Factors Influencing the Thermodynamics of H_2 Oxidative Addition to Vaska-Type Complexes (*trans*-$Ir(PR_3)_2(CO)X$): Predictions from ab Initio Calculations and Experimental Verification

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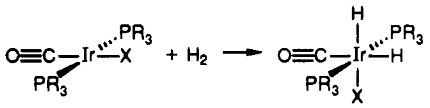
The oxidative addition of nonpolar molecules such as H_2 is one of the most important and characteristic reactions in transition metal chemistry.[1,2] The factors which affect the thermodynamics of H_2 addition are directly relevant to important multistep reactions such as the hydrogenation and hydroformylation of unsaturated substrates and undoubtedly also affect reactions such as hydrosilation and carbon–hydrogen bond activation.[1-4]

Addition of H_2 to Vaska's complex, *trans*-$Ir(PPh_3)_2(CO)Cl$ (R = Ph, X = Cl), is regarded as a paradigm of this reaction class.[1,5] It is widely believed that for this complex,[1a,5b] and more generally as well,[6] the tendency to undergo oxidative addition increases with the electron-donating ability of the ligands. We have conducted a detailed computational study of reaction 1 (R = H) using ab initio electronic structure methods in order to determine quantitatively how the electronic properties of the ligand X affect the thermodynamics of H_2 addition.[7] Very recent computational studies by others have focused on the specific pathway of H_2 addition to Vaska-type complexes and on the relative stabilities of the isomeric products.[8] On the basis of both computational and experimental data we conclude that Ir–X π-interactions dominate the thermodynamics; specifically, *increased* π-donating ability of X *disfavors* H_2 addition. Variation of the σ-donating ability has a more modest effect, with increased σ-donation apparently favoring addition.

trans-$Ir(PR_3)_2(CO)X + H_2 \longrightarrow$ *cis,trans*-$H_2Ir(PR_3)_2(CO)X$ (1)



X = F, Cl, Br, I, CN, OH, SH, H, CH_3, SiH_3, BH_4

A series of ab initio molecular orbital calculations were carried out on reaction 1 (R = H; see Table I).[9] Geometries were optimized at the Hartree–Fock (HF) level using relativistic effective core potentials (ECPs) and double-ζ valence basis sets on all non-hydrogen atoms;[10a-d] hydrogens on the metal were represented by a triple-ζ basis set (311G),[10e] hydrogens on substituent X by a double-ζ basis set (21G),[10f] and the phosphine hydrogens by a minimal basis set (STO-3G).[10g] ECPs representing the maximum number of core electrons were employed for Br, I, and Ir. Improved energies were obtained using Moller–Plesset perturbation theory (MP4(SDTQ)) and larger, polarized basis sets.[10h] Table I shows the computed energies (ΔE) for reaction 1 (R = H); also included are measured enthalpies (R = Ph), as well as observed carbonyl stretching frequencies (ν_{CO}) and half-wave reduction potentials ($\epsilon_{1/2}$) of the reactants.

Inspection of Table I shows that the computed gas-phase energy of reaction 1 (R = H) is about 20 (HF) or 8 (MP4) kcal/mol larger than the measured solution enthalpy (R = Ph) for X = Cl, Br, and I. More importantly, the small energetic differences in the halide series are reproduced very closely by the calculations, even at the single determinant HF level.[11] Although the reaction enthalpies in the cases of X = H, F, and OMe are not known experimentally, qualitative observations indicate that our computed values for these species are consistent with observed reactivity trends.[5b,12] For example, the complexes with X = F or OMe do not add H_2 under normal conditions.

Note that the correlation between ΔH for reaction 1 and ν_{CO} and $\epsilon_{1/2}$ of the reactants is counterintuitive (Table I). The magnitude of ν_{CO} and ease of reduction both increase in the order X = F > Cl > Br > I. Additionally, Angelici has found that the

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Table I. Computed (R = H) and Experimental (R = Ph) Energies for Reaction 1 and Measured Carbonyl Stretching Frequencies and Reduction Potentials of the Reactants[a]

	computed[b]		experimental		
X	ΔE(HF)	ΔE(MP4)	$\Delta H°$	ν_{CO}	$\epsilon_{1/2}$[c]
F	−25.8	−13.6	>−10[d]	1957[g]	−2.55
Cl	−34.2	−22.0	−14[d]	1965[g]	−2.22
Br	−36.2	−24.1	−17[d]	1966[g]	−2.07
I	−39.3	−27.3	−19[d]	1967[g]	−1.96
CN	−38.8	−28.3	−18[e]	1990[g]	
OH	−26.0	−12.8	>−10[f]	1949[g]	
SH	−37.0	−23.7			
H	−45.4	−35.3			
CH_3	−36.1	−23.2		1935[h]	
SiH_3	−48.9	−35.1		1961[i]	
BH_4	−46.4	−51.6			

[a] Reaction energies (ΔE) in kcal/mol; vibrational frequencies (ν_{CO}) in cm^{-1}; reduction potentials ($\epsilon_{1/2}$) in V. [b] Computed values do not include corrections for differences in zero-point vibrational energies. Frequency analysis on the halide complexes resulted in a decrease in exothermicity by about 5 kcal/mol. [c] Schiavon, G.; Zecchin, S.; Pilloni, G.; Martelli, M. *J. Inorg. Nucl. Chem.* **1977**, *39*, 115–117. [d] Experimental values for the halide complexes are from ref 5b, measured in chlorobenzene. [e] ΔH estimated from the equilibrium constant measured in this work (eq 2) and the enthalpy reported above for the iodide complex. [f] Reference 12. [g] Carbonyl stretching frequencies measured in chloroform; from ref 16. [h] Dahlenberg, L.; Nast, R. *J. Organomet. Chem.* **1974**, *71*, C49. [i] ν_{CO} for $Ir(PPh_3)_2(CO)(GeEt_3)$ in chloroform: Glockling, F.; Wilbey, M. D. *J. Chem. Soc. A* **1970**, 1675.

basicity of metal halides decreases in the order Cl > Br > I.[13] These results are all consistent with increasing metal richness as one goes up the halogen period, which is generally considered to imply increasing exothermicity,[5–7] exactly opposite to what is observed and computed. Recently, it has been suggested that the spectroscopic and electrochemical trends for this series (Table I) are dictated by the π-donating ability of the halide.[14] Our computed data for these properties concur with this assessment.[15] In the present study, we find that the exothermicity of H_2 addition is also largely determined by the π-donating ability of X.

The measured ν_{CO} in $Ir(PPh_3)_2(CO)(CN)$ at 1990 cm^{-1} is substantially higher than those measured for the halide complexes (~1965 cm^{-1}),[16] implying a substantial reaction exothermicity if the observed ν_{CO}–ΔH correlation extends beyond the halide series. On the other hand, on the basis of a "conventional" ν_{CO}–ΔH relationship we would expect that the cyanide complex should add H_2 only reluctantly. The computed reaction energy places the complex with X = CN at the same level as that with X = I ($\Delta H = -19$ kcal/mol), i.e., intermediate between these expectations. We have tested this computational prediction by experimental means.

Addition of H_2 to an ambient temperature benzene solution of $Ir(PPh_3)_2(CO)(CN)$ resulted in clean and rapid formation of the previously unreported complex *cis,trans*-$H_2Ir(PPh_3)_2(CO)(CN)$ as determined by ^1H NMR, UV–visible, and IR spectroscopy. When a solution of $Ir(PPh_3)_2(CO)(CN)$ was added to an equimolar solution of $H_2Ir(PPh_3)_2(CO)Cl$, the transfer of hydrogen to the cyanide complex went virtually to completion as monitored by UV absorption. Similar competition experiments with $H_2Ir(PPh_3)_2(CO)I$ (and the reciprocal experiments with $H_2Ir(PPh_3)_2(CO)(CN)/Ir(PPh_3)_2(CO)I$) afforded $K_{eq} = 9$ ($\Delta H = -1.3$ kcal/mol assuming $\Delta S = 0$) for reaction 2 (R = Ph) as determined by NMR spectroscopy. The computed energy for reaction 2 (R = H; data from Table I) is −0.5 kcal/mol (HF) or 1.0 kcal/mol (MP4(SDTQ)), respectively, in remarkable agreement with the derived experimental value.

$$H_2Ir(PR_3)_2(CO)(CN) + Ir(PR_3)_2(CO)I \rightarrow Ir(PR_3)_2(CO)(CN) + H_2Ir(PR_3)_2(CO)I \quad (2)$$

The calculated energy of H_2 addition to the cyanide, thus verified experimentally, allows an interesting comparison with the slightly lower exothermicity calculated for the methyl complex. The CN complex is computed to add H_2 more readily than the CH_3 analogue, although the basicity of CH_3^- is over 40 orders of magnitude[17a] greater than that of CN^-. Clearly, CH_3^- is a much stronger σ-donor than CN^- (Taft parameters $\sigma_I = -0.05$ (CH_3) and 0.56 (CN)), but it is also a significantly stronger π-donor[18] ($\sigma_R = -0.13$ (CH_3) vs 0.08 (CN)).[17b] If σ-donation were the decisive factor determining the reaction exothermicity, then complexes of the weakest σ-donors, e.g. X = F, should add H_2 most readily; in fact, the fluoride complex does not add (Table I). We therefore believe that π-donation plays the major role in determining the thermodynamics of eq 1 and distinctly disfavors H_2 addition. The halide series is more complex since σ-donation increases while π-donation decreases from F to I. We interpret the observed and computed increases in reaction exothermicity to be dominated by the decreasing halide π-donation. The reaction energy differences within the OH/SH and CH_3/SiH_3 pairs of complexes may be similarly rationalized in terms of the relative π-donating abilities of these ligands.

In an attempt to isolate the role played by ligand σ-donation we considered the hypothetical complex $Ir(PH_3)_2(CO)(BH_4)$, i.e., $Ir(PH_3)_2(CO)H$ with BH_3 coordinated to the hydride ligand. The enthalpy of H_2 addition to the BH_4^- complex was calculated to be more favorable than that for $Ir(PH_3)_2(CO)H$ (Table I) even though BH_4^- must be a poorer σ-donor than H^-. This result implies that the effect of varied σ-donation is relatively minor. An attempt to correlate the computed addition energies for all the complexes in Table I to the Taft parameters[17b] for their respective ligands X gives a best fit ($r^2 = 0.87$) with ΔE (kcal/mol) $= -32.3 - 40.4(\sigma_R - 0.2\sigma_I)$. The dominant parameter, σ_R, is essentially a measure of π-donating/withdrawing ability.[17b]

More detailed analysis shows that H_2 addition to these complexes may be considered oxidative in many regards and not reductive as demonstrated by Crabtree[19] for a series of cationic iridium cyclooctadiene complexes. Our study reveals that the carbonyl stretching frequency of the reactant cannot be used as a general predictor for the exothermicity of H_2 addition (eq 1). The present work also demonstrates the ability of high-quality ab initio electronic structure calculations to predict small energy differences among reactions of analogous organometallic complexes. Further experimental and computational investigations are in progress to validate our interpretations and to isolate the dominant components of the overall reaction dynamics.

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