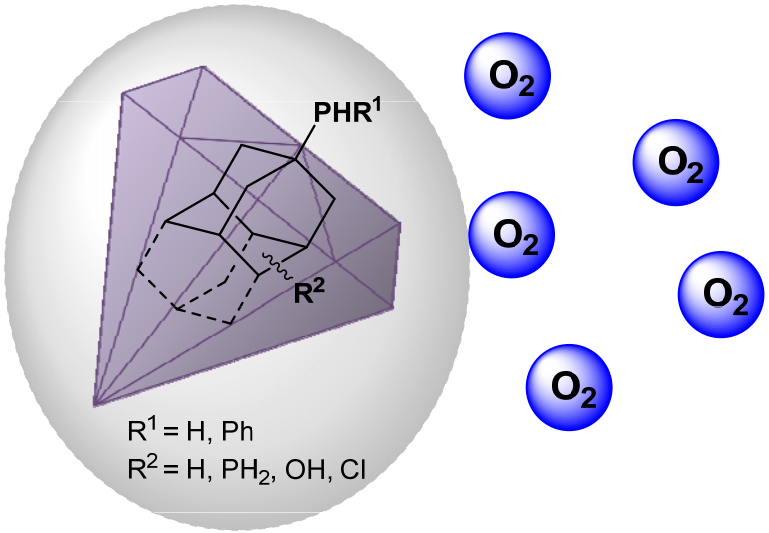
Diamondoid Phosphines: insights concerning air stability and NMR behavior

Seminar talk presented by
Moncea Oana

June 3rd, 2016

Institute of Organic Chemistry
Justus-Liebig-University Giessen



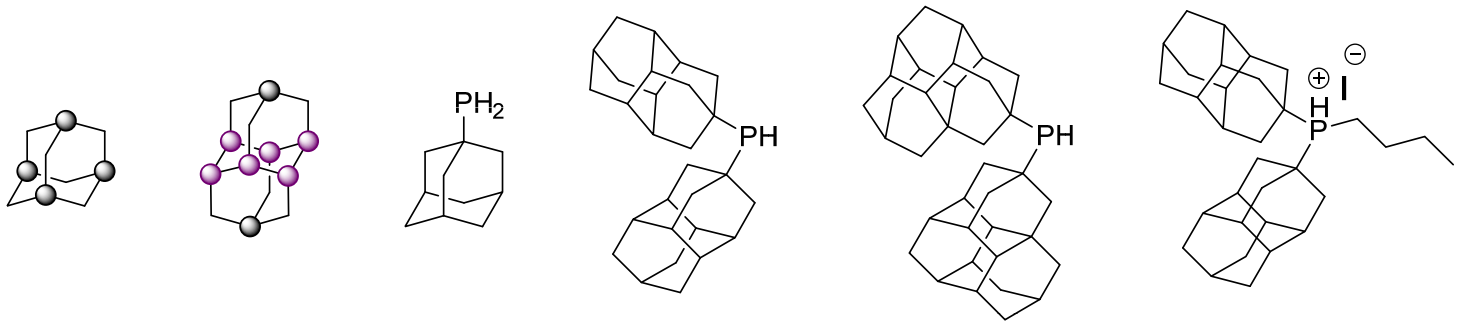
Outline

- Diamnodoid phosphines synthesis
- Diamondoid phoshines characterisation:
    - Air stability
    - VT-NMR studies
- Outlook

Diamnodoid phosphines synthesis

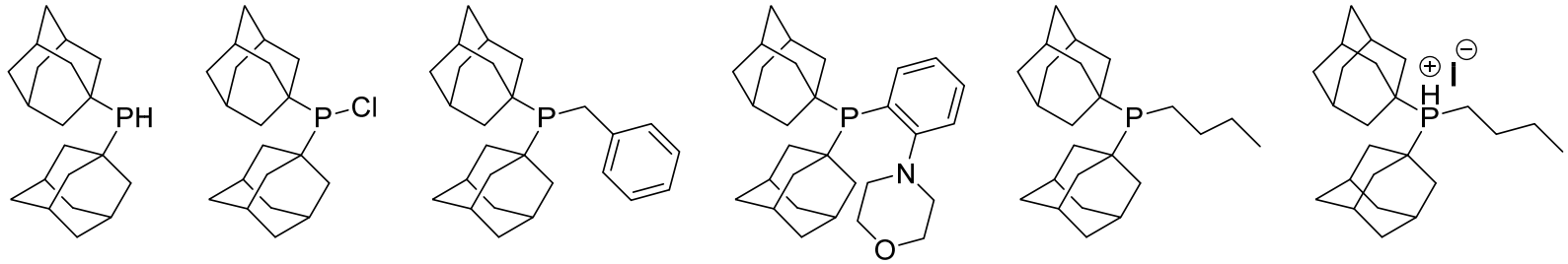
Known diamondoid phosphines and salts:

a)



1 **2** **3** **4a** **4b** **5a**

b)



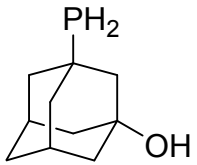
4c **6** **7** **8** **9** **5b**

Stetter, H.; Last, W.-D. *Chem. Ber.* **1969**, *102,* 3364; Ohashi A.; Matsukawa, S.; Imamoto T. *Heterocycles* ***2000****, 52, 905*; Antoni, G.; Schwertfeger, H.; Machuy, M. M.; Würtele, C.; Dahl, J. E. P.; Carlson, R. M. K.; Schreiner, P. R. *Adv. Synth. Catal.* **2010**, *352*, 609***;*** Goerlich, J. R.; Schmutzler, R. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *81,* 141; Goerlich, J. R.; Schmutzler, R. *Phosphorus, Sulfur, and Silicon Relat. Elem.* **1994**, *88*, 241;Tewari, A.; Hein, M.; Zapf, A.; Beller, M. *Synthesis* **2004**, *6*, 935. Hesp, K. D.; Stradiotto, M. *J. Am. Chem. Soc.* **2010**, *132,* 18026; Beller, M.; Ehrentraut, A.; Fuhrmann, C.; Zapf, A. In *WO 02/10178 A1* **2002**.

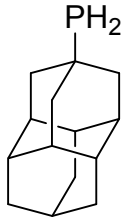
Diamnodoid phosphines synthesis

Novel diamondoid phosphines obtained from their phosphonate homologues:

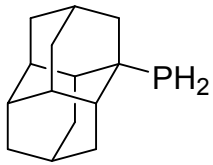
a)



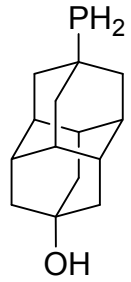
10 (92%)



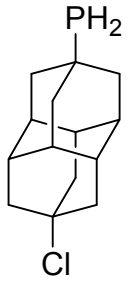
11 (80%)



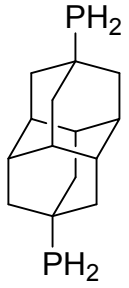
12 (56%)



13 (76%)

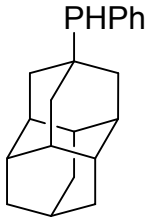


14 (79%)

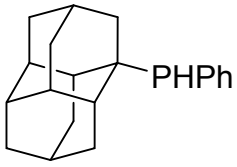


15 (85%)

b)



16 (85%)



17 (75%)

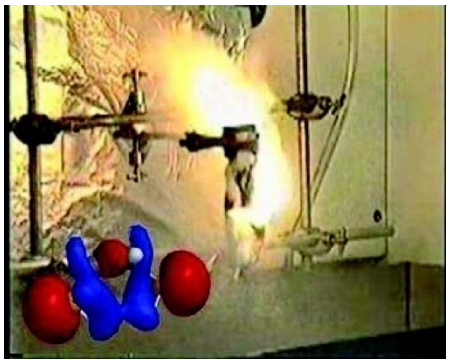
Moncea, O.; Gunawan, M. A.; Poinsot, D.; Cattey, H.; Becker, J.; Yurchenko, R. I.; Butova, E. D.; Hausmann, H.; Šekutor, M.; Fokin, A. A.; Hierso, J.-C.; Schreiner, P. R. *Submitted*

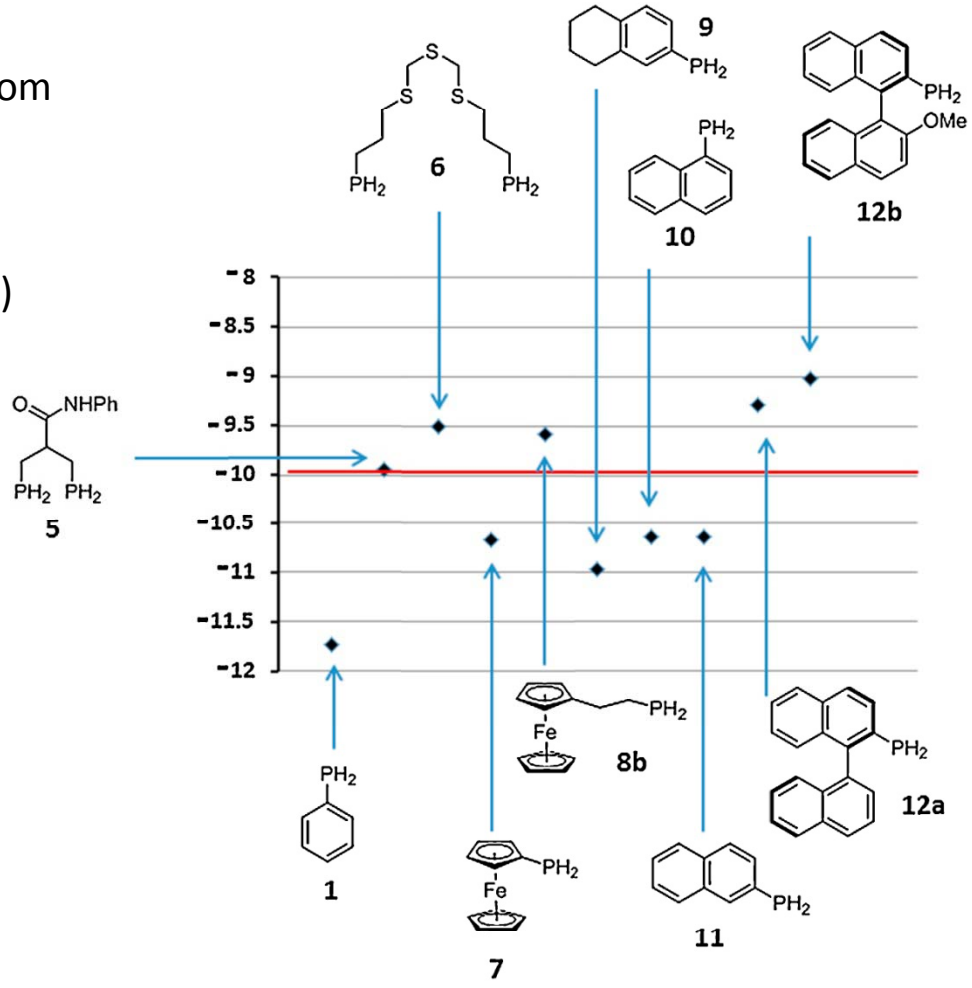
Known air stable primary phosphines:

→ HOMO delocalized away from phosphorous atom

→ extended π–conjugated systems

→ SOMO above -10eV (empirical threshold value)

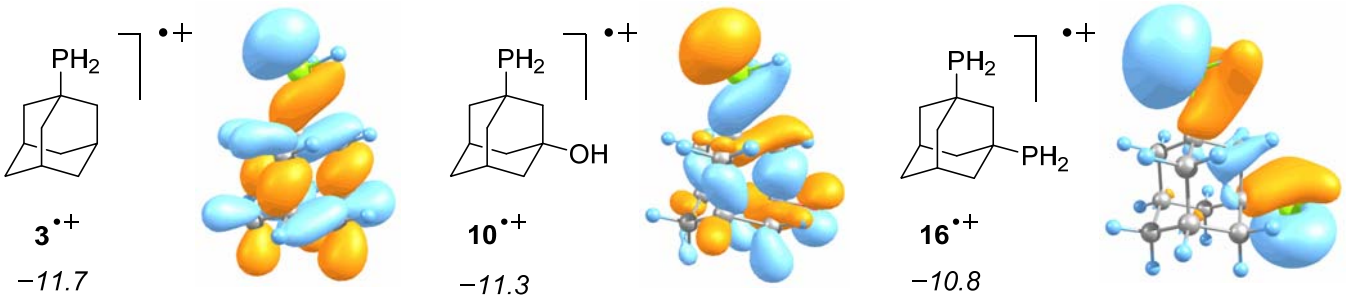


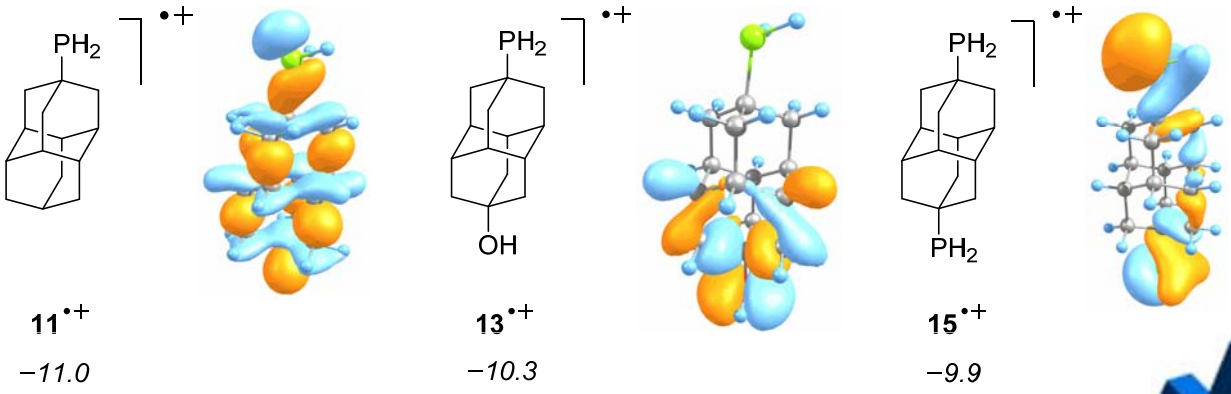


Davies, L. H.; Stewart, B.; Higham, L. J. In *Organometallic Chemistry,* RSC, **2014**, *39*, 51; Fleming, J. T.; Higham, L. J. *Coord. Chem. Rev.* **2015**, *297–298*, 127; Stewart, B.; Harriman, A.; Higham, L. J. *Organometallics* **2011**, *30*, 5338;

Diamondoid phoshines characterisation –Air stability

Diamondoid primary phosphines -air stability trend:



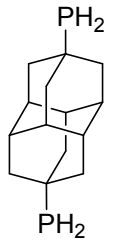


B3LYP/6-311+G(d,p)

Moncea, O.; Gunawan, M. A.; Poinsot, D.; Cattey, H.; Becker, J.; Yurchenko, R. I.; Butova, E. D.; Hausmann, H.; Šekutor, M.; Fokin, A. A.; Hierso, J.-C.; Schreiner, P. R. *Submitted*

Diamondoid phoshines characterisation –NMR study

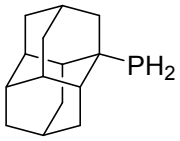
Intriguing behavior in $CDCl_3$ at room temperature for **15**



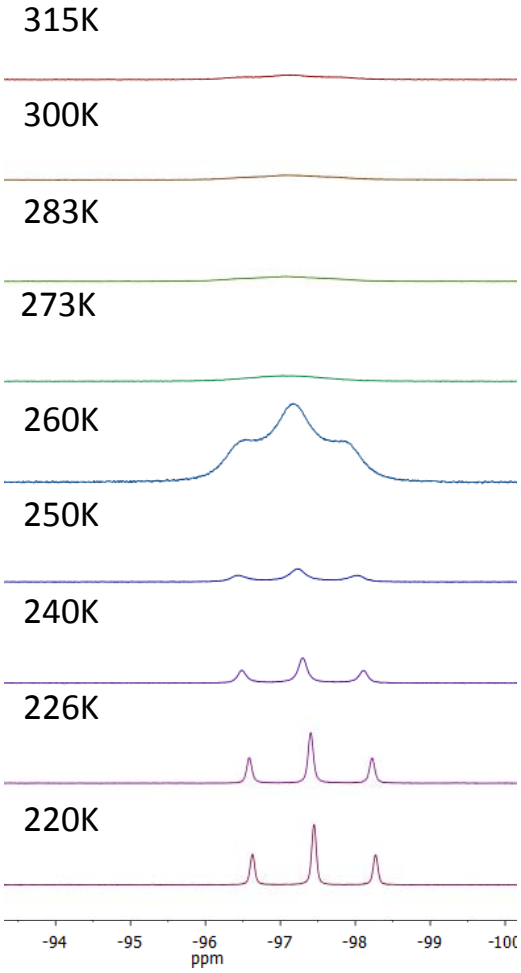
15

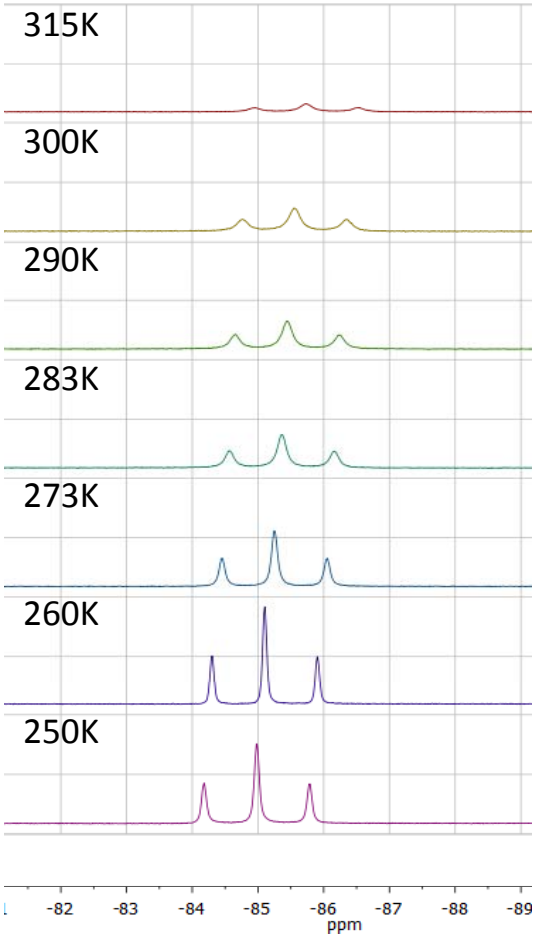
Moncea, O.; Gunawan, M. A.; Poinsot, D.; Cattey, H.; Becker, J.; Yurchenko, R. I.; Butova, E. D.; Hausmann, H.; Šekutor, M.; Fokin, A. A.; Hierso, J.-C.; Schreiner, P. R. *Submitted*

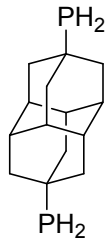
VT- ^{31}P NMR of **12** and **15** in $CDCl_3$ at room temperature



12



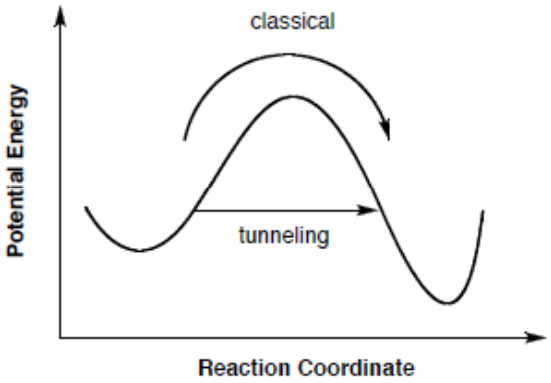




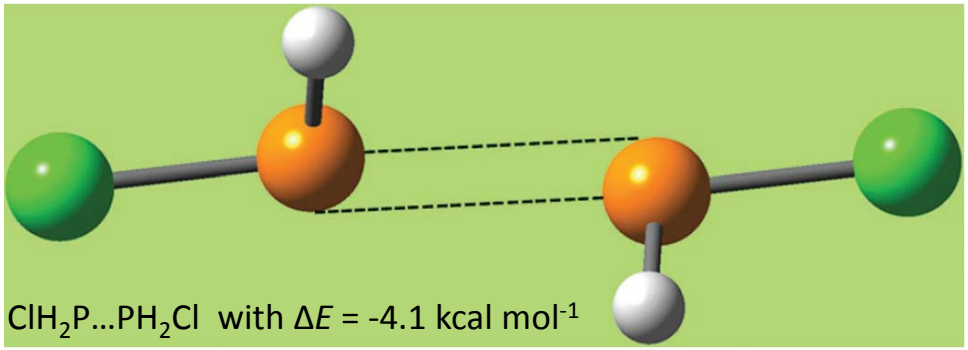
15

Moncea, O.; Gunawan, M. A.; Poinsot, D.; Cattey, H.; Becker, J.; Yurchenko, R. I.; Butova, E. D.; Hausmann, H.; Šekutor, M.; Fokin, A. A.; Hierso, J.-C.; Schreiner, P. R. *Submitted*

- Quantum mechanical tunneling of the molecule



- Pnicogen bonding



$ClH_2P\cdots PH_2Cl$ with ΔE = -4.1 kcal mol^{-1}

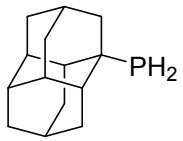
- Proton exchange

Caldin, E. F. *Chem. Rev.* ***1969***, *69*, 135; Politzer, P.; Murray, J. S.; Clark, T. *Phys. Chem. Chem. Phys.* ***2013***, *15*, 11178; Wei, Y.; Li, Q.; Li, W.; Cheng, J.; McDowell, S. A. C. *Phys. Chem. Chem. Phys.* ***2016***, *18*, 11348; Clark, T. *WIREs Comput. Mol. Sci.* ***2013***, *3*, 13; Kolář, M. H.; Deepa, P.; Ajani, H.; Pecina, A.; Hobza, P. In *Halogen Bonding II: Impact on Materials Chemistry and Life Sciences; Metrangolo, P., Resnati, G., Eds.; Springer International Publishing: Cham, 2015, p 1.*

Diamondoid phoshines characterisation –NMR study

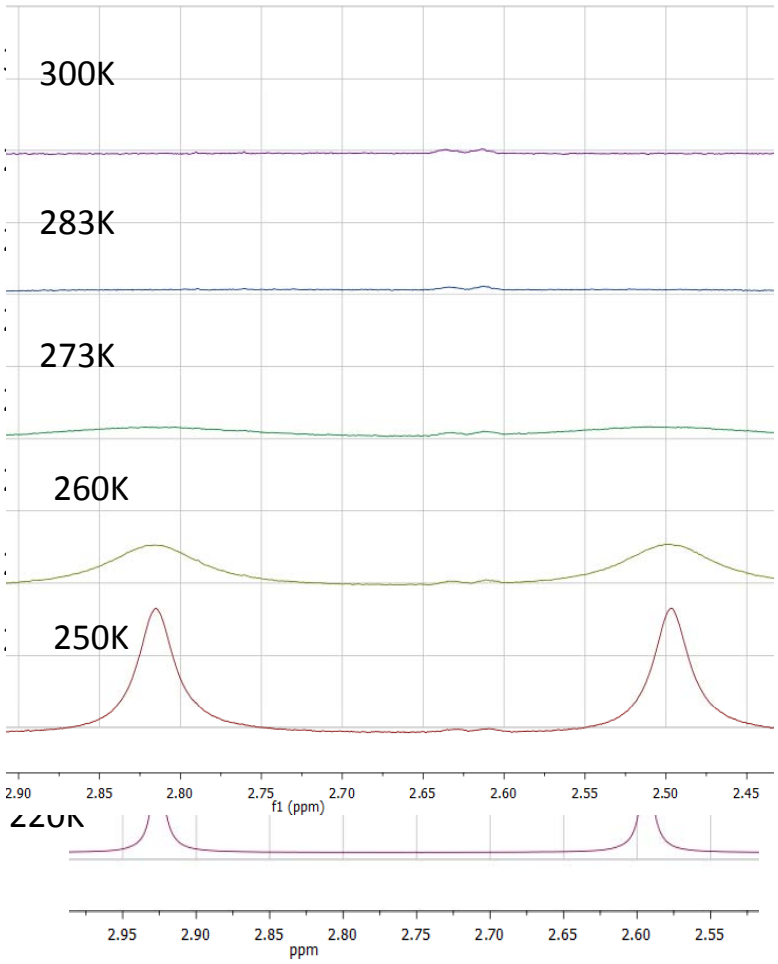
Tunneling ?

NO!

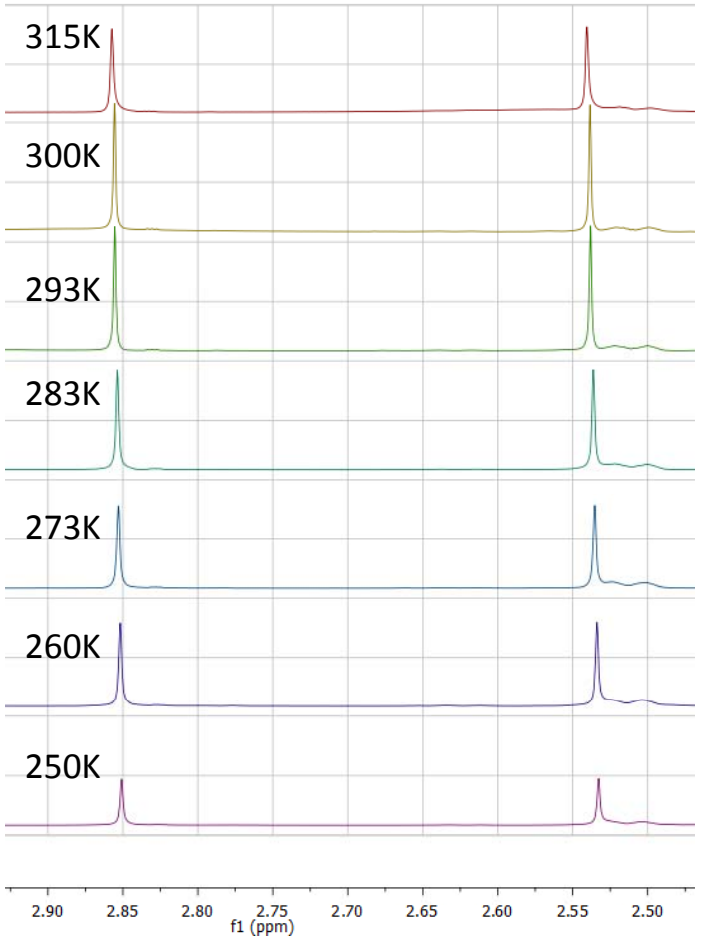


12

In THF-d^8 +HCl



In THF-d^8



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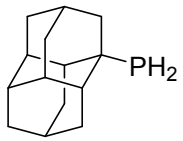
Diamondoid phoshines characterisation –NMR study

Tunneling ?

NO!



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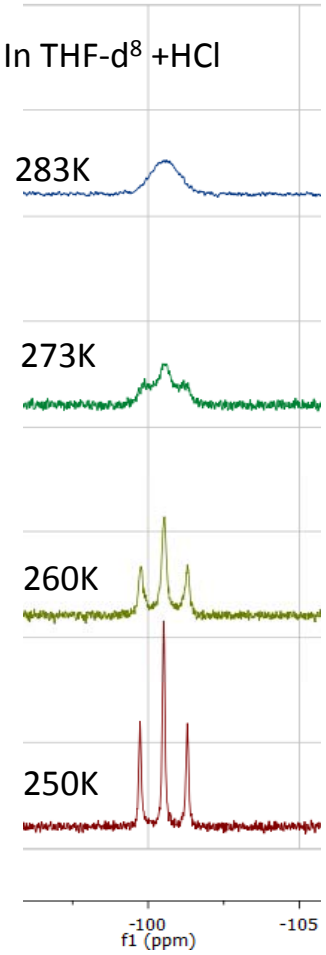

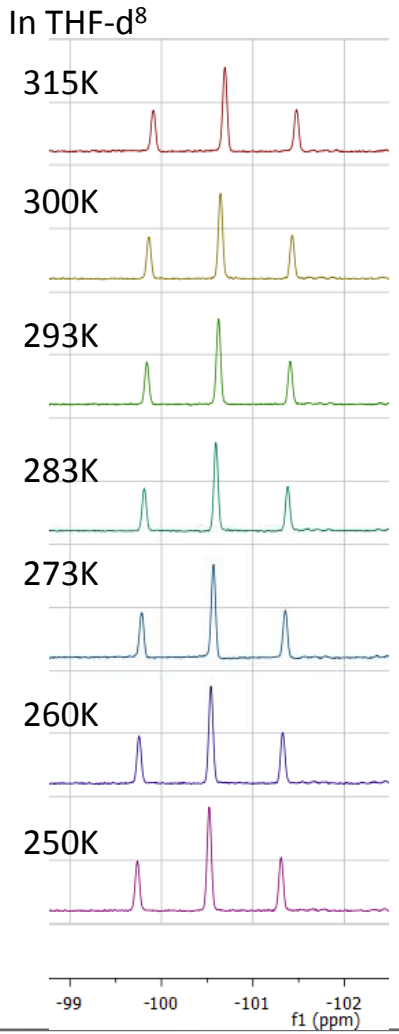

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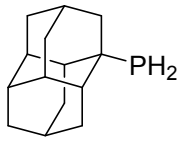
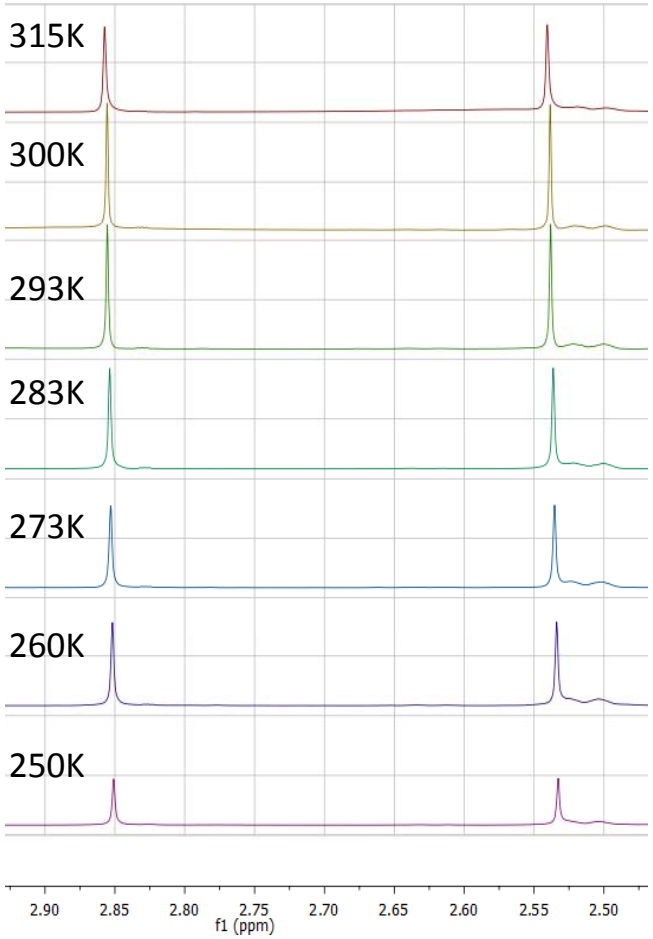
Diamondoid phoshines characterisation –NMR study

σ-hole interaction ?

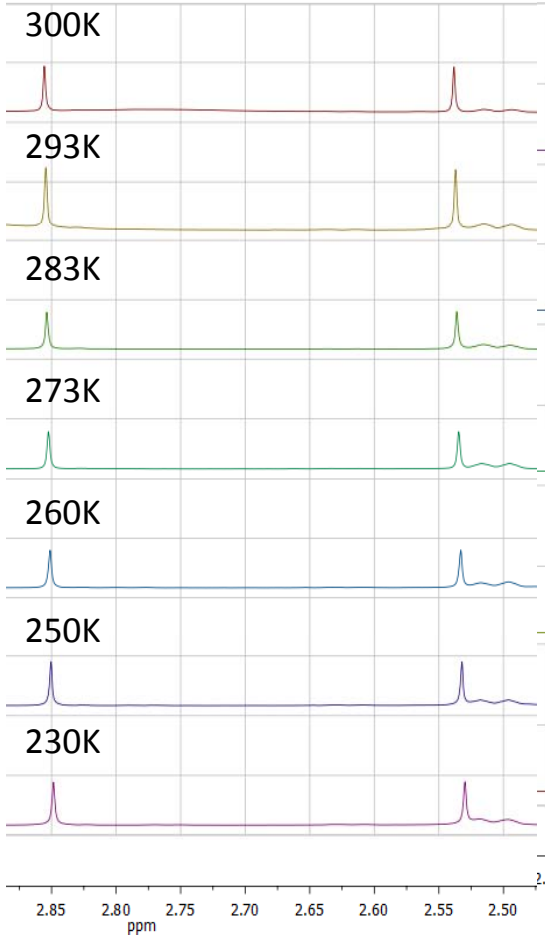


12

In THF-d^8

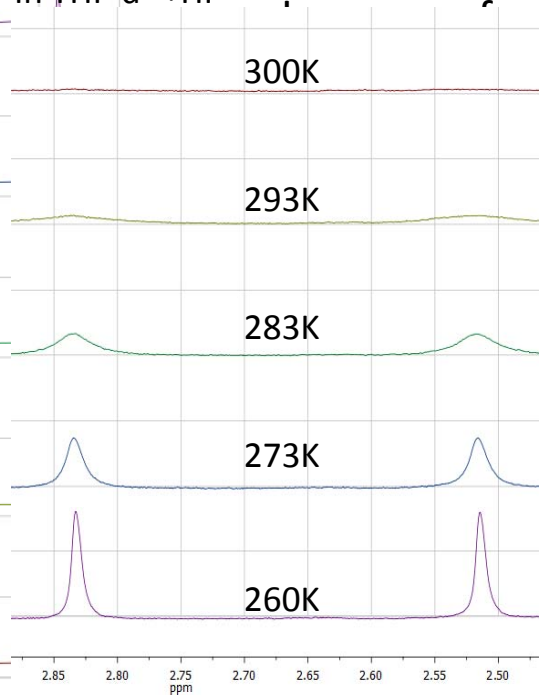


In THF-d^8 + IPh



Impossible to have excess of the salt

In THF-d^8 +HI



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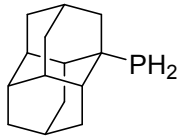
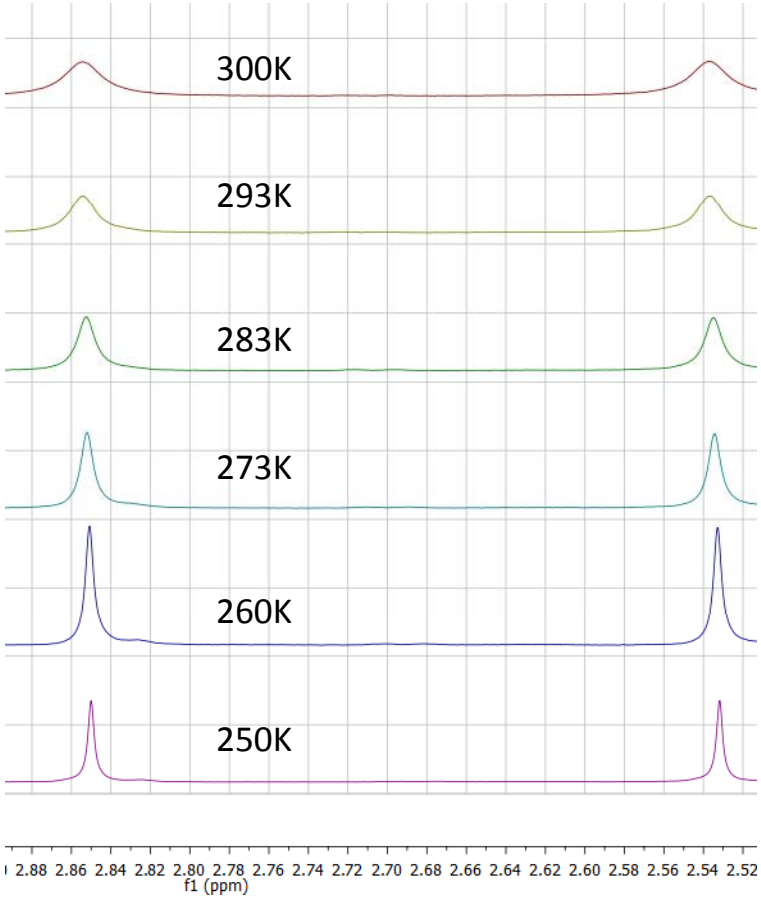
Diamondoid phoshines characterisation –NMR study

Influence of the H^+ ions

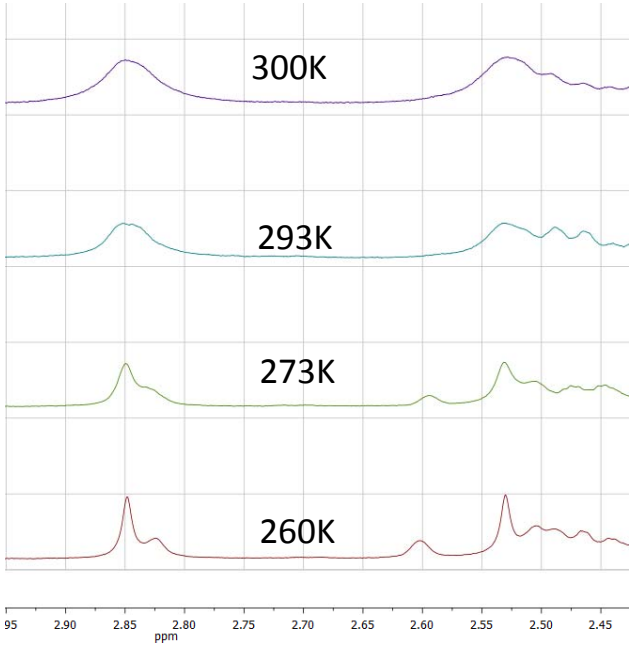


12

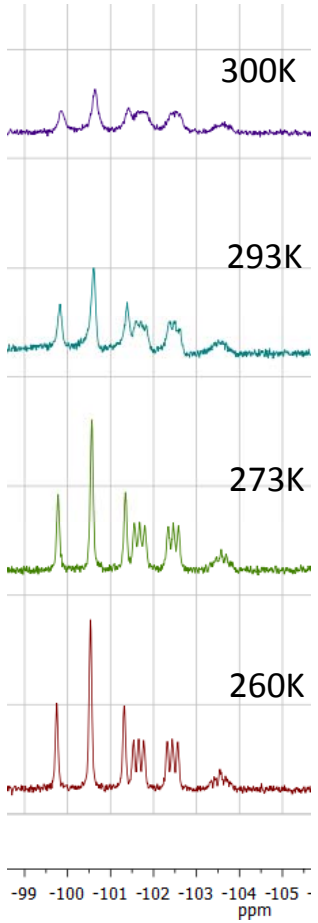
In THF-d^8 +H_2SO_4



In THF-d^8 +D_2SO_4

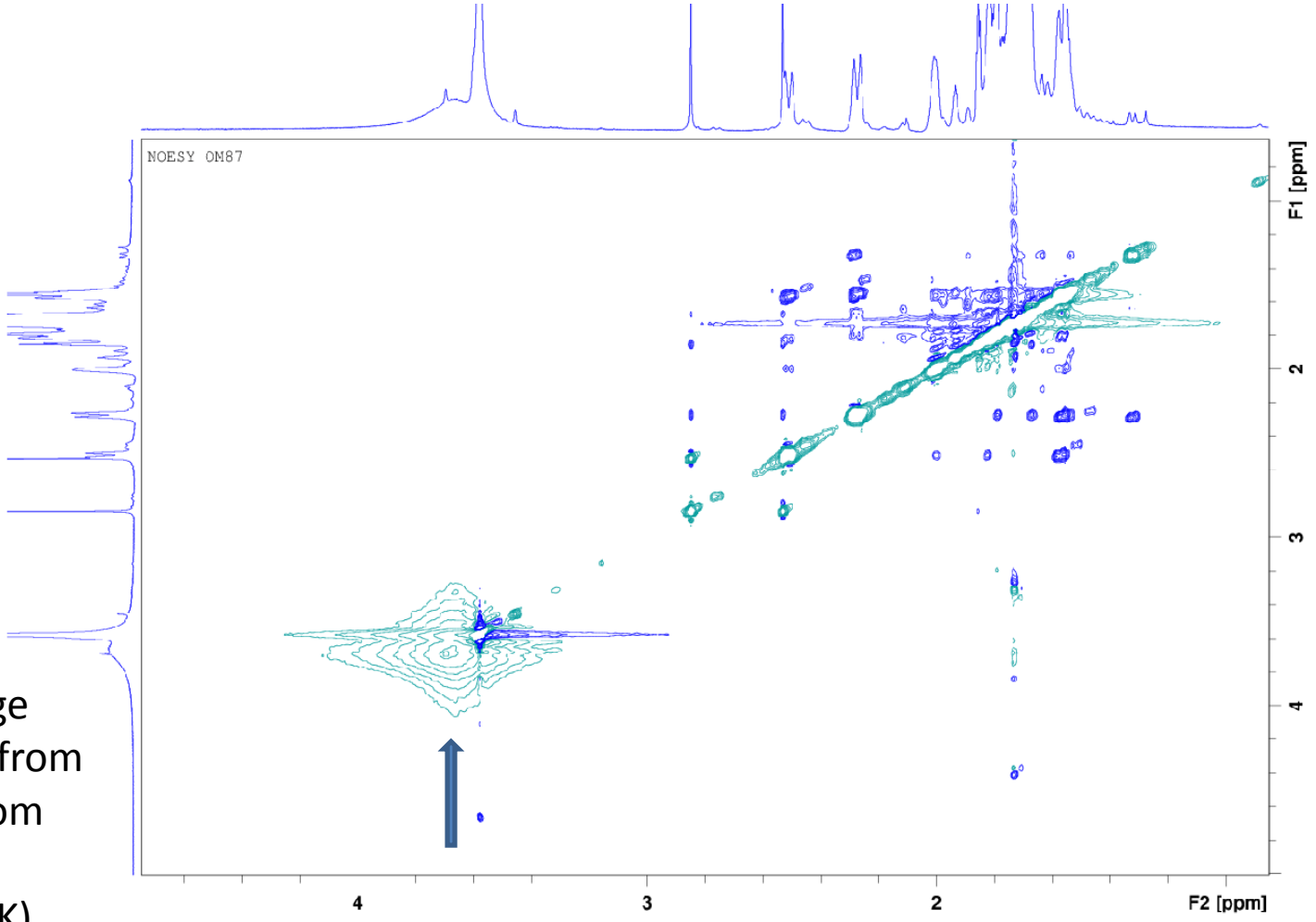


In THF-d^8 +D_2SO_4



Moncea, O.; Gunawan, M. A.; Poinsot, D.; Cattey, H.; Becker, J.; Yurchenko, R. I.; Butova, E. D.; Hausmann, H.; Šekutor, M.; Fokin, A. A.; Hierso, J.-C.; Schreiner, P. R. *Submitted*

For dimondoid primary phosphines → broadening in NMR ^{31}P & ^{1}H corresponds to a fast proton exchange.

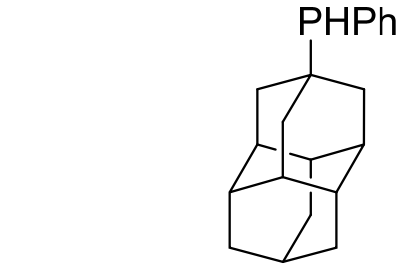


Very slow exchange between protons from PH_2 with water from THF-d^8 at room temperature (298K)

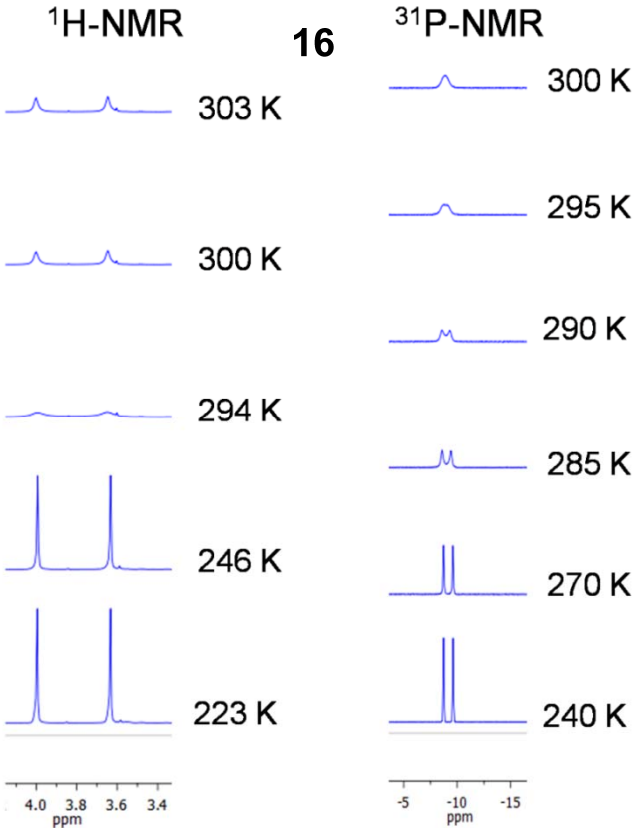
Moncea, O.; Gunawan, M. A.; Poinsot, D.; Cattey, H.; Becker, J.; Yurchenko, R. I.; Butova, E. D.; Hausmann, H.; Šekutor, M.; Fokin, A. A.; Hierso, J.-C.; Schreiner, P. R. *Submitted*

What about the secondary diamondoid phosphines?

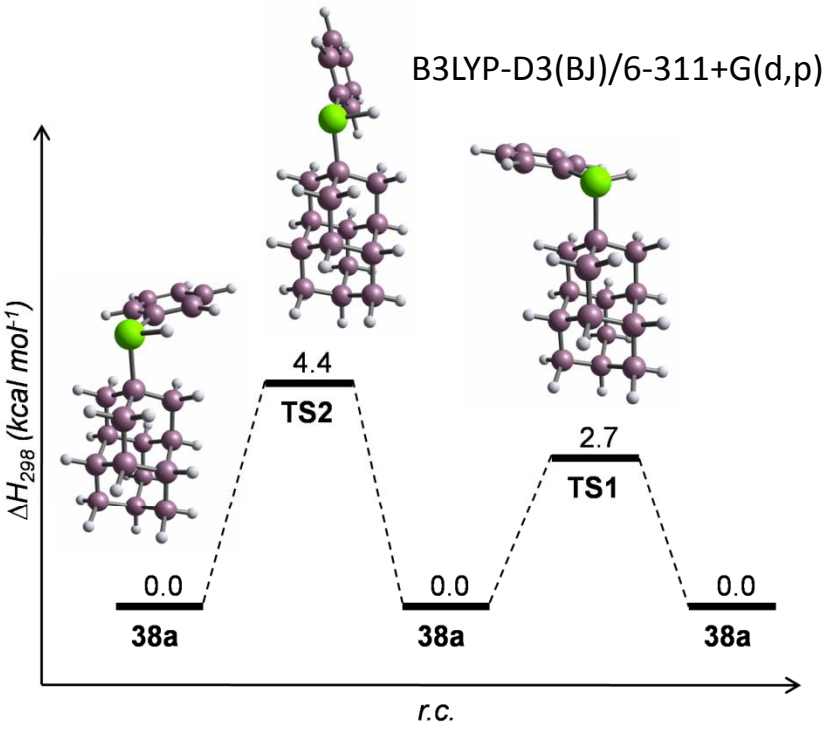
Diamondoid phoshines characterisation –NMR study



16



Is it related to



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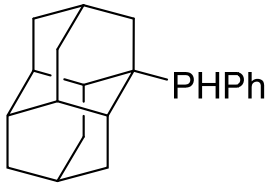

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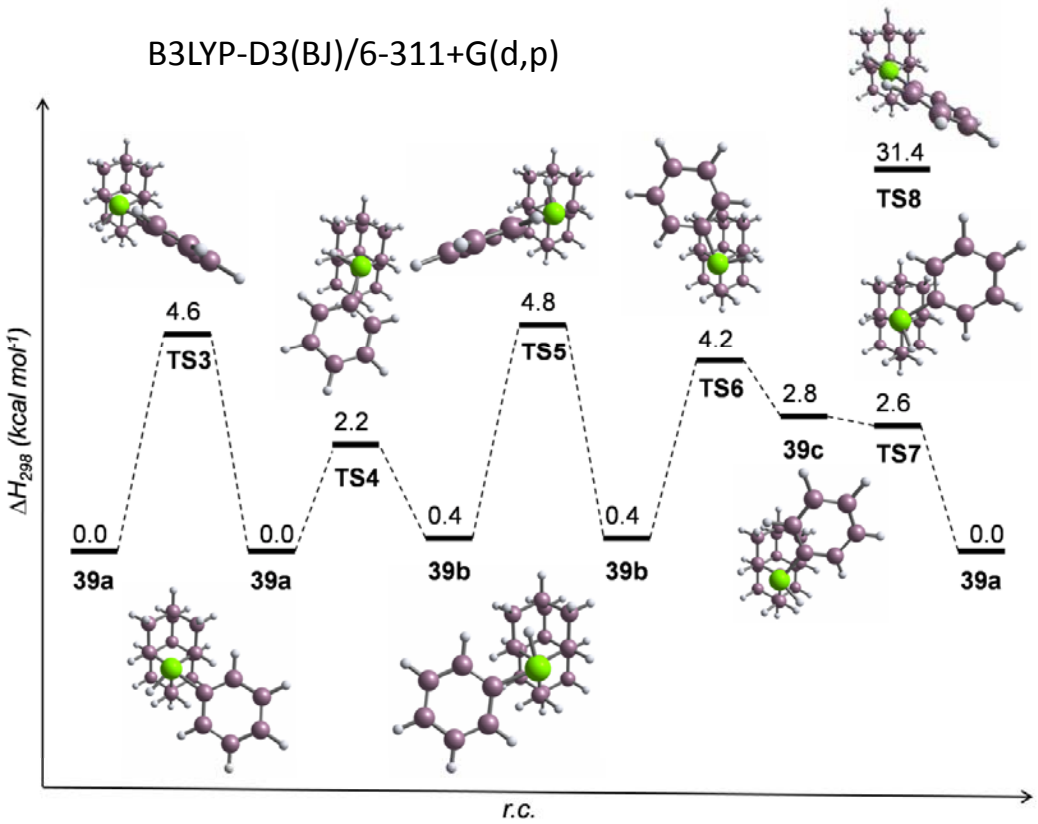
Splitting in 1H NMR of the signals corresponding to the methylene protons→ line shape analysis

B3LYP-D3(BJ)/6-311+G(d,p)



Eyring-Plot (ln(k/T)=f(1/T))

$\Delta H^{\ddagger}$= 10.4 kcal mol^{-1}

To what process is this activation energy corresponding to?

Proton exchange?

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- Unequally 4,9–SH dimondoid phosphonates
- Primary diamantane phosphine post functionalization
- CVD of the novel phosphines => continue work in France
- Primary diamantane phosphines in catalysis => continue work in France

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