

Cation-Cation Bonding in Nitrenium Metal Complexes

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Supplementary Information

General: Oxygen- and moisture-sensitive reactions were carried out under an atmosphere of purified nitrogen in a glovebox equipped with an inert gas purifier. MeCN, THF, ether, DCM, hexane were purified by passing through a column of activated alumina under inert atmosphere. Anhydrous DMF, DMSO, MeOH packed under inert gas were used as purchased. NMR spectra were recorded on a Bruker Avance 500 or on a Bruker Avance III 600 spectrometer at 296K. Residual solvent peaks was used as internal standards for ^1H and ^{13}C respectively (CDCl_3 : δ_{ppm} 7.26/77.2; CD_2Cl_2 : δ_{ppm} 5.31/54.0, CD_3NO_2 : δ_{ppm} 4.33/62.8; THF- d_8 : δ_{ppm} 1.73/25.3; $^1\text{H}/^{13}\text{C}$ NMR). ^{15}N and ^{31}P NMR signals were referenced to neat CH_3NO_2 (or CD_3NO_2) and 85% H_3PO_4 , respectively. ^{103}Rh and ^{195}Pt signals were referenced using Ξ values of 0.031600000 and 0.214967834, respectively, using the IUPAC recommendations.¹ Peak assignment was based on 2D-NMR experiments, such as 1H-COSY and HMQC. NMR data are reported as follows: chemical shift, multiplicity (s=singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, v = virtual), coupling constant(s), integration and assignment, where known. High resolution mass spectra were recorded on Waters LCT Premier Micromass instrument, using an electrospray ionization (ESI+) technique (MeCN/ H_2O 70:30 or THF 100%; flow: 0.2 ml/min).

Abbreviations:

AcOH – Glacial acetic acid

t-BuOK – Potassium tert-butoxide

DCM – Dichloromethane

DMF – N,N-Dimethylformamide

DMSO – Dimethylsulfoxide

Ether – Diethyl ether

EtOH – Ethanol

MeOH – Methanol

MeCN – Acetonitrile

THF – Tetrahydrofuran

Ar – aryl

cy – cyclohexene ring

OTf - trifluoromethanesulfonate

Synthesis

1. Ligands

1,3-Bis-(2'-diphenylphosphinoethyl)-2-¹⁵N-benzotriazolium trifluoromethanesulfonate (1a')

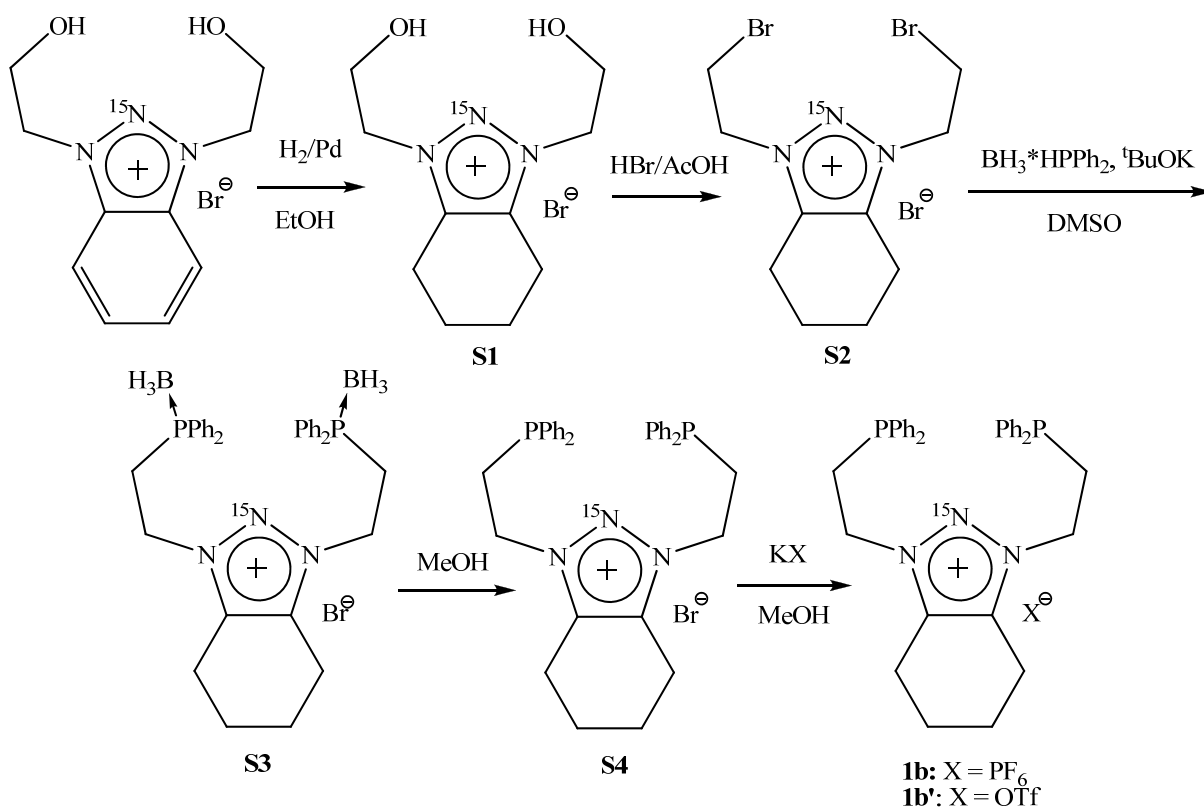
Ligand **1a'** was prepared similarly to the method reported for preparation of ligand **1a**,² except that KOTf instead of KPF₆ was used.

¹H-NMR (500MHz, CDCl₃): δ 7.82 (m, 2H, Ar), 7.76 (m, 2H, Ar), 7.32-7.24 (m, 20H, P-Ar), 4.96 (vq, 4H, N-CH₂), 2.86 (t, 4H, P-CH₂).

¹³C-NMR (125MHz, CDCl₃): δ 135.8 (d, J_(C-P) = 12 Hz, P-Ar), 134.8 (d, J_(C-N) = 1.4 Hz, Ar), 132.8 (d, J_(C-P) = 20Hz, P-Ar), 131.6 (Ar), 129.7 (P-Ar), 129.0 (d, J_(C-P) = 7.2 Hz, P-Ar), 120.9 (q, J_(P-F) = 321 Hz, OTf), 113.6 (Ar), 50.1 (dd, J_(C-P) = 23 Hz, J_(C-N) = 5.0 Hz, N-CH₂), 27.8 (d, J_(C-P) = 17 Hz, P-CH₂); ¹⁵N-NMR (50MHz, CDCl₃): δ -28.9.

³¹P-NMR (200MHz, CDCl₃): δ -21.0.

Ligands **1b** and **1b'** were prepared according to **Scheme S1**.



Scheme S1. Synthesis of *N*-heterocyclic nitrenium based ligands **1b,b'**

1,3-Di-(2'-hydroxyethyl)-2-¹⁵N-tetrahydrobenzotriazolium bromide (S1)

1,3-(2'-hydroxyethyl)-2-¹⁵N-benzotriazolium bromide was prepared from 2-¹⁵N-benzotriazole as previously described.² The crude compound was purified by crystallization from MeOH/DCM. The obtained crystalline material (490 mg, 1.69 mmol) was charged in a 500 ml hydrogenation vessel together with 180 mg of 10% Pd on activated carbon catalyst (0.17 mmol Pd), 10 ml of absolute ethanol and a stirring bar. The air was evacuated and pressurized with 3 atm of H₂. The vessel was then immersed in an oil bath and heated to 70°C with stirring for 20 hours. The reaction mixture was cooled, filtered through a short column of celite and evaporated. The oily residue was dissolved in DCM and small amount of residual KBr that precipitated was removed by filtration through a cotton plug. The obtained clear yellowish solution was once again evaporated, leaving an oily residue that solidified upon prolonged evaporation, yielding 422 mg (1.44 mmol) of the title compound (85%).

¹H-NMR (500MHz, CDCl₃): δ 4.52 (br, 2H, OH), 4.48 (br, 4H), 3.99 (br, 4H), 2.88 (br, 4H, cy), 1.93 (br, 4H, cy). ¹³C-NMR (125MHz, CDCl₃): δ 140.8 (d, J_(C-N) = 1.3 Hz, cy), 60.0 (CH₂-OH), 54.6 (d, J_(C-N) = 4.5 Hz, N-CH₂), 20.9 (cy), 20.6 (cy). ¹⁵N-NMR (50MHz, CDCl₃): δ -44.0.
HR-MS calc. for C₁₀H₁₈N₂¹⁵NO₂⁺ (M⁺): 213.1369, found: 213.1351.

1,3-Di-(2'-bromoethyl)-2-¹⁵N-tetrahydrobenzotriazolium bromide (S2)

Compound **S1** (410 mg, 1.40 mmol) was charged in a 50 ml Schlenk vessel together with 5 ml of 33% HBr in AcOH and a stirring bar. The vessel was sealed with a Teflon cap and heated to 110°C with stirring for 48 hours. Reaction mixture was then evaporated in vacuo at 70°C, the orange oily residue was dissolved in chloroform and filtered through a cotton plug to remove some insoluble black material, dried with Na₂SO₄ and evaporated, yielding 519 mg of the title compound, as a viscous brownish oil (88%).

¹H-NMR (500MHz, CDCl₃): δ 5.12 (br, 4H, N-CH₂), 3.95 (br, 4H, CH₂-Br), 3.05 (br, 4H, cy), 2.03 (br, 4H, cy). ¹³C-NMR (125MHz, CDCl₃): δ 140.9 (d, J_(C-N) = 1.2 Hz, cy), 53.6 (d, J_(C-N) = 5.1 Hz, N-CH₂), 28.6 (CH₂-Br), 21.0 (cy), 20.9 (cy). ¹⁵N-NMR (50MHz, CDCl₃): δ -43.8.
HR-MS calc. for C₁₀H₁₆N₂¹⁵NBr₂⁺ (M⁺): 336.9681, found: 336.9678.

1,3-Bis-(2'-diphenylphosphinoethyl)-2-¹⁵N-tetrahydrobenzotriazolium bromide, bis-borane adduct (S3)

Inside a dry box, 500 mg of compound **S2** (1.19 mmol) were dissolved in 5.0 ml of dry DMSO in a vial. In a separate vial, 267 mg of solid tBuOK (2.38 mmol) were added portionwise to a solution of 478 mg diphenylphosphine-borane adduct (2.38 mmol) in 3.0 ml of dry DMSO with stirring (as an equivalent amount of base is added to the phosphine-borane, the solution color turns orange). The resulting orange solution was then added dropwise to a vigorously stirred solution of **S2**. After the addition, the reaction mixture were taken out of the glove box and transferred to a separation funnel together with ca. 100 ml DCM. This combined organic phase was repeatedly washed with water, dried over Na₂SO₄ and evaporated. The crude product was further purified by flash chromatography on a silica gel (CHCl₃/EtOH 2-11%, the product

comes out at 8-9% EtOH). The eluted fractions were evaporated at room temperature, resulting in 505 mg (0.768 mmol) of the pure title compound as solidified white foam (64%).

Note: This reaction is extremely sensitive to the purity of the solvent DMSO. Significantly reduced yields were obtained when an old DMSO was used.

$^1\text{H-NMR}$ (500MHz, CDCl_3): δ 7.79 (m, 8H, P-Ar), 7.48 (m, 12H, P-Ar), 4.55 (vq, 4H, N- CH_2), 3.23 (vq, 4H, P- CH_2), 2.66 (br, 4H, cy), 1.91 (br, 4H, cy), 0.91 (very br q, 6H, BH_3); $^{13}\text{C-NMR}$ (125MHz, CDCl_3): δ 140.4 (d, $J_{(\text{C-N})} = 1.4$ Hz, cy), 132.5 (d, $J_{(\text{C-P})} = 9.9$ Hz, P-Ar), 132.2 (d, $J_{(\text{C-P})} = 2.5$ Hz, P-Ar), 129.4 (d, $J_{(\text{C-P})} = 10.3$ Hz, P-Ar), 127.3 (d, $J_{(\text{C-P})} = 56$ Hz, P-Ar), 46.4 (vt, $J_{(\text{C-P})} = J_{(\text{C-N})} = 5.6$ Hz, N- CH_2), 25.2 (d, $J_{(\text{C-P})} = 37$ Hz, P- CH_2), 20.6 (cy), 20.2 (cy); $^{15}\text{N-NMR}$ (50MHz, CDCl_3): δ -46.0; $^{31}\text{P-NMR}$ (200MHz, CDCl_3): δ 13.1 (br).
HR-MS calc. for $\text{C}_{34}\text{H}_{42}\text{B}_2\text{N}_2^{15}\text{NP}_2^+$ (M^+): 577.3010, found: 577.3043.

1,3-Bis-(2'-diphenylphosphinoethyl)-2- ^{15}N -tetrahydrobenzotriazolium bromide (S4)

Inside a dry box, 485 mg (0.738 mmol) of **S3** were dissolved in 50 ml of dry deoxygenated MeOH, transferred to a Schlenk vessel equipped with a stirring bar, and sealed tightly with a Teflon cap. The reaction vessel was then taken outside the dry box and heated to 80°C with stirring for 3 hours. After the reaction mixture was cooled to room temperature, the reaction vessel was connected to a vacuum line and the solvent was completely evaporated. The Schlenk vessel was then returned inside the dry box, where the residue was dissolved in DCM, the total volume of which was then reduced to ca. 1 ml by evaporation. The product was then precipitated by adding excess of ether and dried under vacuum, resulting in 406 mg (0.645 mmol) of the pure title compound, as a white crystalline powder (87%).

Note: In several preparations, presence of traces of oxygen resulted in a partial oxidation of the phosphine moieties to the corresponding phosphine oxides, as evident from the additional resonance at 29.2 ppm in $^{31}\text{P-NMR}$. In such cases, an additional reduction step was undertaken. The partially oxidized product is suspended in THF (ca. 5 mg/ml) and AlH_3 in THF, 2.5 mol eq. relative to the amount of the phosphine-oxide (as determined by integration of the corresponding $^{31}\text{P-NMR}$ peaks), are added. The reaction mixture is then heated in a closed vessel to 80°C for one hour, during which the suspension completely dissolves. After cooling to room temperature, the reaction mixture is quenched by careful addition of MeOH and the solvents are removed in vacuo. The residue is then dissolved in DCM and filtrated through celite, the volume of DCM is reduced and the pure product is precipitated by adding excess of ether (90-95%).

$^1\text{H-NMR}$ (500MHz, CDCl_3): δ 7.39 (m, 8H, P-Ar), 7.34 (m, 12H, P-Ar), 4.55 (m, 4H, N- CH_2), 2.74 (t, 4H, P- CH_2), 2.70 (br, 4H, cy), 1.88 (br, 4H, cy); $^{13}\text{C-NMR}$ (125MHz, CDCl_3): δ 139.8 (d, $J_{(\text{C-N})} = 1.3$ Hz, cy), 136.0 (d, $J_{(\text{C-P})} = 12$ Hz, P-Ar), 132.8 (d, $J_{(\text{C-P})} = 19$ Hz, P-Ar), 129.6 (P-Ar), 129.0 (d, $J_{(\text{C-P})} = 7.1$ Hz, P-Ar), 49.3 (dd, $J_{(\text{C-P})} = 23$ Hz, $J_{(\text{C-N})} = 5.1$ Hz, N- CH_2), 27.6 (d, $J_{(\text{C-P})} = 16$ Hz, P- CH_2), 20.6 (cy), 20.4 (cy); $^{15}\text{N-NMR}$ (50MHz, CDCl_3): δ -44.9; $^{31}\text{P-NMR}$ (200MHz, CDCl_3): δ -20.9.

HR-MS calc. for $C_{34}H_{36}N_2^{15}NP_2^+$ (M^+): 549.2355, found: 549.2329.

1,3-Bis-(2'-diphenylphosphinoethyl)-2-¹⁵N-tetrahydrobenzotriazolium hexafluorophosphate (1b)

200 mg of compound **S4** (0.318 mmol) and 88 mg of KPF_6 (0.477 mmol, 1.5 eq.) were dissolved in a minimal amount of MeOH. The solvent was evaporated and the residue dissolved in DCM. The precipitated KBr and the remaining KPF_6 were removed by filtration through celite. The filtrate was evaporated resulting in 214 mg (0.308) mmol of the title compound (97%).

¹H-NMR (500MHz, $CDCl_3$): δ 7.39 (m, 8H, P-Ar), 7.33 (m, 12H, P-Ar), 4.35 (m, 4H, N-CH₂), 2.68 (t, 4H, P-CH₂), 2.50 (br, 4H, cy), 1.80 (br, 4H, cy); ¹³C-NMR (125MHz, $CDCl_3$): δ 139.4 (d, $J_{(C-N)} = 1.2$ Hz, cy), 136.1 (d, $J_{(C-P)} = 12$ Hz, P-Ar), 132.8 (d, $J_{(C-P)} = 20$ Hz, P-Ar), 129.7 (P-Ar), 129.0 (d, $J_{(C-P)} = 7.2$ Hz, P-Ar), 48.7 (dd, $J_{(C-P)} = 25$ Hz, $J_{(C-N)} = 5.7$ Hz, N-CH₂), 27.4 (d, $J_{(C-P)} = 16$ Hz, P-CH₂), 20.4 (cy), 19.7 (cy); ¹⁵N-NMR (50MHz, $CDCl_3$): δ -44.8; ³¹P-NMR (200MHz, $CDCl_3$): δ -21.2, -144.3 (m, $J_{(P-F)} = 713$ Hz).

1,3-Bis-(2'-diphenylphosphinoethyl)-2-¹⁵N-tetrahydrobenzotriazolium trifluoromethanesulfonate (1b')

200 mg of compound **S4** (0.318 mmol) and 90 mg of KOTf (0.477 mmol, 1.5 eq.) were dissolved in a minimal amount of MeOH. The solvent was evaporated and the residue dissolved in DCM. The precipitated KBr and the remaining KOTf were removed by filtration through celite. The filtrate was evaporated resulting in 191 mg (0.273 mmol) of the title compound (86%).

¹H-NMR (500MHz, $CDCl_3$): δ 7.41 (m, 8H, P-Ar), 7.34 (m, 12H, P-Ar), 4.41 (m, 4H, N-CH₂), 2.73 (t, 4H, P-CH₂), 2.59 (br, 4H, cy), 1.86 (br, 4H, cy); ¹³C-NMR (125MHz, $CDCl_3$): δ 139.6 (d, $J_{(C-N)} = 1.3$ Hz, cy), 136.1 (d, $J_{(C-P)} = 12$ Hz, P-Ar), 132.8 (d, $J_{(C-P)} = 20$ Hz, P-Ar), 129.7 (P-Ar), 129.0 (d, $J_{(C-P)} = 7.2$ Hz, P-Ar), 120.9 (q, $J_{(C-F)} = 321$ Hz, OTf), 48.8 (dd, $J_{(C-P)} = 25$ Hz, $J_{(C-N)} = 5.3$ Hz, N-CH₂), 27.5 (d, $J_{(C-P)} = 16$ Hz, P-CH₂), 20.5 (cy), 20.0 (cy); ¹⁵N-NMR (50MHz, $CDCl_3$): δ -45.0; ³¹P-NMR (200MHz, $CDCl_3$): δ -21.1.

2. Complexes

General: All steps of preparation of Rh(I) and Pt(II) complexes were performed in degassed dry solvents under the atmosphere of purified nitrogen inside a glove box, unless specified otherwise. All procedures involving the use of AgPF₆ or AgOTf were performed with the exclusion of light.

2.1. Rh(I) complexes 2-6a,b

1,3-Bis-(2'-diphenylphosphinoethyl)-2-¹⁵N-benzotriazolium rhodium(I) chloride hexafluorophosphate (2a)

Compound **2a** was prepared by a simplified version of the previously reported procedure.¹ 30.0 mg of the ligand **1a** (43.4×10^{-3} mmol) were dissolved in 1 ml of nitromethane and a 1 ml suspension of 8.4 mg [RhCl(C₂H₄)₂]₂ (21.7×10^{-3} mmol, 0.5 eq.) in nitromethane was added dropwise forming an intensely colored dark purple solution, that was stirred for 1 h and then evaporated to dryness, resulting in a quantitative formation of the title compound (36 mg, 43.4×10^{-3} mmol), as a shiny dark purple crystalline powder. Full characterization of **2a** including multinuclear NMR-spectra in d₇-DMF was reported previously.² Here we provide, for comparison, also its NMR-spectra measured in CD₃NO₂ which was used as a deuterated solvent for the NMR characterization of almost all other complexes reported in this paper.

¹H-NMR (500MHz, CD₃NO₂): δ 8.03 (vq, 8H, P-Ar), 7.93 (m, 4H, Ar), 7.55 (t, 4H, P-Ar), 7.51 (t, 8H, P-Ar), 5.14 (br, 4H, N-CH₂), 2.77 (br, 4H, P-CH₂); ¹³C-NMR (125MHz, CD₃NO₂): δ 136.4 (Ar), 135.4 (vt, J_(C-P) = 6.3 Hz, P-Ar), 134.1 (vt, J_(C-P) = 23 Hz, P-Ar), 132.1, 131.5, 129.9 (vt, J_(C-P) = 5.0 Hz, P-Ar), 112.5 (Ar), 49.9 (br, N-CH₂), 22.2 (vt, J_(C-P) = 12 Hz, P-CH₂); ¹⁵N-NMR (50MHz, CD₃NO₂): δ -92.7 (dt, J_(N-Rh) = 29 Hz, J_(N-P) = 3.7 Hz); ³¹P-NMR (200MHz, CD₃NO₂): δ 14.5 (dd, J_(P-Rh) = 130 Hz, J_(P-N) = 3.7 Hz), -143.0 (m, J_(P-F) = 713 Hz).

1,3-Bis-(2'-diphenylphosphinoethyl)-2-¹⁵N-benzotriazolium rhodium(I) iodide hexafluorophosphate (3a)

20.0 mg of compound **2a** (24.1×10^{-3} mmol) were dissolved in 0.5 ml DMF and 0.36 ml of a 10 mg/ml NaI solution in DMF (24.1×10^{-3} mmol NaI, 1.0 eq.) were added. After stirring for 2 h during which the color changed gradually from purple to violet, the solvent was evaporated in vacuo. The residue was dissolved in DCM, forming an ink violet solution that was filtrated through celite to remove the precipitated NaCl. The volume of DCM was then reduced to ca. 0.5 ml and the product was precipitated by addition excess of ether, yielding 18 mg (19.6×10^{-3} mmol) of the title product, as a dark violet powder (80%).

Alternative procedure:

20.0 mg of compound **6a** (20.7×10^{-3} mmol) were dissolved in 2 ml THF and 0.28 ml of 10 mg/ml LiI solution (20.7×10^{-3} mmol, 1 eq.) in THF were added, resulting in a color change from

brown to ink violet. The solution was stirred for 15 min and evaporated in vacuo. The dark violet residue was washed with ether to remove the formed LiPF_6 and dried, yielding 17 mg (18.5×10^{-3} mmol) of the title product (89%).

$^1\text{H-NMR}$ (500MHz, CD_3NO_2): δ 7.99 (m, 12H, Ar + P-Ar), 7.50 (m, 12H, P-Ar), 5.23 (vq, 4H, N- CH_2), 2.79 (br, 4H, P- CH_2); $^{13}\text{C-NMR}$ (125MHz, CD_3NO_2): δ 136.2 (Ar), 135.7 (vt, $J_{\text{C-P}} = 6.1$ Hz, P-Ar), 135.6 (vt, $J_{\text{C-P}} = 23$ Hz, P-Ar), 132.0, 131.9, 129.6 (vt, $J_{\text{C-P}} = 4.9$ Hz, P-Ar), 112.9 (Ar), 50.4 (m, N- CH_2), 23.1 (vt, $J_{\text{C-P}} = 11$ Hz, P- CH_2); $^{15}\text{N-NMR}$ (50MHz, CD_3NO_2): δ -94.1 (dt, $J_{\text{N-Rh}} = 28$ Hz, $J_{\text{N-P}} = 3.3$ Hz); $^{31}\text{P-NMR}$ (200MHz, CD_3NO_2): δ 14.2 (dd, $J_{\text{P-Rh}} = 128$ Hz, $J_{\text{P-N}} = 3.3$ Hz), -143.0 (m, $J_{\text{P-F}} = 713$ Hz).

HR-MS calc. for $\text{C}_{34}\text{H}_{32}\text{N}_2^{15}\text{NP}_2\text{RhI}^+$ (M^+): 775.0142, found: 775.0115.

1,3-Bis-(2'-diphenylphosphinoethyl)-2- ^{15}N -benzotriazolium rhodium(I) tetrahydrofurane bis-hexafluorophosphate (4a)

5.5 mg of AgPF_6 (21.7×10^{-3} mmol, 1.0 eq.) in 0.5 ml THF were added to a stirred solution of 20.0 mg of compound **3a** (21.7×10^{-3} mmol) in 2 ml THF. Upon the addition, the color changed immediately from dark violet to dark brown and a thick precipitate formed. After stirring for 5 min. the precipitate was removed by filtration through celite, and the clear dark brown filtrate was concentrated in vacuo to ~0.5 ml and treated with excess of hexane. The brown precipitate that was formed was collected by filtration through a cotton plug and briefly dried under vacuum, yielding 10 mg (9.9×10^{-3} mmol) of the title compound as a light brown powder (45%). The obtained compound **4a** is soluble in DCM, but graduate formation of decomposition products was observed. It was, therefore, characterized in d_8 -THF, although this solvent polymerizes after prolonged standing, precluding obtaining high resolution $^{13}\text{C-NMR}$ spectrum.

$^1\text{H-NMR}$ (500MHz, d_8 -THF): δ 8.17 (dd, 2H, Ar), 8.03 (br, 8H, P-Ar), 7.81 (dd, 2H, Ar), 7.54 (t, 8H, P-Ar), 7.48 (t, 4H, P-Ar), 5.93 (br, 4H, N- CH_2), 2.98 (very br, 4H, P- CH_2); $^1\text{H-NMR}$ (500MHz, CD_2Cl_2 , major product): 7.91 (dd, 2H, Ar), 7.86 (m, 10H, Ar + P-Ar), 7.55 (m, 12H, P-Ar), 5.72 (br, 4H, N- CH_2), 2.94 (m, 4H, THF), 2.88 (br, 4H, P- CH_2), 0.73 (br, 4H, THF); $^{13}\text{C-NMR}$ (125MHz, d_8 -THF): δ 137.2 (Ar), 135-132 (br, P-Ar), 131.8 (Ar), 130.2 (br, P-Ar), 113.0 (Ar), 52.8 (br, N- CH_2), 24.2 (vt, $J_{\text{C-P}} = 12$ Hz, P- CH_2); $^{15}\text{N-NMR}$ (50MHz, d_8 -THF): δ -92.3 (dt, $J_{\text{N-Rh}} = 31$ Hz, $J_{\text{N-P}} = 4.6$ Hz); $^{31}\text{P-NMR}$ (200MHz, d_8 -THF): δ 19.1 (dd, $J_{\text{P-Rh}} = 130$ Hz, $J_{\text{P-N}} = 4.6$ Hz), -143.1 (m, $J_{\text{P-F}} = 711$ Hz).

Due to its high sensitivity, HR-MS for **4a** could not be obtained.

1,3-Bis-(2'-diphenylphosphinoethyl)-2- ^{15}N -benzotriazolium η^2 -ethylene rhodium(I) bis-hexafluorophosphate (5a)

To a 30.0 mg (43.4×10^{-3} mmol) of ligand **1a** dissolved in 1.0 ml THF 10.9 mg of AgPF_6 (11.0×10^{-3} mmol, 1.0 eq.) in 1.0 ml THF were added dropwise with stirring. A white precipitate

is formed after addition of approximately 0.5 eq. of AgPF_6 , but it dissolves upon addition of the remaining 0.5 eq., yielding finally a clear colorless solution. Separately, 8.4 mg of a freshly prepared $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (21.7×10^{-3} mmol, 0.5 eq.) were dissolved in an additional 1.0 ml of THF and added dropwise with stirring to the first colorless solution, forming a turbid brown suspension that was stirred for additional 10 min. The suspension was filtrated through celite resulting in a dark brown solution. The volume of the solution was reduced to ca. 0.5 ml and the product was precipitated by adding excess of hexane, yielding 28 mg (30.0×10^{-3} mmol) of the title compound, as a brown powder (67%).

$^1\text{H-NMR}$ (500MHz, CD_3NO_2): δ 8.22 (dd, 2H, Ar), 8.09 (dd, 2H, Ar), 7.78 (vq, 8H, P-Ar), 7.62 (t, 4H, P-Ar), 7.58 (t, 8H, P-Ar), 5.93 (vq, 4H, N- CH_2), 3.41 (br, 4H, C_2H_4), 3.11 (br, 4H, P- CH_2); $^{13}\text{C-NMR}$ (125MHz, CD_3NO_2): δ 137.5 (Ar), 135.6, 134.8 (vt, $J_{\text{C-P}} = 6.4$ Hz, P-Ar), 133.3, 130.8 (vt, $J_{\text{C-P}} = 5.2$ Hz, P-Ar), 130.2 (vt, $J_{\text{C-P}} = 24$ Hz, P-Ar), 114.5 (Ar), 68.1 (br d, $J_{\text{C-Rh}} = 12$ Hz, C_2H_4), 53.3 (br, N- CH_2), 24.2 (vt, $J_{\text{C-P}} = 13$ Hz, P- CH_2); $^{15}\text{N-NMR}$ (50MHz, CD_3NO_2): δ -93.5 (dt, $J_{\text{N-Rh}} = 21$ Hz, $J_{\text{N-P}} = 4.0$ Hz); $^{31}\text{P-NMR}$ (200MHz, CD_3NO_2): δ 23.9 (dd, $J_{\text{P-Rh}} = 116$ Hz, $J_{\text{P-N}} = 4.0$ Hz), -143.0 (m, $J_{\text{P-F}} = 707$ Hz).

Due to its high sensitivity, HR-MS for **5a** could not be obtained.

1,3-bis-(2'-diphenylphosphinoethyl)-²N-benzotriazolium triphenylphosphino- rhodium(I) bis-hexafluorophosphate (6a)

To 12.0 mg of compound **3a** (14.1×10^{-3} mmol) dissolved in 2 ml THF 3.3 mg of AgPF_6 (13.0×10^{-3} mmol, 1.0 eq.) in 1 ml THF were added with stirring. Upon addition, the color changed from ink-violet to brown. After stirring for 10 min the reaction mixture was filtered through celite, resulting in a clear brown solution. Finally, 3.7 mg of PPh_3 (14.1×10^{-3} mmol, 1.1 eq.) dissolved in 1 ml THF were added. The obtained dark greenish-yellow solution was evaporated and the solid residue was washed thoroughly with ether from excess of PPh_3 , yielding 14 mg (11.7×10^{-3} mmol) of the title product (89%), as a dark green powder. Single crystals of compound **6a** suitable for an X-ray analysis were obtained by a slow evaporation of its THF solution.

$^1\text{H-NMR}$ (500MHz, CD_3NO_2): δ 8.03 (dd, 2H, Ar), 7.97 (dd, 2H, Ar), 7.51 (m, 8H, P-Ar) 7.39 (t, 4H, P-Ar), 7.33 (t, 8H, P-Ar), 7.22 (m, 15H, PPh_3), 5.88 (br, 4H, N- CH_2), 3.06 (br, 4H, P- CH_2); $^{13}\text{C-NMR}$ (125MHz, CD_3NO_2): δ 137.2 (d, $J_{\text{C-N}} = 1.3$ Hz, Ar), 135.4 (d, $J_{\text{C-P}} = 12$ Hz), 134.7, 134.6 (dt, $^1J_{\text{C-P}} = 51$ Hz, $^3J_{\text{C-P}} = 2.7$ Hz, C_{ipso} of PPh_3), 134.2 (very br), 132.3 (br), 132.2 (d, $J_{\text{C-P}} = 2.3$ Hz), 131.4 (vt, $J_{\text{C-P}} = 23$ Hz), 130.2 (vt, $J_{\text{C-P}} = 5.1$ Hz), 129.9 (d, $J_{\text{C-P}} = 11$ Hz), 113.8 (Ar), 52.2 (br, N- CH_2), 26.0 (vt, $J_{\text{C-P}} = 12$ Hz, P- CH_2); $^{15}\text{N-NMR}$ (50MHz, CD_3NO_2): δ -81.4 (ddt, $J_{\text{N-P trans}} = 38$ Hz, $J_{\text{N-Rh}} = 15$ Hz, $J_{\text{N-P cis}} = 4.2$ Hz); $^{31}\text{P-NMR}$ (200MHz, CD_3NO_2): δ 42.2 (dq, $J_{\text{P-Rh}} = 174$ Hz, $J_{\text{P-P}} = J_{\text{P-N}} = 38$ Hz, PPh_3), 20.1 (ddd, $J_{\text{P-Rh}} = 134$ Hz, $J_{\text{P-P}} = 38$ Hz, $J_{\text{P-N}} = 4.2$ Hz), -143.0 (m, $J_{\text{P-F}} = 707$ Hz); $^{103}\text{Rh-NMR}$ (19MHz, CD_3NO_2): -214.1 (dtd, $J_{\text{Rh-P}} = 174$ Hz, 134 Hz, $J_{\text{Rh-N}} = 15$ Hz).

HR-MS calc. for $C_{52}H_{47}N_2^{15}NF_6P_4Rh^+$ ($M^*PF_6^+$): 1055.1650, found 1055.1655.

1,3-bis-(2'-diphenylphosphinoethyl)-2-¹⁵N-tetrahydrobenzotriazolium η^2 -ethylene-rhodium(I) bis-hexafluorophosphate (5b)

To 30.0 mg of ligand **1b** (43.2×10^{-3} mmol) dissolved in 0.5 ml THF 10.9 mg of $AgPF_6$ (43.2×10^{-3} mmol, 1.0 eq.) in 1.0 ml THF were added dropwise with stirring. A white precipitate is formed after addition of approximately 0.5 eq. of $AgPF_6$, but it dissolves upon addition of the remaining 0.5 eq., yielding finally a clear colorless solution. 8.4 mg of a freshly prepared $[RhCl(C_2H_4)_2]_2$ (21.6×10^{-3} mmol, 0.5 eq.) were dissolved in an additional 1.0 ml of THF and added dropwise with stirring to the first colorless solution, forming a turbid orange-brown suspension that was stirred for additional 10 min. The suspension was filtrated through celite resulting in a clear bright orange solution. The volume of the solution was reduced to ca. 0.5 ml and the product was precipitated out by addition excess of hexane, yielding 35 mg (36.1×10^{-3} mmol) of the title compound, as an orange crystalline powder (83%).

Single crystals suitable for an X-ray analysis were obtained by a slow diffusion of ether into a THF solution of **5b** at $-30^\circ C$.

1H -NMR (500MHz, CD_3NO_2): δ 7.75 (vq, 8H, P-Ar), 7.63 (t, 4H, P-Ar), 7.57 (t, 8H, P-Ar), 5.42 (vq, 4H, N-CH₂), 3.10 (br, 4H, cy), 2.97 (br, 8H, C₂H₄ + P-CH₂), 1.88 (br, 4H, cy); ^{13}C -NMR (125MHz, CD_3NO_2): δ 145.9 (Ar), 134.8 (vt, $J_{(C-P)} = 6.4$ Hz, P-Ar), 133.2 (P-Ar), 130.7 (vt, $J_{(C-P)} = 5.1$ Hz, P-Ar), 130.6 (vt, $J_{(C-P)} = 23$ Hz, P-Ar), 64.4 (br d, $J_{(C-Rh)} = 12$ Hz, C₂H₄), 52.4 (br, N-CH₂), 24.8 (vt, $J_{(C-P)} = 13$ Hz, P-CH₂), 21.8 (cy), 21.2 (cy); ^{15}N -NMR (50MHz, CD_3NO_2): δ -109.8 (dt, $J_{(N-Rh)} = 21$ Hz, $J_{(N-P)} = 4.0$ Hz); ^{31}P -NMR (200MHz, CD_3NO_2): δ 23.2 (dd, $J_{(P-Rh)} = 118$ Hz, $J_{(P-N)} = 4.0$ Hz), -143.0 (m, $J_{(P-F)} = 707$ Hz).

HR-MS calc. for $C_{36}H_{40}N_2^{15}NF_6P_3Rh^+$ ($M^*PF_6^+$): 825.1365, found 825.1353.

1,3-Bis-(2'-diphenylphosphinoethyl)-2-¹⁵N-tetrahydrobenzotriazolium rhodium(I) chloride hexafluorophosphate (2b)

30.0 mg of compound **5b** (30.9×10^{-3} mmol) were dissolved in 2 ml THF and cooled to $-30^\circ C$. Then 1.3 ml of a pre-cooled 1.0 mg/ml LiCl solution in THF (30.9×10^{-3} mmol of LiCl, 1.0 eq.) were added. The resulting solution was kept at $-30^\circ C$ for 5d. During this period a coarse brown crystalline precipitate was formed along with a very fine yellow powder. The brown precipitate was collected, washed with ether and dried, yielding 7.0 mg (8.4×10^{-3} mmol) of pure title product (28%).

1H -NMR (CD_3NO_2 , 500MHz): δ 8.02 (m, 8H, P-Ar), 7.51 (m, 12H, P-Ar), 4.84 (m, 4H, N-CH₂), 2.75 (br, 4H, cy), 2.59 (m, 4H, P-CH₂), 1.92 (br, 4H, cy); ^{13}C -NMR (CD_3NO_2 , 125MHz): δ 140.8 (cy), 135.3 (vt, $J_{(C-P)} = 6.3$ Hz, P-Ar), 134.9 ($J_{(C-P)} = 21$ Hz, P-Ar), 131.8 (P-Ar), 129.8 (vt, $J_{(C-P)} = 4.9$ Hz, P-Ar), 49.4 (br, N-CH₂), 23.0 (vt, $J_{(C-P)} = 12$ Hz, P-CH₂), 22.0 (cy), 21.9 (cy);

^{15}N -NMR (50MHz, CD_3NO_2): δ -103.1 (dt, $J_{(\text{N-Rh})} = 27$ Hz, $J_{(\text{N-P})} = 3.9$ Hz); ^{31}P -NMR (200MHz, CD_3NO_2): δ 14.2 (dd, $J_{(\text{P-Rh})} = 133$ Hz, $J_{(\text{P-N})} = 3.9$ Hz), -143.0 (m, $J_{(\text{P-F})} = 707$ Hz).

HR-MS calc. for $\text{C}_{34}\text{H}_{36}\text{N}_2^{15}\text{NP}_2\text{ClRh}^+$ (M^+): 687.1098, found: 687.1090.

1,3-Bis-(2'-diphenylphosphinoethyl)-2- ^{15}N -tetrahydrobenzotriazolium *rhodium(I)*
tetrahydrofurane bis-hexafluorophosphate (4b)

15.0 mg of a freshly prepared complex **5b** (15.4×10^{-3} mmol) were dissolved with stirring in 3.0 ml of THF, forming a clear yellow-orange solution. Next, 0.2 ml of a 10 mg/ml LiI solution in THF (15.4×10^{-3} mmol LiI, 1.0 eq.) were added and the resulting reddish-brown solution was stirred vigorously for 4 h. The volume of the reaction mixture was then reduced in vacuo to ca. 1 ml and the formed compound **3b** was treated with 3.9 mg of AgPF_6 (15.4×10^{-3} mmol, 1.0 eq.) dissolved in 0.5 ml THF. The reaction mixture immediately turned orange with formation of a thick precipitate. After stirring for 5 min, the reaction mixture was filtrated through celite and the obtained clear orange solution was further concentrated in vacuo until its volume was ca. 0.5 ml. The concentrated solution was cooled to -30°C for 2-3 hours, during which a red-orange crystalline precipitate has formed. The mother liquor was then removed by a pipette and the remained precipitate dried briefly under vacuum. The obtained pure **4b** is soluble in deuterated DCM and unlike the analogous **4a** is sufficiently stable in this solvent for full characterization by multinuclear NMR.

^1H -NMR (600MHz, CD_2Cl_2): δ 7.85 (m, 8H, P-Ar), 7.55 (m, 12H, P-Ar), 5.25 (m, 4H, N- CH_2), 2.83 (m, 4H, THF), 2.74 (br, 4H, cy), 2.69 (br, 4H, P- CH_2), 1.86 (br, 4H, cy), 0.75 (m, 4H, THF); ^{13}C -NMR (150MHz, CD_2Cl_2): δ 143.0 (cy), 133.9 (vt, $J_{(\text{C-P})} = 6.9$ Hz, P-Ar), 132.2 (P-Ar), 132.1 (vt, $J_{(\text{C-P})} = 22$ Hz), 130.2 (vt, $J_{(\text{C-P})} = 5.1$ Hz, P-Ar), 75.7 (THF), 51.7 (m, N- CH_2), 24.9 (THF), 24.7 (vt, $J_{(\text{C-P})} = 12$ Hz, P- CH_2); ^{15}N -NMR (60MHz, CD_2Cl_2): δ -117.5 (dt, $J_{(\text{N-Rh})} = 30$ Hz, $J_{(\text{N-P})} = 4.9$ Hz); ^{31}P -NMR (240MHz, CD_2Cl_2): δ 16.1 (dd, $J_{(\text{P-Rh})} = 133$ Hz, $J_{(\text{P-N})} = 4.9$ Hz), -144.1 (m, $J_{(\text{P-F})} = 711$ Hz).

Due to its high sensitivity, HR-MS for **4b** could not be obtained.

1,3-Bis-(2'-diphenylphosphinoethyl)-2-N-tetrahydrobenzotriazolium *triphenylphosphino-*
rhodium(I) bis-hexafluorophosphate (6b)

20.0 mg of compound **5b** (20.6×10^{-3} mmol) were dissolved in 1.0 ml THF and 5.9 mg of triphenylphosphine (22.5×10^{-3} mmol, 1.1 eq.) in 0.5 ml THF were added. After stirring for 30 min the solvent was evaporated and the residue was washed with ether from excess triphenylphosphine and dried, yielding 22 mg (18.3×10^{-3} mmol) of the title compound, as a crystalline orange powder (89%).

^1H -NMR (600MHz, CD_3NO_2): δ 7.48 (m, 8H), 7.41 (t, 6H), 7.36 (t, 4H), 7.29 (br, 9H), 7.19 (m, 8H), 5.38 (br, 4H, N- CH_2), 2.92 (br, 4H, P- CH_2), 2.69 (br, 4H, cy), 1.73 (br, 4H, cy); ^{13}C -

NMR (150MHz, CD₃NO₂): δ 145.1 (cy), 135.4 (d, J_(C-P) = 11 Hz), 134.9 (br d, J_(C-P) = 50 Hz, C_{ipso} of PPh₃), 134.3 (br), 132.3 (br), 132.0, 131.9 (vt, J_(C-P) = 22 Hz), 130.2 (vt, J_(C-P) = 5.0 Hz), 129.8 (d, J_(C-P) = 10 Hz), 51.3 (N-CH₂), 26.3 (d, J_(C-P) = 12 Hz, P-CH₂), 21.3 (cy), 21.1 (cy); ¹⁵N-NMR (60MHz, CD₃NO₂): δ -99.7 (ddt, J_(N-P trans) = 38 Hz, J_(N-Rh) = 14 Hz, J_(N-P cis) = 4.1 Hz); ³¹P-NMR (240MHz, CD₃NO₂): δ 44.6 (dq, J_(P-Rh) = 178 Hz, J_(P-P) = J_(P-N) = 38 Hz, PPh₃), 20.3 (ddd, J_(P-Rh) = 136 Hz, J_(P-P) = 38 Hz, J_(P-N) = 4.1 Hz, PPh₃), -143.0 (m, J_(P-F) = 707 Hz); ¹⁰³Rh-NMR (19MHz, CD₃NO₂): -311.0 (dtd, J_(Rh-P) = 178 Hz, 136 Hz, J_(Rh-N) = 14 Hz).

HR-MS calc. for C₅₂H₅₁N₂¹⁵NF₆P₄Rh⁺ (M*PF₆⁺): 1059.1963, found 1059.1962.

2.2. Pt(II) complexes 7-10a,b.

1,3-Bis-(2'-diphenylphosphinoethyl)-trifluoromethanesulfonate (7a) *2-¹⁵N-benzotriazolium* *dimethylplatinum(II)*

30.0 mg of ligand **1a'** (43.2*10⁻³ mmol) were dissolved in 1 ml THF and 14.4 mg of (COD)PtMe₂ (43.2*10⁻³ mmol, 1.0 eq.) dissolved in an additional 1 ml THF were added upon stirring. The resulting faintly yellow solution was evaporated and the residue was washed with ether and dried, yielding 40 mg (43.2*10⁻³ mmol) of the title compound as a light yellow powder (quantitative).

¹H-NMR (CD₃NO₂, 500 MHz): δ 8.23 (dd, 2H, Ar), 8.03 (dd, 2H, Ar), 7.78 (br, 4H, P-Ar), 7.46 (br, 6H, P-Ar), 7.35 (br, 6H, P-Ar), 6.98 (br, 4H, P-Ar), 5.50 (br, 4H, N-CH₂), 3.53 (br, 4H, P-CH₂), -0.59 (AB q, J_(H-Pt) = 68 Hz, 6H, Pt-CH₃); ¹³C-NMR (CD₃NO₂, 125 MHz): δ 137.0 (d, J_(C-N) = 1.5 Hz, Ar), 134.2 (br, P-Ar), 133.1 (br, P-Ar), 133.0 (Ar), 131.2 (br d, J_(C-P) = 50 Hz, P-Ar), 129.6 (br, P-Ar), 122.4 (q, J_(C-F) = 320 Hz, OTf), 114.7 (Ar), 49.3 (m, N-CH₂), 23.2 (d, J_(C-P) = 30 Hz, P-CH₂), 8.32 (dd, J_(C-P trans) = 99 Hz, J_(C-P cis) = 8.3 Hz, J_(C-Pt) = 614 Hz, Pt-CH₃); ¹⁵N-NMR (50MHz, CD₃NO₂): δ -27.9 (t, J_(N-P) = 2.0 Hz, J_(N-Pt) = 5.0 Hz); ³¹P-NMR (200MHz, CD₃NO₂): δ 10.7 (d, J_(P-N) = 2.0 Hz, J_(P-Pt) = 1820 Hz).

HR-MS calc. for C₃₆H₃₈N₂¹⁵NP₂Pt⁺ (M⁺): 770.2159, found: 770.2159.

1,3-Bis-(2'-diphenylphosphinoethyl)-trifluoromethanesulfonate (8a) *2-¹⁵N-benzotriazolium* *methylplatinum(II)* *bis-*

30.0 mg of compound **7a** (32.6*10⁻³ mmol) were dissolved in 3 ml DCM and 0.3 ml of a freshly prepared solution of TfOH in ether, 20 mg/ml, (40.0*10⁻³ mmol, 1.2 eq.) were added upon stirring. Upon the addition the yellowish solution became almost colorless. After stirring for 10 min. the solution was evaporated to dryness, and the residue was recrystallized in DCM/ether, yielding 31 mg (29.4*10⁻³ mmol) of the title compound, as a white powder (90%).

$^1\text{H-NMR}$ (CD_3NO_2 , 500 MHz): δ 8.32 (dd, 2H, Ar), 8.21 (dd, 2H, Ar), 7.91 (vq, 8H, P-Ar), 7.71 (t, 4H, P-Ar), 7.65 (t, 8H, P-Ar), 5.62 (vq, 4H, N- CH_2), 3.34 (br m, 4H, P- CH_2), 0.99 (t, $J_{(\text{H-P})} = 7.5$ Hz, $J_{(\text{H-Pt})} = 81$ Hz, 3H, Pt- CH_3); $^{13}\text{C-NMR}$ (CD_3NO_2 , 125 MHz): δ 137.3(Ar), 135.7, 135.3 (vt, $J_{(\text{C-P})} = 6.4$ Hz, P-Ar), 134.0, 130.9 (vt, $J_{(\text{C-P})} = 5.6$ Hz, P-Ar), 127.9 (vt, $J_{(\text{C-P})} = 30$ Hz, P-Ar), 122.1 (q, $J_{(\text{C-F})} = 318$ Hz, OTf), 114.9 (Ar), 51.4 (m, $J_{(\text{C-Pt})} = 16$ Hz, N- CH_2), 24.4 (vt, $J_{(\text{C-P})} = 17$ Hz, P- CH_2), -12.1 (dt, $J_{(\text{C-N})} = 10$ Hz, $J_{(\text{C-P})} = 5.5$ Hz, $J_{(\text{C-Pt})} = 651$ Hz, Pt- CH_3); $^{15}\text{N-NMR}$ (50MHz, CD_3NO_2): δ -92.7 (t, $J_{(\text{N-P})} = 2.2$ Hz, $J_{(\text{N-Pt})} = 49$ Hz); $^{31}\text{P-NMR}$ (200MHz, CD_3NO_2): δ 16.5 (d, $J_{(\text{P-N})} = 2.2$ Hz, $J_{(\text{P-Pt})} = 2903$ Hz).

HR-MS calc. for $\text{C}_{36}\text{H}_{35}\text{N}_2^{15}\text{NO}_3\text{F}_3\text{P}_2\text{SPT}^+$ (M^*OTf^+): 904.1445, found: 904.1446.

1,3-Bis-(2'-diphenylphosphinoethyl)- 2- ^{15}N -benzotriazolium platinum(II) chloride bis-trifluoromethanesulfonate (9a)

A 20 ml vial, equipped with a magnetic stirrer, was charged with 30.0 mg of compound **8a** (28.5×10^{-3} mmol) and 5 ml DCM, forming a white suspension. Then 21 μl of 4M HCl/Dioxane solution (84.0×10^{-3} mmol HCl, 3 eq.) were added by a syringe, yielding a clear yellow solution that was stirred for a few hours, until the $^{31}\text{P-NMR}$ of an aliquot showed a complete consumption of the starting material. The solution was then evaporated, and the yellow crystalline residue was dissolved in DCM, treated with an excess neat TfOH (21 mg, 5 eq.), and evaporated. Finally, the product was recrystallized in DCM/ether, yielding 18 mg (16.8×10^{-3} mmol) of the title compound, as an off-white crystalline powder (59%).

$^1\text{H-NMR}$ (CD_3NO_2 , 500 MHz): δ 8.37 (dd, 2H, Ar), 8.26 (dd, 2H, Ar), 7.98 (vq, 8H, P-Ar), 7.27 (t, 4H, P-Ar), 7.65 (t, 8H, P-Ar), 5.72 (vq, 4H, N- CH_2), 3.27 (br, 8H, P- CH_2); $^{13}\text{C-NMR}$ (CD_3NO_2 , 125 MHz): δ 137.9 (Ar), 136.7, 135.4 (vt, $J_{(\text{C-P})} = 6.2$ Hz, P-Ar), 134.3, 130.8 (vt, $J_{(\text{C-P})} = 5.8$ Hz, P-Ar), 126.9 (vt, $J_{(\text{C-P})} = 32$ Hz, P-Ar), 122.5 (q, $J_{(\text{C-F})} = 320$ Hz, OTf), 115.1 (Ar), 52.0 (br, N- CH_2), 21.8 (vt, $J_{(\text{C-P})} = 18$ Hz, P- CH_2); $^{15}\text{N-NMR}$ (50MHz, CD_3NO_2): δ -134.7 (t, $J_{(\text{N-P})} = 2.9$ Hz, $J_{(\text{N-Pt})} = 471$ Hz); $^{31}\text{P-NMR}$ (200MHz, CD_3NO_2): δ 7.6 (d, $J_{(\text{P-N})} = 2.9$ Hz, $J_{(\text{P-Pt})} = 2295$ Hz).

HR-MS calc. for $\text{C}_{35}\text{H}_{32}\text{N}_2^{15}\text{NO}_3\text{F}_3\text{P}_2\text{SPT}^+$ (M^*OTf^+): 924.0898, found: 924.0903.

1,3-Bis-(2'-diphenylphosphinoethyl)- 2- ^{15}N -benzotriazolium triphenylphosphino- platinum(II) tris-trifluoromethanesulfonate (10a)

To 19.0 mg of compound **9a** (17.7×10^{-3} mmol) dissolved in 0.7 ml CD_3NO_2 5.5 mg of solid AgOTf (21.4×10^{-3} mmol, 1.2 eq.) and 4.6 mg of solid triphenylphosphine (17.7×10^{-3} mmol, 1.0 eq.) were added. After stirring at room temperature for several hours a very fine white precipitate formed. The resulting slurry was filtrated through celite into an NMR tube that was tightly sealed, immersed in an oil bath (outside the glove box) and heated to 80°C overnight. During the heating white precipitate (AgCl) slowly aggregated on the tube walls, while $^{31}\text{P-NMR}$ has shown a gradual conversion of the starting material to the title compound. (sometimes, repeated addition

of sub-equivalent amounts of AgOTf followed by few more hours of heating were required in order to draw the reaction to completion.) The obtained reaction mixture was then cooled to room temperature and filtrated through celite resulting in a clear nearly colorless solution that was subjected to multinuclear NMR analysis.

$^1\text{H-NMR}$ (CD_3NO_2 , 600MHz): δ 8.26 (dd, 2H, Ar), 8.18 (dd, 2H, Ar), 7.65 (t, 4H), 7.54 (m, 15H), 7.45 (m, 8H), 7.37 (t, 8H), 6.13 (4H, br, N-CH₂), 3.66 (4H, br, P-CH₂); $^{13}\text{C-NMR}$ (CD_3NO_2 , 150MHz): δ 138.7 (d, $J_{(\text{C-N})} = 1.7$ Hz, Ar), 138.1, 135.5 (d, $J_{(\text{C-P})} = 11$ Hz), 135.4 ($J_{(\text{C-P})} = 2.9$ Hz), 135.2 ($J_{(\text{C-P})} = 16$ Hz), 134.9, 134.3 (vt, $J_{(\text{C-P})} = 6.0$ Hz), 132.8 (d, $J_{(\text{C-P})} = 2.0$ Hz), 131.6 (vt, $J_{(\text{C-P})} = 6.0$ Hz), 131.6 (d, $J_{(\text{C-P})} = 12$ Hz), 130.7 (d, $J_{(\text{C-P})} = 11$ Hz), 126.6 (dt, $^1J_{(\text{C-P})} = 71$ Hz, $^3J_{(\text{C-P})} = 2.0$ Hz, C_{ipso} of PPh₃), 123.9 (vt, $J_{(\text{C-P})} = 30$ Hz), 122.5 (q, $J_{(\text{C-F})} = 320$ Hz, OTf), 114.9 (Ar), 52.6 (m, N-CH₂), 25.6 (vt, $J_{(\text{C-P})} = 18$ Hz, P-CH₂); $^{15}\text{N-NMR}$ (60MHz, CD_3NO_2): δ -113.5 (dt, $J_{(\text{N-P trans})} = 43$ Hz, $J_{(\text{N-P cis})} = 3.3$ Hz, $J_{(\text{N-Pt})} = 146$ Hz); $^{31}\text{P-NMR}$ (240MHz, CD_3NO_2): δ 14.0 (dd, $J_{(\text{P-P})} = 18$ Hz, $J_{(\text{P-N})} = 3.3$ Hz, $J_{(\text{P-Pt})} = 2320$ Hz), 7.8 (dt, $J_{(\text{P-N})} = 43$ Hz, $J_{(\text{P-P})} = 18$ Hz, $J_{(\text{P-Pt})} = 3812$ Hz, PPh₃); $^{195}\text{Pt-NMR}$ (CD_3NO_2 , 130MHz): δ -4623.7 (dtd, $J_{(\text{Pt-P})} = 3812$ Hz, 2320 Hz, $J_{(\text{Pt-N})} = 146$ Hz).

HR-MS calc. for $\text{C}_{54}\text{H}_{47}\text{N}_2^{15}\text{NO}_6\text{F}_6\text{P}_3\text{S}_2\text{Pt}^+$ (M^+2OTf^+): 1300.1642, found 1304.1644.

1,3-Bis-(2'-diphenylphosphinoethyl)-2-¹⁵N-tetrahydrobenzotriazolium dimethylplatinum(II) trifluoromethanesulfonate (7b)

34.0 mg of ligand **1b'** (48.7×10^{-3} mmol) were dissolved in 1 ml THF and 16.2 mg of (COD)PtMe₂ (48.7×10^{-3} mmol, 1.0 eq.) in an additional 1 ml THF were added upon stirring. The resulting colorless solution was evaporated and the residue was washed with ether and dried, yielding 43 mg (46.5×10^{-3} mmol) of the product, as a white powder (96%).

$^1\text{H-NMR}$ (CD_3NO_2 , 500MHz): δ 7.79 (br, 4H, P-Ar), 7.53 (br, 6H, P-Ar), 7.35 (br, 6H, P-Ar), 6.95 (br, 4H, P-Ar), 5.01 (br, 4H, N-CH₂), 3.35 (br, 4H, N-CH₂), 2.94 (br, 4H, cy), 2.02 (br, 4H, cy), -0.04 (AB q, $J_{(\text{H-Pt})} = 68$ Hz, 6H, Pt-CH₃); $^{13}\text{C-NMR}$ (CD_3NO_2 , 125MHz): δ 141.8 (d, $J_{(\text{C-N})} = 1.3$ Hz, cy), 134.3 (br), 133.2 (br), 131.1 (br d, $J_{(\text{C-P})} = 30$ Hz, P-Ar), 130.0, 129.6 (br), 122.5 (q, $J_{(\text{C-F})} = 320$ Hz, OTf), 48.3 (m, N-CH₂), 23.2 (d, $J_{(\text{C-P})} = 28$ Hz, P-CH₂), 22.0 (cy), 20.9 (cy), 8.0 (dd, $J_{(\text{C-P trans})} = 101$ Hz, $J_{(\text{C-P cis})} = 8.3$ Hz, $J_{(\text{C-Pt})} = 616$ Hz, Pt-CH₃); $^{15}\text{N-NMR}$ (50MHz, CD_3NO_2): δ -41.9 (t, $J_{(\text{N-P})} = 2.0$ Hz, $J_{(\text{N-Pt})} = 4.9$ Hz); $^{31}\text{P-NMR}$ (200MHz, CD_3NO_2): δ 10.9 (d, $J_{(\text{P-N})} = 2.0$ Hz, $J_{(\text{P-Pt})} = 1833$ Hz).

HR-MS calc. for $\text{C}_{36}\text{H}_{42}\text{N}_2^{15}\text{NP}_2\text{Pt}^+$ (M^+): 774.2472, found: 774.2475.

1,3-Bis-(2'-diphenylphosphinoethyl)- 2-¹⁵N-tetrahydrobenzotriazolium methylplatinum(II) bis-trifluoromethanesulfonate (8b)

30.0 mg of compound **7b** (32.4×10^{-3} mmol) were dissolved in 2 ml THF and 5.8 mg (38.6×10^{-3} mmol, 1.2 eq.) of TfOH in 0.5 ml ether (a freshly prepared solution) were added upon stirring.

The resulting colorless solution was evaporated, washed with ether and dried, yielding 34 mg (32.4×10^{-3} mmol) of the title compound, as a colorless powder (quantitative).

Single crystals of compound **8b** suitable for an X-ray analysis were obtained by a slow diffusion of hexane into its DCM solution.

$^1\text{H-NMR}$ (CD_3NO_2 , 500MHz): δ 7.87 (vq, 8H, P-Ar), 7.68 (t, 4H, P-Ar), 7.62 (t, 8H, P-Ar), 5.04 (vq, 4H, N-CH₂), 3.20 (br m, 4H, P-CH₂), 3.00 (br, 4H, cy), 2.03 (br, 4H, cy), 0.79 (t, $J_{(\text{H-P})} = 7.4$ Hz, $J_{(\text{H-Pt})} = 80$ Hz, 3H, Pt-CH₃); $^{13}\text{C-NMR}$ (CD_3NO_2 , 125MHz): δ 145.3 (cy), 135.3 (vt, $J_{(\text{C-P})} = 6.4$ Hz, P-Ar), 133.9 (P-Ar), 130.8 (vt, $J_{(\text{C-P})} = 5.6$ Hz, P-Ar), 128.0, (vt, $J_{(\text{C-P})} = 30$ Hz, P-Ar), 122.1 (q, $J_{(\text{C-F})} = 320$ Hz, OTf), 50.1 (br, $J_{(\text{C-Pt})} = 31$ Hz, N-CH₂), 24.4 (vt, $J_{(\text{C-P})} = 17$ Hz, P-CH₂), 21.9 (cy), 21.4 (cy), -14.1 (dt, $J_{(\text{C-N})} = 10$ Hz, $J_{(\text{C-P})} = 5.7$ Hz, $J_{(\text{C-Pt})} = 646$ Hz, Pt-CH₃); $^{15}\text{N-NMR}$ (50MHz, CD_3NO_2): δ -108.5 (t, $J_{(\text{N-P})} = 2.2$ Hz, $J_{(\text{N-Pt})} = 52$ Hz); $^{31}\text{P-NMR}$ (200MHz, CD_3NO_2): δ 16.4 (d, $J_{(\text{P-N})} = 2.2$ Hz, $J_{(\text{P-Pt})} = 2916$ Hz).

HR-MS calc. for $\text{C}_{36}\text{H}_{39}\text{N}_2^{15}\text{NO}_3\text{F}_3\text{P}_2\text{SPt}^+$ (M^*OTf^+): 908.1758, found: 908.1757.

1,3-Bis-(2'-diphenylphosphinoethyl)- 2-¹⁵N-tetrahydrobenzotriazolium platinum(II) chloride bis-trifluoromethanesulfonate (9b)

Compound **8b** (25.0 mg, 23.6×10^{-3} mmol) was dissolved in 2.5 ml dichloroethane. Then 17 μl (68.0×10^{-3} mmol, 3 eq.) of 4M HCl in dioxane were added by a syringe. The reaction mixture was left unstirred for 2 d, during which the solution gradually turned yellowish and the $^{31}\text{P-NMR}$ spectrum showed a complete consumption of the starting material. The reaction mixture was then evaporated in vacuo, redissolved in dichloroethane and evaporated again several times. During the evaporation the solution decolorizes, giving finally the product as a white crystalline powder, 25 mg (23.2×10^{-3} mmol), in a quantitative yield.

Single crystals of compound **9b** suitable for an X-ray analysis were obtained by a slow evaporation of its DCM solution.

$^1\text{H-NMR}$ (CD_3NO_2 , 500MHz): δ 7.96 (vq, 8H, P-Ar), 7.71 (t, 4H, P-Ar), 7.62 (vt, 8H, P-Ar), 5.16 (m, 4H, N-CH₂), 3.14 (br, 4H, P-CH₂), 3.11 (br, 4H, cy), 2.06 (br, 4H, cy); $^{13}\text{C-NMR}$ (CD_3NO_2 , 125MHz): δ 147.2 (cy), 135.4 (vt, $J_{(\text{C-P})} = 6.0$ Hz, P-Ar), 134.2 (P-Ar), 130.7 (vt, $J_{(\text{C-P})} = 5.6$ Hz, P-Ar), 127.1 (vt, $J_{(\text{C-P})} = 31$ Hz, P-Ar), 122.5 (q, $J_{(\text{C-F})} = 320$ Hz, OTf), 50.8 (br, N-CH₂), 22.5 (cy), 22.0 (vt, $J_{(\text{C-P})} = 18$ Hz, P-CH₂), 21.2 (cy); $^{15}\text{N-NMR}$ (50MHz, CD_3NO_2): δ -152.9 (t, $J_{(\text{N-P})} = 2.9$ Hz, $J_{(\text{N-Pt})} = 477$ Hz); $^{31}\text{P-NMR}$ (200MHz, CD_3NO_2): δ 6.6 (d, $J_{(\text{P-N})} = 2.9$ Hz, $J_{(\text{P-Pt})} = 2320$ Hz).

HR-MS calc. for $\text{C}_{35}\text{H}_{36}\text{N}_2^{15}\text{NO}_3\text{F}_3\text{P}_2\text{SCIPt}^+$ (M^*OTf^+): 928.1211, found: 928.1219.

1,3-bis-(2'-diphenylphosphinoethyl)- 2-¹⁵N-tetrahydrobenzotriazolium triphenylphosphino-platinum(II) tris-trifluoromethanesulfonate (10b)

15.0 mg of compound **9b** (13.9×10^{-3} mmol) were dissolved in 0.7 ml CD_3NO_2 and added to 3.8 mg of solid AgOTf (15.3 mmol, 1.1 eq.) and 3.6 mg of solid triphenylphosphine (13.9×10^{-3} mmol, 1.0 eq.). The resulting fine suspension was filtrated through celite into an NMR tube that was tightly sealed, immersed in an oil bath (outside the glove box) and heated to 80°C overnight. During the heating white precipitate (AgCl) slowly aggregated on the tube walls, while ^{31}P -NMR has shown a gradual conversion of the starting material to the title compound. The obtained reaction mixture was then cooled to room temperature and filtrated through celite resulting in a clear colorless solution that was subjected to multinuclear NMR analysis.

Single crystals of compound **10b** suitable for an X-ray analysis were obtained by a slow diffusion of ether into its solution in CD_3NO_2 .

^1H -NMR (CD_3NO_2 , 600MHz): δ 7.64-7.39 (m, 35H, P-Ar + PPh_3), 5.58 (br, 4H, N- CH_2), 3.51 (br, 4H, (P- CH_2)), 2.88 (br, 4H, cy), 1.80 (br, 4H, cy); ^{13}C -NMR (CD_3NO_2 , 1505MHz): δ 149.9 (d, $J_{(\text{C-N})} = 1.3$ Hz, cy), 135.5 (d, $J_{(\text{C-P})} = 11$ Hz), 135.2 (d, $J_{(\text{C-P})} = 16$ Hz), 135.2 ($J_{(\text{C-P})} = 3.0$ Hz), 134.9, 134.4 (vt, $J_{(\text{C-P})} = 6.2$ Hz), 132.8 (d, $J_{(\text{C-P})} = 2.0$ Hz), 131.6 (vt, $J_{(\text{C-P})} = 5.9$ Hz), 131.3 (d, $J_{(\text{C-P})} = 12$ Hz), 130.7 (d, $J_{(\text{C-P})} = 11$ Hz), 126.7 (dt, $^1J_{(\text{C-P})} = 70$ Hz, $^3J_{(\text{C-P})} = 2.2$ Hz, C_{ipso} of PPh_3), 122.5 (q, $J_{(\text{C-F})} = 320$ Hz, OTf), 124.2 (vt, $J_{(\text{C-P})} = 31$ Hz), 51.4 (br, N- CH_2), 25.6 (vt, $J_{(\text{C-P})} = 19$ Hz, P- CH_2), 21.9 (cy), 20.5 (cy); ^{15}N -NMR (60MHz, CD_3NO_2): δ -129.9 (dt, $J_{(\text{N-P trans})} = 44$ Hz, $J_{(\text{N-P cis})} = 3.3$ Hz, $J_{(\text{N-Pt})} = 143$ Hz); ^{31}P -NMR (240MHz, CD_3NO_2): δ 13.6 (dd, $J_{(\text{P-P})} = 18$ Hz, $J_{(\text{P-N})} = 3.3$ Hz, $J_{(\text{P-Pt})} = 2329$ Hz), 7.4 (dt, $J_{(\text{P-N})} = 44$ Hz, $J_{(\text{P-P})} = 18$ Hz, $J_{(\text{P-Pt})} = 3788$ Hz, PPh_3); ^{195}Pt -NMR (CD_3NO_2 , 130MHz): δ -4630.8 (dtd, $J_{(\text{Pt-P})} = 3788$ Hz, 2329 Hz, $J_{(\text{Pt-N})} = 143$ Hz).

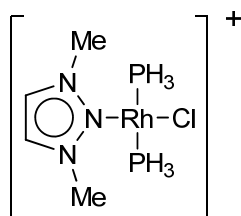
HR-MS calc. for $\text{C}_{54}\text{H}_{51}\text{N}_2^{15}\text{NO}_6\text{F}_6\text{P}_3\text{S}_2\text{Pt}^+$ ($\text{M} \cdot 2\text{OTf}^+$): 1304.1955, found: 1304.1956.

Calculations

The geometries were calculated with the PBE functional including the density fitting approximation. The basis set for these calculations was called SDD(d), and it was based on the D95 basis set with an additional polarization function on the second row atoms, and the Stuttgart/Dresden ECP basis set for the transition metals. Single point energies were calculated with the PBE0 functional (also called PBE1PBE), with the SDB-cc-pVDZ basis set, that is the Dunning cc-pVDZ basis set, and the Stuttgart/Dresden ECP basis set with an added f polarization function on the transition metals. Additionally, a dispersion correction was added with the D3 method of Grimme *et al.*³ on the single point energies. All QM calculations were carried out with Gaussian09.⁴

1. XYZ coordinates of the optimized structured

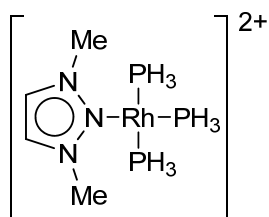
L-RhCl(PH₃)₂⁺



Rh	0.665807	0.000002	0.000128
P	0.968423	2.14221	-0.847836
P	0.968695	-2.142501	0.847008
H	-0.114845	3.004561	-1.215787
H	1.70989	-3.048101	0.036204
H	-0.114634	-3.00538	1.213542
H	1.72988	-2.228055	2.046039
H	1.708978	3.048749	-0.037481
H	1.730284	2.226722	-2.046496
Cl	3.04327	0.000308	0.000313
N	-2.153152	-0.816466	-0.727313
N	-1.283957	-0.000068	0.000125

C	-1.598615	-1.78959	-1.681438
H	-0.605607	-1.41818	-1.997218
C	-3.47925	-0.520899	-0.458248
H	-4.303829	-1.053955	-0.923114
C	-1.598431	1.789591	1.681588
H	-4.303729	1.054166	0.923337
N	-2.153078	0.816424	0.727582
C	-3.479198	0.521067	0.458431
H	-1.484066	-2.779734	-1.20492
H	-2.27635	-1.864744	-2.548088
H	-0.60533	1.418266	1.997173
H	-2.276005	1.864727	2.548364
H	-1.484033	2.779735	1.205021

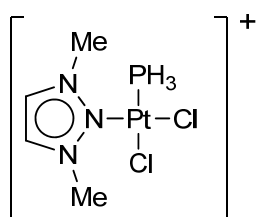
***L-Rh(PH₃)₃*²⁺**



Rh	-0.73539	-0.00027	0.006305
H	2.018923	-1.19524	2.902042
H	-3.7049	1.115605	-0.57615
H	0.532225	-0.31015	2.364591
P	-0.82507	-2.32543	-0.17643
H	1.931522	0.603997	3.059216

H	1.997849	1.192911	-2.9006
H	-3.71267	-1.0586	-0.65083
P	-0.81025	2.32901	0.158143
H	0.520514	0.293442	-2.35938
H	-3.66311	-0.03782	1.277095
H	1.926232	-0.60612	-3.06159
H	0.366391	-3.03424	-0.51474
H	-1.74388	3.040874	-0.6494
H	0.368086	3.071787	-0.15305
H	-1.11425	2.915699	1.422657
H	-1.21396	-3.07829	0.97135
H	-1.71062	-2.90091	-1.133
P	-3.02524	0.004986	0.00289
N	2.186096	-0.12219	1.080472
N	1.33737	-0.00306	0.001778
C	1.634425	-0.26583	2.44815
C	3.508233	-0.07884	0.689684
H	4.335538	-0.15529	1.392495
C	1.62235	0.259313	-2.44745
H	4.327785	0.151118	-1.40481
N	2.179873	0.116886	-1.08161
C	3.504322	0.074271	-0.69758

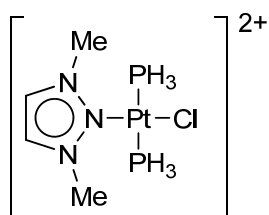
***L*-PtCl₂(PH₃)⁺**



Pt	-0.60124	-0.01769	0.003001
H	0.865452	0.539639	2.697039
H	-0.69046	3.171236	0.376333
H	1.184461	-1.19383	2.334415
Cl	-2.8417	-0.72001	-0.08577
H	2.456543	-0.19114	3.170899
H	1.14317	-0.43498	-2.59798
H	-2.37884	2.449535	-0.83884
Cl	0.217139	-2.29199	-0.26576
H	0.837765	1.32983	-2.42493
H	-2.41039	2.196097	1.347497
H	2.41517	0.761089	-3.11719
P	-1.54433	2.036652	0.23357
N	2.219205	0.166165	1.112255
N	1.377557	0.349974	0.043233
C	1.644604	-0.19254	2.426719
C	3.53649	0.198657	0.71316
H	4.363443	0.064661	1.404937
C	1.612289	0.545242	-2.39487
H	4.346642	0.491777	-1.37702

N	2.2057	0.495402	-1.04166
C	3.52813	0.410222	-0.66728

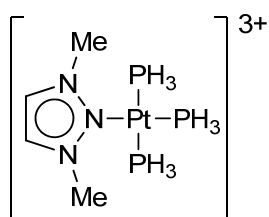
***L*-PtCl(PH₃)₃²⁺**



Pt	-0.56749	0.000001	-3E-06
H	0.793669	0.184084	2.519795
H	0.237132	3.163439	-0.60797
H	2.478045	0.309728	3.157438
Cl	-2.93492	-0.00015	0.000015
H	1.674476	1.759984	2.440851
H	1.67369	-1.75971	-2.44077
H	-1.66771	2.554274	-1.56895
P	-0.88102	-2.30184	0.41596
H	0.793886	-0.18328	-2.52006
H	-1.60563	2.958176	0.612154
H	2.478257	-0.31005	-3.15746
H	-1.60527	-2.95825	-0.61209
H	-1.66736	-2.55443	1.569027
H	0.237538	-3.16332	0.608013
P	-0.88131	2.301826	-0.41588
N	2.320094	0.279068	1.055295

N	1.478768	0.000087	-0.00002
C	1.777977	0.661945	2.382201
C	3.639305	0.179309	0.675686
H	4.466361	0.365091	1.358505
C	1.777881	-0.66173	-2.38225
H	4.466333	-0.36522	-1.35854
N	2.320073	-0.27898	-1.05535
C	3.639285	-0.17936	-0.67573

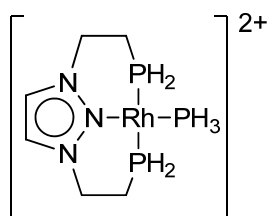
***L*-Pt(PH₃)₃³⁺**



Pt	0.641067	-0.0003	-0.00319
H	-0.73843	-0.18886	2.466921
H	-0.61049	-3.00465	-0.06619
H	-2.03135	0.979054	2.956322
P	2.959974	-0.00094	0.013126
H	-2.32669	-0.79704	3.069606
H	-2.32593	0.831796	-3.04267
H	1.350165	-2.98493	-1.11137
P	0.67044	2.386836	-0.00551
H	-0.75585	0.151958	-2.46804
H	1.272638	-3.0047	1.113322

H	-2.09776	-0.95582	-2.96342
H	3.496264	0.041636	1.328809
H	-0.60714	3.003928	-0.09222
H	1.383577	2.992546	-1.07602
H	1.23883	2.999075	1.145479
H	3.577596	-1.1355	-0.57839
H	3.5759	1.09298	-0.65191
P	0.668636	-2.38674	-0.01634
N	-2.35598	-0.0113	1.099612
N	-1.52116	0.000939	0.003192
C	-1.82518	-0.0016	2.491101
C	-3.67433	-0.00897	0.71455
H	-4.50241	-0.01494	1.424859
C	-1.849	0.007688	-2.48343
H	-4.51482	0.009617	-1.39196
N	-2.36559	0.011049	-1.08603
C	-3.68048	0.005441	-0.689

***Pincer-LRh(I)PH₃*²⁺**

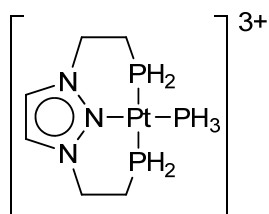


Rh	-0.837746	-0.007369	0.010456
H	0.572493	4.107687	-0.280888

H	1.358974	3.193469	1.034328
H	2.488896	-2.84207	1.289254
H	-3.820808	1.170067	-0.383555
H	1.407502	-3.148057	-1.054973
C	0.822422	-3.074583	-0.119445
H	0.665637	-4.100937	0.259428
P	-0.833775	-2.276131	-0.476205
H	0.978949	-2.041401	1.834519
H	2.412625	2.878137	-1.318255
H	-3.78896	-0.947576	-0.889531
P	-0.871154	2.259312	0.506296
C	0.7606	3.091092	0.109984
H	-3.769708	-0.330822	1.201199
H	0.911153	2.040173	-1.833177
H	-1.816075	3.072103	-0.187867
H	-1.132781	2.691561	1.840044
H	-1.74117	-3.10134	0.253136
H	-1.130418	-2.724337	-1.797127
P	-3.125225	-0.022482	-0.03262
N	2.124592	-0.984403	0.414544
N	1.26219	0.010895	0.004175
C	1.605527	-2.272693	0.953561
C	3.444124	-0.613687	0.248953
H	4.278005	-1.259802	0.514032
C	1.545859	2.294543	-0.964131

H	4.24412	1.33496	-0.564771
N	2.098548	1.021517	-0.422081
C	3.427324	0.674204	-0.283063

Pincer-LPt(II)PH₃³⁺



Pt	-0.6977	-0.00213	-0.00296
H	0.746574	4.113781	-0.32095
H	1.53699	3.221938	1.004289
H	2.591976	-2.85481	1.338374
H	-3.62799	1.131313	-0.57462
H	1.55885	-3.21245	-1.00665
C	0.951302	-3.09624	-0.08941
H	0.764029	-4.11108	0.31169
P	-0.68497	-2.31912	-0.52597
H	1.087355	-2.04597	1.87049
H	2.583905	2.862985	-1.33389
H	-3.63987	-1.09289	-0.6613
P	-0.70218	2.320848	0.516119
C	0.93496	3.100658	0.084058
H	-3.5639	-0.06458	1.321727
H	1.086442	2.044721	-1.87166

H	-1.68799	3.07438	-0.17965
H	-0.96087	2.644834	1.876743
H	-1.67469	-3.07455	0.162798
H	-0.94148	-2.63404	-1.88923
P	-3.01591	-0.00816	0.011264
N	2.246363	-0.99398	0.442788
N	1.402316	0.00269	0.002141
C	1.713758	-2.2835	0.991103
C	3.562047	-0.63447	0.289789
H	4.395926	-1.27506	0.579348
C	1.706785	2.28824	-0.98947
H	4.392152	1.296089	-0.55962
N	2.243389	1.003225	-0.43475
C	3.56018	0.651081	-0.27436

2. Energy scanning

The scanning of the dissociation of the monodentate nitrenium system was carried out fixing the angle of the ligand, but not the internal coordinates of the complex and the nitrenium. In this way the process involves only a linear trajectory of the fragments without any rotation of the nitrenium, and only the strength of the N-M bond was measured. In the case of the tridentate systems these constraints were not applied, as the arms of the ligand do not permit the linear trajectory of the dissociation. The energies and geometries were calculated at the same level as the rest of the complexes, with PBE0/SDB-cc-pVDZ//PBE/SDD(d).

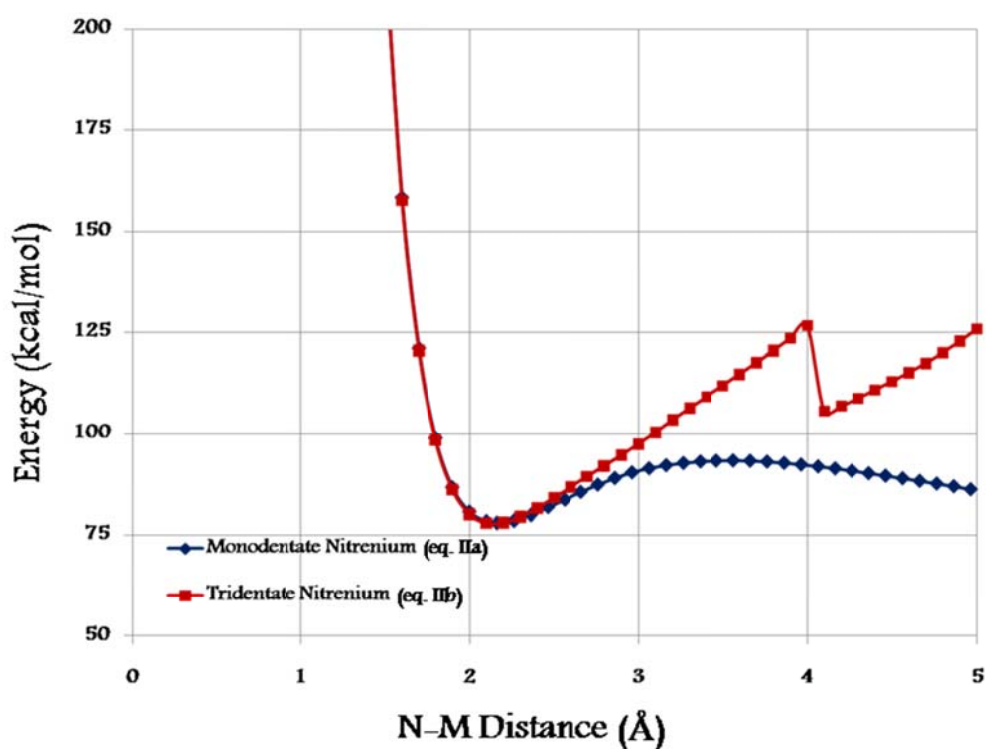


Figure S1. Energy scanning for the monodentate and tridentate nitrenium- $Pt(II)^{2+}$ systems. For convenience of comparison, point of zero energy for the tridentate system was arbitrarily equaled to the binding energy of the monodentate system.

References:

¹ Harris, R.K., Becker, E.D., Cabral de Menezes, S.M., Goodfellow, R., and Granger, P. *Pure Appl. Chem.*, **73**, **2001**, 1795-818.

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