

1,3-butadiene telomerization with methanol catalyzed by heterogenized palladium complexes

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Abstract

The heterogenization of palladium complexes on silica as well as on functionalized styrene/divinylbenzene crosslinked resins and linear poly(styrene) is described. In particular, palladium (0) and palladium (II) derivatives were anchored to the above polymeric systems through their functionalization with bidentate ligands such as acetylacetonate and 1,3-bis(diphenylphosphino)propane moieties. The resulting heterogenized complexes were checked in the catalytic telomerization of 1,3-butadiene with methanol. Their performances were studied in terms of activity and selectivity to telomers. Whereas the heterogenization of palladium complexes either on silica or on polymer resins via the acetylacetonate ligand resulted labile during the catalytic cycle, the polymer-bound palladium complexes via the diphosphine ligand, when activated by an alkoxide, displayed activity and selectivity comparable with those of the corresponding homogeneous counterparts, without appreciable metal leaching in solution. © 1999 Elsevier Science B.V. All rights reserved.

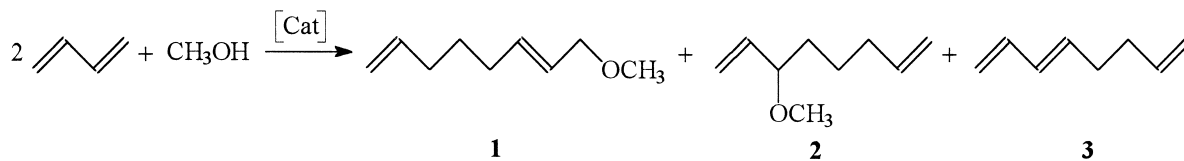
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1. Introduction

Catalytic telomerization of 1,3-butadiene with alcohols, as represented in Scheme 1 for methanol, has recently gained industrial interest as it allows to promote selectively the synthesis of linear unsaturated ethers, thus strongly reducing the formation of undesired dimeric products.

Indeed, the linear telomers, after hydrogenation, may be used as components of diesel fuels, owing to their excellent cetane number and cold flow properties [1]. Homogeneous palladium catalysts have been extensively applied to the above process, due to the high activity and selectivity of the reaction, particularly when an additional phosphine ligand is used [2,3]. In this context, we have recently re-visited this reaction in the homogeneous phase, by focusing our attention on the influence of

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Scheme 1.

alcohol/diene and P/Pd molar ratios, as well as of the nature of the phosphine ligand and reaction temperature on the activity and selectivity to unsaturated linear ethers [4].

Despite the extensive research work dealing with homogeneous palladium telomerization catalysts, only few data were available concerning the use of heterogenized systems [5–10], although these catalysts appear very attractive from industrial point of view as not only they may be easily separated from the reaction products and recycled, but also because anchored metal catalysts may assure a greater stability. However, the heterogenized catalysts described up to now for the telomerization reaction usually showed a progressive leaching of palladium into the reaction medium and a reduced activity with respect to the homogeneous counterparts, owing to a labile fixation of the metal on the inorganic or organic polymeric matrix, probably due to the use of monodentate ligands.

Therefore, in this paper the synthesis of palladium catalysts, anchored to inorganic and polystyrene matrices through bidentate moieties, will be described with the aim to obtain a permanent heterogenization. Moreover, the activity and selectivity of the above catalytic systems will be investigated in the telomerization reaction of 1,3-butadiene with methanol and compared with those obtained with the corresponding homogeneous counterpart. Indeed, among all the reactions catalyzed by heterogenized metal systems, telomerization appears as one of the most severe test to verify the strength of the linkage between the anchoring moiety and the metal, due to the competitive presence of phosphine and 1,3-butadiene coordinating species [2].

2. Experimental

2.1. Materials

All manipulations as well as catalytic reactions were carried out under dry purified argon or nitrogen using standard Schlenk techniques.

Solvents and methanol (J.T. Baker) were carefully dried and freshly distilled just before the use. Anhydrous methanol was obtained by refluxing over Mg/I₂.

Commercial 1,3-butadiene (99%) (Rivoira) was flash distilled prior to use in order to avoid contamination from 4-vinyl-cyclohexene and peroxides.

Phosphine ligands (Fluka) were stored under nitrogen and used as received.

A DOW-C macroporous resin (Dow Chemical), constituted by crosslinked poly(styrene/divinylbenzene) beads containing 8 mol% of divinylbenzene units and having a 65 m² g⁻¹ surface area, and a Merrifield powdered (200–400 mesh) resin (Fluka), consisting of a crosslinked chloromethylated poly(styrene/divinylbenzene) containing 2 mol% of divinylbenzene units and 4.3 meq g⁻¹ of chloromethyl groups (about 56 mol% of chloromethylated styrene units), were used for functionalization reactions in order to obtain bidentate ligands bound to solid polymeric matrices.

SiO₂ (Sud Chemie) in spherical particles (250 m² g⁻¹ surface area, 0.46 g ml⁻¹ density) was activated according to the following procedure: firstly, it was progressively (3 h) heated to 300°C in an oven under vacuum, then it was kept at that temperature for additional 12 h, subsequently it was cooled at 200°C and finally transferred and stored in a dryer until room temperature was reached.

Bis(acetylacetonato)palladium (II) [Pd(acac)₂] (99.9%) (Aldrich) was used as received.

Palladium dibenzylideneacetone [Pd(dba)₂] was prepared as previously reported [11].

Palladium acetate [Pd(OAc)₂] was prepared from Pd (99.9%, Aldrich) and acetic acid as previously described [12].

2.1.1. Synthesis of the SiO₂-supported palladium complex

2.86 g of Pd(acac)₂ were introduced in a 500 ml flask and dissolved in acetonitrile to obtain a concentration of 18.61 mmol l⁻¹ of Pd (determined by UV–VIS spectroscopy). Then 80 ml of the above solution (1.49 mmol of Pd) was transferred under argon into a 250 ml flask and 19.3 g of activated silica were added under stirring. After 24 h the liquid was separated from the silica by filtration, washed with acetonitrile and finally dried under vacuum. The content of palladium in the solution was determined by UV–VIS spectroscopy and the amount of adsorbed metal on the silica to give the heterogenized palladium complex (SiO₂-acac-Pd) was evaluated by difference (Pd = 0.2%).

2.1.2. Synthesis of the heterogenized palladium complex by anchoring the metal to acetylacetonate moieties bound to a Merrifield resin

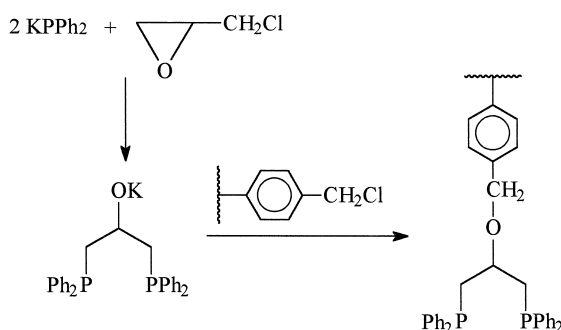
1 g of acac-functionalized Merrifield resin (1.63 mmol of acac groups, 23 mol% of acac-styrene co-units), obtained as previously described [13,14], was swelled under dry argon in 100 ml of anhydrous THF at room temperature for 1 h, then 50 ml of a THF solution of NaH (3.87 mmol) were added dropwise and the reaction mixture was refluxed for 48 h under mild stirring. The reacted resin was filtered off under dry argon, washed several times with anhydrous THF and dried under high vacuum to give 1.37 g of yellow Na-acac-functionalized resin.

1 g of the above Na-acac-functionalized resin, according to a modified procedure with respect to that reported for the synthesis of the corresponding homogeneous complex [15,16], was suspended into 100 ml of anhydrous THF, under dry argon, then 50 ml of a THF solution of Pd(OAc)₂ (3.87 mmol) were added dropwise at 0°C under stirring. The reaction mixture was allowed to slowly warm up to room temperature and then heated at 40°C for 48 h. The reacted resin was filtered off under dry argon, washed several times with THF until uncoloured washings were obtained. After drying 1.38 g of brown-coloured anchored palladium (II)-resin (Res-acac-Pd), with 1.8 wt.% of Pd (2.4 mol% of palladium containing co-units, corresponding to about 10% loading of acac-styrene co-units), as determined by X-rays fluorescence analysis, were obtained.

2.1.3. Synthesis of heterogenized palladium complexes by anchoring the metal to DPPP moieties bound to a DOW-C resin

The functionalization of both DOW-C resin and linear poly(styrene) with the bis(diphenylphosphine)propane (DPPP) ligand was performed according to Scheme 2. More details are reported in the subsequent sections.

Chloromethylation of DOW-C resin was carried out, by using freshly prepared hexylchloromethylether, in the presence of SnCl₄, as previously described [17]. After reaction, a chloromethylated resin with 6.5 wt.% of Cl (1.8 meq of Cl g⁻¹ and 20.3 mol% of chloromethylated styrene units) was obtained.



Scheme 2.

The anchoring of DPPP moieties on DOW-C resin was performed according to Scheme 2, following the previously reported procedure [18–20].

A DPPP-functionalized DOW-C resin, containing 2.64 wt.% of P (5 mol% of phosphinated styrene units), as determined by ^{31}P -MAS-NMR analysis, was thus obtained.

According to a modified procedure with respect to that reported for the synthesis of the corresponding homogeneous complex [21], 1 g (0.37 meq of bidentate phosphine ligand) of the above resin was swelled for 1 h into 60 ml of anhydrous toluene, under dry argon, and subsequently reacted with a solution of 0.43 mmol of $\text{Pd}(\text{dba})_2$ in 50 ml of toluene, slowly added at room temperature. The exchange reaction was continued for 24 h, then the resulting resin, after filtration under dry argon, was washed with toluene until filtrate became colorless and finally dried under high vacuum to give 1.26 g of diphosphine-anchored palladium (0) DOW-C resin (Dow-DPPP-Pd (0)), containing 2.38 wt.% of Pd (3.3 mol% of Pd-containing units), corresponding to a 66% loading of the DPPP-functionalized styrene units.

1 g (0.37 meq of bidentate phosphine ligand) of the DPPP-functionalized DOW-C resin was submitted to reaction with $\text{Pd}(\text{OAc})_2$, as previously described for diphenylphosphinated resins [5], to give 1.3 g of diphosphine-anchored palladium (II) DOW-C resin (Dow-DPPP-Pd (II)) containing 3.60 wt.% of Pd (~ 5 mol% of Pd-containing units, corresponding to about 100% loading of the DPPP-moieties).

2.1.4. Synthesis of [1,3-bis(diphenylphosphino)-2-benzyloxy-propane]-palladium (II)diacetate[(BzO-DPPP)-Pd(OAc) $_2$]

2.61 mmol of benzyl chloride in 10 ml of anhydrous THF were added dropwise under dry argon to 3.87 mmol of the potassium salt of 2-hydroxy-1,3-bis(diphenylphosphino)propane in THF, prepared as previously reported [18,19]. The reaction mixture was refluxed for 12 h, then the solvent was removed under vacuum and the residue treated with water and aq. 3 M HCl. The resulting mixture was extracted with methylene chloride and the extracts washed with water and dried on CaCl_2 . After removing the solvent under vacuum, the residue was purified by chromatography on silica gel by using $\text{CH}_2\text{Cl}_2/n$ -hexane 1:1(v/v) as eluent, to give 1.06 mmol (41% yield) of an oily product which resulted pure 1,3-bis(diphenylphosphino)-2-benzyloxy-propane (BzO-DPPP).

$\{^1\text{H}\}$ - ^{31}P -NMR (CDCl_3): $\delta = -22.7$ ppm. ^1H -NMR (CDCl_3): $\delta = 7.7$ – 6.9 (m, 25 H, aromatic protons); 4.31 (s, 2H, O- CH_2 -Ar); 3.52 (m, 1H, BzO-CH-); 2.54 (d, 4H, - CH_2PPh_2) ppm.

FT-IR (KBr pellet): 3055 (ν_{CH} , aromatic); 2991–2903 (ν_{CH} , aliphatic); 1614, 1587 ($\nu_{\text{C}=\text{C}}$); 1457 ($\delta_{\text{s}(\text{CH}_2)}$, PhCH_2O -); 1436 ($\delta_{\text{s}(\text{CH}_2)}$, $\text{CH}_2\text{-P}$); 1103, 1084, 1066 ($\nu_{\text{P-Ph}}$ and ν_{COC}); 745, 695 (δ_{CH} , aromatic) cm^{-1} .

0.25 g (0.48 mmol) of BzO-DPPP were added, under dry argon, to 0.08 g (0.36 mmol) of Pd(OAc)₂ dissolved in 10 ml of acetone. After few minutes a white microcrystalline product was formed. The product was filtered under dry argon, washed with cool acetone and finally dried under vacuum to give 0.19 g of pure (BzO-DPPP)Pd(OAc)₂ (70% yield).

¹H}-³¹P-NMR (CDCl₃): δ = +21.2 ppm. ¹H-NMR (CDCl₃): δ = 7.9–7.1 (m, 25H, aromatic protons); 4.5 (d, 2H, O–CH₂–Ar); 3.5 (m, 1H, BzO–CH–); 2.7 (m, 4H, –CH₂PPh₂) and 1.5 (d, 6H, CH₃COO–Pd) ppm.

2.1.5. Synthesis of the poly(styrene)-bound palladium (II) complex by anchoring the metal to DPPP moieties (Pst-DPPP-Pd (II))

The polymer ligand was prepared by free radically initiated copolymerization of styrene (St) with 1,3-bis(diphenylphosphino)-2-[(4-vinylbenzyloxy)-propane (StMO-DPPP), a new monomer properly synthesized in 30% yield with the same procedure as previously described for BzO-DPPP, starting from 4-chloromethylstyrene and the potassium salt of 2-hydroxy-1,3-bis(diphenylphosphino)propane (refluxing the reaction mixture at 60°C for 1 week).

¹H-NMR (CDCl₃): δ = 7.8–6.9 (m, 24 H, aromatic protons); 6.70 (m, 1H, Ar–CH=); 5.75 and 5.25 (2d, 2H, Ar–CH₂=); 4.32 (s, 2H, O–CH₂–Ar); 3.54 (m, 1H, BzO–CH–); 2.56 (d, 4H, CH₂PPh₂) ppm.

¹H}-³¹P-NMR (CDCl₃): δ = –22.7 ppm.

The copolymerization was carried out in benzene solution at 60°C in a glass vial under argon, by using 1.5 g of comonomers mixture containing 7 mol% of StMO-DPPP, in the presence of 8.9 mg of AIBN, as radical initiator. After 70 h, 1.12 g of poly(St-co-StMO-DPPP), containing 5 mol% of StMO-DPPP co-units, as determined by ¹H-NMR analysis (2.5 wt.% of P and 0.403 meq of StMO-DPPP co-units g⁻¹), were obtained.

¹H-NMR (CDCl₃): δ = 7.8–6.3 (aromatic protons); 4.2–3.9 (O–CH₂–Ar); 3.6–3.4 (–O–CH–); 2.6–2.4 (–CH₂PPh₂); 2.2–1.1 (CH and CH₂ in the main chain) ppm. ¹H}-³¹P-NMR (CDCl₃): δ = –22.8 ppm.

FT-IR (KBr pellet): 3081–3025 (ν_{CH}, aromatic); 2921–2849 (ν_{CH}, aliphatic); 1601–1584, 1493 (ν_{C=C}, aromatic); 1452 (δ_{s(CH₂)}, main chain CH₂ and PhCH₂O–); 1435 (δ_{s(CH₂)}, CH₂-P); 1182–1069 (ν_{P-Ph} and ν_{COC}); 748, 698 (δ_{CH}, aromatic) cm⁻¹.

0.75 g of the copolymer was reacted with Pd(OAc)₂ in acetone solution as described for BzO-DPPP, a yellow precipitate occurring after 30 min to give 0.54 g of Pst-DPPP-Pd (II) having 3.87 wt.% of Pd (~ 5 mol% of Pd-containing units, corresponding to about 100% loading of DPPP moieties on the polymer).

2.2. Catalytic experiments and analyses

Catalytic experiments were carried out in a 150 ml mechanically stirred stainless steel autoclave, equipped with an inner glass beaker, a substrate inlet vessel, a liquid sampling valve and an internal thermocouple for temperature control.

In a typical procedure, the desired amounts of methanol, palladium catalyst, benzene (as internal standard for GC analysis) and eventually solvent, phosphine ligand and sodium methoxide activator were introduced under dry argon in the nitrogen purged autoclave. Then, 1,3-butadiene was charged and the system pressurized with nitrogen to 1–4 MPa. The autoclave was heated to the desired temperature in a thermostated oil bath. Products samples were periodically removed via the liquid sampling valve, collected in pre-cooled capped vials and immediately analysed by GC. At the end of

the reaction the autoclave was cooled at room temperature and, after removing unreacted 1,3-butadiene, the products analyzed. In recycle experiments of the catalyst, the liquid solution of the products, after catalyst sedimentation, was removed under dry argon and fresh methanol and 1,3-butadiene were added in the proper quantities. When the products solution was recycled, the reaction mixture was analyzed and removed under argon from the autoclave. Then the catalyst was settled, the solution, including the unreacted methanol, was again transferred under argon in the autoclave and fresh 1,3-butadiene was charged in the appropriate molar ratio with methanol.

Quantitative analyses of telomerization products were performed by a SIGMA 3B Perkin–Elmer gas-chromatograph, equipped with a P.C. PE NELSON integrator, a flame ionization detector and a 25 m HP5 capillary column (5% cross-linked methyl–phenyl–silicone). The identification of the telomerization products was carried out both by GC-MS and NMR analyses.

The content of palladium released during catalytic experiments in the liquid reaction products was determined by UV–VIS spectrophotometric analysis at 408 nm, according to the literature [22]. Calibration curve was obtained with 5 standard solutions of sodium tetraiodopalladate at different concentration.

The content of phosphorus in the phosphinated resin was determined by ^{31}P -MAS-NMR analysis, by using as internal standard $\text{NH}_4\text{H}_2\text{PO}_4$. A calibration curve was obtained by using different amounts of solid PPh_3 and the overmentioned internal standard.

2.3. Physico–chemical measurements

IR spectra were recorded on a FT-IR Perkin–Elmer 1750 spectrophotometer. The samples were prepared as KBr pellets or as liquid and solid films on KBr discs.

^1H -, ^{13}C - and ^{31}P -NMR spectra of the samples in CDCl_3 or $\text{DMSO}-d_6$ solution were carried out at 200, 50.3 and 80.95 MHz, respectively, on a Varian XL Gemini 200 spectrometer by using TMS as internal standard or H_3PO_4 85% as external standard.

^{13}C - and ^{31}P -NMR spectra in the solid state were performed on a AMX 300 BRUKER spectrometer, equipped with a CP-MAS apparatus, working at 8000 Hz.

Elemental analyses were carried out at the Analytical Laboratory of Pharmacy Faculty of the University of Pisa.

UV–VIS analyses were accomplished by using a Pharmacy-NOVASPEC II unibeam spectrophotometer.

X-rays fluorescence analyses were performed on a Philips P.W. 1460/10 spectrometer, according to the literature [23,24].

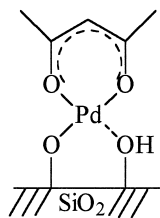
GC-MS spectra of the telomerization products were carried out by a Hewlett-Packard 5995 A spectrometer.

3. Results and discussion

3.1. Synthesis of heterogenized palladium catalysts on solid inorganic and organic supports through chelate moieties

The first approach for obtaining heterogenized palladium catalysts for 1,3-butadiene telomerization with methanol was to anchor a palladium derivative on an activated silica. Indeed, sepiolite-bound palladium complexes have been reported [10] to display in the above telomerization reaction

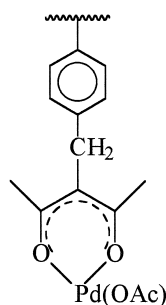
comparable catalytic activity to that of homogeneous counterparts and were claimed to maintain the activity after recycle, although no analytical data were reported for excluding any metal leaching during the catalytic process. In order to achieve a deeper insight on this point, activated SiO_2 was reacted with $\text{Pd}(\text{acac})_2$ to give silica-bound Pd(II) species ($\text{SiO}_2\text{-acac-Pd}$) whose proposed structure, according to the nucleophilic substitution mechanism of the acetylacetonate ligand on the metal [25,26], is represented below:



$\text{SiO}_2\text{-acac-Pd}$

$\text{SiO}_2\text{-acac-Pd}$ (0.2 wt.% of Pd) may be reduced in situ to Pd (0) under the reaction conditions ($T > 50^\circ\text{C}$) [10] to give the effective heterogenized catalyst.

With the aim to investigate the possibility to use other heterogeneous supports, the synthesis of palladium complexes anchored to crosslinked styrene/divinylbenzene resins functionalized with chelating moieties, such as acetylacetonate and 1,3-bis(diphenylphosphino)propane groups, was explored. Indeed, the presence of chelating groups on the support would in principle assure a nearby permanent fixation of the metal on the polymer surface and hence the possibility to obtain telomerization catalysts with a very high stability. Therefore, a macroporous chloromethylated styrene/divinylbenzene Merrifield resin (8 mol% of crosslinking) was reacted (see Section 2) with the sodium acetylacetonate and the resulting functionalized resin, which was previously applied for the heterogenization of nickel catalysts active in the oligomerization and polymerization of α -olefins [27], was exchanged with $\text{Pd}(\text{OAc})_2$ to give an acetylacetonate-anchored palladium (II) resin (Res-acac-Pd) (1.8 wt.% of Pd and about 10% loading by palladium of acac groups present on the resin) whose proposed structure is represented below:

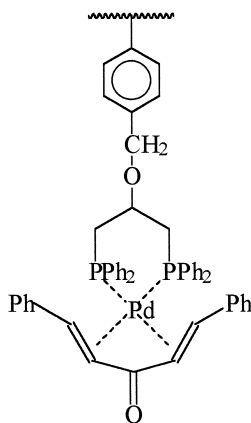


Res-acac-Pd

The above structure is confirmed by IR analysis. Indeed, an intense band at 1560 cm^{-1} is present, assignable to the diketone ligand coordinated to palladium, whereas the bands at 1690 and

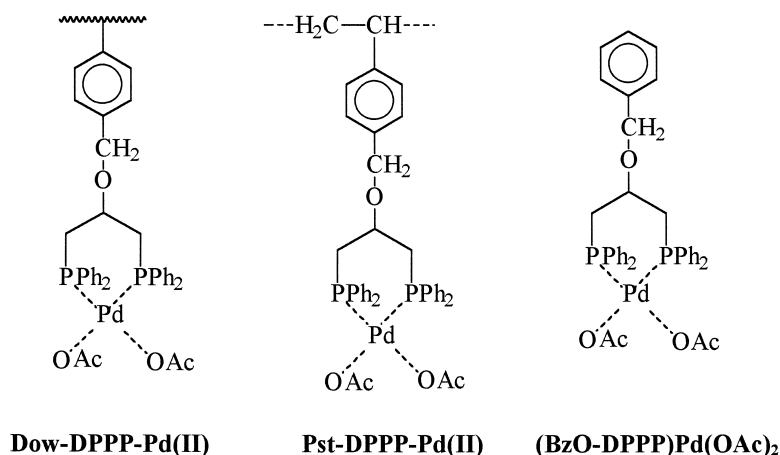
1720 cm^{-1} , typical of stretching vibrations of the ketone groups in the uncoordinated acetylacetonate ligand are absent; moreover, a new band at 1640 cm^{-1} is observed, connected with the asymmetric stretching vibration of metal-bound acetate group.

A styrene/divinylbenzene crosslinked (2%) resin was also functionalized in order to obtain a bis(diphenylphosphino)propane ligand directly bound to the polymer matrix (see Section 2). This type of diphosphine ligand was previously prepared by Tkatchenko [18–20] for synthesizing different heterogeneous transition metal complexes, including palladium derivatives. However, no data were available concerning the use of these latter complexes as catalysts for telomerization reactions. The above phosphinated resin was submitted to exchange reaction with $\text{Pd}(\text{dba})_2$ to give a diphosphine-anchored palladium (0) DOW-C resin (Dow-DPPP-Pd(0)) containing 2.38 wt.% of metal, corresponding to a 66% loading of the DPPP-groups present on the resin. The proposed structure of the above complex is represented below:



Dow-DPPP-Pd(0)

With the aim to increase the loading of $\text{P}^{\text{(III)}}$ by palladium, the above resin was reacted with $\text{Pd}(\text{OAc})_2$. Indeed, in this case about 100% of the diphosphine ligands bound to the resin was loaded by palladium to give diphosphine-anchored palladium (II) DOW-C resin (Dow-DPPP-Pd(II)) whose proposed structure is represented below:



Dow-DPPP-Pd(II)

Pst-DPPP-Pd(II)

(BzO-DPPP)Pd(OAc)₂

An analogous homogeneous complex was also prepared, as low molecular weight model compound of Dow-DPPP-Pd(II), not only for comparing the performances of homogeneous and heterogenized catalysts in the telomerization reaction, but also for a deeper insight on the structure of the heterogenized complex at molecular level.

Therefore, the novel ligand 2-benzyloxy-1,3-bis(diphenylphosphino)propane was reacted with Pd(OAc)₂, by using the same procedure adopted for the phosphinated DOW-C resin, to give the complex (BzO-DPPP)Pd(OAc)₂ above represented. Indeed, ¹H-NMR spectrum of (BzO-DPPP)Pd(OAc)₂ (see Section 2) confirms the above structure. In fact it shows a signal at about 1.5 ppm, assignable to the protons of the methyl groups of the two acetate ligands when coordinated to palladium, analogously to what found for the Pd(diphenylphosphinoethane)(OAc)₂ complex [28]. The effective coordination of the metal to the diphosphine ligand is furthermore confirmed by the shift of the signal of the methylene protons adjacent to the phosphorus atoms from 4.31 to 4.5 ppm after the reaction with Pd(OAc)₂. Finally, the presence of only one signal at +21.2 ppm in the {¹H}-³¹P-NMR spectrum of (BzO-DPPP)Pd(OAc)₂, against a signal at -22.7 ppm in the corresponding spectrum of BzO-DPPP, not only indicates that both phosphorus atoms of the diphosphine ligand are coordinated to the metal, but also proves their magnetic equivalence according to the chelate structure above represented.

An analogous palladium (II) acetate complex was obtained by reacting Pd(OAc)₂ with linear and soluble poly(St-co-StMO-DPPP), containing 5 mol% of phosphinated styrene units (see Section 2). The resulting complex [Pst-DPPP-Pd(II)], having the proposed structure above represented, was checked in the telomerization reaction in order to study the steric effect of main chain coiling on the catalytic performances of the system.

3.2. Catalytic telomerization of 1,3-butadiene with methanol in the presence of heterogenized SiO₂-acac-Pd

As reported in Table 1, in all the experiments an ancillary phosphine ligand was used as it plays an important role in stabilizing Pd(0) species [10]. P(ⁿBu)₃ was chosen because alkyl phosphines favour the achievement of higher selectivity to telomers [4]. Reaction temperatures below 75°C (runs 1–3) did not substantially promote any butadiene conversion, the system becoming active at 85°C (run 4).

Table 1

Telomerization of 1,3-butadiene with methanol in the presence of heterogenized SiO₂-acac-Pd^a

Run	P/Pd (mol/mol)	T (°C)	Reaction time (h)	Conv. (%) C ₄ H ₆	Products (mol%)			Released Pd (%)
					1	2	3	
1	2	50	18	0.4	17.6	0.0	82.4	15.6
2	2	60	18	1.0	71.5	0.0	28.5	n.d.
3	2	75	18	4.2	79.6	4.9	15.5	17.6
4	2	85	6	46.7	86.6	7.9	5.5	26.0
5	0.5	85	18	7.0	40.4	2.1	55.1	n.d.
6	15	60	6	0.4	24.0	0.0	76.0	64.0
7	2	85	18	83.4	84.1	8.9	7.1	n.d.
8 ^b	2	85	18	0.0	—	—	—	—
9 ^c	2	85	18	83.1	71.8	8.5	19.7	—

^aAncillary ligand: P(ⁿBu)₃; MeOH/C₄H₆ = 1.3 mol/mol; C₄H₆/Pd = 2.3 × 10⁴ mol/mol.

^bSolid catalyst was recycled from run 7.

^cCatalytic solution was recycled from run 7.

A molar ratio $P/Pd = 2$ was generally adopted. Indeed, a defect of phosphine with respect to Pd strongly reduces the catalytic activity and dimeric products prevail (run 5). On the other hand, a large excess of phosphine ($P/Pd = 15$, run 6) not only prevented the reaction but more than 60% of the metal was released into solution even under mild conditions ($T = 60^\circ\text{C}$). This occurrence may be explained taking into account that at high concentration of phosphine this ligand is preferentially coordinated to the metal with respect to the reagents and is able also to cleavage silica-metal linkages on the surface. As far as selectivity is concerned, an increase of the reaction temperature not only favours the formation of telomers with respect to dimers, but also significantly enhances the extent of the linear telomer 1-methoxy-2,7-octadiene (1) with respect to 3-methoxy-1,7-octadiene (2). A significant release of the metal into solution is observed also at $P/Pd = 2$, particularly at high temperature, which is however necessary for activating the system. When the catalyst is separated from the liquid products and recycled (run 8) under the same conditions as the fresh catalyst (run 7) no activity was observed. On the contrary, the recycled products solution (run 9), with addition of fresh 1,3-butadiene in order to obtain the same $\text{MeOH}/\text{C}_4\text{H}_6$ molar ratio (1.3), displays substantially the same activity and selectivity of the original experiment. These results clearly indicate that the heterogenized SiO_2 -acac-Pd complex does not display any activity under the adopted reaction conditions, the observed activity being fully related to the released palladium into solution.

3.3. Catalytic telomerization of 1,3-butadiene with methanol in the presence of heterogenized Res-acac-Pd

All the experiments were performed at 60°C using the heterogenized palladium complex Res-acac-Pd in the presence of P^nBu_3 as ancillary ligand. A constant $\text{MeOH}/\text{C}_4\text{H}_6$ molar ratio (1.5) was used in all runs. Preliminarily, the effect of the P/Pd ratio was investigated by varying its value in the 0.3–3 range (runs 10–13, Table 2). The selectivity in telomers 1 and 2 was found to increase with increasing the P/Pd ratio. However, the selectivity to the linear telomer 1 was scarcely affected by the above ratio and in all cases was higher than 93%, whereas the activity reached a maximum for a P/Pd equal to 2. The above behavior is substantially similar to that found for analogous homogeneous systems [4]. An increase of activity was observed by enhancing the $\text{C}_4\text{H}_6/Pd$ ratio (run 14).

Table 2

Telomerization of 1,3-butadiene with methanol in the presence of heterogenized Res-acac-Pd^a

Run	P/Pd (mol/mol)	$\text{C}_4\text{H}_6/Pd$ (mol/mol)	Conv. (%) C_4H_6	Products (mol%)			S^b (%)	T.N. ^c (h^{-1})	Released Pd (%)
				1	2	3			
10	0.3	18000	4.4	30.7	1.4	67.9	95.5	40	35
11	1.2	18000	11.8	56.1	2.4	41.5	95.9	180	45
12	2.0	18000	23.8	68.1	3.8	28.1	94.7	920	76
13	3.0	18000	21.5	90.7	6.5	2.8	93.3	770	n.d.
14	3.0	34000	38.8	92.6	6.0	1.4	93.9	1290	n.d.
15 ^d	3.0	18000	28.8	81.6	4.1	2.1	94.2	n.d.	—
16 ^e	3.0	18000	0.0	—	—	—	—	—	—

^aAncillary ligand: P^nBu_3 ; $\text{MeOH}/\text{C}_4\text{H}_6 = 1.5$ mol/mol; $T = 60^\circ\text{C}$; Reaction time: 6 h.

^bSelectivity to the linear telomer 1, expressed as $[1 \text{ (mol)}/1 \text{ (mol)} + 2 \text{ (mol)}] \times 100$.

^cTurn over expressed as: $\text{g (products)}\text{g}^{-1} \text{ (Pd)} \times \text{h}$.

^dRecycled products solution from run 13.

^eRecycled solid catalyst from run 13.

With the aim to check if the catalytic system was really heterogeneous, the products solution, separated from the solid catalyst, was recycled (run 15) charging fresh butadiene up to a MeOH/C₄H₆ equal to 1.5 as in the original experiment (run 13). As shown in Table 2, the data clearly indicate that the recycled solution has substantially the same activity as that of run 13. Therefore, the activity has to be addressed to organometallic species of palladium present in the solution. This means that during the catalytic process the palladium (II) species, initially anchored to the polymer matrix through the acetylacetonate ligand, were released from the support. Indeed, the presence in solution of butadiene and phosphine ligand would stabilize the released palladium species, thus assuring a comparable activity in the subsequent catalytic cycle. The occurrence of leaching phenomena is also confirmed by the analysis of palladium content in the reaction mixture at the end of the catalytic experiments (Table 2). The above results were also confirmed by the inactivity of the solid catalyst recovered from run 13 and recycled under the same conditions (run 16). The strict correlation between the extent of metal release and concentration of free phosphine in solution clearly indicates that the presence of this ancillary ligand works as driving force for metal detaching from the support. For this reason a chelating diphosphine ligand was directly bound to the polymeric support.

3.4. Catalytic telomerization of 1,3-butadiene with methanol in the presence of heterogenized Dow-DPPP-Pd (0), Dow-DPPP-Pd (II) and Pst-DPPP-Pd (II)

Preliminary experiments were carried out at different reaction temperatures by using a MeOH/C₄H₆ molar ratio equal to 1.5. As reported in Table 3, the palladium complexes anchored to the resin display (runs 17–21) a very low activity, even at high temperature (80–100°C). Moreover, the reaction was mainly oriented to dimerization and cyclodimerization, products 3 and 4-vinylcyclohexene being mainly formed. Taking into account that the low activity observed for the above systems could derive from the inaccessibility of the catalytic sites on the resin, due to its high degree of crosslinking (8%) and shrinkage in methanol, which is a non solvent for polystyrene, a telomerization experiment (run 22) was performed in the presence of toluene in order to favour the swelling of the resin. However, the results reported in Table 3 clearly indicate that also under the above conditions the activity of Dow-DPPP-Pd (II) system is very low. An analogous result was obtained (run 23) also

Table 3

Telomerization of 1,3-butadiene with methanol in the presence of homogeneous and heterogenized diphosphine palladium complexes^a

Run	Precursor	T (°C)	Conv. (%) C ₄ H ₆	Products (mol%)			S ^b (%)
				1	2	Dim. ^c	
17	Dow-DPPP-Pd(0)	60	0.2	0.9	traces	99.1	–
18	Dow-DPPP-Pd(0)	80	0.4	2.3	2.6	95.2	47.0
19	Dow-DPPP-Pd(0)	100	1.6	0.4	1.0	98.6	28.0
20	Dow-DPPP-Pd(II)	60	1.7	0.7	0.3	99.0	70.0
21	Dow-DPPP-Pd(II)	80	0.1	7.5	23.5	69.0	24.0
22	Dow-DPPP-Pd(II) ^d	60	0.7	9.9	3.8	86.0	72.3
23	Pst-DPPP-Pd(II) ^d	60	0.3	~ 0	~ 0	~ 100	–
24	(BzO-DPPP)Pd(OAc) ₂ ^{d,e}	60	6.4	84.2	5.1	10.7	94.3

^aPd: 0.05 mmol; C₄H₆/Pd and MeOH/C₄H₆ = 6500 and 1.5 mol/mol, respectively; Reaction time: 18 h.

^bSelectivity to the linear telomer 1.

^c1,3,7-octatriene (3) + 4-vinylcyclohexene.

^dIn the presence of 15 ml of toluene.

^eIn homogeneous phase.

by using Pst-DPPP-Pd (II) in toluene where the system, although not soluble due to the contemporary presence of methanol, however resulted much more expanded as compared with crosslinked Dow-DPPP-Pd (II). Therefore, the poor activity of the above systems would be mainly attributed to the intrinsic nature of the palladium species anchored to the polymer matrix. Indeed, the diphosphine chelating ligand would give an excessive stability to the polymer-bound metal complexes. Moreover, the low selectivity to telomers would be explained assuming that the metal coordination sphere is too sterically hindered, thus preventing the nucleophilic attack of methanol after the insertion of two butadiene molecules. In order to confirm this hypothesis, a telomerization experiment was performed (run 24, Table 3) in the presence of the homogeneous complex (BzO-DPPP) Pd (OAc)₂ under the same conditions. The quite low activity but the much higher selectivity to telomers with respect to the corresponding heterogenized system confirmed the above picture. Therefore, with the aim to improve the activity and selectivity of the above polymer-bound palladium complexes, the use of sodium methoxide as promoter was explored. Indeed, it is well known that phenoxides and methoxides of alkaline metals are able to activate less reactive palladium precursors, such as halogenides, favouring the reduction of Pd (II) species [29] and acting as nucleophiles in the catalytic cycle. In this context, telomerization experiments with both the heterogenized diphosphine palladium complexes were performed at 60°C by using a MeONa/Pd equal to 10 and comparing their performances with those obtained with Pst-DPPP-Pd (II) as well as with Pd (OAc)₂ and (BzO-DPPP) Pd (OAc)₂, these last two complexes operating in homogeneous phase. As reported in Table 4, the heterogenized Dow-DPPP-Pd(II) complex showed in the presence of MeONa (run 25) a much higher activity than in its absence (run 20, Table 3), a turn over (T.N.) of 195 h⁻¹ being obtained. Moreover, a very large improvement of selectivity to telomers and in particular towards the linear one was observed. Better performances (T.N. = 220 h⁻¹) were found (run 26) when all reaction components were doubled, the poisoning effect of impurities being reduced. An analogous result was obtained when Pst-DPPP-Pd(II) was tested in the presence of MeONa (run 27), by adding *n*-hexane in the reaction medium. This

Table 4

Telomerization of 1,3-butadiene with methanol by using homogeneous and heterogenized diphosphine palladium complexes in the presence of MeONa as promotor^a

Run	Precursor	MeOH/C ₄ H ₆ (mol/mol)	Conv. (%) C ₄ H ₆	Products (mol%) ^b			S ^c (%)	T.N. ^d (h ⁻¹)
				1	2	3		
25	Dow-DPPP-Pd(II)	1.5	87.0	80.1	6.0	7.9	93.0	195
26	Dow-DPPP-Pd(II) ^e	1.5	97.0	87.5	5.5	7.0	94.1	220
27	Pst-DPPP-Pd(II) ^f	1.5	83.1	82.0	7.2	10.2	92.0	192
28	Pst-DPPP-Pd(II) ^g	1.5	66.2	73.2	8.9	16.6	89.3	156
29	Pst-DPPP-Pd(II) ^h	1.5	24.3	29.7	2.9	66.0	91.2	49
30	Pd(OAc) ₂	1.5	9.3	65.5	1.0	33.5	98.5	–
31	(BzO-DPPP)Pd(OAc) ₂ ^f	1.5	83.4	84.8	7.0	7.2	92.4	190
32	Dow-DPPP-Pd(0)	1.5	68.0	87.0	7.0	6.0	91.6	160
33	Dow-DPPP-Pd(0)	3.0	98.0	86.5	6.8	6.8	92.7	230

^aPd: 0.04 mmol; C₄H₆/Pd and MeONa/Pd = 6500 and 10 mol/mol, respectively; Reaction time: 18 h; T: 60°C.

^bWhen 1 + 2 + 3 < 100, trimers are also present to some extent.

^cSelectivity to the linear telomer 1.

^dTurn over calculated as g (products) g⁻¹ (Pd) × h.

^ePd: 0.08 mmol.

^fIn the presence of 20 ml of *n*-C₆H₁₄.

^gIn the presence of 20 ml of toluene.

^hIn the presence of 20 ml of THF.

result definitely confirms the expected activation effect by alkoxides, *n*-hexane presence not affecting the catalytic activity. Taking into account that Pst-DPPP-Pd(II), owing to the linearity of the polymeric ligand, is expected to be more sensitive to solvent effect than Dow-DPPP-Pd(II), the influence of reaction medium was further investigated (runs 28 and 29, Table 4). The collected data clearly indicate that both activity and selectivity to telomers decrease going from *n*-hexane to toluene and dramatically drop down in the presence of THF, i.e., increasing the electron donor character of the reaction medium. Indeed, π -electrons system of toluene phenyl ring may slightly interact with the metal species thus reducing 1,3-butadiene coordination and insertion rates, whereas THF may compete with the reagents in the coordination to the metal by the ethereal electron pair. When Pd(OAc)₂ was used as precursor in homogeneous phase (run 30, Table 4), the activity of the system was very low and a drop of selectivity to telomers also occurred. However, the model compound (BzO-DPPP)Pd(OAc)₂ displayed (run 31, Table 4) substantially the same activity and analogous selectivity as those observed for the heterogenized system. The above results substantiate that the activity in runs 25–29 is to be addressed to the heterogeneous catalyst and not to free Pd(OAc)₂ eventually absorbed on the polymer matrix. In addition a phosphine ligand seems to be necessary for the activation of the catalyst, even in the presence of the alkoxide promoter. When Dow-DPPP-Pd(0) precursor was used (run 32, Table 4) a much higher activity was observed with respect to that of the experiment performed in the absence of MeONa (run 17, Table 3), but lower as compared with Dow-DPPP-Pd(II) (run 25). However, the activity of the Dow-DPPP-Pd(0) precursor could be improved by increasing the relative amount of methanol (run 33), the same performances as with Dow-DPPP-Pd(II) being substantially reached when a MeOH/C₄H₆ molar ratio equal to 3 was used. On the basis of all reported data, it may be concluded that the above heterogenized polymer-bound palladium complexes, when added with an alkoxide promoter, display comparable activity as that of the homogeneous counterpart and high selectivity to telomers (> 85%), particularly towards the linear telomer (> 92%). In this respect, our attention was also focused on the stability of the above catalysts, in terms of metal leaching and hence possibility to be recycled. In particular, the activity of the catalyst deriving from Dow-DPPP-Pd(II) was examined after several recycles, as reported in Table 5, by performing a series of experiments under the same conditions as previously described, but with a shorter duration (3 h). The improved performances of the catalyst during the 1st recycle suggests that the system is characterized by a certain induction period. The overall data clearly indicate that the catalyst substantially maintains the same performances in subsequent cycles, only 5% of metal being

Table 5

Telomerization of 1,3-butadiene with methanol by fresh and recycled catalysts derived from the heterogenized Dow-DPPP-Pd(II) complex in the presence of MeONa as promoter^a

Precursor	Conv. (%) C ₄ H ₆	Products (%) ^b		S ^c (%)	Released Pd ^d (%)
		Telomers	Dimers		
Dow-DPPP-Pd(II)	13.4	76.1	22.1	94.6	1.6
1st Recycle	19.9	94.1	4.9	94.9	1.4
2nd Recycle	11.3	91.7	7.6	94.5	1.1
3rd Recycle	11.4	88.8	10.2	94.5	0.6
4th Recycle	10.5	86.8	12.1	95.0	0.3

^a Pd = 0.08 mmol; C₄H₆/Pd, MeOH/C₄H₆ and MeONa/Pd = 6500, 1.5 and 10 mol/mol, respectively; Reaction time: 3 h; T: 60°C; 20 ml of *n*-hexane.

^b When telomers + dimers < 100 trimers are also present to some extent.

^c Selectivity to the linear telomer 1.

^d Expressed in weight and referred to the amount of Pd originally present in the precursor.

released into solution after 5 catalytic cycles. The progressive slight reduction of activity has probably to be addressed to the impossibility to recover all the catalyst to be used for the subsequent cycle, rather than to a real decrease of activity. Moreover, the phosphorus content determined in the catalyst after the last recycle was found to be the same (2.6 wt.%) as that of the original precursor, thus proving that no release at all of the diphosphine ligand bound to the polymer matrix occurred during the catalytic cycles. Therefore, it may be concluded that under the adopted conditions the polymer-bound palladium complexes via a chelating diphosphine ligand really work as heterogenized catalysts

4. Final remarks

On the basis of the obtained results the following conclusions can be drawn.

Palladium (II) complexes anchored on activated silica, differently to what previously claimed for analogous systems supported on sepiolite, in the presence of an ancillary phosphine ligand do not display any activity as heterogenized catalysts in the telomerization of 1,3-butadiene with methanol, the activity observed at high temperatures being due only to the released metal in solution.

Palladium (II) complexes anchored to crosslinked styrene/divinylbenzene resins through acetylacetonate chelating moieties, in the presence of an ancillary phosphine ligand, result active for the telomerization reaction even in absence of alkoxide promoters. However, they do not work as really heterogenized systems. Indeed, the above activity must be mainly related to palladium leaching into solution, in turn directly connected with the concentration of phosphine ligand in the reaction medium. Therefore diketonate ligands are not suitable to permanently fix palladium species on the polymer matrix.

Palladium complexes anchored to crosslinked styrene/divinylbenzene resins through 1,3-diphosphine chelating ligands display poor activity in the telomerization reaction in absence of an alkoxide promoter, probably due to an intrinsic stability of the catalytic system under the reaction conditions. However, the use of MeONa as promoter generates catalytic species with appreciable activity and high selectivity towards the linear telomer. The above heterogenized systems display substantially the same catalytic performances as those found for analogous complexes operating either in homogeneous phase [BzO-DPPP-Pd(II)] or in heterogeneous phase but in more swollen conditions [Pst-DPPP-Pd(II)], thus suggesting that activity and selectivity of the telomerization reaction are not appreciably affected by diffusion properties and steric hindrance of the support on which the palladium species are anchored. Finally, recycle experiments allow one to conclude that the palladium is permanently anchored to the polymer matrix via 1,3-diphosphine ligands and the resulting catalysts really work as heterogenized systems without appreciable releasing of metal species into the reaction medium. Therefore, the above anchored chelate ligands may be successfully used for heterogenizing different metal species to be applied for several catalytic reactions, even under drastic conditions.

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References

- [1] M. Marchionna, R. Patrini, F. Giavazzi, G.C. Pecci, Preprints 212th National Meeting of the Am. Chem. Soc., Div. Petr. Chem., Vol. 41 (1996) p. 585.
- [2] A. Behr, in: R. Ugo (Ed.), Aspects of Homogeneous Catalysis, Vol. 5, D. Reidel, Dordrecht, 1984, p. 3.
- [3] N. Yoshimura, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, Vol. 1, VCH, Weinheim, 1996, p. 351.
- [4] R. Patrini, M. Lami, M. Marchionna, F. Benvenuti, A.M. Raspolli Galletti, G. Sbrana, *J. Mol. Catal. A: Chem.* 129 (1998) 179.
- [5] C.U. Pittman Jr., S.E. Jacobson, *J. Catal.* 44 (1976) 87.
- [6] C.U. Pittman Jr., Q. Ng, *J. Organometal. Chem.* 153 (1978) 85.
- [7] K. Kaneda, H. Kurosaki, M. Terasawa, T. Imanaka, S. Teranishi, *J. Org. Chem.* 46 (1981) 2356.
- [8] K. Kaneda, H. Yamamoto, T. Imanaka, S. Teranishi, *J. Mol. Catal.* 29 (1985) 99.
- [9] K. Kaneda, M. Higuchi, T. Imanaka, *Chem. Express* 3 (1988) 335.
- [10] U. Schuchardt, E.N. Dos Santos, F.S. Dias, *J. Mol. Catal.* 55 (1989) 340.
- [11] M.F. Rettig, P.M. Maitlis, *Inorg. Synth.* 28 (1990) 110.
- [12] T.A. Stephenson, S.M. Morehouse, A.R. Powell, J.P. Heffer, J. Wilkinson, *J. Chem. Soc.* (1965) 3632.
- [13] R.S. Wright, N.J. Coville, *S. Afr. Chem.* 3 (1989) 42.
- [14] S. Sugai, H. Ikawa, T. Okazaki, S. Akaboshi, S. Ikegami, *Chem. Lett.* (1982) 597.
- [15] A.R. Siedle, R.H. Crabtree, in: A.P. Ginsberg (Ed.), *Inorg Synth.* 27 (1990) 317.
- [16] I.E. Uflyand, I.A. Ilchenko, U.N. Sheinker, *React. Polym.* 14 (1991) 41.
- [17] A. Warshawsky, A. Deshe, *J. Polym. Sci.: Polym Chem. Ed.* 23 (1985) 1839.
- [18] M.I. Tkatchenko, *Soc. Nat. Petroles d'Aquitaine, Belg. Pat.* 831,084 (1976).
- [19] M.I. Tkatchenko, *Chem. Abstr.* 85 (1976) 94934n.
- [20] M.I. Tkatchenko, *C. R. Acad. Sci. Paris (Ser. C)* 282 (1976) 229.
- [21] T. Ukai, H. Kawazura, Y. Ishii, J.J. Bonnet, J.A. Ibers, *J. Organometal. Chem.* 65 (1974) 253.
- [22] S. Fisher, J. Porter, *Anal. Chem.* 36 (1964) 1159.
- [23] C.U. Pittman Jr., D.E. Leyden, J.C. Lennox, *Anal. Chim. Acta* 64 (1973) 143.
- [24] G. Braca, G. Sbrana, L. Leoni, E. Giannetti, *Anal. Chem.* 80 (1975) 176.
- [25] R.G. Pearson, *Angew. Chem.* 77 (1965) 361.
- [26] S. Baba, T. Ogura, S. Kawgushi, *Bull. Chem. Soc. Jpn.* 47 (1974) 665.
- [27] F. Benvenuti, C. Carlini, A.M. Raspolli Galletti, G. Sbrana, M. Marchionna, P. Ferrarini, *Polym. Adv. Technol.* 9 (1998) 113.
- [28] E. Benazzi, C.J. Cameron, H. Mimoun, *J. Mol. Catal.* 69 (1991) 299.
- [29] W. Kuran, A. Musco, *Inorg. Chim. Acta* 12 (1975) 187.