Nitro-Redox Reactions at a Frustrated Borane/Phosphane Lewis Pair

Guo-Qiang Chen, Gerald Kehr, Constantin G. Daniliuc‡ and Gerhard Erker*

Organisch-Chemisches Institut der Universität Münster, Corrensstraße 40, 48149 Münster (Germany)

‡ X-Ray structure analysis.

Supporting Information

| General Information            | S2 |
| Synthesis of compound 8       | S4 |
| Synthesis of compound 9a      | S12|
| Synthesis of compound 9b      | S18|
| Synthesis of compound 10      | S24|
General Procedure. All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Solvents were dried and stored under an argon atmosphere. NMR spectra were recorded on an Agilent DD2- 500 MHz (\(^1\)H: 500 MHz, \(^{13}\)C: 126 MHz, \(^{19}\)F: 470 MHz, \(^{11}\)B: 160 MHz, \(^{31}\)P: 202 MHz) and on an Agilent DD2- 600 MHz (\(^1\)H: 600 MHz, \(^{13}\)C: 151 MHz, \(^{19}\)F: 564 MHz, \(^{11}\)B: 192 MHz, \(^{31}\)P: 243 MHz). \(^1\)H NMR and \(^{13}\)C NMR: chemical shifts are given relative to TMS and referenced to the solvent signal. \(^{19}\)F NMR: chemical shifts are given relative to CFCl\(_3\) (δ = 0, external reference), \(^{11}\)B NMR: chemical shifts are given relative to BF\(_3\)Et\(_2\)O (δ = 0, external reference), \(^{31}\)P NMR: chemical shifts are given relative to H\(_3\)PO\(_4\) (85% in D\(_2\)O) (δ = 0, external reference). NMR assignments were supported by additional 2D NMR experiments. Elemental analyses were performed on an Elementar Vario El III. Melting points and decomposition points were obtained with a DSC 2010 (TA Instruments).

X-Ray diffraction: For compound 9a data sets was collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, Methods Enzymol. 1997, 276, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, Acta Crystallogr. 2003, A59, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, Acta Crystallogr. 1990, A46, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, Acta Crystallogr. 2008, A64, 112-122) and graphics, XP (BrukerAXS, 2000). For compound 9b data sets were collected with a KappaCCD APEXII Bruker diffractometer. For compounds 8 and 10 data sets were collected with a D8 Venture Dual Source 100 CMOS diffractometer. Programs used: data collection: APEX2 V2014.5-0 (Bruker AXS Inc., 2014); cell refinement: SAINT V8.34A (Bruker AXS Inc., 2013); data reduction: SAINT V8.34A (Bruker AXS Inc., 2013); absorption correction, SADABS V2014/2 (Bruker AXS Inc., 2014); structure solution SHELXT-2014 (Sheldrick, 2014); structure refinement SHELXL-2014 (Sheldrick, 2014) and graphics, XP (Bruker AXS Inc., 2014). \(R\)-values are given for observed reflections, and \(wR^2\) values are given for all reflections. Exceptions and special features: For compound 8 one disordered over two positions.
C(Me)(CH=CH$_2$) unit and two dichloromethane molecules were found in the asymmetric unit. For 9a one disordered pentane molecule was found in the asymmetric unit. Compound 9b crystallized with two molecules in the asymmetric unit. Corresponding, two disordered C(Me)(CH=CH$_2$) units were found. Compound 10 shows again the disordered C(Me)(CH=CH$_2$) group. For all these compounds several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. For compound 8 additionally one half disordered dichloromethane molecule and for compound 10 two badly disordered dichloromethane molecules were found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (A. L. Spek J. Appl. Cryst., 2003, 36, 7-13) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecules. CCDC deposition numbers are 1450866 to 1450870.

**Materials.** P/B FLPs 6a, 6b [P. Moquist, G.-Q. Chen, C. Mück-Lichtenfeld, K. Bussmann, C. G. Daniliuc, G. Kehr and G. Erker, Chem. Sci. 2015, 6, 816.] were prepared according to the literature.
Synthesis of compound 8

Compound 6a (136.7 mg, 0.2 mmol) and nitrosobenzene (42.8 mg, 0.4 mmol) were dissolved in CH₂Cl₂ (2 mL). The reaction mixture was stirred at room temperature for 1 day. All volatiles were removed in vacuo and the residue was washed with cold pentane (3x1 mL). After dried in vacuo compound 8 (142.7 mg, 80%) was obtained as a white solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound 8 in dichloromethane at -35 °C. **Decomp.**: 214 °C. **Anal. Calc.** for C₄₇H₄₀BF₁₀N₂O₃P: C: 62.96; H: 4.50; N: 3.12. Found: C: 59.57; H: 4.16; N: 3.15.

The solution of the white solid in CD₂Cl₂ showed two isomers [53:47 (¹H)]

¹H NMR (500 MHz, 299 K, CD₂Cl₂): δ = without assignment to an isomer: 7.26 (1H), 7.25 (1H), 7.06 (2H), 6.80 (1H), 6.72 (1H), 6.51 (2H)(each m, m-Mes), 3.65 (3H, o), 3.63 (3H, o), 2.91 (3H, o), 2.90 (3H, o), 2.34 (3H, p), 2.33 (3H, p), 2.23 (6H, p), 1.75 (3H, o), 1.68 (3H, o), 1.22 (3H, o), 1.20 (3H, o)(each s, CH₃Mes), [Ph not listed]. Major isomer: 5.16 (dd, 3JHH = 17.7 Hz, 3JHH = 10.9 Hz, 1H, =CH), 4.76 (dd, 3JHH,trans = 17.7 Hz, 2JHH = 0.9 Hz, 1H, =CH), 4.75 (dd, 2JPH = 19.6 Hz, 2JHH = 14.1 Hz, 1H, CH₂), 4.35 (dd, 3JHH,cis = 10.9 Hz, 2JHH = 0.9 Hz, 1H, =CH₂), 3.01 (dd, 2JHH = 14.1 Hz, 2JPH = 1.7 Hz, 1H, CH₂), 1.50 (d, J = 5.3 Hz, 3H, CH₃). Minor isomer: 6.87 (dd, 3JHH = 17.8 Hz, 3JHH = 11.0 Hz, 1H, =CH), 5.17 (dd, 3JHH,cis = 11.0 Hz, 2JHH = 0.9 Hz, 1H, =CH₂), 4.84 (dt, 3JHH,trans = 17.8 Hz, 2JHH ~ J = 0.9 Hz, 1H, =CH₂), 4.77 (dd, 2JPH = 20.1 Hz, 2JHH = 14.4 Hz, 1H, CH₂), 2.92 (d, 3JHH = 14.4 Hz, 1H, CH₂), 0.44 (s, 3H, CH₃).

¹³C[¹H] NMR (126 MHz, 299 K, CD₂Cl₂): δ = without assignment to an isomer: 145.00 (d, 4JPC = 2.4 Hz), 144.98 (d, 4JPC = 2.3 Hz), 143.73 (d, 4JPC = 1.5 Hz), 143.70 (d, 4JPC = 1.5 Hz)(p-Mes), 144.8 (d, 2JPC = 10.8 Hz, 2 x), 144.6 (d, 2JPC = 8.8 Hz), 144.0 (d, 2JPC = 4.8 Hz), 142.7 (d, 2JPC = 8.4 Hz), 142.6 (d, 2JPC = 9.3 Hz), 140.4 (d, 2JPC = 14.4 Hz), 139.4 (d, 2JPC = 14.3 Hz)(o-Mes), 132.94 (d, 3JPC = 12.4 Hz), 132.87 (d, 3JPC = 12.4 Hz), 132.6 (d, 3JPC = 11.9 Hz), 132.5 (d, 3JPC = 11.8 Hz), 132.2 (d, 3JPC = 11.3 Hz), 132.1 (d, 3JPC = 11.5 Hz), 132.0 (d, 3JPC = 11.0 Hz), 131.9 (d, 3JPC = 12.4 Hz)(m-Mes), 129.1 (d, 1JPC = 53.4 Hz, 2 x), 123.6 (d, 1JPC = 94.6 Hz), 123.5 (d, 1JPC = 94.4 Hz)(i-Mes), 26.2 (2 x, o), 3.25 (br, o), 2.49 (br, o), 23.7 (d, 3JPC = 4.2 Hz), 23.6 (d, 3JPC = 4.2 Hz), 23.5 (d, 3JPC = 6.0 Hz), 23.4 (d, 3JPC = 6.0 Hz), 21.1 (4 x, p)(CH₃Mes), [Ph, C(F)ₛ not listed, tentatively assigned]. Major isomer: 140.8 (d, 3JPC = 2.0 Hz, =CH), 114.4 (=CH₂), 68.8 (d, 2JPC = 8.3 Hz, NC), 46.6 (d, 1JPC = 68.6 Hz, CH₂), 20.5 (d, 3JPC = 20.7 Hz, CH₃). Minor isomer: 142.7 (=CH), 114.6 (d, 4JPC = 2.8 Hz, =CH₂), 67.2 (d, 2JPC = 7.0 Hz, NC), 43.7 (d, 1JPC = 64.2 Hz, CH₂), 20.3 (CH₃).
$^{11}$B$^{1}$H NMR (160 MHz, 299 K, CD$_2$Cl$_2$): $\delta = 4.3$ ($\nu_{1/2} \sim 65$ Hz).

$^{31}$P$^{1}$H NMR (202 MHz, 299 K, CD$_2$Cl$_2$): $\delta = 49.46$ ($\nu_{1/2} \sim 2$ Hz, 52 mol%), 49.52 ($\nu_{1/2} \sim 2$ Hz, 48 mol%).

$^{19}$F NMR (470 MHz, 253 K, CD$_2$Cl$_2$): $\delta =$ major isomer (53 mol%): -131.7, -132.3, -133.6, -134.8 (each m, each 1F, o), -162.62, -163.24 (each t, $^3J_{FF} = 20.6$ Hz, each 1F, p), -166.6 (1F), -167.4 (2F), -167.7 (1F)(each m, m)(C$_6$F$_5$). Minor isomer (47 mol%): -132.0, -132.5, -133.8, -134.8 (each m, each 1F, o), -161.59, -163.20 (each t, $^3J_{FF} = 20.5$ Hz, each 1F, p), -166.6 (1F), -167.4 (2F), -167.7 (1F)(each m, m)(C$_6$F$_5$).

$^1$H NMR (500 MHz, 299 K, CD$_2$Cl$_2$) of compound 8

$^1$H NMR (500 MHz, 299 K, CD$_2$Cl$_2$) of compound 8 [the error of the integration value of the $m$-Mes + Ph + $=CH$ (29) is due to some impurities]
$^1$H NMR (500 MHz, 299 K, CD$_2$Cl$_2$) of compound 8

$^{13}$C($^1$H) NMR (126 MHz, 299 K, CD$_2$Cl$_2$) of compound 8
$^{13}$C-$^1$H NMR (126 MHz, 299 K, CD$_2$Cl$_2$) of compound 8

$^{13}$C-$^1$H NMR (126 MHz, 299 K, CD$_2$Cl$_2$) of compound 8
$^{19}$F NMR (470 MHz, 253 K, CD$_2$Cl$_2$) of compound 8
$^{1}H, ^{13}C$-GHSQC (500 MHz / 126 MHz, 253 K, CD$_2$Cl$_2$) of compound 8
\( ^1H, ^13C \)-GHSQC (500 MHz / 126 MHz, 253 K, CD\(_2\)Cl\(_2\)) of compound 8

\( ^{11}B\{^1H\} \) NMR (160 MHz, 299 K, CD\(_2\)Cl\(_2\)) and \( ^{31}P\{^1H\} \) NMR (202 MHz, 299 K, CD\(_2\)Cl\(_2\)) of compound 8

**X-ray crystal structure analysis of compound 8:** A colorless prism-like specimen of C\(_{47}\)H\(_{40}\)BF\(_{10}\)N\(_2\)O\(_2\)P \cdot 2 \times \text{CH}_2\text{Cl}_2 approximate dimensions 0.174 mm x 0.203 mm x 0.326 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 654 frames were collected. The total exposure time was 2.02 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a
total of 9132 reflections to a maximum θ angle of 25.44° (0.83 Å resolution), of which 9132 were independent (average redundancy 1.000, completeness = 99.6%, R_{int} = 4.48%, R_{sig} = 3.61%) and 7188 (78.71%) were greater than 2σ(F^2). The final cell constants of a = 11.5431(4) Å, b = 11.9456(4) Å, c = 19.9373(7) Å, α = 97.0860(10)°, β = 106.3400(10)°, γ = 105.7710(10)°, volume = 2478.64(15) Å^3, are based upon the refinement of the XYZ-centroids of 9905 reflections above 2σ(I) with 4.666° < 2θ < 50.81°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.975. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8940 and 0.9420. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, C_{49}H_{44}BCl_{4}F_{10}N_{2}O_{2}P. The final anisotropic full-matrix least-squares refinement on F^2 with 703 variables converged at R1 = 4.62%, for the observed data and wR2 = 12.10% for all data. The goodness-of-fit was 1.039. The largest peak in the final difference electron density synthesis was 0.684 e/Å^3 and the largest hole was -0.595 e/Å^3 with an RMS deviation of 0.061 e/Å^3. On the basis of the final model, the calculated density was 1.429 g/cm^3 and F(000), 1092 e^-.

The Me and vinyl group at C2 are disordered with 67% to 33%.

rac-S-8 (67%)
Synthesis of compound 9a

Compound 6a (136.7 mg, 0.2 mmol) and nitrobenzene (24.6 mg, 0.2 mmol) were dissolved in CH$_2$Cl$_2$ (2 mL). The reaction mixture was stirred at room temperature overnight. All volatiles were removed in vacuo and the residue was washed with cold pentane (3x1 mL). After dried in vacuo compound 9a (145.7 mg, 90 %) was obtained as a white solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound 9a in dichloromethane at -35 °C. Decom: (DSC): 216 °C. Anal. Calc. for C$_{41}$H$_{35}$BF$_{10}$NO$_2$P: C: 61.14; H: 4.38; N: 1.74. Found: C: 60.84; H: 4.15; N: 1.80.

The solution of the white solid in CD$_2$Cl$_2$ showed two isomers [50:50 ($^{31}$P)]

$^1$H NMR (500 MHz, 203 K, CD$_2$Cl$_2$): δ = without assignment to an isomer: 7.27 (m, 4H, o-Ph), 7.13, 7.10 (each m, each 2H, m-Ph), 6.96, 6.93 (each m, each 1H, p-Ph), 6.92 (1H), 6.91 (1H), 6.85 (1H), 6.82 (2H), 6.80 (1H), 6.67 (1H), 6.65 (1H)(each m, m-
Mes), 2.941 (3H, o), 2.936 (3H, o), 2.32 (3H, o), 2.30 (3H, o), 2.27 (6H, p), 2.208 (3H, p), 2.204 (3H, p), 2.13 (6H, o), 1.91 (3H, o), 1.86 (3H, o)(each s, CH$_3^{Mes}$). Isomer1: 6.77 (dd, $^3$J$_{HH,trans}$ = 17.7 Hz, $^3$J$_{HH,cis}$ = 11.1 Hz, 1H, =CH), 5.02 (d, $^3$J$_{HH,cis}$ = 11.1 Hz, 1H, =CH$_2$), 4.73 (d, $^3$J$_{HH,cis}$ = 17.7 Hz, 1H, =CH$_2$), 3.65 (dd, $^2$J$_{PH} = 16.9$ Hz, $^2$J$_{HH} = 14.6$ Hz, 1H, CH$_2$), 2.39 (d, $^2$J$_{HH} = 14.6$ Hz, 1H, CH$_2$), 0.79 (s, 3H, CH$_3$). Isomer2: 5.49 (dd, $^3$J$_{HH,trans}$ = 17.5 Hz, $^3$J$_{HH,cis}$ = 11.0 Hz, 1H, =CH), 4.79 (d, $^3$J$_{HH,trans}$ = 17.5 Hz, 1H, =CH$_2$), 4.63 (d, $^3$J$_{HH,cis}$ = 11.0 Hz, 1H, =CH$_2$), 3.63 (dd, $^2$J$_{PH} = 15.9$ Hz, $^2$J$_{HH} = 14.6$ Hz, 1H, CH$_2$), 2.50 (d, $^2$J$_{HH} = 14.6$ Hz, 1H, CH$_2$), 1.29 (s, 3H, CH$_3$).

$^{13}$C$^1$H NMR (126 MHz, 203 K, CD$_2$Cl$_2$): δ = without assignment to an isomer: 148.5, 148.2 (i-Ph), 145.0 (d, $^2$J$_{PC} = 5.9$ Hz), 144.7 (d, $^2$J$_{PC} = 5.9$ Hz), 143.2 (2 x d, $^2$J$_{PC} = 8.4$ Hz), 139.0 (d, $^2$J$_{PC} = 19.2$ Hz), 138.8 (d, $^2$J$_{PC} = 19.2$ Hz), 138.25 (d, $^2$J$_{PC} = 13.4$ Hz), 138.19 (d, $^2$J$_{PC} = 13.3$ Hz)(o-Mes), 143.6 (d, $^4$J$_{PC} = 2.8$ Hz), 143.5 (d, $^4$J$_{PC} = 2.9$ Hz), 143.2 (2 x d, $^4$J$_{PC} = 2.4$ Hz)(p-Mes), 132.34 (d, $^3$J$_{PC} = 11.8$ Hz), 132.28 (d, $^3$J$_{PC} = 11.8$ Hz), 131.6 (2 x d, $^3$J$_{PC} = 11.0$ Hz), 131.3 (d, $^3$J$_{PC} = 13.9$ Hz), 131.2 (d, $^3$J$_{PC} = 14.1$ Hz), 130.46 (d, $^3$J$_{PC} = 13.4$ Hz), 130.39 (d, $^3$J$_{PC} = 13.1$ Hz)(m-Mes), 126.8, 126.7 (m-Ph), 124.1, 123.6 (p-Ph), 123.1, 122.1 (o-Ph), 124.8 (d, $^1$J$_{PC} = 98.8$ Hz), 124.7 (d, $^1$J$_{PC} = 99.2$ Hz), 120.9 (d, $^1$J$_{PC} = 106.4$ Hz), 120.7 (d, $^1$J$_{PC} = 106.3$ Hz)(i-Mes), 25.1 (br, 2 x), 22.2 (br, 2 x), 21.5 (d, $^3$J$_{PC} = 7.3$ Hz), 21.4 (d, $^3$J$_{PC} = 7.2$ Hz), 20.75 (br, 2 x)(o-CH$_3^{Mes}$), 20.71 (2 x), 20.4 (2 x)(p-CH$_3^{Mes}$), [CaF$_3$ not listed, 1 tentatively assigned]. Isomer1: 141.4 (br d, $^1$J$_{PC} = 12.4$ Hz, =CH), 114.1 (br, =CH$_2$), 68.8 (d, $^2$J$_{PC} = 6.2$ Hz, NC), 40.8 (d, $^1$J$_{PC} = 48.4$ Hz, CH$_2$), 20.8 (CH$_3$). Isomer2: 140.1 (=CH), 115.2 (br, =CH$_2$), 71.1 (d, $^2$J$_{PC} = 6.2$ Hz, NC), 43.1 (d, $^1$J$_{PC} = 52.0$ Hz, CH$_2$), 19.2 (d, $^3$J$_{PC} = 12.0$ Hz, CH$_3$).

$^{11}$B$^1$H NMR (192 MHz, 299 K, CD$_2$Cl$_2$): δ = 5.0 ($v_{1/2} \sim 260$ Hz).

$^{31}$P$^1$H NMR (243 MHz, 299 K, CD$_2$Cl$_2$): δ = 62.1 ($v_{1/2} \sim 2$ Hz, 50%); 61.8 ($v_{1/2} \sim 2$ Hz, 50%).

$^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$): δ = -132.6 (m, 4F, o), -160.1 (t, $^3$J$_{FF} = 20.0$ Hz, 2F, p), -165.6 (m, 4F, m)(CaF$_3$)[δ$^{19}$F$_{mp}$ = 5.5], -132.7 (m, 2F, o), -160.9 (t, $^3$J$_{FF} = 20.3$ Hz, 1F, p), -166.5 (m, 2F, m)(CaF$_3$)[δ$^{19}$F$_{mp}$ = 5.7], -132.7 (m, 2F, o), -161.0 (t, $^3$J$_{FF} = 20.3$ Hz, 1F, p), -166.6 (m, 2F, m)(CaF$_3$)[δ$^{19}$F$_{mp}$ = 5.7].
$^1$H NMR (500 MHz, 203 K, CD$_2$Cl$_2$) of compound 9a
\(^{13}\text{C}({}^1\text{H})\text{ NMR}\) (126 MHz, 203 K, CD\(_2\)Cl\(_2\)) of compound 9a

\(^{13}\text{C}({}^1\text{H})\text{ NMR}\) (126 MHz, 203 K, CD\(_2\)Cl\(_2\)) of compound 9a
$^1$H, $^{13}$C-GHSQC (500 MHz / 126 MHz, 203 K, CD$_2$Cl$_2$) of compound 9a
$^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) of compound 9a

$^{11}$B$^{[1]H}$ NMR (192 MHz, 299 K, CD$_2$Cl$_2$) and $^{31}$P$^{[1]H}$ NMR (243 MHz, 299 K, CD$_2$Cl$_2$) of compound 9a

X-ray crystal structure analysis of compound 9a: formula C$_{41}$H$_{35}$BF$_{10}$NO$_2$P · C$_5$H$_{12}$, $M = 877.63$, colourless crystal, 0.18 x 0.08 x 0.06 mm, $a = 13.2257(3)$, $b = 13.5489(6)$, $c = 13.5621(4)$ Å, $\alpha = 72.298(1)$, $\beta = 69.121(2)$, $\gamma = 72.966(1)^o$, $V = 2116.1(1)$ Å$^3$, $\rho_{\text{calc}} = 1.377$ gcm$^{-3}$, $\mu = 0.149$ mm$^{-1}$, empirical absorption correction (0.973 $\leq$ T $\leq$ 0.991), $Z = 2$, triclinic, space group $P\overline{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 223(2)$ K, $\omega$ and $\varphi$ scans, 19084 reflections collected ($\pm h$, $\pm k$, $\pm l$), 7206 independent ($R_{int} = 0.061$) and 5118 observed reflections [$I > 2\sigma(I)$], 602 refined parameters, $R = 0.086$, $wR^2 = 0.204$, max. (min.) residual electron density 0.44 (-0.56) e.Å$^{-3}$, hydrogen atoms were calculated and refined as riding atoms.
Synthesis of compound 9b

Compound 6b (111.6 mg, 0.2 mmol) and nitrobenzene (24.6 mg, 0.2 mmol) were dissolved in CH₂Cl₂ (2 mL). The reaction mixture was stirred at room temperature overnight. All volatiles were removed in vacuo and the residue was washed with cold pentane (3x1 mL). After dried in vacuo compound 9b (108.2 mg, 80 %) was obtained as a white solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound 9b in dichloromethane at -35 °C. Decomp.: 198 °C. Anal. Calc. for C₃₁H₃₁BF₁₀NO₂P: C: 54.65; H: 4.59; N: 2.06. Found: C: 54.32; H: 4.34; N: 2.05.

The solution of the white solid in CD₂Cl₂ showed two isomers [49 : 51 (³¹P)]

¹H NMR (500 MHz, 299 K, CD₂Cl₂): δ = without assignment to an isomer: 7.21-6.97 (m, 10H, Ph), 1.66 (d, ³ J₉H = 15.1 Hz, 9H, 'Bu), 1.63 (d, ³ J₉H = 15.3 Hz, 9H, 'Bu), 1.20
(d, $^3J_{PH} = 14.5$ Hz, 9H, 'Bu), 1.19 (d, $^3J_{PH} = 14.3$ Hz, 9H, 'Bu). Isomer1: 7.05 (dd, $^3J_{HH,trans} = 17.9$ Hz, $^3J_{HH,cis} = 10.0$ Hz, 1H, =CH), 5.21 (dd, $^3J_{HH,cis} = 11.0$ Hz, $^3J_{PH} = 0.8$ Hz, 1H, =CH$_2$), 4.92 (d, $^3J_{HH,trans} = 17.9$ Hz, 1H, =CH$_2$), 2.93 (dd, $^2J_{HH} = 16.0$ Hz, $^2J_{PH} = 14.3$ Hz, 1H, CH$_2$), 2.28 (dd, $^2J_{HH} = 16.0$ Hz, $^2J_{PH} = 3.7$ Hz, 1H, CH$_2$), 1.28 (s, 3H, CH$_3$). Isomer2: 6.37 (dd, $^3J_{HH,trans} = 17.5$ Hz, $^3J_{HH,cis} = 11.2$ Hz, 1H, =CH), 5.05 (d, $^3J_{HH,cis} = 11.2$ Hz, 1H, =CH$_2$), 5.04 (d, $^3J_{HH,trans} = 17.5$ Hz, 1H, =CH$_2$), 2.94 (t, $^2J_{HH} = 15.8$ Hz, 1H, CH$_2$), 2.44 (dd, $^2J_{HH} = 15.8$ Hz, $^2J_{PH} = 2.9$ Hz, 1H, CH$_2$), 1.59 (d, $^4J_{PH} = 2.4$ Hz, 3H, CH$_3$).

$^{13}$C($^1$H) NMR (126 MHz, 299 K, CD$_2$Cl$_2$): δ = without assignment to an isomer: 148.2 (i), 148.1 (i), 127.02, 126.97 (br), 126.94 (br), 125.9 (p), 125.7 (p)(Ph), 37.3 (2 × 'Bu*'), 36.8 (2 × 'Bu'), 27.8 (br, 2 × 'Bu'), 27.1 (′Bu'), 27.0 (′Bu). Isomer1: 142.4 (d, $^3J_{PC} = 5.7$ Hz, =CH), 114.5 (=CH$_2$), 67.4 (d, $^2J_{PC} = 6.2$ Hz, NC), 32.2 (d, $^1J_{PC} = 39.9$ Hz, CH$_2$), 25.2 (d, $^3J_{PC} = 2.6$ Hz, CH$_3$). Isomer2: 143.1 (=CH), 115.1 (=CH$_2$), 68.8 (d, $^2J_{PC} = 7.7$ Hz, NC), 33.0 (d, $^1J_{PC} = 41.2$ Hz, CH$_2$), 22.7 (d, $^3J_{PC} = 7.7$ Hz, CH$_3$); [C$_6$F$_5$ not listed, $^3$J$_{PC}$ not assignable]

$^{11}$B($^1$H) NMR (160 MHz, 299 K, CD$_2$Cl$_2$): δ = 5.2 (ν$_{1/2}$ ~ 130 Hz).

$^{31}$P($^1$H) NMR (202 MHz, 299 K, CD$_2$Cl$_2$): δ = 87.1 (ν$_{1/2}$ ~ 3 Hz, 49%); 86.8 (ν$_{1/2}$ ~ 3 Hz, 51%).

$^{19}$F NMR (470 MHz, 183 K, CD$_2$Cl$_2$): δ = -133.5, -133.6 (each m, each 1F, o), -158.97 (t, $^3J_{FF} = 21.0$ Hz, 1F, p), -164.0 (m, 2F, m)(C$_6$F$_5$)[Δ$^1$F$_{mp}$ = 5.0], -134.6, -134.7 (each m, each 1F, o), -159.05 (t, $^3J_{FF} = 21.0$ Hz, 1F, p), -164.9 (m, 2F, m)(C$_6$F$_5$)[Δ$^1$F$_{mp}$ = 5.8], -133.8, -134.0 (each m, each 1F, o), -160.65 (t, $^3J_{FF} = 21.8$ Hz, 1F, p), -165.6 (m, 2F, m)(C$_6$F$_5$)[Δ$^1$F$_{mp}$ = 4.9], -130.7 (m, 2F, o), -160.70 (t, $^3J_{FF} = 21.8$ Hz, 1F, p), -167.8 (m, 2F, m)(C$_6$F$_5$)[Δ$^1$F$_{mp}$ = 7.1].

$^1$H NMR (500 MHz, 299 K, CD$_2$Cl$_2$) of compound 9b
**$^{1}H$ NMR (500 MHz, 299 K, CD$_2$Cl$_2$) of compound 9b**

**$^{13}C$($^{1}H$) NMR (126 MHz, 299 K, CD$_2$Cl$_2$) of compound 9b**
$^{13}\text{C}^{1\text{H}} \text{NMR}$ (126 MHz, 299 K, CD$_2$Cl$_2$) of compound 9b

$^{11}\text{B}^{1\text{H}} \text{NMR}$ (160 MHz, 299 K, CD$_2$Cl$_2$) and $^{31}\text{P}^{1\text{H}} \text{NMR}$ (202 MHz, 299 K, CD$_2$Cl$_2$) of compound 9b

$^{19}\text{F} \text{NMR}$ (470 MHz, 183 K, CD$_2$Cl$_2$) of compound 9b
**X-ray crystal structure analysis of compound 9b:** A colorless prism-like specimen of C$_{31}$H$_{31}$BF$_{10}$NO$_2$P, approximate dimensions 0.080 mm x 0.100 mm x 0.100 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1963 frames were collected. The total exposure time was 22.71 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 51154 reflections to a maximum θ angle of 66.69° (0.84 Å resolution), of which 10572 were independent (average redundancy 4.839, completeness = 96.9%, R$_{int}$ = 8.26%, R$_{sig}$ = 6.17%) and 7527 (71.20%) were greater than 2σ(F$^2$). The final cell constants of a = 12.0754(8) Å, b = 14.3703(9) Å, c = 18.9938(13) Å, α = 77.355(4)°, β = 73.434(4)°, γ = 85.944(4)°, volume = 3082.4(4) Å$^3$, are based upon the refinement of the XYZ-centroids of 8252 reflections above 20 σ(I) with 9.866° < 2θ < 132.2°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.875. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8550 and 0.8810. The final anisotropic full-matrix least-squares refinement on F$^2$ with 897 variables converged at R1 = 5.26%, for the observed data and wR2 = 12.57% for all data. The goodness-of-fit was 1.037. The largest peak in the final difference electron density synthesis was 0.246 e/Å$^3$ and the largest hole was -0.411 e/Å$^3$ with an RMS deviation of 0.059 e/Å$^3$. On the basis of the final model, the calculated density was 1.468 g/cm$^3$ and F(000), 1400 e$^-$. Two independent molecules; the Me and vinyl group at C2 are disordered with 60% to 40% and 56% to 44%, respectively.
Compound 6a (102.3 mg, 0.15 mmol) and trans-β-nitrostyrene (22.5 mg, 0.15 mmol) were dissolved in CH₂Cl₂ (2 mL). The reaction mixture was stirred at room temperature overnight. All volatiles were removed in vacuo and the residue was washed with cold pentane (3x1 mL). After dried in vacuo compound 10 (114.2 mg, 91 %) was obtained as a white solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound 10 in dichloromethane at room temperature. Decomp. (DSC): 169 °C. Anal. Calc. for C₄₃H₇₇BF₁₀NO₃P: C: 62.11; H: 4.49; N: 1.68. Found: C: 62.33; H: 4.58; N: 1.73.

The solution of the white solid in CD₂Cl₂ showed two isomers [27 : 73 (1H)]

1H NMR (500 MHz, 253 K, CD₂Cl₂): δ = major isomer: 7.14 (m, 2H, m-Ph), 7.07 (m, 1H, m-Mes⁴), 7.04 (m, 2H, o-Ph), 6.98 (m, 1H, p-Ph), 6.93 (m, 1H, m-Mes⁵), 6.83 (m, 1H, m'-Mes²), 6.66 (m, 1H, m'-Mes⁵), 6.62 (d, 3JHH = 13.5 Hz, 1H, NCH=), 6.04 (d, 3JHH = 13.5 Hz, 1H, PhCH=), 5.47 (dd, 3JHH,trans = 17.4 Hz, 3JHH,cis = 10.9 Hz, 1H, =CH), 5.20 (d, 3JHH,trans = 17.4 Hz, 1H, =CH2), 4.84 (d, 3JHH,cis = 10.9 Hz, 1H, =CH2), 3.61 (dd, 2JPH = 16.1 Hz, 2JHH = 14.8 Hz, 1H, PCH2), 2.93 (s, 3H, o-CH₃Mes), 2.51 (dd, 2JPH = 14.8 Hz, 2JHH = 14.8 Hz, 2JPH = 2.8 Hz, 1H, PCH2), 2.33 (s, 3H, o-CH₃Mes), 2.31 (s, 3H, p-CH₃Mes), 2.23 (s, 3H, p-CH₃Mes), 2.13 (s, 3H, o'-CH₃Mes), 1.90 (s, 3H, o'-CH₃Mes), 1.58 (d, 3JHH = 3.5 Hz, 3H, CH₃). Minor isomer: 7.16 (m, 2H, m-Ph), 7.07 (m, 1H, m-Mes⁴), 7.06 (m, 2H, o-Ph), 6.99 (m, 1H, p-Ph), 6.93 (m, 1H, m-Mes⁵), 6.87 (m, 1H, m'-Mes²), 6.67 (d, 3JHH = 13.5 Hz, 1H, NCH=), 6.66 (m, 1H, m'-Mes⁵), 6.53 (dd, 3JHH,trans = 17.6 Hz, 3JHH,cis = 10.8 Hz, 1H, =CH), 6.09 (d, 3JHH = 13.5 Hz, 1H, PhCH=), 5.21 (d, 3JHH,cis = 10.8 Hz, 1H, =CH2), 5.10 (d, 3JHH,trans = 17.6 Hz, 1H, =CH2), 3.69 (dd, 2JPH = 16.5 Hz, 2JHH = 15.0 Hz, 1H, PCH2), 2.92 (s, 3H, o-CH₃Mes), 2.39 (dd, 2JHH = 15.0 Hz, 2JPH = 1.9 Hz, 1H, PCH2), 2.33 (s, 3H, o-CH₃Mes), 2.21 (s, 3H, p-CH₃Mes), 2.23 (s, 3H, p-CH₃Mes), 2.16 (s, 3H, o'-CH₃Mes), 1.96 (s, 3H, o'-CH₃Mes), 1.07 (s, 3H, CH₃).

13C{1H} NMR (126 MHz, 253 K, CD₂Cl₂): δ = major isomer: 145.5 (d, 2JPC = 6.0 Hz, o-Mes⁴), 144.19 (d, 4JPC = 3.1 Hz, p-Mes⁴), 144.0 (d, 4JPC = 2.6 Hz, p-Mes⁵), 143.9 (d, 2JPC = 9.1 Hz, o-Mes⁵), 139.6 (d, 2JPC = 19.0 Hz, o'-Mes⁴), 139.3 (=CH), 138.70 (d, 2JPC = 13.2 Hz, o'-Mes⁵), 137.9 (i-Ph), 134.1 (NCH=), 132.95 (d, 3JPC = 12.1 Hz, m-Mes⁴), 132.3 (d, 3JPC = 11.1 Hz, m-Mes⁵), 131.6 (d, 3JPC = 13.9 Hz, m'-Mes²), 130.89 (d, 3JPC = 13.4 Hz, m'-Mes⁵), 128.41 (m-Ph), 124.82 (d, 1JPC = 98.6 Hz, i-Mes⁴), 124.76 (p-Ph), 124.6 (o-Ph), 121.1 (d, 1JPC = 107.0 Hz, i-Mes⁵), 117.0 (=CH₂), 107.7 (PhCH=), 69.4 (d, 2JPC = 7.3 Hz, NC), 43.0 (d, 1JPC = 52.1 Hz, PCH2), 25.2 (d, 3JPC = 1.6 Hz, o'-CH₃Mes), 23.0 (br d, 2JPC = 12.8 Hz, CH₃), 22.2 (br, o-CH₃Mes), 21.8 (d, 3JPC = 7.7 Hz,
$^{13}$C NMR (160 MHz, 299 K, CD$_2$Cl$_2$): 145.7 (d, $^2$J$_{CP}$ = 6.0 Hz, o-Mes$^a$), 144.22 (d, $^4$J$_{CP}$ = 3.2 Hz, p-Mes$^a$), 144.0 (d, $^4$J$_{CP}$ = 2.6 Hz, p-Mes$^b$), 143.9 (d, $^2$J$_{CP}$ = 9.1 Hz, o-Mes$^b$), 143.0 (d, $^3$J$_{CP}$ = 12.4 Hz, =CH), 139.4 (d, $^2$J$_{PC}$ = 18.7 Hz, o’-Mes$^a$), 138.67 (d, $^2$J$_{PC}$ = 13.2 Hz, o’-Mes$^b$), 137.8 (i-Ph), 133.0 (NCH=), 132.96 (d, $^3$J$_{PC}$ = 12.1 Hz, m-Mes$^a$), 132.3 (d, $^3$J$_{PC}$ = 11.1 Hz, m-Mes$^b$), 131.8 (d, $^3$J$_{PC}$ = 13.4 Hz, m’-Mes$^a$), 130.94 (d, $^3$J$_{PC}$ = 13.6 Hz, m’-Mes$^b$), 128.44 (m-Ph), 124.9 (d, $^1$J$_{PC}$ = 98.1 Hz, =CH), 124.76 (p-Ph), 124.7 (o-Ph), 121.0 (d, $^1$J$_{PC}$ = 106.6 Hz, i-Mes$^a$), 114.0 (=CH$_2$), 108.1 (PhCH=), 67.9 (d, $^2$J$_{PC}$ = 6.3 Hz, NC), 40.6 (d, $^1$J$_{PC}$ = 49.0 Hz, PCH$_2$), 25.3 (d, $^3$J$_{PC}$ = 1.5 Hz, o’-CH$_3$Mes$^b$), 22.2 (br, o’CH$_3$Mes$^a$), 21.9 (d, $^3$J$_{PC}$ = 7.8 Hz, o’-CH$_3$Mes$^a$), 21.2 (d, $^3$J$_{PC}$ = 1.2 Hz, p’-CH$_3$Mes$^b$), 20.5 (CH$_3$).

$^{11}$B$^{[1]}$H NMR (160 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ = 5.1 ($\nu_{1/2}$ ~ 200 Hz).

$^{31}$P$^{[1]}$H NMR (202 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ = 62.89 ($\nu_{1/2}$ ~ 3 Hz, 64 mol%), 62.87 ($\nu_{1/2}$ ~ 3 Hz, 36 mol%).

$^{19}$F NMR (470 MHz, 299 K, CD$_2$Cl$_2$): $\delta$ = major isomer (69 mol%): -132.7 (m, 2F, o), -159.6 (t, $^3$J$_{FF}$ = 20.0 Hz, 1F, p), -165.3 (m, 2F, m)(C$_6$F$_5$)[$\Delta\delta^{19}$F$_{m,p}$ = 5.7], -133.1 (m, 2F, o), -160.3 (t, $^3$J$_{FF}$ = 20.3 Hz, 1F, p), -166.1 (m, 2F, m)(C$_6$F$_5$)[$\Delta\delta^{19}$F$_{m,p}$ = 5.8]. Minor isomer (31 mol%): -132.4 (m, 2F, o), -159.7 (t, $^3$J$_{FF}$ = 20.0 Hz, 1F, p), -165.4 (m, 2F, m)(C$_6$F$_5$)[$\Delta\delta^{19}$F$_{m,p}$ = 5.7], -133.2 (m, 2F, o), -160.4 (t, $^3$J$_{FF}$ = 20.3 Hz, 1F, p), -166.2 (m, 2F, m)(C$_6$F$_5$)[$\Delta\delta^{19}$F$_{m,p}$ = 5.8].

$^1$H NMR (500 MHz, 253 K, CD$_2$Cl$_2$) of compound 10
$^{1}H$ NMR (500 MHz, 253 K, CD$_2$Cl$_2$) of compound 10
$^1$H NMR (500 MHz, CD$_2$Cl$_2$) of compound 10

$^{13}$C($^1$H) NMR (126 MHz, 253 K, CD$_2$Cl$_2$) of compound 10
$^{13}\text{C}^{[1\text{H}]}\text{NMR}$ (126 MHz, 253 K, CD$_2$Cl$_2$) of compound 10

$^{19}\text{F}\text{NMR}$ (470 MHz, 299 K, CD$_2$Cl$_2$) of compound 10

$^{11}\text{B}^{[1\text{H}]}\text{NMR}$ (160 MHz, 299 K, CD$_2$Cl$_2$) and $^{31}\text{P}^{[1\text{H}]}\text{NMR}$ (202 MHz, 299 K, CD$_2$Cl$_2$) of compound 10
**X-ray crystal structure analysis of compound 10**: A colorless plate-like specimen of C_{43}H_{37}BF_{10}NO_{2}P, approximate dimensions 0.050 mm x 0.100 mm x 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 476 frames were collected. The total exposure time was 5.29 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 7780 reflections to a maximum θ angle of 25.03° (0.84 Å resolution), of which 7780 were independent (average redundancy 1.000, completeness = 99.7%, R_{int} = 7.88%, R_{sig} = 4.03%) and 6088 (78.25%) were greater than 2σ(F^2). The final cell constants of a = 14.2252(8) Å, b = 21.5455(12) Å, c = 15.6095(10) Å, β = 112.746(2)°, volume = 4412.1(5) Å³, are based upon the refinement of the XYZ-centroids of 9649 reflections above 20 σ(I) with 4.892° < 2θ < 54.72°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.921. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9840 and 0.9930. The final anisotropic full-matrix least-squares refinement on F^2 with 559 variables converged at R1 = 6.25%, for the observed data and wR2 = 16.95% for all data. The goodness-of-fit was 1.070. The largest peak in the final difference electron density synthesis was 0.570 e/Å³ and the largest hole was -0.347 e/Å³ with an RMS deviation of 0.078 e/Å³. On the basis of the final model, the calculated density was 1.252 g/cm³ and F(000), 1712 e^−.

The Me and vinyl group at C2 are disordered with 50% to 50%.

![Diagram of compound 10](image-url)
rac-S-10 (50%)