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Is the Polymerization of Linear α-Olefins by Transition-Metal Carbene Complexes a Viable Process? A Theoretical Study Based on Density Functional Theory

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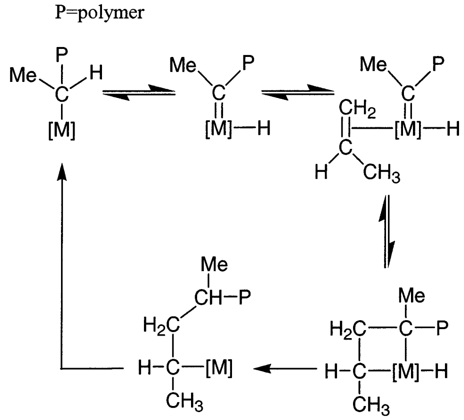
Gradient-corrected density functional theory has been used to study the mechanism of α-olefin polymerization catalyzed by transition-metal carbene complexes. Taking the $[CH_2{=}Re(NO)_2(PMe_3)]^+$ complex as an example, we investigated the possible elementary steps of the polyethylene formation. This "carbene-to-metallacycle" style mechanism based on a pure carbene intermediate starts with the coordination of the ethylene. Then ethylene reacts with the carbene complex by a [2 + 2] addition. Metallacyclobutane decomposition to a new carbene complex takes place by an α-hydrogen transfer reaction. We have also investigated the possible side reactions for the metallacyclobutane decomposition by metathesis reaction, cyclization, and β-hydride transfer reactions. Calculations have been performed on the monomer and carbene complexes, on the possible intermediates, ethylene π-complexes, metallacyclobutanes, cyclopropyl complexes, cyclopropyl hydride complexes, propylidene complexes, propene π-complexes, allyl−hydride intermediates, and transition states. The results show that when the $[CH_2{=}Re(NO)_2(PMe_3)]^+$ complex is used as a catalyst, the β-hydride transfer is both kinetically and thermodynamically favored over the α-hydride transfer reaction; therefore, ethylene polymerization is not viable. Modifying the catalyst by changing the metal center does not change the preference for the β-elimination products. However, the application of strongly electron donating ligands can make the metal center sufficiently electron rich to stabilize the new propylidene ligand over the formation of an olefin π-complex.

Introduction

Ordinary coordination olefin polymerization has been formulated to proceed via a hydride carbene with subsequent [2 + 2] addition of olefin and reductive elimination by Green and Brookhart. This mechanism has also been called the "carbene-to-metallacycle" mechanism, since the intermediate after [2 + 2] addition is a metallacycle[1] (see Scheme 1). A tantalum model system by Schrock further indicated that the Green mechanism can be involved in olefin polymerization. The tantalum carbene hydride can undergo reversible self-insertion of its carbene ligand to form an alkyl complex. It also shows evidence for metallacyclobutane formation and will produce a polymer in the presence of ethylene.[2]

Careful investigations by Brookhart[3] have shown that the C−H bond is never fully broken to form the hydride carbene. Instead the C−H bond forms a weak so-called α-agostic interaction with the metal. Thus, the M−H−C linkage can be considered as a three-center two-electron bond rather than the terminal hydride structure.[4] Therefore, there is a parallel between agostic hydride olefin complexes and analogous alkyl−olefin complexes which can undergo the chain propagation reaction.

Scheme 1



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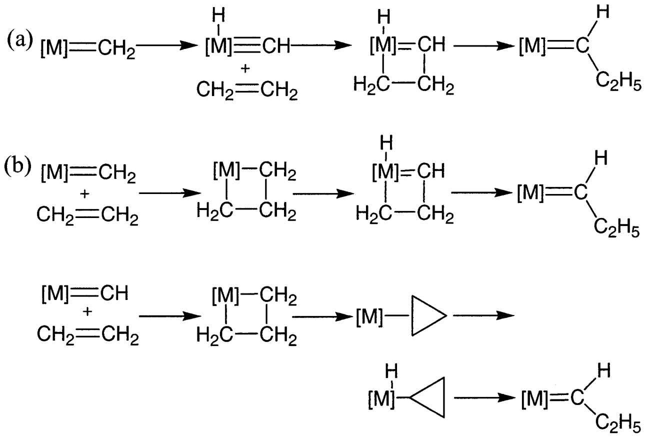
Scheme 2

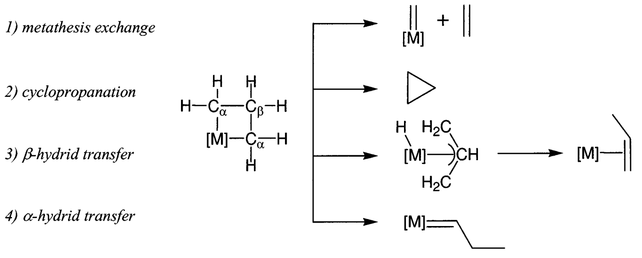


However, the mechanism proposed by Green and Brookhart has prompted us to speculate whether metal carbenes could be used to polymerize α-olefins according to a mechanism that in the spirit of Green and Brookhart involved α-elimination. We present three possible pathways in Scheme 2.

α-Olefins are known to react with carbenes in a number of alternative ways that might compete with the desired α-hydrogen transfer.[5] Thus, the metallacycle in Scheme 2 might undergo metathesis exchange[6] more readily than the desired rearrangement to a new carbene by α-hydride transfer. Moreover, metallacycle decomposition can take place along two other major pathways via cyclopropanation[7] and β-hydride transfer reactions,[8] leading to cyclopropane and olefin π-complex products, respectively (see Scheme 3).

Processes are known in which metal carbenes can work as catalysts for the polymerization[9] or oligomerization[10] of olefins. However, these processes are only applicable to cyclic olefins[11] and diolefins.[12] Thus, cyclic olefins can undergo ring-opening metathesis polymerization (ROMP)[13] in which the cyclic backbone is a necessary condition for the polymerization. Alternatively, α,ω-diolefins can be polymerized by metal carbene catalysts in acyclic diene metathesis polymerization (ADMET).[14] The ROMP and ADMET processes are different from the type of the polymerization we are looking at here, since they involve a metathesis reaction as the key step.

Scheme 3. Metallacyclobutane Decomposition Pathways



We shall in the following study the energetics and kinetics of the different processes depicted in Schemes 2b and 3. The study will initially be based on the carbene model compound $[CH_2{=}Re(NO)_2(PMe_3)]^+$. Related complexes have been newly synthesized by Berke et al.[15] Finally, on the basis of the $[CH_2{=}Re(NO)_2(PMe_3)]^+$ investigations we shall comment on how changing the metal or ligands might help to make the α-H transfer mechanism more feasible.

In our study, we investigated a possible use of metal–carbene complexes as olefin polymerization catalysts from a theoretical point of view. The density functional methodology we use (see Computational Details) has become a reliable tool for understanding the chemistry of the transition-metal-catalyzed polymerization reactions.[16,17]

Computational Details

Molecular geometries have been optimized at the gradient-corrected density functional theory level using the Becke–Perdew exchange correlation functional.[18–20] The calculations have been carried out with the Amsterdam Density Functional (ADF 2000) program package developed by Baerends et al.,[21,22] vectorized by Ravenek.[23,24] The numerical integration scheme applied for the calculations was developed by te Velde et al.[25] The geometry optimization procedure was based on the method

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(5) Heterogeneous catalytic aspects of the reaction with similar elementary steps involving transition-metal carbene intermediates have been reviewed in a recent article: Turner, M. L.; Marsih, N.; Mann, B. E.; Quyoum, R.; Long, H. C.; Maitlis, P. M. *J. Am. Chem. Soc.* **2002**, *124*(35), 10465.

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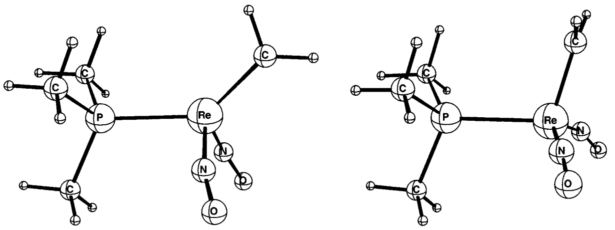
of Versluis and Ziegler.[26] For the transitin-metal elements a standard triple-ζ STO basis set from the ADF database IV was employed with 1s−4d electrons treated as a frozen core for the elements Re, Os, Ir, and Pt. The same database was employed with 1s−3d electrons as a frozen core for the elements Ru, Rh, and Pd. For the nonmetal elements a standard double-ζ basis set with one set of polarization functions (ADF database III) was applied, with frozen cores including 1s electrons for O, N, and C and 1s2s2p for P.[27,28] The auxiliary[29] s, p, d, f, and g STO functions centered on all nuclei were used to fit the Coulomb and exchange potentials during the SCF process. The reported relative energies include scalar relativistic corrections,[30−32] since it was shown that such an approach is sufficient for the systems containing the 4d and 5d transition metals.[33] All structures shown correspond to minimum points on the potential surface, except those prefixed by TS, which represent transition states. Transition states were fully optimized using the algorithm of Banerjee et al.,[34,35] starting from the structures obtained by linear transit calculations. No symmetry constraints were used.

Here one should note the following. (1) The energetics discussed below do not include zero-point vibrational energy and entropy corrections. Due to the large size of the systems, we could not perform vibrational analysis. (2) At this stage of our work, we did not carry out investigation of the solvent and counterion effects. From our experience with the Brookhart catalyst, counterion effects are not important for the late transition metals.[17m,n] Also, we do not expect solvation effects to be important as long as no charge separation is involved.

Results

Catalyst. The complex $[CH_2{=}Re(NO)_2(PMe_3)]^+$ has two possible conformations with, respectively, pyramidal (**1a**) and T-shaped (**1b**) geometries (Figure 1). Thermodynamically they are nearly on the same energy level. The T-shaped alkylidene complex is lower in energy by 1.7 kcal mol^{-1}. This isomerism will give rise to a wide variety of conformations among the products and intermediates during the polymerization reactions. All energies given later are relative to the separate monomer and the most stable form (T-shaped, **1b**) of the catalyst. Relative energies of the stationary points and the transition-state energies of the calculated species are listed in Table 1.



1a
Pyramidal

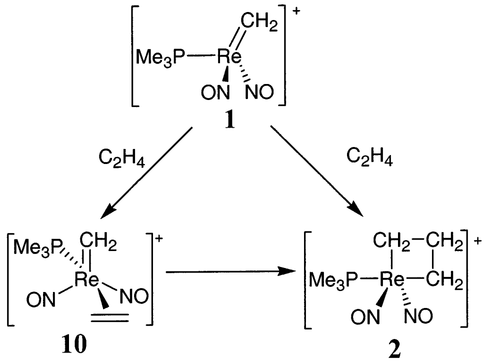
1b
T-shape
($\Delta E_{T\text{-}Pyr} = -1.7$ kcal mol^{-1})

Figure 1. The two possible geometrical forms of the rhenium carbene complex.

Table 1. Calculated Relative Energies (ΔE_{rel}, kcal mol^{-1}) of Reactants, Intermediates, Products, and Barriers ($\Delta E^‡$, kcal mol^{-1}) of Transition States

complex description	species	ΔE_{rel}	$\Delta E^‡$
$[H_2C{=}Re(NO)_2(PMe_3)]^+ + C_2H_4$	**1** + Et	0.0	
metallacyclobutane	**2**	−33.4	
cyclopropane complex	**3**	−34.3	
cyclopropyl hydrido complex	**4**	−25.8	
primary propylidene complex	**5**	−34.9	
cyclopropenyl hydrido complex	**6**	−27.4	
secondary propylidene complex	**7**	−41.7	
allyl hydrido π-complex	**8**	−51.4	
propene π-complex	**9**	−56.4	
ethylene π-complex	**10**	−20.9	
β-H transfer	TS[**2**-**8**]	−30.3	3.1
H-elimination	TS[**8**-**9**]	−47.7	3.7
1,3-H shift	TS[**2**-**5**]	−3.1	30.3
α-hydride transfer	TS[**2**-**4**]	−5.6	27.8
H elimination	TS[**4**-**5**]	−4.8	21.0
H migration	TS[**4**-**6**]	+10.0	35.8
cyclization	TS[**2**-**3**]	−21.5	11.9
α-hydride transfer	TS[**3**-**4**]	−17.4	17.0
H elimination	TS[**6**-**7**]	−17.1	17.2

Scheme 4. π-Complex and Metallacycle Formation



Metallacycle Formation with Ethylene. Depending on the orientation of the two double bonds, the reaction of the alkylidene and olefin leads to two possible species (Scheme 4). Formation of the olefin

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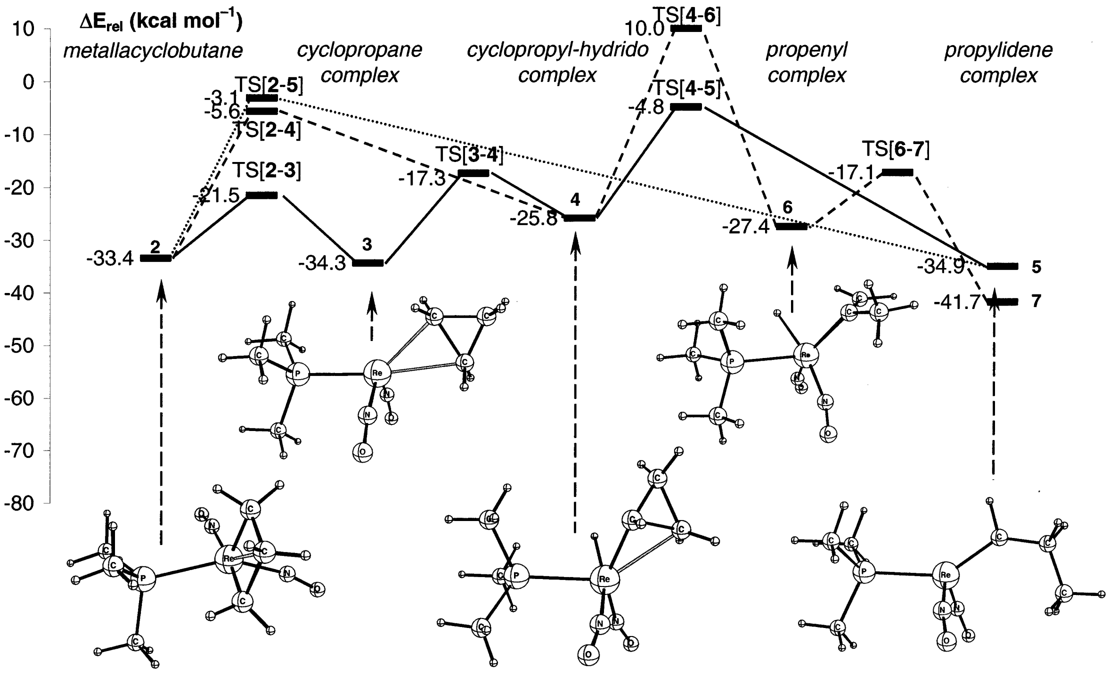


Figure 2. Energy profile of the α-hydride transfer pathway of metallacyclobutane rearrangement.

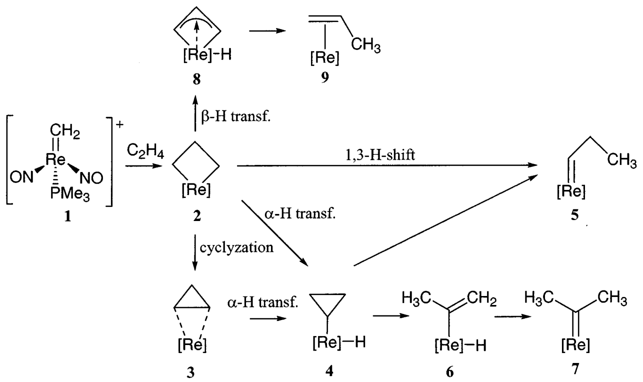
π-complex **10** is possible when the ethylene bond is perpendicular to the Re=C bond. Formation of the olefin complex **10** is exothermic by 21 kcal mol^{-1}, and the resulting π-complex is a minimum on the potential energy surface. On the other hand, four-membered metallacyclobutane complexes **2** are formed when the C=C and Re=C double bonds become parallel to each other. The [2 + 2] addition of ethylene to the Re=C bond is even more exothermic by 3−10 kcal mol^{-1} than the formation of the π-complex **10** and proceeds via a very low barrier (<1 kcal mol^{-1}). We have located eight different isomers on the potential energy surface. Among these isomers there are three pyramidal metallacycle conformers with different agostic bonds between an α-hydrogen and the metal center. The carbon−hydrogen bonds, which are involved in an α-agostic interaction with rhenium, are about 0.06 Å longer than the ideal C(sp^3)−H bond lengths. These α-agostic bonds have the potential to undergo a further α-hydrogen transfer reaction to the metal center. The most stable isomer ($E_{\rm rel}$ = −33.4 kcal mol^{-1}) has a T-shaped geometry, but it can transform with an energy barrier of 5.3 kcal mol^{-1} to a pyramidal conformation ($E_{\rm rel}$ = −27.7 kcal mol^{-1}).

Cyclization and α-Hydride Transfer Reactions. The energy profile for the cyclization and α-hydride transfer reactions, starting from metallacyclobutane **2**, is presented in Figure 2 and Scheme 5. Relative energies of the stationary points and energies for the transition states are listed in Table 1.

The metallacyclobutane complex **2** can undergo a cyclization process in which a new C−C bond is formed to produce the cyclopropane complex **3** (see Scheme 5). After the cyclization **2** → **3**, the most stable cyclopropane isomer **3** has an energy of −34.3 kcal mol^{-1}, which is 0.9 kcal mol^{-1} lower than the most stable metallacyclobutane (Figure 2). The cyclization reaction has a barrier of 11.9 kcal mol^{-1}.

Alternatively, an α-hydrogen can migrate to the metal center to afford the hydrido cyclopropyl complex **4** (Scheme 5). The reaction is endothermic by 7.6 kcal mol^{-1} (Figure 2) and has a barrier of 27.8 kcal mol^{-1}. The complex **4** can also be formed from **3** by α-hydrogen transfer from the cyclopropane ring to the metal. This process (**3** → **4**) is endothermic by 8.5 kcal mol^{-1} but has a much lower barrier of 17.0 kcal mol^{-1} than **2** → **4**. Thus, if formed, **4** is likely to be a product of the two-stage process **2** → **3** → **4** rather than the direct path **2** → **4** (Figure 2).

Scheme 5. Metallacyclobutane Decomposition Pathways by Cyclization and α- and β-Hydrogen Transfer Reactions



Another product accessible from **2** by α-hydrogen transfer is the primary propylidene complex **5**. It can be reached directly from **2** in a 1,3-hydride shift (Scheme 5) that is exothermic by 1.6 kcal mol^{-1} and has a barrier of 30.2 kcal mol^{-1}. Alternatively, the product **5** can be reached in a **2** → **3** → **4** → **5** stepwise reaction for which the highest lying transition state TS[**4-5**] has an energy comparable to that, TS[**2-5**], for the direct process.

The most stable product available with an α-hydrogen transfer from **2** is the secondary propylidene complex **7**. It can be reached in the three-step reaction **2** → **4** → **6** → **7**, where **6** is a propenyl complex (Scheme 5 and Figure 2). The secondary propylidene complex **7** has an energy of −41.7 kcal mol^{-1} and is thus 8.3 kcal mol^{-1}

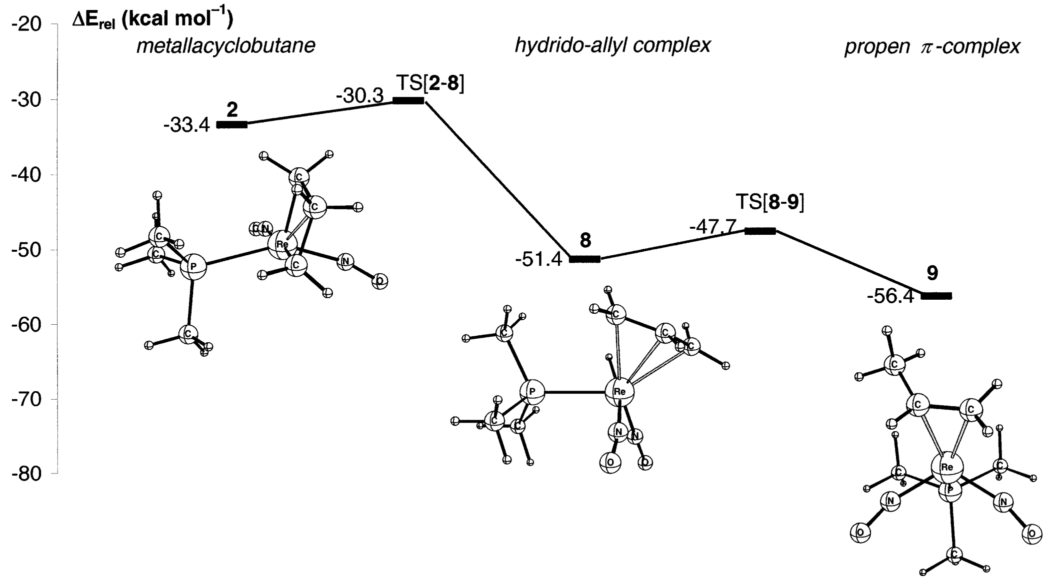


Figure 3. Energy profile of the β-hydride transfer pathway of metallacyclobutane rearrangement.

more stable than **2**. However, the transition state, TS[**4-6**], has an energy of 10.0 kcal mol^{-1}, which makes it unlikely that **7** would be formed from **2**.

β-Hydride Transfer Reactions. The energy profile for the β-hydride transfer reaction starting from the metallacyclobutane **2** is presented in Figure 3. Relative energies of the stationary points and energies of the transition states are listed in Table 1.

In the β-hydride transfer reaction one of the $C_\beta{-}H$ bonds breaks and generates a Re−H bond. This process is fairly exothermic. We find that the most stable π-allyl complex **8** has an energy of −51.4 kcal mol^{-1}, which is lower than that of the metallacyclobutane by 18 kcal mol^{-1}. The estimated barrier of the β-hydride transfer reaction **2** → **8** is very low, less than 3.1 kcal mol^{-1}. The geometry of the transition state TS[**2-8**] is very close to the metallacyclobutane structure, and the corresponding $Re{-}C_\beta$ and $C_\beta{-}H$ distances are 2.94 and 1.10 Å, respectively.

In the second step the hydrido−π-allyl intermediate **8** is transformed into the propylene π-complex **9** by breaking the Re−H bond and transferring the hydrogen to one of the α-carbons (Scheme 5). The most stable β-elimination product is the propylidene π-complex **9** with an energy of −56.4 kcal mol^{-1}. The **8** → **9** transformation is associated with a fairly low barrier of ∼3.7 kcal mol^{-1}. The geometry of the optimized transition state geometry TS[**8-9**] has a Re−H bond distance of 1.72 Å, which is only 0.02 Å longer than the bond lengths in the π-allyl structure **8**.

The β-hydride transfer product π-complex **9** is lower in energy than the α-hydride transfer product **5** by 21.5 kcal mol^{-1}. When the barriers of the two hydride transfer reactions are compared, the barrier for the β pathway is lower than the barrier for the α-hydride transfer process by 25.5 kcal mol^{-1}. Thus, our calculations show that when metallacyclobutane **2** is the starting material, the β-hydride elimination pathway is preferred both thermodynamically and kinetically over α-hydride transfer.

Modifications of the Metal Complex by Varying the Metal Atom and the Ligands. To reverse the preference for α-elimination over β-elimination, we have changed the NO ligands to tertiary phosphine ligands. This was done in order to make the metal center more electron rich and thus stabilize the carbene ligand, which should be more electrophilic than ethylene. The relative energies of the calculated complexes are shown in Table 2 and Figure 4. Using simple phosphine ligands, where R = H, already decreased the relative energy difference between the alkylidene and π-complex to 12.8 kcal mol^{-1}. By this modification of the rhenium complex the energy difference between α- and β-hydride transfer products is reduced by 8.7 kcal mol^{-1} (see Figure 4). Using the more electron donating ligand trimethylphosphine reduces the energy difference between the olefin and propylidene complex to only 6.8 kcal mol^{-1}. By the application of one the most electron donating phosphines, *tert*-butyldipyrrolidinylphosphine,[36] the difference is −15.2 kcal mol^{-1}. Thus, it is possible to make an α-elimination product the thermodynamically most favorable species.

Table 2. Calculated Relative Energies (ΔE_{rel}, kcal mol^{-1}) of Rhenacyclobutane Complexes and Their Decomposition Products by α- and β-Hydride Transfer Reactions for Different PR_3 Tertiary Phosphine Ligands, Where R = H, Me, t-Bu, $N(CH_2)_4$

complex	ΔE_{rel}
$[Re]{=}CH_2$ + ethylene	0.0
$[(PMe_3)(NO)_2Re(\eta^2\text{-}CH_2{=}CHCH_3)]^+$	−56.4
$[(PMe_3)(NO)_2Re({=}CHCHCH_3)]^+$	−34.9
$[(PMe_3)(NO)_2Re({-}CH_2CH_2CH_2{-})]^+$	−33.4
$[(PH_3)_3Re(\eta^2\text{-}CH_2{=}CHCH_3)]^-$	−39.6
$[(PH_3)_3Re({=}CHCH_2CH_3)]^-$	−26.8
$[(PH_3)_3Re({-}CH_2CH_2CH_2{-})]^-$	−32.8
$[(PMe_3)_3Re(\eta^2\text{-}CH_2{=}CHCH_3)]^-$	−32.9
$[(PMe_3)_3Re({=}CHCH_2CH_3)]^-$	−26.7
$[(PMe_3)_3Re({-}CH_2CH_2CH_2{-})]^-$	−30.2
$[(P(t\text{-}Bu)(N(CH_2)_4)_2)_3Re(\eta^2\text{-}CH_2{=}CHCH_3)]^-$	E_1
$[(P(t\text{-}Bu)(N(CH_2)_4)_2)_3Re({=}CHCH_2CH_3)]^-$	E_2
	$E_2 - E_1 = -15.2$

Considering other metal centers with a similar d^6 electron count might also help stabilize the alkylidene

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[36] (a) Clarke, M. L.; Holliday, G. L.; Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **2002**, 1093. (b) Clarke, M. L.; Cole-Hamilton, D. J.; Slawin, A. M. Z.; Woollins, J. D. *Chem. Commun.* **2000**, 2065. (c) Moloy, K. G.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 7696.

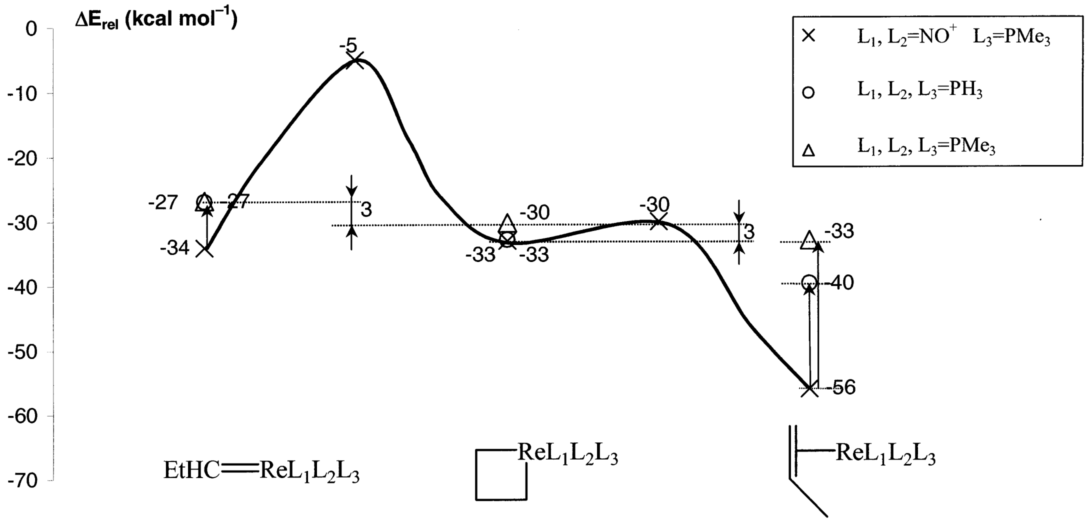

Figure 4. Relative energy (kcal mol^{-1}) changes of the ligand change to the metallacyclobutane complex and its decomposition products.

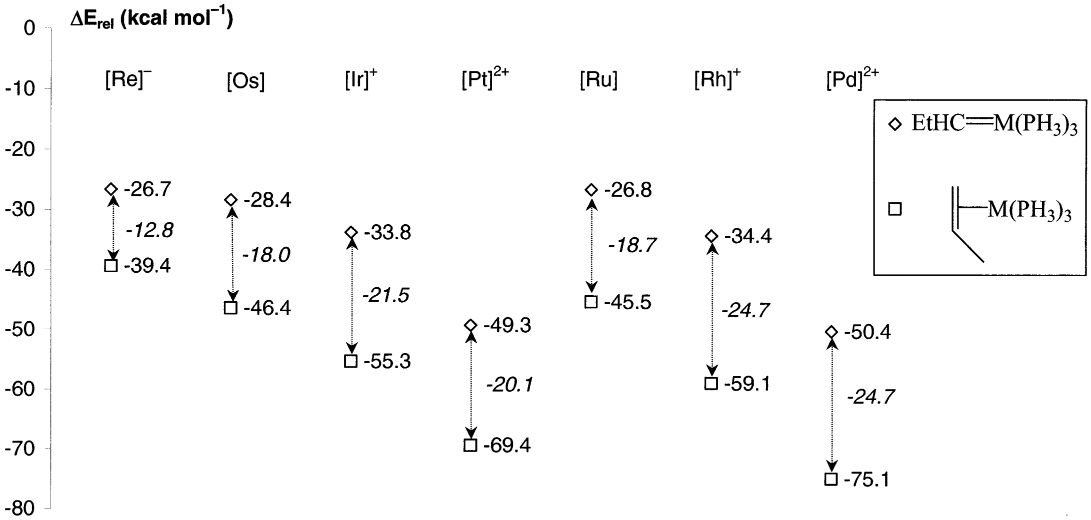

Figure 5. Relative energy (kcal mol^{-1}) differences for the hydride transfer products alkylidene and π-complexes.

intermediate relative to the olefin complex. Therefore, we have carried out a series of calculations on Ru, Rh, Pd, Os, Ir, and Pt transition-metal complexes. The relative energies of the possible α- and β-hydride transfer products are shown in Figure 5. The application of transition metals later than rhenium makes both the α- and β-hydride transfer products thermodynamically more stable but does not affect significantly the relative energy of the metallacycle intermediates. The platinum alkylidene and platinum olefin π-complexes are lower in energy than the corresponding rhenium complexes by 35.7 and 23.7 kcal mol^{-1} (relative to the metallacycles), respectively. On the other hand, the relative energy difference between the alkylidene and π-complexes increases by the application of transition metals later than rhenium. The differences between the 4d and 5d elements are not significant. Complexes of the 5d elements are slightly lower in energy than those of the 4d elements by 2−5 kcal mol^{-1}. However, the energy differences between the alkylidene and olefin complexes are about the same. On the basis of the data summarized in Figure 5, we can conclude that choosing transition metals later than rhenium does not help in stabilizing the alkylidene complexes with respect to the olefin compounds.

Conclusions

We have studied the feasibility of using metal carbenes as catalysts for the polymerization of linear α-olefins according to the α-elimination mechanism of Scheme 2b. Our investigation reveals that the reaction of ethylene with $[CH_2{=}Re(NO)_2PMe_3]^+$ initially leads to a metallacyclobutane intermediate, **2**, as anticipated. However, **2** does not decompose to the required secondary propylidene complex, **7**, by α-elimination. Instead, **2** results in a propene π-complex, **9**, via a β-elimination mechanism as the both kinetically and thermodynamically most favorable product.

To reverse these trends, the application of more electron donating ligands instead of nitrosyl groups, such as trialkylphosphines (PR_3, R = alkyl group) or their P−N derivatives ($PR'R''_2$; R′ = t-Bu and R″ = pyrrolydinyl), seem to be very promising. The application of a $[(PR_3)_3Re{=}CH_2]^-$ (R = H, Me) complex decreases the thermodynamic preference of the propylidene π-complex product to 12.8 kcal mol^{-1} (R = H) and 6.2 kcal mol^{-1} (R = CH_3), respectively. The best results were obtained for the *tert*-butyldipyrrolidinylphosphine, where the α-elimination product **7** is now favored over the β-elimination product **9** by 13.7 kcal mol^{-1}.

We have also carried out calculations with various isoelectronic metal complexes for the smallest anionic triphosphine alkylidenes and π-complexes. These calculations indicate that the use of a later transition metal as the central atom increases the thermodynamic stability of the hydride transfer products but the β-hydride transfer products are still preferred over those from the α-hydride transfer reaction.

According to our calculations a rhenium carbene complex designed with very strong electron donor ligands might make the rhenium center sufficiently electron rich to stabilize the new propylidene ligand over the formation of an olefin complex and thus make α-olefin polymerization by a metal carbene catalyst feasible.

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Supporting Information Available: Tables giving optimized geometries of the structures discussed (Cartesian coordinates, in Å). This material is available free of charge via the Internet at http://pubs.acs.org.

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