Supplementary Material (ESI) for Dalton Transactions

Supplementary Information

Synthesis of η^2-Cyclooctene Iridium and Rhodium Complexes Supported by a Novel P,N-Chelate Ligand and Their Reactivity toward Hydrosilanes: Facile Cl Migration from Metal to Silicon via Silylene Complex Intermediates and Formation of a Base-Stabilised Silylene Complex

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1. The details of X-ray crystal structure analysis of 1, 3·C_7H_8, 5, 7·C_7H_8, 8·C_7H_8, 9, 10·C_7H_8, 11·0.5C_4H_8O and 12·CH_2Cl_2·C_5H_{12}

One molecule of toluene was found in the asymmetric unit cell for **3**, **7**, **8** and **10**. One half molecule of THF for **11** and one molecule each of CH_2Cl_2 and pentane for **12** were found in their asymmetric unit cell. For **1**, all non-hydrogen atoms except two carbon atoms of a cyclohexyl group were refined anisotropically, while all hydrogen atoms were placed in their geometrically calculated positions and fixed. The two carbon atoms (C26, C27) were disordered in two positions with occupancy factors 73% and 27% and refined isotropically. For **3**, all non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were placed in their geometrically calculated positions and fixed. For **5**, because of low quality of the crystal, all carbon and nitrogen atoms had to be refined with isotropic thermal parameters and other non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in their calculated positions and fixed. Although a "checkCIF report" for **5** suggests the existence of some problems concerning to solvents, we could not solve them because any solvents could not be found properly. We also tried to get better crystals by repeated recrystallisation for many times but have never succeeded. For **7**, one of cyclohexyl ligands was disordered in two positions with occupancy factors of 52% and 48%. Non-hydrogen atoms except C1 and the disordered carbon atoms (C15 ~ C24) were refined anisotropically and the hydrogen atoms except IrH were placed in their calculated positions and fixed. The hydrogen atom of IrH was not found. For **8**, all non-hydrogen atoms were refined anisotropically while hydrogen atoms except IrH were placed in their calculated positions and fixed. The hydrogen atom (H1) of IrH was found from the Fourier-difference electron-density and refined isotropically. For **9**, all non-hydrogen atoms except C22 were refined anisotropically and the C22 atom was refined isotropically. The three hydrogen atoms of IrH_3 was not found and not analysed. The hydrogen atoms except IrH_3 were placed in their calculated positions and fixed. For **10**, the carbon atoms of C22 and Cl1 were disordered in two positions with occupancy factors of 59% and 41%. Non-hydrogen atoms except the disordered atoms and the carbon atoms of toluene were refined with anisotropic thermal parameters. The hydrogen atom (H1) of RhH was found from the Fourier-difference electron-density and refined isotropically. The hydrogen atoms on toluene and disordered carbon atoms were not analysed. The other hydrogen atoms were placed in calculated positions and fixed. For **11**, non-hydrogen atoms except oxygen and carbon atoms of THF were refined with anisotropic thermal parameters. Oxygen and carbon atoms of THF were refined with isotropic thermal parameters. The hydrogen atoms of SiH and IrH, which were not found, and hydrogen atoms of THF were not analysed. The other hydrogen atoms were placed in their calculated positions and fixed. For **12**, non-hydrogen atoms except some of carbon atoms of pentane were refined with anisotropic thermal parameters. Some of carbon atoms (C45 ~ C49) were refined isotropically. The hydrogen atom (H1) of IrH was found from the Fourier-difference electron-density and refined isotropically, while the two hydrogen atoms of SiH_2 were not found. The other hydrogen atoms were placed in their calculated positions and fixed.

2. X-ray crystal structure analysis of $P^{cy}N$, **2** and **4**·C_7H_8

Table S1. Crystallographic Data for Complexes $P^{cy}N$, **2** and **4**·C_7H_8

	$P^{cy}N$	**2**	**4**·C_7H_8
Formula	$C_{21}H_{34}NP$	$C_{29}H_{48}ClNPRh$	$C_{39}H_{49}ClIrNP_2$·C_7H_8
Fw	331.46	580.01	913.52
T, K	150(2)	150(2)	150(2)
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a, Å	9.2587(4)	9.6574(8)	16.4500(6)
b, Å	11.4129(4)	11.9410(8)	10.3053(3)
c, Å	18.1566(8)	13.8776(11)	24.0221(10)
α, deg	89.9315(9)	105.204(3)	
β, deg	91.1041(13)	108.539(3)	93.5386(16)
γ, deg	90.0392(13)	98.699(4)	
Z	4	2	4
V, Å^3	1918.23(14)	1422.23(17)	4064.5(3)
ρ, Mg/m^3	1.148	1.361	1.493
μ, mm^{-1}	0.144	0.772	3.462
Crystal size, mm^3	0.19 × 0.18 × 0.13	0.10 × 0.09 × 0.09	0.20 × 0.18 × 0.15
2*θ* range, deg	2.11 – 27.46	1.64 – 27.45	1.24 – 27.41
F(000)	728	612	1856
no. of unique data	4309	6414	8906
no. of data with $I > 2\sigma(I)$	3732	4762	5572
no. of params	211	300	439
GOF on F^2	1.201	1.232	1.193
*R*1, *wR*2 [$I > 2\sigma(I)$]	0.0716, 0.1483	0.1091, 0.2206	0.0637, 0.1440
*R*1, *wR*2 (all data)	0.0864, 0.1566	0.1519, 0.2450	0.0835, 0.1611

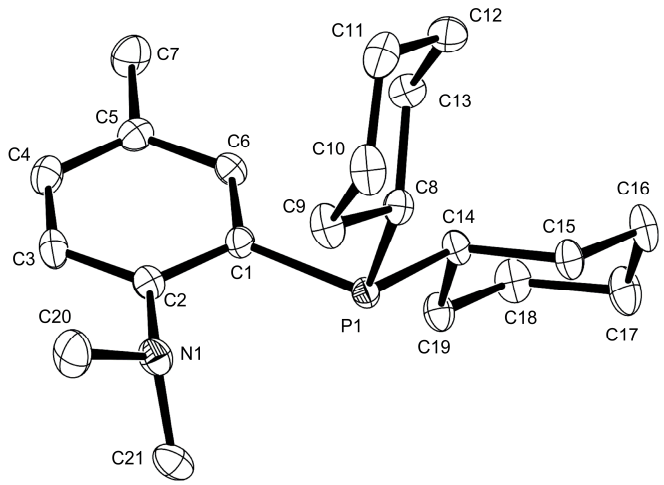

Figure S1. ORTEP view of $P^{cy}N$.

Table S2. Selected bond lengths (Å) and angles (deg) for $P^{cy}N$

P1–C1	1.858(2)	P1–C8	1.866(3)	P1–C14	1.859(3)
N1–C2	1.438(3)	N1–C20	1.450(3)	N1–C21	1.462(3)
C1–P1–C8	104.07(11)	C8–P1–C14	102.23(11)	C14–P1–C1	102.31(11)
C2–N1–C20	115.5(2)	C20–N1–C21	111.0(2)	C21–N1–C2	113.6(2)
P1–C1–C2–N1	3.7(3)				

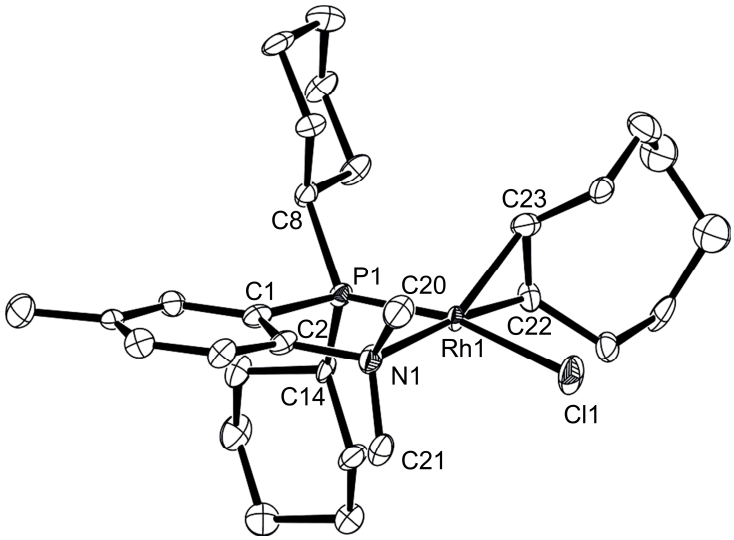

Figure S2. ORTEP view of (P^{cy}N-*P*,*N*)RhCl(η^2-coe) (**2**).

Table S3. Selected bond lengths (Å) and angles (deg) for **2**

Rh1–P1	2.193(2)	Rh1–N1	2.200(9)	Rh1–Cl1	2.449(3)
Rh1–C22	2.140(10)	Rh1–C23	2.106(10)	C22–C23	1.400(14)
P1–Rh1–N1	84.5(2)	N1–Rh1–Cl1	88.3(2)	Cl1–Rh1–C22	94.4(3)
C22–Rh1–P1	91.0(3)	Cl1–Rh1–C23	95.6(3)	C23–Rh1–P1	95.6(3)
C22–Rh1–C23	38.5(4)				

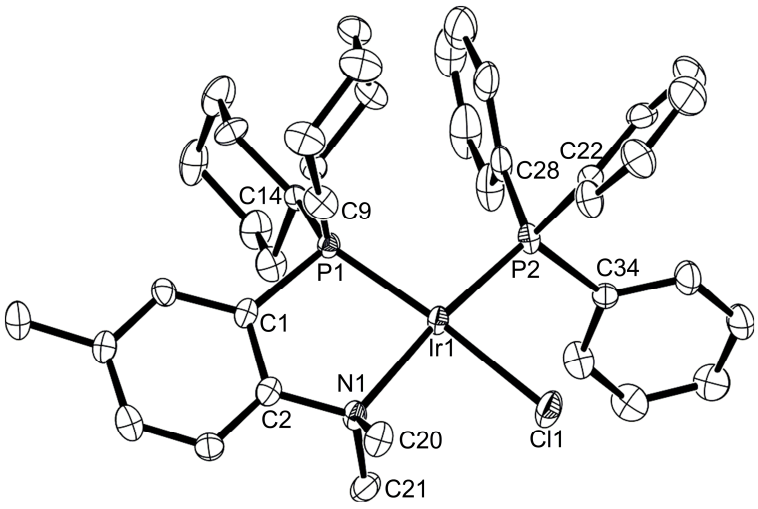

Figure S3. ORTEP view of (P^{cy}N-*P*,*N*)IrCl(PPh_3) (**4**)·C_7H_8.

Table S4. Selected bond lengths (Å) and angles (deg) for **4**·C_7H_8

Ir1–P1	2.192(2)	Ir1–P2	2.221(2)	Ir1–N1	2.215(6)
Ir1–Cl1	2.412(2)				
P1–Ir1–N1	84.4(2)	N1–Ir1–Cl	187.8(2)	Cl1–Ir1–P2	87.49(7)
P2–Ir1–P1	101.25(7)				