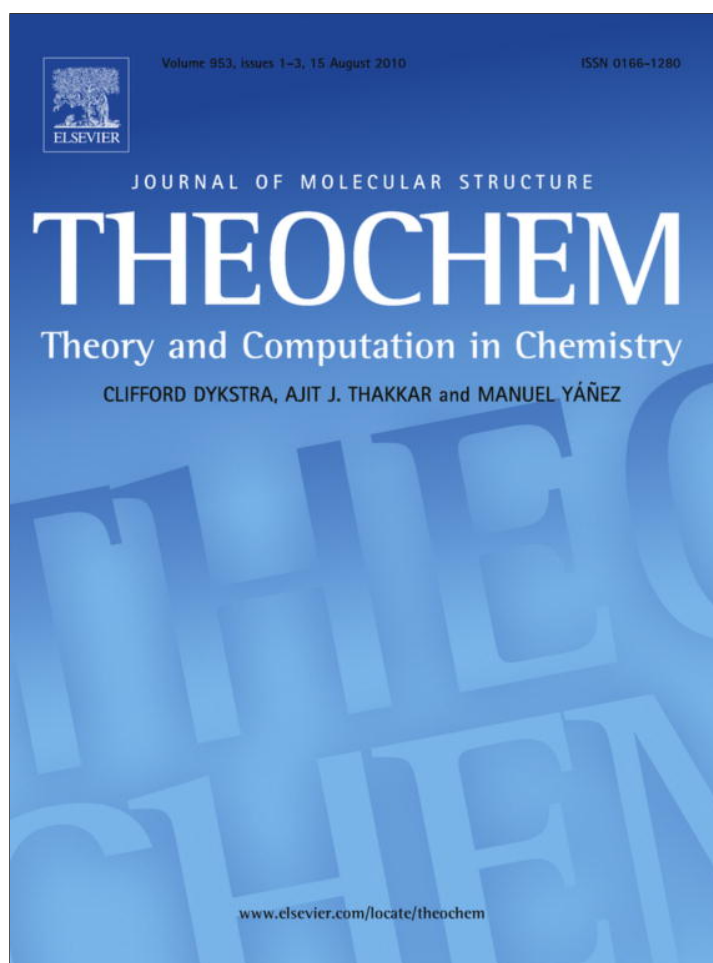


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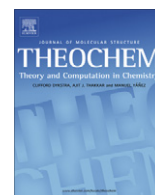
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Towards a rational design of enantioselective heterogeneous catalysts: Modeling of chiral organotin precursors

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ABSTRACT

In this work, the modeling of organotin compounds of general formula Men-Sn-R₃ (Men = menthyl, R = alkyl or alkoxyalkyl) is carried out. These compounds can be employed as precursors for obtaining enantioselective heterogeneous catalysts, prepared by means of Surface Organometallic Chemistry on Metals techniques. Both Molecular Mechanics and Molecular Dynamics, as well as Density Functional Theory (DFT), were used to give an insight into the relative stability of the Sn–C bonds of several different organotin compounds. The calculations carried out on the molecules Men-Sn-(iso-Bu)₃ and Men-Sn-((1-OCH₃)-Et)₃ showed that if these molecules are used as precursor compounds to prepare heterogeneous organobimetallic catalysts, the probability of losing the menthyl group in a dissociation process is lower, leading to a better performance of the resulting catalysts, in terms of enantiomeric excess.

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1. Introduction

In recent decades, chiral synthesis has received much attention due to the increasing requirements of the pharmaceutical and agrochemical industries, among others [1–3]. For economic, environmental, and social reasons, the trend towards using optically pure compounds is undoubtedly increasing. Among the various methods for the selective production of a single enantiomer, asymmetric catalysis is the most attractive from the point of view of atom economy [4–9].

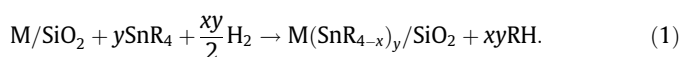
Despite the undoubted advantages of asymmetric heterogeneous catalysis, as yet few achiral substances can be converted into optically pure products with acceptable performance at the production level. One of the very interesting heterogeneous catalytic processes is the enantioselective hydrogenation using metallic catalysts modified with chiral compounds [5,10–15]. What has been termed the “classical approach” within heterogeneous asymmetric catalysis refers to catalytic systems derived from the interaction of a supported transition metal with an optically pure modifier and a prochiral substrate, determining the chirality of the product formed during the hydrogenation reaction. Only two such systems have been extensively studied to date: a nickel catalyst modified with tartrate/NaBr for the hydrogenation of β -keto esters [16,17] and Pt(Pd) catalysts modified with cinchona alkaloids for the hydrogenation of α -keto esters [10–15].

1.1. The Surface Organometallic Chemistry on Metals (SOMC/M) approach

There are several other approaches for obtaining enantioselective heterogeneous catalysts [19,20], among which is the methodology deeply studied in our research group, consisting in the preparation of asymmetric heterogeneous catalysts using SOMC/M techniques [21,22].

Surface organometallic chemistry can be defined as the area of chemistry that results from the overlap between organometallic chemistry and surface science. This field deals with the reactivity of organometallic compounds with the surface of oxides, typically employed as catalyst supports, and also with zeolites and related materials. When this type of reaction occurs on the surface of a metal, there is always a formation step of an organometallic fragment anchored to the surface, giving rise to a particular catalytic site where the interaction with the substrate to be reacted will take place. For only the desired reaction (selectivity) to occur, the catalytic site formed should be well-defined and have the same composition throughout the catalyst surface.

In 1984, Travers et al. [23] and Margitfalvi et al. [24] simultaneously described this application of SOMC for the preparation of bimetallic catalysts. The preparation of a catalyst through SOMC/M techniques involves reacting a supported transition metal (M) with an organometallic compound (usually of a group-14 metal, M') in a hydrogen atmosphere, according to the following equation:



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These kinds of catalytic systems with $M(\text{SnR}_{4-x})_y$ stable species supported on SiO_2 have shown unusual properties of activity and selectivity in many hydrogenation reactions of interest in the field of fine chemicals, for example, in the hydrogenation of α,β -unsaturated aldehydes, aromatic ketones, etc. [24–29].

All the steps in the reaction between an organotin compound of the type tetra-*n*-alkyltin and Pt particles supported on SiO_2 are shown in Fig. 1.

The species proposed in each formation step, are based on chemical analysis studies, XPS and EXAFS performed on a $\text{Pt}(\text{SnBu}_{4-x})_y/\text{SiO}_2$ catalysts [30]. The XP spectra in the region corresponding to Pt $4f_{7/2}$ (around 71 eV) only showed one peak, indicating the complete reduction of platinum. In considering this peak, in the tin-modified systems, a shift is observed in the binding energy (BE) towards lower values of approximately 0.7–1 eV with respect to the Pt/SiO_2 catalyst. In relation to the $\text{Pt}(\text{SnBu}_{4-x})_y/\text{SiO}_2$ sample, two peaks are also observed around 485 and 487 eV (Sn $3d_{5/2}$ region), which could be assigned to metallic tin [Sn(0)] and ionic tin [Sn(II, IV)], respectively. These species are found in similar proportions. EXAFS experiments of Pt/SiO_2 and the tin-modified platinum catalysts demonstrated that Sn addition had strong effects on Pt structures. The $\text{Pt}(\text{SnBu}_{4-x})_y/\text{SiO}_2$ sample showed a quite complicated radial distribution function: at least two different scatterer atoms must be present to obtain such a result. The coordination number for the Pt–Pt shell in the organotin sample is smaller than that of the monometallic sample. Because of the presence of PtSnBu_x entities on the surface of the $\text{Pt}(\text{SnBu}_{4-x})_y/\text{SiO}_2$ catalyst, a Pt–C shell has to be considered when this sample was analyzed. Taking into consideration these results, i.e., Bu groups remaining grafted on the surface and Sn in the form of Sn(0) and Sn(II, IV) in similar proportions, an image of the active phase would be represented by Fig. 1.

The ability to selectively add the organometallic promoter onto the transition metal and to stabilize the organic fragments on the supported bimetallic phase, modifying the chemoselectivity while maintaining the hydrogenating activity, is a quality of this preparation technique that has opened up interesting perspectives for its use in asymmetric heterogeneous catalysis. In this case, the chirality would not be given by the adsorption of a chiral modifier on the metal surface, as in the so-called “classic” systems, but by the chiral organometallic fragments remaining on the supported metal after the preparation reaction. Many of the organometallic com-

pounds used as precursors for the preparation of these enantioselective heterogeneous catalysts are organotin compounds of the type SnR_3R^* , where R^* is an organic fragment having a chiral center and R are organic fragments, equal or not, that have no chiral centers [31]. In this case, by using SOMC/M techniques, heterogeneous chiral catalysts of very good quality in terms of chemo- and enantioselectivity, as well as good stability and reuse capability, have been obtained [21,22]. As an example, Table 1 lists the results from the enantioselective hydrogenation of acetophenone with Pt-based systems modified with different organotin compounds: MenSnBu_3 , $\text{MenSnPh}_2\text{Me}$, Men_3SnMe , and $\text{Men}_3\text{SnSnMen}_3$. Enantiomeric excess values (*ee*%) for the catalysts prepared with the different synthesized chiral modifiers are included in the table. As can be deduced, the enantiodifferentiation capacity of the systems is similar, irrespective of the modifier used, enantiomeric excesses being greater than 20%, with preferential formation of the (*S*)-1-phenylethanol enantiomer. These results are particularly interesting since they exceed literature values for the hydrogenation of nonactivated simple aromatic ketones, such as acetophenone where enantiomeric excess values of 20% or less have been reported for Pt-based systems modified with cinchonidine [32,33]. For the (*S*)-proline-modified Pd/C system, the greatest enantiomeric excess obtained was 22% for 78% conversion [34]. When considering the heterogeneous enantioselective hydrogenation of this simple aromatic ketone and its derivatives, some successful catalytic results have been reported for Ru-based catalysts. In that sense, Zhao et al. reported 1,2-diphenylethylene-diamine and phosphine modified 5%Ru/ γ - Al_2O_3 for the enantioselective hydrogenation of acetophenone with an enantiometric excess of 60.5% [35] and recently, Jiang et al. described the highly enantioselective heterogeneous hydrogenation of aromatic ketones (*ee*% = 83 for acetophenone) catalyzed by Ph3P stabilized Ru/ γ - Al_2O_3 , and modified by chiral diamines derived from cinchona alkaloids. [36].

It is also worth noting that, in our case, enantiomeric excesses have high chemoselectivity to 1-phenylethanol, which are close to 100% for total conversion.

The potential benefit of such controlled method of catalyst preparation lies in the possibility of designing active sites by selecting the nature of the ligands, the oxidation state of both metals, and other chemical properties that are appropriate for a given hydrogenation reaction [27].

Despite the extensive work done by the groups of Vargas at ETH (Zurich) and the group of Murzin at Turku in Finland on enantioselective catalytic systems based on the adsorption of a chiral modifier on a supported transition metal catalyst [11,12,18,37–39], the mechanism of enantioselective hydrogenation reactions employing catalytic systems prepared through SOMC/M techniques is far from being known in detail, so any contribution leading to the knowledge of the structure of the transition-state complex in the key step of enantiodifferentiation may provide an important guide for the rational development of new catalytic systems. In this regard, as a first step towards designing a chiral heterogeneous catalyst we propose modeling the organotin precursor compound that would optimize the catalyst that would finally be obtained.

Table 1
Acetophenone hydrogenation. Enantiomeric excess and selectivity to 1-phenylethanol at 100% conversion.^a

Catalyst	<i>ee</i> %	(<i>S</i>)-1-phenylethanol (%)
PtSn-OM (Pt-SnBu ₄)	0	>99
Pt-MenSnBu ₃	23	97
Pt-MenSnPh ₂ Me	23	>99
Pt-Men ₃ SnMe	24	>99
Pt-Men ₃ SnSnMen ₃	21	98

^a Experimental conditions: 0.25 g catalyst, 4.6 mmol acetophenone, 60 mL 2-propanol (solvent), 80 °C, H₂ pressure 10 atm.

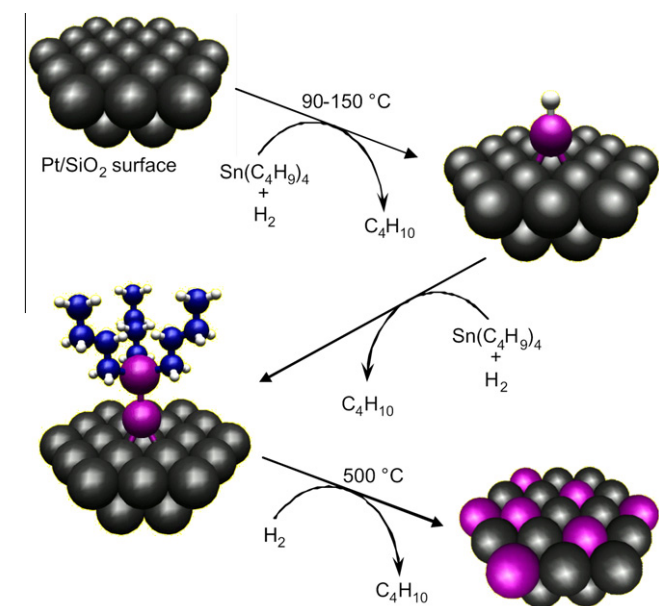


Fig. 1. Steps in the reaction of tetra-*n*-butyltin with a silica supported platinum surface.

For this purpose, in this work molecular modeling tools, both Molecular Mechanics and Molecular Dynamics, as well as Density Functional Theory (DFT), were used to give an insight into the relative stability of the Sn–C bonds of several different chiral organotin compounds that could potentially be used as precursors for the preparation of organometallic chiral heterogeneous catalysts using SOMC/M techniques.

2. Computational methods

Both the calculations at Molecular Mechanics level and the Molecular Dynamics simulations were carried out using the TINKER program [40]. A study of the conformational space of each one of the selected molecules was conducted in the first place. To do this, molecular dynamics simulations were performed using a force field of the mm3 type. For the simulations, a temperature of 1000 K was chosen in order to consider as many conformations as possible. The simulations were performed for 505 ps, and geometries were saved every 1 ps. The time interval for integrating the motion equations was 0.5 fs. Once obtained, these 505 geometries were preoptimized at a Molecular Mechanics level, again using a mm3 force field. A convergence criterion for the energy gradient as a function of the nuclear coordinate lower than 0.05 kcal/mol/Å was chosen. Out of the 505 already preoptimized geometries, 10 corresponding to the conformers with the lowest energy were chosen to be optimized to a higher level of theory using DFT calculations. The geometries of these 10 conformers were optimized using the Vosko, Wilk, and Nusair (VWN) local exchange and correlation functional [41] and a double-zeta (DZ) basis set quality valence space. Then, the geometries of these 10 conformers were reoptimized using the local Vosko, Wilk, and Nusair functional, but now with a triple-zeta (TZP) basis set quality valence space plus a set of polarization functions. Basis sets of this quality are required in order to have a sufficiently small basis set superposition error (BSSE) to warrant its neglect in most situations [42]. The procedure of successive optimizations at different levels of theory is applied to minimize the computational cost, since a direct optimization of the geometries obtained from the Molecular Dynamics simulation, using a calculation level as the one mentioned in the previous paragraph, would require a great computational effort.

On the fully optimized geometries, a series of self-consistent calculations were performed using, in all cases, a triple-zeta basis set plus a set of polarization functions, employing the exchange and correlation functional proposed by Perdew and Wang, 1991, (PW91) [43], which introduces corrections for the density gradient. These calculations were made in order to obtain more accurate energies for the different geometries of each conformer. A further optimization using GGA (generalized gradient approximation) functional did not introduce a substantial improvement in geometry, and it was a time-consuming calculation. The frozen core approximation up to the 1s orbital for O and C atoms and up to the 4d orbital for the tin atom was utilized.

The binding energies of the Sn–C bonds were calculated as the difference between the total energy of the molecule (more stable conformer) and the energy of the fragments originated in a virtual homolytic cleavage of the bond. The calculation of the energy of these fragments was run unrestricted. All DFT calculations were performed using the Amsterdam Density Functional (ADF) program package [44].

3. Results and discussion

In Fig. 2, a schematic representation of the molecules studied in this work, together with the nomenclature used, is presented.

Full geometric optimization of these molecules allowed obtaining the structural parameters of the Sn atom environment, as displayed in Tables 2 and 3. By analyzing the bond lengths and bond angles found, it can be said that the Sn atom retains its tetrahedral environment, with only a slight deformation being observed.

As shown in Table 2, all the Sn–C bond lengths are very similar for all the molecules studied, with some interesting variations as a function of the substituent bond to the Sn atom. Whenever R1, R2, and R3 are alkyl fragments, Sn–C(R1), Sn–C(R2), and Sn–C(R3) bond lengths are shorter than the Sn–C(Men) bond length, except for the Men-Sn-(iso-Bu)₃ molecule. In this molecule, the Sn–C(Men) bond length is equal to the Sn–C(R3) bond length (2.219 Å), and only about 0.005 Å longer than the other two Sn–C bonds (2.214 Å). Variations in the Sn–C bond lengths are more notorious when the substituents are alkoxy fragments. For the Men-Sn-((1-OCH₃)Et)-Et₂ molecule, the Sn–C(Men) bond length is longer than the Sn–C(Et) bond lengths (designated Sn–C(R1) and Sn–C(R3) in Table 2), but shorter than the Sn–C((1-OCH₃)Et) bond length (designated Sn–C(R2) in Table 2). Finally, for the Men-Sn-((1-OCH₃)-Et)₃ molecule, the Sn–C(Men) is the shortest of the four bonds involving the tin atom.

Concerning the bond angles, in Table 2 it can be seen that, although they all have values close to those of a regular tetrahedron, the angle formed between C(Men) and Sn–C(R3) (angle 3 in Table 3) is always wider than the rest. This can be attributed to the bulkiness of the menthyl group.

During the preparation of a chiral organotin catalyst *via* SOMC/M procedures, the organotin compound must lose one of the organic fragments bonded to the tin atom, in order to allow the formation of a ≡Sn–M/Support (M = transition metal) species, characteristic of this kind of catalyst [18,23]. As a measure of the probability that such organic groups would remain bonded to the Sn atom once the organotin precursor has reacted with the supported metal catalyst, the BE for each of the four Sn–C bonds in each of the proposed molecules was calculated by the following equation:

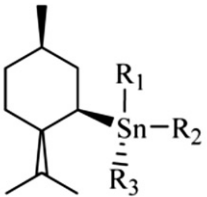
$$BE = [E_{\text{molec}} - (E_{r1} + E_{r2})],$$

where E_{molec} is the total energy of each organotin parent molecule calculated from its constituent atoms in their ground state in a restricted way, and E_{r1} and E_{r2} are the energies of the radical fragments in which the molecule would dissociate. The energies of these fragments are calculated from their component atoms in their ground state in an unrestricted way, taking into account the partial occupation of one of its molecular orbitals.

First, these calculations were performed for the Men-Sn-R₃ molecules where R is an alkyl fragment. In Table 4 the values for the BE of each one of the four bonds involving the Sn atom are presented for the six molecules studied. From these results, some general trends in their behavior can be observed. In the first place, for those molecules in which R is a linear alkyl fragment (entries 1, 2, 3, 4, and 5), the BE for the Sn–C(Men) bond is lower than the BE for any of the other three Sn–C bonds (Sn–C(R1), Sn–C(R2), and Sn–C(R3)). Also, for these last three bonds, the following order for the BE values is observed: Sn–C(R1) > Sn–C(R2) > Sn–C(R3). This trend in binding energies may be due to steric reasons. Fig. 3 shows the optimized geometries for all the molecules studied and, as can be seen, the alkyl fragment generically called R3 is the one that presents the greatest steric hindrance due to its proximity to the menthyl group. This fact is in agreement with the widest bond angle found for C(Men)–Sn–C(R3) (angle 3 in Table 3).

Table 4 also includes the results of BE for the Men-Sn-(iso-Bu)₃ molecule (entry 6). In this case, it is noted that the BE for the Sn–C(Men) bond is higher than that for the other three bonds.

The analysis of the BE values presented in Table 4 let us infer what the behavior of these molecules would be when they react



Entry	Nomenclature	R	Compounds
1	MenSnMe ₃	CH ₃	trimethylmenthyltin
2	MenSnEt ₃	C ₂ H ₅	triethylmenthyltin
3	MenSnPr ₃	C ₃ H ₇	tripropylmenthyltin
4	MenSnBu ₃	C ₄ H ₉	tributylmenthyltin
5	MenSn-(iso-Bu) ₃	C ₄ H ₉	trisobutylmenthyltin
6	MenSnPen ₃	C ₅ H ₁₁	tripentylmenthyltin
7	MenSn-((1-OCH ₃)Et)-Et ₂	2 C ₂ H ₅ , 1 C ₂ H ₄ OCH ₃	1-methoxyethyldiethylmenthyltin
8	MenSn-((1-OCH ₃)Et) ₃	C ₂ H ₄ OCH ₃	tri-1-methoxyethylmenthyltin

Fig. 2. Schematic representation of the organotin molecules studied and nomenclature employed in the paper.

Table 2

Optimized geometrical parameters: bond lengths (Å) of the tin atom environment.

Entries	Molecules	Bond lengths (Å)			
		Sn-C(Men)	Sn-C(R1)	Sn-C(R2)	Sn-C(R3)
1	Men-Sn-Me ₃	2.211	2.188	2.188	2.189
2	Men-Sn-Et ₃	2.213	2.199	2.203	2.202
3	Men-Sn-Pr ₃	2.212	2.197	2.199	2.196
4	Men-Sn-Bu ₃	2.210	2.195	2.199	2.198
5	Men-Sn-(iso-Bu) ₃	2.219	2.214	2.214	2.219
6	Men-Sn-Pen ₃	2.212	2.197	2.200	2.202
7	Men-Sn-((1-OCH ₃)Et)-Et ₂	2.213	2.203	2.223	2.201
8	Men-Sn-((1-OCH ₃)Et) ₃	2.205	2.213	2.218	2.219

Table 3

Optimized geometrical parameters: bond angles (°) of the tin atom environment. Angle labels: **1** C(Men)-Sn-C(R1), **2** C(Men)-Sn-C(R2), **3** C(Men)-Sn-C(R3), **4** C(R1)-Sn-C(R2), **5** C(R1)-Sn-C(R3), **6** C(R2)-Sn-C(R3).

Molecules	Bond angles (°)					
	1	2	3	4	5	6
Men-Sn-Me ₃	107.05	107.98	113.47	108.80	109.16	110.24
Men-Sn-Et ₃	107.18	108.83	112.54	107.72	107.85	112.47
Men-Sn-Pr ₃	107.11	109.31	113.12	108.79	107.74	110.62
Men-Sn-Bu ₃	107.60	108.96	113.33	108.21	107.47	111.07
Men-Sn-(iso-Bu) ₃	105.34	111.98	113.83	105.81	112.60	107.07
Men-Sn-Pen ₃	107.57	108.93	113.82	108.56	107.42	110.34
Men-Sn-((1-OCH ₃)Et)-Et ₂	107.15	108.43	115.62	108.95	108.14	108.40
Men-Sn-((1-OCH ₃)Et) ₃	108.52	109.70	114.07	107.57	105.12	111.52

with a metal surface to form an organometallic catalyst (see Fig. 1). When the cleavage of one bond takes place to form a superficial organotin entity, the probability that the menthyl group would remain bonded to the tin atom is lower than the probability for any of the other three fragments, due to its lower BE, except in the case of Men-Sn-(iso-Bu)₃. For this molecule, although the difference between the BE of the four bonds involving the tin atom is small, one could say that the anchored organotin fragment would be of the type Men(iso-Bu)₂Sn-M/Support, thus leading to a chiral heterogeneous catalyst. Besides, according to the BE values found, for the

molecules corresponding to entries 1–5, the surface organotin entity would be achiral, of the type R₃Sn-M/Support (R = alkyl fragment). It should be noted, however, that as is shown in Table 1, an organotin catalyst prepared from the MenBu₃Sn compound allowed obtaining 23% enantiomeric excess in the hydrogenation of acetophenone to 1-(S)-phenylethanol, indicating that a menthyl group remained bonded to the Sn atom, forming a surface chiral entity. The result could be explained in terms of kinetic effects in the Sn-C bond breaking, which has not been addressed in this work.

Table 4

Computed binding energies (BE, kcal/mol) for the four Sn–C bonds of the different Men–Sn–R (R = alkyl fragments) studied molecules.

Molecules	BE (kcal/mol)			
	Sn–C(Men)	Sn–C(R1)	Sn–C(R2)	Sn–C(R3)
Men–Sn–Me ₃	45.58	53.06	52.79	52.10
Men–Sn–Et ₃	44.28	47.74	46.94	46.86
Men–Sn–Pr ₃	44.81	49.06	48.45	48.30
Men–Sn–Bu ₃	44.71	48.99	48.44	47.81
Men–Sn–Pen ₃	44.57	48.91	48.29	47.80
Men–Sn–(iso-Bu) ₃	42.20	42.16	42.13	41.04

In analyzing the influence of the alkyl chain length of the Men–Sn–R₃ compounds on the BE, it was found that the molecule that presented the lowest BE values for the four bonds involving the tin atom was the Men–Sn–(Et)₃, as shown in Fig. 4. The difference

between the BE of the Sn–C(Men) bond and each one of the other three Sn–C bonds was also calculated, and the results are displayed in Fig. 5. As can be seen, the lowest BE difference corresponds to the Men–Sn–(Et)₃ molecule, and among the bonds of this molecule the smallest difference is between the Sn–C(Men) and Sn–C(R3) bonds.

On the basis of these results, the computational study of an organotin compound that could eventually be synthesized and employed as a precursor for the preparation of a chiral catalyst was proposed. Thus, we proceeded to model a molecule having a methyl group and three ethyl fragments possessing a substituent that weakens the Sn–C(Ri) bond even more. So, two molecules were modeled: Men–Sn–((1-OCH₃)Et)–Et₂, in which one ethyl group has a methoxy substituent in position 1, and Men–Sn–((1-OCH₃)Et)₃ with three OCH₃Et fragments. The results for the BE calculated for these two molecules are listed in Table 5, and the fully optimized geometries for these molecules are shown in Fig. 3.

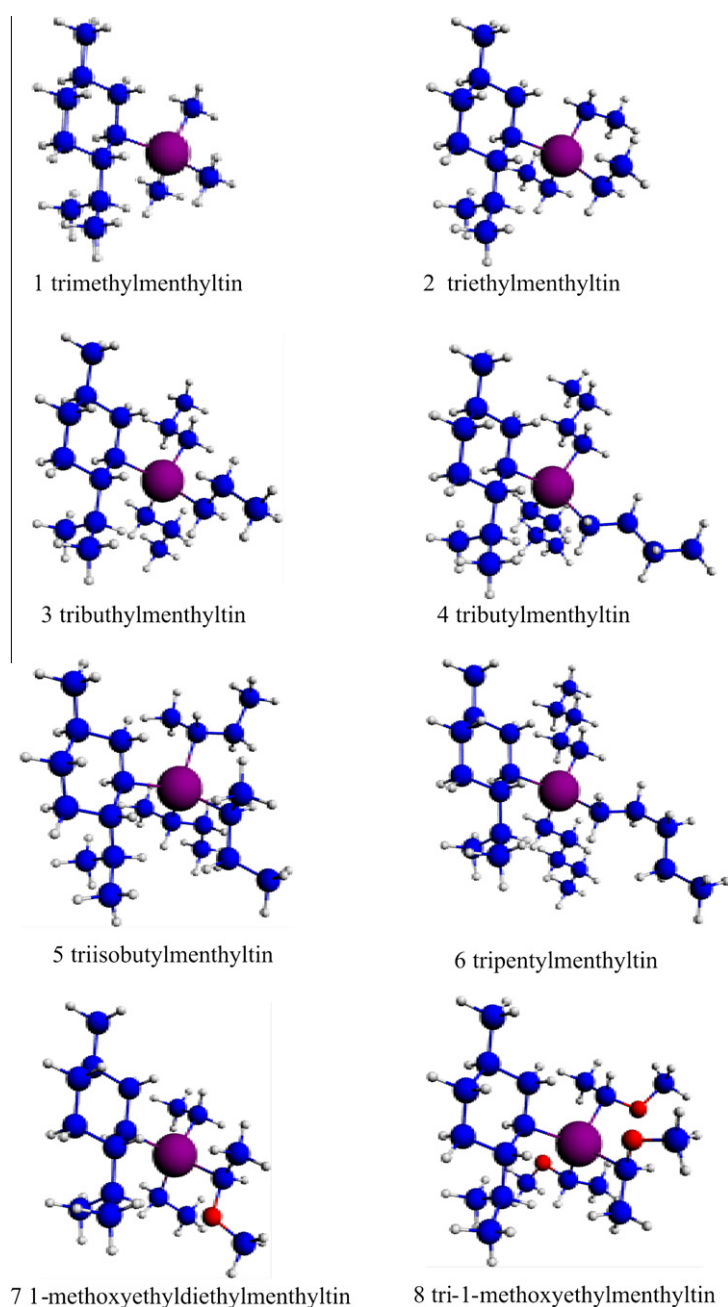


Fig. 3. Fully optimized geometries for all the studied molecules.

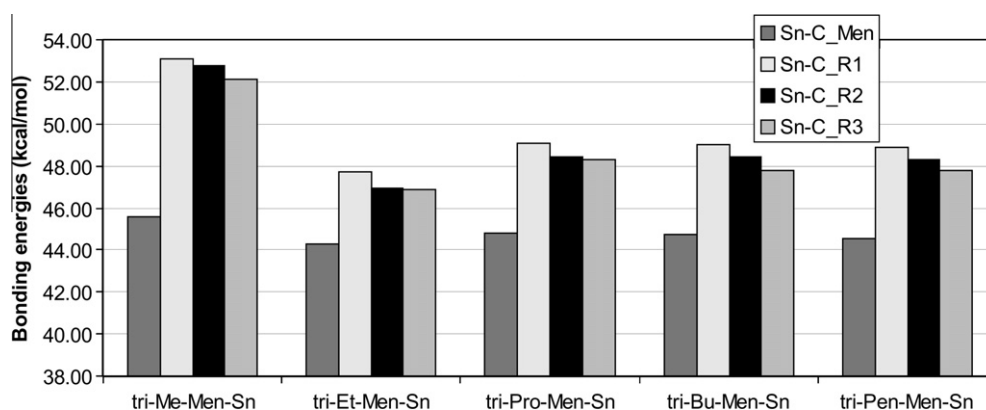


Fig. 4. Binding energies (BE, kcal/mol) for the four Sn–C bonds for the Men–Sn–R molecules studied (R = alkyl fragment).

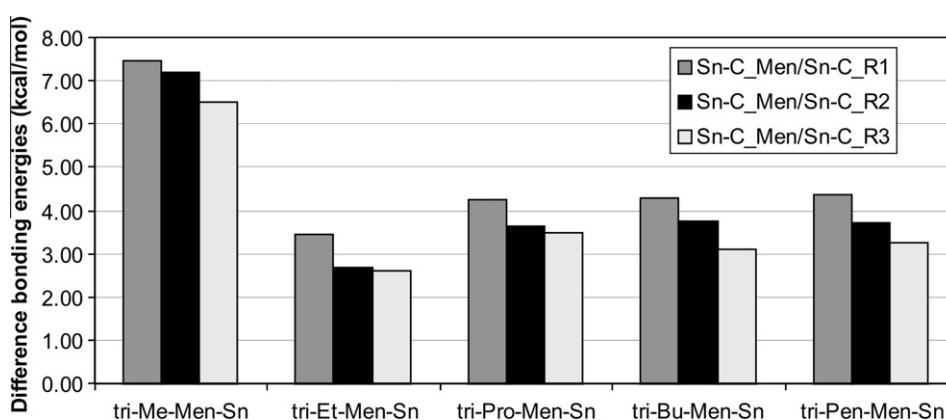


Fig. 5. Energy difference between the Sn–C(Men) bond and each one of the other Sn–C bonds, for the Men–Sn–R molecules studied (R = alkyl fragment).

Table 5
Computed binding energies (BE, kcal/mol) for the four bonds involving the tin atom.

Molecules	BE (kcal/mol)			
	Sn–C(Men)	Sn–C(R1)	Sn–C(R2)	Sn–C(R3)
Men–Sn–((1–OCH ₃)Et) ₂	43.97	47.26	43.38	46.57
Men–Sn–((1–OCH ₃)Et) ₃	43.53	42.33	42.79	42.33

By analyzing the Men–Sn–((1–OCH₃)Et)₂ molecule in the first place, it can be seen that the binding energies calculated for the Sn–C(R1) and Sn–C(R3) bonds are higher than that of the Sn–C(Men), similarly to what was found for the Men–Sn–Et₃ molecule. On the other hand, the Sn–C(R2) bond (the one between Sn and the (1–OCH₃)Et fragment) is the weakest of the four bonds involving the tin atom, due to the presence of the methoxy group linked to the carbon atom bonded to tin. Calculations on the Men–Sn–((1–OCH₃)Et)₃ molecule led to the expected result, that is, that the BE for the Sn–C(Men) bond would have the greatest of the four values (Table 5). The calculated value is even higher than that obtained for the same bond in the Men–Sn–(iso–Bu)₃ molecule (Table 4). So, it may be said that if this molecule is used as precursor to prepare an organometallic heterogeneous catalyst using SOMC/M techniques, the probability that the menthyl group would remain anchored to the surface is greater than the probability that only the achiral (1–OCH₃)Et fragments would, due to their higher BE.

4. Conclusions

Computational methods were used, including *ab initio* calculations (DFT) and molecular mechanics and dynamics, to try to ratio-

nalize the structure of a possible precursor for the production of enantioselective heterogeneous catalysts, prepared by techniques derived from SOMC/M.

The fully optimized geometries for all molecules studied showed the tin atom kept its tetrahedral environment, slightly deformed in the angle between the Sn–C(Men) and Sn–C(R3) bonds, because of the bulkiness of the menthyl group.

Of the molecules studied, only the Men–Sn–(iso–Bu)₃ and the Men–Sn–((1–OCH₃)Et)₃ resulted in the highest BE for the Sn–C(Men) bond. This result indicates that the probability of losing the menthyl group in a dissociation process is lower only for these two molecules.

These results allow speculating that the preparation of enantioselective heterogeneous catalysts, using either Men–Sn–(iso–Bu)₃ or Men–Sn–((1–OCH₃)Et)₃ as precursor compounds, would lead to a better performance of the resulting catalysts.

Acknowledgements

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