Electronic Supplementary Information

Synthesis and X-ray structures of cyclometalated iridium complexes including the hydrides

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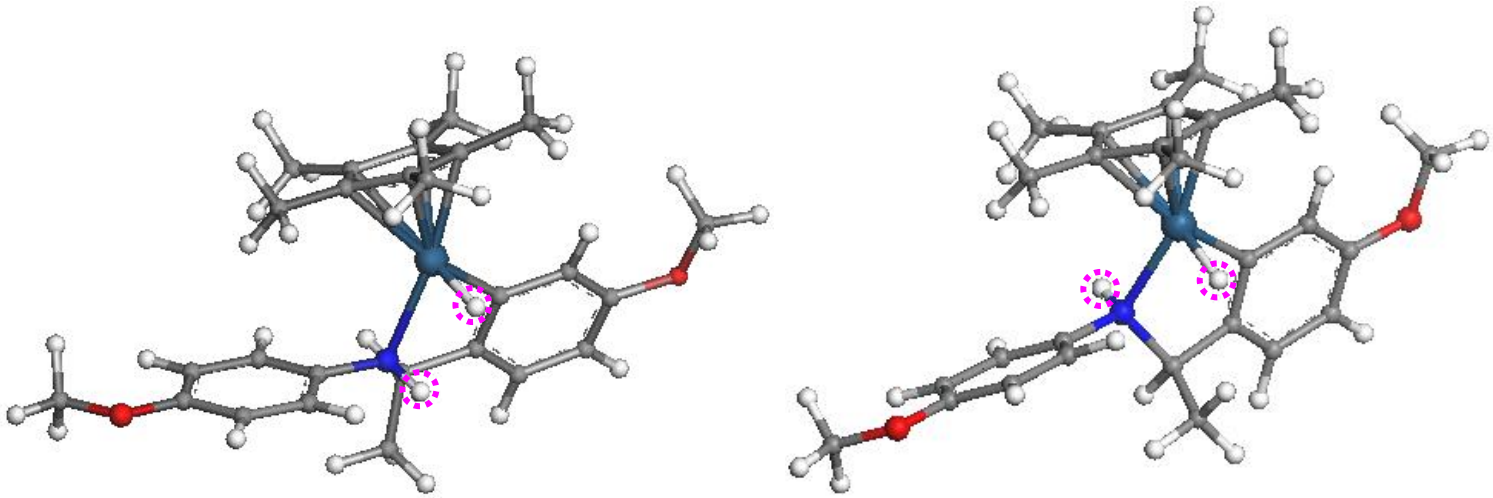

Figure S1 The structures of *cis*-**7** (left) and *trans*-**7** (right).

The bond lengths and angles of the complexes **4**, **5** and **7** were computed at different levels of theory using the DMol[3] and Gaussian codes. The structural properties of the complexes **4** and **5** from experiment are shown in Table S1, which reveals that for both complexes **4** and **5**, the differences between computational and experimental bond lengths and angles are within 2%, indicating our computational settings are reasonable. There is no experimental for the complex **7**. We compare the structural properties of *trans*-**7** and *cis*-**7** in terms of computational results.

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Table S1 Structural properties of complexes **4**, **5** and **7** from experimental data and DFT calculations. The units are [Å] for bond length and [°] for bond angles.

Catalyst	**4**	**5**	**4**	**4**	**4**	**5**	**5**	**5**	***cis*-7**	***cis*-7**	***trans*-7**	***trans*-7**
Code	**Exp**	**Exp**	**DMol^3**	**G03**	**G03**	**DMol^3**	**G03**	**G03**	**DMol^3**	**G03**	**DMol^3**	**G03**
XC	**—**	**—**	**PBE**	**PBE0**	**PBE0**	**PBE**	**PBE0**	**PBE0**	**PBE**	**PBE0**	**PBE**	**PBE0**
Basis Set	**—**	**—**	**DNP**	**LANL2DZ/ 6-31G****	**SDD/ 6-31G****	**DNP**	**LANL2DZ/ 6-31G****	**SDD/ 6-31G****	**DNP**	**LANL2DZ/ 6-31G****	**DNP**	**LANL2DZ/ 6-31G****
Ir_1-N_1	2.09	2.03	2.07	2.06	2.07	2.08	2.06	2.07	2.20	2.18	2.19	2.17
Ir_1-H_1	1.75	1.71	1.60	1.59	1.59	1.60	1.59	1.59	1.60	1.59	1.60	1.58
Ir_1-C_3	2.04	2.05	2.02	2.00	2.01	2.02	2.00	2.01	2.04	2.02	2.05	2.03
N_1-C_1	1.31	1.32	1.33	1.31	1.31	1.33	1.31	1.31	1.51	1.50	1.53	1.51
C_2-C_3	1.47	1.44	1.44	1.44	1.44	1.44	1.44	1.44	1.42	1.41	1.42	1.41
Ir_1-C	2.26	2.27	2.29	2.26	2.25	2.29	2.26	2.26	2.30	2.28	2.31	2.30
(π-ring)	2.29	2.26	2.35	2.31	2.31	2.35	2.31	2.31	2.36	2.33	2.34	2.32
[Å]	2.27	2.25	2.33	2.30	2.30	2.33	2.30	2.30	2.33	2.30	2.32	2.29
	2.26	2.23	2.27	2.25	2.25	2.27	2.26	2.26	2.25	2.23	2.25	2.22
[°]	2.21	2.17	2.22	2.19	2.19	2.22	2.19	2.19	2.19	2.15	2.20	2.17
N_1-Ir_1-H_1	81.32	88.77	85.71	85.04	85.14	85.02	84.87	84.95	82.36	82.82	86.81	86.54
H_1-Ir_1-C_3	87.10	86.45	81.61	81.30	81.26	80.45	81.37	81.23	83.60	82.66	81.92	81.65
C_3-Ir_1-N_1	76.63	77.66	77.65	77.75	77.56	77.90	77.97	77.79	76.73	76.83	77.96	77.86