**Supplementary Materials:**

*Article*

**Theoretical investigations of *para*-methoxystyrene/styrene polymerization** **catalyzed by cationic methyl- and** **dibenzobarrelene-based *α*-diimine** **palladium complexes**

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Table S1**.** Calculated thermodynamic corrections for Gibbs free energies (Δ*G*cor in hartree), solution-phase single-point energies (Δ*E*sol in hartree) and Solution-phase Gibbs free energies (Δ*G*sol in hartree)

|  |  |  |  |
| --- | --- | --- | --- |
| **Computational level: B3LYP**-**D3/BS2/SMD// B3LYP**-**D3/BS1** | | | |
| species | **Δ*G*cor** | **Δ*E*sol** | **Δ*G*sol** |
| **A+** | 0.589031 | -1368.740345 | -1368.148286 |
| *p*MOS | 0.131494 | -424.3140170 | -424.1794952 |
| **A1*p*MOS12** | 0.751903 | -1793.101148 | -1792.346217 |
| **ATS1*p*MOS12** | 0.748681 | -1793.066324 | -1792.314615 |
| **A2*p*MOS12** | 0.751096 | -1793.093742 | -1792.339618 |
| **A3*p*MOS12** | 0.754741 | -1793.113277 | -1792.355508 |
| **A1*p*MOS21** | 0.747329 | -1793.098027 | -1792.347670 |
| **ATS1*p*MOS21** | 0.747455 | -1793.069567 | -1792.319084 |
| **A2*p*MOS21** | 0.750782 | -1793.102454 | -1792.348644 |
| **A3*p*MOS21** | 0.753112 | -1793.131353 | -1792.375213 |
| **A4*p*MOS12** | 0.912289 | -2217.452638 | -2216.537321 |
| **A4*p*MOS21** | 0.913534 | -2217.450693 | -2216.534131 |
| **ATS2*p*MOS12** | 0.909943 | -2217.415032 | -2216.502061 |
| **ATS2*p*MOS21** | 0.911982 | -2217.422206 | -2216.507196 |
| **A5*p*MOS12** | 0.906978 | -2217.443310 | -2216.533304 |
| **A5*p*MOS21** | 0.913090 | -2217.448198 | -2216.532080 |
| **A6*p*MOS12** | 0.910847 | -2217.459783 | -2216.545908 |
| **A6*p*MOS21** | 0.912994 | -2217.475457 | -2216.559435 |
| **B+** | 0.700826 | -1828.571891 | -1827.868037 |
| **B1*p*MOS21** | 0.863195 | -2252.929948 | -2252.063725 |
| **BTS1*p*MOS21** | 0.865875 | -2252.898732 | -2252.029829 |
| **B2*p*MOS21** | 0.865582 | -2252.928584 | -2252.059974 |
| **B3*p*MOS21** | 0.867710 | -2252.962945 | -2252.092207 |
| **B1*p*MOS12** | 0.866335 | -2252.930785 | -2252.061422 |
| **BTS1*p*MOS12** | 0.863143 | -2252.896592 | -2252.030421 |
| **B2*p*MOS12** | 0.865585 | -2252.923873 | -2252.05526 |
| **B3*p*MOS12** | 0.869316 | -2252.943943 | -2252.071599 |
| **B4*p*MOS21** | 1.026075 | -2677.281431 | -2676.252328 |
| **BTS2*p*MOS21** | 1.027151 | -2677.247513 | -2676.217334 |
| **B5*p*MOS21** | 1.025224 | -2677.280574 | -2676.252322 |
| **B6*p*MOS21** | 1.025873 | -2677.309320 | -2676.280419 |
| **B4*p*MOS12** | 1.027118 | -2677.272653 | -2676.242507 |
| **BTS2*p*MOS12** | 1.027912 | -2677.243106 | -2676.212166 |
| **B5*p*MOS12** | 1.026058 | -2677.272074 | -2676.242988 |
| **B6*p*MOS12** | 1.023177 | -2677.281685 | -2676.255480 |
| **B4′*p*MOS12** | 1.024475 | -2677.273902 | -2676.246399 |
| **BTS2′*p*MOS12** | 1.022872 | -2677.245205 | -2676.219305 |
| **B5′*p*MOS12** | 1.023841 | -2677.273094 | -2676.246225 |
| **B6′*p*MOS12** | 1.031198 | -2677.291073 | -2676.256847 |
| **B4′*p*MOS21** | 1.024005 | -2677.274089 | -2676.247056 |
| **BTS2′*p*MOS21** | 1.027604 | -2677.247174 | -2676.216542 |
| **B5′*p*MOS21** | 1.027149 | -2677.280962 | -2676.250785 |
| **B6′*p*MOS21** | 1.029150 | -2677.311724 | -2676.279546 |
| **B7′*p*MOS12BHE** | 0.860772 | -2252.933311 | -2252.069511 |
| **BTS3′*p*MOS12BHE** | 0.859189 | -2252.927658 | -2252.065441 |
| **B8′*p*MOS12BHE** | 0.864825 | -2252.933579 | -2252.065726 |
| **BTS4′*p*MOS12diss** | 0.864041 | -2252.907296 | -2252.040227 |
| **B9′*p*MOS12diss** | 0.861191 | -2252.920338 | -2252.056119 |
| **B10diss** | 0.677693 | -1789.236327 | -1788.555606 |
| **P12BHE** | 0.158492 | -463.643343 | -463.4818232 |
| **B11′*p*MOS12diss** | 0.837489 | -2213.582690 | -2212.742173 |
| **BTS5′*p*MOS12diss** | 0.838667 | -2213.576445 | -2212.734750 |
| **B12′*p*MOS12** | 0.836227 | -2213.597455 | -2212.758200 |
| **B13′*p*MOS12ass** | 1.021225 | -2677.260787 | -2676.236534 |
| **BTS6′*p*MOS12ass** | 1.023291 | -2677.243138 | -2676.216819 |
| **B14′*p*MOS12ass** | 1.019350 | -2677.265455 | -2676.243077 |
| **C+** | 0.778117 | -2438.442402 | -2437.661257 |
| **C1*p*MOS21** | 0.955135 | -2862.823496 | -2861.865333 |
| **CTS1*p*MOS12** | 0.948741 | -2862.785345 | -2861.833576 |
| **CTS1*p*MOS21** | 0.956809 | -2862.789528 | -2861.829691 |
| **CP12** | 0.958400 | -2862.835085 | -2861.873657 |
| **CP21** | 0.778117 | -2438.442402 | -2437.661257 |
| **D+** | 0.908436 | -2595.777820 | -2594.866356 |
| **D1*p*MOS21** | 1.065503 | -3020.124240 | -3019.055709 |
| **DTS1*p*MOS12** | 1.064710 | -3020.092317 | -3019.024579 |
| **DTS1*p*MOS21** | 1.069149 | -3020.091481 | -3019.019304 |
| **DP12** | 1.069959 | -3020.135211 | -3019.062224 |
| **DP21** | 0.956464 | -2862.848918 | -2861.889426 |
| **E+** | 1.100947 | -3362.949278 | -3361.845303 |
| **E1*p*MOS21** | 1.260743 | -3787.302108 | -3786.038337 |
| **ETS1*p*MOS12** | 1.261157 | -3787.270910 | -3786.006725 |
| **ETS1*p*MOS21** | 1.260752 | -3787.262304 | -3785.998524 |
| **EP12** | 1.266244 | -3787.317091 | -3786.047819 |
| **EP21** | 1.265614 | -3787.329742 | -3786.061100 |
| **styrene** | 0.101704 | -309.7514990 | -309.6467672 |
| **B1St21** | 0.834844 | -2138.365745 | -2137.527873 |
| **BTS1St21** | 0.836969 | -2138.339030 | -2137.499033 |
| **B2St21** | 0.837511 | -2138.369416 | -2137.528877 |
| **B3St21** | 0.837317 | -2138.395091 | -2137.554746 |
| **B1St12** | 0.836908 | -2138.366762 | -2137.526826 |
| **BTS1St12** | 0.833580 | -2138.333693 | -2137.497085 |
| **B2St12** | 0.836121 | -2138.361537 | -2137.522388 |
| **B3St12** | 0.836410 | -2138.376346 | -2137.536908 |
| **B4St21** | 0.966776 | -2448.148064 | -2447.178260 |
| **BTS2St21** | 0.969159 | -2448.121153 | -2447.148966 |
| **B5St21** | 0.971641 | -2448.163115 | -2447.188446 |
| **B6St21** | 0.965534 | -2448.179520 | -2447.210958 |
| **B4St12** | 0.967972 | -2448.153997 | -2447.182997 |
| **BTS2St12** | 0.967725 | -2448.115328 | -2447.144575 |
| **B5St12** | 0.966784 | -2448.147227 | -2447.177415 |
| **B6St12** | 0.965318 | -2448.157003 | -2447.188657 |