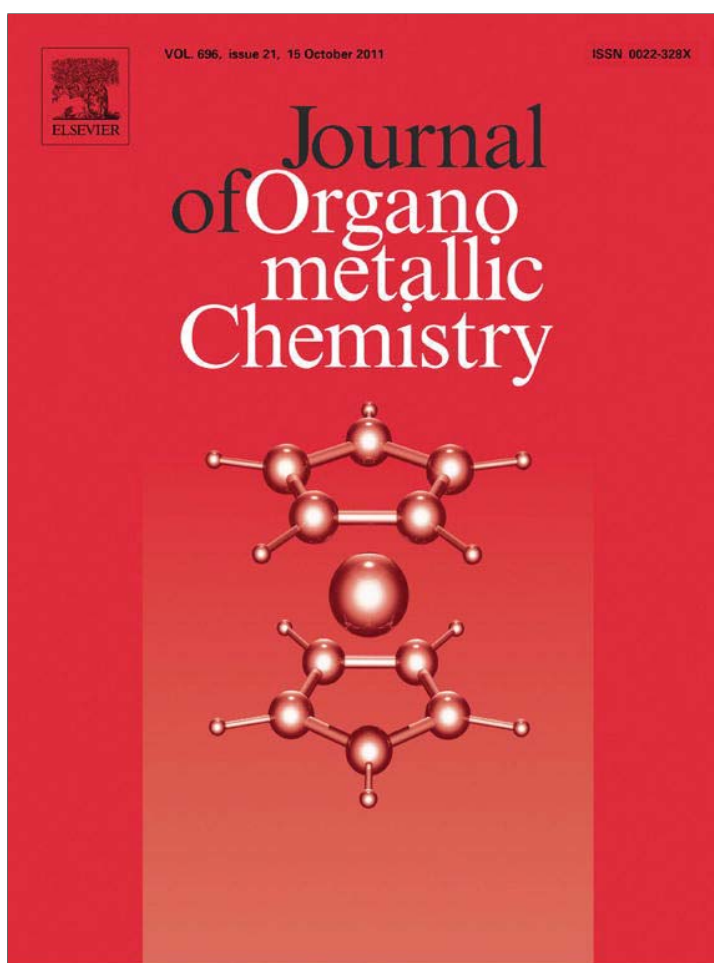


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Journal of Organometallic Chemistry

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Note

Synthesis of new (–)-menthylgermanium derivatives and its use in heterogeneous bimetallic catalysis

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ARTICLE INFO

Article history:

Received 12 May 2011

Received in revised form

6 July 2011

Accepted 7 July 2011

Dedicated to Prof. Dr. Pelayo Camps (University of Barcelona, Spain) on the occasion of his 65th birthday.

Keywords:

Tri-(–)-menthylgermanium chloride

Tri-(–)-menthylmethylgermanium

Tri-(–)-menthylgermanium hydride

Bimetallic catalyst

ABSTRACT

The syntheses and physical properties of tri-(–)-menthylgermanium chloride (**2**), tri-(–)-menthylmethylgermanium (**5**), and tri-(–)-menthylgermanium hydride (**6**) are reported. The preparation of a bimetallic catalyst derived from **5** and Pt supported on SiO₂ and its use in the enantioselective catalytic hydrogenation of acetophenone is also reported.

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1. Introduction

In previous studies we have shown that organotin compounds with (–)-menthyl ligands react with a monometallic catalyst generating an organometallic phase – retaining the organic groups on the surface – with remarkable properties for the selective hydrogenation of carbonyl compounds [1]. Alleged toxicity of the organotin derivatives aroused the interest for developing new organometallic reagents that could replace the organotins. For this reason, and as part of our ongoing studies on the preparation of bimetallic catalysts derived from chiral organometallic compounds in order to use them in heterogeneous catalysis [1,2], we consider it of interest to carry out the preparation of bimetallic systems derived from chiral organogermanium compounds and Pt supported on SiO₂. Bimetallic systems were prepared by controlled surface reactions, using techniques derived from the Surface Organometallic Chemistry on Metals (SOMC/M). This approach

implies the selective reaction of organometallic compounds of several metals, such as Sn, Ge, Pb, with the surface of transition metals, giving rise to different types of surface structures, such as grafted organometallic fragments, adatoms or bimetallic alloys.

A key step in the preparation of asymmetric heterogeneous catalysts based on silica-supported platinum chemically modified with chiral organometallic compounds is the synthesis of optically pure organometallic derivatives. In order to carry out our studies, we decided to attach the (1R,2S,5R)-(–)-menthyl [(–)-Men] group to the germanium atom as chiral ligand. From our own experience in organotin chemistry we knew that the direct attachment of the (–)-menthyl group to the metal atom in germanium tetrachloride might take place enantioselectively [2].

In the chemical literature there are few examples of organogermanium compounds containing (–)-menthyl groups attached to the germanium atom. Thus, in a fairly recent paper Schiesser et al. reported a four steps synthesis of (–)-menthyl diphenylgermane in an overall yield of 40% starting from the alkylation of GeCl₄ with (–)-menthylmagnesium chloride (**1**) in THF using a molar ratio Grignard reagent/GeCl₄ = 1:1 [3]. Santini et al. [4] obtained (–)-menthylgermanium trihydride via oxidative addition of germylene GeCl₂ into the carbon-chloride bond of (–)-menthyl chloride; this reaction led to the organogermanium hydride in 60% yield but a partial racemization was observed.

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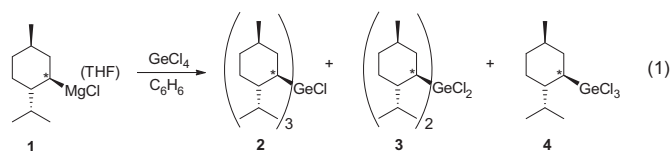
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These organogermanium compounds with chiral ligands are being used at present to modify supported Pt heterogeneous asymmetric catalysts and to study their enantioselectivity in hydrogenation reactions. In order to illustrate these studies, in this paper we report the results obtained in the synthesis of some new (–)-menthyl substituted organogermanium derivatives, and in the hydrogenation of acetophenone using a catalytic system of Pt modified with tri-(–)-menthylmethyl germanium (5).

2. Results and discussion

2.1. Synthesis of tri-(–)-menthylgermanium derivatives

Our target was the synthesis of tri-(–)-menthylgermanium derivatives. Taking into account our previous experience in organotin chemistry [2b], we considered it possible to obtain organogermanium compounds with three (–)-menthyl groups attached to the Ge atom *via* the direct synthesis using higher Grignard reagent **1**/GeCl₄ molar ratios than those used by Schiesser et al. In order to determine the best reaction conditions needed to obtain the desired triorganogermanium derivative in higher proportion, we carried out the reaction between GeCl₄ and **1** in THF under different reaction conditions, as shown in Equation (1)



In all the experiments the Grignard reagent was added dropwise to the solution of germanium tetrachloride in benzene. The results obtained are summarized in Table 1.

Compounds **2** and **3** were separated by column chromatography (silica gel 60). Table 1 shows that, according to the ratio **1**/GeCl₄, in all cases were obtained varying mixtures of chlorides **2** and **3**, and that in one case (entry 1) was detected the formation of (–)-menthylgermanium trichloride (**4**). These reactions were carried out by using titrated solutions of **1** in THF, and the figures given in Table 1 are an average of 6 experiments. Using higher ratios **1**/GeCl₄ did not improve the yield of **2**, and even using a ratio **1**/GeCl₄ = 10 neither the formation of tetra (–)-menthylgermanium nor of hexa(–)-menthyldigermane was detected. This might be connected with the steric hindrance of the voluminous (–)-menthyl group. On the other hand, ¹H NMR of these

Table 1
Alkylation of GeCl₄ with (–) menthylmagnesium chloride.

Entry	1 /GeCl ₄ Ratio	Reaction conditions ^a	Yield (%) ^b	Product Ratios (%) ^c		
				R ₃ GeCl (2)	R ₂ GeCl ₂ (3)	RGeCl ₃ (4)
1	4	1) 0 °C; 2) reflux 12 h; 3) rt 4 h	82	30	70 ^d	
2	5	1) rt; 2) reflux 12 h; 3) rt 15 h	79	53	47	
3	6	1) rt; 2) reflux 3 h; 3) rt 15 h	80	60	40	
4	6	1) rt; 2) reflux 20 h; 3) rt 15 h	89	70	30	

^a All the reactions were carried out by adding the Grignard reagent in THF onto a solution of GeCl₄ in benzene; rt = room temperature; rfx = reflux.

^b After chromatography.

^c By CG-MS; R = (–)-menthyl.

^d Compounds **3** and **4** could not be separated; however, NMR spectra of chromatographic fractions enriched in both **3** and known compound **4** enabled us to establish the composition of these mixtures by comparison with the reported data for compound **4** [2].

compounds demonstrate that the alkylations take place without epimerization this demonstrating that direct alkylation of GeCl₄ takes place enantioselectively.

Starting from tri-(–)-menthylgermanium chloride (**2**) we were able to obtain the new organogermanium derivatives tri-(–)-menthylmethylgermanium (**5**), tri-(–)-menthylgermanium hydride (**6**), and tri-(–)-menthylgermanium bromide (**7**), according to Scheme 1. Thus, alkylation of compound **2** with methylmagnesium iodide afforded compound **5** in 86% yield. On the other hand, reduction of **2** with lithium aluminum hydride leads in 98% yield to the corresponding organogermanium hydride **6**.

To estimate its reactivity, hydride **6** was allowed to react with carbon tetrachloride. It was found that the decomposition of a 0.077 M solution of **6** in carbon tetrachloride at 25 °C takes place in about 10 h. The reaction was followed by IR spectroscopy by observing the disappearance of the Ge–H absorption at 2000 cm⁻¹. On the other hand, the reaction between hydride **6** and carbon tetrabromide led after 72 h to a mixture of hydride **6** and tri-(–)-menthylgermanium bromide (**7**), the former in higher proportion. We were not able to separate this mixture by column chromatography on silica gel 60. However, ¹³C NMR spectrum of the mixture showed the 10 resonances corresponding to each compound and this enabled us to establish the signals belonging to bromide **7**.

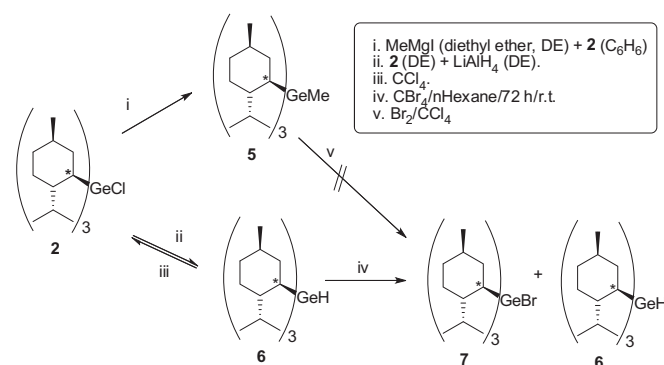
In order to study the reactivity of the Ge–C bonds in tri-(–)-menthylmethylgermanium (**5**), we carried out the addition of bromine in carbon tetrachloride to a solution of **5** in the same solvent. No reaction was detected after 48 h at r.t., tetralkylgermanium **5** being recovered pure.

¹³C NMR characteristics of the new organogermanium compounds **2**, **3**, **5**, and **6** are collected in Table 2.

These organogermanium compounds with chiral ligands are being used at present to modify supported Pt heterogeneous asymmetric catalysts and to study their enantioselectivity in hydrogenation reactions. In order to illustrate these studies, in this paper we report the results obtained in the hydrogenation of acetophenone using a catalytic system of Pt modified with tri-(–)-menthylmethyl germanium (**5**).

2.2. Preparation and characterization of the catalysts

The preparation of the monometallic Pt/SiO₂ catalyst (1 wt% Pt, measured by atomic absorption spectrometry) was achieved by means of ionic exchange, a procedure that allowed obtaining a catalytic phase with high dispersion (H/Pt = 0.65 and 0.55, measured by H₂ and CO chemisorption, respectively) [5]. Results obtained by TEM showed a rather uniform distribution of metallic particle size, centered around 2 nm. These characteristics of surface homogeneity and dispersion are essential to assure a correct preparation of organometallic catalysts through SOMC/M



Scheme 1. Synthesis of derivatives of tri-(–)-menthylgermanium chloride (**2**).

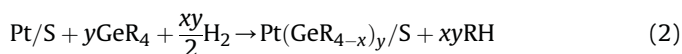
Table 2
¹³C{¹H} NMR spectra of compounds **2**, **3**, **5**, and **6**.^a

C _n	Compound N ^o			
	Compound 2	Compound 3	Compound 5	Compound 6 ^b
C ₁	39.01	36.31	34.80	34.91
C ₂	45.24	45.22	45.49	46.42
C ₃	26.48	26.43	26.71	26.61
C ₄	35.32	35.37	35.71	35.97
C ₅	34.57	34.53	32.66	30.56
C ₆	38.83	38.80	39.90	41.00
C ₇	22.78	22.84	23.02	23.10
C ₈	30.75	31.07	30.61	30.46
C ₉	21.93	22.05	22.16	22.23
C ₁₀	16.82	16.48	16.74	16.23
Z	–	–	–1.67	–

^a In CDCl₃ solution except when otherwise stated; chemical shifts, \square , in ppm with respect to central peak of chloroform.

^b In C₆D₆.

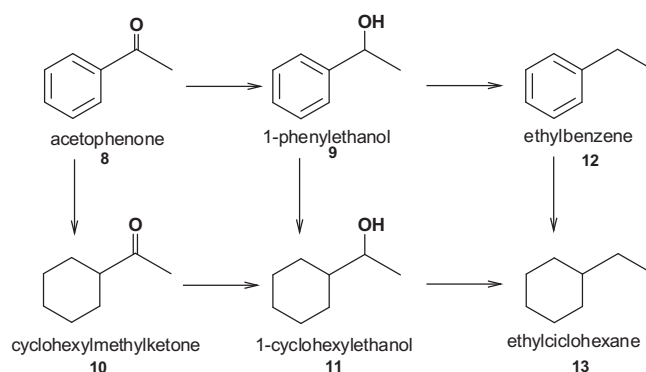
techniques. Germanium-modified catalysts were obtained by a controlled surface reaction between the monometallic catalyst, previously reduced, and a solution of the organometallic germanium compound in a paraffinic solvent, such as n-decane. The reaction takes place between 363 and 423 K and results in a system with organogermanium moieties anchored to the surface. Equation (2) represents the above mentioned process.



R represents the remaining organic fragment bonded to germanium, that is, methyl or (–)-menthyl groups. The amount of germanium fixed was measured to determine the stoichiometry of the bimetallic phase, expressed as the atomic ratio between Ge and Pt through the “y” value ($y = \text{Ge}/\text{Pt} = 0.4$). In order to study the specificity of the interaction between the monometallic catalyst and the organogermanium compounds, blank experiments were conducted in which the germanium precursor was contacted with SiO₂. No detectable amounts of germanium on the support were observed under the experimental conditions of this work. Unfortunately, it has not been possible to characterize in detail the chiral catalytic systems, in particular as regards the structure of the organogermanium phase attached to the platinum surface. However, the results presented below, and other published previously for organotin compounds [1a,b], show that these systems induce enantioselectivity in the hydrogenation of certain prochiral carbonyl compounds, concluding that at least some (–)-menthyl groups are anchored on the catalyst.

2.3. Catalytic tests

The main products of acetophenone (**8**) hydrogenation are shown in Scheme 2. If the C=O bond is hydrogenated, 1-phenylethanol (**9**) is obtained, a product of interest in pharmaceutical and perfume industry. On the other hand, the hydrogenation of the aromatic ring leads to the production of cyclohexylmethylketone (**10**). Finally, the subsequent hydrogenation of **9** or **10** leads to 1-cyclohexylethanol (**11**), a product used in the manufacture of certain polymers. The formation of ethylbenzene (**12**) and ethylcyclohexane (**13**) could be explained by hydrogenolysis of the C–O bond of the intermediate alcohols or, as it has



Scheme 2. Reaction scheme for acetophenone hydrogenation.

been proposed in the literature, by the initial C=O hydrogenation followed by dehydration and addition of hydrogen to the newly formed C=C bond [6]. In general, the required product is 1-phenylethanol (**9**).

Fig. 1 shows the results of selectivity, enantiomeric excess, and conversion to 1-phenylethanol (**9**) at 180 min of reaction for the hydrogenation of acetophenone, Pt, Pt–GeBu₄ and Pt–Men₃GeMe systems. As can be seen, in terms of activity, the catalysts behave quite differently. The monometallic catalyst is more active than the germanium modified system (reached conversion was 95, 66 and 64% for Pt, Pt–GeBu₄ and Pt–Men₃GeMe respectively). To explain these facts it is necessary to take into account the variations in the characteristics of the active sites for hydrogenation that could appear by the addition of either a nonchiral (GeBu₄) or a chiral **5** (Men₃GeMe) organogermanium modifier. Pt-based catalytic systems modified with SnBu₄, similar to those used in this work, have been characterized by our research group using EXAFS, XANES and XPS techniques in order to clarify the nature of the active sites [7]. Those studies revealed that in organobimetallic systems there is a convergence of geometric (dilution of Pt sites) and electronic (increased electron density of Pt) effects due to the presence of second metal. It was also found by XPS that metal modifier is present on the surface of Pt both in ionic form and in metallic. Both monometallic and organobimetallic systems presented in the region corresponding to Pt 4f7/2 binding energy (BE) a single peak, which is characteristic of platinum in the metallic state. The organobimetallic sample presented a shift of this peak toward lower BE. This fact is indicative of the existence of an electronic effect of tin on platinum. The Sn 3d5/2 spectrum for PtSn presents two bands, one that can be ascribed to reduced tin, and another one at higher BE,

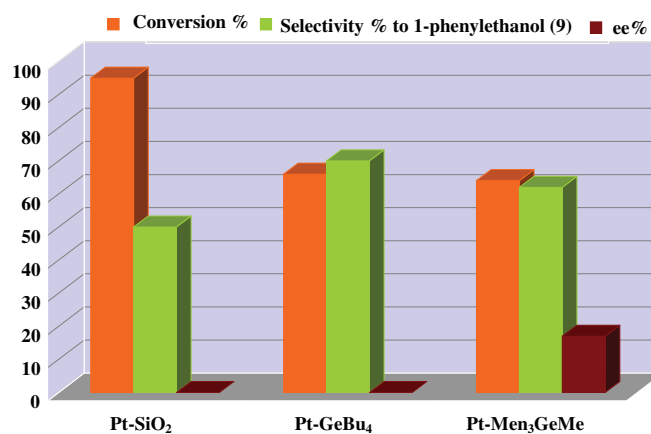


Fig. 1. Conversion, selectivity, and enantiomeric excess for the hydrogenation of acetophenone at 180 min of reaction.

which is attributed to oxidized tin (Sn(II) and Sn(IV)). Thus, the presence of organotin fragments blocks some active sites for the hydrogenation on the Pt surface and, as a consequence, the catalytic activity is reduced.

Concerning the selectivity, Fig. 1 shows that the addition of organogermanium compounds favors the formation of 1-phenylethanol (**9**). In the case of Pt–GeBu₄ and Pt–Men₃GeMe catalysts, the aromatic ring hydrogenation is strongly inhibited perhaps by a dilution effect of Pt atoms, besides the electronic effects produced by the presence of ionic germanium, as shown by EXAFS/XANES [8]. Both effects would favor the acetophenone molecule interaction in this catalyst through the oxygen atom of the C=O group, and not *via* the aromatic ring, facilitating in this way the formation of 1-phenylethanol (**9**). The existence of an additional steric effect due to the presence of GeR_x fragments on the surface should not be discarded. Thus, the selectivity of 1-phenylethanol obtained was 50%, 70 and 62% for Pt, Pt–GeBu₄ and Pt–Men₃GeMe respectively.

The Pt–Men₃GeMe system also proved to be enantioselective; the enantiomeric excess reaching values of 17% for 1-phenylethanol (**9**).

2.4. Conclusions

The main findings of this study are:

- It has been possible to prepare organobimetallic catalysts by the selective reaction of an organogermanium compound (GeBu₄ and Men₃GeMe) and a Pt-monometallic catalyst. These systems have been obtained through controlled surface reactions, using techniques derived from SOMC/M.
- These solids proved to be active catalysts in the hydrogenation of acetophenone. The monometallic catalyst is more active than the germanium modified system, possibly due to a dilution effect of the active sites on the Pt surface, due to the presence of Ge.
- The addition of organogermanium compounds favors the formation of 1-phenylethanol. In the Pt–GeBu₄ and Pt–Men₃GeMe catalysts, the aromatic ring hydrogenation is strongly inhibited perhaps by a dilution effect of Pt atoms, besides the electronic effects produced by the presence of ionic germanium. The existence of an additional steric effect due to the presence of GeR_x fragments on the surface should not be discarded.
- The Pt–Men₃GeMe catalyst proved to be enantioselective in the hydrogenation of acetophenone, reaching values of enantiomeric excess of 17% for 1-phenylethanol.

3. Experimental

3.1. General methods

NMR spectra were recorded on a Bruker ARX 300 instrument, using CDCl₃ as solvent; chemical shifts (δ) are reported in ppm with respect to TMS for ¹H and ¹³C NMR spectra. Infrared spectra were recorded with a Nicolet Nexus FT spectrometer. CG-Mass spectra were obtained with a GC/MS instrument (HP5-MS capillary column, 30 m × 0.25 mm × 0.25 μ m) equipped with 5972 mass selective detector operating at 70 eV (EI). Program: 50 °C for 2 min with increase 10 °C/min to 280 °C. Elemental analyses (C, H) were performed at UMYMFOR (Universidad de Buenos Aires) and University of Cologne (Germany). Melting points were determined in a Kofler hot stage and are uncorrected. Specific rotations were determined with a Polar L- μ P, IBZ messtechnik. All the solvents and reagents used were analytical reagent grade. Germanium

tetrachloride was purchased and (1R,2S,5R)-(–)-menthylmagnesium chloride (**1**) was obtained following known procedures [9].

3.2. Synthesis of (1R,2S,5R)-(–)-trimethylgermanium chloride (**2**) and (1R,2S,5R)-(–)-dimethylgermanium dichloride (**3**)

To a vigorously stirred solution of GeCl₄ (5.64 g, 26 mmol) in dry benzene (27 mL) at room temperature and placed in a two-necked round-bottomed flask with a pressure-equalizing funnel and a reflux condenser with a nitrogen seal attached, was added dropwise a solution of (1R,2S,5R)-(–)-menthylmagnesium chloride (**1**) in dry THF (98.7 mL of a 1.58 M solution, 156 mmol). The mixture was heated under reflux for 20 h and then was left for 15 h with stirring at room temperature. HCl was then added (ca. 20 mL of a 10% solution), and the mixture was transferred to a separatory funnel. After Et₂O addition (ca 150 mL), the organic layer was decanted, washed three times with water, and then dried with anhydrous MgSO₄. The solvent was removed under reduced pressure. The chromatogram of the crude product (12.3 g) showed a mixture of two compounds: (1R,2S,5R)-(–)-trimethylgermanium chloride (**2**) (R_f: 24.12 min) and (1R,2S,5R)-(–)-dimethylgermanium dichloride (**3**) (R_f: 22.88 min) in a ratio **2**/**3** = 70:30. Column chromatography (silica gel 60) of the mixture afforded **2** (8.4 g, 16 mmol, 62%) and **3** (2.3 g, 5.4 mmol, 21%) in the fractions eluted with 99:1 and 93:7 hexane–diethyl ether, respectively. Compound **2**: mp 104–105 °C; [α]_D²² = –79.5° (c 1, C₆H₆); ¹H NMR (CDCl₃, Me₄Si) δ ppm: 0.80 [d, 9H, ³J(H,H) 6.7]; 0.89 [d, 9H, ³J(H,H) 6.4]; 0.94 [d, 9H, ³J(H,H) 6.8]; 0.97–2.10 (m, 30H). MS (*m/z*, relative intensity): 387 [34, (M – C₁₀H₁₉)⁺], 249 [37, (M – C₂₀H₃₈)⁺], 137 (76), 55 (100). Anal. Calcd. for C₃₀H₅₇GeCl: C 68.53; H 10.93. Found: C 68.66; H 10.97. Compound **3**: mp 83–84 °C; [α]_D²² = –82.3° (c 1, C₆H₆); ¹H NMR (CDCl₃, Me₄Si) δ ppm: 0.80 [d, 6H, ³J(H,H) 6.9]; 0.87 [d, 6H, ³J(H,H) 6.5]; 0.93 [d, 6H, ³J(H,H) 7.0]; 0.99–2.00 (m, 20H). MS (*m/z*, relative intensity): 388 [79, (M – Cl)⁺], 352 [17, (M – 2Cl)⁺], 249 [15, (M – Cl – C₁₀H₁₉)⁺], 213 [9, (M – 2Cl – C₁₀H₁₉)⁺], 137 (5), 55 (100). Anal. Calcd. for C₂₀H₃₈GeCl₂: C 56.91; H 9.08. Found: C 57.03; H 9.10.

3.3. Synthesis of (1R,2S,5R)-(–)-trimethylmethylgermanium (**5**)

To a solution of **2** (3.0 g, 5.7 mmol) in dry benzene (12 mL) at 0 °C under nitrogen, was added slowly and dropwise with stirring a solution of the methylmagnesium iodide in diethyl ether (3.7 mL of a 1.53 M solution, 5.7 mmol). The mixture was heated under reflux for 3 h. After cooling at 0 °C, the reaction mixture was decomposed with a solution of HCl (ca 5 mL of a 10% solution). The organic layer was separated and the aqueous layer was extracted three times with diethyl ether (ca 2 mL each). The combined organic extracts were dried over anhydrous MgSO₄, and the solvent was removed under reduced pressure. Column chromatography (silica gel 60) gave **5** as a white solid (2.48 g, 4.9 mmol, 86%); mp 65–66 °C; [α]_D²² = –43.7° (c 1, C₆H₆); ¹H NMR (CDCl₃, Me₄Si) δ ppm: 0.23 (s, 3H); 0.77 [d, 9H, ³J(H,H) 6.9]; 0.88 [d, 9H, ³J(H,H) 6.6]; 0.93 [d, 9H, ³J(H,H) 6.9]; 0.98–1.86 (m, 30H). MS (*m/z*, relative intensity): 367 [1, (M – C₁₀H₁₉)⁺], 228 [41, (M – C₂₀H₃₈)⁺], 137 (100). Anal. Calcd. for C₃₁H₆₀Ge: C 73.67; H 11.96. Found: C 73.48; H 11.92.

3.4. Synthesis of (1R,2S,5R)-(–)-trimethylgermanium hydride (**6**)

To a suspension of LiAlH₄ (0.14 g, 3.6 mmol) in dry diethyl ether (8 mL) under atmosphere of nitrogen at room temperature, was added dropwise a solution of (1R,2S,5R)-(–)-trimethylgermanium chloride (**2**) (1.9 g, 3.6 mmol) in dry diethyl ether (20 mL). The mixture was heated under reflux for 7 h and a saturated solution of ammonium chloride was then added (ca 10 mL). The organic layer was separated, and the aqueous was extracted three times with

diethyl ether. The combined organic extracts were dried over anhydrous MgSO_4 . Removal of the solvent under reduced pressure gave **6** as a white solid (1.73 g, 3.5 mmol, 98%). IR (NaCl, cm^{-1}): $\nu_{\text{Ge-H}}$ 2000 [4]; mp 90–91 °C; $[\alpha]_{\text{D}}^{22} = -105.3^\circ$ (c 1, C_6H_6); ^1H NMR (C_6D_6 , Me_4Si) δ ppm: 0.89 [d, 9H, $^3\text{J}(\text{H,H})$ 6.9]; 0.92 [d, 9H, $^3\text{J}(\text{H,H})$ 6.2]; 1.00 [d, 9H, $^3\text{J}(\text{H,H})$ 6.9]; 1.21–2.28 (m, 30H); 4.35 (s, 1H, Ge–H). MS (m/z , relative intensity): 353 [16, ($\text{M} - \text{C}_{10}\text{H}_{19}$) $^+$], 215 [50, ($\text{M} - \text{C}_{20}\text{H}_{38}$) $^+$], 137 (100). Anal. Calcd. for $\text{C}_{30}\text{H}_{58}\text{Ge}$: C 73.33; H 11.90. Found: C 73.06; H 11.86.

3.5. Catalysts preparation

The monometallic catalyst was prepared by ion exchange, using SiO_2 as support, previously treated with ammonia solution. At pH between 9 and 11, SiO_2 behaves as a cationic exchanger, and under this condition, was contacted with an aqueous solution of $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ in an appropriate concentration so as to obtain 1 wt% Pt in the resulting catalyst. After 24 h of exchange at room temperature, the solid was separated by filtration, washed and dried at 378 K, and subsequently reduced in H_2 flow at 773 K for 2 h.

The modification of monometallic catalysts by germanium addition was carried out by using surface organometallic chemistry on metals (SOMC/M) techniques [10]. Based on the deep analysis of catalytic systems analogous to the ones here presented, but containing tin, the experimental conditions were selected so as to achieved the desired Ge/Pt atomic ratio [7a,11]. After the reduction stage, a definite quantity of the monometallic catalyst (0.25 g) was put to react in H_2 atmosphere with GeBu_4 dissolved in *n*-decane at 393 K. Once the reaction was complete, the catalyst was washed with several portions of *n*-heptane in Ar atmosphere. This catalyst, which has a molar ratio Ge/Pt = 0.4, is denominated Pt– GeBu_4 and corresponds to a solid containing butyl groups anchored on the metallic surface. The preparation of the chiral organometallic catalyst was performed by following an analogous procedure, but using a solution of the chiral organotin compound tri(–)-menthylmethylgermanium in *n*-decane. The Ge/Pt ratio used was also 0.4. This catalyst is denominated Pt– Men_3GeMe .

3.6. Catalysts characterization

The monometallic catalyst was characterized by atomic absorption spectrometry (Varian Spectra AA55), temperature-programmed reduction (TPR) (Quantachrome, 25 $\text{cm}^3 \text{min}^{-1}$, 5% H_2 in N_2 , 10 K min^{-1}), and H_2 and CO chemisorption with a catalyst characterization equipment RXM-100 (Advanced Scientific Designs Inc., USA). The specific surface area of the support was also measured (Micromeritics ASAP 2020, N_2 adsorption at 77 K). The content of Ge fixed in each organobimetallic catalyst was obtained by chromatographic analysis of the solution containing the organometallic compound, as a function of reaction time, using a Varian CP-3800 gas chromatograph, equipped with a capillary column Factor-Four CP8907 (VF-1 ms, 15 m 0.25 mm i.d., DF = 0.25) and a FID detector. These results were consistent with the values obtained from the analysis of the metal content of bimetallic catalysts carried out by atomic absorption spectrometry [11a]. Measurements of the metal contents after the catalysts have been used in the hydrogenation reaction showed no variation, indicating that there is no metal leaching. The metal particle size distribution of all catalysts used was measured by transmission electron microscopy (TEM), in a JEOL 100 Cx microscope.

3.7. Hydrogenation reactions

Both the racemic and the enantioselective hydrogenations of acetophenone were carried out in a stirred autoclave type reactor at a H_2 pressure of 1 MPa and a temperature of 353 K, using 0.25 g catalyst, and 2-propanol as solvent. In each test, 0.5 mL of acetophenone and 60 mL of 2-propanol were used (0.07 M). The experimental conditions for the catalytic tests were chosen so that the reaction rate was not influenced by mass transfer. The course of the reaction was followed in a Varian CP-3800 gas chromatograph equipped with a capillary column CP wax 52 CB (30 m, i.d. 0.53 mm) and a FID detector. The reaction products were identified using a GC/MS Shimadzu QP5050 with a capillary column SUPELCO SPBMTM-5 (30 m, i.d. 0.25 mm). The enantiomeric excess (ee) was calculated according to the following expression: $\text{ee}\% = 100(\text{S} - \text{R}) / (\text{S} + \text{R})$, taking into account data obtained with a BETA DEX™ 120 capillary column (30 m length and i.d. 0.25 mm) in a Varian CP-3800 gas chromatograph.

Acknowledgments

JCP acknowledge grants from ANPCyT (Capital Federal, Argentina/BID 1728/OC-AR PICT N° 2467), CONICET (Buenos Aires, Argentina, PIP 112-200801-02272), and Universidad Nacional del Sur (Bahía Blanca, Argentina, PGI 24/Q024). MLC and VV gratefully acknowledge CONICET (PIP 0185) and Universidad Nacional de La Plata (Project X487) for the financial support. A grant for a short visit to Germany of one of us (JCP) from the Alexander von Humboldt Foundation is also gratefully acknowledged.

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