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J. Am. Chem. Soc. **1998,** *120,* 9256−9266

Thermodynamics of Addition of H$_2$, CO, N$_2$, and C−H Bonds to M(P^{i}Pr$_3$)$_2$Cl (M = Ir, Rh). An Unprecedented Metal−Carbonyl Bond Strength

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Received December 2, 1997. Revised Manuscript Received June 3, 1998

Abstract: The thermodynamics of interconversion of various complexes containing the unit IrL*$_2$Cl (L* = P(^{i}Pr)$_3$) have been investigated by calorimetry and equilibrium measurements. These complexes span a wide range of configurations including four- and five-coordinate d^8 (IrL*$_2$ClL′, IrL*$_2$Cl(CO)$_2$) and five- and six-coordinate d^6 (IrL*$_2$ClRH and IrL*$_2$ClRH(CO)). On the basis of kinetic experiments, a lower limit to the Ir−N$_2$ bond dissociation enthalpy (BDE) of IrL*$_2$Cl(N$_2$) has been determined (36 kcal/mol). Using this value as an "anchor", in conjunction with the relative addition enthalpies obtained calorimetrically, it is possible to derive lower limits for the absolute exothermicities of H$_2$ (48 kcal/mol) and CO (72 kcal/mol) addition to IrL*$_2$Cl; estimates can also be made for the addition of benzene and acetylene C−H bonds. These values are unusually high; indeed, the magnitude of the Ir−CO BDE is unprecedented. In addition, kinetic methods have been used to determine a lower limit of 29 kcal/mol to the Rh−N$_2$ BDE of RhL*$_2$Cl(N$_2$). Combined with previous calorimetric measurements on rhodium complexes, this value permits the calculation of lower limits to the absolute exothermicities of addition to RhL*$_2$Cl for numerous small molecules including H$_2$, CO, N$_2$, C$_2$H$_4$, and aldehydic C−H bonds. The results of electronic structure calculations (approximate DFT; PMe$_3$ used to model P^{i}Pr$_3$) are in excellent agreement with the relative experimental enthalpies, while the absolute values calculated for addition to IrL$_2$Cl are significantly greater than the experimentally determined lower limits. Addition of a methane C−H bond is calculated to be significantly less favorable than addition of benzene or acetylene C−H bonds, in accord with the fact that IrL*$_2$Cl(alkyl)H complexes have not been reported. The significant differences in the enthalpies of addition for these three types of C−H bonds are briefly analyzed.

Introduction

The addition reactions of H$_2$ and CO to transition metal centers are certainly among the most important reactions in transition metal chemistry. These fundamental reactions (and their respective microscopic reverses) are ubiquitous in transition-metal-catalyzed chemistry. Hydrogenations and carbonylations are of tremendous industrial importance and many important processes, such as hydroformylation and homogeneous Fischer−Tropsch analogues, involve both CO *and* H$_2$ addition.[1] A related reaction, which has been the subject of intense study for about 15 years, is the addition of C−H bonds; development of systems incorporating this reaction into useful catalytic cycles is considered a "Holy Grail" of transition-metal-based catalysis.[2] It should also not be overlooked that the reverse reaction, C−H bond elimination, is involved for example in all of the above-mentioned catalytic reactions of CO and/or H$_2$.[1] Yet despite the obvious importance of these fundamental reactions, our understanding of the factors that determine their thermodynamics is quite limited.

Complexes of the group 9 metals play a particularly important role in catalyses of the type noted above. For example, probably the best known catalyst precursors for these respective processes are Rh(PPh$_3$)$_3$Cl (olefin hydrogenation), Co$_2$(CO)$_8$ (hydroformylation), and RhI$_3$ (alcohol carbonylation).[1] In the field of homogeneous hydrocarbon C−H bond activation, Rh and Ir, particularly as phosphine complexes, have played a dominant role in the development of both stoichiometric and catalytic reactions.[2]

We have recently elucidated the relative thermodynamics pertaining to a variety of reactions involving the fragment RhL*$_2$Cl (L* = P^{i}Pr$_3$), including the addition of CO, N$_2$, H$_2$, and aldehydic C−H bonds.[3] Herein we report our determination of the relative enthalpies for addition of CO, N$_2$, and H$_2$ to the iridium congener, IrL*$_2$Cl. In addition, the iridium manifold includes 18-electron complexes such as IrL*$_2$Cl(CO)H$_2$ and IrL*$_2$Cl(CO)PhH. This permits us to determine the absolute enthalpy, for example, of H$_2$ addition to IrL*$_2$Cl(CO) and CO addition to IrL*$_2$Cl(H)$_2$. We also report on kinetic experiments which enable us to estimate upper limits to the *absolute* enthalpies of the additions to both the rhodium and iridium 14-

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Addition of H₂, CO, N₂, and C−H Bonds to M(P^{i}Pr₃)₂Cl

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electron fragments ML*₂Cl. The corresponding M−H and M−CO bond dissociation enthalpies (BDE's) are surprisingly high; indeed, in the case of the L*₂ClIr−CO bond, the magnitude of the obtained BDE is, to our knowledge, unprecedented. Finally, ab initio electronic structure calculations provide quantitative estimates for the absolute energetics of these elementary reactions in full support of the experimentally derived data.

Results

Kinetic Determination of a Lower Limit to the Ir−N₂ BDE of IrL*₂Cl(N₂). On the basis of kinetic experiments we are able to estimate a lower limit for the absolute BDE for the dinitrogen complex IrL*₂Cl(N₂).[4]

The dinitrogen complex is found to be very photosensitive. Even stray room light effects irreversible decomposition to give a product which can be characterized as cyclometalated HIrL*Cl[P(^{i}Pr)₂(CHMeCH₂)] (**A**). The decomposition is unaffected by the presence of N₂ atmosphere. These results suggest that thermal dissociation of N₂ from IrL*₂Cl(N₂) (if it were to occur) would be irreversible and would likely give the same cyclometalated product. At elevated temperature (120 °C), thermolysis of **A** in toluene is found to give predominantly the dihydride complex, IrL*₂Cl(H)₂.

In contrast with its photosensitivity, IrL*₂Cl(N₂) was found to be quite resistant to thermolysis. Decomposition in toluene, which gives predominantly IrL*₂Cl(H)₂, occurs only at elevated temperatures. The rate of decomposition (130−170 °C) is unaffected by the presence of N₂ atmosphere. Under ^{15}N₂ atmosphere (200 Torr, 150 °C), no incorporation of labeled N₂ is observed by IR. Thus, dissociation of N₂ (if it occurs) is irreversible and the rate can be no greater than the rate of decomposition.

An Eyring plot of the decomposition kinetics over the range 130−170 °C yields values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of 31.8 ± 1.6 kcal/mol and −6 ± 2 eu, respectively. The negative value of $\Delta S^\ddagger$ strongly implies a reaction with at least some associative character, and therefore, it does not *directly* yield any information about the Ir−N₂ BDE. However, the observed rates may at least be used as upper limits for the rate of dissociative loss of N₂, which we can then use to calculate lower limits for the activation enthalpy. We assume that $\Delta S^\ddagger$ for dissociation of the Ir−N₂ bond must be at least +10 eu, consistent with the only reported activation entropy for M−N₂ dissociation (21.5 eu for Ni(CO)₃(N₂)[5]) and with the somewhat more abundant data available for dissociation of isostructural M−CO bonds.[6] With this assumption, and using the observed rate of decomposition at 170 °C, $k = 8.21 \times 10^{-5}$ s^{-1}, we obtain 39.0 kcal/mol as a lower limit to $\Delta H^\ddagger$ for dissociation of N₂ from IrL*₂Cl(N₂).

Ford has found that CO reacts with Ir(PPh₃)₂Cl at a rate of 2.7×10^8 M^{-1} s^{-1}; even the bulky ligand PPh₃ adds rapidly to Ir(PPh₃)₂Cl (1.3×10^7 M^{-1} s^{-1}).[7] These rates suggest activation enthalpies less than 1 kcal/mol. Extrapolation from fast addition of CO to fast addition of N₂ can be based on some precedent: Poliakoff et al. have found that N₂ adds to CpV(CO)₃ slightly faster than does CO (1.5×10^8 and 1.3×10^8 M^{-1} s^{-1},
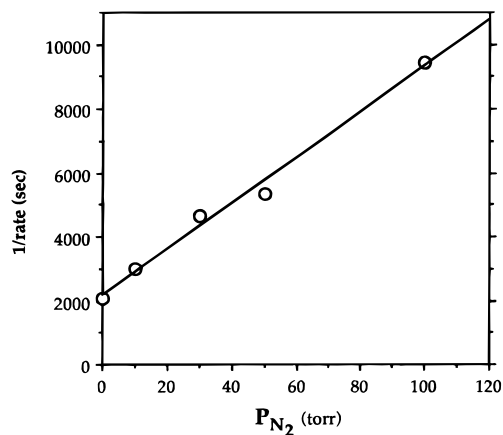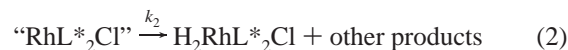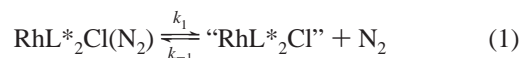

Figure 1. Effect of varying partial pressure of dinitrogen on the rate of decomposition of RhL*₂Cl(N₂).

respectively).[8] Even the less kinetically facile additions to CpNb(CO)₃ and CpTa(CO)₃ (10^6–10^7 M^{-1} s^{-1}) showed rates for N₂ which were equal, within a factor of 2, to those for CO addition.[8] Thus, we assume that the back-reaction of IrL*₂Cl with N₂ has a very low activation enthalpy (≤3 kcal/mol). We therefore obtain a value of 36 kcal/mol as a conservative *lower* limit to the Ir−N₂ BDE of IrL*₂Cl(N₂).

Kinetic Determination of a Lower Limit to the Rh−N₂ BDE of RhL*₂Cl(N₂). The kinetics of RhL*₂Cl(N₂) decomposition in cyclooctane solvent were measured. The major products are H₂RhL*₂Cl and H₂[L*₂Rh(μ-Cl)₂RhL*(cyclooctene)],[9] both of which are presumably derived from the dehydrogenation of cyclooctane. These products have also been obtained from thermolysis of [RhL*₂Cl]₂ in cyclooctane (under argon),[9] and it seems likely that in both cases they are derived from a common intermediate, i.e., monomeric "RhL*₂Cl".

In contrast with the behavior of IrL*₂Cl(N₂), the decomposition of RhL*₂Cl(N₂) is strongly inhibited by the presence of dinitrogen even at very low partial pressures. This may suggest a much lower reactivity on the part of rhodium toward the solvent and/or the ligand alkyl groups. The difference in the effect of N₂, compared with the iridium chemistry, presumably does *not* reflect much higher reactivity of the rhodium fragment, ML*₂Cl, toward N₂ (note that Ford has found that Rh(PPh₃)₂Cl reacts less rapidly than Ir(PPh₃)₂Cl with CO: 6.9×10^7 vs 2.7×10^8 M^{-1} s^{-1}).[7]

The kinetics of decomposition of RhL*₂Cl(N₂) under varying pressures of N₂ at 80 °C are consistent with the following scheme:

$$\text{RhL*}_2\text{Cl(N}_2) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{“RhL*}_2\text{Cl”} + \text{N}_2 \qquad (1)$$

$$\text{“RhL*}_2\text{Cl”} \overset{k_2}{\longrightarrow} \text{H}_2\text{RhL*}_2\text{Cl} + \text{other products} \qquad (2)$$

$$\text{d[RhL*}_2\text{Cl(N}_2)]/\text{d}t = k_{obs}[\text{RhL*}_2\text{Cl(N}_2)] =$$
$$k_1 k_2 [\text{RhL*}_2\text{Cl(N}_2)]/(k_{-1}[\text{N}_2] + k_2) \qquad (3)$$

$$1/k_{obs} = k_{-1}[\text{N}_2]/k_1 k_2 + 1/k_1 \qquad (4)$$

Thus a plot of $1/k_{obs}$ vs $P(\text{N}_2)$ yields a straight line (Figure 1). It should be noted, however, that this does not imply that the

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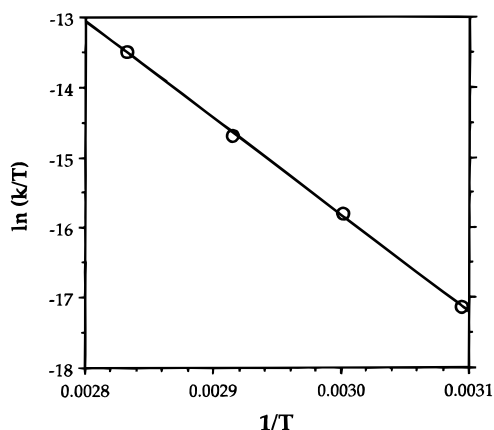(9) Shih, K.; Goldman, A. S. *Organometallics* **1993**, *12*, 3390−3392.

Figure 2. Eyring plot for decomposition of RhL*$_2$Cl(N$_2$).

species "RhL*$_2$Cl" is unsolvated or that the initial step is necessarily dissociative.

In the absence of added N$_2$ atmosphere (under 800 Torr Ar) the observed rate of decomposition of RhL*$_2$Cl(N$_2$) is dependent upon variables related to the rate at which N$_2$ escapes from solution. The reaction proceeds more slowly in an NMR tube than in an unstirred vessel with a larger ratio of surface area to liquid volume, and the rate is further increased by magnetic stirring in such a vessel. These results imply that even the residual N$_2$ in solution, produced by the decomposition, inhibits the reaction in the absence of stirring. However, when the reaction is conducted with stirring (ca. 1.5 mL with 7 cm^2 surface in a vessel with 60 cm^3 total volume) the intercept of the plot of $1/k_{obs}$ vs P(N$_2$) coincides exactly with the rate observed in the absence of added N$_2$ (Figure 1). This implies that under such conditions the pressure of N$_2$ is effectively "zero", i.e., the escape of N$_2$ from solution is much faster than the back reaction with "RhL*$_2$Cl" and is effectively irreversible.

Under ^{15}N$_2$ atmosphere (250 Torr), incorporation of ^{15}N$_2$ was monitored by IR spectroscopy as indicated by loss of the absorption band at 2107 cm^{-1} and concomitant growth of a band at 2037 cm^{-1}. The rate of exchange at 80 °C was found to be 5.92×10^{-4} s^{-1}, approximately equal to the rate of decomposition observed in the absence of N$_2$ atmosphere, 4.88×10^{-4} s^{-1} at 80 °C, in strong support of the scheme of eqs 1–4. The slight discrepancy between these two rates may be due to a small contribution by an associative pathway for N$_2$ exchange, but this possibility was not investigated further (for our purposes it was sufficient to demonstrate that reversible loss of N$_2$ does not occur significantly faster than decomposition in the absence of N$_2$ atmosphere).

An Eyring plot of the decomposition of RhL*$_2$Cl(N$_2$) (Figure 2) yields values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 27.4 ± 0.6 kcal/mol and 3.5 ± 1.7 eu, respectively. The activation entropy value is too high for a true associative pathway. Taking into account that an associative pathway would presumably involve a "reactant" with a concentration of 119 M, i.e., the cyclooctane C–H bond, we may convert the first-order rate constants to second-order; this yields an activation entropy of -6.0 ± 0.9 eu, which still seems significantly too high for a true associative process. However, the value of $\Delta S^{\ddagger}$ seems rather low for a true dissociative pathway. A priori, since the substitution reactions of four-coordinate d^8 complexes are generally associative, it would seem likely that solvent or a ligand alkyl group would play some role in the departure of the N$_2$ ligand. Thus it seems possible, though by no means certain, that the reaction has an associative component. To the extent that this is the case, $\Delta H^{\ddagger}$ for a simple dissociation must be greater than the observed value

of 27.4 kcal/mol. We therefore use 27.4 kcal/mol as a lower limit although the actual value may be equal or only slightly greater. Using an argument similar to the one used above for the iridium analogue, we can then estimate 24 kcal/mol as a *lower* limit to the Rh–N$_2$ BDE, with the distinction being that this lower limit may more closely approximate the actual value than in the iridium case.

Thermodynamics of N$_2$ Substitution by CO: Addition of CO and H$_2$ to IrL*$_2$Cl(CO). The dinitrogen complex IrL*$_2$Cl(N$_2$) undergoes a rapid substitution reaction with CO (eq 5). The enthalpy change associated with dissolving

$$IrL*_2Cl(N_2) + CO \rightarrow IrL*_2Cl(CO) + N_2 \qquad \Delta H_5 \quad (5)$$

IrL*$_2$Cl(N$_2$) in a CO-saturated benzene solution under CO atmosphere in the calorimeter is $-26.9(3)$ kcal/mol. Correcting for the (endothermic) heat of solvation of IrL*$_2$Cl(N$_2$) in benzene gives a solution phase value of $-36.1(4)$ kcal/mol for reaction 5. However, in addition to reaction 5, an equilibrium between monocarbonyl IrL*$_2$Cl(CO) and the dicarbonyl CO adduct is established (eq 6).

$$IrL*_2Cl(CO) + CO \rightleftharpoons IrL*_2Cl(CO)_2 \qquad \Delta H_6 \quad (6)$$

On the basis of equilibrium measurements (NMR), ΔH_6 was determined to be -8.9 kcal/mol (in good agreement with the previously reported enthalpy for addition of CO to Ir(PPh$_3$)$_2$-(CO)Cl[10]). At 50 °C, the temperature at which the calorimetric measurement was conducted, the equilibrium ratio of IrL*$_2$Cl-(CO)$_2$:IrL*$_2$Cl(CO) is 0.024 under 1.0 atm of CO. As only 2.4% of the complex in solution exists as dicarbonyl, and since the enthalpy of addition for the second carbonyl is small, only a minor correction is needed to obtain the enthalpy of reaction 5 from the reaction of IrL*$_2$Cl(N$_2$) with CO: $0.024 \times \Delta H_6 = 0.2$ kcal/mol. ΔH_5 is thus -35.9 kcal/mol, which may be added to the Ir–N$_2$ BDE of IrL*$_2$Cl(N$_2$) (≥ 36 kcal/mol) to obtain a *lower* limit to the Ir–CO BDE of IrL*$_2$Cl(CO) as 72 kcal/mol.

Addition of H$_2$ to IrL*$_2$Cl(CO) occurs in analogy with the well-known addition of H$_2$ to other Vaska-type complexes.

$$IrL*_2Cl(CO) + H_2 \rightleftharpoons IrL*_2Cl(CO)H_2 \qquad \Delta H_7 \quad (7)$$

Because of the very slow rate of equilibration of H$_2$ between gas and solution phases in an NMR tube, this reaction was monitored by UV–visible spectroscopy using a temperature-controlled spectrophotometer with magnetic stirring capability. Equilibrium measurements obtained over a 40–60 °C temperature range yielded values of $-10.3(12)$ kcal/mol and $-27(4)$ eu for ΔH and ΔS of reaction 7, respectively. This is in excellent agreement with values obtained by Vaska for addition of H$_2$ to closely related complexes.[11]

Reactions of IrL*$_2$ClH$_2$. The coordinatively unsaturated dihydride IrL*$_2$ClH$_2$ undergoes rapid addition of CO.

$$IrL*_2ClH_2 + CO \rightarrow IrL*_2Cl(CO)H_2 \qquad \Delta H_8 \quad (8)$$

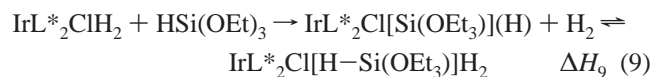The enthalpy of reaction 8 was calorimetrically determined to be $-34.3(5)$ kcal/mol. Note that loss of H$_2$ from the product, IrL*$_2$Cl(CO)H$_2$, is very slow; independent experiments monitored by NMR confirmed that, under the conditions and the time scale of the calorimetry experiment, conversion of IrL*$_2$Cl(CO)H$_2$ to IrL*$_2$Cl(CO) does not proceed to any significant extent.

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We find that the dihydride reacts with silanes to give a mixture of exchange product and adduct (eq 9).[12] Calorimetric

$$IrL^*_2ClH_2 + HSi(OEt)_3 \rightarrow IrL^*_2Cl[Si(OEt_3)](H) + H_2 \rightleftharpoons$$
$$IrL^*_2Cl[H-Si(OEt_3)]H_2 \quad \Delta H_9 \quad (9)$$

measurement of this reaction yields an enthalpy of $-6.1(2)$ kcal/mol. Unfortunately, the equilibrium within eq 9 does not lie to either extreme. It is therefore difficult to obtain a precise enthalpy for the reaction of interest (eq 10) particularly because

$$IrL^*_2ClH_2 + HSi(OEt)_3 \rightarrow IrL^*_2Cl[Si(OEt_3)](H) + H_2$$
$$\Delta H_{10} \quad (10)$$
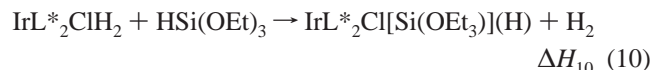
the concentration of H_2 in solution is difficult to estimate under the conditions of the calorimetric measurement. However, we may assume that H_2 addition to $IrL^*_2Cl[Si(OEt_3)](H)$ is exothermic (as it must be to counter the unfavorable entropy of addition) and therefore use ΔH_9 as an upper limit to the exothermicity of eq 10: $\Delta H_{10} \geq -6$ kcal/mol.
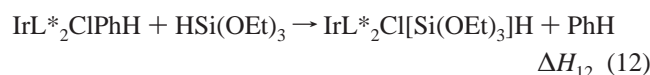
IrL*₂ClPhH and IrL*₂Cl(CCR)H. Addition of PⁱPr₃ (L*) to benzene solutions of [(cyclooctene)₂IrCl]₂ results in formation of IrL*₂ClPhH.[13] This is an unusual example of C—H bond addition to give an unsaturated late-metal hydrocarbyl complex. The phenyl hydride is very closely related to the presumed intermediates of several important examples of organometallic-catalyzed hydrocarbon functionalization.[14–18]

Like the dihydride, the phenyl hydride readily adds CO to give the six-coordinate adduct[13] which is indefinitely stable at 50 °C, the temperature at which the reaction was monitored calorimetrically.

$$IrL^*_2ClPhH + CO \rightarrow trans,trans\text{-}IrL^*_2ClPhH(CO)$$
$$\Delta H_{11} \quad (11)$$
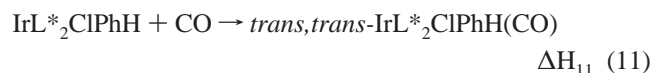
The reaction enthalpy is, within experimental error, equal to that of CO addition to the dihydride (eq 8); $\Delta H_{11} = -33.3(7)$ kcal/mol vs $\Delta H_8 = -34.3(5)$ kcal/mol.

IrL*₂ClPhH has been reported to rapidly react with H_2 to give IrL*₂ClH₂.[13] We did not investigate this reaction (or any other reaction of H_2) directly in the calorimeter because H_2 has a low solubility in organic solvents and the dihydride gives a significant equilibrium concentration of IrL*₂Cl(H₂)(H)₂ under H_2 atmosphere,[19] somewhat similar to the behavior of the silyl hydride (eq 9). We were able, however, to obtain the reaction enthalpy of IrL*₂ClPhH with HSi(OEt)₃ (eq 12); $\Delta H_{12} = -22.5(2)$ kcal/mol.[20]

$$IrL^*_2ClPhH + HSi(OEt)_3 \rightarrow IrL^*_2Cl[Si(OEt)_3]H + PhH$$
$$\Delta H_{12} \quad (12)$$

Table 1. Relative and Absolute Enthalpies (Experimental Lower Limits) (kcal/mol) of Addition to IrL₂Cl (L = PⁱPr₃, Experimental; L = PMe₃, Density Functional Theory Calculations)

addendum	ΔH_{rel}(exptl)	ΔH_{rel}(DFT)	ΔH_{abs}(exptl)	ΔH_{abs}(DFT)
N₂	0	0	≤ -36	-49.3
CO	$-35.9(4)$	-35.2	≤ -72	-84.4
H₂	$-11.9(14)$	-8.0	-48	-57.2
H—Ph	$>4.5(14)$	$+1.7^a$		-47.5^a
H—CCR	$\leq$ca. -12	-15.2	$\leq$ca. -48	-64.4
H—CH₃		$+11.7$		-37.6

^{a} ΔE value.[27]

A series of complexes IrL*₂ClH(C≡CR) has been reported by Werner.[21] Like the phenyl hydride, these complexes readily add CO to give six-coordinate adducts. Calorimetry reveals a reaction enthalpy approximately equal to that for CO addition to the dihydride or the phenyl hydride, $\Delta H_{13} = -32.5(3)$ kcal/mol.

$$IrL^*_2ClH(C≡CPh) + CO \rightarrow IrL^*_2Cl(CO)H(C≡CPh)$$
$$\Delta H_{13} \quad (13)$$
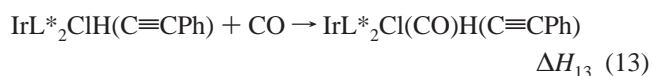
Computed Reaction Enthalpies. Most of the reactions investigated experimentally here were also studied computationally using ab initio electronic structure methods (see Computational Details). These calculations, and calculations on a few closely related reactions, were carried out using both L = PH₃ and L = PMe₃ as phosphine models. In a recent systematic study of the σ- and π-contributions to the orbital interaction energies in a large number of Fe(CO)₄PR₃ complexes, it was concluded that all PR₃ ligands were essentially σ-donors.[22] However, PMe₃ (and PⁱPr₃) was a "pure" σ-donor phosphine in which the π-contribution was less than 20% of the σ-contribution, whereas PH₃ was an intermediate ligand for which the magnitude of the π-contribution was slightly more than 20% of the σ-contribution. Van Wüllen has concluded in a computational study of M(CO)₅X (M = Cr, Mo, W; X = PH₃ and PMe₃) that the π-accepting abilities of PMe₃ and PH₃ are probably similar, but PMe₃ is a stronger σ-donor.[23] Although Tolman parameters indicate that PMe₃ remains slightly less electron donating than the experimentally used L* = PⁱPr₃,[24] it is clearly a considerably more realistic model phosphine ligand, electronically and sterically, than the phosphine ligand more commonly used in computational work, L = PH₃. Hence, results quoted in the text will refer to data from B3LYP calculations on complexes with L = PMe₃, unless otherwise noted.

The BDE for N₂ in M(PMe₃)₂Cl(N₂) is computed at the B3LYP level as 49.2 kcal/mol when M = Ir (Table 1) and 31.6 kcal/mol when M = Rh. The former value is approximately 13 kcal/mol above the (conservatively) estimated experimental lower limit, whereas the latter value is about 8 kcal/mol above the estimated lower limit. The computed difference in M–N₂ BDE's (M = Ir vs Rh) is 18 kcal/mol, whereas a highly tentative experimental value, derived from the difference in the two estimated lower limits, is about 12 kcal/mol. There does not

(12) Several analogues of IrL*₂Cl[Si(OEt₃)](H) have been reported, for example: Yamashita, H.; Kawamoto, A. M.; Tanaka, M.; Goto, M. *Chem. Lett.* **1990**, 2107−2110.

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(19) Le-Husebo, T.; Jensen, C. M. *Inorg. Chem.* **1993**, *32*, 3797−3798.

(20) Berry et al. have found that the analogous reaction of Cp₂Ta-(PMe₃)Ph with HSiMe₃, to yield Cp₂Ta(PMe₃)(SiMe₃) and benzene, is 12.3(6) kcal/mol exothermic: Jiang, Q.; Pestana, D. C.; Carroll, P. J.; Berry, D. H. *Organometallics* **1994**, *13*, 3679−3691.

(21) Höhn, A.; Otto, H.; Dziallas, M.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1987**, 852−854.

(22) Gonzalez-Blanco, O.; Branchadell, V. *Organometallics* **1997**, *16*, 5556−5562.

(23) van Wüllen, C. *J. Comput. Chem.* **1997**, *18*, **1997**, *18*, 1985−1992.

(24) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

appear to be an activation energy barrier for the addition of N_2 to either tricoordinate ML_2Cl complex.

Calculations on B3LYP-optimized $M(PH_3)_2Cl(N_2)$ geometries at the CCSD(T) level predict $M-N_2$ dissociation energies of 32.2 and 16.0 kcal/mol when M = Ir and Rh, respectively. The corresponding values at the B3LYP level are 11−15 kcal/mol higher at 43.7 and 31.0 kcal/mol, respectively. If we include the energetic effects of phosphine alkylation ($PH_3 \rightarrow PMe_3$) computed at the B3LYP level and furthermore convert to enthalpies (see Computational Details), we arrive at "predicted CCSD(T)" BDE's of 37.8 kcal/mol for $Ir-N_2$ and 16.6 kcal/mol for $Rh-N_2$. The former value is very close to the experimentally derived lower limit of 36 kcal/mol, whereas the latter value falls well below the experimentally derived lower limit of 24 kcal/mol.

Single point calculations at the CCSD(T) level predict an $Ir-CO$ dissociation energy of 68.7 kcal/mol for $Ir(PH_3)_2Cl(CO)$, again about 10 kcal/mol less than the B3LYP value (78.3 kcal/mol). The calculated $Ir-CO$ BDE in $Ir(PMe_3)_2Cl(CO)$ is 84.4 kcal/mol (B3LYP; Table 1). The CCSD(T) dissociation energy for $Ir(PH_3)_2Cl(CO)$ translates to a "predicted CCSD(T)" $Ir-CO$ BDE of 74.8 kcal/mol in $Ir(PMe_3)_2Cl(CO)$, close to the experimentally determined lower limit of 72 kcal/mol. The computed reaction enthalpy for the N_2/CO substitution reaction 5 becomes $\Delta H_5 = 49.2 - 84.4$ kcal/mol $= -35.2$ kcal/mol or $\Delta H_5 = 37.8 - 74.8$ kcal/mol $= -37.0$ kcal/mol; both values are in excellent agreement with the experimentally derived value of -35.9 kcal/mol. Szilagyi and Frenking have calculated the first M-CO dissociation energy in a series of metal hexacarbonyls (neutral and charged) at both the B3LYP and CCSD(T) level of theory using effective metal core potentials and basis sets similar to the ones used here.[25] Their B3LYP and CCSD(T) determined M−CO energies differed in all cases by less than 3 kcal/mol. For $W(CO)_6$, where a comparison could be made to an experimental value (46 ± 2 kcal/mol), the B3LYP and CCSD(T) values both compared extremely favorably at 45.9 and 48.0 kcal/mol, respectively. Our computed B3LYP − CCSD(T) difference is larger for the $Ir-CO$ BDE (~10 kcal/mol), and if the experimentally derived lower limit is in fact quite close to the true value, we might infer that our B3LYP BDE's are somewhat too large and that the CCSD(T) method, presumably the more accurate method, does produce the more accurate $Ir-X$ BDE for X = CO and N_2.

Although no measurements were made on CO addition to RhL^*_2Cl in the present work, we mention for completeness that the calculated $Rh-CO$ BDE in $Rh(PMe_3)_2Cl(CO)$ is 59.0 kcal/mol, about 25 kcal/mol less than the analogously computed $Ir-CO$ BDE. The $Rh-CO$ binding energy in $Rh(PH_3)_2Cl(CO)$ is computed at 57.5 kcal/mol at both the B3LYP and CCSD(T) levels of theory, and thus our "predicted CCSD(T)" $Rh-CO$ BDE in $Rh(PMe_3)_2Cl(CO)$ would also be 59.0 kcal/mol.

We have considered the oxidative addition of H_2, $H-CH_3$, Ph-H, and $H-C_2H$ to ML_2Cl as representative of reactions which yield M−H and M−C bonds. For the addition of H_2 to $Ir(PMe_3)_2Cl$, we obtain a ΔH of -57.2 kcal/mol (B3LYP; Table 1), whereas the computed exothermicity is considerably less for H_2 addition to $Rh(PMe_3)_2Cl$ (-28.1 kcal/mol). The computed exothermicities for addition of $H-C_2H$ and Ph−H to $Ir(PMe_3)_2Cl$ (-64.4 kcal/mol, $H-C_2H$;[26] -47.5 kcal/mol,[27] Ph−H) bracket the value obtained for H_2. For late-metal

systems, the addition of aryl C−H bonds is well established to be thermodynamically more favorable than addition of simple alkyl C−H bonds;[28] our calculations predict $\Delta H = -37.6$ kcal/mol for $H-CH_3$ addition to $Ir(PMe_3)_2Cl$, which is ca. 10 kcal/mol less exothermic than the addition of H−Ph.

The computed values for CO or H_2 addition to the four-coordinate $Ir(PMe_3)_2Cl(CO)$ complex (Table 2) are $\Delta H_6 = -12.6$ kcal/mol and $\Delta H_7 = -11.1$ kcal/mol, in good agreement with the experimental values determined here (-8.9 and -10.3 kcal/mol, respectively) or in previous computational work.[29] Whereas addition of $H-C_2H$ to $Ir(PMe_3)_2Cl(CO)$ remains in the exothermic range ($\Delta H = -7.5$ kcal/mol), the addition of Ph-H is predicted to be endothermic ($\Delta H \sim 8$ kcal/mol[27]). The computed exothermicity for $H-C_2H$ adding to IrL_2Cl exceeds that of Ph−H by 16.9 kcal/mol (see above); when adding to $IrL_2Cl(CO)$, the difference is only slightly smaller (15.4 kcal/mol).

Finally, additions of CO to the five-coordinate IrL_2ClHR complexes (R = H, Ph, and C_2H) are computed to be significantly exothermic (Table 2) with computed and measured exothermicities in good agreement. The experimental values cluster around 33 kcal/mol, whereas the computed values (ΔH(R = H) $= -38$ kcal/mol $< \Delta H$(R = Ph) $= -29$ kcal/mol[27] $< \Delta H$(R = C_2H) $= -27$ kcal/mol) display approximately the same mean but a larger spread.

Discussion

Knowledge of the enthalpies of reactions 5−12 permits calculation of the enthalpy of interconversion between any of the iridium complexes involved in these equations. For example,

$$IrL^*_2Cl(N_2) + H_2 \rightarrow IrL^*_2ClH_2 + N_2 \qquad (14)$$

$$\Delta H_{14} = \Delta H_5 + \Delta H_7 - \Delta H_8 = -11.9(14) \text{ kcal/mol}$$

$$IrL^*_2ClH_2 + PhH \rightarrow IrL^*_2ClPhH + H_2 \qquad (15)$$

$$\Delta H_{15} = \Delta H_{10} - \Delta H_{12} \geq 16.4(3) \text{ kcal/mol}$$

$$IrL^*_2Cl(CO) + PhH \rightarrow IrL^*_2Cl(CO)PhH \qquad (16)$$

$$\Delta H_{16} = \Delta H_7 - \Delta H_8 + \Delta H_{10} - \Delta H_{12} + \Delta H_{11} \geq$$
$$7.1(16) \text{ kcal/mol}$$

These results are summarized in Scheme 1 and Tables 1 and 2. In addition, on the basis of the determination of a lower limit for the $Rh-N_2$ BDE, the relative enthalpies previously reported for the rhodium manifold can now be used to obtain analogous lower limits for addition reactions of RhL^*_2Cl (Table 3).

Absolute Enthalpies of Addition to IrL^*_2Cl and RhL^*_2Cl. Kinetic studies of ligand substitution reactions have proven very

(25) Szilagyi, R. K.; Frenking, G. *Organometallics* **1997**, *16*, 4807−4815.

(26) The vinylidene isomer, $Ir(PMe_3)_2Cl(C{=}CH_2)$, is computed to be 13.4 kcal/mol lower in enthalpy than $Ir(PMe_3)_2ClH(C{\equiv}CH)$, in accord with numerous such isomerizations reported by Werner.[21]

(27) Normal-mode analysis could not be carried out on the H−Ph adducts. However, for the additions of $H-CH_3$ and $H-CCH$, it is calculated that ΔE is equal to ΔH within ± 0.2 kcal/mol. Thus values of ΔE are used in lieu of ΔH for the H−Ph additions.

(28) For excellent discussions of trends in M−C bond strengths, see: (a) Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1993**, *115*, 554−562. (b) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1997**, *119*, 10696−10719.

(29) (a) Abu-Hasanayn, F.; Krogh-Jespersen, K.; Goldman, A. S. *Inorg. Chem.* **1993**, *32*, 495−496. (b) Abu-Hasanayn, F.; Goldman, A. S.; Krogh-Jespersen, K. *J. Phys. Chem.* **1993**, *97*, 5890−5896. (c) Abu-Hasanayn, F.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **1993**, *115*, 8019−8023. (d) Abu-Hasanayn, F.; Krogh-Jespersen, K.; Goldman, A. S. *Inorg. Chem.* **1994**, *33*, 5122−5130.

Scheme 1

Scheme 1 (reaction network for Ir complexes, L* = PⁱPr₃):

- Cl–Ir(L*)₂(CO) with H and Ph ligands ← +H-Ph [≥ +7.1 (16)]
- + CO, −33.3 (7) connects to Cl–Ir(L*)₂(H)(Ph)
- Cl–Ir(L*)₂(H)(Ph) ← +H-Ph [≥ +4.3 (14)] ← Cl–Ir(L*)₂(N₂)
- Cl–Ir(L*)₂(N₂) → +CO −N₂, −35.9 (4) → Cl–Ir(L*)₂(CO)
- +H-SiR₃, −22.5 (2) down to Cl–Ir(L*)₂(H)(SiR₃)
- +H₂ / −N₂ [−11.9 (14)] from N₂ complex to Cl–Ir(L*)₂(H)(H)
- +H₂, −10.3 (12) from Cl–Ir(L*)₂(CO) to OC/Cl–Ir(L*)₂(H)(H)
- +H-Ph [≥ +16.4 (3)] diagonal
- Cl–Ir(L*)₂(H)(SiR₃) ← +H-SiR₃ [≥ −6.1 (2)] ← Cl–Ir(L*)₂(H)(H)
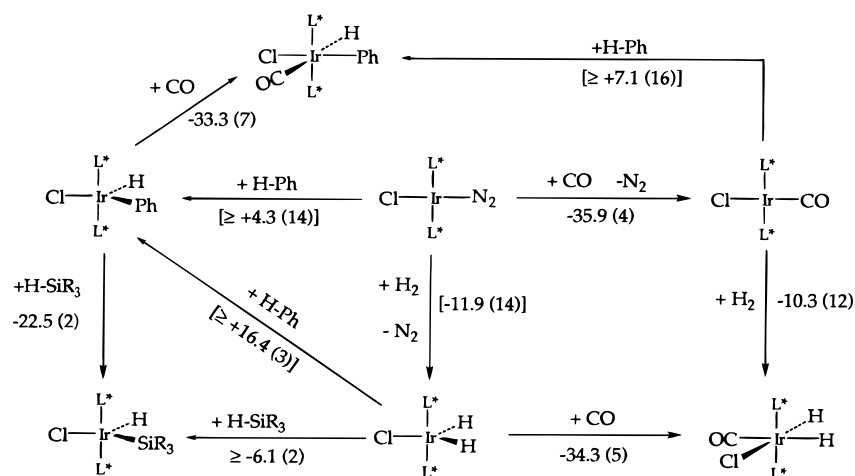- Cl–Ir(L*)₂(H)(H) → +CO, −34.3 (5) → OC/Cl–Ir(L*)₂(H)(H)

Table 2. Enthalpies (kcal/mol) of Addition to IrL₂Cl(CO) and IrL₂ClRH (L = PⁱPr₃, Experimental; L = PMe₃, Density Functional Theory Calculations)

complex	addendum	ΔH(exptl)	ΔH(DFT)
IrL₂Cl(CO)	H₂	−10.3(12)	−11.1
IrL₂Cl(CO)	CO	−8.9(16)	−12.6
IrL₂Cl(CO)	H−Ph	>ca. 7	+7.8[a]
IrL₂Cl(CO)	H−CCR	≤ca. −10	−7.5
IrL₂ClH₂	CO	−34.3(5)	−38.4
IrL₂ClPhH	CO	−33.3(7)	−31.2[a]
IrL₂ClH(CCR)	CO	−32.5(3)	−27.4

[a] ΔE value.[27]

Table 3. Relative Enthalpies[a] (ΔH, kcal/mol) and Lower Limits for the Absolute Enthalpy for Addition of XY to Rh(PⁱPr₃)₂Cl

XY	ΔH_rel	ΔH_abs
N₂	0	≤−24
CO	−31.7(10)	≤−55
ᵗBuNC	−25.9(9)	≤−49
C₂H₄	−8.3(9)	≤−31
PhC≡CPh	−6.3(11)	≤−29
H₂[a]	−16.0(9)	≤−39
C₈H₁₇C(O)H	−7.6(8)	≤−31
C₈H₁₇C(O)Cl	−17.0(8)	≤−40

[a] From ref 3.

useful for the estimation of absolute metal−ligand BDEs of 18-electron transition metal complexes. Such methods are not generally applicable toward 16-electron complexes since their substitution reactions generally proceed through facile *associative* pathways which disallow the determination of any much slower dissociative path. We have been fortunate in the present case to obtain rather slow upper limits for the rate of dissociation of N₂; this is only possible because there are no associative pathways or any associative pathways which do exist are not very facile. These upper limits to the rates afford lower limits to the M−N₂ BDE's as discussed above. From the enthalpy of interconversion with the N₂ complexes, one can then calculate lower limits for formation, from the fragments ML*₂Cl, of the iridium complexes discussed in this work (Table 1) and rhodium complexes investigated previously.

Metal−CO BDE's. The lower limit of 55 kcal/mol for the Rh−CO BDE of RhL*₂Cl(CO) is approximately equal to that of the strongest metal−CO bond previously reported (CpMn-(CO)₃;[30] see Table 4 for additional examples of M−CO BDE's). This high lower limit is consistent with previous theoretical

Table 4. First M−CO BDE's (Experimental and Theoretical; kcal/mol) of Some Stable Metal Carbonyl Complexes

complex	M−CO BDE	ref
Cr(CO)₆	36.8 ± 2	72
Mo(CO)₆	40.5 ± 2	72
W(CO)₆	46.0 ± 2	72
Fe(CO)₅	41 ± 2	72
Ru(CO)₅	27.6 ± 0.4	73
Os(CO)₅	30.6 ± 0.4	74
Ni(CO)₄	22−25	75 (refs 31 and 32)
Pd(CO)₄	9.6 (theory)	75
Pt(CO)₄	13.0 (theory)	75
Ru(dmpe)₂(CO)	43.0 ± 2	76
Mn(CO)₆⁺	32 ± 5	77
V(CO)₆⁻	30.8 ± 3.5	78
Mn(CO)₅⁻	40.6 ± 3.9	78
Co(CO)₄⁻	39.7 ± 3.7	78
CpV(CO)₄	35 ± 5	8
CpMn(CO)₃	55	30
(η⁶-C₆H₆)Cr(CO)₃	45 (theory)	30 (ref 45)
CpRh(CO)₂	46 (theory)	79
CpRh(PH₃)(CO)	44 (theory)	79
CpIr(CO)₂	57 (theory)	79
CpIr(PH₃)(CO)	56 (theory)	79
Ir(CO)₆³⁺	77.5 (theory)	25
Mn(CO)ₙ⁺ (n = 1−5)	≤31 ± 6	77
Cr(CO)ₙ⁻ (n = 1−5)	≤43.9 ± 3.9	78
Rh(PH₃)Cl(CO)	73 (theory)	31
Rh(PH₃)₂Cl(CO)	66 (theory)	32
Rh(PH₃)₂Cl(H)(CH₃)(CO)	23.9 (theory)	32

calculations by Morokuma[31] and by Ziegler[32] which predicted very high Rh−CO binding energies for Rh(PH₃)₂(CO)Cl (73 kcal/mol[31] and 66 kcal/mol,[32,33] respectively). Our calculated binding energies are 58 kcal/mol (L = PH₃) and 60.9 kcal/mol (L = PMe₃), and we obtain BDE's of 55.6 and 59.0 kcal/mol, respectively.

Consistent with the generally greater M−CO BDE's of third- vs second-row transition metals,[34] the M−CO BDE is much greater for IrL*₂Cl(CO) than for the rhodium analogue; indeed, the value of more than 72 kcal/mol is significantly greater than

(30) Burkey, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 8329−8333.

(31) Musaev, D. J.; Morokuma, K. *J. Organomet. Chem.* **1995**, *504*, 93−105.

(32) Margl, P.; Ziegler, T.; Blochl, P. E. *J. Am. Chem. Soc.* **1995**, *117*, 12625−12634.

(33) We use Ziegler's results for the *trans*-phosphine isomers only since with a phosphine as bulky as L* (as compared with the PH₃ used for the calculations) we assume that the *cis*-phosphine isomers would be much less stable.

(34) Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486-494 and references therein.

any previously reported M−CO BDE but consistent with our calculated BDE, 84.4 kcal/mol. Both the rhodium and iridium values may be taken to suggest that d^8 square planar complexes contain unusually strong M−CO bonds; however, factors not specific to the d^8 four-coordinate configuration may be at least as relevant. The nature of the ancillary ligands, i.e., the strong σ-donor (L*) and/or the π-donor in a trans position (chloride), probably plays an important role. By contrast, most known M−CO BDE's pertain to homoleptic carbonyls (Table 4). While homoleptic carbonyls offer advantages of simplicity and symmetry for both experimental and theoretical studies, their BDE values may, with the notable exception of the heavily charged $[Ir(CO)_6]^{3+}$,[25] be anomalously low and any direct comparison with values from this work is of uncertain significance. It is noteworthy, we believe, that organometallic chemistry is still at a stage in its development where we cannot even estimate the range of "typical" metal−CO BDE's.

For the Ir(III) complexes IrL*$_2$Cl(CO)RH (R = H, Ph, CCPh) absolute Ir−CO BDE's are obtained (not lower limits). The three values, which are all nearly equal (33 ± 2 kcal/mol), are in a range similar to many previously reported M−CO BDE's (Table 4); it is noteworthy that this is so despite several factors that might weaken the L*$_2$ClRHIr−CO bond, including the high (formal) oxidation state, the strong trans-influence ligand (H), and the ability of chloride to π-donate and stabilize an unsaturated species.[35] Thus these modest BDE's, like the very high BDE of IrL*$_2$Cl(CO), may be used to argue that previously determined M−CO BDE's are in some sense anomalously low. A very direct comparison may be made with the nearly analogous rhodium species RhL*$_2$Cl(CO)RH, where R = η^1-acyl. In these cases the Rh−CO BDE is experimentally estimated as ca. 13−16 kcal/mol.[36] Computationally, Moro-kuma and Ziegler have both calculated that the Rh−CO BDE of Rh(PH$_3$)$_2$Cl(CO)(CH$_3$)H is ca. 22 kcal/mol, i.e., 40−50 kcal/mol less than that calculated for Rh(PH$_3$)$_2$Cl(CO).[31−33]

Enthalpies of R−H Addition: Ir−R BDE's (R = H, Ph, CCPh). The exothermicity of H$_2$ addition to IrL*$_2$Cl is equal to (BDE$_{Ir−N2}$ − ΔH$_{14}$) ≥ 48 kcal/mol. The average Ir−H BDE is thus ≥76 kcal/mol.[37] This value lies just at the upper limit of the wide range of previously reported metal−hydrogen BDE's;[38] notably, comparable values are reported for other species which activate C−H bonds including Cp$_2$W[39] and Cp*Ir(PMe$_3$).[40] The high exothermicity of H$_2$ addition to IrL*$_2$Cl is in good agreement with previous calculations on CH$_4$ and H$_2$ addition to Ir(PH$_3$)$_2$Cl by Cundari and by us.[41,42] Our present calculations produce ΔH = −57.2 kcal/mol for the addition of H$_2$ to Ir(PMe$_3$)$_2$Cl which translates to an average Ir−H BDE of 81 kcal/mol. The addition of H$_2$ to RhL*$_2$Cl, previously found to be 16.0 kcal/mol more exothermic than

addition of N$_2$,[3] is now experimentally determined to be exothermic by more than 39 kcal/mol, corresponding to an average Rh−H BDE ≥ 72 kcal/mol. The computed exothermicity for H$_2$ addition to Rh(PMe$_3$)$_2$Cl is somewhat less at 28.1 kcal/mol,[43] corresponding to an average Rh−H BDE of 66 kcal/mol. These values are all fairly high, consistent with the ability of RhL*$_2$Cl to dehydrogenate alkanes, but they are less than the analogous iridium values in accord with the generally greater bond strengths of third- vs second-row metals.[44,45]

Addition of a benzene C−H bond to IrL*$_2$Cl is found to be at least 16 kcal/mol less exothermic than H$_2$ addition. This is a somewhat surprising observation; for example, on the basis of the Bryndza−Bercaw relationship[46] (eq 17) the enthalpy of

$$BDE_{M−X} − BDE_{M−Y} = BDE_{H−X} − BDE_{H−Y} \quad (17)$$

Ph−H addition is predicted to be equal to that of H$_2$ addition. While M−H BDE's are frequently greater than predicted on the basis of eq 17, the observed difference in this case, ≥16 kcal/mol, seems rather high. For example, Bergman and Hoff found that the enthalpy of H$_2$ addition to Cp*Ir(PMe$_3$) is approximately equal to that of Ph−H addition.[40] Bercaw has found that addition to Cp*$_2$Hf is only 6.0(3) kcal/mol more favorable for H$_2$ than Ph−H, and σ-bond metathesis of Cp*$_2$-ScH by Ph−H is endothermic by ca. 7 kcal/mol.[47] Likewise, Wolczanski recently reported that Ph−H addition to (silox)$_2$Ti= NSi^{t}Bu$_3$ is 7.0 kcal less favorable than addition of H$_2$.[28b]

In contrast to the difference between Ph−H and H$_2$ addition (≥16 kcal/mol favoring the latter), the exothermicity of acetylene C−H bond addition appears to be at least comparable to that of H$_2$ addition; this is evidenced by the observation of eq 18 as first reported by Werner.[48] We find that eq 18 proceeds

$$IrL*_2ClH_2 + HC≡CPh → IrL*_2ClH(C≡CPh) + H_2$$
$$ΔH_{18} \quad (18)$$
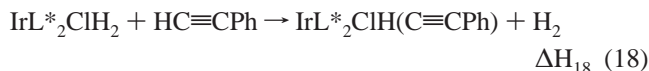
rapidly and to apparent completion in a sealed NMR tube (0.5 mL of solution; 2.0 mL of gas phase). However, in the closed system of the calorimeter cell, where the ratio of gas-phase volume to solution-phase volume is very small, secondary reactions of the H$_2$ product occur to a very significant extent (including the formation of significant concentrations of styrene). This precludes any accurate calorimetric measurement. Nevertheless, the fact that reaction 18 proceeds so readily in a sealed NMR tube strongly suggests that it is exothermic or at most only slightly endothermic. In conjunction with the relative H−H and H−CCR BDE's,[49] this result implies that the Ir−CCPh BDE of IrL*$_2$ClH(C≡CPh) is 27 kcal/mol stronger than the Ir−H BDE of IrL*$_2$ClH$_2$. As is commonly done in analyses of this type, we can then use the *average* Ir−H BDE of IrL*$_2$ClH$_2$ (≥76 kcal/mol) to estimate an Ir−CCPh BDE of ≥103 kcal/

(35) The importance of π-donation in the stabilization of coordinatively unsaturated species has been well demonstrated by Caulton and others, including the particular case of Ir(PR$_3$)$_2$ClH$_2$. See for example: Hauger, B. E.; Gusev, D.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 8−214.

(36) Wang, K. Ph.D. Thesis, Rutgers University, 1995.

(37) The BDE of H$_2$ is 104.21 kcal/mol: *CRC Handbook of Chemistry and Physics*; 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1990; pp 9−102.

(38) For numerous metal−hydrogen BDE values and a good lead reference, see: Wang, D.; Angelici, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 935.

(39) Calado, J. C. D.; Dias, A. R.; Simões, J. A. M.; Silva, M. A. V. R. D. *J. Organomet. Chem.* **1979**, *174*, 77−80.

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mol. To the best of our knowledge this value is significantly greater than any previously reported metal—carbon single-bond dissociation enthalpy. The electronic structure calculations predict $\Delta H_{18} = -7.2$ kcal/mol. Using the same reasoning as above, the Ir—CCH BDE would be estimated as 115 kcal/mol; direct calculation of the Ir—CCH BDE yields a value of 111 kcal/mol.

Presumably, the unusually high value of the Ir—CCR BDE largely reflects the "intrinsic" tendencies of both the alkynyl group and the IrL*$_2$Cl unit to form strong bonds, i.e., the same factors (not specific to the Ir—CCR interaction) which lead to the high C—H BDE of acetylenes and the high Ir—H BDE's of IrL*$_2$ClH$_2$. These factors are explicitly reflected in eq 19 (a

$$BDE_{M-R} = BDE_{M-H} + BDE_{H-R} - BDE_{H-H} \quad (19)$$

rearranged form of eq 17 in which X = H and Y = R). However, it should be noted that M—R bonds are usually weaker than would be predicted on the basis of eq 19. Yet eq 19 seems to often hold reasonably well in the specific case of R = alkynyl, i.e., metal—alkynyl bonds are typically found to be very strong even *after* accounting for the intrinsically strong bonding of the alkynyl unit.[46,47,50] An excellent detailed discussion of metal—alkynyl bonding is found in a recent paper by McGrady et al.[51]

R—H Addition to IrL*$_2$Cl(CO). The value of the enthalpy of addition of H$_2$ to IrL*$_2$Cl(CO), -10.3 kcal/mol, is well precedented by analogues with ligands other than P^{i}Pr$_3$.[11] This is at least 38 kcal/mol less exothermic than addition to the three-coordinate IrL*$_2$Cl. The value corresponds to an average Ir—H BDE of 57 kcal/mol. However, it seems unlikely that the first and second Ir—H BDE's are approximately equal.

$$IrL*_2Cl(CO)H_2 \rightarrow IrL*_2Cl(CO)H^\bullet + H^\bullet \quad (20)$$

$$IrL*_2Cl(CO)H^\bullet \rightarrow IrL*_2Cl(CO) + H^\bullet \quad (21)$$

Formation of the H—IrL*$_2$Cl(CO) bond (the reverse of eq 21) probably involves a significant promotional energy which would imply that formation of the H—IrL*$_2$Cl(CO)H bond (the reverse of eq 20) is considerably more exothermic than the mean value. Spectroscopic evidence (as well as calculations; see below) supports this idea: the Ir—H vibrational frequencies (and thus the force constants) of IrL*$_2$Cl(CO)H$_2$ (2097, 2205 cm^{-1}) are only slightly less than those of IrL*$_2$ClH$_2$ ($\nu_{sym} = 2255$ cm^{-1}, $\nu_{asym} < 2255$ cm^{-1}).[52,53]

The *relative* enthalpies for addition of H$_2$, Ph—H, and H—CCR to the four-coordinate carbonyl IrL*$_2$Cl(CO) are essentially the same as for addition to the three-coordinate fragment, IrL*$_2$Cl. (This follows from the experimental observation that the enthalpies of CO addition to the respective IrL*$_2$ClRH complexes are approximately equal.) Addition of benzene to IrL*$_2$Cl(CO) is found to be endothermic by at least 6 kcal/mol, in contrast with the very exothermic addition to IrL*$_2$Cl. Accordingly, elimination of benzene from IrL*$_2$Cl-(CO)PhH is observed to occur although surprisingly high

temperatures are required: at 120 °C the complex slowly eliminates benzene to give complete conversion to IrL*$_2$Cl-(CO).[54]

In contrast with the benzene addition, the acetylene C—H addition should be at least comparable to that for H$_2$ addition and thus exothermic. Accordingly, the acetylide hydride is completely stable at 120 °C. However, we have been unable to observe the C—H addition reaction; at temperatures of 120 °C or above a solution containing IrL*$_2$Cl(CO) and HCCPh undergoes decomposition to give unidentified products.

R—H Addition: Calculations. Computed reaction enthalpies of R—H addition (R = H, Ph, CCH) to both Ir(PMe$_3$)$_2$Cl and Ir(PMe$_3$)$_2$Cl(CO) are in good agreement with the experimental data discussed above. Furthermore, addition of methane (R = CH$_3$) is calculated to be less favorable than the other additions (Table 1), in accord with the fact that no complexes of the form Ir(PR$_3$)$_2$Cl(alkyl)H have been isolated. The agreement between theory and experimental results furnishes some confidence in the validity of those calculations for which we have no directly comparable experimental data. These calculations prove valuable in analyzing the factors which contribute to the addition enthalpies. In particular, the calculations afford individual M—R BDE's in addition to the overall R—H addition enthalpies. Additionally, they allow us to examine the effects of varying the nature of the PR$_3$ ligand by comparing PMe$_3$ complexes with their PH$_3$ analogues.

As noted above, whereas the average (experimentally determined) Ir—H BDE of Ir(PR$_3$)$_2$Cl(CO)H$_2$ is 57 kcal/mol, the enthalpies of eqs 20 and 21 need not be similar. Indeed, the first Ir—H BDE of Ir(PMe$_3$)$_2$Cl(CO)H$_2$ (eq 20) is calculated to be 83.7 kcal/mol, comparable to that of the average Ir—H BDE of Ir(PMe$_3$)$_2$ClH$_2$. The second BDE of Ir(PMe$_3$)$_2$Cl(CO)H$_2$ is calculated to be dramatically less: only 32.0 kcal/mol. Thus according to the above reasoning, the promotional energy required for addition of H$^\bullet$ to Ir(PR$_3$)$_2$Cl(CO) is on the order of 50 kcal/mol.

In contrast with Ir(PR$_3$)$_2$Cl(CO)H$_2$, the two Ir—H BDE's of Ir(PH$_3$)$_2$ClH$_2$ are very similar: 76.2 and 79.6 kcal/mol for the first and second BDE's, respectively. Thus, the second BDE is slightly higher than the first, in contrast with the 50 kcal/mol difference favoring the first BDE of Ir(PH$_3$)$_2$Cl(CO)H$_2$. The contrast is even more striking for the PMe$_3$ complexes where the first and second BDE's are calculated to be 71.7 and 90.0 kcal/mol, respectively. The origin of the large difference between the two Ir—H BDE's in the PMe$_3$ complex is unclear.

As noted above, calculations and experimental results indicate that the M—R BDE's, particularly for R = alkyl, are much weaker than would be predicted on the basis of the M—H BDE's and the Bercaw—Bryndza equation (eqs 17 and 19). This phenomenon, while perhaps especially pronounced in the case of the present study, seems fairly general for d^n complexes ($n > 0$). Ziegler has concluded that the large difference in M—H vs M—CH$_3$ BDE's for d$^{n>0}$ transition metal centers is due to unfavorable interactions between electrons in the occupied metal and methyl orbitals ("filled—filled repulsions").[55] This idea finds support in the context of the present system. The much more favorable addition of H—Ph and H—C$_2$H versus H—CH$_3$ can be attributed to the presence of low-lying π^* acceptor orbitals on the phenyl and alkynyl fragments, which are capable

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(54) Detailed kinetics of this reaction are reported elsewhere: Rosini, G. P.; Wang, K.; Patel, B.; Goldman, A. S. *Inorg. Chim. Acta* **1998**, *270*, 537—542.

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Table 5. Calculated (B3LYP) Enthalpies of Addition (kcal/mol) and Effects of Phosphine Methylation (substitution of PMe_3 for PH_3)

metal center	addendum	ΔH (L = PH$_3$)	ΔH (L = PMe$_3$)	$\Delta\Delta H$
IrL$_2$Cl	H–H	−51.2	−57.2	−6.0
IrL$_2$Cl	H–CH$_3$	−27.2	−37.6	−10.4
IrL$_2$Cl	H–Ph	−32.9[a]	−47.5[a]	−14.6
IrL$_2$Cl	H–CCH	−49.8	−64.4	−14.6
IrL$_2$Cl	N$_2$	−42.0	−49.3	−7.3
IrL$_2$Cl	CO	−76.2	−84.4	−8.2
IrL$_2$ClH•	•H	−76.2	−71.7	+4.5
IrL$_2$ClH•	•CH$_3$	−51.9	−51.8	+0.1
IrL$_2$ClH•	•Ph	−67.7	−71.8	−4.1
IrL$_2$ClH•	•CCH	−107.0	−111.1	−4.1
IrL$_2$Cl(CO)	H–H	−3.8	−11.1	−7.3
IrL$_2$Cl(CO)	H–CH$_3$	+20.4	+14.9	−5.5
IrL$_2$Cl(CO)	H–Ph	+15.1[a]	+7.8[a]	−7.3
IrL$_2$Cl(CO)	H–CCH	+0.7	−7.5	−8.1
IrL$_2$Cl(CO)	CO	−6.3	−12.6	−6.3
IrL$_2$ClH$_2$	CO	−28.8	−38.3	−9.3

[a] ΔE value.[27]

of mitigating repulsive filled−filled interactions. Furthermore, in a case of d^0 metal−hydrocarbyl bond formation, Wolczanski has found that H−CH$_3$ adds slightly *more* favorably than H−Ph (by 0.9 kcal/mol) to (silox)$_2$Ti=NSi^{t}Bu$_3$.[28b] In the present work, additions of all substrates considered, H$_2$, CH$_3$−H, Ph-H, and H−C$_2$H, as well as CO and N$_2$, are calculated to be more favorable for the more electron-rich PMe$_3$ complexes; however, the magnitude of the difference varies between substrates, particularly for addition to IrL$_2$Cl (Table 5). Computationally substituting PMe$_3$ for PH$_3$ (i.e., methylating the phosphines and thereby increasing electron-donating ability of the ancillary ligands) favors H−CH$_3$ addition to IrL$_2$Cl by less (−10.4 kcal/mol) than it favors addition of H−C$_2$H or H−Ph (−14.6 kcal/mol). Since there are no filled−filled repulsions in the M−H interaction, the effect lies solely in the M−R interaction and is illustrated most markedly when the individual Ir−R BDE's of IrL$_2$ClRH are considered. In this case, methylation of the phosphines results in increased Ir−Ph and Ir−C$_2$H BDE's (∼4 kcal/mol) but has no effect on the Ir−CH$_3$ BDE (51.8 kcal/mol vs 51.9 kcal/mol for the PH$_3$ complex).[56]

Anderson has recently determined by spectroscopic (ESR and near-IR) methods that π-interaction with a methyl group raises the energy of an electron in Cp*$_2$Ti−Me by 1963 cm^{-1} relative to Cp*$_2$Ti−H.[57] One might make the very crude approximation that in IrL$_2$ClHR or IrL$_2$ClHR(CO) there are two full orbitals of π-symmetry which can interact with the methyl group, and thus, the total energy of the π-interactions should be four times that in Cp*$_2$Ti−Me, or 22.5 kcal/mol. This value is centered between our calculated differences for CH$_3$−H and H−H addition, 19.6 and 26.1 kcal/mol, to IrL$_2$Cl and IrL$_2$Cl(CO), respectively. While the level of agreement is probably fortuitous, it would appear that filled−filled repulsions of approximately the same magnitude are indeed operative in both cases. The importance of such an effect can hardly be understated as it may significantly influence almost every reaction which involves d^n (n > 0) transition metal alkyl complexes as either reactants, products, or intermediates.

Conclusions

Current understanding of the energetics associated with organometallic addition reactions (Lewis bases, L, or covalently bonded species, X−Y) is still quite limited. Most of the relevant data refer to addition to 16-electron species, and much of that involves species which may be rather unrepresentative; for example, M−CO BDE's in homoleptic carbonyls may be anomalously low and additions to Vaska-type complexes are undoubtedly disfavored by the high stability of the four-coordinate d^8 configuration. In this study we have elucidated a thermodynamic manifold which includes a wide range of very important and distinct configurations including three-, four-, and five-coordinate d^8 (IrL*$_2$Cl, IrL*$_2$ClL′, and IrL*$_2$Cl(CO)$_2$) and five- and six-coordinate d^6 (IrL*$_2$ClRH and IrL*$_2$ClRH(CO)).

Even though it is a lower limit, the value of 72 kcal/mol for the Ir−CO BDE is, to our knowledge, much greater than any previously reported M−CO BDE. Likewise, the estimated lower limit for the Ir−CCR (homolytic) BDE, 105 kcal/mol, is the highest M−C BDE reported to date. To some extent, these high values apparently reflect a tendency of the L*$_2$IrCl fragment to form very strong bonds. However, these BDE's may actually be more "typical" than one might infer on the basis of the limited set of existing organometallic thermochemical data.

Our electronic structure calculations produce reaction energies that are in excellent agreement with the experimental results found in this work. For example, the directly measured enthalpies of addition of H$_2$ and CO to IrL$_2$(CO)Cl and the addition of CO to IrL$_2$ClH$_2$ are reproduced within a few kilocalories per mole (Tables 1 and 2). While these values are consistent with the experimental lower limits, it must also be taken into account that the experimental and calculated values do refer to different phases. Thus, even if we could obtain "absolute" enthalpies in solution, such values might differ from idealized gas-phase values due to significant interactions between the highly unsaturated ML$_2$Cl species and solvent. The computational method applied (approximate density functional theory) permits the use of realistic ligands, which is clearly important for establishing successful correlations between experimental and computational data.

The range of bond strengths of typical metal−carbon bonds is surely one of the most fundamental issues of organometallic chemistry. We believe that this work has broad implications concerning this issue; perhaps to an even greater extent, however, it serves to highlight the present deficiency of relevant thermochemical data and demonstrates the need for additional experimental and computational studies.

Experimental Section

General Considerations. All manipulations involving organo-iridium complexes were performed under inert atmospheres of argon or nitrogen using standard high vacuum or Schlenk tube techniques or in a Vacuum/Atmospheres glovebox containing less than 1 ppm of oxygen and water. Solvents were dried and distilled under dinitrogen before use employing standard drying agents.[58] Only materials of high purity as indicated by IR and NMR spectroscopies were used in the calorimetric experiments. NMR spectra were recorded using either a Varian Gemini 300-MHz spectrometer or a Varian XL-400 spectrometer. IR spectra were obtained using a Mattson Genesis Series FTIR spectrophotometer. Irradiations were conducted using a 200-W Hg-arc Oriel lamp. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction[59] or the enthalpy of solution for KCl in water.[60]

(56) While the absolute effect of phosphine methylation upon the Ir−CH$_3$ BDE is striking, we place a greater confidence in both the validity and the importance of the calculated relative effects upon the various Ir−R BDE's. In other words, regardless of the absolute change, the less favorable (or more unfavorable) effect vis-à-vis Ir−Ph, Ir−C$_2$H, and especially Ir−H is the more significant observation.

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The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described,[61] and typical procedures are described below. $IrL_2*Cl(N_2)$,[4] $IrL_2*Cl(CO)$,[4] $IrL_2*Cl(H)(C_6H_5)$,[13] $IrL_2*Cl(H)(C\equiv CR)$,[21] and IrL_2*ClH_2[13] were prepared as previously reported.

Infrared Titrations. Prior to every set of calorimetric experiments involving CO, an accurately weighed amount (±0.1 mg) of the organoiridium complex was placed in a test tube fitted with a septum, and C_6H_6 was subsequently added. The solution was then exposed to excess CO, followed by vigorous shaking. The reactions were monitored by infrared spectroscopy, and the reactions were found to be rapid, clean, and quantitative under experimental calorimetric (temperature and concentration) conditions necessary for accurate and meaningful calorimetric results. These conditions were satisfied for all organoiridium reactions investigated involving CO.

NMR Titrations. Prior to every set of calorimetric experiments involving a new reaction, an accurately weighed amount (±0.1 mg) of the organometallic complex was placed in a Wilmad screw-capped NMR tube fitted with a septum and C_6D_6 was subsequently added. The solution was titrated with a solution of the ligand of interest by injecting the latter in aliquots through the septum with a microsyringe, followed by vigorous shaking. The reactions were monitored by ^1H and ^{31}P NMR spectroscopy, and the reactions were found to be rapid, clean, and quantitative under experimental calorimetric conditions. These conditions were satisfied for all organometallic reactions investigated.

Thermolysis of $IrL_2*Cl(N_2)$. Samples (0.5 mL) of 20 mM $IrL_2*Cl(N_2)$ in toluene were heated in a GC oven at 130−170 °C, and the decomposition was monitored by ^{31}P NMR spectroscopy (at room temperature). It was found that, in addition to the formation of IrL_2*ClH_2, $IrL_2*Cl(CO)$ was also formed. Presumably, the carbonyl complex arises from an oxygenated impurity in the solvent which has yet to be identified.

Photolysis of $IrL_2*Cl(N_2)$. Short-term photolysis of samples of $IrL_2*Cl(N_2)$ in benzene or toluene resulted in the formation of several new species, the major species being the product derived from the cyclometalation of an isopropyl group, as evidenced by the large J_{P-P} = 357 Hz, and the observation of a hydride resonance when the irradiation is conducted in perdeuterio solvent.

Reaction of $IrL_2*Cl(N_2)$ with CO. A 0.5-mL sample of 20 mM $IrL_2*Cl(N_2)$ in C_6D_6 was placed in a J. Young resealable NMR tube, and the sample then placed under 1 atm of CO. After vigorous shaking of the sample, ^{31}P NMR spectroscopy and IR spectroscopy showed the immediate disappearance of $IrL_2*Cl(N_2)$ and the formation of $IrL_2*Cl(CO)$ (see below for discussion regarding the presence of $IrL_2*Cl(CO)_2$.)

Equilibrium of $IrL_2*Cl(CO)$ with H₂. A 0.5 mM solution (2.5 mL) of $IrL_2*Cl(CO)$ in benzene was placed with a magnetic stir bar in a specially designed UV−visible cell (1-cm path length, equipped with a Teflon stopcock seal and an O-ring joint to enable attachment to a high vacuum line for the addition of H₂). The sample was then freeze−pump−thawed and placed under 100 Torr of H₂. The UV−vis instrument was equipped with a stirrer to aid in problems associated with slow H₂ dissolution times. The equilibrium was examined from 40 to 60 °C by monitoring the absorbances of $IrL_2*Cl(CO)$ at 379.1 and 431.8 nm until equilibrium was reached, and then the data were fitted exponentially to obtain $t_∞$ absorbance values. The equilibrium constant was then determined at each wavelength and then averaged to give K values of 23.19, 15.33, and 8.53 at 40, 50, and 60 °C, respectively. A plot of ln K vs $1/T$ gives $\Delta H = -10.3(12)$ kcal/mol and $\Delta S = -27(4)$ eu.

Reaction of IrL_2*ClH_2 with HC≡CR. To a 5-mL sample of 20 mM IrL_2*ClH_2 in C_6D_6 was added 1 equiv (approximately 10 μL) of either phenylacetylene or methyl propiolate (R = Ph, C(O)OMe) via microsyringe. The solution immediately turned a deep red color, and ^1H and ^{31}P NMR spectroscopies showed the complete and immediate

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conversion to $IrL_2*Cl(H)(C\equiv CR)$, without the concurrent formation of any rearranged vinylidene product under the calorimetric conditions.

Reaction of $IrL_2*Cl(H)(C\equiv CPh)$ with CO. A 0.5-mL sample of 20 mL of $IrL_2*Cl(H)(C\equiv CPh)$ in C_6D_6 was placed in a J. Young NMR tube and then placed under 1 atm of CO. Upon vigorous shaking of the tube, the color immediately changed from a dark red to a colorless solution. Spectroscopic characterization showed the complete disappearance of $IrL_2*Cl(H)(C\equiv CPh)$ and the formation of a single new organometallic product. On the basis of the data, the complex can be unequivocally assigned as being the simple CO adduct (with the H trans to CO), $IrL_2*Cl(H)(CO)(C\equiv CPh)$. ^1H NMR (C_6D_6): 7.30 (d, J_{H-H} = 7.5 Hz, ortho, 2 H), 7.09 (t, J_{H-H} = 7.5 Hz, meta, 2 H), 6.92, (t, J_{H-H} = 7.5 Hz, para, 1 H), 2.86 (m, P(C*H*Me₂)₃, 6 H), 1.25 (d of vt, J_{P-H} ≈ J_{H-H} = 7 Hz, P(CH*Me₂*)₃, 36 H), −8.45 (t, J_{P-H} = 30.5 Hz, Ir-*H*, 1 H). IR (C_6D_6): $\nu_{C\equiv O}$ = 2000 cm⁻¹ (2024 cm⁻¹ for IrL_2*Cl-(D)(CO)(C≡CPh), $\nu_{C\equiv C}$ = 2130 cm⁻¹.

Reaction of IrL_2*ClH_2 and $IrL_2*Cl(H)(Ph)$ with HSi(OEt)₃. To a 5-mL sample of 20 mM dihydride or phenylhydride in C_6D_6 was added 1 equiv (approximately 20 μL) of HSi(OEt)₃ via microsyringe. ^1H and ^{31}P NMR spectroscopies showed the complete and immediate conversion to a single new organometallic species, which can be unequivocally assigned as being the simple silane adduct $IrL_2*Cl(H)$-(Si(OEt)₃). No other species were observed under the conditions used for calorimetry. ^1H NMR (C_6D_6): 3.98 (qt, J_{H-H} = 6.8 Hz, Si(OC*H₂*-CH₃)₃, 6 H), 2.86 (m, P(C*H*Me₂)₃, 6 H), 1.32 (d of vt, J_{P-H} ≈ J_{H-H} = 6.4 Hz, P(CH*Me₂*)₃, 18 H), 1.31 (d of vt, J_{P-H} ≈ J_{H-H} = 6.4 Hz, P(CH*Me₂*)₃, 18 H), 1.20 (t, J_{H-H} = 7.2 Hz, Si(OCH₂C*H₃*)₃, 9 H), −20.26 (t, J_{P-H} = 13.2 Hz, Ir-*H*, 1 H).

Calorimetric Measurement for Enthalpies of Solution in C_6H_6. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. A 20−30-mg sample of IrL_2*ClH_2, $IrL_2*Cl(N_2)$, or $IrL_2*Cl(H)(Ph)$ was accurately weighed into the lower vessel, and it was then closed and sealed with 1.5 mL of mercury. Benzene (4 mL) was added, and the remainder of the cell was assembled, removed from the glovebox, and inserted in the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no iridium complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30.0 °C (about 2 h) the reaction was initiated by inverting the calorimeter. The reported enthalpies of solution represent the average of five individual calorimetric determinations. They were determined to be 5.2 ± 0.1 kcal/mol for IrL_2*ClH_2, 9.2 ± 0.1 kcal/mol for $IrL_2*Cl(N_2)$, and 7.1 ± 0.1 kcal/mol for $IrL_2*Cl(H)(Ph)$.

Calorimetric Measurement for Reactions with CO. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. A 20-mg sample of iridium complex was accurately weighed into the lower vessel, and it was then closed and sealed with 1.5 mL of mercury. Benzene solution (3 mL) saturated with CO was added, and the rest of the space in the vessel was purged with carbon monoxide. The remainder of the cell was assembled, removed from the glovebox, and inserted in the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no iridium complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30.0 °C (about 2 h), the reaction was initiated by inverting the calorimeter. When the thermal equilibrium was reached again after the end of the reaction (1−2 h), the vessels were then removed from the calorimeter, taken into the glovebox, and opened and the infrared cell was filled under inert atmosphere. Conversion to desired product was found to be quantitative under these reaction conditions. Each enthalpy of reaction represents the average of five individual calorimetric determinations. The enthalpy of reaction of IrL_2*ClH_2 with CO was determined to be −29.1 ± 0.4 kcal/mol. The enthalpy of reaction of $IrL_2*Cl(H)(Ph)$ with CO was determined to be −33.3 ± 0.7 kcal/mol. The enthalpy of reaction of $IrL_2*Cl(N_2)$ with CO was determined to be −26.9 ± 0.3 kcal/mol. The enthalpy of reaction of $IrL_2*Cl(H)$-(C≡CPh) with CO was determined to be −32.5 ± 0.3 kcal/mol.

Computational Details. Ab initio electronic structure calculations were carried out using the GAUSSIAN 94 series of programs on

Hewlett-Packard 735 and Silicon Graphics Indigo workstations.[62] The large majority of the calculations employed the B3LYP hybrid density functional,[63] effective core potentials (ECP's) on the metal atoms, and basis sets of double-ζ or better quality. The Hay−Wadt relativistic small-core ECP's and corresponding basis sets (split valence double-ζ) were used for Rh and Ir (LANL2DZ model).[64] We used the Dunning/Huzinaga all-electron, full double-ζ plus polarization function basis set for the second- and third-row elements (C, N, O, P, and Cl).[65] Hydrogen atoms formally existing as hydrides in the product complexes were described by the 311G(p) basis set;[66] hydrogen atoms in the methyl groups received an STO-3G description;[67] all other hydrogen atoms carried a 21G basis set.[68] Proper basis set substitutions were made in the reactants (H_2, CH_4, C_2H_2, C_6H_6) for the presence of "hydrides". Restricted Hartree−Fock theory was used for both closed and open shell systems.

Geometries were fully optimized[69] under appropriate symmetry constraints (typically C_{2v} or C_s). When L = PH_3, the stationary points were fully characterized by normal-mode analysis (numerical differentiation of analytical gradients), and the total energies at the stationary points along with the (unscaled) vibrational frequencies formed the basis for the calculation of reaction energies (ΔE, $T = 0$ K). The thermodynamic corrections for finite temperature required to convert reaction energies to enthalpies (ΔH, $T = 298$ K) were evaluated using standard statistical mechanical formulas.[70] Since the experiments were carried out in a condensed phase, the enthalpy contributions arising from changes in volume (e.g., two molecules going to one) have been ignored in the thermodynamic calculations. The zero-point energies and corrections for finite temperature found when L = PH_3 were then assumed to apply also when L = PMe_3, the computational model for L* = P^iPr_3.

For $M(PH_3)_2Cl(N_2)$ and $M(PH_3)_2Cl(CO)$ (M = Ir and Rh) and their constitutive fragments improved total energies were obtained at the CCSD(T) level of theory[71] through single point calculations at the B3LYP-optimized geometries with the core potentials and basis sets described above.

Supporting Information Available: Tables containing the optimized geometries and total energies (29 pages, print/PDF) of most of the structures discussed in the present work. See any current masthead page for ordering information and Web access instructions.

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