Electronic Supplementary Information

1. Experimental Part

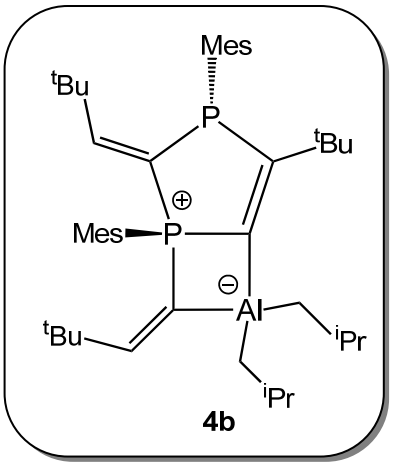
2. Molecular Structures and Important Bond Lengths and Angles

3. Calculated Structures at the B3PW91/6-31+(d,p) Level of Theory

1. Experimental Part

General: All manipulations were carried out under dry argon, using standard Schlenk techniques. Solvents were distilled from drying agents (*n*-pentane, *n*-hexane and cyclopentane over $LiAlH_4$; diethyl ether, tetrahydrofurane and toluene over Na/benzophenone; 1,2-difluoro- and pentafluorobenzene over molecular sieves; acetonitrile over CaH_2, stored over molecular sieves) and degassed. NMR spectra were recorded in benzene-d_6, toluene-d_8, THF-d_8 or chloroform-d_1 at ambient probe temperature on a Bruker Avance I (^{1}H, 400.13; ^{13}C, 100.6 MHz; ^{31}P, 161.94 MHz) or Avance III spectrometer (^{1}H, 400.03; ^{13}C, 100.59) and referenced internally to residual solvent resonances (chemical shift data in δ). ^{13}C and ^{31}P NMR spectra were all proton-decoupled. The chemical shifts were assigned on the basis of homo- and heteronuclear 2D NMR experiments (COSY, HSQC, HMBC, ROESY). Elemental analysis was determined by the microanalytic laboratory of the Westfälische Wilhelms Universität Münster. IR-spectra were recorded as Nujol mull between CsI plates on a Shimadzu Prestige 21 spectrometer, electron impact mass spectra on a Varian mass spectrometer. The compounds **4a** and Mes-P(C≡C-^{t}Bu)$_2$ (H. Westenberg, J. C. Slootweg, A. Hepp, J. Kösters, S. Roters, A. W. Ehlers, K. Lammertsma and W. Uhl, *Organometallics* 2010, **29**, 1323–1330) and **2** (S. Roters, C. Appelt, H. Westenberg, A. Hepp, J. C. Slootweg, K. Lammertsma and W. Uhl, *Dalton Trans.* 2012, **41**, 9033-9045) were obtained according to literature procedures. (Et_2Al-C≡C-CMe_3)$_2$ was synthesized by a standard procedure (W. Uhl, F. Breher, S. Haddadpour, R. Koch and M. Matar, *Z. Anorg. Allg. Chem.* 2004, **630**, 1839–1845). Experimental details are given below. Diisobutylaluminium hydride was applied as purchased (Sigma Aldrich).

1.1 Synthesis of the bicyclic compound 4b



4b

Di(*iso*-butyl)aluminium hydride, $^{i}Bu_2AlH$, (1.18 g, 8.31 mmol, 1.5 mL) was added to a solution of bis(3,3-dimethyl-1-butinyl)mesitylphosphine, Mes-P(C≡C-^{t}Bu)$_2$, (2.59 g, 8.30 mmol) in *n*-hexane (150 mL) at room temperature. An intermediate was formed after 19 h in relatively high purity. It could be isolated as an amorphous solid upon concentration of the reaction mixture and cooling to -30 °C (48% yield). However, rearrangement started immediately and the isolated product contained 10 to 20% of the rearranged compound **4b**. We suppose that it contains a racemate of the S,S- and R,R-isomers of **4b** with the mesityl groups on the same side of the bicycle. Its spectroscopic and analytical characterisation is given below. Single crystals could not be generated. Complete rearrangement to yield the final product **4b** [racemate of **(R,S)- and (S,R)-4b**] with the mesityl groups on different sides of the bicycle required stirring of the mixture at room temperature for 17 d. Concentration of the reaction mixture in vacuum to 25% of the original volume and cooling to -30 °C afforded compound **4b** in its R,S/S,R-form as yellow crystals which were washed two times with 5 mL of *n*-pentane. Yield: 1.65 g, 2.40 mmol (58%).

Characterisation of (S,S/(R,R))-4b:

$^{31}P\{^{1}H\}$ NMR (C_6D_6, 162 MHz, 300 K): δ = 11.3 (d, $^{2}J_{PP}$ = 13.0 Hz, $(C{=}C)_2P$), 55.1 (d, $^{2}J_{PP}$ = 13.0 Hz, $(C{=}C)_3P$). **^{1}H NMR** (C_6D_6, 400 MHz, 300 K): δ = 0.07 (dd, $^{2}J_{HH}$ = 4.2 Hz, $^{3}J_{HH}$ = 6.9 Hz, 2H, AlCH_2^{i}Pr), 0.56 (dd, $^{2}J_{HH}$ = 4.3 Hz, $^{3}J_{HH}$ = 7.0 Hz, 1H, AlCH_2^{i}Pr), 0.68 (dd, $^{3}J_{HH}$ = 6.8 Hz, $^{4}J_{HH}$ = 13.7 Hz, 1H, AlCH_2^{i}Pr), 0.76 (s, 9H, $P_2C{=}C(H)^{t}Bu$), 1.09 (d, $^{3}J_{HH}$ = 6.4 Hz, 6H, $AlCH_2CHMe_2$), 1.23 (s, 9H, P-(Al)C=C(H)^{t}Bu), 1.33 (s, 9H, Al-(P)-C=C(P)^{t}Bu), 1.37 (pseudo-t, $^{3}J_{HH}$ = 6.1 Hz, 3H, $AlCH_2CHMe_2$), 1.39 (pseudo-t, $^{3}J_{HH}$ = 6.1 Hz, 3H,

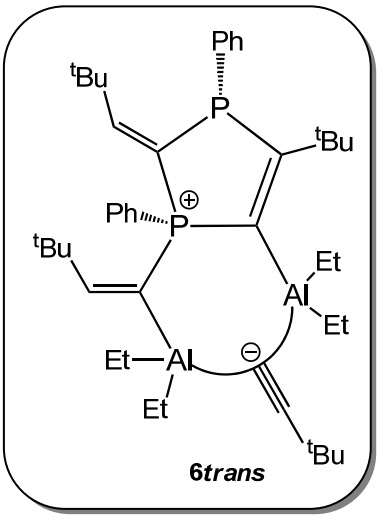
$AlCH_2CHMe_2$), 1.85 (m, 1H, $AlCH_2CHMe_2$), 1.97 (s, 3H, *p*-CH_3 von $(C=C)_3$P-Mes), 2.01 (s, 3H, *p*-CH_3 of $(C=C)_2$P-Mes), 2.40 (m, 1H, $AlCH_2CHMe_2$), 2.44 (s, 3H, *o*-CH_3 of $(C=C)_2$P-Mes), 2.73 (br. s, 6H, *o*-CH_3 of $(C=C)_3$P-Mes), 2.91 (s, 3H, *o*-CH_3 of $(C=C)_2$P-Mes), 6.60 (br. s, 1H, *m*-H of $(C=C)_2$P-Mes), 6.70 (br. s, 2H, *m*-H of $(C=C)_3$P-Mes), 6.72 (d, $^3J_{HP}$ = 82.7 Hz, 1H, P-(Al)-C=C-*H*), 6.78 (s, 1H, *m*-H of $(C=C)_2$P-Mes), 6.87 (dd, $^3J_{HP}$ = 20 Hz, $^3J_{HP}$ = 23 Hz, 1H, P_2-C=C-*H*). **$^{13}C\{^1H\}$ NMR** (C_6D_6, 101 MHz, 300 K): δ = 20.7 (s, *p*-CH_3 of $(C=C)_3$P-Mes), 21.0 ((s, 3H, *p*-CH_3 of $(C=C)_2$P-Mes), 22.9 (br., $AlCH_2{}^iPr$), 23.0 (s, *o*-CH_3 of $(C=C)_2$P-Mes), 23.1 (d, $^3J_{CP}$ = 29.3 Hz, *o*-CH_3 of $(C=C)_3$P-Mes), 25.1 (s, *o*-CH_3 of $(C=C)_2$P-Mes), 25.1 (s, *o*-CH_3 of $(C=C)_3$P-Mes), 27.5 (s, $AlCH_2CHMe_2$), 27.5 (s, $AlCH_2CHMe_2$), 27.8 (br., $AlCH_2{}^iPr$), 28.4 (s, $AlCH_2CHMe_2$), 28.5 (s, $AlCH_2CHMe_2$), 28.5 (br., m, $^4J_{CP}$ = 1.5 Hz, $^4J_{CP}$ = 3.8 Hz, P_2-C=C(H)CMe_3), 29.2 (s, $AlCH_2CHMe_2$), 29.3 (s, $AlCH_2CHMe_2$), 29.4 (d, $^4J_{CP}$ = 2 Hz, P-(Al)-C=C(H)CMe_3), 31.5 (s, Al-(P)-C=C(P)CMe_3), 36.6 (s, P_2C=C(H)CMe_3), 39.4 (d, $^3J_{CP}$ = 16.4 Hz, P-(Al)-C=C(H)CMe_3), 40.9 (dd, $^2J_{CP}$ = 29.9 Hz, $^3J_{CP}$ = 19.6 Hz, Al-(P)-C=C(P)CMe_3), 127.4 (partially covered, $^1J_{CP}$ = about 77 Hz, $^3J_{CP}$ = 5.4 Hz, *ipso.-C* of $(C=C)_3$P-Mes), 130.1 (s, *m*-C von $(C=C)_2$P-Mes), 130.4 (d, $^3J_{CP}$ = 8.0 Hz, *m*-*C* of $(C=C)_2$P-Mes), 131.6 (br., *m*-*C* of $(C=C)_3$P-Mes), 131.9 (d, $^1J_{CP}$ = 5.4 Hz, *ipso.-C* of $(C=C)_2$P-Mes), 139.6 (dd, $^1J_{CP}$ = 40.3 Hz, $^1J_{CP}$ = 26.0 Hz, P_2-*C*=C-H), 140.6 (d, $^4J_{CP}$ = 1.8 Hz, *p*-*C* of $(C=C)_2$P-Mes), 141.4 (d, $^4J_{CP}$ = 2.8 Hz, *p*-*C* of $(C=C)_3$P-Mes), 144 (br., *o*-*C* of $(C=C)_3$P-Mes), 144.5 (dd, $^2J_{CP}$ = 37.1 Hz, $^4J_{CP}$ = 3.1 Hz, *o*-*C* of $(C=C)_2$P-Mes), 145.3 (d, $^2J_{CP}$ = 5.4 Hz, *o*-*C* of $(C=C)_2$P-Mes), 146.5 (d, $^2J_{CP}$ = 24.6 Hz, P-(Al)-*C*=C-H), 153.9 (d, $^2J_{CP}$ = 17.4 Hz, P-(Al)-C=*C*-H), 157.6 (br., Al-(P)-*C*=C-P), 164.1 (dd, $^2J_{CP}$ = 3.1 Hz, $^2J_{CP}$ = 16.8 Hz, P_2-C=*C*-H), 172.3 (dd, $^1J_{CP}$ = 28.2 Hz, $^2J_{CP}$ = 1.5 Hz, Al(P)-C=*C*-P). **MS** (EI, 20 eV, 353 K): m/z (%) = 629 (100), 630 (41), 631 (9) $[M - Bu]^+$; 573 (18), 574 (7), 575 (1) [M – butene – $Bu]^+$; 489 (2) $[M - butene - AlBu_2]^+$. **CHN**: ($C_{44}H_{69}AlP_2$, 686.9): Found: C, 76.0; H, 10.4; calcd.: C, 76.9; H, 10.1.

Characterisation of 4b [(R,S)-4b]:

$^{31}P\{^{1}H\}$ NMR (C_6D_6, 162 MHz, 300 K): δ = 13.4 (d, $^{2}J_{PP}$ = 24.0 Hz, $(C{=}C)_2P$), 62.6 (d, $^{2}J_{PP}$ = 24.0 Hz, $(C{=}C)_3P$). **^{1}H NMR** (C_6D_6, 400 MHz, 300 K): δ = 0.27 (d, $^{3}J_{HH}$ = 6.9 Hz, 2H, $AlCH_2^{i}Pr$), 0.64 (dd, $^{2}J_{HH}$ = 12.9 Hz, $^{3}J_{HH}$ = 6.8 Hz, 1H, $AlCH_2^{i}Pr$), 0.70 (dd, $^{2}J_{HH}$ = 12.9 Hz, $^{3}J_{HH}$ = 6.8 Hz, 1H, $AlCH_2^{i}Pr$), 0.72 (s, 9H, $P_2C{=}C(H)^{t}Bu$), 1.05 (d, $^{3}J_{HH}$ = 6.5 Hz, 3H, $AlCH_2CHMe_2$), 1.08 (d, $^{3}J_{HH}$ = 6.5 Hz, 3H, $AlCH_2CHMe_2$), 1.31 (s, 9H, $P\text{-}(Al)C{=}C(H)^{t}Bu$), 1.35 (s, 9H, $Al\text{-}(P)\text{-}C{=}C(P)^{t}Bu$), 1.38 (d, $^{3}J_{HH}$ = 4.3 Hz, 3H, $AlCH_2CHMe_2$), 1.39 (d, $^{3}J_{HH}$ = 4.3 Hz, 3H, $AlCH_2CHMe_2$), 1.89 (m, 1H, $AlCH_2CHMe_2$), 1.95 (s, 3H, *p*-CH_3 of $(C{=}C)_3P$-Mes), 2.01 (s, 3H, *p*-CH_3 of $(C{=}C)_2P$-Mes), 2.29 (s, 3H, *o*-CH_3 of $(C{=}C)_2P$-Mes), 2.43 (dt, $^{3}J_{HH}$ = 6.5 Hz, $^{3}J_{HH}$ = 13.1 Hz, 1H, $AlCH_2CHMe_2$), 2.72 (s, 6H, *o*-CH_3 of $(C{=}C)_3P$-Mes), 2.90 (s, 3H, *o*-CH_3 of $(C{=}C)_2P$-Mes), 6.62 (br. s, 1H, *m*-H of $(C{=}C)_2P$-Mes), 6.65 (br. s, 2H, *m*-H of $(C{=}C)_3P$-Mes), 6.77 (dd, $^{3}J_{HP}$ = 17.0 Hz, $^{3}J_{HP}$ = 21.9 Hz, 1H, $P_2\text{-}C{=}C\text{-}H$), 6.79 (d, $^{4}J_{HP}$ = 5.4 Hz, 1H, *m*-H of $(C{=}C)_2P$-Mes), 7.02 (d, $^{3}J_{HP}$ = 47.8 Hz, 1H, $P\text{-}(Al)\text{-}C{=}C\text{-}H$). **$^{13}C\{^{1}H\}$ NMR** (C_6D_6, 101 MHz, 300 K): δ = 20.8 (s, *p*-CH_3 of $(C{=}C)_3P$-Mes), 21.1 (s, *p*-CH_3 of $(C{=}C)_2P$-Mes), 23.1 (d, $^{3}J_{CP}$ = 28.8 Hz, *o*-CH_3 of $(C{=}C)_2P$-Mes), 23.6 (br., $AlCH_2^{i}Pr$), 23.6 (br., *o*-CH_3 of $(C{=}C)_3P$-Mes), 24.6 (s, *o*-CH_3 of $(C{=}C)_2P$-Mes), 27.4 (s, $AlCH_2CHMe_2$), 27.5 (s, $AlCH_2CHMe_2$), 28.4 (dd, $^{4}J_{CP}$ = 1.4 Hz, $^{4}J_{CP}$ = 4.4 Hz $P_2\text{-}C{=}C(H)CMe_3$), 28.9 (s, $AlCH_2CHMe_2$), 28.9 (s, $AlCH_2CHMe_2$), 28.9 (s, $AlCH_2CHMe_2$), 29.1 (s, $AlCH_2CHMe_2$), 29.4 (br., $AlCH_2^{i}Pr$), 29.4 (d, $^{4}J_{CP}$ = 1.4 Hz, $P\text{-}(Al)\text{-}C{=}C(H)CMe_3$), 31.3 (d, $^{3}J_{CP}$ = 6.8 Hz, $Al\text{-}(P)\text{-}C{=}C(P)CMe_3$), 36.4 (dd, $^{3}J_{CP}$ = 1.8 Hz, $^{3}J_{CP}$ = 12.1 Hz, $P_2C{=}C(H)CMe_3$), 37.2 (d, $^{3}J_{CP}$ = 30.8 Hz, $P\text{-}(Al)\text{-}C{=}C(H)CMe_3$), 40.9 (dd, $^{2}J_{CP}$ = 18.9 Hz, $^{3}J_{CP}$ = 29.4 Hz, $Al\text{-}(P)\text{-}C{=}C(P)CMe_3$), 126.4 (dd, $^{1}J_{CP}$ = 68.9 Hz, $^{3}J_{CP}$ = 3.9 Hz, *ipso.-C* of $(C{=}C)_3P$-Mes), 130.4 (s, *m*-C of $(C{=}C)_2P$-Mes), 130.4 (s, *m*-C of $(C{=}C)_2P$-Mes), 131.6 (d, $^{1}J_{CP}$ = 30.5 Hz, *ipso-C* of $(C{=}C)_2P$-Mes), 131.6 (br., d, $^{3}J_{CP}$ = 10.2 Hz, *m-C* von $(C{=}C)_3P$-Mes), 131.6 (br., d, $^{3}J_{CP}$ = 10.2 Hz, *m-C* of $(C{=}C)_3P$-Mes), 134.9 (dd, $^{1}J_{CP}$ = 10.1 Hz, $^{1}J_{CP}$ = 39.7 Hz, $P_2\text{-}C{=}C\text{-}H$), 140.7 (d, $^{4}J_{CP}$ = 1.7 Hz, *p-C* of $(C{=}C)_2P$-Mes), 141.9 (d, $^{4}J_{CP}$ = 2.7 Hz, *p-C* of $(C{=}C)_3P$-Mes), 144 (br. HMBC, *o-C* of

(C=C)$_3$P-Mes), 144.4 (dd, $^2J_{CP}$ = 36.2 Hz, $^4J_{CP}$ = 3.4 Hz, *o-C* of (C=C)$_2$P-Mes), 145.3 (d, $^2J_{CP}$ = 5.4 Hz, *o-C* of (C=C)$_2$P-Mes), 147.4 (d, $^2J_{CP}$ = 25.2 Hz, P(Al)-*C*=C-H), 158.1 (br., Al(P)-*C*=C-P), 160.9 (dd, $^2J_{CP}$ = 1.1 Hz, $^2J_{CP}$ = 15.3 Hz, P$_2$-C=*C*-H), 164.5 (d, $^2J_{CP}$ = 10.2 Hz, P(Al)-C=*C*-H), 174.1 (dd, $^1J_{CP}$ = 31.0 Hz, $^2J_{CP}$ = 1.7 Hz, Al(P)-C=*C*-P). **MS** (EI, 20 eV, 298 K): m/z (%) = 630 (100), 631 (42), 632 (9) [M – butene]$^+$; 573 (18), 574 (7), 575 (1) [M – butene – Bu]$^+$; 489 (3) [M – butene – AlBu$_2$]$^+$. **IR** (CsI plates, paraffin, cm^{-1}): 3178 vw, 2951 to 2851 vs (paraffin); 1730 w, 1692 w, 1678w, 1647 w, 1603 vs, 1576 w, 1566 w, 1537 w, 1514 w, 1499 w νC=C, phenyl; 1460 vs (paraffin); 1404 w δCH$_3$; 1375 vs (paraffin); 1310 m, 1290 w, 1246 m δCH$_3$; 1198 m, 1167 s, 1155 s, 1055 s, 1030 m, 1009 m, 962 s, 916 w, 891 w, 849 vs, 812 m, 777 m, 747 w νC-C, δC-H; 723 vs (paraffin); 665 m δphenyl; 592 w, 573 w, 550 w, 515 w, 469 w, 442 w, 430 w δC-C, νAl-C, νP-C. **CHN** (C$_{44}$H$_{69}$AlP$_2$, 686.9): Found: C, 76.7; H, 10.1; calcd.: C, 76.9; H, 10.1. **Mp** (argon, sealed capillary): 156 °C (dec).

1.2 Synthesis of the dialkylaluminium alkynide insertion product 6*trans*



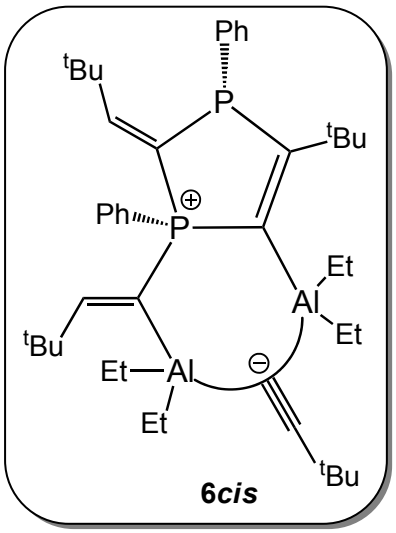
The heterocyclic compound **2**, [(Ph)(^{t}Bu-C≡C)P-C{=C(H)-^{t}Bu}-AlEt$_2$]$_2$, (1.13 g, 1.59 mmol) was dissolved in 40 mL of toluene. The solution was stirred at 50 °C for 1 h. After cooling to room temperature the mixture was concentrated in vacuum to a few mL and treated with 1 mL of *n*-hexane. Cooling to -45 °C gave colourless crystals of ***6trans*** which were washed in the cold (-45 °C) with 2 mL of *n*-hexane. Yield: 0.235 g, 0.33 mmol (21%). An equilibrium mixture was detected in benzene solution which contained ***6trans***, the dimeric aluminium alkynide Et$_2$Al-C≡C-CMe$_3$ and probably the bicyclic compound **5** (^{31}P NMR: δ =

18.4 and 57.6; $^{2}J_{PP}$ = 17.0 Hz). The low concentration of **5** did not allow a further characterization.

^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 300 K):δ = 9.7 (d, $^{2}J_{PP}$ = 7.1 Hz, (C=C)$_2$P), 59.1 (d, $^{2}J_{PP}$ = 7.1 Hz, (C=C)$_3$P). **^{1}H NMR** (C_6D_6, 400 MHz, 300 K): δ = 0.02 (dq, $^{2}J_{HH}$ = 16.3 Hz, $^{3}J_{HH}$ = 8.1 Hz, 1H, AlC*H*$_2$CH$_3$), 0.36 (dq, $^{2}J_{HH}$ = 16.0 Hz, $^{3}J_{HH}$ = 8.0 Hz, 1H, AlC*H*$_2$CH$_3$), 0.55 (m, 1H, AlC*H*$_2$CH$_3$), 0.60 (m, 1H, AlC*H*$_2$CH$_3$), 0.65 (m, 4H, AlC*H*$_2$CH$_3$), 0.69 (s, 9H, P$_2$C=C(H)^{t}*Bu*), 0.99 (s, 9H, C≡C^{t}*Bu*), 1.19 (s, 9H, P-(Al)-C=C(H)^{t}*Bu*), 1.39 (s, 9H, Al-(P)-C=C(P)^{t}*Bu*), 1.59 (t, $^{3}J_{HH}$ = 8.0 Hz, 3H, AlCH$_2$C*H*$_3$), 1.61 (m, $^{3}J_{HH}$ = 6.5 Hz, 3H, AlCH$_2$C*H*$_3$), 1.62 (3H, AlCH$_2$C*H*$_3$), 1.64 (t, $^{3}J_{HH}$ = 7.9 Hz, 3H, AlCH$_2$C*H*$_3$), 6.48 (dd, $^{3}J_{HP}$ = 16.4 Hz, $^{3}J_{HP}$ = 23.0 Hz, 1H, P$_2$-C=C-*H*), 6.93 (m, 1H, *p*-H von (C=C)$_2$P-Ph), 6.94 (m, $^{3}J_{HH}$ = 7.3 Hz, 2H, *m*-H of (C=C)$_2$P-Ph), 7.08 (br., m, $^{3}J_{HH}$ = 7.4 Hz, $^{4}J_{PH}$ = 1.4 Hz, 1H, *p*-H of (C=C)$_3$P-Ph), 7.19 (br., m, $^{3}J_{HH}$ = 7.4 Hz, $^{3}J_{PH}$ = 2.7 Hz, 2H, *m*-H of (C=C)$_3$P-Ph), 7.46 (d, $^{3}J_{HP}$ = 73.8 Hz, 1H, P-(Al)-C=C-*H*), 7.50 (m, $^{3}J_{HP}$ = 7 Hz, $^{3}J_{HH}$ = 7.6 Hz, 2H, *o*-H of (C=C)$_2$P-Ph), 7.96 (m, $^{3}J_{HP}$ = 11 Hz, $^{3}J_{HH}$ = 7 Hz, 2H, *o*-H of (C=C)$_3$P-Ph). **^{13}C{^{1}H} NMR** (C_6D_6, 101 MHz, 300 K): δ = 4.7 (br., Al*C*H$_2$CH$_3$), 5.7 (br., Al*C*H$_2$CH$_3$), 5.9 (br., Al*C*H$_2$CH$_3$), 9.7 (br., Al*C*H$_2$CH$_3$), 11.0 (s, AlCH$_2$*C*H$_3$), 11.1 (s, AlCH$_2$*C*H$_3$), 11.3 (s, AlCH$_2$*C*H$_3$), 11.7 (s, AlCH$_2$*C*H$_3$), 28.4 (dd, $^{4}J_{CP}$ = 5.1 Hz, $^{4}J_{CP}$ = 1.2 Hz, P$_2$-C=C(H)C*Me*$_3$), 29.9 (s, C≡C-*C*Me$_3$), 30.0 (s, C≡C-C*Me*$_3$), 31.6 (dd, $^{4}J_{CP}$ = 4.6 Hz, $^{6}J_{CP}$ = 1.5 Hz, P-(Al)-C=C(H)C*Me*$_3$), 32.7 (d, $^{3}J_{CP}$ = 9.0 Hz, $^{4}J_{CP}$ = 1.9 Hz, Al-(P)-C=C(P)C*Me*$_3$), 37.0 (dd, $^{3}J_{CP}$ = 2.0 Hz, $^{3}J_{CP}$ = 13.5 Hz, P$_2$-C=C(H)*C*Me$_3$), 38.5 (d, $^{3}J_{CP}$ = 12.1 Hz, P-(Al)-C=C(H)*C*Me$_3$), 42.3 (dd, $^{2}J_{CP}$ = 22.9 Hz, $^{3}J_{CP}$ = 26.9 Hz, Al-(P)-C=C(P)*C*Me$_3$), 90.9 (s, *C*≡C-CMe$_3$), 128.4 (d, $^{3}J_{CP}$ = 11.1 Hz, *m*-C of (C=C)$_3$P-Ph), 128.7 (d, $^{3}J_{CP}$ = 7.9 Hz, *m*-C of (C=C)$_2$P-Ph), 130.0 (d, $^{4}J_{CP}$ = 1.3 Hz, *p-C* von (C=C)$_2$P-Ph), 131.7 (d, $^{4}J_{CP}$ = 2.5 Hz, *p-C* of (C=C)$_3$P-Ph), 132.9 (dd, $^{1}J_{CP}$ = 83.1 Hz, $^{3}J_{CP}$ = 1.3 Hz, *ipso-C* of (C=C)$_3$P-Ph), 133.0 (d, $^{3}J_{CP}$ = 8.8 Hz, *o*-C of (C=C)$_3$P-Ph), 133.5 (br., P-(Al)-*C*=C-H), 134.1 (dd,$^{1}J_{CP}$ = 18.6 Hz, $^{1}J_{CP}$ = 29.4 Hz, P$_2$-*C*=C-H), 135.8 (dd, $^{2}J_{CP}$ = 19.7 Hz, $^{4}J_{CP}$ = 1.0 Hz, *o-C* of (C=C)$_2$P-Ph), 138.9 (d, $^{1}J_{CP}$ = 26.6 Hz, *ipso-C* of (C=C)$_2$P-Ph), 147.2 (br., Al-(P)-*C*=C-P),

156.1 (s, C≡*C*-CMe_3), 163.5 (dd, $^2J_{CP}$ = 2.8 Hz, $^2J_{CP}$ = 12.7 Hz, P_2-C=*C*-H), 171.0 (d, $^2J_{CP}$ = 9.3 Hz, P-(Al)-C=*C*-H), 185.6 (d, $^1J_{CP}$ = 29.5 Hz, Al-(P)-C=*C*-P). **MS** (EI, 20 eV, 333 K): m/z (%) = 569 (12), 570 (4) [M – 2Et – ethene – Bu]$^+$; 517 (100), 518 (36), 519 (6) [M – $AlEt_3$ – C≡C^{t}Bu]$^+$; 489 (10), 490 (3) [M – $AlEt_3$ – ethene – C≡C^{t}Bu]$^+$; 487 (9), 488 (3) [M – $AlEt_2$ – 2Et – C=C(H)^{t}Bu]$^+$; 407 (9), 408 (2) [M – $AlEt_3$ – ethene – C≡C^{t}Bu – C=C(H)^{t}Bu]$^+$. **IR** (CsI plates, paraffin, cm^{-1}): 3055 vs, 2951 to 2848 vs (paraffin); 2798 vs ν=C-H); 2132 w, 2043 vs νC≡C; 2013 vw, 1969 w, 1954 m, 1899 w, 1886 w, 1809 w, 1763 vw, 1707 vw, 1663 w, 1584 to 1551 br. vs νC=C, phenyl; 1454 br. vs (paraffin); 1450 vs, 1412 m δCH_3; 1375 vs (paraffin); 1333 vw, 1306 s, 1240 br. vs δCH_3; 1202 br. vs, 1180 vs, 1155 vw, 1107 vs, 1088 w, 1069 w, 1034 vs, 978 br. vs, 947 vs, 928 vs, 870 vs, 831 w, 791 vs, 742 vs νC-C, δC-H; 719 s (paraffin); 698 m δphenyl; 675 m, 646 s, 629 to 611 br. s, 586 m, 573 m, 557 m, 515 s, 492 w, 475 m, 455 m, 440 s δC-C, νAl-C, νP-C. **CHN** ($C_{44}H_{68}Al_2P_2$, 712.9): Found: C, 74.1, H, 9.5; calcd.: C, 74.1, H, 9.6. **Mp** (argon, sealed capillary): 145 °C (dec).

1.3 Synthesis of the dialkylaluminium alkynide insertion product 6*cis*



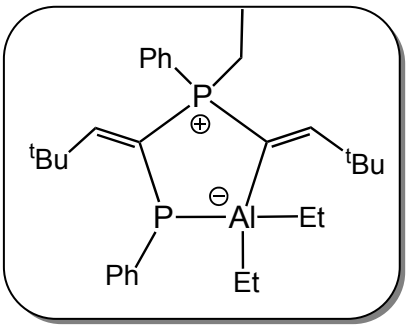
Compound ***6trans*** (0.286 g, 0.40 mmol) was dissolved in 20 mL of toluene. The mixture was stirred at 60 °C for 16 h. After cooling to room temperature the solvent was removed in vacuum. The residue was dissolved in 1 mL of cyclopentane. Cooling to -45 °C gave colourless platelets of ***6cis*** which were washed with 2 mL of *n*-hexane. Yield: 0.148 g, 0.21 mmol (52%).

$^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz, 300 K): δ = 3.3 (d, $^2J_{PP}$ = 17.0 Hz, (C=C)$_2$P), 77.3 (d, $^2J_{PP}$ = 17.0 Hz, (C=C)$_3$P). **^{1}H NMR** (C_6D_6, 400 MHz, 300 K): δ = 0.49 (m, 2H, AlCH_2CH$_3$), 0.53 (m, 2H, AlCH_2CH$_3$), 0.64 (m, 2H, AlCH_2CH$_3$), 0.70 (s, 9H,

$P_2C=C(H)^tBu$), 0.77 (m, 2H, $AlCH_2CH_3$), 0.98 (s, 9H, $C\equiv C^tBu$), 1.28 (s, 9H, P-(Al)-C=C(H)^t*Bu*), 1.33 (s, 9H, Al-(P)-C=C(P)^t*Bu*), 1.60 (m, 6H, $AlCH_2CH_3$), 1.62 (m, 6H, $AlCH_2CH_3$), 5.89 (dd, $^3J_{HP}$ = 16.4 Hz, $^3J_{HP}$ = 21.1 Hz, 1H, P_2-C=C-*H*), 6.97 (d, $^3J_{HP}$ = 45.7 Hz, 1H, P-(Al)-C=C-*H*), 6.98 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{PH}$ = 1.5 Hz, 1H, *p*-H of $(C=C)_2$P-Ph), 7.04 (m, $^3J_{HH}$ = 7.3 Hz, 2H, *m*-H of $(C=C)_2$P-Ph), 7.09 (br., m, $^3J_{HH}$ = 7.4 Hz, $^4J_{PH}$ = 1.4 Hz, 1H, *p*-H of $(C=C)_3$P-Ph), 7.20 (br. dt, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 2.6 Hz, 2H, *m*-H of $(C=C)_3$P-Ph), 7.63 (m, $^3J_{HP}$ = 7.2 Hz, $^3J_{HH}$ = 6.9 Hz, 2H, *o*-H of $(C=C)_2$P-Ph), 7.96 (m, 2H, *o*-H of $(C=C)_3$P-Ph). **^{13}C{^{1}H} NMR** (C_6D_6, 101 MHz, 300 K): δ = 5.7 (br., $AlCH_2CH_3$), 6.7 (br., $AlCH_2CH_3$), 9.3 (br., $AlCH_2CH_3$), 9.6 (br., $AlCH_2CH_3$), 11.2 (s, $AlCH_2CH_3$), 11.5 (s, $AlCH_2CH_3$), 11.6 (s, $AlCH_2CH_3$), 11.7 (s, $AlCH_2CH_3$), 28.8 (dd, $^4J_{CP}$ = 5.2 Hz, $^4J_{CP}$ = 1.2 Hz, P_2-C=C(H)CMe_3), 29.9 (s, C≡C-CMe_3), 30.1 (C≡C-*C*Me_3), 30.1 (d, $^4J_{CP}$ = 2.1 Hz, P-(Al)-C=C(H)CMe_3), 32.8 (dd, $^3J_{CP}$ = 7.9 Hz, $^4J_{CP}$ = 1.3 Hz, Al-(P)-C=C(P)CMe_3), 36.8 (dd, $^3J_{CP}$ = 2.5 Hz, $^3J_{CP}$ = 13.1 Hz, P_2-C=C(H)*C*Me_3), 37.8 (d, $^3J_{CP}$ = 28.2 Hz, P-(Al)-C=C(H)*C*Me_3), 42.2 (dd, $^2J_{CP}$ = 21.7 Hz, $^3J_{CP}$ = 26.9 Hz, Al-(P)-C=C(P)*C*Me_3), 91.2 (s, *C*≡C-CMe_3), 128.4 (P_2-*C*=C-H), 128.7 (d, $^3J_{CP}$ = 11.2 Hz, *m*-C of $(C=C)_3$P-Ph), 128.9 (d, $^3J_{CP}$ = 7.9 Hz, *m*-C of $(C=C)_2$P-Ph), 130.0 (br., s, *p-C* von $(C=C)_2$P-Ph), 131.2 (dd, $^1J_{CP}$ = 74.2 Hz, $^3J_{CP}$ = 1.5 Hz, *ipso-C* of $(C=C)_3$P-Ph), 132.1 (d, $^4J_{CP}$ = 2.6 Hz, *p-C* of $(C=C)_3$P-Ph), 132.4 (br. P-(Al)-*C*=C-H), 133.3 (d, $^3J_{CP}$ = 9.3 Hz, *o*-C of $(C=C)_3$P-Ph), 135.5 (dd, $^2J_{CP}$ = 19.8 Hz, $^4J_{CP}$ = 1.1 Hz *o-C* of $(C=C)_2$P-Ph), 139.7 (d, $^1J_{CP}$ = 24.8 Hz, *ipso-C* of $(C=C)_2$P-Ph), 147.3 (br., Al-(P)-*C*=C-P), 159.4 (s, C≡*C*-CMe_3), 165.4 (d, $^2J_{CP}$ = 11.7 Hz, P_2-C=*C*-H), 173.5 (d, $^2J_{CP}$ = 5.3 Hz, P-(Al)-C=*C*-H), 186.3 (d, $^1J_{CP}$ = 29.3 Hz, Al-(P)-C=*C*-P). **MS** (EI, 20 eV, 333 K): m/z (%) = 569 (12), 570 (5) [M – 2Et – ethene – Bu]$^+$; 517 (100), 518 (33), 519 (6) [M – $AlEt_3$ – C≡C^{t}Bu]$^+$; 487 (31), 488 (10), 489 (8), [M – $AlEt_2$ – 2Et – C=C(H)^{t}Bu]$^+$; 407 (12), 408 (3) [M – $AlEt_3$ – ethene – C≡C^{t}Bu – C=C(H)^{t}Bu]$^+$. **IR** (CsI plates, paraffin, cm^{-1}): 3050 m, 2951 to 2850 vs (paraffin); 2712 w νC=C-H; 2313 w, 2290 w, 2120 w, 2037 vs νC≡C; 1973 w, 1956 w, 1902 w, 1888 vw, 1811 w, 1765 w, 1727 w, 1711 w, 1692 w, 1661 s, 1584 vs, 1551 vs νC=C, phenyl; 1465 to 1450

br. vs, 1371 vs (paraffin); 1306 m, 1260 m δ H_3); 1200 w, 1182 w, 1113 s, 1088 m, 1034 s, 976 m, 949 w, 916 w, 870 w, 831 m, 785 m, 758 vw, 742 vs νC-C, δC-H; 721 w (paraffin); 694 w δphenyl; 675 w, 650 w, 629 w, 467 w, 433 w δC-C, νAl-C, νP-C. **CHN** ($C_{44}H_{68}Al_2P_2$, 712.9): Found: C, 73.9, H 9.7; calcd.: C, 74.1, H 9.6. **Mp** (argon, sealed capillary): 150 °C (dec).

1.4 Synthesis of *cyclo*-Ph-P-Al(Et)$_2$-C(=CH-^{t}Bu)-P(Ph)Et-C(=CH-^{t}Bu)

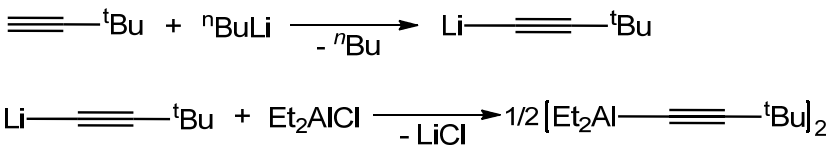


Compound **2** (0.287 g, 0.40 mmol) was dissolved in 15 mL of toluene, treated with triethylaluminium, Et_3Al, (55.6 mg, 0.49 mmol, 67 µL, 1.2 equivalents) and stirred at 110 °C for 2 h. A mixture of two unknown compounds (**A**, 47%, $^{31}P\{^1H\}$ δ = –31.7(s); **B**, 22%, $^{31}P\{^1H\}$ δ = –3.4 and 85.6, $^2J_{PP}$ = 9.3 Hz), ***6cis*** (4%), [Ph(Et)P-C(=CH-^{t}Bu)-$AlEt_2$]$_2$ (17%) and 9% of the expected product was obtained. All volatiles were removed in vacuum. The residue was dissolved in 5 mL of *n*-hexane. A mixture of compound **B** and the alkenylaluminium compound precipitated as an amorphous solid and was removed. Repeated concentration of the filtrate and cooling to +2 or -45 °C gave two further fractions of this amorphous solid. Few crystals of the yellow five-membered heterocycle crystallized as the fourth fraction after further concentration and cooling to -45 °C.

$^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz, 300 K): δ = -90.5(d, $^2J_{PP}$ = 21.5Hz, P-Al), 42.2 (d, $^2J_{PP}$ = 21.5 Hz, P-CH_2CH_3). **^1H NMR** (C_6D_6, 400 MHz, 300 K): δ = 0.58 (dt, $^3J_{HP}$ = 17.6 Hz, $^3J_{HH}$ = 7.6 Hz, P-CH_2CH_3), 0.59 (m, H, AlCH_2CH_3), 0.67 (m, H, AlCH_2CH_3), 0.72 (m, H, AlCH_2CH_3), 0.85 (m, H, AlCH_2CH_3), 1.11 (s, 9H, P-(Al)C=C(H)^t*Bu*), 1.27 (s, 9H, P_2C=C(H)^t*Bu*), 1.46 (t, $^3J_{HH}$ = 8.1 Hz 3H, $AlCH_2CH_3$), 1.74 (t, $^3J_{HH}$ = 8.0 Hz, 3H,

$AlCH_2CH_3$), 1.68 (m, 1H, P-CH_2CH_3), 2.01 (m, 1H, $^2J_{HH}$ = 15.4 Hz, $^3J_{HH}$ = 7.6 Hz, P-CH_2CH_3), 6.41 (dd, $^3J_{HP}$ = 16.3 Hz, $^3J_{HP}$ = 26.6 Hz, 1H, P_2-C=C-*H*), 6.66 (d, $^3J_{HP}$ = 39.4 Hz, 1H, P-(Al)-C=C-*H*), 6.96 (m, 2H, *m*-H of $(C=C)_2$P-Ph), 6.97 (m, 1H, *p*-H of Al-P-Ph), 7.00 (m, 2H, *p*-H of $(C=C)_2$P-Ph), 7.10 (m, $^3J_{HH}$ = 6.8Hz, 2H, *o*-H of $(C=C)_2$P-Ph), 7.16 (m, 2H, *m*-H of Al-P-Ph), 7.53 (m, $^3J_{HH}$ = 7.1 Hz, 2H, *o*-H of Al-P-Ph). **^{13}C{H} NMR** (C_6D_6, 101 MHz, 300 K): δ = 2.4 (br., $AlCH_2CH_3$), 5.4 (br., $AlCH_2CH_3$), 6.3 (d, $^2J_{CP}$ = 4.9 Hz, P-CH_2CH_3), 11.3 (s, $AlCH_2CH_3$), 11.6 (s, $AlCH_2CH_3$), 17.0 (d, $^1J_{CP}$ = 50.1 Hz, P- CH_2CH_3), 29.3 (d, $^4J_{CP}$ = 1.8 Hz, P-(Al)-C=C(H)CMe_3), 30.3 (d, $^4J_{CP}$ = 6.7 Hz, P_2-C=C(H)CMe_3), 37.4 (d, $^3J_{CP}$ = 17.6 Hz, P_2C=C(H)CMe$_3$), 38.4 (d, $^3J_{CP}$ = 27.4 Hz, P-(Al)-C=C(H)CMe$_3$), 123.5 (s, *p*-*C* of Al-P-Ph), 124.3 (dd, $^1J_{CP}$ = 53.7 Hz, $^3J_{CP}$ = 1.8 Hz, *ipso*.-*C* of $(C=C)_2$P-Ph), 127.9 (*m*-C of Al-P-Ph), 128.8 (dd, $^1J_{CP}$ = 51 Hz, $^1J_{CP}$ = 66 Hz, P_2-*C*=C-H), 129.2 (d, $^3J_{CP}$ = 9.8 Hz, *m*-C of $(C=C)_2$P-Ph), 130 (br., P-(Al)-*C*=C-H), 130.0 (d, $^2J_{CP}$ = 16.6 Hz, *o*-C of Al-P-Ph), 132.2 (s, *p*-*C* of $(C=C)_2$P-Ph), 133.6 (d, $^2J_{CP}$ = 6.9 Hz, *o*-*C* of $(C=C)_2$P-Ph), 172.4 (dd, $^2J_{CP}$ = 9.5 Hz, $^2J_{CP}$ = 14.1 Hz, P_2-C=*C*-H), 174.2 (dd, $^2J_{CP}$ = 3.9 Hz, $^4J_{CP}$ = 2.0 Hz, P-(Al)-C=*C*-H).

1.5 Synthesis of the dimeric aluminium alkynide (3,3-dimethyl-1-butinyl)-diethylaluminium, $[Et_2Al\text{-}C{\equiv}C\text{-}^tBu]_2$

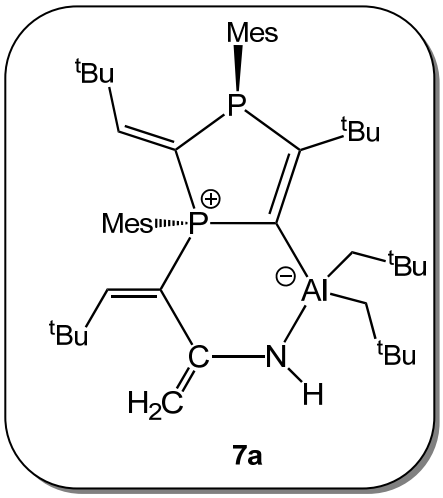


A solution of *n*-butyllithium in *n*-hexane (1.6 M, 9.60 mmol, 6 mL) was added to a cooled (-78 °C) solution of 3,3-dimethyl-1-butyne, H-C≡C-^{t}Bu, (0.79 g, 9.63 mmol, 1.2 mL) in 50 mL of *n*-hexane. The mixture was stirred at -78 °C for 0.5 h, warmed to room temperature and stirred for 1.5 h. After cooling to -78 °C a solution of diethylaluminium chloride, Et_2AlCl, (1.15 g, 9.55 mmol, 1.2 mL) in 40 mL of *n*-hexane was slowly added. The mixture was stirred at room temperature for 16 h and filtrated. The residue was washed with 10 mL of *n*-hexane.

The solvent of the filtrate was removed in vacuum. The remaining oil was purified by distillation (10^{-3} mbar, 85-100 °C) and trapped in a Schlenk vessel cooled with liquid nitrogen. Yield: 1.11 g, 3.34 mmol (based on the dimer, 70%) of a highly viscous, extremely air-sensitive liquid which spontaneously ignites on contact with air. Due to this extreme sensitivity determination of elemental analysis was not successful.

^{1}H NMR (200 MHz, C_6D_6, 300 K): δ = 0.45 (q, $^{3}J_{HH}$ = 8.1 Hz, 4H, AlCH_2CH$_3$), 1.01 (s, 9H, ^{t}Bu), 1.42 (t, $^{3}J_{HH}$ = 8.1 Hz, 6H, AlCH$_2$CH_3). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 300 K): δ = 3.6 (AlCH$_2$CH$_3$), 9.7 (AlCH$_2$$CH_3$), 29.5 ($C$(CMe$_3$)$_3$), 29.8 (C($CMe_3$)$_3$), 81.6 (Al-$C$≡C), 149.5 (Al-C≡$C$). **MS** (EI, 20 eV, 298 K): m/z (%) = 303 (100), 304 (19), 305 (2) [M – Et]$^{+}$; 275 (27), 276 (5) [M – Et – ethene]; 247 (6) [M – AlEt$_2$]$^{+}$; 137 (34), 138 (5) [1/2 M – Et]$^{+}$; 109 (10) [1/2 M – Et – ethene]$^{+}$. **IR** (CsI plates, neat, cm^{-1}): 3321 vw, 2972 to 2864 br., vs, 2787 s, 2721 w νCH$_3$; 2145 s, 2075 vs νC≡C; 1969 vw, 1829 vw, 1736 vw, 1476 vs, 1459 vs, 1406 s, 1364 vs, 1246 vs δCH$_3$; 1227 vs, 1202 vs; 1103 w, 1065 w, 993 s, 949 s, 918 m, 897 w, 847 vw, 816 vw, 723 vs νC-C; 656 br., s, 532 s, 462 to 440 br., vs δC-C, νAl-C.

1.6 Synthesis of the acetonitrile insertion product 7a



7a

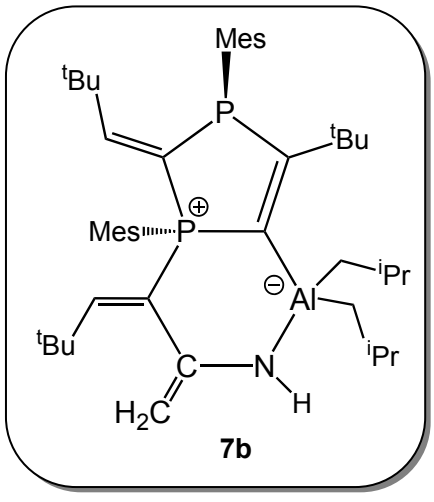
The crude product obtained from the synthesis of **4a** (0.715 g, 1.00 mmol) was dissolved in *n*-hexane (15 mL) and treated with acetonitrile (0.123 g, 3.00 mmol, 0.16 mL, 3 equivalents). The mixture was stirred for 3 days. Insoluble by-products of unknown composition were removed by filtration. The solvent of the filtrate was removed in vacuum. The oily residue was dissolved in 3 mL of cyclopentane. A yellow solid of **7a** crystallized upon cooling to -80 °C. Yield: 0.230 g, 0.304 mmol (30%).

^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 300 K): δ = 5.9 (d, $^{2}J_{PP}$ = 56.1 Hz, (C=C)$_2$P), 61.3 (d, $^{2}J_{PP}$ = 56.1 Hz, (C=C)$_3$P). **^{1}H NMR** (C_6D_6, 400 MHz, 300 K): δ = 0.61 (br. s, 2H, AlCH_2^{t}Bu), 0.69

(s, 9H, P_2-C=C(H)^tBu), 0.72 (br., 1H, AlCH_2^tBu), 0.87 (br., 1H, AlCH_2^tBu), 1.29 (s, 9H, AlCH$_2^t$Bu), 1.36 (s, 9H, Al-(P)-C=C(P)^tBu), 1.49 (s, 9H, P-(Al)-C=C(H)^tBu), 1.52 (s, 9H, AlCH$_2^t$Bu), 1.87 (s, 3H, *p*-CH_3 of (C=C)$_3$P-Mes), 1.99 (s, 3H, *p*-CH_3 of (C=C)$_2$P-Mes), 2.35 (s, 3H, *o*-CH_3 of (C=C)$_2$P-Mes), 2.83 (s, 3H, *o*-CH_3 of (C=C)$_2$P-Mes), 2.84 (s, 3H, *o*-CH_3 of (C=C)$_3$P-Mes), 2.86 (s, 3H, *o*-CH_3 of (C=C)$_3$P-Mes), 3.65 (s, 1H, N-*H*), 3.83 (d, $^4J_{PH}$ = 1.8 Hz, 1H, N-(C)-C=CH_2), 4.23 (s, 1H, N-(C)-C=CH_2), 6.51 (d, $^3J_{HP}$ = 27.2 Hz, 1H, P-(Al)-C=C-*H*), 6.57 (br., 1H, *m*-H of (C=C)$_3$P-Mes), 6.57 (br., 1H, *m*-H of (C=C)$_2$P-Mes), 6.71 (br., 1H, *m*-H of (C=C)$_3$P-Mes), 6.75 (d, $^4J_{HP}$ = 5.6 Hz, 1H, *m*-H of (C=C)$_2$P-Mes), 7.08 (dd, $^3J_{HP}$ = 21.6 Hz, $^3J_{HP}$ = 14.6 Hz, 1H, P_2-C=C-*H*). **^{13}C{^{1}H} NMR** (C_6D_6, 101 MHz, 300 K): δ = 20.6 (d, $^5J_{CP}$ = 1.0 Hz, *p*-CH_3 of (C=C)$_3$P-Mes), 21.0 (s, *p*-CH_3 of (C=C)$_2$P-Mes), 23.2 (d, $^3J_{CP}$ = 28.9 Hz, *o*-CH_3 of (C=C)$_2$P-Mes), 24.5 (d, $^3J_{CP}$ = 3.0 Hz, 1H, *o*-CH_3 of (C=C)$_3$P-Mes), 25.6 (s, *o*-CH_3 of (C=C)$_2$P-Mes), 25.9 (dd, $^3J_{CP}$ = 6.4 Hz, $^5J_{CP}$ = 3.6 Hz, 1H, *o*-CH_3 of (C=C)$_3$P-Mes), 28.5 (dd, $^4J_{CP}$ = 0.8 Hz, $^4J_{CP}$ = 3.9 Hz, P_2-C=C(H)CMe_3), 30.2 (s, P-(Al)-C=C(H)CMe_3), 31.9 (d, $^3J_{CP}$ = 7.2 Hz, Al-(P)-C=C(P)CMe_3), 32.6 (s, AlCH$_2$CMe_3), 32.9 (s, AlCH$_2$CMe_3), 33.3 (br., AlCH_2CMe_3), 35.5 (s, AlCH$_2$CMe_3), 35.8 (s, AlCH$_2$CMe_3), 36.2 (br., AlCH_2CMe_3), 36.7 (dd, $^3J_{CP}$ = 3.0 Hz, $^3J_{CP}$ = 12.4 Hz, P_2-C=C(H)CMe_3), 36.8 (d, $^3J_{CP}$ = 16.7 Hz, P-(Al)-C=C(H)CMe_3), 42.3 (dd, $^2J_{CP}$ = 20.1 Hz, $^3J_{CP}$ = 31.2 Hz, Al-(P)-C=C(P)CMe_3), 88.7 (d, $^3J_{CP}$ = 8.9 Hz, N-(C)-C=CH_2), 122.6 (dd, $^1J_{CP}$ = 78.4 Hz, ^{3}J$_{CP}$ = 2.3 Hz, *ipso*-*C* of (C=C)$_3$P-Mes), 130.1 (s, *m*-C of (C=C)$_2$P-Mes), 130.6 (d, $^3J_{CP}$ = 8.0 Hz, *m*-C of (C=C)$_2$P-Mes), 131.4 (HMBC, P_2-*C*=C-H), 131.4 (HMBC, *ipso*-*C* of (C=C)$_2$P-Mes), 131.9 (d, $^3J_{CP}$ = 10.1 Hz, *m*-*C* of (C=C)$_3$P-Mes), 131.9 (HMBC, N-(C)-*C*=CH$_2$), 132.2 (d, $^3J_{CP}$ = 11.6 Hz, *m*-*C* of (C=C)$_3$P-Mes), 141.2 (d, $^4J_{CP}$ = 1.7 Hz, *p*-*C* of (C=C)$_2$P-Mes), 141.3 (d, $^4J_{CP}$ = 2.9 Hz, *p*-*C* of (C=C)$_3$P-Mes), 142.0 (d, $^2J_{CP}$ = 7.2 Hz, *o*-*C* of (C=C)$_3$P-Mes), 144.5 (d, $^2J_{CP}$ = 11.1 Hz, *o*-*C* of (C=C)$_3$P-Mes), 145.2 (d, $^2J_{CP}$ = 5.9 Hz, *o*-*C* of (C=C)$_2$P-Mes), 145.4 (dd, $^2J_{CP}$ = 36.6 Hz, $^4J_{CP}$ = 3.4 Hz, *o*-*C* of (C=C)$_2$P-Mes), 148.7 (d, $^1J_{CP}$ = 5.8 Hz, P-(Al)-*C*=C-H), 154.0 (d, $^2J_{CP}$ = 9.2 Hz, P-(Al)-C=*C*-H), 154.4 (HMBC br., Al-(P)-*C*=C-P), 160.1 (d, $^2J_{CP}$ =

13.6 Hz, P_2-C=*C*-H), 179.0 (dd, $^1J_{CP}$ = 30.4 Hz, $^2J_{CP}$ = 3.0 Hz, Al-(P)-C=*C*-P). **MS** (EI, 20 eV, 329 K): m/z (%) = 684 (100), 685 (45), 684 (11) [M – neopentyl]$^+$; 643 (64), 644 (28), 645 (6) [M – neopentyl – CH_3CN]$^+$; 587 (4), 588 (1) [M – neopentyl – CH_3CN – butene]$^+$; 464 (25), 465 (9) [MesP-{C(H)=C^{t}Bu}-MesP-{C(H)=C^{t}Bu}]$^+$. **IR** (CsI plates, paraffin, cm^{-1}): 3364 vw, 3179 vw, 30100 vw νN-H; 2953 to 2853 vs (paraffin); 1886 vw, 1886 vw, 1724 vw, 1680 vw, 1602 vs, 1572 vw, 1555 vw, 1539 vw, 1528 vw, 1503 vw νC=C, phenyl, δN-H; 1458 vs (paraffin); 1404 vw δCH_3; 1375 vs (paraffin); 1364 vs, 1335 vw, 1314 vw, 1290 w, 1267 w, 1250 vw δCH_3; 1221 m, 1198 m, 1169 vw, 1153 vw, 1117 m, 1098 w, 1055 vw, 1034 w, 1011 w, 997 w, 959 m, 930 vw, 914 vw, 851 vs, 773 s, 745 m νC-C, νC-N; 721 m (paraffin); 669 m δphenyl; 656 w, 642 vw, 625 s, 610 w, 583 w, 556 w, 536 vw, 519 w, 496 w, 461 m, 442 vw, 428 vw, 419 vw δC-C, νAl-C, νAl-N, νP-C. **CHN** ($C_{48}H_{76}AlNP_2$, 756.1): Found: C, 76.3; H, 10.3; N, 1.5; calcd.: C, 76.3, H, 10.1, N 1.9. **Mp** (argon, sealed capillary): 183°C (dec).

1.7 Synthesis of the acetonitrile insertion product 7b



7b

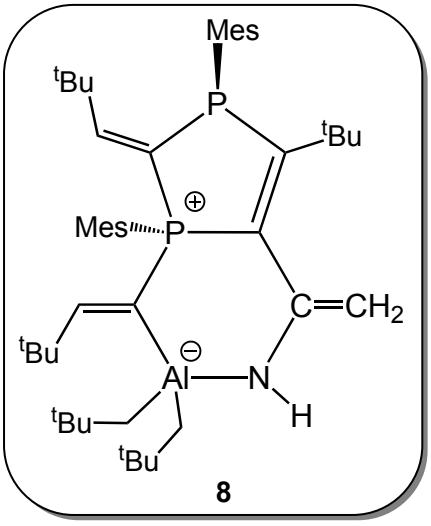
Acetonitrile (0.108 g, 2.63 mmol, 0.14 mL, two equivalents) was added to a solution of the bicyclic compound **4b** (0.900 g, 1.31mmol) in 20 mL of toluene at room temperature. The solution was stirred for 6 days. All volatiles were removed in vacuum. The oily residue was dissolved in 1.6 mL of *n*-hexane. Light yellow blocks of **7b** were obtained upon cooling to -45 °C. They were washed two times with 1.5 mL of *n*-pentane to remove oily impurities. Yield: 42 mg, 0.058 mmol (4%).

^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 300 K): δ = 5.3 (d, $^2J_{PP}$ = 55.1 Hz, (C=C)$_2$P), 60.3 (d, $^2J_{PP}$ = 55.1 Hz, (C=C)$_3$P). **^{1}H NMR** (C_6D_6, 400 MHz, 300 K): δ = 0.41 (m, 1H, AlCH_2^iPr), 0.44 (m, 1H, AlCH_2^iPr), 0.45 (m, 1H, AlCH_2^iPr), 0.57 (m, 1H, AlCH_2^iPr), 0.69 (s, 9H, P_2-C=C(H)^t*Bu*),

1.22 (d, $^{3}J_{HH}$ = 6.4 Hz, 3H, AlCH$_2$CH*Me*$_2$), 1.26 (d, $^{3}J_{HH}$ = 6.4 Hz, 3H, AlCH$_2$CH*Me*$_2$), 1.34 (s, 9H, Al-(P)-C=C(P)^{t}*Bu*), 1.41 (d, $^{3}J_{HH}$ = 6.4 Hz, 3H, AlCH$_2$CH*Me*$_2$), 1.43 (d, $^{3}J_{HH}$ = 6.4 Hz, 3H, AlCH$_2$CH*Me*$_2$), 1.48 (s, 9H, P-(Al)-C=C(H)^{t}*Bu*), 1.84 (s, 3H, *p*-C*H*$_3$ of (C=C)$_3$P-Mes), 1.99 (s, 3H, *p*-C*H*$_3$ of (C=C)$_2$P-Mes), 2.10 (m, 1H, AlCH$_2$C*H*Me$_2$), 2.35 (s, 3H, *o*-C*H*$_3$ of (C=C)$_2$P-Mes), 2.42 (dq, $^{3}J_{HH}$ = 6.8 Hz, $^{3}J_{HH}$ = 20.2 Hz, 1H, AlCH$_2$C*H*Me$_2$), 2.80 (s, 3H, *o*-C*H*$_3$ of (C=C)$_3$P-Mes), 2.82 (s, 3H, *o*-C*H*$_3$ of (C=C)$_2$P-Mes), 2.85 (s, 3H, *o*-C*H*$_3$ of (C=C)$_3$P-Mes), 3.58 (s, 1H, N-*H*), 3.81 (d, $^{4}J_{PH}$ = 2.2 Hz, 1H, N-(C)-C=C*H*$_2$), 4.15 (s, 1H, N-(C)-C=C*H*$_2$), 6.51 (d, $^{3}J_{HP}$ = 26.9 Hz, 1H, P-(Al)-C=C-*H*), 6.56 (br., 1H, *m*-H of (C=C)$_3$P-Mes), 6.57 (br. s, 1H, *m*-H of (C=C)$_2$P-Mes), 6.70 (br., 1H, *m*-H of (C=C)$_3$P-Mes), 6.75 (d, $^{4}J_{HP}$ = 4.7 Hz, 1H, *m*-H of (C=C)$_2$P-Mes), 7.11 (dd, $^{3}J_{HP}$ = 14.7 Hz, $^{3}J_{HP}$ = 23 Hz, 1H, P$_2$-C=C-*H*). **^{13}C{^{1}H} NMR** (C$_6$D$_6$, 101 MHz, 300 K): δ = 20.6 (s, *p*-*C*H$_3$ of (C=C)$_3$P-Mes), 21.0 (s, *p*-*C*H$_3$ of (C=C)$_2$P-Mes), 23.3 (d, $^{3}J_{CP}$ = 29.0Hz, *o*-*C*H$_3$ of (C=C)$_2$P-Mes), 24.5 (d, $^{3}J_{CP}$ = 3.0 Hz, 1H, *o*-*C*H$_3$ of (C=C)$_3$P-Mes), 25.5 (s, *o*-*C*H$_3$ of (C=C)$_2$P-Mes), 25.9 (dd, $^{3}J_{CP}$ = 4.7 Hz, $^{5}J_{CP}$ = 3.2 Hz, 1H, *o*-*C*H$_3$ of (C=C)$_3$P-Mes), 26.5 (br., Al*C*H$_2$^{i}Pr), 27.7 (s, AlCH$_2$*C*HMe$_2$), 27.8 (s, AlCH$_2$*C*HMe$_2$), 28.5 (s, Al*C*H$_2$^{i}Pr), 28.5 (dd, $^{4}J_{CP}$ = 4 Hz, $^{4}J_{CP}$ = 9 Hz, P$_2$-C=C(H)C*Me*$_3$), 29.2 (s, AlCH$_2$CH*Me*$_2$), 29.2 (s, AlCH$_2$CH*Me*$_2$), 29.4 (s, AlCH$_2$CH*Me*$_2$), 29.5 (s, AlCH$_2$CH*Me*$_2$), 30.1 (d, $^{4}J_{CP}$ = 1.1 Hz, P-(Al)-C=C(H)C*Me*$_3$), 31.7 (d, $^{3}J_{CP}$ = 6.7 Hz, Al-(P)-C=C(P)C*Me*$_3$), 36.7 ($^{3}J_{CP}$ = 15 Hz, $^{3}J_{CP}$ = 2 Hz, P$_2$C=C(H)*C*Me$_3$), 36.7 ($^{3}J_{CP}$ = 16.4 Hz, P-(Al)-C=C(H)*C*Me$_3$), 42.1 (dd, $^{2}J_{CP}$ = 31.4 Hz, $^{3}J_{CP}$ = 19.9 Hz, Al-(P)-C=C(P)*C*Me$_3$), 87.7 (d, $^{3}J_{CP}$ = 8.9 Hz, N-(C)-C=*C*H$_2$), 122.1 (dd, $^{1}J_{CP}$ = 78.6 Hz, $^{3}J_{CP}$ = 2.1 Hz, *ipso*-*C* of (C=C)$_3$P-Mes), 130.2 (s, *m*-C of (C=C)$_2$P-Mes), 130.6 (d, $^{3}J_{CP}$ = 7.8 Hz, *m*-C of (C=C)$_2$P-Mes), 131 (HMBC, *ipso*-*C* of (C=C)$_2$P-Mes), 131 (HMBC, P$_2$-*C*=C-H), 131.9 (d, $^{3}J_{CP}$ = 10.7 Hz, *m*-*C* of (C=C)$_3$P-Mes), 132.2 (d, $^{3}J_{CP}$ = 11.7 Hz, *m*-*C* of (C=C)$_3$P-Mes), 132.3 (dd, $^{1}J_{CP}$ = 60.1 Hz, $^{3}J_{CP}$ = 4.0 Hz, N-(C)-*C*=CH$_2$), 141.3 (d, $^{4}J_{CP}$ = 1.6 Hz, *p*-*C* of (C=C)$_2$P-Mes), 141.5 (d, $^{4}J_{CP}$ = 2.8 Hz, *p*-*C* of (C=C)$_3$P-Mes), 142.2 (d, $^{2}J_{CP}$ = 7.9 Hz, *o*-*C* of (C=C)$_3$P-Mes), 144.6 (d, $^{2}J_{CP}$ = 11.5 Hz, *o*-*C* of (C=C)$_3$P-Mes), 145.2 (m, *o*-*C* of (C=C)$_2$P-

Mes), 145.4 (dd, $^{2}J_{CP}$ = 34.2 Hz, $^{4}J_{CP}$ = 3.9 Hz, *o-C* of (C=C)$_2$P-Mes), 149.2 (d, $^{1}J_{CP}$ = 5.8 Hz, P-(Al)-*C*=C-H), 153.9 (d, $^{2}J_{CP}$ = 9.3 Hz, P-(Al)C=*C*-H), 154.5 (HMBC br., Al-(P)-*C*=C-P), 159.8 (d, $^{2}J_{CP}$ = 13.1 Hz, P$_2$-C=*C*-H), 179.2 (dd, $^{1}J_{CP}$ = 30.3 Hz, $^{2}J_{CP}$ = 3.0 Hz, Al-(P)-C=*C*-P). **MS** (EI, 20 eV, 353 K): m/z (%) = 670 (65), 671 (30), 672 (6) [M – Bu]$^+$; 629 (100), 630 (45), 631 (9) [M – CH_3CN – Bu]$^+$; 614 (4), 615 (1) [M – butene – Bu]$^+$; 573 (23), 574 (9), 575 (2) [M – CH_3CN – Bu – butene]$^+$; 530 (3), 531 (2) [M – CH_3CN – $AlBu_2$ – Me]$^+$. **IR** (CsI plates, paraffin, cm^{-1}): 3352 vw, 3177 vw, 3100 vw (νN-H); 2951 to 2853 br. vs (paraffin); 1601 vs, 1568 w, 1526 vw, 1515 vw νC=C, phenyl, δN-H; 1460 vs (paraffin); 1404 vw δCH_3; 1375 vs (paraffin); 1356 s, 1310 w, 1288 vw, 1267 w, 1250 vw δCH_3; 1221 m, 1198 m, 1167 w, 1086 vw, 1051 to 1024 br. s, 999 m, 959 m, 932 vw, 918 vw, 856 s, 847 vs, 814 w, 756 s, 745 w νC-C, νC-N; 721 w (paraffin); 676 s δphenyl; 658 m, 625 s, 594 w, 573 w, 565 vw, 549 w, 521 w, 496 vw, 465 vw, 440 vw δC-C, νAl-C, νAl-N, νP-C. **CHN** ($C_{46}H_{72}AlNP_2$, 728.0): Found: C, 76.0; H, 10.0; N, 1.8; calcd.: C, 75.9; H 10.0; N, 1.9.

1.8 Synthesis of the acetonitrile insertion product 8



8

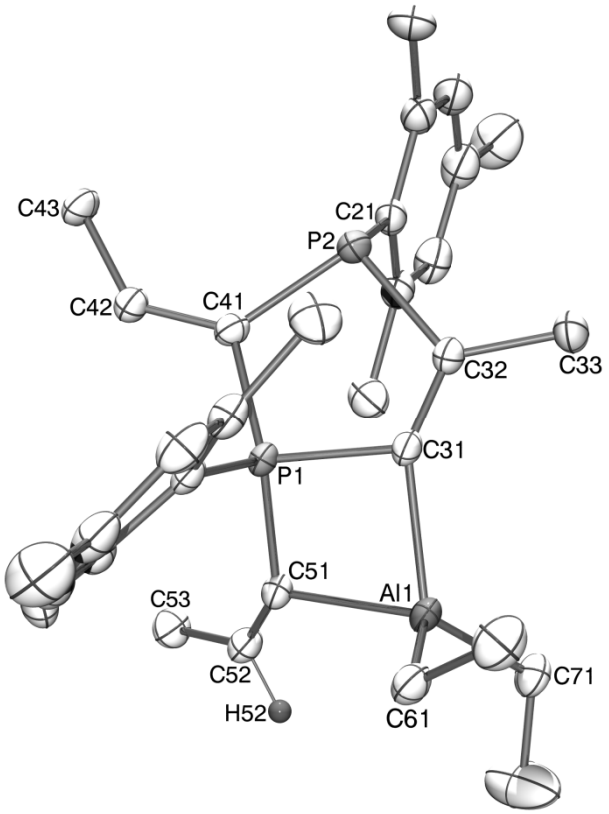
A solution of compound **3a** (Aryl = mesityl, R = $CH_2{}^tBu$) (0.129 g, 0.18 mmol) was dissolved in 25 mL of toluene and treated with an excess of acetonitrile (3.90 g, 9.50 mmol, 5 mL, large excess) at -10 °C. The mixture was warmed to room temperature and stirred for 10 min. The solvent was removed in vacuum. A mixture of many unidentified compounds resulted. Few crystals of **8** were obtained upon cooling of a solution in 1,2-difluorobenzene (1 mL) to -45 °C.

^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 300 K): δ = 2.0 (d, $^{2}J_{PP}$ = 6.6 Hz, (C=C)$_2$P), 60.3 (d, $^{2}J_{PP}$ = 6.6 Hz, (C=C)$_3$P). **^{1}H NMR** (C_6D_6, 400 MHz, 300 K): δ = 0.72 (s, 9H, ^tBu), 1.34 (s, 9H, ^tBu), 1.41 (s, 9H, ^tBu), 1.54 (9 H, s, ^tBu), 1.55 (9 H, s, ^tBu), 1.84 (s, 3H, *p*-CH_3 of P-Mes), 1.99 (s,

3H, *p*-C*H*$_3$ of P-Mes), 2.48 (s, 3H, *o*-C*H*$_3$ of P-Mes), 2.70 (s, 3H, *o*-C*H*$_3$ of P-Mes), 2.83 (s, 3H, *o*-C*H*$_3$ of (C=C)$_3$P-Mes), 2.85 (s, 3H, *o*-C*H*$_3$ of (C=C)$_2$P-Mes), 3.72 (s, 1H, N-H), 3.75 (d, $^4J_{PH}$ = 2.2 Hz, 1H, C=C*H*$_2$), 4.01 (s, 1H, C=C*H*$_2$), 6.34 (*pseudo*-t , $^3J_{HP}$ = 20.5 Hz, 1H, C=C-*H*), 6.85(d, $^3J_{HP}$ = 50.5 Hz, 1H, C=C-*H*).

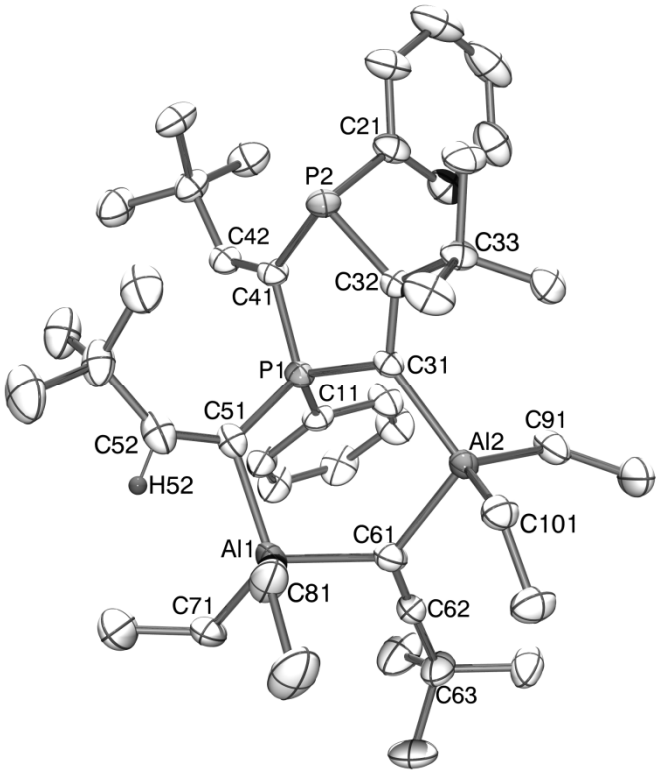
2. Molecular Structures and Important Bond Lengths and Angles#

Figure 1: Molecular structure of compound **4b**



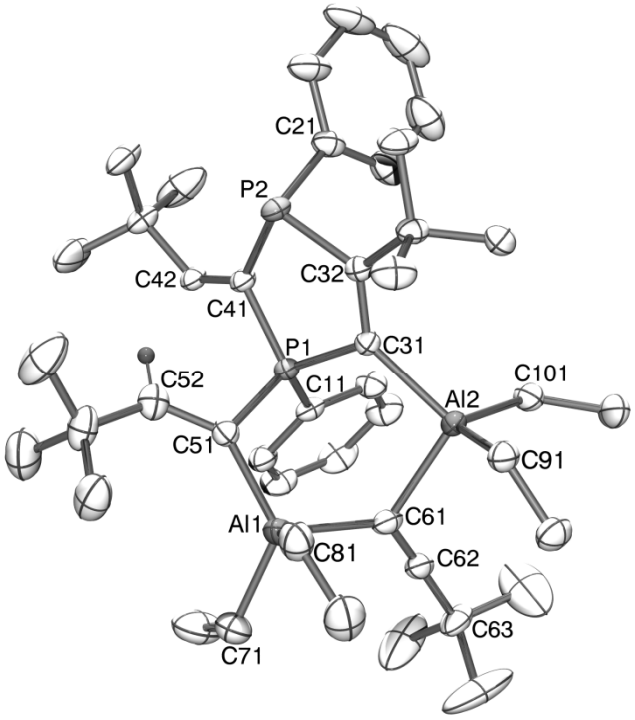
Displacement ellipsoids are drawn at the 40% level. Methyl groups of C43, C33, C53, C62 and C72 and hydrogen atoms with the exception of H52 are omitted. Important bond lengths [pm] and angles [°]:
P(1)-C(11) 184.1(3), P(1)-C(31) 178.3(2), P(1)-C(41) 183.8(3), P(1)-C(51) 179.5(3), P(2)-C(21) 184.7(3), P(2)-C(32) 186.1(3), P(2)-C(41) 184.5(3), Al(1)-C(31) 204.6(3), Al(1)-C(51) 210.5(3), Al(1)-C(61) 198.5(3), Al(1)-C(71) 199.4(3), C(31)-C(32) 134.3(4), C(41)-C(42) 133.8(4), C(51)-C(52) 133.3(4), C(11)-P(1)-C(41) 110.1(1), C(11)-P(1)-C(51) 106.5(1), C(31)-P(1)-C(41) 101.4(1), C(31)-P(1)-C(51) 91.9(1), C(41)-P(1)-C(51) 133.2(1), C(21)-P(2)-C(32) 105.2(1), C(21)-P(2)-C(41) 110.5(1), C(32)-P(2)-C(41) 96.4(1), C(31)-Al(1)-C(51) 76.5(1), C(31)-Al(1)-C(61) 113.0(1), C(31)-Al(1)-C(71) 116.7(1), C(51)-Al(1)-C(61) 113.2(1), C(51)-Al(1)-C(71) 110.8(1), C(61)-Al(1)-C(71) 119.0(1), P(1)-C(31)-Al(1) 92.0(1), P(1)-C(31)-C(32) 114.4(2), Al(1)-C(31)-C(32) 145.6(2), P(2)-C(32)-C(31) 118.1(2), P(2)-C(32)-C(33) 118.6(2), C(31)-C(32)-C(33) 122.8(2), P(1)-C(41)-P(2) 107.8(1), P(1)-C(41)-C(42) 119.5(2), P(2)-C(41)-C(42) 131.4(2), P(1)-C(51)-Al(1) 89.8(1), P(1)-C(51)-C(52) 140.3(2), Al(1)-C(51)-C(52) 126.3(2).

Figure 2: Molecular structure of compound ***6trans***



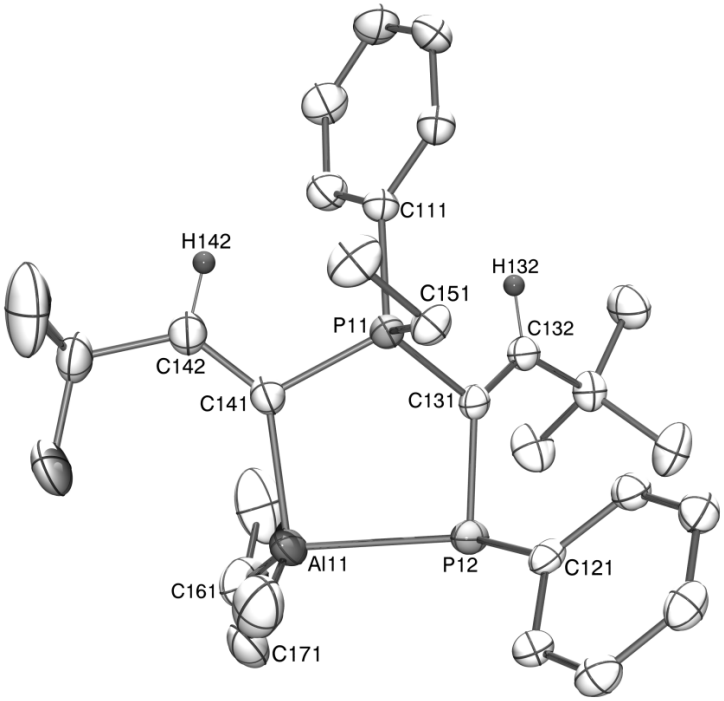
Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms with the exception of H52 are omitted. Important bond lengths [pm] and angles [°]:
P(1)-C(11) 180.9(2), P(1)-C(31) 177.7(2), P(1)-C(41) 180.9(2), P(1)-C(51) 176.7(2), P(2)-C(21) 184.6(2), P(2)-C(32) 186.2(2), P(2)-C(41) 182.8(2), Al(1)-C(61) 207.7(3), Al(1)-C(51) 203.2(2), Al(1)-C(71) 199.5(3), Al(1)-C(81) 201.4(6), Al(2)-C(61) 209.6(3), Al(2)-C(31) 205.5(2), Al(2)-C(91) 198.7(2), Al(2)-C(101) 198.7(2), C(31)-C(32) 136.9(2), C(41)-C(42) 134.2(3), C(51)-C(52) 133.9(4), C(61)-C(62) 120.9(3), C(11)-P(1)-C(41) 102.3(9), C(11)-P(1)-C(51) 106.3(1), C(31)-P(1)-C(41) 121.9(1), C(31)-P(1)-C(51) 107.6(1), C(41)-P(1)-C(51) 121.9(1), C(21)-P(2)-C(32) 100.1(1), C(21)-P(2)-C(41) 102.3(9), C(32)-P(2)-C(41) 94.5(9), C(31)-Al(2)-C(61) 103.17(8), C(31)-Al(2)-C(91) 107.3(1), C(31)-Al(2)-C(101) 120.54(9), C(61)-Al(2)-C(91) 106.3(1), C(61)-Al(2)-C(101) 102.4(9), C(91)-Al(2)-C(101) 115.4(1), C(61)-Al(1)-C(51) 105.96(1), C(61)-Al(1)-C(71) 107.8(1), C(61)-Al(1)-C(81) 110.3(4), C(51)-Al(1)-C(71) 111.0(1), C(51)-Al(1)-C(81) 103.2(3), C(71)-Al(1)-C(81) 118.9(4), P(1)-C(31)-Al(2) 116.97(9), P(1)-C(31)-C(32) 110.2(2), Al(2)-C(31)-C(32) 132.8(2), P(2)-C(32)-C(31) 121.2(2), P(2)-C(32)-C(33) 115.6(1), C(31)-C(32)-C(33) 122.8(2), P(1)-C(41)-P(2) 108.6(1), P(2)-C(41)-C(42) 132.9(2), P(1)-C(41)-C(42) 118.5(2), C(41)-C(42)-C(43) 131.7(2), P(1)-C(51)-Al(1) 116.6(1), P(1)-C(51)-C(52) 134.6(2), Al(1)-C(51)-C(52) 108.5(2), C(51)-C(52)-C(53) 136.9(2), Al(2)-C(61)-Al(1) 113.1(1), Al(1)-C(61)-C(62) 119.2(2), Al(2)-C(61)-C(62) 127.4(2), C(61)-C(62)-C(63) 178.0(2).

Figure 3: Molecular structure of compound **6*cis***



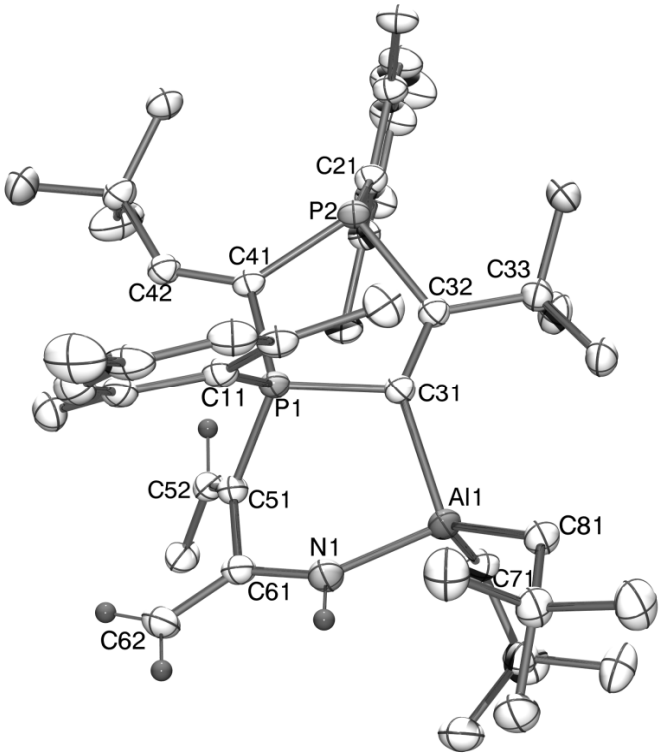
Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms with the exception of H52 are omitted. Important bond lengths [pm] and angles [°]:
P(1)-C(11) 180.5(3), P(1)-C(31) 177.8(2), P(1)-C(41) 180.9(2), P(1)-C(51) 179.6(3), P(2)-C(21) 184.8(3), P(2)-C(32) 186.5(3), P(2)-C(41) 182.5(3), Al(1)-C(61) 210.5(3), Al(1)-C(51) 203.3(3), Al(1)-C(71) 198.9(3), Al(1)-C(81) 199.9(3), Al(2)-C(61) 198.5(3), Al(2)-C(31) 205.2(2), Al(2)-C(91) 199.0(3), Al(2)-C(101) 213.7(3), C(31)-C(32) 136.2(3), C(41)-C(42) 133.3(3), C(51)-C(52) 135.8(4), C(61)-C(62) 120.6(4), C(11)-P(1)-C(41) 106.5(1), C(11)-P(1)-C(51) 109.9(1), C(31)-P(1)-C(41) 102.7(1), C(31)-P(1)-C(51) 109.0(1), C(41)-P(1)-C(51) 113.7(1), C(21)-P(2)-C(32) 100.0(1), C(21)-P(2)-C(41) 102.4(1), C(32)-P(2)-C(41) 94.7(1), C(61)-Al(1)-C(51) 101.9(1), C(61)-Al(1)-C(71) 104.8(1), C(61)-Al(1)-C(81) 108.0(1), C(51)-Al(1)-C(71) 115.5(1), C(51)-Al(1)-C(81) 114.3(1), C(71)-Al(1)-C(81) 111.2(2), C(31)-Al(2)-C(61) 98.9(1), C(31)-Al(2)-C(91) 122.6(1), C(31)-Al(2)-C(101) 105.9(1), C(61)-Al(2)-C(91) 102.4(1), C(61)-Al(2)-C(101) 111.5(1), C(91)-Al(2)-C(101) 114.3(1), P(1)-C(31)-Al(2) 116.2(1), P(1)-C(31)-C(32) 109.9(2), Al(2)-C(31)-C(32) 133.9(2), P(2)-C(32)-C(31) 121.1(2), P(2)-C(32)-C(33) 122.8(8), C(31)-C(32)-C(33) 122.8(2), P(1)-C(41)-P(2) 107.9(1), P(2)-C(41)-C(42) 133.3(2), P(1)-C(41)-C(42) 118.6(2), C(41)-C(42)-C(43) 132.4(2), P(1)-C(51)-Al(1) 115.1(1), P(1)-C(51)-C(52) 111.5(2), Al(1)-C(51)-C(52) 133.0(2), C(51)-C(52)-C(53) 132.6(3), Al(2)-C(61)-Al(1) 113.4(1), Al(1)-C(61)-C(62) 129.6(2), Al(2)-C(61)-C(62) 116.4(2), C(61)-C(62)-C(63) 178.8(3)

Figure 4: Molecular structure of *cyclo*-Ph-P-Al(Et)$_2$-C(=CH-^{t}Bu)-P(Ph)Et-C(=CH-^{t}Bu)



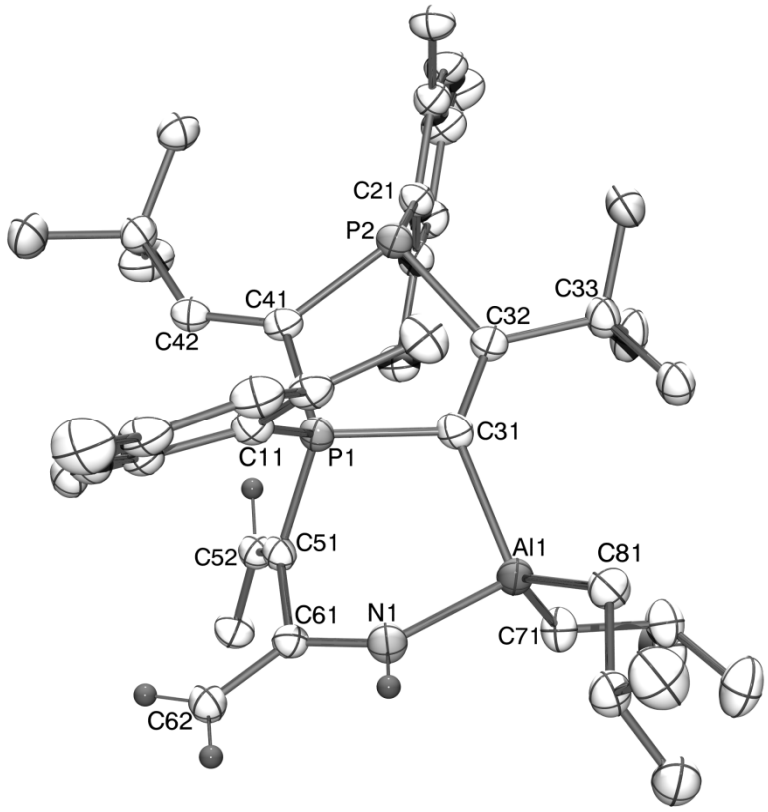
Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms with the exception of H132 and H142 are omitted. Important bond lengths [pm] and angles [°] (data in square brackets are from the second, independent molecule):
P(11)-C(141) 178.9(3) [178.1(3)], P(11)-C(131) 180.7(3) [181.0(3)], P(11)-C(111) 181.0(3) [181.4(3)], P(11)-C(151) 181.4(3) [181.2(3)], C(151)-C(152) 152.7(5) [152,3(5)], C(131)-C(132) 135.0(4) [133.0(4)], C(131)-P(12) 183.9(3) [186.2(3)], C(141)-C(142) 133.8(5) [134.1(5)], C(141)-Al(11) 205.4(3) [204.4(3)], P(12)-C(121) 183.3(3) [182.8(3)], P(12)-Al(11) 246.1(1) [246.1(1)], Al(11)-C(171) 198.4(4) [200.3(4)], Al(11)-C(161) 199.1(5) [197.7(3)], C(141)-P(11)-C(131) 108.9(2) [108.6(1)], C(141)-P(11)-C(111) 113.4(2) [115.0(1)], C(131)-P(11)-C(111) 109.8(2) [109.3(1)], C(141)-P(11)-C(151) 107.5(2) [106.8(2)], C(131)-P(11)-C(151) 109.7(2) [108.2(2)], C(111)-P(11)-C(151) 107.4(2) [108.7(2)], C(132)-C(131)-P(11) 117.8(2) [119.6(2)], C(132)-C(131)-P(12) 128.5(2) [128.0(2)], P(11)-C(131)-P(12) 113.4(2) [111.8(2)], C(131)-C(132)-C(133) 129.5(3) [130.3(3)], C(142)-C(141)-P(11) 113.6(3) [116.9(2)], C(142)-C(141)-Al(11) 135.7(3) [134.3(2)], P(11)-C(141)-Al(11) 110.6(2) [108.6(2)], C(141)-C(142)-C(143) 130.0(3) [128.6(3)], C(121)-P(12)-C(131) 101.8(1) [103.2(1)], C(121)-P(12)-Al(11) 111.4(1) [108.2(1)], C(131)-P(12)-Al(11) 96.5(1) [98.4(1), C(171)-Al(11)-C(161) 116.5(2) [115.9(2)], C(171)-Al(11)-C(141) 116.5(2) [112.5(1)], C(161)-Al(11)-C(141) 111.0(2) [116.4(1)], C(171)-Al(11)-P(12) 112.6(1) [113.6(1)], C(161)-Al(11)-P(12) 101.5(2) [100.7(1)], C(141)-Al(11)-P(12) 95.9(1) [95.0(1)].

Figure 5: Molecular structure of compound **7a**



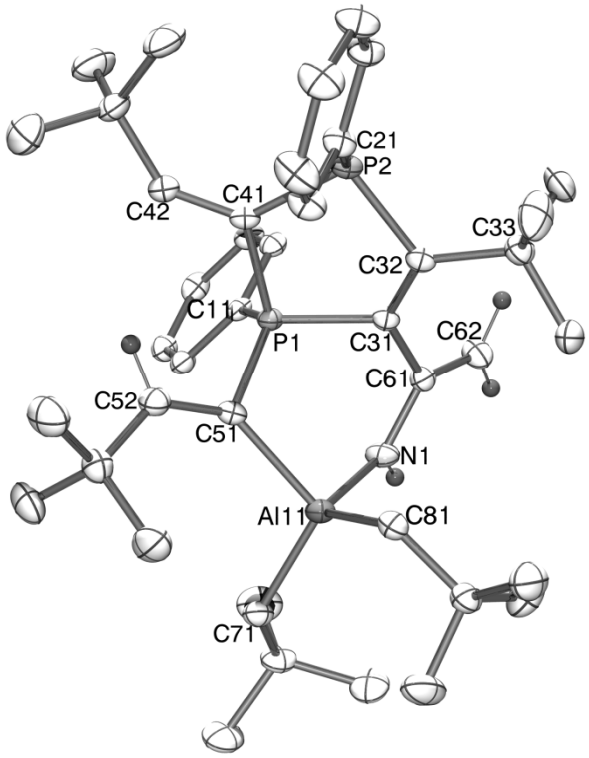
Displacement ellipsoids are drawn at the 40% level. Methyl groups of C53 and hydrogen atoms with the exception of the C=CH_2 and N-H protons are omitted. Important bond lengths [pm] and angles [°]:
P(1)-C(31) 178.7(2), P(1)-C(41) 181.5(2), P(1)-C(51) 182.2(2), P(1)-C(11) 182.9(2), P(2)-C(41) 183.1(2), P(2)-C(21) 184.0(2), P(2)-C(32) 186.9(2), C(31)-C(32135.8(2), C(31)-Al(1) 208.5(2), C(41)-C(42) 134.5(2), C(51)-C(52) 133.7(3), C(51)-C(61) 149.1(3), C(61)-C(62) 134.7(3), C(61)-N(1) 137.6(2), N(1)-Al(1) 187.8(2), N(1)-H(1) 89(3), Al(1)-C(71) 200.8(2), Al(1)-C(81) 201.6(2), C(31)-P(1)-C(41) 102.64(8), C(31)-P(1)-C(51) 106.46(8), C(41)-P(1)-C(51) 115.00(8), C(41)-P(1)-C(11) 108.71(8), C(51)-P(1)-C(11) 108.06(8), C(41)-P(2)-C(21) 107.26(8), C(41)-P(2)-C(32) 95.13(8), C(21)-P(2)-C(32) 107.96(8), C(32)-C(31)-P(1) 111.1(1), C(32)-C(31)-Al(1) 139.1(1), P(1)-C(31)-Al(1) 108.70(9), C(31)-C(32)-C(33) 124.5(2), C(31)-C(32)-P(2) 118.3(1), C(33)-C(32)-P(2) 116.5(1), C(42)-C(41)-P(1) 120.2(1), C(42)-C(41)-P(2) 133.8(1), P(1)-C(41)-P(2) 105.53(9), C(52)-C(51)-C(61) 131.5(2), C(52)-C(51)-P(1) 118.3(1), C(61)-C(51)-P(1) 110.2(1), C(51)-C(52)-C(53) 132.7(2), C(62)-C(61)-N(1) 126.4(2), C(62)-C(61)-C(51) 120.2(2), N(1)-C(61)-C(51) 112.8(2), C(61)-N(1)-Al(1) 131.9(2), C(61)-N(1)-H(1) 109(2), Al(1)-N(1)-H(1) 118(2), N(1)-Al(1)-C(71) 111.40(9), N(1)-Al(1)-C(81) 109.49(8), C(71)-Al(1)-C(81) 119.17(9), N(1)-Al(1)-C(31) 98.27(7), C(71)-Al(1)-C(31) 101.99(8), C(81)-Al(1)-C(31) 114.43(8).

Figure 6: Molecular structure of compound **7b**



Displacement ellipsoids are drawn at the 40% level. Methyl groups of C53 and hydrogen atoms with the exception of the C=CH_2 and N-H protons are omitted. Important bond lengths [pm] and angles [°]:
P(1)-C(31) 178.1(3), P(1)-C(41) 182.2(3), P(1)-C(51) 182.4(3), P(1)-C(11) 183.0(4), P(2)-C(41) 183.7(4), P(2)-C(21) 185.3(3), P(2)-C(32) 186.9(3), C(31)-C(32) 136.0(4), C(31)-Al(1) 208.5(3), C(41)-C(42) 134.5(5), C(51)-C(52) 133.6(5), C(51)-C(61) 150.0(4), C(61)-C(62) 134.0(5), C(61)-N(1) 137.2(2), N(1)-Al(1) 188.5(3), N(1)-H(1) 89(4), Al(1)-C(71) 200.9(4), Al(1)-C(81) 200.3(4), C(31)-P(1)-C(41) 102.6(2), C(31)-P(1)-C(51) 106.5(2), C(41)-P(1)-C(51) 115.6(2), C(41)-P(1)-C(11) 109.2(2), C(51)-P(1)-C(11) 107.3(2), C(41)-P(2)-C(21) 107.3(2), C(41)-P(2)-C(32) 95.1(2), C(21)-P(2)-C(32) 107.4(2), C(32)-C(31)-P(1) 111.4(3), C(32)-C(31)-Al(1) 138.2(3), P(1)-C(31)-Al(1) 109.5(2), C(31)-C(32)-C(33) 123.8(3), C(31)-C(32)-P(2) 118.3(3), C(33)-C(32)-P(2) 117.2(2), C(42)-C(41)-P(1) 120.8(3), C(42)-C(41)-P(2) 133.6(3), P(1)-C(41)-P(2) 105.2(2), C(52)-C(51)-C(61) 130.8(3), C(52)-C(51)-P(1) 118.8(2), C(61)-C(51)-P(1) 110.3(2), C(51)-C(52)-C(53) 132.7(3), C(62)-C(61)-N(1) 126.5(3), C(62)-C(61)-C(51) 120.3(3), N(1)-C(61)-C(51) 112.7(3), C(61)-N(1)-Al(1) 132.2(2), C(61)-N(1)-H(1) 112(3), Al(1)-N(1)-H(1) 116(3), N(1)-Al(1)-C(71) 108.6(2), N(1)-Al(1)-C(81) 104.0(2), C(71)-Al(1)-C(81) 122.4(2), N(1)-Al(1)-C(31) 98.2(2), C(71)-Al(1)-C(31) 107.2(2), C(81)-Al(1)-C(31) 113.6(2).

Figure 7: Molecular structure of compound **8**



Displacement ellipsoids are drawn at the 40% level. Methyl groups of the mesityl rings and hydrogen atoms with the exception of the C=CH_2 and N-H protons are omitted. Important bond lengths [pm] and angles [°]:
P(1)-C(51) 180.7(3), P(1)-C(31) 180.9(3), P(1)-C(41) 181.1(3), P(1)-C(11) 183.3(3), P(2)-C(41) 184.2(3), P(2)-C(21) 185.3(3), P(2)-C(32) 186.0(3), C(31)-C(32) 136.0(4), C(31)-C(61) 149.1(4), C(41)-C(42) 134.2(5), C(51)-C(52) 135.1(5), C(51)-Al(1) 207.5(3), N(1)-C(61) 138.4(4), N(1)-Al(1) 187.4(3), N(1)-H(1) 75(3), C(61)-C(62) 133.6(5), Al(1)-C(81) 201.0(4), Al(1)-C(71) 202.2(3), C(51)-P(1)-C(31) 106.3(2), C(51)-P(1)-C(41) 114.0(2), C(31)-P(1)-C(41) 99.4(2), C(51)-P(1)-C(11) 116.8(2), C(41)-P(1)-C(11) 107.7(1), C(41)-P(2)-C(21) 109.7(2), C(41)-P(2)-C(32) 96.8(2), C(21)-P(2)-C(32) 112.2(2), C(32)-C(31)-C(61) 134.3(3), C(32)-C(31)-P(1) 115.4(3), C(61)-C(31)-P(1) 110.3(2), C(31)-C(32)-C(33) 126.1(3), C(31)-C(32)-P(2) 115.3(3), C(33)-C(32)-P(2) 116.9(2), C(42)-C(41)-P(1) 115.7(3), C(42)-C(41)-P(2) 133.1(3), P(1)-C(41)-P(2) 109.9(2), C(41)-C(42)-C(43) 134.6(3), C(52)-C(51)-P(1) 113.9(3), C(52)-C(51)-Al(1) 137.5(3), P(1)-C(51)-Al(1) 108.6(2), C(51)-C(52)-C(53) 130.8(3), C(61)-N(1)-Al(1) 129.8(3), C(61)-N(1)-H(1) 108(2), Al(1)-N(1)-H(1) 121(2), C(62)-C(61)-N(1) 125.9(3), C(62)-C(61)-C(31) 120.9(3), N(1)-C(61)-C(31) 112.3(3), N(1)-Al(1)-C(81) 110.7(2), N(1)-Al(1)-C(71) 112.9(1), C(81)-Al(1)-C(71) 118.0(2), N(1)-Al(1)-C(51) 97.4(1), C(81)-Al(1)-C(51) 105.4(1), C(71)-Al(1)-C(51) 110.2(1).

3. Calculated Structures at the B3PW91/6-31+(d,p) Level of Theory#

4' -1.586,4006069 a.u. (ZPE 0,344115 a.u.)

C	-2.17565	-0.17606	3.93777
C	-2.27836	-1.27210	3.08278
C	-1.47229	0.96139	3.53395
C	-1.68078	-1.23572	1.82212
C	-0.87876	1.00401	2.27571
C	2.07908	-2.86199	1.40465
C	-0.98308	-0.09504	1.41120
C	-0.13237	-1.67627	-0.93312
C	-1.00195	-2.29603	-1.74645
C	1.57957	0.15185	-0.19462
C	3.08772	-2.44497	-1.81441
C	-2.31796	-1.82186	-2.28569
C	-1.97970	1.96967	-1.14782
C	-0.70422	1.58465	-0.97005
C	-2.43939	3.29774	-1.65622
C	2.01241	1.31389	-0.72745
C	3.45396	1.63053	-1.00913
H	-2.81778	-2.16126	3.39682
H	-1.38433	1.81422	4.20118
H	1.39465	-2.50012	2.18179
H	1.89559	-3.93852	1.28378
H	-0.71801	-3.29742	-2.08482
H	-2.77534	1.26112	-0.90825
H	4.14520	-2.32100	-1.54340
H	2.91337	-1.86761	-2.73086
Al	1.88611	-1.89934	-0.32467
P	-0.19344	-0.02359	-0.23270
P	0.78896	2.64253	-1.19005
H	2.95136	-3.50579	-2.06575
H	3.09923	-2.75793	1.79899
H	0.95169	2.53536	-2.60448
H	3.78974	2.48926	-0.41428
H	4.08629	0.77256	-0.76959
H	3.60649	1.89371	-2.06380
H	-1.62417	4.02586	-1.69559
H	-2.85849	3.19889	-2.66620
H	-3.23965	3.69699	-1.02221
H	-1.74136	-2.09544	1.16111
H	-2.63759	-0.20796	4.92069
H	-0.33239	1.89205	1.96867
H	-2.29491	-1.78145	-3.38238
H	-3.12069	-2.52099	-2.01784
H	-2.58484	-0.82938	-1.91423

MeCN -132,7088994 a.u. (ZPE 0,045393 a.u.)

N	0.00000	0.00000	1.43849
C	0.00000	0.00000	0.27764
C	0.00000	0.00000	-1.17831
H	0.00000	1.02644	-1.55516
H	-0.88892	-0.51322	-1.55516
H	0.88892	-0.51322	-1.55516

9' -1.719,0966993 a.u. (ZPE 0,390181 a.u.)

C	3.59663	-0.55024	-3.16876
C	8.90718	-1.10515	-0.11320
C	3.71898	-1.02945	-1.74435
C	4.14086	-0.41946	-0.62185
C	8.59055	1.38529	2.20748
C	6.54161	1.30533	-0.45799
C	8.51094	2.35643	-1.65881
C	7.04309	2.14203	-1.40033
C	3.16049	3.08394	-1.89687
C	4.39434	2.59243	-1.68999
C	2.88920	1.32832	1.61519
C	2.78302	4.16750	-2.85608
C	4.05922	1.87433	1.07687
C	2.33090	1.86739	2.77473
C	4.66928	2.96082	1.71459
C	2.94812	2.94460	3.41261
C	4.11911	3.48853	2.88215
H	9.31024	-1.81536	0.62137
H	8.33768	-1.68295	-0.85198
H	3.41666	-2.08188	-1.64097
H	9.29422	2.12535	1.80369
H	2.33309	2.65401	-1.32695
H	7.83494	1.94107	2.77703
H	1.41537	1.44526	3.18153
H	4.60570	4.32398	3.37814
N	6.45744	-0.88470	1.74326
Al	7.78799	0.27227	0.77585
P	4.73404	1.21996	-0.49574
P	5.93772	3.21149	-2.44578
H	5.97276	2.40654	-3.62692
H	9.14281	1.70487	-1.04889
H	8.75296	2.15799	-2.71105
H	8.79417	3.39724	-1.46014
H	2.14048	4.91016	-2.36830
H	2.20658	3.75711	-3.69620
H	3.66076	4.67793	-3.26364
H	2.43420	0.47366	1.11940
H	2.51871	3.35909	4.32083
H	5.57931	3.38931	1.30239
H	2.56643	-0.66028	-3.53468
H	4.22499	-1.16574	-3.82677
H	3.89657	0.49352	-3.28681
H	9.15372	0.77134	2.92286
H	9.77000	-0.67385	-0.63722
C	5.50982	-1.50927	1.95754
C	4.31779	-2.28562	2.20553
H	3.63854	-2.03044	1.38109
H	3.87744	-2.00861	3.16686
H	4.55271	-3.35337	2.19634

9'-isom -1.719,1027755 a.u. (ZPE 0,390437 a.u.)

C	0.84812	-1.14809	-1.32025
C	6.94968	0.07021	0.33835
C	1.46443	0.22434	-1.33482
C	2.12625	0.76019	-0.28896

C	6.68892	2.97896	2.11007
C	4.62605	2.39960	-0.48977
C	6.60213	3.14366	-1.89338
C	5.13339	3.00871	-1.59034
C	1.23402	3.60130	-2.43414
C	2.48411	3.33222	-2.01733
C	1.00241	3.06317	1.51566
C	0.85382	4.34700	-3.67423
C	2.20856	3.39461	0.88780
C	0.48807	3.87970	2.52315
C	2.89850	4.54648	1.28336
C	1.18094	5.02585	2.91603
C	2.38689	5.35703	2.29613
H	7.33839	-0.48563	1.20232
H	6.36877	-0.63306	-0.27138
H	1.32188	0.74690	-2.29477
H	7.39807	3.61658	1.56556
H	0.40056	3.25252	-1.82043
H	5.94840	3.64549	2.57002
H	-0.45283	3.62073	3.00199
H	2.93151	6.24591	2.60257
N	4.50577	0.71374	2.10700
Al	5.85880	1.61949	0.92867
P	2.81876	2.36029	-0.49228
P	4.03484	3.85420	-2.82713
H	4.12476	2.86503	-3.85441
H	7.22864	2.62527	-1.16235
H	6.83503	2.72642	-2.88155
H	6.89994	4.19897	-1.91667
H	0.12982	5.13733	-3.44200
H	0.36740	3.67882	-4.39678
H	1.72051	4.80300	-4.16182
H	0.48103	2.15837	1.21175
H	0.78286	5.65948	3.70413
H	3.83917	4.80480	0.80407
H	1.28272	-1.77894	-2.10780
H	-0.23155	-1.10246	-1.51956
H	1.00614	-1.64285	-0.35725
H	7.25249	2.50511	2.92484
H	7.82111	0.37008	-0.25812
C	3.55432	0.16893	2.46934
C	2.34758	-0.50501	2.88491
H	1.67386	-0.42597	2.02018
H	1.91610	-0.00914	3.75824
H	2.55794	-1.55283	3.11527

10’ -1.719,1476198 a.u. (ZPE 0,393868 a.u.)

C	-2.37916	-2.85413	-2.23212
C	3.61025	-2.26067	-0.82474
C	-1.81124	-1.58771	-1.67442
C	-0.99526	-1.43892	-0.61128
C	3.11769	-0.77207	2.18703
C	1.43792	0.26849	-0.53402
C	3.13908	1.30324	-2.07642
C	1.74719	1.12014	-1.54072
C	-2.20492	1.97135	-1.33285
C	-0.94374	1.50576	-1.36775

C	-1.96914	0.13880	2.00845
C	-2.75859	3.08212	-2.16435
C	-0.78090	0.62725	1.45209
C	-2.34795	0.52822	3.29202
C	0.02927	1.49926	2.18901
C	-1.54143	1.40069	4.02342
C	-0.35333	1.88268	3.47275
H	3.84910	-3.25842	-0.43213
H	3.18370	-2.40300	-1.82641
H	-2.07669	-0.69109	-2.23596
H	3.87968	0.01305	2.08223
H	-2.91074	1.50746	-0.64029
H	2.35676	-0.39912	2.88452
H	-3.26692	0.14201	3.72380
H	0.28395	2.54888	4.04691
N	0.82458	-2.39719	0.67633
Al	2.36843	-1.32621	0.42599
P	-0.31541	0.21003	-0.25120
P	0.45519	2.20579	-2.33757
H	0.29146	1.44134	-3.53327
H	3.83561	0.62167	-1.58431
H	3.17469	1.11070	-3.15664
H	3.48194	2.33464	-1.92647
H	-3.30153	3.79677	-1.53491
H	-3.48268	2.69318	-2.89203
H	-1.97594	3.61493	-2.71119
H	-2.58886	-0.55581	1.44741
H	-1.83401	1.69736	5.02677
H	0.96470	1.85659	1.76788
H	-2.11495	-2.93499	-3.29362
H	-3.47580	-2.83558	-2.18711
H	-2.02683	-3.75063	-1.72454
H	3.60560	-1.62656	2.67546
H	4.56644	-1.73329	-0.94607
C	-0.37322	-2.49457	0.29394
C	-1.26548	-3.64783	0.73892
H	-2.33245	-3.39888	0.72629
H	-0.96850	-3.93306	1.75085
H	-1.11224	-4.52494	0.09900

7' -1.719,1588862 a.u. (ZPE 0,394804 a.u.)

C	-1.62898	-2.23505	-3.27363
C	3.38266	-1.97102	-1.51009
C	-1.40953	-3.48219	-0.26419
C	-1.33903	-1.12046	-2.32183
C	-0.49541	-2.47511	-0.32574
C	-0.84117	-1.23236	-1.07421
C	3.30825	-1.50896	1.84138
C	1.44787	0.40083	-0.27746
C	3.26001	1.90222	-1.17823
C	1.83042	1.55503	-0.87216
C	-2.17003	2.16969	-1.06346
C	-0.87779	1.81517	-0.95447
C	-2.19428	-0.41291	1.78018
C	-2.68586	3.46029	-1.61128
C	-0.96197	0.19473	1.51072
C	-2.70631	-0.39321	3.07685

C	-0.24381	0.81385	2.54122
C	-1.99373	0.22876	4.10202
C	-0.76219	0.82907	3.83395
H	3.65833	-3.03289	-1.44406
H	2.81563	-1.84590	-2.44239
H	-2.37967	-3.39020	-0.73734
H	-1.20336	-4.39154	0.29362
H	-1.53234	-0.11621	-2.69924
H	0.79284	-3.18719	0.98642
H	4.20123	-0.86871	1.84350
H	-2.93353	1.46173	-0.73407
H	2.68814	-1.20243	2.69399
H	-3.65757	-0.87408	3.28649
H	-0.19970	1.30237	4.63362
N	0.70569	-2.41434	0.33285
Al	2.34082	-1.42014	0.10107
P	-0.31942	0.26151	-0.18155
P	0.58691	2.86243	-1.33696
H	0.64110	2.65589	-2.74913
H	3.92517	1.07614	-0.91865
H	3.39142	2.12955	-2.24395
H	3.57207	2.79448	-0.62138
H	-3.43337	3.89111	-0.93506
H	-3.19088	3.29592	-2.57206
H	-1.88733	4.19147	-1.76473
H	-2.73732	-0.92376	0.99031
H	-2.39356	0.23878	5.11222
H	0.72303	1.26458	2.33446
H	-1.24798	-1.98257	-4.27010
H	-2.71163	-2.38327	-3.38105
H	-1.19235	-3.17784	-2.93824
H	3.66097	-2.52911	2.05011
H	4.32144	-1.41105	-1.62462