Phosphanylphosphaalkenes as precursors for metallaphosphaalkene complexes

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A. Experimental section

All synthetic reactions were conducted under an argon atmosphere using a standard Schlenk technique. Toluene, THF and pentane were dried over Na/benzophenone and were freshly distilled under argon prior to use. Lithium salts of diphosphanes $(Et_2N)_2P$-$P(SiMe_3)Li{\cdot}n$THF and tBu$_2$P-P(SiMe$_3$)Li·nTHF were synthesized according to the literature.[1, 2] Benzophenone, 4,4'-dibenzyl-benzophenone and dichloro(*p*-cymene)ruthenium(II) dimer were purchased commercially. Elemental analysis for solid were recorded on Elementar Vario El Cube CHNS.

A. 1. Synthesis of ***2***

A suspension of 4,4'-dibenzyl-benzophenone (0.200 g; 0.598 mmol) in 15 mL of toluene was added to a solution of tBu$_2$P-P(SiMe$_3$)Li·2.5THF (0.321 g; 0.598 mmol) in 10 mL of toluene at RT (room temperature). Immediately formed a clear, intense orange solution, which was stirred for about 30 min. After this time, the toluene was evaporated, and the oily residue was treated with 15 mL of pentane and filtered. The resulting filtrate was concentrated to $^1/_3$ of its original volume and stored at +4˚C. After several hours, dark orange crystals of the expected product precipitated from the solution. Yield of isolated crystals 0.230 g (78%). Anal. Calcd. for $C_{33}H_{36}P_2$: C, 80.14; H, 7.34 %. Found: C, 80.12; H, 7.38 %.

^{1}H NMR (400 MHz, Toluene-d$_8$, 298 K) δ 7.66 – 6.98 (18 H, aromatic protons, (**biph**)$_2$C=P-PtBu$_2$) 1.17 (d, 18H, $J_{P\text{-}H}$ = 11.0 Hz, (biph)$_2$C=P-P***t*****Bu**$_2$) ppm;

^{13}C{^{1}H} NMR (100.6 MHz, Toluene-d$_8$, 298 K) δ 206.00 (dd, $J_{P\text{-}C}$ = 54.9 Hz, $J_{P\text{-}C}$ = 16.8 Hz, (biph)$_2$**C**=P-PtBu$_2$), 145.55 (dd, $J_{P\text{-}C}$ = 23.6 Hz, $J_{P\text{-}C}$ = 4.5 Hz, (**biph**)$_2$C=P-PtBu$_2$), 144.54 (dd, $J_{P\text{-}C}$ = 14.53 Hz, $J_{P\text{-}C}$ = 5.4 Hz, (**biph**)$_2$C=P-PtBu$_2$), 142.26 (d, $J_{P\text{-}C}$ = 5.4 Hz, (**biph**)$_2$C=P-PtBu$_2$), 140.94 (s, (**biph**)$_2$C=P-PtBu$_2$), 140.68 (s, (**biph**)$_2$C=P-PtBu$_2$), 140.13 (s, (**biph**)$_2$C=P-PtBu$_2$), 130.40 (q, $J_{P\text{-}C}$ = 6.5 Hz, $J_{P\text{-}C}$ = 4.4 Hz (**biph**)$_2$C=P-PtBu$_2$), 128.70 (s, (**biph**)$_2$C=P-PtBu$_2$), 128.57 (s, (**biph**)$_2$C=P-PtBu$_2$), 127.80 (d, $J_{P\text{-}C}$ = 19.9 Hz, (**biph**)$_2$C=P-PtBu$_2$), 127. 06 (s, (**biph**)$_2$C=P-PtBu$_2$), 126.94 (s, (**biph**)$_2$C=P-PtBu$_2$), 126.84 (s, (**biph**)$_2$C=P-PtBu$_2$), 126.70 (s, (**biph**)$_2$C=P-PtBu$_2$), 126.16 (s, (**biph**)$_2$C=P-PtBu$_2$), 34.10 (dd, $J_{P\text{-}C}$ = 30.0 Hz, $J_{P\text{-}C}$ = 4.1 Hz, (biph)$_2$C=P-P***t*****Bu**$_2$), 31.11 (dd, $J_{P\text{-}C}$ = 14.5 Hz, $J_{P\text{-}C}$ = 5.5 Hz, (biph)$_2$C=P-P***t*****Bu**$_2$) ppm;

^{31}P{^{1}H} NMR (162 MHz, Toluene-d$_8$, 298 K) δ 277.31 (d, $J_{P\text{-}P}$ = 229.4 Hz, (biph)$_2$C=**P**-PtBu$_2$), 27.86 (d, $J_{P\text{-}P}$ = 229.4 Hz, (biph)$_2$C=P-**P**tBu$_2$) ppm.

*A. 2. Synthesis of compounds **3a** and **3***

A solution of benzophenone (0.093 g; 0.510 mmol) in 5 mL of toluene was added to a solution of $(Et_2N)_2P$-$P(SiMe_3)Li$·1.5THF (0.200 g; 0.510 mmol) in 5 mL of toluene at RT. The resulting solution immediately adopted a dark orange color. The mixture was stirred for 1 hour at RT, and after that time the solvent was removed under reduced pressure. The oily residue was treated with pentane (15 mL) and filtered, and the resulting solution was concentrated to half of its volume. The final solution was stored at +4˚C for 24 hours resulting in the formation of yellow crystals (**3a**). Yield of isolated crystals 0.145 g (76%). Anal. Calcd. for $C_{42}H_{60}N_4P_4$: C, 67.73; H, 8.12; N, 7.52 %. Found: C, 67.68; H, 8.09; N, 7.56 %.

The crystals of **3a** were dissolved in C_6D_6 and the resulting solution immediately characterized by NMR spectroscopy, allowing to detect the signals of **3** and **3a**. The measurement was repeated 3 and 6 hours after dissolution. After this time, only signals from the monomer (**3**) were observed.

<u>NMR Data for **3**:</u>

^{1}H NMR (400 MHz, C_6D_6, 298 K) δ 7.56 – 6.89 (18 H, aromatic protons, **Ph**$_2$C=P-P(NEt$_2$)$_2$), 3.02 (m, 4 H, $J_{H\text{-}H}$ = 6.9 Hz, Ph$_2$C=P-P{N(C**H**$_2$CH$_3$)$_2$}$_2$), 2.92 (broad m, 4 H, $J_{H\text{-}H}$ = 6.9 Hz, Ph$_2$C=P-P{N(C**H**$_2$CH$_3$)$_2$}$_2$), 0.05 (t, $^3J_{H\text{-}H}$ = 6.9 Hz, 12 H, Ph$_2$C=P-P{N(CH$_2$C**H**$_3$)$_2$}$_2$) ppm;

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K) δ 198.62 (dd, $J_{P\text{-}C}$ = 52.7 Hz, $J_{P\text{-}C}$ = 23.6 Hz, Ph$_2$**C**=P-P(NEt$_2$)$_2$), 146.38 (dd, $J_{P\text{-}C}$ = 19.9 Hz, $J_{P\text{-}C}$ = 4.5 Hz, **Ph**$_2$C=P-P(NEt$_2$)$_2$), 145.20 (dd, $J_{P\text{-}C}$ = 13.6 Hz, $J_{P\text{-}C}$ = 7.3 Hz, **Ph**$_2$C=P-P(NEt$_2$)$_2$), 137.91 (s, **Ph**$_2$C=P-P(NEt$_2$)$_2$), 131.74 (s, **Ph**$_2$C=P-P(NEt$_2$)$_2$), 129.88 (s, **Ph**$_2$C=P-P(NEt$_2$)$_2$), 129.37 (t, $J_{P\text{-}C}$ = 2.5 Hz, **Ph**$_2$C=P-P(NEt$_2$)$_2$), 128.75 (d, $J_{P\text{-}C}$ = 4.4 Hz, **Ph**$_2$C=P-P(NEt$_2$)$_2$), 128.00 (d, $J_{P\text{-}C}$ = 0.8 Hz, **Ph**$_2$C=P-P(NEt$_2$)$_2$), 127.31 (s, **Ph**$_2$C=P-P(NEt$_2$)$_2$), 45.42 (dd, $J_{P\text{-}C}$ = 15.6 Hz, $J_{P\text{-}C}$ = 6.7 Hz, Ph$_2$C=P-P(N**Et**$_2$)$_2$), 15.15 (d, $J_{P\text{-}C}$ = 3.6 Hz, Ph$_2$C=P-P(N**Et**$_2$)$_2$) ppm;

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K) δ 271.39 (d, $J_{P\text{-}P}$ = 244.9 Hz, Ph$_2$C=**P**-P(NEt$_2$)$_2$), 103.68 (d, $J_{P\text{-}P}$ = 244.9 Hz, Ph$_2$C=P-**P**(NEt$_2$)$_2$) ppm.

<u>NMR Data for **3a**:</u>

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K) δ -21.3 (m, P$_2$$P^A$C), 111.2 (m, N$_2$$P^X$P), multiplets simulated as AA'XX' pattern with $^1J_{AA'}$ = -106 Hz, $^1J_{AX}$ = -106 Hz, $^2J_{AX'}$ = 236 Hz, $^3J_{XX'}$ = 0 Hz.

*A. 3. Synthesis of compounds **4a** and **4***

A suspension of 4,4'-dibenzyl-benzophenone (0.185 g; 0.510 mmol) in 10 mL of toluene was added to a solution of $(Et_2N)_2P\text{-}P(SiMe_3)Li\cdot1.5THF$ (0.200 g; 0.510 mmol) in 5 mL of toluene at RT. The resulting mixture immediately adopted a dark orange color. The initially cloudy mixture quickly became clear, and after 1 hour at RT, the solvent was removed under reduced pressure. The oily residue was treated with pentane (15 mL) and filtered, and the resulting solution was concentrated to half its volume. The final solution was stored at +4˚C for 24 hours, resulting in the formation of dark yellow crystals of **4a**. Yield of isolated crystals 0.172 g (60%). Anal. Calcd. for $C_{71}H_{88}N_4P_4 \cdot C_5H_{14}$: C, 76.05; H, 7.91; N, 5.00 %. Found: C, 75.80; H, 7.74; N, 5.12 %.

The crystals of **4a** were dissolved in C_6D_6. NMR spectra recorded immediately after dissolution showed signals attributable to **4** and **4a**. After 1 hour, only signals from the monomer (**4**) were observed.

<u>NMR Data for **4**:</u>

^{1}H NMR (400 MHz, Toluene-d_8, 298 K) δ 7.77 – 7.09 (18 H, aromatic protons, (**biph**)$_2$C=P-P(NEt$_2$)$_2$), 3.20 (sept, 4 H, $J_{H\text{-}H}$ = 6.7 Hz, (biph)$_2$C=P-P{N(C**H**$_2$CH$_3$)$_2$}$_2$), 3.10 (broad sept, 4 H, $J_{H\text{-}H}$ = 6.9 Hz, (biph)$_2$C=P-P{N(C**H**$_2$CH$_3$)$_2$}$_2$), 1.03 (t, $J_{H\text{-}H}$ = 6.9 Hz, 12 H, (biph)$_2$C=P-P(CH$_2$C**H**$_3$)$_2$}$_2$) ppm;

^{13}C{^{1}H} NMR (100.6 MHz, Toluene-d_8, 298 K) δ 197.41 (dd, $J_{P\text{-}C}$ = 53.0 Hz, $J_{P\text{-}C}$ = 24.1 Hz, (biph)$_2$**C**=P-P(NEt$_2$)$_2$), 145.32 (dd, $J_{P\text{-}C}$ = 20.1 Hz, $J_{P\text{-}C}$ = 4.1 Hz, (**biph**)$_2$C=P-P(NEt$_2$)$_2$), 144.08 (dd, $J_{P\text{-}C}$ = 13.9 Hz, $J_{P\text{-}C}$ = 6.6 Hz, (**biph**)$_2$C=P-P(NEt$_2$)$_2$), 141.68 (d, $J_{P\text{-}C}$ = 4.5 Hz, (**biph**)$_2$C=P-P(NEt$_2$)$_2$), 140.94 (s, (**biph**)$_2$C=P-P(NEt$_2$)$_2$), 140.62 (s, (**biph**)$_2$C=P-P(NEt$_2$)$_2$), 140.07 (s, (**biph**)$_2$C=P-P(NEt$_2$)$_2$), 130.52 (s, (**biph**)$_2$C=P-P(NEt$_2$)$_2$), 128.65 (s, (**biph**)$_2$C=P-P(NEt$_2$)$_2$), 128.05 (d, $J_{P\text{-}C}$ = 2.5 Hz, (**biph**)$_2$C=P-P(NEt$_2$)$_2$), 127.16 (d, $J_{P\text{-}C}$ = 10.6 Hz, (**biph**)$_2$C=P-P(NEt$_2$)$_2$), 126, 83 (s, (**biph**)$_2$C=P-P(NEt$_2$)$_2$), 126.75 (s, (**biph**)$_2$C=P-P(NEt$_2$)$_2$), 126.69 (s, (**biph**)$_2$C=P-P(NEt$_2$)$_2$), 45.48 (dd, $J_{P\text{-}C}$ = 15.5 Hz, $J_{P\text{-}C}$ = 6.8 Hz, (biph)$_2$C=P-P(N**Et**$_2$)$_2$), 15.15 (d, $J_{P\text{-}C}$ = 3.6 Hz, (biph)$_2$C=P-P(N**Et**$_2$)$_2$) ppm;

^{31}P{^{1}H} NMR (162 MHz, Toluene-d_8, 298 K) δ 272.02 (d, $J_{P\text{-}P}$ = 248.6 Hz, (biph)$_2$C=**P**-P(NEt$_2$)$_2$), 104.13 (d, $J_{P\text{-}P}$ = 248.6 Hz, (biph)$_2$C=P-**P**(NEt$_2$)$_2$) ppm.

<u>NMR Data for **4a**:</u>

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K) δ -20.5 (m, P_2P^AC), 111.3 (m, N_2P^XP), multiplets simulated as AA'XX' pattern with $^1J_{AA'}$ = -106 Hz, $^1J_{AX}$ = -108 Hz, $^2J_{AX'}$ = 238 Hz, $^3J_{XX'}$ = 0 Hz.

*A. 4. Synthesis of compounds **5** and **7***

Compound **3a** (0.150 g; 0.201 mmol) was treated with 5 mL of THF and stirred for 6 hours at room temperature to allow complete conversion to monomer **3**. During this time, a change in the color of the solution from yellow to intense orange was noticed. Next, a suspension of dichloro(*p*-cymene)ruthenium(II) dimer (0.369 g; 0.603 mmol) in 5 mL of THF was transferred to the solution, resulting in an immediate change of the color to dark red. The mixture was stirred for 24 hours. To the residue obtained after evaporation of THF, 10 mL of toluene was added and the mixture was filtered. The resulting filtrate was concentrated to $^{1}/_{3}$ of its volume, and the solution was kept at room temperature for 24 hours. After this time, dark red crystals separated, which were isolated to give 0.306 g (44%) of [(*p*-cym)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)] (**5**), Anal. Calcd. for $C_{40}H_{46}Cl_3P_1Ru_2$: C, 55.46; H, 5.35 %. Found: C, 55.41; H, 5.40 %. The supernatant solution was transferred to a Schlenk flask. Next, all volatile substances were removed by evaporation under low pressure. To the residue, 10 mL of pentane was added and the mixture was filtered. The resulting filtrate was concentrated to 1 mL and the solution was stored at -30°C. After 48 h, red crystals of [(*p*-cym)RuCl$_2$(η^1-P(Cl)(NEt$_2$)$_2$] (**7**) were collected. Yield of isolated crystals 0.191 g (46%). Anal. Calcd. for $C_{18}H_{34}Cl_3P_1Ru_2$: C, 41.83; H, 6.63; N, 5.42 %. Found: C, 41.80; H, 6.59 N, 5.46 %.

<u>NMR data for **5**:</u>

^{1}H NMR (400 MHz, Toluene-d$_8$, 298 K) δ 7.13 – 7.01 (10 H, aromatic protons, [(*p*-cym)(Cl)Ru(μ^2-P=C**Ph$_2$**)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 4.68 (d, 2H, $J_{H\text{-}H}$ = 6.0 Hz, [(***p*-cym**)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 4.50 (dd, 2H, $J_{H\text{-}H}$ = 6.0 Hz, $J_{P\text{-}H}$ = 1.0 Hz, [(***p*-cym**)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 4.34 (dd, 2H, $J_{H\text{-}H}$ = 6.0 Hz, $J_{P\text{-}H}$ = 1.1 Hz, [(***p*-cym**)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 3.77 (d, 2H, $J_{H\text{-}H}$ = 5.9 Hz, [(***p*-cym**)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 3.10 (sept, 2 H, $J_{H\text{-}H}$ = 6.9 Hz, [(***p*-cym**)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 2.19 (s, 6H, [(***p*-cym**)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 1.20 (d, 6H, $J_{H\text{-}H}$ = 6.8 Hz, [(***p*-cym**)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 1.01 (d, 6H, $J_{H\text{-}H}$ = 6.8 Hz, [(***p*-cym**)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]) ppm;

^{13}C{^{1}H} NMR (100.6 MHz, Toluene-d$_8$, 298 K) δ 147.97 (s, [(*p*-cym)(Cl)Ru(μ^2-P=C**Ph$_2$**)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 128.92 (s, [(*p*-cym)(Cl)Ru(μ^2-P=C**Ph$_2$**)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 128.11 (s, [(*p*-cym)(Cl)Ru(μ^2-P=C**Ph$_2$**)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 126.64 (d, $J_{P\text{-}C}$ = 2.7 Hz, [(*p*-cym)(Cl)Ru(μ^2-P=C**Ph$_2$**)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 125.26 (s, [(*p*-cym)(Cl)Ru(μ^2-P=C**Ph$_2$**)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 111.85 (d, $J_{P\text{-}C}$ = 4.4 Hz, [(*p*-cym)(Cl)Ru(μ^2-P=C**Ph$_2$**)(μ^2-Cl)Ru(Cl)(*p*-cym)], 101.83 (s, [(***p*-cym**)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 86.97 (d, $J_{P\text{-}C}$ = 4.4 Hz, [(***p*-cym**)(Cl)Ru(μ^2-

P=CPh$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]) 84.19 (d, $J_{P\text{-}C}$ = 3.6 Hz, [(***p*-cym**)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 81.85 (s, [(***p*-cym**)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 80.88 (s, [(***p*-cym**)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 30.43 (s, [(***p*-cym**)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 23.49 (s, [(***p*-cym**)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 19.07 (s, [(***p*-cym**)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]) ppm;

^{31}P{^{1}H} NMR (162 MHz, Toluene-d$_8$, 298 K) δ 327.3 [(*p*-cym)(Cl)Ru(μ^2-**P**=CPh$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)] ppm.

NMR data for **7**:

^{1}H NMR (400 MHz, THF-d$_8$, 298 K) δ 5.49 (m, 4H, $J_{P\text{-}H}$ = 18.8 Hz, $J_{H\text{-}H}$ = 6.2 Hz, [(***p*-cym**)RuCl$_2$(η^1-P(Cl)(NEt$_2$)$_2$]), 3.15 (m, 8H, $J_{H\text{-}H}$ = 7.1 Hz, [(*p*-cym)RuCl$_2$(η^1-P(Cl){N(C**H**$_2$CH$_3$)$_2$}$_2$]), 2.91 (sept, 1H, $J_{H\text{-}H}$ = 7.0 Hz, [(***p*-cym**)RuCl$_2$(η^1-P(Cl)(NEt$_2$)$_2$]), 2.02 (s, 3H, [(***p*-cym**)RuCl$_2$(η^1-P(Cl)(NEt$_2$)$_2$]), 1.16 (d, 6H, $J_{H\text{-}H}$ = 7.0 Hz, [(***p*-cym**)RuCl$_2$(η^1-P(Cl)(NEt$_2$)$_2$]), 1.00 (t, 12H, $^3J_{H\text{-}H}$ = 7.1 Hz, [(*p*-cym)RuCl$_2$(η^1-P(Cl) {N(CH$_2$C**H**$_3$)$_2$}$_2$]) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, THF-d$_8$, 298 K) δ 108.45 ($J_{P\text{-}C}$ = 1.4 Hz, [(***p*-cym**)RuCl$_2$(η^1-P(Cl)(NEt$_2$)$_2$]), 97.00 (s, [(***p*-cym**)RuCl$_2$(η^1-P(Cl)(NEt$_2$)$_2$]), 90.48 (d, $J_{P\text{-}C}$ = 6.14 Hz, [(***p*-cym**)RuCl$_2$(η^1-P(Cl)(NEt$_2$)$_2$]), 90.36 ($J_{P\text{-}C}$ = 7.7 Hz, [(***p*-cym**)RuCl$_2$(η^1-P(Cl)(NEt$_2$)$_2$]), 41.48 (d, $J_{P\text{-}C}$ = 5.8 Hz, [(*p*-cym)RuCl$_2$(η^1-P(Cl)(N**Et**$_2$)$_2$]), 30.43 (s, $J_{P\text{-}C}$ = 7.7 Hz, [(***p*-cym**)RuCl$_2$(η^1-P(Cl)(NEt$_2$)$_2$]), 21.42 (s, [(***p*-cym**)RuCl$_2$(η^1-P(Cl)(NEt$_2$)$_2$]), 16.53 (s, [(***p*-cym**)RuCl$_2$(η^1-P(Cl)(NEt$_2$)$_2$]), 13.56 (d, $J_{P\text{-}C}$ = 3.2 Hz, [(*p*-cym)RuCl$_2$(η^1-P(Cl)(N**Et**$_2$)$_2$]) ppm.

^{31}P{^{1}H} NMR (162 MHz, THF-d$_8$, 298 K) δ 145.30 (s, [(*p*-cym)RuCl$_2$(η^1-**P**(Cl)(NEt$_2$)$_2$]) ppm.

*A. 5. Synthesis of compounds **6** and **7***

Compound **4a** (0.150 g; 0.143 mmol) was treated with 5 mL of THF and the mixture stirred for 6 hours at room temperature to allow for complete conversion to compound **4**. A change in the color of the solution from dark yellow to red was observed. A suspension of dichloro(*p*-cymene)ruthenium(II) dimer (0.263 g; 0.429 mmol) in 5 mL of THF was transferred to the solution of 4. The reaction mixture immediately took on a dark red color. The mixture was stirred for 24 hours. Next, all volatile substances were removed in vacuo and the residual solid was dissolved in 10 mL of toluene. The resulting filtrate was concentrated to $^{1}/_{3}$ of its volume, and the solution was kept at room temperature for 24 hours. At that time, dark red crystals separated, which were collected to yield 0.222 g (42%) of [(*p*-cym)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)] (**6**). Anal. Calcd. for $C_{45}H_{46}Cl_3P_1Ru_2$: C, 58.35; H, 5.01 %. Found: C, 5.29; H, 5.09

<u>NMR data for **6**:</u>

^{1}H NMR (400 MHz, Toluene-d$_8$, 298 K) δ 7.75 – 7.73 (18 H, aromatic protons, [(*p*-cym)(Cl)Ru(μ^2-P=C(**biph**)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 4.61 (d, 2H, J_{H-H} = 6.0 Hz, [(***p*-cym**)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 4.41 (dd, 2H, J_{H-H} = 5.6 Hz, J_{P-H} = 0.8 Hz, [(***p*-cym**)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 4.28 (dd, 2H, J_{H-H} = 5.8 Hz, J_{P-H} = 1.1 Hz, [(***p*-cym**)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)], 3.79 (d, 2H, J_{H-H} = 5.8 Hz, [(***p*-cym**)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 3.02 (sept, 2 H, J_{H-H} = 6.8 Hz, [(***p*-cym**)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 2.09 (s, 6H, [(***p*-cym**)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 1.1 (d, 6H, J_{H-H} = 6.8 Hz, [(***p*-cym**)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 0.97 (d, 6H, J_{H-H} = 6.8 Hz, [(***p*-cym**)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]) ppm;

^{13}C{^{1}H} NMR (100.6 MHz, Toluene-d$_8$, 298 K) δ 146.46 (s, [(*p*-cym)(Cl)Ru(μ^2-P=C(**biph**)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 144.73 (s, [(*p*-cym)(Cl)Ru(μ^2-P=C(**biph**)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 140.59 (s, [(*p*-cym)(Cl)Ru(μ^2-P=C(**biph**)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 140.08 (s, [(*p*-cym)(Cl)Ru(μ^2-P=C(**biph**)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 139.43 (s, [(*p*-cym)(Cl)Ru(μ^2-P=C(**biph**)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 136.84 (d, J_{P-C} = 5.9 Hz, [(*p*-cym)(Cl)Ru(μ^2-P=C(**biph**)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 136.78 (d, J_{P-C} = 4.8 Hz, [(*p*-cym)(Cl)Ru(μ^2-P=C(**biph**)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 130.51 (s, [(*p*-cym)(Cl)Ru(μ^2-P=C(**biph**)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)]) 127.16 (s, [(*p*-cym)(Cl)Ru(μ^2-P=C(**biph**)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 126.74 (s, [(*p*-cym)(Cl)Ru(μ^2-P=C(**biph**)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 126.64 (s, [(*p*-cym)(Cl)Ru(μ^2-P=C(**biph**)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 126.23 (s, [(*p*-cym)(Cl)Ru(μ^2-P=C(**biph**)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)]), 102.11 (s, [(***p*-cym**)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 87.02 (d, J_{P-C} = 3.6 Hz, [(***p*-cym**)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 84.50 (broad s, [(***p*-cym**)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 82.11 (s, [(***p*-cym**)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(***p*-**

cym)]), 80.95 (s, [(***p*-cym**)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 30.48 (s, [(***p*-cym**)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 23.57 (s, [(***p*-cym**)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]), 19.11 (s, [(***p*-cym**)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(***p*-cym**)]) ppm;

^{31}P{^{1}H} NMR (162 MHz, Toluene-d$_8$, 298 K) δ 330.3 (s, [(*p*-cym)(Cl)Ru(μ^2-**P**=CPh$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)]) ppm.

%. By analogy to the reaction of compound **3** with ruthenium(II) complex, compound **7** was isolated from the supernatant solution and identified by single crystal XRD and NMR spectroscopy. Yield of isolated crystals of 7 0.133 g (45%).

B. NMR spectra

^{1}H, ^{31}P and ^{13}C NMR spectra in solution were recorded on a Bruker AV400 MHz spectrometer. Chemical shifts were referenced to tetramethylsilane (for ^{1}H and ^{13}C or 85% H_3PO_4 (for ^{31}P), respectively, as external standards. Coupling constants are given as absolute numbers except for compounds 3a and 4a whose higher order ^{31}P NMR spectra were analyzed by spectral simulation. These simulations were carried out using the DAISY module incorporated in the Bruker TopSpin software with the assumption that $^{1}J_{PP}$ coupling constants have negative signs.

B.1. Spectra of $(Et_2N)_2P$-$P(SiMe_3)Li\cdot1.5THF$

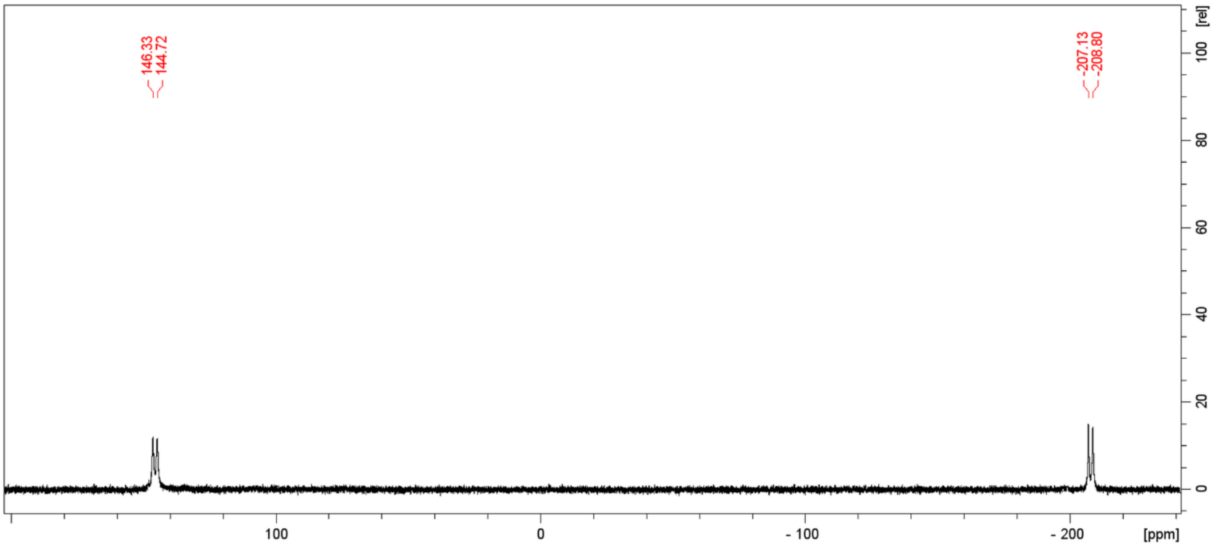

Figure S1. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K) spectrum of isolated $(Et_2N)_2P$-$P(SiMe_3)Li\cdot1.5THF$.

- 145.54 ppm, broad d, $J_{P\text{-}P}$ = 265.2 Hz, $(Et_2N)_2$**P**-$P(SiMe_3)Li$;
- -207.95 ppm, broad d, $J_{P\text{-}P}$ = 265.2 Hz, $(Et_2N)_2P$-**P**$(SiMe_3)Li$;

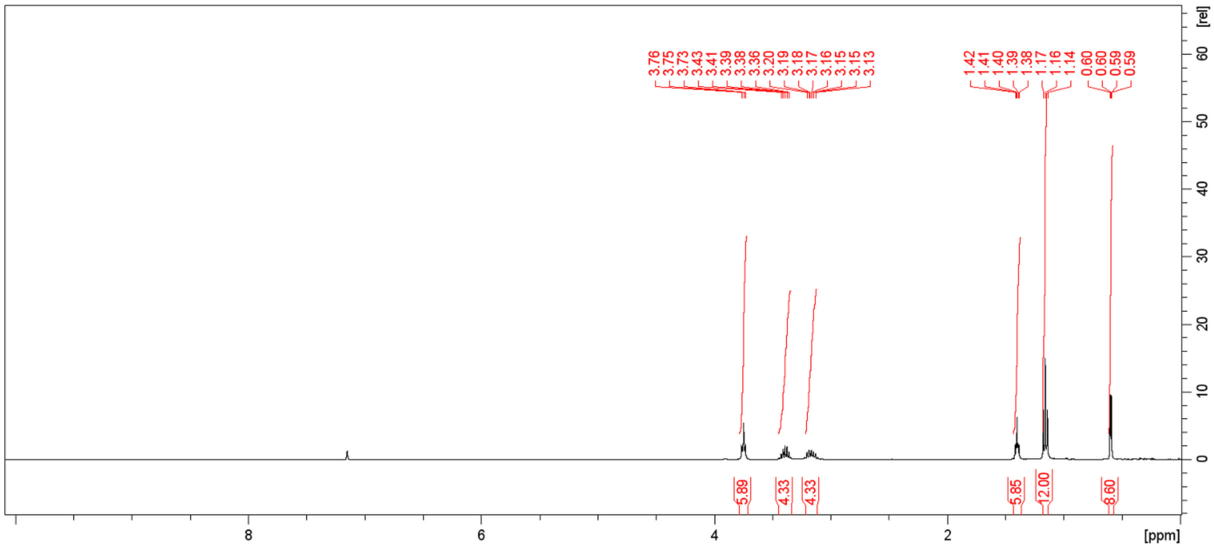

Figure S2. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectra of isolated lithium salt of diphosphane $(Et_2N)_2P$-$P(SiMe_3)Li$·1.5THF.

- 3.75 ppm, m, 4 H, $J_{H\text{-}H}$ = 3.42 Hz, THF;
- 3.39 ppm, m, 4 H, $J_{H\text{-}H}$ = 7.1 Hz, $\{(CH_3C\mathbf{H}_2)_2N\}_2P$-$P(SiMe_3)Li$·1.5THF;
- 3.17 ppm, broad m, 4 H, $J_{H\text{-}H}$ = 7.1 Hz, $\{(CH_3C\mathbf{H}_2)_2N\}_2P$-$P(SiMe_3)Li$·1.5THF;
- 1.40 ppm, quin, 4 H, $J_{H\text{-}H}$ = 3.42 Hz, THF;
- 1.16 ppm, t, 12 H, $J_{H\text{-}H}$ = 7.1 Hz, $\{(C\mathbf{H}_3CH_2)_2N\}_2P$-$P(SiMe_3)Li$·1.5THF;
- 0.59 ppm, dd, 9H, $J_{P\text{-}H}$ = 3.7 Hz, $J_{P\text{-}H}$ = 1.1 Hz, $\{(CH_3CH_2)_2N\}_2P$-$P(Si\mathbf{Me}_3)Li$·1.5THF;

B.2. Reaction of *t*Bu$_2$P-P(SiMe$_3$)Li·2.5THF with (biph)$_2$C=O

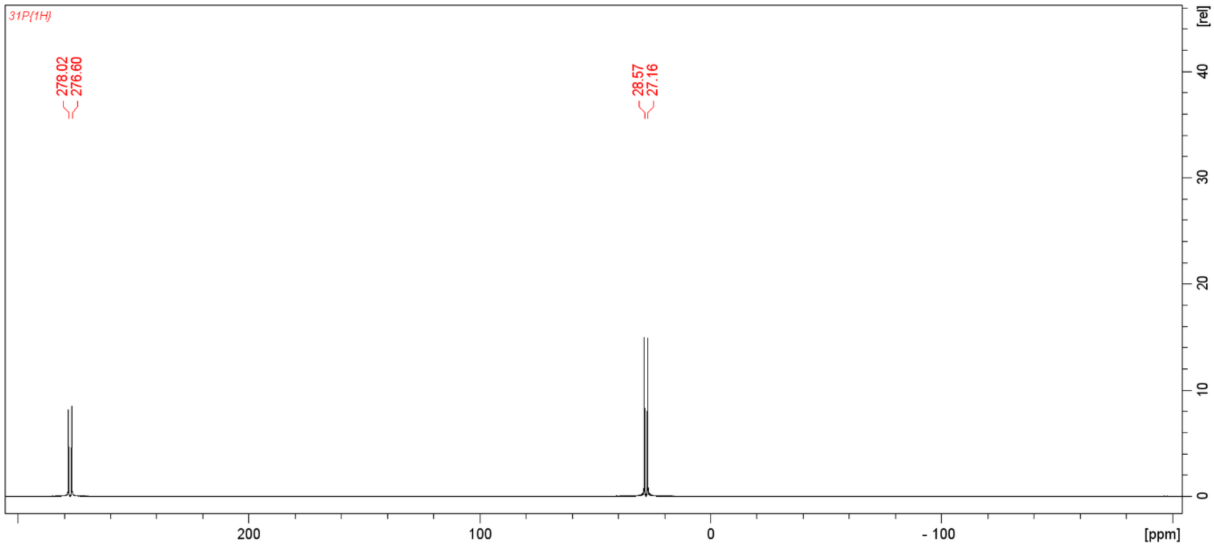

Figure S3. ^{31}P{^{1}H} NMR (162 MHz, Toluene-d$_8$, 298 K) spectrum of isolated (biph)$_2$C=P-P*t*Bu$_2$ (**2**).

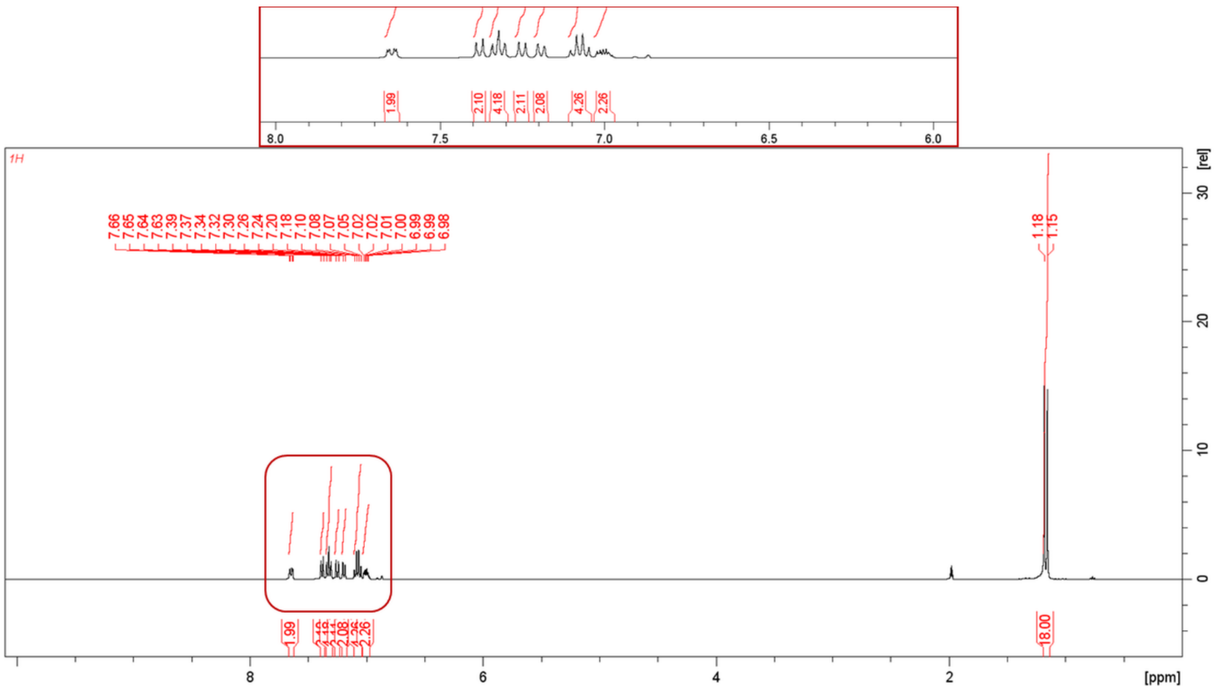

Figure S4. ^{1}H NMR (400 MHz, Toluene-d$_8$, 298 K) spectrum of isolated (biph)$_2$C=P-P*t*Bu$_2$ (**2**).

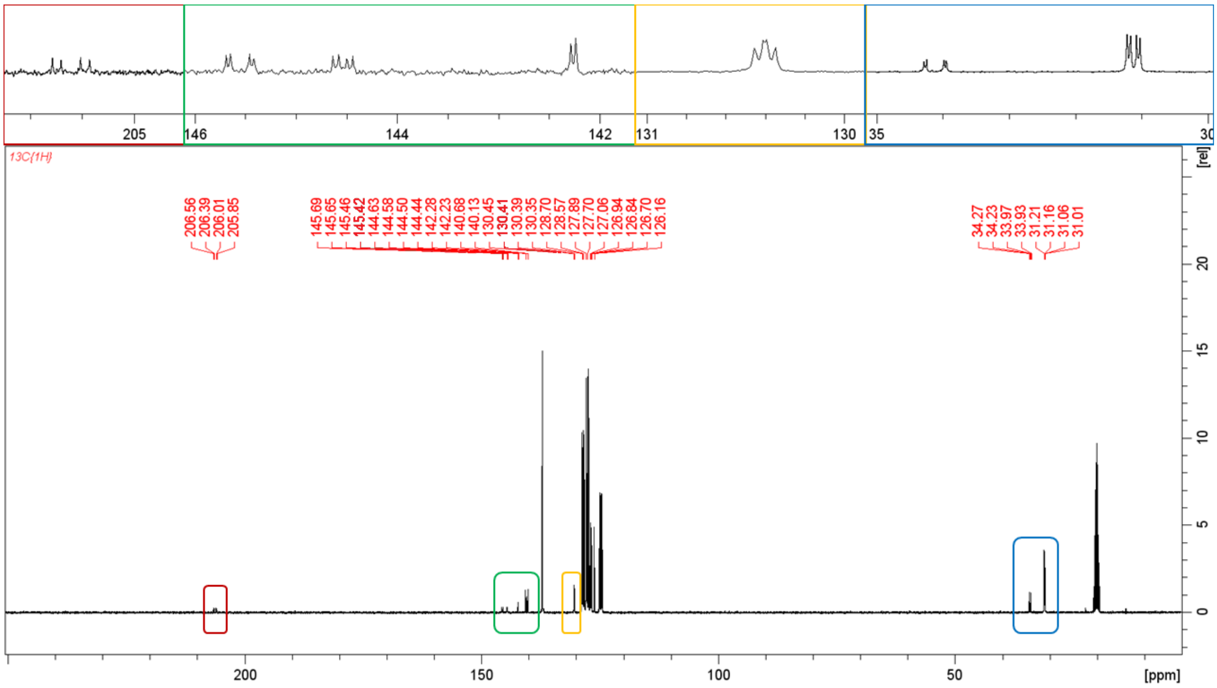

Figure S5. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, Toluene-d_8, 298 K) spectrum of isolated $(biph)_2C{=}P{-}P\mathit{t}Bu_2$ (**2**).

B.3. Reaction of $(Et_2N)_2P$-$P(SiMe_3)Li \cdot 1.5THF$ with selected ketones

B.3.1. with benzophenone.

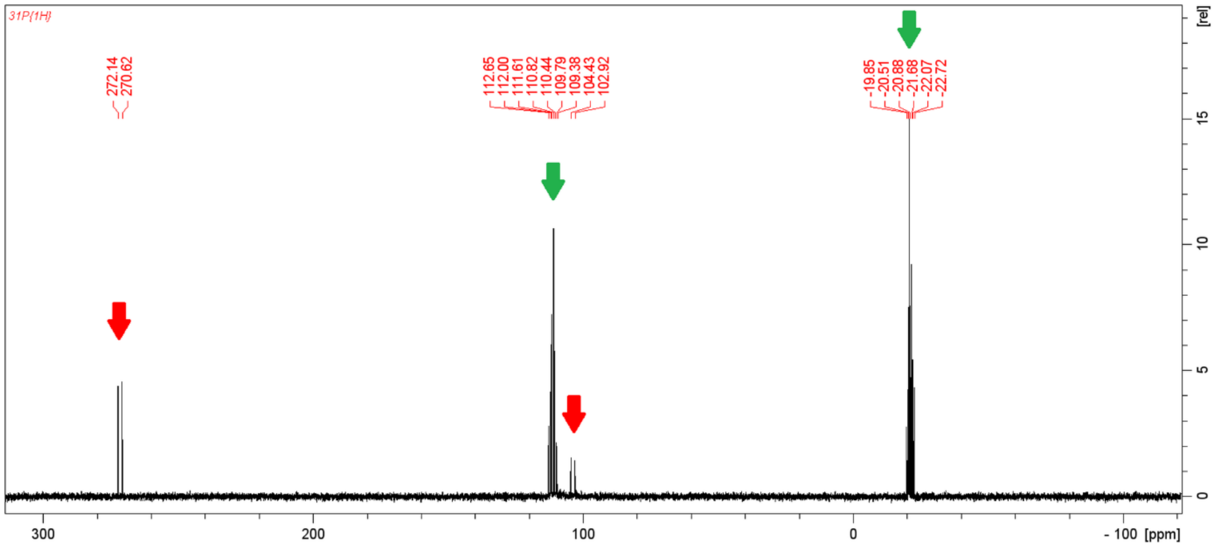

Figure S6. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K) spectrum of isolated **3a** measured directly after dissolution in C_6D_6 (red color – **3**, green color –**3a**)

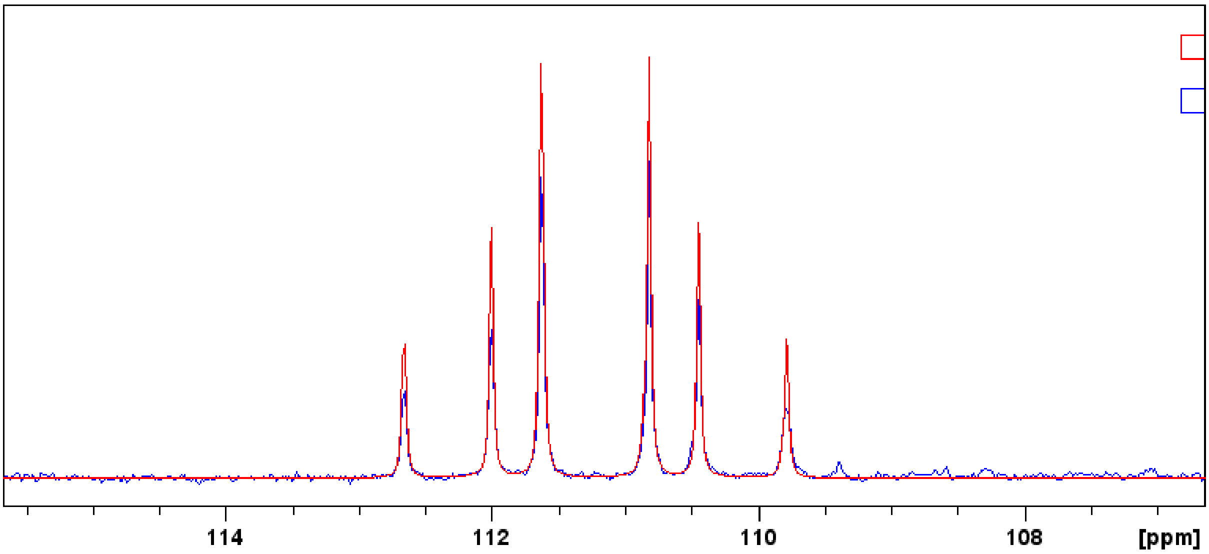

Figure S7. Expansion of the $^{31}P\{^1H\}$ NMR spectrum (162 MHz, C_6D_6, 298 K) of Figure S6 showing the signal at 111.2 ppm attributable to dimer **3a** (blue line) together with the result of a spectral simulation (red line).

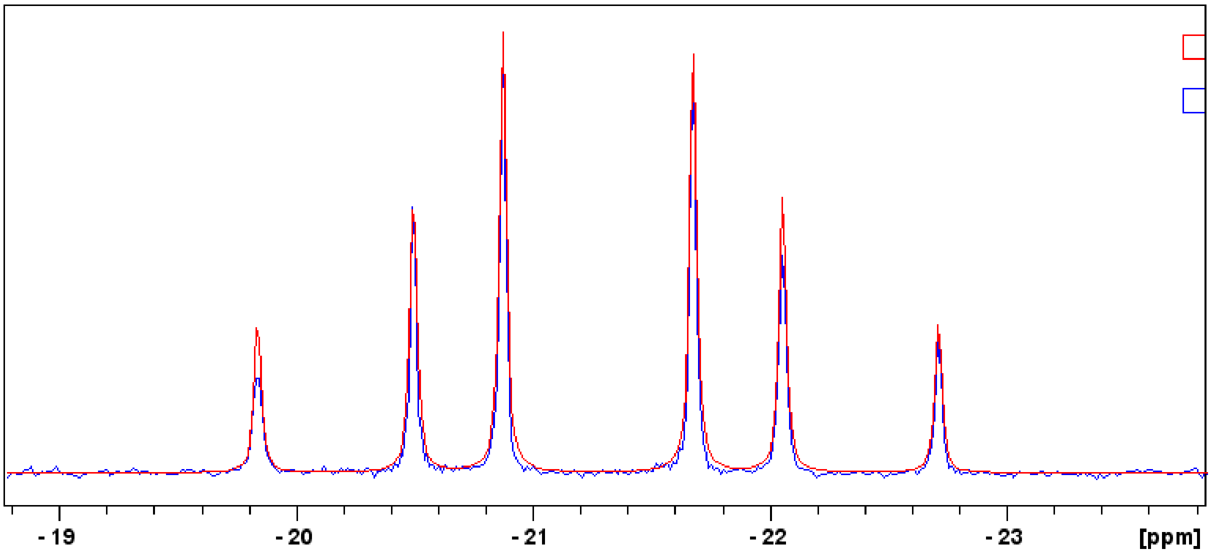

Figure S8. Expansion of the $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, C_6D_6, 298 K) of Figure S6 showing the signal at -21.3 ppm attributable to dimer **3a** (blue line) together with the result of a spectral simulation (red line).

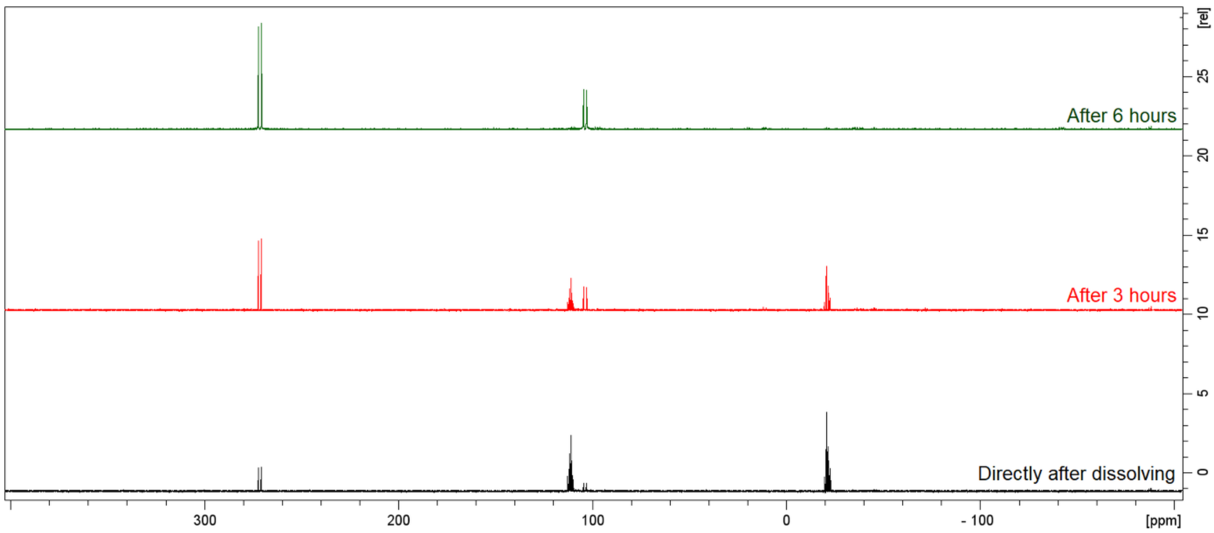

Figure S9. $^{31}P\{^{1}H\}$ NMR spectra (162 MHz, C_6D_6, 298 K) showing the transformation of dimer **3a** to phosphanylphosphaalkene **3** over time.

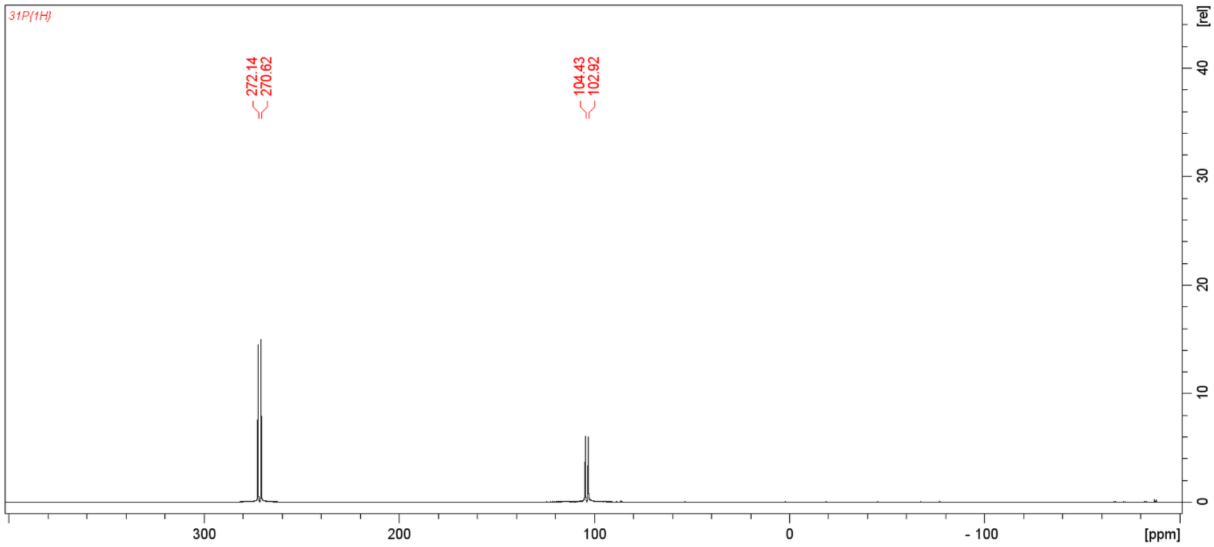

Figure S10. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K) spectrum of isolated $Ph_2C{=}P{-}P(NEt_2)_2$ (**3**).

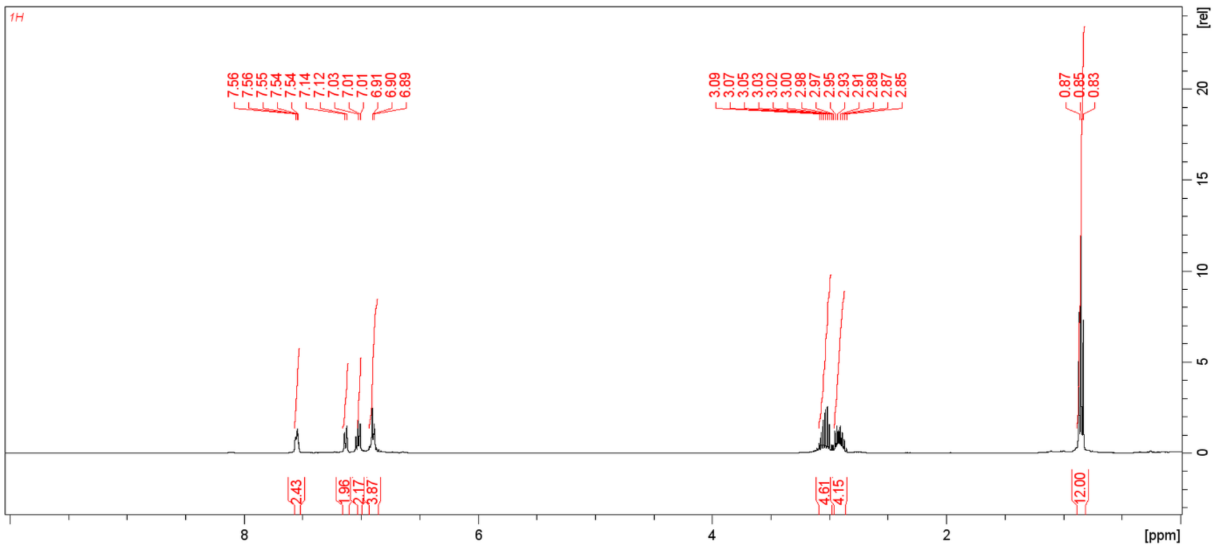

Figure S11. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated $Ph_2C{=}P{-}P(NEt_2)_2$ (**3**).

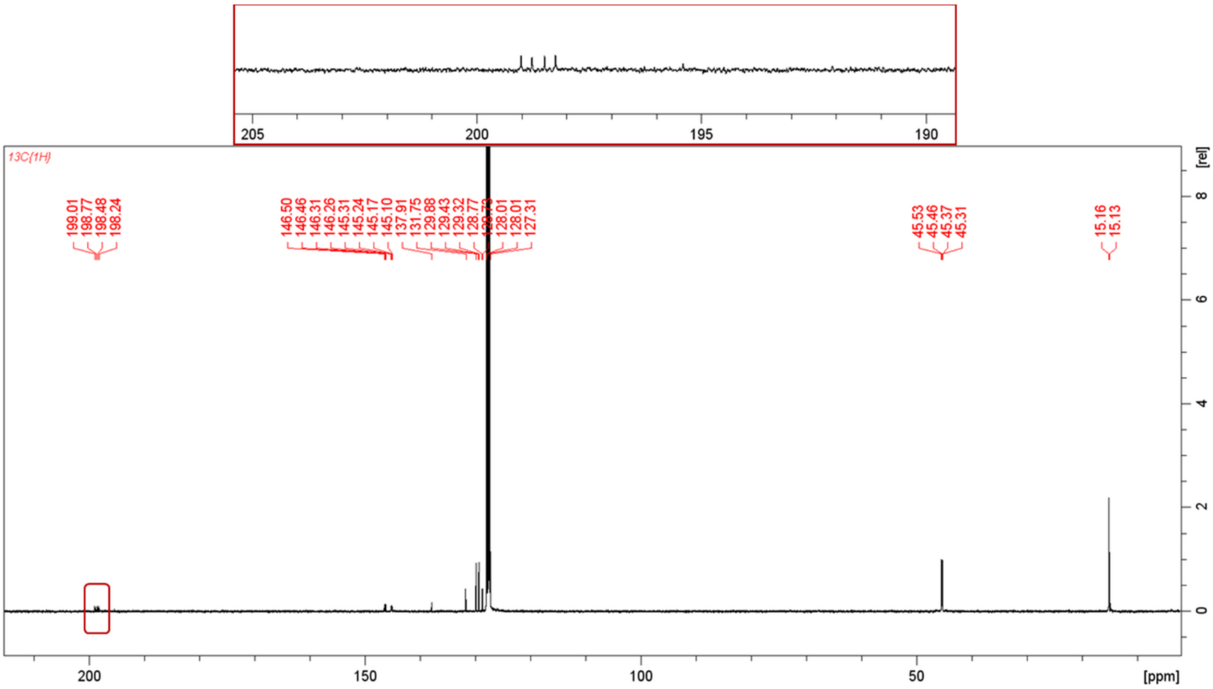

Figure S12. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, C_6D_6, 298 K) spectrum of isolated $Ph_2C{=}P{-}P(NEt_2)_2$ (**3**).

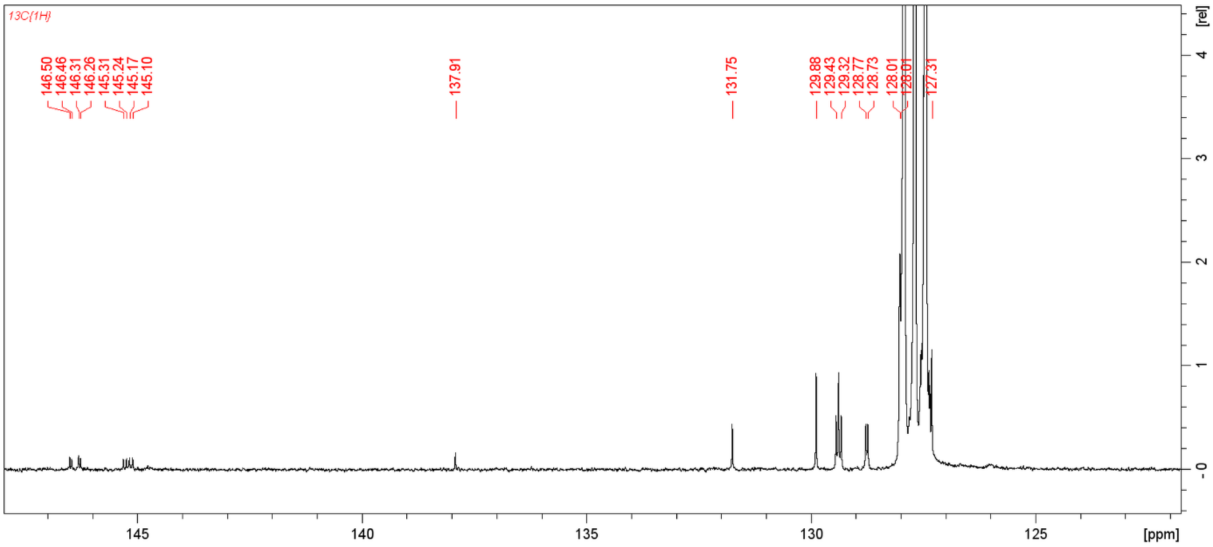

Figure S13. Expansion of the $^{13}C\{^{1}H\}$ NMR (100.6 MHz, C_6D_6, 298 K) spectrum of isolated $Ph_2C{=}P{-}P(NEt_2)_2$ (**3**) showing the range from 150 ppm to 120 ppm.

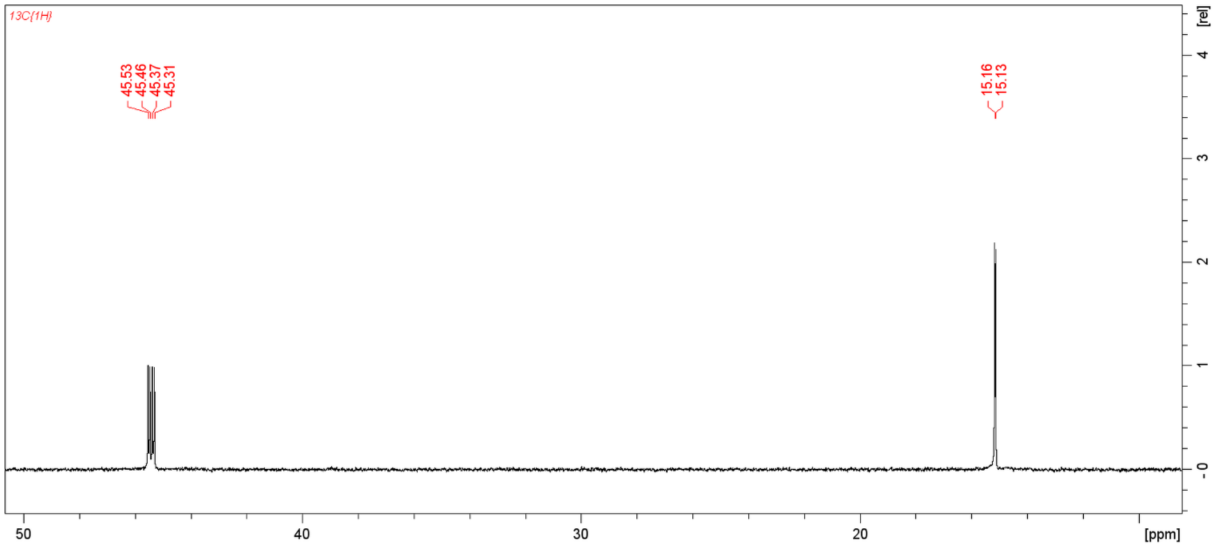

Figure S14. Expansion of the $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K) spectrum of isolated $Ph_2C{=}P$-$P(NEt_2)_2$ (**3**) showing the range from 50 ppm to 10 ppm.

B.3.2. with 4,4'-diphenylbenzophenone

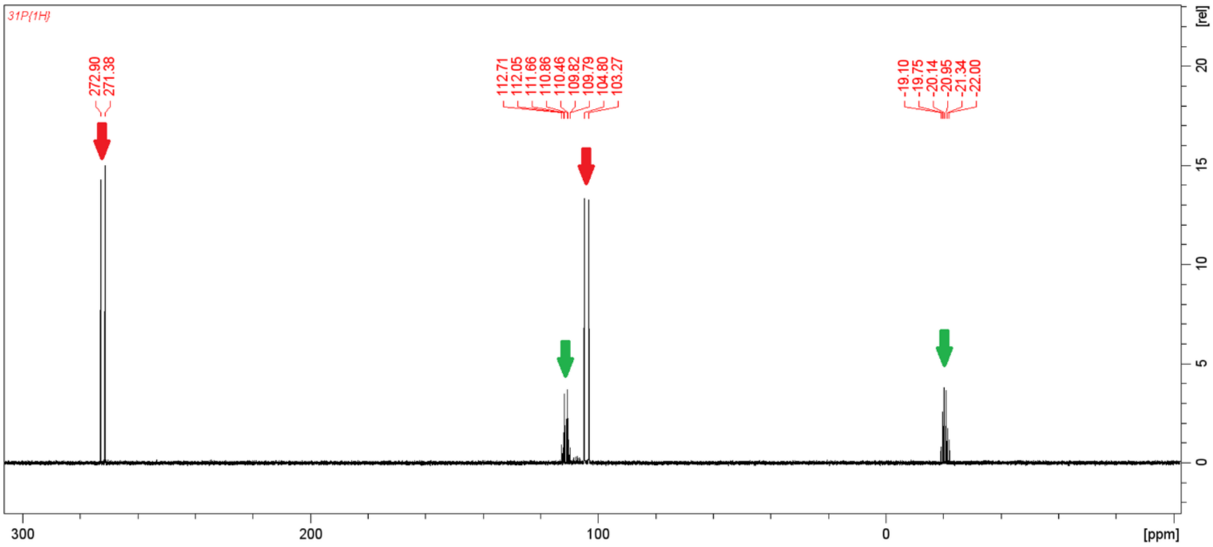

Figure S15. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, Toluene-d_8, 298 K) of isolated (**4a**) measured directly after dissolution in C_6D_6 (red color – **4**, green color – dimer **4a**).

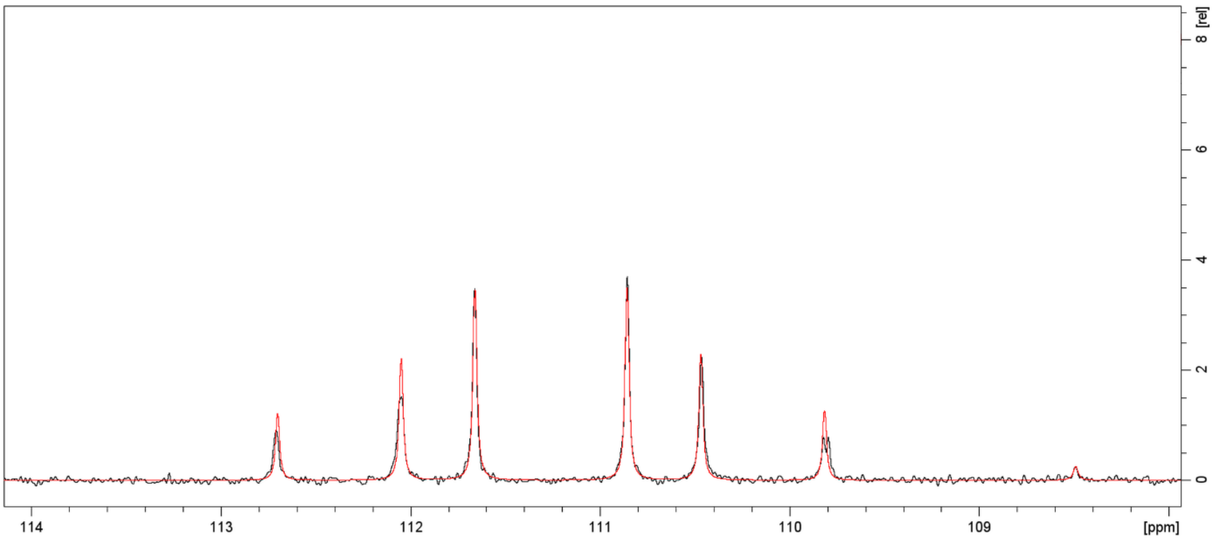

Figure S16. Expansion of the $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, C_6D_6, 298 K) of Figure S15 showing the signal at 111.3 ppm attributable to dimer **4a** (black line) together with the result of a spectral simulation (red line).

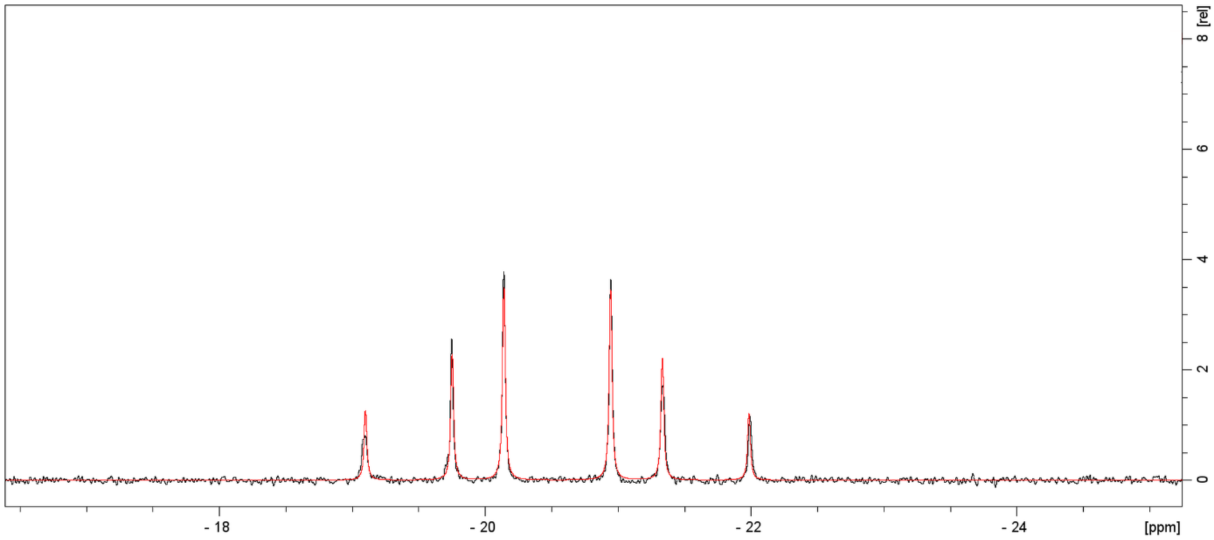

Figure S17. Expansion of the $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, C_6D_6, 298 K) of Figure S15 showing the signal at -20.5 ppm attributable to dimer **4a** (black line) together with the result of a spectral simulation (red line).

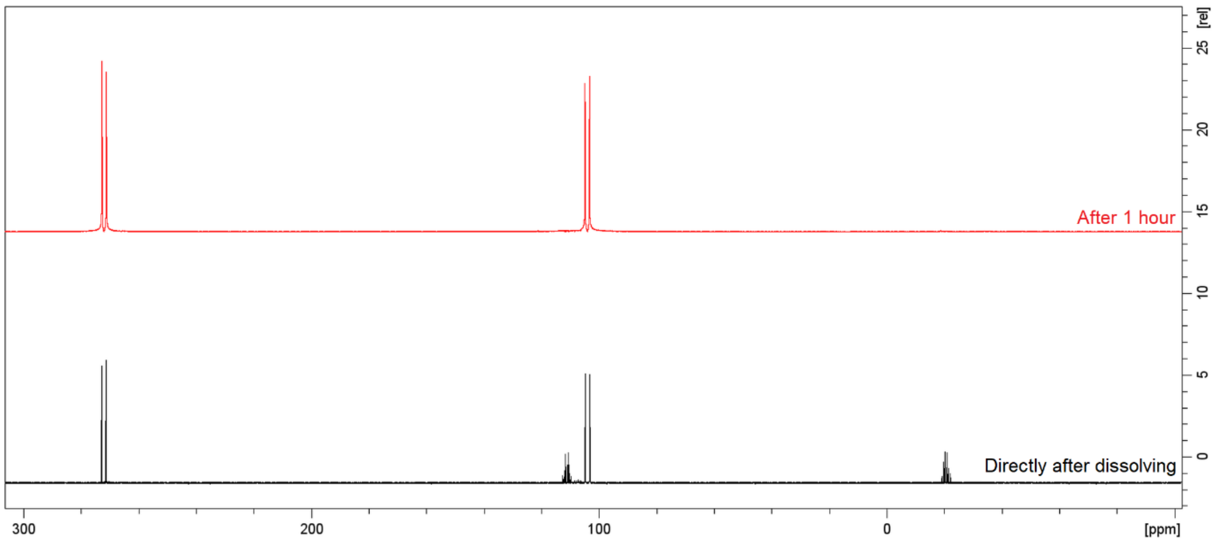

Figure S18. $^{31}P\{^{1}H\}$ NMR spectra (162 MHz, C_6D_6, 298 K) showing the transformation of dimer **4a** to phosphanylphosphaalkene **4** over time.

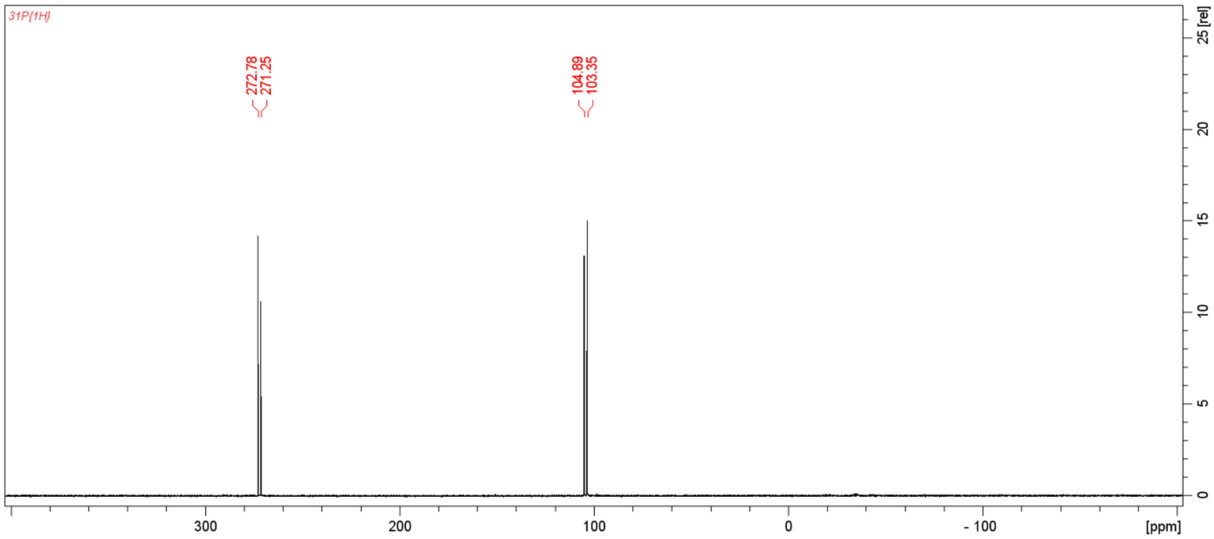

Figure S19. $^{31}P\{^1H\}$ NMR (162 MHz, Toluene-d$_8$, 298 K) spectrum of $(biph)_2C{=}P{-}P(NEt_2)_2$ (**4**).

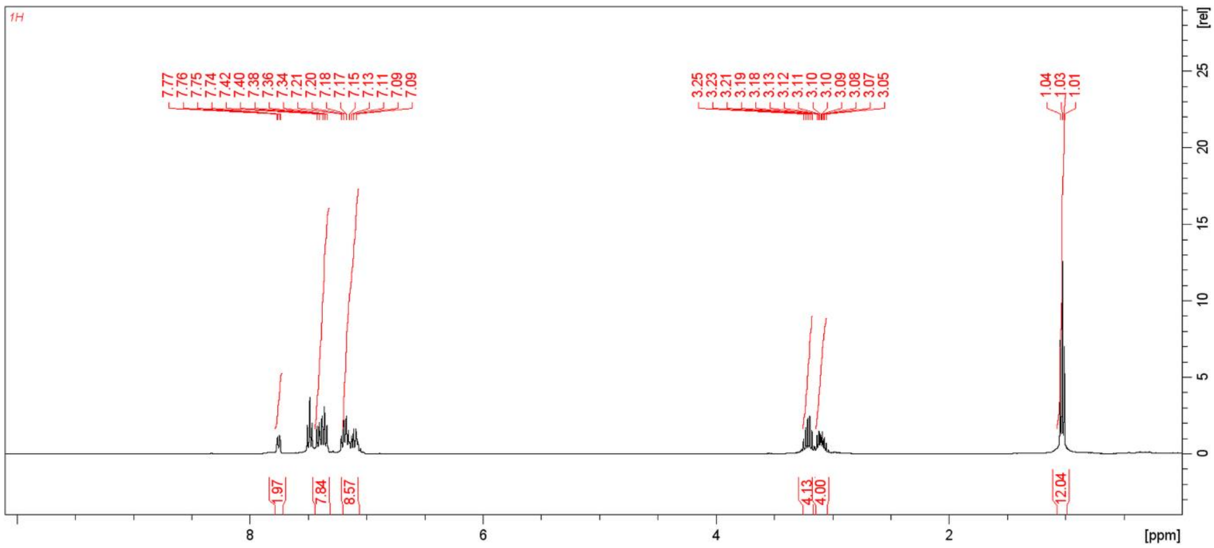

Figure S20. ^1H NMR (400 MHz, Toluene-d$_8$, 298 K) spectrum of $(biph)_2C{=}P{-}P(NEt_2)_2$ (**4**).

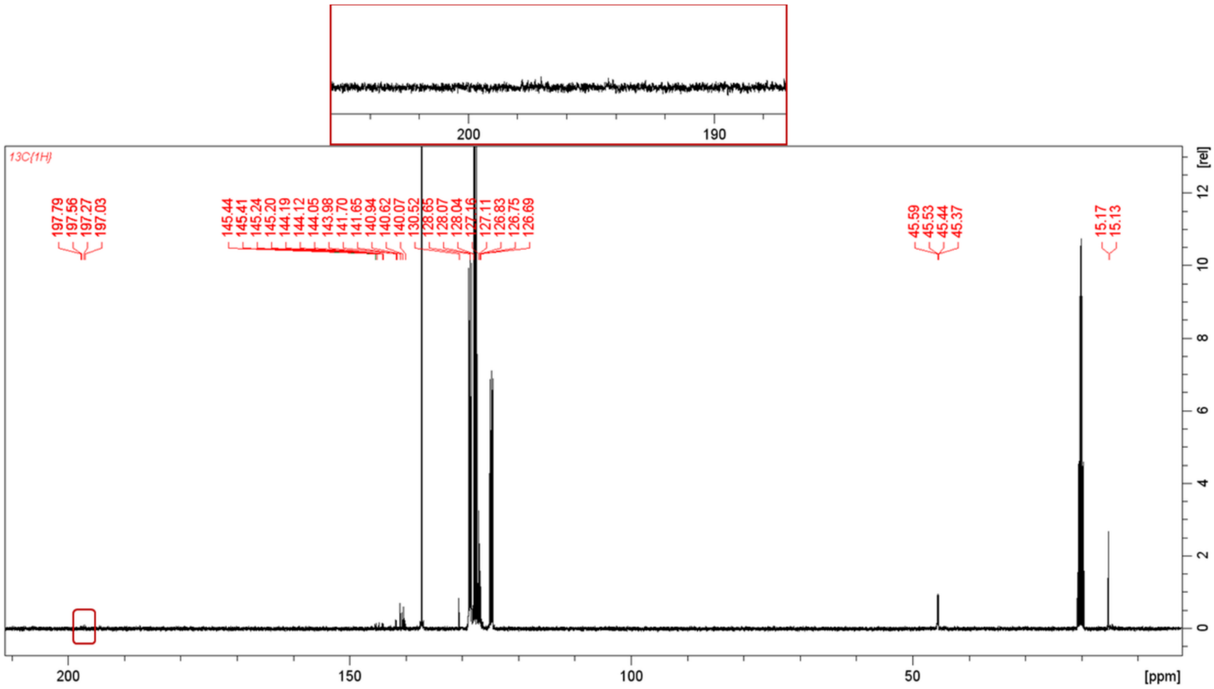

Figure S21. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, Toluene-d$_8$, 298 K) spectrum of (biph)$_2$C=P-P(NEt$_2$)$_2$ (**4**).

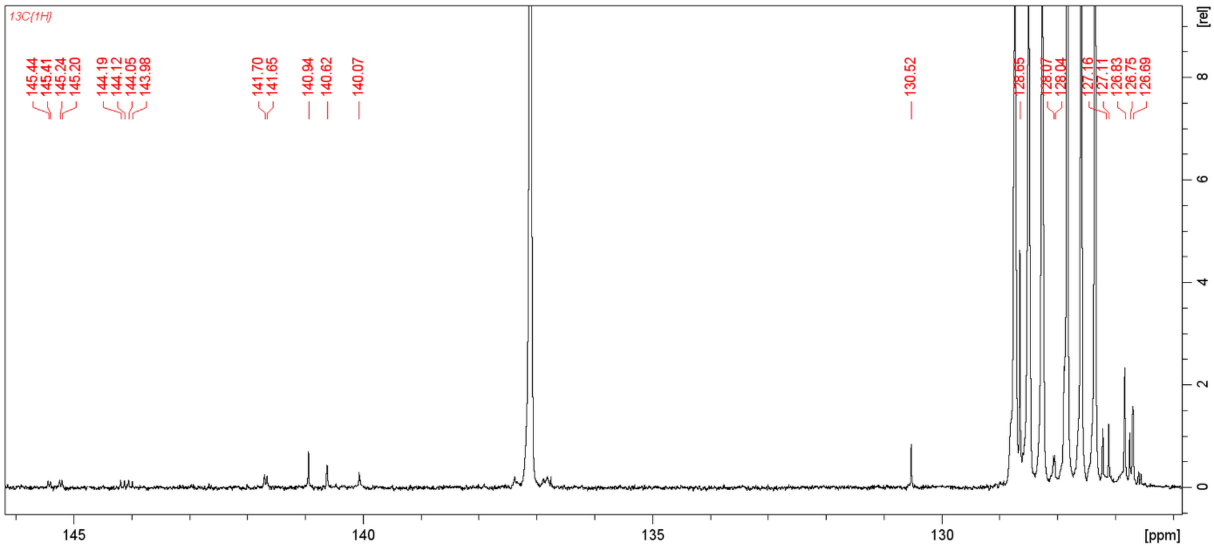

Figure S22. Expansion of the $^{13}C\{^{1}H\}$ NMR (100.6 MHz, Toluene-d$_8$, 298 K) spectrum of (biph)$_2$C=P-P(NEt$_2$)$_2$ (**4**) showing the range from 150 ppm to 120 ppm.

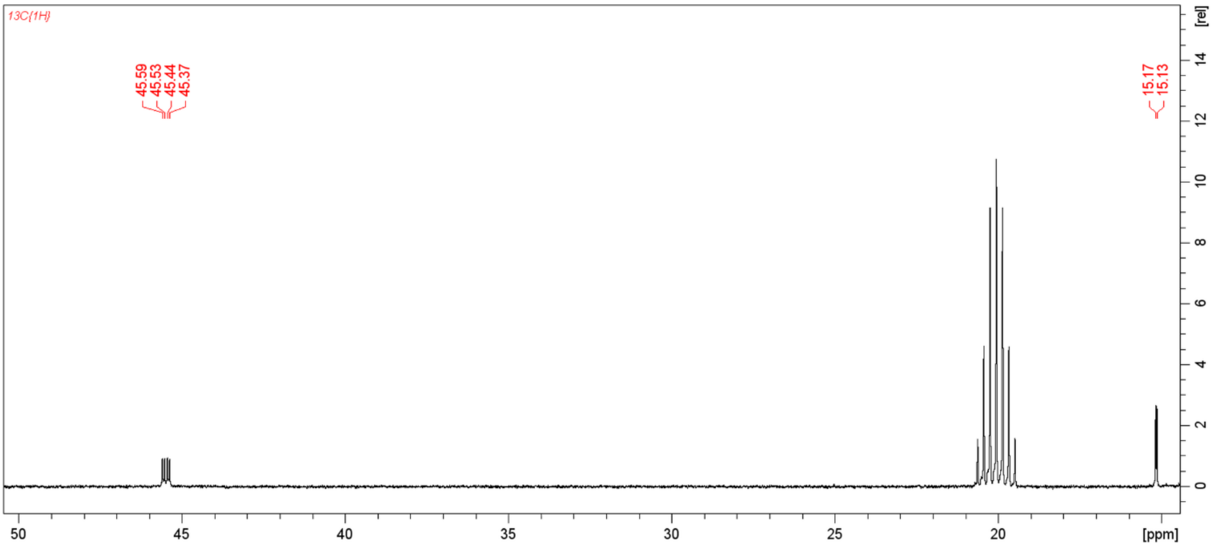

Figure S23. Expansion of the $^{13}C\{^{1}H\}$ NMR (100.6 MHz, Toluene-d_8, 298 K) spectrum of $(biph)_2C{=}P{-}P(NEt_2)_2$ (**4**) showing the range from 50 ppm to 10 ppm.

B.4. Reactions of $[(p\text{-cym})RuCl_2]_2$ with phosphanylphosphaalkenes

*B.4.1. with $Ph_2C{=}P\text{-}P(NEt_2)_2$ (**3**)*

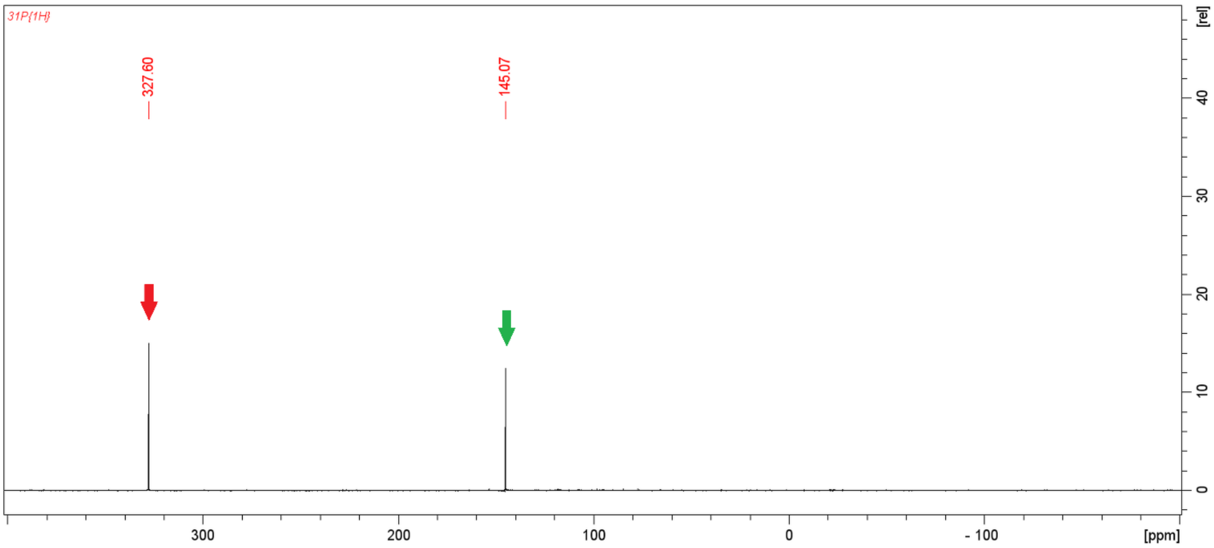

Figure S24. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, THF-d_8, 298 K) of the reaction mixture of **3** with $[(p\text{-cym})RuCl_2]_2$; **5** (red arrow), **7** (green arrow).

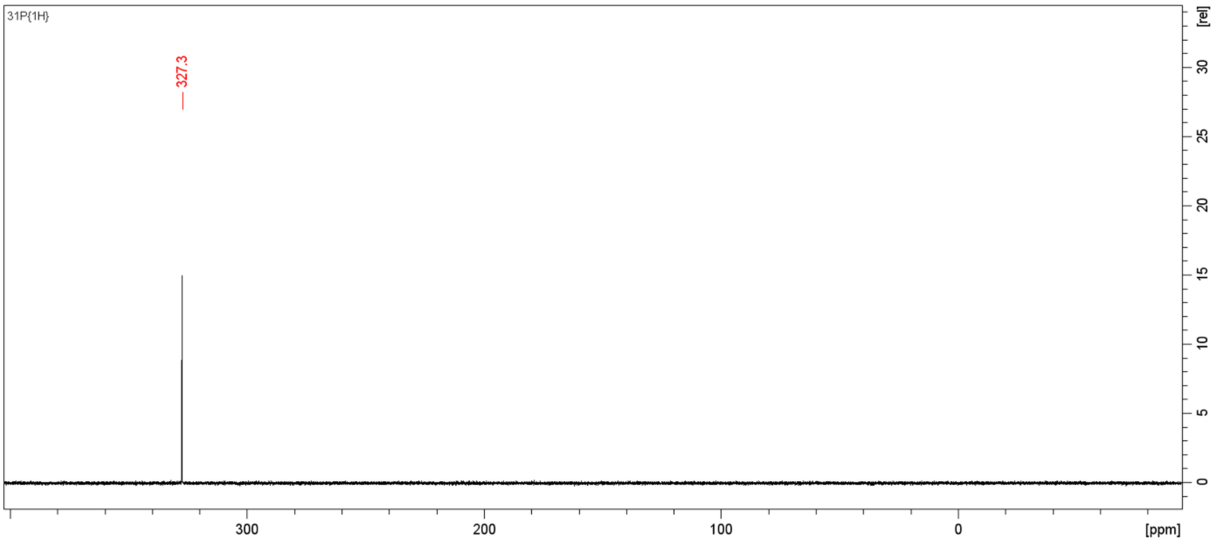

Figure S25. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, Toluene-d_8, 298 K) of isolated $[(p\text{-cym})(Cl)Ru(\mu^2\text{-}P{=}CPh_2)(\mu^2\text{-}Cl)Ru(Cl)(p\text{-cym})]$ (**5**).

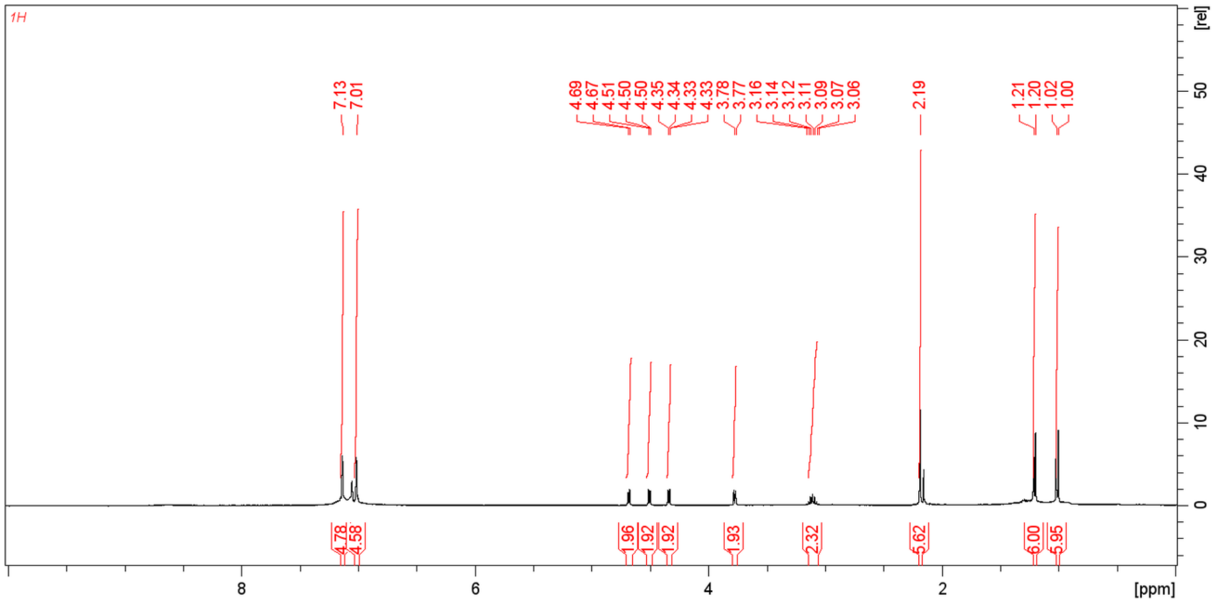

Figure S26. ^{1}H NMR spectrum (400 MHz, Toluene-d$_8$, 298 K) of isolated [(*p*-cym)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)] (**5**).

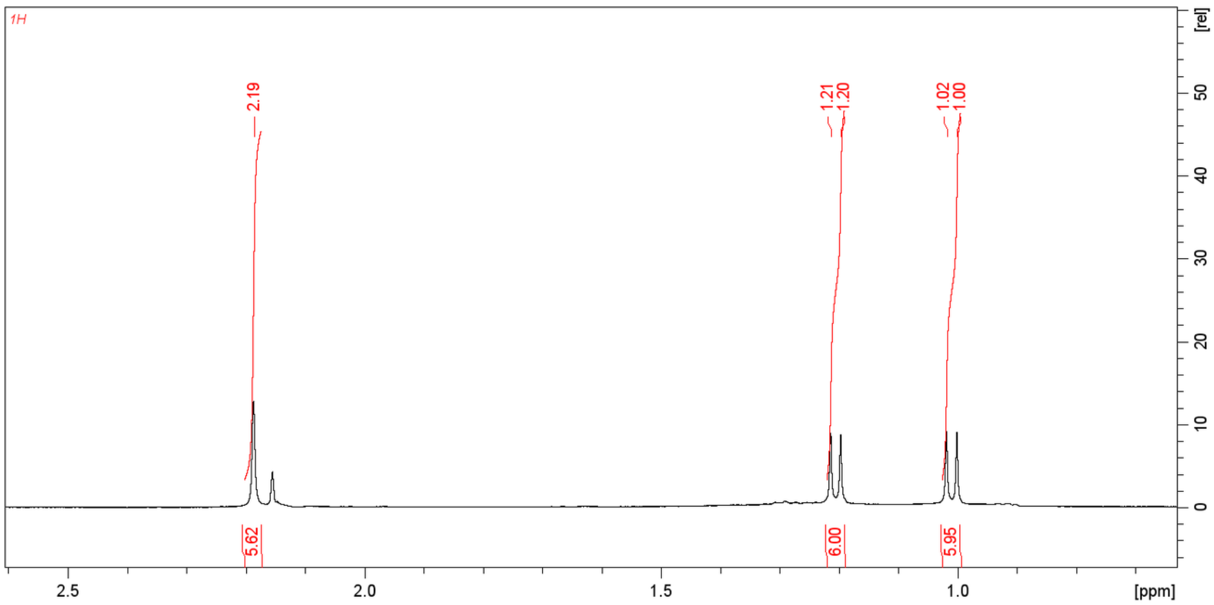

Figure S27. Expansion of the ^{1}H NMR spectrum (400 MHz, Toluene-d$_8$, 298 K) of isolated [(*p*-cym)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)] (**5**) showing the range from 2.5 ppm to 0.5 ppm.

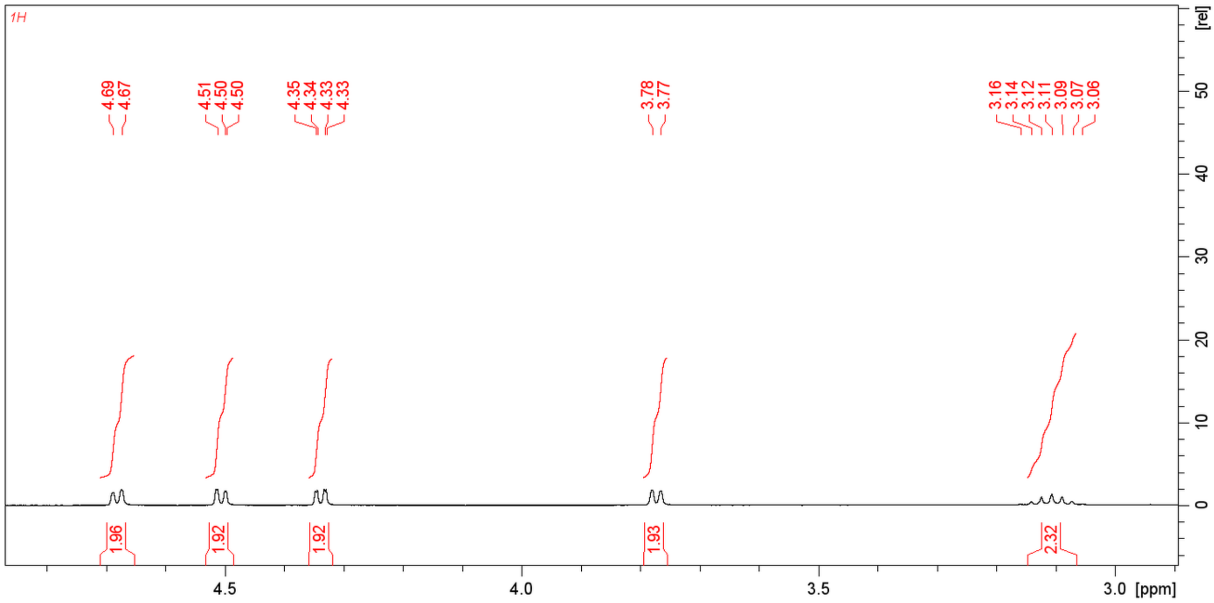

Figure S28. ^{1}H NMR spectrum (400 MHz, Toluene-d$_8$, 298 K) of isolated [(*p*-cym)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)] (**5**) in the range from 5.0 ppm to 3.0 ppm.

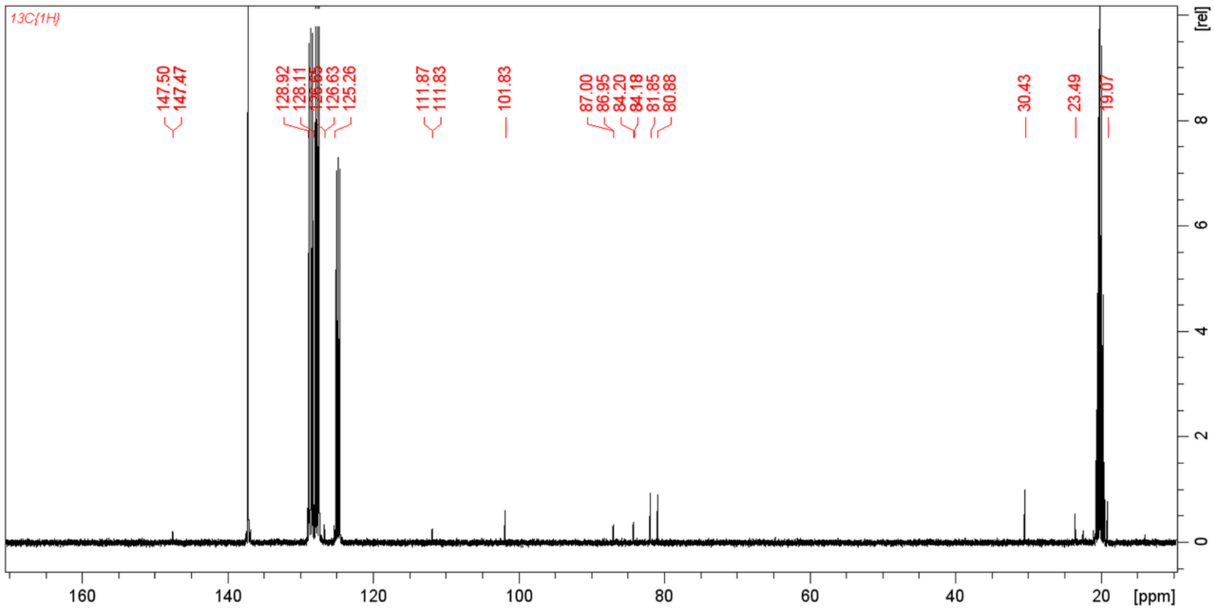

Figure S29. ^{13}C{^{1}H} NMR spectrum (100.6 MHz, Toluene-d$_8$, 298 K) of isolated [(*p*-cym)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)] (**5**).

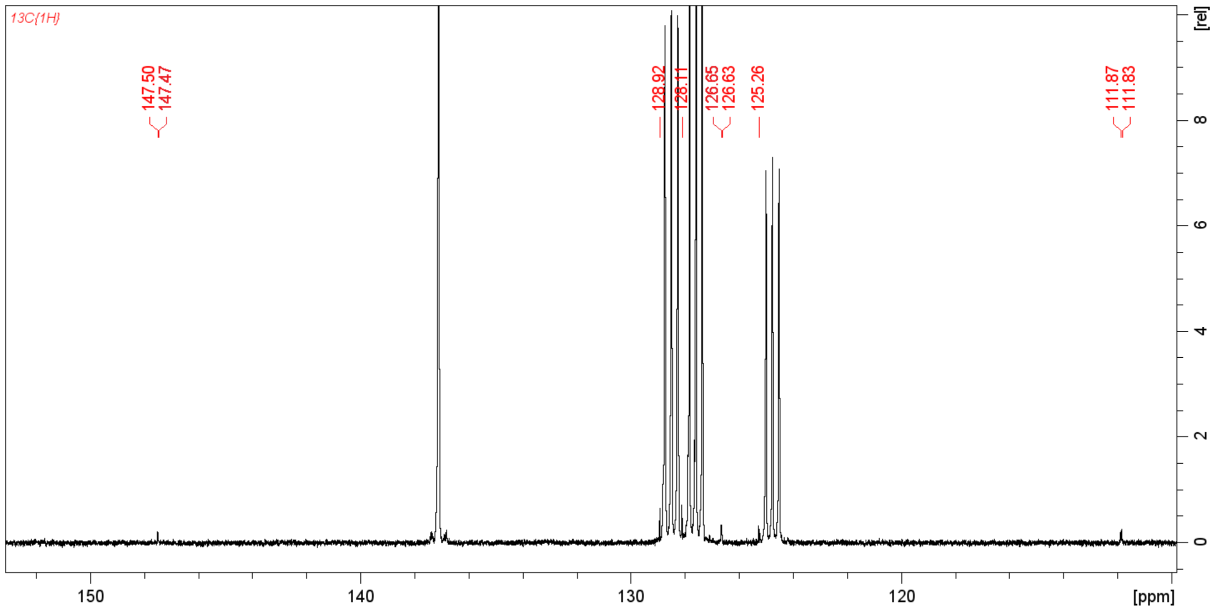

Figure S30. Expansion of the $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, Toluene-d_8, 298 K) of isolated [(*p*-cym)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)] (**5**) showing the range from 150 ppm to 100 ppm.

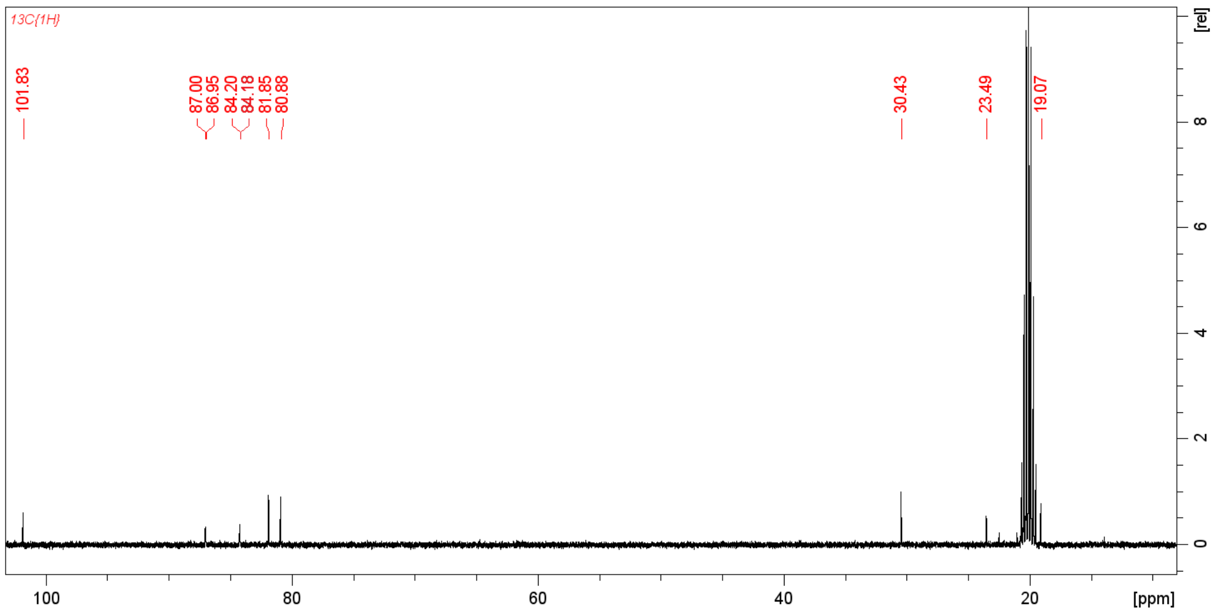

Figure S31. Expansion of the $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, Toluene-d_8, 298 K) of isolated [(*p*-cym)(Cl)Ru(μ^2-P=CPh$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)] (**5**) showing the range from 100 ppm to 0 ppm.

*B.4.2. with $(biph)_2C{=}P{-}P(NEt_2)_2$ (**4**)*

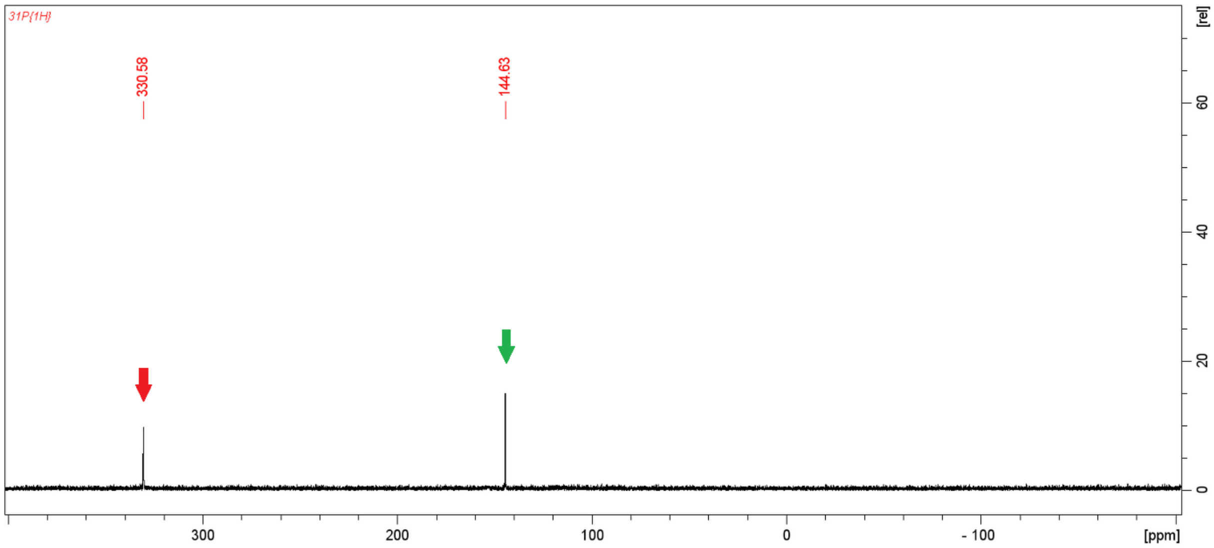

Figure S32. $^{31}P\{1H\}$ NMR spectrum (162 MHz, C_6D_6, 298 K) of reaction mixture of **4** with [(*p*-cym)$RuCl_2]_2$; **6** (red arrow), **7** (green arrow).

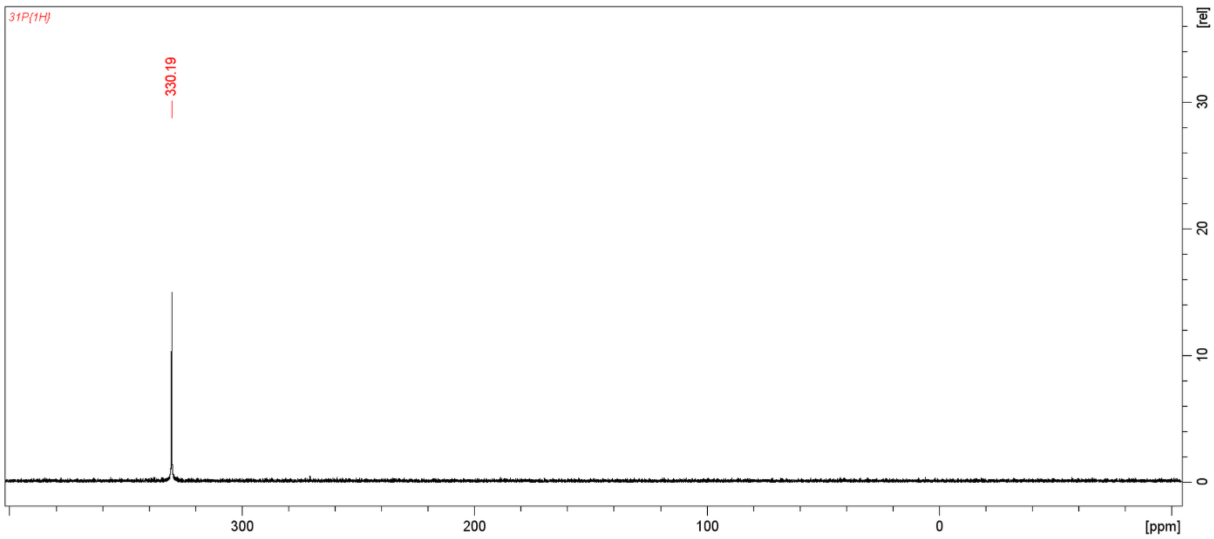

Figure S33. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, Toluene-d_8, 298 K) of isolated [(*p*-cym)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)] (**6**).

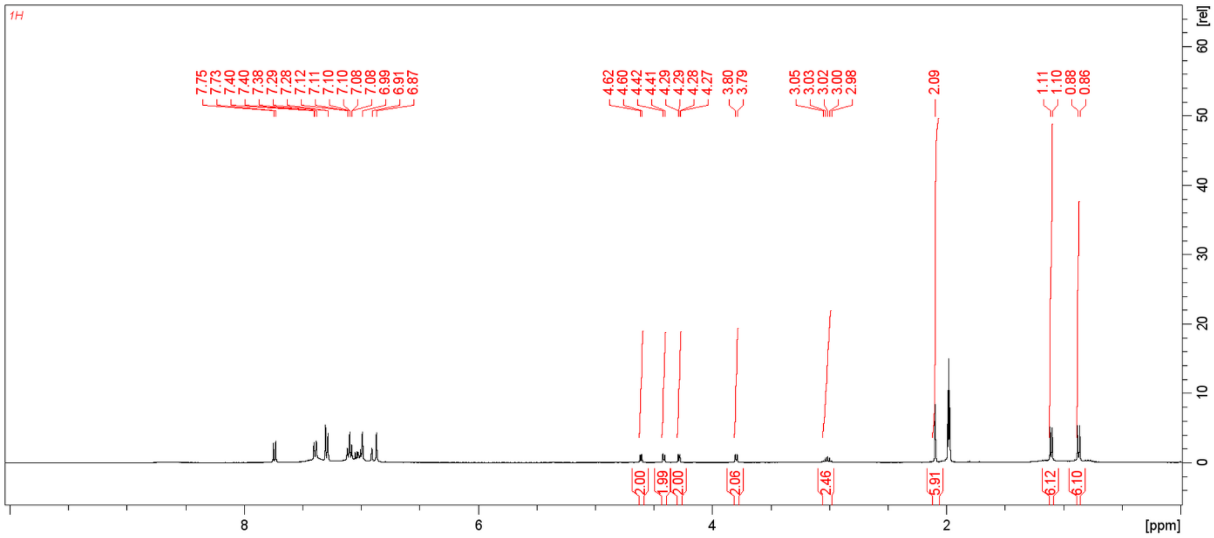

Figure S34. ^{1}H NMR spectrum (400 MHz, Toluene-d_8, 298 K) of isolated [(*p*-cym)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)] (**6**).

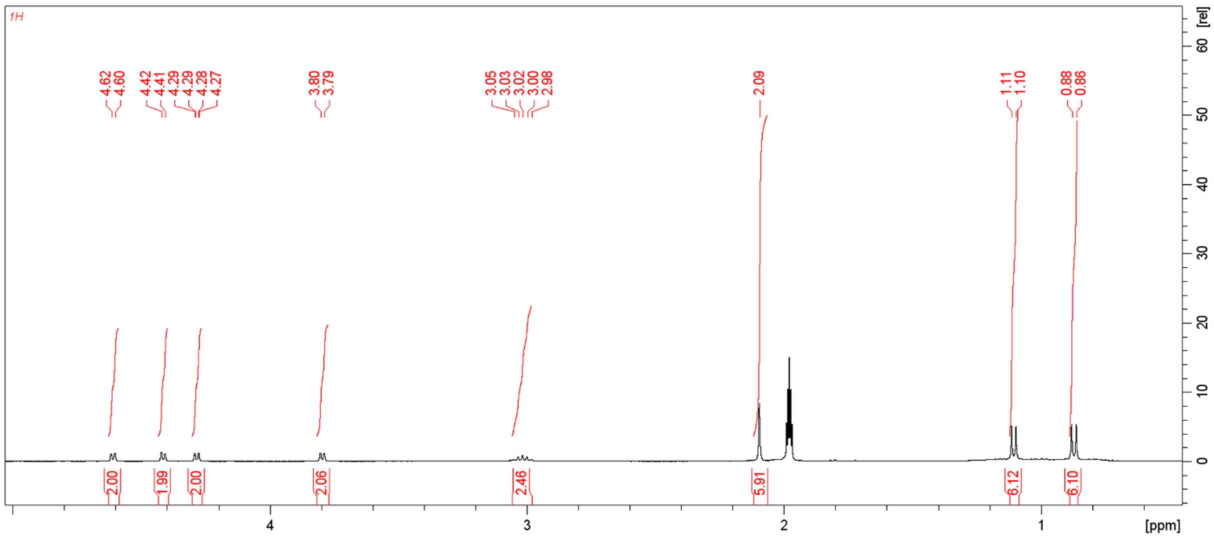

Figure S35. Expansion of the ^{1}H NMR spectrum (400 MHz, Toluene-d_8, 298 K) of isolated [(*p*-cym)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)] (**6**) showing the range from 5.0 ppm to 0.5 ppm.

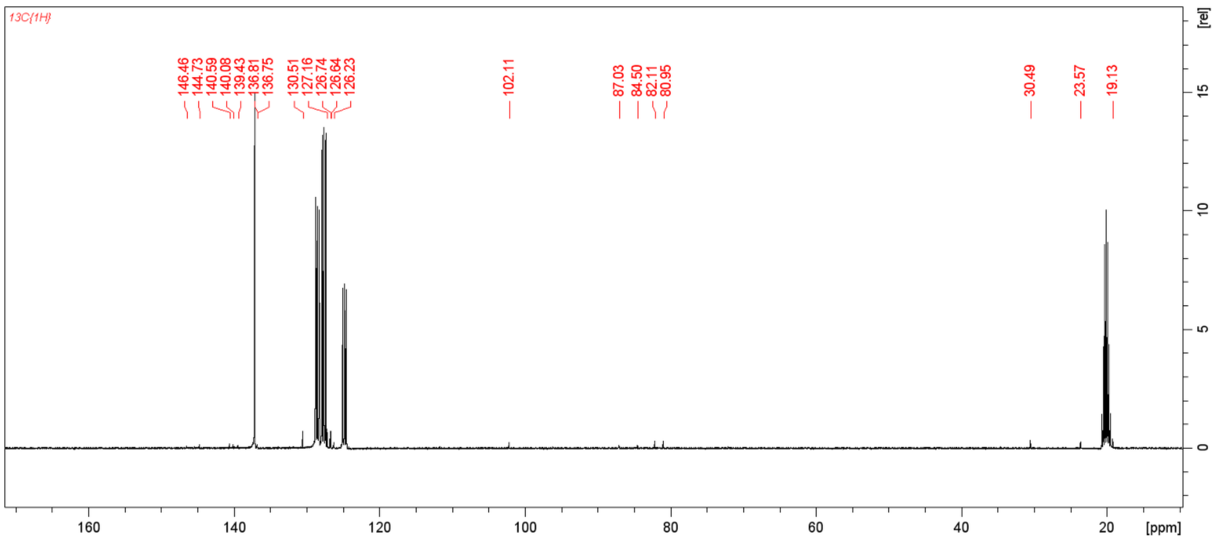

Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, Toluene-d$_8$, 298 K) of isolated [(*p*-cym)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)] (**6**).

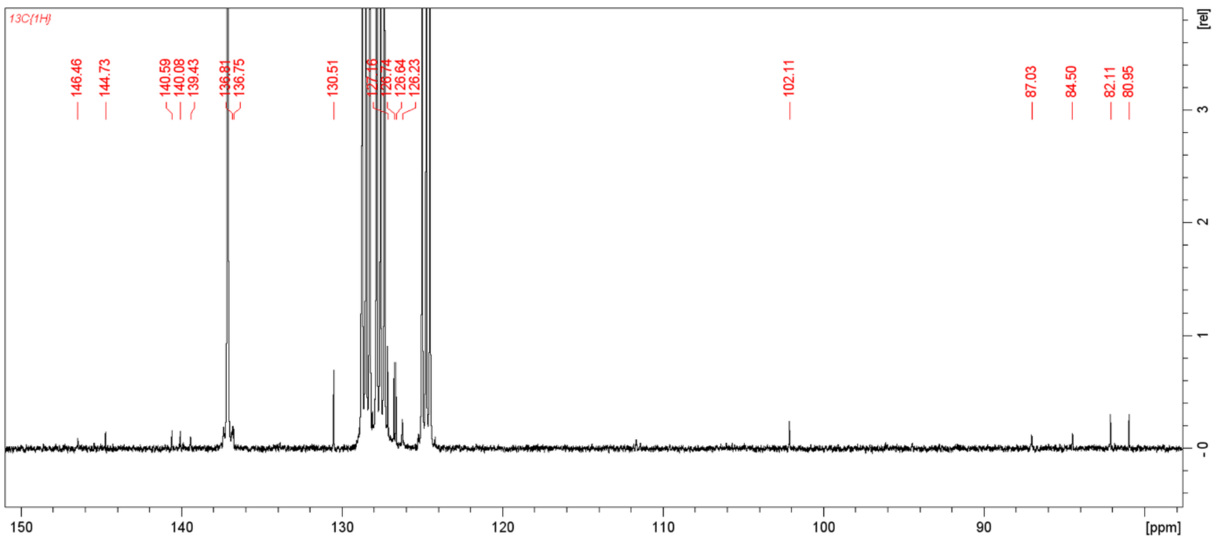

Figure S37. Expansion of the $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, Toluene-d$_8$, 298 K) of isolated [(*p*-cym)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)] (**6**) showing the range from 150 ppm to 80 ppm.

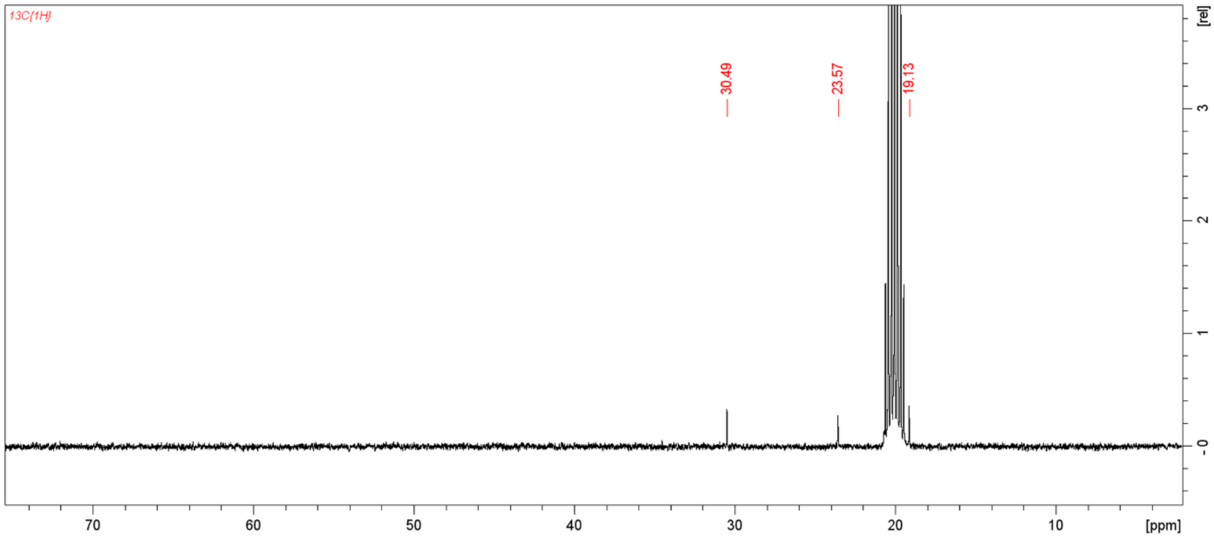

Figure S38. Expansion of the $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, Toluene-d$_8$, 298 K) of isolated [(*p*-cym)(Cl)Ru(μ^2-P=C(biph)$_2$)(μ^2-Cl)Ru(Cl)(*p*-cym)] (**6**) showing the range from 70 ppm to 0 ppm.

*B.4.3. [(p-cym)RuCl$_2$(η^1-P(Cl)(NEt$_2$)$_2$)] (**7**)*

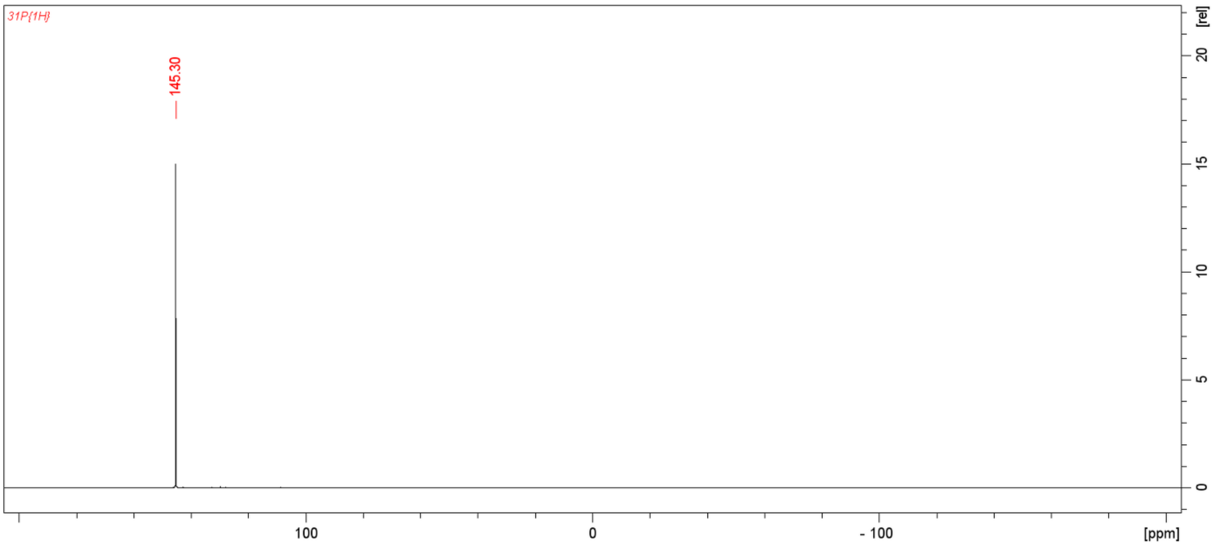

Figure S39. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, THF-d$_8$, 298 K) of isolated [(*p*-cym)RuCl$_2$(η^1-P(Cl)(NEt$_2$)$_2$)] (**7**).

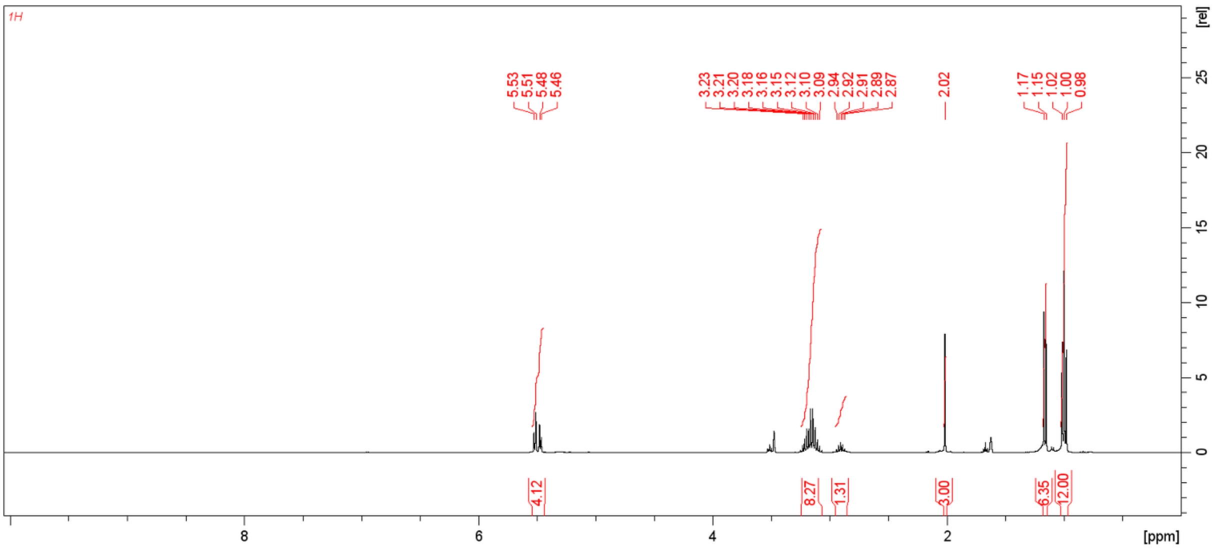

Figure S40. ^1H NMR spectrum (400 MHz, THF-d$_8$, 298 K) of isolated [(*p*-cym)RuCl$_2$(η^1-P(Cl)(NEt$_2$)$_2$)] (**7**).

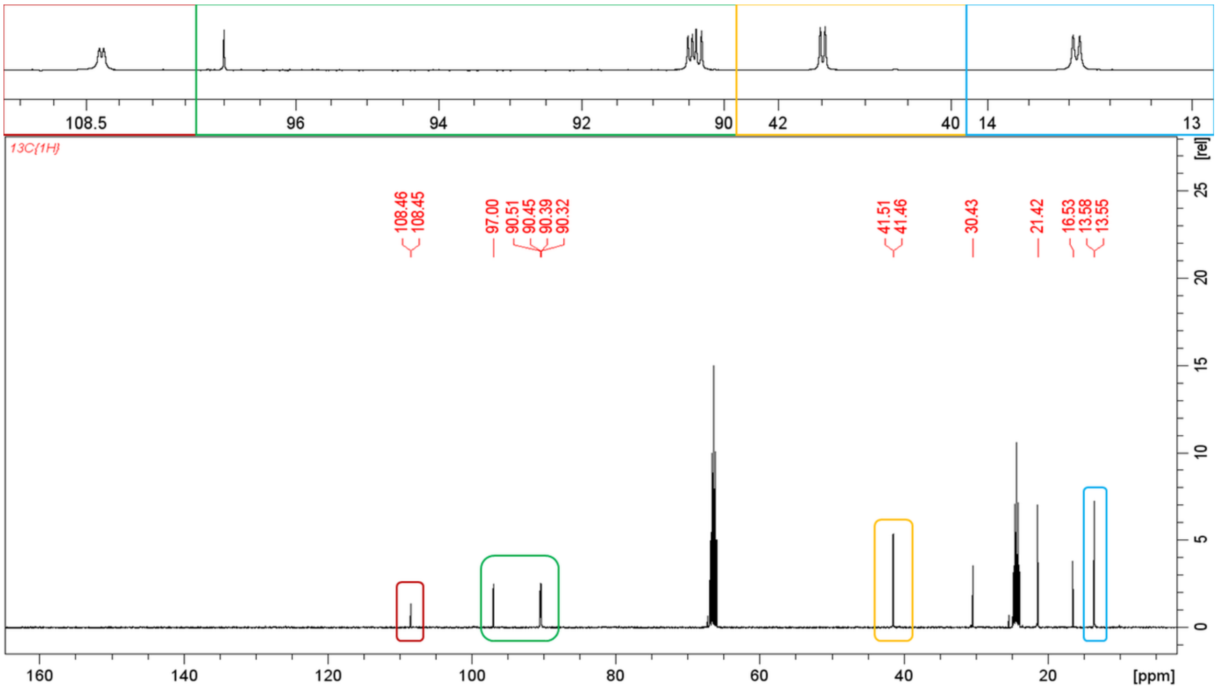

Figure S41. $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, THF-d_8, 298 K) of isolated [(*p*-cym)$RuCl_2$(η^1-P(Cl)($NEt_2)_2$)] (**7**).

C. X-Ray diffraction data

The X-ray diffraction data for $[(Et_2N)_2P\text{-}P(SiM_3)Li\cdot THF]_2$, **2**, **3a**, **4a**, **5**, **6** and **7** were measured with an IPDS2T diffractometer equipped with an STOE image plate detector system and microfocus X-ray sources providing Kα radiation by high-grade multilayer X-ray mirror optics for Mo (λ = 0.71073 Å, $[(Et_2N)_2P\text{-}P(SiM_3)Li\cdot THF]_2$, **2**, **3a**, **4a**, **5**, **6**) and Cu (λ = 1.54186 Å, **7**). The measurements were carried out at 120 K. The structures were solved by direct methods and refined against F^2 with the Shelxs-2008 and Shelxl-2008 programs[3] run under WinGX.[4] Non-hydrogen atoms were refined with anisotropic displacement parameters. The isotropic displacement parameters of all hydrogens were fixed to 1.2 U_{eq} for aromatic, CH, CH_2 and 1.5 UK_{eq} for methyl groups. For **5,** the contribution to the scattering of the disordered solvent molecule (THF) was removed with the SQUEEZE routine of the PLATON program.[5]

The crystallographic data for all structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publications No. CCDC 2386108-2386114. Copies of the data can be obtained free of charge upon application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; E mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystallographic data for **[(Et$_2$N)$_2$P-P(SiM$_3$)Li·THF]$_2$, 2** and **3a**.

	[(Et$_2$N)$_2$P-P(SiM$_3$)Li·THF]$_2$	**2**	**3a**
Empirical formula	$C_{30}H_{74}Li_2N_4O_2P_4Si_2$	$C_{33}H_{36}P_2$	$C_{42}H_{60}N_4P_4$
Formula weight	716.87	494.56	744.82
Radiation source	Mo-*Kα*	Mo-*Kα*	Mo-*Kα*
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Orthorhombic	Monoclinic
Space group	*C2/c*	*Pbcn*	*C2/c*
a [Å]	19.6660(9)	9.8631(4)	17.1259(16)
b [Å]	9.8948(3)	20.3925(11)	10.8384(7)
c [Å]	23.2825(11)	28.0508(14)	23.062(2)
α [°]	90	90	90
β [°]	104.656(4)	90	106.613(8)
γ [°]	90	90	90
V [Å3]	4383.2(3)	5641.9(5)	4102.0(6)
Z	4	8	4
Calculated Density [g·cm-1]	1.086	1.164	1.206
T [K]	120(2)	120(2)	120(2)
μ [mm-1]	0.255	0.173	0.218
Theta range for data collection [°]	2.32-29.54	2.41-29.39	2.29-27.80
Index ranges	-19 ≤ h ≤ 25 -13 ≤ k ≤ 12 -30 ≤ l ≤ 30	-12 ≤ h ≤ 10 -26 ≤ k ≤ 22 -35 ≤ l ≤ 35	-21 ≤ h ≤ 21 -13 ≤ k ≤ 13 -29 ≤ l ≤ 29
Data / restraints / parameters	5238/0/206	6100/0/323	4450/0/231
Goodness-of-fit on F^2	1.028	1.209	1.012
Final R indices	0.0444	0.0998	0.1031
[*I*>2σ(I)]	0.0977	0.188	0.2545
R indices (all data)	0.0907	0.1532	0.1790
[*I*>2σ(I)] (all data)	0.1115	0.1932	0.3186
Largest diff. peak and hole [e.Å-3]	0.055 and -0.232	0.361 and -0.363	0.121 and -0.715
CCDC	**2386111**	**2386114**	**2386112**

Table S2. Crystallographic data for **4a, 5** and **6**.

	4a	**5**	**6**
Empirical formula	$C_{71}H_{88}N_4P_4$	$C_{40}H_{46}Cl_3P_1Ru_2$	$C_{45}H_{46}Cl_3P_1Ru_2$
Formula weight	1121.33	866.23	926.28
Radiation source	Mo-*Kα*	Mo-*Kα*	Mo-*Kα*
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	*P*-1	*P*-1
a [Å]	14.2680(10)	10.1085(4)	16.3325(5)
b [Å]	23.3514(16)	14.1466(6)	16.6265(5)
c [Å]	18.7576(13)	14.9037(7)	16.9118(5)
α [°]	90	66.843(3)	74.161(2)
β [°]	96.391(5)	72.498(3)	78.653(2)
γ [°]	90	83.439(3)	87.765(2)
V [Å3]	6210.8(7)	1868.80(15)	4331.2(2)
Z	4	2	4
Calculated Density [g·cm-1]	1.199	1.539	1.421
T [K]	120(2)	120(2)	120(2)
μ [mm-1]	0.167	1.093	0.948
Theta range for data collection [°]	2.09-29.57	2.24-29.66	2.09-29.57
Index ranges	-15 ≤ h ≤ 19 -31 ≤ k ≤ 30 -25 ≤ l ≤ 25	-13 ≤ h ≤ 13 -19 ≤ k ≤ 19 -17 ≤ l ≤ 20	-22 ≤ h ≤ 22 -23 ≤ k ≤ 22 -23 ≤ l ≤ 23
Data / restraints / parameters	16647/0/722	9036/0/523	23279/0/931
Goodness-of-fit on F^2	1.111	1.090	1.015
Final R indices	0.0839	0.0702	0.0481
[*I*>2σ(I)]	0.11429	0.2138	0.1186
R indices (all data)	0.1605	0.0896	0.0655
[*I*>2σ(I)] (all data)	0.1775	0.2326	0.1327
Largest diff. peak and hole [e.Å-3]	0.086 and -0.445	0.244 and -1.711	0.863 and -1.556
CCDC	**2386108**	**2386109**	**2386113**

Table S3. Crystallographic data for **7**.

	7
Empirical formula	$C_{18}H_{34}Cl_3N_2P_1Ru_1$
Formula weight	516.86
Radiation source	Cu-*Kα*
Wavelength [Å]	1.54186
Crystal System	Triclinic
Space group	*P*-1
a [Å]	7.4357(4)
b [Å]	11.5604(6)
c [Å]	13.4708(6)
α [°]	94.140(4)
β [°]	94.656(4)
γ [°]	98.498(4)
V [Å3]	1137.28(10)
Z	2
Calculated Density [g·cm-1]	1.509
T [K]	120(2)
μ [mm-1]	9.512
Theta range for data collection [°]	3.30-67.54
Index ranges	-8 ≤ h ≤ 8 -13 ≤ k ≤ 13 -15 ≤ l ≤ 15
Data / restraints / parameters	3811/0/205
Goodness-of-fit on F^2	1.131
Final R indices	0.0544
[*I*>2σ(I)]	0.1403
R indices (all data)	0.0644
[*I*>2σ(I)] (all data)	0.1528
Largest diff. peak and hole [e.Å-3]	0.167 and -1.186
CCDC	**2386110**

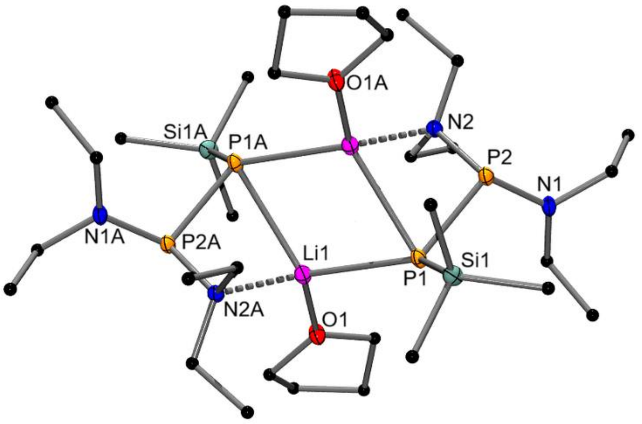

Figure 42. Molecular structure of $[(Et_2N)_2P\text{-}P(SiM_3)Li{\cdot}THF]_2$ (thermal ellipsoids drawn at the 50% probability level for N, O, P, Si and Li and ball representation for carbon atoms; H atoms have been omitted for clarity). Selected distances (Å) and angles (deg): P1-P2 2.1781(7), P1-Si1 2.2178(8), P1-Li1 2.677(4), P1-Li1A 2.628(3), P2-N1 1.6987(18), P2-N2 1.7713(17), Li1-O1 1.914(4), Li1···N2 2.145(4), Li1···P2 2.830(3); P1-P2-N1 106.89(7), P1-P2-N2 98.49(6), Li1-P1-P2 63.05(7), P1-Li1-P1A 112.21(12), Li1-P1-Li1A 67.79(13); Symmetry operations: A: 0.5-x, 1.5-y, 1-z.

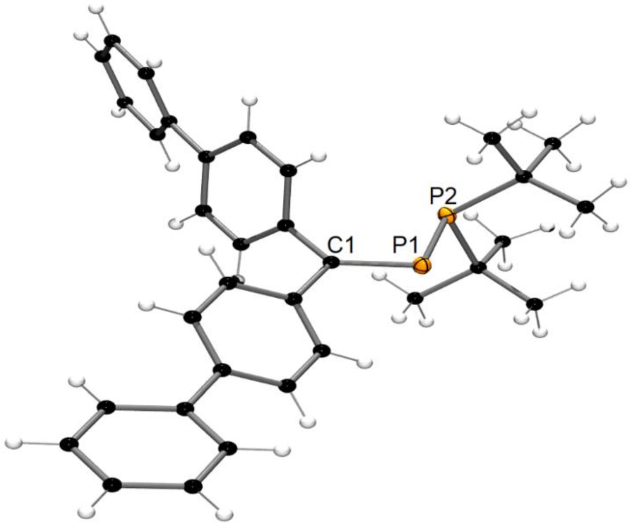

Figure S43. Molecular structure of $(biph)_2C{=}P\text{-}P\textit{t}Bu_2$ (**2**) (thermal ellipsoids drawn at the 50% probability level for P; carbon atoms presented as balls). Selected distances (Å) and angles (deg): P1-P2 2.2216(18), P1-C1 1.692(5), C1-P1-P2 104.26(17).

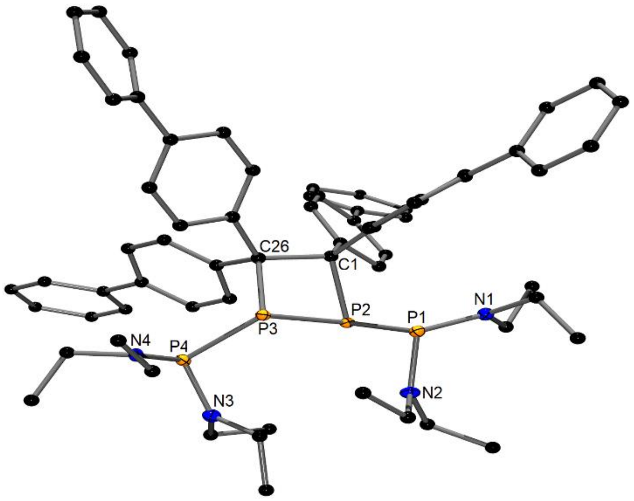

Figure S44. Molecular structure of (biph)$_2$C=P-P*t*Bu$_2$ (**2**) (thermal ellipsoids drawn at the 50% probability level for P; carbon atoms presented as balls). Selected distances (Å) and angles (deg): P1-P2 2.2216(18), P1-C1 1.692(5), C1-P1-P2 104.26(17).

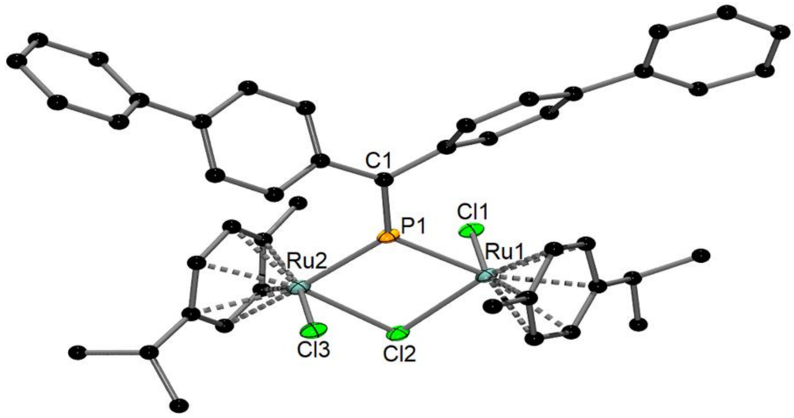

Figure S45. Molecular structure of **6** (thermal ellipsoids drawn at the 50% probability level for Ru, Cl, P; carbon atoms presented as balls; H atoms omitted for clarity). Selected distances (Å) and angles (deg)**:** Ru1-P1 2.3163(9), Ru2-P1 2.3226(9), Ru1-Cl1 2.4154(8), Ru1-Cl2 2.4599(8), Ru2-Cl2 2.4645(8), Ru2-Cl3 2.4083(8), P1-C1 1.697(3); Ru1-P1-Ru2 107.38(3), Ru1-Cl2-Ru2 98.77(3), Ru1-P1-C1 126.74(12), Ru2-P1-C1 125.85(12), ΣP1 = 359.97(10).

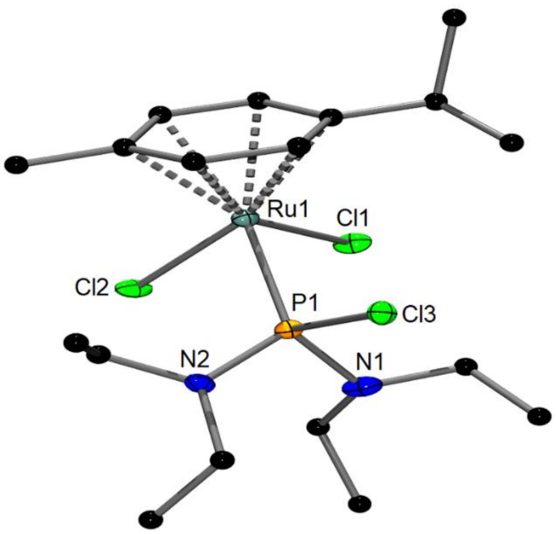

Figure 46. Molecular structure of **7** (carbon atoms represented as balls and all other heavy atoms as thermal ellipsoids drawn at the 50% probability level; the H atoms have been omitted for clarity). Selected distances (Å) and angles (deg): Ru1-Cl1 2.4106(18), Ru1-Cl2 2.4154(16), Ru1-P1 2.3179(17), P1-Cl3 2.112(2), P1-N1 1.653(6), P1-N2 1.619(6); Cl1-Ru1-Cl2 85.17(7), Cl1-Ru1-P1 89.66(6), Cl2-Ru1-P1 85.29(6), Ru1-P1-Cl3 110.43(9).

D. Computational Studies

DFT quantum chemical calculations were performed using the Turbomole 7.7.1 software package.[6-9] Molecular geometries were optimized using the resolution-of-the-identity approximation[10, 11] and multiple accelerated resolution of the identity approximation.[12] def2-SV(P)[10, 11, 13, 14] or def2-TZVP[10, 11, 13, 14] basis sets together with the BP86[15] functional were applied. Selected calculations include D4 empirical dispersion correction.[16, 17] Energetic minima were confirmed by analytical calculations of vibrations with the aoforce module.[18-20] Using the computed vibrational energies, standard (T = 298.15 K, p = 0.1 MPa) thermodynamic data were calculated. Graphics and population analyses were generated with the BIOVIA Tmolex 2024 software.[21] Population Analysis Based On Occupation Numbers (PABOON),[22] Natural Population Analysis (NPA)[23] and Wiberg bond indices[24] calculated for **5** and **6**.

D.1. Phosphanylphosphaalkenes

Table S4. Selected data from the DFT calculations of (**I**) to (**VI**) ((DFT: def2-TZVP/BP86).

Compound	Total energy	Dipole moment	HOMO-LUMO gap
	H	**D**	**eV**
Me_2C=P-P*t*Bu_2 (**I**)	-1116.5866	0.63	2.68
Me(Ph)C=P-P*t*Bu_2 (**II**)	-1308.38271	2.26	2.17
Ph_2C=P-P*t*Bu_2 (**III**)	-1500.19443	2.20	2.03
Me_2C=P-P$(NEt_2)_2$ (**IV**)	-1227.34712	1.28	2.61
Me(Ph)C=P-P$(NEt_2)_2$ (**V**)	-1419.15658	1.28	2.33
Ph_2C=P-P$(NEt_2)_2$ (**VI**)	-1610.97142	1.36	2.00

Result obtained in Population Analysis Based On Occupation Numbers (PABOON)[22], and Wiberg bond indices[24] of phosphanylphosphaalkenes I to VI are presented in tables S5 and S6.

Table S5. Results of the Population Analysis Based On Occupation Numbers for (**I**) to (**VI**).

Compound	Two center shared electron numbers					Atomic charges with multicenter corrections					
	N^1-P^1	N^2-P^1	N-$P_{avg.}$	P-P	P-C	N^1	N^2	$N_{avg.}$	P^1	P^2	C
(I)				1.12	1.89				0.07	-0.08	-0.03
(II)				1.13	1.84				0.09	-0.08	-0.03
(III)				1.17	1.77				0.13	-0.04	-0.07
(IV)	1.13	1.15	1.14	1.09	1.89	-0.18	-0.18	-0.18	0.28	-0.11	-0.04
(V)	1.16	1.13	1.15	1.08	1.87	-0.17	-0.17	-0.17	0.28	-0.10	-0.03
(VI)	1.15	1.13	1.14	1.08	1.80	-0.18	-0.17	-0.17	0.29	-0.11	-0.03

Table S6. Wiberg bond indices.

Compound	Wiberg bond index				
	N^1-P	N^2-P	N-$P_{avg.}$	P-P	P-C
(I)				1.06	1.77
(II)				1.10	1.69
(III)				1.17	1.59
(IV)	1.09	0.97	1.03	1.06	1.70
(V)	1.10	1.12	1.11	1.05	1.76
(VI)	1.08	1.10	1.09	1.04	1.67

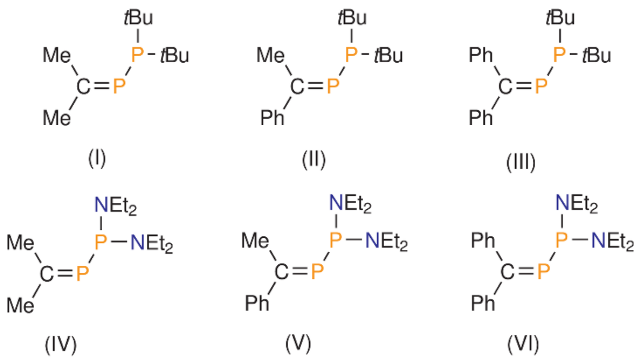

Figure 47. Molecular structures of the model compounds.

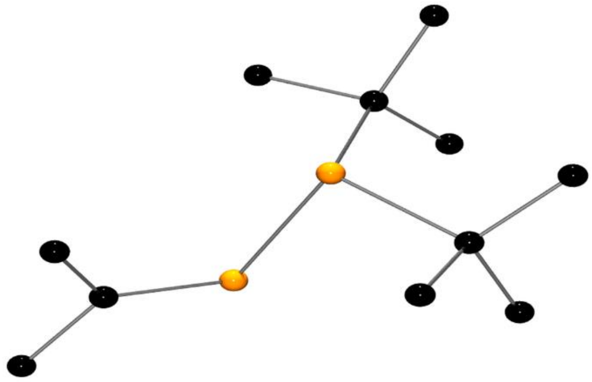

Figure S48. Optimized molecular structures of **I**.

Below are presented xyz coordinates for optimized geometry of **I**:

P	0.2539780	-0.3804578	0.3504828
C	1.8223406	0.7348688	0.4402178
C	0.0744008	-1.2002189	-1.3891418
P	-1.3169969	1.2102995	0.1879722
C	-2.5110431	0.7359576	1.3030082
C	-2.5470897	-0.4594221	2.2070950
C	-3.7190777	1.6342957	1.4078450
H	-4.6405887	1.0733008	1.1757644
H	-3.6593568	2.4978219	0.7318920
H	-3.8328371	2.0057615	2.4407936
C	3.0361769	-0.1809265	0.6925640
C	1.6156678	1.6004584	1.6993531
C	2.0960383	1.6469000	-0.7633369
C	1.3120536	-2.0698110	-1.6662720
C	-0.1766630	-0.2618509	-2.5796753
C	-1.1483799	-2.1258439	-1.2229165
H	-1.6286261	-1.0560325	2.1553454
H	-3.4042408	-1.1059795	1.9497970
H	-2.7105326	-0.1392871	3.2507208
H	1.1159911	-2.7196968	-2.5357012
H	1.5572981	-2.7177799	-0.8118096
H	2.1963675	-1.4637632	-1.9054255
H	-1.3142264	-2.6876555	-2.1571329
H	-2.0632639	-1.5535877	-1.0097765
H	-1.0000810	-2.8506060	-0.4095111
H	-0.3349735	-0.8620226	-3.4922678
H	0.6681332	0.4112942	-2.7693713
H	-1.0737213	0.3561987	-2.4302864
H	2.8659297	-0.8431137	1.5537324
H	3.9230968	0.4376027	0.9104277
H	3.2767869	-0.8083732	-0.1748837
H	1.3819663	0.9844815	2.5806975
H	0.8024135	2.3294873	1.5694613
H	2.5408486	2.1608134	1.9133097
H	2.9531712	2.3059838	-0.5417184
H	1.2349570	2.2884438	-0.9980675

H	2.3540825	1.0724591	-1.6631853

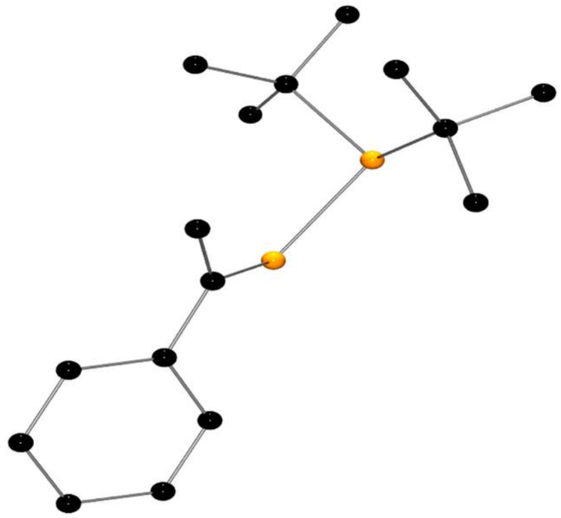

Figure S49. Optimized molecular structures of **II**.

Below are presented xyz coordinates for optimized geometry of **II**:

P	1.2410361	-1.1428255	0.5154489
C	2.5065146	0.0580725	-0.3183663
C	0.6745543	-2.5458284	-0.6699328
P	-0.6816364	-0.2956183	1.2814364
C	-1.3384258	1.0577606	0.4554668
C	-0.9694312	1.5668283	-0.9073868
C	3.8822868	-0.5692477	0.0093402
C	2.4046852	1.3914370	0.4427095
C	2.4372437	0.3015359	-1.8326500
C	1.9161611	-3.3098293	-1.1632900
C	-0.1743889	-2.0841899	-1.8631552
C	-0.1615093	-3.5006705	0.2070744
H	-0.6184162	2.6117210	-0.8704284
H	-1.8464495	1.5608293	-1.5748282
H	-0.2008603	0.9447089	-1.3710069
H	1.5934624	-4.2067303	-1.7179637
H	2.5455009	-3.6422182	-0.3253347
H	2.5356961	-2.7110243	-1.8442912
H	-0.4588403	-4.3769543	-0.3927478
H	-1.0785438	-3.0209248	0.5772912
H	0.4108521	-3.8581341	1.0744382
H	-0.4884457	-2.9598246	-2.4575046
H	0.3778544	-1.4130785	-2.5334035
H	-1.0825126	-1.5654151	-1.5257871
H	4.0036884	-0.7265180	1.0896880
H	4.6816555	0.1096155	-0.3330285
H	4.0291764	-1.5355856	-0.4913033
H	2.4445384	1.2359135	1.5310684
H	1.4792762	1.9329832	0.2123949
H	3.2558954	2.0355671	0.1661487
H	3.2656172	0.9685869	-2.1275109
H	1.5064524	0.7858733	-2.1500845
H	2.5524848	-0.6268315	-2.4075161

C	-2.4422170	1.7538289	1.1542330
C	-3.5310129	2.3053130	0.4413511
C	-4.5914945	2.9206354	1.1038926
C	-4.5946993	3.0179245	2.4984141
C	-3.5190571	2.4961391	3.2222303
C	-2.4567895	1.8822410	2.5616658
H	-3.5647119	2.2261936	-0.6453244
H	-5.4237670	3.3258912	0.5259256
H	-5.4217988	3.5073194	3.0144377
H	-3.4975662	2.5833618	4.3096965
H	-1.6020582	1.5111683	3.1284924

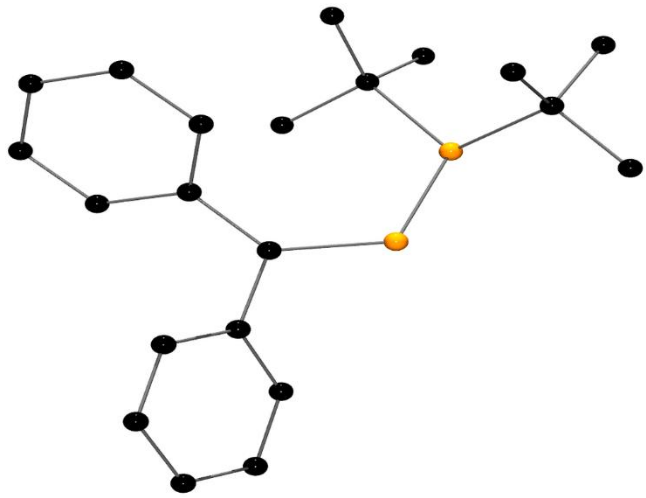

Figure S50. Optimized molecular structures of **III**.

Below are presented xyz coordinates for optimized geometry of **III**:

P	1.4455961	-1.4385711	0.1248834
C	3.0649525	-0.6205592	0.7743994
C	1.2834668	-1.3403422	-1.7877443
P	-0.0408066	-0.5761709	1.5152028
C	-1.4258945	0.2638770	0.9313327
C	4.2704689	-1.1644256	-0.0118794
C	3.2092857	-1.0770770	2.2412606
C	3.0571181	0.9150912	0.7166136
C	2.1417546	-2.5009645	-2.3392370
C	1.6922143	-0.0286265	-2.4661192
C	-0.1885870	-1.6691415	-2.0935824
H	1.9612055	-2.5896791	-3.4236510
H	1.8718053	-3.4581731	-1.8713150
H	3.2170135	-2.3410167	-2.1949570
H	-0.3016338	-1.8367778	-3.1773941
H	-0.8634956	-0.8556151	-1.8061919
H	-0.5104510	-2.5866027	-1.5784489
H	1.5206302	-0.1117187	-3.5531702
H	2.7580219	0.1955612	-2.3226822
H	1.1027511	0.8215949	-2.1040037
H	4.2921253	-2.2633525	-0.0192688
H	5.1976998	-0.8152352	0.4719664
H	4.2908290	-0.8077688	-1.0500958
H	3.2399031	-2.1726669	2.3203097
H	2.3871035	-0.7130513	2.8719668
H	4.1517122	-0.6768086	2.6507435
H	4.0148756	1.3072162	1.1001371
H	2.2506149	1.3292069	1.3379046
H	2.9298357	1.2918834	-0.3066350
C	-2.5480366	0.2877736	1.8992989
C	-2.8671003	-0.8318809	2.6984984
C	-3.8790223	-0.7689648	3.6567518
C	-4.6139826	0.4060177	3.8307758
C	-4.3279274	1.5198783	3.0327876
C	-3.3149062	1.4625417	2.0792619

H	-2.3216516	-1.7624279	2.5369256
H	-4.1073260	-1.6512124	4.2570192
H	-5.4126473	0.4515628	4.5724900
H	-4.8961872	2.4429105	3.1598182
H	-3.0902677	2.3426386	1.4757332
C	-1.6151802	1.0399261	-0.3127320
C	-2.7847873	0.8870642	-1.0872575
C	-2.9930877	1.6541689	-2.2326230
C	-2.0530273	2.6162216	-2.6168212
C	-0.9010893	2.7977430	-1.8473354
C	-0.6810932	2.0137934	-0.7129423
H	-3.5280836	0.1484459	-0.7836597
H	-3.8976939	1.5067270	-2.8248316
H	-2.2234828	3.2276619	-3.5039656
H	-0.1713779	3.5594613	-2.1271223
H	0.2078432	2.1698636	-0.1004146

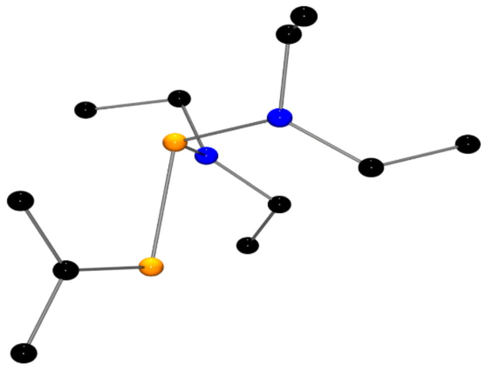

Figure S51. Optimized molecular structures of **IV**.

Below are presented xyz coordinates for optimized geometry of **IV**:

P	-0.0289277	-0.2656449	0.6243101
N	1.5464321	0.4404750	0.6753276
N	-0.3198382	-1.1457544	-0.8280964
P	-1.1111774	1.6656736	0.2802902
C	-2.6790589	1.3429568	0.8505348
C	-3.6529475	2.4950243	0.8532948
C	-3.2415270	0.0513930	1.3662821
H	-3.7585481	0.2134842	2.3276016
H	-2.4764569	-0.7226634	1.5031110
H	-4.0043669	-0.3358312	0.6682037
C	2.5245534	-0.2315368	1.5528510
C	2.1146876	1.3282907	-0.3436980
C	-0.4050921	-0.5888288	-2.1819802
C	-0.2976596	-2.6119696	-0.7280124
H	-4.0143805	2.6938682	1.8771846
H	-4.5446748	2.2502376	0.2504628
H	-3.2101250	3.4183489	0.4566133
H	-1.3328279	-0.9433391	-2.6661548
C	0.7857420	-0.9056003	-3.0945437
H	-0.5207768	0.5010904	-2.0852216
C	-1.5620936	-3.2984868	-1.2539307
H	-0.1686341	-2.8533643	0.3380629
H	0.5863517	-3.0276871	-1.2481207
C	2.5833741	0.3432961	2.9706121
H	3.5179665	-0.1703432	1.0759385
H	2.2792053	-1.3046304	1.6128356
C	2.8335476	2.5562110	0.2210420
H	1.2941970	1.6670716	-0.9925990
H	2.8150259	0.7629358	-0.9920548
H	2.8500463	1.4087444	2.9621219
H	3.3281519	-0.1961232	3.5764045
H	1.6051239	0.2437213	3.4615034
H	3.2095902	3.1833094	-0.6013836
H	3.6956731	2.2759612	0.8427871
H	2.1471876	3.1584256	0.8323052
H	-1.4952159	-4.3837773	-1.0876262
H	-1.7032546	-3.1420317	-2.3327833
H	-2.4556132	-2.9241379	-0.7347302
H	1.7296534	-0.5532678	-2.6556423

H	0.6553595	-0.4112286	-4.0686590
H	0.8813274	-1.9842719	-3.2844443

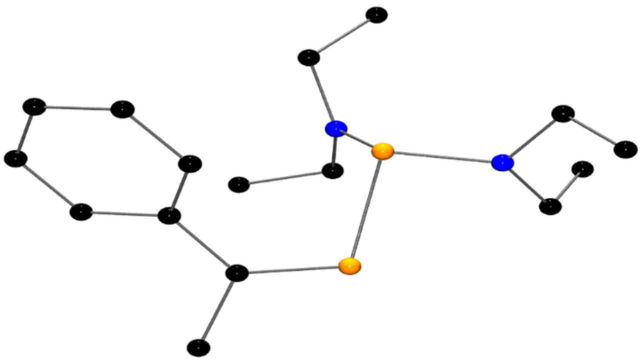

Figure S52. Optimized molecular structures of **V**.

Below are presented xyz coordinates for optimized geometry of **V**:

C	-0.7852673	-0.3838722	2.6400462
P	0.3572210	-1.1799525	1.6581426
P	0.7557878	0.2010006	-0.0706576
N	-0.5249067	-0.1809300	-1.1471953
N	2.2484549	-0.5475907	-0.5160919
C	-1.1826504	-1.1010718	3.9116756
C	-1.4495485	0.9227652	2.4214914
C	-2.8557077	1.0149722	2.4067427
C	-3.4941297	2.2414084	2.2201231
C	-2.7426355	3.4101391	2.0714305
C	-1.3476597	3.3379547	2.1051943
C	-0.7074835	2.1093068	2.2719511
H	-3.4553483	0.1104618	2.5225619
H	-4.5843323	2.2841551	2.1961673
H	-3.2411872	4.3709985	1.9362078
H	-0.7503228	4.2454468	2.0028993
H	0.3803681	2.0597845	2.3018276
C	2.4623642	-1.9740935	-0.7812834
C	2.3918641	-2.3746366	-2.2609021
H	1.7149096	-2.5431317	-0.2080729
H	3.4434156	-2.2726171	-0.3722131
H	2.5581492	-3.4569978	-2.3680478
H	1.4108046	-2.1338093	-2.6918533
H	3.1598934	-1.8626802	-2.8580572
C	3.3496023	0.3449946	-0.9030615
C	4.5609262	0.2719107	0.0323713
H	2.9513698	1.3708384	-0.9040251
H	3.6695889	0.1337576	-1.9406022
H	4.2754197	0.5486748	1.0567755
H	4.9985776	-0.7361023	0.0623165
H	5.3472665	0.9619701	-0.3086879
C	-0.9356716	0.8762312	-2.0820585
C	-0.3746582	0.7363076	-3.5024947
H	-0.6064748	1.8336809	-1.6509225
H	-2.0376261	0.9166564	-2.1217746
H	-0.7368022	1.5591746	-4.1372015
H	0.7238887	0.7673429	-3.4950006
H	-0.6860367	-0.2054791	-3.9772735
C	-1.1336751	-1.4991783	-1.3490099

C	-2.6286420	-1.5557968	-1.0188360
H	-0.6041897	-2.2167139	-0.7048922
H	-0.9739763	-1.8417680	-2.3892862
H	-3.0084383	-2.5779710	-1.1659416
H	-2.8024289	-1.2656268	0.0261613
H	-3.2197334	-0.8888258	-1.6618257
H	-2.2690011	-1.2884932	3.9349064
H	-0.9558469	-0.4781049	4.7928715
H	-0.6654909	-2.0644902	4.0154050

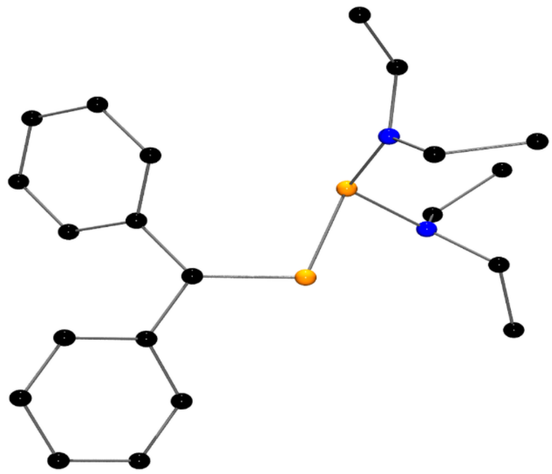

Figure S53. Optimized molecular structures of **VI**.

Below are presented xyz coordinates for optimized geometry of **VI**:

C	-0.3673917	-0.0255856	2.0557881
P	0.8873068	0.2231362	0.9077851
P	-0.0081366	-0.3653716	-1.0632190
N	-0.1655598	1.1489650	-1.8715726
N	1.4033813	-1.2288842	-1.5802987
C	0.0491977	-0.0099114	3.4799782
C	1.2707884	-0.5717230	3.9061744
C	1.6701699	-0.4976097	5.2399807
C	0.8574521	0.1334215	6.1861744
C	-0.3634867	0.6845693	5.7849092
C	-0.7660232	0.6090718	4.4526401
H	1.8941766	-1.0870000	3.1741977
H	2.6157635	-0.9486539	5.5454077
H	1.1679698	0.1862744	7.2306643
H	-1.0060081	1.1797249	6.5149240
H	-1.7150113	1.0511870	4.1470446
C	-1.8021627	-0.2416639	1.7792380
C	-2.5083395	-1.2543934	2.4632332
C	-3.8543823	-1.4961077	2.1953964
C	-4.5374799	-0.7143048	1.2579682
C	-3.8577931	0.3042479	0.5857683
C	-2.5044935	0.5336535	0.8370389
H	-1.9822895	-1.8648962	3.1983473
H	-4.3750957	-2.2965701	2.7235409
H	-5.5946322	-0.8950448	1.0578897
H	-4.3864576	0.9280378	-0.1369003
H	-1.9786942	1.3372222	0.3204700
C	1.1669268	-2.5062542	-2.2656885
C	1.2848496	-2.4515546	-3.7939890
H	0.1533812	-2.8326403	-1.9885800
H	1.8596288	-3.2675926	-1.8684635
H	1.0763364	-3.4420316	-4.2252279
H	0.5655265	-1.7356769	-4.2171441
H	2.2923414	-2.1559238	-4.1200675
C	2.7584408	-0.6758425	-1.6674735

C	3.8458732	-1.5774972	-1.0757136
H	2.7614709	0.2796665	-1.1241546
H	3.0142121	-0.4351622	-2.7176053
H	3.6198182	-1.8150986	-0.0269488
H	3.9532131	-2.5208501	-1.6288821
H	4.8170734	-1.0625686	-1.1133748
C	0.6821100	2.3360415	-1.7074164
C	1.6005165	2.6607042	-2.8916921
H	1.2839558	2.1904645	-0.7979463
H	0.0429781	3.2137012	-1.5016299
H	2.2286298	3.5304121	-2.6485874
H	2.2626254	1.8172151	-3.1311022
H	1.0301905	2.9116012	-3.7974991
C	-1.0803199	1.1633555	-3.0229497
C	-2.0819075	2.3217891	-3.0161083
H	-1.6275317	0.2083249	-3.0026877
H	-0.5165245	1.1769802	-3.9756459
H	-2.7702796	2.2234608	-3.8681404
H	-2.6773792	2.3230236	-2.0924040
H	-1.5889246	3.3001614	-3.1054461

D.2. Dimerization

Table S7. Selected calculated standard thermodynamic parameters for **3**, **3a**, **4,** and **4a** (DFT: def2-TZVP/BP86).

Compound	**Total energy**	**HOMO-LUMO gap**	**H°**	**S°**	**G°**
	H	eV	kJ·mol^{-1}	kJ·mol^{-1}·K	kJ·mol^{-1}
3	-1610.97142	2.00	-4228343.38440	0.81688	-4228587.223
***trans*-3a**	-3221.9296	1.3555	-8456645.7577	1.3555	-8457049.898
***cis*-3a**	-8459126.53	2.46	-8456595.9921	1.3679	-8457003.8221
4	-2073.25657	1.36	-5441639.98870	1.0335	-5441948.500
***trans*-4a**	-2073.25657	1.36	-5441639.98870	1.0335	-5441948.500
***cis*-3a**	-10886612.04	2.21	-10883214.7489	1.7898	-10883748.3889

Table S8. Selected DFT calculated standard thermodynamic parameters of **3**, **3a**, **4** and **4a** (RIDFT: def2-TZVP / BP86).

Compound	**Total energy**	**HOMO-LUMO gap**	**H°**	**S°**	**G°**
	H	eV	kJ·mol^{-1}	kJ·mol^{-1}·K^{-1}	kJ·mol^{-1}
3	-4229899.6141	2.01	-4228635.9041	0.80942	-4228877.2327
***trans*-3a**	-8459948.1658	2.87	-8457412.1358	1.32235	-8457412.1458
***cis*-3a**	-8459903.5320	2.52	-8457367.1120	1.32462	-8457367.1120
4	-5443749.6526	1.33	-5442052.1526	1.02094	-5442052.1526
***trans*-4a**	-10887677.9179	2.45	-10884273.6079	1.73316	-10884273.6079
***cis*-34a**	-10887676.7499	2.50	-10884275.5049	1.72500	-10884275.5049

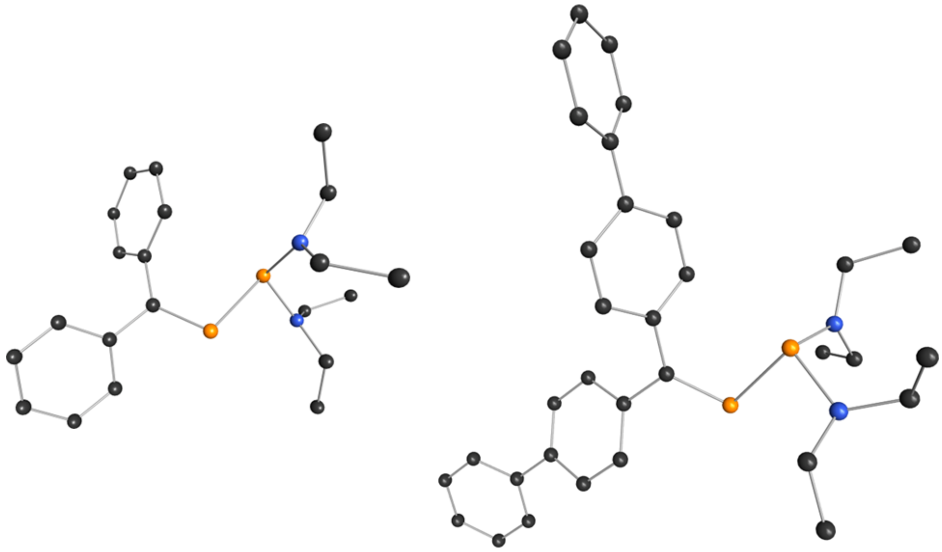

Figure S54. Optimized molecular structures of **3** (left) and **4** (right) (DFT: def2-SV(P)/BP86).

Below are presented xyz coordinates for optimized geometry of **3**:

C	-0.3673917	-0.0255856	2.0557881
P	0.8873068	0.2231362	0.9077851
P	-0.0081366	-0.3653716	-1.0632190
N	-0.1655598	1.1489650	-1.8715726
N	1.4033813	-1.2288842	-1.5802987
C	0.0491977	-0.0099114	3.4799782
C	1.2707884	-0.5717230	3.9061744
C	1.6701699	-0.4976097	5.2399807
C	0.8574521	0.1334215	6.1861744
C	-0.3634867	0.6845693	5.7849092
C	-0.7660232	0.6090718	4.4526401
H	1.8941766	-1.0870000	3.1741977
H	2.6157635	-0.9486539	5.5454077
H	1.1679698	0.1862744	7.2306643
H	-1.0060081	1.1797249	6.5149240
H	-1.7150113	1.0511870	4.1470446
C	-1.8021627	-0.2416639	1.7792380
C	-2.5083395	-1.2543934	2.4632332
C	-3.8543823	-1.4961077	2.1953964
C	-4.5374799	-0.7143048	1.2579682
C	-3.8577931	0.3042479	0.5857683
C	-2.5044935	0.5336535	0.8370389
H	-1.9822895	-1.8648962	3.1983473
H	-4.3750957	-2.2965701	2.7235409
H	-5.5946322	-0.8950448	1.0578897
H	-4.3864576	0.9280378	-0.1369003
H	-1.9786942	1.3372222	0.3204700
C	1.1669268	-2.5062542	-2.2656885
C	1.2848496	-2.4515546	-3.7939890
H	0.1533812	-2.8326403	-1.9885800
H	1.8596288	-3.2675926	-1.8684635
H	1.0763364	-3.4420316	-4.2252279
H	0.5655265	-1.7356769	-4.2171441

H	2.2923414	-2.1559238	-4.1200675
C	2.7584408	-0.6758425	-1.6674735
C	3.8458732	-1.5774972	-1.0757136
H	2.7614709	0.2796665	-1.1241546
H	3.0142121	-0.4351622	-2.7176053
H	3.6198182	-1.8150986	-0.0269488
H	3.9532131	-2.5208501	-1.6288821
H	4.8170734	-1.0625686	-1.1133748
C	0.6821100	2.3360415	-1.7074164
C	1.6005165	2.6607042	-2.8916921
H	1.2839558	2.1904645	-0.7979463
H	0.0429781	3.2137012	-1.5016299
H	2.2286298	3.5304121	-2.6485874
H	2.2626254	1.8172151	-3.1311022
H	1.0301905	2.9116012	-3.7974991
C	-1.0803199	1.1633555	-3.0229497
C	-2.0819075	2.3217891	-3.0161083
H	-1.6275317	0.2083249	-3.0026877
H	-0.5165245	1.1769802	-3.9756459
H	-2.7702796	2.2234608	-3.8681404
H	-2.6773792	2.3230236	-2.0924040
H	-1.5889246	3.3001614	-3.1054461

Below are presented xyz coordinates for optimized geometry of **3**:

C	-1.8764466	0.5751278	1.1345855
C	-0.8782198	-0.1784691	0.4810534
C	-1.3007420	-1.2450095	-0.3353872
C	-2.6523906	-1.5431486	-0.4919721
C	-3.6469591	-0.7760689	0.1392255
C	-3.2259249	0.2947133	0.9525950
C	0.5475070	0.1607413	0.6501362
C	1.0264323	0.3866825	2.0318583
C	2.0449184	1.3171803	2.3294004
C	2.5228213	1.4767796	3.6249933
C	2.0057895	0.7212109	4.6954110
C	0.9814459	-0.1995129	4.4035674
C	0.4997884	-0.3596746	3.1087692
P	1.7174201	0.2832215	-0.6098566
P	0.5110201	0.2377787	-2.5547802
N	1.0511285	-1.1967478	-3.3115542
C	2.4528232	-1.6323756	-3.3324807
C	2.7754054	-2.7977531	-2.3918645
N	1.5608950	1.4307291	-3.3322707
C	1.5734719	1.4393539	-4.8016428
C	0.2864786	1.9259253	-5.4866748
C	1.5544929	2.7634431	-2.7132482
C	2.9371854	3.4188314	-2.6917624
C	0.0446105	-2.1252119	-3.8350078
C	0.1335417	-2.3677107	-5.3456856
H	2.4395957	1.9382544	1.5240332
H	3.2836569	2.2338331	3.8218752

C	2.5133955	0.8955052	6.0746973
H	0.5787711	-0.8247780	5.2021256
H	-0.2774612	-1.0993630	2.9134822
H	-0.5470478	-1.8666393	-0.8201844
H	-2.9441606	-2.3728876	-1.1376843
C	-5.0841547	-1.0856523	-0.0374312
H	-3.9711736	0.8953738	1.4766515
H	-1.5801384	1.4008117	1.7831219
H	-0.9403882	-1.6999446	-3.5898782
H	0.1070804	-3.0949494	-3.3071646
H	-0.6569178	-3.0649672	-5.6606282
H	0.0047440	-1.4298843	-5.9039817
H	1.0963584	-2.8110119	-5.6369443
H	3.0663954	-0.7573508	-3.0724505
H	2.7339734	-1.9061127	-4.3656090
H	2.5513583	-2.5303721	-1.3492223
H	2.2091103	-3.7049103	-2.6470741
H	3.8449404	-3.0470042	-2.4565611
H	1.2005789	2.6543462	-1.6735560
H	0.8266480	3.4353807	-3.2081100
H	2.8817942	4.4125404	-2.2220192
H	3.6459377	2.8012654	-2.1234494
H	3.3392308	3.5551339	-3.7059219
H	1.7982968	0.4176429	-5.1387804
H	2.4229113	2.0633518	-5.1248547
H	0.3998252	1.8858926	-6.5804060
H	-0.5717554	1.2975089	-5.2081549
H	0.0429632	2.9634053	-5.2177456
C	1.6536690	0.7885834	7.1844330
C	2.1333825	0.9516870	8.4840569
C	3.4858352	1.2245444	8.7068349
C	4.3530691	1.3331454	7.6162338
C	3.8725669	1.1717415	6.3167464
H	0.5906823	0.6030597	7.0223570
H	1.4453486	0.8736152	9.3273889
H	3.8612833	1.3518219	9.7230551
H	5.4128372	1.5361203	7.7786847
H	4.5646556	1.2317207	5.4753282
C	-6.0434575	-0.0576413	-0.1053107
C	-7.3973534	-0.3478493	-0.2749299
C	-7.8263048	-1.6738782	-0.3784276
C	-6.8868358	-2.7064272	-0.3119212
C	-5.5328648	-2.4156500	-0.1440297
H	-5.7178859	0.9824651	-0.0532325
H	-8.1206138	0.4669588	-0.3354973
H	-8.8851158	-1.9010198	-0.5094792
H	-7.2111998	-3.7459272	-0.3823852
H	-4.8125596	-3.2315249	-0.0654882

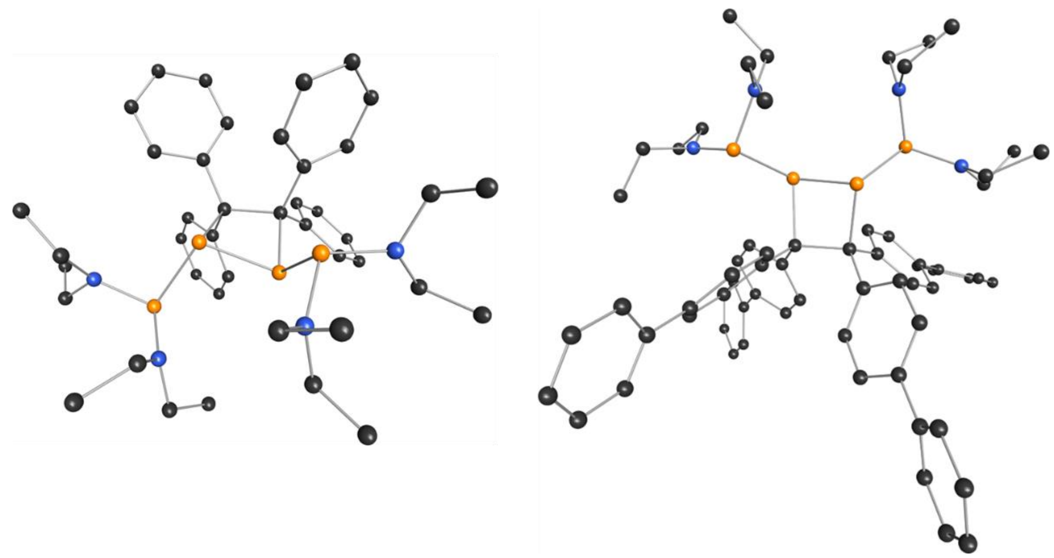

Figure S55. Optimized molecular structures of ***trans*-3a** and ***trans*-4a** (trans configuration) (DFT: def2-SV(P)/BP86).

Below are presented xyz coordinates for optimized geometry of ***trans*-3a**:

C	-1.0147201	1.6671468	-0.2937648
C	0.6260893	1.7327594	-0.3653717
P	-1.1172964	-0.1517060	0.4612245
P	0.9189638	-0.2138271	-0.4227057
P	-2.2904798	-1.4448423	-1.0040639
P	2.1803974	-0.8218147	1.4113091
C	-1.6723850	2.6574280	0.6777087
C	-2.7698570	2.2598682	1.4538834
C	-3.4516435	3.1551071	2.2815197
C	-3.0438665	4.4875987	2.3587274
C	-1.9512309	4.9051206	1.5963527
C	-1.2790783	4.0039660	0.7681062
H	-3.0978040	1.2207223	1.4117889
H	-4.3015739	2.8050371	2.8698086
H	-1.6087549	5.9397874	1.6491118
H	-0.4187701	4.3620754	0.2065312
C	-1.6822201	1.7687373	-1.6746382
C	-2.7849497	2.6128807	-1.8970992
C	-3.3666959	2.7364056	-3.1630569
C	-2.8654753	2.0152881	-4.2462380
C	-1.7829950	1.1560696	-4.0411670
C	-1.2092282	1.0309251	-2.7775755
H	-3.1974577	3.1965146	-1.0763127
H	-4.2170321	3.4077436	-3.2954665
H	-1.3780037	0.5751702	-4.8712467
H	-0.3654439	0.3510376	-2.6499045
C	1.2516336	2.3867000	0.8779926
C	2.2428332	3.3796620	0.7681992
C	2.7638384	4.0204181	1.8970474
C	2.3153954	3.6820865	3.1734861
C	1.3516180	2.6784543	3.3055057

C	0.8359735	2.0393812	2.1788922
H	2.6070475	3.6765637	-0.2137544
H	3.5239369	4.7930857	1.7681192
H	0.9932762	2.3876519	4.2941673
H	0.0816146	1.2629628	2.3163203
C	1.1984265	2.3742409	-1.6378677
C	0.6917679	3.5747532	-2.1664267
C	1.2812846	4.1895416	-3.2725795
C	2.4012875	3.6230540	-3.8851049
C	2.9169819	2.4295371	-3.3785685
C	2.3167607	1.8181774	-2.2745629
H	-0.1934817	4.0331640	-1.7303237
H	0.8526367	5.1145285	-3.6614786
H	3.7866644	1.9639979	-3.8455069
H	2.7209900	0.8738880	-1.9076075
N	-1.6987192	-2.9887803	-0.5090742
C	-1.7092911	-3.5250669	0.8569576
N	-3.8958377	-1.1755912	-0.4110796
C	-4.9462399	-1.5141597	-1.3992402
N	3.7779773	-0.3384671	1.0046047
N	2.0395957	-2.5183828	1.1966314
C	2.1488282	-3.2960202	-0.0422283
C	1.8096357	-3.2946366	2.4287032
H	1.2935094	-4.2270426	2.1404763
H	1.1084173	-2.7336755	3.0664247
C	3.0603489	-3.6275820	3.2507112
C	4.4655407	-0.5514783	-0.2699298
C	5.8650766	-1.1665065	-0.1530875
H	4.5556917	0.4118217	-0.8102727
H	3.8342235	-1.2006415	-0.8930167
C	-1.4294324	-4.0146770	-1.5359135
H	-0.6885138	-4.7081700	-1.0969005
C	-0.8790061	-3.4910501	-2.8594063
H	-2.3321886	-4.6235561	-1.7356438
C	-4.3117242	-1.2960431	0.9920051
C	-5.4977202	-0.4110506	1.3861393
H	-3.4439804	-1.0383265	1.6183384
H	-4.5734439	-2.3471935	1.2307514
C	5.2608048	0.0128717	3.0305641
C	4.4056220	0.6334442	1.9210438
H	4.6405821	-0.6143128	3.6861547
H	6.0718131	-0.6108285	2.6319258
H	5.7090788	0.8052786	3.6498454
H	3.6187979	1.2464543	2.3831890
H	5.0123121	1.3272003	1.3144101
H	2.7823055	-4.2091956	4.1434261
H	3.5545271	-2.7062520	3.5877117
H	3.7902647	-4.2114683	2.6751098
H	5.8418073	-2.1128246	0.4046806
H	6.5627127	-0.4882974	0.3570832
H	6.2718280	-1.3635249	-1.1563965
C	3.3603441	-4.2295543	-0.1509808

H 2.1485221 -2.5875947 -0.8824578
H 1.2303187 -3.9014245 -0.1596335
H 3.3704829 -4.7084284 -1.1421094
H 4.3044248 -3.6833916 -0.0244339
H 3.3264361 -5.0312253 0.5997037
H -4.4828502 -2.0911874 -2.2160979
C -5.6596612 -0.3038958 -2.0041971
H -5.6748653 -2.1948031 -0.9218245
H -6.1701906 0.2960722 -1.2397696
H -4.9385262 0.3462321 -2.5175154
H -6.4109353 -0.6352110 -2.7381882
H -5.3064920 0.6457901 1.1554621
H -5.6820761 -0.5041068 2.4669154
H -6.4204321 -0.7105277 0.8703231
H -0.6154620 -4.3440300 -3.5026220
H -1.6105836 -2.8725569 -3.3939221
H 0.0208403 -2.8803458 -2.6991958
C -2.7502678 -4.6199582 1.1256073
H -0.7068360 -3.9371024 1.0783561
H -1.8562355 -2.6867038 1.5514995
H -3.7687482 -4.2746304 0.8982326
H -2.7189075 -4.9144298 2.1850596
H -2.5569324 -5.5212171 0.5272841
H -3.5657087 5.1901725 3.0100555
H 2.7141126 4.1868978 4.0547158
H 2.8591958 4.1010386 -4.7522800
H -3.3131453 2.1168049 -5.2360943

Below are presented xyz coordinates for optimized geometry of ***trans*-4a**:

C -0.9144392 0.1723268 -0.3202468
C 0.5787859 0.6110974 0.2058259
P -0.7155118 -1.7502732 0.0750820
P 1.4208129 -1.1529704 -0.0398064
P -1.0016304 -2.8812045 -1.8828591
P 2.1893965 -1.8955623 2.0050033
C -2.0890120 0.7374511 0.4872593
C -3.2110628 -0.0578339 0.7568885
C -4.3359182 0.4444810 1.4091236
C -4.3927361 1.7826650 1.8333674
C -3.2699404 2.5851471 1.5667944
C -2.1505260 2.0761144 0.9107590
H -3.2085465 -1.1009143 0.4383969
H -5.1951078 -0.2092217 1.5695496
H -3.2545494 3.6206279 1.9106982
H -1.2996364 2.7379126 0.7620304
C -1.1292146 0.4433615 -1.8154287
C -2.3097943 1.0363205 -2.2964039
C -2.4904813 1.3181896 -3.6515207
C -1.5016007 1.0184478 -4.6015811
C -0.3284243 0.4046815 -4.1269216
C -0.1523830 0.1201802 -2.7774638

H	-3.1126596	1.2884243	-1.6060384
H	-3.4342039	1.7604013	-3.9757425
H	0.4768442	0.1695716	-4.8246156
H	0.7802163	-0.3508937	-2.4630366
C	0.5827175	1.0684641	1.6716668
C	1.2296876	2.2501688	2.0769581
C	1.1742115	2.7029628	3.3960273
C	0.4734986	1.9957822	4.3856784
C	-0.1480114	0.7964985	3.9909920
C	-0.0888096	0.3443281	2.6765973
H	1.7683127	2.8521517	1.3470817
H	1.6596400	3.6473296	3.6488229
H	-0.6693994	0.1901095	4.7332939
H	-0.5847883	-0.5952187	2.4272391
C	1.2973007	1.6478630	-0.6669770
C	0.6554466	2.7985873	-1.1570865
C	1.3481100	3.7749970	-1.8698723
C	2.7239978	3.6547892	-2.1325570
C	3.3675387	2.5031105	-1.6505999
C	2.6665164	1.5285814	-0.9409347
H	-0.4152063	2.9308083	-1.0134183
H	0.7988673	4.6324636	-2.2620389
H	4.4393210	2.3761651	-1.8131960
H	3.2029492	0.6446214	-0.5934626
N	-0.1404728	-4.3216293	-1.4826808
C	-0.3761358	-5.1759568	-0.3131505
N	-2.7132408	-3.1389981	-1.8118844
C	-3.3108618	-3.4510579	-3.1315405
N	3.6192226	-0.9848375	2.2780412
N	2.6206477	-3.4745485	1.4896795
C	3.3234784	-3.8773129	0.2667601
C	2.2634234	-4.5628878	2.4180732
H	2.1541139	-5.4845060	1.8202887
H	1.2702522	-4.3454862	2.8415794
C	3.2448912	-4.8062459	3.5705525
C	4.6902324	-0.7144590	1.3177612
C	6.1044746	-1.0206763	1.8243380
H	4.6560530	0.3502043	1.0123813
H	4.4926148	-1.3055476	0.4123738
C	0.7036469	-4.9596730	-2.5123846
H	1.4520210	-5.5658285	-1.9694063
C	1.4400411	-3.9998870	-3.4426760
H	0.1175342	-5.6754567	-3.1203410
C	-3.4384053	-3.6969129	-0.6626477
C	-4.8966150	-3.2446031	-0.5442686
H	-2.8935711	-3.4025945	0.2473390
H	-3.4253382	-4.8054405	-0.6960300
C	3.4601196	4.6930757	-2.8904937
C	3.1506113	6.0574736	-2.7372407
C	3.8452306	7.0368179	-3.4477122
C	4.8667812	6.6756817	-4.3303887
C	5.1856904	5.3250798	-4.4950554

C	4.4908947	4.3463558	-3.7837756
H	2.3722499	6.3532900	-2.0319550
H	3.5925841	8.0888008	-3.3050935
H	5.4094707	7.4411132	-4.8867382
H	5.9741230	5.0304228	-5.1895755
H	4.7293203	3.2934220	-3.9423192
C	-1.6865787	1.3287615	-6.0378330
C	-2.3790549	2.4837902	-6.4478018
C	-2.5547602	2.7763533	-7.8004883
C	-2.0416855	1.9208534	-8.7793161
C	-1.3509708	0.7700931	-8.3897878
C	-1.1759673	0.4783631	-7.0367333
H	-2.7602802	3.1738617	-5.6934192
H	-3.0872610	3.6832434	-8.0920042
H	-2.1782764	2.1496630	-9.8371436
H	-0.9526446	0.0900423	-9.1447159
H	-0.6576259	-0.4365736	-6.7456613
C	0.3934767	2.4859893	5.7809332
C	1.4751375	3.1596130	6.3792697
C	1.3971369	3.6233311	7.6928392
C	0.2343606	3.4249010	8.4423318
C	-0.8491759	2.7587121	7.8631958
C	-0.7703710	2.2953300	6.5496383
H	2.3976537	3.2989295	5.8133813
H	2.2527048	4.1352779	8.1365820
H	0.1729026	3.7872339	9.4694213
H	-1.7664487	2.6071514	8.4345761
H	-1.6333573	1.8025970	6.0993548
C	-5.5804463	2.3217020	2.5357342
C	-6.3135948	1.5269027	3.4367422
C	-7.4333773	2.0337863	4.0968624
C	-7.8482572	3.3492309	3.8722777
C	-7.1311509	4.1519312	2.9808990
C	-6.0115019	3.6442768	2.3213774
H	-5.9834920	0.5070473	3.6410312
H	-7.9798055	1.4004830	4.7977452
H	-8.7235746	3.7460369	4.3883135
H	-7.4504477	5.1780190	2.7911634
H	-5.4754560	4.2724153	1.6080940
C	4.2528629	-0.8457034	4.7290134
C	3.6311781	-0.1649869	3.5054524
H	3.6734821	-1.7375608	5.0060729
H	5.2905034	-1.1567114	4.5497238
H	4.2424006	-0.1592985	5.5895700
H	2.5988453	0.1243359	3.7491602
H	4.1639859	0.7742215	3.2784846
H	2.8906684	-5.6381243	4.1989391
H	3.3218034	-3.9126533	4.2046576
H	4.2522042	-5.0532815	3.2109844
H	6.1896366	-2.0592312	2.1724680
H	6.3877215	-0.3595789	2.6547524
H	6.8335573	-0.8636638	1.0152320

C	4.7248454	-4.4703612	0.4553183
H	3.3767407	-2.9995446	-0.3923861
H	2.7007251	-4.6182233	-0.2694426
H	5.1754276	-4.6740467	-0.5281008
H	5.3854286	-3.7822807	0.9992200
H	4.6950424	-5.4212514	1.0051329
H	-2.4957449	-3.6818106	-3.8366098
C	-4.1605823	-2.3252981	-3.7227450
H	-3.9051790	-4.3785993	-3.0404535
H	-5.0108704	-2.0703640	-3.0770948
H	-3.5541409	-1.4194426	-3.8558939
H	-4.5548649	-2.6241610	-4.7064965
H	-4.9805625	-2.1493902	-0.5262822
H	-5.3290833	-3.6420077	0.3861085
H	-5.5101056	-3.6184202	-1.3754655
H	2.1152335	-4.5749701	-4.0938911
H	0.7491653	-3.4341681	-4.0799834
H	2.0363372	-3.2752364	-2.8700724
C	-1.0764501	-6.5095001	-0.6054228
H	0.5980685	-5.3922780	0.1639349
H	-0.9552575	-4.5986829	0.4204431
H	-2.0442618	-6.3574904	-1.1039425
H	-1.2583444	-7.0514758	0.3344156
H	-0.4638864	-7.1583916	-1.2467975

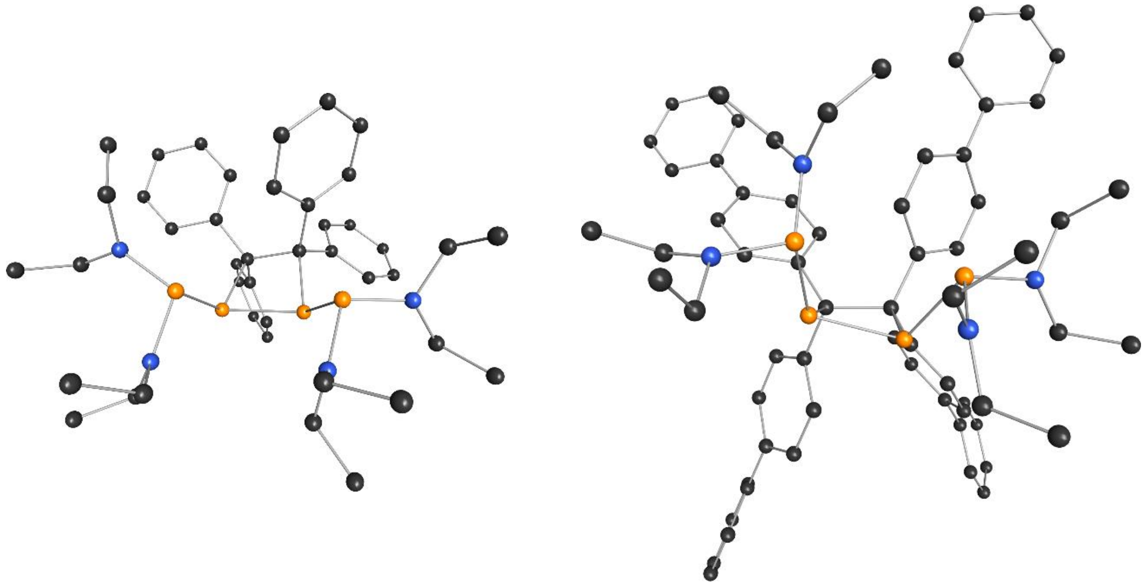

Figure S56. Optimized molecular structures of ***cis*-3a** and ***cis*-4a** (cis configuration) (DFT: def2-SV(P)/BP86).

Below are presented xyz coordinates for optimized geometry of ***cis*-3a**:

C	-1.2253276	1.8201260	-0.1607045
C	0.3981897	1.9574774	-0.0344783
P	-1.3746690	-0.0329956	-0.8615878
P	0.7933181	0.4395881	-1.2054558
P	-1.3796660	-1.8376045	0.6304261
P	2.3399599	-0.8930386	-0.1448522
C	-2.0921072	2.0930360	1.0646018
C	-3.4280094	1.6525523	1.0256518
C	-4.3492682	2.0077374	2.0088680
C	-3.9549750	2.8070541	3.0859262
C	-2.6319396	3.2409929	3.1537631
C	-1.7148517	2.8949669	2.1539750
H	-3.7588556	1.0525013	0.1753102
H	-5.3829615	1.6662814	1.9291296
H	-2.3010929	3.8648599	3.9857112
H	-0.6962415	3.2654797	2.2377183
C	-1.7707911	2.6804877	-1.3383982
C	-2.6722856	3.7375319	-1.1175767
C	-3.1663902	4.5128244	-2.1703195
C	-2.7744739	4.2567735	-3.4834950
C	-1.8724650	3.2187815	-3.7246783
C	-1.3827040	2.4454893	-2.6718227
H	-3.0007187	3.9726610	-0.1070934
H	-3.8637375	5.3237182	-1.9524870
H	-1.5434975	3.0023370	-4.7424921
H	-0.6696898	1.6516533	-2.8988956
C	0.9750593	1.7571307	1.3739680
C	1.9907996	2.5949912	1.8737670
C	2.5153678	2.4234902	3.1595434

C	2.0466384	1.4031714	3.9858257
C	1.0535712	0.5485826	3.4993568
C	0.5328596	0.7226777	2.2193819
H	2.3791251	3.4035293	1.2574336
H	3.2970980	3.1000182	3.5099140
H	0.6803941	-0.2666500	4.1212458
H	-0.2315368	0.0302413	1.8700799
C	0.9292197	3.2686912	-0.6326055
C	0.4352336	4.5106100	-0.1930048
C	0.9500676	5.7111181	-0.6819845
C	1.9816098	5.7065577	-1.6252865
C	2.4844984	4.4852160	-2.0721395
C	1.9594403	3.2856893	-1.5802895
H	-0.3676620	4.5455500	0.5424290
H	0.5384802	6.6566435	-0.3249835
H	3.2859245	4.4588577	-2.8125942
H	2.3472128	2.3383856	-1.9570886
N	-2.7063543	-1.7076495	1.7085702
C	-2.4030487	-1.9142931	3.1332786
N	3.7777831	-0.0662729	-0.6206805
N	2.1902632	-2.2796275	-1.1473732
C	1.6612360	-2.3803794	-2.5123504
C	2.5637275	-3.5504066	-0.5029126
H	1.9642321	-4.3517391	-0.9684440
H	2.2584088	-3.5024299	0.5556284
C	4.0511556	-3.9193758	-0.5688354
C	4.1814920	0.2491161	-1.9908603
C	5.5009730	-0.3887481	-2.4428037
H	4.2663192	1.3472342	-2.1081373
H	3.3715361	-0.0708587	-2.6617551
C	-4.1223747	-1.6324994	1.3437804
C	-4.9545544	-2.8474179	1.7732562
C	5.6675310	-0.4420116	1.0318248
C	4.6010242	0.5000965	0.4614621
H	5.1935565	-1.3258274	1.4817720
H	6.3748013	-0.7848635	0.2651118
H	6.2397110	0.0697797	1.8211753
H	3.9396060	0.8165989	1.2812074
H	5.0714513	1.4223243	0.0788919
H	4.2245571	-4.8792040	-0.0575586
H	4.6633359	-3.1552333	-0.0721264
H	4.4041077	-4.0168774	-1.6040977
H	5.4756456	-1.4804075	-2.3224486
H	6.3555780	-0.0014259	-1.8711830
H	5.6837885	-0.1587433	-3.5035939
C	2.6119629	-2.9673385	-3.5623081
H	1.3550422	-1.3712435	-2.8280667
H	0.7375180	-2.9899821	-2.4933114
H	2.1231108	-2.9546994	-4.5484068
H	3.5433524	-2.3890416	-3.6348301
H	2.8738264	-4.0114591	-3.3404868
C	-2.8507513	-0.7798528	4.0557627

H -4.6709406 3.0869256 3.8599026
H 2.4508379 1.2703720 4.9904023
H 2.3824638 6.6453108 -2.0104132
H -3.1626240 4.8580097 -4.3070886
H -3.9416115 -0.6440529 4.0417438
H -2.3897186 0.1745350 3.7687716
H -2.5623730 -1.0091062 5.0926476
H -5.0367665 -2.9213448 2.8666596
H -5.9760390 -2.7578696 1.3751802
H -4.5189082 -3.7851816 1.4023571
H -2.8511033 -2.8654269 3.4786415
H -1.3130352 -2.0472963 3.2078747
H -4.5739156 -0.7221605 1.7741130
H -4.1795986 -1.5161689 0.2525737
N -1.7859757 -2.9624872 -0.6131771
C -2.6949558 -2.8255981 -1.7620503
C -1.1032446 -4.2624441 -0.4997547
H -0.0776110 -4.0796439 -0.1477429
H -1.0209834 -4.6879656 -1.5157231
C -1.7600821 -5.2798840 0.4422175
H -3.0487321 -1.7867725 -1.7901487
H -2.1091546 -2.9661797 -2.6910748
C -3.8908246 -3.7838274 -1.8008625
H -1.7901385 -4.8883850 1.4687417
H -1.1771737 -6.2140651 0.4548299
H -2.7866987 -5.5237126 0.1395079
H -4.5233355 -3.6871652 -0.9084057
H -4.5086333 -3.5559199 -2.6829192
H -3.5768247 -4.8335106 -1.8856678

Below are presented xyz coordinates for optimized geometry of ***cis*-4a**:

C -0.8662918 -0.9245072 0.0717879
C 0.7143062 -0.7285366 -0.2864300
P -0.8815564 -0.1041078 1.9058598
P 1.3013097 -0.3866449 1.5482099
P -1.1842637 2.0354874 2.6635708
P 2.3102097 1.6517877 1.8378356
C -1.9221783 -0.3395801 -0.8531021
C -3.2244225 -0.1736971 -0.3425831
C -4.2849482 0.2441080 -1.1396151
C -4.0998745 0.5294997 -2.5061591
C -2.8056624 0.3598115 -3.0215732
C -1.7452370 -0.0694298 -2.2190612
H -3.4091840 -0.4006031 0.7094018
H -5.2710351 0.3735658 -0.6901235
H -2.6225017 0.5349151 -4.0830316
H -0.7698306 -0.1961563 -2.6834228
C -1.2104462 -2.4049041 0.3556387
C -2.1611032 -3.1021498 -0.4113372
C -2.4813153 -4.4348903 -0.1528122
C -1.8717206 -5.1458365 0.8924149

C	-0.9134839	-4.4565099	1.6564344
C	-0.5932488	-3.1276707	1.3956964
H	-2.6734760	-2.6012489	-1.2309324
H	-3.2445808	-4.9212367	-0.7629603
H	-0.3876345	-4.9781066	2.4579590
H	0.1726566	-2.6506878	2.0099408
C	1.0551457	0.4558023	-1.1953439
C	1.9715508	0.3270409	-2.2574157
C	2.2536235	1.3877033	-3.1189697
C	1.6391531	2.6400842	-2.9652543
C	0.7561163	2.7825663	-1.8785828
C	0.4799947	1.7280595	-1.0131933
H	2.4573788	-0.6294904	-2.4410403
H	2.9403913	1.2205247	-3.9508055
H	0.2924228	3.7521480	-1.6911144
H	-0.1933062	1.9045205	-0.1749483
C	1.3409985	-2.0141539	-0.8431319
C	0.7957227	-2.6418160	-1.9784178
C	1.3789872	-3.7749087	-2.5377873
C	2.5434798	-4.3446768	-1.9899824
C	3.0875996	-3.7228636	-0.8556665
C	2.4970094	-2.5865259	-0.2991654
H	-0.1123337	-2.2462855	-2.4332278
H	0.9038900	-4.2467339	-3.3994902
H	4.0023502	-4.1190221	-0.4112574
H	2.9418572	-2.1405982	0.5912070
N	-1.4599234	3.2813329	1.5369545
C	-2.4287847	3.2918842	0.4315844
N	3.7924062	1.4951653	0.9884885
N	2.5953538	1.4193364	3.5159884
C	3.1576474	0.2447764	4.1929793
C	2.1956168	2.5315573	4.3941797
H	2.0131021	2.1069240	5.3961831
H	1.2217717	2.9156901	4.0475519
C	3.1962165	3.6878855	4.4903214
C	4.6011069	0.2799500	0.8576482
C	6.1059067	0.4792413	1.0642426
H	4.4364626	-0.1701682	-0.1415580
H	4.2319104	-0.4502817	1.5911992
C	-0.9520625	4.6025962	1.9608497
C	-0.1911855	5.3586576	0.8722211
C	4.9726045	3.6884439	0.5372886
C	4.0779005	2.5622351	0.0100378
H	4.4922958	4.1962810	1.3852008
H	5.9482788	3.3163731	0.8767606
H	5.1451296	4.4365706	-0.2518770
H	3.1245957	2.9927836	-0.3307682
H	4.5333367	2.0957560	-0.8797814
H	2.8161085	4.4627313	5.1743527
H	3.3431672	4.1514558	3.5047712
H	4.1768584	3.3572131	4.8577415
H	6.3202611	0.9277962	2.0441782

H	6.5408574	1.1257438	0.2897188
H	6.6199481	-0.4918995	1.0079868
C	4.5334481	0.4574213	4.8350889
H	3.2077081	-0.5756199	3.4641172
H	-2.9944733	0.5337176	5.2446239
H	4.8980454	-0.4895287	5.2617110
H	5.2669568	0.8091194	4.0970657
H	4.4926641	1.1919487	5.6514975
C	-3.6805911	4.1472170	0.6604397
H	-3.4393408	5.2167321	0.7387517
H	-4.2118931	3.8552975	1.5764793
H	-4.3678964	4.0270741	-0.1895385
H	-0.8273727	5.5970271	0.0077074
H	0.1788044	6.3124288	1.2760776
H	0.6701995	4.7736769	0.5236435
H	-1.9241078	3.6465639	-0.4843647
H	-2.7139063	2.2521508	0.2289409
H	-1.7808101	5.2275537	2.3424944
H	-0.2804143	4.4278968	2.8140087
N	-2.6155661	1.8048348	3.6045993
C	-3.8866603	1.3300635	3.0480793
C	-2.3562648	1.4011449	5.0034865
H	-1.3189535	1.0407544	5.0857830
C	-2.5729594	2.5297619	6.0145492
H	-3.9224323	1.6271989	1.9923149
H	-3.9096688	0.2204585	3.0664433
C	-5.1294340	1.8712697	3.7583949
H	-1.8953574	3.3685407	5.8013022
H	-2.3674395	2.1750243	7.0364647
H	-3.6019175	2.9121415	5.9839244
H	-5.1431939	2.9704455	3.7509346
H	-6.0360883	1.5097452	3.2511512
H	-5.1825139	1.5360795	4.8033397
C	3.1648811	-5.5512633	-2.5840493
C	3.1868315	-5.7436255	-3.9781066
C	3.7744177	-6.8781800	-4.5385951
C	4.3542278	-7.8496276	-3.7180745
C	4.3394213	-7.6744732	-2.3316469
C	3.7519421	-6.5394773	-1.7719920
H	2.7599248	-4.9797313	-4.6300971
H	3.7867856	-7.0002596	-5.6229649
H	4.8130015	-8.7372495	-4.1558241
H	4.7790126	-8.4316997	-1.6803388
H	3.7198233	-6.4279704	-0.6870391
C	-2.2200222	-6.5564449	1.1782051
C	-2.5168333	-7.4566484	0.1375865
C	-2.8452730	-8.7853929	0.4073718
C	-2.8855881	-9.2479605	1.7256193
C	-2.5932413	-8.3672714	2.7706221
C	-2.2644064	-7.0386631	2.4999155
H	-2.4607545	-7.1145630	-0.8970158
H	-3.0614222	-9.4662635	-0.4176156

H	-3.1421400	-10.2870062	1.9368274
H	-2.6297603	-8.7146882	3.8045409
H	-2.0638522	-6.3537727	3.3253898
C	-5.2221286	0.9804887	-3.3614130
C	-5.0168051	1.9133286	-4.3953457
C	-6.0729322	2.3367401	-5.2026813
C	-7.3619680	1.8381779	-4.9958590
C	-7.5830610	0.9111719	-3.9736439
C	-6.5264373	0.4880171	-3.1669475
H	-4.0200110	2.3292323	-4.5504706
H	-5.8894478	3.0666707	-5.9928436
H	-8.1878801	2.1689584	-5.6269842
H	-8.5832527	0.5070421	-3.8091479
H	-6.7073609	-0.2576052	-2.3909701
C	1.9122852	3.7605092	-3.8939810
C	3.1846275	3.9349635	-4.4711387
C	3.4402823	4.9897461	-5.3476834
C	2.4296933	5.8997541	-5.6696974
C	1.1607407	5.7418615	-5.1057957
C	0.9059582	4.6860392	-4.2302590
H	3.9901408	3.2474318	-4.2084237
H	4.4376123	5.1070019	-5.7748734
H	2.6293298	6.7250014	-6.3545376
H	0.3607367	6.4405367	-5.3564886
H	-0.0964316	4.5583349	-3.8185906
H	2.4473570	-0.0893885	4.9730828

Table S9. Selected Results of Population Analyses Based on the Occupation Numbers for **3** to **4** (DFT: def2-TZVP/BP86).

Compound	Two center shared electron numbers					Atomic charges with multicenter corrections					
	N^1-P	N^2-P	N-$P_{avg.}$	P-P	P-C	N^1	N^2	$N_{avg.}$	P^2	P^1	C
3	1.15	1.13	1.14	1.08	1.80	-0.18	-0.17	-0.17	0.29	-0.11	-0.03
4	1.05	1.25	1.15	1.00	1.81	-0.18	-0.27	-0.23	0.27	-0.14	0.01

Table S10. Selected Wiberg bond indices for **3** and **4** (DFT: def2-TZVP/BP86).

Compound	R^1	R^2	R^3	Wiberg bond index				
				N^1-P	N^2-P	N-$P_{avg.}$	P^2-P^1	P^1-C
3	Et_2N	Ph	Ph	1.08	1.10	1.09	1.04	1.67
4	Et_2N	Ph(C_6H_5)	Ph(C_6H_5)	1.11	0.97	1.04	1.01	1.66

D.3. Ruthenium complexes

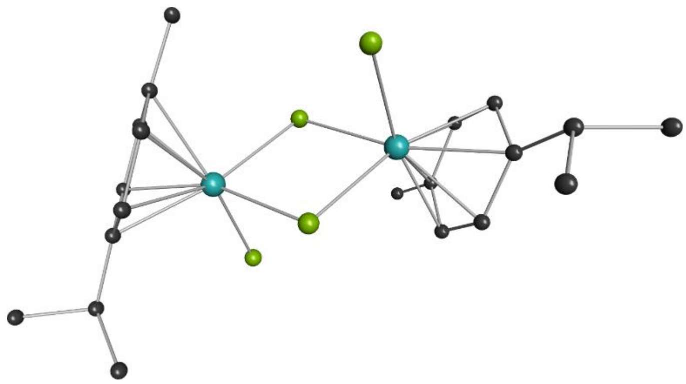

Figure S57. Optimized molecular structure of [(*p*-cym)$RuCl_2$]$_2$ (DFT: def2-TZVP/BP86).

Below are presented xyz coordinates for optimized geometry of [(*p*-cym)$RuCl_2$]$_2$:

Ru	-1.7740443	-0.5945329	-0.5995969
Cl	-0.8544170	-2.8007013	-0.6072918
Cl	0.0000000	0.0000000	0.9944550
Cl	0.0000000	-0.0000000	-2.1973321
C	-3.0473152	1.0231346	-1.4281816
C	-3.3910943	-0.2575001	-1.9959087
H	-3.3216152	-0.3951134	-3.0757351
C	-3.6983470	-1.3708553	-1.1740899
H	-3.8484401	-2.3479705	-1.6344507
C	-3.6677819	-1.2735483	0.2632247
C	-3.2964986	-0.0129118	0.8113869
H	-3.1315690	0.0719837	1.8851197
C	-3.0075350	1.1234917	-0.0152418
H	-2.6286526	2.0373658	0.4421641
C	-2.6699265	2.1841331	-2.2998411
H	-3.5579437	2.8088975	-2.4894412
H	-2.2783733	1.8437266	-3.2663430
H	-1.8981780	2.8005307	-1.8201352
C	-3.9666111	-2.4994984	1.1029287
H	-3.5518110	-3.3544289	0.5432772
C	-5.4934256	-2.6840944	1.2147440
H	-5.9515675	-1.8504574	1.7684124
H	-5.7250660	-3.6150344	1.7517678
H	-5.9715786	-2.7357050	0.2260583
C	-3.3013290	-2.4888627	2.4827834
H	-2.2165818	-2.3401108	2.3972619
H	-3.4730831	-3.4517807	2.9835072
H	-3.7180430	-1.7060066	3.1350590
Ru	1.7740443	0.5945329	-0.5995969
Cl	0.8544170	2.8007013	-0.6072918
C	3.0473152	-1.0231346	-1.4281816
C	3.3910943	0.2575001	-1.9959087
C	3.6983470	1.3708553	-1.1740899
H	3.3216152	0.3951134	-3.0757351

H	3.8484401	2.3479705	-1.6344507
C	3.6677819	1.2735483	0.2632247
C	3.2964986	0.0129118	0.8113869
C	3.9666111	2.4994984	1.1029287
H	3.5518110	3.3544289	0.5432772
C	5.4934256	2.6840944	1.2147440
H	5.9515675	1.8504574	1.7684124
H	5.7250660	3.6150344	1.7517678
H	5.9715786	2.7357050	0.2260583
C	3.3013290	2.4888627	2.4827834
H	2.2165818	2.3401108	2.3972619
H	3.4730831	3.4517807	2.9835072
H	3.7180430	1.7060066	3.1350590
H	3.1315690	-0.0719837	1.8851197
C	3.0075350	-1.1234917	-0.0152418
C	2.6699265	-2.1841331	-2.2998411
H	3.5579437	-2.8088975	-2.4894412
H	2.2783733	-1.8437266	-3.2663430
H	1.8981780	-2.8005307	-1.8201352
H	2.6286526	-2.0373658	0.4421641

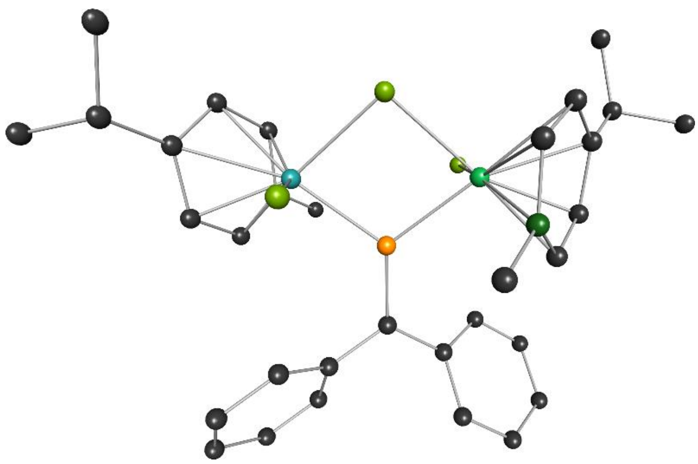

Figure S58. Optimized molecular geometry of **5** (DFT: def2-TZVP/BP86).

Below are presented xyz coordinates for optimized geometry of **5**:

H	1.2389587	-1.9482467	-2.1595505
C	0.5320584	2.6704177	-1.8806426
C	-0.9765066	1.4640282	-4.0745406
C	0.3656140	1.0357161	-3.7479216
H	0.8161558	0.2160279	-4.3069316
C	1.1167096	1.6589061	-2.7143970
H	2.1442812	2.7150283	-0.4514431
C	-1.7010721	0.7884546	-5.2198799
H	-1.4504883	-0.2833169	-5.1367578
C	-3.2259424	0.9096715	-5.1573791
H	-3.6153624	0.5261253	-4.2047299
H	-3.6783412	0.3213825	-5.9677592
Cl	-1.4196319	-1.4282942	-2.4362697
Ru	-0.6856209	0.7988515	-1.8696672
C	2.7506851	-0.8890174	-1.0298841
C	4.0911316	-0.4443580	-1.0502192
H	4.4893745	0.0824644	-0.1815956
C	4.9053698	-0.6611574	-2.1613992
H	5.9353083	-0.2999668	-2.1543179
C	4.4075649	-1.3401747	-3.2787070
H	5.0473584	-1.5189432	-4.1441758
C	3.0875181	-1.8006377	-3.2675757
H	2.6935796	-2.3516347	-4.1237610
C	2.2672557	-1.5812238	-2.1588194
H	2.1307304	1.3144567	-2.5127786
C	-0.8412978	2.9582523	-2.1068526
H	-1.3627623	3.6132821	-1.4084835
C	-1.5643178	2.4174557	-3.2301247
H	-2.6139882	2.6806233	-3.3505909
C	1.3116419	3.3448172	-0.7897924
H	1.7327287	4.2918539	-1.1646875
C	-1.1494687	1.3118216	-6.5621776
H	-1.3845864	2.3787015	-6.6941095
H	-1.6004310	0.7585905	-7.3982846

H	-0.0584500	1.1958267	-6.6293386
H	-3.5609864	1.9507213	-5.2849802
C	1.9054020	-0.6428046	0.1648627
C	2.5290149	-0.8929357	1.4880738
C	2.3934819	0.0100984	2.5620716
H	1.8114971	0.9230519	2.4210300
C	2.9943271	-0.2513915	3.7953944
H	2.8858968	0.4705115	4.6071296
C	-1.4800912	-2.3501589	1.7978663
C	-2.7646754	-1.7417842	1.7945558
H	-3.4602801	-1.9876717	0.9918360
C	-3.1791795	-0.8169952	2.8192024
H	-4.1793275	-0.3901170	2.7634547
C	-2.2742519	-0.3651023	3.7911468
C	-0.9139670	-0.8468861	3.6971580
H	-0.1535499	-0.4339676	4.3593458
C	-0.5410985	-1.8500797	2.7614362
H	0.4922359	-2.1952279	2.7360076
C	-1.1076172	-3.4153428	0.8081980
H	-1.4065437	-4.4032115	1.1948968
H	-0.0239880	-3.4333511	0.6358600
H	-1.6031882	-3.2507969	-0.1574683
C	-2.6117874	0.6693445	4.8443442
H	-1.7595041	1.3706625	4.8530948
C	-3.8733694	1.4831218	4.5443759
H	-4.7800598	0.8588701	4.5675268
H	-3.8052651	1.9731699	3.5637880
H	-3.9990710	2.2665760	5.3045908
C	-2.6953629	-0.0083354	6.2276946
H	-3.5398094	-0.7126897	6.2694321
H	-2.8448192	0.7480509	7.0113423
H	-1.7786785	-0.5659326	6.4663898
Cl	-0.6361564	2.1224342	2.2518915
Cl	-2.5232931	0.8480269	-0.2219694
P	0.2936938	-0.0986229	0.0243116
Ru	-1.3078087	-0.1262047	1.6935517
C	3.7458651	-1.4143603	3.9886970
H	4.2184729	-1.6125374	4.9518691
C	3.8989518	-2.3148466	2.9289832
H	4.4865103	-3.2246510	3.0642806
C	3.3048962	-2.0549518	1.6943702
H	3.4330942	-2.7609724	0.8723324
H	0.6746333	3.5615055	0.0775698

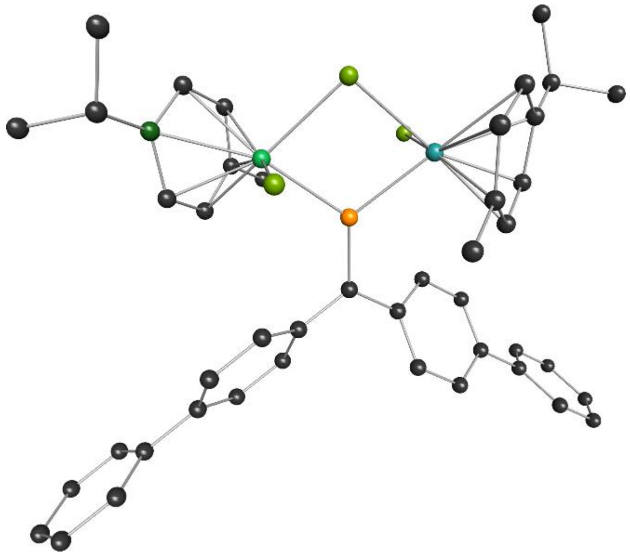

Figure S59. Optimized molecular geometry of **6** (DFT: def2-TZVP/BP86).

Below are presented xyz coordinates for optimized geometry of **6**:

C	-0.0979505	-0.5949075	-0.4613122
C	1.0352739	-1.1926573	-1.2054786
C	2.0046431	-0.4066579	-1.8610680
H	1.9297479	0.6818665	-1.8162077
C	3.0575994	-0.9968609	-2.5565551
H	3.7949015	-0.3545171	-3.0419974
C	3.1990257	-2.3952697	-2.6356007
C	2.2252381	-3.1801788	-1.9875257
H	2.2825097	-4.2682275	-2.0512242
C	1.1673302	-2.5957355	-1.2980428
H	0.4220906	-3.2331330	-0.8195246
C	4.3185286	-3.0167008	-3.3790480
C	4.8230625	-2.4312171	-4.5560993
H	4.3616861	-1.5205175	-4.9411688
C	5.8787970	-3.0161642	-5.2556227
H	6.2449085	-2.5477340	-6.1706966
C	6.4583408	-4.2020172	-4.7960743
H	7.2836845	-4.6595465	-5.3431802
C	5.9696540	-4.7966802	-3.6295111
H	6.4192228	-5.7182502	-3.2561080
C	4.9134037	-4.2116862	-2.9308718
H	4.5586828	-4.6726943	-2.0075840
C	-1.4320931	-1.2060789	-0.6647976
C	-1.8565511	-1.5772282	-1.9597098
H	-1.1876732	-1.4140422	-2.8062189
C	-3.1073505	-2.1468415	-2.1769556
H	-3.3916419	-2.4357360	-3.1903077
C	-3.9951481	-2.3917927	-1.1110456
C	-3.5644690	-2.0370703	0.1814912
H	-4.2260018	-2.2068182	1.0331842
C	-2.3163204	-1.4595691	0.4035257

H	-2.0179188	-1.1920618	1.4193346
C	-5.3222092	-3.0070169	-1.3404415
C	-5.8838448	-3.8943628	-0.4024134
H	-5.3180804	-4.1545896	0.4935175
C	-7.1351133	-4.4722933	-0.6176612
H	-7.5439160	-5.1644187	0.1203390
C	-7.8581323	-4.1777038	-1.7768586
H	-8.8365170	-4.6296433	-1.9452953
C	-7.3153135	-3.2992961	-2.7186695
H	-7.8737654	-3.0550333	-3.6238202
C	-6.0637196	-2.7222078	-2.5031788
H	-5.6632873	-2.0181277	-3.2344224
C	-2.0611585	3.0320518	-0.5585957
C	-2.9020990	1.9076730	-0.2608790
H	-2.9296826	1.0598932	-0.9449865
C	-3.6379586	1.8426692	0.9538531
H	-4.2035365	0.9394203	1.1808555
C	-3.6560603	2.9450964	1.8895400
C	-2.7959891	4.0208195	1.6237778
H	-2.6726231	4.8160122	2.3573382
C	-1.9585594	4.0271970	0.4509960
H	-1.2246954	4.8244516	0.3299879
C	-1.2854046	3.1233914	-1.8402159
H	-1.8543439	3.7121507	-2.5780770
H	-1.1074267	2.1279443	-2.2665943
H	-0.3116390	3.6048651	-1.6813258
C	-4.5020224	2.8286250	3.1401590
H	-4.3727803	1.7893102	3.4887661
C	-4.0680184	3.7532182	4.2805837
H	-3.0126632	3.5943215	4.5402295
H	-4.2158830	4.8145567	4.0277598
C	-5.9877998	3.0370191	2.7808606
H	-6.6187306	2.8603206	3.6635166
H	-6.3170433	2.3514895	1.9872992
H	-6.1674416	4.0661106	2.4348499
C	2.5218642	-0.2881134	2.7109367
C	2.7826701	0.9148864	3.4217137
H	2.2153129	1.1223021	4.3293825
C	3.7752756	1.8645450	2.9859365
H	3.9318262	2.7645943	3.5783691
C	4.4312558	1.7085087	1.7559262
C	4.0442150	0.5763181	0.9437002
H	4.4441475	0.4808461	-0.0654061
C	3.1556421	-0.4210949	1.4299334
H	2.9037193	-1.2663048	0.7898409
C	1.5877316	-1.3346465	3.2444893
H	2.1401984	-2.0261731	3.9012647
H	1.1458842	-1.9222901	2.4297893
H	0.7700437	-0.8808796	3.8194619
C	5.4211383	2.7070634	1.1936626
H	5.1398432	2.8376681	0.1342957
C	5.3676958	4.0860224	1.8566494

H	4.3560402	4.5108963	1.8074051
H	6.0479749	4.7742993	1.3361684
H	5.6864263	4.0480628	2.9098384
C	6.8434726	2.1118643	1.2466127
H	7.1716796	1.9715447	2.2875066
H	7.5555071	2.7893075	0.7541483
H	6.8986595	1.1376746	0.7406488
Cl	-1.6573881	0.6791296	3.3437428
Cl	0.5122495	3.0689088	2.4026126
Cl	2.2711906	2.9983502	-0.4605018
P	0.1243770	0.7400195	0.5836318
Ru	-1.5386053	2.1176159	1.4110448
Ru	2.1425407	1.4961264	1.4225089
H	-4.6703436	3.5457594	5.1758931

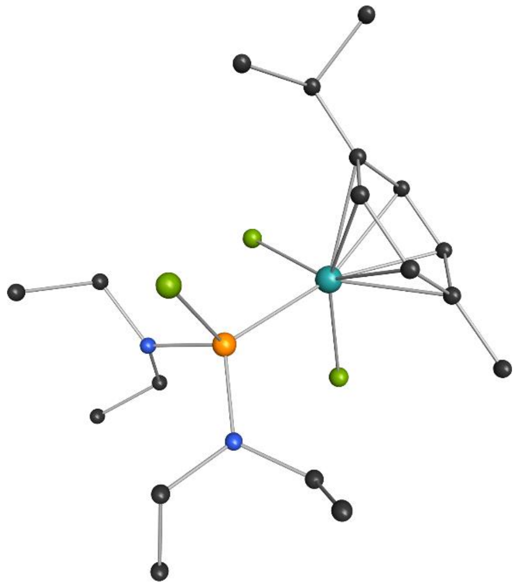

Figure S60. Optimized molecular structure of [RuC_2(η^6-cymene){$PCl(NEt_2)_2$}] (DFT: def2-TZVP/BP86).

Below are presented xyz coordinates for optimized geometry of **7**:

Ru	-0.0858681	1.1315171	-1.1079358
Cl	1.5261435	-0.6368194	1.6965423
P	-0.2017928	-0.6648839	0.3842434
Cl	-1.8894334	0.0297485	-2.2716594
Cl	-1.7813334	2.2057021	0.2291908
N	-0.1793671	-2.2229163	-0.2298052
C	2.0139048	1.7293709	-0.7171788
H	2.5884009	1.4692395	0.1695252
N	-1.4051584	-0.7718093	1.5685133
C	1.2324987	2.9109658	-0.7286816
C	0.4315291	3.1660495	-1.9045095
H	-0.2498034	4.0168486	-1.9010631
C	0.4028932	2.2700647	-2.9796001
H	-0.2936140	2.4372777	-3.8014055
C	1.9846156	0.8109045	-1.8155699
H	2.5682312	-0.1083288	-1.7589842
C	1.1749664	1.0515176	-2.9570690
C	1.9808301	5.1963877	-0.0572491
H	3.0475864	4.9814358	-0.2228463
H	1.9082444	5.9742307	0.7162124
H	1.5709397	5.6099125	-0.9895696
C	1.2252104	3.9292874	0.3939089
H	0.1647145	4.1914994	0.5495583
C	-0.2340503	-3.3860111	0.6793619
H	-0.5553944	-3.0156693	1.6592706
H	0.7821490	-3.7963418	0.8087796
C	1.7769109	3.4075533	1.7225506
H	1.2601071	2.4934013	2.0422928
H	1.6381883	4.1664883	2.5049303
H	2.8552388	3.1936770	1.6633768

C	1.1234997	0.1114878	-4.1257035
H	1.6968654	-0.8034887	-3.9328247
H	1.5486220	0.5957392	-5.0186221
H	0.0815651	-0.1625710	-4.3489278
C	-1.1847459	-4.4844779	0.2024648
H	-0.8547450	-4.9481691	-0.7374128
H	-2.2009151	-4.0956052	0.0515771
H	-1.2302126	-5.2790366	0.9609771
C	-2.7777714	-1.0199901	1.0528953
H	-2.6878039	-1.5032971	0.0716129
H	-3.2666606	-0.0488703	0.8708587
C	-1.3433388	0.0758690	2.7821864
H	-2.2922839	0.6296888	2.8428256
H	-0.5682472	0.8427114	2.6600045
C	0.2978767	-2.5014527	-1.5917470
H	0.2232819	-1.5657626	-2.1554023
H	-0.4180984	-3.1893676	-2.0686183
C	-1.0894450	-0.7170647	4.0658305
H	-0.1124506	-1.2168747	4.0305985
H	-1.8611214	-1.4801736	4.2339430
H	-1.0923908	-0.0350901	4.9299116
C	1.7125511	-3.0832550	-1.6682033
H	2.0082790	-3.1970737	-2.7214380
H	1.7839668	-4.0768612	-1.2041303
H	2.4441291	-2.4305526	-1.1706114
C	-3.6255744	-1.8818504	1.9872116
H	-4.6054318	-2.0592497	1.5200234
H	-3.8082937	-1.3882439	2.9516447
H	-3.1585938	-2.8574176	2.1839451

Table S11. Comparison between calculated (DFT) and experimental (XRD) distances for **5** and **6**.

Bond	**Distance [Å]**			
	5		**6**	
	DFT	XRD	DFT	XRD
Ru^1-P	2.322	2.303(2)	2.321	2.3163(9)
Ru^1-P	2.322	2.309(2)	2.321	2.3226(9)
Ru-$P_{avg.}$	2.322	2.306(2)	2.321	2.31945(9)
P=C	1.718	1.689(8)	1.721	1.697(3)

Table S12. Selected DFT calculated data for **5** and **6** (DFT: def2-TZVP/BP86).

Compound	**Unit**	**5**	**6**
Total energy	H	-3191.33838	-3653.126368
Dipole moment	D	0.22	0.06
HOMO-LUMO	eV	1.98	1.91

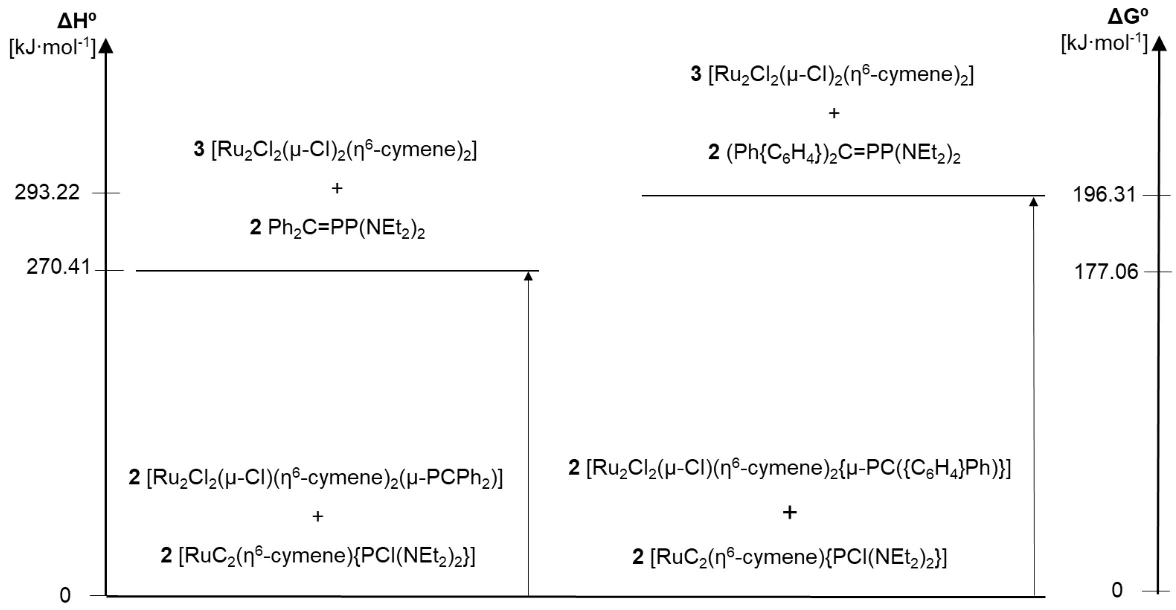

Figure S61. Energetic diagram of the reactions of Ph_2C=P-P$(NEt_2)_2$ (**3**) or $(biph)_2C$=P-P$(NEt_2)_2$ (**4**) with [(*p*-cym)$Ru_2Cl_2]_2$.

Table S13. Selected DFT calculated standard thermodynamic parameters.

Compound	**Total energy**	**HOMO-LUMO gap**	**°H**	**°S**	**°G**
	[kJ·mol^{-1}]	[eV]	[kJ·mol^{-1}]	[kJ·mol^{-1}·K]	[kJ·mol^{-1}]
5	-8384355.445	2.03	-8382662.195	1.08679	-8382986.221
6	-9598096.882	1.94	-9595970.202	1.29749	-9596357.048
7	-6914639.877	2.30	-6913283.707	0.88323	-6913547.042
[(*p*-cym)$Ru_2Cl_2]_2$	-7379498.691	1.98	-7378311.541	0.87313	-7378571.865

To cast some light on the bonding situation in **5** and **6** Population Analysis Based On Occupation Numbers (PABOON),[22] Natural Population Analysis (NPA)[23] and Wiberg bond indices[24] were calculated (table S13).

Table S14. Population analysis of the selected bonds in **5** and **6**.

Population analysis based on occupation numbers			
		5	**6**
Two center shared electron numbers	Ru1-P	0.56	0.56
	Ru2-P	0.56	0.56
	$Ru\text{-}P_{avg}$	0.56	0.56
	P-C	1.65	1.63
Atomic charges with multicenter corrections	Ru1	0.19	0.19
	Ru2	0.19	0.19
	$Ru_{avg.}$	0.19	0.19
	P	0.49	0.49
	C	-0.22	-0.22
Wiberg bond indices			
Wiberg bond order	Ru1-P	0.84	0.85
	Ru2-P	0.84	0.84
	$Ru\text{-}P_{avg.}$	0.84	0.84
	P-C	1.55	1.53
Natural Population Analysis			
Occupation of P atom	Core (1s)	2.00	2.00
	Valence (2s)	0.95	0.95
	Valence ($2p_x$)	1.09	1.21
	Valence ($2p_y$)	1.20	1.18
	Valence ($2p_z$)	1.19	1.09
Atomic charges	Ru1	0.01	0.01
	Ru2	0.01	0.01
	$Ru_{avg.}$	0.01	0.01
	P	0.82	0.82
	C	-0.45	-0.45

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