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Activation of the C=P bond in phosphanylphosphaalkenes (C=P–P bond system) in the reaction with nucleophilic reagents: MeLi, *n*BuLi and *t*BuLi†

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Three reactions of phosphanylphosphaalkene (**1**) with nucleophiles were performed to activate the diphosphorus monomer. We observed similar results in the reactions with MeLi and *n*BuLi, in which the P–P bond is cleaved and triphosphorus systems [P(Me)₂–CH(biph)–CH(biph)–P–(PtBu)₂][–] (**1a**) and [P(*n*Bu)₂–CH(biph)–CH(biph)–P–(PtBu)₂][–] (**1b**), respectively, are formed depending on the nucleophilic reagent (biph = biphenyl). In the case of *t*BuLi, the P–P bond remains intact; on the phosphorus atom, only one *t*Bu group is substituted, and as a result, [(biph)(H)C–P(*t*Bu)–PtBu₂][–] (**1c**) is generated as a stable carbanion. We additionally investigated the effect of substitution in the phenyl ring in the course of these reactions by involving two other phosphanylphosphaalkenes (**3** and **4**). All initial reactions were conducted in tetrahydrofuran (THF) solution at ambient temperature.

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Introduction

Compounds containing a C=P bond, namely, phosphalkenes, are well investigated in organophosphorus chemistry. The various methods of synthesis of these systems are widely described.^{1–4} However, not only the synthesis is of interest to many scientists, but also the use of their properties which are due to the presence of a reactive P=C bond. One important area is the synthesis and engagement of phosphalkene complexes in catalysis.⁵ The most studied metal complexes originate from nickel and copper groups. Alcohol allylation, cyclodehydration, hydroamination, hydroamidation and dehydrogenative silylation of ketones are some of the examples where platinum or palladium complexes supported with P=C ligands are employed as catalysts.^{6–10} Copper complexes exhibit activity in CO₂ hydrogenation and hydrosilylation, while gold-containing phosphalkene complex was used in alkoxycyclization of 1,6-enyne intramolecular cyclizations to afford heterocyclic structures or in hydration reactions of terminal acetylenes.^{11,12} Phosphalkene species are used in many organic syntheses, *inter alia*, in Diels–Alder reaction with dienes or *via* dimerization for *e.g.* 1-phosphabutadienes.¹³ Cycloaddition of

phosphaalkenes to an arene ring (N-bound), the effect of which was bicyclic product may also be considered as specific application. Additionally, the authors demonstrated the reversibility of the process and the establishing equilibrium between the phosphalkene and the phosphabicyclic product.¹⁴ A significant aspect is research on phosphalkene polymerization and the importance of phosphorus polymers. In the literature, anion-, cation- and radical-initiated processes have been reported.^{15–19} In the first type of reaction, MeLi or *n*BuLi was most often used, while in the second type, triflic acid or Lewis acids (MCl₃; M = Al, Ga, In) was mainly employed. In the third case, the most frequent choice was VAZO or TEMPO. The main starting monomer thus far has included MesP=CPh₂ compound and *m*-XylP=CPh₂ in a lesser extended, due to their moderate stability.^{20–23} Although, it should be emphasized that Mes*P=CH₂ was employed as monomer in cationic polymerization and AlCl₃ was used as the initiator. However this led to intramolecular C–H activation of the Mes* substituent.¹⁹ Gates and coworkers demonstrated anionic polymerization of MesP=C(Fc)Ph, which is a *C*-ferrocenyl-substituted phosphalkene.²⁴ However, no phosphalkene with an aldehyde derivative was used for this purpose. In the following years, studies reported the polymerization of phosphalkenes with the use of other substituents on carbon (*C*-aryl), including 1-naphthyl and 9-phenanthryl moieties.²⁵ Another example is phosphalkene bearing a *C*-pyrenyl substituent, MesP=C(Ph)Pyr, which is subjected to anionic polymerization.²⁶ Changing the substituent on the phosphorus atom with a phosphanyl group leads to the formation of phosphanylphosphaalkene (C=P–P).^{27–32} These diphosphorus analogs are a considerable and lesser

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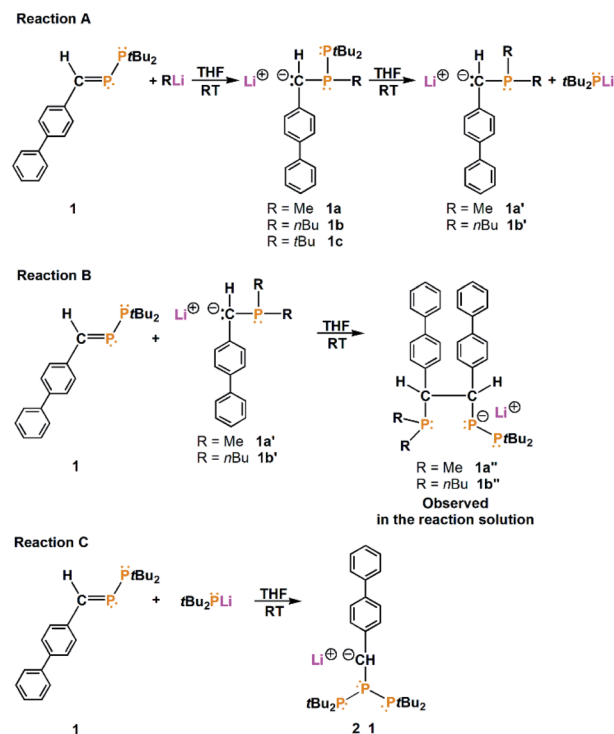
† Electronic supplementary information (ESI) available: X-ray crystallographic data and details, molecular structure of **1a*** and **2_1** and **3**. NMR spectra, DFT calculations details. CCDC 2114106, 2114107 and 2163558. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1ra09215d



known group of compounds, and their reactivity is practically unknown. Our main goal was to perform the first step of anionic polymerization in solution (tetrahydrofuran, THF) at room temperature; for this purpose, we chose (biph)(H)C=P-PtBu₂ (1), (3,5-*t*Bu₂C₆H₃)(H)C=P-PtBu₂ (3) and (*p*-Me₂N-C₆H₄)(H)C=P-PtBu₂ (4) containing an aldehyde derivative. We conducted reactions with three initiators (MeLi, *n*BuLi, *t*BuLi) and presented the results of our research.

Results and discussion

Initially, we mixed MeLi with (biph)(H)C=P-PtBu₂ in THF-*d*₈. The ³¹P{¹H} nuclear magnetic resonance (NMR) spectrum obtained 24 hours later revealed that the signals of phosphanylphosphaalkene disappeared, whereas new signals were visible: 54.20 ppm (d, *J*_{PP} = 325.2 Hz), −48.52 ppm (d, *J*_{PP} = 108.4 Hz), and −56.33 ppm (dd, *J*_{PP} = 325.2 Hz, *J*_{PP} = 108.4 Hz) for one of the new compounds, 47.12 ppm and −51.41 ppm (d, *J*_{PP} = 313.2 Hz) for another new compound and an additional two singlets at 40.28 ppm and −62.31 ppm (see ESI, Fig. S4 and S5†). The ³¹P{¹H}/¹H HMQC NMR spectrum shows that the phosphorus atom observed at 47.12 ppm correlates with protons at 1.21 ppm (*t*Bu groups) and with protons at 2.91 ppm (weak correlation), while the phosphorus atom observed at −51.41 ppm indicates a strong correlation with protons at 2.91 ppm and a very weak correlation with protons observed at 1.03 ppm (see ESI, Fig. S11 and S12†). The integration revealed that at 2.91 ppm 1H, at 1.21 ppm 18H and at 1.03 ppm 3H protons are located. The obtained result shows that in the reaction, the anion [(biph)(H)C=P(Me)-PtBu₂][−] (**1a**) is formed, and the P=C bond is activated. Similar C=P bond activation by using nucleophilic reagents was described previously in the literature as the initiation step of the anionic polymerization of phosphoalkenes. Gates and coworkers presented the reactions of (Ph)₂C=PMe₃ with MeLi and *n*BuLi, where the ionic compounds (Ph)₂C=P(Me)(Me) and (Ph)₂C=P(Me)(*n*Bu), respectively, were generated.^{20–22} The other signals in the ³¹P{¹H} NMR spectrum (especially singlets at 40.28 ppm and −62.31 ppm) may indicate that in the reaction of (biph)(H)C=P-PtBu₂ with MeLi, the P-P bond is not stable, and monophosphorus compounds are formed. In the ³¹P{¹H}/¹H HMBC spectrum, the phosphorus atom observed at 40.28 ppm correlates only with the doublet at 1.33 ppm (*J*_{PH} = 10.1 Hz) from *t*Bu groups (see ESI, Fig. S11†). The obtained result may suggest the formation of *t*Bu₂PLi, which confirms the cleavage of the P-P bond. For comparison, the signals of *t*Bu₂PLi (s) found in the literature lie in the range from 38.51 ppm (Li₄ unit)³³ to 46.6 ppm.³⁴ Another compound observed in the ³¹P{¹H} NMR spectrum is a singlet (−62.31 ppm) correlated with protons at 2.61 ppm (*J*_{PH} = 5.4 Hz), 0.98 ppm (*J*_{PH} = 2.4 Hz) and 0.89 ppm (*J*_{PH} = 2.9 Hz) (see ESI, Fig. S11†). The obtained results reveal further reaction of **1a** with MeLi remaining in the reaction solution and attachment of the second methyl group to the phosphorus atom. Substitution of the second methyl group leads to P-P bond cleavage and the formation of ionic compound with the formula [Li(solvent)_{*n*}]⁺[(biph)(H)C=P(Me)₂][−] (**1a'**) and *t*Bu₂PLi (integration for compound **1a'** is shown in ESI Fig. S10†). All reactions of (biph)(H)C=P-PtBu₂ with RLi (R =



Scheme 1 Reactions of phosphanylphosphaalkene (**1**) with RLi in THF solution (R = Me, *n*Bu, *t*Bu).

Me, *n*Bu, *t*Bu) observed in the reaction mixture are presented in Scheme 1.

Furthermore, the signals observed at 54.20 ppm (d, *J*_{PP} = 325.2 Hz), −48.52 ppm (d, *J*_{PP} = 108.4 Hz), and −56.33 ppm (dd, *J*_{PP} = 325.2 Hz, *J*_{PP} = 108.4 Hz) may suggest the formation of compounds with three different phosphorus atoms in solution. Repeating this reaction in THF and crystallization from dimethoxyethane (DME) allowed us to obtain good-quality crystals for X-ray measurements. Interestingly, we isolated two types of crystals from this reaction solution: deep red blocks and bright red needles. X-ray analysis of the red block crystals revealed an ionic compound with the formula [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-PtBu₂][−] (**1a***). **1a*** crystallizes in the triclinic space group *P* $\bar{1}$ with two molecules in the unit cell. The independent part of the unit cell contains a total of **1a***; therefore, four stereocenters (C9, C22, C45, C58) can be distinguished. In one organic ligand, the carbon stereocenter atoms have the same configurations, C9, C22 – *R*, *R* and C45, C58 – *S*, *S*. The molecular structure of the anion of **1a*** is presented in Fig. 1.

The X-ray structure of the anionic part of **1a*** indicates a four-coordinate lithium compound between tetrahedral and square-planar geometry at the metal center ($\tau_4 = 0.57(3)$, $\tau'_4 = 0.54(6)$).^{35,36} The P-P interatomic distances in **1a*** differ slightly from one another (2.1585(15) Å and 2.1685(15) Å) and lie slightly below the lower limit of a single P-P bond (the range given by Corbridge for a P-P single bond is 2.17–2.24 Å).³⁷ The geometries around P1, P2, P4 and P5 in **1a*** are more pyramidal ($\Sigma_{P1} = 338.31(12)^\circ$, $\Sigma_{P2} = 316.03(16)^\circ$, $\Sigma_{P4} = 325.65(12)^\circ$ and $\Sigma_{P5} =$



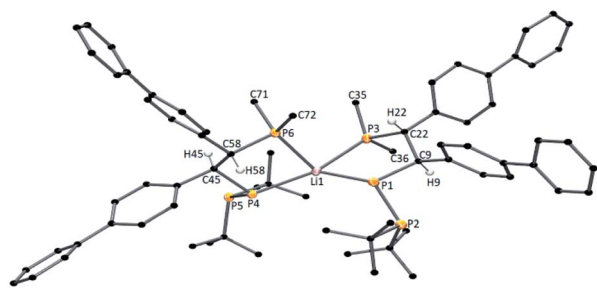


Fig. 1 Molecular structure of the anion of **1a*** (ellipsoids 30%, the H atoms have been omitted for clarity, except H9, H22, H45 and H58). Important distances (Å) and angles (deg): Li1–P1 2.479(7), Li1–P3 2.556(6), Li1–P4 2.517(6), Li1–P6 2.531(7), P1–P2 2.1585(15), P4–P5 2.1685(15), C9–C22 1.531(5), C45–C58 1.548(5).

315.81(11)° and finally confirmed the single bond character between two phosphorus atoms (P1–P2 and P4–P5). The Li–P distances in **1a*** are also differ from each other (2.479(7) Å, 2.556(6) Å, 2.517(6) Å, 2.531(1) Å). Similar Li–P distances are found in the following: [(Dipp)₂P]Li(THF)₃, 2.482(3) Å;³⁸ iPrP{C₆H₄-2-CH(C₆H₄-2-CH₂NMe₂)NMe₂}Li(THF)₂, 2.509(6) Å;³⁹ *t*Bu(Ph)P–P(SiMe₃)Li(THF)₃, 2.518(17) Å;⁴⁰ and [(Et₂O)₂Li{(Ph₂P)₂CH}], 2.581(4) Å and 2.583(4) Å.⁴¹ The ³¹P{¹H} NMR spectrum conducted from the **1a*** crystals revealed signals from six different phosphorus atoms: 29.07 ppm (*J*_{PP} = 247.7 Hz, *J*_{PP} = 17.2 Hz), –44.57 ppm (*J*_{PP} = 73.4 Hz, *J*_{PP} = 17.2 Hz), –67.56 ppm (*J*_{PP} = 247.7 Hz, *J*_{PP} = 73.4 Hz), 29.45 ppm (*J*_{PP} = 239.3 Hz), –44.92 ppm (*J*_{PP} = 36.5 Hz) –82.62 ppm (*J*_{PP} = 239.3 Hz, *J*_{PP} = 36.5 Hz) (see ESI, Fig. S13 and S14†). The Mulliken population analysis calculated for **1a*** revealed different partial atomic charges on the phosphorus atoms: [P^(–0.225)(Me)₂–CH(biph)–CH(biph)–P^(–0.583)–(P^(–0.414)*t*Bu₂)₂][–] and second ligand [P^(–0.025)(Me)₂–CH(biph)–CH(biph)–P^(–0.030)–(P^(–0.255)*t*Bu₂)₂]. It shows that electron density on corresponding P atoms is not distributed equally after complexation (see ESI, Fig. S57 and S58†). Despite the seemingly analogous chemical environment, derived results indicate different coordination of the organophosphorus ligand to the lithium cation. Moreover it justifies presence of separate signal for each P atom in the ³¹P{¹H} NMR spectrum of dissolved compound **1a***.

The second type of crystals isolated in the reaction as bright red needles were characterized as a symmetrical triphosphane with the formula [Li(DME)₃]⁺[*t*Bu₂P–P–{C(H)–(biph)}–P*t*Bu₂][–] (**2_1**) (the molecular structure of **2_1** is shown in ESI Fig. S2†). Furthermore, the reaction conducted at high concentrations of adducts led only to a mixture of **1a**, **1a'** and **1a''**, while compound **2_1** was observed only at lower concentrations of adducts. The collected observations allowed us to eliminate compound **2_1** from the reaction by selecting the appropriate concentration of the reagents.

The reaction of (biph)(H)C=P–*Pt*Bu₂ with *n*BuLi was also conducted in THF-*d*₈ and investigated by NMR technique. The ³¹P{¹H} NMR spectrum revealed the formation of analogous compounds, as in the reaction with MeLi: [{(biph)(H)C–P(*n*Bu)–*Pt*Bu₂}][–] (**1b**, d, 39.22 ppm, –37.43 ppm, *J*_{PP} = 326.3 Hz),

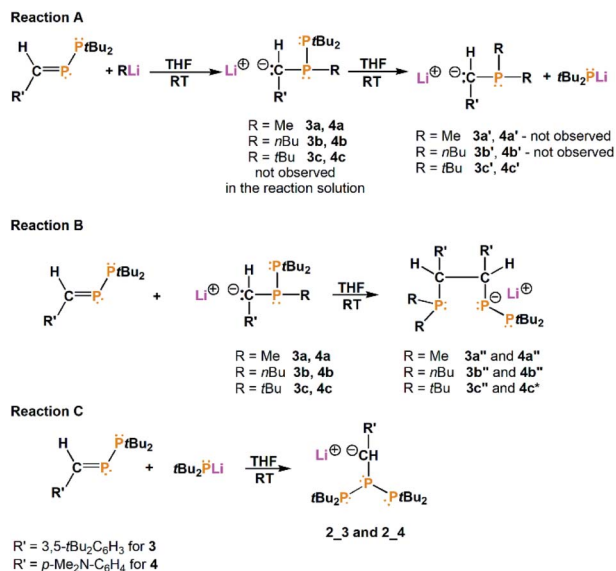
[(biph)(H)C–P(*n*Bu)₂][–] (**1b'**, s, –41.56 ppm) and [P(*n*Bu)₂–CH(biph)–CH(biph)–P–(*Pt*Bu₂)₂][–] (**1b''**, d, 54.91 ppm, *J*_{PP} = 326.0 Hz; d, –24.16 ppm, *J*_{PP} = 102.4 Hz and dd, –59.24 ppm, *J*_{PP} = 102.4 Hz, *J*_{PP} = 326.0 Hz) (all NMR spectra of the reaction mixture are shown in ESI Fig. S25–S39†). To isolate compound **1b''**, the reaction was repeated in nondeuterated THF, and then, crystallization was conducted from organic solvents (DME, THF and toluene). Unfortunately, all attempts to isolate **1b''** failed, and we isolated only a small amount of **2_1**.

Because the reactions of (biph)(H)C=P–*Pt*Bu₂ with MeLi and *n*BuLi lead to substitution of two alkyl groups on the phosphorus atom and, in turn, P–P bond cleavage, we decided to examine another nucleophilic reagent – *t*BuLi. The reaction of (biph)(H)C=P–*Pt*Bu₂ with *t*BuLi was investigated by NMR spectroscopy and revealed the formation of only one compound. The ³¹P{¹H} NMR spectrum obtained from the reaction mixture shows only two doublets at 30.08 ppm and –4.05 ppm, with a coupling constant of 333.3 Hz. The ³¹P{¹H}/¹H HMBC NMR spectrum revealed a correlation of the phosphorus atom observed at 30.08 ppm with only protons at 1.31 ppm (two doublets, *J*_{PH} = 13.2 Hz and 13.7 Hz) from the *t*Bu groups. Interestingly, the signal at –4.05 ppm correlates with a doublet of doublets at 3.15 ppm (*J*_{PH} = 7.6 Hz, *J*_{PH} = 1.3 Hz) and with a doublet at 1.14 ppm (*J*_{PH} = 12.7 Hz) (all NMR spectra of the reaction mixture are shown in ESI Fig. S30–S32†). The obtained results evidently point out substitution of the phosphorus atom with only one *t*Bu group and formation of a new carbanion-containing compound with the formula [(biph)(H)C–P(*t*Bu)–*Pt*Bu₂][–] (**1c**). Stopping the reaction at this stage is probably associated with steric hindrance of the *t*Bu groups. Despite all efforts, it was not possible to isolate the compound **1c** in a crystalline form.

In order to investigate the influence of substituents on the phenyl ring, we synthesized a new phosphanylphosphaalkene with the formula (3,5-*t*Bu₂C₆H₃)(H)C=P–*Pt*Bu₂ (**3**) and we used previously synthesized phosphanylphosphaalkene (*p*-Me₂N–C₆H₄)(H)C=P–*Pt*Bu₂ (**4**) additionally. In comparison to compound **1**, in which the phenyl group was substituted with phenyl in the *para* position, compounds **3** and **4** constitute respectively examples where the phenyl is substituted with *t*Bu groups (*meta* positions) and NMe₂ (*para* position).

All reactions were performed in THF-*d*₈ and stirred for 24 hours before NMR measurements. The obtained results show that independently of the substituents in the phenyl ring and used lithium compounds, these reactions do not stop at the mono-substitution stage (compounds **3a–c** and **4a–c** were not observed in the reaction solutions) (Scheme 2). ³¹P{¹H} NMR spectra of the reaction solution revealed that in each of these reactions appropriate triphosphane is formed: [*t*Bu₂P–P–{C(H)(3,5-*t*Bu₂C₆H₃)–*Pt*Bu₂}][–] (**2_3**, 66.12 ppm, *J*_{PP} = 347.5 Hz, *J*_{PP} = 62.5 Hz; 57.98 ppm, *J*_{PP} = 231.7 Hz, *J*_{PP} = 62.5 Hz; –67.30 ppm, *J*_{PP} = 347.5 Hz, *J*_{PP} = 231.7 Hz) and [*t*Bu₂P–P–{C(H)(*p*-Me₂N–C₆H₄)–*Pt*Bu₂}][–] (**2_4**, 64.62 ppm, *J*_{PP} = 348.2 Hz, *J*_{PP} = 62.6 Hz; 56.85 ppm, *J*_{PP} = 239.6 Hz, *J*_{PP} = 62.6 Hz; –69.64 ppm, *J*_{PP} = 348.2 Hz, *J*_{PP} = 239.6 Hz). Additionally, the ³¹P{¹H} NMR spectra show the compounds formation with a new C–C bond (**3a''–3c''** and **4a''–4c''**) and with three different





Scheme 2 Reactions of phosphanylphosphaalkenes (3,5-*t*-Bu₂C₆-H₃)(H)C=P-PtBu₂ (**3**) and (*p*-Me₂N-C₆H₄)(H)C=P-PtBu₂ (**4**) with RLi in THF solution (R = Me, *n*Bu, *t*Bu).

phosphorus atoms, analogous to **1a''** and **1b''** compounds (see ESI Fig. S34–S47†). Importantly, the **4c''** compound occurs in the reaction solution as a system of two three-phosphorus molecules coordinated to the lithium ion (³¹P{¹H} NMR: 51.56 ppm, dd, *J*_{PP} = 326.9 Hz, *J*_{PP} = 5.3 Hz; 49.51 ppm, dd, *J*_{PP} = 281.7 Hz, *J*_{PP} = 51.5 Hz; 41.07 ppm, dd, *J*_{PP} = 139.5 Hz, *J*_{PP} = 5.3 Hz; 3.81 ppm, dd, *J*_{PP} = 111.3 Hz, *J*_{PP} = 51.5 Hz; –55.98 ppm, dd, *J*_{PP} = 281.7 Hz, *J*_{PP} = 111.3 Hz; –57.56 ppm, dd, *J*_{PP} = 326.9 Hz, *J*_{PP} = 139.5 Hz, the spectra see ESI, Fig. S44–S47†). For comparison, an analogous compound **1a''** was obtained in the reaction of **1** with MeLi, however, was not observed in the reaction solution, but it revealed in the crystallization process.

Experimental

Materials and methods

All synthetic procedures were performed under inert gas (Ar) and were carried out using mBraun glovebox and standard Schlenk techniques. THF, DME, toluene and pentane were dried over Na/Ph₂CO and distilled under argon atmosphere. All spectra in solution were recorded on Bruker AV400 MHz spectrometer (external standard tetramethylsilane for ¹H, ¹³C; 85% H₃PO₄ for ³¹P). Elemental analysis for solid and liquid samples were recorded on Elementary Vario El Cube CHNS. (biph)(H)C=P-PtBu₂ and (*p*-Me₂N-C₆H₄)(H)C=P-PtBu₂ were prepared according to procedure in the literature.³² MeLi, *n*BuLi and *t*BuLi were commercially purchased.

Synthesis of (3,5-*t*-Bu₂C₆H₃)(H)C=P-PtBu₂ (**3**)

To a solution of *t*Bu₂PP(SiMe₃)Li·3THF (0.500 g; 1.058 mmol) in 8 mL of toluene, a solution of 3,5-di-*tert*-butylbenzaldehyde (0.231 g; 1.058 mmol) in 5 mL of toluene was added. Almost immediately solution turned yellow-orange. After 1 hour the solvent was evaporated, and the solid residue was treated with

20 mL of pentane. The mixture was filtered and concentrated more than half its volume. The solution was stored at +4 °C for 24 hours. The desired compound (3,5-*t*-Bu₂C₆H₃)(H)C=P-PtBu₂ was obtained in the form of yellow crystals (0.320 g; 80%). Anal. calcd for C₂₃H₄₀P₂: C, 72.98; H, 10.65%. Found: C, 72.89; H, 10.72%.

Reactions of (biph)(H)C=P-PtBu₂ with MeLi, *n*BuLi, *t*BuLi respectively

Reaction of (biph)(H)C=P-PtBu₂ with MeLi. To a solution of (biph)(H)C=P-PtBu₂ (0.200 g; 0.584 mmol) in 4–5 mL of THF a MeLi (0.365 mL; 0.584 mmol; 1.6 M) was dropwise added. The color immediately changed from orange to dark red. After 24 hours of stirred, the solvent was evaporated, and 10 mL of DME was added. The solution was slowly concentrated to about half then allowed to crystallize at –23 °C. After 5–6 hours, the red block appeared which were characterized as [Li(DME)₃]⁺[{P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li}][–] (**1a''**) (M = 1423.48 g mol^{–1}; 0.105 g, 13%). Anal. calcd for C₈₄H₁₁₈Li₂O₆P₆: C, 70.87; H, 8.36%. Found: C, 71.03; H, 8.45%. The crystals were isolated and concentrated one half more, and the solution was left at –23 °C again to afforded bright red needles, X-ray-quality crystals of [Li(DME)₃]⁺[tBu₂P-P-{C(H)(biph)}-PtBu₂][–] (**2_1**) (M = 764.86 g mol^{–1}, 0.045 g, 10%). Anal. calcd for C₄₁H₇₆Li₁O₆P₃: C, 64.38; H, 10.01%. Found: C, 64.25; H, 10.15%.

NMR data of isolated 1a'' in THF-d₈. ¹H NMR (400 MHz, C₆D₆, 298 K) δ: 7.5–6.98 (aromatic protons), 3.85 (m, 1H, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻), 3.67 (m, 1H, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻), 3.61 (small amount of THF from THF-d₈), 3.46 (DME protons), 3.44 (1H, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻), 3.41 (m, 1H, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻), 3.30 (DME protons), 1.76 (small amount of THF from THF-d₈), 1.40 (d, *J*_{PH} = 11.2 Hz, 9H, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻), 1.39 (d, *J*_{PH} = 11.0 Hz, 9H, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻), 1.17 (d, *J*_{PH} = 11.2 Hz, 9H, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻), 1.11 (d, *J*_{PH} = 4.5 Hz, 3H, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻), 1.01 (d, *J*_{PH} = 11.6 Hz, 9H, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻), 0.73 (d, *J*_{PH} = 3.9 Hz, 3H, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻), 0.73 (d, *J*_{PH} = 4.3 Hz, 3H, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻), 0.66 (d, *J*_{PH} = 4.0 Hz, 3H, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻) ppm.

¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K) δ: 142.04–125.43 (aromatic C atoms), 71.79 (DME), 66.42 (THF-d₈), 57.93 (DME), 52.79 (d, *J*_{PC} = 19.4 Hz, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻), 52.72 (d, *J*_{PC} = 17.8 Hz, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻), 44.67 (d, *J*_{PC} = 16.2 Hz, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻), 42.87 (d, *J*_{PC} = 18.7 Hz, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻), 31.54 (dd, *J*_{PC} = 28.8 Hz, *J*_{PC} = 1.7 Hz, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻), 31.51 (dd, *J*_{PC} = 28.7 Hz, *J*_{PC} = 3.7 Hz, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻), 30.61 (dd, *J*_{PC} = 15.0 Hz, *J*_{PC} = 1.6 Hz, [Li(DME)₃]⁺[P(Me)₂-CH(biph)-CH(biph)-P-(PtBu₂)₂Li]⁻).



$\{C(CH_3)_3\}_2\}^-$, 30.52 (dd, $J_{PC} = 14.0$ Hz, $J_{PC} = 0.8$ Hz, $[Li(DME)_3]^+[P(Me)_2-CH(biph)-CH(biph)-P\{C(CH_3)_3\}_2]^-$), 30.10 (dd, $J_{PC} = 13.1$ Hz, $J_{PC} = 8.6$ Hz, $[Li(DME)_3]^+[P(Me)_2-CH(biph)-CH(biph)-P\{C(CH_3)_3\}_2]^-$), 30.08 (dd, $J_{PC} = 14.3$ Hz, $J_{PC} = 1.2$ Hz, $[Li(DME)_3]^+[P(Me)_2-CH(biph)-CH(biph)-P\{C(CH_3)_3\}_2]^-$), 24.34 (THF- d_8), 13.42 (d, $J_{PC} = 17.5$ Hz, $[Li(DME)_3]^+[P(Me)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$), 13.03 (d, $J_{PC} = 15.5$ Hz, $[Li(DME)_3]^+[P(Me)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$), 10.45 (d, $J_{PC} = 18.7$ Hz, $[Li(DME)_3]^+[P(Me)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$), 9.92 (d, $J_{PC} = 19.5$ Hz, $[Li(DME)_3]^+[P(Me)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$) ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6 , 298 K) δ : 29.45 (d, $J_{PP} = 239.3$ Hz, $[Li(DME)_3]^+[P(Me)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$), 29.07 (dd, $J_{PP} = 245.7$ Hz, $J_{PP} = 17.2$ Hz, $[Li(DME)_3]^+[P(Me)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$), -44.57 (dd, $J_{PP} = 73.4$ Hz, $J_{PP} = 17.2$ Hz, $[Li(DME)_3]^+[P(Me)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$), -44.92 (d, $J_{PP} = 36.5$ Hz, $[Li(DME)_3]^+[P(Me)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$), -67.56 (dd, $J_{PP} = 245.7$ Hz, $J_{PP} = 73.4$ Hz, $[Li(DME)_3]^+[P(Me)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$), -82.62 ppm, (dd, $J_{PP} = 239.3$ Hz, $J_{PP} = 36.5$ Hz, $[Li(DME)_3]^+[P(Me)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$) ppm.

NMR data of isolated **2_1** in THF- d_8 . 1H NMR (400 MHz, C_6D_6 , 298 K) δ : 7.68–6.07 (aromatic protons), 3.46 (s, DME protons), 3.30 (s, DME protons), 3.22 (broad d, $J_{PH} = 5.3$ Hz, 1H, $[Li(DME)_3]^+[tBu_2P-P\{C(H)-Ph-Ph\}-PtBu_2]^-$), 1.32 (broad s, 36H, $[Li(DME)_3]^+[tBu_2P-P\{C(H)-Ph-Ph\}-PtBu_2]^-$) ppm.

$^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6 , 298 K) δ : 143.38–112.13 (aromatic C atoms), 71.79 (s, DME), 57.92 (s, DME), 54.80 (dt, $J_{PC} = 17.4$ Hz, $J_{PC} = 3.9$ Hz, $[Li(DME)_3]^+[tBu_2P-P\{C(H)-Ph-Ph\}-PtBu_2]^-$), 31.85 (broad dd, $J_{PC} = 15.0$ Hz, $J_{PC} = 7.0$ Hz, $[Li(DME)_3]^+[tBu_2P-P\{C(H)-Ph-Ph\}-PtBu_2]^-$), 31.24 (dd, $J_{PC} = 24.9$ Hz, $J_{PC} = 2.3$ Hz, $[Li(DME)_3]^+[tBu_2P-P\{C(H)-Ph-Ph\}-PtBu_2]^-$), 31.09 (dd, $J_{PC} = 28.2$ Hz, $J_{PC} = 2.4$ Hz, $[Li(DME)_3]^+[tBu_2P-P\{C(H)-Ph-Ph\}-PtBu_2]^-$) ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6 , 298 K) δ : 40.11 (d, $J_{PP} = 285.4$ Hz, $[Li(DME)_3]^+[tBu_2P-P\{C(H)(biph)-PtBu_2]^-$), 40.10 (d, $J_{PP} = 284.8$ Hz, $[Li(DME)_3]^+[tBu_2P-P\{C(H)(biph)-PtBu_2]^-$), -54.71 (dd, $J_{PP} = 285.4$ Hz, $J_{PP} = 284.8$ Hz, $[Li(DME)_3]^+[tBu_2P-P\{C(H)(biph)-PtBu_2]^-$) ppm.

Reaction of (biph)(H)C=P-PtBu₂ with *n*BuLi. To a solution of (biph)(H)C=P-PtBu₂ (0.08 g; 0.234 mmol) in 1 mL of THF- d_8 a *n*BuLi (0.093 mL; 0.234 mmol; 2.5 M) was dropwise added. The color immediately changed from orange to dark red, and after 24 hours the solution was transferred to a NMR-tube and measurements were performed.

1H NMR (400 MHz, C_6D_6 , 298 K) δ : 7.55–6.57 (aromatic protons), 3.80 (broad m, 1H, $[P(nBu)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$, **1b''**), 3.52 (dd, $J_{PH} = 11.5$ Hz, $J_{PH} = 3.7$ Hz, 1H, $[P(nBu)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$, **1b''**), 2.95 (dd, $J_{PH} = 7.8$ Hz, $J_{PH} = 1.5$ Hz, 1H, $[(biph)(H)C-P(nBu)-PtBu_2]^-$, **1b**), 2.73 (d, $J_{PH} = 5.3$ Hz, $[(biph)(H)C-P(nBu)-PtBu_2]^-$, **1b'**), 1.65 (broad m, $[P(nBu)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$, **1b''**), 1.57 (broad m, $[P(nBu)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$, **1b''**), 1.56 (broad m, $[(biph)(H)C-P(nBu)-PtBu_2]^-$, **1b**), 1.48 (broad m, $[(biph)(H)C-P(nBu)-PtBu_2]^-$, **1b'**), 1.45 (broad m, $[P(nBu)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$, **1b''**), 1.42 (broad m, $[(biph)(H)C-P(nBu)-PtBu_2]^-$, **1b'**), 1.34

(d, $J_{PH} = 12.2$ Hz, 18H, $[P(nBu)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$, **1b''**), 1.32 (d, $J_{PH} = 12.2$ Hz, 18H, $[(biph)(H)C-P(nBu)-PtBu_2]^-$, **1b**), 1.32 (d, $J_{PH} = 10.9$ Hz, 18H, tBu_2PLi), 1.32 (DME protons), 1.15 (broad m, $[P(nBu)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$, **1b''**), 0.96 (d, $J_{PH} = 11.6$ Hz, 18H, $[P(nBu)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$, **1b''**), 0.92 (DME protons) ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6 , 298 K) δ : 54.91 (d, $J_{PP} = 326.0$ Hz, $[P(nBu)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$, **1b''**), 41.80 (broad singlet, tBu_2PLi), 39.22 (d, $J_{PP} = 326.3$ Hz, $[(biph)(H)C-P(nBu)-PtBu_2]^-$, **1b**), -24.16 (d, $J_{PP} = 102.4$ Hz, $[P(nBu)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$, **1b''**), -37.43 (d, $J_{PP} = 326.3$ Hz, $[(biph)(H)C-P(nBu)-PtBu_2]^-$, **1b**), -41.56 (s, $[(biph)(H)C-P(nBu)_2]^-$, **1b'**), -59.24 (dd, $J_{PP} = 102.4$ Hz, $J_{PP} = 326.0$ Hz, $[P(nBu)_2-CH(biph)-CH(biph)-P(PtBu_2)]^-$, **1b''**) ppm.

Reaction of (biph)(H)C=P-PtBu₂ with *t*BuLi. To a solution of (biph)(H)C=P-PtBu₂ (0.08 g; 0.234 mmol) in 1 mL of THF- d_8 a *t*BuLi (0.123 mL; 0.234 mmol; 1.9 M) was dropwise added. The color immediately changed from orange to very dark red, and after 24 hours the solution was transferred to a NMR tube and measurements were performed.

1H NMR (400 MHz, C_6D_6 , 298 K) δ : 7.58–6.07 (aromatic protons), 3.15 (dd, $J_{PH} = 7.6$ Hz, $J_{PH} = 1.3$ Hz, 1H, $[(biph)(H)C-P(tBu)-PtBu_2]^-$, **1c**), 3.10 (d, $J_{PH} = 198.4$ Hz, tBu_2PH), 1.36 and 1.34 (hexane protons from 2.5 M solution of *t*BuLi in hexane), 1.31 (d, $J_{PH} = 13.2$ Hz, $[(biph)(H)C-P(tBu)-PtBu_2]^-$, **1c**), 1.31 ($J_{PH} = 13.7$ Hz, $[(biph)(H)C-P(tBu)-PtBu_2]^-$, **1c**), 1.14 (d, $J_{PH} = 12.7$ Hz, $[(biph)(H)C-P(tBu)-PtBu_2]^-$, **1c**), 1.09 (d, $J_{PH} = 12.3$ Hz, tBu_2PH), ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6 , 298 K) δ : 30.08 (d, $J_{PP} = 333.28$ Hz, $[(biph)(H)C-P(tBu)-PtBu_2]^-$, **1c**), 19.87 (s, tBu_2PH), -4.05 (d, $J_{PP} = 333.28$ Hz, $[(biph)(H)C-P(tBu)-PtBu_2]^-$, **1c**) ppm.

Reactions of (3,5-*t*Bu₂C₆H₃)(H)C=P-PtBu₂ (**3**) with MeLi, *n*BuLi, *t*BuLi respectively

Phosphanylphosphaalkene (80 mg, 0.223 mmol) was dissolved in 0.7 mL of THF- d_8 and lithium compound was dropwise added. After 24 hours solution was transferred to NMR-tube and appropriate measurements were performed.

Reaction with MeLi (0.223 mmol, 0.140 mL, 1.6 M solution in Et₂O). 1H NMR (400 MHz, C_6D_6 , 298 K) δ : 7.61–6.66 (aromatic protons), 4.10 (dd, $J_{PH} = 9.8$ Hz, $J_{HH} = 6.4$ Hz $[tBu_2P-P\{C(H)(3,5-*t*Bu_2C_6H_3)\}-PtBu_2]^-$), 3.65 (broad d, $J_{HH} = 6.1$ Hz, $[P(Me)_2-CH(3,5-*t*Bu_2C_6H_3)-CH(3,5-*t*Bu_2C_6H_3)-P(PtBu_2)]^-$), 3.48 (broad dd, $J_{HH} = 6.0$ Hz, $J_{PH} = 1.9$ Hz $[P(Me)_2-CH(3,5-*t*Bu_2C_6H_3)-CH(3,5-*t*Bu_2C_6H_3)-P(PtBu_2)]^-$), 1.41 (d, $J_{PH} = 11.7$ Hz, tBu_2PLi), 1.39 (d, $J_{PH} = 10.1$ Hz, $[tBu_2P-P\{C(H)(3,5-*t*Bu_2C_6H_3)\}-PtBu_2]^-$), 1.26 (broad d, $J_{PH} = 11.3$ Hz, $[P(Me)_2-CH(3,5-*t*Bu_2C_6H_3)-CH(3,5-*t*Bu_2C_6H_3)-P(PtBu_2)]^-$), 1.24 (d, $J_{PH} = 11.1$ Hz, $[tBu_2P-P\{C(H)(3,5-*t*Bu_2C_6H_3)\}-PtBu_2]^-$), 1.21 (broad d, $J_{PH} = 11.3$ Hz, $[P(Me)_2-CH(3,5-*t*Bu_2C_6H_3)-CH(3,5-*t*Bu_2C_6H_3)-P(PtBu_2)]^-$), 1.03 (d, $J_{PH} = 10.9$ Hz, $[tBu_2P-P\{C(H)(3,5-*t*Bu_2C_6H_3)\}-PtBu_2]^-$), 1.01 (d, $J_{PH} = 10.9$ Hz, $[tBu_2P-P\{C(H)(3,5-*t*Bu_2C_6H_3)\}-PtBu_2]^-$), 0.89 ($J_{PH} = 12.3$ Hz, $[P(Me)_2-CH(3,5-*t*Bu_2C_6H_3)-CH(3,5-*t*Bu_2C_6H_3)-P(PtBu_2)]^-$), 0.69 (d, $J_{PH} = 2.4$ Hz, $[P(Me)_2-CH(3,5-*t*Bu_2C_6H_3)-CH(3,5-*t*Bu_2C_6H_3)-P-$



$(\text{PtBu}_2)]^-$, 0.55 (d, $J_{\text{PH}} = 2.4$ Hz, $[\text{P}(\text{Me})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 298 K) δ : 66.12 (dd, $J_{\text{PP}} = 347.5$ Hz, $J_{\text{PP}} = 62.5$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$), 57.98 (dd, $J_{\text{PP}} = 231.7$ Hz, $J_{\text{PP}} = 62.5$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$), 53.01 (d, $J_{\text{PP}} = 324.1$ Hz, $[\text{P}(\text{Me})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), 39.78 (s, $t\text{Bu}_2\text{PLi}$), 19.81 (s, $t\text{Bu}_2\text{PH}$), -48.80 (d, $J_{\text{PP}} = 97.6$ Hz, $[\text{P}(\text{Me})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), -56.70 (broad dd, $J_{\text{PP}} = 324.1$ Hz, $J_{\text{PP}} = 97.6$ Hz $[\text{P}(\text{Me})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), -67.30 (dd, $J_{\text{PP}} = 347.5$ Hz, $J_{\text{PP}} = 231.7$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$) ppm.

Reaction with $n\text{BuLi}$ (0.223 mmol, 0.089 mL, 2.5 M solution in hexane). ^1H NMR (400 MHz, C_6D_6 , 298 K) δ : 4.10 (dd, $J_{\text{PH}} = 9.8$ Hz, $J_{\text{HH}} = 6.4$ Hz $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$), 3.71 (broad m, $[\text{P}(n\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), 3.47 (broad dd, $J_{\text{PH}} = 9.8$ Hz, $J_{\text{HH}} = 6.4$ Hz $[\text{P}(n\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), 1.65 (broad m, $[\text{P}(n\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), 1.57 (broad m, $[\text{P}(n\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), 1.39 (d, $J_{\text{PH}} = 10.3$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$), 1.31 (broad d, $J_{\text{PH}} = 10.3$ Hz, $[\text{P}(n\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), 1.27 (broad d, $J_{\text{PH}} = 12.5$ Hz, $[\text{P}(n\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), 1.25 (d, $J_{\text{PH}} = 12.2$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$), 1.18 (broad d, $[\text{P}(n\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), 1.03 (broad m, $[\text{P}(n\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), 1.03 (d, $J_{\text{PH}} = 11.0$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$), 1.00 (d, $J_{\text{PH}} = 10.9$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$), 0.91 (broad m, $[\text{P}(n\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$) 0.88 (broad d, $J_{\text{PH}} = 12.1$ Hz, $[\text{P}(n\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 298 K) δ : 66.05 (dd, $J_{\text{PP}} = 347.5$ Hz, $J_{\text{PP}} = 62.5$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$), 57.88 (dd, $J_{\text{PP}} = 231.7$ Hz, $J_{\text{PP}} = 62.5$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$), 54.07 (dd, $J_{\text{PP}} = 325.2$ Hz, $J_{\text{PP}} = 2.6$ Hz, $[\text{P}(n\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), -24.07 (dd, $J_{\text{PP}} = 96.8$ Hz, $J_{\text{PP}} = 2.6$ Hz, $[\text{P}(n\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), -60.36 (dd, $J_{\text{PP}} = 325.2$ Hz, $J_{\text{PP}} = 96.8$ Hz, $[\text{P}(n\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), -67.42 (dd, $J_{\text{PP}} = 347.5$ Hz, $J_{\text{PP}} = 231.7$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$) ppm.

Reaction with $t\text{BuLi}$ (0.223 mmol, 0.117 mL, 1.9 M solution in pentane). ^1H NMR (400 MHz, C_6D_6 , 298 K) δ : 4.17 (broad m, $[\text{P}(t\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), 4.11 (dd, $J_{\text{PH}} = 9.8$ Hz, $J_{\text{HH}} = 6.4$ Hz $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$), 3.72 (broad m, $[\text{P}(n\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), 2.49 (d, $J_{\text{PH}} = 10.4$ Hz, $[(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)(\text{H})\text{C-P}(\text{tBu})_2]$), 1.53 (d, $J_{\text{PH}} = 11.2$ Hz, $[\text{P}(t\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), 1.39 (d, $J_{\text{PH}} = 10.3$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$), 1.27 (broad d, $J_{\text{PH}} = 11.3$ Hz, $[\text{P}(t\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), 1.26 (d, $J_{\text{PH}} = 11.7$ Hz, $[\text{P}(t\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), 1.24 (d, $J_{\text{PH}} = 12.2$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$), 1.20 (d,

broad d, $J_{\text{PH}} = 12.1$ Hz, $[\text{P}(t\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), 1.12 (d, $J_{\text{PH}} = 10.4$ Hz, $[(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)(\text{H})\text{C-P}(\text{tBu})_2]$), 1.11 (d, $J_{\text{PH}} = 9.8$ Hz, $[(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)(\text{H})\text{C-P}(\text{tBu})_2]$), 1.03 (d, $J_{\text{PH}} = 10.9$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$), 1.02 (d, $J_{\text{PH}} = 10.1$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$), 0.88 (broad d, $J_{\text{PH}} = 10.6$ Hz, $[\text{P}(t\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 298 K) δ : 65.94 (dd, $J_{\text{PP}} = 347.5$ Hz, $J_{\text{PP}} = 62.5$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$), 57.96 (dd, $J_{\text{PP}} = 231.7$ Hz, $J_{\text{PP}} = 62.5$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$), 48.79 (dd, $J_{\text{PP}} = 314.6$ Hz, $J_{\text{PP}} = 35.3$ Hz, $[\text{P}(t\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), 39.78 (s, $t\text{Bu}_2\text{PLi}$), 19.84 (s, $t\text{Bu}_2\text{PH}$), 8.18 (dd, $J_{\text{PP}} = 114.7$ Hz, $J_{\text{PP}} = 35.3$ Hz, $[\text{P}(t\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$), -67.49 (dd, $J_{\text{PP}} = 347.5$ Hz, $J_{\text{PP}} = 231.7$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\}\text{-PtBu}_2]$), -67.54 (dd, $J_{\text{PP}} = 314.6$ Hz, $J_{\text{PP}} = 114.7$ Hz, $[\text{P}(t\text{Bu})_2\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-CH}(3,5\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)\text{-P}(\text{PtBu}_2)]^-$) ppm.

Reactions of $(p\text{-Me}_2\text{N-C}_6\text{H}_4)(\text{H})\text{C}=\text{P-PtBu}_2$ (4) with MeLi, $n\text{BuLi}$, $t\text{BuLi}$ respectively

Phosphanylphosphaalkene (80 mg, 0.257 mmol) was dissolved in 0.7 mL of THF- d_8 and lithium compound was dropwise added. After 24 hours solution was transferred to NMR-tube and appropriate measurements were performed.

Reaction with MeLi (0.257 mmol, 0.160 mL, 1.6 M solution in Et $_2\text{O}$). ^1H NMR (400 MHz, C_6D_6 , 298 K) δ : 4.01 (dd, $J_{\text{PH}} = 9.5$ Hz, $J_{\text{HH}} = 6.4$ Hz $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}\text{-PtBu}_2]$), 3.50 (broad m, $[\text{P}(\text{Me})_2\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-P}(\text{PtBu}_2)]^-$), 3.18 (broad d, $J_{\text{PH}} = 11.6$ Hz, $[\text{P}(\text{Me})_2\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-P}(\text{PtBu}_2)]^-$), 2.86 (s, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}\text{-PtBu}_2]$), 2.83 (s, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}\text{-PtBu}_2]$), 2.80 (s, $[\text{P}(\text{Me})_2\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-P}(\text{PtBu}_2)]^-$), 2.71 (s, $[\text{P}(\text{Me})_2\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-P}(\text{PtBu}_2)]^-$), 1.42 (d, $J_{\text{PH}} = 11.7$ Hz, $t\text{Bu}_2\text{PLi}$), 1.38 (d, $J_{\text{PH}} = 9.9$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}\text{-PtBu}_2]$), 1.29 (broad d, $J_{\text{PH}} = 11.3$ Hz, $[\text{P}(\text{Me})_2\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-P}(\text{PtBu}_2)]^-$), 1.24 (d, $J_{\text{PH}} = 9.8$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}\text{-PtBu}_2]$), 1.05 (d, $J_{\text{PH}} = 10.0$ Hz, $t\text{Bu}_2\text{PH}$), 0.91 (d, $J_{\text{PH}} = 10.3$ Hz, $[\text{P}(\text{Me})_2\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-P}(\text{PtBu}_2)]^-$), 0.90 (d, $J_{\text{PH}} = 3.0$ Hz, $[\text{P}(\text{Me})_2\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-P}(\text{PtBu}_2)]^-$), 0.60 (d, $J_{\text{PH}} = 2.3$ Hz, $[\text{P}(\text{Me})_2\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-P}(\text{PtBu}_2)]^-$) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 298 K) δ : 64.62 (dd, $J_{\text{PP}} = 348.2$ Hz, $J_{\text{PP}} = 62.6$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}\text{-PtBu}_2]$), 56.85 (dd, $J_{\text{PP}} = 239.6$ Hz, $J_{\text{PP}} = 62.6$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}\text{-PtBu}_2]$), 54.44 (d, $J_{\text{PP}} = 324.7$ Hz, $[\text{P}(\text{Me})_2\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-P}(\text{PtBu}_2)]^-$), 39.77 (s, $t\text{Bu}_2\text{PLi}$), 19.84 (s, $t\text{Bu}_2\text{PH}$), -47.08 (d, $J_{\text{PP}} = 111.51$ Hz, $[\text{P}(\text{Me})_2\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-P}(\text{PtBu}_2)]^-$), -64.84 (dd, $J_{\text{PP}} = 324.7$ Hz, $J_{\text{PP}} = 111.51$ Hz, $[\text{P}(\text{Me})_2\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)\text{-P}(\text{PtBu}_2)]^-$), -69.64 (dd, $J_{\text{PP}} = 348.2$ Hz, $J_{\text{PP}} = 239.6$ Hz, $[\text{tBu}_2\text{P-P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}\text{-PtBu}_2]$) ppm.



Reaction with *n*BuLi (0.257 mmol, 0.103 mL, 2.5 M solution in hexane). ^1H NMR (400 MHz, C_6D_6 , 298 K) δ : 4.01 (dd, $J_{\text{PH}} = 9.6$ Hz, $J_{\text{HH}} = 6.5$ Hz [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$), 3.69 (broad m, [$n\text{Bu}_2\text{P}-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}^-$), 3.25 (broad dd, $J_{\text{PH}} = 11.8$ Hz, $J_{\text{HH}} = 3.1$ Hz [$n\text{Bu}_2\text{P}-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}^-$), 2.88 (s, [$n\text{Bu}_2\text{P}-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}^-$), 2.86 (s, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$), 2.82 (s, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$), 2.81 (s, [$n\text{Bu}_2\text{P}-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}^-$), 1.67 (broad m, [$n\text{Bu}_2\text{P}-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}^-$), 1.57 (broad m, [$n\text{Bu}_2\text{P}-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}^-$), 1.38 (d, $J_{\text{PH}} = 10.0$ Hz, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$), 1.31 (broad d, $J_{\text{PH}} = 10.8$ Hz, [$n\text{Bu}_2\text{P}-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}^-$), 1.26 (broad d, $J_{\text{PH}} = 11.2$ Hz, [$n\text{Bu}_2\text{P}-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}^-$), 1.25 (d, $J_{\text{PH}} = 9.8$ Hz, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$), 1.06 (d, $J_{\text{PH}} = 10.4$ Hz, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$), 1.05 (broad m, [$n\text{Bu}_2\text{P}-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}^-$), 0.92 (broad m, [$n\text{Bu}_2\text{P}-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}^-$), 0.92 (d, $J_{\text{PH}} = 10.5$ Hz, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 298 K) δ : 64.73 (dd, $J_{\text{PP}} = 348.2$ Hz, $J_{\text{PP}} = 62.6$ Hz, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$), 57.05 (dd, $J_{\text{PP}} = 237.7$ Hz, $J_{\text{PP}} = 62.6$ Hz, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$), 54.84 (d, $J_{\text{PP}} = 328.6$ Hz, [$n\text{Bu}_2\text{P}-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}^-$), 39.77 (s, $t\text{Bu}_2\text{PLi}$), 19.81 (s, $t\text{Bu}_2\text{PH}$), -22.45 (d, $J_{\text{PP}} = 109.6$ Hz, [$n\text{Bu}_2\text{P}-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}^-$), -67.41 (dd, $J_{\text{PP}} = 328.6$ Hz, $J_{\text{PP}} = 109.6$ Hz, [$n\text{Bu}_2\text{P}-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}^-$), -69.52 (dd, $J_{\text{PP}} = 348.2$ Hz, $J_{\text{PP}} = 237.7$ Hz, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$) ppm.

Reaction with *t*BuLi (0.257 mmol, 0.135 mL, 1.9 M solution in hexane). ^1H NMR (400 MHz, C_6D_6 , 298 K) δ : 4.00 (dd, $J_{\text{PH}} = 9.6$ Hz, $J_{\text{HH}} = 6.5$ Hz [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$), 3.84 (broad d, $J_{\text{PH}} = 10.9$ Hz, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), 3.76 (broad m, $J_{\text{PH}} = 4.4$ Hz, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), 3.69 (broad d, $J_{\text{PH}} = 11.5$ Hz, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), 3.52 (broad m, $J_{\text{HH}} = 5.4$ Hz, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), 2.90 (s, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), 2.88 (s, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$), 2.86 (s, [$\{p\text{-Me}_2\text{N-C}_6\text{H}_4\}(\text{H})\text{C}-\text{P}(t\text{Bu}_2)_2\}^-$), 2.84 (s, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$), 2.82 (s, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), 2.80 (s, [$\{p\text{-Me}_2\text{N-C}_6\text{H}_4\}(\text{H})\text{C}-\text{P}(t\text{Bu}_2)_2\}^-$), 2.78 (s, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), 2.71 (s, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), 1.44 (d, $J_{\text{PH}} = 10.9$ Hz, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), 1.39 (broad d, $J_{\text{PH}} = 10.2$ Hz, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), 1.38 (d, $J_{\text{PH}} = 10.1$ Hz, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$), 1.28 (broad d, $J_{\text{PH}} = 10.8$ Hz, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), 1.24 (d, $J_{\text{PH}} = 10.14$ Hz, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), 1.24 (d, $J_{\text{PH}} = 9.8$ Hz, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$), 1.23 (d, $J_{\text{PH}} = 10.14$ Hz, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), 1.15 (d, $J_{\text{PH}} = 10.9$ Hz, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), 1.14 (d, $J_{\text{PH}} = 10.4$ Hz, [$\{p\text{-Me}_2\text{N-C}_6\text{H}_4\}(\text{H})\text{C}-\text{P}(t\text{Bu}_2)_2\}^-$), 1.05 (d, $J_{\text{PH}} = 9.8$ Hz, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$), 1.05 (d, $J_{\text{PH}} = 10.8$ Hz, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$), 0.98 (d, $J_{\text{PH}} = 10.0$ Hz, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 298 K) δ : 64.65 (dd, $J_{\text{PP}} = 348.2$ Hz, $J_{\text{PP}} = 62.6$ Hz, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$), 57.03 (dd, $J_{\text{PP}} = 237.7$ Hz, $J_{\text{PP}} = 62.6$ Hz, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$), 51.56 (dd, $J_{\text{PP}} = 326.9$ Hz, $J_{\text{PP}} = 5.3$ Hz, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), 49.51 (dd, $J_{\text{PP}} = 281.7$ Hz, $J_{\text{PP}} = 51.5$ Hz, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), 41.07 (dd, $J_{\text{PP}} = 139.5$ Hz, $J_{\text{PP}} = 5.3$ Hz, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), 31.44 (s, [$\{p\text{-Me}_2\text{N-C}_6\text{H}_4\}(\text{H})\text{C}-\text{P}(t\text{Bu}_2)_2\}^-$), 3.81 (dd, $J_{\text{PP}} = 111.3$ Hz, $J_{\text{PP}} = 51.5$ Hz, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), -55.98 (dd, $J_{\text{PP}} = 281.7$ Hz, $J_{\text{PP}} = 111.3$ Hz, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), -57.56 (dd, $J_{\text{PP}} = 326.9$ Hz, $J_{\text{PP}} = 139.5$ Hz, [$\{P(t\text{Bu})_2-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{CH}(p\text{-Me}_2\text{N-C}_6\text{H}_4)-\text{P}(\text{PtBu}_2)\}_2\text{Li}\}^-$), -69.59 (dd, $J_{\text{PP}} = 348.2$ Hz, $J_{\text{PP}} = 237.7$ Hz, [$t\text{Bu}_2\text{P}-\text{P}\{-\text{C}(\text{H})(p\text{-Me}_2\text{N-C}_6\text{H}_4)\}-\text{PtBu}_2\}^-$) ppm.

Conclusions

The performed experiments undoubtedly display that $\text{C}\equiv\text{P}$ bond activation in the phosphanylphosphaalkene (biph)(H) $\text{C}\equiv\text{P}-\text{PtBu}_2$ occurs with each of the three selected reagents. However, the reactions with MeLi and *n*BuLi ultimately lead to substitution of two organic groups (Me and *n*Bu) on the phosphorus atoms and, consequently, to cleavage of the P-P bond. From the point of view of further research related to the polymerization of phosphanylphosphaalkenes, both MeLi and *n*BuLi are not suitable reagents for anionic activation. The research shows that the best reagent for anionic activation is *t*BuLi, because only one *t*Bu group is substituted on the phosphorus atom. Additionally, in this substitution the new item (Scheme 2) is given in the text reaction of the second group (*t*Bu), cleavage of the P-P bond was not observed. Moreover, replacement the -Ph group in the *para* position, with *t*Bu groups (*meta* position) and NMe₂ group (*para* position) does not improve the stability of the products after the first stage of the reaction – i.e. the activation of the $\text{P}=\text{C}$ bond consisting in the mono-substitution of the Me, *n*Bu or *t*Bu groups to the phosphorus atom. The obtained result indicates that (biph)(H) $\text{C}\equiv\text{P}-\text{PtBu}_2$ (1) is the best phosphanylphosphaalkene to activate the $\text{P}=\text{C}$ bond as proved by its reaction with *t*BuLi.

Conflicts of interest

There are no conflicts to declare.



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