Composition of catalyst resting states of hydroformylation catalysts derived from bulky mono-phosphorus ligands, rhodium dicarbonyl acetylacetonate and syngas

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ABSTRACT

The paper describes the composition of the resting states of several catalysts for alkene hydroformylation derived from bulky monophosphorus ligands. The results presented assess how bulky ligands compete with CO for the rhodium, and hence the role of 'unmodified' catalysts in alkene hydroformylation in the presence of these ligands. High Pressure Infra-Red (HPIR) spectroscopy was carried out at the rhodium and syngas concentrations typically used during catalysis experiments. These HPIR studies revealed that two ligands previously studied in Rh-catalysed hydroformylation react with $[Rh(acac)(CO)_2]$ and H_2/CO to give the unmodified rhodium cluster, $[Rh_6(CO)_{16}]$, as the only detectable species. Both less bulky phosphoramidites, and 1,3,5,7-Tetramethyl-6-phenyl-2,4,8-trioxa-6-phosphaadamantane, on the other hand, do not show the presence of $[Rh_6(CO)_{16}]$, and hence catalysis proceeds by purely ligand modified species under normal conditions. In the case of the Rh/phosphaadamantane catalysts, anecdotal evidence that this only forms a particularly useful catalyst above a certain pressure threshold can be understood in terms of how the catalyst composition varies with pressure. The ligands discussed have all been assessed in the hydroformylation of propene to separate their innate branched selectivity from their ability to isomerise higher alkenes to internal isomers.

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Introduction

As is often remarked, hydroformylation of alkenes is one of the most important reactions in homogenous catalysis. Rh catalysts derived from bidentate ligands are particularly useful for linear-selective hydroformylation of terminal alkenes, and, generally using substrates biased towards branched products, asymmetric hydroformylation [1,2]. Bulky monophosphorus ligands have also played a prominent role in hydroformylation catalysis. Bulky phosphites are known to give remarkably active catalysts. Detailed studies of *ortho*-substituted triarylphosphite systems show that, while a mixture of Rh species can be formed during hydroformylation, the high reactivity and high isomerisation activity can be ascribed to mono-ligated rhodium catalysts [3]. The resting state of a mono-ligated pathway is a complex of type $[Rh(H)L(CO)_3]$. *In situ* spectroscopic studies have also been carried out on some supramolecular assemblies formed from bulky monodentate phosphoramidites; these also form mono-ligated catalysts of type $[Rh(H)L(CO)_3]$ [4]. These are in contrast to less reactive catalysts derived from less bulky triphenylphosphine and triphenylphosphite that tend to form a complex mixture of resting states: $[Rh(H)L(CO)_3]$, $[Rh(H)L_2(CO)_2]$ (2 isomers), $[Rh(H)L_3(CO)_1]$ in varying proportions depending on the reaction conditions [5]. Carbonyl clusters with bridging carbonyl ligands and coordinated phosphorus ligands can also form, although these can be converted back to the hydride-carbonyl complexes above under hydroformylation conditions. Finally, all of these species can potentially be in competition with unmodified Rh catalysts, $[Rh(H)(CO)_4]$ or $[Rh_6(CO)_{16}]$.

There are other interesting reports describing performance in hydroformylation for other types of Rh/bulky monophosphorus ligand catalysts. However, few of these have been interrogated spectroscopically. In connection with our work aimed at developing alkene hydroformylations with branched regioselectivity [6], we wished to identify if certain ligand types were worthy of further development: three catalysts derived from bulky monophosphrous

ligands seemed to us to require greater understanding of catalyst composition.

Ojima and co-workers [7] reported the use of enantiopure mono-dentate phosphoramidites in the enantioselective hydroformylation of allyl cyanide. Allyl cyanide does tend to give preference for the branched aldehyde [7,8] but the regioselectivity reported for ligand **1** is unusually high (B:L 96:4). Related ligand **2** gave no enantioselectivity and reduced regioselectivity. Another paper reporting unusual branched regioselectivity used trinaphthylphosphine, ligand **1-Np₃P** [9]. However, in this work on 1-hexene hydroformylation, extensive isomerisation occurs, so it is not known if the Rh/**1-Np₃P** catalyst system has a tendency to form branched aldehydes, or that the products almost exclusively stem from hydroformylation of the isomerised alkenes hex-2-ene and hex-3-ene. The adamantyl cage phosphine, 1,3,5,7-Tetramethyl-6-phenyl-2,4,8-trioxa-6-phosphaadamantane, ^{Me}**CgP-Ph** has been used often, as its Rh catalyst has several desirable characteristics: air and moisture stable during reaction set up, ability to hydroformylate less reactive highly substituted alkenes, high reactivity and a tendency to form an unusually large amount of branched products in the hydroformylation of hex-1-ene [6b,6d,6e]. However, unlike a lot of hydroformylation catalysts that operate best at low pressures (2–10 bar), we have observed on many occasions that Rh/^{Me}**CgP-Ph** catalysts do not readily exhibit their best performance until at least 10 bar of syngas pressure (at the concentration and temperatures they are typically used at).

During hydroformylation using strong chelating bidentate ligands, providing the ligands are used in >1:1 ratio to rhodium, there is no contribution from 'unmodified catalysts' (with no ligands present except carbon monoxide and hydrogen). This means that catalyst resting states have often been studied using NMR spectroscopy backed up by IR spectroscopy, and in some cases catalyst resting states have been isolated and fully characterised. It is important to note that using monophosphorus ligands this is not the case. An equilibrium exists under hydroformylation conditions in which many resting states can co-exist, and indeed each of these could lead to a distinct catalytic cycle that produces product. This includes the unmodified Rh catalysts which could also contribute towards forming aldehyde products. A key aspect of this equilibrium is controlled by the concentration of CO and phosphorous ligand. In order to shed light on which cycles are dominant during hydroformylation, it is important to study the catalyst resting states under similar conditions to those used in a hydroformylation reaction: these are generally too dilute to study using NMR spectroscopy. In particular while NMR characterisation can be performed on the reaction between a Rh precursor, syngas and ligands at high concentrations, this pushes the equilibrium away from unmodified species and towards the more highly ligated compounds. We wished to assess if: (i) the bulky monophosphoramidites can sometimes form both unmodified catalysts and ligated catalytic pathways, (ii) if hydroformylation using **1-Np₃P** as a ligand primarily operates through unmodified catalysts, (iii) whether the ^{Me}**CgP-Ph** ligand exclusively forms mono-ligated catalysts, or has a contribution from unmodified species, and why >10 bar syngas pressure is generally required. In this project, we have carried out HPIR studies under conditions close to those used in catalysis to shed light on the number the phosphorus ligands coordinated to rhodium during hydroformylation. We also report the use of the ligands in Fig. 1 in rhodium-catalysed hydroformylation of propene.

Results and Discussion

The majority of the ligands examined in this study were well known and prepared according to the literature or purchased. However, ligand **3** is a new compound and was fully characterised. The
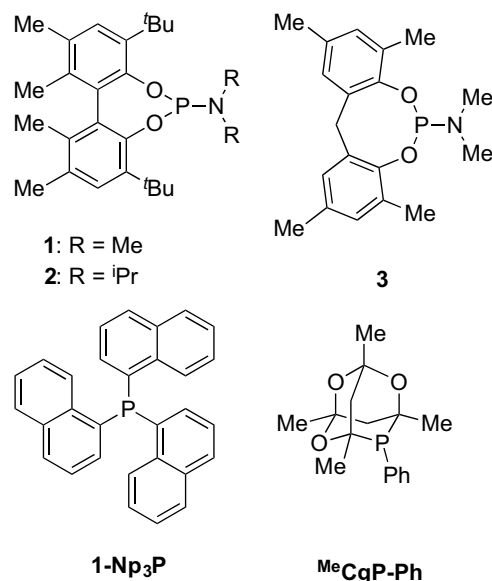

Fig. 1. Structures of ligands used in this study.

Table 1
Hydroformylation of propene.

Entry	Ligand	TON	% iso
1[a]	none	684	56
2[b]	none	590	56
3	1	1023	48
4	2	712	54
5	3	542	37
5	PPh₃	903	37
6	1-Np₃P	124	57
7	^{Me}CgP-Ph	1013	41

[Rh(acac)(CO)₂] (5.12 µmol) and ligand (0.020 mmol)(Rh:L 1:4) stirred in toluene (20 mL) at 90 °C under syngas (CO:H₂ 1:1, 20 bar) for 1 h, prior to running reaction for 1 h under propene/syngas (20 bar (Propene:hydrogen:CO = 2:9:9). Products determined by GC using 1-methylnaphthalene as an internal standard.

[a] Pre-Catalyst = [Rh(acac)(CO)₂] no ligand.
[b] Pre-Catalyst = [Rh₂(2-ethylhexanoate)₄], no ligand.

ligands were tested in the hydroformylation of propene to see if the catalysts derived from these ligands demonstrated unusually high *iso*-selectivity (Table 1); over 50% branched selectivity is near to the state of the art; few catalysts have been reported to give higher *iso*-selectivity than simple unmodified catalysts. The use of [Rh(acac)(CO)₂] without added ligand gives around 56% branched selectivity, similar to the more bulky of the ligands **1-Np₃P** and **2**. The TON measured after one hour is an average TOF; this measure of conversion at this arbitrary point in time provides a useful estimation of activity, although these values are not initial turnover frequencies, since some of these reactions are nearing completion, while some are near their peak rate after one hour (100% conversion corresponds to TON from gas uptake of ~1350). This was sufficient to show that the catalyst derived from ligand **2** is less active than Rh/ligand **1** catalyst, and **1-Np₃P**/Rh is a less active catalyst than less bulky PPh₃/Rh catalysts.

HPIR spectroscopy has often been used successfully to confirm the structures of Rh catalysts derived from *bis*-phosphorus ligands [10]. In these cases, the main species are limited to *bis*-equatorial isomers and axial-equatorial isomers, along with some inactive resting states. These are often independent of catalyst