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Specific solvent effect on R_2ZrCl_2 (R = butyl, ethyl) reactivity, a density functional study

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Abstract

The reactivity of $ZrCl_2Bu_2$ is modeled for the formation of $ZrCl_2$(butene). Two pathways are computed: the β- and the γ-Hydrogen migration. It is found that the β-H pathway is favored by about 13 kcal mol^{-1}. The specific effect of dimethyl ether as a model of the THF solvent is analyzed and found to greatly facilitate the reaction. Solvent or ligand complexation on the zirconium is found more important in product $ZrCl_2$(butene) than in the reagent $ZrCl_2Bu_2$. These results are commented in regard to the experimental evidences of reactivity differences depending on the solvent used.

Keywords: Zirconium; β-Hydrogen migration; Density functional theory; Solvent effects

1. Introduction

Since the discovery by Ei-ichi Negishi of a practical method for the generation of zirconocene like reagent 'Cp_2Zr' [1], the synthetic reactions employing organometallic zirconium compounds are being widely developed [2]. Among these species, dialkylzirconocenes [1] are currently of special interest as they can lead to both polymerization catalysts [3] and stoechiometric reagents for organic synthesis [2]. Their synthesis is commonly prepared by the action of two equivalents of an alkyllithium, like *n*-BuLi, on a zirconocene dichloride at low temperature in ether, usually tetrahydrofuran (THF). The zirconocene dichloride is usually made starting from lithiated cyclopentadienyl ligands that react on $ZrCl_4$. However, a particularly interesting strategy for the synthesis of the starting zirconocene dichloride is being developed by Eisch et al. [4] starting from dialkylzirconium dichloride (**1**) and fulvene (Scheme 1).

Noteworthy, depending on the solvent used in the synthesis, either bridged or unbridged metallocene can be obtained. For instance, ether solvents (R_2O) favor the obtention of bridged zirconocenes, through the '$ZrCl_2$' intermediate, as shown in Scheme 1, while unbridged products are to be obtained in hydrocarbon solvents. As mentioned by Eisch, the key of the selectivity is believed to hold in the formation of this intermediate '$ZrCl_2$' species, which has not been characterized [4].

Because both butane and butene gas are detected during the reaction in ether solvents, the reaction is likely to occur through a hydrogen migration from one alkyl chain onto the other (for instance in a β-hydrogen migration as shown in Scheme 2).

In this paper we investigate the specific solvent effect on the formation of **2** as a precursor of the putative $ZrCl_2$ key species. While we focus on the dialkyl zirconium dichloride reactivity (ie $ZrCl_2Bu_2$), we shall use some insights from the reactivity of analogous

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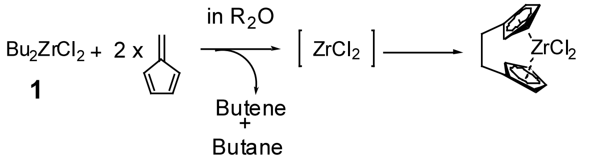
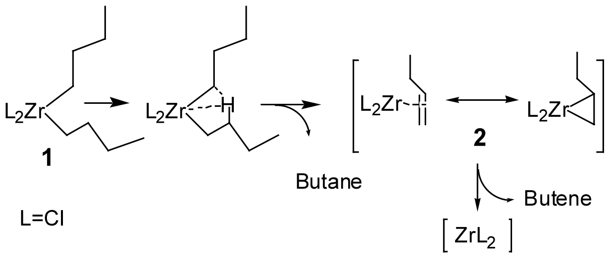


Scheme 1.

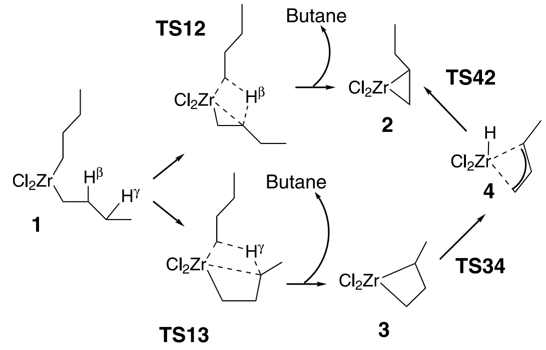


Scheme 2.

dialkyl zirconocene ($ZrCp_2Bu_2$) that has been subject to mechanistic studies [5,6].

The corresponding conversion of dialkylzirconocene to zirconacyclopropane is usually believed to follow an associative pathway [7] and to proceed via a β-hydrogen migration. However, we are not aware of any theoretical investigation for this mechanism that would concern neutral zirconocenes [8].[1] The zirconocene-alkenes complexes obtained are too reactive to be isolated alone. They react generally with π-donor ligands (e.g. alkenes) and lead to either a ligand exchange product and/or a C–C coupling reaction product (e.g. zirconacyclopentane) [1,2,9]. However, they have been trapped with a coordinating ligand (typically PMe_3) and some X-ray structures are available in the litterature [10]. The parallel between the Cp_2ZrBu_2 and the Cl_2ZrBu_2 reactivities also suggested the possibility of a γ-elimination mechanism that has been proposed for the analogous zirconocene [6].

In this paper, we shall thus study the effect of the ether solvent and the one of phosphines on the reaction paths described in Scheme 3.



Scheme 3.

2. Computational details

The calculations reported in this work have been performed using the GAUSSIAN-98 suite of program [11]. Both geometry and energy calculations were performed using the B3LYP hybrid functional [12]. The basis set we used was grounded on the LANL2DZ 'basis set' [13], which combined either a relativistic effective core potential (RECP) plus a double-ζ Gaussian basis (for phosphorus, chlorine, and zirconium) after Hay and Wadt, or simply an all electron double-ζ Gaussian basis (for hydrogen, carbon, and oxygen) after Dunning and Hay [14]. The LANL2DZ basis set as parametrized in Gaussian has been supplemented with polarisation and diffuse functions taken from D95 [14] as follow: the polarisation functions were added to the C, O, P and Cl atoms with the exponant values $d_C = 0.75$, $d_O = 0.85$, $d_P = 0.37$ and $d_{Cl} = 0.6$ respectively. In order to save computational requirements for the assisted mechanism, the carbon atoms of the ligands (PMe_3, OMe_2) did not held any polarization functions all along this study. For the chlorine atoms we added s and p diffuse functions to complete their description (exponant value from D95 $sp_{Cl} = 0.0483$).

Each molecular structure has been fully optimized and characterized as minima or transition states by second derivatives analysis. Transition states were characterized by a unique imaginary frequency. Although our calculations were held in a gas phase approximation, the results we obtained should be representative of the mechanism of the formation of these important species in solvent, thanks to the inclusion of their specific effects in the calculations.

3. Results and discussion

The β-H mechanism involves a simple hydrogen transfer from the β-carbon atom of an alkyl onto the α-carbon of the other alkyl (Scheme 3). We shall first have a quick look at the dissociative path that goes through a metal hydride (Fig. 1, **H**). In this dissociative pathway, we found the intermediate **H** as a minimum that is about 30 kcal mol^{-1} higher in energy than the reagent **1**. This result indicates that the transition states are even higher in energy than 30 kcal mol^{-1}. Such a dissociative path will not be discussed further due to both the high energy of this intermediate and the fact that previous kinetic studies have shown a second order

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[1] Most of the computational studies on the zirconium reactivity are rather devoted to polymerization mechanisms, and involve cationic species.

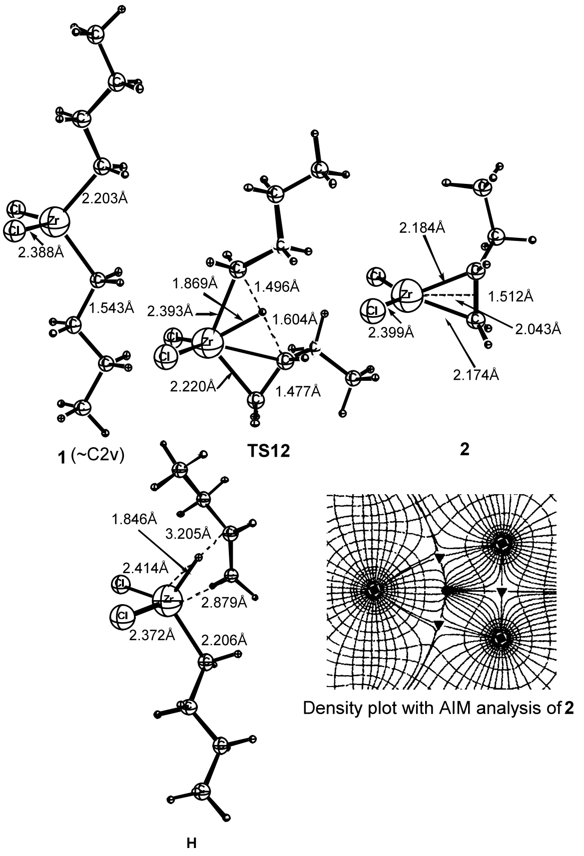

Fig. 1. Main geometrical parameters for the β-H migration and AIM analysis of **2**. On the density map, the RCP is symbolized using a circle, bond critical points (BCP) with a triangle and the nucleus by square.

process, incompatible with such a first order dissociative path [7].[2]

For the associative path, the hydrogen transfer is assisted in the transition state by the Zr center (Zr···H = 1.869 Å, **TS12**, see Fig. 1). The C–C bond distance in structure **2** is found to be closer to a single rather than a double bond. This result is in favor of the zirconacyclopropane description rather than to an ethylene-zirconium complex [15]. Furthermore, Bader's atom in molecule (AIM) [16][3] analysis of **2** unambiguously shows the cyclic nature of the system with a ring critical point (RCP) in the triangle formed by the Zr–C–C atoms (Fig. 1).

The energetics we obtained for this associative β-H path (Table 1) are not consistent with a low temperature (0 °C) spontaneous reaction: the reaction is endothermic (16.4 kcal mol^{-1}). These computational results can be compared to the zirconocene analogue, which has been experimentally characterized by X-ray diffraction. As a matter of fact, experimental structure of **2** has only been characterized in the presence of ligands, phosphines or ethers [2b,10]. This point, added to the solvent effect described by Eisch, prompted us to study the influence of ether 'ligands' on this hydrogen migration mechanism (vide infra).

The γ-H mechanism involves a two step sequence through a zirconacyclobutane intermediate (**TS13** → **3**) followed by a rearrangement (**3** → **TS34** → **4** → **TS42** → **2**, Scheme 3).

In **TS13**, a hydrogen migrates from C^{γ} of an alkyl chain to C^{α} of the other. The zirconacyclobutane (**3**) formed following this mechanism must rearrange for **2** is to be obtained. In **TS34**, a hydrogen migrates from C^{β} in the zirconacyclobutane to the Zr atom, leading to an allylic zirconium hydride (**4**), and this hydrogen is then transferred on the C^{γ} position (**TS42**) to lead to the zirconacyclopropane (**2**). The optimized structures of the complete mechanism are displayed in Fig. 2 and the energies are presented in Table 1.

In this dichloride system the energies involved for the γ-H migration are significantly higher than for the β-H mechanism ($\Delta E_{\text{ZPC}} = 41.1$ kcal mol^{-1} vs. 28.4 for the β-H migration). This remark also holds for the second step of the mechanism, the allylic rearrangement, which requires an even higher energy: 43.9 kcal mol^{-1}. The Zr–H distance is nearly 0.1 Å larger in the γ-H migration (1.945 Å) than in the β-H migration (1.869 Å). This suggests a weaker assistance from the Zr to the γ-H migration.

The intermediates zirconacyclobutane (**3**) and allylic zirconium hydride (**4**) are not high in energy. They are

Table 1
Energetics of the β- and γ-elimination (the corresponding structures are in Fig. 1 and Fig. 2)

	E [a]	ZPC [a]	ΔE [b]	ΔE_{ZPC} [b,c]
1	−392.37426	0.24268	0.0	0.0
TS12	−392.32670	0.24032	29.8	28.4
2 [d]	−392.34784	0.24241	16.6	16.4
H	−392.32801	0.23907	29.0	26.8
TS13	−392.30581	0.23974	42.9	41.1
3 [d]	−392.35872	0.24189	9.8	9.3
TS34 [d]	−392.29940	0.23784	47.0	43.9
4 [d]	−392.35279	0.23875	13.5	11.0
TS42 [d]	−392.33749	0.23870	23.1	20.6

[a] Absolute energies in au.
[b] Relative energies in kcal mol^{-1}, relative to **1**.
[c] ZPC included.
[d] A butane molecule is included.

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[2] More details on this structure can be found in the supplementary materials (structure **H**).

[3] The plot diagram was obtained using AIM 2000, with the wavefunction calculated at the B3LYP/DZVP level with GAUSSIAN-98. Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Lab., Pacific Northwest Lab., Richland, Washington, DC (DZVP: N. Godbout, D. R. Salahub, J. Andzelm, E. Wimmer, Can. J. Chem. 70 (1992) 560). See http://www.emsl.pnl.gov:2080/forms/basisform.html.

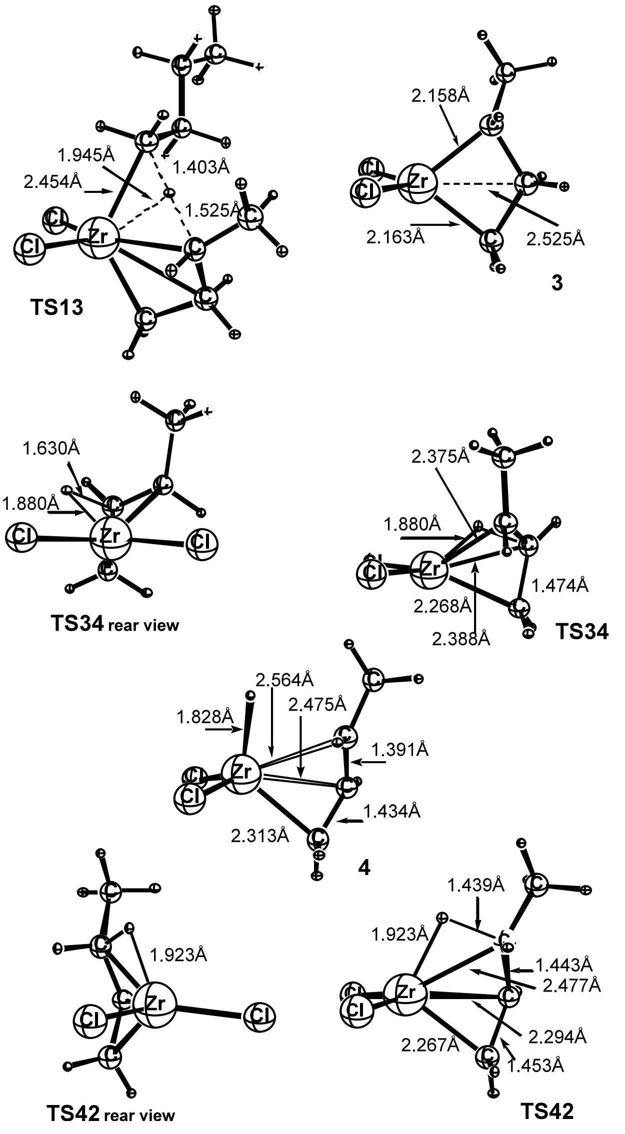

Fig. 2. B3LYP optimized structures for the γ-H mechanism and subsequent allylic rearrangement.

even about 5 kcal mol^{-1} more stable than the product (**2**). As mentioned for the β-H mechanism, the reaction is endothermic and the solvent effects will also be studied for this mechanism.

The specific solvent/ligand effect on the β-elimination mechanism has been investigated at the same level of theory using the dimethyl ether or the trimethylphosphine as a ligand. The ether ‘ligand’ will be noted using **• O** added to the name: e.g. **2 • O** has one ether molecule coordinated to the Zr atom by the oxygen. A similar notation is used for the trimethylphosphine (**• P**). As described in the computational details, polarisation functions were not added on the C atoms of the ligand.

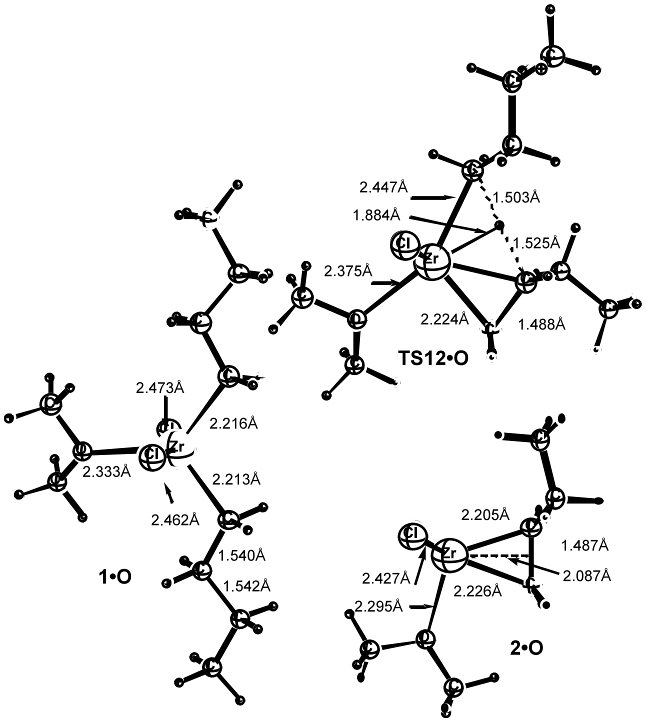

Fig. 3. Main geometrical parameters for the OMe_2 assisted β-H mechanism.

Adding one OMe_2 molecule to **1**, the geometry of the associative complex (**1 • O**) exhibits a strong interaction between the oxygen and the metallic center, the Zr–O bond distance is short (Fig. 3, $d(\text{Zr–O}) = 2.33$ Å) and the stabilization is significant (Table 2, 10.7 kcal mol^{-1}). Noteworthy, the ∠ClZrCl angle is larger in this complex **1 • O** (160°) than in the solvent free analogue (120°). Our solvent stabilized starting material **1 • O** can thus be referred to a trigonal bipyramid pentavalent zirconium where the apical positions are occupied by chlorides. The distance between the chlorides and the zirconium are also elongated (+0.1 Å) compared to the solvent free structure.

In the transition state of the OMe_2 assisted β-H migration (**TS12 • O**), the geometrical parameters are essentially identical to those encountered in the solvent free system. The most important differences lies in (i) the

Table 2
Solvent/ligand assistance in the dibutyl species

Species\X	No ligand	O	P
1 + X	–	10.7 [a]	13.1 [a]
1 · X	0.0	0.0	0.0
TS12 · X	28.4	25.1	24.9
2 · X [b]	16.4	3.5	2.1
TS13 · X	41.1	38.6	38.4
3 · X [b]	9.3	8.8	10.7
TS34 · X [b]	43.9	28.5	26.1
4 · X [b]	11.0	10.4	11.1
TS42 · X [b]	20.6	15.2	15.7

The energies, in kcal mol^{-1}, are relative to the starting material **1** · X, entry 2. They are ZPC corrected.

[a] Energy for the complexation of X on **1**.

[b] A butane molecule is included.

increased distance (+0.04 Å) between the Zr atom and the leaving carbon atom of the butane, (ii) the shorter distance between the carbon atoms where the hydrogen migration takes place; from 3.10 Å (in **TS12**), this C–C distance is reduced to 3.03 Å when one OMe_2 is explicitly used in the calculation. These modifications can simply be attributed to the hindrance around the Zr atom, which moderately forces the two carbons to get together. As a matter of fact the barrier is reduced, but only to a small extend: from 28.4 to ~25 kcal mol^{-1}.

As the β-H migration progresses, a butane molecule is released, and the zirconacyclopropane **2 • O** is obtained. In the calculations, the oxygen of OMe_2 is more tightly bonded to the Zr in **2 • O** than in the reagent **1 • O** (Zr–O = 2.29 vs. 2.33 Å). The distance from the Zr to the midpoint of the 'ethylene' is slightly increased in this product, which is consistent with a small decrease of the C–C bond length. The most interesting result is probably on the energy of the reaction which is now only slightly endothermic (+3.5 kcal mol^{-1}). The inclusion of one molecule of OMe_2 thus stabilizes the product more than the reagent. The explicit consideration of a second molecule of OMe_2 will even magnify this point (vide infra).

It is worth to compare our results to the experimental data obtained by Negishi and co-workers on zirconocenes [5]. It was reported that the reaction rates are virtually unaffected by PMe_3 when the reaction takes place in THF. Negishi has inferred from this result that the role of the phosphine is to trap and stabilize the final product. Our results (Figs. 3 and 4) indicate indeed a strong interaction in the reaction product (**2**) with the trimethyl phosphine or with the dimethyl ether. Both the ligand and the solvent act similarly (Table 2). Our results thus conform to Negishi's conclusions.

Our results also show in the reagent a small although clear Zr atom predilection for the phosphine (13.1 kcal mol^{-1}); larger than for the dimethyl ether molecule (10.7). This ligand affinity is essentially maintained during the reaction. This result is consistent with the experimental fact that, for zirconocenes, in a mixture of THF and PMe_3, the X-ray structures have a PMe_3 molecule bonded to the Zr atom rather than the THF [17].[4]

The specific solvent/ligand effect on the γ-H mechanism is found to also slightly facilitate the γ-H migration step (**TS13**), lowering the energies by roughly the same value (~3 kcal mol^{-1}). The energy barrier is thus still significantly larger, by ~13 kcal mol^{-1}, in the γ-hydrogen migration step than in the β analogous mechanism.

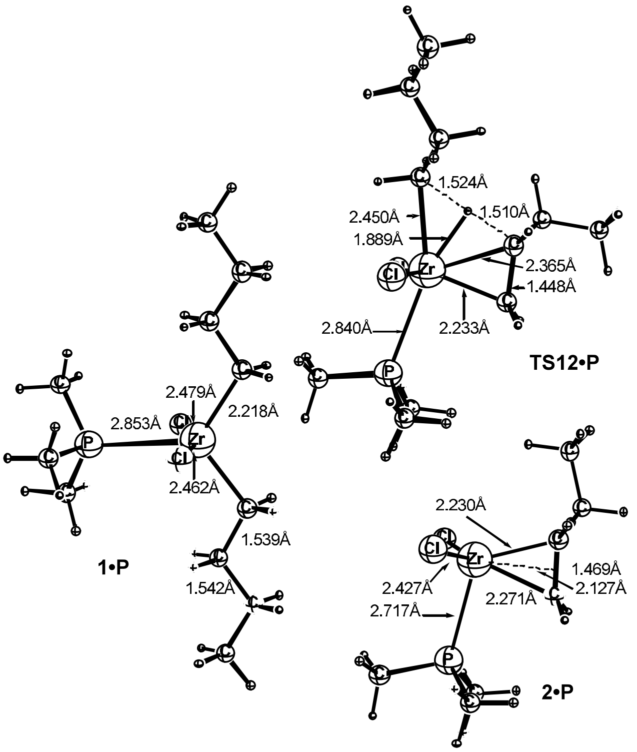

Fig. 4. Main geometrical parameters for the PMe_3 assisted β-H mechanism.

The main effect of the solvent/ligand is actually to lower the energy of the second transition state (**TS34 • X**), that concerns the allylic rearrangement (the energy is decreased from 43.9 to 28.5 and 26.1 kcal mol^{-1} depending on the ligand). However, no large structural (geometrical) differences are found in the X-assisted transition states (Figs. 4 and 5 compared to the structure without ligand **TS34**, Fig. 2).

Because the first transition state of the γ-H mechanism (**TS13 • X**) is significantly higher in energy than that of the β-H mechanism, and because the solvent/ligand effect is small on these transients, we shall in the following focus on further investigating the solvent effect only for the β mechanism.

3.1. Further investigation of the specific solvent/ligand effect on the β-H mechanism

In order to save computational requirements, we used a reduced model of the dibutylzirconium species, the diethylzirconium dichloride. This model that eliminates the mechanistically useless C atoms of the system, will allow us to add up to two OMe_2 or PMe_3 molecules to the β-H reaction path. To differentiate this model from the real system, we shall simply add a e (for ethyl) to the structure numbering (**1e**, **TS12e**, and **2e**). Consistently with the previous notation, the ether are noted '**• O**': e.g.

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[4] As commented in this reference, a number of PMe_3 stabilized zirconocenes have been characterized by X-ray crystallography. When phosphines are available in the reaction mixture, alkene zirconocenes all bear a PMe_3 ligand on the Zr atom. For alkyne zirconocenes, the PMe_3 ligand was even shown to inhibit the catalytic carbomagnesation although THF does not.

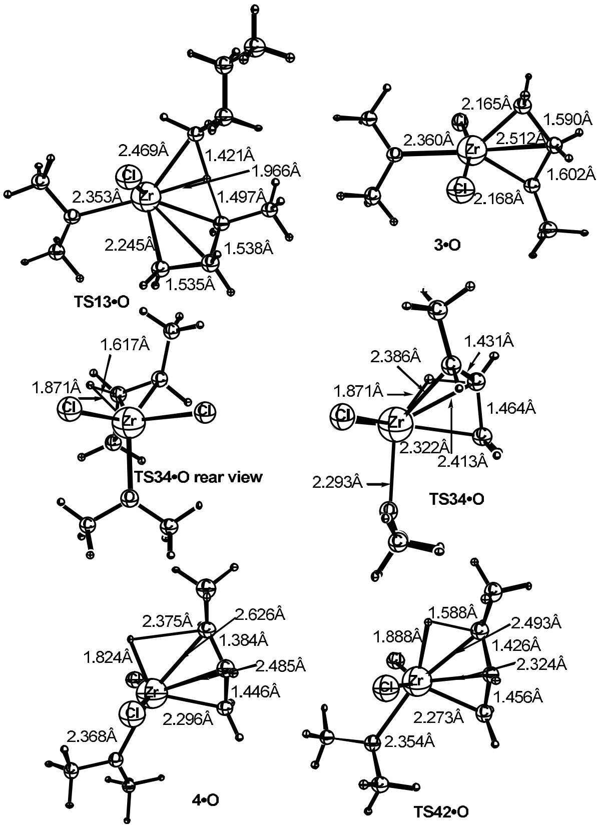

Fig. 5. Main geometrical parameters for the OMe_2 assisted γ-H mechanism on the diethyl model system.

2e•O has one ether ligand while **2e•OO** has two of them coordinated to the Zr atom.

We shall first note that when no or one ligand is used, the reactivity of the diethyl zirconium dichloride is very similar to the one of the dibutyl substituted analogue for both the geometries and the energetics (Fig. 6, Table 3). Probably because of a smaller hindrance, in the model, the reaction is slightly less endothermic (2 kcal mol^{-1} difference) in the ethyl model than in the butyl system. This small difference supports our choice of the model.

In the reagent, as shown on **1e•OO** (Fig. 7) the second OMe_2 molecule stays at a longer distance from the Zr center than the first OMe_2 (Zr–O = 2.60 vs. 2.48 Å). As shown by the energetics in Table 3, both ligands actually stabilize the reagent, the first contributing for 11 kcal mol^{-1} and the second for 5 kcal mol^{-1}. The second molecule plays thus a smaller role in the reagent stabilization. A similar geometry is obtained in **1e•PP**. The structure of the reagents **1e•XX** is close to a distorded octahedra with a trans arrangement only for the chlorine atoms.[5] The β-H migration occurs then in

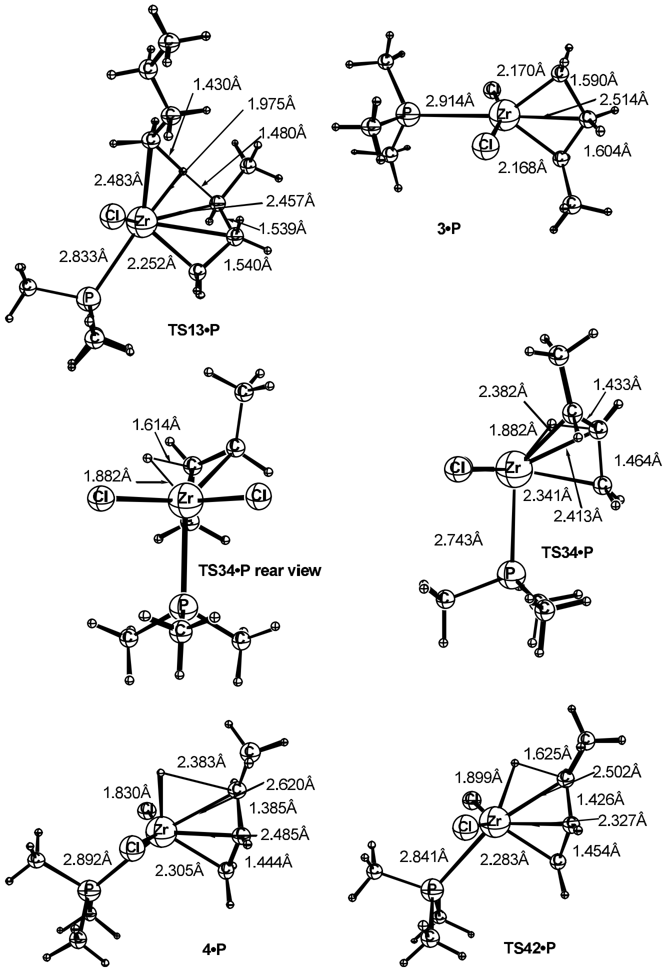

Fig. 6. Main geometrical parameters for the PMe_3 assisted γ mechanism on the diethyl model system.

TS12e•XX whose geometrical parameters are fairly similar to those of the previous case (**TS12e•X**). In the product **2e•XX**, we obtained a nearly C_{2v} structure which can be viewed as a bipyramid with the X moieties at the apical positions. As it was the case previously, the most interesting results are in the energies of the reactions. With the OMe_2 solvent, although the barrier to the β-H migration is indeed only slightly reduced, to about 20 kcal mol^{-1}, the reaction is found to be now exothermic, by some 7 kcal mol^{-1} (Table 3). With the phosphine ligands, the effect of the second molecule is even larger and one obtains an exothermicity for the reaction of about 18 kcal mol^{-1}.

This result is clearly to be attributed to the difference between the stabilization brought by the second phosphine molecule in the reagent (1.4 kcal mol^{-1}) compared to that in the product (~18 kcal mol^{-1}).

3.2. Partition of the interaction energy

The total interaction energy between the metal and the 'ligand', either phosphine or ether, can be parti-

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[5] Other isomers, like all *trans* and all *cis* substituents were not studied due to the fact that the arrangement of the substituents must allow the β-hydrogen migration from the one alkyl chain onto the other, a requirement that dictated a *cis* arrangement at least for the alkyl chains.

Table 3
Summary of the solvent/ligand assistance in the diethyl model system (β-H migration)

X	No ligand	O		P	
	∅	O	OO	P	PP
1e+2X	–	–	16.2	–	14.8
1e · (∅ or X)+X	–	10.8	5.4	13.4	1.4
1e · (X or XX)	0.0	0.0	0.0	0.0	0.0
TS12e · (X or XX)	27.5	24.5	20.2	24.6	17.9
2e · (X or XX)	14.7	1.4	−7.5	0.2	−17.9

The energies, in kcal mol^{-1}, are relative to the complexed starting material 1e · X or 1e · XX, entry 3. They are ZPC corrected.

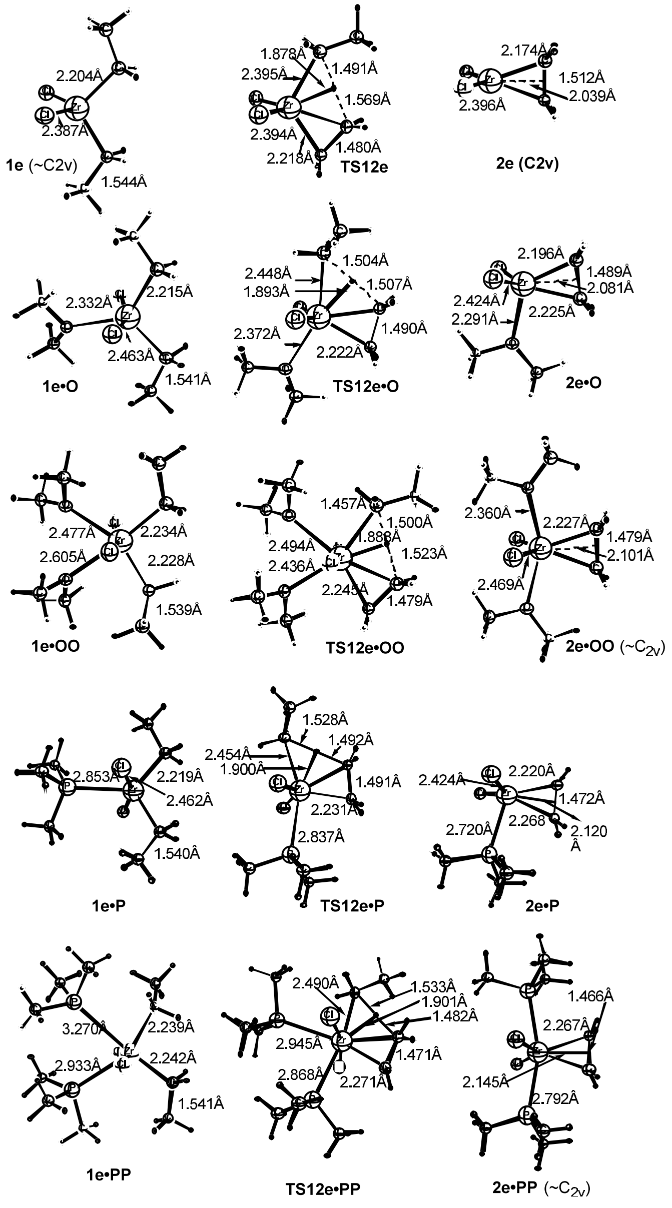
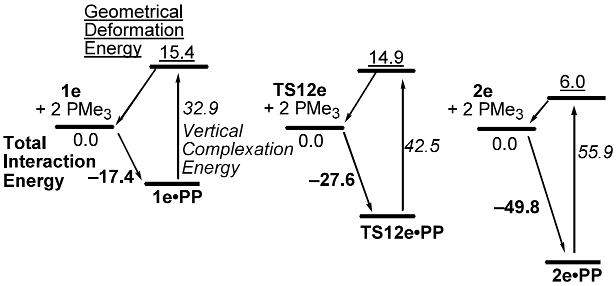


Fig. 7. Main geometrical parameters for the OMe_2 and PMe_3 assisted β-H mechanism on the diethyl model system.

tioned into geometrical constraints and solvent–solute (ligand–metallic core) interaction. The Total Interaction Energy (TIE) between the solute and the solvent is the energy difference between the optimized complex (e.g. **2e • PP**) and the corresponding optimized reagent (e.g. **2e**+2 PMe_3 at infinite separation) (Scheme 4). One shall extract form TIE the 'Vertical Complexation Energy' (VCE) that is obtained by removing the solvent/ligand from the metallic core without any geometrical relaxation. By relaxing the geometry of the different partners one obtains the Geometrical Deformation Energy (GDE). GDE can be further separated into the contributions from either the ligands GDE_{Lig} or the metallic core GDE_M (Table 4).

Such an energy partition is graphically shown on Scheme 4 for the **• PP** case where two PMe_3 strongly interact with the metal. It is shown that the ligands interact better (VCE) and induce a smaller deformation (GDE) in the product than in the reagent or in the transition state. The GDE is for instance reduced from 15.4 to 6.0 kcal mol^{-1} on going from **1e • PP** to **2e • PP**. Of most interest is the fact that this difference is to be attributed to the metallic part of the complex rather than to the ligand. As shown in Table 4, the ligand contribution to the GDE (GDE_{Lig}) is fairly constant all along the reaction, while the metallic part has a contribution (GDE_M) that varies along the reaction with the ClZrCl angle (large GDE_M are obtained for large ∠ ClZrCl). The main deformation of the metallic core occurs thus essentially along this angle that allow the ligand/solvent to bind to the metallic center. Such a result is to be attributed to the better availability on the LUMO orbital in the alkene product (**2e**) compared to that for the dialkyl reagent (**1e**) (Scheme 5).



Scheme 4.

Table 4
Energy partition of the solvent effect

	TIE	VCE	GDE	GDE_M	(∠)[a]	GDE_{Lig}
1e · O	−12.7	−35.5	22.8	11.8	(160°)	11.0
TS12e · O	−15.6	−33.4	17.8	6.9	(142°)	10.9
2e · O	−25.7	−38.3	12.6	1.7	(126°)	10.9
1e · OO	−19.5	−35.0	15.5	14.4	(164°)	1.1
TS12e · OO	−26.9	−41.8	14.9	13.6	(170°)	1.3
2e · OO	−41.3	−44.9	3.0	2.3	(133°)	0.7
1e · P	−15.0	−28.1	13.1	11.1	(159°)	2.0
TS12e · P	−17.8	−25.0	7.2	5.6	(139°)	1.6
2e · P	−29.5	−33.4	3.9	2.0	(129°)	1.9
1e · PP	−17.4	−32.9	15.4	13.6	(158°)	1.8
TS12e · PP	−27.6	−42.5	14.9	13.0	(165°)	1.9
2e · PP	−49.8	−55.9	6.0	3.4	(135°)	2.6

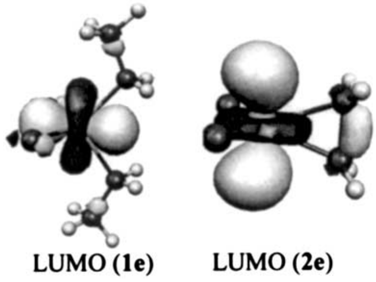
Unlike Tables 1–3, the energies here and in Scheme 4 are ZPC uncorrected.

[a] In parenthesis is the ∠ Cl ZrCl angle, in degrees.

4. Conclusion

Finally, the formation of the key species ('$ZrCl_2$') as produced from the dialkylated reagent is likely to occur through a hydrogen migration from a C^{β} atom of the one alkyl chain to the C^{α} of the leaving alkane (e.g. butane). Such a β−H migration is clearly preferred (by more than 10 kcal mol^{-1}) over the analogous γ-H process. In all the cases we showed that the reaction product is much more stabilized by our model of the solvent (dimethyl ether) and by the phosphine (PMe_3). Such a coordinating solvent/ligand renders feasible (exothermic) a process that would otherwise be endothermic.

In this study of the dialkyl zirconium dichloride reactivity we used some insights from the zirconocene reactivity that has been more extensively studied. Such a comparison should however be used with caution as, for instance, the free space around the Zr atom, available for solvent/ligand coordination, would be significantly reduced in zirconocenes. We showed on the zirconium dichloride a particularly large effect when two molecules of PMe_3 are explicitly used, although it should be somewhat difficult to introduce more than one molecule in the zirconocene analogue. As a matter of fact only one molecule of PMe_3 has been characterized in the X-ray structures available.



Scheme 5.

We mentioned in the introduction that the synthesis of zirconocenes starting from dialkylated zirconium dichloride, as proposed by Eisch, bears a strong solvent effect: the reaction products are not the same in ether or in hydrocarbon (C_nH_m, e.g. hexane). A dihydride zirconium dichloride has been proposed as an intermediate in hydrocarbon solvent rather than the '$ZrCl_2$' β-H migration product. Our study, that shows the compulsory need of solvent/ligand lone pairs to stabilize the '$ZrCl_2$' intermediate, enlightens the reason for this difference. The hydrocarbon solvent can not be expected to play such a role and different intermediates are to be obtained, depending on the solvent used for the synthesis.[6]

5. Supplementary material

XYZ coordinates and energies for all computed structures (24 pages) are available from the author on request.

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[6] The proposal of a dihydride intermediate is currently investigated in our group.

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