

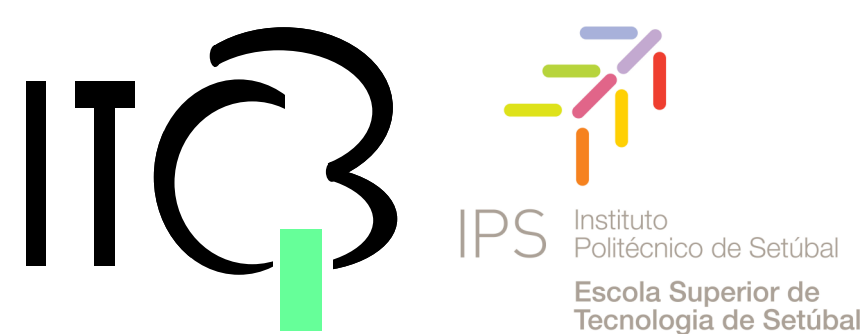
Indenyl ring slippage in crown thioether complexes $[\text{IndMo}(\text{CO})_2\text{L}]^+$ and C–S activation of trithiacyclononane: Experimental and theoretical studies

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Introduction

In complexes of type $[\text{IndMo}(\text{CO})_2\text{L}_2]^+$, trithiacyclononane (ttcn) was the only known neutral sulfur ligand able to induce indenyl ring slippage, affording complex $[(\eta^3\text{-Ind})\text{Mo}(\text{CO})_2(\kappa^3\text{-ttcn})]^+$.^[1] Thus, we extended this work to the macrocyclic ligands 1,3,5-trithiane (tt) and 1,4,7,10-tetrathiacyclododecane (ttcd) in search of other examples of haptotropic shifts. Moreover, the observation that complex $[(\eta^3\text{-Ind})\text{Mo}(\text{CO})_2(\kappa^3\text{-ttcn})]^+$ undergoes elimination of ethylene and CO to produce the Mo(IV) complex $[(\eta^5\text{-Ind})\text{Mo}(\text{CO})_2(\kappa^3\text{-1,4,7-trithiaheptanate})(\text{CO})]^+$ in a very clean process, spurred our curiosity. Here the structural chemistry of $[(\text{Cp}')\text{Mo}(\text{CO})_2(\text{S}_3)]^+$ ($\text{Cp}' = \text{C}_5\text{H}_5, \text{C}_9\text{H}_7; \text{S}_3 = \text{tt, ttcn, ttcd}$) is explored and complemented by a DFT mechanistic study.^[2]

Synthesis and Crystallography

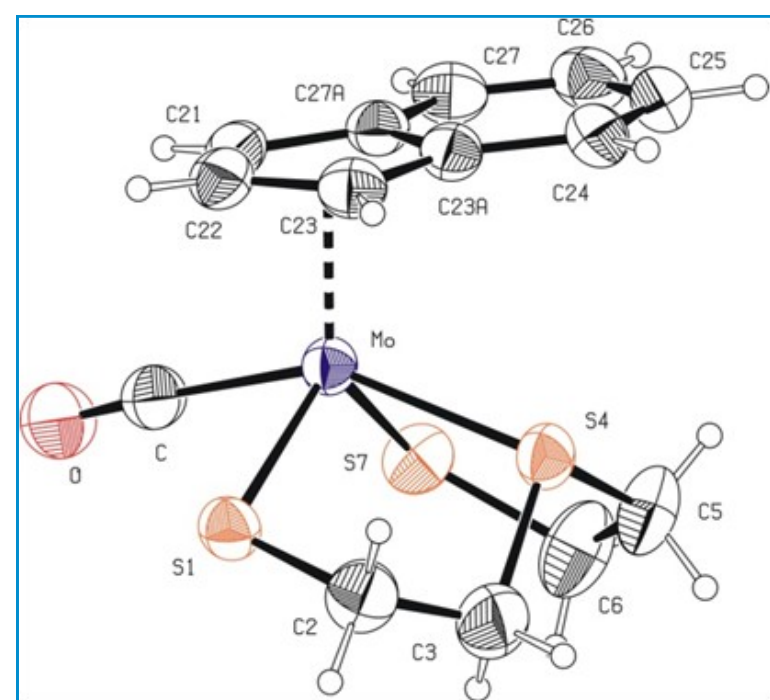
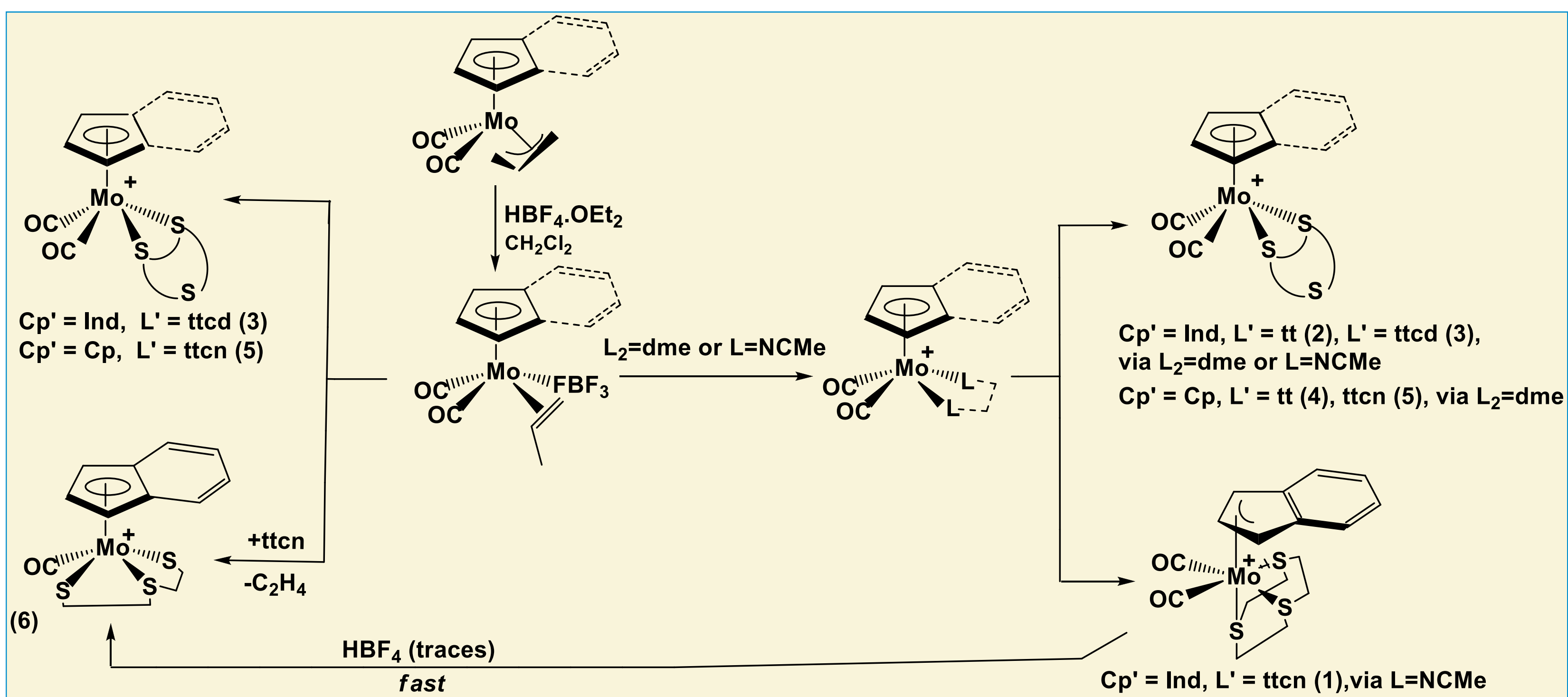
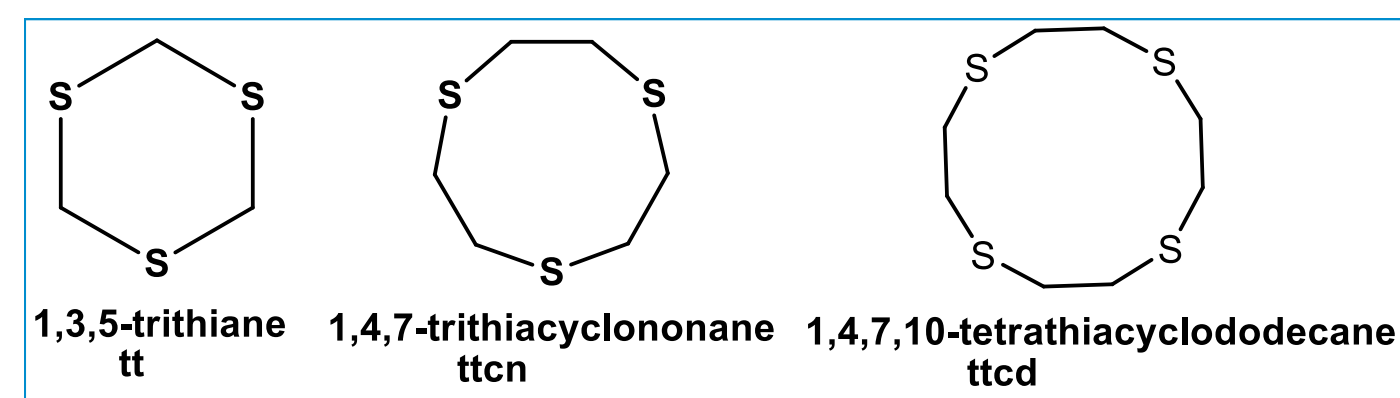


Fig. 3 ORTEP of 6

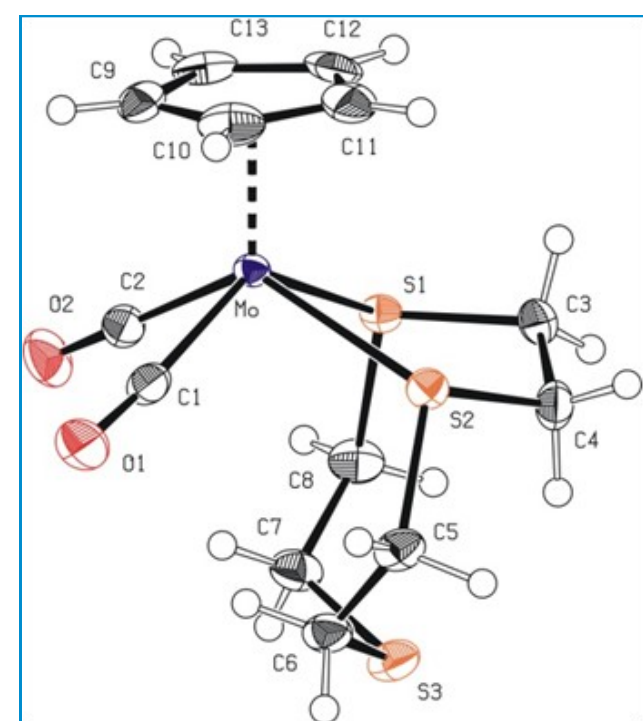


Fig. 1 ORTEP of 5

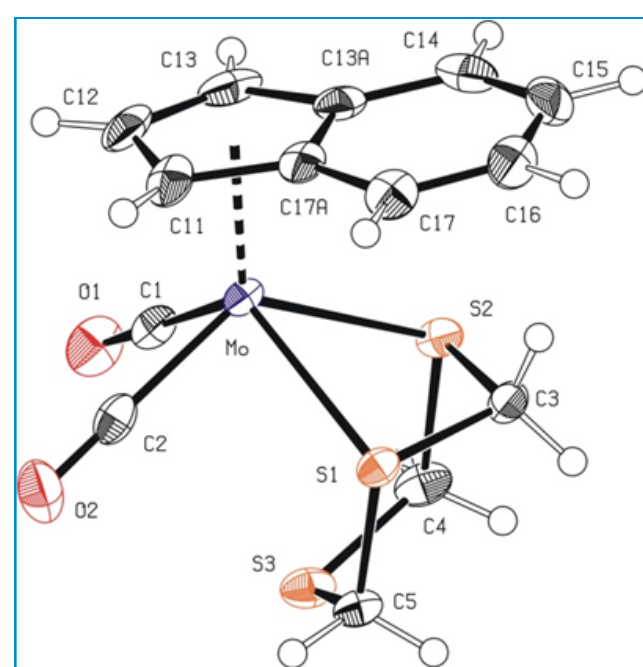


Fig. 2 ORTEP of 2

Computational studies: Why is ttcn the only studied macrocycle able to induce indenyl ring slippage?

Complex	Relative energy (kcal mol ⁻¹)	Complex	Relative energy (kcal mol ⁻¹)
$[(\eta^5\text{-Cp})\text{Mo}(\text{CO})_2(\kappa^2\text{-tt})]^+$	0	$[(\eta^3\text{-Cp})\text{Mo}(\text{CO})_2(\kappa^3\text{-tt})]\text{BF}_4$	33.0
$[(\eta^5\text{-Cp})\text{Mo}(\text{CO})_2(\kappa^2\text{-ttcn})]^+$	0	$[(\eta^3\text{-Cp})\text{Mo}(\text{CO})_2(\kappa^3\text{-ttcn})]^+$	22.2
$[(\eta^5\text{-Cp})\text{Mo}(\text{CO})_2(\kappa^2\text{-ttcd})]^+ (1)$	0	$[(\eta^3\text{-Cp})\text{Mo}(\text{CO})_2(\kappa^3\text{-ttcd})]^+$	16.3
$[(\eta^5\text{-Cp})\text{Mo}(\text{CO})_2(\kappa^2\text{-ttcd})]^+ (2)$	2.6		
$[(\eta^5\text{-Ind})\text{Mo}(\text{CO})_2(\kappa^2\text{-tt})]^+$	0	$[(\eta^3\text{-Ind})\text{Mo}(\text{CO})_2(\kappa^3\text{-tt})]^+$	15.4
$[(\eta^5\text{-Ind})\text{Mo}(\text{CO})_2(\kappa^2\text{-ttcn})]^+ (3)$	0	$[(\eta^3\text{-Ind})\text{Mo}(\text{CO})_2(\kappa^3\text{-ttcn})]^+ (3)$	6.4
$[(\eta^5\text{-Ind})\text{Mo}(\text{CO})_2(\kappa^2\text{-ttcd})]^+ (1)$	0	$[(\eta^3\text{-Ind})\text{Mo}(\text{CO})_2(\kappa^3\text{-ttcd})]^+$	1.24
$[(\eta^5\text{-Ind})\text{Mo}(\text{CO})_2(\kappa^2\text{-ttcd})]^+ (2)$	6.0		

(1) binding through two consecutive sulfur atoms; (2) binding through two opposite sulfur atoms
(3) most stable indenyl conformation selected (see Figs. 4 and 5)

The lowest energy is always found for the $\eta^5\text{-Cp}'$ coordination (as shown in the X-ray structures of (2) and (5)) and $[(\eta^3\text{-Ind})\text{Mo}(\kappa^3\text{-1,4,7-ttcn})(\text{CO})_2]^+$ is not particularly more stable than others (Table 1).

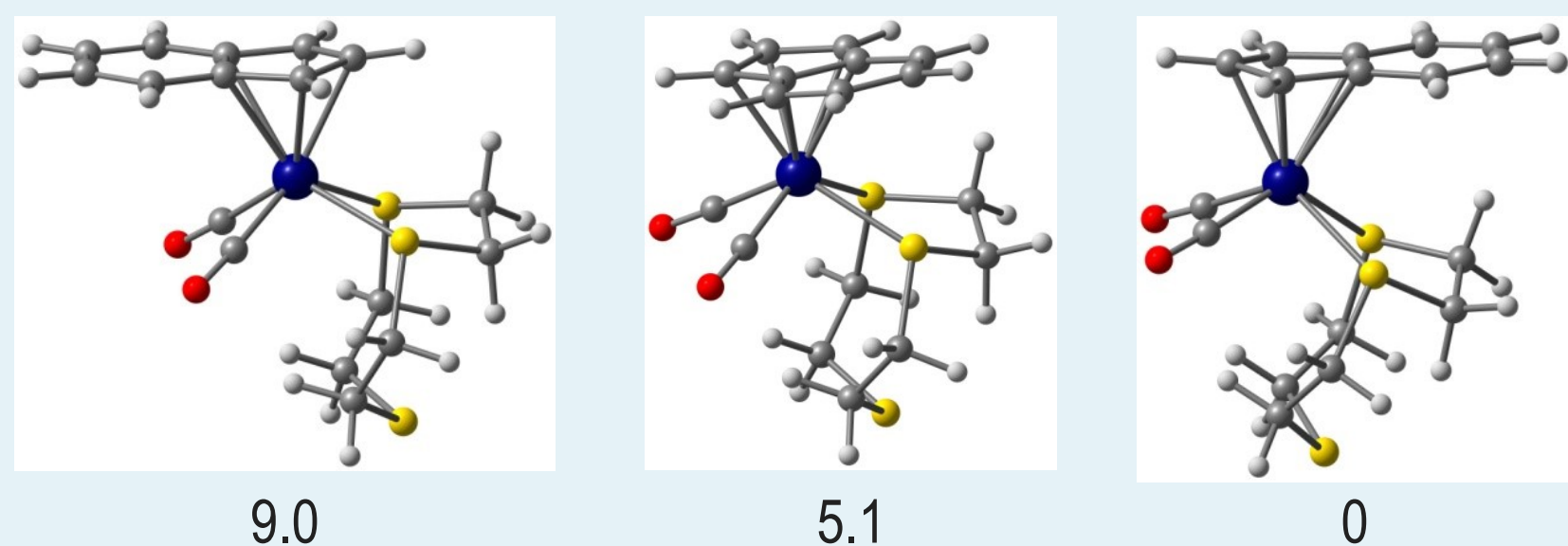


Fig. 4. Optimized geometries of $[(\eta^5\text{-Ind})\text{Mo}(\kappa^2\text{-1,4,7-ttcn})(\text{CO})_2]^+$ and relative energies (kcal mol⁻¹)

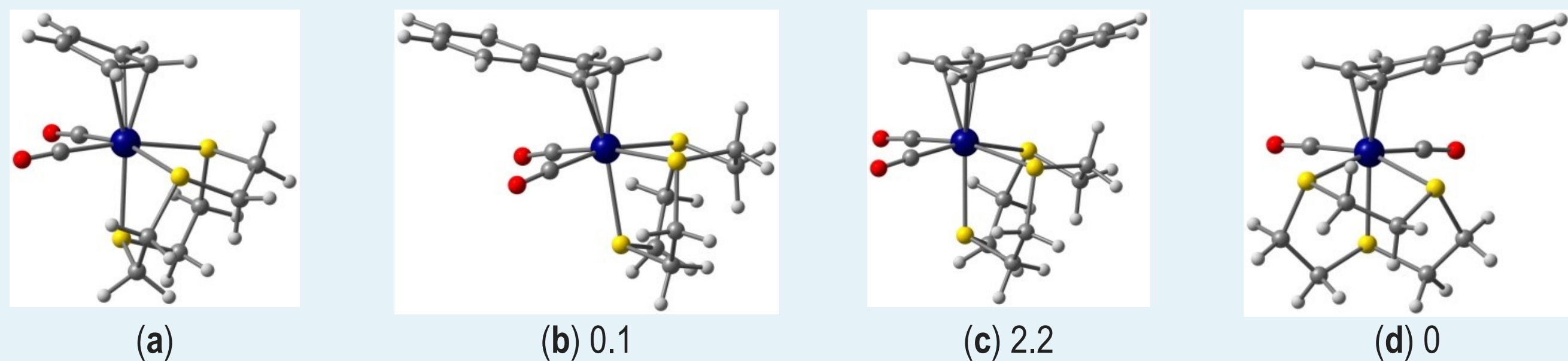


Fig. 5. Optimized geometries of $[(\eta^3\text{-Cp})\text{Mo}(\kappa^3\text{-1,4,7-ttcn})(\text{CO})_2]^+$ (a), $[(\eta^3\text{-Ind})\text{Mo}(\kappa^3\text{-1,4,7-ttcn})(\text{CO})_2]^+$ (b-d) and relative energies (kcal mol⁻¹)

Using Molecular Dynamics:

The ttcn conformers fall into two main clusters:

- 1) all three SCCS dihedral angles are $\pm 60^\circ$ and the three S atoms face the same side;
- 2) only two SCCS dihedral angles are $\pm 60^\circ$ and one S is pointing away from the others.

The first cluster covers 99.7% of all conformations, indicating that almost all the molecules in solution have the three S atoms pointing in the same direction (Fig. 6), the appropriate conformation for $\kappa^3\text{-ttcn}$ coordination (see Scheme below).

Thus, the observed complex $[(\eta^3\text{-Ind})\text{Mo}(\kappa^3\text{-1,4,7-ttcn})(\text{CO})_2]^+$ is the kinetically favored species and not the thermodynamic one.

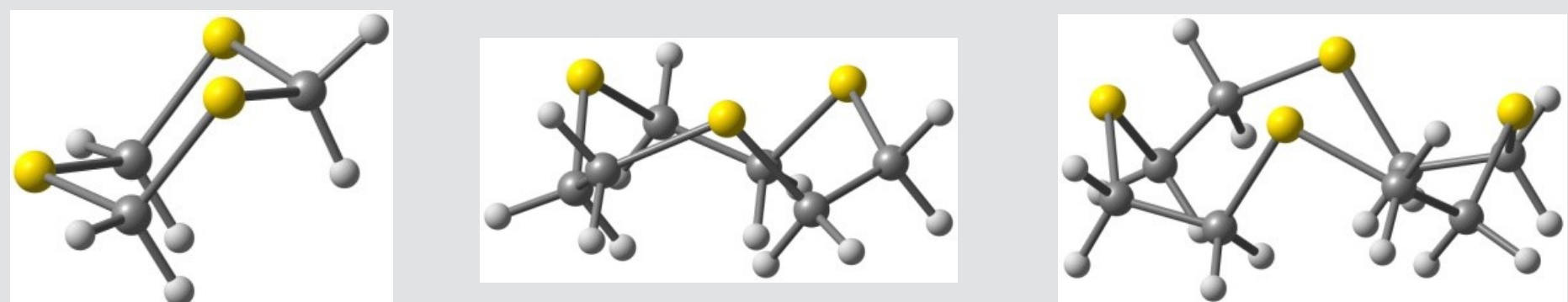
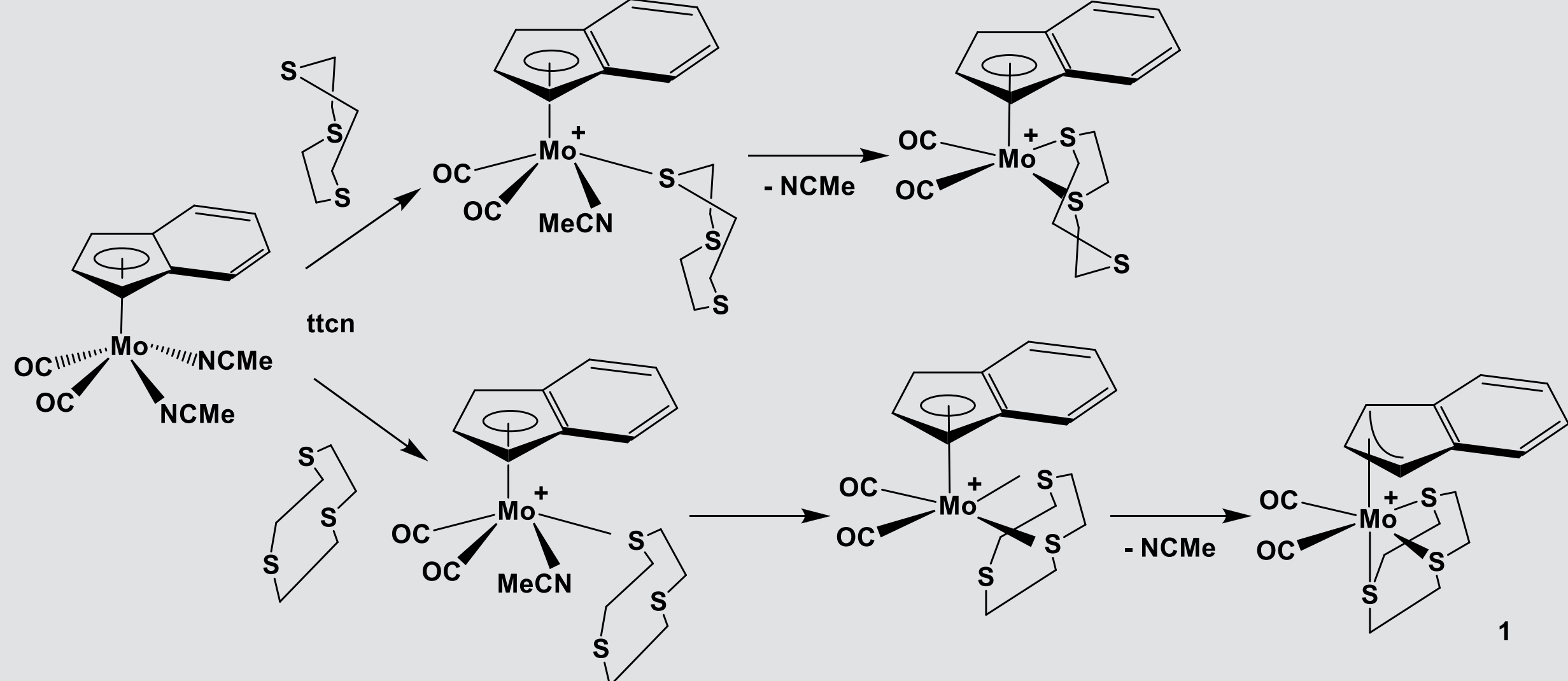


Fig. 6. Optimized geometries of the major conformers of tt (left), ttcn (center) and ttcd (right)



Computational Studies: what is the mechanism for the ttcn ring opening reaction?

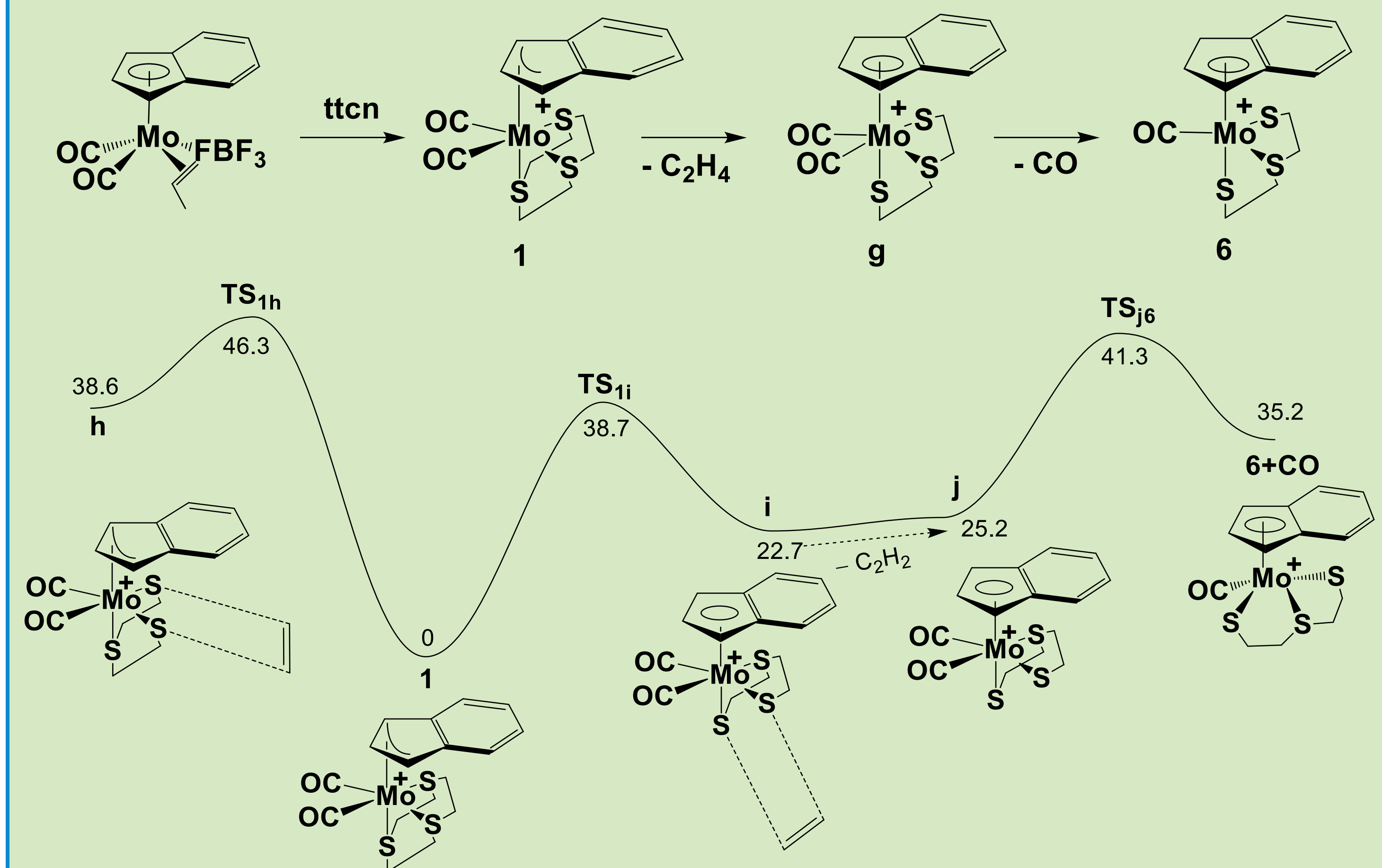


Fig. 7. Energy profile for loss of ethylene and CO from $[(\eta^3\text{-Ind})\text{Mo}(\kappa^3\text{-1,4,7-ttcn})(\text{CO})_2]^+$ (electronic energies, kcal mol⁻¹)

The high formal oxidation state leads to weak Mo–C(O) bonds and long calculated distances of 203.6 and 204.4 pm (i). The reaction is helped by the formation of gaseous products (ethylene and CO). The relatively high barrier (38.7 kcal mol⁻¹) is consistent with the slow uncatalyzed process. The acid catalyzed reaction proceeds much faster.

Conclusions

The macrocycle 1,4,7-trithiacyclononane (ttcn) reacts with $[(\eta^5\text{-Ind})\text{Mo}(\text{CO})_2(\text{NCMe})_2]^+$ to give $[(\eta^3\text{-Ind})\text{Mo}(\text{CO})_2(\kappa^3\text{-ttcn})]^+$ (1), but its reaction with $[(\eta^5\text{-Ind})\text{Mo}(\text{CO})_2(\text{C}_3\text{H}_5)(\text{FBF}_3)]^+$ affords the C–S bond cleavage product $[(\eta^5\text{-Ind})\text{Mo}(\text{CO})_2(\kappa^3\text{-1,4,7-trithiaheptanate})]\text{BF}_4$ (6), characterised by X-ray crystallography. In contrast to ttcn, the macrocycles 1,3,5-trithiane (tt) and 1,4,7,10-tetrathiacyclododecane (ttcd) fail to induce indenyl ring slippage: tt and ttcd react with $[(\eta^5\text{-Ind})\text{Mo}(\text{CO})_2(\text{NCMe})_2]^+$ to give $[(\eta^5\text{-Ind})\text{Mo}(\text{CO})_2(\kappa^2\text{-tt})]^+$ (2) and $[(\eta^5\text{-Ind})\text{Mo}(\text{CO})_2(\kappa^2\text{-ttcd})]^+$ (3), respectively.

DFT calculations showed that the $\eta^5\text{-Ind/Cp}$ coordination mode is always the most stable. However, a Molecular Dynamics study of the macrocycles conformations revealed that the major conformer of ttcn was a chair, which favoured κ^3 coordination. As indenyl complexes undergo slippage with a small barrier (<10 kcal mol⁻¹), the kinetically preferred species $[(\eta^3\text{-Ind})\text{Mo}(\text{CO})_2(\kappa^3\text{-ttcn})]^+$ (1) is the observed one. The ttcn ring opening reaction of 1 proceeds stepwise, with loss of ethylene followed by loss of CO, as calculated by DFT.

References

- [1] a) J. R. Ascenso, I. S. Gonçalves, E. Herdtweck and C. C. Romão, *J. Organomet. Chem.*, 1996, **508**, 169; b) M. J. Calhorda, C. A. Gamelas, I. S. Gonçalves, E. Herdtweck, C. C. Romão and L. F. Veiros, *Organometallics*, 1998, **17**, 2597.
- [2] C. A. Gamelas, N. A. G. Bandeira, C. C. L. Pereira, M. J. Calhorda, E. Herdtweck, M. Machuqueiro, C. C. Romão, L. F. Veiros, *Dalton Trans.* 2011, **40**, 1-13.

Acknowledgments

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