Parahydrogen-NMR Spectroscopy Applications in Catalysis

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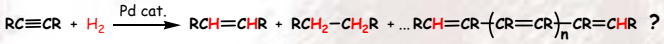
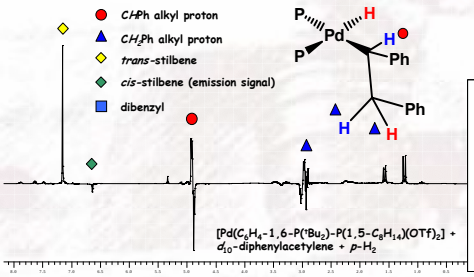
Unravelling the mechanism by which metal complexes catalyses a reaction can lead to great improvements in the efficiency of the processes. Achieving this requires a combination of kinetics, synthetics and theoretical studies.

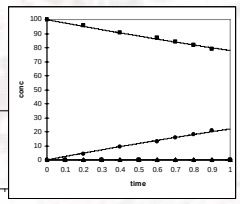
- Catalytic reactions involve multistep mechanisms where a series of **short-lived intermediates** are **continously generated**.
- The detection of such species is essenstial to understand the mechanism but is generally difficult due to their **low concentration**.
- **Parahydrogen NMR** allows the **identification of** such **intermediates** in many reactions of academic and **industrial interest** like **Hydrogenation** of alkenes, **Hydrofomylation** or **Hydrosilylation** of alkenes.

Hydrogenation (vs oligomerisation)

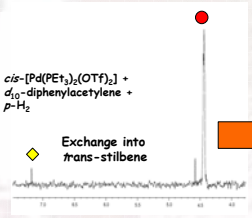


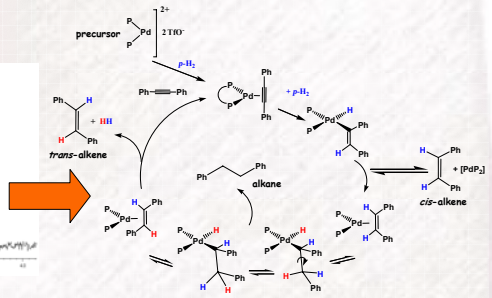
Palladium complexes are used as homogeneous catalysts in a wide range of reactions. We are **currently** studying the reactivity of palladium diphosphine complexes with alkynes and H_2. These complexes catalyse the semihydrogenation of alkynes to alkenes, but also isomerize the *cis* alkenes to the *trans* species. Detection of alkyl hydrides has allowed us to propose the mechanism sumarized in below. This observation also helps to understand the formation of alkanes depending on the phosphine chosen. We hope in the inmediate furure these observations will permit the **rational design of catalysts** which will favour either **semihydrogenation** (with or without isomerization), **double hydrogenation** or the **alkyne oligomerisation**. J. P. Dunne, S. Aiken, S. B. Duckett, D. Konya, K. Q. Almeida Leñero and E. Drent. J. Am. Chem. Soc. **2004**, *126*, 16708.





- **Kinetic measurements.**
- **Determination of thermodynamic parametres $\Delta H^{\neq}$ and $\Delta H^{\neq}$.**





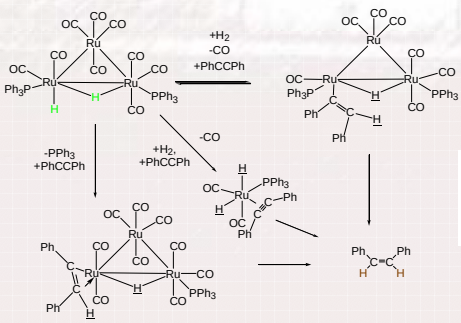
Characterization of reaction intermediates (the technique can look at more than metal hydrides)

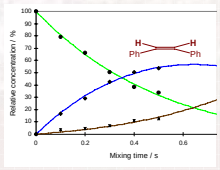
Deduction of the catalytic cycle

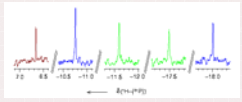
Cluster based Catalysis

Transition metal clusters are of interest because they share some of the phenomena typical of **polynuclear surfaces** but act as **homogeneous catalysts**.

Parahydrogen allows the **distinction between true intact cluster catalysis and pathways involving mononuclear fragmentation products**. D. Blazina, S. B. Duckett, P. J. Dyson and J. A. B. Lohman. Chem. Eur. J. **2003**, 9(5), 1046.

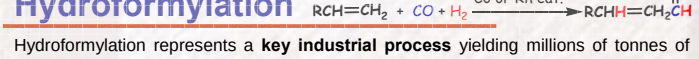






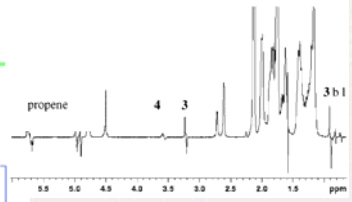
EXSY Spectroscopy allows magnetisation transfer from H to be monitored at 301 K

Hydroformylation



Hydroformylation represents a **key industrial process** yielding millions of tonnes of aldehydes annually that feed into a wide range of end products. Co and Rh systems with phosphine donors are used as industrial catalysts.

C. Godard, S. B. Duckett, S. Polas*, R. Tooze* and A. C. Whitwood. J. Am. Chem. Soc. **2005**, *127*, 4944.
C. Godard, S. B. Duckett, C. Henry, S. Polas*, R. Toose* and A. C. Whitwood. Chemm. Commun., **2004**, 1826.



- **Mapping of the hydroformylation reaction using a Co catalyst.**
- **The PHIP effect allows the detection of both key reaction intermediates and their hydroformylation products at very early reaction times.**

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