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.

Keywords: hydroformylation; unmodified catalysts; *in situ* monitoring; phosphoramidites; IR spectroscopy

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 connections 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-Np$_3$P**.[9] However, in this work on 1-hexene hydroformylation, extensive isomerisation occurs, so it is not known if the Rh/**1-Np$_3$P** 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-Np$_3$P** 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.

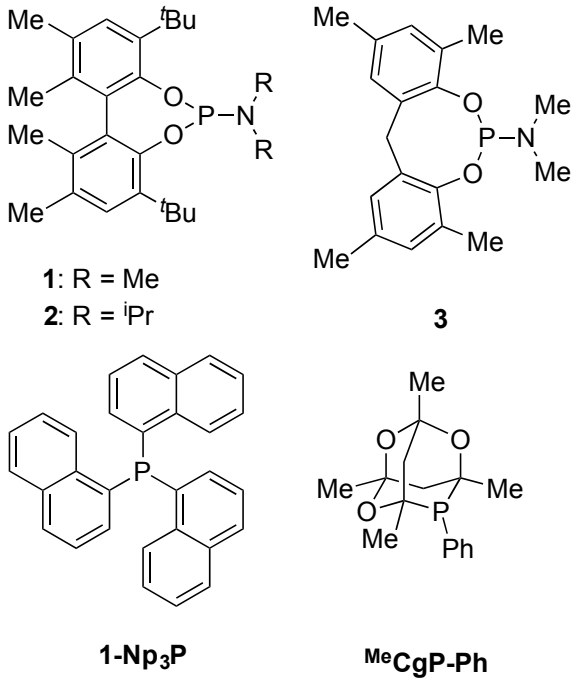


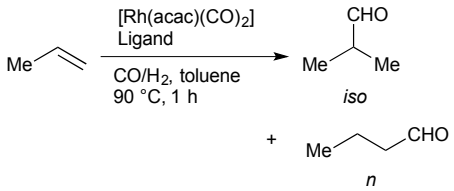
Figure 1: Structures of ligands used in this study

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 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-Np$_3$P** 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-Np$_3$P** / Rh is a less active catalyst than less bulky PPh_3 / Rh catalysts.

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	**PPh_3**	903	37
6	**1-Np$_3$P**	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 ($CO:H_2$ 1:1, 20 bar) for 1 hour, prior to running reaction for 1 hour 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 = [Rh_2(2-ethylhexanoate)$_4$], no ligand.

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 concentration. As previously discussed, it is common for many mono-phosphorus ligands to form quite

complex catalyst compositions. Our primary aim was to assess if the unmodified catalysts were formed for any of the ligands, but to also get a snapshot of the types of resting state that were favoured. In this study, we were able to get good spectra at concentrations of [1-2 mM]: similar to those used in catalysis (Ref. 7: 1 mM; Ref 9: 0.23 mM).

$[Rh_6(CO)_{16}]$ has large carbonyl stretching vibrations at 2074 and 1821 cm^{-1} with a weak band at 2045 cm^{-1}.[11] An IR spectrum of a sample generated under our conditions is archived in the ESI and is in agreement with the above assignment. This can be formed from $[Rh(acac)(CO)_2]$ or from $[Rh_2(hexanoate)_4]$. Garland and co-workers [12] have demonstrated that $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ converts into $[RhH(CO)_4]$ during studies on the hydroformylation of dimethylbut-1-ene.

There is some useful literature on the position of the carbonyl absorption bands for Rh catalysts derived from certain ligands that give relatively simple catalyst compositions under the conditions of the HPIR experiment.[1,4,5a,10] $[RhH(CO)_2(PPh_3)_2]$ with PPh_3 in the axial and equatorial positions contains bands at 1992 and 1947 cm^{-1} in 2-methyltetrahydrofuran at around 60 mM concentration.[1,5a] The *bis*-equatorial species is assigned to bands at 2042 and 1981 cm^{-1}. Triphenylphosphite forms the 2 isomers of $[RhH(CO)_2(P(OPh)_3)_2]$ displaying carbonyl stretches at 2034 and 1992 cm^{-1} for the axial equatorial isomer, and 2053 and 2018 cm^{-1} for the *bis*-equatorial isomer. $[RhH(CO)(P(OPh)_3)_3]$ has also been detected with a stretch at 2070 cm^{-1}.[5b] As expected, the electron-withdrawing ligand shifts the carbonyl stretches to higher wavenumber. A mono-ligated Rh complex of a phosphoramidite ligand shows bands at 2054, 2000 and 1982 cm^{-1} if the phosphorus ligand is in the equatorial plane and 2055, 2022, 1998 cm^{-1} if the phosphorus ligand is in the apical position.[4d] With these comparisons in hand, most of the components (unmodified cluster, mono or *bis*-ligated Rh complexes) in the catalyst mixtures can be assigned, and the presence of the unmodified clusters can be unequivocally determined.

The catalysts formed from ligand **1** and bulkier ligand, **2** were studied by *in situ* HPIR spectroscopy (**Figure 3**). The IR spectra obtained from $[Rh(acac)(CO)_2]$, ligand **1** and syngas shows a number of bands around 1950-2050 cm^{-1}, typical for $[RhH(CO)_n(L)_{3-n}]$ complexes. In particular, bands at 2062/2009 cm^{-1} and 2037/1996 cm^{-1} are suggestive of the two isomers of a *bis*-ligated species. In the original paper

on the use of this ligand in enantiomerically pure form, DFT calculations supported a *bis*-ligated pathway, and this result is in agreement with this.

In contrast, the reaction of ligand **2,** $[Rh(acac)(CO)_2]$ and syngas leads to almost exclusive formation of the rhodium cluster, $[Rh_6(CO)_{16}]$ either at 70 ºC and 90 ºC. In the previous work by Ojima and co-workers [7], the enantiomerically pure form of ligand **2** gave poorer regioselectivity and no enantioselectivity in hydroformylation. It therefore seems very likely that this bulky ligand does not coordinate to rhodium under hydroformylation conditions, and that the higher branched selectivity observed for propene hydroformylation with ligand **2** relative to ligand **1** (**Table 1**), is almost certainly due to the unmodified catalyst.

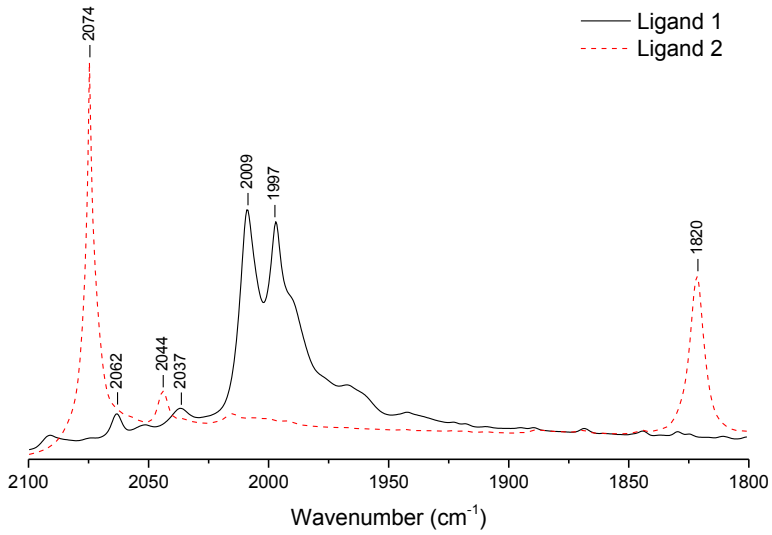


Fig. 3: HPIR spectra of rhodium catalysts from $[Rh(acac)(CO)_2]$ 70 °C in hexane, under 20 bar syngas ($CO:H_2$ 1:1); from ligand **1** (black) and ligand **2** (red)

The least bulky phosphoramidate ligand **3**, was found to give the lowest branched selectivity. HPIR spectroscopy confirms that no rhodium clusters were formed. The carbonyl bands at 2061/2015 cm^{-1} and 2026/1983 cm^{-1} are assigned to both isomers of $[RhH(CO)_2(L)_2]$ (**Figure 4**).

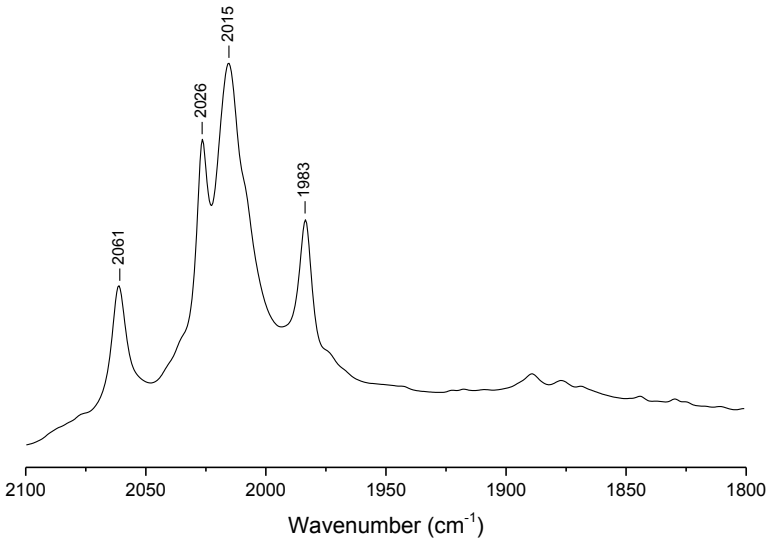


Figure 4: HPIR spectrum of rhodium catalysts formed from less bulky ligand, **3** at 70 ^{o}c and 20 bar syngas in hexane (L:Rh = 4:1).

To provide a comparison under our conditions, the frequently used ligand PPh_3 and $[Rh(acac)(CO)_2]$ forms multiple catalyst species, with a number of carbonyl bands present between 1950-2060 cm^{-1} including both isomers of $[RhH(CO)_2(PPh_3)_2]$ as discussed in previous reports (see ESI).[1,5a] In contrast, $[Rh(acac)(CO)_2]$, **1-Np$_3$P** and syngas react together to form only the rhodium cluster as the main detectable Rh-carbonyl species (**Figure 5**).

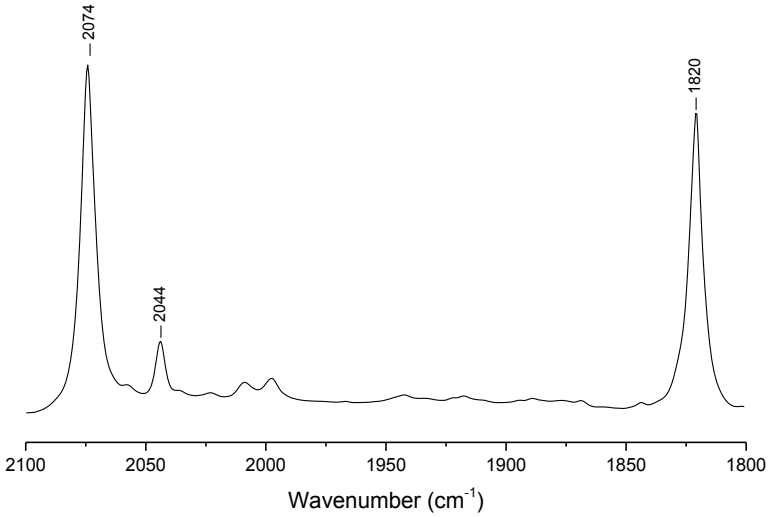


Figure 5: HPIR spectrum of rhodium catalyst formed with **1-Np$_3$P** ligand at 70 ^{o}c and 20 bar syngas in hexane (L:Rh = 4:1); this matches that formed when no ligand is present and is assigned to [Rh_6CO_{16}]

It is very likely that the high branched selectivity observed for the hydroformylation of 1-hexene by Bajaj and co-workers [9] (as well the similar regioselectivities shown in propene hydroformylation using [Rh(acac)$(CO)_2$] alone) stems primarily or entirely from catalysis by the unmodified catalyst. The spectroscopic experiment on the Rh/**1-Np$_3$P** system was repeated at 110 ^{o}C, the reaction temperature that was used in reference 9, and gave the same carbonyl bands in the IR spectrum. The **1-Np$_3$P** ligand concentration in the HPIR experiment is slightly higher than that used in the propene hydroformylation. The known implication of higher ligand concentration is to form more ligand-associated species, and hence at low ligand and catalyst concentrations, unmodified catalysts resting states are even more likely. The lower activity observed relative to unmodified catalysts is most likely due to some inactive ligated Rh compound being present, at least at some point, and the effective concentration of hydroformylation catalyst being different in the presence of **1-Np$_3$P**. The ligand therefore can still have an impact on the catalysis, especially with higher alkenes where the regioselectivity is strongly influenced by the degree of alkene isomerisation that has occurred at a given point in the reaction, *even if it doesn't coordinate to Rh during aldehyde formation*. For the hydroformylation of higher alkenes especially then, some difference in the results observed in the presence of ligand between a

control experiment of ligandless hydroformylation does not serve as evidence that the main catalysis going on is ligand modified. At the end of the reactions of [Rh(acac)(CO)$_2$] with syngas and ligands **1,** **^{Me}CgP-Ph** and **1-Np$_3$P**, the reaction mixtures were concentrated and examined by $^{31}P\{^1H\}$ NMR. While the former two gave a mixture of compounds: the exact identity of which are not likely to be of particular significance to catalysis (since the composition is related to [CO]), there were several species that clearly displayed a $J_{P\text{-}Rh}$ coupling: these either directly represent (or are derived from) Rh catalysts formed from these ligands. In contrast, the hydroformylation reaction mixture from reactions using **1-Np$_3$P** as ligand showed only free ligand (δ_P = -32) and its oxide (δ_P = +38). If a sample was taken from the reaction of **1-Np$_3$P** with [Rh(acac)(CO)$_2$] and syngas after a shorter time period there is a small amount of a Rh species formed, which can be assigned as [Rh(acac)(1-Np$_3$P)(CO)] (δ_P = 46.5, br. d, $J_{P\text{-}Rh}$ = 173 Hz) , which we also prepared independently (see ESI). We also monitored the reaction of [Rh(acac)(**1-Np$_3$P**)(CO)], 3 equivalents of **1-Np$_3$P** and syngas by IR (this time using hexane/CH_2Cl_2 mixture for solubility reasons) and found this converts into [$Rh_6(CO)_{16}$]. There is a small additional carbonyl band observed at 1886 cm^{-1}, but no sign of [$RhH(CO)_n(L)_{3-n}$] complexes. This peak cannot be assigned, and could be an inactive phosphine modified cluster, or another type of unmodified cluster. In any case, it is shown that **1-Np$_3$P** cannot compete with the relatively high pressures of CO for Rh used under catalysis conditions.

The IR spectra obtained from [Rh(acac)(CO)$_2$], **^{Me}CgP-Ph** and syngas were complex and a number of experiments were carried out, at increasing ligand concentration and syngas pressure, to assist in the assignment of the bands (**Figure 6**). Above an initial pressure of 5 bar syngas, an activation period of roughly 20 minutes was observed with formation of the activated species complete in a further 20 minutes. Below 5 bar of syngas pressure, catalyst activation to [$RhH(CO)_n(L)_{3-n}$] complexes does not take place. The rate at which the [$RhH(CO)_n(L)_{3-n}$] species formed were observed to decrease as ligand loading increased and were sigmoidal in nature. Changes in adsorption band height were faster than the acquisition time of the experiment when the pressure of syngas was altered.

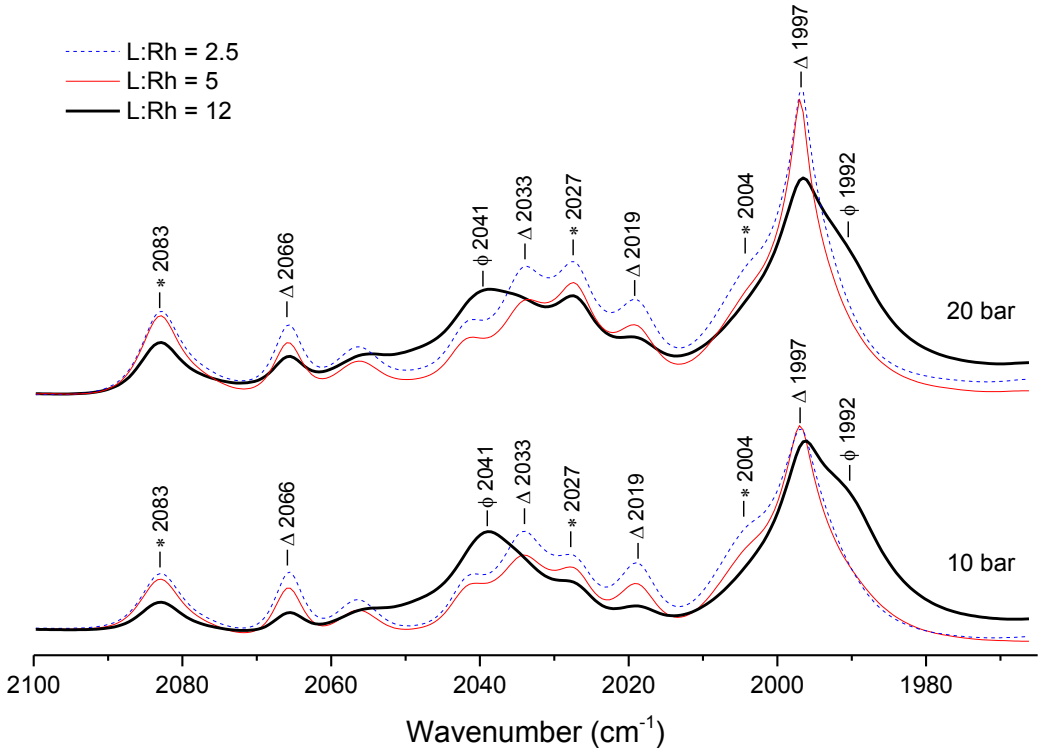


Fig. 6: HPIR spectra of rhodium catalysts from $[Rh(acac)(CO)_2]$ at 50 °C in hexane, under 10 or 20 bar syngas ($CO:H_2$ 1:1) with **^{Me}CgP-Ph** at increasing loadings relative to rhodium; L:Rh = 2.5 (blue), L:Rh = 5 (red), L:Rh = 12 (black). Assigned complexes are labelled *mono* = *, *bis* = Δ, and *tris* = ϕ.

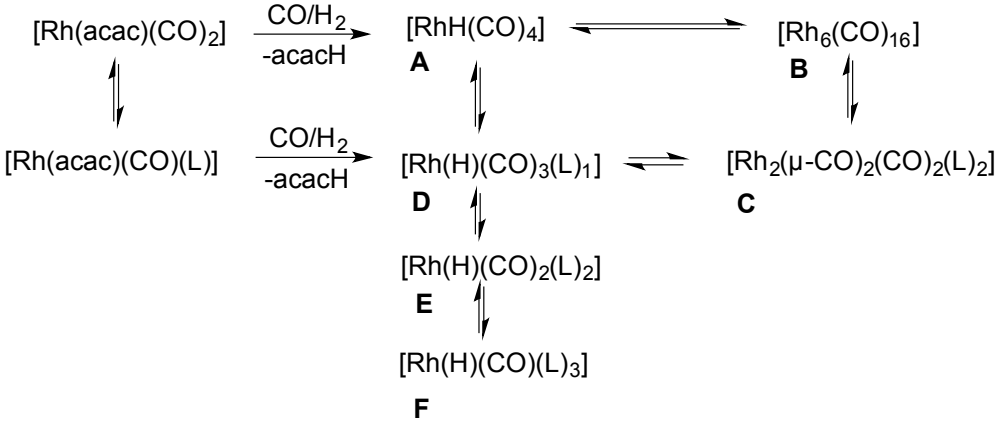
At high ligand concentration (L:Rh = 12), the major species displayed one distinct adsorption bands at 2041 cm^{-1} that decreases in intensity on increasing pressure of syngas; we assign this as the *tris*-ligated complex (as the equilibrium between $[Rh(H)(L)_3(CO)]$ and $[Rh(H)(L)_2(CO)_2]$ and $[Rh(H)(L)_1(CO)_3]$ should shift away from the former as the CO concentration is increased). A further correlated band is present at 1992 cm^{-1}, we assign this as the possible hydride of the *tris*-ligated complex. At lower ligand concentration, major bands that decrease in intensity as the pressure of syngas increases are assigned as the two isomers of *bis*-ligated complexes, $[Rh(H)(L)_2(CO)_2]$. Due to the differences in intensities of these stretches we assign

2066 and 2019 cm^{-1} as the *bis*-equatorial complex and 2033 and 1997cm^{-1} as the equatorial-axial complex. These are the shifts expected given the literature data on the *bis*-ligated complexes of $P(OPh_3)_3$.[5a,b] Finally, we assign bands at 2083, 2027, and 2004 cm^{-1} to the *mono*-ligated species, $[Rh(H)(L)_1(CO)_3]$. These are present in the greatest amount at the lowest ligand concentration, L:Rh = 2.5, and at each ligand concentration increase in intensity on increase in pressure of syngas. At each ligand concentration and pressure examined peaks at 1821, 1800, and 1779 cm^{-1} are observed, but there is no sign of the 3 correlated peaks that belong to $[Rh_6(CO)_{16}]$. This suggests that while some form of bridging Rh-carbonyl species may indeed be a minor component in these reaction mixtures, there is no strong evidence for the unmodified catalyst being present to any great extent, and the reaction mixture is primarily composed of every possible type of $[Rh(H)(L)_n(CO)_{3-n}]$ complex. Since higher pressure of syngas pushes the equilibrium towards $[Rh(H)(L)_1(CO)_3]$ complexes, that are known for other ligands to be especially reactive, this is why the Rh / **^{Me}CgP-Ph** catalyst does not show significantly increased reactivity if the CO concentration is not high enough. This will be more pronounced for sterically hindered alkenes, and the combination of a relative low partial pressure of CO and a very small alkene in the propene hydroformylation experiments is probably why the **^{Me}CgP-Ph/** Rh catalysts gave broadly similar rates to PPh_3/ Rh catalyst in the propene hydroformylation experiments, while **^{Me}CgP-Ph/** Rh catalysts are much more active under some conditions.[6c,d, 13]

Conclusions

A number of monodentate ligands have been investigated in the hydroformylation of propene. Two of the bulky ligands gave unusually high branched selectivity of propene, similar to what is observed with unmodified catalysts. However, this was due to the bulkier ligands dissociating from the rhodium, since under conditions similar to those used in catalysis using HPIR spectroscopy there was no evidence for phosphine modified catalysts. In hydroformylation using monodentate ligands the following equilibrium is set up (**Scheme 1**). For the bulky ligands **1-Np$_3$P** and **2,** the equilibrium lies in the top right part of the scheme. For ligand **1**, the evidence suggested that the main species formed was *bis*-ligated and hence able to control enantioselectivity in the similar way that these ligands have done before in

asymmetric hydrogenation. For **^{Me}CgP-Ph,** despite its significant bulk, it is able to form a mixture of ligand-modified species. This even includes the tri-ligated complex of type [Rh(H)(L)$_3$(CO)], generally considered to be unreactive. This species can be down-regulated by increases in CO pressure, allowing a greater concentration of highly reactive mono-ligated Rh species to predominate and deliver highly reactive catalysts. This shows the importance of ensuring ligand coordination has occurred when using monodentate ligands in hydroformylation. It is also now clear that despite some ligands significantly bulkier than **1** being used with success in other transition metal catalysed reactions, when they have to compete with the strong ligand CO the situation is different. The cage phosphine is a little different from the bulky phosphites and phosphoramidites known in that the highly reactive mono-ligated Rh catalysts are very much the major species reported, whereas **^{Me}CgP-Ph** shows more complex coordination behaviour. Any future studies involving modification of either phosphoramidites or phosphaadamantane ligands with bulky substituents to deliver more selective catalysts need to ensure the desired Rh catalysts are generated.



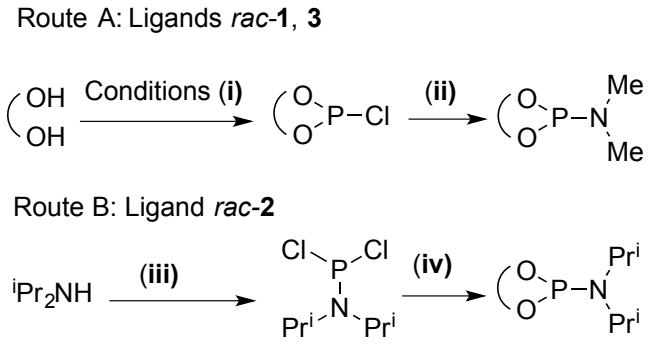
Scheme 1: Formation of catalyst resting states from [Rh(acac)(CO)$_2$] and monophosphine ligands: It is proposed that the equilibrium heavily favours unmodified species, **A**, and **B** for bulky ligands **2**, and **1-Np$_3$P**. the other ligands discussed form mixtures containing varying proportions of compounds **C**-**F**.

Experimental

All manipulations were carried out under an inert atmosphere of nitrogen or argon using standard Schlenk techniques. Solvents, *N*-Methylpyrrolidine, triethylamine and $CDCl_3$ were dried and degassed before use. Common starting materials were

purchased commercially and used as received. Propene/CO/H_2 (10/45/45) and CO/H_2 were obtained from BOC.

$[Rh_2(2\text{-ethylhexanoate})_4]$ as a 1% solution in 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate was provided by Eastman Chemical Company. $[Rh(acac)(CO)_2]$ and ligands **1-Np3P** were purchased. **^{Me}CgP-Ph** is available from Strem Chemicals. Ligands (*rac*)-**1** (59% yield), **3** (14% yield) were made according to **Route A** (**Scheme 2**), while ligand (*rac*)-**2** (71% yield), was made according to **Route B** (see ESI for full details and characterisation data).



Scheme 2: Ligand synthesis. **Conditions: (**i): *N*-methylpyrrolidine (3 equiv.), PCl_3 (1.3 equiv.), toluene, rt, 48 h. **(ii)**: *N*-methylpyrrolidine (1.2 equiv.), $HNMe_2$ (1.2 equiv.), toluene, rt, 18 h. **(iii)**: Et_3N (1.5 equiv.), PCl_3 (1.5 equiv.), CH_2Cl_2, rt, 18 h. **(iv)**: Et_3N (1.5 equiv.), diol (0.8 equiv.), CH_2Cl_2, rt, 18 h.

General procedure for hydroformylation of propene.

Hydroformylation reactions were performed in a Parr 4590 Micro Reactor fitted with a gas entrainment stirrer, comprising of a hollow impeller, to enhance gas-liquid mass transfer. Ligand (20.48 μmol (Rh:L 1:4)) was added to a Schlenk tube, which was then purged with nitrogen. $[Rh(acac)(CO)_2]$ (5.12 μmol) was added in a toluene stock solution (2 mg mL^{-1}). Toluene was then added to make up to 20 mL total volume, and internal standard 1-methylnaphthalene (0.2 mL) was added. The solution was transferred *via* syringe to the pressure vessel (which had been purged with CO/H_2) through the injection port. CO/H_2 (1:1, 20 bar) was added and the heating jacket set to 90 °C while stirring. Once the temperature reached 90 °C, the reaction was stirred for 1 hour to fully activate the catalyst. Then pressure was then released and replaced with propene/CO/H_2 (10:45:45, 20 bar). The reaction was then run for 1 hour, before immediate GC analysis.

General procedure for HPIR analysis.

HPIR studies were performed in a Parr high pressure IR CSTR vessel constructed from Hastelloy C, fitted with CaF_2 windows and rated to 275 bar. The adjustable path-length was set to 4 mm. Spectra were recorded using an Avatar 360 FT-IR spectrometer with a mercury-cadmium-telluride detector. [Rh(acac)$(CO)_2$] (0.06 mmol) and ligand (0.075 mmol (Rh:L 1:4) were added to a Schlenk tube, which was then purged with nitrogen. Hexanes (30 mL) was added to dissolve rhodium and ligand, and then transferred *via* syringe to the pressure vessel (which had been purged with N_2) through the injection port. CO/H_2 (1:1, 20 bar) was added and the heating jacket set to the desired temperature while stirring. Once the vessel reached the desired temperature a spectrum was recorded every two to 15 minutes. A background spectrum of hexane under appropriate temperature and pressure of CO/H_2 was subtracted from the spectra for analysis.

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

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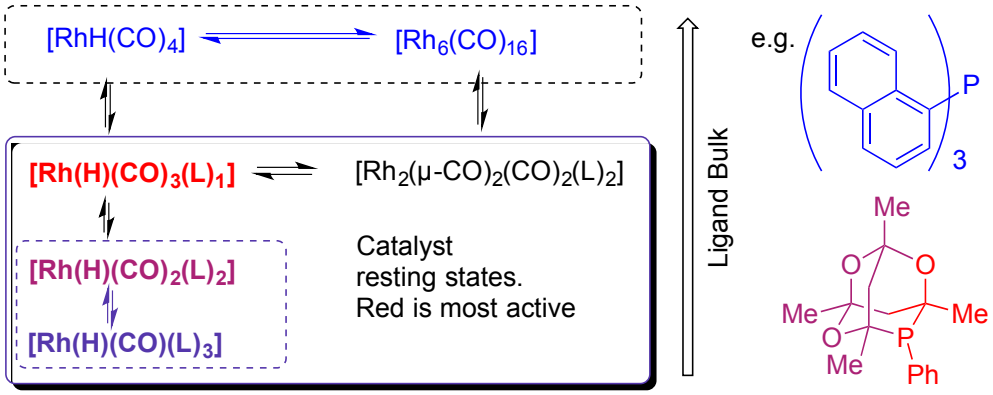

Highlights:

- **In situ spectroscopic study of hydroformylation catalysts at typical reaction concentrations.**
- **Two ligands in the literature found to not coordinate to rhodium in the presence of syngas.**
- **The highly active Rh / 1,3,5,7-Tetramethyl-6-phenyl-2,4,8-trioxa-6-phosphaadamantane catalyst system studied by in situ HPIR spectroscopy and found to be mixture of resting states, with the composition tuneable by reaction conditions.**