Molecular Orbital Study of Bonding, Conformations, and Reactivity of Transition-Metal Complexes Containing Unsaturated Organic Ligands. Electrophilic and Nucleophilic Additions to Acetylide, Vinylidene, Vinyl, and Carbene Ligands

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We carried out nonparametrized molecular orbital calculations on the following complexes: FpCCH, Fp′CCH, Fp′NCH$^+$, MpCCH$_2$, FpCCH$_2$$^+$, Fp′CCH$_2$$^+$, Fp′CHCH$_2$, and Fp′CH$_2$$^+$, where symbols Fp, Fp′, and Mp stand for CpFe(CO)$_2$$^+$, CpFe(PH$_3$)$_2$$^+$, and CpMn(CO)$_2$, respectively. Acetylide (CCH), nitrile (NCH), and vinyl (CHCH$_2$) ligands form weak π bonds with the metal atoms, whereas vinylidene (CCH$_2$) and carbene (CH$_2$) ligands form strong π bonds. The metal–vinylidene bond is between double and triple, which permits facile rotation of the ligand. In the vinyl complex Fp′CHCH$_2$, the repulsive, four-electron π interaction between Fp′ and CHCH$_2$ is stronger than the attractive, two-electron π interaction. The optimal position of the vinyl ligand is one that minimizes the repulsive overlap although the attractive overlap is also minimized. The energy criterion confirms this unusual conformational preference. The preferred position of the π-accepting carbene ligand in Fp′CH$_2$$^+$ is one that maximizes the attractive π overlap; the calculated barrier is close to the value obtained by NMR spectroscopy. Additions to these complexes conform to a rather general rule: terminal, unsaturated organic ligands bonded to late transition metals undergo α attack by nucleophiles and β attack by electrophiles. The calculations indicate that nucleophilic additions are directed by the character and localization of the LUMO's in the substrates, whereas the electrophilic additions are directed chiefly by the charge distribution in the substrate molecules. We cautiously predict that, if electrophiles add to vinylidene ligands in these complexes, the attack will be at ligand β-carbon atoms. We do not expect nucleophilic additions to α-carbon atoms in acetylide and vinyl ligands.

Introduction

Electronic structures and reactivities of organic compounds change, often drastically, when they coordinate to transition metals to form organometallic complexes. These complexes are versatile synthetic reagents, intermediates in many catalyzed industrial processes, and a challenge to theorists.[1] Kinetically controlled addition reactions are particularly suited for molecular orbital investigations because they are single-step processes, accompanied by relatively small strucural changes in the reactants. The most important aspect of these additions is their regioselectivity—the choice of the site of attack in the substrate. When organometallic substrate contains several unsaturated ligands, the problem of regioselectivity becomes rather complicated. Empirical and semitheoretical rules for explaining and predicting selectivity abound in organic chemistry and are emerging in organometallic chemistry as this discipline matures.

One such generalization was made by Davison and Selegue, who succeeded in reducing an alkynyliron complex to an alkyliron complex in a sequence of four addition reactions.[2] They concluded that η^1-carbon ligands bonded to late transition metals tend to undergo α attack by nucleophiles and β attack by electrophiles.[2,3] The same tendency is evident in the reactions reported by Bruce and his co-workers[4] and by several other groups. To explain these interesting observations, we examined bonding in the starting compound and in three intermediates of this stepwise synthesis, which had all been isolated and characterized by Davison and Selegue. Symbols Fp, Fp′, and Mp stand for the metal-containing fragments CpFe(CO)$_2$$^+$, CpFe(PH$_3$)$_2$$^+$, and CpMn(CO)$_2$, respectively. We carried out calculations on the following compounds: FpCCH, Fp′CCH, Fp′NCH$^+$, MpCCH$_2$, FpCCH$_2$$^+$, Fp′CCH$_2$$^+$, Fp′CHCH$_2$, and Fp′CH$_2$$^+$. These complexes contain a variety of terminal (η^1) organic ligands: acetylide (CCH), nitrile (NCH), vinylidene (CCH$_2$), vinyl (CHCH$_2$), and carbene (CH$_2$). Besides reactivity, we discuss conformational preferences of the planar ligands (vinylidene, vinyl, and carbene) in terms of overlap and energy criteria.

This paper is the fourth part of our study of bonding, structure, and reactivity of transition-metal complexes containing unsaturated organic ligands.[5–7] In the first two parts,[5,6] we examined carbyne complexes of manganese and chromium and concluded that nucleophilic additions to their carbyne ligands are frontier controlled and apparently not charge controlled. In the third part,[7] we suggested that optimal conformations of carbene and carbyne ligands (and possibly some others) are those that minimize orbital energies and not necessarily maximize overlaps in the dominant metal–carbon π interactions.

Details of the Calculations

An approximation to the Hartree-Fock-Roothaan technique, the Fenske–Hall self-consistent field (SCF) method, has been described elsewhere[8] and some of its applications have been reviewed.[9,10] The method is devoid of adjustable or empirical parameters so that results of a calculation (eigenvalues and eigenvectors) are completely determined

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by molecular geometry and the basis functions.

We partitioned every complex molecule into two closed-shell moieties: the metal-containing fragment and the ligand that undergoes addition. Such cleavage allows inspection of crucial interactions that affect the reactivity and spatial orientation of the ligand. After the SCF portion of the calculation would converge in the atomic basis set, the molecular orbitals of the complex were transformed into a basis set of the fragment orbitals. This transformation and redistribution of charge between the fragmens to make them closed shells have no effect upon the results of calculations but make 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 the complete molecules. These energies differ slightly from one compound to another because they reflect the influences of the molecular environment upon the moieties "ready for bonding". To expedite calculations on the large molecules, we used $(PH_3)_2$, CCH, CCH_2, $CHCH_2$, CH_2, and NCH as models for ligands dppe [bis(diphenylphosphino)ethane], CCMe or CCPh, $CCMe_2$ or CCHPh, $CHCMe_2$, CH(*t*-Bu), and NCMe, respectively. Comparative calculations on the real ligands and their models did not reveal any significant differences in the electronic structures and bonding abilities that would be due to substitution of hydrogen atoms for the larger groups. In fact, several compounds with ligands CCH, CCH_2, and CH_2 are known, and their reactions are analogous to those of the complexes with bulkier ligands. Therefore we believe that these simplifications, routinely made in nonrigorous as well as in ab initio calculations, are justified. We determined relative stabilities of conformations from the differences in summed eigenvalues of the sets of occupied molecular orbitals that include the orbitals affected by internal rotation.

The basis functions were the same as in our previous studies.[5,6]

Structures. We took the geometry of the vinylidene complex $MpCCH_2$ from the crystal structure of $MpCCMe_2$.[11] Bond distances and angles in our model fragment Fp′ were the same as in $CpFe(dppe)NCMe^+$.[12] The geometry of the fragment Fp was taken from the structure of FpCCPh.[13] The distances between the fragments in the alkynyl, vinylidene, and nitrile complexes were taken from the actual structures, mentioned above; this distance was made 1.85 Å in the vinyl complex and 1.80 Å in the carbene complex. To see whether the metal–carbon bond lengths affect the electronic structures, we carried out calculations on the vinylidene complex $Fp'CCH_2^+$ using Fe–C distances of 1.65 and 1.85 Å. This change in the bond length did not affect the ordering of the molecular orbitals; the eigenvectors and net atomic charges changed only slightly and the characteristics of bonding in the two cases were the same. The reported results were obtained with 1.65 Å. The angles in the ligands were idealized: 109.5, 120, and 180° at the tetra-, tri-, and dicoordinate atoms, respectively. The common interatomic distances were used in the ligands: 1.45, 1.34, and 1.09 Å for P–H, double C–C, and C–H bonds, respectively. The metal atom was always at the origin of the coordinate system whose z axis pointed toward the carbon atom in the terminal organic ligand. The metal-containing fragments had C_s symmetry: the mirror plane (yz) of the fragment is called vertical and the xz plane is called horizontal. They are shown in Figure 1.

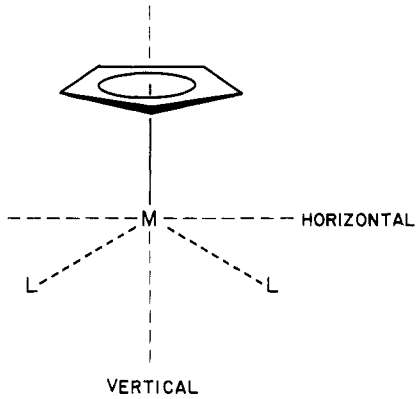

Figure 1. Two reference planes in the $CpML_2$ fragment.

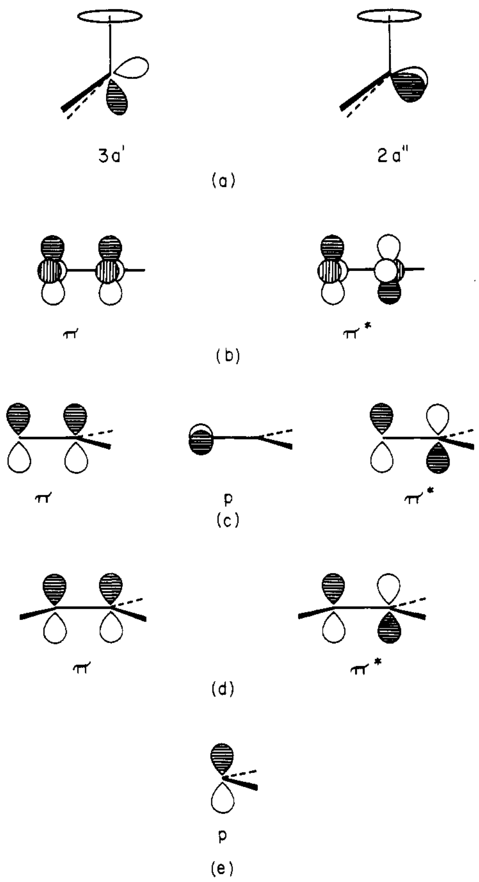

Figure 2. Crucial π-type molecular orbitals in (a) $CpML_2$ fragments, (b) acetylide or nitrile, (c) vinylidene, (d) vinyl, and (e) carbene ligands. Orbitals 3a′, 2a″, and those designated π are filled, whereas others are vacant.

Bonding Abilities of the Fragments

In our discussion of the fragments we shall emphasize those molecular orbitals that are essential for bonding in the complete molecules. They are shown in Figure 2. The crucial set of orbitals in a fragment is usually isolated in energy from the lower lying occupied and the higher lying vacant orbitals. A fragment orbital is classified as σ or π in character according to its bonding ability with respect to another fragment. The same designations, e.g., σ or π*, are often used for orbitals in different ligands, but it should be clear from the context which ligand is meant.

Metal-Containing Fragments. The electronic structures of isoelectronic fragments Mp and Fp are very similar. They are presented in detail elsewhere,[5,14] so only the

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Table I. Energies and Percent Compositions of Important Orbitals in CpFe(PH$_3$)$_2$$^+$

orbital	ε, eV	Fe d_{z^2}	Fe $d_{x^2-y^2}$	Fe d_{xy}	Fe d_{xz}	Fe d_{yz}	Fe s	Fe p	Cp e_1''	(PH$_3$)$_2$ lone pairs
4a′ (LUMO)	−12.26	33	7			5	7	30	13	
3a′ (HOMO)	−15.00		35			56				
2a″	−15.25			8	73			7	3	
2a′	−15.67	26	39			25				
1a″	−18.86			6	11			8	65	3
1a′	−19.00	16	6			3		4	63	

salient features will be summarized here. The six important fragment orbitals, ordered by the increasing energies, are 1a′, 1a″, 2a′, 3a′, 2a″ (the HOMO), and 4a′ (the LUMO). The π-type orbitals 1a′ and 1a″ are very close in energy and consist primarily of the HOMO level, e_1'', of the Cp ligand which is doubly degenerate in that free ligand. (In our first paper[5] we designated these two orbitals together as "Cp" and began symmetry labeling from the next higher orbital). The other four fragment orbitals are chiefly localized on the metal (iron or manganese) atom and are composed largely of its 3d orbitals; 2a′ and 4a′ have σ character, whereas 3a′ and 2a″ have π character. Orbital 2a′ provides metal–CO bonding within the fragment and practically does not contribute to the bonding between the metal fragment and the organic ligand. Orbitals 3a′ and 2a″, split by about 0.3 eV, are particularly important for interfragment bonding. Orbital 3a′ can π donate in the vertical plane of the metal fragment, whereas the HOMO 2a″ can π donate in the horizontal plane.

The electronic structure of Fp′ is similar to the electronic structures of Fp and Mp. The most important consequence of substituting phosphines for carbonyl ligands is the inversion of the two highest occupied orbitals—3a′ is now the HOMO and 2a″ is below it, as Table I shows. Orbital 3a′ in Fp is somewhat stabilized by its mixing with 2π orbitals of the CO ligands; when carbonyls are replaced by phosphines, this bonding interaction disappears and the energy of 3a′ increases. In every complex, orbital 2a″ overlaps better than 3a′ with the π-type orbitals in the ligands because 2a″ has somewhat greater contribution from the metal 4p orbitals than 3a′.

Ligands. The crucial orbital of acetylide, HC≡C:$^-$, are its two π bonds (a level designated π), a lone pair (σ), and two π-antibonding orbitals (level π*) of high energy. Nitrile, HC≡N:, has analogous orbitals—which therefore have the same designations—except the π-bonding level is more stable because nitrogen is more electronegative than carbon. Vinylidene, $H_2C{=}C$:, may be viewed as containing sp- and sp^2-hybridized carbon atoms with a π bond between them. Its important orbitals are a π bond (π), a lone pair (σ), an empty π-type p orbital of the ligating carbon atom (p), and a π-antibonding orbital (π*) of high energy. Vinylidenes resemble aminocarbynes[5-7] in their bonding abilities. Vinyl, $H_2C{=}\ddot{C}H^-$, is derived from ethene and its crucial orbitals are a π bond (π), a lone pair (σ), and a high-lying π-antibonding orbital (π*). Carbene, H_2C:, has a lone pair (σ) and a vacant π-type p orbital (designated p).

The lone pair, σ, is the HOMO in every one of these ligands. The linear ligands (acetylide and nitrile) each have degenerate π-type orbitals, a bonding and an antibonding level in each ligand. Vinylidene has two nonequivalent π-accepting orbitals: p lies in the ligand plane, whereas π* is perpendicular to that plane. The vinyl and carbene ligands each contain only one π-accepting orbital, which is perpendicular to the ligand plane. Clearly, vinylidene has different abilities for π bonding with the metal in the two planes, whereas vinyl and carbene can π-bond only in the plane perpendicular to the ligand. Because of such bonding abilities, these three nonlinear ligands exhibit conformational preferences when bonded to low-symmetry metal fragments such as CpML$_2$.

Table II. Energies and Percent Compositions of Important MO's in CpFe(CO)$_2$CCH

ε, eV	CpFe(CO)$_2$ 1a′	1a″	2a′	3a′	2a″	CCH π	π*
−11.87 (HOMO)					43	54	2
−12.09			3	35		59	1
−13.78			76	5			
−14.98	14			53		28	1
−14.98		9			52	37	1
−16.20	70		7	5		12	1
−16.23		89				8	

Table III. Energies and Percent Compositions of Important MO's in CpFe(PH$_3$)$_2$CCH

ε, eV	CpFe(PH$_3$)$_2$ 1a′	1a″	2a′	2a″	3a′	CCH π	π*
−8.42 (HOMO)			9		65	18	4
−8.50				71		22	5
−9.18			73		16		
−12.09	19				11	63	
−12.52		4		20		72	

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, 4a′, of the metal fragment to form a σ bond. The metal–ligand π bonds are formed largely by back-donation from 2a″ or 3a′ or both orbitals of the metal fragments into the π-accepting orbitals of the ligands. The interactions of the filled ligand orbitals, designated π, with the metal-based orbitals can also be significant, as will be shown later. The metal–ligand π interactions are crucial for bonding and conformations; the σ interactions are rather simple and are not sensitive to rotation about the metal–ligand axis. The frontier orbitals, particularly the LUMO's, of the complexes are most likely to affect chemical reactivity, and we shall examine them in some detail. The electronic structures of these molecules are rather complicated because their low symmetry permits extensive mixing of many orbitals. Only the crucial interactions will be identified in the molecular orbital diagrams and the accompanying tables will provide the details.

Alkynyl Complexes FpCCH and Fp′CCH. The electronic structures of these two complexes are similar, as Figures 3 and 4 and Tables II and III show. The important finding is that the acetylide ligand is essentially pure σ donor; since its π* level lies high above the filled metal-based orbitals, back-donation is weak. The total

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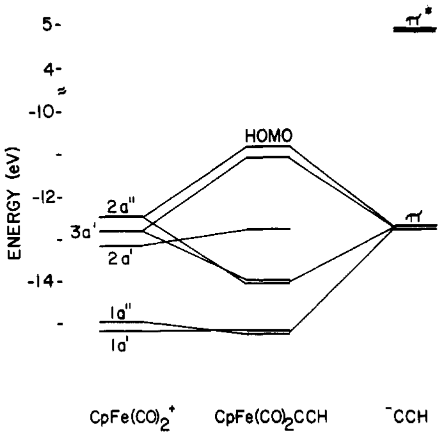

Figure 3. The most important orbital interactions in CpFe-$(CO)_2CCH$.

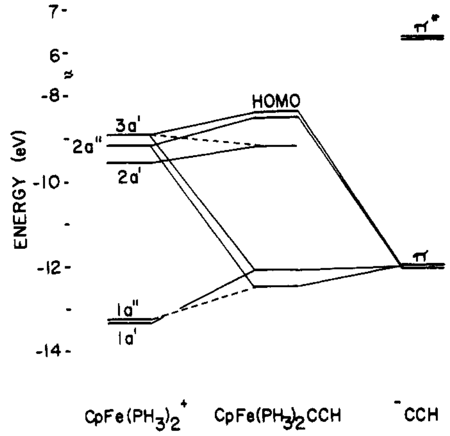

Figure 4. The most important orbital interactions in CpFe-$(PH_3)_2CCH$.

population of the π* level (two orbitals) is 0.22 e in the complex containing strong donors, phosphines, and 0.14 e in the complex with strong acceptors, carbonyls. This finding is consistent with infrared spectra of the two kinds of alkynyl complexes.[15] The important metal orbitals are energetically matched with the acetylide *filled* π level, and therefore the main interactions between the fragments are four-electron, destabilizing ones. The HOMO is 10% localized on the acetylide β-carbon atom in the Fp′ complex and 30% in the Fp complex. Similarly, the next highest occupied molecular orbital is 12 and 33% localized on the β-carbon atom in the Fp′ and Fp complex, respectively. The reason for the greater polarization of molecular orbitals in Fp′CCH than in FpCCH is evident in Figures 3 and 2. The metal-based orbitals in the former complex lack the stabilization provided by the π-accepting CO ligands in the latter complex; because of that, the energy matching between the fragment orbitals in Fp′CCH is poorer than in FpCCH. The LUMO's in both complexes are entirely confined to the respective metal fragments, the LUMO in FpCCH being somewhat localized on the CO ligands. In each complex, the LUMO lies close to other vacant molecular orbitals.

Nitrile Complex Fp′NCH$^+$. The main features of bonding in this molecule are presented in Figure 5 and Table IV. The π-accepting ability of nitrile is comparable to that of acetylide—the total population of its π* level is 0.26 e—which means that nitrile is also a weak π acceptor. Its π level has low energy and does not interact appreciably with the metal-based orbitals. Consequently, the high-lying filled molecular orbitals are essentially localized in the Fp′ fragment. The LUMO is somewhat delocalized on the ligand, but it is not π antibonding between the fragments; the importance of this will become clear later. As in the alkynyl complexes, the LUMO belongs to a manifold of several rather closely spaced vacant orbitals.

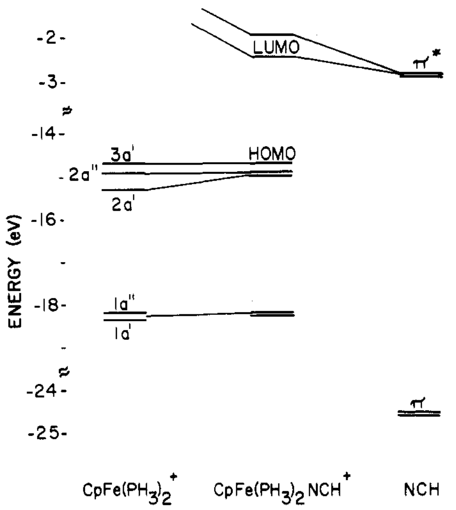

Figure 5. The most important orbital interactions in CpFe-$(PH_3)_2NCH^+$.

Table IV. Energies and Percent Compositions of Important MO's in $CpFe(PH_3)_2NCH^+$

	CpFe(PH$_3$)$_2$					NCH	
ε, eV	1a′	1a″	2a′	2a″	3a′	π	π*
−14.71 (HOMO)					93	2	4
−14.89				88		3	6
−14.96			85				
−18.20	63	35					
−18.22	34	65					

Table V. Energies and Percent Compositions of Important MO's in $CpMn(CO)_2CCH_2$ Containing Horizontal Vinylidene Ligand

	CpMn(CO)$_2$					CCH$_2$		
ε, eV	1a′	1a″	2a′	3a′	2a″	π	p	π*
−3.53 (LUMO)					42		54	
−9.36 (HOMO)				72		19		8
−10.37			92					
−12.28		12			50		37	
−13.10	77		3			10		
−13.70		88			6		5	
−15.30	13			14		69		2

Table VI. Energies and Percent Compositions of Important MO's in $CpMn(CO)_2CCH_2$ Containing Vertical Vinylidene Ligand

	CpMn(CO)$_2$					CCH$_2$		
ε, eV	1a′	1a″	2a′	3a′	2a″	π	p	π*
−4.17 (LUMO)				37			56	
−9.02 (HOMO)					71	18		10
−10.38			91					
−12.08	22		3	49			22	
−13.34		95				5		
−13.85	67			11			16	
−15.28		5			16	74		2

Vinylidene Complexes $MpCCH_2$, $FpCCH_2^+$, and $Fp'CCH_2^+$. The main results of the calculations are shown in Figure 6 and Tables V and VI.

In the conformer containing the horizontal ligand, its orbitals π and π* interact with metal-based orbitals of a′ symmetry and orbital p interacts with orbitals of a″ sym-

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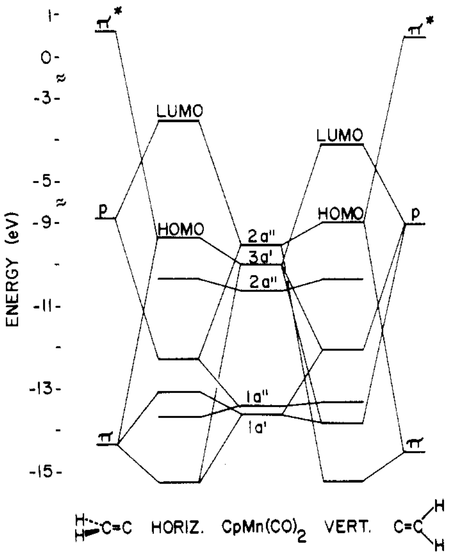

Figure 6. The most important orbital interactions in the two conformations of $CpMn(CO)_2CCH_2$.

metry. In the conformer with the vertical ligand, the interactions are reversed: π and π* with a'' and p with a'. The metal–vinylidene back-donation is nearly the same in the two conformations of $MpCCH_2$: about 0.85 e in orbital p and about 0.24 e in orbital π*. Clearly, metal–ligand π bonding is stronger in the ligand plane than in the plane perpendicular to the ligand; this is also evident by inspection of the overlaps and overlap populations corresponding to these two interactions. Although back-bonding involving π* is appreciable, the manganese–vinylidene cannot be considered triple and the reported length of 1.68 Å in MpCCHPh may not be quite accurate; the error may have been caused by rapid decomposition of the crystals, reported by the authors.[16a,b] Our finding that the multiplicity of this bond is between 2 and 3 is borne out by the comparison of the Mn–carbene formal double bond in $MpCMe_2$ (1.87 Å),[16c] Mn–vinylidene bond in $MpCCMe_2$ (1.79 Å),[11] and Cr–carbyne triple bonds in many carbyne complexes (average about 1.70 Å).[17] The vinylidene ligand is similar to aminocarbyne ligand, CNR_2, whose bonds with metals are also between double and triple.[6,17–19] This analogy may be worth exploring experimentally. The notion of extensive back-bonding to the vinylidene ligand is further supported by infrared data for a series of MpL complexes with various ligands L, which show that vinylidene is stronger π acceptor than CO, CPh_2, and several other ligands.[20] Mössbauer parameters of an iron–vinylidene complex also indicate that this ligand is a strong π acceptor.[21]

Table VII. Energies and Percent Compositions of Important MO's in $CpFe(CO)_2CCH_2^+$ Containing Horizontal Vinylidene Ligand

	$CpFe(CO)_2$					CCH_2		
ε, eV	1a'	1a''	2a'	3a'	2a''	π	p	π*
-7.85 (LUMO)					20		66	
-17.41 (HOMO)				26		65		5
-20.16	8		71					
-21.35		43			47		8	
-21.67	51		7	35		4		
-22.71		54			26		10	
-23.56	28		5	30		26		3

Table VIII. Energies and Percent Compositions of Important MO's in $CpFe(CO)_2CCH_2^+$ Containing Vertical Vinylidene Ligand

	$CpFe(CO)_2$					CCH_2		
ε, eV	1a'	1a''	2a'	3a'	2a''	π	p	π*
-8.55 (LUMO)				15			68	
-17.12 (HOMO)					32	60		7
-20.18	8		72					
-21.52	31		4	57			4	
-21.59		69			22	8		
-22.84	48		8	22			12	
-23.46		28			34	25		3

Table IX. Energies and Percent Compositions of Important MO's in $CpFe(PH_3)_2CCH_2^+$ Containing Horizontal Vinylidene Ligand

	$CpFe(PH_3)_2$					CCH_2		
ε, eV	1a'	1a''	2a'	2a''	3a'	π	p	π*
-5.64 (LUMO)				25			61	
-14.84 (HOMO)			7		35	47		8
-16.67			67		17			
-18.63	53				24	15		
-18.84		29		50			19	
-19.62		70		19			6	
-20.68	37		7		14	34		

Table X. Energies and Percent Compositions of Important MO's in $CpFe(PH_3)_2CCH_2^+$ Containing Vertical Vinylidene Ligand

	$CpFe(PH_3)_2$					CCH_2		
ε, eV	1a'	1a''	2a'	2a''	3a'	π	p	π*
-6.27 (LUMO)			5		18		65	
-14.70 (HOMO)				42		47		10
-16.76			68		15			
-18.13	23		3		56		10	
-19.30		88		4		6		
-20.08	66		9		9		12	
-20.46		10		38		36		

Most π-type molecular orbitals in the complex have contributions from both sets of metal-based orbitals (1a', 1a'' and 3a', 2a'') and from more than one ligand orbital (π, p, and π*). For example, the molecular orbital at −12.08 eV in the conformer containing vertical ligand consists of an in-phase (bonding) combination of p with 3a' and an out-of-phase (antibonding) combination of p with 1a'. This complexity makes it difficult to predict optimal conformation solely by considering orbital overlaps. The energy criterion indicates that the horizontal position of the vinylidene is preferred over the vertical by about 4 kcal mol^{-1}; the preference is small because the Mn–C bond is partly triple. Indeed, NMR studies of several complexes in solutions showed that the vinylidene ligand rotates easily about its bond with the metal atom.[3,21–23] In the solid state, the vinylidene plane is indeed horizontal,[11,16a,b] in

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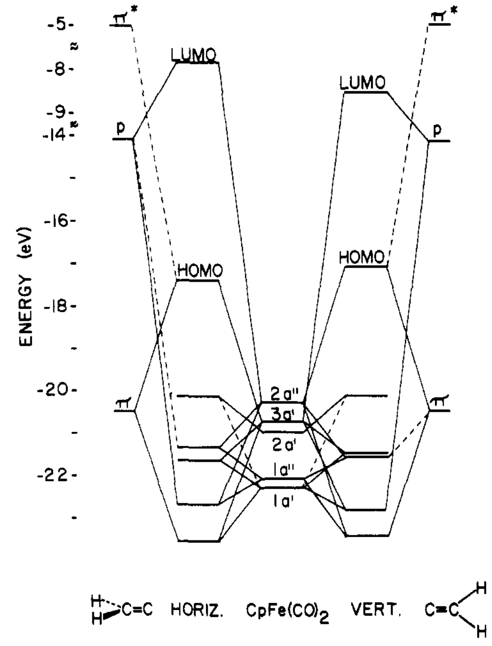

Figure 7. The most important orbital interactions in the two conformations of $CpFe(CO)_2CCH_2^+$.

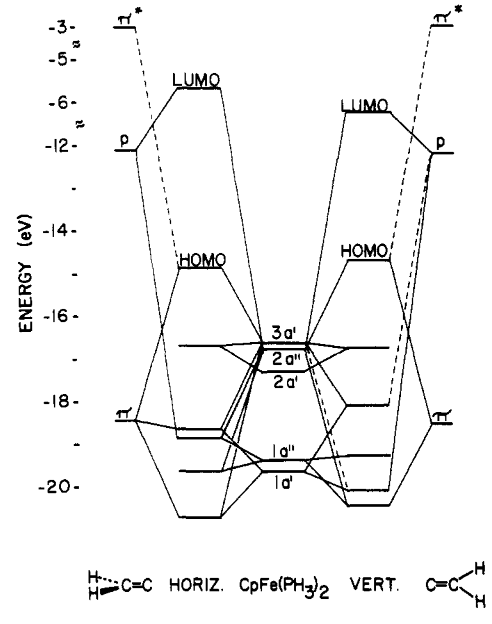

Figure 8. The most important orbital interactions in the two conformations of $CpFe(PH_3)_2CCH_2^+$.

accord with our result. Schilling et al., who briefly examined such a complex before us, calculated the horizontal position to be more stable than the vertical one by 3.6 kcal mol^{-1}.[14] The LUMO in $MpCCH_2$ is π-antibonding between the Mn and vinylidene α-C atoms, 50% localized on this α carbon atom, and well isolated in energy (more than 3 eV) from other vacant molecular orbitals.

Complex $FpCCH_2^+$ resembles the corresponding manganese compound, as Figure 7 and Table VII and VIII show, and has the same slight conformational preference. The populations of p and π* are about 0.46 and 0.23 e, respectively. The HOMO is about 30% localized on the β-carbon atom in the vinylidene ligand. The π-antibonding LUMO is about 60% localized on the α-carbon atom and is separated from the other virtual orbitals by about 3 eV.

The electronic structure of $Fp'CCH_2^+$ is summarized in Figure 8 and Tables IX and X. The back-donation in it is slightly stronger than in $FpCCH_2^+$—populations of the vinylidene p and π* orbitals are about 0.57 and 0.28 e, respectively—because phosphine is a better donor than carbonyl. The two conformations have nearly the same total orbital energies—the calculated values differ by less than 2 kcal mol^{-1}. The frontier orbitals have the characteristics found in other vinylidene complexes: the HOMO is about 25% localized on the β-carbon atom, whereas the π-antibonding, energetically isolated (by about 4 eV) LUMO is about 60% localized on the α-carbon atom in the ligand.

Table XI. Energies and Percent Compositions of Important MO's in $CpFe(PH_3)_2CHCH_2$ Containing Horizontal Vinyl Ligand

	$CpFe(PH_3)_2$					$CHCH_2$	
ε, eV	1a'	1a''	2a'	2a''	3a'	π	π*
−8.10 (HOMO)			6		66	17	5
−8.29				92			
−8.74			72		13		
−11.84	24				10	56	
−13.01		98					
−13.27	59		4			25	

Table XII. Energies and Percent Compositions of Important MO's in $CpFe(PH_3)_2CHCH_2$ Containing Vertical Vinyl Ligand

	$CpFe(PH_3)_2$					$CHCH_2$	
ε, eV	1a'	1a''	2a'	2a''	3a'	π	π*
−7.92 (HOMO)				70		25	5
−8.15			6		90		
−8.76			79		7		
−12.21		3		22		70	
−12.27	71		3				
−13.00		96				3	

Vinyl Complex $Fp'CHCH_2$. The nature of the metal–vinyl interactions in this complex makes the investigation of its conformational preference somewhat unusual and interesting.

The most popular method for molecular orbital analysis of organometallic conformations involves examination of dominant overlaps along the axis of intramolecular rotation. Since most complexes studied by such methods contain rather strongly *π-accepting* ligands—so that the occupied molecular orbitals are *stabilized* by contributions from the ligand orbitals—it became customary to find the dominant overlaps *maximized* in the optimal conformations; thus the term "maximum-overlap criterion".

Assuming that vinyl ligand is a π acceptor, as many unsaturated organic molecules are, one would expect the principal π interaction in the complex to be back-donation from 2a'' or 3a' of the metal fragment into *vacant* π* of the ligand. Since this two-electron interaction is *attractive*, the optimal position of the ligand should be one that *maximizes* it. The pertinent overlaps, shown in Figure 9, are 0.145 and 0.109; thus, the vinyl ligand may be expected to lie in the vertical plane. If, however, vinyl is not a π acceptor, the principal π interaction in the complex should occur between 2a'' or 3a' of the metal fragment and *filled* π of the ligand. This *repulsive* four-electron interaction should be *minimized* in the optimal conformation. The overlaps (0.152 and 0.096) indicate this time that the ligand should lie in the horizontal plane! Clearly, overlaps alone do not permit a conclusive prediction of the stable conformation.

This dilemma can be resolved in two ways. If one wishes to remain in the framework of overlap analysis, one has to decide which π interaction—attractive or repulsive—dominates the metal–vinyl bonding. Figure 9 and Tables XI and XII show that π mixes more than π* with the metal-based orbitals, so that the repulsive interactions

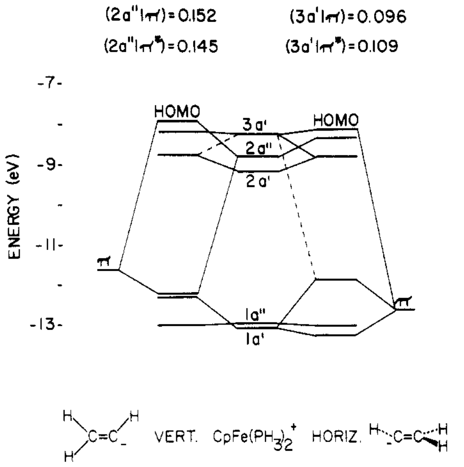

Figure 9. The most important orbital interactions and overlaps in the two conformations of $CpFe(PH_3)_2CHCH_2$. The high-lying σ^* orbital of the vinyl ligand is not shown.

Table XIII. Energies and Percent Compositions of Important MO's in $CpFe(PH_3)_2CH_2^+$ Containing Vertical Carbene Ligand

	CpFe(PH₃)₂					CH₂
ε, eV	1a'	1a''	2a'	2a''	3a'	p
−9.56 (LUMO)				35		61
−15.77 (HOMO)			10		82	
−16.22			69		14	
−18.41		16		54		29
−18.89	88		4			
−19.26		82		10		5

seem to prevail. Indeed, populations of orbital π^*, a measure of back-bonding, is relatively small: 0.14 e when the vinyl is horizontal and 0.15 e when it is vertical. All this indicates that the optimal position of the ligand should be horizontal. Another approach, and less ambiguous one, is to compare total orbital energies in the two conformations. Again, the horizontal position of the vinyl ligand is predicted to be more stable than the vertical one by about 5 kcal mol^{-1}. Evidently, the attractive π interactions are weak despite the sizable overlaps of π^* with the metal-based orbitals because π^* lies high in energy above those metal-based orbitals. This prediction of the conformational preference agrees with the known structure of a similar vinyl complex.[24]

The HOMO in $Fp'CHCH_2$ belongs chiefly to the metal fragment. The LUMO is not π-antibonding between the fragments. It is somewhat localized on the vinyl ligand but is close in energy to other vacant orbitals, particularly so in the more stable conformation.

Carbene Complex $Fp'CH_2^+$. The electronic structure of this compound resembles that of $Fp'CCH_2^+$ by rather strong metal–ligand π bonding with concomitant back-donation into the ligand orbital p; its average population in the two rotamers (horizontal and vertical carbene) is about 0.72 e. Figure 10 and Tables XIII and XIV contain other data about bonding. Orbital p of the carbene ligand mixes with the low-lying as well as the high-lying orbitals of the metal fragment and its overlaps with the former ones are not negligible (see Figure 10). For example, the molecular orbital at −17.76 eV in the rotamer containing horizontal carbene is bonding with respect to 3a' and p but antibonding with respect to 1a' and p. When a molecule has such a low symmetry (C_s) and complicated electronic structure, we do not discuss its conformational preference solely in terms of orbital overlaps but prefer to use the energy criterion. The vertical orientation of the carbene (in which the dominant overlap is indeed maximized) turned out to be more stable than the horizontal one by about 11 kcal mol^{-1}; this is our prediction of the barrier for interconversion between the two equivalent rotamers containing vertical carbene ligand. The actual value, obtained in a variable-temperature NMR study of that compound, is close: 10.4 kcal mol^{-1}.[25]

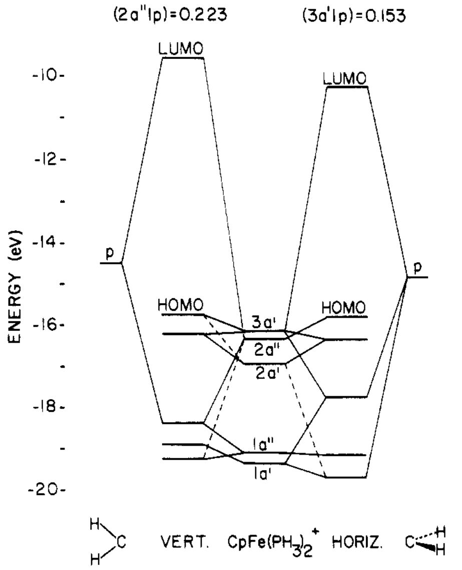

Figure 10. The most important orbital interactions and overlaps in the two conformations of $CpFe(PH_3)_2CH_2^+$.

Table XIV. Energies and Percent Compositions of Important MO's in $CpFe(PH_3)_2CH_2^+$ Containing Horizontal Carbene Ligand

	CpFe(PH₃)₂					CH₂
ε, eV	1a'	1a''	2a'	2a''	3a'	p
−10.26 (LUMO)			6		25	64
−15.81				94		
−16.33			67		16	
−17.76	22				52	16
−19.13		98				
−19.72	66		9		7	15

The HOMO in the carbene complex is contained chiefly in the metal fragment. The π-antibonding LUMO is about 60% localized on the carbene carbon atom and its separation in energy from the next virtual orbital is very large—about 8 eV.

Electrophilic and Nucleophilic Additions

Having examined the electronic structures of the complexes, we turn to investigation of regioselectivity of electrophilic and nucleophilic additions that they undergo. These reactions are known for a multitude of complexes containing $CpFe(CO)_2^+$,[3,24,26–29a] $CpFe(dppe)^+$,[2,3,29b] $CpRuL_2^+$,[4,23a,30,31] and $CpMn(CO)_2$[11,32,33] fragments and

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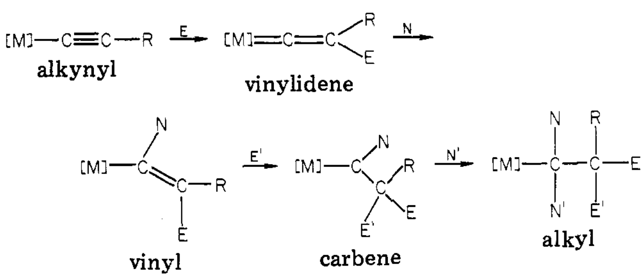
Scheme I



[M] represents a metal-containing fragment, E and E′ represent electrophiles, and N and N′ represent nucleophiles

Table XV. Charges of Coordinatively Unsaturated Atoms

	organic ligand		CO[b]			
molecule	α-C	β-C	C	O	C_{Cp}[b]	N
FpCCH	−0.05	−0.27	0.34	−0.14	0.02	
Fp′CCH	−0.09	−0.37			−0.01	
$Fp'NCH^+$		−0.02			0.01	0.20
$MpCCH_2$[a]	−0.39	−0.09	−0.09	0.03	−0.12	
$FpCCH_2^+$[a]	0.29	−0.35	0.40	0.07	0.06	
$Fp'CCH_2^+$[a]	0.19	−0.38			0.04	
$Fp'CHCH_2$[a]	−0.10	−0.26			−0.02	
$Fp'CH_2$[a]	0.02				0.03	

[a] Average value for two conformations. [b] Average value for all similar atoms.

various addends (Scheme I). Several analogous types of reactions, involving more or less different kinds of complexes, are also known.[4,20,22,23b,34–37]

All the various reactions in Scheme I conform to a simple rule: nucleophiles add to the α-carbon atoms in the terminal unsaturated organic ligands, whereas electrophiles add to the β-carbon atoms. Attacks at the other unsaturated ligands in these complexes (Cp and CO) and at the metal atoms have not been reported. The electrophilic complexes (those attacked by nucleophiles) are usually cationic, and the nucleophilic ones (those attacked by electrophiles) are electroneutral, but charges are not included in Scheme I. We believe that overall positive charge of a molecule enhances its *reactivity* toward nucleophiles and that it would greatly retard its *reactivity* toward electrophiles, but overall charges probably are not critically important for the *regioselectivity* in the reactions. Even in charge-controlled reactions, it is the *distribution* of electron density that determines the site of attack. The gross atomic charges in the unsaturated ligands, calculated by Mulliken population analysis,[8,38] presented in Table XV. Before discussing these numbers, we want to repeat the words of Schaefer, which express a consensus among theorists: "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".[39a]

Let us examine Table XV with this in mind. The numbers themselves may not be true in the absolute sense, but they reveal an interesting pattern: the β-carbon atom is the most negative ligand atom in every iron-containing complex. Its charge is rather high—on the average about −0.30. Whereas few molecular orbitals are important in bonding, many of them contribute to the charge distribution; this often obscures the origin of atomic charges. In the previous discussion of the compounds, we mentioned the molecules whose HOMO's and the next highest occupied molecular orbitals contributed noticeably to the accumulation of electron density at the β-carbon atoms. This accumulation may be due to polarization of the π and π* orbitals in the ligand by the 2a″ or 3a′ or both (in the alkynyl complex) orbitals in the metal fragment. Second-order perturbation theory shows that the ligand π system is polarized away from the metal fragment, a π-donating substituent.[39b] The electrophilic attacks at polarized ligands are directed by charge and orbital factors in concert. The cationic iron vinylidene complexes, for which electrophilic additions have not been reported, also carry substantial negative charges on their β-carbon atoms. This finding perhaps adds some credence to a recent proposal by Caulton and his co-workers that vinylidene complexes may be turned into carbyne complexes by electrophilic addition.[40a] To effect such a transformation, the overall charges of the reactants should be matched judiciously. A similar *net* reaction has very recently been accomplished:[37b] HCl adds to the unsaturated C–C bond in $CpFe(CO)(PPh_3)CCH_2^+$ to yield a chloro(methyl)carbene complex, $CpFe(CO)(PPh_3)C(Cl)Me$, which means that the H atom (or ion) of HCl becomes attached to the β-carbon atom in the vinylidene ligand.

Deprotonation of dppe ligand in $CpFe(dppe)CCMe_2^+$ by bases was attributed to enhanced acidity of the H atoms in α positions with respect to the coordinated P atom and related to the known fact that phosphonium salts are more acidic than their parent phosphines.[40b] Our calculations show that the P atoms in $Fp'CCH_2^+$ are indeed akin to phosphonium centers—their charges are +0.92 because phosphine ligands are poor π acceptors—and thus support the above explanation.

In the preceding discussion of bonding, we emphasized that the LUMO's in the vinylidene and carbene complexes, which are electrophilic, have three characteristics in common: they are π antibonding between the metal and the ligand, substantially localized at the ligand α-carbon atom (possibly another consequence of polarization), and separated in energy from other virtual orbitals. The LUMO's of the alkynyl and vinyl complexes, which have not been repoted to add nucleophiles, lack some or all of these attributes (see above). Thus, the nucleophilic additions seem to be frontier controlled. An incoming nucleophile donates electron density from its HOMO (the lone pair) to the LUMO in the organometallic substrate, thus destroying a metal–carbon π bond and reducing the bond order between these atoms; this overall change is evident in Scheme I. Substantial localization of the LUMO at the α-carbon atom causes the attack to be regioselective. Isolation in energy is needed to ensure that the HOMO of the nucleophile will interact preferentially with the LUMO of the substrate. It seems that charge distribution is not important for regioselectivity of nucleophilic attack (see Table XV). There is no experimental indication that the carbonyl carbon atoms in FpCCH and $FpCCH_2^+$, which carry

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positive charges, are electrophilic; also the electrophilic α-carbon atom in $MpCCH_2$ bears considerable negative charge. The same situation was found in carbyne complexes, to which many various nucleophiles add.[5,6]

In the last years, nucleophilic additions to several kinds of organometallic complexes have been recognized as frontier controlled,[5–7,41–46] but no electrophilic additions have been attributed solely to frontier orbitals.[46] This deserves further study.

In view of the preceding discussion, we would be surprised to learn about nucleophilic attack at the α-carbon atoms in the acetylide and vinyl ligands bonded to $CpML_2$ fragments. The LUMO in FpCCH is such that, if a nucleophile adds to that molecule, we would expect it to attack the carbonyl atom. These beliefs of ours perhaps have some support in the behavior of complexes CpFe(dppe)$NCMe^{+}$[47] because nitrile is similar to acetylide. Various anions, some of them potent nucleophiles, replace the nitrile ligand without any apparent side reactions such as additions. This is not a proof of the hypothesis, but it is consistent with our finding that the LUMO in $Fp'NCH^+$ does not have the properties that would make this complex electrophilic.

Several other ligands in transition-metal complexes undergo α attack by nucleophiles and β attack by electrophiles. Among them are N_2,[48] CS,[49] CSe,[3] CN^-,[3] and NC^-.[3] These regioselective additions are fairly common, and the causes to which we attribute them in this study may be rather general.

Acknowledgment. We are grateful to several colleagues for their comments and information about the chemical reactions we examined. S. G. Harsy and Professor P. M. Treichel, both of this department, read the manuscript and commented upon it. Professors M. I. Bruce of University of Adelaide, K. G. Caulton of Indiana University, A. Davison of Massachusetts Institute of Technology, and R. P. Hughes of Dartmouth College kindly informed us about their experimental work. The research was supported by the National Science Foundation, Grant CHE 7950005. N.M.K. has been a Fulbright Fellow since 1978 and is a Procter and Gamble Fellow for 1981–1982.

Registry No. $CpFe(PH_3)_2^+$, 81616-25-3; $CpFe(CO)_2CCH$, 33029-77-5; $CpFe(PH_3)_2CCH$, 81616-26-4; $CpFe(PH_3)_2NCH^+$, 816616-27-5; $CpMn(CO)_2CCH_2$, 81616-28-6; $CpFe(CO)_2CCH_2^+$, 81616-29-7; $CpFe(PH_3)_2CCH_2^+$, 81616-30-0; $CpFe(PH_3)_2CHCH_2$, 81616-31-1; $CpFe(PH_3)_2CH_2^+$, 81616-32-2.

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Hydrido and Hydroxycarbonyl Compounds of the Carbonyl(η-cyclopentadienyl)nitrosylrhenium Group

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Reaction of $[(\eta\text{-}C_5H_5)Re(NO)(CO)_2][BF_4]$ (2) with $Et_3N\text{–}H_2O$ in acetone at 50 °C affords thermally robust $(\eta\text{-}C_5H_5)Re(NO)(CO)H$ (1) in excellent yield as low-melting orange crystals. The stable yellow metallocarboxylic acid $(\eta\text{-}C_5H_5)Re(NO)(CO)COOH$ (3) precipitates when base (Et_3N or NaOH) is added to a solution of 2 in water. Although 3 is stable in anhydrous THF, catalytic amounts of strong bases produce 1 rapidly and quantitatively at room temperature, establishing the instability of the carboxylate anion 5 presumed to be formed by deprotonation of 3 under these conditions. The latter anion is more stable in water and is a probable intermediate in the above synthesis of 1. The high thermal stability of 1 and the more facile loss of CO_2 from the carboxylate 5 than from 3 itself are discussed in terms of the strength of the Re–CO bond. The bromide $(\eta\text{-}C_5H_5)Re(NO)(CO)Br$ is formed in good to excellent yield from 1 and CBr_4, Br_2, or *N*-bromosuccinimide. Hydride abstraction from 1 by $[Ph_3C][PF_6]$ in the presence of donor ligands yields salts $[(\eta\text{-}C_5H_5)Re(NO)(CO)L][PF_6]$ (L = acetonitrile, tetrahydrofuran, acetone).

Introduction

A 1972 communication from this laboratory described the synthesis of the new rhenium hydride $(\eta\text{-}C_5H_5)Re(NO)(CO)H$, 1.[1,2] Its rather high thermal and oxidative stability were noted, but no reactions were reported. It was only the second example of a nitrosyl hydride, the first having been prepared in 1962 by Hieber and Tengler.[3] Hydride 1 was obtained by reaction of the carbonyl cation 2 with triethylamine and water in acetone (eq 1).[1] The intermediacy of 3 was proposed, but no attempt was made to isolate such a species. We report here details of the preparation of 1 and several of its reactions, which suggest that it will become a useful starting point in synthesis. The results demonstrate a lack of acidity for 1; its reactions are

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