Supporting Information

PPh_3 Propeller Diastereomers. The Bonding Motif Ph_{PPh3} Face-on π-Ar in Half-Sandwich Compounds $[(\pi\text{-Ar})LL'MPPh_3]$

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Table S1. Crystallographic data for the complexes

Complex	(R_{Ru},S_C)-[CyRu(1O-2N)Cl]	(R_{Ru},S_C)-[CyRu(1O-2N)PPh_3]PF_6	(R_{Ru},S_C)-[CyRu(2O-1N)PPh_3]PF_6
Empirical formula	$C_{29}H_{30}ClNORu$	3($C_{47}H_{45}NOPRu$),3(F_6P)	$C_{47}H_{45}NOPRu$, F_6P, 2(CH_2Cl_2)
Formula weight	545.06	916.85	1001.78
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1$	$P2_1$
a (Å)	9.044(3)	10.50060(10)	10.429(5)
b (Å)	13.524(3)	17.86340(10)	16.431(5)
c (Å)	20.436(5)	34.44680(10)	14.060(5)
α (^{o})	90	90	90
β (^{o})	90	98.100(1)	98.590(5)
γ (^{o})	90	90	90
V (Å)^3	2499.4(12)	6396.99(7)	2382.3(16)
Z	4	2	2
ρcalcd (mg/m^3)	1.449	1.428	1.515
Abs coeff (mm^{-1})	0.756	4.219	0.567
Abs correct	multi-scan	multi-scan	multi-scan
Transmiss max/min	1.0000/0.7317	1.0000/0.46716	1.0000/ 0.7749
F (000)	1120	2850	1108
Crystal size (mm)	0.36 x 0.32 x 0.27	0.19 x 0.06 x 0.02	0.51 x 0.38 x 0.20
Radiation (A)	Mo Kα/0.71073	Cu Kα/1.54184	Mo Kα/0.71073
Θ range (^{o})	3.01- 27.48	3.5650-66.5840	3.17-27.48
Rflns/unique	19688/4388	48030/21912	18634/8291
R_{int}	0.037	0.0318	0.0334
Data/params	4392/298	21912/1567	8291/578
Goodness of fit F^2	1.065	1.012	1.057
R_1/wR_2 ($I>2\sigma(I)$)	0.0325/0.0875	0.0414/0.1086	0.0561/0.1479
R_1/wR_2 (all data)	0.0335/0.0885	0.0427/0.1100	0.0600/0.1519
Largest diff. peak and hole (e Å^{-3})	2.300/-0.519	1.259/ -0.798	2.326/-0.605
Flack-Parameter	-0.004(14)	-0.014(3)	-0.029(14)
CCDC No.	1519530	1519531	1519532

Table S2. Rotation angles ρ and angles φ plane Ph/plane π-Ar in diastereomers, [(π-Ar)LL'MPPh$_3$], which only differ in the configuration of the PPh$_3$ ligand

CSD symbol or CCDC number[a] *(ref.)*	Formula	Ph face-on π-Ar			Ph edge-on π-Ar		
		C_i-P-M-Ar_{cent} ρ / °	C_o-C_i-P-M τ / °	plane Ph_{face}/ plane π-Ar φ / °	C_i-P-M-Ar_{cent} ρ / °	C_o-C_i-P-M τ / °	plane Ph_{edge}/ plane π-Ar φ / °
HEDYIY *(1)*	(R_{Ru},S_C)-[(π-C_6H_6)Ru(O-N)PPh_3]PF_6	37.3	53.7	27.6	-82.4	23.9	58.2
HEDYOE *(1)*	(R_{Ru},S_C)-[(π-C_6H_6)Ru(O-N)PPh_3]PF_6	-28.7	-62.1	28.6	89.2	-16.0	51.2
1519532	(R_{Ru},S_C)-[CyRu(2O-1N)PPh_3]PF_6	35.2	44.3	26.8	-86.0	25.6	67.2
1519531 [1]	(R_{Ru},S_C)-[CyRu(1O-2N)PPh_3]PF_6	45.5	44.7	17.3	-80.6	6.4	50.6
1519531 [2]	(R_{Ru},S_C)-[CyRu(1O-2N)PPh_3]PF_6	47.0	44.0	17.8	-76.7	14.2	58.8
1519531 [3]	(R_{Ru},S_C)-[CyRu(1O-2N)PPh_3]PF_6	-33.2	-69.5	18.2	87.3	-25.2	66.0
VOWTUW[1] *(2)*	[CpFe{CO(C=CH_2)-OBn}(CO)PPh_3]	-36.8	-65.7	25.9	82.7	-3.1	39.4
VOWTUW[2] *(2)*	[CpFe{CO(C=CH_2)-OBn}(CO)PPh_3]	38.8	55.0	23.5	-81.1	12.1	48.0
GIRYIP[1] *(3)*	[CpFe(C_4F_5)(CO) PPh_3]	64.1	14.3	34.8	-57.3	39.5	87.9
GIRYIP[2] *(3)*	[CpFe(C_4F_5)(CO) PPh_3]	33.4	63.7	27.9	-85.7	10.2	44.5
ZINXOJ[1] *(4)*	[CpRe{S(CH_2CH=CH_2)$_2$}(NO)PPh_3]SbF_6	42.6	32.1	26.1	-75.7	63.7	79.1
ZINXOJ[2] *(4)*	[CpRe{S(CH_2CH=CH_2)$_2$}(NO)PPh_3]SbF_6	-31.5	-62.3	38.8	87.2	-38.8	67.3
FOMZEN[1] *(5)*	[CpFe($CNBPh_3$)(CO)-PPh_3]	-42.5	-53.3	21.6	79.2	-14.9	48.9
FOMZEN[2] *(5)*	[CpFe($CNBPh_3$)(CO)-PPh_3]	36.7	67.3	34.5	-83.7	7.4	45.1
RCMXFE[1] *(6)*	[CpFe{COO($C_{10}H_{19}$)}-(CO)PPh_3]	43.2	55.1	16.2	-76.8	12.1	45.8
RCMXFE[2] *(6)*	[CpFe{COO($C_{10}H_{19}$)}-(CO)PPh_3]	-40.8	-53.4	13.7	80.5	-14.7	51.1
SEPZUI[1,2] *(7)*	[CpRu(IC_6H_4Me-*p*)-(CO)PPh_3]PF_6	-44.4	-51.9	20.9	74.3	-8.9	44.2

[a]Brackets [] indicate independent molecules.

Table S3. Rotation angles ρ and angles φ plane Ph/plane π-Ar for the 140 cases of the 119 compounds, [(π-C_6R_6)RuLL'PPh_3], which only differ in the configuration of the PPh_3 ligand. Only three-legged half-sandwich compounds considered.

Ent-ry	CSD Symbol[a]	Ph_{face}-on π-Ar			Ph_{edge}-on π-Ar		
		C_i-P-M-Ar_{cent} ρ / °	C_o-C_i-P-M τ / °	plane Ph_{face}/ plane π-Ar φ / °	C_i-P-M-Ar_{cent} ρ / °	C_o-C_i-P-M τ / °	plane Ph_{edge}/ plane π-Ar φ / °
1	NEZKOT[1]	-59.193	-84.91	45.708	62.228	46.035	4.257
2	GIZMUY	-55.649	-61.41	8.194	65.846	-3.078	56.864
3	DITNID(1)	-55.634	-22.249	27.409	61.272	70.159	39.371
4	NEZKOT[2]	-54.837	-82.745	41.227	62.834	35.449	13.515
5	HESHAP[2]	-54.154	85.321	46.943	64.811	41.675	6.697
6	SIGKEZ(1)	-53.992	-72.808	35.882	62.11	21.912	22.749
7	QENJUO	-53.279	-61.244	27.638	63.267	9.335	36.853
8	LIRDEW	-53.176	-74.038	34.949	64.963	23.813	22.404
9	YUTKON	-50.193	77.453	47.697	68.061	18.331	28.728
10	ESOLUT(1)	-50.074	-72.851	31.491	66.459	12.086	29.882
11	WAKXUB(2)	-50.019	-76.357	41.363	67.175	10.931	27.542
12	WUVMAD	-49.524	-36.168	16.749	70.404	-17.083	57.63
13	NEZJIM	-46.889	-48.217	17.336	72.396	-4.243	54.473
14	SIGJUO	-46.573	-63.872	28.046	67.914	-3.44	45.012
15	WUVMOR	-46.348	-41.141	16.361	73.436	-25.137	68.144
16	TEYZOM	-46.234	-63.366	31.13	71.968	14.989	28.447
17	SIGJOI	-46.179	-77.246	33.769	70.461	13.344	28.339
18	VICZOW	-45.525	-62.972	20.349	73.144	-2.235	44.964
19	EHABEU	-45.099	-80.29	32.795	74.764	16.096	26.688
20	BEDNII	-44.73	-74.678	36.472	73.037	21.164	20.714
21	PEHHOB[2]	-44.607	-54.613	18.022	77.002	1.299	41.181
22	PEHJET[1]	-44.588	-55.781	17.963	77.232	2.807	40.273
23	HIZNIN(2)	-43.93	-50.162	21.196	74.259	-2.489	41.917
24	VIQQOB	-43.792	-67.564	20.8	76.719	9.789	37.532
25	WAKXUB(1)	-43.309	-59.457	28.888	71.221	-7.79	46.704
26	ZESRUK	-43.228	-64.888	34.182	74.437	5.103	33.124
27	MACVAO	-42.979	-62.763	24.392	74.933	2.128	36.576
28	BULDIW	-42.123	-58.955	26.731	76.671	-7.469	46.175
29	ESOLUT(2)	-42.014	-63.279	26.317	76.924	-64.189	77.214
30	XOSWUY	-41.721	-63.284	30.087	76.199	1.685	42.828
31	ECIQAJ	-41.666	-65.405	38.421	75.919	11.713	30.479

32	TUKYAB	-41.472	-66.908	26.144	77.159	7.967	33.699
33	AMEJEH	-41.22	-73.532	33.262	75.812	9.562	29.811
34	IKEKOY[2]	-41.033	-60.149	23.332	75.68	-3.135	40.938
35	RIRDUS	-41.005	-40.947	26.636	80.215	-27.094	66.857
36	SIGKEZ(2)	-40.078	-70.334	32.985	80.86	-62.566	77.094
37	TOPCUW	-39.751	-48.954	20.178	80.449	-28.285	64.371
38	OVUFUI	-39.517	-52.025	17.376	82.481	-32.482	74.131
39	YOGDOO	-39.338	-53.547	18.552	80.987	-9.718	53.027
40	FOKVUY	-38.324	-44.41	23.969	83.52	-3.353	45.553
41	TIPXIA	-36.569	-70.587	38.502	79.436	2.387	35.075
42	NABXAQ	-36.283	-57.832	23.868	85.283	-9.29	47.3
43	TOPCOQ[1]	-34.609	-58.99	27.26	83.559	-15.425	53.015
44	JUCNAW	-34.581	-53.541	22.743	87.667	-21.305	58.122
45	LOMXER	-34.262	-59.267	25.107	87.131	5.407	35.437
46	PAWJAY	-33.94	-53.165	21.599	86.023	-18.351	59.96
47	PEQTUC	-32.718	-60.301	28.384	85.599	-25.804	59.879
48	VOTYUY10[1]	-32.448	-76.404	27.804	84.984	-29.698	67.907
49	ZUQNII	-32.091	-49.895	20.668	88.302	-23.668	59.757
50	TOPCOQ[2]	-31.844	-58.925	21.973	87.206	-22.093	59.281
51	IKEKUE[2]	-31.34	-55.186	20.485	88.088	-48.97	85.932
52	IMUDEZ	-30.833	-53.639	24.374	82.976	-17.175	55.225
53	NUHTEQ	-30.498	-56.048	20.706	88.87	-18.803	53.855
54	PAWHUQ	-29.921	-51.392	25.109	89.779	-18.287	60.341
55	HEDYOE	-28.739	-62.078	28.602	89.289	-15.964	51.235
56	FUZCAG	-27.613	-85.708	30.004	90.051	-39.207	76.399
57	ZOJYEE	-27.123	-53.376	22.913	93.975	-31.232	67.591
58	ZOJXUT	-26.379	-48.565	27.736	94.637	-40.221	78.805
59	ZOJYAA	-25.74	-56.778	23.805	94.857	-31.954	71.074
60	IMUDOJ	-25.389	-64.189	28.49	87.455	-13.999	50.402
61	DITNID(2)	-25.142	-74.768	26.43	91.992	-34.255	70.389
62	WAKNII	-24.328	-48.548	29.735	98.536	-22.856	65.342
63	IMUDID	-24.11	-64.971	28.773	88.945	-18.622	53.579
64	GIKNOE	-23.677	-55.995	27.035	96.796	-32.261	71.015
65	MOQSAO	-17.257	-58.514	28.671	102.07	-44.98	80.732
66	MUCXAJ(1)	-16.661	-76.041	34.926	98.983	-40.125	73.98
67	VAKFIX(1)	-15.158	-85.028	35.804	100.425	-35.508	71.995
68	DITNEZ(1)	12.866	66.08	30.564	-103.741	45.869	82.236
69	LOMXAN	17.046	66.048	29.743	-103.346	19.715	52.945
70	HIZNIN(1)	20.088	74.047	26.761	-96.253	46.167	82.155
71	MIMHEW[1]	21.931	78.52	29.329	-95.555	29.333	68.795
72	YOGFIK	23.482	47.938	30.109	-98.46	20.849	68.818
73	ZOJYOO	25.817	56.395	23.498	-95.072	32.62	72.212

74	LUKPIR	26.426	49.912	28.438	-92.461	41.24	74.952
75	FAPSEV	27.316	50.958	26.966	-92.725	28.887	65.028
76	LIZZIE	28.294	62.699	32.936	-88.018	-3.405	42.718
77	YOGFOQ	29.025	50.767	25.553	-92.898	27.316	69.457
78	FAPSUL	29.384	50.823	24.563	-90.803	39.484	73.47
79	MIMHEW[2]	29.435	80.324	31.802	-89.555	7.478	50.868
80	WEQHAD(2)	29.95	59.016	22.017	-88.623	65.529	73.865
81	MUNVEW	30.661	66.601	25.113	-84.126	35.65	67.521
82	KIVLUY	31.531	69.629	23.459	-87.459	0.048	40.801
83	NEZJOS	31.664	57.157	24.086	-87.652	-0.071	46.413
84	YOGCON	31.814	70.091	24.456	-84.256	10.705	49.853
85	XAWPOA	32.582	76.908	26.448	-82.689	16.916	54.356
86	BULDES	32.928	71.079	36.151	-87.112	9.747	44.468
87	FUZBUZ	32.933	-83.651	39.065	-85.184	47.543	87.343
88	NEZKEJ	33.326	49.635	21.895	-91.074	18.681	62.982
89	MABKUW[2](2)	33.91	64.838	24.788	-80.331	19.642	54.997
90	IKEKUE[1]	33.941	55.352	20.205	-85.32	41.616	76.582
91	KADVER	34.094	72.823	35.679	-81.029	13.498	46.246
92	DITNEZ(2)	34.163	56.994	16.37	-84.549	8.627	46.385
93	YOGDAA	34.877	57.254	18.678	-84.039	13.802	59.1
94	ECIPUC	36.525	67.349	34.262	-79.578	12.457	51.967
95	MABKUW[1](1)	36.661	70.176	26.883	-76.405	10.857	48.033
96	GAQDAE	37.011	65.53	14.705	-84.025	10.262	54.635
97	LIZZOK	37.284	54.263	24.542	-80.868	6.877	49.048
98	GIZMOS	37.339	56.334	24.499	-82.321	6.786	55.414
99	HEDYIY	37.341	53.703	27.625	-82.424	23.893	58.178
100	VIQRES	38.204	71.361	18.688	-81.579	9.552	50.582
101	NEPRAC	39.267	74.199	35.745	-77.974	-2.195	33.424
102	MUCXAJ(2)	40.978	51.933	21.601	-75.061	47.277	84.756
103	LOMWOA	41.181	57.242	23.836	-79.129	0.506	41.597
104	AQAYIA	41.613	67.56	32.039	-77.141	-15.078	25.571
105	IKEKOY[1]	42.141	64.797	26.566	-73.998	-3.044	35.789
106	WEQHAD(1)	42.217	55.424	19.553	-76.638	1.004	41.436
107	NEZJUY	42.743	49.139	15.834	-79.895	7.219	53.297
108	YUSWUE	42.977	46.366	20.538	-79.257	12.701	55.308
109	AXIVEI[1]	43.135	65.513	24.111	-74.143	-8.487	31.836
110	TOLVEV[1]	43.823	53.827	27.473	-71.481	4.889	39.57
111	DITZIR	44.216	60.929	36.099	-70.107	12.086	48.175
112	NEZKAF	44.282	42.17	20.171	-76.95	12.401	55.325
113	ZESSAR	44.506	54.028	19.133	-74.93	-1.998	39.763
114	VIJREL	45.293	55.289	12.556	-73.829	-2.689	44.803
115	YEBDOY	45.694	59.759	11.938	-77.185	-4.492	44.94

116	PEHHOB[1]	45.932	75.475	35.372	-72.698	-20.666	20.688
117	AXIVEI[2]	46.089	65.21	24.828	-72.229	-1.013	43.476
118	GIRMAX	46.126	57.542	15.417	-76.881	-10.775	33.238
119	GILQOI	46.129	49.38	14.341	-76.391	-2.206	44.837
120	PEHJET[2]	46.236	75.928	36.661	-72.529	-22.302	19.796
121	ECIQOX	46.289	68.776	29.419	-73.067	-17.657	27.704
122	KEKFOV	46.565	54.579	10.925	-74.191	-3.103	45.9
123	RUJHOT	46.616	63.144	22.349	-74.907	9.972	54.241
124	MUNGEH	46.629	62.535	17.017	-75.286	-9.769	41.903
125	JEXFAU	46.639	75.527	31.856	-69.499	-2.877	36.415
126	TOLVEV[2]	47.659	56.779	28.893	-67.762	0.469	36.447
127	JEXDUM	47.78	60.335	26.741	-66.418	-8.53	34.722
128	UCODUM	47.892	-76.348	52.987	-70.68	-33.265	7.963
129	VOTYUY10[2]	48.005	51.258	20.303	-74.051	1.531	44.088
130	VIQRUI	48.371	49.903	11.958	-74.582	1.734	49.092
131	PEHJAP	48.433	74.07	34.55	-72.114	-15.901	29.323
132	HIVWOY	48.501	53.763	21.538	-69.796	-1.883	35.56
133	BONXAD	48.522	65.647	12.109	-72.994	-4.389	41.534
134	JEXDOG	49.927	61.583	16.337	-67.13	25.543	64.352
135	MABKUW[1](2)	50.871	66.092	27.136	-64.373	-3.489	37.813
136	TOLVIZ	51.065	71.014	38.638	-64.145	-11.545	25.658
137	VAKFIX(2)	53.115	40.208	20.457	-64.232	14.072	55.35
138	MABKUW[2](1)	53.28	70.566	32.166	-59.477	-10.175	32.754
139	XOSWOS	53.684	69.646	32.051	-65.4	-20.733	28.022
140	HESHAP[1]	53.766	81.436	41.884	-66.238	-36.44	10.777

[a]Brackets [] indicate independent molecules and parentheses () different ligands in the same molecule.

Table S4. CH/π interactions between π-Ar and Ph of the CHMePh substituent (β-phenyl effect) in the compounds $[(\pi\text{-}C_6R_6)Ru(O\text{-}N)PPh_3]PF_6$

Entry *(ref.)*	CSD symbol[a] CCDC number	Formula	ArCH-$C_{i/o}$ (Å)
1 *(1)*	HEDYIY	(R_{Ru},S_C)-$[(\pi\text{-}C_6H_6)Ru(O\text{-}N)PPh_3]PF_6$	H-C_i: 2.93, H-C_o: 2.79
2 *(1)*	HEDYOE	(R_{Ru},S_C)-$[(\pi\text{-}C_6H_6)Ru(O\text{-}N)PPh_3]PF_6$	H-C_i: 2.56, H-C_o: 2.75, H-$C_{o'}$: 2.96
3	1519532	(R_{Ru},S_C)-$[CyRu(2O\text{-}1N)PPh_3]PF_6$	H-C_i: 2.81
4	1519531[1]	(R_{Ru},S_C)-$[CyRu(1O\text{-}2N)PPh_3]PF_6$	H-C_i: 2.86 H-C_o: 2.54
5	1519531[2]	(R_{Ru},S_C)-$[CyRu(1O\text{-}2N)PPh_3]PF_6$	H-C_i: 2.64, H-C_o: 2.93, H-$C_{o'}$: 2.99
6	1519531[3]	(R_{Ru},S_C)-$[CyRu(1O\text{-}2N)PPh_3]PF_6$	H-C_i: 2.58, H-C_o: 2.76, H-$C_{o'}$: 2.89

[a]Brackets indicate independent molecules [1], [2], and [3].

Table S5. Relative energy and torsion angle of the optimized geometries of the cations in HEDYIY and HEDYOE at the RI-B3LYP/def2-TZVP level of theory

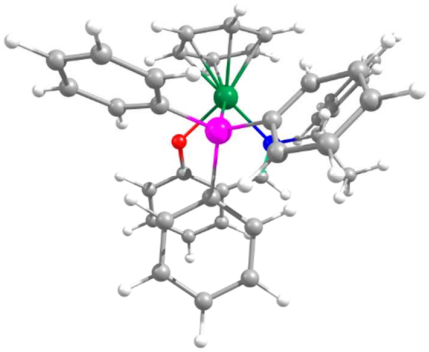
	HEDYIY	HEDYOE
Relative energy / kJ·mol^{-1}	2.68	0
ρ /°	47.4	

Table S6. Relative energy and torsion angle of the optimized geometries with restraints of the cation in HEDYIY at the RI-B3LYP/def2-TZVP level of theory

ρ (°)	47.4	1.1[a)]	21.9	50.3	59.4[a)]
relative energy / kJ·mol^{-1}	0	24.31	13.50	0.75	4.66

a) Two torsion angles have been fixed (C_i-P-Ru-C71 and C_i-P-Ru-C75).

Table S7. Cartesian coordinates of the optimized geometry of the cation in HEDYIY at the RI-B3LYP/def2-TZVP level of theory. Total Energy: -2072.84032804932 a.u.

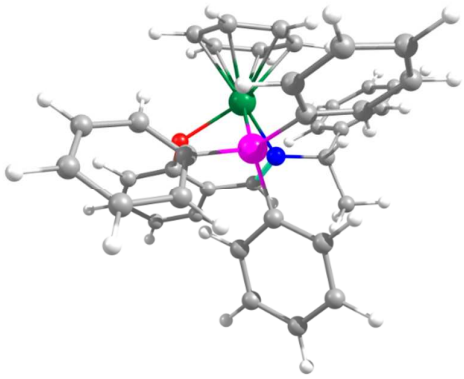


Atom	x	y	z
Ru	-2.1321834	-0.0994331	7.9225526
P	-4.4213110	-0.2845909	8.6564295
O	-2.9155617	1.4031439	6.7472479
N	-2.5019374	-1.4633959	6.3391995
C	-2.8328183	-1.0779682	5.1478912
H	-2.9413078	-1.8522739	4.3934321
C	-2.2608573	-2.9246020	6.5447783
H	-2.4864567	-3.0991544	7.5945122
C	-3.1832039	-3.8495772	5.7322072
H	-4.2299675	-3.5632374	5.8306111
H	-3.0701536	-4.8648483	6.1128051
H	-2.9230185	-3.8795409	4.6741905

C	-6.3149936	1.0888780	7.0362961
H	-6.0830133	1.9812979	7.5975746
C	-7.2560621	1.1641099	6.0153843
H	-7.7307615	2.1123744	5.7982269
C	-7.5913793	0.0322354	5.2838287
H	-8.3273844	0.0931327	4.4924805
C	-6.9832433	-1.1825170	5.5814185
H	-7.2475412	-2.0740805	5.0267922
C	-6.0422629	-1.2589429	6.5989159
H	-5.5996246	-2.2167217	6.8341017
C	-5.6940567	-0.1243882	7.3402767
C	-5.2993060	0.8416677	11.1165303
H	-5.5371242	-0.1626400	11.4363452
C	-5.5277590	1.8992348	11.9929892
H	-5.9371215	1.6981672	12.9748027
C	-5.2373804	3.2018645	11.6109267
H	-5.4219883	4.0231143	12.2915342
C	-4.7022981	3.4454501	10.3489846
H	-4.4695018	4.4582436	10.0445703
C	-4.4600745	2.3935383	9.4756574
H	-4.0188612	2.5903919	8.5069538
C	-4.7698746	1.0759053	9.8451508
C	-6.3026140	-2.0586294	9.7678265
H	-7.0496433	-1.3600001	9.4152180
C	-6.7079634	-3.1948219	10.4545207
H	-7.7622897	-3.3649540	10.6314802
C	-5.7657513	-4.1117570	10.9114712
H	-6.0843614	-4.9981835	11.4448237
C	-4.4159640	-3.8860323	10.6760181
H	-3.6771522	-4.5964904	11.0246844
C	-4.0101624	-2.7463123	9.9882910
H	-2.9581217	-2.5873515	9.8025985
C	-4.9429255	-1.8161375	9.5277491
C	-0.0549265	-2.8627976	5.2408381
H	-0.4703580	-2.1309908	4.5598561
C	1.2452863	-3.3119040	5.0329202
H	1.8144325	-2.9338226	4.1929848
C	1.8128355	-4.2441101	5.8951187

H	2.8241287	-4.5932668	5.7317058
C	1.0684782	-4.7283668	6.9648824
H	1.4966991	-5.4602086	7.6381676
C	-0.2300994	-4.2748589	7.1706824
H	-0.8052113	-4.6682979	8.0022862
C	-0.8079735	-3.3334180	6.3172142
C	-3.0767537	1.4073608	5.4517543
C	-3.2980699	2.6499849	4.8141306
H	-3.2982318	3.5400610	5.4299174
C	-3.5124739	2.7278879	3.4561160
H	-3.6791137	3.6969431	3.0011646
C	-3.5188205	1.5748521	2.6551655
H	-3.6903809	1.6461799	1.5901269
C	-3.3023290	0.3573927	3.2515826
H	-3.3033989	-0.5452191	2.6506617
C	-3.0671070	0.2381876	4.6426896
C	-1.3587439	1.0244702	9.7482337
H	-1.9284407	1.6865296	10.3818501
C	-0.7127093	1.5152029	8.6095159
H	-0.8224765	2.5568759	8.3418921
C	0.0462191	0.6545982	7.7670832
H	0.5413800	1.0475600	6.8910194
C	0.1068669	-0.7091986	8.0660267
H	0.6490295	-1.3776903	7.4142008
C	-0.6001666	-1.2398526	9.1762398
H	-0.5551705	-2.2982392	9.3851650
C	-1.3380080	-0.3735075	10.0045178
H	-1.8769491	-0.7656839	10.8558060

Table S8. Cartesian coordinates of the optimized geometry of the cation in HEDYOE at the RI-B3LYP/def2-TZVP level of theory. Total Energy: -2072.84135001407 a.u.



Atom	x	y	z
Ru	-0.5551222	-1.1941653	0.5615494
P	0.0320906	1.0298932	1.2898331
O	1.3858732	-1.6691813	1.0689390
N	0.1554937	-0.8071572	-1.4030076
C	1.2962526	-1.2382870	-1.8341565
H	1.5322560	-1.0528286	-2.8787207
C	-0.7282327	-0.1167501	-2.3880857
H	-1.3894057	0.4994134	-1.7820352
C	0.0191799	0.8316832	-3.3411411
H	0.6900326	1.4927531	-2.7928450
H	-0.7143416	1.4429141	-3.8676767
H	0.5860587	0.2968609	-4.1031982
C	0.7274168	3.2823365	-0.3308506
H	-0.2420031	3.7041520	-0.1085037
C	1.6123453	4.0102708	-1.1219551
H	1.3108137	4.9751702	-1.5094588
C	2.8768933	3.5093507	-1.4018058
H	3.5651309	4.0793709	-2.0127946
C	3.2598436	2.2759917	-0.8817345
H	4.2484149	1.8832638	-1.0830562
C	2.3801205	1.5466575	-0.0945880

H	2.6995003	0.5995096	0.3184204
C	1.0996706	2.0393929	0.1860086
C	1.5515343	2.2962222	3.2744268
H	1.4784379	3.1756101	2.6479321
C	2.2299054	2.3808542	4.4821162
H	2.6726854	3.3217303	4.7829740
C	2.3450957	1.2599584	5.2990620
H	2.8787022	1.3257383	6.2386890
C	1.7830967	0.0547860	4.8986347
H	1.8834901	-0.8247229	5.5218584
C	1.1010517	-0.0320404	3.6889638
H	0.7060024	-0.9828316	3.3687635
C	0.9697355	1.0882293	2.8678977
C	-1.8142429	2.4526199	2.9025875
H	-1.1747467	2.2115474	3.7398768
C	-2.9848975	3.1722708	3.1295323
H	-3.2381631	3.4727884	4.1382448
C	-3.8177229	3.5096309	2.0714583
H	-4.7234458	4.0751484	2.2487586
C	-3.4802749	3.1163014	0.7791600
H	-4.1216817	3.3772567	-0.0531910
C	-2.3200249	2.3884459	0.5535062
H	-2.0817248	2.0851762	-0.4578798
C	-1.4628671	2.0532532	1.6106491
C	-2.8989448	-0.6399451	-3.5424255
H	-3.2521791	0.3292792	-3.2059821
C	-3.7276703	-1.4288376	-4.3315908
H	-4.7154987	-1.0739662	-4.5970714
C	-3.2872957	-2.6694783	-4.7795615
H	-3.9288617	-3.2868240	-5.3947934
C	-2.0145613	-3.1075972	-4.4336803
H	-1.6593161	-4.0695852	-4.7814384
C	-1.1867874	-2.3137228	-3.6445731
H	-0.2019870	-2.6824133	-3.3885903
C	-1.6181007	-1.0691896	-3.1855155
C	2.3139461	-2.1344362	0.2769671
C	3.4028179	-2.8259440	0.8565199
H	3.3996642	-2.9627382	1.9299633

C	4.4388678	-3.3007657	0.0823042
H	5.2573885	-3.8265916	0.5590411
C	4.4528809	-3.1120816	-1.3088886
H	5.2722205	-3.4875483	-1.9060436
C	3.4097516	-2.4362171	-1.8934771
H	3.4062492	-2.2702925	-2.9651444
C	2.3223430	-1.9455346	-1.1325298
C	-1.2238944	-3.3750071	0.8807182
H	-0.6170462	-4.2600509	0.7507614
C	-1.2035783	-2.6762816	2.1255247
H	-0.5722978	-3.0378008	2.9249808
C	-1.9664195	-1.5174963	2.3041010
H	-1.9576887	-0.9984182	3.2518435
C	-2.7164724	-0.9973353	1.2093076
H	-3.2726515	-0.0793406	1.3260388
C	-2.7047185	-1.6562176	-0.0248728
H	-3.2579358	-1.2566521	-0.8613320
C	-1.9702107	-2.8698570	-0.1804714
H	-1.9502401	-3.3597009	-1.1432470

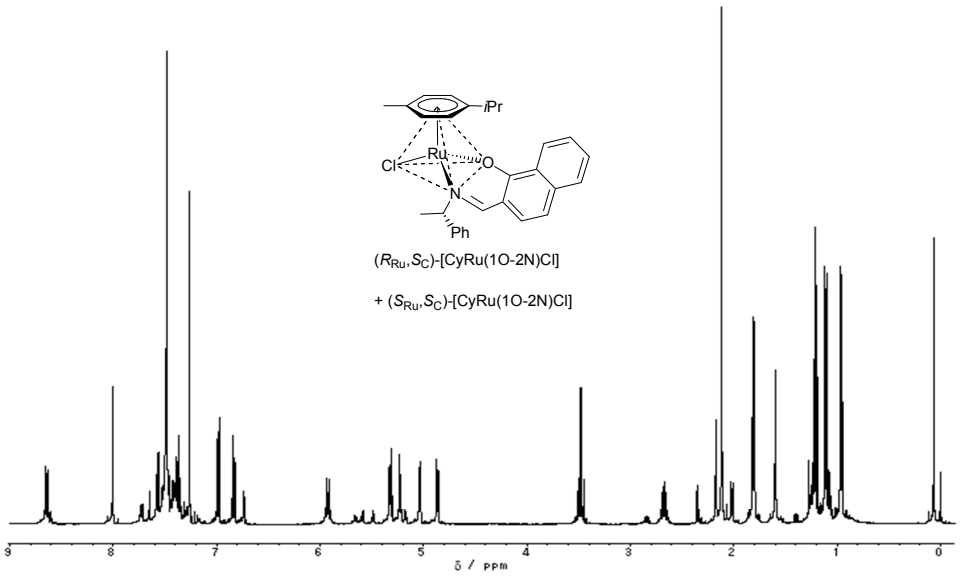


Figure S1. ^{1}H NMR spectrum of (R_{Ru},S_C)/(S_{Ru},S_C)-[CyRu(1O-2N)Cl] in $CDCl_3$.

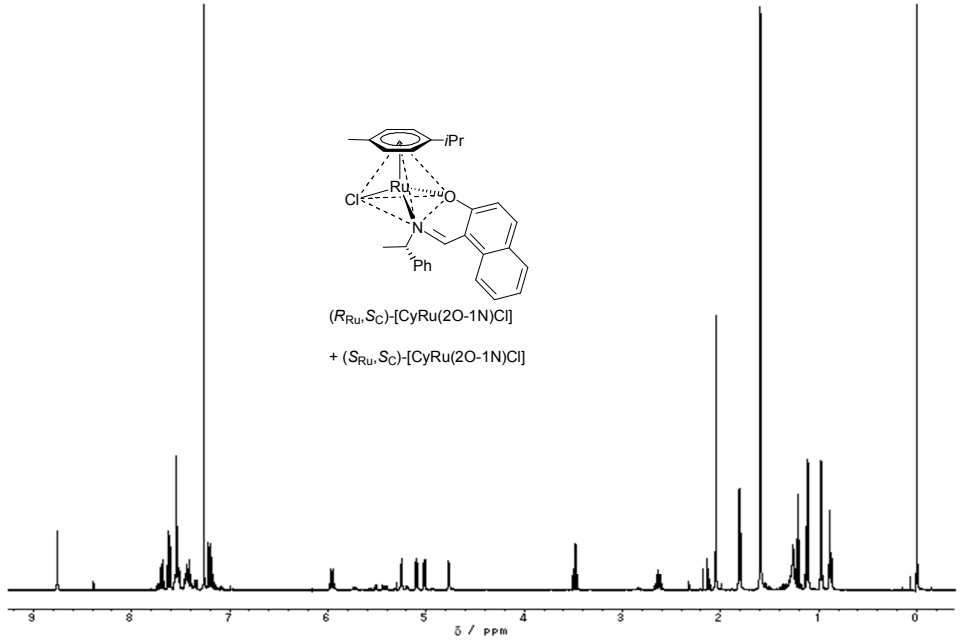


Figure S2. ^{1}H NMR spectrum of (R_{Ru},S_C)/(S_{Ru},S_C)-[CyRu(2O-1N)Cl] in $CDCl_3$.

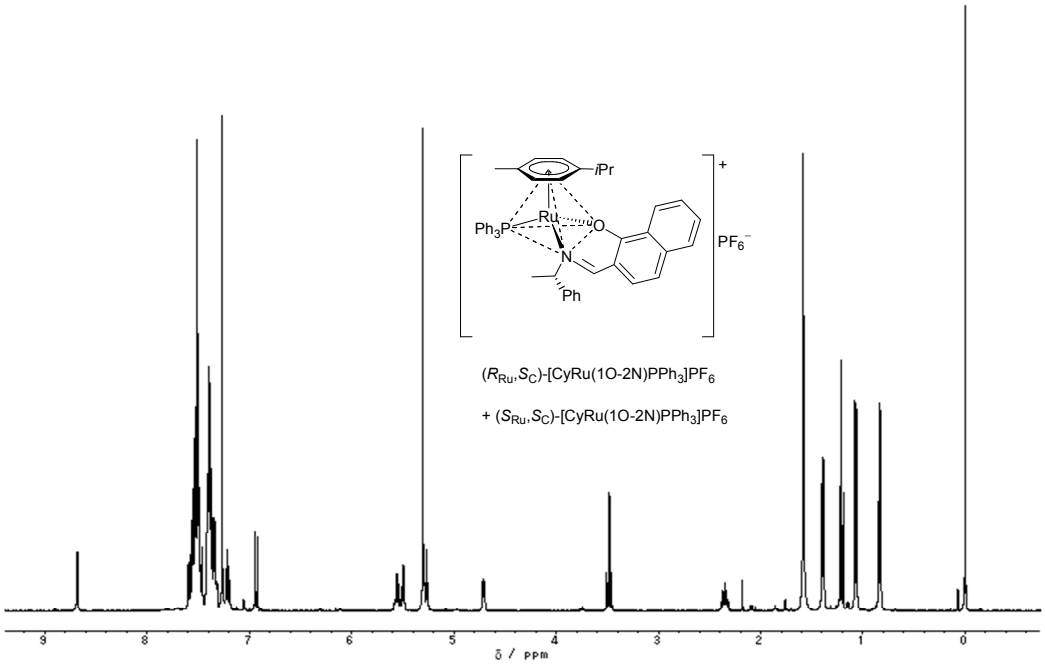


Figure S3. ^{1}H NMR spectrum of (R_{Ru},S_C)/(S_{Ru},S_C)-[CyRu(1O-2N)PPh$_3$]PF$_6$ in CDCl$_3$.

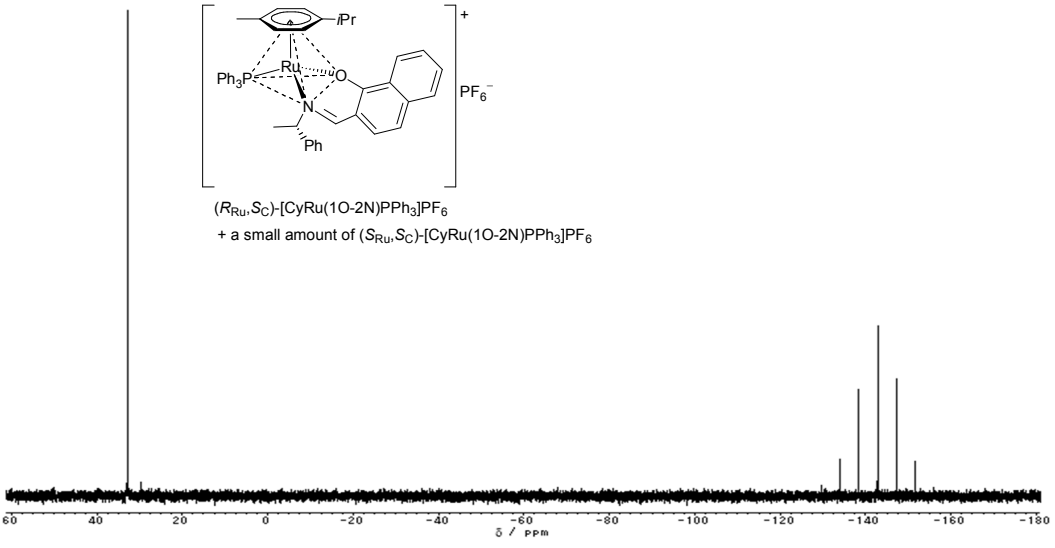


Figure S4. ^{31}P{^{1}H} NMR spectrum of (R_{Ru},S_C)-[CyRu(1O-2N)PPh$_3$]PF$_6$ and a small amount of (S_{Ru},S_C)-[CyRu(1O-2N)PPh$_3$]PF$_6$ in CDCl$_3$.

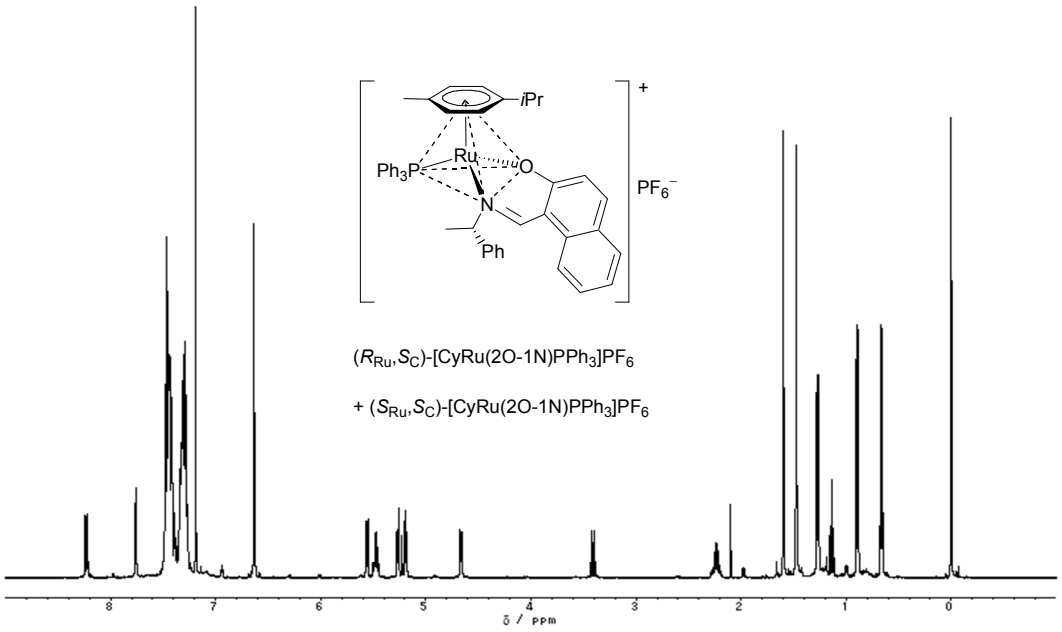


Figure S5. ^{1}H NMR spectrum of (R_{Ru},S_C)/(S_{Ru},S_C)-[CyRu(2O-1N)PPh$_3$]PF$_6$ in CDCl$_3$.

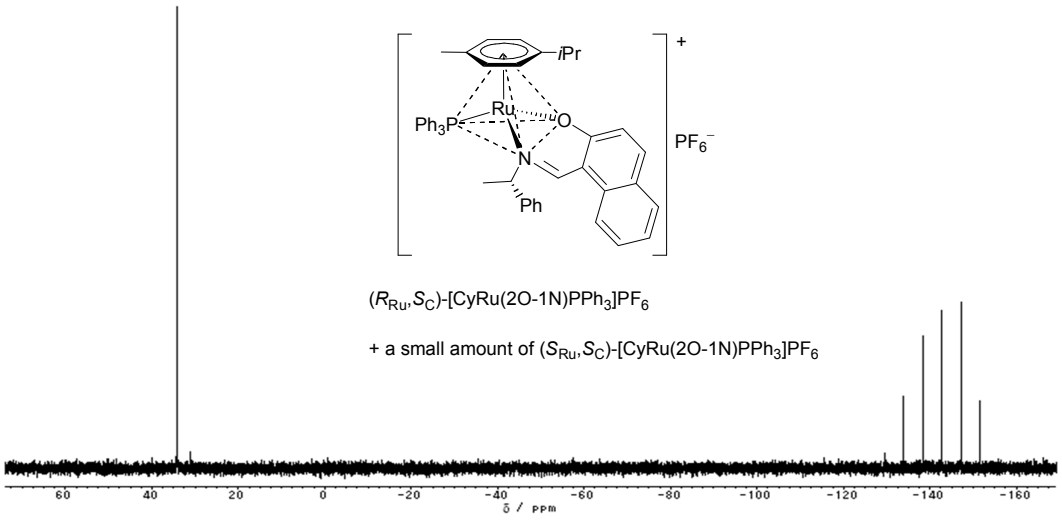


Figure S6. ^{31}P{^{1}H} NMR spectrum of (R_{Ru},S_C)-[CyRu(2O-1N)PPh$_3$]PF$_6$ and a small amount of (S_{Ru},S_C)-[CyRu(2O-1N)PPh$_3$]PF$_6$ in CDCl$_3$.

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