Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

for

Angew. Chem. Int. Ed. Z52231

69451 Weinheim, Germany

Mechanism of the Aliphatic Hydroxylation Mediated by a Bis(μ-oxo)dicopper(III) Complex**

Philipp Spuhler and Max C. Holthausen*

[*] Dipl.-Chem. P. Spuhler, Dr. M. C. Holthausen, Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg (Germany), FAX: (+49) 6421-282-5566, e-mail: Max.Holthausen@chemie.uni-marburg.de

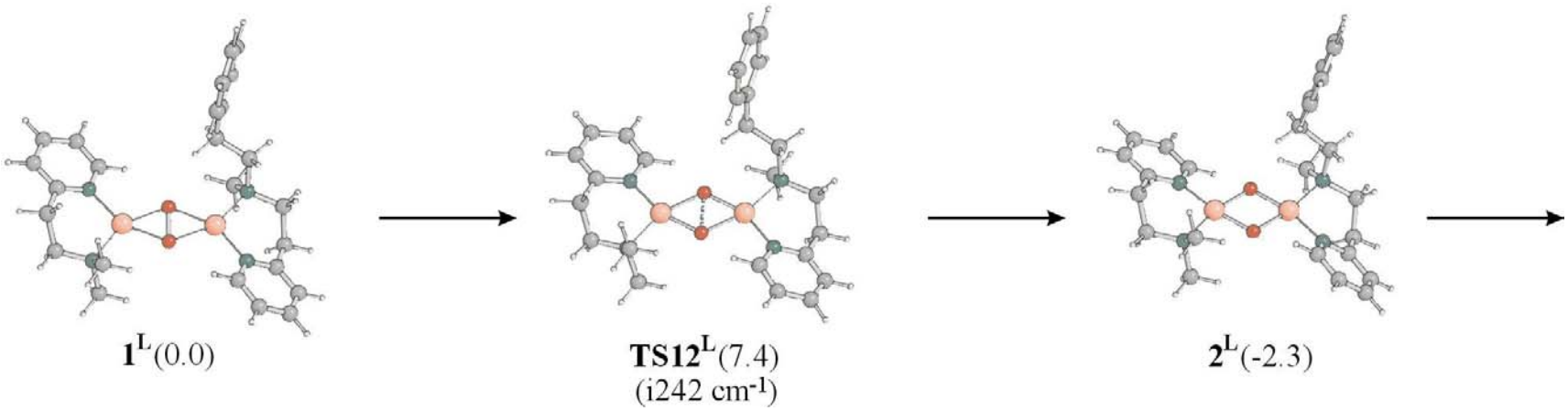

Figure 4: Stationary points (minima and transition structures) along the reaction path of the hydroxylation of the benzylic C–H bonds in the large computational model $[Cu_2L^3L^4(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)]^{2+}$; relative energies ($\Delta G^{-80°C}$ in kcal/mol, 1 atm, acetone) are given in parentheses.

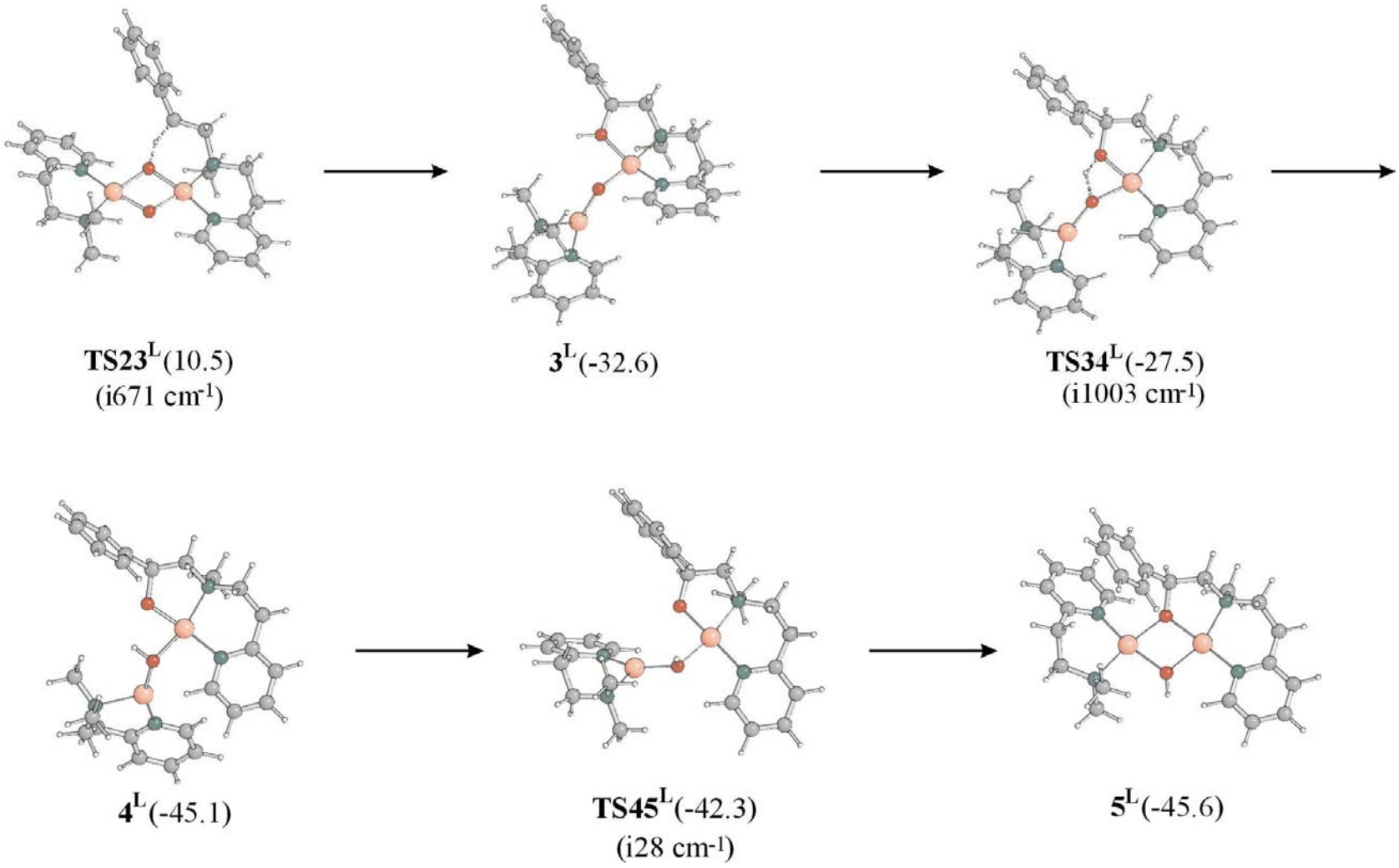

Figure 4 (continued)

Table 3: Energies relative to **1** in kcal/mol. Geometries, zero point vibrational energies, and thermal contributions were obtained at the B3LYP/LANL2DZ (BS1) level. Final energies were obtained from single point energy calculations at the B3LYP/BS2 level including solvation contributions computed employing the COSMO continuum model.

Species	Model[a]	ΔE_{tot}(BS1)	ΔE_G[b]	ΔE_{tot}(BS2)	ΔE_{Solv}(BS2)[c]	ΔG[d]	$\Delta G^{\ddagger}(\rightarrow)$[e]	$\Delta G^{\ddagger}(\leftarrow)$[f]
1	small	0.0	0.0	0.0	0.0	0.0	-	-
	large	0.0	0.0	0.0	0.0	0.0	-	-
TS12	small	7.9	-0.9	9.2	-2.3	6.1	6.1	10.0
	large	6.7	1.0	7.4	-1.0	7.4	7.4	9.7
2	small	3.1	-0.1	0.5	-4.4	-4.0	-	-
	large	1.4	2.4	-2.9	-1.8	-2.3	-	-
TS23	small	3.3	-1.1	2.9	-1.6	0.2	4.2	39.3
	large	7.4	-0.5	9.1	1.9	10.5	12.7	43.0
3	small	-39.8	0.3	-41.5	2.0	-39.2	-	-
	large	-35.0	2.3	-37.3	2.4	-32.6	-	-
TS34	small	-27.7	-2.0	-29.5	0.6	-30.9	8.3	21.9
	large	-27.9	-0.2	-29.6	2.3	-27.5	5.0	17.6
4	small	-46.1	-0.3	-51.8	-0.7	-52.8	-	-
	large	-42.5	1.4	-47.4	0.8	-45.1	-	-
TS45	small	-43.1	0.0	-50.0	-0.9	-50.9	1.9	7.7
	large	-38.4	1.4	-44.1	0.3	-42.3	2.8	3.3
5	small	-60.6	1.5	-61.2	1.0	-58.6	-	-
	large	-53.3	3.1	-53.9	5.2	-45.6	-	-

[a] Computational model, small: $\mathbf{L^1}$, $\mathbf{L^2}$, large: $\mathbf{L^3}$, $\mathbf{L^4}$. [b] Correction for zero point vibrational energies and thermal contributions (-80°C, 1atm, BS1). [c] Correction for solvation energy (BS2, acetone, $\varepsilon = 20.7$). [d] $\Delta G = \Delta E$(BS2) + ΔE_G (BS1) + ΔE_{Solv} (BS2). [e] Gibbs free energy of activation for the forward reaction. [f] Gibbs free energy of activation for the reverse reactionf