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Review

Mechanism in homogeneous catalysis; NMR as a prime mover

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Abstract

An overview of the contribution of NMR to the development of our understanding of homogeneous catalysis is presented, with an emphasis on work from the author's research group.

Keywords: NMR; Catalysis; Enantioselectivity; Reactive intermediates; Rhodium; Ruthenium; Palladium; Zinc

The progression of synthetic organic chemistry is very much driven by experimental observation. Researchers test an idea, and if it works then optimisation and application follow. The initial discovery procedure does not require deep insights into the specific reaction mechanism. In the longer run however, progress would stall if reaction pathways were not probed in detail. This leads not only to the delineation of a specific process, but also to general rules and paradigms that have a much broader consequence. The new understanding that ensues leads to fresh ideas, and then naturally to new reactions, or to novel ways of carrying out existing reactions. Thus, the overall pattern of development in synthesis is iterative; insight, discovery, understanding, leading to fresh insight.

By their nature catalytic reactions are mechanistically more complex than stoichiometric ones. The reactants and reagents have pre-defined structures, or at the very least pre-defined functionalities are involved in the desired transformation. No such constraints are necessary for the catalyst structure, the sole concern being in its ability to fulfil the objectives of the researcher. These may be concerned with reactivity and yield, but are as likely to involve the selectivity of product formation. In turn, this may address diverse aspects; chemoselectivity, regioselectivity or stereoselectivity. It is frequently the case that all of these need to be considered concurrently. The additional complexity of catalytic reactions indicates that reaction mechanism is a more significant concern in synthetic planning, there being a need to limit choices within the wider set of parameters, and enhanced understanding may be crucial in achieving that aim. A further facet that needs to be considered is the additional challenge to be faced in the study of catalytic mechanism, inherent in the increased complexity. A catalytic cycle proceeds through a sequence of steps, and at each step the catalyst is associated with reactants and/or reagents. By the nature of successful catalytic reactions, the intermediates requiring structural definition are short-lived and provide a challenge for conventional techniques.

Although not the first recorded example of homogeneous catalysis, the demonstration that Wilkinson's catalyst, $ClRh(PPh_3)_3$ was effective for the hydrogenation of a range of alkenes under bench-top conditions had a powerful effect on the organic community. Up to then, there had not been a general concern about the way in

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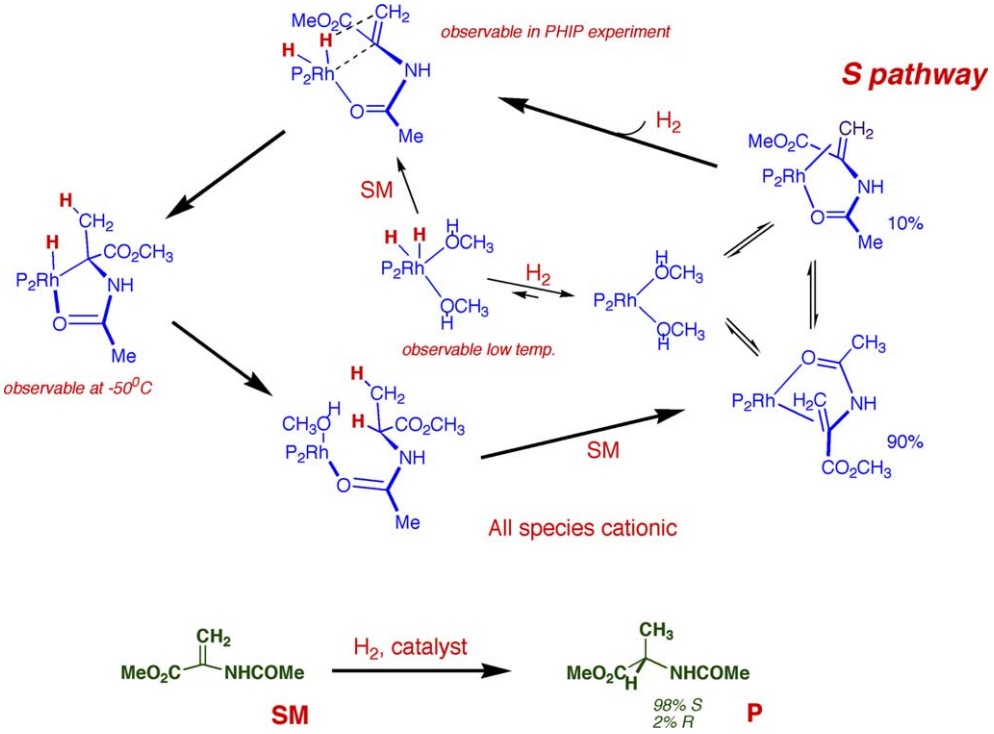
which transition metals interact with organic molecules, that being more of a proper concern for inorganic chemistry. The rapid subsequent development by Knowles [1] and Kagan [2] of effective procedures for asymmetric hydrogenation greatly enhanced the level of interest. The procedures had been developed empirically, based on how the space around a reacting metal centre could be controlled by the right ligands. At the time of its publication, it provided a challenge, perhaps even *the* challenge, for the application of mechanistic techniques to catalysis. Of course there was already a tradition in place, based largely on careful kinetic studies of catalytic processes. This tradition was largely established through the study of enzymes [3], and although the experimental problems are distinct, the principles derived from enzymology can be applied to kinetic studies of homogeneous catalysis [4]. The results were, and continue to be, a central plank in understanding of the discipline. Kinetic analysis provides fundamental information on the molecularity of the ground state and turnover-limiting transition state. By the variation of individual concentrations and of reaction conditions, insights into the steps leading to and from the two denoted states can be obtained. By indirect techniques such as isotopic labelling, structure variation in reactants and catalyst and LFEs, indirect information on the detailed nature of the individual reaction steps can be obtained. That is in itself important and fundamental information, and plays an essential part if the catalytic reaction is used as an industrial process. To an organic chemist, knowledge of the structure of the reactive intermediates that make up the catalytic cycle is at least as important. This information can enable the researcher to improve the design of the catalyst and understand how it can be adapted to other substrates. In asymmetric catalysis, structural information is essential to an understanding of the origin of enantioselectivity, and by implication how that can be enhanced. A problem is that the structural techniques are by definition static, and it is essential to correlate what is observed by spectroscopy, diffraction or other techniques with the realities of catalysis under proper turnover conditions.

At an early stage in his career, the author was impressed and influenced by the comment that "*NMR is the cornerstone of Chemistry*". Since this was made long before the advent of FT protocols and superconducting magnets, it was as prescient as it was accurate. NMR provided the incentive for the study of reactive intermediates in asymmetric hydrogenation. This required a certain leap of faith, since there was a considered view that true catalytic intermediates, being reactive by definition, were most probably inaccessible to structural characterisation. Hence it was with the naivety of a rank beginner, that the challenge of the structure of reactive intermediates in asymmetric hydrogenation was enjoined. Over 25 years later, the basic achievements of the NMR approach to this problem are summarised in Scheme 1 [5]. It has to be said that rhodium asymmetric



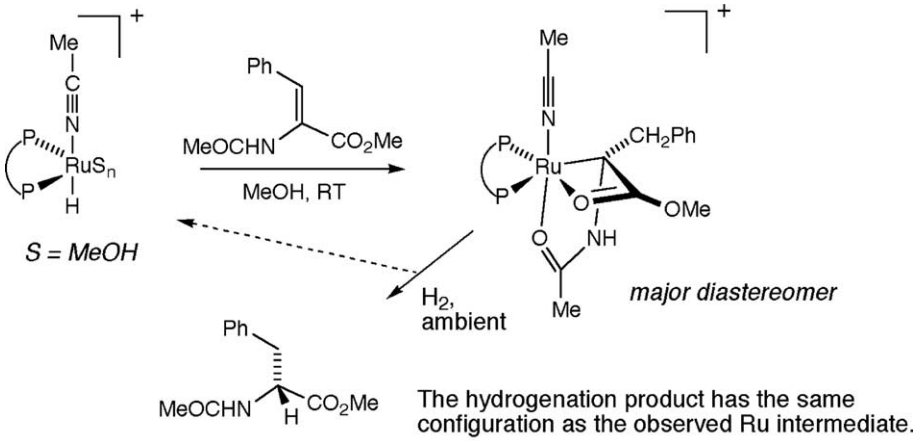
Scheme 1. The currently accepted pathway for rhodium catalysed asymmetric hydrogenation. All the intermediates have been observed and characterised by NMR, and the dynamics of reversible interconversion between solvate and enamide complexes has been defined.

hydrogenation is rather a special case. The application of NMR methods is most effective where there are nuclear spins that identify connectivities and local molecular environment. The intermediates in this process have an abundance of spin 1/2 nuclei, ^{103}Rh, ^{31}P, ^{13}C and ^{1}H. This peculiarly fortunate circumstance permits detailed information to be obtained, not only on the structure of several key intermediates, but also on their configuration. The accord between this work and the extremely thorough kinetic study of asymmetric hydrogenation by Landis and Halpern is most gratifying [6]. The NMR work even identifies one important component of the reaction – the intramolecular interconversion of stereoisomeric substrate Rh complexes – that remained hidden to the direct kinetic analysis. It remained for Gridnev and Imamoto to make the picture more complete by identifying solvate dihydride complexes [7], and our own collaboration with Bargon's group indicated the possibility of a substrate dihydride complex, as will be discussed later on [8].

Most of the work described was completed more than 15 years ago, and in the interim period there have been remarkable advances in NMR methodologies, both in terms of sensitivity and in the extraction of structural and dynamic information through myriad pulse sequences. To provide a complete cover of the ways in which NMR analyses have enhanced our knowledge of homogeneous catalysis would be impossible in the limited space available, and the discussion will be confined to individual contributions that highlight the power of this family of techniques. In making a selection from such a broad and wide-ranging literature, a bias towards the writer's own work may be perceived by the reader!

Although rhodium complexes were the first ones that demonstrated high enantioselectivity in asymmetric hydrogenation, the related ruthenium complexes indelibly associated with Noyori demonstrate a wider range of applicability, being effective in the hydrogenation of both alkenes and ketones [9]. Since ruthenium (with an even atomic number) possesses a range of stable isotopes, none of which has a nuclear spin quantum number = 1/2, it is already more difficult to utilise NMR in the determination of the catalytic mechanism than in the rhodium case. For the case of alkene reduction, formal mechanistic and kinetic work had been carried out by Noyori and Kitamura [10]. In addition, Bergens has conducted very elegant NMR experiments that demonstrate how the ruthenium mechanism differs from the rhodium case [11]. Here ruthenium monohydrides are observable under turnover conditions, and play a significant role in the pathway. For rhodium, both hydrogens added to the substrate come from the same molecule of H_2, but in the ruthenium case one remains from the previous cycle and one arises from the new dihydrogen molecule [12]. Aspects of the mechanism in which NMR played an important part are indicated in Scheme 2.

Using NMR as a tool to probe the asymmetric reduction of carbonyl compounds is a formidable challenge since the spin systems of the ligand and substrate are less intimately connected than in the alkene case. Daley and Bergen's contribution is a beautiful illustration of the power of modern NMR techniques in the determination of catalytic mechanism [13]. A substrate that gave modest e.e.'s in hydrogenation was deliberately chosen, so that more than one diastereoisomeric intermediate could be identified. An additional factor affecting the choice of reactant was stabilisation of the alkoxide intermediate formed by addition of the resting state Ru–H complex to the reacting carbonyl group. In this way two diastereomeric Ru alkyls were formed at low temperatures, and the predominant one could be fully characterised by a combination of HETCOR (^{31}P–^{1}H) and ROESY experiments. The absolute configuration, determined by protonolysis, was the same as that of the product from catalytic hydrogenation. The rate-determining step is inferred to be the hydrogenolysis of the O–Ru bond, with

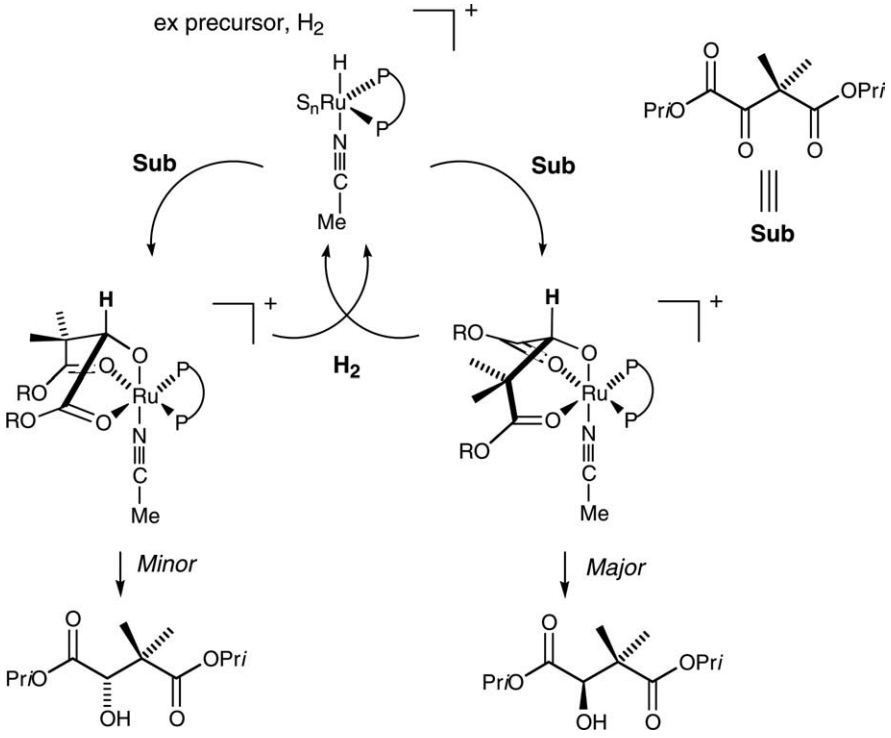


Scheme 2. An NMR-characterised intermediate in the ruthenium-BINAP catalysed hydrogenation of dehydroamino acid esters.

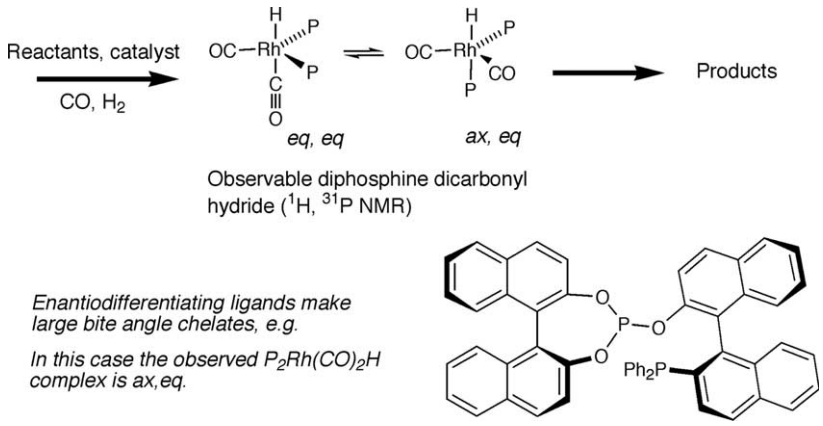
some possibility of reversibility in the formation of the observed alkoxide under true turnover conditions (Scheme 3).

Hydroformylation has advanced from its status as a precursor of commodity chemicals to a reaction that can be utilised in fine chemical synthesis, through the demonstration of directive stereochemical control [14], and asymmetric catalysis [15]. In early work we had demonstrated that the assumed intermediate in simple hydroformylations $HRh(CO)_2(PPh_3)_2$ has a fluxional trigonal bipyramidal structure in solution, and the equilibrium ration between the (H *trans* P) and (H *trans* CO) forms is changed when PPh_3 is replaced by a diphosphine chelate [16]. The ligands that have proved effective in asymmetric hydroformylation are unsymmetrical diphosphines or phosphinophosphites, that possess a large bite angle at rhodium. The disposition of the chelate ligand between the possible *eq–eq* and *ax–eq* TBP conformers, the former being favoured by increased bite angle, plays an important part in determining the stereoselectivity of the catalytic reaction. This ratio can be determined in solution by direct NMR analysis, although on an intermediate that is before the enantiodifferentiating step [17] (Scheme 4).

For many experiments the power of NMR is limited by its sensitivity. This in turn depends on the Boltzmann distribution of nuclear spin states, and for the case of proton NMR means that only one in 10^7 nuclei contributes to the observed phenomenon at ambient temperature. A simple trick removes this limitation. If hydrogen is stored over paramagnetic material (Fe_3O_4) at very low temperature the *ortho*- and *para*-nuclear spin states equilibrate, and the latter predominates strongly. When the *para*-enriched hydrogen is transferred to a substrate (e.g., in a hydrogenation reaction), then the ^1H NMR spectrum of the initial product is polarised, with strongly enhanced emission or adsorption provided that the two hydrogens remain coupled. PHIP (*para*-hydrogen induced polarisation) was adventitiously discovered by Bowers and Weitekamp [18], and developed as a tool in catalysis by Eisenberg, Duckett and especially Bargon [19]. This procedure appeared to us to present new possibilities for the observation of transient species in asymmetric hydrogenation, and was further encouraged by the synthesis of a ligand (PHANEPHOS) whose rhodium complex was effective in asymmetric hydrogenation when hydrogen was bubbled through the reaction mixture at −40 °C [20]. The collaborative work centred on the direct characterisation of the previously elusive dihydride formed in the asymmetric hydrogenation of a dehydroamino acid ester [8]. The observed species had unusual spectral characteristics, with one polarised hydridic hydrogen at rather low field (−2 ppm) and one resonating more conventionally at −19 ppm. The transient structure was solved with the help of ^{13}C NMR labelling of the reactant α-carbon, thereby



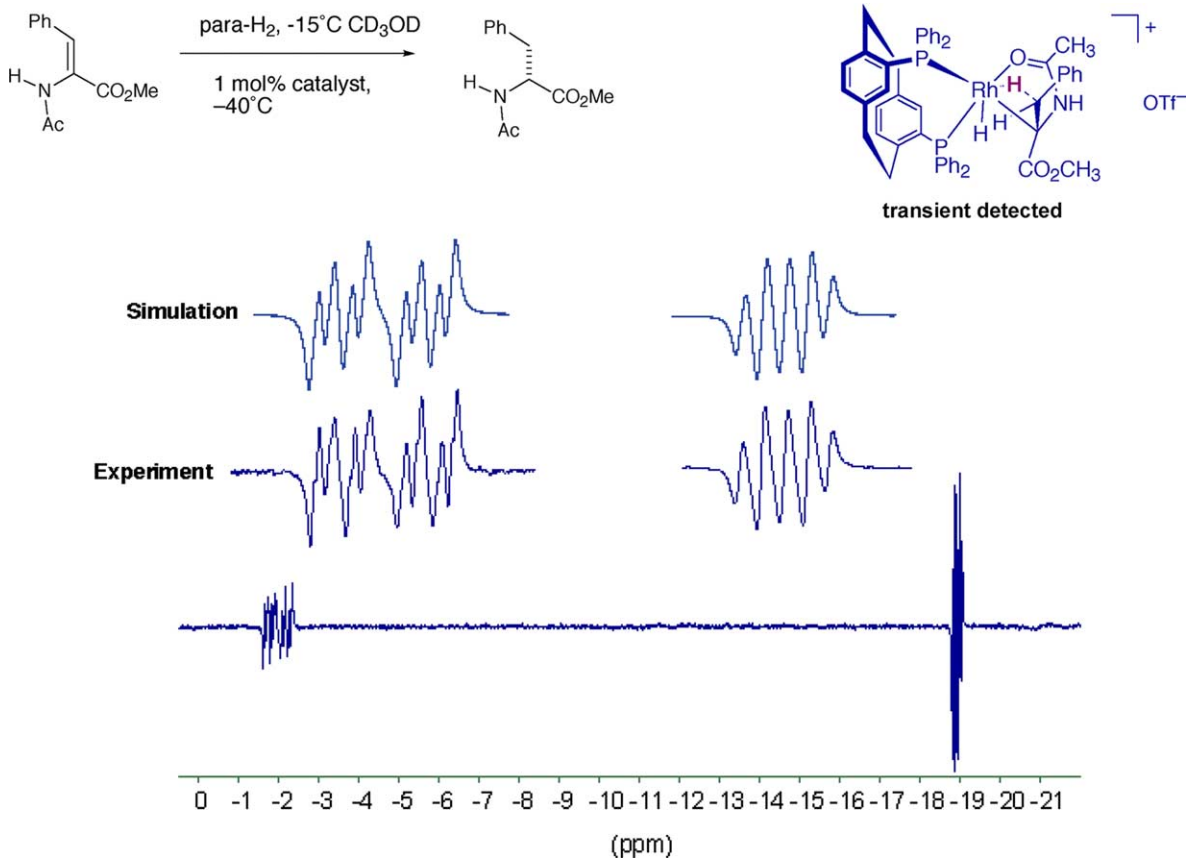
Scheme 3. Intermediates in the ruthenium-catalysed asymmetric hydrogenation of an α,β′-ketodiester, from NMR spectra taken at −30 °C in d_8-THF. The intermediates were characterised by HETCOR, ROESY and HMBC NMR experiments. The major observed species is the main product precursor. PP = (*R*)-BINAP; S = MeCN or THF.



Scheme 4. The NMR-characterisable $HRhP_2CO_2$ intermediate in hydroformylation.

demonstrating that the hydrogen was agostic and bridged between rhodium and carbon, providing a snapshot of the hydrogen transfer process (Scheme 5).

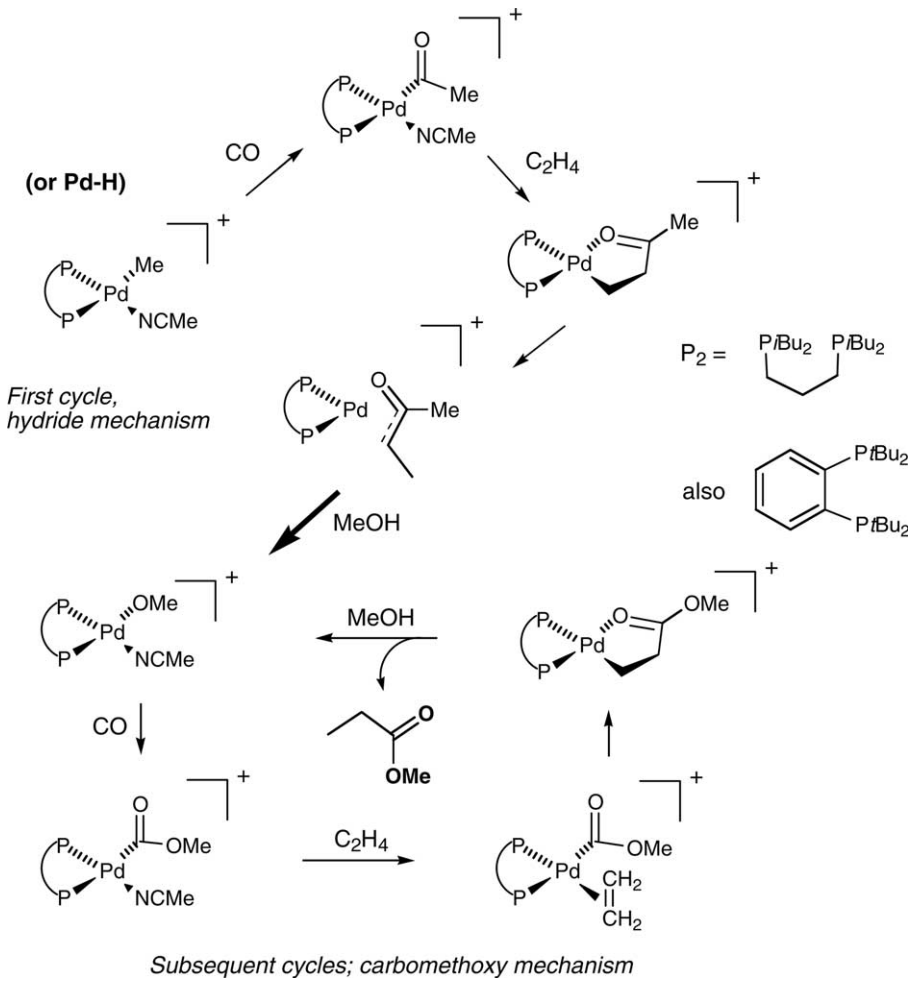
The application of NMR methods to define the structure of true intermediates in catalysis is by no means confined to catalytic reactions in which hydrogen is transferred to the substrate. Much of the insight into the mechanism of important polymerisation processes stems from NMR investigations. The work can involve direct alkene polymerisation or alkene/CO polymerisation. These simple reactions can give rise to a rich array of intermediates that can be characterised by NMR, usually requiring sub-ambient temperatures. For direct alkene polymerisation, Brookhart has employed both



Scheme 5. Detection of a dihydride intermediate in the rhodium-PHANEPHOS catalysed hydrogenation of MAC, using *para*-enriched dihydrogen. The spin excitation manifested by characteristic emission–adsorption multiplets is maintained in the initial hydrogenation product.

palladium and nickel diimine complexes. The reaction proceeds through a set of NMR-observable intermediates, with the linear/branching process being mediated by an isomerising β-agostic Pd or Ni alkyl. The structure and dynamics of the agostic intermediates can be studied in detail, especially in the nickel series [21]. For the copolymerisation of simple alkenes and acrylates with cationic palladium diimine complexes, a remarkable sequence of 4-, 5- and 6-ring chelate complexes can be characterised from methyl acrylate and the parent MePd cation [22]. For ethylene/CO copolymerisation with a Pd diphosphine complex, accurate data on the initiation and propagation steps can be obtained from low temperature NMR [23]. That and related polymerisations can be terminated by methanol and under appropriate conditions the reaction course can be diverted to carbomethoxylation of the alkene. By similar techniques and with a similar outcome, the intermediates in this catalytic cycle can be fully characterised by NMR, The propagation follows a "hydride" or "carbomethoxy" catalytic cycle depending on whether the initial catalytic steps involve insertion of CO into an alkyl or an alkoxypalladium complex. Both of these have been fully delineated [24] (Scheme 6).

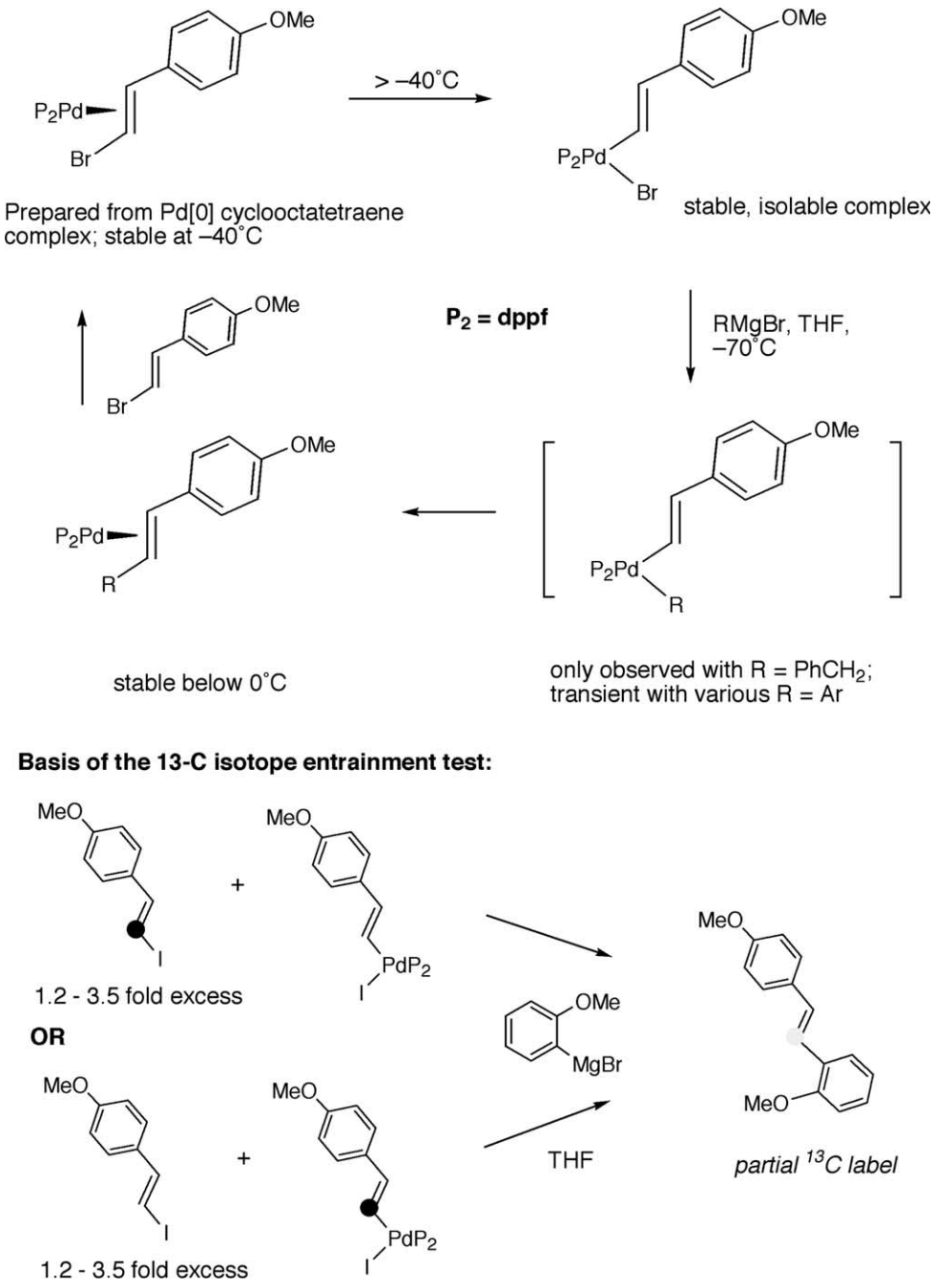
In general, palladium-catalysed coupling reactions have been studied by a different community, but often involve similar chemistry and similar intermediates to the polymerisation reactions described above. Our own contributions to the mechanism of asymmetric Heck couplings have included the characterisation of the resting state in the reaction of phenyl triflate with 2,3-dihydrofuran. The most interesting aspect of this is the rapid dyotropic shift involved. A single diastereomer, precursor to a single enantiomer of the observed major product is formed by a three stage process at −70 °C: Pd–Ph addition to the alkene, followed by a double Pd–H dissociation and return. Full characterisation of the intermediate formed required HETCOR and HMBC techniques [25]. Many further examples of the characterisation of intermediates in C–C and C–N coupling reactions have been presented. A question that always arises from such work is whether the observed



Scheme 6. Catalytic cycles for the conversion of ethene into methyl propanoate, with CO in methanol. The specified intermediates have been characterised by NMR, and link to related work on the Heck reaction and ethene/CO co-polymerisation.

intermediate is a true component of the catalytic sequence. The NMR snapshot inevitably reveals a stoichiometric situation, unless it is carried out under turnover conditions. In some cases the proposed intermediate in the catalytic cycle can be isolated and we devised an experiment on this basis termed the ''isotope entrainment test''. The reactive intermediate is employed as catalyst in one isotopomeric form in a reaction where the related substrate is added as a different isotopomer. After a few cycles of catalysis, deliberately limited by reagent availability, the product is isolated. Accurate analysis of the isotopic constitution of the product enables the extent of incorporation of the putative catalyst to be determined. In addition, different models for the catalytic mechanism can be tested against the predictions of models, based on comparison between the predicted and observed distribution of isotopomers [26] (Scheme 7).

Allylic alkylation is a special case of palladium coupling chemistry, distinguished by the exometallic

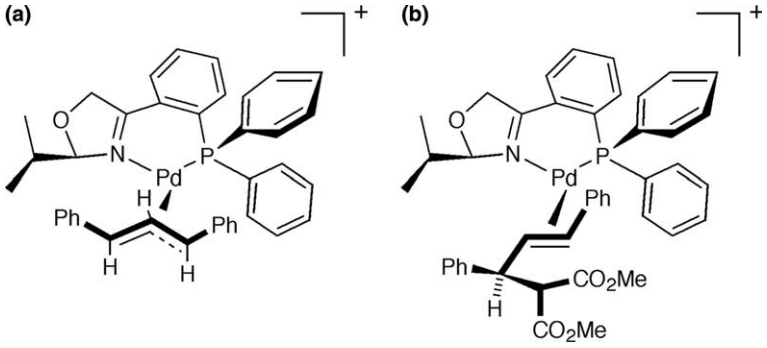


Scheme 7. Intermediates in palladium catalysed cross-coupling characterised by NMR. The linkage between the observed alkenylpalladium iodide and turnover conditions was established through the described isotope entrainment experiment.

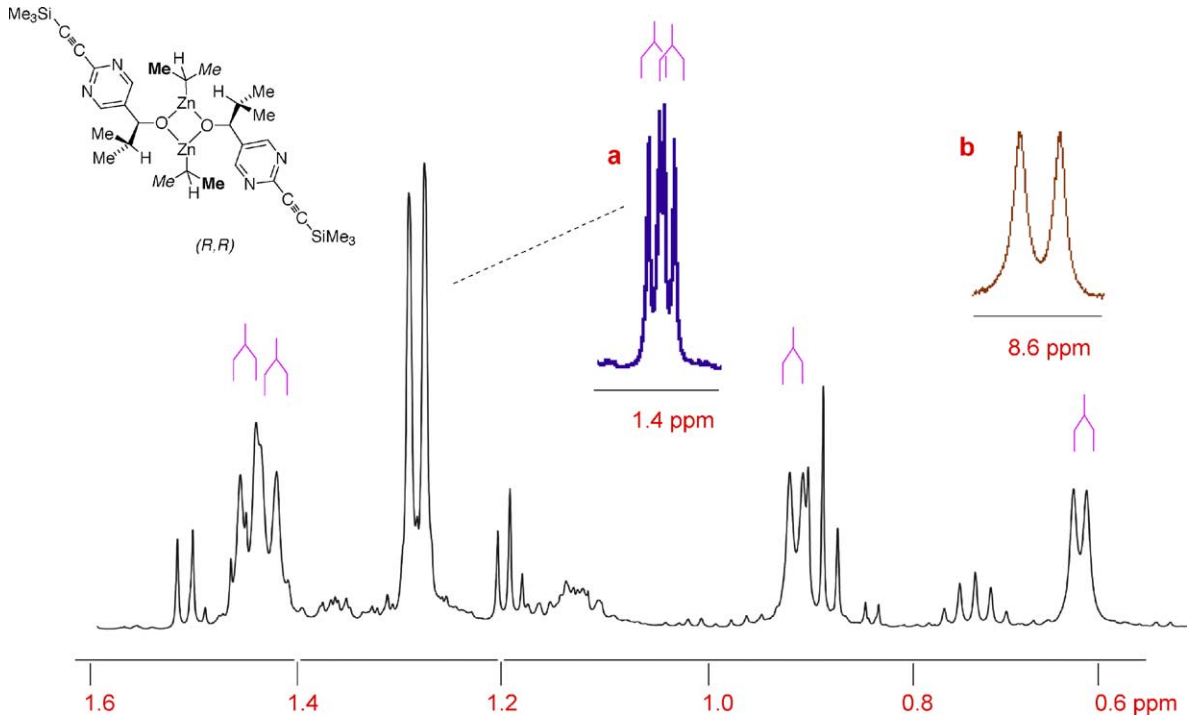
mechanism; a cationic Pd allyl normally reacts with a nucleophile which does not attach to the palladium but rather approaches from the opposite side of the allylic fragment. The initial product is an η^2-alkene palladium complex, which dissociates and thus permits the catalytic cycle to continue. PHOX ligands are highly effective in catalytic asymmetric allylations, and clearly the structure of the alkene complex in a case with exemplary selectivity would give a snapshot of the reaction pathway by which it is formed. It transpires that this labile intermediate can be prepared and fully characterised by NMR at low temperature [27]. A technique that is widely useful in ligand substrate complexes was applied here, and to a high level of sophistication. The structure of the ligand metal fragment is well appreciated, and normally supported by X-ray data. This can be utilised to locate the bound reactant, using through-space mapping by NOESY and ROESY experiments. In this way a full structure and conformation of the alkene complex can be obtained, because the results permit accurate distance mapping. The results obtained were extended by a systematic analysis of the structure and dynamics of related allylpalladium complexes by NMR [28]. They were further augmented by a formal structure determination of the aforementioned η^2-alkene complex [29] (Scheme 8). The application of cross-correlated relaxation techniques alone to the structure of the complex gave a rather diffuse result. When the NMR results were combined with distance and angle restraints arising from published X-ray data on Pd-alkene complexes, a unique result, save for the expected conformational flexibility about aryl linkages, was obtained. Structural information at this level of sophistication gives information of comparable quality and rigour to that obtained by X-ray analysis. The difference is that high-quality crystals are not required. Interestingly, the formal solution of structure by NMR is far more advanced in the protein structure community than in the catalysis community; the PDB database contains several thousand entries for which the protein structure solution was carried out in entirety by NMR methods [30].

In the examples described thus far NMR reveals details of the structure and dynamics of species that have a significant lifetime on the timescale of nuclear spin relaxation. This corresponds to a lifetime of a second or more. If the species is dynamic then characterisation provides a greater challenge. One of the discoveries in asymmetric catalysis that has attracted most attention is the autocatalytic zinc alkyl additions to heterocyclic aldehydes arising from Soai's work [31]. This has in addition provided the first authenticated examples of absolute asymmetric synthesis [32]. Although the mechanism of simpler zinc alkylations is well understood and the structure of intermediates established [33], there had been no previous work on the nature of intermediates in autocatalysis. Kinetic studies established that the resting state in autocatalysis was a reactive dimer [34], in contrast to the monomeric reactive entity described earlier [33]. NMR studies are clearer in thf (where the species is less dynamic) than in toluene, and it was first established that the structure is a dimeric zinc–oxygen square, based on the fact that the methyl protons of Zn-bound isopropyl groups are diastereotopic in the enantiopure, but isochronous in the racemic dimer. The same structure pertains in toluene, and interchange between the homo-and heterochiral forms can be measured above ambient temperature by line-shape analysis. Below ambient, further aggregation to highly unsymmetrical tetramers and other oligomers is observed. The association of Zn*i*Pr$_2$ with the dimeric Zn alkoxide (moderate, and permitting rapid alkyl–alkyl exchange between reagent and catalyst) and the reactant aldehyde (low) can be studied, aided by the synthesis of ^{15}N-labelled pyrimidine substrate. The findings are summarised in Scheme 9. The difficulties in obtaining reliable NMR information, from a system with a limited range of readily accessible spin 1/2 nuclei, exacerbates the problem of structure solution in a dynamic system [35]. Only with modern pulse techniques, spectrometer dispersion and sensitivity was the outcome possible.

The current status of NMR techniques available to the well-found synthetic laboratory permits the determi-



Scheme 8. (a) η^3-Allyl and (b) η^2-ethene product complexes involved in the asymmetric allylic alkylation of 1,3-diphenylprop-2-enyl acetate by dimethyl malonate anion. The fully detailed structures and spatial dispositions were established by NMR techniques.



Scheme 9. Section of the ^{1}H NMR spectrum of the resting state homochiral dimeric species in Soai's autocatalytic system in C_7D_8, showing the $ZnCHMe_2$ diastereotopic methyl groups at 1.4 ppm and the $ZnO(CHAr)CHMe_2$ diastereotopic methyl groups at 0.9 and 0.6 ppm. Inset (a) diastereotopic separation of the deshielded $Zn(CHMe_2)_2$ signal (from excess reagent) at 253K, (b) the aromatic region of the NMR spectrum of a racemic sample, showing signals due the the homochiral and heterochiral species in comparable amounts.

nation of complex structure in solution with a level of accuracy that goes largely unappreciated. In addition, modern multidimensional NMR dynamics can give insights into reactivity, and supply information that assists the construction of a complete mechanistic picture. As an additional possibility, molecular aggregation can be studied with exquisite precision by diffusion-ordered spectroscopy (DOSY), a powerful and as yet under-applied technique in catalysis [36].

Acknowledgement

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