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On the Mechanism of Polymerization of Acrylates by Zirconocene Complexes, an ab Initio and Density Functional Theory MO Study

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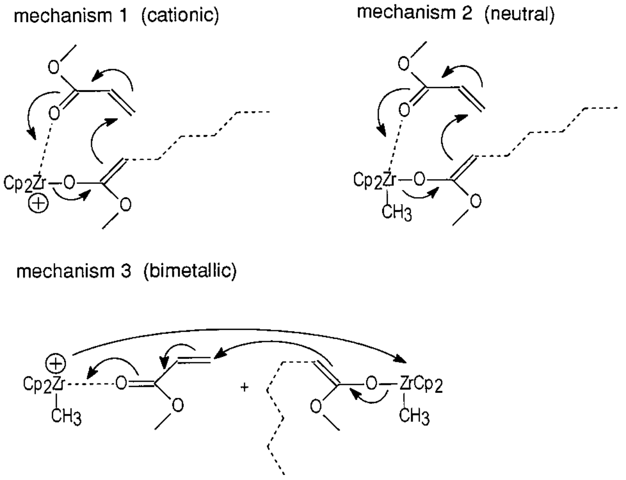
ABSTRACT: RHF/3-21G ab initio, density functional theory (B3LYP/3-21G), and single-point calculations using an effective core potential (B3LYP/6-31G*-ECP(S)//3-21G) are performed for different mechanisms of polymerization of acrylic acid and methyl acrylate by dicyclopentadienyl−zirconocene enolate complexes. Polymerization is considered involving a cationic zirconocene complex and a neutral zirconocene complex, respectively. In addition, a mechanism proposed by Collins is treated which involves a neutral and a cationic zirconocene complex in the CC bond-forming step at the same time. Catalytic cycles can be devised in all cases which suggest that all three mechanisms may be realizable under suitable conditions. However, the "bimetallic" mechanism proposed by Collins shows the lowest energy of activation for the propagation step. It is shown that bridging of the cyclopentadienyl rings should be important not only with respect to reactivity but also with respect to the possible catalytic cycle. Methyl methacrylate is not included in the treatment; i.e., the problem of tacticity in these polymerizations is not addressed.

Introduction

The polymerization of alkyl acrylates or methacrylates has industrial significance and, therefore, has been the subject of intensive experimental investigations and practical applications. A few years ago, zirconocene complexes have been introduced as catalyst or catalyst precursors for the polymerization of methyl methacrylate.[1] This stimulated investigations with the goal to elucidate the scope and limitations of this approach. Several investigations are based on a modification of dimethylzirconocene or derivatives thereof as catalyst precursors.[2] Proposals were made regarding the catalytically active species and the mechanism of polymerization. Of particular interest is the generation of the actual catalyst and the nature of the propagation step. Bridged and nonbridged zirconocene derivatives have been studied. Most of these studies have in common that, in the initial preparation of the active catalyst, methyl groups are eliminated from dimethylzirconocene complexes in order to provide a cationic intermediate with a vacant ligand site which can be used by an acrylate molecule or, in view of the catalytic activity, by an ester enolate molecule. The latter is presumed to be formed in situ prior to polymerization. Several catalytic cycles have been proposed which were either replaced or refined over the years.

Three mechanisms which have been proposed on the basis of experimental studies were considered in detail in this computational study (Scheme 1). A zirconium ester enolate subunit is common to all of them. Mechanism 1 is based on a positively charged dicyclopentadienyl zirconium subunit.[2a−c] Acrylate is attached to zirconium via the carbonyl oxygen atom. The terminal C atom of acrylate forms a CC bond with the β-C atom of the enolate, acrylate now becoming the new enolate unit. The catalytic cycle is terminated by removing the methoxycarbonyl group, formerly the enolate, from zirconium. Mechanism 2 is similar but incorporates a neutral zirconium complex, that is, a dicyclopentadienyl methylzirconium unit bound to an enolate.[2b,2c] The third mechanism is different insofar as two dicyclopentadienyl methylzirconium units are involved,[2b,c] one being connected to an ester enolate and the other to an acrylate molecule. CC bond formation is a bimolecular reaction. During the process, the positively charged complex becomes neutral and vice versa.

Scheme 1



A number of theoretical studies have been carried out on ethene or propene polymerization by metallocene complexes. In part, they are based on RHF, on DFT calculations, or on a combination of MO and force-field procedures.[3] The present ab initio molecular orbital and density functional theory investigation was initiated in order to gain insight into the polymerization process of acrylates by metallocene catalysts. We have decided to systematically investigate three different catalytic cycles and to compare the results with experiment. If the complexes are cationic no attempt is made to elucidate the role of counterions although they may be important.[2g] Only acrylic acid (AA) and its derivatives will be considered; thus the question of tacticity in methyl

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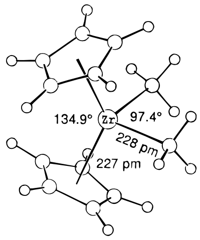
methacrylate polymerizations will not be addressed here. Although many experimental studies have been carried out on bridged dicyclopentadienyl units or even on indenyl−zirconocene complexes our study emphasizes nonbridged dicyclopentadienyl−zirconocene complexes. Some reactions, however, are considered where the cyclopentadienyl rings are bridged by a methano, a silano, or an ethano group. Some bridged [$Cp_2Zr(CH_3)$-enolate] complexes are investigated in order to see the effect of bridging on the nature of enolate zirconocene complexes.

Computational Procedures

The calculations were carried out with the serial and parallel version of the program GAUSSIAN 94.[4] Due to the complexity of the molecular structures the 3-21G basis set was used for all atoms including zirconium. RHF/3-21G and density functional theory calculations, B3LYP/3-21G, were performed, the latter predominantly as single-point calculations on the computed RHF/3-21G structures. Single-point calculations on stationary points and transition structures were also performed using the effective core potential approach for zirconium, developed by the Stuttgart group (denoted as ECP(S)) (B3LYP/6-31G*-ECP(S)//3-21G).[5] Due to the high number of atoms to be considered in the complexes of the catalytic cycle, the systems had to be simplified in many cases. One approximation concerns the replacement of alkyl groups in enolates by hydrogen atoms. Also, many calculations were done with free carboxy groups instead of methoxy carbonyl. When acrylic acid as model for methyl acrylate is part of a structure, it has to be ensured that no artifacts are introduced by this simplification. Whereas the possible conformations of methyl acrylate differ only slightly in energy, this is not the case for acrylic acid, as hydrogen bonding between OH and C=O is possible, thus rendering the conformation allowing this stabilization energetically more favorable.[6] In cases where ambiguities might arise from choosing acrylic acid, the calculation is repeated with methyl acrylate. Further, multiatom systems may pose problems concerning local energy minima due to the existence of several stable conformations. Therefore, sometimes reasonable choices have to be made. In general, all degrees of freedom were energy minimized, except for the reaction coordinate, which was chosen as the distance of the β-C atom of a zirconium bound enolate and the β-C atom of acrylic acid or methyl acrylate. Calculations at various distances of the reacting atoms, for which all other parameters were optimized, indicated that the transition structure (TS) of CC coupling lies at a separation of 220−230 pm of the reacting centers. This presumption was confirmed in one case where a TS was successfully located. An analysis of the Hessian matrix provided only one negative vibrational frequency. This calculation proved that the potential energy surface is flat in the region of the TS and justifies single-point calculations on higher levels of theory. Although small structural changes of the stationary points or transition structures may be possible if the theoretical level is changed, the energetic situation should not be altered to such an extent that conclusions on the mechanistic pathway will be influenced by this approach. For reasons of computation time the calculations were terminated when the change in total energy was $\leq 10^{-4}$ a.u. between two cycles.

Results and Discussion

Zirconocene Complexes for the Construction of Catalyst Precursors, Catalysts, and Catalytic Cycles. Dicyclopentadienyldimethylzirconocene, dicyclopentadienylmethylzirconocene cation, and dicyclopentadienylzirconium dication are reference molecules for the construction of catalytic cycles. The molecules were examined both on the RHF/3-21G and on the B3LYP/3-21G density functional theory levels by allowing the optimization of all degrees of freedom without any symmetry constraints. The structures as obtained by B3LYP/3-21G calculations are presented in formulas **1**−**3**. The RHF/3-21G results do not differ significantly. Generally, bond lengths tend to be slightly shorter when determined by B3LYP/3-21G. Dimethylzirconocene (**1**) has been analyzed by X-ray diffraction.[7] The experimental bond distances and bond angles are very similar to the calculated values. Thus, the calculated Zr−CH_3 distance of 228 pm (B3LYP/3-21G) is identical to the experimental value; the metal−cyclopentadienyl centroid distance of 227 pm differs only slightly from the measured value of 223 pm. A similar good agreement exists for the bond angles. The structure of the dicyclopentadienylmethylzirconocene cation can also be compared with published X-ray data of complexes containing this subunit[8] and other quantum-chemical calculations using density functional theory (LDA approximation).[3b,9] Both the LDA calculation and the X-ray data are in reasonable agreement with our results. Our calculated Zr−CH_3 bond lengths are 226 pm (RHF/3-21G) and 224 pm (B3LYP/3-21G), in good agreement with the X-ray determined value of 222 pm. The cation is not planar; the angle between the plane spanned by the lines connecting zirconium and the centroids of the cyclopentadienyl rings and the Zr−CH_3 bond is 46°, similar to the LDA calculation by Ziegler.[3b] As in Ziegler's work, some indication of an agostic interaction of a hydrogen atom of the methyl group and zirconium is observed.



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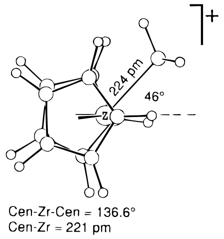

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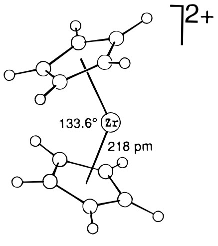

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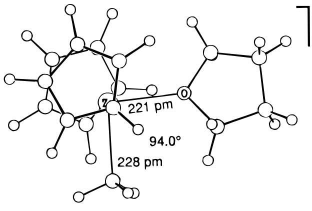

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For the purpose of structural comparison with literature data,[10] we also calculated the structure of the THF adduct of the dicyclopentadienylmethylzirconocene cation **4** (RHF/3-21G). The structure of **4** is very close to that obtained by X-ray diffraction of the same complex although the counterion tetraphenylborate was not considered in the calculation. The zirconium−oxygen and the Zr−CH_3 bond lengths are 221 and 228 pm as compared to 212 and 226 pm in the crystal. The angle O(THF)−Zr−CH_3 is obtained as 94.0° and measured as 97.4°. Other calculations on different levels of theory[11] support our experience that the basis set chosen provides reliable structural data of organometallic complexes.

Some energetic considerations evolving from these calculations are of interest (Table 1). In view of the

Table 1. Δ*E*(SCF, 0 K) on Complexing Metallocene Fragments to Various Components (kcal mol^{-1}) Where All Compounds Were Geometry Optimized on the RHF/3-21G Level, Except Where Noted Otherwise

	formula	Δ*E* (kcal mol^{-1})
2 + THF	**4**	−59.6
2 + $H_2C{=}CH{-}CO_2H$	**5**	−59.9
2 + $(H_2C{=}CH{-}CO_2H)_2$	**6a**	−78.1
2 + $(H_2C{=}CH{-}CO_2H)_2$	**6b**	−78.2
2 + $H_2C{=}C(OH)O^-$	**7a**	−195.1
2 + $H_2C{=}C(OCH_3)O$	**7b**	−195.3
2 + $(H_3C)_2C{=}C(OCH_3)O^-$	**8**	−194.9
2 + $(H_3C)_2C{=}C(OCH_3)O^-$	**8**	−211.3[a]
2 + CH_3OH		−55.8
2 + $H_2C{=}CH{-}CO_2H$ + THF		−71.0
3 + $H_2C{=}C(OH)O^-$	**9**	−314.7
3 + $H_2C{=}C(OH)O^-$ + $H_2C{=}CH{-}CO_2CH_3$		−377.1
3 + $H_2C{=}C(OH)O^-$ + THF		−372.5
$H_4C_2Cp_2Zr(CH_3)^+$ + $(H_3C)_2C{=}C(OCH_3)O^-$	**29**	−209.4[a]
$Me_2SiCp_2Zr(CH_3)^+$ + $(H_3C)_2C{=}C(OCH_3)O^-$	**30**	−210.3[a]
$Me_2CCp_2Zr(CH_3)^+$ + $(H_3C)_2C{=}C(OCH_3)O^-$	**31**	−210.6[a]
2 + $H_2C{=}CH{-}CO_2CH_3$		−62.2
2 + $(H_2C{=}CH{-}CO_2CH_3)_2$		−71.8
2 + $(H_2C{=}CH{-}CO_2CH_3)_2$		−68.2

[a] **8**, **29**−**31** B3LYP/3-21G-optimized, single-point B3LYP/3-21G calculations on geometries of fragments as obtained from separating **8**, **29**−**31**.

reactions to be considered, the strength of the interaction between $[Cp_2ZrCH_3]^+$ (**2**) and the oxygen atom of THF is remarkable. On complexation of THF, −59.6 kcal mol^{-1} is liberated. This may be an indication why polymerization reactions of alkenes do not occur in THF solution[10] as the solvent molecules would prohibit the coordination of an alkene molecule. According to the result for **4**, it is not surprising that the oxygen atom of methanol adds to the $[Cp_2ZrCH_3]^+$ fragment with a comparable gain in stability of −55.8 kcal mol^{-1}. The zirconium−oxygen distance is 222 pm in this case. This demonstrates the similarity of the interaction of oxygen and zirconium in both complexes. The covalent bond is mainly formed by zirconium p- and oxygen s-orbitals (see below). When the carbonyl oxygen atom of acrylic acid assumes the function of the bonding atom to zirconium (**5**), −59.9 kcal mol^{-1} is gained, an amount comparable to that found for the THF or methanol adduct. It is interesting to note that the interaction of **5** with a second molecule of acrylic acid (**6a/b**) leads to an additional stabilization of −18.2/−18.3 kcal mol^{-1}.

The proposed mechanisms of polymerization of acrylates, based on one molecule of zirconocene, involve either a neutral complex between $[Cp_2ZrCH_3]^+$ (**2**) and an ester enolate or a cationic complex between $[Cp_2Zr]^{2+}$ (**3**) and an ester enolate. These complexes are postulated (see above) to take part in the propagation step of the polymerization. To simulate these situations we determined the interaction of **2** with the enolates of acetic acid (**7a**), methyl acetate (**7b**), and methyl isobutyrate (**8**), with respect to the interaction of **3** with the enolate of acetic acid (**9**) (Figure 1). The THF adduct of $[Cp_2Zr(OC(OH){=}CH_2)]^+$ was included because a THF adduct of an ester enolate complex of **3** has been used as polymerization catalyst.[2b] The enolate complexes are characterized by a covalent zirconium−oxygen bond. In addition, however, the total binding energies of −195.1 for **7a**, of −195.3 for **7b**, and of −194.9 kcal mol^{-1} for **8,** which are about −140 kcal mol^{-1} higher than for the THF and acrylic acid adducts **4** and **5,** must include an electrostatic component between the charged species. The total binding energy of **3** to the enolate of acetic acid amounts to −314.7 kcal mol^{-1}; if THF is added to this complex, it increases to −372.5 kcal mol^{-1}.

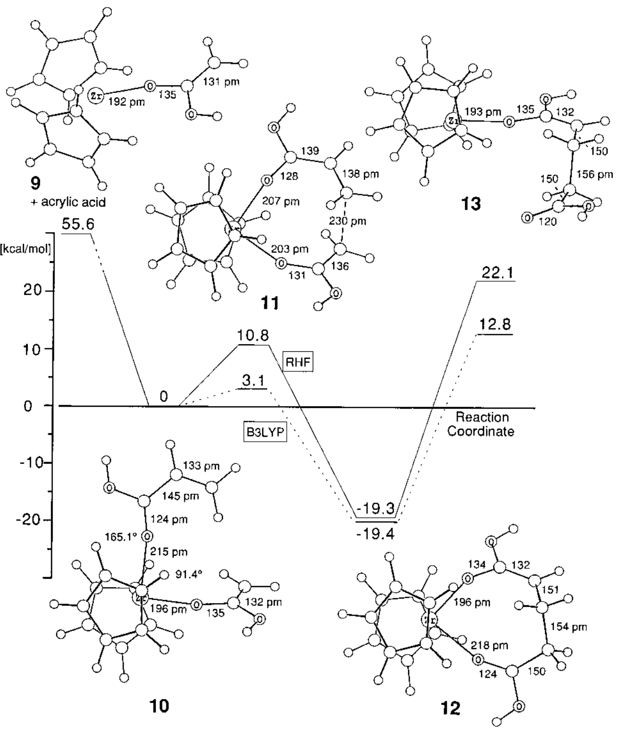


Figure 1. Reaction coordinate (kcal mol^{-1}) of a catalytic cycle for polymerization of acrylates based on the cationic metallocene complex $[Cp_2Zr(OC(OH){=}CH_2)]^+$. Structures **9**−**13** are positively charged. Full lines: RHF/3-21G results. Broken lines: B3LYP/6-31G*-ECP(S)//3-21G results.

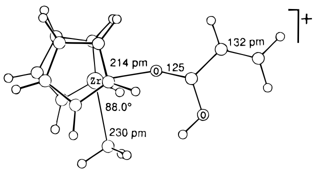
The Cationic Mechanism. In the course of his studies, Collins proposed $[Cp_2Zr(OC(OMe)C{=}CMe_2)(THF)]^+$ as a catalyst for polymerization of methyl methacrylate (MMA) and established a weak polymerization activity for this complex,[2b] as well as a fast reaction of the same complex in the presence of **1**.[2a] Soga investigated the polymerization of MMA with the catalyst systems *rac*-$Et(Ind)_2Zr(CH_3)_2/Ph_3CB(C_6F_5)_4$, *rac*-$Et(IndH_4)_2Zr(CH_3)_2/Ph_3CB(C_6F_5)_4$, and *rac*-$Me_2Si(Ind)_2Zr(CH_3)_2/Ph_3CB(C_6F_5)_4$ in the presence of Lewis acids such as Et_2Zn, in particular with respect to the tacticity of the product.[2e] Experiments were also carried out with $Cp_2Zr(CH_3)_2$ under similar conditions.[2d] It was claimed that $Zn(C_2H_5)_2$ takes part in the initiation reaction and is not involved in the propagation step. The nature of the initiation reaction was not further detailed. Collins suggested in his early work that a cationic $[Cp_2Zr(enolate)]^+$ complex might be the active species in analogy to the proposed mechanism of MMA polymerization mediated by lanthanocene complexes.[12]

In a first approximation to the cationic catalytic system we chose the enolate complex **9** (see Figure 1) and determined its interaction with a molecule of acrylic acid, allowing optimization of all geometrical variables except the conformation of acrylic acid, which was fixed as displayed. The numerical results are displayed in Table 2, entry 1. A minimum in the potential energy surface is found for structure **10** (Figure 1). The angle Zr−O=C is determined to be 165.1°, the angle O(enolate)−Zr−O(acrylic acid) amounts to 91.4°. The two oxygen zirconium distances are 196 pm (O−enolate) and 215 pm (O−acrylic acid). Thus, the enolate appears to be bound slightly stronger to zirconium than acrylic

Table 2. Relative Energies (kcal mol^{-1}) of Stationary Points and Approximate Transition Structures in the Propagation Sequence of Polymerization of Acrylic Acid (AA) or Methyl Acrylate (MA)[a]

entry	organomet fragment	alkene		E^b		approximate TS		metallacycle		enolate complex
1	$[Cp_2Zr(OC(OH{=}CH_2)]^+$	AA	**10**	55.6	**11**	10.8 [1.2; 3.1]	**12**	−19.3 [−21.0; −19.4]	**13**	22.1 [17.4; 12.8]
2	$[Cp_2Zr(OC(OH){=}CH_2)$-$(H_2C{=}CHCO_2H)]^+$	AA		24.4		17.0 [7.3; 5.9]	**12a**	−10.7 [−11.6; −13.4]		−7.3 [−8.3; −17.2]
3	$[Cp_2Zr(OC(OH){=}CH_2))THF]^+$	AA		24.4		17.5 [7.9; 6.5]		−8.1 [−9.4; −12.3]		−3.0 [−6.4; −15.2]
4	$[Cp_2Zr(CH_3)(OC(OCH_3){=}CH_2)]$	MA	**18**	11.5	**14**	13.9 [3.3; 10.0]	**19**	−20.7 [−22.6; −17.5]	**20**	−24.9 [−26.5; −26.8]
5	$[Cp_2Zr(CH_3)(OC(OCH_3){=}CH_2)]$	MA	**18**	11.5	**15**	15.3 [5.1; 9.4]		−20.1 [−22.2; −18.1]		−26.0 [−26.3; −28.4]
	$[Cp_2Zr(CH_3)(OC(OCH_3){=}CH_2)]$	MA	**18**	11.5	**16**	25.9 [14.4; 20.0]				
	$[Cp_2Zr(CH_3)(OC(OCH_3){=}CH_2)]$	MA	**18**	11.5	**17**	22.4 [8.8; 15.7]				
6	$[Cp_2Zr(CH_3)(OC(OH){=}CH_2)]$	AA		11.7		16.0 [5.6; 10.3]		−18.4 [−19.8; −15.1]		−23.0 [−23.6; −24.5]
	ΔZPVE for entry 6[c])				**21**	1.29		3.65		3.04
7	$[Cp_2Zr(CH_3)(OC(OCH_3){=}CH_2)]$	AA		10.9		14.7 [4.4; 9.6]		−19.8 [−21.2; −17.2]		−25.0 [−25.0; −27.2]
8	$[H_2SiCp_2Zr(OC(OH){=}CH_2)]^+$	AA		64.0		11.1 [1.6; 2.7]		−19.3 [−21.2; −19.9]		−11.4 [21.0; 12.0]
9	$[H_2SiCp_2Zr(CH_3)(OC(OH){=}CH_2)]$	AA		11.6		14.1 [4.6; 6.1]		−16.5 [−18.6; −17.6]		−20.2 [−19.9; −26.2]
10	$[C_2H_4Cp_2Zr(CH_3)(OC(OH){=}CH_2)]$	AA		9.9		12.5 [1.9; 6.4]		−17.0 [−21.1; −17.3]		−24.7 [−24.8; −26.6]
11	$[Cp_2ZrCl(OC(OH){=}CH_2)]$	AA		13.6		12.9 [4.4; 4.8]		−25.9 [−26.4; −25.2]		−19.1 [−20.9; −29.4]
12	$[Cp_2ZrCl(OC(OCH_3){=}CH_2)]$	AA		10.5		11.6 [3.2; 5.3]		−26.4 [−25.1; −25.5]		−25.2 [−26.7; −34.9]

[a] Reference point (0.0 kcal mol^{-1}) is the initial complex between the organometallic fragment and AA or MA. RHF/3-21G values are given in square brackets: B3LYP/3-21G//RHF/3-21G (first) and B3LYP/6-31G*-ECP(S)//RHF/3-21G (second). [b] Energy of organometallic fragment + AA or + MA relative to the initial complex (0.0 kcal mol^{-1}). [c] ZPVE corrections for stationary points of entry 6 (fully converged) and TS **21** relative to the initial complex (0.0 kcal mol^{-1}).



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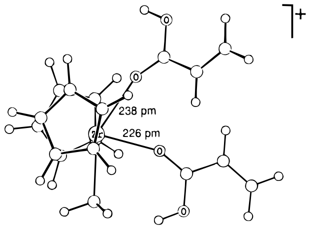

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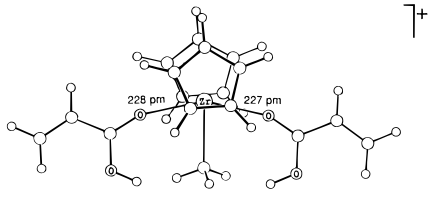

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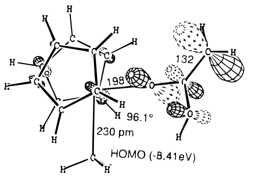

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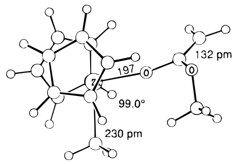

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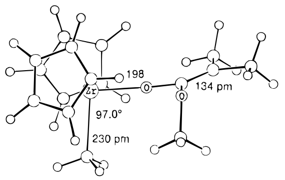

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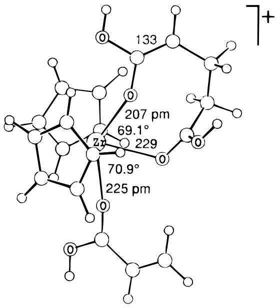
acid, in agreement with an electrostatic component in this interaction. This is confirmed by the binding energies of $Cp_2ZrCH_3^+$ to acrylic acid (**5**) and to the enolate of methyl acetate (**7b**) (see Table 1), where Zr−O bond lengths are observed that are very similar to those in **10**. The carbonyl−oxygen bond stretches only slightly on complexation (124 pm as compared to 120 pm in the free acid), the CC double bond remains unaffected. The bonding energy is −55.6 kcal mol^{-1}, a value which is roughly identical to the complexation energy of acrylic acid with **2**.

The CC distance of the atoms forming the new CC bond was chosen as the reaction coordinate. Within a range of 210−240 pm, the total energy was calculated at intervals of 10 pm, optimizing all geometrical variables. A maximum of the energy was found at a separation of 230 pm of the reacting atoms (**11**). Due to the complexity of the system, no attempt to locate the exact TS was undertaken. The two Zr−O bond distances are not equal, the one to the enolate oxygen being 203 pm and the one to the carbonyl oxygen atom being 207 pm. The approximate activation energy is 10.8 kcal mol^{-1}. On formation of the CC bond, the system relaxes to structure **12**, which is characterized by an eight-membered ring involving zirconium and two oxygen atoms. The two oxygen atoms are again not equivalent; the carboxy group of the incoming acrylic acid is converted into an enolate moiety, and the former enolate oxygen becomes the carbonyl oxygen atom of a carboxy group. Formally, both ligands, the incoming acrylate and the enolate, can be interconverted. This is supported by the Zr−O distances of 196 and 218 pm in **12** in comparison to structure **10**. If the reaction coordinate describes the propagation step properly, then the termination of the catalytic cycle must be the dissociation of the carboxy group from zirconium to give the enolate complex **13**. This separation process requires 41.4 kcal mol^{-1} of energy, somewhat less than the energy gain on associating acrylic acid to **9**. The energy requirement of this last step raises doubts whether this kind of propagation sequence would lead to polymerization. To see the effect of electron correlation, single-point B3LYP/3-21G and B3LYP/6-31G*-ECP(S) calculations were carried out on the geometries of the stationary points and transition structures. Broken lines in Figure 1 describe the results of the effective core potential calculations. The activation energy for CC bond formation is reduced to 3.1 kcal mol^{-1}, the energy of **12** remains almost identical, and **13** is lowered in energy by about 9 kcal mol^{-1}. The bond breaking process remains endothermic. In the B3LYP/3-21G approximation, the activation energy for CC coupling is further reduced to 1.2 kcal mol^{-1}. Thus, CC bond formation requires only little activation in the cationic mechanism.

According to these calculations, the polymerization should stop after formation of an eight-membered metallacycle (**12**). This conclusion might be tested by reacting a cationic enolate complex, e.g., the complex $[Cp_2Zr(OC(OMe)C{=}CMe_2)(THF)][BPh_4]$ of Collins[2b] under noncatalytic conditions with acrylate. To our knowledge, this has not been done so far. A comparable organolanthanide(III) complex, however, with high activity in methyl methacrylate polymerization has been isolated by Yasuda et al.[12] There are striking similarities between the X-ray determined structure of this eight-membered metallacycle and our calculated structure.

A second approach to the cationic mechanism was based on the reasoning that polymerizations are carried out in the presence of a large excess of acrylate and that a second molecule of acrylate, represented in our calculation by acrylic acid might be involved in the catalytic cycle. Indeed, if a second molecule of acrylic acid interacts with complex **10**, −24.4 kcal mol^{-1} of energy is liberated (Table 2, entry 2), leading to an almost symmetrical structure (similar to **6b**, however with enolate instead of methyl) in which the two carbonyl oxygen−zirconium distances are 230 pm. However, the distances of the β-C atoms of the two acrylic acid molecules from the β-C atom of the enolate are different, being 384 and 470 pm, respectively. If the shorter separation is chosen as the reaction coordinate CC bond formation requires 17.0 kcal mol^{-1} of activation energy to form the metallacycle **12a**, which lies −10.7 kcal mol^{-1} below the energy of the first complex. The final step, separation of the carboxy group from zirconium, is slightly endothermic and in the ECP calculation is even slightly exothermic. This reaction sequence has the further advantage that the product produced in the last step serves directly as the educt for the next propagation step as it corresponds to **10**.



12a

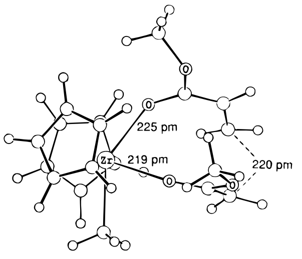
Collins reported that $[Cp_2Zr(enolate)THF]^+$ polymerizes methyl methacrylate, although not very efficiently.[2b] This led us to investigate the influence of a THF molecule on the shape of the reaction coordinate. The reaction coordinate, including the first molecular complex, transition structure, reaction product, and separated polymer chain, follows from the data in Table 2, entry 3. Two features are remarkable: In all cases the activation energy for CC bond formation is higher than in the absence of THF and the scission of the carbonyl oxygen atom from zirconium in the last step requires a much smaller amount of energy than in the absence of THF. The presence of THF facilitates in particular the separation step. Thus, it has to be assumed that in Collins polymerization with $[Cp_2Zr(enolate)THF]^+$ THF remains attached to zirconium during the polymerization or, as in the previous case, a molecule of acrylate assumes this function via a dissociation/association equilibrium.

It might be argued that acrylic acid could bind as well or even better via the oxygen atom of the hydroxy group and not via the carbonyl oxygen of acrylic acid to zirconium. This possibility was considered. The minimization procedure leads to a complex which is 18 kcal mol^{-1} higher in energy than **5**, thus eliminating this possibility. Furthermore, if methyl acrylate is used instead of acrylic acid, complexation via the oxygen atom of the methoxy group does not lead to a stable situation. When the energy is minimized, the complex transforms to that in which the carbonyl oxygen is connected to zirconium. Simple alkenes, e.g., ethene or propene, are π-bound to zirconium. This possibility was also tested for acrylic acid. If a complex of a π-bound acrylic acid and dicyclopentadienylmethylzirconium is chosen as the starting point of a calculation without geometry restraints, then the energy minimization procedure leads to a complex where acrylic acid is bound via the oxygen atom of the carbonyl group. These calculations demonstrate that the preferred complex of acrylate with zirconium is that in which the carbonyl oxygen atom is attached to zirconium.

The "Neutral" Mononuclear Mechanism. Collins originally proposed the cationic zirconium−enolate complex **9** (Figure 1) as the reactive catalyst.[2a] In subsequent, very detailed studies, he reached the conclusion that a neutral zirconocene−enolate and a cationic zirconocene−acrylate complex were involved at the same time (Scheme 1).[2b,c] In the course of this development a neutral zirconocene−enolate complex also was discussed as the single active species. The catalytically active species is prepared by reacting dicyclopentadienyldimethylzirconocene (**1**) or derivatives thereof, preferably with $Ph_3C^+B(C_6F_5)_4^-$, which leads to dealkylation of **1** and formation of **2**. Complex **2** is transformed to a neutral enolate complex, analogous to **7** or **8**, from which the polymerization is believed to start.

When the approach of methyl acrylate (MA) to complex **7b** is considered, four possibilities exist, all of which were analyzed computationally (**14**−**17**). MA may interact in a syn- or antiperiplanar arrangement of the CO and CC double bonds, and for each conformation there exist two arrangements which correspond to a rotation of the MA molecule by 180°. A priori, it is not possible to decide which of the four approaches leads to the lowest activation energy for CC coupling and might, therefore, be responsible for the polymerization. The mode of approach also determines the tacticity in methyl methacrylate (MMA) polymerizations based on a mononuclear catalytic cycle.

The approximate energies of activation of CC bond formation for the four cases were determined by assuming that in the transition structure the separation of the carbon atoms which form the new bond is 220 pm. This distance is the result of a reaction coordinate calculation for the CC bond forming step between dicyclopentadienylmethylzirconiumenolate and acrylic acid (entry 6 of Table 2) and is used in all cases where a neutral zirconocene complex serves as the catalytically active species. As will be shown below such a choice is very reasonable. Keeping this distance fixed, all other degrees of freedom were optimized, which led to the four approximate transition states **14**−**17**. Among these structures **16** and **17**, resulting from the antiperiplanar conformation of MA, are higher in energy than **14** and **15**. With regard to the approximations made, it has to be concluded that the activation energies of CC bond formation in arrangements **14** and **15** are roughly identical.



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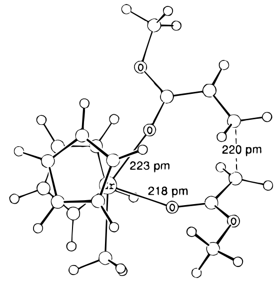

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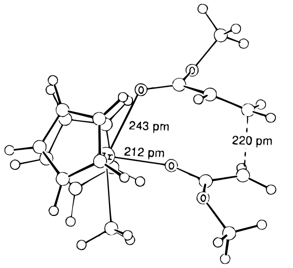

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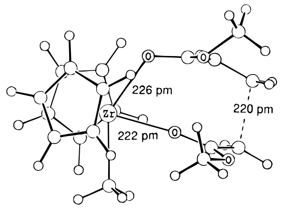

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Catalytic cycles involving **14** and **15** were selected for more detailed calculations. The modeling was started from the neutral zirconocene−enolate complex [$Cp_2Zr(OC(OCH_3){=}CH_2)(CH_3)$] (**7b**). The approach of determining the activation energy for polymerization of MA was identical to the previous calculation for the cationic zirconium−enolate complex (Figure 1). Thus, a monomer molecule of methyl acrylate was complexed to **7b**, which leads to an energy gain of −11.5 kcal mol^{-1} (**18**) (Table 2, entry 4, Figure 2). The carbonyl oxygen atom of the incoming acrylic acid remains at a distance of 389 pm from zirconium. Structure **18** should, therefore, be stabilized by dipole−dipole interactions and not by covalent bonding. This type of complex formation is frequently found in calculations and results from the isolated molecule approach not taking into account solvation effects. As in nucleophilic substitutions by the S_N2 mechanism this type of complex will not exist in solution.[13] The situation is quite different from structure **10** (Figure 1) where the carbonyl oxygen atom of the incoming acrylic acid binds at a distance of 215 pm, characteristic for covalent interactions. The oxygen(enolate)−Zr distances in structures **10** and **18** are very similar (196−197 pm). The approximate transition structure is **14**, from where reaction product **19** is formed, liberating −34.6 kcal mol^{-1}. Transition structure **14** is characterized by two slightly different Zr−oxygen bonds, 225 pm for the incoming acrylicacid ester and 219 pm for the enolate, thus the two molecules still retain their identity in the TS. In **19** the situation is reversed, enolate and ester are interconverted, leading to Zr−O distances of 210 and 233 pm, respectively. For this catalytic cycle the activation energy is 3.1 kcal mol^{-1} higher than for the cationic case above. The main difference between both catalytic cycles consists of the final step of the propagation reaction sequence, i.e., the scission of the CO−Zr bond leading to the new carboxy group. In contrast to the previous cycle (Figure 1), no activation barrier could be located; the methoxycarbonyl group is more or less expelled from the eight-membered ring complex with an exothermicity of 3.9−9.3 kcal mol^{-1}. No assistance of acrylate is required for this step.

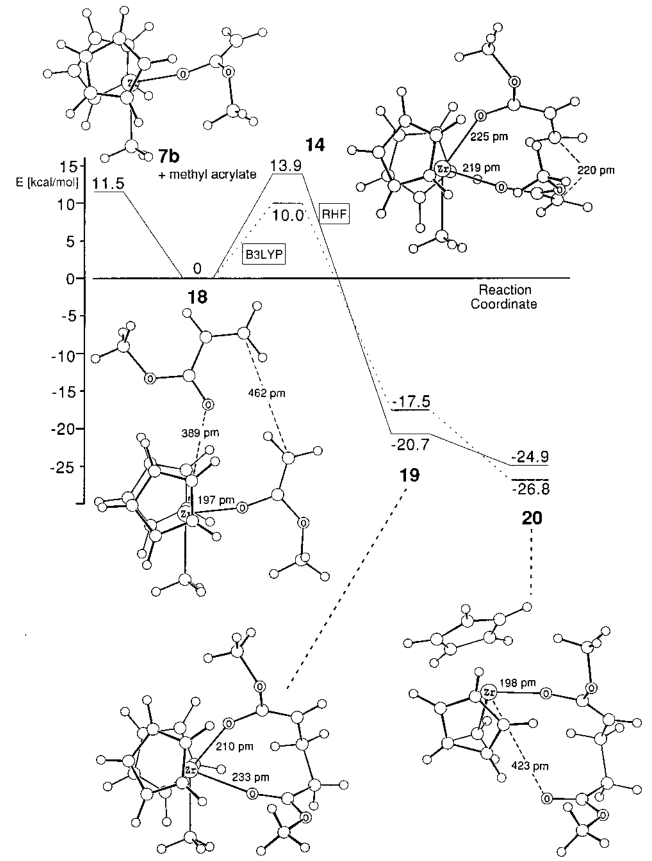
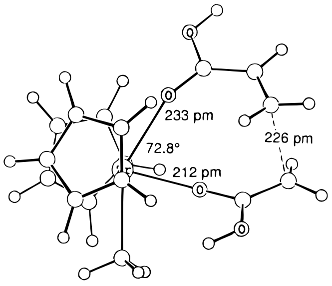


Figure 2. Reaction coordinate (kcal mol^{-1}) of a catalytic cycle for polymerization of methyl acrylate based on the neutral metallocene complex [$Cp_2Zr(CH_3)(OC(OCH_3){=}CH_2)$]. Full lines: RHF/3-21G results. Broken lines: B3LYP/6-31G*-ECP(S)//3-21G results.

If complex **15** instead of **14** is chosen as starting point for a reaction coordinate calculation, comparable results are obtained (Table 2, entry 5). Similarly, calculations starting from **7a** (entry 6) or **7b** (entry 7) and acrylic acid as monomer lead to similar conclusions. Thus the results are consistent and do not depend on the replacement of methyl groups by hydrogen.

The question arises as to how close the approximate structures are to fully characterized TS. To check this, a prototypal complete transition structure search was performed on **7a** plus acrylic acid (RHF/3-21G). A fully characterized first-order TS (**21**) could be located. In TS **21** the separation of the reacting atoms is 226 pm, very close to the separation of 220 pm obtained for the energy maximum in the reaction coordinate calculation. The two Zr−oxygen bonds remain different, 233 and 212 pm, respectively. The activation energy for CC coupling is 15.4 kcal mol^{-1} as compared to 16.0 kcal mol^{-1} from the reaction coordinate calculation (entry 6 in Table 2). The test calculation demonstrates that our approach of calculating reaction coordinates leads to reliable results concerning structure and energies of the transition states. Formulas **22** and **23** display the molecular orbitals which describe the zirconium−oxygen bonds, both being of similar nature involving mainly zirconium p-orbitals and oxygen s-orbitals. These interactions explain the approximate 90° angle between the two oxygen atoms and zirconium. The effect of zero-point vibrational energy (ZPVE) corrections can be elucidated in this case. The ΔZPVE values in Table 2 (energies relative to the initial complex (0.0 kcal mol^{-1})) show that the activation energy is raised by ca. 1 kcal mol^{-1}, and the metallacycle and the enolate are respectively destabilized by ca. 3 kcal mol^{-1}. Assuming that similar corrections hold for all the other examples where the TS structures are only approximate, it can be stated that these corrections will not alter the general conclusions regarding the catalytic cycles.



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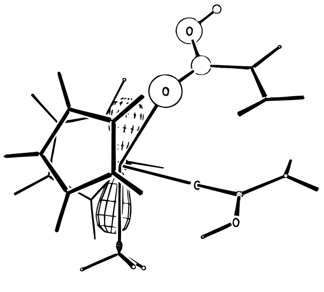

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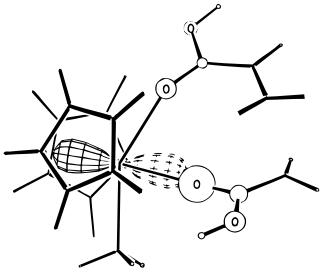


23

The effect of groups other than methyl as the ligand at zirconium on the polymerization of acrylates was studied briefly. Entries 11 and 12 in Table 2 describe the influence of a chlorine atom. A decrease of 4 or 5 kcal mol^{-1} in the approximate activation energy is found. Thus, chlorine substitution should be favorable for acrylate polymerization.

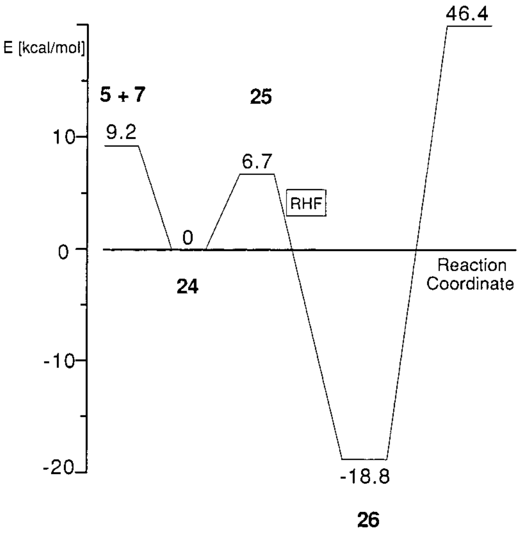
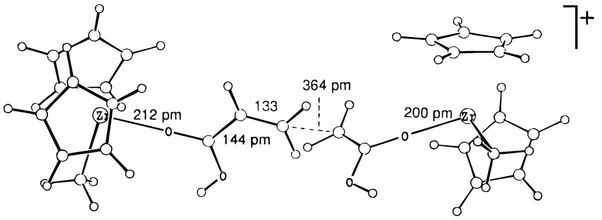


Figure 3. Reaction coordinate (kcal mol^{-1}) of a catalytic cycle for metallocene polymerization of acrylates based on a mechanism involving both a neutral and a cationic zirconocene complex (RHF/3-21G results).

The Binuclear Mechanism. Collins provided evidence that the polymerization of acrylates occurs most easily via a bimetallic reaction involving a neutral zirconocene−enolate complex and a cationic complex $[Cp_2Zr(CH_3)(acrylate)]^+$ (Scheme 1).[2b,2c] Thus, the enolate and acrylate moieties which are coupled are not attached to the same zirconium center. It is assumed that the association of methyl acrylate to the cationic $[Cp_2Zr(CH_3)]^+$ complex (**2**) activates the monomer even stronger than if it is bound to a $[Cp_2Zr(CH_3)(enolate)]$ complex (**7**/**8**). If the energy gain on complexing acrylic acid to $[Cp_2ZrCH_3]^+$ to yield **5** (−59.9 kcal mol^{-1}) or complexing methyl acrylate to $[Cp_2Zr(CH_3)(O(OCH_3)C{=}CH_2)]$ to give **18** (−11.5 kcal mol^{-1}), respectively, is taken as a measure for this activation, then Collins' proposal should indeed be correct. More important, however, might be the activating effect of $[Cp_2ZrCH_3]^+$ (**2**) as a Lewis acid on the π-system of acrylic acid, which should lower the HOMO and the LUMO of the CC double bond and prepare it for a stronger interaction with the HOMO of the C=C double bond of the zirconium−enolate complex. The structure of the HOMO, which is confined to the acrylate subunit, and the energy (−8.41 eV) according to the RHF/3-21G calculation are indicated in formula **7a**. The RHF/3-21G calculated HOMO and LUMO energies of the π system of acrylic acid are −10.91 and +2.89 eV. On formation of **5,** these energies change to −15.11 and −2.07 eV. Thus, the energy of both molecular orbitals is lowered, the LUMO energy by almost 5 eV. This has to be compared with the LUMO energy of +2.07 eV for the C=C bond of acrylic acid attached to $[Cp_2Zr(O(OH)C{=}CH_2)(CH_3)]$. On formation of ($[Cp_2Zr(O(OH)C{=}CH_2)(CH_3)(OC(OH)C{-}CH{=}CH_2)]$), the HOMO energy of the C=C− double bond of the enolate moiety is raised from −8.41 to −7.71 eV. From these numbers HOMO−LUMO gaps (according to the frontier molecular orbital model measures for the extent of interaction of the reaction partners, and, hence, their reactivity), of 6.34 eV (−8.41 − (−2.07)) for the binuclear mechanism and of 9.78 eV (−7.71 − (+2.07)) for the neutral mononuclear one are calculated. This is a clear indication that acrylic acid is more strongly activated by complex formation with $[Cp_2ZrCH_3]^+$ (**5**) than with $[Cp_2ZrCH_3(enolate)]$.

When the mononuclear complexes **5** and **7a** are brought together, a molecular complex (**24**) is formed which is −9.2 kcal mol^{-1} lower in energy than the components. The geometry of **24** is such that the reacting C atoms are still 364 pm apart. When the CC bond is closed, a maximum in energy is reached at a distance of 230 pm (**25**); the energy of this approximate transition state is 6.7 kcal mol^{-1} above that of the precomplex **24**. Notably, the activation energy for CC bond formation is indeed the lowest for the three mechanisms considered. Transition structure **25** collapses to **26** as the most stable compound. The former enolate moiety again develops into a carboxy compound and the carboxy group of acrylic acid becomes the new enolate. This is reflected by the corresponding Zr−oxygen bond distances which are 200 and 213 pm, respectively. The critical point of this mechanism is the scission of the zirconium−oxygen (carbonyl) bond of the carboxy group which is generated on closing the new CC bond. As this is the inverse process of complexing an acrylic acid molecule to $[Cp_2Zr(CH_3)]^+$, it is not surprising that this reaction requires an energy of +65.2 kcal mol^{-1}. Figure 3 displays schematically the corresponding reaction coordinate.



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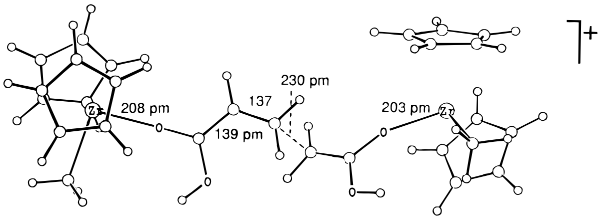

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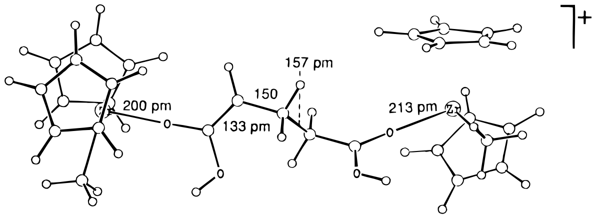

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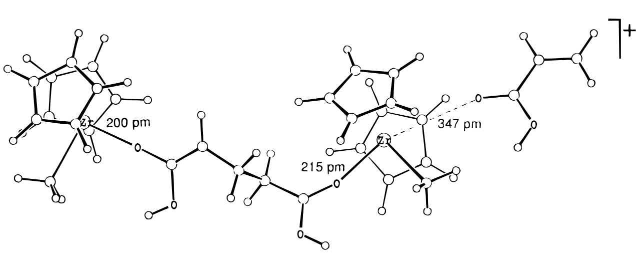

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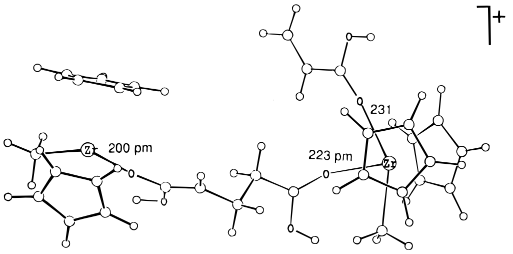

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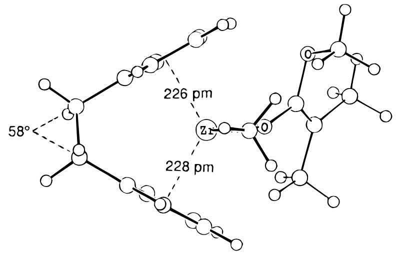
An unassisted separation of $[Cp_2Zr(CH_3)]^+$ (**2**) from **26** is therefore energetically not feasible. The most attractive solution to this problem seems to be the assistance of a monomer in the separation process. This may be described as a bimolecular substitution process. The substitution process may proceed by one of several different pathways. Two of these were investigated computationally, a backside (**27**) and a front-side (**28**) attack of acrylic acid on the carboxy-complexed $[Cp_2Zr(CH_3)]^+$ unit of **26**. Backside attack leads first to complex **27**, lying energetically 7.8 kcal mol^{-1} below **26**. The separation of **27** into $[Cp_2Zr(CH_3)OC(OH){=}CHR]$, where R represents the growing polymer chain with a carboxy end group, and $[Cp_2Zr(CH_3)O{=}C(OH)CH{=}CH_2]^+$ requires only 13.1 kcal mol^{-1} instead of the 65.2 kcal mol^{-1} for separation into $[Cp_2Zr(CH_3)O(OH)C{=}CHR]$ and $[Cp_2ZrCH_3]^+$. Front-side attack leads to **28**, where the carbonyl oxygen−zirconium bond is 231 pm, i.e., slightly longer than the second carbonyl oxygen−zirconium distance of 223 pm. Splitting this complex into $[Cp_2Zr(CH_3)(O(OH)C{=}CHR]$, R again representing the growing polymer chain, and $[Cp_2Zr(CH_3)(OC(OH)CH{=}CH_2)]^+$ requires 18.3 kcal mol^{-1}. This would mean that for the substitution process backside attack is more favorable than front-side attack.

An attempt was made to calculate approximate reaction coordinates for the front-side and backside substitution processes using a complex as a model that is analogous to **5** but with OCH_3 instead of OH. Backside attack of the carbonyl oxygen atom of methyl acrylate on this complex leads to a molecular complex stabilized by −13.4 kcal mol^{-1} relative to the energy of the components and displaying an oxygen−zirconium distance of 440 pm. This compound further converts to a symmetrical structure, similar to **6b** (OCH_3 instead of OH, with Zr−O distances of 231 pm) which lies −6.0 kcal mol^{-1} below the energy of the components but +7.4 kcal mol^{-1} above the primary complex. In contrast to common S_N2 reactions, this structure is a minimum on the potential energy surface and not a TS. Dissociation of this complex follows the reverse pathway leading via the molecular complex to the separated molecules. Assuming that the primary complex is a isolated molecule (“gas phase”) phenomenon which does not exist in solution and presuming that the energy barrier for substitution does not involve any appreciable activation energy, the 6.0 kcal mol^{-1} would correspond to the required activation energy of substitution. The second process considered for the separation into the fragments considers a front-side attack of methyl acrylate on a complex that is analogous to **5** but with OCH_3 instead of OH, leading to a structure similar to **6a** (OCH_3 instead of OH). No primary complex is found. This complex is −9.5 kcal mol^{-1} lower in energy than the reactants. As the reverse process requires at least 9.5 kcal mol^{-1} for the separation in the products, assuming as in the previous case no additional activation energy, this front-side substitution process requires 3.5 kcal mol^{-1} more energy than the backside attack. All attempts to locate transition structures for the association or dissociation processes failed. Summarizing, it can be stated that the substitution processes lead to the conclusion that backside attack is likely to be favored over front-side attack.

Effect of Bridging of the Cyclopentadienyl Units. When cyclopentadienyl or indenyl groups are connected by various bridges, the polymerization of methyl methacrylate becomes more feasible and the tacticity of the polymer is influenced. While we are not concerned with the aspect of tacticity, the influence of the connecting bridges is of concern. Some model calculations were performed where the ester−enolate of methyl methacrylate is attached to the dicyclopentadienyl methylzirconium cation **2**. A methano bridge, a silano bridge, and an ethano bridge between two cyclopentadienyl units were considered, and their influence on the structure of the resulting complex was studied. Special attention was paid to the influence of the bridging on the angle between the cyclopentadienyl rings and the position of the zirconium atom relative to the center of the rings. In **29**, **30**, and **31** the structures of the complexes as obtained from 3-21G density functional theory calculations (B3LYP) are presented. The angle between the rings widens, changing from 50° in the nonbridged (**8**, B3LYP) to ca. 72° in the methano-bridged complex **31**. The zirconium ion is positioned at the intersection of the lines, starting at the center of the rings and being oriented perpendicular to the plane of the five-membered rings. The cyclopentadienyl−centroid distance does not vary significantly (227 ± 2 pm). If the angle between the rings widens, zirconium becomes more accessible, hence offering more space for incoming acrylate molecules by reduced steric hindrance. This, however, should be important only if a mononuclear mechanism is operating. In view of the fact that bridging of the cyclopentadienyl units will prohibit backside attack on a complex similar to **26** (with bridged Cp rings) and considering that polymerization is faster with bridged zirconium complexes as catalysts, it is tempting to postulate that polymerization in these cases occurs via mononuclear catalytic cycles.



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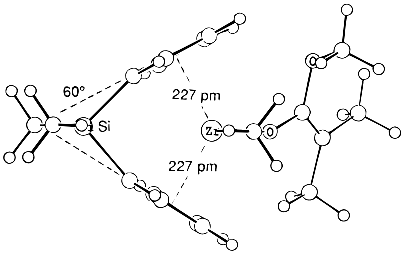

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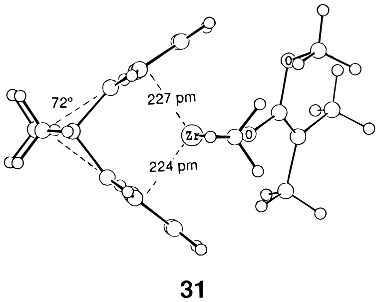

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RHF/3-21G reaction coordinates were determined for three cases. The cationic mechanism was tested for the SiH$_2$-bridged cyclopentadienyl rings. However, no change of the approximate activation energy was observed, compare entries one and eight in Table 2. The neutral mechanism, entries 9 and 10 in Table 2, seems to gain from bridging. With regard to the experimental observation of higher activity of bridged zirconocene derivatives, the calculated decrease of 3−4 kcal mol^{-1} in the activation energy by bridging the cyclopentadienyl rings indeed could be taken as argument that the neutral mechanism (mechanism 2 in Scheme 1) is followed experimentally.

Concluding Remarks

The comparison of organometallic structures determined by X-ray diffraction with those obtained by RHF/3-21G and B3LYP/3-21G density functional theory calculations showed very good agreement, indicating that the chosen basis set reproduces the metal organic situation properly. Transition structures determined by reaction coordinate calculations appear to be very good approximations to fully characterized transition states, as demonstrated in a case where a complete transition structure search was carried out. The computed activation energy differs only slightly from the approximate value, showing that the potential energy surface is rather flat in this region. B3LYP/3-21G and B3LYP/6-31G*-ECP(S) single-point calculations on stationary points and transition structures of the RHF/3-21G potential energy surface reduce the height of the activation barriers but do not lead to changes in the general conclusions.

Three possible catalytic cycles were calculated and shown to be realistic alternatives: The cationic mechanism (mechanism 1 in Scheme 1), originally favored by several groups,[2a−c] followed from mechanistic studies on the polymerization of simple alkenes by metallocene catalysts. A cationic species $[Cp_2Zr(OC(OR){=}CR_2)]^+$ is assumed to add an acrylate molecule which then reacts with an enolate (Scheme 1, Figure 1). The drawback of the cationic mechanism is the breaking of an oxygen−zirconium bond, a very energy-consuming process to start a new propagation step. It was shown that a slightly modified catalytic cycle starting with a second molecule of acrylic acid interacting with a zirconium enolate, which becomes the chain propagating molecule after scission of the zirconium−oxygen bond (entry 2 in Table 2), removes the disadvantage of the cycle of Figure 1.

The second catalytic cycle (mechanism 2 in Scheme 1), starting with a mononuclear, neutral zirconocene complex formed formally from $[Cp_2Zr(CH_3)]^+$ and an ester−enolate (Figure 2), yielded a slightly higher activation energy of CC coupling than the first cycle. In contrast to the cationic mechanism, the scission step, i.e., the separation of the newly generated carboxy group from zirconium, proved to be exothermic and did not require assistance by an acrylate molecule.

The third ("bimetallic") mechanism (mechanism 3 in Scheme 1) delineated from experiments by Collins' group[2b,2c] presumes that $[Cp_2Zr(OC(OR){=}CR_2)(CH_3)]$ reacts with $[Cp_2Zr(CH_3)(O{=}C(OR)CH{=}CH_2)]^+$. CC coupling via this mechanism requires the lowest activation energy of the three cases considered. A rationalization of the higher reactivity in terms of a Lewis acid function of $[Cp_2Zr(CH_3)]^+$ on methyl acrylate is provided. To be competitve with the other two catalytic cycles, the final step, that is the separation of $[Cp_2Zr(CH_3)]^+$ from the product complex, must be assisted by acrylate. Two possibilities, backside or front-side attack of the carbonyl oxygen of acrylate on the zirconium fragment were considered and found to be possible alternatives, although backside attack was slightly favored.

The influence of bridging by SiH_2, $(H_3C)_2C$, and C_2H_4 on the structure and the reactivity of the ester−enolate complex in polymerization was studied. A widening of the angle between the planes of the cyclopentadienyl units from 50 to about 70° is observed with the consequence that the metal center can be reached easier. Reaction coordinate calculations provided evidence that the neutral mononuclear mechanism profits from the increase in angle widening. Chlorine instead of methyl at zirconium seems to have an activating effect (Table 2, entries 11 and 12).

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Supporting Information Available: Tables of absolute energies of organometallic complexes and reference molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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