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A R T I C L E S

Combined Computational and Experimental Study of Substituent Effects on the Thermodynamics of H₂, CO, Arene, and Alkane Addition to Iridium

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Abstract: The thermodynamics of small-molecule (H_2, arene, alkane, and CO) addition to pincer-ligated iridium complexes of several different configurations (three-coordinate d^8, four-coordinate d^8, and five-coordinate d^6) have been investigated by computational and experimental means. The substituent para to the iridium (Y) has been varied in complexes containing the (Y-PCP)Ir unit (Y-PCP = η^3-1,3,5-C_6H_2[CH_2-PR_2]$_2$Y; R = methyl for computations; R = *tert*-butyl for experiments); substituent effects have been studied for the addition of H_2, C−H, and CO to the complexes (Y-PCP)Ir, (Y-PCP)Ir(CO), and (Y-PCP)Ir(H)$_2$. Para substituents on arenes undergoing C−H bond addition to (PCP)Ir or to (PCP)Ir(CO) have also been varied computationally and experimentally. In general, increasing electron donation by the substituent Y in the 16-electron complexes, (Y-PCP)Ir(CO) or (Y-PCP)Ir(H)$_2$, *disfavors* addition of H−H or C−H bonds, in contradiction to the idea of such additions being oxidative. Addition of CO to the same 16-electron complexes is also disfavored by increased electron donation from Y. By contrast, addition of H−H and C−H bonds or CO to the three-coordinate parent species (Y-PCP)Ir is favored by increased electron donation. In general, the effects of varying Y are markedly similar for H_2, C−H, and CO addition. The trends can be fully rationalized in terms of simple molecular orbital interactions but not in terms of concepts related to oxidation, such as charge-transfer or electronegativity differences.

Introduction

The addition of CO and the "oxidative" addition of molecules belonging to the general class R−H (where R = H or a group of comparable electronegativity such as silyl or hydrocarbyl) are requisite steps in most organometallic catalytic cycles.[1] Even catalyses that do not directly involve these reactions frequently contain at least one such reaction in reverse (e.g., C−H elimination in the case of polymerization or oligomerization of olefins). A thorough understanding of the factors (electronic, steric, etc.) that govern the thermodynamics of these reactions is therefore critical to any attempts at rational design or even fine-tuning of organometallic catalysts.[2] It is our belief, however, that the present level of understanding of such factors is remarkably limited. For example, currently a primary guiding principle concerning the thermodynamics of these reactions is that increased electron richness favors addition of either CO[3,4]

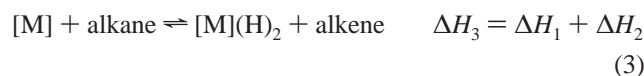or R−H.[5,6] We present evidence that this principle may be seriously flawed.

The functionalization of alkanes is an area where the development of efficient catalysts is of great interest.[7] In the past few years, complexes containing "pincer"-ligated iridium fragments, (PCP)Ir (where PCP = η^3-1,3-C_6H_3[CH_2PR_2]$_2$; in this paper, R = methyl for computations, R = *tert*-butyl for experiments), have been found to be among the most efficient[8,9] and certainly the most selective[10] catalysts for the dehydrogenation of alkanes. The thermodynamics of H_2 addition to the catalytic species (eq 1) is of particular interest in the context of dehydrogenation, since the catalytic cycle presumably involves the transfer of hydrogen from an alkane to the metal center (eq 3). Equation 3 is less exothermic than simple addition of H_2 by an amount equal to the enthalpy of alkane dehydrogenation (ca.

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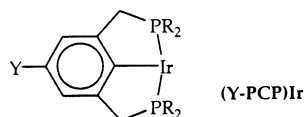
(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 523−668.

(2) Martinho Simoes, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629−688.

(3) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 931−941.

(4) (a) Sulfab, Y.; Basolo, F.; Rheingold, A. L. *Organometallics* **1989**, *8*, 2139−43. (b) Basolo, F. *Polyhedron* **1990**, *9*, 1503−35.

(5) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988; pp 1189−1194.

(6) Collman, J. P. *Acc. Chem. Res.* **1968**, *1*, 136−143.

(7) For some recent reviews of homogeneously catalyzed hydrocarbon functionalization, see (a) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154−162. (b) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879−2932. (c) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550−557. (d) Guari, Y.; Sabo-Etiennne, S.; Chaudret, B. *Eur. J. Inorg. Chem.* **1999**, 1047−1055.

(8) (a) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083−2084. (b) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840−841.

(9) Xu, W.; Rosini, G. P.; Gupta, M.; Jensen, C. M.; Kaska, W. C.; Krogh-Jespersen, K.; Goldman, A. S. *Chem. Commun.* **1997**, 2273−2274.

(10) Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086−4087.

23−30 kcal/mol),[11] shown in eq 2.

$$[M] + H_2 \rightleftharpoons [M](H)_2 \qquad \Delta H_1 \qquad (1)$$

$$\text{alkane} \rightleftharpoons H_2 + \text{alkene} \qquad \Delta H_2 \approx 23-30 \text{ kcal/mol} \quad (2)$$

$$[M] + \text{alkane} \rightleftharpoons [M](H)_2 + \text{alkene} \qquad \Delta H_3 = \Delta H_1 + \Delta H_2 \tag{3}$$

On a more fundamental level, the PCP ligand affords an excellent opportunity to vary ligand X in a fragment of the general form *trans*-ML$_2$X and to observe the resulting effect on the thermodynamics of small-molecule additions. *trans*-ML$_2$X fragments (M = Co, Rh, Ir; L typically a phosphine; X typically an anionic group, especially halide) are found in a wide range of important catalysts.[1] Varying halides and related ligands results in changes at the metal center that are substantial and fairly complex; this has been particularly well established with respect to energies of H$_2$ addition.[12−19] We have found that the lighter, more electronegative halogens result (paradoxically) in increased electron density at the metal center of *trans*-IrL$_2$X(CO)[20] and a decreased tendency toward oxidative addition of H$_2$;[21] however, partly because bond lengths and other factors are affected, elucidating the relative importance of steric, electrostatic, and σ/π effects is a complex task. In the case of the PCP ligand, the phenyl group is the equivalent of X in *trans*-ML$_2$X; systematic changes of the substituent at the position para to the metal allow us to leave the ligand qualitatively unchanged while varying electronic factors (exclusively) in an incremental and controlled fashion.

(Y-PCP)Ir

We report both theoretical and experimental approaches toward the study of substituent effects for addition of small molecules to complexes (Y-PCP)Ir and several other complexes that contain the (Y-PCP)Ir unit.

We have synthesized the *p*-methoxy (Y = OCH$_3$) and *p*-methoxycarbonyl [Y = C(O)OCH$_3$] substituted PCP ligands, which represent electron-rich and electron-poor derivatives of the parent ligand, respectively. The effect of these substituents on the thermodynamics of H$_2$ addition to (Y-PCP)Ir(CO) are measured directly. We recently reported the products of arene C−H addition to (PCP)Ir;[22] equilibrium measurements reveal the effects of derivatizing the arene undergoing C−H addition. First-principles electronic structure calculations render the study of a much wider range of para substituents feasible, and more importantly, a fuller range of reactions may be examined. The experimentally observed substituent effects are in excellent agreement with the computed values; therefore, for the closely related reactions where experimental values are not accessible, we feel that we have excellent reason to be confident in the accuracy of the calculated substituent effects.

Computational and Experimental Methods

Density Functional Calculations. Standard computational methods based on density functional theory[23] and implemented in the GAUSS-IAN98 series of computer programs[24] have been employed. Specifically, we have made use of the three-parameter exchange functional of Becke[25] and the correlation functional of Lee, Yang, and Parr[26] (B3LYP). The Hay−Wadt relativistic, small-core effective core potential and corresponding basis set (split valence double-ζ) were used for the Ir atom (LANL2DZ model),[27] and the second- and third-row elements carried all-electron, full double-ζ plus polarization function basis sets (Dunning−Huzinaga D95(d)[28] for Li, B, C, N, O, F; McLean−Chandler[29] for P). Hydrogen atoms in H$_2$ or a hydrocarbon, which formally become hydrides in the product complexes, were described by the triple-ζ plus polarization 311G(p) basis set;[30] regular hydrogen atoms present in the PCP ligand or in alkyl, aryl, boryl, and amino groups carried a double-ζ 21G basis set.[31]

(11) NIST Standard Reference Database Number 69, February 2000 release: http://webbook.nist.gov/chemistry/.
(12) The M(PMe$_3$)$_4$X$_2$ (M = Mo, W) systems have been especially well studied in this respect. Complexes of the lighter halides were found to react more favorably with H$_2$, providing an important contrast with H$_2$ addition to IrL$_2$(CO)X, which is closely related to the (Y-PCP)Ir(CO) system examined in the present work. More generally, however, conclusions drawn from the Mo/W work are in good agreement with those of the present study concerning the dominance of specific orbital interactions (filled−filled or filled−empty), and in particular π donation from the ligand being varied, in determining substituent effects. (a) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 353−354. (b) Murphy, V. J.; Rabinovich, D.; Hascall, T.; Klooster, W. T.; Koetzle, T. F.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 4372−4387. (c) Hascall, T.; Rabinovich, D.; Murphy, V. J.; Beachy, M. D.; Friesner, R. A.; Parkin, G. *J. Am. Chem. Soc.* **1999**, *121*, 11402−11417.
(13) (a) Rachidi, I. E.-I.; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, *14*, 671−677. (b) Riehl, J.-F.; Jean, Y.; Eisenstein, O.; Pélissier, M. *Organometallics* **1992**, *11*, 729.
(14) Clot, E.; Eisenstein, O. *J. Phys. Chem. A* **1998**, *102*, 3592−3598.
(15) (a) Lunder, D. M.; Lobkovsky, E. B.; Streib, W. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1991**, *113*, 1837−1838. (b) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190−3191. (c) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25−41.
(16) Hauger, B. E.; Gusev, D.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 208−214.
(17) Albinati, A.; Bakhmutov, V. I.; Caulton, K. G.; Clot, E.; Eckert, J.; Eisenstein, O.; Gusev, D. G.; Grushin, V. V.; Hauger, B. E.; Klooster, W. T.; Koetzle, T. F.; McMullan, R. K.; O'Loughlin, T. J.; Pélissier, M.; Ricci, J. S.; Sigalas, M. P.; Vymenits, A. B. *J. Am. Chem. Soc.* **1993**, *115*, 7300−7312.
(18) (a) Le-Husebo, T.; Jensen, C. M. *Inorg. Chem.* **1993**, *32*, 3797−3798. (b) Lee, D. W.; Jensen, C. M. *J. Am. Chem. Soc.* **1996**, *118*, 8749−8750. (c) Lee, D. W.; Jensen, C. M. *Inorg. Chim. Acta* **1997**, *259*, 359−362.
(19) Li, S. H.; Hall, M. B.; Eckert, J.; Jensen, C. M.; Albinati, A. *J. Am. Chem. Soc.* **2000**, *122*, 2903−2910 and references therein.

(20) The inverse halide order for electron richness has been reported in other systems; see, for example, Zietlow, T. C.; Hopkins, M. D.; Gray, H. B. *J. Am. Chem. Soc.* **1986**, *108*, 8266−8267.
(21) (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. *Inorg. Chem.* **1994**, *33*, 5122−5130.
(22) Kanzelberger, M.; Singh, B.; Czerw, M.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 11017−11018.
(23) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; University Press: Oxford, U.K., 1989.
(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Mailick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98 (Revision A.5); Gaussian Inc.: Pittsburgh, PA, 1998.
(25) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(26) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(27) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
(28) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1976; pp 1−28.
(29) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.
(30) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.
(31) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

Reactant and product geometries were fully optimized by gradient methods.[32] The (PCP)Ir fragment has the aryl group canted relative to the P−Ir−P axis (C_2 point group), so most of the complexes studied possess no molecular symmetry (C_1). In selected cases, higher symmetry (C_s, C_{2v}) was imposed to illustrate the importance of σ vs π effects. Although a few calculations used $PR_2 = PH_2$, our general computational model for (PCP)Ir has methyl groups attached to the phosphorus atoms [i.e., $PR_2 = P(CH_3)_2$], a compromise between the use of hydrogen atoms and the alkyl groups actually employed in the catalytic systems (e.g., *i*Pr or *t*Bu). The computed reaction energies represent purely electronic energies and are not corrected for thermal or vibrational effects.

Experimental. General experimental methods are included in the Supporting Information. Also in the Supporting Information are spectroscopic data, elemental analyses, and synthetic procedures for the following compounds: 1,3-bis[di(*tert*-butyl)phosphinomethyl]-5-methoxybenzene (MeO-PCP-H), (MeO-PCP)IrHCl, (MeO-PCP)IrH₄, (MeO-PCP)IrH₂, methyl 3,5-bis[di(*tert*-butyl)phosphinomethyl]benzoate (CH₃OC(O)-PCP-H), [CH₃OC(O)-PCP]IrHCl, and [CH₃OC(O)-PCP]-IrH₄. Syntheses of the ligands, like those for the corresponding iridium hydrido chlorides, were based on syntheses reported by Moulton and Shaw[33] for the parent ligand. Reduction of the hydrido chlorides to the hydrides followed the methods of Kaska and Jensen and co-workers.[34,35] Spectroscopic data and methods for in situ generation of the (PCP)Ir aryl hydrides are also included in the Supporting Information.

Linear Free-Energy Relationship (LFER) Analysis. Since all substituent effects examined involved phenyl para substituents, the standard Hammett substituent parameter, σ_p, was initially used for a linear free energy analysis of all data sets. Reasonably good correlations of calculated ΔE values with σ_p were found for all reactions with multiple data points. The resulting reaction single parameters are expressed as ρ_{sp}, to distinguish them from dual-parameter ρ values (see below), and likewise, standard Hammett substituent parameters are written as σ_{sp}. In an attempt to dissect the substituent effects further into σ and π effects, we analyzed these six reactions using dual-parameter models wherein calculated ΔE values are fit to an equation of the following form (σ is the substituent parameter and ρ is the reaction parameter; R and I denote resonance and inductive, respectively):

$$\Delta E = \rho_R \sigma_R + \rho_I \sigma_I$$

"Resonance" effects are assumed to be largely attributable to π interactions, while inductive effects are assumed to correlate with σ donation. It should be noted, however, that these parameters are derived empirically on the basis of para- and meta-substituent effects, and the π/resonance and σ/inductive correlations are in no way rigorous.[37,38] Thus, the parameters only crudely reflect the π/σ properties of the para carbon. Numerous dual-parameter models have been proposed, all of which prove valuable but with limited generality.[37] In particular, several resonance parameter scales (σ_R) have been proposed by Taft et al.[37] and by others.[38] These scales complement several scales applicable for inductive effects. Of these perhaps the most widely used is the benzoic acid scale [$\sigma_{R(BA)}$] based upon the reaction used by Hammett as the standard for the original σ_P treatment.[37] We investigated six different

(32) Schlegel, H. B. *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific Publishing: Singapore, 1994; pp 459−500.
(33) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020−1024.
(34) Nemeh, S.; Jensen, C.; Binamira-Soriage, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442−1447.
(35) (a) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083−2084. (b) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840−841.
(36) Morales-Morales, D.; Redon, R.; Wang, Z.; Lee, D. W.; Yung, C.; Magnuson, K.; Jensen, C. M. *Can. J. Chem.* **2001**, *79*, 823−829.
(37) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. In *Progress in Physical Organic Chemistry*; Streitwieser, A. S., Taft, R. W., Eds.; John Wiley & Sons: 1973; Vol. 10, pp 1−80.
(38) Wells, P. R. In *Linear Free Energy Relationships*; Academic Press: London, 1968; pp 1−45.

Table 1. Substituent Parameters Used for LFER Fits

Y	$\sigma_{sp}{}^a$	$\sigma_{R(BA)}{}^b$	$\sigma_I{}^c$
NH₂	−0.66	−0.82	0.12
OCH₃	−0.27	−0.61	0.27
F	0.06	−0.45	0.50
H	0.00	0.00	0.00
C(O)OCH₃	0.52	0.14	0.30
NO₂	0.78	0.15	0.65

[a] Reference 79. [b] Based on benzoic acid pH; ref 37. [c] Inductive effect; ref 37.

Table 2. Computed LFER Parameters for Addition Reactions of Eqs 4, 6, and 9−16, Varying Y (Y-PCP) or Z (Z-C₆H₅ or Z-C₆HMe₂)[a]

eq	reaction	ρ_{sp}	ρ_R	ρ_I
4	[Y-M] + H₂ → [Y-M]H₂	4.0(5)	4.4(7)	2.7(12)
6	[Y-M] + Ph-H → [Y-M](Ph)(H)	2.3(3)	2.5(1)	1.9(1)
6	[Y-M] + n-Bu-H → [Y-M](n-Bu)(H)	3.2(5)	3.7(2)	2.0(3)
	[M] + Z-Ar−H → [M](Z-Ar)H	−6.0(9)	−4.5(10)	8.2(17)
9	[M] + Z-Ar−H → [M](Z-Ar-horizontal)H		−8.2	−6.3
10	[M] + Z-Ar−H → [M](Z-Ar-vertical)H		0.7	−7.2
11	[Y-M](CO) + H₂ → *trans*-[Y-M](CO) H₂	−1.3(2)	−1.6(1)	−0.4(1)
11	[Y-M](CO) + H₂ → *cis*-[Y-M](CO)H₂	−1.3(2)	−1.6(1)	−0.4(1)
12	[Y-M](CO) + Ph-H → [Y-M](CO)H(Ph)	−0.9(4)	−1.4(2)	−0.04(15)
12	[M](CO) + Z-Ar−H → [M](CO)(Z-Ar)H		−4.7	−7.0
13	[Y-M]H₂ + H₂ → [Y-M]H₄	−2.5(5)	−3.0(2)	−1.2(3)
14	[Y-M] + CO → [Y-M](CO)	2.7(4)	2.9(5)	2.1(10)
15	[Y-M]H₂ + CO → *trans*-[Y-M]H₂(C O)	−2.6(4)	−3.1(2)	−1.1(3)
15	[Y-M]H₂ + CO → *cis*-[Y-M]H₂(CO)	−2.5(3)	−2.9(2)	−1.3(3)
16	[Y-M](CO) + CO → [Y-M](CO)₂	−1.5(3)	−1.9(2)	−0.6(2)

[a] Positive values of ρ indicate that addition is favored by increasing electron donation by Y or Z. M = (PCP)Ir; [Y-M] = (Y-PCP)Ir.

dual-parameter models. For all reactions investigated, the signs (positive or negative) of the reaction parameters were the same for all six scales used. Thus, the answers to the questions of major concern here are independent of the choice of dual-parameter model. Overall, good fits were obtained with all the dual-parameter scales (for each model, the r^2 values averaged over all reactions ranged from 0.955 to 0.978). For the single-parameter Hammett para-substituent model, the average r^2 value was 0.935. The standard Taft−Lewis dual-parameter model gave correlations as good or better than the others (average $r^2 = 0.978$), so we invoke only this dual-parameter model and the accompanying $\sigma_{R(BA)}$ scale in our discussions of individual reactions (Table 1).

For all reactions and for all six scales, much better correlations were found for the π/resonance than for the σ/inductive parameters. On the basis of both the calculated magnitudes of the reaction parameters and the quality of the correlations, it appears that π/resonance effects are generally considerably more important than σ/inductive effects. Calculated reaction parameters are summarized in Table 2. A more detailed description of the LFER analysis is in the Supporting Information.

Results and Discussion

Addition of H₂ to (Y-PCP)Ir (Standard Linear Free-Energy Relationships). Perhaps the two most effective systems for catalytic alkane dehydrogenation are those that contain the fragments (PCP)Ir[8−10] or Rh(PMe₃)₂Cl.[39,40] We have previously calculated that H₂ addition to either fragment is exoergic by ca. 25−30 kcal/mol, approximately the enthalpy of alkane dehydrogenation (eq 2).[9] Thus, eq 3 is approximately thermo-neutral for these fragments, and we believe this is a critical factor contributing to the catalytic effectiveness of these species (particularly for transfer−dehydrogenation). By contrast, (PCP)-Rh adds H₂ only weakly, and consequently alkane dehydroge-

(39) (a) Maguire, J. A.; Goldman, A. S. *J. Am. Chem. Soc.* **1991**, *113*, 6706−6708. (b) Maguire, J. A.; Petrillo, A.; Goldman, A. S. *J. Am. Chem. Soc.* **1992**, *114*, 9492−9498.
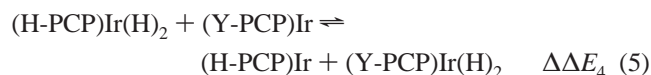(40) Rosini, G. P.; Soubra, S.; Wang, S.; Vixamar, M.; Goldman, A. S. *J. Organomet. Chem.* **1998**, *554*, 41−47.

Table 3. Computed Absolute and Relative Reaction Energies for Addition of H_2 to (Y-PCP)Ir[a]

Y	ΔE	$\Delta\Delta E$	symmetry imposed (C_{2v})[b]	
			ΔE	$\Delta\Delta E$
NH_2	−26.37	−2.36	−27.68	−2.97 (NH_2 coplanar)
NH_2(90)			−24.87	−0.17 (NH_2 orthogonal)
OCH_3	−25.80	−1.78		
F	−24.94	−0.93		
Li	−24.82	−0.81		
H	−24.01	0.00	−24.71	0.00
C(O)OCH_3	−22.11	1.90		
NO_2	−20.89	3.13	−21.34	3.36 (NO_2 coplanar)
NO_2(90)			−23.95	0.76 (NO_2 orthogonal)
BH_2	−20.51	3.51	−20.51	3.63 (BH_2 coplanar)
BH_2(90)			−24.92	−0.21 (BH_2 orthogonal)

[a] Reaction energies, in kilocalories per mole, were calculated from eqs 4 and 5. [b] NH_2(90), BH_2(90), and NO_2(90) refer to calculations in which the respective group is held orthogonal to the PCP aryl ring. In all other calculations the group was either coplanar (constrained symmetry) or approximately coplanar with the aryl ring (unconstrained).

nation by this fragment is strongly endoergic.[9] Conversely, H_2 addition to Ir(PMe$_3$)$_2$Cl is too highly exoergic (ca. 60 kcal/mol; eq 1) for this species to act as a dehydrogenation catalyst. Obviously, the thermodynamics of the alkane dehydrogenation step and, more generally, the catalytic effectiveness of fragments *trans*-ML$_2$X are strongly dependent on the electronic properties of X. Thus, both for reasons specific to the (PCP)Ir system and for reasons much more general, it is of interest to explore the energetic effects resulting from systematic variations in the electronic properties of the aryl group in (PCP)Ir.

As seen in Table 3, the computed energy of H_2 addition to (Y-PCP)Ir fragments (ΔE_4, eq 4) generally becomes more negative with increasing electron-donating ability of Y. This is most conveniently described in terms of $\Delta\Delta E$, the energy for the homodesmotic (isodesmic) reaction 5:[41]

$$(\text{Y-PCP})\text{Ir} + H_2 \rightleftharpoons (\text{Y-PCP})\text{Ir}(H)_2 \qquad \Delta E_4 \qquad (4)$$

$$(\text{H-PCP})\text{Ir}(H)_2 + (\text{Y-PCP})\text{Ir} \rightleftharpoons$$
$$(\text{H-PCP})\text{Ir} + (\text{Y-PCP})\text{Ir}(H)_2 \qquad \Delta\Delta E_4 \quad (5)$$

The magnitudes of these substituent effects are on the order of several kilocalories per mole (Table 3), which implies that they have the potential to affect reaction rates by several orders of magnitude, if they are manifest in any way in a rate-determining transition state (directly or in a preequilibrium). For the single-parameter LFER analysis, the value of ρ_{sp} (the single-parameter reaction coefficient, see Methods section and Table 2) is 4.0(5) ($P = 0.15\%$; errors in parentheses represent one standard deviation in all cases); the one exception to the correlation of $\Delta\Delta E$ with σ_{sp} (the standard Hammett substituent parameter) is fluorine ($\sigma_{sp} = 0.06$; $\Delta\Delta E_4 = -0.93$ kcal/mol). Fluorine, however, is π-donating as well as σ-withdrawing. If only resonance effects are considered, no anomalies are found among the substituents examined. The energy of H_2 addition is found to increase with increasing value of the resonance parameter (see Methods section) as follows: $NH_2 < OCH_3 < F < H < C(O)OCH_3 < NO_2$. By use of the $\sigma_{R(BA)}/\sigma_I$ dual-parameter model, reaction exoergicity is found to correlate with both inductive and resonance substituent values with the reaction parameters $\rho_R = 4.4(7)$ and $\rho_I = 2.7(12)$. The importance of resonance effects is therefore greater, not only because $\rho_R > \rho_I$ but also because the range of σ_R values is greater; the implied

(41) Sung, K. *J. Org. Chem.* **1999**, *64*, 8984−8989 and references therein.

resonance effects span a range of 4.3 kcal/mol, whereas inductive effects span only 1.8 kcal/mol. Independent of the greater value of ρ_R, in this as in all other cases the statistical certainty of the correlation with resonance effects is also greater (the P value associated with ρ_R is $P_R = 0.7\%$; $P_I = 10\%$ for ρ_I).

**Addition of H_2 to (Y-PCP)Ir: Supporting Evidence for the Importance of π Effects.** Further evidence for the importance of resonance or π effects is obtained from calculations conducted with C_{2v} symmetry imposed on the (Y-PCP)Ir fragment. The presence of the mirror planes establishes a rigorous σ/π separation, and rotation of the locally planar NH_2, NO_2, or BH_2 groups by 90° from coplanarity with the aryl group will virtually eliminate their π-accepting/donating ability.
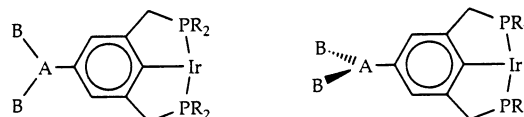
rotation of the Y-group in (Y-PCP)Ir prior to substrate addition

The BH_2 group (for which there are no published substituent values), when oriented in the PCP aryl plane, is the most unfavorable substituent examined for eq 5: $\Delta E_4 = 3.6$ kcal/mol, which may be compared with $\Delta E_4 = -3.0$ kcal/mol for the most favorable substituent, the NH_2 group. Rotating NO_2, NH_2, or BH_2 perpendicular to the aryl ring plane, so that conjugation cannot occur with the aryl π system, results in very small absolute values of ΔE_4 for all three substituents. Upon 90° rotation of the group, the small ΔE_4 values are almost identical in the case of NH_2 (−0.17 kcal/mol) and BH_2 (−0.21 kcal/mol), the strongest π donor and π acceptor, respectively.

Calculations on *p*-Li-substituted (Y-PCP)Ir afford $\Delta E_4 = -0.85$ kcal/mol, which is surprisingly close to the value found when Y = F: $\Delta E_4 = -0.93$ kcal/mol. Li is obviously not an intrinsic π donor; however, as a strong σ donor it effects a significant build-up of negative charge in the σ-type orbitals of the carbon to which it is bound. This excess negative charge in the σ system results in a polarization of the π cloud toward the metal and thus Li-PCP may be significantly π-donating relative to unsubstituted H-PCP. To further gauge the "π-donating" ability of Li we have calculated the barrier to rotation around the B−C bond of several derivatives (*p*-Y)C$_6$H$_4$-BH$_2$ (i.e., the difference in energy between the ground-state conformation, which has coplanar BH_2 and phenyl units, and the conformer in which the two units are perpendicular).
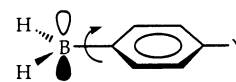
rotation about the H$_2$B−C bond as a measure of the π-donating ability of Y

The magnitude of this barrier is expected to primarily reflect the double-bond character in the B−C bond and hence provide a measure of the π-donating/accepting ability of Y as transmitted to the carbon adjacent to B. The calculated B−C rotational barriers are 9.2, 10.5, 11.5, and 13.3 kcal/mol for Y = C(O)OCH$_3$, H, F, and OCH$_3$, respectively, and they correlate reasonably well with the $\sigma_{R(BA)}$ parameters: $\rho = -4.6(10)$; $r^2 = 0.92$. The calculated B−C rotational barrier for Y = Li (12.7 kcal/mol) lies between those for F and OCH$_3$, indicating that

p-LiC$_6$H$_4$ is a better π donor than is p-FC$_6$H$_4$ [42] and thus implying that Li-PCP is more π-donating than F-PCP. If increased Y-PCP $\rightarrow$ Ir σ donation were to significantly favor the addition, then Li-PCP, at least comparable to F-PCP as a π donor and undoubtedly a better σ donor than F-PCP, would be expected to engender a significantly greater exoergicity for H$_2$ addition, in contrast with the calculated result (Table 3). This suggests that, despite the positive value of ρ_I for reaction 4, increased σ donation has a negligible or even unfavorable effect on the thermodynamics of H$_2$ addition to (PCP)Ir.

In summary, statistical analysis of the energetic effects produced by substituents with known σ values, in conjunction with calculations on less conventional substituents (e.g., Li, BH$_2$), strongly supports the conclusion that the exoergicity of H$_2$ addition to (Y-PCP)Ir is highly sensitive to the π-donating/withdrawing ability of Y (favored by π donation). This is consistent with our previous study on addition to L$_2$IrX complexes in which it was also found that H$_2$ addition energies are determined largely by the degree of π-donating/withdrawing ability of X,[43] and with earlier work by Eisenstein in which the importance of X $\rightarrow$ M π donation in L$_2$IrX(H)$_2$ complexes was elucidated.[13,14] Dual-parameter analysis suggests that σ donation also favors H$_2$ addition, albeit to a significantly lesser extent than π donation; however, the statistical support for this conclusion is weak, and additional calculations (Y = Li, rotated NH$_2$, and BH$_2$) seem to indicate that any such effect is negligible or even inverse.

Addition of Arene C$-$H bonds to (PCP)Ir: Para-Substituted PCP Ligands. The thermodynamics of C$-$H addition to (PCP)Ir and the related substituent effects are, obviously, of interest in the context of (PCP)Ir-catalyzed hydrocarbon functionalization:

$$(\text{Y-PCP})\text{Ir} + \text{R}-\text{H} \rightleftharpoons (\text{Y-PCP})\text{Ir(R)(H)} \quad (6)$$
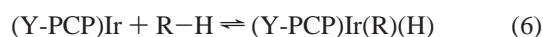
More generally, substituent effects on the thermodynamics of C$-$H addition to transition metal complexes are not well elucidated. It seems reasonable to presume that substituent effects for C$-$H addition would correlate with those for H$_2$ addition, but the quality of this correlation (assuming it does exist) is not clearly established.[44,45]

Unlike the alkyl hydrides (presumed intermediates in (PCP)-Ir-catalyzed alkane dehydrogenation), the aryl hydrides have recently been observed and isolated.[22] Thus, in the interest of keeping the calculations as closely related as possible to experimental efforts, we focus more on aryls than alkyls in this paper. It is important to note, however, that the geometry of the aryl hydrides is calculated to be pseudo-square-pyramidal with apical hydride (C$_{PCP}$$-Ir-C_{phenyl}$ $\sim$ 174°; H$-$Ir$-$C$_{phenyl}$ $\sim$ 90°).[46] In contrast, the dihydrides (C$_{PCP}$$-Ir-$H $\sim$ 151°; H$-$Ir$-$H $\sim$ 58°) and alkyl hydrides (C$_{PCP}$$-Ir-C_{butyl}$ $\sim$ 159°;
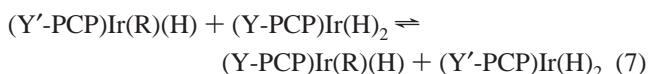
Table 4. Computed Absolute and Relative Reaction Energies for Benzene and n-Butane C$-$H Addition to (Y-PCP)Ir[a]

Y	R = Ph		R = n-butyl	
	ΔE	$\Delta\Delta E$	ΔE	$\Delta\Delta E$
OCH$_3$	-7.73	-1.07	2.57	-1.62
H	-6.66	0.00	4.19	0.00
C(O)OCH$_3$	-5.84	0.82	5.46	1.27
NO$_2$	-5.08	1.58	5.28	1.89

[a] Reaction energies, in kilocalories per mole, were calculated from eq 6.

H$-$Ir$-$C$_{butyl}$ $\sim$ 71°) are best described as distorted trigonal-bipyramidal.[47] This complicates any attempt at direct comparisons of H$-$H and aryl$-$H additions to (PCP)Ir.

We have restricted the calculations to examinations of benzene and n-butane adding to the parent complex (Y = H), the two derivatives we have actually synthesized [Y = OCH$_3$ and C(O)OCH$_3$], and the nitro complex (Y = NO$_2$). It can be seen from Table 4 that increased electron donation favors addition of phenyl$-$H bonds to (Y-PCP)Ir. However, the effects appear to be slightly weaker than found for addition of H$_2$ [single-parameter model, ρ_{sp} = 2.3(3) for arene versus 4.0(5) for addition of H$_2$; dual-parameter model, ρ_R = 2.5(1) and ρ_I = 1.9(1) for arene versus ρ_R = 4.4(7) and ρ_I = 2.7(12) for H$_2$]. Thus, the equilibrium for an arene$-$H$_2$ exchange reaction (eq 7) is calculated to lie slightly to the right when Y$'$ is more electron-donating than Y:

$$(\text{Y}'\text{-PCP})\text{Ir(R)(H)} + (\text{Y-PCP})\text{Ir(H)}_2 \rightleftharpoons$$
$$(\text{Y-PCP})\text{Ir(R)(H)} + (\text{Y}'\text{-PCP})\text{Ir(H)}_2 \quad (7)$$

Note that any mechanism for (Y-PCP)Ir-catalyzed alkane dehydrogenation, olefin hydrogenation, or several other catalytic reactions presumably involves species of the type (Y-PCP)Ir-(R)(H) and (Y-PCP)Ir(H)$_2$, though not necessarily the species (Y-PCP)Ir. Thus, in that context, the *relative* substituent effects for R$-$H versus H$_2$ addition (as expressed in eq 7) are arguably as important as are the substituent effects for each reaction individually (i.e., eqs 4 and 6).

We have experimentally measured the equilibrium constant for eq 7 for Y$'$/Y = OCH$_3$/H and R = Ph. Starting with either (CH$_3$O-PCP)Ir(Ph)(H) and (H-PCP)Ir(H)$_2$ or the converse pair, the same value is obtained, K = 3.9 $\pm$ 0.2 (25 °C), corresponding to ΔG_7 = -0.8 kcal/mol. Assuming that $\Delta S \approx 0$ (as seems reasonable in view of the closely related nature of the species involved) and that $\Delta H_7 \approx \Delta E_7$, we obtain an experimental ΔE_7 $\approx$ -0.8 kcal/mol, in excellent agreement with the calculated value of -0.7 kcal/mol [Tables 3 and 4; $-1.78 - (-1.07)$ = -0.71 kcal/mol].

The above experimental results are consistent with the results from the full range of arenes used to calculate ΔE_6: increased electron donation by Y-PCP favors Ph$-$H addition but to a lesser extent than it favors H$_2$ addition. This is probably due to increased π donation stabilizing the distorted trigonal-bipyramidal structure (calculated for the dihydrides) more than the square-pyramidal structures (calculated for the aryl hydrides); this differential stabilization has been reported previously for isomeric ML$_2$XH$_2$ complexes.[13] Consistent with this conclusion,

(42) Calculated electron populations in the "unoccupied" p orbital of the BH$_2$ group of p-Y-C$_6$H$_4$BH$_2$ are in accord with the rotational barrier being comparable for Y = MeO and Y = Li. These populations for several substituents Y are as follows: C(O)OMe, 0.120; H, 0.130; F, 0.136; MeO, 0.157; Li, 0.160. Direct evidence for polarization by Li is revealed by calculations on Y-C$_6$H$_5$. Populations of the p$_\pi$ orbitals at the C1 and C4 positions, respectively, are calculated as follows for the respective substituents Y: H (1.000, 1.000); Li (0.891, 1.028); F (0.965, 1.031).

(43) Krogh-Jespersen, K.; Goldman, A. S. In *Transition State Modeling for Catalysis*; ACS Symposium Series 721; American Chemical Society: Washington, DC, 1998; pp 151$-$162.

(44) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444$-$1456.
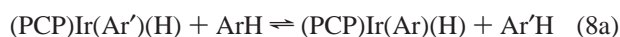
(45) Labinger, J. A.; Bercaw, J. E. *Organometallics* **1988**, *7*, 926$-$928.

(46) Krogh-Jespersen, K.; Czerw, M.; Kanzelberger, M.; Goldman, A. S. *J. Chem. Inf. Comput. Sci.* **2001**, *41*, 56$-$63.
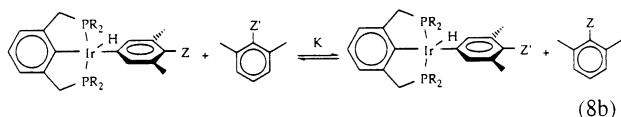
(47) See Supporting Information for selected structural parameters (bond lengths and angles) for all calculated parent complexes and derivatives.

the addition of the alkyl−H bonds is *more* favored by increased electron donation [$\rho_{sp} = 3.2(5)$] than is addition of the *less* electron-rich aryl−H bonds [$\rho_{sp} = 2.3(3)$; see Table 4 and the discussion of alkyl−H bond addition below]. This result is obviously inconsistent with charge-transfer effects but can be explained in terms of the alkyl hydrides possessing a structure that is much closer to the trigonal-bipyramidal geometry of (PCP)IrH$_2$.

Addition of Arene C−H Bonds to (PCP)Ir: Para-Substituted Arenes. The direct observation of C−H addition products that undergo arene exchange affords the opportunity to directly measure the thermodynamic effects of substituents located on the arene addendum. We have recently reported that 1,3-xylene undergoes addition selectively at the 5-position (giving a 3,5-dimethylphenyl hydride).[22] The equilibrium constant for eq 8a (Ar′ = xylyl; Ar = phenyl) is ca. 40 at −38 °C, which corresponds to ca. 7 on a per-C−H bond basis and $\Delta G = -0.9$ kcal/mol. This is in perfect agreement with the calculations, which predict $\Delta E_8 = -0.9$ kcal/mol for benzene/xylene [$-6.66 - (-5.74) = -0.92$ kcal/mol].

$$(PCP)Ir(Ar')(H) + ArH \rightleftharpoons (PCP)Ir(Ar)(H) + Ar'H \quad (8a)$$

Monosubstituted benzenes can add to (PCP)Ir to yield several phenyl hydride isomers and rotamers. To simplify the determination of equilibrium constants for eq 8, which involves two arenes and therefore potentially twice as many isomers, we therefore chose to compare ortho-substituted *m*-xylenes, i.e., 2-Z-1,3-dimethylbenzenes (eq 8b). For each of these species, only one aryl C−H bond undergoes addition.

(8b)

We were successful for two xylyl substituents: nitro and chloro. The relative equilibrium constants at −38 °C are K_{NO_2}: K_{Cl}:$K_H = 4600$:43:1. The corresponding experimental values of $\Delta\Delta G_{8b} \approx \Delta\Delta E_{8b}$ are −3.9 and −1.8 kcal/mol, in good agreement with calculated values of −5.1 and −1.6 kcal/mol, respectively. It bears noting that the effect of the nitro group is calculated to be less when on xylene (−5.1 kcal/mol) than on benzene (−6.2 kcal/mol). This is presumably due to the neighboring methyl groups forcing the NO$_2$ group out of coplanarity with the ring and thus decreasing its ability to act as a π acceptor (the calculated dihedral angle between the NO$_2$ and phenyl planes is ∼50°). Likewise, the computed substituent effect of MeO is negligible in the xylene case (0.01 vs 1.12 kcal/mol on benzene) because the MeO methyl group rotates to form a dihedral angle of 90° with the aryl plane, effectively eliminating π conjugation by the oxygen lone pair.

For all substituents examined in arene (p-ZC$_6$H$_4$-H) addition to (Y-PCP)Ir, the effect on the arene ring undergoing addition is opposite in sign to the effect exerted when the same substituent is positioned on the PCP aryl ring: electron-rich substituents favor addition when on the PCP ring [$\rho_{sp} = 2.3(3)$] and disfavor it when on the addendum ring [$\rho_{sp} = -6.0(9)$]. The magnitudes of the relative effects, however, are highly dependent on the location of the substituent. The nitro group, when substituted on an adding benzene ring, yields a strikingly high value for $|\Delta\Delta E|$, a value more than 5 times that of
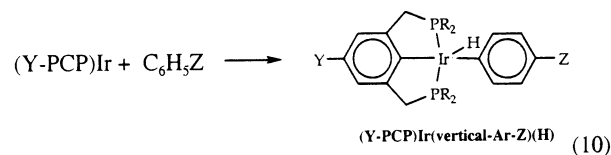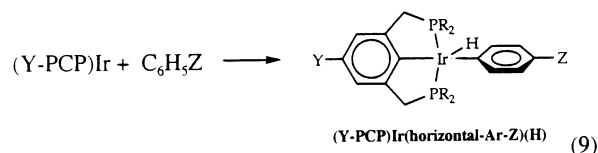
Table 5. Computed Absolute and Relative Reaction Energies for Addition of Arene ([p-Z-R$_2$C$_6$H$_2$]-H) C−H Bond to (PCP)Ir[a]

	product					
	unconstrained (C_1)		aryl horizontal (C_s)		aryl vertical (C_s)	
Z	ΔE	$\Delta\Delta E$	ΔE	$\Delta\Delta E$	ΔE	$\Delta\Delta E$
NO$_2$	−12.83	−6.18	−8.65	−5.30	−6.74	−4.56
C(O)OCH$_3$	−8.67	−2.01				
Cl	−8.40	−1.74				
H	−6.66	0.00	−3.35	0.00	−2.18	0.00
OCH$_3$	−5.54	1.12				
NH$_2$	−4.41	2.25	2.63	+5.98	−3.61	−1.43

[a] Reaction energies are given in kilocalories per mole.

methoxy: 6.2 vs 1.1 kcal/mol. In contrast, the effect exerted by a nitro group on the PCP ring of the iridium complex is only slightly greater than that of the methoxy group: 1.6 vs 1.1 kcal/mol (Table 5). The nitro group has both large electron-withdrawing inductive and resonance effects, whereas methoxy has an electron-withdrawing inductive effect but an electron-donating resonance effect. Thus, these results suggest that both π and σ electron-withdrawing groups (Z) on the benzene ring very strongly favor addition, in contrast to the effects on the PCP ring (Y), where π donation favors addition but the effect of σ donation is much less significant or even unfavorable. The relatively greater importance of π versus σ effects, for Y versus Z, is reflected in the reaction parameters: varying Y in (Y-PCP)Ir gives $\rho_R = 2.5(1)$ and $\rho_I = 1.9(1)$ (Table 2), while varying Z for addition of the C−H bond at the 4-position in C$_6$H$_5$Z gives $\rho_R = -4.5(10)$ and $\rho_I = -8.2(17)$.

Despite the negligible or even unfavorable effect of increasing σ donation from Y-PCP, in all cases discussed above the addition is favored by electron-donating substituents, Y, on PCP as well as by electron-withdrawing substituents, Z, on the arene undergoing addition. This generalization would appear to support, at least on a qualitative level, the concept of C−H addition being an "oxidative" process, i.e., a process driven in large part by the transfer of charge from metal to addendum. We believe, however, that this is not the case. The aryl hydride product has two empty d orbitals, only one of which is of π symmetry with respect to either the axis of the metal−carbon bond formed upon C−H addition or the axis of the metal−carbon(PCP) bond. That empty d(π) orbital is of appropriate symmetry to overlap with the PCP π orbitals in accord with the favorable effect of increased π donation from PCP. By contrast, the π orbitals of the added arene overlap with a filled d orbital, since the resulting aryl ligand is approximately perpendicular to the PCP plane as in the structure labeled (Y-PCP)Ir(horizontal-Ar-Z)(H).

(Y-PCP)Ir(horizontal-Ar-Z)(H)

(9)

(Y-PCP)Ir(vertical-Ar-Z)(H)

(10)

Due at least in part to steric factors, the horizontal structure represents the most favorable geometry, even with methyl groups on the P atoms. However, if we computationally replace the methyl groups with H atoms, it becomes possible for the phenyl group to rotate 90° without encountering excessive steric stress, and its π orbitals can now interact with the same empty d(π) orbital that overlaps with the PCP π orbitals. The energies calculated for formation of the two isomers, with mirror symmetry (C_s) imposed in both cases, are shown in Table 5. For (Y-PCP)Ir(horizontal-Ar-H)(H), the geometry and the reaction thermodynamics are similar to the system with methylated P atoms and no imposed symmetry. Formation of the vertical isomer (eq 10) is less favorable than that of the horizontal isomer (eq 9) for Y = Z = H, but only by 1.2 kcal/mol (3.35− 2.18). Much more importantly, however, *the effect of varying substituent Z is very different for eqs 9 and 10*. In particular, horizontal addition (eq 9) is disfavored by the strongly π-donating NH$_2$ in the Z position ($\Delta\Delta E$ = 6.0 kcal/mol versus Z = H; Table 5). In contrast, when the arene is added vertically (eq 10), Z = NH$_2$ exerts a favorable effect on the reaction energy ($\Delta\Delta E$ = −1.4 kcal/mol versus Z = H). Evidently, π donation from the para substituent on the arene can *favor* addition to (PCP)Ir, depending upon the isomer formed, in contradiction with the idea of the reaction being driven or promoted largely by transfer of charge from metal to ligand.

When located in the Y position, NH$_2$ favors either horizontal (eq 9) or vertical addition of arene (eq 10) ($\Delta\Delta E$ = −2.7 and −1.9 kcal/mol, respectively; Z = H). For vertical addition (eq 10), the favorable effect of Y = NH$_2$ (−1.9 kcal/mol) is quite similar to the effect exerted by NH$_2$ at the Z position (−1.4 kcal/mol). The fact that a substituent can exert effects of the same direction and magnitude when located on either addendum or ancillary ligand is obviously inconsistent with the idea that substituent effects are dominated by the transfer of charge from the metal to the addendum (or from addendum to metal). Instead, this result is fully consistent with the proposal that the major effect of the NH$_2$ substituent derives from π donation into the empty d orbital, which overlaps equally with both the PCP and the addendum aryl groups of (Y-PCP)Ir(vertical-Ar-Z)(H).

In contrast to NH$_2$, which exerts a substituent effect that is predominantly π (σ_R = −0.82; σ_I = 0.12), NO$_2$ exerts predominantly a σ effect (σ_R = 0.15; σ_I = 0.65). Whereas Z = NH$_2$ affects eqs 9 and 10 in opposite directions, the effect of Z = NO$_2$ is found to be favorable for both eqs 9 and 10. The value of $\Delta\Delta E$ is less favorable for vertical (−4.6 kcal/mol) than for horizontal addition (−5.3 kcal/mol), presumably due to the energetically unfavorable effect of π withdrawal for eq 10, but apparently the strongly σ-withdrawing effect of NO$_2$ is much more important than the relatively weak π withdrawal (which, by itself, should make a positive contribution to $\Delta\Delta E$ of eq 10). In addition to the much greater value of σ_I versus σ_R for NO$_2$, this observation is in accord with the very large inductive parameter (ρ_I = −8.2) determined in the symmetry-unconstrained reactions; ρ_I is expected to be, and apparently is, approximately independent of the aryl group orientation.[48]

Addition of Alkyl C−H Bonds to (PCP)Ir. We have recently reported calculations[46] on the thermodynamics of addition for different hydrocarbon C−H bonds to (H-PCP)Ir. A large energy difference between alkane and arene addition is calculated; Table 4 shows a difference of 11 kcal/mol favoring benzene vs the primary C−H bond of *n*-butane.[49] This result is experimentally well precedented for late-metal systems; for example, Wick and Jones[50] have found a difference of 9.35 kcal/mol between addition of benzene and *n*-pentane C−H bonds. Early metal systems show much smaller differences (e.g., 1.2 kcal/mol for benzene vs *n*-butane addition to [^{t}Bu$_3$SiO]$_2$Ti= NSi^{t}Bu$_3$).[51,52] In terms of the present system, the difference may be attributable to a combination of σ effects (cf. the large value of ρ_I = −8.2 for addition of H−C$_6$H$_4$Z) and π effects, with alkyl being more π donating as it lacks the capacity of aryl to act as a π acceptor. Although π donation into the empty metal d(π) orbital should be favorable, this may be outweighed by unfavorable interactions between filled d(π) orbitals present in late metals and filled orbitals in alkyl ligands (Pauli steric repulsion).[53] Note in this context that the unfavorable effect of the NH$_2$ group for the horizontal addition of aminobenzene ($\Delta\Delta E_9$ = +6.0 kcal/mol; Table 5) is of much greater magnitude than the favorable effect for the vertical addition ($\Delta\Delta E_{10}$ = −1.4 kcal/mol).

Concerning ancillary ligand substituent effects, electron-donating substituents on the PCP ligand favor addition of alkane but less so than addition of H$_2$. Thus the values of ΔE_7 are positive for alkyl−H addition also but less so than for phenyl−H; i.e., the favorable effect of increased electron donation by Y-PCP increases as phenyl−H < alkyl−H < H−H. The alkyl hydride geometries are quite similar to those of the dihydrides (C$_{PCP}$−Ir−C$_{butyl}$ ~ 160° and C$_{butyl}$−Ir−H ~ 70° vs C$_{PCP}$−Ir−H = 150° and H−Ir−H ~ 60°); thus, alkyl−H addition probably provides a better comparison with H$_2$ addition. It is difficult to distinguish π effects from σ effects but the major conclusions concerning ancillary ligand effects for either arene or alkane addition seem clear: C−H addition to (Y-PCP)Ir is favored by increased electron donation from Y but to a lesser degree than is H$_2$ addition.

H$_2$ and C−H Addition to (Y-PCP)Ir(CO): Para-Substituted PCP Ligands. The calculated and experimental results discussed above demonstrate an increased tendency toward H−H and C−H addition for the more electron-rich (Y-PCP)Ir derivatives and an increased tendency for addition of more electron-deficient arenes. The single exception to this generalization is the effect of the π-donating NH$_2$ group on benzene, when the aryl group is added perpendicular to the equatorial plane. It may be tempting to consider this one exception to be a mere anomaly and to rationalize the general effects in terms of the definition of "oxidative addition", i.e., a reaction that

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(48) Accordingly, dual-parameter analysis for the vertical addition gives ρ_R = 0.7 and ρ_I = −7.2; since there are only three data points, there is no overdetermination and no error analysis is possible.

(49) *n*-Butane was chosen, rather than a smaller alkane, to allow for future studies on primary vs secondary C−H addition and internal vs terminal β-elimination reactions.

(50) Wick, D. D.; Jones, W. D. *Organometallics* **1999**, *18*, 495−505.

(51) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1997**, *119*, 10696−10719.

(52) For excellent discussions of the kinetic and thermodynamic selectivity exhibited by transition metal complexes toward C−H bonds, particularly in terms of factors other than steric, see the following and references therein: (a) Bennett, J. L.; Vaid, T. P.; Wolczanski, P. T. *Inorg. Chim. Acta* **1998**, *270* (1−2), 414−423. (b) Wick, D. D.; Jones, W. D. *Organometallics* **1999**, *18*, 495−505.

(53) (a) Ziegler, T.; Tschinke, V.; Becke, A. *J. Am. Chem. Soc.* **1987**, *109*, 1351−1358. (b) Ziegler, T.; Tschinke, V.; Versluis, L.; Baerends, E. J.; Ravenek, W. *Polyhedron* **1988**, *7*, 1625−1637.
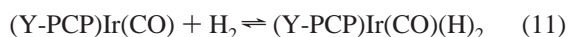
Table 6. Computed Absolute and Relative Reaction Energies for Addition of H_2, Ph–H, and CO to (Y-PCP)Ir(CO)[a]

	product					
	(Y-PCP)Ir(CO)H_2		(Y-PCP)Ir(CO)HPh		(Y-PCP)Ir(CO)$_2$	
Y	ΔE	$\Delta\Delta E$	ΔE	$\Delta\Delta E$	ΔE	$\Delta\Delta E$
BH_2	−10.89	−0.76			−13.09	−1.08
NO_2	−10.70	−0.57	12.93	−0.22	−12.76	−0.75
$C(O)OCH_3$	−10.51	−0.39	12.84	−0.32	−12.54	−0.53
H	−10.13	0.00	13.15	0.00	−12.01	0.00
Li	−9.70	0.42			−12.03	−0.02
F	−9.61	0.51			−11.41	0.60
OCH_3	−9.20	0.93	13.94	0.78	−11.15	0.86
NH_2	−8.91	1.21	14.20	1.04	−10.81	1.20

[a] Reaction energies, in kilocalories per mole, were calculated from eqs 11, 12, and 16.

involves removal of charge from the metal and therefore should be favored by increased electron density on the metal center. However, in the case of four-coordinate d^8 complexes IrL_2-(CO)X, we have previously argued that increased electron density (more specifically, increased π donation) *disfavors* addition of H_2.[21] Unfortunately, the comparison between complexes with different ligands X (mostly halides) is not straightforward: complexes of the less electronegative halogens add H_2 more readily (seemingly consistent with the oxidative addition concept) but paradoxically, their complexes are *less* electron-rich.[20] Close examination reveals that significant variables other than electron-donating ability are involved, including the extent of orbital overlap and the metal–ligand bond length, which results in greater electrostatic effects for the smaller halides.[21] The present (PCP)Ir systems, involving different substituents at the para position, are in some respects much more amenable to analysis. We therefore examined addition of H_2 to (PCP)Ir(CO) derivatives for the sake of comparison with both the corresponding three-coordinate PCP complexes and the four-coordinate carbonyl halide (Vaska-type) analogues.

Addition of H_2 to either (PCP)Ir(CO) or $(C(O)OCH_3$-PCP)-Ir(CO) results in the formation of both cis and trans isomeric dihydrides, in accord with a report by Milstein for addition to the di(isopropyl)phosphino analogue:[54]

$$(Y\text{-PCP})Ir(CO) + H_2 \rightleftharpoons (Y\text{-PCP})Ir(CO)(H)_2 \quad (11)$$

The substituent effects are very similar for both isomers but we have focused on the more symmetrical trans isomer, which was found by Milstein and co-workers[54] to be thermodynamically favored in accord with our calculations. The reaction energies, shown in Table 6, clearly illustrate that *H_2 addition is disfavored by increasing electron donation by the para substituent on PCP* [$\rho_{sp} = -1.3(2)$; $P_{sp} = 0.3\%$]. Note that varying the PCP para substituent raises none of the complicating factors introduced when the halide is varied in IrL_2(CO)X; for example, upon substituting H with Li (or, experimentally, methoxycarbonyl with methoxy), the primary result can only be an increase of electron density at the para carbon. The concept of "oxidative addition" as proposed by Vaska and co-workers[55,56] was in large part based on substituent effects; for

example, the heavier, more electropositive halogens were found to favor H_2 addition to IrL_2(CO)X (although it was not realized that such complexes were actually less electron-rich). With reaction energies as the substituent effect criterion, the calculated values in Table 6 lead squarely to the conclusion that the prototypical "oxidative addition" reaction represented by eq 11 is not really oxidative at all. The Taft–Lewis reaction parameters are $\rho_R = -1.64(6)$ and $\rho_I = -0.45(11)$; thus the unfavorable effect of increased electron donation is not large, but the statistical significance is high ($P_R = 0.01\%$; $P_I = 2.7\%$) and clearly in the direction opposite that of an "oxidative" addition. On the basis of these values, the range of resonance effects (1.6 kcal/mol) is significantly greater than the range of inductive effects (0.3 kcal/mol).

Experimental results unambiguously corroborate the calculated trend: addition of H_2 to $([(CH_3O)C(O)]$-PCP)Ir(CO) (ν_{CO} = 1930.0 cm^{-1}) is more favorable than to the unsubstituted complex (ν_{CO} = 1927.7 cm^{-1}), while H_2 addition to the electron-rich MeO-PCP complex (ν_{CO} = 1925.5 cm^{-1}) (2 atm of H_2) was not observable ($K < 0.01$ atm^{-1}). Measured values of K_{11} (22 °C) are as follows: $C(O)OCH_3$-PCP, $K_{11} = 0.056$ atm^{-1}; H-PCP, $K_{11} = 0.036$ atm^{-1}.[57−59]

Addition of Arene C–H Bonds to (PCP)Ir(CO): Para-Substituted Arenes. Like addition of H_2, the addition of C–H bonds to (Y-PCP)Ir(CO) (eq 12) is disfavored (computationally) by increased electron-donating ability of Y-PCP (Table 6).

$$(Y\text{-PCP})Ir(CO) + ZC_6H_5 \rightleftharpoons \quad (12)$$

Although we have recently reported the isolation of the benzene CH addition product shown in eq 12 (Z = H), (PCP)-Ir(CO)(Ph)(H),[22] the substituent effects for addition are difficult to test experimentally for two reasons: (i) presumably the equilibrium lies far toward benzene elimination, precluding equilibrium studies, and (ii) the kinetics of elimination are extremely slow even at 110 °C, precluding calorimetric studies. Nevertheless, in view of the experimentally confirmed substituent effects for H_2 addition, there appears to be no reason to doubt the validity of these calculated results.

Does the correlation between ΔE and the electron-donating ability of Y suggest that addition of H_2 or C–H bonds to (Y-PCP)Ir(CO) is best viewed as a "reductive addition"?[60] Such a concept would imply a transfer of electron density from the

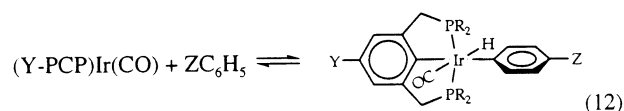(54) Rybtchinski, B.; Vigalok, A.; Bendavid, Y.; Milstein, D. *Organometallics* **1997**, *16*, 3786−3793.
(55) Vaska, L. *Acc. Chem. Res.* **1968**, *1*, 335−344.
(56) Vaska, L.; Werneke, M. F. *Ann. N.Y. Acad. Sci.* **1971**, *172*, 546−562.

(57) Although the $\Delta\Delta E$ values (i.e., the substituent effects) are the focus of this work, it should be noted that the calculated and absolute values for the thermodynamics of addition are reasonably consistent (especially considering the different alkyl groups on the phosphorus atoms in experiments versus calculations). For example, for unsubstituted (PCP)Ir-(CO), the experimental values for H_2 addition are $K_{cis} = 0.068$ atm^{-1} and $K_{trans} = 0.036$ atm^{-1}. Converting to reciprocal molar units gives $\Delta G = -1.66$ kcal/mol and -1.29 kcal/mol (ref 55). By use of the value for the entropy of addition of H_2 to Vaska's complex, -29 eu (based on H_2 in solution; refs 55 and 58) gives $\Delta H = -10.22$ and -9.85 kcal/mol, respectively. This compares with the respective calculated values of $\Delta E = -6.50$ and -10.13 kcal/mol.
(58) Based upon the solubility of H_2 in 1-octene at 298 K, 0.0040 M/atm^{-1}: Purwanto; Deshpande, R. M.; Chaudhari, R. V.; Delmas, H. *J. Chem. Eng. Data* **1996**, *41*, 1414−1417.
(59) For formation of the cis isomer, the same trend is observed: $[(CH_3O)C-(O)]$-PCP, $K_{11} = 0.19$; H-PCP, $K_{11} = 0.068$. It also bears note that addition of H_2 to the di(*tert*-butyl)phosphino analogue (the actual ligand used in all experiments described in this work) is significantly less favorable than to the isopropyl analogue.[54]
(60) Crabtree, R. H.; Quirk, J. M. *J. Organomet. Chem.* **1980**, *199*, 99−106.

addendum to the metal center; this should be *favored* by increased electron richness on the para position of a benzene derivative (p-ZC$_6$H$_4$-H) undergoing C−H addition. To the contrary, there appears to be a strong *inverse* correlation based on the two substituents that we have calculated: methoxybenzene adds less favorably to (PCP)Ir(CO) than benzene by 1.0 kcal/mol, and nitrobenzene adds more favorably by 5.3 kcal/mol.

Thus, somewhat counterintuitively, C−H addition to (Y-PCP)Ir(CO) is favored by electron-withdrawing para substituents on either the PCP ring (Y) or the adding arene (Z). [This is analogous to the case of addition to (Y-PCP)Ir being favored by electron-donating p-NH$_2$ located on either the PCP ring or the adding arene, for arene adding vertically to (Y-PCP)Ir (eq 10).] The arene addendum effect for eq 12 shows a greater magnitude as might be expected, since the bond being formed is closer to the substituent. However, less predictably, the relative importance of inductive and resonance effects is apparently quite different for the Y and Z substituents. The limited data yield reaction parameters $\rho_R = -4.7$ and $\rho_I = -7.0$, implying comparable resonance and inductive contributions if the full range of substituents were varied at the Z position. In contrast, for substitution on the Y-PCP ring reaction parameters are $\rho_R = -1.4(2)$ and $\rho_I = -0.04(15)$. This is consistent with the reaction parameters obtained for addition of H$_2$ to (Y-PCP)-Ir(CO) [$\rho_R = -1.64(6)$ and $\rho_I = -0.45(11)$], where the resonance effect is much greater than the inductive effect (by a factor of >5 over the full range of substituents).

In our study of H$_2$ addition to Vaska's complex, we considered several factors to explain the observation that the lighter halides disfavored H$_2$ addition.[21] There appeared to be an initial-state effect, wherein the better π donors such as X = F stabilized the square-planar complex via donation into the empty Ir(p$_z$) orbital. An apparently more important effect was manifest in the product: repulsive interactions (electrostatic and/or covalent) between the lone pairs on X and the additional electrons resulting from H$_2$ addition. The present observations support the explanation of repulsive interactions between the ancillary ligand (X or PCP) and the electron density contributed by the addendum (hydride and hydrocarbyl ligands): increased π electron density from either PCP or the adding aryl group is clearly indicated to result in a less favorable addition reaction. This cannot be explained solely in terms of either initial-state effects or charge transfer.

Minimizing electron−electron repulsion is apparently the dominant driving force within the π system. Sigma withdrawal by substituents on the adding arene (Z) is strongly favorable; however, the relative importance of σ effects is much less pronounced for the PCP substituents (Y). While electron−electron repulsion probably also plays a role in the σ system, detailed analysis of the results suggests that there is an additional component to the effects, one that is indicative of a true oxidative addition. Such a charge-transfer component would partially offset the unfavorable effect of increased electron donation (resulting in increased Pauli repulsion) in the case of the PCP substituent, whereas it would enhance the already favorable effect of an electron-withdrawing group on the arene undergoing addition. Hence the reaction parameters for eq 12 (especially ρ_I) are much greater for Z than for Y.
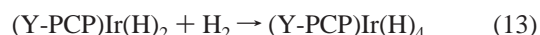
Table 7. Computed Absolute and Relative Reaction Energies for Addition of H$_2$ and CO to (Y-PCP)Ir(H)$_2$[a]

	[M]H$_4$[b]		*trans*-[M](CO)H$_2$		*cis*-[M](CO)H$_2$	
Y	ΔE	$\Delta \Delta E$	ΔE	$\Delta \Delta E$	ΔE	$\Delta \Delta E$
BH$_2$	−15.79	−1.62	−47.09	−1.79	−43.56	−1.87
NO$_2$	−15.46	−1.30	−46.64	−1.34	−43.14	−1.45
C(O)OCH$_3$	−15.18	−1.01	−46.29	−0.99	−42.79	−1.10
H	−14.17	0.00	−45.30	0.00	−41.69	0.00
F	−13.47	0.70	−44.44	0.86	−41.05	0.64
Li	−13.43	0.74	−44.79	0.51	−41.06	0.63
OCH$_3$	−12.81	1.36	−43.77	1.54	−40.36	1.33
NH$_2$	−12.15	2.02	−43.18	2.13	−39.68	2.01

[a] Reaction energies, in kilocalories per mole, were calculated from eqs 13 and 15. [b] [M] = (Y-PCP)Ir.

H$_2$ Addition to (Y-PCP)Ir(H)$_2$. Although addition to Ir(I) is far more common, many examples are known of H$_2$ addition to Ir(III). Addition of H$_2$ to complexes of the type IrL$_2$X(H)$_2$, where X is a halide, has received the most attention;[14,16−19] the products have been shown to be dihydrogen complexes, viz., IrL$_2$X(H)$_2$(H$_2$). The addition has been studied theoretically and experimentally. The lighter halides have been shown to disfavor coordination of H$_2$, and this has been proposed to be due to increased X → M π bonding[14,16] although, as discussed above in the context of varying X in species IrL$_2$X(CO), it is difficult to conclusively rule out other factors when the halide ligand is varied.

H$_2$ can also add to Ir(III) to give Ir(V) complexes. (P^{i}Pr$_3$)$_2$-IrH$_5$ was shown by neutron diffraction to be a classical pentahydride[61] and has been shown to undergo reversible elimination of H$_2$.[62] (PCP)IrH$_4$ was reported by Kaska and Jensen and co-workers[35] and, on the basis of T_{1min} values, was proposed to be a classical tetrahydride.[63,64] Our calculations on this species indicate that the tetrahydride is indeed the most stable isomer, though the dihydrogen complexes *cis*- and *trans*-(PCP)Ir(H)$_2$(H$_2$) are calculated to be only slightly higher in energy. Further investigation of the dihydrogen/dihydride equilibria is beyond the scope of this paper; herein we focus on the full oxidative addition:

$$(\text{Y-PCP})\text{Ir(H)}_2 + \text{H}_2 \rightarrow (\text{Y-PCP})\text{Ir(H)}_4 \qquad (13)$$

The results of calculations of eq 13 are shown in Table 7. It is found that increased electron donation by Y strongly *disfavors* the addition. Dual-parameter analysis indicates that π donation is the dominant factor [$\rho_R = -3.0(2)$; $\rho_I = -1.2(3)$]. Y = Li and Y = F show similar reaction energies, an indication that increased σ donation probably does not play a significantly disfavorable role. The π donation effect is presumably due in part to stabilization of the coordinatively unsaturated (Y-PCP)-Ir(H)$_2$ complex [as proposed for addition to IrL$_2$X(H)$_2$[13]]. There is also structural evidence for destabilizing effects in the product; this is probably best described in terms of repulsive interactions between the PCP π orbitals and the additional electron density contributed by H$_2$ to the conjugating (formally empty) orbital

(61) Garlaschelli, L.; Khan, S. I.; Bau, R.; Longoni, G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1985**, *107*, 7212−13.
(62) Goldman, A. S.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 7537−7539.
(63) Gupta, M. Ph.D. Thesis, University of Hawaii, 1997.
(64) McLoughlin, M. A.; Flesher, R. J.; Kaska, W. C.; Mayer, H. A. *Organometallics* **1994**, *13*, 3816−3822.
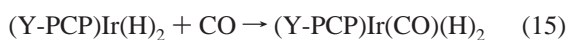
in the plane perpendicular to the P−Ir−P axis.[13] The evidence for this is presented in more detail in the Geometries section below.

CO Addition to (Y-PCP)Ir. Addition of CO to the parent three-coordinate fragment (H-PCP)Ir is calculated to be exoergic by 59.2 kcal/mol (eq 14, Y = H):
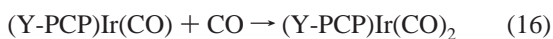
$$(Y\text{-PCP})Ir + CO \rightarrow (Y\text{-PCP})Ir(CO) \qquad (14)$$

This is 25 kcal/mol less than the calculated value for addition of CO to $Ir(PMe_3)_2Cl$ (84 kcal/mol); this large difference is similar to that for H_2, which is computed to add to $Ir(PMe_3)_2Cl$ 33 kcal/mol more favorably than to (H−PCP)Ir.[65] As might be expected, increasing electron richness on the PCP ligand favors the thermodynamics of CO addition, presumably due to improved $Ir(d)−CO(\pi^*)$ back-bonding. The magnitude of the effect (see Supporting Information) is less than that for H_2 addition to (Y-PCP)Ir, but the ordering of relative energies is essentially the same as observed for H_2 addition (Table 3). This trend is also reflected by reaction parameters [$\rho_R = 2.9(5)$; $\rho_I = 2.1(10)$] that are both ca. 70% of the corresponding values for H_2 addition (4.4 and 2.7). As with H_2, this indicates a greater overall energy range for resonance effects than for inductive effects (2.9 vs 1.7 kcal/mol). Also, as with H_2, consideration of the nonparametrized substituents such as (rotated) NH_2, BH_2, NO_2, or Li (see Supporting Information) suggests that σ donation is even less significant than indicated by the dual-parameter LFER analysis.

CO Addition to (Y-PCP)Ir(H)₂. Like the oxidative addition of H_2 or C−H bonds, the addition of CO to late transition metal centers is generally assumed to be favored by increased electron richness at the metal center.[3,4] The above example of CO addition to (Y-PCP)Ir (eq 14) conforms to this expectation. In contrast to addition to (PCP)Ir, however, addition of CO to (PCP)Ir(H)₂

$$(Y\text{-PCP})Ir(H)_2 + CO \rightarrow (Y\text{-PCP})Ir(CO)(H)_2 \qquad (15)$$

is found to be *disfavored* by increased electron-donating ability of the Y-PCP ligand (Table 7); the reaction parameters [$\rho_{sp} = -2.6(4)$; $\rho_R = -3.1(2)$; $\rho_I = -1.1(3)$][66] are of the same magnitude—but opposite direction—as those for CO addition to (PCP)Ir. This result is closely related to the inverse dependence on electron-donating ability of Y-PCP found for the "converse" reaction: addition of H_2 to (PCP)Ir(CO) (eq 11) to give the same product as in eq 15. (Indeed, these are not fully independent results: from the calculations of eqs 4, 11, and 14, a thermodynamic cycle can be completed: eq 15 = eq 11 + eq 14 − eq 4.)

CO Addition to (Y-PCP)Ir(CO). As discussed above, an *inverse* correlation between electron donation and M−CO bond dissociation energy is found for (Y-PCP)Ir(CO)(H)₂. Is this an anomalous result? It would appear not to be: addition of CO to (Y-PCP)Ir(CO) is also calculated to show such an inverse correlation:
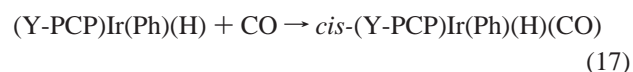
$$(Y\text{-PCP})Ir(CO) + CO \rightarrow (Y\text{-PCP})Ir(CO)_2 \qquad (16)$$

(calculations shown in Table 6). The reaction parameters are markedly similar to those found for addition of H_2 to the same complex: $\rho_{SP} = -1.5(3)$; $\rho_R = -1.9(1)$; $\rho_I = -0.6(2)$ (cf. −1.3, −1.6, and −0.4, respectively, for H_2 addition[66]). Presumably these results are closely related; most obviously in terms of initial-state stabilization and likely also in terms of filled−filled orbital repulsions in the products. One difference of note is the effect when Y = Li: for H_2 addition, Li and F have very similar effects, but for CO addition, Li is significantly more favorable. This indicates that increased σ donation favors addition of CO relative to H_2; perhaps this is due to the absence of a ligand trans to PCP in the CO adduct.

The addition of CO to (Y-PCP)Ir(Ph)(H), eq 17, is formally analogous to CO addition to the dihydride, eq 15:

$$(Y\text{-PCP})Ir(Ph)(H) + CO \rightarrow cis\text{-}(Y\text{-PCP})Ir(Ph)(H)(CO) \qquad (17)$$

However, the phenyl hydrides possess a square-pyramidal geometry (H apical) rather than the distorted trigonal-bipyramidal (tbp) geometry of (PCP)Ir(H)₂. Since the distorted tbp structure has been shown to be particularly well stabilized by π donation,[13] the inverse correlation of Ir−CO bond dissociation energy and electron richness might not be expected in the case of eq 17. Indeed, there is no clear correlation with the electron-donating ability of Y-PCP. The reaction parameters are $\rho_R = -0.7(1)$ and $\rho_I = +1.0(1)$. These values are very small and the only examples in this work where ρ_R and ρ_I are of opposite sign. Thus, we give them little weight; however, the absence of a significant correlation with electron-donating ability does at least offer one additional example contradicting the notion that increasing electron richness should necessarily result in *increased* M-CO bond strengths.[67−69]

Overview of R−H and CO Addition to (PCP)Ir: Geometries and Structural Trends. Experimentally, X-ray crystal structures have been determined previously for two of the complexes calculated in this work: (PCP)IrH₂[8b] and (PCP)Ir-(CO)[36] [both with bis(*tert*-butyl)phosphino groups]. Calculated iridium−ligand bond distances and angles are in excellent agreement with the crystallographic values (within 0.01 Å and 1°, respectively).[70]

The calculated lengths of the Ir−H and Ir−C bonds that are formed upon R−H and CO addition to (Y-PCP)Ir show no significant variations as functions of the substituent Y. However, the (Y-PCP)C−Ir bond lengths show distinct variations that are small but clearly systematic (Table 8).[47,71] The correlation between bond lengths and σ_{sp} can be parametrized according to eq 18, where δ_{sp} is the correlation factor (in units of

(65) Rosini, G. P.; Liu, F.; Krogh-Jespersen, K.; Goldman, A. S.; Li, C.; Nolan, S. P. *J. Am. Chem. Soc.* **1998**, *120*, 9256−9266.

(66) Values given are for formation of the trans dihydride; values for the cis isomer are equal within the statistical margin (see Table 7).

(67) Results concerning these six-coordinate d⁶ carbonyls are no doubt closely related to reports, both computational (ref 68) and experimental (ref 69), demonstrating that M−CO bond dissociation energies in complexes of the form [M(CO)₅X⁻] (M = Cr, Mo, W) vary inversely with the π-donating ability of X.

(68) Macgregor, S. A.; MacQueen, D. *Inorg. Chem.* **1999**, *38*, 4868−4876.

(69) (a) Graham, J. R.; Angelici, R. J. *Inorg. Chem.* **1967**, *6*, 2082. (b) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113.

(70) Crystallographic and calculated values, respectively, are as follows for (PCP)IrH₂ (ref 8b): C−Ir, 2.124(13) vs 2.120; P−Ir, 2.308(2) vs 2.304; C−Ir−P, 82.41(6) vs 81.8. For (PCP)Ir(CO) (ref 36) (molecule 1 of the two molecules in the unit cell): (PCP)C−Ir, 2.102(8) vs 2.106; (CO)C−Ir, 1.873(10) vs 1.878; P−Ir, 2.298(2) vs 2.314; (PCP)C−Ir−P, 81.800(2) vs 80.7.

Table 8. Computed C_{PCP}–Ir Bond Lengths[a] and Correlation with Hammett Parameter (σ_{sp}) for (Y-PCP)Ir and Its H_2 and CO Adducts[71]

Y	M[b]	MH_2	M(CO)	MH_4	$M(CO)_2$	$M(CO)H_2$
H	1.979	2.120	2.106	2.142	2.172	2.124
F	1.980	2.117	2.104	2.142	2.173	2.123
OCH_3	1.983	2.112	2.104	2.141	2.176	2.125
CO_2CH_3	1.967	2.121	2.103	2.137	2.160	2.115
NO_2	1.960	2.120	2.098	2.131	2.149	2.108
NH_2	1.985	2.108	2.102	2.145	2.178	2.126
Li	1.985	2.116	2.106	2.147	2.180	2.129
BH_2	1.962	2.123	2.099	2.133	2.151	2.111
δ_{sp}[c]	−1.8(3)	0.9(2)	−0.2(2)	−0.9(2)	−2.0(4)	−1.3(3)

[a] Bond lengths are given in angstroms. [b] [M] = (Y-PCP)Ir. [c] Correlations are given in picometers.

picometers):

$$d(C_{PCP}\text{-Ir}) = D + \sigma_{sp}\delta_{sp} \qquad (18)$$

For the parent 14-electron complex, C_{PCP}–Ir bond lengths increase with increasing electron richness [$\delta_{sp} = -1.8(3)$]. For example, the C_{PCP}–Ir bond length of electron-rich (NH_2-PCP)-Ir is 0.025 Å greater than that of (NO_2-PCP)Ir (Table 8). Addition of CO to give (Y-PCP)Ir(CO) results in a much smaller range of C_{PCP}–Ir bond lengths among the various complexes [with low statistical significance; $\delta_{sp} = -0.2(2)$]; presumably, $C_{PCP} \rightarrow Ir$ π donation becomes more favorable (or less unfavorable) due to decreased electron density in the d_{xy} orbital (see Figure 3 below for definition of axes), which results from Ir $\rightarrow$ CO back-bonding. Addition of H_2 to give (Y-PCP)Ir(H)$_2$ results in an *inverse* correlation with electron richness: $\delta_{sp} = 0.9(2)$, presumably reflecting $C_{PCP} \rightarrow Ir$ π donation into the "empty" d_{xy} orbital in the equatorial plane. If either CO or H_2 is added to (Y-PCP)Ir(H)$_2$, the correlation reverses back to give negative values of δ_{sp}: −1.3(3) and −0.9(4) for (Y-PCP)Ir(H)$_4$ and *trans*-(Y-PCP)Ir(CO)(H)$_2$, respectively. Likewise, addition of CO to (Y-PCP)Ir(CO), to give (Y-PCP)Ir(CO)$_2$, also results in longer (PCP)C–Ir bonds for electron-richer derivatives: $\delta_{sp} = -2.0(2)$.

The directions and magnitudes of these correlations with C_{PCP}–Ir bond lengths, and particularly the differences between the various complexes [e.g., the value of δ_{sp} for (Y-PCP)IrH$_2$ as compared with that for (Y-PCP)Ir(CO)H$_2$], may be easily rationalized in terms of simple molecular orbital (MO) interactions. In the case of the 14-electron parent complex, (Y-PCP)-Ir, there is a d^8 configuration and a filled d orbital of the correct symmetry to interact with the PCP p(π) orbitals. Accordingly, C_{PCP}–Ir distances are longer for the more electron-rich species such as (H_2N-PCP)Ir, reflecting a greater filled–filled repulsion. This is illustrated in Figure 1. (Alternatively the trend may reflect a diminished favorable interaction with the empty PCP
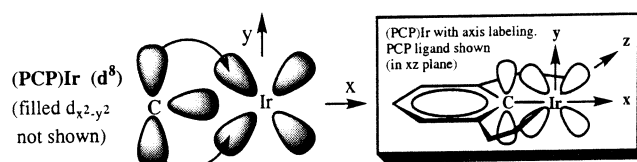

Figure 1. Schematic illustration of the interaction between the C_{PCP} p(π) orbital and the filled d_{xy} orbital of (PCP)Ir, indicating that increased π donation by the PCP ring (or decreased π withdrawal) is energetically *unfavorable*. Thus the most π-electron-rich species, (H_2N-PCP)Ir, has the longest C_{PCP}–Ir bond. Orbital shading indicates occupancy. Orientation and axes are indicated in the box.
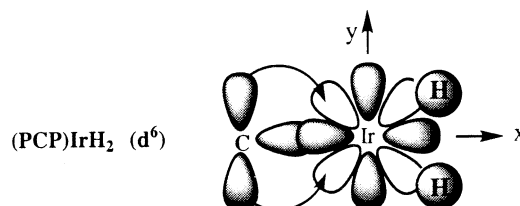

Figure 2. Schematic illustration of the interaction between the C_{PCP} p(π) orbital and the empty (PCP)Ir d_{xy} orbital of (PCP)IrH$_2$, indicating that increased π donation by the PCP ring (or decreased π withdrawal) is energetically *favorable*. Thus the most π-electron-rich derivative, (H_2N-PCP)IrH$_2$, has the *shortest* C_{PCP}–Ir bond.

π^* orbitals; it is difficult to choose between these two possibilities, but the implications for the addition reactions are the same and the difference does not have a bearing on our major conclusions. For the sake of simplicity we frame the following discussion, and Figures 1−3, in terms of interactions with the filled PCP π orbitals.)

The unfavorable interaction indicated in Figure 1 is mitigated by the addition of CO, owing to Ir–CO π donation; accordingly, the magnitude of δ_{sp} decreases substantially [from −1.8(3) to −0.2(2)]. Even more pronounced is the effect of H_2 addition, which results in a formally unoccupied d_{xy} orbital. (Note that this does not necessarily imply that the metal is "oxidized"; donation by the "hydrides" into other Ir orbitals must also be accounted for, but the occupancy of the d_{xy} orbital is reduced.) Increased π donation by C_{PCP} is now favorable, and the correlation with electron-donating ability of Y is inverse: $\delta_{sp} = 0.9(2)$. This interaction (see Figure 2) is strictly analogous to that proposed in seminal work by Eisenstein and co-workers[13] on ML$_2$XH$_2$ systems and is related in a more general sense to work by Caulton and others on the stabilization of unsaturated complexes by X $\rightarrow$ M π bonding.[15,72]

Addition of CO to (PCP)IrH$_2$ effects another reversal of the sign of δ_{sp} as the d-orbital occupancy is rearranged so that the PCP p(π) orbitals again interact with a (formally) filled d_{xy} orbital. In addition to the occupied d_{xy} orbital, the C_{PCP} p(π) orbital can interact, unfavorably, with the hydride orbitals and/ or with the Ir(p$_y$) orbital (partially occupied due to donation by the hydrides). This is indicated in Figure 3.

Thus, C_{PCP}–Ir bond lengths are calculated to be consistently greater for the more electron-rich derivatives of all the 18-electron complexes. This suggests that the additions to the corresponding 16-electron complexes are not less favorable merely because of stabilization of the 16-electron reactants. Apparently, increased π donation from the PCP ligand also results in *destabilization* of all the calculated 18-electron

(71) The *P* values for the regression analysis of the correlation of the C_{PCP}–Ir bond length with the single-parameter σ, σ_{sp}, range from 0.3% to 2.1% as follows (percent values): (Y-PCP)Ir, 0.3; (Y-PCP)IrH$_2$, 2.1; (Y-PCP)IrH$_4$, 1.0; (Y-PCP)IrH$_2$(CO), 0.9; (Y-PCP)Ir(CO)$_2$, 0.6. Further support for the significance of these correlations is obtained with substituents Y = Li and Y = BH$_2$, for which σ_{sp} values are unavailable. For example, for all complexes that give an inverse correlation of σ_{sp} with C_{PCP}–Ir bond length (negative δ_{sp}), the BH$_2$ derivative gives the second shortest C_{PCP}–Ir bond length (after Y = NO$_2$). In addition the correlations found between the different complexes that are essentially zero; for example, for the 18-electron species (Y-PCP)IrH$_4$, (Y-PCP)IrH$_2$(CO), and (Y-PCP)-Ir(CO)$_2$, the respective *P* values are 1.6×10^{-5}, 3.5×10^{-5}, and 5.8×10^{-5}. Note that the geometries for each set of derivatives are obtained independently.

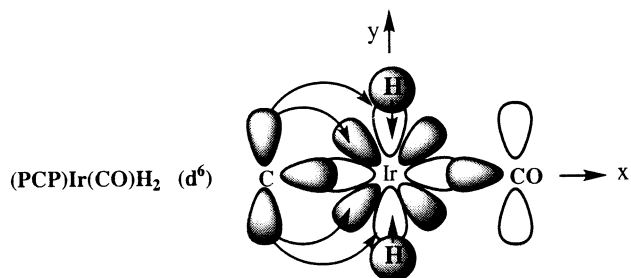(72) Bryndza, H. E.; Domaille, P. J.; Paciello, R. A.; Bercaw, J. E. *Organometallics* **1989**, *8*, 379−385.

Figure 3. Schematic illustration of the interaction between the C_{PCP} p(π) orbital and the filled (PCP)Ir d_{xy} orbital of (PCP)Ir(CO)H$_2$, indicating that increased π donation by the PCP ring (or decreased π withdrawal) is energetically *unfavorable*. Thus the most π-electron-rich derivative, (H$_2$N-PCP)Ir(CO)H$_2$, has the *longest* C_{PCP}–Ir bond.

Figure 4. Effect of increased π donation by Y-PCP (or decreased π withdrawal) on the thermodynamic relationships between the H$_2$/CO adducts of (Y-PCP)Ir.

products [including (PCP)IrH$_4$, (PCP)Ir(CO)(R)(H) and (PCP)-Ir(CO)$_2$] due to the effect of increased repulsive interactions between filled orbitals.

Overview of R–H and CO Addition to (PCP)Ir: Thermodynamics. Using (PCP)Ir as the core metal fragment, we have examined substituent effects for the addition of small molecules (hydrocarbons, H$_2$, and CO) to late-metal complexes with several prototypical configurations including d^8 three-coordinate, d^8 four-coordinate, and d^6 five-coordinate. Five classes of complexes resulting from the addition of R–H (R = H or hydrocarbyl) and/or CO to (PCP)Ir have been investigated: (PCP)Ir(R)(H), (PCP)Ir(CO), (PCP)Ir(CO)$_2$, (PCP)Ir-(CO)(R)(H), and (PCP)Ir(H)$_4$.

The substituent effects on the thermodynamic relationships between these species can be fully rationalized in terms of fundamental MO interactions—but not in terms of electron richness or oxidation/reduction. Key considerations are as follows:

(i) The parent complex, (PCP)Ir, is destabilized by increased π donation from the PCP π system (Figure 1).

(ii) The 16-electron distorted tbp complex, (PCP)Ir(H)$_2$, is strongly stabilized by π bonding from the PCP π system (Figure 2).[13]

(iii) The 16-electron (PCP)Ir(CO) complex and quasi-square-pyramidal (PCP)Ir(aryl)(H) are also stabilized by π donation from PCP, though probably to a lesser extent than (PCP)Ir-(H)$_2$.[13]

(iv) The 18-electron species (PCP)Ir(CO)(H)$_2$, (PCP)Ir(CO)-(R)(H), and (PCP)Ir(CO)$_2$ are destabilized by increasing π donation from PCP; in all cases this likely results from filled–filled interaction of the PCP π orbital with increased electron density in the Ir d_{xy} and/or p$_y$ orbitals.

The thermodynamic relationships indicated in Figure 4 all readily follow from the simple considerations noted in points i–iv.

As a result of the (relative) stabilizing/destabilizing effects noted in points i–iii, addition of R–H or CO to 14-electron three-coordinate (Y-PCP)Ir is significantly *favored* by increased electron-donating ability of Y; this *appears* to suggest that such additions are "oxidative" (Tables 2–4). Furthermore, the addition of *p*-ZC$_6$H$_4$–H to (PCP)Ir is favored by electron-withdrawing Z groups, when the arene is added perpendicularly to the PCP plane (Table 5); this is also consistent with C–H addition being an "oxidative" process. However, if the phenyl group is added so that it is coplanar with the PCP ligand, a strongly π-donating group (Z) on the arene (*p*-amino) favors
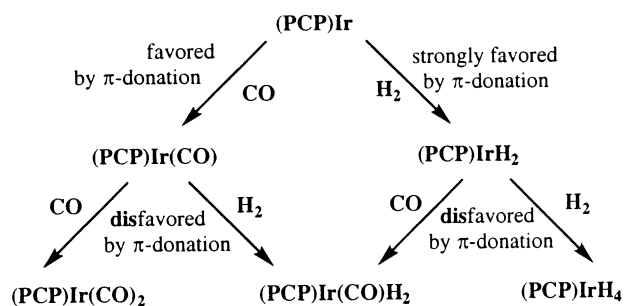
the addition reaction; this is completely *inconsistent* with the substituent effects being determined primarily by charge-transfer components. Instead, these results can all be explained in terms of addition of R–H or CO to (PCP)Ir resulting in decreased electron density in one of the d orbitals in the *xy* plane, a process that may be favored by increased π donation from either the PCP carbon or the vertically added phenyl.

Computationally (and experimentally for H$_2$ addition), increased electron-donating ability of the para substituent Y is found to disfavor R–H or CO addition to (Y-PCP)Ir(CO) (Table 6). The H$_2$ result in particular is somewhat ironic since (PCP)-Ir(CO) is a derivative of Vaska's complex, the system that was the basis for the original characterization of H$_2$ addition as an "oxidative" process.[55,56] However, the observed substituent effect does not imply the converse, i.e., that the process is a "reductive addition"; increased electron donation from the substituent Z disfavors addition of the *p*-C–H bond of ZC$_6$H$_5$ with an even stronger substituent effect than found for Y in Y-PCP. The trend is best explained in terms of additional Pauli (filled–filled) repulsions operative in the 18-electron products (point iv, above) as compared with the 16-electron reactants (points ii and iii); thus increased electron donation from either ancillary ligand (PCP) or addendum (arene) is unfavorable.

Increased electron-donating ability of the para substituent Y is found to *disfavor* H–H or CO addition to (Y-PCP)Ir(H)$_2$ (Figure 4; Table 7). In the case of CO addition, there is widespread agreement that metal–π* back-bonding plays a more important role than CO-to-metal σ donation in determining bond dissociation energies (at least in the case of anionic and neutral metal carbonyls);[73] increased electron richness is, accordingly, widely believed to generally favor increased M–CO bond dissociation energies.[3,4] However, as with H$_2$ addition to (Y-PCP)Ir(CO), the interactions described above (points ii and iv) are apparently dominant.

The fact that the direction of the observed trends for C–H and H–H addition can be successfully explained without invoking oxidative/reductive components (i.e., charge transfer or polarity) does not eliminate the possibility that such factors do contribute to the reaction energies. Indeed, close examination of the complete body of reaction parameters seems to suggest that the C–H additions (and therefore, presumably, H$_2$ additions as well) are in fact somewhat oxidative. In particular, the very negative values of ρ_I derived for all three additions of *p*-ZC$_6$H$_4$–H in which the Z is varied [vertical and horizontal addition to (PCP)Ir and addition to (PCP)Ir(CO)] would seem

(73) Davidson, E. R.; Kunze, K. L.; Machado, F. B. C.; Chakravorty, S. J. *Acc. Chem. Res.* **1993**, *26*, 628–635.

to suggest as much. However, any such oxidative component is apparently not dominant; for example, in the case of addition to (Y-PCP)Ir(CO) it is not sufficiently strong to offset the increased electron−electron repulsion resulting from C−H addition, and thus increasing electron donation from Y disfavors addition of C_6H_6 to (Y-PCP)Ir(CO).

In varying aryl ring substituents (as in this work) and in the case of varying halides,[12−21] it seems that π effects and the effects of specific orbital interactions are dominant. In addressing the question of a genuinely oxidative component, it may prove helpful to focus on other types of ligands, though complications presented by other ligands may prove equally problematic. Considering other systems, it is known that the tris(*p*-tolyl)-phosphine and tris(*p*-methoxyphosphine) analogues of Vaska's complex [Ir(PPh₃)₂(CO)Cl] add H_2 more favorably than the parent, though the difference is slight ($\Delta\Delta G$ = 0.2 and 0.3 kcal/mol, respectively);[56] this suggests a small favorable effect of increased σ donation. More generally, the fairly limited examples of metal−hydrogen BDEs that have been determined (enthalpies of single H-atom addition to odd-electron complexes) indicate dependencies on the electron-donating ability of the ancillary ligands that range from small and positive to small and inverse. Tilset found negligible effects in comparing several neutral-complex couples including $CpMo(CO)_3H$ (Cp = C_5H_5, C_5Me_5), $Co(CO)_3LH$ [L= PPh₃, P(OPh)₃], and $(C_5H_5)W(CO)_2$-LH (L = PMe₃, CO);[74] a comparison of $LM(CO)_3$ complexes (L = Tp, Tp′, Cp; M = Mo, W) indicated an inverse relationship between M−H BDE and electron richness.[75] The most extensive study of M−H BDEs was conducted by Wang and Angelici[76] on cationic complexes; a slight dependence on ancillary ligand electron-donating ability was found for complexes of Fe, Mo, Os, and W, while zero dependence was found for [CpIr(CO)-(PR₃)H]⁺ (varying R) or [(C₅MeₙH₅₋ₙ)Ir(cyclooctadiene)H]⁺.

Conclusion. Substituent effects have been investigated, experimentally and computationally, for manifold small-molecule addition reactions with (PCP)Ir as the core metal fragment. The experimentally observed substituent effects are all in excellent agreement with the computed values. Addition

of either CO or RH to the 14-electron species (Y-PCP)Ir is favored by increased electron donation from the para substituent Y. However, further addition of either CO or RH to the resulting 16-electron complexes, (Y-PCP)IrRH or (Y-PCP)Ir(CO), is generally *disfavored* by increased electron donation by Y. The trends for the energies of CO addition, H−H addition, and C−H bond addition to the (Y-PCP)Ir complexes are all found to be very similar. All the trends elucidated, encompassing the effects of varying both the PCP ligand as well as added arene, may be simply explained in terms of filled−filled and filled−empty MO interactions operative in the respective reactants and products, rather than by any net transfer of charge to or from the addenda. Thus, despite widespread assumptions, electron-rich ancillary ligands do not appear to generally favor the thermodynamics of addition of H_2, hydrocarbons, or CO. Undoubtedly there are true charge-transfer components influencing substituent effects in the present systems and others; however, this work indicates that such effects are not generally dominant.[77,78]

Supporting Information Available: Experimental details and complete data for computed absolute and relative reaction energies of all reactions investigated (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(74) Tilset, M. P.; Vernon D. *J. Am. Chem. Soc.* **1989**, *111*, 6711−17.
(75) Skagestad, V.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 5077−83.
(76) Wang, D.; Angelici, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 935.
(77) With respect to our conclusion we feel that it is important to note an important caveat: *relative* energies of addition are often more important than absolute energies. Even assuming that addition of CO or R−H is not oxidizing (or even if such additions are assumed to be reducing), increased electron donation by ancillary ligands such as Y-PCP probably does favor the addition of CO or R−H *relative* to the addition of "classical" two-electron donor ligands (e.g., amines or trialkylphosphines) that engage in a significant net transfer of charge to the metal center (ref 78). In other words, equilibria such as the following (e.g., L = NR₃ or PR₃) will presumably be pushed to the right by increased electron donation by ancillary ligands: M−L + RH = M(R)(H) + L; M−L + CO = M(CO) + L.
(78) For example, Bryndza and Bercaw reported that π-donating ancillary ligands (X) substantially accelerate the rates of dissociation of PMe₃ from Cp*-(PMe₃)₂RuX; presumably these kinetics correlate closely with the Ru−P BDEs: Bryndza, H. E.; Domaille, P. J.; Paciello, R. A.; Bercaw, J. E. *Organometallics* **1989**, *8*, 379−385.
(79) Exner, O. In *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum Publishing Company: New York, 1972; pp 28−29.