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Molecular mechanical studies on the olefin metathesis reaction

I. Development and evaluation of tungsten carbene parameters: METMOD1

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Abstract

Molecular mechanics studies have been carried out on WCl_4CHR (R = H, CH_3, or CH_2CH_3) complexes using the PCMODEL-PI V4.0 program with the new METMOD1 force field, developed for this particular application. The PCMODEL program previously provided a semi-quantitative guide to structures of transition metal carbenes using only the stretching, van der Waals, and 1,3-interactions. METMOD1 uses all of the six original energy terms of MMX: stretching, van der Waals, stretch-bend, bending, torsion, and electronic (dipole-dipole or charge) interactions. Only experimentally determined data for relevant compounds were used for parameterization. Trigonal-bipyramidal structures with equatorial parallel carbene conformations are found to be favoured. Coordination of α-hydrogen appears to be an option. Bond lengths, rotational barriers (16 ± 2 kcal) and the rotational profile for $W{=}C_c$ bonds are in good agreement with the experimental data. Structures calculated by PCMODEL, METMOD1, and *ab initio* methods are compared with the relevant experimental data.

Key words: Tungsten; Carbene; Molecular mechanics; Ab initio; Olefin metathesis; Polymerization

1. Introduction

Olefin metathesis is of great value in organic and polymer synthesis [1]. The reactions do not occur spontaneously. They all require the presence of a catalyst system containing a transition metal compound, frequently in conjunction with a second compound (cocatalyst) and sometimes a third (promoter). Transition metal carbenes formed in these systems trigger the *trans*alkylidenation (*i.e.* metathesis) of olefins. The carbene mechanism is now well documented and accepted: olefin coordination to the complex carbene leads to a metallacyclobutane, which rearranges to give a new olefin and a new metallacarbene [2] (Scheme 1).

These reactions are mostly stereoselective [3,4]. The theories developed to account for the experimental information have been outlined in some excellent reviews [5]. The importance of the nature of the transition metal, the carbene, and even the ancillary ligands has been recognised. However, except in one recent case [5a], actual atomic and molecular parameters are not used in the analyses. The use of terms such as "larger", "smaller", "bulkier" etc. indicate the qualitative nature of the treatment. Even in the case of well-defined unicomponent carbene catalysts, it is hard in this way to make a reliable prediction of the structure of the products [6], not to mention the case of the ill-defined catalyst systems.

We have chosen an alternative, complementary approach to this problem. The aim of our work is to provide satisfactory models to allow investigation of the catalysts, the intermediates, and the products of the metathesis reactions represented in Scheme 1. We believe that molecular mechanics can provide precise quantitative estimates of intramolecular effects governing the course of the reaction. An essential requirement for this strategy was the development of the parameters of the force fields for the organometallic chain-carriers **1–3** in conjunction with an accessible

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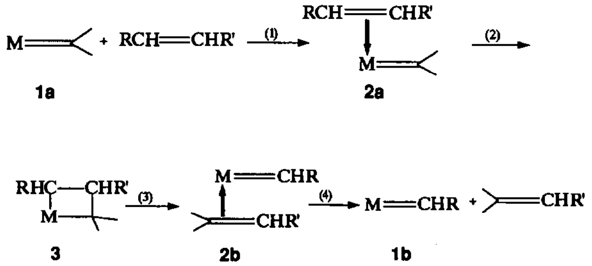

Scheme 1. Mechanism of olefin metathesis.

and well-documented computational procedure such as the PCMODEL-PI V4.0 [7]. Some of our encouraging preliminary results on molecular mechanics studies on ring-opening polymerization of norbornene were recently briefly reported [8]. Now, in the first part of a series of papers we define and test a detailed and refined version of the force field (termed METMOD1) of the WCl_4CHR carbenes (**1a** and **1b**) formed in the $WCl_6/SnMe_4$-initiated metathesis reactions (and probably in hundreds of catalyst systems in which WCl_6 is used as a catalyst precursor). This will be followed in subsequent papers by the provision of supplementary parameters for the so-called well-defined carbene catalysts [9], of the force fields of π-complexes (**2a** and **2b**) and metallacycles (**3**), and by analysis of the reactions (1)–(4). We hope that METMOD1 will also provide an easily accessible tool for experimental chemists working in the field of carbene chemistry.

2. Experimental details

2.1. The use of the PCMODEL-PI V4.0

The PCMODEL is parametrized for transition metals in general, mainly using data for iron derivatives with corrections applied for other metals [10]. The bending functions and all torsion potentials involving the metal atom are removed and the 1,3-interaction and an $1/r^2$ attractive terms are introduced instead. Rotation barriers are set to zero in each case, in contrast to the experimental findings [11].

The PCMODEL general transition metal force field, provides a good means of deriving a possible geometry with informative values for tungsten carbenes. The carbene group is placed in equatorial parallel position, in agreement with the experimental results [12,13]. However, even after introducing the torsion and bending terms, and also providing experimental parameters for the stretching term, reliable quantitative data were not obtained. Because of some built-in van der Waals correction, the program indicated longer inter-atomic distances than are observed. Ideal bond angles were reproduced satisfactorily and rotational barriers were acceptable, but the geometry was still somewhat distorted because of the lack of an appropriate torsion profile.

2.2. The METMOD1 force field

The original force field of the PCMODEL left unsatisfactory features in the modelling of tungsten carbenes even after major adjustment of the parameters. For that reason, we abandoned the use of the general transition metal central atom method and instead constructed a force field for the specific handling of tungsten carbene species, termed METMOD1.

The energy terms used, identical with those for the MMX of the PCMODEL [7,10], are shown in Scheme 2. In eqns. 1–7, E_1 represents stretching energies, E_2 bending energies, E_3 stretching–bending energies, E_4 van der Waals energies, E_5 dihedral angle energies, and E_6 charge or dipole interaction energies. All variables and constants are defined in the subsequent discussion.

In the light of our preliminary molecular mechanical studies and the results of some recent *ab initio* studies on WCl_4CH_2 [14], a trigonal-bipyramidal structure with equatorial parallel carbene position was assumed for the WCl_4CHR carbenes. This is in accord with the

$$E_{TOTAL} = \sum_{BL} E_1 + \sum_{BA} E_2 + \sum_{SB} E_3 + \sum_{vdW} E_4 + \sum_{DA} E_5 + \sum_{EL} E_6$$

where

$$(1) \qquad E_1 = \frac{1}{2} \cdot 143.88 \cdot k_s \cdot (1 + \mathrm{CST} \cdot (r - r_0))\,(r - r_0)^2$$

CST = −2.00, is the cubic stretch term

$$(2) \qquad E_2 = \frac{1}{2} \cdot 0.043828 \cdot k_b \cdot (\theta_0 - \theta)^2\,(1 + \mathrm{SF} \cdot (\theta_0 - \theta)^4)$$

$\mathrm{SF} = 7 \cdot 10^{-8}$, is the sextic bending constant

$$(3) \qquad E_3 = 2.51118 \cdot k_{sb} \cdot \theta \cdot (r_{12} + r_{23})$$

θ is the angle 1—2—3

r_{ij} is distance between atoms i and j

$$(4) \qquad E_4 = \varepsilon \cdot 290000 \cdot e^{-12.5/p} - 2.25 \cdot p^6$$

$$\varepsilon = \sqrt{\varepsilon_i \cdot \varepsilon_j}$$

$$p = \frac{r_{vdW,i} + r_{vdW,j}}{r_0}$$

if $p \geq 3.311$ then

$$E_4 = \varepsilon \cdot 336.176 \cdot p^2$$

$$(6) \qquad E_5 = \frac{V_1}{2}(1 + \cos\omega) + \frac{V_2}{2}(1 - \cos 2\omega) + \frac{V_3}{2}(1 + \cos 3\omega)$$

sign of angle A—B—C—D is positive when looking through B, toward C, if D is counterclockwise from A

$$(7) \qquad E_6 = 14.39418 \cdot 4.80298^2 \cdot \frac{Q_i \cdot Q_k}{r_{i,k}}$$

$$\mu_{i,k} = 2.385 \cdot l_0\,(Q_i - Q_j)$$

$$E_6 = 14.39418 \cdot \frac{\mu_{i,k} \cdot \mu_{m,n}}{D \cdot r^3}(\cos\chi - 3 \cdot \cos A \cdot \cos B)$$

D is the dielectric constant

Scheme 2. The energy terms used in METMOD1.

structure of the well-characterized five-coordinate tungsten-carbenes [11c,13c,13d].

Extensive use of experimental data, mainly X-ray bond lengths and angles for various carbene complexes, was made in the parametrization of METMOD1 [11–13].

2.2.1. Atom types of METMOD1

The METMOD1 in its present state employs six new atom types in addition to the original MMX type set for the description of WCl_4CHR carbenes (Table 1).

The first unparametrized atom (Ge, type 31) of the PCMODEL was converted to tungsten. An ordinary sp^2 carbon was used for carbene carbon C_c based on the assumption of a totally covalent $W{=}C_c$ bond [15]. Chlorines are differentiated according to their positions within the structure as axial Cl_a and equatorial Cl_e ones. Coordination of the α-hydrogen is considered as an alternative option on the basis of numerous recent X-ray results [12a,c]. To create an opportunity for this kind of option a new type of hydrogen H^*, and a new type of sp^3 carbon C^* (the carbon atom attached to the carbene carbon) were defined.

2.2.2. Stretching parameters of METMOD1

The ideal bond lengths and stretching force constants (k_s) used in METMOD1 are listed in Table 2.

No experimental force constant for the $W{=}C_c$ bond was found. The force constant used in MMX (2.0) seems to be too small compared to the experimental value for a $Ta{=}C_c$ bond of 5.96 mdyn $Å^{-1}$ [11d]. The latter was used in the program as an approximation. Values calculated from IR spectroscopic data [16] by solving the secular determinant method for unidimensional bonds [17] fall into the range of 8.176–3.310 mdyn $Å^{-1}$, justifying our choice. The force constant of the W–Cl bond was accepted as MMX default, while the experimental values are somewhat lower (1.73 mdyn $Å^{-1}$ [18]).

TABLE 2. Bond lengths and stretching force constants used in METMOD1

Bond type		k_s (mdyn $Å^{-1}$)	r_0 (Å)	μ (Debye)
C_c	W	5.96	1.877	0.506
C_c	H^*	4.40	1.100	−0.200
C	C^*	4.40	1.523	0.000
C_c	C^*	5.00	1.497	0.300
H	C^*	4.60	1.113	0.000
W	Cl_e	2.00	2.384	−2.081
W	Cl_a	2.00	2.384	−2.081

H^* was chosen as bridging hydrogen from the MMX type set, and its parameters are made identical with those of the hydrogen attached to an sp^2 carbon. The bond lengths for C^* are not different from those for an ordinary sp^3 carbon.

2.2.3. Bending parameters of METMOD1

While in the hydrocarbon part, the carbene carbon C_c is defined as an ordinary sp^2 carbon, the tungsten-containing bond angles are changed to those from average X-ray data. In five-coordinate species the $W{=}C_c{-}C$, $W{=}C_c{-}H$ and $H{-}C_c{-}H$ angles correspond to those of a normal organic sp^2 system. When α-hydrogen coordination is assumed, the $W{=}C_c{-}C^*$ and $W{=}C_c{-}H^*$ bond angles are set to 149.73° and 72.2° respectively [12a,c].

The chlorines are given angles ideal for an ordinary trigonal-bipyramidal structure (Table 3).

Force constants for $W{=}C_c{-}H^*$, $Cl{-}W{=}C_c$, and $Cl{-}W{-}Cl$ are made somewhat larger than MMX defaults to fit X-ray structures as closely as possible. For the same reason the k_b used for the $W{=}C_c{-}C^*$ angle (0.50) is smaller than that found for $Ta{-}C_c{-}C$ (0.596 Å) [11d].

TABLE 1. New atom types used in METMOD1 in addition to MMX

Element	Atom type	Description of atom type	r_{vdW} (Å)	ϵ (kcal mol^{-1})	MMX symbol replaced
W	31	tungsten	1.390	0.400	Ge
Cl_e	58	equatorial Cl	2.030	0.240	Z2
Cl_a	59	axial Cl	2.030	0.240	Z4
C_c	2	carbene C	1.940	0.044	C
H^*	32	coordinated H	1.500	0.047	Sn
C^*	33	α-C in coordination	1.900	0.044	Pb

Atom types C_{sp^3} (1), C_{sp^2} (2), and H (5) attached to C used as MMX defaults.

TABLE 3. Bond angles and bending force constants used in METMOD1

Angle type			k_b (mdyn Å rad^{-2})	θ_0 (degree)
C	C	C^*	0.45	109.47
H	C	C^*	0.36	109.39
C	C^*	C_c	0.45	109.47
H	C^*	C_c	0.36	109.39
C	C^*	H	0.36	109.39
H	C^*	H	0.32	109.40
C	C_c	W	0.55	130.00
C	C_c	H^*	0.36	118.20
W	C_c	H^*	0.40	72.20
W	C_c	C^*	0.50	149.73
H^*	C_c	C^*	0.36	138.07
H	C_c	W	0.36	115.00
H	C_c	H^*	0.36	119.00
C_c	W	Cl_e	0.50	100.00
C_c	W	Cl_a	0.50	95.00
Cl_a	W	Cl_a	0.30	170.50
Cl_e	W	Cl_e	0.30	135.00
Cl_e	W	Cl_a	0.30	88.50

2.2.4. *Stretching-bending and van der Waals parameters*

The MMX defaults are accepted and used unchanged in METMOD1.

2.2.5. *Dihedral angle parameters of METMOD1*

For the rotation of C_c–C, or C_c–C^*, bonds, the 1–1–2–2 or 5–1–2–2 MMX defaults are used.

From NMR data for five-coordinate carbene complexes [11d–11f] the activation energy barrier for the W=C_c rotation is assumed to be 15.6 kcal mol^{-1}, smaller than that found for four-coordinate species (16.8–21.6 kcal mol^{-1}) [12a]. Rotation around this bond involves eight interactions: *i.e.* in the case of an ethylidene carbene there are four H(H^*)–C_c=W–Cl interactions and four C(C^*)–C_c=W–Cl interactions. The two-fold barrier with respect to the equatorial chlorines has two maxima at 90° and −90°, and two minima at 0° and 180°; $V_2 > 0$, as is usual in the case of sp^2-sp^2 connections. In the case of the axial chlorines the two-fold barrier has two minima at 90° and −90°, and two maxima at 0° and 180°, $V_2 < 0$ (Table 4). The potential energy curve for the rotation around the W=C_c bonds is analogous to that for the equatorial isomer of $(CO)_4Fe{=}CH(OH)$ [11f].

2.2.6. *Electronic interaction energy*

Net atomic charges calculated by partial equalization of orbital electronegativity (PEOE) method [19] or their transformation to bond dipole moments [20] were used for parameterization. Orbital electronegativity values used for PEOE calculations are given in Table 5.

TABLE 4. Torsional parameters for METMOD1

Dihedral Angle type				Parameters (kcal mol^{-1})		
				V_1	V_2	V_3
C	C	C_c	W	−0.44	0.24	0.06
C	C	C_c	H^*	0.00	0.00	0.01
C	C^*	C_c	W	−0.44	0.24	0.06
C	C^*	C_c	H^*	0.00	0.00	0.01
C_c	C^*	C	H	0.00	0.00	0.50
H	C^*	C	H	0.00	0.00	0.24
H	C	C_c	W	0.00	0.00	−0.24
H	C	C_c	H^*	0.00	0.00	0.52
H	C^*	C_c	W	0.00	0.00	−0.24
H	C^*	C_c	H^*	0.00	0.00	0.52
C	C_c	W	Cl_e	0.00	1.95	0.00
C	C_c	W	Cl_a	0.00	−1.95	0.00
C^*	C_c	W	Cl_e	0.00	1.95	0.00
C^*	C_c	W	Cl_a	0.00	−1.95	0.00
H	C_c	W	Cl_e	0.00	1.95	0.00
H	C_c	W	Cl_a	0.00	−1.95	0.00
H^*	C_c	W	Cl_e	0.00	1.95	0.00
H^*	C_c	W	Cl_a	0.00	−1.95	0.00

2.2.7. *Ab initio calculations*

In an ideal case the METMOD1 structures of WCl_4CHR-type carbenes should be checked by comparison with appropriate X-ray structural data. Unfortunately such data are not yet available.

In order to provide some check on our molecular mechanical geometries, structures of the carbene complexes generated on entirely independent bases, such as *ab initio* calculations were used. The calculations were carried out by using GAMESS (Version 13 November 1992) quantum chemistry program [22]. All geometry optimizations were performed at the Restricted Hartree-Fock level utilizing the Stevens-Bach-Krauss (SBK) [23] basis set for the tungsten and the chlorine atoms, and STO 3G basis set for the others. Stationary points on the potential energy surfaces were located by the Schlegel method [24].

2.3. *Hardware*

An IBM AT 80386-33 MHz + 80387 arithmetic coprocessor was used for the structuring and a MicroVAX for the MM calculations. The *ab initio* calculations were performed by using IBM RISC6000 320H and Silicon Graphics Iris Indigo R3000 workstations.

TABLE 5. Parameters used for PEOE calculations

Atom type	$a_{i,v}$ (eV)	$b_{i,v}$ (eV)	$c_{i,v}$ (eV)	Reference
C sp^2	8.790	9.320	1.510	19
C sp^3	7.980	9.180	1.880	19
Cl	11.000	9.690	1.450	19
H	7.170	6.240	−0.560	19
W	4.378	5.806	1.836	21

3. Results and discussion

3.1. Testing the METMOD1 parameters

3.1.1. Methylidene–tungsten–tetrachloride

Methylidene–tungsten–tetrachloride is one of the simplest and more realistic tungsten(IV) carbenes that can be considered and actually generated *e.g.* [25]:

$WCl_6 + Sn(CH_3)_4 \rightarrow WCl_4CH_2 + CH_4.$

When Bertran *et al.* [14a] carried out their theoretical study, no structural data for this compound were available, and this is still true. Nevertheless, structural data for closely related carbene complexes can be found in the literature.

The *ab initio* calculation and each of our molecular mechanics studies indicate the preference of a trigonal-bipyramidal structure with the equatorial parallel carbene conformation [14a]. The W=C$_c$ and W–Cl bond lengths in the METMOD1 structure correspond well to those known from X-ray studies for tungstacarbenes, and the bond angles are close to the ideal values (Table 6).

If one of the α-H-s is assumed to be coordinated to the central metal atom, the W=C$_c$ bond length becomes shorter and W–Cl bond lengths longer, while the relative bond lengths of the equatorial and axial chlorines W–Cl$_e$/W–Cl$_a$ are reversed, making W–Cl$_a$ shorter. The W=C$_c$–H* angle is far from the experimental value. The idea of establishing one W...H bond and defining another α-H to get a better fit was rejected, however, since in the case of longer alkylidene groups the problem can be solved in another way (see later).

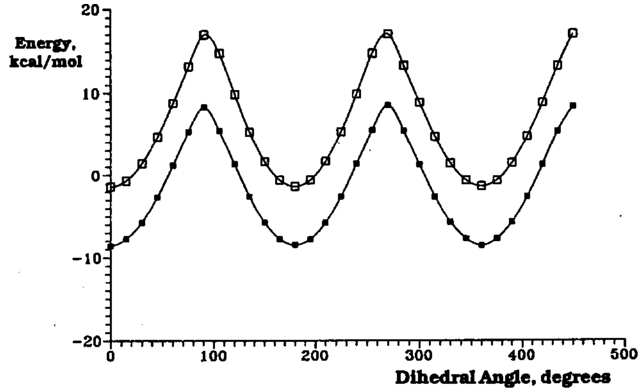

Fig. 1. Energy of rotation for WCl$_4$CH$_2$ complex (□ αH-coordinated, ■ αH-non-coordinated).

Instead of using the ROT-E conformational analysis option for the PCMODEL, the energy profile for the W=C$_c$ bond rotation was constructed by calculating the minimum energy content of 24 conformations with increasing dihedral angles, allowing the chlorines to relax after each rotational step (Fig. 1). The barrier about the W=C$_c$ bond, known experimentally for tungstacarbenes, is well reproduced. The equatorial perpendicular conformations correspond to the highest energy content, in agreement with the results of the *ab initio* calculations [14a]. The favoured equatorial parallel conformation is demonstrated in Fig. 2.

3.1.2. Ethylidene-and propylidene–tungsten–tetrachloride

Methylidene–tungsten–tetrachloride in the presence of linear chain olefins is easily converted into

TABLE 6. Geometrical parameters for the methylidene carbene complex

	METMOD1	METMOD1 αH-coordinated	MMX	*ab initio* [14]	GAMESS	Experimental	References
Bond lengths (Å)							
W=C$_c$	1.872	1.873	1.92	2.077	1.877	1.859, 1.882, 2.032	12, 15
W–Cl$_e$	2.365	2.367	2.44	2.464	2.320	2.389	12b–d
W–Cl$_a$	2.383	2.383	2.45	2.558	2.434	2.379	12c
Interatomic distances (Å)							
W...H	2.584	2.410	2.65	–	2.637	1.835	12a
Cl$_e$...H	3.339	3.094	3.92	–	3.403	–	–
Bond angles (degrees)							
Cl$_e$–W–Cl$_e$	146.56	145.69	115.85	135.4	145.80	120.0	a
Cl$_e$–W–Cl$_a$	88.66	88.61	89.96	88.9	88.22	90.0	a
Cl$_e$–W=C$_c$	106.72	107.15	133.74, 115.36	112.3	107.10	120.0	a
Cl$_a$–W=C$_c$	94.67	94.72	90.08	91.1	96.08	90.0	a
W=C$_c$–H	118.46	104.89	119.91	123.1	122.40	72.2	12a
Dihedral Angle (degrees)							
Cl$_e$–W=C$_c$–H	0.00	0.11	1.02	0.00	0.00	0.00	b

[a] Ideal trigonal-bipyramidal structure [b] C$_c$, W, H(H*), C(C*), Cl$_e$ are in equatorial plane [12,13,15]

other alkylidene carbenes, *e.g.* [26]:

$$WCl_4CH_2 + CH_3CH{=}CHCH_2CH_3 \rightleftharpoons WCl_4CHCH_2CH_3 + CH_2{=}CHCH_3$$

$$WCl_4CH_2 + CH_3CH{=}CHCH_2CH_3 \rightleftharpoons WCl_4CHCH_3 + CH_2{=}CHCH_2CH_3$$

Calculated data for $CH_3CH/CH_3CH_2CHWCl_4$ carbenes (*i.e.* the chain-carrying tungstacarbenes in the $WCl_6/SnMe_4$-initiated metathesis of 2-pentene) are given in Table 7, together with some relevant experimental data. There are no significant changes in the bond lengths and in the relative positions of the chlorine ligands upon variation of the hydrocarbon chain length, but there are more definite changes in the bond angles; these changes may be attributed to the relative bulk of the CH_3 and C_2H_5 groups.

A potential energy surface is defined by the rotation of the $W{=}C_c$ and $C_c{-}C$ bond (Fig. 3). The dihedral angel $\theta_1 = 0$ when the $C_c{-}H$ bond is eclipsed with the $Cl_e{-}W$ and $\theta_2 = 0$ when the C–H bond is eclipsed with the $W{=}C_c$ bond. The geometry optimization was performed for each of the θ_1 *vs.* θ_2 combinations (15° increment), and the intermediate points were generated by quadratic spline interpolation. The energy needed for the transformation can be read from the levels. Structures of the conformers and one of the transition states chosen for representation are also shown in Fig. 3. The distortion of the trigonal-bipyramidal structure at the highest energy (perpendicular carbene) conformation can be easily observed.

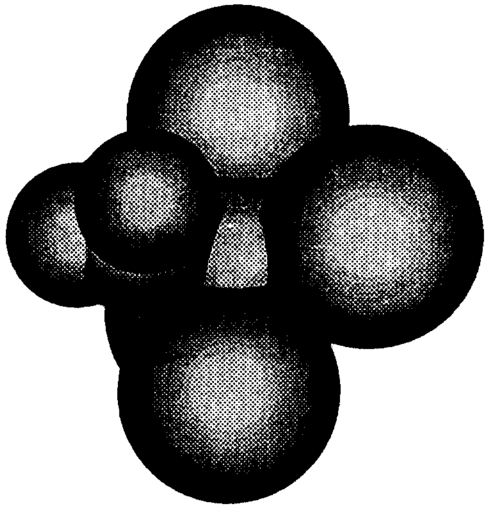

Fig. 2. CPK model and the WCl_4CH_2 complex calculated by METMOD1.

When the charge interaction or the dipole interaction is taken into account the E_{total} energy is increased, but because they have no effect on the geometry they can be ignored in this phase of the investigations.

The symmetrical energy profile is distorted when H-coordination is included (Fig. 4). The structure becomes much more rigid, the minima and the transitional states are more definite, and the $W{=}C_c$ barrier is increased by 1 kcal mol^{-1}.

Bond angles $H{-}C_c{-}C^*$ in H-coordinated carbene groups are much larger than those in the correspond-

TABLE 7. Geometrical parameters for WCl_4CHR ($R = CH_3/CH_2CH_3$) carbene complexes

	METMOD1	METMOD1 αH-coordinated	MMX	GAMESS	Experimental	References
Bond lengths (Å)						
$W{=}C_c$	1.873/1.872	1.876/1.976	1.92/1.92	1.897/1.897	1.859, 1.882, 2.032	12, 15
$W{-}Cl_e$	2.366/2.366	2.370/2.370	2.44/2.44	2.326/2.326	2.389	12b–d
$W{-}Cl_a$	2.383/2.383	2.385/2.385	2.45/2.45	2.445/2.445	2.379	12c
Interatomic distances (Å)						
W...H	2.514/2.514	1.918/1.919	2.65/2.65	2.562/2.570	1.835	12a
W...H	3.056/3.057	3.245/3.246	2.94/2.94	3.109/3.111	–	–
Cl_e...H	3.224/3.223	2.706/2.706	3.83/3.82	3.275/3.285	–	–
Cl_e...C	3.724/3.723	4.048/4.043	4.18/4.15	3.779/3.772	–	–
Bond angles (degrees)						
$Cl_e{-}W{-}Cl_e$	145.59/145.62	143.85/149.90	113.90/115.07	144.20/144.27	120.0	[a]
$Cl_e{-}W{-}Cl_a$	88.72/88.82	88.66/88.70	89.93/89.87	99.97/88.90	90.0	[a]
$Cl_e{-}W{=}C_c$	106.46/107.95	111.20/111.21	118.73/118.44	107.17/107.15	120.0	[a]
$Cl_a{-}W{=}C_c$	94.62/94.64	94.91/94.88	89.71/89.99	94.53/94.95	90.0	[a]
$W{=}C_c{-}C$	129.66/129.61	148.21/147.98	119.30/119.31	130.62/130.22	168.0, 140.6	12b, c
$W{=}C_c{-}H$	112.81/112.80	75.14/75.19	119.67/119.65	114.54/115.01	72.2	12a
Dihedral angles (degrees)						
$Cl_e{-}W{=}C_c{-}H$	0.00/1.19	0.10/0.21	1.75/0.84	0.03/2.250	0.0	[b]

[a] Ideal trigonal-bipyramidal structure [b] C_c, W, H(H*), C(C*), Cl_e are in equatorial plane [12,13,15].

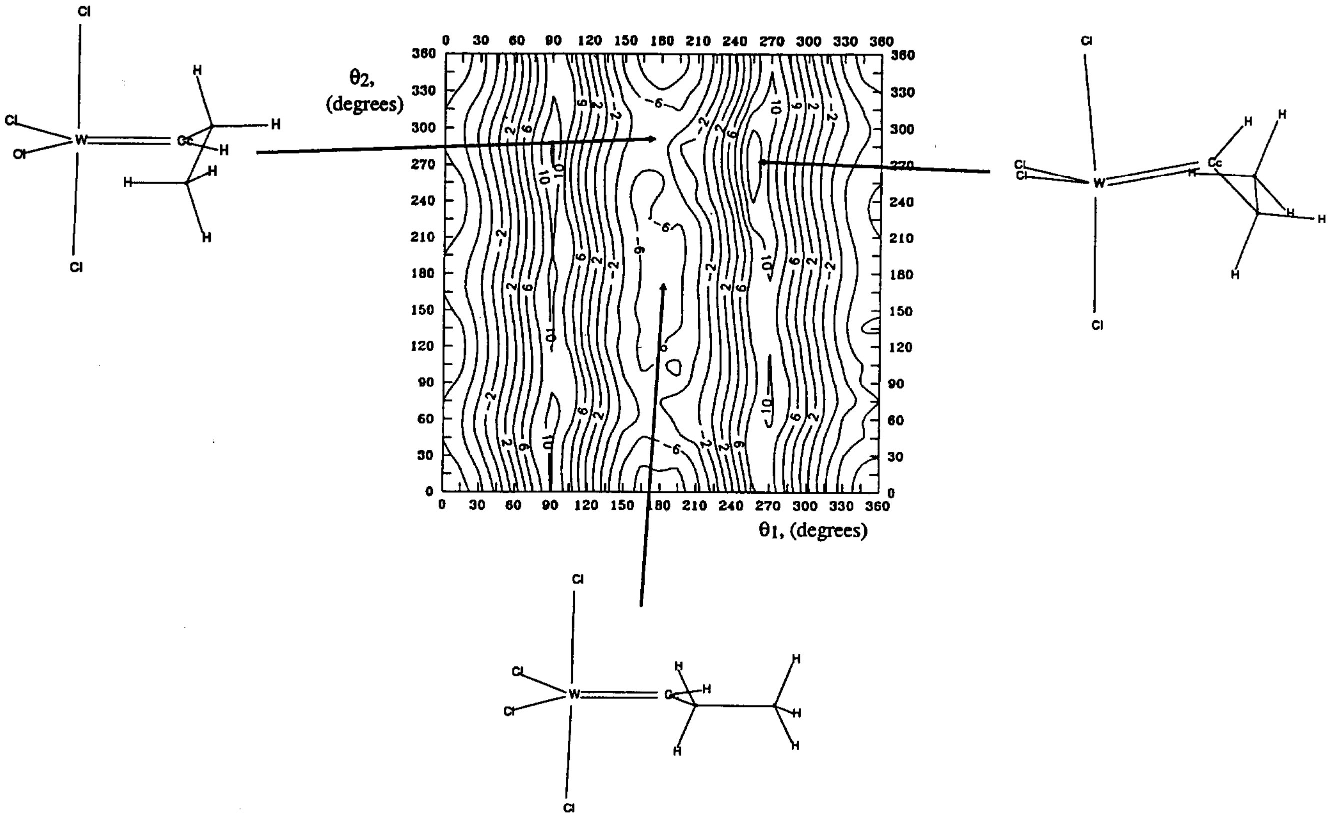

Fig. 3. Potential energy surface $E = f(\theta_1, \theta_2)$ for $WCl_4CHC_2H_5$ complex, and structures of chosen conformations.

ing methylene carbene. Positive net atomic charges accumulated on W and α-H do not seem to favour the W...H coordinative bond in these particular cases. This option will have an importance in the subsequent analyses of more complex and well-documented carbenes.

3.2. *Verifications of* METMODI

A model is generally verified by comparing the data with experimental information. However, the necessary experimental data are still missing, and so we at-

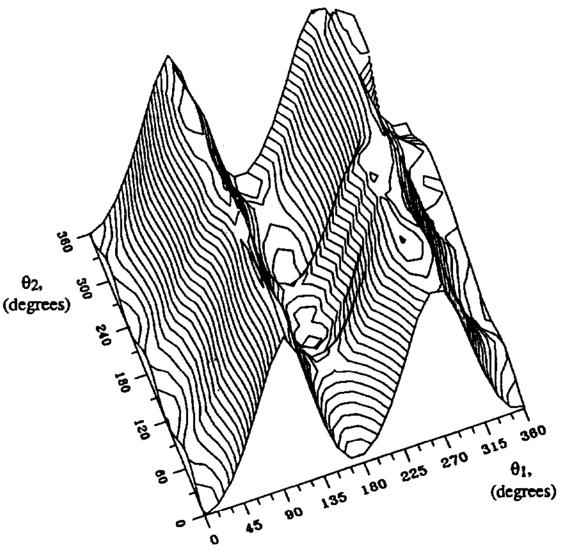

Fig. 4. Potential energy surface $E = f(\theta_1, \theta_2)$ for αH-coordinated complex WCl_4CHCH_3.

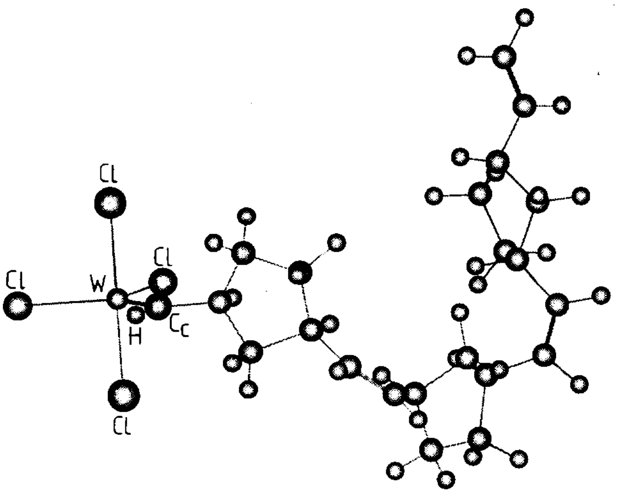

Fig. 5. METMODI structure of $WCl_4(=CHC_5H_8CH=)_3CH_2$ carbene.

tempted to find an independent method for the generation of the structure of $RCHWCl_4$-type carbenes, and so carried out *ab initio* calculations on them.

Geometric data derived from our *ab initio* calculations are given in Tables 6 and 7 under the heading of "GAMESS". Without making a detailed analysis of the data presented, it can be seen that our calculations support the previous assumption of the slightly distorted trigonal-bipyramidal structure with the equatorial parallel carbene conformation. The structural data are much closer to the relevant experimental data than were those obtained in earlier calculations [14a].

In a comparison of the corresponding *ab initio* and METMOD1 structures with inclusion of H atoms as well as the heavy atoms, the average error and the RMS value in the worst case ($R = C_2H_5$) were 0.054 Å and 0.057 Å respectively. When shorter hydrocarbon chains or only the heavy atoms are considered the match was even better (0.048 Å and 0.051 Å). RMS values below 0.1 Å are generally regarded as acceptable in molecular mechanics calculations [27].

The use of METMOD1 can be extended far beyond the above three carbenes. Combining large numbers of WCl_6-containing metathesis catalyst systems [1] with the various possible linear chain and/or cyclo-olefins results in a countless number of $RCHWCl_4$ carbenes. A propagating polymer carbene in a CH_2WCl_4-initiated polymerization of norbornene is shown as an example in Fig. 5.

The METMOD1 force field described above, when supplemented with some additional parameters [9], was found to reproduce the X-ray structures of the Osborn carbenes [13c] with excellent accuracy.

4. Conclusions

Our earlier studies indicated the potential of molecular mechanics for studying the origin of the stereoselectivity in olefin metathesis. To give improve these calculations for predicting product structures, a new force field treatment, termed METMOD1 has been developed. For that purpose the MMX force field of the PCMODEL is parametrized by fully experimental data for the treatment of metallacarbenes, π-complexes and metallacycles as reaction intermediates. In this first part of a planned series of papers, the refined and detailed version of the force fields of the WCl_4CHR ($R = H, CH_3$ or CH_2CH_3) carbenes formed in the $WCl_6/SnMe_4$-catalyzed metathesis reactions of 2-pentene is defined and tested. Six new atom types are introduced and four additional energy terms are introduced and parametrized for the calculations. Slightly distorted trigonal-bipyramidal structures with equatorial parallel carbene conformations are favoured for the active species. Bond lengths, rotation barriers and rotational profiles for $W{=}C_c$ bonds are in good agreement with the relevant experimental data. The validity of the METMOD1 force field is assessed by comparison with the results of *ab initio* calculations.

We believe that the goal of providing an easily excessible and versatile tool for laboratory chemists working in the field of olefin metathesis is fulfilled by METMOD1.

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References

1 (a) K.J. Ivin, *Olefin Metathesis*, Academic Press, London, 1983; (b) V. Dragutan, A.T. Balaban and M. Dimonie, *Olefin Metathesis and Ring-Opening Polymerization of Cyclo-Olefins*, John Wiley & Sons, Chichester, 1985.

2 (a) J.L. Herrison and Y. Chauvin, *Makromol. Chem.*, (1970) 141, 161; (b) T.J. Katz, J. McGinnis and C. Altus, *J. Am. Chem. Soc., 98* (1976) 606; (c) T.J. Katz and W.H. Hersh, *Tetrahedron Lett.*, (1977) 585; (d) T.J. Katz, S.J. Lee and M.A. Shippey, *J. Mol. Catal., 8* (1980) 219; (e) J. Kress, M. Wesolek and J.A. Osborn, *J. Chem. Soc., Chem. Commun.*, (1982) 514; (f) R. Schrock, S. Rocklage, J. Wengrovius, G. Rupprecht and J. Fellman, *J. Mol. Catal., 8* (1980) 73; (g) C.P. Casey and T.J. Burkhardt, *J. Am. Chem. Soc., 96* (1974) 7808; (h) J. McGinnis, T.J. Katz and S. Hurwitz, *J. Am. Chem. Soc., 98* (1976) 605.

3 (a) S. Furukawa, *Kogyo Kagaku Zasshi, 74* (1971) 2471; (b) E.S. Davie, D.A. Whan and J. Kemball, *J. Catal., 24* (1972) 272; (c) A. Ismayel-Milanovic, J.M. Basset, H. Praliaud, M. Dufaux and L. de Mourges, *J. Catal., 31* (1973) 408; (d) N. Calderon, E.A. Ofstead, J.P. Ward, W.A. Judy and K.W. Scott, *J. Am. Chem. Soc., 90* (1968) 4133; (e) J.L. Wang and H.R. Menapace, *J. Org. Chem., 33* (1968) 3794; (f) J.M. Basset, J.M. Bilhou, R. Mutin and J. Theolier, *J. Am. Chem. Soc., 97* (1975) 7376; (g) M. Leconte and J.M. Basset, *J. Am. Chem. Soc., 101* (1979) 7296; (h) M. Leconte and J.M. Basset, *Ann. N.Y. Aca and. Sci., 333* (1980) 165.

4 (a) G. Natta, G. Dall'Asta, G. Mazzanti and G. Motroni, *Macromol. Chem., 69* (1963) 163; (b) G. Natta, G. Dall'Asta and L. Porri, *Makromol. Chem., 81* (1965) 253; (c) T.J. Katz, J. McGinnis, S.J. Lee and N. Acton, *Tetrahedron Lett.*, (1976) 4246; (d) G. Dall'Asta and G. Motroni, *Angew. Makromol. Chem., 16/17* (1971) 51; (e) K.J. Ivin, L.-M. Lam and J.J. Rooney, *Makromol. Chem., 182* (1981) 1847; (f) H.H. Thoi, K.J. Ivin and J.J. Rooney, *J. Mol. Catal., 15* (1982) 245.

5 (a) J.-M. Basset, D. Boutarfa, E. Custodero, M. Leconte and C. Paillet, in Y. Imamoglu, B. Zumreoglu-Karan and A.J. Amass (eds.), *Olefin Metathesis and Polymerization Catalysts*, Kluwer Academic Publishers, Dordrecht, 1989, p. 45; (b) K.J. Ivin, in Y. Imamoglu, B. Zumreoglu-Karan and A.J. Amass (eds.), *Olefin Metathesis and Polymerization Catalysts*, Kluwer Academic Publishers, Dordrecht, 1989, p. 187.

6 R.M.E. Greene, K.J. Ivin, J. Kress, J.A. Osborn and J.J. Rooney, *Brit. Polym. J., 21* (1989) 237.

7 Serena Software, P.O. Box 3076, Bloomington, IN 47402-3076, USA.

8 (a) L. Bencze and R. Szilagyi, *J. Mol. Catal., 76* (1992) 145–156; (b) L. Bencze and R. Szilagyi, *NATO ASI Metal-Ligand Interactions: from Atoms, to Clusters, to Surfaces, Cetraro (I)*, June 10–22, 1991, Abstr. p. 37.

9 L. Bencze and R. Szilagyi, *Xth Int. Symp. on Olefin Metathesis and Polymerization (ISOM-10), Tihany June 27–July 2, 1993*, p. 77.

10 J.J. Gajewski, K.E. Gilbert and J. McKelvey, in D. Liotta (ed.), *Advances in Molecular Modelling*, JAI Press, London, 1990, Vol. 2, Chapter 2.

11 (a) R.R. Schrock, L.W. Messerle, C.D. Wood and L.J. Guggenberger, *J. Am. Chem. Soc., 100* (1978) 3973; (b) L.J. Guggenberger and R.R. Schrock, *J. Am. Chem. Soc., 97* (1975) 6578; (c) J. Kress and J.A. Osborn, *J. Am. Chem. Soc., 109* (1987) 3959; (d) J. Ushiro, H. Nakatsuji and T. Yonezawa, *J. Am. Chem. Soc., 106* (1984) 5892.

12 (a) J.H. Wengrovius, R.R. Schrock, M.R. Churchill and H.J. Wasserman, *J. Am. Chem. Soc., 104* (1982) 1739; (b) M.R. Churchill, A.L. Rheingold, W.J. Youngs, R.R. Schrock and J.H. Wengrovius, *J. Organomet. Chem., 204* (1981) C17; (c) M.R. Churchill, J.R. Missert and W.J. Youngs, *Inorg. Chem., 20* (1981) 3388; (d) M.R. Churchill and A.L. Rheingold, *Inorg. Chem., 21* (1982) 1357.

13 (a) C.P. Casey, A.J. Shusterman, W. Vollendorf and K.J. Haller, *J. Am. Chem. Soc., 104* (1982) 2417; (b) C.A. Toledano, J. Levisalles, M. Rudler, J.-C. Daran and Y. Jeannin, *J. Organomet. Chem., 228* (1982) C7; (c) M.T. Youniou, J. Kress, J. Fisher, A. Augero and J.A. Osborn, *J. Am. Chem. Soc., 110* (1988) 1488; (d) J. Kress, N. Wesolek and J.A. Osborn, *J. Chem. Soc., Chem. Commun.*, (1982) 514.

14 (a) M. Sodupe, J.M. Lluch, A. Oliva and J. Bertran, *Organometallics, 8* (1989) 1837; (b) T.R. Cundari and N.S. Gordon, *Organometallics, 11* (1992) 55.

15 A.K. Rappe and W.A. Goddard, *J. Am. Chem. Soc., 104* (1982) 448.

16 I. Feinstein-Jaffe, D. Gibson, S.J. Lippard, R.R. Schrock and A. Spool, *J. Am. Chem. Soc., 106* (1984) 6305.

17 E.B. Wilson, J.C. Decius and P.C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, 1955.

18 (a) D.M. Adams, *Metal Ligands and Related Vibrations*, Edward Arnold Publishers, London, 1967; (b) *Handbook of Chemistry and Physics*, 56th edn., CRC-Press, Boca Raton, Cleveland (1975).

19 (a) J. Gasteiger and M. Marsili, *Tetrahedron Lett., 34* (1978) 3181; (b) J. Gasteiger and M. Marsili, *Tetrahedron, 36* (1980) 3219.

20 (a) L. Dosen-Micovic, D. Jeremic and N.L. Allinger, *J. Am. Chem. Soc., 105* (1983) 1716; (b) L. Dosen-Micovic, D. Jeremic and N.L. Allinger, *J. Am. Chem. Soc., 105* (1983) 1723.

21 *Gmelin Handbook of Inorganic Chemistry*, 8th edn., Springer Verlag, Berlin, 1987; W, Supplement, Vol. A2, Physical properties.

22 M.W. Schmidt, K.K. Baldridge, J.A. Boatz, J.H. Jensen, S. Koseki, M.S. Gordon, K.A. Nguyen, T.L. Windus and S.T. Elbert, *GAMESS (General Atomic and Molecular Electronic Structure System), QCPE Bulletin, 10* (1990) 52.

23 M. Krauss, W.J. Stevens and H. Bach, unpublished results.

24 H.B. Schlegel, *J. Comput. Chem., 3* (1982) 214.

25 (a) N.B. Bespalova, E.D. Babich and V.M. Vdovin, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1979) 1403; (b) E. Thorn-Csanyi, *Angew. Makromol. Chem., 94* (1981) 181; (c) K.J. Ivin, D.T. Laverty, J.H. O'Donnell, J.J. Rooney and C.D. Steward, *Makromol. Chem., 180* (1979) 1989; (d) H.R. Grubbs and C.R. Hoppin, *J. Chem. Soc., Chem. Commun.*, (1977) 634.

26 (a) J.L. Bilhou, J.-M. Basset, R. Mutin and W.F. Graydon, *J. Chem. Soc., Chem. Commun.*, (1976) 970; (b) R.H.A. Bosma, X.D. Xu and J.C. Mol, *J. Mol. Catal., 15* (1982) 187.

27 K.A. Durkin, M.J. Sherrod and L. Dennis, in D. Liotta (ed.), *Advances in Molecular Modelling*, JAI Press, London, 1990, Vol. 2, Chapter 3.