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Supplementary Information

Application of phosphorus-bridged rigid bent bis(NHCs) as dipodal ligands in main group and transition metal chemistry

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Table of contents

1. General methods

All reactions were performed under dried and deoxygenated argon atmosphere using Schlenk or glovebox techniques. The used argon (>99.998%) was purified by a system of three columns (deoxygenation by a BTS copper catalyst (BASF PuriStar® R3-15S) at ca. 100 °C, removing moisture with silica gel, phosphorus pentoxide desiccant with indicator (Sicapent®) and calcium chloride). Glassware, spatulae, cannulae as well as filter papers were dried in a compartment dryer at 80 °C for at least one hour. Additionally, the glassware was heated with a heat gun (up to 550 °C) under active vacuum (< $5 \cdot 10^{-2}$ mbar) and filled with argon. Sterile syringes were purged with argon three times before use. The solvents were dried by standard procedures by refluxing over proper desiccants under an argon atmosphere (*n*-pentane and toluene over sodium wire (Ø = 2 mm); diethyl ether stabilised with 3,5-di-*t*-butyl-4-hydroxytoluene (BHT) and tetrahydrofuran over benzophenone and sodium wire; dichloromethane over calcium hydride) for several days and distilled before use. Alternatively, diethyl ether and toluene were dried using a MBraun SPS-800 solvent purification system. For filtration Schlenk frits or stainless steel cannulae (Ø = 1 mm and 2 mm) with Whatman® glass microfiber filters (grade GF/A) were used. After use, devices made of stainless steel were cleaned with deionised water and acetone and glassware by storage in a concentrated solution of potassium hydroxide in isopropanol for at least two days and in diluted hydrochloric acid for at least four hours. Afterwards, the glassware was washed with water and soap, deionised water and acetone. All joints were greased with OKS 1112 grease or with PTFE paste (Carl Roth). Vacuum was applied by a rotary vane pump (vacuubrand RZ6) enabling pressures $<10^{-2}$ mbar.

NMR spectra were recorded on a Bruker Avance I 300 MHz, Bruker Avance I 400 MHz, Bruker Avance I 500 MHz or Bruker Avance III HD Ascend 500 MHz spectrometer at the NMR department of the University of Bonn and subsequently analysed by the program *MestReNova 14.2*. The calibration of the ^{1}H and ^{13}C NMR spectra was done via the solvent residual signals relative to tetramethylsilane (<1% in $CDCl_3$) (C_6D_6: $\delta(^{1}H)$ = 7.16 ppm and $\delta(^{13}C)$ = 128.06 ppm, CD_2Cl_2: $\delta(^{1}H)$ = 5.32 ppm and $\delta(^{13}C)$ = 53.84 ppm).[1] All lock frequencies were calibrated internally against the ^{1}H signals of solutions of tetramethylsilane with a volume fraction of $\phi \leq 1\%$ in the corresponding deuterated solvent. The deuterated solvents were used without further purification and dried by storing over 3 Å (CD_2Cl_2) or 4 Å (C_6D_6) molecular sieves. The chemical shift (δ) is given in parts per million (ppm) and the coupling constant ($^{n}J_{X,Y}$) in Hertz (Hz) as absolute values neglecting the sign where *n* is the number of bonds between the coupling nuclei X and Y. For assigning the multiplicity following abbreviations were used: s = singlet, d = doublet, dd = doublet of doublets, m = multiplet, sat = satellites and br = broad. For ^{1}H NMR spectra additionally the number of nuclei is given accordingly which is determined via integration. The ^{1}H and ^{13}C NMR signals of compounds were assigned by a combination of COSY, HSQC and HMBC experiments to unequivocally assign protons and carbon resonances if necessary. All measurements were performed at ambient temperature (298 K) if not stated otherwise.

Mass spectrometry using electrospray ionisation (ESI) or atmospheric-pressure chemical ionization (APCI) was performed on a Thermo Fisher Scientific Orbitrap XL mass spectrometer. Only selected data are given for detected ions. The peaks are given in mass-to-charge ratio (m/z) while only the isotopomer with the highest relative abundance is represented. Additionally, the relative intensities of the peaks are given in parentheses and the proposed molecule fragments in square brackets if not stated otherwise.

UV/vis spectra were recorded in the spectral range of 200–700 nm on a *Shimadzu UV-1650PC* spectrometer with a double-beam optic photometric system with a maximum wavelength range of 190.0 to 1100 nm, a spectra band width of 2 nm and a wavelength accuracy of ±0.5 nm with an automatic wavelength correction. An automatic baseline correction with the pure solvent was performed before the analyte solution was measured. The detector is a silicon photodiode with a photometric range of −0.5 to 3.999 absorbance. Quartz glass cuvettes (*Hellma* precision cells *110-QC*) with dimensions of 46 mm × 12.5 mm × 12.5 mm, a light path length of 10 mm and a chamber volume of 350 µL were used and closed with PTFE caps before measurement. Measurements were started with a circa 10^{-5} molar solution of the respective compound and diluted until a sufficient spectrum was recorded. All spectra are normed to an absorbance of 1 a.u.; no extincition coefficient were determined. Absorbance wavelengths are given in nanometers (nm) with the relative absorbance (max. 1) and assignment to the associated transition in parentheses.

IR spectra of solids were recorded in the spectral range of 4000-400 cm^{-1} on a Bruker Alpha FTIR spectrometer with a single-reflection diamond ATR measurement or a Shimadzu IRSpirit FTIR spectrometer with a single-reflection germanium ATR measurement attachment in a glovebox at ambient temperature. All analyses were performed using the programs *EZ OMNIC 7.3* of Fisher Scientific and *OPUS* of Bruker. Only selected wavenumbers of the absorption bands are given using reciprocal centimetres (cm^{-1}). The intensities of the bands are marked as very strong (vs), strong(s), medium (m), weak (w).

Elemental analyses were performed on a Elementar Vario Micro analysis device in quadruplicate or triplicate for each sample. All samples were prepared and weighed up in tin or silver sample containers using a micro-analytical balance in a glovebox. The mean C, H and N values are given for each compound.

Melting points were measured using a MPM-H2 device or a Büchi melting point determination device according to Dr. Tottoli. The samples were grease-sealed in a glass capillary (Ø = 0.1 mm) in a glovebox and heated quickly (ca. 10 K/min) for a rough determination of the melting point or decomposition temperature. Afterwards, a heating rate of approximately 1 K/min was used until the sample melted or decomposed. No internal or external temperature corrections were performed.

Single crystal X-ray diffraction analyses were performed on a Bruker D8-Venture diffractometer at 100 K by using monochromated Cu-Kα radiation (λ = 1.54178 Å) (**2a**, **6b**), a STOE IPDS-2T diffractometer at 123 K by using monochromated Mo-Kα radiation (λ = 0.71073 Å) (**4a**) or a STOE STADIVARI diffractometer at 100 K by using monochromated Cu-Kα radiation (λ = 1.54178 Å) (**5a**,**b**). Intensities were measured by fine-slicing ϕ and ω scans and corrected background, polarisation and Lorentz effects. A semi-empirical absorption correction was applied for the data sets following Blessing's method.[2] The structure was solved by direct methods and refined anisotropically by the least-squares procedure implemented in SHELX program system.[3] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included isotropically refined using a riding model at the bound carbon atoms. The program *Olex2 1.5 of OlexSys*[4] was used for analyses and the ellipsoid representations of the molecular structures with the probability level set to 50%. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2301879 (**2a**) and CCDC- 2301880 (**5a**), which can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

2. Experimental procedures and characterisation

2.1. 1,4-Diphosphabarrelene 2a

To a solution of 2.000 g (3.47 mmol, 1.0 eq.) of **1** in 60 mL dichloromethane 3.00 mL (24.1 mmol, 7.0 eq.) *trans*-3-hexene were added dropwise. After stirring for 7 d at ambient temperature the solution had turned red and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting slightly pink residue was washed four times with 20 mL *n*-pentane each (until the washing solution is not pink anymore) and the orange solid was dried for 2 h (≤ 0.02 mbar). Yield: 1.71 g (2.58 mmol, 74 %). Mp: 120 °C (dec.). Elemental analysis: Found: C, 50.2; H, 7.2; N, 8.6. Calc. for $C_{28}H_{48}N_4P_2Se_2$: C, 50.9; H, 7.3; N, 8.5 %. ***2a*** *slowly decomposes at room temperature.* IR: $\tilde{\nu}_{max}$/cm^{-1} = 2957m and 2928m ($\nu_{as}(CH_3)$, $\nu_s(CH_2)$), 2860m ($\nu_s(CH_3)$, $\nu_{as}(CH_2)$). ^{1}H NMR (500.04 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 0.97 (t, $^3J_{H,H}$ = 7.4 Hz, 12H, CH_3(*n*-Bu)), 1.10 (t, $^3J_{H,H}$ = 7.2 Hz, 6H, CH_3(Et)), 1.15–1.27 (m, 2H, PCHCH_2), 1.31–1.45 (m, 8H, NCH$_2$CH$_2$CH_2), 1.46–1.57 (m, 2H, PCHCH_2), 1.63–1.85 (m, 10H, NCH$_2$CH_2, PCH), 4.15–4.23 (m, 2H, NCH_2), 4.24–4.34 (m, 6H, NCH_2). ^{13}C{^{1}H} NMR (125.75 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 11.4 (s, CH_3(*n*-Bu)), 13.9 (m, CH_3(Et)), 20.3 (m, NCH$_2$CH$_2$CH_2), 28.3 (m, PCHCH_2), 32.3 (m, NCH$_2$CH_2), 46.4 (dd, $J_{P,C}$ = 5.5 Hz, PCH), 49.0 (m, NCH$_2$), 137.1 (dd, $J_{P,C}$ = 8.0 Hz, $J_{P,C}$ = 5.5 Hz, P*C*), 139.8 (d, $J_{P,C}$ = 4.3 Hz, P*C*), 159.6 (s_{sat}, $^1J_{Se,C}$ = 235.1 Hz, *C*Se). ^{31}P NMR (202.44 MHz, 298.0 K, CD_2Cl_2): δ / ppm = −86.3 (m). ^{31}P{^{1}H} NMR (202.44 MHz, 298.0 K, CD_2Cl_2): δ / ppm = −86.3 (s). ^{77}Se NMR (57.24 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 31.2 (s). MS (positive ESI): *m/z* = 663.176 (<1 %) [M+H]$^+$, 583.259 (100) [M−Se+H]$^+$, 579.262 (20) [M−hexene]$^+$, 499.165 (43) [M−hexene−Se+H]$^+$. HR-MS (positive ESI): found: 663.1756. Calc. for [$C_{28}H_{48}N_4P_2Se_2H$]$^+$ 663.1763.

2.2. 1,4-Diphosphabarrelene 2b

To a solution of 1.001 g (1.74 mmol, 1.0 eq.) of **1** in 30 mL dichloromethane 0.73 mL (8.68 mmol, 5.0 eq.) 1-hexene were added dropwise. After stirring for 3 d at ambient temperature the solution had turned yellow and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting yellow residue was washed twice with 10 mL diethyl ether each and four times with 10–20 mL *n*-pentane each and the beige solid was dried for 2 h (≤ 0.02 mbar). Yield: 0.765 g (1.16 mmol, 67 %). Mp: 142 °C (dec.). Elemental analysis: Found: C, 50.35; H, 7.3; N, 8.6. Calc. for $C_{28}H_{48}N_4P_2Se_2$: C, 50.9; H, 7.3; N, 8.5 %. ***2b*** *slowly decomposes at room temperature.* IR: $\tilde{\nu}_{max}$/cm^{-1} = 2956m and 2927m ($\nu_{as}(CH_3)$, $\nu_s(CH_2)$), 2860m ($\nu_s(CH_3)$, $\nu_{as}(CH_2)$). ^{1}H NMR (500.04 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 0.89 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, CH_3(PCH(*n*-Bu))), 0.92–1.92 (m, 12H, CH_3(N(*n*-Bu))), 1.14–1.22 (m, 1H, PCH_2), 1.23–1.32 (m, 4H, PCHCH$_2$CH_2CH_2), 1.32–1.46 (m, 8H, NCH$_2$CH$_2$CH_2), 1.45–1.55 (m, 2H, PCHCH_2), 1.63–1.86 (m, 8H, NCH$_2$CH_2), 1.96 (m, 1H, PCH), 2.13 (m, 1H, PCH_2), 4.18–4.37 (m, 8H, NCH_2). ^{13}C{^{1}H} NMR (125.75 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 14.0 (m, CH_3), 20.4 (m, NCH$_2$CH$_2$CH$_2$), 22.8 (s, PCHCH$_2$CH$_2$CH$_2$), 28.2 (dd, $^1J_{P,C}$ = 9.5 Hz, $^2J_{P,C}$ = 4.1 Hz, PCH$_2$), 31.6 (d, $J_{P,C}$ = 15.3 Hz, PCHCH$_2$CH$_2$), 32.3 (m, NCH$_2$CH$_2$), 32.4 (d, $J_{P,C}$ = 2.6 Hz, PCHCH$_2$), 36.3 (dd, $^1J_{P,C}$ = 7.3 Hz, $^2J_{P,C}$ = 2.5 Hz, PCH), 49.0 (m, NCH$_2$), 136.2 (dd, $J_{P,C}$ = 11.4 Hz, $J_{P,C}$ = 3.2 Hz, PC), 137.5 (dd, $J_{P,C}$ = 6.3 Hz, $J_{P,C}$ = 2.9 Hz, PC), 138.9 (dd, $J_{P,C}$ = 5.7 Hz, $J_{P,C}$ = 2.9 Hz, PC), 139.9 (dd, $J_{P,C}$ = 6.0 Hz, $J_{P,C}$ = 3.7 Hz, PC), 159.3 (s, CSe), 159.7 (s, CSe). ^{31}P NMR (202.44 MHz, 298.0 K, CD_2Cl_2): δ / ppm = −91.4 (m, *P*CH$_2$), −87.0 (m, *P*CH). ^{31}P{^{1}H} NMR (202.44 MHz, 298.0 K, CD_2Cl_2): δ / ppm = −91.4 (d, $^3J_{P,P}$ = 17.3 Hz, *P*CH$_2$), −87.0 (d, $^3J_{P,P}$ = 17.6 Hz, *P*CH). ^{77}Se NMR (57.24 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 27.7 (s), 30.5 (s). MS (positive ESI): *m/z* = 663.174 (<1 %) [M+H]$^+$, 583.258 (61) [M−Se+H]$^+$. HR-MS (positive ESI): found: 663.174. Calc. for [$C_{28}H_{48}N_4P_2Se_2H$]$^+$ 663.176.

2.3. Se-methylated imidazolium salt 3a

To a solution of 1.202 g (1.82 mmol, 1.0 eq.) of **2a** in 25 mL dichloromethane 0.44 mL (4.00 mmol, 2.2 eq.) MeOTf were added dropwise. After stirring for 2 h at ambient temperature the former light red solution had turned yellow and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting oily residue was washed three times with 10–20 mL diethyl ether each and three times 20 mL *n*-pentane at −50 °C. After drying for 3 h (≤ 0.02 mbar) a yellow, sticky solid in 97 % purity (3 % **4a**) was obtained. Yield: 1.349 g (1.36 mmol, 75 %). IR: $\tilde{\nu}_{max}$/cm^{-1} = 2962m and 2935m (ν_{as}(CH$_3$), ν_s(CH$_2$)), 2876m (ν_s(CH$_3$), ν_{as}(CH$_2$)). ^{1}H NMR (500.04 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 1.01 (tm, $^3J_{H,H}$ = 7.4 Hz, 12H, CH_3(*n*-Bu)), 1.18 (t, $^3J_{H,H}$ = 7.3 Hz, 6H, CH_3(Et)), 1.30–1.35 (m, 2H, PCHCH_2), 1.40–1.54 (m, 8H, NCH$_2$CH$_2$CH_2), 1.63–1.74 (m, 2H, PCHCH_2), 1.76–1.92 (m, 10H, NCH$_2$CH_2, PC*H*), 2.48 (s, 6H, SeCH_3), 4.36–4.59 (m, 8H, NCH_2). ^{13}C{^{1}H} NMR (125.75 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 11.2 (s_{sat}, $^1J_{Se,C}$ = 56.1 Hz, Se*C*H$_3$), 13.7 (s, *C*H$_3$(*n*-Bu)), 13.8 (s, *C*H$_3$(*n*-Bu)), 13.9 (dd, $J_{P,C}$ = 7.3 Hz, *C*H$_3$(Et)), 20.2 (m, NCH$_2$CH$_2$*C*H$_2$), 27.9 (dd, $J_{P,C}$ = 9.4 Hz, PCH*C*H$_2$), 33.7 (dd, $J_{P,C}$ = 2.0 Hz, NCH$_2$*C*H$_2$), 33.9 (dd, $J_{P,C}$ = 2.0 Hz, NCH$_2$*C*H$_2$), 45.1 (dd, $J_{P,C}$ = 5.2 Hz, P*C*H), 51.1 (dm, $J_{P,C}$ = 29.8 Hz, N*C*H$_2$), 121.0 (q, $^1J_{F,C}$ = 320.8 Hz, *C*F$_3$), 138.9 (s_{sat}, $^1J_{Se,C}$ = 181 Hz, *C*SeCH$_3$), 142.3 (m, P*C*), 145.6 (dd, $J_{P,C}$ = 8.9 Hz, $J_{P,C}$ = 6.5 Hz, P*C*). ^{31}P NMR (202.44 MHz, 298.0 K, CD_2Cl_2): δ / ppm = −87.0 (m). ^{31}P{^{1}H} NMR (202.44 MHz, 298.0 K, CD_2Cl_2): δ / ppm = −87.0 (s). ^{77}Se NMR (57.24 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 105.8 (s). MS (positive ESI): *m/z* = 841.166 (100) [M−OTf]$^+$, 346.107 (41) [M−2OTf]$^{2+}$, 304.060 (45) [M−hexene−2OTf]$^{2+}$. HR-MS (positive ESI): found: 841.1677 Calc. for [$C_{31}H_{54}F_3N_4O_3P_2SSe_2$]$^+$ 841.1674.

2.4. Se-methylated imidazolium salt 3b

To a solution of 0.500 g (0.76 mmol, 1.0 eq.) of **2b** in 15 mL dichloromethane 0.18 mL (1.67 mmol, 2.2 eq.) MeOTf were added dropwise. After stirring for 2 h at ambient temperature the former dark yellow solution had turned light yellow and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting oily residue was washed three times with 5 mL diethyl ether each and three times with 5 mL *n*-pentane each. After drying for 3 h (≤ 0.02 mbar) a light yellow, sticky solid was obtained. IR: $\tilde{\nu}_{max}$/cm^{-1} = 2961m and 2934m (ν_{as}(CH$_3$), ν_s(CH$_2$)), 2874m (ν_s(CH$_3$), ν_{as}(CH$_2$)). ^{1}H NMR (300.13 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 0.90 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, CH_3(PCH(*n*-Bu))), 0.96–1.07 (m, 12H, CH_3(N(*n*-Bu))), 1.24–1.40 (m, 5H, PCH_2, PCHCH$_2$CH_2CH_2), 1.40–1.60 (m, 10H, PCHCH_2, NCH$_2$CH$_2$CH_2), 1.75–1.93 (m, 8H, NCH$_2$CH_2), 2.33–2.46 (m, 1H, PC*H*), 2.55–2.74 (m, 1H, PCH_2), 2.47 (s, 3H, SeCH_3), 2.49 (s, 3H, SeCH_3), 4.36–4.60 (m, 8H, NCH_2). ^{13}C{^{1}H} NMR (75.48 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 11.1 (s, Se*C*H$_3$), 11.3 (s, Se*C*H$_3$), 13.7 (br s, *C*H$_3$(N(*n*-Bu))), 14.0 (s, *C*H$_3$(PCH(*n*-Bu))), 20.3 (m, NCH$_2$CH$_2$*C*H$_2$), 22.7 (s, PCHCH$_2$CH$_2$*C*H$_2$), 26.4 (m, P*C*H$_2$), 31.5 (d, $J_{P,C}$ = 15.3 Hz, PCHCH$_2$*C*H$_2$), 33.7 (m, NCH$_2$*C*H$_2$), 34.1 (d, $J_{P,C}$ = 2.6 Hz, PCH*C*H$_2$), 35.3 (m, P*C*H), 50.9–51.2 (m, N*C*H$_2$), 120.9 (q, $^1J_{F,C}$ = 320.8 Hz, *C*F$_3$), 138.3 (m, *C*SeCH$_3$), 138.4 (m, *C*SeCH$_3$), 141.9 (dd, $J_{P,C}$ = 19.4 Hz, $J_{P,C}$ = 3.5 Hz, P*C*), 142.1 (dd, $J_{P,C}$ = 13.2 Hz, $J_{P,C}$ = 3.5 Hz, P*C*), 144.9–145.2 (m, P*C*). ^{31}P NMR (121.51 MHz, 298.0 K, CD_2Cl_2): δ / ppm = −91.2 (m, *P*CH$_2$), −87.0 (m, *P*CH). ^{31}P{^{1}H} NMR (121.51 MHz, 298.0 K, CD_2Cl_2): δ / ppm = −91.2 (d, $^3J_{P,P}$ = 16.7 Hz, *P*CH$_2$), −87.0 (d, $^3J_{P,P}$ = 16.7 Hz, *P*CH). ^{77}Se NMR (57.24 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 102.8 (s), 103.5 (s). MS (positive ESI): *m/z* = 841.172 (100) [M−OTf]$^+$, 346.110 (88) [M−2OTf]$^{2+}$, 304.062 (92) [M−hexene−2OTf]$^{2+}$. HR-MS (positive ESI): found: 841.1673. Calc. for [$C_{31}H_{54}F_3N_4O_3P_2SSe_2$]$^+$ 841.1674.

2.5. Imidazolium salt 4a

To a solution of 1.016 g (1.03 mmol, 1.0 eq.) of **3a** in 20 mL methanol 0.194 g (5.13 mmol, 5.0 eq.) $NaBH_4$ were added at −20 °C which resulted in a darkening of the yellow solution and gas formation (MeSeH). After stirring for 20 min the gas evolution had stopped and 0.438 g (3.18 mmol, 3.1 eq.)

[Et_3NH]Cl were added. The suspension was let warm up to ambient temperature and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting yellow, oily residue was filtered over a bed of celite® and silica (d = 4 cm, h = 1 cm each) with 250 mL tetrahydrofuran. After solvent removal *in vacuo* (≤ 0.05 mbar), extraction with three times 5–10 mL dichloromethane, followed by solvent evaporation, the yellow residue was washed with three times 10 mL *n*-pentane at –20 °C and dried for 3 h (≤ 0.02 mbar) yielding a waxy, yellow solid. Yield: 0.540 g (66 %). IR: $\tilde{\nu}_{max}$/cm^{-1} = 3113w and 3043w (*ν*(CH)), 2963w and 2934m ($\nu_{as}(CH_3)$, $\nu_s(CH_2)$), 2874m ($\nu_s(CH_3)$, $\nu_{as}(CH_2)$). ^{1}H NMR (500.04 MHz, 298.0 K, CD_2Cl_2): *δ* / ppm = 0.93–1.01 (m, 12H, C*H*$_3$(*n*-Bu)), 1.15 (t, $^3J_{H,H}$ = 7.2 Hz, 6H, C*H*$_3$(Et)), 1.24–1.33 (m, 2H, PCHC*H*$_2$), 1.30–1.46 (m, 8H, NCH$_2$CH$_2$C*H*$_2$), 1.57–1.66 (m, 2H, PCHC*H*$_2$), 1.66–1.73 (m, 2H, PC*H*), 1.81–1.91 (m, 8H, NCH$_2$C*H*$_2$), 4.24–4.32 (m, 4H, NC*H*$_2$), 4.32–4.42 (m, 4H, NC*H*$_2$), 9.03 (t, $^4J_{P,H}$ = 2.9 Hz, C*H*). ^{13}C{^{1}H} NMR (125.75 MHz, 298.0 K, CD_2Cl_2): *δ* / ppm = 13.5 (s, *C*H$_3$(*n*-Bu)), 13.6 (s, *C*H$_3$(*n*-Bu)), 13.8 (m, *C*H$_3$(Et)), 19.9 (m, NCH$_2$CH$_2$*C*H$_2$), 20.0 (m, NCH$_2$CH$_2$*C*H$_2$), 28.0 (m, PCH*C*H$_2$), 33.0 (m, NCH$_2$*C*H$_2$), 33.2 (m, NCH$_2$*C*H$_2$), 45.1 (dd, $J_{P,C}$ = 5.4 Hz, P*C*H), 50.0 (tm, $J_{P,C}$ = 4.1 Hz, N*C*H$_2$), 121.0 (q, $^1J_{F,C}$ = 320.2 Hz, *C*F$_3$), 139.6 (s, *C*H), 141.1 (dd, $J_{P,C}$ = 12.8 Hz, $J_{P,C}$ = 8.1, P*C*), 143.9 (dd, $J_{P,C}$ = 8.8 Hz, $J_{P,C}$ = 6.6 Hz, P*C*). ^{31}P NMR (202.44 MHz, 298.0 K, CD_2Cl_2): *δ* / ppm = −90.4 (m). ^{31}P{^{1}H} NMR (202.44 MHz, 298.0 K, CD_2Cl_2): *δ* / ppm = −90.4 (s). MS (positive ESI): *m/z* = 653.304 (100) [M−OTf]$^+$, 252.176 (15) [M−2OTf]$^{2+}$, 210.129 (35) [M−2OTf−hexene]$^{2+}$. MS (negative ESI): *m/z* = 149.0 (100) [OTf]$^-$. HR-MS (positive ESI): found: 653.3027. Calc. for [$C_{29}H_{50}F_3N_4O_3P_2S$]$^+$ 653.3025.

2.6. Imidazolium salt 4b

To a solution of 0.563 g (0.57 mmol, 1.0 eq.) of **3b** in 9 mL methanol 0.108 g (2.84 mmol, 5.0 eq.) $NaBH_4$ were added at −20 °C which resulted in a darkening of the yellow solution and gas formation (MeSeH). After stirring for 20 min the gas evolution had stopped and 0.243 g (1.76 mmol, 3.1 eq.) [Et_3NH]Cl were added. The suspension was let warm up to ambient temperature and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting light yellow, oily residue was filtered over a bed of celite® and silica (d = 2 cm, h = 1 cm each) with 100 mL tetrahydrofuran. After solvent removal *in vacuo* (≤ 0.05 mbar), extraction with three times 5–10 mL dichloromethane, followed by solvent evaporation, the light yellow residue was washed with five times 8 mL *n*-pentane at –20 °C and dried for 2 h (≤ 0.02 mbar) yielding a sticky, beige solid. Yield: 0.207 g (46 %). IR: $\tilde{\nu}_{max}$/cm^{-1} = 3117w and 3042w (*ν*(CH)), 2962w and 2934m ($\nu_{as}(CH_3)$, $\nu_s(CH_2)$), 2875m ($\nu_s(CH_3)$, $\nu_{as}(CH_2)$). ^{1}H NMR (500.04 MHz, 298.0 K, CD_2Cl_2): *δ* / ppm = 0.90 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, C*H*$_3$(PCH(*n*-Bu))), 0.93–1.01 (m, 12H, C*H*$_3$(N(*n*-Bu))), 1.26–1.34 (m, 4H, PCHCH$_2$C*H*$_2$C*H*$_2$), 1.34–1.42 (m, 8H, NCH$_2$CH$_2$C*H*$_2$), 1.42–1.56 (m, 3H, PCHC*H*$_2$, PC*H*$_2$), 1.79–1.92 (m, 8H, NCH$_2$C*H*$_2$), 2.27–2.37 (m, 1H, PC*H*), 2.45–2.56 (m, 1H, PC*H*$_2$), 4.26–4.42 (m, 8H, NC*H*$_2$), 8.88 (dd, $^4J_{P,H}$ = 3.0 Hz, C*H*), 9.06 (dd, $^4J_{P,H}$ = 2.9 Hz). ^{13}C{^{1}H} NMR (125.75 MHz, 298.0 K, CD_2Cl_2): *δ* / ppm = 13.5 (s, *C*H$_3$(N(*n*-Bu))), 13.9 (s, *C*H$_3$(PCH(*n*-Bu))), 20.0 (m, NCH$_2$CH$_2$*C*H$_2$), 22.7 (s, PCHCH$_2$CH$_2$*C*H$_2$), 26.5 (dd, $J_{P,C}$ = 10.1 Hz, $J_{P,C}$ = 3.5 Hz, P*C*H$_2$), 31.5 (d, $J_{P,C}$ = 15.6 Hz, PCHCH$_2$*C*H$_2$), 33.1 (m, NCH$_2$*C*H$_2$), 35.1 (d, $J_{P,C}$ = 16.3 Hz, PCH*C*H$_2$), 35.4 (dd, $J_{P,C}$ = 7.2 Hz, $J_{P,C}$ = 1.9 Hz, P*C*H), 50.0 (m, N*C*H$_2$), 120.8 (q, $^1J_{F,C}$ = 320.1 Hz, *C*F$_3$), 138.8 (s, *C*H), 139.4 (s, *C*H), 140.4 (dd, $J_{P,C}$ = 17.8 Hz, $J_{P,C}$ = 4.3 Hz, P*C*), 141.6 (dd, $J_{P,C}$ = 12.4 Hz, $J_{P,C}$ = 4.0 Hz, P*C*), 143.3 (dd, $J_{P,C}$ = 12.2 Hz, $J_{P,C}$ = 4.0 Hz, P*C*), 143.7 (dd, $J_{P,C}$ = 11.4 Hz, $J_{P,C}$ = 4.7 Hz, P*C*). ^{31}P NMR (202.44 MHz, 298.0 K, CD_2Cl_2): *δ* / ppm = −94.4 (m, *P*CH$_2$), −91.0 (m, *P*CH). ^{31}P{^{1}H} NMR (202.44 MHz, 298.0 K, CD_2Cl_2): *δ* / ppm = −94.4 (d, $^3J_{P,P}$ = 16.0 Hz, *P*CH$_2$), −91.0 (d, $^3J_{P,P}$ = 16.0 Hz, *P*CH). MS (positive ESI): *m/z* = 653.301 (100) [M−OTf]$^+$, 252.174 (55) [M−2OTf]$^{2+}$, 210.128 (39) [M−2OTf−hexene]$^{2+}$. MS (negative ESI): *m/z* = 149.0 (100) [OTf]$^-$. HR-MS (positive ESI): found: 653.3029. Calc. for [$C_{29}H_{50}F_3N_4O_3P_2S$]$^+$ 653.3025.

2.7. Bis(NHC) 5a

To a solution of 0.561 g (0.70 mmol, 1.0 eq.) of **4a** in 7.5 mL THF 0.338 g (1.69 mmol, 2.2 eq.) KHMDS in two portions of 1–1.5 mL THF each were added via a syringe, resulting in an orange, slightly turbid solution. After stirring for 15 min at ambient temperature the solvent was removed *in vacuo* (≤ 0.05 mbar) at the same temperature. The resulting yellow solid mixed with an orange, oily residue was extracted with three times 3–6 mL *n*-pentane. After removal of the solvent *in vacuo* (≤ 0.05 mbar) at ambient temperature and drying for 6 h (≤ 0.02 mbar) an orange oil was obtained (still containing traces of HMDS). Yield: 0.15 g (43 %). IR: $\tilde{\nu}_{max}$/cm^{-1} = 2957w and 2931m (ν_{as}(CH$_3$), ν_s(CH$_2$)), 2872m (ν_s(CH$_3$), ν_{as}(CH$_2$)). ^{1}H NMR (500.04 MHz, 298.0 K, C$_6$D$_6$): δ / ppm = 0.84 (t, $^3J_{H,H}$ = 7.3 Hz, 12H, C*H*$_3$(*n*-Bu)), 0.96 (t, $^3J_{H,H}$ = 7.2 Hz, 6H, C*H*$_3$(Et)), 1.05–1.11 (m, 2H, PCHC*H*$_2$), 1.14–1.21 (m, 2H, PC*H*CH$_2$), 1.21–1.37 (m, 10H, NCH$_2$CH$_2$C*H*$_2$, PCHC*H*$_2$), 1.79–1.95 (m, 8H, NCH$_2$C*H*$_2$), 4.19–4.31 (m, 8H, NC*H*$_2$). ^{13}C{^{1}H} NMR (125.75 MHz, 298.0 K, C$_6$D$_6$): δ / ppm = 13.9–14.1 (m, *C*H$_3$(*n*-Bu), *C*H$_3$(Et)), 20.1 (s, NCH$_2$CH$_2$*C*H$_2$), 28.4 (m, PCH*C*H$_2$), 35.1 (br s, NCH$_2$*C*H$_2$), 35.2 (br s, NCH$_2$*C*H$_2$), 46.2 (dd, $J_{P,C}$ = 6.0 Hz, P*C*H), 50.0 (s, N*C*H$_2$), 50.1 (s, N*C*H$_2$), 139.3 (m, P*C*), 141.7 (m, P*C*), 218.4 (br s, *C*^{2}). ^{31}P NMR (202.44 MHz, 298.0 K, C$_6$D$_6$): δ / ppm = −86.2 (m). ^{31}P{^{1}H} NMR (202.44 MHz, 298.0 K, C$_6$D$_6$): δ / ppm = −86.2 (s). MS (APCI): *m/z* = 539.364 (60) [M+H+2 H$_2$O]$^+$, 521.353 (100) [M+H+H$_2$O]$^+$, 503.343 (1) [M+H]$^+$, 437.259 (36) [M−hexene+H+H$_2$O]$^+$, 419.249 (4) [M−hexene+H]$^+$. HR-MS (APCI): found: 503.3425. Calc. for [C$_{28}$H$_{48}$N$_4$P$_2$H]$^+$ 503.3427.

2.8. Bis(NHC) 5b

0.147 g (0.18 mmol, 1.0 eq.) of **4b** and 0.080 g (0.40 mmol, 2.2 eq.) KHMDS were dissolved in 3 mL THF, resulting in an orange, slightly turbid solution. After stirring for 15 min at ambient temperature the solvent was removed *in vacuo* (≤ 0.05 mbar) at the same temperature. The resulting colourless solid mixed with an yellow, oily residue was extracted with three times 5 mL diethyl ether. After removal of the solvent *in vacuo* (≤ 0.05 mbar) at ambient temperature and drying for 5 h (≤ 0.02 mbar) a yellow-orange oil was obtained (still containing traces of HMDS). Yield: 0.050 g (54 %). IR: $\tilde{\nu}_{max}$/cm^{-1} = 2956w and 2928m (ν_{as}(CH$_3$), ν_s(CH$_2$)), 2872m (ν_s(CH$_3$), ν_{as}(CH$_2$)). ^{1}H NMR (500.04 MHz, 298.0 K, C$_6$D$_6$): δ / ppm = 0.78–0.86 (m, 15H, C*H*$_3$(PCH(*n*-Bu)), C*H*$_3$(N(*n*-Bu))), 0.87–0.91 (m, 1H, PC*H*$_2$), 0.92–0.99 (m, 2H, PCHCH$_2$CH$_2$C*H*$_2$), 1.21–1.32 (m, 10H, NCH$_2$CH$_2$C*H*$_2$, PCHCH$_2$C*H*$_2$), 1.33–1.39 (m, 8H, NCH$_2$CH$_2$C*H*$_2$), PCHC*H*$_2$), 1.59–1.66 (m, 1H, PC*H*), 1.66–1.75 (m, 1H, PC*H*$_2$), 1.79–1.98 (m, 8H, NCH$_2$C*H*$_2$), 4.22–4.31 (m, 8H, NC*H*$_2$). ^{13}C{^{1}H} NMR (125.75 MHz, 298.0 K, C$_6$D$_6$): δ / ppm = 13.9–14.0 (m, *C*H$_3$), 20.1–20.2 (m, NCH$_2$CH$_2$*C*H$_2$), 22.8 (s, PCHCH$_2$CH$_2$*C*H$_2$), 28.2 (dd, $^1J_{P,C}$ = 9.1 Hz, $^2J_{P,C}$ = 4.8 Hz, P*C*H$_2$), 31.7 (d, $J_{P,C}$ = 14.9 Hz, PCH*C*H$_2$), 34.9–35.3 (m, NCH$_2$*C*H$_2$), 35.7–35.8 (m, P*C*H), 35.9 (br s, PCHCH$_2$*C*H$_2$), 49.8–50.0 (m, N*C*H$_2$), 138.7 (d, $J_{P,C}$ = 13.7 Hz, P*C*), 139.7 (d, $J_{P,C}$ = 9.0 Hz, P*C*), 140.7 (d, $J_{P,C}$ = 8.6 Hz, P*C*), 142.0 (d, $J_{P,C}$ = 8.3 Hz, P*C*), 219.9 (t, $^3J_{P,C}$ = 2.7 Hz, *C*^{2}), 220.5 (t, $^3J_{P,C}$ = 3.0 Hz, *C*^{2}). ^{31}P NMR (202.44 MHz, 298.0 K, C$_6$D$_6$): δ / ppm = −92.0 (m, *P*CH$_2$), −86.4 (m, *P*CH). ^{31}P{^{1}H} NMR (202.44 MHz, 298.0 K, C$_6$D$_6$): δ / ppm = −92.0 (d, $^3J_{P,P}$ = 19.7 Hz, *P*CH$_2$), −86.4 (d, $^3J_{P,P}$ = 19.4 Hz, *P*CH). MS (APCI): *m/z* = 539.364 (100) [M+H+2 H$_2$O]$^+$, 521.353 (77) [M+H+H$_2$O]$^+$, 503.343 (<1) [M+H]$^+$, 419.249 (1) [M−hexene+H]$^+$. HR-MS (APCI): found: 503.3429. Calc. for [C$_{28}$H$_{48}$N$_4$P$_2$H]$^+$ 503.3427.

2.9. BCl_3-Bis(NHC) adduct 6a

To a solution of 0.116 g (0.23 mmol, 1.00 eq.) **5a** in 4 mL toluene 0.438 mL (0.438 mmol, 1.9 eq.) BCl_3 (1M in hexane) were added dropwise yielding a colourless solution and orange precipitate. After 3 h the solvent was removed *in vacuo* ($5 \cdot 10^{-2}$ mbar). The residue was extracted with three times 5 mL

toluene and the solvent evaporated. After washing with two times 3 mL *n*-pentane at −40 °C and drying for several hours the adduct was obtained as colourless solid. Yield: 0.010 g (6 %). Mp: 150 °C (dec.). IR: $\tilde{\nu}_{max}$/cm^{-1} = 2963w and 2932m (ν_{as}(CH$_3$), ν_s(CH$_2$)), 2875m (ν_s(CH$_3$), ν_{as}(CH$_2$)). ^{1}H NMR (500.04 MHz, 298.0 K, C$_6$D$_6$): 0.77-0.86 (m, 18H, C*H*$_3$(*n*-Bu), C*H*$_3$(Et)), 0.93-0.99 (m, 2H, P-C*H*CH$_2$CH$_3$), 1.00-1.09 (m, 2H, P-CHC*H*$_2$CH$_3$), 1.18-1.35 (m, 10H, NCH$_2$CH$_2$C*H*$_2$CH$_3$, P-CHC*H*$_2$CH$_3$), 1.78-2.02 (m, 8H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 4.68-4.92 (m, 8H, NC*H*$_2$CH$_2$CH$_2$CH$_3$). ^{13}C{^{1}H} NMR (125.75 MHz, 298.0 K, C$_6$D$_6$): 13.6-13.8 (m, *C*H$_3$(*n*-Bu), *C*H$_3$(Et)), 20.0 (s, NCH$_2$CH$_2$*C*H$_2$CH$_3$), 20.1 (s, NCH$_2$*C*H$_2$CH$_2$CH$_3$), 27.5 (m, P-CH*C*H$_2$CH$_3$), 34.6-34.8 (m, NCH$_2$*C*H$_2$CH$_2$CH$_3$), 45.8 (t, $J_{P,C}$ = 6.0 Hz, P-*C*HCH$_2$CH$_3$), 50.2-50.4 (m, NCH$_2$CH$_2$CH$_2$CH$_3$), 139.6 (m, P-C), 142.7 (m, P-C). *Due to its quartet splitting the C^2 was not observed.* ^{31}P NMR (202.44 MHz, 298.0 K, C$_6$D$_6$): δ / ppm = −86.8 (m). ^{31}P{^{1}H} NMR (202.44 MHz, 298.0 K, C$_6$D$_6$): δ / ppm = −86.8 (s). ^{11}B{^{1}H} NMR (160.14 MHz, 298.0 K, C$_6$D$_6$): δ / ppm = 2.6 (s). MS (positive ESI): *m/z* = 619.258 (9) [M+H−BCl$_3$]$^+$, 252.175 (100) [M+2 H−2 BCl$_3$]$^{2+}$, 210.128 (87) [M+2 H−2 BCl$_3$−hexene]$^+$. HR-MS (positive ESI): found: 619.2582. Calc. for [C$_{28}$H$_{48}$BCl$_3$N$_4$P$_2$H]$^+$ 619.2592.

2.10. CS$_2$-Bis(NHC) adduct 7a

To a solution of 0.094 g (0.187 mmol, 1.00) **5a** in 3 mL toluene 0.023 mL (0.029 g, 0.374 mmol, 2.00 eq.) CS$_2$ was added dropwise yielding an immediate colour change to dark red. After 1 h the solvent was removed *in vacuo* ($5 \cdot 10^{-2}$ mbar) and the red, oily residue was extracted with three times 2–5 mL toluene. After solvent removal, washing with three times 3–5 mL *n*-pentane at −60 °C and drying for several hours the adduct was obtained as burgundy coloured solid. Yield: 61 %. Mp: 96 °C. Elemental analysis: Found: C, 54.6; H, 7.1; N, 8.5. Calc. for C$_{30}$H$_{48}$N$_4$P$_2$S$_4$: C, 55.0; H, 7.4; N, 8.6 %. UV/vis: λ_{max}(toluene)/nm (abs.) = 290 (0.65, NCN), 363 (1, CS$_2$). IR: $\tilde{\nu}_{max}$/cm^{-1} = 2956w and 2930m (ν_{as}(CH$_3$), ν_s(CH$_2$)), 2870m (ν_s(CH$_3$), ν_{as}(CH$_2$)), 1469m (ν_{as}(NCN$^+$)), 1054s (ν_{as}(CS$_2^-$). ^{1}H NMR (500.04 MHz, 298.0 K, C$_6$D$_6$): 0.79 (dm, $^3J_{H,H}$ = 7.3 Hz, 12H, C*H*$_3$(*n*-Bu)), 0.86-0.93 (m, 8H, C*H*$_3$(Et), P-CHC*H*$_2$CH$_3$), 1.10-1.27 (m, 12H, NCH$_2$CH$_2$C*H*$_2$CH$_3$, P-C*H*CH$_2$CH$_3$), 1.75-1.85 (m, 2H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.92 (tt, $^3J_{H,H}$ = 7.6 Hz, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.97-2.05 (m, 2H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 4.23-4.43 (m, 8H, NC*H*$_2$CH$_2$CH$_2$CH$_3$). ^{13}C{^{1}H} NMR (125.75 MHz, 298.0 K, C$_6$D$_6$): 13.8 (s, *C*H$_3$(*n*-Bu), *C*H$_3$(Et)), 13.8 (s, *C*H$_3$(*n*-Bu), *C*H$_3$(Et)), 20.3-20.4 (m, NCH$_2$CH$_2$*C*H$_2$CH$_3$), 27.7 (dd, $J_{P,C}$ = 9.1 Hz, P-CH*C*H$_2$CH$_3$), 33.3 (m, NCH$_2$*C*H$_2$CH$_2$CH$_3$), 33.4 (m, NCH$_2$*C*H$_2$CH$_2$CH$_3$), 46.2 (dd, $J_{P,C}$ = 6.0 Hz, P-*C*HCH$_2$CH$_3$), 48.3-48.5 (m, NCH$_2$CH$_2$CH$_2$CH$_3$), 139.6 (dd, $J_{P,C}$ = 10.6 Hz, $J_{P,C}$ = 7.0 Hz, P-*C*), 138.9 (m, P-*C*), 152.7 (s, *C*-CS$_2$), 223.8 (s, *C*S$_2$). ^{31}P NMR (202.44 MHz, 298.0 K, C$_6$D$_6$): δ / ppm = −87.1 (m). ^{31}P{^{1}H} NMR (202.44 MHz, 298.0 K, C$_6$D$_6$): δ / ppm = −87.1 (s). MS (positive ESI): *m/z* = 655.230 (47) [M+H]$^+$. HR-MS (positive ESI): found: 655.2312. Calc. for [C$_{30}$H$_{48}$N$_4$P$_2$S$_4$H]$^+$ 655.2310.

2.11. PPh$_2$-Bis(NHC) adduct 8a

To a solution of 0.097 g (0.12 mmol, 1.00 eq.) **4a** in 9 mL THF 0.053 g (0.27 mmol, 2.20 eq.) KHMDS were added in 4 mL THF at −80 °C. After 5 minutes Ph$_2$PCl was added and after stirring for 0.5 h the solution had turned colourless and the solvent was removed *in vacuo* ($5 \cdot 10^{-2}$ mbar) leaving a colourless, oily residue. After extraction with three times 4-10 mL toluene, evaporation of the solvent, washing with three times 5-10 mL *n*-pentane and drying for several hours the adduct was obtained as a yellow solid. Yield: 0.084 g (59 %). Mp: 108 °C. IR: $\tilde{\nu}_{max}$/cm^{-1} = 2961w and 2932m (ν_{as}(CH$_3$), ν_s(CH$_2$)), 2874m (ν_s(CH$_3$), ν_{as}(CH$_2$)). ^{1}H NMR (400.13 MHz, 298.0 K, C$_6$D$_6$): δ / ppm = 0.54-0.68 (m, 12H, NCH$_2$CH$_2$CH$_2$C*H*$_3$), 0.71-0.96 (m, 8H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.26 (t, $^3J_{H,H}$ = 7.25 Hz, 6H, PCHCH$_2$C*H*$_3$), 1.20-1.34 (m, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.35-1.4 (m, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.50-1.66 (m, 2H, PCHC*H*$_2$CH$_3$), 1.78-1.97 (m, 2H, PCHC*H*$_2$CH$_3$), 2.42-2.55 (m, 2H, PC*H*CH$_2$CH$_3$), 4.37-4.57 (m, 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 4.65-4.76

(m, 2H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 4.79-4.91 (m, 2H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 6.98-7.7.09 (m, 4H, *para*-CH), 7.15-7.23 (m, 4H, *meta*-CH), 7.29-7.39 (m, 4H, *meta*-CH), 7.51-7.64 (dt, $^3J_{P,H}$ = 15.4 Hz, $^3J_{H,H}$ = 7.8 Hz, 8H, *ortho*-CH). $^{13}C\{^1H\}$ NMR (100.63 MHz, 298.0 K, C_6D_6): δ / ppm = 13.5 (s, NCH$_2$CH$_2$CH$_2$*C*H$_3$), 13.6 (s, NCH$_2$CH$_2$CH$_2$*C*H$_3$), 13.9 (m, PCHCH$_2$*C*H$_3$), 19.9 (s, NCH$_2$CH$_2$*C*H$_2$CH$_3$), 20.0 (s, NCH$_2$CH$_2$*C*H$_2$CH$_3$), 28.1 (m, PCH*C*H$_2$CH$_3$), 33.4 (m, NCH$_2$*C*H$_2$CH$_2$CH$_3$), 44.4 (m, P*C*HCH$_2$CH$_3$), 50.5 (dm, $^3J_{P,C}$ = 9.9 Hz, N*C*H$_2$CH$_2$CH$_2$CH$_3$), 50.8 (dm, $^3J_{P,C}$ = 10.2 Hz, N*C*H$_2$CH$_2$CH$_2$CH$_3$), 122.2 (q, $^1J_{F,C}$ = 322.0 Hz, (*C*F$_3$)OTf), 133.8 (d, $^2J_{P,C}$ = 20.5 Hz, *ortho*-C), 130.0 (d, $^3J_{P,C}$ = 7.3 Hz, *meta*-C), 130.3 (d, $^3J_{P,C}$ = 7.5 Hz, *meta*-C), 130.7 (d, $^4J_{P,C}$ = 9.1 Hz, *para*-C), 143.5-143.8 (m, P*C*), 146.1-146.3 (m, P*C*), 147.1 (d, $^1J_{P,C}$ = 59.1 Hz, *C*-PPh$_2$). *Despite also analysing the ^{13}C-^1H-HSQC/HMBC spectra and without the possibilty to record ^{31}P-^{13}C-HSQC/HMBC spectra,* d*ue to the signal's low intensity the ipso-C resonance could not be assigned.* ^{31}P NMR (162.00 MHz, 298.0 K, C_6D_6): δ / ppm = −84.3 (m), −25.3 (m). $^{31}P\{^1H\}$ NMR (162.00 MHz, 298.0 K, C_6D_6): δ / ppm = −84.3 (s), −25.3 (s). MS (positive ESI): *m/z* = 436.219 (100) [M-2OTf]$^{2+}$, 394.172 (80) [M-2OTf-1-Hexene]$^{2+}$, 344.198 (60) [M-2OTf-PPh$_2$+H]$^{2+}$, 302.151 (51) [M-2OTf-PPh$_2$+H-1-Hexene]$^{2+}$, 185.052 (16) [PPh$_2$]$^+$. MS (negative ESI): *m/z* = 149.0 (100) [OTf]$^-$.

2.12. Fe(CO)$_4$-Bis(NHC) complex 9a

A solution of 0.412 g (0.82 mmol, 1.00 eq.) **5a** in 10 mL toluene was cooled to −80 °C and transferred to a to −80 °C cooled suspension of 0.268 g (0.738 mmol, 0.90 eq.) Fe$_2$(CO)$_9$ in 10 mL toluene with additionally 5 mL toluene. After letting warm up to room temperature and stirring for 5 days, the solvent was removed *in vacuo* ($5 \cdot 10^{-2}$ mbar). The orange, oily residue was filtered over a bed of silica and celite (d = 2 cm, h = 1 cm each) with 150 mL THF in total and solvent was evaporated. After extraction with three times 10–20 mL *n*-pentane, solvent removal and drying for several hours the complex was obtained as orange solid. Yield: 0.314 g (46 %). Mp: 121 °C (dec.). IR: $\tilde{\nu}_{max}$/cm^{-1} = 2961w and 2932m (ν_{as}(CH$_3$), ν_s(CH$_2$)), 2874m (ν_s(CH$_3$), ν_{as}(CH$_2$)), 2037s (ν(CO)), 1909vs (ν(CO)). ^1H NMR (500.04 MHz, 298.0 K, C_6D_6): δ / ppm = 0.75 (t, $^3J_{H,H}$ = 6.8 Hz, 6H, C*H*$_3$(Et)) 0.85 (tm, $^3J_{H,H}$ = 7.4 Hz, 12H, C*H*$_3$(*n*-Bu)), 0.89 (m, 2H, PC*H*CH$_2$CH$_3$), 0.94-1.00 (m, 4H, P-CHC*H*$_2$CH$_3$), 1.21-1.38 (m, 8H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.67-1.84 (m, 8H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 4.15-4.30 (m, 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 4.38-4.54 (m, 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$). $^{13}C\{^1H\}$ NMR (125.75 MHz, 298.0 K, C_6D_6): δ / ppm = 13.4 (m, *C*H$_3$(Et)), 13.8 (m, *C*H$_3$(*n*-Bu)), 27.7 (m, PCH*C*H$_2$CH$_3$), 20.2 (m, NCH$_2$CH$_2$*C*H$_2$CH$_3$), 34.0 (m, NCH$_2$*C*H$_2$CH$_2$CH$_3$), 45.7 (t, $^1J_{P,C}$ = 6.3, P*C*HCH$_2$CH$_3$), 51.0 (m, N*C*H$_2$CH$_2$CH$_2$CH$_3$), 141.0 (dd, $J_{P,C}$ = 8.0 Hz, $J_{P,C}$ = 5.3 Hz, P-*C*), 143.6 (dd, $J_{P,C}$ = 4.3 Hz, P-*C*), 187.8 (t, $^3J_{P,C}$ = 2.7 Hz, *C*^{2}), 218.7 (s, *C*O). ^{31}P NMR (202.44 MHz, 298.0 K, C_6D_6): δ / ppm = −82.2. $^{31}P\{^1H\}$ NMR (202.44 MHz, 298.0 K, C_6D_6): δ / ppm = −82.2 (s). MS (positive ESI): *m/z* = 671.255 (100) [M−Fe(CO)$_4$+H]$^+$, 643.261 (6) [M−Fe(CO)$_4$−CO+H]$^+$, 587.162 (2) [M−Fe(CO)$_4$−hexene+H]^2. HR-MS (ESI(+)): found: 671.2575. Calc. for [C$_{32}$H$_{48}$FeN$_4$O$_4$P$_2$H]$^+$ 671.2577.

2.13. Attempted synthesis of tri-/tetranuclear Fe(CO)$_4$-Bis(NHC) complex

In a Schlenk tube 0.015 g (0.03 mmol, 1.00 eq.) **5a** and 0.025 g (0.07 mmol, 2.3 eq.) Fe$_2$(CO)$_9$ were suspended in 1.5 mL toluene and stirred at ambient temperature. $^{31}P\{^1H\}$ NMR monitoring after three days and 20 days showed the same spectrum with approximately 40 % conversion to a trinuclear complex. $^{31}P\{^1H\}$ NMR (121.51 MHz, 298.0 K): δ / ppm = −91.7 (d, $^3J_{P,P}$ = 9 Hz, *P*CH$_2$), 45.1 (br m, *P*CH$_2$Fe(CO)$_4$).

2.14. Bis(NHC) 5c via trapping reaction of 11

In a *J Young®* NMR tube 0.007 g (0.01 mmol, 1.0 eq.) **5a** were dissolved in 0.45 mL (2.85 mmol, 285 eq.) 1-octene and heated to 120 °C. After 2 h the $^{31}P\{^1H\}$ NMR spectrum showed complete conversion.

$^{31}P\{^{1}H\}$ NMR (121.51 MHz, 298.0 K): δ / ppm = −91.8 (d, $^{3}J_{P,P}$ = 20.1 Hz, *P*CH_2), −86.1 (d, $^{3}J_{P,P}$ = 20.1 Hz, *P*CH).

2.15. $Fe(CO)_4$-Bis(NHC) complex 9c via trapping reaction of 12

In a *J Young®* NMR tube 0.01 g (0.01 mmol, 1.0 eq.) **9a** were dissolved in 0.45 mL (2.85 mmol, 285 eq.) 1-octene and heated to 100 °C. After 5 h the $^{31}P\{^{1}H\}$ NMR spectrum showed complete conversion. $^{31}P\{^{1}H\}$ NMR (121.51 MHz, 298.0 K): δ / ppm = −89.1 (d, $^{3}J_{P,P}$ = 18.2 Hz, *P*CH_2), −83.7 (d, $^{3}J_{P,P}$ = 18.2 Hz, *P*CH).

3. NMR and UV/vis spectra

*Impurities (solvent peaks, grease peaks) are marked with * in the spectra.*

3.1. 1,4-Diphosphabarrelene 2a

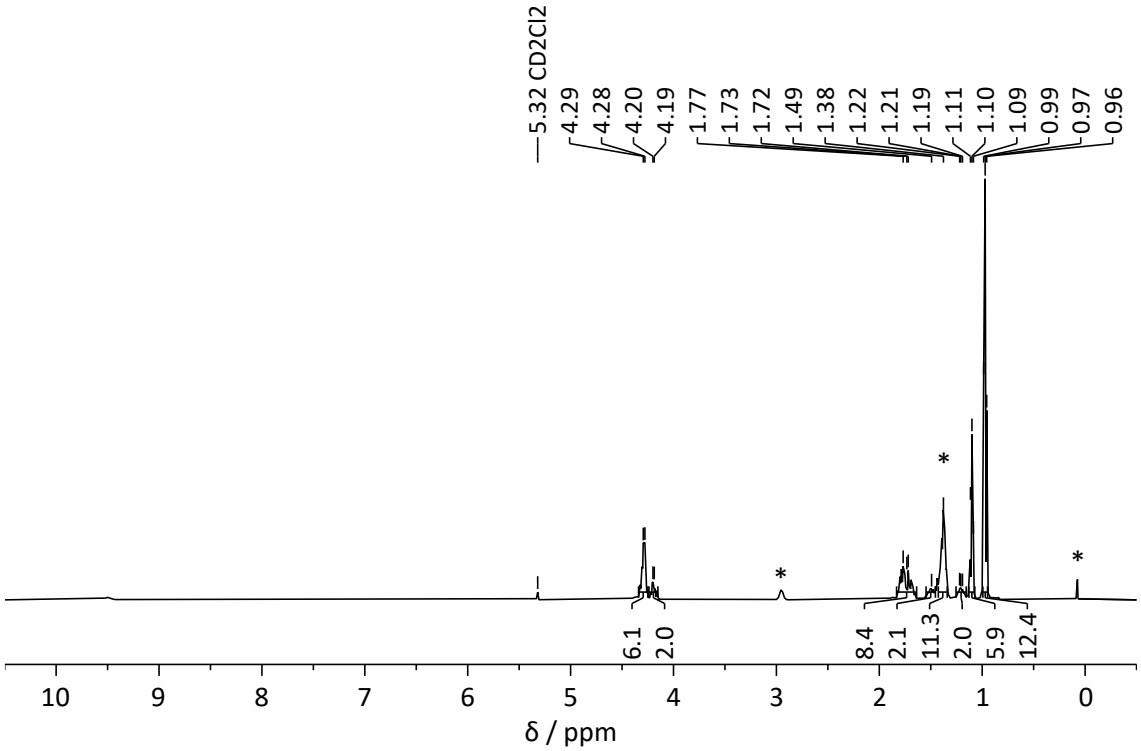

Figure S1 *^{1}H NMR spectrum (CD_2Cl_2, 500.04 Hz, 298.0 K) of **2a**.*

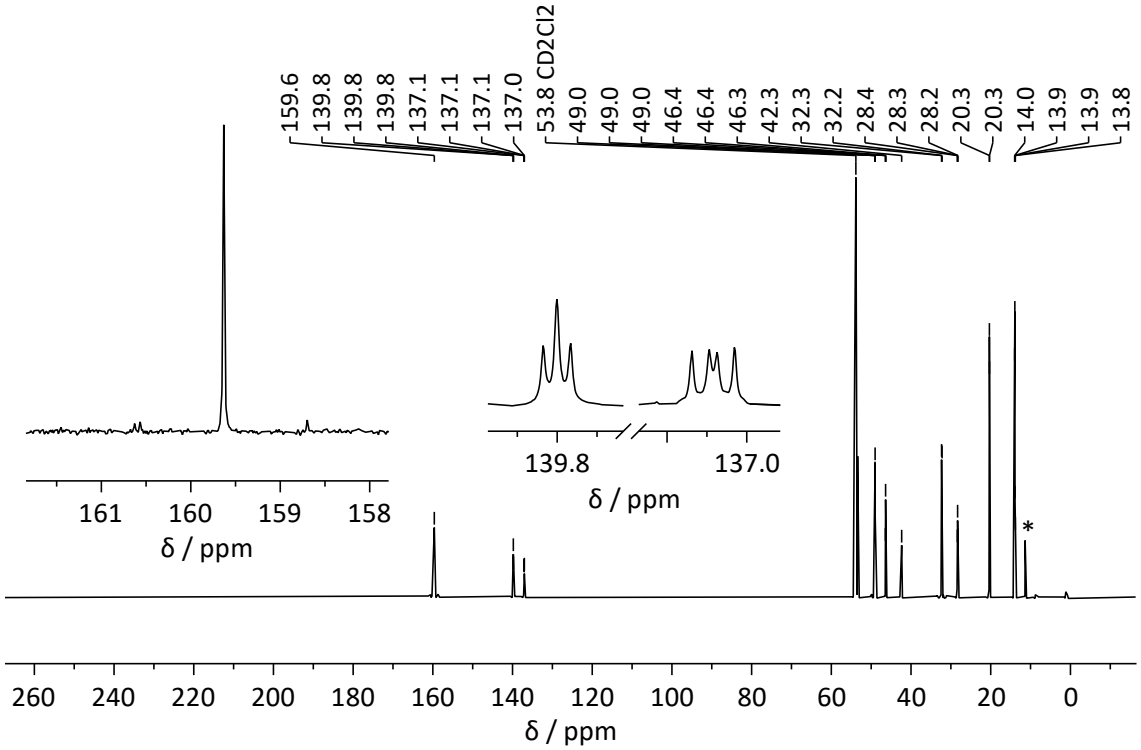

Figure S2 *$^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 125.75 Hz, 298.0 K) of **2a**.*

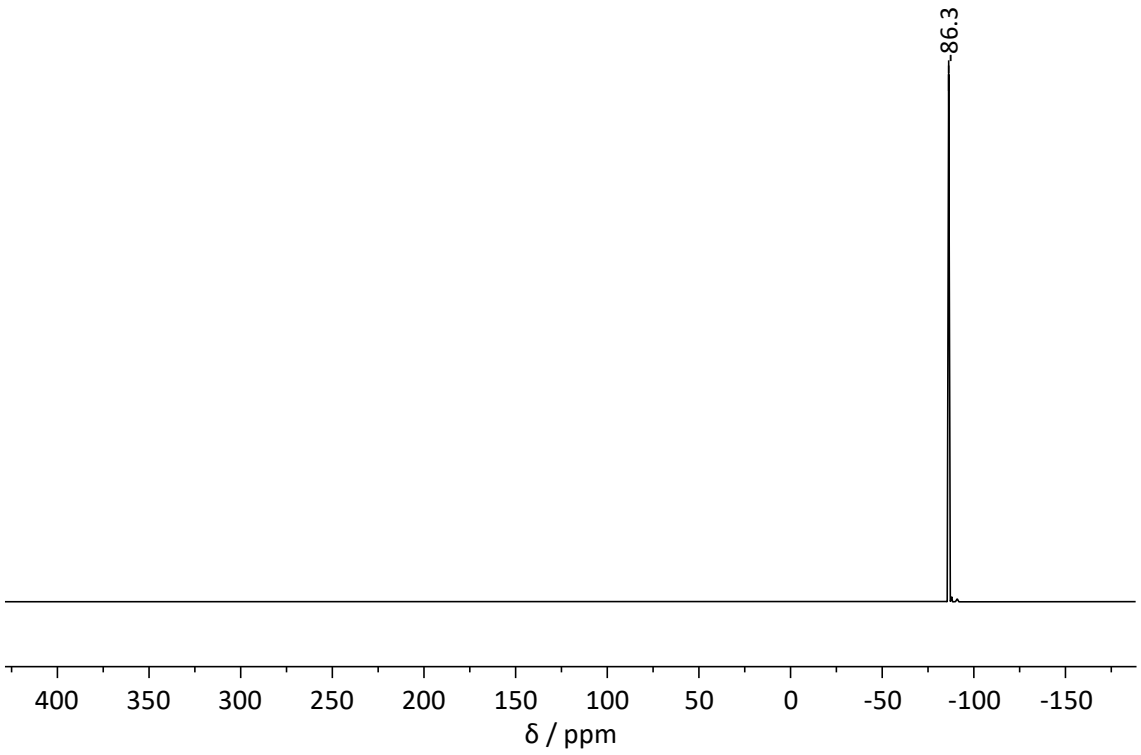

Figure S3 *$^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 202.44 Hz, 298.0 K) of **2a**.*

3.2. 1,4-Diphosphabarrelene 2b

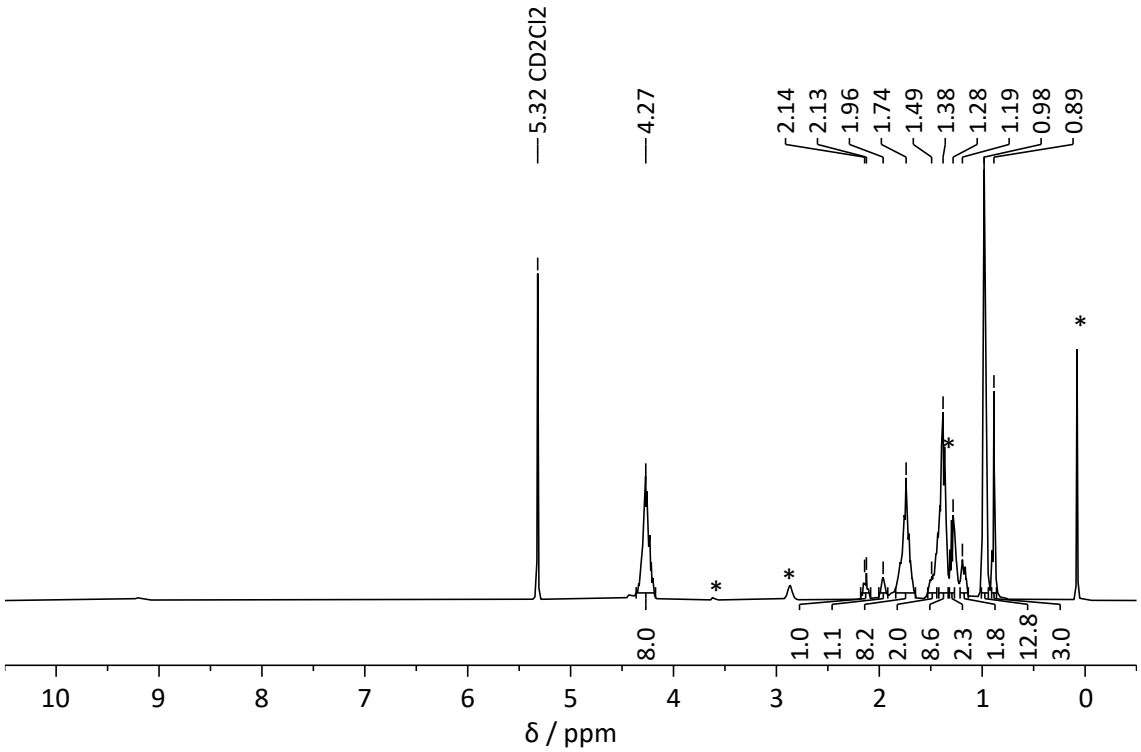

Figure S4 *^{1}H NMR spectrum (CD_2Cl_2, 500.04 Hz, 298.0 K) of **2b**.*

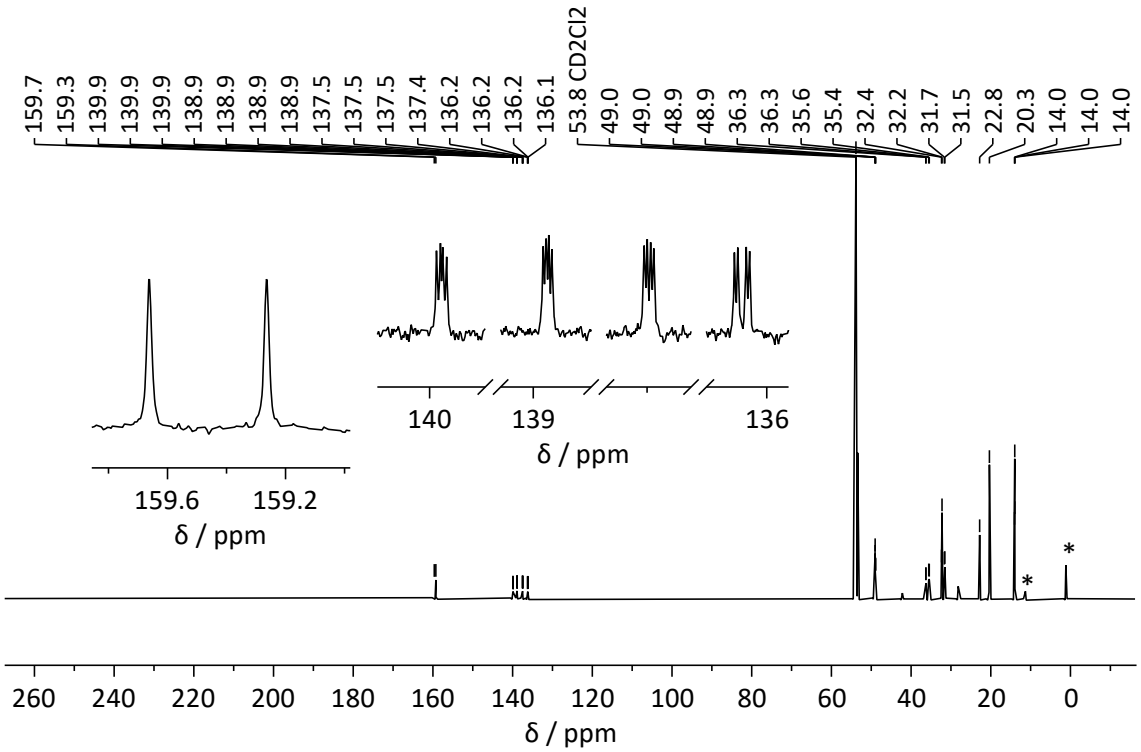

Figure S5 *$^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 125.75 Hz, 298.0 K) of **2b**.*

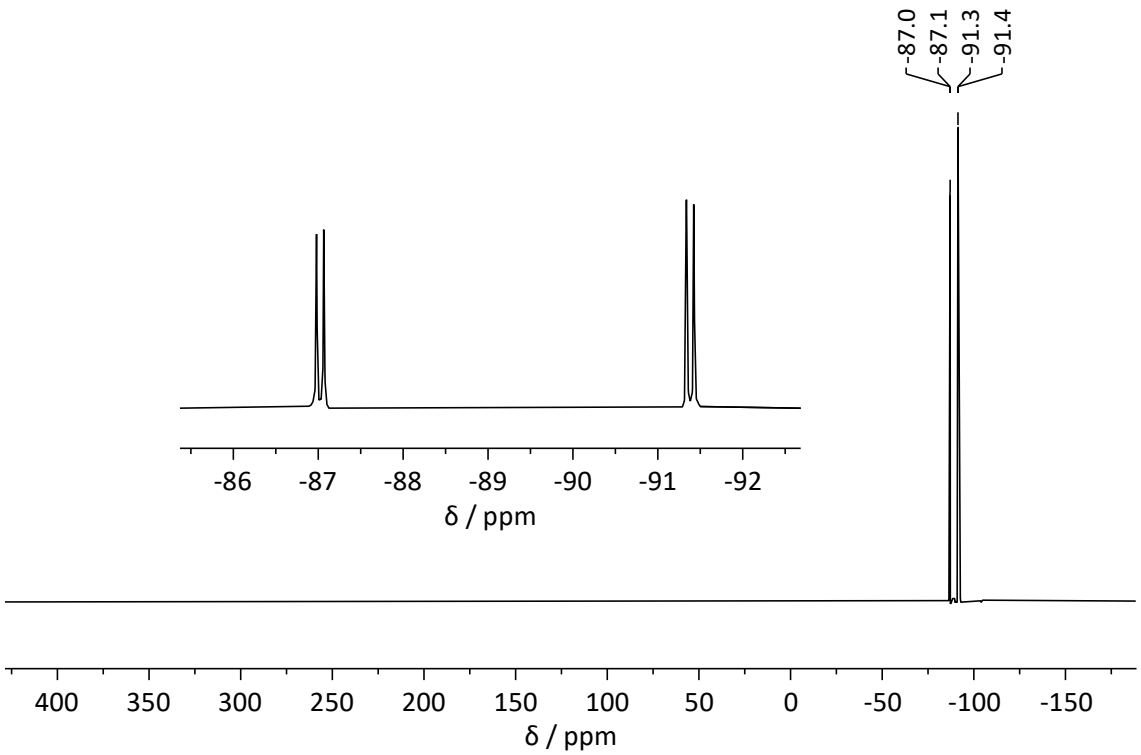

Figure S6 *$^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 202.44 Hz, 298.0 K) of* ***2b****.*

3.3. Se-methylated imidazolium salt 3a

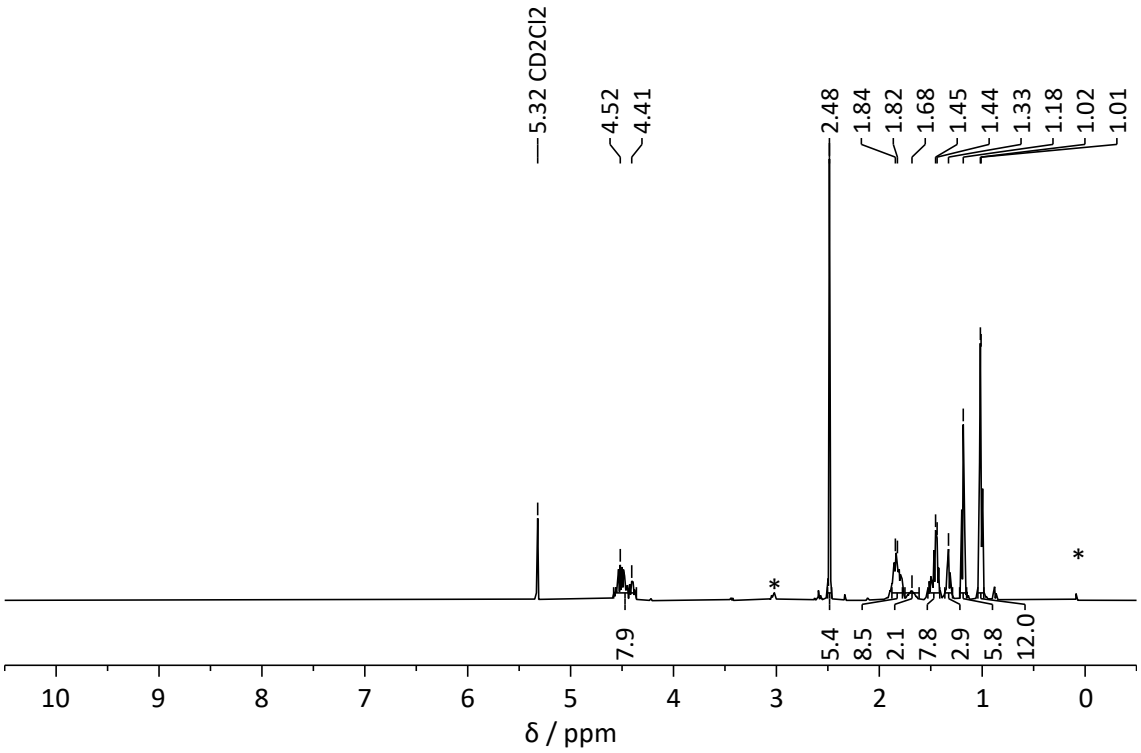

Figure S7 *^{1}H NMR spectrum (CD_2Cl_2, 500.04 Hz, 298.0 K) of* ***3a****.*

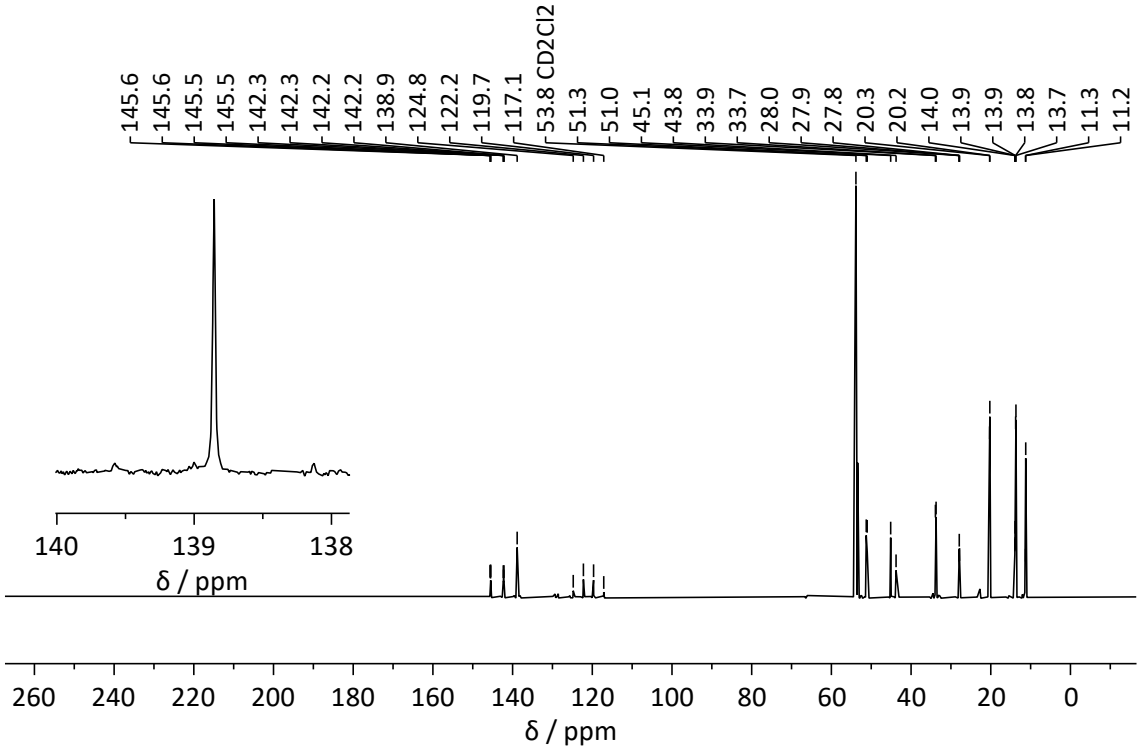

Figure S8 *$^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 125.75 Hz, 298.0 K) of **3a**.*

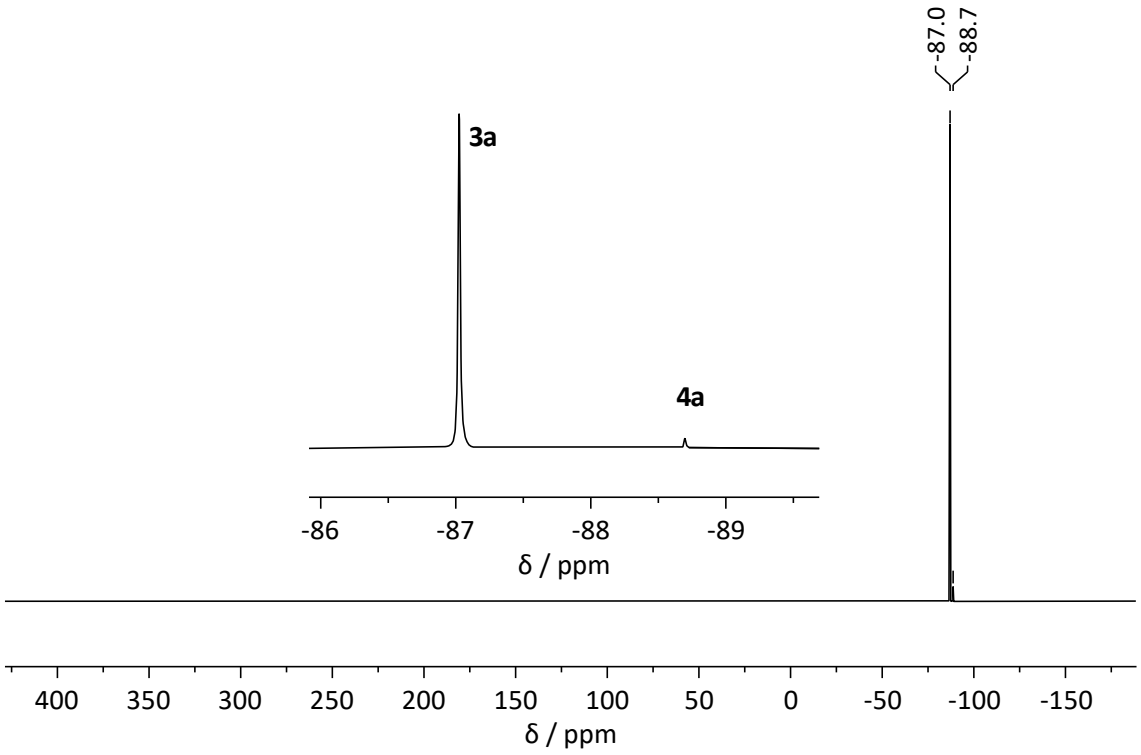

Figure S9 *$^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 202.44 Hz, 298.0 K) of **3a** (with impurity of **4a**).*

3.4. Se-methylated imidazolium salt 3b

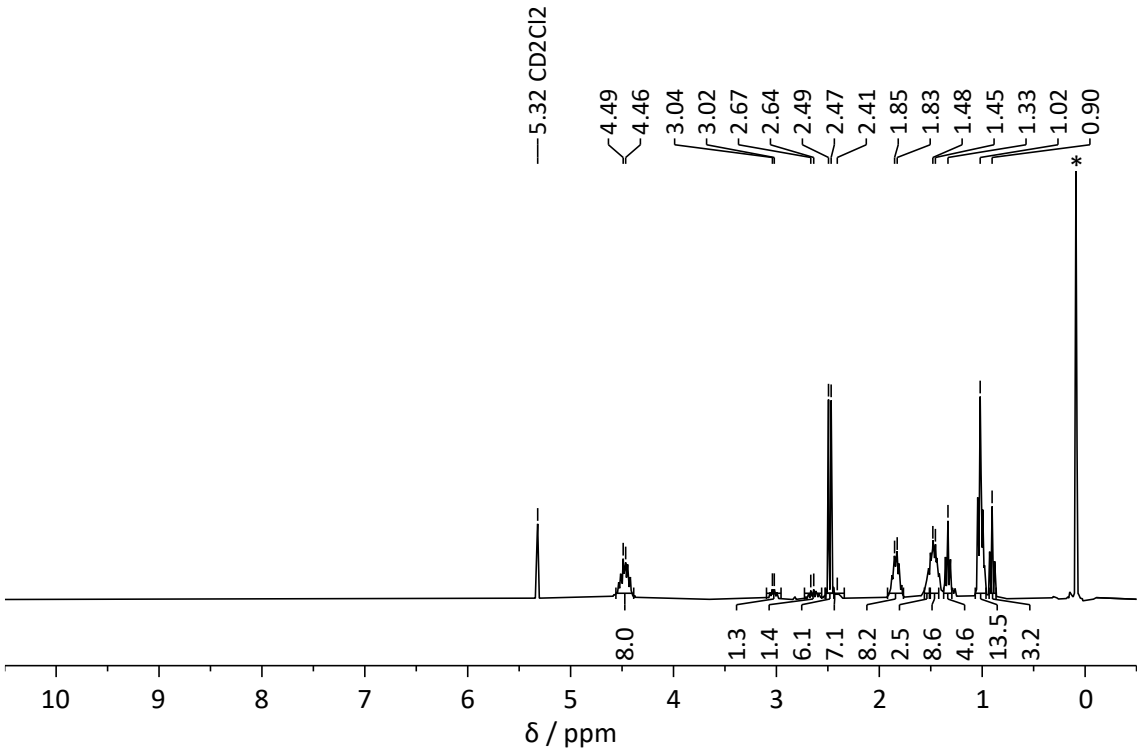

Figure S10 *^{1}H NMR spectrum (CD_2Cl_2, 300.13 Hz, 298.5 K) of **3b**.*

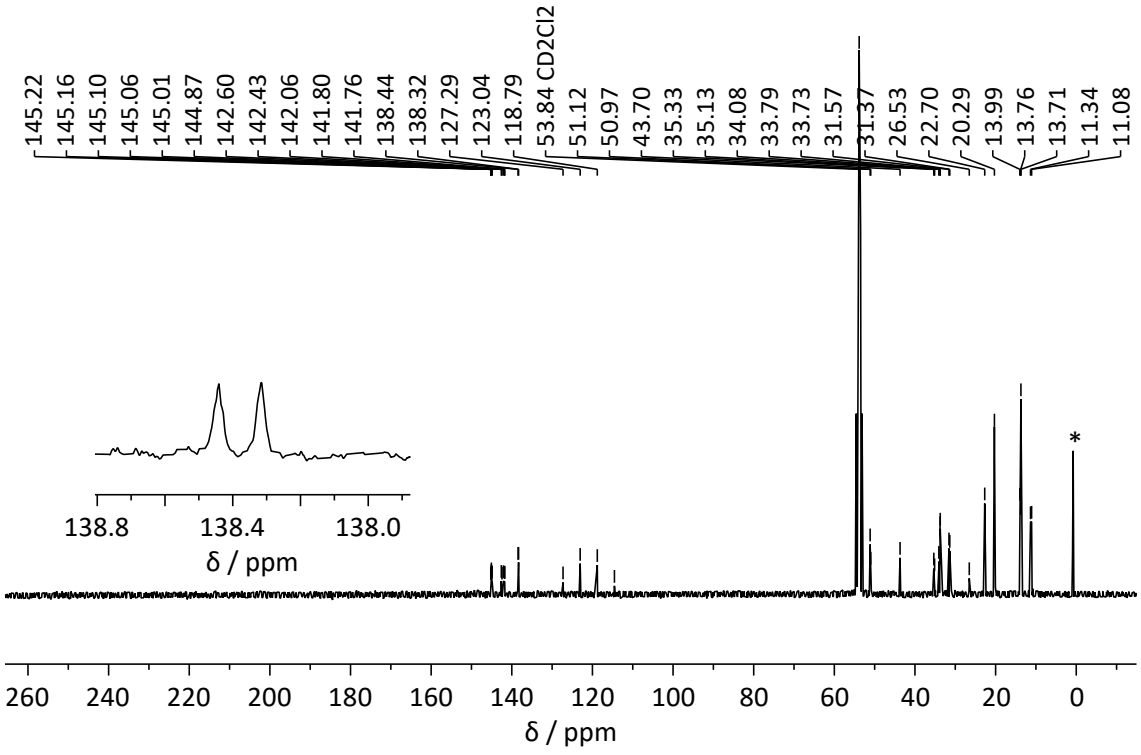

Figure S11 *$^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 75.48 Hz, 298.7 K) of **3b**.*

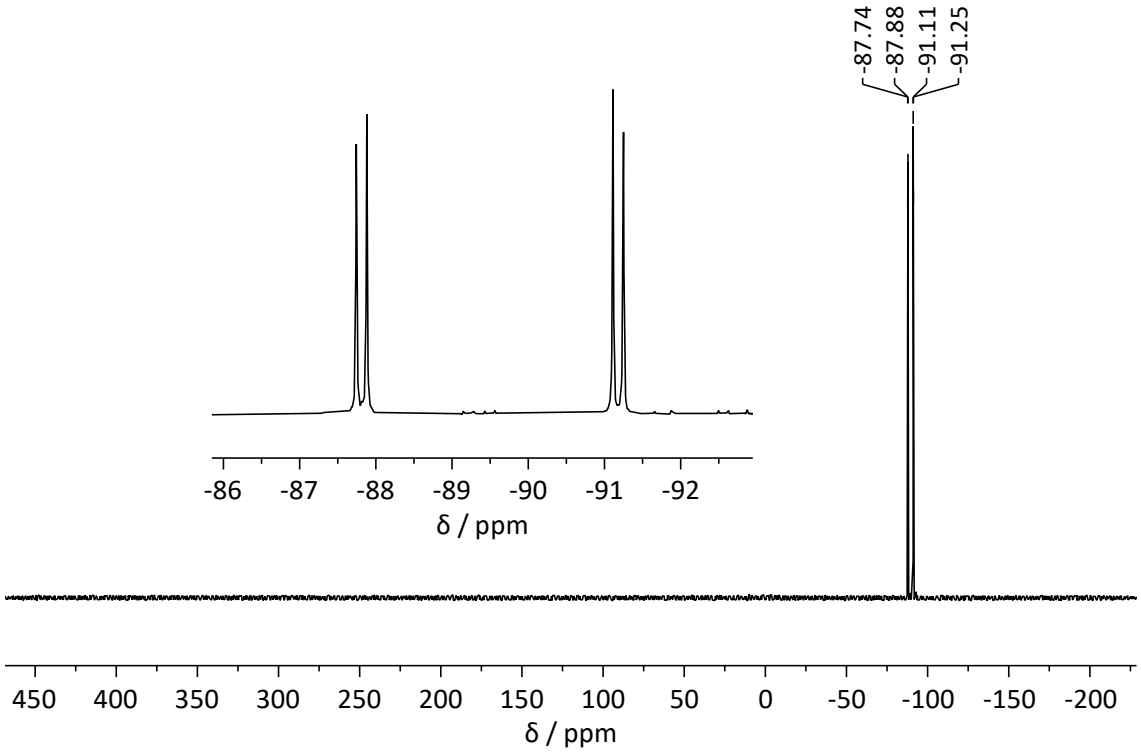

Figure S12 *$^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 121.51 Hz, 298.5 K) of* ***3b****.*

3.5. Imidazolium salt 4a

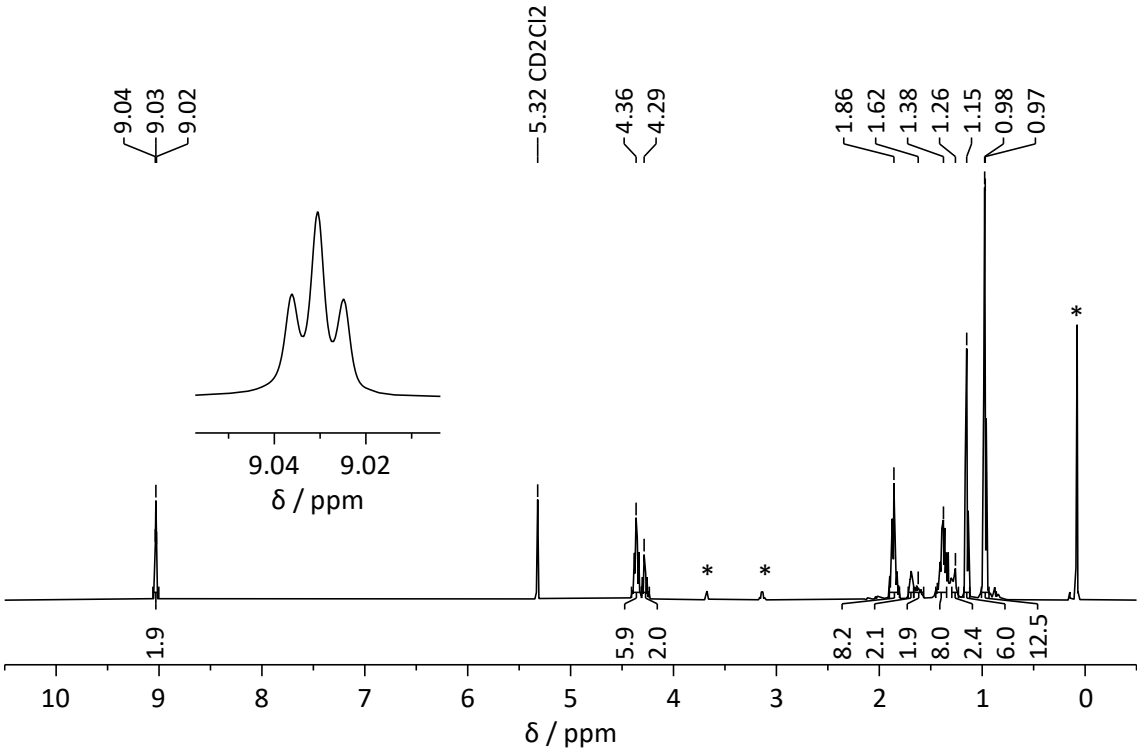

Figure 13 *^{1}H NMR spectrum (CD_2Cl_2, 500.04 Hz, 298.0 K) of* ***4a****.*

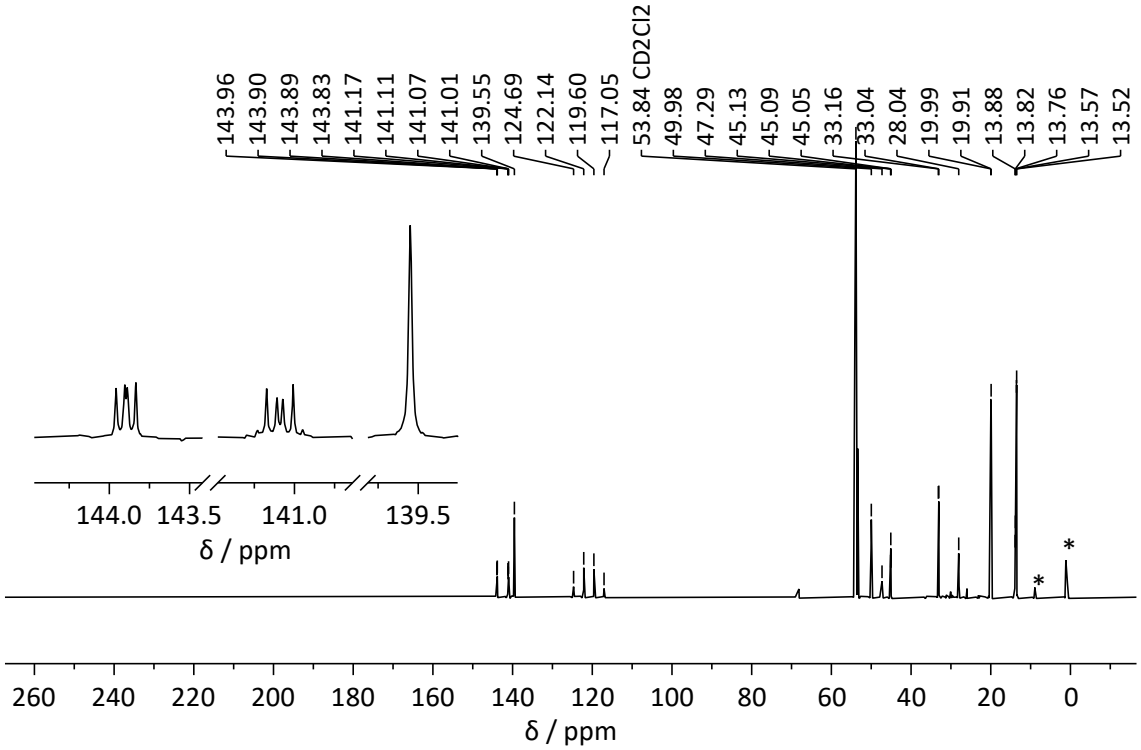

Figure S14 *$^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2, 125.75 Hz, 298.0 K) of **4a**.*

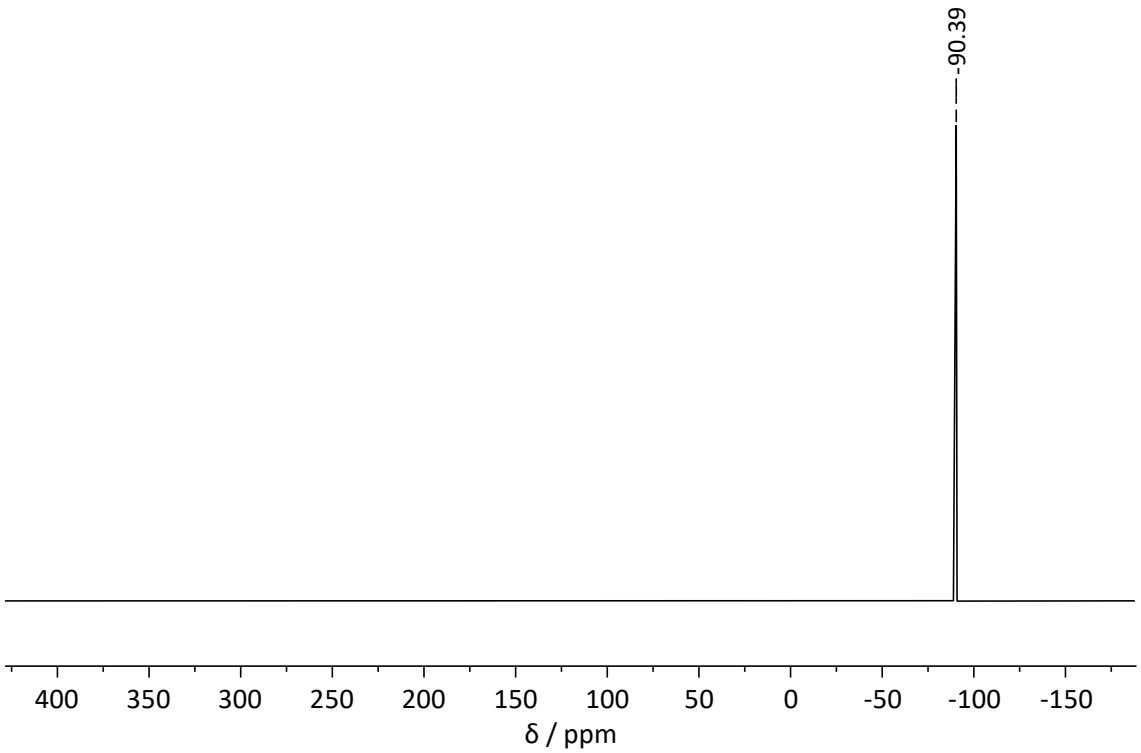

Figure S15 *$^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 202.44 Hz, 298.0 K) of **4a**.*

3.6. Imidazolium salt 4b

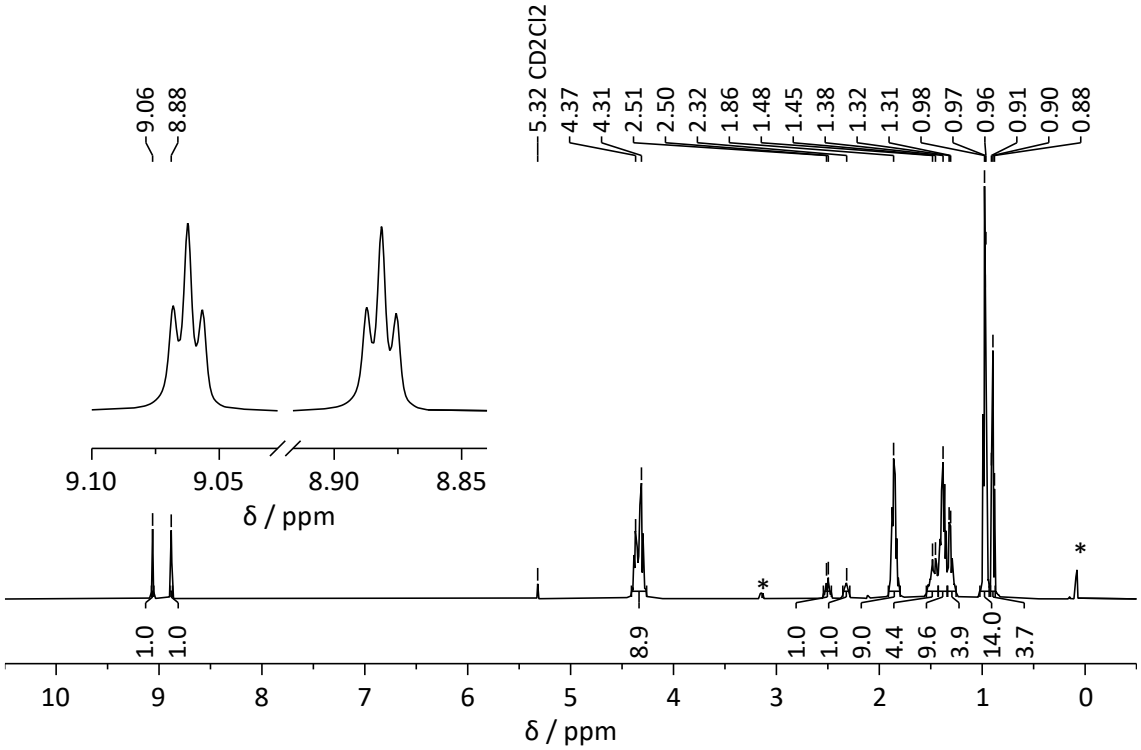

Figure S16 *^{1}H NMR spectrum (CD_2Cl_2, 500.04 Hz, 298.0 K) of* ***4b****.*

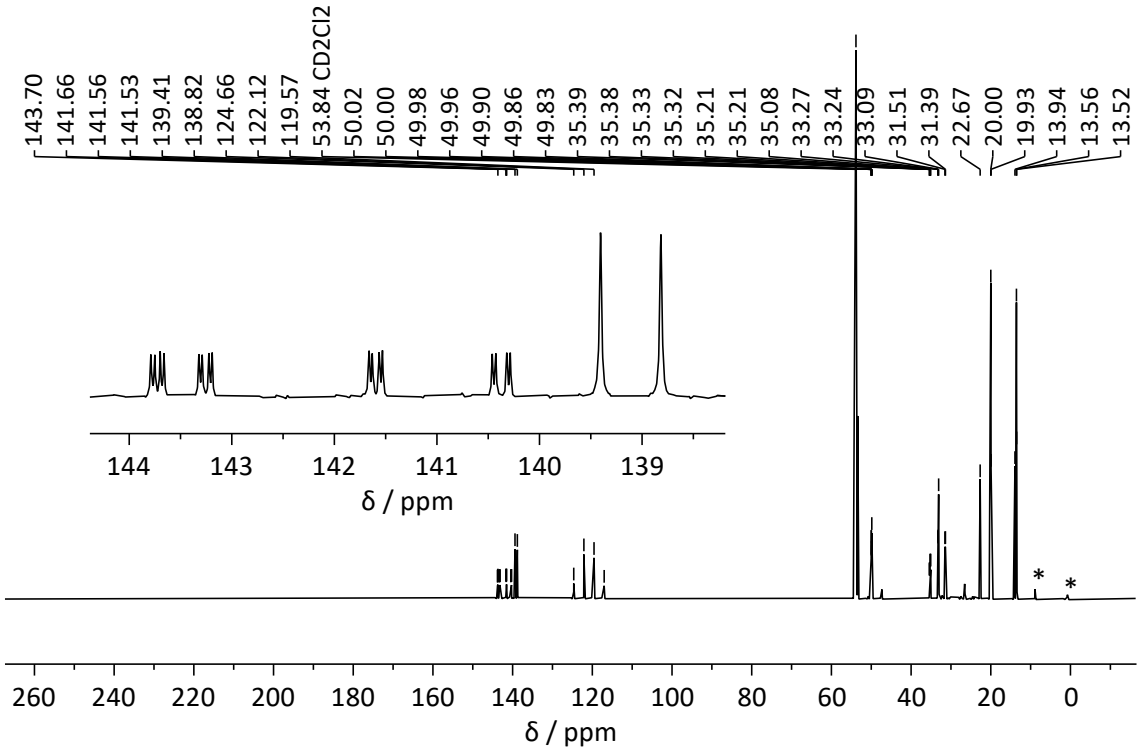

Figure S17 *$^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 125.75 Hz, 298.0 K) of* ***4b****.*

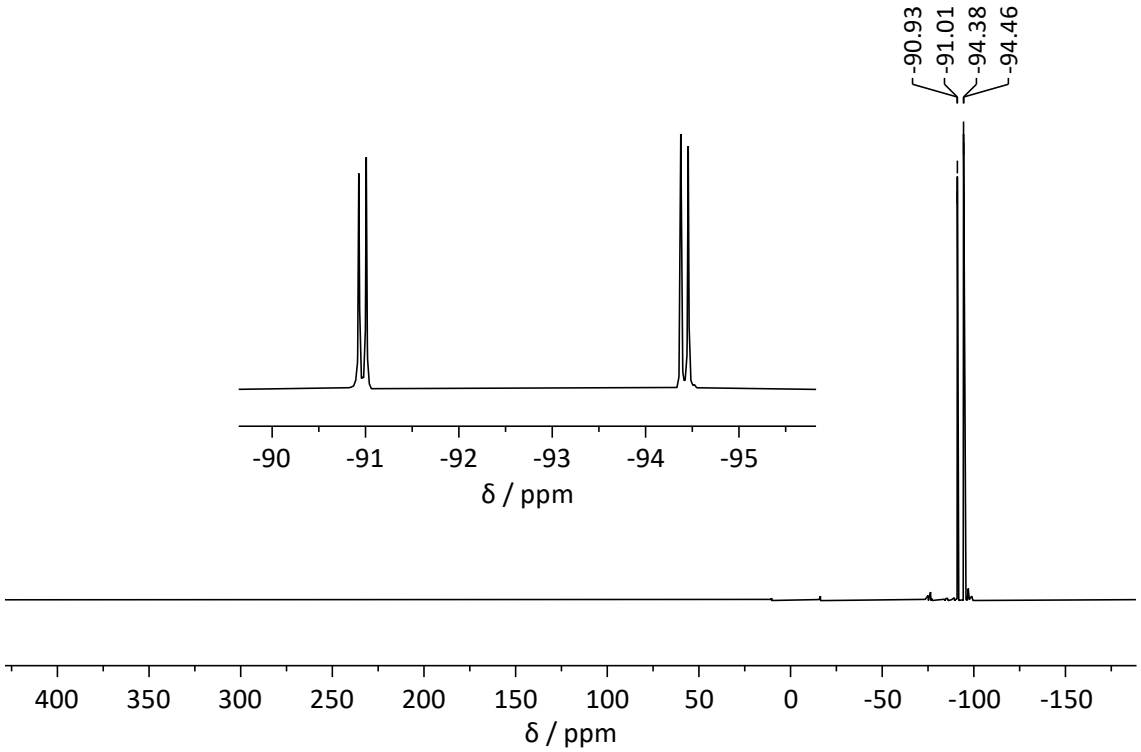

Figure S18 *$^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 202.44 Hz, 298.0 K) of* ***4b****.*

3.7. Bis(NHC) 5a

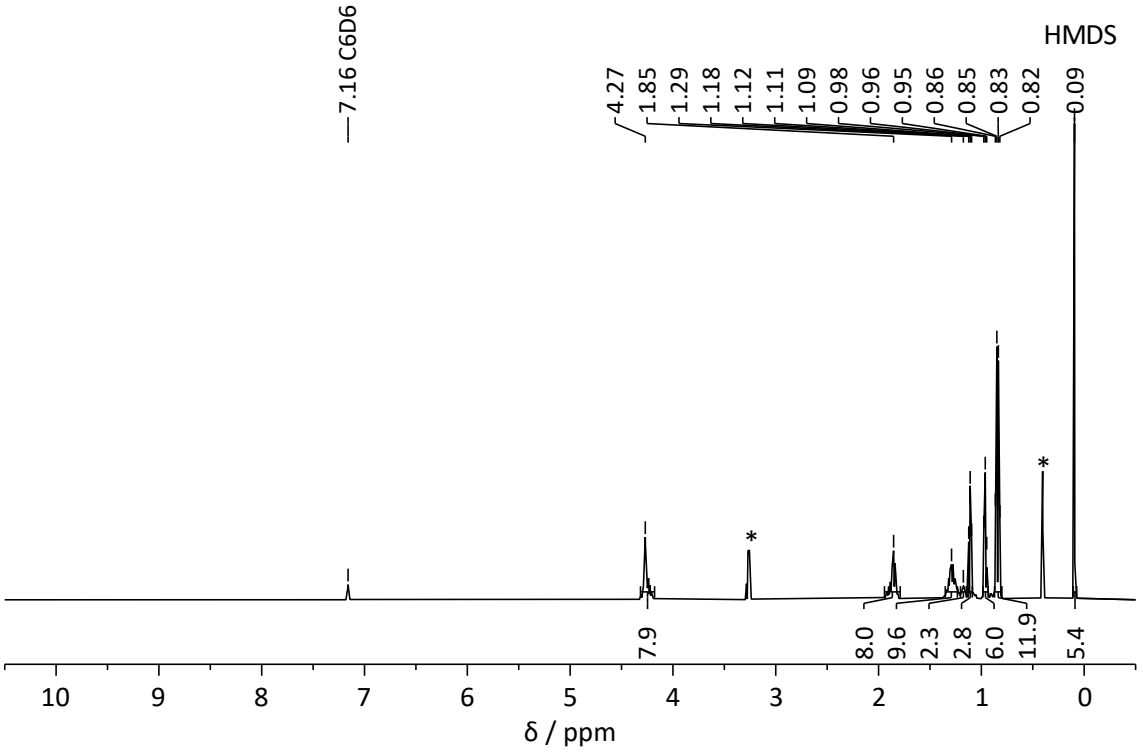

Figure S19 *^{1}H NMR spectrum (C_6D_6, 500.04 Hz, 298.0 K) of* ***5a****.*

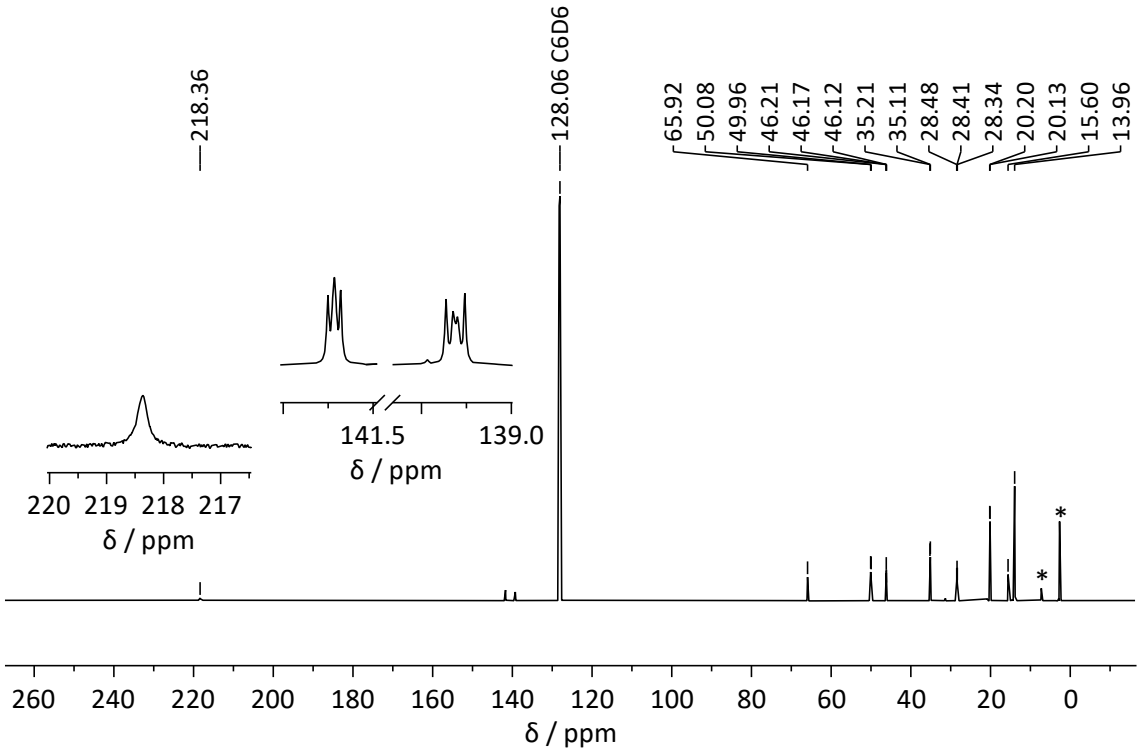

Figure S20 *$^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 125.75 Hz, 298.0 K) of* ***5a****.*

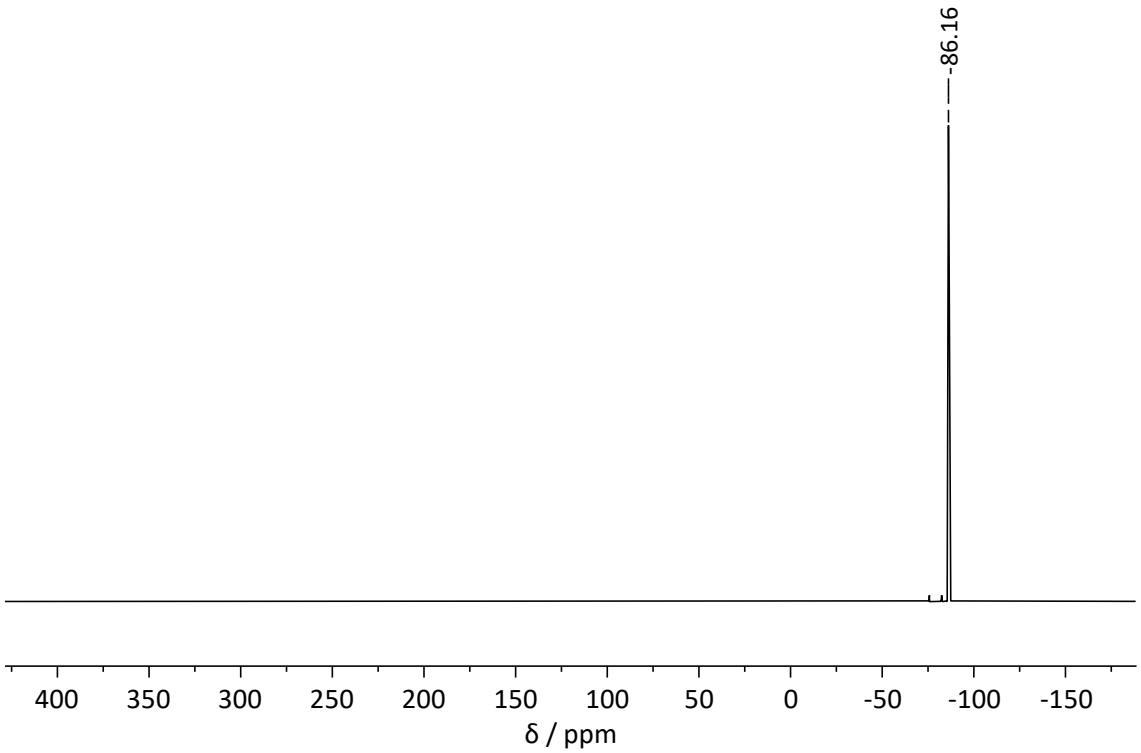

Figure S21 *$^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 202.44 Hz, 298.0 K) of* ***5a****.*

3.8. Bis(NHC) 5b

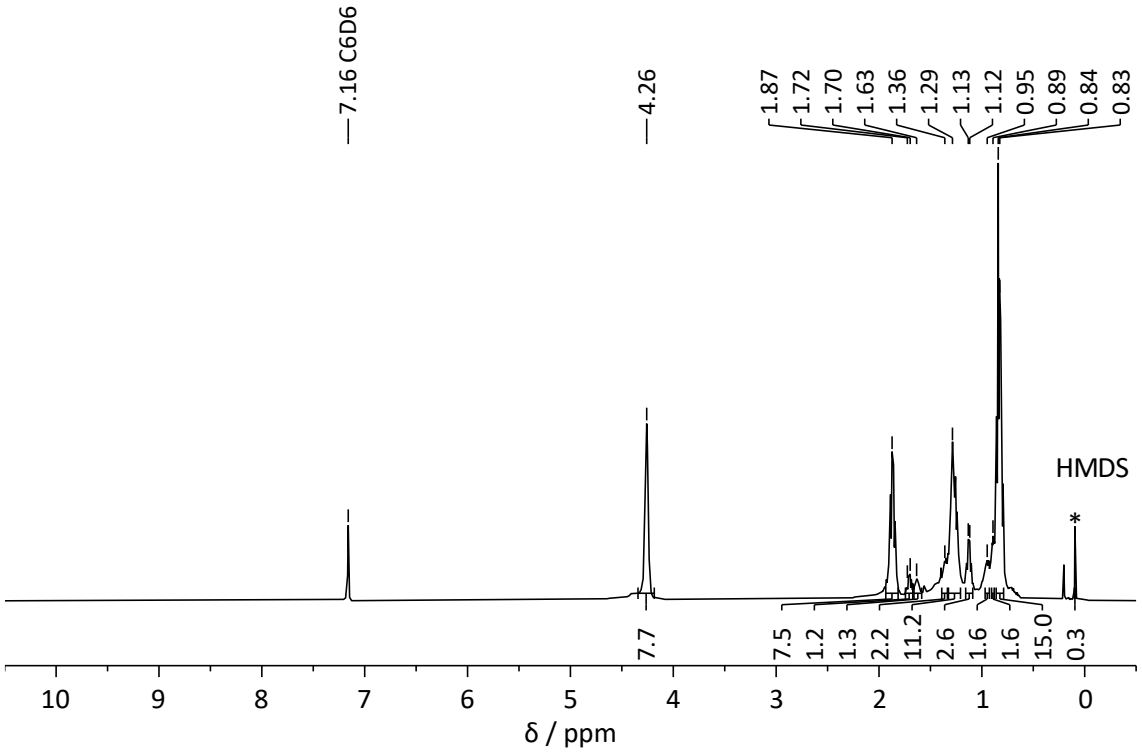

Figure S22 *^{1}H NMR spectrum (C_6D_6, 500.04 Hz, 298.0 K) of* ***5b****.*

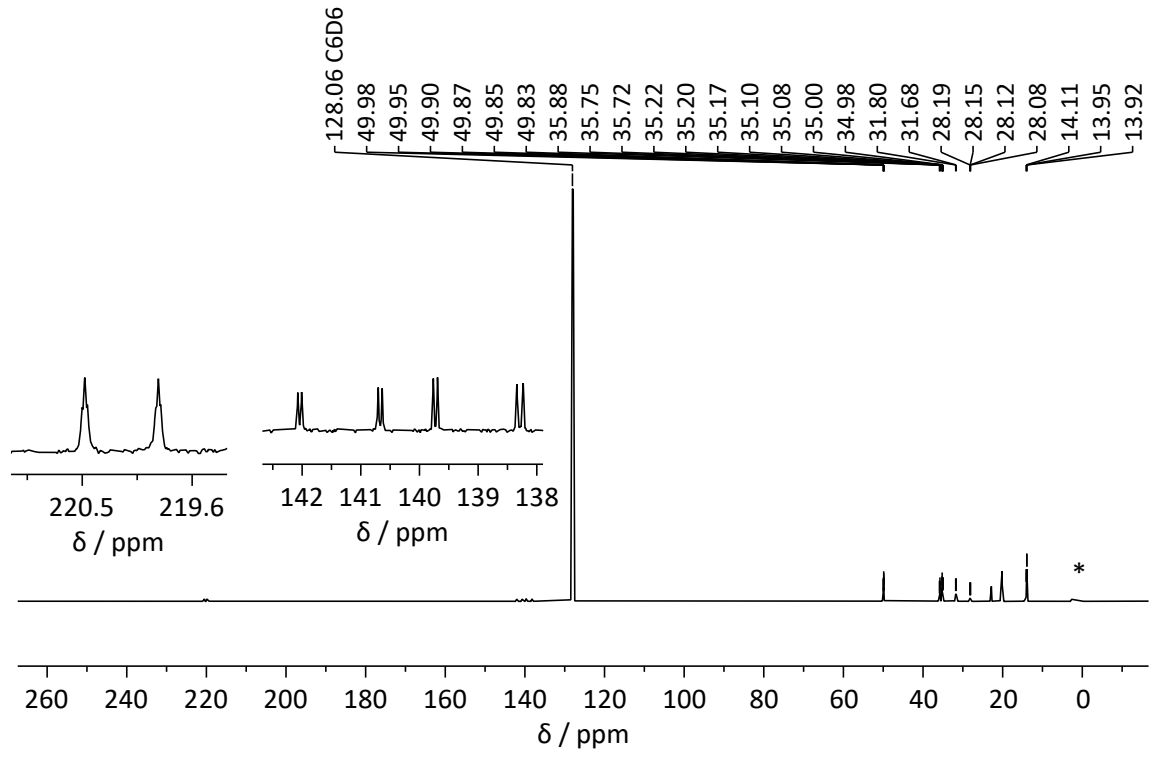

Figure S23 *$^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 125.75 Hz, 298.0 K) of* ***5b****.*

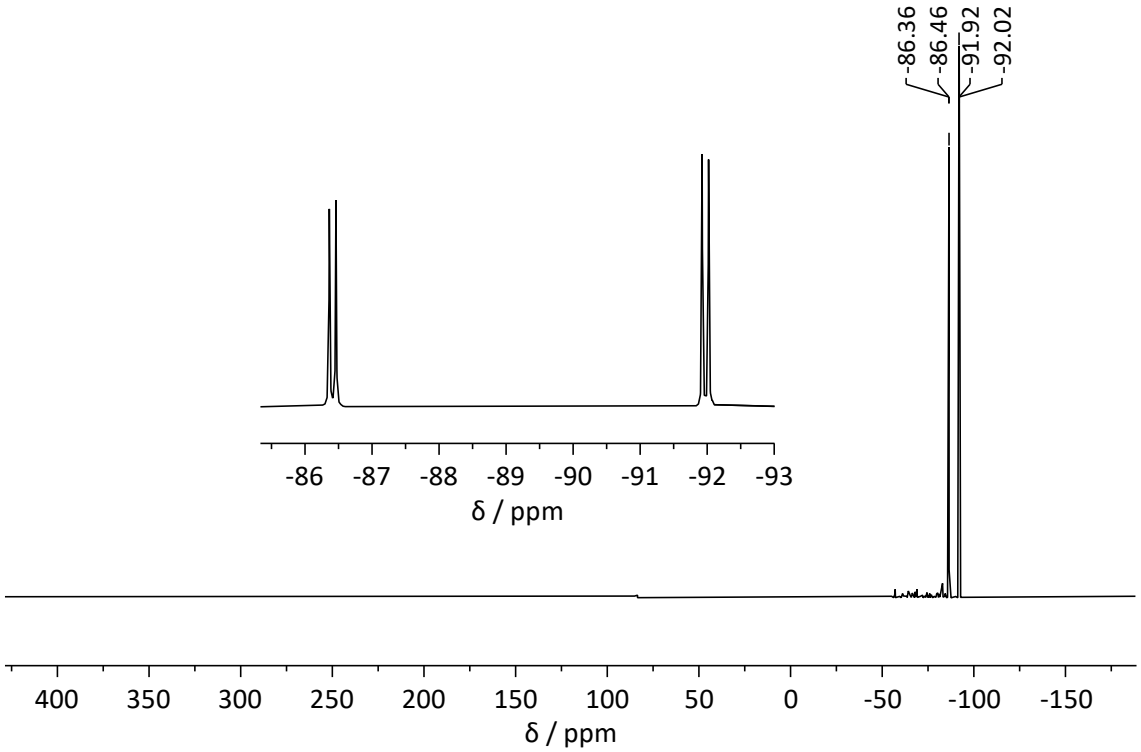

Figure S24 *$^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 202.44 Hz, 298.0 K) of* ***5b****.*

3.9. BCl_3-Bis(NHC) adduct 6a

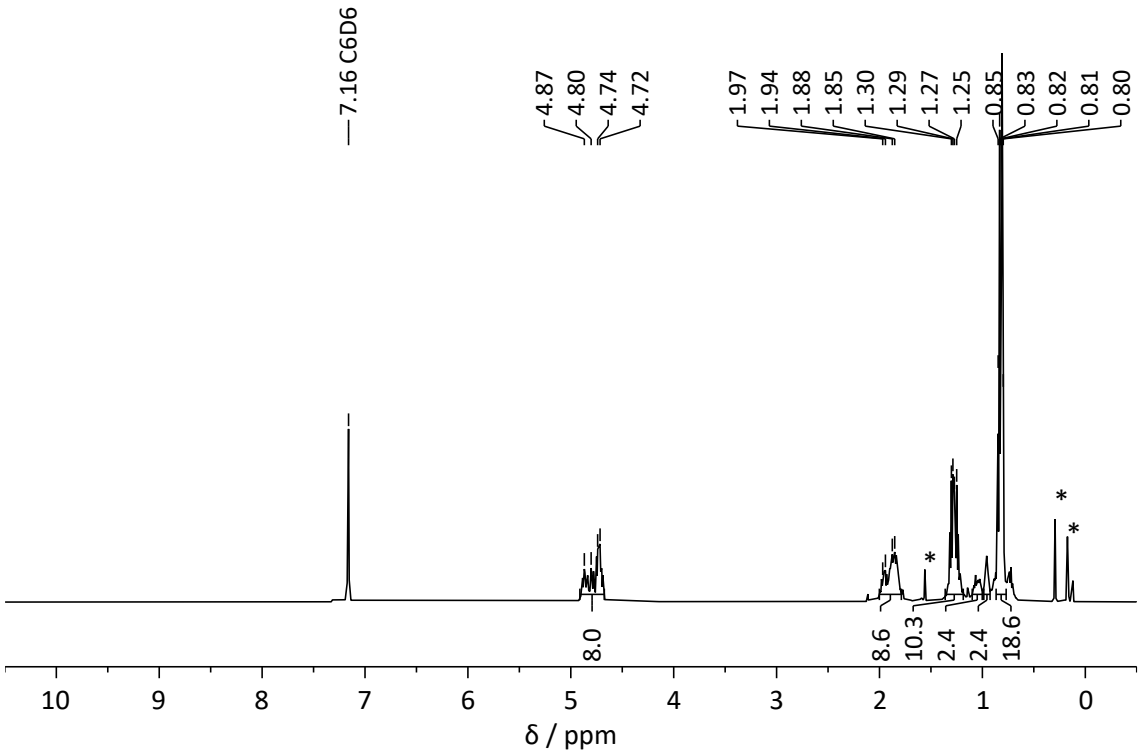

Figure S25 *^{1}H NMR spectrum (C_6D_6, 499.13 Hz, 297.9 K) of* ***6a****.*

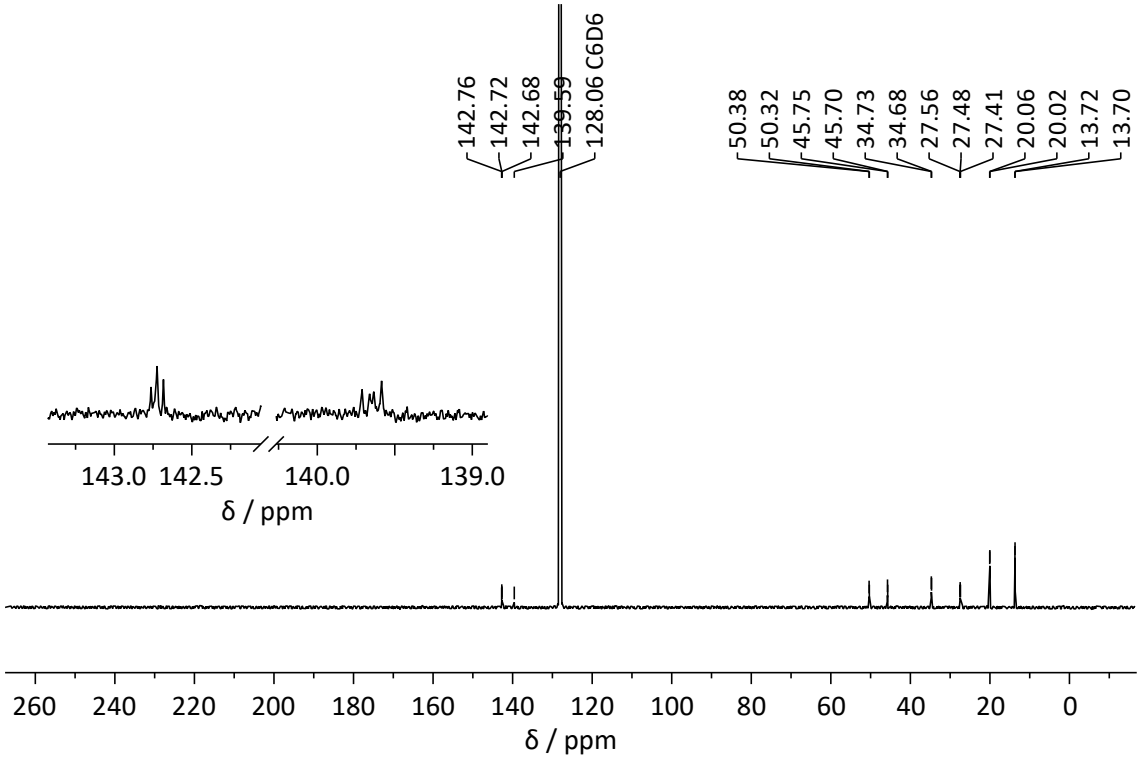

Figure S26 *$^{13}C\{^1H\}$ NMR spectrum (C_6D_6, 125.52 Hz, 298.0 K) of* ***6a****.*

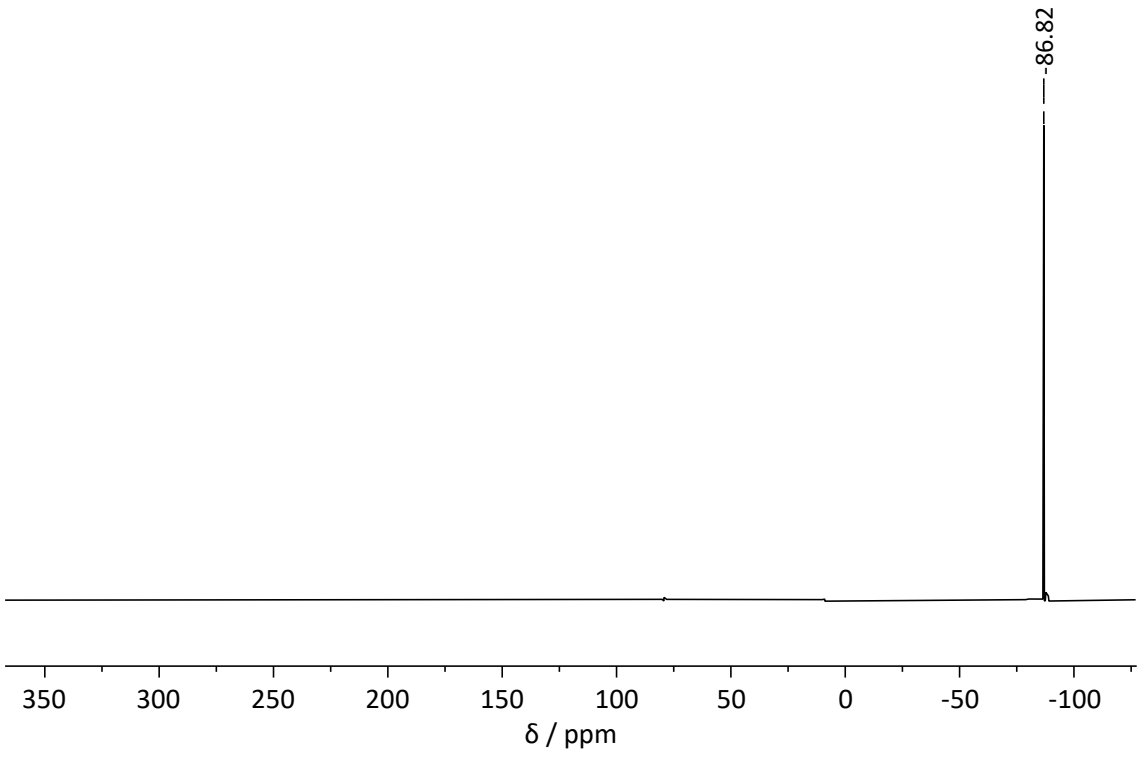

Figure S27 *$^{31}P\{^1H\}$ NMR spectrum (C_6D_6, 202.08 Hz, 297.8 K) of* ***6a****.*

3.10. CS_2-Bis(NHC) adduct 7a

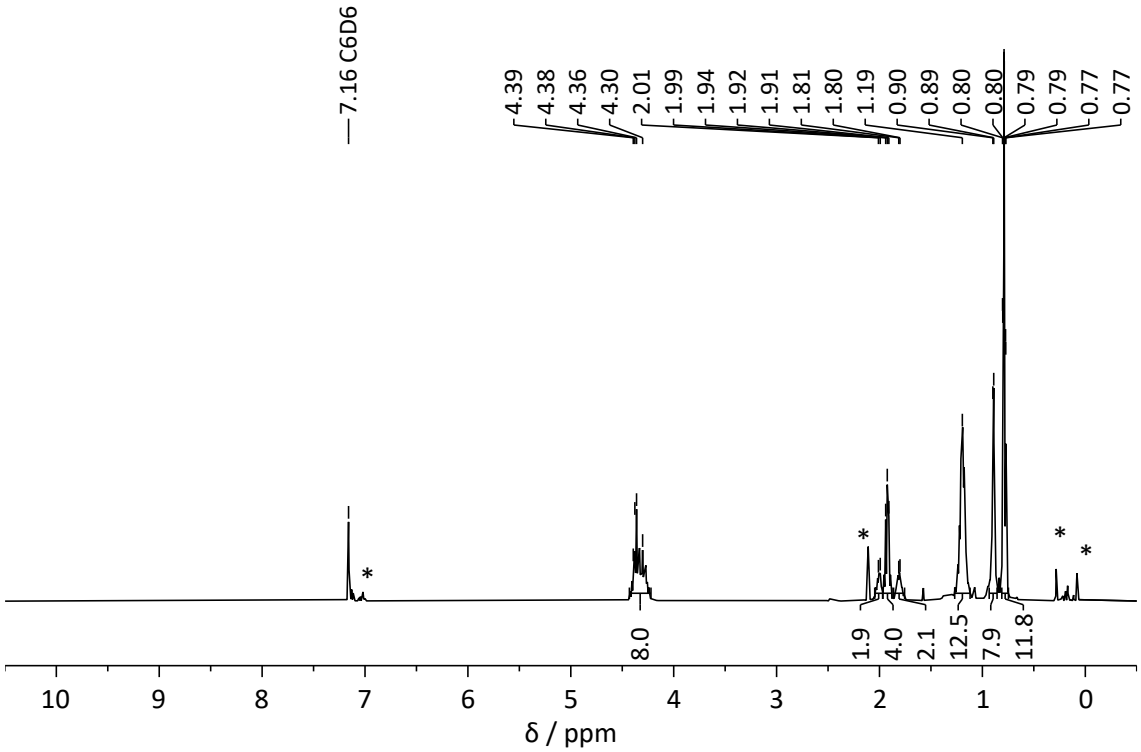

Figure S28 *^{1}H NMR spectrum (C_6D_6, 499.96 Hz, 298.0 K) of **7a**.*

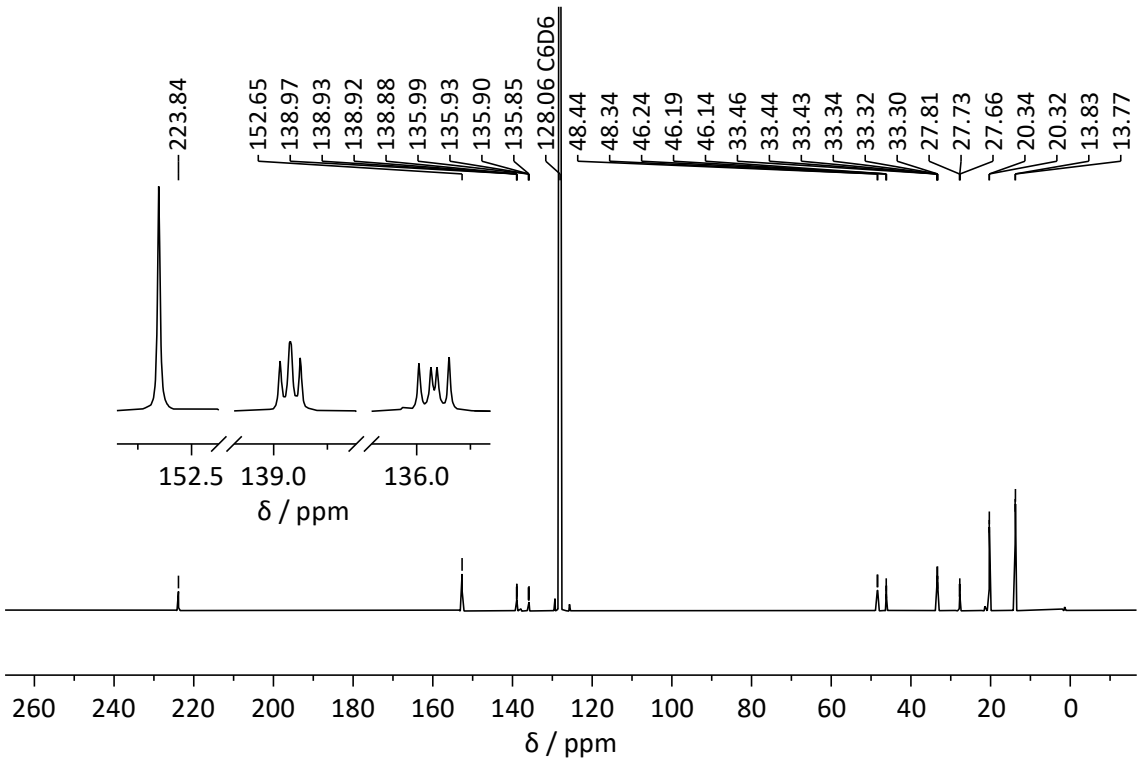

Figure S29 *$^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 125.73 Hz, 298.0 K) of **7a**.*

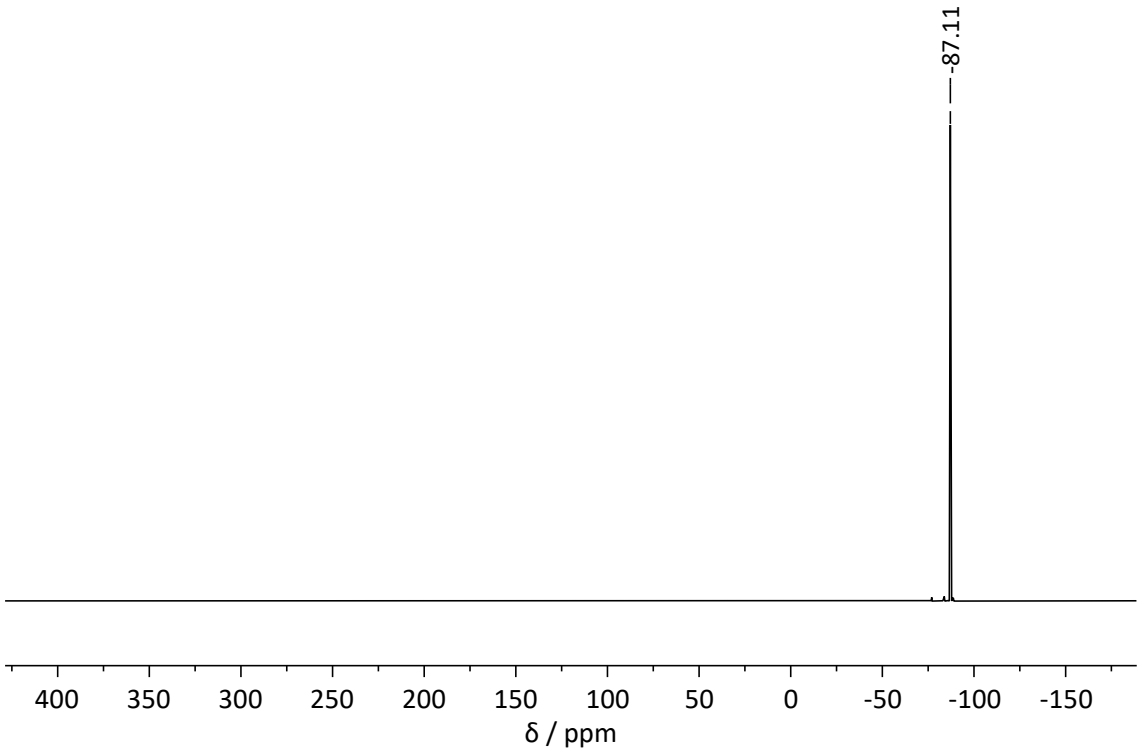

Figure S30 *$^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 202.41 Hz, 298.0 K) of **7a**.*

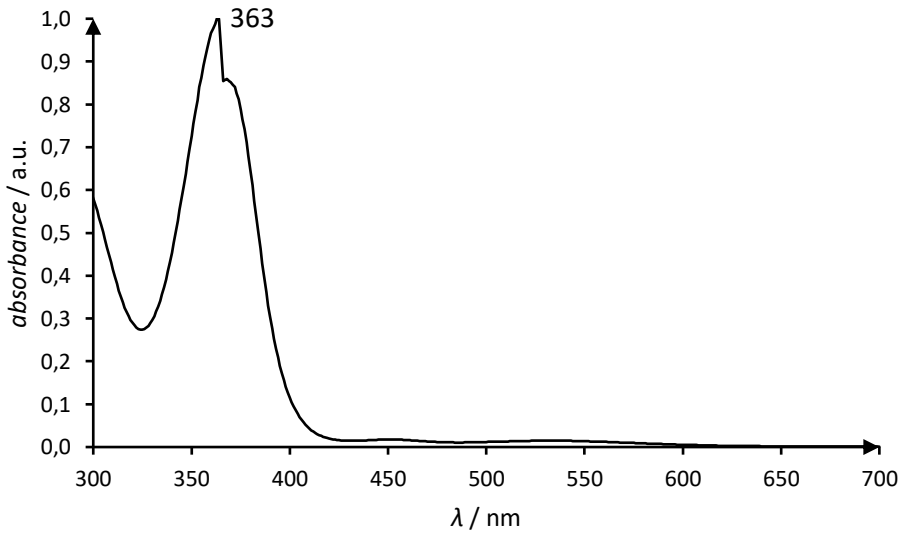

Figure S31 *UV/vis spectrum of **7a** (toluene, ca. 10^{-6} mol L^{-1}, r.t).*

3.11. PPh_2-Bis(NHC) adduct 8a

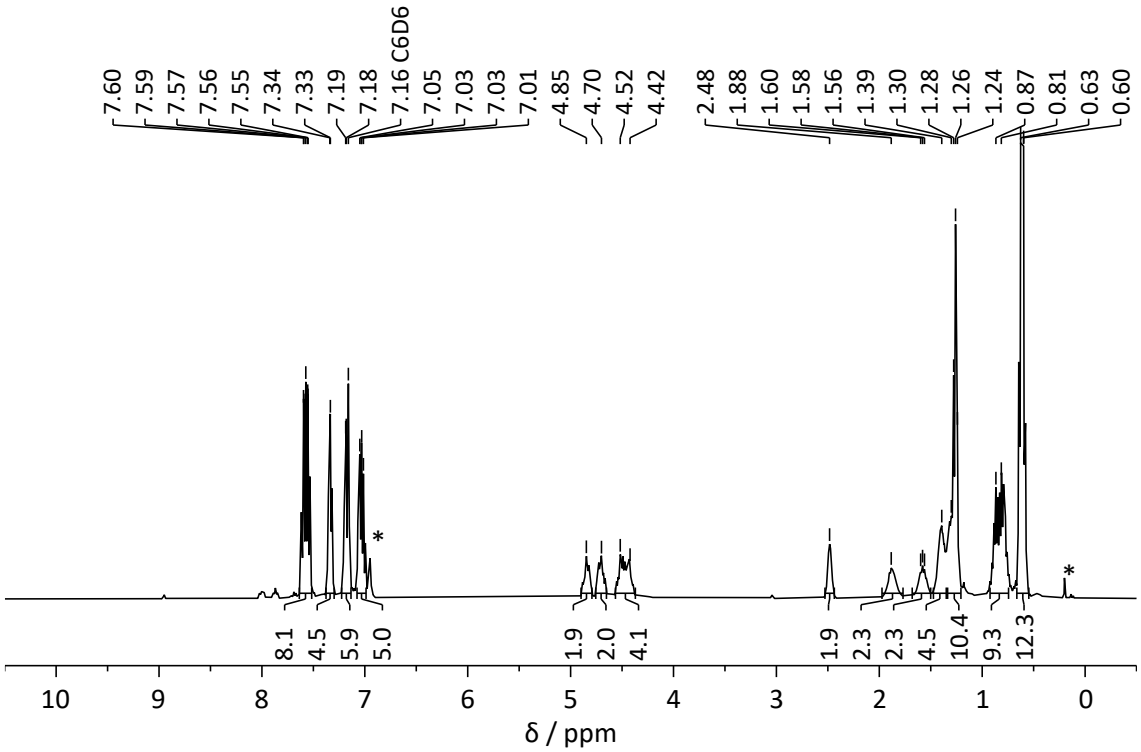

Figure S32 *^{1}H NMR spectrum (C_6D_6, 400.13 Hz, 298.0 K) of **8a**.*

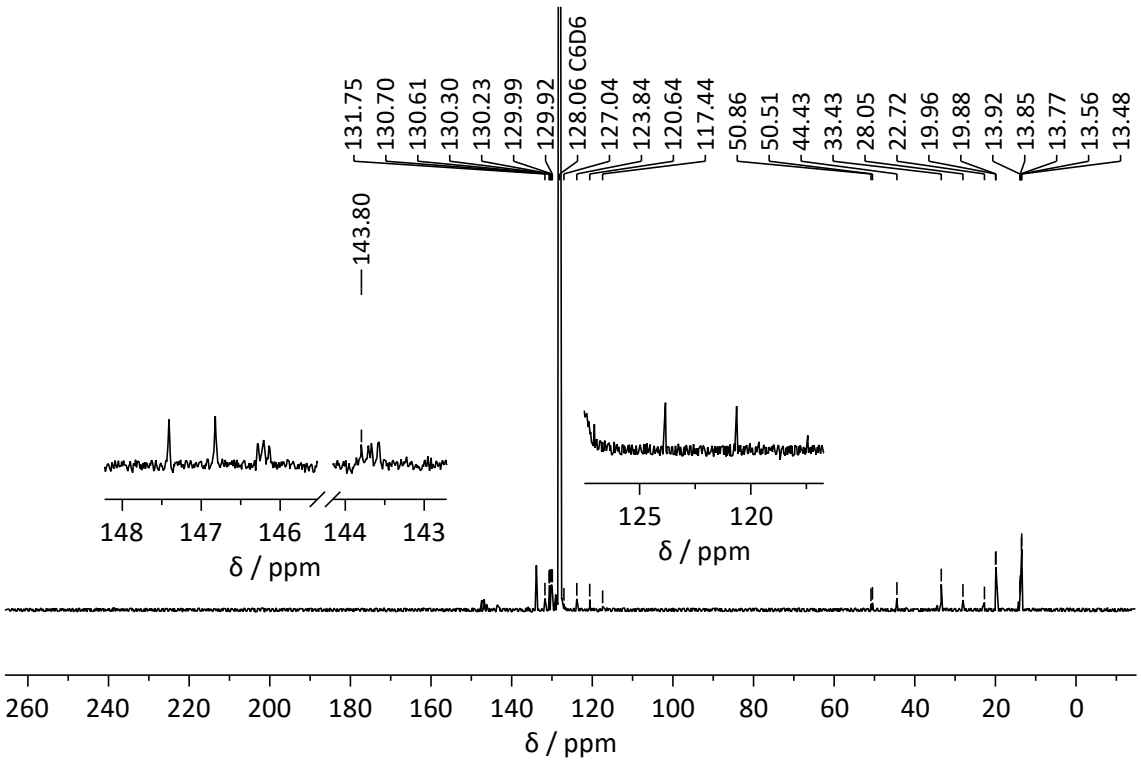

Figure S33 *$^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 100.63 Hz, 298.0 K) of **8a**.*

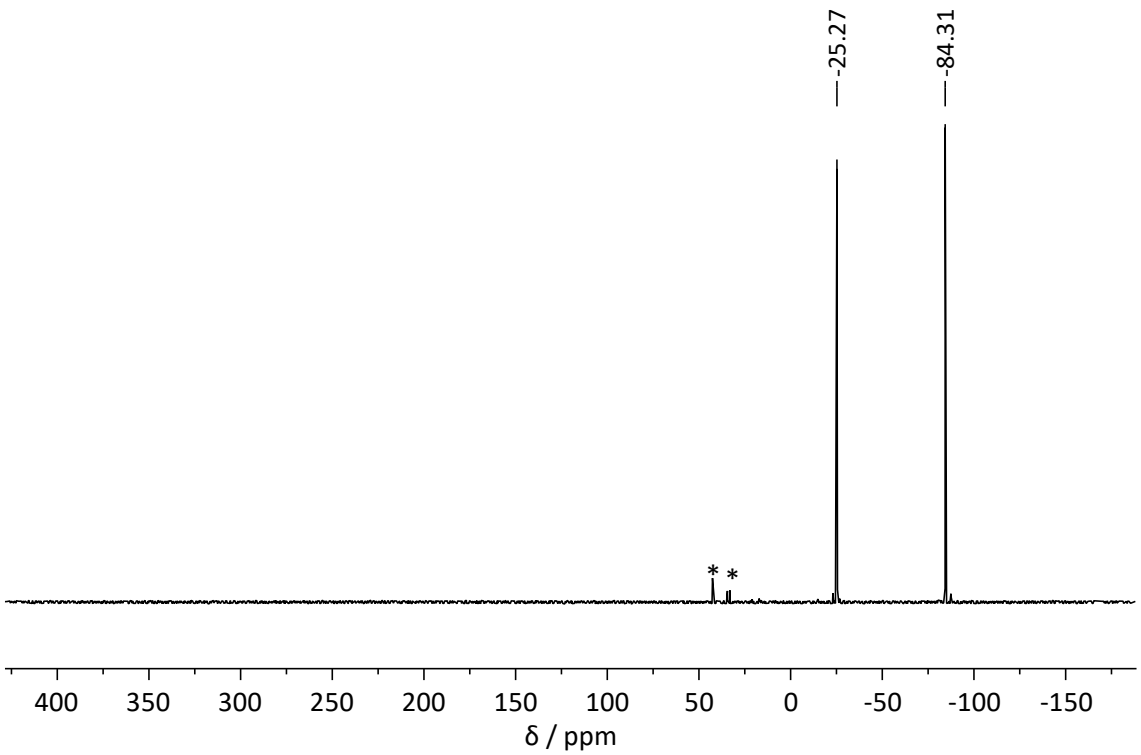

Figure S34 *$^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 162.00 Hz, 298.0 K) of **8a**.*

3.12. $Fe(CO)_4$ Bis(NHC) complex 9a

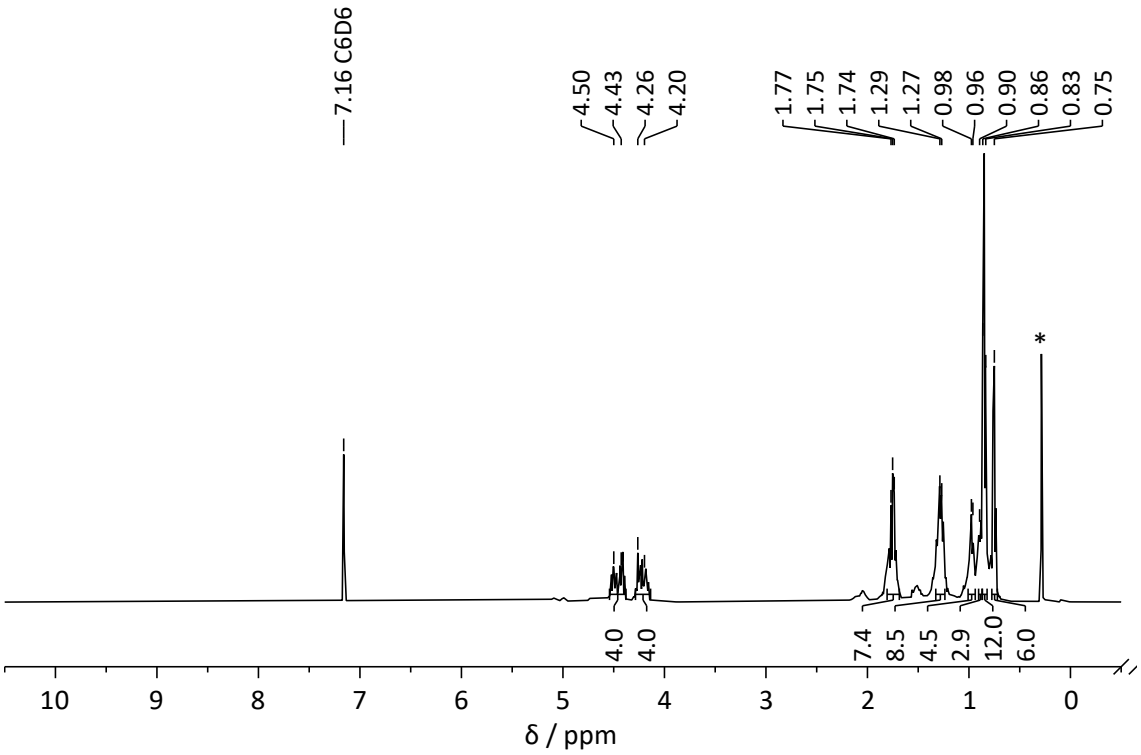

Figure S35 *^{1}H NMR spectrum (C_6D_6, 500.04 Hz, 298.0 K) of **9a**.*

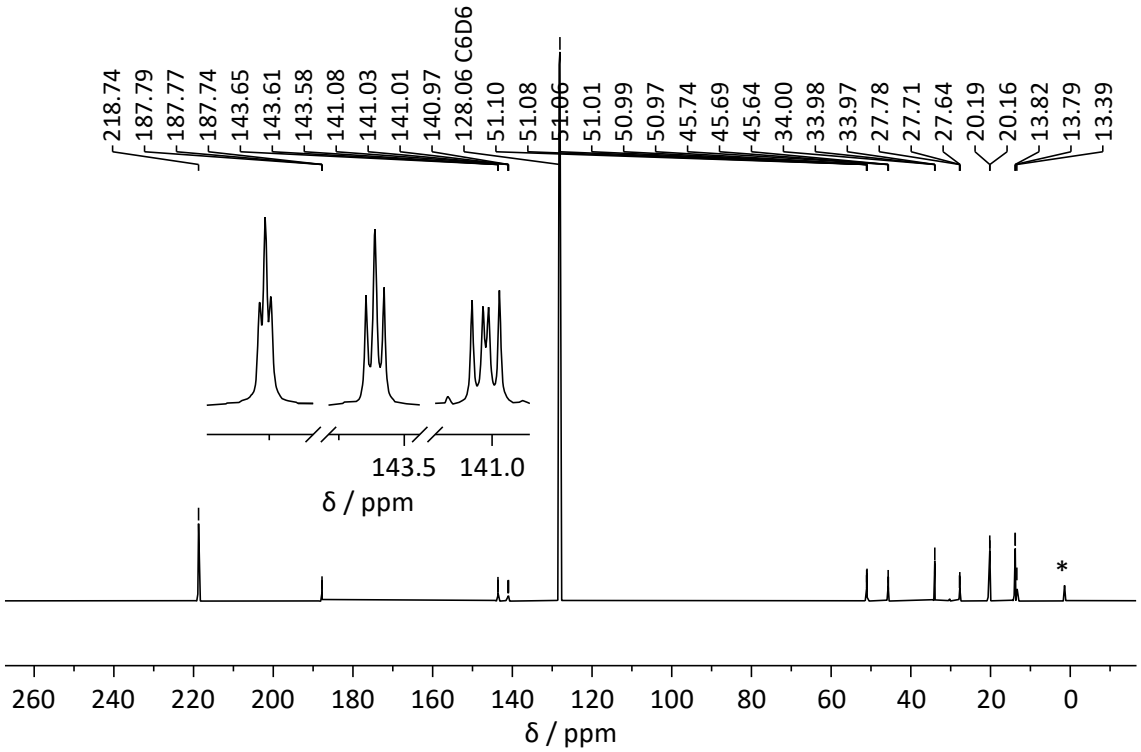

Figure S36 *$^{13}C\{^1H\}$ NMR spectrum (C_6D_6, 125.75 Hz, 298.0 K) of **9a**.*

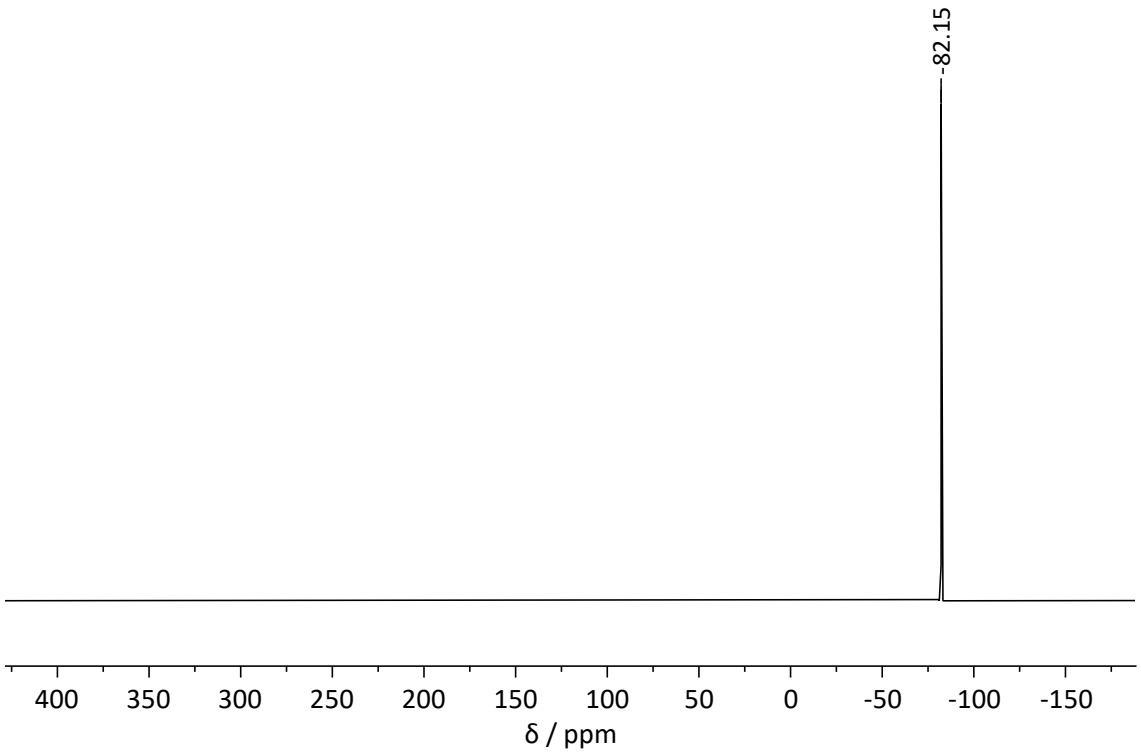

Figure S37 *$^{31}P\{^1H\}$ NMR spectrum (C_6D_6, 202.44 Hz, 298.0 K) of **9a**.*

3.13. Attempted synthesis of tri-/tetranuclear $Fe(CO)_4$-Bis(NHC) complex

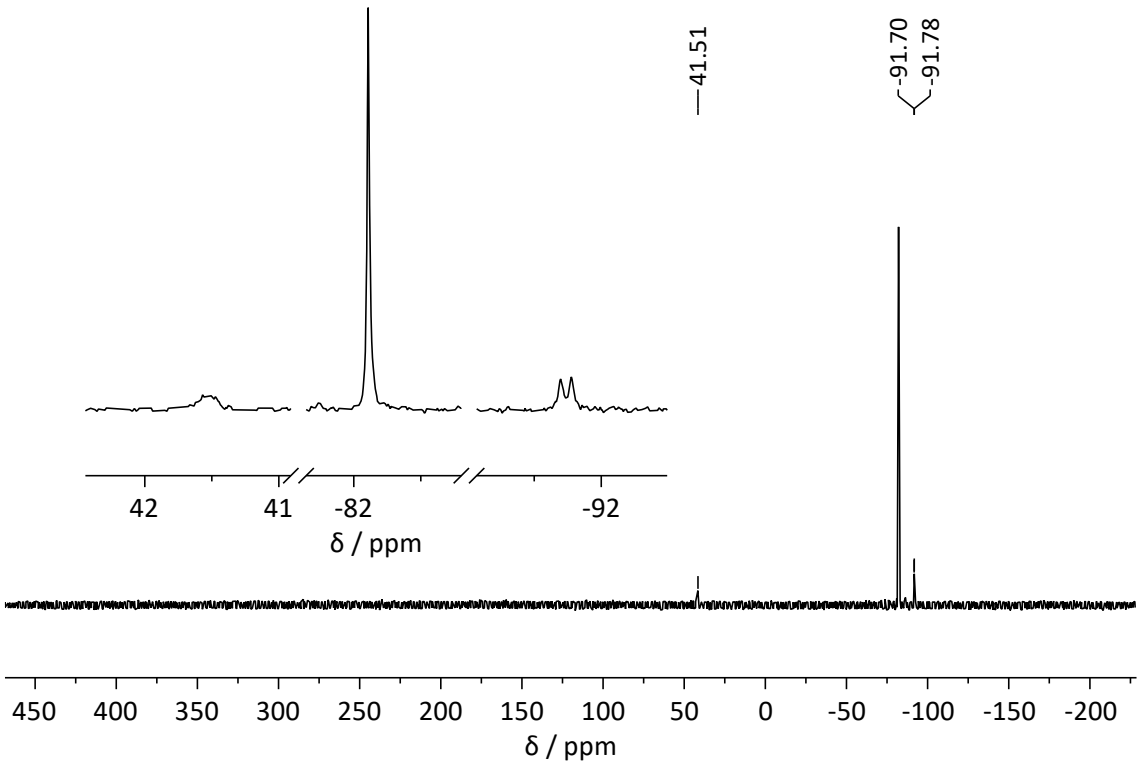

Figure S38 *$^{31}P\{^{1}H\}$ NMR spectrum (toluene, 121.51 Hz, 298.0 K) of **5a** with 2.3 eq. $Fe_2(CO)_9$ in reaction mixture.*

3.14. Temperature dependent equilibrium between 1 and 2b

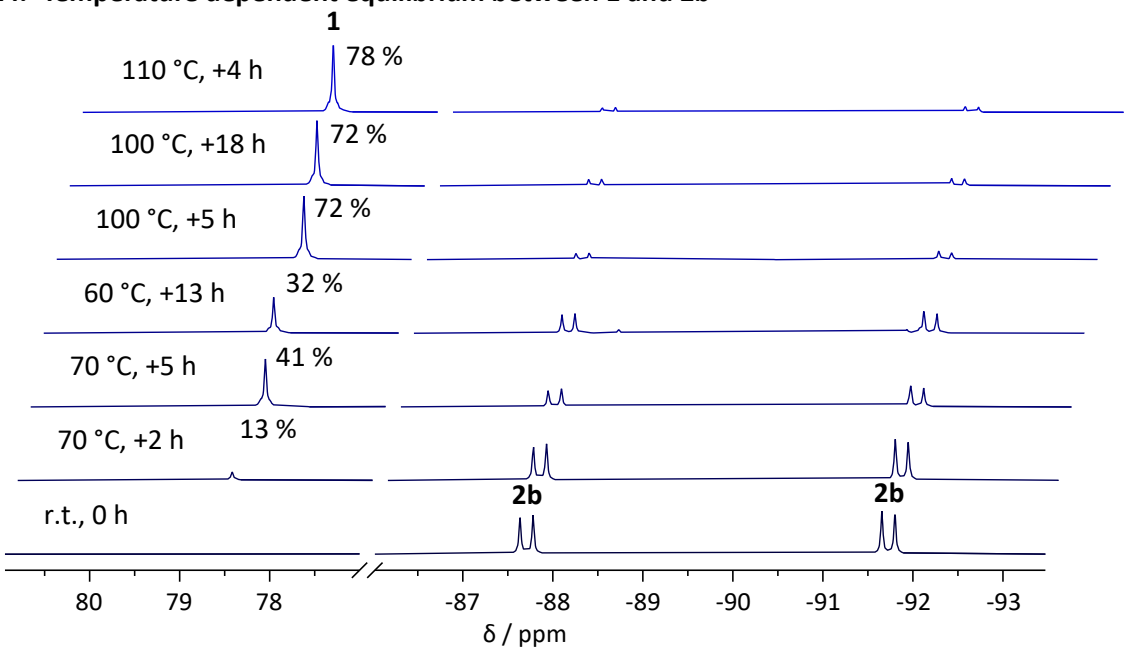

Figure S39 *$^{31}P\{^{1}H\}$ NMR spectra of **2b** in toluene in a J Young® NMR tube after heating at different temperatures.*

3.15. Bis(NHC) 5c

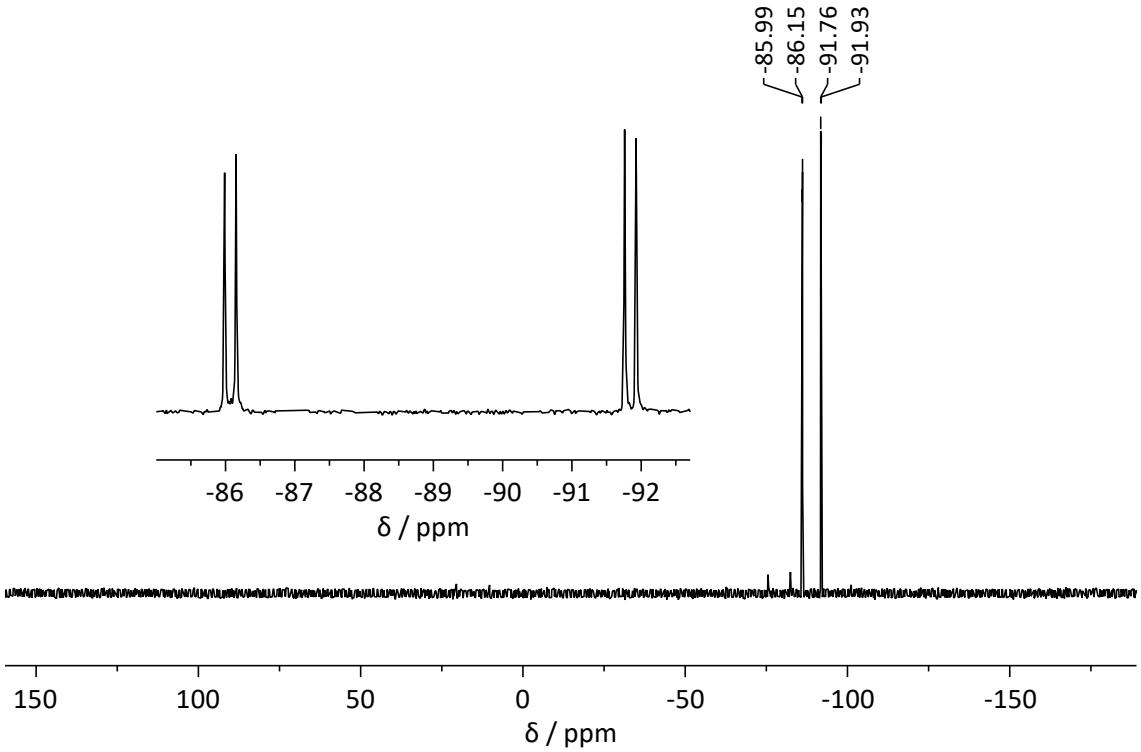

Figure S40 *$^{31}P\{^{1}H\}$ NMR spectrum (1-octene, 121.51 Hz, 298.0 K) of **5c** in reaction mixture.*

3.16. $Fe(CO)_4$ Bis(NHC) complex 9c

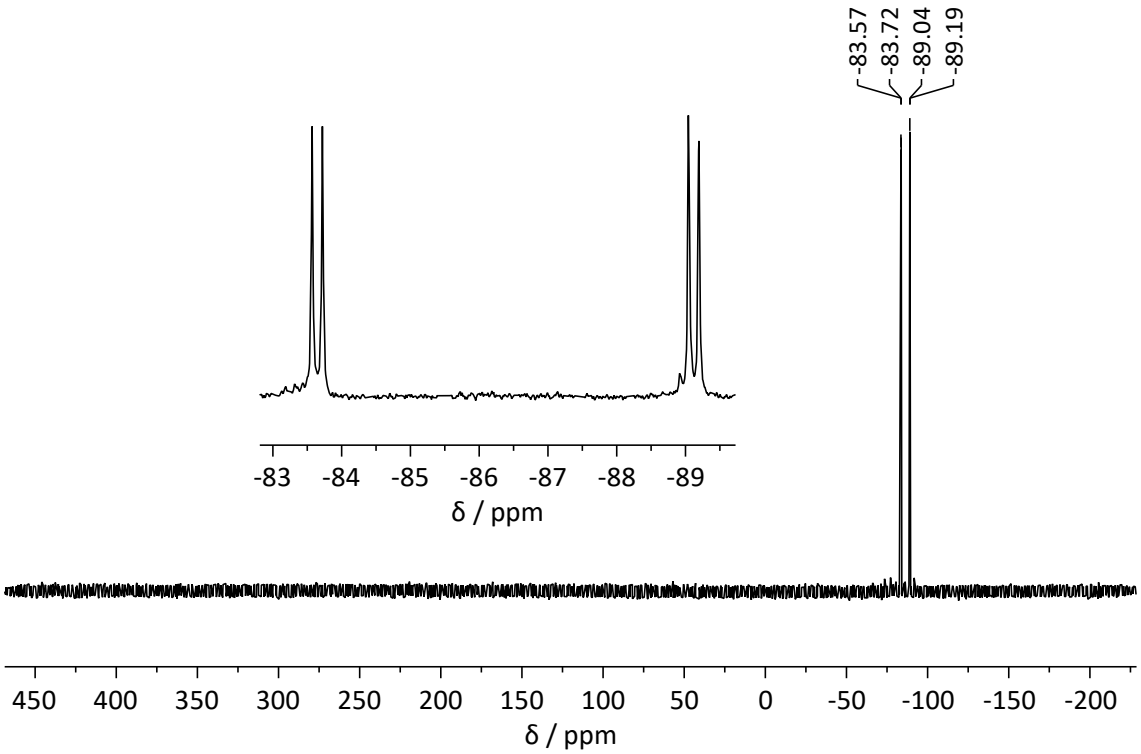

Figure S41 *$^{31}P\{^{1}H\}$ NMR spectrum (1-octene, 121.51 Hz, 298.0 K) of **9c** in reaction mixture.*

3.17. Retro-[4+2] cycloaddition of 5a

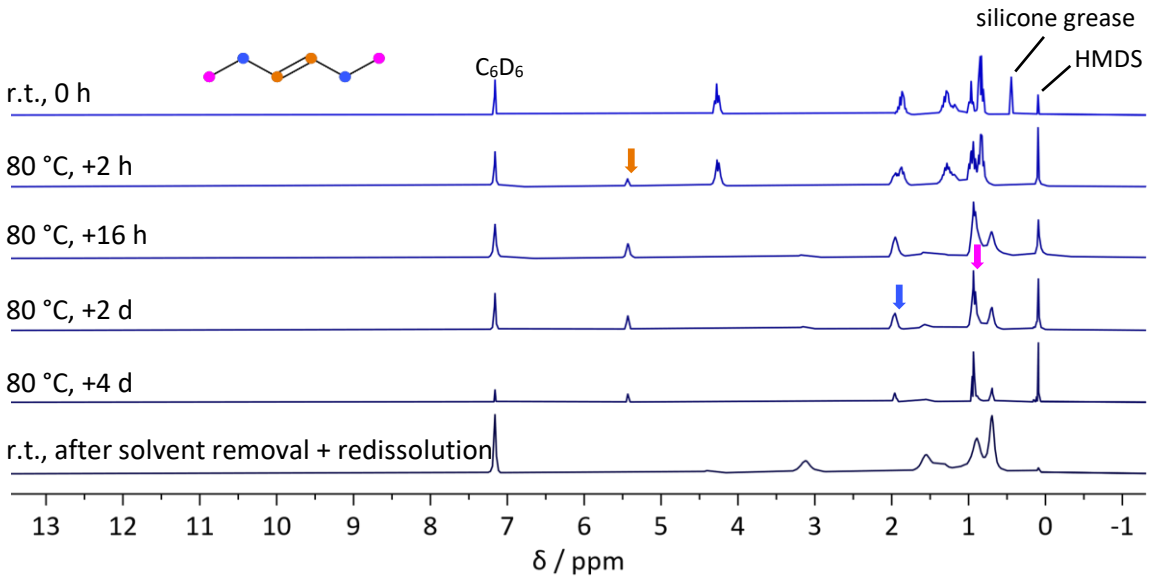

Figure S42 *^{1}H NMR spectra of the of heating a solution of **5a** in C_6D_6.The emergences of ^{1}H NMR resonances for 3-hexene are marked with coloured arrows at the point where the signal can clearly be identified.*

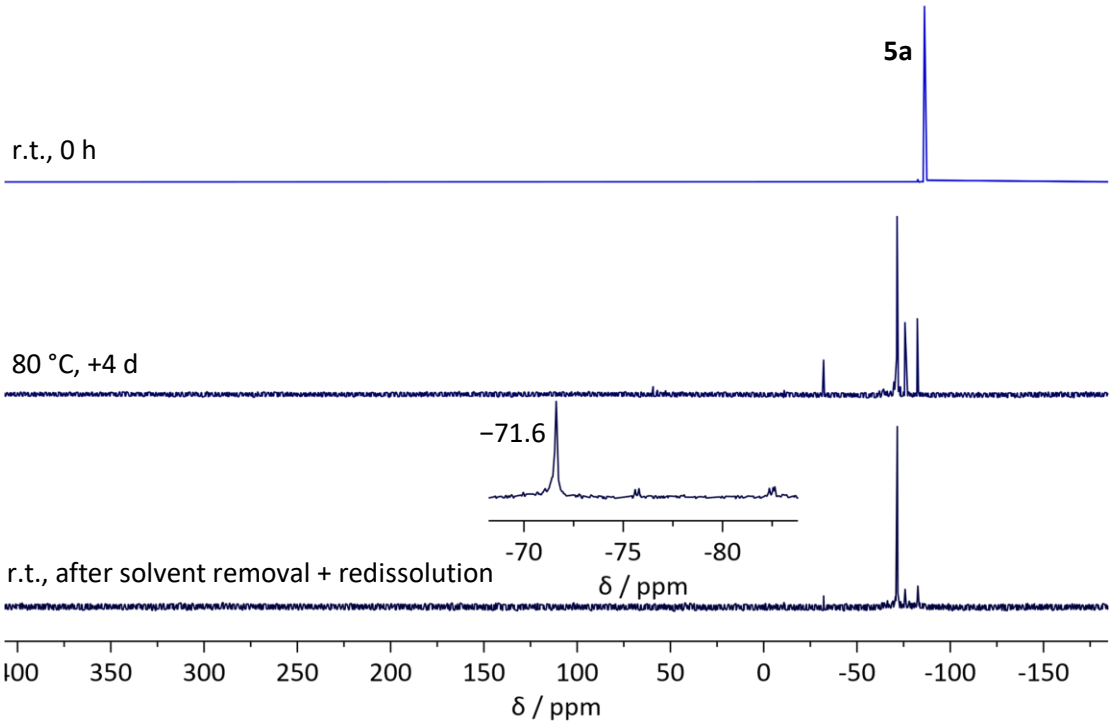

Figure S43 *$^{31}P\{^{1}H\}$ NMR spectra of the of heating a solution of **5a** in C_6D_6.*

4. Single crystal X-ray diffraction studies

4.1. 1,4-Diphosphabarrelene 2a

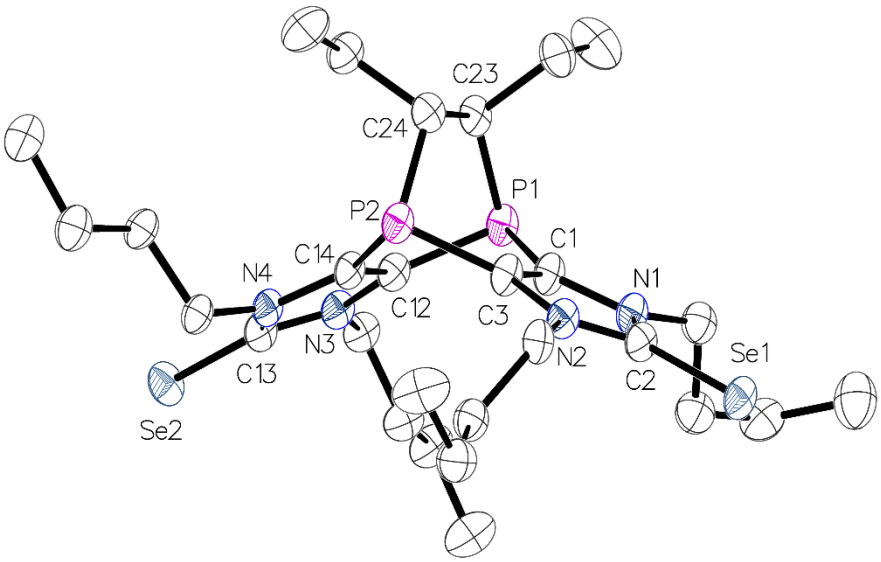

Figure S44 *ORTEP-drawing of molecular structure of* ***2a*** *in the crystal. H atoms were omitted for clarity. Ellipsoids set at 50 % probability level.*

Table S1 *Crystal data and structure refinements for 2a.*

Identification code	GSTR750, TT-500 // GXraycu_6823f
Crystal habitus	clear colourless plank
Device type	Bruker D8 Venture
Empirical formula	$C_{28}H_{48}N_4P_2Se_2$
Moiety formula	$C_{28}H_{48}N_4P_2Se_2$
Formula weight / g mol^{-1}	660.56
T / K	100
Crystal system	triclinic
Space group	*P*–1
a / Å	10.1836(4)
b / Å	11.7770(5)
c / Å	14.4181(6)
α / °	108.515(2)
β / °	95.741(3)
γ / °	97.957(3)
V / Å^3	1604.70(12)
Z	2
ρ_{calc} / g cm^{-3}	1.367
μ / mm^{-1}	3.988

F(000)	684.0
Crystal size / mm^3	0.241 × 0.039 × 0.037
Absorption correction	empirical
T_{min}; T_{max}	0.4152; 0.7535
Radiation	Cu-K$_\alpha$ (λ = 1.54178 Å)
2Θ range for data collection / °	6.542 to 135.462
Completeness to Θ	0.970
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 14$, $-17 \le l \le 17$
Reflections collected	19425
Independent reflections	5640 (R_{int} = 0.0612, R_{sigma} = 0.0598)
Data / restraints / parameters	5640 / 285 / 331
Goodness-of-fit on F^2	1.141
Final *R* indexes ($I \ge 2\sigma(I)$)	R_1 = 0.0700, ωR_2 = 0.2027
Final *R* indexes (all data)	R_1 = 0.0829, ωR_2 = 0.2108
Largest diff. peak / hole / e Å^{-3}	1.22 / −0.65

4.2. Bis(NHC) 5a

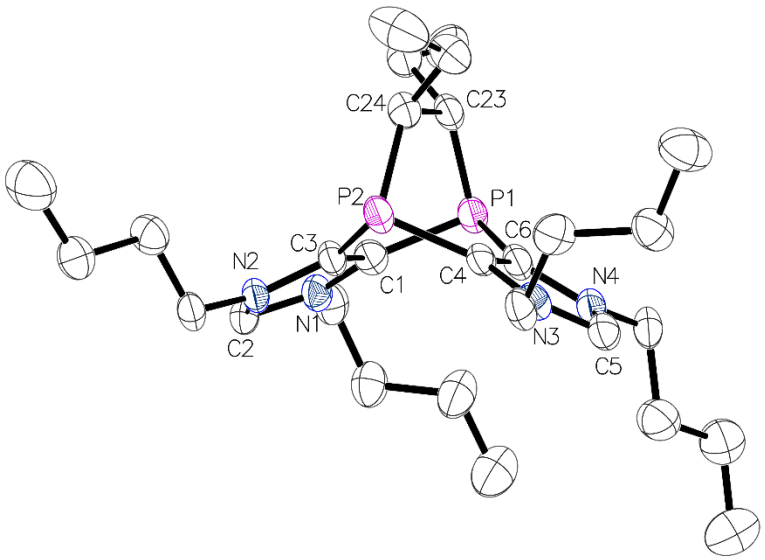

Figure S45 *ORTEP-drawing of molecular structure of 5**a** in the crystal. H atoms were omitted for clarity. Ellipsoids set at 50 % probability level.*

Table S2 *Crystal data and structure refinements for **5a**.*

Identification code	GSTR778, TT-592 // GXray6966
Crystal habitus	clear colourless plate
Device type	Stadivari
Empirical formula	$C_{28}H_{48}N_4P_2$
Moiety formula	$C_{28}H_{48}N_4P_2$
Formula weight / g mol^{-1}	502.64

T / K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	17.3905(7)
b / Å	14.4115(4)
c / Å	24.3244(11)
α / °	90
β / °	103.089(3)
γ / °	90
V / Å^3	5937.9(4)
Z	8
ρ_{calc} / g cm^{-3}	1.125
μ / mm^{-1}	1.482
F(000)	2192.0
Crystal size / mm^3	0.2 × 0.2 × 0.01
Absorption correction	multi-scan
T_{min}; T_{max}	0.6694; 0.8969
Radiation	Cu-K$_\alpha$ (λ = 1.54186 Å)
2Θ range for data collection / °	7.18 to 135.492
Completeness to Θ	0.978
Index ranges	$-15 \le h \le 20$, $-17 \le k \le 14$, $-29 \le l \le 27$
Reflections collected	73734
Independent reflections	10503 (R_{int} = 0.1397, R_{sigma} = 0.0720)
Data / restraints / parameters	10503 / 541 / 636
Goodness-of-fit on F^2	1.043
Final R indexes ($I \ge 2\sigma(I)$)	R_1 = 0.0890, ωR_2 = 0.2054
Final R indexes (all data)	R_1 = 0.1519, ωR_2 = 0.2474
Largest diff. peak / hole / e Å^{-3}	0.49 / −0.50

4.3. BCl_3-Bis(NHC) addut 6a

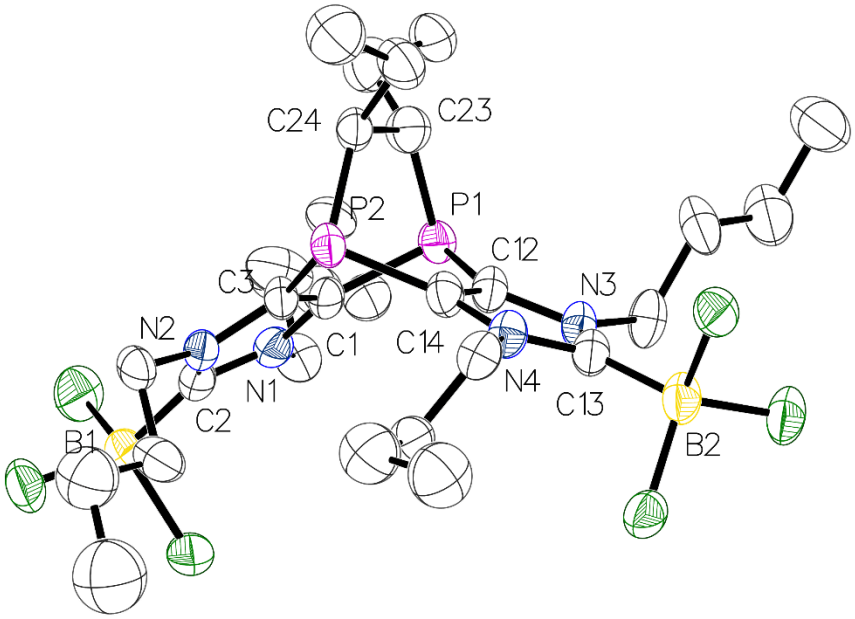

Figure S46 *ORTEP-drawing of molecular structure of 6**a** in the crystal. H atoms were omitted for clarity. Ellipsoids set at 50 % probability level.*

4.4. $Fe(CO)_4$-Bis(NHC) complex 9a

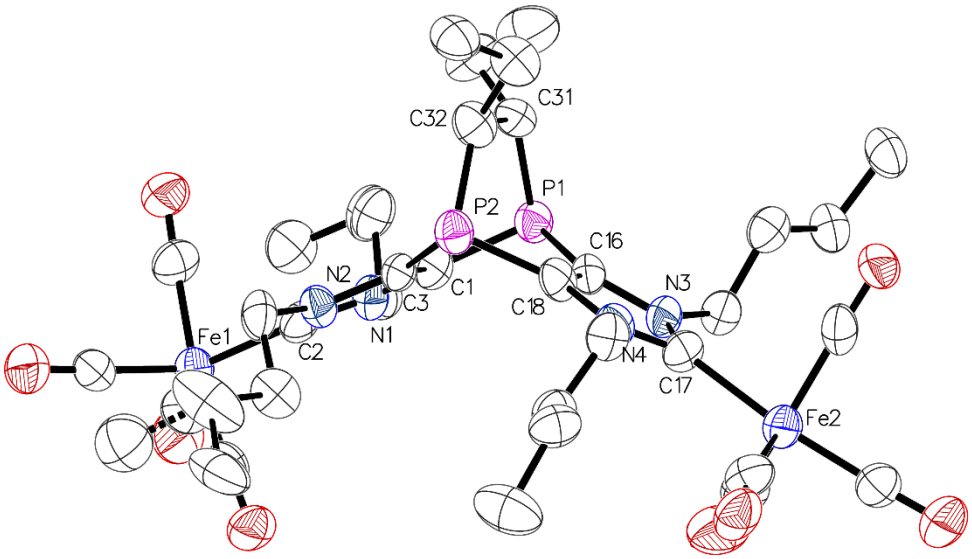

Figure S47 *ORTEP-drawing of molecular structure of 9**a** in the crystal. H atoms were omitted for clarity. Ellipsoids set at 50 % probability level.*

5. Computational details

All geometric optimisation and energy calculations were performed with *ORCA 5.0*.[5,6] Structures were optimised at the TPSS-D4/def2-TZVP/$CPCM_{THF}$ level of theory which combines the TPSS[7] meta-GGA density functional with the charge dependent atom-pairwise DFT-D4 dispersion correction which uses the D4(EEQ)-ATM dispersion model[8] and the def2-TZVP basis set[9–12] using the conductor-like polarisable continuum model (CPCM)[13] for THF (ε = 7.25). The minimum or transition state nature of the compounds has been determined by numerical frequency calculations. All minima have zero imaginary frequencies below −50 cm^{-1} which can be the numerical error according to the *ORCA 5.0.4* manual.[14] If single imaginary frequencies between 0 and −50 cm^{-1} appeared they were checked carefully and in all cases only belonged to small rotations of *N*-Me substituent whose contributions in energy difference fall within the method's error margins. Transition states possess only one imaginary frequency that describes the transition from starting material to product. The transition states have been computed with the help of the nudge elastic band optimiser (NEB)[6,15] as implemented in *ORCA 5.0*. Single-point calculations were performed at the PW6B95-D4/def2-QZVP/$CPCM_{THF}$ level of theory which combines the PW6B95 hybrid-meta-GGA functional[16] with the larger def2-QZVP basis set.[9–12] NICS(1) values were calculated at the B3LYP-D4/def2-TZVPPD level of theory combining the hybrid functional B3LYP[16] with the def2-TZVPPD basis set[9–12] and using the NMR module of ORCA 5.0 utilising Gauge including atomic orbitals (GIAOs).[17] Values were obtained by calculating the NICS(1) value of benzene at the same levels of theory. The B3LYP functional was chosen here for general comparability as it is often used, performed well for the synthesised systems in a self-conducted small study and gave reliable results with relatively low resource cost. The density-fitting RI-J (def2/J)[9,17] approach was used to accelerate geometry optimisations, numerical frequency and single point energy calculations.

The graphical representations of the calculated structures and their frontier molecular orbitals (FMOs) were generated with *UCSF Chimera 1.15*.[18]

Below are listed the optimised cartesian coordinates (in Å) with electronic energies (in Hartree) in THF solution. All structures of new compounds were computed as model compounds with *N*-methyl instead of *N*-*n*-butyl substitution to save computational costs. Zero point energies (E_{ZPE}), thermal corrections (E_T) at 298.15 K and entropy corrections (E_S) were taken from the optimisation calculations.

5.1. 1,4-Diphosphinine Me-1

E = − 6097.14773569006
E_{ZPE} = 0.21546057
E_T = 0.01970719
E_S = −0.06819458

C	-6.63659639604487	-6.76349954779763	-0.57437989494840
C	-7.01810281038773	-5.46793769503506	-0.98979277550357
C	-4.58925997056719	-4.59092680656701	-0.48861089151771
C	-4.20812501952794	-5.88621426362723	-0.07201944422323
P	-6.11504632344754	-3.97316931032637	-1.07857002716934
P	-5.11073904930460	-7.38130306527148	0.01539260018824
N	-7.76343167323847	-7.56271540650167	-0.71509567477563
N	-8.35412542067073	-5.55730274052072	-1.35752668735538
N	-3.46236502488408	-3.79177491126075	-0.34809678467092
N	-2.87256135163947	-5.79650218136778	0.29726426623751
C	-9.13715627156274	-4.42944132870743	-1.84950185040084

H	-9.15478659860490	-3.64135607172510	-1.09138366195778
H	-8.68711916939980	-4.04651203792609	-2.76984811339602
H	-10.14785880432339	-4.78917335772211	-2.04431854452550
C	-7.79636573754305	-8.98342537610885	-0.38622870594260
H	-7.06122100701810	-9.51543426627857	-0.99657340216856
H	-7.56282362851465	-9.11692771566574	0.67388376285446
H	-8.80107938203511	-9.34834796592270	-0.60112625486687
C	-2.08981735200652	-6.92415149805342	0.79013012127655
H	-2.05535426100451	-7.70532782936717	0.02541818776488
H	-1.08449120628588	-6.55997413695446	1.00359763985677
H	-2.55169749250347	-7.31810341610561	1.69985784847377
C	-3.42922396171315	-2.37115287972720	-0.67734494170440
H	-2.42210444849058	-2.00828098769303	-0.47040169710144
H	-3.67087585443098	-2.23765498358184	-1.73562382751375
H	-4.15839116956245	-1.83730667470270	-0.06143332927126
Se	-0.70977823540036	-3.90794120454322	0.48230109174520
C	-2.40380846072507	-4.51870859053487	0.13231596637379
C	-8.82249584556139	-6.83539934713249	-1.19380113133125
Se	-10.51669807360122	-7.44603440327164	-1.54318384442673

5.2. 1,4-Diphosphabarrelene Me-2a

E = −6333.43866871791
E_{ZPE} = 0.38173882
E_T = 0.02732074
E_S = −0.08286413

P	7.35624341239364	5.63915417540039	5.84925366042591
P	5.08170920093830	6.67855235722052	8.06455140005477
N	7.23186120375796	8.47597915907024	5.25405278733431
N	5.77153929549200	9.16106232069358	6.73387673260759
N	3.69277502274990	4.46096756723462	6.81640676278227
N	5.19789012001919	3.75774564850488	5.39078017152605
C	6.77443833386490	7.35566584111325	5.92886574841748
C	6.61208809463244	9.59558457703808	5.74371203291806
C	5.86539268780132	7.78199708232352	6.85686643474727
C	4.77084794977499	5.32697253453042	6.89470335001461
C	3.94777381057381	3.48813754422329	5.88243579870651
C	5.71351911074939	4.88779320835554	6.00905080462092
C	8.21378516440371	8.49194858154322	4.17428121191606
C	4.90870544493200	10.04359982944466	7.51321840121403
C	2.47138382486157	4.56233311546466	7.61084095206870
C	5.85859843984302	2.96381189646964	4.35889221657969
C	7.80485871455491	5.56264828750473	7.69860710200930
C	6.69714553225507	5.91488425579716	8.72907616583978
C	9.06111178666299	6.42320275637364	7.94332958372970
C	10.26612538528977	6.06244548923349	7.07133439160715
C	6.35117609527563	4.69103075479542	9.60001151173911
C	5.41757556864323	4.98957354296809	10.77577627106464
H	7.75600168659086	8.89411073347040	3.26752160564536
H	8.54383332052652	7.46584154502716	4.00747926172763
H	9.06050670272746	9.12017866796213	4.45946054011360
H	4.31960521199971	9.42448368933307	8.19088512297787

H	4.25263453205861	10.59908014790104	6.83935159040186
H	5.52057411873013	10.74835118452757	8.08111310604392
H	1.99505930083498	5.52793987670827	7.42658748599395
H	2.71588758197258	4.46632200551515	8.67140396459549
H	1.81228114063075	3.74992129763574	7.30208368607004
H	5.24129890870117	2.94819281702845	3.45800260181502
H	5.99972088476047	1.94130486941036	4.71635351763439
H	6.82349544699987	3.42698788870003	4.14871516473445
H	8.06912128653990	4.50561803507988	7.83510417793890
H	7.08491154293490	6.71096528182100	9.37886031683053
H	8.79534761108648	7.47929279897690	7.80355616560509
H	9.32997461572789	6.30982080471287	9.00146302353947
H	11.14060261731659	6.65110353993091	7.36744634109967
H	10.07352925852339	6.26042360976937	6.01105988300072
H	10.51912001573812	5.00071997750067	7.17266467737973
H	5.91870771468669	3.91111854903911	8.95922468300756
H	7.29726026997375	4.28661287361363	9.98219712307451
H	5.28902644949339	4.09717828710503	11.39708474068826
H	4.42529300148162	5.30740598719873	10.43714319755294
H	5.82762168581111	5.78751389735268	11.40562230825551
Se	2.84864497804221	2.09798178920121	5.35831324174368
Se	6.85029591664021	11.33363932017481	5.17317898060494

5.3. *Trans*-3-hexene

E = −236.265093679682
E_{ZPE} = 0.16211694
E_T = 0.00817955
E_S = −0.0409027

C	-4.80070142793797	-0.48323146733284	0.14402445255520
H	-4.40330364761575	-1.48679963469822	0.33177243751068
H	-4.41535761741107	-0.13519373357744	-0.82071352554108
H	-5.89126427572447	-0.56129278086869	0.06579682547295
C	-4.40092521823713	0.48102463439091	1.27559302499868
H	-4.77203917944567	1.48554067821021	1.02491742262931
H	-3.30796354335326	0.54954777905405	1.33868918154215
C	-4.95555168043475	0.06318870265969	2.60836663619785
H	-6.04547977595689	0.01287937559236	2.68037535381037
C	-4.22453775928559	-0.26595556934958	3.67863263340918
H	-3.13460989678030	-0.21557642505567	3.60664706213067
C	-4.77916343521612	-0.68388822956714	5.01137766067772
H	-4.40799504237458	-1.68839497558424	5.26201345321946
H	-5.87212003562952	-0.75247217470859	4.94825870251290
C	-4.37946281009056	0.28033860489384	6.14299772473285
H	-4.77691142524214	1.28389410518437	5.95528759058947
H	-4.76480771069156	-0.06776447206509	7.10771197689427
H	-3.28890551857260	0.35845558282207	6.22125138665732

5.4. Transition state Me-2a-TS

E = −6333.39757299952
E_{ZPE} = 0.37861033
E_T = 0.027709

E_S = −0.08386964

imf = −241.86 cm^{-1}

C	-0.46919300327267	-1.62558617401646	-0.08429841734242
C	-1.05624131887346	-0.82988308542107	-1.05880148211223
C	1.07305476586562	0.75454446921844	-1.05242755950148
C	1.69634705794336	-0.09340061754341	-0.14750827437810
P	-0.65935840920250	0.86535113263578	-1.40428838346347
P	0.88072986576841	-1.19390831839693	0.98031065607624
N	-1.27133657823376	-2.75568920559278	0.04712795134412
N	-2.19549713984452	-1.50328157771409	-1.48914045138205
N	2.03855871134683	1.65753507430122	-1.48745474366012
N	3.02307962867663	0.31953076940947	-0.06537353359933
C	-3.10179897751426	-1.07051807853353	-2.54935668823880
H	-4.09086485396021	-0.86628495940921	-2.13365318032027
H	-2.68882026107807	-0.16549919580103	-2.99756945377312
H	-3.18217779456930	-1.86139792738800	-3.29825528469440
C	-1.02662468718875	-3.86409840322374	0.96409791666628
H	-1.58226129582360	-3.71573100818097	1.89430588613367
H	-1.35836071464480	-4.78715087521347	0.48633268896751
H	0.04386767303876	-3.90250735984168	1.17458910238310
C	4.07490071419382	-0.32278408728936	0.71850857840816
H	3.64724790337777	-1.20524933401997	1.19713242506189
H	4.89327689082276	-0.61209278813812	0.05546890526107
H	4.45111838891293	0.37024667018206	1.47390982886301
C	1.80365001930650	2.73558223732442	-2.44219811029130
H	1.17970374386361	2.35567601873637	-3.25425296887410
H	1.29971309196569	3.57181875600227	-1.94906408243438
H	2.77341296927984	3.06172530019206	-2.82067492301920
Se	4.84584604873612	2.25607414683696	-1.14591087023859
C	3.24050410545897	1.38928751174841	-0.89104117260494
C	-2.32833459197707	-2.68848061956594	-0.81770530342387
Se	-3.65761450384879	-3.93935162904777	-1.05909803099163
H	-0.70233522949679	0.12295487108928	2.62654688220129
C	-0.29652982622621	0.81062625343658	1.88355680487997
C	-1.23071598596696	1.35281220287730	0.97871342487578
C	0.88320974125172	1.65131590141783	2.32565216044869
H	-1.06898912426580	2.39562062468434	0.70351188020488
C	-2.67306805329799	0.89378803796879	1.02903457066561
H	0.48093865004023	2.58051734496081	2.75577349279014
H	1.46220751828908	1.96518379992598	1.44806809190381
H	-3.03660956006439	1.07175135297845	2.05200117956053
H	-2.72255315852580	-0.19328595864451	0.88893759573001
C	1.78881394573483	0.98704198380637	3.36294644697576
H	2.59812259534587	1.66189081198435	3.65838502366424
H	1.21777870746732	0.72319932125029	4.26020786020704
H	2.24122195098798	0.06566250427007	2.98096995740864
C	-3.60391597478456	1.60733068565030	0.04838900290736
H	-4.63241743887299	1.25120894394426	0.16292833260421
H	-3.59385240232989	2.68879986427100	0.22442314198769
H	-3.30313380381153	1.44150461187851	-0.99165687383696

5.5. 1,4-Diphosphabarrelene Me-2b

E = −6333.43874187026
E_{ZPE} = 0.38270019
E_T = 0.02773531
E_S = −0.08395965

P	7.35324715794990	5.58740026899647	5.87018515412861
P	5.08660273100894	6.62896071038327	8.09260046386955
N	7.29755651008531	8.43585968569669	5.33937412231956
N	5.82305586118484	9.12424966161496	6.80313688842223
N	3.65377089489239	4.46949633831810	6.77571261029871
N	5.16372997596546	3.76150782079822	5.35711142147264
C	6.78952542595899	7.31058188119815	5.96955387609573
C	6.70042800628011	9.55994432476056	5.84596262307867
C	5.87022294916352	7.74042947573468	6.88781311721107
C	4.75819366149418	5.29657366818273	6.90415780275358
C	3.89725601875693	3.51970794807070	5.81793292000337
C	5.70280850180806	4.85488173638437	6.02056944681447
C	8.31032283030060	8.45149335305016	4.28828440220520
C	4.96509180939634	10.01088576310114	7.58352885520689
C	2.40306424284876	4.57119105063729	7.52190472104988
C	5.81555272865310	2.97618259995423	4.31349614230284
C	7.81338408894774	5.50303932397594	7.72111067765033
C	6.69100316546922	5.85957235919764	8.72608034977366
C	9.04992908590912	6.39399847771829	7.95526071750287
C	10.24964581351845	6.09303142407676	7.05384418460189
H	7.90775750962497	8.94325208731717	3.40003484856555
H	8.57336823858156	7.41728252395380	4.06274188213538
H	9.19087938032497	8.99717822448319	4.63520988474235
H	4.33783802199358	9.39176202434708	8.22598897630269
H	4.34629523730038	10.60540375798474	6.90776616566166
H	5.58120894132338	10.67991468426852	8.18879554160404
H	1.57434538778096	4.72587484824012	6.82735066736442
H	2.48680406833175	5.41758505421375	8.20462310157373
H	2.23517602480196	3.64868003339630	8.08241127941519
H	5.20392629241812	2.99315346676858	3.40873566897748
H	5.93284403283270	1.94321915477562	4.64935967763397
H	6.79148487340639	3.42282373860245	4.11934876569488
H	8.09143316952688	4.45187416117334	7.86357884659271
H	7.07602237406138	6.57254271989620	9.46371886415372
H	8.75173093874332	7.44509324830714	7.83788029668066
H	9.34795506520910	6.27471704039960	9.00563934010786
H	9.97041908586729	6.22757943405548	5.99962362953581
H	10.53405869032698	5.03692139168895	7.16334874151537
H	6.36319333245076	4.96905876546744	9.27173171368606
C	11.45563303035401	6.98682708842764	7.36291423791453
H	11.75486508051718	6.84208556257767	8.40989488579949
H	11.15431347018314	8.03884156492178	7.26666014228391
C	12.64654600340164	6.70617803987788	6.44128813572427
H	13.49619463299158	7.35590743901582	6.67786581441437
H	12.97962666339748	5.66591864121860	6.53841811503891
H	12.37498127573185	6.87369202237103	5.39210526106114

Se	7.00250292660400	11.30511944992228	5.32971727738705
Se	2.74500479232008	2.19352596047688	5.25432774167046

5.6. 1-Hexene

E = −236.265093679682
E_{ZPE} = 0.16248643
E_T = 0.00799746
E_S = −0.04057872

C	-5.69009835057238	0.90689948263830	0.33079839780943
H	-5.35885615609771	0.26507473116964	1.14573137954423
H	-6.76314400060383	1.02910521231955	0.20651076222321
C	-4.81558171566253	1.51174994681208	-0.47726615930880
H	-5.19001479303475	2.14970008182438	-1.28064617489499
C	-3.32216328022187	1.40836285744762	-0.36716481412739
H	-2.91789207196854	0.99531153705298	-1.30373787998114
H	-3.05662735615058	0.70880356264658	0.43567708115025
C	-2.65042823142816	2.77096053420846	-0.11263055688819
H	-3.02842725072187	3.18785006174475	0.83082828866939
H	-2.94361423709547	3.47318468797234	-0.90561208903649
C	-1.12170572045561	2.67695972179767	-0.05559244428268
H	-0.75227727292685	2.25696736239681	-1.00119305512334
H	-0.83358605377120	1.96853702582698	0.73307312435313
C	-0.45473549946595	4.03199488988521	0.20201278966999
H	-0.78876361640233	4.45687742097103	1.15619441167912
H	0.63644880535100	3.93938680512156	0.23805059250916
H	-0.70663319877133	4.74837407816403	-0.58913365396490

5.7. Transition state Me-2b-TS

E = −6333.3954898991
E_{ZPE} = 0.37924521
E_T = 0. 02828747
E_S = −0.0852108

imf = −293.61 cm^{-1}

C	-0.52286878019228	-1.79668789705918	-0.27456195410037
C	-1.09328457859622	-0.86703986038526	-1.13278330559859
C	1.06546632659667	0.66160900133197	-0.90265657445049
C	1.65366655730010	-0.29083977491280	-0.07999341559233
P	-0.65479230360715	0.84150525676970	-1.26433517116014
P	0.82932666866203	-1.55951446756529	0.83630306092808
N	-1.37836439807218	-2.89352408900244	-0.24934250020790
N	-2.27699351645801	-1.42815537084012	-1.60040392108465
N	2.04616482321637	1.60814690495181	-1.18636101658201
N	2.97365478626658	0.10791590661719	0.10669159269772
C	-3.20522677068588	-0.79197870477716	-2.53073402908657
H	-2.66107392249879	-0.02150007791977	-3.07984793101946
H	-3.58919512643672	-1.55105628510562	-3.21401686820584
H	-4.03800471215525	-0.34070517428377	-1.98433145231743
C	-1.15405569154843	-4.10598676751852	0.53109659442347
H	-0.09955005930074	-4.38101581112493	0.45613390166952

H -1.41723729843485 -3.93393591536377 1.57881829560188
H -1.78737380737367 -4.89135719828233 0.11654676815731
C 3.99498146903365 -0.62798447703474 0.84760676299314
H 3.55368034818067 -1.56569338061108 1.18914054495523
H 4.84372929534217 -0.82731141308412 0.18984068255515
H 4.33223265853432 -0.03827648174537 1.70220706006989
C 1.85311777385022 2.79222775884541 -2.01658825018590
H 2.82675798747807 3.09130000808225 -2.40727744958764
H 1.17197056363274 2.53738886383343 -2.83130021471444
H 1.43018605290323 3.60714034899628 -1.42202623412010
C 3.22138943925723 1.26926189349252 -0.57500039996512
C -2.45708929814979 -2.67448909126925 -1.06434833950173
C -0.47059233522216 0.41985811233321 1.96962922883739
C -1.24743081096013 1.11578238075761 1.03664151368435
H -0.93578501446789 -0.40424806613543 2.50546121322838
H -1.06246223351988 2.18337435860990 0.93140076471401
H -2.27298294570060 0.80407783169392 0.86020677456190
Se -3.85881292335025 -3.82146681085881 -1.40070072967681
Se 4.83043777547728 2.16035087698713 -0.65446763854748
C 0.68733848879913 1.12504143844093 2.63622731344168
H 0.27175453585503 1.96307577100807 3.21799322375075
H 1.31720925535356 1.59372512673414 1.86776973174186
C 1.54282266604045 0.26997441633448 3.57038726791882
H 0.90495723074248 -0.16286342214306 4.35348801396047
H 1.96060652462145 -0.58225339797667 3.01764842204292
C 2.68449366509128 1.06426222042768 4.21250790543148
H 3.29312546839119 1.51900625299687 3.41902042159539
H 2.26372940978528 1.89521798225322 4.79478413549397
C 3.57289411025647 0.20001592632103 5.11221239636501
H 4.38062548653086 0.78977319046695 5.55906979716417
H 2.98932987007877 -0.24553947250451 5.92668486952714
H 4.02812728945337 -0.61770842078166 4.54075913819368

5.8. Se-methylated imidazolium salt $[Me\text{-}3a]^{2+}$

E = −6413.039854786058
E_{ZPE} = 0.45768220
E_T = 0.03276212
E_S = −0.09379375

P 7.42926122773285 5.65380328550391 5.72156151436226
P 5.10311624483394 6.64609881541212 7.96076172401896
N 7.24600946076204 8.49248459035661 5.16689108191312
N 5.78197620387660 9.14233990404116 6.66204883118551
N 3.73266976831893 4.48303738072227 6.60445342406002
N 5.25299149499797 3.83030687082284 5.16758485803462
C 6.81714031623791 7.36564302438838 5.83592457868433
C 6.61321389578071 9.57623032062059 5.68343568075273
C 5.89292668566888 7.76972905161835 6.76633984737995
C 4.81373509523805 5.32930131768067 6.73823920879289
C 4.00835433833329 3.56871912688130 5.64078484137665
C 5.77160722951194 4.91221989444106 5.84949992733259
C 8.22760897772877 8.52172907685021 4.07543433753927

C	4.88997140199117	9.99749716888985	7.45920511489565
C	2.47935529949354	4.57550377773502	7.36737047102667
C	5.93598821864706	3.07798013775983	4.10759348368553
C	7.83986176356670	5.54371621175056	7.57579949405350
C	6.72105646588909	5.87361658174984	8.60185616379977
C	9.09788080756397	6.39367044492997	7.85101063315505
C	10.31217382560284	6.03669901539266	6.99098420311460
C	6.37165024372843	4.63382409592663	9.45091620554819
C	5.43683652944466	4.91192958728943	10.63029075865557
H	8.00811507803816	9.38389016799039	3.44435177029306
H	8.12715616720886	7.59799395567785	3.50619012772996
H	9.23466648833034	8.59963960496973	4.48947723781143
H	4.61382405211999	9.44517416176283	8.35671467118726
H	3.99835931521176	10.23733565190355	6.87702915857381
H	5.42493531500776	10.91047037045826	7.72085159297925
H	1.81121988620810	5.28924569816348	6.88162520112197
H	2.72056534488700	4.91030200506826	8.37598614327498
H	2.02110170892892	3.58739631310965	7.39051051600803
H	5.17590785919756	2.63467307481273	3.46313600657151
H	6.55608064011162	2.29812390523563	4.55394340192600
H	6.55594912084378	3.77419797886068	3.54328874089150
H	8.09800519692222	4.48266334639975	7.68786041168682
H	7.09836665847186	6.66192865992949	9.26651020714416
H	8.84127969339143	7.45433170204672	7.72878120131156
H	9.34759836469987	6.25731637095895	8.91049436133765
H	11.18402780029336	6.61747357628588	7.30793931899495
H	10.13834467432751	6.24876305661574	5.92987854408473
H	10.55833151758510	4.97306957955663	7.08417407422296
H	5.94380004375951	3.86236705622422	8.79659057220457
H	7.31910983309967	4.22780256621634	9.82605034655046
H	5.30745079430940	4.00689012214864	11.23200838522050
H	4.44389715470928	5.23658139737755	10.29930176768847
H	5.84767239929798	5.69559766644432	11.27652987871748
Se	2.81882762185717	2.23516322947405	5.02096391654629
Se	6.76895856880818	11.36794700008713	5.10452218853043
C	8.65314613741221	11.66334440916905	5.62400823237657
H	9.31276980376973	11.05464858392735	5.00841489016781
H	8.81536986391116	12.72407376207132	5.42542439816570
H	8.76212934873181	11.44740721881267	6.68530914537255
C	3.81077854879017	0.65411356183543	5.67239591619702
H	3.15227752136111	-0.18263238100742	5.43259154001399
H	4.75672096341669	0.56092369592906	5.14216635508106
H	3.94717102003082	0.74380325072024	6.74859339664756

5.9. Imidazolium salt [Me-4a]$^{2+}$

E = −1528.889624617097
E_{ZPE} = 0.40448133
E_T = 0.02408162
E_S = −0.07456163

P	6.93612965543109	5.23745943729860	5.78000781883852
P	5.57233161174581	7.15453868260381	8.21024450858014

N	7.84033025179025	7.89205120493268	5.02594363843423
N	6.98420607236881	9.12057688773433	6.61838461175763
N	3.25206662447911	5.72378565908866	7.20519215591510
N	4.14415169967846	4.46413121182811	5.65724899527436
C	7.09587676969756	7.05050714292398	5.83339427833488
C	7.75343759459670	9.13493376532487	5.52119310831278
C	6.56124603408305	7.81933483590349	6.83509676689322
C	4.59688131160789	6.04338728239410	7.14549078346254
C	3.00617258049622	4.77054063579891	6.29509256530556
C	5.15870396455467	5.25159435838151	6.17676094201345
C	8.60614047049704	7.50187795850194	3.83137263729621
C	6.65292956368914	10.29683509463021	7.43844794939761
C	2.25372103126870	6.31663669109436	8.10945254287920
C	4.27453926161406	3.46182876571299	4.58722047664341
C	7.53240030826872	5.00598297694695	7.57278269864677
C	6.81632067016938	5.79887180893132	8.70071642821196
C	9.05640282485957	5.24346500976283	7.62113529027480
C	9.87120428911539	4.36657069613689	6.66754897219275
C	6.13565415446416	4.83383388698787	9.69366893222634
C	5.53851990352786	5.50391703268735	10.93284087910533
H	9.06262604213655	8.39731284065043	3.41167781930270
H	7.92567116374666	7.04935464919118	3.10887851164607
H	9.37649496736964	6.78697205921229	4.12390901954478
H	5.56832413452625	10.40868142418983	7.47160798925895
H	7.10942616688375	11.17176039372319	6.97730582571708
H	7.04822830879703	10.15118171877691	8.44481537911708
H	2.20520119362436	7.39080303516936	7.92552881109016
H	2.55272617710815	6.12287008701527	9.14063595092029
H	1.28983203974391	5.85334970507317	7.90312950054414
H	3.28836989341508	3.04321411603051	4.39076106853520
H	4.95836868132493	2.67815978120406	4.91649120277932
H	4.66379245453403	3.95051852263836	3.69293036901664
H	7.33684818178209	3.93851940725404	7.73806281678519
H	7.57689040469112	6.38011646160362	9.23826693316277
H	9.25731810773947	6.30602706392914	7.43015933769745
H	9.37454582166616	5.05202496276723	8.65340857884183
H	10.94181982840569	4.52849890672141	6.82705467679117
H	9.65314881920904	4.59082455464509	5.61717700976421
H	9.65773241887393	3.30500128467148	6.83508277153237
H	5.36544279972302	4.26098521516416	9.16028516317335
H	6.89849867632634	4.10852906736805	10.00260945021332
H	5.16294048544128	4.74631020753600	11.62775018296515
H	4.70269937641832	6.16559403542026	10.67810829137198
H	6.29284446508581	6.10253882121839	11.45559411926302
H	8.22095488753183	10.01082890412968	5.09652435990594
H	2.04118785589184	4.32656174909100	6.10070788106289

5.10. 1,4-Diphosphinine bis(imidazolium) salt Me-10

E = − 1292.58199919564
E_{ZPE} = 0.2383914
E_T = 0.02452739
E_S = −0.05945547

C	-6.60694454009715	-6.77380451356824	-0.55924848141760
C	-7.00010433918370	-5.48892586076798	-1.01040141042677
C	-4.60945654255116	-4.58941897216928	-0.53406441166126
C	-4.21628797100843	-5.87430134479169	-0.08292867823547
P	-6.12866708510565	-3.98287887658266	-1.14164789507881
P	-5.08769188073346	-7.38038076629193	0.04819206524757
N	-7.73642354461580	-7.58772392700137	-0.68421158394823
N	-8.34293365149731	-5.60574859513886	-1.38050800844144
N	-3.48004843828219	-3.77543693135598	-0.40887612974348
N	-2.87350776098095	-5.75742974196338	0.28734574779098
C	-9.18019531251430	-4.52108689194563	-1.91359845137435
H	-10.17065071934334	-4.92535584336807	-2.11677519971881
H	-9.24292472214378	-3.72396330668987	-1.16990781852073
H	-8.72921187401193	-4.14624090159223	-2.83464016868462
C	-7.80510116843384	-9.01347175684341	-0.33113695750033
H	-7.58005205372639	-9.12510859248132	0.73148732850962
H	-7.07842567067648	-9.56231657040898	-0.93348955476240
H	-8.81308063753424	-9.36751507122863	-0.54252194195777
C	-2.03629408270536	-6.84202096852517	0.82066257190800
H	-2.48681098134117	-7.21608332840027	1.74225270884565
H	-1.04555257131487	-6.43797024471653	1.02287751809450
H	-1.97432825232492	-7.63966687768899	0.07747030605480
C	-3.41140141965578	-2.34966558045472	-0.76186118036076
H	-2.40343747530532	-1.99560785205503	-0.55042704677187
H	-4.13811126141170	-1.80087707328869	-0.15949891155103
H	-3.63641994352600	-2.23797218234437	-1.82448603779597
C	-2.47552576687784	-4.50241649354154	0.07986058807335
C	-8.74096995707209	-6.86071784125392	-1.17286221811763
H	-9.73565942443404	-7.23434689524531	-1.37297302817023
H	-1.48088095159057	-4.12874619829571	0.28011627971510

5.11. Transition state Me-4a-TS

E = −1528.84068709559
E_{ZPE} = 0.40243271
E_T = 0.02475636
E_S = −0.07639928

imf = −139.65 cm^{-1}

C	-0.42615849057393	-1.62137991292223	-0.11031072006584
C	-1.02316458029262	-0.81841830672733	-1.08559212652584
C	1.05729875071408	0.77073334915987	-1.05791879376905
C	1.69304188273687	-0.08711681529722	-0.15678624806325
P	-0.64753973899940	0.85677134781542	-1.49696746126497
P	0.95988021209041	-1.27434913743748	0.92286788024128
N	-1.21297262459431	-2.76831881652244	-0.00685951719758
N	-2.13922346154970	-1.52120913021255	-1.54349408216699
N	2.02570024792182	1.67616130397031	-1.49107016926890
N	3.02579632766764	0.32464784212277	-0.09587946353508
C	-3.04996029511638	-1.09914032132034	-2.61919626694684
H	-3.62952125058750	-0.23696910588067	-2.28675346545105
H	-2.45395764011746	-0.83926636728028	-3.49569742184372
H	-3.71545679636111	-1.93103420708236	-2.84693140606541

C	-0.96380357791389	-3.90329334330763	0.89315144349498
H	-1.05865740860117	-3.56688985684690	1.92737656300926
H	-1.70154490088431	-4.67588387555182	0.68041302047108
H	0.04425625506375	-4.28041735410143	0.70992428887559
C	4.09863394099139	-0.32287546293866	0.67488312767120
H	3.87045528906582	-0.25321019344847	1.73899866438616
H	4.16493401669552	-1.36907027392670	0.37048574559349
H	5.03243445385565	0.19481731792882	0.45923313838619
C	1.81001064172172	2.77446870495414	-2.44334200265726
H	1.39891665326415	2.36243745596462	-3.36693457643973
H	1.11249175651724	3.49237602375539	-2.00734896183978
H	2.76952202069237	3.25258792480723	-2.63549179794125
C	3.18878425122565	1.36991589272437	-0.91200735998104
C	-2.21395471149370	-2.68201811098118	-0.88594982316238
H	-0.67443259218440	0.06748001631344	2.62944588822875
C	-0.35167971649729	0.86426558791728	1.95843709750067
C	-1.29271832736927	1.36858486706360	1.08316645687786
C	0.85984648456743	1.66175016290461	2.38061075022039
H	-1.12491354359369	2.37712497474008	0.70373642095751
C	-2.71410590202881	0.85779037660891	1.05053724462009
H	0.50672395716726	2.65117377807111	2.70272437658347
H	1.50747633343704	1.86079688717130	1.51784213930401
H	-3.09660557908240	0.89318758008982	2.08023064575066
H	-2.73440249396068	-0.20461022872805	0.77800745792458
C	1.65151113780059	1.01871705853190	3.52014019692245
H	2.51202000287164	1.63669802941500	3.79282276251246
H	1.02016195299095	0.90089383101569	4.40724749545188
H	2.02004140623703	0.02371751466340	3.24471900123631
C	-3.64268109120776	1.67415519955545	0.15035742853593
H	-4.66301612901655	1.28140546232983	0.18717740500185
H	-3.66682883239486	2.72027802462417	0.47364007561861
H	-3.31073472764124	1.66258810462385	-0.89416088352280
H	-2.95864536051055	-3.44536266876426	-1.05940312482615
H	4.12534179727698	1.87820887043558	-1.09048104284185

5.12. Bis(NHC) Me-5a

E = −1527.922647933374
E_{ZPE} = 0.37774859
E_T = 0.02452739
E_S = −0.07552661

P	7.35948585359040	5.64679510336920	5.85609456316249
P	5.08871615612200	6.68523354082703	8.06050493436604
N	7.20329182103525	8.49817450591914	5.24745295329980
N	5.77297095823725	9.16841213590438	6.69548104402762
N	3.71388871089242	4.43456122982387	6.80885542862453
N	5.19142698627704	3.74909614757939	5.41667570093473
C	6.78054496542208	7.36471275449580	5.92777517623523
C	6.58850645032551	9.64094647853520	5.69778736106680
C	5.86992407613064	7.79103812583091	6.85461809496979
C	4.77746729435637	5.32125589888716	6.90501208829086
C	3.93663886189192	3.44523980344302	5.88258835459879

C	5.72330266264579	4.88242387254854	6.02029118848573
C	8.18160264854458	8.49142179733646	4.16232800631161
C	4.89830699268787	10.03153318555756	7.48577807930821
C	2.48527092385163	4.53284354756178	7.59331848775134
C	5.87190762154131	2.96463778119049	4.38909919369065
C	7.81363513013002	5.57131478660269	7.70796065799866
C	6.70664620528718	5.93012593851411	8.73598542708334
C	9.07379269165839	6.42452200139800	7.95549002986499
C	10.28448767260239	6.04456547215210	7.09947771200913
C	6.36537071832326	4.71098409944322	9.61501400296317
C	5.42492710759018	5.01024011093074	10.78528694901153
H	8.28600773458019	9.51627533161302	3.80718593079681
H	7.83534925196381	7.84855707026672	3.34844210052577
H	9.14572246935859	8.12427598692819	4.52501667943907
H	3.85883822861001	9.70795350783602	7.38352197642844
H	5.01032520778000	11.04727744603075	7.10736740493707
H	5.18375049631910	9.99534424818842	8.54086204953974
H	1.98426938715788	5.48387656763011	7.39249721311344
H	2.71364288817094	4.46568143340789	8.66063894340547
H	1.84079761891843	3.70450914327983	7.30010180400446
H	5.20224925965071	2.15654486912426	4.09568100025632
H	6.80297174752069	2.54913943311644	4.78470180026584
H	6.09818253330216	3.59370886016697	3.52378620173299
H	8.07268541538727	4.51318452999783	7.84744870384336
H	7.09365883903282	6.73080517547303	9.38073655016413
H	8.81699360560251	7.48052191102364	7.79915302680360
H	9.33438860836910	6.32362139920704	9.01732976539077
H	11.15970414650718	6.63506320492274	7.39062193531636
H	10.09856660361288	6.22264578633041	6.03467117338223
H	10.53298466477132	4.98383630282987	7.22198645625887
H	5.93820291048224	3.92611605426596	8.97688080602818
H	7.31133680561653	4.31213894761077	10.00433090093561
H	5.29970523046590	4.12146851440789	11.41287190837235
H	4.43253350593798	5.31934413786202	10.43935328568199
H	5.82612033173785	5.81563182062895	11.41163694932152

5.13. 1,4-Diphosphinine bis(NHC) 11

E = −1291.63449637021
E_{ZPE} = 0.21141758
E_T = 0.016036
E_S = −0.05881653

C	-6.64086335742516	-6.76536869380257	-0.57391999338451
C	-7.02256952600040	-5.46852957049974	-0.99078536871886
C	-4.58525114248717	-4.58887608016498	-0.48811179929905
C	-4.20361572482122	-5.88566119658256	-0.07101036883099
P	-6.11253521953128	-3.98176474167471	-1.07557372918042
P	-5.11353105521129	-7.37251964122356	0.01338342564425
N	-7.78738817184910	-7.54711887317104	-0.72344720989348
N	-8.36498560210227	-5.58456557599199	-1.35467855956516
N	-3.43874654896541	-3.80711024411983	-0.33851018627329
N	-2.86131757070249	-5.76953249529376	0.29328210621154

C	-9.15976351077456	-4.46524898567058	-1.84967529608347
H	-9.20372506318590	-3.67309756208004	-1.09548550480179
H	-8.71448994744352	-4.06421827976202	-2.76570906093525
H	-10.16220117017392	-4.83833453111036	-2.05590352101232
C	-7.83406176180321	-8.96932511183855	-0.39942509862407
H	-7.11171153562390	-9.51817157914899	-1.01186938637263
H	-7.59692175236354	-9.12108950106447	0.65834238385137
H	-8.84316861390391	-9.32202295133692	-0.60888570736886
C	-2.06651449466225	-6.88888273768744	0.78815168420276
H	-2.01937378263963	-7.67946687966841	0.03250250678926
H	-1.06514978287964	-6.51495709865621	0.99803991227712
H	-2.51392467891263	-7.29231845301248	1.70208051694472
C	-3.39210769179051	-2.38487427984614	-0.66241133712719
H	-2.38257840272753	-2.03252740447764	-0.45440517453954
H	-3.63075892935769	-2.23295226200045	-1.71981378481008
H	-4.11337731844573	-1.83584126383631	-0.04885770186784
C	-2.36318973450611	-4.50462892644812	0.13959750521361
C	-8.86307790970995	-6.84949507983008	-1.20110125244582

5.14. Transition state Me-5a-TS

E = −1527.88158508944
E_{ZPE} = 0.37475281
E_T = 0.02472331
E_S = −0.07596483

imf = −218.93 cm^{-1}

C	-0.43523771041973	-1.63766066612687	-0.10066734641844
C	-1.04138103174645	-0.84834834551541	-1.06803550899478
C	1.06453665276813	0.78628020676859	-1.06430696198739
C	1.70653135957251	-0.05253199734332	-0.16381218727812
P	-0.66859013631270	0.84946319593699	-1.41846338618003
P	0.92081978038575	-1.19007446953913	0.94698632855525
N	-1.22015583023773	-2.78825420198188	-0.00700495065076
N	-2.15204669521503	-1.57425146322090	-1.50314388988049
N	2.03938552902064	1.68300233190835	-1.50494476434039
N	3.03207025278952	0.38521780801978	-0.12279216546358
C	-3.05671059475374	-1.12688982086026	-2.55910424077135
H	-3.58411677770097	-0.22008159323225	-2.25211556784433
H	-2.49092812560542	-0.92176969426951	-3.47270623594729
H	-3.77546135190335	-1.92643304690932	-2.73675020638969
C	-0.92882669142672	-3.89637609240814	0.89770003490854
H	-1.00541744331343	-3.56726032609343	1.93837960539163
H	-1.65992887945619	-4.68103959607237	0.70480893950200
H	0.08245472414890	-4.27184280261889	0.71427920775128
C	4.07885801686985	-0.24803108333154	0.67538625023537
H	3.87588080450281	-0.12450429686642	1.74237036782521
H	4.13140623861666	-1.31523586287809	0.44096100355545
H	5.02148469814658	0.23694240110917	0.42303901000542
C	1.78402641195825	2.74799183244343	-2.47028427823179
H	1.36358840095508	2.32715605794756	-3.38858651203548
H	1.08028478006188	3.47592306592817	-2.05513970780256

H	2.73511001024636	3.23553314139686	-2.68295826468414
H	3.27145771975994	1.44336232951190	-0.95977324661815
C	-2.27362190091621	-2.78891192632174	-0.88067487434213
H	-0.74986380891187	0.05563744459441	2.59201795283255
C	-0.32232969353962	0.77171363163732	1.88922001614747
C	-1.23043437994395	1.34390053161740	0.97938477595530
C	0.84508702785397	1.59000727966004	2.40660292644966
H	-1.04344058788774	2.38516658750939	0.71527600673099
C	-2.68518608400445	0.91577069813299	1.00087494256390
H	0.44795349153501	2.55041670581616	2.76642858559936
H	1.52152157400550	1.84174990137443	1.58051525967188
H	-3.04062634371926	0.99527730106352	2.03872988487155
H	-2.76536680866900	-0.14762770319311	0.74381029842798
C	1.61468535485173	0.91966780094687	3.54641215747529
H	2.44177786152730	1.55237816164207	3.88404957145234
H	0.95442019061400	0.73608403575544	4.40177848429344
H	2.02892549010852	-0.04593379786896	3.23670377288399
C	-3.59761791402016	1.75672493345848	0.10633702539504
H	-4.63449098884610	1.41251520949078	0.17591164404551
H	-3.56702866400719	2.81034553723962	0.40678767725762
H	-3.29175792774186	1.70513065574184	-0.94428743392318

5.15. BCl_3-bis(NHC) adduct Me-6a

E = −4341.63837446506
E_{ZPE} = 0.40004788
E_T = 0.03503724
E_S = −0.09767531

P	6.92985487138357	5.22391849782558	5.77344789468587
P	5.57993653570549	7.14797240909333	8.17263444110973
N	7.86009481147842	7.86576850083367	5.00212726265568
N	7.01687546888365	9.09329197502479	6.58901739126232
N	3.26085519928267	5.71186135416027	7.18996940071912
N	4.14008739234719	4.43858683248939	5.65959743176713
C	7.10266146491263	7.03316982649405	5.80505359699447
C	7.81231214597986	9.13804465741093	5.48482180688108
C	6.57802030422758	7.80299541839784	6.80402551373782
C	4.59911970760443	6.03218523597301	7.12333145991674
C	2.97110056751779	4.72835773970533	6.29237304934766
C	5.15541757318949	5.23225973951796	6.16557454171925
C	8.55938439918025	7.37303264126039	3.80381480519738
C	6.64487445747521	10.22307020597991	7.45322052415536
C	2.32564501879030	6.35910252426790	8.12135510018005
C	4.36749494773319	3.46946266946700	4.57449986360936
C	7.54528074166193	5.00987802958128	7.56095282295024
C	6.80629068889471	5.78494445363383	8.68642444687852
C	9.05947615754279	5.30268458169048	7.60166442649788
C	9.89857936270643	4.47590598053299	6.62457622323983
C	6.09542351962356	4.80959789449846	9.64601978991086
C	5.46050862622716	5.46813952778388	10.87275434843963
H	8.24204546144593	7.94155586540270	2.93180371526111
H	8.28212319667138	6.32461178597254	3.68872370483326

H	9.63623312783550	7.46309792075532	3.93802697113118
H	5.67258768907867	9.99186781601545	7.89001532269284
H	6.58163686569656	11.12748509729799	6.85237654026731
H	7.39089014870406	10.34497937283881	8.23965154018698
H	2.72234171950108	7.35052231057192	8.34277571120876
H	2.25297698520635	5.76884506519267	9.03548949871832
H	1.34906460107976	6.44016092433856	7.64901539508092
H	3.70395809746172	3.68841743354068	3.74011683237903
H	4.19134624114216	2.45805531317225	4.93722589523911
H	5.40764122158773	3.58189065365493	4.26669127612834
H	7.38909825865474	3.93713733929494	7.73465359578627
H	7.55735195543147	6.35159349641328	9.25241300370150
H	9.21845916669561	6.37467473146496	7.42594510919439
H	9.39508500045350	5.10595358145654	8.62768846015091
H	10.96450384595225	4.66841694606863	6.78317483722301
H	9.66786897205931	4.71921735783608	5.58133231881721
H	9.71987517990206	3.40387954733928	6.76581875699585
H	5.33960652347614	4.24542625085087	9.08401038153696
H	6.84573545334713	4.07803958061725	9.97171397802629
H	5.05597986872905	4.70565090715305	11.54606868328021
H	4.63906300892393	6.13869591453772	10.59640496379311
H	6.20039738172796	6.05657551767391	11.42722414911427
B	8.49378516841409	10.49648653152168	4.92844981872054
B	1.48666155782307	4.11667166289223	6.08708272219259
Cl	9.43973342044877	11.30246651689268	6.34248278826605
Cl	7.10133174129238	11.62867698106320	4.34524617376390
Cl	9.68220309895731	10.24187949702941	3.52296412574880
Cl	0.85738441685907	3.53586545381957	7.76333857311436
Cl	0.38951999135310	5.50039542229230	5.42054563164454
Cl	1.39951667173901	2.67787650940535	4.91407338394506

5.16. CS_2-bis(NHC) adduct Me-7a

E = −3198.536145627476
E_{ZPE} = 0.39823083
E_T = 0.03248970
E_S = −0.09342132

P	6.90161190450980	5.25257825388020	5.76283559863749
P	5.56921571774576	7.17210658828880	8.17675761354588
N	7.85241305792519	7.88871553337383	5.00633916348226
N	7.02946313180810	9.12375304915591	6.61329611742107
N	3.23628891028023	5.73361389641793	7.21784366000059
N	4.11619831660015	4.45847674564056	5.67352037046518
C	7.08276024891871	7.05931364282330	5.80623587348154
C	7.81174116791427	9.14157565529479	5.51259816213048
C	6.56879840845253	7.82983140383011	6.81350430658511
C	4.57799391959260	6.06802113633987	7.12737004606449
C	2.97175547168313	4.75053376076325	6.32885822531838
C	5.13170992456872	5.26649746048437	6.16641103831338
C	8.61715525119305	7.49731124276202	3.81778234669176
C	6.75276909015848	10.29184032310330	7.45571534249772
C	2.25247793443123	6.30482799884746	8.14327713668405

C	4.24314302755877	3.42424181543412	4.64140296643521
C	7.52577681816467	5.02809667175144	7.54965727641601
C	6.78662333114151	5.79333392260706	8.68047183664144
C	9.03910894986982	5.32492541883084	7.58710117540660
C	9.87551167540982	4.51188578070811	6.59634197126751
C	6.06497901345023	4.81110881688145	9.62482493334840
C	5.41932973350960	5.45967615456003	10.85129308865391
H	8.39082997852259	8.19400210795584	3.00947222378444
H	8.31411771833292	6.48702176170322	3.54436500951716
H	9.68423901806917	7.52086792053863	4.04807324820772
H	5.83427821436649	10.09753425635856	8.00928305473264
H	6.62765322493800	11.16532107737518	6.81533862664534
H	7.58463444697886	10.44984689460729	8.14521794756750
H	2.65234797237954	7.24772848433794	8.51554695978480
H	2.08611151469501	5.61069744846517	8.96941813000420
H	1.31956648373845	6.47760643836028	7.60556566325638
H	3.36081861087288	3.46018788898500	4.00151638154944
H	4.32577727404273	2.44355953564026	5.11494884730839
H	5.13994520009159	3.63781145093669	4.06030844523209
H	7.37267018570978	3.95379792293547	7.71615614125840
H	7.53822862027164	6.34910924633309	9.25641556400807
H	9.19471221317055	6.39922460106323	7.42318013717751
H	9.38024849925569	5.11717820184955	8.60912957878302
H	10.94167593029918	4.70633221127993	6.75082994238193
H	9.63783931288403	4.76595428304838	5.55717531894359
H	9.70119704199493	3.43771564788118	6.72642013372362
H	5.31356232607128	4.25311249760957	9.05106283134559
H	6.81074541075310	4.07521841569776	9.95118215578950
H	5.01027398273698	4.69161337909647	11.51547468021439
H	4.59901195572949	6.13111520702823	10.57349914219967
H	6.15362648990115	6.04510027125491	11.41627020699425
C	8.50410891668458	10.32712221033436	4.95987737581749
C	1.65674907462709	4.10314115468469	6.12284651240562
S	0.77115739835022	4.71308483651704	4.83195989911608
S	1.32833361814886	2.88795588099271	7.23708546423773
S	9.93760640406655	10.70343021913618	5.75302036853720
S	7.71670795742962	11.04694327621371	3.66132175998694

5.17. Ph_2P-bis(NHC) adduct Me-8a

E = −3139.317756536563
E_{ZPE} = 0.74493356
E_T = 0.04818169
E_S = −0.12269537

P	7.38361135423154	5.71599154177564	5.79458531348403
P	5.04560835896998	6.65744827391425	8.04746394921090
N	7.09963323656389	8.54015374077476	5.21729986614627
N	5.63186536235216	9.15510453182498	6.71466081576548
N	3.74105702671536	4.43870840755009	6.72392313238928
N	5.27245250058802	3.80356629572758	5.29982982342191
C	6.71367476842796	7.40656485418817	5.89461515254798
C	6.43621109122249	9.61470916557359	5.71989992506515

C	5.79532161561808	7.79294249159613	6.83833765988693
C	4.78988018769140	5.32159561713517	6.83769401727701
C	4.03525237033654	3.50620087940303	5.77946016952294
C	5.75538125773242	4.91818796143541	5.95007268956802
C	8.04494200750770	8.56440121412904	4.09049248384814
C	4.73406263146355	9.96919516183661	7.54682064069196
C	2.47843760996650	4.53062721453531	7.47283515567836
C	5.99258400987527	3.07189388664582	4.24711097436934
C	7.81193352589970	5.64081428602574	7.64755121110115
C	6.69066526297605	5.93763065080746	8.68106171804482
C	9.04222313217176	6.53500503526800	7.90840621169241
C	10.27093475036947	6.19508766748933	7.06235763277268
C	6.38727593949265	4.68900011260227	9.53484086459759
C	5.43420183020335	4.93250383115945	10.70700559807923
H	8.38293646750106	9.59071188786974	3.94933176905456
H	7.53828935773099	8.20709530821899	3.19210124190568
H	8.88698285741743	7.91598918809877	4.33247672437133
H	3.92764550541742	9.32158494725987	7.89110171789620
H	4.33202402908003	10.78199603202368	6.94574096186413
H	5.28816347827605	10.36722345625867	8.39836731178891
H	2.70669867569012	4.82697140950699	8.49643470236756
H	1.99916603759878	3.55192473521860	7.45628363460713
H	1.83445688235937	5.27304238562617	6.99778495412510
H	5.27707938586780	2.72266388859412	3.50553348594644
H	6.52445221286663	2.22621492871848	4.68595550364561
H	6.69779996169690	3.76575657767663	3.78978842823392
H	8.10823055096217	4.59042935061251	7.76681130387906
H	7.04690274210722	6.73912002275183	9.34154183313813
H	8.75599791328104	7.58527354320161	7.76391667407869
H	9.29136812463157	6.42780479854056	8.97141200027626
H	11.12214588082294	6.81164202423380	7.36755189861149
H	10.09642618421414	6.37365368395766	5.99533735857363
H	10.55023938597133	5.14267208428116	7.18476916940215
H	5.99685056303737	3.89625492865327	8.88260055422392
H	7.34903459159979	4.32573759363363	9.91758173244263
H	5.34384062247552	4.02715684536534	11.31534005009487
H	4.42886689723349	5.20718434179991	10.36835381803041
H	5.80333091077610	5.73989134209877	11.34924896965822
P	2.93629656313015	2.08271250706064	5.42914805189983
P	6.76707466181924	11.33152999942951	5.16967759830887
C	2.35642447305454	2.46569788641846	3.74083188372708
C	1.47025856161127	1.53946187864962	3.16542812964975
C	2.67213164639935	3.63758672901158	3.04049364010897
C	0.94386129542547	1.76469143023912	1.89565764264326
H	1.19325920181729	0.64021883571136	3.71049286843066
C	2.12769989666558	3.86711018665545	1.77643912128652
H	3.33379587994799	4.38177627215014	3.47402652791753
C	1.27125588057687	2.92974122210901	1.19836452891333
H	0.26957792267487	1.03536340581571	1.45633470853971
H	2.37861995095545	4.77952123118104	1.24297479583415
H	0.85386623932272	3.10919024894378	0.21190195272204
C	4.19390576363709	0.76548684329421	5.22894618792275

C	4.93060871539342	0.41959650540536	6.37271315082055
C	4.39245303571509	0.05798504205897	4.03858320069665
C	5.88023617044111	-0.59814331497146	6.31254609584307
H	4.76623528633700	0.95090112421513	7.30785888209383
C	5.32936402207427	-0.97451170156691	3.98945390981472
H	3.82907716803596	0.31719730685634	3.14757018658108
C	6.07908072690059	-1.29973853826458	5.12091147409370
H	6.45565556818007	-0.85116789704768	7.19847138346695
H	5.47798658007298	-1.51962572304602	3.06162775869473
H	6.81165825434984	-2.10040068417942	5.07701737170683
C	5.16626656092907	11.79615440902820	4.42635660081552
C	5.04926413451244	13.11740954560376	3.96239674177047
C	4.11582050453789	10.89626007307064	4.20198397896405
C	3.88468989759481	13.53745633795067	3.32382398989181
H	5.86932331819839	13.81774559899368	4.10135341861375
C	2.95874262615902	11.31768095517021	3.54602317459168
H	4.19239886835399	9.86240012599197	4.52625023673596
C	2.83679314655443	12.63832049063636	3.11354517844502
H	3.80142036673928	14.56444341642361	2.98030871831016
H	2.15136734253296	10.61089731611735	3.37682147888336
H	1.93304331358551	12.96465395597461	2.60736456389982
C	6.81735418068888	12.14781237612191	6.81079089444838
C	7.87265913419368	11.77171349336879	7.65691229107163
C	5.92640578298983	13.14571289238156	7.21957088627509
C	8.01158388830091	12.36383306787615	8.91025496556369
H	8.58247272749277	11.01138511532524	7.33758213282858
C	6.08254556759123	13.75049869490575	8.46734330761427
H	5.10473274957090	13.44510913539192	6.57618988691521
C	7.11819724956728	13.35799446957210	9.31660968496525
H	8.82342830611949	12.05803819969519	9.56397055042225
H	5.38666326148243	14.52494999704300	8.77732191779297
H	7.23230455877359	13.82802141162716	10.28906354608478

5.18. $Fe(CO)_4$ Bis(NHC) complex Me-9a

E = −4965.19975317778
E_{ZPE} = 0.44826923
E_T = 0.04625442
E_S = −0.12115881

P	7.34560728442715	5.65465135099572	5.81560166717885
P	5.08361814558475	6.67822121757706	8.05422476313553
N	7.20113576515107	8.50082018345176	5.24201230567106
N	5.77758292347627	9.16923141998580	6.73182428769756
N	3.69443429465251	4.46158406921318	6.79106648730768
N	5.18393280316913	3.76394344915441	5.38058757212252
C	6.75554733611431	7.36857770614993	5.90446134772642
C	6.60107601241005	9.61919122343894	5.74280659462025
C	5.85833502105114	7.78854894227753	6.84703755769642
C	4.76566836512495	5.33538137890534	6.87670361507976
C	3.94102100801509	3.48443454482255	5.86987695708352
C	5.70699617747231	4.89688729514820	5.98811618745610
C	8.18346125569563	8.50232813057080	4.15572054140708

C	4.91736368723660	10.02945226194968	7.54796192270238
C	2.47740145319326	4.55884153069796	7.59846570030617
C	5.86791719018372	2.97682854092615	4.35216437606266
C	7.81280694807725	5.58920059471504	7.66240583193064
C	6.70039191210406	5.89860572747103	8.70059165079412
C	9.04094963860418	6.49230478167298	7.89813441139140
C	10.24664609876450	6.18376399773400	7.00718596586822
C	6.35666297475002	4.64327559273678	9.52705617297288
C	5.38213701997236	4.88390846895254	10.68267887881079
H	7.76830800325590	9.02110689935380	3.29149703969742
H	8.40260050378415	7.46429673723182	3.90199444117380
H	9.09599502929461	9.00508628516165	4.48090621153999
H	4.43864431576102	9.40428397257134	8.30278393496077
H	4.15910952945191	10.49974081607878	6.91961394006220
H	5.52352770451862	10.79888912128517	8.02663226853478
H	2.35119019324489	5.59884814880992	7.90237356682782
H	2.56272240120301	3.92431403764030	8.48411968751251
H	1.63328292616810	4.23097202003191	6.99353294877870
H	5.28675551888093	2.98457383103124	3.42902960130752
H	5.99072618669931	1.95002980712202	4.69879165510109
H	6.84370980600577	3.43235261884844	4.17785064766354
H	8.11500543524364	4.54189207963089	7.79487218188916
H	7.08147322531796	6.67316354428576	9.37951074236550
H	8.73712541688931	7.53986416714971	7.77326179963409
H	9.32768299266431	6.37794982627706	8.95136115679300
H	11.10269799381618	6.80124083342485	7.29830827070098
H	10.03395721633737	6.38491564291760	5.95132559969467
H	10.53923968026118	5.13105069358574	7.09454159555992
H	5.96101995737998	3.87151497959932	8.85368255305227
H	7.30101838769000	4.24998724556207	9.92470573087036
H	5.25797605778108	3.96980883145405	11.27255627436777
H	4.39210017026713	5.18734289180090	10.32467459636931
H	5.75209223666452	5.67205292988698	11.34864921251812
Fe	6.87495232398136	11.49657398645484	5.15699204364232
Fe	2.75918141834698	1.96608093649002	5.37008473115824
C	8.25687700642436	11.42843483082000	6.28952213816422
C	6.09692023234541	12.84491385591867	6.01031570116956
C	7.90371020347506	11.88923822321421	3.76452451065769
C	5.44026810310339	11.17439611701609	4.13884309857647
C	3.30743006909298	1.29352652914000	6.93413628289202
C	1.04671123763961	1.83374468069617	5.81937409379988
C	3.43094937047717	0.62989640030621	4.41249036176928
C	2.39077738781538	2.98056871103962	3.94394993817784
O	9.13982093393705	11.32953602217293	7.03451938668509
O	8.57401983237822	12.17985024408312	2.85718122438873
O	5.59833392902804	13.75154434910679	6.54548067564256
O	4.50902692604824	10.91544178534822	3.49907320182354
O	3.69195607199029	0.90287315152325	7.95565458277766
O	-0.07667269059986	1.71244636221899	6.10249833407649
O	3.82671343657044	-0.26477464917723	3.78072811346072
O	2.18187000413390	3.67424809433839	3.03927112913940

5.19. $Fe(CO)_4$-1,4-diphosphinine bis(NHC) complex Me-12

E = −4728.90574667237
E_{ZPE} = 0.28163534
E_T = 0.03773719
E_S = −0.10438937

C	-6.66963352485028	-6.72633410075835	-0.46539540995532
C	-6.97950768907129	-5.50397224014887	-1.09867679198574
C	-4.55665206140921	-4.62782420806539	-0.59614913255104
C	-4.24674510378165	-5.85024065771565	0.03700858119202
P	-6.01481701131244	-4.07658675117638	-1.38274741192225
P	-5.21144065096057	-7.27760227877434	0.32114604057687
N	-7.82177882672513	-7.50248790374792	-0.55881322666344
N	-8.30257152746000	-5.62062394047003	-1.51646994083548
N	-3.40456280918360	-3.85162171596582	-0.50259873207211
N	-2.92368801379622	-5.73357269033344	0.45483081982206
C	-9.00564257568039	-4.54083390675204	-2.20430386447985
H	-8.83613396952915	-3.60625457222162	-1.66263821027576
H	-8.63423076630855	-4.44478211908353	-3.22838472797346
H	-10.06692501306760	-4.78136501216762	-2.21036215788931
C	-7.89386117935680	-8.86417025160256	-0.03471340054242
H	-7.01685757816436	-9.42190331370238	-0.37476921621940
H	-7.91561121824677	-8.84366653085181	1.05848965033948
H	-8.80096664293982	-9.32523774833133	-0.42050395908144
C	-2.22058299916118	-6.81344347992326	1.14249757769659
H	-2.38971147267215	-7.74787705311022	0.60045729223813
H	-1.15935910150805	-6.57267643792480	1.14896848250286
H	-2.59229885658066	-6.90994265480905	2.16642752877629
C	-3.33254165773970	-2.48983857348534	-1.02644801223344
H	-2.42544357799778	-2.02882129117288	-0.64057379875752
H	-3.31079485298665	-2.51012979541518	-2.11965579941021
H	-4.20957278293476	-1.93221595248855	-0.68628105053238
C	-2.39451498303471	-4.51535625281877	0.13460687919991
C	-8.83179605880963	-6.83877353478290	-1.19608341482148
Fe	-10.66349603958477	-7.49639052017284	-1.57191915036646
Fe	-0.56289680237507	-3.85768493466998	0.51053462242405
C	-12.05386247139297	-6.40435543799346	-1.77301420418945
C	-10.85450436585563	-7.52404399857742	0.21037857617270
C	-11.04296972543216	-9.22733061672699	-1.73281953224321
C	-10.19253579726015	-7.36583051132970	-3.29684160044140
C	-0.18307501152209	-2.12685981472689	0.67177818597995
C	-1.03391072303407	-3.98835992254393	2.23544688313897
C	-0.37181981771488	-3.82954479468329	-1.27175788276691
C	0.82742235030776	-4.94983412336204	0.71145127536650
O	-10.94618517168379	-7.52594631356467	1.36363864435107
O	-11.34347182642686	-10.34570488474409	-1.83876635272006
O	-9.85498574128952	-7.27456517075751	-4.39960998492224
O	-12.99190746525684	-5.73293840708420	-1.91977669876070
O	-1.37158037602727	-4.07963889086633	3.33817731060604
O	0.11771579351805	-1.00858020238702	0.77792900866027
O	1.76562831657829	-5.62104784933789	0.85812177171506

O -0.28012262027799 -3.82738863867079 -2.42501546614619

5.20. Transition state Me-9a-TS

E = −4965.1590436321
E_{ZPE} = 0.44596688
E_T = 0.04600367
E_S = −0.1198402

imf = −183.34 cm^{-1}

C -0.47191559293774 -1.61395382464748 -0.05928862296270
C -1.05457416567720 -0.83335460460962 -1.04658455012946
C 1.06353560745226 0.75934364816023 -1.04098932144105
C 1.68942870597473 -0.08577246722572 -0.13672735489912
P -0.66338822788426 0.85635602320821 -1.41649060788569
P 0.88602470571957 -1.18953135547372 0.99509158245337
N -1.27898389158562 -2.74160006464247 0.07413744057832
N -2.18075113815007 -1.53170251849034 -1.47817382178197
N 2.03693962607853 1.65814984754530 -1.47284665470399
N 3.01970061216275 0.32595611120104 -0.07780017634653
C -3.06402262951767 -1.08695406747083 -2.55852320748379
H -4.03392715431104 -0.78816156787847 -2.15755192087089
H -2.59150087160544 -0.23424507157436 -3.04961282571834
H -3.19690173336410 -1.90170658652560 -3.26986834203319
C -1.00574486954789 -3.81584881109624 1.02638650625144
H -0.92617202446982 -3.39713964022654 2.03254018440809
H -1.83594851297720 -4.51875841356411 0.97942473885663
H -0.07007130511990 -4.31467565910915 0.76013135715293
C 4.05712211416253 -0.35046977719044 0.70394854691559
H 3.63386750547845 -1.28043309342945 1.08824801554802
H 4.90774783126625 -0.56678992668325 0.05765648804988
H 4.37968119929973 0.27599983586844 1.53714350820629
C 1.77075370389315 2.73218926168771 -2.42736254761624
H 1.56256458118109 2.30910290748336 -3.41372003121868
H 0.90943139413441 3.31209641302670 -2.08714217049201
H 2.65452076833204 3.36711061900403 -2.46746432265244
C 3.24521365271601 1.38933152130983 -0.90345810695006
C -2.31959145346975 -2.71012125028370 -0.80429369676974
H -0.68351518471660 0.15480695220805 2.63888431900534
C -0.30576525434357 0.84859523795045 1.88723835414274
C -1.25638626357042 1.35545182548587 0.98630092255735
C 0.87396421208844 1.70479378299629 2.29437968440259
H -1.11559154050313 2.39262058245496 0.68072684230657
C -2.68413812453566 0.85600291414235 1.03515056602720
H 0.47086974200539 2.63568675485014 2.72015503699629
H 1.43202398286450 2.01222020008812 1.40160008378602
H -3.05419931547568 1.02035563662716 2.05794058030190
H -2.70050262101292 -0.23125514177619 0.89322845924446
C 1.80480039558544 1.06244770143792 3.32244269876067
H 2.60663296761347 1.75222074759329 3.60227182489674
H 1.25068200312728 0.79442073153987 4.22897662799501
H 2.26605810326649 0.14626259715313 2.93870168324077

C	-3.63300362022886	1.54405900618044	0.05399567865868
H	-4.64857486052575	1.14982229171384	0.15645385289039
H	-3.66353127691522	2.62354647097476	0.23928814493930
H	-3.31696364467087	1.39931818236785	-0.98475192433217
Fe	4.97638785697983	2.32270274541666	-1.18888264952085
Fe	-3.74705066403866	-4.06818651819081	-1.07376420550909
C	4.70435028631856	2.92882509089554	0.47209513097708
C	5.16029209212920	3.97020683376888	-1.82730569813610
C	6.49254750037561	1.49190363117855	-0.77804871931283
C	4.88485333878362	1.60911954576284	-2.82841805392210
C	-4.76311729502252	-2.88070086149165	-0.20252537477926
C	-4.14089987201799	-5.36717129500034	0.07221209093222
C	-2.43682625457666	-5.01584549953581	-1.84198500761152
C	-4.74226694876826	-4.02709471107527	-2.54456853034507
O	4.48621595577775	3.30416131682151	1.54634503302561
O	5.32324901055852	5.04405923944798	-2.24672345664350
O	7.51245048691027	0.99592025072164	-0.51645372837654
O	4.78341333929587	1.12892166269378	-3.87744907714767
O	-5.38027163682314	-2.08240585435004	0.36723390408613
O	-4.42976010451967	-6.23609646100946	0.79153072917788
O	-1.55742270556251	-5.59087163159032	-2.32952159466427
O	-5.42554252308600	-4.03704144682524	-3.48696431451444

5.21. Benzene

E = − 232.664908030522
E_{ZPE} = 0.09878993
E_T = 0.00446923
E_S = −0.03226501

C	-1.95157515664963	-1.94181934194898	0.00123964360573
C	-0.55451034892333	-1.94187599422772	0.00167952666477
C	0.14406955309208	-0.73212590832029	0.00113048235510
C	-0.55442426849691	0.47771364661745	0.00014360049289
C	-1.95145687573065	0.47777029081972	-0.00029632909168
C	-2.65005291912501	-0.73200663881849	0.00025269425661
H	-2.49494331228158	-2.88301125882164	0.00166329347121
H	-0.01124572085226	-2.88312819979092	0.00246102019623
H	1.23086778614158	-0.73211910991074	0.00148510813606
H	-0.01095887139054	1.41884936534224	-0.00027981981910
H	-2.49481857563281	1.41896658235759	-0.00107745735864
H	-3.73685129015094	-0.73191343329822	-0.00010176290916

5.22. FMOs of Me-2a and $[Me\text{-}4a]^{2+}$

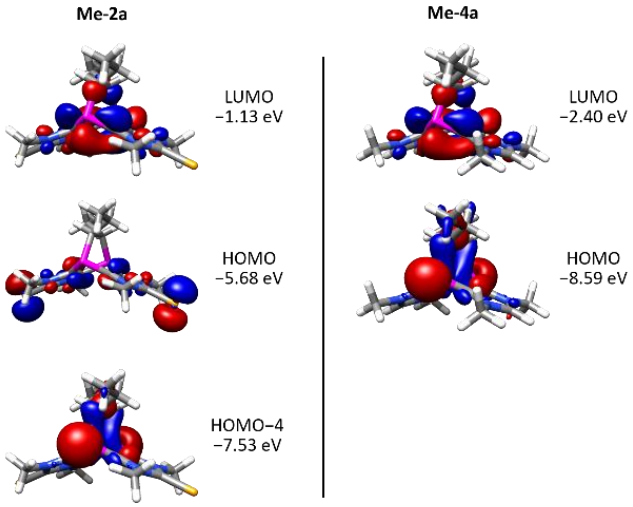

Figure S48 *Calculated FMOs of* ***Me-2a*** *and* ***[Me-4a]$^{2+}$*** *including P-centred LUMOs and P lone pair with large s-character in the HOMO−4 or HOMO, respectively.*

5.23. LUMO to HOMO−5 of Me-5a

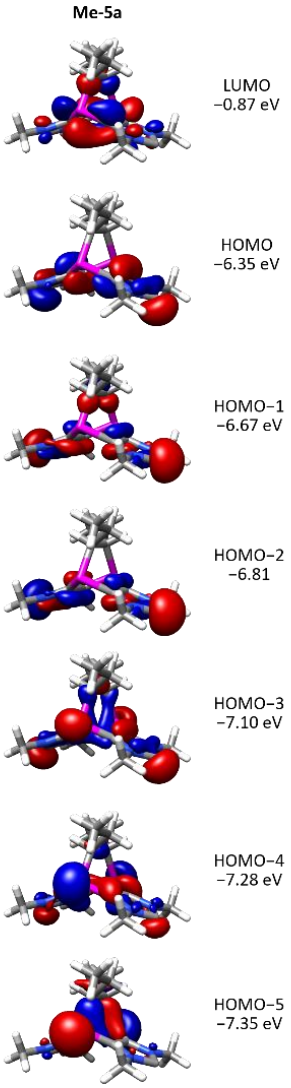

Figure S49 *Calculated carbene and/or P-centred FMOs of* ***Me-5a****.*

5.24. FMOs of Me-9a

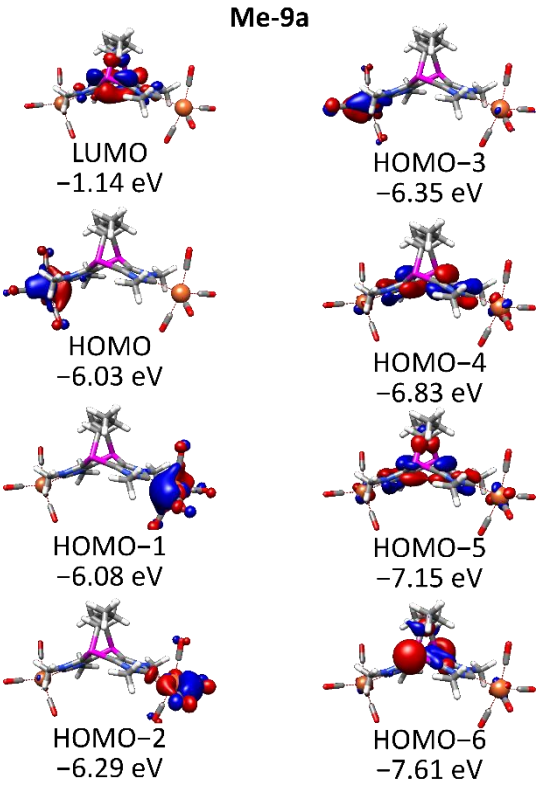

Figure S50 *Calculated FMOs of* ***Me-9a****.*

5.25. HOMO and LUMO of Me-10

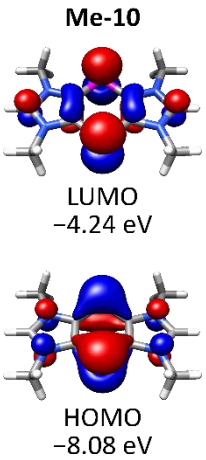

Figure S51 *Calculated HOMO and LUMO of* ***Me-10****.*

5.26. FMOs of Me-11

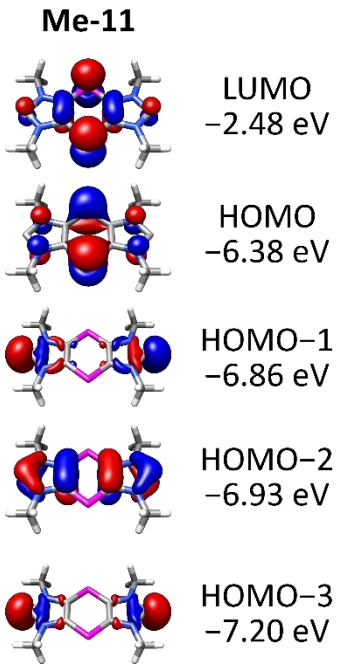

Figure S52 *Calculated FMOs of* ***Me-11***

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