

# Hydroformylation studies using Nafion supported rhodium based homogeneous catalysts

D.E. Bryant\*, M. Kilner

Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, UK

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## Abstract

A series of rhodium complexes of the form  $[\text{Rh}(\text{L})_2\text{NBD}]\text{BF}_4$  where L represents a phosphine ligand and  $[\text{Rh}(\text{L}-\text{L})\text{NBD}]\text{BF}_4$  where (L–L) represents a diphosphine ligand and NBD = norbornadiene have been prepared. The complexes have been incorporated into Nafion by ion-exchange and the supported catalysts thus obtained have been compared with their homogeneous precursors for their activity as catalysts for the hydroformylation of hex-1-ene. The overall yield and the ratio of normal heptanal to branched products are reduced in all cases by introduction of the catalyst into Nafion. The modification of Nafion to produce a polymeric phosphine and its use as a ligand for hydroformylation using rhodium is also described.

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## 1. Introduction

We have recently reported the use of Nafion to support transition metal complexes for the catalytic hydrogenation of cyclohexene, dimethylmaleate and nitrotoluene [1]. The catalysts retained their activity when supported in Nafion, producing yields of hydrogenated materials comparable or better than yields obtained homogeneously, with improved rates of reaction over those reported in other studies. In this present study Nafion is used to support a series of rhodium complexes for the catalytic hydroformylation of hex-1-ene.

Hydroformylation using supported catalysis has been previously reported in the literature. In general, the catalysts are grafted onto polymeric supports by ligand exchange. A polymer with pendant benzyl

chloride groups can be phosphorylated by reaction with bisarylphosphinolithium and the resultant polymeric diphosphine used to replace  $\text{PPh}_3$  groups from the homogeneous catalyst precursor. One danger with this strategy comes when neighbouring pendant groups are in close proximity. Partial phosphorylation can lead to quaternisation which in turn gives a very poor hydroformylation catalyst [2].

Despite this potential drawback, Evans et al. reported [3] the exchange of *trans*- $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$  with a diphenylphosphine based polymer derived from chloromethylated polystyrene. The resultant polymer was active for the hydroformylation of 1-pentene. The linear to branched ratio was 3:1 and no alcohols were produced. A variation on this theme was provided by Allum et al. [4] who incorporated  $[\text{Rh}(\text{acac})(\text{CO})_2]$  into diphosphine derivatised cross-linked polystyrene beads. They achieved a 41% yield of aldehyde after 4 h at 80 °C under an atmosphere of 43 bar 1:1  $\text{H}_2$ :CO. The molar ratio of alkene to rhodium was  $10^4$ :1. Given

\* Corresponding author. Fax: +44-113-343-6565.

E-mail address: d.bryant@chem.leeds.ac.uk (D.E. Bryant).

that the normal to branched ratio using the supported catalyst was 2.5:1, much higher than that expected from  $[\text{Rh}(\text{acac})(\text{CO})_2]$  in solution, the authors concluded that the polymeric phosphine had played a role in the reaction. Pittman et al. [5] showed that increases in the polymer bound  $\text{PPh}_2$  to rhodium ratio led to increases in normal to branched product ratios but at the cost of overall yields.

Asymmetric hydroformylation has also been accomplished using rhodium supported catalysts [6] formed from chiral phosphine ligands functionalised with vinyl groups for subsequent polymerisation. Introduction of  $[\text{Rh}(\text{acac})(\text{CO})_2]$  afforded an active catalyst capable of 2000 turnovers in the hydroformylation of styrene. Branched products were around 80% of the total and these were in enantiomeric excesses of up to 90%. Balue and Bayon [7] report the immobilisation of a rhodium thiolate binuclear catalyst by protonation of amine groups, pendant from the sulphur bridges, using a sulphonic acid ion-exchange resin. The products of hydroformylation were methyl acetals rather than aldehydes, formed almost quantitatively, with branched products exceeding linear products by 4:1.

## 2. Experimental

Unless otherwise stated, all syntheses were carried out under a dry, oxygen-free, nitrogen or argon atmosphere, using standard Schlenk techniques. Solvents used in syntheses were dried using the appropriate drying agents. Hydrocarbons and ethers were distilled from sodium wire, dichloromethane and acetonitrile were distilled from  $\text{CaH}_2$  and methanol was dried with activated, Linde type 4A molecular sieves. Methanol and deionised water were deoxygenated by bubbling nitrogen gas through prior to use. The remaining solvents were deoxygenated by three freeze-pump-thaw cycles and stored in solvent pots in the dark.

### 2.1. High pressure reactions

All catalytic testing was performed in a purpose-built high pressure laboratory using a stainless steel reaction vessel capable of withstanding 750 atm. The vessel has a capacity of  $150\text{ cm}^3$ , a drain plug and

is fitted with a thermocouple and dip-tube. Provision is made for continuous stirring and there are connections via 1/8 stainless steel “Swagelok” tubing to a bursting disc for emergency pressure release, an analogue pressure gauge, pressure transducer and the manifold for introduction and removal of gases. Reaction solutions are contained in a glass liner. The whole autoclave is electrically heated by a concentric band heating element. Products were determined using a HP 5890 Series II gas chromatograph with flame ionisation detector, containing a SE30 capillary column and fitted with an integrator. Product peaks were identified by either a HP 5890 Series II GC coupled to a VG Analytical Trio 1000 mass spectrometer or by comparing retention times with authentic samples.

### 2.2. Ligands used for hydroformylation studies

A number of ligands was synthesised (see Fig. 1) and these were used to form complexes by displacement of NBD from  $[\text{Rh}(\text{NBD})_2]\text{BF}_4$ , which was prepared according to the procedure of Schenk et al. [8]. The resulting rhodium–phosphine complexes were used for a comparative study of the hydroformylation of hexene. The ligands were chosen to be capable of protonation and cover a range of types. Diphenylphosphino-2-pyridine ( $\text{PPh}_2\text{py}$  (7)) was supplied by the Aldrich chemical company. The remaining aminophosphines, bis( $N,N'$ -diphenylphosphino) phenylenediamine ( $\text{dppphn}$  (1)), di- $N$ -piperidylphenylphosphine ( $\text{d}(\text{pip})\text{pp}$  (4)), diphenylphosphino- $N$ -methylaniline ( $\text{dppnma}$  (6)), bis( $N,N'$ -diphenylphosphino-methyl)ethylenediamine ( $\text{dppmen}$  (5)) [9] were synthesised from the corresponding chlorophosphines and amines. Phosphines, diisopropylphosphinoferrrocene ( $\text{dippf}$  (2)) [10], diphenylphosphinoquinoline ( $\text{dppq}$  (3)) [11] were prepared following literature procedures.

### 2.3. The modification of Nafion functionality

The sulphonic acid groups that form the ion-exchange sites in Nafion resin are also reactive centres which can be modified using suitable reagents in a manner analogous to solution chemistry. The inert nature of the fluorinated polymer chains in Nafion allows the use of aggressive reagents without the

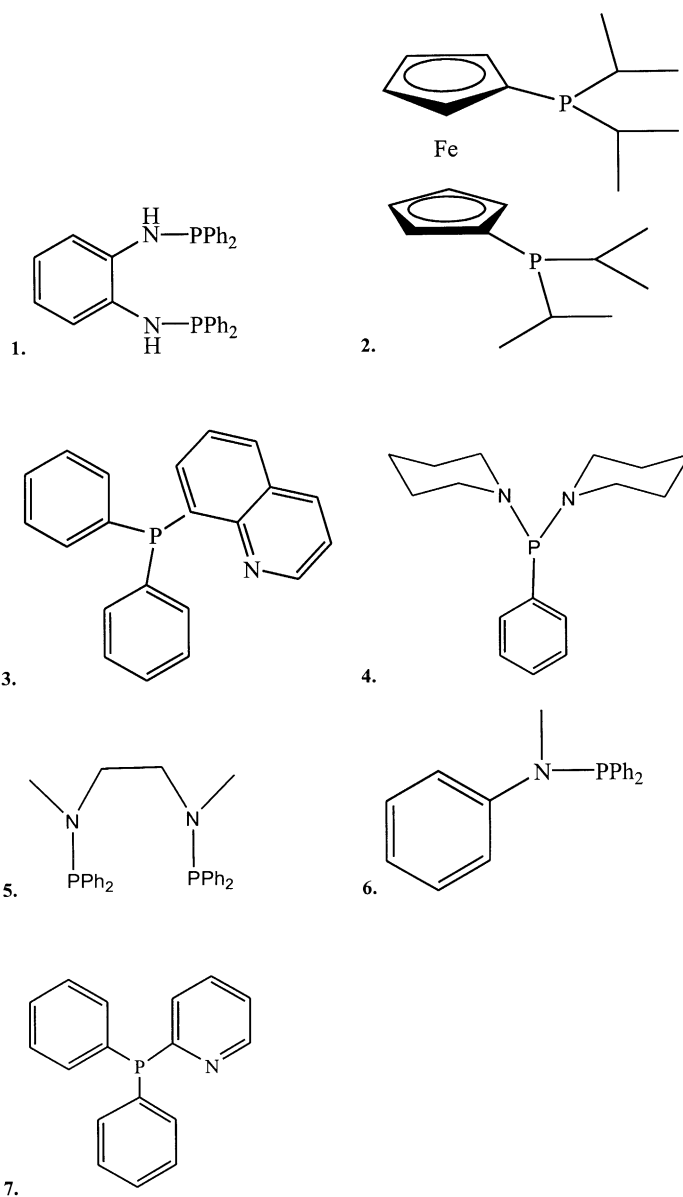
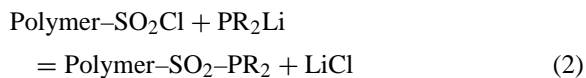
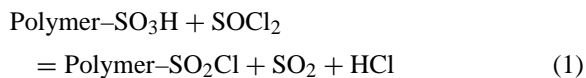


Fig. 1. Phosphine ligands used to complex rhodium.

complication of unwanted side reactions.



#### 2.4. The synthesis of Nafion diphenylphosphine

Nafion-H beads (5 g) were refluxed overnight under nitrogen gas in 10 ml thionyl chloride. The beads, which had become opaque in appearance, were rinsed with  $3 \times 10$  ml  $\text{CH}_2\text{Cl}_2$  and pumped dry.

Nafion sulphonyl chloride (0.7 g) was weighed into a two-necked round-bottomed flask. In a second, similar flask, triphenylphosphine (1.0 g, 3.8 mmol) and lithium wire (0.14 g, 20 mmol) were stirred rapidly under an argon atmosphere. On addition of THF (10 ml) and a little warming, reaction started to generate diphenylphosphinolithium. When conversion of  $\text{PPh}_3$  was complete, confirmed by  $^{31}\text{P}$  NMR, the THF solution of  $\text{PPh}_2\text{Li}$  was transferred by cannula filter to the flask containing the modified Nafion. The beads were stirred at room temperature for an hour before the THF solution was decanted and the beads rinsed thoroughly with fresh THF and methanol.

Solid state MAS  $^{31}\text{P}\{^1\text{H}\}$  NMR showed a singlet at  $\delta = 34.5$  ppm.

The resultant polymer was clear and flexible. Modification of Nafion in this way has not been previously reported.

### 2.5. The addition of $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ to Nafion- $\text{PPh}_2$

Beads of Nafion- $\text{PPh}_2$  (0.7 g), were stirred for 7 days in a toluene (10 ml) solution of  $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ , (138 mg, 0.2 mmol) at room temperature under an atmosphere of nitrogen. The complex was completely absorbed. The beads were used for the hydroformylation of hex-1-ene giving a yield of 180 mol/(mol Rh) and a normal to branched ratio of 0.71 with only 1% leaching.

### 2.6. Catalytic hydroformylation studies

All homogeneous runs and runs using Nafion-H were based on cationic rhodium complexes formed by the replacement of norbornadiene from  $[\text{Rh}(\text{NBD})_2]\text{BF}_4$  by either two monodentate ligands or one bidentate ligand. A series of high pressure reactions was performed using a set of standardised conditions, described in Section 2.7. In each case, the catalyst system was formed in situ by addition of the ligand to  $[\text{Rh}(\text{NBD})_2]\text{BF}_4$  and in each case the substrate used was hex-1-ene. For each Nafion supported run, the ligand was allowed to react with  $[\text{Rh}(\text{NBD})_2]\text{BF}_4$  and the reaction solution monitored using phosphorus NMR spectroscopy to establish that ligand replacement had indeed occurred and was complete before the resultant solution was stirred with Nafion beads.

### 2.7. Standard conditions used for hydroformylation

#### 2.7.1. Homogeneous case

$[\text{Rh}(\text{NBD})_2]\text{BF}_4$  (0.01 g,  $2.7 \times 10^{-5}$  mol) was added to a slight molar excess of ligand in the glass sleeve of the reaction vessel. To this was added 10 ml each of hex-1-ene, methanol (to swell the beads and act as an internal standard) and *N*-methylpyrrolidinone (NMP). The sleeve was fitted to the autoclave and the autoclave flushed with nitrogen. The autoclave was pressurised to 40 bars of  $\text{H}_2/\text{CO}$  (50:50) and heated to 120 °C for 5 h.

#### 2.7.2. Supported case

$[\text{Rh}(\text{NBD})_2]\text{BF}_4$  (0.01 g,  $2.7 \times 10^{-5}$  mol) was added to a slight molar excess of ligand in a 100 ml round bottomed flask and dissolved in degassed methanol. The mixture was stirred for 2–3 h before a sample was removed for monitoring by  $^{31}\text{P}$  NMR. In all cases the signal for free ligand could no longer be detected and a new pattern for the complex had been generated. To the flask was added 1 g of vacuum dried Nafion-H beads and stirring continued overnight under nitrogen. The solution was removed by syringe from the beads which were rinsed in methanol before being transferred to the reaction vessel sleeve. The procedure then continued as described in Section 2.7.1 above.

## 3. Results

The catalysts used for the hydroformylation of hex-1-ene also facilitate its isomerisation. In the presence of the catalyst hex-1-ene can isomerise to *cis*- and *trans*-hex-2-ene and *cis*- and *trans*-hex-3-ene. Each of these can undergo hydroformylation to produce both linear and branched aldehyde isomers.

Reaction solutions were distilled and analysed by gas liquid chromatography. Peaks were identified by GC-MS in the first instance and thereafter by retention times. In some cases only three isomers of hexene were seen and in some cases four isomers were seen (internal alkenes can be *cis* or *trans*). Their peaks were assigned on the basis of literature values for their boiling points, on the assumption that the lowest boiling fraction elutes first. This is not sufficiently unambiguous to allow identification of *cis* and

Table 1  
High pressure results comparing homogeneous to Nafion supported hydroformylation of hex-1-ene

Phosphine	Leaching	Yield of hexene isomers (%)		Yield (mol/(mol Rh))		Yield aldehyde (%)		Aldehyde <i>n:b</i> ratio	
		H	N	H	N	H	N	H	N
None <sup>a</sup>	Complete	n/a	73.3	n/a	296	n/a	9.3	n/a	0.36
dppphn (1)	None	66.4	70.5	1045	1195	13.1	12.9	1.33	0.75
dippf (2)	20%	79.8	73.4	1696	1428	11.2	9.5	0.74	0.55
dppq (3)	Complete	63.4	71.9	412	454	13.8	15.2	1.10	0.52
d(pip)pp (4)	15%	59.3	76.3	610	253	20.4	8.5	1.37	0.59
dppmen (5)	Complete	41.0	54.7	1754	1158	44.4	29.3	2.28	0.94
dppnma (6)	Heavy	53.4	64.3	1303	801	43.6	26.8	1.29	0.62
dpp(py) (7)	Slight	45.8	75.3	1083	208	36.3	7.0	1.91	1.65
Blank <sup>b</sup>	n/a	n/a	15.3	n/a	Nil	n/a	Nil	n/a	n/a

Conditions: [Rh(NBD)<sub>2</sub>]BF<sub>4</sub> (0.01 g, 2.7 × 10<sup>-5</sup> mol) was added to a slight molar excess of ligand dissolved in 10 ml each of hex-1-ene, methanol and *N*-methylpyrrolidinone (NMP). Pressure: 40 bars of H<sub>2</sub>/CO (50:50). Temperature: 120 °C for 5 h.

<sup>a</sup> Catalyst [Rh(NBD)<sub>2</sub>]BF<sub>4</sub>.

<sup>b</sup> No rhodium used; H = homogeneous, N = Nafion supported.

*trans* isomers. In all cases, the three possible aldehyde products were identified (*n*-heptanal, 5-methylhexanal and 4-ethylhexanal). For the purposes of establishing the percentage normal product, the area of integration produced by the normal isomer is divided by the areas generated by all isomers added together. There was no evidence for the production of alcohols or alkanes. Yields and isomer distributions are displayed in Table 1.

#### 4. Discussion

In order to study hydroformylation using Nafion supported complexes, the complexes chosen must be capable of being absorbed by Nafion. Initially the use of cationic rhodium phosphine complexes appeared appropriate. However, early trials using the complex [Rh(NBD)(dcpe)]BF<sub>4</sub> showed that very serious leaching had occurred. It was likely that during catalysis a neutral intermediate, perhaps of the form [HRhL<sub>2</sub>(CO)], had formed during the reaction and had leached out from the beads. The results obtained were very ambiguous, in that catalysis could have taken place in the solution as well as in the beads. In order to ensure that the rhodium complexes were retained within the Nafion throughout the catalytic cycle, it was decided to form cationic complexes containing phosphine ligands which were themselves

capable of protonation. The group of ligands included monodentate and bidentate phosphines, monodentate aliphatic and aromatic aminophosphines and bidentate aliphatic and aromatic aminophosphines.

A set of standard conditions was chosen (see Section 2) to enable a fair comparison across the range of ligands and between the complexes used homogeneously and the complexes supported in Nafion. The complexes were allowed to form in situ from the reaction between [Rh(NBD)<sub>2</sub>]BF<sub>4</sub> and the corresponding phosphine. To complete the data set, a hydroformylation reaction run was carried out using Nafion without any [Rh(NBD)<sub>2</sub>]BF<sub>4</sub>, designated as “blank” and a run was carried out using [Rh(NBD)<sub>2</sub>]BF<sub>4</sub> without any added phosphine ligand.

From Table 1 it can be seen that, in most cases, the overall yield is reduced by introduction of the catalyst into Nafion. There does not appear to be any pattern across the series of ligands with regard to yields obtained when the catalyst is used homogeneously. However, on introduction into Nafion, the three bidentate ligands consistently outperform the monodentate ligands. Dppq (3) could be considered as a bidentate ligand in homogeneous solution but in Nafion it will be protonated and can therefore be classified among the monodentate ligands. The distribution of products is clearly altered by introduction into Nafion. The ratio of normal heptanal to branched products, is reduced in all cases by supporting the catalysts.

Interestingly, this remains the case despite leaching occurring in the majority of cases which suggests that the support has a strong influence despite leaching occurring and that perhaps the leaching occurs after the reaction is complete. The trend across the range of ligands for production of normal aldehyde using homogeneous catalysts is closely followed by the supported catalysts. In most cases, more of the two and three isomers are produced by the supported catalysts. The data show that isomerisation occurs faster than hydroformylation, and leads to a decrease in normal heptanal production, particularly for the supported catalysts. This increase in isomerisation products in the supported case can be attributed to the action of Nafion–H itself, since hex-1-ene was isomerised in the “blank” experiment (Table 1).

## 5. Conclusions

Rhodium–phosphine complexes supported in Nafion are capable of catalysing the hydroformylation of hex-1-ene albeit at a reduced overall yield. The ratio of normal to branched products is lower than that obtained by the same catalyst systems used ho-

mogeneously. Nafion can be modified into a polymeric phosphine ligand which can form a rhodium based supported catalyst. Yields obtained for the hydroformylation of hex-1-ene are lower than those obtained using Nafion–H absorbed rhodium complexes.

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