Mechanism of Ethene Trimerization at an *ansa*-(Arene)(cyclopentadienyl) Titanium Fragment

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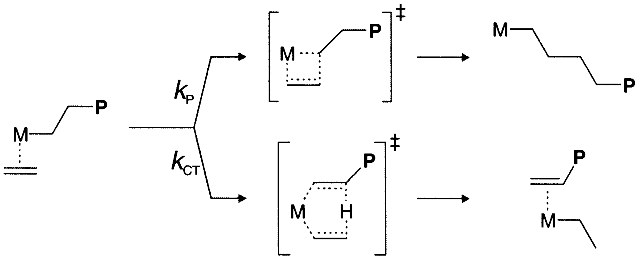
A theoretical study of ethene trimerization at a cationic ($C_6H_5CH_2C_5H_4$)Ti fragment generally supports the metallacycle mechanism proposed earlier for this reaction. However, the crucial formation of the 1-hexene complex from a titanacycloheptane intermediate occurs by direct $C_\beta \rightarrow C_{\alpha'}$ hydrogen transfer rather than by the more traditional β-elimination/reductive elimination sequence. The pendant arene moiety "breathes" during the reaction, being more strongly bound at the Ti^{II} stage than at the Ti^{IV} stage of the reaction. Its main role is to make the olefin complex formation more endothermic, thus increasing the barriers for formation of titanacyclopentane and titanacycloheptane intermediates. For the "naked" (C_5H_5)Ti system, which lacks this effect, further ring growth wins over hexene formation. But even for the bridged ($C_6H_5CH_2C_5H_4$)Ti system, we find that the various reactions are very delicately balanced.

Introduction

Ethene can be polymerized by a wide variety of catalysts, many of them based on early transition metals.[1] The polymerization invariably follows the standard Cossee−Arlman coordination−migratory insertion mechanism[2] for propagation. Chain transfer occurs by β-elimination or (more usually) by β-hydrogen transfer to monomer.[3]



By increasing the rate of chain transfer (k_{CT}) relative to that of propagation (k_P), selectivity can be shifted toward mixtures of ethene *oligomers*, with an average degree of polymerization close to k_P/k_{CT}; if chain transfer becomes very fast, the *dimer* 1-butene will be produced exclusively.[4] However, *selective* conversion into a single higher olefin other than butene cannot be achieved by the standard polymerization mechanism. Nevertheless, a limited number of catalysts, based on various metals, are known to trimerize ethene selectively to 1-hexene. Clearly, their catalysis follows a mechanism different from standard insertion polymerization; this mechanism is believed to involve metallacycle intermediates.[5] Most catalysts reported to date for this reaction are based on chromium.[6] Recently, new catalysts based on titanium[7] and tantalum[8] have been reported. Possible metallacycle intermediates have been isolated for a chromium system,[9] supporting the generally proposed mechanism. The titanium system ($C_6H_5CMe_2C_5H_4$)$TiCl_3$/MAO, discovered by Deckers and co-workers,[7] is one of the first examples of a well-defined catalyst, where the nature of the active species seems to be clear. Because of its structural analogy to a titanocene, one could expect this to be an ethene polymerization catalyst. In fact, it does form some polymer, but the main product upon exposure to ethene is the trimerization product, 1-hexene. The authors originally proposed the mechanism shown in Scheme 1 for the catalyst activation and trimerization steps,[7a] similar to the one proposed earlier for in situ hexene generation in a system lacking the pendant arene moiety.[7c]

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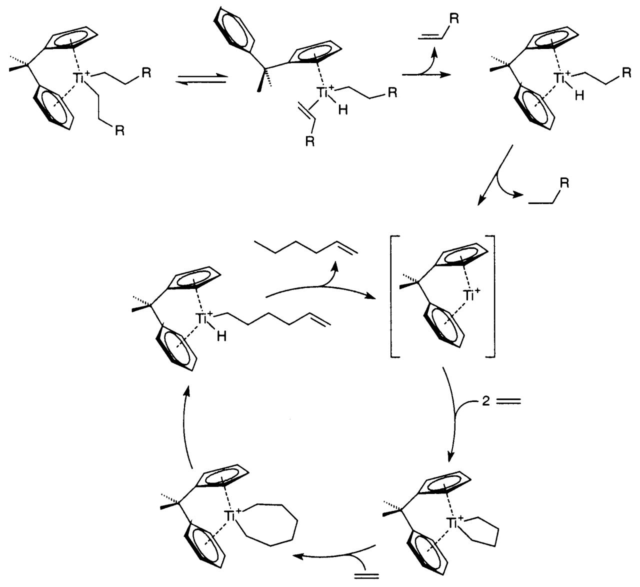
Scheme 1. Trimerization Cycle as Proposed by Deckers et al.[7a]



In this proposal, the catalyst precursor upon activation with MAO forms a cationic dimethyl complex in which the arene moiety of the ligand coordinates to the metal center.[10] The dimethyl complex can undergo multiple ethene insertions to produce bis(*n*-alkyl) compounds. These complexes supposedly are in equilibrium with alkyl-olefin-hydride species which would have the arene moiety detached. Displacement of the olefin by another ethene, which rapidly inserts into the M−H bond, would lead to the normal chain transfer process of catalytic ethene polymerization. However, the olefin can also be displaced by the pendant arene moiety to yield an alkyl-hydride complex, which can then undergo reductive elimination to give an alkane and a Ti^{II} species. This has been proposed as the key step for the switch from polymerization to trimerization. The Ti^{II} species then coordinates two molecules of ethene and couples them to give a titana(IV)cyclopentane. Migratory insertion of a third molecule of ethene results in the formation of a titana(IV)cycloheptane. This can undergo β-elimination and reductive elimination steps similar to the dialkyl species discussed above, now leading to 1-hexene formation. A mechanism like this can explain the high selectivity for 1-hexene formation, provided that the free energy barrier for ethene insertion into the titanacycloheptane is higher than the barrier for 1-hexene formation from the same species. Throughout this mechanism the hemilabile character of the arene-Cp ligand supposedly is the driving force of this particular reactivity.

We now have performed a detailed theoretical study to check the validity of this proposed mechanism. The model system chosen for this study, containing the $C_6H_5CH_2C_5H_4$ ligand, is not as efficient and selective at ethene trimerization as the CMe_2-bridged system, but should still be able to capture the essentials of the chemistry. Our findings confirm the general features of the catalytic cycle but differ significantly in its mechanistic details, particularly regarding the mode of formation of the Ti^{II} intermediate. After the initial submission of this work, a theoretical study by Yu and Houk appeared[21b] which analyzes trimerization at $TaCl_5$/MeLi[8] and reaches similar mechanistic conclusions.

Table 1. Final Relative Energies and Effective Barriers (kcal/mol) Calculated for Trimerization at $BzCpTiR_2^+$ and $CpTiR_2^+$

		system			
		BzCp (a)		Cp (b)	
$LTi(C_2H_4)$	**1**	0.00		0.00	
$LTi(C_2H_4)_2$	**2**	6.89		−1.62	
$LTi(C_2H_4{\cdots}C_2H_4)$ TS	**3**	15.43	15.43	7.06	8.68
$LTi(CH_2)_4$	**4**	1.48		−6.53	
$LTi(CH_2)_4(C_2H_4)$	**5**	16.44		−4.45	
$LTi(CH_2)_4{\cdots}C_2H_4$ TS	**6**	20.14	20.14	1.50	8.02
$LTi(CH_2)_6$	**7**	−4.11		−13.24	
$LTi(CH_2)_6$ transfer TS	**8**	15.38	19.49	8.05	21.29
LTi(hexene)	**9**	−8.25		−8.34	
$LTi(C_4H_7{\cdots}H)$ β-elim TS	**10**	24.97	24.97		
$LTi(H)(C_4H_7)$	**11**	23.91			
$LTi(H{\cdots}C_4H_7)$ red.elim TS	**12**	40.63	40.63		
LTi(butene)	**13**	−2.33			
$LTiEt_2$	**14**	15.54		3.05	
$LTi(Et{\cdots}H{\cdots}C_2H_4)$ TS	**15**	32.29	16.75	20.66	17.61
$LTi(C_2H_4)(C_2H_6)$	**16**			5.90	
$LTiEt_2(C_2H_4)$	**17**	28.99			
$LTi(Et)(Et{\cdots}C_2H_4)$ TS	**18**	32.91	17.37		

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Table 2. Corrections on Going from DZ/6-31G/6-31G Energies to Final Free Energies**

			basis set			ZPE+thermal		
	system		total	excl "BSSE"[a]	BSSE	total	excl C_2H_4/C_2H_6[b]	solvation
BzCp	$LTi(C_2H_4)$	**1a**	0.00	−0.87	0.00	0.00	0.00	0.00
	$LTi(C_2H_4)_2$	**2a**	4.86	0.58	2.95	11.31	1.36	2.91
	$LTi(C_2H_4\cdots C_2H_4)$ TS	**3a**	5.02	0.74	2.95	12.10	2.15	4.19
	$LTi(CH_2)_4$	**4a**	5.16	0.88	2.95	11.68	1.73	4.15
	$LTi(CH_2)_4(C_2H_4)$	**5a**	9.70	2.02	4.68	23.03	3.14	5.60
	$LTi(CH_2)_4\cdots C_2H_4$ TS	**6a**	7.46	−0.22	4.68	23.91	4.01	5.21
	$LTi(CH_2)_6$	**7a**	10.15	2.46	4.68	26.75	6.86	2.33
	$LTi(CH_2)_6$ transfer TS	**8a**	7.69	0.01	4.68	25.36	5.47	4.24
	LTi(hexene)	**9a**	8.16	0.48	4.68	26.14	6.25	2.21
	$LTi(C_4H_7\cdots H)$ β-elim TS	**10a**	4.72	0.44	2.95	10.25	0.30	3.42
	$LTi(H)(C_4H_7)$	**11a**	5.33	1.05	2.95	9.11	−0.84	4.27
	$LTi(H\cdots C_4H_7)$ redelim TS	**12a**	5.25	0.97	2.95	9.96	0.01	3.30
	LTi(butene)	**13a**	3.45	−0.83	2.95	13.21	3.27	2.49
	$LTiEt_2$	**14a**	2.47	−1.80		9.73	−1.25	5.78
	$LTi(Et\cdots H\cdots C_2H_4)$ TS	**15a**	3.99	−0.29		9.18	−1.80	2.79
	$LTiEt_2(C_2H_4)$	**17a**	5.19	−2.49	1.69	20.20	−0.72	7.54
	$LTi(Et)(Et..C_2H_4)$ TS	**18a**	4.55	−3.13	1.69	19.95	−0.97	6.34
Cp	$LTi(C_2H_4)$	**1b**	0.00	1.46	0.00	0.00	0.00	0.00
	$LTi(C_2H_4)_2$	**2b**	2.76	0.24	3.50	11.54	1.59	5.93
	$LTi(C_2H_4\cdots C_2H_4)$ TS	**3b**	3.00	0.47	3.50	12.43	2.48	6.95
	$LTi(CH_2)_4$	**4b**	3.02	0.49	3.50	13.32	3.37	6.32
	$LTi(CH_2)_4(C_2H_4)$	**5b**	6.56	0.04	5.09	24.97	5.08	10.32
	$LTi(CH_2)_4\cdots C_2H_4$ TS	**6b**	6.27	−0.25	5.09	25.54	5.65	10.28
	$LTi(CH_2)_6$	**7b**	6.46	−0.06	5.09	28.64	8.74	8.93
	$LTi(CH_2)_6$ transfer TS	**8b**	7.32	0.81	5.09	27.66	7.77	8.59
	LTi(hexene)	**9b**	7.42	0.91	5.09	28.86	8.97	8.59
	$LTiEt_2$	**14b**	1.42	−1.11		11.45	0.47	9.69
	$LTi(Et\cdots H\cdots C_2H_4)$ TS	**15b**	1.23	−1.30		10.98	0.00	9.33
	$LTi(C_2H_4)(C_2H_6)$	**16b**	0.82	−1.71		12.67	1.69	9.98

[a] Contribution per ethene/ethane estimated by linear regression. [b] Excluding the ethene/ethane translational entropy component.

Computational Details

Structures were optimized at the B3LYP[11] level of theory with SV 6-31G (ligand), SV 6-31G** (reactive part), and DZ (Ti) basis sets.[12−14] Minima were optimized with the GAMESS-UK package,[15] and transition states were located with the Gaussian98 suite.[16] All optimizations were performed without imposing any constraints. All minima and transition states were checked by a frequency analysis within the same basis set. Thermochemical analysis was performed at 5 bar pressure and a temperature of 303.15 K, corresponding to the actual reaction conditions of the experiments by Deckers and co-workers; for all cationic species and free hexene and butene, the translation component of the entropy was deleted to approximate the effect of having these species in solution rather than in the gas phase.[17] More accurate energies, BSSE corrections, and solvent corrections were calculated in a larger basis set (TZV 6-311G**[18] on all atoms). The BSSE corrections were obtained following the counterpoise procedure.[19] Solvent corrections were done with the CPCM continuum model[20] with toluene solvent (energies for ethene and ethane, which were calculated for the gas phase, were not corrected for solvent effects[17]). Table 1 lists the final relative free energies for all species relevant to initiation and trimerization; the individual corrections used to arrive at these numbers are listed in Table 2 and are discussed in more detail in the text.

Results

The Trimerization Cycle. The basic properties of the mechanism presented in Scheme 1 are supported by our computational study. Figure 1 shows the calculated energy diagram for our more detailed version of the trimerization cycle. Starting from a Ti^{II} monoethene complex, coordination of the second ethene unit and formation of a titana(IV)cyclopentane has a barrier of about 15 kcal/mol. Coordination and insertion of the next ethene molecule, to give a titana(IV)cycloheptane, is slightly more difficult, with a calculated barrier of about 20 kcal/mol. This last complex shows a notable β-agostic interaction, placing a hydrogen atom in an ideal position for β-elimination. However, the last and crucial step of 1-hexene formation does not involve a discrete olefin hydride complex. Instead, we find a *direct* hydrogen transfer from C_β to $C_{\alpha'}$ with a free energy barrier that is about 19 kcal/mol.[21] All of these barriers are compatible with a reaction that is fast at room temperature. Figure 2 shows the calculated geometries for the reactant, transition state, and product of the hydrogen transfer step. The transition state for this reaction shows a near-linear C···H···C configuration reminiscent of transition states in σ-bond metathesis reactions.[22] The finding of such a direct transfer step has significant consequences:

(a) In the two-step mechanism one could expect ethene insertion in the alkyl-hydride species to compete with hexene formation, leading not only to longer-chain oligomers or polymers but also to diolefin and alkane byproducts; in the direct transfer mechanism one would not expect such complications.

(b) Hexenyl derivatives such as the one proposed in the two-step mechanism tend to cyclize to cyclohexyl or cyclopentylmethyl species.[23] Again, this complication would not be expected in the direct-transfer mechanism, since no hexenyls are ever formed.

Formation of the Trimerization Catalyst. If elimination of 1-hexene from the titanacycloheptane involves direct $C_\beta \rightarrow C_{\alpha'}$ hydrogen transfer, it stands to reason that formation of a Ti^{II} olefin complex from a Ti^{IV} dialkyl

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(23) See e.g.: Perch, N. S.; Widenhoefer, R. A. *Organometallics* **2001**, *20*, 5251.

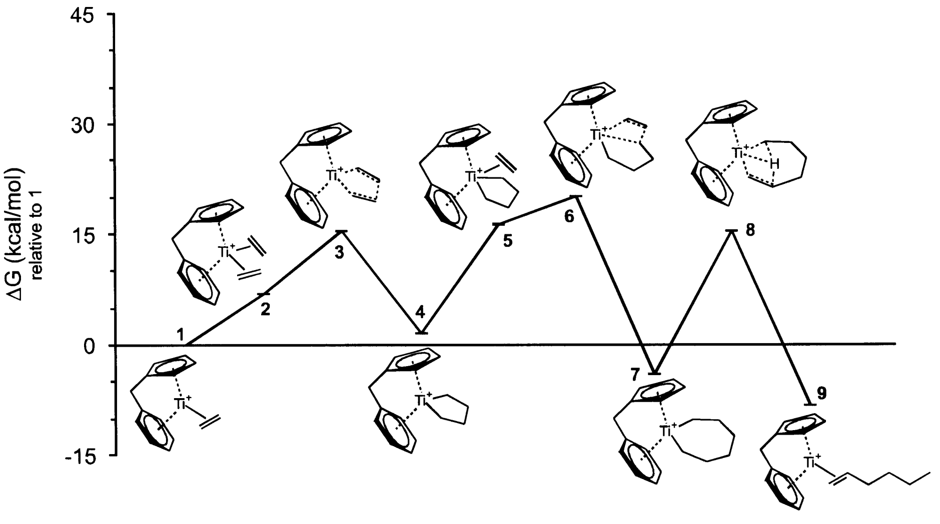

Figure 1. Calculated energy diagram for trimerization.

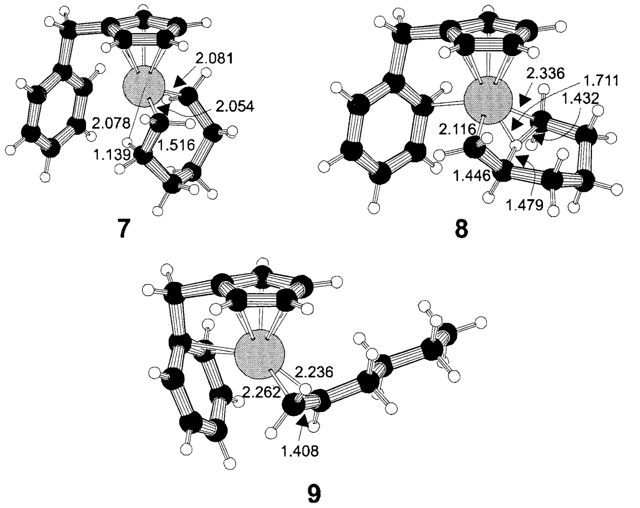

Figure 2. Calculated geometries of (**7**) titanacycloheptane, (**8**) H transfer TS, and (**9**) 1-hexene complex.

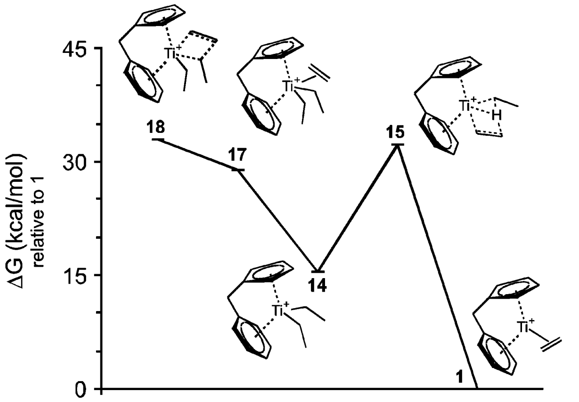

Figure 3. Calculated energy diagram for competing hydrogen transfer and olefin insertion in $(C_6H_5CH_2C_5H_4)TiEt_2^+$.

can also proceed via this route. Indeed, we find that the lowest-energy path for formation of a Ti^{II} ethene complex from a Ti^{IV} diethyl proceeds via this direct transfer mechanism (see Figure 3).[21] The calculated barrier is ca. 3 kcal/mol lower than that found for the direct transfer in the titanacycloheptane, demonstrating that the presence of the seven-membered ring imposes some steric constraints on this reaction. $C_\beta \rightarrow C_{\alpha'}$ transfer wins over olefin insertion in the Ti−Et bond of $LTiEt_2^+$, but only barely (by ca. 1 kcal/mol in our results). Thus, it might be that some oligomer or polymer is formed before the catalyst enters the trimerization cycle. However, once the catalyst has entered the cycle, it is more likely to stay there, as argued below.

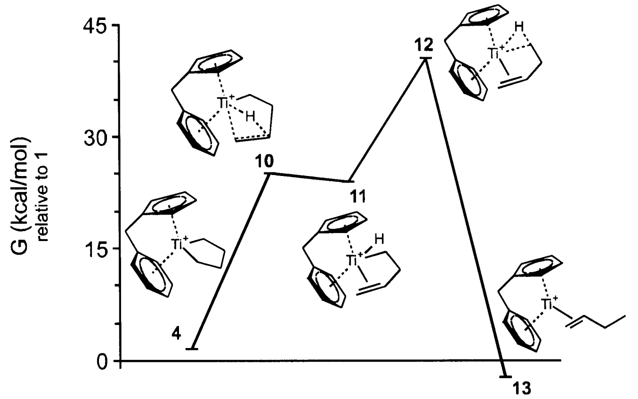

Figure 4. Calculated energy diagram for two-step formation of 1-butene.

Derat et al.[21a] recently concluded from a theoretical study of the decomposition of $(n\text{-Bu})_2ZrCl_2$ that also in that case direct $C_\beta \rightarrow C_{\alpha'}$ hydrogen transfer is the lowest-energy pathway for alkane elimination. Their calculated transition states show the same near-linear C···H···C as our structures **8** and **15**. Similarly, Houk proposed hydrogen transfer from a propyl to a methyl group as a (model for) generation of the active species in Ta-catalyzed trimerization.[21b]

Trimerization versus Dimerization. The preference for trimerization over dimerization can be explained on the basis of the very high reaction barrier for 1-butene elimination from the titanacyclopentane. Whereas the titanacycloheptane undergoes direct $C_\beta \rightarrow C_{\alpha'}$ hydrogen transfer through a transition state with a near-linear C···H···C arrangement, the titanacyclopentane eliminates 1-butene via a two-step pathway (as shown in Figure 4) due to the geometrical constraints of the five-membered ring. First a β-hydride is transferred to the metal to give a discrete Ti^{IV} butenyl-hydride complex with internal coordination of the butenyl double bond. In the second step, this complex undergoes reductive elimination to a Ti^{II} butene complex. The free energy barrier for the β-elimination step is high (24 kcal/mol), and this step is strongly endothermic (22 kcal/mol). The subsequent 1-butene reductive elimination also has a significant barrier (17 kcal/mol), so that the effective barrier for 1-butene formation amounts to 41 kcal/mol (energy difference between **1** and **12**). Clearly, this reaction cannot compete with titanacycloheptane formation. In practice, one would never expect 1-butene to be formed following this path. Even if the butenyl-hydride were formed, then rather than going through the high-energy elimination transition state it would rapidly bind and insert ethene, leading to a Ti^{IV} ethyl-butenyl species. This could then undergo chain growth and/or $C_\beta \rightarrow C_{\alpha'}$ transfer like the Ti^{IV} dialkyls discussed above, which would lead to alkanes and diolefins as byproducts. The fact that these have not been observed experimentally demonstrates that even this first step on the dimerization path, β-elimination from titanacyclopentane **4**, does not occur.

These results also illustrate why the two-step mechanism will not be followed for hexene formation. It might be that β-elimination from metallacycle **7** would be easier than from **4**. However, since the β-elimination is strongly endothermic, the effective barrier for 1-butene formation is the energy difference between **1** and **12**. For the C_6 system the corresponding difference should be very similar and, therefore, much too high to compete with either olefin insertion or $C_\beta \rightarrow C_{\alpha'}$ hydrogen transfer.

Trimerization versus Further Growth of the Seven-Membered Ring. If one accepts the steps presented here for formation of hexene from ethene, what is to prevent the titanacycloheptane intermediate from inserting further ethene monomers and producing tetramers, pentamers, etc.? To answer this question, we would have to calculate the insertion barrier for ethene in the metallacycle. Unfortunately, this is a very flexible system, and even if we found a transition state, it would be hard to make sure we have the lowest one. However, the following arguments make it plausible that further growth of the metallacycle is not likely:

1. For the $TiEt_2$ precursor, insertion is already slightly *disfavored* over $C_\beta \rightarrow C_{\alpha'}$ transfer. The transfer reaction is a bit more difficult in the metallacycloheptane due to steric constraints, but this would also be expected for insertion. Thus, one could already expect elimination to be slightly favored over further insertion for the metallacycle.

2. Transfer should be slightly more favorable (relative to insertion) for a longer chain or a metallacycle than for an ethyl group, since a more stable substituted olefin is produced. Normally, this contributes about 2–3 kcal/mol to barrier differences.

3. Further growth would result in a nine-membered ring, which is the least favorable medium-sized ring.[24] It should be disfavored relative to the seven-membered ring by about 6–7 kcal/mol, which means that at the transition state one would already expect a contribution of ca. 3 kcal/mol. Indeed, Houk found that in the simpler $TaCl_3$ system insertion in the seven-membered ring is also more difficult than in the five-membered ring.[21b] This also means that, *if* a nine-membered ring were formed, it would be more likely to grow to an 11- or 13-membered ring: the decrease in ring strain on further growth of the ring would favor insertion over elimination. In other words, one would never expect much octene, but formation of some (linear) decene or dodecene would be more reasonable.[25]

Thus, the catalyst is most likely to eliminate an olefin at the titanacycloheptane stage.

Role of the Arene Moiety. In all calculated structures, the arene ring is relatively weakly bound to the metal ion. This is true in particular for all Ti^{IV} species, where the metal–ring distances are so large that it is not immediately clear whether the ring should really be considered as coordinating to the metal center at all.[26] To assess the importance of the metal–ring interaction, we have also studied the complete catalytic cycle for a model lacking the pendant arene. In the remainder of the paper, **1a**, **2a**, etc., indicate species having the pendant arene, which is lacking in the corresponding species **1b**, **2b**, ...

Qualitatively, the results are similar to those obtained for the arene-containing catalyst. The main difference is that all olefin binding energies are higher by ca. 10–15 kcal/mol (e.g., **1a** → **2a** $\Delta G = +7$ kcal/mol, **1b** → **2b** -2 kcal/mol; **4a** → **5a** $+15$ kcal/mol, **4b** → **5b** $+2$ kcal/mol). Because of this, the effective barriers for formation of the five- and seven-membered rings are much lower than for the arene-containing system, but the barrier for hexene elimination is nearly the same. Hence, the naked system should not stop at a seven-membered ring but give a polymer. Moreover, the naked Ti dialkyl cation would not even enter the trimerization cycle because also there insertion wins over $C_\beta \rightarrow C_{\alpha'}$ transfer. Finally, the $C_\beta \rightarrow C_{\alpha'}$ transfer is always *endothermic* in the system lacking the pendant arene. This agrees with the observation by Derat[21a] that donor molecules (ether or phosphine) are required to make the transfer in $(n\text{-Bu})_2ZrCl_2$ exothermic. Thus, the arene moiety, despite its large distance to the metal, exerts a significant influence on the chemistry at the metal center and should be considered bound to the metal. It also agrees with experiment in the sense that half-sandwich complexes lacking a pendant arene produce mainly polymer and only a little hexene, which is incorporated into the polymer.[7c]

Of course, the above comparison is not quite fair, in the sense that there would never be a "real" catalyst as open as the naked model mentioned above. Instead, a Ti catalyst lacking the pendant arene would grab a solvent molecule (usually an arene[26c]) or one or more additional ethene molecules to relieve its coordinative unsaturation. Thus, it is perhaps more relevant to the

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(24) See e.g.: Allinger, N. L.; Cava, M. P.; de Jongh, D. C.; Johnson, C. R.; Lebel, N. A.; Stevens, C. L. *Organic Chemistry*; Worth: New York, 1971; p 40.

(25) Comparison of this prediction with the experimental results[7b] is not straightforward. The $(C_6H_5CH_2C_5H_4)Ti$ catalyst produces about equal amounts of linear hexene and high-MW PE; whether the PE is (partly) produced by "$(C_6H_5CH_2C_5H_4)Ti^+$" or by a catalyst degradation product is not clear. Some C_{10} olefin is produced; this is mainly a hexene/ethene co-trimer. In addition, much smaller amounts of C_8, C_{12}, and higher olefins are produced, but again it is not clear whether these are formed at the same catalytic center as the trimer.

(26) NMR data clearly demonstrate that in $(C_6H_5CMe_2C_5H_4)TiR_2^+$ cations the arene moiety coordinates.[10] However, the only structural data that are available are for a Ti^{III} complex.[10b] See also: Deckers, P. J. W.; Hessen, B. *Organometallics* **2002**, *21*, 5564.

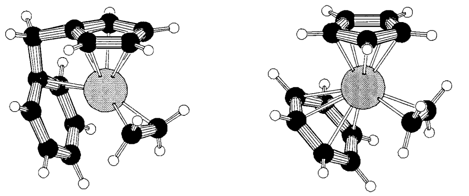
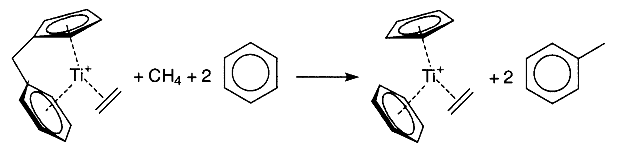
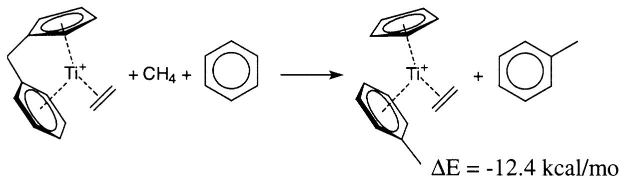


Figure 5. Calculated structures of $(C_6H_5CH_2C_5H_4)Ti(C_2H_4)^+$ and $(C_6H_6)(Cp)Ti(C_2H_4)^+$. The cutoff for drawing M−C bonds was arbitrarily set at 2.6 Å.

experiment to compare the intramolecular coordination of the arene in **1** to that of an external arene molecule. The following isodesmic equations can be used to compare the coordination energies of internal and external arenes:



ΔE = -9.2 kcal/mol



ΔE = -12.4 kcal/mol

From these equations, we calculate that coordination of free benzene is ca. 9 kcal/mol *stronger* than intramolecular coordination of the pendant arene. However, entropy will favor intramolecular coordination at room temperature, so that in arene solution at room temperature the free energies of intra- and intermolecularly coordinated states should be similar. The calculation also shows that toluene coordinates more strongly than benzene by ca. 3 kcal/mol.

The stronger *inter*molecular binding of arenes is understandable from the geometries of the two types of complexes. In Figure 5, they are compared at the stage of the monoethene complex. It is clear that a separate benzene molecule not only approaches the metal atom more closely but also prefers to be further away from the Cp ring, thus filling more of the space around the metal atom. In the case of the pendant arene, coordination of the ring can only be accommodated by a deformation of several bond angles of the ligand, and even if this happens, the arene moiety is forced to stay close to the Cp ring.

The difference in coordination geometries between intra- and intermolecularly coordinated arene may be germane to the catalytic activity of the complex. The reduced amount of space around the metal in the free arene complex will oppose further ethene coordination at every stage of the reaction. Thus, one would expect much lower reaction rates in the system not having a bridge between arene and cyclopentadienyl groups. Use of a C_2 instead of a C_1 bridge, which also reduces the available space around the metal, indeed leads to a dramatic drop in catalyst activity.[7b] It remains possible that in the reaction of Ti half-sandwich complexes with ethene in arene solvent, the resting state is a Ti-arene complex,[26c] while polymerization still occurs at a Ti center lacking the arene ligand.

Table 3. Metal−Ring Geometries for Calculated Structures

		M−ring plane	slippage
$LTi(C_2H_4)$	**1**	2.184	0.372
$LTi(C_2H_4)_2$	**2**	2.229	2.445
$LTi(C_2H_4\cdots C_2H_4)$ TS	**3**	2.255	2.339
$LTi(CH_2)_4$	**4**	2.409	2.287
$LTi(CH_2)_4(C_2H_4)$	**5**	3.023	2.620
$LTi(CH_2)_4\cdots C_2H_4$ TS	**6**	3.449	2.869
$LTi(CH_2)_6$	**7**	2.581	2.059
$LTi(CH_2)_6$ transfer TS	**8**	2.261	2.390
LTi(hexene)	**9**	2.214	0.433
$LTi(C_4H_7\cdots H)$ β-elim TS	**10**	2.431	2.235
$LTi(H)(C_4H_7)$	**11**	2.302	2.339
$LTi(H\cdots C_4H_7)$ red. elim TS	**12**	2.535	1.858
LTi(butene)	**13**	2.264	0.496
$LTiEt_2$	**14**	2.501	2.207
$LTi(Et\cdots H\cdots C_2H_4)$ TS	**15**	2.351	2.175
$LTiEt_2(C_2H_4)$	**17**	3.099	2.757
$LTi(Et)(Et..C_2H_4)$ TS	**18**	3.587	3.270

Table 4. Effect of Basis Set Expansion on the Activation Energy of the β-Hydrogen Transfer Step

basis set on: Ti/active/ligand	Δ*E*
LANL2DZ/3-21G/3-21G	17.7
LANL2DZ/6-31G/3-21G	19.9
LANL2DZ/6-31G/6-31G	27.8
3-21G/3-21G/3-21G	24.8
DZ/3-21G/3-21G	16.6
DZ/6-31G/6-31G	26.7
DZ/6-31G**/6-31G	25.1
6-31G/6-31G**/6-31G	25.9
6-31G**/6-31G**/6-31G	25.9
6-311G**/6-311G**/6-31G**	22.1
6-311G**/6-311G**/6-311G**	23.2

During the reaction, the pendant arene moiety of the *ansa* catalyst undergoes considerable movement. It is always coordinated in an asymmetric fashion, so that the shortest Ti−C distance is to one of the *ortho* carbons. Coordination is strongest at the Ti^{II} stage (in particular in the monoethene complex), but even then the metal−arene interaction is much weaker than the metal−Cp interaction. Table 3 lists the metal−ring geometric parameters for all species studied.

Theoretical Aspects: Going from DFT Energies to Solution-Phase Free Energies. A large number of factors have to be taken into account to convert DFT energies to free energies that can be related to experimental results, and we cannot yet handle all of them satisfactorily. In the present study, we have considered the following corrections (values for the individual corrections are collected in Table 2):

Basis Set Extension. Geometries were optimized at the DZ/SV6-31G**/SV6-31G level, but single-point energies were also obtained at the TZV6-311G** level to estimate the basis set dependence. In fact, the present system seems to be rather sensitive to basis set size and choice of pseudopotential. We have studied this aspect in more detail for the $C_\beta \rightarrow C_{\alpha'}$ transfer step, which appears to be the most sensitive one. Table 4 lists energies obtained from single-point calculations with different basis sets. The results suggest that from TZV6-311G** on the basis set dependence will be rather modest.

Comparing the basis set effects between our optimization level (DZ/SV6-31G**/SV6-31G) and the level used for the final energies (TZV6-311G**), we can see that the larger basis set systematically disfavors the larger molecules. This can be traced back to the lower BSSE in this basis. If the data are corrected for this, the remaining corrections are modest and do not show clear trends. Most barriers go up a little with the larger basis set; $LTiEt_2^+$, its ethene complex, and the insertion transition state are stabilized by ca. 2 kcal/mol.

Basis Set Superposition Error (BSSE). Ideally, BSSE should be taken into account in an integrated approach, to provide a correction to the potential energy surface *during* geometry optimization. However, no satisfactory procedures have yet been implemented for doing this. We calculated the BSSE at the olefin complex stage and then assumed that the error is constant from that point on. Since the correction is only ca. 2 kcal per molecule of ethene, the *error* in this correction should not be very large.

Zero-Point Energy and Thermal Corrections. DFT energies are routinely converted to gas-phase free energies using standard thermochemical analysis procedures. However, the present reactions do not occur in the gas phase but in solution. For ethene this is not a problem, since in the actual reaction dissolved ethene is in equilibrium with gas-phase ethene and hence has the same free energy. However, the charged metal-containing species cannot be considered to be in equilibrium with the gas phase at any reasonable pressure, so calculation of their free energies is nontrivial. As a zeroth-order approximation, we have taken the gas-phase free energy but excluded the translational component, which should be mostly quenched in solution. The dominant effect in the thermal corrections is due to the contributions of free, gaseous ethene and ethane (ca. 10 kcal/mol per free molecule of each). For all steps in which ethene is incorporated, this contribution dominates over the calculated barrier in determining the final free energy of activation. If the contribution is excluded, the remaining corrections (listed separately in Table 2) are small. The larger molecules are again systematically destabilized by a few kcal/mol, but most barriers change by less than 1 kcal/mol.

Solvent and Counterion. Including a discrete counterion in our calculations would not have been possible. Also, it is not clear whether an ion-pair model would provide a more reasonable description than an isolated cation. Therefore, we did not attempt to take any counterion into account. Solvent effects were included using the CPCM continuum solvation model. This should provide a reasonable description of solvated ions derived from the *ansa*(arene)(cyclopentadienyl) ligand; the “naked” system is discussed separately below. As expected, solvation corrections preferentially stabilize the more open species, in particular $LTi(C_2H_4)^+$. The larger molecules are again slightly disfavored. However, the influence on the individual reaction steps is small, typically 1−2 kcal/mol, which is not surprising given the low polarity of the solvent used (toluene) and the crowding around the small Ti atom. The most notable effect is on the $C_\beta \rightarrow C_{\alpha'}$ transfer in $LTiEt_2^+$, where solvation lowers the barrier by 3 kcal/mol; surprisingly, transfer in the metallacycloheptane is hardly affected by solvation.

For unsubstituted Cp derivatives in an arene solvent, the “real” system would undoubtedly have a discrete arene coordinated to the metal. Therefore, our studies on this system can be useful in modeling a hypothetical “naked” system and hence understanding the role of the pendant arene in the trimerization catalyst, but cannot be expected to reproduce the experimental results for the “real” Cp system without the arene moiety.

Conclusions

Our calculations support the metallacycle mechanism for ethene trimerization at a cationic *ansa*(arene)(cyclopentadienyl) titanium fragment. The main difference from earlier proposals is that, like Houk,[21b] we predict the crucial olefin elimination step to occur by a direct $C_\beta \rightarrow C_{\alpha'}$ hydrogen transfer rather than a two-step β-elimination/reductive elimination sequence. This could be the explanation for the absence of any products derived from insertion in the previously proposed (hydride)(alkyl) intermediate. The role of the pendant arene, compared with a “naked” system, is to reduce the olefin coordination energy and thus promote $C_\beta \rightarrow C_{\alpha'}$ transfer over further growth of the metallacycle. The difference between a pendant arene and an independent arene auxiliary ligand is the strong reduction of free space around Ti in the latter case.

The insertion and transfer steps of the present mechanism appear to be very delicately balanced. On the basis of our results, we predict that even small changes to the system can have a dramatic effect on the balance between trimerization, oligomerization, and polymerization. This seems to agree with the experimental observations: for example, just changing the bridge between the arene and cyclopentadienyl groups from CH_2 to CMe_2 already changes trimerization selectivity from 42 to 83%.[7b] In fact, the differences we calculate are small enough that we could not predict with any certainty, based on calculations only, that the system studied would indeed trimerize rather than oligomerize or polymerize. However, given that trimerization is observed, it seems very plausible that the mechanism we calculate is indeed the one followed experimentally.

Note Added after ASAP: One of the author names in reference 21b was incorrect in the version posted ASAP on 5/23/2003; it is correct in the version posted 6/5/2003, and in print.

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