J. Am. Chem. Soc. **1980**, *102*, 7667-7676

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$_2$.[30] Ortho and meta carbon exchange were treated separately as a two spin exchange between two different populated sites. 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 Strasbourgh-Cronenbourg, France.

Temperature Measurements. The temperature was measured before and after each spin-transfer experiment by use of a chemical shift thermometer (CH_3OH in a mixture of $CHCl_2F$-$CHClF_2$, 1:1, v/v).[27a,b]

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

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(30) Binsch, G.; Kleier, A., DNMR$_2$ program No. 141, QCPE, University of Indiana, Bloomington.

Unusual M–C–H Angles, C–H Bond Activation, and α-Hydrogen Abstraction in Transition-Metal Carbene Complexes

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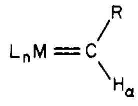
Abstract: Alkylidene complexes of electron-deficient transition metals display an interesting structural deformation in which the carbene appears to pivot in place while the C_α–H bond weakens. A molecular orbital analysis of these carbene complexes traces the deformation to an intramolecular electrophilic interaction of acceptor orbitals of the metal with the carbene lone pair. Bulky substituents on the metal and carbene protect the metal center from intermolecular reactions and control the extent of carbene pivoting. While a secondary interaction weakens the C–H_α bond and attracts the α-hydrogen to the metal, full transfer of hydride 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 α-elimination mode characteristic of the reactions of these compounds. The complexed carbene centers are unusually electron-rich, nucleophilic, by comparison with 18-electron d^6 stabilized carbene 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 equalized, as in dienes. Substituents bend toward or away from the metal, as in cyclopolyenes. But there is no precedent for the remarkable structural change that occurs in the electron-deficient alkylidene complexes recently synthesized by Schrock and coworkers.[2,3] These have the general composition $L_nM(CHR)$. However, their geometry differs substantially from what might have been expected for a classical carbene complex, **1**. The carbene ligand appears to pivot in place (**2**) so that remarkably small M–C–H angles, down to 78°, and correspondingly large M–C–R angles, up to 170°, are seen. The analysis of this deformation is the subject of this paper.



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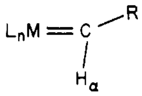

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The geometrical anomaly is only one of several unusual electronic and chemical properties of these alkylidene complexes of Ta, Nb, and W. They appear to be formed in α-elimination reactions of the type given by eq 1.

$$L_nM\begin{matrix}CH_2R\\R'\end{matrix} \longrightarrow L_nM-CHR + R'H \qquad (1)$$

The Schrock alkylidene complexes are nucleophilic rather than electrophilic.[2] The contrast with the heteroatom-substituted carbene complexes of the Fischer type[4] is sharp—it seems strange that a carbene 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,[5] two of these neutron diffraction structures which are a necessity for

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(1) To whom correspondence should be addressed.

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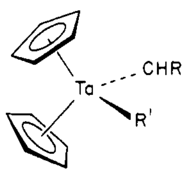
Table I. Selected Geometric Parameters of Carbene Complexes

no.	molecule	electron count at M	metal oxidation state CH$_2$	metal oxidation state CH$_2^{2-}$	angles (deg) and dist (Å) ∠RCH	∠MCH	∠MCR(θ)	MC	CH	M···H	ref
3	$TaCp_2(CH_2)(CH_3)$	18	III	V		126.5	126.5^a	2.026			5a
3	$TaCp_2(CHPh)(CH_2Ph)$	18	III	V			135.2	2.07			5b
3	$TaCp_2(CHCMe_3)Cl$	18	III	V		111.0	150.4	2.03			5c
4	$Ta(C_5Me_5)(CHCMe_3)C_2H_4(PMe_3)$	16	I	III	111.9	78.1	170.0	1.946	1.135	2.042	5d
5	$Ta(CHCMe_3)_2(Me_3C_6H_2)(PMe_3)_2$	14	I	V			168.9	1.932			5e
							154.0	1.955			
6	$[Ta(CHCMe_3)Cl_3(PMe_3)]_2$	14	III	V	114	84.8	161.2	1.898	1.131	2.119	5f
7	$TaCp(CHCMe_3)Cl_2$	14	III	V			165.0				5g
8	$Ta(CH_2CMe_3)_3CCMe_3Li(dmp)$	10	III	V			165.0	1.76	2.19^b		5h
9	$W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(P_2C_6H_6)$	16					149.7	1.982			5c

^{a} R = H. ^{b} CLi instead of CH.

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 I.



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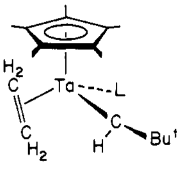
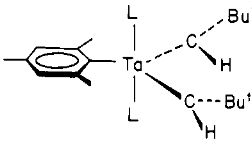


4, L = PMe$_3$



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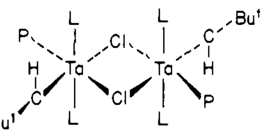
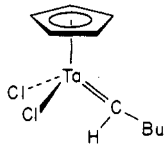


6, L = Cl, P = PMe$_3$



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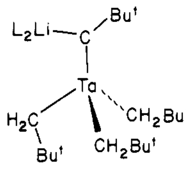
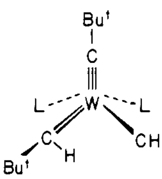


8, L$_2$ = dmp



9, L$_2$ = dmpe

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 TaCH$_\alpha$ 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–H$_\alpha$ bond is accordingly lengthened, to 1.135 and 1.131 Å. C–H$_\alpha$ bond weakening is also apparent in the strongly lowered C–H stretching frequencies and NMR coupling constants.[2]

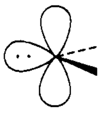
For the other complexes in Table I we have X-ray crystallographic structure determinations. While these do not allow us to follow the α-hydrogen so closely, we see the effects of the deformation in the enormous M–C–R angle and the correlated decrease in M–C bond length. Incidentally the fantastic structure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

The observed dimunitions of the M–C–H$_\alpha$ 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 α-hydrogen. To put it another way, the R–C–H$_\alpha$ angle does not deviate nearly as much from its normal angle as do the other two angles around the α-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 carbyne complex, in Table I.[5h] However, a comparison of the structural details of this molecule, $Ta(CH_2CMe_3)_3(CCMe_3)Li(dmp)$, 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···H$_\alpha$ interaction be of sufficient intensity for hydrogen transfer to occur? Does the M···H$_\alpha$ interaction activate H$_\alpha$ for transfer to another metal-bound ligand? What is the origin of the nucleophilicity of these complexed carbenes? 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, **10**, 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.



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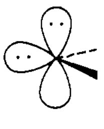

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(6) For alkylidyne complexes see also: McLain, S. J.; Wood, C. D.; Messerle, L. W.; Schrock, R. R.; Hollander, F. J.; Youngs, J. W.; Churchill, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 5962–5964; Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 171–176.

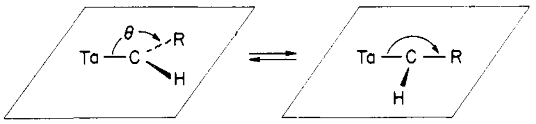
(7) Goddard, R. J.; Jemmis, E. D.; Hoffmann, R. to be submitted for publication.

Alternatively we can begin from a starting point of a CH_2^{2-} ligand, an excellent π 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**, $Ta(CHCMe_3)_2(mesityl)(PMe_3)_2$. 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 $Ta(CHCH_3)_2(H)(PH_3)_2$ to $Ta(CHCH_3)_2(H)Cl_2^{2-}$ to $Ta(CHCH_3)H_2Cl_2^{3-}$ to $Ta(CH_2)H_4^{3-}$. 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 adjacently 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 θ shown in **12**. Thus the Ta–C–H angle is $240 - \theta°$. On the left $\theta = 120°$, which we will term the undistorted geometry; on the right $\theta = 180°$, the bent geometry.



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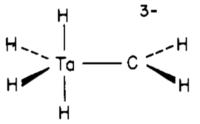
Our final model is $Ta(CH_2)H_4^{3-}$ (**13**), a 14-electron Ta(I) (or Ta(III) if the carbene is taken as CH_2^{2-}) methylene complex.



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We calculate the model complex with the distorted carbene geometry ($\theta = 180°$) 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 $[H_4Ta]^{3-}$ and CH_2 is shown in Figure 1.

The frontier orbitals of the ML_4 fragment are well-known;[8] those of $[H_4Ta]$ comprise an orbital set, a_1,a_2,b_2, derived from the t_{2g} set of an octahedron lying beneath b_1 and a_1 orbitals descended from e_g. Alternatively the latter may be viewed as linear combinations of two hybrids pointing toward the missing octahedral ligands. The local symmetry is C_{2v}. Under this point group p_y on the metal mixes into b_1 in a stabilizing way, and the orbital hybridizes in the direction of the vacant octahedral coordination sites.[9] This, we shall see, will be an important factor contributing to the stabilization of the bent carbene.

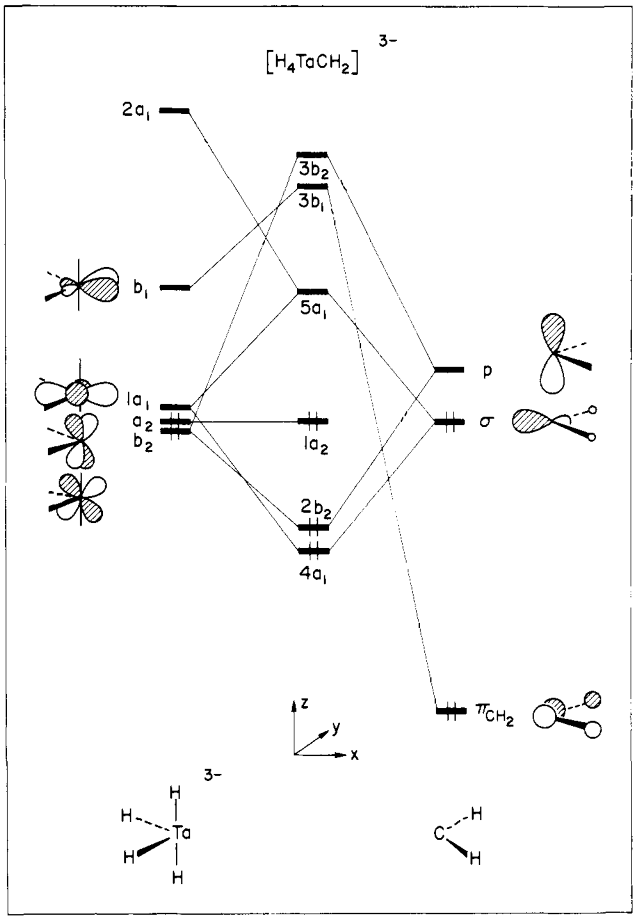

Figure 1. Diagram to show the interaction of the frontier orbitals of H_4M with those of CH_2 in $[H_4TaCH_2]^{3-}$.

The frontier orbitals of methylene are given on the right-hand side of Figure 1. We shall be mainly concerned with σ (the donor orbital), p (the acceptor orbital), and, to a lesser extent, a lower lying σ orbital of local π symmetry, π_{CH_2}.[10] The primary interactions are a donation of electron density from σ of the carbene to $1a_1$ (and to a lesser extent $2a_1$) of the ML_4 fragment and a back-donation from metal b_2 to carbene p. These interactions yield the $4a_1$ and $2b_2$ orbitals in which most of the metal–carbene bonding is contained. There is a further interaction between the b_1 hybrid of ML_4 and the π_{CH_2} orbital of the methylene. One metal orbital (a_2) is unaffected by carbene complexation.

Even at this point we can comment on the nucleophilicity of the coordinated carbene. The carbene p 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 $2b_2$ orbital, which is 64% on TaH_4, and 36% on the carbene. The b_2–p interaction is excellent—the Ta d orbital and the carbene p 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^4 Ta(I), then the b_2–p interaction transfers 0.72 electron into the carbene p orbital. One might as well have started out from a CH_2^{2-} and a d^2 Ta(III) and transferred 1.28 electrons to the TaH_4 fragment.

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(8) (a) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058–1076. (b) Burdett, J. K. *J. Chem. Soc., Faraday Trans.* **1974**, *70*, 1599–1613. (c) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1977**, 602–610; *Adv. Organomet. Chem.* **1977**, *15*, 1–51. (d) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456–3467. (e) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *Ibid.* **1979**, *101*, 3801–3812.

(9) For an analysis of this hybridization see: Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365–374.

(10) For a description of the orbitals of methylene and other carbenes see: Hoffmann, R.; Zeiss, G. D.; VanDine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485–1499. Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971; especially the chapter by J. F. Harrison. The localized orbitals of a CH_2 group are discussed and illustrated in: Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals", Academic Press: New York, 1973; pp 5–7, 63.

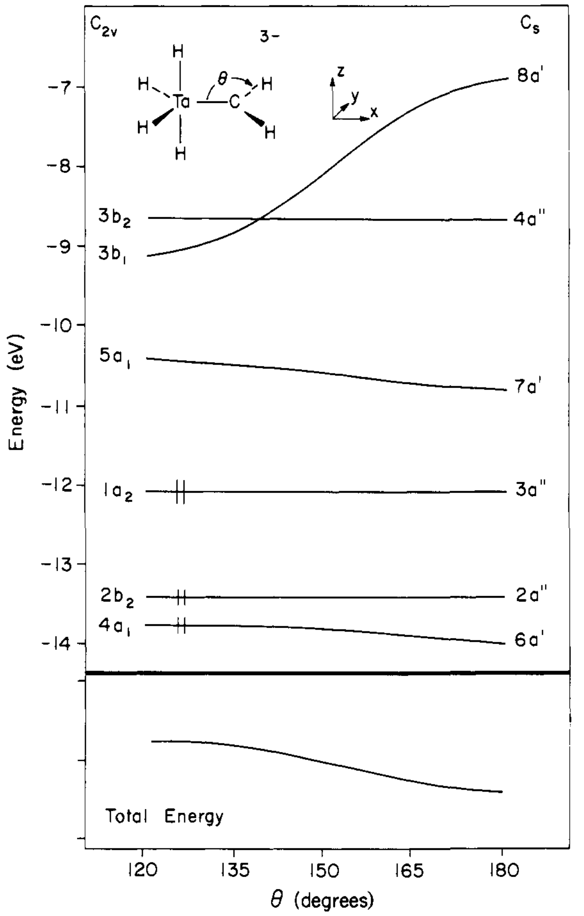
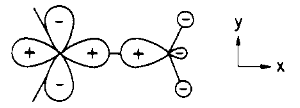


Figure 2. The Walsh diagram for the bending of the methylene group in $[H_4TaCH_2]^{3-}$. The total energy curve is shown at the bottom, on a graph with scale markings 1 eV apart.

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 θ 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_s. 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_s, 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 ($\theta = 120°$), this ligand is bound primarily through the σ–$1a_1(x^2 - y^2)$ interaction (**14**), orbital $4a_1$. Bending decreases this overlap, from 0.23 at $\theta = 120°$ to 0.15 at $\theta = 180°$. But at the same time a new and important interaction is turned on. This is between the b_1 hybrid of the MH_4 fragment and the carbene σ, an overlap that is zero at $\theta = 120°$ but rises quickly to 0.30 at $\theta = 180°$ (**15**). The hybridization of b_1 is responsible for its excellent overlap with the carbene donor orbital. Note also the M–H_α 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 θ and by the corresponding increase in population of that fragment orbital.



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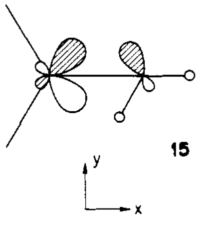

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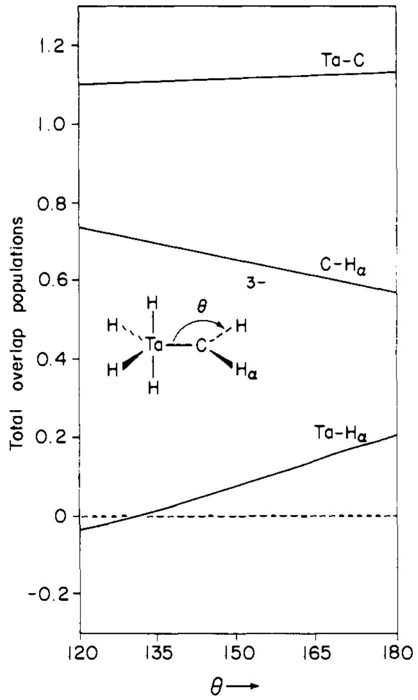

Figure 3. Total overlap populations in the triad, Ta–C, C–H_α, and Ta–H_α, as a function of θ.

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 (σ of the CH_2). Other orbitals of the carbene, e.g., π_{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 σ orbital is at lower energy, engaging more weakly in intramolecular electrophilic interactions. It appears that such a deformation occurs in *trans*-((adamantyl)NH)$_2$Mo(OSiMe$_3$)$_4$[11a] 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 σ donor and acceptor effects by changing the electronegativity of the equatorial ligands and a π effect by CN and NH_2 equatorial substituents. Both σ and π 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 $\theta = 180°$ and $\theta = 120°$. The evolution of the overlap populations

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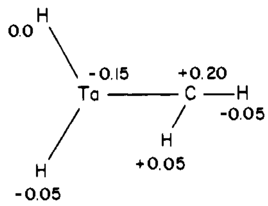
(11) (a) Nugent, W. A.; Harlow, R. L., private communication. (b) Heath, C.; Hursthouse, M. B. *Chem. Commun.* **1971**, 143–144. Bradley, D. C.; Chisholm, M. H.; Heath, C.; Hursthouse, M. B. *Ibid.* **1969**, 1261.



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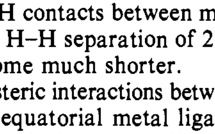
is displayed in Figure 3. The changes in the Ta–C–H_α triangle are all consistent with the observed structural perturbations. Note that in the calculations the Ta–C_α and C–H_α distances are kept fixed, so that any changes in these overlap populations are indeed reflections of an underlying electronic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

The Ta–H_α 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_α interaction is spread out over many orbitals, and (c) the eventual barrier, to be discussed later, to the consummation 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 $5a_1$–$7a'$ 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 $3b_1$, 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, $Ta(CHCH_3)(CH_3)_2H_2^{3-}$ (**17**). In this molecule an increase in θ from 120° is sterically differentiated from a decrease in that angle. The potential energy curve generated is presented in Figure 4, which for comparison shows the energy of a simple CH_2 group so rotated.



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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 electrophilicity 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 MCH_2 plane. We have done both. Calculations on a neutral model for **4**, $TaCp(C_2H_4)(PH_3)(CH_2)$, place a charge of +0.39 on Ta and –0.66 on the methylene carbon. We have already mentioned the result that in $Ta(CH_2)H_4^{3-}$ the methylene $2p_z$ orbital, orthogonal to the local MCH_2 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.

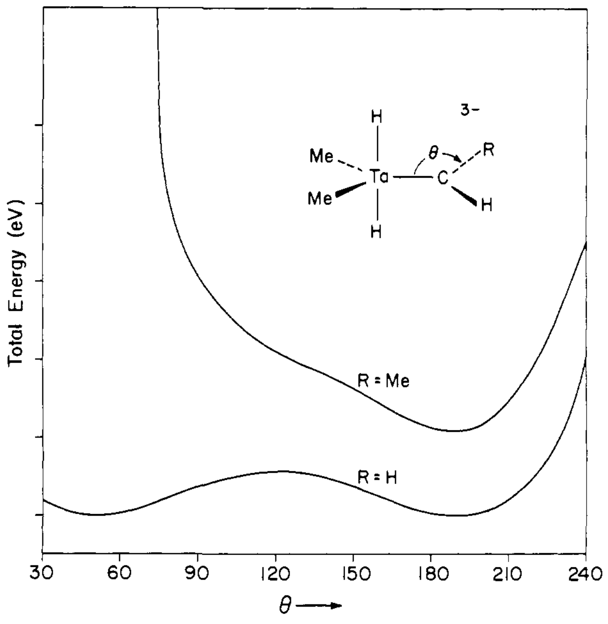


Figure 4. Potential energy curve for bending of an ethylidene ligand at a sterically crowded metal atom. The corresponding energy curve for a simple methylene is also included for comparison. The two curves are drawn on the same but arbitrary energy scale, markings 1 eV apart.

Table II. Coulomb Integrals and Overlaps in 13, 18, and 19

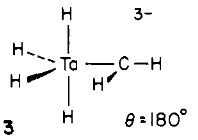
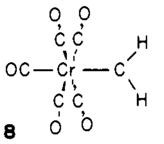
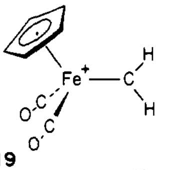
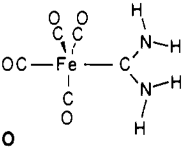
metal	molecule	H_{ii}, eV	H_{ii} of t_{2g} in ML_n, eV	⟨M d|C 2p⟩
Ta	13	−12.10	−12.10	0.249
Fe	18	−12.70	−12.35	0.135
Cr	19	−11.23	−12.58	0.178

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 $Cr(CO)_5CH_2$ (**18**), $CpFe(CO)_2CH_2^+$ (**19**), and $Fe(CO)_4C(NH_2)_2$ (**20**) and compared these with **13**. **18** and **19** are models for unstabilized methylenes on d^6 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 carbenes of the d^6 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

	Charge on $C_{carbene}$	Population of carbene 2p
 **13**	0.0	0.82
 **18**	0.08	0.49
 **19**	0.09	0.54
 **20**	0.49	0.63

denominator or numerator of a typical perturbation theoretic term governing the interaction:

$$\Delta E = |H_{ij}|^2/(E_i - E_j)$$

The energy argument would operate as follows. Given a carbene 2p above the metal d function that interacts with it in π 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**.

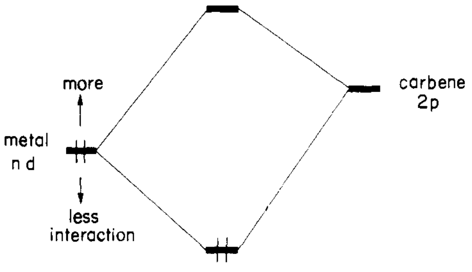


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Table II shows the Coulomb integrals, measuring the energy of the unperturbed metal d function in our calculations. But instead of looking at these H_{ii}'s, one should examine the d orbital energy in the ML_n fragment, incorporating the effect of the other ligands on the metal. This is shown in the second column. The carbene 2p orbital is at −11.4 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 nucleophilicity 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 π interaction is sufficiently strong that the M d–C 2p π-antibonding combination is pushed up substantially higher—it is $3b_2$–$4a''$ 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.

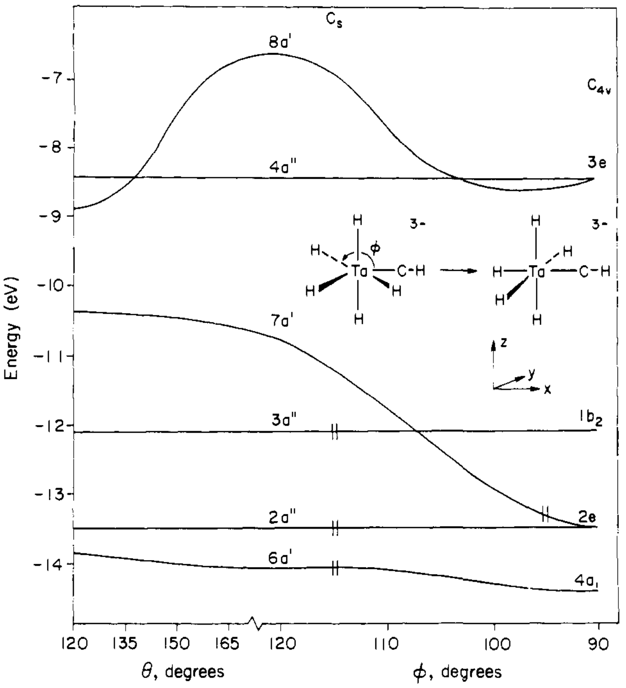
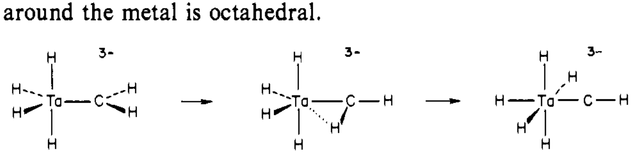


Figure 5. The Walsh diagram for the transfer of hydrogen to tantalum (at right) appended to a similar diagram for the first stage of the reaction, carbene pivoting (at left).

The Hydrogen Transfer

In the course of the extensive reorientation of the complexed methylene we find that the C_α–H bond weakens significantly, a result consistent with the long C–H distances, where these have been determined accurately,[5d,f] low C–H stretching frequencies,[2a,d] and low ${}^1J_{CH}$ coupling constants[2a,d,h] 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.



22 **23** **24**

At θ = 180°, 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-bipyramidal 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** → **23** → **24**. φ = 120° for the deformed methylene complex, and 90° for the methyne complex.

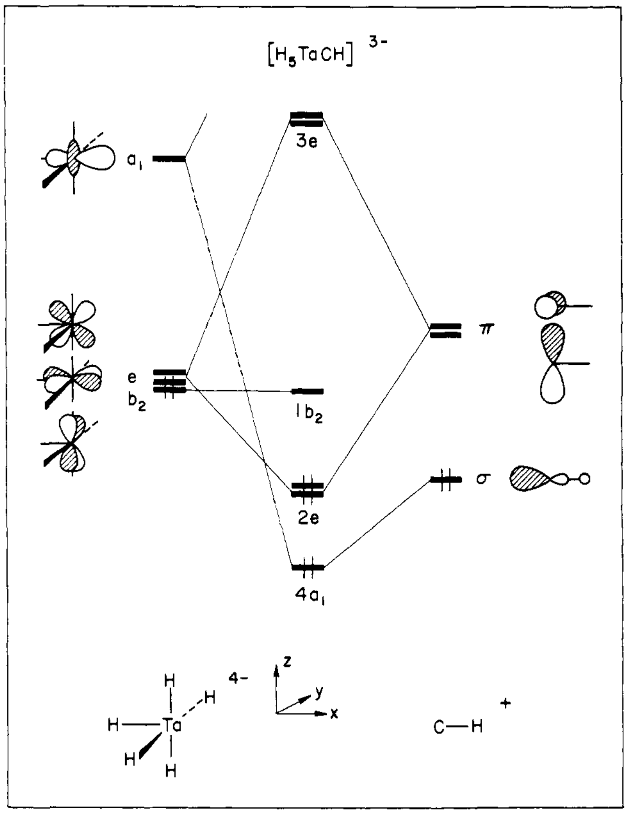
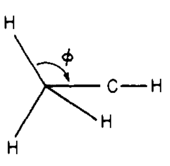


Figure 6. The interaction of the frontier orbitals for TaH_5 with CH in $[H_5TaCH]^{3-}$.

The other two equatorial hydrogens follow the motion proportionally.



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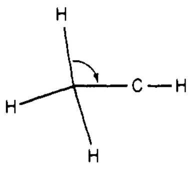

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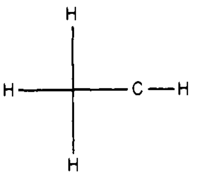

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The calculated Walsh diagram for this slice through the surface is shown in Figure 5, along with a condensed version of the preceding part of the deformation coordinate. The striking aspect of this correlation diagram is a level crossing, between 7a′ and 3a″. The consummation 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_5[8] and of methyne. Note the excellent π 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, $\theta = 180°$, 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 θ 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 π 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_α bonding and C–H_α antibonding in the region of intermediate φ.

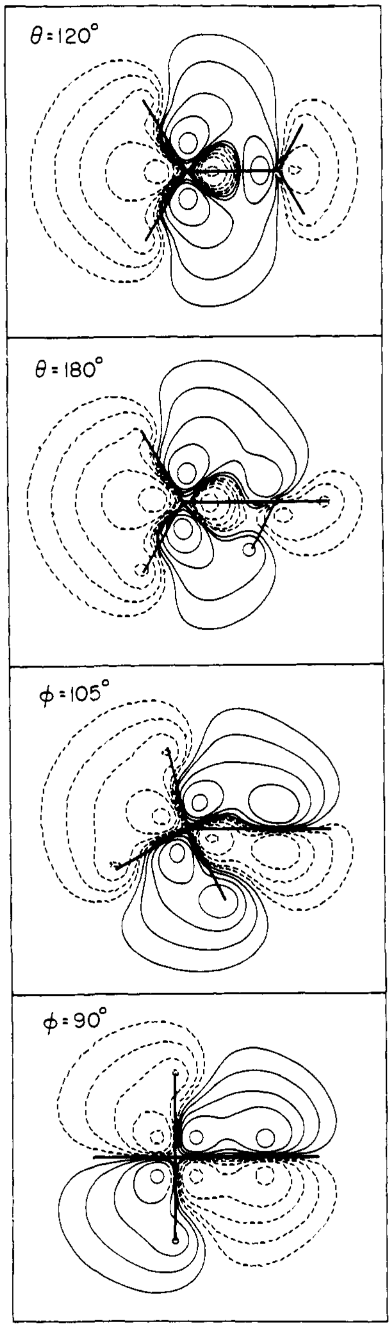


Figure 7. Contour plots in the equatorial plane, showing the development of the 7a′ orbital in **14**. From top to bottom: at the undistorted geometry, $\theta = 120°$; with the carbene bent, $\theta = 180°$; at an intermediate geometry during the hydrogen transfer, $\varphi = 105°$; after complete transfer of the hydrogen, $\varphi = 90°$. The contour values in each diagram: 0.2, 0.1, 0.555, 0.025, 0.01.

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_α–H 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 $\varphi = 120°$ just becomes more positive.

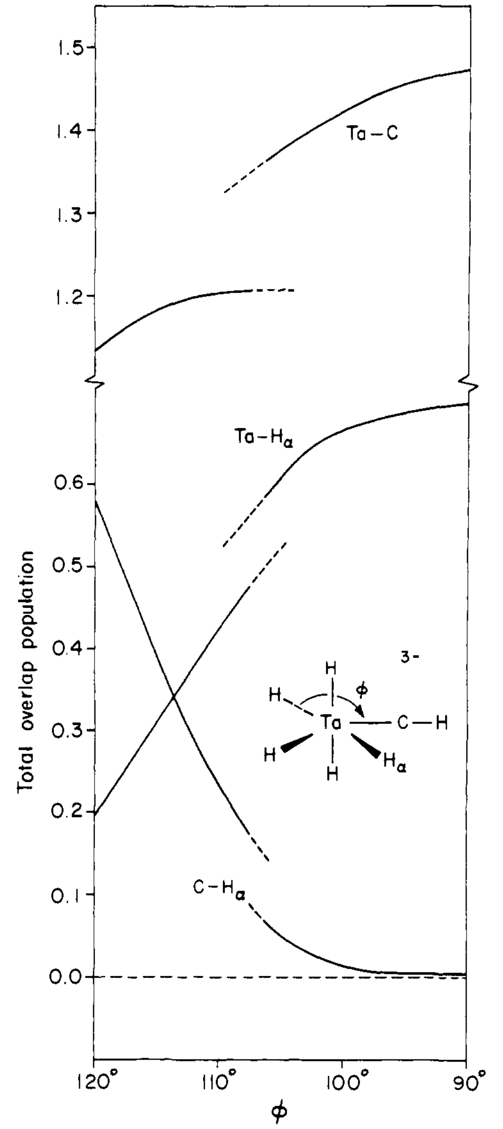
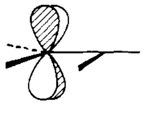
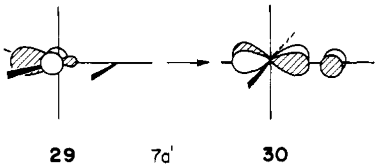


Figure 8. The overlap population changes in the Ta-C, C-H_α, and Ta-H_α bonds along the hydrogen-transfer coordinate, showing the discontinuities that follow from the level crossing.

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.



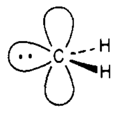
28, 3a''



29 7a' **30**

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



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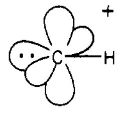

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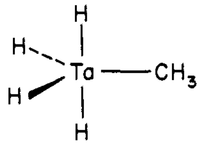
metal orbital such as **32**, which cannot interact by symmetry with any carbene orbital. When a hydride is transferred to the metal, an empty p orbital becomes available on the carbyne carbon. This orbital will find a match on the metal, but it will be of a different symmetry from the metal orbital containing the two extra electrons. A level crossing follows.

One might think that a level crossing could be avoided by destabilizing 3a''-1b_2 relative to 7a'-2e (see Figure 5). This can be accomplished for instance by axial π-donor substitution. But the result is unwelcome—7a' is metal-CH_2 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 $CpTa(C_6H_4)Me_2$,[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 $H_4Ta(CH_3)^q$, q = 2- and 4- (**33**), the



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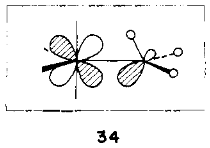
two choices of charge corresponding to Ta(III), d^2 and Ta(I), d^4, respectively. The five-coordinate trigonal-bipyramidal structure was studied not so much because of a direct correspondence to known compounds ($Ta(CH_3)_5$ is known, but not its structure,[13] and $(Me_3CCH_2)(Me_3CCH)_2(PMe_3)_2Ta$ is reasoned to be trigonal bipyramidal by analogy with 5^{5e}) 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 CH_3 and TaH_4 units. Note that the level pattern is closer to that of a trigonal-bipyramidal ML_5 paradigm (**15**) than the carbene complex. 3a'' and 7a' are related to e'' and 8a' and 4a'' to e'. There is only a small energy gap between 3a'' and 7a'. From this one might conclude that the d^2 complex would have a high-spin ground state. However the magnitude of the gap could depend on the π-bonding characteristics of the real ligands.

The methyl ligand could deform in two ways: (a) canting its local 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.



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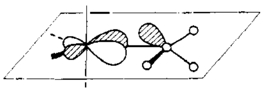

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For the d^2 complex, 3a'' in Figure 9 filled, we find a very flat curve, essentially no energy change for 50° bending of the threefold axis in the equatorial plane, a fairly small stabilization of 7

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[12] McLain, S.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263-265. Churchill, M. R.; Youngs, W. J. *Inorg. Chem. 18*, 1697-1702.

[13] Schrock, R. R.; Meakin, P. *J. Am. Chem. Soc.* **1974**, *96*, 5288-5290.

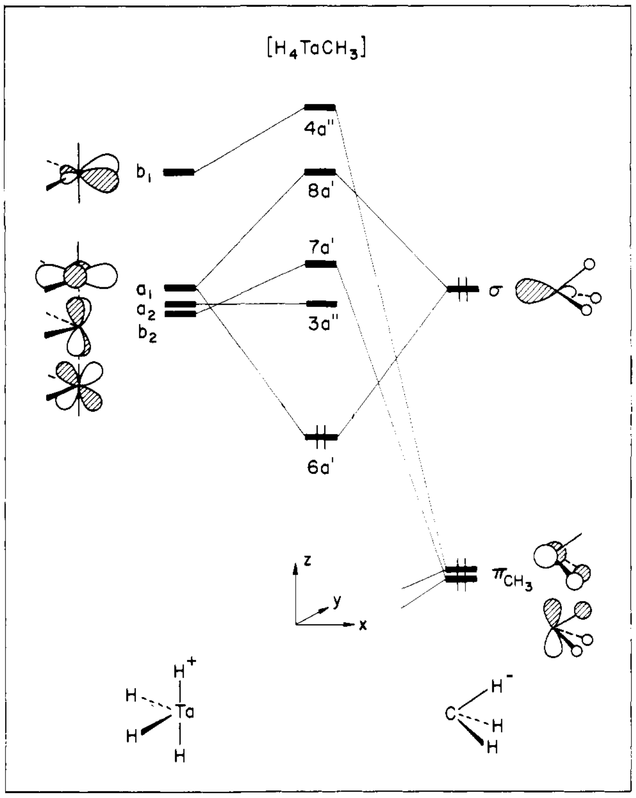


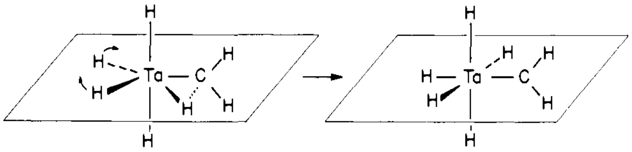
Figure 9. The interaction of the frontier orbitals of MH_4, with Me in $[H_4TaCH_3]$.

kcal/mol for an equal degree of bending in the axial plane. In each case the appropriate CH_3 conformation, **34** or **35**, was used. It appears that the energy denominator in a perturbation expression controls the direction of bending. The effect is clearly there, though it may be somewhat diminished relative to the carbene. The TaH_α overlap population grows in positive and $C–H_\alpha$ diminishes for either bending mode.

When two more electrons are added, forming the d^4 $TaH_4(CH_3)^{4-}$, they enter the 7a′ orbital. Electrophilicity in the axial plane is now gone, and the methyl group encounters a substantial barrier when it tries to tilt its threefold axis in that plane. Bending in the equatorial plane gains 7 kcal/mol for a 50° excursion.

Recalling the steric influence on carbene bending, we calculated a potential energy surface for canting of an equatorial methyl in pentamethyltantalum. The bulk of the methyl groups imposed barriers on bending in the axial plane but still allowed substantial canting in the equatorial plane.

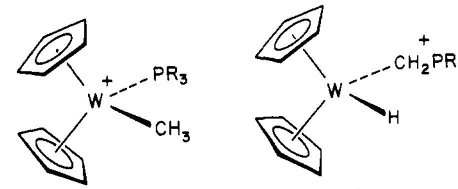
Hydride transfer to the metal, α-hydrogen abstraction, is a possible first step in the decomposition of pentaalkylniobium and -tantalum complexes.[14] We examined a hypothetical transfer of this type along a model reaction coordinate **36** patterned after our carbene study. The reaction is allowed for the d^0 Ta(V) case, but it encounters a barrier of some 30 kcal/mol. No doubt that computed barrier would be lowered if full geometry optimization were allowed. The observed decomposition of the pentaalkyls proceeds at room temperature for Ta and at still lower temperatures for Nb. There is a kinetic deuterium isotope effect on the decomposition implicating a rate-determining C–H cleavage, though not necessarily intramolecular.[14]



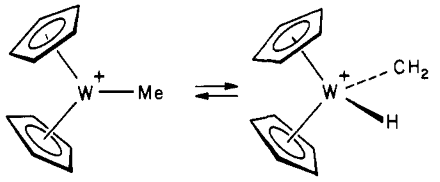
36

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

Green, Cooper, and Canestrari[15] have found that Cp_2WMe^+ forms two different adducts with phosphines, **37a** and **b**. They conclude that there is a facile equilibrium between the Cp_2WMe^+ (**38**) and a carbene hydride complex **39** and suggest that the latter is more stable.



a **37** b

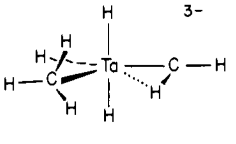


38 **39**

We have studied this reaction as well. The hindrance to methyl tilting is small. The calculated carbene 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 carbene complex orients with the CH_2 plane perpendicular to the CMH plane, as expected.[16] There is a relatively low-lying LUMO in **39**, available for phosphine attack. It is the antibonding combination of the carbene p orbital with $1a_1$ of the Cp_2M fragment.[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 ractivity in this field is α-elimination, from a metal dialkyl to a free alkane and a complexed carbene and from a metal alkyl carbene to an alkane and a coordinated carbyne.[2] In calculations on our model $TaH_4(CH_2)^{3-}$, we noted a small positive overlap population between the carbene 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 carbene hydrogen and the methyl carbon.



40

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 Å from the carbene carbon atom to one 1.09 Å from the methyl carbon atom. The transfer encountered no symmetry barrier though the

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[14] Schrock, R. R. *J. Organomet. Chem.* **1976**, *122*, 209–225.

[15] (a) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121–1127. (b) Canestrari, M.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1979**, 913–914.

[16] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742.

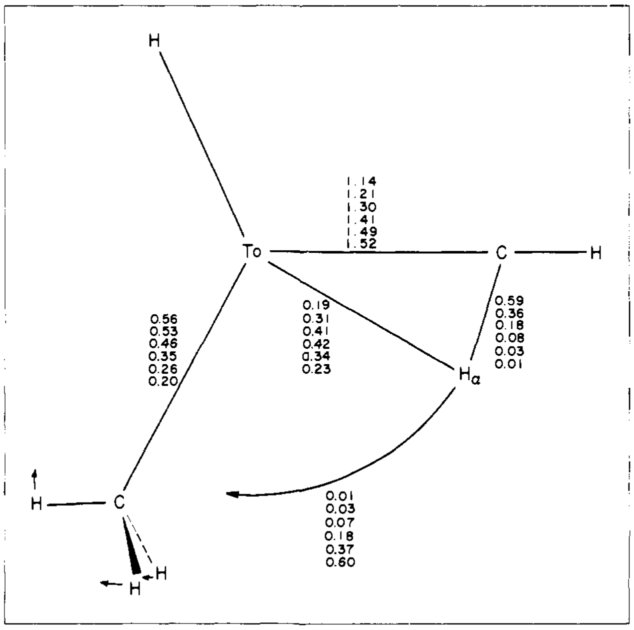
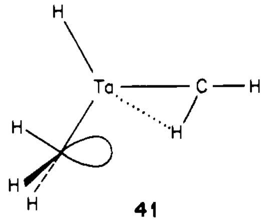


Figure 10. The evolution of the overlap populations during H transfer from a carbene to a methyl group in the idealized reaction path described in the text. Each stack of numbers indicates the evolution of a given overlap population along a hypothetical H-transfer reaction coordinate.

energy rose by ca. 1 eV. The overlap populations indicated the expected C_α–H weakening and C_{methyl}–H strengthening but also showed clearly an increase in C_α–Ta and a decrease in C_{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 σ 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.

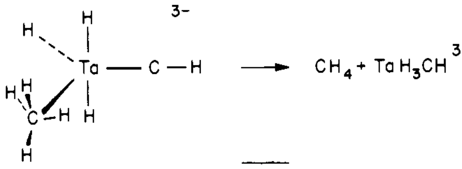


41

The hydrogen transfer is now exothermic by 1 eV. This is for $TaH_3(CH_3)(CH_2)^{3-}$, a Ta(I), d^4 system (if CH_2 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_α–H bond and the formation of C_{methyl}–H in its place, note the large increase in M–C_α 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 α-hydrogen to the methyl group.

The Ta–C_{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 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.



(2)

Table III. Parameters Used in Extended Hückel Calculations

orbital	H_{ii}, eV	ζ_1	ζ_2	$C_1{}^a$	$C_2{}^a$
Ta 5d	−12.10	4.08	1.64	0.640	0.552
6s	−10.10	1.89			
6p	−6.86	1.85			
C 2s	−21.4	1.625			
2p	−11.4	1.625			
N 2s	−26.0	1.95			
2p	−13.4	1.95			
O 2s	−32.30	2.275			
2p	−14.80	2.275			
H 1s	−13.60	1.30			
Cl 3s	−30.0	2.033			
3p	−15.0	2.033			
P 3s	−18.6	1.60			
3p	−14.0	1.60			
Fe 3d	−12.6	5.35	2.00	0.551	0.626
4s	−9.10	1.90			
4p	−5.32	1.90			
Cr 3d	−11.2	4.95	1.80	0.506	0.675
4s	−8.66	1.70			
4p	−5.24	1.70			

[a] Contraction coefficients used in the double-ζ expansion.

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Appendix

All calculations were of the extended Hückel type,[17] and weighted H_{ij}'s were used.[18] Coulomb integrals and orbital exponents are listed in Table III, and these were taken from earlier work.[19] For the model calculations idealized geometries were assumed with Ta–C(carbene) = 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_4TaCH_2, $(CO)_5CrCH_2$, $Cp(CO)_2FeCH_2{}^+$, and $(CO)_5FeC(NH_2)_2$ the metal to carbene carbon distances were fixed at 2.0 Å. The geometries for the remaining part of the molecules were modeled after $(CO)_5Cr(PPh_3)$,[20a] $[CpFe(CO)_2]_2C_4H_4$,[20b] and $(CO)_4FeC(NMe)_2C_2H_4$.[20c]

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