

leading to a smaller band gap.

Acknowledgment. The work at North Carolina State University was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. At Cornell University support derived from the National Science Foundation through MSC Grant DMR-7681083

Appendix

The exponents ζ_{μ} and the valence state ionization potentials $H_{\mu\mu}$ of the Slater-type atomic orbitals χ_{μ} employed in our calculations are summarized in Table I.

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Criteria of Maximum Overlap and Minimum Orbital Energy in Molecular Orbital Studies of Conformations of Transition-Metal Carbene and Carbyne Complexes

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Abstract: We carried out nonparameterized molecular orbital calculations on various conformations of several transition-metal complexes containing carbene or carbyne ligands. In the preferred conformations of $\text{CpMn}(\text{CO})_2\text{CMe}_2$ and $\text{CpMn}(\text{CO})_2\text{C}(\text{OMe})\text{Ph}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), the carbene lies in the symmetry plane of the metal fragment; in the latter compound, the Cp and Ph rings tend to be anti. In the preferred conformation of $\text{BzCr}(\text{CO})_2\text{C}(\text{OMe})\text{Ph}$ ($\text{Bz} = \eta^6\text{-C}_6\text{H}_6$), however, the carbene is perpendicular to the symmetry plane of the metal fragment. The rotation about the metal-carbyne triple bonds in $\text{CpMn}(\text{CO})_2\text{CPh}^+$ and $\text{BzCr}(\text{CO})_2\text{CPh}^+$ is very facile. These theoretical findings agree with crystal structures and NMR spectra of the complexes. We found that conformational preferences of certain organometallic compounds can better be explained and predicted by the criterion of minimum orbital energy than by the criterion of maximum metal-ligand overlap. Stabilizing and destabilizing effects of nonbonding molecular orbitals, as well as those of bonding and antibonding orbitals, need to be considered in the study of conformational preferences. A striking example is $\text{BzCr}(\text{CO})_2\text{C}(\text{OMe})\text{Ph}$. It adopts a conformation with smaller chromium-carbene π overlap because this leaves the more stable of the two π -type metal orbitals as the nonbonding HOMO for the whole complex molecule. $\text{CpMn}(\text{CO})_2\text{CMe}_2$ and $\text{CpMn}(\text{CO})_2\text{C}(\text{OMe})\text{Ph}$ also adopt conformations that minimize total orbital energies. The maximum overlap criterion cannot be applied without ambiguity to molecules in which several bonds are appreciably affected by internal rotation. On the basis of calculations, we expect the heterocarbene complexes to undergo frontier-controlled nucleophilic additions.

From ethane to biological macromolecules, experimental and theoretical chemists have sought to explain and predict relative stabilities of different conformations, to measure and calculate barriers to rotation about chemical bonds, and to understand the physical origin of these barriers.¹ Theoretical studies have been carried out with various nonempirical and semiempirical methods of quantum chemistry and empirical methods based on classical mechanics. The rigor of such studies depends mainly on the size and complexity of the molecules in question and upon the computational requirements of the problem. Not surprisingly, conformational studies of transition-metal complexes began only

several years ago. Since even small organometallic molecules are still too large to allow close approach to the Hartree-Fock limit in ab initio calculations,² less rigorous methods are indispensable for studying chemically interesting and practically important compounds. Roald Hoffmann and his co-workers have systematically examined conformations of various transition-metal compounds with extended Hückel calculations in conjunction with overlap and symmetry arguments.³ They concluded that barriers to rotation of organic ligands about their bonds to metal atoms stem mainly from electronic causes.³ Others have also examined conformations of transition-metal complexes by qualitative theory and by calculations, emphasizing electronic effects.⁴ A single

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Slater determinant cannot adequately represent the electronic structure of a molecule while it is twisted about a multiple bond. Hence, any attempt to describe a potential surface for such twisting would require calculations beyond the Hartree-Fock level. But it is appropriate to represent limiting, closed-shell conformations with single determinants and to compare them, without inferences about the intermediate stages of the intramolecular rotation. This procedure is used widely.^{1,3,4}

Understanding the geometries of unsaturated ligands in low-valent transition-metal complexes, their steric properties, and rearrangements is important for studies of surface chemistry and heterogeneous catalysis.⁵ The accepted mechanism of olefin metathesis involves carbene complexes as homogeneous catalysts; the carbene ligands are exchanged with the alkylidene fragments from the olefins in the propagation steps of metathesis.⁶ These important chemical transformations and many others⁷ probably depend in some respect on conformations of the carbene complexes involved. A good deal is known about mononuclear transition-metal carbene complexes,⁸ but studies of their practical applications have begun only recently. The polynuclear complexes with bridging carbene ligands seem to be intermediates in some organic reactions⁹ and we believe that mononuclear complexes will find such use as well. The recent finding that certain alkylidyne complexes metathesize acetylenes¹⁰ is a step toward that aim.

This is a part of our theoretical study of bonding, geometry, and reactivity of transition-metal complexes containing carbyne,¹¹ carbene,^{12a-c} and other unsaturated ligands.^{12d} We want to contribute to the understanding of conformational preferences of relatively large, *sterically unstrained* organometallic molecules of interest to experimental chemists, to qualitatively account for the origin or absence of rotational barriers in these molecules, and

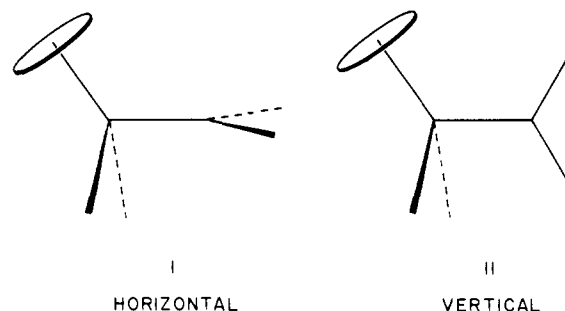


Figure 1. Two important planes of $\text{CpMn}(\text{CO})_2$ and $\text{BzCr}(\text{CO})_2$ and corresponding positions of planar ligands (e.g., carbenes) bonded to them.

to estimate the heights of the barriers.

Details of the Calculations

An approximation to the Hartree-Fock-Roothaan technique, the Fenske-Hall self-consistent-field (SCF) method, has been described elsewhere¹³ and some of its applications have been reviewed.¹⁴ The method is devoid of adjustable or empirical parameters so that results of a calculation (eigenvalues and eigenvectors) are completely determined by the geometry of the molecule and by the basis functions. In the calculations of the Fock matrix elements, the small but discernible effects of the intramolecular interactions upon the energy levels are taken into account implicitly. This feature of the method adds to its usefulness for conformational studies of large molecules with low symmetry.

We partitioned every organometallic molecule into a metal-containing fragment and a carbene or carbyne ligand. Such cleavage at the bond about which intramolecular rotation occurs allows inspection of crucial interactions between the fragments in different conformations. After the SCF part of the calculation converged in the atomic basis set, the molecular orbitals of the complex were transformed into a basis set of the fragment orbitals. This transformation has no effect upon the results of calculations but makes them easier to interpret. The energies of the fragment orbitals in the molecular orbital diagrams are diagonal elements of the Fock matrices from the calculations on complete molecules. These energies differ slightly from one conformation to another because they reflect the influences of the molecular environment upon the moieties "ready for bonding".

We determined relative stabilities of conformations from the differences in summed eigenvalues of all of those occupied molecular orbitals that are affected by internal rotation. Since different rotamers of a molecule contain the same number of bonds among the same atoms, interelectron and internuclear repulsions are about the same in rotamers and changes in total energy can be approximated by changes in summed orbital energies.¹⁵ It is gratifying to note that conformational studies of transition-metal complexes with *ab initio* and semiempirical calculations often yield results that agree well qualitatively and even semiquantitatively with each other. Among many such cases, particularly relevant to this study is the concord between approximately^{3b} (ignoring interelectron repulsion) and rigorously^{4a} calculated rotational barrier in a prototype carbene complex and in some olefin complexes.^{3m,4e} These and other examples justify the use of orbital energies when the total energies are practically not calculable. This method is widely used in the studies of large molecules, when chemical insight is needed more than highly accurate numbers.^{1,3,4}

The basis functions were the same as in our previous study.^{11a} **Structures.** We took geometries of two key molecules directly from the crystal structures of $\text{CpMn}(\text{CO})_2\text{CMe}_2$ ¹⁶ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$)

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and $\text{BzCr}(\text{CO})_2\text{C}(\text{OMe})\text{Ph}^{17}$ ($\text{Bz} = \eta^6\text{-C}_6\text{H}_6$). For the remaining three compounds we used bond distances and angles from these two structures and from several others related to them.^{11a,18} The metal was always at the origin of the coordinate system whose z axis pointed toward the carbon atom in the ligand. The fragments $\text{CpMn}(\text{CO})_2$ and $\text{BzCr}(\text{CO})_2$ have C_s symmetry; the mirror plane (yz) of the fragment is called vertical and the xz plane is called horizontal throughout this paper. They are shown in Figure 1.

Bonding Abilities of the Fragments

In our discussion of the fragments we will emphasize those molecular orbitals that are essential for bonding in the complete molecules. The crucial set of orbitals in a fragment is usually isolated in energy from the lower-lying occupied and the higher-lying vacant levels. Fragment orbitals are customarily designated as σ or π according to their principal bonding abilities with respect to another fragment.

Metal-Containing Fragments. Detailed accounts of the electronic structure of $\text{CpMn}(\text{CO})_2$ can be found elsewhere,^{3c,11a} so only its salient features will be summarized here. The crucial orbitals, largely localized on the Mn atom, are the highest occupied molecular orbital (HOMO) a'' and orbital $2a'$ about 0.3 eV below. Both have π character; a'' lies in the horizontal plane and $2a'$ lies in the vertical plane.

The electronic structure of $\text{BzCr}(\text{CO})_2$ is similar to that of $\text{CpMn}(\text{CO})_2$. The two highest-lying orbitals—the HOMO $2a'$ and orbital a'' —are of π type, mainly localized on the Cr atom, and separated by 0.2 eV. However, in this fragment the HOMO lies in the vertical plane and the more stable orbital lies in the horizontal plane. This difference between the two fragments will be important in the discussion of conformations adopted by their complexes.

The orbital beneath these two π orbitals in both metal fragments is $1a'$, essentially σ in nature. The lowest unoccupied molecular orbital (LUMO) in both fragments, designated $3a'$, is σ accepting.

Ligands. The three crucial orbitals of CMe_2 are designated hy , σ (the HOMO), and p (the LUMO). Orbital hy is a hyperconjugative combination of the p orbitals of the three carbon atoms and has π -bonding ability in the carbene plane; orbital σ corresponds to an sp^2 hybrid of the carbene carbon atom; and orbital designated p is practically pure p orbital of the carbene carbon atom, perpendicular to the ligand plane.

The electronic structures of carbene ligands that contain heteroatoms have been described elsewhere.^{12a} The crucial orbitals of $\text{C}(\text{OMe})\text{Ph}$ are its HOMO, marked σ , which is essentially a lone pair of electrons in the carbon atom, and the LUMO, designated π^* , which is mainly an antibonding combination of carbon and oxygen p orbitals perpendicular to the ligand plane.

Detailed discussions of bonding abilities of carbyne ligands can be found in our earlier papers.¹¹ The most important orbitals of CPh^+ are the following: the HOMO, designated σ , which is a lone pair of the carbyne carbon atom; the LUMO, marked 4π , which is perpendicular to the phenyl ring and partly delocalized over it; and the vacant orbital 5π , only 0.5 eV above the LUMO, which is practically pure p orbital of the carbyne carbon atom and lies in the phenyl plane. Clearly, CPh^+ has different abilities for π bonding in the two perpendicular planes.

Bonding in the Complexes and Their Conformations

From the preceding discussion of the fragments it is clear how the bonds between them are formed. The HOMO, σ , of the ligand donates electron density to the LUMO, $3a'$, of the metal fragment to form a σ bond. The metal–ligand π bonds are formed by back-donation from the a'' or $2a'$ or both orbitals of the metal

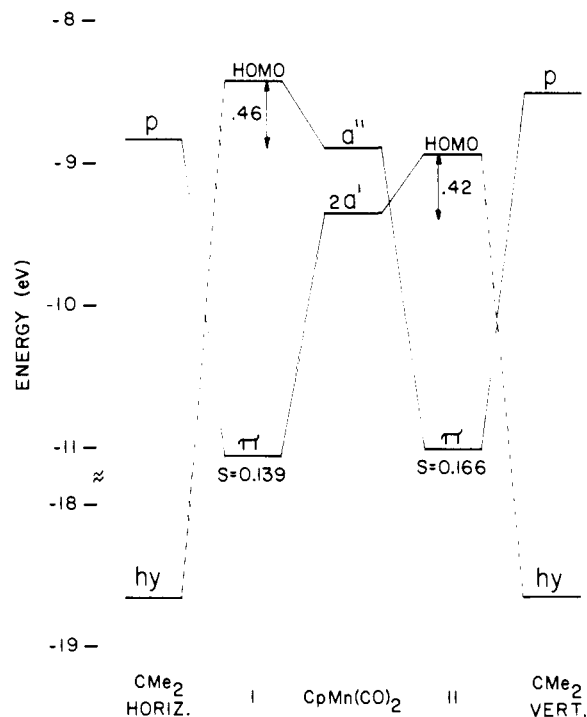


Figure 2. The most important interactions in the two conformations of $\text{CpMn}(\text{CO})_2\text{CMe}_2$.

fragment into the π -accepting orbitals of the ligands—one orbital in the carbenes and two such orbitals in the carbyne. In the discussion of conformations we will emphasize the metal–ligand π interactions; the σ interactions are not sensitive to rotation about the metal–carbon axis.

$\text{CpMn}(\text{CO})_2\text{CMe}_2$. The two limiting positions of the carbene ligand in this molecule are in the horizontal and vertical planes of the metal fragment, as Figure 1 shows. In several complexes containing CpMLL' fragments and π -accepting ligands, these ligands are parallel with the bond between M and the more π accepting of the two different ligands L and L'.^{3d,19} In $\text{CpMn}(\text{CO})_2\text{CMe}_2$ ligands L and L' are the same (CO), but to allow for the unlikely skewed rotamers we also examined the structure in which the carbene ligand makes angles of 45° with the horizontal and vertical planes of the $\text{CpMn}(\text{CO})_2$ fragment.

Our calculations indicate that the vertical orientation of the carbene is more stable than the horizontal one by 9 kcal mol⁻¹; the skewed orientation has intermediate stability. This means that two indistinguishable conformers containing vertical carbene are separated by a twofold rotational barrier of about 9 kcal mol⁻¹; the structure containing horizontal carbene corresponds to a transition state for interconversion between the conformers.

The vertical orientation is preferred over the horizontal one owing to an interplay between a stabilizing 2-electron interaction and a destabilizing 4-electron interaction and the influence of nonbonding molecular orbitals. Involved are the nonequivalent π -donating orbitals a'' and $2a'$ of the metal fragment and two π -type orbitals of the carbene ligand—accepting π and donating hy . The most important interactions in the horizontal and vertical orientations are shown in Figure 2. Orbitals a'' and $2a'$ are orthogonal and so are orbitals p and hy , which makes their interactions easy to visualize. When the carbene is vertical, p is horizontal and interacts with a'' (the overlap integral is 0.166) to form a π -bonding molecular orbital at -11.02 eV; the more stable metal orbital, $2a'$, then remains essentially nonbonding except for some destabilization owing to weak interaction with the low-lying occupied orbital hy . When the carbene is horizontal,

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p is vertical and interacts with $2a'$ (the overlap integral is 0.139) to yield a π -bonding orbital at -11.06 eV; now it is the less stable metal orbital, a'' , that remains practically nonbonding except for some destabilization by orbital hy. The overlaps of p with a'' and $2a'$ are somewhat different, but the greater overlap with the less stable metal orbital (a'') and the smaller overlap with the more stable metal orbital ($2a'$) produce π -bonding molecular orbitals of practically the same stability; although the "stabilization energies" (energy lowerings) of a'' and $2a'$ are different in I and II, the bonding interaction does not seem to cause a difference in stabilities of the two orientations. Destabilization of the filled metal orbital by its 4-electron interaction with the filled carbene orbital is also practically the same in the two orientations, as Figure 2 shows, and does not contribute appreciably to the conformational preference. We conclude that the vertical orientation is more stable than the horizontal because orbital $2a'$ is more stable than a'' . The preferred conformation is the one in which the less stable metal-based orbital participates in the stabilizing π interaction so that the more stable orbital remains as the HOMO of the complex molecule. The unfavorable conformation has the less stable metal-based orbital as its HOMO. Our conclusion agrees with all known structures of $\text{CpMn}(\text{CO})_2$ ^{16,18a,20} and analogous $\text{CpRe}(\text{CO})_2$ ^{21a} complexes containing carbene ligands that are not bulky. Our conclusion that the rotational barrier is low agrees with that drawn from NMR spectra of $\text{CpMn}(\text{CO})_2\text{CMe}_2$ ^{21b} and $\text{CpMn}(\text{CO})_2\text{C}(\eta^1\text{-C}_5\text{H}_5)\text{Me}$ ^{21c}

Schilling, Hoffmann, and Lichtenberger studied conformational preferences in $\text{CpM}(\text{CO})_2\text{CR}_2$ complexes before us.^{3e} They carried out extended Hückel calculations on model compound $\text{CpFe}(\text{CO})_2\text{CH}_2^+$ and reached the same qualitative conclusion as we did—that vertical orientation of the carbene is more stable than horizontal—but explained this preference differently from us. Although they seem to have used an energy criterion to calculate rotational barrier, their explanation of the conformational preference rests mainly upon the maximum overlap criterion²²—the carbene orbital p tends to maximize its overlap with a π -donating orbital of the metal fragment. The difference between the overlap integrals in the two conformations was 0.017. Our calculations also showed somewhat better overlap—by 0.027—in the vertical than in the horizontal orientation of the carbene, but we do not attribute the conformational preference to that. The difference in overlaps is offset by the difference in energies of the metal orbitals so that the Mn–C π molecular orbitals have practically the same stability in the two conformations. Indeed, the manganese-to-carbene back-donation, represented by the population of the orbital p of CMe_2 , is almost the same in the two conformations: 0.91 e when CMe_2 is vertical and 0.85 e when it is horizontal. These rather large numbers indicate that carbene ligands without heteroatoms are strong π acceptors.

The criteria of minimum orbital energy and maximum overlap lead to the same prediction of optimal conformation of $\text{CpMn}(\text{CO})_2\text{CMe}_2$ but attribute this preference to different causes. Next we discuss a compound for which the two criteria predict different optimal conformations.

$\text{BzCr}(\text{CO})_2\text{C}(\text{OMe})\text{Ph}$. The most important interactions in the two conformations of this complex are shown in Figure 3. The energies of the fragment orbitals differ slightly in these conformations because their environments (neighboring atoms) differ. These influences were hardly noticeable in $\text{CpMn}(\text{CO})_2\text{CMe}_2$ because CMe_2 is a symmetric ligand, but they are more pronounced with $\text{C}(\text{OMe})\text{Ph}$ because OMe and Ph substituents are

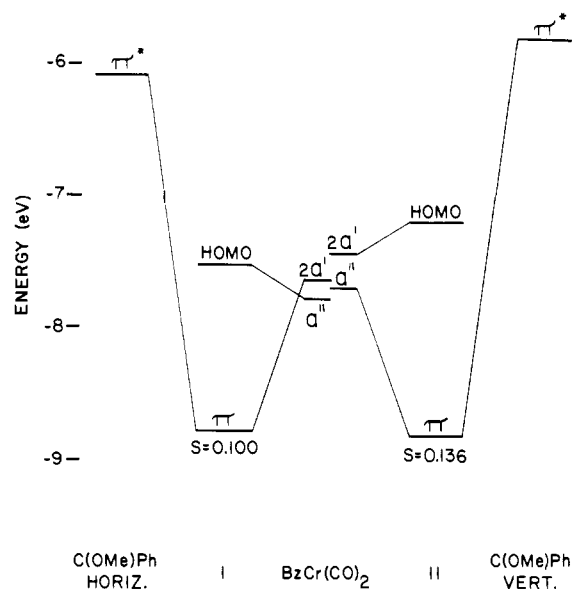


Figure 3. The most important interactions in the two conformations of $\text{BzCr}(\text{CO})_2\text{C}(\text{OMe})\text{Ph}$.

sterically and electronically different. The perturbations of the metal fragment and the ligand are slight and almost the same (about 0.2 eV or less), which indicates that they indeed arise from intramolecular interactions. In such a large molecule without any overall symmetry it is not possible to attribute them to any particular cause. The lower-lying hyperconjugative orbital of the carbene, which corresponds to orbital hy of CMe_2 , is not shown in the molecular orbital diagram because it does not contribute to the difference between the conformations. The a'' - π^* metal–ligand overlap (when the carbene is vertical) is 0.04 larger than the $2a'$ - π^* overlap (when the carbene is horizontal). Nevertheless, the energies of the π -bonding molecular orbitals in the two conformations are practically the same (they differ by 0.04 eV) and so are the "stabilization energies" of $2a'$ and a'' (they differ by 0.01 eV). The crucial difference between the two orientations of the carbene does not seem to be in the bonding interactions but rather in the choice of the HOMO for the complex. Vertical carbene interacts with a'' and leaves the less stable orbital $2a'$ as the HOMO, whereas horizontal carbene interacts with $2a'$ and leaves the more stable orbital a'' as the HOMO. The horizontal conformation is calculated to be more stable by 8 kcal mol⁻¹. Indeed, the carbene ligand in $\text{BzCr}(\text{CO})_2\text{C}(\text{OMe})\text{Ph}$ lies in the horizontal plane of the metal fragment.¹⁷

The optimal structures of molecules in condensed phases or in mixtures may differ from structures of the free molecules. However, medium effects were found to be important mainly in conformational equilibria involving very facile rotations.²³ In general, crystalline fields affect neutral molecules weakly^{24a} and crystal structures are widely used to test and complement theoretical studies of conformations.^{1,3,4}

This carbene complex is not the first compound whose optimal conformation cannot be attributed to maximization of overlap in the dominant bond. Hoffmann pointed out^{3f} that the maximum overlap criterion fails when applied to as simple a molecule as ethane^{24b,c} because *antibonding* effects are important there. Our study shows that the criterion may be inadequate if different conformations contain *nonbonding* orbitals of considerably different energies. Since high-lying nonbonding orbitals are common in organometallic molecules, the criterion of minimum orbital energy is particularly useful in organometallic stereochemistry. Even when one conformationally sensitive π interaction dominates

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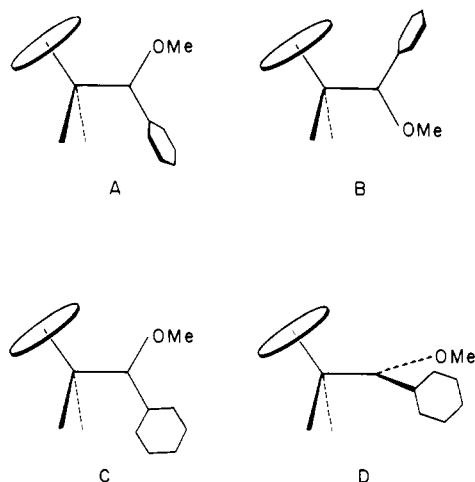


Figure 4. Conformations of $\text{CpMn}(\text{CO})_2\text{C}(\text{OMe})\text{Ph}$.

in the molecule, the overlap criterion may prove inapplicable if the overlap can be maximized only at the expense of leaving occupied molecular orbitals at high energy. We expect this to happen in $\text{BzCr}(\text{CO})_2$ complexes with various π -acid ligands: η^2 -olefin (whose π^* orbital is topologically equivalent to the π -accepting LUMO of a carbene), η^1 - CO_2 , η^1 - SO_2 , η^1 -acyl, and others. This prediction may be tested when the compounds become available.

$\text{CpMn}(\text{CO})_2\text{C}(\text{OMe})\text{Ph}$. We examined bonding in four different conformations of this molecule (shown in Figure 4). In structures A, B, and C the carbene ligand is vertical and in structure D it is horizontal. In A and C the Cp and Ph rings are anti (trans with respect to the metal-carbene bond), whereas in B they are syn (cis) to each other. In C the Ph ring is in the carbene plane, whereas in the other three structures it is perpendicular to that plane. The comparisons among these four conformations permit conclusions regarding preferred orientation of the carbene plane (vertical or horizontal), the phenyl ring (in the carbene plane or perpendicular to it), and the two rings (syn or anti). The approximate energies of these four structures in kcal mol^{-1} (relative to the least stable one, D) are the following: C, -19; A, -17; B, -5; and D, 0. Evidently, in the absence of steric effects the carbene plane prefers to be vertical with the two rings anti to each other (conformations A and C). Our conclusion that little stability is gained as the Ph ring is aligned with the carbene plane (stabilities of A and C differ little) is in accord with crystallographic findings that the $\text{C}_{\text{carbene}}\text{-Ph}$ bond is practically single.^{18a,20a,25a} Molecular models and calculations of interatomic distances showed that putting the Ph ring into the carbene plane in conformation B would cause serious steric crowding of the Ph and Cp rings. This conclusion agrees with the crystal structures of phenylcarbene complexes. In $\text{CpMn}(\text{CO})_2\text{CPh}_2$ the Ph ring that is syn to the Cp ring is perpendicular to the vertical carbene plane.^{20d} Such twist is not possible in the planar anthrone-derived carbene ligand and its complex with $\text{CpMn}(\text{CO})_2$ is not stable.^{25b} The molecule of known structure whose composition and bonding most resemble that of $\text{CpMn}(\text{CO})_2\text{C}(\text{OMe})\text{Ph}$ is $\text{CpMn}(\text{CO})_2\text{C}(\text{COPh})\text{Ph}$.^{18a} This molecule adopts vertical-anti conformation, which turned out to be the most stable one by our calculations. The preference for the vertical orientation of the carbene ligand can be explained as in $\text{CpMn}(\text{CO})_2\text{CMe}_2$, i.e., stabilization of the less stable orbital (the HOMO a'') of the metal fragment so that the more stable one ($2a'$) remains as the HOMO in the molecule. Again, a difference in overlaps (about 0.02) does not seem to cause stabilization of either conformation. The finer details of molecular shape, such as the syn or anti position of the two rings and the position of the Ph ring with respect to the

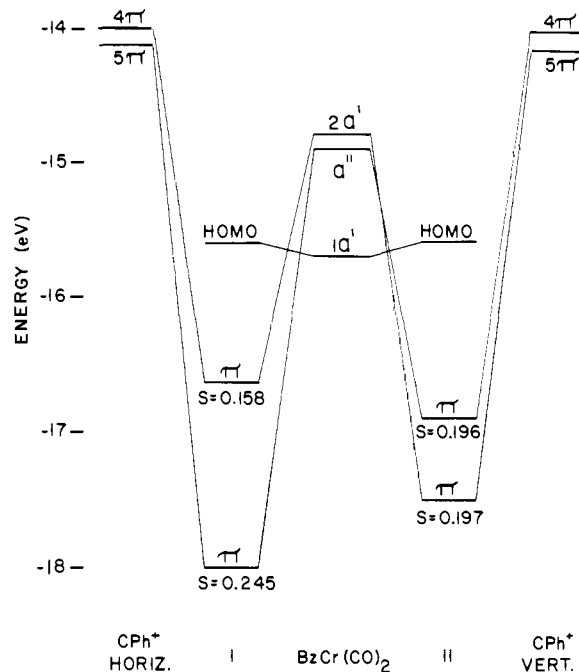


Figure 5. The most important interactions in the two conformations of $\text{BzCr}(\text{CO})_2\text{CPh}^+$.

carbene plane, lent themselves to investigation by the energy arguments; our attempts to analyze them by examining overlaps proved inconclusive.

$\text{CpMn}(\text{CO})_2\text{CPh}^+$ and $\text{BzCr}(\text{CO})_2\text{CPh}^+$. Carbyne complexes contain triple metal-carbon bonds with two π interactions of comparable strengths.¹¹ The conformational preference of such a molecule cannot be analyzed unambiguously by the maximum-overlap criterion because neither interaction dominates the metal-ligand π bonding. We will use the chromium complex in our discussion, but the conclusions apply to the manganese complex as well.

The crucial interactions between the two fragments in the molecule are shown in Figure 5. The π -accepting orbitals of CPh^+ (the LUMO 4π and the next empty orbital 5π) have similar energies but differ in their localization, as mentioned above. The metal fragment perturbs them enough to invert their ordering in the complex molecule in comparison to that in the free carbyne, as is evident in Figure 5. The perturbations of the metal-based orbitals by the ligand are small and could not be shown in the figure. The metal orbital a'' overlaps better than $2a'$ with the given carbyne orbital; the carbyne orbital 5π overlaps better than 4π with the given metal orbital. The horizontal orientation of the carbyne maximizes one overlap and minimizes another; these two overlaps differ substantially (by 0.09) and so do the energies of the corresponding π -bonding orbitals (by 1.4 eV). When the carbyne is vertical, the two overlaps are practically the same and the two π -bonding orbitals are closer in energy (split by 0.6 eV). In both conformations the HOMO of the complex molecule is the unaltered σ orbital $1a'$ of the metal fragment; since it is not affected by rotation about the Cr-C bond, it does not discriminate between the two orientations of the carbyne ligand. In both manganese and chromium complexes the stabilities of the two conformations differ only by 2 kcal mol^{-1} . Examination of these two orientations of the carbyne ligand (that is, of its phenyl ring) indicates that there is virtually no barrier to rotation about the metal-carbon triple bonds (that is, about the carbon-phenyl bonds).²⁶ This process should be facile even at very low temperatures. The ^{13}C NMR spectra of $\text{CpMn}(\text{CO})_2\text{CPh}^{+27}$ and $\text{BzCr}(\text{CO})_2\text{CPh}^{+28}$ at low temperatures are compatible with free

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(26) The notion of free rotation about triple bonds was introduced long ago (see ref 22c, p 1379) but has not been widely assimilated yet.

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rotation on the NMR time scale.

Aminocarbynes, CNR_2^+ , have two very different π -accepting orbitals. The LUMO is essentially pure carbon p orbital in the ligand plane. The next vacant orbital, perpendicular to the ligand plane, is unstable and delocalized and thus less available for bonding with metals.^{11,29} These ligands are somewhat similar to carbenes,^{11b} except they prefer to π bond *in* the ligand plane. Compounds $\text{X}(\text{CO})_4\text{MCNR}_2$ ($\text{M} = \text{Cr}$, $\text{R} = \text{Et}$, $\text{X} = \text{Cl}$, Br , or I ; $\text{M} = \text{W}$, $\text{R} = \text{Me}$, $\text{X} = \text{Cl}$, Br , or I)³⁰ and $(\text{CO})_5\text{CrCNR}_2^+$ ($\text{R} = \text{Me}$ ³¹ or Et ³²) are known but $\text{CpMn}(\text{CO})_2\text{CNR}_2^+$ has not been prepared. Reasoning as we did about $\text{CpMn}(\text{CO})_2\text{CMe}_2$, we expect that the preferred orientation of the aminocarbyne ligand will be horizontal. The barrier to rotation should be smaller than in $\text{CpMn}(\text{CO})_2\text{CMe}_2$ because there will be some back-donation into the less stable π -accepting orbital of the carbyne ligand.

Nucleophilic Additions to Carbene Ligands

All three carbene complexes examined in this study have metal-carbene π -antibonding orbitals as their LUMO's. We expect two of them, $\text{CpMn}(\text{CO})_2\text{C}(\text{OMe})\text{Ph}$ and $\text{BzCr}(\text{CO})_2\text{C}(\text{OMe})\text{Ph}$, to undergo frontier-controlled nucleophilic additions to the carbene carbon atoms. An incoming nucleophile can donate an electron pair from its HOMO to the LUMO of the substrate, thus destroying the metal-carbon π interaction and converting that bond into a single one. Additions of nucleophiles to carbyne,¹¹ carbene,^{12c,d} and vinylidene^{12d} complexes were shown to be frontier controlled. The third complex, $\text{CpMn}(\text{CO})_2\text{C}(\text{CH}_3)_2$, contains hydrogen atoms in the α position with respect to the carbene carbon atom. These atoms may be removed by basic nucleophiles in a reaction that would compete with addition.

Concluding Remarks

We studied conformational preferences of rather complex organometallic molecules containing carbene and carbyne ligands and examined the criteria of maximum overlap and minimum orbital energy for explaining and predicting optimal positions of these ligands. We believe that conclusions from this study have some generality and can be used in theoretical conformational analysis of various kinds of organometallic and inorganic complexes.

Undoubtedly, many molecules adopt conformations in which dominant metal-ligand π overlaps are maximized. Since shapes

of many such molecules are chiefly determined by bonding (stabilizing) interactions, maximization of this overlap may be taken as the cause of the conformational preferences. But antibonding (destabilizing) and nonbonding molecular orbitals are often important in determining the shape of molecules. Even if such a molecule contains one dominant bonding interaction and the corresponding overlap is maximized in the optimal conformation, the causes for the conformational preference should be sought in the interplay of various influences, not only in the bond whose overlap is at the maximum. The effects of bonding and antibonding molecular orbitals upon conformations of organometallic complexes have been studied extensively.^{1,3,4} In this study we point out the role that metal-ligand nonbonding molecular orbitals play in organometallic stereochemistry. The importance of these orbitals is strikingly exemplified by $\text{BzCr}(\text{CO})_2\text{C}(\text{OMe})\text{Ph}$; this molecule sacrifices the overlap in the dominant metal-carbene bond in order to achieve lower orbital energy. We expect several other complexes with organic and inorganic ligands to behave similarly. It seems to us that the maximum overlap criterion cannot be applied without ambiguity to molecules in which several interactions of comparable magnitudes are affected by internal rotation; the examples are carbyne complexes. The lower the symmetry of the molecule, the more difficult it is to carry out unambiguous analyses of overlaps because of extensive mixing of orbitals. We believe that in studying these more complex stereochemical problems the criterion of minimum orbital energy should be used not only quantitatively—to determine the relative stabilities of conformations—but also, with proper analysis, qualitatively—to explain the conformational preferences. This approach is intended to augment, rather than replace, the often useful analysis of orbital overlaps.

Acknowledgment. The authors are grateful to Professor Charles Casey and to Stephen Harsy, both of the University of Wisconsin—Madison, for useful comments. This work was supported by the National Science Foundation, Grant CHE 8024820. N.M.K. has been a Fulbright Fellow since 1978 and is a Procter and Gamble Fellow for 1981–1982.

Note Added in Proof. After this paper was submitted for publication, U. Schubert determined the structure of $\text{CpMn}(\text{CO})_2\text{C}(\text{OEt})\text{Ph}$ and found it to adopt conformation B of Figure 4. The difference between the predicted conformation of the methoxy complex and the observed conformation of the ethoxy complex may well be caused by intramolecular steric interactions rather than by electronic (orbital) interactions. Since steric effects are not treated explicitly in our molecular orbital calculations, we chose to study the uncrowded methoxy complex.

Registry No. $\text{CpMn}(\text{CO})_2\text{CMe}_2$, 59831-13-9; $\text{BzCr}(\text{CO})_2\text{C}(\text{OMe})\text{Ph}$, 32611-32-8; $\text{CpMn}(\text{CO})_2(\text{OMe})\text{Ph}$, 12245-61-3; $\text{CpMn}(\text{CO})_2\text{CPh}^+$, 59831-17-3; $\text{BzCr}(\text{CO})_2\text{CPh}^+$, 59366-13-1.

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