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Ab Initio Molecular Orbital Study of Substituent Effects in Vaska Type Complexes (*trans*-IrL$_2$(CO)X): Electron Affinities, Ionization Potentials, Carbonyl Stretch Frequencies, and the Thermodynamics of H$_2$ Dissociative Addition

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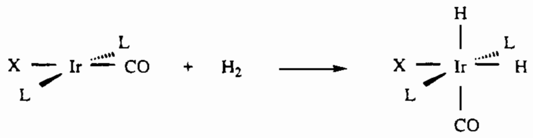
Ab initio electronic structure calculations are used to study substituent effects in Vaska-type complexes, *trans*-IrL$_2$(CO)X (**1-X**) (X = F, Cl, Br, I, CN, H, CH$_3$, SiH$_3$, OH, and SH; L = PH$_3$). Both the electron affinity and the ionization potential of **1-X** are computed to increase upon descending the halogen series of complexes, which indicates, surprisingly, that the complexes with more electronegative halogens are more difficult to reduce and easier to oxidize. The computed electron affinity trend is consistent with the half-wave reduction potential trend known for **1-X** (L = PPh$_3$; X = F, Cl, Br, and I). Computed carbonyl stretch frequencies for **1-X** are greater than experimental values (L = PPh$_3$), but observed trends are well reproduced. The redox and spectroscopic trends are discussed in terms of the substituent effects on the electronic structure of **1-X**, particularly as revealed in the molecular orbital energy level diagrams of these complexes. The reaction energy for H$_2$ addition to **1-X**, leading to the *cis,trans*-(H)$_2$IrL$_2$(CO)X (**2-X**) product, has been computed. After electron correlation effects are included (MP4(SDTQ)), the reaction enthalpy computed for **1-Cl** is −18.4 kcal/mol (L = PH$_3$) as compared to a reported experimental value of −14 kcal/mol (L = PPh$_3$). Compared with available experimental data, the electronic effects of L (L = PH$_3$, NH$_3$, or AsH$_3$) and X on the thermodynamics of the H$_2$ addition reaction are accurately reproduced by the model calculations at all levels of theory (HF and MPn). Formation of the hypothetical products *cis,trans*- and *trans,trans*-(H)$_2$IrL$_2$(CO)X (**2-X** and **3-X**) (X = BH$_2$, NH$_2$, and PH$_2$) is used to demonstrate that π-acceptor substituents promote the H$_2$ addition reaction to **1-X** while π-donor substituents disfavor addition.

Introduction

Accurate estimates of ligand substituent effects on elementary reaction energies are indispensable to any attempt at rational design or fine-tuning of transition metal based reagents or catalysts. The dissociative addition of H$_2$ to a transition metal center is a fundamental elementary step in numerous important catalytic processes.[1] H$_2$ addition is normally considered oxidative with respect to the metal center;[2] accordingly, it is generally accepted that increased electron donation from the ligands to reacting metal centers increases the reaction exothermicity.[3] In particular, this view receives support from studies of various *trans*-Ir(PR$_3$)$_2$(CO)Cl complexes, which demonstrate that more basic phosphines slightly increase the exothermicity of H$_2$ addition.[3] Systematic data concerning the effect of varying the anionic substituents on the thermodynamics of H$_2$ addition are more ambiguous. While replacement of Cl in *trans*-Ir(PPh$_3$)$_2$(CO)Cl by I increases the exothermicity of addition,[3b] the same substitution in W(PMe$_3$)$_4$Cl$_2$ yields the opposite effect.[4] Analysis of substituent effects by anionic ligands is further complicated by the absence of a definitive classification pertaining to the "electron-donating" properties of anionic substituents. On the basis of the electronegativity of the neutral halogens, for example, the electron-donating strength of the halides is expected to increase descending the halogen group. Many observations, however, are more consistent with a classification of lighter halides as the better electron donors; for example, Rottink and Angelici have recently reported a gradual decrease in the protonation energy of CpOs(PR$_3$)$_2$X as X is changed from Cl to I,[5] and Doherty and Hoffman[6] have discussed the carbonyl stretch frequency and half-wave reduction potential trends observed in *trans*-M(PPh$_3$)$_2$(CO)X (M = Rh or Ir) complexes in terms of increased halogen-to-metal π-donation by the lighter halogens.

Recent developments in computer technology and computational quantum chemistry have made it possible to carry out high level electronic structure calculations on chemically relevant transition metal complexes.[7] A feasible and potentially useful application of such calculations is the prediction of substituent effects on the reaction energies of various metal complexes and fragments. In the present work, we explore this possibility in a detailed *ab initio* computational study of substituent effects on the reaction energy for H$_2$ addition to Vaska type complexes, **1-X**, equation 1, where L = PH$_3$ and X is formally an anionic 2-electron donating ligand (F, Cl, Br, I,

$$trans\text{-IrL}_2\text{(CO)X} + \text{H}_2 \rightarrow cis,trans\text{-(H)}_2\text{IrL}_2\text{(CO)X} \quad (1)$$



1-X **2-X**

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CN, H, CH_3, SiH_3, OH, or SH). The effect of varying L has been investigated for L = NH_3 and AsH_3 (X = Cl), and calculations were also made on complexes containing L = PMe_3 (X = Cl and I).

The literature on theoretical studies of H_2 addition to transition metal complexes is extensive.[8] Previous work on H_2 addition to d^8 square planar complexes has focused primarily on the general mechanism of the activation process[9] and on the factors that determine the stereospecificity of addition.[10] In contrast, the primary objective of the present study is to estimate quantitatively the small differences in reaction energies associated with changing the substituents in Vaska-type model complexes. The performance of the employed theoretical method in describing redox and spectroscopic properties of **1-X** is also examined. Available experimental data provide a gauge of the accuracy and limitations of the computational method in describing this particular reaction system. In addition, by consideration of a large number of complexes, a qualitative interpretation of the role played by substituents in the H_2 addition process may be realized, and correlations between seemingly disjointed properties may be elucidated. A preliminary communication of this work[11a] and studies of substituent effects on the activation energy[11b] and the kinetic[11b] and equilibrium isotope effects[11c] of reaction 1 have been published.

Computational Details

Ab initio electronic structure calculations[12] were carried out with the Gaussian 90 and Gaussian 92 series of programs[13,14] on a Cray YMP-832 computer at the Pittsburgh Supercomputer Center and on a local Convex C-220 minisupercomputer. Relativistic effective core potentials (ECPs) and corresponding basis sets generated by Ermler, Christiansen, and co-workers[15] were used for all non-hydrogen atoms. Experience has shown these potentials to accurately describe a number of properties in transition metal complexes.[16] The larger core ECP-1 type potentials, which include 68 electrons in the core for Ir, were employed, thus leaving only the outermost Ir 5d and 6s electrons and the valence (s, p) electrons of other atoms for explicit treatment via basis functions. For the sake of comparison, a few calculations were also made with the Ir ECP-2 type potential, which covers a 60-electron Ir core.

Stationary points on the potential energy surfaces were located by optimizing all geometrical parameters within appropriate overall molecular point group constraints (C_{2v} or C_s) at the single determinant restricted Hartree–Fock level (RHF)[17] using analytical energy gradient methods.[18] Normal mode analysis was carried out to verify the identity of stationary points and resulting harmonic vibrational frequencies were used to obtain zero point energies (ZPEs). The iridium basis set was contracted as (3s, 3p, 4d) → [1, 1, 1 / 2, 1 / 3, 1], and the basis sets on all other non-hydrogen atoms (B, C, O, N, F, Cl, Br, I, S, and P) were split into double-ζ quality by liberating the outermost primitive into a separate function, (4s, 4p) → [3, 1 / 3, 1] or (3s, 3p) → [2, 1 / 2, 1]. The H_2 molecule and hydrogens directly bonded to Ir were described by a 311G basis set;[19a] hydrogens in the X groups (OH, Me etc.) carried a 21G basis set,[19b] and hydrogens on L carried the minimal STO-3G[19c] basis set. Complexes containing PMe_3 ligands were optimized with a minimal STO-3G basis set on the Me carbon atoms and imposed constraints of C_s symmetry and frozen methyl group rotation.

Single point calculations (at the optimized geometries of the neutral four-coordinate complexes) on the monocationic and monoanionic radical species of **1-X** at both the unrestricted (UHF)[20] and restricted open shell (ROHF)[21] HF levels were used to estimate vertical ionization potentials and electron affinities.

To obtain improved reaction energies, Møller–Plesset perturbation theory[22] was applied fully through fourth order, MP4(SDTQ), at the optimized geometries. For this purpose, the basis sets described above were augmented by additional diffuse d functions on iridium (exponent 0.038) and a diffuse set of sp functions on the central atom of the substituent X (exponents: H–Cl,[23] Br (0.043), I (0.038)). The energies of the PMe_3-containing complexes were only computed at the level of second-order perturbation theory (MP2) without enlarging the basis set.

Results and Discussion

I. Electronic Structure of 1-X. Electrostatic Field Substituent Effects. The calculated orbital energies of the higher occupied and lower unoccupied molecular orbitals (MOs) may

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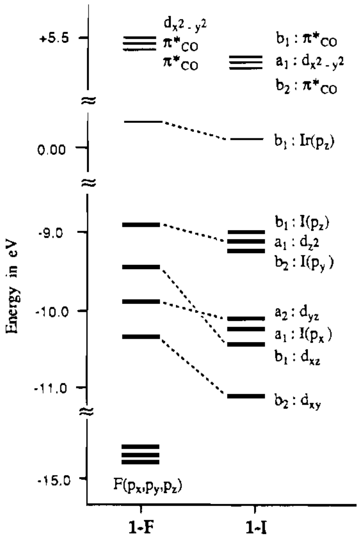

Figure 1. Molecular orbital energy level diagram for *trans*-Ir$(PH_3)_2$(CO)X (X = F and I). Bold lines represent doubly occupied orbitals and single lines represent empty orbitals.

Table 1. Mulliken Net Atomic Charges on Ir (q_{Ir}) and X (q_X) in **1-X**, Electron Occupancy of the Ir σ-Orbitals in **1-X** (σ_X), Orbital Energy of the σ-X MO in **1-X** ($E_{\sigma\text{-X}}$, eV), Orbital Energy of the Unpaired Electron in the Free Radical Fragment **X** ($E_{radical}$, eV), and Absolute Electronegativity[a] of the Free Radical Fragment **X** (μ, eV)

X	q_{Ir}	q_X	σ_X[b]	$E_{\sigma\text{-X}}$	$E_{radical}$	μ
			L = PH_3			
F	+0.11	−0.62	1.30	−14.45	−6.43	10.41
Cl	−0.18	−0.42	1.63	−11.73	−5.36	8.31
Br	−0.25	−0.37	1.70	−10.99	−4.98	7.60
I	−0.35	−0.35	1.75	−10.04	−4.54	6.76
CN	−0.29	−0.27	1.91	−12.95	−6.27	8.92
H	−0.47	0.00	2.14	−10.53	−3.40	7.17
CH_3	−0.29	−0.14	1.95	−10.04	−2.69	4.96
SiH_3	−0.50	−0.13	2.04	−9.06	−3.05	4.78
			L = NH_3[c]			
Cl	+0.07	−0.44	1.70[d]	−11.81	−5.36	8.31

[a] Values from ref 30. [b] Total electron occupancy in the s, p_x and d_{x^2} Ir orbitals. [c] The two σ-L_2 MOs in **1-X** transform as a_1 and b_2. The corresponding energy levels (eV) are $a_1(NH_3) = -16.87$, $a_1(PH_3) = -14.58$; $b_2(NH_3) = -14.85$, and $b_2(PH_3) = -12.65$. [d] Corresponding σ_y values for the total sigma electron occupation in orbitals along the y-axis are 0.86 and 1.06 for L = NH_3 and PH_3, respectively (X = Cl).

be used to illustrate some of the substituent effects on the electronic structure of **1-X**. The complexes with X = F and I (**1-F** and **1-I**) will be considered in particular because the differences in electronic properties between F and I are sufficiently large to allow qualitative distinctions to be made among various components of the full Ir−X interaction. The descriptive label of a particular frontier MO (Figure 1) as predominantly metal or ligand in character is based on the magnitude of the largest atomic orbital coefficients contributing to that MO. In the fluoro and iodo complexes there is no ambiguity in such assignments. In most other complexes, however, delocalization can be extensive and assignments of orbitals as belonging exclusively to metal or ligand may be questionable. The symmetry labels pertain to the C_{2v} molecular point group in a coordinate system chosen so that the molecule lies in the x−y plane with the substituent X, Ir, and the carbonyl group on the principal rotation (x) axis; this choice positions the two phosphines essentially along the y-axis.

The gross energetic features displayed in Figure 1 may be understood on the basis of simple electrostatic field arguments.[24,25] Crystal field effects influence the energies of both filled and empty metal orbitals and play a significant role in determining their availability for covalent bond formation. Due to the smaller size of the fluorine atom, its closer proximity to the metal, and its larger net negative charge in **1-X**, it exerts a much stronger electrostatic field on the metal orbitals than does the iodine atom. As a result, corresponding metal-based orbitals (occupied and unoccupied) in **1-X** are always higher in energy when X = F than when X = I. In addition, the orbital energy gap between the occupied Ir(d_{z^2}) and unoccupied Ir($d_{x^2-y^2}$) orbital ($\epsilon(d_{x^2-y^2}) - \epsilon(d_{z^2})$; ϵ = orbital energy) is distinctly larger in **1-F** (14.0 eV) than in **1-I** (13.3 eV).[26] The orbital energy of the Ir(d_{yz}) orbital may be used to further illustrate the relative strengths of the halogen electrostatic fields. Within the C_{2v} point group of **1-X**, the a_2 symmetry of the Ir(d_{yz}) orbital does not match any combination of ligand orbitals. Accordingly, this metal orbital may be considered as purely nonbonding and its energy may be used as a "nonbiased" indicator of substituent field effects. The energy of the Ir(d_{yz}) orbital in **1-F** is 0.30 eV higher than in **1-I**, a result showing the stronger field effect exerted by F. The significance of this result is highlighted when it is noted that the charge on Ir is computed (Mulliken scheme) to be positive in **1-F** (q_{Ir} = +0.11) but negative in **1-I** (q_{Ir} = −0.35) (Table 1). Among other related substituents, the electrostatic field effects, as indicated by $\epsilon(d_{yz})$, decrease on descending a group, i.e., F > Cl > Br > I; CH_3 > SiH_3; and NH_3 > PH_3. To gain more detailed insight into the electronic structure of **1-X**, we now consider the individual metal and ligand orbitals and the electron donor/acceptor properties of the Ir and X constituents.

Substituent σ-Effects. As is typical of d^8 square planar complexes,[27] covalent metal−ligand interactions take place in **1-X** primarily between the empty metal (formally Ir^+) 6s, $6p_x$, $6p_y$ and $5d_{x^2-y^2}$ orbitals and the doubly occupied ligand group and metal $5d_{z^2}$ orbitals. This leads to the principal formation of four bonding MOs. Three of these MOs belong to the a_1 irreducible symmetry representation and can be described as mainly σ-CO, σ-X, and σ-L_2 in character; one MO belongs to the b_2 representation and is essentially L_2 in character and locally of π-symmetry (π-L_2). As a result of these interactions, the doubly occupied $5d_{z^2}$ orbital acquires weak σ-antibonding character while the empty $6p_z$ and doubly occupied $5d_{xy}$, $5d_{xz}$, and $5d_{yz}$ metal orbitals remain formally nonbonding but available to interact with ligand MOs of appropriate symmetry through π-type interactions. In discussing the σ-property differences among the various substituents in **1-X**, it is helpful to relate the final Ir−X σ bond in the complex to an initial σ-interaction taking place between two radical fragments: X and *trans*-IrL_2(CO). Figure 2 shows a MO interaction diagram between the *trans*-Ir$(PH_3)_2$(CO) radical fragment (computed using the corresponding geometrical parameters from **1-Cl**) and the singly occupied orbital in X ($E_{radical}$, orbital energies are given in Table 1). For all substituents, the singly occupied orbital in X has a much lower energy than the singly occupied metal orbital ($5d_{x^2-y^2}$). Consequently, when the Ir−X bond is formed, the

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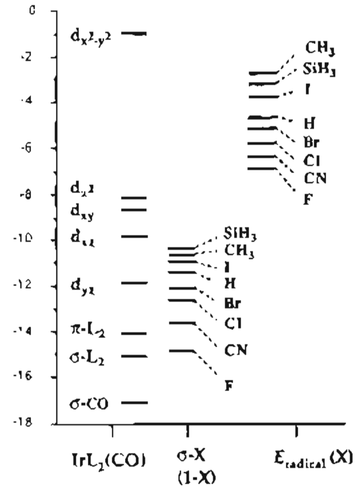

Figure 2. Molecular orbital interaction diagram between *trans*-Ir(PH$_3$)$_2$(CO) and the σ-MO of the free radical substituents ($d_{x^2-y^2}$ and X are singly occupied). σ-X is the energy of the Ir–X σ-orbital in the product, 1-X.

σ-X MO will be polarized toward X (and thus X becomes formally anionic in **1-X**) to an extent largely determined by the initial E_{radical} value.

The order exhibited by the E_{radical} values qualitatively correlates well with the electronegativity order (Pauling,[28] Mulliken,[29] or absolute[30]) of **X**, in accord with the common practice of using electronegativity as a criterion for classifying the σ-donating strength of ligands. Solely on the basis of this factor, substituents like F and CN would be expected to have a large polarizing influence on the σ-X MO (the corresponding anions will be weak σ-donors). A complete description of σ bonding differences among various substituents, however, requires consideration of other properties of X as well, including the spatial extent of its σ-orbital and its ability to accommodate negative charge. Although these factors are more difficult to elucidate qualitatively than the orbital energy factor, their relevance becomes evident when the atomic orbital populations in **1-X** are examined. Assuming that the total σ donation from CO and PH$_3$ to Ir in **1-X** does not significantly change when X is varied, then the total occupancy of the metal $d_{x^2-y^2}$,[31] p_x, and s orbitals (denoted henceforth by "σ_X") can be taken as an indicator of the σ-donating strength of X. Table 1 shows the σ_X values in **1-X** as determined by the Mulliken population analysis scheme.[29,32] According to the σ_X criterion, the σ-donating abilities of the halides follow the order I (1.75) > Br (1.70) > Cl (1.63) ≫ F (1.30) as would have been expected based on the halogen electronegativities. However, on the basis of these considerations, it would also be expected that the energy levels of the occupied d_{z^2} and unoccupied $d_{x^2-y^2}$ orbitals would be higher in **1-I** than in **1-F**, in distinct disagreement with the calculated values (Figure 1).

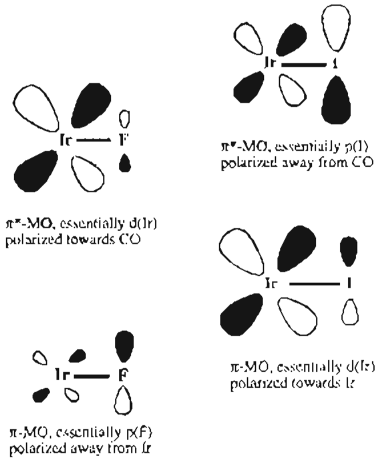

Figure 3. Schematic illustration of the differences in the halide–metal p–d π-type interaction in **1-F** and **1-I**.

The fact that the halogen electronegativities correlate well with σ_X, but do not determine the energy levels of the metal-based σ-orbitals, suggests that the crystal field of X plays an important role in determining the electronic structure of **1-X**. Further considerations demonstrate that electronegativity cannot be viewed as the dominant factor in the determination of substituent σ-properties. For example, H is significantly more electronegative than CH$_3$ but the σ_X value for **1-H** is significantly greater than that for **1-CH$_3$**; disparate abilities to accommodate negative charge may play an important role in this case. When X = CN, σ_X is 1.91, which is unexpectedly high in view of the large electronegativity of CN. Two factors are likely to be responsible for this result. First, the particularly suitable directionality of the σ-orbital in CN (sp hybrid) promotes overlap with the metal σ-orbitals and accordingly increases the σ_X occupancy. Second, electron back donation from Ir to CN through the π-system (see below) may synergistically enhance the CN-to-Ir σ-donation. These examples also illustrate the significant complications that are encountered in trying to draw a general and meaningful "σ-donation" scale for ligands that differ widely in electronic properties.

Substituent π-Effects. The formally nonbonding halide p_z and metal d_{xz} orbitals overlap in **1-X** and produce two π-type MOs of b_1 symmetry; similarly, the halide p_y and metal d_{xy} orbitals give two π-type MOs of b_2 symmetry. Since all these orbitals are doubly occupied, their net π-type interactions (four electrons in two orbitals) are repulsive. Part of this repulsion is ameliorated by π back-bonding to the b_1 and b_2 π^*-MOs of the carbonyl group. In **1-F**, the atomic orbital coefficients of the Ir–X π-MOs show that the lower energy MOs are almost purely F(p) in character while the higher ones are predominantly Ir(d), indicating minimal interaction. This may be attributed to the large energy separation between the relevant fluorine and metal orbitals (ca. 4–5 eV in the complex, Figure 1) and the mismatch in orbital size. In **1-I**, on the other hand, the energy levels are closely spaced with the higher π-MOs having predominantly I(p) character but reflecting a more extensive ligand(p)–metal(d) orbital overlap than in **1-F**. On the basis of these considerations, a perhaps simplistic picture of the Ir(d)–halide(p) π-interaction in **1-X** may be proposed as illustrated in Figure 3. The metal d_{xy} and d_{xz} orbitals in **1-F** possess some antibonding character and are accordingly slightly polarized away from the Ir–F bond toward CO. In **1-I**, however, the metal d orbitals have bonding character with respect to the halide and are concentrated within the Ir–I bond.

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(28) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1962.

(29) Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782.

(30) Pearson, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 7684.

(31) Calculations were carried out with six cartesian d-type basis functions.

(32) We do not make any attempt to draw conclusions based on the absolute values of the charges in Table 1. Rather, we will be concerned with trends which are reproducible by other population analysis methods as well. Similar trends in atomic charges are obtained, for example, from the natural bond orbital (NBO) scheme developed by Weinhold *et al.* ((a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 89). Although the NBO method largely resolves the basis set dependence problem encountered in the Mulliken population analysis method, the results it produces when applied to transition metal complexes depend strongly on the choice of the metal atomic orbitals as "valence" or "Rydberg", see for example: Maseras, F.; Morokuma, K. *Chem. Phys. Lett.* **1992**, *195*, 500.

The differences in Ir−X π-bonding influence the interactions between the Ir(p,d) orbitals and the π^* orbitals on the CO ligand, thus affecting, for example, the carbonyl stretch frequency of **1-X**.

Additional π-interaction in the Ir−X bond could potentially take place via overlap between the empty metal p_z orbital and the doubly occupied halide p_z orbital. However, the population analysis shows relatively low electron occupancy in Ir(p_z) (q_{p_z} = 0.06 and 0.07 for X = F and I; respectively),[33] suggesting only a minor role for this type of bonding, which is perhaps not surprising given the poor energy match between the two orbitals involved and the very diffuse nature of the metal 6p orbitals. Since the energy and size of F(p_z) renders it unsuitable for overlap with Ir(p_z), the higher Ir(p_z) orbital energy computed in **1-F** than in **1-I** (Figure 1) seems to be more a consequence of the stronger crystal field effect of F than the result of an extensive F(p_z)−Ir(p_z) bonding overlap interaction.

In **1-CN**, the two empty CN π^*-MOs are of relatively low energy and are polarized toward the occupied metal d-orbitals; as a result, CN acts as a good π-acceptor. The CH_3 and SiH_3 groups in their respective complexes have two occupied MOs of π-symmetry with largely bonding C−H or Si−H character and two corresponding empty π^* type MOs, all potentially available for hyperconjugative interactions.[34] The occupied CH_3 π-MOs have predominantly C(p) character (in **1-CH$_3$**, the atomic charges in the CH_3 group are $q_H = +0.13$ and $q_C = -0.53$), and the energy match with the occupied Ir(d) orbitals is poor. The corresponding CH_3 π^*-MOs have dominant H(s) character and high orbital energies. Thus, CH_3 lacks any π-accepting qualities but may still exert some π-donating character. On the other hand, the occupied SiH_3 π-MOs in the Ir−SiH_3 bond have significant H(s) character (in **1-SiH$_3$**, atomic charges in the SiH_3 group are $q_H = -0.23$ and $q_{Si} = -0.13$) and are directed away from the metal, whereas the corresponding π^*-MOs have dominant Si(p) character and relatively low orbital energies. Consequently, SiH_3 is a weak π-acceptor and exhibits reduced π-repulsion in the Ir−X bond relative to that of CH_3.[35] The presence of low-lying unoccupied π^*-MOs on X has a stabilizing influence on the Ir(p_z) orbital. In CN and SiH_3, for example, the energy of the Ir(p_z) (in eV) orbital is 1.55 and 1.74, respectively, as compared to 1.96 (I), 2.18 (H), and 2.70 (CH_3). A similar orbital and charge analysis of the NH_3 and PH_3 ligands leads to the classification of NH_3 ($q_N = -0.59$; $q_H = +0.22$) as a poor π-acceptor and a ligand exhibiting strong π-repulsion character and PH_3 ($q_P = -0.04$; $q_H = +0.06$) as a ligand with π-accepting properties. Several studies have demonstrated that the antibonding P−R MOs of phosphines (PR_3, where R can be a hydrogen) play an important π-accepting role in metal−phosphine bonding.[36]

II. Redox and Spectroscopic Properties of 1-X. It is of interest to see if trends observed for the physical properties of **1-X** can be reproduced computationally and to relate their origins to the electronic structure of **1-X**.

Redox Properties. The reduction process provides information on the radical state of lowest energy in **1-X** and hence, in a one-electron picture, information regarding the LUMO of **1-X**. The radical anions of **1-X** are computed to possess $^2B_1$ (X = halogen, H or CN) or $^2A'$ (X = CH_3 or SiH_3) ground states with the unpaired electron predominantly residing in the Ir($6p_z$) orbital. In the anion of **1-Cl**, for example, the spin density distribution shows 0.73 electrons allocated to the Ir(p_z) orbital, 0.10 electrons to the CO(π^*) orbital (C(p_z) = 0.07, O(p_z) = 0.03)) and 0.14 electrons to Ir(d_{xz}).[37] The vertical electron affinity (EA) of **1-Cl** is computed to be −1.66 and −1.56 eV at the ROHF and UHF levels, respectively; i.e., the addition of an electron to **1-X** is disfavored in agreement with the experimental data (Table 2). Computed EAs are not numerically accurate at these theoretical levels[38] but the computed trend should be reliable. In the halide series of complexes, the calculations predict a sharp (F−Cl) and then a gradual (Cl−I) increase in EA upon descending the series; this result is fully consistent with the experimental half-wave reduction potential trend known for the L = PPh_3 complexes of **1−X**.[39] Substituents that raise the energy of the b_1 MOs in **1-X** (Ir(p_z) and CO(π^*)) such as F (Figure 1) tend to disfavor the one-electron reduction reactions both experimentally and computationally. In accord with the low Ir(p_z) energy levels computed for the CN and SiH_3 complexes, the calculations predict more facile reductions for these complexes than for the halides. The π-accepting orbitals on these ligands delocalize the unpaired electron; substituent spin densities computed for the radical anions are 0.10 (CN) and 0.04 (SiH_3) compared with values of less than 0.01 for the halides and CH_3. Among all the complexes studied, the methyl complex is the least susceptible to reduction. We interpret this to reflect the combined effects of a large electrostatic field, a repulsive interaction between the filled methyl π-orbitals and the added electron, and a disfavoring strong σ-donation exerted by the methyl group. Finally, we note that replacing PH_3 by NH_3 disfavors reduction of **1-Cl** by

Table 2. Measured Half-Wave Reduction Potential ($\epsilon°_{1/2}$, eV), Computed Electron Affinity (EA_{UHF} and EA_{ROHF}, eV) and Ionization Potential (IP_{UHF}, eV), and Measured and Computed Carbonyl Stretching Frequencies (ν_{CO}, cm^{-1}) for **1-X**

X	$\epsilon°_{1/2}$[a]	EA_{ROHF}	EA_{UHF}	IP_{UHF}	$(\nu_{CO})_{exp}$[b]	$(\nu_{CO})_{comp}$
			L = PH_3			
F	−2.55	−1.99	−1.87	5.47	1957	2033
Cl	−2.22	−1.66	−1.56	5.62	1965	2046
Br	−2.07	−1.55	−1.43	5.62	1966	2047
I	−1.96	−1.41	−1.30	5.61	1967	2051
CN		−1.10	−0.91	5.56	1990	2073
H		−1.77	−1.62	4.75		2043[c]
CH_3		−2.07	−1.94	4.80	1935	2023
SiH_3		−1.26	−1.11	5.13	1961	2050
			L = NH_3			
Cl		−1.97	−1.84	5.69		2046

[a] Measured in CH_3CN against Ag/Ag$^+$; L = PPh_3.[39] [b] X = halide or CN;[41a] X = Me;[41b] experimental value shown for SiH_3 is actually the value measured for X = $GeEt_3$;[41c] in all cases L = PPh_3. [c] Tabulated value is for the deuteride complex (**1-D**) since the CO and Ir−H stretches are strongly coupled in **1-H**. The computed ν_{M-H} and ν_{CO} values in **1-H** are 1984 and 2083 cm^{-1}, respectively.

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[33] This result does not change when additional contracted or diffuse p orbitals are added to the metal.

[34] For thorough discussions of bonding in metal−methyl systems see: (a) Ziegler, T.; Tschinke, V.; Becke, A. *J. Am. Chem. Soc.* **1987**, *105*, 1351. (b) Ziegler, T.; Cheng, W.; Baerends, E. J.; Ravenek, W. *Inorg. Chem.* **1988**, *27*, 3458.

[35] Lichtenberger, D. L.; Rai-Chaudhuri, A. *J. Am. Chem. Soc.* **1991**, *113*, 2923.

[36] (a) Pacchioni, G.; Bagus, P. S. *Inorg. Chem.* **1992**, *31*, 4391. (b) Marynick, D. S. *J. Am. Chem. Soc.* **1984**, *106*, 4064. (c) Xiao, S.-X.; Trogler, W. C.; Ellis, D. E.; Berkovitch-Yellin, Z. *J. Am. Chem. Soc.* **1983**, *105*, 7033.

[37] The spin distribution is very likely to change when the geometric parameters of the radical anion complex are reoptimized. Allowing the O−C−Ir angle to bend, for example, may enhance spin delocalization on CO (see for example: (a) Astruc, D. *Acc. Chem. Res.* **1991**, *24*, 36. (b) Tyler, R. D. *Acc. Chem. Res.* **1991**, *24*, 325). For the purposes of this study and for the sake of obtaining information regarding the electronic structure of the neutral complex, it seems appropriate to keep the geometric parameters fixed.

[38] At the MP4(SDTQ) level, the electron affinity and ionization potential values for **1-Cl** are −1.40 and 7.37 eV; respectively.

[39] Schiavon, G.; Zecchin, S.; Pilloni, G.; Martelli, M. *J. Inorg. Nucl. Chem.* **1977**, *39*, 115.

about 0.3 eV, a result which can be rationalized in terms of the better π-accepting character of PH_3.

Experimental data on the oxidation properties of **1-X** are not available. Table 2 includes ionization potentials (IPs) computed for the formation of the lowest radical cationic state of **1-X** ($^2A_1$ in C_{2v} symmetry complexes, $^2A'$ in C_s complexes). The unpaired electron in the cations of **1-X** is largely localized in the Ir(d_{z^2}) orbital and the oxidation potential trend is computed to follow the corresponding Ir(d_{z^2}) orbital energy trend. For example, oxidation of **1-F** is computed to be 0.14 eV easier than the oxidation of **1-I** as would have been anticipated based on the relative energy levels for Ir(d_{z^2}) shown in Figure 1.[40] With the exception of the hydride and methyl complexes, the IP values vary within a fairly narrow range (0.22 eV). In contrast with the marked effect noted on the reduction potential of **1-Cl**, replacing PH_3 by NH_3 is computed to have only a small effect on the IP (~0.1 eV). Both strong σ-donation (X = H, CH_3, or SiH_3) and strong field effects (X = F) seem to lower the oxidation potential of **1-X**.

Carbonyl Stretch Frequencies. The computed carbonyl stretch frequencies (ν_{CO}) for **1-X** are about 10% greater than the experimental values[41] (Table 2), a common discrepancy in vibrational frequency calculations that ignore vibronic anharmonicity and electron correlation effects.[42,43] Nevertheless, the observed changes in ν_{CO} accompanying ligand substitution are reproduced very well by the employed theoretical model. Experiments show, for example, that the substitution of Cl by F or CN changes ν_{CO} in **1-X** by -8 and $+15$ cm^{-1}, respectively, whereas the computations predict shifts of -7 and $+17$ cm^{-1}.

The carbonyl stretch frequency in transition metal complexes is generally expected to decrease with increasing $M \rightarrow CO(\pi^*)$ back-donation and to increase with increasing $CO \rightarrow M$ σ-donation.[44] In the present system, the observed and computed ν_{CO} frequencies increase upon descending the halide group (computed values are 2033, 2046, 2047, and 2051 cm^{-1} for X = F, Cl, Br, and I, respectively), opposite to the trend that would be expected based solely on halide σ-donating properties for two reasons. First, as σ-donation increases with the heavier halides, $CO \rightarrow Ir$ σ-donation would be expected to decrease. Second, increased σ-donation results in increased electron density on the metal and is thus expected to induce stronger $Ir \rightarrow CO$ back-bonding.[45] An explanation of the trend based on increased $Ir \rightarrow CO(\pi^*)$ donation due singularly to increased $X \rightarrow Ir$ π-donation by the lighter halides seems inconsistent with the calculated low energies and small size of the F(p) orbitals noted in the previous section. Rather, we attribute the observed ν_{CO} trend partly to the greater electrostatic field strength of the lighter halides, which raises the energy of the Ir(d) orbitals and increases delocalization of d-electrons onto CO. A second relevant factor inducing a small ν_{CO} value is the relative energy ordering of the π-orbitals in the Ir−X bond. Particularly when X = F, the antibonding character of the d-orbitals makes them more suitable for back-bonding to CO as illustrated in Figure 3, even though the overlap may be relatively small. The high ν_{CO} value computed and observed in **1-CN** (2073 and 1990 cm^{-1}, respectively) is consistent with the high π-accepting capacity of CN. Finally, the larger ν_{CO} value when X = SiH_3 (2050 cm^{-1}) as compared with CH_3 (2023 cm^{-1}) follows from the stronger field effect of CH_3 and the ability of SiH_3 to engage in π back-bonding.

The experimental and computed ν_{CO} trends displayed in **1-X** are preserved in the dihydride and dicarbonyl products resulting from H_2 and CO addition, respectively, to **1-X**.[46,47] Similar substituent effects on ν_{CO} are also observed in other related transition metal−halide complexes like $RuH(X)(CO)(PR_3)_2$[48a] and its pyridine adduct.[48b]

III. Thermodynamics of H_2 Addition to 1-X. The gas phase reaction energies for H_2 addition to **1-X** (eq 1) have been computed for a series of substituents that span a wide range in electronic properties. The results are given in Table 3 along with available experimental solution enthalpies. At the Hartree−Fock level, the reaction energies are computed to be too exothermic, for example $\Delta E_{HF} = -34.2$ kcal/mol for H_2 addition to **1-Cl**.[49] Accounting for electron correlation effects (see Computational Details) brings this value to $\Delta E_{MP4} = -22.0$ kcal/mol. Addition of the differential zero point energy for the reaction ($\Delta ZPE = 5.9$ kcal/mol) and the corrections for thermal vibrational, translational, and rotational excitations to ΔE_{MP4} yields a computed reaction enthalpy of $\Delta H_{MP4} = -18.4$ kcal/mol (L = PH_3). This value agrees well with the corresponding experimental value of -14 kcal/mol reported for H_2 addition to Vaska's complex (**1-Cl**, L = PPh_3). More importantly, Table 3 shows that at all levels of theory the observed gradual increase in exothermicity (ca. 2 kcal/mol) upon going from Cl to Br to I is reproduced extremely well by the calculations. A comparable result is also obtained with the more realistic PMe_3 ligands (X = Cl or I). When the alternative Ir(ECP-2) potential, which liberates the penultimate 5s and 5p electrons (60 electrons left in the Ir core), is used in the calculations, the computed reaction energies are uniformly less exothermic than those obtained with the Ir(ECP-1) core, especially at the HF level. The MPn calculations have different effects on the reaction energies depending on the Ir(ECP) used, in particular at the MP2 level where the reaction exothermicity with Ir(ECP-1) is decreased relative to its HF value and is increased with Ir(ECP-2). The experimentally determined enthalpic substituent effects are, however, reproduced equally well by the reaction energies computed with either Ir ECP at any computational level (HF−

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(40) Although Figure 1 shows the HOMO in **1-I** to be a halide p orbital (b_1 symmetry), the cationic $^2B_1$ state is much higher in energy than the $^2A_1$ state.

(41) (a) Peone, J.; Vaska, L. *J. Chem. Soc., Chem. Commun.* **1971**, 418. (b) Dahlenberg, L.; Nast, R. *J. Organomet. Chem.* **1974**, *71*, C49. (c) Glockling, F.; Wilbey, M. D. *J. Chem. Soc. A* **1970**, 1675.

(42) Blomberg, M.; Brandemark, U.; Johansson, J.; Siegbahn, P.; Wennerberg, J. *J. Chem. Phys.* **1988**, *88*, 4324.

(43) (a) Hout, R. F.; Levi, B. A.; Hehre, W. J. *J. Comput. Chem.* **1982**, *3*, 234. (b) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (c) Thomas, J. R.; DeLeeuw, B. L.; Vaceck, G.; Schaefer, H. F., III. *J. Chem. Phys.* **1993**, *98*, 1336. (d) Margareta, R. A.; Siegbahn, P. E. M.; Lee, T. J.; Rendell, A. P.; Rice, J. E. *J. Chem. Phys.* **1991**, *95*, 5898.

(44) For cases where ν_{CO} of a bound CO is larger than ν_{CO} of free CO see: (a) Veldcamp, A.; Frenking, G. *Organometallics* **1993**, *12*, 4613. (b) Beattie, I. R.; Jones, P. J.; Young, N. A. *J. Am. Chem. Soc.* **1992**, *114*, 6146. (c) Sodupe, M.; Bauschlicher, C. W.; Lee, T. J. *Chem. Phys. Lett.* **1992**, *189*, 266.

(45) For example, complexes with more basic phosphines have lower ν_{CO} values, see: Wilkinson, S. G. *Comprehensive Organometallic Chemistry,* 1st ed.; Pergamon Press: Oxford, U.K., 1984; Vol. 5, p 549.

(46) Experimental ν_{CO} for **3-X** (L = PPh_3) are 1975, 1982, and 1995 cm^{-1} for X = Cl, Br, and I, respectively. Halpern J.; Chock P. B. *J. Am. Chem. Soc.* **1966**, *88*, 3511. The computed values are 2135 (F), 2151 (Cl), 2155 (Br) and 2156 cm^{-1} (I). In these complexes, however, the CO and M−H stretching modes are coupled. The computed ν_{CO} values for the deuterated complex are 2163 (F), 2176 (Cl) and 2177 cm^{-1} (I).

(47) In *trans*-$Ir(PPh_3)_2(CO)_2X$ (trigonal bipyramid with axial phosphines) the two carbonyl stretching frequency values (antisymmetric, symmetric) measured in toluene are: (1928, 1978 cm^{-1}) for X = Cl, (1931, 1983 cm^{-1}) for X = Br, and (1934, 1988 cm^{-1}) for X = I. Abu-Hasanayn, F. Unpublished results.

(48) (a) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190. (b) Poulton, J. T.; Sigalas, M. P.; Folting, K.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 1476.

(49) Application of the counterpoise method predicts a BSSE of +2.3 kcal/mol at this level.

Table 3. Computed[a] and Measured[b] Reaction Energies (kcal/mol) for H_2 Addition to **1-X**

X	ΔE_{HF}	ΔE_{MP2}	ΔE_{MP4}	ΔH_{exp}
		$L = PH_3$		
F	−25.8	−20.3	−13.6	>−10
Cl	−34.2	−29.3	−22.0	−14[b]
Br	−36.2	−31.6	−24.1	−17[b]
I	−39.3	−35.0	−27.3	−19[b]
		$L = PMe_3$		
Cl	−40.4	−30.9		−14[b]
I	−44.4	−33.4		−19[b]
		$L = PH_3$ (ECP-2)[c]		
Cl	−11.0	−18.0	−8.7	−14[b]
I	−15.2	−24.1	−14.4	−19[b]
		$L = PH_3$		
CN	−38.8	−35.9	−28.3	−18[d]
H	−45.4	−38.6	−35.3	
CH_3	−36.1	−31.2	−23.2	
SiH_3	−48.9	−44.1	−35.1	
OH	−26.0	−19.8	−12.8	
SH	−37.0	−31.4	−23.7	
BH_4[e]	−44.6	−40.4	−32.2	
		$L = NH_3$		
X = Cl	−29.3	−18.8	−13.8	
		$L = AsH_3$		
X = Cl	−34.6	−29.9	−22.4	−15[f]

[a] ΔE given without ZPE corrections; "MP4" refers to MP4(STDQ) calculations. [b] L = PPh_3; measured in chlorobenzene.[3b] [c] Calculations carried out with the Ir(ECP-2) type potential. [d] L = PPh_3; measured in benzene.[11a] [e] Our previously reported[11a] values when X = BH_4 are in error. [f] Estimated value.[54,55]

MPn). A detailed assessment of the two types of potentials on the geometries of the reactants and products and on the energetics of H_2 and CO addition to **1-X** will be presented elsewhere.[50,51]

The computed reaction energies (ΔE_{MP4}) for X = H (−35.3 kcal/mol), F (−13.6 kcal/mol), and OH (−12.8 kcal/mol) are consistent with qualitative observations of the reactivities of these complexes. For example, $H_3Ir(PPh_3)_2(CO)$ is a known complex[52] (unlike $HIr(PPh_3)_2(CO)$), while **1-F** and **1-OMe**[53] (L = PPh_3) do not add H_2 under ambient conditions. Significant increases in reaction exothermicity, ca. 10 kcal/mol, are computed when OH is replaced by SH and also when CH_3 is replaced by SiH_3, similar to the computed effect of replacing F by Cl. The computations predict that the reaction energy for H_2 addition to **1-CN** should be comparable to that for **1-I**. Since the cyano complexes are very different electronically from the halide species, we were interested in determining the reliability of these calculated relative energies and have accordingly tested this theoretical prediction by experimental means (see Experimental Details). Competition experiments revealed that K_{eq} = 9 for eq 2 (L = PPh_3) and therefore ΔH_{eq} = −1.3 kcal/mol

$$H_2IrL_2(CO)(CN) + IrL_2(CO)I \rightleftharpoons IrL_2(CO)(CN) + H_2IrL_2(CO)I \quad (2)$$

(assuming ΔS_{eq} = 0). This value is in very reasonable agreement with the computed results of $\Delta E_{eq\text{-}HF}$ = −0.5 kcal/mol or $\Delta E_{eq\text{-}MP4}$ = 1.0 kcal/mol for eq 2 when L = PH_3 (Table 3).

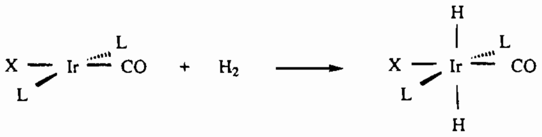
The small energetic effects observed experimentally upon replacing PPh_3 by $AsPh_3$ in equation 1 ($\Delta\Delta H$ = −0.2 kcal/mol)[54,55] are also well reproduced by the model calculations with L = AsH_3 ($\Delta\Delta E_{MP4}$ = −0.4 kcal/mol). Amine complexes analogous to **1-X** are not known; model calculations predict these to add H_2 much less favorably than their phosphine and arsine counterparts.

The data presented above and in Table 3 demonstrate unequivocally that the employed computational model is accurate in providing quantitative estimates of substituent effects on the energetics of this reaction system. It should be reemphasized that the computed trends are identical at the HF and correlated (MPn) levels of theory. This is an important result to consider in computations of substituent effects in larger systems. Furthermore, most discussions using qualitative molecular orbital concepts are only possible based on data obtained at the HF level. It continues to be of conceptual and practical interest to relate the reaction energy trend to commonly used qualitative notions based on the general electronic properties of the substituents.

As noted in the introduction, H_2 addition to Vaska type complexes is generally considered "oxidative" and ligands which increase "electron richness" (strong electron donors) at the metal center should tend to favor "oxidative addition".[3] Such a hypothesis is consistent with the reaction enthalpy trend observed for the halide complexes, if the electron richness of the metal is assumed to decrease with increased halogen electronegativity. However, the redox and spectroscopic properties of **1-X** are inconsistent with the implications of the above hypothesis: complexes of the more electronegative halogens are actually more susceptible to one-electron oxidation, are much less prone to one-electron reduction, and exhibit more extensive metal-to-ligand back-bonding. All these results are opposite to the properties expected from "electron poor" metal centers. Furthermore, the expected inverse correlation between substituent electronegativity and reaction exothermicity observed for H_2 addition to the halide complexes does not continue to hold when the full series of complexes is considered. For example, CN is clearly much more electronegative than CH_3, yet **1-CN** is computed to add H_2 5 kcal/mol more exothermically than **1-CH₃**. Similarly, though CH_3 and SiH_3 have comparable electronegativities, H_2 addition to **1-SiH₃** is 12 kcal/mol more exothermic than to **1-CH₃**. Thus, ligand electronegativity is clearly not the dominant variable influencing the relative enthalpies of eq 1. In this regard we also note that H_2 addition to some cationic iridium complexes has been described as reductive with respect to the metal,[2] and many studies have emphasized the highly covalent (and not ionic) nature of metal−hydrogen bonds.[56]

In order to more easily examine how the electronic properties of a substituent can influence the energetics of H_2 addition to **1-X**, we consider the formation of the hypothetical *trans,trans*-$(H)_2Ir(PH_3)_2(CO)X$ product, **3-X**, eq 3. Analysis of the H_2

$$trans\text{-}IrL_2(CO)X + H_2 \rightarrow trans,trans\text{-}(H)_2IrL_2(CO)X \quad (3)$$



1-X **3-X**

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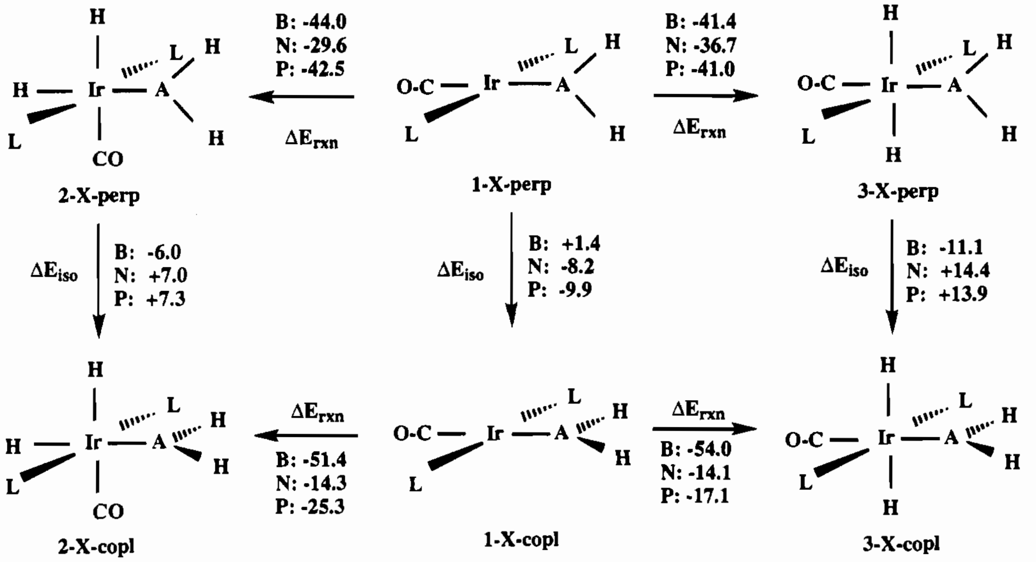

Figure 4. Isomerization (ΔE_{iso}) and H_2 addition reaction energies (ΔE_{rxn}) for the AH_2 complexes **1-X**, **2-X**, and **3-X** (in kcal/mol). Calculations were carried out at the HF level.

addition process is greatly simplified in eq 3 since the molecular symmetry and the *trans* CO−X configuration of **1-X** are preserved in **3-X**. We consider **1-X** and **3-X** with X = AH_2 and A = B, N, and P (Figure 4) in an attempt to resolve substituent π and σ effects. Preservation of a coplanar arrangement of the atoms in the Ir−AH_2 fragment leaves a single nonbonding atomic p orbital on AH_2. When AH_2 lies in the $IrL_2(CO)$ plane, the AH_2 nonbonding orbital (A(p_z)) has b_1 symmetry and the corresponding complexes are denoted "**1-X-copl**" and "**3-X-copl**". When the AH_2 group is oriented perpendicular to the $IrL_2(CO)$ plane, the nonbonding orbital (A(p_y)) is of b_2 symmetry and the corresponding complexes are denoted "**1-X-perp**" and "**3-X-perp**". Variation of the orientation of AH_2 with respect to the $IrL_2(CO)$ plane in **1-X** and **3-X** permits large changes in the π-interactions between AH_2 and $IrL_2(CO)$ while only minimally affecting σ-interactions.[57]

According to the computations (HF level), the **1-BH₂-perp** conformer is 1.4 kcal/mol lower in energy than **1-BH₂-copl**. In contrast, when X = NH_2 or PH_2, the **1-X-copl** conformer is computed to be more stable than **1-X-perp** by 8.2 and 9.9 kcal/mol, respectively (see Figure 4). The relevant π-interactions in **1-X-perp** are primarily between A(p_y) and Ir(d_{xy}) and between A(p_y) and the occupied MO formed from the two *trans*-PH_3 ligands, π-L_2. Both of these interactions are repulsive in the NH_2 and PH_2 complexes where A(p_y) is doubly occupied. In **1-X-copl**, π-interaction involves A(p_z), the occupied Ir(d_{xz}) and the unoccupied Ir(p_z) orbitals. When X = NH_2 or PH_2, the A(p_z)−Ir(p_z) interaction is attractive (bonding). Thus, when the nonbonding AH_2 p orbital is occupied, isomerization of **1-X-copl** to **1-X-perp** is strongly disfavored because it replaces a bonding A(p_z)−Ir(p_z) interaction with a repulsive A(p_y)−(π-L_2) interaction. Analogous isomerization of the BH_2 complex, on the other hand, is favored because the process allows an additional bonding interaction to take place between the empty B(p_y) and the occupied π-L_2 orbitals. The small magnitude of this stabilization (1.4 kcal/mol) suggests that π-L_2 is only weakly "π-active".

Adding two H atoms to **1-AH₂** (relative AH_2 orientation retained in the product) results in an additional occupied b_1 (π-symmetry) MO in either isomer. H_2 addition to **1-BH₂-copl** is computed to be favored by 12.6 kcal/mol over addition to **1-BH₂-perp**, indicating a significant stabilizing interaction between the occupied π-H_2 MO and the empty B(p_z) orbital. In striking contrast, H_2 addition to the **1-X-copl** isomers of the NH_2 and PH_2 complexes is 22.6 (NH_2) and 24.8 (PH_2) kcal/mol less favored than H_2 addition to the **1-X-perp** isomers, showing that the presence of an occupied π-orbital of b_1 symmetry on X strongly disfavors the addition reaction. In the latter cases, H_2 addition to **1-AH₂-copl** (A = N or P) results in both the loss of a favorable Ir(p_z)−A(p_z) interaction and the creation of additional π-H_2−A(p_z) repulsion, whereas H_2 addition to **1-AH₂-perp** (A = N or P) leaves the π-interactions in the system qualitatively unchanged.

The above ideas concerning substituent π-effects appear directly transferable to the relative energies of the cis-$(H)_2$ products (**2-X**). Addition of H_2 to the **1-X-perp** conformer produces complexes in which p_y (a″ symmetry, C_s point group) is formally the nonbonding orbital on AH_2 (**2-X-perp**, Figure 4). Alternatively, addition of H_2 to the **1-X-copl** conformer yields products (**2-X-copl**, Figure 4) in which p_z is the nonbonding AH_2 orbital (a′ symmetry). As in the case of the trans-$(H)_2$ product, these addition reactions formally replace the two electrons in Ir(d_{z^2}) with two occupied metal−ligand orbitals along the *z*-axis. The formation of **2-BH₂-copl** from **1-BH₂-copl** is computed to be 7.4 kcal/mol more exothermic than the formation of **2-BH₂-perp** from **1-BH₂-perp**. This can be explained in terms of a stabilizing interaction taking place between the empty B(p_z) orbital in **2-BH₂-copl** and occupied ligand orbitals along the *z*-axis. In particular, the MO corresponding to the Ir−H bond of the hydride trans to CO appears to be significantly involved in this interaction because its energy level is much higher than that of the σ-MO corresponding to Ir−CO and thus energetically more suitable to interact with the empty p orbital on BH_2. When AH_2 = NH_2 or PH_2, on the other hand, the A(p_z) orbital is doubly occupied and exerts a

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(55) The measured equilibrium constants (K_c) for the reversible H_2 addition to $Ir(PPh_3)_2(CO)Cl$ and $Ir(AsPh_3)_2(CO)Cl$ are 3.22 and 4.31, respectively, giving $\Delta\Delta H = -0.17$ kcal/mol. See ref 54.

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(57) The two A−H bonds in AH_2 afford one occupied and one unoccupied MO of π-symmetry (b_1 or b_2 symmetry depending on the orientation of AH_2) that can contribute to the π interactions taking place between M and AH_2 in a way similar to that discussed for CH_3 and SiH_3. The contribution from this interaction to the total energetic differences among the AH_2 complexes is assumed to be small relative to the effects involving the nonbonding p orbital.

repelling effect on the ligands along the z-axis; accordingly, the formation of **2-AH$_2$-perp** is computed to be more exothermic than the formation of **2-AH$_2$-copl** by 15.3 (NH_2) and 17.2 kcal/mol (PH_2). The important role of the interaction between the σ-IrH MO (H trans to CO) and the nonbonding orbital of AH_2 is further revealed by the magnitude of the corresponding H−Ir−A angle. In **2-AH$_2$-perp**, this angle is computed to be comparable for the three substituents: 85° (BH_2), 87° (NH_2), and 88° (PH_2). Isomerization of the BH_2 complex into **2-BH$_2$-copl** decreases the value significantly (to 80°), reflecting the bonding interaction between σ-IrH and the empty B(p_z) orbital. The corresponding isomerization of the NH_2 or PH_2 complexes, despite an expected decrease in steric effects, slightly increases the value of this angle (88° (NH_2) and 90° (PH_2)) and hence reflects the developed repulsion between σ-IrH and the occupied N(p_z) or P(p_z) orbitals. Consideration of the AH_2 complexes in Figure 4 demonstrates that the presence of π-accepting orbitals on the substituents strongly promotes H_2 addition to Vaska-type complexes, while the presence of occupied π-symmetry substituent orbitals disfavors addition.

In an attempt to isolate σ-effects, eqs 1 and 3 were examined for X = BH_4 in a fixed linear Ir−H−B arrangement.[58] This ligand may be regarded as a hydride having its σ-donating tendencies reduced due to the coordination of the additional BH_3 moiety. The reaction energies for the formation of **2-BH$_4$** (−44.6 kcal/mol, Table 3) and **3-BH$_4$** (−41.2 kcal/mol) are similar to those for the H_2 addition to **1-H** (−45.4 kcal/mol; note that **2-H** and **3-H** are identical), suggesting that the reaction energies for H_2 addition to **1-X** are not very sensitive to the σ-properties of X.

The HF reaction energies for *trans*-H_2 addition, eq 3, for other substituents are as follows (kcal/mol): −28.1 (F), −30.8 (I), −45.4 (H), and −37.6 (CN), indicating that the substituent effects on the energetics of the formation of **3-X** are different than those for the formation of **2-X** (Table 3). In particular, the reaction energies for X = F and I are much less different in the formation of **3-X** than **2-X**. The much lower exothermicity computed when X = halogen as compared to H or CN is consistent with a disfavoring effect from the occupied halogen π-orbitals although a significant energetic contribution from differences in σ-bonding properties cannot be ruled out.

Concluding Remarks

The relative importance of the numerous factors which affect the electronic structure and bonding in the low symmetry complexes **1-X** has proven difficult to determine. The differences in the electronic structures do not follow predominantly from the σ-donating properties of the substituents. Both electrostatic field properties and π-donating/accepting abilities of the substituents play large roles in shaping the detailed electronic structure of **1-X**. These properties have been analyzed with the use of the standard electronic structure tools, viz., molecular orbital energy and interaction diagrams as well as electron population analysis. The calculated spectroscopic trends are fully consistent with the electronic structure model developed for **1-X**, in particular with respect to the frontier orbital energy levels and their compositions.

The preceding section demonstrates that experimental relative enthalpies of H_2 addition to **1-X** for a wide range of substituents, X, can not only be reproduced but can also be accurately predicted using model electronic structure calculations. *Ab initio* calculations are therefore of significant potential value in the "fine-tuning" of transition metal based reagents or catalysts. Simplified calculations involving hypothetical *trans,trans*-H_2-$Ir(PH_3)_2(CO)AH_2$ (A = B, N, or P) complexes show clearly that the π-properties of the substituents play an important role in determining the thermodynamics of the addition reaction: the presence of occupied π-orbitals on the substituents has a strongly disfavoring effect and the presence of π-accepting orbitals has a significant stabilizing effect. While the significance of other variables cannot be ruled out, comparisons such as the H_2 addition to **1-H** vs **1-BH$_4$** or **1-CH$_3$** vs **1-SiH$_3$** indicate that the reaction energies are much less sensitive to σ- than to π-effects. Consistent with our conclusion of the importance of specific π-interactions, e.g. between X(p_z) and Ir(p_z) orbitals in **1-X** or between X(p_z) and π-H_2 orbitals in **3-X** , the observed trends do not necessarily carry over to other systems having electronic structures very different from **1-X**. For example, as noted above, $W(PMe_3)_4X_2$ adds H_2 more favorably when X = Cl than when X = I. Furthermore, the 14e fragments *trans*-$Rh(PH_3)_2X$ and *trans*-$Ir(PH_3)_2X$ have been calculated to add H_2 less exothermically when X = H than when X = Cl.[59,60] In our study of $Rh(PH_3)_2X$ we find that for X = halide the substituent effect on the reaction energy of H_2 addition is much smaller than that found for equation 1.[61]

Experimental Details

$Ir(PPh_3)_2(CO)Cl$ was prepared according to published methods.[62] $Ir(PPh_3)_2(CO)I$ (**1-I**, L = PPh_3) and $Ir(PPh_3)_2(CO)(CN)$ (**1-CN**, L = PPh_3) were prepared from **1-Cl** (L = PPh_3) by metathesis using NaI/acetone and LiCN/dimethylformamide (DMF), respectively, and were characterized by IR and UV absorptions in accord with literature data. These complexes add H_2 readily and give dihydride products characterized by two triplets of doublets in their ^{1}H NMR: **2-Cl**, $\delta_1 = -6.67$, $^2J_{P-H} = 17.0$, $^2J_{H-H} = 4.5$; $\delta_2 = -17.50$, $^2J_{P-H} = 14.0$; **2-I**, $\delta_1 = -8.47$, $^2J_{P-H} = 17.3$, $^2J_{H-H} = 4.2$; $\delta_2 = -14.82$, $^2J_{P-H} = 13.7$; **2-CN**, $\delta_1 = -9.10$, $^2J_{P-H} = 16.9$, $^2J_{H-H} = 4.0$; $\delta_2 = -11.71$, $^2J_{P-H} = 15.5$.

To measure K_{eq} of eq 2, equal volumes of 5 mM benzene solutions of **2-CN** (prepared by exposing a solution of **1-CN** to 2 atm of H_2 and freeze−pump−thawing the resulting solution twice) and **1-I** were added to an NMR tube, which was sealed, and ^{1}H NMR spectra were then recorded. Shortly after mixing, peaks due to **2-I** became apparent. The concentrations of **2-I** and **2-CN** were estimated from the integrands of their low field hydride peaks. The concentration of **1-CN** was then equated with [**2-I**] and that of **1-I** with [**2-CN**]. When the spectra ceased to change (3 days), equilibrium was assumed to have been reached and K_{eq} was calculated as 9 ± 1. At the end of the experiment, H_2 was added to the NMR solution mixture to convert all complexes to dihydride species. The NMR spectrum was recorded and confirmed that **2-I** and **2-CN** had the same concentration. The reciprocal experiment, starting with **1-CN** and **2-I**, afforded a similar K_{eq} value.

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