Synthesis and Catalytic Activity of (η^6-*p*-Cymene)(phosphane)ruthenium(II) Complexes Supported on Poly(biphenoxyphosphazene) or Chiral Poly(binaphthoxyphosphazene) Copolymers

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The polyphosphazene random copolymer containing diphenylphosphane ligands $\{[NP(OC_6H_4PPh_2)_2]_{0.4}[NP(O_2C_{12}H_8)]_{0.6}\}_n$ (**1a**) ($O_2C_{12}H_8$ = 2,2′-dioxy-1,1′-biphenyl), and the chiral binaphthoxy analogues $\{[NP(OC_6H_4PPh_2)_2]_{0.1}[NP(O_2C_{20}H_{12})]_{0.9}\}_n$ [$O_2C_{20}H_{12}$ = (*R*)-2,2′-dioxy-1,1′-binaphthyl] (**1b**) and $\{[NP(OC_6H_4PPh_2)_2]_{0.2}[NP(O_2C_{20}H_{10}Br_2)]_{0.8}\}_n$ [$O_2C_{20}H_{10}Br_2$ = (*R*)-2,2′-dioxy-6,6′-dibromo-1,1′-binaphthyl] (**1c**), reacted in dichloromethane at room temperature with appropriate amounts of the dimeric complex $[Ru(\eta^6\text{-}p\text{-cymene})Cl(\mu\text{-}Cl)]_2$ to give the corresponding polymeric (phosphane)Ru^{II} complexes $\{[NP(OC_6H_4PPh_2[RuCl_2(\eta^6\text{-}p\text{-cymene})]_x)_2]_{0.4}[NP(O_2C_{12}H_8)]_{0.6}\}_n$ [*x* = 0.5 (**2a**), 1 (**2b**)], $\{[NP(OC_6H_4PPh_2[RuCl_2(\eta^6\text{-}p\text{-cymene})])_2]_{0.1}[NP(O_2C_{20}H_{12})]_{0.9}\}_n$ (**3**) and $\{[NP(OC_6H_4PPh_2[RuCl_2(\eta^6\text{-}p\text{-cymene})])_2]_{0.2}[NP(O_2C_{20}H_{10}Br_2)]_{0.8}\}_n$ (**4**). The isolated products are soluble reddish solids, and are thermally very stable with very high glass transition temperatures. The reaction of **1b** or **1c** with the cationic precursor $[RuCl(PPh_3)_2(\eta^6\text{-}p\text{-cymene})][PF_6]$ in refluxing THF gave the crosslinked insoluble cationic polymeric complexes $\{[NP(OC_6H_4PPh_2)_2]_{0.1}[NP(O_2C_{20}H_{12})]_{0.9}[RuCl(\eta^6\text{-}p\text{-cymene})(PF_6)]_{0.05}\}_n$ (**5**) and $\{[NP(OC_6H_4PPh_2)_2]_{0.2}[NP(O_2C_{20}H_{10}Br_2)]_{0.8}[RuCl(\eta^6\text{-}p\text{-cymene})(PF_6)]_{0.08}\}_n$ (**6**). All the complexes were active catalysts in transfer hydrogenation of acetophenone by propan-2-ol, but the C_2-pockets containing the catalytic centers gave no enantioselectivity because of the conformational behavior of the chiral derivatives.

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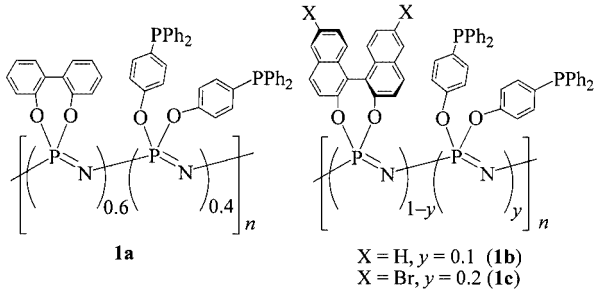
Introduction

Although many linear polyphosphazenes[1−5] $(N{=}PR_2)_n$, carrying ligands as lateral groups, can be used to form transition metal complexes,[6−12] the resulting materials have not been extensively characterized as polymer-supported catalysts.[13] Recently, according to the synthesis of the homopolymers $[NP(O_2C_{12}H_8)]_n$ ($O_2C_{12}H_8$ = 2,2′-dioxy-1,1′-biphenyl)[14] and the chiral analogue $[NP(O_2C_{20}H_{12})]_n$ [$O_2C_{20}H_{12}$ = (*R*)-2,2′-dioxy-1,1′-binaphthyl],[15] we reported the preparation of phosphazene random copolymers bearing diphenylphosphane groups (Scheme 1) $\{[NP(OC_6H_4PPh_2)_2]_x[NP(O_2C_{12}H_8)]_{1-x}\}_n$ (*x* = 0.4; **1a**),[16] $\{[NP(OC_6H_4\text{-}PPh_2)_2]_{0.1}[NP(O_2C_{20}H_{12})]_{0.9}\}_n$ [$O_2C_{20}H_{12}$ = (*R*)-2,2′-dioxy-1,1′-binaphthyl] (**1b**),[17] and $\{[NP(OC_6H_4\text{-}PPh_2)_2]_{0.2}[NP(O_2C_{20}H_{10}Br_2)]_{0.8}\}_n$ (**1c**) [$O_2C_{20}H_{10}Br_2$ = (*R*)-2,2′-dioxy-6,6′-dibromo-1,1′-binaphthyl].[17] The latter chiral polymers **1b**, **1c** were considered of potential interest in catalysis because they have the phosphane ligands located in the space (chiral pocket) defined by two consecutive



Scheme 1. Polyphosphazenes **1a**, **1b**, **1c**

$[NP(O_2C_{20}H_{10}X_2)]_n$ (X = H, Br) units,[18] and the very high glass transition temperatures of the polymers indicate their stereochemical rigidity.

(Arene)ruthenium(II) complexes have been widely used in homogeneous catalysis and have proven to be efficient precatalysts in a wide number of organic transformations of academic and industrial interest.[19] In particular, they have shown outstanding performance in catalytic transfer hydrogenations.[20] In order to explore the actual potential of the polyphosphazenes as supporting polymers, we considered the synthesis of well-defined complexes containing (arene)-ruthenium(II) fragments. It is well known that the development of cleaner and low-cost catalytic processes requires

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the immobilization of catalysts through coordination to functionalized polymers, and this immobilization has been revealed as one of the most reliable methodologies.[21]

Herein, we describe the synthesis and characterization of novel neutral or cationic polymeric (η^6-*p*-cymene)ruthenium(II) complexes supported by diphenylphosphane ligands in the achiral polyphosphazene **1a** and in the chiral polyphosphazenes **1b** and **1c**. They have proven to be active and recyclable catalysts in transfer hydrogenation of acetophenone by propan-2-ol although no enantiomeric excesses were observed when using the chiral derivatives. The stereochemical factors, which may determine this lack of selectivity by the chiral binaphthoxy derivatives, are also discussed.

Results and Discussion

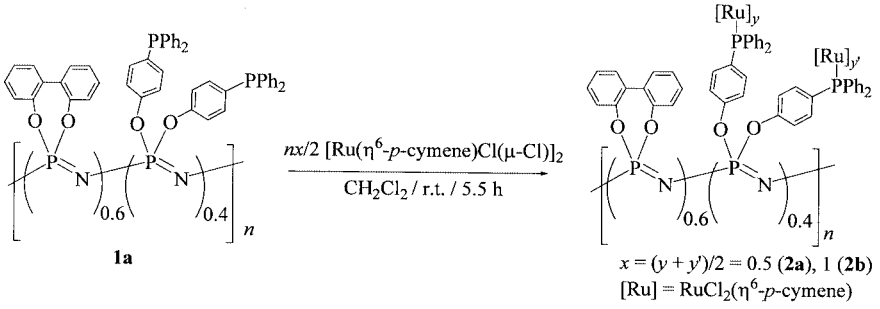
Synthesis and Characterization of (Arene)(Linear and crosslinked polymeric phosphazene−phosphane)Ru^{II} Complexes

The reaction of the polyphosphazene−phosphane $\{[NP(OC_6H_4PPh_2)_2]_{0.4}[NP(O_2C_{12}H_8)]_{0.6}\}_n$ (**1a**) with $0.4x$ equiv. (x = 0.5, 1) of [Ru(η^6-*p*-cymene)Cl(μ-Cl)]$_2$ per polymeric unit in dichloromethane at room temperature gave the well-defined polymeric (phosphane)ruthenium(II) complexes $\{[NP(OC_6H_4PPh_2[RuCl_2(\eta^6\text{-}p\text{-cymene})]_x)_2]_{0.4}[NP(O_2C_{12}H_8)]_{0.6}\}_n$ [x = 0.5 (**2a**), 1 (**2b**)] (83 and 92% yield, respectively) (Scheme 2). The reaction was monitored by the decrease in intensity of the $^{31}P\{^1H\}$ singlet resonance due to the PPh_2 groups in **1a** ($\delta \approx -6$ ppm) and the appearance of a new singlet at δ = 23.7 ppm, arising from the coordinated PPh_2 groups in **2a**, **2b**. The final relative intensities of the phosphorus resonances were in agreement with the expected value for each polymer. Thus, all the diphenylphosphanyl groups available in complex **2b** were coordinated to ruthenium centers, while in **2a** 50% of the ligands remained free.

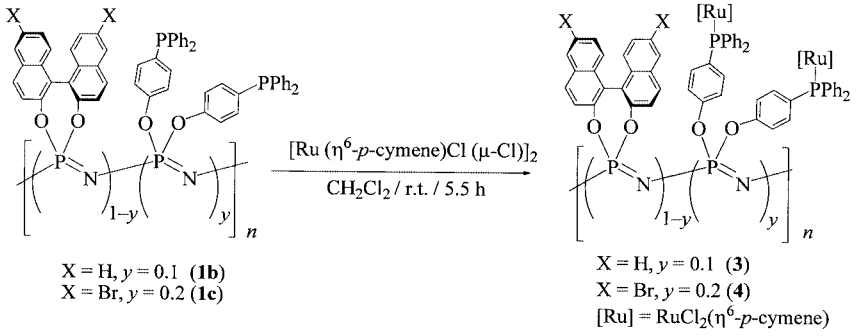
According to a similar procedure (Scheme 3), the ruthenium(II) polymeric complexes $\{[NP(OC_6H_4PPh_2[RuCl_2(\eta^6\text{-}p\text{-cymene})])_2]_{0.1}[NP(O_2C_{20}H_{12})]_{0.9}\}_n$ (**3**) and $\{[NP(OC_6H_4PPh_2[RuCl_2(\eta^6\text{-}p\text{-cymene})])_2]_{0.2}[NP(O_2C_{20}H_{10}Br_2)]_{0.8}\}_n$ (**4**) were obtained (90 and 88% yield) by treating the chiral polyphosphazenes **1b** and **1c** with 0.1 and 0.2 equiv., respectively, of [Ru(η^6-*p*-cymene)Cl(μ-Cl)]$_2$ per polymeric unit. The high ratio of binaphthoxy/diphenylphosphanyl groups of the polymers **1b**, **1c** ensured the location of the ruthenium fragments within the potentially chiral pocket formed by two consecutive binaphthoxy units.

Complexes **2a**, **2b, 3** and **4** were isolated as red, air-stable solids, which are soluble in dichloromethane but insoluble in hexane or propan-2-ol. Analytical and spectroscopic data (IR and ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR) supported the proposed formulations (see Exp. Sect. for details). As expected, the NMR signals of the polymers were broad to very broad and several of the weaker peaks could not be observed clearly.

The presence of the organometallic moiety [Ru(η^6-*p*-cymene)] was shown in the ^1H and $^{13}C\{^1H\}$ NMR spectra by the expected resonances for the nuclei of the aromatic ring, as well as for the methyl and isopropyl substituents. $^{31}P\{^1H\}$ NMR spectra contain resonances at $\delta \approx 23$ ppm corresponding to the coordinated diphenylphosphanyl groups, which compare well with those of the analogous



Scheme 2



Scheme 3

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complex $[RuCl_2(PPh_3)(\eta^6\text{-}p\text{-cymene})]$ (δ = 23.1 ppm). In the case of **2a**, a signal corresponding to the uncoordinated PPh_2 groups (δ = −6.2 ppm) was also observed. The spectra also showed two broad signals corresponding to the distribution of chemical shifts of the two different phosphazene repeating units present in the polymeric chains, one at $\delta \approx -5$ ppm $[NP(O_2C_{12}H_8)]$ or $\delta = -3$ ppm $\{[NP(O_2C_{20}H_{12})]$ or $[NP(O_2C_{20}H_{10}Br_2)]\}$, and another at $\delta \approx -23$ ppm $[NP(OC_6H_4PPh_2)_2]$. In all cases, the relative intensities were in agreement with the chemical formulae proposed.

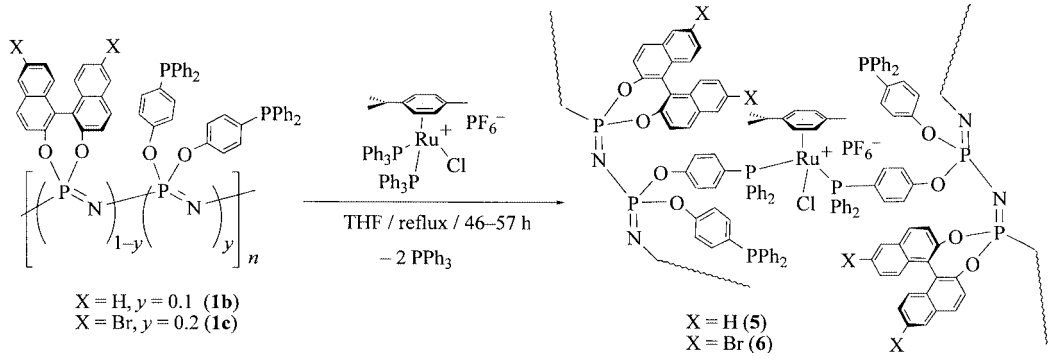
The DSC curves of the polymeric complexes **2a** and **2b** showed a well-defined glass transition. The measured T_g values (149 and 189 °C) were, as expected,[22] higher than that of the starting polymer **1a** (95 °C) and increased with increasing metal content. The glass transition could not be detected for the chiral binaphthoxy derivatives **4** and **5**, but they should be higher than those of the corresponding polymers **1b** (268 °C) and **1c** (256 °C). These values, and the very broad NMR spectra observed at room temperature, are clear indicators of the high stereochemical rigidity of the polymeric chains, a factor that should favor the stereochemical selectivity of the chiral sites in asymmetric processes.[23]

In order to investigate whether the inclusion of the Ru^{II} active centers inside a solid chiral matrix would result in the expected[24] enhanced enantiomeric induction, the crosslinked polymeric complexes $\{[NP(OC_6H_4PPh_2)_2]_{0.1}[NP(O_2C_{20}H_{12})]_{0.9}[RuCl(\eta^6\text{-}p\text{-cymene})(PF_6)]_{0.05}\}_n$ (**5**) and $\{[NP(OC_6H_4PPh_2)_2]_{0.2}[NP(O_2C_{20}H_{10}Br_2)]_{0.8}[RuCl(\eta^6\text{-}p\text{-cymene})(PF_6)]_{0.08}\}_n$ (**6**) were synthesized (Scheme 4) by treating the ligands $\{[NP(OC_6H_4PPh_2)_2]_{0.1}[NP(O_2C_{20}H_{12})]_{0.9}\}_n$ (**1b**) and $\{[NP(OC_6H_4PPh_2)_2]_{0.2}[NP(O_2C_{20}H_{10}Br_2)]_{0.8}\}_n$ (**1c**) with the appropriate amount of the cationic precursor $[RuCl(PPh_3)_2(\eta^6\text{-}p\text{-cymene})][PF_6]$ in refluxing THF. The displacement of the PPh_3 ligands in the cationic complex by the PPh_2 groups attached to the polymer was favored by the insolubility of the final products. Therefore, this substitution method is very convenient for the preparation of crosslinked polymeric complexes with controlled composition, as has been already observed in other cases with phosphazenes carrying pyridine ligands.[25]

Materials **5** and **6**, isolated (95 and 94 yield%) as air-stable, slightly red and green solids, respectively, were insoluble in common organic solvents. Microanalysis (including Ru and P) and spectroscopic data (IR and ^{31}P NMR) support the proposed formulation. Their ^{31}P NMR spectra in the solid state show broad signals at δ = 24.4, 23.2 (**5**) and 24 (**6**) ppm corresponding to the coordinated diphenylphosphanyl groups, and a very broad resonance at δ = −8.5 (**5**) and −9.3 (**6**) ppm for the phosphorus atoms of the polymeric chain. The composition and structure were also confirmed by the IR spectra that showed the absorptions (i) at $\tilde{\nu}$ = 2965 (m) and 2855 (w) cm^{-1} due to the *p*-cymene fragment, (ii) at $\tilde{\nu}$ = 838 cm^{-1} from the PF_6^- anion, and (iii) in the $\tilde{\nu}$ = 1200−1300 cm^{-1} region for the stretching ν(PN) modes of the phosphazene chain.

Catalytic Activity in the Transfer Hydrogenation of Ketones

In order to test the catalytic activity and enantioselectivity of the Ru^{II} complexes supported on the chiral phosphazenes, the transfer hydrogenation of acetophenone by propan-2-ol was investigated, in the presence of catalytic amounts of **2a**, **2b**, **3**, **4**, **5** and **6** (Scheme 5). For comparative purposes, the efficiencies of the analogous homogeneous ruthenium(II) catalysts, $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PPh_3)]$ and $[RuCl(\eta^6\text{-}p\text{-cymene})(PPh_3)_2][PF_6]$, were also observed under the same reaction conditions. In a typical experiment, NaOH was added to either a suspension of the supported ruthenium catalyst precursor (**2a**, **2b**, **3**−**6**) or a solution of the respective mononuclear complex and acetophenone (0.25 M) in propan-2-ol (ketone/Ru/base = 500:1:24) at reflux. The reactions were monitored by gas chromatography. Table 1 shows the catalytic performances. Supported ruthenium(II) complexes **2a**, **2b, 3** and **4** afforded high conversions after ca. 24 h (TON = 450−475; Table 1, Entries 3−6). It is interesting to note that a fast initial rate is observed in the reduction of acetophenone by complex **4**, giving a yield of 53% after 1 h (TOF = 265 h^{-1}). As expected, complexes $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PPh_3)]$ and $[RuCl(\eta^6\text{-}p\text{-cymene})(PPh_3)_2][PF_6]$ were active under homogeneous conditions, showing comparable efficiencies (TON = 475 and 480, respectively) to those of the supported catalysts, but with higher rates (4.5 h) (Table 1, En-



Scheme 4

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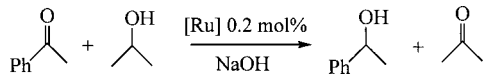
tries 1 and 2). The crosslinked supported complexes **5**−**6** were also active catalysts although they were less efficient than their linear analogues **3** and **4** (Table 1, Entries 7 and 8).



Scheme 5

Table 1. Transfer hydrogenation of acetophenone

Entry[a]	Catalyst	Yield [%][b]	Time [h]	TON[c]
1	$[RuCl_2(PPh_3)(p\text{-cymene})]$	95	4.5	475
2	$[RuCl(PPh_3)_2(p\text{-cymene})][PF_6]$	96	4.5	480
3	**2a**	90	24	450
4	**2b**	92	24	460
5	**3**	92	24	460
6	**4**	95	24	475
7	**5**	70	24	350
8	**6**	65	24	325

[a] Conditions: reactions were carried out at 82 °C using 5 mmol of acetophenone (0.25 M in propan-2-ol); ketone/Ru/NaOH = 500:1:24. [b] Yield in 1-phenylethanol, determined by GC. [c] Turnover number, TON = mol of 1-phenylethanol/mol of Ru.

In order to take advantage of the insolubility of the immobilized catalysts in propan-2-ol, the catalytic activity of the supported ruthenium(II) complexes was examined by successive runs after recycling by simple decantation (see Exp. Sect. for details). Catalysts **2b**, **3**−**6** were active in the second run (40−60% yields) but with a notable reduction in efficiency (Table 2). In contrast, catalyst **2a** showed only a slight loss of activity after six successive runs (Figure 1) with a cumulative turnover number of 2430.

Table 2. Transfer hydrogenation of acetophenone; second run for complexes **2b**, **3**−**6**

Entry[a]	Catalyst	Yield [%][b]	Time [h]	Cumulative TON[c]
1	**2b**	57	24	745
2	**3**	60	24	760
3	**4**	47	24	710
4	**5**	54	24	620
5	**6**	40	24	525

[a] Conditions: reactions were carried out at 82 °C using 5 mmol of acetophenone (0.25 M in propan-2-ol); ketone/Ru/NaOH = 500:1:24. [b] Yield in 1-phenylethanol, determined by GC. [c] Turnover number calculated over the two runs.

Although we made no attempt to characterize the recycled catalysts, it is apparent that the active catalytic species show a moderate to good stability after the first run has been completed. As is well established from a variety of mechanistic studies, transient ruthenium(II) hydride derivatives are the active species in this type of transfer hydrogenation.[26] These species are formed during the first catalytic

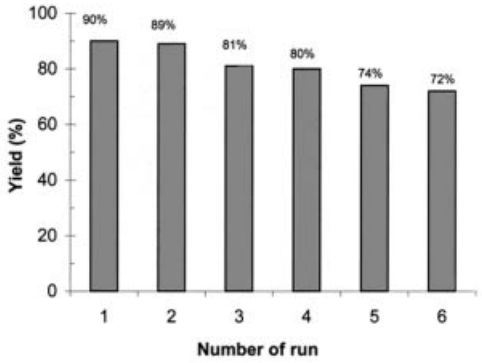


Figure 1. Transfer hydrogenation of acetophenone by **2a**; conditions: reaction carried out at 82 °C using 5 mmol of acetophenone (0.25 M in propan-2-ol); ketone/Ru/NaOH = 500:1:24; yield of 1-phenylethanol after 24 h determined by GC; global TON for six uses = 2430

cycle in which the supported pre-catalyst undergoes a chloride/isopropoxide ligand exchange followed by β-elimination. Although in the first run the required excess of NaOH (24 mol per mol of Ru) for the formation of the active species is used, we observed that better conversions are achieved by addition of NaOH in each run.[27]

In all cases, the leaching of ruthenium from the support during the catalytic experiments was determined by atomic absorption spectroscopy of the metal in solution, after removal of the polymer. When complex **2a** was used, the leaching never exceeded 5% of the initial quantity of ruthenium, in agreement with its recyclability. In contrast, the polymers **2b**, **3** and **4** suffered a greater loss of ruthenium during the first use (ca. 35−50%), which probably accounts for the large decrease in their catalytic activity. As expected in the case of the crosslinked polymers **5** and **6**, the ruthenium leaching is very low and their poor catalytic performances most likely reflect the low accessibility of the active center.

Unfortunately, enantiomeric excesses were observed with neither linear nor crosslinked chiral polymers. As the presence of the active centers within the chiral pockets is unquestionable, these results seem to indicate that in the overall average arrangement of the solid matrix, the local conformations of the polymer chains bearing the chiral sites are too open to induce enantioselectivity. However, another more subtle factor could be the helical secondary structure found for analogous phosphazene chains with binaphthoxy groups.[28] It is well known that the helical polymers form good enantioselective catalysts,[29] but the combination of the secondary helical structure and the centrochiralities present in the main chain may be counterproductive.[30] In this case, it might be better to use a catalyst with either one or another of these features.

Conclusions

This work shows that neutral $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]$ and cationic $[Ru(\eta^6\text{-}p\text{-cymene})Cl]^+$ fragments can be supported by chiral and achiral polyphosphazenes, giving rise to linear

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or crosslinked polymeric complexes (**2a**, **2b**, **3**−**6** in Schemes 2−4) in which the metal fragments are linked to the polymeric backbone through phosphane lateral groups.

These materials are active polymer-supported catalysts for the transfer hydrogenation of acetophenone with high conversions. Complex **2a** was also recyclable and, in contrast with its homogeneous counterparts which were active only in one run, it could be recovered without significant ruthenium leaching after various catalytic transformations (cumulative TON = 2430 after 6 runs). The activity of **2a** is similar to that of the previously described ruthenium(II) catalyst supported on commercially available R_2P-Merrifield-type polymers.[21f]

Although the active centers supported in polymers **3**−**6** are situated in the chiral pockets generated by two consecutive chiral binaphthoxyphosphazene units, no enantiomeric excess of the resulting secondary alcohol was observed. This may be due to the conformational characteristics of the polymeric chains with pockets that are too wide to induce enantioselectivity. Our observations may represent another experimental example of the combination of chiral polymeric units within a secondary helical structure being counterproductive in asymmetric induction.[30]

Experimental Section

General Comments: All reactions were carried out under nitrogen. The polymeric ligand $\{[NP(OC_6H_4PPh_2)_2]_{0.4}[NP(O_2C_{12}H_8)]_{0.6}\}_n$ (**1a**) was prepared by a method described elsewhere,[16] using $[NPCl_2]_n$ obtained by the procedure described by Magill et al.[31] The product had less than 0.14% of unchanged chlorine, a negligible fraction of oxidized phosphane sites (ca. 3.5%), and contained 0.7 units of polytetrahydrofuran (PTHF). Therefore, its actual degree of functionalization with PPh_2 groups was 1.87 mmol per gram of polymer $(FD)_P = 1.87$. As observed with the previously published analogue,[16] the GPC chromatogram was poorly defined indicating a very broad distribution with an estimated average M_w of 300000 ($M_w/M_n = 12.5$). The T_g (DSC) occurred at 95 °C ($\Delta C_p = 0.19\ Jg^{-1}K^{-1}$). In the polymers $\{[NP(OC_6H_4PPh_2)_2]_{0.1}[NP(O_2C_{20}H_{12})]_{0.9}\}_n$ [17] (**1b**) and $\{[NP(OC_6H_4PPh_2)_2]_{0.2}[NP(O_2C_{20}H_{10}Br_2)]_{0.8}\}_n$,[17] (**1c**) a fraction of the $-PPh_2$ sites had been oxidized to $-P(=O)Ph_2$ (20% and 12%, respectively) and their actual degrees of functionalization with active PPh_2 ligands (the values used to calculate the stoichiometric amounts of Ru complex below) were $(FD)_P = 0.45$ mmol/g and $(FD)_P = 0.69$ mmol/gram, respectively. The precursor complexes $[RuCl_2(PPh_3)(\eta^6\text{-}p\text{-cymene})]$[32] and $[Ru(\eta^6\text{-}p\text{-cymene})Cl(\mu\text{-}Cl)]_2$ [33] were prepared as described previously. $[RuCl(PPh_3)_2(\eta^6\text{-}p\text{-cymene})][PF_6]$ was prepared similarly to the analogous complexes described in the literature.[34] THF was treated with KOH and distilled twice from Na in the presence of benzophenone. The IR spectra were recorded with a Perkin−Elmer FT Paragon 1000 spectrometer. NMR spectra were recorded with Bruker AC-200, AC-300, DPX-300 and Avance 300 instruments, using $CDCl_3$ as solvent unless otherwise stated. ^{31}P NMR spectra of the insoluble polymers were obtained from $[D_6]$DMSO or $CDCl_3$ suspensions using a Varian Unity plus (300 MHz) instrument at the Universitat de Barcelona (Serveis Cientifico-Tècnics). ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are given in δ relative to TMS. $^{31}P\{^1H\}$ NMR chemical shifts are given in δ relative to external 85% aqueous H_3PO_4. Coupling constants are in Hz. C, H, N analyses were performed with a Perkin−Elmer 240 microanalyzer. Ru analyses were performed by Galbraith Laboratories. T_g values were measured with a Mettler DSC 300 differential scanning calorimeter in the second heating cycle unless otherwise stated. Thermal gravimetric analyses were performed with a Mettler TA 4000 instrument. The polymer samples were heated at a rate of 10 °C/min from ambient temperature to 800 °C under a constant flow of nitrogen. Gas chromatographic measurements were carried out with a Hewlett Packard HP6890 instrument. HP-INNOWAX cross-linked polyethylene glycol (30 m, 250 μm) or Supelco Beta-Dex™ 120 (30 m, 250 μm) columns were used.

General Procedure for Catalytic Transfer Hydrogenation of Acetophenone: Under an inert gas, acetophenone (5 mmol), the ruthenium catalyst precursor (0.01 mmol of Ru, 0.2 mol %) and propan-2-ol (17.5 mL) were introduced into a Schlenk tube fitted with a condenser, and heated at 82 °C for 15 min. Then NaOH (2.5 mL of a 0.096 M solution in propan-2-ol, 4.8 mol %) was added and the reaction monitored by gas chromatography. Acetone and 1-phenylethanol were the only products detected in all cases. The recycling process was carried out as follows: After cooling the reaction mixture to room temperature, the insoluble polymer was decanted and washed twice with 10 mL of propan-2-ol. Then, propan-2-ol (17.5 mL), acetophenone (5 mmol) and NaOH (2.5 mL of a 0.096 M solution in propan-2-ol, 4.8 mol %) were added and the mixture heated at 82 °C.

$\{[NP(OC_6H_4PPh_2[RuCl_2(\eta^6\text{-}p\text{-cymene})]_x)_2]_{0.4}[NP(O_2C_{12}H_8)]_{0.6}\}_n$ [x = 0.5 (2a); 1 (2b)]: The dimer $[Ru(\eta^6\text{-}p\text{-cymene})Cl(\mu\text{-}Cl)]_2$ (0.043 g, 0.14 mmol of Ru) was added to a solution of $\{[NP(OC_6H_4PPh_2)_2]_{0.4}[NP(O_2C_{12}H_8)]_{0.6}\}_n$ (**1a**) (0.15 g, 0.28 mmol of PPh_2 groups) in CH_2Cl_2 (15 mL), and the mixture stirred at room temperature for 5.5 h. The resulting solution was concentrated to ca. 1 mL and poured dropwise into hexane (500 mL) to give **2a** as a slightly reddish solid that was dried in vacuo. Yield 0.16 g, (83%). The reddish complex **2b** was prepared similarly using $\{[NP(OC_6H_4\text{-}PPh_2)_2]_{0.4}[NP(O_2C_{12}H_8)]_{0.6}\}_n$ (**1**) (0.20 g, 0.37 mmol of PPh_2 groups) and the dimer $[Ru(\eta^6\text{-}p\text{-cymene})Cl(\mu\text{-}Cl)]_2$ (0.114 g, 0.37 mmol of Ru) and stirring for 5.5 h. The yield was 0.29 g (92%).

2a: $^{31}P\{^1H\}$ NMR (25 °C): δ = 23.7 (m, $C_6H_4PPh_2Ru$), −5.6 [m, $N{=}P(O_2C_{12}H_8)$], −6.2 ($C_6H_4PPh_2$), −22.5 [m, $N{=}P(OC_6H_4PPh_2)_2$] ppm. ^1H NMR (25 °C): δ = 7.5, 7.3, 7.1, 6.7 (aromatic rings); 4.9, 4.7 [$CH_3C_6H_4CH(CH_3)_2$]; 3.4, 1.6 (PTHF), 2.7 [$CH_3C_6H_4CH(CH_3)_2$], 1.5 [$CH_3C_6H_4CH(CH_3)_2$], 0.9 [$CH_3C_6H_4CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (25 °C): δ = 152.5, 135, 121.5 (PC_6H_4O), 138, 134, 129 [$P(C_6H_5)_2$], 149, 130.5, 129, 126, 123 ($PO_2C_{12}H_8$); 96, 89.5, 87, 30.5, 22 (*p*-cymene), 71, 27 (PTHF) ppm. FTIR (KBr): $\tilde{\nu}$ = 3054 (m, C−H str., arenes), 2937 (m, C−H str., PTHF), 2855(m, C−H str., PTHF), 1587 (w), 1491 (m), 1477 (m), 1435 (s, C=C str., *p*-cymene), 1374 (m), 1268(s, sh, PO−C str.), 1246 (vs, N−P str.), 1197 (vs, N−P str.), 1169 (vs), 1095 (vs, P−OC str.), 1015 (w), 931 (vs, br, POC def.), 834 (m), 785 (s, PNP def.), 749 (s), 717 (w), 696 (s), 609 (m), 586 (sh), 524 (m, br) cm^{-1}. $C_{28.4}H_{27.2}Cl_{0.8}NO_{2.7}P_{1.8}Ru_{0.4}$ (550.27): calcd. C 62.0, H 4.98, N 2.54; found C 61.1, H 5.35, N 2.54 (calcd. values include the 0.7 PTHF content). TGA: Continuous loss of mass from 170 °C, with maxima at 220 °C (6%), 340 °C (21%), 430 °C (16%). Residue at 800 °C: 41%. T_g (DSC) = 149 °C. $\Delta C_p = -0.113\ J[gK]^{-1}$. Only observed during the second cooling cycle.

2b: $^{31}P\{^1H\}$ NMR (25 °C): δ = 23.6 (m, $C_6H_4PPh_2Ru$), −5.4 [m, $N{=}P(O_2C_{12}H_8)$], −23.5 [m, $N{=}P(OC_6H_4PPh_2)_2$] ppm. ^1H NMR

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(25 °C): δ = 7.5, 7.3, 7.2, (br, aromatic rings); 5.0, 4.8 [$CH_3C_6H_4CH(CH_3)_2$], 3.4, 1.6 (PTHF); 2.7 [$CH_3C_6H_4CH(CH_3)_2$], 0.9 [$CH_3C_6H_4CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 134, 129 [$P(C_6H_5)_2$]; 98, 87, 30.5, 22 (*p*-cymene); 71, 27 (PTHF) ppm. FTIR (KBr): $\tilde{\nu}$ = 3057 (m, C−H str., arene), 2941 (m, C−H str., PTHF), 2864 (m, C−H str., PTHF), 1588 (w), 1492 (m), 1480 (m), 1435 (s, C=C str., *p*-cymene), 1376 (m), 1246 (vs, N−P str.), 1212 (vs, N−P str.), 1198 (vs, N−P str.), 1172 (vs), 1117 (m), 1094 (vs, P−OC str.), 1016 (w), 935 (v, br, POC def.), 840 (w), 786 (m, PNP def.), 752 (m), 717 (w), 696 (m), 609 (w), 524 (s, br) cm^{-1}. $C_{32.4}H_{32.8}Cl_{1.6}NO_{2.7}P_{1.8}Ru_{0.8}$ (672,74): calcd. C 57.8, H 4.91; N 2.08.; found C 56.9, H 4.38, N 2.18 (calcd. values include the 0.7 PTHF content). TGA: Continuous loss of mass from 180 °C, with maxima at 260 °C (24%), 480 °C (23%), 720 °C (10%). Residue at 800 °C: 43%. T_g (DSC) = 189 °C, ΔC_p= 0.139 J[gK]$^{-1}$.

{[NP(OC$_6$H$_4$PPh$_2$[RuCl$_2$(η^6-*p*-cymene)])$_2$]$_{0.1}$[NP(O$_2$C$_{20}$H$_{12}$)]$_{0.9}$}$_n$ (3): The reddish complex **3** was prepared by stirring a solution of {[NP(OC$_6$H$_4$PPh$_2$)$_2$]$_{0.1}$[NP(O$_2$C$_{20}$H$_{12}$)]$_{0.9}$}$_n$ (**1b**) (0.50 g, 0.225 mmol of PPh_2 groups) in CH_2Cl_2 (30 mL) with the dimer [Ru(η^6-*p*-cymene)Cl(μ-Cl)]$_2$ (0.0735 g, 0.24 mmol of Ru) at room temperature for 5.5 h. The polymer was isolated according to the procedure described previously for **2a**. The yield was 0.51 g (90%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 26.8 (m, Ph_2P=O), 23.0 (m, $C_6H_4PPh_2Ru$), −2.8 [m, N=$P(O_2C_{20}H_{12})$], −23.5 [m, N=$P(OC_6H_4PPh_2)_2$] ppm. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.3 (v br, aromatic rings); 5.0 [v br, $CH_3C_6H_4CH(CH_3)_2$], 2.6 [v br, $CH_3C_6H_4CH(CH_3)_2$], 0.9 [v br, $CH_3C_6H_4CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 149, (NPO*C* naphthalene ring), 136, 134, 130, 124 (v, br naphthalene and phosphane ring), 32, 24 (br, *p*-cymene) ppm. FTIR (KBr): $\tilde{\nu}$ = 3054 (m, C−H str., arenes), 2960 (m, C−H str., *p*-cymene), 2866 (m, C−H str., *p*-cymene), 1620 (w), 1592 (m), 1508 (m), 1465 (w), 1434 (m), 1398 (m), 1363 (m), 1317 (s), 1256 (sh, s, N−P str.), 1219 (vs, N−P str.), 1190 (sh, vs, N−P str.), 1154 (sh, m), 1095 (w), 1072 (s, P−OC str.), 1030 (w), 963 (vs, br, POC def.), 895 (m), 868 (s), 811(s, PNP def.), 772 (w), 746 (s), 713 (m), 694 (m), 655(m), 571 (s), 523 (m), 487 (m) cm^{-1}. $C_{23.2}H_{15.84}Cl_{0.32}NO_{2.04}P_{1.2}Ru_{0.16}$ (405.94): calcd. C 68.6, H 3.93, N 3.45 (calcd. values take into account the 20% of oxidized phosphane sites); found C 66.3, H 4.01, N 3.42. TGA: Continuous loss of mass from 180 °C, with maxima at 212 (6%), 500 (31%) and 790 °C (7%). Residue at 800 °C: 56%. No T_g was observed in the DSC thermogram up to 300 °C.

{[NP(OC$_6$H$_4$PPh$_2$[RuCl$_2$(η^6-*p*-cymene)])$_2$]$_{0.2}$[NP(O$_2$C$_{20}$H$_{10}$Br$_2$)]$_{0.8}$}$_n$ (4): The dimer [Ru(η^6-*p*-cymene)Cl(μ-Cl)]$_2$ (0.095 g, 0.31 mmol of Ru) was added to a solution of {[NP(OC$_6$H$_4$PPh$_2$)$_2$]$_{0.2}$[NP(O$_2$C$_{20}$H$_{10}$Br$_2$)]$_{0.8}$}$_n$ (**1c**) (0.50 g, 0.345 mmol of PPh_2 groups) in CH_2Cl_2 (30 mL), and the mixture was stirred at room temperature for 5.5 h. The resulting solution was concentrated to ca. 1 mL and poured dropwise into hexane (500 mL) to give **4** as an orange solid that was dried in vacuo. Subsequently, the product was reprecipitated from CH_2Cl_2/diethyl ether, washed with Et_2O (2 × 30 mL) and dried under vacuum at room temperature for 1 d. Yield 0.53 g (88%). $^{31}P\{^1H\}$ NMR (25 °C): δ = 27.5 (m, Ph_2P=O), 23.1 (m, $C_6H_4PPh_2Ru$), −4.3 [m, N=$P(O_2C_{20}H_{10}Br_2)$], −20.0 [m, N=$P(OC_6H_4PPh_2)_2$] ppm. ^1H NMR (25 °C): δ = 7.3 (v br, aromatic rings); 1.8 [br, $CH_3C_6H_4CH(CH_3)_2$], 1.3 [br, $CH_3C_6H_4CH(CH_3)_2$] ppm. FTIR (KBr): $\tilde{\nu}$ = 3055 (m, C−H str., arenes), 2958 (w, C−H str., *p*-cymene), 2865 (w, C−H str, *p*-cymene), 1585 (m), 1493 (m), 1436 (w), 1354 (m), 1317 (s), 1253 (sh, s, N−P str.), 1218 (vs, N−P str.), 1191 (sh, s, N−P str.), 1154 (s), 1117 (w), 1066 (m, P−OC str.), 959 (vs, br, POC def.), 943 (sh, s), 874 (m), 826 (m), 808 (m, PNP def.), 779 (w), 748 (w), 728 (w), 692 (m), 656(w), 602 (w), 570 (m), 521(m), 474 (w) cm^{-1}. $C_{26.7}H_{18.5}Br_{1.6}Cl_{0.70}NO_{2.05}P_{1.4}Ru_{0.35}$ (617.54): calcd. C 51.93, H 3.02, N 2.27 (calcd. values take into account the 12% of oxidized phosphane sites); found C 50.8, H 2.95, N 2.35. TGA: Continuous loss of mass from 180 °C, with maxima at 210 °C (7%), 490 (37%) and 780 (16%). Residue at 800 °C: 40%. No T_g was observed in the DSC thermogram up to 300 °C.

{[NP(OC$_6$H$_4$PPh$_2$)$_2$]$_{0.1}$[NP(O$_2$C$_{20}$H$_{12}$)]$_{0.9}$[RuCl(η^6-*p*-cymene)(PF$_6$)]$_{0.05}$}$_n$ (5): The complex [RuCl(η^6-*p*-cymene)(PPh_3)$_2$][PF_6] (0.061 g, 0.065 mmol) was added to a solution of {[NP(OC$_6$H$_4$PPh$_2$)$_2$]$_{0.1}$[NP(O$_2$C$_{20}$H$_{12}$)]$_{0.9}$}$_n$ (**1b**) (0.50 g, 0.225 mmol of PPh_2 groups) in THF (30 mL) and the resulting mixture was refluxed for 48 h. Then the solvent was evaporated and the free PPh_3 was extracted with diethyl ether (3 × 20 mL). The reddish solid residue was dried under vacuum at room temperature for 6 h. Yield 0.50 g (95%). $^{31}P\{^1H\}$ NMR ([D$_6$]DMSO suspension, 25 °C): δ = 24.4, 23.2 (m, $C_6H_4PPh_2Ru$), −8.5 [v br, N=$P(O_2C_{20}H_{12})$, N=$P(OC_6H_4PPh_2)_2$], −148 (m, PF_6^-) ppm. FT IR (KBr): $\tilde{\nu}$ = 3053 (m, C−H str., arenes), 2965 (m, C−H str, *p*-cymene), 2855 (w, C−H str., *p*-cymene), 1620 (w), 1591 (m), 1506 (w), 1436 (m), 1398 (m), 1362 (m), 1317 (s), 1258 (sh,s, N−P str.), 1218 (vs, N−P str.), 1186 (sh,vs, N−P str.), 1148 (sh, s), 1116 (m), 1069 (m, P−OC str.), 961 (s, br, POC def.), 943 (sh, s), 895 (m), 865 (s), 838 (m, P−F str., PF_6^-), 808 (s, PNP def.), 772 (w), 745 (s), 712 (m), 693 (s), 654 (m), 571 (s), 560 (sh,m, P−F str., PF_6^-), 538 (m), 486 (m), 472 (m), 450 (m) cm^{-1}. $C_{22.1}H_{14.3}Cl_{0.05}F_{0.3}NO_{2.02}P_{1.25}Ru_{0.05}$ (377.42): calcd. C 70.3, H 3.82, Cl, F 1.98, N 3.71, P 10.3, Ru 1.34 (calcd. values take into account the 20% of oxidized phosphane sites); found C 67.0, H 3.81, Cl, F 1.53, N 3.52, P 8.83, Ru 1.11. TGA: Continuous loss of mass from 60 °C, with maxima at 510 °C (42.6%). Residue at 800 °C: 57.4%. No T_g was observed in the DSC thermogram up to 300 °C.

{[NP(OC$_6$H$_4$PPh$_2$)$_2$]$_{0.2}$[NP(O$_2$C$_{20}$H$_{10}$Br$_2$)]$_{0.8}$[RuCl(η^6-*p*-cymene)(PF$_6$)]$_{0.08}$}$_n$ (6): The complex [RuCl(η^6-*p*-cymene)(PPh_3)$_2$][PF_6] (0.074 g, 0.079 mmol) was added to a solution of {[NP(OC$_6$H$_4$PPh$_2$)$_2$]$_{0.2}$[NP(O$_2$C$_{20}$H$_{10}$Br$_2$)]$_{0.8}$}$_n$ (**1c**) (0.50 g, 0.345 mmol of PPh_2 groups) in THF (30 mL) and the resulting mixture was refluxed for 57 h. Then the solvent was evaporated and the free PPh_3 was extracted with diethyl ether (5 × 20 mL). The green solid residue was dried under vacuum at room temperature for 12 h. Yield 0.50 g (94%). $^{31}P\{^1H\}$ NMR ($CDCl_3$ suspension, 25 °C): δ = 24 (m, $C_6H_4PPh_2Ru$), − 9.3 [v br, N=$P(O_2C_{20}H_{10}Br_2)$, N=$P(OC_6H_4PPh_2)_2$]. FT IR (KBr): $\tilde{\nu}$ = 3053 (m, C−H str., arenes), 2960 (m, C−H str., *p*-cymene), 2852 (m, C−H str., *p*-cymene), 1584 (m), 1492 (m), 1437 (m), 1393 (m), 1354 (m), 1317 (s), 1258 (s, N−P str.), 1216 (vs, N−P str.), 1187 (sh,vs, N−P str.), 1115 (s), 1065 (s, P−OC str.), 956 (s, br, POC def.), 942 (vs), 872 (s), 838 (sh, P−F str., PF_6^-), 826 (s), 805 (s, PNP def.), 777 (s), 748 (m), 726 (s), 690 (s), 654 (m), 601 (m), 568 (s), 560 (sh, P−F str., PF_6^-), 533 (s), 514 (s), 492 (s), 472 (s) cm^{-1}. $C_{24}H_{14.72}Br_{1.6}Cl_{0.08}F_{0.48}NO_{2.05}P_{1.48}Ru_{0.08}$ (543.63): calcd. C 53.0, H 2.73, N 2.58, P 8.43; Ru 1.49 (calcd. values take into account the 12% oxidized phosphane sites); found C 51.5, H 2.74, N 2.54, P 7.34, Ru 1.35. TGA: Continuous loss of mass from 160 °C, with maxima at 220 °C (9%), 470 °C (40%), and 770 °C (9%). Residue at 800 °C: 39%. No T_g was observed in the DSC thermogram up to 300 °C.

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[1] [1a] C. W. Allen, *Coord. Chem. Rev.* **1994**, *130*, 137. [1b] I. Manners, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1602. [1c] R. De Jaeger, M. Gleria, *Prog. Polym. Sci.* **1998**, *23*, 179. [1d] R. De Jaeger, M. Gleria (Eds.), *Phosphazenes: A Worldwide Insight*, NOVA Science Publishers, New York, **2004**.

[2] [2a] H. R. Allcock, *Appl. Organomet. Chem.* **1998**, *12*, 659. [2b] H. R. Allcock, M. A. Hofmann, C. M. Ambler, R. V. Morford, *Macromolecules* **2002**, *35*, 3484. [2c] M. A. Hofmann, C. M. Ambler, A. E. Maher, E. Chalkova, X. Y. Zhou, S. N. Lvov, H. R. Allcock, *Macromolecules* **2002**, *35*, 6490.

[3] H. R. Allcock, *Chem. Mater.* **1994**, *6*, 1476.

[4] G. A. Carriedo, J. I. Fidalgo Martínez, F. J. García Alonso, E. Rodicio González, A. Presa Soto, *Eur. J. Inorg. Chem.* **2002**, 1502.

[5] G. A. Carriedo, F. J. García Alonso, P. A. González, *Macromol. Rapid Commun.* **1997**, *18*, 371.

[6] H. R. Allcock, J. L. Desorcie, G. H. Riding, *Polyhedron* **1987**, *6*, 119.

[7] K. B. Visscher, H. R. Allcock, *Chem. Mater.* **1994**, *6*, 2040.

[8] H. R. Allcock, A. A. Dembek, E. H. Klingenberg, *Macromolecules* **1991**, *24*, 5208.

[9] H. R. Allcock, E. N. Silverberg, C. J. Nelson, W. D. Coggio, *Chem. Mater.* **1993**, *5*, 1307.

[10] G. A. Carriedo, F. J. García Alonso, J. L. García Álvarez, C. Díaz Valenzuela, N. Yutronic Sáez, *Polyhedron* **2002**, *21*, 2587.

[11] G. A. Carriedo, F. J. García Alonso, P. A. González, C. Díaz Valenzuela, N. Yutronic Sáez, *Polyhedron* **2002**, *21*, 2579.

[12] C. Díaz, P. Castillo, G. A. Carriedo, P. Gómez Elipe, F. J. García Alonso, *Macromol. Chem. Phys.* **2002**, *203*, 1912.

[13] [13a] H. R. Allcock, K. D. Lavin, N. M. Tollefson, T. L. Evans, *Organometallics* **1983**, *2*, 267. [13b] R. A. Dubois, P. E. Garrou, K. D. Lavin, H. R. Allcock, *Organometallics* **1986**, *5*, 460. [13c] V. Chandrasekhar, A. Athimoolam, *Org. Lett.* **2002**, *4*, 2113. [13d] V. Janout, P. Cefelin, D. R. Tur, S. V. Vinogradova, *Polym. Bull.* **1986**, *15*, 303. [13e] B. Valter, B. Masar, V. Janout, H. Hrudkova, P. Cefelin, D. R. Tur, S. V. Vinogradova, *Makromol. Chem.* **1991**, *192*, 1549.

[14] G. A. Carriedo, L. Fernández-Catuxo, F. J. García Alonso, P. Gómez-Elipe, P. A. González, *Macromolecules* **1996**, *29*, 5320.

[15] G. A. Carriedo, F. J. García Alonso, P. A. González, J. L. García Álvarez, *Macromolecules* **1998**, *31*, 3189.

[16] G. A. Carriedo, F. J. García Alonso, P. A. González, P. Gómez Elipe, *Polyhedron* **1999**, *18*, 2853.

[17] G. A. Carriedo, F. J. García Alonso, A. Presa Soto, *Eur. J. Inorg. Chem.* **2003**, 4341.

[18] S. D. Dreher, T. J. Katz, K.-C. Lam, A. L. Rheingold, *J. Org. Chem.* **2000**, *65*, 815.

[19] [19a] T. Naota, H. Takaya, S.-I. Murahashi, *Chem. Rev.* **1998**, *98*, 2599. [19b] B. M. Trost, F. D. Toste, A. B. Pinkerton, *Chem. Rev.* **2001**, *101*, 2067.

[20] [20a] G. Zassinovich, G. Mestroni, S. Gladiali, *Chem. Rev.* **1992**, *92*, 1051. [20b] R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97. [20c] M. J. Palmer, M. Wills, *Tetrahedron: Asymmetry* **1999**, *10*, 2045. [20d] R. Noyori, M. Yamakawa, S. Hashiguchi, *J. Org. Chem.* **2001**, *66*, 7931. [20e] D. Carmona, M. P. Lamata, L. A. Oro, *Eur. J. Inorg. Chem.* **2002**, 2239. [20f] K. Everaere, A. Mortreux, J. F. Carpentier, *Adv. Synth. Catal.* **2003**, *345*, 67.

[21] [21a] D. J. Bayston, C. B. Travers, M. E. C. Polywka, *Tetrahedron: Asymmetry* **1998**, *9*, 2015. [21b] K. Polborn, K. Severin, *Eur. J. Inorg. Chem.* **2000**, 1687. [21c] K. Polborn, K. Severin, *Chem. Eur. J.* **2000**, *6*, 4604. [21d] A. J. Sandee, D. G. I. Petra, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Chem. Eur. J.* **2001**, *7*, 1202. [21e] Y. C. Chen, T. F. Wu, J. G. Deng, H. Liu, Y. Z. Jiang, M. C. K. Choi, A. S. C. Chan, *Chem. Commun.* **2001**, 1488. [21f] N. E. Leadbeater, *J. Org. Chem.* **2001**, *66*, 2168. [21g] S. Laue, L. Greiner, J. Wöltinger, A. Liese, *Adv. Synth. Catal.* **2001**, *343*, 711. [21h] C. Saluzzo, M. Lemaire, *Adv. Synth. Catal.* **2002**, *344*, 915 and references cited herein. [21i] Y. C. Chen, T. F. Wu, J. G. Deng, H. Liu, X. Cui, J. Zhu, Y. Z. Jiang, M. C. K. Choi, A. S. C. Chan, *J. Org. Chem.* **2002**, *67*, 5301. [21j] R. Akiyama, S. Kobayashi, *Angew. Chem. Int. Ed.* **2002**, *41*, 2602. [21k] S. Kobayashi, R. Akiyama, *Chem. Commun.* **2003**, 449. [21l] E. Dulière, M. Devillers, J. Marchand-Brynaert, *Organometallics* **2003**, *22*, 804. [21m] J. Q. Yu, H. C. Wu, C. Ramarao, J. B. Specer, S. V. Ley, *Chem. Commun.* **2003**, 678. [21n] S. B. Wendicke, E. Burri, R. Scopelliti, K. Severin, *Organometallics* **2003**, *22*, 1894. [21o] P. N. Liu, Y. C. Chen, X. Q. Li, Y. Q. Tu, J. G. Deng, *Tetrahedron: Asymmetry* **2003**, *14*, 2481.

[22] H. R. Allcock, A. A. Dembek, E. H. Klingenberg, *Macromolecules* **1991**, *24*, 5208.

[23] L. Pu, *Chem. Rev.* **1998**, *98*, 2405.

[24] P. Hesemann, J. J. Moreau, *Tetrahedron: Asymmetry* **2000**, *11*, 2183.

[25] G. A. Carriedo, F. J. García Alonso, A. Presa Soto, *J. Inorg. Organomet. Polym.* **2004**, *14*, 29.

[26] J. E. Bäckvall, *J. Organomet. Chem.* **2002**, *652*, 105.

[27] In the case of catalyst **2b**, the second run in the absence of base leads to only 50% of 1-phenylethanol after 24 h.

[28] [28a] G. A. Carriedo, F. J. García Alonso, J. L. García Álvarez, G. M. Lombardo, G. C. Pappalardo, F. Punzo, *Chem. Eur. J.*, in press. [28b] G. A. Carriedo, J. L. García Álvarez, F. J. García Alonso, A. Presa Soto, M. P. Tarazona, F. mendicuti, G. Marcelo, *Macromolecules*, in press.

[29] L. Pu, *Tetrahedron: Asymmetry* **1998**, *9*, 1457.

[30] M. Reggelin, M. Schultz, M. Holbach, *Angew. Chem. Int. Ed.* **2002**, *41*, 1614.

[31] A. N. Mujumdar, S. G. Young, R. L. Merker, J. H. Magil, *Macromolecules* **1990**, *23*, 14.

[32] M. A. Bennett, A. K. Smith, *J. Chem. Soc., Dalton* **1974**, 233.

[33] M. A. Bennett, T.-N. Huang, T. W. Matheson, A. K. Smith, *Inorg. Synth.* **1982**, *21*, 75.

[34] H. Werner, R. Werner, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 683.

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