

Hydrometalation or Condensation in the Reaction of Cl_2ZrEt_2 with H_2CO . A Theoretical Account

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Specific solvent effects on the reactivity of Cl_2ZrEt_2 with formaldehyde is investigated with density functional theory (B3LYP). Polar solvents are modeled with dimethyl ether molecules, while hydrocarbon solvents are treated as in a vacuum. When initiated in polar solvents, the reaction is found to involve a cyclization that costs only 6 kcal·mol⁻¹. For the hydrozirconation, initiated in hydrocarbon solvent, a zirconium dihydride intermediate (Cl_2ZrH_2) is found 66.8 kcal·mol⁻¹ higher than the reactive species. A direct hydrozirconation mechanism is detailed and found likely to occur ($\Delta H^\ddagger \approx 10$ kcal·mol⁻¹).

Introduction

Group IV metallocene synthesis is an active field in organometallic chemistry due to their catalytic activity in olefin polymerization, and their structure as a catalyst is known to greatly influence the type of polymer obtained.^{1,2} For instance, *ansa*-zirconocenes catalysts, with a bridge between the cyclopentadienyl moieties, have been shown to influence the stereochemistry of the polymer.^{3,4}

Among many possible syntheses of these catalysts, particularly noteworthy is the recent strategy reported by Eisch et al.,^{5–7} where either metallocenes or *ansa*-metallocenes can be obtained starting from a single reagent (Cl_2ZrBu_2) and a single cyclopentadienyldiene substrate (fulvene). The key to the selectivity lies in the solvent used in the initial step of the reaction (Scheme 1), apolar solvents (hydrocarbon) leading to unbridged species, while polar solvents giving rise to the bridged compound. This selectivity is also observed with other substrates, such as aldehydes or imines.⁵ Such a control of the substitution gives access to a broad range of zirconium-containing compounds that can be used not only for catalysis but for stoichiometric synthesis as well.^{8,9}

Yet this difference, obviously due to the solvent, has not been explained and is the subject of the present

computation of the specific solvent effect on this selectivity. Although metallocene synthesis is of primary importance for synthetic applications, their large size as well as the aromatic structure of their cyclopentadienyl ligands would substantially complicate the reading of our computational study. On the other hand, aldehyde substrates also give rise to the same solvent selectivity and can be considered as a handy model to report our study. We used in the present contribution the simplest (unsubstituted) aldehyde (i.e., formaldehyde). Aryl-substituted aldehydes as well as fulvenes have been left apart for a forthcoming study of the conjugation and aromatic effects on such mechanisms. The outermost part of the butyl chains in the Cl_2ZrBu_2 reagent is unlikely to play any role in the mechanism but would complicate the analysis of our results. The reagent will be modeled in the present paper with Cl_2ZrEt_2 , **1**.

The mechanism in polar solvent, which leads to bridged compounds, can be described as follow:^{5,6} if an octahedral coordination is preferred about the Zr center, one shall consider that two solvent molecules can coordinate to the metal (Scheme 2, pathway 1). The resulting structure shall be noted **1·SS** to show that two solvent molecules (**S**) are coordinated to structure **1**. A single β -hydride elimination between the alkyl chains produces the key species of the synthesis: the Cl_2Zr -(alkene) stabilized by the solvent's lone pair **2·SS**. Upon warming, such a species is considered to release its ligands and behave as its titanium analogue, which forms a TiCl_2 black suspension.¹⁰ The " ZrCl_2 " suspension can be considered as an aggregation of multiple Cl_2Zr units, possibly stabilized by a number of ether ligands. Such a solid structure has not been further

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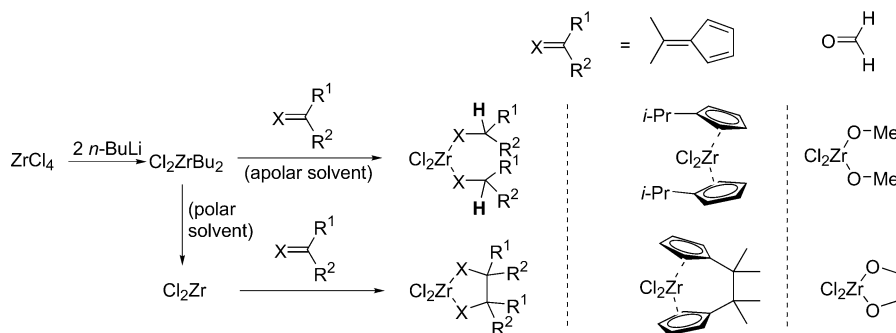
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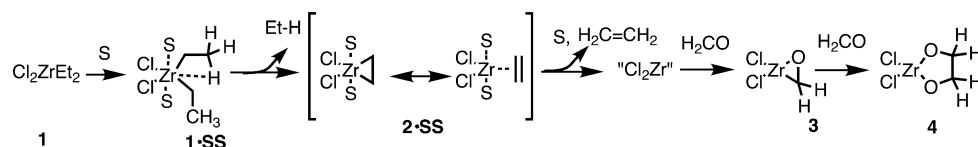
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Scheme 1

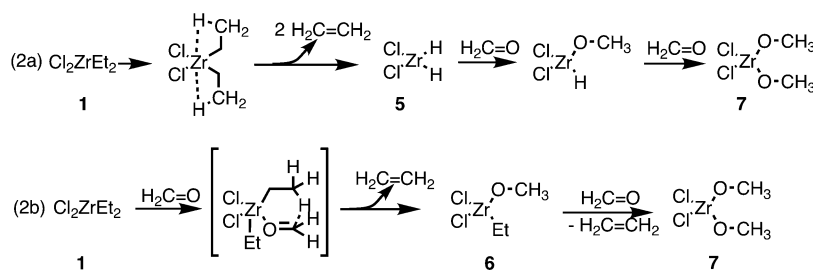


Scheme 2

pathway 1 (polar solvent S)



pathways 2 (hydrocarbon solvent):



studied herein. We rather considered the whole exothermicity of the ligand exchange around the metal ($2\cdot\text{SS} \rightarrow 3$). Incoming aldehydes would form a reactive species **3** and couple reductively to produce the dioxazirconacyclopentane species **4**. We recently studied¹¹ the first step of this reaction with ether solvent, $1 \rightarrow 2\cdot\text{OO}$, where **O** notes the coordination of ether molecules by one of their oxygen lone pairs. We showed how dialkylated zirconium dichloride can undergo a single β -hydride migration between the chains. We showed that this migration becomes exothermic when strong σ -coordinating ligands (ether or phosphines) interact with the metal. Most of the exothermicity is due to the stabilization of the migration product by the lone pairs of the ligand (or solvent) ($2\cdot\text{OO}$, $2\cdot\text{SS}$).

The selectivity in hydrocarbon solvent can be deciphered by two concurrent hypotheses from the literature.⁶ By extension of the polar solvent model, a stabilizing octahedral coordination can be obtained by two $\text{Zr}\cdots\text{H}-\text{C}_\beta$ agostic interactions (Scheme 2, pathway 2a). They would preorient the alkyl chains for two β -hydride migrations to the Zr center (and subsequent alkene eliminations) ($1 \rightarrow 5$). The zirconium dihydride (**5**) is the key intermediate for this hypothesis. The hydrometalation of the aldehyde simply originates from the $\text{C}=\text{O}$ insertion into the $\text{Zr}-\text{H}$ bonds ($5 \rightarrow 7$). The formation of the unbridged compound (**7**) requires two successive hydrometalations.

The second hypothesis is the direct transfer of a $\text{C}-\text{H}$ bond from the alkyl chains to the organic substrate, via a six-membered ring complex (Scheme 2, path 2b).

We shall in the following use Cl_2ZrEt_2 , dimethyl ether, and formaldehyde to (i) investigate the possibility of $\text{Zr}\cdots\text{H}-\text{C}_\beta$ agostic interactions in the dialkylated starting material (Cl_2ZrEt_2); the hypothesis of a zirconium dihydride intermediate shall also be discussed; (ii) investigate the possibility of a six-membered ring intermediate or transition state for the direct hydride transfer; (iii) describe the bridged system formation that occurs in polar solvent; (iv) propose a complete picture of the two reactions processes, with and without strong σ -coordinating ligands.

Computational Details

The calculations reported herein have been performed using the Gaussian98 suite of program.¹² Both geometry and energy calculations were performed using the B3LYP hybrid func-

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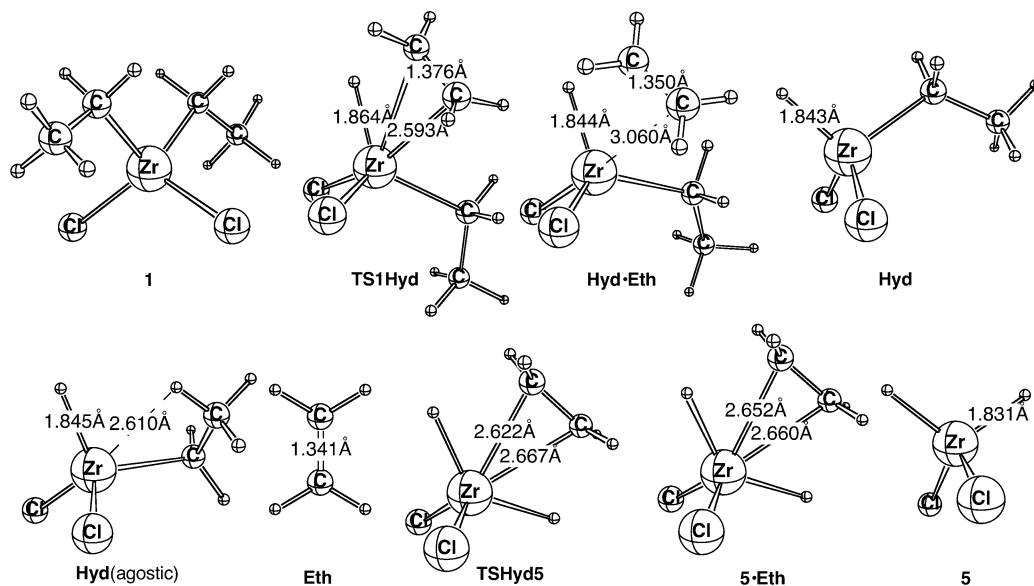


Figure 1. Geometries of the structures for the dihydride formation.

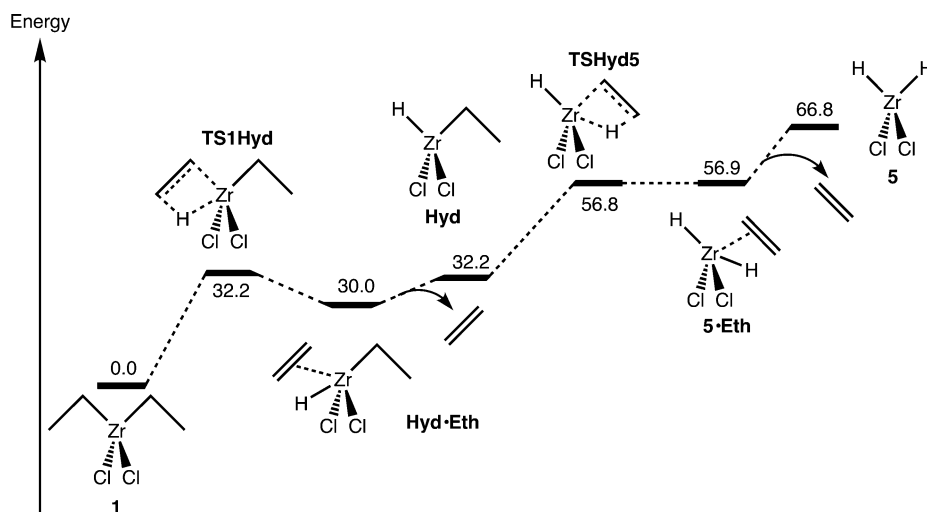


Figure 2. Energy and shape of the intermediates and transition states from Cl_2ZrEt_2 (**1**) to the dihydride Cl_2ZrH_2 (**5**). The energies, in $\text{kcal}\cdot\text{mol}^{-1}$, include the zero-point correction.

tional.¹³ 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.

The basis set we used is grounded on the Hay and Wadt LANL2DZ basis set¹⁴ that combines a relativistic effective core potential (RECP) plus a double- ζ Gaussian basis (for chlorine and zirconium) and Dunning's all electron (D95) double- ζ Gaussian basis (for hydrogen, carbon, and oxygen).¹⁵ This basis has been supplemented with polarization and diffuse functions taken from the D95 basis set as follow: The polarization functions added to the C, O, and Cl atoms have the following exponents: $d_c = 0.75$, $d_o = 0.85$, and $d_{cl} = 0.6$, respectively. Chlorine atoms have additional s and p diffuse functions with the exponent $sp_{cl} = 0.0483$.

To save computational requirements for the polar solvent assisted mechanism, the carbon atoms of the solvent model (OMe_2) did not hold any polarization functions all along this

study. Test computations with the PCM continuous model showed a rather small influence on the key step of the reaction in polar solvent. These nonspecific solvent effects were thus disregarded, and we focused only on the specific solvent effects in polar medium. The mechanisms in hydrocarbon solvent were also modeled with a simple gas phase approximation.

Results and Discussion

Hydrometalation: Apolar Solvent, Agostic Interaction, and Dihydride (Cl_2ZrH_2). An important point in the dihydride mechanism is that an agostic interaction can stabilize the system and preorient the conformation of the alkyl chains for the hydride migration (Scheme 2, pathway 2a). Within such a hypothesis, the intermediate between **1** and **5** is drawn as a bicyclic-like (spiro) compound. A similar interaction was found weak in $\text{ZrCl}_3(\text{ethyl})$, and one should not expect a large agostic interaction.¹⁶ We made several careful attempts to locate a minimum structure with one or two agostic $\text{C}_\beta\text{-H}\cdots\text{Zr}$ stabilized structures. All these attempts

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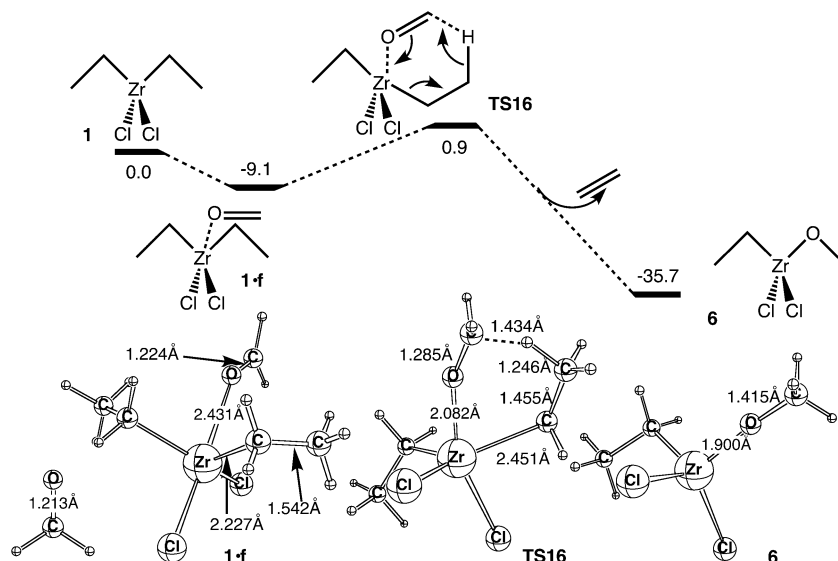


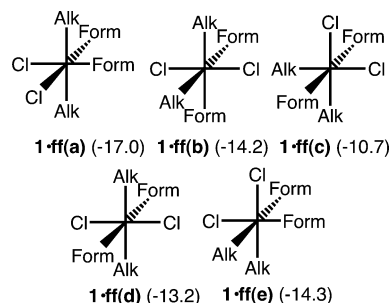
Figure 3. Reaction profile and structures for the six-membered ring direct mechanism with one formaldehyde molecule. The energies, in $\text{kcal}\cdot\text{mol}^{-1}$, include the zero-point correction.

failed and led rather to the C_{2v} symmetric conformation, a structure with the ethyl chains spreading apart from one another (Figure 1, **1**).¹⁷ This suggests that no large agostic interaction (if any) can stabilize the starting materials in a bicyclic-like conformation; neither can it preorient the side chains to facilitate the first hydride transfer.

The formation of the zirconium dihydride **5**, if any, likely occurs step by step from **1** (Figure 2), through a transfer of a hydrogen in β position of one of the ethyl chains onto the metal. This leads to the first hydride (noted **Hyd**). The transition state **TS1H_{Hyd}** for this step is located $32.2 \text{ kcal}\cdot\text{mol}^{-1}$ above **1**. It is a rather late transition state, with the C=C and the Zr–H bonds almost completely formed (1.376 and 1.864 Å, respectively). The Zr–H bond in the isolated hydride is close to the latter value, 1.843 Å (Figure 2). The product **Hyd·Eth** is the dissociative complex of an ethylene that weakly interacts with the hydride. Both **Hyd·Eth** and **Hyd** are high in energy ($\sim 30.0 \text{ kcal}\cdot\text{mol}^{-1}$). The hydride **Hyd** can resemble a loose agostic structure, noted herein “**Hyd**(agostic)”; see Figure 2. It has a short $\text{Zr}\cdots\text{H}$ distance and a very bent $\angle\text{ZrCC}$ angle (96°).¹⁸ The second ethylene abstraction goes through **TSHyd5**, which is located at a significantly high energy, $56.8 \text{ kcal}\cdot\text{mol}^{-1}$ above **1**, which is $24.6 \text{ kcal}\cdot\text{mol}^{-1}$ above the hydride **Hyd**. This transfer of the second hydrogen is thus less difficult than the first one, as far as the barrier is concerned. The structure resulting from this late transition state corresponds to a long distance interaction (2.565 Å) between an ethylene and the dihydride. This dihydride, Cl_2ZrH_2 **5**, is located $66.8 \text{ kcal}\cdot\text{mol}^{-1}$ above **1**. With such a high energy no dihydride intermediate could be further envisaged for the reactivity in hydrocarbon solvent.¹⁹

Hydrometalation: Apolar Solvent, Direct Hydride Transfer. We shall now consider the hypothesis of a direct hydride transfer to the aldehyde, via a six-membered ring intermediate or transition state. Starting from the dialkylated zirconium dichloride **1**, one could add one or more formaldehyde molecules and perform the direct hydrometalation. A single molecule

Scheme 3



can be used to analyze the mechanism (Figure 3). The formaldehyde first interacts by one of its lone pairs with the zirconium center. The first complex is thus noted **1·f** (we use the same convention throughout the present paper). This is a moderately stabilizing interaction (**1·f** is $9.1 \text{ kcal}\cdot\text{mol}^{-1}$ lower than **1**). Our calculations show that the six-membered ring intermediate is a transition state, noted herein **TS16**, located only $0.9 \text{ kcal}\cdot\text{mol}^{-1}$ above the starting materials (**1**). This corresponds to a small barrier (only $10 \text{ kcal}\cdot\text{mol}^{-1}$) that can be passed at room temperature. The ethylene abstraction down from **TS16** is an exothermic process that leads to the zirconium monoalkoxide **6**, $35.7 \text{ kcal}\cdot\text{mol}^{-1}$ below the starting materials. The energies are clearly in favor of such a direct transfer rather than through the hydrides.^{20,21}

The complete mechanism for the present aldehyde hydrozirconation involves more than a single formaldehyde molecule. When two formaldehydes are associ-

(17) As such an interaction usually involves a hydride (negatively charged hydrogen), we added to the basis set diffuse and polarization functions on the hydrogen atoms to favor their hydride potentiality. The coefficients were taken from the D95++(d,p) basis set as implemented in Gaussian 98 ($s_H = 0.036$ and $p_H = 1.0$). This did not change the result of the optimization; no agostic minimum structure was obtained.

(18) **Hyd** and **Hyd**(agostic) were found at the same energy ($32.2 \text{ kcal}\cdot\text{mol}^{-1}$ relative to **1**). The cost to fold the alkyl chain is identical to the energy gained by the agostic interaction.

(19) It has been experimentally established on a similar system that the formation of the hydride is not favored. See for instance: Fujita, K.; Yorimitsu, H.; Shinokubo, H.; Matsubara, S.; Oshima, K. *J. Am. Chem. Soc.* **2001**, *123*, 12115.

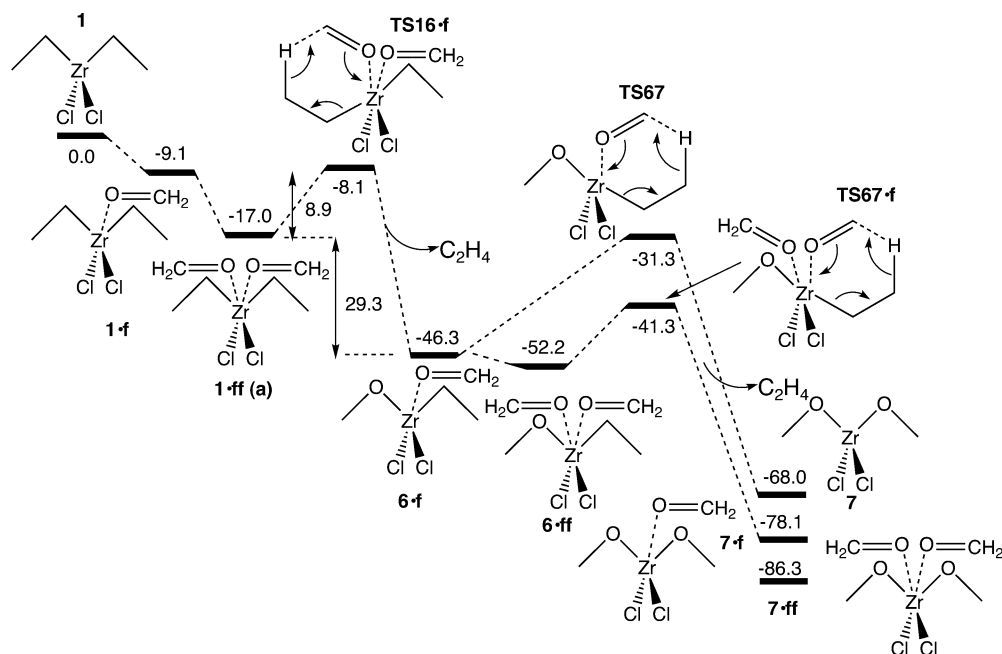


Figure 4. Reaction profile for the direct hydrometalation of the organic substrate from the dialkylated zirconium dichloride to the alkoxyde product $\text{Cl}_2\text{Zr}(\text{OMe})_2$. The energies, in $\text{kcal}\cdot\text{mol}^{-1}$, include the zero-point correction.

ated to the dialkylated zirconium dichloride, they can lead to five possible stereoisomers of **1·ff**, schematically drawn in Scheme 3 with the corresponding energies, in $\text{kcal}\cdot\text{mol}^{-1}$, relative to the isolated moieties.²² Structure **1·ff(a)** has the alkyl chains *trans* from one another (chlorines and formaldehydes all being *cis*). In **1·ff(b)** the chlorines are *trans*, and in **1·ff(c)** the formaldehydes are *trans*. In **1·ff(d)** all ligands are *trans* to one another, and in **1·ff(e)** all of them are *cis*.

The energies show that structure **1·ff(a)** is the most stable, and we used it as a starting species to describe the direct hydrometalation (Figures 4 and 5). One can actually use any of these conformations as a starting structure for the hydrogen transfer because they all possess an alkyl *cis* to a formaldehyde, which is required for the hydrogen transfer from the alkyl to the aldehyde. The energy required to perform the aldehyde reduction from **1·ff(a)** is low enough so we did not further investigate the question of the starting structure. From **1·ff(a)**, one easily connects to **6·f**, with a small activation barrier ($8.9 \text{ kcal}\cdot\text{mol}^{-1}$) and a large exothermicity ($29.3 \text{ kcal}\cdot\text{mol}^{-1}$). From **6·f** one can, in principle, either add a third formaldehyde molecule, to have an octahedral zirconium environment **6·ff**, or directly go to the second direct hydrometalation through **TS67**. The activation energy is slightly lower in the former case (10.9 vs $15.0 \text{ kcal}\cdot\text{mol}^{-1}$), and we suggest that an excess of formaldehyde can facilitate the second hydrometalation.

Both paths are exothermic by more than $20 \text{ kcal}\cdot\text{mol}^{-1}$. Finally, an excess of formaldehyde might further stabilize the reaction products and lead to **7·ff**, which is $86.3 \text{ kcal}\cdot\text{mol}^{-1}$ beneath the starting materials.

The hydrosirconation mechanism goes unambiguously through the direct, stepwise, process with two successive six-membered ring transition states. The highest barrier is so small ($10 \text{ kcal}\cdot\text{mol}^{-1}$) that it can be almost considered as a spontaneous reaction.

Condensation: Polar Solvent, Formation of the Zirconacycle. As shown in our previous report,¹¹ polar solvents such as THF, and more generally ethers, favor the formation of a $\text{Cl}_2\text{Zr}(\text{alkene})$ species, with the $\text{C}=\text{C}$ double bond coordinated to the zirconium (Scheme 2, **2·SS**). This species is also called a zirconacyclopropane due to the CC elongation ($\sim 1.5 \text{ \AA}$) and the short $\text{Zr}-\text{C}$ bonds ($\sim 2.2 \text{ \AA}$) (Figure 7). The most likely mechanism for the bridged system synthesis is a reductive coupling between two aldehyde molecules (Scheme 2, from **3** to **4**).

Starting from the isolated dialkylated species **1**, one can first validate the octahedral model. Structure **1·OO**, with two ethers coordinated by their lone pair to the metal, is indeed $16.2 \text{ kcal}\cdot\text{mol}^{-1}$ more stable than **1** + 2 OMe_2 , in a quasi octahedral arrangement (Figures 6 and 7). The formation of **2·OO** requires $20.2 \text{ kcal}\cdot\text{mol}^{-1}$ and is exothermic by $7.5 \text{ kcal}\cdot\text{mol}^{-1}$.¹¹ The alkane gas that is rejected from the reaction medium is unlikely to recombine back to the metal, making this reaction clearly irreversible. Upon the experimental workup (moderated heating to ca. $20 \text{ }^\circ\text{C}$), the ligands and the alkene can be removed from the Zr center to obtain the “ ZrCl_2 ” intermediate.

Disregarding the description of this “ ZrCl_2 ” solid intermediate, we studied globally the step for going from **2·OO** to **3·ff**. In this formal reaction, three formaldehyde molecules replace the ether ligands and the ethylene and act as σ -donating ligands. The stabilization of the oxazirconacyclopropane **3** is about $20 \text{ kcal}\cdot\text{mol}^{-1}$ for each

(20) This mechanism might be extended to alkene and alkyne hydrosirconation with $\text{Cp}_2\text{ZrCl}(\text{alkyl})$ studied by Negishi et al. Such a reaction might also occur via a similar six-membered ring transition state. (a) Negishi, E.; Miller, J. A.; Yoshida, T. *Tetrahedron Lett.* **1984**, 25, 3407. (b) Swanson, D. R.; Nguyen, T.; Noda, Y.; Negishi, E. *J. Org. Chem.* **1991**, 56, 2590. (c) Makabe, H.; Negishi, E. *Eur. J. Org. Chem.* **1999**, 969.

(21) Ketone reduction to alcohol can however be catalyzed by Cp_2ZrH_2 , in specific conditions; see for instance: Ishii, Y.; Nakano, T.; Inada, A.; Kishigami, Y.; Sakurai, K.; Ogawa, M. *J. Org. Chem.* **1986**, 51, 240.

(22) A similar study on formaldehyde complexation onto ZrCl_4 has been recently published: Bernardi, N.; Bottoni, A.; Casolari, S.; Tagliavini, E. *J. Org. Chem.* **2000**, 65, 4783.

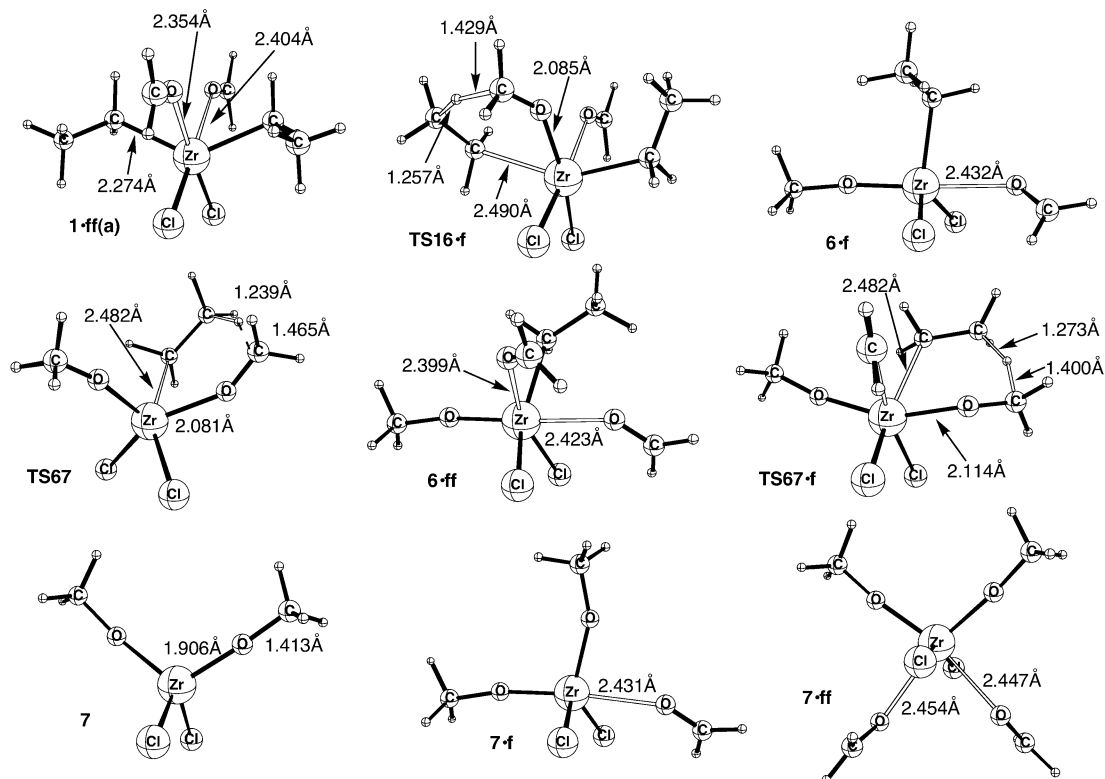


Figure 5. Shape of the structures for the six-membered ring mechanism with more than one formaldehyde molecules. The energies, in $\text{kcal}\cdot\text{mol}^{-1}$, include the zero-point correction.

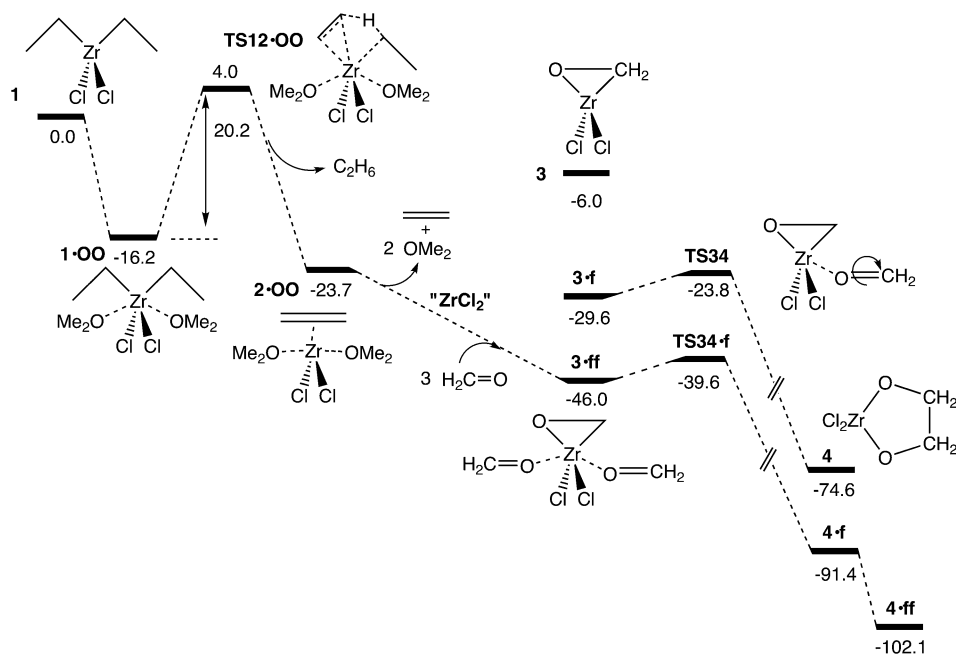


Figure 6. Reaction profile for the bridged system synthesis in polar solvent, from Cl_2ZrEt_2 to the dioxazirconacycle **4**. The energies (in $\text{kcal}\cdot\text{mol}^{-1}$) include the zero-point correction. For the geometry of these structures, see Figure 7.

ligand (Figure 6). The reductive C–C coupling is a facile process that costs about $6 \text{ kcal}\cdot\text{mol}^{-1}$ and is very exothermic ($-45 \text{ kcal}\cdot\text{mol}^{-1}$), the dioxazirconacycle **4** being $74.6 \text{ kcal}\cdot\text{mol}^{-1}$ below the starting materials.

Once **2-OO** is formed, followed by the “ ZrCl_2 ” suspension obtained by heating, the reaction that leads to **4** is to be considered as a barrierless process.

Hydrometalation or Condensation? We showed herein that the direct “hydride” transfer (Figure 4) is clearly the preferred mechanism for the aldehyde hy-

drometalation process in hydrocarbon solvent. Two β -hydride transfers from the alkyl chains onto the formaldehydes make the hydrozirconation irreversible by rejecting an alkene molecule (a gas) that could not return onto the zirconium. Once the first direct transfer is accomplished, which requires only $8.9 \text{ kcal}\cdot\text{mol}^{-1}$ and is exothermic by about $22 \text{ kcal}\cdot\text{mol}^{-1}$, the unbridged compound is obtained.

We also showed how, in ether solvent, the dioxazirconacycle (bridged species) can originate from the zir-

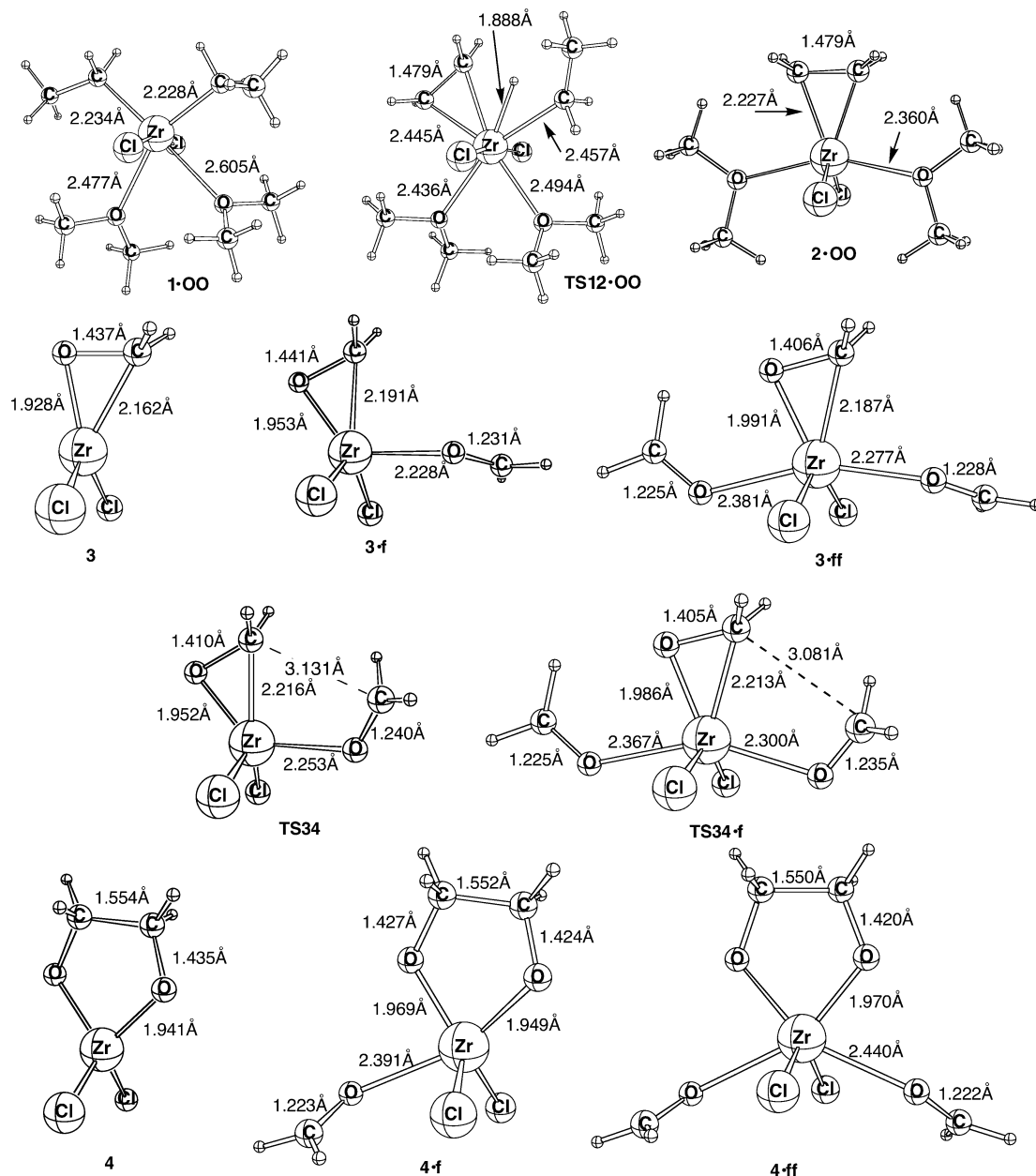


Figure 7. Shape of the structures for the bridged system synthesis in polar solvent, from Cl_2ZrEt_2 (**1-00**) to the dioxazirconacycle (**4**), disregarding the “ ZrCl_2 ” aggregates.

conacyclopropane intermediate (Figure 6, **2-00**). Disregarding the solvent abstraction to form the “ ZrCl_2 ” species, we found that the limiting step in this reaction is the β -hydride transfer from the alkyl chains in the starting material (**1** \rightarrow **TS12** \rightarrow **2**). In hydrocarbon solvent when no ether molecule can facilitate this reaction, one shall consider that the σ -donating oxygens’ lone pairs of the formaldehyde could act as those of the ether solvent.

As shown in Figure 8, we found that the formaldehydes barely change the activation energy compared to the reaction profile computed with dimethyl ether ($\Delta H^\ddagger \approx +21 \pm 1 \text{ kcal}\cdot\text{mol}^{-1}$ in both cases). Formaldehyde stabilizes the product even slightly more than does dimethyl ether (-27.7 vs $-23.7 \text{ kcal}\cdot\text{mol}^{-1}$). The Cl_2Zr -(alkene) formation can thus also be envisaged in hydrocarbon solvent. However, the initial step of the aldehyde hydrometalation to form **6-f** and **7** is more exothermic and easier than the formation of **2-ff** (see

Figure 9) and **4** ($\Delta H^\ddagger = +8.9$ vs $+21.7 \text{ kcal}\cdot\text{mol}^{-1}$). Our comparison is consistent with the experimental finding that only the aldehyde hydrometalation product is detected in hydrocarbon solvents.

Conclusion

We finally disclosed the mechanisms that allow the synthesis of bridged and unbridged dialkoxyzirconium dichloride by solvent modulation. From our results one shall conclude that unbridged species issue from a two-step reaction involving a direct transfer of the hydride from the alkyl chains to the substrate. It involves two successive six-membered ring transition states and low barriers (they can be smaller than $10 \text{ kcal}\cdot\text{mol}^{-1}$). The number of organic substrates actually involved in the reaction cannot be exactly determined, although moderate excess of formaldehyde should stabilize the reaction product in a quasi-octahedral coordination and facilitate

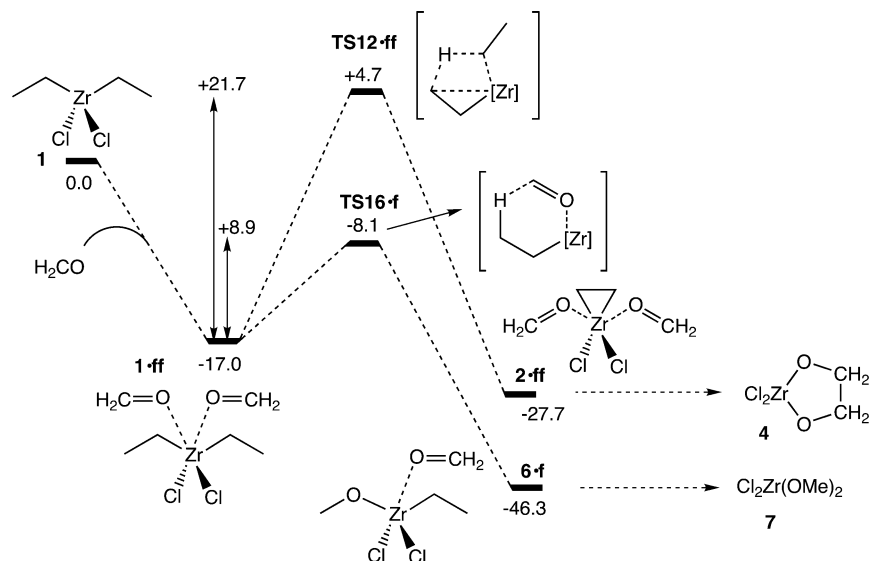


Figure 8. Reaction profile comparing the hydrometalation and the β -H abstraction. The energies (in kcal·mol⁻¹) include the zero-point correction. For the geometries of these structures, see Figures 5 and 9.

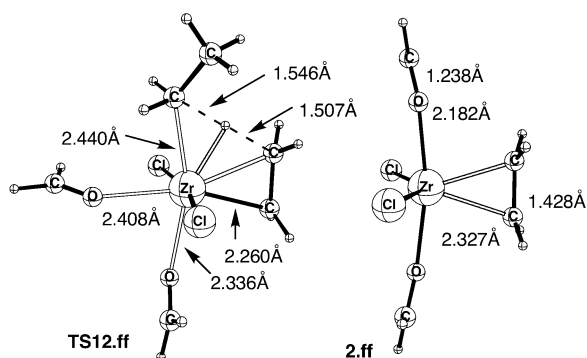


Figure 9. Structures for the formation of $\text{Cl}_2\text{Zr}(\text{alkene})$ assisted by formaldehyde.

the reaction. The zirconium hydrides are energetically high and should not be further envisaged in the present cases.

These reaction mechanisms can be extended to the reactivity of other substrates such as substituted aldehydes, fulvenes, and Bronsted acids. The detailed study of these reactions, where conjugation effects are impor-

tant, is currently in progress in our groups and is the subject of a forthcoming publication.

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Supporting Information Available: XYZ coordinates and energies for all computed structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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