Available online at www.sciencedirect.com

SCIENCE DIRECT®

Coordination Chemistry Reviews 248 (2004) 377–395

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Supported catalysts from polymerizable transition metal complexes

Piero Mastrorilli, Cosimo Francesco Nobile*

Department of Water Engineering and Chemistry, Polytechnic of Bari, via Orabona, 4 I-70125 Bari, Italy

Received 13 October 2003; accepted 10 February 2004

Contents

Abstract

This review covers the last 12 years of research on the synthesis and use of heterogeneous catalysts obtained by co-polymerization of suitable metal containing monomers (MCM). The catalytic applications of these supported metal complexes are subdivided into three areas. Hydrogenation of alkenes and functionalized olefins are covered first. Oxidation of several substrates such as olefins, sulfides, alcohols, and aldehydes are then considered. Of particular interest in this framework is the use of chiral salen metal containing monomers for the stereoselective epoxidation of hindered olefins. Alkene and alkyne polymerizations, Heck and Heck-type reactions, allylic alkylation, and Michael additions are discussed in the field of carbon–carbon bond forming reactions. A common factor emerging from this survey is the application of metal containing monomers for the synthesis of molecularly imprinted polymers to be used as catalysts or catalyst supports.

Keywords: Metal containing monomers; Polymerizable complexes; Supported metal catalysts; Hydrogenation; Oxidation; C–C bond forming reaction

1. Introduction

Supported metal complexes continuously attract the interest of a growing part of the scientific community for the advantages that they offer with respect to their soluble counterparts [1]. Some of these advantages are the robustness, the increased air and moisture stability, ease of separation, and the potential recyclability, when used as heterogeneous catalysts.

The supports on which metal complexes have been immobilized are inorganic or organic polymers. Typical inorganic supports are oxides bearing surface hydroxyl groups, acting as [2,3] (or being precursors of) ligands for suitable metal containing moieties [4–7].

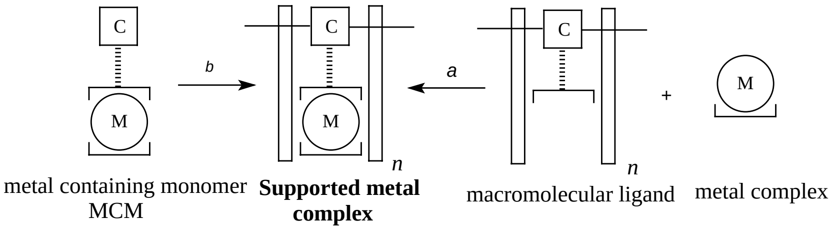
Using organic co-polymers as supports for transition metal complexes allows one to conjugate a controllable flexibility of the matrix with the possibility to fine-tune the physical properties (polarity, swellability, morphology, etc.) of the

---

Abbreviations: aaema, deprotonated form of 2-(acetoacetoxy)ethyl methacrylate; BINOL, binaphthol; BSA, *N*,*O*-bis(trimethylsilyl)acetamide; cod, 1,5-cyclooctadiene; *m*-CPBA, *meta*-chloroperbenzoic acid; (+)-diop, (*S*,*S*)-4,5-bis(diphenylphosphinomethyl)-2,2′-dimethyl-1,3-dioxolane; DMAA, *N*,*N*-dimethylacrylamide; DMF, *N*,*N*-dimethylformamide; DMG, *N*,*N*-dimethylglyicine; DVB, divinylbenzene; ee, enantiomeric excess; EGDMA, ethylene glycol dimethacrylate; EMA, ethyl methacrylate; [(*R*,*S*)-JOSIPHOS], (*R*)-(–)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethyldicyclohexylphosphine; MBAA, *N*,*N*′-methylenebisacrylamide; MCM, metal containing monomer; MCP, metal containing polymer; (*S*)-MeObiphep, (*S*)-(–)-2,2′-bis-(diphenylphosphino)-6,6′-dimethoxy-1,1′-biphenyl; NMO, *N*-methylmorpholine-*N*-oxide; [(*R*,*R*)-NORPHOS], (2*R*,3*R*)-(–)-2,3-bis(diphenylphosphino)-bicyclo[2.2.1]hept-5-ene; PhIO, iodosobenzene; poly-, co-polymer of; [(*R*,*S*)-PPFA], (–)-(*R*)-*N*,*N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]-ethylamine; salen, *N*,*N*′-disalicylidene-ethylenediamine; t.o.f., turn over frequency

* Corresponding author. Tel.: +39-080-5963605; fax: +39-080-5963611.
E-mail address: c.f.nobile@poliba.it (C.F. Nobile).

0010-8545/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2004.02.003



Scheme 1. Synthesis of supported metal complexes.

material by suitable combination of co-monomers and cross-linkers. The first example of an organic polymer supported metal complex was proposed in 1969 by Haag and Whitehurst [8] and consisted of sulfonated polystyrene bearing cationic Pt(II) complexes. Since then, practically all classes of organic polymers, including natural ones such as silk [9], starch [10], cellulose [11], chitosan [12,13], have been investigated as supports for metal complexes. Variously cross-linked *p*-chloromethylstyrene/divinylbenzene co-polymers, functionalizable for the insertion of ligands or ligand precursors as pendant groups, are also commercially available.

Although the principal application of metal complexes supported onto organic matrices is catalysis [14], other properties such as luminescence of these materials have been studied [15,16]. They have also found some uses in electrochemistry [17–19], for the detection and degradation of organo-phosphotriester pesticides [20] and as adhesion promoters between glass and an organic polymer [21–24].

The simplest synthetic route for synthesizing an organic polymer supporting a metal complex is depicted as route *a* of Scheme 1. It envisages the synthesis of a macromolecular ligand and subsequent anchoring of a metal salt or complex, and is by far the most investigated strategy which has led to uncountable examples concerning in particular the use of polystyrene as support [25,26].

A rather overlooked albeit intriguing alternative (route *b*) is the incorporation of a metal onto a support by polymerization of a suitable metal containing monomer (MCM). Two advantages are associated with this approach: (i) the possibility to study the MCM as a homogeneous catalyst before polymerization [27–29]; (ii) the possibility to use MCMs for the synthesis of imprinted materials with controllable “outer sphere” morphology [30]. Moreover, route *b* can lead to a more uniform distribution of the metal complex in the matrix with respect to route *a*, and to a higher dispersion of the metal, a beneficial property when the material is to be used as heterogeneous catalyst.

Last but not least, the knowledge of the structure of the metal center, which can be inferred by analyzing the MCM in solution, may also shed light on catalytic pathways in the heterogeneous catalysis [31].

The issue of MCM polymerization has been addressed intensively by several authors and a monograph updated to 1991 on the subject is available [32]. A more recent review on the same topic focuses on catalysts obtained from MCMs for applications on hydrogen peroxide decomposition [33].

Supported metal complexes obtained from MCM polymerization have been proposed for other potential applications than catalysis, such as nanosized technology [34,35], biomimetic systems [36,37], materials science [38,39], chromatographic separations [40], and electrochemistry [18,41].

This review is aimed at providing the reader with a report on the last 12 years of research on the subject and will be focused on heterogeneous catalysts obtained from MCM polymerization. The catalytic reactions have been subdivided into hydrogenation, oxidation and C–C bond forming reactions.

In Table 1 are listed the MCMs and the organic co-monomers used to achieve the metal containing polymers (MCP) discussed throughout the paper along with their use in catalysis.

2. Hydrogenation reactions

Hydrogenation of organic substrates is, without doubt, one of the most useful and widely investigated benchmarks for the study of heterogeneous catalysis. Materials obtained by polymerization of MCMs have been used for hydrogenation reactions both by dihydrogen addition or by hydrogen transfer.

The cationic rhodium complex bearing isopropenylphenyl diphosphines **1** has been co-polymerized with EGDMA in the presence of DMF as porogen and the resulting material proved to be an active and recyclable catalyst for the hydrogenation of several alkenes with yields ranging from 88 to 99% (Table 2) [42]. Although the supported metal complex was less active than its homogeneous counterpart, the catalyst used in the hydrogenation of 3-acryloyloxazolidinone could be reused as many as six times with only a slight decrease in activity (the time to reach reaction completion changed from 30 min in the first run to 60 min in the sixth run). The use of this supported rhodium complex in fluorous biphasic solvent system has been also reported [43].

Several unsaturated substrates have been hydrogenated with yields ranging from 64 to 100% using the co-polymer of Rh(cod)(aaema) (**2**) with MBAA and DMAA as catalyst [44] (Table 3). The hydrogenation of 1-heptene, cyclohexene, carvone, citral, and nitrobenzene was carried out at 1 bar H_2, whereas cinnamaldehyde, benzonitrile, and valeronitrile required 20 bar H_2 to be reduced (Table 3) [45]. Supported complex poly-**2** retained its activity for several cycles when used in the hydrogenation of olefins.

Substituting the cod ligand with the chiral ligand (+)-diop and co-polymerizing the resulting complex **3** with DMAA and MBAA afforded a chiral catalyst that facilitated the hydrogenation of methyl-(Z)-α-*N*-acetamidocinnamate with ee's up to 53% [46]. The reason for the unsatisfactory enentioselectivity of the catalyst (under comparable conditions the [(+)-diopRh(aaema)] gave an ee of 67%) was the partial oxidation of the chiral ligand during the polymerization of the MCM, as indicated by CP/MAS ^{31}P NMR experiments.

Table 1
Polymerizable complexes used as precursors of supported catalysts

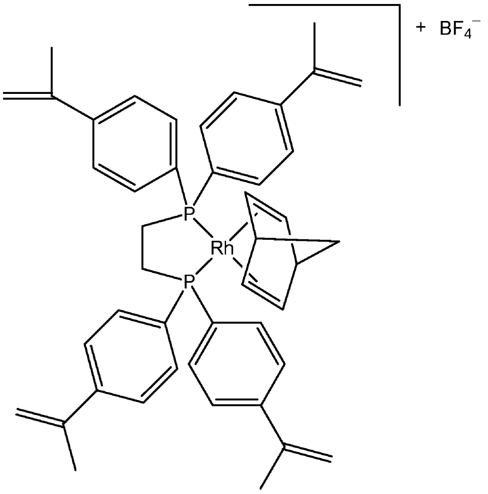
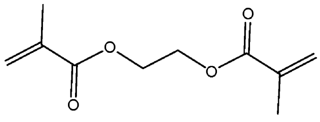
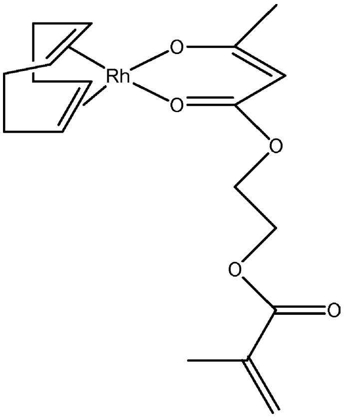
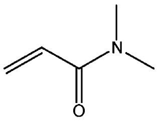
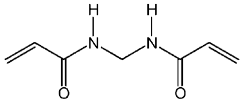
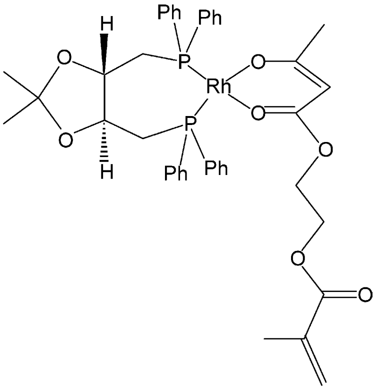
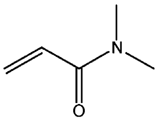
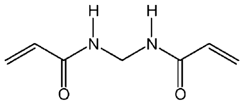
Metal containing monomer	Co-monomers	Use in Catalysis
 **1**	 EGDMA	Hydrogenation [42,43] and hydroboration [42]
 **2**	 DMAA and  MBAA	Hydrogenation [44,45] and polymerization of phenylacetylene [88,89]
 **3**	 DMAA and  MBAA	Enantioselective hydrogenation [46]

Table 1 (*Continued*)

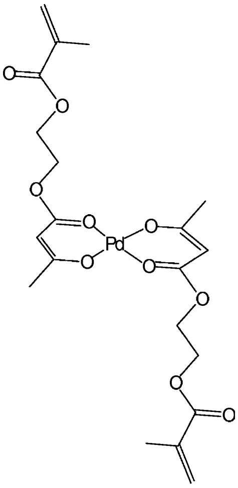
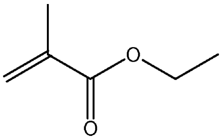
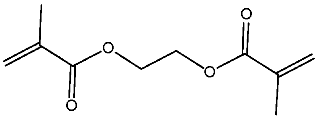
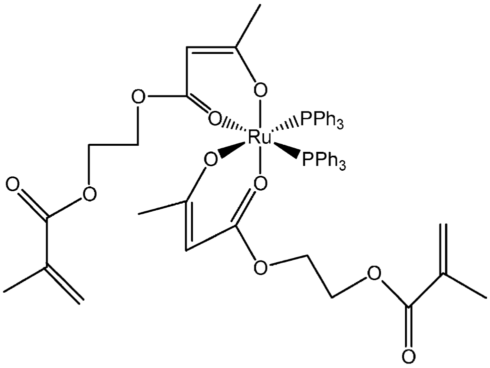
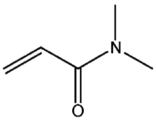
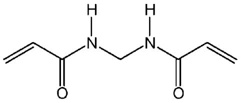
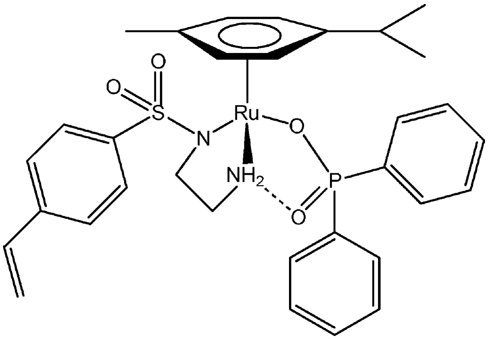
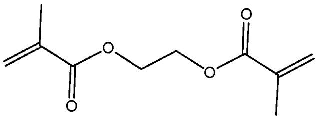
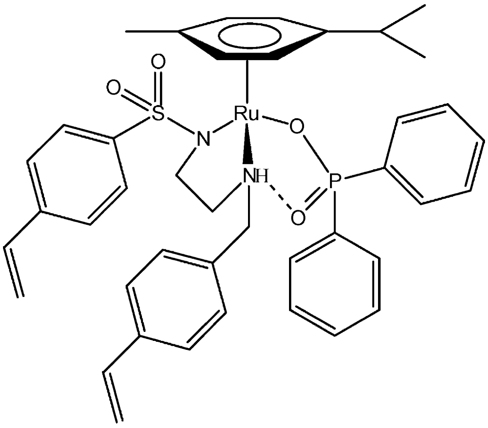
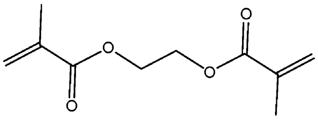
Metal containing monomer	Co-monomers	Use in Catalysis
 **4**	 EMA and  EGDMA	Hydrogenation [44,47], Heck cross-coupling [90,91] and asymmetric allylic alkylation [93]
 **5**	 DMAA and  MBAA	Hydrogenation [48]
 **6**	 EGDMA	Reduction of aromatic ketones [50,51]
 **7**	 EGDMA	Reduction of aromatic ketones [51]

Table 1 (*Continued*)

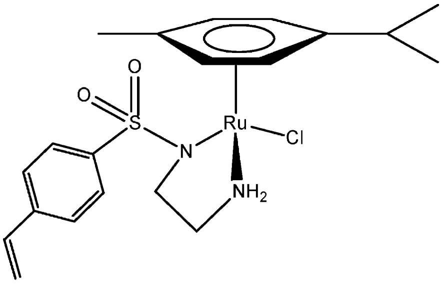
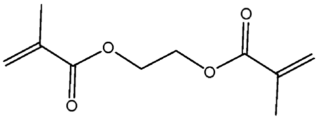
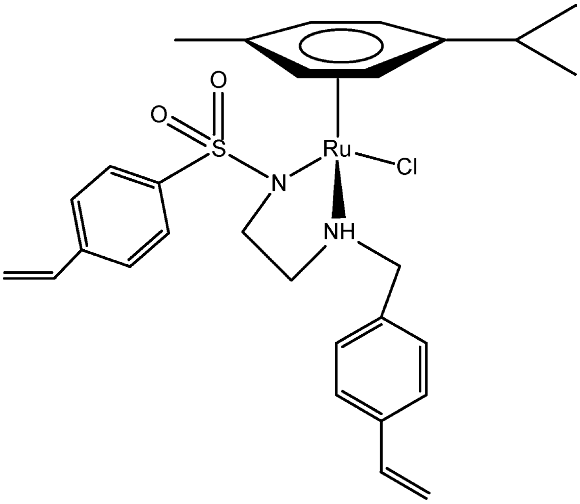
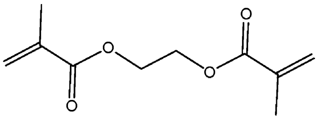
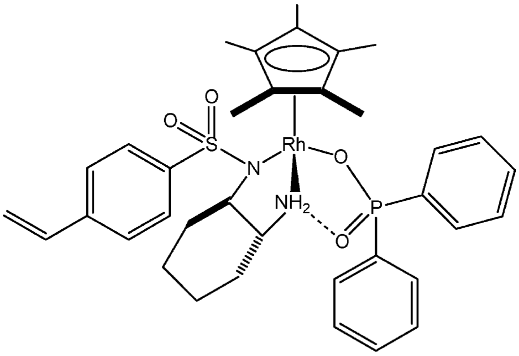
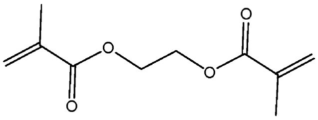
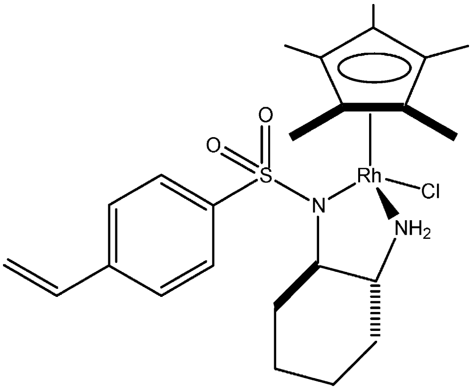
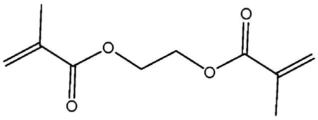
Metal containing monomer	Co-monomers	Use in Catalysis
 **8**	 EGDMA	Reduction of aromatic ketones [50,51]
 **9**	 EGDMA	Reduction of aromatic ketones [51]
 **10**	 EGDMA	Reduction of aromatic ketones [52]
 **11**	 EGDMA	Reduction of aromatic ketones [52]

Table 1 (*Continued*)

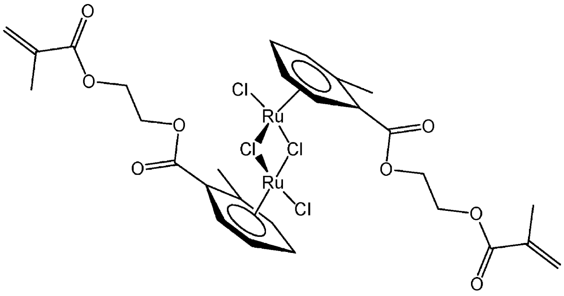
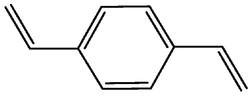
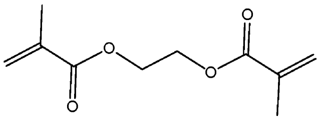
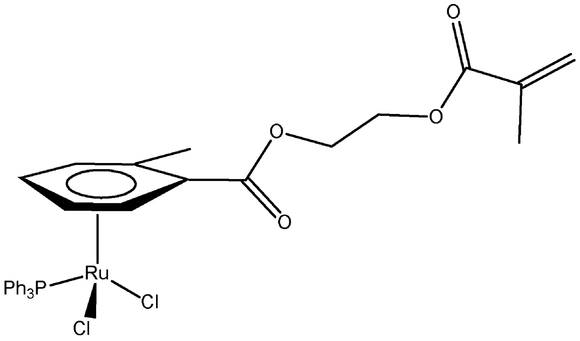
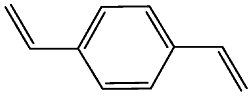
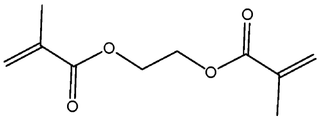
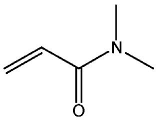
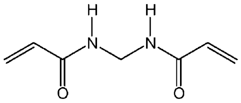
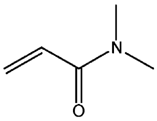
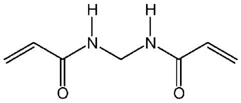
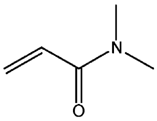
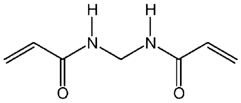
Metal containing monomer	Co-monomers	Use in Catalysis
 **12**	 DVB or  EGDMA	Reduction of aromatic ketones [53]
 **13**	 DVB or  EGDMA	Reduction of aromatic ketones [53]
Fe(aaema)$_3$ **14**	 DMAA and  MBAA	Epoxidation [56,57], oxidation [58] and coupling between acyl chlorides and Grignard reagents [87]
Ni(aaema)$_2$ **15**	 DMAA and  MBAA	Epoxidation [56,57] and Michael addition [86]
Co(aaema)$_2$ **16**	 DMAA and  MBAA	Epoxidation [56,57], oxidation [58–62], and Michael addition [86]

Table 1 (*Continued*)

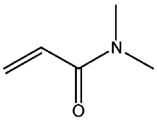
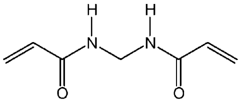
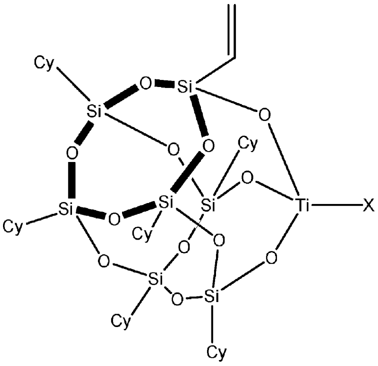
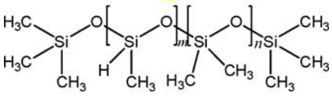
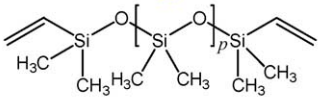
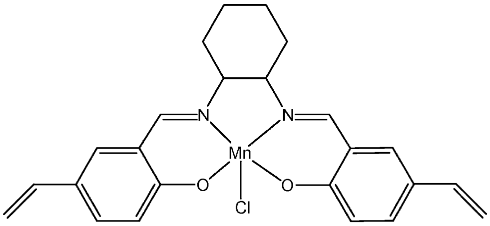
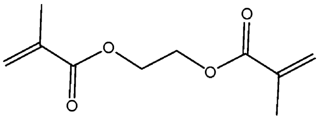
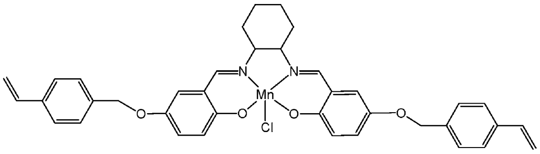
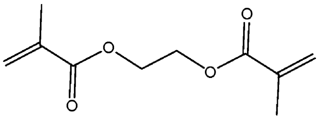
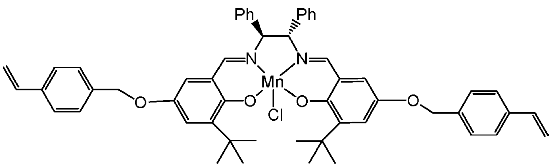
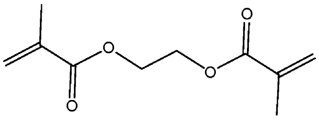
Metal containing monomer	Co-monomers	Use in Catalysis
Cu(aaema)$_2$ **17**	 DMAA and  MBAA	Oxidative coupling of 2-naphthol [63]
 **a**: x = η^5-C_5H_5 **b**: x = OiPr **18 a-b**	 HMS-301 Mw = 1900-2000 m = 6.4 n = 19.3 and  DMS-V05 Mw = 770, p = 7.7	Epoxidation [64]
 **19**	 EGDMA	Epoxidation [67]
 **20**	 EGDMA	Epoxidation [67]
 **21**	 EGDMA	Chiral epoxidation [68,69]

Table 1 (*Continued*)

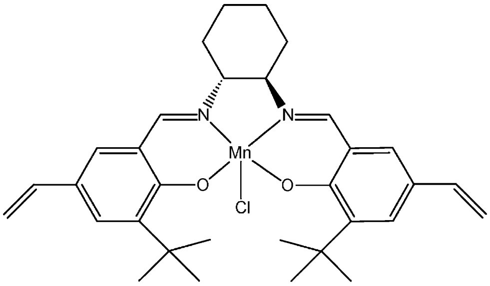
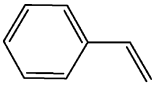
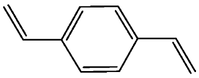
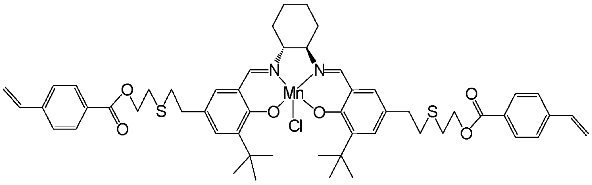
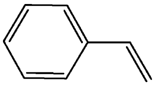
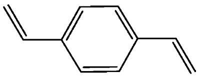
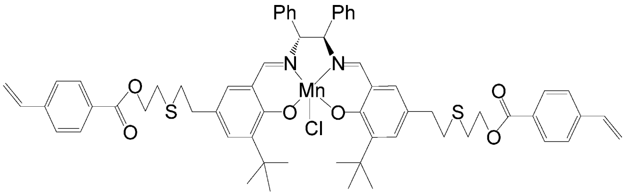
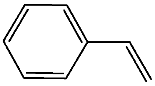
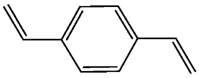
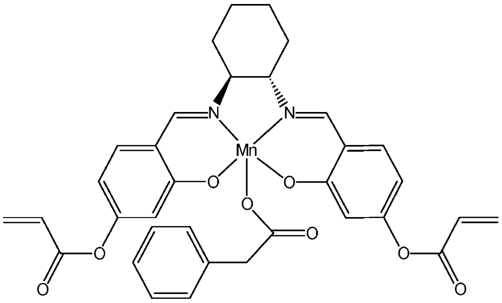
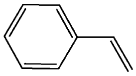
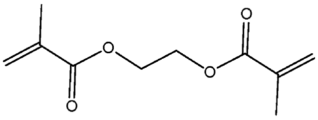
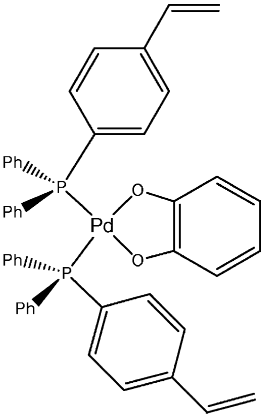
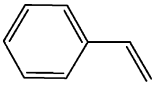
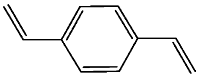
Metal containing monomer	Co-monomers	Use in Catalysis
 **22**	 and  DVB	Chiral epoxidation [70]
 **23**	 and  DVB	Chiral epoxidation [71]
 **24**	 and  DVB	Chiral epoxidation [71]
 **25**	 and  EGDMA	Chiral epoxidation [72]
 **26**	 and  DVB	Stille and Suzuki cross-coupling [76]

Table 1 (*Continued*)

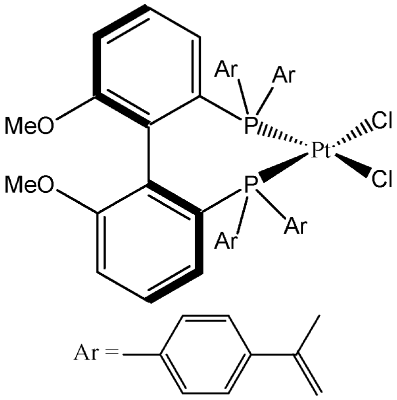
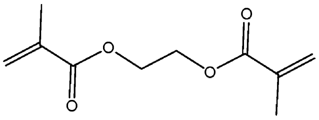
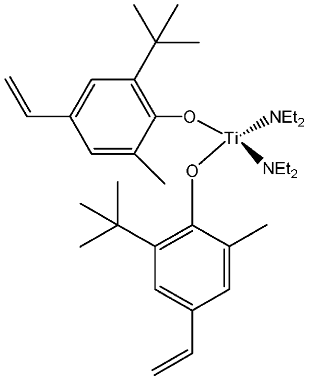
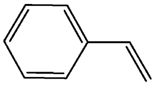
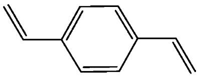
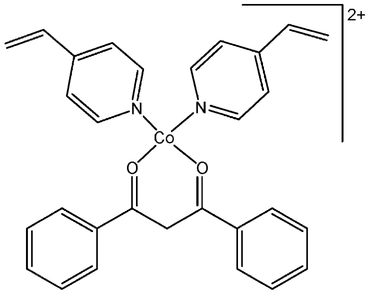
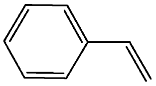
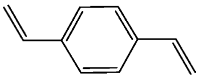
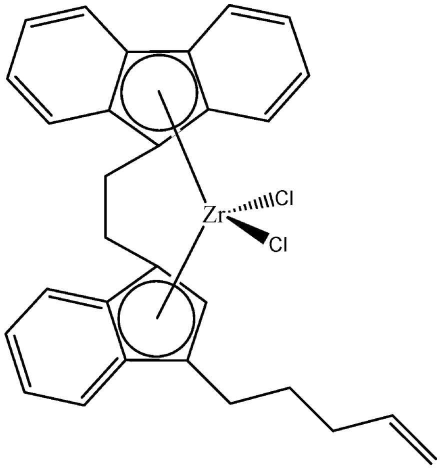
Metal containing monomer	Co-monomers	Use in Catalysis
 **27**	 EGDMA	Ene reaction [78]
 **28**	 and  DVB	Diels–Alder reaction [79]
 **29**	 and  DVB	Aldol condensation [80]
 **30**	–	Ethylene polymerization [81]

Table 1 (*Continued*)

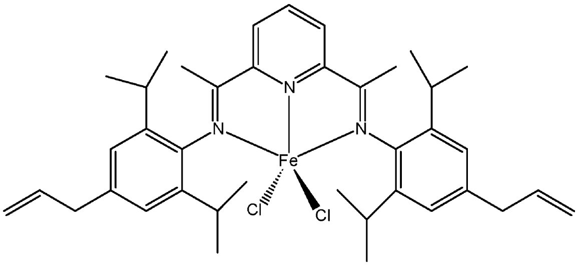
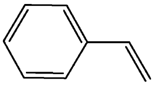
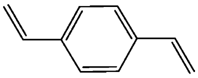
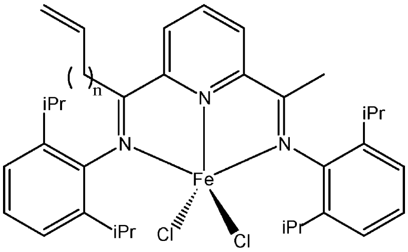
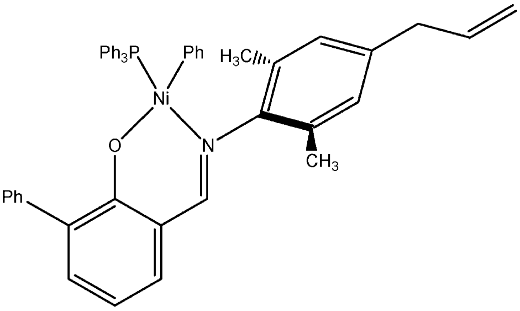
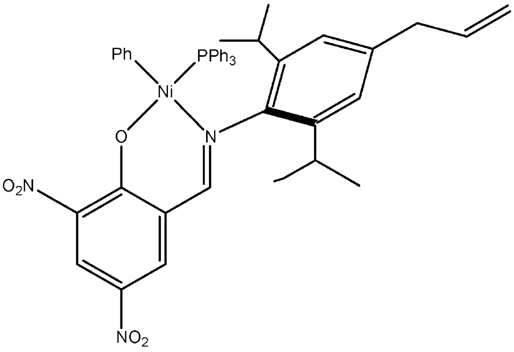
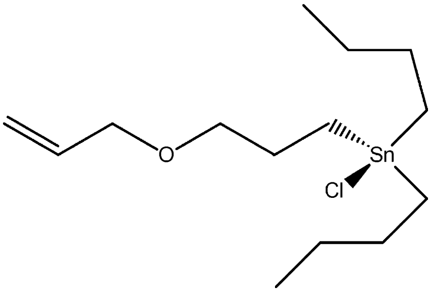
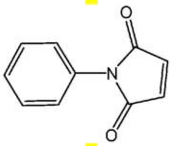
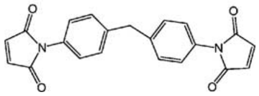
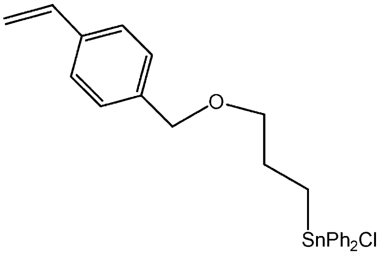
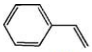
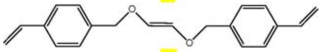
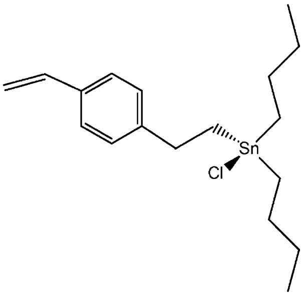
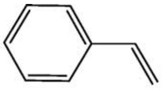
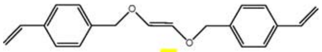
Metal containing monomer	Co-monomers	Use in Catalysis
 **31**	 and  DVB	Ethylene polymerization [82]
 **32** n = 2, 3, 4	–	Ethylene polymerization [83]
 **33**	–	Ethylene polymerization [84]
 **34**	–	Ethylene polymerization [85]

Table 1 (*Continued*)

Metal containing monomer	Co-monomers	Use in Catalysis
 **35**	 and/or 	Reduction of 1-bromoadamantane [95]
 **36**	 and 	Reduction of 1-bromoadamantane [96]
 **37**	 and  DVB or 	Reduction of 1-bromoadamantane and radical cyclization [94,97]

An active and reusable palladium based catalyst was obtained by co-polymerizing Pd(aaema)$_2$ (**4**) with EMA and EGDMA [44]. Olefins, alkynes, α,β-unsaturated aldehydes, citral, carvone, and nitro compounds were hydrogenated at ambient conditions with yields exceeding 90% in most cases (Table 4) [47]. Benzaldehyde required 10 bar H_2 to be transformed first into benzyl alcohol ($t = 1$ h) and then into toluene (4 h).

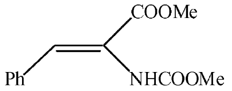
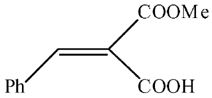
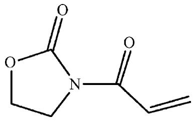
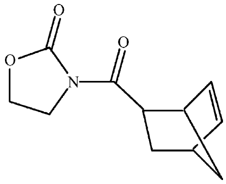
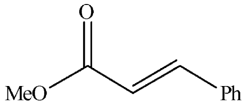
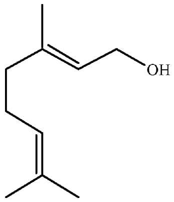
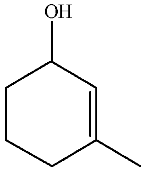
Ruthenium(II) was supported onto an acrylamidic resin by co-polymerization of Ru(PPh$_3$)$_2$(aaema)$_2$ (**5**) with DMA and MBAA [48]. The resulting material was used in the hydrogenation of alkenes, alkynes, and aldehydes under 10–35 bar H_2, with turn over frequency (t.o.f.) ranging from 3.2 to 16 h^{-1} (Table 5).

An important field in which MCMs have recently been employed as a source of catalytically active centers is molecular imprinting [49]. The strategy used for molecular imprinting is the co-polymerization of a MCM bearing the imprint species with suitable co-monomers and cross-linkers. Removal of the imprint species produces sites topographically complementary to the print species in terms of shape and chemical functionalities. Following this approach Severin's group has described the activity and selectivity of Ru-based imprinted co-polymers poly-**6**–**9** towards the reduction of benzophenone [50,51], and the enantioselective reduction of aromatic ketones by supported Rh (poly-**10**–**11**) [52] or Ru (poly-**12**–**13**) [53] catalysts.

3. Oxidation reactions

Transition metal catalyzed oxidations have recently received much interest [54] because of the potential selectivity which can be attained using suitable metal complexes. Since

Table 2
Hydrogenation of unsaturated substrates catalyzed by supported complex poly-**1**

Entry	Substrate	*P* (bar)	Time (h)	Yield (%)
1		1	6	93
2		6.8	12	93
3		1	3.5	99
4		10	3	99
5		10	24	97
6		2	10	96
7		10	18	88

the discovery of Mukaiyama that olefins can be epoxidized using a catalytic system comprised of a β-diketonato complex, dioxygen and a sacrificial aldehyde [55], much effort has been devoted to the application of this catalytic system to the oxidation of several organic substrates. In this framework, the materials obtained by the co-polymerization of the MCMs Fe(aaema)$_3$ (**14**), Ni(aaema)$_2$ (**15**), and Co(aaema)$_2$ (**16**) with suitable co-monomers have been used as heterogeneous catalysts for the aerobic epoxidation of olefins in the presence of a sacrificial aldehyde [56] (Table 6).

Notably, cyclic olefins are smoothly epoxidized with yields ranging from 86 to 100%. Moreover, the stereoselectivity observed in the epoxidation of cholesteryl acetate was

Table 3
Hydrogenation of unsaturated substrates catalyzed by supported complex poly-**2** at ambient pressure of H_2 and r.t.

Entry	Substrate	Product (% yield)	t.o.f. (h^{-1})
1	1-Heptene	*n*-Heptane (>99)	40
2	Cyclohexene	Cyclohexane (>99)	80
3	(–)-Carvone	Carvotanacetone (77)	25
4	Citral	Citronellal (64)	2.6
5[a]	Cinnamaldehyde	3-Phenylpropanal (68)	19
6[a]	Valeronitrile	Dipentylamine (85)	27
7	Nitrobenzene	Aniline (>99)	8.9

[a] At 20 bar H_2.

Table 4
Hydrogenation of unsaturated substrates catalyzed by the supported complex poly-**4** at ambient pressure of H_2 and r.t.

Entry	Substrate	Product (% yield)	t.o.f. (h^{-1})
1	1-Heptene	*n*-Heptane (>99)	80
2	Cyclohexene	Cyclohexane (>99)	80
3	1-Octyne	*n*-Octane (99)	32
4	Phenylacetylene	Ethylbenzene (99)	23
5	Diphenylacetylene	1,2-Diphenylethane (>99)	29
6	2-Cyclohexen-1-one	Cyclohexanone (91)	80
7	2-Cyclopenten-1-one	Cyclopentanone (>99)	53
8	Cinnamaldehyde	3-Phenylpropanal (83)	4.8
9	Citral	Citronellal (70)	15
10	(–)-Carvone	Carvomenthone (70)	23
11[a]	Benzaldehyde	Benzyl alcohol (95)	160
12[a]	Benzaldehyde	Toluene (>99)	40
13	Nitrobenzene	Aniline (>99)	63
14	2-Nitrotoluene	*o*-Toluidine (>99)	63
15	2,4-Dinitrotoluene	2,4-Diaminotoluene (>99)	3.3

[a] At 10 bar H_2.

Table 5
Hydrogenation of unsaturated substrates catalyzed by the supported complex poly-**5** at 65 °C

Entry	Substrate	*P* (bar)	Product (% yield)	t.o.f. (h^{-1})
1	Cyclohexene	10	Cyclohexane (95)	16
2	1-Heptene	20	*n*-Heptane (100)	16
3[a]	Benzaldehyde	35	Benzyl alcohol (93)	6.0
4	Cinnamaldehyde	35	3-Phenyl-1-propanol (87)	4.0
5	2-Hexenal	35	Hexanol (95)	4.0
6	Phenylacetylene	35	Ethylbenzene (>99)	4.0
7	Diphenylacetylene	35	Stilbenes (>99)	3.2

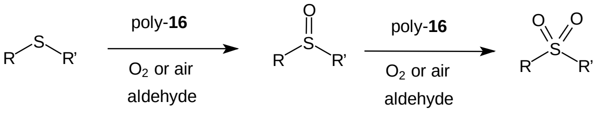
[a] At 80 °C.

Table 6
Catalytic epoxidation of alkenes by supported complexes poly-**14**, poly-**15**, and poly-**16** under Mukaiyama's conditions

Entry	Substrate	MCP	Time (h)	Yield (%)
1	Norbornene	Fe(III)	46	>99
2	Norbornene	Ni(II)	46	98
3	Norbornene	Co(II)	46	93
4	Cyclohexene	Fe(III)	40	>99
5	Cyclohexene	Ni(II)	40	86
6	Cyclohexene	Co(II)	40	>99
7	Cholesteryl acetate	Fe(III)	24	>99
8	Cholesteryl acetate	Ni(II)	24	>99
9	Cholesteryl acetate	Co(II)	24	95
10	1-Octene	Fe(III)	45	43
11	1-Octene	Ni(II)	45	28
12	1-Octene	Co(II)	45	26

Table 7
Aerobic oxidation of α-hydroxyketones by supported complexes poly-**16** and poly-**14** under Mukaiyama's conditions

Entry	Substrate	MCP	Yield (%)
1	Anisoin	Co(II)	87
2	Anisoin	Fe(III)	65
3	Benzoin	Co(II)	94
4	Benzoin	Fe(III)	95
5	4,4′-Dimethyl-benzoin	Co(II)	66
6	4,4′-Dimethyl-benzoin	Fe(III)	46



Scheme 2. Aerobic oxidation of sulfides by supported cobalt complex.

in all cases directed towards the formation of the β-epoxide, whereas using the relevant MCM as homogeneous catalyst, no stereoselectivity was observed [57]. The heterogeneous catalytic systems were recyclable without loss of activity except for the epoxidation of open chain olefins.

Supported complexes poly-**14** and poly-**16** have been used as heterogeneous catalysts for the aerobic oxidation of α-hydroxyketones to α-diketones under Mukaiyama's conditions [58] (Table 7). The supported Co(II) catalyst poly-**16** was more active then the corresponding Fe(III) based poly-**14**. Both catalysts were easily separable from the reaction mixture and recyclable.

The use of a sacrificial aldehyde in combination with molecular oxygen and a metal β-ketoesterate was also applied to the selective oxidation of sulfides to sulfoxides or sulfones [27,28], Co(II) being outstanding in terms of activity and selectivity. The supported complex poly-**16** was therefore employed as a recyclable heterogeneous catalyst for the selective oxidation of disubstituted sulfides to sulfoxides and sulfones under Mukaiyama's conditions [59] (Scheme 2 and Table 8). When dried air was used as oxidant in place of pure dioxygen the reaction was more selective towards the formation of the intermediate sulfoxide.

The reaction conditions optimized for monosulfides have been applied to the oxidation of bis-sulfides. The catalytic system air/supported cobalt/aldehyde was used for the regioselective oxidation of 2-(2-*p*-tolylsulfanyl-ethylsulfanyl)-benzothiazole yielding the corresponding sulfoxide 2-[2-(toluene-4-sulfinyl)-ethylsulfanyl]-benzothiazole in 93% yield [60] (Scheme 3).

Table 8
Aerobic oxidation of sulfides by supported complex poly-**16** under Mukaiyama's conditions

Entry	Substrate	Oxidant	Time (h)	Yield in sulfoxide (%)	Yield in sulfone (%)
1	$(CH_3)_2S$	Air	8	80	–
2	$(CH_3)_2S$	Air	20	–	>99
3	$(n\text{-Bu})_2S$	Air	21	83	10
4	$(n\text{-Bu})_2S$	Air	37	8	92
5	$(t\text{-Bu})_2S$	O_2	3	–	>99
6	$(PhCH_2)_2S$	O_2	8	–	>99
7	*p*-Tol-S-CH_3	O_2	2	–	>99

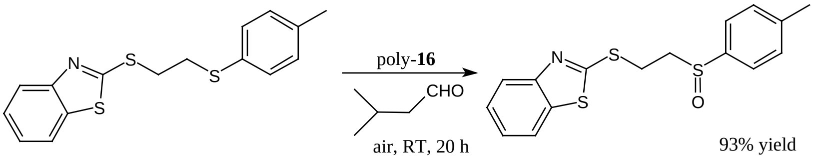
Supported complex poly-**16** was also used as a recyclable heterogeneous catalyst for the oxidation of triphenylphosphine to the corresponding oxide [61], and for the oxidation of benzylic and secondary alcohols [62] (Table 9). In the latter reaction, yields higher than 65% were obtained in times ranging from 2 to 9 h.

The oxidation of di-*t*-butylphenol using the supported complex poly-**16** resulted in a mixture of the corresponding quinone (37% yield) and diphenoquinone (31%) (Scheme 4).

The supported copper complex poly-**17**, obtained from co-polymerization of Cu(aaema)$_2$ with DMAA and MBAA, was reported active in the oxidative coupling of 2-naphthol [63] (Scheme 5).

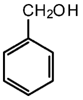
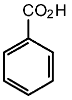
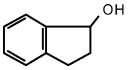
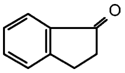
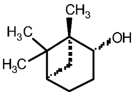
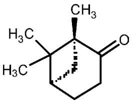
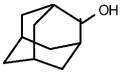
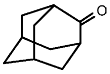
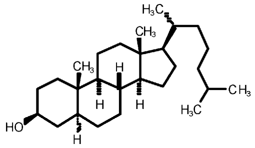
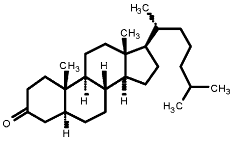
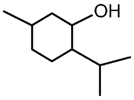
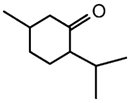
Interesting catalysts for heterogeneous oxidations have been obtained by suitable polymerization of the titanium(IV) silsesquioxanes **18a**–**b**. The polymers so obtained were tested as catalysts for the epoxidation of cyclooctene with equimolar amounts of *t*-butylhydroperoxide [64]. The most active system was obtained for **18b** (epoxide yield 73%). Cyclododecene and 1-octene could also be epoxidized with this titanium(IV) supported catalyst using hydrogen peroxide as oxidant with yields of 45 and 62%, respectively.

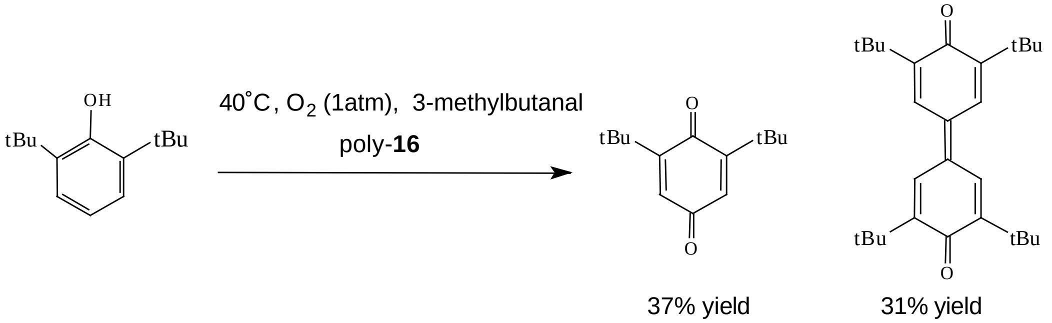
Stereoselective oxidations are among the most useful organic transformations and, in particular, olefin chiral epoxidation can be considered a key step for the synthesis of pharmaceuticals and biologically active compounds. Therefore almost parallel to the discovery of chiral Mn(III)-salen complexes as olefin epoxidation catalysts [65,66], efforts have been devoted to the immobilization of these catalysts onto an organic or inorganic support, mainly aiming at potential catalyst recycling and minimization of deactivation pathways. The polymerization of MCM is one of the strategies which has been used to synthesize manganese(III)-salen supported complexes. An early result was obtained by Dahl and coworkers [67] who synthesized for preliminary studies



Scheme 3. Regioselective oxidation of a bis-sulfide by supported cobalt complex.

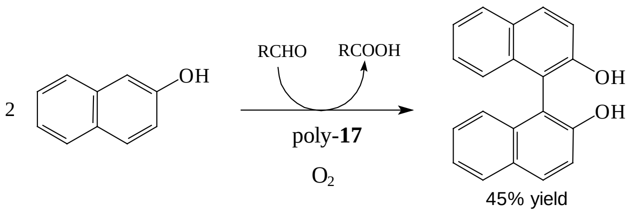
Table 9
Aerobic oxidation of alcohols by supported complex poly-**16** under Mukaiyama's conditions

Entry	Substrate	Product	Time (h)	Yield (%)
1			6	94
2			2	99
3			4	97
4			7	95
5			7	86
6			9	75

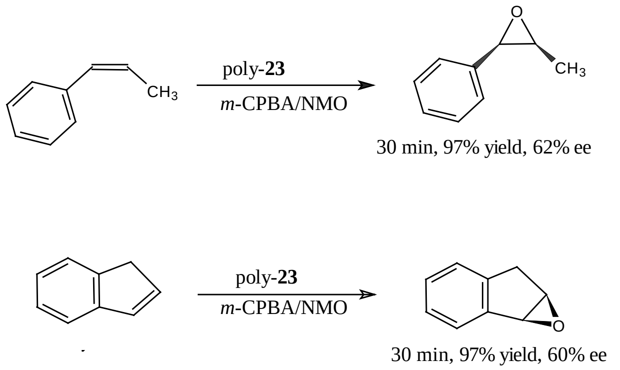


Scheme 4. Aerobic oxidation of di-*t*-butylphenol by supported cobalt complex.

the racemic MCMs **19** and **20** and tested their activity in the epoxidation of several substrats by PhIO. Lower activity was observed for the heterogeneous catalysts poly-**19** and poly-**20**: an induction period of 30 min was measured and ca. 24 h were required to bring the reaction to acceptable conversions. Notwithstanding these drawbacks, in most cases, the reaction catalyzed by the MCP selectively yielded the corresponding epoxides. The better selectivity observed was ascribed to defined structures and site isolation of metal centers in the polymer matrix. As a development of this work the Mn(III) containing vinyl monomer **21** bearing a rigid *t*-butyl group in the *ortho* position respect to the phenoxide group was synthesized [68,69]. Complex **21** was co-polymerized with EGDMA and turned out to be active, although poorly enantioselective. The best results were obtained in the epoxidation of dihydronaphthalene (68% yield, 30% ee). The low enantioselectivity observed with poly-**21** was counterbalanced by an increase in chemical stability: the supported metal complex retained its catalytic activity for at least five cycles. A quite similar approach was reported by Salvadori and coworkers [70] who used the Mn(III) containing monomer **22** co-polymerized with styrene and DVB. Using various oxidants, styrene and *cis* β-methylstyrene were smoothly epoxidized, although enantioselectivities did not exceed 41%. Also in this case the catalyst retained its activity and selectivity unmodified for five cycles. As a follow-up of this work [71], the MCMs **23** and **24** were synthesized, in which the vinyl moiety is spaced from the metal complex.



Scheme 5. Aerobic oxidation of 2-naphthol by supported copper complex.



Scheme 6. Enantioselective epoxidations by supported manganese complex.

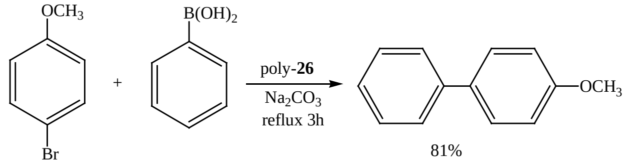
After co-polymerization with styrene and DVB, poly-**23** and poly-**24** gave better ee's compared with poly-**22** (Scheme 6).

As a general trend, the heterogeneous Mn(III)-salen complexes obtained from MCM polymerization showed lower enantioselectivities with respect to their homogeneous counterparts. This was ascribed to a perturbation of the catalyst–substrate interaction due to the polymeric matrix. An attempt was put forward in this respect [72] by co-polymerizing the Mn(III) complex **25** containing the phenylacetate moiety co-ordinated to the metal in order to "imprint" the polymer with a cavity aimed at a non-constrained approach of the real substrate. After removal of the template the heterogeneous catalyst was used in the epoxidation of styrene by *m*-CPBA or PhIO. Although the catalyst was active and recyclable, its enantioselectivity did not exceed 14%.

4. C–C bond forming reactions

Transition metal catalyzed C–C bond forming reactions represent some of the most powerful and versatile tools available for synthetic organic chemistry [73,74]. Until recently, nearly all reports of polymer supported metal catalyzed C–C bond forming process describe the use of insoluble catalysts obtained by reaction between macromolecular ligands and transition metal salts or complexes (route *a* of Scheme 1). There are only few examples of supported catalysts synthesized via polymerization of MCM and suitable co-monomers and cross-linkers (route *b* of Scheme 1). A crucial issue for this class of reactions is the leaching of the metal from the polymeric matrix (whatever the synthetic procedure) which, in many cases, renders the reaction mechanism homogeneous [75]. However the catalyst can be recycled if a controlled release of a little amount of soluble catalytically active species warrants the necessary amount of catalyst in order to trigger the reaction in subsequent cycles.

Cammidge and coworkers [76] carried out a comparative studies on two polymer supported triphenylphosphine palladium complexes in Stille and Suzuki reactions. The first MCP was prepared from commercial polystyrene bound triphenylphosphine treated with K_2PdCl_4, whereas the second MCP was obtained by polymerization of the Pd(II) MCM **26**. These studies highlighted a higher activity of the supported catalyst prepared via route *b* respect to that synthesized via route *a*. The authors ascribe this behavior to the easier tunability of the reactive site in the MCM, in which the two polymerizable phosphine ligands were co-ordinated in a *cis*-square planar geometry on the palladium(II) center, thus favoring the catalytic cycle [77]. In the reaction between *p*-bromoanisole and phenylboronic acid (Scheme 7) the catalyst prepared via route *a* led to a 56% yield, while the catalyst prepared via route *b* led to a consistently higher yield (81%). The $PdCl_2/PPh_3$ homogeneous system gave a yield (55%) comparable with that obtained using the commercial polymeric ligand. Recycling the insoluble catalyst obtained via route *a* led to a slight reduction of the yield, while the MCP prepared by route *b* was recyclable without loss of activity.

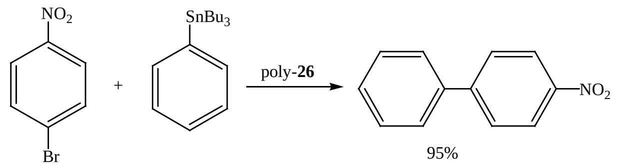


Scheme 7. Suzuki reaction promoted by supported palladium complex.

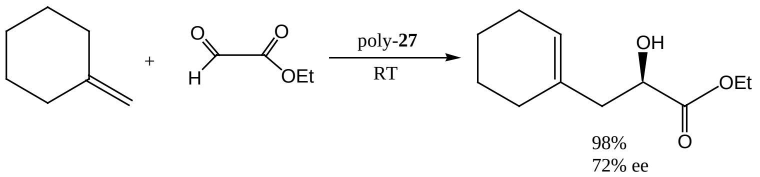
In the Stille coupling of 4-nitrobromobenzene with tributylphenyltin (Scheme 8) the catalyst prepared via route *a* was inactive, while MCP poly-**26** yielded 95% of 4-nitrobiphenyl.

Another example of MCM bearing polymerizable phospanyl ligands is the [(*S*)-MeObiphepPtCl$_2$] complex (**27**) used in asymmetric catalysis by molecular imprinting [78]. The process of interest is the ene reaction between methylenecyclohexane and ethyl glyoxylate (Scheme 9) and the best results (98% conversion, 72% ee) were obtained using (*S*)-BINOL as templating agent. In another work, Gagné and coworkers [79] used the molecular imprinting technique to incorporate the titanium(IV) complex **28** containing polymerizable aryloxide ligands into a rigid and porous polystyrene/DVB-based matrix to yield a polymer which, after replacement of chlorides for the NEt$_2$ groups, acted as a catalyst for the Diels–Alder reaction (Scheme 10).

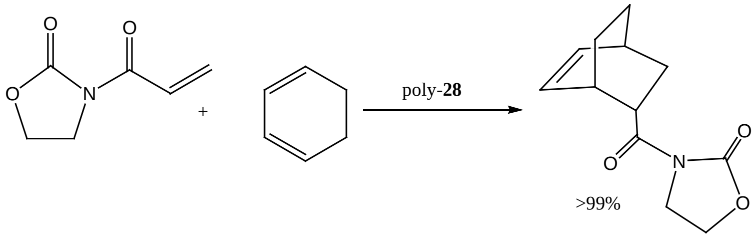
A MCP embodying dibenzoylmethane as templating agent, obtained by polymerization of the Co(II) complex **29**, was used in the aldol condensation of acetophenone and benzaldehyde to yield chalcone (Scheme 11) [80].



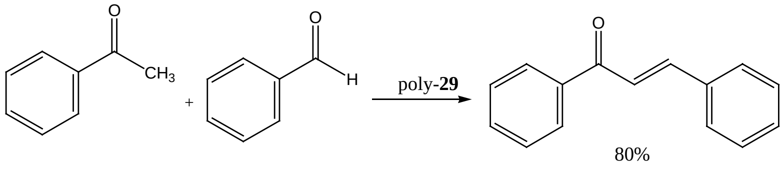
Scheme 8. Stille reaction promoted by supported palladium complex.



Scheme 9. Ene reaction promoted by supported platinum complex.



Scheme 10. Diels–Alder reaction promoted by supported titanium complex.

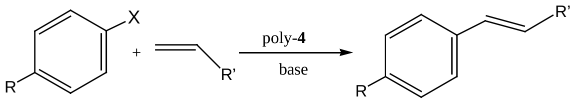


Scheme 11. Aldol condensation promoted by supported cobalt complex.

Heterogenization of catalysts for olefin polymerization has also recently been achieved by using MCMs. In these cases the MCM, initially homogeneously dispersed in the olefin slurry, undergoes co-polymerization with the substrate yielding a “self-immobilized” MCP, which acts as a heterogeneous catalyst, thus avoiding the drawbacks of fouling on the reactor walls. The first example of this heterogenization strategy was applied by Alt [81], who used titanium, zirconium and hafnium metallocenes as co-monomers in ethylene polymerization. The length of the polymerizable alkenyl substituent on the metallocene complexes determines the activity of the catalyst and the molecular weight of the resulting polyethylene. The highest activity was obtained with complex **30** bearing a 5-pentenyl substituent.

Other “self-immobilized” catalysts were obtained from 2,6-bis(imino)pyridyl iron(II) complexes **31**–**32**, and salicylaldimate phenyl nickel(II) complexes **33**–**34** which were used in ethylene polymerization [82–85].

The MCPs obtained from complexes Ni(aaema)$_2$ (**15**) and Co(aaema)$_2$ (**16**) were also used as heterogeneous catalysts for Michael addition reactions (Scheme 12) [86].



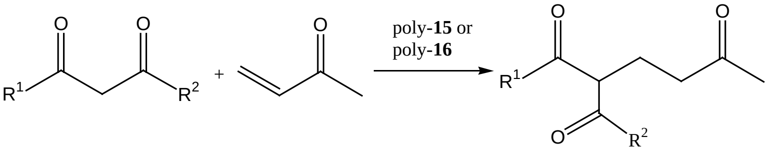
X = I, Br
R = H, CH_3, NO_2, $COCH_3$
R' = $COOCH_3$, CN, C_6H_5

Scheme 13. Heck reaction catalyzed by supported palladium complex.

Among the two supported metals, Co(II) turned out to be more active than Ni(II) (Table 10).

Supported Fe(III) complex poly-**14** catalyzed the coupling reaction between acyl chlorides and Grignard reagents, affording ketones with yields up to 96% at room temperature [87].

Supported Rh(I) poly-**2** was also employed as the first heterogeneous catalyst for the polymerization of phenylacetylene and *p*-tolylacetylene [88]. The supported complex is more active than its homogeneous analogue (cod)Rh(aaema) (**2**) yielding 98% of poly(phenylacetylene) in thf. The



$R^1 = R^2 = CH_3$
$R^1 = CH_3$, $R^2 = OCH_3$
$R^1 = R^2 = OC_2H_5$

Scheme 12. Michael addition promoted by supported nickel or cobalt complexes.

Table 10
Addition of Michael donors to methyl vinyl ketone by supported complexes poly-**15** and poly-**16** at 75 °C

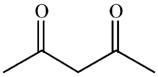
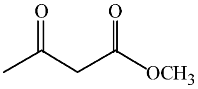
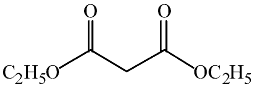
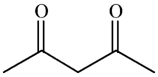
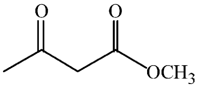
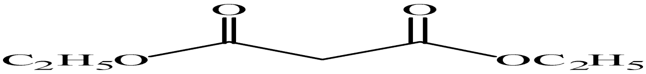
Entry	Michael donor	Supported metal	Time (h)	Yield (%)
1		Ni(II)	46	66
2		Ni(II)	19	92
3		Ni(II)	92	34
4		Co(II)	19	88
5		Co(II)	19	97
6		Co(II)	39	68

Table 11
Heck coupling reactions of aryl halides catalyzed by supported poly-**4**

Entry	Aryl halide	Alkene	t.o.f. (h^{-1})
1	Iodobenzene	Styrene	167
2	Iodobenzene	Acrylonitrile	167
3	Iodobenzene	Methyl acrylate	500
4	*p*-Iodotoluene	Styrene	250
5	*p*-Iodotoluene	Acrylonitrile	167
6	*p*-Iodotoluene	Methyl acrylate	250
7[a]	Bromobenzene	Styrene	42
8[a]	*p*-Bromonitrobenzene	Styrene	50
9[a]	*p*-Bromoacetophenone	Styrene	50

[a] In the presence of DMG.

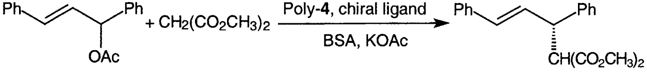
heterogeneous nature of the catalyst seems to affect the morphology of the product [89].

Supported Pd(aaema)$_2$ (poly-**4**) was used as phosphane-free catalyst for the Heck reaction of aryl iodides and bromides with different olefins, in the presence of potassium or sodium acetate as base (Scheme 13) [90].

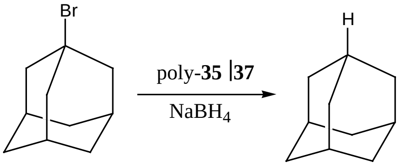
Table 11 summarizes the results obtained in poly-**4** promoted Heck reactions of aryl iodides and bromides with different olefins.

In all cases the MCPs recovered were employed in subsequent runs with slight loss of activity. However, when the reaction mixture was hot filtered at 20% conversion, the activity of the mother liquor was comparable to that of fresh poly-**4**. On the contrary, the activity of the mother liquors was negligible when the filtration was carried out after aryl iodide consumption. It was concluded that poly-**4** acted as

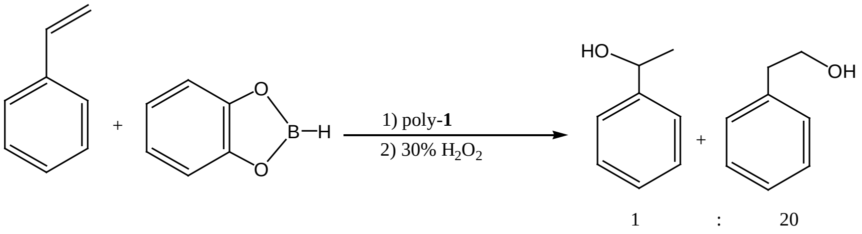
Table 12
Asymmetric allylic alkylation of *rac*-1,3-diphenyl-2-propenyl acetate with dimethyl malonate catalyzed by poly-**4**



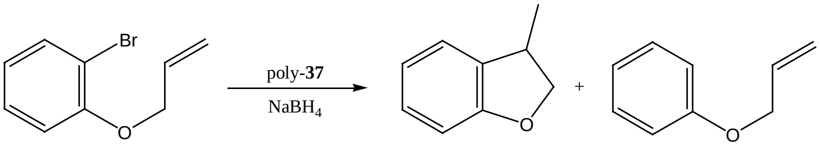
Entry	Chiral ligand	Time (h)	Yield (%)	ee (%)
1	(*R*,*S*)-PPFA	14	80	60
2	(*R*,*S*)-JOSIPHOS	96	90	93
3	(*R*,*R*)-NORPHOS	14	60	69



Scheme 15. Reduction of bromoadamantane promoted by supported organotin compound.



Scheme 14. Hydroboration of styrene promoted by supported rhodium complex.



Scheme 16. Radical cyclization of 1-bromo-2-(prop-2-enyloxy)benzene promoted by supported organotin compound.

a reservoir of catalytically active palladium soluble species, which deactivated when the aryl halide was consumed [91].

A homogeneous mechanism was found to be operating also in the asymmetric allylic alkylation reaction [92] promoted by poly-**4** in the presence of chiral ligands [93], such as [(*R*,*S*)-PPFA], [(*R*,*S*)-JOSIPHOS], [(*R*,*R*)-NORPHOS]. Table 12 summarizes the results obtained in the reaction between *rac*-1,3-diphenyl-2-propenyl acetate with dimethyl malonate in the presence of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and a catalytic amount of KOAc.

The system reached a maximum enantioselectivity of 93% but suffered from severe metal leaching.

5. Other reactions

The co-polymer of rhodium complex **1** has been used in the hydroboration of styrene to give, after oxidative workup, good yields of phenylethanols [42] (Scheme 14).

Deleuze and coworkers [94–97] have synthesized several polymerizable organotin chlorides **35**–**37**, the co-polymers of which turned out to be active catalysts for the reduction of bromoadamantane by sodium borohydride (Scheme 15) and for the radical cyclization of 1-bromo-2-(prop-2-enyloxy)benzene [97] (Scheme 16).

6. Conclusions

Polymerization of MCM remains nowadays a valuable tool for the synthesis of supported catalyst. In the last few years, several examples of their application have been put forward, covering the most important reaction classes. Chemical homogeneity of the active center and potential tailoring of the support properties are recognized points of strength of the MCM co-polymerization concept. A more extensive application of these advantages can be expected not only in catalysis but also in other areas of interest (i.e. as electrode modifiers or luminescent materials), where combining the features of a well-defined metal center with the processability of a polymer matrix could bring about the necessary breakthrough for large scale production.

Acknowledgements

The authors thank Prof. G.P. Suranna, Dr. M.M. Dell'Anna and Dr. G. Romanazzi for helpful discussions and suggestions.

References

[1] F.R. Hartley, Supported Metal Complexes, D. Reidel Publishing Company, Dordrecht, 1985.

[2] F. Lefebvre, J. Thivolle-Cazat, V. Dufaud, G.P. Niccolai, J.M. Basset, Appl. Catal. A 182 (1999) 1.

[3] J.M. Basset, F. Lefebvre, C. Santini, Coord. Chem. Rev. 178–180 (1998) 1703.

[4] J. Guzman, B.C. Gates, Dalton Trans. (2003) 3303.

[5] C.E. Song, S.-G. Lee, Chem. Rev. 102 (2002) 3495.

[6] A.K. Kakkar, Chem. Rev. 102 (2002) 3579.

[7] I.F.J. Vankelecom, P.A. Jacobs, in: D.E. De Vos, I.F.J. Vankelecom, P.A. Jacobs (Eds.), Chiral Catalyst Immobilization and Recycling, Wiley-VCH, Weinheim, 2000, p. 19.

[8] W.O. Haag, D.D. Whitehurst, German Patent 1,800, 371; Chem. Abs. 71 (1969) 114951.

[9] H. Sajiki, T. Ikawa, H. Yamada, K. Tsubouchi, K. Hirota, Tetrahedron Lett. 44 (2003) 171.

[10] K. Huang, L. Xue, Y.-C. Hu, M.-Y. Huang, Y.-Y. Jiang, React. Funct. Polym. 50 (2002) 199.

[11] K. Huang, L. Xue, Y.-C. Hu, M.-Y. Huang, Y.-Y. Jiang, Polym. Adv. Technol. 13 (2002) 165.

[12] C.-C. Guo, G. Huang, X.-B. Zhang, D.-C. Guo, Appl. Catal. A 247 (2003) 261.

[13] J. Zhang, C.-G. Xia, J. Mol. Catal. A 206 (2003) 59.

[14] A.D. Pomogailo, Catalysis by Polymer-Immobilized Metal Complexes, Gordon and Breach, New York, 1998.

[15] F. Embert, A. Mehdi, C. Reyè, R.J.P. Corriu, Chem. Mater. 13 (2001) 4542.

[16] D.A. Friesen, T. Kajita, E. Danielson, T.J. Meyer, Inorg. Chem. 37 (1998) 2756.

[17] S.P. Hendry, M.F. Cardosi, A.P.F. Turner, E.W. Neuse, Anal. Chim. Acta 281 (1993) 453.

[18] G.N.A. Nallas, K.J. Brewer, Inorg. Chim. Acta 257 (1997) 27.

[19] C.N. Myer, C.W. Allen, Polym. Prepr. 41 (2000) 558.

[20] T. Yamazaki, E. Yilmaz, K. Mosbach, K. Sode, Anal. Chim. Acta 435 (2001) 209.

[21] R.D. Archer, B. Wang, Chem. Mater. 5 (1993) 317.

[22] B. Wang, R.D. Archer, Polym. Mater. Sci. Eng. 59 (1988) 120.

[23] R.D. Archer, B. Wang, Polym. Mater. Sci. Eng. 61 (1989) 101.

[24] R.D. Archer, B. Wang, Polym. Mater. Sci. Eng. 60 (1989) 710.

[25] N.E. Leadbeater, M. Marco, Chem. Rev. 102 (2002) 3217, and references therein.

[26] C. A McNamara, M.J. Dixon, M. Bradley, Chem. Rev. 102 (2002) 3275, and references therein.

[27] R. Giannandrea, P. Mastrorilli, C.F. Nobile, G.P. Suranna, J. Mol. Catal. 94 (1994) 27.

[28] P. Mastrorilli, C.F. Nobile, Tetrahedron Lett. 35 (1994) 4193.

[29] L. Lopez, P. Mastrorilli, G. Mele, C.F. Nobile, Tetrahedron Lett. 35 (1994) 3633.

[30] N.M. Brunkan, M.R. Gagnè, J. Am. Chem. Soc. 122 (2000) 6217.

[31] P. Mastrorilli, C.F. Nobile, G.P. Suranna, L. Lopez, Tetrahedron 51 (1995) 7943.

[32] A.D. Pomogailo, V.S. Savost'yanov, Polymerization of Metal Containing Monomers, CRC Press, 1994, ISBN 0-8493-2863-2.

[33] G.I. Dzhardimalieva, A.D. Pomogailo, Kinet. Catal. 39 (1998) 821.

[34] A.S. Rozenberg, A.V. Raevskii, E.I. Aleksandrova, O.I. Kolesova, G.I. Dzhardimalieva, A.D. Pomogailo, Russ. Chem. Bull. Int. Ed. 50 (2001) 901.
[35] A.S. Rosenberg, G.I. Dzhardimalieva, A.D. Pomogailo, Polym. Adv. Technol. 9 (1998) 527.
[36] A.D. Pomogailo, V.F. Razumov, I.S. Voloshanovskii, J. Porphyrins Phthalocyanines 4 (2000) 45.
[37] D. Wohrle, J. Porphyrins Phthalocyanines 4 (2000) 418.
[38] G.I. Dzhardimalieva, A.D. Pomogailo, Macromol. Symp. 186 (2002) 147.
[39] S.I. Pomogailo, G.I. Dzhardimalieva, V.A. Ershova, S.M. Aldoshin, A.D. Pomogailo, Macromol. Symp. 186 (2002) 155.
[40] K. Sreenivasan, J. Appl. Polym. Sci. 80 (2001) 2795.
[41] E. Hofer, E. Steckhan, B. Ramos, W.R. Heineman, J. Electroanal. Chem. 402 (1996) 115.
[42] R.A. Taylor, B.P. Santora, M.R. Gagnè, Org. Lett. 2 (2000) 1781.
[43] S.L. Vinson, M.R. Gagnè, Chem. Commun. (2001) 1130.
[44] M.M. Dell'Anna, P. Mastrorilli, A. Rizzuti, G.P. Suranna, C.F. Nobile, Inorg. Chim. Acta 304 (2000) 21.
[45] P. Mastrorilli, A. Rizzuti, G.P. Suranna, C.F. Nobile, Inorg. Chim. Acta 304 (2000) 17.
[46] P. Mastrorilli, A. Rizzuti, G. Romanazzi, G.P. Suranna, R. Gobetto, C.F. Nobile, J. Mol. Catal. A 180 (2002) 177.
[47] M.M. Dell'Anna, M. Gagliardi, P. Mastrorilli, G.P. Suranna, C.F. Nobile, J. Mol. Catal. A 158 (2000) 515.
[48] P. Mastrorilli, C.F. Nobile, G.P. Suranna, M.R. Taurino, M. Latronico, Inorg. Chim. Acta 335 (2002) 107.
[49] M. Tada, Y. Iwasawa, J. Mol. Catal. A 199 (2003) 115.
[50] K. Polborn, K. Severin, Chem. Commun. (1999) 2481.
[51] K. Polborn, K. Severin, Chem. Eur. J. 6 (2000) 4604.
[52] K. Polborn, K. Severin, Eur. J. Inorg. Chem. (2000) 1687.
[53] S.B. Wendicke, E. Burri, R. Scopelliti, K. Severin, Organometallics 22 (2003) 1894.
[54] R.A. Sheldon, J.K. Kochi, Metal Catalyzed Oxidation of Organic Compounds, Academic Press, New York, 1981.
[55] T. Mukaiyama, in: D.H.R. Barton, A.E. Martell, D.T. Sawyer (Eds.), The Activation of Dioxygen and Homogeneous Catalytic Oxidation, Kluwer, New York, 1993, p. 133.
[56] M.M. Dell'Anna, P. Mastrorilli, C.F. Nobile, G.P. Suranna, J. Mol. Catal. A 103 (1995) 17.
[57] P. Mastrorilli, C.F. Nobile, J. Mol. Catal. 99 (1994) 19.
[58] M.M. Dell'Anna, P. Mastrorilli, C.F. Nobile, L. Lopez, J. Mol. Catal A 111 (1996) 33.
[59] M.M. Dell'Anna, P. Mastrorilli, C.F. Nobile, J. Mol. Catal. A 108 (1996) 57.
[60] M.M. Dell'Anna, P. Mastrorilli, C.F. Nobile, M.R. Taurino, V. Calò, A. Nacci, J. Mol. Catal. A 151 (2000) 61.
[61] P. Mastrorilli, F. Muscio, C.F. Nobile, G.P. Suranna, J. Mol. Catal. A 148 (1999) 17.
[62] S.R. Cicco, M. Latronico, P. Mastrorilli, G.P. Suranna, C.F. Nobile, J. Mol. Catal. A 165 (2001) 135.
[63] P. Mastrorilli, F. Muscio, G.P. Suranna, C.F. Nobile, M. Latronico, J. Mol. Catal. A 165 (2001) 81.
[64] M.D. Skowronska-Ptasinska, M.L.W. Vorstenbosch, R.A. van Santen, H.C.L. Abbenhuis, Angew. Chem. Int. Ed. 41 (2002) 637.
[65] W. Zhang, J.L. Leobach, S.R. Wilson, E.N. Jacobsen, J. Am. Chem. Soc. 112 (1990) 2801.
[66] T. Katsuki, Coord. Chem. Rev. 140 (1995) 189.
[67] B.B. De, B.B. Lohray, S. Sivaram, P.K. Dhal, Macromolecules 27 (1994) 1291.
[68] B.B. De, B.B. Lohray, S. Sivaram, P.K. Dahl, Tetrahedron: Asymmetry 6 (1995) 2105.
[69] B.B. De, B.B. Lohray, S. Sivaram, P.K. Dahl, J. Polym. Sci. A: Polym. Chem. 35 (1997) 1809.
[70] F. Minutolo, D. Pini, P. Salvadori, Tetrahedron Lett. 37 (1996) 3375.
[71] F. Minutolo, D. Pini, A. Petri, P. Salvadori, Tetrahedron: Asymmetry 7 (1996) 2293.
[72] D. Di Salvo, D.B. Dellinger, J.W. Gohdes, React. Funct. Polym. 53 (2002) 103.
[73] E.-I. Negishi (Ed.), Handbook of Organopalladium Chemistry for Organic Synthesis, vols. 1–2, John Wiley & Sons, Inc., Hoboken, NJ, 2002.
[74] F. Diederich, P.J. Stang (Eds.), Metal-Catalyzed Cross-Coupling Reactions, Wiley-VCH, Weinheim, 1998.
[75] K. Kohler, R.G. Heidenreich, J.G.E. Krauter, J. Pietsch, Chem. Eur. J. 8 (2002) 622, and references therein.
[76] A.N. Cammidge, N.J. Baines, R.K. Bellingham, Chem. Commun. (2001) 2588.
[77] I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009, and references therein.
[78] J.H. Koh, A.O. Larsen, P.S. White, M.R. Gagné, Organometallics 21 (2002) 7.
[79] B.P. Santora, A.O. Larsen, M.R. Gagné, Organometallics 17 (1998) 3138.
[80] J. Matsui, I.A. Nicholls, I. Karube, K. Mosbach, J. Org. Chem. 61 (1996) 5414.
[81] H.G. Alt, J. Chem. Soc., Dalton Trans. (1999) 1703 and references therein.
[82] C. Liu, G. Jin, New J. Chem. 10 (2002) 1485.
[83] F.A.R. Kaul, G.T. Puchta, H. Schneider, F. Bielert, D. Mihalios, W.A. Herrmann, Organometallics 21 (2002) 74.
[84] D. Zhang, G.-X. Jin, N.-H. Hu, Chem. Commun. (2002) 574.
[85] D. Zhang, G.-X. Jin, N.-H. Hu, Eur. J. Inorg. Chem. (2003) 1570.
[86] P. Mastrorilli, C.F. Nobile, G.P. Suranna, J. Mol. Catal. A 103 (1995) 23.
[87] M.M. Dell'Anna, P. Mastrorilli, C.F. Nobile, G. Marchese, M.R. Taurino, J. Mol. Catal. A 161 (2000) 239.
[88] P. Mastrorilli, C.F. Nobile, A. Rizzuti, G.P. Suranna, D. Acierno, E. Amendola, J. Mol. Catal. A 178 (2002) 35.
[89] P. Mastrorilli, C.F. Nobile, G.P. Suranna, A. Corradi, C. Leonelli, P. Veronesi, Appl. Organomet. Chem. 17 (2003) 711.
[90] M.M. Dell'Anna, P. Mastrorilli, F. Muscio, C.F. Nobile, G.P. Suranna, Eur. J. Inorg. Chem. (2002) 1094.
[91] M.M. Dell'Anna, P. Mastrorilli, F. Muscio, C.F. Nobile, Sci. Technol. Catal. 145 (2003) 133.
[92] B.M. Trost, Chem. Pharm. Bull. 50 (2002) 1.
[93] M.M. Dell'Anna, P. Mastrorilli, C.F. Nobile, G.P. Suranna, J. Mol. Catal. A 201 (2003) 131.
[94] A. Chemin, H. Deleuze, B. Maillard, Eur. Polym. J. 34 (1998) 1395.
[95] A. Chemin, H. Deleuze, B. Maillard, J. Chem. Soc., Perkin Trans. 1 (1999) 137.
[96] A. Chemin, H. Deleuze, B. Maillard, J. Appl. Polym. Sci. 79 (2000) 1297.
[97] A. Mercier, H. Deleuze, B. Maillard, O. Mondain-Monval, Adv. Synth. Catal. 344 (2002) 33.