

Equilibrium Between a Self-Assembled M_3L_2 Molecular Cage and M_6L_4 Molecular Bowl

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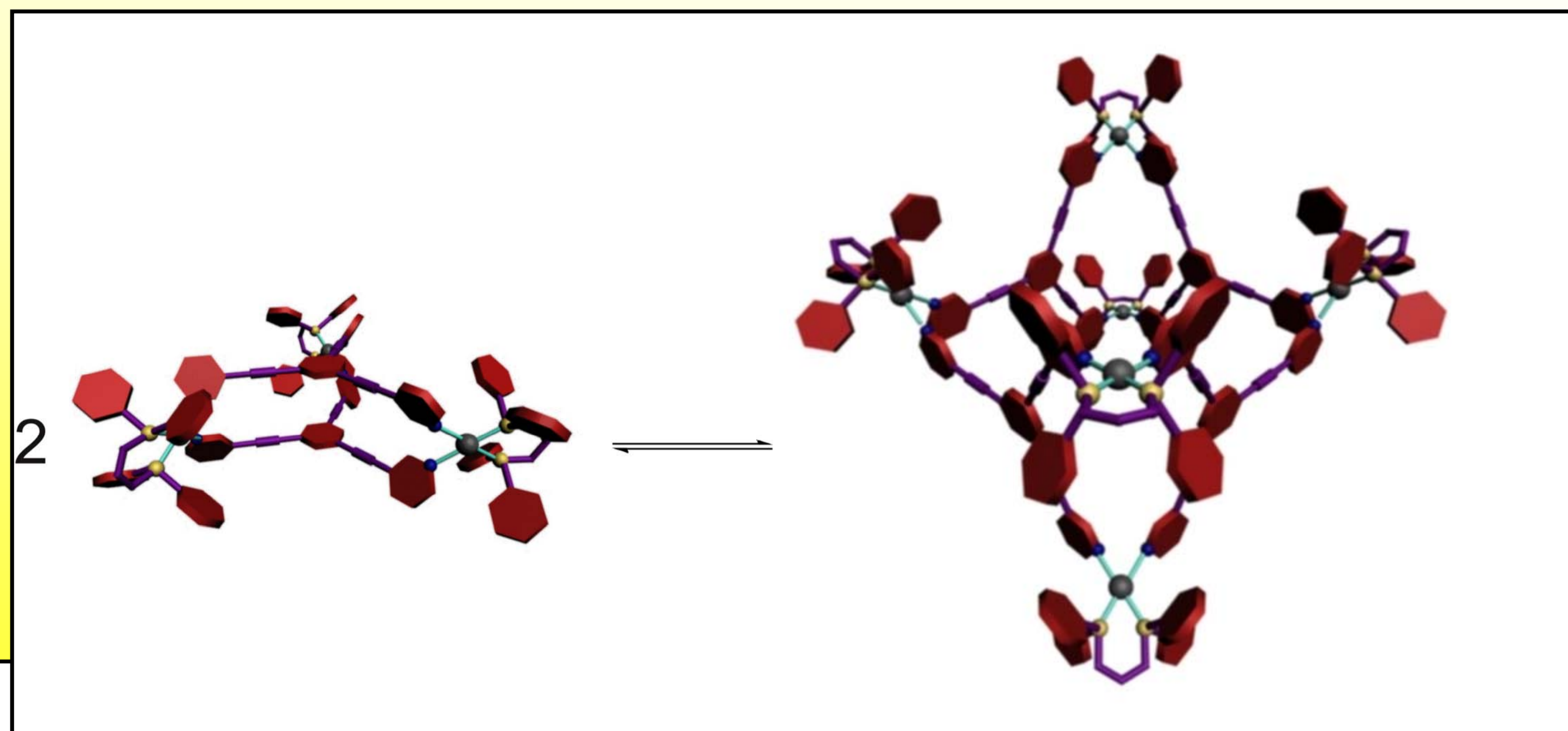
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Introduction

In the early stages of designing discrete 3D assemblies by combining an organic ligand with a *cis*-protected metal, the use of a template was mandatory.^[1] Later, solely the choice of a rigid ligand could shift the equilibrium from an unspecific assembly to a discrete, thermodynamically favored 3D assembly, making the use of a template unnecessary.^[2]

This in mind, we synthesized a tritopic pyridine ligand (**1**), which combines the properties of being rigid, but still having a rotational flexibility between the acetylene units.



After combining ligand **1** with $M(dppp)OTf_2$ ($M = Pd(II), Pt(II)$; $dppp =$ diphenylphosphino-propane) in a 1 : 1.5 ratio, we interestingly observed an equilibrium between a 3:2 and 6:4 ($M:L$) assembly when using the *cis*-protected $Pd(II)$ metal and only a 3:2 assembly for the *cis*-protected $Pt(II)$ metal at room temperature.

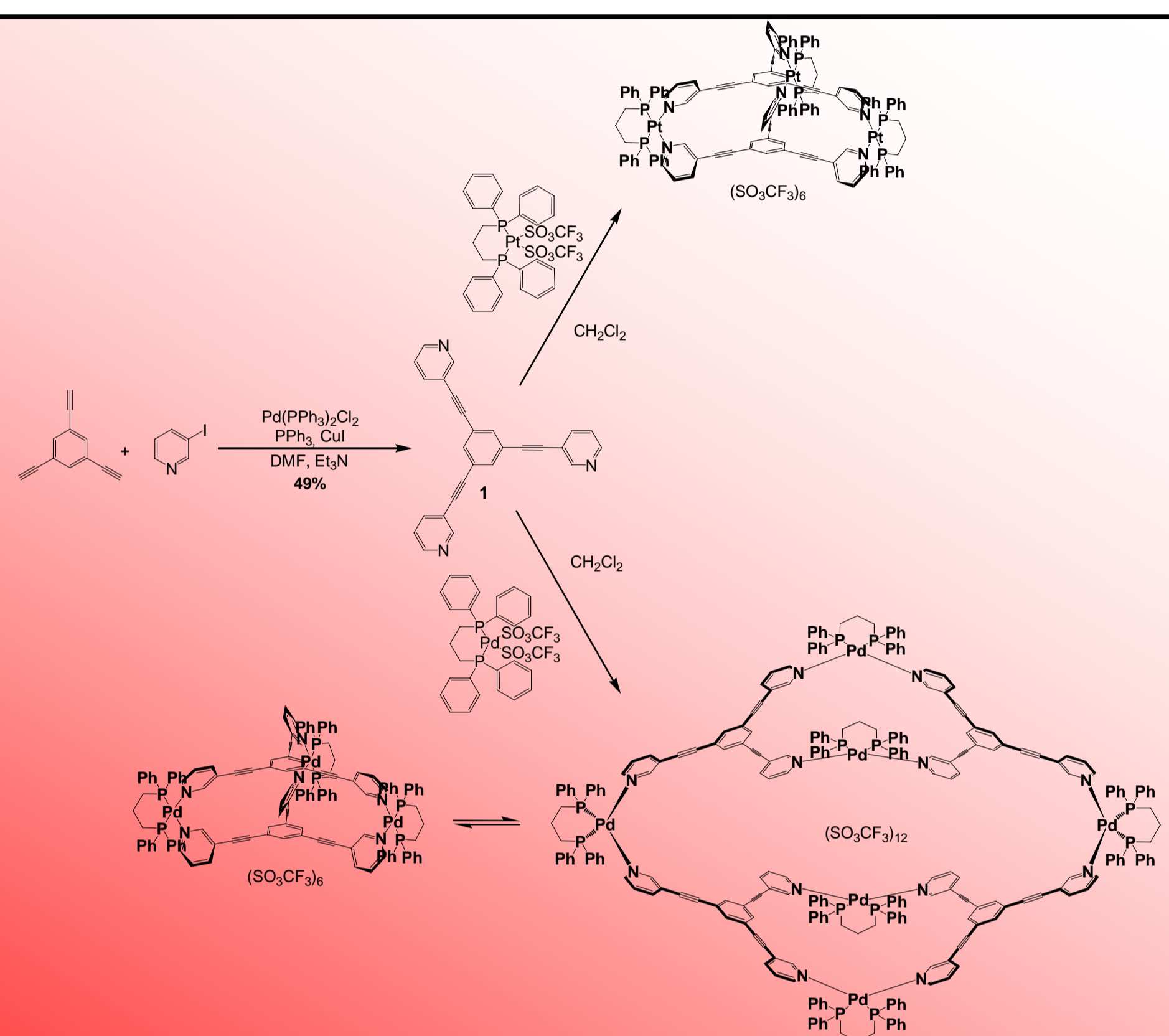
Both assemblies were investigated and confirmed by 1H -, ^{31}P -NMR and ESI MS experiments.

Synthesis

Tritopic pyridine ligand **1** is synthesized by a Sonogashira cross coupling reaction.

When combining the tritopic pyridine ligand **1** with a *cis*-protected $Pd(II)$ metal in a 1 : 1.5 ratio, an equilibrium of a 3:2 and 6:4 assembly is observed.

In case of the *cis*-protected Pt metal only the 3:2 assembly is formed at room temperature.

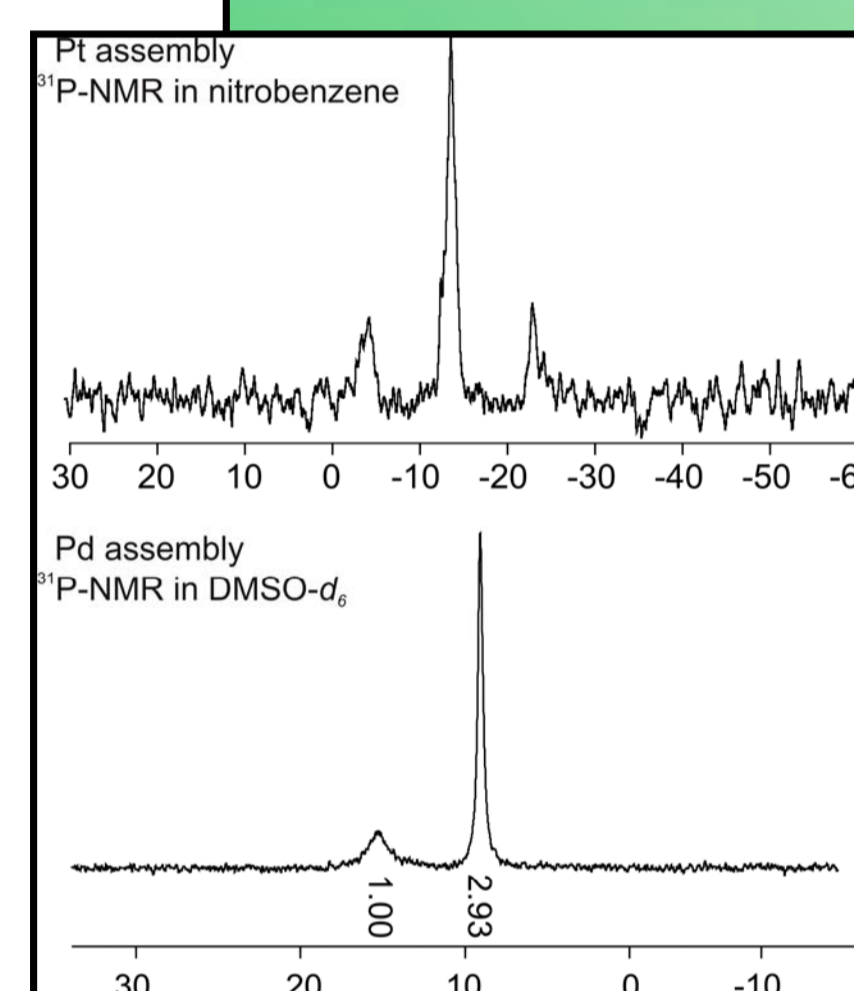


NMR Spectroscopy

The 1H -NMR shows the tritopic pyridine ligand **1** and the Pd assembly in a 1 : 1.5 ratio in CD_2Cl_2 .

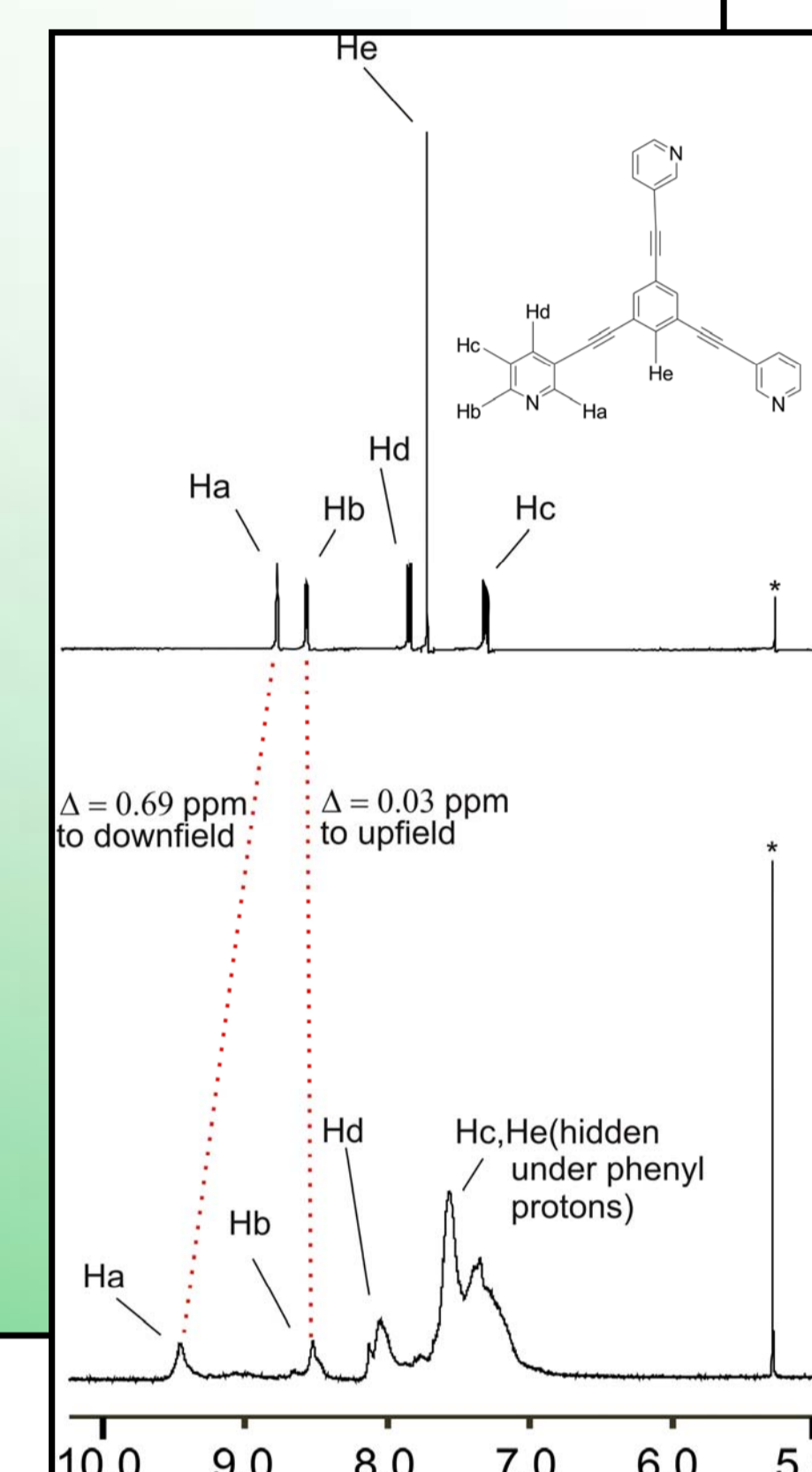
The α -pyridyl protons (**Ha**) are downfield shifted indicating a coordination to the metal and the second α -pyridyl protons (**Hb**) are upfield shifted due to the phenyls of $dppp$.

A broadening of the signals may indicate an equilibrium of two or more assemblies.



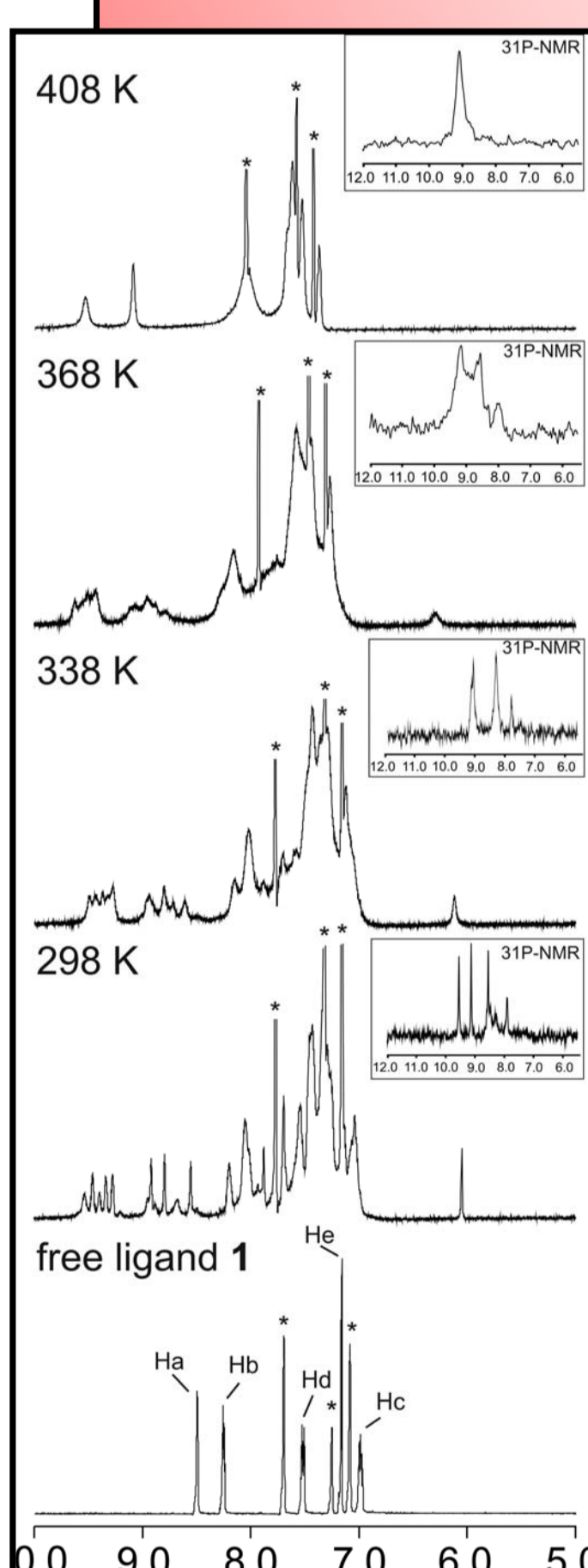
In the $^{31}P\{^1H\}$ -NMR of the Pd assembly in $DMSO-d_6$ two signals are evident representing the 3:2 and 6:4 assemblies (latter more upfield shifted), while three peaks are observed in nitrobenzene under identical conditions. In contrast, the $^{31}P\{^1H\}$ -NMR of the Pt assembly in nitrobenzene shows only one signal.

This confirms the observed equilibrium between the 3:2 and 6:4 assemblies and its solvent dependency.



NMR Experiments

1H - and ^{31}P -NMR high temperature depending measurements with the Pd assemblies in nitrobenzene- d_5 were performed



at r.t. at least two species are present

raising the temperature causes a broadening of the signals

at approximately 380 K coalescence temperature in ^{31}P -NMR is reached

at higher temperatures the entropically favored 3:2 assembly is the only species present

All changes were fully reversible on cooling the solution to the starting temperature, confirming that the system is in equilibrium.

Tandem Mass Spectrometry Experiments

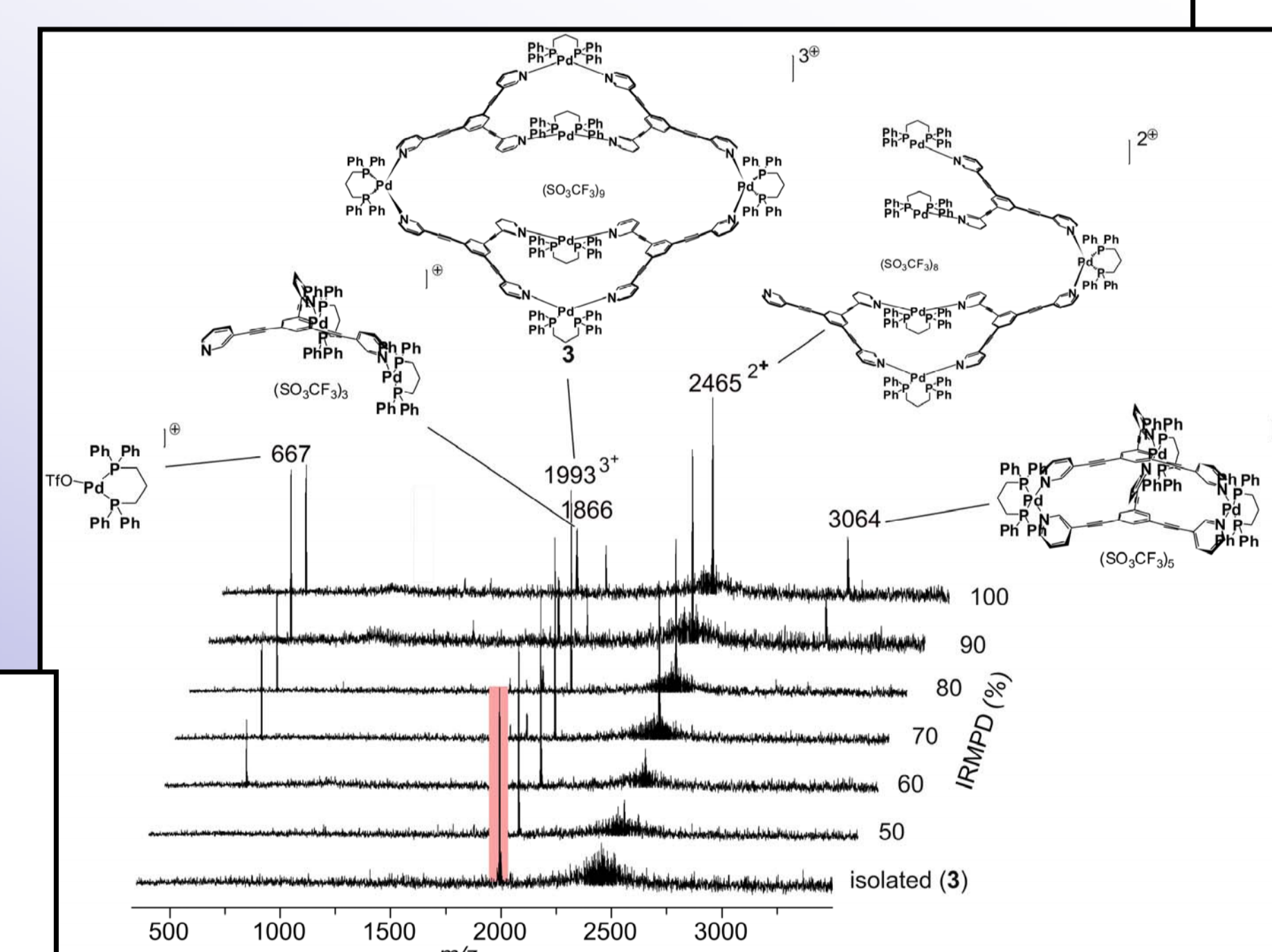
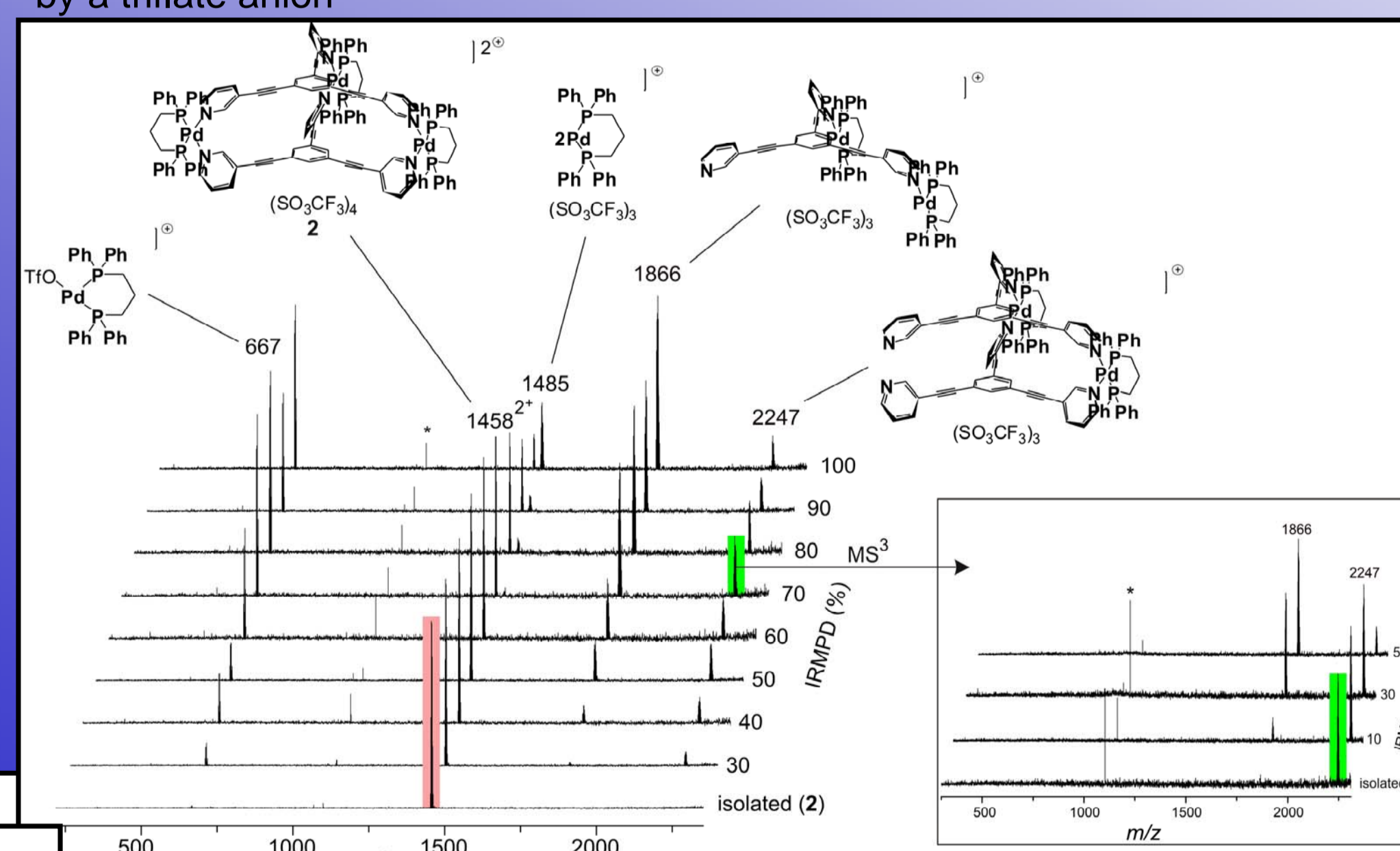
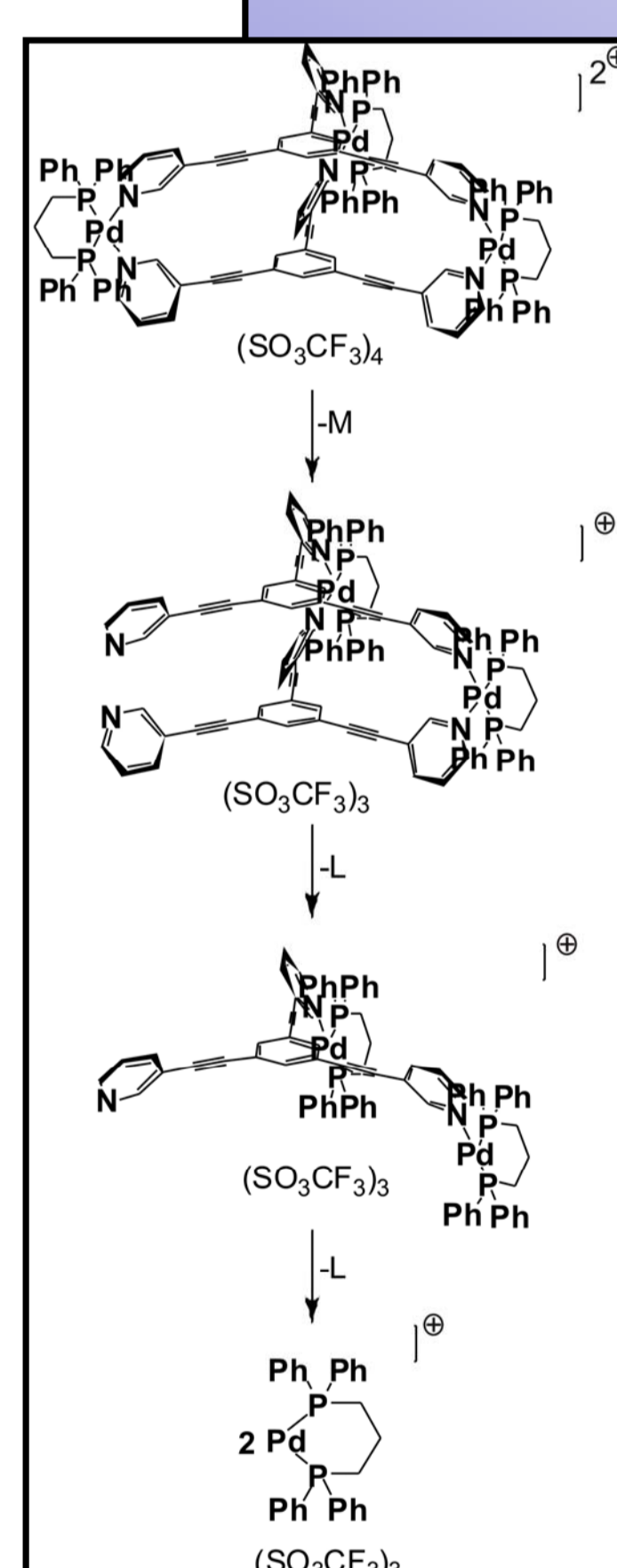
Isolation of the double charged cage (**2**) or triple charged bowl (**3**) and the initiated fragmentation by an IRMPD CO_2 Laser unclosed the possibility:

to study the fragmentation mechanism of the M_3L_2 molecular cage, which was reconfirmed by MS^3 experiments and

to ensure the 6:4 assembly is not a dimer of the 3:2 assembly

Fragmentation mechanism of the Pd assembly (M_3L_2):

- loss of $Pd(II)$ corner
- loss of neutral ligand **1**
- loss of second ligand **1**, simultaneously forming two $Pd(II)$ corners linked by a triflate anion



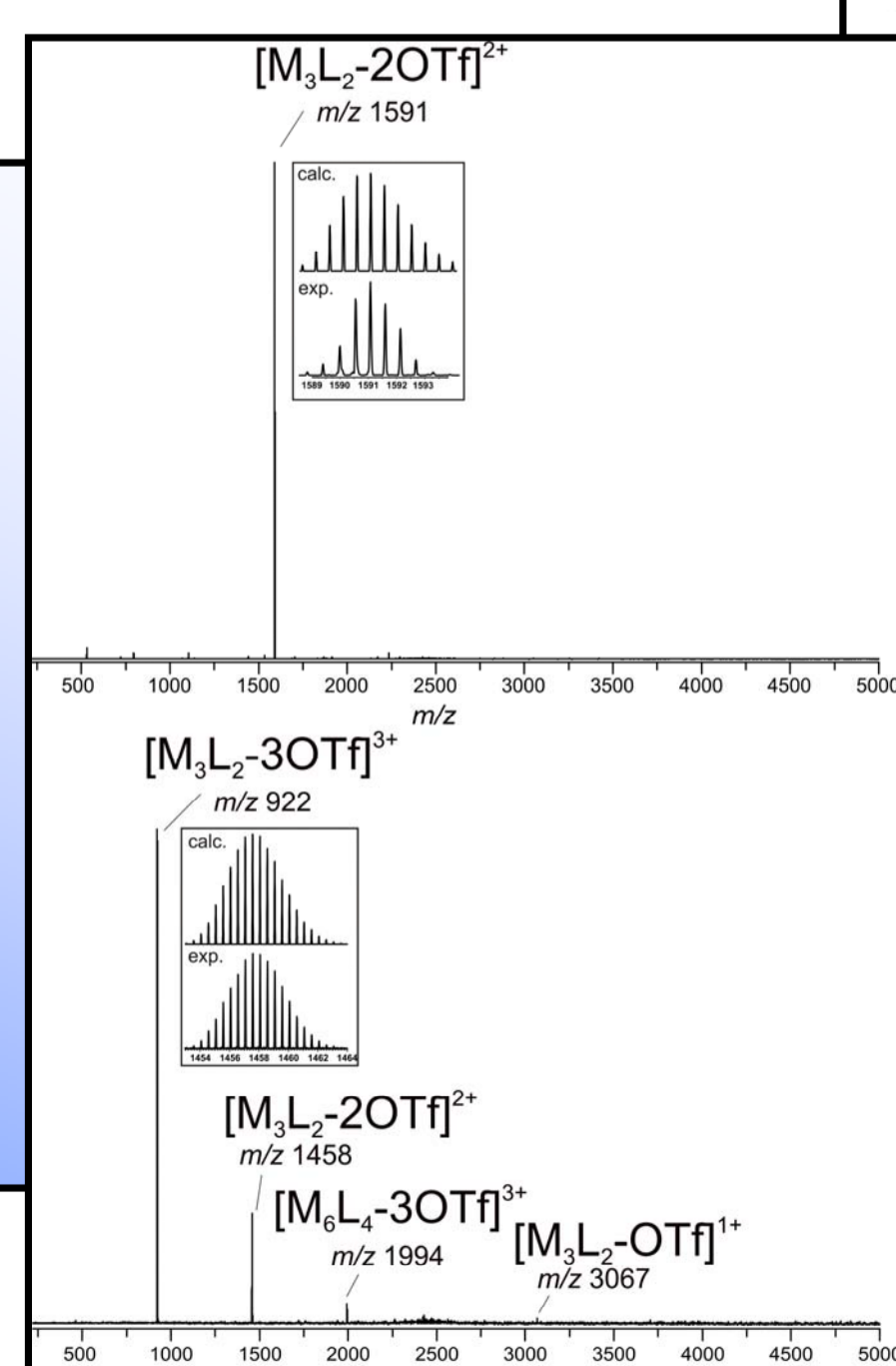
A different fragmentation pathway is observed for the Pd assembly (M_6L_4):

- loss of $Pd(II)$ corner + ligand **1**
- loss of two $Pd(II)$ corners + ligand **1**, forming the 3:2 assembly via back side attack of the free pyridyl unit at the appropriate Pd corner

Mass Spectrometry

The ESI mass spectrum of the Pt assembly after 24 h of stirring results in only one peak showing the formation of only the 3:2 assembly.

The ESI mass spectrum of the Pd assembly after only 10 min of stirring already confirms the formation of a 3:2 and 6:4 assembly



Conclusion

- We observed an equilibrium between a self-assembled M_3L_2 -cage and a M_6L_4 -bowl when mixing tritopic ligand **1** and *cis*-protected Pd -metal in a ratio of 1:1.5.
- The equilibrium was confirmed by NMR spectroscopy and ESI mass spectrometry.
- Tandem mass spectrometry enabled us to study the fragmentation mechanism of the 3:2 and 6:4 assemblies.
- High-temperature NMR measurements show a shift of the equilibrium towards the entropically favored 3:2 assembly.

References

- [1] a) M. Fujita, S. Nagao, K. Ogura, *J. Am. Chem. Soc.* **1995**, *117*, 1649-1650; S. Hiraoka, M. Fujita, *J. Am. Chem. Soc.* **1999**, *121*, 10239-10240.
- [2] a) U. Radhakrishnan, M. Schweiger, P. J. Stang, *Org. Lett.*, **2001**, *20*, 3141-3143; b) M. Fujita, K. Umamoto, M. Yoshizawa, N. Fujita, T. Kusakawa, K. Biradha, *Chem. Commun.*, **2001**, 509-518; c) P. S. Mukherjee, N. Das, P. J. Stang, *J. Org. Chem.* **2004**, *69*, 3526-3529; d) J. E. Beves, B. E. Chapman, P. W. Kuchel, L. F. Lindoy, J. McMurtrie, M. McPartlin, P. Thordarson, G. Weia, *Dalton Trans.*, **2006**, 744-750.

Acknowledgments

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