The Role of Virtual Halogen d Orbitals in the Stability and Reactivity of Rhenium Alkyl Halide Complexes of the Form [(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(XR)]$^+$

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The electronic structure of the transition-metal Lewis acid [(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)]$^+$ and its coordination to the Lewis bases I$^-$, ICH$_3$, and CH$_2$Cl$_2$ are investigated via Fenske–Hall molecular orbital calculations on the prototype species [(η^5-C$_5$H$_5$)Re(NO)(PH$_3$)]$^+$. In each case, electron density is transferred from the ligand to the metal center in a classic Lewis acid–base interaction. The alkyl halide ligands alkylate a variety of nucleophiles, and the reaction coordinate for these processes is studied. From the calculations it is revealed that extra virtual d orbitals must be included in the basis set of the halogen atoms in order to explain the reaction chemistry. Use of this extended basis set places a significant portion of the LUMO's wave function on the halogen atom, as suggested by experiment. The activation of halocarbon ligands occurs as a consequence of the character and geometry of the lowest virtual levels of the complexes and not a prior weakening due to coordination with the metal.

Introduction

The oxidative addition of an alkyl halide to a coordinatively unsaturated transition-metal fragment is a key step in a number of important catalytic and stoichiometric processes.[1] Hence, the variety of new, stable transition-metal alkyl halide complexes that have recently become available can be expected to aid our understanding of the mechanisms of these reactions. Further, there is the potential that alkyl halide complexes may exhibit unusual reactivity that can be applied in organic and organometallic synthesis.

In a paper coauthored by one of the authors of this present work the experimental studies of an easily accessible class of *chiral* alkyl halide complexes is described.[2] The fragment [(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)]$^+$ is found to make isolable complexes of alkyl iodides and somewhat more labile complexes of alkyl bromides and chlorides. It has been suggested[3] that in the alkyl halide complexes a bonding interaction between filled metal d orbitals and the C–X σ^* antibonding orbital may supplement the weak Lewis basicity of the ligand. Yet, subsequent crystal structures[2,3] have shown that the C–X bond lengths change little, if at all, from those in the free ligand. Nevertheless, when the alkyl halide complex is reacted with most nucleophiles, cleavage of the C–X bond preferentially occurs. Furthermore, these rates are much faster than those for the corresponding reactions of the free ligand.

The goal of this study is to (1) explain the nature of the bonding in these alkyl halide complexes and (2) understand the basis for the unusually high reactivity of the alkyl halide ligand toward nucleophiles. In the calculations to follow, the PH$_3$ ligand was utilized instead of the computationally more complex PPh$_3$ ligand. For the sake of brevity, the term "Re$^+$ fragment" will be substituted for [(Cp)Re(NO)(PH$_3$)]$^+$ and the symbol "Cp" will be used to designate the (η^5-C$_5$H$_5$) ligand. We have studied the Re$^+$ fragment along with its I$^-$, CH$_3$I, and CH$_2$Cl$_2$ adducts by using Fenske–Hall and natural bond theory calculations.

Calculational Details

The calculations in this work were completed on a VAX 8650 computer using the Fenske–Hall approximate MO

method[4] as well as the natural bond orbital (NBO) analysis of Weinhold and co-workers.[5] Interatomic distances and angles were idealized from X-ray crystallographic data.[2] The P–Re–I–C torsion angle in the methyl iodide complex was set at 180°. The description of bonding in the compounds studied is not altered by these structural modifications. Triphenylphosphine (PPh$_3$) ligands were modeled by PH$_3$ in order to make the computations more tractable. All Cp rings were idealized to D_{5h} symmetry with C–C distances of 1.41 Å and C–H distances of 1.09 Å.

The STO basis functions for carbon, nitrogen, and oxygen were those of Clementi.[6] Double-ζ representations were kept for the valence p orbitals of each atom. The other s and p functions were curve fit to single-ζ in order to minimize the number of exponents. The hydrogen exponent was set at 1.16. The "best atom" functions were used for chlorine and iodine. As will be discussed later, two sets of calculations, with and without extra halogen d orbitals, were carried out. These extra virtual d orbitals were Schmidt orthogonalized to the core orbitals and given an exponent of 1.30. The rhenium functions were obtained by projecting an atomic Xα–SW calculation on a set of optimized, orthonormal Slater-type orbitals.[7] The 6s and 6p exponents on the metal were set at 2.30. These functions are less diffuse than atomic results but are found to describe bonding in organometallic complexes more accurately.[8]

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Table I. Mulliken and Natural Electron Populations of Key Atomic Orbitals in (Cp)Re(NO)(PH₃)(I), before and after Coordination

	I 5p_z		Re 5$d_{x^2-y^2}$		Re 6s		Re 6p_y	
	I⁻	Re–I[a]	Re⁺[b]	Re–I	Re⁺	Re–I	Re⁺	Re–I
Mulliken	2.000	1.355	0.748	0.859	0.300	0.359	0.067	0.228
NBO	2.000	1.455	0.743	0.857	0.382	0.503	0.019	0.048

[a] Re–I refers to (Cp)Re(NO)(PH₃)(I). [b] Re⁺ refers to the fragment [(Cp)Re(NO)(PH₃)]⁺.

All calculations were performed by using the transformed basis approach.[9] Initially, the ligands were converged as discrete molecules: nitrosyl as NO⁺, cyclopentadienyl as Cp⁻, and PH₃, CH₃I, and CH₂Cl₂ as neutral species. Then, the resulting molecular orbitals were allowed to interact with the central rhenium atom in a final run.[10]

The molecular orbital wave functions were analyzed via the natural bond orbital (NBO) procedure of Weinhold et al.[5] In the NBO method, any wave function, regardless of origin,[11] is essentially localized into the "best" possible Lewis structure of NBOs. The NBOs are constructed from natural hybrid orbitals (NHOs) that are not unlike the traditional hybrid orbitals used so frequently in organic chemistry. The method attempts to localize the NBOs specifically as core orbitals, lone pairs, bonds, and antibonds. Since NBOs do not form a basis for an irreducible representation of the exact wave function, a calculated Lewis structure cannot totally represent the wave function. However, over 97% of the electron density is accounted for in the calculated Lewis description in the rhenium system. Departures from the ideal structure occur with partial occupancy of antibonding and Rydberg (non-Lewis type) orbitals.

In addition, we have made use of a feature of the NBO method called natural population analysis. The procedure provides an alternative to the Mulliken population analysis.[5d] In the Mulliken scheme, diffuse "unfilled" metal s and p orbitals are often overemphasized when electrons are summed in transition-metal compounds. This results in a metal atom having more negative charge than intuition would suggest. Use of natural orbitals eliminates the overlap partitioning problem of the traditional scheme while retaining important features such as generality, simplicity, and ease of application.

Bonding in the Complexes

a. [(Cp)Re(NO)(PPh₃)]⁺ and (Cp)Re(NO)(PPh₃)(I). The d⁶, 16-valence-electron Lewis acid [(Cp)Re(NO)-(PPh₃)]⁺ coordinates a variety of Lewis bases. Its reaction chemistry occurs with retention of configuration at the rhenium center, suggesting a chiral, pyramidal ground state.[2] Theory agrees with this formulation of the fragment as a pseudooctahedral complex with an empty coordination site.[12]

Our calculations indicate that the LUMO of the Re⁺ fragment is primarily a rhenium hybrid directed toward the empty site. The orbital contour plot of this wave function, shown in Figure 1, illustrates this clearly. The Re 5$d_{x^2-y^2}$, 6s, and 6p_y atomic orbitals make up about two-thirds of its character. It is this orbital that accepts

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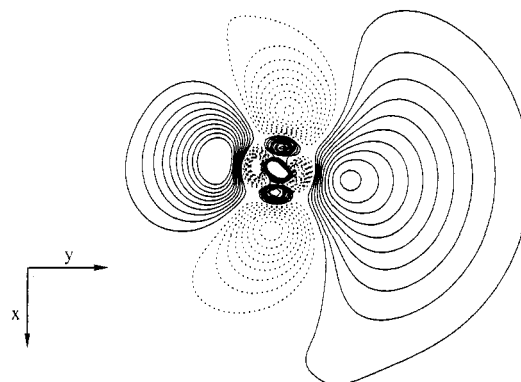

Figure 1. Contour diagram for the LUMO of [(Cp)Re(NO)-(PH₃)]⁺. Values shown are ±0.025, ±0.050, ±0.075, ±0.100, ±0.125, ±0.150, ±0.175, ±0.200, ±0.225, ±0.250. Negative values are indicated by dashed contours. A partial local coordinate system for the rhenium atom is shown.

electron density from a donor lone pair.

We analyzed the stable iodide complex (CP)Re(NO)(PH₃)(I) in order to view the donor–acceptor relationship of a ligand and the Re⁺ fragment.
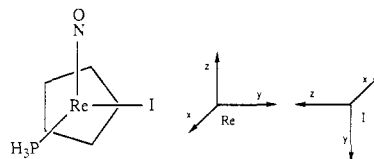
By observing atomic orbital populations before and after coordination, we see from Table I that more than half of an electron is lost from the iodine 5p_z orbital, while the population of the orbitals in the metal fragment increases. The result of the interaction is the formation of a single bond of σ symmetry, polarized toward the iodine atom. The loss of electron density in the iodine 5p_z orbital is not fully accounted for in the gains that occur in the listed rhenium orbitals. The additional density is delocalized in small increases in other centers throughout the molecule as a whole.

b. CH₃I and [(Cp)Re(NO)(PPh₃)(ICH₃)]⁺. Next, we examined the similarities and differences between the electronic structure of the neutral methyl iodide molecule and that of the methyl iodide ligand in [(Cp)Re(NO)-(PPh₃)(ICH₃)]⁺. Of primary concern is the effect of coordination upon the C–I bond. The results of MO calculations should show whether or not a metal d → σ* interaction is responsible for the stability of this species and its partial activation of the C–I bond which would facilitate cleavage of the bond. In addition, we carried out calculations on each species with and without extra halogen d orbitals in order to view any possible alterations in the bonding description due to their inclusion.

MO diagrams of methyl iodide are presented in Figure 2. It is clear that the occupied molecular orbitals in the ground-state electronic structure of this compound are unaffected by the expansion of the basis set to include iodine 5d functions. The filled orbitals that are shown fall into three categories: levels 6, 8, and 9 are the carbon–

Table II. Mulliken and Natural Electron Population of Key Atomic Orbitals in [(Cp)Re(NO)(PH₃)(ICH₃)]⁺, before and after Coordination

	I 5p$_z$		Re 5d$_{x^2-y^2}$		Re 6s		Re 6p$_y$	
	CH₃I	Re–I–CH₃⁺	Re⁺ [b]	Re–I–CH₃⁺	Re⁺	Re–I–CH₃⁺	Re⁺	Re–I–CH₃⁺
Mulliken	1.952	1.470	0.748	0.856	0.300	0.357	0.067	0.243
	1.956[c]	*1.418*		*0.825*		*0.384*		*0.259*
NBO	1.954	1.556	0.743	0.830	0.382	0.502	0.019	0.052
	1.950[c]	*1.501*		*0.874*		*0.510*		*0.055*

[a] Re–I–CH₃⁺ refers to [(Cp)Re(NO)(PH₃)(ICH₃)]⁺. [b] Re⁺ refers to the fragment [(Cp)Re(NO)(PH₃)]⁺. [c] Use of italics indicates that the iodine basis set included 5d orbitals.
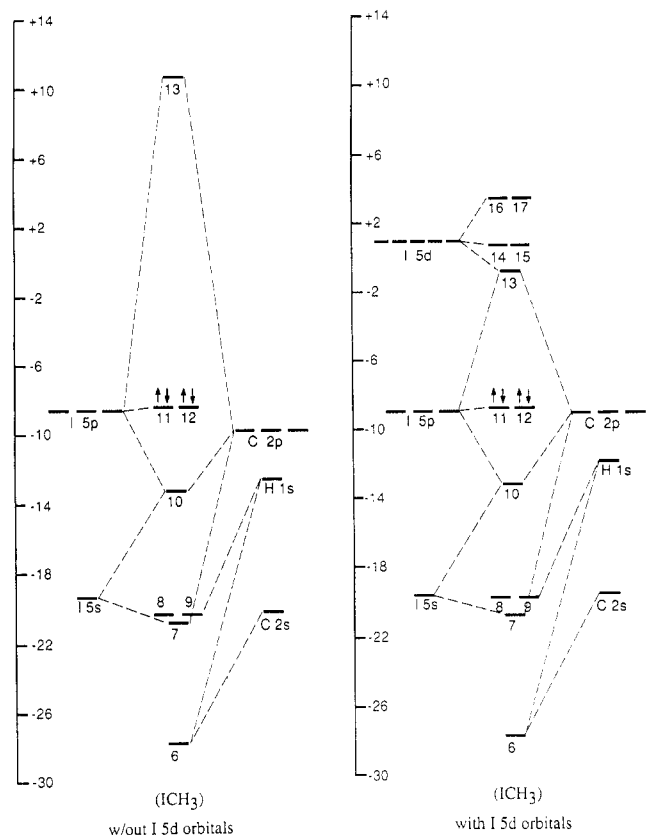

Figure 2. Molecular orbital diagrams for ICH₃ with a minimal basis set and an extended basis set including iodine 5d orbitals. Energies are expressed in electronvolts.

Figure 3. Molecular orbital diagrams for [(Cp)Re(NO)(PH₃)-(ICH₃)]⁺ with a minimal basis set and an extended basis set including iodine 5d orbitals. L refers to ICH₃ ligand molecular orbitals, PH4 to the phosphine HOMO lone pair, and Cp12 and Cp13 to the degenerate set of highest filled levels in C₅H₅⁻. Ld indicates the use of the I 5d functions. Energies are expressed in electronvolts.

hydrogen bonding set, levels 11 and 12 are iodine p lone pairs, and levels 7 and 10 are part of a three-orbital interaction between carbon and iodine. In general three atomic orbitals that interact yield a bonding MO, a nonbonding MO, and an antibonding MO. Our diagram suggests the characterization of level 7 as a bonding orbital and level 10 as a nonbonding orbital.

While the occupied molecular orbitals of CH₃I are essentially unaffected by inclusion of the 5d functions on the iodine, the characters and energetics of the *unfilled* molecular orbitals are substantially altered. For example, in a minimal basis set the LUMO of methyl iodide, the carbon–iodine antibond MO 13, is quite high in energy at 19 eV above the HOMO. Use of the 5d orbitals allows mixing to occur, resulting in a LUMO which is now over 50% iodine d in character. In addition, the mixing forces MO 13 to a position only 8 eV above the iodine p lone pairs. Thus, we see that the 5d orbitals are not important in the bonding of the isolated ligand yet help ensure a more realistic placement of the virtual molecular orbitals.[8]

When methyl iodide coordinates to the Re⁺ fragment, the resultant complex [(Cp)Re(NO)(PH₃)(ICH₃)]⁺ exhibits similar bonding characteristics to those when iodide ion is the ligand. By monitoring Mulliken and natural popu-

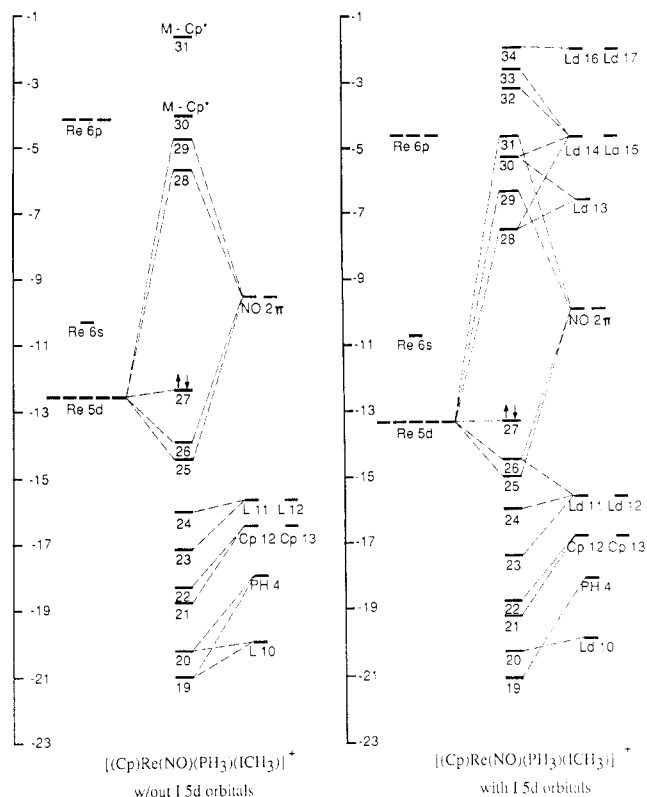lations in the same manner as above, we can evaluate the donating ability of this ligand. The atomic orbital populations, found in Table II, indicate that the amount of electron density donated to the metal is about 75% of that in (Cp)Re(NO)(PH₃)(I).

The MO calculations of the Re⁺–ICH₃ complex, with and without I 5d orbitals, indicate that electronic rearrangement upon bond formation proceeds as expected. The interaction diagrams in Figure 3 show that, in general, the highest filled ligand MOs interact with the rhenium d orbitals in order to lower their energy. A net donation of electron density from the ligand to the metal occurs. Of course, the nitrosyl ligand takes part in a classic backbonding interaction with the metal atom resulting in levels 25 and 26. Also, one d orbital, the d$_{xy}$, comes across essentially unperturbed, due to the fact that no ligand orbitals are of appropriate symmetry to interact with it to any great extent.

In light of our stated goals, we are also interested in observing how the unfilled orbitals of the methyl iodide ligand are affected. The NBO method, being a type of the localized valence bond theory, calculates the population

Table III. Mulliken and Natural Populations of Key Orbitals in [(Cp)Re(NO)(PH₃)(ICH₃)]⁺ with and without Attacking PH₃

	Mulliken pop. of MO 13[a]		natural pop. of I–C σ^*	
	without I 5d	with I 5d	without I 5d	with I 5d
no PH₃	0.012e	*0.038e*	0.020e	*0.038e*
2.50 Å	0.182e	*0.380e*	0.164e	*0.149e*

[a] MO 13 is the LUMO in the Fenske–Hall calculation of methyl iodide (see Figure 2). Recall that MO 13 and I–C σ^* are *unfilled* before coordination to the rhenium atom.

of antibonds and Rydberg levels as part of its usual procedure. This function is useful in monitoring delocalization from bonding orbitals or lone pairs into unfilled levels. It may then be possible to spot electronic instability in a bond. Analogous information is derived in the Fenske–Hall approach by the use of transformed basis sets. One can observe fragment or ligand molecular orbitals being populated or depopulated when placed in a new environment.

For example, the partial occupation of the LUMO of methyl iodide, MO 13, can be indicative of potential weakening of the iodine–carbon σ bond. This is due to the fact that although MO 13 is substantially localized on the iodine atom, it is technically antibonding between the iodine and the carbon. As shown in Table III, the orbital becomes only slightly populated when bound to the Re⁺ fragment. The calculated values are miniscule when compared to classic back-bonding situations. The population of MO 13 is about 0.038e whereas the two nitrosyl 2π orbitals, which are π antibonding in character, have natural populations of about 0.45 electron each. Therefore, we conclude from our calculations that there is little or no weakening of the iodine–carbon σ bond in methyl iodide as a consequence of coordination to the Re⁺ moiety.

The differences between the use of a minimal basis set as opposed to including I 5d functions are analogous to those in the discrete ligand; that is, in the ground-state description of the molecule, unfilled halogen d orbitals play little or no part in the bonding, while the character of the unfilled molecular orbitals changes drastically. Later, we will examine calculations that suggest the use of the extended basis set is necessary in helping to explain the site of nucleophile attack and the cleavage of the iodine–carbon bond in this system.

c. [(Cp)Re(NO)(PPh₃)(ClCH₂Cl)]⁺. The dichloromethane complex [(Cp)Re(NO)(PPh₃)(ClCH₂Cl)]⁺ has been characterized by NMR and IR and has been shown to be a versatile precursor for a number of substitution and exchange reactions.[2d] In addition, the related pentamethylcyclopentadienyl species [(η⁵-C₅Me₅)Re(NO)(PPh₃)(ClCH₂Cl)]⁺ undergoes similar substitution reactions, while thermal decomposition affords the oxidative addition product [(η⁵-C₅Me₅)Re(NO)(PPh₃)(Cl)(CH₂Cl)]⁺.[2c] Calculations on the dichloromethane complexes were thus undertaken to supplement the foregoing work on the methyl iodide complex as well as yield information about some important reaction chemistry.

Coordinated dichloromethane perturbs the Re⁺ fragment in a manner very similar to methyl iodide. Transfer of electron density from a chlorine p orbital into a rhenium d hybrid occurs. CH₂Cl₂ is an useful ligand because we can observe any back-bonding in relation to a sort of "control" σ^* bond, the other Cl–C pair:
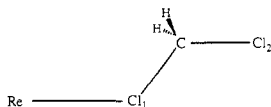
Table IV. Natural Bond Orbital Populations of Cl–Cσ^* Antibonds in CH₂Cl₂ and [(Cp)Re(PH₃)(ClCH₂Cl)]⁺

	natural pop.	
	without Cl 3d	with Cl 3d
Cl–Cσ^* in CH₂Cl₂	0.020e	*0.019e*
Cl₁–Cσ^* in complex	0.036e	0.097e
Cl₂–Cσ^* in complex	0.015e	0.015e
Cl₁–Cσ^* in complex after Br⁻ attack	0.071e	0.145e

There is evidence that the Cl₁–C σ^* antibond is mildly affected by coordination to the rhenium center (Table IV). In addition, the inclusion of virtual 3d functions in the chlorine basis set enhances the delocalization; we see that the Cl₁–C σ^* antibond has an occupation nearly 0.080e greater than in the discrete dichloromethane molecule. However, the observed magnitudes do not indicate that back-bonding or the "π-acidity" of the ligand is *primarily* responsible for the stability of the molecule although such effects may influence conformation.[13]

Reactions with Nucleophiles

In the experimental studies on this class of compounds it has been noted that alkyl halide complexes of the form [(Cp)Re(NO)(PPh₃)(XR)]⁺ BF₄⁻ are particularly reactive alkylating agents.[2a] For example, in the methyl iodide complex, the C–I bond is cleaved with the addition of triphenylphosphine, giving the phosphonium salt Ph₃PR⁺BF₄⁻ and Re⁺–I⁻. Similar reactions are observed with ethyl and propyl iodide complexes. Also, coordinated dichloromethane is activated by Br⁻ yielding Re⁺–Cl⁻ and CH₂ClBr.[2d] By performing calculations with the incoming nucleophiles (PH₃ or Br⁻) at various distances and geometries, one is able to observe a weakening of the halogen-carbon bond by a substantial increase in the population of the antibond and a lowering of overlap populations.

These calculations are informative for a number of reasons. First, they clearly indicate that d orbitals should be included in the basis set for molecules of this type. When a minimal basis set is used, the two lowest molecular orbitals of [(Cp)Re(NO)(PH₃)(ICH₃)]⁺ are obviously the antibonding counterparts of the Re d → NO $2\pi^*$ antibonding interaction (Figure 3). In addition, in the field of the Re⁺ fragment, methyl iodide MO 13 has an energy of +5.08 eV. In light of this information, the observed chemistry would seem to run counter to the general rule that orbitally controlled nucleophilic attack occurs at the LUMO.[14] However, as mentioned earlier, the character of the MOs in the Re⁺–ICH₃ complex is altered significantly with the use of iodine 5d functions. The countour plot of the LUMO, with d orbitals, indicates that iodine is the principle contributor to this orbital (Figure 4).

Although it cannot be specified from the contour diagram or the percent characters of the orbitals in the LUMO whether the I–C or the Re–I bond will be broken upon reaction with a phosphine, the calculations do provide a good orbitally based argument that nucleophilic attack by PH₃ at the iodine atom in the Re⁺–ICH₃ complex would facilitate the observed exchange reactions. To understand the breaking of the I–C bond, one must turn to Mulliken and natural orbital populations. The values presented in Table III show that the carbon–iodine bond begins to weaken when the attacking PH₃ ligand approaches to

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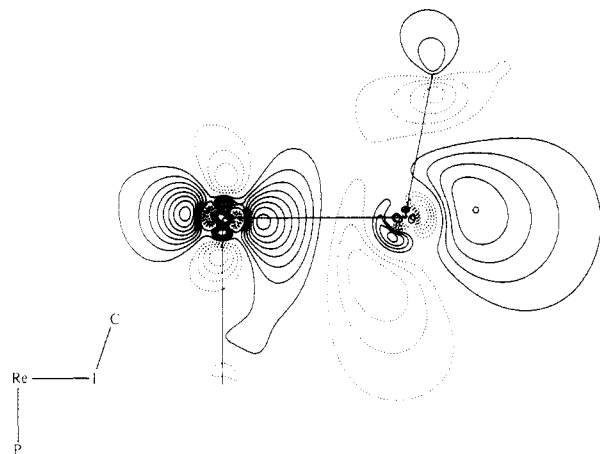
Figure 4. Contour diagram for the LUMO of [(Cp)Re(NO)-(PH$_3$)(ICH$_3$)]$^+$. Values shown are ±0.025, ±0.050, ±0.075, ±0.100, ±0.125, ±0.150, ±0.175, and ±0.200. Negative values are indicated by dashed contours. The plane that is plotted contains the atoms P, Re, I, and C in the geometry shown. The primary percent characters of the LUMO are I 5d$_{z^2}$ (36.7%), I 5p$_z$ (15.6%), Re 5d$_{x^2-y^2}$ (15.2%), and NO 2π (10.6%).

Table V. Atomic Overlap Populations of the Principle Iodine/Carbon and Rhenium/Iodine Interactions in [(Cp)Re(NO)(PH$_3$)(ICH$_3$)]$^+$, with and without Attacking PH$_3$[a]

	overlap pop.	
AO interaction	before attack	after attack
I 5p$_x$/C 2p$_z$	0.379e	0.318e
Re 6s/I 5p$_z$	0.107e	0.080e
Re 6p$_y$/I 5p$_z$	0.157e	0.119e
Re 6p$_y$/I 5d$_{z^2}$	0.002e	0.044e
Re 5d$_{xy}$/I 5d$_{xz}$	0.127e	0.151e
Re 5d$_{yz}$/I 5d$_{yz}$	0.072e	0.093e
Re 5d$_{x^2-y^2}$/I 5p$_z$	0.131e	0.112e
Total—6 chief Re–I interactns	0.596e	0.599e

[a] The iodine–phosphorus distance is 2.5 Å after attack.

within 2.5 Å of the iodine atom along the iodine negative z axis. The approximate atomic separation for a phosphorus–iodine bond is 2.5 Å.[15]

Atomic overlap populations are another measure of the extent of bonding between two atoms (see Table V). The carbon 2p$_z$/iodine 5p$_x$ interaction is the primary one involved in the carbon–iodine bond. There is a marked decrease in this overlap population on approach by PH$_3$. Though the description of the perturbation of the rhenium–iodine bond is slightly more complex, the sum of the atomic overlap populations that are principally involved is virtually unchanged after attack. This information shows that approach of the phosphine lone pair prefer-

entially weakens the I–C bond rather than the Re–I bond.

The contour plot *does* reveal why attack at the iodine atom is so effective along the iodine negative z axis. The large lobe extending out the back of the metal–halogen bond is mainly I 5d in character and is easily accessible to the lone pair of the phosphine. These results strongly suggest that nucleophilic attack at the iodine will result in *retention* of configuration at the carbon center in marked contrast to the conventional view of S$_N$2 attack at carbon which results in *inversion* of configuration. Studies to examine this proposal are currently in progress.

The same procedure was applied to the dichloromethane complex with bromide ion acting as the nucleophile. Although no molecular orbital is clearly identifiable as the Cl$_1$–C σ^* antibond, the localized natural bond description does identify such an orbital. Approach of the bromide ion toward Cl$_1$ in the identical fashion as above causes the same changes as in the methyl iodide complex; the nucleophile increases the occupation of the Cl$_1$–C antibonding orbital (Table IV).

The nature of the NBO approach yields another piece of information that reinforces our conclusions. In determining the best possible Lewis structure of a molecule with a given wave function, natural bond orbitals as applied to metal complexes have been required to fulfill an occupation threshold of 1.5e in order for a bond to be described.[11] The rest of the valence electrons are then distributed as lone pairs. In Re$^+$–CH$_2$Cl$_2$, the threshold was not met, indicating a highly ionic interaction between the fragments. However, attack by Br$^-$ results in the construction of a single bond of σ symmetry between Re and Cl$_1$, while simultaneously resulting in the aforementioned occupation of the Cl$_1$–C antibond, thus setting the stage for elimination of CH$_2$ClBr. Therefore, the NBO localized description of the bonding in this molecule rationalizes the observed chemistry.

Summary

Our calculations show that the bonding of halide and alkyl halide ligands to (Cp)Re(NO)(PPH$_3$)$^+$ occurs through a simple acid–base, donor–acceptor interaction. The nature of the carbon–halogen bonds is not perturbed to any great extent. Contrary to some speculation, the postulated stabilization effect of metal d → carbon–halogen σ backbonding is not seen in the Fenske–Hall *or* NBO approach. The inclusion of extra virtual d orbitals on the halogen atoms significantly affects the character of nearby unfilled levels, but no change is seen in the bonding of the ground-state parent molecules. The extended basis set is necessary to explain the observed weakening of the C–X bond during nucleophilic attack. Therefore, this study concludes that the activation of the ligands occurs due to the identity of the lowest virtual levels and not a prior weakening due to coordination with the metal.

(15) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, 1984; pp 568, 966.