

Gold–Gold Cooperation in the Addition of Methanol to Alkynes

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INTRODUCTION

Gold catalysis is one of the hot topics in current organic synthesis.

It started with the discovery that gold can efficiently catalyze the addition of nucleophiles, to alkynes.

Nowadays gold is efficiently used for the construction of complex structures through reaction cascades based on π activations of multiply unsaturated molecules.

key steps are often based on couplings between a C-C triple bond and a C-C double bond.

The accepted reaction mechanism for the gold(I)-mediated addition of either water or methanol to an alkyne involves coordination of cationic gold to the C-C triple bond, which promotes the addition of the nucleophile.

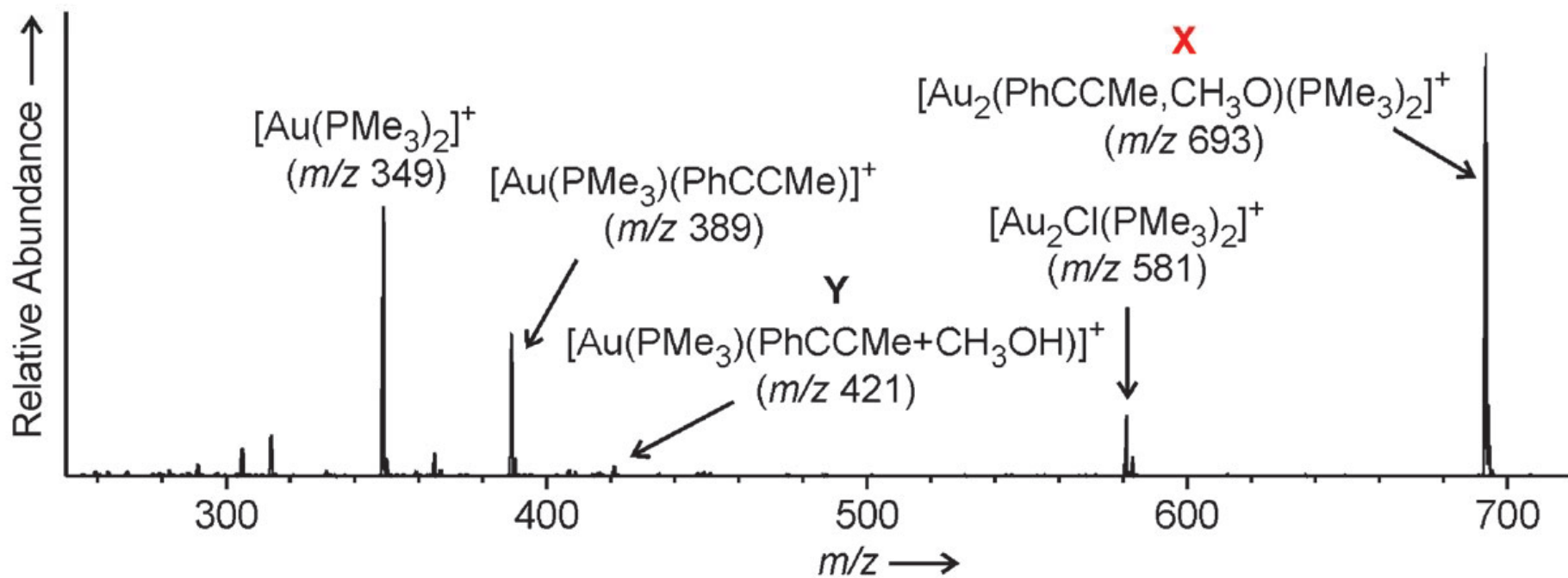
The addition is completed by the migration of a proton bound to the oxygen atom of the incoming nucleophile to the second carbon atom of the multiple bond. The proton migration is assisted by solvent molecules.

IN THIS PAPER

An investigation of the gold(I)-mediated ($[\text{AuCl}(\text{PMe}_3)]$) addition of methanol to an alkyne (1-Phenylpropyne, $\text{Ph-C}\equiv\text{C-Me}$) by electrospray ionization mass spectrometry (ESI-MS), NMR experiments, and DFT calculations.

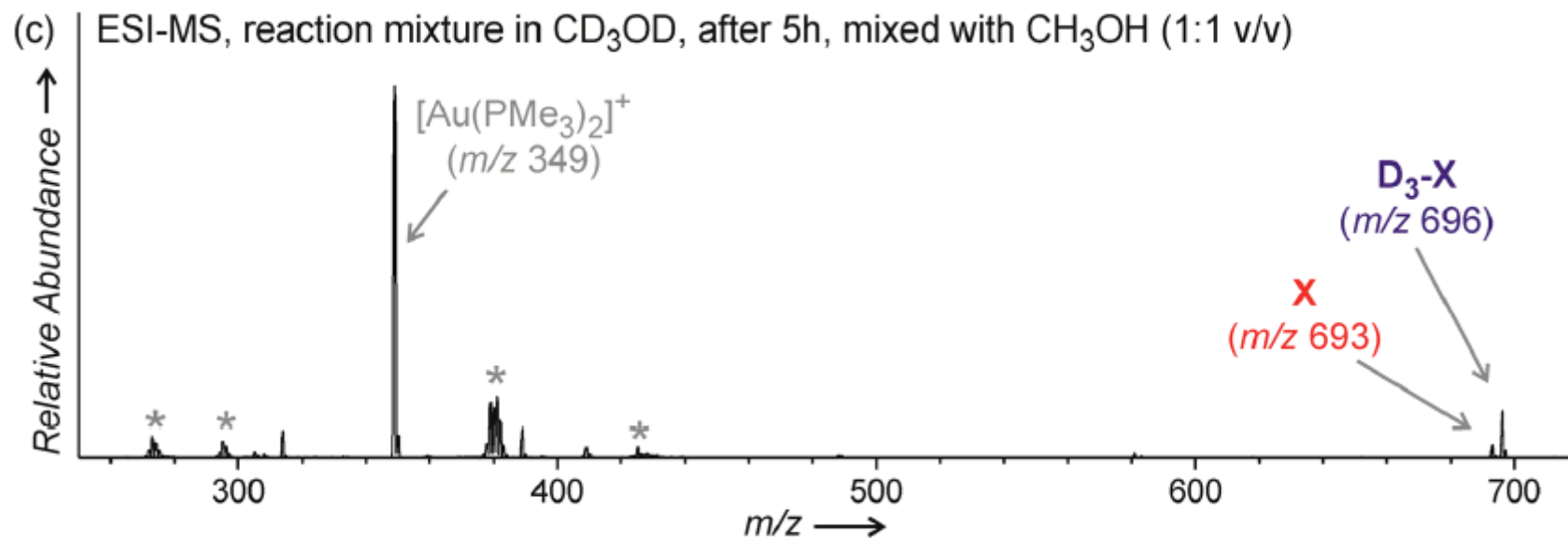
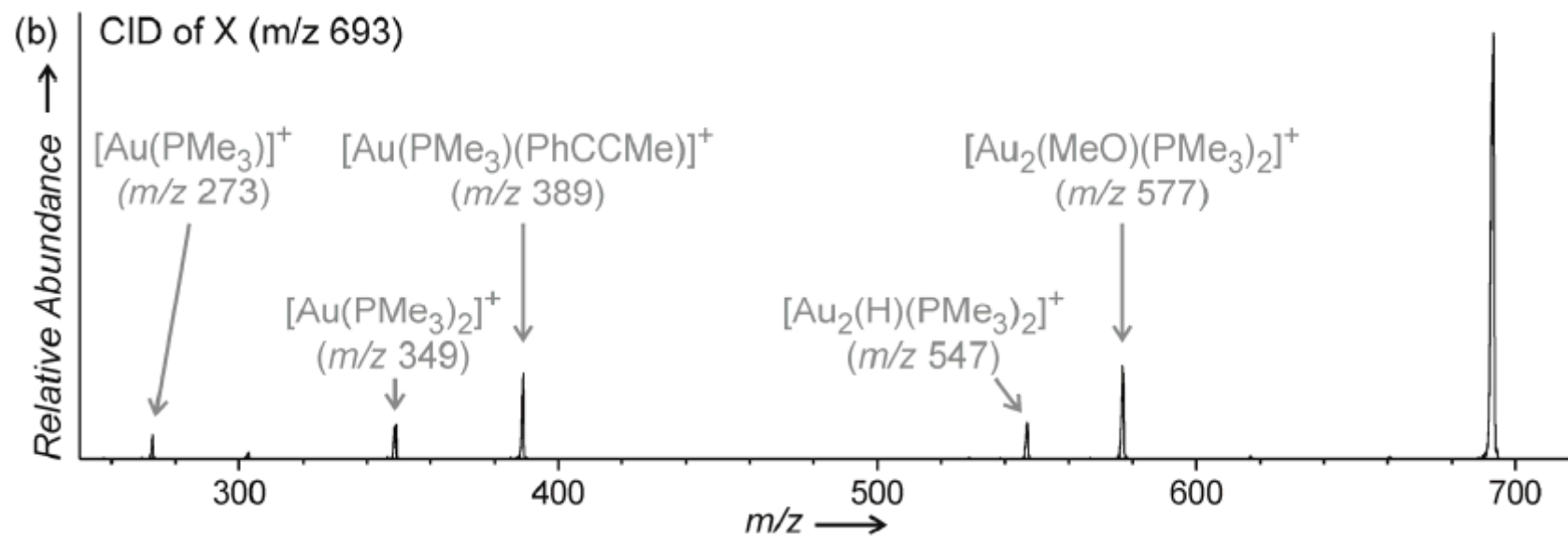
Furthermore, the key reaction intermediate is characterized by IR multiphoton dissociation (IRMPD) spectroscopy.

RESULT AND DISCUSSIONS

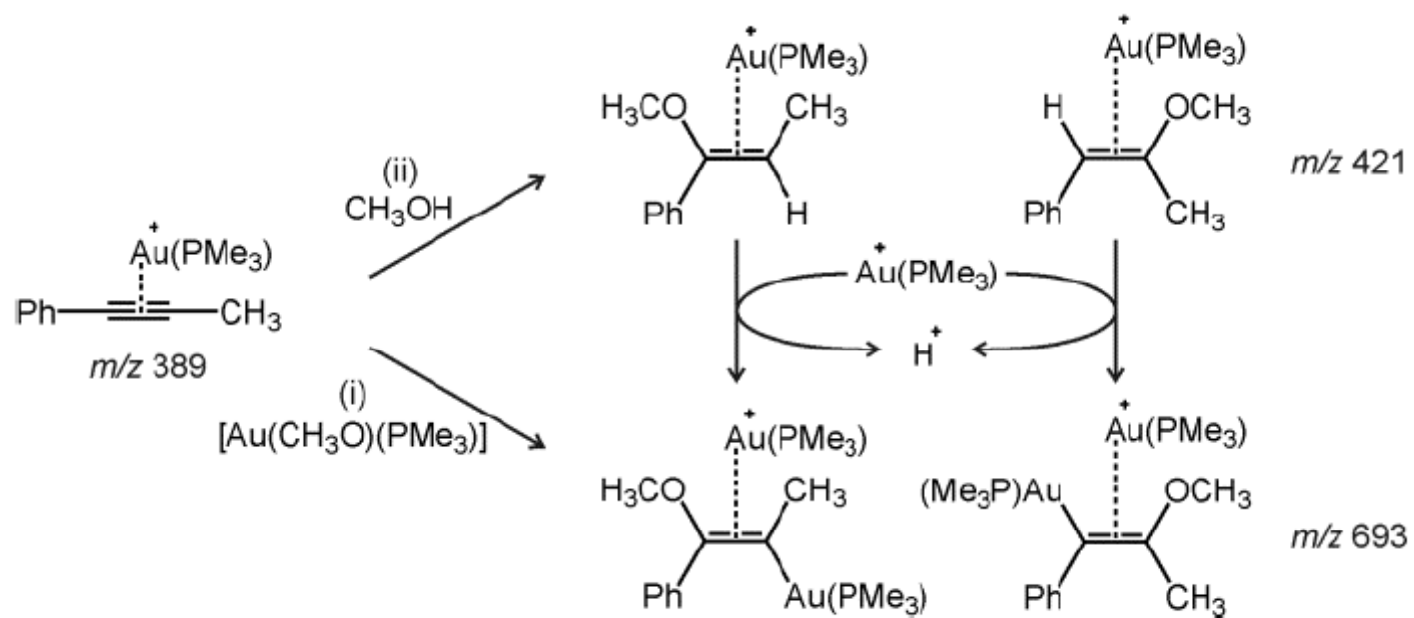


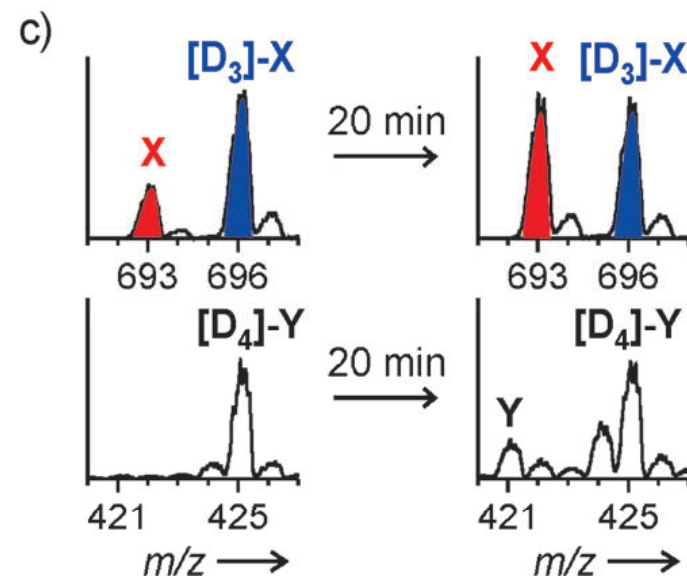
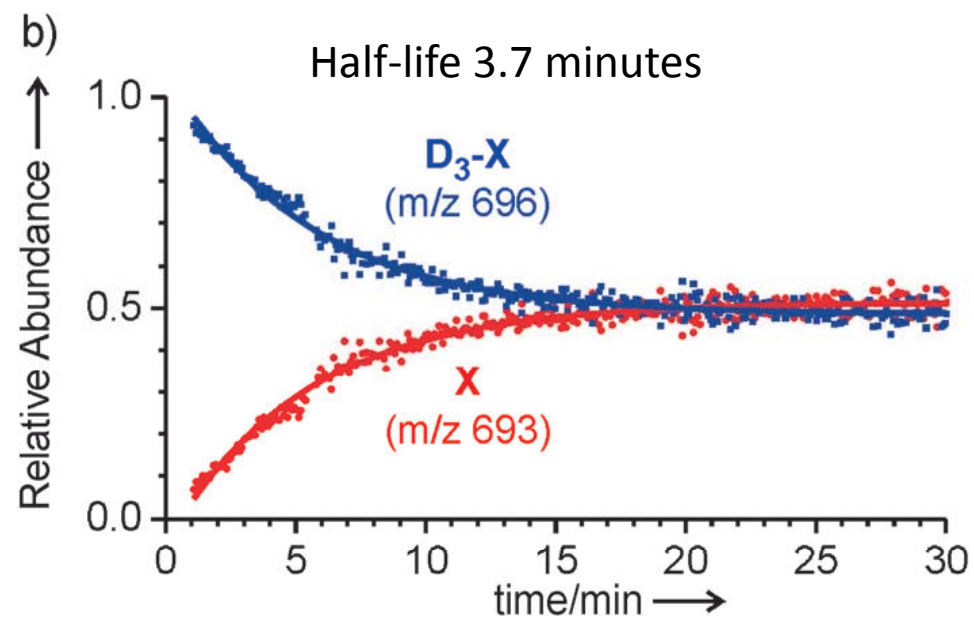
ESI-MS data of a MeOH solution of 1-phenylpropyne with catalyst.

Identification of m/z 693 peak, an intermediate



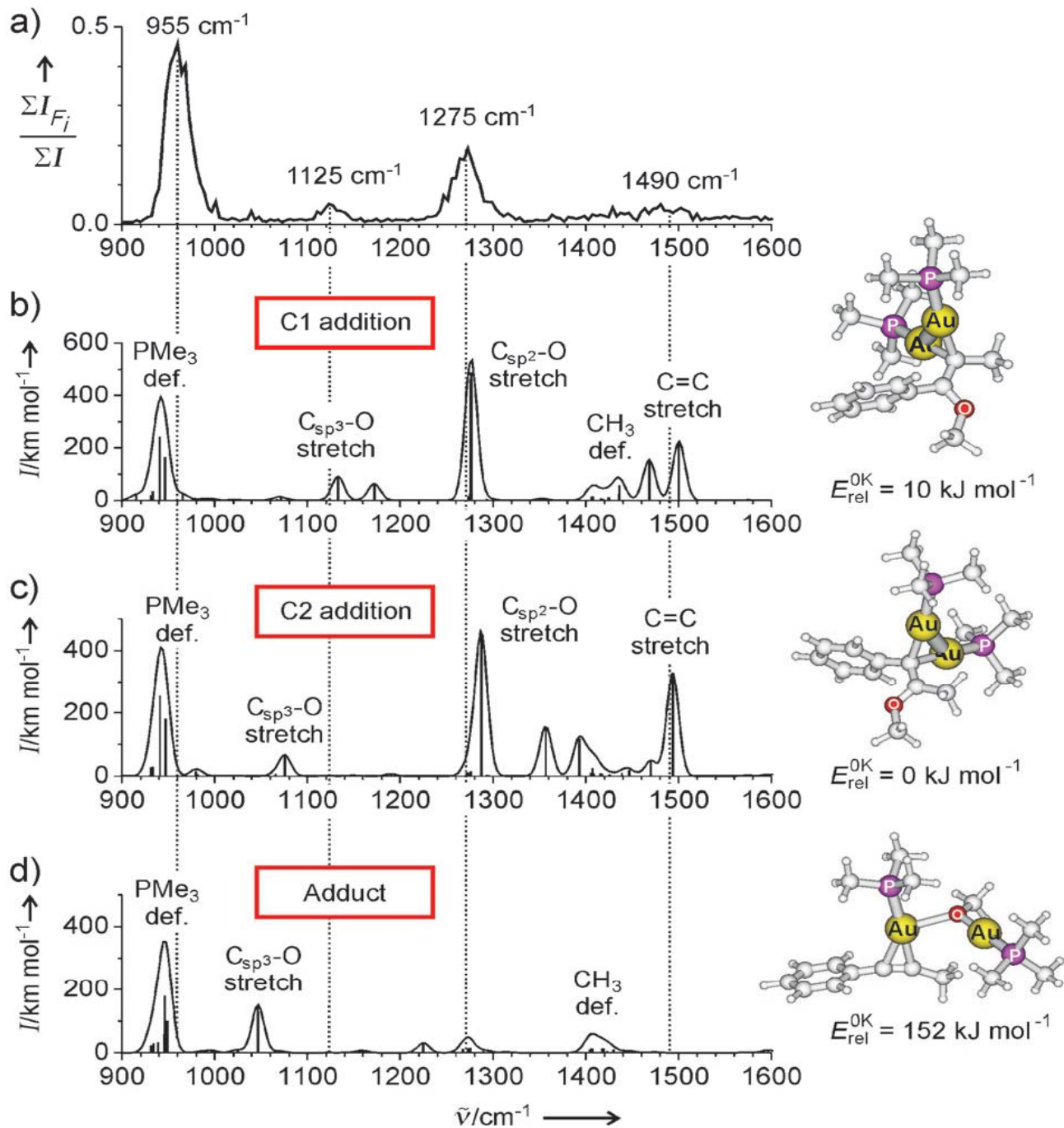
Possible pathways for the formation of X



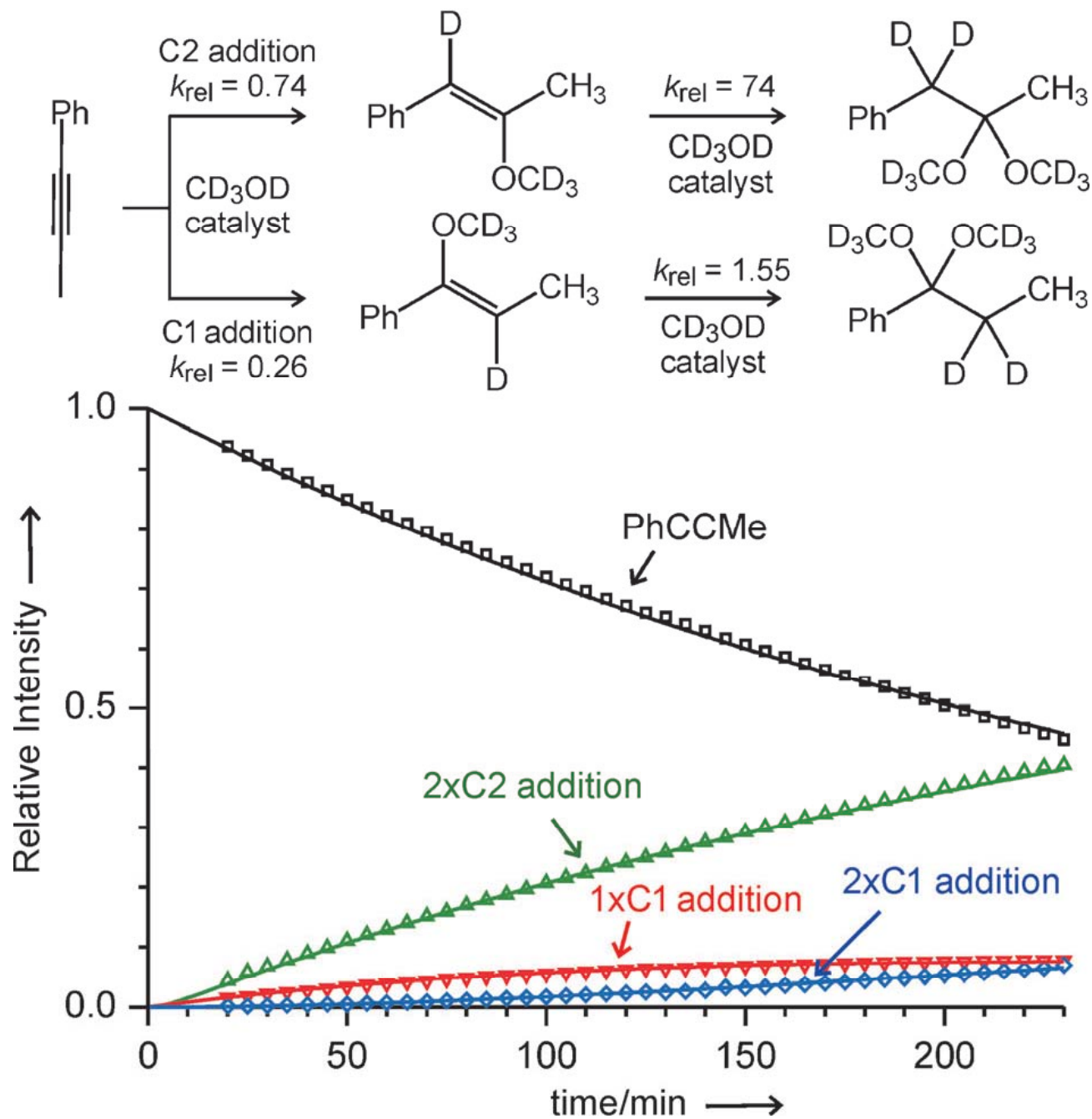


Time dependence of the relative abundances of $[D_3]$ -X and X upon adding CH_3OH to a solution of 1-phenylpropyne in CD_3OD and the catalyst (CH_3OH/CD_3OD 1:1 (v/v)) after 1 hour reaction time.

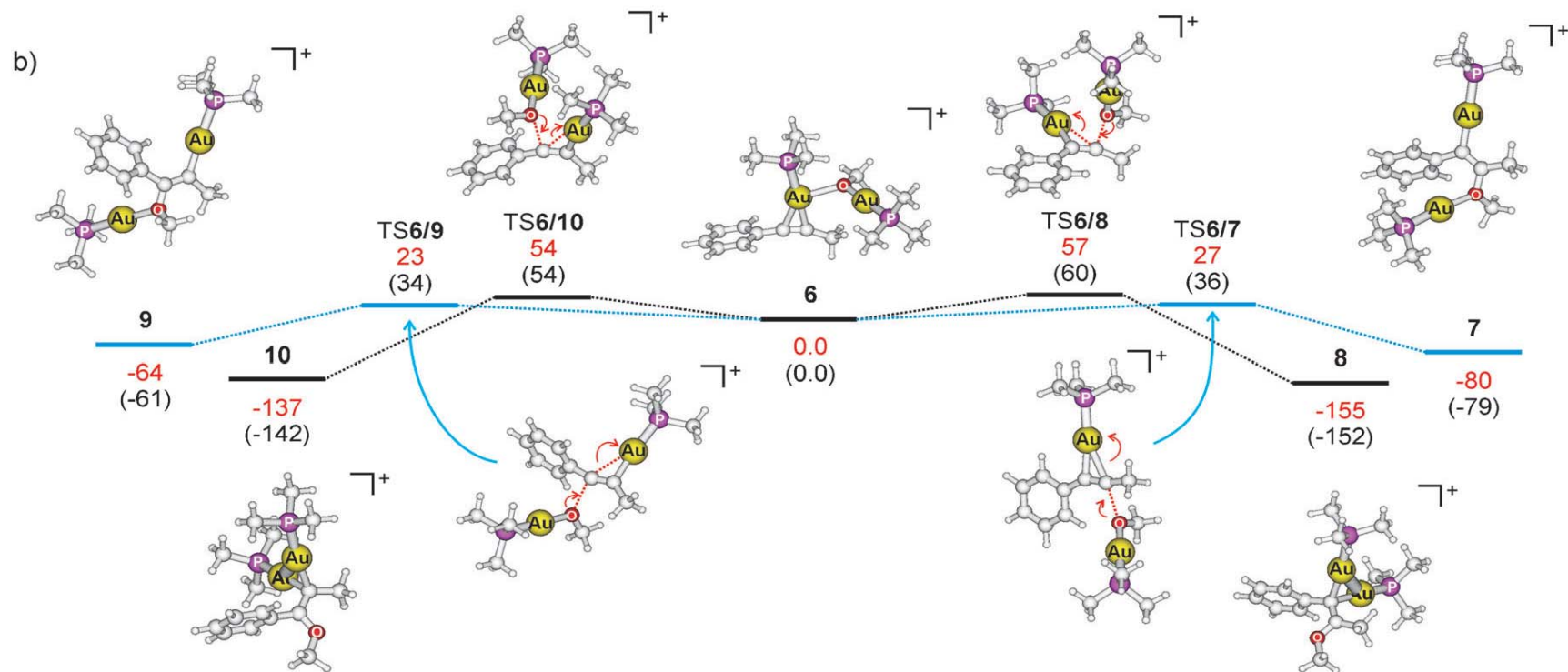
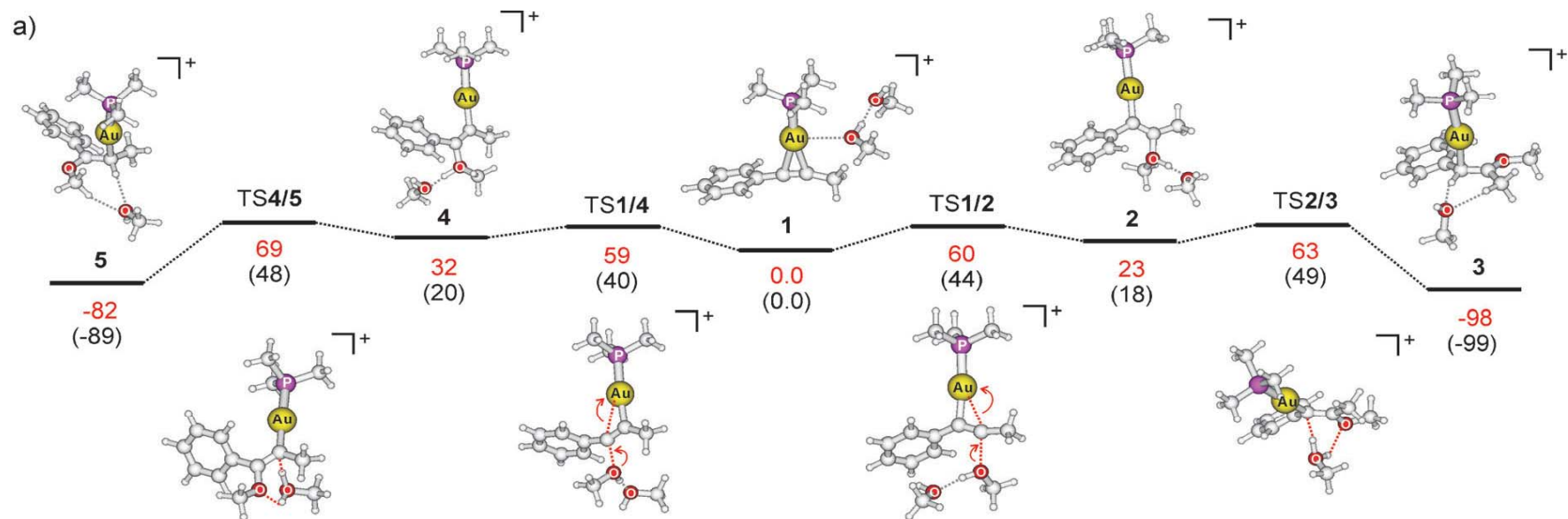
Structure determination of X by IRMPD spectroscopy



NMR spectroscopic investigation of the reaction



DFT calculations



SUMMARY AND CONCLUSIONS

The results presented herein demonstrate that the addition of methanol to a C-C triple bond proceeds with a dual activation mechanism; the triple bond is activated by the coordination with the gold catalyst and methanol is added in the form of gold methanolate.

The dual activation mechanism results in direct formation of gem-diaurated intermediates.

Additions of O-nucleophiles can have a substantial effect on the mechanistic understanding of the gold-catalyzed reactions.

As the addition of alcohol represents an initial step of many cascade reactions involving alkynes, the understanding of the mechanistic aspects may guide in designing new synthetic methods.

FUTURE POSSIBILITIES

Small gold cluster can be used for similar catalytic reaction, without modifications in the helium gas line.

Possibility of doing gas phase IR spectroscopic measurements of mass selected ions in the new ice instrument, if attached an ESI source.

THANK YOU