2 | 99 | - |
| 1e       | tBuBr| 4.3 | 70 | 21 | 19 | - |

While iodomethane gave the corresponding derivative [Ph\textsubscript{2}PCH\textsubscript{2}PPh\textsubscript{2}CH\textsubscript{3}]I (1a) in excellent yield after short reaction time as also known from the literature,\textsuperscript{10b} other substrates required more
forcing reaction conditions. An increase of the bulkiness of the alkyl group R in primary haloalkanes R-CH₂-X from R = H to R = CH₃ and further to R = tBu results in longer reaction times and lower yields in case of [Ph₂PCH₂PPh₂CH₂CH₃]Br (1b) and no transformation at all in case of neopentyl bromide as substrate. This significantly reduced reactivity is in agreement with earlier studies of S₂N₂ reactions of neopentyl systems, which are often accompanied by rearrangement to the corresponding 2-methyl-2-butyl derivatives.¹¹

As expected for S₂N₂ reactions, longer reaction times and an excess of substrate were also necessary in case of secondary haloalkanes such as 2-iodopropane to obtain the desired product. A yield of only 37% of [Ph₂PCH₂PPh₂CH(CH₃)₂]I (1c) after one week is far from satisfying but the straightforward product isolation just by filtration and the easy recovery of unreacted dppm by removing all volatiles of the mother liquor partially compensate this downside.

Prolonged reaction times of three weeks make even the t-butyl derivative [Ph₂PCH₂PPh₂C(CH₃)₃]Br (1e) accessible, but the yields remained low (19%). Even longer reaction times resulted in additional product formation, but also led to the formation of by-products, which may arise from O₂ or H₂O leaking into the reaction flask during these extremely long reaction times. One by-product, namely [Ph₂MePH]+Br⁻ (3), was identified by X-ray diffraction experiments.

In case of benzyl derivatives, excellent yields were achieved as demonstrated for the (2,4,6-trimethylphenyl)methyl derivative [Ph₂PCH₂PPh₂CH₂Mes]Br (1d). The corresponding chloride derivative gives the same yield under identical reaction conditions.¹⁰a Tables 2 and 3 summarize selected NMR data and structural parameters of the isolated compounds 1a-e. The molecular structures of 1c and 1d are shown in Figure 1 as representative examples.
Figure 1. Molecular structures and numbering schemes of 1c (top) and 1d (bottom). Co-crystallized CHCl₃ in 1c is omitted for clarity. The ellipsoids represent a probability of 50%, the H atoms are shown with arbitrary radii.

Table 2. Selected bond lengths and angles of 1, 2 and 4

| Entry | Bond lengths [Å] | Angle [°] |
|-------|------------------|-----------|
|       | P^III_C1 | P^III_C(Ph)^a | P^V_C1 | P^V_C2 | P^V_C(Ph)^a | P^III_C1-P^V |
| Phosphonium salts |
| 1a  | c | 1.782(5) | 1.802(5) | 1.792(5) |
| 1b  | d | 1.861(2) | 1.832(2) | 1.796(2) | 1.804(2) | 1.793(2) | 114.69(11) |
| 1c  | 1.872(5) | 1.831(5) | 1.810(5) | 1.827(5) | 1.798(5) | 110.7(2) |
| 1d  | 1.867(2) | 1.838(2) | 1.797(2) | 1.819(2) | 1.792(2) | 111.48(10) |
| 1e  | 1.889(3) | 1.834(3) | 1.803(3) | 1.859(3) | 1.801(3) | 111.41(17) |
| Ylides |
| 2a  | 1.767(3) | 1.845(3) | 1.687(3) | 1.812(4) | 1.815(3) | 119.64(19) |
| 2b  | 1.7642(14) | 1.8438(14) | 1.6866(14) | 1.8267(15) | 1.8178(14) | 120.25(8) |
| 2c  | 1.764(3) | 1.846(3) | 1.690(3) | 1.824(3) | 1.818(3) | 121.23(16) |
| 2d  | 1.773(2) | 1.842(2) | 1.700(2) | 1.848(2) | 1.818(2) | 117.79(13) |
| Lithium complex |
| 4a  | 1.753(3) | 1.838(3) | 1.696(3) | 1.719(3) | 1.839(3) | 117.71(15) |

^a^ Average value. ^b^ Molecule A of two independent molecules. ^c^ No accurate values are available due to a disorder of the –CH₂PPh₂ group of the molecule. ^d^ Data of 1b·toluene was used.
Table 3. Selected NMR data of compounds 1, 2 and 4

| Entry | $^1$H NMR $\delta$ P-CH$_2$-P | $^2$J$_{H,H}$ [Hz] | $^1$C NMR $\delta$ P-CH$_2$-P | $^1$J$_{C,P}$ [Hz] | $^3$P NMR $\delta$ P$^III$ | $\delta$ P$^V$ | $^2$J$_{P,P}$ [Hz] |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| **Phosphonium salts** | | | | | | | |
| 1a    | 4.12            | 14.7            | 22.5            | 51.2; 34.7      | -22.3           | 26.7            | 59.7            |
| 1b    | 4.20            | 14.3            | 20.2            | 49.8; 34.1      | -23.2           | 33.8            | 58.2            |
| 1c    | 4.05            | 13.0            | 18.7            | 48.7; 33.3      | -24.6           | 38.1            | 58.7            |
| 1d    | 4.45            | 13.8            | 22.0            | 47.7; 32.9      | -23.8           | 25.8            | 61.3            |
| 1e    | 3.95            | 12.3            | 18.4            | 46.2; 35.7      | -23.0           | 41.2            | 60.5            |
| **Ylides** | | | | | | | |
| 2a    | 1.23            | 11.4; 1.6       | 8.5             | 118.9; 11.2     | -16.3           | 19.4            | 158.3           |
| 2b    | a               | a               | 3.9             | 117.3; 10.6     | -16.3           | 27.7            | 150.7           |
| 2c    | 1.10            | ~10; 1.3        | 0.0             | 116.2; 10.7     | -15.7           | 33.7            | 135.7           |
| 2d    | 1.06            | 11.2; 2.7       | 10.5            | 117.0; 10.3     | -15.8           | 24.2            | 150.6           |
| **Lithium complex** | | | | | | | |
| 4a    | 1.12            | 11.0; 8.9       | 14.5            | 135.0; 19.2     | -13.5           | 36.4            | 139.3           |

$^a$ Accurate value is not available due to overlapping signals.

Phosphonium salts of the type 1 can easily be deprotonated by strong bases such as Me$_3$PCH$_2$, NaNH$_2$, or KOrBu to form the corresponding ylides. Depending on the nature of the substituent R, deprotonation either takes place in the bridging P-CH$_2$-P group or in the substituent (see scheme 2).

**Scheme 2.** Substituent dependent regioselective deprotonation of 1 with R being hydrocarbon groups.

While in substituents containing for instance β-carbonyl groups the anionic charge of an adjacent ylide is greatly stabilized and consequently deprotonation takes place in the substituent (outer deprotonation), simple alkyl-substituted phosphonium salts like 1a-c are deprotonated in the bridge (inner deprotonation). Like for the parent benzyl derivative, inner deprotonation was found for 1d, indicating that a Ph$_3$P group provides superior stabilization for the formed ylide. In contrast, deprotonation within the substituent was reported for the related fluorenyl
Beside a simple deprotonation reaction, the rearrangement of in situ generated (1-diphenylphosphino-1-methylethyl)methylene(diphenylphosphorane offers an alternative strategy to [Ph$_3$PCHPPh$_2$CH(CH$_3$)$_2$] (2c) in low yield.$^{12}$

The phosphonium ylides 2a-d were isolated as off-white to pale yellow substances and characterized by NMR spectroscopy. Selected NMR data of these compounds is summarized in table 2. Additionally, the molecular structures of all four compounds were determined by X-ray diffraction experiments to elucidate the structural changes accompanying the deprotonation. Figure 2 shows the molecular structures of 2c and 2d as typical examples.

Figure 2. Molecular structures and numbering schemes of 2c (top) and 2d (bottom). Co-crystallized Et$_2$O (2c) is omitted for clarity. The ellipsoids represent a probability of 50%, the H atoms are shown with arbitrary radii.
In comparison to the data of the phosphonium salts, shortening of both P-C bonds around the ylidic carbon by roughly 0.1 Å was observed, indicating a certain amount of charge delocalization towards the Ph$_2$P fragment. The P-C-P angle in all four derivatives is close to 120° with [Ph$_2$PCHPPh$_2$CH$_2$Mes] (2d) showing the largest deviation with 117.79°. In this derivative, some degree of pyramidalization at C1 was found, resulting in an angle sum of 353.7°.

Aside from the potential use of phosphonium ylides of type 2 in the Wittig reaction$^{13}$ or as mono- or bidentate neutral ligands, they are also easy-to-handle precursors for monoanionic ligands. The deprotonation of [Ph$_2$PCHPPh$_2$CH$_3$] (2a) at the CH$_2$ group by methyllithium or $n$-butyllithium has been reported earlier$^{10b,14}$ and the resulting solutions have been used to transfer the anionic ligand to e.g. yttrium or nickel complexes,$^{14,15}$ but little is known about the intermediately formed lithium compound itself.

This lithium compound can be isolated in pure form, when the deprotonation by $n$-butyllithium is performed in toluene. Due to the lack of additional neutral donor ligands, a polymeric structure of the product has to be assumed making it sparingly soluble in toluene and facilitating the isolation. The obtained very moisture sensitive white powder of [Li(Ph$_2$PCHPPh$_2$CH$_2$)]$_n$ (4) is soluble in donor solvents like diethyl ether, THF or THP. In THF solution the polymer is split into monomeric units probably containing two coordinated thf molecules to fill the coordination sites at lithium. A complete dissociation into a [Li(thf)$_4$]$^+$ cation and a liberated anionic ligand as observed for related [Li(dme)$_3$][H$_2$BPPh$_2$CHPPh$_2$BH$_2$] can safely be excluded.$^8$ In the $^7$Li{H} NMR as well as in the $^{31}$P{H} NMR spectrum a $^1$J$_{PLi}$ coupling of approximately 36 Hz was observed even at ambient temperature, allowing the description of 4 as a strong contact ion pair in THF solution. The observed coupling constant is rather small but falls into the same order of magnitude as observed for other compounds.$^{16}$ For the closely related Li[Ph$_2$PCHP(S)Ph$_2$] in diethyl ether a coupling constant of 54 Hz was reported.$^{16c}$

Recrystallization of 4 from $N,N,N',N'$-tetramethylethylenediamine (tmeda) yielded the mononuclear [(tmeda)Li(Ph$_2$PCHPPh$_2$CH$_2$)] (4a) resembling the bonding situation of the thf solvate. NMR measurement in [D$_8$]THF indicates, that the tmeda ligand can be replaced by THF and identical spectra as in case of 4 were observed for 4a aside from the signals of non-coordinated tmeda. The molecular structure of 4a is displayed in Figure 3.

The lithium atom is in a distorted tetrahedral coordination sphere surrounded by a phosphorus atom and a carbon atom of the ylidic ligand and the two nitrogen donors of tmeda. The bond lengths within the organometallic five-membered ring indicate electron delocalization and partial multiple bond character throughout the whole CPCP fragment. In comparison to the structurally characterized nickel complex [Ni(Ph$_2$PCHPPh$_2$CH$_2$)$_2$]$^{15}$ and the yttrium complex [Y(Ph$_2$PCHPPh$_2$CH$_2$)$_3$]$^{14}$ containing the same ligand, slight differences become obvious. Especially, an increasing P-CH$_3$ bond length from lithium (1.719(3) Å) to yttrium (1.744(7)-1.751(6) Å) and nickel (1.772(7) Å) was found and interpreted as decreasing multiple bond character between these atoms. This observation is in agreement with the assumed increasing σ-bond character of the metal-carbon bond to the CH$_2$ group in this row, leading to formal $sp^3$
hybridization of this carbon atom in the nickel complex, whereas the lithium complex 4a can be regarded as an ion pair.

![Molecular structure and numbering scheme of 4a](image)

**Figure 3.** Molecular structure and numbering scheme of 4a. H-atoms and co-crystallized tmeda are omitted for clarity. The ellipsoids represent a probability of 50%. Selected bond lengths (Å) and angles (deg): Li1-N1 2.091(5), Li1-N2 2.084(5), Li1-C2 2.161(5), Li1-P1 2.549 (5), N1-Li1-N2 88.89(19), N1-Li1-C2 115.7(2), N2-Li1-C2 120.6(2), N1-Li1-P1 116.1(2), N2-Li1-P1 129.2(2), C2-Li1-P1 88.87(16).

**Conclusions**

The S_N2 reaction of dppm and haloalkanes offer a straightforward access to phosphonium salts, even for secondary or tertiary haloalkanes. The lower yields and long reaction times are partially compensated by the efficient workup of the products and the easy recovery of unreacted dppm. The phosphonium salts can be deprotonated by KOrBu to obtain neutral phosphonium ylides in good yields.
Further deprotonation with n-butyllithium in toluene allows the isolation of lithium complexes containing the corresponding monoanionic ylidic ligands as demonstrated by the synthesis of \([\text{Li(Ph}_3\text{PCHPPh}_2\text{CH}_2])_n\).

The neutral compounds and the monoanionic ylides are promising new ligands for s-block and d-block metal complexes, shielding the metal fragment and offering a sensitive \(^{31}\text{P}\) NMR probe.

**Experimental Section**

**General.** All manipulations were carried out in an argon atmosphere under anaerobic conditions. Prior to use, all solvents, except of CDCl\(_3\), were thoroughly dried and distilled under an argon atmosphere.

\(^1\text{H}, \ ^{31}\text{P}\{\text{H}\}, \ ^{13}\text{C}\{\text{H}\}\) and \(^7\text{Li}\{\text{H}\}\) NMR spectra were recorded at ambient temperature on Bruker AC 200 MHz; AC 400 MHz or AC 600 MHz spectrometers. \(^1\text{H}\) and \(^{13}\text{C}\{\text{H}\}\) NMR spectra were referenced to the residual solvent signals of 98% perdeuterated THF or CDCl\(_3\) as an internal standard. Melting points were measured with a Reichert-Jung Apparatus Type 302102 and are uncorrected. Elemental analyses were performed on a Leco CHNS-932 at the Institute of Organic Chemistry and Macromolecular Chemistry, FSU Jena.

1,1-Bis(diphenylphosphino)methane (dppm) and the haloalkanes were purchased from Aldrich and used without further purifications. [((Diphenylphosphino)methyl]methylidiphenylphosphonium iodide (1a) was synthesized according to a known procedure.\(^{10b}\)

**Analytical data of [(diphenylphosphino)methyl]methylidiphenylphosphonium iodide (1a).**

1a. White solid. \(^1\text{H}\) NMR (600MHz, CDCl\(_3\)): \(\delta\)H 2.72 (3H, d, \(^2\text{J}_\text{HP} = 13.5\) Hz, P-CH\(_3\)), 4.15 (2H, d, \(^2\text{J}_\text{HP} = 14.7\) Hz, P-CH\(_2\)-P), 7.20-7.30 (6H, m, CH Ph), 7.45-7.57 (8H, m, CH Ph), 7.59-7.67 (2H, m, CH Ph), 7.78 (4H, m, CH Ph). \(^{13}\text{C}\{\text{H}\}\) NMR (150.9 MHz, CDCl\(_3\)): \(\delta\)C 10.5 (1C, dd, \(^1\text{J}_\text{CP} = 56.7\) Hz, \(^3\text{J}_\text{CP} = 3.1\) Hz, P-CH\(_3\)), 22.5 (1C, dd, \(^1\text{J}_\text{CP} = 51.2\) Hz, \(^1\text{J}_\text{CP} = 34.7\) Hz, P-CH\(_2\)-P), 119.5 (2C, d, \(^1\text{J}_\text{CP} = 86.5\) Hz, i-C Ph), 129.0 (4C, d, \(\text{J}_\text{CP} \sim 7\) Hz, CH Ph), 129.9 (4C, d, \(\text{J}_\text{CP} = 12.8\) Hz, CH Ph), 130.0 (2C, s, p-CH Ph), 132.9 (4C, d, \(\text{J}_\text{CP} = 10.3\) Hz, CH Ph), 133.6 (4C, d, \(\text{J}_\text{CP} = 21.4\) Hz, CH Ph), 134.5 (2C, d, \(^1\text{J}_\text{CP} = 10.5\) Hz, \(^3\text{J}_\text{CP} = 8.0\) Hz, i-C Ph), 134.7 (2C, d, \(^4\text{J}_\text{CP} = 3.1\) Hz, p-CH Ph). \(^{31}\text{P}\{\text{H}\}\) NMR (81MHz, CDCl\(_3\)): \(\delta\)P -22.3 (1P, d, \(^2\text{J}_{\text{PP}} = 59.7\), 26.7 (1P, d, \(^2\text{J}_{\text{PP}} = 59.7\) Hz). Anal. Calcd for C\(_{26}\)H\(_{25}\)P\(_2\): C, 59.33 H, 4.79; I, 24.11%. Found: C, 59.38; H, 4.77; I, 24.23%. Suitable crystals of the composition 1a·2 CHCl\(_3\) were obtained from a saturated solution of 1a in CHCl\(_3\) at ambient temperature.

**Synthesis of [(diphenylphosphino)methyl]ethylidiphenylphosphonium bromide (1b).**

Dppm (5.0 g, 13.0 mmol) was dissolved in toluene (60 ml) and bromoethane (8.6 g, 78.9 mmol) was added. The reaction mixture was heated to 50 °C for seven days. The resulting white
precipitate of the composition 1b·0.5 toluene was collected by filtration, washed with toluene (2 × 20 ml) and dried in vacuum.

1b·0.5 toluene. White solid, yield 51%, 3.60 g, 1H NMR (200MHz, CDCl3): δH 1.08 (3H, dt, JHP = 20.4 Hz, JHH = 7.5 Hz, CH3 Et), 2.29 (1.5H, s, CH3 toluene), 3.35 (2H, dq, JHP = 12.9 Hz, JHH = 7.4 Hz, P-CH2 Et), 4.20 (2H, d, JCP = 14.3 Hz, P-CH2-P), 7.02-7.28 (8.5H, m, CH Ph + toluene), 7.38-7.66 (10H, m, CH Ph), 7.70-7.87 (4H, m, CH Ph). 13C{H} NMR (100.6 MHz, CDCl3): δC 6.1 (1C, d, JCP = 5.0 Hz, CH3 Et), 16.9 (1C, dd, JCP = 51.5 Hz, JCP = 3.8 Hz, CH2 Et), 20.2 (1C, dd, JCP = 49.8 Hz, JCP = 34.1 Hz, P-CH2-P), 21.3 (0.5C, s, CH3 toluene), 117.4 (2C, d, JCP = 84.0 Hz, i-C Ph), 125.1 (0.5C, s, p-CH toluene), 128.0 (1C, s, m-CH toluene), 128.7 (4C, d, JCP = 8.0 Hz, CH Ph), 128.8 (1C, s, o-CH toluene), 129.6 (2C, s, p-CH Ph), 129.7 (4C, d, JCP = 12.4 Hz, CH Ph), 133.2 (4C, d, JCP = 22.1 Hz, CH Ph), 133.3 (4C, dd, JCP ∼ 10 Hz, JCP = 1.2 Hz, o-CH Ph), 134.4 (2C, d, JCP = 2.6 Hz, p-CH Ph), 134.8 (2C, dd, JCP = 11.4 Hz, JCP = 7.8 Hz, i-C Ph) 137.6 (0.5C, s, i-C toluene). 31P{H} NMR (81MHz, CDCl3) δP -23.2 (1P, d, JPP = 58.2 Hz), 33.8 (1P, d, JPP = 58.2 Hz). For X-ray diffraction experiments and elemental analysis, crystals of the composition 1b·toluene, obtained directly from the reaction mixture at ambient temperature, were used. Anal. Calcd for C34H33P2Br (585.51): C, 69.75; H, 6.03; Br, 13.65%. Found: C, 69.69; H, 5.84; Br 13.88%. This crop still contained a very small amount of crystals of the composition 1b·0.5 toluene, suitable for X-ray diffraction measurements.

Synthesis of [(diphenylphosphino)methyl]isopropylidiphenylphosphonium iodide (1c).

Dppm (4.4 g, 11.4 mmol) was dissolved in toluene (50 ml) and 2-iodopropane (8.0 g, 47.1 mmol) was added. The reaction mixture was heated to 80 °C for seven days. The resulting white precipitate of the composition 1c·toluene was collected by filtration, washed with toluene (2 × 20 ml) and dried in vacuum.

1c·toluene. White solid, yield 37%, 2.6 g, 1H NMR (200MHz, CDCl3): δH 1.18 (6H, dd, JHP = 18.9 Hz, JHH = 7.0 Hz, CH3 iPr), 2.31 (3H, s, CH3 toluene), 4.05 (2H, d, JHP = 13.0 Hz, P-CH2-P), 4.20 (1H, dsept, JHP = 11.6 Hz, JHH = 7.1 Hz, P-CH2 Et), 7.00-7.30 (11H, m, CH Ph + toluene), 7.40-7.90 (14H, m, CH). 13C{H} NMR (50.3 MHz, CDCl3): δC 15.6 (2C, d, JCP = 1.4 Hz, CH3 iPr), 18.7 (1C, dd, JCP = 48.7 Hz, JCP = 33.3 Hz, P-CH2-P), 21.4 (1C, s, CH3 toluene), 23.9 (1C, dd, JCP = 46.7 Hz, JCP = 2.2 Hz, CH iPr), 115.0 (2C, d, JCP = 81.9 Hz, i-C Ph), 125.2 (1C, s, p-CH toluene), 128.2 (2C, s, m-CH toluene), 128.8 (4C, d, JCP = 8.9 Hz, CH Ph), 128.9 (2C, s, o-CH toluene), 129.7 (2C, s, p-CH Ph), 129.8 (4C, d, JCP = 11.8 Hz, CH Ph), 133.3 (4C, d, JCP = 22.4 Hz, CH Ph), 134.1 (4C, dd, JCP = 8.5 Hz, JCP = 1.4 Hz, o-CH Ph), 134.6 (2C, dd, JCP = 10.7 Hz, JCP = 7.5 Hz, i-C Ph), 134.7 (2C, d, JCP = 3.0 Hz, p-CH Ph), 137.8 (1C, s, i-C toluene). 31P{H} NMR (81MHz, CDCl3) δP -24.6 (1P, d, JPP = 58.7 Hz), 38.1 (1P, d, JPP = 58.7 Hz). Anal. Calcd for C53H37P2I (646.53): C, 65.02; H, 5.77; I, 19.63%. Found: C, 65.06; H, 5.72, 19.54%. Suitable crystals of the composition 1c·CHCl3 for X-ray diffraction experiments were obtained by slow diffusion of Et2O into a saturated solution of 1c·toluene in CHCl3.
Synthesis of [(diphenylphosphino)methyl]diphenyl[2,4,6-trimethylphenyl]methylphosphonium bromide (1d). Dppm (3.59 g, 9.34 mmol) was dissolved in toluene (40 ml) and 2-bromomethyl-1,3,5-trimethylbenzene (1.99 g, 9.34 mmol) was added. The reaction mixture was heated to 80 °C for two days. The resulting white precipitate of 1d was collected by filtration, washed with toluene (2 × 20 ml) and dried in vacuum.

1d. White solid, yield 99%, 5.53 g, mp 240-241 °C; 1H NMR (600MHz, CDCl3): δH 1.68 (6H, s, o-CH3 Mes), 2.10 (3H, d, 2JHP = 2.7 Hz, p-CH3 Mes), 4.45 (2H, d, 2JHP = 13.8 Hz, P-CH2-P), 4.79 (2H, d, 2JHP = 14.5 Hz, P-CH2), 6.56(2H, s, m-CH Mes), 7.18-7.23 (6H, m, CH Ph), 7.26-7.32 (4H, m, CH Ph), 7.50-7.58 (10H, m, CH Ph). 13C{H} NMR (100.6 MHz, CDCl3): δC 20.7 (1C, d, 6JCP = 1.4 Hz, P-CH3 Mes), 21.0 (2C, d, 4JCP = 1.0 Hz, o-CH3 Mes), 22.0 (1C, dd, 1JCP = 47.7 Hz, 1JCP = 32.9 Hz, P-CH2-P), 30.3 (1C, d, 1JCP = 45.4 Hz, P-CH2), 116.9 (2C, d, 1JCP = 82.6 Hz, i-C Ph), 123.1 (1C, d, JCP = 9.5 Hz, C Mes), 128.9 (4C, d, JCP = 8.6 Hz, CH Ph), 129.2 (4C, d, JCP = 12.1 Hz, CH Ph), 129.5 (2C, d, 4JCP = 3.6 Hz, m-CH Mes), 129.7 (2C, s, p-CH Ph), 133.4 (4C, d, JCP = 22.6 Hz, CH Ph), 134.0 (4C, dd, 2JCP = 8.9 Hz, 4JCP = 2.7 Hz, o-CH Ph), 134.4 (2C, d, 4JCP = 2.9 Hz, p-CH Ph), 135.0 (2C, dd, 1JCP = 11.2 Hz, 3JCP = 8.0 Hz, i-C Ph), 137.7 (1C, d, JCP = 4.4 Hz, C Mes), 137.8 (2C, d, 3JCP = 5.4 Hz, o-C Mes). 31P{H} NMR (161.9MHz, CDCl3) δP -23.8 (1P, d, 2JPP = 61.3 Hz), 25.8 (1P, d, 2JPP = 61.3 Hz). Anal. Calcd for C35H35P2Br (597.52): C, 70.36 H, 5.90; Br, 13.37%. Found: C, 70.20; H, 5.96; Br, 13.51%. Suitable crystals of 1d for X-ray diffraction experiments were obtained by slow diffusion of Et2O into a saturated solution of 1d in CHCl3.

Synthesis of tert-butyl[(diphenylphosphino)methyl]diphenylphosphonium bromide (1e) and formation of methylidiphenylphosphonium bromide (3). Dppm (6.5 g, 16.9 mmol) was dissolved in toluene (50 ml) and 2-bromo-2-methylpropane (10.0 g, 73.0 mmol) was added. The reaction mixture was heated to 70 °C for three weeks. The resulting white precipitate of 1e was collected by filtration, washed with toluene (2 × 20 ml) and dried in vacuum.

1e. White solid, yield 19 %, 1.64 g. Suitable crystals of 1e·2CH2Cl2 for X-ray diffraction experiments were obtained by cooling a saturated solution of 1e in a mixture of Et2O and dichloromethane from ambient temperature to -20 °C. 1H NMR (200MHz, CDCl3): δH 1.47 (9H, d, 3JHP = 17.1 Hz, CH3 tBu), 3.95 (2H, d, 2JHP = 12.3 Hz, P-CH2-P), 7.1-7.8 (20H, m, CH Ph). 13C{H} NMR (50.3 MHz, CDCl3): δC 18.4 (1C, dd, 1JCP = 46.2 Hz, 3JCP = 35.7 Hz, P-CH2-P), 26.5 (3C, s, CH3 tBu), 34.4 (1C, d, 1JCP = 42.0 Hz, P-C tBu), 116.4 (2C, dd, 1JCP = 79.5 Hz, 3JCP = 1.8 Hz, i-C Ph), 128.8 (4C, d, JCP = 8.4 Hz, CH Ph), 129.6 (4C, d, JCP = 11.7 Hz, CH Ph), 129.6 (2C, s, p-CH Ph), 133.2 (4C, d, JCP = 22.7 Hz, CH Ph), 134.2 (4C, dd, 2JCP = 8.2 Hz, 4JCP = 1.8 Hz, o-CH Ph), 134.5 (2C, d, 4JCP = 2.7 Hz, p-CH Ph), 134.8 (2C, dd, 1JCP = 12.1 Hz, 3JCP = 7.6 Hz, i-C Ph). 31P{H} NMR (81MHz, CDCl3) δP -23.0 (1P, d, 2JPP = 60.5 Hz), 41.2 (1P, d, 2JPP = 60.5 Hz). MS [ESI in CHCl3/CH3OH] (m/z, %): 441.2 (M+, 100). HRMS: calcd for the cation C29H31P2, 441.1901; found 441.1887.

Further crops of product 1e were obtained by heating of the mother liquor of the reaction for additional weeks, but these fractions contained by-products. A few crystals of one of those by-
products grew at the wall of the Schlenk tube right above the solvent level, when the reaction mixture was kept undisturbed at ambient temperature for several days after heating. The compound was identified as [Ph₂MePH]⁺Br⁻ (3) by X-ray diffraction experiments.

3. Colorless crystals. \(^1\)H NMR (400MHz, CDCl₃): \(\delta_H\) 2.57 (3H, d, \(^2\)J\(_{HP}\) = 14.6 Hz, CH₃), 7.56 (4H, m, CH Ph), 7.67 (2H, m, CH Ph), 7.97 (4H, m, CH Ph), the signal of the P-H group was not observed, probably due to exchange with D₂O or DCI present as impurities in the used CDCl₃. \(^13\)C{\(\text{H}\)} NMR (100.6 MHz, CDCl₃): \(\delta_C\) 7.3 (1C, d, \(^1\)J\(_{CP}\) = 53.3 Hz, P-CH₃), 117.6 (2C, d, \(^1\)J\(_{CP}\) = 83.0 Hz, i-C Ph), 130.1 (4C, d, \(J_{CP}\) = 13.0 Hz, CH Ph), 133.1 (4C, d, \(J_{CP}\) = 10.9 Hz, CH Ph), 134.7 (2C, d, \(J_{CP}\) = 2.4 Hz, p-CH Ph). \(^{31}\)P{\(\text{H}\)} NMR (81MHz, CDCl₃) \(\delta_P\) -2.4 (s).

**Synthesis of [(diphenylphosphino)methylene]methylidiphenylphosphorane (2a).** A solution of KOrBu in THF (6.8 ml, 1M) was added to a stirred suspension of 1a (3.6 g, 6.84 mmol) in THF (40 ml) at ambient temperature. The resulting mixture was stirred for an additional hour and filtered over diatomaceous earth to remove precipitated KBr. The obtained yellow solution was reduced to dryness and dried in vacuum. A second crop of product was afterwards isolated by filtration and dried in vacuum. A second crop of product was obtained by cooling a saturated solution in Et₂O from ambient temperature to -20 °C.

**Synthesis of [(diphenylphosphino)methylene]ethylidiphenylphosphorane (2b).** A solution of KOrBu in THF (5.7 ml, 1M) was added to a stirred suspension of 1b-0.5 toluene (3.07 g, 5.69 mmol) in THF (35 ml) at ambient temperature. The reaction mixture was stirred for an additional hour and filtered over diatomaceous earth to remove precipitated KBr. The obtained yellow solution was reduced to dryness and dried in vacuum. The resulting solid foam was taken up in diethyl ether (20 ml) and the suspension obtained was stirred for 30 minutes. The formed product was afterwards isolated by filtration and dried in vacuum. A second crop of product was obtained by cooling a saturated solution in Et₂O from ambient temperature to -20 °C.
obtained in form of well shaped pale yellow crystals, suitable for X-ray diffraction experiments, by storing the mother liquor at -10 °C over night.

2b. Pale yellow crystals, yield 81%, 1.89 g, mp 120-123 °C. 1H NMR (200MHz, [D₈]THF): δH 1.00-1.25 (4H, m, P-CH=P + CH₃), 2.57 (2H, dq, 2J_HP = 12.5 Hz, 3J_HH = 7.3 Hz, P-CH₂), 7.00-7.25 (6H, m, CH Ph ), 7.30-7.48 (6H, m, CH Ph), 7.48-7.62 (4H, m, CH Ph), 7.68-7.84 (4H, m, CH Ph). 13C{H} NMR (150.9 MHz, [D₈]THF): δC 3.9 (1C, dd, 1J_CP = 117.3 Hz, 1J_CP = 10.6 Hz, P-CH=P), 7.1 (1C, pseudo-t, 2J_CP = 4J_CP = 3.7 Hz, CH₃ Et), 20.6 (1C, dd, 1J_CP = 63.8 Hz, 3J_CP = 8.5 Hz, CH₂ Et), 126.7 (2C, s, p-CH Ph), 128.0 (4C, d, J_CP = 6.2 Hz, CH Ph), 129.0 (4C, d, J_CP = 10.9 Hz, CH Ph), 131.6 (2C, d, 4J_CP = 2.0 Hz, p-CH Ph), 132.3 (4C, d, 4J_CP = 18.7 Hz, CH Ph), 132.7 (4C, d, J_CP = 8.9 Hz, CH Ph), 133.9 (2C, dd, 1J_CP = 81.4 Hz, 3J_CP = 3.5 Hz, i-C Ph), 148.6 (2C, pseudo-t, 1J_CP = 3J_CP = 10.6 Hz, i-C Ph). 31P{H} NMR (81MHz, [D₈]THF) δP -16.3 (1P, d, 2J_PP = 150.7 Hz), 27.7 (1P, d, 2J_PP = 150.7 Hz). Anal. Calcd for C₂₇H₂₆P₂ (412.45): C, 78.63; H, 6.35%. Found: C, 78.59; H, 6.33%.

Synthesis of [(diphenylphosphino)methyleneisopropylidiphenylphosphorane (2c). A solution of KOrBu in THF (1.8 ml, 1M) was added to a stirred suspension of 1c·toluene (1.1 g, 1.70 mmol) in THF (15 ml) at ambient temperature. The resulting mixture was stirred for an additional hour and filtered over diatomaceous earth to remove precipitated KI. The obtained yellow solution was reduced to dryness and dried in vacuum. The resulting solid foam was taken up in diethyl ether (20 ml) and the solution was filtered and stored at -20 °C over night. (The solution tends to oversaturate and in some cases lower temperatures and longer storage times were necessary to induce crystallization.) A pale yellow crystalline solid of the composition 2c·0.5 Et₂O was obtained, isolated by filtration and gently dried in vacuum. The crystals partially lose the co-crystallized Et₂O upon prolonged drying. Yield 57%, 0.45 g, pale yellow crystals. 1H NMR (200MHz, [D₈]THF): δH 1.10 (1H, dd, 2J_HP ~ 10 Hz, 2J_HP = 1.3 Hz, P-CH=P), 1.12 (3H, t, 3J_HH = 7.0 Hz,CH₃ Et₂O), 1.15 (6H, dd, 3J_HP = 16.9 Hz, 3J_HH = 7.0 Hz, CH₃ iPr), 2.96 (1H, dd, δJ = 116.2 Hz, J_CP = 10.7 Hz, P-CH=P), 15.5 (1C, s, CH₃ Et₂O), 16.7 (2C, d, 2J_CP = 2.7 Hz, CH₃ iPr), 26.5 (1C, dd, 1J_CP ~ 60 Hz, 3J_CP = 1.8 Hz, CH iPr), 66.2 (1C, s, CH₂ Et₂O), 126.7 (2C, s, p-CH Ph), 128.0 (4C, d, J_CP = 6.1 Hz, CH Ph), 129.0 (4C, d, J_CP = 10.8 Hz, CH Ph), 131.6 (2C, d, 4J_CP = 2.6 Hz, p-CH Ph), 132.3 (4C, d, J_CP = 18.7 Hz, CH Ph), 132.5 (2C, dd, 1J_CP ~ 80 Hz, 3J_CP = 3.2 Hz, i-C Ph), 133.3 (4C, dd, 2J_CP = 8.4 Hz, 4J_CP = 1.9 Hz, o-CH Ph), 148.9 (2C, dd, 1J_CP = 12.2 Hz, 3J_CP = 9.4 Hz, i-C Ph). 31P{H} NMR (81MHz, [D₈]THF) δP -15.7 (1P, d, 2J_PP = 135.7 Hz), 33.7 (1P, d, 2J_PP = 135.7 Hz). Anal. Calcd for C₃₀H₃₃P₂O₀.₅ (463.54): C, 77.73; H, 7.18%. Found: C, 77.49; H, 7.28%. Suitable crystals of 2c·0.5 Et₂O for X-ray diffraction experiments were obtained directly from the reaction mixture.
Synthesis of [(diphenylphosphino)methylene]diphenyl([2,4,6-trimethylphenyl)methyl]phosphorane (2d). A solution of KOtBu in THF (7.7 ml, 1M) was added to a stirred suspension of 1d-(4.61 g, 7.71 mmol) in THF (40 ml) at ambient temperature. The resulting mixture was stirred for an additional hour and filtered over diatomaceous earth to remove precipitated KBr. The obtained yellow solution was reduced to dryness and dried in vacuum. The resulting solid foam was taken up in diethyl ether (40 ml). A small amount of formed solid (~0.4 g) was removed by filtration and discarded. The yellow solution was reduced to dryness, leaving an off-white solid. This residue was suspended in heptane (20 ml), isolated by filtration and dried in vacuum.

2d. Pale yellow solid, yield 82%, 3.27 g, mp 138-140 °C. 1H NMR (200MHz, [D8]THF): δH 1.06 (1H, dd, 2JHP = 11.2 Hz, 3JHP = 2.7 Hz, P-CH=P), 1.87 (6H, s, o-CH3 Mes), 2.20 (3H, d, JHP = 2.1 Hz, p-CH3 Mes), 4.11 (2H, d, 2JHP = 14.7 Hz, P-CH2), 6.68 (2H, s, CH Mes), 7.04-7.34 (10H, m, CH Ph ), 7.37-7.58 (10H, m, CH Ph). 13C{H} NMR (100.6 MHz, [D8]THF): δCP C8 10.5 (1C, dd, 1JCP = 117.0 Hz, 1JCP = 10.3 Hz, P-CH=P), 20.8 (1C, s, p-CH3 Mes), 21.3 (2C, s, o-CH3 Mes), 32.2 (1C, dd, 1JCP = 57.5 Hz, 3JCP = 12.1 Hz, P-CH2), 126.8 (2C, s, p-CH Ph), 128.0 (4C, d, JCP = 6.2 Hz, CH Ph), 128.5 (4C, d, JCP = 11.2 Hz, CH Ph), 128.8 (1C, d, 2JCP = 8.0 Hz, i-C Mes), 129.6 (2C, d, 3JCP = 2.7 Hz, m-CH Mes), 131.7 (2C, d, 4JCP = 2.3 Hz, p-CH Ph), 132.5 (4C, d, JCP = 19.0 Hz, CH Ph), 133.6 (2C, dd, 1JCP ~ 80 Hz, 3JCP = 1.5 Hz, i-C Ph), 133.9 (4C, d, JCP = 9.2 Hz, CH Ph), 136.6 (1C, d, 5JCP = 3.6 Hz, p-C Mes), 138.4 (2C, d, 2JCP = 4.6 Hz, o-C Mes), 148.6 (2C, pseudo-t, 1JCP = 1JCP = 10.5 Hz, i-C Ph). 31P{H} NMR (81MHz, [D8]THF) δP-15.8 (1P, d, 2JP = 150.6 Hz), 24.2 (1P, d, 2JP = 150.6 Hz). Anal. Calcd for C35H34P2 (516.60): C, 81.37 H, 6.63%. Found: C, 81.25; H, 6.76%. Suitable crystals of 2d for X-ray diffraction experiments were obtained by cooling a saturated solution in Et2O from ambient temperature to -20 °C.

Synthesis of lithium-[(diphenylphosphino)methylene](methylene)diphenylphosphorane (4). A solution of n-butyllithium in hexane (0.72 ml, 1.6M) was added to a stirred yellowish solution of 2a-(0.46 g, 1.15 mmol) in toluene (15 ml) at ambient temperature. The initially clear reaction mixture was stirred for an additional hour resulting in precipitation of a white solid. Afterwards, the formed product was collected by filtration, washed with cold toluene (5 ml) and dried in vacuum.

4-0.5 toluene. Off-white solid, yield 67%, 0.35 g. 1H NMR (200MHz, [D8]THF): δH -0.29 (2H, d, 2JHP = 9.3 Hz, Li-CH2-P), 1.12 (1H, dd, 2JHP = 11.0 Hz, 3JHP = 8.9 Hz, P-CH=P), 2.32 (1.5H, s, CH3 toluene), 7.0-7.3 (14.5, m, CH Ph + toluene), 7.5-7.8 (8H, m, CH Ph). 13C{H} NMR (100.6 MHz, [D8]THF): δC -2.1 (1C, br, Li-CH2-P), 14.5 (1C, dd, 1JCP = 135.0 Hz, 1JCP = 19.2 Hz, PCH=P), 21.4 (0.5C, s, CH3 toluene), 125.9 (0.5C, s, p-CH toluene), 126.4 (2C, s, p-CH Ph), 127.7 (4C, d, JCP ~ 10 Hz, CH Ph), 127.8 (4C, d, JCP ~ 7 Hz, CH Ph), 128.3 (2C, d, 4JCP = 1.8 Hz, p-CH Ph), 128.8 (1C, s, m-CH toluene), 129.6 (1C, s, o-CH toluene), 131.3 (4C, d, JCP = 9.2 Hz, CH Ph), 132.3 (4C, d, JCP = 16.2 Hz, CH Ph), 138.3 (0.5C, s, i-C toluene), 145.9 (2C, d, 1JCP = 67.3 Hz, i-C Ph), 148.8 (2C, d, 1JCP = 8.3 Hz, i-C Ph). 31P{H} NMR (81MHz, [D8]THF): δP -
13.4 (1P, dq, $^{2}J_{PP} = 140.1$ Hz, $^{1}J_{LiP} = 36.5$ Hz), 36.4 (1P, d, $^{2}J_{PP} = 139.5$ Hz). $^{7}$Li{H} NMR (155.5MHz, [D$_{8}$]THF): $\delta_{Li}$ 0.09 (d, $^{1}J_{LiP} = 35.3$ Hz).

A small portion of 4·0.5 toluene was recrystallized from $N,N,N',N'$-tetramethylethylediamine (tmeda) to obtain suitable crystals of the formula [(tmeda)Li(Ph$_{2}$PCHPPh$_{2}$CH$_{2}$)]·0.5 tmeda (4a) for X-ray diffraction experiments.

**Supporting Information available.** Crystal data and refinement details of 1a-4a, molecular structures and numbering schemes of 1a, 1b, 1e, 2a, 2b, and 3. Additionally, crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-842321 for 1a·2CHCl$_{3}$, CCDC-842322 for 1b·0.5toluene, CCDC-847440 for 1b·toluene, CCDC-842323 for 1c·CHCl$_{3}$, CCDC-842324 for 1d, CCDC-856224 for 1e·2CH$_{2}$Cl$_{2}$, CCDC-842325 for 3, CCDC-842326 for 2a, CCDC-842327 for 2b, CCDC-842328 for 2c·0.5Et$_{2}$O, CCDC-842329 for 2d, and CCDC-842330 for 4a·0.5tmeda. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E- mail: deposit@ccdc.cam.ac.uk].

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