Supporting Information for A Cooperative Model for Metallocene Catalyst Activation by Methylaluminoxane

Dr. Scott Collins, Prof. Mikko Linnolahti

Department of Chemistry, University of Eastern Finland, Joensuu Campus, Yliopistokatu 7, FI-80100, Joensuu, Finland.

Contents

Table S-1 Energies for Structures Reported[a]

Structure[b]	E	H	H-qh	TS-tr	TS-qh-tr
C_3H_6	-117.878183	-117.793937	-117.793942	0.023788	0.023788
	-117.782651	*-117.698852*	*-117.698857*	*0.023839*	*0.023839*
$AlMe_3$ C_{3h}	-362.140460	-362.024446	-362.025875	0.036047	0.034694
	-361.974980	*-361.860048*	*-361.861630*	*0.037565*	*0.034916*
Al_2Me_6 C_{2v}	-724.314410	-724.079599	-724.081892	0.054038	0.053323
	-723.987850	*-723.754997*	*-723.757140*	*0.053883*	*0.053227*
$SBIZrMe_2$	-1189.238147	-1188.824312	-1188.826836	0.070837	0.069246
	-1188.521689	*-1188.110250*	*-1188.112741*	*0.070868*	*0.069373*
n6m4	-3595.040208	-3594.288773	-3594.299951	0.152287	0.143350
	-3593.562769	*-3592.818476*	*-3592.829337*	*0.152489*	*0.143289*
n7m5	-4314.959611	-4314.042318	-4314.054397	0.174046	0.165779
	-4313.189059	*-4312.280424*	*-4312.291396*	*0.171414*	*0.165035*
n26m9	-12560.677149	-12558.396156	-12558.428074	0.409009	0.382067
2a	-9086.022396	-9084.149019	-9084.174417	0.325863	0.302539
	-9082.135703	*-9080.279223*	*-9080.303617*	*0.324664*	*0.303217*
3a	-9448.179901	-9446.187904	-9446.214605	0.342228	0.317484
	-9444.141304	*-9442.167495*	*-9442.193650*	*0.343309*	*0.319595*
2b	-5142.053697	-5140.838970	-5140.854508	0.210555	0.196120
	-5139.731508	*-5138.526696*	*-5138.542029*	*0.210543*	*0.196813*
3b	-5504.206768	-5502.873463	-5502.890969	0.230185	0.213948
	-5501.728391	*-5500.406035*	*-5500.422967*	*0.229773*	*0.213880*
2c	-4784.301049	-4783.132799	-4783.147577	0.202264	0.188026
	-4782.116060	*-4780.957689*	*-4780.971923*	*0.201541*	*0.188693*

3c	-5146.463282	-5145.176566	-5145.193404	0.219733	0.204612
	-5144.122715	*-5142.846509*	*-5142.863152*	*0.220854*	*0.205342*
2d	-13387.779277	-13385.200584	-13385.235589	0.445130	0.411815
3d	-13749.938665	-13747.241356	-13747.277736	0.461403	0.426897
2e	-8737.107133	-8735.137494	-8735.165499	0.343991	0.313835
	-8733.312316	*-8731.360215*	*-8731.387708*	*0.344919*	*0.314969*
3e	-9099.271337	-9097.184180	-9097.214484	0.366013	0.331712
	-9095.322466	*-9093.253551*	*-9093.282577*	*0.362788*	*0.331261*
2b π-C_3H_6 *syn*	-5259.932767	-5258.630332	-5258.646842	0.220962	0.206463
2b TS *syn*	-5259.909891	-5258.607704	-5258.624348	0.221115	0.203723
2c TS *syn*	-4902.160573	-4900.905315	-4900.921598	0.214944	0.196058
2d TS *syn*	-13505.642635	-13502.976612	-13503.012274	0.450175	0.418197
2e π-C_3H_6 *syn*	-8854.997093	-8852.942430	-8852.972383	0.357818	0.325312
2e TS *syn*	-8854.979055	-8852.922956	-8852.952742	0.356421	0.322087
2e γ-CH	-8854.993756	-8852.935725	-8852.965787	0.358580	0.323545
2f SBIZrMe-μ-Me-cage-*16,6*	-9086.034106	-9084.157091	-9084.178405	0.308512	0.289302
2f TS syn[c]	-9203.889020	-9201.923878	-9201.944868	0.310554	0.292475

a. M06-2X/TZVP energies in atomic units at 298.15 K in toluene PCM with MN15/def2-TZVP results in italics. Note that G-tr = H−TS-tr and G-qh-tr = H-qh−TS-qh-tr where those values were used to calculate ΔG-tr and ΔG-qh-tr values in Tables 1-3. b. For coordinate files, see electronic supporting information Table S-1.xyz. For coordinate and energy data for C_3H_6, $AlMe_3$, Al_2Me_6, $SBIZrMe_2$, **2a**, **3a**, insertion intermediates and the transition structure corresponding to CIP **2a** listed in Table 1 see S. Collins, M. Linnolahti, *ChemPhysChem* **2024**, *25*, e202300856 and its Supporting Information. c. The insertion barrier for this *16,6* cage structure (S. Collins, M. Linnolahti, *ChemPhysChem* **2023**, *24*, e202300342) is $\Delta E^{‡}$ = 61.1 and $\Delta G^{‡}$-qh-tr = 126.3 kJ mol^{-1}.

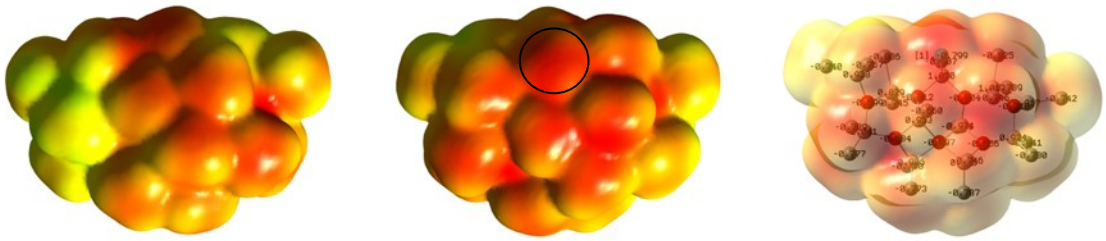

Figure S-1 - Electrostatic potential surfaces of the [*7,4*]$^{-}$ anion showing negative charge localized differently to each face and top edge of sheet. Right – Mulliken charges with terminal Me group highlighted as being most negative (-0.799). That group is circled in the middle picture.

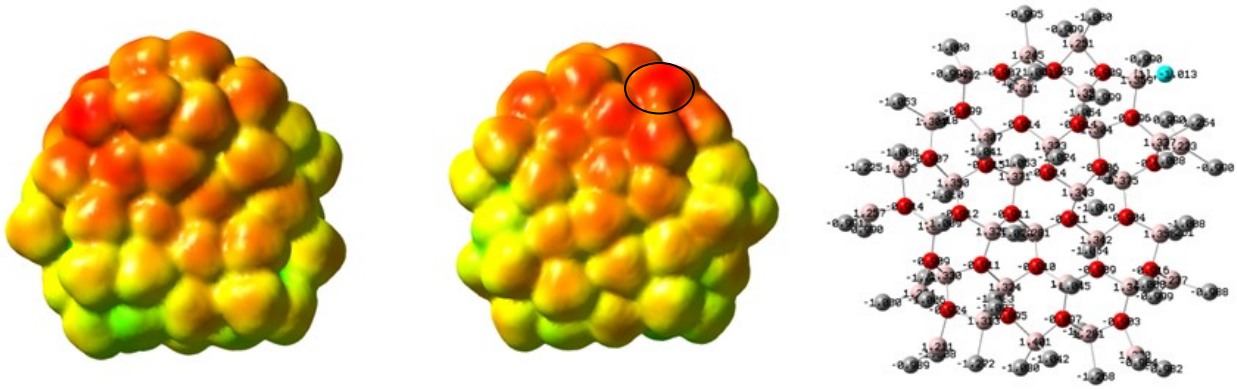

Figure S-2 - Electrostatic potential surfaces of the [*26,8*]$^{-}$ anion showing negative charge localized to each face and top edge of sheet. Right – Mulliken charges with terminal Me group highlighted as being most negative (-1.013).

Figure S-3 - Electrostatic potential surface of the [*13,8*]$^{-}$ anion showing the most electron rich face. Centre – Mulliken charges with several exposed, terminal Me groups highlighted. Right – Gaussian input file with [SBIZrMe]$^{+}$ cation placed above the most electron rich face.