Supplementary Material (ESI) for New Journal of Chemistry

Supplementary Information for

Iminophosphorane based [P_2N_2] rhodium complexes: synthesis, reactivity, and a catalytic application.

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Table S1. Crystal data and structural refinement details for complexes **2_BF4** and **3_cl**

Compound	**2_BF_4**	**3_Cl**
Molecular formula	$C_{52}H_{48}N_2P_4Rh,_2(CH_2Cl_2),BF_4$	$C_{52}H_{48}Cl_2N_2P_4Rh,Cl,C_2H_3N$
Molecular weight	1184.38	1221.55
Crystal habit	Pale Yellow Block	Orange Needle
Crystal dimensions(mm)	0.20x0.14x0.06	0.32x0.04x0.04
Crystal system	orthorhombic	orthorombic
Space group	$P2_12_12_1$	$P2_12_12$
a(Å)	12.299(1)	19.416(1)
b(Å)	19.674(1)	24.922(1)
c(Å)	22.075(1)	10.803(1)
α(°)	90.00	90.00
β(°)	90.00	90.00
γ(°)	90.00	90.00
V($Å^3$)	5341.5(6)	5227.4(6)
Z	4	4
d($g\text{-}cm^{-3}$)	1.473	1.552
F(000)	2416	2504
μ(cm^{-1})	0.692	0.799
Absorption corrections	multi-scan ; 0.8739 min, 0.9596 max	multi-scan ; 0.7841 min, 0.9687 max
λ(Å)	0.71069	0.71069
Monochromator	graphite	graphite
T (K)	150.0(1)	150.0(1)
Scan mode	phi and omega scans	phi and omega scans
Maximum θ	30.02	25.01
HKL ranges	-17 10 ; -27 26 ; -22 31	-22 22 ; -29 29 ; -12 12
Reflections measured	36847	8882
Unique data	15419	8882
Rint	0.0429	0.1246
Reflections used	12655	5203
Criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Refinement type	Fsqd	Fsqd
Hydrogen atoms	constr	mixed
Parameters refined	631	560
Reflections / parameter	20	9
wR2	0.0777	0.1394
R1	0.0354	0.0610
Flack's parameter	-0.045(15)	-0.10(5)
Weights a, b	0.0328 ; 0.0000	0.0595 ; 0.0000
GoF	0.993	0.931
difference peak / hole (e $Å^{-3}$)	0.680(0.066) / -0.679(0.066	0.842(0.106) / -0.426(0.106)
CCDC number	772852	772854

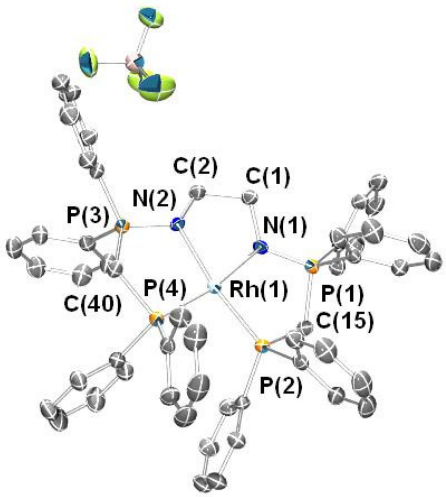

Figure S1. Molecular structure of complex **2_BF$_4$**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (◦): P2–Rh1 2.1937(6), N1–Rh1 2.091(2), N2–Rh1 2.095(2), P4–Rh1 2.1911(5), Rh1–B1 10.661, P1–N1 1.606(2), P3–N2 1.610(2), P1–C15 1.803(2), P2–C15 1.875(2), P3–C40 1.802(2), P4–C40 1.882(2); P4–Rh1–P2 100.28(2), N1–Rh1–N2 80.55(7), P4–Rh1–N2 89.78(5), P2–Rh1–N1 89.41(5), P1-N1-Rh1 117.6(1), P1–C15–P2 106.6(1), C15-P2-Rh1 104.80(7), C40-P4-Rh1 105.35(7), P4–C40–P3 107.5(1), N(2)-P(3)-C(40) 105.0(1), P3-N2-Rh1 117.2(1), N1–P2–P4–N2 -0.83(3), P1–P2–P4–P3 15.21(2), P2–N1–N2–P4 1.03(4), P2–P1–P3–P4 8.85(2).

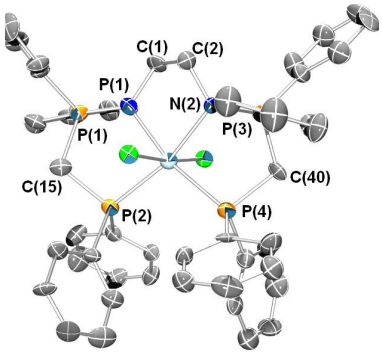

Figure S2. Molecular structure of complex **3_BF$_4$**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (◦):P2–Rh1 2.291(2), N1–Rh1 2.087(7), N2–Rh1 2.102(6), P4–Rh1 2.308(2), Rh1–Cl1 2.351(2), Rh1–Cl2 2.362(2), Rh1–Cl3 6.604, P1–N1 1.593(8), P3–N2 1.578(7), P1–C15 1.787(8), P2–C15 1.88(1), P3–C40 1.794(8), P4–C40 1.840(8); P4–Rh1–P2 105.66(8), N1–Rh1–N2 80.9(3), P4–Rh1–N2 86.9(2), P2–Rh1–N1 86.9(2), Cl1–Rh1–Cl2 173.56(8), Cl1–Rh1–P2 86.55(8), Cl1–Rh1–P4 96.34(8), Cl1–Rh1–N2 87.4(2), Cl1–Rh1–N1 87.0(2), Cl2–Rh1–P2 96.12(8), Cl2–Rh1–P4 88.60(8), Cl2–Rh1–N2 88.8(2), Cl2–Rh1–N1 87.3(2), P(3)-N(2)-Rh(1) 121.8(3); N(2)-P(3)-C(40) 104.2(4); C(40)-P(4)-Rh(1) 100.6(3); C(15)-P(2)-Rh(1) 101.9(3); N(1)-P(1)-C(15) 105.5(4); P(1)-N(1)-Rh(1) 122.8(4), P1–C15–P2 109.0(5), P4–C40–P3 109.6(4), N1–P2–P4–N2 5.31(17), P1–P2–P4–P3 5.40(11), P2–N1–N2–P4 7.16(44), P2–P1–P3–P4 3.39(9).