electron units), may be somewhat surprising, since alkyl substituents are generally regarded as donating electronic charge to carbocations and thereby stabilizing them.[27-29] The results suggest instead that the stabilization may come about from the electrostatic interaction between the negative methyl carbon and the positive ring site. Based on our calculated charges, the magnitude of this effect should then be para > ortho ≫ meta.

The stabilization energies of these σ complexes, calculated with eq 2, are fully in accord with the prediction. (See Table I.) The least stable is the benzene complex, in which no ring activation or alkyl sustituent effect can occur, while the stabilities of the toluene system isomers increase in the expected order, meta < ortho < para. These findings are in complete agreement wht experimental observations of relative reactivities and orientational preferences.[2]

In these σ complexes, there is a very sizable transfer of charge from the aromatic molecule to the NO_2 group, amounting to 1.06–1.09 electron units (Figure 2). The original +1 charge of the latter is more than neutralized. (In contrast, for protonated benzene and toluene, we found only about 0.85 electron units to be transferred, and the tetrahedral carbons had negative charges of approximately −0.14, whereas they are 0.00 in Figure 2. This shows the strong electron-withdrawing effect of the NO_2 group.) Thus, the NO_2 is carrying out its well-known function of deactivating the aromatic system toward electrophilic attack.[4,26] Roughly half of this transferred electronic charge comes from the hydrogens, including those of the methyl groups in the toluene complexes. It is notable that the methyl carbon has virtually the same charge in all the systems shown in Figure 2.

(27) Reference 4, pp 351–356.
(28) Kemp, D. S.; Vellaccio, F. "Organic Chemistry"; Worth Publishers: New York, 1980; Section 7.6.
(29) NO_2^+: ref 16. Benzene: Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619. Toluene: Pang, F.; Boggs, J. E.; Pulay, P.; Fogarasi, G. *J. Mol. Struct.* **1980**, *66*, 281.

Summary

Our intention in this work has not been to try to conclusively settle the controversial points related to the mechanism of aromatic nitration but rather to provide quantitative descriptions and a better understanding of some systems that may be involved in these processes. We have accordingly presented and discussed the structures, atomic charge redistributions, and stabilization energies associated with the formation of both weakly and strongly bound benzene-NO_2^+ and toluene-NO_2^+ complexes that are possible intermediate stages in the nitration of these aromatic molecules.

Certain interesting and consistent patterns can be seen in our results. One of these is the fact that the same type of resonance structure appears to be the dominant contributor to each of the four σ complexes that have been studied. Another is the picture that has emerged of the two functions performed by the methyl group in toluene and its complexes: First, it induces a rearrangement of charge within the aromatic ring whereby the carbon to which it is attached becomes more positive, by essentially the same increment in each case. The resulting electrostatic interaction,
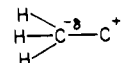
may be responsible for the various stabilization effects in the toluene-NO_2^+ σ complexes that result in the well-known ortho, para-directing properties of CH_3. Second, the methyl group, under the stimulus of the strong electron-attracting power of the NO_2, is a source of electronic charge, which comes from its hydrogens. This is observed in the weakly bound complex as well as the strongly bound ones.

Factors Favoring an M···H—C Interaction in Metal–Methyl Complexes. An MO Analysis[†]

O. Eisenstein* and Y. Jean*

Contribution from the Laboratoire de Chimie Théorique (U.A. 506), Bâtiment 490, Centre Paris-Sud, 91405 Orsay Cedex, France. Received July 5, 1984

Abstract: Electron-deficient alkyl complexes of transition metals sometimes exhibit striking structures in which the alkyl group is distorted in such a way that a C–H bond interacts with the metal atom, leading to an electron donation from the C–H bond to the metal and to a weakening of that bond. In particular, this is the case for the octahedral d^0 complex **4**. However, in the tetrahedral d^0 complex **7**, no significant distortion of the methyl group appears. Model octahedral and tetrahedral complexes, $H_5TiCH_3^{2-}$ and H_3TiCH_3, respectively, have been studied by extended Hückel calculations in order to understand the reasons for the different structures of **4** and **7**. It is shown that a distortion of the methyl group is likely to occur only if a strong interaction between the σ_{Ti-C} orbital and a low-lying d orbital of proper symmetry develops upon distortion. In both octahedral and tetrahedral complexes such an interaction exists, but it is much larger in the former. The stability of the distorted structure originates more from an electronic reorganization of the M–C bond than from a direct C–H electron donation into the metal. Substituent effects have also been analyzed: π donors disfavor distortion in the plane in which they are lying, while π acceptors have the opposite effect; a ligand trans to the metal-methyl bond favors distortion. Finally, the role of electron number in the complexes and that of the ligand field around the metal were discussed, and comparison with experimental data was made when available.

Current interests in aliphatic C–H bond activation by transition metal arise from the need for homogeneous catalytic systems capable of selectively functionalizing aliphatic hydrocarbons.

Although C–H bonds of a hydrocarbon are considered as chemically inert, numerous reactions involve the insertion of a transition metal into a C–H bond. Intramolecular reactions such as α and β eliminations commonly occur and are responsible for the instability of many alkyl–metal complexes.[1] Examples of insertion

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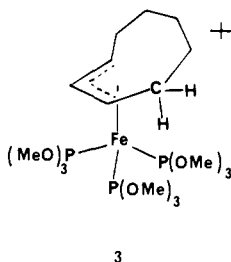[†] Dedicated to J. D. Dunitz on the occasion of his 60th birthday.

are also known.[2] The intermolecular insertion of a metal into a C–H bond, a very important reaction for its industrial applications, is much rarer, presumably because of the unfavorable entropy effects that arise when metal complex and hydrocarbon approach together. Nevertheless, recently considerable progress has been achieved in this field.[3]

Interest in the intramolecular reactions has been recently renewed by the discovery of electron-deficient transition metal complexes that exhibit in their ground state an interaction between the metal center and a nearby C–H bond.[4] In such complexes, the C–H bond has been considered as an electron donor toward the electron-deficient metal center. The M···H···C geometry does not seem to be specific. It varies from a linear M···H···C situation 1, in which the metal essentially does not interact with the carbon atom, to a triangular-type geometry 2, in which the metal interacts with both the carbon and hydrogen atoms.

1   2

The group that brings a C–H bond within bonding distance to the metal is called "agostic" by Brookhart and Green.[4] In their opinion, agostic groups are much more numerous than one may have thought, although a few are known so far.

Complexes having an agostic group can be divided in two classes. In one class, the M···H···C interaction can be geometrically achevied without any noticeable distortion of the C–H containing ligand geometry (3 is the first of such complexes characterized by neutron diffraction).[5] No strain is built in the ligand, and energy stabilization is expected to result from the partial electron donation from the C–H bond to the metal center. Some of these complexes present interesting fluxional behavior.[6,7] The second

3

class of compounds is more striking. The M···H···C interaction is made at the expense of a strong geometrical distortion of the organic ligand. In this category one finds the 12-electron complexes 4[8] and 5.[9] The Ti–C–H angle in 4 is 93.7° from neutron

a = 93.7°   a = 85.9°

4   5
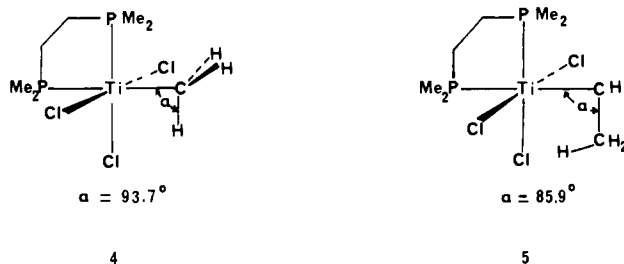
diffraction studies,[8] and the Ti–C–C angle in 5 is 86°.[9] The 14-electron titanium complex 6 appears to have one agostic CH₃ group although the H atoms have not been accurately located yet.[10]

6
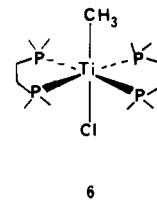
These distorted methyl structures are related to the distorted alkylidenes in electron-deficient tantalum alkylidene complexes characterized by Schrock and co-workers.[11]

Electron deficiency is a necessity if one wants the complex to have an agostic group. For instance, if one replaces the titanium by iron in complex 6 (and the chlorine atom by a methyl group), both methyl groups have a normal tetrahedral structure.[10] It is nevertheless important to note that electron deficiency in a complex is not sufficient by itself to give rise to an agostic group. Consider Cl_3TiCH_3, 7.[4] Although it is only an eight-electron complex, there is no evidence for a Ti–C–H interaction. The methyl group is slightly flattened and all Ti–C–H angles are 104° (X-ray diffraction results). Similarly, the high-spin 13-electron complex 8 does not present any Mn–C–H interaction.[12]

a = 104°

7   8
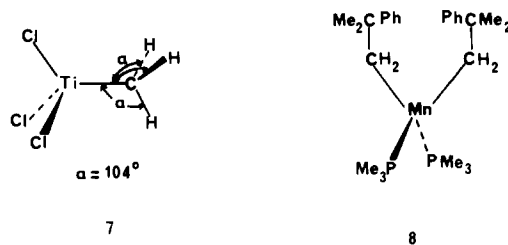
Among the 16-electron complexes, one also finds some which have a M–C–H interaction and some which have none. The cyclopentadienylcobalt cation 9 has the α hydrogen 1.46 Å from the cobalt atom and the Co–C–C angle equal to 74°.[13]   In 10,

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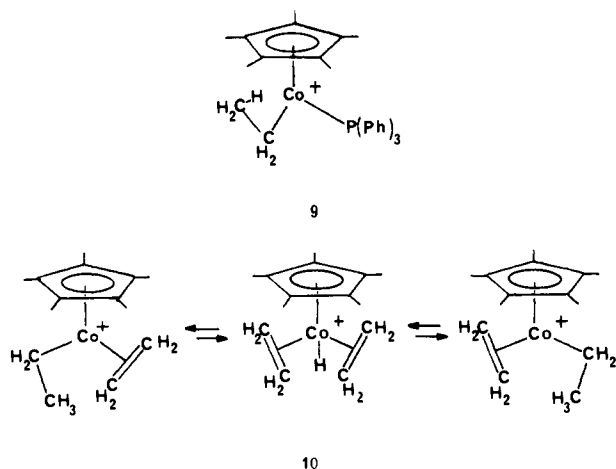
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M···H—C Interaction in Metal-Methyl Complexes

J. Am. Chem. Soc., Vol. 107, No. 5, 1985 1179

9

10

no structural information was obtained. However, spectroscopic data and fluctional properties, according to which a β-hydrogen migration exchanges the olefin and the ethyl group, are in agreement with a noticeable Co–H interaction in the ground state of the molecule.[14] Biscyclopentadienyl 16-electron complexes may also have agostic methyl groups.[15]

In contrast, in the cycloheptatrienyltitanium complex, **11**, neither H_α nor H_β interacts with the metal.[4]

$a = 115°$

11
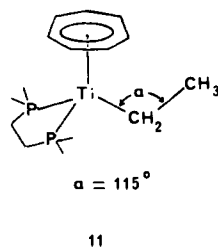
Thus, it is necessary to look for a better understanding of the factors which are responsible for the occurence of an agostic group. Such knowledge is especially important for a more rational approach to the C–H activation problem. Furthermore, factors that favor a M···H···C interaction in the ground state may also be important in the transition state of the insertion of the metal into a C–H bond. Theoretical work is scarce in this domain. Ittel and co-workers have shown by EHT calculations that a M···H···C interaction is favored in a 16-electron η^3 alkenyl complex but not in an 18-electron one.[16] Hoffmann and co-workers have analyzed the tantalum alkylidene complex and have predicted that a methyl group could in principle also distort.[17] Morokuma and co-workers have done ab initio pseudo-potential calculations on models of the titanium complexes **5**[18] and **4**[19] and have obtained optimized structural parameters in good agreement with experiment. Nevertheless, the factors which favor or disfavor the occurrence of an agostic group in any type of electron-deficient transition metal complexes are still unclear.

In this work, the influence of the ligand field, the electronic nature of the ligands, the role of the electron deficiency in the occurrence of a M···H···C interaction in methyl complexes are discussed with the help of extended Hückel calculations. *We show in particular why an electron deficiency at the metal is not sufficient to systematically induce a M···H···C interaction.*

(14) Brookhart, M.; Green, M. L. H.; Pardy, R. B. A. *J. Chem. Soc., Chem. Commun.* **1983**, 691.

(15) The reactivity of $Cp_2WCH_3^+$ (ref 1b) has been reinterpreted in that fashion (ref 4).

(16) Harlow, R. L.; McKinney, R. J.; Ittel, S. D. *J. Am. Chem. Soc.* **1979**, *101*, 7496.

(17) Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1980** *102*, 7667.

(18) Koga, N.; Obara, S.; Morokuma. K. *J. Am. Chem. Soc.* **1984**, *106*, 4625.

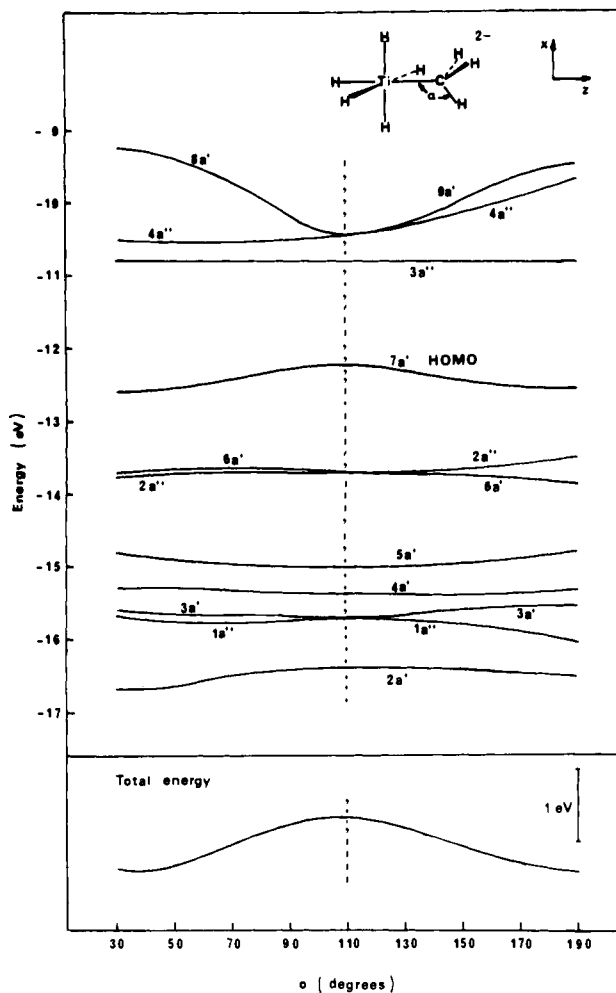(19) Obara, S.; Koga, N.; Morokuma, K. *J. Organomet. Chem.* **1984**, *270*, C33.

Figure 1. Walsh diagram and total energy variation as a function of α in $H_5TiCH_3^{2-}$.

Octahedral Complex

Calculations were first performed on the d^0 $H_5TiCH_3^{2-}$ complex to check whether the methyl distortion was an intrinsic property of a 12-electron octahedral complex. In the first set of calculations, the distortion was described by a single parameter (α angle) whose value is 109.47° in the undistorted structure **12**. The angles

12
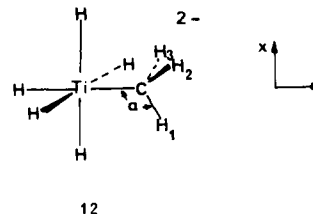
between the C–H bonds have been kept constant to their tetrahedral value. Other structural parameters are given in the Appendix.

The variation of α away from the reference value (109.47°) toward either smaller or larger values results in a lowering of the total energy (Figure 1). The two minima which appear at $\alpha = 40°$ and at $\alpha = 190°$ have approximately the same energy. The rather large energy stabilization upon distortion should not be taken in a quantitative sense. We, nevertheless, consider that the qualitative behavior of the energy is well reproduced. The correlation diagram (Figure 1) shows that some orbitals are quite affected by the structural change. The behavior of the HOMO (7a') is especially interesting. It nicely parallels the behavior of the total energy. As in the case of the total energy, the stabilization of the HOMO is equivalent for small and large α angles. In contrast to the behavior of the HOMO, one of the low-lying empty orbital (8a') is strongly destabilized by the structural change. We
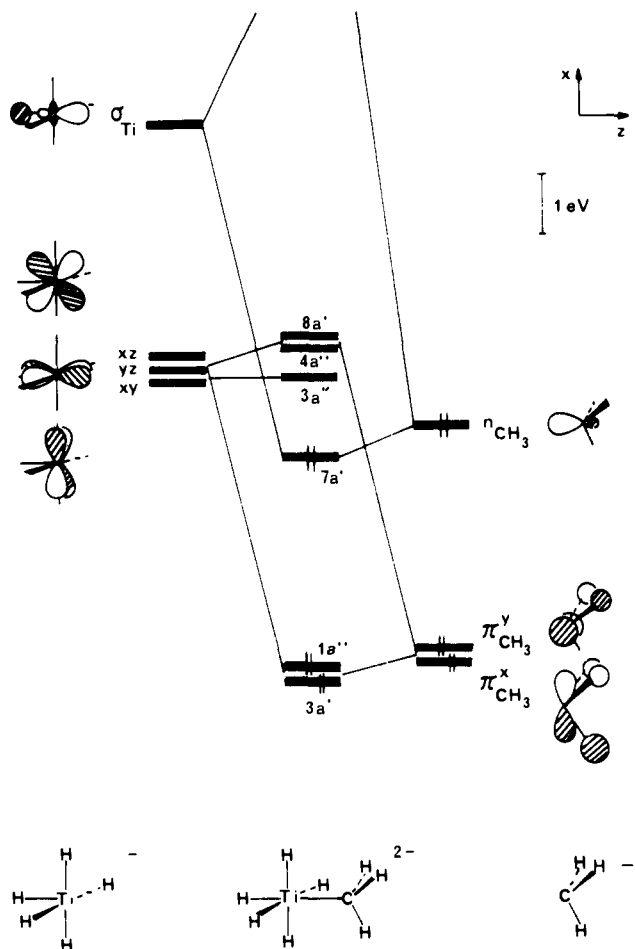
Figure 2. Interaction diagram between the H_5Ti^- and CH_3^- fragments.
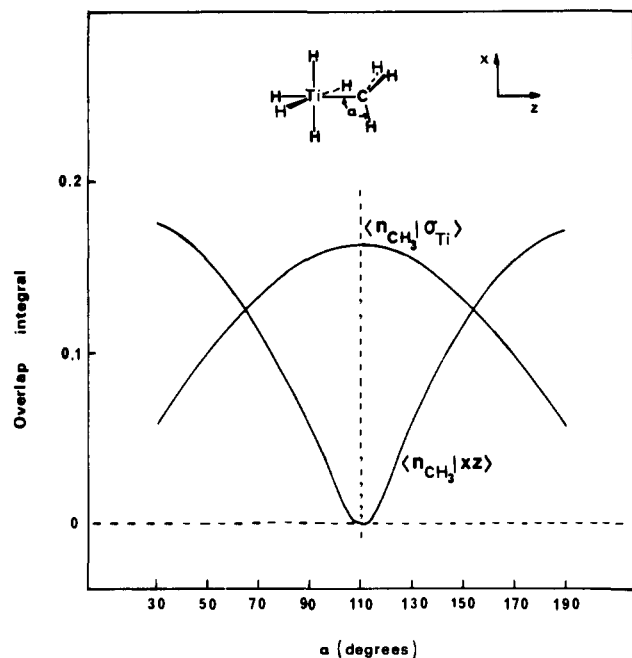

Figure 3. Overlap between some fragment molecular orbitals. See Figure 2 for the labels of the orbitals.

will show that the reasons for the occurrence of an agostic methyl group are mostly contained in the two above orbitals. Other orbitals follow a more shallow and complicated pattern which will be analyzed in due time.

In order to understand the above energy scheme, we consider the molecule as made of two fragments TiH_5^- and CH_3^-. The well-known molecular orbitals of these fragments are given in

Table I. Mulliken Overlap Population in Complexes **12** and **18**

	octahedron			tetrahedron		
α, deg	50	109.47	170	50	109.47	170
Ti–C	0.390	0.330	0.402	0.471	0.483	0.468
C–H$_1$	0.679	0.772	0.796	0.683	0.771	0.785
C–H$_{2,3}$	0.782	0.772	0.720	0.778	0.771	0.727
Ti–H$_1$	0.098	−0.015	−0.034	0.116	−0.013	−0.031
Ti–H$_{2,3}$	−0.023	−0.015	0.051	−0.0203	−0.013	0.0511

Figure 2. TiH_5^- has a set of three low-lying degenerate d orbitals (xy, xz, and yz in our coordinate system) and a high-lying hybrid orbital σ_{Ti}, made of a mixture of z^2, s and p_z pointing toward the vacant site. The $x^2 - y^2$ orbital is even higher in energy and is not necessary in this bonding scheme. All of these orbitals are empty. CH_3^- possesses a set of degenerate $\pi^x_{CH_3}$ and $\pi^y_{CH_3}$ orbitals rather deep in energy and a high-lying n_{CH_3} hybrid. All of these orbitals are occupied. We neglect the empty orbitals of CH_3 because they are very high in energy and do not participate in the bonding with the metal fragment. The main molecular orbitals of the undistorted $H_5TiCH_3^{2-}$ system are easily derived by combining the above fragment orbitals. The HOMO of the complex is the bonding combination of σ_{Ti} and n_{CH_3}. It characterizes the Ti–C σ bond. $\pi^x_{CH_3}$ and $\pi^y_{CH_3}$ match xz and yz, respectively. The bonding interaction between these orbitals is not very large owing to the large energy gap between the interacting orbitals. Consequently the xz and yz orbitals are only very weakly destabilized by the methyl π orbitals and remain essentially nonbonding.

When the α angle is moved away from 109.47° the HOMO, which is the σ_{Ti-C} bond, is mostly affected. To understand what happens to this orbital, two effects have to be considered. First, the overlap between σ_{Ti} and n_{CH_3} decreases (**13**), because these

13

two fragment orbitals do not point toward each other anymore (Figure 3). This is an unfavorable factor which should have resulted in a destabilization of the σ_{Ti-C} orbital.

Secondly, at $\alpha = 109.47°$ n_{CH_3} cannot overlap with xz by symmetry. When α takes a different value, the symmetry is lowered and n_{CH_3} overlaps with xz (Figure 3). Because of the symmetry property of xz, the overlap is the same for small and large α angles, **14**. As xz is vacant, this is clearly a stabilizing


$\alpha < 109.47°$ $\alpha > 109.47°$

14

interaction which in turn causes the destabilization of xz (8a′, Figure 1). This overlap arises mainly from the carbon sp^3 hybrid and to a much smaller extent to the hydrogen atom(s) since the coefficient(s) on the hydrogen(s) is less than 0.1.

Therefore these two opposite effects will add when the methyl group is tilted. In the octahedral complex discussed here, the HOMO is eventually stabilized. Thus the stabilization coming from the intervention of the xz is larger than the destabilization resulting from the weakening of the bonding interaction between σ_{Ti} and n_{CH_3}. In Figure 3, we show the variation of the overlap between n_{CH_3}, σ_{Ti}, and xz as a function of α. It is clear that the overlap between n_{CH_3} and xz increases fast as α departs from 109.47°. In contrast, the overlap between n_{CH_3} and σ_{Ti} decreases in a much slower fashion. In addition, xz is lower in energy than σ_{Ti}. Thus the overall stabilization upon distortion is not suprising. The distortion does not actually weaken the σ_{Ti-C} bond, but rather induces a reorganization of the orbitals involved in that bond; the lower participation of σ_{Ti} is compensated by a larger mixing with xz. The Mulliken overlap populations given in Table I shows that

indeed the Ti–C bond is slightly reinforced. Note that a similar analysis has been proposed by Hoffmann and co-workers in their studies of the alkylidene tantalum complexes.[17]

It is noticeable that the above analysis only involves the evolution of the metal–carbon bond energy upon distortion, and not a possible increase of the electron donation from the C–H bond to the metal center. This is not consistent with the description of the agostic complexes given in the introduction, namely, with the fact that the C–H bond close to the metal center is generally thought as a new ligand giving electrons to the electron-deficient metal center. Therefore, although the evolution of the total energy can be rationalized only by looking at the HOMO evolution, we need to analyze the role of the deeper molecular orbitals characterizing the C–H bonds. They are the (i) $\pi^x_{CH_3}$ and (ii) $\pi^y_{CH_3}$ in weak bonding interaction with xz and yz, respectively (Figure 2).

(i) When α is smaller than 109.47°, H_1 gets closer to the metal. This modifies the nature of the overlap between xz and $\pi^x_{CH_3}$ as shown in **15**. The diminished overlap between the carbon p_x and
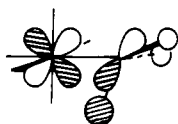
15

xz is counterbalanced by the larger overlap between H_1 and xz. Consequently, the overlap between the two group orbitals xz and $\pi^x_{CH_3}$ weakly increases ($S = 0.146$ for $\alpha = 109.47°$; $S = 0.167$ for $\alpha = 50°$).

When α is larger than 109.47°, H_2 and H_3 gets closer to the metal. However, the overlap between xz and $\pi^x_{CH_3}$ decreases because of the loss of overlap between xz and p_x orbitals ($S = 0.092$ for $\alpha = 170°$), **16**. In contrast with the case of $\alpha < 109.47°$,
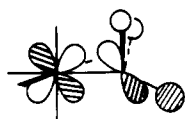
16

H_2 and H_3 do not overlap sufficiently with xz, because of the out-of-plane position of hydrogens and of the smaller coefficients carried by these atoms.

(ii) For small values of α, the overlap between $\pi^y_{CH_3}$ and yz remains almost constant ($S = 0.146$ and 0.131 for $\alpha = 109.47$ and $50°$, respectively) because the hydrogen atoms have almost no overlap with yz even in the undistorted structure. In contrast $\pi^y_{CH_3}$ overlaps much stronger with yz at a large α angle because H_2 and H_3 get now closer to yz ($S = 0.146$ for $\alpha = 109.47°$ and 0.212 for $\alpha = 170°$), **17**.
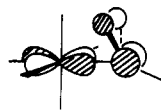
17

It therefore appears that a distortion toward small values of α stabilizes $\pi^x_{CH_3}$ through increasing interaction with xz (8a', Figure 1) while a distortion toward large values of α stabilizes $\pi^y_{CH_3}$ through increasing interaction with yz (4a″, Figure 1). The behavior of deeper orbitals which have CH_3 characters (3a' and 1a″ for $\alpha = 109.47°$, Figure 1) are thus easily understood. For small values of α, $\pi^x_{CH_3}$, which is now spread in 3a' and 2a', is stabilized, while $\pi^y_{CH_3}$ (1a″) remains unaffected. For large values of α, the deep a' orbitals are not modified (2a' is slightly stabilized and 3a' destabilized) while $\pi^y_{CH_3}$ (1a″) is stabilized. The stabilization gained by these interactions is almost the same for small and large α angles because xz and yz are degenerate as well as $\pi^x_{CH_3}$ and $\pi^y_{CH_3}$. The behavior of the occupied orbitals is nicely

reflected in the behavior of the empty xz (8a') and yz (4a″) orbitals. For small α, xz interacts with both n_{CH_3} and $\pi^x_{CH_3}$ and for large α only with n_{CH_3}. Therefore, xz (8a') is more destabilized at small α. In contrast, yz (4a″) is destabilized for large values of α (increasing interaction with 1a″) and remains unchanged for small ones.

The consequence of the interaction of specific π_{CH_3} orbitals with empty d orbitals when CH_3 tilts in one direction or the other is the weakening of specific C–H bonds and partial formation of Ti–H bonds. Table I summarizes the Mulliken overlap population. For small α angles, C–H$_1$ is weakened (the overlap population decreases from 0.783 for $\alpha = 109.47°$ to 0.690 for $\alpha = 40°$), while Ti–H$_1$ is strengthened since its overlap population varies from an antibonding situation (overlap population -0.02 for $\alpha = 109.47°$) to a bonding one ($+0.097$ for $\alpha = 40°$). For large α angles, C–H$_2$ and C–H$_3$ bonds are weakened, while Ti–H$_2$ and Ti–H$_3$ bonds are strengthened. However, the Ti–H bond orders created in the agostic structures remain small when compared with a terminal Ti–hydrogen bond order (0.47). It is clear that the C–H bond is a very weak base as it can be expected from the deep energy level of its occupied orbitals.

We can already draw some conclusions concerning an agostic methyl group in an octahedron d^0 complex.

(i) The occupied n_{CH_3} orbital is bonded to the empty σ_{Ti} and xz simultaneously. This new bonding situation is more stable than the normal σ_{Ti-C} bond made of only σ_{Ti} and n_{CH_3}.

(ii) For small α angles, xz interacts in a bonding fashion with the C–H$_1$ bond through $\pi^x_{CH_3}$. For large α angles, the empty yz interacts with the C–H$_2$ and C–H$_3$ bonds through $\pi^y_{CH_3}$. Weakening of C–H bonds and partial Ti–H bonds results from these interactions.

(iii) The two energy minima, one for $\alpha \simeq 40°$ and the other one for $\alpha \simeq 190°$, are almost the same in energy. Note that all examples of distorted methyl groups known so far have small values for α. We show later in this paper that the preference for this minimum is related to the ligand effects at the metal center.

The Tetrahedron Case

Calculations were first performed on the d^0 H$_3$TiCH$_3$ complex, in a staggered conformation **18**, to check whether or not the absence of methyl distortion in Cl$_3$TiCH$_3$ (**7**) is an intrinsic property of a eight-electron tetrahedral complex.
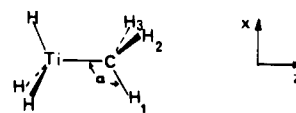
18

As in the previous system, the structural change was described by the Ti–C–H$_1$ α angle. Molecular orbital energies and total energy variations are given in Figure 4. In contrast with the octahedron case, any departure of the α angle away from 109.47° is weakly destabilizing. Results are very similar for an eclipsed conformation of the complex. This finding agrees nicely with experimental results on Cl$_3$TiCH$_3$ (**7**). Moreover, the HOMO evolution closely follows that of the total energy. It is therefore crucial to understand why the HOMOs of tetrahedral and octahedral complexes behave so differently since in both cases their evolutions almost parallel that of the total energy.

Let us first discuss the shapes and the energies of the molecular orbitals of H$_3$TiCH$_3$ built as linear combinations of the fragment molecular orbitals of H$_3$Ti$^+$ and CH$_3^-$ (Figure 5). H$_3$T$_i^+$ has three low-lying vacant orbitals of e and a$_1$ symmetry (looking like the three nonbonding orbitals of the octahedron) and, much higher in energy, a set of three hybrids of e and a$_1$ symmetry, made up of a mixture of d, s, and p atomic orbitals. On the methyl moiety are the usual $\pi^x_{CH_3}$ and $\pi^y_{CH_3}$ bonding orbitals and the nonbonding n_{CH_3} orbital (of e and a$_1$ symmetry, respectively). Taking into account the energy gap between the fragment molecular orbitals, it is clear that a metal–methyl bond in the undistorted d^0 complex mainly involves interactions between the methyl orbitals and the
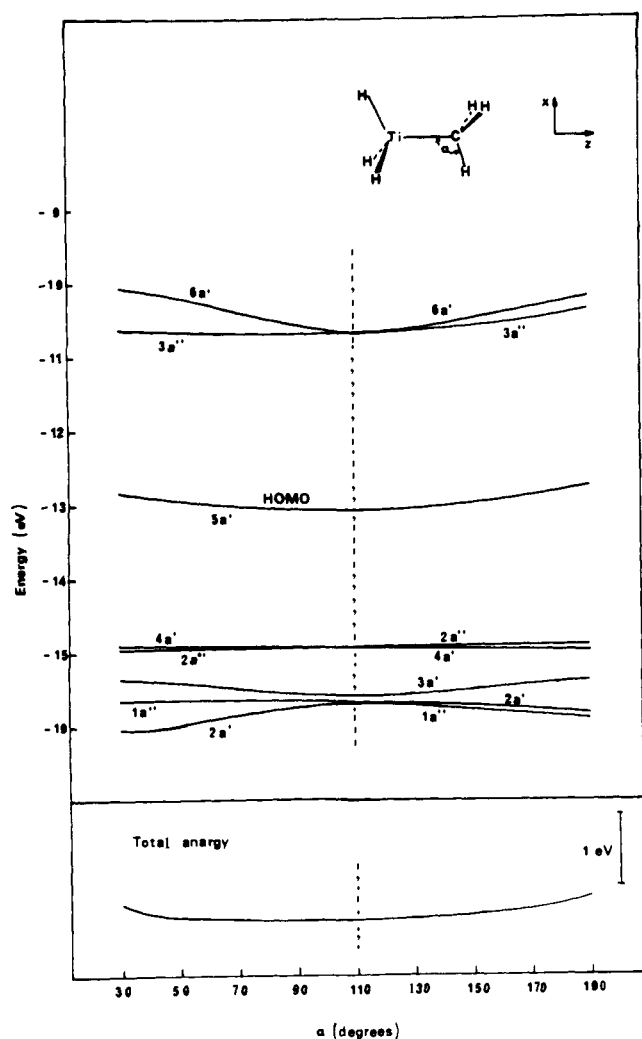
Figure 4. Walsh diagram and total energy variation as a function of α in H_3TiCH_3.

lower set ($1e$, $1a_1$) of vacant orbitals on H_3Ti^+. In particular, the σ_{Ti-C} bond results from the bonding combination of $1a_1$ and n_{CH_3} orbitals, while $\pi^x_{CH_3}$ and $\pi^y_{CH_3}$ are stabilized by e orbitals on H_3Ti^+ (mainly $1e$, closer in energy). On the other hand, both e sets on TiH_3^+ are slightly destabilized, while the $1a_1$ orbital energy is strongly raised by its antibonding combination with n_{CH_3}. The classical splitting associated with the tetrahedron, two orbitals below three, results from these interactions.

Now, our analysis of methyl distortion in H_3TiCH_3 follows exactly the one developed for the octahedron. As CH_3 is tilted, the bonding interaction between $1a_1$ and n_{CH_3} diminishes, **19**, which

19   20
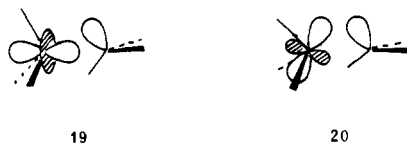
is unfavorable. On the other hand, n_{CH_3} can now interact in a bonding way with the empty orbitals of the e sets (i.e., $1e_s$ and $2e_s$) which are symmetrical with respect to the xz plane. The interaction with $1e_s$, **20**, closer in energy, is expected to be dominant. At this point, it seems that the tilt of CH_3 should have similar consequences in the tetrahedron and in the octahedron. However, calculations have shown that the HOMO of tetrahedron is destabilized while that of octahedron is stabilized. An examination of the *quantitative* aspects of the interaction in both systems reveals the reasons for the different behaviors.

In usual perturbational analysis, the strength of interaction depends both on the energy gap and on the overlap between interacting orbitals. Let us first consider the energy gap criteria.
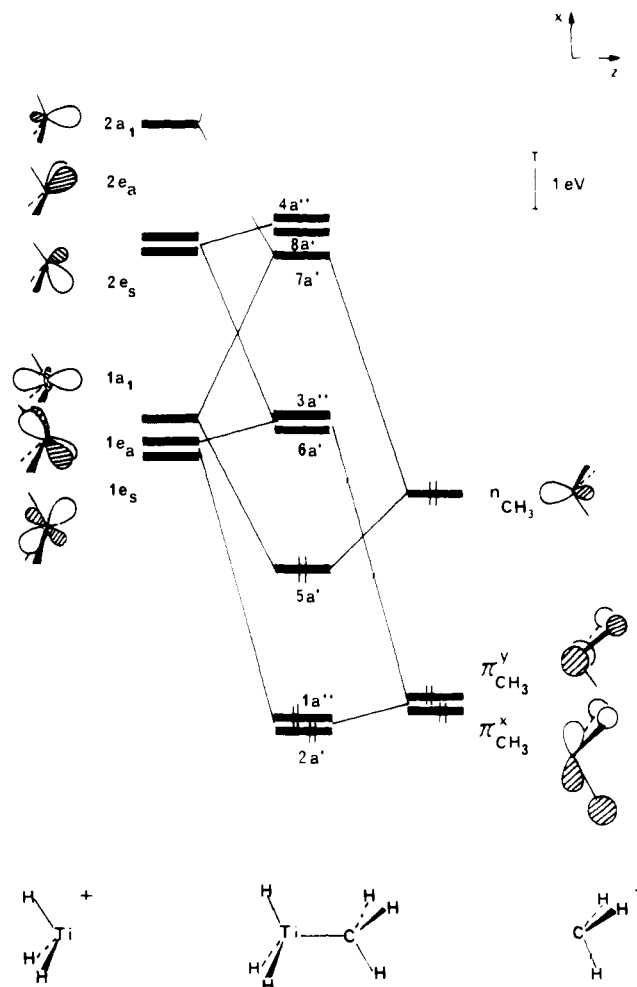
Figure 5. Interaction diagram between the H_3Ti^+ and CH_3^- fragments.
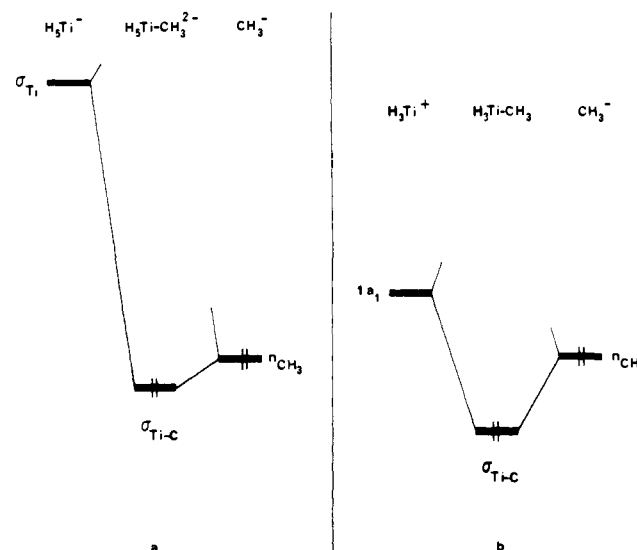
Figure 6. Formation of the σ_{Ti-C} bond in the octahedron complex (a) and in the tetrahedron one (b).

While the energy of empty orbitals are approximately the same (-10.63 eV in the tetrahedron vs. -10.43 eV in the octahedron), the energy level of the HOMO (associated with the σ_{Ti-C} bond) is much lower in the tetrahedron case (-13.05 instead of -12.25 eV), leading to a greater energy gap (2.42 eV/1.82 eV). The reason why the σ_{Ti-C} orbital energy depends on the ligand field can be easily understood. In the octahedral complex, the σ_{Ti-C} bond results from the interaction between n_{CH_3} and a hybrid orbital carried by H_5Ti^- fragment (Figure 6a). The latter is high in

energy because it is destabilized by an antibonding interaction with the hydrogen atom lying on the hybrid axis (hydrogen trans to the methyl group in $H_5TiCH_3{}^{2-}$). Because of the large energy gap between these two fragment orbitals, their interaction is small and the resulting bonding molecular orbital still high in energy. On the contrary, the $1a_1$ fragment orbital carried by H_3Ti^+ which interacts with n_{CH_3} to form σ_{Ti-C} is a low-energy orbital. It is a nonbonding orbital since no ligands can overlap with it (Figure 6b). Thus the energy gap between interacting orbitals is small, and the bonding interaction is strong, which leads to the σ_{Ti-C} orbital of low energy. As a consequence of this analysis, the existence of a *ligand trans to the CH_3 group* in the complex (as is the case for the octahedron and not for the tetrahedron) is *a factor which raises the energy level of the HOMO and thus favors (all other things being equal) the methyl distortion.*

Let us now examine the overlap criteria between the HOMO and the vacant orbital of proper symmetry. In the octahedral complex, the vacant orbital is a pure xz one, which is entirely contained in the plane of methyl distortion. Therefore, the methyl distortion entails a large overlap between the HOMO and the vacant orbital. On the contrary, the $1e_s$ orbital in the tetrahedron has contribution both of xz (60%) and $x^2 - y^2$ (37%) types, the latter being inefficient to stabilize the HOMO since the overlap between $x^2 - y^2$ and n_{CH_3} is zero. The remaining part of the xz atomic orbital can be found in the higher $2e_s$ orbital, which is too high in energy to interact strongly wiith the HOMO in the distorted structure. Therefore, the overlap between the HOMO and the vacant orbital is smaller because of the shape of the vacant orbital. This overlap also depends on the shape of the HOMO. Only the contributions carried by the methyl group can overlap with the vacant orbital on the metal: the greater these contributions, the larger the overlap. Remembering the discussion about the HOMO energy level (Figure 5), it is easy to see that the HOMO is more concentrated on the methyl group in the octahedron case, since the energy gap between the fragment molecular orbitals is larger. Therefore, both the shape of the vacant orbital and that of the HOMO contribute to decrease the overlap in the case of the tetrahedron complex.

It is clear that two factors are responsible for the different behavior of the HOMOs: a larger energy gap and a smaller overlap between the interacting MOs in the tetrahedron than in the octahedron. From the viewpoint of Jahn–Teller concept, we can say that the second-order Jahn–Teller distortion is easier in the octahedron since the excited state is closer in energy and the matrix element is larger.

As in the octahedron, the distortion also modifies the metal to π_{CH_3} bonding pattern. Diminishing the α angle increases the overlap between $\pi^x{}_{CH_3}$ and $1e_s$, while increasing the α angle increases the overlap between $\pi^y{}_{CH_3}$ and $1e_a$.

The above analysis expresses itself nicely in the Mulliken overlap population (Table I). The Ti–C bond is slightly weakened by the distortion in contrast to the reinforcement which occurs in the octahedron. Hydrogen atoms that are getting closer to the metal become partially bonded to the metal, and the corresponding C–H bonds are slightly weakened in a very similar fashion to the case of the octahedron. However, the increased electron transfer from the C–H bond to the metal is not large enough to compensate for the destabilization of the HOMO so that the total energy curve for tilt of CH_3 is eventually slightly repulsive. Therefore, it seems that *electrons donation from C–H to the metal does not differentiate the two complexes, while the metal to carbon bonding reorganization does.*

This comparison of the results on octahedron and tetrahedron complexes makes clear the factors which favor agostic structures: (a) a low-lying vacant orbital of proper symmetry, entirely contained in the distortion place; (b) a high-lying σ_{Ti-C} orbital; and (c) a good overlap between the distorted σ_{Ti-C} bond and the vacant orbital.

Focusing upon these three factors, it is now possible to analyze the role of substituents in a given ligand field, and the relative ability of various coordination spheres at the metal to favor agostic strutures.
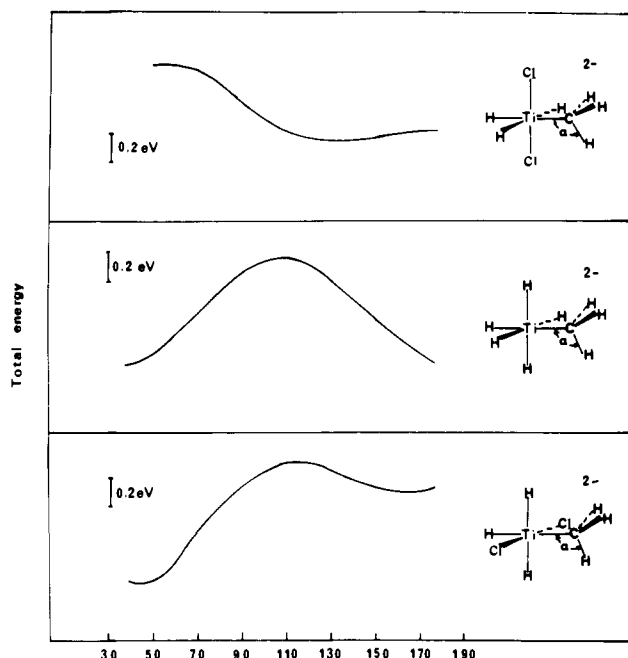

**Figure 7.** Variation of the total energy as a function of α in three octahedral complexes.

Ligand Effects

We specially discuss how the nature of the ligands modifies the energy levels and shapes of the relevant orbitals in the octahedral complex. The three low–lying orbitals xz, yz, xy, can be influenced only by the π orbitals of the ligands. Figure 7 shows the consequence of π donor substitution at different positions in the octahedron.

It is clear that π donor ligands have a negative influence on the distortion because they raise some or all of these three d orbitals. Suppose a π donor such as Cl in the xz distortion plane. If it is at the trans position, the p_x orbital mixes in an antibonding way with xz (**21**), and the p_y orbital with the yz orbital (**22**). When the substituents are in the cis position (**23**), the xz and yz orbitals are destabilized. In both cases, the higher level of xz
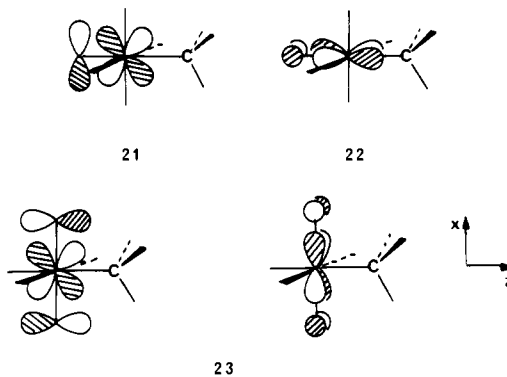
makes the CH_3 group more difficult to distort. The unfavorable influence is especially pronounced for a chlorine atom in a cis position since the p_z orbital of Cl also has antibonding interaction with n_{CH_3} in the distorted structure, **24**. In the case of two chlorine
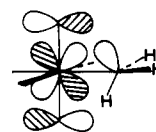

atoms on the x axis, the deep minima found in the unsubstituted case disappear. The total energy curve is strongly repulsive for small value of α, since xz stabilizes neither σ_{Ti-C} nor $\pi^x{}_{CH_3}$ effi-

ciently. For large value of α, yz is still stabilizing $\pi^y_{CH_3}$ in an efficient way since it is not affected by the chlorine lone pairs. Consequently the total energy curve is almost flat for large α (Figure 7).

Suppose now that the Cl atoms are introduced on the y axis, that is, perpendicular to the plane of distortion. The xz orbital cannot overlap by symmetry with the Cl lone pairs, while xy and yz are raised in energy. Therefore, xz is still efficient in stabilizing both the σ_{Ti-C} bond and the $\pi^x_{CH_3}$ orbital so the tilt of CH_3 toward small α is as favorable as in the absence of Cl atoms (Figure 7). In contrast, the distorted structure corresponding to a large value of α is less favorable (the stabilization energy is -0.18 vs. -0.79 eV in the absence of Cl atoms) since the stabilizing interaction between $\pi^y_{CH_3}$ and yz is now very small. This is due first to the higher level of yz and second to the out-of-phase overlap of the H_2 and H_3 orbitals with the p_z lone pairs of Cls, **25**. Figure 7
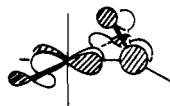

25

shows how the minimum corresponding to a small α value remains unchanged with respect to the unsubstituted case while the minimum corresponding to a large α value is much less favorable.

The ligands effect can be summarized in the following way. π donors are strongly unfavorable for the agosticism if they are introduced in the plane of distortion. If they are introduced along the perpendicular axis, they serve to favor one minima ($\alpha < 109.47°$) over the other ($\alpha > 109.47°$). These results agree nicely with the experimental structure **4**. The distortion characterized by a small value of α occurs in the plane that contains only one chlorine atom.

We have performed some model calculations on $H_2Cl_3TiCH_3^{2-}$ (**26**) in which one Cl is lying in the distortion plane and two are
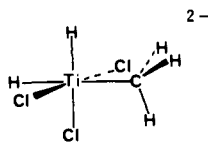
26

on the axis orthogonal to that plane, as it is in **4**. In agreement with the above analysis a small well (-0.15 eV) is found for a small value of α.

The analysis developed in the case of the octahedron should apply to all ligand fields. Therefore, Cl_3TiCH_3 would resist distortion even more than our model H_3TiCH_3. It is clear that π acceptors have the reverse influence. However, it is unlikely that an electron-deficient complex with acceptor ligands could be synthetized.

Rotational Barrier of the Methyl Group

We have seen that the distortion of CH_3 occurs in a specific plane when the metal complex is unsymmetrically substituted. This raises the point of the possibility of a rotational barrier of the methyl group. Two types of rotation can be envisaged. The rotation about the metal–carbon bond keeps the same hydrogen atom in proximity to the metal. The rotation about the local C_3 axis of the methyl group brings successively each hydrogen atom close to the metal. In the first rotation type, one H remains different from the two other ones and should in principle be distinguishable by NMR spectroscopy. In the second type of rotation, all hydrogen atoms become equivalent.

We first discuss the rotation about the Ti–C bond. Let us start with a distorted structure with $\alpha < 109.47°$, in the unsubstituted $H_5TiCH_3^{2-}$. The barrier is fourfold and cannot be large. This can be easily understood in the following way. In **27** the distortion occurs in the xz plane, and in **28** the distortion is in the yz plane. In **27** xz serves as the stabilizing orbital, while in **28**, it is yz that
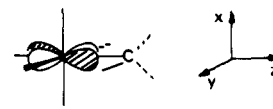

27   28

plays the role. As xz and yz are degenerate, the interactions are equal. For structures that are intermediate between **27** and **28**, a suitable linear combination of xz and yz can always be found. Therefore, the potential energy curve associated with the rotation about the Ti–C bond is flat. The same argument applies to a rotation in a distorted structure with a large α value.

Larger rotational barriers are expected in the case of ligand substitution that strongly differentiates xz and yz planes. For instance, with two chlorine atoms along the y axis, the rotational barrier around the Ti–C bond is equal to the energy difference between the agostic structures in the xz and yz planes. However, the latter is not stable with respect to the undistorted structure (Figure 7), and the rotational mechanism should not actually involve a simple rotation around the Ti–C axis.

Let us see now the rotation about the local C_3 axis of the CH_3 group. Rotation of 180° about this axis leads from **29** (small value of α) to **30** (large value of α). For instance, $\alpha = 40°$ in **29** (energy
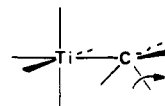
29   30

minimum for $\alpha < 109.47°$) leads to $\alpha = 178°$ in **30** (close to the energy minimum for $\alpha > 109.47°$). The calculated energy curve between **29** and **30** is rather flat, the activation energy being simply equal to the energy difference between **29** and **30** (~ 1 kcal/mol). When ligands are different, a higher barrier is expected.

Actual rotation of methyl group is likely to involve a combination of both mechanisms described above: the greater the differentiation of xz and yz planes, the larger the energy barrier. However, it cannot be larger than the energy difference between agostic and nondistorted structures. In **4**, this difference is rather low since even the distortion plane contains a chlorine atom, and it could be why NMR spectroscopy cannot differentiate the three H atoms of the methyl group.

Distortion and Number of Electrons at the Metal

The analysis we have done previously applied to a d^0 octahedral or tetrahedral complex. For another electron count, depending on the number of electrons added, a distortion can or cannot occur.

In the octahedron, Figure 1 shows that xy remains unperturbated by the distortion of the CH_3 group because of its symmetry. Therefore, the addition of two electrons in this orbital should not prevent the methyl group from being agostic. As a matter of fact, the low-spin d^2 trans $TiMeCl(dmpe)_2$[10] **6** appears to have an agostic methyl group. The addition of more electrons starts filling up the xz and yz orbitals. A priori, electron occupation of yz should still allow for a distortion in the xz plane. Although the d^3 $VMe_2(dmpe)_2$ complex could not be analyzed by X-ray diffraction, the infrared C–H stretching frequency is lower than it should be for a normal CH_3 group bound to a transition metal.[10] The low-spin $CrMe_2(dmpe)_2$ also has a ν_{C-H} value that is slightly lower than the normal one expected.[10] In addition, an X-ray analysis gives the Cr–C–H angles to be 108, 108 and 121°.[20] This rather strange distortion was said to be chemically insignificant. In our opinion it would not be too surprising if the tilt of the CH_3 group is an easy motion in both of these complexes. In the tetrahedron series, an agostic structure is unlikely whatever the electron occupancy at the metal. One therefore understand why the 13-electron, d^5, high-spin $Mn(CH_2CMe_2Ph)_2(PMe_3)_2$ has no agostic alkyl groups.[12]

(20) Girolami, G.; Salt, J. E.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 5954.

Other Coordination Modes

By comparing the octahedron to the tetrahedron, we have seen that the tendency for agosticism varies strongly with the ligand field at the metal. A similar analysis performed on other types of coordination gives a ranking of the various complexes with respect to their ability to have an agostic methyl group. For the sake of comparison, all calculations were done with the parameters of titanium and the electron count is kept to d^0 for the basic analysis.

A pentacoordinated L_4MCH_3 can have either a square-basis pyramid or a trigonal-bipyramid structure. Test calculations on H_4MCH_3 (d^0) show that the square basis pyramid is more stable. Nevertheless, the preference for the square-basis pyramid structure cannot be extremely large. As a matter of fact, in some inorganic complexes of Ti(IV) and V(IV) both structures have been observed. The interesting point is that the two structures differ markedly in their ability to have an agostic methyl group.

The case of the square-basis pyramid is best studied by starting from an octahedron which has lost one ligand. The structure thus obtained has the metal in the plane of the four basal ligands. In this particular type of square-basis pyramid, the methyl group can occupy the apical or the basal site.

Suppose that the methyl is at the apical site **31**. The absence of a trans ligand lowers the energy of the orbital characteristic of the metal–carbon bond. Therefore, although this structure has the same set of three low-lying nonbonding d orbitals as the octahedron, the tendency for a methyl distortion is considerably diminished.

31
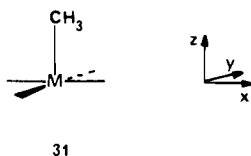
The transformation of this particular square-basis pyramid in a more general one (angle between two trans basal ligands less than 180°) makes the distortion even less likely. It comes from the fact that the empty xz and yz orbitals of **31** are raised in energy by the basal ligands that are no longer in the nodal planes of these orbitals, **32**. With a low-lying metal–carbon σ bond and high-lying empty xz and yz, the system has no chance to be agostic.

32
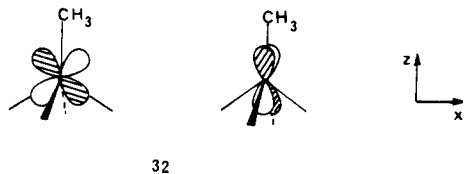
If the CH_3 group occupies the basal site of **31**, the ease for distortion is larger since the presence of a trans ligand places the metal carbon in a situation very much similar to that of the octahedron. When the angle between the basal ligands is diminished, the distortion becomes less favorable (xz and yz are raised in energy and no group is really trans to the basal metal–carbon bond).

In the trigonal bipyramid one also finds that the axial site favors the distortion more than the equatorial one. At the axial position (**33**) the metal–carbon σ bond orbital, destabilized by the other axial ligand, makes use of one of the orbitals of the lower e set, **34** (xz or yz), to stabilize a distorted structure.

33   **34**
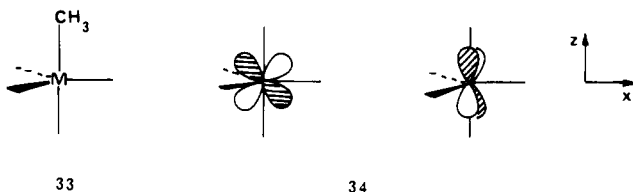
For a methyl in an equatorial site one should distinguish a distortion in the plane which contains the axial ligands (**35**) from that in the plane which contains the equatorial ligands (**36**).

35   **36**
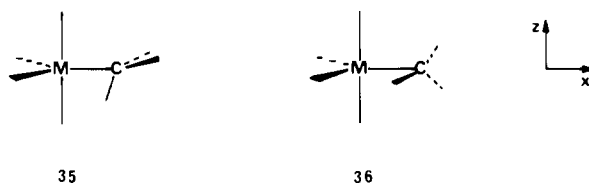
In **35**, the available empty orbital is xz of the lower e set of the metal d orbital. In **36**, the empty orbital that has the good symmetry to stabilize the distorted metal carbon bond belongs to the higher e set ($x^2 - y^2$ or xy). Consequently the equatorial position is not favorable for distortion because of the absence of a trans ligand, the worst situation being a distortion in the equatorial plane itself.

One can quickly analyze the square-planar and trigonal complexes by examining the relationships between the octahedron and the square planar, on one hand, and that between the trigonal bipyramid and the trigonal complex, on the other hand.

The square-planar L_3MCH_3 d^0 complex should easily have an agostic methyl group as there is always a ligand trans to the methyl group, and one can use the xz orbital for a distortion in the plane perpendicular to the molecular plane **37**. The distortion in the

37   **38**
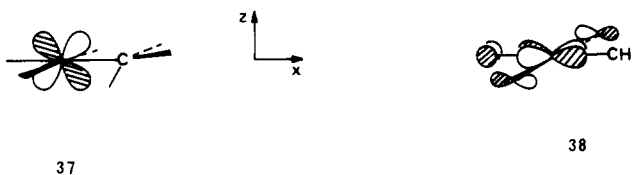
molecular plane has to involve xy. In the absence of any π donor ligand, xy has the same energy as xz or yz so that a distortion in the molecular plane can occur in principle. A more realistic situation puts π donor ligands around the metal, as shown in **38**, thus raising first of all the energy of xy. This disfavors especially the molecular plane as a plane for distortion.

Although we believe that a d^0 square-planar complex should favor an agostic methyl group with a plane of distortion perpendicular to the molecular plane, we should note that such planar complexes may not exist. All tetracoordinated d^0 systems prefer a tetrahedral structure, and our calculations actually agree with that experimental fact. Consequently, considerable strain may have to be introduced in the ligand in order to force a tetracoordinated d^0 system to become more planar. It should also be noted that additional electrons would not help for the distortion since they will first fill the xz and yz orbitals, which should stay empty for stabilizing the agostic structure.

A trigonal complex L_2MCH_3 should not favor an agostic methyl group. A methyl group in such complex would behave like a methyl at the equatorial site of a trigonal bipyramid. Consequently, a distortion in the molecular plane should be very unfavorable, while the one in a perpendicular plane (**39**) would be

39
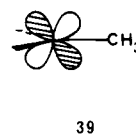
easier although still difficult. More d electrons would feel the xz which makes the distortion even more difficult.

One may thus understand the unexpected chemical inactivity of $R_2Mn(PR_3)_2$. This complex easily loses a phosphine group to give a tricoordinate Mn(II) complex, which despite its high electron deficiency shows no propensity for β elimination.[21] This chemical inertness may be related to the difficulty for the system to build a M···H···C interaction via an agostic structure.

We have therefore been able to order the unsubstituted d^0 complexes in three classes. In the class that strongly favors a

(21) Girolami, G. S.; Howard, C. G.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B., submitted for publication.

Table II. Extended Hückel Parameters

orbital	H_{ii}, eV	ζ_1	ζ_2	$C_1{}^a$	$C_2{}^a$
H_{1s}	−13.60	1.30			
C_{2s}	−21.4	1.625			
C_{2p}	−11.4	1.625			
Cl_{3s}	−30.0	2.033			
Cl_{3p}	−15.0	2.033			
Ti_{4s}	−8.97	1.075			
Ti_{4p}	−5.44	0.675			
Ti_{3d}	−10.81	4.55	1.40	0.4206	0.7839

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

distortion, one finds the octahedron, an hypothetical d⁰ square-planar complex, and the axial site of a trigonal bipyramid. In a borderline case one finds the basal position of a square-basis pyramid, the equatorial site of a trigonal bipyramid with a distortion in the plane containing the axial ligand, the trigonal complex with a distortion in the plane perpendicular to the molecular plane, and the tetrahedron. In the most unfavorable case one finds the trigonal bipyramid (CH₃ equatorial) and the trigonal complexes for a distortion in the equatorial and molecular plane, respectively.

This order should be the same for all metals, but one should be aware that the *boundary between a possible and an unfavorable distortion may be very much dependant on the nature of the metal.* For instance, methyl distortion in H₄Ta(CH₃)²⁻ complex (**40**) leads

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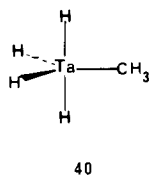
to a flat energy curve in the equatorial plane and to a small stabilization on the axial plane.[17] We saw here that a similar system with Ti as metal leads to large and small destabilizations, respectively. Clearly, the same trend is found, but Ta seems to be more efficient in favor of agostic structures. In the same way, calculations on d⁰ octahedral and tetrahedral complexes of tantalum lead to a stabilization in both systems, but the one in the octahedron is twice the one in the tetrahedon. The reason lies in the lower energy level of d orbitals used on the calculations (−12.10 and −10.8 eV for Ta and Ti, respectively): the lower the d orbital level, the smaller the energy gap between the σ_{M-C} and the low-lying empty orbitals. The diffuseness of d orbitals might

also play a role by increasing the overlap between the orbitals. However, since increasing diffuseness usually corresponds to increasing energy of d orbitals, a more quantitative analysis would be required to make predictions.

Conclusions

In this paper, we have proposed a rationale for the unexpected structure of some electron-deficient methyl complexes. A reorganization of the metal–carbon bond seems to be at the heart of the problem. Such a reorganization is possible if the metal–carbon σ bond lies at a high energy level and if an empty low-lying orbital of adequate symmetry on the metal can stabilize this high-lying metal–carbon bond. In these electron-deficient complexes, electron donation from a C–H bond to the metal center always provides a stabilization in the distorted structure. However, when the distortion is too costly in energy for the metal–carbon bond, this factor is not large enough to lead to an overall stabilization. We have discussed how the agoticism is affected by the electronic nature of the ligands and the coordination mode. The results presented may help to control the agosticism of yet unknown systems. The study of ethyl complexes is in progress. We are also investigating the distortion of the ligand field away from the ideal octahedral field in the methyl and ethyl complexes.

Appendix

The calculations were of the extended Hückel type and weighted H_{ij}'s were used.[22] Idealized geometries were assumed with Ti–C = 2.15 Å, Ti–H = 1.60 Å, C–H = 1.09 Å, and Ti–Cl = 2.30 Å. All angles at the metal were taken to be 90° in the octahedron and 110° in the tetrahedron. Coulomb integrals and orbital exponents are listed on Table II, and these were taken from earlier work.[23]

Registry No. 4, 85944-68-9; **7**, 2747-38-8; H₅TiCH₃²⁻, 94138-09-7; H₃TiCH₃, 78499-82-8.

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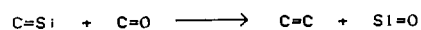# Ab Initio Study of the Reaction of Silene with Formaldehyde

Steven M. Bachrach and Andrew Streitwieser, Jr.*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received July 16, 1984

Abstract: The reaction of silene with formaldehyde to give silanone and ethylene was examined at the SCF level by using the 3-21G, 3-21G(*), and 3-21G* basis sets. All compounds were fully optimized, including the proposed intermediate, 1,2-silaoxetane (**5**), for which the structure and vibrational frequencies are reported. While the reaction is exothermic by approximately 30 kcal mol⁻¹, the proposed intermediate is more stable than both the products and reactants by at least 50 kcal mol⁻¹. However, if the product is taken to be the dimer of silanone (cyclodisiloxane), **6**, the reaction is more exothermic, with the products lying 25 kcal mol⁻¹ below 1,2-silaoxetane. A mechanism is proposed for this reaction based on the energetics and the integrated spatial electron populations. In addition, the unusual geometry of cyclodisiloxane is explained by MO arguments to be caused primarily by large oxygen–oxygen lone-pair repulsions.

Interest in the formation of multiple bonds to silicon has been increasing over the past few years, and many experimental[1–9] and

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(5) Barton, T. J. *Pure Appl. Chem.* **1980**, *52*, 615.
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Scheme I

C=Si + C=O ⟶ C=C + Si=O

theoretical[10–15] papers on this subject have appeared recently in the literature. The growing body of known chemistry of the silenes

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