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Molecular mechanical studies on the olefin metathesis reaction

III. * Modelling of the "well-defined" carbenes

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Abstract

A new force field termed METMOD had been originally constructed to simulate the carbene complexes that initiate the metathesis of cyclic and acyclic olefins with or without the application of a Lewis acid cocatalyst. The largest and most studied group of them are the so-called Osborn carbenes. They can be regarded as derivatives of the WX_4CR_2 (X ≡ Cl, Br or I; R ≡ H or alkyl group) carbenes in which one or more W–X bonds are substituted to W–O bonds, *e.g.* $WX_{4-n}(OY)_nCR_2$, where $n = 1$–4, Y ≡ R, SO_2CF_3 or $SiPh_3$. In the present part of the work the force field is extended to all the mononuclear Osborn carbenes and some other structures related to them. Trigonal bipyramidal (TBP) structures are proposed for these compounds in which the carbene ligand occupies an equatorial site with its two substituents and with the two neopentoxo groups lying in the trigonal plane of the TBP. Parameter development was based on experimental NMR, X-ray and IR data as well as on *ab-initio* calculations. METMOD1 is composed of 16 new atom types and 571 new data in addition to the MMX parameters, and it is used within the well-documented computational software of PCMODEL-PI V4.0. The general transition metal force field of the original software is abandoned while all the seven MMX interactions are turned on and parametrized. Simulated structures fit *ab initio* and X-ray structures with high accuracy. Experimental (NMR) rotational barriers for W=Cc bonds are simulated with an average error of 0.563 kcal mol^{-1}.

Key words: Tungsten; Ab initio; Carbene; Molecular mechanics; Olefin; Metathesis

1. Introduction

A large number of catalyst systems are known to initiate the metathesis of olefins [1]. There is overwhelming evidence that the transition metal carbenes generated *in situ* by these systems trigger the transalkylidenation of the olefins [2]. The structure of the products are in close relation to the structure of the active species. The theories developed to rationalize the experimental results are summarized in some excellent reviews [3]. The elucidation of the direct links is, however, rather difficult since the precise nature, number and relative position of the ligands round the central metal atom is seldom known. We believe that computational chemistry might help to overcome the problem until skilful preparative work fills this gap.

A new force field termed METMOD1 had been originally constructed to simulate the WCl_4CHR (R ≡ H or alkyl group) carbenes [4] formed in WCl_6–$SnMe_4$ initiated metathesis reactions and most probably in hundreds of catalytic systems in which WCl_6 is used as catalyst precursor [5]. In the past few years, several carbene complexes have been synthesized which initiated the metathesis of cyclic and acyclic olefins even alone, without the application of a Lewis acid cocatalyst. The largest and most studied group of them are the so-called Osborn carbenes [2e]. They can be regarded to be the derivatives of the WX_4CR_2 (X ≡ Cl, Br or I; R ≡ H or alkyl group) carbenes in which one or more W–X bonds are substituted for W–O bonds, *e.g.* $WX_{4-n}(OY)_nCR_2$, where n = 1–4, Y ≡ R, SO_2CF_3 or $SiPh_3$.

Most of these simple five-coordinated complexes are oil-soluble liquids. Their compositions and some of their structural features are well known and documented [6,7]. Therefore they would make the most

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* For Part II, see ref. 8.

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promising candidates for catalyst *vs.* product structure studies. In our previous work the X-ray structures of derivatives of an Osborn carbene $\{W[\overline{C(CH_2)_3C}H_2](OCH_2{}^tBu)_2Br_2\}_2$ (**1**) and $W[\overline{C(CH_2)_3C}H_2](OCH_2{}^tBu)_2Br_2 \cdot GaBr_3$ (**2**) [7] were studied to derive additional parameters to our METMODI force field [8].

The aim of this work is to extend the force field parameters now to all the mononuclear Osborn carbenes and structures related to them to provide an easily available tool for theoretical studies on complex carbenes and carbene-initiated catalytic reactions.

2. Experimental details

2.1. Software

METMODI parameters are used within the well-documeted computational software of PCMODEL-PI V4.0 [9]. The general transition metal force field of the original software is abandoned and all the seven MMX interactions turned on and parametrized [4a,b,8]. *Ab-initio* calculations were carried out using GAUSSIAN'92 [10].

2.2. Hardware

Silicon Graphics Iris Indigo R3000 and IBM RISC 6000 workstations were used to help the calculations.

2.3. Parametrization

Types and general formulae of the compounds parametrized are given in Scheme 1.

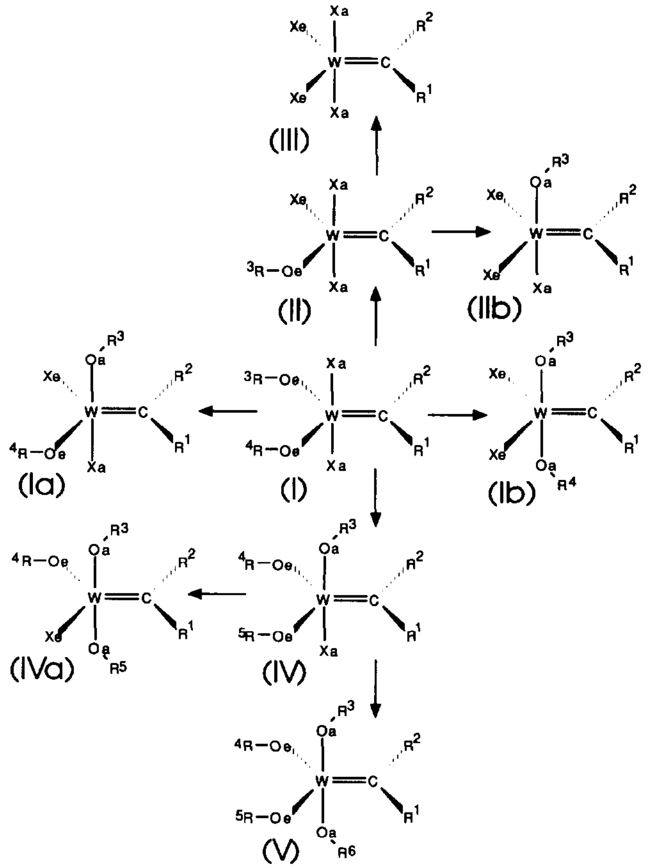
The fundamental compound of this work is represented by the general formula **I** since the compound $W[\overline{C(CH_2)_3C}H_2](OCH_2{}^tBu)_2Br_2$ (**3**) is the only one for which some closely relevant X-ray data are available [7].

On the basis of NMR and IR studies, trigonal bipyramidal (TBP) structures are proposed for these compounds in which the carbene ligand occupies an equatorial site with its two substituents and with the two neopentoxo groups lying in the equatorial plane. The bromine atoms Br_a are in the *trans* axial position. Basically similar structures apply for all the complexes covered in Scheme 1.

To model these compounds some new parameters are needed in addition to those already published in refs. 4b and 8.

The procedure applied for parametrization is shown in Scheme 2.

Actually only the Br_a–W–Br_a bond angle has to be defined as an additional parameter necessary to simulate the complexes of type **I**. Considering the relevant values of **1** and **2** as initial values, after optimization 178° was chosen as the parameter together with a relatively small force constant (0.35).



Scheme 1. Complexes modelled containing halo and/or alkoxo ligands.

In the tribromo derivatives (type **II**) one bromine atom is placed in an equatorial position and it is defined as a new atom type Br_e.

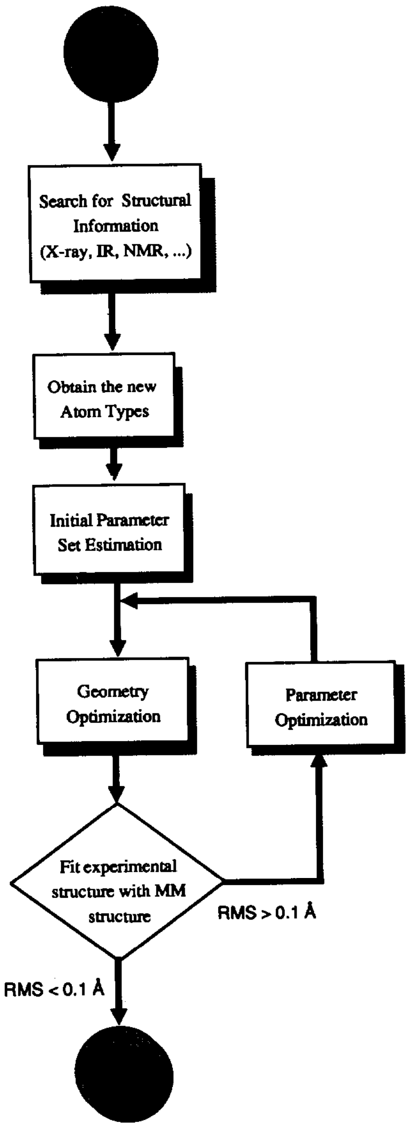
The bond length, the corresponding force constant and the r_{vdW} radius are identical with those of Br_a. A small increase in the r_{vdW} for Br_e resulted in enhanced accuracy.

The bond angle Br_e–W–O_e was chosen to be 140° to serve as a general parameter for all the compounds studied with the smallest average error.

Br_e–W–Br_a is close to but necessarily smaller than 90°.

To determine the ideal Br_e–W–C_c angle, comparison of the corresponding values in **1**, **2** and the *ab-initio* structure gave very reliable indications (Table 1). The earlier force constants were accepted unchanged.

Torsion angles and profiles for C_c=W bonds were fitted for the complexes by solving a linear first-order inhomogeneous equation system involving eight variables. Each variable was attributed to a particular interaction such as Br_e–W=C_c–C, Br_e–W=C_c–H, O_e–W=C_c–C etc. Parameters were optimized using NMR data published for eight to ten different Osborn carbenes [6].



Scheme 2. Parameter optimization procedure.

No quantitative data are available for rotation barrier around the W–O bond. On the basis of some qualitative information [11], electronic similarity may be found between the $W{=}C_c$ and the W–O bond; the W–O–C bond is straightening out like the $W{=}C_c{-}C$ bond (106.8° → 140.0°, and 120° → 140.0° respectively), indicating the double-bond character of the W–O bond. The profile of the W–O bond rotation is similar to that of the $W{=}C_c$ bond while the energy barriers were set to 40–50% of the latter.

Other torsion angles within the hydrocarbon group are used as MMX defaults.

The tetrabromo-tungstacarbenes (type **III**) are not Osborn carbenes by definition but genetically may be regarded as one of the a borderlines of Scheme 1.

Only one parameter has to be defined now, the $Br_e{-}W{-}Br_e$ bond angle. The parameter derived upon considering the available sources and optimization is set to 140°, equal to the $Br_e{-}W{-}Br_e$ angle.

Compounds of type **IV** may be derived from type **I** by substituting a bromine for an alkoxide ligand.

The third alkoxide ligand placed necessarily into axial position, and a new atom type, axial oxygen O_a, has to be defined therefore. The alkoxide group is computed with original MMX defaults but the MMX atom type of O_a is assigned for 58.

The W–O bond length and C–O–W bond angle defined earlier are assumed to be valid here, too.

The relative position of O_a with respect to the neighbouring ligands has to be determined by the corresponding bond angles.

The bond angles $Br_a{-}W{-}O_a$ and $O_a{-}W{-}O_a$ are derived from the corresponding Br–W–Br values and set to 175° and 88° respectively to emphasize the distortion of the ideal TBP structure.

Prior to optimization, numerous sources were considered (Table 1) for setting the bond angle for $O_a{-}W{-}C_c$ at 93°.

MMX defaults for torsion interactions of aliphatic ligands are used unchanged.

Torsion angles for $C{-}C_c{=}W{-}O_a$, $H{-}C_c{=}W{-}O_a$, $C{-}O_a{-}W{-}O_e$, $C{-}O_a{-}W{=}C_c$ and $C{-}O_a{-}W{-}Br_a$ were calculated as described above in connection with compound type II. The W–O rotation barrier is significantly lower in the axial position than in the equatorial position in [11].

The $C{-}O_a{-}W{-}O_e$ torsion interaction represents a peculiar case. The energy profile of the $O_a{-}W$ rotation has to be described with the usual equation of

$$F(\omega) = \tfrac{1}{2}V_1(1 + \cos\omega) + \tfrac{1}{2}V_2[1 - \cos(2\omega)] + \tfrac{1}{2}V_3[1 + \cos(3\omega)] + \dots$$

having a minimum at ±70° and at ±110° and a maximum at 0° and 140°.

Using five parts of the above equations would be more accurate for an efficient calculation of the profile, but the three parts provided by PCMODEL, where $V_1 = 0.5$, $V_2 = 1.0$ and $V_3 = 0.5$ still gives sufficiently good results. Detailed description of the calculation of the torsion parameters has been described elsewhere [12].

The tetraalkoxo-tungstacarbenes (type **V**) are the other extremes at the borderline of the Osborn carbenes. Two more parameters should be defined here. The $O_a{-}W{-}O_a$ bond angle and the $O_a{-}W{-}O_a{-}C$ torsion angle. Since no reliable data on the $O_a{-}W{-}O_a$ bond angle were found in the literature for carbene complexes, the $O_a{-}W{-}Br_a$ data were adapted by analogy. Parametrization of the torsion angle is fundamentally based on the $O_a{-}W{=}C_c{-}C$ by analogy, superimposing a new interaction ($V_1 > 0$) to keep the alkyl group of the alkoxid ligand away from the carbene.

TABLE 1. Data considered for bond angle parametrization

Geometry variable	WCl_4CHR-type carbene complexes				$WBr_2(OCH_2{}^tBu)[\overline{C(CH_2)_3CH_2}]$ derivatives			Angle (°), *Ab initio* structures of $WBr_4CR^1R^2$			
	Angle (°) k_b(mdyn $Å^{-1}$ deg^{-1})	Simulated angle (°)			Angle (°), X-rays		Angle (°) k_b(mdyn Å deg^{-1})	$R^1 = H$ $R^2 = H$	$R^1 = H$ $R^2 = CH_3$	$R^1 = H$ $R^2 = CH_2CH_3$	$R^1 = CH_3$ $R^2 = CH_3$
		$R = H$	$R = CH_3$	$R = CH_2CH_3$	Dimer	$GaBr_3$ adductum					
L_e-W-L_e	135.0 (0.30)	146.6	145.6	145.6	159.37(16)	159.13(24)	152.5 (0.52)	145.4	141.6	141.2	132.8
L_a-W-L_e	88.5 (0.30)	88.7	88.7	88.8	Br_c 91.93(45) Br_a 86.22(70)	Br_c 89.44(695) Br_a 95.59(18)	88.0 (0.31)	88.2(2)	α-H 89.3(1) α-C 88.5(0)	α-H 89.2(3) α-C 88.3(0)	89.6(2)
L_a-W-L_a	17.0 (0.3)	170.7	170.8	170.9	167.05(2)	166.83(3)	163.5 (0.60)	167.6	173.4	172.6	177.9
C_c=W-L_e	100.0 (0.50)	106.7	100.5	108.0	100.12(11)	98.06(123)	103.0 (0.41)	107.3(0)	α-H 108.5 α-C 109.9	α-H 108.4 α-C 110.4	113.6(1)
C_c=W-L_a	95.0 (0.50)	94.7	94.6	94.6	Br_c 92.39(18) Br_a 100.56(18)	Br_c 96.39(22) Br_a 96.76(22)	102.5 (0.40)	96.4(0)	93.2(2)	93.7(6)	91.1(2)

TABLE 2. Parameter set for $WBr_n(CR^1R^2)(OR^3)_{4-n}$ in addition to METMOD1

Symbol	Element	r_{vdW}	ε (kcal mol^{-1})
Br_e	13	2.680	0.478
O_a	58	1.740	0.050

Bond type		k_s (mdyn Å^{-1})	l_0 (Å)	μ (D)
A	B			
C	O_a	5.360	1.407	0.719
LP	O_a	4.500	0.600	−0.286
O_a	W	4.200	1.812	−1.234
Br_e	W	2.500	2.550	−1.894

Angle type			k_b (mdyn Å deg^{-2})	θ_0 (°)
A	B	C		
C	C	O_a	0.70	107.50 [a]
C	C	O_a	0.70	107.70 [b]
C	C	O_a	0.70	107.40 [c]
H	C	O_a	0.54	106.70
C	O_a	LP	0.10	105.16
LP	O_a	LP	0.24	131.00
LP	O_a	W	0.40	105.115
C	O_a	W	0.41	147.75
O_e	W	O_a	0.30	88.00
O_e	W	Br_e	0.30	140.00
O_a	W	C_c	0.50	93.00
O_a	W	O_a	0.50	175.00
O_a	W	Br_e	0.40	88.00
O_a	W	Br_a	0.40	175.00
Br_e	W	C_c	0.40	105.00
Br_e	W	Br_e	0.35	140.00
Br_e	W	Br_a	0.30	89.00
Br_a	W	Br_a	0.35	178.00

Dihedral angle type				Parameters (kcal mol^{-1})		
A	B	C	D	V_1	V_2	V_3
C	C	C	O_a	0.10	0.10	0.18
C	C	O_a	LP	0.00	0.00	0.00
C	C	O_a	W	0.40	0.52	0.467
C	C_c	W	O_a	0.00	3.73	0.00
C	C_c	W	Br_e	0.00	2.70	0.00
C_a	C_a	C_c	W	0.00	15.00	0.00
C_a	C_c	W	O_e	0.00	11.50	0.00
C_a	C_c	W	O_a	0.00	5.75	0.00
C_a	C_c	W	Br_a	0.00	5.75	0.00
H	C	C	O_a	0.00	0.00	0.18
H	C	O_a	W	0.00	0.00	0.53
H	C_c	W	O_a	0.00	7.47	0.00
H	C_c	W	Br_e	0.00	5.40	0.00
C	O_e	W	O_a	0.00	1.00	0.00
C	O_e	W	Cl_e	0.00	1.00	0.00
C	O_e	W	Cl_a	0.00	1.00	0.00
C	O_e	W	Br_e	0.00	1.00	0.00
C	O_a	W	C_c	0.00	3.00	0.00
C	O_a	W	O_e	0.50	1.00	0.50
C	O_a	W	O_a	0.00	0.50	0.00
C	O_a	W	Cl_e	0.50	1.00	0.50
C	O_a	W	Cl_a	0.00	1.00	0.00
C	O_a	W	Br_e	0.50	1.00	0.50
C	O_a	W	Br_a	0.00	1.00	0.00
[d]	[d]	O_a	LP	0.00	0.00	0.00

Notes to table 2:
[a] $>CR_2$ type.
[b] $>CRH$ type.
[c] $>CH_2$ type.
[d] Any atom.

There are some indications of the existence of positional isomers. In theory, excluding mirror images, type **I** compounds may have two isomers (**Ia** and **Ib**), and type **II** and **IV** may have one additional isomer each (**IIb** and **IVa** respectively). The Br_e–W–O_a bond angle is chosen to be equal to Br_e–W–Br_a and O_e–W–Br_a.

The Br_e–W–O_a–C torsion is analogous with the other W–O_a rotation profile and energy barriers (V_1,V_3 > 0; $V_2 < 1$; Table 2).

For the X ≡ Cl case the bond lengths have already been given [4b]. For the cases where X ≡ F and I the data from the literature and the *ab initio* data were used the same way as described for chlorine [13] (Table 3).

The bond angle parameters were determined corresponding to the atomic radii and the hardness of the elements involved.

All torsion parameters assigned to halide derivatives other than those of bromine were calculated as described for compounds of type II.

Electronic interactions were calculated by the PEOE method [14]. Tungsten parameters necessary for the calculation are listed in the first part of this series [4b]. Since isomers in this respect are essentially not different from the parent compound types, "only" 16 complexes had to be built for the calculation of the net atomic charges for F, Cl, Br and I derivatives. The results are summarized in Table 4.

It is worth mentioning that in the bond momentum calculation based on the equation

$$\mu = Cl_0(Q_i - Q_j)$$

the value $C = 2.835$ is generally used [15]. For some reason that is still unknown to us, in the case of the PCMODEL version used, $C = 4.73$ is adequate for obtaining the desired bond momentum.

Osborn carbenes containing Y groups other than hydrocarbons are listed in Scheme 3. X-ray structures for this kind of compound are not published. A good structure approximation may be achieved by adapting the corresponding C parameters to Si (Table 5).

For the CF_3SO_2 group the use of the parameters published in ref. 16 is supported.

3. Results and discussion

The majority of the Osborn carbenes are hydrocarbon-soluble liquids, except for the $W(CR^1R^2)$-

TABLE 3. Parameter set for $WX_n(CR^1R^2)(OR^3)_{4-n}$ in addition to METMOD1 (X = Cl, I or F)

Symbol	Element	r_{vdW} (Å)	ε (kcal mol^{-1})
F_a	61	1.650	0.078
I_e	14	2.750	0.714
I_a	62	2.320	0.424

Bond type		k_s (mdyn Å^{-1})	l_0 (Å)	μ (D)
A	B			
F_e	W	3.000	1.800	−2.500
F_a	W	3.000	1.800	−2.500
I_e	W	3.000	2.700	−1.977
I_a	W	3.000	2.700	−1.977

Angle type			k_b, (mdyn Å deg^{-2})	θ_0 (°)
A	B	C		
C_c	W	F_e	0.50	109.50
F_e	W	F_e	0.30	141.50
O_e	W	F_e	0.25	137.00
O_a	W	F_e	0.25	85.00
C_c	W	F_a	0.50	105.00
F_e	W	F_a	0.30	84.00
F_a	W	F_a	0.30	147.00
O_e	W	F_a	0.21	85.00
O_a	W	F_a	0.40	160.00
O_e	W	Cl_e	0.25	135.00
O_e	W	Cl_a	0.21	85.00
O_a	W	Cl_e	0.25	85.00
O_a	W	Cl_a	0.40	170.00
C_c	W	I_e	0.30	110.00
O_e	W	I_e	0.25	142.00
O_a	W	I_e	0.25	89.00
I_e	W	I_e	0.35	135.00
C_c	W	I_a	0.35	95.00
O_e	W	I_a	0.21	89.00
O_a	W	I_a	0.40	177.00
I_e	W	I_a	0.25	90.00
I_a	W	I_a	0.45	178.00

Dihedral angle type				Parameters (kcal mol^{-1})		
A	B	C	D	V_1	V_2	V_3
C	C_c	W	F_e	0.00	1.50	0.00
C	C_c	W	F_a	0.00	1.50	0.00
C	C_c	W	I_e	0.00	2.70	0.00
C	C_c	W	I_a	0.00	1.97	0.00
H	C_c	W	F_e	0.00	1.50	0.00
H	C_c	W	F_a	0.00	1.50	0.00
H	C_c	W	I_e	0.00	5.40	0.00
H	C_c	W	I_a	0.00	3.93	0.00
C	O_e	W	F_e	0.00	1.00	0.00
C	O_a	W	F_e	0.50	1.00	0.50
C	O_e	W	F_a	0.00	1.00	0.00
C	O_a	W	F_a	0.00	1.00	0.00
I_e	W	O_e	C	0.00	1.00	0.00
I_a	W	O_e	C	0.00	1.00	0.00
I_e	W	O_a	C	0.50	1.00	0.50
I_a	W	O_a	C	0.00	1.00	0.00

TABLE 4. Average net atomic charges calculated by the PEOE method for $W(CH^tBu)(OCH_2{}^tBu)_nX_{4-n}$ complexes

Atom	Net atomic charge			
	X = F	X = Cl	X = Br	X = I
W	1.100	0.784	0.701	0.684
X	−0.295	−0.185	−0.157	−0.152
C_c	0.015	−0.090	−0.113	−0.118
α-H	0.044	0.034	0.032	0.032

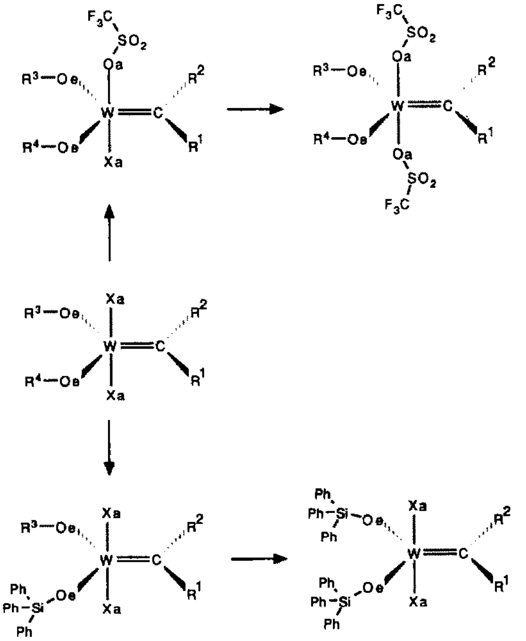
$(OCH_2{}^tBu)_2Br_2$-type complexes with tertiary carbene carbon, which are yellow powders. On the basis of NMR and IR studies, TBP structures are proposed for these compounds in which the carbene ligand occupies an equatorial site with its two substituents and with the two neopentoxo groups lying in the trigonal plane of the TBP [6].

3.1. Verification of the model

This group of carbenes is well documented but its parametrization is still a rather laborious task. The structure of compound $W[\overline{C(CH_2)_3C}H_2](OCH_2{}^tBu)_2Br_2$ (3) built by METMOD1 parameters is shown in Fig. 1.

The distortion of the TBP structure is very characteristic. The two axial ligands try to escape from the repulsing effect of the carbene group and force, even causing the two equatorial ligands to open up their O–W–O angle from 120° to about 155°.

While these carbene complexes seem to be monomeric in solution, the only X-ray diffraction study published so far shows 3 to be dimeric (1) in the solid state. The two pentacoordinated mononuclear units are weakly interacting via two long asymmetric tung-



Scheme 3. Complexes modelled containing CF_3SO_3 and Ph_3SiO ligands.

TABLE 5. Parameter set for $WX_n(CR^1R^2)(OR^3)_{4-n}$ in addition to METMOD1 extended complexes (X = F, Br, Cl or I; $R^3 = SO_2CF_3$ or $SiPh_3$)

Bond type A	Bond type B	k_s (mdyn Å^{-1})	l_0 (Å)	μ (D)
S	O_a	7.000	1.570	−1.000
Si	O_e	5.500	1.630	−0.400

Angle type A	Angle type B	Angle type C	k_b (mdyn Å deg^{-2})	θ_0 (°)
Si	O_e	LP	0.10	105.16
Si	O_e	W	0.41	147.75
S	O_a	LP	0.10	105.16
S	O_a	W	0.41	147.75
S	C	F	0.65	109.50
S	O	LP	0.50	120.00
C	S	O_a	0.45	109.00
O	S	O_a	0.45	117.00
C_c	Si	C_c	0.60	109.50
C_c	Si	O_e	0.40	110.20

Dihedral angle type A	B	C	D	Parameters (kcal mol^{-1}) V_1	V_2	V_3
C_a	C_a	C_a	Si	0.00	15.00	0.00
C_a	C_a	Si	C_a	0.10	0.00	0.50
C_a	C_a	Si	O_e	0.10	0.00	0.50
F	C	S	O_a	0.00	0.00	1.00
F	C	S	O	0.00	0.00	1.00
C	S	O	LP	0.00	0.00	0.00
O	S	O	LP	0.00	0.00	0.00
C	S	O_a	W	0.00	0.00	2.00
O	S	O_a	W	0.00	0.00	2.00
C_c	Si	O_e	W	0.00	0.00	0.20
C_c	W	O_e	Si	0.00	5.00	0.00
O_e	W	O_e	Si	0.00	0.50	0.00
F_a	W	O_e	Si	0.00	1.00	0.00
Cl_a	W	O_e	Si	0.00	1.00	0.00
Br_a	W	O_e	Si	0.00	1.00	0.00
I_a	W	O_e	Si	0.00	1.00	0.00
C_c	W	O_a	S	0.00	3.00	0.00
O_e	W	O_a	S	0.50	1.00	0.50
O_a	W	O_a	S	0.00	0.50	0.00
F_a	W	O_a	S	0.00	0.50	0.00
Cl_a	W	O_a	S	0.00	0.50	0.00
Br_a	W	O_a	S	0.00	1.00	0.00
I_a	W	O_a	S	0.00	0.50	0.00
C_c	Si	O_e	LP	0.00	0.00	0.00

sten-bromide bridges. Each tungsten atom thus possesses a slightly distorted octahedral coordination geometry in which the two neopentoxo oxygen atoms as well as the two bromo ligands are mutually *trans*, and the carbene carbon occupies the position *trans* to the W–Br bridge.

The other reliable source of information related to complexes type I is the X-ray structure of 2 that is a $GaBr_3$ adduct of 3. The molecular structure of 2 is analogous to that of the dimer, one pentacoordinate monomeric unit of 1 being replaced by a tricoordinate $GaBr_3$ group [6].

The most striking initial observation concerning the structures of 1 and 2 is their similarity. In both cases, tungsten atoms are hexacoordinate, but given the extremely long W...Br coordinate bond the complexes might be regarded as slightly perturbed pentacoordinated structures exposed to a weak sixth interaction. If we bear these structures in mind, our force field might be verified by comparing them with the METMOD1 structures.

The structure of the dimer (1) was built by orienting two (3) complexes properly to each other. The appropriate Br...W coordinating bonds were set by fixing the distance first at 10 Å. The distance was decreased stepwise and the energy of the structure was minimized after each step.

The system reached the steric energy minimum at the W...Br_a distance of 4 Å (Fig. 2) and in this position the atom type of the bridging bromine was changed to Br_c and the structure minimized to obtain the equilibrium structure of the model of 1 (Fig. 3).

The X-ray structure of 1 [6] was fitted to the model. Considering the seven central atoms of the monomeric units, the average fitting error and the r.m.s. are 0.053 Å and 0.061 Å respectively. Extending the number of atoms involved in the comparison the fitting errors rise above 0.1 Å. These alterations may not be fully attributed to the crystal packing effect and cannot be balanced without changing the original organic MMX parameters [8]. Fitting errors for comparing METMOD1 and X-ray structures of 2 are slightly larger than those of the dimer.

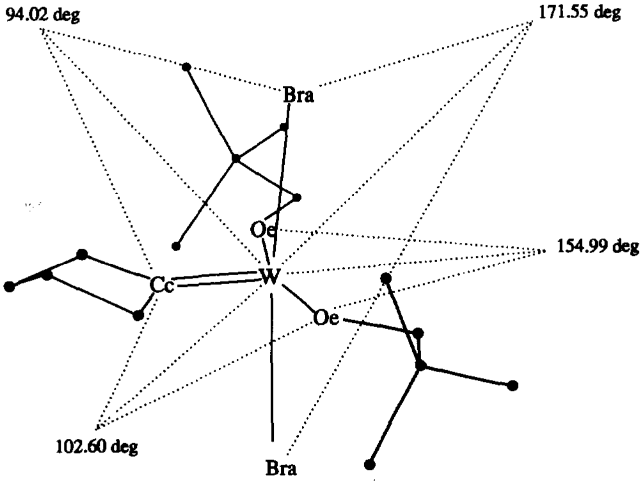


Fig. 1. Molecular structure of $W[\overline{C(CH_2)_3C}H_2]Br_2(OCH_2{}^t(Bu)_2$ (hydrogen atoms are omitted).

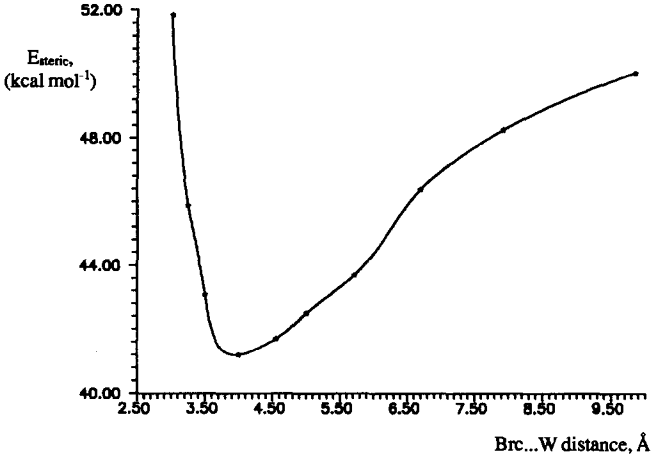


Fig. 2. Potential function of the 3 → 3 collision.

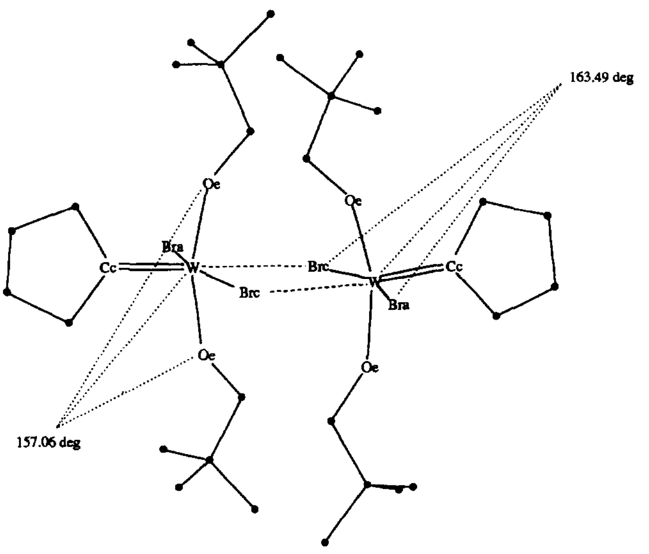


Fig. 3. METMOD1 structure of $\{W[\overline{C(CH_2)_3CH_2}]Br_2(OCH_2{}^tBu)_2\}_2$ (hydrogen atoms are omitted).

TABLE 7. Barrier heights of W=C_c bond rotation

Complex	Barrier height (kcal mol^{-1})	
	Calculated	Experimental
$W(CH^tBu)(OCH_2{}^tBu)_4$	8.06	8.0
$W(CH^tBu)(OCH_2{}^tBu)_3Br$	12.51	13.1
$W(CH^tBu)(OCH_2{}^tBu)_2Br_2$	17.27	17.2
$W[\overline{C(CH_2)_3CH_2}](OCH_2{}^tBu)_2Br_2$	21.42	23.0
$W(CH^tBu)(OCH_2{}^tBu)Br_3$	10.57	9.1 [a]

[a] Estimated value.

TABLE 8. Bond lengths (Å), bond angles (°) and dihedral angles (°) for $W(CH^tBu)(OCH_2{}^tBu)_2Br_2$ (4)

Bond lengths			
W–C_c	1.889(0)	W–Br_a	2.568(1)
W–O_e	1.824(3)		
Bond angles			
W=C_c–C	140.24(0)	O_e–W–O_e	150.97(0)
W–O_e–C	144.47; 151.33 [a]	O_e–W–Br_a	88.99(12)
C_c=W–O_e	98.96; 110.07 [a]	Br_a–W–Br_a	172.01(0)
C_c=W–Br_a	94.98(2)		
Dihedral angles			
C–C_c=W–O_e	0.53	C–O_e–W–O_e	−1.82
C–C_c=W–Br_a	90.85	C–O_e–W–Br_a	93.90
C–O_e–W=C_c	2.01		

[a] Next to the hydrocarbon group of the carbene ligand.

In fact, the monomeric unit of the dimer and the corresponding mononuclear complex (3) are very similar. It is interesting to note, however, how the Br–W–Br and O–W–O bonds behave under (163.5°, 157.0°; Fig. 3) or without (172.0°, 151.0°; Fig. 1) the influence of the sixth ligand.

Results of the fitting of the METMOD1 and *ab initio* structures for several F, Cl, Br and I carbene complexes are given in Table 6.

One-dimensional conformation analysis of the models was carried out for the W=C_c bond for five well-characterized Osborn carbenes. Experimental (NMR) rotation barriers are reproduced by our calculations with high accuracy (Table 7).

3.2. Application of the model

Numerous Osborn carbenes have been isolated [5] and several more were detected and identified within

TABLE 6. Results of fitting the $WX_4CR^1R^2$ models with *ab-initio* structures

R^1; R^2	R.M.S. fitting error (Å)							
	X = F		X = Cl		X = Br		X = I	
	All atoms	α atoms [a]	All atoms	α atoms [a]	All atoms	α atoms [a]	All atoms	α atoms [a]
H; H	0.048	0.052	0.050	0.051	0.091	0.079	0.095	0.090
H; CH_3	0.079	0.045	0.052	0.050	0.063	0.047	0.066	0.049
H; CH_2CH_3	0.074	0.045	0.072	0.052	0.086	0.045	0.108	0.053
CH_3; CH_3	0.054	0.065	0.072	0.068	0.063	0.078	0.061	0.074

[a] α atoms: W, and C_c, X_{e_1}, X_{e_2}, X_{a_1}, X_{a_2} atoms directly bonded to tungsten.

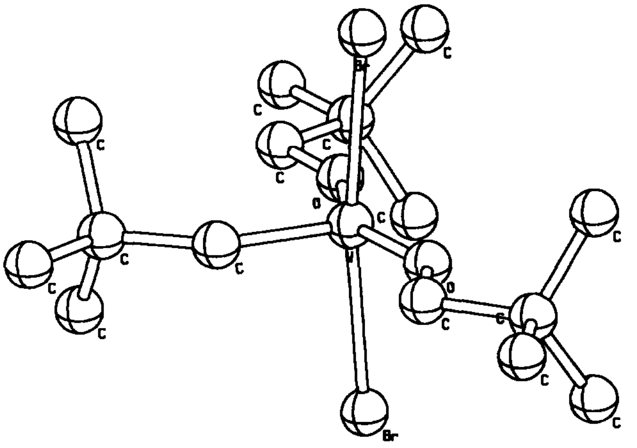


Fig. 4. ORTEP view of W(CH^{t}Bu) Br$_2$(OCH$_2$^{t}Bu)$_2$ complex.

catalytic conditions [17]. Using the METMODI force field, reliable molecular structures may be derived and used in various studies and in forecasting physical properties.

Geometric data derived by the model for one of the most frequently employed carbene complex catalysts (**4**) are given in Table 8 and Figure 4. We believe that these kinds of model are adequate and might be used until skilful preparative work and subsequent X-ray investigations provide the necessary corrections.

The use of the models is aimed mostly at the study of the homogeneous catalytic reactions of the carbenes in metathesis and other reactions as initiators and chain carriers. Having the reliable structures, the interactions of the catalysts and the monomers may be simulated and the most probable products described.

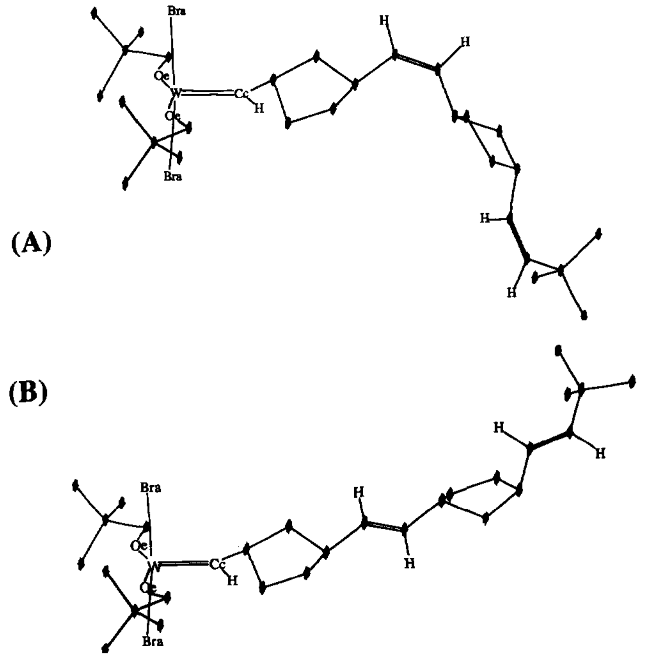


Fig. 5. (A) P_2CC and (B) P_2TT propagating carbene complexes.

The models of two propagating carbenes detected in the ring-opening polymerization of norbornene [17] are shown in Fig. 5 as examples.

Compound **A** is a living carbene in which both the initial step and the first propagating step resulted in *cis* double-bond formation, while in compound **B** both C, C-double bonds formed in the ring-opening reactions are *trans*. Detailed conformation analysis of such structures will hopefully help to describe the intimate details of the primary (propagation) and secondary (*e.g.* degradation) reactions and the probability of their occurrences, as well.

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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*, Wiley, Chichester, West Sussex, 1985.

2 (a) J.L. Herrison and Y. Chauvin, *Makromol. Chem.*, *161* (1970) 141; (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) 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, Dordrecht, 1989, p. 45; (b) K.J. Ivin, in Imamoglu, B. Zumreoglu-Karan and A.J. Amass (eds.), *Olefin Metathesis and Polymerization Catalysts*, Kluwer, Dordrecht, 1989 p. 187.

4 (a) L. Bencze and R. Szilagyi, *J. Mol. Catal.*, *76* (1992) 14; (b) L. Bencze and R. Szilagyi, *J. Organomet. Chem.*, *465* (1994) 211.

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

6 J. Kress and J.A. Osborn, *J. Am. Chem. Soc.*, *109* (1987) 3953.

7 M.T. Youinou, J. Kress, J. Fisher, A. Augero and J.A. Osborn, *J. Am. Chem. Soc.*, *110* (1988) 1488.

8 L. Bencze and R. Szilagyi, *J. Mol. Catal.*, (1994) in press.

9 Serena Software, P.O. Box 3076, Bloomington, IN.

10 M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W.Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. Defrees, J. Baker, J.J.P. Stewart and J.A. Pople, GAUSSIAN 92, Revision C, Gaussian, Inc., Pittsburgh, PA, 1992.

11 (a) P.J. Blower, M.H. Chisholm, D.L. Clark and B.W. Eichhorn, *Organometallics, 5* (1986) 2125; (b) A.R. Rossi and R. Hoffmann, *Inorg. Chem., 14* (1975) 365.

12 L. Bencze and R. Szilagyi, to be published.

13 F.A. Cotton, W. Schwotzer and E.S. Shamshoum, *Inorg. Chem., 23* (1984) 4111.

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

15 S. Wolfe, D.F. Weaver and K. Yang, *Can. J. Chem., 66* (1988) 2687

16 J.P. Bowen, and N.L. Allinger, *J. Am. Chem. Soc. 106* (1984) 765

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

Appendix A: Nomenclature

Atom types

H	aliphatic hydrogen
C	sp^3 carbon
C_a	aromatic carbon
W	tungsten
C_c	carbene carbon
Br_a	axial bromine
Br_e	equatorial bromine
Br_c	bridging bromine
O_a	axial oxygen
O_e	equatorial oxygen
LP	lone pair

MM parameters

k_b	bending force constant (mdyn $Å^{-1}$ deg^{-1})
k_s	stretching force constant (mdyn $Å^{-1}$)
l_0	strain-free bond length (Å)
r_{vdW}	van der Waals radius (Å)
V_i	i-fold rotational barrier (kcal mol^{-1})
ε	hardness (kcal mol^{-1})
θ_0	strain-free bond angle (°)
μ	bond dipole moment (D)