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Molecular Orbital Study of the Anionic Carbonyl Cluster $Fe_2Co(CO)_9CCO^-$ and the Products of Its Reactions with Phosphines

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The anionic trinuclear ketenylidene cluster $Fe_3(CO)_9CCO^{2-}$ reacts with electrophiles, which generally attack at the most negatively charged sites in the cluster, the α-carbon atom or the oxygen atom of the ketenylidene, CCO, group. The cationic cluster $Co_3(CO)_9CCO^+$ reacts with nucleophiles, which attack at the most positively charged site in the cluster, the β-carbon atom of the ketenylidene group. The mixed metal ketenylidene cluster, $Fe_2Co(CO)_9CCO^-$, reacts both with electrophiles and with nucleophiles. In particular, the reactions of $Fe_2Co(CO)_9CCO^-$ with phosphines yield the interesting result of an incoming nucleophile bonded to the negatively charged α-carbon atom of the ketenylidene group. It was this unusual reaction product which caused us to investigate the electronic structure of $Fe_2Co(CO)_9CCO^-$ and its reaction products with phosphines using Fenske–Hall molecular orbital calculations. The results show that both orbital and charge considerations favor attack by phosphines at the cobalt atom. Occupation of the $Fe_2Co(CO)_9CCO^-$ LUMO by the electrons of the incoming nucleophile results in rupture of a Co–Fe bond, allowing the phosphine to associatively attach at the Co atom. Migration of the phosphine to the carbide follows because the phosphine–carbide interaction is so favorable.

Introduction

The cationic ketenylidene cluster $Co_3(CO)_9CCO^+$ undergoes numerous reactions with nucleophiles such as alcohols, mercaptans, and amines. The site of interaction with these nucleophiles is always at the positively charged β-carbon of the ketenylidene group.[1,2] The anionic ketenylidene clusters $M_3(CO)_9CCO^{2-}$, where M is Fe, Ru, or Os, generally react with electrophiles at negatively charged sites in the cluster.[3-7] The anionic cluster $Fe_2Co(CO)_9CCO^-$, shown in Figure 1, reacts both with nucleophiles and with electrophiles.[8] The only electrophile that it has been found to react with is H^+. The product of this reaction is $Fe_2Co(CO)_{10}CH$,[9] which is analogous to the reaction of the proton with $Fe_3(CO)_9CCO^{2-}$. Despite its negative charge, $Fe_2Co(CO)_9CCO^-$ reacts with several nucleophiles. For the most part these reactions occur in much the same fashion as do the reactions of nucleophiles with $Co_3(CO)_9CCO^+$, attack is at the β-carbon atom of the ketenylidene group.[8] Nucleophiles which react with $Fe_2Co(CO)_9CCO^-$ in this way are $LiCH_3$, $NaOCH_3$, and $KB(C_2H_5)_3H$.

The reactions of $Fe_2Co(CO)_9CCO^-$ with phosphines are very unusual in that the product, $Fe_2Co(CO)_9CPR_3^-$, shown in Figure 2, has the nucleophile bonded to the α-carbon atom of the ketenylidene group, the most negatively charged site in the cluster.[9,10] This unusual result led to mechanistic studies of these reactions which showed that the initial site of attack by the phosphines is at the cobalt atom.[11,12] Subsequent migration to the α-carbon atom gives the final product. In order to examine this unusual reaction, we have done molecular orbital calculations on $Fe_2Co(CO)_9CCO^-$, $Fe_2Co(CO)_9CPMe_3^-$, PMe_3, PEt_3, and $Fe_2CoPMe_3(CO)_8CCO^-$, as well as the hypothetical fragment $Fe_2Co(CO)_9C^-$.

Table I. Molecular Orbital Results for $Fe_2Co(CO)_9CCO^-$

atom	charge	main orbital in LUMO	percentage in LUMO
Co	−0.20	$3d_{xy}$	15.2
Fe1	+0.05	$3d_{x^2-y^2}$	14.1
Fe2	+0.09	$3d_{x^2-y^2}$	9.2

Experimental Section

X-ray structural results were taken from the literature[8,10] for both $Fe_2Co(CO)_9CCO^-$ and $Fe_2Co(CO)_9CPMe_3^-$. Coordinates for the atoms in PMe_3, PEt_3, and $Fe_2CoPMe_3(CO)_8CCO^-$ were obtained from molecular mechanics calculations using PC Model, an interactive modeling program available from Serena Software.[13] The Fenske–Hall calculations[14] used Herman–Skillman[15] atomic basis functions as modified by the method of Bursten and Fenske.[16] The double-ζ functions for the 1s and 2s wave functions were reduced to single-ζ functions for these calcuations. The resulting molecular wave functions were used to compute Mulliken populations, atomic charges, and overlap populations. The phosphorus calculations included phosphorus atomic d orbital functions.

Results and Discussion

The products of the reactions of most nucleophiles with $Fe_2Co(CO)_9CCO^-$ have the nucleophile bound at the β-

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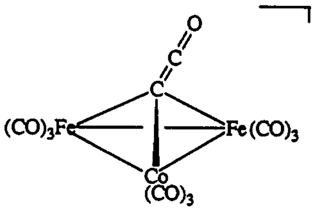

Figure 1. Structure of the anionic carbonyl cluster $Fe_2Co(CO)_9CCO^-$.

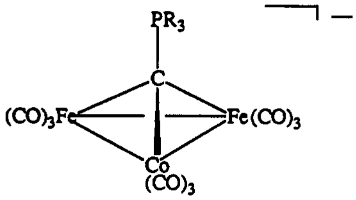

Figure 2. Structure of the product of the reaction of $Fe_2Co(CO)_9CCO^-$ and phosphines.

carbon atom of the ketenylidene group, the most positively charged site in the complex.[8] In $Fe_2Co(CO)_9CCO^-$, for example, our calculations indicate that the β-carbon atom has a charge of +0.50; in $Co_3(CO)_9CCO^+$ the β-carbon atom has a charge of +0.51. Nucleophilic attack by phosphines upon the anionic $Fe_2Co(CO)_9CCO^-$ cluster gives an unusual result.[9-12] The product has the nucleophile bound to the negatively charged α-carbon atom of the ketenylidene group instead of to the positively charged β-carbon atom. The computed charge on the α-carbon atom in the reactant $Fe_2Co(CO)_9CCO^-$ is −0.61. Thus the lone pair on the phosphorus atom is donated to the atom with the least favorable coulombic interaction. The molecular orbital calculations shed light on this reaction. The reaction is slow enough that it can be experimentally followed by both IR and NMR spectroscopy.[9-12] Such studies show that the final site of bonding, the α-carbon atom of the ketenylidene group, is not the initial site of attack. Instead, the incoming phosphine initially bonds to the cobalt atom. The evidence for this comes from the ^{31}P and ^{59}Co NMR spectra.[9,10] The ^{31}P NMR peak is broadened because the phosphorus atom is attached to the quadrupolar Co nucleus. The ^{59}Co NMR peaks are considerably shifted when a phosphorus atom is bound to them.

In all cases, i.e. several different phosphines, the phosphorus atom attacks at the Co atom, never at an iron atom. Though no experimental reason for this is found or suggested,[10,11] our calculations reveal that both orbital and charge considerations favor attack at the Co atom. As shown in Table I, the atomic orbital that has the highest percentage contribution to the LUMO of the starting $Fe_2Co(CO)_9CCO^-$ is the d_{xy} of the Co atom. Figure 3 is a view of this cluster from the positive x-axis. This perspective, computed by geometry optimization using PC Model, shows how open the cobalt atom is to attack from this direction. This orbital points in a sterically favorable direction. In addition, the charge on the Co atom, −0.20, aids in attracting the positively charged P atom (+0.47 in PMe_3). The charges on the iron atoms in $Fe_2Co(CO)_9CCO^-$, +0.09 and +0.05, repel rather than attract the phosphorus atom. The ketenylidene group is absent from the LUMO.

Donation of the phosphorus lone pair into the LUMO of $Fe_2Co(CO)_9CCO^-$ changes the bonding in the cluster. Recently, the effect of addition of electrons to the LUMO of a triiron cluster has been examined electrochemically and theoretically using extended Hückel molecular orbital calculations.[17] We have used this approach to elucidate the mechanism of the reaction of trimethylphosphine with $Fe_2Co(CO)_9CCO^-$. It has been proposed that the mechanism of the reaction involves rupture of either a Co–Fe bond or of the Co–α-C bond.[11] Table II shows the effect of occupation of the LUMO on the overlap populations between the relevant atoms. These calculations were done in two ways. The effect of LUMO occupancy on the overlap populations was initially done using the molecular orbitals of $Fe_2Co(CO)_9CCO^-$. These results are given in column 3 of Table II. Column 4 gives the results of the same calculation using the results of a Fenske–Hall calculation done on $Fe_2Co(CO)_9CCO^{3-}$. In this way a comparison can be made of the validity of using a virtual orbital versus using an optimized orbital for the LUMO. As seen in Table II, the results computed in these two ways are nearly the same. They show that occupation of the LUMO weakens the interaction between the cobalt atom and the α-carbon atom by 10% and actually strengthens the interaction between the cobalt atom and terminal carbon atoms. On the other hand, the metal–metal bonds are weakened. In particular, the Co–Fe interactions become repulsive. Thus the calculations clearly favor the mechanism in which the α-carbon atom remains triply bridging and a Co–Fe bond breaks.

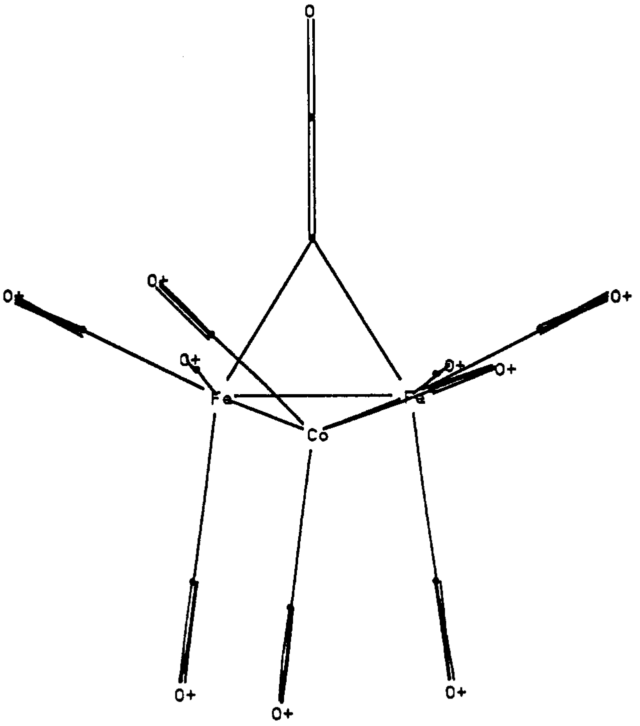

Figure 3. View along the x-axis of the geometry-optimized structure of $Fe_2Co(CO)_9CCO^-$.

Table II. Effect of LUMO Occupancy on Overlap Populations

	overlap population		
bond	LUMO empty	$Fe_2Co(CO)_9CCO^-$ LUMO occupied	$Fe_2Co(CO)_9CCO^{3-}$ LUMO occupied
Co–α-C	+0.42	+0.39	+0.38
Co–t-C	+0.82	+0.86	+0.81
Co–Fe1	+0.09	−0.10	−0.10
Co–Fe2	+0.11	−0.04	−0.08
Fe1–Fe2	+0.13	+0.02	+0.01

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Table III. Comparison of Bonding of Carbide to CO and PMe$_3$

cluster	HOMO–LUMO overlap population	electrons lost from HOMO	ligand charge	donor atom charge
$Fe_2Co(CO)_9CCO^-$	0.16	0.82	−0.52	−0.12
$Fe_2Co(CO)_8CPMe_3^-$	0.25	1.04	+0.50	+0.47

Once attached to the Co atom, the phosphine then migrates to the α-carbon atom of the ketenylidene group. Our calculations demonstrate that this migration is quite reasonable. Molecular orbital calculations were done on $Fe_2Co(CO)_9CPMe_3^-$ using both the atomic basis and the fragment basis approaches. Table III compares how the carbide bonds to the two ligands, CO and PMe$_3$. The overlap populations between the carbide and the two ligands are comparable. The total overlap population between the carbide and the carbon atom of CO is 1.54; the total overlap population between the carbide and the phosphorus atom of PMe$_3$ is 1.40. On the other hand, when the orbitals of PMe$_3$ and the hypothetical fragment $Fe_2Co(CO)_9C^-$ are used as input for the calculation on $Fe_2Co(CO)_9CPMe_3^-$, the results show that the overlap population between the HOMO of the incoming nucleophile PMe$_3$ and the LUMO of $Fe_2Co(CO)_9C^-$ has a value of 0.25. Similar calculations done with CO instead of PMe$_3$ gives a smaller overlap population of 0.16 between the HOMO of $Fe_2Co(CO)_9C^-$ and an incoming CO.

The amount of electron density transferred from the incoming nucleophile to the $Fe_2Co(CO)_9C^-$ framework is greater when PMe$_3$ is attached than when CO is attached to the carbide. The fragment basis calculations on $Fe_2Co(CO)_9CPMe_3^-$ reveal that the HOMO of PMe$_3$ loses 1.04 electrons to $Fe_2Co(CO)_9C^-$. This transfer of electrons is 27% larger than the 0.82 electrons lost by the CO HOMO when $Fe_2Co(CO)_9CCO^-$ is formed. Another way of viewing the electron flow onto the metal framework is by using the net charge on the two groups. The computed charge on PMe$_3$ is +0.50 in $Fe_2Co(CO)_9CPMe_3^-$. The net charge on the CO of CCO in $Fe_2Co(CO)_9CCO^-$ is −0.52. Thus the $Fe_2Co(CO)_9C$ framework has one full electron more when bonded to PMe$_3$ than when bonded to CO.

And, finally, the charge on the phosphorus atom of PMe$_3$ is +0.47 compared with a charge on the C, i.e. the β-carbon atom, of CO of −0.12. Our calculations reveal that nucleophiles which attach at the β-carbon atom all have negative charges on the atom that bonds to the positively charged β-carbon atom. For example, the charge on the carbon atom in LiCH$_3$ is −0.63; the charge on the oxygen atom in NaOCH$_3$ is −0.84. Thus the calculations show that the phosphorus atom in PMe$_3$ is quite different from these other nucleophiles.

Fenske–Hall calculations on triethylphosphine indicate a charge of +0.38 on the phosphorus atom. Less coulombic attraction exists, therefore, between the cobalt atom and the phosphorus atom in triethylphosphine than between the cobalt atom and the phosphorus in trimethylphosphine. One expects, then, that the rate of reaction of the cluster with trimethylphosphine will be faster than its reaction with triethylphosphine. It is known that trimethylphosphine reacts with $Fe_2Co(CO)_9CCO^-$ at a rate that is 13 times faster than the rate of the reaction with triethylphosphine.[11] We consider the charge difference between the phosphorus atoms in the two phosphines to be too small to wholly account for this rate difference. In addition, our calculations show that the HOMO's of the two phosphines are essentially identical. Both HOMO's are mainly composed of the p_z orbital of the phosphorus atom. The trimethylphosphine has 75% p_z of the phosphorus atom, while the triethylphosphine has 72% p_z of the phosphorus atom. The electronic similarity of the two phosphines supports the suggestion that steric effects play an important role in the relative rates of these associatively activated reactions.[11]

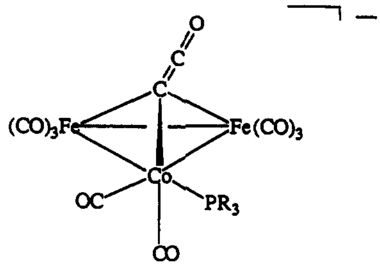

Figure 4. Intermediate in the reaction between $Fe_2Co(CO)_9CCO^-$ and phosphines.

Our calculations are in agreement with experimental data that support the idea that PMe$_3$ bonds better to the carbide atom in this trinuclear cluster than does CO. When the phosphine replaces the CO on the carbide position, the ^{13}C NMR peaks of the terminal carbonyls are shifted in the proper direction for increased electron density being present.[10] The IR peaks of the terminal carbonyls are shifted to lower frequencies when the more basic phosphines are present, indicating a better transfer of electrons.[10] It has also been noted that when the phosphorus atom is bound to the carbide atom, the terminal CO IR peaks are at lower frequencies than when the phosphorus atom is bound to the Co atom.[10] This suggests that the phosphorus atom donates electrons to the cluster better when it is on the carbide than when it is attached at a metal site. Comparison of the results of our calculations on $Fe_2CoPMe_3(CO)_8CCO^-$, shown in Figure 4, and $Fe_2Co(CO)_9CPMe_3^-$ demonstrates that the migration of the phosphorus to the carbide position is possible not only because the phosphorus bonds better to the carbide than does the CO, but also because the phosphorus bonds better to the carbide than it does to the cobalt atom. Atomic basis calculations indicate that in $Fe_2Co(CO)_9CPMe_3^-$ the total overlap population between the phosphorus atom and the carbide is +1.40. In $Fe_2CoPMe_3(CO)_8CCO^-$ the total overlap population between the phosphorus atom and the cobalt atom is only +0.70. The charge on PMe$_3$ in $Fe_2Co(CO)_9CPMe_3^-$ is +0.50, whereas in $Fe_2CoPMe_3(CO)_8CCO^-$ the charge on PMe$_3$ isn only +0.15. Both the overlap population and the amount of electron density transferred indicate that bonding of the phosphorus atom to the carbide is favored over bonding the phosphorus to the cobalt atom. Thus the migration occurs and the added electron density transferred to the metal framework causes the observed spectral changes.

The reaction of $Fe_2Co(CO)_9CCO^-$ with PMe$_3$, seemingly at odds with the reactions of other nucleophiles with trinuclear carbonyl clusters, is made understandable by the Fenske–Hall calculations. The phosphine attacks at the Co atom because the cobalt has the greatest percentage contribution to the LUMO of the complex as well as the most negative charge of the metal atoms. The addition of the phosphine's electrons to the LUMO causes the Co–Fe interaction to become repulsive. Thus that bond breaks and the phosphorus atom attaches to the cobalt atom. The phosphine then rearranges to the carbide position because the bonding between the phosphorus atom and the carbide is more favorable than the bonding between the carbide and the β-carbon atom of the ketenylidene group and more favorable than the bonding between the phosphorus atom and the cobalt atom.

If the phosphine cluster, $Fe_2Co(CO)_9CPMe_3^-$, is reacted with acid, the H^+ ends up bridging the two Fe atoms, never bonded to the Co. The molecular orbital calculations reveal that the nature of the HOMO of $Fe_2Co(CO)_9CPMe_3^-$ is perfectly suited for this position of attack. The HOMO of $Fe_2Co(CO)_9CPMe_3^-$ is composed of 29% Fe1 and 28% Fe2 orbitals and only 3% Co orbitals. Migration to the carbide, which occurs in $Fe_2Co(CO)_9CCO^-$, is prevented by the superior bonding of the phosphorus atom to the carbide.

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Comparison of the Dynamics and Thermodynamics of the Redox-Promoted Carbonylation of (η-Cp)(CO)(L)FeMe in Methylene Chloride and Acetonitrile. Applications of the Quantitative Analysis of Ligand Effects (QALE)

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The redox-catalyzed carbonylations of 19 complexes, (η-Cp)(CO)(L)FeMe (L = PMe_3, $PPhMe_2$, PEt_3, PPh_2Me, PEt_2Ph, PPh_2Et, $P(i\text{-}Bu)_3$, $P(p\text{-}Me_2NC_6H_4)_3$, $P(p\text{-}MeOC_6H_4)_3$, $P(p\text{-}MeC_6H_4)_3$, PPh_3, $P(p\text{-}FC_6H_4)_3$, $P(p\text{-}ClC_6H_4)_3$, $P(p\text{-}CF_3C_6H_4)_3$, PPh_2Cy, $PPh_2\text{-}t\text{-}Bu$, $P(i\text{-}Pr)_3$, $PPhCy_2$, PCy_3), in acetonitrile have been studied by cyclic and square-wave voltammetry coupled with computer simulation methods. The mechanism appears to involve oxidation of (η-Cp)(CO)(L)FeMe and rapid formation of (η-Cp)(AN)(L)$FeCOMe^+$ followed by rate-limiting reaction of (η-Cp)(AN)(L)$FeCOMe^+$ with CO. Quantitative analysis of the ligand effect data shows that the second-order transformation of (η-Cp)(CO)(L)$FeMe^+$ to (η-Cp)(AN)(L)$FeCOMe^+$ is accelerated by poorer electron donor ligands and inhibited by the larger ligands. The first-order back-reaction of (η-Cp)(AN)(L)$FeCOMe^+$ to (η-Cp)(CO)(L)$FeMe^+$, in contrast, is relatively insensitive to the electron-donor capacity and the size of L. The second-order reaction between (η-Cp)(AN)(L)$FeCOMe^+$ and CO is accelerated by better electron-donor ligands; the steric profile is complex and shows sequential regions of no steric effects, steric acceleration, and steric inhibition. The results of the studies are compared with those obtained when methylene chloride is the solvent.

Introduction

Recently, we reported results of electrochemical studies of the redox-promoted carbonylation of (η-Cp)(CO)(L)FeMe in methylene chloride containing tetrabutylammonium hexafluorophosphate.[1] The carbonylation proceeds via the iron(III) complexes (η-Cp)(CO)(L)$FeMe^+$ and apparently involves two steps (Scheme I). We suggested that the rate-limiting first step is the nucleophilically (PF_6^- or CH_2Cl_2) assisted alkyl to acyl rearrangement. This result is consisted with the earlier reports of Bergman,[2] Halpern,[3] Cotton,[4] Norton,[5] and Trogler,[6] who pointed out the importance of solvent participation in the alkyl to acyl rearrangement. The nature of the second step, the reaction between the solvent-coordinated acyl complex and CO, could not be probed, unfortunately, since this fast step is kinetically invisible in this medium. Analysis of the kinetic data for alkyl to acyl rearrangement in methylene chloride, as a function of the stereoelectronic properties of the ancillary phosphorus(III) ligands (L), revealed that the transition state for the rearrangement is electron rich compared to the ground state. The reaction is sterically inhibited for complexes containing L with cone angles (θ) <149°. For larger L, the reaction is sterically accelerated. These observations led us to suggest that the transition state possesses a very weakly bonded entering nucleophile (CH_2Cl_2 or PF_6^-) and an extensively formed acyl ligand.

In this paper, we report our study of the carbonylation of (η-Cp)(CO)(L)$FeMe^+$ in acetonitrile (0.1 M TBAH) under 1 atm of CO at 0 °C. Under these conditions the reaction of the solvent-coordinated acyl complex (η-Cp)(AN)(L)$FeCOMe^+$ with CO is rate-limiting, thereby allowing us to study the steps leading to the carbonylation product (η-Cp)(CO)(L)$FeCOMe^+$.

Experimental Section

General Considerations. All manipulations, preparations, and electrochemical experiments were carried out under argon using standard techniques as previously described.[1] Acetonitrile (AN, HPLC grade) was distilled from calcium hydride immediately before use. Mixtures of CO and argon were prepared using Matheson flow meters. The flow meters were calibrated by measuring the volume of pure gases and mixtures of gases that

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