Molecular Orbital Calculations on Carbyne Complexes $CpMn(CO)_2CR^+$ and $(CO)_5CrCNEt_2^+$. Frontier-Controlled Nucleophilic Addition to Metal-Carbon Triple Bond

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Abstract: The electronic structures and bonding capabilities of the carbyne ligands CMe^+, $CSiMe_3^+$, CPh^+, and $CNEt_2^+$ and the metal-containing fragments $CpMn(CO)_2$ and $Cr(CO)_5$ are examined by a nonparametrized MO method. The LUMO and the next lowest unoccupied MO in CPh^+ and $CNEt_2^+$ are differently localized and are not degenerate; energy splitting is small in the former carbyne and big in the latter. Calculations were carried out on four carbyne complexes made from these fragments: $CpMn(CO)_2CMe^+$, $CpMn(CO)_2CSiMe_3^+$, $CpMn(CO)_2CPh^+$, and $(CO)_5CrCNEt_2^+$. Each complex contains a triple metal-carbon bond. Donation from the HOMO of the carbyne ligand into the LUMO of the metal fragment creates a σ bond. Two π bonds are formed by back-donation from the two highest occupied orbitals of the metal fragment into the two lowest empty orbitals of the carbyne. The two lowest unoccupied molecular orbitals in each complex are π antibonding between metal and carbon. In frontier-controlled reactions, various nucleophiles add to the carbyne carbon atom, although it is invariably the most negative ligand site in the carbyne complex. Our findings differ from a recent claim that nucleophilic addition to the cationic carbyne complexes is charge controlled. An experiment is proposed to examine the relative importance of frontier and charge controls in these reactions.

Many transient organic species which are unstable because they do not satisfy some valence requirements (such as the Lewis or Hückel rule) are found as ligands in stable complexes with transition metals. Carbynes (CR) are radicals containing monovalent carbon atoms with five valence electrons. The simplest member of the family, CH, is fairly well characterized spectroscopically.[1] Relatively little is known about the chemical behavior of carbynes,[2] but it seems fair to generalize that those species are extremely reactive, with rates often approaching the frequencies of molecular collisions in gases.[3]

Probably the first complex of a carbyne ligand was $CH_3CCo(CO)_9$. Its serendipitous preparation[4] in 1958 marked the beginning of the chemistry of alkylidynetricobalt nonacarbonyl complexes, which has been developed largely by Seyferth and co-workers.[5] Wilkinson and co-workers prepared dinuclear carbyne-bridged complexes of Nb, Ta, Mo, W, and Re.[6] The first mononuclear carbyne complexes of group 6 metals were reported by E. O. Fischer and co-workers in 1973. Their skillful work has resulted in about seventy articles so far, including several very useful reviews.[7,8] Other contributions to the chemistry of carbyne complexes have come from the laboratories of Angelici,[9] Chatt and Pombeiro,[10] Schrock,[11] Churchill,[12] Stone,[13,14] Rosenblum,[15] Dolgoplosk,[16] Herrmann,[17] Roper,[18] Lappert,[19] Bino,[20] and Vollhardt.[21] Prompted by the work of these experimental chemists, particularly by that of Fischer's group, we undertook a comprehensive study of the electronic structures, bonding, reactivity, and geometries of carbyne complexes by means of nonempirical molecular orbital calculations. Since complexes of general types $CpMn(CO)_2L$ and $(CO)_5CrL$ are among the most widely studied ones in experimental and theoretical organometallic chemistry, we devote our first article to compounds $CpMn(CO)_2CCH_3^+$, $CpMn(CO)_2CC_6H_5^+$, $CpMn(CO)_2CSi(CH_3)_3^+$, and $(CO)_5CrCN(C_2H_5)_2^+$. This work is the first molecular orbital treatment of compounds containing important metal-carbon triple bonds and the first theoretical interpretation of some of their reactions.

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Details of MO Calculations

An approximation to Hartree–Fock–Roothaan LCAO MO technique, the Fenske–Hall SCF method, has been described[22] and some of its applications have been reviewed.[23] The method is devoid of parameters so that the results of calculations (eigenvectors and eigenvalues) are completely determined by the geometry of the molecule as well as by the nature and size of an atomic basis set.

Basis Functions. Clementi's free-atom double-zeta HF functions[24] were used for C, N, O, and Si. Only the valence-shell p functions were kept as double-zeta and all other functions (s in valence shells and all core functions) were curve-fit to single-zeta forms by using the criterion of maximum overlap[25] so that the number of exponents is minimized. The single exponent of 1.45 was chosen for d functions of Si.[26] A value of 1.16 was used for the hydrogen exponent, because it minimizes the energy of methane.[27] Functions from 1s through 3d for Cr and Mn were taken from the tables of Richardson et al.[28] for atoms of 1+ charge. Exponents of 4s and 4p functions were, respectively, 2.0 and 1.6 for chromium and 2.2 and 2.2 for manganese. To see how sensitive the results of our calculations are to the choice of basis functions, we performed several calculations with single-zeta valence p functions for C, O, and N atoms and with an exponent of 1.20 for H. The changes in eigenvalues, eigenvectors, and orbital populations were minimal; in particular, no inversions of MO energies were detected.

Structures. The same C_s geometry of the $CpMn(CO)_2$ fragment was used for all three complexes, so that differences in electronic structures caused by changing carbyne ligands are not obscured by geometry effects. Interatomic distances were taken from the crystal structure of the parent molecule, $CpMn(CO)_3$;[29] one CH group was put into the symmetry plane of the fragment, which is the *yz* plane of our coordinate system. The Cp ring was given an idealized D_{5h} geometry. Actual Cr–CO bond lengths (equatorial 1.90, apical 1.975 Å) and C–O distances (equatorial 1.15, apical 1.155 Å) were used for the $(CO)_5CrCNEt_2^+$ complex;[30] CH_3–CH_2 distances were made 1.54 Å, and N–CH_2 distances were set at 1.47 Å. All OC–M–CO angles in both metal fragments were made 90°. The lengths of the C–C bonds in the ligands CCH_3^+ and $CC_6H_5^+$ were taken from crystal structures of the octahedral carbyne complexes.[31] All Si–C distances in $CSiMe_3^+$ were set at 1.85 Å, which is very close to the average value of 1.86 Å, found in $CpW(CO)_2CSiPh_3$.[32] All C–H distances were fixed at 1.10 Å. Tetrahedral angles were used at alkyl carbon atoms and at Si; bonds to N make 120° angles, and the phenyl ring was given D_{6h} symmetry. The observed value[30] of 175° was used for the bond angle at the carbyne C atom in the Cr compound, but that angle was set at 180° in the Mn complexes. The carbyne CNC_2 plane in the chromium compound bisects the OC–Cr–CO angles; the phenyl ring in the CPh^+ ligand is kept in the symmetry plane (*yz*) of the $CpMn(CO)_2$ moiety.

The length of the Mn–C triple bond was estimated in the following way. The Mn–C double bond in the "nonstabilized" carbene complex $CpMn(CO)_2CMe_2$ is 1.87 Å long,[33] and the shortest Cr–C bond in the "stabilized" carbene (heterocarbene) complex of $Cr(CO)_5$ was taken to be 2.02 Å long.[34] The latter is assumed to be a double bond, and it is 0.32 Å longer than the average length, 1.70 Å, of a Cr–C triple bond.[31a] If the difference between Mn–C double and triple bond lengths is also 0.32 Å, then a Mn–C triple bond should be 1.87 − 0.32 = 1.55 Å long. To see whether our somewhat arbitrary choice of the Mn–C bond length affects the predicted electronic structures, we did calculations on $CpMn(CO)_2CMe^+$ and $CpMn(CO)_2CPh^+$ using Mn–C distances of 1.55 and 1.68 Å. The change in bond length did not affect the ordering of MO's in either compound; differences in the eigenvectors and in the net atomic charges were small and did not alter the description of bonding.

Table I. Energies and Percent Compositions of Frontier Orbitals of CMe^+

		carbyne C			methyl C			H
MO[a]	ε, eV	s	p_π	p_σ	s	p_π	p_σ	s
π	−19.67		89			2		9
σ	−24.74	26		64			8	2

[a] σ is HOMO and π are LUMO's.

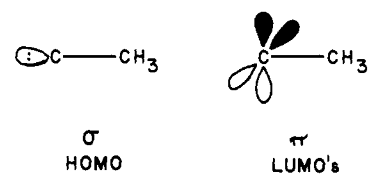

Figure 1. Frontier orbitals of CMe^+.

Clarification of Calculational Results. After the SCF portion of a calculation would converge in the atomic basis set, the MO's were transformed into a basis of fragment orbitals to simplify discussion of bonding. It is especially convenient to partition the complex molecule into just two moieties: the carbyne ligand and the metal-containing fragment.[35] Inspection of interactions between the two moieties would often reveal that many MO's of the complex had practically the same energies and compositions as certain orbitals in the separate fragments, i.e., that these fragment orbitals were not significantly perturbed by bonding. This justified deletion of such orbitals from the variational procedure, which saved computer time and clarified the picture of bonding without really affecting its validity. This so-called frozen-orbital approximation has been discussed in detail elsewhere.[36]

Ligands and Metal Fragments

Prior to this work, there has only been one MO study of a complex of a carbyne ligand.[37] It dealt with $HCCo_3(CO)_9$, in which CH was used as a model for a triply bridging carbyne. In this work, we present a treatment of complexes of four types of carbynes, CR, in which R is alkyl, trialkylsilyl, aryl, and dialkylamine. This choice represents the majority of ligands found in well characterized carbyne complexes. The metal-containing fragments are $CpMn(CO)_2$ and $Cr(CO)_5$. In order to simplify bonding considerations, each complex was partitioned into two closed-shell moieties: a positive carbyne and a neutral metal fragment. It is useful to first consider them separately and then build complex molecules from them.

Carbyne Ligands. The fragment CMe^+ has 10 valence electrons in 5 orbitals, quite similar to the well-known ligand CO. As might be expected from that analogy, it is the frontier orbitals of carbyne which are almost entirely responsible for bonding with the metal. Their characteristics are given in Table I and their shapes in Figure 1. Assuming C_{3v} symmetry, the carbyne's filled σ-donating

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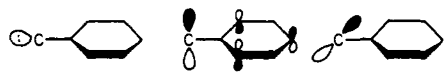
Table II. Energies and Percent Compositions of Important Orbitals of $CSiMe_3^+$

		carbyne C			Si			methyl C		H
MO[a]	ϵ, eV	s	p_π	p_σ	s	p	d	s	p	s
2π	−20.77		75				13	1	10	1
σ	−22.69	9		68		7	3		8	2
1π	−23.89		12			22	4	1	52	9

[a] σ is HOMO and 2π are LUMO's.



σ HOMO 4π LUMO 5π

Figure 2. Crucial orbitals of CPh^+.

HOMO (labeled σ) belongs to a_1 representation, and its two empty degenerate π-accepting LUMO's (labeled π) are of e type. In the language of valence-bond theory, the σ lone pair is an sp hybrid, whereas the π orbitals are "unhybridized" p orbitals of carbyne carbon atom with some hyperconjugative contribution from the three C–H bonds. The σ orbital is 6.5 eV above the next highest filled level, and the next virtual orbital is well above the π set. This isolation in energy, combined with heavy localization on the carbyne carbon atom, makes the frontier orbitals of CMe^+ practically the only ones that make the bond to the metal.

The ligand $CSiMe_3^+$ can be considered as having C_{3v} symmetry (if the Me groups are treated as single atoms), and its frontier orbitals are similar to those of CMe^+ but there are some notable differences. The energy gap between the σ HOMO and the 2π LUMO here is less than 2 eV. Participation of d orbitals of Si causes the frontier MO's to be somewhat less localized on the carbyne carbon than they were in CMe^+. A new feature in $CSiMe_3^+$ is a pair of hyperconjugative molecular orbitals (labeled 1π) immediately below the HOMO, which are primarily composed of the three Si–C σ bonds. The corresponding hyperconjugative MO's in CMe^+ are made of C–H bonds, whose substantial H 1s character stabilizes them so much that they do not effectively interact with the π-type orbitals of the metal fragment. Sizable contributions from the carbon p orbitals and the silicon d orbitals place the 1π orbitals of $CSiMe_3^+$ relatively high in energy and make them potentially useful for bonding to the metal fragment (see Table II).

The carbyne CPh^+ qualitatively differs from the two ligands discussed above in that its low-lying empty π orbitals are not degenerate. The energy splitting between them is only 0.5 eV, but this can, and does, give rise to interesting bonding phenomena. The LUMO, labeled 4π, is perpendicular to the phenyl ring and is stabilized by appreciable delocalization over the ortho and para positions of the ring, just like in benzyl species. The next lowest virtual level, orbital 5π, lies in the plane of the Ph ring; except for some hyperconjugation with C–C and C–H bonds, it is essentially a p orbital of the carbyne carbon atom. The orbitals 1π, 2π, and 3π are related to the three C–C π bonds in a Kekulé formula for the phenyl ring or benzene. The σ-donating HOMO is very much like an sp hybrid on the carbyne carbon atom (see Table III and Figure 2).

The ligand $CNEt_2^+$ has four crucial MO's: 1π, σ(HOMO), 2π(LUMO), and 3π(next lowest virtual orbital). The orbital 1π is 2 eV above the next highest level and the 3π is far below the next virtual orbital, so that the set is energetically quite isolated. An important feature of this ligand is the delocalization of a filled p orbital of nitrogen (its "lone pair") by interaction with a p orbital of the carbyne carbon atom, as shown in Figure 3. The orbital 1π corresponds to a C–N π bond perpendicular to the ligand plane. About 50% of the 1π comes from an in-phase p_C–p_N combination and the other 50% is contributed by the hyperconjugative system of the two ethyl groups, which contain methylene carbons in the nitrogen trigonal plane while the methyl carbons are out of that plane. As in the other ligands, the HOMO is essentially a "lone pair" on the carbyne carbon atom, akin to an sp hybrid. The

Table III. Energies and Percent Compositions[a] of Important Orbitals of CPh^+

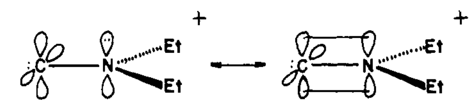
		carbyne C			α-C	o-C	m-C	p-C
MO[b]	ϵ, eV	s	p_π	p_σ	p	p	p	p
5π	−16.01		91		1	5	1	
4π	−16.50		56		1	27		16
σ	−21.37	23		63	7	3	2	
3π	−21.67					51	49	
2π	−23.16		18		16		33	33
1π	−26.42		10		33	34	17	6

[a] Contributions from s orbitals of ring carbons and hydrogens are small and are deleted. [b] σ is HOMO, 4π is LUMO.

Table IV. Energies and Percent Compositions of Important Orbitals of $CNEt_2^+$

		carbyne C			N			Et groups	
MO[a]	ϵ, eV	s	p_π	p_σ	s	p_π	p_σ	s	p
3π	−9.56		57			37		2	4
2π	−15.65		89			1		1	8
σ	−22.93	36		54			4	2	3
1π	−23.60		31			20		10	39

[a] σ is HOMO, 2π is LUMO.



I II

Figure 3. Resonance representation of interaction between p orbitals of C and N in $CNEt_2^+$. When the orbitals combine in phase, II corresponds to partial C–N π bond, i.e., MO 2π; when the combination is out of phase, II corresponds to the π-antibonding MO 3π.

LUMO is an almost pure in-plane p orbital of the carbyne carbon atom. The orbital 3π is destabilized by about 6 eV relative to the LUMO due to out-of-phase mixing of the nitrogen's orbital into the carbyne carbon's p orbital; in fact, the 3π can be viewed as a C–N π antibond, the counterpart of the π-bonding orbital 1π (see Table IV).

Nonequivalence of the two empty levels in the carbynes CPh^+ and $CNEt_2^+$ makes them unique among the π-accepting ligands in their ability to form two nonequivalent π bonds even with metal fragments whose symmetries are high enough to permit equivalent (i.e., doubly degenerate) π-donating orbitals on the metal. Some bonding consequences of those effects will be briefly mentioned later in this account. A more complete treatment of the stereochemical and bonding phenomena caused by nonequivalence of the two metal–carbon π interactions in a number of carbyne complexes will be presented elsewhere.[38]

Metal Fragments. All calculations on the metal fragments and carbyne complexes were carried out using right-hand Cartesian coordinate system, with the z axis pointing toward the vacant coordination site or toward the carbyne carbon. This facilitates examination of the metal–carbon bonding, which is the most interesting interaction in the carbyne complexes. This choice of coordinates puts the two CO ligands of the $CpMn(CO)_2$ fragment and its complexes into the xy plane. It places Cr at the origin and all the Cr–C bonds along the Cartesian axes.

$CpMn(CO)_2$ Fragment. The electronic structure and bonding capabilities of $CpM(CO)_2$ fragments with C_s symmetry have been analyzed by Schilling, Hoffmann, and Lichtenberger.[39] The overall bonding picture which emerged from the present calculations on $CpMn(CO)_2$ agrees well with their qualitative conclusions, which makes it unnecessary to duplicate the symmetry arguments and discuss the relationship between $CpMn(CO)_2$ and its parent, $CpMn(CO)_3$.[39,40] The four high-lying molecular

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Table V. Energies and Percent Compositions of Crucial Orbitals of $CpMn(CO)_2$ Fragment

		Mn							Cp	$(CO)_2$ 2π		
MO[a]	ϵ, eV	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}	s	p	e_1''	a_1	a_2	b_1
3a′	−4.83	53	2				9	6	12	2		12
a″	−7.29			4	67			3	7		12	
2a′	−8.29	2	3			71	1	1		2		18
1a′	−8.95	10	54			2		1		25		

[a] a″ is HOMO, 3a′ is LUMO.

Table VI. Energies and Percent Compositions of Important Orbitals of $Cr(CO)_5$ Fragment

		Cr						$(CO)_4$		CO	
MO[a]	ϵ, eV	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	$d_{xz,yz}$	s	p	5σ	2π	5σ	2π
3σ	−5.45	35				6	22		37		
2π	−7.68				62				25		12
2δ	−8.41			54					45		
2σ	−16.34	19					10	10		55	
1δ	−16.38		38					56			
1π	−16.85						22	74			
1σ	−18.83					9		67		11	

[a] 2π are HOMO's, 3σ is LUMO.

orbitals of the fragment (the three highest filled MO's and the LUMO) are crucial for the formation of the Mn-carbyne bond and will be described more quantitatively. Adopting the symmetry labels from the previous study,[39] these four molecular orbitals are 1a′, 2a′, a″, and 3a′ in the order of increasing orbital energies. Both orbitals 1a′ and 2a′ from the extended Hückel calculations were capable of σ and π interactions along the z axis and therefore had to be rehybridized to obtain new orbitals a'_σ and a'_π, which respectively had σ and π character.[39]

Bonding within $CpMn(CO)_2$ is clarified by partitioning this fragment into moieties: Mn^+, Cp^-, and $(CO)_2$, whose orbitals constitute a transformed basis set. Besides the orbitals of the metal, the crucial ones are e''_1 HOMO's of the Cp^- ring and those 2π orbitals of $(CO)_2$ that belong to the a_1, b_1, and a_2 representations of C_{2v} point group. By using $(CO)_2$ rather than two CO groups, ligand–ligand interactions are taken into account (see Table V). This calculation immediately produced orbitals equivalent to a'_σ and a'_π of Schilling et al., but we still call them 1a′ and 2a′, respectively. Our orbital 1a′ represents π interaction in the *xy* plane between $d_{x^2-y^2}$ orbital of Mn and a_1 representation of 2π orbitals of $(CO)_2$. A small contribution from d_{z^2} is equivalent to partial hybridization of d_{z^2} and $d_{x^2-y^2}$ into a $d_{z^2-y^2}$ orbital, which gives the 1a′ some ability for σ bonding along the z axis. A very small addition of d_{yz} is not sufficient to tilt the 1a′ orbital in the *yz* plane and give it any significant π character. The orbital 2a′ is largely d_{yz} and therefore can π donate to the carbyne ligand in the *yz* plane. Some contribution from a b_1 representation of the 2π orbitals of $(CO)_2$, which is perpendicular to the *xy* plane, shows that orbital 2a′ is essentially a Mn–CO π-bonding one. The HOMO is the only one of those four orbitals which is antisymmetric with respect to the *yz* plane and thus has a″ symmetry. It is mainly a d_{xz} orbital, with contributions from the e_1'' of Cp^- and from an out-of-plane a_2 representation of 2π orbitals of the $(CO)_2$ group. The HOMO can π donate to the carbyne ligand in the *xz* plane. The LUMO, labeled 3a′, is essentially a σ-accepting orbital. About a half of it comes from the d_{z^2} and the rest from the e_1'' of the Cp^- and the b_1 orbital of $(CO)_2$. The latter two small contributions give the 3a′ orbital some π-accepting ability in the *yz* plane, which explains why the 3a′ participates a little in the Mn–carbyne π interactions. This set of four important fragment orbitals is separated from the next lowest virtual MO by more than 5 eV.

Two more orbitals of $CpMn(CO)_2$ contribute to bonding in the carbyne complexes. In the fragment, they lie below the 1a′ and are energetically quite separated from that level. Both orbitals are made primarily from the e_1'' HOMO's of the Cp^- ring and are therefore labeled Cp. The one at −12.58 eV has a″ symmetry,

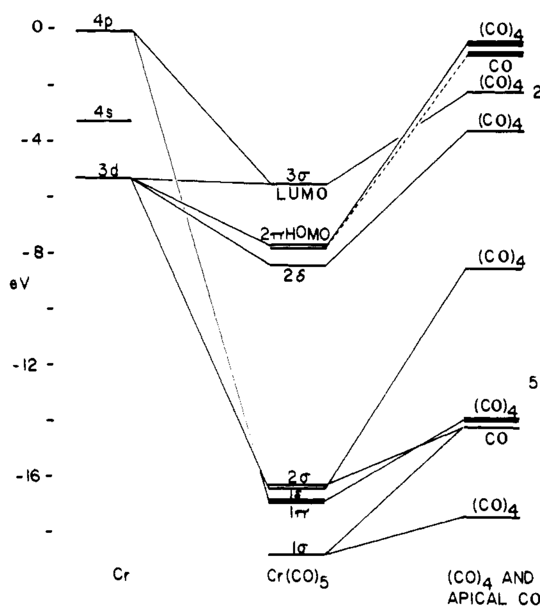

Figure 4. MO diagram of $Cr(CO)_5$. High-lying 2π levels of CO's are omitted. Dashed lines represent small contributions from the orbitals of the moieties to the MO's of the complete species.

whereas the one at −12.79 eV has a′ symmetry. They can mix with the HOMO and the 2a′ of the $CpMn(CO)_2$ fragment, respectively, but orbitals Cp are far less important for the Mn–carbyne bonding than the four fragment MO's which were examined in detail and included in Table V.

$Cr(CO)_5$ Fragment. Bonding capabilities of this species were examined by Elian and Hoffmann,[41] with emphasis on the high-lying orbitals, derived from the $t_{2g} + e_g$ pattern of $Cr(CO)_6$ by removal of one CO ligand. This set of orbitals includes a σ-type LUMO of a_1 symmetry, a π-type doublet (HOMO's) of e symmetry, and a δ-type orbital of b_2 symmetry. The orbitals are classified as σ, π, or δ according to their bonding abilities toward the missing sixth ligand and not by their nature with respect to the $Cr(CO)_5$ fragment itself.

To simplify the discussion of the electronic structure of $Cr(CO)_5$ with C_{4v} symmetry, we partitioned this species into a Cr atom, a D_{4h} equatorial set $(CO)_4$, and an apical CO ligand. The levels a_1, e, and b_2 of Elian and Hoffmann correspond to our levels 3σ, 2π, and 2δ, respectively. (Label 2π here designates two filled MO's of $Cr(CO)_5$; elsewhere in this article it designates virtual orbitals

(40) Lichtenberger, D. L.; Fenske, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 50.

(41) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

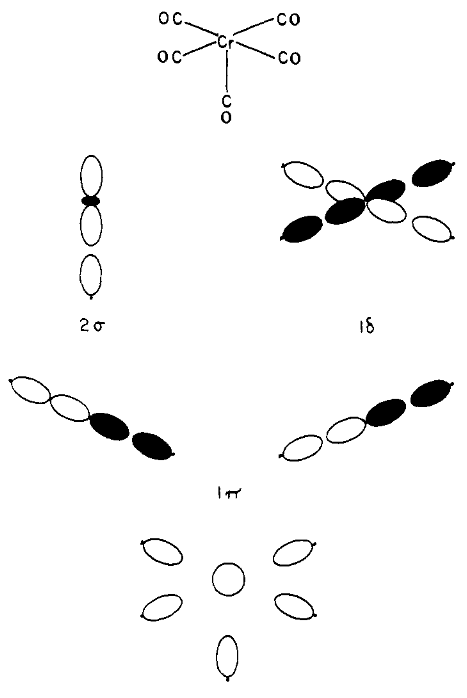

Figure 5. Orbitals of $Cr(CO)_5$ constructed from the Cr–CO σ bonds.

of CO, $CSiMe_3^+$, and $CNEt_2^+$, as well as a filled MO of CPh^+ It will be clear from the context what 2π stands for; see Table VI and Figure 4.) The MO's 2π andd 2δ of $Cr(CO)_5$ physically represent π interactions between Cr and the CO ligands. For a more complete discussion of the carbyne complex, it is necessary to also consider a lower-lying group of orbitals which are mainly composed of 5σ "lone pairs" of the CO ligands, interacting with the metal d and p orbitals of appropriate symmetry. These fragment orbitals can be thought of as the five Cr–CO σ bonds, but again they are labeled according to their symmetries relative to the missing sixth ligand: 1σ, 1π, 1δ, and 2σ (see Figure 5). The two sets of fragment orbitals are energetically isolated from each other.

Bonding in the Complexes

All the energies of the fragment orbitals are diagonal Fock matrix elements from the calculations on carbyne complexes, and they often greatly differ from the eigenvalues of those orbitals in the free fragments, listed in Tables I through VI. Results of a calculation, including the Fock matrix elements, on the whole carbyne complex do not depend on the way the molecule is fragmentized. It is convenient to choose the fragments to be closed-shell species, which makes the carbyne ligands positive and the metal fragments neutral, but those charges are arbitrary and stabilization of the MO's in the free carbynes due to the positive charge is not significant in the discussion of the complexes. There is another reason why molecular orbitals have different energies in the free fragments and in those same fragments when they are in molecular environments. In the calculation of a diagonal element of the Fock matrix, and consequently in determining the MO energy, our method takes into account the effects of the charges on all neighboring atoms.[22] The resulting perturbations of the orbitals in the metal fragments are usually small, but they can get so large in the carbyne ligands that the very ordering of the orbitals of the ligands "ready for bonding" is altered from that in the free ligand. This "scrambling" of energy levels is very evident in the MO diagram in Figure 8, as will be discussed later.

From the previous discussion of the electronic structures of the fragments it is clear how the triple metal–carbon bonds are formed. In each instance the σ-type HOMO of the carbyne donates electron density to the LUMO of the metal fragment, while the two empty π-type orbitals of the carbyne ligand, the LUMO and the next virtual orbital, accept electron density from the two

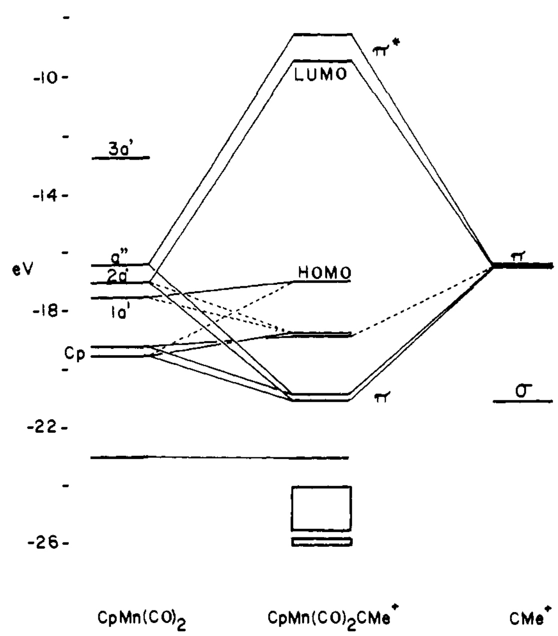

Figure 6. MO diagram of $CpMn(CO)_2CMe^+$ in which Mn–carbyne σ interaction is not explicitly shown. MO's between −24.0 and −25.5 eV primarily belong to $CpMn(CO)_2$; those between −25.8 and −26.0 eV primarily belong to CMe^+.

Table VII. Energies and Percent Compositions of Important MO's of $CpMn(CO)_2CMe^+$

	$CpMn(CO)_2$				CMe^+
ϵ, eV	a''	2a'	1a'	Cp	π
−8.47	42				45
−9.35(LUMO)		37		4	47
−16.87(HOMO)			77	11	
−18.73		22	17	51	5
−18.79	11			77	11
−20.81	40			22	33
−20.97		33		27	35
−22.97				94	

highest occupied π orbitals of the metal fragment. The σ-bonding molecular orbital is so stable that it is omitted from some MO diagrams. More interesting are the two or more π-bonding MO's, the high-lying essentially nonbonding orbitals, and the low-lying virtual orbitals. It is these interactions and the resulting MO's that will be treated in some quantitative detail.

$CpMn(CO)_2CMe^+$. A molecular orbital diagram for this complex is given in Figure 6. The carbyne π orbitals are practically degenerate, although, strictly speaking, they are in nonequivalent molecular environments. The HOMO and the next two highest filled MO's in the complex are strongly localized within the metal fragment and have small contributions from the π orbitals of the carbyne. The metal–carbyne π-bonding interactions are represented by the two close levels at about −21 eV. Their antibonding counterparts are the LUMO and the next lowest virtual orbital. In Table VII, the MO's can be identified by their energies. Our calculations fully confirm the conclusions of Fischer and co-workers about the existence of triple metal–carbon bonds in carbyne complexes. The overlap population between the 3a′ and the carbyne σ is 0.552, between the a″ and one of the two carbyne π orbitals it is 0.410, and between the 2a′ and another π orbital of the carbyne it is 0.340. These relatively large positive numbers suggest that all three interactions are quite strongly bonding but that the two π bonds are not equivalent (see also Table XI).

$CpMn(CO)_2CSiMe_3^+$. The three uppermost filled MO's are quite similar to the corresponding orbitals in $CpMn(CO)_2CMe^+$, as can be seen by comparing Tables VII and VIII and Figures 6 and 7. The next two closely spaced orbitals are the hyperconjugative 1π orbitals of the $CSiMe_3^+$ ligand, which do not have

Table VIII. Energies and Percent Compositions of Important MO's of $CpMn(CO)_2CSiMe_3^+$

	CpMn(CO)$_2$				CSiMe$_3^+$	
ε, eV	a''	2a'	1a'	Cp	2π	1π
−10.94	46				45	3
−11.65(LUMO)		41			48	3
−17.30(HOMO)			72	15		
−19.13				71	16	2
−19.23		17	20	50	7	1
−19.97					14	74
−20.03				11	13	74
−21.83	36			15	23	19
−21.87		32		14	24	19

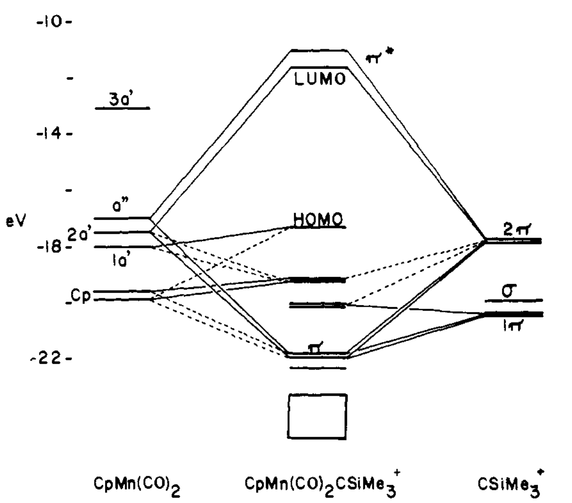

Figure 7. MO diagram of $CpMn(CO)_2CSiMe_3^+$ from which Mn–carbyne σ interaction is omitted.

counterparts in the CMe^+. Interestingly, the π-bonding MO's at about −21.8 eV contain comparable contributions from the hyperconjugative 1π and the p,d-type 2π orbitals of $CSiMe_3^+$ ligand. The empty π-antibonding MO's have minimal contributions from the 1π's. Again, overlap populations testify about the existence of a Mn–C triple bond: 0.425 for the σ interaction between the 3a' and the carbyne σ, and values 0.363 and 0.308 for the π interactions of the carbyne 2π with a'' and 2a', respectively. Interactions of the 1π orbitals with the a'' and 2a' are nonbonding, as evident from their near-zero ovelap populations.

$CpMn(CO)_2CPh^+$. In the calculation on this molecule, all orbitals of CPh^+ except the crucial ones (1π, 2π, 3π, σ, 4π, and 5π) were "frozen" in the form, i.e., with percent compositions of atomic orbitals, that they have in the free ligand. This did not significantly alter the eigenvalues and the eigenvectors of the complex and simplified the MO diagram and its interpretation (Figure 8). As mentioned before, the energy levels (diagonal elements of the Fock matrix) of the six important CPh^+ orbitals are scrambled compared to their ordering in the free ligand, given in Table III. Orbitals 2π and 4π are perpendicular to the ligand plane, and they interact with the a'' to produce two π-type M–C orbitals at −17.39 and −20.85 eV. The former MO has a larger contribution from the frontier 4π than from the ring 2π, whereas the latter is much more 2π than 4π in character (see Table IX). This suggests that of those two MO's the one at −17.39 eV is truly bonding between the Mn and the carbyne carbon atom. The overlap populations of a'' with the 4π and the 2π are, respectively, 0.337 and 0.011, which supports the conclusion derived from the extent of their mixing. The second Mn–carbyne π interaction, represented by the MO at −20.45 eV, occurs between the 2a' and the 5π and has an overlap population of 0.344. Unlike the two previous molecules, $CpMn(CO)_2CPh^+$ has an energy gap of more than 3 eV between the two Mn–carbyne π-bonding MO's, but the π-antibonding orbitals are still very close in energy. The σ-bonding interaction between orbitals 3a' and σ gives rise to an MO at −25.92 eV.

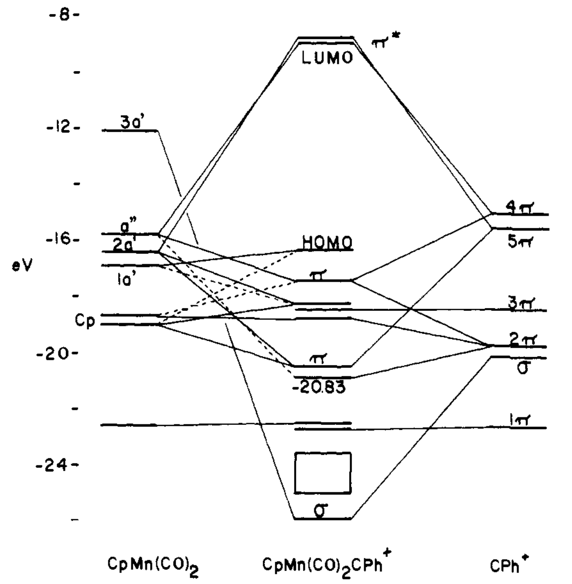

Figure 8. MO diagram of $CpMn(CO)_2CPh^+$ with Ph ring in the *yz* plane. MO's between −23.5 and −25.0 eV primarily belong to $CpMn(CO)_2$.

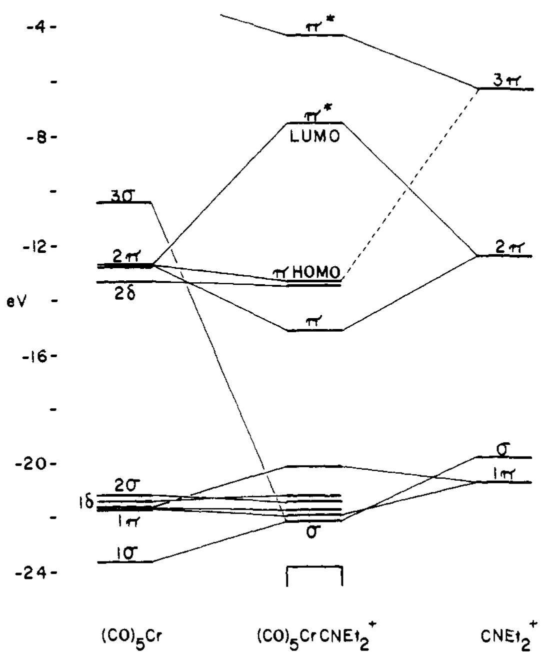

Figure 9. MO diagram of $(CO)_5CrCNEt_2^+$.

Table IX. Energies and Percent Compositions of Important MO's of $CpMn(CO)_2CPh^+$

	CpMn(CO)$_2$					CPh$^+$				
ε, eV	3a'	a''	2a'	1a'	Cp	2π	3π	σ	4π	5π
−8.68			36							48
−8.88(LUMO)		45							47	
−16.33(HOMO)	6			79	10					
−17.39		25			11	26			35	
−18.20			24	15	51					6
−18.39							100			
−18.72					80	18				
−20.45			34		28					33
−20.85		22			7	52			10	
−25.92	20				14			45		

$(CO)_5CrCNEt_2^+$. Figure 9 reveals why, in the treatment of separate fragments, we considered some lower-lying orbitals, namely, the hyperconjugative 1π of the carbyne and the Cr–CO σ-bonding orbitals 1σ and 1π. The less stable carbyne orbitals

Table X. Energies and Percent Compositions of Important MO's of $(CO)_5CrCNEt_2^+$

	Cr(CO)$_5$							CNEt$_2^+$			
ϵ, eV	3σ	2π	2δ	2σ	1δ	1π	1σ	3π	2π	σ	1π
−7.51(LUMO)		38							53		
−13.27(HOMO)		81						15			3
−13.36			100								
−15.09		60							37		
−20.13						22					71
−21.20					100						
−21.36				99							
−21.69						95			4		
−21.93						76					21
−22.13	20						31			38	

2π and 3π interact with the 2π doublet of the metal, whereas the more stable 1π orbital of the carbyne has an energetically close partner in the 1π level of $Cr(CO)_5$. Since the carbyne plane bisects the OC–Cr–CO angles, there occurs mixing of the two degenerate orbitals within each of the two e-symmetry levels 1π and 2π of $Cr(CO)_5$ and also mixing of the two atomic p_π orbitals on the ligand atoms in the 1π, 2π, and 3π orbitals of the $CNEt_2^+$ (see Table X). The HOMO of the complex is almost pure one of the two 2π orbitals of $Cr(CO)_5$, because its partner by symmetry, the 3π of the carbyne, is delocalized over nitrogen and hence less available for bonding with the metal fragment. A consequence of this is relatively low total overlap population between the 2π orbitals of $Cr(CO)_5$ and the 3π orbital of carbyne—only 0.178. The MO at −15.09 eV represents a true π-bonding interaction between the fragments; it has a total 2π–2π overlap population of 0.299, because the ligand 2π orbital is heavily localized on the carbyne carbon. The MO's at −20.13 and −21.93 eV signify 1π–1π π interaction but they are essentially nonbonding, as evident from the corresponding overlap populations, which are very close to zero. The orbitals 1δ and 2δ of $Cr(CO)_5$ have no partners of appropriate symmetry on the carbyne and therefore remain strictly nonbonding. The orbital 2σ, which binds Cr to the apical CO ligand in $Cr(CO)_5$, is not affected by coordination of the carbyne ligand trans to it and remains nonbonding as well. The metal–carbon σ bond can be identified with an MO at −22.13 eV. As in all other carbyne complexes, the LUMO is π antibonding between the two fragments.

Back-Donation. Partial multiple characters of metal–ligand bonds have been studied a great deal, both experimentally and theoretically, over the past 20 years. In particular, detailed examination of the π bonding between CO and metals in a myriad of complexes of various types has led to the conclusion that the CO ligand is one of the best π acceptors. Since carbynes form triple bonds with metals, as the present calculations confirm, one would expect these ligands to withdraw electrons even stronger than CO does. Table XI shows this expectation to be true. For example, the CMe^+ ligand withdraws a total of 1.859 electrons. For comparison with the CO we have to consider neutral CMe, which would withdraw 0.859 electrons. This value is much larger than the value (0.631 e) for a CO in the metal fragment even *before* a strongly π-accepting carbyne is attached to it. It is probably safe to state that *carbynes are among the best π-acid ligands*. As Table XI shows, the two orthogonal π-accepting orbitals in every coordinated carbyne ligand have unequal electron occupations; these orbitals also have different overlap populations with the orbitals of the metal fragment and their numerical values are given above. Clearly, the two metal–carbon π bonds in the carbyne complexes studied are not equivalent.

Atomic Charges. Our MO method calculates atomic charges by Mulliken population analysis.[22,42] The values for the important atoms in the molecules of the complexes are given in Table XII. Since the Cr–C–N angle in $(CO)_5CrCNEt_2^+$ slightly deviates from 180°, the charges of the four equatorial C and O atoms differ insignificantly in the third decimal place; the values given for

(42) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

Table XI. Populations of π-Accepting Ligand Orbitals

	orbital population	
molecule	cationic carbyne^a	CO $2\pi^{b,c}$
$CpMn(CO)_2$		0.631
$CpMn(CO)_2CMe^+$	π_{xz} 0.975	
	π_{yz} 0.884	
$CpMn(CO)_2CSiMe_3^+$	π_{xz} 1.086	
	π_{yz} 0.994	
$CpMn(CO)_2CPh^+$	4π 0.956	
	5π 0.858	
$Cr(CO)_5$		eq 0.491
		ax 0.527
$(CO)_5CrCNEt_2^+$	2π 0.833	
	3π 0.346	

^{a} Separate populations of the two orbitals. ^{b} Combined populations of the two 2π orbitals per CO ligand. ^{c} Partitioning of the molecules of the complexes into just two fragments prevents us from reporting the populations of the CO 2π orbitals in the carbyne complexes.

cis-CO ligand are the averages. Charges of atoms in the Cp and organic groups within the carbyne ligands never differ from zero by more than 0.1 electron.

Before discussing these numbers, we want to repeat the words of Schaefer: "Any scheme (such as a population analysis) for assigning charges to atoms in a molecule is arbitrary. However, comparison of population analyses for a series of molecules does allow one to make qualitative conclusions concerning changes in electron distribution."[43] Indeed, limitations of Mulliken method have been recognized,[42,44] and cases have been found where it failed.[45] An earlier study[46] of TiF_6^{3-} showed that diffuse 4s and 4p orbitals of the metal strongly overlap with filled 2p orbitals of the F^- ligands so that when the Mulliken method assigns half of the overlap populations from those interactions to the metal, an unrealistically large amount of electron density is transferred from the ligands to the metal.

Let us examine Table XII with this in mind. The numbers themselves are certainly not true in the absolute sense, but they reveal an interesting pattern: of all the ligand atoms, the carbyne carbon is invariably the most negative. It is also much more negative than Mn in three complexes. In particular, it is significantly more negative, by 0.26 to 0.69 e, than any carbonyl carbon in all the compounds. Much of the discussion of reactivity in the next section depends on this result, and hence we decided to make sure it is not purely an artifact of our calculations. We corrected for the effect of inevitable diffuseness of the 4s and 4p functions on Mn in $CpMn(CO)_2CMe^+$ by assigning to the metal the *total* overlap population (instead of just one half of it, as the Mulliken method does) between the 4s and 4p orbitals of Mn and the σ and π orbitals of the carbyne ligand. This reduced the negative charge on the carbyne carbon from −0.35 to −0.20, made the carbonyl carbon a little more negative (from 0.00 to −0.08) due to increased back-donation, but the carbyne was still considerably more negative of the two. It is generally agreed that X-ray photoelectron spectroscopy can directly tell the distribution of charge in large molecules,[47] but it may be difficult to apply this technique to the thermolabile carbyne complexes.

Addition of Nucleophiles

Fischer's group has experimentally studied the reactivity of carbyne complexes,[8] particularly the addition of nucleophiles to

(43) Schaefer, H. F., III "The Electronic Structure of Atoms and Molecules"; Addison-Wesley: Reading, MA, 1972; p 384.
(44) Cinllo, G.; Piovesana, O. *Inorg. Chem.* **1980**, *19*, 2871.
(45) Brown, D. A.; Chambers, W. J.; Fitzpatrick, N. J. *Inorg. Chim. Acta Rev.* **1972**, 7 and references therein.
(46) Fenske, R. F.; Caulton, K. G.; Radtke, D. D.; Sweeney, C. C. *Inorg. Chem.* **1966**, *5*, 951.
(47) (a) Brant, P.; Feltham, R. D. *Inorg. Chem.* **1980**, *19*, 2673 and references cited therein. (b) For a review, see: Jolly, W. L. *Top. Curr. Chem.* **1977**, *71*, 149.

Table XII. Gross Atomic Charges

molecule	metal	carbyne C	C in CO	O in CO	other
$CpMn(CO)_2CMe^+$	1.16	−0.35	0.00	0.12	
$CpMn(CO)_2CSiMe_3{}^+$	1.26	−0.70	0.01	0.13	Si 1.23
$CpMn(CO)_2CPh^+$	1.16	−0.40	0.00	0.11	
$(CO)_5CrCNEt_2{}^{+\,a}$	−0.30	−0.07	cis 0.19 trans 0.20	cis −0.03 trans 0.02	N 0.16

[a] CO's are cis and trans relative to carbyne.

metal–carbon triple bonds. Their findings, together with a few results by Lappert and co-workers,[19] are summarized in eq 1–3.

$$CpM(CO)_2CR^+ + Nu^{0,-} \rightarrow CpM(CO)_2C(R)Nu^{+,0} \text{ (ref 48)} \quad (1)$$

$$(CO)_5CrCNR_2{}^+ + Nu^- \rightarrow (CO)_5CrC(NR_2)Nu \text{ (ref 49)} \quad (2)$$

$$(\eta^6\text{-Ar})Cr(CO)_2CPh^+ + Nu^{0,-} \rightarrow (\eta^6\text{-Ar})Cr(CO)_2C(Ph)Nu^{+,0} \text{ (ref 50)} \quad (3)$$

For details, see ref 48–50. A brief review is given in ref 65. Considering various metals M, groups R, nucleophiles Nu, and rings Ar, there are more than 50 reported additions of nucleophiles to carbyne carbon atoms.[48-50] The products of these reactions are carbene complexes, some of which contain relatively rare "nonstabilized" carbenes, those without heteroatoms adjacent to the carbene carbon atom.

The problem of selectivity and orientation in reactions is among the fundamental ones in chemistry. Why do different carbyne complexes react with so many various agents in the same way? It has been proposed that the positive charge in the cationic carbyne complexes undergoing reactions 1–3 is highly localized at the respective carbyne carbon atoms.[8b] More recently, this view has been modified to suggest that the positive charge in $(CO)_5CrCNEt_2{}^+$ is delocalized over the entire Cr–C–N unit, but the reactivity is still attributed to a partial positive charge of the carbyne carbon atom.[30] These explanations fully agree with chemical intuition.

However, nucleophiles do not always attack the most positive (or the least negative) sites in the substrate molecules. Mainly through the work of Fukui[66,67] and some other scientists,[68] the idea has emerged that much of chemical reactivity can be explained by examining the interactions among the frontier orbitals of the reactants. This approach to the problem is best summarized in Fukui's general orientation rule,[67] which says that most chemical reactions occur in such a way as to maximize the overlap of the HOMO and LUMO of the respective reactants. Klopman goes further in his generalized perturbation theory of reactivity and distinguishes between frontier-controlled and charge-controlled chemical reactions.[69] From this latter point of view, the proposed explanation of reactions 1–3 is tantamount to saying that addition of nucleophiles to carbyne complexes is charge controlled.

Present MO calculations suggest that the aforementioned additions may be frontier controlled. Moreover, the observed orientation seems to be opposite to the expectation for a charge-controlled process, because the reactive site (carbyne carbon) is the most negative ligand atom in every complex we studied. See Table XII and the accompanying discussion. The MO diagrams for all four carbyne complexes (Figures 6–9) show that the two lowest virtual orbitals are M–C π antibonds, energetically isolated from the occupied and from the higher virtual levels. An incoming nucleophile donates electron density from its HOMO (the "lone pair") to the LUMO of the substrate, which destroys one M–C π bond and converts the starting carbyne complex into a carbene complex. We also carried out MO calculations on $(\eta^6\text{-}C_6H_6)Cr(CO)_2CPh^+$ and observed exactly the same features of bonding (low-lying energetically isolated LUMO and the next virtual orbital, both with Cr–C π-antibonding character) and the characteristic charge distribution (carbyne C is −0.27, carbonyl C is 0.08). Full details of those calculations will be presented in a different context.[38]

There have appeared several reports of frontier-controlled reactions involving organotransition-metal compounds. This study was prompted by an explanation by Block et al. of nucleophilic attack on a carbene complex.[70a] Other studies dealt with amination of a thiocarbonyl ligand,[71] addition of carbanions to $ArCr(CO)_3$,[72] and nucleophilic and electrophilic attack on $ArCr(CO)_3$;[73] nucleophilicity of alkylidene ligands in their complexes with early transition metals was found not to be due to frontier orbitals.[74]

Although the *orientation* of nucleophilic attack seems to be frontier controlled, we believe that the gross positive charge of

(48) Anionic nucleophile, neutral carbene complex. M = Mn: R = Ph, Nu = RO^-,[51] ArO^-,[51] CN^-,[52] SCN^-,[52] OCN^-,[53] Me^-;[54] R = Me, Nu = Me^-;[33,54] M = Re: R = Ph, Nu = CN^-,[52] SCN^-,[52] Me^-,[55] H^-;[56] R = $SiPh_3$,[57] Nu = Me^-, H^-. Neutral nucleophile, cationic carbene complex: M = Mn, R = Ph, Nu = RNC,[58,59] PMe_3;[60] M = Re, R = Ph, Nu = PMe_3.[60]

(49) R = Me,[19] Nu = CN, Me_2N. R = Et, Nu = Br,[61] I,[61] OCN,[61] SCN,[61] Ph_3Sn,[62] F,[63] Ph_2As.[30]

(50) Anionic nucleophile, neutral carbene complex:[64] Ar = C_6H_6, MeC_6H_5, 1,4-$Me_2C_6H_4$, 1,3,5-$Me_3C_6H_3$; Nu = NH_2^- (from NH_3), NMe_2^- (from $HNMe_2$). Neutral nucleophile, cationic carbene complex:[60] Ar = C_6H_6, 1,4-$Me_2C_6H_4$, 1,3,5-$Me_3C_6H_3$; Nu = PMe_3.

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the substrate molecule enhances its overall *reactivity* toward nucleophiles, which might be related to the quite high yields of carbene complexes in most reactions. However, orientation does not necessarily depend on those same factors that govern reactivity, as measured by the reaction rates or by the equilibrium constants.

The relative importance of charge and orbital controls can perhaps be examined by attempting nucleophilic additions to $CpMn(CO)_2CSiMe_3^+$. The calculation shows the low-lying energetically isolated virtual orbitals to have Mn–C π-antibonding character, but there is also a high negative charge on the carbyne carbon atom (–0.70). Will any reaction occur? If it does, will it be addition to form a carbene complex or some other process? These questions can only be answered by appropriate experiments.

The generalization that reactions between hard acids and hard bases tend to be charge controlled whereas the reactions between soft species are more likely to be frontier controlled[75] does not hold in these reactions because there are hard as well as soft bases[75] among the nucleophiles that are found to effectively attack soft carbyne carbon.[48-50]

Triethylphosphine reacts with $(CO)_5CrCNMe_2^+$ to form *trans*-$Et_3PCr(CO)_4CNMe_2^+$ at a higher temperature than that used for reaction 2.[19] Schubert proposed a plausible explanation: the positive charge of the substrate compound is partly localized on the metal, thus decreasing the Cr–CO back-bonding so that the CO trans to the carbyne is replaced by phosphine, which has a higher σ-donor/π-acceptor ratio than CO does.[8a]

The importance of the reaction conditions is illustrted by the following two examples: Substitution[19] at –10 °C

$$[(CO)_5CrCNMe_2]BF_4 + t\text{-}Bu_4NI \rightarrow trans\text{-}ICr(CO)_4CNMe_2 + t\text{-}Bu_4NBF_4$$

Addition[61] at –60 °C

$$[(CO)_5CrCNEt_2]BF_4 + Me_4NI \rightarrow (CO)_5CrC(NEt_2)I + Me_4NBF_4$$

The orientation and selectivity in the reactions of carbyne complexes will continue to challenge experimentalists and theorists alike.

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Dynamics of Light-Induced Water Cleavage in Colloidal Systems

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Abstract: A transparent TiO_2 sol (particle radius 200 Å) is produced via hydrolyis of titanium tetraisopropoxide in acid aqueous solution. When loaded simultaneously with ultrafine Pt and RuO_2 deposits, these particles display extremely high activity as water decomposition catalysts. Band-gap excitation of the TiO_2 generates H_2 with a quantum yield of 30 ± 10%. Oxygen is produced in stoichiometric proportion. When $Ru(bpy)_3^{2+}$ or rhodamine B is used as a sensitizer, water is decomposed by visible light. Addition of methyl viologen (MV^{2+}) increases significantly the H_2 yield. Laser photolysis experiments performed with the $Ru(bpy)_3^{2+}/MV^{2+}$ system illustrate the high rate and specificity of the catalytic reactions leading to hydrogen and oxygen production from water.

The observation of light-induced oxygen evolution on illuminated TiO_2 single crystals reported by Honda et al.[1] has stimulated extensive investigations[2] in the photoelectrochemical behaviour of this semiconductor. While developing mixed Pt/RuO_2 catalysts for the mediation of water decomposition by visible light,[3-9] we became intrigued with the outstanding performance of TiO_2 particles as a support material. In the presence of a suitable sensitizer such a bifunctional redox catalyst affords sustained water cleavage over more than 20 days, the quantum yield being in excess of 5%. For understanding and further improvement of this system it is mandatory to perform detailed investigations on titania-based Pt/RuO_2 catalysts of different composition and structure. On crucial parameter to be explored is the effect of particle size. It appears desirable to synthesize TiO_2 particles of truly colloidal dimensions. As scattering effects are small, these solutions can be subjected to a detailed photochemical analysis by both conventional and flash photolysis techniques. Water decomposition studies with such transparent TiO_2 sols are reported in this paper.

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