Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information: Metal–ring interactions in Group 2 *Ansa*–Metallocenes: Assessed with the Local Vibrational Mode Theory

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1 Linear Metallocene complexes investigated

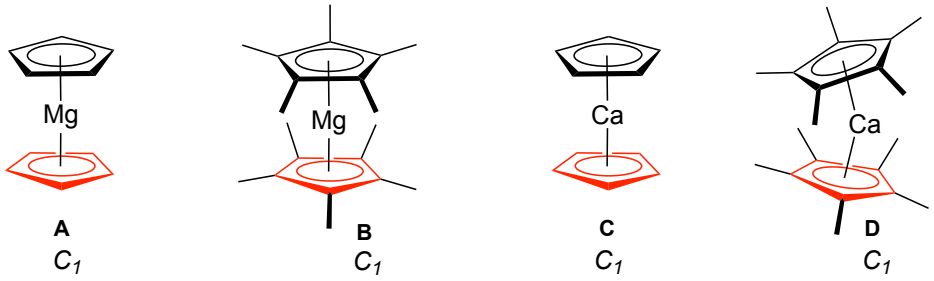

Figure S1: Linear complexes investigated in this work. **A** is $MgCp_2$, **B** is $MgCp^*_2$, **C** is $CaCp_2$, and **D** is $CaCp^*_2$

Table S1: Calculated linear metallocenes M–Cp distances (M = Mg, Ca) d (Å), local mode force constants k^a(M–Cp) (mdyn/Å), Cp–M–Cp angles A (°), and corresponding local mode force constants k^a(Cp–M–Cp) (mdynÅ/Rad^2), as well as NBO charges for the metal. For structures whose distances and local force constants of M–Cp differ, the top row corresponds to the top Cp ring, while the bottom row corresponds to the bottom Cp ring (for more information, see text). B3LYP-D3/def2-TZVP level of theory.

Structure	d	k^a(M-Cp)	A	k^a(Cp-M-Cp)	e
A	1.999	1.680	180.0	0.197	1.806
B	1.966	1.789	180.0	0.129	1.877
C	2.350	1.439	179.5	0.026	1.776
D	2.322	1.477	155.1	0.291	1.786
	2.322	1.482			

2 Laplacian Plots

Selected Laplacian plots are shown below.

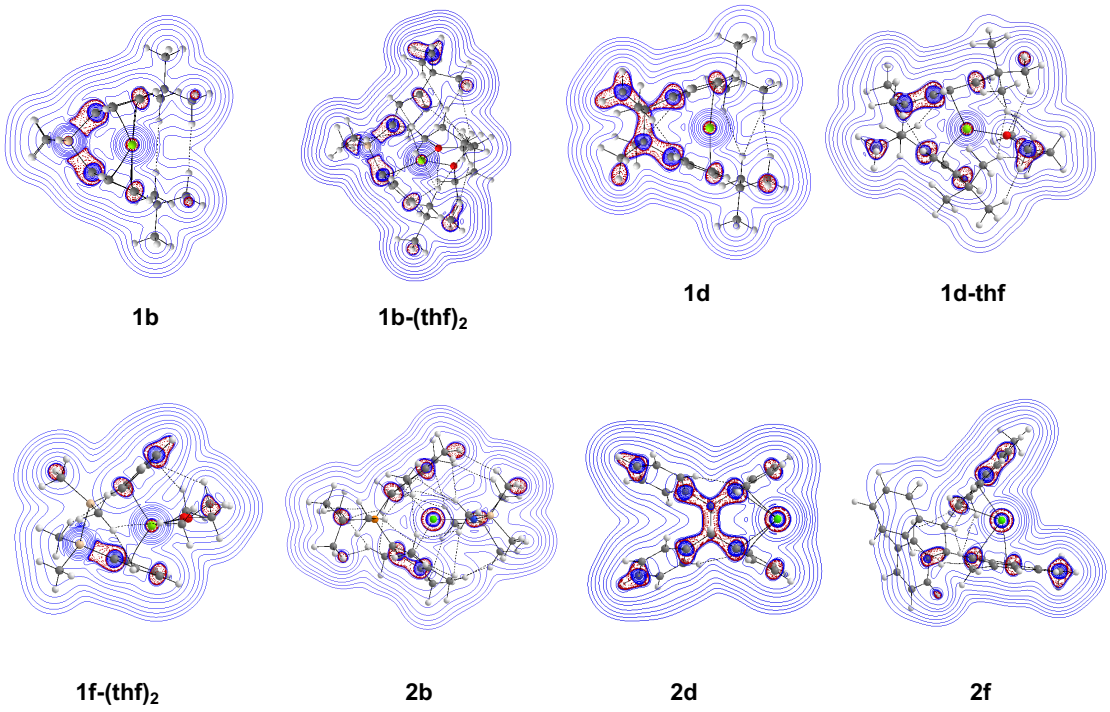

Figure S2: Contour plots displaying the Laplacian of the electron density within the Cp–M–Cp plane for **1b**, **1b-(thf)**$_2$, **1d**, **1d-thf**, **1f-(thf)**$_2$, **2b**, **2d**, and **2e**. Blue solid lines account for positive $\nabla^2(\rho(\mathrm{r})$ values (depletion of charge) while red dashed lines represent negative $\nabla^2(\rho(\mathrm{r}))$ values (concentration of charge). B3LYP-D3/def2-TZVP level of theory.

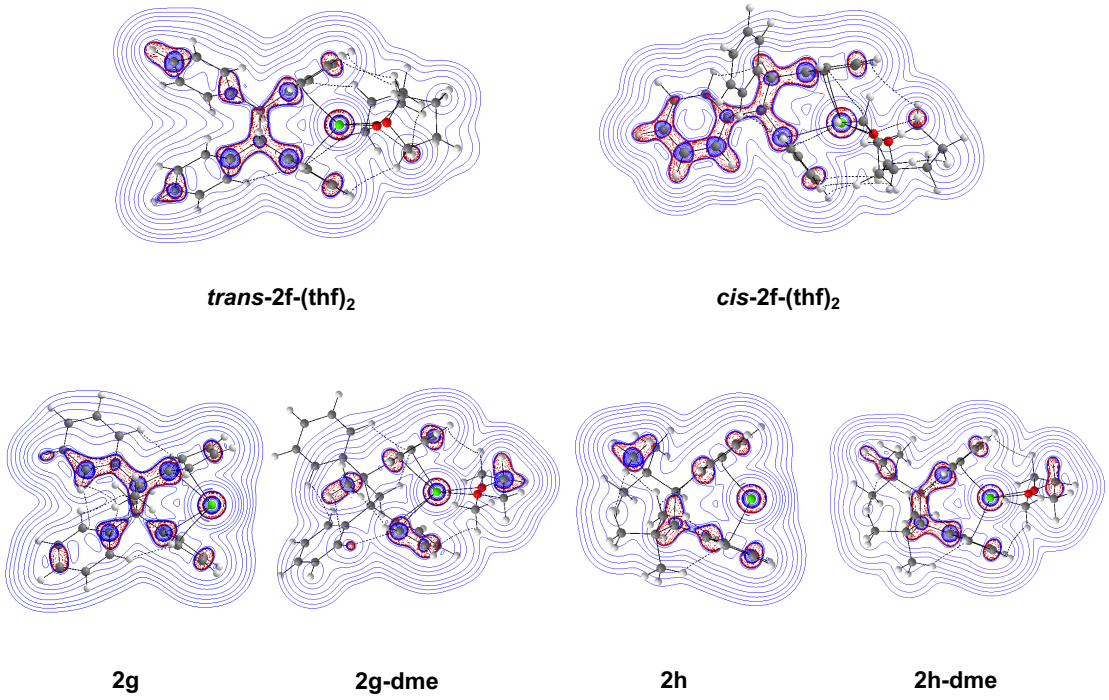

Figure S3: Contour plots displaying the Laplacian of the electron density within the Cp–M–Cp plane for ***trans*-2f-(thf)$_2$**, ***cis*-2f-(thf)$_2$**, **2g**, **2g-dme**, **2h**, and **2h-dme**. Blue solid lines account for positive $\nabla^2(\rho(\mathrm{r})$ values (depletion of charge) while red dashed lines represent negative $\nabla^2(\rho(\mathrm{r}))$ values (concentration of charge). B3LYP-D3/def2-TZVP level of theory.