SUPPLEMENTARY DATA

for

Buckling Under Strain: Relief of Steric Pressure Occurs Differently for Sm^{III} Porphyrinogen Complexes of the π-Bound Auxiliary Ligands Cyclopentadienyl and Cyclooctatetraenediyl

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SYNTHESIS OF 6.

SYNTHESIS OF 7.

TABLE S1: XYZ Coordinates for the DFT optimized structure of *N*-methylpyrrole.

TABLE S2: XYZ Coordinates for the DFT *N*-Me distorted structure of *N*-methylpyrrole.

TABLE S3: XYZ Coordinates for the DFT optimized structure of pentamethylcyclopentadienide.

TABLE S4: XYZ Coordinates for the DFT Me distorted structure of pentamethylcyclopentadienide.

FIGURE S1: Full labelled ORTEP representations of the structure of **6**.

FIGURE S2: Full labelled ORTEP representations of the structure of **7**.

SYNTHESIS OF 6.

*t*BuCl (1.25 mL of 0.46 M THF solution, 0.58 mmol) was added to a toluene solution (20 mL) of the Sm^{II} precursor* (0.50 g, 0.58 mmol) at 0 °C. The mixture was stirred for 1 h then cooled to -35 °C. A suspension of $Na(C_5H_5)$ (0.051 g, 0.58 mmol) in toluene (5 mL) at -35 °C was added dropwise with stirring and the mixture warmed to rt and stirred for 1.5 h, during which time the color changed from pale brown to orange. The mixture was then cooled to -50 °C and filtered. Solvent was removed from the filtrate in vacuo at -20 °C to give an orange solid. Hexanes (5 mL) were added and the flask briefly warmed to rt to form a uniform suspension. Overnight cooling to -80 °C, removal of the supernatant and drying of the orange powder in vacuo afforded the product (0.21 g, 46 %). Crystals suitable for X-ray diffraction were obtained by cooling a hot, saturated hexane solution. Elemental analysis (%) calcd for $C_{43}H_{59}N_4Sm$: C 66.01, H 7.60, N 7.16; found: C 66.06, H 7.55, N 6.77. ^{1}H NMR (299.888 MHz, [D_8]toluene, 20 °C): δ=-0.50 (t, 12H, CH_3 ethyl), 1.05 (m, 4H, CH_2 ethyl), 1.26 (s, 4H, CH *N*-Mepyrrolyl), 1.43 (m, 4H, CH_2 ethyl), 1.54 (t, 12H, CH_3 ethyl), 2.08 (m, 4H, CH_2 ethyl), 2.75 (m, 4H, CH_2 ethyl), 3.84 (s, 6H, *N*-CH_3), 6.94 (s, 4H, CH pyrrolyl), 9.22 ppm (s, 5H, CH Cp ligand); ^{13}C NMR (75.407 MHz, [D_8]toluene, 20 °C): δ=8.2 (CH_3 ethyl), 9.7 (CH_3 ethyl), 23.9 (CH_2 ethyl), 32.3 (CH_2 ethyl), 35.0 (*N*-CH_3), 45.0 (*C* meso), 102.0 (CH, *N*-Mepyrrolyl), 104.6 (CH, pyrrolyl), 111.5 (CH, Cp ligand), 134.8 (C, *N*-Mepyrrolyl), 154.5 (C, pyrrolyl).

* J. Wang, A. K. J. Dick, M. G. Gardiner, B. F. Yates, E. J. Peacock, B. W. Skelton and A. H. White, *Eur. J. Inorg. Chem.* **2004**, 1992.

SYNTHESIS OF 7.

Cyclooctatetraene (60 μL of 1.92 M toluene solution, 0.12 mmol) was added to a toluene solution (15 mL) of the Sm^{II} precursor* (0.20 g, 0.23 mmol) producing a green precipitate over 5 min. The colorless supernatant was removed and the precipitate rinsed with toluene (10 mL) and dried in vacuo to give the product (0.15 g, 82 %). Crystals suitable for X-ray diffraction were obtained by diffusion of cyclooctatetraene vapour into a toluene solution of the Sm^{II} precursor. Elemental analysis (%) calcd for $C_{84}H_{116}N_8Sm_2$: C 65.57, H 7.60, N 7.28; found: C 65.07, H 7.32, N 7.04.

* J. Wang, A. K. J. Dick, M. G. Gardiner, B. F. Yates, E. J. Peacock, B. W. Skelton and A. H. White, *Eur. J. Inorg. Chem.* **2004**, 1992.

TABLE S1: XYZ Coordinates for the DFT optimized structure of *N*-methylpyrrole.

C	0.009658	0.022099	0.009275
C	0.010249	-0.014216	1.387351
C	1.370392	-0.016322	1.807969
C	2.148973	0.018788	0.670820
N	1.315935	0.049149	-0.424970
H	-0.805103	0.034198	-0.701463
H	-0.866735	-0.022377	2.020770
H	1.736703	-0.026426	2.825865
H	3.222753	0.027787	0.544189
C	1.743872	-0.014083	-1.808968
H	2.705235	0.495276	-1.919393
H	1.852278	-1.049301	-2.156494
H	1.011473	0.493629	-2.442723

TABLE S2: XYZ Coordinates for the DFT *N*-Me distorted structure of *N*-methylpyrrole.

C	0.007812	-0.004238	-0.022405
C	0.005781	-0.008036	1.350633
C	1.371248	-0.007296	1.773301
C	2.145302	-0.003253	0.639193
N	1.318436	0.002702	-0.473098
C	1.701752	-0.663901	-1.710435
H	2.716312	-0.364413	-1.990311
H	1.669201	-1.755044	-1.604984
H	1.022927	-0.364400	-2.514697
H	-0.808575	-0.040605	-0.731132
H	-0.869065	0.040416	1.985730
H	1.734307	0.041549	2.791566
H	3.219344	-0.038865	0.515676

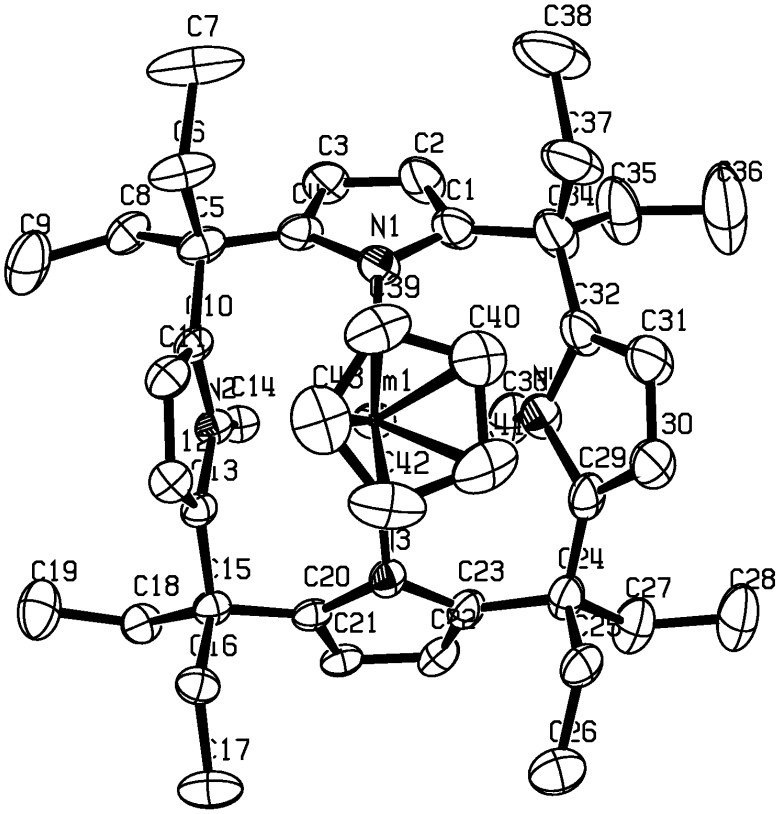
TABLE S3: XYZ Coordinates for the DFT optimized structure of pentamethylcyclopentadienide.

C	-0.005178	0.020017	-0.039509
C	0.015323	-0.029019	1.378392
C	1.370997	-0.046801	1.796849
C	2.188314	-0.008937	0.637628
C	1.780994	0.091422	-1.933419
H	2.751981	-0.405287	-2.086537
H	1.066472	-0.406785	-2.607772
H	1.903748	1.117187	-2.334521
C	1.337798	0.032418	-0.497304
C	3.692311	-0.002108	0.618028
H	4.119700	-0.562302	1.464911
H	4.094904	-0.464592	-0.296790
H	4.148092	1.006832	0.668162
C	1.858689	-0.085228	3.219095
H	2.817663	-0.619228	3.313145
H	2.026439	0.911263	3.674066
H	1.148648	-0.599915	3.885254
C	-1.189102	-0.046777	2.279330
H	-0.988950	-0.574890	3.224821
H	-1.560059	0.956226	2.570012
H	-2.047227	-0.556385	1.812970
C	-1.234395	0.063179	-0.905105
H	-1.601877	1.084126	-1.130760
H	-1.067510	-0.414697	-1.883429
H	-2.084494	-0.462245	-0.441907

TABLE S4: XYZ Coordinates for the DFT Me distorted structure of pentamethylcyclopentadienide.

C	-0.000171	0.000508	0.000522
C	-0.000369	-0.000933	1.415275
C	1.352045	-0.000697	1.854058
C	2.182538	0.001661	0.708700
C	1.350959	-0.016608	-0.445965
C	1.787056	-0.551240	-1.785373
H	2.804340	-0.226698	-2.059397
H	1.801239	-1.657759	-1.826663
H	1.126414	-0.227735	-2.606534
C	-1.208433	-0.091723	-0.894272
H	-1.071496	0.474764	-1.828713
H	-1.469520	-1.122988	-1.204845
H	-2.110612	0.315895	-0.414140
C	-1.196300	0.103664	2.322589
H	-1.293792	1.082516	2.831974
H	-2.137168	-0.053207	1.776519
H	-1.178577	-0.646322	3.132805
C	1.786823	0.108075	3.290639
H	1.280959	-0.626973	3.940718
H	2.865646	-0.068247	3.405300
H	1.584266	1.094936	3.751452
C	3.686033	-0.090450	0.693910
H	4.079161	-1.119001	0.568926
H	4.127314	0.497882	-0.126138
H	4.131720	0.291940	1.624165

FIGURE S1: Full labelled ORTEP representations of the structure of **6**.



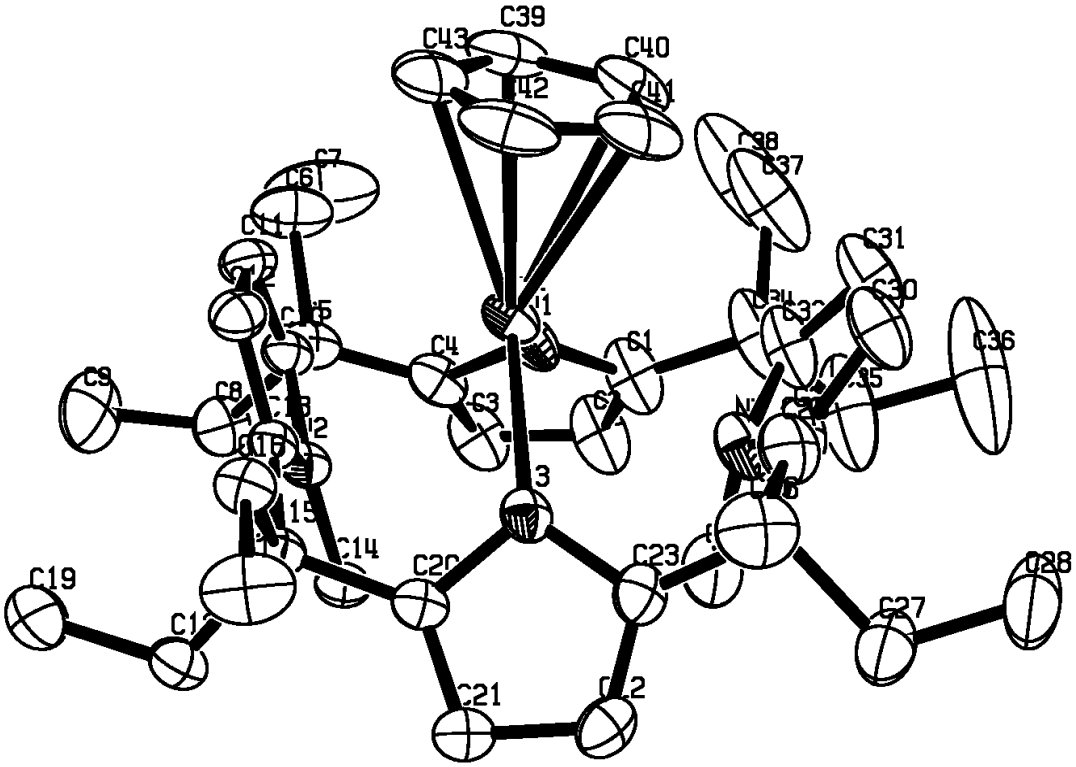
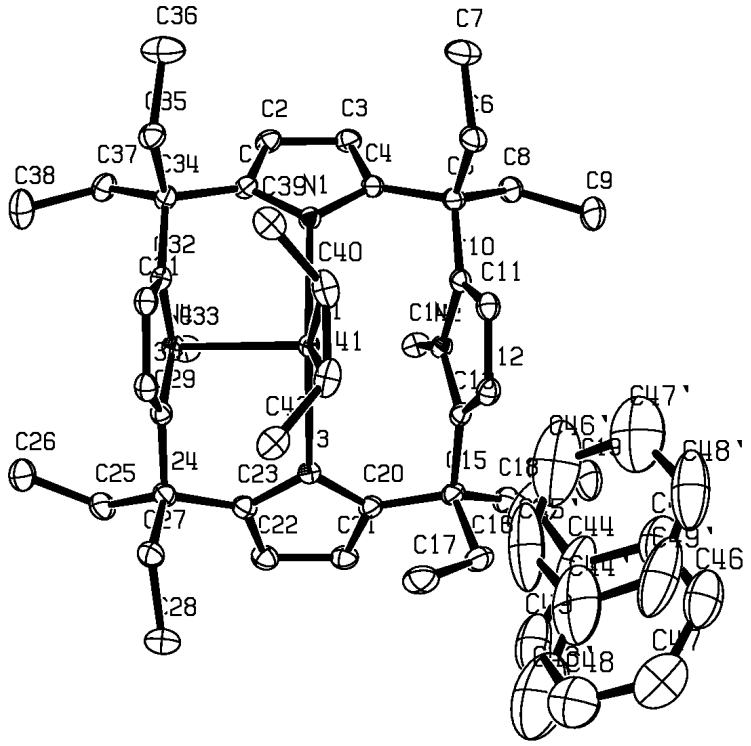
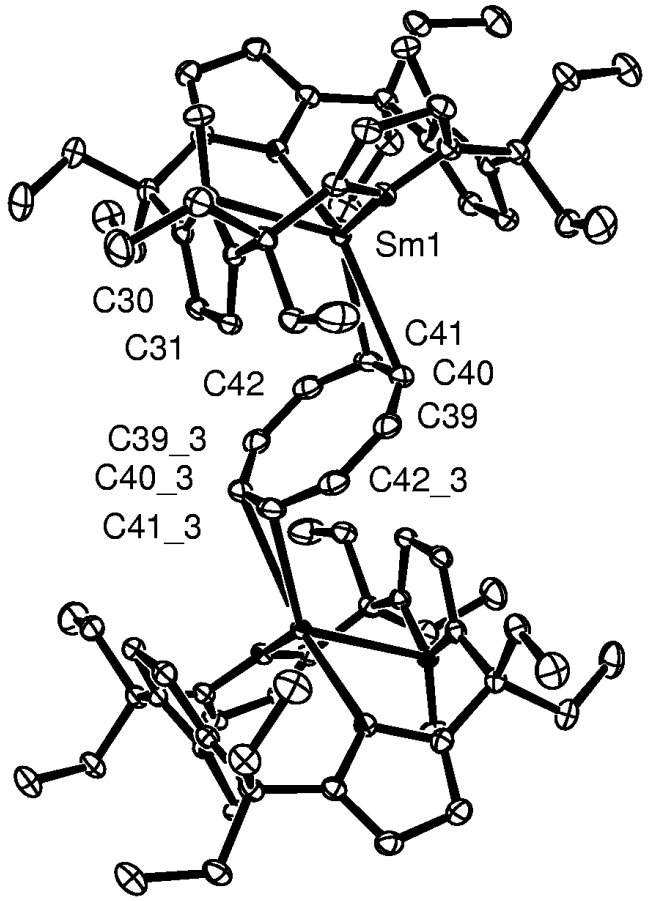



FIGURE S2: Full labelled ORTEP representations of the structure of **7**.