Supplementary information.

Table S1. Molecular mechanics data for ligand dimethyl esters (figure 2)

Ligand (diester)	Intercarbonyl distance/Å	ΔE /kJmol^{-1}	Symmetry number s	Population
5	8.80	0.00	2	0.52
	6.80	5.30	4	0.12
	8.00	5.30	1	0.03
	9.40	5.40	1	0.03
	7.30	6.60	4	0.07
	8.70	7.00	4	0.06
	4.60	7.10	4	0.06
	8.80	8.30	4	0.04
	8.80	8.40	4	0.04
	8.60	8.90	4	0.03
6	8.25	0.00	2	0.20
	6.50	0.62	4	0.31
	4.60	0.67	2	0.15
	8.25	4.18	4	0.08
	5.92	5.14	4	0.05
	6.66	6.15	4	0.03
	4.42	6.46	4	0.03
	7.96	7.24	4	0.02
	4.11	7.58	4	0.02
	7.93	7.63	4	0.02
	6.27	8.03	4	0.02
	8.03	8.03	4	0.02
	6.29	8.16	4	0.02
	7.08	9.03	4	0.01
	6.41	9.20	4	0.01
	5.58	9.47	4	0.01
	4.26	10.68	4	0.01
7	4.53	0.00	4	0.59
	6.68	2.05	4	0.26
	5.77	6.25	4	0.05
	6.40	7.92	4	0.02
	8.59	8.33	2	0.01
	8.21	8.63	4	0.02
	6.66	8.67	4	0.02
	6.65	8.81	4	0.02
	4.56	10.66	4	0.01
8	4.30	0.00	4	0.29
	4.50	1.70	4	0.15
	4.40	1.90	4	0.13
	4.50	3.40	2	0.04

	5.00	4.10	4	0.06
	4.90	4.60	4	0.05
	4.40	4.80	4	0.04
	5.00	5.90	4	0.03
	5.00	5.90	2	0.01
	7.30	6.00	4	0.03
	5.20	6.30	4	0.02
	5.90	6.60	4	0.02
	8.30	6.80	2	0.01
	7.40	8.00	4	0.01
	7.00	8.00	4	0.01
	7.10	8.10	4	0.01
	6.60	8.20	4	0.01
	5.20	8.30	4	0.01
	4.80	8.30	4	0.01
	5.40	8.40	4	0.01
	7.40	8.60	4	0.01
	6.90	8.70	4	0.01
	7.40	9.00	4	0.01
	6.20	9.20	4	0.01
	8.20	9.30	4	0.01
	8.50	9.50	4	0.01
	7.50	9.60	4	0.01
	6.40	9.70	4	0.01
9	4.30	0.00	4	0.31
	4.20	0.10	4	0.30
	4.30	1.60	2	0.08
	4.30	2.20	2	0.06
	4.60	3.70	4	0.07
	5.00	4.20	2	0.03
	4.20	4.30	2	0.03
	4.25	5.70	4	0.03
	4.30	6.88	4	0.02
	4.32	7.21	4	0.02
	4.50	7.30	4	0.02
	4.17	7.55	4	0.02
	4.67	8.05	4	0.01
	4.31	8.68	4	0.01
	4.20	10.70	4	0.00
10	4.50	0.00	4	0.26
	4.20	0.90	4	0.18
	4.50	1.70	4	0.13
	4.30	1.90	4	0.12
	4.20	3.30	4	0.07
	4.40	4.20	4	0.05
	4.84	4.34	4	0.05
	4.40	5.60	4	0.03

	4.80	5.60	4	0.03
	4.41	6.23	4	0.02
	4.80	6.70	4	0.02
	5.50	7.40	4	0.01
	4.63	8.26	4	0.01
	5.90	9.00	4	0.01
	6.00	9.30	2	0.00
	5.10	9.60	4	0.01
	5.30	10.30	4	0.00
11	5.71	0.00	4	0.16
	5.07	1.07	4	0.11
	6.00	1.46	4	0.09
	4.55	1.53	4	0.09
	7.27	1.78	4	0.08
	5.40	2.68	4	0.06
	8.00	2.71	2	0.03
	6.24	2.85	4	0.05
	4.90	3.48	2	0.02
	5.90	3.78	4	0.04
	5.50	3.84	4	0.04
	6.00	4.48	2	0.01
	4.34	4.80	4	0.02
	7.44	5.19	4	0.02
	4.54	5.26	4	0.02
	7.33	5.48	4	0.02
	7.50	5.50	4	0.02
	4.55	5.55	4	0.02
	5.38	5.56	4	0.02
	6.31	5.77	4	0.02
	5.74	5.92	4	0.02
	6.46	6.35	2	0.01
	4.63	6.37	4	0.01
	8.04	6.45	4	0.01
	6.05	7.96	4	0.01
	7.51	8.02	4	0.01
	5.60	9.19	4	0.00
	8.13	9.23	2	0.00
	6.39	9.31	4	0.00
	7.50	9.45	4	0.00
	6.45	9.71	4	0.00
13	6.80	0.00	4	0.16
	8.40	0.60	2	0.06
	8.20	0.65	4	0.13
	6.90	0.82	4	0.12
	8.20	1.74	4	0.08
	7.10	2.00	4	0.07
	5.70	2.20	2	0.03

	7.00	2.40	4	0.06
	7.20	3.50	4	0.04
	5.90	4.40	4	0.03
	8.20	4.40	4	0.03
	5.90	4.50	4	0.03
	6.10	4.70	4	0.02
	4.90	5.20	4	0.02
	6.90	5.40	4	0.02
	8.30	5.70	4	0.02
	8.60	5.90	4	0.02
	8.20	6.90	4	0.01
	6.00	7.60	4	0.01
	4.60	7.90	4	0.01
	4.60	8.10	4	0.01
	6.00	8.20	4	0.01
	7.50	8.80	2	0.00
	5.80	9.10	4	0.00
	5.00	9.20	4	0.00
	4.90	9.60	4	0.00
	8.30	9.90	4	0.00
14	5.40	0.00	4	0.17
	4.80	0.30	4	0.16
	6.50	2.00	4	0.08
	5.20	2.40	4	0.07
	7.50	2.60	4	0.06
	9.10	2.60	2	0.03
	7.50	2.60	4	0.06
	5.00	2.60	4	0.06
	8.60	3.10	2	0.03
	8.70	3.10	4	0.05
	7.90	3.30	4	0.05
	6.70	3.80	2	0.02
	8.20	3.90	2	0.02
	6.60	5.70	2	0.01
	7.90	6.00	4	0.02
	5.10	6.10	4	0.02
	8.70	6.40	4	0.01
	7.50	6.50	4	0.01
	6.60	6.90	4	0.01
	6.50	7.40	4	0.01
	7.50	7.50	4	0.01
	7.40	7.90	4	0.01
	7.70	8.00	4	0.01
	6.40	8.00	4	0.01
	5.40	8.50	4	0.01
	8.50	8.60	4	0.01
	7.60	8.70	4	0.01
	8.00	8.90	4	0.00

	6.60	9.80	4	0.00
	5.30	9.90	4	0.00
	5.30	10.50	4	0.00
15	8.00	0.00	4	0.19
	6.90	0.23	4	0.17
	7.00	0.58	4	0.15
	8.00	1.14	4	0.12
	7.40	2.44	4	0.07
	7.80	3.20	4	0.05
	5.50	4.40	4	0.03
	6.70	5.30	4	0.02
	5.80	6.10	4	0.02
	7.90	6.10	4	0.02
	5.10	6.50	4	0.01
	6.90	7.50	4	0.01
	8.00	7.60	4	0.01
	6.80	7.70	4	0.01
	8.00	7.80	4	0.01
	7.40	7.90	4	0.01
	5.60	8.00	4	0.01
	6.20	8.00	4	0.01
	6.80	8.30	4	0.01
	7.00	8.40	4	0.01
	7.60	8.40	4	0.01
	7.00	8.40	4	0.01
	7.80	8.70	4	0.01
	8.00	8.80	4	0.01
	8.00	8.80	4	0.01
	7.00	8.90	4	0.01
	5.30	9.00	4	0.01
	6.90	9.00	4	0.01
	6.00	9.10	4	0.00
	7.30	9.20	4	0.00
	7.10	9.40	4	0.00
	7.80	9.60	4	0.00
	7.70	9.60	4	0.00
	7.30	9.60	4	0.00
	7.40	9.70	4	0.00
	7.40	9.70	4	0.00
	7.70	9.70	4	0.00
	7.80	10.00	4	0.00
	7.80	10.00	4	0.00

Table S2. DFT Energies of lowest conformations of ligand dimethyl esters and corresponding monochelate complexes (pBP/DN*).

	E_{ligand}/au	$E_{chelate}$ /au	ΔE^a/kJmol^{-1}	$\Delta\Delta E^b$/kJmol^{-1}
5	-917.3803	-10672.2849	26	0
6	-1231.9318	-10986.8432	8	-18
7	-6065.1741	-15820.0828	15	-11
8	-1074.6669	-10829.5790	6	-20
9	-1389.2182	-11144.1292	9	-17
10	-6222.4639	-15977.3769	4	-22
13	-1613.1351	-11368.0154	90	64
14	-845.5425	-10600.4410	0	-26
15	-842.1371	-10597.0344	45	19

[a] $\Delta E = 2625\{(E_{chelate} + 2E_{MeOAc}) - (E_{ligand} + E_{Rh2(OAc)4})\}$
$= 2625\{E_{chelate} - E_{ligand} + 9754.9144\}$.
$Rh_2(OAc)_4$ = -10291.9001 au, MeOAc = -268.4929 au
[b] $\Delta\Delta E = \Delta E - 26$.