Supplementary Materials

Coordination-induced Self-Assembly of a Heteroleptic Paddlewheel-type Dirhodium Complex

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Contents

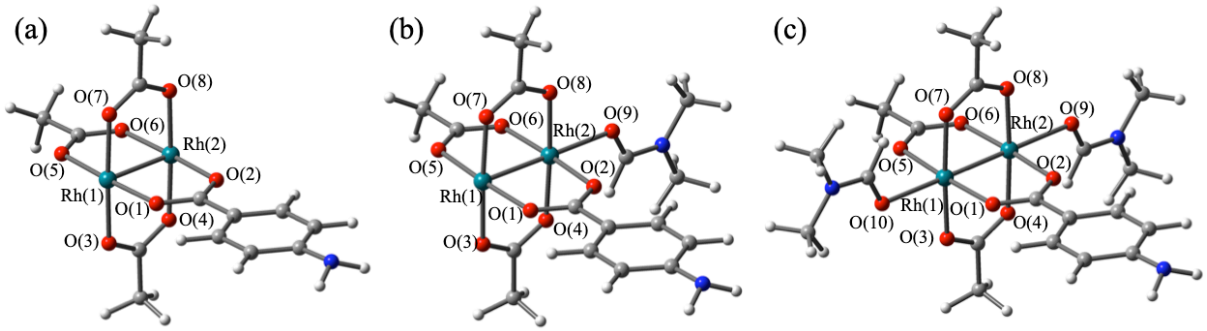

Figure S1. Optimized geometries of (a) $[Rh_2(O_2CCH_3)_3(PABC)]$, (b) $[Rh_2(O_2CCH_3)_3(PABC)(DMF)]$, and (c) $[Rh_2(O_2CCH_3)_3(PABC)(DMF)_2]$ (**1D**).

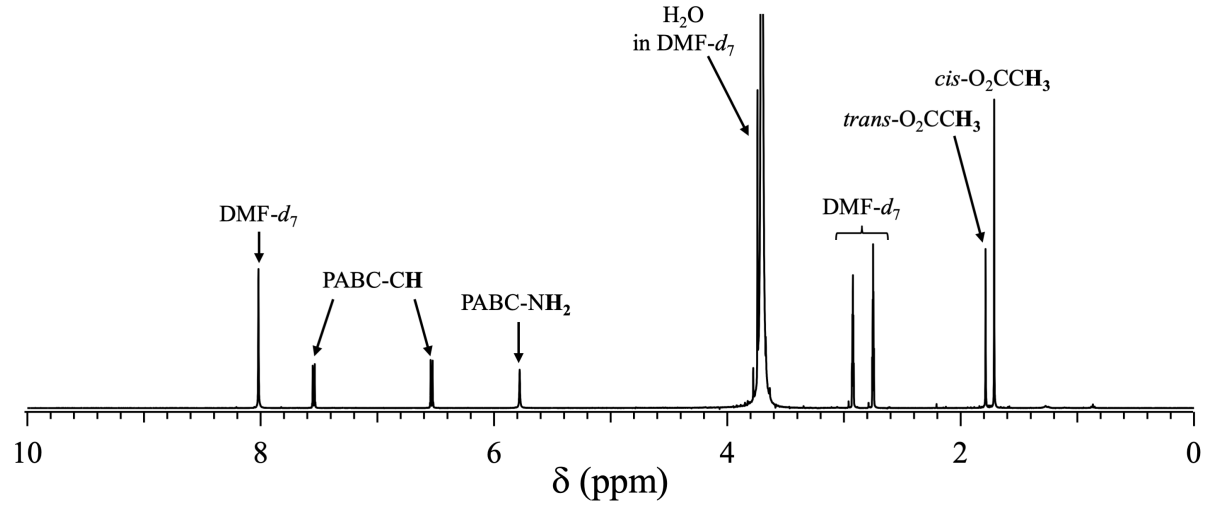

Figure S2. ^{1}H NMR spectrum of $[Rh_2(O_2CCH_3)_3(PABC)]$ (**1**) in DMF-d_7.

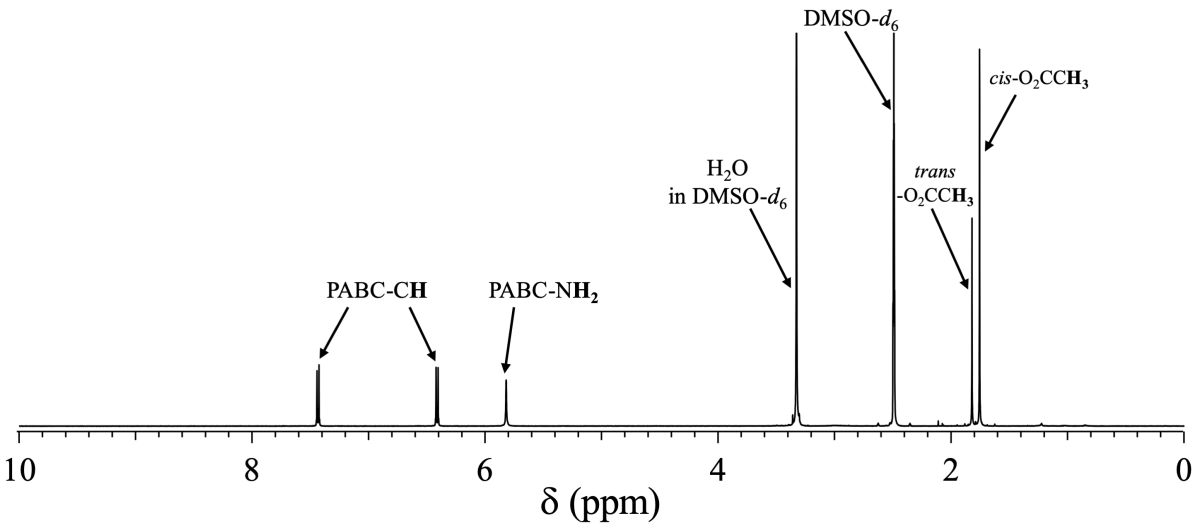

Figure S3. ^{1}H NMR spectrum of $[Rh_2(O_2CCH_3)_3(PABC)]$ (**1**) in DMF-d_7.

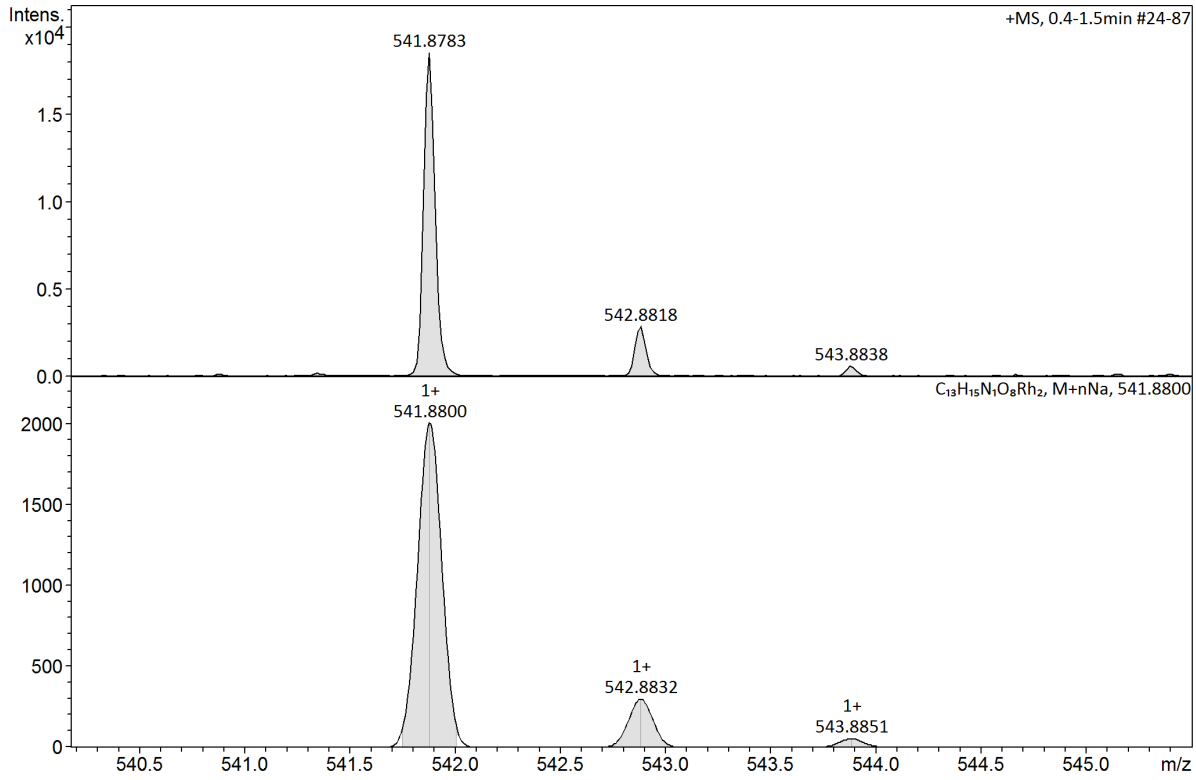

Figure S4. Observed (top) and simulated (down) ESI-TOF-MS spectra of $[Rh_2(O_2CCH_3)_3(PABC)]$ (**1**).

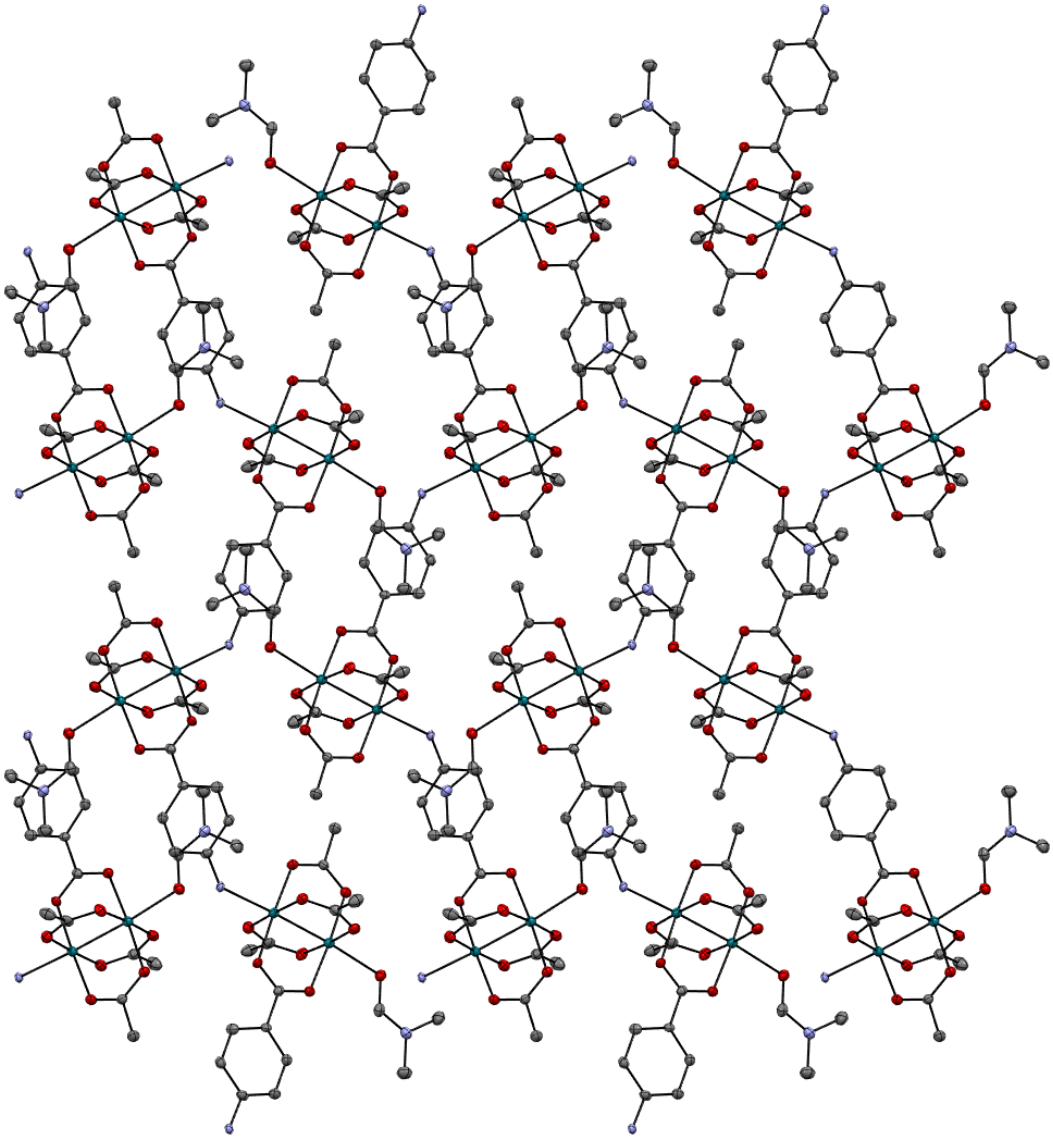

Figure S5. Packing view (along a axis) of crystal structure of $[Rh_2(O_2CCH_3)_3(PABC)(DMF)]_n$ (**1P**). Hydrogen atoms are omitted for clarity.

Table S1. Coordinate of optimized geometry of $[Rh_2(O_2CCH_3)_3(PABC)]$.

Rh	0	0	0
Rh	0	0	2.38121138
O	2.05160758	0	0.05765033
O	2.0505158	0.00113604	2.32476207
O	0.00109151	2.05718748	0.05808655
O	-0.00286575	2.05562824	2.32418248
O	-2.05682089	0.00235241	0.0565767
O	-2.05892845	0.00594686	2.32210207
O	0.00267541	-2.05658093	0.05731559
O	-0.00337387	-2.05795709	2.32348758
N	8.33676634	0.18997002	1.18583212
H	8.80574159	-0.12701467	2.0276077
H	8.80296904	-0.11880834	0.33946141
C	2.64615047	0.00958283	1.19133538
C	4.12655108	0.0363007	1.19095792
C	4.84193821	0.05626685	-0.01929742
H	4.28825752	0.04641398	-0.95854205
C	6.23024677	0.08748984	-0.02476063
H	6.77246578	0.1063721	-0.97400593
C	6.95369413	0.09975489	1.18750337
C	6.23333177	0.07771269	2.4014981
H	6.77805066	0.08847093	3.34942826
C	4.84487659	0.0468107	2.39949559
H	4.2938862	0.02860088	3.34024356
C	0.00828103	2.63948098	1.19149232
C	0.06153102	4.14722707	1.19334952
H	-0.4244996	4.54707162	0.2938961
H	1.11863764	4.46015504	1.1825371
H	-0.40608017	4.54402801	2.10375153
C	-2.64081898	-0.0018319	1.18896608
C	-4.14919927	-0.0481069	1.18791302
H	-4.54592132	0.43625199	2.08962569
H	-4.46814317	-1.10350345	1.19475479
H	-4.54485523	0.42504181	0.2798828
C	0.01209507	-2.64007382	1.19014401
C	0.07416108	-4.1476857	1.18845272
H	-0.39634183	-4.55033566	2.09479642
H	1.13324501	-4.45412276	1.18320791
H	-0.40360999	-4.54788538	0.28473129

Table S2. Coordinate of optimized geometry of $[Rh_2(O_2CCH_3)_3(PABC)(DMF)]$.

Rh	0	0	0
Rh	0	0	2.40690251
O	2.06348853	0	0.07131192
O	2.05728623	0.00430028	2.34023434
O	-0.00333857	2.05985053	0.0719609
O	-0.00479395	2.05724312	2.34112414
O	-2.06657839	-0.00972308	0.06711644
O	-2.06419813	0.00689476	2.33513383
O	0.00275522	-2.07617071	0.06416325
O	-0.00219363	-2.06994114	2.33120934
N	8.34843537	0.22953498	1.22250983
H	8.80900117	-0.11172599	2.06001905
H	8.81284388	-0.08575307	0.37699813
C	2.64812395	0.01490259	1.20855149
C	4.13408124	0.05046616	1.21080531
C	4.85369025	0.09126945	0.00478658
H	4.30154928	0.09405689	-0.93547963
C	6.24305795	0.13004249	0.00421311
H	6.78881653	0.16656346	-0.94282327
C	6.96217598	0.12977867	1.21796319
C	6.23792508	0.08863418	2.42794238
H	6.77932184	0.09096886	3.37805914
C	4.84868306	0.05030672	2.42061057
H	4.29293339	0.01814306	3.35820922
C	0.00464037	2.63599179	1.20775496
C	0.05734121	4.14625569	1.20635685
H	-0.44770841	4.54499619	0.31663366
H	1.11354891	4.46068697	1.1716754
H	-0.39191824	4.54455297	2.12538974
C	-2.642907	-0.00643978	1.2037371
C	-4.15433206	-0.05083738	1.20415052
H	-4.5485561	0.43831193	2.10455918
H	-4.47719055	-1.10512266	1.21656825
H	-4.55184214	0.42080665	0.29588507
C	0.0119498	-2.65194919	1.20493114
C	0.07205847	-4.16278716	1.20503393
H	-0.29207387	-4.56009076	2.16088693
H	1.12138326	-4.47414646	1.07221852
H	-0.51067412	-4.56946623	0.36697552
O	-0.0119837	0.00703667	-2.24764092
C	-0.08555162	-1.07402812	-2.84855043
N	-0.14054651	-1.18213372	-4.19099414
H	-0.10951427	-2.03561903	-2.30285448
C	-0.22512545	-2.47846739	-4.83809135
H	-1.14985668	-2.55926086	-5.43540585
H	0.63481079	-2.63760521	-5.51155318
H	-0.22735383	-3.27235674	-4.07837613
C	-0.12327485	0.00203973	-5.03780975
H	-0.06260327	0.88833892	-4.39567583
H	0.74677239	-0.02376227	-5.71567245
H	-1.04130688	0.05013918	-5.6478016

Table S3. Coordinate of optimized geometry of $[Rh_2(O_2CCH_3)_3(PABC)(DMF)_2]$.

Rh	0	0	0
Rh	0	0	2.41797192
O	2.06729059	0	0.07659744
O	2.06707225	0.00459235	2.34547445
O	-0.00057946	2.06971103	0.0816717
O	0.00353977	2.07431012	2.34951237
O	-2.06977514	-0.00861701	0.07204294
O	-2.07134248	0.01646838	2.34029194
O	-0.00237259	-2.07551659	0.06933213
O	-0.00762251	-2.07020738	2.33711715
O	-0.00010035	0.02436904	4.76180143
N	8.35861005	0.22605349	1.20226865
H	8.81815897	-0.1543696	2.02384464
H	8.81187726	-0.07857825	0.34631849
N	0.05821796	1.29171476	6.66395181
C	2.65097935	0.01358555	1.21072834
C	4.14063816	0.04806969	1.20907668
C	4.85383822	0.11921633	0.0012258
H	4.29509872	0.14512524	-0.93483667
C	6.24381507	0.15849161	-0.00587097
H	6.78431271	0.21942017	-0.95481817
C	6.96937503	0.12581869	1.20277916
C	6.25206656	0.0522714	2.41454403
H	6.79930651	0.02689995	3.36124677
C	4.86186071	0.01517361	2.41366575
H	4.31000541	-0.0449895	3.35226718
C	0.00967561	2.64814286	1.20965361
C	0.0578845	4.16078805	1.21104578
H	-0.25903355	4.55676846	0.23805728
H	1.0945259	4.48251642	1.40430058
H	-0.57434358	4.55951044	2.01698323
C	-2.64540558	-0.00273193	1.20626052
C	-4.15855448	-0.05243398	1.20514462
H	-4.55809745	0.41753614	2.1134844
H	-4.47763647	-1.10795439	1.19511346
H	-4.55642187	0.43460874	0.30488577
C	0.00505576	-2.64882728	1.20930191
C	0.05982541	-4.16145284	1.20993763
H	-0.27478582	-4.557622	2.17697458
H	1.10221428	-4.47789861	1.03994265
H	-0.55265916	-4.56540816	0.39158725
C	0.03918585	1.12384005	5.32059289
H	0.06146953	2.06815438	4.74247939
C	0.03284258	0.14457304	7.55713151
H	-0.85192273	0.1869241	8.21567872
H	0.93747488	0.12617635	8.18945314
H	-0.00685024	-0.76639851	6.94818248
C	0.10644038	2.61361232	7.2568757
H	-0.77508907	2.79216573	7.89778685
H	0.12181945	3.37435325	6.46369635
H	1.01156299	2.73575304	7.87782892
O	-0.01952821	-0.02946306	-2.34620676
C	-0.13989761	-1.12698062	-2.89702069
N	-0.22759942	-1.29804875	-4.23733293
H	-0.18389728	-2.06718811	-2.31350663
C	-0.36714844	-2.61804813	-4.81976099
H	-1.30550395	-2.69863787	-5.39663734
H	0.47339093	-2.84154875	-5.50044827
H	-0.38124277	-3.37419086	-4.02217522
C	-0.1902221	-0.15612501	-5.13671626
H	-0.09563297	0.75491578	-4.5339521
H	0.6687242	-0.23316623	-5.82574708
H	-1.11523673	-0.10682823	-5.73691121

Table S4. Selected geometrical parameters of optimized geometries of $[Rh_2(O_2CCH_3)_3(PABC)]$, $[Rh_2(O_2CCH_3)_3(PABC)(DMF)]$, and $[Rh_2(O_2CCH_3)_3(PABC)(DMF)_2]$ (**1D**).

Bond lengths	$[Rh_2(O_2CCH_3)_3(PABC)]$	$[Rh_2(O_2CCH_3)_3(PABC)(DMF)]$	$[Rh_2(O_2CCH_3)_3(PABC)(DMF)_2]$
Rh(1)-Rh(2)	2.381	2.407	2.418
Rh(1)-O(1)	2.051	2.058	2.068
Rh(1)-O(3)	2.059	2.071	2.072
Rh(1)-O(5)	2.060	2.065	2.073
Rh(1)-O(7)	2.056	2.058	2.075
Rh(2)-O(2)	2.052	2.065	2.069
Rh(2)-O(4)	2.057	2.077	2.077
Rh(2)-O(6)	2.058	2.070	2.071
Rh(2)-O(8)	2.058	2.061	2.071
Rh(1)-O(10)	-	-	2.346
Rh(2)-O(9)	-	2.248	2.344

Table S5. Sum of electronic and thermal free energies of optimized geometries of $[Rh_2(O_2CCH_3)_3(PABC)]$, $[Rh_2(O_2CCH_3)_3(PABC)(DMF)]$, $[Rh_2(O_2CCH_3)_3(PABC)(DMF)_2]$ (**1D**), and DMF.

Complexes	Sum of electronic and thermal free energies (a.u.)
$[Rh_2(O_2CCH_3)_3(PABC)(DMF)_2]$	-1877.026166
$[Rh_2(O_2CCH_3)_3(PABC)(DMF)]$	-1628.573634
$[Rh_2(O_2CCH_3)_3(PABC)]$	-1380.113947
DMF	-248.450286