quencies and infrared intensities are very similar to the ordinary SCF results, while the TCSCF dipole moment for vinylidenesilene is 0.77 debye.

For silylenylaetylene (**3**) the lowest energy TCSCF wave function has the form

$$\Psi = C_1\ 7a'^2 8a'^2 9a'^2 10a'^2 2a''^2 11a'^2 12a'^2\ +$$
$$C_2\ 7a'^2 8a'^2 9a'^2 10a'^2 2a''^2 11a'^2 3a''^2 \quad (3)$$

At the DZ+P TCSCF equilibrium geometry of silylenylacetylene, $C_1 = 0.982$ and $C_2 = 0.187$, and the TCSCF energy is 0.017 47 hartrees below the analogous single configuration SCF energy. For the parent silylene (SiH_2), the TCSCF/SCF energy difference is about 0.02 hartrees. On this basis we see that the TCSCF treatment is less essential for all three structures **1**, **2**, and **3** considered here than for the parent, unsubstituted SiH_2. For silylenylacetylene we see the largest TCSCF/SCF structural difference encountered in this research, for the Si–C distance. There we predict $r_e(\text{Si–C, SCF}) = 1.853$ Å and $r_e(\text{Si–C, TCSCF}) = 1.856$ Å, still a difference of only 0.0034 Å. Like the other principal species (**1** and **2**) studied here, **3** has a moderate dipole moment: 0.63 debye at the TCSCF level of theory.

For our final large basis set predictions of the relative energies of **1**, **2**, and **3**, CI with all single and double excitations was carried out with respect to both TCSCF reference functions (see wave functions (1), (2), and (3), respectively). With the restrictions discussed earlier, there are totals of 27 083 (**1**), 26 988 (**2**), and 52 714 (**3**) configurations included. DZ+P TC-CISD total energies are −366.064 47, −366.036 50, and −366.031 21 hartrees, respectively. These total energies place vinylidenesilene 17.6 kcal above **1** and silylenylacetylene 20.9 kcal above **1**. With the TCSCF-CISD Davidson correction,[26] **2** falls to within 16.4 kcal of **1**, and **3** lies 21.6 kcal above **1**. These results, of course, are qualitatively similar to our one reference CI predictions.

Conclusions

The global minimum on the C_2SiH_2 singlet potential energy hypersurface is 3-silacyclopropenylidene (**1**) which has a relatively short carbon–silicon bond.

It is appropriate to note at this point that the analogous hydrocarbon compound cyclopropenylidene has recently been synthesized by the group of Maier and Hoffmann.[24] Cyclopropenylidene was identified with the help of theoretical predictions[15] of the vibrational frequencies and IR intensites, much like those reported here for the sila-substituted **1**. We note in this regard that DZ+P SCF vibrational frequencies (such as those reported in Table III) are typically ~10% higher than the observed fundamentals.[25]

After structure **1** come vinylidenesilene **2** and silylenylacetylene **3**, which are 17 and 22 kcal/mol higher in energy at the DZ+P CI level of theory. Five more minima have been identified theoretically, but they are all much higher in energy, and it will be difficult to identify them experimentally. It is hoped that the theoretically determined vibrational frequencies and IR intensities will help in identifying the three C_2SiH_2 low-lying isomers.

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Theoretical Study of the Conformation of Cis Carbene–Olefin–Transition Metal Complexes: Back-Donation vs. Ligand–Ligand Interaction

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Abstract: The conformation of several cis carbene–olefin–transition metal complexes (d^6 octahedral, d^4 pseudooctahedral, and d^8 trigonal-bipyramidal) have been studied by means of Extended Hückel calculations. In the case of d^6 tungsten octahedral complexes, it is shown that the two main factors which determine the optimal conformations are metal-to-ligand back-donation and direct ligand–ligand interaction. The relative amounts of both factors depend strongly on the electronic nature of the ligands at the metal. When they are innocent ligands with no π acceptor properties, maximization of the back-donation from the metal to the carbene and the olefin determines the best conformations. This is obtained when the two π acceptor orbitals overlap with two different d nonbonding orbitals. Four-electron repulsion between the occupied nonbonding orbitals and the occupied ligand orbitals then distinguishes between the conformations which have an equivalent amount of back-donation. When the ligands are π acceptor ligands (such as CO), ligand–ligand interaction takes a determining influence. This interaction is optimal when the π systems of the carbene and olefin are coplanar (that is when back-donation is minimized). The introduction of the π donor group on the carbene carbon increases also the importance of the ligand–ligand interaction. The structures of d^4 pseudooctahedral tantalum and d^8 trigonal-bipyramid carbene–olefin complexes are also discussed.

Cis metal–carbene–olefin complexes have been proposed as key intermediates in the olefin metathesis,[1] cyclopropanation of al-

kenes,[2] and the Ziegler–Natta polymerization of alkenes.[3] Considerable effort has been spent in the isolation and charac-

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terization of such complexes. Many such complexes[4] were known, but most of them did not take part in either olefin metathesis or cyclopropanation and even fewer of them were characterized by X-ray analysis. Of special interest among these complexes are those in which the carbene and the olefin group are well-separated groups, both linked to the metal. In the late 1970, only two such complexes, 1[5] and 2,[6] were known, but their characterization by spectroscopic means did not allow full structural assignation.


1

2

3
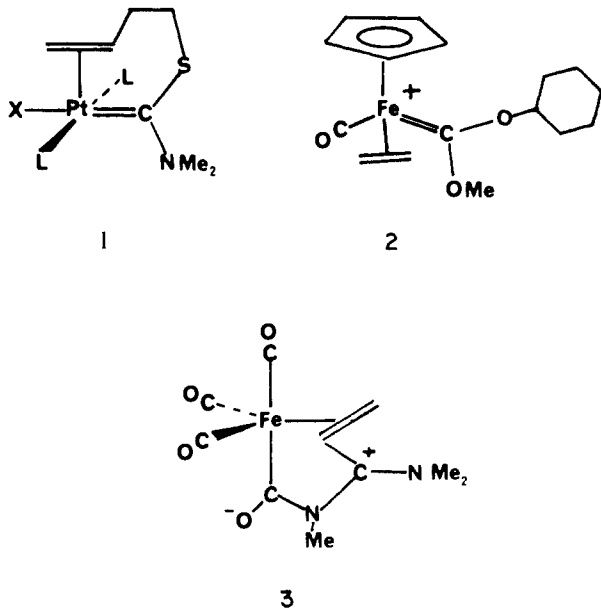
Detailed structural information is known about 3.[7] In this trigonal bipyramid, the carbene occupies the axial site and the olefin lies in the equatorial plane. In addition, the plane of the carbene is perpendicular to the metal–olefin plane. For this system, no reaction of the type mentioned above has been reported.

Considerable progress has been made recently, and some interesting points have been raised concerning the structure and reactivity of metal–carbene–olefin complexes.

$(CO)_5W(CR_2)$, R = phenyl and tolyl, is known to catalyze the metathesis of olefins.[8] Casey[9] and Rudler[10] independently suceeded in isolating and structurally characterizing cis $(CO)_4W$-(CXY)–olefin $(X = OR, NR_2; Y = alkyl)$ complexes obtained by reacting the metal–carbene and the olefin. Both have reached similar results. In order to force the cis arrangement of the carbene and the olefin, the two groups are linked by a relatively short saturated chain and are thus chelating the metal. The chelation is necessary since trans carbene–olefin–metal complexes are

probably more stable.[11] These complexes are Fisher-type carbenes in which the carbon carbene carries a π donor group such as an amino or an alkoxy group inside or outside the saturated chain. These complexes are schematically represented as 4,[10a] 5,[10b] 6,[10c] 7,[9a] 8,[9b] and 9[9b] (8 and 9 are two conformers of the same complex; see below for the definition of α and β). Two conformations have
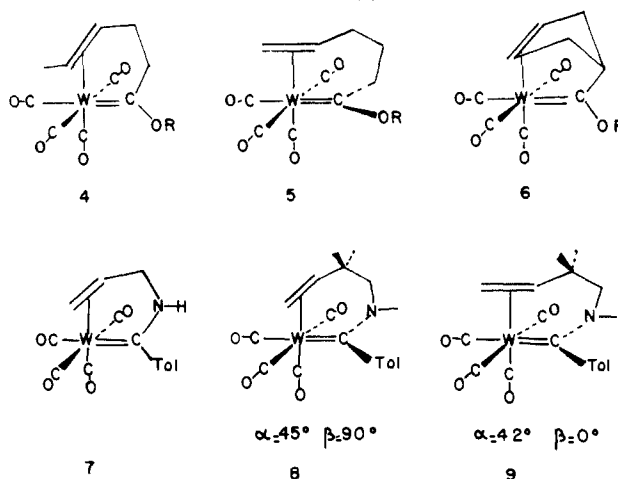
been basically observed. In one of them, the C–C olefin bond is almost perpendicular to the metal–carbene bond and the carbene ligands lie in the carbene carbon–W–olefin midpoint plane (4, 6, and 7). In the other one, the olefin is almost parallel to the metal–carbene bond and the carbene plane is perpendicular to the carbene carbon–W–olefin midpoint plane (5). Structures 8 and 9 are intermediate between the two previous idealized geometries.[9b]

The interesting point is that the reactivity of these complexes is closely related to their structure. The complex in which the olefin is parallel to the tungsten–carbene bond (5) yields cyclopropane,[10b] while the complexes in which the olefin is perpendicular to the tungsten–carbene bond (4, 6, and 7) are unreactive.[9a,10] In no case are olefin metathesis products observed.

A d^4 complex of tantalum (counting the carbene as a neutral ligand; see ref 18) has been isolated and structurally characterized by neutron diffraction, 10.[12] In many aspects, this complex differs

10
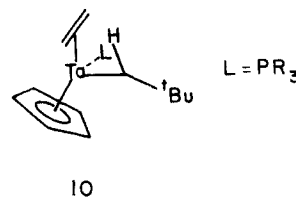
from the precedent ones. It is an alkylidene complex since the carbon shows a strong nucleophilic character. The alkylidene is strongly distorted away from a classical geometry (Ta–C–H angle is 78°). Such distortions which are now commonly found in electron-deficient complexes[13] have been discussed theoretically.[14] Finally, an additional interesting aspect of this molecule is provided by its abnormally long C=C double bond, 1.49 Å. No olefin metathesis, cyclopropanation, or olefin polymerization has been reported for that system. In this case as in the nonreactive W(0) complexes, the olefin bond is perpendicular to the metal–carbene direction. In addition, the hydrogen of the CHR group lies in the carbene–Ta–olefin midpoint plane.

Much theoretical work has been devoted to olefin–transition metal[15,17] and to carbene–transition metal[16,17] complexes. But

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Cis Carbene–Olefin–Transition Metal Complexes

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Table I. Analysis of the Rotational Barrier of (a) $H_4W(CH_2)(C_2H_4)^{4-}$, (b) $(CO)_4W(CH_2)(C_2H_4)$, and (c) $(CO)_4W(CHOH)(C_2H_4)$

complex	(0,0)	(90,0)	(0,90)	(90,90)
		a		
$E_T{}^a$	17.4	39.5	3.9	0.0
$\sum d^b$	7.9	51.7	1.4	0.0
$\sum \sigma^c$	18.5	0.0	21.7	19.9
		b		
E_T	16.2	3.2	6.0	0.0
$\sum d$	12.0	14.3	4.6	0.0
$\sum \sigma$	12.5	0.0	18.0	16.6
		c		
E_T	11.8	0.0	4.2	1.2
$\sum d$	4.2	5.5	3.2	0.0
$\sum \sigma$	7.9	0.0	10.6	11.6

$^a E_T$ = total energies (kcal/mol) of the four representative conformations relative to the most stable one. $^b \sum d$ = sum of the energies of three highest occupied d orbitals (kcal/mol) relative to the most stable situation. $^c \sum \sigma$ = sum of the energies of the two orbitals below the d levels (kcal/mol) relative to the most stable situation (see text).

apart from some preliminary work,[17b] little is known about carbene–olefin complexes. A better understanding of these im-
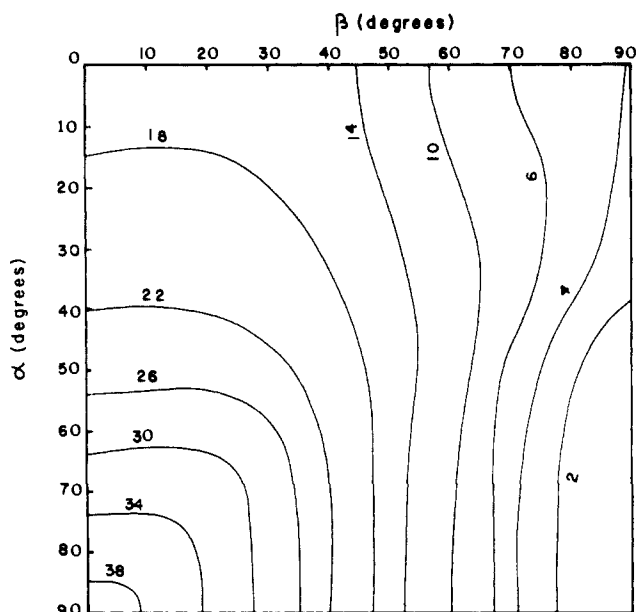
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Figure 1. Potential energy surface $E = f(\alpha,\beta)$ for $H_4W(CH_2)(C_2H_4)^{4-}$.

portant intermediates requires a discussion of the factors controlling their conformational preferences. In this work, we discuss the conformational properties of these complexes by means of Extended Hückel calculations. It is shown that the conformational preference of these complexes is highly sensitive to the nature of the ligands on the metal. In particular, it is shown that the conformation which can produce cyclopropane can only be reached if some specific conditions are met.

$H_4W(CH_2)(C_2H_4)^{4-}$. The first complex that has been studied is $H_4W(CH_2)(C_2H_4)^{4-}$, a model for $(CO)_4W(CXY)(C_2H_4)$. It corresponds to the usual simplification according to which all carbonyl ligands are replaced by hydride ions and the carbene and alkene ligands by methylene and ethylene, respectively. The total charge of the system is set to 4– to keep a d^6 configuration[18] at the metal.

Two angles α and β are sufficient to fully describe the conformation of these systems. The α angle defines the twist between the plane of the carbene carbon, the metal, and the ethylene midpoint and the plane of the carbene. The β angle between the plane defined by the carbene carbon, the metal, and the midpoint of the alkene ligand and the plane defined by the metal and the two carbons of the alkene moiety determine whether the carbon–carbon double bond of the alkene and the carbene carbon-to-metal bond are parallel ($\beta = 0°$) or perpendicular ($\beta = 90°$). Four limiting structures, each one referred by its α and β value as (α,β) are **11–14**. The experimentally observed conformations are **13** ($\alpha = 0°, \beta = 90°$), model for **4, 6**, and **7**, and **12** ($\alpha = 90$, $\beta = 0$), model for **5**. As we just mentioned above, the conformation **12** gives cyclopropane, while the conformation **13** is unreactive.

(α,β)	(0,0)	(90,0)	(0,90)	(90,90)
	11	12	13	14
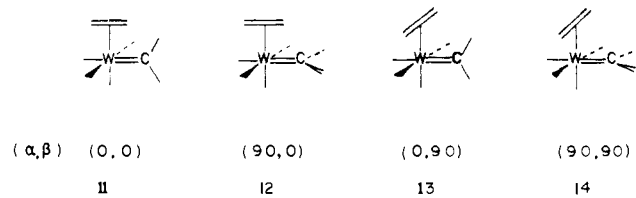
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(18) The tungsten complexes are Fisher-type carbene complexes for which it is well-accepted that the carbene ligand should be considered as a neutral ligand. For consistancy, we always consider the carbene as neutral, even in the tantalum complexes although it is better represented as an alkylidene complex. It is important to realize that our argument does not depend on the formal charge affected to the carbene and that the alternative choice (doubly negatively charged carbene) would lead to analogous discussion and results.

We have verified by calculating the full potential energy surface $E(\alpha,\beta)$, Figure 1, that these four conformations characterize adequately the shape of the surface. Their relative energies are reported in Table Ia. This calculated order is clearly at odds with the experimental one. (90,0) is the most unfavorable conformation by a large amount (39.5 kcal/mol) although it turns out to be one of the experimentally observed structure. The other observed geometry (0,90) is also not the calculated optimal conformation, but it lies only 3.9 kcal/mol above the minimum. In these d^6 octahedrons, the three low-lying nonbonding d orbitals (the t_{2g} set of a pure octahedron) are doubly occupied. The contribution to the total energy of these three orbitals, $\sum d$, is reported relative to the lowest value. The variation of this term nicely parallels that of the total energy. Consequently, the three low-lying d orbitals are responsible for the calculated relative total energy. The energy level of the three d orbitals is only influenced by π effects which can be either stabilizing or destabilizing. The stabilization provided by the ethylene π^* and the carbene p_C orbitals is well-known as the back-donation effect and deserves no additional comments. The destabilizing factors originate from the occupied ethylene π^+ (**15**), π^- (**16**), and carbene π_{CH_2} (**17**).

| 15 | 16 | 17 |
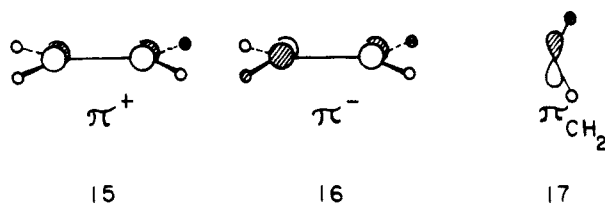
The interaction between a d orbital and π^- is only weakly destabilizing since the overlap between the two orbitals is of Δ type, while the destabilization created by π^+ and π_{CH_2} is more important since the overlap is of Π type. The change in energy of a d orbital is also accompanied by a more or less large delocalization of that orbital on the ligand orbital. The delocalization of d on ethylene π^* or carbene p_C is large, while that on ethylene π^+ and carbene π_{CH_2} is considerably smaller and that on ethylene π^- is even smaller.

With this simple set of ideas in mind, one can understand the relative energies of the four conformers **11**, **12**, **13**, and **14**. The way their d orbitals mix with the ligands occupied and empty orbitals is illustrated in Figure 2. In the following discussion, we shall consider the ethylene fragment interacting with $WH_4CH_2^{4-}$. In this way, the d orbitals interact primarily with the carbene orbitals and the notation is as follow: $(xy + \lambda p_C)$ refers to the in-phase combination of xy with $2p_C$ and $(xz - \epsilon\pi_{CH_2})$ to the out-of-phase combination of xz with $2p_C$.

Compare first (0,90) to (90,90). In (0,90), π^* stabilizes yz, while π^- and π^+ destabilizes, respectively, $(xy + \lambda p_C)$ and $(xz - \epsilon\pi_{CH_2})$. In (90,90), π^* stabilizes also yz, while π^- destabilizes $(xy - \epsilon\pi_{CH_2})$ and π^+ destabilizes $(xz + \lambda p_C)$. These conformations differ only by the way π^+ and π^- destabilize their respective partners. We have seen above that the perturbation originating from π^+ is larger than that originating from π^-; thus, we can limit ourselves to the role of π^+. It turns out that in these compounds, the destabilization by π^+ is under the control of the overlap. Therefore, $(xz - \epsilon\pi_{CH_2})$, being more localized on the metal than $(xz + \lambda p_C)$, is more destabilized by π^+ so that *(0,90) is less stable than (90,90)*.

Compare now (0,0) to (90,0). π^* interacts with different orbitals in the two conformations. In (0,0), it overlaps with $(xz - \epsilon\pi_{CH_2})$, which is high in energy and only slightly delocalized on the ligands. In (90,0), π^* overlaps with $(xz + \lambda p_C)$, which is low in energy and strongly delocalized on the carbene carbon p_C orbital. According to energy and overlap criteria (the in-phase overlap between the closest carbene and ethylene carbon p_C orbitals is not sufficient to lead to a large stabilization of xz), π^* stabilizes $(xz - \epsilon\pi_{CH_2})$ much more than $(xz + \lambda p_C)$. Thus, it is not surprising that *(0,0) is considerably more stable than (90,0)*. π^+ and π^- also participate in a different manner in the two conformers, but their influence is too small to reverse the energetical preference created by π^*.

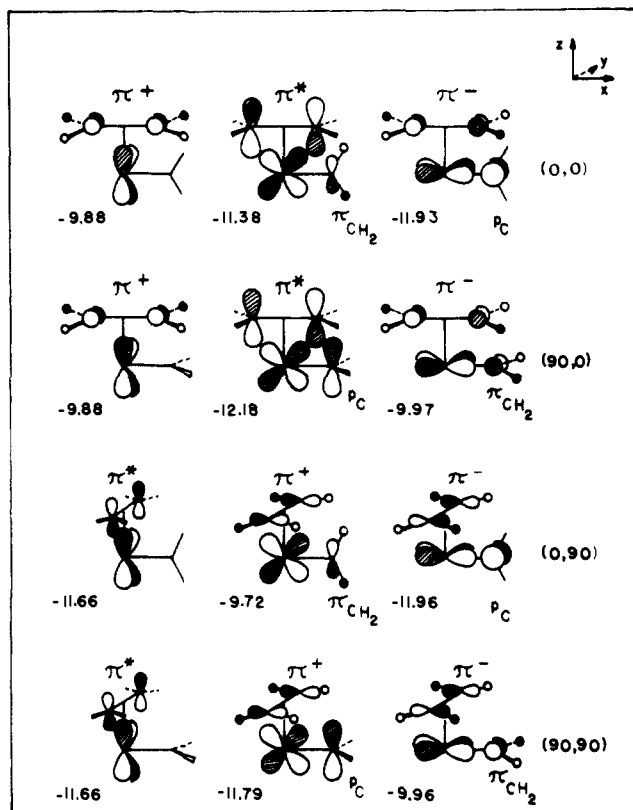In order to finally rank all the conformations, we need now to

Figure 2. Shape of the three low-lying d orbitals of $L_4W(CH_2)(C_2H_4)$ in the four limit conformations. π^+, π^-, and π_{CH_2} are defined in the text (see **15**, **16**, and **17**).

compare (0,90) to (0,0). π^* stabilizes yz in (0,90) and $(xz - \epsilon\pi_{CH_2})$ in (0,0). The energy criteria favor the second one, and the overlap criteria favor the first one. Both effects almost compensate; thus, the mixing with π^* slightly favors the (0,90) conformation. In this case, π^+ has a role to play. In (0,0), π^+ destabilizes yz, and in (0,90), it destabilizes $(xz - \epsilon\pi_{CH_2})$. yz is entirely localized on the metal so that the destabilization is larger in (0,0). Consequently, *(0,90) is more stable than (0,0)*. It should be noted that in addition to these orbital effects, some steric difficulties also disfavor (0,0).

We have now understood why these four conformations are in a decreasing order of stability (90,90), (0,90), (0,0), (90,0). The main result concerns the high energy of (90,0). In this conformation, a single d orbital is stabilized by π^* and p_C, while two d orbitals are stabilized in the other conformations. As it appears from this study, the stabilization of one d orbital by two vacant ligand orbitals is less than the stabilization of two independent d orbitals interacting each one with one empty ligand orbital, a fact that has been demonstrated in the general case[19] and applied in the case of *trans*-bis(ethylene)[15a] and *trans*-bis(carbene)[16c] complexes. This result seems to be also true in the case of cis complexes. It is clear that the stabilization of a d orbital by one empty ligand orbital diminishes considerably an additional stabilization provided by the other empty ligand orbital.

$(CO)_4W(CH_2)(C_2H_4)$. A model system closer to the experimental complexes is $(CO)_4W(CH_2)(C_2H_4)$. Table Ib gives the relative energies of the four representative conformations. Considerable changes have occurred upon replacement of H^- by the CO group. First the differences in energy between the various conformations have dropped drastically. Second and more important, their relative ordering has been modified. The most stable conformation remains (90,90), but the formely very unfavorable (90,0) is now second in the list and only 3.2 kcal/mol above (90,90). Third, whereas with H^- ligands the variation of $\sum d$ parallels that of the total energy, this is not any more the case

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with CO ligands (see Table Ib). According to $\sum d$, the hierarchy of the conformations would have been the same for H^- and CO ligands, and in particular (90,0) would have remain the most unfavorable conformation, although in a less dramatic way. Clearly, stabilization of other orbitals than the occupied d block is favoring (90,0).

The reason $\sum d$ disfavors (90,0) considerably less with CO ligands is simple to understand. The CO π^*'s depress the energies of xy, yz, and xz and thus diminish the amount of back-donation from these orbitals into the ethylene π^* and carbene p_C. For this reason, there are less energetical difference between conformations (0,0), (0,90), or (90,90) in which the back-donation is at its best and (90,0) in which the back-donation is at its worst. To understand why (90,0) has been so much stabilized, one has to take into account orbitals deeper than the d "nonbonding" block. The two orbitals below are characteristic of the bonding between the metal and the ethylene and carbene ligands. In these orbitals, the ethylene uses its π orbital, the carbene its σ_C orbital, and the metal the d orbitals that are pointing toward these ligands. Schematically, the bonding between C_2H_4 and W involves π and z^2, **18**, and the bonding between CH_2 and W involves σ_C and $x^2 - y^2$, **19**. In fact, the lack of symmetry allows full mixing of these two molecular orbitals.
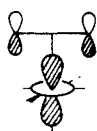
18   19

These metal–ligand orbitals can be stabilized by a vacant orbital centered on the other ligand. Consider **18** and the empty p_C on the carbene. As shown in **20** for (90,0), for example, p_C overlaps solely with the part of **18** that is centered on the ethylene in a through-space manner. This interaction can thus be viewed as

(α,β)	(90,0)	(90,90)	(0,0)	(0,90)
S	0.086	0.024	0	0
	20	21	22	23

a ligand–ligand stabilizing interaction. The overlap S (reported with the structures) between π ethylene and p_C is large because the ethylene orbital points toward p_C. The S overlap is considerably smaller in (90,90), **21**, and null in the two other conformations, **22** and **23**.

Similar considerations apply to **19** which can be stabilized by π^* (S' being the overlap between π^* and σ_C) in (90,0) and in (0,0) but not in (0,90) and (90,90) as it is shown in structures **24–27**.

(α,β)	(90,0)	(90,90)	(0,0)	(0,90)
S'	0.082	0	0.079	0
	24	25	26	27

(90,0) is stabilized by these two ligand–ligand interactions in a greater manner. (90,90) and (0,0) are taking advantage of one of these interactions, while none of them are present in (0,90). A numerical evaluation of these interactions is shown in Table Ib. $\sum \sigma$, which is the sum of the energy of the two orbitals below the d block, gives a good estimate of the energetics of these interactions since they contain the major part of **18** and **19**. While

Table II. Carbon–Carbon Mulliken Overlap Population within the Olefin $(C_1–C_2)$ and between the Olefin and the Carbene $(C_1–C_3)$ in (a) $H_4W(CH_2)(C_2H_4)^{4-}$ and (b) $(CO)_4W(CHOH)(C_2H_4)$

complex	(0,0)	(90,0)	(0,90)	(90,90)
		a		
$C_1–C_2$	0.943	0.967	0.938	0.938
$C_1–C_3$	-0.010	0.154	-0.006	-0.009
		b		
$C_1–C_2$	0.972	0.956	0.967	0.964
$C_1–C_3$	0.007	0.142	-0.005	-0.005

none of $\sum d$ or $\sum \sigma$ can independently account for the variation of the total energy, the sum of these terms reasonably follows the total energy, although they actually even overemphasize the stability of (90,0).

$(CO)_4W(CHOH)(C_2H_4)$. In the experimental complexes, a π donor group (alkoxy or amino group) which is linked to the carbene carbon diminishes the acceptor capability of the carbene group. The results on $\sum d$, $\sum \sigma$, and the total energies of the four conformations are shown in Table Ic. (90,0) becomes now the most stable conformer although (90,90) and (0,90) are very close in energy. In principal, any of these three conformations could be attained experimentally. Other effects than those included in these calculations, such as steric effects or strain energy, may determine the experimental preference.

The analysis for this compound follows very closely that done for the previous complex with CO ligands. The back-donation is even smaller since the oxygen lone pair diminishes the acceptor capability of the carbene p_C orbital. Consequently $\sum \sigma$ takes a determining role although $\sum d$ and $\sum \sigma$ are necessary for the understanding of the conformational preferences.

Back-Donation vs. Ligand–Ligand Stabilization. In summary, essentially two interactions control the stability of metal–carbene–olefin complexes. The first interaction is the well-known back-donation from the metal d into the empty orbitals of the ligands. To take maximum advantage of it, the vacant ligand orbitals should overlap with different d orbitals. The second interaction is a stabilizing ligand–ligand interaction involving the occupied orbital of one ligand and the empty orbital of the other one. For the carbene–olefin complex, it reaches its maximum value when the p orbitals of both ligands are coplanar, that is, when the stabilization by back-donation is minimum. A third type of interaction, an order less in magnitude according to perturbation argument, arises from a four-electron repulsion between occupied orbitals on the metal and the ligands and provides a fine tuning to the stability order determined by the two other interactions.

The important point that remains to be discussed is under which conditions one of these interactions dominates. The precise determination of the frontier is of course beyond the reliability of our method of calculation. Nevertheless, trends can be determined. For that purpose, let us go back to the H^- ligand complex and estimate the strength of the ligand–ligand interaction. $\sum \sigma$ for $H_4W(CH_2)(C_2H_4)^{4-}$ is given in Table Ia. It favors (90,0) by 19.9 kcal/mol but not enough to reverse the order imposed by $\sum d$ which is in favor of (90,90) by about 51.7 kcal/mol. Replacing H^- by CO diminishes $\sum d$ much more than $\sum \sigma$ (compare Table Ia and Ib) so that the effects of back-donation ($\sum d$) and ligand–ligand ($\sum \sigma$) interaction begin to compete. Adding π donor ligands to the carbene diminishes more $\sum d$ than $\sum \sigma$ (see (C-O)$_4$W(CHOH)(C$_2$H$_4$); compare Table Ib and Ic) and increases that tendency. One can thus safely propose the following trend. *If the metal has high-lying d orbitals (no π acceptor ligand and early transition metal of especially the third period), the back-donation determines the preferential conformation. On the contrary, if the metal has deep d orbitals (presence of π acceptor ligand and/or late transition metal of especially the first period), the ligand–ligand interaction determines the most stable conformation.*

A last comment concerns the overlap population between the carbon atoms. The $C_1–C_2$ (within the olefin) and $C_1–C_3$ (between the olefin and the carbene) overlap populations are given in Table

II for two of the model systems we have studied: H_4W-$(CH_2)(C_2H_4)^{4-}$ and $(CO)_4W(CHOH)(C_2H_4)$. The C_1-C_2 overlap population is the largest for (90,0) in the H^--substituted case and the smallest for the same conformation in the CO-substituted case that is fully consistent with our arguments. The less-efficient back-donation in (90,0) (H^- case) results in less occupancy of π^*_{CC} and thus less weakening of the C_1-C_2 bond. On the opposite, in the CO-substituted case, ligand–ligand interaction more than compensates for the lack of back-donation so that the C_1-C_2 bond is more weakened for this conformation. The C_1-C_3 overlap population is large, and a partial bond between the two atoms is formed. (90,0) seems clearly to be the only reactive conformation for either olefin metathesis as noted in a previous work[17b] or cyclopropanation.[20]

$(C_5H_5)Ta(CHCMe_3)(C_2H_4)(PMe_3)$. This d^4 tantalum complex (counting CHR as a neutral ligand for sake of comparison with the other systems) contains a metal that has high-lying d occupied orbitals and ligands, C_5H_5 (Cp) and PMe_3, that are not strong acceptor groups. From the preceding study, back-donation effects from the tantalum into the carbene and the ethylene are expected to be large and thus to determine the preferential conformation. Two experimental facts support this point of view. First, the carbene behaves like a nucleophile and is more an alkylidene than a carbene which indicates a large back-donation from the metal into the carbene p_C. Second, the C–C bond of the ethylene is the longest observed for coordinated olefins that is commonly interpreted as due to a large donation into the π^* orbital of the unsaturated ligand.

Since the ligand field around the tantalum is pseudooctahedral, it is interesting to see if one can deduced the conformation of this complex from the pure octahedral situation. The closest model is the one with H^- ligands (absence of π acceptor groups). Among the four limit conformations studied before, the one that has the lowest energy for two occupied d orbitals is (0,90), which is indeed the conformation of this complex as shown previously in **10**.

To what extent are the pseudooctahedron and the pure octahedron related to each other? The analogy (shape, orientation, and energy splitting, **3** below **2**) between their d orbitals is actually rather significant. The tantalum complex can be viewed as made of a $CpTa(CHCMe_3)(PMe_3)$ moiety and C_2H_4. The fragment molecular orbitals have been already derived,[21] and we will use here the results that are germane to our analysis.

The three low-lying d orbitals of $CpMLL'L''$ viewed down the $M-L''$ bond are shown in **28**. They are directly related to those of ML_6. For our purpose, it is more convenient to redraw them in a perspective identical with the one used for $L_4M(CH_2)(C_2H_4)$ as shown in **29**. The characteristic shape of the nonbonding set
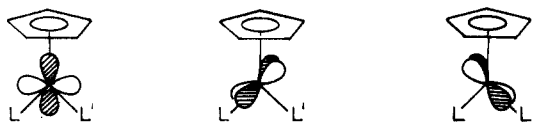

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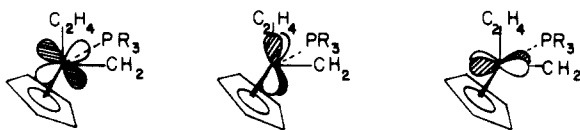
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we have been using previously is thus obvious. Although these orbitals are not degenerate in energy as they are in the real octahedron, their difference in energy is not significant enough

to impair our argument. We can thus repeat the analysis as it was done previously, and this leads us to account for the preferred conformer, (0,90).

This complex has another interesting property which concerns the structural distortion of the $CHCMe_3$ group (Ta–C–H angle equal to 78°). Many such distortions are now known. Groups that undergo this type of distortion have been called agostic by Green and Brookhart.[13] Theoretical analyses of agostic carbene[14a] and alkyl[14b] groups have been done. The essential conditions that should be met for a group to become agostic are the following. In a nonagostic structure, the donating pair of the carbene or alkyl ligand interacts with a σ-type hybrid on the metal, **30**, to make a classical metal–carbon σ bond. An agostic structure is favored if an additional empty d orbital can overlap with the ligand lone pair in the distorted structure, **31**. The lower in energy the d orbital is, the more stable is the agostic structure.
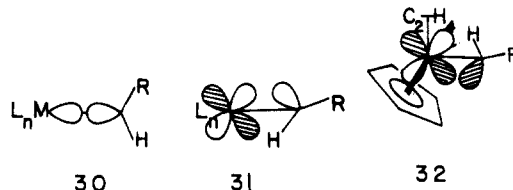
In the (0,90) conformation, the xy and yz orbitals are doubly occupied and stabilized by back-bonding. The xz orbital is empty and is adequately situated to distort the $CHMe_3$ group in the xz plane, **32**. Therefore, the orbital arrangement of this conformer is perfectly adapted to be stabilized by back-donation and to allow agostic interaction.

Trigonal-Bipyramidal Carbene–Olefin Complexes. Such complexes have potentially many more isomers than the octahedral complexes since the apical (a) and equatorial (e) sites are not equivalent in a trigonal bipyramid. A detailed study of the conformational properties of all possible isomers is beyond the scope of this work. We will focus on models of **3**, a d^8 iron complex with a chelating carbene–olefin group in which the carbene occupies the apical site and the olefin the equatorial. Due to the relatively short length of the chain between the carbene and the olefin, an aa isomer is precluded. Molecular models also show the ee isomer to have a lot of strain. An ae isomer is the only remaining choice.

The preferred site occupancy in a trigonal bipyramid has been discussed by Rossi and Hoffmann.[17a] They show that two factors determine the site preference. A strong π acceptor group prefers the equatorial site and a single faced π acceptor ligand is orientated such as to have its π orbital in the equatorial plane. The σ releasing group prefers the apical site. It is clear that competing effects are present and that a detailed understanding of the ligand organization in a trigonal bipyramid requires the knowledge of the σ and π electronic properties of each ligand. We will thus only look at the essential tendencies. Highly stabilized carbenes (as it is the case in **3**) are weak π acceptor groups and show experimentally a preference for the apical site,[22] in agreement with SCF calculations on $(CO)_4Fe(CHOH)$.[16b] As discussed by Dedieu, the formyl group which can formally be considered as a highly stabilized carbene also prefers the apical site.[23] To our knowledge, no nonstabilized carbene of d^8 trigonal-bipyramid complexes has been synthesized but one could imagine that such a carbene would be a better candidate for the equatorial site. In contrast, ethylene always prefers the equatorial site, and its conformation is such as the two carbons lie in the equatorial plane as it is well-known from both experimental and theoretical[15] studies. It is therefore interesting to check whether the presence of the other ligand (carbene or olefin) in **3** modifies the individual preference. As indicated above, we will limit our study to the ae

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Table III. Relative Total Energies (kcal/mol) for Representative Conformations (X, Y) of (a) $FeH_3(NH_2CO^-)(C_2H_4)^{3-}$ and (b) $Fe(CO)_3(NH_2CO^-)(C_2H_4)$. X and Y Refer, Respectively, to the Position of the Carbene and the Olefin

Y		X			
		a_0	a_{90}	e_0	e_{90}
e_0	a	72.0	28.8		
	b	59.6	20.4		
e_{90}	a	1.0	0.0		
	b	0.0	1.4		
a_0	a			71.8	32.9
	b			69.4	24.5
a_{90}	a			34.8	37.0
	b			29.6	25.0

Table IV. Extended Hückel Parameters with Double-ζ Expansion Coefficients (*)

orbital		H_{ij}, eV	ζ_1	ζ_2	$c_1{}^*$	$c_2{}^*$
W	5d	−10.3	4.982	2.06	0.567 53	0.646 73
	6s	−8.26	2.341			
	6p	−5.17	2.309			
Fe	3d	−12.6	5.35	2.00	0.550 5	0.626
	4s	−9.10	1.90			
	4p	−5.32	1.90			
C	2s	−21.4	1.625			
	2p	−11.4	1.625			
N	2s	−26.0	1.95			
	2p	−13.4	1.95			
O	2s	−32.3	2.275			
	2p	−14.8	2.275			
H	1s	−13.6	1.3			

isomers. The notation for describing the position of the ligands is shown in **33**.
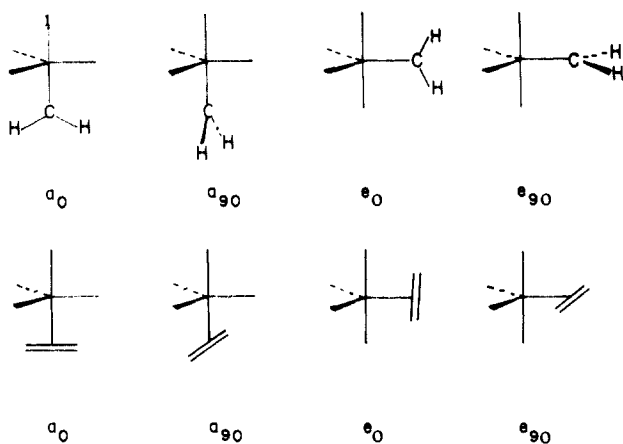
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Table III gives the relative energies of the various (X,Y) (position of the carbene and ethylene, respectively) isomers of $L_3Fe(NH_2CO^-)(C_2H_4)$ (L = H⁻, CO). The two more stable conformers are (a_0,e_{90}) and (a_{90},e_{90}) independently of the nature of L. Therefore, the intrinsic site and orientation preference of each ligand are maintained in this complex.

As in the monosubstituted complexes, the ethylene prefers the e_{90} orientation and the carbene can take either the a_0 or a_{90} orientation (it is indeed known that there is no rotational barrier for a single-face π ligand at the apical site). The situation is thus quite different from that of the octahedron since the ligand–ligand interaction cannot modify the intrinsic preference of each ligand individually. The two conformers in which the two π systems are coplanar, (a_{90},e_0) and (e_{90},a_0), remain high in energy.

Conclusion

The conformational preference for carbene–olefin complexes results from a subtle balance between two factors: back-donation and ligand–ligand interaction. These two factors favor different conformations, the relative importance of each of them depending on the nature of ligands at the metal, of the substituents at the

carbene, and the ligand field at the metal.

In the octahedral complexes, ligand–ligand interaction dominates the situation for a metal that is coordinated to π acceptor ligands and with π donor groups on the carbene. In contrast, for an ae-substituted trigonal bipyramid, the back-donation factor remains dominant whatever the ligand type at the metal and substituent at the carbene.

A complete knowledge of the hierarchy between the different limit isomers requires the analysis of the four-electron repulsion occurring between the occupied d block and the low-lying orbitals of the ligand. In some cases, several conformations can be reached from an electronic point of view. As a matter of fact, structures intermediate between our limit conformations have been experimentally observed. It seems to be the case for an amino-substituted carbene as observed by Casey[9b] (tungsten complex) and very recently by Templeton[24] (manganese complex).

Appendix

The calculations were of the Extended Hückel type, and weighted H_{ij}'s were used.[25] Coulomb integrals and orbital exponents are listed in Table IV. In the tungsten complexes, the following bond lengths were taken: W–H, 1.8 Å; W–C(CO), 2.0 Å; C–O, 1.14 Å; W–C(carbene), 2.1 Å; W–C(ethylene), 2.03 Å; C–C, 1.42 Å; C–H, 1.08 Å; H–C–C, 116°; H–C–C–W, 110°. For the iron complexes, the following bond lengths were taken: Fe–H, 1.65 Å; Fe–C(CO), 1.8 Å; C–O, 1.14 Å; Fe–C(carbene), 1.97 Å; Fe–C(ethylene), 2.05 Å. Other distances within the organic ligands were given standard values.[26]

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