Supporting Information

Novel Heteroleptic NHC Rhodium Complexes with Pyridine-Derived Ligands: Synthetic Accessibility and Reactivity Towards Oxygen.

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Table S1: Crystallographic data for compounds **2**, **3-6,** and **10**.

Complex	**2**	**3**	**5**	**6**	**7**	**8•2 Cl**
Formula	$C_{70} H_{100} Cl_2 N_4 Rh_2$	$C_{36} H_{49} Cl N_3 Rh$	$C_{43} H_{50} Cl N_4 Rh$	$C_{48} H_{53} Cl N_4 Rh$	$C_{35.25} H_{49.25} Cl N_4 Rh$	$C_{54.15} H_{67.15} Cl_3 N_6 Rh$
Fw	1274.26	662.14	761.23	824.30	667.40	1011.35
Crystal dimensions (mm^3)	0.10 x 0.08 x 0.08	0.30 x 0.25 x 0.25	0.30 x 0.20 x 0.10	0.33 x 0.30 x 0.15	0.20 x 0.06 x 0.04	0.10 x 0.08 x 0.06
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	*P*-1	*C*2/c	*P*-1	*P*2(1)/*n*	*P*-1	*P*-1
a (Å)	12.4202(2)	36.8292(4)	10.6065(2)	10.6281(2)	10.7301(16)	12.5027(4)
b (Å)	12.5006(2)	10.36610(10)	12.9410(2)	11.9529(2)	17.553(3)	20.8414(6)
c (Å)	13.7005(2)	19.8406(2)	15.3621(2)	33.2439(5)	20.621(3)	21.4998(6)
V ($Å^3$)	1643.31(4)	6772.56(12)	1922.18(5)	4178.35(12)	3492.6(9)	5299.7(3)
Z	1	8	2	4	4	4
T (K)	293(2) K	180(2)	180(2)	180(2)	180(2)	180(2)
D_{calcd} (g cm^{-3})	1.288	1.299	1.315	1.310	1.269	1.268
μ (mm^{-1})	0.626	0.611	0.549	0.510	0.594	0.514
F (000)	672	2784	796	1724	1403	2120
θ range (deg)	1.68 - 26.00°.	2.49 - 26.00	3.44 -26.00	1.95- 26.00	1.29- 26.00	1.54 to 26.00
Index ranges (*h, k, l*)	±15, ±15, -16-15	-45-38, -12-8, -23-24	-13-12, -15-12, ±18	±13, -14-12, -41-40	±13, -19-21, 0-25	±15, ±25, ±26

No. of rflns collected	18399	12449	14674	34993	13703	53751
No. of independent rflns/R_{int}	6350	6613 /0.0115	7498 / 0.0224	8185/ 0.0184	13703/0.0976	20736 /0.0810
No. data/restraints/params	6350 / 8 / 350	6613 / 0 / 396	7498 / 30 / 455	8185 / 36 / 527	13703 / 0 / 703	20736 / 198 / 1111
R1/wR2 ($I > 2\sigma(I)$)	0.0324/0.0787	0.0207/0.0526	0.0325/0.0761	0.0300/0.0659	0.0708/ 0.1464	0.0636/0.1364
R1/wR2 (all data)	0.0391/0.0830	0.0236/ 0.0551	0.0405/0.0806	0.0316/0.0666	0.1350/ 0.1647	0.1290/0.1643
GOF (on F^2)	1.034	1.044	1.052	1.227	0.989	1.018
largest diff peak/hole (e Å^{-3})	0.612 / -0.686	0.305 / -0.276	1.531/ -0.534	0.279/ -0.603	0.789/ -0.973	0.791/ -0.803

Table S2: Week non-covalent van-der Waals type of interactions in complex **8•2BF$_4$**

Atoms	Bond length, Å	% van der Waals radii
H(10C)-Cl(4)	2.240	75.93
H(12D)-Cl(4)	2.369	80.30
H(10B)-Cl(6)	2.386	80.88
H(3A)-Cl(6)	2.534	85.90
H(64A)-Cl(6)	2.808	95.18
H(68A)-Cl(4)	2.850	96.61
H(93A)-Cl(4)	2.8555	96.78
H(49A)-Cl(6)	2.876	97.40
H(72A)-Cl(4)	2.880	97.63
H(93A)-Cl(4)	2.8555	96.78
H(72B)-Cl(6)	2.887	97.86
H(70A)-Cl(2)	2.857	96.84

Experimental aspects of the crystallography:

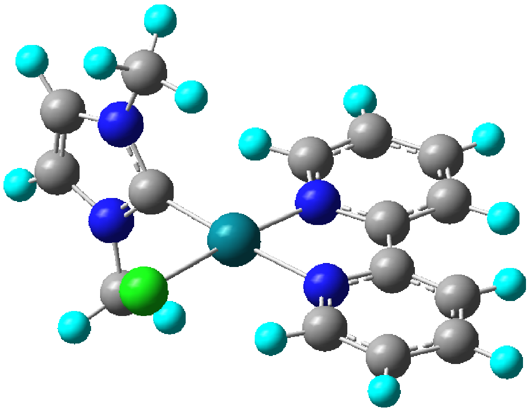
Data collection and processing: Crystals were mounted on a glass fiber with grease and cooled to -93 °C in a stream of nitrogen gas controlled with Cryostream Controller 700. Data collection was performed on a Bruker SMART APEX II X-ray diffractometer with graphite-monochromated Mo K$_{\square}$ radiation (λ = 0.71073 Å), operating at 50 kV and 30 mA. Data were processed on a PC using the Bruker AXS Crystal Structure Analysis Package:[1] Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT (Bruker, 2005); structure solution: XPREP (Bruker, 2005) and SHELXTL (Bruker, 2000); structure refinement: SHELXTL; molecular graphics: SHELXTL; publication materials: SHELXTL. Neutral atom scattering factors were taken from Cromer and Waber.[2]

Solution and refinement: All structures were solved by direct methods. Full-matrix least-square refinements minimizing the function $\sum w\, (F_o^2 - F_c^2)^2$ were applied to the compounds. All non-hydrogen atoms were refined anisotropically. All H atoms were placed in geometrically calculated positions, with C-H = 0.95 (aromatic), 0.99 Å (CH_2) and 0.98 Å (CH_3), and refined as riding atoms, with Uiso(H) = 1.5 UeqC(methyl), or 1.2 Ueq(other C).

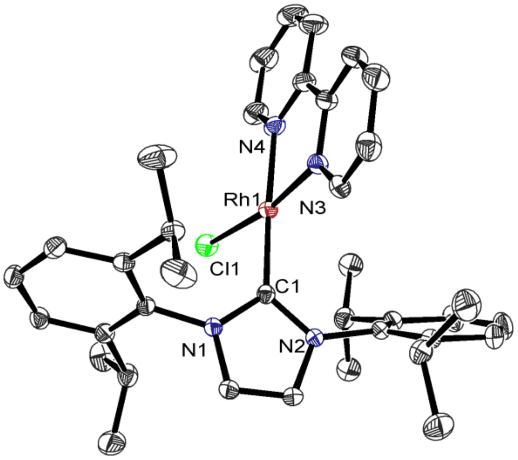
For complex **4** (cc110): The H atoms on ethylene were located from difference Fourier maps and refined without any restraints. For complex **5**: (cc119): One of the isopropyl groups is disordered with its two methyl groups. The two methyl groups were thus split into 3 groups. SHELX commands, SUMP, PART, SADI and EADP were applied to refine the disorder. For complex **6** (cc94): The methyl groups were refined with AFIX 137, which allowed the rotation of the methyl groups whilst keeping the C-H distances and X-C-H angles fixed. One of the solvent benzene molecules is disordered. SHELX commands, PART, AFIX and SAME were applied to resolve the disorder. For complex **8** (cc126:) All non-hydrogen atoms were refined anisotropically, except some of them in the solvent molecules. All H atoms were placed in geometrically calculated positions, with C-H = 0.95 (aromatic), and 0.99 Å (CH_2), and refined as riding atoms, with Uiso(H) = 1.2 Ueq C or N. Some of the solvent benzene molecules are disordered. SHELX commands, DFIX, EADP and SAME were applied to resolve the disorder.

Computational Details:

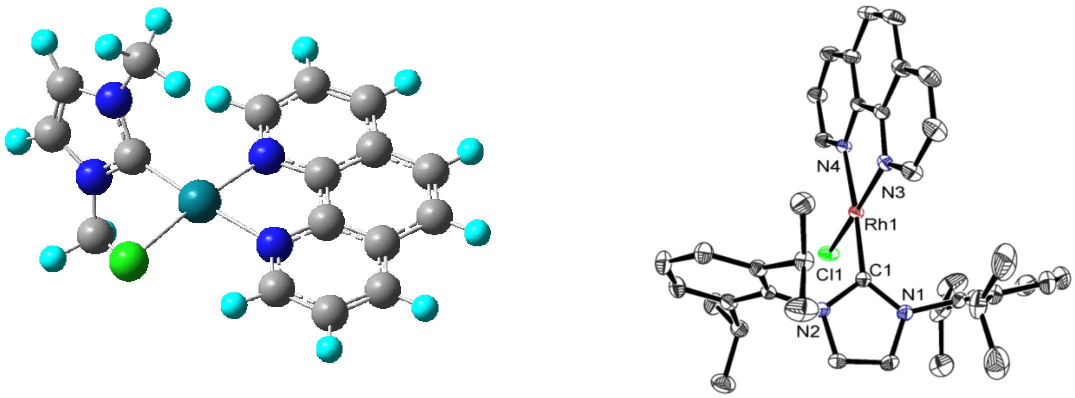
General Considerations: All calculations were performed using density functional theory with the CAM-B3LYP exchange-correlation functional. The Rh atom was treated with the LANL2DZ effective core potential basis set. All other atoms (C, H, N, and Cl) were treated with the 6-31G(d,p) basis set. The Polarizable Continuum Model (PCM) was used to simulate solvent effects. For computational simplicity, the IPr ligand was replaced with IMe (IMe = *N,N'*-bis(methyl)imidazol-2-ylidene). Optimized geometries are in good correlation with the experimentally determined X-ray structures reported herein.



$\mathbf{5}^{\mathbf{IMe}}$



$\mathbf{5}^{\mathbf{IPr}}$



6^{IMe} **6^{IPr}**

Figure S1. Calculated and experimentally determined structures of complexes **5** and **6**.

Table S3: Relevant bond lengths of complexes **5^{IMe}, 5^{IPr}**, **6^{IMe}** and **6^{IPr}** for comparison.

Bond lengths (Å)	**Calculated (5^{IMe})**	**Experimental (5^{IPr})**	**Calculated (6^{IMe})**	**Experimental (6^{IPr})**
Rh(1)-Cl(1)	2.438	2.3530(7)	2.433	2.3480(5)
Rh(1)-N(3)	2.044	1.990(2)	2.052	2.0085(16)
Rh(1)-N(4)	2.105	2.063(2)	2.118	2.0729(16)
Rh(1)-C(1)	2.019	1.986(2)	2.014	1.9896(19)
C(1)-N(1)	1.359	1.375(3)	1.361	1.382(2)
C(1)-N(2)	1.359	1.377(3)	1.358	1.378(3)

Table S4: Relevant bond angles of complexes **5^{IMe}, 5^{IPr}**, **6^{IMe}** and **6^{IPr}** for comparison.

Angles (°)	**Calculated (5^{IMe})**	**Experimental (5^{IPr})**	Calculated (6^{IMe})	Experimental (6^{IPr})
N(1)-C(3)-C(4)-N(2)	**0.00**	**0.90**	**0.07**	**0.56**
Cl(1)-Rh(1)-C(1)	**89.41**	89.45(7)	**90.19**	88.28(5)
C(1)-Rh(1)-N(3)	**97.12**	98.50(9)	**96.48**	101.92(7)
N(4)-Rh(1)-Cl(1)	**94.87**	92.65(7)	**93.91**	89.94(5)