Even the normal is abnormal: N-Heterocyclic carbene C^2 binding to a phosphaalkene without breaking the P=C bond

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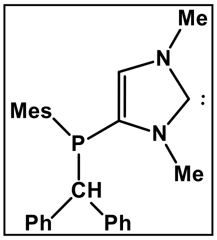
Supporting Information

Experimental Section

All reactions were performed under an argon atmosphere, using common Schlenk techniques or glove box and dry solvents. Tetrahydrofuran, diethyl ether, *n*-pentane and toluene were dried over sodium wire/benzophenone and further purified by subsequent distillation. The phosphaalkene ($MesP=CPh_2$ – M. Yam, et al. *Inorg. Chem.* **2006**, *45*, 5225-5234) and $[M(CO)_5(CH_3CN)]$ complexes (M = Cr, Mo, W - U. Koelle, *J. Organomet. Chem.* **1977**, *133*, 53-58) were synthesized according to published procedures. The $[Rh(cod)Cl]_2$ was used as obtained from Strem. All other chemicals were used as purchased. All NMR spectra were recorded on a Bruker AX-300.1 spectrometer (300.1 MHz for ^1H, 75.5 MHz for ^{13}C, 121.5 MHz for ^{31}P). The ^1H and ^{13}C NMR spectra were referenced to the residual proton resonances and the ^{13}C NMR signals of the deuterated solvents and ^{31}P to 85% H_3PO_4 as external standard, respectively. Melting points were determined in one-side melted off capillaries using a Büchi Type S or a Carl Roth Type MPM-2 apparatus, they are uncorrected. Mass spectrometric data were collected on a Kratos MS 50 spectrometer using EI, 70 eV. IR spectra of all compounds were recorded on a Thermo IR spectrometer with an attenuated total reflection (ATR) attachment. The X-ray analysis was performed on a STOE IPDS2T or Bruker X8-KappaApexII diffractometer. The structures were solved by direct methods refined by full-matrix least-squares technique in anisotropic approximation for non-hydrogen atoms using SHELXS97 and SHELXL97 program packages. Hydrogen atoms were located from Fourier synthesis and refined isotropically. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1428162 (**1**$\cdot BH_3$), 1428161 (**2**) which can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of *P*-functional NHC 1

In a Schlenk tube, 1,3-dimethyl-imidazolium iodide (1.31 g, 5.8 mmol) was dissolved in tetrahydrofuran (35 mL) and cooled to -78 °C. ^{n}BuLi (1.6 M in *n*-hexane, 3.5 mL, 5.66 mmol)[†] was added to it and the reaction mixture was slowly warmed up to -40 °C. It was stirred for 2 h at this temperature. The reaction mixture was cooled again to -78 °C. Then phosphaalkene (MesP=CPh$_2$) (1.8 g, 5.75 mmol) in tetrahydrofuran (5 mL) was added and the reaction mixture was stirred overnight while warming up to ambient temperature. The yellowish red colored solution was concentrated to dryness *in vacuo* (8 × 10^{-3} mbar) and the residue was taken up in toluene to remove traces amount of unreacted imidazolium iodide and formed lithium iodide via filtering cannulation. The filtrate was collected and the solvent was removed *in vacuo* (8 × 10^{-3} mbar) and washed with *n*-pentane several times to remove little excess of unreacted phosphaalkene and then dried *in vacuo* (8 × 10^{-3} mbar).



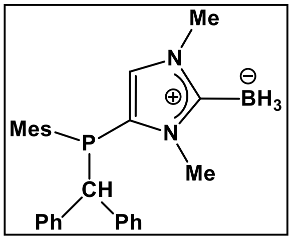
Yield: (1.82 g, 4.41 mmol, 78 %), yellow solid, m.p. 110 °C (dec.). ^{1}H NMR (300.1 MHz, THF-d$_8$, 25°C): δ = 2.17 (s, 3H, Mes-*p*-C*H*$_3$), 2.33 (s, 6H, Mes-*o*-C*H*$_3$), 3.30 (s, 3H, N-C*H*$_3$), 3.66 (s, 3H, N-C*H*$_3$), 5.33 (d, $^2J_{\mathrm{P,H}}$ = 6.5 Hz, 1H, CPh$_2$*H*), 6.60 (d, $^3J_{\mathrm{P,H}}$ = 2.6 Hz, 1H, C^5- *H*), 6.95-7.36 (m, 10H, C$_6$H$_5$-*H*), 7.74-7.79 (m, 2H, Mes-*H*). ^{13}C{^{1}H} NMR (75.5 MHz, THF-d$_8$, 25°C): δ = 20.1 (s, Mes-*C*H$_3$), 21.9 (d, $^3J_{\mathrm{P,C}}$ = 18.5 Hz, Mes-*C*H$_3$), 35.8 (d, $^3J_{\mathrm{P,C}}$ = 7.5 Hz, N-*C*H$_3$), 37.1 (s, N-*C*H$_3$), 48.5 (d, $^1J_{\mathrm{P,C}}$ = 11.2 Hz, *C*Ph$_2$H), 125.6 (d, $J_{\mathrm{P,C}}$ = 5.4 Hz), 125.9 (d, $J_{\mathrm{P,C}}$ = 2.4 Hz), 126.6 (d, $J_{\mathrm{P,C}}$ = 2.0 Hz), 127.6 (d, $J_{\mathrm{P,C}}$ = 0.9 Hz), 128.2 (d, $J_{\mathrm{P,C}}$ = 6.9 Hz), 128.5 (d, $J_{\mathrm{P,C}}$ = 0.6 Hz), 128.9 (d, $J_{\mathrm{P,C}}$ = 13.6 Hz), 129.7 (d, $J_{\mathrm{P,C}}$ = 4.4 Hz), 139.7 (d, $J_{\mathrm{P,C}}$ = 1.3 Hz), 141.1 (d, $J_{\mathrm{P,C}}$ = 11.4 Hz), 141.8 (d, $J_{\mathrm{P,C}}$ = 14.4 Hz), 144.9 (d, $J_{\mathrm{P,C}}$ = 15.8 Hz), 222.5 (bs, C^2). ^{31}P NMR (121.5 MHz, THF-d$_8$, 25°C): δ = -37.2 (s). MS (EI, 70 eV): *m/z* (%) 412 (12) [M]$^{\cdot+}$, 398 (12) [M-CH$_3$]$^+$, 316 (10) [MesPCHPh$_2$]$^+$, 245 (10) [M-Ph$_2$CH]$^+$, 167 (58) [Ph$_2$CH]$^+$.

Synthesis of [*P*-functional NHC·BH$_3$] complex 1·BH$_3$

To a solution of *P*-functional imidazol-2-ylidene **1** (0.22 g, 0.55 mmol) in tetrahydrofuran (8 mL), borane-dimethyl sulfide (BH$_3$·SMe$_2$) (0.05 mL, 0.55 mmol) was added at ambient temperature. The reaction mixture was stirred for 16h at ambient temperature at which point the volatiles were removed *in vacuo* (8 × 10^{-3} mbar) followed by washing with *n*-pentane (2 × 4 mL)

[†] A sub-stoichiometric amount nBuLi is used as excess would induce polymerization of MesP=CPh$_2$. The excess imidazolium iodide cannot be removed and traces of iodide have prevented us obtaining successful elemental analyses for new compounds and complexes reported herein.

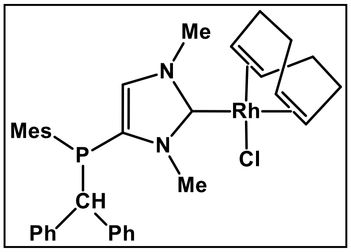
and then dried *in vacuo* (8×10^{-3} mbar). Single crystals suitable to X-ray diffraction were obtained by cooling a saturated THF solution of the crude product at -20 °C for ca. 1 month.



Yield of both isomer: (0.22 g, 0.52 mmol, 95%), white solid, m.p. 210 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25°C): δ = -37.8 (s, 95%) and -38.1 (s, 5%). ^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C) (major isomer): δ = 1.23 (q, $^1J_{B,H}$ = 83.0 Hz, 3H, $\mathrm{B}H_3$), 2.10 (s, 3H, Mes-*p*-$\mathrm{C}H_3$), 2.15 (s, 6H, Mes-*o*-$\mathrm{C}H_3$), 3.16 (s, 3H, N-$\mathrm{C}H_3$), 3.46 (s, 3H, N-$\mathrm{C}H_3$), 5.07 (d, $^2J_{P,H}$ = 6.7 Hz, 1H, $\mathrm{CPh_2}H$), 6.61 (d, $^3J_{P,H}$ = 2.8 Hz, 1H, C^5- *H*), 6.95-7.98 (m, 6H, C_6H_5-*H*), 7.25-7.32 (m, 4H, C_6H_5-*H*), 7.53-7.57 (m, 2H, Mes-*H*). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25°C) (major isomer): δ = 20.0 (s, Mes-$C\mathrm{H_3}$), 21.5 (d, $^3J_{P,C}$ = 17.6 Hz, Mes-$C\mathrm{H_3}$), 33.2 (d, $^3J_{P,C}$ = 8.6 Hz, N-$C\mathrm{H_3}$), 34.8 (s, N-$C\mathrm{H_3}$), 47.2 (d, $^1J_{P,C}$ = 11.3 Hz, $C\mathrm{Ph_2H}$), 122.8 (d, $J_{P,C}$ = 16.9 Hz), 122.9 (d, $J_{P,C}$ = 3.0 Hz), 125.6 (d, $J_{P,C}$ = 2.6 Hz), 126.3 (d, $J_{P,C}$ = 1.8 Hz), 127.0 (d, $J_{P,C}$ = 1.4 Hz), 127.2 (d, $J_{P,C}$ = 6.8 Hz), 127.7 (d, $J_{P,C}$ = 13.3 Hz), 128.1 (d, $J_{P,C}$ = 0.8 Hz), 128.5 (d, $J_{P,C}$ = 22.5 Hz), 129.2 (d, $J_{P,C}$ = 4.7 Hz), 138.9 (d, $J_{P,C}$ = 12.3 Hz), 139.5 (d, $J_{P,C}$ = 1.5 Hz), 139.6 (d, $J_{P,C}$ = 13.1 Hz), 143.9 (d, $J_{P,C}$ = 18.0 Hz). ^{11}B{^{1}H} NMR (96.6 MHz, $CDCl_3$, 25°C): δ = -36.9 (s) and -37.1 (s). IR (ATR, ũ [cm^{-1}]): ũ = 2954 (br), 2277 (br), 1601 (s), 1555 (w), 1447 (s), 1289 (w), 1260 (w), 1165 (s), 1118 (w), 1074 (w), 1074 (w), 1029 (s), 877 (s), 765 (w), 735 (w), 697 (vs). UV/Vis (CH_2Cl_2): λ_{max} [nm] (abs.): 230 (0.725). MS (EI, 70 eV): *m/z* (%) 426 (8) $[M]^{\cdot+}$, 425 (20) $[M-H]^+$, 318 (12) $[C_{22}H_{22}P]^+$, 258 (12) $[M-Ph_2CH_2]^+$, 167 (58) $[CHPh_2]^+$, 109 (58) $[M-MesPCHPh_2]^+$.

Synthesis of [*P*-functional NHC-(1,2,5,6-)-1,5-cyclooctadiene]chlororhodium(I)] complex 1·Rh(cod)Cl

To a solution of $[(cod)RhCl]_2$ (0.11 g, 0.23 mmol) in tetrahydrofuran (5 mL) was added a solution of *P*-functional imidazol-2-ylidene **1** (0.19 g, 0.46 mmol) in tetrahydrofuran (5 mL). The reaction mixture was heated at 60 °C for 16h, at which point the volatiles were removed *in vacuo* (8×10^{-3} mbar). The crude product was washed with *n*-pentane (2 × 6 mL) and then dried *in vacuo* (8×10^{-3} mbar).

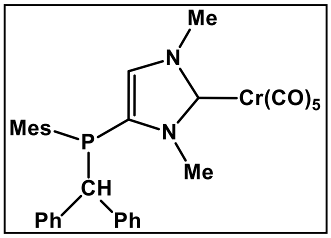


Yield of both isomer: (266 mg, 0.40 mmol, 88%), yellowish red solid, m.p. 148 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25°C): δ = -36.7 (s, 58 %) and -37.1 (s, 42 %). ^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C) (major isomer): δ = 1.67 (m, 4H, cod), 1.83 (m, 4H, cod), 2.04 (s, 3H, Mes-*p*-$\mathrm{C}H_3$), 2.16 (s, 6H, Mes-o-$\mathrm{C}H_3$), 3.32 (s, 3H, N-$\mathrm{C}H_3$), 3.64 (m, 2H, cod), 3.69 (s, 3H, N-CH_3), 4.97 (d, $^2J_{P,H}$ = 6.9 Hz, 1H, CPh$_2H$), 5.05 (m, 2H, cod), 6.03 (d, $^3J_{P,H}$ = 2.6 Hz, 1H, C^5- H), 7.26-7.33 (m, 10H, C$_6$H$_5$-H), 7.52-7.57 (m, 2H, Mes-H). ^{1}H NMR (300.1 MHz, CDCl$_3$, 25°C) (minor isomer): δ = 1.72 (m, 4H, cod), 1.88 (m, 4H, cod), 2.08 (s, 3H, Mes-*p*-CH_3), 2.12 (s, 6H, Mes-o-CH_3), 3.36 (s, 3H, N-CH_3), 3.66 (m, 2H, cod), 3.70 (s, 3H, N-CH_3), 4.89 (d, $^2J_{P,H}$ = 6.6 Hz, 1H, CPh$_2H$), 5.13 (m, 2H, cod), 6.01 (d, $^3J_{P,H}$ = 2.6 Hz, 1H, C^5- H), 7.18-7.24 (m, 10H, C$_6$H$_5$-H), 7.50-7.54 (m, 2H, Mes-H). ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$, 25°C) (major isomer): δ = 19.9 (s, Mes-CH_3), 21.9 (d, $^3J_{P,C}$ = 17.8Hz, Mes-CH_3), 28.7 (s, cod), 31.3 (s, N-CH$_3$), 31.5 (s, cod), 36.7 (d, $^3J_{P,C}$ = 7.8 Hz, N-CH_3), 48.3 (d, $^1J_{P,C}$ = 12.9 Hz, CPh$_2$H), 70.0 (d, $^1J_{Rh,C}$ = 14.2 Hz, cod), 94.8 (d, $^1J_{Rh,C}$ = 6.7 Hz, cod), 123.2 (d, $J_{P,C}$ = 16.6 Hz), 124.4 (d, $J_{P,C}$ = 4.8 Hz), 125.4 (d, $J_{P,C}$ = 2.5 Hz), 127.3 (d, $J_{P,C}$ = 6.3 Hz), 128.0 (d, $J_{P,C}$ = 0.9 Hz), 129.0 (d, $J_{P,C}$ = 3.8 Hz), 130.6 (d, $J_{P,C}$ = 1.0 Hz), 130.9 (d, $J_{P,C}$ = 1.1 Hz), 139.0 (d, $J_{P,C}$ = 11.5 Hz), 140.1 (d, $J_{P,C}$ = 13.2 Hz), 182.2 (dd, $^1J_{Rh,C}$ = 48.9 Hz, $^3J_{P,C}$ = 2.0 Hz, C^2). ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$, 25°C) (minor isomer): δ = 20.0 (s, Mes-CH_3), 21.2 (d, $^3J_{P,C}$ = 17.6 Hz, Mes-CH_3), 28.5 (s, cod), 30.9 (s, cod), 31.1 (s, N-CH$_3$), 35.7 (d, $^3J_{P,C}$ = 6.5 Hz, N-CH_3), 48.2 (d, $^1J_{P,C}$ = 13.4 Hz, CPh$_2$H), 70.3 (d, $^1J_{Rh,C}$ = 14.1 Hz, cod), 94.8 (d, $^1J_{Rh,C}$ = 6.8 Hz, cod), 124.1 (d, $J_{P,C}$ = 18.7 Hz), 124.6 (d, $J_{P,C}$ = 4.9 Hz), 126.1 (d, $J_{P,C}$ = 2.3 Hz), 127.3 (d, $J_{P,C}$ = 6.4 Hz), 128.2 (d, $J_{P,C}$ = 0.8 Hz), 129.1 (d, $J_{P,C}$ = 3.6 Hz), 130.8 (d, $J_{P,C}$ = 1.1 Hz), 131.1 (d, $J_{P,C}$ = 1.0 Hz), 139.1 (d, $J_{P,C}$ = 10.9 Hz), 139.5 (d, $J_{P,C}$ = 13.3 Hz), 182.6 (dd, $^1J_{Rh,C}$ = 48.9 Hz, $^3J_{P,C}$ = 2.0 Hz, C^2). IR (ATR, ῦ [cm^{-1}]): ῦ = 2963 (w), 2933 (w), 2912 (w), 2871 (vs), 2826 (w), 1601 (s), 1549 (w), 1491 (w), 1447 (s), 1374 (s), 1304 (s), 1182 (s), 1075 (s), 1029 (s), 918 (w), 850 (s), 783 (s), 695 (vs). UV/Vis (CH$_2$Cl$_2$): λ_{max} [nm] (abs.): 400 (0.035), 231 (1.198). MS (EI, 70 eV): *m/z* (%) 433 (84) [C$_{18}$H$_{19}$ClN$_2$PRh]$^+$, 307 (40) [M-MesPCHPh$_2$-Cl]$^+$, 198 (22) [M- MesPCHPh$_2$-cod(Cl)]$^+$, 167 (58) [Ph$_2$CH]$^+$.

General synthesis of [*P*-functional NHC-M(CO)$_5$] complexes 1·M(CO)$_5$

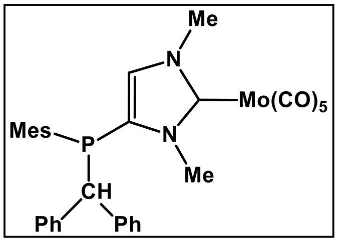
A solutions of [M(CO)$_5$(CH$_3$CN)] (M = Cr-W) (0.412 mmol each) in tetrahydrofuran (5 mL) was added to a solution containing the *P*-functional imidazol-2-ylidene **1** (0.17 g, 0.412 mmol) in tetrahydrofuran (5 mL) at ambient temperature. The reaction mixture was heated at 60 °C for 16h. The yellow colored solutions were then concentrated *in vacuo* to dryness (8 × 10^{-3} mbar) followed by recrystallization from toluene (6 mL) and washed with *n*-pentane (1 × 4 mL) and then dried *in vacuo* (8 × 10^{-3} mbar).

[*P*-functional NHC-Pentacarbonylchromium(0)] complex 1·Cr(CO)$_5$



Yield of both isomer: (0.218 g, 0.361 mmol, 86%), orange solid, m.p. 144 °C. ^{31}P NMR (121.5 MHz, CDCl$_3$, 25°C): δ = -36.7 (s, 77%) and -37.8 (s, 23%). ^{1}H NMR (300.1 MHz, CDCl$_3$, 25°C) (major isomer): δ = 2.11 (s, 3H, Mes-*p*-C*H*$_3$), 2.35 (s, 6H, Mes-*o*-C*H*$_3$), 3.29 (s, 3H, N-C*H*$_3$), 3.60 (s, 3H, N-C*H*$_3$), 5.02 (d, $^2J_{P,H}$ = 6.6 Hz, 1H, CPh$_2$*H*), 6.23 (d, $^3J_{P,H}$ = 2.5 Hz, 1H, C^5- *H*), 6.95-7.00 (m, 6H, C$_6$H$_5$-*H*), 7.18-7.25 (m, 4H, C$_6$H$_5$-*H*), 7.53-7.55 (m, 2H, Mes-*H*). ^{1}H NMR (300.1 MHz, CDCl$_3$, 25°C) (minor isomer): δ = 1.90 (s, 6H, Mes-*o*-C*H*$_3$), 2.19 (s, 3H, Mes-*p*-C*H*$_3$), 3.22 (s, 3H, N-C*H*$_3$), 3.72 (s, 3H, N-C*H*$_3$), 5.17 (d, $^2J_{P,H}$ = 7.5 Hz, 1H, CPh$_2$*H*), 6.29 (d, $^3J_{P,H}$ = 2.8 Hz, 1H, C^5- *H*), 7.00-7.03 (m, 6H, C$_6$H$_5$-*H*), 7.28-7.36 (m, 4H, C$_6$H$_5$-*H*), 7.56-7.62 (m, 2H, Mes-*H*). ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$, 25°C) (major isomer): δ = 19.9 (s, Mes-*C*H$_3$), 21.4 (d, $^3J_{P,C}$ = 18.1 Hz, Mes-*C*H$_3$), 36.8 (d, $^3J_{P,C}$ = 10.3 Hz, N-*C*H$_3$), 38.2 (s, N-*C*H$_3$), 47.9 (d, $^1J_{P,C}$ = 12.3 Hz, *C*Ph$_2$H), 123.4 (d, $J_{P,C}$ = 16.9 Hz), 125.6 (d, $J_{P,C}$ = 2.6 Hz), 126.6 (d, $J_{P,C}$ = 4.2 Hz), 127.2 (d, $J_{P,C}$ = 6.7 Hz), 127.8 (d, $J_{P,C}$ = 12.8 Hz), 127.0 (d, $J_{P,C}$ = 1.2 Hz), 138.9 (d, $J_{P,C}$ = 12.0 Hz), 139.8 (d, $J_{P,C}$ = 13.1 Hz), 139.4 (d, $J_{P,C}$ = 1.3 Hz), 143.7 (d, $J_{P,C}$ = 16.8 Hz), 191.3 (d, $^3J_{P,C}$ = 2.3 Hz, C^2), 213.9 (s, *cis*-CO), 216.8 (s, *trans*-CO). ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$, 25°C) (minor isomer): δ = 20.0 (s, Mes-*C*H$_3$), 21.7 (d, $^3J_{P,C}$ = 17.1 Hz, Mes-*C*H$_3$), 34.4 (d, $^3J_{P,C}$ = 7.2Hz, N-*C*H$_3$), 35.6 (s, N-*C*H$_3$), 47.4 (d, 1$J_{P,C}$ = 11.4 Hz, *C*Ph$_2$H), 120.5 (d, $J_{P,C}$ = 14.6 Hz), 124.8 (d, $J_{P,C}$ = 1.9 Hz), 126.3 (d, $J_{P,C}$ = 2.0 Hz), 127.4 (d, $J_{P,C}$ = 5.3 Hz), 127.6 (d, $J_{P,C}$ = 12.7 Hz), 128.1 (d, $J_{P,C}$ = 0.8 Hz), 137.4 (d, $J_{P,C}$ = 13.6 Hz), 138.3 (d, $J_{P,C}$ = 12.5 Hz), 141.1 (d, $J_{P,C}$ = 1.7 Hz), 143.5 (d, $J_{P,C}$ = 15.7 Hz), 190.7 (d, $^3J_{P,C}$ = 1.8 Hz, C^2), 214.5 (s, *cis*-CO), 216.9 (s, *trans*-CO). IR (ATR, ῦ [cm^{-1}]): ῦ = 2962 (w), 2053 (s), 1972 (s), 1888 (br), 1602 (w), 1448 (w), 1260 (s), 1087 (s), 1020 (s), 798 (s), 703 (w), 679 (w). UV/Vis (CH$_2$Cl$_2$): λ_{max} [nm] (abs.): 230 (0.740). MS (EI, 70 eV): *m/z* 604 (14) $[M]^{\cdot+}$, 492 (22) $[M\text{-}4CO]^+$, 464 (64) $[M\text{-}5CO]^+$, 287 (10) $[M\text{-}MesPHCPh_2]^+$, 192 (12) $[Cr(CO)_5]^+$, 176 (28) [M-MesPCHPh$_2$-4CO], 167 (20) $[Ph_2CH]^+$, 79 $[C_4H_4N_2]^+$. HR-MS (C$_{32}$H$_{29}$CrN$_2$O$_5$P): found: 604.1474, calc: 604.1219.

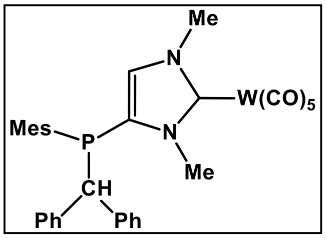
[P-functional NHC-Pentacarbonylmolybdenum(0)] complex 1·Mo(CO)$_5$



Yield of both isomer: (0.226 g, 0.35 mmol, 85 %), yellow solid, m.p. 165 °C (dec.). ^{31}P NMR (121.5 MHz, CDCl$_3$, 25°C): δ = -36.7 (s, 85%) and -37.9 (s, 15%). ^{1}H NMR (300.1 MHz, CDCl$_3$, 25°C) (major isomer): δ = 2.11 (s, 6H, Mes-*o*-C*H*$_3$), 2.16 (s, 3H, Mes-*p*-

CH_3), 3.26 (s, 3H, N-CH_3), 3.67 (s, 3H, N-CH_3), 5.03 (d, $^2J_{P,H}$ = 6.4 Hz, 1H, CPh$_2$*H*), 6.61 (d, $^3J_{P,H}$ = 2.7 Hz, 1H, C^5- *H*), 6.94-6.98 (m, 6H, C$_6$H$_5$-*H*), 7.27-7.36 (m, 4H, C$_6$H$_5$-*H*), 7.53-7.55 (m, 2H, Mes-H). ^{1}H NMR (300.1 MHz, CDCl$_3$, 25°C) (minor isomer): δ = 2.14 (s, 6H, Mes-*o*-CH_3), 2.17 (s, 3H, Mes-*p*-CH_3), 3.76 (s, 3H, N-CH_3), 3.77 (s, 3H, N-CH_3), 5.14 (d, $^2J_{P,H}$ = 7.3 Hz, 1H, CPh$_2$*H*), 6.70 (d, $^3J_{P,H}$ = 3.1 Hz, 1H, C^5- *H*), 6.99-7.02 (m, 6H, C$_6$H$_5$-*H*), 7.17-7.24 (m, 4H, C$_6$H$_5$-*H*), 7.56-7.58 (m, 2H, Mes-*H*). ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$, 25°C) (major isomer): δ = 19.9 (s, Mes-*C*H$_3$), 21.5 (d, $^3J_{P,C}$ = 18.0 Hz, Mes-*C*H$_3$), 37.5 (d, $^3J_{P,C}$ = 9.5 Hz, N-*C*H$_3$), 38.8 (s, N-*C*H$_3$), 47.9 (d, $^1J_{P,C}$ = 12.3 Hz, *C*Ph$_2$H), 123.4 (d, $J_{P,C}$ = 17.0 Hz), 125.6 (d, $J_{P,C}$ = 2.6 Hz), 125.8 (d, $J_{P,C}$ = 4.1 Hz), 126.3 (d, $J_{P,C}$ = 2.0 Hz), 127.0 (d, $J_{P,C}$ = 1.1 Hz), 127.2 (d, $J_{P,C}$ = 7.0 Hz), 127.8 (d, $J_{P,C}$ = 12.8 Hz), 128.1 (d, $J_{P,C}$ = 0.8 Hz), 129.1 (d, $J_{P,C}$ = 4.6 Hz), 131.0 (d, $J_{P,C}$ = 23.0 Hz), 139.0 (d, $J_{P,C}$ = 12.0 Hz), 139.4 (d, $J_{P,C}$ = 1.3 Hz), 139.8 (d, $J_{P,C}$ = 13.2 Hz), 143.7 (d, $J_{P,C}$ = 16.5 Hz), 188.9 (d, $^3J_{P,C}$ = 2.2 Hz, C^2), 205.5 (s, *cis*-CO), 210.8 (s, *trans*-CO). ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$, 25°C) (minor isomer): δ = 20.0 (s, Mes-*C*H$_3$), 21.6 (d, $^3J_{P,C}$ = 15.7 Hz, Mes-*C*H$_3$), 35.9 (d, $^3J_{P,C}$ = 10.9 Hz, N-*C*H$_3$), 39.1 (s, N-*C*H$_3$), 47.4 (d, $^1J_{P,C}$ = 10.8 Hz, *C*Ph$_2$H); other signals were not assigned. IR (ATR, ῦ [cm^{-1}]): ῦ = 2961 (w), 2061 (s), 1989 (s), 1911 (br), 1601 (w), 1447 (s), 1259 (w), 1157 (w), 1079 (w), 1028 (w), 730 (w), 697 (s), 684 (s). UV/Vis (CH$_2$Cl$_2$): λ_{max} [nm] (abs.): 231 (0.505), 207 (0.140), 200 (0.158). MS (EI, 70 eV): *m/z* 468 (22) [M-Me-Ph$_2$CH]$^+$, 412 (64) [M-Mo(CO)$_5$]$^+$, 333 (8) [M-MesPCHPh$_2$]$^+$, 237 (10) [Mo(CO)$_5$]$^+$, 167.0 (74) [Ph$_2$CH]$^+$. HR-MS ($C_{32}H_{29}MoN_2O_5P$): found: 650.1446, calc: 650.0868.

[P-functional NHC-Pentacarbonyltungsten(0)] complex 1·W(CO)$_5$

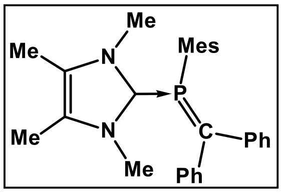


Yield of both isomer: (0.265 g, 0.36 mmol, 86 %), orange red solid, m.p. 108 °C. ^{31}P NMR (121.5 MHz, CDCl$_3$, 25°C): δ = -36.4 (s, 92 %) and -37.8 (s, 8 %). ^{1}H NMR (300.1 MHz, CDCl$_3$, 25°C) (major isomer): δ = 2.21 (s, 6H, Mes-*o*-CH_3), 2.26 (s, 3H, Mes-*p*-CH_3), 3.36 (s, 3H, N-CH_3), 3.68 (s, 3H, N-CH_3), 5.14 (d, $^2J_{P,H}$ = 6.6 Hz, 1H, CPh$_2$*H*), 6.73 (d, $^3J_{P,H}$ = 2.6 Hz, 1H, C^5- *H*), 7.04-7.08 (m, 6H, C$_6$H$_5$-*H*), 7.29-7.44 (m, 4H, C$_6$H$_5$-*H*), 7.63-7.67 (m, 2H, Mes-*H*). ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$, 25°C) (major isomer): δ = 19.9 (s, Mes-*C*H$_3$), 21.5 (d, $^3J_{P,C}$ = 17.4 Hz, Mes-*C*H$_3$), 38.4 (d, $^3J_{P,C}$ = 9.9 Hz, N-*C*H$_3$), 39.7 (s, N-*C*H$_3$), 47.9 (d, $^1J_{P,C}$ = 12.2 Hz, *C*Ph$_2$H), 123.3 (d, $J_{P,C}$ = 16.7 Hz), 125.6 (d, $J_{P,C}$ = 2.1 Hz), 126.3 (d, $J_{P,C}$ = 1.9 Hz), 127.0 (d, $J_{P,C}$ = 1.2 Hz), 127.3 (d, $J_{P,C}$ = 6.8 Hz), 127.8 (d, $J_{P,C}$ = 12.8 Hz), 128.1 (d, $J_{P,C}$ = 0.7 Hz), 129.2 (d, $J_{P,C}$ = 4.5 Hz), 130.9 (d, $J_{P,C}$ = 23.6 Hz), 138.9 (d, $J_{P,C}$ =

12.0 Hz), 139.5 (d, $J_{P,C}$ = 1.3 Hz), 139.7 (d, $J_{P,C}$ = 13.1 Hz), 143.7 (d, $J_{P,C}$ = 16.2 Hz), 180.5 (d, $^3J_{P,C}$ = 2.1 Hz, C^2), 197.1 (s_{sat}, $^1J_{C,W}$ = 126.4 Hz, *cis*-CO), 200.2 (s, *trans*-CO). IR (ATR, $\tilde{\upsilon}$ [cm^{-1}]): $\tilde{\upsilon}$ = 2962 (w), 2060 (s), 1971 (s), 1878 (vs), 1602 (w), 1492 (w), 1448 (w), 1345 (w), 1260 (s), 1076 (br), 1017 (br), 796 (s), 747 (w), 696 (s). UV/Vis (CH_2Cl_2): λ_{max} [nm] (abs.): 231 (0.515), 214 (0.171), 207 (0.154), 199 (0.145). MS (EI, 70 eV): *m/z* (%) 736 (32) $[M]^{\cdot+}$, 708 (32) $[M\text{-}CO]^+$, 706 (18) [M-2Me], 680 (24) $[M\text{-}2CO]^+$, 652 (60) $[M\text{-}3CO]^+$, 596 (18) $[M\text{-}5CO]^+$, 419 (12) $[M\text{-}MesPCHPh_2]^+$, 167 (40) $[Ph_2CH]^+$.

Reaction of Me_2IMe with a phosphaalkene derivative; synthesis of 2

In a glove box, phosphaalkene (MesP=CPh_2) (0.316 g, 1 mmol) was added to the Me_2IMe (0.124 g, 1 mmol) in diethyl ether (10 mL) solution at ambient temperature and then stirred for one hour. The red colored solution containing ca. 93% **2** along with other products was then concentrated to dryness *in vacuo* (8 × 10^{-3} mbar) following which a red solid was obtained. Single crystals were obtained by slow evaporation of a saturated diethyl ether solution of the crude product in a glovebox (ca. 24 h) at ambient temperature. Compound **2** showed poor long term stability (≥2 days) in diethyl ether or thf solution and could not be isolated in > 93% purity according to 31P NMR spectroscopy. Thus, a yield could not be determined.



^{1}H NMR (300.1 MHz, C_6D_6, 25°C): δ = 1.53 (s, 6H, $C^{4/5}$-C*H*$_3$), 2.01 (s, 3H, Mes-*p*-C*H*$_3$), 2.26 (s, 6H, Mes-*o*-C*H*$_3$), 3.31 (s, 6H, N-C*H*$_3$), 6.54-7.74 (m, 12H, Ar-*H*). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 25°C): δ = 8.5 (s, $C^{4/5}$-*C*H$_3$), 20.9 (s, Mes-*C*H$_3$), 22.3 (d, $^3J_{P,C}$ = 18.5 Hz, Mes-*C*H$_3$), 34.4 (d, $^3J_{P,C}$ = 7.5 Hz, N-*C*H$_3$), 120.3-129.4 (Ar), 136.5 (d, $J_{P,C}$ = 38.4 Hz), 138.2 (s, Ar), 140.6 (d, $J_{P,C}$ = 8.2 Hz, Ar); other missing signals could not resolved. ^{31}P NMR (121.5 MHz, C_6D_6, 25°C): δ = 200.7 (bs, $w_{1/2}$ = 231 Hz).

NHC displacement reactions

In a glove box, to a freshly prepared diethyl ether (3 mL) solution of **2** (0.2 mmol), triphenyl borane or tris(pentafluorophenyl)borane (0.2 mmol each) was added and stirred for one hour at ambient temperature. The formation of free phosphaalkene (MesP=CPh_2) was confirmed by ^{31}P NMR and NHC·BR_3 complexes by ^{11}B NMR spectroscopy.

Crystal data and structure refinement for 1·BH$_3$

Device Type	STOE IPDS2T
Empirical formula	$C_{58}H_{72}B_2N_4OP_2$
Moiety formula	$2(C_{27}H_{32}BN_2P)$, C_4H_8O
Formula weight	924.76
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C* 2/*c*
Unit cell dimensions	a = 25.984 Å α = 90°
	b = 9.734 Å β = 108.32°
	c = 21.550 Å γ = 90°
Volume	5174.2 Å^3
Z	4
Calculated density	1.187 mg/m^3
Absorption coefficient	0.128 mm^{-1}
F(000)	1984
Crystal size	0.15 × 0.09 × 0.03 mm
Theta range for data collection	2.96 to 25.25°
Limiting indices	$-31 \leq h \leq 31$, $-11 \leq k \leq 11$, $-21 \leq l \leq 25$
Reflections collected / unique	33310 / 33319 [R(int) = 0.103]
Completeness to theta = 25.25	99.8 %
Absorption correction	Integration
Max. and min. transmission	0.9962 and 0.9811
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	33319 / 58 / 340
Goodness-of-fit on F^2	0.754
Final R indices [I>2sigma(I)]	$R_1 = 0.0777$, $wR_2 = 0.1454$
R indices (all data)	$R_1 = 0.2228$, $wR_2 = 0.1936$
Largest diff. peak and hole	0.469 and -0.322 e.Å^{-3}

Crystal data and structure refinement for 2

Device Type	Bruker X8-KappaApexII
Empirical formula	$C_{29}H_{33}N_2P$
Moiety formula	C29 H33 N2 P
Formula weight	440.54
Temperature	100
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 11.3578(19) Å α = 90°
	b = 9.9307(13) Å β = 102.838(13)°
	c = 22.539(5) Å γ = 90°
Volume	2478.6(8) Å^3
Z	4
Calculated density	1.181 mg/m^3
Absorption coefficient	0.130 mm^{-1}
F(000)	944.0
Crystal size	0.1 × 0.08 × 0.05 mm
Theta range for data collection	5.51 to 55.998°
Limiting indices	$-15 \leq h \leq 14$, $-13 \leq k \leq 13$, $-29 \leq l \leq 28$
Reflections collected	21757 [R(int) = 0.0752]
Completeness to theta	0.997
Absorption correction	empirical
Max. and min. transmission	0.7459 and 0.5954
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5947 / 0 / 296
Goodness-of-fit on F^2	1.006
Final R indices [I>2sigma(I)]	$R_1 = 0.0462$, $wR_2 = 0.1023$
R indices (all data)	$R_1 = 0.0909$, $wR_2 = 0.1218$
Largest diff. peak and hole	0.27 and -0.44 e.Å^{-3}

Computational Details

DFT Calculations: Initial geometries for all molecules were obtained from crystallographic coordinates (where available) or constructed from standard models. Geometry optimizations and numerical frequency calculations were performed using version 3.0.3 of the ORCA computational chemistry package. (ref: Frank Neese in *ORCA – an ab initio, DFT, and Semiempirical Electronic Structure Package*, version 3.0.3. The Max Planck Institute for Chemical Energy Conversion, Muelheim a. d. Ruhr, Germany, 2015.) Scalar relativistic effects were taken in to account using ZORA corrections as implemented in ORCA. (refs: J. Chem. Phys. 1993, 99, 4597 & J. Chem .Phys. 1998, 109, 392.) Calculations were performed with a very dense integration grid (ORCA Grid6). Molecular geometries were optimized using the B3LYP functional and all electron basis sets (def2-TZVP) for all atoms. Computational efficiency was improved by applying the RI approximation (RIJCOSX) for the hybrid functional. (ref: J. Chem. Phys. 2009, 356, 98-109)

NBO Analysis: NBO analysis was performed using .47 files generated from Gaussian03 recalculation of the ORCA-derived geometries at the B3LYP/6-31G(d) level of theory. (ref: Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.) NRT analysis was performed using NBO6.(ref: NBO 6.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, and F. Weinhold (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2013);

http://nbo6.chem.wisc.edu/) The presence of three aromatic rings in MesP=CPh$_2$ and four in the corresponding NHC-adduct resulted in very large numbers of contributing structures based on electron delocalization in the rings systems. The system was simplified by applying an energy threshold limit (NRTTHR=10) and by excluding the Mes ring from the analysis as it does not contribute significantly to the overall electronics of the systems under investigation (see SI for further details).

S1. Optimized Geometries (ORCA 3.0.3: B3LYP/TZVP/ZORA)

Geometries for all computed structures were obtained using ORCA v3.0.3 run on either departmental servers at UBC or though the WestGrid supercomputing center. A representative input file is given below (note that geometries and/or electron density distributions did not change significantly when comparing gas phase vs. COSMO-based solvent calculations in diethyl ether, THF, or toluene).

```
! RKS B3LYP def2-TZVP def2-TZVP/C   RIJCOSX ZORA TightSCF
! OPT NumFreq
! Grid6 NoFinalGrid
! Normalprint

* xyzfile 0 1 xtalstructureinput.xyz
```

Frequency analysis confirmed that each computed geometry was in a true minimum in the energy surface. All coordinates below are final gas phase optimized geometries in Cartesian coordinates (Å):

MesP=CMe$_2$

C	1.931364	-0.142668	-3.307989
P	1.270236	1.234384	-2.607309
C	0.610442	0.731906	-0.954690
C	1.243190	1.186560	0.218361
C	2.563478	1.916054	0.178927
H	2.812616	2.316401	1.163001
H	2.551548	2.747220	-0.530033
H	3.373754	1.249073	-0.127016
C	0.648838	0.944398	1.456814
H	1.140919	1.302929	2.354969
C	-0.560037	0.269846	1.576922
C	-1.174351	0.019563	2.929239
H	-2.243482	0.247749	2.928789
H	-0.702385	0.628287	3.700379
H	-1.061470	-1.028601	3.223465
C	-1.177398	-0.171471	0.408445
H	-2.127659	-0.692148	0.473629
C	-0.620389	0.049404	-0.849496
C	-1.356178	-0.437591	-2.072843
H	-1.509477	0.367584	-2.795173
H	-2.331013	-0.845996	-1.804555
H	-0.799334	-1.220005	-2.592397
C	2.056217	-1.521599	-2.735723
C	2.463608	-0.003235	-4.709091
H	1.924415	-0.670150	-5.390306
H	2.366456	1.015634	-5.086179
H	3.518596	-0.298179	-4.755869
H	1.463389	-2.232288	-3.323598
H	3.094911	-1.864276	-2.807065
H	1.737057	-1.584749	-1.696669

Me$_2$IMe

C	-1.086338	-0.999466	0.049539
N	-0.144973	-0.017437	0.010707
C	-0.692787	1.266025	-0.031296
C	-2.040378	1.093033	-0.026685
N	-2.245935	-0.287218	0.027881
C	1.276203	-0.303765	0.015614

C	-3.547375	-0.923547	0.046851
C	-3.147661	2.087493	-0.075073
H	1.774498	0.164365	-0.835770
H	-4.178237	-0.501796	0.831432
C	0.123470	2.510920	-0.053825
H	1.750296	0.054209	0.933185
H	1.393843	-1.382099	-0.049051
H	-4.060977	-0.808747	-0.911306
H	-3.390075	-1.980919	0.242976
H	-0.522353	3.385218	-0.129047
H	0.725053	2.622850	0.853582
H	0.813263	2.536752	-0.902206
H	-3.790790	1.939870	-0.947630
H	-3.787074	2.034994	0.810893
H	-2.745117	3.098624	-0.131791

Mes$_4$+MesP=CMe$_2$

C	2.467915	9.498870	6.917104
P	2.158161	11.058015	6.326547
C	1.745933	12.149865	7.780140
C	0.359215	12.274178	8.059544
C	-0.695255	11.550240	7.260825
H	-0.612198	11.762957	6.192682
H	-0.597626	10.468208	7.375422
H	-1.690877	11.845888	7.593758
C	-0.075058	13.065922	9.117276
H	-1.140557	13.134627	9.312926
C	0.809021	13.763326	9.935485
C	0.303260	14.600903	11.080504
H	1.119692	15.105720	11.599455
H	-0.396586	15.364563	10.731003
H	-0.230380	13.985991	11.810845
C	2.161841	13.631778	9.666073
H	2.875972	14.145267	10.302317
C	2.649147	12.838427	8.619524
C	4.154623	12.762001	8.503463
H	4.550905	13.432822	7.737502
H	4.611726	13.056428	9.450251
H	4.494945	11.755919	8.264345
C	3.737884	12.088287	5.668993
N	3.631952	13.272474	5.018080
C	2.453097	14.118926	5.110613
H	2.486639	14.876773	4.332350
H	1.566167	13.497771	4.976931
H	2.392174	14.603489	6.084982
C	4.764735	13.525142	4.246118
C	4.953330	14.787417	3.479461
H	4.202918	14.912091	2.694176
H	4.897209	15.662554	4.133273
H	5.930671	14.796381	2.999380
C	5.586128	12.454066	4.410001
C	6.946947	12.194541	3.860411
H	7.239517	13.000304	3.189248
H	7.700002	12.136685	4.652051
H	6.993309	11.262570	3.291292
N	4.933059	11.580994	5.284476
C	5.442201	10.274720	5.692020
H	6.513756	10.239688	5.509883
H	4.952439	9.482128	5.127658
H	5.251655	10.107362	6.748549
C	2.360887	8.341098	5.955121
C	3.010197	9.150720	8.275952
H	1.748764	7.529046	6.373103
H	1.904880	8.637958	5.006438
H	3.334344	7.876899	5.712052
H	2.495737	8.272951	8.689669
H	4.085837	8.880006	8.274542
H	2.885744	9.960591	8.997066

MesP=CPh$_2$

H	1.899603	-0.171571	-3.216093
H	0.710818	1.044299	-2.733267
C	1.278715	0.175782	-2.389705
H	3.887481	-0.229327	-2.173322
H	0.555356	-0.608599	-2.163593
H	-4.762531	2.650473	-1.678128
H	-2.361218	2.129109	-1.533205
C	3.501044	0.232280	-1.270702
C	2.138086	0.510856	-1.195744
H	-2.019597	-1.817299	-1.319255
H	-1.339335	-4.170253	-1.098939
C	-4.421510	1.875806	-1.002600
H	6.037314	-0.513365	-1.138309
C	-3.065741	1.588545	-0.915571
C	-1.287647	-2.094877	-0.571494
H	6.412061	1.136475	-0.654154
C	-0.905094	-3.423503	-0.445392
H	-6.395578	1.381013	-0.315598
C	5.853175	0.239105	-0.370931
C	4.382587	0.535268	-0.239450
C	-5.337747	1.160324	-0.241005
P	-0.126252	1.681108	0.065690
C	1.621780	1.104336	-0.023540
C	-2.589080	0.588253	-0.053717
C	-1.136728	0.313222	0.087011
C	-0.730593	-1.100826	0.248646
H	0.323755	-4.832386	0.624194
C	0.028431	-3.795710	0.517906
C	-4.885747	0.152705	0.607181
H	6.273654	-0.126431	0.568361
C	-3.530906	-0.133331	0.697736
C	3.862834	1.144675	0.899463
C	2.506396	1.439231	1.024280
C	0.204113	-1.495488	1.214898
C	0.577281	-2.825672	1.349340
H	-5.592801	-0.412095	1.202416
H	-3.192074	-0.914062	1.365845
H	4.529161	1.402634	1.716884
H	0.625859	-0.751592	1.875392
H	1.296337	-3.105979	2.108851
H	1.307932	2.882705	2.123649
C	2.019868	2.074889	2.306521
H	1.506126	1.348257	2.943986
H	2.853824	2.485299	2.877333

Me$_2$IMe+MesP=CPh$_2$

P	2.582742	9.409032	6.778258
N	2.115862	12.156728	6.287425
N	1.835565	11.727422	8.386942
C	1.381282	8.874511	5.465601
C	1.957170	8.008697	4.497482
C	1.232016	7.655234	3.366456
H	1.693192	6.996964	2.637817
C	-0.057969	8.128492	3.133039
C	-0.626505	8.938348	4.103970
H	-1.643646	9.292513	3.967747
C	0.054752	9.310645	5.268446
C	3.357177	7.462284	4.639665
H	4.104241	8.258737	4.589533
H	3.565665	6.748500	3.842014
H	3.506509	6.960658	5.596963
C	-0.790823	7.776294	1.865420
H	-0.281175	8.194333	0.992888
H	-1.809409	8.166917	1.873663
H	-0.842920	6.694603	1.718596
C	-0.720182	10.154824	6.250395
H	-0.431206	9.958393	7.280772
H	-1.785895	9.938640	6.157770
H	-0.591319	11.225645	6.060857
C	1.992265	11.135319	7.177718
C	2.044537	13.384726	6.936164
C	1.889133	13.115446	8.259338
C	2.392497	11.971223	4.873433
H	1.486432	11.723355	4.320871
H	3.101817	11.149844	4.763986
H	2.829877	12.881163	4.470830
C	2.107977	14.685398	6.214008
H	3.087141	14.866858	5.761631
H	1.901606	15.503812	6.901402
H	1.363852	14.734913	5.415211
C	1.826870	14.047533	9.419512
H	0.845825	14.056360	9.902116
H	2.045544	15.061484	9.087968
H	2.566533	13.786758	10.179558
C	1.610205	11.028531	9.651550
H	0.916684	10.205336	9.508627
H	1.185076	11.733350	10.361252
H	2.542276	10.622844	10.041906
C	2.731320	8.393895	8.182507
C	4.141296	8.161740	8.573280
C	5.121800	9.172946	8.562870
H	4.833563	10.185932	8.307320
C	6.454331	8.911591	8.861476
H	7.173318	9.723188	8.838432
C	6.865320	7.630593	9.207739
H	7.901134	7.426256	9.448850
C	5.912356	6.613896	9.247799
H	6.210064	5.604683	9.509695
C	4.587392	6.873010	8.935901
H	3.872550	6.059980	8.952829
C	1.655778	7.740645	8.931020
C	1.813264	7.434214	10.305777
H	2.758069	7.650488	10.787065
C	0.795584	6.871198	11.060458
H	0.972816	6.656569	12.109032
C	-0.443797	6.585845	10.491753
H	-1.239797	6.150693	11.082572
C	-0.625109	6.864653	9.141700
H	-1.569954	6.629231	8.664085
C	0.396273	7.418764	8.380363
H	0.224432	7.574602	7.325786

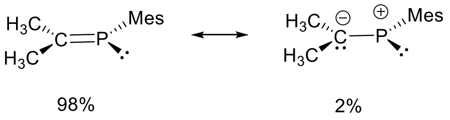
S2. Computational Thermochemistry

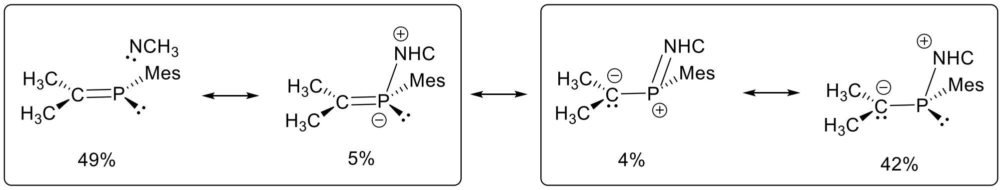
S3. Natural Resonance Theory Analysis Results (G04: B3LYP/6-31G(d)/NBO6)

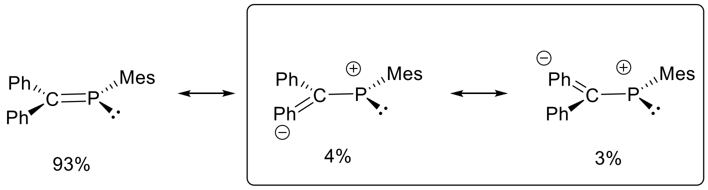
NRT analyses were performed using optimized geometries given in section S1 using NBO6. The NRT analysis did not include the mesitylene group in any of the analyses (as it was shown to contribute very little to the overall changes in bonding upon adduct formation) and omitted all of the hydrogen atoms using the NRT <ATOM#> key. In addition, a minimum threshold was set (NRTTHR=10) to restrict possible resonance structures to only the most important contributions. This was important to allow for reasonable computation of resonance contributors in the largest system. No significant differences were observed between using NRTTHR=10 and NRTTHR=8 although computational time was increased significantly in the latter case. The same parameters were used for all systems. A representative NBO6 input sequence is shown below:

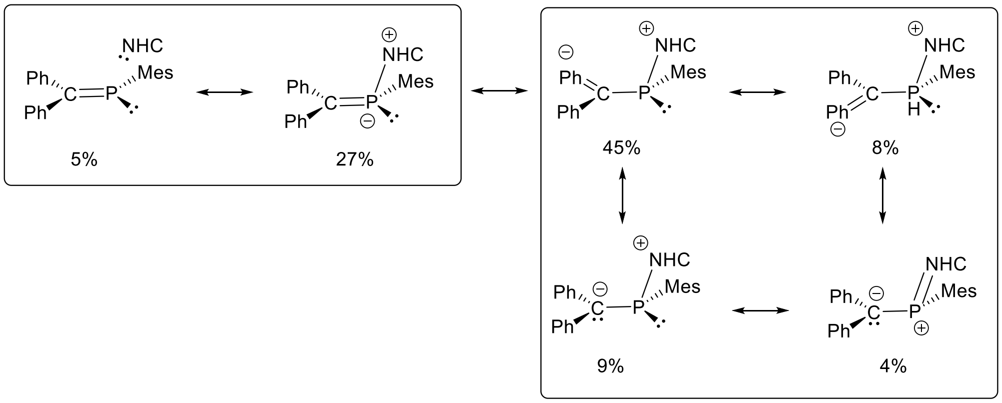
```
$NBO nrt <4 5 6 7 8 9 26 27 28 30 32 34 36 38 39 41 43 45 47>  nrtfdm nrtres=1500 nrtthr=10
nrtcml  $END
```

The resulting resonance decompositions are summarized below.



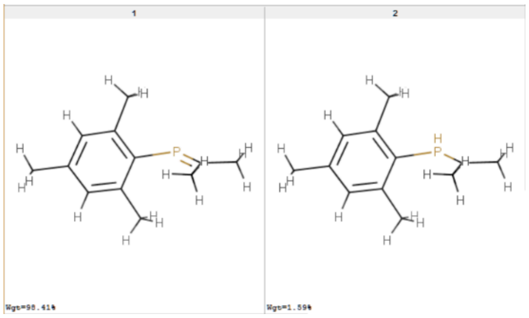




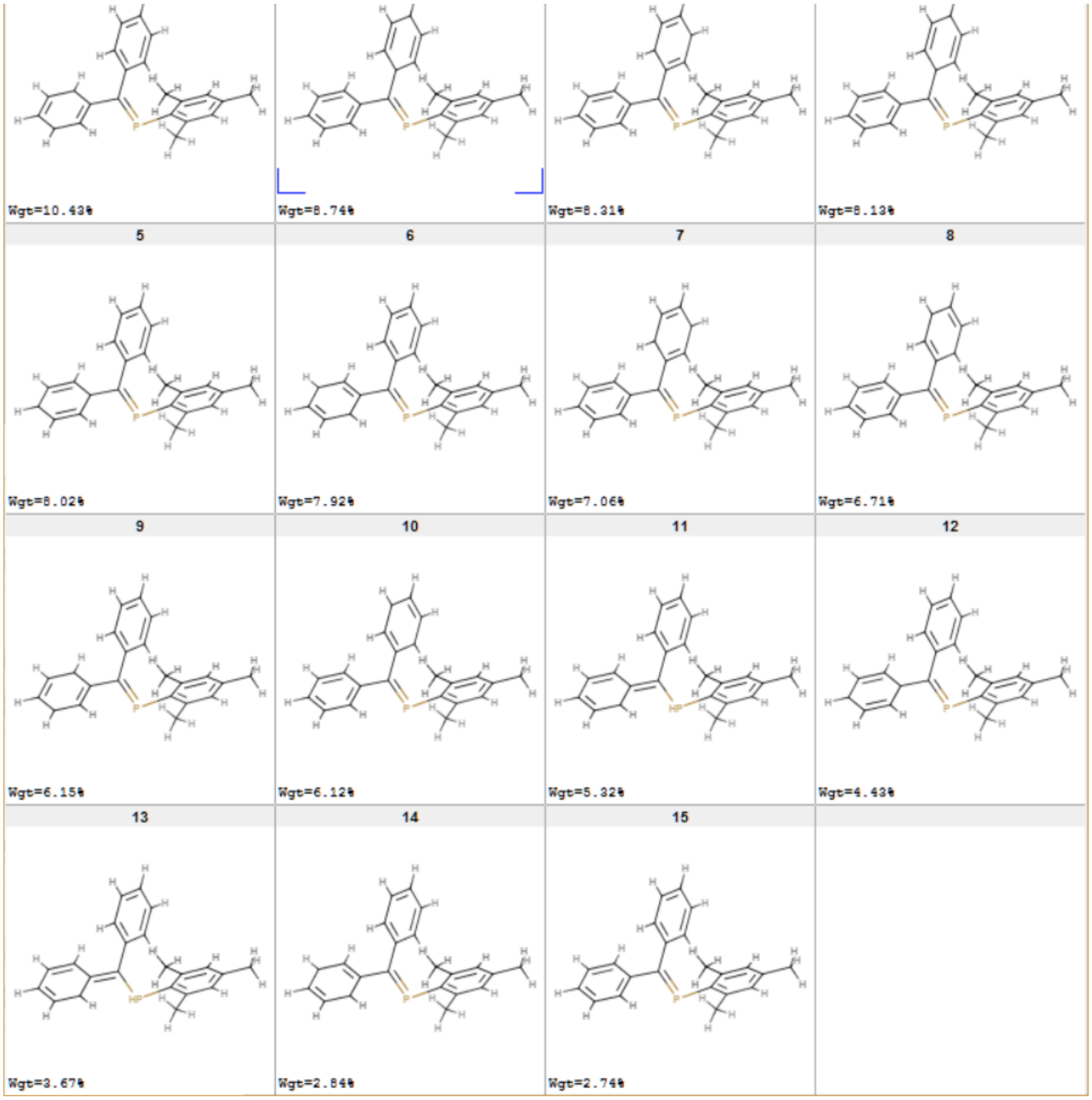


Selected output from the NRT analysis are given below (cml output visualized in MarvinSketch):

MesP=CMe$_2$

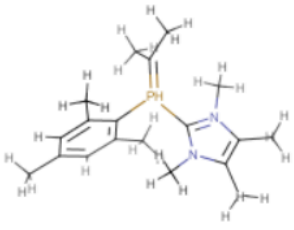


MesP=CPh$_2$



Me$_2$IMe---MesP=CMe$_2$

1



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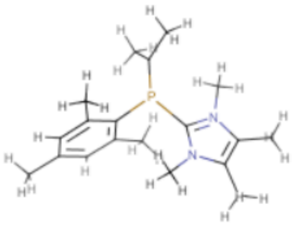
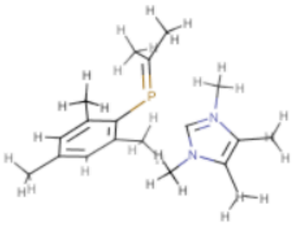


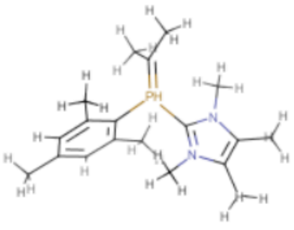
Wgt=14.75%

3



Wgt=10.96%

4



Wgt=7.29%

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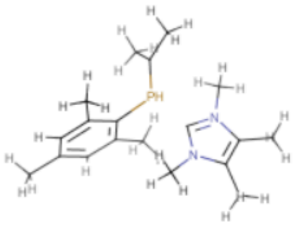

Wgt=6.46%

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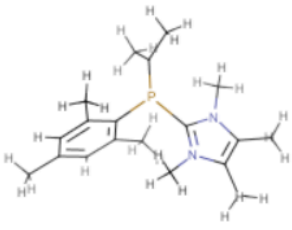

Wgt=6.21%

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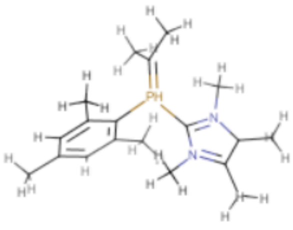

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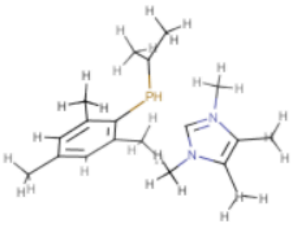

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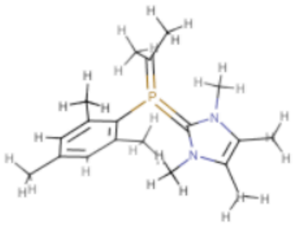

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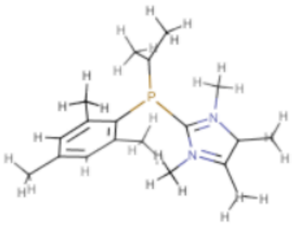

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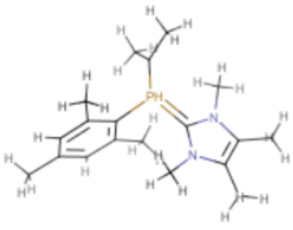

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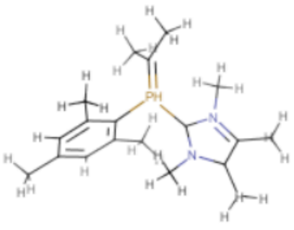

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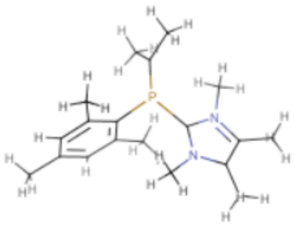

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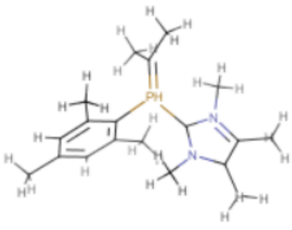

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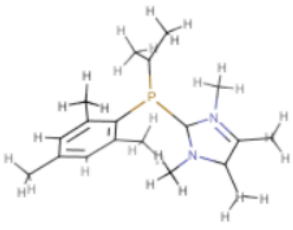

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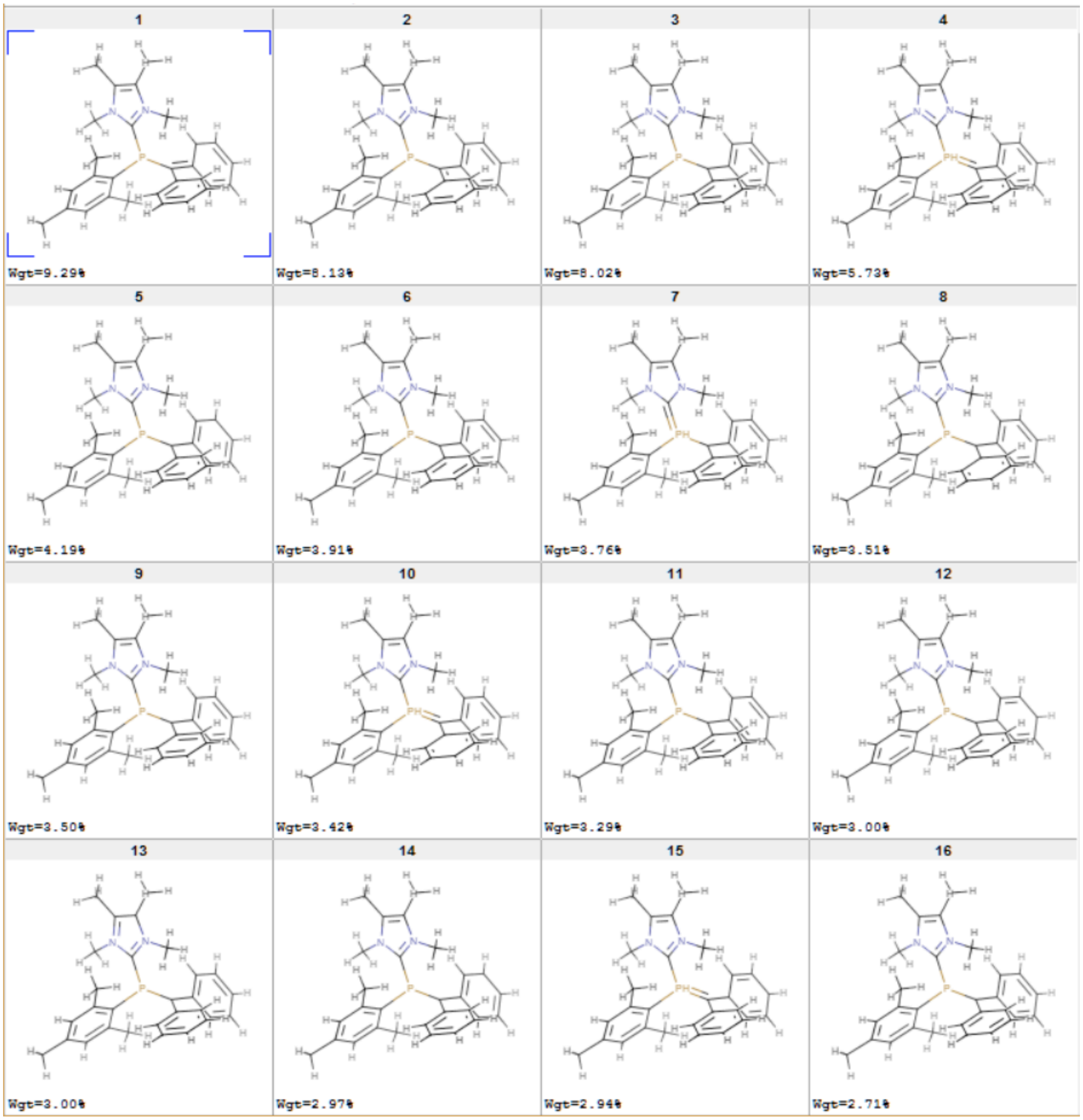
Me$_2$IMe---MesP=CPh$_2$



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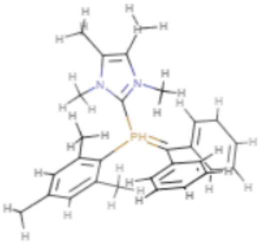
Wgt=9.29%	Wgt=8.13%	Wgt=8.02%	Wgt=5.73%
5	**6**	**7**	**8**
Wgt=4.19%	Wgt=3.91%	Wgt=3.76%	Wgt=3.51%
9	**10**	**11**	**12**
Wgt=3.50%	Wgt=3.42%	Wgt=3.29%	Wgt=3.00%
13	**14**	**15**	**16**
Wgt=3.00%	Wgt=2.97%	Wgt=2.94%	Wgt=2.71%

17



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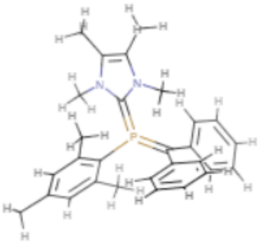

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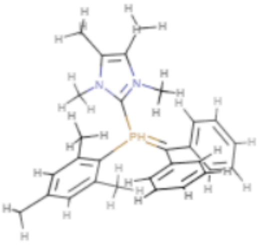

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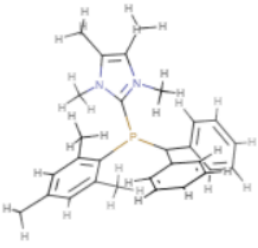

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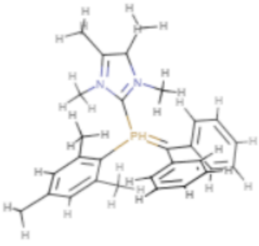

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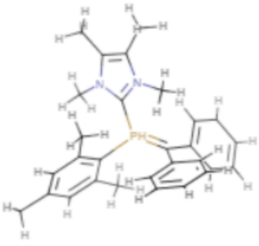

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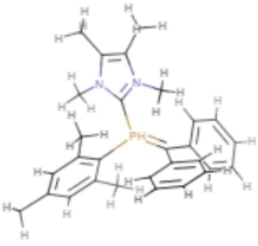

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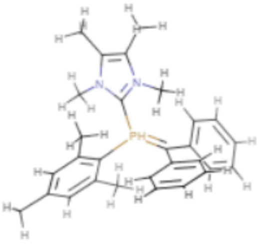

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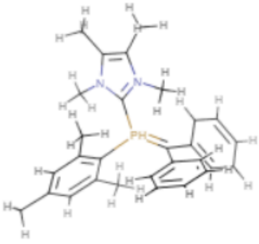

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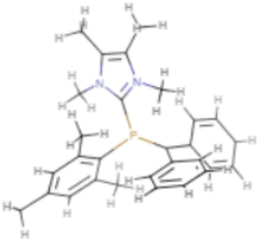

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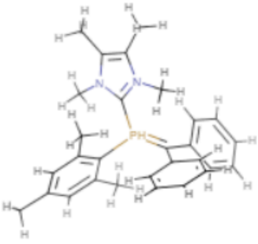

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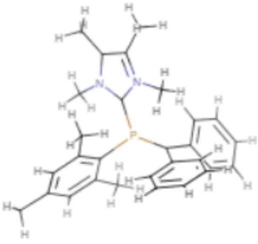

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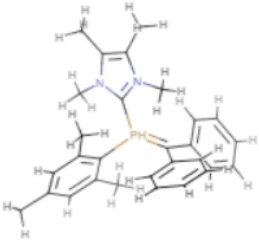

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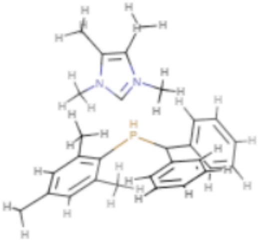

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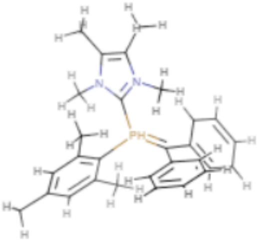

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Selected Spectra for new compounds

Figure S1: $^{31}P\{^{1}H\}$ NMR spectrum of **1** in THF-d8 (121.5 MHz, 25 °C)

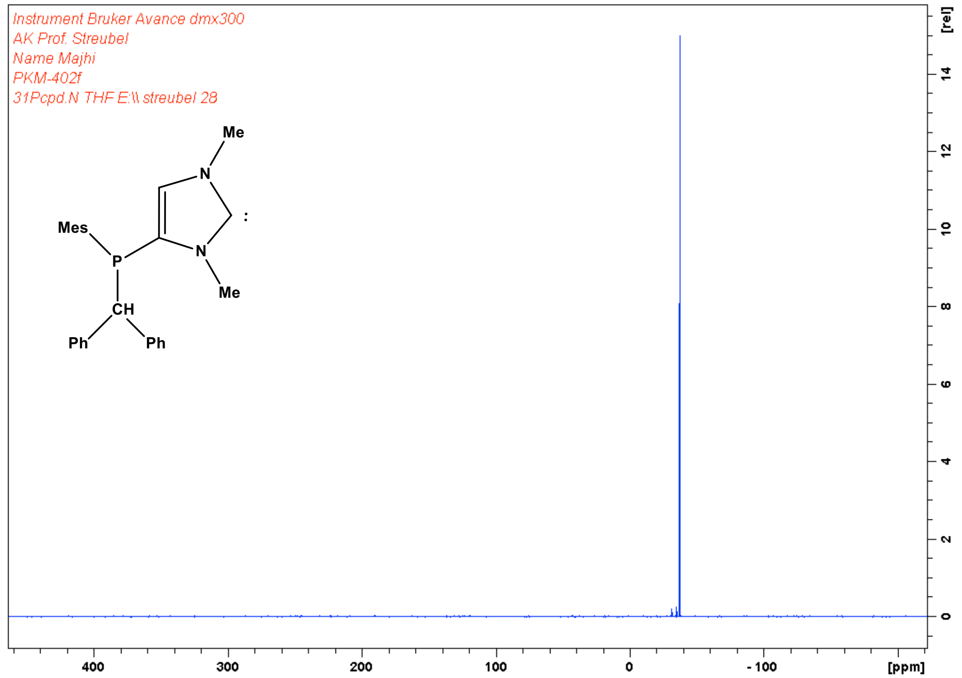

Figure S2: ^{1}H NMR spectrum of **1** in THF-d8 (300.1 MHz, 25 °C)

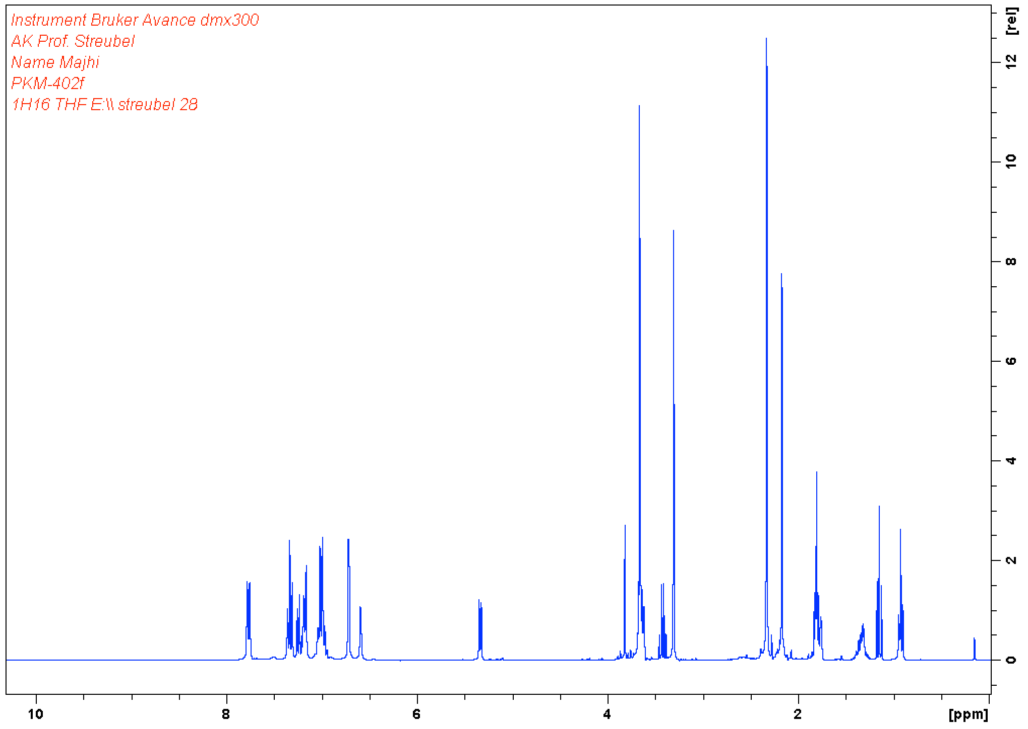

Figure S3: $^{13}C\{^{1}H\}$ NMR spectrum of **1** in THF-d8 (75.5 MHz, 25 °C)

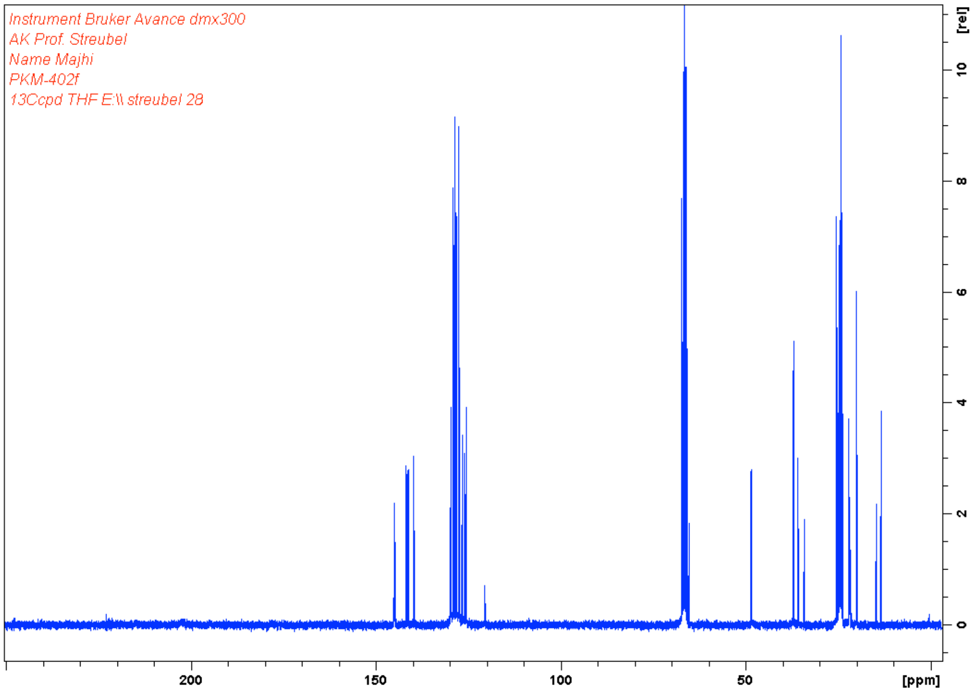

Fig. S4: $^{31}P\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 (121.5 MHz, 25 °C)

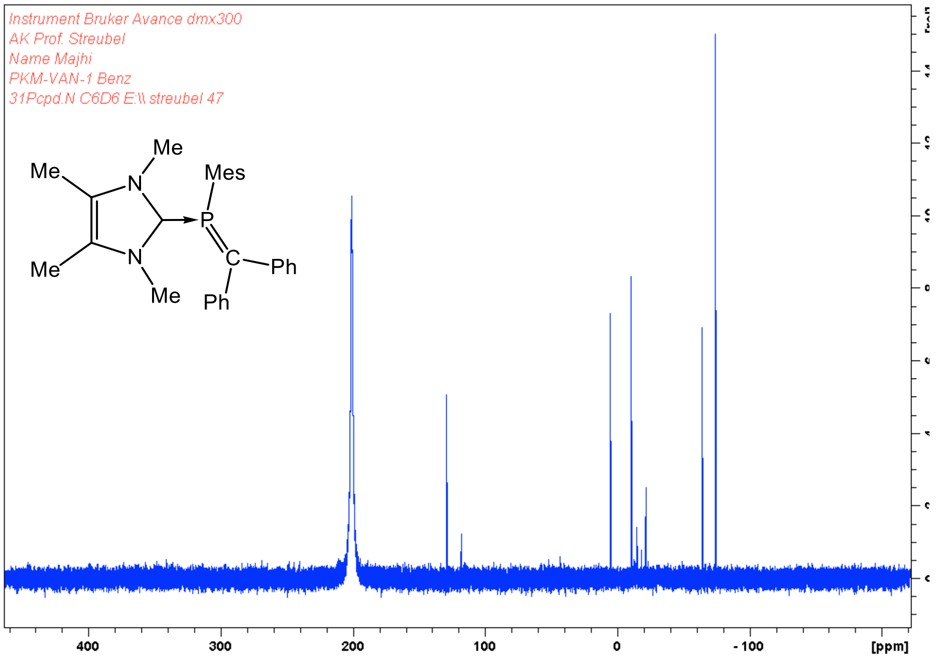

Fig. S5: ^{1}H NMR spectrum of **2** in C_6D_6 (300.1 MHz, 25 °C)

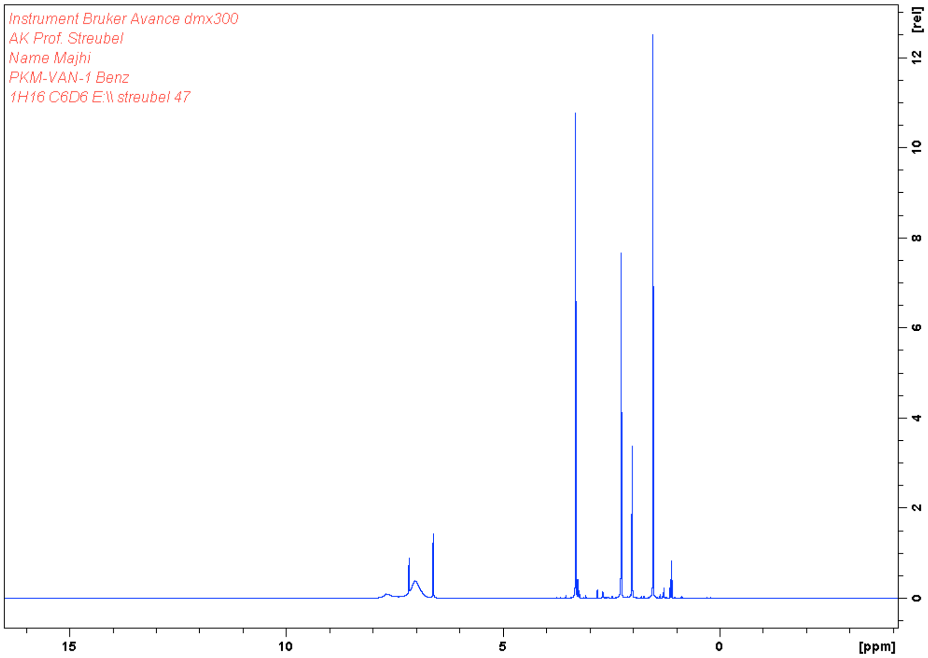

Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 (75.5 MHz, 25 °C)

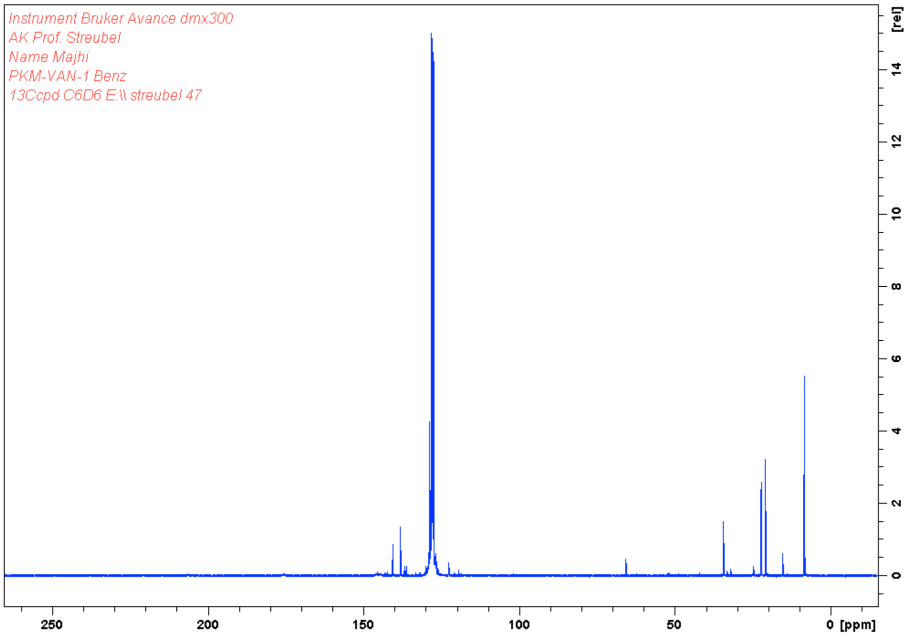

Figure S7: $^{31}P\{^{1}H\}$ NMR spectrum of **1·BH₃** in $CDCl_3$ (121.5 MHz, 25 °C)

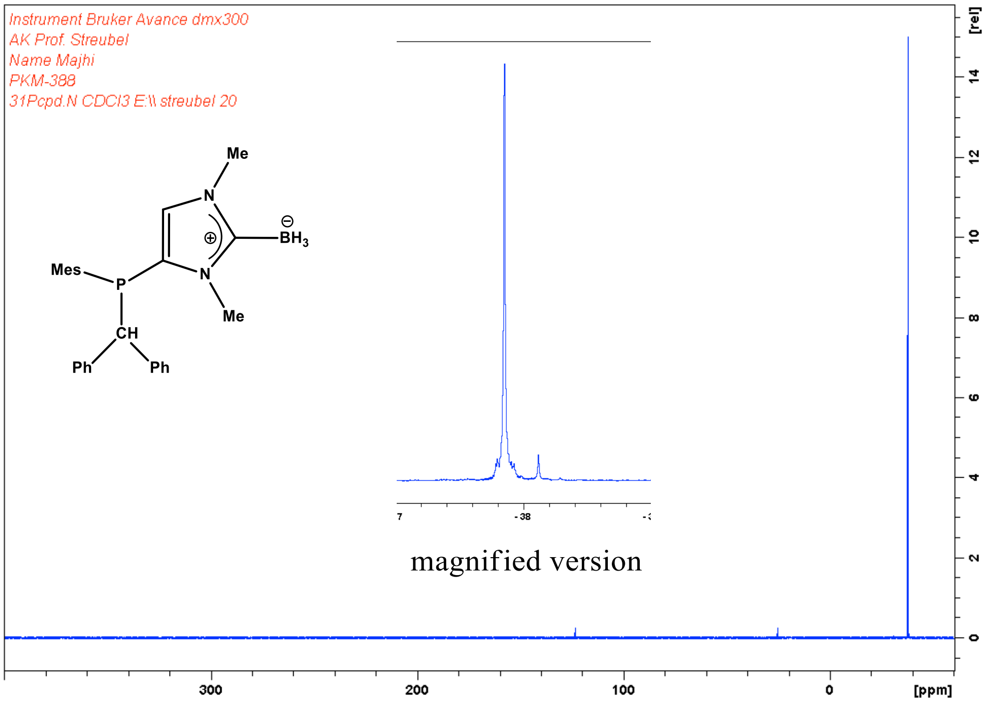

Figure S8: ^{1}H NMR spectrum of **1·BH₃** in $CDCl_3$ (300.1 MHz, 25 °C)

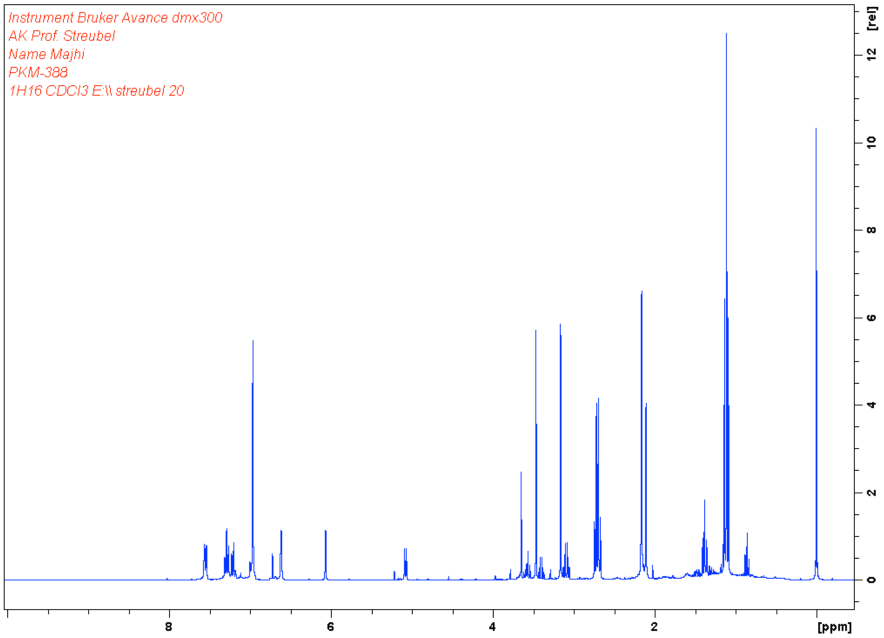

Figure S9: $^{13}C\{^1H\}$ NMR spectrum of **1·BH$_3$** in CDCl$_3$ (75.5 MHz, 25 °C)

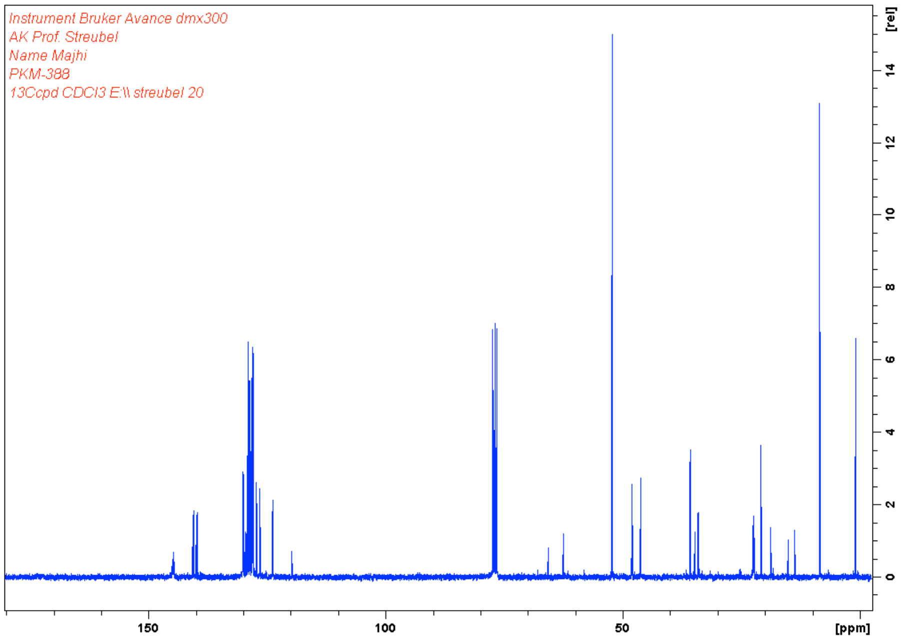

Figure S10: $^{31}P\{^1H\}$ NMR spectrum of **1·Rh(cod)Cl** in CDCl$_3$ (121.5 MHz, 25 °C)

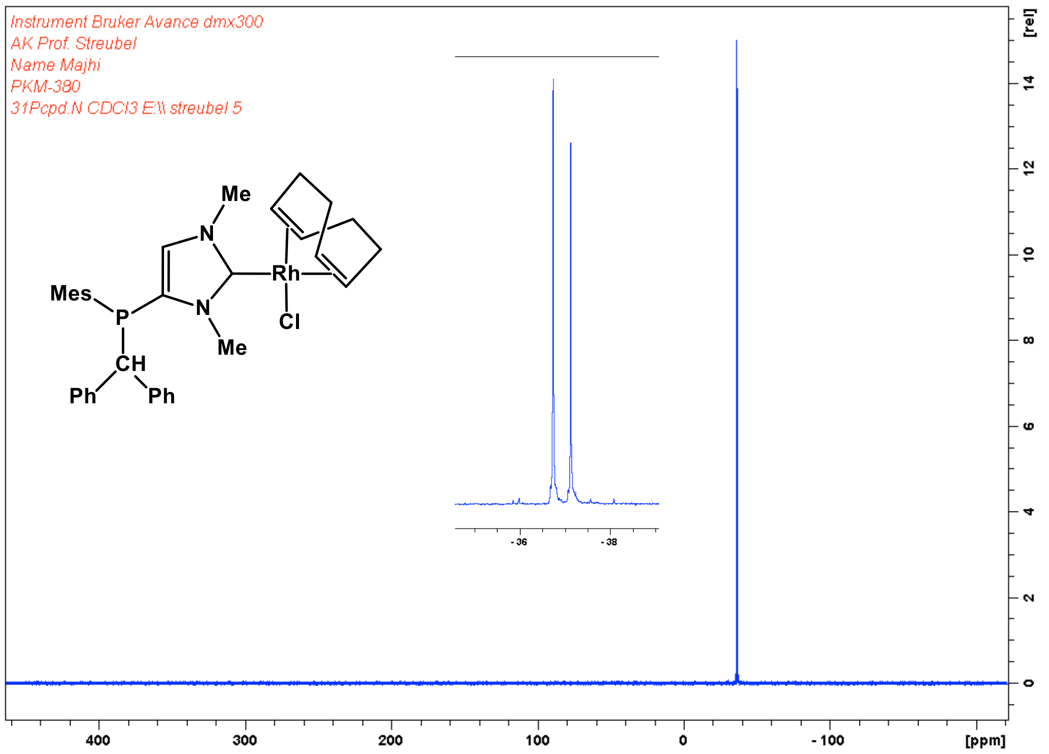

Figure S11: ^{1}H NMR spectrum of **1·Rh(cod)Cl** in CDCl$_3$ (300.1 MHz, 25 °C)

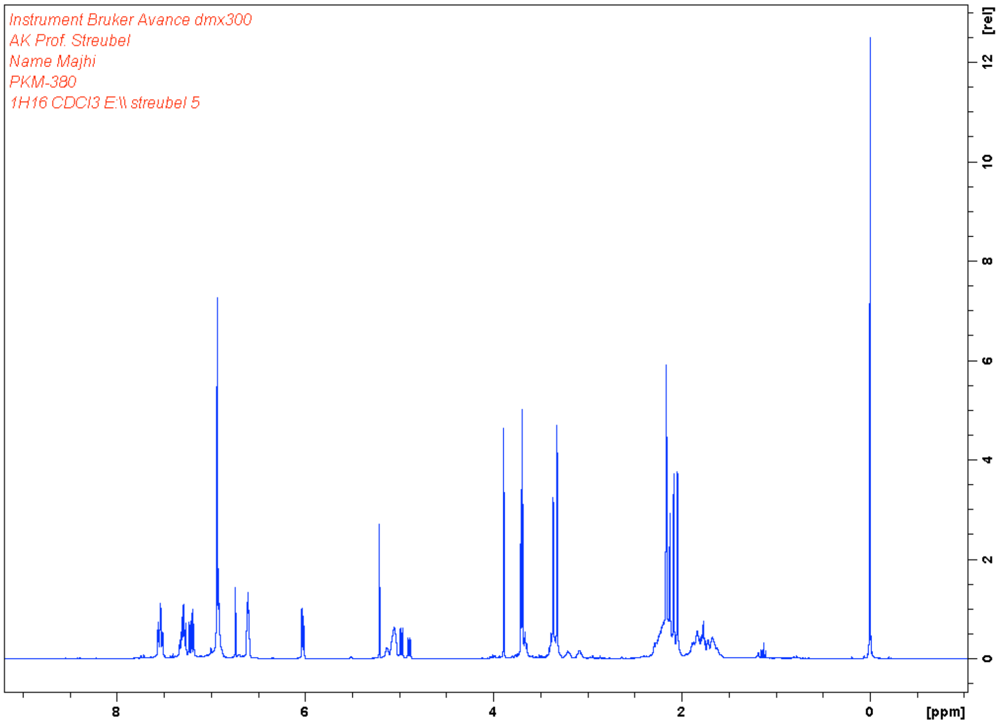

Figure S12: ^{13}C{^{1}H} NMR spectrum of **1·Rh(cod)Cl** in CDCl$_3$ (75.5 MHz, 25 °C)

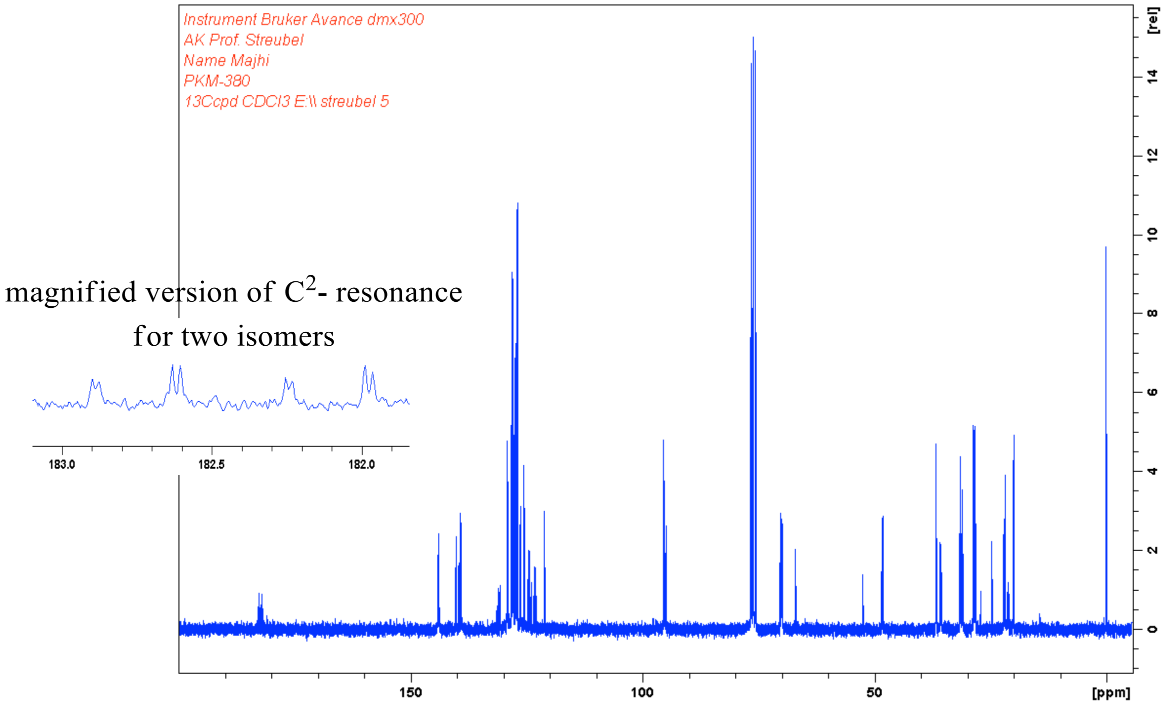
magnified version of C^2- resonance for two isomers

Figure S13: ${}^{31}P\{{}^{1}H\}$ NMR spectrum of **1·Cr(CO)$_5$** in $CDCl_3$ (121.5 MHz, 25 °C)

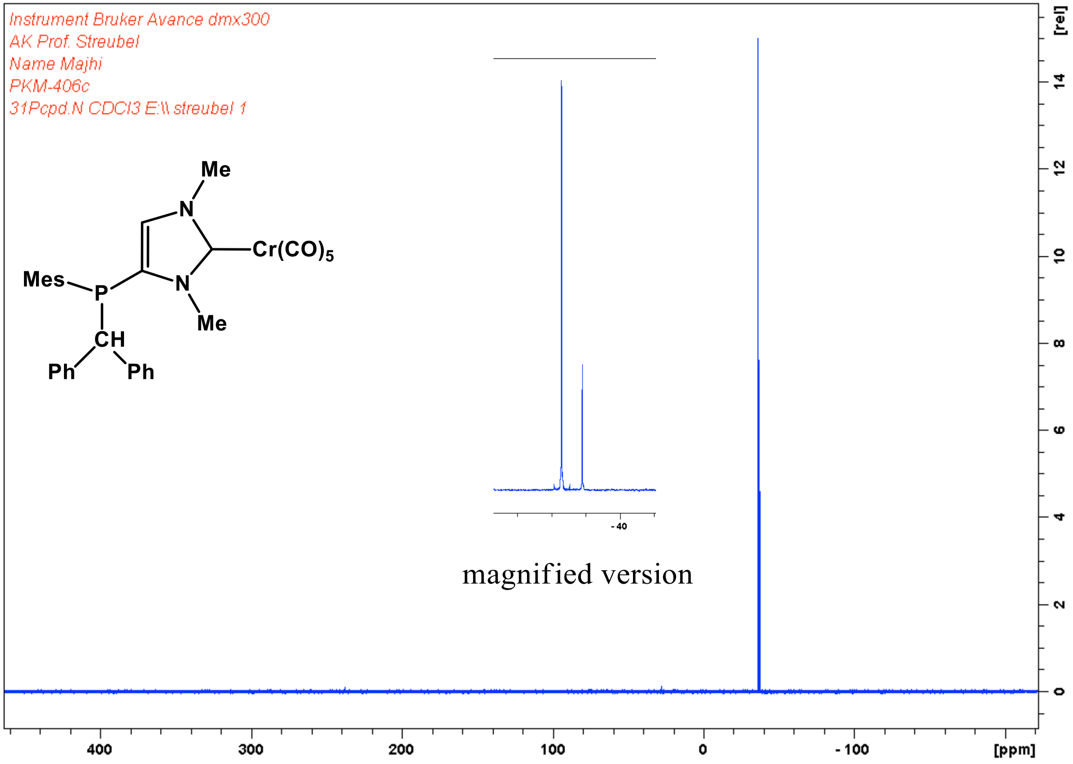

Figure S14: ${}^{1}H$ NMR spectrum of **1·Cr(CO)$_5$** in $CDCl_3$ (300.1 MHz, 25 °C)

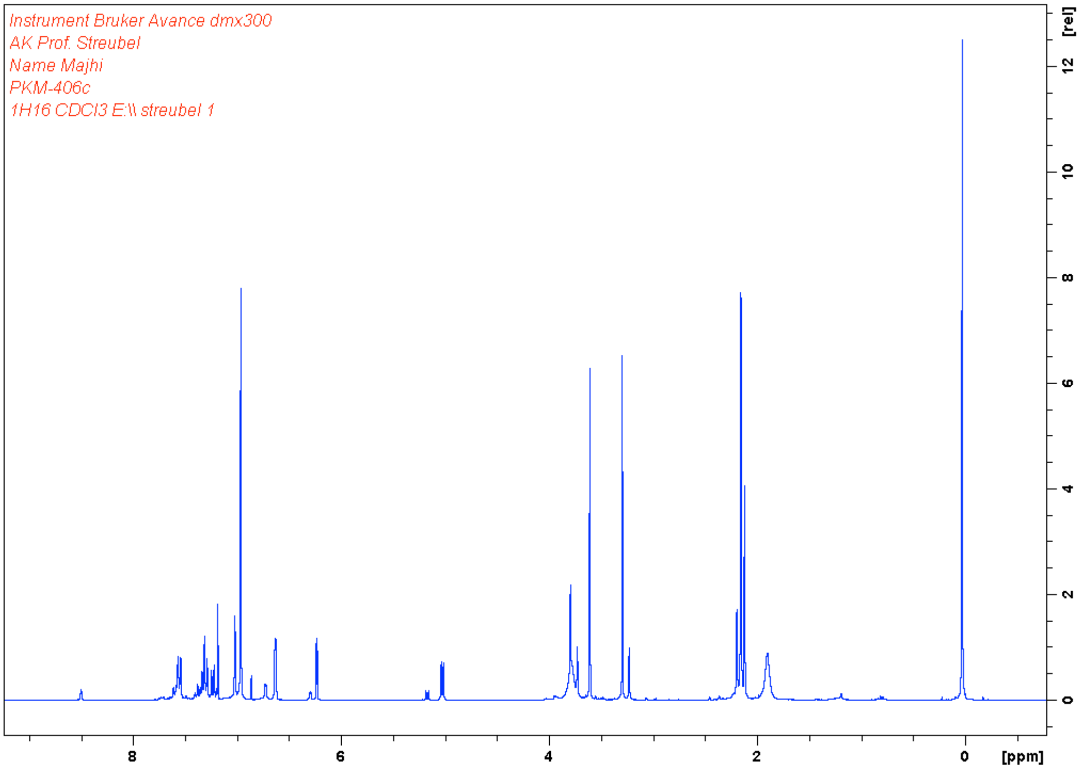

Figure S15: $^{13}C\{^1H\}$ NMR spectrum of **1·Cr(CO)$_5$** in $CDCl_3$ (75.5 MHz, 25 °C)

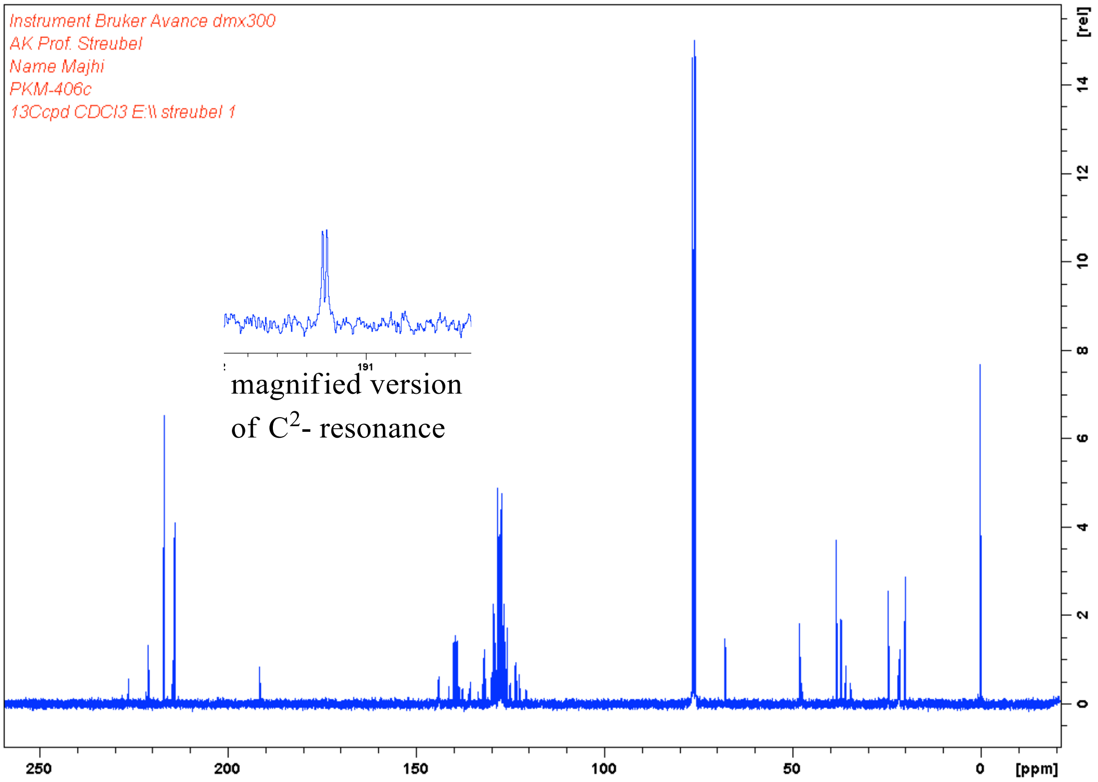

Figure S16: IR (ATR) spectrum of **1·Cr(CO)$_5$**

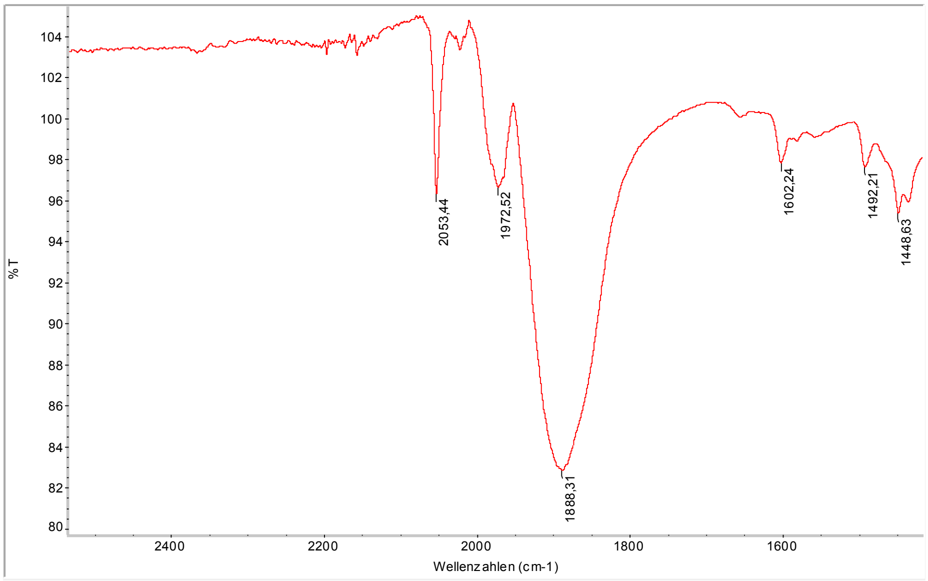

Figure S17: $^{31}P\{^{1}H\}$ NMR spectrum of **1·Mo(CO)$_5$** in $CDCl_3$ (121.5 MHz, 25 °C)

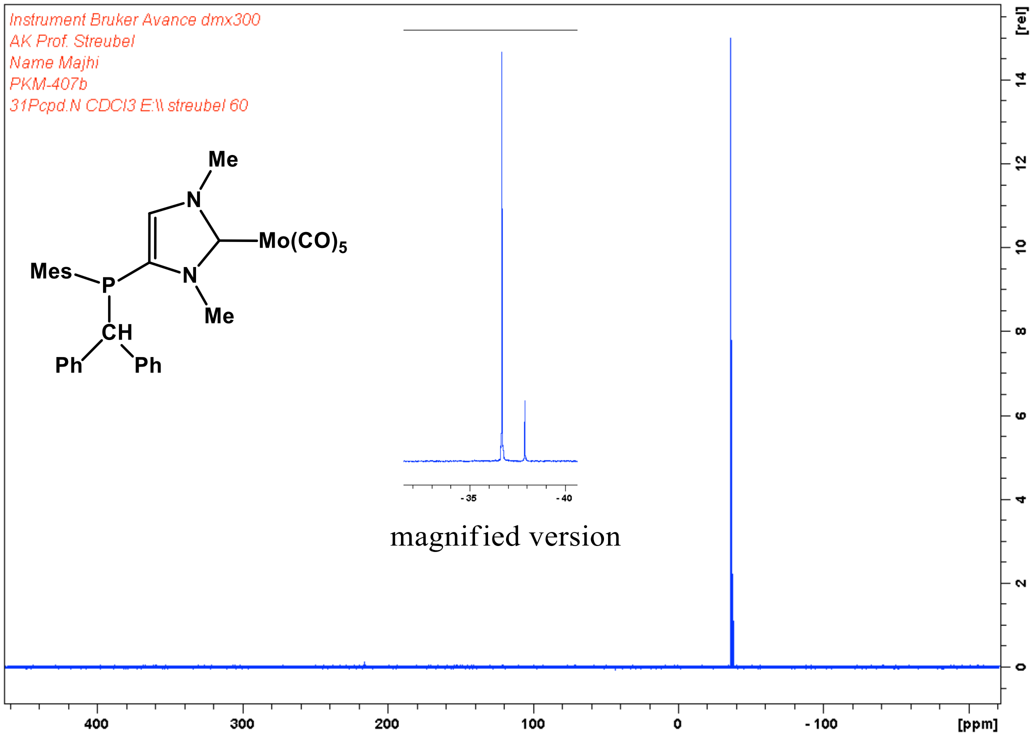

Figure S18: ^{1}H NMR spectrum of **1·Mo(CO)$_5$** in $CDCl_3$ (300.1 MHz, 25 °C)

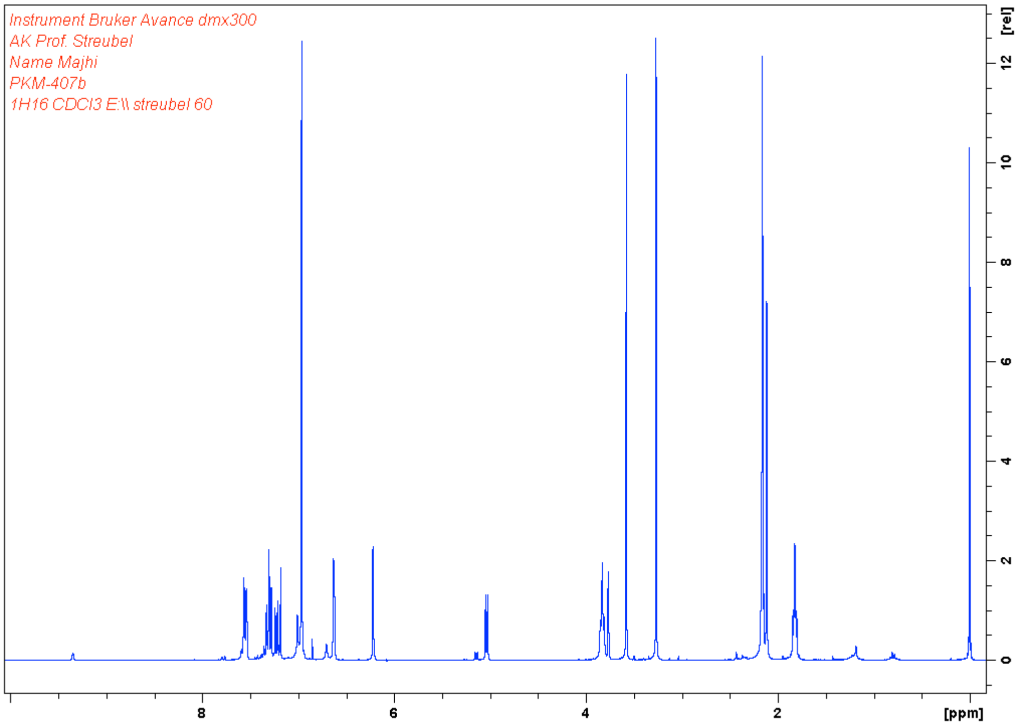

Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of **1·Mo(CO)$_5$** in $CDCl_3$ (75.5 MHz, 25 °C)

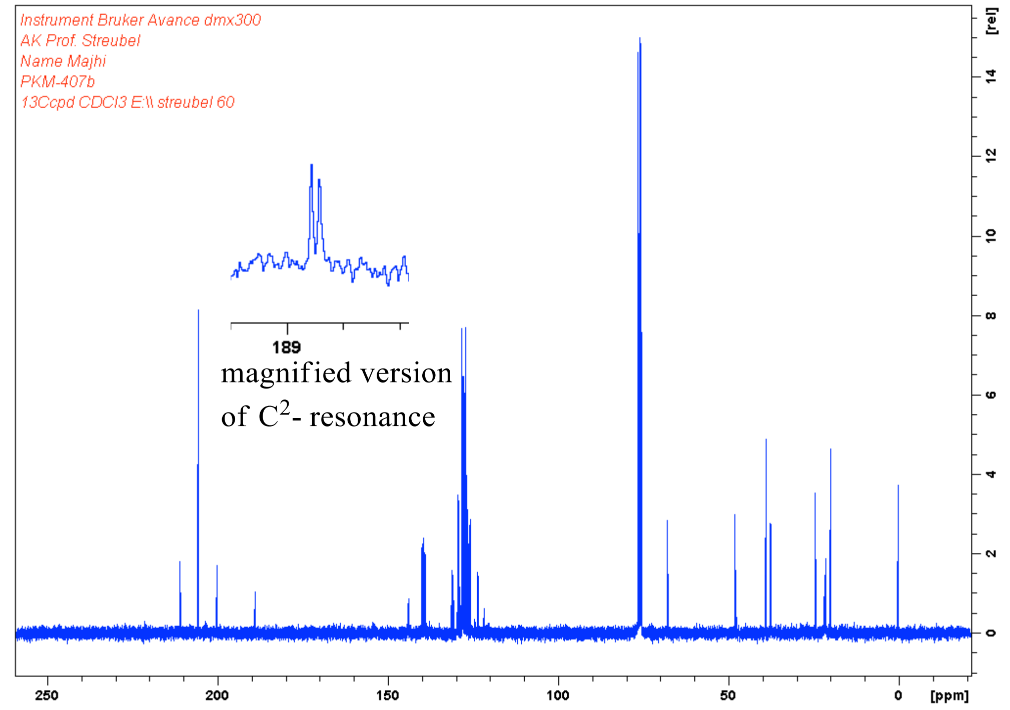

Figure S20: IR (ATR) spectrum of **1·Mo(CO)$_5$**

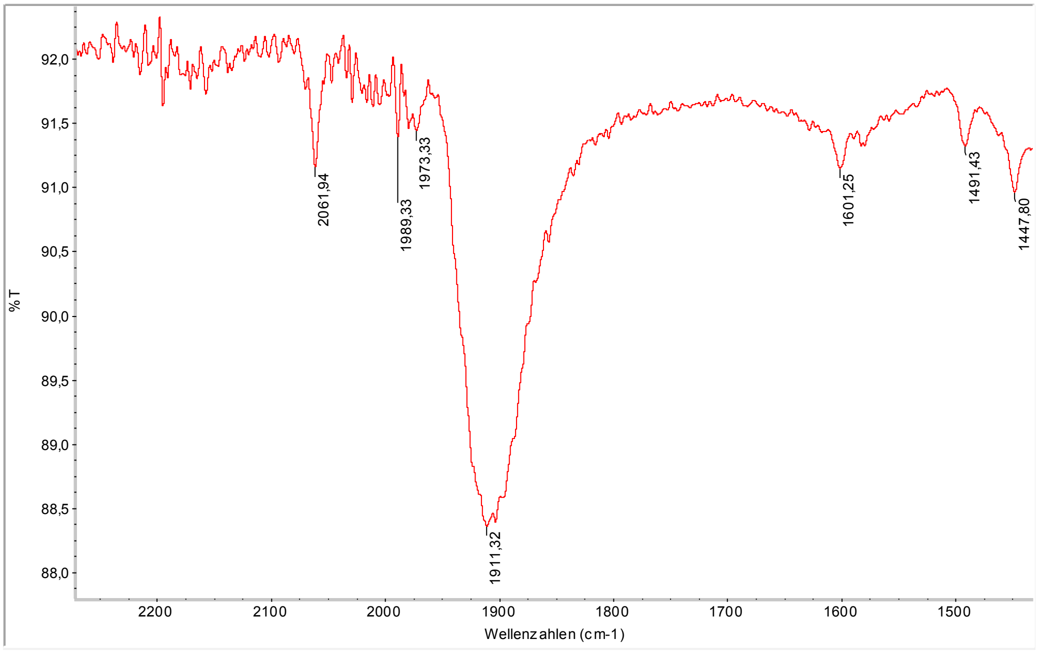

Figure S21: $^{31}P\{^{1}H\}$ NMR spectrum of **1·W(CO)₅** in $CDCl_3$ (121.5 MHz, 25 °C)

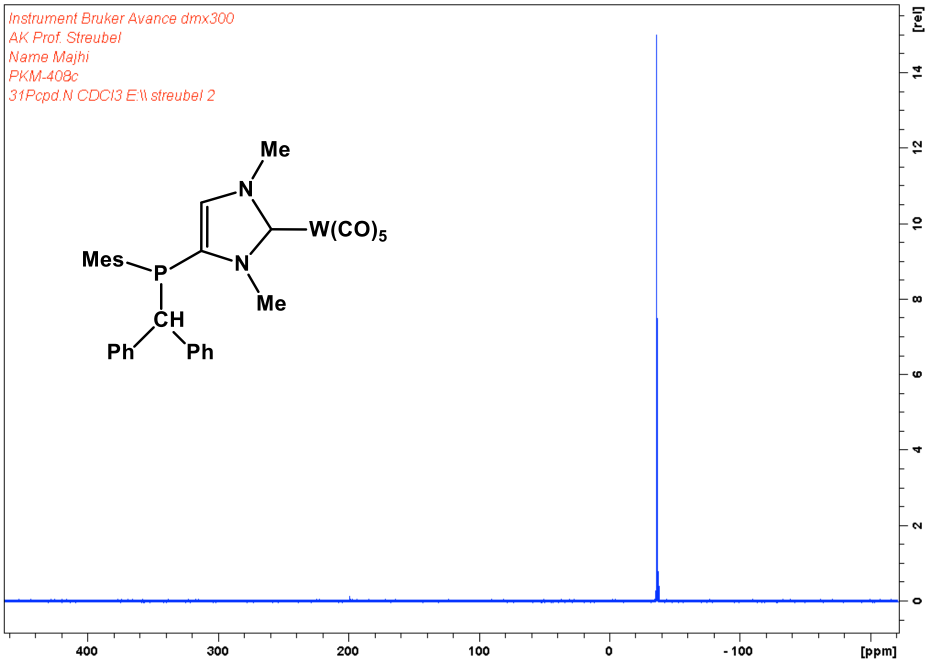

Figure S22: ^{1}H NMR spectrum of **1·W(CO)₅** in $CDCl_3$ (300.1 MHz, 25 °C)

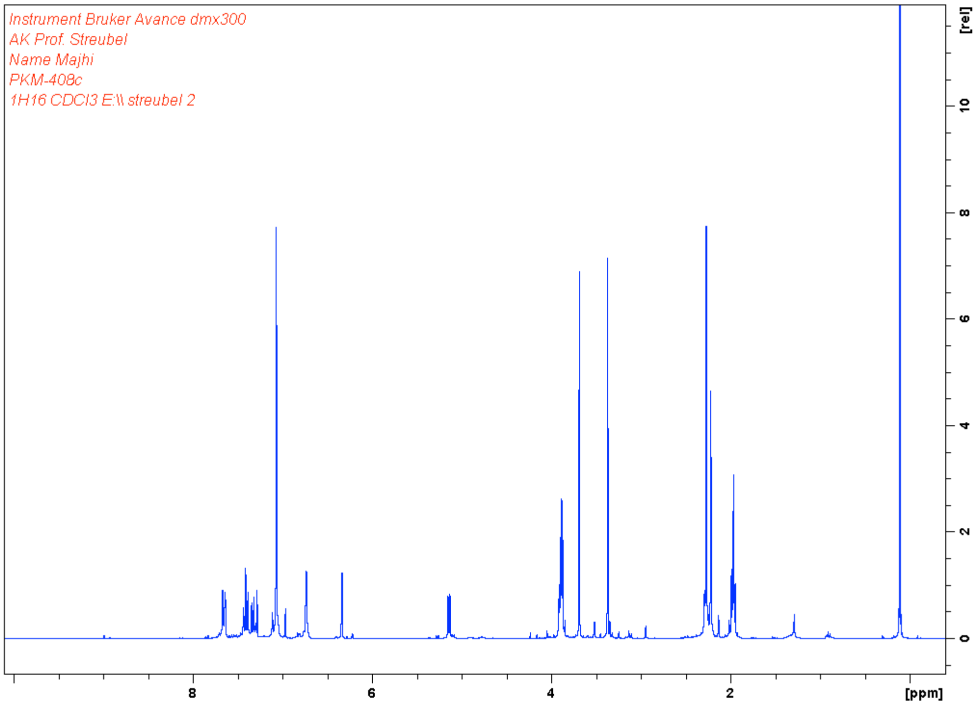

Figure S23: $^{13}C\{^1H\}$ NMR spectrum of **1·W(CO)$_5$** in $CDCl_3$ (75.5 MHz, 25 °C)

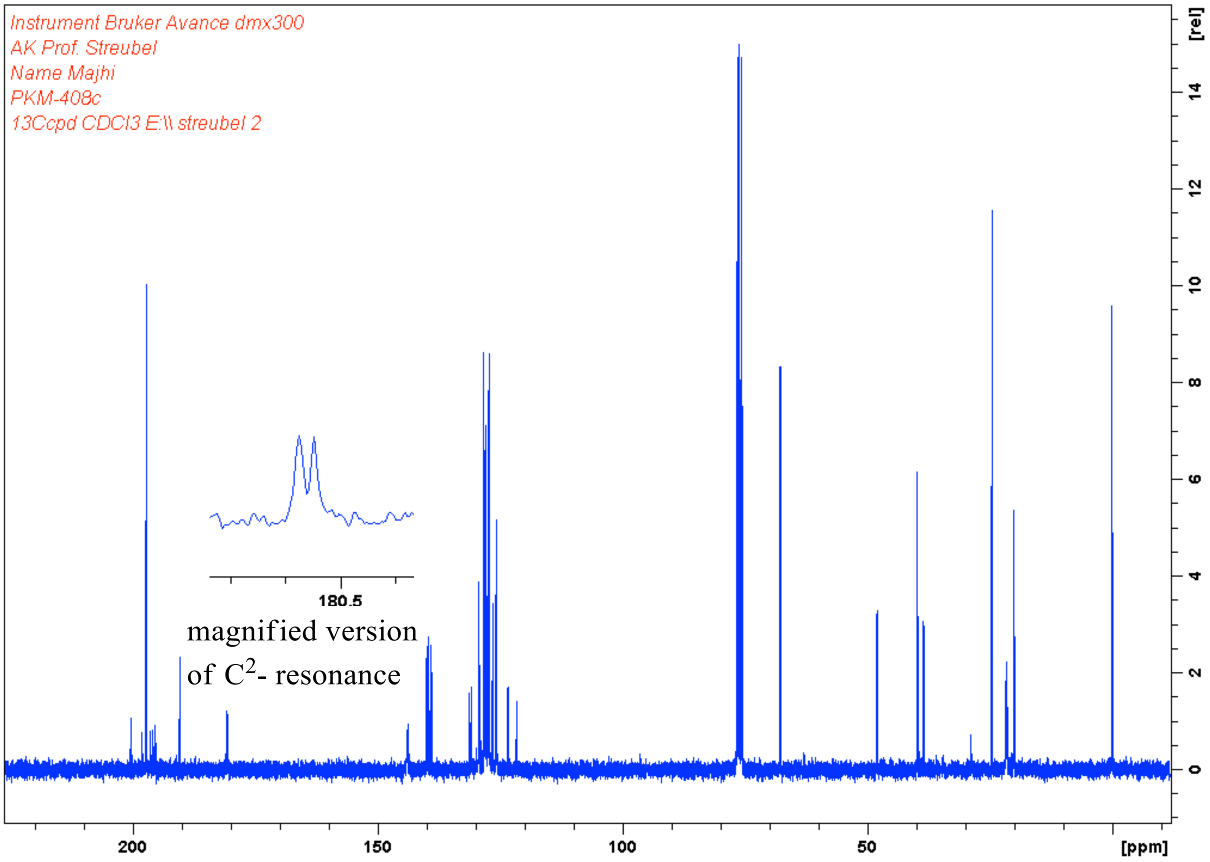

Figure S24: IR (ATR) spectrum of **1·W(CO)$_5$**