Supporting Information for:

Combined Computational and Experimental Study of Substituent Effects on the Thermodynamics of H_2, CO, Arene, and Alkane Addition to Iridium

Karsten Krogh-Jespersen*, Margaret Czerw, Keming Zhu, Bharat Singh, Mira Kanzelberger, Nitesh Darji, Patrick D. Achord, Kenton B. Renkema and Alan S. Goldman*

General experimental. All manipulations were conducted under argon atmosphere unless noted otherwise. NMR spectra were obtained using Varian Mercury 300- and Unity 400-MHz spectrometers.

Synthesis of 1,3-di(bromomethyl)-5-methoxybenzene (1). A mixture of 3,5-dimethylanisole (9.80 g, 72.1 mmol), N-bromosuccinimide (26.94 g, 151.3 mmol), and benzoyl peroxide (0.25 g, 1.0 mmol) in carbon tetrachloride (100 mL) was heated under reflux with stirring for 1.5 hr, and then cooled down to room temperature. The floating white solid succinimide was removed by filtration. The filtrate was evaporated, resulting in 17.2 g of solid, which contained 46% of the desired product **1** (determined by GC). The purified product **1** (9.23 g, 43.5%) was obtained by passing the mixed brominated products through a silica gel column with (20/80) methylene chloride/petroleum ether. ^{1}H NMR (C_6D_6): δ 6.57 (s, 2 H, Ar*H*), 6.54 (s, 1H, Ar*H*), 3.85 (s, 4 H, CH_2), 3.15 (s, 3 H, CH_3O). MS (EI) *m/z* 294 (M^+), 214, 134, 91, 65, 39.

Synthesis of 1,3-bis[di(t-butyl)phosphinomethyl]-5-methoxybenzene (*p*-OCH$_3$-PCP-H) (2). Synthesis of this ligand, like that for the corresponding iridium hydrido chloride as well as the ester derivatives, were based on reported syntheses by Shaw for the parent ligand.[33] To 1.5 g of **1** (5.1 mmol) in 15 mL of degassed acetone was added 1.89 mL of di-tert-butylphosphine (10.2 mmol) (Aldrich) at room temperature. This mixture was heated under reflux with stirring for 45 min under an argon atmosphere, and the solvent was removed *in vacuo.* The solid was dissolved in degassed deionized water (10 mL) and treated with a solution of sodium acetate (2.6 g, 31.7 mmol) in degassed deionized water (10 mL). The diphosphine was extracted with degassed ether (3 x 20 mL) and dried over $MgSO_4$, and the ether solution was filtered under argon pressure. The ether solvent was evaporated under vacuum, giving 1.37 g (63.4%) of the ligand **2** as a white solid. ^{31}P{^{1}H} NMR (C_6D_6): δ 31.94 (s). ^{1}H NMR (C_6D_6): δ 7.22 (s, 1H, *Ar*), 7.02 (s, 2 H, *Ar*), 3.46 (s, 3 H, CH_3O), 2.79 (bs, 4 H, CH_2), 1.10 (d, J_{HP} =10.2 Hz, 36 H, C(CH_3)$_3$). MS (EI) *m/z* 424 (M^+), 368, 312, 255, 199, 165, 135, 91, 57, 41; Anal. Calcd. For $C_{25}H_{46}OP_2$: C, 70.72; H, 10.92; O, 3.77; P, 14.59. Found: C, 70.59; H, 11.11; P, 13.89.

Synthesis of (CH$_3$O-PCP)IrHCl (3). To 1.19 g of **2** (2.8 mmol) in 40 mL of toluene was added 1.26 g of $[IrCl(COE)_2]_2$ at room temperature. This mixture was refluxed overnight with stirring under an argon atmosphere, and the solvent was removed *in vacuo*. The product was recrystallized from toluene/pentane, giving 1.73 g (94.5%) of **3** as dark-red crystals. ^{31}P{^{1}H} NMR (C_6D_6): δ 67.47. ^{1}H NMR (C_6D_6): δ 6.78 (s, 2 H, *Ar*), 3.57 (s, 3 H, CH_3O), 3.03 (ABX$_2$, Δδ = 0.06 ppm, J_{HH} = 17.6 Hz, J_{HP} = 3.2 Hz, 4 H, CH_2), 1.30 (vt, J_{HP} = 6.8 Hz, 18 H, CH_3), 1.25 (vt, J_{HP} = 7.2 Hz, 18 H, CH_3), -43.11 (t, J_{HP} =12.8 Hz, 1H, Ir-*H*). Anal. Calcd. For $C_{25}H_{46}ClOP_2Ir$: C, 46.04; H, 7.11; Cl, 5.44; O, 2.45; P, 9.50; Ir, 29.47. Found: C, 45.19; H, 7.04; Cl, 5.35; P, 8.50; Ir, 29.64.

Synthesis of (MeO-PCP)IrH$_4$ (4) and (MeO-PCP)IrH$_2$ (5). Conversion of **3** to **4**, and the analogous reduction of the ester-PCP derivative, was based upon syntheses reported by Kaska and Jensen.[34,35] 0.53 mL of 1 M $LiBEt_3H$ in THF (0.53 mmol) was added dropwise to a solution of **3** (0.30 g, 0.46 mmol) in 150 mL of pentane at room temperature under argon atmosphere. The solution turned lighter color and some white precipitate was found at the bottom of the flask. After the addition of $LiBEt_3H$ was completed, one cycle of freeze-pump-thaw was done to remove the argon atmosphere and the flask was filled with H_2 (800 torr). The solution was stirred overnight at room temperature under H_2; the H_2 atmosphere was removed and the precipitate was filtered out. The solvent was removed *in vacuo,* giving 0.22 g (78%) of **5** as brown crystals containing ca. 25% **4**. NMR data for **4**: ^{31}P{^{1}H} NMR (C_6D_6): δ 73.54 (s). ^{1}H NMR (C_6D_6): δ 6.83 (s, 2 H, *Ar*), 3.59 (s, 3 H, CH_3O), 3.25 (vt, J_{HP} = 4.4 Hz, 4 H, CH_2), 1.20 (vt, J_{HP} = 6.8 Hz, 36 H, C(CH_3)$_3$), -9.11 (t, J_{HP} = 9.2 Hz, 4 H, IrH_4). NMR data for **5**: ^{31}P{^{1}H} NMR (C_6D_6): δ 86.40 (s). ^{1}H NMR (C_6D_6): δ 7.02 (s, 2 H, *Ar*), 3.58 (s, 3 H, CH_3O), 3.52 (vt, J_{HP} = 3.2 Hz, 4 H, CH_2), 1.27 (vt, J_{HP} = 6.4 Hz, 36 H, C(CH_3)$_3$), -19.71 (t, J_{HP} = 8.8 Hz, 2 H, IrH_2). Anal. Calcd. For $C_{25}H_{47}OP_2Ir$ (75%) + $C_{25}H_{49}OP_2Ir$ (25%) : C, 48.56; H, 7.74; O, 2.59; P, 10.02; Ir, 31.09. Found: C, 47.91; H, 7.76; P, 10.06; Ir, 30.88.

Methyl 3,5-bis(bromomethyl)benzoate (6). In a 500-mL flask, methyl 3,5-dimethylbenzoate (4.989 g, 0.030 mol), NBS (11.400 g, 0.064 mol) and AIBN (0.499 g, 0.003 mol) were dissolved in 250 mL CH_2Cl_2 and brought to reflux. After 12 hours CH_2Cl_2 was removed and the solid redissolved in CCl_4. The solution was washed three times with a saturated solution of Na_2SO_3 to remove a golden yellow impurity. CCl_4 was removed by rotovap to yield a fine white solid. The product was dry-loaded on a column and 300 mL of 10:1 hexane/ethyl acetate were used to elute the sample. Recrystallizations from hexane/CH_2Cl_2 concluded purification (15% yield). ^{1}H NMR (C_6D_6, 25 °C): 3.44, (3 H, s, OCH_3), 3.73, (4 H, s, CH_2Br), 6.91, (1H, s, 4-Ar*H*), 7.83, (2 H, s, 2,6-Ar*H*).

Methyl 3,5-bis(di-t-butylphosphinomethyl)benzoate (CH$_3$OC(O)-PCP-H). The compound was prepared from **6**, in analogy to previously reported syntheses.[33] Di-t-butyl phosphine (1.15mL, 6.21 mmol) was added to a solution of **6** (1.00g, 3.14 mmol) in acetone. The solution was refluxed for two hours yielding a white precipitate. The solvent was removed and the solid was washed with diethyl ether (3 x 5mL). The solid was then dissolved in water (5 mL) and deprotonated with a solution of sodium acetate (2g/5mL). The product was extracted with diethyl ether (5x5mL) and dried over $MgSO_4$. Filtering the solution and removal of diethyl ether resulted in a white solid weighing 1.03g (73%). ^{1}H NMR (C_6D_6, 25 °C): 1.04, (36 H, d, J_{PH} = 10.8 Hz, C(CH_3)$_3$), 2.75 (4 H, d, PCH_2, J_{PH} = 2.4 Hz), 3.48, (3 H, s, OCH_3), 7.85, (1 H, s, 4-Ar*H*), 8.26, (2 H, s, 2,6-Ar*H*). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): 34.1, (s).

[CH$_3$OC(O)-PCP]IrHCl. The compound was prepared from $CH_3OC(O)$-PCP-H analogously to previously reported syntheses.[33] $[IrCl(COE)_2]_2$, (0.0991g, 0.111 mmol) was added to a toluene solution (10mL) of ligand $CH_3OC(O)$-PCP-H (0.100 g, 0.221 mmol). Stirring the solution at reflux for sixteen hours under argon produced a dark red-orange color. Removal of solvent and recrystallization from a toluene-petroleum ether (1:2) solvent system produced a clean, deep red solid (38% yield). ^{1}H NMR (C_6D_6, 25 °C): -42.1, (1 H, t, J_{PH} = 16.8 Hz), 1.18, (18 H, vt, CCH_3, J_{PH} = 9.20 Hz), 1.22, (18 H, vt, J_{PH} = 9.20 Hz), 2.87, 3.00, (4 H, (ABX$_2$), PCH_2, J_{HH} = 23.2 Hz, J_{PH} = 5.2 Hz), 3.68, (3

H, bs, OC*H*$_3$), 7.91, (2 H, bs, 3,5-Ar*H*). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): 68.1, (s).

[CH$_3$OC(O)-PCP]IrH$_4$. KH (0.075 g, 1.9 mmol) and the above mentioned hydrido-chloro complex (0.0402 g, 0.0591 mmol) were dissolved in benzene and stirred for three days at room temperature under 1400 torr H_2. The compound was then extracted and filtered using benzene. Solvent was removed to give a brown oil (96% yield). ^{1}H NMR (C_6D_6, 25 °C): -9.02, (4 H, t, J_{PH} = 12.8 Hz), 1.13, (36 H, t, C(C*H*$_3$)$_3$, J_{PH} = 8.40 Hz), 3.18, (4 H, t, PC*H*$_2$, J_{PH} = 8.4 Hz), 3.67, (3 H, s, OC*H*$_3$), 7.98, (2 H, s, 3,5-Ar*H*). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): 73.7, (s).

Reactions of (Y-PCP)IrH$_4$ and (Y-PCP)IrH$_2$. The dihydride and tetrahydride derivatives are readily interconvertible and typically synthesized as mixtures. When pure dihydride was required the mixture was dissolved in toluene, which was then removed under vacuum with warming; the remaining solid was pure dihydride. Pure tetrahydride was easily obtained *in situ,* when required, by adding H_2 atmosphere. For most purposes, the mixture of dihydride and tetrahydride is satisfactory; for example, the reaction with norbornene (>2 equivalents) and arenes to give the corresponding aryl hydrides proceeds equally well with either species. The corresponding carbonyls (Y–PCP)Ir(CO) are obtained quantitatively by bubbling CO through solutions of dihydride and/or tetrahydride and identified by ^{31}PNMR and IR. ^{31}P{^{1}H} NMR (C_6D_6): (H-PCP)Ir(CO),[36] 81.9, (MeOC(O)-PCP)Ir(CO), 81.0, (MeO-PCP)Ir(CO), 82.3. IR (cyclooctane): (H-PCP)Ir(CO), 1927.7 cm^{-1} (s) ν_{CO}; (MeO-PCP)Ir(CO), 1925.5 cm^{-1} (s) ν_{CO}; (MeOC(O)-PCP)Ir(CO), 1930.0 cm^{-1} (s) ν_{CO}, 1720 cm^{-1} (m) $\nu_{MeOC=O}$.

Equilibrium measurements. All equilibrium measurements were determined by integration of both ^{31}P NMR and ^{1}H NMR (monitoring hydrides and/or PCP-methylenes) spectra. Error limits are set to be consistent with values obtained from both methods.

Equilibrium measurements; addition of para-substituted xylene C-H bonds to (PCP)Ir. Reactions were monitored by ^{31}P NMR at -38 °C (at higher temperatures the compounds undergo rapid arene exchange to give coalescence and a single singlet in the ^{31}P NMR spectrum[22]). The parent complex, (PCP)Ir(H)(3,5-dimethylphenyl) has been reported.[22] To a mesitylene (0.6 mL) solution of this complex containing m-xylene (60 μL), was added 3.0 μL of 2-chloro-*m*-xylene resulting in the growth of a new doublet (at -38 °C) at δ 66.6 ppm, J_{PH} = 13.0 Hz, attributable to (PCP)Ir(H)(3,5-dimethyl-4-chlorophenyl) (cf. δ 66.5 ppm, J_{PH} = 13.0 Hz for the parent complex.). The ratios of the peak heights of the two doublets (incomplete resolution precluded the use of integrals) was used to determine the equilibrium constant for xylene/chloroxylene C-H addition (eq 8b; Z, Z' = H, Cl).

To determine the equilibrium constant for addition of 2-nitro-*m*-xylene, a mesitylene solution of (PCP)Ir(H)(3,5-dimethyl-4-nitrophenyl) was prepared containing excess 2-nitro-*m*-xylene (δ 67.0 in pure mesitylene). In analogy with the above procedure, increasing amounts of 2-chloro-*m*-xylene were added resulting in the growth of another doublet at δ 66.5 (J_{PH} = 13.0 Hz), attributable to (PCP)Ir(H)(3,5-dimethyl-4-chlorophenyl) (a slight upfield solvent shift of ca. 0.1 ppm is caused by the presence of 2-chloro-*m*-xylene cf. 66.6 in pure mesitylene); the equilibrium constant for eq 8b (Z, Z' = Cl, NO_2) was then determined using the integrals of these baseline-resolved peaks.

(PCP)Ir(H)(3,5-dimethyl-4-chlorophenyl) and (PCP)Ir(H)(3,5-dimethyl-4-nitrophenyl) were also generated, independently, in mesitylene-d_{12} solutions in order to obtain low temperature ^{1}H NMR spectra. For the chloro case, (PCP)IrH$_4$ in neat 2-chloro-*m*-xylene was reacted with excess norbornene in a valved NMR tube. Solvent and volatiles (norbornene and norbornane) were removed, and the resulting film was redissolved in mesitylene-d_{12}. In the nitro case, a mesitylene-d_{12} solution of (PCP)IrH$_4$ was reacted with norbornene in the presence of 2-nitro-*m*-xylene, giving a solution of the desired C-H addition product. Samples for equilibrium measurements and ^{1}H NMR spectra were all ca. 30 mM in total (PCP)Ir. (PCP)Ir(H)(3,5-dimethyl-4-chlorophenyl): ^{1}H NMR (mesitylene-d_{12}, -35 °C): -45.69, (1H, t, J_{PH} = 13.0 Hz), 0.89, 0.91, (36 H, 2vt, C(C*H*$_3$)$_3$, (overlapping and incompletely resolved)), 2.55, 2.58, (2 x 3H, 2s, Ar-C*H*$_3$), 3.21, (4 H, m (unresolved AB pattern), PC*H*$_2$), 7.02, (1H, t, 4-Ar*H* , J_{HH} = 7.4 Hz), 7.17, (2 H, d, 3,5-Ar*H*, J_{HH} = 7.5 Hz), 7.45, 7.53, (2 x 1H, 2s, 2,6-chloroxylyl Ar*H*). (PCP)Ir(H)(3,5-dimethyl-4-nitrophenyl): ^{1}H NMR (mesitylene-d_{12}, -38 °C): -45.51, (1H, t, J_{PH} = 13.5 Hz), 0.83, 0.85, (36 H, 2vt, C(C*H*$_3$)$_3$, (overlapping and incompletely resolved)), 2.45, 2.48, (2 x 3 H, 2s, Ar-C*H*$_3$), 3.20, (4 H, m (unresolved AB pattern), PC*H*$_2$), 7.02, (1H, t, 4-Ar*H* , J_{HH} = 7.4 Hz), 7.15, (2 H, d, 3,5-Ar*H*, J_{HH} = 7.5 Hz), 7.48, 7.55, (2 x 1H, 2s, 2,6-nitroxylyl Ar*H*).

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. For each of six reactions, represented by eqs 4, 6, 11, 14-16, we have calculated reaction energies with six substituents (NO_2, $C(O)OCH_3$, F, H, OCH_3, NH_2) for which substituent parameters are available. 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 based on para- and meta-substituent effects, and the pi/resonance and sigma/inductive correlations are in no way rigorous.[37,38] Thus, the parameters only crudely reflect the pi/sigma 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. and by others.[37,38] 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] The σ^-_R resonance scale is most applicable to reactions wherein the degree of π-acceptance by the substituent plays a major role. Conversely, σ^+_R values (based upon stabilization of benzylic cations) are presumably applicable to reactions wherein substituent π-donation is important. The Dewar-Grisdale parameters appear to represent an attempt to achieve greater generality.[38] We have applied Dewar-Grisdale parameters in their original form, and in a form "corrected" according to Wells.[38] Finally, we have combined the Taft σ^-_R and σ^+_R scales, using the former values for π-acceptors

(NO_2, $C(O)OCH_3$) and the latter values for π-donors (F, NH_2, OCH_3) to give a "$\sigma^{+/-}_R$" scale.

Thus, six different dual-parameter models with respective sets of parameters were applied to six different reactions (regression analysis performed with Microsoft Excel 98), yielding 36 reaction parameter pairs (inductive and resonance, or pi and sigma). *For all six reactions, 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 as follows (average r-squared values for the six reactions are in parentheses): standard Taft-Lewis $\sigma_{R(BA)}$ (0.978); uncorrected Dewar-Grisdale (0.976); "corrected" Dewar-Grisdale, (0.970); Taft σ^+_R (0.914); Taft σ^-_R (0.950); $\sigma^{+/-}_R$ (0.955). For the single-parameter standard Hammett *para*-substituent model, the average r-squared value was 0.935. The standard Taft-Lewis dual-parameter model gave correlations as good or better than the others, so we will invoke only this dual-parameter model and the accompanying $\sigma_{R(BA)}$ scale in our discussions of individual reactions.

For all six reactions and all six scales, better correlations were found for the pi/resonance than for the sigma/inductive parameters. The correlation with resonance effects is in all cases excellent (P_R < 1.3% for all six reactions using the $\sigma_{R(BA)}$ scale) and resonance effects are apparently the energetically more important factor in view of both the greater ρ_R values obtained for all six reactions and the greater spread of σ_R values (-0.82 to 0.15 versus 0.0 to 0.65 for σ_I). Standard errors for the resonance reaction parameter were smaller relative to the actual value, and P-values were generally much smaller for the resonance reaction parameters (1.3%, in the worst case, versus 13% for the inductive reaction parameter). This does not reflect the greater range found for the resonance versus the inductive values, since relative standard errors and P-values are independent of the absolute parameter values. Based on both the calculated magnitudes of the reaction parameters and the quality of the correlations, it appears that pi/resonance effects are generally considerably more important than sigma/inductive effects.

Complete data set of computed LFER parameters, absolute and relative reaction energies

Table 1. Computed LFER parameters, absolute and relative reaction energies (kcal/mol) for H_2 addition to (Y-PCP)Ir, eqs 4 and 5.

(Y-PCP)Ir + H_2 → (Y-PCP)Ir($H)_2$

Y	ΔE	ΔΔE
NH_2	-26.37	-2.36
OCH_3	-25.80	-1.78
F	-24.94	-0.93
Li	-24.82	-0.81
H	-24.01	0.00
$C(O)OCH_3$	-22.11	1.90
NO_2	-20.89	3.13
BH_2	-20.51	3.51

ρ_{sp} = 4.0(5); P_{sp} = 0.0015; r^2 = 0.937
ρ_R = 4.4(7); ρ_I = 2.7(12); P_R = 0.007; P_I = 0.10; r^2 = 0.969

(Y-PCP)Ir + H_2 → (Y-PCP)Ir($H)_2$
Symmetry imposed (C_{2v})[a]

Y	ΔE	ΔΔE
NH_2	-27.68	-2.97
NH_2(90)	-24.87	-0.17
H	-24.71	0.00
NO_2	-21.34	3.36
NO_2(90)	-23.95	0.76
BH_2	-21.08	3.63
BH_2(90)	-24.92	-0.21

a) "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 co-planar (constrained symmetry) or approximately co-planar with the aryl ring (unconstrained).

Table 2. Computed LFER parameters, absolute and relative reaction energies (kcal/mol) for benzene and *n*-butane C-H addition to (Y-PCP)Ir, eq 6

(Y-PCP)Ir + R-H → (Y-PCP)Ir(R)(H)

Y	R	ΔE	ΔΔE
OCH_3	Ph	-7.73	-1.07
H	Ph	-6.66	0.00
$C(O)OCH_3$	Ph	-5.84	0.82
NO_2	Ph	-5.08	1.58

ρ_{sp} = 2.3(3); P_{sp} = 0.015; r^2 = 0.970
ρ_R = 2.5(1); ρ_I = 1.9(1); P_R = 0.03; P_I = 0.05; r^2 = 0.999

(Y-PCP)Ir + R-H → (Y-PCP)Ir(R)H

Y	R	ΔE	ΔΔE
OCH_3	n-butyl	2.57	-1.62
H	n-butyl	4.19	0.00
$C(O)OCH_3$	n-butyl	5.46	1.27
NO_2	n-butyl	5.28	1.89

ρ_{sp} = 3.2(5); P_{sp} = 0.022; r^2 = 0.955
ρ_R = 3.7(2); ρ_I = 2.0(3); P_R = 0.03; P_I = 0.08; r^2 = 0.998

Table 3. Computed LFER parameters, absolute and relative reaction energies (kcal/mol) for addition of arene ([*p*-Z-$R_2C_6H_2$]-H) C-H bond to (PCP)Ir

(PCP)Ir + (*p*-Z-C_6H_4)-H → (PCP)Ir(*p*-Z- C_6H_4)(H)

Z	ΔE	ΔΔE
NO_2	-12.83	-6.18
$C(O)OCH_3$	-8.67	-2.01
Cl	-8.40	-1.74
H	-6.66	0.00
OCH_3	-5.54	1.12
NH_2	-4.41	2.25

ρ_{sp} = -6.0(9); P_{sp} = 0.022; r^2 = 0.955
ρ_R = -4.5(10); ρ_I = -8.2(17); P_R = 0.14; P_I = 0.13; r^2 = 0.986

(PCP)Ir + (*p*-Z-*m,m*-$Me_2C_6H_2$)-H → (PCP)Ir(*p*-Z-*m,m*-$R_2C_6H_2$)(H)

Z	ΔE	ΔΔE
NO_2	-10.82	-5.08
Cl	-7.36	-1.63
H	-5.74	0.00
OCH_3	-5.72	0.01
Li	-2.82	2.92

(PCP)Ir + (*p*-Z-C_6H_4)-H → (PCP)Ir(horizontal-*p*-Z-C_6H_4)(H);
C_s symmetry; aryl ligand contained in the imposed plane of symmetry (eq 9)

Z	ΔE	ΔΔE
NO_2	-8.65	-5.30
H	-3.35	0.00
NH_2	2.63	+5.98

ρ_R = -8.2; ρ_I = -6.3

(PCP)Ir + (*p*-Z-C_6H_4)-H → (PCP)Ir(vertical-*p*-Z-C_6H_4)(H)
C_s symmetry; aryl ligand perpendicular to the imposed plane of symmetry (eq 10)

Z	ΔE	ΔΔE
NO_2	-6.74	-4.56
NH_2	-3.61	-1.43
H	-2.18	0.00

ρ_R = 0.7; ρ_I = -7.2

Table 4. Computed LFER parameters, absolute and relative reaction energies (kcal/mol) for H_2 addition to (Y-PCP)Ir(CO), eq 11.

(Y-PCP)Ir(CO) + H_2 → *trans*-(Y-PCP)Ir(CO)$(H)_2$

Y	ΔE	ΔΔE
BH_2	-10.89	-0.76
NO_2	-10.70	-0.57
$C(O)OCH_3$	-10.51	-0.39
H	-10.13	0.00
Li	-9.70	0.42
F	-9.61	0.51
OCH_3	-9.20	0.93
NH_2	-8.91	1.21

ρ_{sp} = -1.3(2); P_{sp} = 0.003; r^2 = 0.907
ρ_R = -1.6(1); ρ_I = -0.4(1); P_R = 0.0001; P_I = 0.027; r^2 = 0.996

(Y-PCP)Ir(CO) + H_2 → *trans*-(Y-PCP)Ir(CO)$(H)_2$
Symmetry imposed (C_{2v})

Y	ΔE	ΔΔE
BH_2	-10.18	-0.96
BH_2(90)	-9.06	0.17
NO_2	-9.99	-0.77
NO_2(90)	-9.40	-0.17
H	-9.23	0.00

(Y-PCP)Ir(CO) + H_2 → *cis*-(Y-PCP)Ir(CO)$(H)_2$

Y	ΔE	ΔΔE
NO_2	-7.20	-0.70
$C(O)OCH_3$	-7.01	-0.52
H	-6.50	0.00
F	-6.23	0.27
Li	-5.97	0.53
OCH_3	-5.79	0.71
NH_2	-5.42	1.08

ρ_{sp} = -1.3(2); P_{sp} = 0.003; r^2 = 0.907
ρ_R = -1.6(1); ρ_I = -0.4(1); P_R = 0.0001; P_I = 0.027; r^2 = 0.996

Table 5. Computed LFER parameters, absolute and relative reaction energies (kcal/mol) for arene (C_6H_5Z) C-H addition to (Y-PCP)Ir(CO), eq 12

(Y-PCP)Ir(CO) + C_6H_6 → (Y-PCP)Ir(CO)(H)(C_6H_5)

Y	ΔE	ΔΔE
$C(O)OCH_3$	12.84	-0.32
NO_2	12.93	-0.22
H	13.15	0.00
OCH_3	13.94	0.78
NH_2	14.20	1.04

ρ_{sp} = -0.9(4); P_{sp} = 0.14; r^2 = 0.74
ρ_R = -1.4(2); ρ_I = -0.04(15); P_R = 0.07; P_I = 0.9; r^2 = 0.989

(PCP)Ir(CO) + H-(*p*-Z-C_6H_4) → (PCP)Ir(CO)(*p*-Z-C_6H_4)H

Z	ΔE	ΔΔE
NO_2	7.89	-5.26
H	13.15	0.00
OCH_3	14.10	0.95

ρ_R = -4.7; ρ_I = -7.0

Table 6. Computed LFER parameters, absolute and relative reaction energies (kcal/mol) for H_2 addition to (Y-PCP)Ir$(H)_2$, eq 13

(Y-PCP)Ir$(H)_2$ + H_2 → (Y-PCP)Ir$(H)_4$

Y	ΔE	ΔΔE
BH_2	-15.79	-1.62
NO_2	-15.46	-1.30
$C(O)OCH_3$	-15.18	-1.01
H	-14.17	0.00
F	-13.47	0.70
Li	-13.43	0.74
OCH_3	-12.81	1.36
NH_2	-12.15	2.02

ρ_{sp} = -2.5(5); P_{sp} = 0.013; r^2 = 0.906
ρ_R = -3.0(2); ρ_I = -1.2(3); P_R = 0.004; P_I = 0.04; r^2 = 0.994

Table 7. Computed LFER parameters, absolute and relative reaction energies (kcal/mol) for CO addition to (Y-PCP)Ir, eq 14

(Y-PCP)Ir + CO → (Y-PCP)Ir(CO)

Y	ΔE	ΔΔE
NH_2	-60.63	-1.44
OCH_3	-60.36	-1.17
Li	-59.91	-0.72
F	-59.77	-0.58
H	-59.19	0.00
$C(O)OCH_3$	-57.89	1.30
NO_2	-56.83	2.36
BH_2	-56.71	2.47

ρ_{sp} = 2.7(4); P_{sp} = 0.002; r^2 = 0.922
ρ_R = 2.9(5); ρ_I = 2.1(10); P_R = 0.013; P_I = 0.12; r^2 = 0.935

(Y-PCP)Ir + CO → (Y-PCP)Ir(CO)
Symmetry imposed (C_{2v})

Y	ΔE	ΔΔE
NH_2	-61.15	-1.85
NH_2(90)	-59.47	-0.16
H	-59.31	0.00
NO_2	-56.91	2.40
NO_2(90)	-58.73	0.57
BH_2	-56.82	2.49
BH_2(90)	-59.49	-0.18

Table 8. Computed LFER parameters, absolute and relative reaction energies (kcal/mol) for CO addition to $(PCP)Ir(H)_2$, eq 15

(Y-PCP)$Ir(H)_2$ + CO → *trans*-(Y-PCP)$Ir(CO)(H)_2$

Y	ΔE	ΔΔE
BH_2	-47.09	-1.79
NO_2	-46.64	-1.34
$C(O)OCH_3$	-46.29	-0.99
H	-45.30	0.00
Li	-44.79	0.51
F	-44.44	0.86
OCH_3	-43.77	1.54
NH_2	-43.18	2.13

ρ_{sp} = -2.6(4); P_{sp} = 0.002; r^2 = 0.922
ρ_R = -3.1(2); ρ_I = -1.1(3); P_R = 0.0004; P_I = 0.04; r^2 = 0.992

(Y-PCP)$Ir(H)_2$ + CO → *trans*-(Y-PCP)$Ir(CO)(H)_2$
Symmetry imposed (C_{2v})

Y	ΔE	ΔΔE
BH_2	-45.92	-2.09
BH_2(90)	-43.62	0.20
NO_2	-45.56	-1.73
NO_2 (90)	-44.18	-0.36
H	-43.83	0.00
NH_2	-41.05	2.78
NH_2(90)	-43.75	0.08

(Y-PCP)$Ir(H)_2$ + CO → *cis*-(Y-PCP)$Ir(CO)(H)_2$

Y	ΔE	ΔΔE
BH_2	-43.56	-1.87
NO_2	-43.14	-1.45
$C(O)OCH_3$	-42.79	-1.10
H	-41.69	0.00
Li	-41.06	0.63
F	-41.05	0.64
OCH_3	-40.36	1.33
NH_2	-39.68	2.01

ρ_{sp}= -2.5(3); P_{sp} = 0.0008; r^2 = 0.954
ρ_R = -2.9(2); ρ_I = -1.3(3); P_R = 0.0004; P_I = 0.02; r^2 = 0.993

Table 9. Computed LFER parameters, absolute and relative reaction energies (kcal/mol) for CO addition to (PCP)Ir(CO), eq 16

(Y-PCP)Ir(CO) + CO → (Y-PCP)$Ir(CO)_2$

Y	ΔE	ΔΔE
BH_2	-13.09	-1.08
NO2	-12.76	-0.75
$C(O)OCH_3$	-12.54	-0.53
Li	-12.03	-0.02
H	-12.01	0.00
F	-11.41	0.60
OCH_3	-11.15	0.86
NH_2	-10.81	1.20

ρ_{sp} = -1.5(3); P_{sp} = 0.02; r^2 = 0.866
ρ_R = -1.9(2); ρ_I = -0.6(2); P_R = 0.0006; P_I = 0.097; r^2 = 0.989

Table 10. Computed absolute and relative reaction energies (kcal/mol) for CO addition to (Y-PCP)$IrH(C_6H_4$-Z), eq 17
(Y-PCP)$IrH(C_6H_4$-Z) + CO → (Y-PCP)$IrH(C_6H_4$-Z)(CO)

Y	Z	ΔE	ΔΔE
H	NO_2	-40.29	-0.92
H	OCH_3	-39.55	-0.17
$C(O)OCH_3$	H	-39.23	0.17
H	H	-39.38	0.00
NO_2	H	-38.81	0.57
OCH_3	H	-38.70	0.68