Indenyl ring slippage in crown thioether complexes [IndMo(CO)2L]^+ and C–S activation of trithiacyclononane: Experimental and theoretical studies


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Introduction

In complexes of type [IndMo(CO)2L]^+: trithiacyclononane (ttcn) was the only known neutral sulfur ligand able to induce indenyl ring slippage, affording complex [Cy(Ind)Mo(CO)(S2)]^+. Thus, we extended this work to the macrocyclic ligands 1,3,5-tetrathiacyclohexadecane (ttcd) in search of other examples of hopfitalopic shifts. Moreover, the observation that complex [IndMo(CO)(S2)]^+ undergoes elimination of ethylene and CO to produce the Mo(V) complex [IndMo(CO)(S2)]^+ via a [4+2]-cycloaddition/CO insertion is a very clean process, spurred our curiosity. Here the structural chemistry of [Cy2(Ind)Mo(CO)2(S2)]^+ (Cy = C6H5), S2 = 8, 10, nNcMe) is explored and complemented by a DFT mechanistic study.

Synthesis and Crystallography

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

Using Molecular Dynamics:

The ttcn conformers fall into two main clusters:
1) all three SCCS dihedral angles are 60° and the three S atoms face the same side;
2) only two SCCS dihedral angles are 60° 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. The appropriate conformation for the ttcn coordination (see Scheme below).

Thus, the observed complex [IndMo(CO)(S2)]^+ is the kinetically favored species and not the thermodynamic one.

Conclusions

The macrocycle 1,4,7-trithiacyclononane (ttcn) reacts with [IndMo(CO)2(NCMe)]^+ to give [Cy(Ind)Mo(CO)(S2)]^+, but its reaction with [IndMo(CO)2(C6H5)]^+ affords the C–S bond cleavage product [Cy(Ind)Mo(CO)2(1,3,5-tetrathiacyclohexadecane)][BF4]4. Characterized by X-ray crystallography, in contrast to ttcn, the macrocycles 1,3,5-tetrathiacyclohexadecane (ttcd) fail to induce indenyl ring slippage. It and ttcn react with [IndMo(CO)(NMe2)]^+ to give [IndMo(CO)(NMe2)(S2)]^+ (2) and [IndMo(CO)(NMe2)(S2)][BF4] (3), respectively. DFT calculations showed that the y^2-Ind coordination mode is always the most stable. However, a Computational Dynamics study of the macrocycles conformations revealed that the major conformer of ttcn was a chair, which favoured coordination. As indenyl complexes undergo slippage with a small barrier (<10 kcal mol^-1), the kinetically preferred species [y^2-IndMo(CO)(S2)]^+ (1) is the observed one. The ttcn opening reaction of 1 proceeds stepwise, with loss of ethylene followed by loss of CO, as calculated by DFT.

References


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