Electronic Supplementary Material (ESI) for RSC Advances

Supplementary Information for

C(Naphthyl)-H Bond Activation by Rhodium: Isolation, Characterization and TD-DFT Study of the Cyclometallates

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Supplementary Information S1

Crystal Structure of 2a

The compound **2a** was found to be crystallized in monoclinic form with C2/c space group at room temperature. The structure was found to be disordered. We tried to solve the structure in lower symmetry space group such as C2 in anticipation of seeing two ordered molecules related by a screw. But we could not solve it in the C2 space group and hence failed to get rid of the disorder.

Crystal Structure of 3a & *intra-/intermolecular interaction in solid state*

The crystal packing arrangement of (**3a**) (Figure S1) has been found to be stabililized by two intermolecular C-H…π interaction C48-H48A···Cg4 [where Cg4 is the centroid of the C5—C9 ring at -x,-1/2+y,1/2-z] and C54-H54A···Cg10 [where Cg10 is the centroid of the C39—C44 ring at x,1/2-y,-1/2+z] (Figure S2, Table S2). There are no aromatic π···π interactions in the crystal structure of **3a**. However five intra-molecular H bonding interactions are there (Table S3).

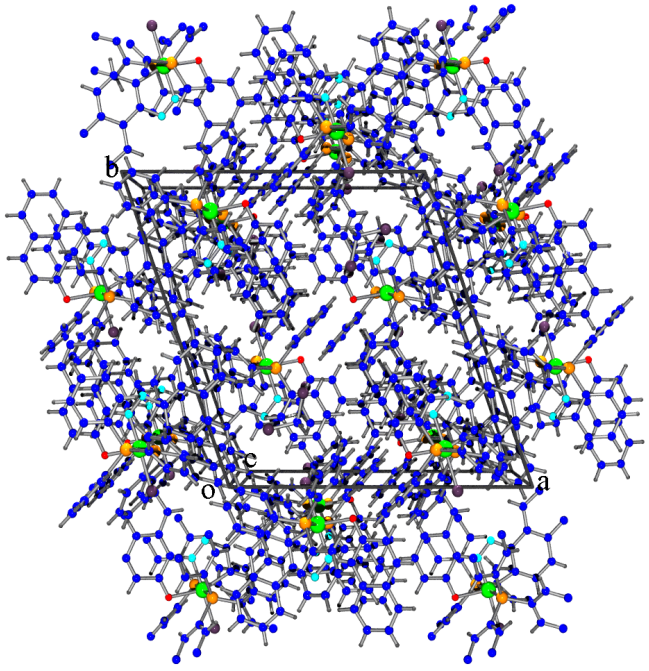


Figure S1 Packing arrangement in **3a**.

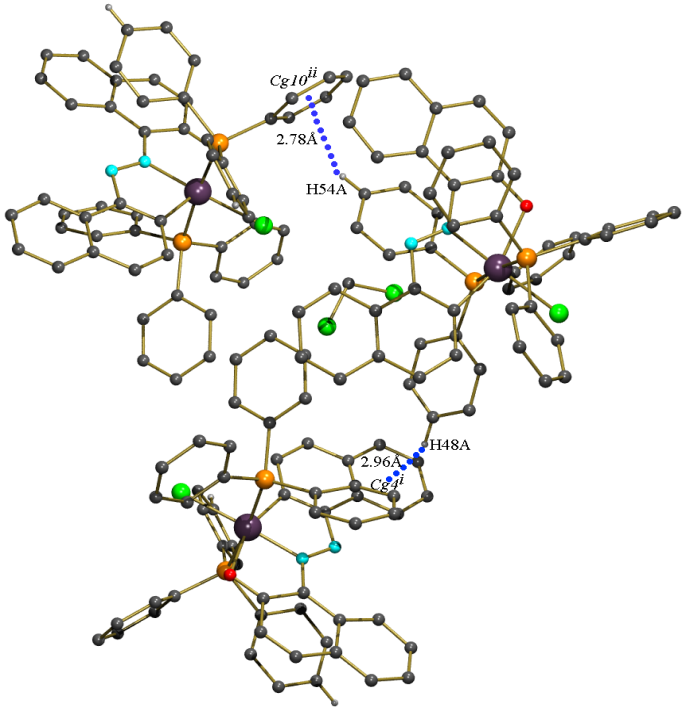


Figure S2 Intermolecular C-H… π interaction in **3a**. Symmetry code: (i) -x,-1/2+y,1/2-z; (ii) x,1/2-y,-1/2+z . Cg(4) and Cg(4) are the centroids of C5-C9 and C39-C44 rings respectively.

Crystal Structure of* 4a & *intra- /intermolecular interaction in solid state

The crystal packing of **4a** (Figure S3) is found to be stabilized by an intermolecular C-H… π interaction C50-H50A···Cg6 [where Cg6 is the centroid of the C18—C23 ring at 1-x, 1-y, 1-z.] (Figure S4a). Moreover there are two intra-molecular π···π interactions involving the aryl ring C5-C10 and two phenyl rings of two triphenyl phosphine moieties. The centroid-centroid distances are 3.954(3) & 3.779 (3) Å with no slippages (Table S1, Figure S4b).

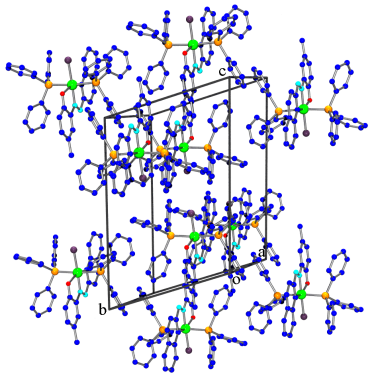
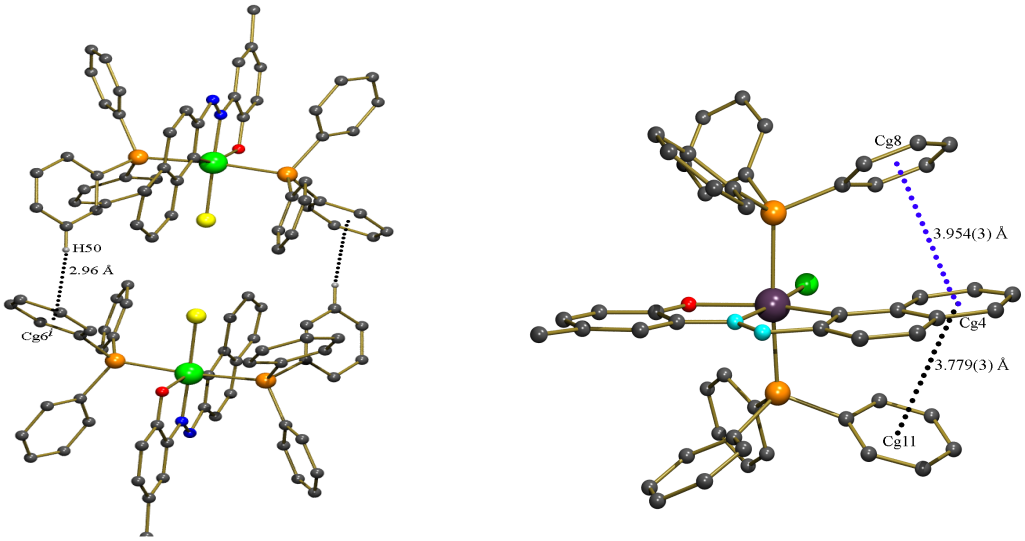


Figure S3 Packing arrangement in **4a**.



(a) **(b)**

Figure S4 (a) Intermolecular C-H… π interaction in **4a**. Symmetry code: (i) 1-x, 1-y, 1-z. Cg(6) is the centroid of C18-C23 ring; (b) Intramolecular π···π interactions in **4a**. Cg(4), Cg(8) and Cg(11) are the centroids of C5-C9, C30-C35 and C48-C53 rings respectively.

Crystal Structure of* 4b & *intra- /intermolecular interaction in solid state

The crystal packing in **4b** (Figure S5) has also been found to be stabilized by two intermolecular C-H… π interactions; C26-H26···Cg8 [where Cg8 is the centroid of the C30—C35 ring at -x,1-y,-z] and C38-H38···Cg7 [where Cg7 is the centroid of the C24—C29 ring at 1-x,1-y,-z] (Figure S6). These intermolecular C-H… π interactions arrange the molecules in parallel fashion. There is an intra-molecular π···π interactions involving the aryl rings C1-C9 and C30-C35. The centroid-centroid distance is 3.815(3) Å and the corresponding perpendicular distance is 3.653 Å with no slippage. Geometric parameters of all the interactions are compiled in Table S1- S3.

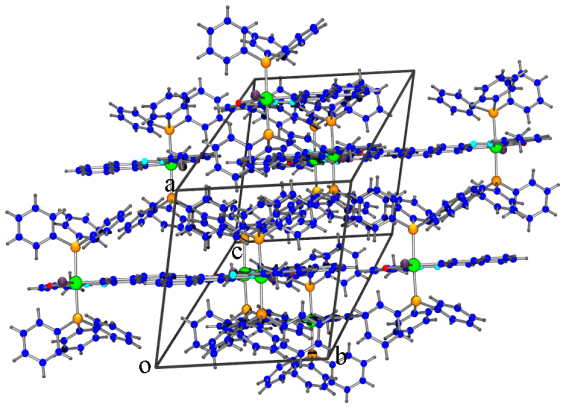


Figure S5 Packing arrangement in the cyclometallate **4b**.

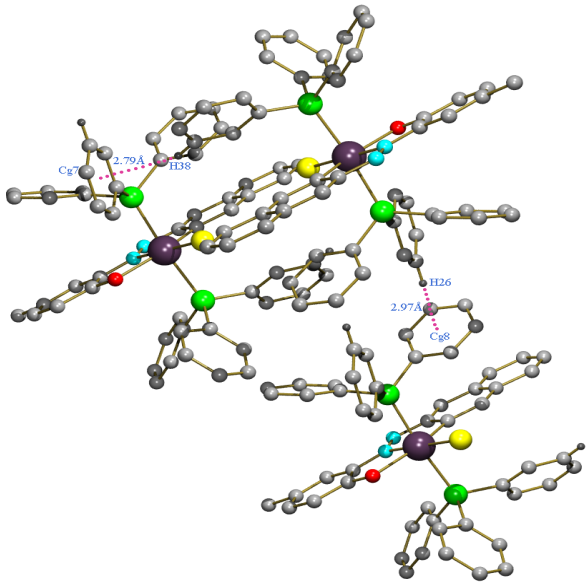


Figure S6 Intermolecular C-H… π interactions in **4b**. Symmetry code: (i) -x, 1-y,-z; (ii) 1-x,1-y,-z . Cg(8) and Cg(7) are the centroids of C30-C35 and ring C24-C29 respectively.

Crystal Structure of 5b & intra- /intermolecular interaction in solid state

The crystal packing in **5b** is shown in Figure S7. The crystal packing in **5b** has been found to be stabilized by an intermolecular C-H… π hydrogen bonding interactions (Figure S8) where C37 atom in the molecule acts as a hydrogen-bond donor, *via* H37 to the Cg(11) of another molecule at 1/2-x, 1/2+y, 1/2-z. Between these two molecular units there exist an intermolecular C-H…Cl hydrogen bonding interaction (Figure S8). Various intra-molecular hydrogen bonding interactions in the compound are shown in Figure S9.

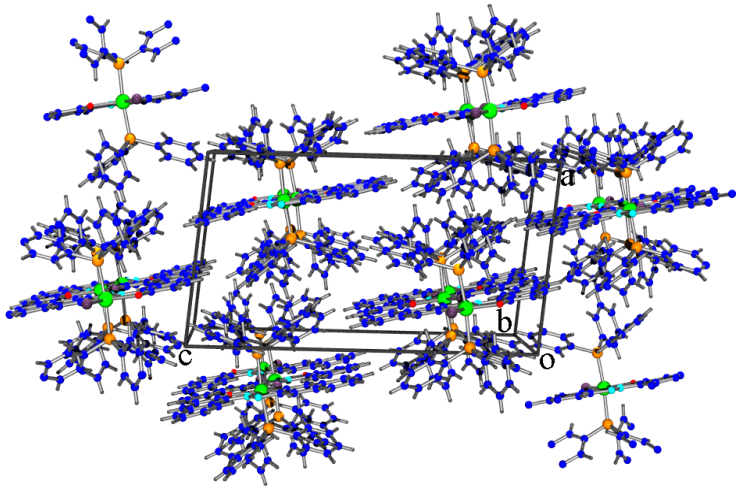


Figure S7 Packing arrangement in the cyclometallate **5b**.

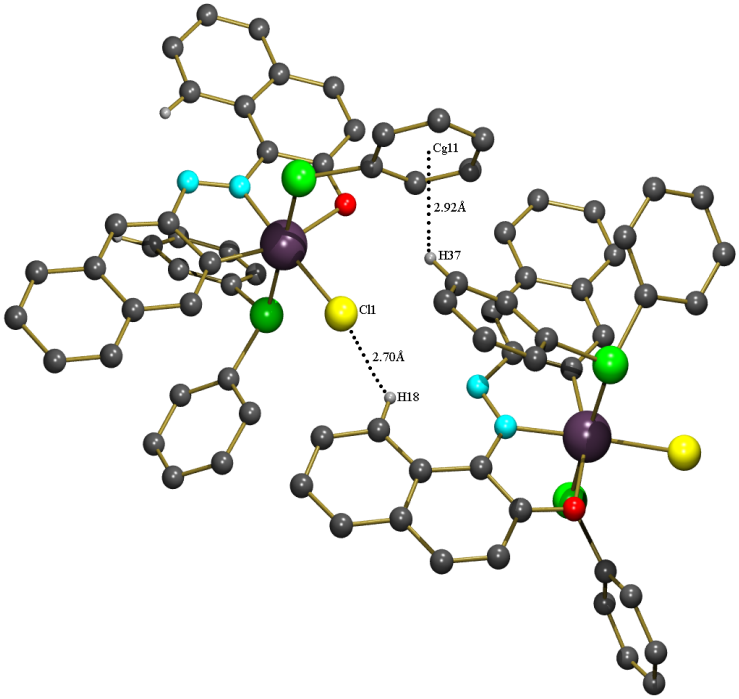


Figure S8 Intermolecular C-H…π and C-H…Cl interactions in **5b**. Symmetry code: 1/2-x, 1/2+y, 1/2-z. Cg(11) is the centroids of C45-C50 ring.

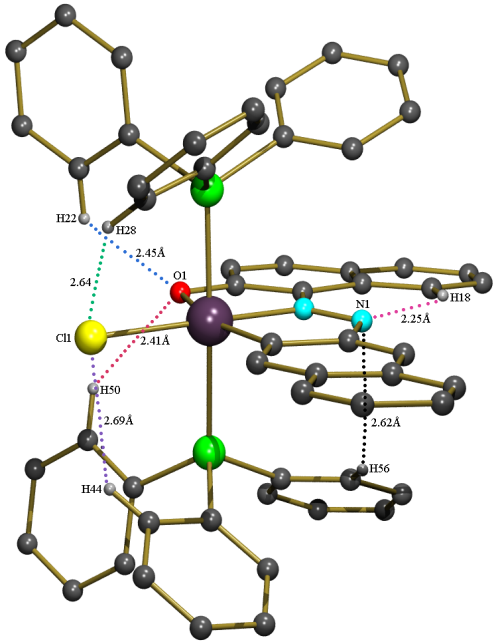


Figure S9. Intramolecular hydrogen bonding interactions in **5b.**

Table S1 Geometric parameters of the π···π interactions

	π···π	Cg···Cg/Å	CgI_Perp/Å	CgJ_Perp/Å	Slippage/Å	Symm. Op.
4a[a]	Cg(4)→Cg(11)	3.779(3)	3.729	3.952		x, y, z
	Cg(4)→Cg(8)	3.954(3)	3.952	3.729		x, y, z
4b[b]	Cg(3)→Cg(8)	3.815(3)	3.653	3.420		x, y, z
	Cg(8)→Cg(3)	3.815(3)	3.420	3.653		x, y, z

[a] Cg (4) and Cg(11) are the centroids of C5-C9 and C48-C53 rings respectively.
[b] Cg(3) and Cg(8) are the centroids of C1-C9 and C30-C35 rings respectively.

Table S2 Geometric parameters of the C-H···π interactions

		H···Cg/Å	γ[a]	C-H···Cg/ º	C···Cg/Å	Symm. Operation on Cg
3a[b]	C48-H48A···Cg(4)	2.96	14.54	132	3.644(7)	-x,-1/2+y,1/2-z
	C54-H54A···Cg(10)	2.78	8.58	152	3.631(8)	x,1/2-y,-1/2+z
4a[c]	C50 –H50 ...Cg(6)	2.96	21.35	155	3.826(5)	1-x, 1-y, 1-z
4b[d]	C26-H26···Cg(8)	2.95	13.77	148	3.788(6)	-x,1-y,-z
	C38-H38···Cg(7)	2.79	8.07	148	3.613(5)	1-x,1-y,-z
5b[e]	C37-H37···Cg(11)	2.92	8.58	141	3.689(11)	1/2-x,1/2+y,1/2-z

[a]γ= angle defined by a line connecting center of gravity of the aromatic ring with H atom and the normal to the aromatic ring.
[b] Cg(4) and Cg(10) are the centroids of C5-C9 and C39-C44 rings respectively.
[c] Cg(6) is the centroid of C18-C23 ring.
[d] Cg(8) and Cg(7) are the centroids of C30-C35 and C24-C29 rings respectively.
[e] Cg(11) is the centroids of C45-C50 ring.

Table S3 Geometric parameters of the hydrogen bonding interactions

		d(D-H)/ Å	d(H···A)/ Å	d(D···A)/ Å	D-H···A/º	Symm. Operation on A
3a	*C18-H18···N2	0.93	2.29	2.893(7)	122	x, y, z
	*C26-H26A···Cl1	0.93	2.71	3.495(8)	143	x, y, z
	*C34-H34A···O1	0.93	2.39	3.094(6)	133	x, y, z
	*C40-H40A···O1	0.93	2.31	3.143(6)	149	x, y, z
	*C46-H46A···Cl1	0.93	2.61	3.453(5)	152	x, y, z
4a	*C8-H8···Cl1	0.93	2.58	3.443(5)	155	x, y, z
	*C19-H19···O1	0.93	2.39	3.156(6)	139	x, y, z
	*C29-H29···N1	0.93	2.62	3.086(5)	155	x, y, z
	*C41-H41···N1	0.93	2.52	3.086(5)	120	x, y, z
	*C47-H47···O1	0.93	2.23	3.101(6)	155	x, y, z
	*C49-H49···Cl1	0.93	2.78	3.505(5)	135	x, y, z
4b	*C19-H19···N1	0.93	2.60	3.142(7)	117	x, y, z
	*C29-H29···O1	0.93	2.55	3.314(6)	140	x, y, z
	*C37-H37···Cl1	0.93	2.74	3.530(6)	143	x, y, z
	*C43-H43···N1	0.93	2.55	3.116(7)	120	x, y, z
	*C49-H49···O1	0.93	2.32	3.195(6)	156	x, y, z
5b	C18-H18···Cl1	0.93	2.70	3.448(9)	137	1/2-x,1/2+y,1/2-z
	*C18-H18···N1	0.93	2.25	2.872(10)	124	x, y, z
	*C22-H22···O1	0.93	2.45	3.172(10)	135	x, y, z
	*C28-H28···Cl1	0.93	2.64	3.419(10)	142	x, y, z
	*C44-H44···Cl1	0.93	2.69	3.433(11)	137	x, y, z
	*C50-H50···O1	0.93	2.41	3.202(9)	142	x, y, z
	*C56-H56···N1	0.93	2.62	3.009(10)	106	x, y, z

* Intramolecular hydrogen bond

Supplementary Information S2

Table S4 Cyclic voltammetric data of the rhodium(III) cyclometallates.[a]

Compound	E, V vs SCE	
	Oxidation[b]	Reduction[c]
$[Rh(PPh_3)_2(L^1)Cl]$, **2a**	1.09, 0.79	-0.97
$[Rh(PPh_3)_2(L^2)Cl]$, **3a**	1.12	-1.05
$[Rh(PPh_3)_2(L^2)Cl]$, **3b**	1.15	-0.79
$[Rh(PPh_3)_2(L^3)Cl]$, **4a**	1.02	-1.10
$[Rh(PPh_3)_2(L^3)Cl]$, **4b**	1.09	-0.93
$[Rh(PPh_3)_2(L^4)Cl]$, **5a**	0.97	-1.20
$[Rh(PPh_3)_2(L^4)Cl]$, **5b**	1.06	-0.96

[a] In 1:9 dichloromethane-acetonitrile; supporting electrolyte, TBAP; scan rate 50 mVs^{-1}; [b] E_{pa} values; [c] E_{pc} values.

Supplementary Information S3

Table S5 Energies and Percentage Composition of the Lowest Unoccupied and Highest Occupied Kohn-Sham Orbitals of **4a** in terms of Rh and the ligand fragment[a]

MO	occ	E(eV)	Rh	Ligand
154	0	-1.734		77.52
153a	0	-1.812	2.61(d_{x2-y2}); 2.39(d_{z2}).	70.73
152a	0	-1.830	10.82(d_{z2}); 7.39(d_{x2-y2}); 2.97 (d_{xz}).	48.92
151a	0	-1.859		75.72
150a	0	-2.067	9.48(d_{x2-y2}); 8.70(d_{z2}); 6.81 (d_{yz}).	47.79
149a	0	-3.123	3.32 (d_{yz}).	85.53
148a	2	-4.563	9.19 (d_{xy}).	77.54
147a	2	-5.035	35.04 (d_{xz}); 3.38 (d_{z2}); 3.29(d_{xy}).	49.95
146a	2	-5.252	2.19 (d_{yz}).	72.29
145a	2	-5.622	6.22 (d_{yz}); 1.89 (d_{z2}); 1.38(d_{xy}).	67.32
144a	2	-5.810	4.59(d_{yz}); 1.52(d_{z2}).	68.34
143a	2	-5.934	7.93 (d_{yz}); 2.55 (d_{z2}); 1.35 (d_{xy}).	60.98

Bold characters are used for the HOMO (148a) and the LUMO (149a).

Table S6 Energies and Percentage Composition of the Lowest Unoccupied and Highest Occupied Kohn-Sham Orbitals of **4b** in terms of Rh and the ligand fragment[a]

MO	occ	E(eV)	Rh	Ligand
154a	0	-1.710		70.54
153a	0	-1.799	2.84(d_{z2}) ; 1.42(d_{yz}) ; 1.37(d_{x2-y2}); 1.25(d_{xy}).	73.01
152a	0	-1.843	2.25(d_{z2}); 1.41 (d_{yz}).	69.90
151a	0	-1.859	1.87(d_{xy}).	75.72
150a	0	-2.067	9.48(d_{x2-y2}); 8.70(d_{z2}); 6.81 (d_{yz}).	47.79
149a	0	-3.123	3.32 (d_{yz}).	85.53
148a	2	-4.563	9.19 (d_{xy}).	77.54
147a	2	-5.035	35.04 (d_{xz}); 3.38 (d_{z2}); 3.29(d_{xy}).	49.95
146a	2	-5.252	2.19 (d_{yz}).	72.29
145a	2	-5.622	6.22 (d_{yz}); 1.89 (d_{z2}); 1.38(d_{xy}).	67.32
144a	2	-5.810	4.59(d_{yz}); 1.52(d_{z2}).	68.34
143a	2	-5.934	7.93 (d_{yz}); 2.55 (d_{z2}); 1.35 (d_{xy}).	60.98

[a]Bold characters are used for the HOMO (148a) and the LUMO (149a).