

(P,C)-Cyclometallated complexes deriving from naphthyl phosphines: versatile and powerful tools in organometallic chemistry

Julien Monot, Enrico Marelli, Blanca Martin-Vaca, Didier Bourissou*

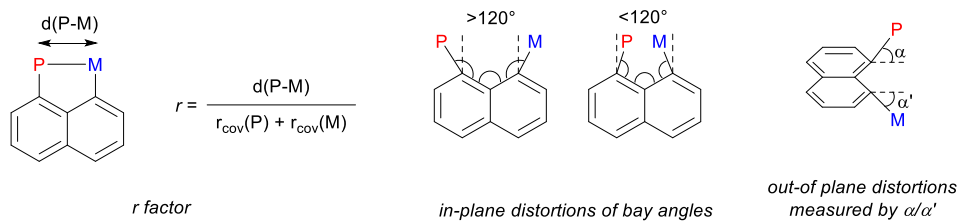
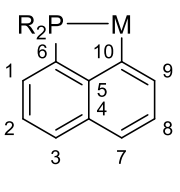
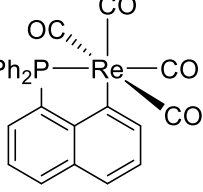
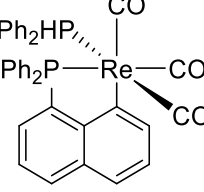
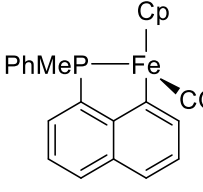
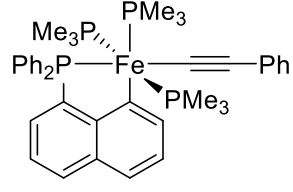
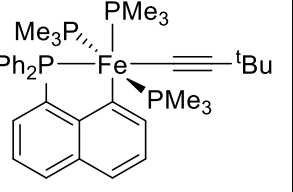
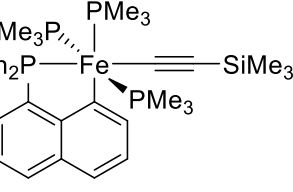
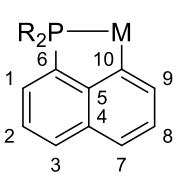
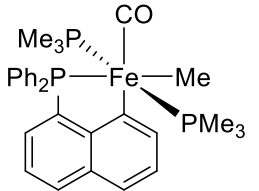
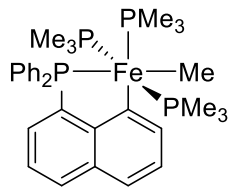
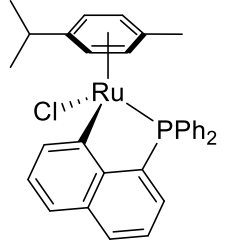
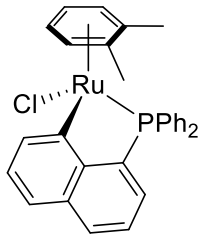
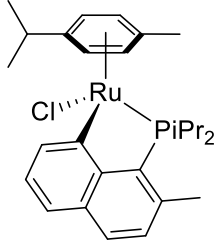
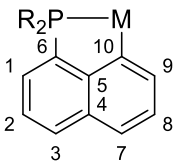
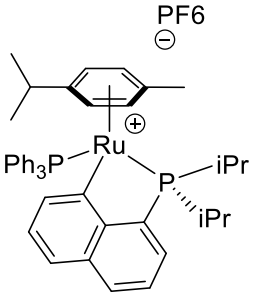
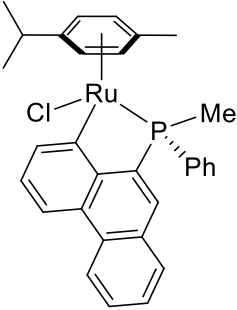
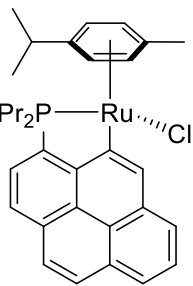
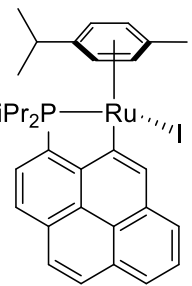
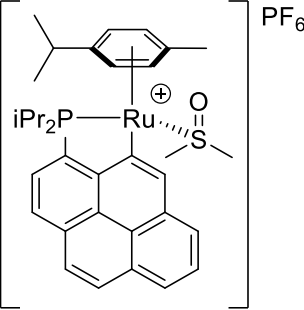
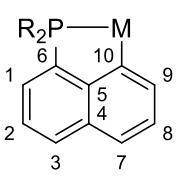
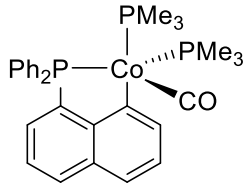
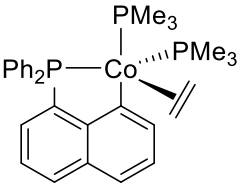
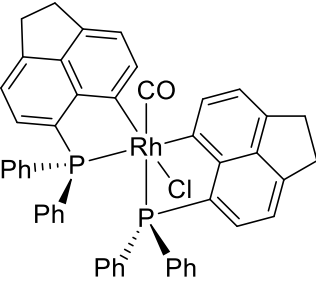
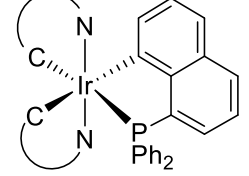
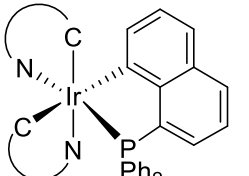


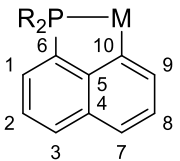
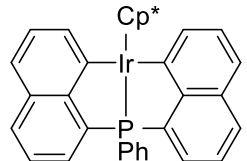
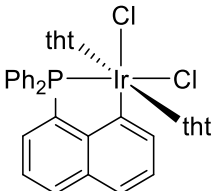
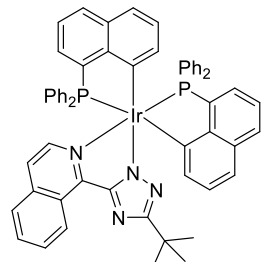
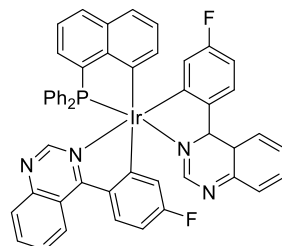
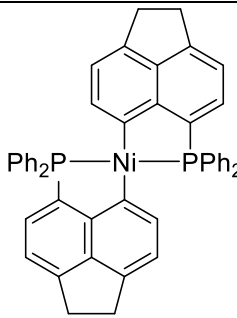
Table S1. Selected geometric parameters (Å, °) of the 77 (P,C)-naphthyl cyclometalated complexes deposited in the CCDC database.

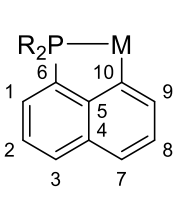
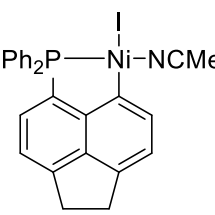
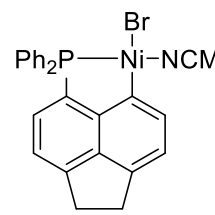
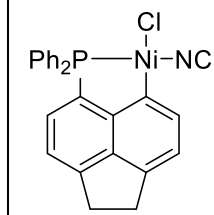
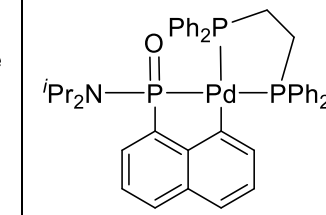
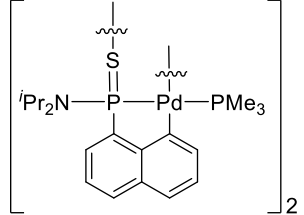
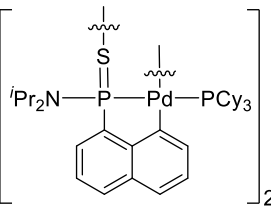
							
Reference		1	2	3	4	5	5
r factors							
d(P-M)		2.418(6)	2.4203	2.1662	2.2485	2.2270	2.2396
$\Sigma r_{\text{cov}}(\text{P-M})$		2.58	2.58	2.39	2.39	2.39	2.39
r(P-M)		0.937	0.938	0.906	0.941	0.932	0.937
d(M-C10)		2.215(5)	2.2249	1.9915	2.015	2.0243	2.0058
$\Sigma r_{\text{cov}}(\text{M-C10})$		2.24	2.24	2.05	2.05	2.05	2.05
r(M-C10)		0.989	0.993	0.971	0.983	0.987	0.978
P-M-C10		79.48	79.04	84.49	84.05	83.57	83.99
Bay angles							
M-C10-C5		119.48	119.89	119.90	119.97	119.48	120.06
C5-C6-P		115.0	114.88	110.90	111.95	110.86	111.46
Out-of plane distortions							
α (C3-C6-P)		0.32	3.77	5.39	8.43	8.03	6.56
α' (C7-C10-M)		4.70	4.07	1.11	1.99	5.74	5.74

					
Reference	5	5	6	6	6
r factors					
d(P-M)	2.2068	2.219(1)	2.296(1)	2.2768	2.3030
$\Sigma r_{\text{cov}}(\text{P-M})$	2.58	2.39	2.53	2.53	2.53
r(P-M)	0.855	0.928	0.907	0.900	0.910
d(M-C10)	2.0578	2.020(7)	2.084(6)	2.0772	2.0730
$\Sigma r_{\text{cov}}(\text{M-C10})$	2.24	2.05	2.19	2.19	2.19
r(M-C10)	0.918	0.985	0.951	0.948	0.946
P-M-C10	84.37	84.00	80.94	80.54	79.97
Bay angles					
M-C10-C5	117.78	118.75	120.95	121.18	122.11
C5-C6-P	111.31	110.66	111.17	111.20	109.41
Out-of plane distortions					
$\alpha(\text{C3-C6-P})$	1.12	8.58	2.30	3.99	12.19
$\alpha'(\text{C7-C10-M})$	1.83	5.61	3.95	6.98	1.32

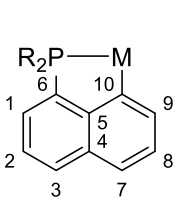
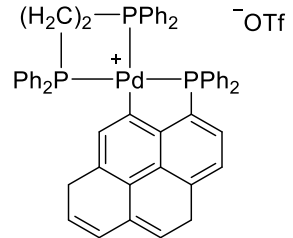
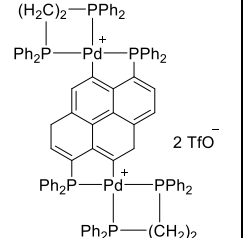
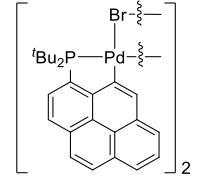
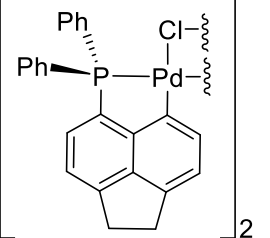
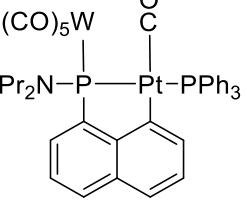
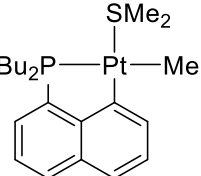
					
Reference	6	7	8	8	8
r factors					
d(P-M)	2.3328	2.282(3)	2.3060	2.3130	2.3230 2.3280
$\Sigma r_{\text{cov}}(\text{P-M})$	2.53	2.53	2.53	2.53	2.53
r(P-M)	0.922	0.902	0.911	0.914	0.918 0.920
d(M-C10)	2.0933	2.094(8)	2.0840	2.0880	2.0650 2.0640
$\Sigma r_{\text{cov}}(\text{M-C10})$	2.19	2.19	2.19	2.19	2.19
r(M-C10)	0.956	0.956	0.951	0.953	0.943 0.942
P-M-C10	79.83	80.41	81.24	80.96	80.10 80.31
Bay angles					
M-C10-C5	121.62	121.80	120.61	120.74	120.94 122.15
C5-C6-P	111.41	111.95	112.85	113.04	111.76 112.02
Out-of plane distortions					
$\alpha(\text{C3-C6-P})$	6.41	8.23	5.81	7.51	12.61 7.62
$\alpha'(\text{C7-C10-M})$	4.92	3.32	3.50	1.17	1.27 5.18

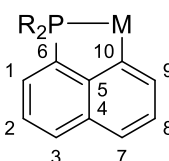
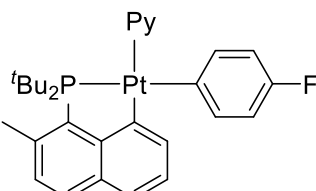
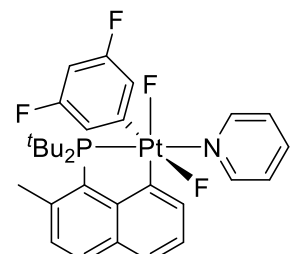
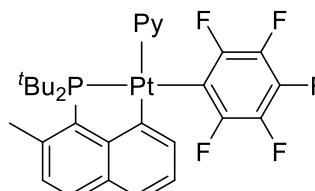
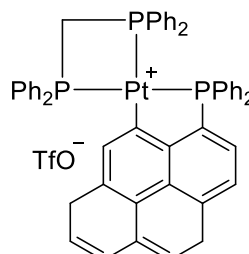
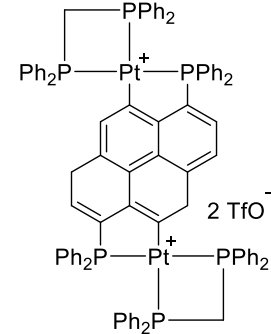
					
Reference	9	9	10	10	10
r factors					
d(P-M)	2.175(3)	2.1831	2.3748 2.3814	2.330(2)	2.2470(9)
$\Sigma r_{\text{cov}}(\text{P-M})$	2.33	2.33	2.49	2.48	2.48
r(P-M)	0.933	0.937	0.954 0.956	0.900	0.906
d(M-C10)	1.996(3)	2.0007	2.0929 2.0616	2.114(6)	2.122(4)
$\Sigma r_{\text{cov}}(\text{M-C10})$	1.99	1.99	2.15	2.14	2.14
r(M-C10)	1.003	1.00	0.973 0.959	0.988	0.991
P-M-C10	84.00	83.81	82.85 82.53	82.0(2)	81.4(1)
Bay angles					
M-C10-C5	117.91	118.57	117.68 116.70	120.1(5)	117.9(3)
C5-C6-P	110.17	111.01	112.80 111.65	113.5(5)	112.0(3)
Out-of plane distortions					
α (C3-C6-P)	5.69	5.55	6.69	2.33	6.57
α' (C7-C10-M)	11.69	11.43	2.43	1.66	6.69

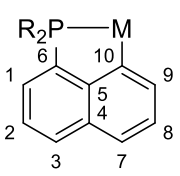
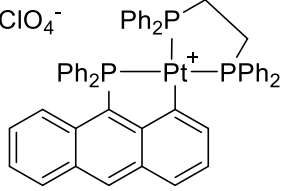
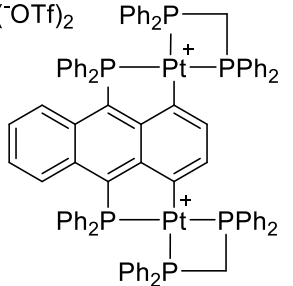
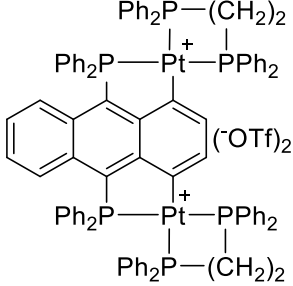
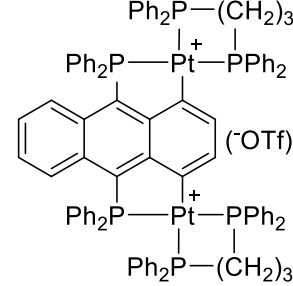
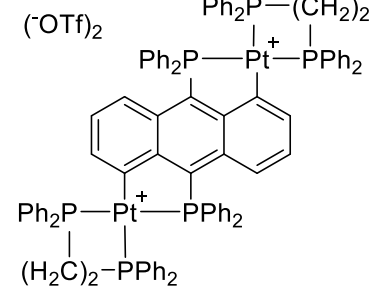
					
Reference	11	12	12	13	14
r factors					
d(P-M)	2.223(1)	2.2485	2.3360 2.2814	2.2470	2.1740
$\Sigma r_{\text{cov}}(\text{P-M})$	2.48	2.48	2.48	2.48	2.31
r(P-M)	0.896	0.906	0.942 0.920	0.906	0.941
d(M-C10)	2.069(4) 2.045(6)	2.0529	2.07 2.0844	2.1215	1.9690
$\Sigma r_{\text{cov}}(\text{M-C10})$	2.14	2.14	2.14	2.14	1.97
r(M-C10)	0.967 0.955	0.959	0.967 0.974	0.991	0.999
P-M-C10	80.9(1) 82.3(1)	84.20	83.63 82.76	81.38	85.99
Bay angles					
M-C10-C5	119.8(4) 120.8(4)	119.12	118.68 120	117.85	117.17
C5-C6-P	109.8(4) 111.3(4)	113.56	113.77 114.77	111.98	109.25
Out-of plane distortions					
$\alpha(\text{C3-C6-P})$	3.28 11.71	2.48	6.56 1.19	9.36	9.47
$\alpha'(\text{C7-C10-M})$	3.44 4.93	3.15	1.35 1.09	7.85	5.68

						
Reference	14	14	14	15	15	15
r factors						
d(P-M)	2.1557	2.1639	2.1631	2.286	2.2628 2.2636	2.2531 2.2595
$\Sigma r_{\text{cov}}(\text{P-M})$	2.31	2.31	2.31	2.46	2.46	2.46
r(P-M)	0.933	0.937	0.936	0.929	0.920 0.920	0.916 0.918
d(M-C10)	1.9278	1.9212	1.9262	2.092	2.0466 2.0391	2.0769 2.0783
$\Sigma r_{\text{cov}}(\text{M-C10})$	1.97	1.97	1.97	2.12	2.12	1.12
r(M-C10)	0.978	0.975	0.978	0.987	0.965 0.962	0.980 0.980
P-M-C10	86.01	85.97	85.99	83.65	83.23 83.14	82.99 83.49
Bay angles						
M-C10-C5	118.13	118.15	118.23	118.67	120.01 119.08	119.28 119.06
C5-C6-P	107.92	105.05	108.00	114.74	112.50 111.77	112.77 113.16
Out-of plane distortions						
$\alpha(\text{C3-C6-P})$	1.68	1.63	1.19	3.46	7.29 11.95	3.61 2.56
$\alpha'(\text{C7-C10-M})$	1.12	6.86	6.50	5.63	2.42 5.69	1.26 2.13

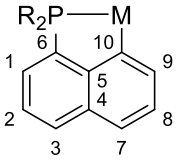
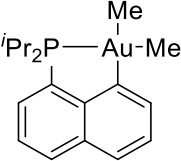
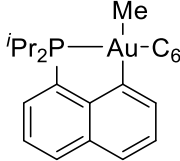
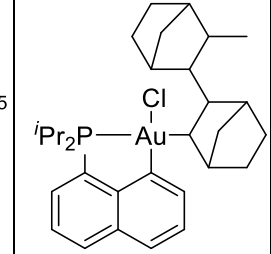
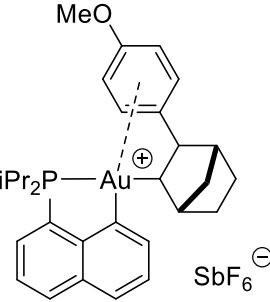
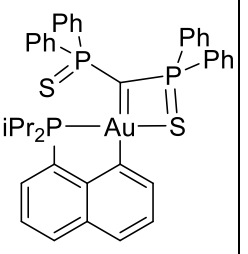
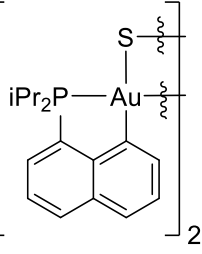
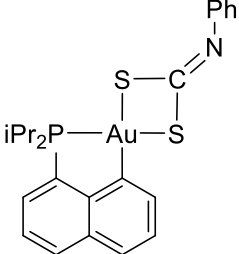
Reference	15	15	16	17	18	19
r factors						
d(P-M)	2.2585(5) 2.2596(4)	2.2546(9) 2.2456(8)	2.2190	2.229	2.1937 2.1960	2.2180 2.2117
$\Sigma r_{cov}(P-M)$	2.46	2.46	2.46	2.46	2.46	2.46
r(P-M)	0.918 0.918	0.916 0.913	0.902	0.906	0.891 0.892	0.902 0.899
d(M-C10)	2.069(2) 2.070(2)	2.027(3) 2.044(3)	1.9863	2.012	1.9888 1.9860	1.9843 1.9832
$\Sigma r_{cov}(M-C10)$	2.12	2.12	2.12	2.12	2.12	2.12
r(M-C10)	0.976 0.976	0.956 0.964	0.937	0.949	0.938 0.937	0.936 0.935
P-M-C10	84.17(6) 84.17(6)	83.74(8) 83.77(8)	83.61	83.19	83.45 83.48	83.01 83.39
Bay angles						
M-C10-C5	118.5(2) 118.5(2)	118.8(2) 119.1(2)	121.49	120.20	121.17 121.02	119.94 120.07
C5-C6-P	113.6(2) 113.2(2)	112.3(2) 112.3(2)	110.95	111.25	109.69 109.92	107.00 112.97
Out-of plane distortions						
α (C3-C6-P)	1.64 2.83	3.03 3.42	0.23	3.37	0.37 0.98	9.99 10.45
α' (C7-C10-M)	2.04 1.91	8.42 3.87	2.38	6.45	2.84 0.39	6.39 1.29

						
Reference	20	20	21	10	22	23
r factors						
d(P-M)	2.2977	2.3033	2.2587	2.2227	2.337	2.2991
$\Sigma r_{\text{cov}}(\text{P-M})$	2.46	2.46	2.46	2.46	2.43	2.43
r(P-M)	0.934	0.936	0.918	0.903	0.962	0.946
d(M-C10)	2.0821	2.0800	2.0285	2.0038	2.073	2.0358
$\Sigma r_{\text{cov}}(\text{M-C10})$	2.12	2.12	2.12	2.12	2.09	2.09
r(M-C10)	0.982	0.981	0.957	0.945	0.992	0.974
P-M-C10	82.95	83.16	83.38	84.12	84.59	83.82
Bay angles						
M-C10-C5	118.58	118.54	119.16	117.70	118.45	119.89
C5-C6-P	114.49	113.75	112.05	109.23	115.50	113.18
Out-of plane distortions						
$\alpha(\text{C3-C6-P})$	1.58	0.94	0.53	1.54	2.95	2.94
$\alpha'(\text{C7-C10-M})$	2.08	1.16	5.77	6.26	1.44	2.88

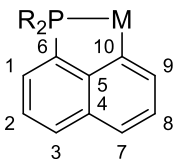
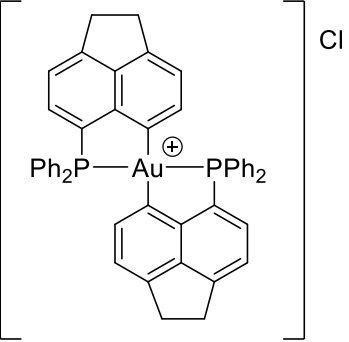
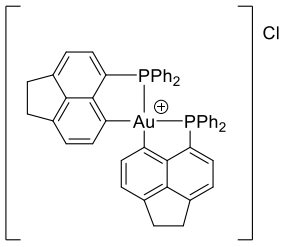
					
Reference	24	24	24	20	20
r factors					
d(P-M)	2.3335	2.3210	2.3122	2.2597	2.2849
$\Sigma r_{\text{cov}}(\text{P-M})$	2.43	2.43	2.43	2.43	2.43
r(P-M)	0.960	0.955	0.951	0.930	0.940
d(M-C10)	2.0082	2.0063	2.0106	2.0512	2.0516
$\Sigma r_{\text{cov}}(\text{M-C10})$	2.09	2.09	2.09	2.09	2.09
r(M-C10)	0.961	0.960	0.962	0.981	0.981
P-M-C10	82.93	82.61	83.00	83.63	84.07
Bay angles					
M-C10-C5	122.34	120.69	121.73	118.35	117.73
C5-C6-P	110.61	109.86	111.08	112.65	113.47
Out-of plane distortions					
$\alpha(\text{C3-C6-P})$	7.88	11.62	5.67	3.55	3.32 1.24
$\alpha'(\text{C7-C10-M})$	3.62	4.11	2.76	2.05	1.28 2.80

					
Reference	25	25	25	25	25
r factors					
d(P-M)	2.2923	2.2703	2.2814 2.2883	2.2800	2.2817
$\Sigma r_{\text{cov}}(\text{P-M})$	2.43	2.43	2.43	2.43	2.43
r(P-M)	0.943	0.934	0.939 0.941	0.938	0.939
d(M-C10)	2.0770	2.0422	2.1056 2.0641	2.0789	2.0734
$\Sigma r_{\text{cov}}(\text{M-C10})$	2.09	2.09	2.09	2.09	2.09
r(M-C10)	0.994	0.977	1.007 0.987	0.995	0.992
P-M-C10	82.77	83.74	82.38 81.63	80.81	82.54
Bay angles					
M-C10-C5	118.91	118.81	118.09 122.34	120.81	119.78
C5-C6-P	112.08	110.46	113.09 112.57	112.50	112.29
Out-of plane distortions					
$\alpha(\text{C3-C6-P})$	6.05	0.99	3.97 5.86	4.09	7.20
$\alpha'(\text{C7-C10-M})$	2.77	2.89	1.54 2.72	4.12	2.94

Reference	25	26	26	27	27	28	29
r factors							
d(P-M)	2.2817	2.284(1)	2.2728	2.3498	2.3678	2.3433	2.330
$\Sigma r_{\text{cov}}(\text{P-M})$	2.43	2.43	2.43	2.43	2.43	2.43	2.43
r(P-M)	0.939	0.940	0.935	0.967	0.974	0.964	0.959
d(M-C10)	2.0639	2.070(4)	2.0518	2.0372	2.0798	2.0569	2.0313
$\Sigma r_{\text{cov}}(\text{M-C10})$	2.09	2.09	2.09	2.09	2.09	2.09	2.09
r(M-C10)	0.987	0.990	0.982	0.975	0.995	0.984	0.972
P-M-C10	80.86	84.4(1)	84.52	84.66	83.99	84.87	84.63
Bay angles							
M-C10-C5	120.17	117.2(3)	118.19	118.36	117.84	118.89	118.78
C5-C6-P	111.61	114.1(3)	112.82	114.94	114.22	115.25	115.76
Out-of plane distortions							
α (C3-C6-P)	7.34	4.81	1.49	4.42	6.66	3.81	2.52
α' (C7-C10-M)	7.64	2.09	0.60	1.97	3.87	0.80	2.56

							
Reference	30	30	30	28	31	31	31
r factors							
d(P-M)	2.3161	2.3399	2.3534	2.4000	2.2880 2.2760	2.2860	2.2920
$\Sigma r_{\text{cov}}(\text{P-M})$	2.43	2.43	2.43	2.43	2.43	2.43	2.43
r(P-M)	0.953	0.963	0.968	0.988	0.941 0.937	0.941	0.943
d(M-C10)	2.1016	2.0849	2.0450	2.0370	2.0740 2.0710	2.0710	2.0580
$\Sigma r_{\text{cov}}(\text{M-C10})$	2.09	2.09	2.09	2.09	2.09	2.09	2.09
r(M-C10)	1.00	0.997	0.978	0.975	0.992 0.992	0.991	0.985
P-M-C10	83.36	82.86	84.35	84.15	83.88 83.51	83.85	83.89
Bay angles							
M-C10-C5	118.42	118.15	117.55	118.02	118.72 118.98	118.15	118.65
C5-C6-P	114.92	113.81	114.03	114.65	114.26 113.53	113.58	113.87
Out-of plane distortions							
$\alpha(\text{C3-C6-P})$	3.11	9.21	6.75	5.23	4.70 6.43	5.84	4.82
$\alpha'(\text{C7-C10-M})$	4.29	4.54	1.60	4.47	1.51 1.82	2.03	1.39

Reference	31	32	33	33	34	34	35
r factors							
d(P-M)	2.3050	2.2616	2.3058	2.2975	2.3380	2.3770	2.2864
$\Sigma r_{cov}(P-M)$	2.43	2.43	2.43	2.43	2.43	2.43	2.43
r(P-M)	0.948	0.931	0.949	0.945	0.962	0.978	0.941
d(M-C10)	2.0640	2.0045	2.0599	2.0778	2.0970	2.1180	2.0429
$\Sigma r_{cov}(M-C10)$	2.09	2.09	2.09	2.09	2.09	2.09	2.09
r(M-C10)	0.987	0.959	0.985	0.994	1.003	1.013	0.977
P-M-C10	84.29	84.13	84.88	84.33	83.00	84.28	85.08
Bay angles							
M-C10-C5	118.44	118.81	117.61	117.64	119.36	117.39	115.68
C5-C6-P	114.05	112.95	114.56	114.53	113.64	116.52	111.49
Out-of plane distortions							
α (C3-C6-P)	4.86	2.76	2.69	4.77	4.90	1.85	6.82
α' (C7-C10-M)	1.68	5.33	0.95	3.41	1.59	5.55	7.17

		
Reference	35	36
r factors		
d(P-M)	2.3290	2.3700 2.3716
$\Sigma r_{\text{cov}}(\text{P-M})$	2.43	2.43
r(P-M)	0.958	0.975 0.976
d(M-C10)	2.1001	2.0933 2.0890
$\Sigma r_{\text{cov}}(\text{M-C10})$	2.09	2.09
r(M-C10)	1.005	1.00 0.999
P-M-C10	83.84	83.51 83.22
Bay angles		
M-C10-C5	116.12	115.69 115.80
C5-C6-P	113.16	112.93 112.72
Out-of plane distortions		
$\alpha(\text{C3-C6-P})$	0.86	5.73 9.08
$\alpha'(\text{C7-C10-M})$	1.90	2.98 1.63

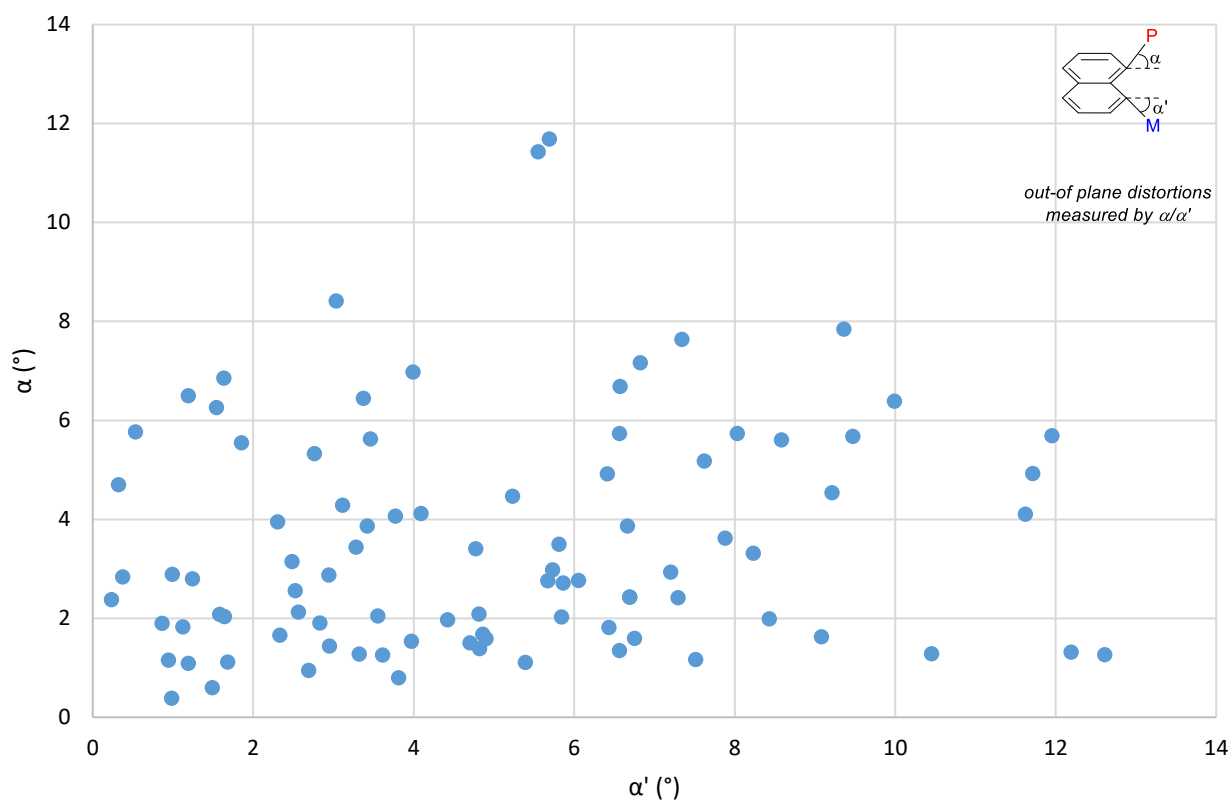


Chart S1. Plot of the out-of-plane distortion angle α against the out-of-plane distortion angle α' .

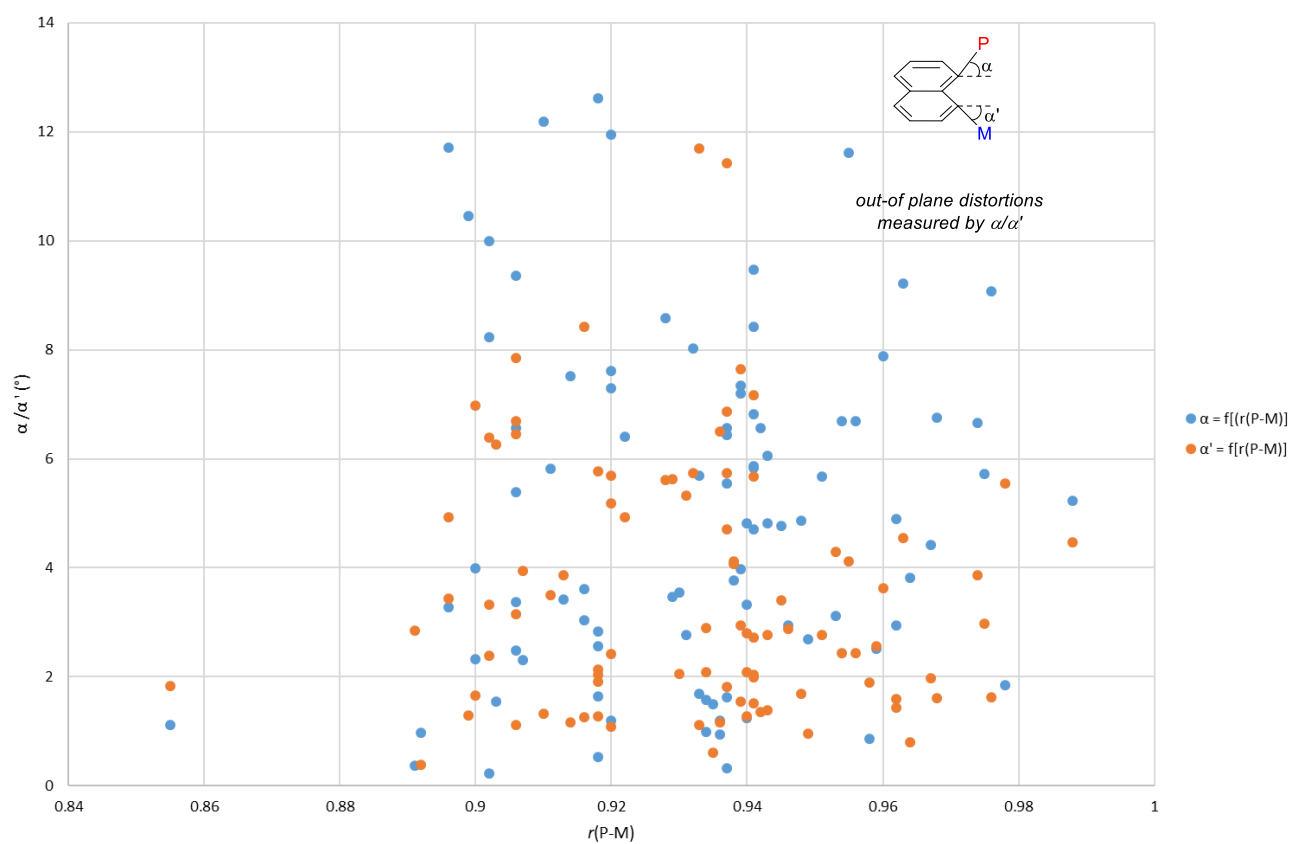


Chart S2. Plot of the out-of plane distortion angle α against the $r(P-M)$ factor (in blue) and plot of the out-of plane distortion angle α' against the $r(P-M)$ factor (in orange).

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