Synthesis, Structure and Reactivity of NO^+, $NO^\cdot$ and NO^- Pincer PCN-Rh Complexes

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Supporting Information

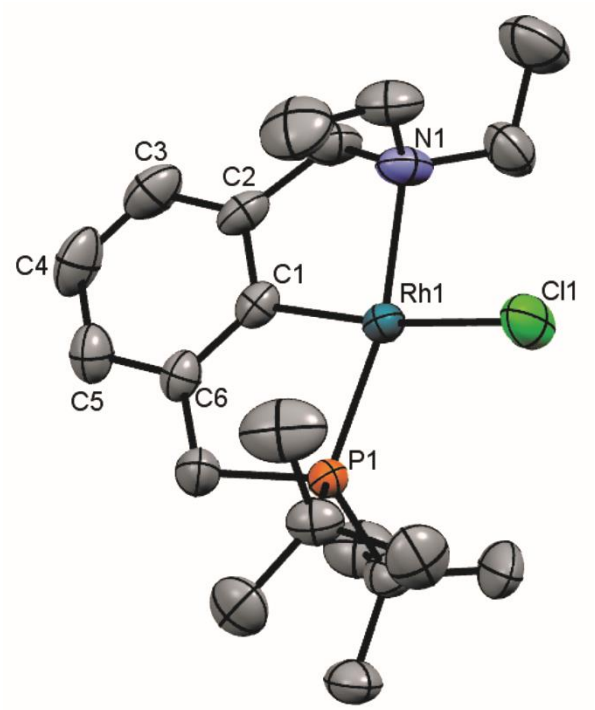


Figure S1. *Ortep plot of* ***(1)*** *at the 50% probability level. Hydrogen atoms are omitted for clarity.*

Table 1. Selected bond lengths (Å) and angles (deg.) for (2)

Rh(1)-P(1)	2.241(1)	Cl(1)-Rh(1)-N(1)	97.6(1)
Rh(1)-Cl(1)	2.443(2)	Cl(1)-Rh(1)-C(1)	169.3(1)
Rh(1)-N(1)	2.192(4)	P(1)-Rh(1)-Cl(1)	101.25(5)
Rh(1)-C(1)	1.972(4)	P(1)-Rh(1)-N(1)	166.0(1)
C(1)-C(2)	1.400(8)	P(1)-Rh(1)-C(1)	83.6(1)
C(2)-C(3)	1.380(8)	N(1)-Rh(1)-C(1)	82.3(2)
C(3)-C(4)	1.373(8)		
C(4)-C(5)	1.380(1)		
C(5)-C(6)	1.385(7)		
C(6)-C(1)	1.401(6)		

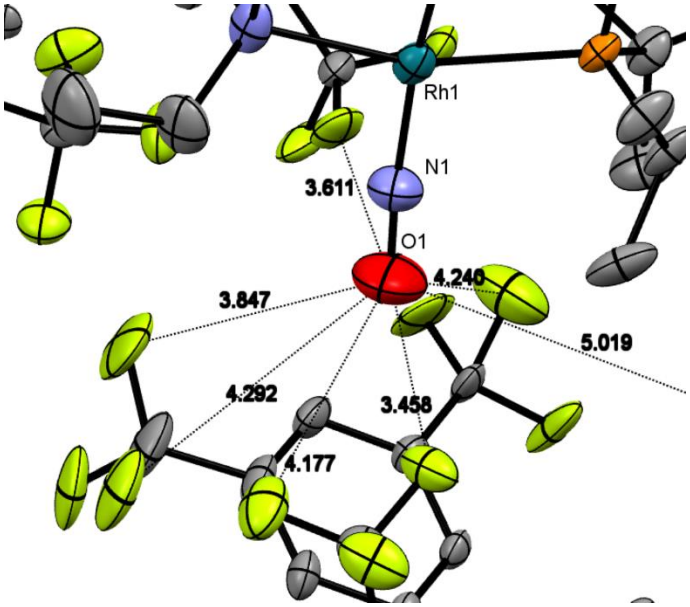


Figure S2. *Ortep plot of* ***(3^{+})*** *at the 50% probability level. Hydrogen atoms and disordered fluorine atoms are omitted for clarity. A close-up of the counteranion facing the NO ligand including distances from fluorine atoms to the oxygen atom is presented.*

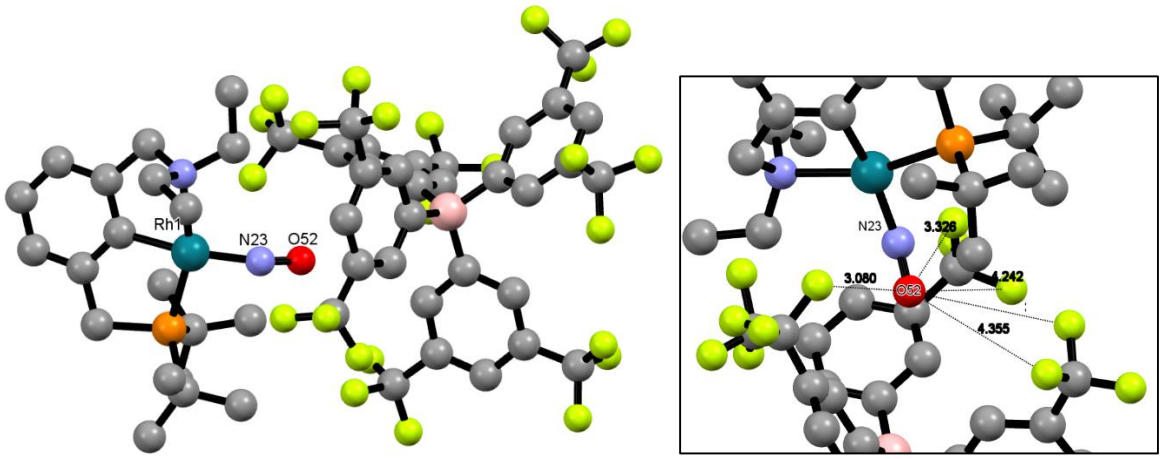
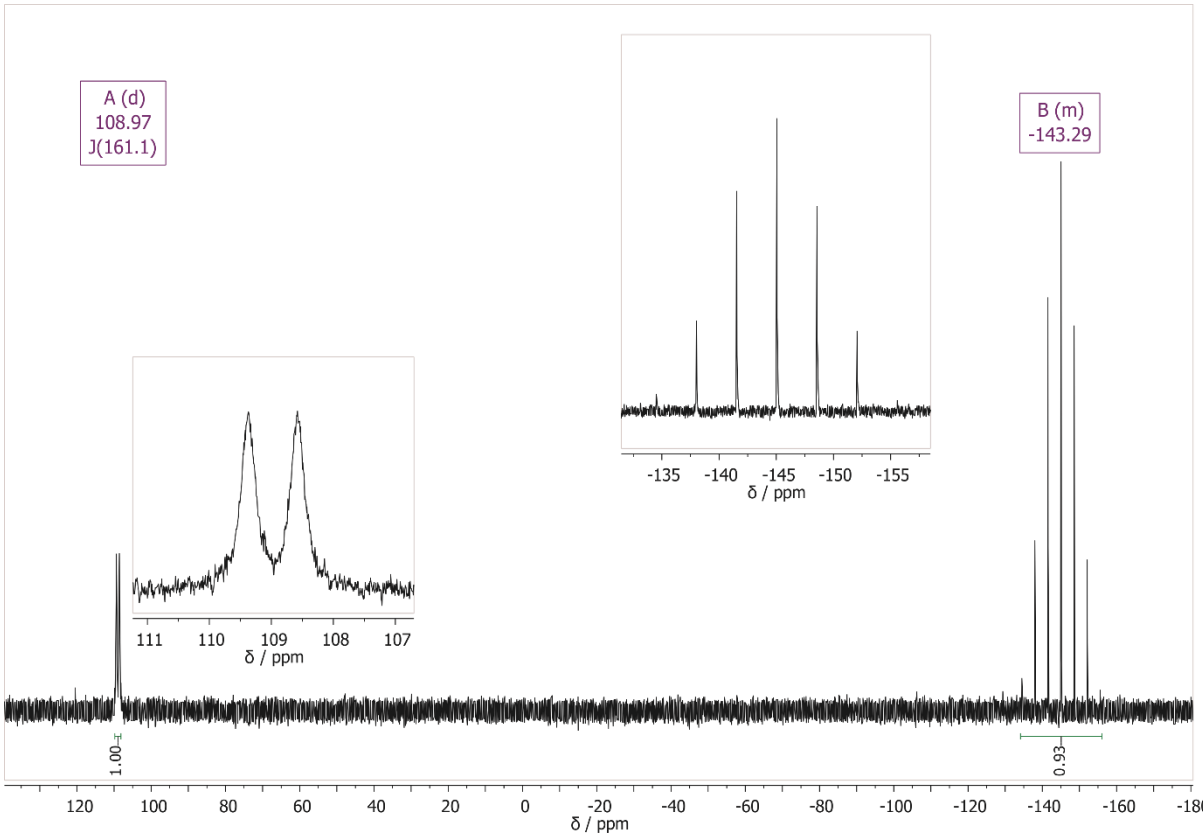
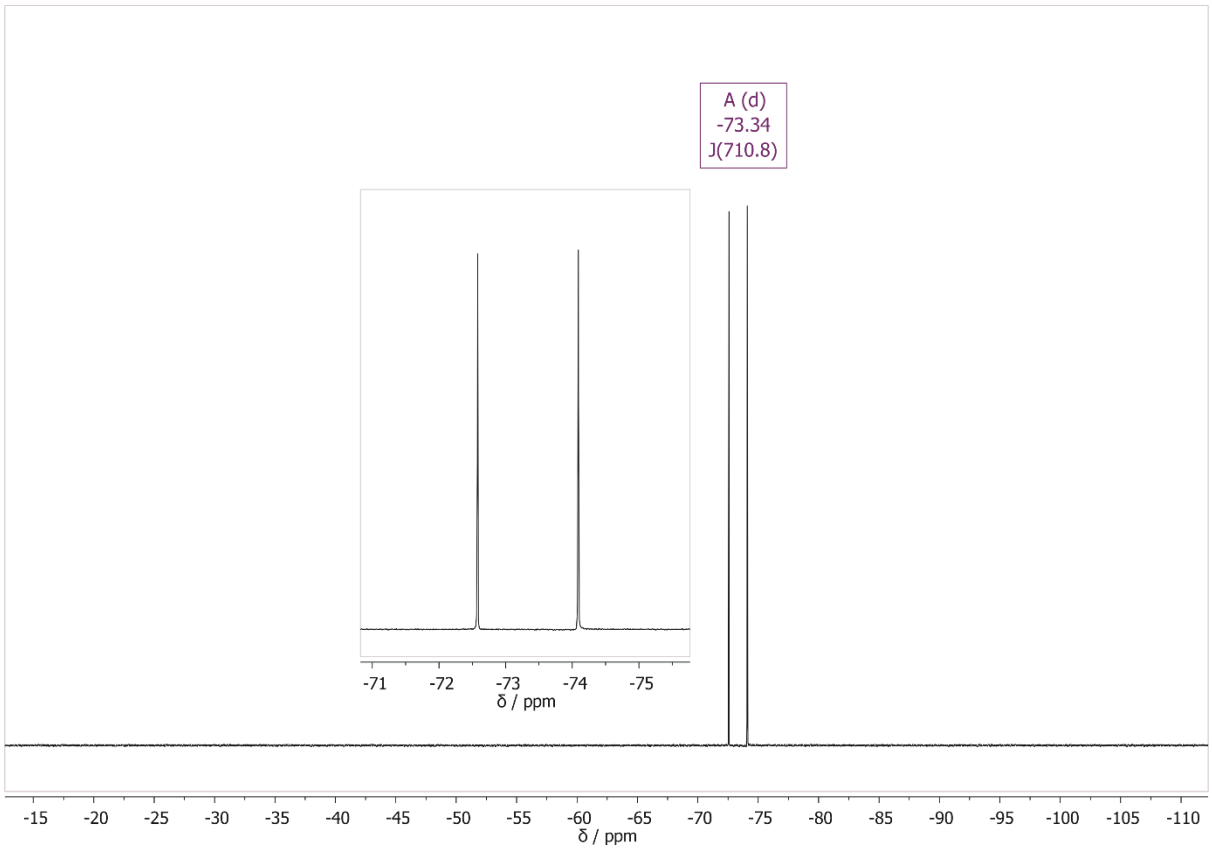


Figure S3. *DFT-optimized structure for* ***(3-BArF)****. Hydrogen atoms are omitted for clarity. A close-up of the counteranion facing the NO ligand including distances from fluorine atoms to the oxygen atom is presented.*

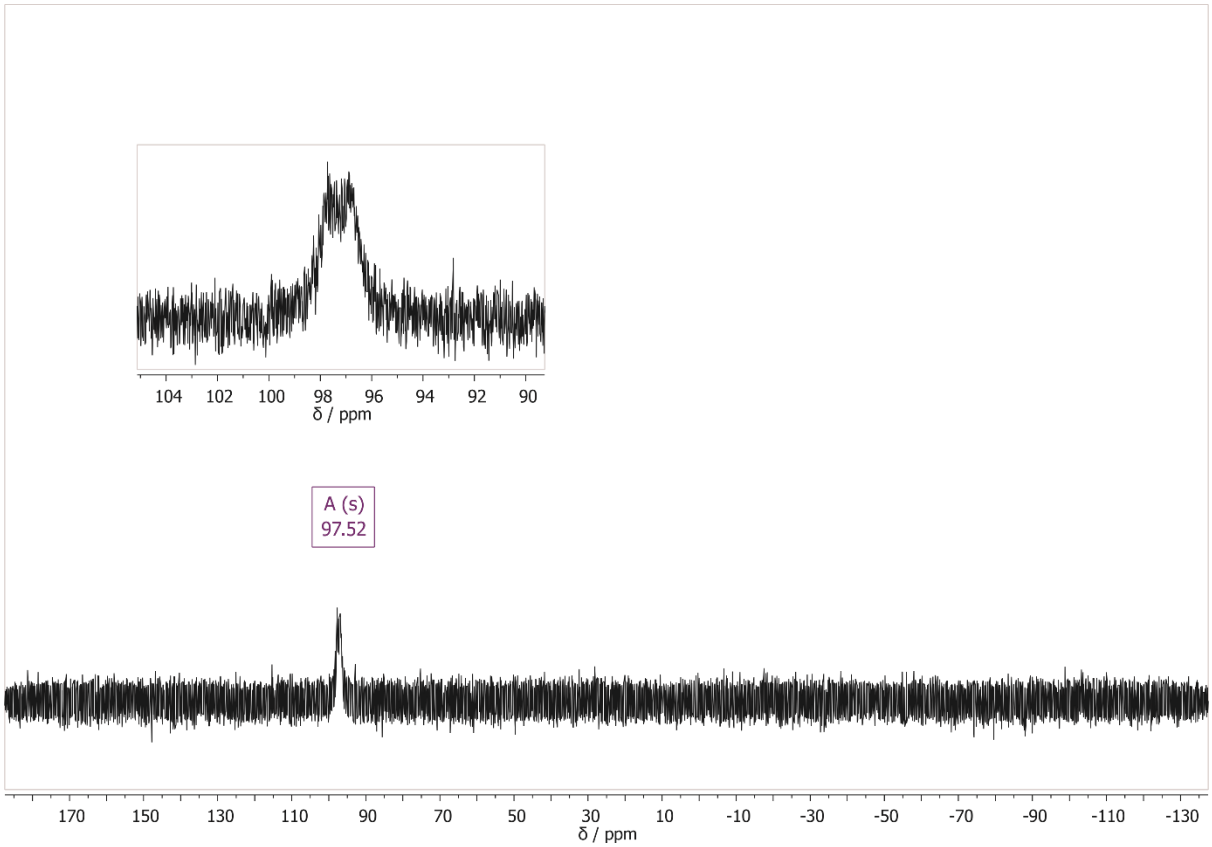


(a)

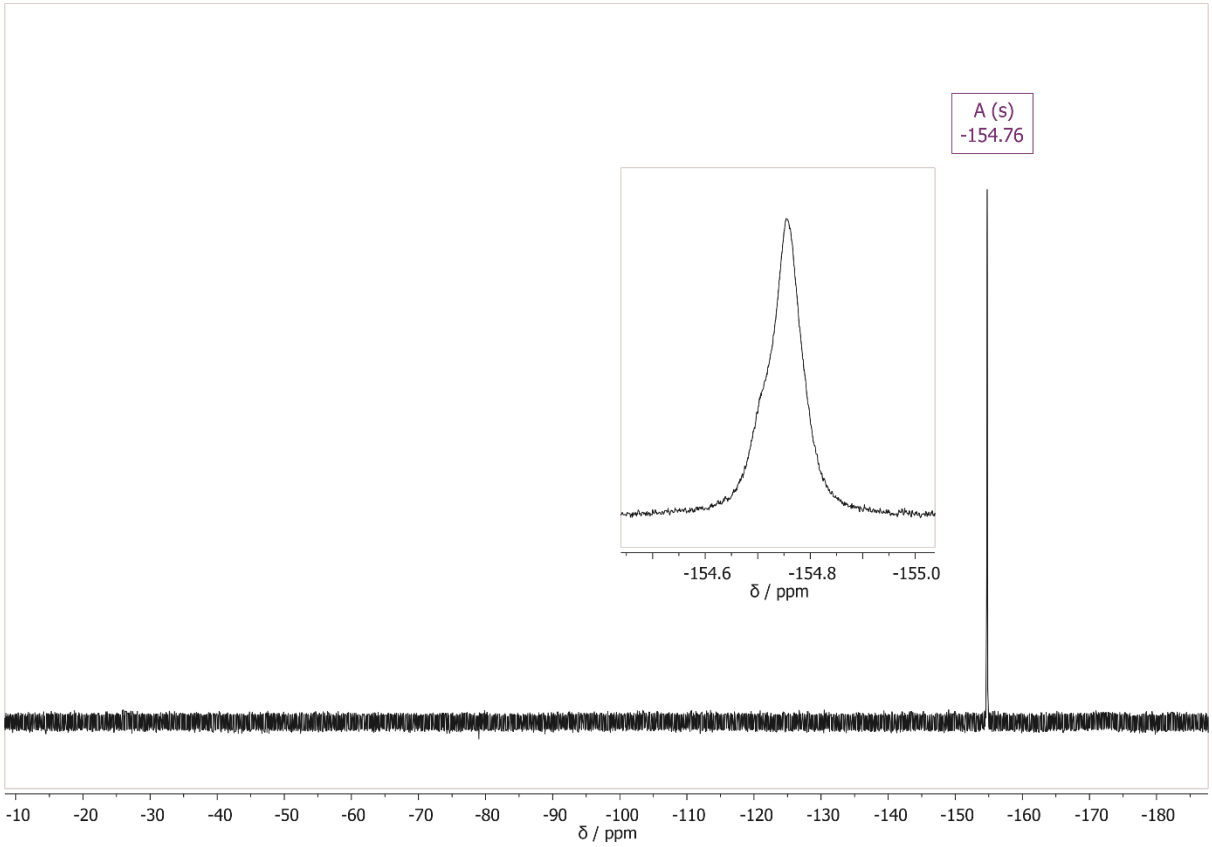


(b)

Figure S4. *500 MHz NMR spectra obtained upon treatment of a dichloromethane solution of* ***(2)*** *with $TlPF_6$.* ***(a)*** *^{31}P-NMR;* ***(b)*** *^{19}F-NMR.*

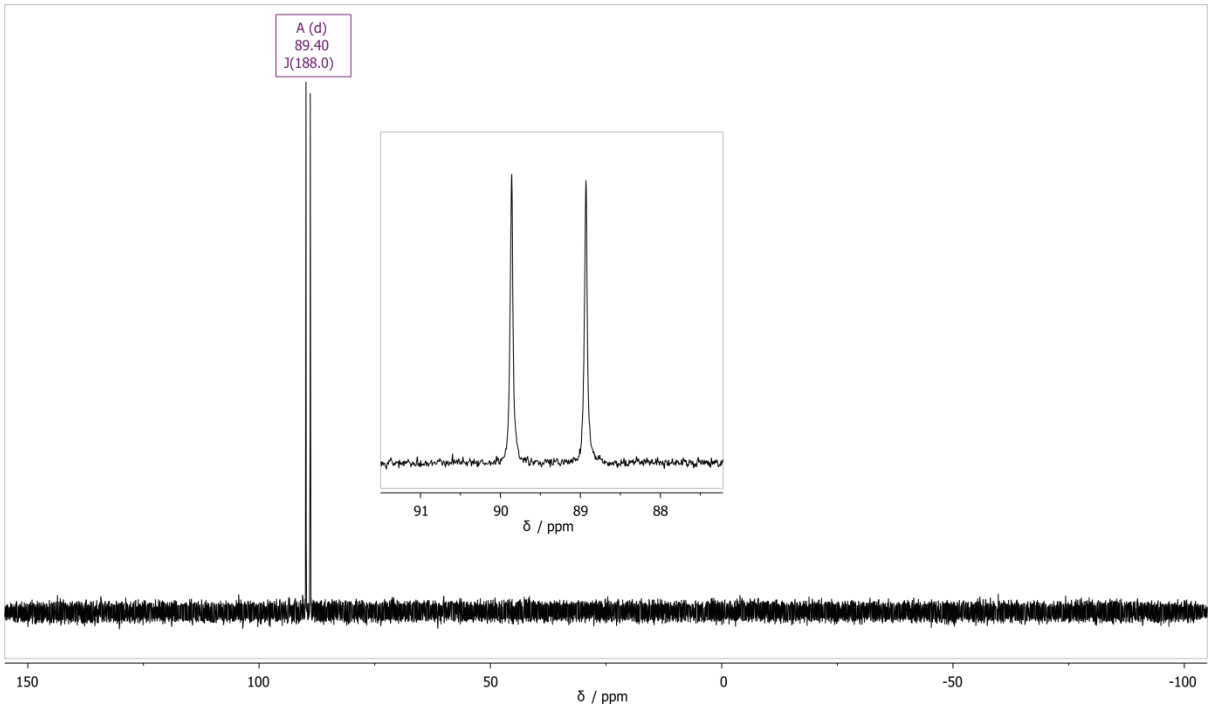


(a)

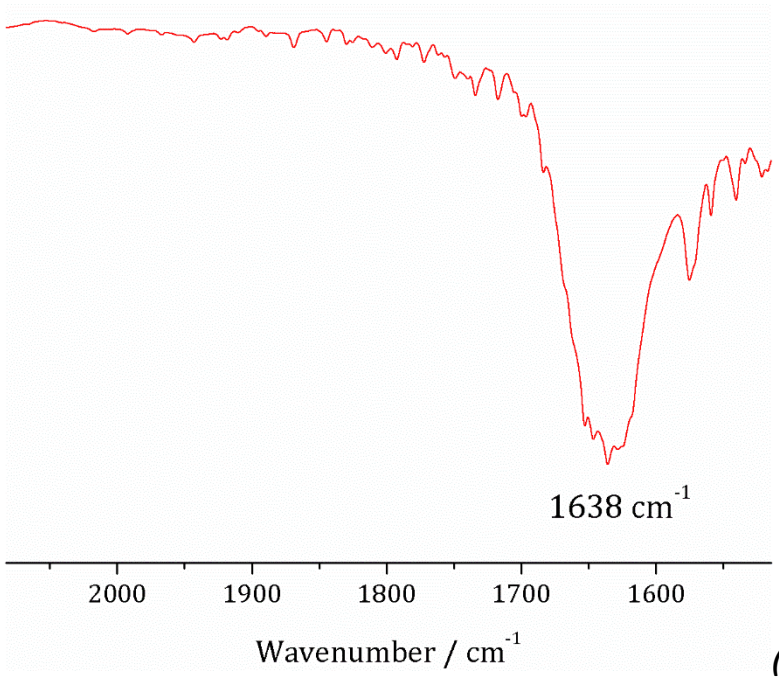


(b)

Figure S5. *500 MHz NMR spectra obtained upon treatment of a dichloromethane solution of* ***(2)*** *with $TlBF_4$.* ***(a)*** *^{31}P-NMR;* ***(b)*** *^{19}F-NMR.*

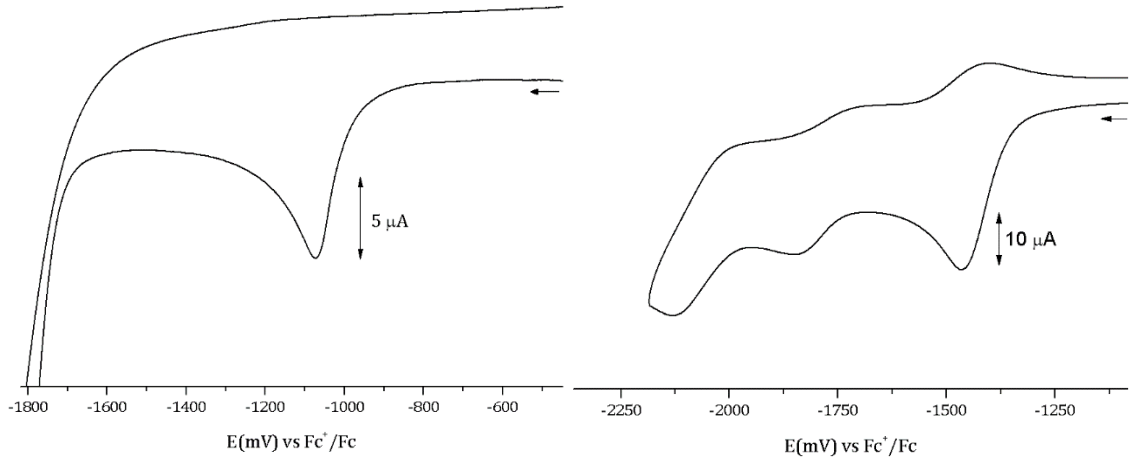


(a)



(b)

Figure S6. *Spectra obtained upon treatment of a dichloromethane solution of* ***(2)*** *with silver triflate.* ***(a)*** *^{31}P-NMR,* ***(b)*** *FTIR.*



(a) ***(b)***

Figure S7. *Cyclic voltammograms of negative potential sweep of* ***(a)*** *Complex* ***(3^+)*** *in CH_2Cl_2 / 0.25 M Bu_4NPF_6.* ***(b)*** *Complex* ***(4^+)*** *in CH_3CN / 0.25 M Bu_4NPF_6.*

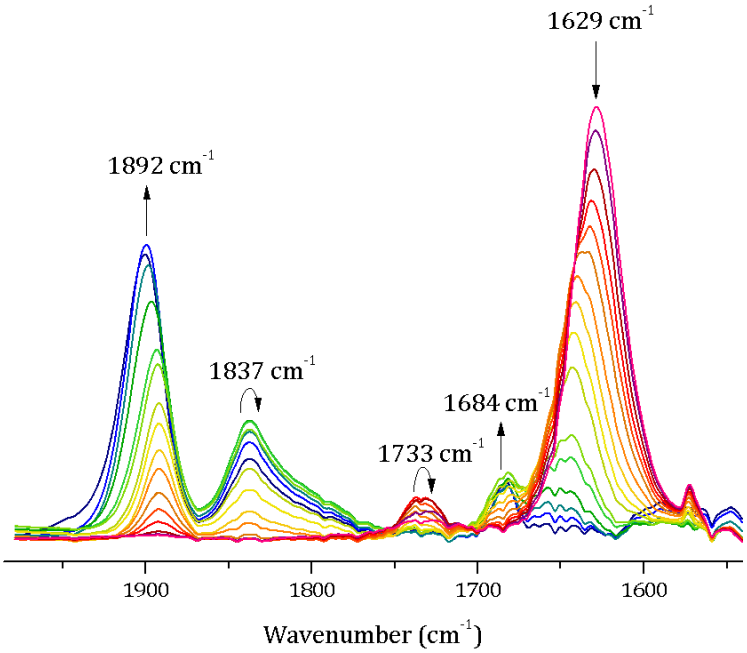


Figure S8. *IR spectral changes observed during electrolytic oxidation of* ***(2)*** *in $ClCH_2CH_2Cl$ / 0.25 M Bu_4NPF_6. The signal at 1684 cm^{-1} reached a peak and then remained constant. The signal at 1837 cm^{-1} was identified as complex* ***(3^+)****, given the characteristic ν(NO) signal and also given its oxidation at higher potentials which shielded a small signal around 1918 cm^{-1}, distorting the 1890 cm^{-1} peak and diminishing the 1837 cm^{-1} peak*

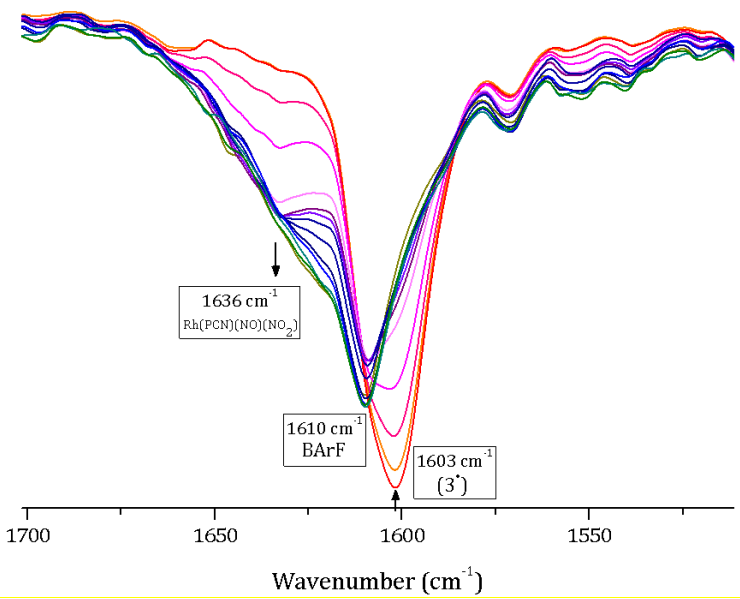
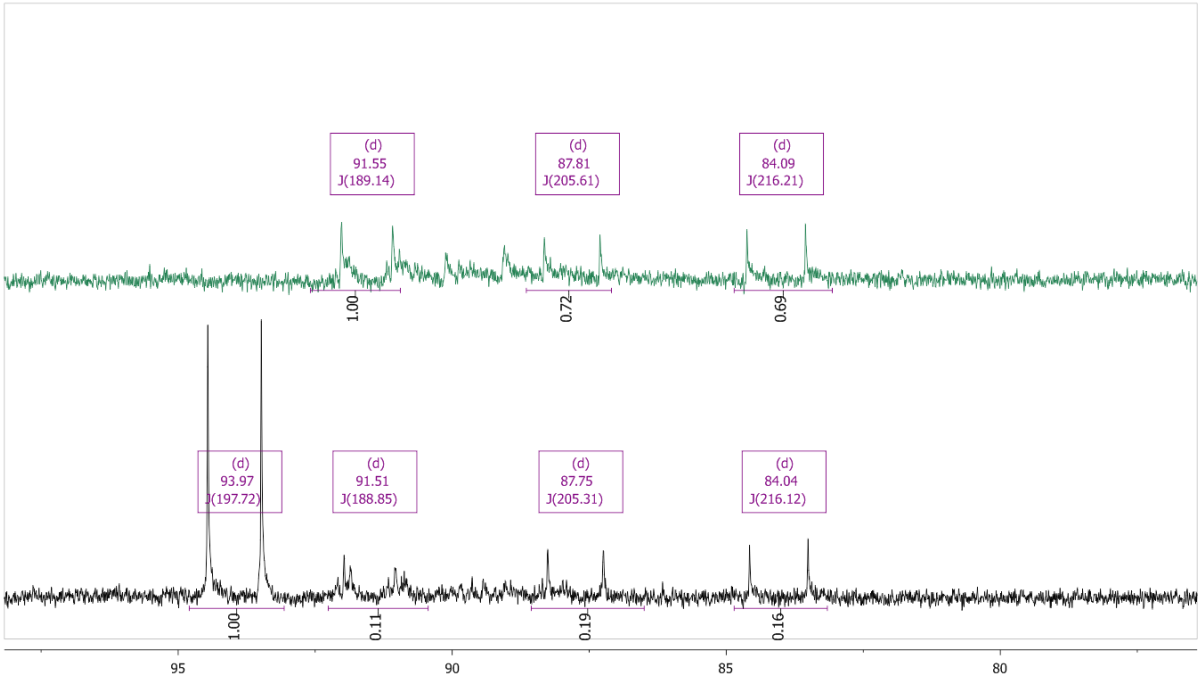
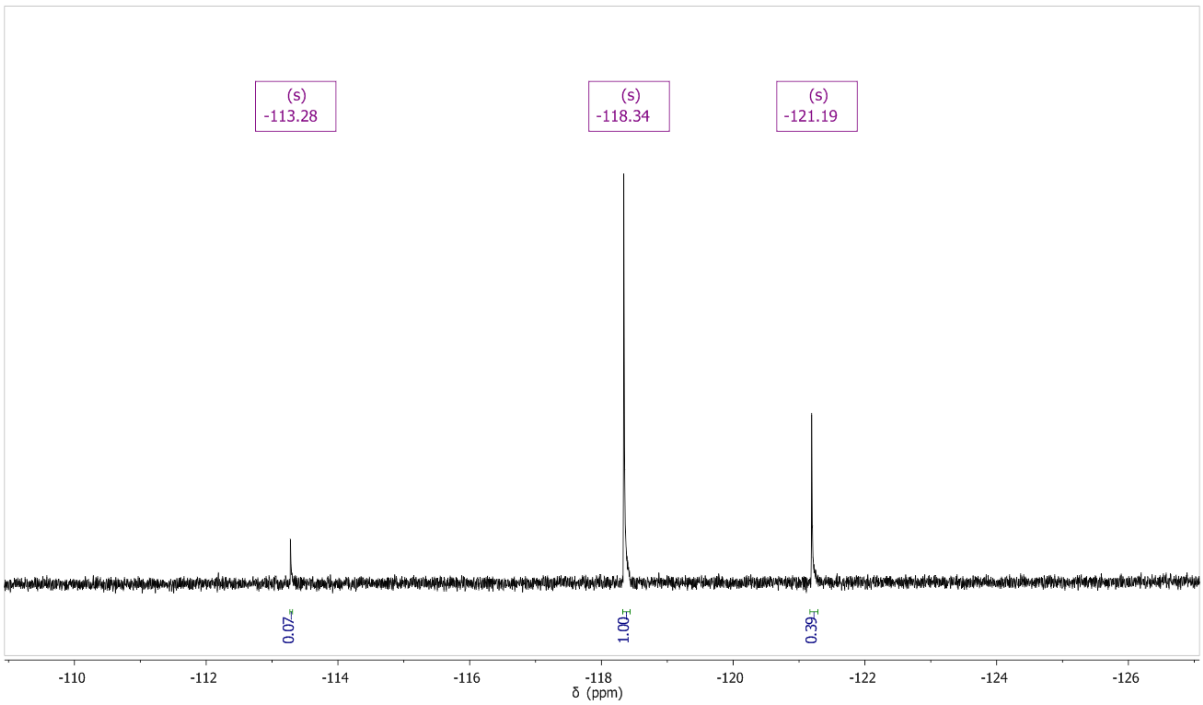


Figure S9. *FTIR monitoring of decomposition of* ***(3•)*** *by air in THF solution. The band at 1610 cm^{-1} which can also be seen corresponds to the BArF^{-} counterion.*

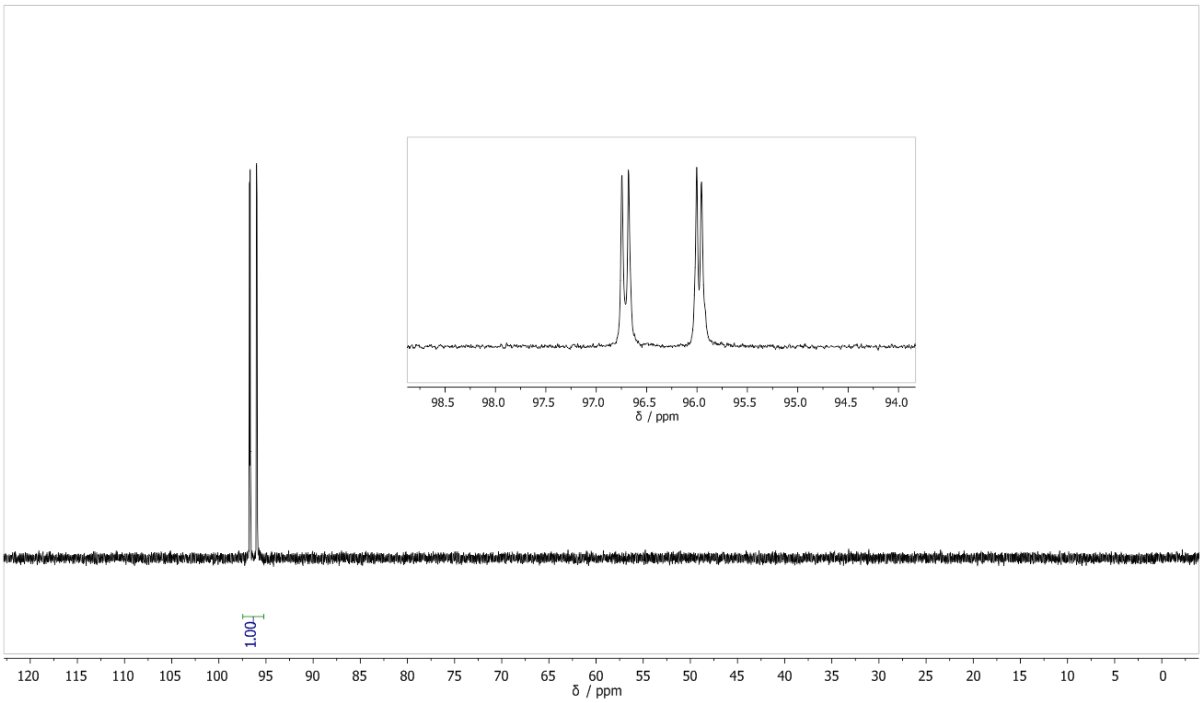


(a)

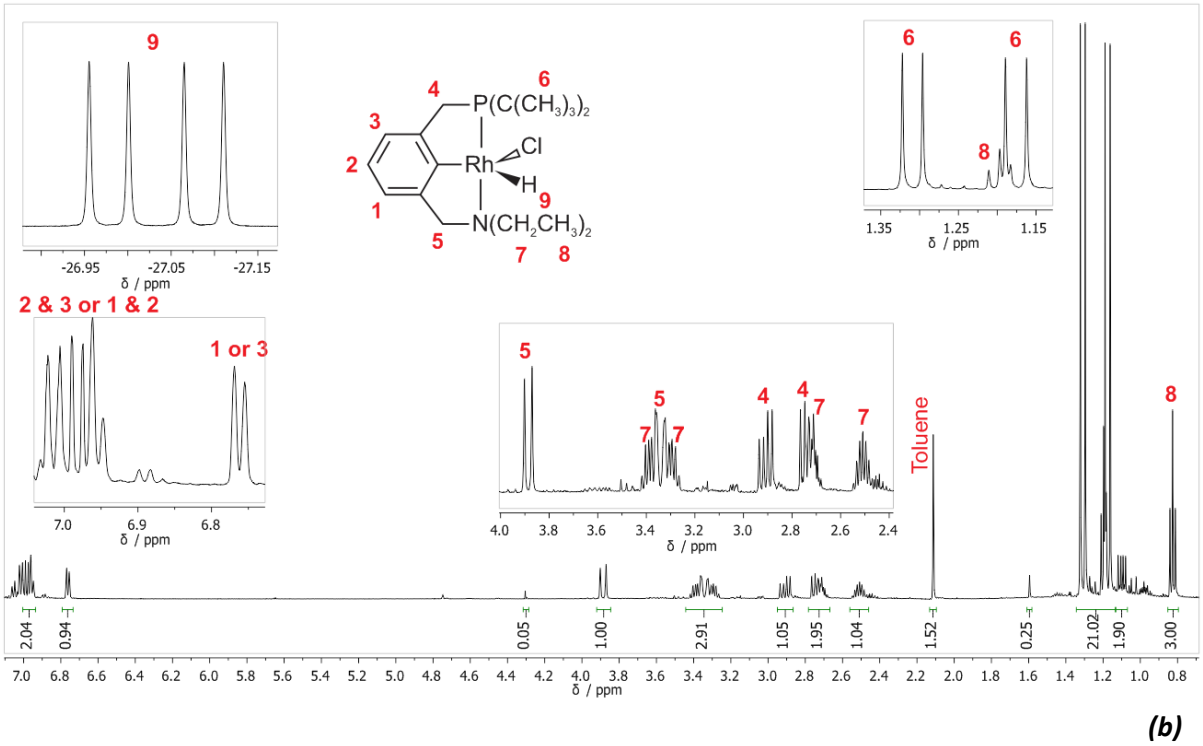


(b)

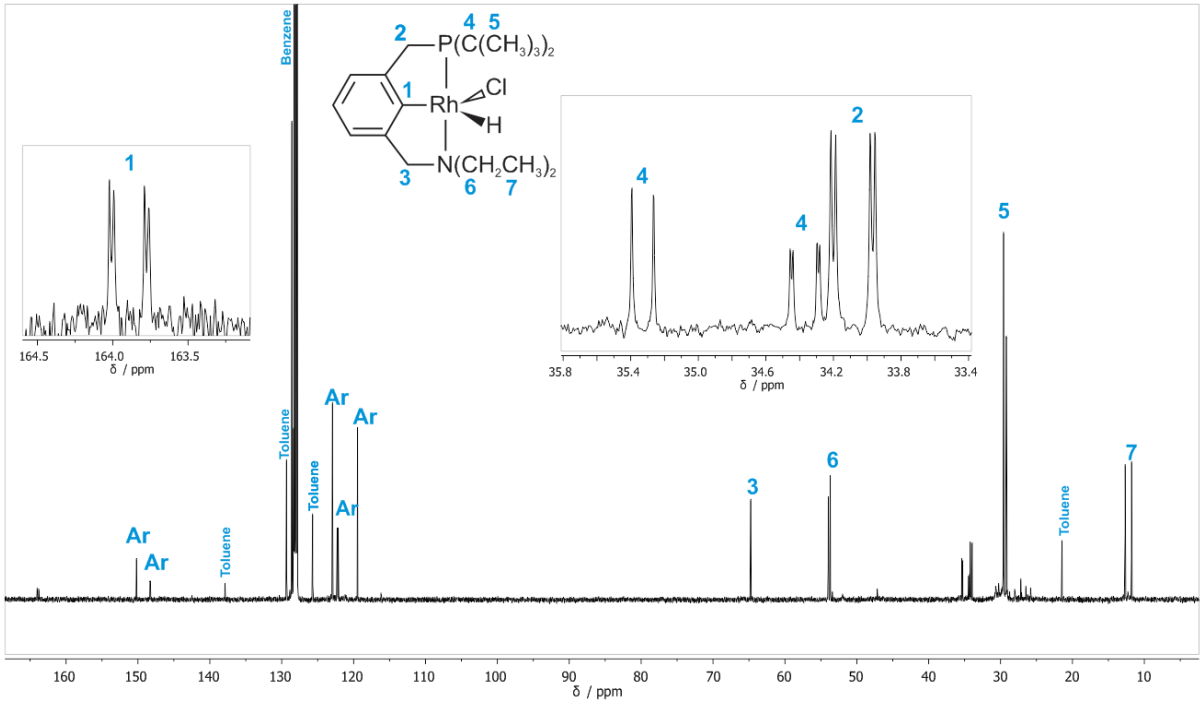
Figure S10. (a) *500 MHz ^{31}P-NMR of complex* ***(3•)*** *in benzene (green) and of complex* ***(3•)*** *after addition of 1 equivalent of 2-fluoroiodobenzene (black).* ***(b)*** *500 MHz ^{19}F-NMR of complex* ***(3•)*** *in benzene after addition of 1 equivalent of 2-fluoroiodobenzene.*



(a)

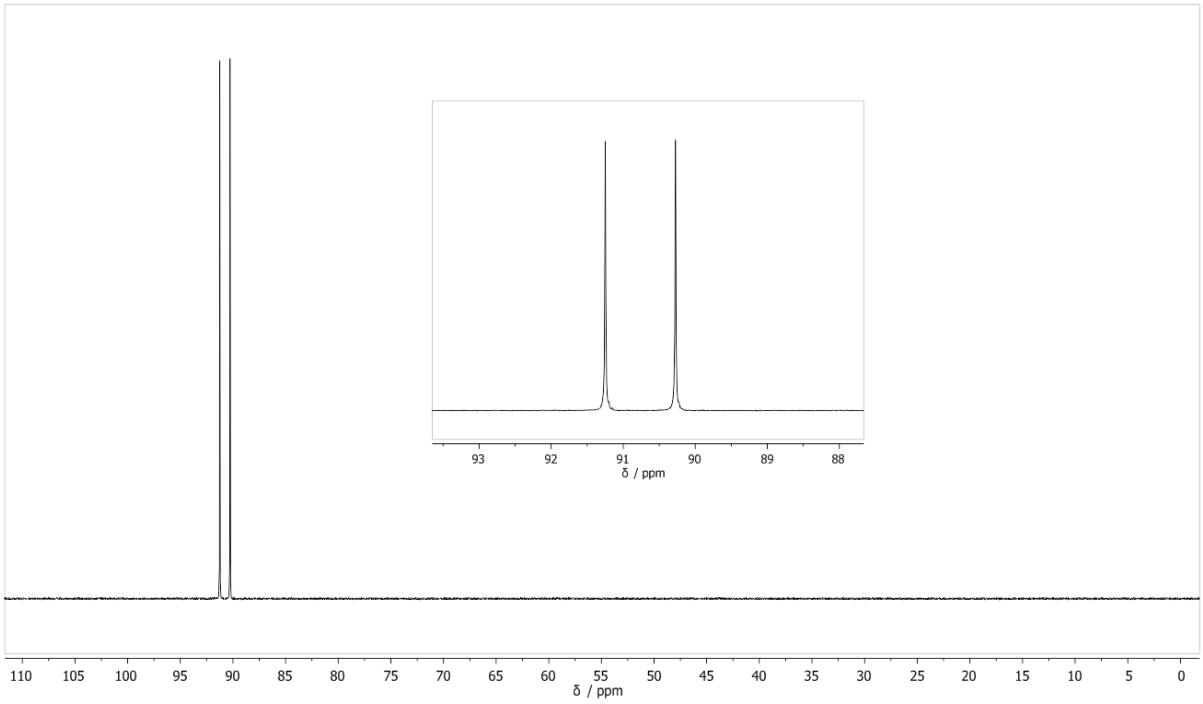


(b)

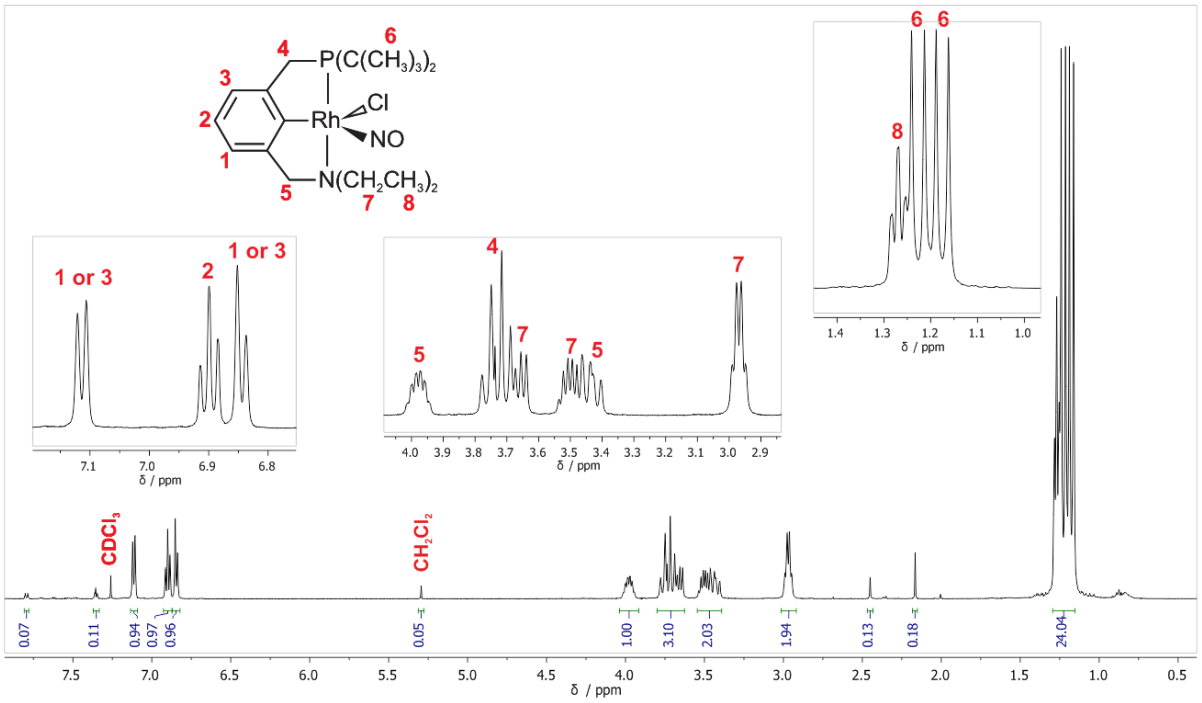


(c)

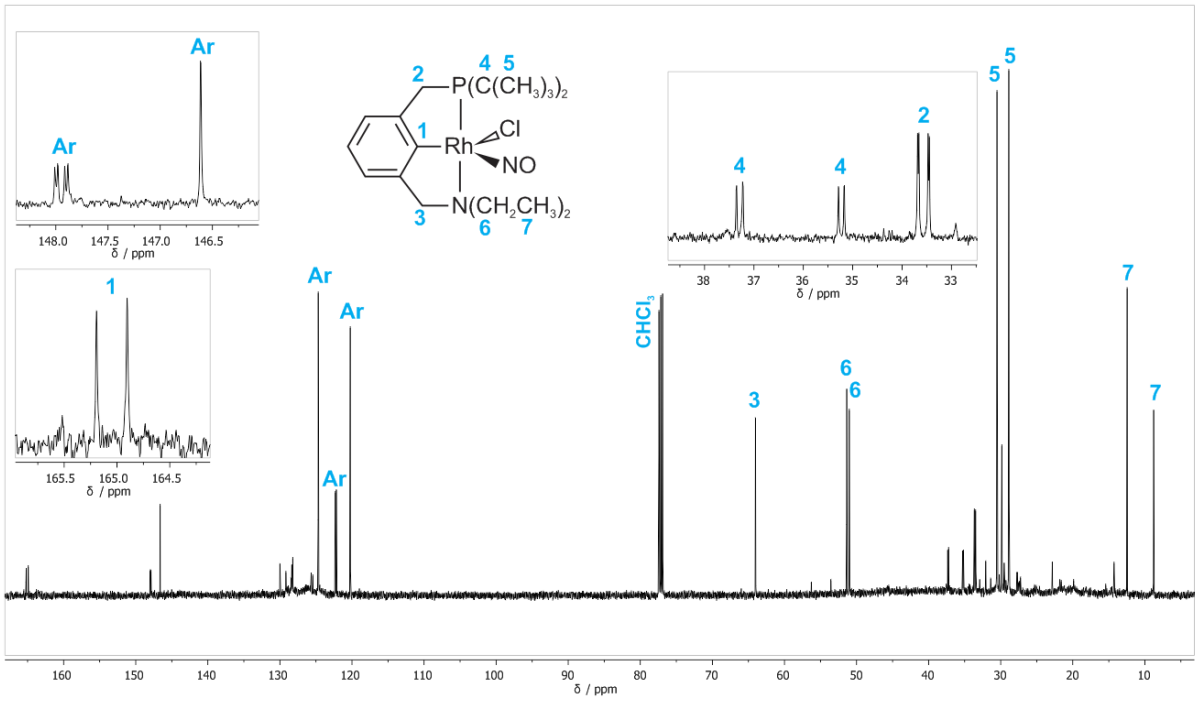
Figure S11. *500 MHz NMR spectra of complex* ***(1)*** *in d_6-benzene:* ***(a)*** *^{31}P-NMR,* ***(b)***^{1}*H-NMR,* ***(c)*** *^{13}C-NMR.*


93 92 91 90 89 88
δ / ppm
110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
δ / ppm

(a)

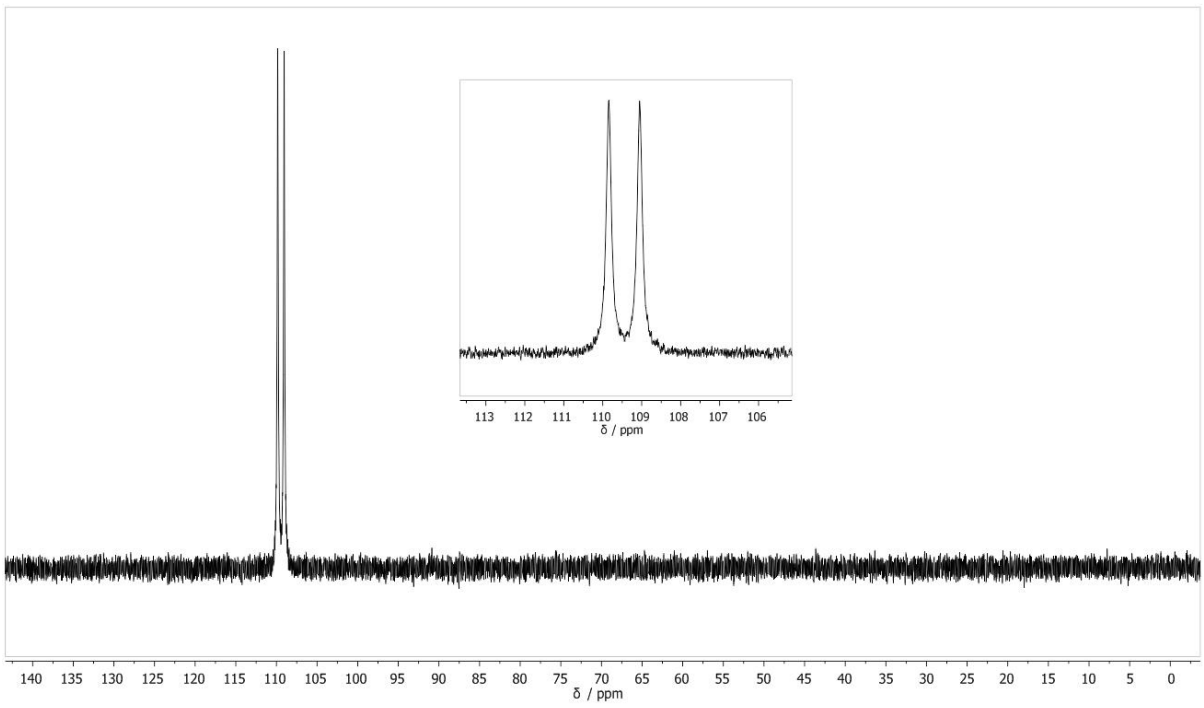

P(C(CH3)3)2
Rh
Cl
NO
N(CH2CH3)2
1 or 3
2
1 or 3
5
4
7
7
5
7
6 6
8
CDCl3
CH2Cl2
0.07
0.11
0.94
0.97
0.96
0.05
1.00
3.10
2.03
1.94
0.13
0.18
24.04
δ / ppm

(b)

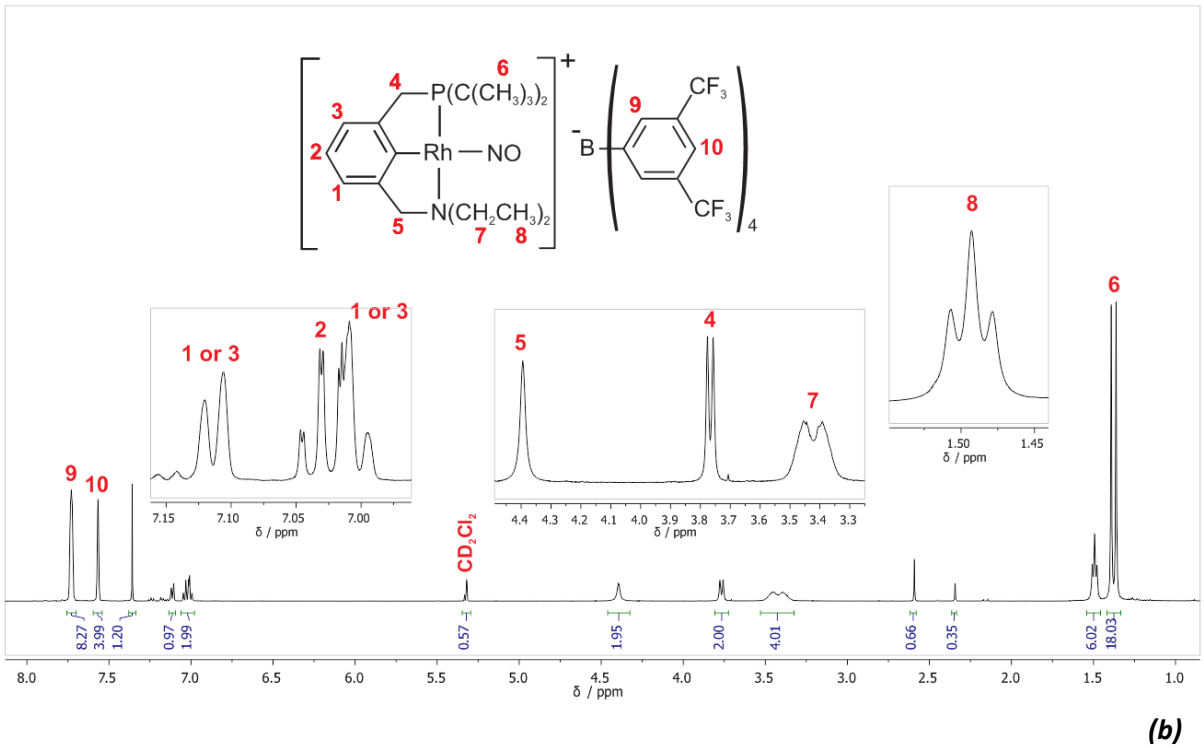


(c)

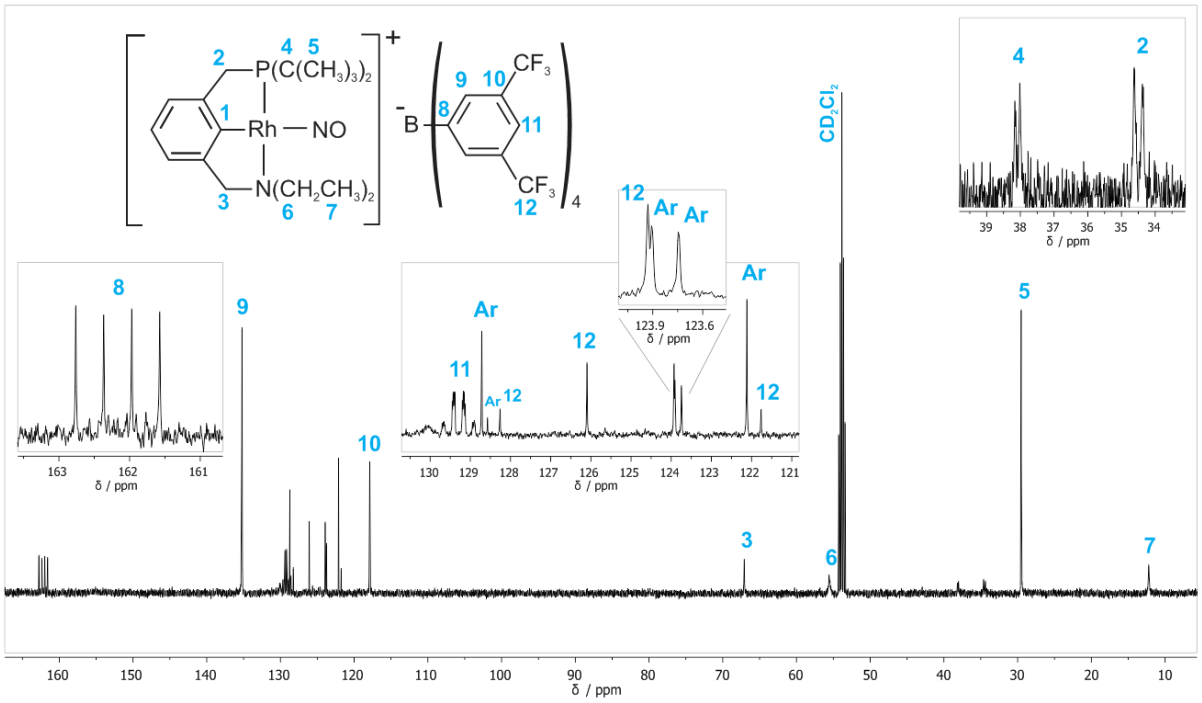
Figure S12. *500 MHz NMR spectra of complex* ***(2)*** *in* $CDCl_3$*:* ***(a)*** ^{31}*P-NMR,* ***(b)*** ^{1}*H-NMR,* ***(c)*** ^{13}*C-NMR.*



(a)



(b)



(c)

Figure S13. *500 MHz NMR spectra of complex* ***(3⁺)*** *in CD_2Cl_2:* ***(a)*** *^{31}P-NMR (in CH_2Cl_2),* ***(b)*** *^{1}H-NMR,* ***(c)*** *^{13}C-NMR.*

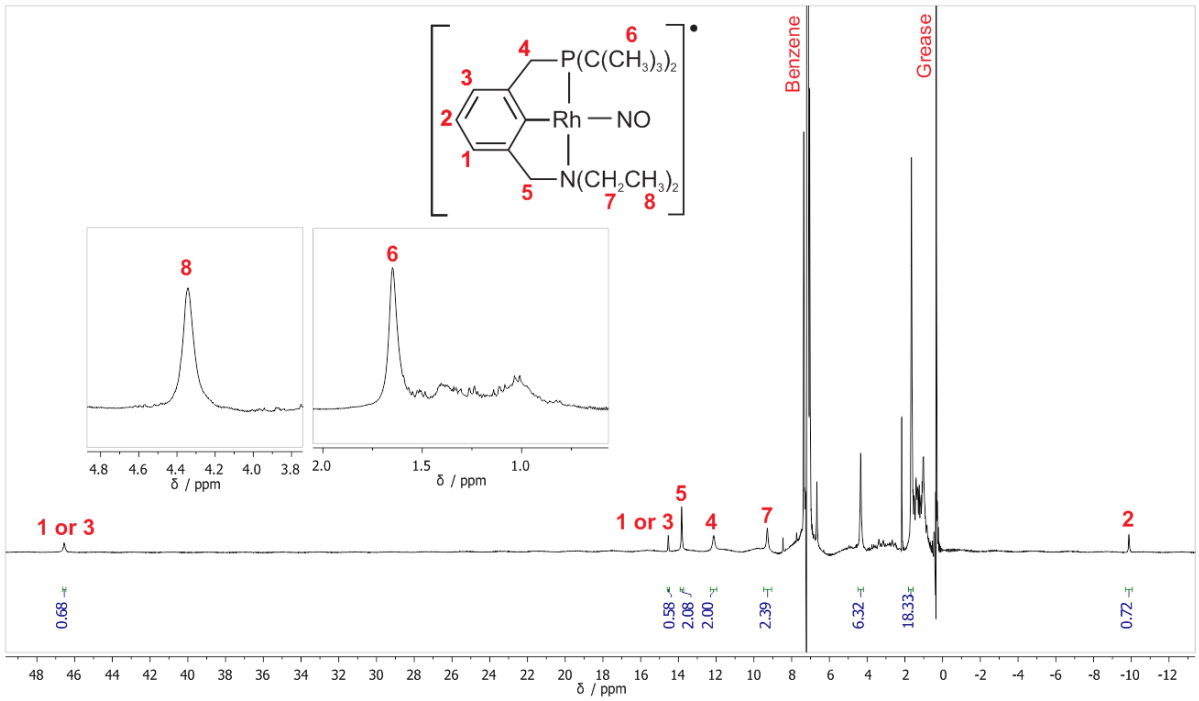
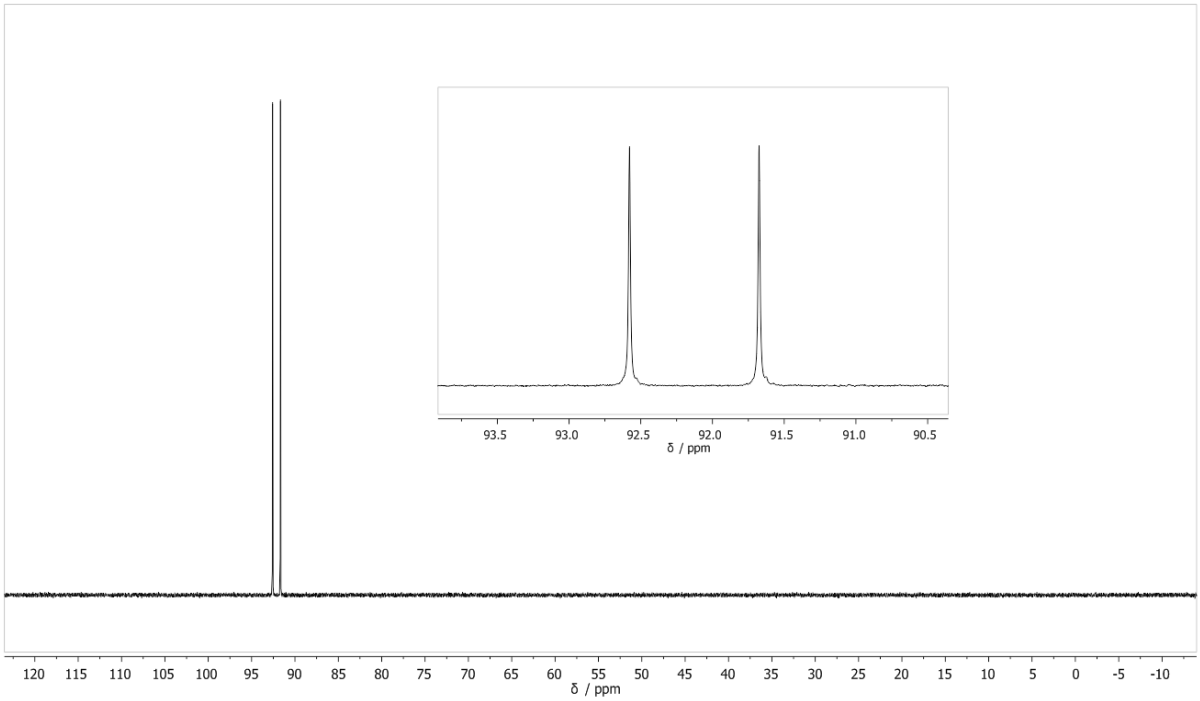


Figure S14. *500 MHz ^{1}H-NMR spectra of complex* ***(3•)*** *in benzene.*



(a)

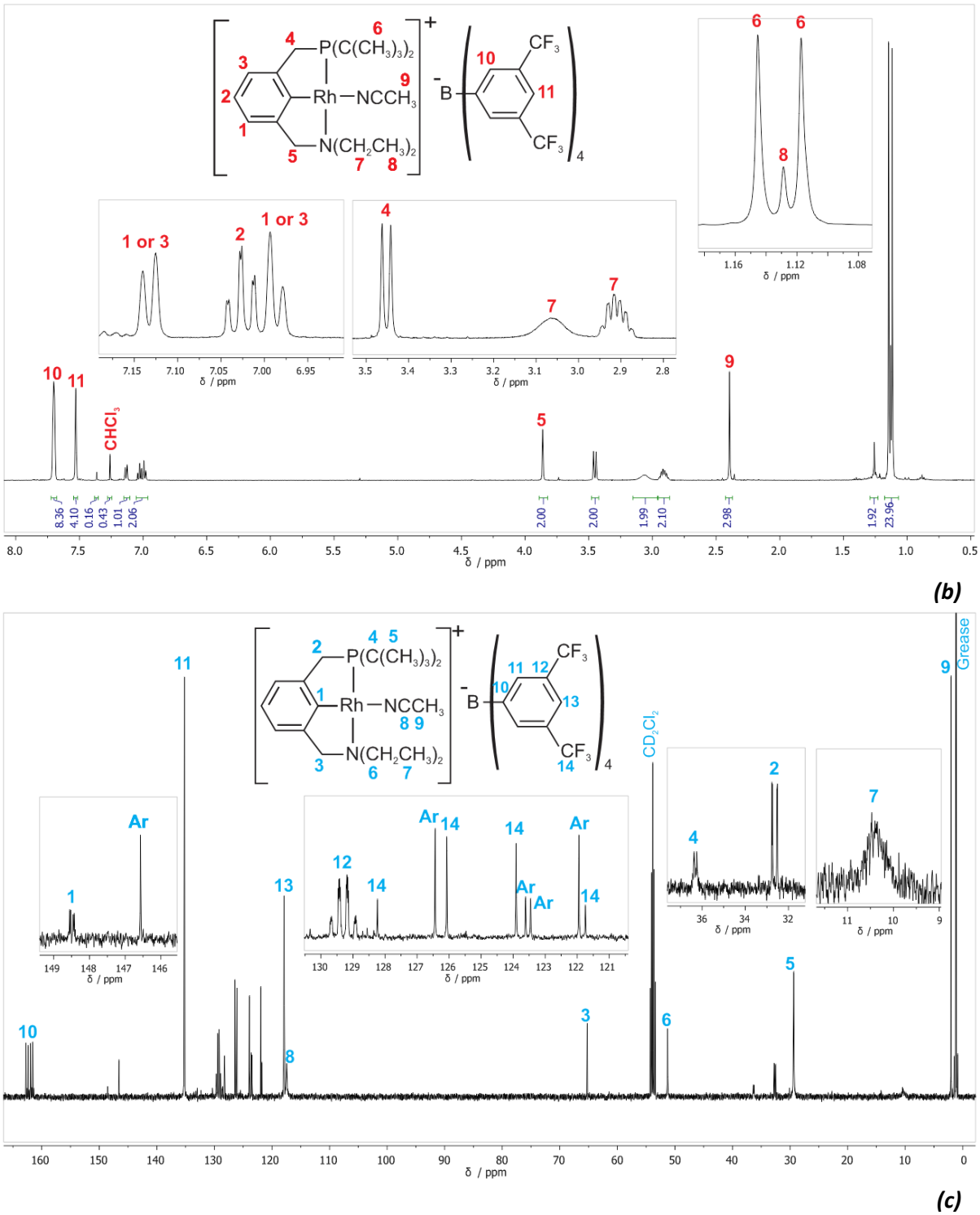
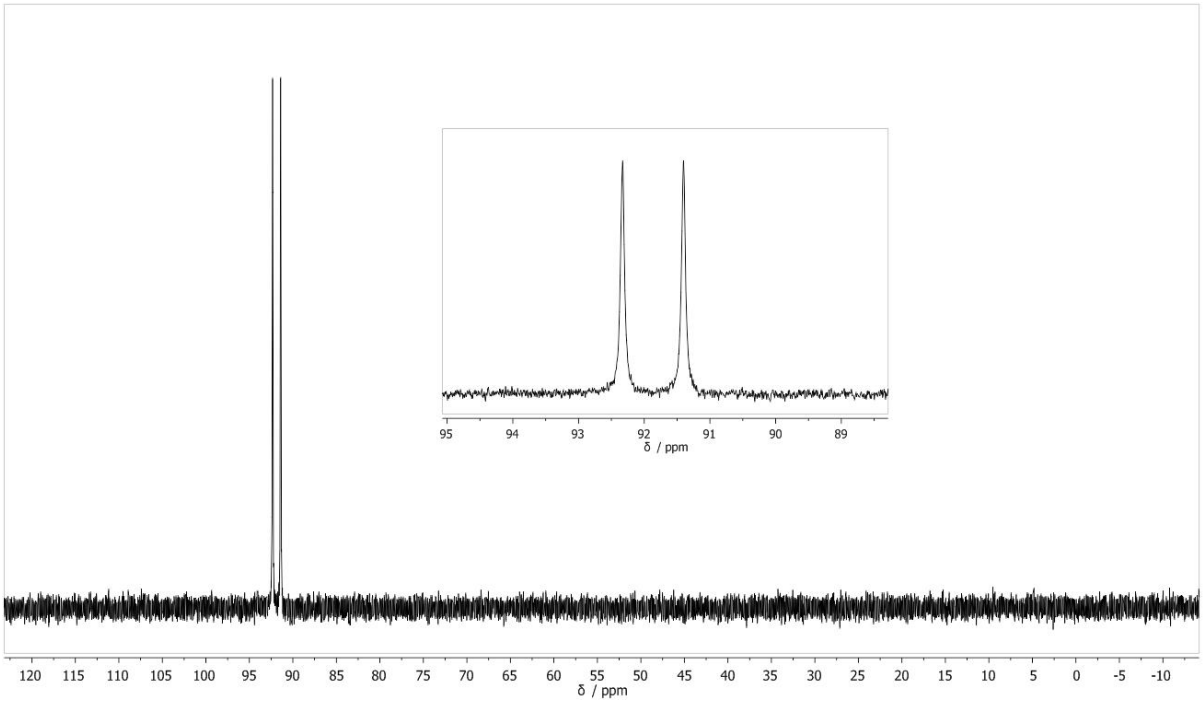
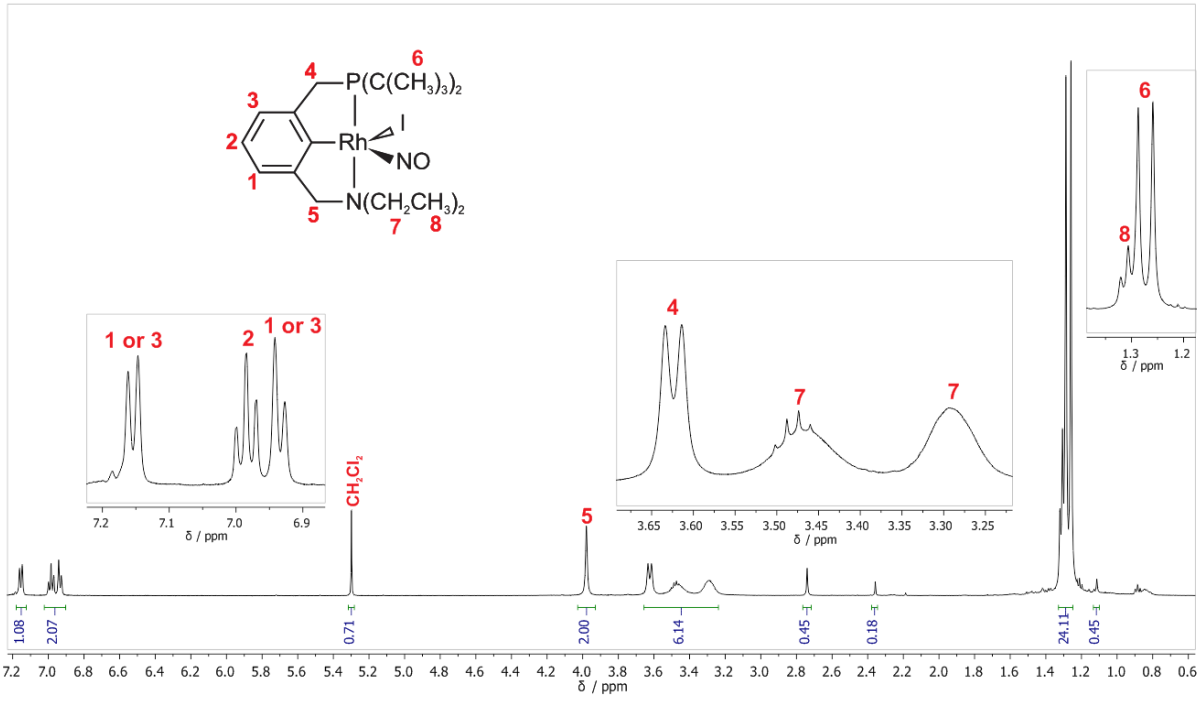


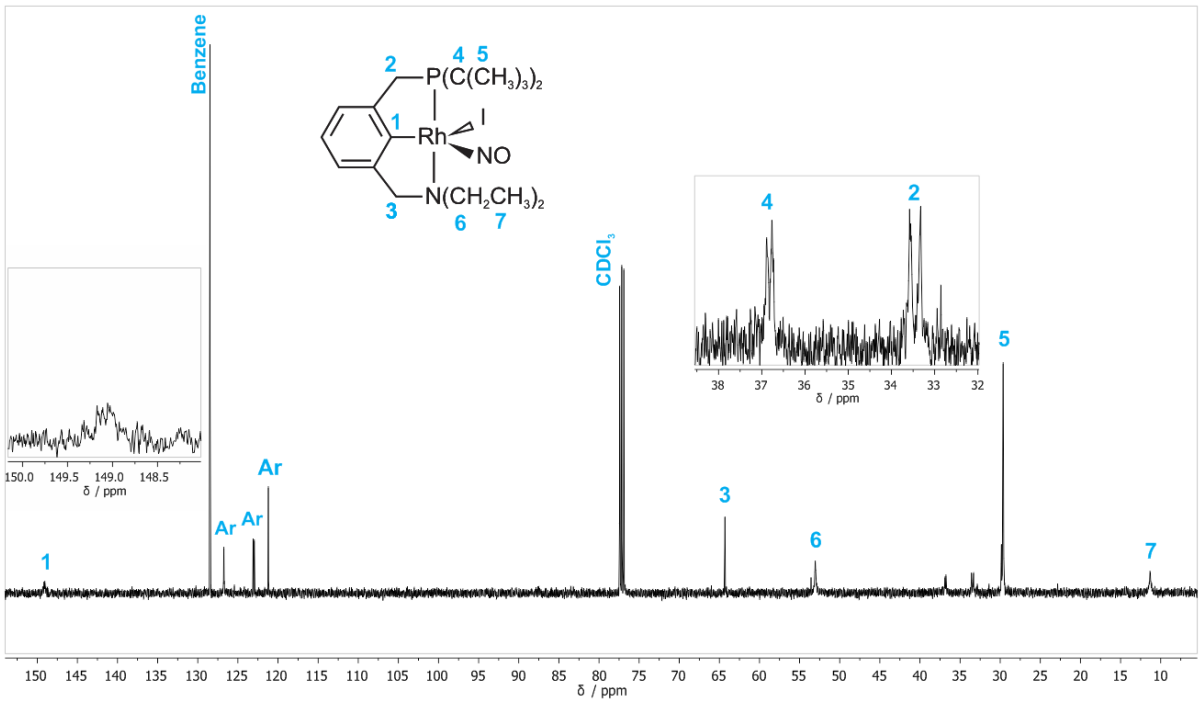
Figure S15. *500 MHz NMR spectra of complex* ***(4⁺)*** *in* $CDCl_3$: ***(a)*** ^{31}*P-NMR,* ***(b)*** ^{1}*H-NMR,* ***(c)*** ^{13}*C-NMR (in* CD_2Cl_2*).*


95 94 93 92 91 90 89
δ / ppm
120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10
δ / ppm

(a)


P(C(CH3)3)2
Rh
I
NO
N(CH2CH3)2
1 or 3
2
1 or 3
CH2Cl2
5
4
7
7
6
8
1.08
2.07
0.71
2.00
6.14
0.45
0.18
24.11
0.45
δ / ppm

(b)



(c)

Figure S16. *500 MHz NMR spectra of complex* ***(5)*** *in* $CDCl_3$*:* ***(a)*** ^{31}*P-NMR,* ***(b)*** ^{1}*H-NMR,* ***(c)*** ^{13}*C-NMR.*

Cartesian coordinates from optimizations

Rh(PCN)(NO)(Cl) ***(2)***

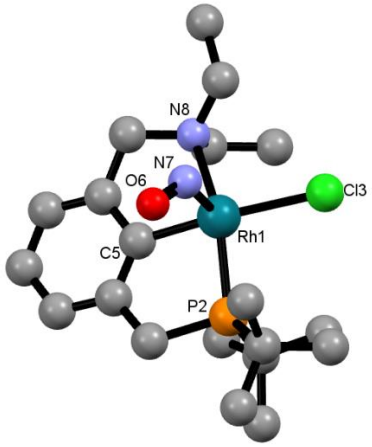


Figure S17. *DFT-optimized structure for* ***(2)****. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg.): Rh1-N7 1.900, N7-O6 1.190, Rh1-N7-O6 128.0.*

	X	Y	Z
Rh	-0.41971500	-0.46933100	-0.34819500
P	1.77062600	0.13154000	0.03575800
Cl	-0.08644300	-2.90008600	-0.03463300
C	-2.91702200	-0.43026400	1.61070800
C	-0.72157400	1.51674500	-0.16332400
O	-0.23779900	0.41797600	-2.99245800
N	-0.75942100	-0.31237200	-2.21066700
N	-2.70655000	-0.43497500	0.12896800
C	-2.06672900	1.94616500	-0.12099200
C	1.73285700	1.96931200	-0.33809900
C	2.19196000	0.04311700	1.91529900
C	-3.40051500	-1.55780300	-0.56448800
C	3.19811900	-0.57285300	-1.03437400
C	-2.36561800	3.30590700	0.07038800
C	0.32219500	2.46817900	-0.11733400
C	1.14562100	0.91122100	2.64989900
C	3.64136700	-1.95075000	-0.50253300
C	2.06299700	-1.40166300	2.44025600
C	4.40236200	0.38820200	-1.11641300
C	3.59876100	0.58826300	2.23127600
C	2.62250600	-0.77446100	-2.45198200
C	-1.32504000	4.24099200	0.18010800
C	0.01216400	3.82823200	0.06919200
C	-3.11727500	0.89969100	-0.40704200
C	-2.57198900	-1.73435500	2.32326900
C	-4.92327700	-1.61592300	-0.39530000
H	0.81650500	4.57072000	0.12188200

H	-1.55624700	5.29881300	0.33742300
H	-3.40892000	3.63793400	0.12123300
H	-2.29959700	0.39727800	1.99912400
H	-3.97269700	-0.15423700	1.81745400
H	2.49572900	2.53378800	0.22538200
H	1.99141400	2.06496400	-1.40984700
H	-3.13577600	-1.46234200	-1.63140800
H	-2.92403400	-2.48751300	-0.21544600
H	1.18231100	1.97292000	2.36112800
H	0.12060700	0.54919200	2.46794500
H	1.34115200	0.84685000	3.73527900
H	4.20647100	-1.87506500	0.43952700
H	2.77874100	-2.62139500	-0.35371700
H	4.31203700	-2.41572300	-1.24732900
H	1.10730000	-1.86378100	2.14799600
H	2.86567300	-2.05691100	2.07529200
H	2.12599500	-1.38047200	3.54322700
H	4.13292700	1.35946800	-1.56190300
H	4.87189600	0.57594200	-0.13998800
H	5.16877900	-0.06656900	-1.76957000
H	4.39453700	-0.06034400	1.83484600
H	3.75935800	1.61129000	1.85213500
H	3.72553000	0.62472600	3.32838100
H	1.80509600	-1.51191700	-2.44612400
H	2.24693000	0.16031100	-2.89810200
H	3.42707100	-1.15609200	-3.10591700
H	-3.20730100	0.77747600	-1.50418100
H	-4.11511400	1.19732800	-0.02598600
H	-2.60369300	-1.56504200	3.41184100
H	-3.29120000	-2.53628600	2.09247000
H	-1.57013600	-2.09804400	2.04497100
H	-5.22276500	-1.76350400	0.65506000
H	-5.42191100	-0.70685700	-0.76972600
H	-5.31641400	-2.46874000	-0.97171800

[Rh(PCN)(NO)]⁺ ***(3⁺)***

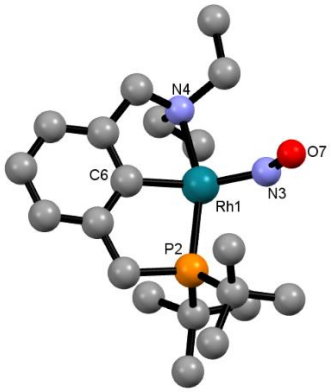


Figure S18. *DFT-optimized structure for* ***(3⁺)****. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg.): Rh1-N3 1.827, N3-O7 1.177, Rh1-N3-O7 143.5.*

	X	Y	Z
Rh	-0.46279200	-0.54604600	-0.13735200
P	1.79014300	0.11427000	0.06746700
N	-0.27000400	-2.11203900	-1.05760400
N	-2.68530200	-0.47554200	0.08189500
C	-2.07926200	1.83404400	-0.51021700
C	-0.72814400	1.43171500	-0.35420000
O	-0.26745000	-2.58015200	-2.13798000
C	0.29463300	2.40626800	-0.25865400
C	-3.10177600	0.74583500	-0.68797400
H	-4.11343400	1.07177200	-0.38343500
H	-3.15523600	0.45192300	-1.75172900
C	3.03243600	-0.50369200	-1.24792100
C	2.35767100	-0.27723100	-2.62092000
H	1.43457600	-0.86161300	-2.74231800
H	3.06146300	-0.59498000	-3.40934500
H	2.11841100	0.78201900	-2.80861600
C	-0.05413700	3.77016300	-0.28279200
H	0.72880100	4.53104100	-0.20041100
C	1.73477400	1.96444300	-0.17321800
H	2.29194700	2.47543700	0.63106700
H	2.26449600	2.20423500	-1.11162100
C	3.32923900	-2.00327300	-1.05122900
H	3.94121400	-2.18987000	-0.15509900
H	3.90499600	-2.36724500	-1.91927100
H	2.41635100	-2.61571200	-0.98333600
C	2.31422500	-0.19041600	1.87942100
C	-1.39225900	4.16099000	-0.41728200
H	-1.64855200	5.22384000	-0.43336900
C	-2.40607800	3.19704100	-0.53143200
H	-3.44972500	3.50942200	-0.63979400
C	2.08607100	-1.67839400	2.22210100

H	1.03679200	-1.97609500	2.05626100
H	2.31599800	-1.83777200	3.28955600
H	2.72963000	-2.35361900	1.63970300
C	1.37026900	0.66686300	2.75302700
H	1.50663300	1.74896100	2.60109900
H	1.58575700	0.45301700	3.81396500
H	0.30921800	0.42477100	2.57159400
C	-3.35250300	-1.70857900	-0.47028500
H	-2.91442200	-2.57246500	0.05259800
H	-3.04150800	-1.77724200	-1.52589500
C	4.35412700	0.29510300	-1.20749300
H	4.20674500	1.37525600	-1.36426500
H	4.99431600	-0.06265300	-2.03237400
H	4.91420500	0.15333300	-0.27345300
C	3.77654800	0.20395700	2.15805500
H	4.49012400	-0.48265300	1.67803600
H	3.95508400	0.14976100	3.24604600
H	4.00916100	1.23342300	1.84024200
C	-2.99232800	-0.26578600	1.54113400
H	-2.48690400	0.66997100	1.82876300
H	-4.07935300	-0.08726700	1.64464000
C	-2.55696700	-1.40911800	2.45156500
H	-1.48037000	-1.62576700	2.34317900
H	-3.11732900	-2.33833500	2.26521600
H	-2.73906100	-1.12128900	3.49883500
C	-4.87960400	-1.74681900	-0.37231400
H	-5.23474200	-2.67181700	-0.85330000
H	-5.35846000	-0.90429400	-0.89493200
H	-5.23818300	-1.76386300	0.66817600

Alternative structure for$[Rh(PCN)(NO)]^+$ ***(3$^+$)***

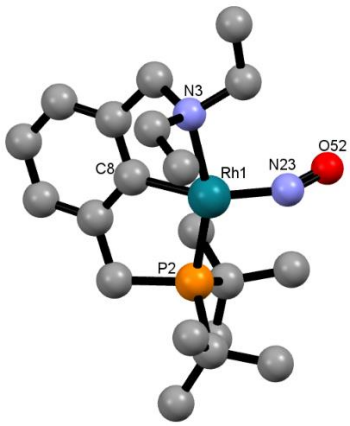


Figure S19. *DFT-optimized structure for* ***(3$^+$)*** *(alternative structure). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg.): Rh1-N23 1.822, N3-O7 1.175, Rh1-N3-O7 146.8.*

	X	Y	Z
Rh	0.48736100	-0.56871800	-0.07838500
P	-1.78675600	0.03367700	0.16213500
N	2.72370700	-0.41780400	0.00737100
C	1.99865600	1.91635800	-0.22521100
C	2.27177900	3.28630700	-0.10322400
H	3.27269700	3.67021600	-0.32519600
C	-0.30451700	2.30909800	0.52646400
C	0.70446700	1.42700400	0.07248900
C	-1.63487200	1.72743900	0.93688500
H	-2.49191500	2.37112100	0.67583800
H	-1.66844600	1.58674800	2.03213700
C	3.02062500	0.90068100	-0.65668200
H	4.05088100	1.22860100	-0.42513100
H	2.96250000	0.73122300	-1.74683400
C	-0.01725900	3.68255700	0.63232500
H	-0.79064400	4.37578600	0.97857900
C	1.25749100	4.16629700	0.30701700
H	1.46883900	5.23583700	0.39110900
C	3.13950700	-0.35031100	1.45308800
H	2.63513300	0.53259900	1.87522700
H	4.22684700	-0.15098900	1.49233400
C	-2.70248400	-1.04615200	1.44568600
N	0.34651700	-2.02926900	-1.15844400
C	-2.74612900	0.32392300	-1.46889900
C	3.40146500	-1.54630600	-0.72473300
H	3.04350700	-2.48328600	-0.27137500
H	3.01677700	-1.51784200	-1.75753100
C	-3.90750700	-0.31419700	2.07437200
H	-3.61708300	0.61727500	2.58590100
H	-4.35409200	-0.97512400	2.83731900
H	-4.69312300	-0.07857700	1.34382700
C	-1.66563300	-1.35249100	2.55042500
H	-0.81781800	-1.94059600	2.16191900
H	-2.15459300	-1.94599700	3.34247600
H	-1.26645100	-0.44042700	3.02545500
C	-2.03639600	1.48100800	-2.20560800
H	-2.10459000	2.43914200	-1.66786900
H	-2.52576800	1.61675200	-3.18544200
H	-0.97171000	1.26179400	-2.38522200
C	2.79724600	-1.59283700	2.26756200
H	1.71891600	-1.82154400	2.21575600
H	3.05209600	-1.40890000	3.32300200
H	3.35828500	-2.48391200	1.94611900
C	-3.15811500	-2.37101800	0.80344600

H	-3.97761000	-2.22677300	0.08294600
H	-3.53499600	-3.03934400	1.59652900
H	-2.33059000	-2.89561300	0.29735000
C	-4.21435100	0.70606200	-1.19230400
H	-4.79940000	-0.14131300	-0.80359400
H	-4.67854000	1.01256000	-2.14558700
H	-4.31621400	1.55388100	-0.49589600
O	0.38743400	-2.44899900	-2.25467200
C	-2.69446500	-0.93024300	-2.36490600
H	-1.67152000	-1.14675100	-2.70385000
H	-3.30091000	-0.73724500	-3.26624900
H	-3.10462000	-1.82845200	-1.88116000
C	4.93224200	-1.51750300	-0.74016600
H	5.33439300	-0.59968300	-1.19640200
H	5.28755700	-2.36486200	-1.34755200
H	5.37076400	-1.63167700	0.26309200

[Rh(PCN)(NO)][BArF] ***(3-BArF)***

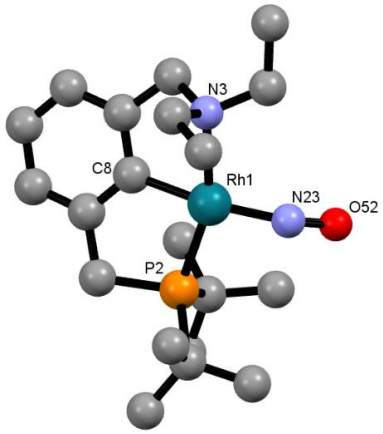


Figure S20. *DFT-optimized structure for* ***(3-BArF)****. Hydrogen atoms and the counteranion were omitted for clarity. Selected bond lengths (Å) and angles (deg.): Rh1-N23 1.819, N23-O52 1.165, Rh1-N23-O52 155.0.*

	X	Y	Z
Rh	-4.04045000	-0.62059000	-0.32898700
P	-5.02821800	1.51186000	-0.39384400
N	-3.80172600	-2.81834800	0.00747000
C	-5.79748800	-2.26147800	1.33093300
C	-6.96250300	-2.66302000	2.00127700
H	-6.99600900	-3.62868000	2.51651600
C	-6.90137500	-0.18123800	0.65816800
C	-5.75864300	-1.01551300	0.66005200
C	-6.83290600	1.11145200	-0.11785500
H	-7.36307500	1.94485400	0.37496300
H	-7.29419700	0.98415800	-1.11379300

C	-4.53681100	-3.07983000	1.29334800
H	-4.73811000	-4.16104900	1.41189600
H	-3.85786700	-2.77468100	2.10918500
C	-8.06024800	-0.59025500	1.34260400
H	-8.94744800	0.05170000	1.34776800
C	-8.08550100	-1.82071700	2.01432200
H	-8.99067400	-2.13080800	2.54450700
C	-4.47310900	-3.54754400	-1.12287600
H	-5.51310300	-3.18593500	-1.15173500
H	-4.51103200	-4.62490200	-0.86953000
C	-4.96168600	2.37300200	-2.09940700
N	-2.32528000	-0.05553200	-0.54527500
C	-4.54360900	2.63491800	1.08091000
C	-2.35244300	-3.20890900	0.14876800
H	-1.84923600	-2.94095000	-0.79120100
H	-1.94273500	-2.56789900	0.94096100
C	-6.07058200	3.43510900	-2.25959900
H	-7.08081100	3.01685200	-2.12210600
H	-6.02197400	3.83108100	-3.28904600
H	-5.95053800	4.28502900	-1.57476100
C	-5.18558500	1.25412900	-3.14357200
H	-4.38036100	0.50441100	-3.11583100
H	-5.18750800	1.70965100	-4.14958300
H	-6.15270600	0.73889900	-3.01637400
C	-5.03573500	1.93629800	2.36774300
H	-6.13285600	1.86281800	2.42817500
H	-4.69383000	2.53458800	3.23028600
H	-4.61173400	0.92483100	2.46787000
C	-3.79571400	-3.34983700	-2.47721400
H	-3.62844000	-2.28083200	-2.69394500
H	-4.44472700	-3.76056900	-3.26687000
H	-2.82711200	-3.86954900	-2.53963600
C	-3.57789100	3.00656500	-2.33986000
H	-3.36216300	3.84422900	-1.66046500
H	-3.55110800	3.40665700	-3.36849000
H	-2.76189700	2.27171500	-2.26477300
C	-5.19694000	4.02684200	0.96781700
H	-4.75984400	4.62568800	0.15420800
H	-5.01343400	4.57349000	1.90913800
H	-6.28943100	3.97856400	0.82604200
O	-1.31244800	0.40397100	-0.19747200
C	-3.01071300	2.77797500	1.17039000
H	-2.54171300	1.83471700	1.48545100
H	-2.77387700	3.52895100	1.94355700
H	-2.53738600	3.12099400	0.24054300

C	-2.09102300	-4.67762300	0.49038100
H	-2.53291700	-4.96517500	1.45678800
H	-1.00339000	-4.82337700	0.56420600
H	-2.45303800	-5.36783400	-0.28723000
C	2.75620300	1.63708200	-0.34085600
C	1.61625900	2.45639400	-0.17956400
H	0.72300400	2.03547000	0.29350200
C	1.75405000	-0.78132000	-1.00627700
C	1.96355200	0.03850000	1.59082200
C	3.88710700	2.26514900	-0.90603500
H	4.80856000	1.69318000	-1.05006700
C	1.58265300	3.79797800	-0.59421700
C	4.85492900	-0.87242000	-1.09077000
H	4.40664300	-0.53802100	-2.03258000
C	4.14932800	-0.67555500	0.12174100
C	1.01194800	-0.16353800	-2.03792000
H	1.03017700	0.92584000	-2.13393100
C	2.71594100	4.39254200	-1.16263400
H	2.70046400	5.43433200	-1.48785100
C	2.53695500	0.82294400	2.62503300
H	3.46533500	1.36760700	2.42612400
C	3.87298900	3.61415400	-1.30316000
C	1.68505500	-2.19610300	-0.96063300
H	2.24782700	-2.73189700	-0.18922100
C	0.24167900	-0.89958900	-2.95633200
F	0.41328400	5.87588600	-0.76278600
F	-0.20098400	4.48900600	0.82399700
F	4.85664700	5.27072600	-2.70199900
C	6.11633800	-1.48466300	-1.13527600
C	4.78016400	-1.15939600	1.28568900
H	4.28147200	-1.05551300	2.25456700
C	0.76260100	-0.61971600	1.91697700
H	0.28480700	-1.25343700	1.16262500
C	6.72287100	-1.94783700	0.04148200
H	7.70477300	-2.42295400	0.01395300
C	0.92455400	-2.94064400	-1.87821100
C	6.04164800	-1.78294100	1.25128100
C	0.19744200	-2.29708900	-2.89183600
H	-0.38453500	-2.87252800	-3.61545100
F	-2.16751600	-0.60085800	2.58508500
C	0.14415400	-0.47524600	3.17792200
F	-0.21636700	1.05799900	-4.24245500
F	1.17623600	-4.92225200	-0.57716500
F	-0.78324100	-0.87721600	-5.11083800
F	5.85601400	-3.24122300	3.11594800

F	5.92311300	3.36228000	-2.48590600
B	2.67019500	0.04504700	0.09782100
F	-0.69098200	4.04361700	-1.25997100
F	5.88184500	4.79066600	-0.82774900
C	1.95494800	0.93874700	3.89383700
C	0.73778200	0.29965700	4.17854900
H	0.26977100	0.40249400	5.15938700
C	5.13160100	4.25471500	-1.83321000
F	6.56898000	-0.68055500	-3.32812600
F	8.13722700	-1.86032600	-2.33994600
F	-0.32653400	-4.94200500	-2.18495800
C	-0.64036500	-0.19279100	-3.94654900
C	0.29779200	4.56160100	-0.44612000
C	-1.18767100	-1.11859900	3.42456700
C	0.90805800	-4.44514900	-1.82705600
F	6.32155500	-2.83959400	-3.07635600
F	2.42980700	1.28752600	6.19595600
F	-1.92756200	-0.05109200	-3.43439300
F	-1.64558100	-0.95694700	4.68796500
F	6.75660500	-1.28012000	3.46050500
C	6.63885400	-2.28093100	2.54205900
C	6.78864000	-1.71117000	-2.46486500
F	1.80684600	-5.00848100	-2.67171800
F	-1.18354300	-2.46533700	3.16508700
F	7.87690500	-2.82140700	2.37037500
F	1.97992200	3.05020100	4.97997700
F	3.90017900	2.02322100	4.73824000
C	2.57469300	1.82143000	4.94868200

[Rh(PCN)(NO)]$^{2+}$ ***(3^{2+})***

	X	Y	Z
Rh	-0.50928100	-0.49334200	-0.12299500
P	1.83117500	0.13021600	-0.13740100
N	-0.20879700	-2.24399500	0.42494600
N	-2.75216300	-0.41661400	-0.11644800
C	-2.08471900	1.93821700	-0.28880800
C	-0.72575100	1.49063400	-0.24097800
O	0.05139900	-3.25222900	0.92280400
C	0.34375900	2.43871100	-0.18341500
C	-3.10881700	0.91862300	-0.69907600
H	-4.13332300	1.20844700	-0.40720800
H	-3.10147500	0.82704200	-1.80086900
C	2.70894900	-0.68288900	-1.62073300
C	1.64988700	-0.70163600	-2.74723600
H	0.78064600	-1.33648300	-2.48588100

H	2.09920500	-1.13693400	-3.65669800
H	1.28561000	0.30412500	-3.01548500
C	0.03865200	3.77366100	0.10723900
H	0.83892700	4.51102800	0.22091700
C	1.72655200	1.95374700	-0.50576600
H	2.52259200	2.51431900	0.01082800
H	1.90411600	2.08587300	-1.58933400
C	3.13087000	-2.12365800	-1.27390800
H	3.94611700	-2.15566200	-0.53596100
H	3.50461300	-2.60816500	-2.19142000
H	2.29374200	-2.73839000	-0.90497200
C	2.67525800	0.01758000	1.57575700
C	-1.30746100	4.18216400	0.20368900
H	-1.53393100	5.23601100	0.39217000
C	-2.37005400	3.27467500	-0.00908700
H	-3.40501500	3.62882500	0.02057100
C	2.56143800	-1.40536700	2.15661300
H	1.52278000	-1.65114600	2.42606500
H	3.14614600	-1.44239500	3.09085000
H	2.96263800	-2.18579800	1.49407800
C	1.93801700	0.99890900	2.51288400
H	2.05275300	2.05306300	2.21782100
H	2.37400600	0.89823800	3.52112500
H	0.86216200	0.77050500	2.59636700
C	-3.24821700	-1.54695600	-0.98585200
H	-2.93600000	-2.48501200	-0.50321800
H	-2.69686700	-1.46693000	-1.94021800
C	3.93605800	0.13919200	-2.07025400
H	3.67925000	1.16210500	-2.38693600
H	4.37693100	-0.36186100	-2.94926200
H	4.71960200	0.19451200	-1.30192900
C	4.16044700	0.42059200	1.43893700
H	4.74889700	-0.32382600	0.88226500
H	4.58867700	0.47879600	2.45432900
H	4.30452300	1.40880500	0.97339000
C	-3.28685000	-0.46446100	1.30059300
H	-2.92858100	0.45338700	1.79419800
H	-4.38647600	-0.37989300	1.22338400
C	-2.92380700	-1.68782700	2.12893000
H	-1.85084800	-1.72496900	2.37575800
H	-3.22589900	-2.63767400	1.66100300
H	-3.46436600	-1.62324800	3.08658200
C	-4.75685900	-1.56663400	-1.25118100
H	-4.97383300	-2.41755300	-1.91573300
H	-5.11320600	-0.65902800	-1.76154800

H	-5.34267900	-1.71452900	-0.33124800

Alternative structure for $[Rh(PCN)(NO)]^{2+}$ ***(3^{2+})***

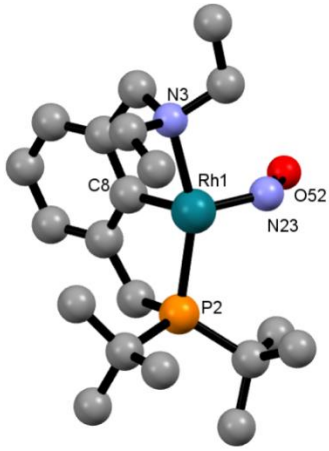


Figure S21. *DFT-optimized structure for* ***(3^{2+})*** *(alternative structure). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg.): Rh1-N23 1.854, N23-O52 1.169, Rh1-N23-O52 139.0.*

	X	Y	Z
Rh	0.48196700	-0.59185900	-0.13453800
P	-1.84129300	0.04993800	-0.00035100
N	2.66588800	-0.55995300	0.27351300
C	2.12116700	1.72685700	-0.48365000
C	2.39154400	3.09543400	-0.51815800
H	3.42187600	3.45782400	-0.44921100
C	-0.32326400	2.22843400	-0.71496400
C	0.75429800	1.30431000	-0.51632000
C	-1.72430600	1.69883500	-0.86693900
H	-1.93284900	1.51695000	-1.93683900
H	-2.48771200	2.41086800	-0.51371600
C	3.18359900	0.66281700	-0.42932400
H	4.10813100	1.02589200	0.05301900
H	3.45481300	0.36918700	-1.45998700
C	-0.01114500	3.59295300	-0.74625500
H	-0.80856600	4.33441600	-0.85492100
C	1.33053000	4.01864600	-0.65888500
H	1.55662500	5.08741300	-0.71834200
C	2.77286800	-0.38389400	1.76889700
H	2.29726200	0.58253500	2.00770400
H	3.84147100	-0.28709100	2.03072300
C	-2.22958500	0.39903700	1.84533300
N	0.47579100	-1.50753800	-1.74685400
C	-3.09570100	-1.06946100	-0.91856700
C	3.36326500	-1.81308800	-0.21052200
H	2.82194800	-2.66970900	0.22216700
H	3.20860500	-1.84780500	-1.30116800

C	-3.45417900	1.32656300	1.99371300
H	-3.29188300	2.31990400	1.54689400
H	-3.62289800	1.48857400	3.07257900
H	-4.37759100	0.89907400	1.58263700
C	-0.99720600	1.09990700	2.45815900
H	-0.09329100	0.46478100	2.42226600
H	-1.20630700	1.30082400	3.52275800
H	-0.76662700	2.06430100	1.97882400
C	-2.93994700	-0.82998900	-2.43614800
H	-3.33669900	0.14754800	-2.75197400
H	-3.53340300	-1.59662600	-2.96204400
H	-1.90511100	-0.92855000	-2.79754100
C	2.13153900	-1.51954800	2.56188900
H	1.07397900	-1.69468100	2.27723300
H	2.13237400	-1.25997500	3.63198400
H	2.67109800	-2.47226000	2.45467300
C	-2.46902100	-0.94270200	2.56884600
H	-3.38664700	-1.44726100	2.23392600
H	-2.58646900	-0.73983200	3.64665500
H	-1.62342000	-1.64343500	2.45985400
C	-4.54667400	-0.73392400	-0.50912600
H	-4.76918600	-0.99295000	0.53592800
H	-5.21887200	-1.33956600	-1.14099800
H	-4.80458900	0.32264900	-0.68362400
O	0.67223000	-1.29905600	-2.88022000
C	-2.76557500	-2.54028000	-0.58262400
H	-1.76089400	-2.83586200	-0.92772200
H	-3.48838800	-3.18605200	-1.10895500
H	-2.84954300	-2.76630000	0.49036800
C	4.85541000	-1.90147700	0.11318000
H	5.42963900	-1.05886400	-0.30256200
H	5.25024100	-2.81964400	-0.34964500
H	5.05845500	-1.97340400	1.19248200

[Rh(PCN)(NO)(CH$_3$CN)]$^+$ ***(4$^+$)***

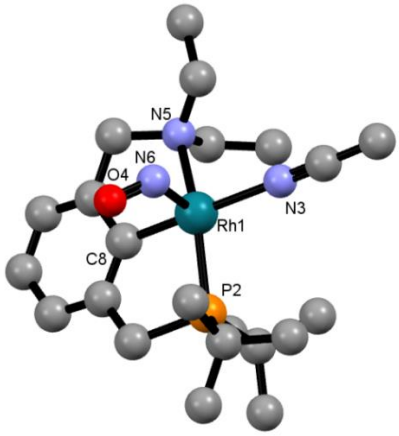


Figure S22. *DFT-optimized structure for* ***(4$^+$)****. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg.): Rh1-N6 1.926, N6-O4 1.182, Rh1-N6-O4 125.9.*

	X	Y	Z
Rh	0.44094900	0.32055400	-0.28344100
P	-1.79253900	-0.32205400	0.05420200
N	0.20928400	2.52313100	-0.17232500
O	0.39327100	-0.44097200	-2.96516100
N	2.68007900	0.27672500	0.16915700
N	0.71247100	0.39096500	-2.18842800
C	2.07572300	-2.08725700	-0.20982600
C	0.72647500	-1.66467100	-0.21027400
C	0.09479600	3.68833500	-0.15547900
C	-0.30942300	-2.62513500	-0.17283900
C	3.12368200	-1.02818100	-0.42909600
H	4.11097100	-1.32802500	-0.02988400
H	3.25056400	-0.84928500	-1.51376300
C	-3.20949300	0.36935200	-1.03645200
C	-2.63970200	0.51249000	-2.46411300
H	-1.83460800	1.26239300	-2.50365800
H	-3.44933400	0.84928000	-3.13444400
H	-2.25178500	-0.43539500	-2.87095600
C	0.01544200	-3.98910200	-0.05526000
H	-0.78341800	-4.73699000	-0.01308400
C	-1.73302500	-2.14717800	-0.33102400
H	-2.46034700	-2.71361500	0.27586500
H	-2.05012500	-2.25861000	-1.38482000
C	-3.64823300	1.76394500	-0.54956800
H	-4.16996700	1.72957400	0.41857400
H	-4.35291500	2.19036900	-1.28443000
H	-2.79407700	2.45626300	-0.46791700
C	-2.18997900	-0.21097900	1.92980000
C	1.35570600	-4.39830900	-0.00153300
H	1.59679400	-5.46011100	0.09812200

C	2.38640800	-3.45210500	-0.08913800
H	3.43210200	-3.77724400	-0.07407400
C	-0.04900700	5.13547300	-0.13589200
H	-1.11361200	5.41367500	-0.19135500
H	0.47780300	5.57934200	-0.99567600
H	0.37695900	5.54780500	0.79277500
C	-1.97851700	1.23472800	2.42595400
H	-0.95520100	1.58861000	2.21968000
H	-2.12816300	1.26062000	3.51938700
H	-2.68332200	1.94998100	1.97869300
C	-1.18405700	-1.12699000	2.66213600
H	-1.30078500	-2.18922400	2.39889400
H	-1.35186700	-1.03021400	3.74894900
H	-0.13954300	-0.84257400	2.45359500
C	3.39639400	1.43456600	-0.45562000
H	2.94314700	2.35006000	-0.04565100
H	3.13746100	1.40874000	-1.52757400
C	-4.42352800	-0.58432200	-1.07712100
H	-4.16513700	-1.57663400	-1.47826900
H	-5.18144600	-0.15174500	-1.75339900
H	-4.89946800	-0.72120900	-0.09626300
C	-3.62108000	-0.67893300	2.25857400
H	-4.38906600	0.00879300	1.87397500
H	-3.73675400	-0.71494200	3.35606100
H	-3.83280300	-1.69119300	1.87753800
C	2.87490000	0.20344400	1.65528900
H	2.32970100	-0.69507500	1.98752200
H	3.94698000	0.01603800	1.85996500
C	2.40455500	1.42896200	2.43125200
H	1.34754500	1.66197100	2.22312800
H	3.00528300	2.32561900	2.21208100
H	2.49940000	1.22667000	3.50963300
C	4.91720800	1.46613100	-0.27490600
H	5.31913300	2.33951000	-0.81239000
H	5.40788400	0.57297300	-0.69192300
H	5.21691000	1.56611900	0.78019400

[Rh(PCN)(NO)(CH$_3$CN)][BArF] ***(4-BArF)***

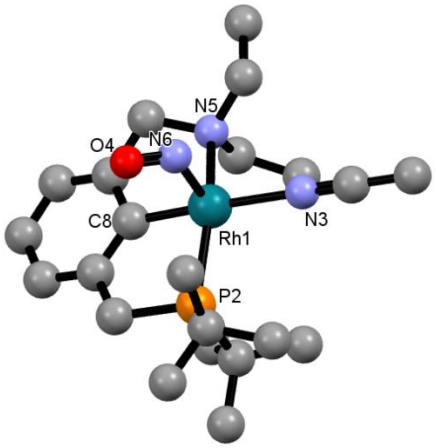


Figure S23. *DFT-optimized structure for* ***(4-BArF)****. Hydrogen atoms and the counteranion were omitted for clarity. Selected bond lengths (Å) and angles (deg.): Rh1-N6 1.926, N6-O4 1.180, Rh1-N6-O4 126.0.*

	X	Y	Z
Rh	-4.22022700	-0.36285900	0.13447400
P	-5.53543200	1.56007000	-0.15512200
N	-2.63555300	0.48146700	1.42001200
O	-3.44763800	-0.38008000	-2.54488600
N	-3.86008100	-2.53960900	0.71137900
N	-3.09298400	-0.47499400	-1.42332700
C	-5.72343100	-2.63274800	-0.90548300
C	-5.76088400	-1.22170000	-0.82055800
C	-1.80539800	0.91894200	2.12006000
C	-6.83806900	-0.51666000	-1.40451900
C	-4.46447700	-3.30732400	-0.42981900
H	-4.63848700	-4.36184700	-0.14298800
H	-3.70840800	-3.31294600	-1.23724200
C	-4.81085800	3.19303600	-0.85330000
C	-3.73469200	2.78526900	-1.88170100
H	-2.88240700	2.27614400	-1.41002400
H	-3.34731300	3.69717700	-2.36862000
H	-4.13086800	2.13428300	-2.67773800
C	-7.90442000	-1.22961500	-1.98223900
H	-8.74729400	-0.68574500	-2.42268400
C	-6.75798500	0.99034300	-1.44786700
H	-7.73641300	1.49070300	-1.34493600
H	-6.34405200	1.30837800	-2.42329800
C	-4.14505200	4.02603000	0.25920500
H	-4.88018900	4.48431900	0.93877800
H	-3.57217600	4.84601100	-0.20745500
H	-3.42858100	3.43550800	0.84849700
C	-6.58108500	1.85213600	1.42687400

C	-7.88947500	-2.63190100	-2.00824800
H	-8.72743100	-3.17776200	-2.45115100
C	-6.79550000	-3.33403800	-1.48279500
H	-6.77092000	-4.42815100	-1.53084800
C	-0.77924700	1.46236500	2.99170600
H	-0.76160100	2.56015400	2.91579000
H	0.20519300	1.06918300	2.68677200
H	-0.97022000	1.15141900	4.02984800
C	-5.64754800	2.06874300	2.63633200
H	-4.94704500	1.22755400	2.76065100
H	-6.26010400	2.13694300	3.55266600
H	-5.05707200	2.99280800	2.56112000
C	-7.40475100	0.56887400	1.67761300
H	-8.12549500	0.35706200	0.87297400
H	-7.97374400	0.69742400	2.61532300
H	-6.75972300	-0.31781900	1.79187400
C	-2.39744700	-2.84785800	0.84901300
H	-1.99766500	-2.19112100	1.63389200
H	-1.93406300	-2.53622400	-0.10039500
C	-5.88712200	4.03881500	-1.56828700
H	-6.32158100	3.51809200	-2.43594300
H	-5.40541500	4.95544000	-1.95154400
H	-6.70638200	4.35006700	-0.90476000
C	-7.54924900	3.04377000	1.29092100
H	-7.02343200	4.00821500	1.22905900
H	-8.19450300	3.07949400	2.18656400
H	-8.21207900	2.95101200	0.41516600
C	-4.63872000	-2.85952400	1.95188400
H	-5.69794800	-2.67662000	1.70406900
H	-4.54087400	-3.94482200	2.15001600
C	-4.23841600	-2.06839200	3.19278700
H	-4.36395300	-0.98415800	3.03900800
H	-3.19670000	-2.24849700	3.49803700
H	-4.89029100	-2.36682500	4.02958000
C	-2.04558100	-4.30793300	1.14695200
H	-0.95151500	-4.40967700	1.11886900
H	-2.44929800	-4.99709600	0.38990800
H	-2.38167700	-4.63149300	2.14455100
F	0.39996200	1.06440400	-4.81882700
F	0.72593300	-4.68742900	-0.80788000
F	7.34186500	-0.45396700	-4.53779000
F	0.73877900	-4.76085600	-2.99804800
F	5.48032800	0.70932700	-4.62910300
F	7.19611000	1.47366400	-3.50761900
F	-1.12196000	-4.30909900	-1.94127000

F	-1.22013500	1.39820400	-3.38991700
F	-1.04992500	3.28718900	0.20629700
F	-1.35072200	-0.25926700	-4.82461600
F	4.43263700	1.18329900	5.31107100
F	-0.26868900	4.52670300	1.83624600
F	0.15318400	-3.39948100	3.20648900
F	-0.29805800	5.31134000	-0.20298500
F	-0.80107600	-1.49642700	3.71212500
F	5.96283800	0.22599700	4.06899700
F	6.60437600	-4.33695600	-0.77118300
F	6.87477200	-3.25557300	1.11252800
F	4.58459800	6.12994500	-0.09481900
F	4.98873700	-0.89991600	5.68488300
C	2.75205700	-0.47599000	1.45730300
C	4.34267100	-0.47869400	-0.75016900
C	1.49002300	2.23351800	0.15234000
H	0.60701700	1.58694700	0.16527300
F	8.37822400	-3.08722100	-0.48038100
C	4.81988500	0.08236100	-1.95616100
H	4.24651400	0.87823600	-2.44349600
C	1.31112200	3.61755400	0.29177800
C	1.11298400	0.10143900	-2.11761700
H	1.31797200	1.17296800	-2.20646700
C	1.76670400	-0.64793900	-1.11711000
C	0.54716400	-2.61462900	-1.98040700
C	6.50370300	0.33720100	-3.81015100
C	3.69891700	-0.43847900	3.74193500
C	2.76199500	1.64562200	-0.03944200
C	0.24103700	-4.08651600	-1.92992800
C	2.41601100	4.48361800	0.26488400
H	2.29063800	5.56433600	0.35900100
C	3.77014500	-0.12130100	2.38012400
H	4.65200900	0.41607700	2.01736200
C	6.00548100	-0.35542500	-2.56765900
C	0.19464800	-0.47315700	-3.01621900
C	1.64564000	-1.15923800	2.00137200
H	0.82584900	-1.46166200	1.34045800
F	0.43535800	-2.53359800	5.19967100
C	-0.10345400	-1.83639400	-2.95300600
H	-0.82181600	-2.28260100	-3.64389000
C	2.59074400	-1.13219300	4.25439900
H	2.54001200	-1.39970300	5.31141000
C	6.29582600	-1.98163500	-0.81543200
C	5.11441800	-1.52737400	-0.20496600
H	4.79868400	-2.00727200	0.72610900

C	1.46736400	-2.03310400	-1.09498400
H	1.97128000	-2.68095200	-0.37108300
C	1.56525100	-1.48703500	3.37336800
C	3.85372500	2.53844900	-0.05846900
H	4.86495200	2.14859200	-0.21400800
C	-0.48862000	0.41891900	-4.01858700
C	3.68821600	3.92893000	0.09339300
C	6.75619100	-1.39377000	-2.00014700
H	7.67717600	-1.73797900	-2.47460000
F	5.80997000	4.46389400	-0.83522700
C	0.36686900	-2.23460700	3.88078300
C	-0.05878500	4.18585400	0.51641900
F	5.54602500	4.75508900	1.31618500
B	2.90258300	0.00372500	-0.11633600
C	4.77782400	0.01411700	4.69503100
C	7.03892600	-3.15780800	-0.23606200
C	4.90530100	4.82116600	0.11434300

$[Rh(PCN)(NO)(CH_3CN)]^{2+}$ ***(4^{2+})***

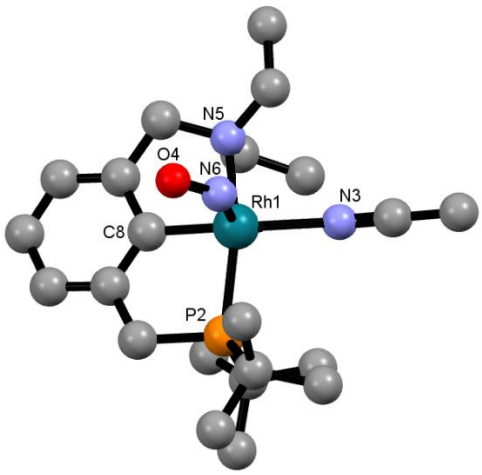


Figure S24. *DFT-optimized structure for* ***(4^{2+})****. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg.): Rh1-N6 1.881, N6-O4 1.171, Rh1-N6-O4 132.8.*

	X	Y	Z
Rh	0.46431300	0.29188600	-0.27464000
P	-1.84553200	-0.32590100	0.04933200
N	0.18421400	2.51804900	-0.10779400
O	0.72339000	-0.49901500	-2.95967800
N	2.67888700	0.29220000	0.15407000
N	0.53743500	0.33028600	-2.15400100
C	2.11019900	-2.07857600	-0.20287000
C	0.74381900	-1.65568200	-0.23199700
C	0.05599600	3.68165500	-0.10112900
C	-0.31818700	-2.61493300	-0.20063800

C	3.15347700	-1.01509200	-0.41395100
H	4.12777800	-1.29603600	0.02318100
H	3.31888600	-0.86920100	-1.49731600
C	-3.20485800	0.39288300	-1.09253000
C	-2.60304100	0.51749100	-2.50740900
H	-1.80041100	1.27095100	-2.55059500
H	-3.39991500	0.84860100	-3.19444500
H	-2.22335600	-0.43953200	-2.90241100
C	0.00489300	-3.96337700	-0.00482200
H	-0.78805800	-4.71448100	0.06184100
C	-1.73435400	-2.13754500	-0.38315000
H	-2.46410000	-2.73319700	0.19099700
H	-2.02617300	-2.23495700	-1.44594000
C	-3.64546400	1.78604600	-0.60471300
H	-4.18869700	1.74662200	0.35074500
H	-4.33595600	2.21258700	-1.35154200
H	-2.79486500	2.47943700	-0.50645100
C	-2.21841600	-0.23169900	1.92984000
C	1.35215700	-4.36531800	0.08717900
H	1.58774400	-5.42556900	0.21665600
C	2.40475200	-3.42811600	-0.00994100
H	3.44287400	-3.76832700	0.05269600
C	-0.09977900	5.12498700	-0.09018500
H	-1.16795500	5.39317200	-0.13302800
H	0.41256100	5.56600100	-0.96090800
H	0.33596700	5.54564100	0.83086600
C	-2.03961100	1.21783500	2.42671100
H	-1.01762400	1.59150900	2.25259500
H	-2.21777500	1.23450100	3.51523500
H	-2.74791300	1.92127200	1.96804900
C	-1.19906900	-1.13758200	2.65335600
H	-1.27835400	-2.19755500	2.36701000
H	-1.39474400	-1.07615300	3.73728600
H	-0.15791200	-0.81092000	2.48901100
C	3.38280900	1.45810000	-0.49497000
H	2.89542600	2.36970900	-0.11964200
H	3.15596500	1.39192000	-1.57216700
C	-4.41513000	-0.56979500	-1.14043900
H	-4.16137200	-1.55798900	-1.55420900
H	-5.16668000	-0.12682200	-1.81612700
H	-4.89822900	-0.71043800	-0.16409800
C	-3.64843300	-0.72797700	2.22776700
H	-4.42096300	-0.04872800	1.83931100
H	-3.77373200	-0.76655900	3.32376000
H	-3.84234500	-1.74366000	1.84724900

C	2.86643300	0.25818300	1.65330600
H	2.34858300	-0.64745500	2.00982300
H	3.94315500	0.10425200	1.85076800
C	2.37020800	1.48929900	2.40096100
H	1.30016000	1.68622100	2.22277100
H	2.93710100	2.39753400	2.14595100
H	2.50082500	1.31791600	3.48079100
C	4.89556000	1.52491900	-0.27511700
H	5.28687800	2.38394700	-0.84247500
H	5.41916600	0.63018400	-0.64574200
H	5.16830700	1.68338200	0.77928400

*[Rh(PCN)(NO)]• **(3•)***

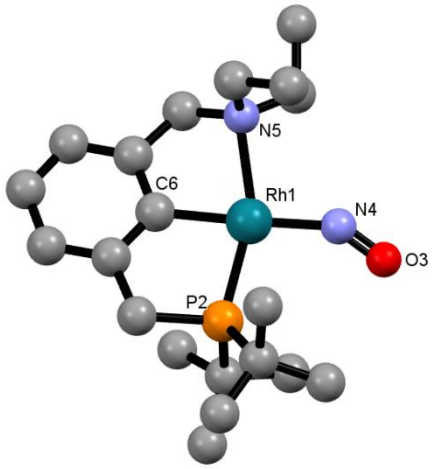


Figure S25. *DFT-optimized structure for **(3•)**. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg.): Rh1-N4 1.923, N4-O3 1.205, Rh1-N4-O3 147.2.*

	X	Y	Z
Rh	-0.45836900	-0.53552800	0.04541300
P	1.70661000	0.09886900	-0.09892600
O	0.40484700	-3.27526400	0.93729100
N	-0.31241900	-2.38196100	0.56288000
N	-2.76874400	-0.45248100	0.08533200
C	-0.75842400	1.46057900	-0.14457100
C	-2.06965800	1.93118200	0.11018800
C	-2.38617100	3.29001900	-0.04850600
H	-3.40433500	3.65057300	0.14102300
C	-1.38719200	4.19506600	-0.44401300
H	-1.63039600	5.25575100	-0.56278800
C	-0.08050900	3.74762400	-0.69417700
H	0.68763800	4.46477500	-1.00631500
C	0.23597100	2.38339000	-0.55328600
C	1.61411700	1.82917300	-0.84403600
H	2.43062600	2.48351700	-0.48855400

H	1.75909900	1.71603200	-1.93398600
C	2.84217700	-0.85213600	-1.32263300
C	1.94030900	-1.17723500	-2.53512500
H	1.06715700	-1.77621400	-2.23050200
H	2.52426900	-1.74845000	-3.27993200
H	1.56450700	-0.26706700	-3.03237200
C	3.31468500	-2.17789000	-0.69417600
H	3.80387700	-2.79239800	-1.47183800
H	2.47708300	-2.76062300	-0.27792100
H	4.05502200	-2.01456000	0.10504900
C	4.05893300	-0.04118600	-1.81278200
H	3.76619900	0.90381100	-2.29806300
H	4.60298300	-0.63800500	-2.56769300
H	4.77020000	0.19377600	-1.00807800
C	2.56451700	0.37354400	1.59914200
C	4.04340800	0.78841400	1.49911800
H	4.68118800	-0.02617700	1.12131300
H	4.41320500	1.04929200	2.50754600
H	4.19159600	1.67459700	0.85890900
C	1.77189300	1.49223200	2.31080400
H	1.86861400	2.46772400	1.80812400
H	2.16193600	1.60376000	3.33875100
H	0.69954000	1.24548200	2.36652000
C	2.43029100	-0.91292500	2.43898000
H	1.37405300	-1.20787700	2.53627300
H	2.83503600	-0.72735200	3.45062600
H	2.97954100	-1.76368300	2.00906900
C	-3.06680100	0.91594600	0.62010200
H	-4.11025200	1.21482200	0.38754600
H	-2.98831400	0.84693900	1.72061900
C	-3.26302100	-0.53798000	-1.32141300
H	-2.79908500	0.30747800	-1.85442200
H	-4.36065500	-0.37005900	-1.33894900
C	-2.91642900	-1.84463500	-2.02895400
H	-3.41763300	-2.71608400	-1.57766900
H	-1.82749600	-2.01721200	-2.00176100
H	-3.23667600	-1.78468200	-3.08181400
C	-3.34094100	-1.51018300	0.96951500
H	-2.89160400	-1.34821800	1.96379600
H	-2.94778000	-2.47643300	0.61658300
C	-4.87040000	-1.55802600	1.08166300
H	-5.15390000	-2.33965800	1.80509500
H	-5.35442600	-1.80806200	0.12400200
H	-5.29453800	-0.60644200	1.44128700

Experimental Section

Reaction of [Rh(PCN)(H)(Cl)] (1) with Diazald®. Formation of [Rh(PCN)(NO)(Cl)] (2). Reaction of **(1)** with potassium tert-butoxide yielding dehydrochlorination product [Rh(PCN)(N_2)] followed by nitrosylation with $NOBF_4$ in THF was also tested, but instead of obtaining the expected product $[Rh(PCN)(NO)]^+$, complex **(2)** was found to be the main product, presumably because of considerable amounts of chloride remaining in solution after reaction with KOtBu. A few attempts at accomplishing nitrosylation via reaction of **(1)** with isoamyl nitrite and mild heating were also carried out but in this case conversion was scarce and prolonging of reaction times only resulted in decomposition of **(1)**. Therefore, for the final synthesis pathway the Diazald® reaction was chosen for having the best yield.