### Solution Thermochemical Study of Ligand Steric Influences on Substitution Enthalpies in the L<sub>2</sub>Fe(CO)<sub>3</sub> System

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The enthalpies of reaction of  $(BDA)Fe(CO)_3$   $(BDA = (C_6H_5)CH=CHO(CH_3)$ , benzylideneacetone) with a series of sterically demanding phosphine ligands, leading to the formation of  $(L)_2Fe(CO)_3$  complexes (L = phosphine) have been measured by solution calorimetry in THF at 50 °C. The range of reaction enthalpies spans some 7 kcal/mol. The overall relative order of stability established is as follows  $(PR_3; -\Delta H, \text{kcal/mol})$ : PPh<sub>3</sub> < PCy<sub>2</sub>Ph < PCyPh<sub>2</sub> < PCy<sub>3</sub> < P<sup>i</sup>Pr<sub>3</sub> < PPh<sub>2</sub>Et < PBz<sub>3</sub>. A quantitative analysis of ligand effect of the present and previously obtained data for L<sub>2</sub>Fe(CO)<sub>3</sub> complexes helps clarify the exact steric versus electronic ligand contributions to the enthalpy of reaction in this system. Results of a singlecrystal diffraction study for the complex *diaxial*-(PPh<sub>2</sub>Cy)<sub>2</sub>Fe(CO)<sub>3</sub> (2) show the molecule to be monoclinic, P2<sub>1</sub>/n, with a = 12.393(5) Å, b = 15.811(6) Å, c = 18.029(7) Å,  $\alpha = \gamma = 90^{\circ}$ ,  $\beta = 108.00(2)^{\circ}$ , V = 43360(5) Å<sup>3</sup>, Z = 4,  $d_{calcd} = 1.337$  g cm<sup>-1</sup>,  $n_{obsd} = 3130$ , and R = 0.052. Electronic effects are overwhelmingly important in this system, yet a steric threshold of 135° can be extracted from the QALE treatment which shows at which point steric factors begin to influence and contribute to the measured enthalpy of ligand substitution.

### Introduction

The importance of tertiary phosphine ligands in organometallic chemistry and catalysis is undeniable.<sup>1</sup> A large number of processes exhibit marked selectivity and reactivity differences according to the nature of the phosphine borne on the transition metal center.<sup>2</sup> A prototypical example of the importance of phosphine as an ancillary ligand is illustrated by the Noyori catalyst which mediates the asymmetric hydrogenation of olefins<sup>3</sup> (eq 1).



Kinetic, catalytic, and structural studies have been

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conducted on this and related catalytic systems.<sup>3</sup> In spite of the vast amount of information focusing on  $PR_3$ -transition metal complexes, few thermodynamic data regarding heats of binding of these ligands to metal centers exist.<sup>4,5</sup> Manzer and Tolman<sup>6</sup> have reported the solution calorimetry of square-planar platinum(II) complexes, shown in eq 2, for a series of phosphine ligands.

$$trans - [CH_3PtQ_2(THF)]^+ + PR_3 \rightarrow trans - [CH_3PtQ_2(PR_3)]^+ + THF (2)$$

$$Q = P(CH_3)_2 Ph$$

A similar series was then investigated for Ni(0) complexes<sup>7</sup> shown in eq 3. Detailed thermochemical inves

$$Ni(COD)_2 + 4PR_3 \rightarrow Ni(PR_3)_4 + 2COD$$
 (3)

(5)

tigations of two related Mo(0) systems have been reported by Hoff and co-workers<sup>8</sup> (eqs 4 and 5). At a

$$(\operatorname{arene})\operatorname{Mo(CO)}_3 + 3\operatorname{PR}_3 \rightarrow fac-(\operatorname{PR}_3)_3\operatorname{Mo(CO)}_3 + \operatorname{arene} (4)$$

$$(\text{NBD})\text{Mo(CO)}_4 + 2\text{PR}_3 \rightarrow cis-(\text{PR}_3)_2\text{Mo(CO)}_4 + \text{NBD}$$

#### NBD = norbornadiene

more basic level of understanding lies the question of

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<sup>(2)</sup> Pignolet, L. H., Ed. Homogeneous Catalysis with Metal Phosphine Complexes; Plenum: New York, 1983.

<sup>(3)</sup> Noyori, R. Asymmetric Catalysis in Organic Synthesis; Wiley and Sons, Inc.: New York, 1994, and references cited therein.

<sup>(5)</sup> Nolan, S. P.; Lopez de la Vega, R.; Hoff, C. D. Organometallics 1986, 5, 2529–2537.

<sup>(6)</sup> Manzer, L. E.; Tolman, C. A. J. Am. Chem. Soc. **1975**, 97, 1955–1986.

<sup>(7)</sup> Tolman, C. A.; Reutter, D. W.; Seidel, W. C. J. Organomet. Chem. 1976, 117, C30-C33.

<sup>(8) (</sup>a) Nolan, S. P.; Hoff, C. D. J. Organomet. Chem. 1985, 290, 365–373.
(b) Mukerjee, S. L.; Nolan, S. P.; Hoff, C. D.; de la Vega, R. Inorg. Chem. 1988, 27, 81–85.

the relative importance of steric vs electronic ligand effects in organometallic systems bearing phosphine ligands.

We have addressed this question with the help of solution calorimetric techniques, having previously reported on the importance of enthalpy electronic and steric components for phosphine ligands binding to organogroup 8 systems:<sup>9,10</sup>

$$\frac{\text{Cp*Ru(COD)Cl}_{(\text{soln})} + 2\text{PR}_{3(\text{soln})} \frac{\text{THF}}{30 \, ^{\circ}\text{C}}}{\text{Cp*Ru(PR}_{3})_{2}\text{Cl}_{(\text{soln})} + \text{COD}_{(\text{soln})}} (6)$$

$$\begin{array}{c} CpRu(COD)Cl_{(soln)}+2PR_{3(soln)} \xrightarrow{THF} \\ CpRu(PR_{3})_{2}Cl_{(soln)}+COD_{(soln)} \end{array} (7) \end{array}$$

$$(BDA)Fe(CO)_{3(soln)} + 2PR_{3(soln)} \xrightarrow{\text{THF}}_{50\ \circ\text{C}} trans-(PR_3)_2Fe(CO)_{3(soln)} + BDA_{(soln)} (8)$$

 $Cp = C_5H_5$ ;  $Cp^* = C_5Me_5$ ; BDA = PhCH=CHCOMe;  $PR_3$  = tertiary phosphine

We recently extended this work to emphasize the importance of electronic factors in a series of parasubstituted triphenylphosphine ligands within this  $(L)_2$ -Fe $(CO)_3$  system<sup>10c</sup> (eq 9).

$$(BDA)Fe(CO)_{3} + 2 PR_{3} \xrightarrow{\text{THF}} 0C \xrightarrow{PR_{3}} bCO + BDA (9)$$

$$PR_{3} = P(p-XC_{6}H_{4})_{3} ; X = H, Cl. F, Me, MeO, CF_{3}$$

We now wish to complete the thermochemical investigation of this iron-based system by reporting on the thermochemical investigation of ligand substitution reactions of sterically demanding tertiary phosphine ligands (eq 10).

$$(BDA)Fe(CO)_3 + 2 PR_3 \qquad \frac{THF}{50^{\circ}C} \qquad OC - Fe + BDA \qquad (10)$$

 $PR_3 = PCy_2Ph$ ,  $PCyPh_2$ ,  $PCy_3$ ,  $P^iPr_3$ ,  $PPh_2Et$ ,  $PBz_3$ 

### **Experimental Section**

General Considerations. All manipulations involving organoiron complexes were performed under inert atmospheres of argon or nitrogen using standard high-vacuum or Schlenk tube techniques or in a Vacuum/Atmospheres glovebox containing less than 1 ppm oxygen and water. Ligands were purchased from Strem Chemicals and used as received. Tetrahydrofuran was stored over sodium wire, distilled from sodium benzophenone ketyl, stored over Na/K alloy, and vacuum transferred into flame-dried glassware prior to use. The organoiron complex  $(BDA)Fe(CO)_3$  (1) was synthesized according to literature procedures.<sup>11</sup> Only materials of high purity as indicated by IR and NMR spectroscopies were used in the calorimetric experiments. Synthesis and characterization of iron tricarbonyl phosphine complexes have been previously reported.<sup>12,13</sup> Infrared spectra were recorded using a Perkin-Elmer FT Model 1760 spectrometer in 0.1 mm NaCl cells. NMR spectra were recorded using a Varian Gemini 300 MHz spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction<sup>14</sup> or the enthalpy of solution of KCl in water.<sup>15</sup> The experimentally determined enthalpies for these two standard calibration reactions are the same within experimental error as literature values. This calorimeter has been previously described,<sup>16</sup> and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits.

<sup>1</sup>H NMR Titrations. Prior to every set of calorimetric experiments involving a new ligand, an accurately weighed amount ( $\pm 0.1 \text{ mg}$ ) of the organoiron complex was placed in a Wilmad screw-capped NMR tube fitted with a septum, and THF- $d_8$  was subsequently added. The solution was titrated with a solution of the ligand of interest by injecting the latter in aliquots through the septum with a microsyringe, followed by vigorous shaking. The reactions were monitored by <sup>1</sup>H NMR spectroscopy, and the reactions were found to be rapid, clean, and quantitative under experimental calorimetric conditions (50 °C). These conditions are necessary for accurate and meaningful calorimetric results and were satisfied for all organoiron reactions investigated. Only reactants and products were observed in the course of the NMR titration.

Calorimetric Measurement for Reaction of (BDA)Fe-(CO)<sub>3</sub> and Tricyclohexylphosphine. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. A 20-30 mg sample of recrystallized (BDA)Fe(CO)<sub>3</sub> was accurately weighed into the lower vessel; it was closed and sealed with 1.5 mL of mercury. A 4 mL volume of a 25% stock solution of PCy<sub>3</sub> [1 g of PCy<sub>3</sub> in 25 mL of THF; >10:1 molar ratio of PCy<sub>3</sub>:BDAFe- $(CO)_3$ ] was then added, and the remainder of the cell was assembled, removed from the glovebox, and inserted into the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no organoiron complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 50.0 °C (about 2 h) the calorimeter was inverted thereby allowing the reactants to mix. After the reaction reached completion and the calorimeter had once again reached thermal equilibrium (ca. 2 h), the vessels were removed from the calorimeter, taken into the glovebox, and opened, and the infrared cell was filled under inert atmosphere. An infrared spectrum of each product was recorded using this IR cell filling procedure. Conversion to (PCy<sub>3</sub>)<sub>2</sub>Fe- $(CO)_3$  was found to be quantitative under these reaction conditions. The enthalpy of reaction,  $-24.2 \pm 0.1$  kcal/mol, represents the average of five individual calorimetric determinations. The enthalpy of solution of  $(BDA)Fe(CO)_3^{10a}$  (6.5  $\pm$  0.2 kcal/mol) was then added to this value to obtain a value of  $-30.7 \pm 0.2$  kcal/mol for all species in solution.

**Synthesis.** (BDA)Fe(CO)<sub>3</sub> was synthesized according to the literature procedure.<sup>11</sup> The identities of all calorimetry prod-

<sup>(9)</sup> For organoruthenium systems see: (a) Nolan, S. P.; Martin, K. L.; Stevens, E. D.; Fagan, P. J. Organometallics 1992, 11, 3947-3953.
(b) Luo, L.; Fagan, P. J.; Nolan, S. P. Organometallics 1993, 12, 3405-3411.
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1993, 32, 2410-2415. (c) Li, C.; Nolan, S. P. Organometallics 1995, 14, 1327-1332.

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<sup>(16)</sup> Nolan, S. P.; Hoff, C. D. J. Organomet. Chem. 1985, 282, 357-362.

# Table 1. Enthalpies of Substitution (kcal/mol) in<br/>the Reaction

 $(\text{BDA})\text{Fe}(\text{CO})_{3(\text{soln})} + 2L_{(\text{soln})} \frac{\text{THF}}{50\,^\circ\text{C}} \\ (L)_2\text{Fe}(\text{CO})_{3(\text{soln})} + \text{BDA}_{(\text{soln})}$ 

L	complex	$(\mathrm{cm}^{-1})^{a}$	$-\Delta H_{ m rxn}{}^b$
AsPh <sub>3</sub>	(Ph <sub>3</sub> As) <sub>2</sub> Fe(CO) <sub>3</sub>	1886	10.2(0.2)
$P(p-CF_3C_6H_4)_3$	$[(p-CF_3C_6H_4)_3P]_2Fe(CO)_3$	1899	$22.4(0.3)^d$
$AsEt_3$	$(\tilde{E}t_3As)_2Fe(CO)_3$	1865	$24.5(0.3)^{\circ}$
$P(p-ClC_6H_4)_3$	$[(p-ClC_6H_4)_3P]_2Fe(CO)_3$	1893	$25.0(0.1)^d$
$P(p-FC_6H_4)_3$	$[(p-FC_6H_4)_3P]_2Fe(CO)_3$	1891	$25.8(0.2)^d$
$P(C_6H_5)_3$	$[(C_6H_5)_3P]_2Fe(CO)_3$	1887	<b>26.9</b> (0.2) <sup>c</sup>
$PCy_2Ph$	$(PCy_2Ph)_2Fe(CO)_3$	1868	$27.1(0.1)^{e}$
$PCyPh_2$	$(PCyPh_2)_2Fe(CO)_3$	1879	$27.5(0.1)^{e}$
$P(p-CH_{3}C_{6}H_{4})_{3}$	$[(p-CH_3C_6H_4)_3P]_2Fe(CO)_3$	1884	$28.2(0.3)^d$
$P(p-CH_3OC_6H_4)_3$	$[(p-CH_3OC_6H_4)_3P]_2Fe(CO)_3$	1882	$30.1(0.2)^d$
PČy <sub>3</sub>	$(\tilde{P}Cy_3)_2Fe(CO)_3$	1854	$30.7(0.2)^{e}$
P <sup>i</sup> Pr <sub>3</sub>	$(P^{i}Pr_{3})_{2}Fe(CO)_{3}$	1860	$31.6(0.1)^{e}$
$PPh_2Et$	$(PPh_2Et)_2Fe(CO)_3$	1881	$32.7(0.1)^{e}$
$PBz_3$	$(PBz_3)_2Fe(CO)_3$	1884	$32.8(0.2)^{e}$
$PPh_2Me$	$(Ph_2MeP)_2Fe(CO)_3$	1878	34.1(0.3) <sup>c</sup>
$PPhMe_2$	$(PhMe_2P)_2Fe(CO)_3$	1875	37.3(0.3) <sup>c</sup>
$PMe_3$	$(Me_3P)_2Fe(CO)_3$	1871	38.9(0.2) <sup>c</sup>
$P^n B u_3$	$(^{n}Bu_{3}P)_{2}Fe(CO)_{3}$	1865	$41.7(0.3)^{\circ}$
$\mathbf{PEt}_3$	$(Et_3P)_2Fe(CO)_3$	1867	$42.4(0.2)^{c}$

 $^a$  Infrared spectra were recorded in THF.  $^b$  Enthalpy values are reported with 95% confidence limits.  $^c$  Taken from ref 10a,b.  $^d$  Taken from ref 10c.  $^e$  This work.

ucts were determined by comparison with reported spectroscopic data<sup>12.13</sup> or with materials independently synthesized. A detailed synthetic procedure for new organoiron complexes is described below:

 $[(C_6H_{11})_2(C_6H_5)P]_2Fe(CO)_3$ . A 100 mL flask was charged with 105 mg (0.37 mmol) of  $(BDA)Fe(CO)_3$  (BDA = benzylideneacetone), 204 mg (0.75 mmol) of PCy<sub>2</sub>Ph (dicyclohexylphenylphosphine), and 20 mL of THF. This clear solution was stirred for 48 h at room temperature during which time the color of solution changed from red orange to orange. The solution was then evaporated to dryness in vacuum, the residue was taken up in a 5 mL of CH<sub>2</sub>Cl<sub>2</sub> /25 mL of pentane mixture, and crystals were grown from this solution by slow cooling. After filtration of the obtained yellow microcrystals and drying under vacuum, 140 mg (56%) of product was obtained.  $^{1}$ H-NMR (THF- $d_8$ ): 8.01 (m, 4H, -Ph), 7.43 (m, 6H, -Ph), 2.53 (m, 4H, -Cy), 2.16-2.13 (m, 4H, -Cy), 1.88-1.68(m, 16H, -Cy), 1.55-1.20 (m, 20H, -Cy). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 7.91 (m, 4H, -Ph), 7.43 (m, 6H, -Ph), 2.41 (br, 4H, -Cy), 2.07 (m, 4H, -Cy), 1.89-1.68 (m, 16H, -Cy), 1.46-1.14 (m, 20H, -Cy), 1.46--Cy). IR [ $\nu_{CO}$  (THF)]: 1867 cm<sup>-1</sup>. Anal. Calcd for C<sub>39</sub>H<sub>54</sub>-FeO<sub>3</sub>P<sub>2</sub>: C, 67.99; H, 7.91. Found: C, 68.26; H, 7.83.

[( $C_6H_5CH_2$ )<sub>3</sub>**P**]<sub>2</sub>Fe(CO)<sub>3</sub>. A 100 mL flask was charged with 118 mg (0.41 mmol) of (BDA)Fe(CO)<sub>3</sub> (BDA = benzylideneacetone), 254 mg (0.836 mmol) of trisbenzylphosphine, and 25 mL of THF. Stirring the solution overnight at room temperature produces a color change of the solution from red orange to orange brown. After reduction the solution volume to 5 mL and addition of 25 mL pentane, the solution was left at room temperature where slow diffusion of pentane occurred through the THF layer. After filtration, this afforded 150 mg product (yield 57%) as greenish-yellow crystals. <sup>1</sup>H-NMR (THF-d<sub>8</sub>): 7.32–7.19 (m, 15H, -Ph); 3.27–3.25 (m, 6H, -CH<sub>2</sub>-). IR [ $\nu_{co}$  (THF)]: 1884 cm<sup>-1</sup>. Anal. Calcd for  $C_{45}H_{42}FeO_3P_2$ : C, 72.17; H, 5.66. Found: C, 72.33; H, 5.56.

Structure Determination of  $(PPh_2Cy)_2Fe(CO)_3$  (2). A rectangular light yellow crystal of 2, grown by evaporation of a saturated CH<sub>2</sub>Cl<sub>2</sub>/pentane solution, having approximate dimensions  $0.25 \times 0.25 \times 0.25$  mm was selected and mounted on the end of a glass fiber using silicone high-vacuum grease, and cooled to 100(2) K in a stream of cold nitrogen gas on an Enraf-Nonius CAD 4 diffractometer. Cell dimensions were

Table 2. Summary of Crystallographic Data for (PCyPh<sub>2</sub>)<sub>2</sub>Fe(CO)<sub>3</sub> (2)

empirical formula	C <sub>39</sub> H <sub>42</sub> O <sub>3</sub> P <sub>2</sub> Fe
space group	$P2_1/n$
unit cell dimensions	-
a, Å	12.393(5)
b, Å	15.811(6)
c, Å	18.029(7)
a, deg	90
$\beta$ , deg	108.00(2)
y, deg	90
V, Å <sup>3</sup>	3360(5)
Z, molecule/cell	4
$d_{\rm calcd},  {\rm g/cm^3}$	1.337
$\mu(Mo), cm^{-1}$	5.766
monochromator	highly ordered graphite crystal
temp, K	100(2)
abs corr	empirical ( $\psi$ -scan method)
diffractometer	Enraf-Nonius CAD 4
scan type	$\theta - 2\theta$
data collcd	$-14 \le h \le 14, 0 \le k \le 18,$
	$0 \leq l \leq 21$
$2\theta$ range, deg	4.0-50.0
no. of colled refins	5891
no. of indep reflns	5891
no. of obsd refins $(I > 3\sigma(I))$	3130
$R_{\rm F}({\rm obsd \ data}), \%$	4.5
R <sub>wF</sub> , %	5.2
goodness of fit	1.6
no. of variables	561

## Table 3. Selected Bond Distances (Å) and Bond<br/>Angles (deg) for (PCyPh\_2)\_2Fe(CO)\_3 (2)

Den J I	an anth an						
Bond Lengths <sup>a</sup>							
2.218(1)	P(1) - C(4)	1.840(4)					
2.218(1)	P(1) - C(10)	1.850(4)					
1.780(5)	P(1) - C(16)	1.846(4)					
1.759(4)	P(2) - C(22)	1.831(5)					
1.773(5)	P(2) - C(28)	1.853(4)					
1.141(5)	P(2) - C(34)	1.839(4)					
1.174(5)	Cy C-C(ave)	1.502(8)					
1.162(5)	Ph C-C(ave)	1.376(8)					
Dand Angles"							
Donu .	Aligies-						
178.45(6)	C(4) - P(1) - C(10)	101.9(2)					
89.5(1)	C(4) - P(1) - C(16)	102.5(2)					
89.5(1)	C(10) - P(1) - C(16)	102.9(2)					
88.8(1)	Fe-P(2)-C(22)	115.6(1)					
89.1(1)	Fe-P(2)-C(28)	117.7(2)					
88.6(1)	Fe-P(2)-C(34)	114.6(2)					
92.5(1)	C(22) - P(2) - C(28)	102.6(2)					
118.1(2)	C(22) - P(2) - C(34)	101.7(2)					
120.0(2)	C(28) - P(2) - C(34)	102.4(2)					
121.9(2)	Fe-C(1)-O(1)	178.5(4)					
115.1(1)	Fe-C(2)-O(2)	177.8(4)					
117.2(2)	Fe-C(3)-O(3)	176.8(4)					
115.3(1)							
	$\begin{array}{r} & \text{Bond I} \\ \hline 2.218(1) \\ 2.218(1) \\ 1.780(5) \\ 1.759(4) \\ 1.773(5) \\ 1.141(5) \\ 1.162(5) \\ \hline \\ & \text{Bond} \\ 178.45(6) \\ 89.5(1) \\ 89.5(1) \\ 88.8(1) \\ 89.5(1) \\ 88.8(1) \\ 92.5(1) \\ 118.1(2) \\ 120.0(2) \\ 121.9(2) \\ 115.1(1) \\ 117.2(2) \\ 115.3(1) \\ \end{array}$	$\begin{array}{r llllllllllllllllllllllllllllllllllll$					

 $^{\boldsymbol{a}}$  Numbers in parentheses are the estimated standard deviations.

determined by least-squares refinement of the measured setting angles of 25 reflections with  $40^{\circ} < 2\theta < 50^{\circ}$  using Mo Ka radiation . The structure was solved by direct methods (MULTAN80) and refined by full matrix least-squares techniques. Crystal data for **2** are summarized in Table 2 and selected bond distances and angles are listed in Table 3. Positional and equivalent isotropic thermal parameters are presented in Table 4. Figure 1 gives an ORTEP drawing of this molecule.

### Results

The  $(BDA)Fe(CO)_3$  complex (BDA = PhCH=CHCOMe, benzylideneacetone) was selected as the entryway into the thermochemistry of the iron tricarbonyl system in view of the labile nature of the BDA ligand as illustrated

Table 4. Fractional Coordinates and Isotropic Thermal Parameters for  $(PCyPh_2)_2Fe(CO)_3$  (2)<sup>a</sup>

atom	x	у	z	$B, Å^2$	atom	x	у	z	$B, Å^2$
Fe	-0.02290(6)	0.21900(4)	0.22950(4)	1.76(1)	C(18)	-0.0364(6)	0.3606(4)	0.4730(3)	4.4(2)
P(1)	-0.1751(1)	0.27812(8)	0.24774(6)	1.79(2)	C(19)	-0.1097(5)	0.4193(4)	0.4833(3)	3.9(1)
P(2)	0.1281(1)	0.15667(8)	0.21263(7)	1.69(2)	C(20)	-0.2019(5)	0.4395(3)	0.4226(3)	3.6(1)
<b>O</b> (1)	-0.0217(3)	0.0934(3)	0.3486(2)	4.0(1)	C(21)	-0.2223(5)	0.3994(3)	0.3509(3)	2.9(1)
O(2)	-0.1492(3)	0.1751(2)	0.0680(2)	3.0(1)	C(22)	0.2410(4)	0.1289(3)	0.3020(3)	1.8(1)
O(3)	0.0931(3)	0.3815(2)	0.2744(2)	4.0(1)	C(23)	0.2681(4)	0.1839(3)	0.3654(3)	2.6(1)
C(1)	-0.0210(4)	0.1431(3)	0.3028(3)	2.5(1)	C(24)	0.3547(5)	0.1664(4)	0.4328(3)	3.0(1)
C(2)	-0.0983(4)	0.1943(3)	0.1322(3)	1.9(1)	C(25)	0.4140(5)	0.0912(4)	0.4296(3)	3.0(1)
C(3)	0.0496(4)	0.3164(3)	0.2558(3)	2.4(1)	C(26)	0.3867(5)	0.0358(3)	0.3786(3)	2.9(1)
C(4)	-0.2873(4)	0.2038(3)	0.2518(3)	1.9(1)	C(27)	0.3008(4)	0.0527(3)	0.3110(3)	2.4(1)
C(5)	-0.3140(4)	0.1356(4)	0.1983(3)	2.9(1)	C(28)	0.2062(4)	0.2144(3)	0.1558(3)	2.5(1)
C(6)	-0.4059(5)	0.0835(4)	0.1930(3)	3.1(1)	C(29)	0.1293(4)	0.2388(4)	0.0759(3)	2.9(1)
C(7)	-0.4733(5)	0.0986(4)	0.2379(3)	<b>3.6(1)</b>	C(30)	0.1960(5)	0.2727(5)	0.0252(3)	4.4(1)
C(8)	-0.4473(5)	0.1627(4)	0.2927(3)	3.8(1)	C(31)	0.2757(5)	0.3420(4)	0.0630(3)	4.2(1)
C(9)	-0.3574(4)	0.2170(4)	0.2970(3)	3.2(1)	C(32)	0.3487(5)	0.3204(5)	0.1442(3)	4.9(2)
C(10)	-0.2548(4)	0.3546(3)	0.1733(3)	2.2(1)	C(33)	0.2794(5)	0.2856(4)	0.1942(3)	4.4(1)
C(11)	-0.1803(5)	0.4159(4)	0.1492(3)	3.5(1)	C(34)	0.0993(4)	0.0541(3)	0.1622(3)	2.6(1)
C(12)	-0.24445(6)	0.4849(4)	0.0963(4)	4.3(2)	C(35)	0.0311(5)	-0.0020(4)	0.1822(4)	5.1(2)
C(13)	-0.3371(5)	0.4511(4)	0.0289(3)	3.7(1)	C(36)	0.0129(6)	-0.0822(5)	0.1483(5)	7.8(2)
C(14)	-0.4109(5)	0.3878(4)	0.0514(3)	3.6(1)	C(37)	0.0676(8)	-0.1082(4)	0.0997(4)	6.7(2)
C(15)	-0.3451(5)	0.3189(4)	0.1025(3)	3.7(1)	C(38)	0.1325(9)	-0.0532(5)	0.0780(4)	10.1(3)
C(16)	-0.1489(4)	0.3378(3)	0.3395(3)	2.3(1)	C(39)	0.1553(8)	0.0280(4)	0.1113(4)	7.6(2)
C(17)	-0.0552(5)	0.3193(4)	0.4031(3)	3.9(1)					

<sup>a</sup> Numbers in parentheses are the estimated standard deviations.

by Angelici and co-workers,<sup>17</sup> who have used this molecule in their synthetic efforts (eq 11). The labile

$$\begin{array}{c} Ph \longrightarrow O \\ OC & Fe \\ OC & CO \end{array} + 2 PPh_3 \\ \hline \begin{array}{c} 25^{\circ}C \\ 20 \text{ hrs} \end{array} & \begin{array}{c} PPh_3 \\ 1 \\ CO \\ Fe \\ PPh_3 \end{array} + BDA \quad (11) \\ PPh_3 \end{array}$$

nature of the BDA complex has also previously been noted by Brookhart and co-workers in their use of this complex as a diene trapping  $agent^{18}$  (eq 12).

$$(BDA)Fe(CO)_3 + \bigcirc \longrightarrow Fe(CO)_3 + BDA$$
 (12)

We have recently reported the enthalpies of reaction of monodentate tertiary phosphines with the (BDA)Fe-(CO)<sub>3</sub> complex<sup>10a-c</sup> as illustrated in eq 13.

 $(BDA)Fe(CO)_3 + 2 PR_3 \xrightarrow{THF} OC \xrightarrow{PR_3} \downarrow CO + BDA (13)$ 

PR3 = tertiary phosphine

We now extend this work to sterically demanding tertiary phosphine donors. All results involving monodentate phosphine ligands investigated for the present study, including those previously reported, are summarized in Table 1. A single-crystal structural study was carried out on one organoiron complex, 2. Tables 2 and 4 give important bond distances and angles as well as positional parameters with an ORTEP drawing of the structure (Figure 4).

### Discussion

With the exception of the few thermodynamic investigations reported by Muetterties<sup>19</sup> and Connor,<sup>20</sup> thermodynamic information focusing on organoiron systems remains scarce. Studies clearly separating steric from electronic contributions are also quite few in number.<sup>21,22</sup> In this section, thermochemical data for sterically demanding tertiary monodentate phosphine ligands are presented. These data enable a complete treatment of ligand effects within the  $L_2Fe(CO)_3$  system,<sup>23</sup> the nature of L ranging from sterically compact (PMe<sub>3</sub>) to spatially demanding (PCy<sub>3</sub>). A quantitative analysis of ligand effects (QALE) analysis is then described which shows the steric/electronic relationship existing in the present system.

Sterically Demanding Monodentate Phosphines Ligands. We have previously shown that the entryway into the thermochemistry of this system lies in the reaction of  $(BDA)Fe(CO)_3$  with excess ligand as illustrated in reaction 14.<sup>10</sup> We now wish to show that this entryway can be extended to sterically demanding

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$$BDAFe(CO)_{3(soln)} + 2 PMe_{3(soln)} \xrightarrow{THF}_{50^{\circ}C} \xrightarrow{PMe_{3}}_{CO} \xrightarrow{PMe_{3}}_{CO} \xrightarrow{PMe_{3}}_{CO} \xrightarrow{PMe_{3}}_{CO} \xrightarrow{PMe_{3}}_{PMe_{3}} \xrightarrow{(14)}_{PMe_{3}} \xrightarrow{\Delta H_{ran} = -38.9 \pm 0.2 \text{ kcal/mol}}$$

tertiary phosphine ligands (eq 15). A complete listing

$$BDAFe(CO)_{3(soln)} + 2 PCy_{3(soln)} \xrightarrow{THF}_{50^{\circ}C} \xrightarrow{PCy_{3}}_{CO} \xrightarrow{PCy_{3}}_{Fe} \xrightarrow{CO}_{Fe} \xrightarrow{PCy_{3}}_{PCy_{3}} + BDA_{(soln)} \quad (15)$$
$$\Delta H_{--} = -30.7 \pm 0.2 \text{ kcal/mol}$$

$$M_{rxn} = -30.7 \pm 0.2 \text{ kcal/mol}$$

of all thermochemical information thus far measured for monodentate ligands in this system is presented in Table 1. This rather extensive tabulation now allows for a detailed analysis of factors affecting the thermochemical stability of iron-phosphine bond enthalpy terms.

We have previously described the overwhelming importance of electronic effects in this system. The enthalpic trends in earlier contributions<sup>10a-c</sup> were described in terms of two-component relationships dealing exclusively with ligand substitution enthalpies and electronic terms quantifying the electronic donating ability of the phosphine ligand. Keeping in mind such considerations and enthalpy data listed in Table 1, it is surprising to find one of the most basic phosphines  $(PCy_3)^{24}$  to have an unusually low enthalpy of ligand substitution. In the present data, involving sterically demanding phosphines, a simple linear relationship correlating the electronic factor associated with the phosphine ligand to the enthalpy of reaction cannot be obtained (Figure 1).

The poor correlation obtained (0.55) is taken to mean that the steric factor contributes in some amount to the magnitude of the ligand substitution reaction. It therefore appears that electronic arguments can explain the enthalpic trend to a point, beyond which both steric and electronic contributions must be considered. This argument has been presented qualitatively and semiquantitatively in a number of systems.<sup>21</sup>

Quantitative Analysis of Ligand Effects (QALE). We now wish to consider the present data in quantitative terms with the help of a relationship and treatment proposed by Giering and Prock.<sup>25</sup> Giering and coworkers have partitioned relative importance of steric and electronic contributions using a variation of a treatment first proposed by Tolman.<sup>24</sup> These researchers have applied this treatment to a number of kinetic and thermodynamic data.<sup>21a,b,f,25</sup> If such a treatment is applied to the present data, the general eq 16 is obtained

$$-\Delta H_{\rm rxn} = -(0.73 \pm 0.10)\chi -$$

$$(0.46 \pm 0.03)(\theta - 135)\lambda -$$

$$(1.69 \pm 0.38)E_{\rm ar} + 46.28 \pm 0.78 \quad (16)$$

$$n = 16 \qquad R^2 = 0.984$$

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Figure 1. Enthalpy of reaction (kcal/mol) versus the phosphine electronic parameter ( $\chi$ ). Slope = -0.456; R = 0.55.



Figure 2. Steric enthalpy contribution (kcal/mol) versus phosphine cone angle (deg).

for 16 different phosphine reactions,<sup>26</sup> where  $\Delta H$  is the enthalpy of reaction (kcal/mol),  $\chi$  is the electronic parameter associated with a given phosphine ligand,  $\theta$ represents the phosphine steric factor,  $\lambda$  is a switching function that turns the steric effect when the size of the ligand exceeds the steric threshold (that is  $\lambda$  equals 0 when  $\theta$  is less than the steric threshold angle and  $\lambda$ equals 1 when  $\theta$  is greater than the threshold angle value), and  $E_{\rm ar}$  is the phosphine aryl substituent contribution. All phosphine parameters values (with the exception of the enthalpy data) utilized in the treatment have previously been reported by Giering and Prock.<sup>25</sup> The correlation coefficient depicts the excellent fit of the data to this model. Once the general formula is derived, individual electronic and steric enthalpic contributions can be back-calculated. Doing this simple analysis affords the graphical representation of the enthalpic contribution associated with steric effects ( $\theta$ ) and is illustrated in Figure 2. Here, it can clearly be seen that a steric threshold of 135° is present in this system. This is taken to mean that phosphine ligands with cone angles greater than 135° will exhibit a steric contribution to the overall enthalpy of reaction. It should also be pointed out that since this is a thermodynamic study as opposed to a kinetic one, the analysis of the data

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<sup>(26)</sup> PBz<sub>3</sub> has not been included in this analysis. Giering<sup>25</sup> has observed that this phosphine proves to be a problem in such analyses.



Figure 3. Electronic enthalpy contribution (kcal/mol) versus phosphine electronic parameter ( $\chi$ ). Slope = -0.733; R = 0.98.

gives a view of  $L_2Fe(CO)_3$  that is independent of mechanism of formation. Thus, the steric threshold observed in the analysis must be attributed to nonlinear steric effects in  $L_2Fe(CO)_3$  and not to a change in mechanism or a change in the nature of the rate-determinating step.

A simple electronic correlation (Figure 3) can also be established in a similar manner (by back-calculating the enthalpic electronic contribution) and shows a fairly good linear relationship denoting the principal electronic influences in this system. Observation of the steric threshold at 135° might be possible in different sets of data.<sup>27</sup> Accordingly, the infrared data reported in this contribution was examined for such a correlation using Giering's treatment. Regression analysis of the full set of data does not provide good results. It appears that a problem in this analysis is the loss of  $D_{3h}$  symmetry and the resulting distortion of the complex when PRR'2 ligands are used. The ORTEP of 2 nicely shows this distortion. In the  $D_{3h}$  symmetric systems  $(R_3P)_2Fe$ - $(CO)_3$ , the C-Fe-C bond angles are expected to be the same and the Fe(CO)<sub>3</sub> group should be planar regardless of the ancillary ligand. The analysis of the IR data for these  $D_{3h}$  complexes<sup>28</sup> is excellent even in the absence of steric threshold limitation. This correlation is presented in eq 17. The best fit, however, the one with the

$$\nu(\text{CO}) = 1.688\chi - 0.0969\theta + 3.633E_{\text{ar}} + 68.04$$
 (17)

$$R^2 = 0.999$$

smallest standard deviation, is given by eq 18, where

$$\nu(\text{CO}) = 1.702\chi - 0.1266(\theta - 135)\lambda + 3.415E_{\text{ar}} + 56.35 (18)$$

$$R^2 = 1.00$$

the steric threshold is identical to the one previously calculated for the enthalpy data. The reason behind the observed good fit of the data without the steric threshold constraint is the relatively small importance of steric effects in this system. The interpretation of the infrared data set analysis (an increase of the phosphine size past the steric threshold causes the carbonyl stretching frequency to shift to a lower wavenumber) might be



Figure 4. ORTEP drawing of  $(PCyPh_2)_2Fe(CO)_3$  with ellipsoids drawn at 50% probability.

explained in terms of diminished steric crowding of the first vibration state vs the ground state or, alternatively, as the phosphines are forced away from the iron center, there is an associated attenuation in the P-Fe  $\pi$  bonding, therefore resulting in an increase in electron density on the Fe available for back-donation with the carbonyl groups. This appears to be the first definitive evidence for phosphine-metal  $\pi$  bonding. More work aimed at elucidating the bonding factors present in this and related systems is currently underway.

Structural Features of (PCyPh<sub>2</sub>)<sub>2</sub>Fe(CO)<sub>3</sub> (2). Figure 4 shows an ORTEP of (PCyPh<sub>2</sub>)<sub>2</sub>Fe(CO)<sub>3</sub>; the important bond lengths and angles are listed in Table 3. The iron complex is best considered a trigonal bipyramid with phosphine ligands occupying the apex in a mutually trans spatial arrangement (P-Fe-P bond angle of  $178.45(6)^{\circ}$ ) with a meridional arrangement of carbonyl groups (C-Fe-C average bond angle of 120.0- $(2)^{\circ}$ ). In view of the steric demands associated with this ligand (cone angle 153°) a slight distortion from pure  $D_{3h}$  might have been expected. In fact, it is slightly distorted from  $D_{3h}$  based on the Fe-C-O bond distances (see Table 3). The crystal structures of  $[(Me_2N)_3P]_2Fe$ - $(CO)_3$  (3)<sup>29</sup> and  $[P(OCH_2)_3P]_2Fe(CO)_3$  (4)<sup>30</sup> indicate that  $(R_3P)_2Fe(CO)_3$  complexes of monodentate phosphines prefer to adopt trigonal-bipyramidal structures in which the phosphine ligands occupy trans axial positions. In these two complexes, the three Fe-CO bond lengths are 1.76 and 1.80 Å, respectively. This compares with Fe-Cbond lengths of 1.780(5), 1.759(4), and 1.773(5) Å present in **2**, leading to a distortion from  $D_{3h}$  symmetry. The C–O bond lengths in **3** and **4** are 1.16 and 1.15 Å. respectively; whereas in 2, C-O bond lengths of 1.141-(5), 1.174(5), and 1.162(5) Å can be found. These important differences in individual bond lengths in 2 compared with the rather uniform bond length values found in the  $Fe(CO)_3$  moiety of 3 and 4 illustrate the presence of a deviation from ideal  $D_{3h}$  symmetry in 2.<sup>31</sup>

<sup>(27)</sup> Giering, W. P. Private communication.

<sup>(28)</sup> All infrared data used for  $D_{3h}$  complexes can be found in Table 1. In addition a value for  $(P^tBu_3)_2Fe(CO)_3$  in THF of 1852 cm<sup>-1</sup> has been included in the treatment.

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<sup>(31)</sup> Casey and co-workers have observed structural distortion in a related  $Fe(CO)_3$  system involving chelating bidentate phosphine ligands: Casey, C. P.; Whiteker, G. T.; Campana, C. F.; Powell, D. R. Inorg. Chem. **1990**, 29, 3376–3381.

### Conclusion

The reported solution calorimetric investigation represents a detailed thermochemical study of organoiron complexes. Relative bond enthalpies are reported, and these help understand the donating ability of the ligands in the present system and the corresponding stabilizing effect on iron complexes. Moreover, a quantitative analysis of ligand effect analysis clearly shows the relative importance of steric and electronic factors in the present system at various phosphine steric requirements. This system to our knowledge is unique in that a complete ligand effect analysis can be performed on a large series of phosphine ligands therefore enabling a concise analysis of the relative importance of steric versus electronic effects. Studies focusing on enthalpic contributions associated with ligand substitution of other ligands/ligand-types in this and related systems are presently underway.

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Supporting Information Available: Tables of hydrogen coordinates and B values, selected distances and angles, anisotropic thermal parameters, and hydrogen bond distances for 2(10 pages). Ordering information is given on any current masthead page.

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