

Electronic supplementary information

REVERSIBLE COORDINATION OF THE CARBONYL LIGANDS IN CYMANTRENE AS A WAY TO CREATE PHOTOACTIVE SYSTEMS

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Table S1. IR and ¹H NMR spectral data for compounds **1–75**

Compound	ν (CO)/cm ⁻¹ , ligand	ν CO/cm ⁻¹ , amide	λ_{\max} /nm (ϵ)	δ (α -H in Cp)/ppm	δ (β -H in Cp)/ppm	δ (CH)/ppm
1	2040, 1930	1717	330 (531)	4.26	3.67	4.58
10	1930, 1857	1666	426 (178), 516 (245)	5.04, 5.10	2.87, 3.36	3.06
2	2020, 1935	1694	330 (725)	Major conformer: 4.24, 4.46; minor conformer: 4.17, 4.52	Major conformer: 3.84, 4.01; minor conformer: 3.84, 4.01	Major conformer: 5.38; minor conformer: 5.07
11	1955, 1854	1640	426 (179), 515 (179)	5.17	2.71, 3.65	3.25
3	2022, 1933	1719	332 (1372)	4.22	3.88	3.52
12	1933, 1856	1668	426 (271), 516 (200)	5.07	2.72	3.11
4	2020, 1936	1690	330 (986)	4.36	3.96	3.68
13	1930, 1857	1650	506 (327)	4.96	3.26	2.80
5	2020, 1937	1675	328 (1185)	4.33	3.92	3.90
14	1930, 1859	1631	438 (887), 533 (339)	5.08	3.33	3.08
6	2021, 1936	1685	331 (1309)	4.31, 4.41	3.92	4.90
15	1932, 1859	1654	392 (146), 506 (67)	4.95, 4.99	3.03, 3.51	3.19
7	2019, 1938	1672	332 (1697)	4.30, 4.33	3.88	5.19
16	1930, 1859	1632	435 (437), 532 (147)	5.09, 5.14	3.19, 3.55	3.36
8	2017, 1938	1673	339 (2089)	4.28, 4.44	3.96, 3.97	5.01
17	1929, 1857	1628	427 (454), 493 (280)	5.08, 5.11	3.09, 3.39	3.23
9	2022, 1940	1691	330 (1086)	4.05, 4.21	3.72, 3.79	5.99
18	1930, 1858	1650	505 (349)	4.71, 4.93	3.02, 3.23	4.17
19	2014, 1933	1697	329 (1244)	4.59, 4.64	3.79	
25	1927, 1853	1632	503 (1300)	4.94	2.96, 3.16	
29	1963, 1896	1695	326 (1230)	4.47, 5.17	3.19, 3.45	
20	2026, 1935	1700	328 (793)	4.32, 4.54	3.91, 4.06	4.97
26	1939, 1870		516 (305)	5.09, 5.14	2.57, 3.56	2.91
30	1977, 1914	1700	341 (700)	4.34, 4.89	2.75, 3.59	2.83
21	2021, 1936	1685	331 (1309)	4.31, 4.41	3.92	4.90
27	1941, 1872	1605	509 (900)	5.01, 5.05	2.53	3.32
31	1975, 1917	1663	331 (1200)	4.27, 4.58	3.59, 3.64	5.52

22	2021, 1935	1700	329 (1037)	3.98	3.95	3.76
24	1964, 1901	1700	334 (885)	4.48, 4.51	3.66, 3.70	2.70
23	2021, 1936	1659	329 (1110)	Major conformer: 4.42; minor conformer: 3.89	Major conformer: 3.87; minor conformer: 3.87	Major conformer: 3.81; minor conformer: 3.82
28	1931, 1856		519	4.88	3.17	2.87
32	1965, 1903	1659	333 (934)	4.32, 4.63	3.58, 3.63	2.13
33	2020, 1936	1673	330 (910)	4.22	3.79	3.75
44	1930, 1856	1634	424 (734); 525 (254)	4.97	3.20	2.88
34	2020, 1937	1673	334(1177)	4.24	3.80	3.79
45	1930, 1858	1633	408 (1169); 525 (668)	4.99	3.19	2.94
35	2020, 1936	1671	334 (1023)	4.23	3.81	3.76
46	1928, 1858	1633	434 (1001); 548 (358)	4.95	3.20	2.86
36	2019, 1938,	1671	337 (958)	4.20, 4.27	3.78, 3.80	5.11
47	1929, 1857	1631	427 (988); 521 (408)	4.97, 5.04	3.03, 3.37	3.24
37	2019, 1937	1672	333 (1295)	4.22, 4.26	3.78, 3.81	5.19
48	1929, 1858	1634	430 (1269); 520 (507)	4.95, 5.01	3.04, 3.40	3.28
38	2019, 1938	1671	341 (775)	4.30, 4.38	3.89, 3.93	5.23
49	1929, 1856	1631	430 (1095); 522 (414)	4.94, 5.01	3.05, 3.36	3.25
39	2020, 1937	1674	335 (1058)	5.15	4.90	4.28
50	1931, 1857	1636	431 (1033); 505 (436)	4.97	3.19	2.93
40	2020, 1936	1673	330 (1522)	5.15	4.91	4.26
51	1930, 1858	1633	419 (856); 511 (285)	4.95	3.20	2.85
41	2020, 1936	1674	329 (1056)			
52	1929, 1857	1634	429 (991); 515 (394)			
42	2019, 1939	1672	335 (1202)			
53	1930, 1859	1632	436 (1111); 534 (412)			
43	2019, 1938	1671	334 (1009)	4.23, 4.26	3.78, 3.80	5.08
54	1929, 1857	1631	439 (887); 533 (330)	4.92, 4.98	3.01, 3.37	3.17
55	2021, 1936	1674	330 (942)	4.17	4.07	4.65
59	1966, 1905	1650	332 (842)	5.13, 5.28	4.18, 4.28	4.85
63	1927, 1857	1631				
56	2019, 1938	1671	328 (1146)	4.50, 4.72	4.05, 4.21	5.26
60	1958, 1896	1671	323 (990)	4.35, 5.09	3.65, 3.95	5.45
64	1927, 1857	1631	532 (505)			
57	2021, 1936	1647	330 (1073)	5.05	4.22	4.89
61	1965, 1904		330 (1333)			
65	1933, 1858	1631	417 (333),			

			520 (123)			
58	2021, 1931 .	1671	330 (1340)			
62	1966, 1903		294 (3400)			
66	1936, 1857		410 (633), 527 (123)			
67	2019, 1940		341 (993)	5.10	4.73	4.96
71	1931, 1861		455 (360); 570 (128)	4.76	3.03	3.16
68	2019, 1938		345 (1054)	5.29	4.73	5.22
72	1931, 1861		460 (360); 565 (168)	4.49, 5.13	2.51, 3.62	4.30
69	2023, 1942		332 (9846)	5.18	4.72	5.46
74	1983, 1930		334 (8156)	5.02	4.45, 4.84	4.58
75	1927, 1853		517 (268)	4.88	2.69	3.65

Table S2. Kinetic data for the thermal ligand exchange

Reaction	$t_{1/2}$	$K_{\text{obs}} \cdot 10^4$
10 – 1	96	1.20 (0.02)
11 – 2	64	1.81 (0.04)
13 – 4	52	2.35(0.03)
14 – 5	64	1.82(0.02)
15 – 6	129	0.89(0.01)
16 – 7	103	1.18(0.03)
17 – 8	115	1.03(0.01)
18 – 9	99	1.17(0.03)
10 + PPh3	144	0.80 (0.01)
17 + PPh3	172	0.67 (0.01)
25 – 29	67	1.72 (0.02)
26 – 30	3	38.51 (0.07)
27 – 31	5	23.12 (0.06)
28 – 32	5	23.18 (0.06)
44 – 33	90	1.28 (0.01)
45-34	76	1.52 (0.02)
46 – 35	142	0.81 (0.005)
47 – 36	210	0.55 (0.005)
48 – 37	136	0.82 (0.005)
49 – 38	91	1.27 (0.01)
50 – 39	184	0.62 (0.005)
51 – 40	162	0.71 (0.005)
52 – 41	120	0.96 (0.005)
53 – 42	136	0.86 (0.005)
54 – 43	116	0.99 (0.005)
63 – 59	10	11.61 (0.05)
64 – 60	124	0.93 (0.01)
65 – 61	10	11.56 (0.05)
66 – 62	127	0.91 (0.01)
71 – 68	3	33.84 (0.09)
72 – 69	53	2.19 (0.02)
74 – 69	575	0.2 (0.005)
75 – 74	3	38.5 (0.1)

Table S3. Ratio of the chelates after irradiation of the tricarbonyl complexes

Irradiated compound	Olefine chelate	Chelate with the Mn–O=C bond
19	1	5
20	3	1
21	1	5
22	1	0
23	4	1
59	2	1
60	2	1
61	2	1
62	2	1