recorded with a Varian CH7 spectrometer (push rod, sample temperature 30 °C, 70-eV electron energy).

# Deviation from the Ideal Octahedral Field vs. Alkyl Distortion in d⁰ Metal–Alkyl Complexes: A MO Study

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The main geometrical features of d⁰ hexacoordinated alkyl complexes (R = CH₃, C₂H₅) are analyzed by means of extended Hückel calculations. Structural distortions from the ideal octahedral field around the metal and distortions at the organic ligand (agostic group) are discussed. The following are shown. (i) The octahedral ligand field around the d⁰ hexacoordinated complex is not a minimum on the potential energy surface. Distortions entailing mixing with low-lying empty d orbitals do occur (second-order Jahn–Teller effect); however, π-donor groups at the metal (chlorine atoms, for instance) help the system to remain close to the octahedron. (ii) Distortions at the organic ligand and around the metal center are antagonizing each other when they occur in the same plane, because they make use of the same vacant metal orbital to stabilize some occupied MO's (in particular the HOMO of the complex). (iii) While the metal C–H interaction is very weak in the methyl complex, it is less so in the ethyl complex, in good agreement with experimental evidence.

The geometrical features of some electron-deficient organometallic complexes suggest an interaction between the metal center and a nearby C–H bond carried by an organic ligand. The group that brings this C–H bond has been called "agostic" by Brookhart and Green.[1] In some cases this interaction is made at the expense of a strong structural distortion of the organic ligand. In particular, octahedral complexes 1 and 2 exhibit unusually small M–
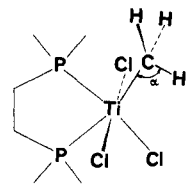
1

(α=93·7°)
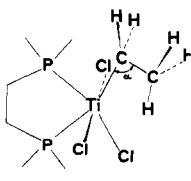
2

(α=85·9°)

C–H angles (93.7° for 1 and 85.9° for 2, respectively), suggesting a strong driving force for the distortion of the

methyl (1) or the ethyl (2) groups.[2] The main chemical interest of these complexes is that they may be regarded as models for the transition states of α (1) and β (2) oxidative addition. Indeed, both 1 and 2 are characterized by a rather short Ti···H distance and by a weakening of the C–H bond interacting with the metal. Related distortions for alkylidene groups have been reported by Schrock and co-workers.[3] Several theoretical studies have been devoted to the understanding of this fascinating class of compounds.[4]

However, the alkyl distortion is not the only structural characteristic of these complexes. One can also note a strong deviation from the ideal octahedral field around the metal center, in both 1 and 2. While two metal–chlorine bonds remain almost exactly perpendicular to the alkyl distortion plane, ligand angles in that plane are far from the ideal 90° value. In particular, the C–Ti–Cl angle is larger (114° in 1 and 128.4° in 2, respectively), while the opposite phosphine angle is only 75°. It may be asked

(1) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* 1983, *250*, 395 and references therein.

(2) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* 1982, 802, 1410. Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K.; Schultz, A. J.; Williams, J. M.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.*, in press.

(3) Schultz, A. J.; Williams, J. M.; Schrock, R. R.; Rupprecht, G.; Fellmann, J. D. *J. Am. Chem. Soc.* 1979, *101*, 1593. Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *Ibid.* 1981, *103*, 169. Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Ibid.* 1982, *104*, 1739.

(4) (a) Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* 1980, *102*, 7667. (b) Koga, N.; Obara, S.; Morokuma, K. *J. Am. Chem. Soc.* 1984, *106*, 4625. Obara, S.; Koga, N.; Morokuma, K. *J. Organomet. Chem.* 1984, *270*, C33. (c) Francl, M. M.; Pietro, W. J.; Hout, R. F.; Hehre, W. J. *Organometallics* 1983, *2*, 281. (d) Eisenstein, O.; Jean, Y. *J. Am. Chem. Soc.* 1985, *107*, 1177 and references therein.

whether or not there is a relationship between the agostic nature of the alkyl group and the distortion around the metal away from the octahedral field. As a matter of fact, the first idea which comes to mind is that steric requirements impose such distortion in order to accommodate the agostic group. The widening of one angle allows the hydrogen atom to interact with the metal, and the opposite angle is diminished because of rehybridization. This seems especially to be the case for the ethyl complex: if the terminal hydrogen of the ethyl group is considered as coordinated to the metal, one has to accommodate five ligands in the equatorial plane of this pseudo-pentagonal bipyramid. All angles around the metal should be around 72° which is approximately the case. A very different point of view can also be taken. The octahedral structure is the optimum structure for a d^6 hexacoordinated complex. Removal of electrons from the metal can lead to a different structure.[5] In particular d^0 hexacoordinated complexes often deviate from octahedral field.[5a-c]

In this study, we will first analyze the driving force for a d^0 hexacoordinated complex to move away from the octahedral field in the way found in complexes 1 and 2 (modeled by 3 → 4). A more complete analysis of distortions in hexacoordinated d^0 systems (in particular comparison between distortion found in 1 and 2 and the more commonly observed deviation toward trigonal prism[5a-c]) is in progress with both ab initio and extended Hückel methods in collaboration with T. A. Albright. In a second part, we will discuss the consequences of the ligand field distortion on the ability of the alkyl groups ($R = CH_3, C_2H_5$), previously studied in the octahedral field in case of CH_3,[4d] to become agostic.

Deviation from the Ideal Octahedral Field in TiH_6^{2-} (3)

In a first set of calculations, we studied the d^0 TiH_6^{2-} complex 3, a model for 1 and 2 in which all the ligands have

3
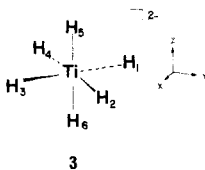
been replaced by hydride ions. This simplified model is used to check whether the deviation from the octahedral

(5) (a) Hoffmann, R.; Howell, J. M.; Rossi, A. R. *J. Am. Chem. Soc.* 1976, *98*, 2484 and references therein. (b) Comba, P.; Sargeson, A. M.; Engelhardt, L. M.; Harrowfield, J. McB.; White, A. H.; Snow, M. R. *Inorg. Chem.* 1985, *24*, 2327. (c) Smith A. E.; Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. *J. Am. Chem. Soc.* 1965, *87*, 5798. Stiefel, E. I.; Eisenberg, R.; Rosenberg, R. C.; Gray, H. B. *Ibid.* 1966, *88*, 2956. Schrauzer, G. N.; Mayweg, V. P. *Ibid.* 1966, *88*, 3235. Stiefel, E. I.; Bennett, L. E.; Dori, Z.; Crawford, T. H.; Simo, C.; Gray, H. B. *Inorg. Chem.* 1970, *9*, 281. Pierpont, C. G.; Eisenberg, R. *J. Chem. Soc. A* 1971, *14*, 2285. Moriarty, R. E.; Ernst, R. D.; Bau, R. *J. Chem. Soc., Chem. Commun.* 1972, 1242. Bennett, M. J.; Cowie, M.; Martin, J. L.; Takats, J. *J. Am. Chem. Soc.* 1973, *95*, 7504. Martin, J. L.; Takats, J. *Inorg. Chem.* 1975, *14*, 73, 1358. Pierpont, C. G.; Buchanan, R. M. *J. Am. Chem. Soc.* 1975, *97*, 4912. Cowie, M.; Bennett, M. J. *Inorg. Chem.* 1976, *15*, 1584, 1589, 1595. Yamanouchi, K.; Enemark, J. H. *Ibid.* 1978, *17*, 2911. Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Hursthouse, M. B.; Amarasiri, S.; Jayaweera, A.; Quick, A. *J. Chem. Soc., Dalton Trans.* 1979, 914. Dilworth, J. R.; Hyde, J.; Lyford, P.; Vella, P.; Venkatasubramanan, K. *Inorg. Chem.* 1979, *18*, 268. Dilworth, J. R.; Dahlstrom, P. L.; Hyde, J. R.; Kustyn, M.; Vella, P. A.; Zubieta, J. *Ibid.* 1980, *19*, 3562. Green, J. C.; Kelly, M. R.; Grebenik, P. D.; Briant, C. E.; McEvoy, N. A.; Mingos, D. M. P. *J. Organomet. Chem.* 1982, *228*, 239. Dorfman, J. R.; Pulla Rao, C.; Holm, R. H. *Inorg. Chem.* 1985, *24*, 453. A related distortion is found in a dioxomolybdenum(VI) species (Pierpont, C. G.; Downs, H. H. *Inorg. Chem.* 1977, *16*, 2970). In this structure the chlorine atoms deviate by 12° from the z axis toward the small angle of the equatorial plane. However, the ligands in the equatorial plane are strongly dissimilar and our reasoning with four equatorial hydrogens is not directly transferable.

Table I. Overlap Populations between Titanium and Hydrogen Atoms in TiH_6^{2-} for Structures 3 (Ideal Octahedron), 4, and 7[a]

structure	Ti-H$_1$	Ti-H$_2$	Ti-H$_3$	Ti-H$_4$	Ti-H$_5$	Ti-H$_6$
3	0.477	0.477	0.447	0.447	0.447	0.447
4	0.499	0.499	0.531	0.531	0.478	0.478
7	0.494	0.494	0.530	0.530	0.573	0.573

[a] See 3 for the numeration of hydrogen atoms.

field is an intrinsic property of the d^0 complex or is due to the presence of an agostic group and/or to the particular nature of the other ligands in 1 or 2.

Let us first discuss a deviation from the octahedral field involving the four ligands lying in the xy equatorial plane, the two remaining Ti-H bonds (not shown in the transformation 3 → 4) being kept perpendicular to that plane. This deformation (3 → 4) mimics the actual structures found for complexes 1 and 2. The structure is described by ϕ_1 (larger than 90°) and ϕ_2 (smaller than 90°).

3   **4**
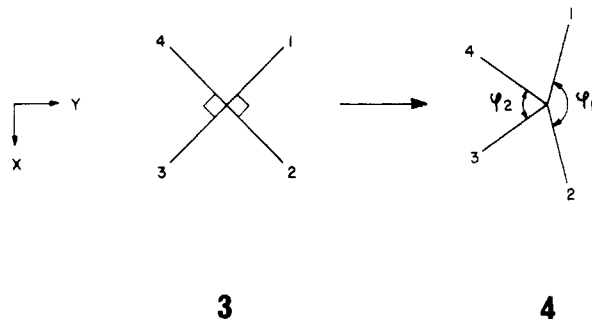
EH calculations lead to a minimum for $\phi_1 = 150°$ and $\phi_2 = 70°$, the stabilization energy with respect to 3 being 1.49 eV.[6] Clearly, there is strong preference for a nonoctrahedral field in the unsubstituted d^0 complex 3. Therefore unusual metal–ligand bond angles found in 1 and 2 are not due to the presence of the agostic alkyl group, as it may have been thought beforehand.

The molecular orbital (MO) shapes and energies of 3 as well as their evolution upon distortion from 3 to 4 are reported on Figure 1. The lowest MO in 3 is the in-phase combination of the metal 4s orbital with the $1s_H$ orbitals. Just above, there is a set of two degenerate MO's involving bonding combinations of xy and z^2 orbitals with 1s orbitals lying in the xy plane and along the z axis, respectively. The three highest occupied MO's arise from the interaction of the 4p orbitals on the metal with combinations of $1s_H$ orbitals of proper symmetry. Finally a set of three degenerate low-lying empty orbitals is formed by the d orbitals which are nonbonding with respect to the ligands ($xz, yz, x^2 - y^2$). We do not include the highest degenerate set made of the antibonding combination of xy and z^2 with the ligands. All these orbitals are labeled within the C_{2v} symmetry group which is preserved upon deformation from 3 to 4.

Upon deformation, there is a reorganization of the orbitals of b_1 symmetry: the $1b_1$ orbital (5) is destabilized because the hydrogen motion reduces the overlap between xy and $1s_H$ orbitals, since the lobes of xy do not point anymore along the M–H bonds. On the other hand, the $2b_1$ orbital is stabilized because the reduced symmetry in 4 allows the participation of the xy orbital. While in 3 the

(6) Preliminary ab initio calculations on CrH_6 indicate also a considerable stabilization upon departure from the ideal octahedron: Albright, T. A., personnal communication.

(7) Cracknell, R. B.; Orpen A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* 1984, 326.

(8) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* 1978, *100*, 3686.

5

xy orbital interacts in an ideal fashion with equatorial hydrogens throughout $1b_1$, its participation with metal hydrides bonds in **4** is spread out into two weaker interactions in orbitals $1b_1$ and $2b_1$. On the whole the energetic evolution of b_1 orbitals is disfavorable (Figure 1). Therefore, the total energy lowering is due to the orbitals of a_1 symmetry. In particular, the $3a_1$ orbital is strongly stabilized because the empty x^2-y^2 orbital, which could not mix in the symmetrical structure **3**, is now allowed to interact (**6**), leading to a lowering of $3a_1$ and, at the same time, to a large energy rise of the vacant $4a_1$ orbital. Table I shows that all the Ti–H bonds are reinforced by intervention of $x^2 - y^2$. Those bonds that are more reinforced are Ti–H_3 and Ti–H_4. This comes from the way $x^2 - y^2$ mixes into $3a_1$ as it is shown in **6**. The resulting orbital ($3a_1$ in **4**) is strongly hybridized toward H_3 and H_4.

3 a₁ in 3   **3a₁ in 4**

6

Deeper MO's of a_1 symmetry ($1a_1$ and $2a_1$) are also stabilized by mixing in with $4a_1$. On the whole, the total energy decreases mainly because of the stabilization of $3a_1$, which overcomes the destabilization of b_1 orbitals. In other words the distorted complex **4** can use two d orbitals (instead of one in **3**) to bind the hydrogen atoms in the *xy* plane. This is a typical lowering of symmetry due to a second-order Jahn–Teller effect. In that motion the four metal–hydrogen bonds lying in the equatorial plane are reinforced while those perpendicular to that plane are unaffected (Table I). It is interesting to note that, despite the angular change in ϕ_1 and ϕ_2, all hydrogen atoms lying in the *xy* plane remain far apart from each other ($H_3\cdots H_4 = H_1\cdots H_4 = H_2\cdots H_3 = 1.83$ Å). The associated overlap populations remain very small (0.006 for $H_3\cdots H_4$, 0.034 for $H_1\cdots H_4$ and $H_2\cdots H_3$, to be compared to 0.003 in the octahedral structure **3**).

Now, one can wonder whether other distortions could stabilize **4**. It is actually the case since there are two nonbonding empty d orbitals in **4** (*xz* and *yz*, Figure 1) which are still not used for bonding with the ligands. Although the actual minimum energy structure of the TiH_6^{2-} complex is out of the scope of this study, we calculated a surface displacing H_5 and H_6 off the *z* axis in the *yz* plane and keeping the other hydrogens as in **4**. In the optimal structure **7** which resembles a bicapped tetrahe-

7

dron, the H_5 and H_6 tilt toward the wide H_1–Ti–H_2 angle (ϕ_1) and the optimal H_5–Ti–H_6 angle is found to be 118°. A further stabilization of 1.35 eV is obtained with respect to **4**. In structure **7**, the *yz* orbital that was not used to bond with the ligands in **4** is now allowed to interact with

Figure 1. Molecular orbitals of TiH_6^{2-} in the ideal octahedral field, **3** (left-hand side), and their evolution upon **3** → **4** transformation.

1s orbitals of H_5 and H_6. This situation is better than that found in **4** since four d orbitals (xy, $x^2 - y^2$, yz, and z^2) are used to bind the metal with the hydride ions while only three were utilized in **4**. In other words, the system distorts itself in order to use the maximum number of d orbitals for bonding with the ligands since there is no electrons to put in the d orbitals as lone pairs. Therefore **4** is far from being the minimum energy structure for TiH_6^{2-}. Nevertheless, it resembles the experimental geometries found for **1** and **2**, in which the "axial" Ti–Cl bonds remain perpendicular to the alkyl distortion plane. We have now to analyze the role of substitutents, in particular that of chlorine atoms, to solve this apparent contradiction.

We first study the d^0 complex $H_4TiCl_2^{2-}$ (**8**) in which the two chlorine atoms lie along the *z* axis. The lone pairs carried by chlorine atoms cannot mix with $x^2 - y^2$ because they do not overlap by symmetry. Therefore no fundamental change occurs in the evolution of the MO's compared to the unsubstituted case for a distortion in the *xy* plane (**9**). Thus deformation from the ideal octahedral structure **8** to **9** ($\phi_1 = 150°$, $\phi_2 = 68°$) leads to a stabilization of the same order of magnitude as that found for **3** distorted into **4** (1.75 eV instead of 1.49 eV).

8   **9**

On the contrary, *xz* and *yz* do interact with chlorine lone pairs and the vacant antibonding combinations (**10** and

11) are raised in energy (-9.36 eV instead of -10.81 eV in the nonsubstituted case). Consequently, these two orbitals are less efficient to stabilize further distortion in **9**, and if one tries to move chlorine atoms off the z axis in the yz plane (as we have done in **7** for hydrogen atoms), a very small stabilization of 0.15 eV is found (instead of 1.35 eV for **4** → **7**) for a weak deviation away from the z axis (10° instead of 31° in **7**). It should be noted that the bonding conterpart of orbitals **10** and **11** remains at almost the same

10   **11**
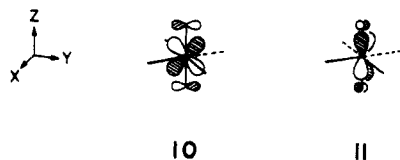
energy when the chlorine atoms deviate slightly away from the z axis since the loss of metal–chlorine π-overlap is compensated by the apparition of some σ-type overlap between the chlorine lone pairs and xz or yz. Therefore, the presence of two chlorine atoms along the z axis reduces the ability of the complex to distort from the ideal octahedral field: only distortion in the xy plane (orthogonal to TiCl bonds) are now allowed, in agreement with the experimental structures of **1** and **2**.

Finally we have studied the $H_3TiCl_3^{2-}$ complex **12** in which the third chlorine atom lies in the xy plane (as it is the case in the experimental structures **1** and **2**).

12
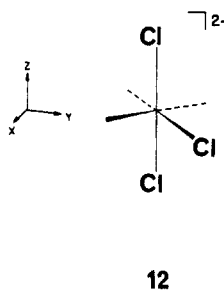
One of the lone pairs of this atom can now interact with the $x^2 - y^2$ orbital, leading to a vacant antibonding combination **13** raised in energy (-10.07 eV instead of -11.8

13

eV in **3** or **8**). The ability of the complex to deviate from the octahedral field in the xy plane is thus reduced but still occurs. The system remains closer to the octahedron ($\phi_1 = 140°$, $\phi_2 = 70°$), and the stabilization upon distortion away from octahedral field is smaller compared to the complexes without chlorine in the xy plane (0.97 eV instead of 1.49 eV for **3** → **4** and 1.75 eV for **8** → **9**). In agreement with structures **1** and **2**, deviation from the octahedral field occurs in the plane containing only one chlorine atom, i.e., the plane which contains the lowest unoccupied d orbital. Additional substitution by π-donor atoms lead to an ideal octahedron, such as WCl_6 and MoF_6. Obviously, π-acceptor should have the opposite effect than π-donor and favors deviations from the octahedral field.

It is clear that *the deviation away from the ideal octahedron for these d^0 complexes is not the consequence of the presence of an alkyl group in need of space. It is due to a tendency of the complex to optimize the metal–ligand σ-bonds as it is for the distortion toward trigonal prism.*[5] This structural reorganization is diminished and even prevented by the presence of π-donor groups.
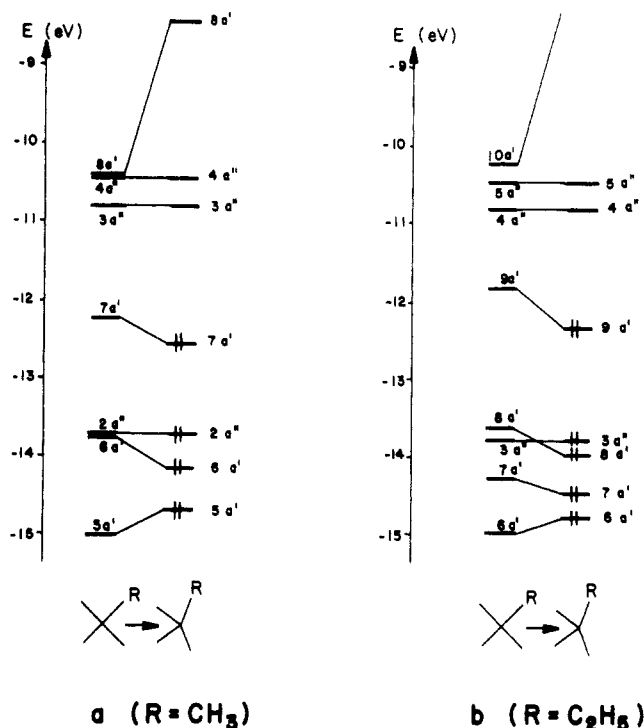

Figure 2. Correlation diagrams for the transformation of octahedral field ($\phi_1 = \phi_2 = 90°$) to optimal (ϕ_1, ϕ_2) values: (a) R = CH_3; (b) R = C_2H_5.

Deviations from Ideal Octahedral Field in Alkyl-Substituted Complexes

We have first looked at the distortion of the ligand field around the metal for $TiH_5CH_3^{2-}$ (**14**) and $TiH_5C_2H_5^{2-}$ (**15**) while *the alkyl groups are maintained in a nonagostic structure*; i.e., the Ti–C–H and Ti–C–C angles are kept to the tetrahedral angle (**14** → **16** and **15** → **17**). The replacement of the hydrogen atom by the alkyl group does not lead to any important change with respect to the behavior of TiH_6^{2-}. In the methyl case, a minimum is found for $\phi_1 = 148°$ and $\phi_2 = 68°$, with a stabilization energy (**14** → **16**) equal to 1.36 eV (instead of 1.49 for **3** → **4**). In the ethyl case, the minimum is found for $\phi_1 = 140°$ and $\phi_2 = 72°$ with a stabilization energy (**15** → **17**) equal to 1.81 eV.

14 R = CH_3 **16** R = CH_3
**15** R = C_2H_5 **17** R = C_2H_5
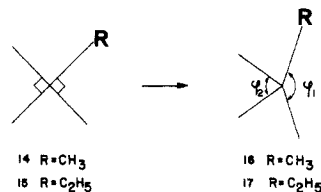
The evolution of the most important MO's upon distortion from the octahedral field are reported on Figure 2, both for methyl (**2a**) and for ethyl (**2b**) substitution. The main features of these diagrams are similar to those found for TiH_6^{2-}, despite the fact that some MO's are no longer degenerate because of the presence of the alkyl group. A bonding orbital (**5a′** in **2a** and **6a′** in **2b**), corresponding to $1b_1$ orbital in Figure 1, is destabilized. It is more than compensated by the stabilization of other bonding orbitals (**6a′** and **7a′** in **2a**; **7a′**, **8a′**, and **9a′** in **2b**) which play the role of $3a_1$ and $2b_1$ in Figure 1. The empty orbital responsible for the stabilization (**8a′** in **2a** and **10a′** in **2b**) is considerably raised in energy in the distorted system as it was the case for $4a_1$ in Figure 1.

We will discuss now how does deviation from the ideal octahedral field modify the ability of the alkyl group to pivot and become agostic.

## Deviation from Ideal Octahedral Field vs. Alkyl Distortion

Methyl Complex. Let first briefly recall the results we got in the case of methyl distortion in a regular octahedral field ($18 \rightarrow 19$). Note that the presentation given below is slightly different, although equivalent, to the one presented in the precedent work.[4d]

18 (α=109°)   **19** (α=40°)
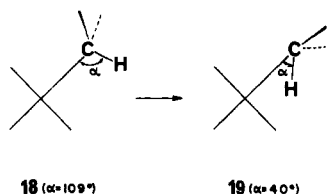
The energy lowering resulting from the pivoting of the methyl group ($18 \rightarrow 19$) is mainly due to the stabilization of the HOMO of the complex, this orbital representing the Ti–C σ-bond. A fragment molecular orbital analysis using TiH_5^- and CH_3^- fragments shows that two orbitals of the metal fragment TiH_5^- are of particular importance for the description of the Ti–C σ-bond. They are a high-lying (–6.89 eV) hybrid orbital, h_1, represented in **20**, pointing toward the vacant site and a low-lying (–10.8 eV) nonbonding $x^2 - y^2$ orbital represented in **21**.

20 (h_1, ε = –6.89 eV)   **21** (x^2-y^2, ε = –10.8 eV)
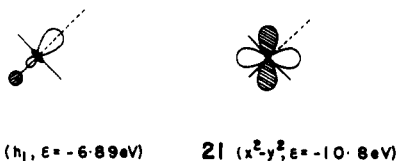
In the nonagostic symmetrical structure **18**, the Ti–C σ-bond results from the bonding interaction of the sp^3 lone pair of CH_3^- (n_{CH_3}), HOMO of CH_3^-, with the high-lying h_1 whereas the interaction between n_{CH_3} and $x^2 - y^2$ is null by symmetry (**22**). Due to the large energy gap between

S large   S =0
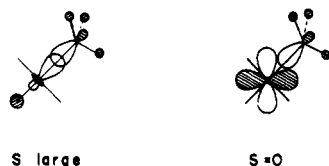
22

h_1 and n_{CH_3} (4.86 eV), their interaction is weak and the resulting bonding combination (HOMO of the complex) remains at a rather high energy.

When the Ti–C–H (α) angle is moved from 109.5° (**18**) to smaller (**19**) or larger values, this interaction pattern is drastically modified: h_1 is no longer pointing toward n_{CH_3} and $\langle n_{CH_3}|h_1\rangle$ overlap decreases as illustrated in **23** and

S small   S large
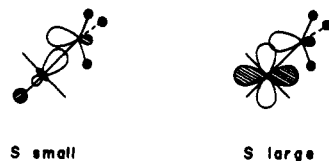
23

shown numerically in Figure 3. On the other hand, a large overlap progressively takes place between n_{CH_3} and $x^2 - y^2$ (**23**, Figure 3). The HOMO of the complex contains now a large part of the low-lying $x^2 - y^2$ orbital. Since the energy gap between the interacting fragment orbitals $x^2 - y^2$ and n_{CH_3} is very small (0.95 eV), the bonding inter-
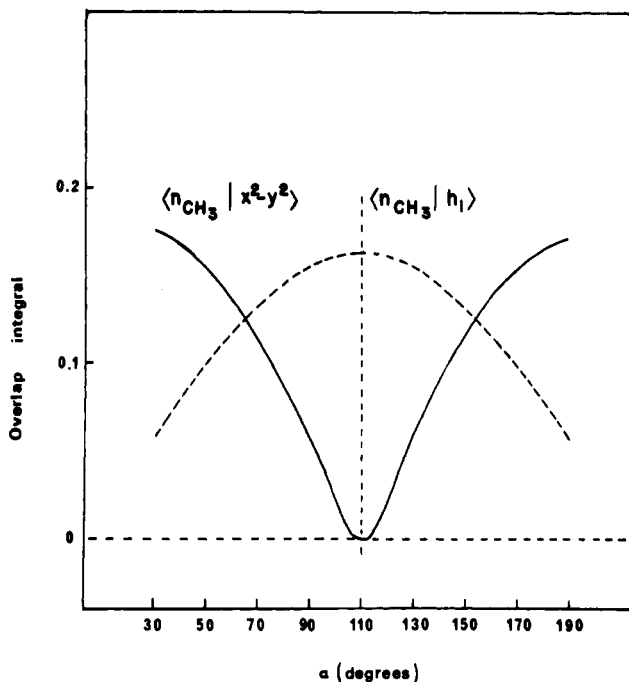

Figure 3. Overlap between h_1 (**20**, dashed line) and $x^2 - y^2$ (**21**, solid line) with n_{CH_3} as a function of CH_3 pivoting in an ideal octahedral field.
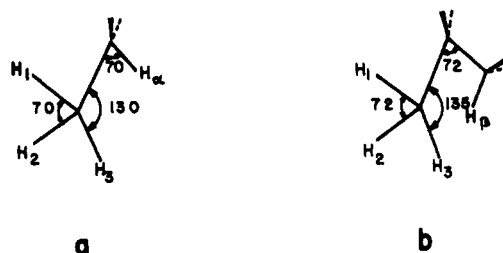

a   **b**

Figure 4. Optimal structures for (a) $H_5TiCH_3^{2-}$ and (b) $H_5TiC_2H_5^{2-}$. In this optimization H_1–Ti–C and H_2–Ti–H_3 angles have been assumed to be equal. In (a) the Ti$\cdots H_\alpha$ distance is equal to 2.051 Å, and in (b) Ti$\cdots H_\beta$ distance is equal to 1.551 Å.

action between Ti and C is stronger than that in the nonagostic system **18** in which the high-lying h_1 hybrid was exclusively used to make the Ti–C σ-bond. Therefore, in going from **18** to **19**, the energy of the HOMO decreases, as the total energy does. The crucial point is that the pivoting of the CH_3 group is made possible by the participation of $x^2 - y^2$ into the Ti–C σ-bond. *Therefore the distortion of the ligand field around the metal as well as the pivoting of the CH_3 group requires the use of the same empty metal orbital $x^2 - y^2$, each of these structural motions shifting up the energy of $x^2 - y^2$. It results that both structural movements are competing.* In other words, each of these structural distortions limits the amplitude of the other one. The optimized structure allowing coupling of these two is found for $\phi_1 = 130°$, $\phi_2 = 72°$, and $\alpha = 70°$ (Figure 4a). This structure is in good agreement with the experimental one. In the ideal octahedral field ($\phi_1 = \phi_2 = 90°$) a much larger distortion of the methyl group was found ($\alpha = 40°$). In contrast, if the methyl group is kept nonagostic, the deviation from the octahedral field was found larger ($\phi_1 = 148°$, $\phi_2 = 68°$ in **16**).
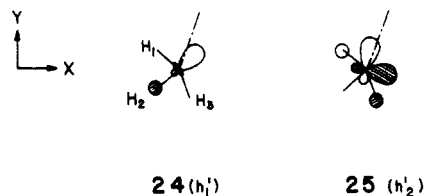
With CH_3^- and the distorted TiH_5^- ($\phi_1 = 130°$, $\phi_2 = 72°$) as fragments, we found the general features of the previous analysis to be still relevant, although the lowering of the symmetry introduces some quantitative changes. The total energy decreases ($\Delta E = 0.28$ eV) as well as the energy of the HOMO, when the methyl is pivoted (α going from 109.5 to 70°) as it is shown in Figure 5. Like in the
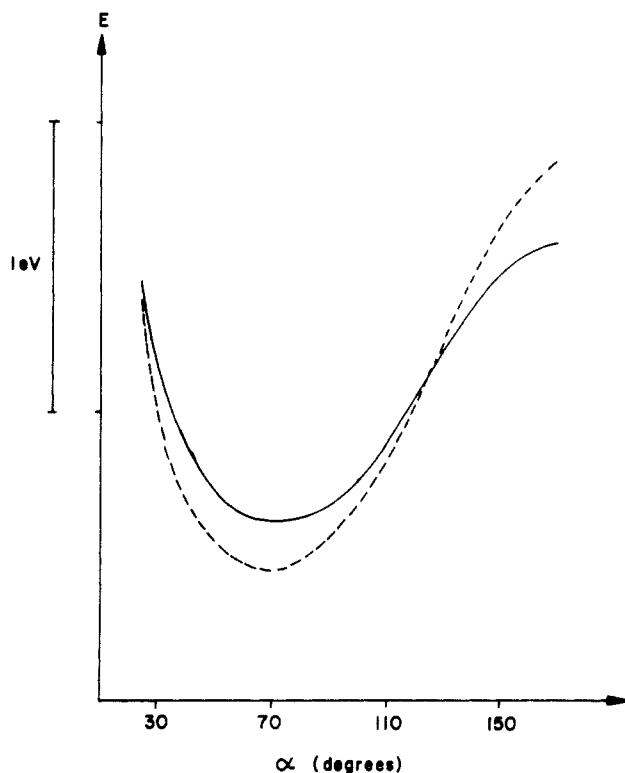
Figure 5. Total energy (solid line) and twice the HOMO energy (dashed line) as a function of CH_3 pivoting in a distorted octahedral field for $H_5TiCH_3^{2-}$.

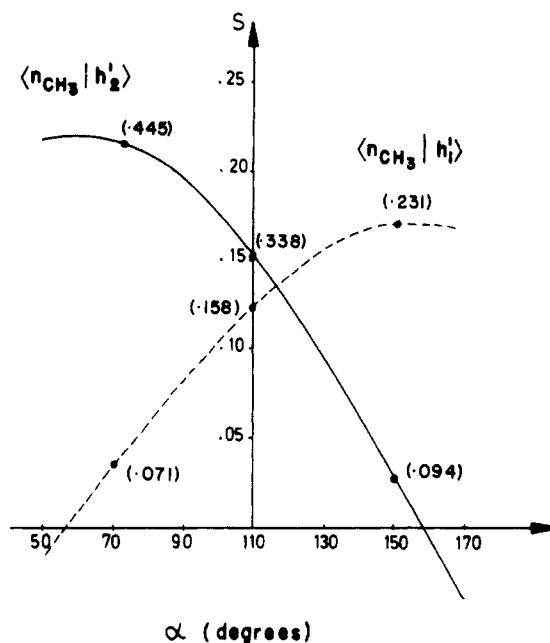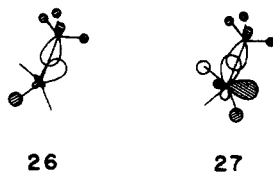**Figure 6.** Overlap between h_1' (24, dashed line) and h_2' (25, solid line) with n_{CH_3} as a function of CH_3 pivoting in a distorted octahedral field. In parentheses are reported the coefficients of h_1' and h_2' in the HOMO of the complex.

nondistorted case, the HOMO is representative of the Ti–C σ-bond.

The two orbitals of the distorted TiH_5^- fragment that are important for the formation of the Ti–C bond are h_1' ($\epsilon = -6.80$ eV) and h_2' ($\epsilon = -9.83$ eV) shown in 24 and 25,

2 4 (h_1')   **2 5** (h_2')

respectively. They are close reminders of the two corresponding orbitals h_1 (20) and $x^2 - y^2$ (21) of the nondistorted TiH_5^- fragment. h_1' has a shape and an energy very similar to those in h_1. h_2' is higher in energy than $x^2 - y^2$ since the three ligands in the xy plane are not anymore in the nodal planes of $x^2 - y^2$. However, h_1' and h_2' have clearly the same ability to bind to incoming ligands as h_1 and $x^2 - y^2$ had.

Formation of the Ti–C bond involves interaction of n_{CH_3} with these two orbitals. The only difference with the case of ideal octahedral field is that, even for $\alpha = 109.5°$ (undistorted methyl group), n_{CH_3} can interact in a bonding fashion with both of them (26 and 27). Evolution of the overlaps between the orbitals of the metal and CH_3 fragments upon CH_3 in-place rotation are reported on Figure 6. Distortion toward small values of α decreases the interaction of n_{CH_3} with the high-lying hybrid orbital (26) but increases that with the low-lying h_2' orbital (27), i.e.,


26   **27**

the same trend as that found in the ideal octahedral field. The participation of the various fragment orbitals inside the HOMO is given in Figure 6, showing the reorganization of the Ti–C bond. The amount of h_1' decreases while that of h_2' increases as the α-angle varies from 109.5 to 70°.

The consideration of the electron transfer confirms the above description. As the methyl group is tilted, there is an increase of the electron transfer from the methyl group to the metal, the electrons going from n_{CH_3} to the low-lying h_2'. Accordingly, the Ti–C bond is slightly reinforced. The Ti–C overlap population increases from 0.356 for $\alpha = 109°5$ to 0.375 for $\alpha = 70°$. Thus all the consequences of the pivoting of the CH_3 are very similar in the ideal octahedron and in the distorted one though the magnitude of all of them are much reduced. α takes the value of 70° instead of 40°. The Ti–C overlap population increases in a smaller extend. As we mentioned above, this is due to the rise in energy of $x^2 - y^2$ associated with the change of the ligand field around the metal.

An important consequence of the reduced ability of the CH_3 group to distort when the structural reorganization of the ligand field is permitted concerns the C–H bond weakening and Ti···H interaction for the hydrogen which comes nearer the metal. Both were found to be rather small in the previous work. It is even more so now. The C–H bond is hardly weakened with respect to a normal C–H bond. The C–H overlap populations are respectively 0.745 in the optimized structure and 0.772 in the nonagostic structure. At the same time the Ti···H overlap population is only 0.035. One can compare these values to the ones found for an agostic CH_3 in an ideal octahedron (C–H = 0.690 and Ti···H = 0.097). It is interesting to compare these results to the experimental facts for 1.[2] According to the neutron diffraction study, the C–H bond involved with the metal is not found to be any longer than a normal C–H bond. In addition no change in the NMR coupling constant J(C–H) is found as it has been noticed for all other agostic structures.[1,2] In our opinion, these experimental results and our theoretical analysis indicate that only a very weak metal H···C interaction is at work in the methyl complex. It is thus likely that the pivoting
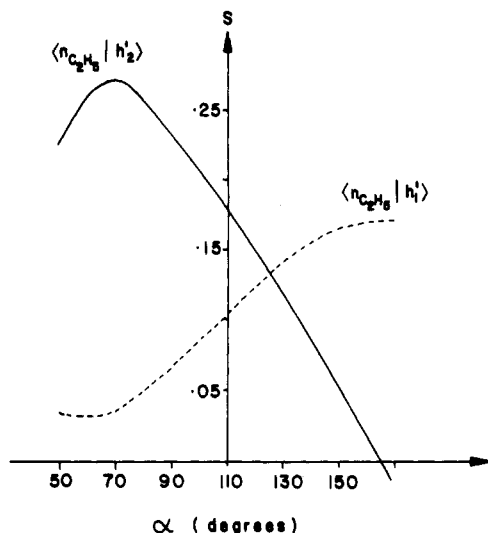
Figure 7. Overlap between h_1' (24, dashed line) and h_2' (25, solid line) with $n_{C_2H_5}$ as a function of C_2H_5 pivoting in a distorted octahedral field.

of the alkyl group is due to other factors such as the increase in the Ti–C interaction as we have suggested.

A last comment concerns the fact that in the ideal octahedron two types of agostic structures were found possible, one for a small α angle and the other one for a large α angle. The last type of agostic structure was found disfavorable when Cl atoms were set on the axis perpendicular (z axis) to the plane of distortion.[4d] In the distorted octahedron the agostic structure with $\alpha < 109.5°$ is the only favorable one even in the absence of any chlorine atoms along the z axis (Figure 5). The pivoting of the CH_3 toward $\alpha > 109.5°$ results in an increase of the energy of the HOMO and the total energy. This can be easily understood by looking at the shape of h_1' and h_2'. When α gets larger than 109.5°, the overlap between n_{CH_3} and h_1' increases while that between n_{CH_3} and h_2' decreases since n_{CH_3} is pointing toward the nodal plane of h_2' as it is illustrated in 28. There is thus a diminished interaction between the


28

carbon and the lowest metal orbital which is not favorable to the system. Therefore the distortion around the metal field commands the direction of the pivoting of CH_3.

Ethyl Complex. As we mentioned previously, the energy lowering associated with the deformation of the octahedral field (keeping a nonagostic ethyl group) is larger in the ethyl case than in the methyl case. Two factors may account for this difference. First, some steric interactions between the closest hydrogen atoms H_β and H_3 (distance = 1.85 Å in the ideal octahedron 29) can be relieved by


29
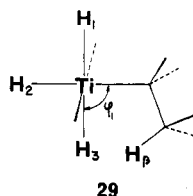
opening the ϕ_1 angle. Second, the stabilizing interaction between the HOMO of C_2H_5 (lone pair on the carbon
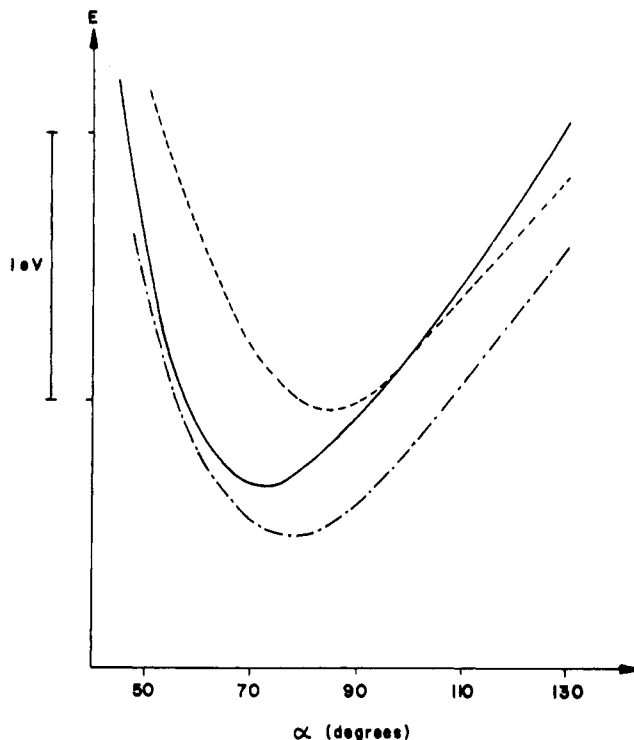

Figure 8. Total energy (solid line), twice the HOMO energy (dashed line) and twice the (HOMO + 8a') energy (dotted dashed line) as a function of C_2H_5 pivoting in a distorted octahedral field for $H_5TiC_2H_5{}^{2-}$.

mixed in an antibonding fashion with π_{CH_3} as shown in 30) and h_2' (25) is larger than that in the methyl case (compare the stabilizations of the two HOMO's, 9a' for the ethyl case and 7a' for the methyl case, Figure 2). Both energy and overlap criteria are responsible for that result. The HOMO of $C_2H_5{}^-$ (–11.25 eV) is higher than that of $CH_3{}^-$ (–11.75 eV), and the overlap with h_2' is larger due to a nonnegligible in phase participation of the β-group (31). As shown in Figure 6 (methyl) and Figure 7 (ethyl), the overlap integrals are respectively 0.158 and 0.180 for $\alpha = 109.5°$.
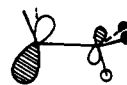
30
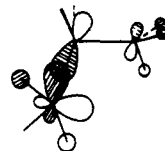
**31**

Let us now turn our attention to the discussion of the pivoting of C_2H_5. This motion presents some features that are different from those found for CH_3 group. If we try to distort the ethyl group in the ideal octahedral field (29), the total energy increases strongly despite a stabilization of the HOMO. This is due to steric interactions between H_β and H_3 atoms that are getting very close to each other. This induces a raise in the energy of deep MO's which dominate all other effects. Therefore the agostic C_2H_5 group can only occur in a distorted octahedral field. The pivoting of C_2H_5 ($\alpha = 70°$) in a nondistorted octahedral field. The pivoting of C_2H_5 ($\alpha = 70°$) in a nonoctahedral field leads to a larger stabilization than for the methyl

(−0.64 eV instead of −0.28 eV). As in the methyl case, the HOMO is made by the bonding combination of the HOMO of the alkyl fragment ($n_{C_2H_5}$, 31) with the metal high-lying h_1' and low-lying h_2' fragment orbitals. When α decreases from 109.5 to 70°, the overlap between $n_{C_2H_5}$ and h_1' decreases while that between h_2' and $n_{C_2H_5}$ increases. The large overlap (Figure 7) between h_2' and $n_{C_2H_5}$ results in a strong stabilization of the HOMO. However, as it can be seen in Figure 8, the minima of energy for the HOMO and for the total energy occur at significantly different angles. The reason for that discrepancy comes from the fact that the diminution of the α-angle results in a mixing between the σ_{Ti-C} orbital (the HOMO 9a′) and a lower orbital of the ethyl group which characterizes the σ_{C-C} bond (8a′, 32). Therefore, the stabilization is spread out in two orbitals (9a′ and 8a′), largely developed upon the fragment molecular orbitals 30 and 32, and the sum of these two orbital energies ($2(\epsilon_{9a'} + \epsilon_{8a'})$) follows the total energy in a very close fashion. Finally a third low-lying orbital comes into play: the $\pi_{C_2H_5}$ orbital mostly centered on the β-carbon and lying in the distortion plane (33). As the ethyl group is tilted, the interaction between 33 and h_2' increases since H_β comes very close to the metal.
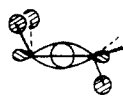
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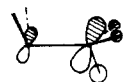
33

The electron transfer is very instructive to examine. The Ti–C bond is slightly weakened, a result opposite to that found in the methyl case. In contrast the C–C bond is reinforced. This is due to the electron transfer from $n_{C_2H_5}$ (C–C antibonding) into the metal orbital h_2'. The system is on its way to form partially a C–C double bond. Simultaneously the C–H_β bond order is significantly reduced (0.661) especially when compared to the corresponding C–H bond in the agostic CH_3 methyl group (0.745). This weakening results from the rather large overlap between h_2' with the C–H part of $n_{C_2H_5}$ (30 and 33) and with the deeper $\pi_{C_2H_5}$ orbital (33). Although we may have exagerated this interaction by having H_β much too close to the

metal in our optimized structure, our results agree well with the general experimental trend. In the experimental structure 2, the C–C bond is found significantly shorter (1.467 Å) than a normal C–C single bond.[2] A similar C–C bond length shortening was observed in an agostic cobalt complex.[7] Simultaneously a large change in the C–H NMR coupling constant has been interpreted in term of a significative C–H_β bond lengthening.[1,2] In other words the ethyl complex has been frozen on the reaction path corresponding to β-elimination.

In conclusion, we have shown in this work that the shift away from the octahedral field in 1 and 2 is not a consequence of the steric demand of the agostic alkyl group but results from the absence of electrons in the d shell. We have put forward the similarities and the differences between the methyl and the ethyl complexes. While we believed that almost no metal C–H interaction is at work in the methyl complex, it is not so in the ethyl complex. Pivoting the alkyl group results for the methyl group in a Ti–C bond reinforcement and results for the ethyl group in a C–C bond reinforcement.

Appendix

The calculations were of extended Hückel type and weighted H_{ij}'s were used.[8] Bond distances are as follows: Ti–C = 2.15 Å, Ti–H = 1.60 Å, C–H = 1.09 Å, C–C = 1.46 Å, and Ti–Cl = 2.30 Å. Coulomb integrals and orbital exponents are listed on Table II, and these were taken from earlier work.[9]

Table II. Extended Hückel Parameters

orbital	H_{ij}, eV	ζ_1	ζ_2	$C_1{}^a$	$C_2{}^a$
H_{1s}	−13.60	1.300			
C_{2s}	−21.40	1.625			
C_{2p}	−11.40	1.625			
Cl_{3s}	−30.00	2.033			
Cl_{3p}	−15.00	2.033			
Ti_{4s}	−8.97	1.075			
Ti_{4p}	−5.44	0.675			
Ti_{3d}	−10.81	4.550	1.40	0.4206	0.7839

^{a} Contraction coefficients in the double-ζ expansion.

(9) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.