

Andrew D. Westwell and Jonathan M. J. Williams*

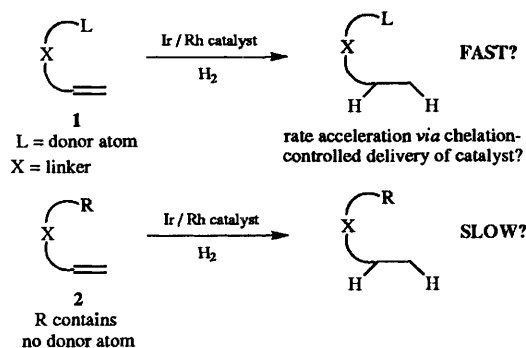
 Department of Chemistry, University of Loughborough, Loughborough, Leicestershire
 LE11 3TU, UK

In competition experiments, alkenes tethered to pyridyl groups were found to undergo iridium catalysed hydrogenation more quickly than alkenes tethered to phenyl groups. This is in marked contrast to the results for hydrogenation of some of the individual substrates where alkenes tethered to pyridyl groups were reduced much more slowly than their phenyl counterparts.

Introduction

The homogeneous catalytic hydrogenation of alkenes can be accomplished using a wide range of transition metal catalysts.¹ In particular, cationic iridium complexes such as [Ir(cod)-{P(c-C₆H₁₁)₃(Py)}]PF₆ (cod = cycloocta-1,5-diene; Crabtree catalyst) have been shown to be highly efficient hydrogenation catalysts.² As part of our studies towards the use of auxiliaries in a catalytic manner, we have been considering the possibility that auxiliaries capable of chelation with an incoming reagent might be able to accelerate reaction rates.³ In a recent communication,⁴ we were able to demonstrate that transition metal catalysed Diels–Alder cycloadditions were accelerated by auxiliaries which could provide chelation to transition metal Lewis acids. We now wish to demonstrate this principle for the iridium catalysed hydrogenation of allylic ethers and enoate esters containing pyridyl auxiliaries.

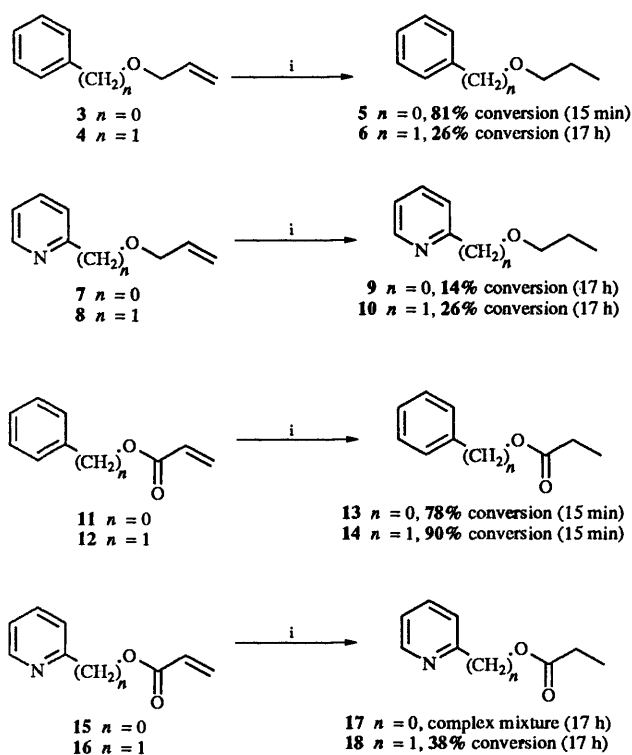
We anticipated that alkenes attached to auxiliaries equipped with a donor atom **1** might accelerate the rate of iridium or rhodium catalysed hydrogenation relative to alkenes tethered to groups without a donor atom **2**.



Results and discussion

We discovered that allyl phenyl ether **3** which is not capable of chelation underwent iridium catalysed hydrogenation in methanol in high conversion within 15 min (Scheme 1). Allyl benzyl ether **4**,⁵ however, reacted much more slowly under the same reaction conditions giving a lower level of conversion even after 17 h. This difference in reactivity is presumably due to the greater Lewis basicity of the oxygen atom in **4** which can poison the iridium catalyst.

However, 2-allyloxypyridine **7**⁶ underwent much slower conversion than the corresponding phenyl substrate **3**, giving lower levels of conversion over a much longer reaction time (17 h compared with 15 min). Allyl picolyl ether **8**⁵ reacted at



Scheme 1 Reagents and conditions: i, Ir cat. (2.5 mol%), H₂ (1 atm.), MeOH, room temp.

the same rate as allyl benzyl ether **4** under the same conditions. We found that methanol was a satisfactory solvent for these reactions, although a similar difference in reactivity between allylic ethers **3** and **7** was observed for hydrogenation under the same conditions in dichloromethane, *i.e.* allyl phenyl ether **3** went to 100% conversion after 15 min whereas 2-allyloxypyridine **7** underwent hydrogenation in only 7% conversion after 17 h. The corresponding reaction using [Rh(cod){Ph₂P(CH₂)₄PPh₂}]⁺BF₄⁻ in dichloromethane gave fairly low levels of conversion for both substrates (7% conversion after 15 min for **3** and 22% conversion after 17 h for **7**).

Thus, the presence of a co-ordinating group (pyridyl nitrogen or a non-aryl ether) dramatically lowers the reactivity of the substrate.

A similar trend to the results for substrates **3** and **7** was observed for the related enoate esters, prepared by reaction of the appropriate alcohol with acryloyl chloride in the presence of triethylamine. Phenyl and benzyl acrylates **11** and **12** underwent rapid iridium catalysed hydrogenation whereas a much longer reaction time was required to achieve a lower conversion for picolyl acrylate **16**. 2-Pyridyl acrylate **15** was found to be unstable on addition of iridium (or rhodium) catalyst, undergoing decomposition in preference to hydrogenation.

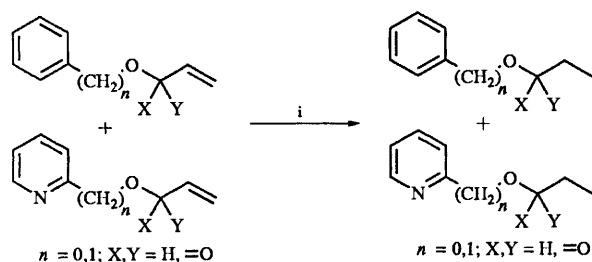
Again, the presence of the pyridyl group has dramatically reduced the rate of catalysed hydrogenation.

We believe that the 2-pyridyl groups (and the non-aryl ethers)

Table 1 Competitive catalytic hydrogenation reactions^a

Substrates	Products	Catalyst	H ₂ (atm)	Solvent	Conversion (%) (Ph)	Conversion (%) (Py)
3 + 7	5 + 9	Ir	1.0	MeOH	2	26
3 + 7	5 + 9	Ir	1.0	CH ₂ Cl ₂	0.8	7
3 + 7	5 + 9	Ir	2.7	MeOH	47	85
3 + 7	5 + 9	Ir	2.0	MeOH	24	68
3 + 7	5 + 9	Ir	4.4	CH ₂ Cl ₂	15	49
3 + 7	5 + 9	Rh ^b	4.4	CH ₂ Cl ₂	4	19
4 + 8	6 + 10	Ir	4.4	MeOH	16	24
11 + 15	13	Ir	4.4	MeOH or CH ₂ Cl ₂	—	Decomp.
12 + 16	14 + 18	Ir	2.0	MeOH	25	33

^a All reactions were run at room temperature for 17 h. ^b Rh catalyst = [Rh(cod){Ph₂P(CH₂)₄PPh₂}]⁺BF₄⁻.



Scheme 2 Reagents and conditions: i, Ir cat. (2.5 mol%), H₂, room temp., 17 h (or Rh⁺ catalyst) (see Table 1)

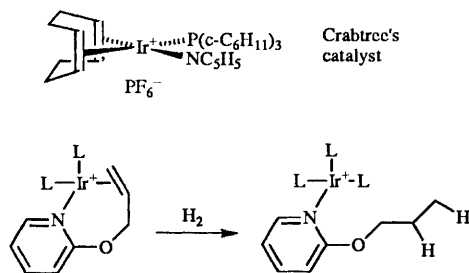


Fig. 1 Auxiliary accelerated hydrogenation

are poisoning the iridium catalyst *via* coordination, thereby reducing the rate of alkene hydrogenation.⁷ Nevertheless, we proceeded to investigate the relative reactivity of phenyl and 2-pyridyl substrates in competition reactions.

In a typical experimental procedure for competitive hydrogenation, such as the comparison between allyl phenyl ether **3** and 2-allyloxypyridine **7**, equimolar quantities of the two substrates were dissolved in the appropriate solvent and then a catalytic amount of catalyst (2.5 mol%) was added (Scheme 2). The reaction mixture was immediately subjected to hydrogenation at the appropriate pressure for 17 h at room temp. in each case. The results are detailed in Table 1.

For all of the competitive catalytic hydrogenation reactions studied, the 2-pyridyl-based (Py) substrates always reacted more quickly than the corresponding phenyl-based (Ph) substrates.

The results for competitive hydrogenation between allyl phenyl ether **3** and 2-allyloxypyridine **7** are particularly noteworthy. In independent catalytic hydrogenation reactions, the phenyl substrate **3** reacts more than 100 times as quickly as the pyridyl substrate **7**. However, in the competition experiment, the relative reactivity is reversed, and substrate **7** reacts at least 10 times as quickly as substrate **3**. However, the reactivity of 2-allyloxypyridine **7** was not greatly affected by the presence of allyl phenyl ether **3**. Competition reactions between allyl benzyl and allyl picolyl ethers **4** and **8**, however, did not give much rate acceleration for the 2-pyridyl substrate. The results for the corresponding esters **12** and **16** showed that the reactivity of benzyl acrylate **12** in iridium catalysed

hydrogenation was greatly reduced by the presence of picolyl acrylate **16**.

Whilst we have shown that the presence of the pyridyl substrate slows down catalytic hydrogenation, the competition experiments do suggest that for the 2-pyridyl substrates such as 2-allyloxypyridine **7** chelation to iridium is accelerating the reaction of tethered alkenes with respect to untethered alkenes, perhaps *via* a complex as illustrated in Fig. 1. Thus, it is the preferential complexation of the pyridyl substrate to the iridium catalyst (*via* the pyridyl nitrogen) which accelerates this reaction relative to the phenyl analogue. Nevertheless, the phenyl analogue reacts rapidly in the absence of the pyridyl substrate, since it does not have to compete for the iridium catalyst.

In summary, we have demonstrated that in competitive iridium catalysed hydrogenation reactions alkenes tethered to 2-pyridyl groups undergo reaction significantly more quickly than the corresponding alkenes tethered to phenyl groups. This finding is in contrast to the reactivity of the substrates in the more usual non-competitive mode of reaction. The design of 2-pyridyl-based auxiliaries based on these systems which can function in a catalytic manner is currently underway.

Acknowledgements

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