Addition of a Carbonyl Functionality to Titanium Carbenes. A Study of the Mechanism and Intermediates in the Tebbe Reaction[†]

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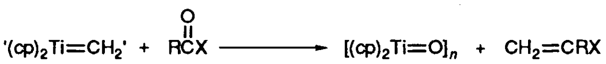
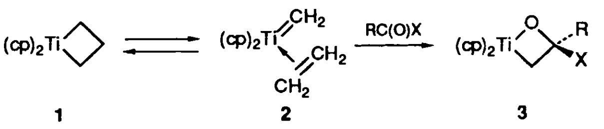
The Tebbe transformation of carbonylic substrates such as aldehydes, ketones, esters and amides into alkenes has been analysed theoretically. The active complex in the Tebbe reaction was modelled by various $X_2Ti{=}CH_2$ ($X = \eta^5\text{-}C_5H_5$, H or Cl) complexes. The extended-Hückel approach was used to obtain a qualitative molecular orbital interaction picture of the reaction giving the expected titanaoxetane intermediate. A concerted path is proposed. A formally $2\pi + 2\pi$ reaction path is made allowed due to the existence of a very polarized titanium–carbon π-type orbital (highest occupied molecular orbital) providing two electrons more for the cycloaddition. The geometrical structures of the titanaoxetanes were analysed by extended-Hückel, semiempirical as well as *ab initio* methods. These indicate that the four-membered ring will take a planar geometry, as puckering of the metallacycle results in weakning of the titanium–oxygen bond. A comparison of the 4- and 3-*exo*-methylenetitanaoxetane isomers revealed that the former is the most stable.

The organometallic parallel to the organic Wittig reaction is the Tebbe reaction[1] where the oxygen atom of a carbonyl function is exchanged by the alkylidene group of a titanium carbene complex,[2] as outlined in Scheme 1. The source of the titanium alkylidene is usually a titanacyclobutane compound **1**,[3] or Tebbe's reagent, $[(cp)_2\overline{TiClCH_2Al}Me]$,[1] of which the former has been proposed to be in equilibrium with a titanium–alkylidene–alkene complex **2** (Scheme 2). The addition of organic substrates such as aldehydes, ketones, esters or amides RC(O)X (X = H, R′, OR′ or NR'_2) to **1** is proposed to lead to the formation of titanaoxetanes, $(cp)_2\overline{TiCH_2CR(X)O}$ **3**, from which the alkene and $[(cp)_2Ti{=}O]_n$ are formed.[2d]

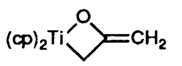


$$\text{'}(cp)_2Ti{=}CH_2\text{'} + R\overset{O}{\overset{\parallel}{C}}X \longrightarrow [(cp)_2Ti{=}O]_n + CH_2{=}CRX$$

Scheme 1 cp = $\eta^5\text{-}C_5H_5$; X = H, R′, OR′ or NR'_2



Scheme 2



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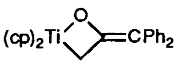

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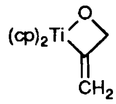

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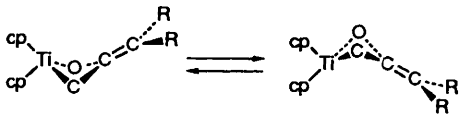

4a R = H **4b**
5a R = Ph **5b**

Metallaoxetanes, such as **3**, have been proposed as intermediates in various transition-metal catalysed oxygen-transfer reactions.[4,5] A few metallaoxetanes, with the metal ranging from the early to the late transition metals, have been characterized from X-ray crystallographic investigations.[6] Still, the existence of metallaoxetanes in oxygen-transfer reactions is a subject of intense debate.[5] Two metallaoxetanes formed in the reaction of transition-metal carbenes (metal = tantalum and molybdenum) with various aldehydes have very recently been characterized by X-ray methods.[6a,b] According to our knowledge no titanaoxetanes have yet been structurally characterized. However, the formation of titanaoxetane **3**, as an intermediate in Scheme 1, has been studied by NMR spectroscopy.[7,8] Grubbs and co-workers[7] studied the structure of the 4-*exo*-methylenetitanaoxetanes **4** and **5** by NMR spectroscopy at several temperatures. They prepared **4** and **5** either by reaction of a titanium ketene with dimethylsulfonium methanide (**4**) or by exchange of a ketene with the alkene of 3-*tert*-butyltitanacyclobutane (**5**).[7]

Reaction of $(cp)_2Ti{=}C{=}CR_2$ with ketones or aldehydes has been proposed to involve the formation of the isomeric 3-*exo*-methylenetitanaoxetane complex **6**.[2c] However, this was not detectable by NMR spectroscopy, as are the 4-*exo*-methylene substituted compounds **4** and **5**.

From the NMR investigations it was suggested that the four-membered rings of compounds **4** and **5** are puckered.[7,8] The interconversion of the two puckered conformers, **4a** ⟶ **4b** and **5a** ⟶ **5b**, respectively, by ring flips was found by dynamic NMR spectroscopy to have activation energies of 13 and 19 kcal mol^{-1}.[7] Grubbs and co-workers[7] suggested that the puckering is due to donation of lone-pair electrons from the oxygen atom of the titanaoxetane into one of the empty orbitals of titanium and that it is required to obtain a better overlap between these two atoms.

This puckering of compounds **4** and **5** is a significant structural difference from the other characterized metallaoxetanes, as these generally are found to have ring structures that are very close to planar.[6] The observed small deviations from planarity in some of these systems are suggested to be caused by steric repulsion between the ligands at the metal atom and the substituents on the carbon atom in the 4-position of the metallacycle.[6a,b] Two metallaoxetanes have been prepared by

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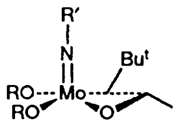
[†] *Non-SI units employed:* cal = 4.184 J, eV ≈ 1.60×10^{-19} J, au ≈ 4.36×10^{-18} J.

reaction of an early transition-metal carbene complex with appropriate aldehydes, giving $(RO)_2(R'N)\overline{MoCH(Bu^t)CH(Ph_F)O}$ 7[6b] and O-*anti*-$\overline{(\eta^5\text{-}C_5Me_5)_2MeTaCH_2CH(Ph)O}$ 8.[6a] These complexes have internal angles that add up to 354 and 355°, respectively, indicating almost planar structures. Furthermore, a dynamic NMR analysis of $(\eta^5\text{-}C_5Me_5)_2Me\overline{TaCH_2CH_2O}$ indicates a planar metallacyclic ring.[6a]



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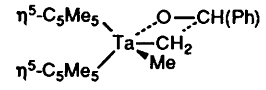

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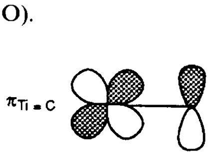
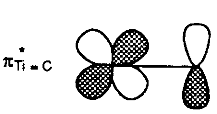
In the present work we want to address the following questions from theoretical observations: (*i*) how does a carbonyl functionality add to the titanium–carbene moiety?; (*ii*) what is the structure of the titanaoxetanes and (*iii*) are the titanaoxetanes puckered from electronic reasons? First, we have used the extended-Hückel[9] approach to describe the addition of the carbonyl function to a titanium–carbene moiety from a frontier-orbital point of view and to analyse possible distortions from planarity of the 4-*exo*-methylenetitanaoxetane structure. Secondly, we have performed a series of semiempirical[10] and *ab initio* calculations[11] on different titanaoxetanes, to obtain more detailed information regarding these questions.

Results and Discussion

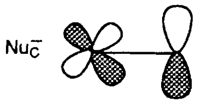
Extended-Hückel Calculations.—Although no titanium carbenes have been structurally characterized, they are believed to be important intermediates in the Tebbe reaction.[2] We will use $(cp)_2Ti{=}CH_2$ as a model for the titanium carbene that reacts with carbonylic substrates, the latter being modelled by formaldehyde. The titanium–carbon bond length of $(cp)_2Ti{=}CH_2$ was estimated from total-energy calculations to be 1.74 Å. In a generalized valence bond analysis of $(cp)_2Ti{=}CH_2$ reacting with alkenes this distance was set to 1.88 Å.[12] The exact distance is not important in this part of the study as we want to develop a qualitative orbital interaction picture. The structure of formaldehyde was taken from literature data,[13] and the $(cp)_2Ti$ fragment is similar to those in other bis(cyclopentadienyl)titanium complexes.[3b] The frontier orbitals of $(cp)_2Ti{=}CH_2$ are the expected $\pi_{Ti=C}$ (I) and $\pi^*_{Ti=C}$ (II) as the two HOMO (highest occupied molecular orbital) and two LUMO (lowest unoccupied molecular orbital), together with two strongly polarized orbitals.[12] These are shown in **III** (HOMO) and **IV** (LUMO).



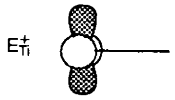
I



II



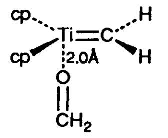
III



IV

It is seen that the HOMO of $(cp)_2Ti{=}CH_2$, *i.e.* **III**, is largely polarized towards the methylene carbon atom, thereby rationalizing the well known nucleophilic character of Schrock-type carbenes[2f,g] by this orbital, and we designate it Nu_C^-. The LUMO is largely located on titanium, and is labelled E_{Ti}^+. Six approaches of formaldehyde to the titanium carbene fragment have been examined, all with a titanium–oxygen separation kept at 2.0 Å in order to be able to compare the different pathways of approach. The total energies of the various approaches are indicated in **V**–**X** together with the most important intermolecular distances.

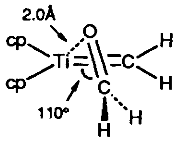
'End on'



$E = -1284.98$ eV

V

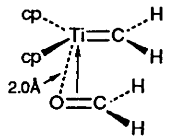
$2\pi_s + 2\pi_a$



$E = -1276.63$ eV

VI

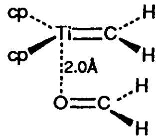
'Side on'



$E = -1280.54$ eV

VII

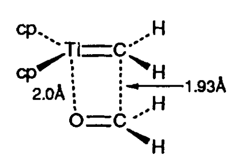
$2\pi + 2\pi$(Ti–O)



$E = -1284.02$ eV

VIII

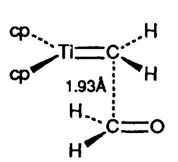
$2\pi + 2\pi$(C–C)



$E = -1284.12$ eV

IX

'Betaine'

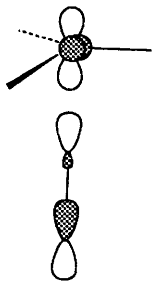


$E = -1283.18$ eV

X

The lowest energy is found for the end-on approach, **V**, where the interaction between the two molecules is favoured by a stabilization of the titanium atom by an oxygen lone pair. This approach therefore represents a likely geometry of an initial interaction between the two molecules involved in the Tebbe reaction as it is only stabilized by 0.06 eV (≈ 1.4 kcal mol^{-1}) relative to the separated molecules. The five structures **VI**–**X** represent intermediates that, by a first glance, could be thought of as involved in the titanaoxetane formation. Formally, the reaction looks like a $2\pi + 2\pi$ cycloaddition, which in order to be allowed should be $2\pi_s + 2\pi_a$,[14] but this precursor, **VI**, is disfavoured by as much as 8 eV (≈ 184 kcal mol^{-1}) and is thus not considered further. The side-on approach shown in **VII**, where the distances from the titanium atom to the carbon and oxygen atoms are equal, is also disregarded from an energetic point of view. The two $2\pi_s + 2\pi_s$ approaches, **VIII** and **IX**, are on the other hand only slightly higher in energy than the preliminary end-on interaction **V**. Finally, a 'betaine' structure similar to the intermediate in the Corey–Chaykovsky transformation of aldehydes to epoxides by sulfur ylides[15] is considered, **X**. This approach is only unfavourable by ≈ 22 kcal mol^{-1} compared to the $2\pi_s + 2\pi_s$ interactions (**VIII** and **IX**), giving an overall instability of ≈ 43 kcal mol^{-1} when compared to the separated molecules. We will focus on structures **V** and **IX**, although **X** cannot be excluded from the energetics above. An orbital picture of the end-on interaction **V** is shown in **XI**.

It is found that the stabilization is mainly caused by donation of electron density from the oxygen lone-pair orbital of formaldehyde to E_{Ti}^+. The former is depleted by 0.21 electron, whereas the latter receives 0.38 electron indicating the electrophilicity of the titanium atom. A titanium-oxygen overlap population of 0.271 is calculated for **XI**. This approach of the aldehyde to $(cp)_2Ti{=}CH_2$ is very similar to the path proposed for the addition of aldehydes to $[Ta(\eta^5\text{-}C_5Me_5)_2(CH_2)Me]$.[16]



XI

The next step in the reaction must be the formation of the titanaoxetane through a tilting of formaldehyde and we will here focus on **IX**. An orbital interaction diagram of this carbon-based $2\pi_s + 2\pi_s$ approach is outlined in Fig. 1. The interaction is rather complex due to the very low symmetry of the system. The Nu_C^- orbital interacts with the LUMO of formaldehyde, the bonding combination is found as the HOMO of **IX**, in which the C–C bonding characteristics dominate; with an overall overlap population of 0.292. The E_{Ti}^+ orbital is also involved in bonding as it interacts strongly with the $\pi_{C=O}$ orbital of formaldehyde. The bonding combination is shown at the bottom centre of Fig. 1 and it is seen that this combination primarily forms the titanium–oxygen bond (overlap population 0.234). The titanium–carbon π-type orbitals are also involved in the bonding as the Ti=C bond is weakened considerably as indicated by the overlap population decrease from 0.811 to 0.611. This weakening is primarily due to a depletion of electrons from $\pi_{Ti=C}$ (0.19 electron lost). From this qualitative orbital picture the reaction can now be formulated in either of two ways. First, we can see that what first looked to be a $2\pi + 2\pi$ reaction is actually a six-electron reaction because Nu_C^- is involved in the bonding. Secondly, the two new bonds (titanium–oxygen and carbon–carbon) result from different orbital interactions, a 'non-symmetric' concerted cycloaddition. This phenomenon can be explained by the hard and soft acids and bases (HSAB) theory,[17] as the bond between the two hard atoms (hard acid, Ti; hard base, O) is a result of an interaction of E_{Ti}^+ and $\pi_{C=O}$, which have a large separation in orbital energies. The carbon–carbon bond, as described above, occurs primarily through interaction of the orbitals Nu_C^- (soft base) and π_{CO}^*, where the carbon atom has soft acid characteristics.

The role of the metal can thus be to 'catalyse' a formally forbidden reaction: the reaction of $(cp)_2Ti{=}CH_2$ with RC(O)X is in principle $2\pi_s + 2\pi_s$, a forbidden reaction,[14] but the presence of titanium generates a HOMO of $(cp)_2Ti{=}CH_2$ which is mainly located at the carbon atom. This orbital is also involved in the reaction, changing it from a four- to a formally six-electron reaction, thus making it allowed.[14] The idea of using transition metals for making forbidden reactions allowed has also been introduced in some similar types of reactions, where oxygen atoms are transferred from oxometal complexes to alkenes[18] and in the reduction of epoxides by low-valent early transition-metal complexes.[19]

The HSAB formulation of the reaction is further stimulated by following the changes in atomic charges that are calculated on going from the separated molecules to **IX**. The general feature in HSAB theory that hard–hard interaction only involves small charge changes[17] is seen here, whereas the soft–soft interaction has more covalant character as ≈0.25 electron is transferred, **XII**. The titanaoxetane, $(cp)_2\overline{TiCH_2CH_2O}$, resulting from **IX** is favoured by 2.3 eV (≈53 kcal mol^{-1}) compared to **IX**, but unstable towards elimination of ethylene by several eV. The overall activation energy for the addition of formaldehyde to $(cp)_2Ti{=}CH_2$ is thus, in the extended-Hückel approximation, ≈0.9 eV (21 kcal mol^{-1}).

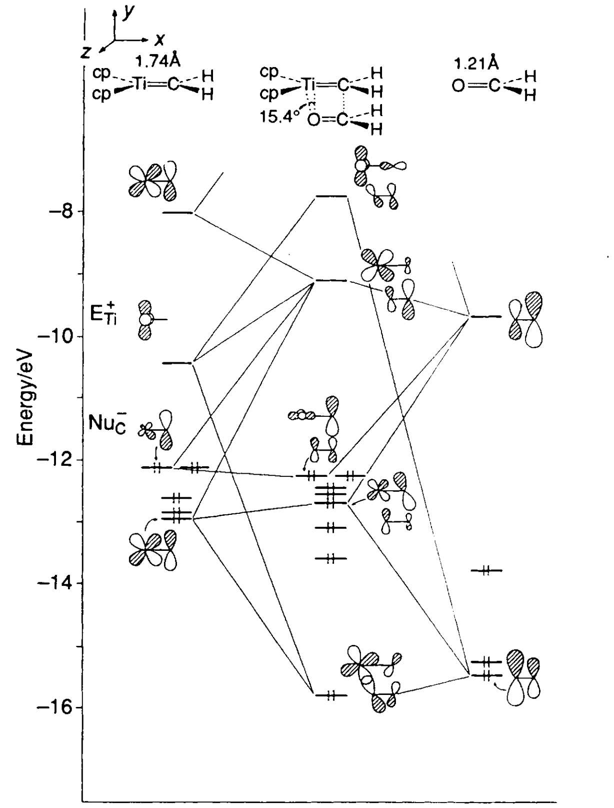
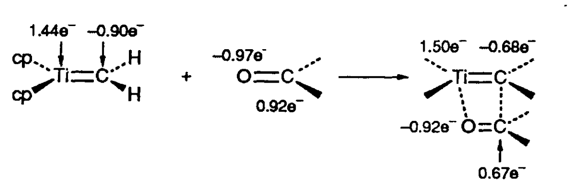
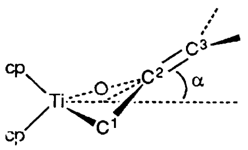


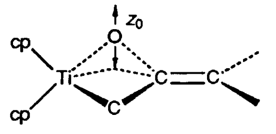
Fig. 1 Interaction diagram for a $2\pi_s + 2\pi_s$ approach involving $(cp)_2Ti{=}CH_2$ and $H_2C{=}O$ forming a titanaoxetane



XII



XIII



XIV

The above analysis indicates how the titanaoxetane intermediate in the Tebbe reaction can be formed. Grubbs and co-workers[7] studied two special titanaoxetanes, **4** and **5**, which have an sp^2-hybridized β-carbon atom. Presumably, these titanaoxetanes are more stable than **3**, because it is allenes that can be eliminated from **4** and **5** and not a simple alkene. Here we will focus on the possible distortions from a planar ring that can account for the dynamic NMR results.[7] The puckering has been proposed to be caused either by donation of electron density from the 4-*exo*-methylene bond into an empty titanium orbital,[7,20] or from maximizing overlap between an oxygen lone pair and an empty a_1 orbital on titanium, presumably E_{Ti}^+.[7] The first electronic feature has been set forth to explain the similar puckering of zirconacyclopentenes.[20] This possibility was studied by varying the angle α in **XIII** keeping all bond distances in the four-membered ring unchanged. The total energy and some important overlap populations calculated for **XIII** are given in Table 1. From an energetic point of view this distortion is uphill, and *not* favourable. Also, bond considerations indicate a destabilized ring upon puckering, as the titanium–oxygen bond is weakened without creating a positive overlap population between the titanium centre and carbon atom C^2.

Another way of puckering is to move the oxygen atom of the four-membered ring out of the plane of the ring, as indicated by the arrows in **XIV**. The calculated total energies and titanium–oxygen overlap populations are listed in Table 2. Again, the distortion, although keeping the bond distances unchanged, results in a decrease in the titanium–oxygen overlap population and thus a weaker bond.

The extended-Hückel calculations thus indicate that ring puckering of compounds **4** and **5** is an unfavourable distortion of the system. Further structural analysis will be based on semiempirical and *ab initio* calculations.

Semiempirical Calculations.—The structures of $(\mathrm{cp})_2\overline{\mathrm{TiCH_2CH_2O}}$, $(\mathrm{cp})_2\overline{\mathrm{TiCH_2C(CH_2)O}}$ and $(\mathrm{cp})_2\overline{\mathrm{TiC(CH_2)CH_2O}}$ have been optimized by the Zernes intermediate neglect of differential overlap (ZINDO) procedure[10] for the singlet states of the systems. Some geometrical results for the titanaoxetanes are presented in Table 3.

The structural optimization of $(\mathrm{cp})_2\overline{\mathrm{TiCH_2CH_2O}}$ yields a planar ring. The Ti–C(cp) bond length is found to be 2.40 Å on average, which is very similar to corresponding values for other cyclopentadienyltitanium compounds.[3b] The titanium–carbon and –oxygen bond lengths agree with similar bonds in characterized titanium complexes.[3b,21a] The HOMO of $(\mathrm{cp})_2\overline{\mathrm{TiCH_2CH_2O}}$ is located at −7.81 eV and it is a $\sigma_{\mathrm{Ti-O}}$ orbital, while the second HOMO is of $\sigma_{\mathrm{Ti-C}}$ character, found at −10.20 eV. The LUMO at −0.31 eV is a combination of d_{z^2} mixed in with a small part of d_{yz} at titanium, while the second LUMO is located at the cp rings at 0.91 eV (a more thorough presentation and discussion of the frontier orbitals of titanaoxetanes is presented in the *ab initio* section). The following atomic charges of the titanaoxetane part are calculated: Ti, 1.11; C^1, −0.31; O, −0.65; and C^2, 0.08. The variation in total energy for a puckering of the four-membered ring as shown in **XIII** has also been investigated. The results obtained by the ZINDO method are similar to those found by the extended-Hückel calculations as a tilting of atom C^2 by 20° out of the titanaoxetane plane causes an increase in energy by 38 kcal $\mathrm{mol^{-1}}$. Starting an optimization of the structure of $(\mathrm{cp})_2\overline{\mathrm{TiCH_2CH_2O}}$ with a non-planar ring leads to a structure where the ring is planar.

Table 1 Changes in total energy and in the overlap populations between titanium and carbon atom C^2 and between titanium and oxygen as a function of the variation in the angle α in **XIII**

α/°	Ti–C^2/Å	Energy/eV	Overlap population	
			Ti–C^2	Ti–O
0	2.437	−1357.24	−0.069	0.408
20	2.402	−1357.14	−0.063	0.405
40	2.300	−1356.78	−0.057	0.397
60	2.133	−1355.42	−0.033	0.383

Table 2 Change in total energy and titanium–oxygen overlap population when moving the oxygen atom out of the titanaoxetane plane, as in **XIV**

z_0/Å	Energy/eV	Overlap population Ti–O
0.00	−1357.24	0.408
0.16	−1357.16	0.407
0.31	−1356.90	0.402
0.61	−1355.68	0.382

Let us continue with a comparison of the two *exo*-methylene substituted isomers **4** and **6**. The NMR investigations revealed that **4** is stable on the NMR time-scale,[7] whereas **6** is unstable.[4] Their geometrical structures have been optimized. The results in Table 3 show that both titanaoxetane rings prefer to be planar, as the sum of the angles is calculated to be 360.0 and 359.7° for **4** and **6**, respectively. Comparing the geometrical results for $(\mathrm{cp})_2\overline{\mathrm{TiCH_2C(CH_2)O}}$ and $(\mathrm{cp})_2\overline{\mathrm{TiC(CH_2)CH_2O}}$ with those for $(\mathrm{cp})_2\overline{\mathrm{TiCH_2CH_2O}}$ shows that the metallaoxetane parts of the three systems are very similar. Only very small variations in bond lengths and angles are found. The length of the exocyclic double bond is similar to that of a normal carbon–carbon double bond. The difference in total energy between the 4- and 3-*exo* isomers is calculated to be 19 kcal $\mathrm{mol^{-1}}$, and the calculations show that the former is most stable in agreement with the experimental results.

We will in the following focus attention on the 4-*exo*-methylene substituted titanaoxetane **4**. The frontier orbitals of **4** will be presented briefly, and discussed in more detail under the *ab initio* section. The HOMO of **4** is mainly the $\pi_{\mathrm{C=C}}$ orbital of the exocyclic double bond found at −5.92 eV. At −6.73 eV is a combination of titanium d_{z^2} and oxygen p_z. The LUMO of **4** is rather high in energy at 5.01 eV as a combination of titanium orbitals, and right above it is $\pi^*_{\mathrm{C=C}}$. The orbital picture indicates that an electrophile would prefer to react at the exocyclic double bond, a prediction that has to be verified experimentally. The charges of the atoms in the titanaoxetane ring are: Ti, 1.17; O, −0.43; C^1, −0.43; C^2, 0.21; and C^3, −0.40. When comparing these with those found for $(\mathrm{cp})_2\overline{\mathrm{TiCH_2CH_2O}}$ it is seen that the oxygen atom and atom C^2 both become more positively charged while C^1 becomes slightly more negative, upon the introduction of the exocyclic double bond.

The structures of the titanaoxetane has been investigated (planar *versus* non-planar) as the exocyclic double bond is tilted out of the plane defined by the four-membered ring, as outlined in **XIII**. Forcing the exocyclic double bond out of the metallaoxetane plane leads in this case also to an increase in the total energy of the system; a 20° movement of the carbon atom leads to an energy increase of 21 kcal $\mathrm{mol^{-1}}$, while a bending of

Table 3 Total energies and some geometrical data for titanaoxetanes[a]

	$(\mathrm{cp})_2\overline{\mathrm{TiCH_2CH_2O}}$	$(\mathrm{cp})_2\overline{\mathrm{TiCH_2C(CH_2)O}}$	$(\mathrm{cp})_2\overline{\mathrm{TiC(CH_2)CH_2O}}$
Energy/au	−107.561	−113.800	−113.769
Ti–C(cp)[b]/Å	2.40	2.40	2.40
Ti–O/Å	2.15	2.16	2.17
Ti–C^1/Å	2.15	2.15	2.12
C^1–C^2/Å	1.49	1.48	1.48
C^2–O/Å	1.40	1.38	1.40
$C^{1,2}$–C^3/Å	—	1.34	1.33
Ti–O–C^2/°	92.6	92.2	91.4
O–C^2–C^1/°	110.0	111.4	110.4
Ti–C^1–C^2/°	90.1	89.9	91.2
C^1–Ti–O/°	66.9	66.5	66.7
$C^{1,2}$–$C^{2,1}$–C^3/°	—	129.0	132.5

[a] For the numbering of the atoms see **XIII**. [b] Average of the Ti–C bond lengths.

Table 4 Calculated bond distances, angles and total energies for $H_2TiCH_2CH_2O$ and $Cl_2TiCH_2CH_2O$[a]

	$H_2TiCH_2CH_2O$		$Cl_2TiCH_2CH_2O$	$H_2TiCH_2CH_2O$
Basis set	STO-3G*	STO-3G*	STO-3G*	GBS
Electronic state	$^1A'$	$^3A''$	$^1A'$	$^1A''$
Energy/au	−992.215	−991.955	−1900.787	−1002.747
Ti–O/Å	1.73	1.68	1.72	1.77
Ti–C^1/Å	2.06	3.91	2.05	2.05
C^1–C^2/Å	1.56	1.53	1.56	1.54
O–C^2/Å	1.47	1.42	1.48	1.52
Ti–O–C^2/°	95.8	143.3	96.1	95.4
O–C^2–C^1/°	104.9	111.6	104.0	103.0
C^2–C^1–Ti/°	81.0	47.6	81.5	84.3
C^1–Ti–O/°	78.3	179.0	78.4	77.3

[a] For the numbering of the atoms see **XIII**.

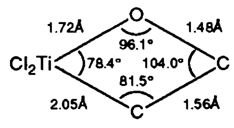
30° destabilizes the complex by as much as 73 kcal mol^{-1}. Furthermore, no orbital interactions between titanium and the methylene-bound carbon atom are observed when moving the exocyclic double bond out of the metallacycle plane. The semiempirical calculations thus indicate that the titanaoxetane prefers to be planar.

Ab Initio *Calculations*.—The geometry of various titanaoxetanes in the singlet state, and some structures in the triplet state, have been optimized using a STO-3G* basis set and a general basis set (GBS) (see Appendix).[11] To reduce computation time the cyclopentadienyl ligands were replaced by chlorine or hydrogen atoms. A similar replacement of the cyclopentadienyl rings of dicyclopentadienyltitanacyclobutane has been shown to be a reasonable structural model for the metal complex in a study of the metal-catalysed alkene metathesis reaction.[12]

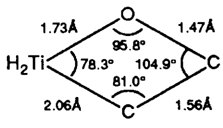
The optimized structures of $Cl_2TiCH_2CH_2O$ and $H_2TiCH_2CH_2O$ in the singlet states with the ring skeleton constrained to be planar as obtained using the STO-3G* basis set, are shown as **XV** and **XVI** respectively. The structural data indicate that the geometry of the titanaoxetane does not change significantly when changing the ligand from chlorine to hydrogen, as only minor changes in bond distances and angles are found. Table 4 gives some structural and electronic results for the optimization of $Cl_2TiCH_2CH_2O$ and $H_2TiCH_2CH_2O$. The electronic states are $^1A'$, and the total energies (including configuration interaction with a frozen-core approximation) are calculated to be −1900.787 and −992.215 au, respectively.

The results in Table 4 show that the singlet state of $H_2TiCH_2CH_2O$ is more stable than the triplet state. The singlet states of $Cl_2TiCH_2CH_2O$ and $H_2TiCH_2CH_2O$, the latter with the STO-3G* basis set as well as the GBS, are found to be more stable than the triplet states (not all shown in the Table). Furthermore, the calculated structure of $H_2TiCH_2CH_2O$ does not change very much when changing the basis set from STO-3G* to GBS. For $H_2TiCH_2CH_2O$ optimized with the STO-3G* basis set the $^1A'$ state is 162 kcal mol^{-1} more stable than the $^3A''$ state. The most significant structural difference between $H_2TiCH_2CH_2O$ in the singlet and triplet states is a lengthening of the titanium–carbon bond. The observed increases in these bond lengths can be traced to population of a titanium–carbon antibonding orbital in the triplet state as outlined in **XVII**.

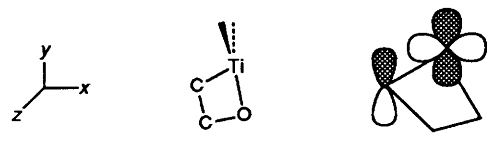
The results in Table 4 also show that replacing the chlorine with hydrogen atoms on titanium does not cause any significant change in the structural data for the four-membered ring in the singlet state. A major difference is found for the $^3A''$ state of $H_2TiCH_2CH_2O$ with the STO-3G* basis set (a similar result is obtained with GBS) in which the titanium–carbon bond breaks and the system ends up as in **XVIII**, which reminds one of the proposed intermediates in the metal-catalysed reductions of epoxides and in various alkene epoxidation reactions.[5,22] It should be noted that a similar cleavage of the titanium–carbon bond in the titanaoxetane is observed when using the ZINDO approach for optimizing this compound. However, we will not comment further on the structure of the triplet states of the titanaoxetanes as our main intention is to discuss the closed-shell states of the systems.



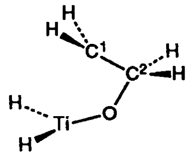
XV



XVI



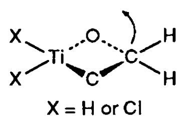
XVII



XVIII

The optimized structures for $H_2TiCH_2CH_2O$ obtained by the *ab initio* and ZINDO approaches have one significant structural difference as the titanium–oxygen bond from the former is about 0.4 Å shorter than the same bond in ZINDO-optimized $(cp)_2TiCH_2CH_2O$. This disagreement is also reflected in the other bond lengths of the titanaoxetane. The titanium–oxygen bond length in $H_2TiCH_2CH_2O$ is rather short compared to single titanium–oxygen bond distances (normally about 2.1 Å [21a,b]) and resembles a double bond (normally about 1.7 Å [21c]).

The results in Table 4 were obtained for structures where the four-membered ring is planar. We have also made a series of calculations with puckered titanaoxetanes **XIX** as starting geometry (the X–Ti–X angle is also optimized). The calculations show that bending atom C^2 out of the plane results in an increase in energy. The planar geometry always ends up as the optimized structure when puckering is an allowed parameter,



X = H or Cl

XIX

and it is thus the most stable form of the titanaoxetanes **XV** and **XVI**.

Let us discuss the electronic structure of $H_2TiCH_2CH_2O$ (see **XVI**) in the singlet state. The frontier orbitals of this system are given to the left of Fig. 2, as found when optimized with GBS. The HOMO is mainly a bonding orbital comprised of p_x orbitals of the carbons and the oxygen mixed with some titanium d_{z^2} character, found at −11.12 eV. The second highest occupied molecular orbital at −11.67 eV, bonding between titanium and oxygen, occurs through interaction of oxygen p_z and titanium d_{xz} orbitals. The third occupied molecular orbital shown is distributed among three atoms: titanium, oxygen and C^2 and is of p_z character at carbon and oxygen and d_{xz} character at titanium. This orbital is found at −13.08 eV. In between the occupied molecular orbitals are orbitals that are either located on the two other titanium ligands or on the hydrogen atoms of the four-membered ring. The lowest unoccupied molecular orbitals are mainly located at the titanium centre. The LUMO is mainly titanium $d_{z^2}(E_{Ti}^+)$, calculated to be at 1.88 eV, while the second LUMO is a combination of d_{xy} and d_{yz} found at 2.28 eV. The calculated atomic net charges on the atoms of the titanaoxetane are as follows: Ti, 1.70; C^1, −0.91; C^1, 0.10, while the oxygen atom has an expected negative charge of −0.82. It is noticeable that the titanium-bound carbon atom of the ring is more negatively charged than is the oxygen atom by this applied method of sharing the molecular charge among the atoms (Mulliken principle).[23] Comparing the frontier orbitals of $H_2TiCH_2CH_2O$ obtained by the *ab initio* calculations with those obtained by the ZINDO procedure, it appears that the LUMOs are very similar but changes are found among the occupied MOs. The atomic charges are also different, the *ab initio* charges being more polarized than those obtained by the semiempirical method.

The found planar arrangement of the titanaoxetanes, $X_2TiCH_2CH_2O$, can be rationalized from the frontier orbitals of the metallaoxetane part shown in Fig. 2. The requirement of $X_2TiCH_2CH_2O$ to pucker is either through an interation of E_{Ti}^+, the LUMO of the system, with the p_z orbital of atom C^2 to improve overlap between these two atoms, or by increase of the titanium–oxygen overlap population. It appears from Fig. 2 that among the occupied frontier orbitals the third highest occupied molecular orbital has amplitude at C^2. However, this amplitude is very small, and probably not enough to build up good overlap with the titaniun d_{z^2} orbital. By bending C^2 out of the plane no increase in the titanium–oxygen overlap population is observed. This indicates that the lone-pair electrons of the oxygen do not donate electron density into an empty orbital on titanium by puckering of the ring. These results show that the metallaoxetane $X_2TiCH_2CH_2O$ is probably planar, and that any deviation from planarity of eventually X-ray characterized titanaoxetanes will be rationalized by steric effects.

The structures of 4-*exo*-$X_2TiCH_2C(CH_2)O$ and 3-*exo*-$X_2TiC(CH_2)CH_2O$ (X = H or Cl) have been optimized using the STO-3G* basis set for X = Cl and the STO-3G* as well as the GBS basis for X = H. In all the calculations a planar geometry was maintained. The results show that the singlet state is preferred for both compounds. For example, the $^1A'$ state of 4-*exo*-$Cl_2TiCH_2C(CH_2)O$ has been calculated to be 49 kcal mol⁻¹ lower in energy than the triplet state. The only major structural difference between the two electronic states is found in the exocyclic carbon–carbon bond. In the $^1A'$ state of *e.g.* 4-*exo*-$Cl_2TiCH_2C(CH_2)O$ the length of this bond is 1.31 Å, corresponding to a normal carbon–carbon double bond, whereas in the $^3A''$ state this length is 1.55 Å, which is similar to a carbon–carbon bond in triplet planar ethylene obtained with the same basis set.

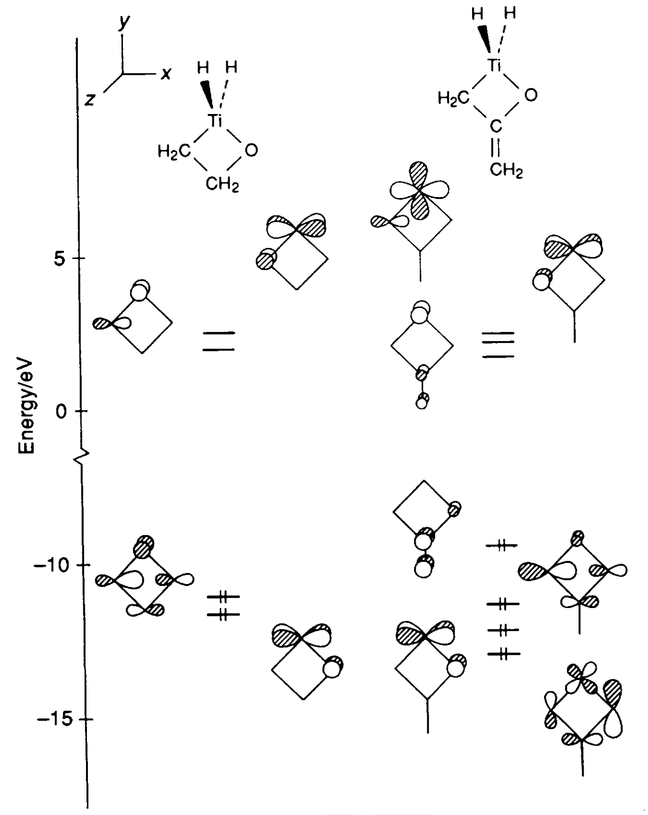


Fig. 2 Frontier orbitals of $H_2TiCH_2CH_2O$ (left) and of 4-*exo*-$H_2TiCH_2C(CH_2)O$ (right)

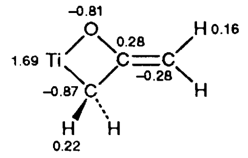
We will in the following focus on the structural calculations for 4-*exo*-$H_2TiCH_2C(CH_2)O$ and 3-*exo*-$H_2TiC(CH_2)CH_2O$ with the GBS basis, as the results obtained for these two systems are representative for the titanaoxetanes. The results for the optimized structures are given in Table 5. It is concluded that the two exocyclic compounds are structurally alike. The only major difference is found in the oxygen–carbon bond length of the four-membered ring, which in 4-*exo*-$H_2TiCH_2C(CH_2)O$ is 0.07 Å shorter than in 3-*exo*-$H_2TiC(CH_2)CH_2O$. This is due to the possibility of an interaction between an oxygen p orbital and the π^*_{C-C} orbital of the exocyclic double bond in the 4-*exo*-methylenetitanaoxetane thereby increasing the overlap population in question. The distribution of charges in the two systems is also at first sight different, as shown in **XX** and **XXI**. In 4-*exo*-$H_2TiCH_2C(CH_2)O$ (see **XX**) the ethylene fragment ($C{=}CH_2$) is slightly positive, whereas in 3-*exo*-$H_2TiC(CH_2)CH_2O$ (see **XXI**) it is negatively charged. On the other hand, if the total charge at the exocyclic double bond is summed and compared to the charge on the sp³-hybridized carbon in the other system at the same place of the metallacycle the values are not very different. The total atomic charge at the ethylene fragment in **XX** is 0.32 relative to 0.27 on the sp³-hybridized CH_2 group in **XXI**, and −0.42 for the exocyclic ethylene fragment in **XXI** relative to −0.43 for the sp³-hybridized CH_2 group in **XX**. The total energies of 4-*exo*-$H_2TiCH_2C(CH_2)O$ and 3-*exo*-$H_2TiC(CH_2)CH_2O$ reveal the former to be more stable by 35 kcal mol⁻¹.

The bending of the exocyclic double bond of compound **4**, as

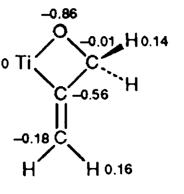
Table 5 Selected electronic and geometrical data for 4-*exo*-$H_2\overline{\mathrm{TiCH_2C(CH_2)O}}$ and 3-*exo*-$H_2\overline{\mathrm{TiC(CH_2)CH_2O}}$*

	$H_2\overline{\mathrm{TiCH_2C(CH_2)O}}$	$H_2\overline{\mathrm{TiC(CH_2)CH_2O}}$
Basis set	GBS	GBS
Electronic state	$^1A'$	$^1A'$
Energy/au	−1040.360	−1040.304
Ti–O/Å	1.80	1.78
O–C^1/Å	1.43	1.50
C^1–C^2/Å	1.52	1.53
C–Ti/Å	2.06	2.05
$C^{1,2}$–C^3/Å	1.32	1.33
Ti–O–C^1/°	97.1	97.7
O–C^1–C^2/°	104.2	100.9
C^1–C^2–Ti/°	84.5	86.5
C^2–Ti–O/°	74.1	74.9
$C^{1,2}$–$C^{2,1}$–C^3/°	133.2	127.9

* Numbering of the atoms is similar to that in **XIII**.



XX



XXI

shown in **XIII** and proposed by Grubbs and co-workers, has been studied. Puckering of the ring which results from bending of the exocyclic double bond out of the plane defined by titanium, carbon and oxygen was analysed. The bending angle was examined over a large range, as it can be imagined that a local minimum would be found for large values of α. Our calculations indicate that the system prefers to be planar as found above for $H_2\overline{\mathrm{TiCH_2CH_2O}}$ and for the early transition metallaoxetanes characterized.[6]

Let us finally discuss the electronic structure of 4-*exo*-$H_2\overline{\mathrm{TiCH_2C(CH_2)O}}$. The frontier orbitals are shown to the right in Fig. 2 and are very similar to those to the left for $H_2\overline{\mathrm{TiCH_2CH_2O}}$. The HOMO of 4-*exo*-$H_2\overline{\mathrm{TiCH_2C(CH_2)O}}$ is located mainly at the exocyclic double bond as $\pi_{C=C}$, while the LUMO comprises titanium d_{z^2} mixed with a small amount of $\pi^*_{C=C}$, followed by primarily titanium d_{xz} and $d_{z^2+y^2}$ orbitals. It is thus seen that the orbitals of a titanaoxetane having an exocyclic double bond are in principle similar to those of $H_2\overline{\mathrm{TiCH_2CH_2O}}$, with the only difference that the carbon–carbon π-bonding and antibonding orbitals are found in between the HOMO and LUMO of $H_2\overline{\mathrm{TiCH_2CH_2O}}$.

Conclusion

A qualitative picture of the Tebbe reaction is set forth. Initial co-ordination of the carbonylic substrate to the titanium of a titanium carbene structure is made possible through donation of electron density from an oxygen lone pair into the titanium $d_{x^2-y^2}$ orbital, which is the LUMO. This activates the carbon–oxygen double bond towards the addition, which formally looks like a $2\pi + 2\pi$ cycloaddition. Two extra electrons located at the methylene carbon atom in the metal complex are then introduced, turning this 'forbidden' reaction into a six-electron interaction, and thus making it 'allowed'.

All the applied theoretical methods, extended Hückel, ZINDO and *ab initio*, indicate that a titanaoxetane ring will be planar for purely electronic reasons. No increases in the overlap populations between the titanium centre and either the oxygen atom of the ring or the β-carbon atom could be found in the calculations. When the two isomers of the *exo*-methylenetitanaoxetanes are compared it is found that the 4-*exo* isomer is more stable than the 3-*exo* isomer, in agreement with the NMR results. This difference is traced to a slightly stronger carbon–oxygen bond in the four-membered ring in the 4-*exo*-methylenetitanaoxetane. The experimentally found puckered structure of the 4-*exo*-methylenetitanaoxetanes cannot be accounted for by this study. In order to trace the electronic consequences of the presence of solvent molecules in the NMR experiments one would need much more advanced theoretical methods.

Appendix

The orbital parameters used in the extended-Hückel calculations are available in the literature.[24] The *ab initio* calculations were carried out with the Gaussian 88 program.[11] The general basis set (GBS) was taken from Poirier and Csizmadia.[25] For titanium an 8s4p2d basis set with the contraction scheme [62111111/5112/32(1)] was used, while for carbon and oxygen we used a 4s2p basis set with contraction schemes [5211/41]; hydrogens were replaced by a 2s [31] basis set.[25] The triplet-state calculations were performed with the unrestricted Hartree–Fock approach.

Acknowledgements

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References

1 F. N. Tebbe, G. W. Parshall and G. S. Reddy, *J. Am. Chem. Soc.*, 1978, **100**, 3611.

2 (*a*) S. H. Pine, R. Zahler, D. A. Evans and R. H. Grubbs, *J. Am. Chem. Soc.*, 1980, **102**, 3270; (*b*) J. R. Stille and R. H. Grubbs, *J. Am. Chem. Soc.*, 1983, **105**, 1664; (*c*) S. L. Buchwald and R. H. Grubbs, *J. Am. Chem. Soc.*, 1983, **105**, 5490; (*d*) K. A. Brown-Wensley, S. L. Buchwald, L. Cannizzo, L. Clawson, S. Ho, D. Meinhardt, J. R. Stille and R. H. Grubbs, *Pure Appl. Chem.*, 1983, **55**, 1733; (*e*) N. A. Petasis and E. I. Bzowej, *J. Am. Chem. Soc.*, 1990, **112**, 6392; (*f*) R. R. Schrock, *J. Am. Chem. Soc.*, 1976, **98**, 5399; (*g*) R. R. Schrock and J. D. Fellmann, *J. Am. Chem. Soc.*, 1978, **100**, 3359; (*h*) J. H. Freudenberger and R. R. Schrock, *Organometallics*, 1986, **5**, 398.

3 (*a*) T. R. Howard, J. B. Lee and R. H. Grubbs, *J. Am. Chem. Soc.*, 1980, **102**, 6878; (*b*) J. B. Lee, G. J. Gajda, W. P. Schaefer, T. R. Howard, T. Ikariya, D. A. Straus and R. H. Grubbs, *J. Am. Chem. Soc.*, 1981, **103**, 7358; (*c*) J. B. Lee, K. C. Ott and R. H. Grubbs, *J. Am. Chem. Soc.*, 1982, **104**, 7491; (*d*) E. V. Anslyn and R. H. Grubbs, *J. Am. Chem. Soc.*, 1987, **109**, 4880.

4 K. B. Sharpless, A. Y. Teranishi and J.-E. Bäckvall, *J. Am. Chem. Soc.*, 1977, **99**, 3120.

5 K. A. Jørgensen and B. Schiøtt, *Chem. Rev.*, 1990, **90**, 1483 and refs. therein.

6 (*a*) L. R. Whinnery, jun., L. M. Henling and J. E. Bercaw, *J. Am. Chem. Soc.*, 1991, **113**, 7575; (*b*) G. C. Bazan, R. R. Schrock and M. B. O'Regan, *Organometallics*, 1991, **10**, 1062; (*c*) J. F. Hartwig, R. G. Bergman and R. A. Andersen, *J. Am. Chem. Soc.*, 1990, **112**, 3234; (*d*) A. A. Zlota, F. Frolow and D. Milstein, *J. Am. Chem. Soc.*, 1990, **112**, 6411; (*e*) R. Schlodder, J. A. Ibers, M. Lenarda and M. Graziani, *J. Am. Chem. Soc.*, 1974, **96**, 6893; (*f*) M. Lenarda, N. B. Pahor, M. Calligaris, M. Graziani and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1978, 279; (*g*) W. A. Herrmann, U. Küsthardt, A. Schäfer and E. Herdtweck, *Angew. Chem.*, 1986, **98**, 818.

7 S. C. Ho, S. Hentges and R. H. Grubbs, *Organometallics*, 1988, **7**, 780.

8 E. V. Anslyn, B. D. Santarsiero and R. H. Grubbs, *Organometallics*, 1988, **7**, 2137.

9 R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **37**, 2872; R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.

10 J. A. Pople, D. L. Beveridge and P. A. Dobosh, *J. Chem. Phys.*, 1967, **47**, 2026; J. Ridley and M. C. Zerner, *Theor. Chim. Acta*, 1973, **32**, 111; M. A. Zerner, G. H. Loew, R. F. Kirscher and U. T. Muller-Westerhoff, *J. Am. Chem. Soc.*, 1980, **102**, 5891.

11 Gaussian 88, M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Raghavachari, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, E. M. Fluder, S. Topiol and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1988.

12 T. H. Upton and A. K. Rappé, *J. Am. Chem. Soc.*, 1985, **107**, 1206.

13 G. Glockler, *J. Phys. Chem.*, 1958, **62**, 1049; K. Takagi and T. Oka, *J. Phys. Soc. Jpn.*, 1963, **18**, 1174.

14 R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, VCH, Weinheim, 1970.

15 E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, 1962, **84**, 867; F. Volatron and O. Eisenstein, *J. Am. Chem. Soc.*, 1987, **109**, 1.

16 B. Schiøtt, K. A. Jørgensen, M. J. Calhorda and A. M. Galvao, *Organometallics*, in the press.

17 T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, 3rd edn., Harper and Row, New York, 1987.

18 K. A. Jørgensen and R. Hoffmann, *J. Am. Chem. Soc.*, 1986, **108**, 1867.

19 F.-M. Su, C. Cooper, S. J. Geib, A. L. Rheingold and J. M. Mayer, *J. Am. Chem. Soc.*, 1986, **108**, 3545; B. Schiøtt and K. A. Jørgensen, *J. Chem. Soc., Dalton Trans.*, 1989, 2099.

20 G. Erker, J. Wicker, K. Engel, F. Rosenfeldt, W. Dietrich and C. Krüger, *J. Am. Chem. Soc.*, 1980, **102**, 6344; P. Hofmann, M. Frede, P. Stauffert, W. Lasser and U. Thewalt, *Angew. Chem.*, 1985, **97**, 693; K. Tatsumi, H. Yasuda and A. Nakamura, *Isr. J. Chem.*, 1983, **23**, 145; G. Erker, K. Engel, C. Krüger and G. Müller, *Organometallics*, 1984, **3**, 128.

21 (*a*) G. Fachinetti, C. Biran, C. Floriani, A. C. Villa and C. Guastini, *Inorg. Chem.*, 1978, **17**, 2995; (*b*) J. D. Williams, S. F. Pedersen, K. B. Sharpless and S. J. Lippard, *J. Am. Chem. Soc.*, 1984, **106**, 6430; (*c*) W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley, New York, 1988, p. 188.

22 S. M. Kupchan and M. Maruyama, *J. Org. Chem.*, 1971, **36**, 1187; D. Ostovic and T. C. Bruice, *J. Am. Chem. Soc.*, 1989, **111**, 6511; Y. Hayashi and J. Schwartz, *Inorg. Chem.*, 1981, **20**, 3473; T. R. Cundari and R. S. Drago, *Inorg. Chem.*, 1990, **29**, 487.

23 J. Lowe, *Quantum Chemistry*, Academic Press, New York, 1978.

24 K. A. Jørgensen, R. A. Wheeler and R. Hoffmann, *J. Am. Chem. Soc.*, 1987, **109**, 3240.

25 R. Poirier and I. G. Csizmadia, *Handbook of Gaussian Basis Sets: Physical Sciences Data*, Elsevier, Amsterdam, 1985, vol. 24.

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