Complete Line-Shape Analysis. Complete line-shape analysis was performed on ions 3, 4, and 6–8.

The experimental spectra, obtained at (at least) ten different temperatures, were simulated with the program DNMR$^3$. Ortho and meta carbon exchange were treated separately as a two spin exchange between different populations. The population dependence on temperature was obtained from spectra below the coalescence and extrapolated for higher temperatures. The chemical shifts are found to be independent of the temperature. The transverse relaxation time $T_2$ was obtained in the coalescence region by monitoring the line width of a nonexchanging carbon. All calculations were performed on the Univac 1110 system of the Laboratoire de Calcul de Strasbourg-Cronenbourg, France.

Temperature Measurements. The temperature was measured before and after each spin-transfer experiment by use of a chemical shift thermometer (CH$_3$OH in a mixture of CHCl$_3$-FCIC$_2$, 1:1, v/v).$^{2ab}$

Acknowledgment. We are indebted to Professor G. A. Olah for critical comments. We wish to thank the Swedish National Science Research Council and the Centre National de la Recherche Scientifique for financial support.

Unusual M–C–H Angles, C–H Bond Activation, and $\alpha$-Hydrogen Abstraction in Transition-Metal Carbone Complexes

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Abstract: Alkylidene complexes of electron-deficient transition metals display an interesting structural deformation in which the carbone appears to pivot in place while the C=H bond weakens. A molecular orbital analysis of these carbone complexes traces the deformation to an intramolecular electrophilic interaction of acceptor orbitals of the metal with the carbone lone pair. Bulky substituents on the metal and carbone protect the metal center from intermolecular reactions and control the extent of carbone pivoting. While a secondary interaction weakens the C–H bond and attracts the $\alpha$-hydrogen to the metal, full transfer of $\alpha$-hydrogen to the metal is a forbidden reaction, at least for a five-coordinate, 14-electron complex. The metal-hydrogen bonding interaction guides the hydride to a neighboring alkyl group, facilitating an $\alpha$-elimination mode characteristic of the reactions of these compounds. The complexed carbone centers are unusually electron-rich, nucleophilic, by comparison with 18-electron d$^4$ stabilized carbone complexes. This is a consequence of an extremely effective Ta–C overlap.

It seems that nature has dealt us extremes in the interaction of transition-metal centers with organic ligands. Bonds may be dismantled completely, as in oxidative additions and kindred reactions. At the other end of the spectrum lies the uninteresting phenomenon of no interaction at all. The common consequence of chemical coordination is structural change, albeit in moderation. Thus CC bonds stretch and CR$_2$ or CR groups bend back, as in coordinated ethylenes and acetylenes. Bond alternation may be dismantled completely, as in oxidative additions and kindred reactions of the type given by eq 1.

\[
\begin{align*}
\text{L}_4\text{M} &= \text{C} \quad \text{R} \\
\text{L}_4\text{M} &= \text{C} \quad \text{R} \\
\text{H}_\alpha \\
\text{H}_\alpha
\end{align*}
\]

The geometrical anomaly is only one of several unusual electronic and chemical properties of these alkylidene complexes of Ta, Nb, and W. They appear to be formed in $\alpha$-elimination reactions of the type given by eq 1.

\[
\begin{align*}
\text{L}_4\text{M} &= \text{C} \quad \text{CHR} \\
\text{L}_4\text{M} &= \text{C} \quad \text{CHR} \\
\text{R} \\
\text{R}
\end{align*}
\]

The Schrock alkylidene complexes are nucleophilic rather than electrophilic. 2 The contrast with the heteroatom-substituted carbone complexes of the Fischer type is sharp—it seems strange that a carbone coordinated to an electron-poor metal atom should be more electron-rich than one bound to an 18-electron d$^6$ center.

The Structural Background

Nine structures of the Schrock carbenes are at hand, two of these neutron diffraction structures which are a necessity for

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accurate location of the crucial hydrogen in a CHR ligand. The complexes in question are of seven basically different structural types, 3–9, and their geometrical parameters are summarized in Table 1.

![Structural diagram](image)

Table 1. Selected Geometric Parameters of Carbene Complexes

<table>
<thead>
<tr>
<th>no.</th>
<th>molecule</th>
<th>electron count at M</th>
<th>CH₂CH₂⁺</th>
<th>metal oxidation state</th>
<th>angles (deg) and dist (Å)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>TaCp₂(CH₂)(CH₂)</td>
<td>18 III V</td>
<td>126.5</td>
<td>126.5⁰</td>
<td>2.026</td>
<td>5a</td>
</tr>
<tr>
<td>3</td>
<td>TaCp₂(CH₂Ph)(CH₂Ph)</td>
<td>18 III V</td>
<td>135.2</td>
<td>2.07</td>
<td>5b</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>TaCp₃(CH₂CMe₃)Cl</td>
<td>18 III V</td>
<td>111.0</td>
<td>2.03</td>
<td>5c</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Ta(CH₂Me₃)(CHMe₃)(CH₂)(PMe₃)</td>
<td>16 I III</td>
<td>111.9</td>
<td>78.1</td>
<td>1.946</td>
<td>1.135</td>
</tr>
<tr>
<td>5</td>
<td>Ta(CH₂CMe₃)₂(Me₂C₂H₅)(PMMe₃)</td>
<td>14 I V</td>
<td>169.8</td>
<td>1.932</td>
<td>5e</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>[Ta(CH₂CMe₃)Cl₂(PMe₃)]</td>
<td>14 III V</td>
<td>114</td>
<td>84.8</td>
<td>1.189</td>
<td>1.131</td>
</tr>
<tr>
<td>7</td>
<td>TaCp(CH₂CMe₃)Cl₂</td>
<td>14 III V</td>
<td>165.0</td>
<td>5g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Ta(CH₂CMe₃)CCMe₃Li(dmpe)</td>
<td>10 III V</td>
<td>165.0</td>
<td>1.76</td>
<td>2.19⁰</td>
<td>5h</td>
</tr>
<tr>
<td>9</td>
<td>W(C₂Me₅)₂(CH₂CMe₃)(CH₂CMe₃)(P₂C₂H₆)</td>
<td>16 III V</td>
<td>149.7</td>
<td>1.982</td>
<td>5c</td>
<td></td>
</tr>
</tbody>
</table>

a R = H. b ClI instead of CH.

In the first three complexes in the table the MCR angle is enlarged, 126.5°–150.4°, but not nearly as opened up as in molecules 3–9, where it ranges between 150 and 170°. The TaCH₃ angle is 78.1° in 4 and 84.8° in 6, the two neutron diffraction structures which give us a good idea of the location of that hydrogen. The distance between the Ta and that hydrogen is 2.04 and 2.12 Å, respectively. The C–H₃ bond is accordingly lengthened, to 1.135 and 1.131 Å. C–H₃ bond weakening is also apparent in the strongly lowered C–H stretching frequencies and NMR coupling constants.²

For the other complexes in Table 1 we have X-ray crystallographic structure determinations. While these do not allow us to follow the a-hydrogen so closely, we see the effects of the deformation in the enormous M–C–R angle and the correlated decrease in M–C bond length. Incidentally the fantastic structure of the tungsten complex 9 gives an "internal calibration" of tungsten–alkyl (2.258 Å), tungsten–carbon (1.942 Å), and tungsten–carbene (1.785 Å) bond lengths.⁶ Similar calibrations are available in some of the other structures.

The observed diminutions of the M–C–H₃ angle to 78 or 85° from an assumed "normal" value around 120° could have been interpreted as the consequence of a bonding interaction with the metal, an incipient abstraction. In fact the structural data make it clear that the alkyl substituent R "follows" the a-hydrogen. To put it another way, the R–C–H₃ angle does not deviate nearly as much from its normal angle as do the other two angles around the a-carbon. It is this observation that made us think of a carbene pivoting in place, 1 → 2, and is a taking-off point for the analysis that will follow.

We have included a tantalum lithium complex 8 earlier thought of as a carbene complex, in Table 1.³⁸ However, a comparison of the structural details of this molecule, Ta(CH₂CMe₃)₂(CCMe₃)Li(dmpe), with (alkylidene)tantalum complexes indicates obvious similarities. The short Ta–C distance is in tune with the large Ta–C–C angle. The C–Li distance of 2.19 Å is within the normal bonding range. The LiCTa angle is considerably smaller than the idealized value, as in the alkylidene complexes. The Ta–Li separation (<2.9 Å) is not unusually large, considering the large radii of Ta and Li. Here we point out only the similarity of this structure to those of alkylidene complexes. Details of bonding in complexes containing transition metals and Li will be discussed elsewhere.⁷

Why does the alkylidene ligand deform in its unusual way? Does it depend on the d-electron configuration and/or the degree of approach to the 18-electron count? Can the extent and direction of bending be controlled by the ligand set? When will the M–H₃ interaction be of sufficient intensity for hydrogen transfer to occur? Does the M–H₃ interaction activate H₃ for transfer to another metal-bound ligand? What is the origin of the nucleophilicity of these complexed carbones? These are some of the questions we will try to answer.

Before we begin the analysis, it is important to set down explicitly the problems in electron counting met in these molecules. Normally a carbene ligand is viewed as neutral, a σ donor and a superlative π acceptor. Within this formalism the Ta in the complexes listed in Table I is in oxidation state either I or III.


(7) Goddard, R. J.; Jemmis, E. D.; Hoffmann, R. to be submitted for publication.
Alternatively we can begin from a starting point of a CH$_2^-$ ligand, an excellent \( \pi \) donor. This has the advantage of making the formal oxidation state of Ta in two 14-electron complexes (5 and 6) identical. It is important to perceive the different starting points in these formalisms, for the oxidation state ambiguity is apparent in the experimental literature on these molecules. Table I classifies the metal atoms in the two extreme ways of counting the carbene electrons.

**Tracing the Basic Distortion**

We chose to model an alkylidene complex of moderate complexity, one which has a clearly defined coordination geometry, shows the typical deformation and has a low electron count. This is the dicarbene 5, Ta(CHMe$_3$)$_2$(mesityl)(PMe$_3$)$_2$. The computations are of the extended Hückel type, parameters specified in the Appendix. A progression of geometrical and electronic simplification was followed from 5 to Ta(CHCH$_3$)$_2$(H)(PMe$_3$)$_2$ to Ta(CHCH$_3$)$_2$(H)$_2$Cl$_2$ to Ta(CHCH$_3$)$_2$(H)$_2$Cl$_2$ to Ta(CHCH$_3$)$_2$(H)$_2$Cl$_2$. In this sequence one of the carbenes is replaced by H-. Exploratory calculations were carried out at each stage to see whether the carbene deformation survived the simplification of the ligand set. It did.

We need to clarify the nature of the distortion in the carbenes. In all cases where this has been determined, the carbene carbon atom and its three adjacent bonded atoms are coplanar. Angles around the carbon atom vary from complex to complex, but as we have mentioned above, the R-C-H angles remain approximately constant. In our model we will fix this angle to be 120° and monitor the bending of the carbene with the angle \( \theta \) shown in 12. Thus the Ta-C-H angle is 240° - \( \theta \). On the left \( \theta = 120^\circ \), which we will term the undistorted geometry; on the right \( \theta = 180^\circ \), the bent geometry.

\[ TaCHCH_3H^+ \]

Our final model is Ta(CH$_2$)H$_2^+$ (13), a 14-electron Ta(I) (or Ta(III)) if the carbene is taken as CH$_2^-$ methylene complex.

\[ TaCHCH_3H^+ \]

We calculate the model complex with the distorted carbene geometry (\( \theta = 180^\circ \)) to be 0.5 eV more stable than that with the undistorted geometry. In order to see how this stabilization can arise, we will first consider the orbitals of the TaH$_4$ and the CH$_2$ fragments and the interaction of these two fragments. Then we will look at the bending process and finally the interaction of the same two fragments at the distorted geometry.

The interaction diagram for [H$_4$Ta]$^+$ and CH$_2$ is shown in Figure 1.

The frontier orbitals of the ML$_4$ fragment are well-known, those of [H$_4$Ta]$^+$ comprise an orbital set, \( \alpha_1, \alpha_2, \beta_2 \), derived from the \( t_2g \) set of an octahedron lying beneath \( \beta_1 \) and \( \alpha_1 \) orbitals descended from \( \epsilon_r \). Alternatively the latter may be viewed as linear combinations of two hybrids pointing toward the missing octahedral coordination sites. This, we shall see, will be an important factor contributing to the stabilization of the bent carbene.

The frontier orbitals of methylene are given on the right-hand side of Figure 1. We shall be mainly concerned with \( \sigma \) (the donor orbital), \( \pi \) (the acceptor orbital), and, to a lesser extent, a lower lying \( \sigma \) orbital of local \( \pi \) symmetry, \( \pi_{CH_2} \). The primary interactions are a donation of electron density from \( \sigma \) of the carbene to \( \alpha_1 \) (and to a lesser extent \( \alpha_2 \)) of the ML$_4$ fragment and a back-donation from metal \( \beta_2 \) to carbene \( \pi \). These interactions yield the \( \alpha_1 \) and \( \alpha_2 \) orbitals in which most of the metal–carbene bonding is contained. There is a further interaction between the \( \beta_2 \) hybrid of ML$_4$ and the \( \pi_{CH_2} \) orbital of the methylene. One metal orbital (\( \alpha_2 \)) is unaffected by carbene complexation.

Even at this point we can comment on the nucleophilicity of the coordinated carbene. The carbene \( \pi \) orbital, its source of electrophilic or nucleophilic reactivity, is completely vacant in a free methylene. In the undeformed metal-complexed structure it is occupied by no less than 0.82 electron. Of these 0.72 electron are derived from the \( \beta_2 \) orbital, which is 64% on TaH$_4$ and 36% on the carbene. The \( \beta_2-\pi \) interaction is excellent—the Ta 3d orbital and the carbene \( \pi \) are very well matched in size; i.e., they have a large overlap. They are also at near resonance with each other in energy. It is here that we see clearly the limitations of any partitioning of electrons: if we start out from a d$^8$ Ta(I), then the \( \beta_2-\pi \) interaction transfers 0.72 electron into the carbene \( \pi \) orbital. One might as well have started out from a CH$_2^-$ and a d$^2$ Ta(III) and transferred 1.28 electrons to the TaH$_4$ fragment.

---


As we will see, the population of the carbene \( p \), and therefore its nucleophilicity, is unaffected by in-plane deformations.

Now we bend the carbene, pivoting it in place and measuring the deformation by the angle \( \theta \) defined in 12. Figure 2 shows the total energy curve and the Walsh diagram for the frontier orbitals. The symmetry is lowered from \( C_{2v} \) to \( C_{v} \). \( a_2 \) and \( b_2 \) orbitals are totally unaffected by the bending, because of the simplicity of the ligand set, while \( a_1 \) and \( b_1 \) orbitals, both \( a' \) in \( C_{2v} \), mix. The Walsh diagram shows that the occupied level responsible for stabilization along the deformation coordinate is \( 4a_1-6a' \). The extreme variation in energy of the unfilled \( 3b_1-8a' \) also provides a vital clue.

When the carbene is in its "normal" position (\( \theta = 120^\circ \)), this ligand is bound primarily through the \( \sigma^\pi 1a_1(x^2-y^2) \) interaction (14), orbital \( 4a_1 \). Bending decreases this overlap, from 0.23 at \( \theta = 120^\circ \) to 0.15 at \( \theta = 180^\circ \). But at the same time a new and important interaction is turned on. This is between the \( \beta \) hybrid of the \( MH_4 \) fragment and the carbene \( \pi \), an overlap that is zero at \( \theta = 120^\circ \) but rises quickly to 0.30 at \( \theta = 180^\circ \) (15). The hybridization of \( b_1 \) is responsible for its excellent overlap with the carbene donor orbital. Note also the \( M-H_a \) bonding interaction explicitly displayed in 15. The involvement of the \( b_1 \) is underscored by the rapid rise in energy of \( 3b_1 \) (mainly \( TaH_4 b_1 \)) with \( \theta \) and by the corresponding increase in population of that fragment orbital.

What we have then is a strong intramolecular electrophilic interaction between an empty orbital of one piece of the molecule (\( b_1 \) of the \( TaH_4 \) fragment, \( xy \)) and a filled orbital of a ligand (\( \pi \) of the \( CH_2 \)). Other orbitals of the carbene, e.g., \( \pi CH_2 \) interact with the metal \( xy \) and a complete analysis must consider these. But the main interaction is between the carbene lone pair and the metal acceptor orbital, and it is this that makes us view the process more as a ligand rotating in place rather than intramolecular electrophilic attack on a \( C-H \) bond or a hydrogen atom.

This effect is to be expected for all carbenes attached to an electron-deficient center, subject to steric effects which we will describe below. Ligand pivoting might also take place in amide (\( NH_2^- \)) complexes isoelectronic with the carbene compounds discussed here. However, the effect is less likely to occur than in the carbene complexes since the amide lone pair \( \sigma \) orbital is at lower energy, engaging more weakly in intramolecular electrophilic interactions. It appears that such a deformation occurs in \textit{trans-}((adamantyl)NH)\textsubscript{2}Mo(OSiMe\textsubscript{3})\textsubscript{4} but not in some other amides.\(^{11b}\)

If the complexed carbene bends as a consequence of an intramolecular interaction with an empty metal fragment orbital, then the extent or efficiency of that bending should be responsive to the metal ligand sets. We modeled \( \sigma \) donor and acceptor effects by changing the electronegativity of the equatorial ligands and \( \pi \) effect by \( CN \) and \( NH_2 \) equatorial substituents. Both \( \sigma \) and \( \pi \) equatorial acceptors induce a greater energy gain on bending, whereas donors work in the opposite direction. This is in qualitative accord with the notion that electron deficiency on the metal induces carbene deformation.

In the deformation a net 0.20 electron is transferred from the carbene to the \( ML_4 \) fragment. The atom-by-atom breakdown of this charge drift is shown in 16, which gives the difference between \( \theta = 180^\circ \) and \( \theta = 120^\circ \). The evolution of the overlap populations

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is displayed in Figure 3. The changes in the Ta–C–H, triangle are all consistent with the observed structural perturbations. Note that in the calculations the Ta–C, and C–H distances are kept fixed, so that any changes in these overlap populations are indeed reflections of an underlying electronic effect.

The Ta–H overlap population increases rapidly, forcing one to consider once again whether it is carbene pivoting or C–H bond activation by the metal which is "leading" the reaction. The theoretical answer is not absolutely clear—both effects are operative. We are led to a conclusion of a dominant role for carbene pivoting by (a) the geometrical facts outlined in the introduction, (b) the fact that the M–H interaction is spread out over many orbitals, and (c) the eventual barrier, to be discussed later, to the consumption of M–H interaction, namely, complete H transfer to the metal.

We might note that occupation of the level scheme by two more electrons, filling 8a1–7a in Figure 2, will not affect the tendency to bend, in fact it may enhance it somewhat. Two electrons more, reaching the 18-electron count, fills 3b1, which then prohibits distortion of the type we have discussed.

Steric Effects

It is clear from the experimental studies that the steric bulk of the neopentylidene ligand must have something to do with the kinetic stability of the Schrock complexes. But what is the role of the steric effect in the deformation? To explore this point, we have studied a model ethylidene complex, Ta(CHCH3)(CH2)H2+. In this molecule an increase in θ from 120° is sterically differentiated from a decrease in that angle. The potential energy curve presented in Figure 4, which for comparison shows the energy of a simple CH2 group so rotated.

Note that the curves are nearly identical on the large θ side, where the carbene methyl group is out of steric trouble. For small θ, where the carbene methyl group is bent toward the equatorial methyl substituents, the energy rises steeply. This is a steric effect, the result of short HH contacts between methyl groups. At θ = 90° our model has a H–H separation of 2.16 Å, and at smaller θ some of these become much shorter.

We conclude that steric interactions between bulky substituents on the carbene and equatorial metal ligands are important in setting the Ta–C–C angle, i.e., the equilibrium tilt of the carbene ligand. Since the electronic impetus to rotate the carbene is relatively mild, the steric effects may lead to a substantial variation in MCC angle. By delimiting access to the electrophilically reactive metal atom, the bulky groups no doubt confer kinetic stability on these complexes. We think that their blocking of reactivity with external bases is indirectly responsible for our being able to observe the peculiar geometrical deformations that are seen.

Charge Distribution and Nucleophilicity

While the methylene carbon atoms in our model complexes are negatively charged, one cannot reason from this finding alone about the nucleophilicity of the carbon. This is because there is an overall 3– charge on the entire complex. One must move to a neutral molecule or focus on the electron density in the orbital perpendicular to the MCH2 plane. We have done both. Calculations on a neutral model for 4, TaCp(C2H4)(PPh3)(CH2), place a charge of +0.39 on Ta and −0.66 on the methylene carbon. We have already mentioned the result that in Ta(CH2)H2+ the methylene 2p orbital, orthogonal to the local MCH2 plane, is occupied by 0.82 electron. In an uncomplexed carbene it is vacant, and in a planar methyl radical it is occupied by one electron.

Bending the carbene to its preferred geometry removes electrons from the carbon and transfers them to the metal. This was already shown in structure 16. One might think that the nucleophilicity of the complexed carbene is thereby decreased. But the effect is entirely in the σ system, and the population of the methylene p orbital is unchanged. If one were doing a self-consistent field calculation, the σ charge drift would affect the p population, but at the extended Hückel level there is no such effect. The bending thus is not expected to modify substantially the basic nucleophilicity of the system.

What about the paradox of a nucleophilic carbene on an electron-poor metal center while the Fischer type carbenes are electrophilic? We have carried out comparative calculations on model carbene complexes Cr(CO)3C2H2 (18), CpFe(CO)3C2H2+ (19), and Fe(CO)5C(NH2)2 (20) and compared these with 13, 18, and 19 are models for unstabilized methylenes on d6 centers, while 20 models a π-donor stabilized carbene.

The carbene carbon of 20 is more positive than those of the other complexes simply because of σ-electron drift to the more electronegative N substituents. This stabilized carbene does have more electrons in its 2p orbital than 19 or 18, the result of N lone pair donation. But neither it nor the unstabilized carbene of the d6 type is as nucleophilic, by the criteria of either carbon charge or carbene 2p population, as the tantalum complex.

The roots of this difference could be looked for in either the energetics of the metal d–carbene p–π interaction or in its efficiency as measured by the respective overlap, i.e., either in the
denominator or numerator of a typical perturbation theoretic term governing the interaction:

\[ \Delta E = \frac{|H_{ij}|^2}{E_i - E_j} \]

The energy argument would operate as follows. Given a carbene 2p orbital and metal d function that interacts with it in \( \pi \) fashion, any increase in the energy of metal d orbitals would result in greater interaction, therefore more population of carbon 2p. This is shown schematically in 21.

Table II shows the Coulomb integrals, measuring the energy of the unperturbed metal d function in our calculations. But instead of looking at these \( \alpha_{ij} \)'s, one should examine the d orbital energy in the ML, fragment, incorporating the effect of the other ligands on the metal. This is shown in the second column. The carbene 2p orbital is at \(-1.14\) eV. The Ta complexes have a slight advantage in interaction on the energy criterion, but it is not great.

The overlap criterion makes a clearer choice. The Ta orbitals, with the parameters we use, are extremely well matched for overlap with carbon 2p functions (See Table II). We believe this factor is the dominant one in making the carbene electron rich in the Ta complexes, though we are very well aware that to some degree we are at the mercy of the parameters in the extended Hückel calculations here, more so than we normally are in drawing our often symmetry-based conclusions.

Another approach to the problem of electrophilicity or nucleophility is the frontier orbital one, focusing on the nature of the lowest unoccupied (LUMO) or highest occupied (HOMO) molecular orbital. In the carbenes 18–20 the LUMO is invariably largely the carbene 2p, so it is not surprising that these react with bases such as phosphines. In the Ta complex the d–p \( \pi \) interaction is sufficiently strong that the M d–C 2p \( \pi \)-antibonding combination is pushed up substantially higher—it is 3b\(_2\)–4a\(^{\prime\prime}\) in Figure 2. In principle the Ta complex is still available for interaction with a base, but less so than in its Fe or Cr counterparts.

The Hydrogen Transfer

In the course of the extensive reorientation of the complexed methylene we find that the C\(_a\)–H bond weakens significantly, a result consistent with the long C–H distances, where these have been determined accurately,\(^{24}\) low C–H stretching frequencies,\(^{22,23}\) and low \( \nu_{C=H} \) coupling constants\(^{24,32}\) that are observed in these molecules. At the same time that the C–H bond is loosened, we calculate that the Ta–H overlap population grows positive, a clear indicator of incipient bonding. It would seem that the hydrogen is being transferred to the metal. Why then does it not go all the way over?

In general one cannot rely on the extended Hückel method to give a trustworthy surface where bond stretching is a critical coordinate. But we thought we could obtain an answer to the above question by exploring a line of points on the surface for complete hydrogen transfer from our model compound 22 to a hypothetical methyne complex 24, where the local symmetry around the metal is octahedral.

At \( \theta = 180^\circ \), a deformed methylene with one Ta–C–H at 180° and one at 60°, the hydrogen atom closest to the metal is only 1.7 Å away, approximately the same distance as the other metal hydrogens. If the hydrogen atom closest to the metal in the bent carbene complex is then regarded as being attached to the metal, then the conversion of the trigonal-bipyrimal carbene complex to the octahedral complex 24 can be easily visualized as the simultaneous gradual motion of three hydrogen atoms in the equatorial plane of the Ta atom. 25–27 illustrates this path by showing beginning, intermediate, and final geometries in the equatorial plane. Please note that this is a different view from those shown previously—it is a series of snapshots taken down the linear H–X–H axis of 22 \( \rightarrow \) 23 \( \rightarrow \) 24. \( \phi = 120^\circ \) for the deformed methylene complex, and 90° for the methyne complex.
The calculated Walsh diagram for this slice through the surface is shown in Figure 5, along with a condensed version of the preceding part of the deformation coordinate. The striking aspect of this correlation diagram is a level crossing, between $7a'$ and $3a''$. The consumption of the hydrogen transfer is a symmetry-forbidden reaction. The computed barrier that results is not large, ~18 kcal/mol, but the very fact that it exists is surprising, given the signs of incipient Ta-H bonding.

To trace the decrease in energy of the $7a'$ orbital that is responsible for the crossing, we need the levels of the carbyne complex. These are built up in Figure 6 from the well-understood orbitals of MH$_2$ and of methyne. Note the excellent bonding which leads to the occupied 2e set. As long as a mirror plane of symmetry is maintained in the course of the hydrogen transfer, the $7a'$ orbital has to correlate with one component of the 2e.

The variation in energy of the $7a'$ can be followed in another way. At the beginning of the deformation, $\theta = 180^\circ$, this orbital is $5a_1$. It is a hybrid of metal $x$ and $x^2 - y^2$, concentrating its electron density away from the methylene. The orbital is shown at the top of Figure 7. It is somewhat Ta-CH$_2$ antibonding, with an overlap population of -0.22 were it occupied by two electrons. As $\theta$ changes from 120 to 180°, this level is only mildly affected, its energy set primarily by the position of the two equatorial ligands in its nodal surfaces. Antibonding with the carbene is slightly decreased, to -0.10.

Once the equatorial hydrogens begin to move in the second stage of the reaction this orbital is more directly affected. It rapidly replaces $x^2 - y^2$ by $xy$ (middle of Figure 7), trying to keep the equatorial hydrogens in its nodal surfaces. Finally it becomes pure $xy$, nicely $\pi$ bonding with a carbyne p orbital. The overlap population for 2 electrons in that orbital is 0.37 at the end. $7a'$ is also weakly Ta-H$_2$ bonding and C-H$_a$ antibonding in the region of intermediate $\phi$.

From Figure 5 it is not entirely clear where an activation energy of 18 kcal/mol could come from since the $7a'$ is uniformly decreasing as it crosses a $3a''$ orbital that is unaffected by the reaction. The barrier is to be found spread out over several lower $a'$ orbitals involved in C$_a$-H$_b$ bonding. It is essentially the disruption of the old C-H bond.

The overlap population changes along the entire hydrogen-transfer coordinate, Figure 8, show the discontinuity that follows from the level crossing. Note that the Ta-H overlap population already positive at $\phi = 120^\circ$ just becomes more positive.
To summarize: when one attempts to transfer the hydrogen completely, one encounters a level crossing, despite an initial attractive interaction and incipient bond formation between Ta and H. The level crossing is between the two metal based levels shown approximately in 28 and 29 – 30. The reaction is symmetry forbidden.

Will one obtain a similar level crossing in other electron-deficient carbene complexes? While we have not yet explored models other than the specific five- and six-coordinate geometries considered above, we think that it is likely that a similar effect will occur in other cases as well. Qualitatively the following argument should apply. If the carbene and carbyne ligands are to be viewed as σ donors and π acceptors, then the carbene is neutral (31) but CH must be taken positive and its p orbitals empty (32). The α-hydrogen is then transferred formally as a base, H−, changing the coordination sphere but not the electron count on the metal.

If the metal has 4 d electrons, one pair of these will be tied up in π bonding with the carbene p in 31. The other pair enters a metal orbital such as 32, which cannot interact by symmetry with any carbene orbital. When a hydride is transferred to the metal, an empty p orbital becomes available on the carbyne carbon. This orbital will find a match on the metal, but it will be of a different symmetry from the metal orbital containing the two extra electrons. A level crossing follows.

One might think that a level crossing could be avoided by destabilizing 3a′−1b2 relative to 7a′−2e (see Figure 5). This can be accomplished for instance by axial σ-donor substitution. But the result is unwelcome—7a′ is metal–CH2 antibonding in the early stages of the reaction, and complexation of the carbene in the first place would be disfavored.

Deformation of an Alkyl Ligand and Hydride Transfer

If a carbene distorts as extensively as it does in the alkylidene complexes, could an alkyl group undergo a similar reorientation? While in the 18-electron alkyls of type 3 or the dimethyltantalum–benzyne complex CpTa(CH2)2Me2,12 there is no sign of that distortion, the MCC angle at the alkyl ligand is slightly enlarged in some of the electron-deficient complexes, to 128° in 8 and 125° in 9.

The model we used was H4Ta(CH3)q, q = 2− and 4− (33), the two choices of charge corresponding to Ta(III), d2 and Ta(I), d4, respectively. The five-coordinate trigonal-bipyramidal structure was studied not so much because of a direct correspondence to known compounds (Ta(CH3)3, is known, but not its structure,13 and (Me3CCH2)(Me3CCH)2(PMe3)2Ta is reasoned to be trigonal bipyramidal by analogy with 55e) but rather because of our familiarity with the related carbene case.

An interaction diagram for the alkyl complex is shown in Figure 9—it is a straightforward coupling of CH3 and TaH4 units. Note that the level pattern is closer to that of a trigonal-bipyramidal ML5 paradigm (15) than the carbene complex.

For the d2 complex, 3a″ in Figure 9 filled, we find a very flat curve, essentially no energy change for 50° bending of the threefold axis in the axial plane, "using" the acceptor ability of 7a′, 34, or (b) tilting in the equatorial plane, using 8a′, 35, as did the carbene.
though not necessarily intramolecular.\(^\text{(14)}\)

For d\(^2\) and d\(^4\) complexes along an analogous reaction coordinate, we get level crossings. These are similar in origin to the carbone to carbyne interconversion (Figure 5). In the present case the reactant alkyl complex has one less \(\pi\) interaction than the product carbone.

Green, Cooper, and Canestrari\(^\text{(15)}\) have found that Cp\(_2\)WMe\(^+\) forms two different adducts with phosphines, 37a and b. They conclude that there is a facile equilibrium between the Cp\(_2\)WMe\(^+\) (38) and a carbone hydride complex 39 and suggest that the latter is more stable.

We have studied this reaction as well. The hindrance to methyl tilting is small. The calculated carbone hydride complex is much more stable, so that if full geometry optimization is allowed we expect that little activation energy will bar the rearrangement of 38 to 39. The carbone complex orients with the CH\(_2\) plane perpendicular to the CMH plane, as expected.\(^\text{(16)}\) There is a relatively low-lying LUMO in 39, available for phosphine attack. It is the antibonding combination of the carbone \(p\) orbital with \(1a\) of the Cp\(_2\)M fragment.\(^\text{(16)}\) The methyl complex 38 has a still lower lying unfilled orbital, in fact it might have a high-spin ground state.

The Elimination Reaction

A characteristic pattern of reactivity in this field is \(\alpha\)-elimination, from a metal dialkyl to a free alkane and a complexed carbone and from a metal alkyl carbone to an alkane and a coordinated carbyne.\(^\text{(2)}\) In calculations on our model TaH\(_4\)(CH\(_3\))\(^3-\) we noted a small positive overlap population between the carbone hydrogen atom closest to the metal and its nearest metal-bound hydrogen. Similarly in 40 we have a slightly positive overlap population, a harbinger of incipient bonding between the near carbone hydrogen and the methyl carbon.

Encouraged by these observations we first considered a simple model for the H transfer. That is: keeping all other geometrical parameters constant, we moved the hydrogen atom in an arc of constant radius about the Ta atom from a position 1.09 \(\AA\) from the carbone carbon atom to one 1.09 \(\AA\) from the methyl carbon atom. The transfer encountered no symmetry barrier though the


we allowed the methyl group to bend, as indicated in the H-transfer process.

and direct its hydrogen atom. We reasoned that if the methyl group were to bend is introduced, whereas with two electrons less the transfer process of that hydrogen to the metal is forbidden. It is as if the metal neutral). With two or four electrons more a substantial barrier showed clearly an increase in C\textsubscript{Ta}-Ta and a decrease in C\textsubscript{methyl}-Ta expected C\textsubscript{Ta}-H weakening and C\textsubscript{methyl}-H strengthening but also overlap population along a hypothetical H-transfer reaction coordinate.

intermediate stages in the reaction, yet recall that total transfer its place, note the large increase in M-C\textsubscript{Ta} bonding and the in-
dismantling of the C\textsubscript{Ta}-H bond and the formation of C\textsubscript{methyl}-H in

energy rose by ca. 1 eV. The overlap populations indicated the expected C\textsubscript{Ta}-H weakening and C\textsubscript{methyl}-H strengthening but also showed clearly an increase in C\textsubscript{Ta}-Ta and a decrease in C\textsubscript{methyl}-Ta bond strengths.

This first attempt at approximating a reaction path for transfer and elimination treated most unfairly the recipient methyl group. A way of easing the barrier for H transfer in our model without changing the metal–hydrogen distance would be to prepare the methyl group in some manner for accepting the in-coming hydrogen atom. We reasoned that if the methyl group were to bend and direct its \(\sigma\) orbital toward the hydrogen atom, then this might stabilize the transition state. And why not? We have seen that such a distortion of a methyl group can occur. So in our model we allowed the methyl group to bend, as indicated in 41, during the H-transfer process.

The hydrogen transfer is now exothermic by 1 eV. This is for Ta\textsubscript{H\textsubscript{2}}(CH\textsubscript{3})\textsubscript{2}(CH\textsubscript{3})\textsuperscript{+}, a Ta(I), \(d^4\) system (if CH\textsubscript{3} is counted as neutral). With two or four electrons more a substantial barrier is introduced, whereas with two electrons less the transfer process remains the same as in the \(d^4\) case.

The evolution of the overlap populations along this improved reaction path is illustrated in Figure 10. Aside from the forced dismantling of the C\textsubscript{Ta}-H bond and the formation of C\textsubscript{methyl}-H in its place, note the large increase in M-C\textsubscript{Ta} bonding and the interesting maximum in Ta-H bonding. It grows quite large at intermediate stages in the reaction, yet recall that total transfer of that hydrogen to the metal is forbidden. It is as if the metal guides the \(\sigma\)-hydrogen to the methyl group.

The Ta–C\textsubscript{methyl} overlap population decreases steadily as the hydrogen is transferred. It is no wonder, for one has a five-coordinate carbon here. As expected it does not take much, some

Figure 10. The evolution of the overlap populations during H transfer from a carbone to a methyl group in the idealized reaction path described in the text. Each stack of numbers indicates the evolution of a given overlap population along a hypothetical H-transfer reaction coordinate.

<table>
<thead>
<tr>
<th>orbital</th>
<th>(H_0) eV</th>
<th>(\varepsilon_1)</th>
<th>(\varepsilon_2)</th>
<th>C\textsubscript{Ta}</th>
<th>C\textsubscript{methyl}</th>
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\(\delta\) Contraction coefficients used in the double-\(\xi\) expansion.

13 kcal/mol in calculated activation energy, to remove the methane to infinity (eq 2). We expect that when a better and more complete potential energy surface is done on this reaction that one will find little or no activation energy for the combined H transfer and methane freeing.

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Appendix

All calculations were of the extended Hückel type, and weighted \(H_0\)'s were used. Coulomb integrals and orbital exponents are listed in Table III, and these were taken from earlier work. For the model calculations idealized geometries were assumed with Ta–C(carbone) = 1.90, Ta–C(methyl) = 2.18, Ta–H = 1.72, and C–H = 1.09 Å. In several exploratory calculations the following bond lengths were used: Ta–Cl = 2.36, Ta–P = 2.57, C–C = 1.50 Å. Otherwise geometries were taken from the literature.

In the comparative calculations of H\textsubscript{2}TaCH\textsubscript{2}, (CO)\textsubscript{2}CrCH\textsubscript{2}, Cp(CO)\textsubscript{3}FeCH\textsubscript{2}, and (CO)\textsubscript{4}FeC(NMe)\textsubscript{2}C\textsubscript{H}\textsubscript{4} the metal to carbene carbon distances were fixed at 2.0 Å. The geometries for the remaining part of the molecules were modeled after (CO)\textsubscript{5}FeC(NH\textsubscript{2})\textsubscript{2} the metal to carbene carbon distances were fixed at 2.0 Å. Otherwise geometries were taken from the literature.