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COMPLEX CATALYSIS

XIV *. STRUCTURE-ACTIVITY RELATIONSHIPS OF COMPLEX CATALYSTS FOR OLEFIN METATHESIS; A THEORETICAL CONSIDERATION

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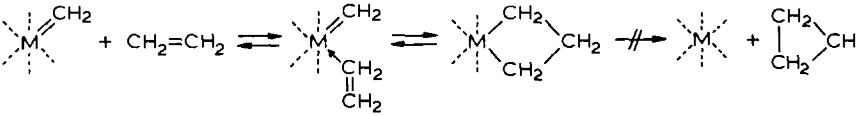
Summary

Some essential constitutional properties for a complex catalyst of olefin metathesis are derived from considerations of bond energy and kinetic stability of the transition metal carbon σ-bond on the basis of the carbene mechanism with the complex fragment X≡M(CHR) ($M = Mo, W$; $X = O, N, C{-}R$) as a model.

As shown by various indirect experimental results [1,2], it seems now to be proved that the catalyst for olefin metathesis is a transition metal carbene complex (A). According to eq. 1, the latter reacts reversibly with the olefin via an olefin carbene complex (B) to give a metallocyclobutane complex (C) without deactivation by reductive elimination of cyclopropane or by any other scission reaction of the transition metal carbon σ-bonds.



(1)

It is well established that the transition metals Mo, W and Re are especially suitable for the generation of metathesis catalysts. However, up to now no plausible theoretical explanation has been advanced for this observation, since the structure of the catalyst complex A had not yet been characterized [3].

Recently Schrock et al. [4] synthesized an oxotungsten(IV) carbene complex

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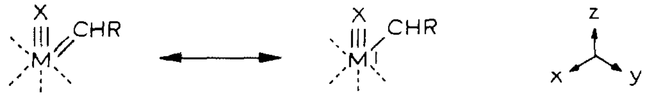
* For part XIII See ref. 15.

$OW^{IV}(CHCMe_3)(PMe_3)Cl_2$ which was identified by X-ray crystal structure analysis. This complex catalyses the olefin metathesis though its activity is rather low. We have found, that nitridomolybdenum(VI) complexes, such as $NMo^{VI}Cl_3(OPPh_3)_2$ or $Bu_4[NMo^{VI}Cl_4]$ for example, after addition of $EtAlCl_2$ (1:6–10) catalyse olefin metathesis with high activity very probably by the formation of a nitridomolybdenum(IV) carbene complex according to eq. 2 [5]:

$$NMo^{VI}Cl_3L_2 + (2+x)EtAlCl_2 \rightarrow \left(NMo^{IV}(CHCH_3)Cl \cdot x\,EtAlCl_2\right) + C_2H_6 + 2\,L \cdot AlCl_3 \quad (2)$$

Further, Fischer et al. [6] have reported that the carbynetungsten complex $CH_3CW(CO)_4Br$ in combination with the Lewis acid $TiCl_4$(1:1) possesses high catalytic activity in the polymetathesis of cycloolefins. Therefore, we conclude that the complex fragment (eq. 3) with the oxidation number +IV and a d_{xy}^2 configuration at the central atom could be essential for the catalytic action.

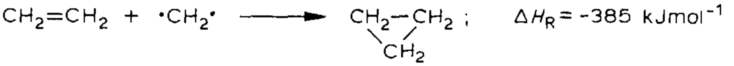


(3)

M = Mo, W ; X = O, N, C—R

Taking into account that the carbene is a neutral ligand, the metallocyclobutane formation with the olefin can be regarded as an oxidative addition which requires a *d*-electron pair at the central atom. The high oxidation number of the transition metal may be a prerequisite for preventing carbene transfer to the olefin from a thermodynamic viewpoint.

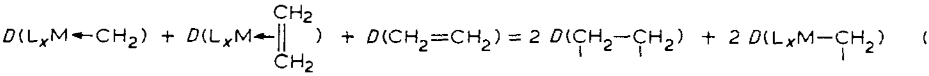
Cyclopropane formation from C by concerted reductive elimination involving the unoccupied d_{xy} orbital at the transition metal is an orbitally allowed reaction according to the principle of conservation of orbital symmetry [7] and therefore, in agreement with experiment, is not strongly hindered kinetically. Under this premise the smallest amount of bond energy necessary to suppress the carbene transfer to the olefin can be derived from the enthalpy of formation of cyclopropane [8] according to eq. 4 i.e. $D(L_xM \leftarrow CH_2) > 385\ kJmol^{-1}$:



$$CH_2{=}CH_2 + {\cdot}CH_2{\cdot} \longrightarrow \underset{CH_2}{CH_2{-}CH_2}\,; \qquad \Delta H_R = -385\ kJmol^{-1} \quad (4)$$

This minimum value for the strength of the transition metal—carbene bond also excludes its decomposition by ethylene formation, since $D(CH_2{=}CH_2) = 720$ kJ-mol^{-1} [8].

The maximum catalytic activity will be achieved, if the free activation enthalpy is the same for both of the reversible reactions in eq. 1, i.e. if B and C are equal in energy. Neglecting influences from entropy and solvation the following equation (eq. 5) must then be valid for the corresponding bond dissociation enthalpies:



$$D(L_xM \leftarrow CH_2) + D\left(L_xM \leftarrow \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}\right) + D(CH_2{=}CH_2) = 2\,D(\overset{|}{C}H_2{-}\overset{|}{C}H_2) + 2\,D(L_xM{-}\overset{|}{C}H_2) \quad (5)$$

Assuming that the coordinative bond energy of the olefin, is 44 kJmol^{-1}, in accordance with calorimetric measurements for the system WCl$_6$-[EtAlCl$_2$]cyclohexene [9], and deriving the C–C bond energy in formula C from the corresponding enthalpies of formation [8] i.e.:

$$D(\underset{|}{C}H_2-\underset{|}{C}H_2) = 1/4[4\Delta H_f{}^{\circ}(\bullet CH_2\bullet) - \Delta H^{\circ}{}_f(\text{cyclobutane})] = 379\ \text{kJmol}^{-1},$$

then since $D(CH_2{=}CH_2) = 720$ kJmol^{-1} the homolytic bond energy of the transition metal carbon σ-bond in formula C, which is needed for optimum catalytic action, obtained from eq. 5 is $D(L_xM-\underset{|}{C}H_2) = 196$ kJmol^{-1}.

A comparison with the average bond energies $D(Mo-CH_3) = 150$ kJmol^{-1} and $D(W-CH_3) = 198$ kJmol^{-1}, determined calorimetrically for $Cp_2Mo(CH_3)$ and $Cp_2W(CH_3)_2$ recently [10], demonstrates that the carbene mechanism for the catalysis of olefin metathesis proposed by Herison and Chauvin [11] is thermodynamically quite plausible. This is supported also by recent quantum chemical calculations [12]. Regarding the constitution of an efficient metathesis catalyst the following conclusions can be drawn:

(1) The coordination bond energy of the carbene at the transition metal must be so large that cyclopropane and olefin formation is prevented thermodynamically.

(2)The homolytic bond energy of the transition metal–carbon σ-bond in the metallocyclobutane complex must be high enough to reach equality in energy with the olefin carbene complex, which is the essential energetic supposition for maximal catalytic activity, cf. the reaction diagram in Fig. 1.

(3) The transition metal must be present in the d_{xy}^2 ground state configuration to initiate, by the d_{xy}–$2p_\pi$–π^* orbital overlap, cf. Fig. 2, the most favourable coordination of the carbene and the olefin for formation of the metallocyclobutane structure.

(4) The transition metal–carbon σ-bond must also be sufficiently kinetically stabilized against heterolytic and homolytic decomposition to diminish irreversible destruction of the complex catalyst.

Carbene complexes of Mo^{IV} and W^{IV} with a triply bonded X-ligand obviously can fullfill more or less these conditions, and in the case of tungsten the higher M–C

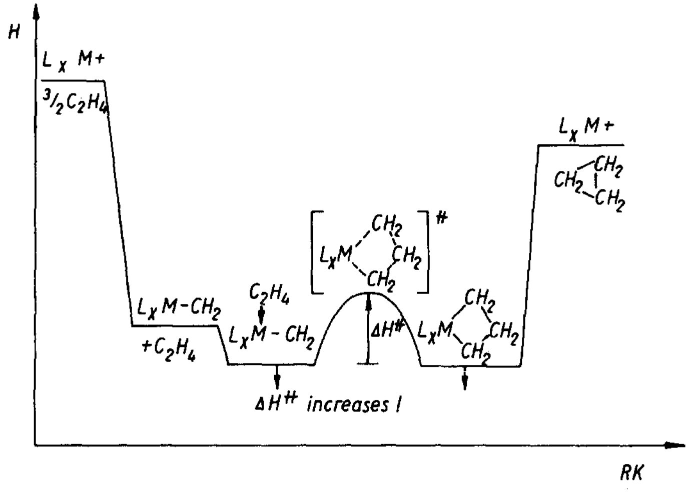


Fig. 1. Reaction diagram for the complex-catalyzed metathesis of ethylene.

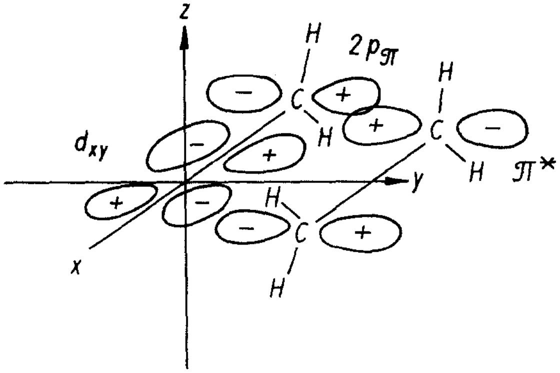


Fig. 2. $d_{xy}-2p_\pi-\pi^*$ overlap in the olefin carbene complex.

dissociation energy should allow a more extended ligand variation.

In general, the strength of the transition metal–carbon σ-bond increases in the order $3d < 4d < 5d$ metal and decreases with increasing oxidation number [13]. By the formation of the triple bond involving the d_{xz} and the d_{yz} orbitals at the transition metal, the effective charge on the hexavalent central atom in C can be reduced strongly and the homolytic M–C bond energy is increased substantially. This effect is expected to become larger in the row of X-ligands O < N < C–R and may be the reason why in going from W to Mo the oxochloro complexes show practically no catalytic activity [5].

The kinetic stabilization of the M–C bond involving *d*-electron-poor transition metals by π-basic ligands is a well known fact [13]. In the X≡M structure a strong destabilization of the d_{xz} and the d_{yz} orbitals arise from the π-bond formation [14], thus a hydride or electron transfer into these orbitals as the first step of decomposition is energetically more difficult. In C an intramolecular electron transfer from the highest occupied M–C σ-orbital into the free d_{xy} orbital also does not lead to a kinetic destabilization, because there exists for the trimethylenediyl group chelate bonded in the same plane a high probability of recombination [13].

This model of a complex catalyst for olefin metathesis does not only allow the recognition of some important constitutional suggestions for catalytic activity but also represents a useful heuristic basis for further investigations to find stable and highly active metathesis catalysts.

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