7). To date, the results indicate that carborane ligands tend to stabilize electron-deficient complexes of high oxidation state much more so than do cyclopentadienides. However, there is not as yet sufficient experimental or theoretical results to provide a basis for understanding of the factors that dictate the stabilities and properties of these complexes. Further studies are currently underway in our laboratories.

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Supplementary Material Available: Listings of mass spectrometric data (Table S-1) of IV–VII, a table of bond angles (Table S-2), a table of anisotropic displacement coefficients of IV, VI, and VII (Table S-3), a table of H-atom coordinates and isotropic displacement coefficients of IV, VI, and VII (Table S-4), and a table of the atomic orbital compositions of the molecular orbitals of IX (Table S-5) (14 pages). Ordering information is given on any current masthead page.

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Addition of Aldehydes to Tantalum–Carbene Complexes and the Reduction of Epoxides by Unsaturated Tantalum Complexes. Theoretical Study of the Reaction Mechanism and Product Structures

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The addition of formaldehyde to $Cp_2Ta(CH_3)(CH_2)$ is studied from a molecular orbital point of view. Two possible isomers of the product, O-*anti*-$Cp_2(CH_3)\overline{Ta(OCH_2CH_2)}$ and O-*syn*-$Cp_2(CH_3)\overline{Ta(OCH_2CH_2)}$, are analyzed. The anti isomer is suggested to be thermodynamically more stable because it has stronger tantalum–carbon bonds. Steric hindrance of the Cp rings may result in the initial formation of the syn isomer only. Different routes for the following rearrangement to the anti isomer are compared. Berry pseudorotation and turnstile rotations are both high-energy processes. Methyl migration via one of the Cp rings is a possible pathway from energetic and bonding considerations. This reaction path is found to be base catalyzed. The possibility of an acid-catalyzed heterolysis of the tantalum–oxygen bond is discussed. The reduction of ethylene oxide by a $Cp_2Ta(CH_3)$ complex is also studied. A direct oxygen abstraction pathway is compared to one involving the formation of the tantalaoxetanes $Cp_2(CH_3)\overline{Ta(OCH_2CH_2)}$. An initial weak coordination of the epoxide through the oxygen atom is suggested. A concerted elimination of the alkene from this precursor is a nonactivated process, opposed to a path that involves formation of tantalaoxetanes by an insertion of tantalum into a carbon–oxygen bond of the epoxide.

The existence of metallaoxetanes as intermediates in various transition-metal-catalyzed oxygen-transfer reactions, such as alkene epoxidation,[1] epoxide reduction,[2] Tebbe-like reactions,[3] and insertion of carbon dioxide into epoxides,[4] has been a subject of intense debate during the past two decades.[5] Reports dealing with theoretical aspects of the chemistry of transition-metal metallaoxetanes have appeared in the literature.[6] This report will discuss the formation of tantalaoxetanes in two of the above reaction types, namely, in the Tebbe-like reaction of a tantalum–carbene complex with aldehydes and in the reduction of epoxides by a tantalum complex. The extended Hückel method[7] is applied throughout the study.

Table I. Atomic Parameters

atom	orbital	H_{ii}, eV	ζ_1	ζ_2	$c_1{}^a$	$c_2{}^a$
Ta	6s	−10.10	2.280			
	6p	−6.86	2.241			
	5d	−12.00	2.762	1.938	0.6600	0.5592
O	2s	−32.20	2.275			
	2p	−14.80	2.275			
C	2s	−21.40	1.625			
	2p	−11.40	1.625			
H	1s	−13.60	1.300			

[a] Coefficients used in a double-ζ expansion of the metal d-orbitals.

The Tebbe-like reaction is the organometallic analogue

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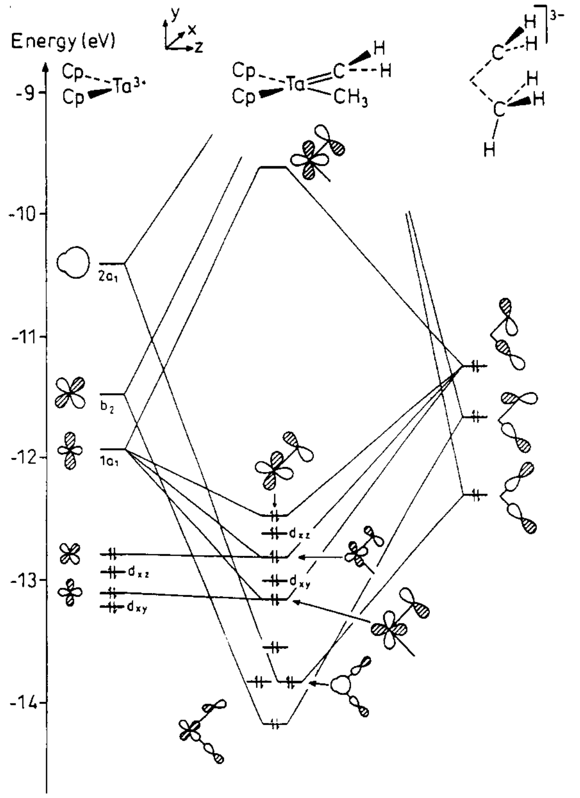
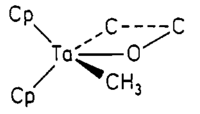


Figure 1. Orbital interaction diagram of Cp_2Ta^{3+} (left) and CH_2^- and CH_3^- (right). No Cp contributions are drawn onto the figure. The occupied orbitals of Cp_2Ta^{3+} are all Ta–Cp bonding with relatively small tantalum contribution, whereas the empty ones are tantalum to Cp antibonding with large tantalum contribution, as indicated by the size of the lobes on tantalum.

of the organic Wittig reaction where a nucleophilic carbenoid reacts with a carbonyl compound giving an oxaphosphetane.[8-10] Only recently the first reports on early-transition-metal metallaoxetanes obtained by reaction of Schrock-type metal carbenes with aldehydes have appeared in the literature.[3e,11,12] A molybdenaoxetane is formed by mixing pentafluorobenzaldehyde and Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (Ar = 2,6-diisopropylphenyl),[11] and two isomeric tantalaoxetanes are obtained by adding aldehydes to $Cp_2^*Ta(CH_3)(CH_2)$.[12] In the latter, Bercaw et al. investigated the possibility of forming tantalaoxetanes in the reduction of epoxides by $Cp_2^*Ta(CH_3)$ and in the addition of aldehydes to $Cp_2^*Ta(CH_2)(CH_3)$.[12] First they established the structures of the O-syn- and the O-anti isomers, 1 and 2, of $Cp_2^*(CH_3)\overline{Ta(OCH_2CH_2)}$ by letting $Cp_2^*Ta(CH_2)(CH_3)$ react with the appropriate aldehyde, then they followed the reduction of ethylene oxide and styrene oxide.[12] As no signals corresponding to either of the tantalaoxetanes were observed by NMR during the reduction, they concluded that tantalaoxetanes are not formed in the course of this reaction.[12] This paper will address these reactions and will be divided into two parts, the first dealing with the formation of the tantalaoxetanes from aldehydes and tantalum carbenes, the second with the reduction of epoxides.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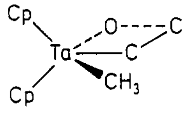
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Formation of $Cp_2^*(CH_3)\overline{Ta(OCH_2CH_2)}$

Let us start with a short description of the 18-electron $Cp_2^*Ta(CH_2)(CH_3)$ complex.[13] Several theoretical analysis concerning metal to CR_2 bonding have appeared in the literature,[14,15] and therefore we will limit ourselves to this

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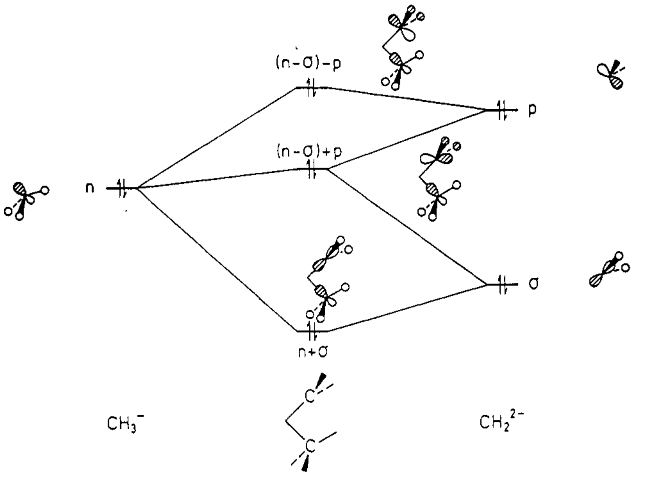
very low symmetry tantalum–carbene complex. For simplicity of the calculations, we will use the cyclopentadienyl analogue, $Cp_2Ta(CH_2)(CH_3)$, which was the first transition metal–methylene complex to be isolated and structurally characterized.[13] The compound has a pseudotetrahedral geometry with a C–Ta–C bond angle of 95.5°.[13] The methylene hydrogens are placed above and under the C–Ta–C plane in order to create a stronger tantalum–carbon bond by overlapping of the p_π orbital on carbon and a tantalum orbital only involved in δ-type bonding with the Cp rings.[13,14]

In Figure 1 is shown an interaction diagram of a Cp_2Ta^{3+} fragment and CH_2^{2-} and CH_3^- closed-shell fragments. On the left-hand side are shown the well-known frontier molecular orbitals of the bent d^0 Cp_2Ta^{3+} fragment.[14] The three lowest unoccupied fragment orbitals are the $1a_1$, b_2, and $2a_1$ as described in an early paper by Lauher and Hoffmann.[14] We have also drawn some of the Ta–Cp bonding orbitals, as they are involved in bonding with the methylene and methyl ligands. The methyl and methylene ligands can form symmetry fragment orbitals that can overlap with the three empty metal centered orbitals. The fragment orbitals of CH_2^{2-} and CH_3^- are shown to the right of Figure 1.

These fragment orbitals are obtained by two sequential first-order mixings,[16] as indicated in **3**. The p and σ orbitals of CH_2^{2-} and the n orbital of CH_3^- are close in energy, with n lying in the middle, so they mix strongly. First the n and σ orbitals interact giving n + σ (bonding) and n − σ (antibonding). The latter is perturbed by the p orbital in a way that decreases the antibonding character between the two carbons.[16] This gives the (n − σ) + p combination shown. The p orbital also interacts with n − σ in an antibonding way resulting in the (n − σ) − p orbital. The orbitals in **3** are analogous to the fragment orbitals of similar trihydride complexes.[17]



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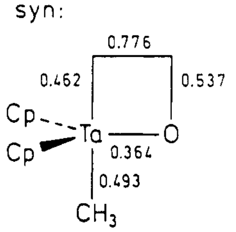
Unoccupied metal-centered orbitals able to interact with these three fragment orbitals are found in Figure 1. Because of the very low symmetry of the molecule, the bonding picture is rather complicated. The LUMO of the compound is the antibonding tantalum–carbon π-type orbital found at −9.7 eV. The tantalum–carbon π bond, which is expected to be involved in a [2 + 2] cycloaddition with an aldehyde, is distributed among at least three occupied orbitals in $Cp_2Ta(CH_2)(CH_3)$, namely, the HOMO and the third and the fifth HOMOs. This results in an overall negative charge of carbon (−0.32) and the Schrock-type nucleophilicity of the complex.[3c] In a similar complex, the Tebbe reagent, "$Cp_2Ti{=}CH_2$", the nucleophilicity of the carbon can be directly traced to one orbital that is nearly entirely centered on the methylene carbon.[18]

Let us proceed with the reaction of $Cp_2Ta(CH_2)(CH_3)$ with aldehydes and the following isomerization reactions. The reaction involves the fairly stable O-*syn*-tantalaoxetane, which rearranges without loss of either the aldehyde (no back reaction) or the alkene to the thermodynamically favored O-*anti*-tantalaoxetane (eq 1).[12] Only the structure

$$Cp_2Ta(CH_3)(CH_2) + H_2C{=}O \rightarrow \text{O-}syn\text{-}Cp_2(CH_3)\overline{Ta(OCH_2CH_2})\rightarrow \text{O-}anti\text{-}Cp_2(CH_3)\overline{Ta(OCH_2CH_2})\rightarrow H_2C{=}CH_2 + Cp_2(CH_3)TaO \quad (1)$$

of the O-*anti*-$Cp_2(CH_3)\overline{Ta(OCH_2CH_2})$ isomer was established by X-ray methods.[12] In the following calculations we will use the structural findings from this analysis on both isomers of the tantalaoxetane. The extended Hückel calculations come out with the O-anti isomer as more stable than the O-syn isomer by ~10 kcal/mol, in agreement with experiments. The calculated overlap populations, which indicate the relative strength of one specific type of bond, are shown in **4** and **5**. The most striking difference between the two isomers is the increase in tantalum to carbon overlap populations accompanying the isomerization reaction. The C–C and Ta–O bonds of the four-membered ring stay unchanged, whereas the C–O bond is slightly weakened during the isomerization. The O-anti isomer can be viewed as a distorted trigonal bypyramid (TBP), as the measured bond angles indicate that the centers of the Cp rings, the tantalum atom, and the tantalum-bound carbon atom of the ring lie exactly in one plane (angles sum up to 360.0°).[12] In this model the ring oxygen and the methyl carbon are the pseudoaxial ligands, whereas the O-syn isomer has two carbons as pseudoaxial ligands of a distorted TBP. It is well-known for d^0–d^4 and d^{10} complexes that good σ donors (the less electronegative elements) will bind stronger in an equatorial site than in an axial site of the TBP and that the poorer σ donors,



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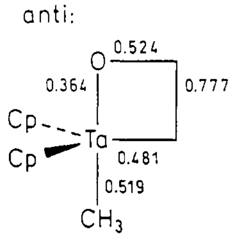

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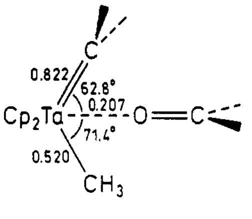
highly electronegative elements, will prefer the axial sites.[17,19] One can then argue that the isomerization can be driven by a desire to increase the bond strength of the tantalum–methylene bond, as carbon is a better σ donor than is oxygen. A similar study on η^2-acylmetallocenes of group 4 metals has been published. Only small differences in the total energies were found for that class of compounds.[20] These compounds are further away from the TBP geometry, as the central coordination is not found in the plane made up by the center of the Cp's and the metal center, and the angle between the outer ligands and the metal center is ~110°.[20] One thus cannot apply the TBP selection rules to the η^2-acyl complexes.

Now we want to address the question of why $Cp_2Ta(CH_3)(CH_2)$ adds aldehydes first, giving the unfavored isomer of tantalaoxetane and not the thermodynamically favored O-*anti*-tantalaoxetane. From the above analysis of the tantalum–carbene compound no obvious electronic reasons are found explaining this observation, as the π-type tantalum carbon orbitals are equally distributed on the syn and the anti side of the bond. When aldehydes react with the Tebbe complex, $Cp_2Ti{=}CH_2$, an initial coordination through the oxygen has been proposed on theoretical grounds.[18] For this reason we have tried to approach a formaldehyde molecule to the tantalum–carbene complex with the oxygen atom pointing towards tantalum. Approaches from both sides of the tantalum–methylene double bond were followed. The energies needed for approaches of formaldehyde to the tantalum carbene complex from either the syn or the anti sides of the tantalum methylene bond are of similar magnitude. In 6 and 7 are shown precursors to a syn isomer, 6, and an anti isomer, 7, with total energies and selected overlap populations indicated. The syn precursor is favored by only ~0.2 eV. From inspection of the frontier orbitals of the involved molecules, it appears that for formaldehyde the most important orbital is the oxygen lone pair, 8, which is depleted by 0.18 electrons in 6 and by 0.14 electrons in 7, respectively. The HOMO and the LUMO of the tantalum carbene are involved in this preliminary coordination. The HOMO looses 0.25–0.26 electrons in both approaches, whereas the LUMO discriminates slightly between the two sides of attack. The syn precursor results in a larger gain of electrons for this orbital than does the anti approach, 0.50 electrons compared to 0.22 electrons. These observations are reflected by the tantalum–methylene overlap population in 6 and 7, which changes from 0.935 in $Cp_2Ta(CH_2)(CH_3)$ to 0.822 (6) and 0.856 (7), respectively.



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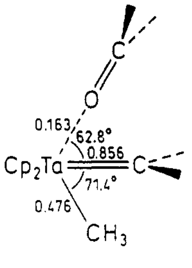
6



-1425.6 eV

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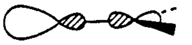

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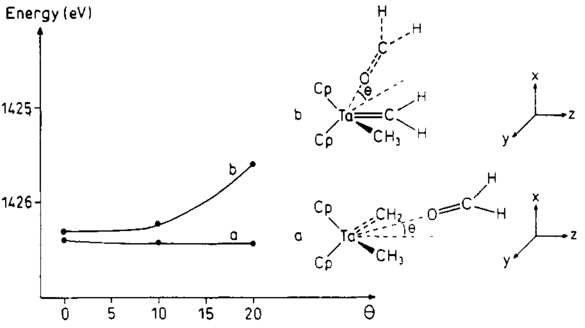

Figure 2. Energy variation when rocking formaldehyde out of the *yz* plane. The syn geometry is outlined in (a) and the anti approach is behind the observations of (b).

The above considerations of the two approaches studied indicate that the syn side leads to a slightly stronger activation of the methylene carbon toward a [2 + 2] reaction, although the energy difference of ~0.2 eV is too low to explain the observed results. Let us therefore explore to a certain extent the sterics of this addition. In 6 and 7 the approach of the formaldehyde molecule is in the C–Ta–C plane. In Figure 2 is shown the variation in the total energy when formaldehyde is tilted out of this plane in order to elucidate the availability of the syn (Figure 2a) and anti sides (Figure 2b) of the bond for an incoming molecule. The tantalum–oxygen distance is kept constant at 2.5 Å. It is obvious from the figure that the solid angle of the reaction is much larger for a molecule approaching from the syn side than from the anti side, due to extensive steric repulsion between the Cp rings and the incoming formaldehyde. The experiments were run with Cp*'s, which will reinforce this effect, favoring a syn approach of an aldehyde to $Cp_2{}^*Ta(CH_3)(CH_2)$. When CO is added to similar Cp_2MRX complexes, the molecule will enter from the anti side.[20] The presence of the two hydrogen atoms in formaldehyde is enough to make this addition site unfavorable and trigger the addition to proceed from the syn side. The next step on the reaction path can then be thought of as being a nucleophilic attack of the methylene carbon at the formaldehyde carbon. Negative charge builts up on the former carbon when the tantalum oxygen interaction is turned on. In 6 and 7 no carbon–carbon interaction is found. We will not go into more detail about the reaction steps going from these precursors to the tantalaoxetane structures as many bond lengths and bond angles need to be changed at the same time.

So far the analysis has given reasons of why the syn isomer can be termed as the kinetic product. This is primarily due to steric reasons, it is much easier for an incoming aldehyde to approach the tantalum carbene bond from the syn side. The *anti*-tantalaoxetane is proposed to be thermodynamically favored because this geometry results in stronger tantalum–carbon bonds. But how is the *syn*-tantalaoxetane isomerized to the *anti*-tantalaoxetane? It was concluded from experiments that the transformation proceeds without loss of either the aldehyde or the alkene.[12] By adding small amounts of weak acids, such as methanol, benzoic acid, or N bases, an acceleration of the molecular rearrangement was observed.[12] Bercaw et al. explained the acid catalysis by a heterolytic cleavage of the tantalum oxygen bond in *syn*-tantalaoxetane, giving $Cp^*_2(CH_3)Ta(CH_2CHPhOH)^+$ which breaks the Ta–O bond and, after rotation, closes to the O-*anti*-tantalaoxetane.[12] They were not able to explain the base catalysis.

In 9 are shown the calculated overlap populations for a protonated form of O-*syn*-tantalaoxetane where the

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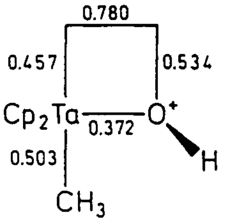
(19) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

(20) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440 and references therein.

Ta–O–H bond angle has been optimized by minimizing the total energy. The tantalum–oxygen overlap population



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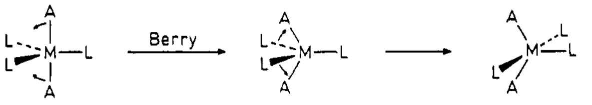
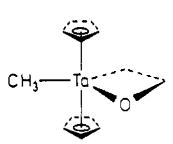
increases slightly, compared to **4**, when binding a proton. Of course these calculations can not exclude the proposed path, just indicate that the tantalum oxygen bond does not necessarily break when acid is added. Ab initio calculations on similar titanaoxetanes reveal that the carbon atom bound to titanium and the oxygen atom have similar negative charges and H^+ may thus add there.[18]

Two mechanisms describing intramolecular rearrangements in five-coordinated compounds are known, namely, Berry pseudorotation and turnstile rotations.[24] Both result in interconversions of the two axial ligands with two of the equatorial ligands, as shown in eqs 2 and 3.[21] The observed isomerisation of O-*syn*-tantalaoxetane to O-*anti*-tantalaoxetane can be reached by either of the above rearrangements reactions. Very recently a Berry-like pseudorotation has been proposed to describe the observed intramolecular rearrangements of similar molybdenacyclobutanes complexes involved in polymerization reactions of alkenes.[22] We have calculated total energies of the assumed intermediates to elucidate if any of the processes are reasonable. An intermediate in a Berry pseudorotation mechanism will have the two cyclopentadienyl ligands in the axial positions, as shown in **10**. It is obtained after one reaction sequence as outlined in eq 2. It is unfavorable by ~5 eV compared to **4** and **5**. The structure of an intermediate in a turnstile rotation has only one Cp ligand in the axial position, as in **11**. The calculations indicate that **11** is also an energetically very unstable compound when compared to the two isomers of tantalaoxetane. Therefore, we conclude that pseudorotations are probably not responsible for the isomerization of O-*syn*-tantalaoxetane to O-*anti*-tantalaoxetane because they are very high energy processes.



(2)

(3)



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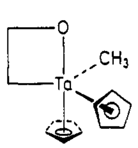

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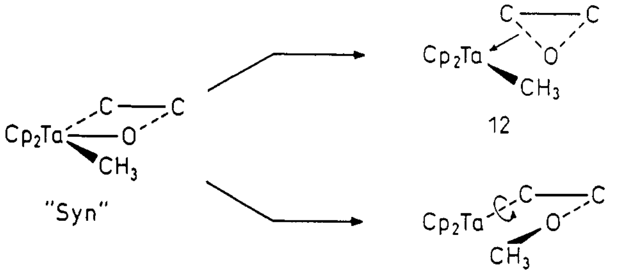
The above statement is in agreement with a study by Parkin and Bercaw of the intramolecular rearrangements of $Cp_2^*W(H)(H)$ when it is deuterated.[23] The first product observed has deuterium in the center position, $Cp_2^*W(H)(D)(H)^+$. This species then rearranges intramolecularly so deuterium takes a lateral position, $Cp_2^*W(H)(H)(D)^+$.[23] They proposed three different mechanisms other than rotations that all could explain the isomerization path.[23] Thus, they were not able to choose one of them as being more likely than the others. For the isomerization of O-*syn*-tantalaoxetane, all but one of these three mechanisms can be excluded from very simple reasoning. The first mechanism involves the formation of a η^2-coordinated dihydride obtained from a coupling of two neighboring ligands in $Cp_2^*W(H)(D)(H)^+$.[23] In the tantalaoxetane case this means the formation of either **12** or **13**. A side-on coordinated epoxide is formed in **12**. This would probably rearrange to an oxygen-bound form (see later on). From the principle of microscopic reversibility **12** is thus eliminated since it is known experimentally that epoxides added to $Cp_2^*Ta(CH_3)$ do not give tantalaoxetanes.[12] The structure **13** cannot give the O-*anti*-tantalaoxetane upon rotation. The second mechanism they proposed in the isomerization of $Cp_2^*W(H)(D)(H)^+$ involved the formation of a coordinated trihydride species.[23] For the tantalum complex this path can be neglected since it would involve a strange hypervalent organic species. The third mechanism involves a migration of a lateral ligand, L, to one of the Cp* rings, giving a η^4-C_5Me_5L, followed by a "Tarzan" type swing over the central ligand and a return of L to the metal center. In the tantalum case this mechanism implies that the methyl group migrates to a Cp ring, which swings over the four-membered ring, whereafter the methyl returns to the tantalum, giving the O-*anti*-tantalaoxetane, as drawn in reaction sequence 4 with side views and top views indicated.



Alkyl migrations from a transition-metal center to a coordinated cyclopentadienyl ligand is a known transformation, though rare.[24] To investigate whether this mechanistic proposal provides a reasonable reaction path

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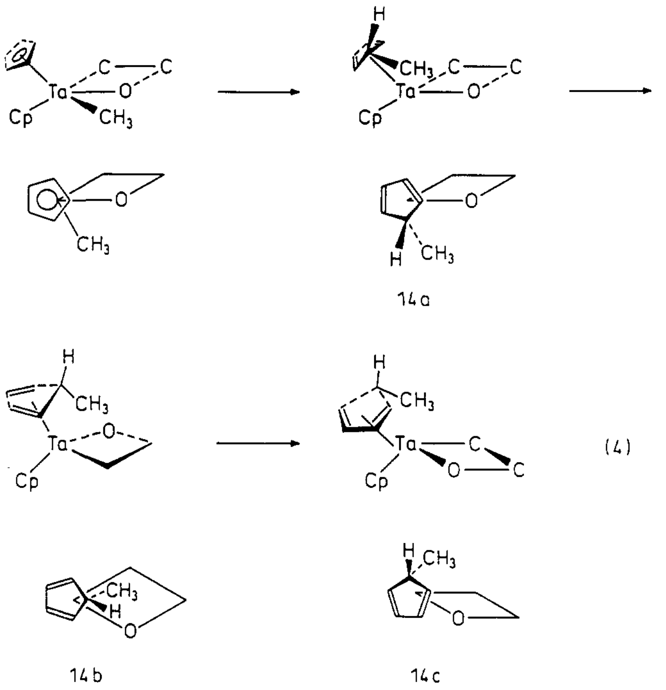
(21) Ugi, I.; Marquarding, D.; Klusacek, H.; Gillespie, P.; Ramirez, F. *Acc. Chem. Res.* **1971**, *4*, 288.

(22) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535. Bazan, G. C.; Oskam, J. H.; Cho, H.-N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899.

(23) Parkin, G.; Bercaw, J. E. *Polyhedron* **1988**, *7*, 2053; *J. Chem. Soc., Chem. Commun.* **1989**, 255.

(24) (a) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324. (b) Canillo, E.; Prout, C. K. *Acta Crystallogr.* **1977**, *B33*, 3916. (c) Elmitt, K.; Green, M. L. H.; Forder, R. A.; Jefferson, I.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1974**, 747. (d) Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1974**, 516. (e) Sim, G. A.; Woodhouse, D. I.; Knox, G. R. *J. Chem. Soc., Dalton Trans.* **1979**, 629. (f) Bunting, H. E.; Green, M. L. H.; Newmann, P. A. *J. Chem. Soc., Dalton Trans.* **1988**, 557. (g) Brookhart, M.; Pinhas, A. R.; Lukacs, A. *Organometallics* **1982**, *1*, 730. (h) McAlister, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966. (i) Rush, P. K.; Noh, S. K.; Brookhart, M. *Organometallics* **1986**, *5*, 1745. (j) This migation has been proposed as being involved in electrophilic substitution of ferrocene and of similar transition-metal coordinated cyclopentadienyl and arene ligands, see, e.g.: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th Ed.; Wiley: New York, 1988; p 1176. Werner, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 794 and references therein. (k) Migration of an acyl group to a cyclopentadienyl ring is also known, see e.g.: Meyer, T. Y.; Messerle, L. *J. Am. Chem. Soc.* **1990**, *112*, 4565.



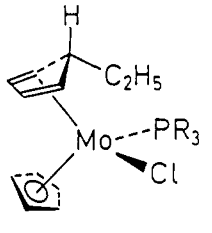
14a

14b

14c

(4)

for the isomerization of O-*syn*-tantalaoxetane, some calculations on the intermediate η^4-diene complexes, **14a–c**, were performed. The structure of the η^4-diene complexes is made analogous to one[24b] of the two[24d] crystal structures that have been published. There, an ethyl (Et) group migrates in $Cp_2Mo(Cl)(Et)$ upon addition of phosphines, PR_3, to give $Cp(\eta^4\text{-}C_5H_5Et)Mo(Cl)(PR_3)$, **15**.[24b] The fifth carbon in the five-membered ring is bent out of the butadiene plane by 30.4° in **15**.[24b] Calculations on the tantalum complex give a smaller activation energy for this migration than for the above regarded pseudorotations, as the intermediates **14a** and **14b** are disfavored by ~3 eV compared to **4** and **5**. The calculated bonding picture agrees well with that determined in the X-ray study of **15**, where it was found that the molybdenum–carbon bond distances for the η^4-C_5H_5Et ligand are shorter than those to the Cp ring.[24b] This is reflected very nicely in the calculations on the tantalum structures **14a** and **14c**, as the average overlap population between tantalum and the five carbons of the Cp ring is 0.18 and the four to C_5H_5Me is 0.21, indicating the stronger bond. The precursor to O-*anti*-tantalaoxetane, **14c**, is favored by ~10 kcal/mol compared to the O-syn precursor, **14a**, and furthermore **14c** is the structure of lowest energy when all rotation angles of the η^4-ligand are included in the analysis. This migration of the methyl group via a cyclopentadienyl ligand is calculated to be base catalyzed, as added phosphines, PR_3 (R = H in the calculations), can coordinate to the open site on tantalum in **14a**, thereby forcing the Tarzan type swing to proceed. The intermediate, **14b**, is stabilized by ~5–10 kcal/mol by the coordination of the phosphine ligand. So far, this third reaction path looks promising, as it has an acceptable (though high) activation barrier and exhibits base catalysis.



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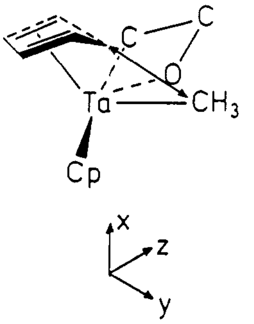
Let us now describe the migration of the methyl group from the tantalum atom to the Cp ring in a molecular orbital picture. In O-*syn*-tantalaoxetane there is no carbon–carbon interaction between methyl and the Cp rings. If one carbon of the Cp ring is bent 20° down from the plane, as in **16**, the carbon–carbon interaction is turned on, as an overlap population of 0.03 is calculated. The energy increase is found to be ~2 eV, slightly less than in **14a–c**. If **16** is divided into two fragments, one being the methyl group the other the rest of the molecule, the following molecular orbital picture emerges from the calculations. The second HOMO of a bent Cp ring, which is localized on the carbon atom sitting out of the plane, can interact with the LUMO of the remaining molecule, being primarily a tantalum to methyl σ^* orbital, **17**. The tantalum to methyl carbon overlap population decreases from 0.488 in O-*syn*-tantalaoxetane to 0.411 in **16**, indicating a weakening of the bond in question. The second HOMO of the bent Cp fragment is depleted by 0.66 electrons and the LUMO of the tantalum fragment accepts 0.87 electrons. The migration of the methyl ligand to the Cp ring can thus be formulated as a nucleophilic attack of one carbon atom in the Cp ring at the frontside of the methyl ligand.



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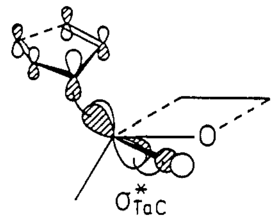


17

One can of course also imagine that the tantalum-bound methylene group of the four-membered ring can migrate to the cyclopentadienyl ring and make a Tarzan type swing over the tantalum oxygen bond and then being transferred back to the tantalum atom in the center position. We have not analyzed in any further detail this path, because it is analogous to a methyl migration via one cyclopentadienyl ring.

Formation of Ethylene from Ethylene Oxide and $Cp_2Ta(CH_3)$

Ethylene oxide interacts with the unsaturated $Cp_2Ta(CH_3)$ fragment, which exists in solution in equilibrium with $Cp_2Ta(H)(CH_2)$, to produce ethylene and a new Ta–O double bond. As a first step toward establishing a model for the reaction, we looked for the most stable geometry of a hypothetical complex between $Cp_2Ta(CH_3)$ and

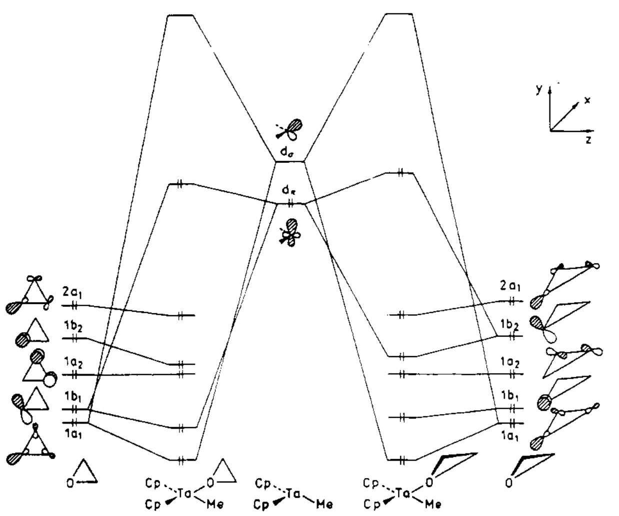
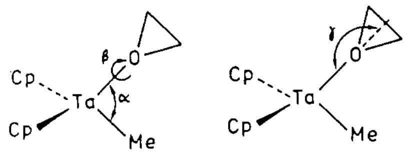


Figure 3. Interaction diagram between the $Cp_2Ta(CH_3)$ fragment and ethylene oxide, OC_2H_4, for the in-plane geometry (left) and the perpendicular geometry (right).

ethylene oxide, three different geometric variables being taken into account, 18.



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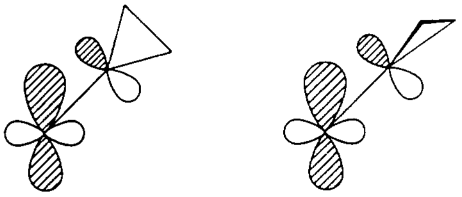
The O–Ta–C angle is followed by varying α; β is the torsion around the Ta–O bond (only two extremes were tested: the O–C–C ring could be in the O–Ta–C plane or perpendicular to it), and γ describes the bending of the ethylene oxide ring away from the O–Ta–C plane. Decreasing the γ angle from 180° (in-plane geometry) to smaller values corresponds to bending the ring away from the *yz* plane. This leads to an increase in energy, although only relatively small changes are found for small bending angles. This possibility was not considered further in the remaining calculations. Supposing then that the ligand lies in the O–Ta–C plane (*yz*), we optimized α. The α angle takes slightly different values according to the orientation of the ethylene oxide ring, 80° for the in-plane geometry and 77° for the perpendicular one. The in-plane geometry was found to be more stable by 0.15 eV. This result can be understood by looking at the interaction diagram shown in Figure 3.

The frontier orbitals of the $Cp_2Ta(CH_3)$ fragment are shown in the center of Figure 3. They have been described in detail before for the analogous Cp_2TiCl^+ fragment[20] and consist of one d_σ and one d_π orbital. The d_σ orbital is empty, while d_π is occupied with two electrons, tantalum in this fragment having a d^2 electronic configuration. The occupied levels of the ethylene oxide ligand are shown to the left of Figure 3. Both $1a_1$ and $2a_1$ may participate in σ-bond formation, while either $1b_1$ or $1b_2$ can be involved in π bonding, depending on the orientation of the ring. The symmetry labels refer to the plane of the epoxide lying in the *xz* plane and will be used without further changes for simplicity. Back donation to $2b_1$ (an unoccupied orbital, not shown in Figure 3) is possible but made negligible by the high energy of this orbital. When ethylene oxide binds to $Cp_2Ta(CH_3)$, we may expect the formation of a σ bond, electrons being transferred from the oxygen lone pair in ethylene oxide to the metal. Furthermore, a four-electron destabilizing interaction will take place between d_π and the appropriate occupied orbital of the ligand. Either $1b_1$ or $1b_2$ can be used in the π interaction, depending on the orientation of the ethylene oxide ring. The interaction involves $1b_1$ if the ring lies in the O–Ta–C plane, while $1b_2$ will be used in the perpendicular geometry, 19. Of course there is a difference in the energy of these orbitals which will affect their ability to π-bond. The π interaction will be a destabilizing interaction because the metal-based d_π orbital is filled. The favored geometry will thus be the one which minimizes interaction. This will be the case for the in-plane geometry where the energy match between d_π and $1b_1$ is poorer than between d_π and $1b_2$. Thus, the ligand will prefer to lie in the *yz* plane. All this is shown together in the molecular orbital diagrams for the two geometries, as depicted in Figure 3.



19

If, as suggested by the experimental evidence, no tantalaoxetanes are formed, one can imagine the reaction to be initiated by the interaction between tantalum and the oxygen atom of ethylene oxide, similar to one of the structures discussed above. Such a complex might lie somewhere on the reaction path. As seen above, however, this complex is not particularly stable, due to a four electron interaction between d_π and either $1b_2$ or $1b_1$. The complex would then decompose to give ethylene. In a slightly different approach, one might consider that as soon as a weak Ta–O interaction develops, it triggers the breaking of the C–O bonds. The problem is then to determine at what stage of Ta–O bond formation the C–O bonds in the ring start to break.

We studied, therefore, different pathways for the reaction, assuming either prior coordination of ethylene oxide through the oxygen atom to Ta followed by breaking of both C–O bonds or formation of the Ta–O bond accompanied by simultaneous breaking of the C–O bonds in the ring. As the results were very similar in all cases, only what happens when starting from a coordinated, in-plane epoxide ligand will be shown. While the molecular orbitals are known for both geometries (Figure 3), there is a symmetry plane for the in-plane one, which aids the analysis. In Figure 4 it is shown how the total energy and some of the relevant overlap populations change along the reaction coordinate chosen (stretching of the C–O bonds and allowing the ethylene molecule to become planar by bending the hydrogens).

There is no activation energy for this process. All the molecular orbitals which are important for the reaction are symmetric relative to the mirror plane (*yz*) and they mix, so that many avoided crossings are found on the reaction path. The energy of the other molecular orbitals remains unchanged. What is happening along all the avoided crossings is the stabilization of the C–O σ^* levels, which takes place as the C–O bonds are stretched. This is shown in Figure 5, where we plot the energy of the C–O σ^* level which becomes ethylene π at the final step of the reaction, along the reaction coordinate described. The energy of this

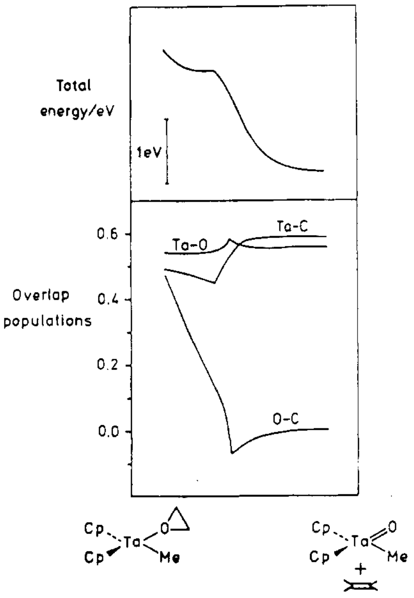


Figure 4. Change in total energy and overlap populations for elimination of ethylene from ethylene oxide coordinated to $Cp_2Ta(CH_3)$.

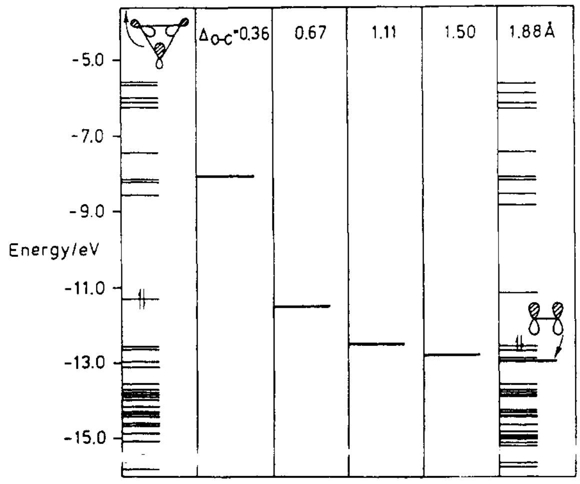


Figure 5. Projection of the molecular orbital of ethylene oxide that becomes ethylene π after reaction with $Cp_2Ta(CH_3)$, at different stages of the reaction measured by the stretching of the C–O bond. All the levels in the energy window considered are shown at the two extremes considered.

orbital is very high in the initial complex and falls outside the energy window shown. As the C–O bond becomes longer and the hydrogen atoms move closer to the nodal plane of the C p orbital it becomes more stable. The two C–O bonds are replaced by the C–C π bond and the Ta–O π bond.

The reduction of epoxides is formally a forbidden one, but the low symmetry makes the activation energy disappear. The similarity between formation of ethylene from ethylene oxide and $Cp_2Ta(CH_3)$ or from ethylene oxide and $WCl_2(PR_3)_4$[25] or from ethylene sulfide on Mo(110)[26] can also be noticed by looking at the schematic Walsh diagram of the reduction of ethylene oxide with the tantalum carbene complex (Figure 5). The picture that emerges is analogous to the one given for the surface reaction[26] and to the published Walsh diagram of the epoxide reduction by the d^2 tungsten complex.[25]

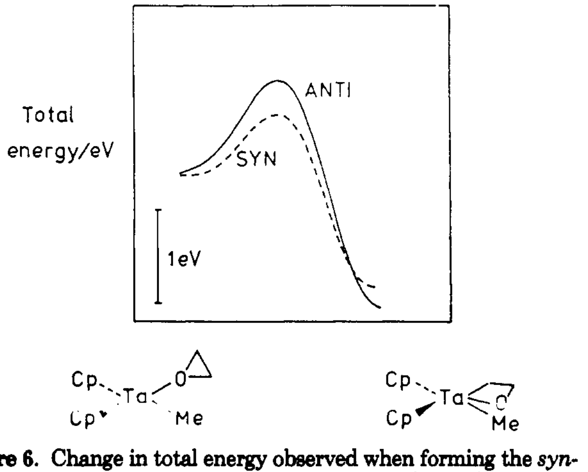
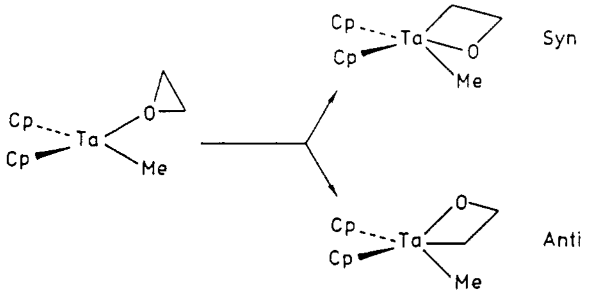


Figure 6. Change in total energy observed when forming the *syn*- or the *anti*-metallaoxetane starting from coordinated, in-plane OC_2H_4.

The evolution of the other C–O σ* level leading to the ethylene π* is similar, but it is always empty and does not contribute to any stabilization. It is the formation of π that may be considered the driving force for the reaction to proceed.

In the reduction of ethylene oxide by $Cp_2Ta(CH_3)$ forming ethylene, no tantalaoxetane intermediates could be experimentally detected.[12] We decided, however, to study theoretically the process of forming tantalaoxetanes so as to compare it with the concerted mechanism described above. To do this, the possibility of forming either the syn or the anti isomer of the metallacycle was taken into account, starting from the precursor complex where ethylene oxide is coordinated through the oxygen, as shown in **20**.



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As one of the carbon atoms of the ethylene oxide ring approaches tantalum, the adjacent C–O bond breaks and the new Ta–C bond starts to form. The activation energy for this process is higher than for the concerted mechanism (estimated as 0.6 eV for the O-syn and 1.0 eV for the O-anti isomer, respectively) as shown in Figure 6.

It is interesting to note that while the anti form is the thermodynamically most stable, these calculations also show the syn isomer to be formed preferentially, as the energy barrier leading to it is lower. The Ta–O bond becomes stronger during this process, even though tantalum is involved in a new bond with carbon. This is due to the fact that no four-electron destabilizing π-type interactions are found in this species.

Comparing the two processes, concerted elimination of ethylene or prior formation of a tantalaoxetane, one might wonder why the first one is preferred, when it involves breaking two carbon–oxygen bonds simultaneously, while

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[25] Schiøtt, B.; Jørgensen, K. A. *J. Chem. Soc., Dalton Trans.* **1989**, 2099.

[26] Calhorda, M. J.; Hoffmann, R.; Friend, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 50.

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in the second one the two bonds are broken successively and the metallacycle intermediate is known to be a stable molecule. The most likely explanation is that there is a thermodynamic drive for the reaction: the Ta(V) complex, $Cp_2TaO(CH_3)$, is much more stable than the metallacycle. The energy of the transition state should also become lower. Again, if the hypothetical ethylene oxide adduct of $Cp_2Ta(CH_3)$ is compared to the tantalaoxetane, it is seen that, on geometrical grounds, forming ethylene from the first requires much less atomic motion than converting it to the second. On the same line of reasoning, as two molecules result from the reaction, the entropic contribution is also clearly in favor of the concerted reaction.

Conclusions

The thermodynamic O-*anti*-tantalaoxetane isomer is rationalized to be more stable than the O-syn isomer because it has stronger tantalum–carbon bonds. In this study it has been explained that aldehydes prefer to add to the syn side of a $Cp_2Ta(CH_2)(CH_3)$ complex due to electronic as well as steric grounds, the latter being more important. The O-*syn*-tantalaoxetane is thus the kinetic product of the reaction. The following isomerisation to the thermodynamically favored form may proceed via ligand (L) migration to a cyclopentadienyl ring followed by a rotation of the hereby formed η^4-C_4H_5L ligand. This path shows base catalysis as the intermediate is stabilized by ~10 kcal/mol by coordination of PH_3. Pseudorotations were excluded from energetic reasoning. The possibility of an acid-catalyzed breaking of the tantalum–oxygen bond cannot be excluded from these calculations as the overlap population of this bond was only slightly affected by binding of hydrogen to the oxygen atom. The reduction of epoxides by a $Cp_2Ta(CH_3)$ complex is proposed to follow a nonactivated direct abstraction pathway of the oxygen atom of the three-membered ring by the tantalum center without formation of tantalaoxetanes.

Acknowledgment. We are thankful to John E. Bercaw and Roald Hoffmann for introducing us to this chemistry prior to publication and for helpful comments. For the careful preparation of the drawings we thank Arne Lindahl and Henrique Nuno. M.J.C. and A.M.G. thank Junta Nacional de Investigação Científica e Tecnológica (PMCT/C/CEN/367/90).

Appendix

The extended Hückel molecular[7] approach is used throughout the study. The bond distances and angles of the various tantalum complexes and of the involved small organic molecules are in accordance with literature data.[12,13,27] Atomic parameters are listed in Table I.

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Study of Metal–Ligand Multiple Bonding in Osmium and Iridium Imido Complexes: Evidence for the Cyclopentadienyl–Imido Analogy

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He I and He II photoelectron spectra are reported for $Os(\eta\text{-}C_6Me_6)NBu^t$, $Os(\eta\text{-}1,4\text{-}(CHMe_2)MeC_6H_4)NBu^t$, and $Ir(\eta\text{-}C_5Me_5)NBu^t$. Photoelectron bands are assigned using simple molecular orbital models for the complexes. The bonding of the osmium and iridium compounds shows similarities to that of the metallocenes but the metal a_1 orbital is more destabilized in the case of the imido complexes.

Introduction

Terminal transition metal imido complexes are known for most transition metal groups.[1] They show varied and interesting reactivity; for example, osmium imido complexes have been used as either stoichiometric or catalytic reagents for oxyamination of a variety of alkenes[2-5] and group IV imido complexes have been implicated in C–H bond activation.[6] They also are increasingly used as ancillary ligands in organometallic chemistry, in which they are widely regarded as analogous to cyclopentadienyl ligands both in their frontier orbitals and in the way that their steric and electronic requirements can be varied by

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