Hydrogenation studies using Nafion-supported homogeneous catalysts with cyclohexene, dimethylmaleate and 4-nitrotoluene

David E. Bryant, Melvyn Kilner*

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

Abstract

Three known high activity hydrogenation catalysts, $[RhCl\{Ph_2P(NC_5H_{10})\}_3]$ (**I**), $[Ir(C_8H_{12})(PPh_2Me)_2]PF_6$ (**II**) and $[Rh(C_7H_8)\{(Pr_2P)_2Fc\}]BF_4$ (**III**, Fc = ferrocenyl), have been incorporated into Nafion by ion-exchange and/or ligand exchange methods, and the supported catalysts so obtained compared with their homogeneous equivalents for activity for hydrogenation of three substrates, cyclohexene, dimethylmaleate and 4-nitrotoluene. The catalysts retain 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. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogenation; Nafion; Homogeneous catalysts

1. Introduction

A serious drawback with the application of transition metal homogeneous catalysts, which limits their wider adoption by industry, is the frequent need for an additional step in a manufacturing process to separate the catalyst from the product stream. Several approaches have been adopted to circumvent this problem, most involving the anchoring of the catalyst, by a variety of ways, onto a solid support, thus achieving the ease of separation of a heterogeneous catalyst, but retaining the design features of a homogeneous catalyst. Tailoring the catalyst to the needs of the reaction is therefore retained with, in principle, elimination of the difficulties of recovery. For this purpose, transition metal complexes have been supported on silica and other refractory oxides [1], in clays, in siloxanes, exchanged into ion-exchange resins and attached to polystyrene [2,3] and other organic polymers [4,5] through bonding to the ligands in the metal complex or by polymerisation of complexes through ligands functionalised to act as monomers [6]. There are many polymers used though polystyrene is the most common.

In the present study, use is made of the ionomeric resin traded by Du Pont under the name "Nafion", an example of a perfluorosulphonic acid resin, consisting of a hydrophobic, fluorinated backbone interspersed with ether linkages and with pendant sulphonic acid groups.

Seminal work on the structure of Nafion resulted from X-ray studies performed by Gierke et al. [7], based on which Hsu and Gierke proposed a cluster network model [8] of two phase-separated domains forming spherical inverted micelles connected by short narrow channels. The two phases are the hydrophobic polymer backbone phase and the hydrophilic sulphonic acid phase. The cluster diameters predicted by the model fall within a range between 2 and 5 nm,

---
* Corresponding author. Fax: +44-191-3861127.
*E-mail address:* mel.kilner@durham.ac.uk (M. Kilner).

depending on the equivalent weight, figures which are borne out by the measurements from small angle X-ray measurements. Thus, sufficient space is available to accommodate metal complexes within these cavities.

Within the hydrophilic cavities, advantage may be taken of the properties of the –SO$_3$H groups to introduce metal complexes, and the following three processes have been explored:

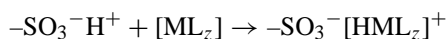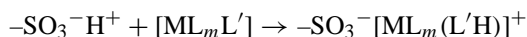1. ion-exchange of protons for cationic metal complexes

   $$-SO_3^-H^+ + [ML_x]^+ \rightarrow -SO_3^-[ML_x]^+ + H^+$$
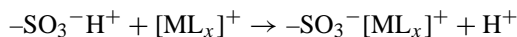
2. ligand exchange by the sulphonate groups

   $$-SO_3^- + [ML_yX] \rightarrow -SO_3[ML_y] + X^-$$
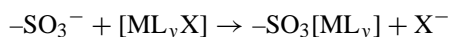
3. protonation of the complex by Nafion and its subsequent retention

   $$-SO_3^-H^+ + [ML_z] \rightarrow -SO_3^-[HML_z]^+$$

   or

 $$-SO_3^-H^+ + [ML_mL'] \rightarrow -SO_3^-[ML_m(L'H)]^+$$

The literature contains a few examples in which Nafion serves as a support for a transition metal complex acting as a catalyst. Toth et al. [9] used Nafion as a support to immobilise chiral phosphine rhodium complexes. Conversion of greater than 95% was achieved for the asymmetric hydrogenation of unsaturated amino acid derivatives in methanol. Enantioselectivities achieved using supported catalysts were found to vary and depend on the substrate, sometimes inferior and sometimes superior to the homogeneous equivalent. However, in all cases, the reaction time for the supported catalyst was two orders of magnitude slower than the homogeneous case. The catalysts were proven for up to six cycles without significant deterioration.

Olefin double bond shift isomerisation has been carried out in Nafion using a nickel phosphite catalyst [Ni{P(OEt)$_3$}$_4$], the active species, [HNi{P(OEt)$_3$}$_3$]$^+$ forming slowly by protonation and loss of ligand within the Nafion-H support [10]. Rates of isomerisation of 1-octene using the supported catalyst were of the order of one-third of that shown by the homogeneous systems, but were improved by partially neutralising the Nafion by exchanging some of the acid sites with Na$^+$.

Seen et al. [11] later describe the dimerisation of ethene using a Nafion-supported nickel(II) complex. Nickel was introduced as [Ni(*o*-tolyl)Br(PPh$_3$)$_2$] in a pyridine/methanol solution containing Nafion. The Nafion assisted in the formation of [Ni(*o*-tolyl)(py)$_2$(PPh$_3$)]$^+$ and subsequently supported the complex. In common with other studies it was found that the supported catalysts had lower turnover numbers per hour but continued to be active for much longer than the comparable homogeneous system. Eventually the yields per mole of catalyst were higher using the supported system.

The same research group also studied palladium catalysts [12] for ethene dimerisation. Cationic Pd(II) species are particularly suited to immobilisation in Nafion by ion-exchange methods and it is thought that catalytic activity is enhanced by non-coordinating anions. The RSO$_3^-$ ion in Nafion is very weakly coordinating with coordination ability between those of PF$_6^-$ or BF$_4^-$ and ClO$_4^-$ [12]. Three Pd(II) species, namely [Pd(1,10-phen)$_2$]$^{2+}$, [Pd(1,10-phen)(py)$_2$]$^{2+}$ and [Pd(2,2'-bipy)$_2$]$^{2+}$ were immobilised in Nafion, and it was found that the level of catalyst loading was significant. Initially, palladium loadings of 2 wt.% were used, which corresponds to about one Pd atom per five SO$_3^-$ ion-exchange sites. At this loading, activities of around 1500 turnovers/h were obtained at 80 °C. Decreasing the catalyst loading steadily increased the activity reaching a maximum of 16,000 turnovers/h with a loading of 0.065% Pd. The exercise was repeated in water with an even more dramatic improvement. At a loading of 0.025% an activity of 80,000 turnovers/h was obtained. Further improvements were reported in a later paper in which an activity of 760,000 turnovers/h was achieved for [Pd(1,10-phen)$_2$]$^{2+}$ supported in powdered Nafion [13]. Several explanations were suggested for these results. Firstly, higher loadings could limit the diffusion of ethene to the centre of the beads; secondly, it is known that exchange of larger cations (than H$^+$) limits the swelling of Nafion in protic solvents, necessary for efficient diffusion of reactants and products to and from the catalytic sites. Thirdly, the swelling of Nafion may reduce steric hindrance in one or more of the catalytic steps of the reaction. Fourthly, and finally, it is known that a common cause of catalyst deactivation is the interaction between intermediates to form dimers and clusters. Low catalyst loadings
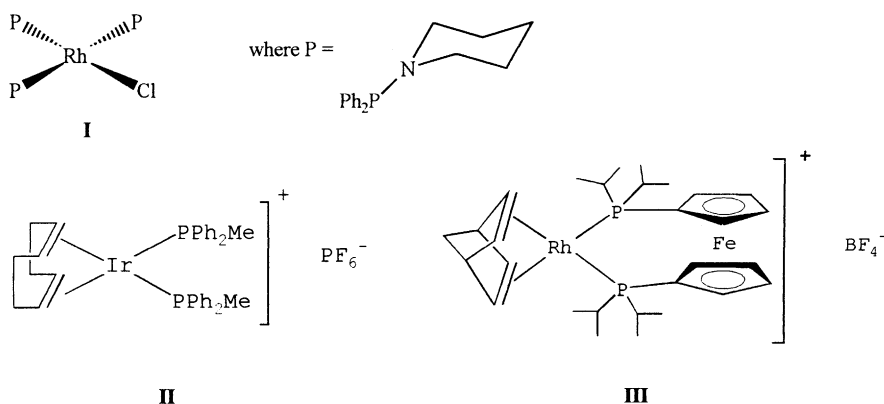
Scheme 1. Homogeneous catalysts used in the study.

would result in a decrease in catalyst deactivation by this process and hence bring an improvement in rates and yields.

In the present study, a comparison is made of the activities of three homogeneous hydrogenation catalysts, $[RhCl\{Ph_2P(NC_5H_{10})\}_3]$ (**I**), $[Ir(C_8H_{12})(PPh_2Me)_2]PF_6$ (**II**) and $[Rh(C_7H_8)\{(Pr_2P)_2Fc\}]BF_4$ (**III**), (see Scheme 1) incorporated into the cavities of Nafion with their homogeneous equivalents, with respect to three different types of substrate, cyclohexene, dimethylmaleate and 4-nitrotoluene.

2. Experimental

Unless otherwise stated, all syntheses were carried out under a dry, oxygen-free, nitrogen or argon atmosphere, using standard vacuum line and Schlenk techniques. Solvents used in syntheses were dried using the appropriate drying agent [18]. Hydrocarbons and ethers were distilled from sodium wire, dichloromethane and acetonitrile were distilled from calcium hydride and methanol was dried with activated, Linde type 4A molecular sieve. Methanol and deionised water were deoxygenated by bubbling through nitrogen gas prior to use. The remaining solvents were deoxygenated by three freeze-pump-thaw cycles and stored in sealed solvent pots under nitrogen in the dark.

2.1. High pressure testing

All catalytic testing was performed using a stainless steel reaction vessel capable of withstanding 750 atm.

The vessel has a capacity of $150 \, cm^3$ and is fitted with a thermocouple and pressure transducer. Provision was made for continuous stirring and there were connections, via 1/8 in. stainless steel tubing, to a manifold for the introduction and removal of gases. Reaction solutions were contained in a glass liner. The whole autoclave was electrically heated by a concentric band heating element. Products were determined using a HP 5890 Series II gas chromatograph, fitted with a SE30 capillary column, integrator and a flame ionisation detector. Product peaks were identified using a HP 5890 Series II GC coupled to a VG Analytical Trio 1000 mass spectrometer, and by comparing GC retention times with those for authentic samples.

2.2. Catalyst testing

The general method used is illustrated as follows. $[RhCl(PPh_2Py)_3]$ (0.01 g) was allowed to absorb into Nafion (1.0 g) in methanol in the presence of a 5 molar excess of ligand (0.014 g). The Nafion was added to hex-1-ene ($2 \, cm^3$) in cyclohexane ($30 \, cm^3$), transferred to the autoclave, pressurised to 50 bar H_2, then heated to 80 °C. Product solutions were then analysed as described above. After 8 h only a trace of hexane was detected.

Tolman and Faller [14] demonstrate that rates of hydrogenation of hex-1-ene for 'Wilkinson' type catalysts, i.e. $RhClL_3$, where $L = a$ mono-dentate phosphine, can vary by up to a factor of 5000. The most active catalyst identified from their review corresponded to $L = Ph_2P(NC_5H_{10})$. However, this

was a misquotation from the original paper by Sajus [15] who reported results for the ligand L = PhP(NC$_5$H$_{10}$)$_2$, and it is the complex of the former ligand which was tested in this work. This complex, [RhCl{Ph$_2$P(NC$_5$H$_{10}$)}$_3$] (**I**), together with two other catalysts of reported high activity, namely [Ir(C$_8$H$_{12}$)(PPh$_2$Me)$_2$]PF$_6$ (**II**) [16] and [Rh(C$_7$H$_8$){(Pr$_2$P)$_2$Fc}]BF$_4$ (**III**) [17], were synthesised following literature procedures (see Scheme 1 for structures of complexes used).

Three substrates were chosen for a comparative study of hydrogenation. Cyclohexene was purified of peroxides following a procedure described by Armarego and Perrin [18], distilled, dried and degassed. Dimethylmaleate was degassed using three freeze-thaw pump cycles, prior to use, 4-nitrotoluene (solid) was used as received.

The general experimental procedure involved the absorption of an accurately weighed amount of each catalyst, approximately 10^{-5} mole, into Nafion-H (1 g) in degassed methanol (10 cm^3). Stirring was continued until the solution colour faded completely and the beads assumed the colour of the original complex. In the case of catalyst **I** (see Scheme 1), unusually, this process did not go to completion. Therefore, yields quoted for reactions involving this catalyst represent minimum values and are based on the assumption that all the metal complex was absorbed by the Nafion. Leaching is a problem with complex **I** for the same reasons that absorption is incomplete. Measurements of leaching by atomic absorption spectrophotometry indicated a 10% loss of catalyst (**I**) during this reaction.

3. Results

A general overview of the results obtained is presented in the Table 1. Yields are quoted in moles of substrate hydrogenated per mole of catalyst used. Rates are in moles of substrate hydrogenated per mole of catalyst used per hour for the full duration of the reaction. Percentage substrate conversion was calculated from GC peak integrals as follows:

where 'FID factor' is the ratio of responses of the flame ionisation detector to starting material and product, based on weighed standards.

The reaction conditions used were not necessarily optimised for each system but were chosen for comparative purposes. For the same purposes, it was found that a sample of Wilkinson's catalyst run under the same standardised conditions, in the absence of Nafion, hydrogenated 1400 mole of cyclohexene per mole of catalyst.

Non-coordinating solvents, especially CH$_2$Cl$_2$, improve the yields of hydrogenation products using [Ir(C$_8$H$_{12}$)(PPh$_2$Me)$_2$]PF$_6$ (**II**) [16]. Consequently, the reaction of complex **II** in Nafion (see Table 1) was repeated with dimethyl maleate in CH$_2$Cl$_2$, and gave a yield of 18,000 mole per mole of catalyst. A yield of 8200 mole/mole catalyst was also obtained for a single run of (**II** + Nafion) with 3 g maleic acid, which was completely converted to the ester 2,3-dimethylbutanedioate in methanol. Also, Nafion was converted to the sodium form and used to absorb catalyst **II**. The beads were used in a run with nitrotoluene in methanol to give 17.8% of the hydrogenated product with a maximum rate of 180 mole/mole h compared with values of 98% and 1600 mole/h mole catalyst for the hydrogen form.

In addition to the high pressure reactions recorded in the Table 1, the catalyst [RhCl{PhP(NC$_5$H$_{10}$)$_2$}$_3$], an analogue of **I** (see Scheme 1), was also used for the hydrogenation of cyclohexene under the same conditions used for all reactions recorded in the Table 1. For both the homogeneous and supported cases a yield of only 16 mole product/mole catalyst was obtained. Furthermore, nearly 90% of the catalyst leached from the Nafion.

Under the conditions used, cyclohexene was hydrogenated to cyclohexane as expected and dimethyl maleate was hydrogenated to the dimethylbutanedioate. Further reduction to the alcohol was not detected. 4-Nitrotoluene was hydrogenated completely in methanol to p-toluidine with great facility in most cases, and hence for these reactions, it is more appropriate to compare rates of reaction. A blank run using Nafion-H and 4-nitrotoluene dissolved in methanol

$$\text{conversion (\%)} = \frac{\text{area of product peak}}{(\text{area of product peak} \times \text{FID factor}) + (\text{area of starting material})} \times 100\%$$

Table 1

Results of high pressure reactions (see Scheme 1 for catalyst identity)[a]

Catalyst	Cyclohexene	Dimethylmaleate	4- Nitrotoluene[b]
	Yield (mole/mole cat.)	Yield (mole/mole cat.)	Rate (mole/h mole cat.) (% converted)
I	100	790	3900 (89)
I + Nafion	260	520	3700 (100)
II	270	670	60 (7)
II + Nafion	800	4400	1600 (98)
III	43	530	5800 (99)
III + Nafion	68	220	4500 (100)

[a] Conditions: each complex (10^{-5} mole) was stirred separately with Nafion (1.0 g) in degassed methanol (10 cm^3) until the solution colour faded completely (or for **I** the colour intensity minimised); each sample of prepared Nafion was then mixed with the substrate in methanol (30 cm^3), subjected to 40 bar H_2 and stirred at 80 °C for 5 h. For comparison, Wilkinson's catalyst in the absence of Nafion, reduced 1400 mole/mole cat. of cyclohexene under comparable conditions.

[b] 4-Nitrotoluene was hydrogenated completely and with great facility in most cases, hence the rates are compared.

remained unchanged after 2 h under the standard reaction conditions.

A study was made of complex **II** in Nafion as a catalyst for hydrogenation under ambient pressure and temperature conditions. Cyclohexene (0.82 g) was dissolved in 20 cm^3 CH_2Cl_2 (0.5 M) in a 100 ml Schlenk tube under nitrogen, connected to a double Schlenk line. The tube was cooled in an ice-bath to 0 °C. A 250 ml round bottomed flask was charged with complex **II** (0.017 g, 0.02 mmole), filled with nitrogen and cooled in the same ice-bath. The cyclohexene solution was cannula transferred by nitrogen pressure to the flask containing the catalyst forming a red solution. The nitrogen supply to the line was disconnected and a H_2 supply connected in its place. The lines were flushed with hydrogen. A 2 l round bottomed flask was evacuated and filled with hydrogen and connected to the reaction flask to act as a reservoir. The reaction flask was carefully evacuated and refilled with hydrogen three times leading to a complete loss of colour of the solution. The stirrer was started and the time noted as time $t = 0$. Samples (0.1 cm^3) were removed at 10 min intervals for analysis by gas chromatography. The maximum rate obtained under these conditions was 1134 mole/mole h.

The procedure described above was then repeated with Nafion beads (1 g) containing complex **II** (0.0113 g), introduced in methanol which was then removed under vacuum. The beads initially had a bright red colour in common with the homogeneous solution. On addition of hydrogen, the beads lost

this colour after only 5 s. On using these beads in an identical reaction to that described above, only a trace of hydrogenation product was formed, and the beads became pale yellow, the colour associated with deactivated catalyst. Several more unsuccessful attempts were made with slight variations in conditions, e.g. using a longer induction period before addition of hydrogen, or using mixtures of methanol and CH_2Cl_2, etc. but in each case the catalyst was quickly deactivated.

4. Discussion

Introduction of the complexes into Nafion was achieved following the procedures described above. The two ionic complexes were readily absorbed from solutions of methanol as expected. Trials were always conducted using freshly prepared samples since overnight storage of beads containing [Ir(COD)(PPh$_2$Me)$_2$]PF$_6$ (catalyst **II**) led to a loss of the initial bright red colour which was indicative of loss of activity. The complexes with aminophosphine ligands, [RhCl{Ph$_2$PNC$_5$H$_{10}$}$_3$] (catalyst **I**), and its analogue [RhCl{PhP(NC$_5$H$_{10}$)$_2$}$_3$], were only slowly absorbed. The P–N bond gives the nitrogen some sp^2 character and as a result it is not strongly protonated [19,20].

The failure of Nafion supported [Ir(COD)(PPh$_2$ Me)$_2$]PF$_6$ (complex **II**) to work in the experiments conducted at low temperature and pressure is readily

explained. In the homogeneous catalytic reaction, when the alkene substrate drops to a low concentration, the catalyst is deactivated due to the formation of the catalytically inactive hydride bridged dimer $[Ir_2H_5(PPh_2Me)_4]PF_6$ [16]. This is also considered to occur when the complex is in Nafion and the reaction conditions are not forcing. The rapid decolouration of the beads on exposure to hydrogen gas indicates that hydrogen is capable of rapidly dissolving into solution and diffusing into the Nafion beads. However, it seems that as the cyclohexene substrate in the beads becomes rapidly depleted by hydrogenation, the rate of diffusion of the alkene back into the beads is much slower than that of hydrogen gas. A consequence of this mass flow restriction is the failure of the iridium centre to maintain a full coordination sphere appropriate for catalysis, and deactivates by forming the bridging hydride mentioned above. It is intriguing that this process does not occur during high pressure reactions. It is possible that at the higher temperatures, the formation of the hydride bridged dimer is disfavoured, or more likely, the dimer is returned by reaction with the alkene to the catalytic cycle for kinetic reasons. In fact, it can be seen from the Table 1 that with all three substrates, supporting complex **II** in Nafion has a very beneficial influence on the complex as an active catalyst. Given the fact that complex **II** achieves its highest rates in non-coordinating solvents such as CH_2Cl_2, the beneficial influence of Nafion could be due to the fact that methanol present in the Nafion cavities is likely to be protonated and therefore also be non-coordinating. To test this hypothesis, a single run was performed in which sodium Nafion was used. The maximum rate achieved was 180 mole/mole h, better than the homogeneous figures but still far short of the value obtained for Nafion-H.

The performance of complex **I** is mixed, and gives results which depend on the substrate used. Supporting the complex in Nafion has only a small influence on the yields and rates of catalytic reactions, with no obvious trends. The poor comparative performance of complex **III** for hydrogenating cyclohexene is not readily explained. The figures were replicated using three batches of catalyst. The same complex hydrogenated dimethylmaleate and 4-nitrotoluene much more effectively, and was particularly active with the latter substrate.

It is generally assumed that supporting a catalyst in a polymer may or may not improve the final yields obtained from a reaction, but that it will certainly have a detrimental effect on rates due to diffusion limitations. It can be seen from the results obtained for 4-nitrotoluene that rates are only slightly reduced by supporting catalysts in Nafion.

It is interesting to explore the differences between the ligands ($Ph_2P\{NC_5H_{10}\}$) and ($PhP\{NC_5H_{10}\}_2$), i.e. replacing one phenyl group with a piperidyl group. Three attempts were made to synthesise the catalyst reported by Sajus [15] as $[RhCl(PhP\{NC_5H_{10}\}_2)_3]$. The first synthesis used $[Rh(COD)Cl]_2$ as starting material. The second and third syntheses used $[Rh(C_2H_4)_2Cl]_2$ with equimolar, and 10 M excess of ligand, respectively. In all cases the same product was formed which displayed only a single phosphorus NMR environment (δ = 27.12 (s) ppm) and metal-chlorine stretching frequencies in the infra-red spectrum characteristic of a bridged dimer (ν(Rh–Cl–Rh) 273 cm^{-1}, 261 cm^{-1}). Also, catalytic reactions were performed using $[Rh(C_2H_4)_2Cl]_2$ and di-*N*-piperidylphenylphosphine (i) in stoichiometric amounts, and (ii) with a 5 molar phosphine excess, in order to form the active species in situ but comparatively low yields of hydrogenation products were always the result. This feature may be explained as arising from electronic features of the ligand. The nitrogen atoms attached to the phosphorus will reduce the electron density on the phosphorus atom making it a poorer nucleophile, less likely to break the chlorine bridge present in $[Rh(C_2H_4)_2Cl]_2$ and form $[RhL_3Cl]$ complexes. Also, it is likely that the very bulky nature of the ligand makes nucleophilic attack more difficult. Interestingly, a similar complex, formed from PCy_3 ligands, exists in solution as an equilibrium mixture of $[RhCl(PCy_3)_2]$ and its dimer $[Rh(PCy_3)_2Cl]_2$, but the equilibrium lies towards the three coordinate monomer, $[RhCl(PCy_3)_2]$, which can be isolated [21]. Further, this complex forms stable adducts, even with atmospheric gases [22], but as a hydrogenation catalyst is relatively poor, reducing cyclohexene at a rate 40 times slower than Wilkinson's catalyst [23]. Thus, steric factors may contribute to the limited effectiveness of the aminophosphine as a suitable ligand for the rhodium hydrogenation catalysts.

5. Conclusions

It has been demonstrated that the complexes $[RhCl\{Ph_2P(NC_5H_{10})\}_3]$, $[Ir(C_8H_{12})(PPh_2Me)_2]PF_6$ and $[Rh(C_7H_8)\{(Pr_2P)_2Fc\}]BF_4$, active for homogeneous catalysed hydrogenation of cyclohexene, dimethylmaleate and 4-nitrotoluene, retain their activity when supported in Nafion. Yields obtained for supported catalysts are comparable or better than yields obtained by the standard homogeneous process, and rates of reaction are not reduced to the extent reported in other studies. The effectiveness of supported catalysts is primarily attributed to the use of low catalyst loadings in Nafion.

References

[1] M. Capka, J. Hetflejs, Coll. Czech Chem. Commun. 39 (1974) 154.
[2] R.H. Grubbs, L.C. Kroll, E.M. Sweet, J. Macromol. Sci. Chem. A 7 (5) (1973) 1047.
[3] G. Strukul, M. Bonivento, M. Graziani, Inorg. Chim. Acta 12 (1975) 15.
[4] D.E. Bergbreiter, R. Chandran, J. Am. Chem. Soc. 109 (1987) 174.
[5] K.G. Allum, R.D. Hancock, I.V. Howell, R.C. Pitkethly, P.J. Robinson, J. Organomet. Chem. 87 (1975) 189.
[6] C.U. Pittman, P.L. Grube, O.E. Ayers, S.P. McManus, M.D. Rausch, G.A. Moser, J. Polym. Sci.: Polym. Chem. Ed. 10 (1972) 379.
[7] T.D. Gierke, G.E. Munn, F.C. Wilson, J. Polym. Sci.: Polym. Phys. Ed. 19 (1981) 1686.
[8] W. Hsu, T. Gierke, Macromolecules 15 (1982) 101.
[9] I. Toth, B. Hanson, M. Davis, J. Organomet. Chem. 397 (1990) 109.
[10] A. Seen, K. Cavell, A. Hodges, A. Mau, J. Chem. Soc., Dalton Trans. (1992) 1381.
[11] A. Seen, K. Cavell, A. Hodges, A. Mau, J. Mol. Catal. 90 (1994) 245.
[12] A. Seen, K. Cavell, A. Hodges, A. Mau, J. Mol. Catal. 94 (1994) 163.
[13] A. Seen, A.T. Townsend, J.C. Bellis, K. Cavell, J. Mol. Catal. 149 (1999) 233.
[14] C. Tolman, J. Faller, Homogeneous Catalysis with Metal Phosphine Complexes, Pignolet.
[15] L. Sajus, Rev. Inst. Franc. Petrole (1969) 1477.
[16] R. Crabtree, Acc. Chem. Res. 12 (1979) 331.
[17] M.J. Burk, T.G.P. Harper, J.R. Lee, C. Kallberg, Tetrahedron Lett. 35 (28) (1994) 4963.
[18] W.L.F. Armerego, W. Perrin, Purification of Laboratory Chemicals, 4th Edition, Wiley, New York, 1997.
[19] C. Romming, J. Songstad, Acta Chem. Scand. A 32 (1978) 689.
[20] N.W. Mitzel, B.A. Smart, K.-H. Dreihäuptel, D.W.H. Rankin, H. Schmidbaur, J. Am. Chem. Soc. 118 (1996) 12673.
[21] H.L.M. van Gaal, F.G. Moers, J.J. Steggerda, J. Organomet. Chem. 65 (1974) C43.
[22] H.L.M. van Gaal, F.L.A. van den Bekerom, J. Organomet. Chem. 134 (1977) 237.
[23] J.A. Osborn, F.H. Jardine, J.F. Young, G. Wilkinson, J. Chem. Soc. A (1966) 1711.