Organoiron Thermochemistry. Solution **Thermochemical Investigation of Tertiary Phosphine** Ligand Electronic Effects in trans-(P(p-XC₆H₄)₃)₂Fe(CO)₃ Complexes

Chunbang Li and Steven P. Nolan*

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

Received October 11, 1994[®]

The enthalpies of reaction of $(BDA)Fe(CO)_3$ $(BDA = (C_6H_5)CH = CHC(O)(CH_3)$, benzylideneacetone) with a series of para-substituted triphenylphosphine ligands, leading to the formation of trans- $(P(p-XC_6H_4)_3)_2Fe(CO)_3$ complexes (X = H, CH₃O, CH₃, Cl, F, CF₃), have been measured by solution calorimetry in THF at 50 °C. The range of reaction enthalpies spans some 7.7 kcal/mol and helps establish a relative order of complex stability for 14 compounds in the iron tricarbonyl system. The relative enthalpy scale for tertiary phosphine complexes, $trans \cdot (P(p-XC_6H_4)_3)_2 Fe(CO)_3$, is as follows $(X, \Delta H_{reacn} \text{ in kcal/mol})$: CF₃, 22.4(0.3); $Cl, 25.0(0.1); F, 25.8(0.2); H, 26.9(0.2); CH_3, 28.2(0.3); CH_3O, 30.1(0.2).$ The thermodynamic investigation of these isosteric tertiary phosphine ligands helps to independently determine the importance of phosphine electronic contribution to the enthalpy of reaction in this system. Correlations of various factors gauging the electron-donating properties of the phosphine ligands clearly show the electronic factor to be the overwhelming contributor to the enthalpy of reaction in the $trans-(PR_3)_2Fe(CO)_3$ system.

Introduction

The field of organometallic thermochemistry has gained recognition as one of great relevance to catalysis.¹ Such valuable investigations have led to a better understanding of bonding and reactivity patterns in a small number of organometallic systems.^{2,3} These studies have also proven to be powerful tools in predicting the thermodynamic feasibility of given reactions or individual steps comprising catalytic cycles.^{3,4} In spite of the general view that such studies are fundamental to a better understanding of organometallic systems,

this area remains one where few complete investigations have been performed.

Tertiary phosphines and chelating tertiary diphosphines have been widely used as ligands in organometallic chemistry.⁵ Kinetic, catalytic, and structural studies have been conducted on such complexes.⁶ In spite of the vast amount of information focusing on transition-metal phosphine complexes, few thermodynamic data regarding heats of binding of these ligands to metal centers exist. Manzer and Tolman⁷ have reported on the solution calorimetry of square-planar platinum(II) complexes, shown in eq 1, for a series of

$$trans - [CH_3PtL_2(THF)]^+ + PR_3 \rightarrow$$

$$trans - [CH_3PtL_2(PR_3)]^+ + THF (1)$$

$$L = P(CH_3)_2Ph$$

phosphine ligands. A similar series was then investigated for Ni(0) complexes,⁸ shown in eq 2.

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

More recently, detailed thermochemical investigations of two related Mo(0) systems have been reported by Hoff and co-workers.9

© 1995 American Chemical Society

^{*} Abstract published in Advance ACS Abstracts, February 1, 1995. (1) For leading references in this area see: (a) Nolan, S. P. Bonding Chem. 1992, 40, 503-561. (c) Martinho Simões, J. A.; Beauchamp, J. L. Chem. Rev. 1990, 90, 629-688. (d) Marks, T. J., Ed. Bonding, E. Chem. 1992, 40, 503-561. (c) Martinho Simões, J. A.; Beauchamp, J. L. Chem. Rev. 1990, 90, 629-688. (d) Marks, T. J., Ed. Bonding, E. Chem. Rev. 1990, 90, 629-688. (d) Marks, T. J., Ed. Bonding, 1993, 1 L. Chem. Rev. 1990, 90, 629-688. (d) Marks, T. J., Ed. Bonding Energetics in Organometallic Compounds; ACS Symposium Series 428; American Chemical Society: Washington, DC, 1990. (e) Marks, T. J., Ed. Metal-Ligand Bonding Energetics in Organotransition Metal Compounds; Polyhedron Symposium-in-Print 7; Pergamon Press: Oxford, U.K., 1988. (f) Skinner, H. A.; Connor, J. A. In Molecular Structure and Energetics; Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1987; Vol. 2, Chapter 6. (g) Skinner, H. A.; Connor, J. A. Pure Appl. Chem. 1985, 57, 79-88. (h) Pearson, R. G. Chem. Rev. 1985, 85, 41-59. (i) Mondal, J. U.; Blake, D. M. Coord. Chem. Rev. 1982, 47, 205-238. (j) Mansson, M. Pure Appl. Chem. 1983, 55, 417-426. (k) Pilcher, G.; Skinner, H. A. In The Chemistry of the Metal-Carbon Bond; Harley, F. R., Patai, S., Eds.; Wiley: New York, 1982; pp 43-90. (l) Connor, J. A. Top. Curr. Chem. 1977, 71, 71-110. (2) (a) Nolan, S. P.; Hoff, C. D.; Stoutland, P. O.; Newman, L. J.; Buchanan, J. M.; Bergamn, R. G.; Yang, G. K.; Peters, K. G. J. Am. Chem. Soc. 1987, 109, 3143-3145, and references therein. (b) Nolan, S. P.; Lopez de la Vega, R.; Hoff, C. D. Organometallics 1986, 5, 2529-

S. P.; Lopez de la Vega, R.; Hoff, C. D. Organometallics 1986, 5, 2529-2537

^{(3) (}a) Nolan, S. P.; Porchia, M. Marks, T. J. Organometallics **1991**, 10, 1450–1457. (b) Nolan, S. P.; Stern, D.; Marks, T. J. J. Am. Chem.

^{10, 1450-1457. (}b) Nolan, S. P.; Stern, D.; Marks, T. J. J. Am. Chem.
Soc. 1989, 111, 7844-7854.
(4) (a) Nolan, S. P.; Stern, D.; Hedden, D.; Marks, T. J. In ref 1d, pp 159-174. (b) Nolan, S. P.; Lopez de la Vega, R.; Mukerjee, S. L.; Gongalez, A. A.; Hoff, C. D. In ref 1e, pp 1491-1498. (c) Marks, T. J.; Gagné, M. R.; Nolan, S. P.; Schock, L. E.; Seyam, A. M.; Stern, D. L. Pure Appl. Chem. 1989, 61, 1665-1672. (d) Schock, L. E.; Marks, T. L. L. Am. Chem. Soc. 1989, 140. 7701 J. J. Am. Chem. Soc. 1988, 110, 7701.

⁽⁵⁾ Tolman, C. A. Chem. Rev. 1977, 77, 313-348.

⁽⁶⁾ Pignolet, L. H., Ed. Homogeneous Catalysis with Metal Phosphine Complexes; Plenum: New York, 1983.
(7) Manzer, L. E.; Tolman, C. A. J. Am. Chem. Soc. 1975, 97, 1955–

¹⁹⁸⁶

⁽⁸⁾ Tolman, C. A.; Reutter, D. W.; Seidel, W. C. J. Organomet. Chem. 1976, 117, C30-C33.

 ^{(9) (}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.

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

$$(\text{NBD})\text{Mo(CO)}_4 + 2\text{PR}_3 \rightarrow cis-(\text{PR}_3)_2\text{Mo(CO)}_4 + \text{NBD} (4)$$

NBD = norbornadiene

In an effort to remedy this dearth of thermodynamic information on metal-phosphine complexes, we have recently reported on three organogroup 8 systems:^{10,11}

$$\begin{array}{c} Cp*Ru(COD)Cl_{(soln)}+2PR_{3(soln)} \xrightarrow{THF} \\ Cp*Ru(PR_{3})_{2}Cl_{(soln)}+COD_{(soln)} \end{array} (5) \end{array}$$

$$CpRu(COD)Cl_{(soln)} + 2PR_{3(soln)} \xrightarrow{\text{THF}} CpRu(PR_3)_2Cl_{(soln)} + COD_{(soln)} (6)$$

$$(BDA)Fe(CO)_{3(soln)} + 2PR_{3(soln)} \xrightarrow{\text{THF}}_{50 \,^{\circ}\text{C}} trans-(PR_3)_2Fe(CO)_{3(soln)} + BDA_{(soln)} (7)$$

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

Noteworthy is that in every one of the phosphinebased organometallic thermochemical investigations mentioned above, interpretations of results are provided in terms of phosphine steric and electronic contributions to the overall enthalpy of reaction. A number of relationships have been used to determine or gauge these relative steric and electronic contributions in kinetic and thermodynamic studies.^{12,13} In the present contribution, we extend our solution calorimetric work on organoiron-based systems¹¹ and report on the relative importance of the tertiary phosphine ligand electronic parameter as it affects metal-ligand bond enthalpies and complex stability. The present thermochemical investigation focuses on a series of isosteric

(11) For organoiron systems see: (a) Luo, L.; Nolan, S. P. Organometallics 1992, 11, 3483-3486. (b) Luo, L.; Nolan, S. P. Inorg. Chem. 1993, 32, 2410-2415.

phosphine ligands binding the iron tricarbonyl system $(-Fe(CO)_3).$

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 of oxygen and water. 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. Infrared spectra were recorded using a Perkin-Elmer FTIR Model 2000 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 reaction¹⁴ or the enthalpy of solution of KCl in water.¹⁵ The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described,16 and typical procedures are described below. The organoiron complex $(BDA)Fe(CO)_3$ (1) was synthesized according to literature procedures. 17 Only materials of high purity as indicated by IR and NMR spectroscopy were used in the calorimetric experiments. All organoiron complexes have been previously reported,¹⁸ with the exception of the $trans-(p-CF_3C_6H_4)_3P)_2Fe(CO)_3$ complex, which was synthesized as described below. All ligands were purchased from Strem Chemicals (Newburyport, MA) or Organometallics, Inc. (East Hampstead, NH), and used as received.

Synthesis and Characterization of trans-(p-CF₃- C_6H_4)₃P)₂Fe(CO)₃. A 100 mL flask was charged with 510 mg of P(p-CF₃C₆H₄)₃ (1.09 mmol), 140 mg (0.49 mmol) of (BDA)- $Fe(CO)_3$ (BDA = benzylideneacetone), and 15 mL of THF. The clear orange solution was stirred at room temperature for 88 h, after which time the solvent was removed under vacuum. The residue was dissolved in 20 mL of CH₂Cl₂ and slowly cooled to -50 °C using a dry ice-acetone bath. Following filtration, washing with 2 mL of pentane and drying under vacuum afforded 288 mg of a golden yellow product (yield 57%). ¹H NMR (d_8 -THF): 7.87 ppm (24 H, m, Ph). IR (THF): v_{co} 1899 cm⁻¹. Anal. Calcd for $C_{45}H_{24}FeP_2O_3F_{18}$: C, 50.40; H, 2.26. Found: C, 50.71; H, 2.43.

Calorimetric Measurement for Reaction Involving (BDA)Fe(CO)₃ and P(p-CF₃C₆H₄)₃. 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)₃ was accurately weighed into the lower vessel; it was closed and sealed with 1.5 mL of mercury. Four milliliters of a stock solution of the phosphine ligand (2 g of the phosphine ligand in 25 mL of THF) was added and the remainder of the cell was assembled, removed from the glovebox, and inserted in the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no organoiron complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 50.0 °C (about 2 h) the reaction was initiated by inverting the calorimeter. At the end of the reaction (1-2h) the vessels were removed from the calorimeter, taken into the glovebox, and opened, and the infrared cell was filled under an inert atmosphere. An infrared spectrum of each product was

⁽¹⁰⁾ 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*, 3953. 3405-3411. (c) Luo, L.; Zhu, N.; Zhu, N.-J.; Stevens, E. D.; Nolan, S. P.; Fagan, P. J. Organometallics 1994, 13, 669-675. (d) Li, C.; Cucullu, M. E.; McIntyre, R. A.; Stevens, E. D.; Nolan, S. P. Organometallics 1994, 13, 3621-3627. (e) Luo, L.; Nolan, S. P. Organometallics 1994 13, 4781-4786. (f) Luo, L.; Li, C.; Cucullu, M. E.; Nolan, S. P. Organometallics 1995, 14, 1333-1338.

^{(12) (}a) Rahman, M. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering,
W. P. Organometallics 1989, 8, 1-7. (b) Liu, H.-Y.; Eriks, K.; Prock,
A.; Giering, W. P. Inorg. Chem. 1989, 28, 1759-1763. (c) Poe, A. J.
Pure Appl. Chem. 1988, 60, 1209-1216 and references cited therein.
(d) Gao, Y.-C.; Shi, Q.-Z.; Kersher, D. L.; Basolo, F. Inorg. Chem. 1988,
27, 188-191. (e) Baker, R. T.; Calabrese, J. C.; Krusic, P. J.; Therien,
M. J.; Trogler, W. C. J. Am. Chem. Soc. 1988, 110, 8392-8412. (f) Rahman, M. M.; Liu, H.-Y.; Prock, A.; Giering, W. P. Organometallics 1987. 6, 650-658.

^{(13) (}a) Huynh, M. H. V.; Bessel, C. A.; Takeuchi, K. J. Abstracts of Papers, 208th National Meeting of the American Chemical Society, Washington, DC, Fall 1994; American Chemical Society: Washington, DC, 1994; Abstract INOR 165. (b) Perez, W. J.; Bessel, C. A.; See, R. F.; Lake, C. H.; Churchill, M. R.; Takeuchi, K. J. Abstracts of Papers, 208th National Meeting of the American Chemical Society, Washington, DC, Fall 1994; American Chemical Society: Washington, DC, 1994; INOP 166. (c) Ching S.; Shirop D. F. J. Am. Chemical Society: 1000 1994; INOR 166. (c) Ching, S.; Shriver, D. F. J. Am. Chem. Soc. 1989, 111, 3238–3243. (d) Lee, K.-W.; Brown, T. L. Inorg. Chem. 1987, 26, 1852 - 1856.

⁽¹⁴⁾ Ojelund, G.; Wadso, I. Acta Chem. Scand. 1968, 22, 1691-1699. (15) Kilday, M. V. J. Res. Natl. Bur. Stand. (U.S.) 1980, 85, 467-481

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

⁽¹⁷⁾ Howell, J. A. S.; Johnson, B. F. G.; Josty, P. L.; Lewis, J. J. Organomet. Chem. 1972, 39, 329–333.
(18) (a) Inoue, H.; Takei, T.; Heckmann, G.; Fluck, E. Z. Naturforsch.
1991, 46B, 682–686. (b) Sowa, J. R.; Zanotti, V.; Facchin, G.; Angelici, R. J. J. Am. Chem. Soc. 1991, 113, 9185–9192.

Table 1. Enthalpies of Substitution (kcal/mol) in the Reaction

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

L	complex	$\delta_{\rm CO} ({\rm cm}^{-1})^a$	$-\Delta H_{\text{reacn}}^{b}$
AsPh ₃	(Ph ₃ As) ₂ Fe(CO) ₃	1886	10.2(0.2) ^c
$P(p-CF_3C_6H_4)_3$	$[(p-CF_{3}C_{6}H_{4})_{3}P]_{2}Fe(CO)_{3}$	1899	$22.4(0.3)^d$
AsEt ₃	(Et ₃ As) ₂ Fe(CO) ₃	1865	24.5(0.3) ^c
$P(p-ClC_6H_4)_3$	$[(p-ClC_6H_4)_3P]_2Fe(CO)_3$	1893	$25.0(0.1)^d$
$P(p-FC_6H_4)_3$	$[(p-FC_{6}H_{4})_{3}P]_{2}Fe(CO)_{3}$	1891	$25.8(0.2)^d$
$P(C_6H_5)_3$	$[(C_6H_5)_3P]_2Fe(CO)_3$	1887	26.9(0.2) ^c
$P(p-CH_3C_6H_4)_3$	$[(p-CH_{3}C_{6}H_{4})_{3}P]_{2}Fe(CO)_{3}$	1884	$28.2(0.3)^d$
$P(p-CH_3OC_6H_4)_3$	$[(p-CH_3OC_6H_4)_3P]_2Fe(CO)_3$	1882	$30.1(0.2)^d$
PPh ₂ Me	(Ph ₂ MeP) ₂ Fe(CO) ₃	1878	34.1(0.3) ^c
PPhMe ₂	$(PhMe_2P)_2Fe(CO)_3$	1875	37.3(0.3) ^c
PMe ₃	$(Me_3P)_2Fe(CO)_3$	1871	38.9(0.2)°
P ⁿ Bu ₃	$(^{n}Bu_{3}P)_{2}Fe(CO)_{3}$	1865	41.7(0.3) ^c
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 11. ^{*d*} This work.

recorded using this procedure. Conversion to trans-(P(p-CF_3C_6H_4)_3)_2Fe(CO)_3 was found to be quantitative under these reaction conditions. The enthalpy of reaction, -15.9 ± 0.1 kcal/mol, represents the average of five individual calorimetric determinations.

Calorimetric Determination of the Enthalpy of Solution of $(BDA)Fe(CO)_3$ in THF. In order to consider all species in solution, the enthalpy of solution of 1 had to be directly measured. The calorimeter cells were loaded in the exact fashion as in the example described above, with the exception that no ligands were introduced in the reaction cell. The measured enthalpy is 6.5 ± 0.1 kcal/mol and represents seven separate determinations. To ensure that no decomposition had occurred during the thermal equilibration at 50 °C, a THF solution of $(BDA)Fe(CO)_3$ was maintained at 50 °C for 3 h; the solvent was then removed and the residue examined by NMR and IR spectroscopy. Both analytical techniques clearly showed the complex to have remained intact during this thermal treatment.

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. In the present study, a series of isosteric tertiary phosphine ligands were investigated by batch solution calorimetry:

$$(BDA)Fe(CO)_{3} + 2P(p-XC_{6}H_{4})_{3} \xrightarrow{THF} trans-(P(p-XC_{6}H_{4})_{3})_{2}Fe(CO)_{3} + BDA (8)$$

All reactions investigated led to a unique product under the calorimetric conditions as determined by infrared and NMR spectroscopy. A list of all enthalpies of reaction involving para-substituted triphenylphosphine ligands is provided in Table 1. All reported enthalpies of reaction are solution-phase values and take into account the enthalpy of solution of (BDA)Fe-(CO)₃ (6.5 \pm 0.1 kcal/mol).

Discussion

With the exception of the few thermodynamic investigations reported by Muetterties¹⁹ and Connor,²⁰ thermodynamic information focusing on organoiron systems remains scarce. The $(BDA)Fe(CO)_3$ complex (BDA =PhCH=CHCOMe, benzylideneacetone) provides easy access to iron tricarbonyl complexes and thermochemical data, in view of the labile nature of the BDA ligand as illustrated by Angelici and co-workers,¹⁸ who have reported its usefulness as a synthon leading to high yields of (phosphine)tricarbonyliron complexes:

Ph
$$\rightarrow$$
 PPh₃
 \downarrow + 2PPh₃ $\xrightarrow{25 \circ C}$ CO \rightarrow CO \rightarrow EDA (9)
 \downarrow CO \rightarrow PPh₃
 \downarrow CO \rightarrow PPh₃
 \downarrow CO \rightarrow PPh₃
 \downarrow PPh₃
 \downarrow CO \rightarrow PPh₃
 \downarrow PPh₃

The labile 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.²¹

$$(BDA)Fe(CO)_3 +$$

We have recently reported the enthalpies of reaction of $(BDA)Fe(CO)_3$ with a series of mono- and bidentate ligands using solution calorimetry in THF at 50 °C according to eqs 11 and 12.¹¹

$$(BDA)Fe(CO)_{3} + 2L' \xrightarrow{\text{THF}}_{50 \text{ °C}} trans(L')_{2}Fe(CO)_{3}(PR_{3})_{2} + BDA (11)$$

L' = monodentate ligand

$$(BDA)Fe(CO)_{3} + L'' \xrightarrow{THF}_{50 \circ C} cis-(L'')Fe(CO)_{3}(PR_{3})_{2} + BDA \quad (12)$$

L'' = bidentate ligand

In the monodentate phosphine study, we have interpreted contributions of steric and electronic phosphine effects by using a relationship first proposed by Tolman and co-workers:⁵

$$-\Delta H^{\circ} = A_0 + A_1 \theta + A_2 \nu \tag{13}$$

where enthalpies of reaction are correlated to steric (θ , cone angle) and electronic (ν , A_2 carbonyl stretching frequency in Ni(CO)₃L (L = tertiary phosphine) factors. The A_1/A_2 ratio can be taken as a measure of the relative importance of steric versus electronic factors. It would be expected that steric factors play only a minor role in this iron system in view of the final trans arrangement

⁽¹⁹⁾ Putnik, C. F.; Welter, J. J.; Stucky, G. D.; D'Aniello, M. J.; Sosinsky, B. A.; Kirner, J. F.; Muetterties, E. L. J. Am. Chem. Soc. 1978, 100, 4107-4109.

 ^{(20) (}a) Brown, D. L. S.; Connor, J. A.; Leung, M. L.; Paz Andrade,
 M. I.; Skinner, H. A.; Zafarani-Moattar, M. T. J. Organomet. Chem.
 1976, 110, 79-89. (b)Connor, J. A.; Demain, C. P.; Skinner, H.
 A.; Zafarani-Moattar, M. T. J. Organomet. Chem. **1979**, 170, 117-130.

^{(21) (}a) Graham, C. R.; Scholes, G.; Brookhart, M. J. Am. Chem. Soc. 1977, 99, 1180-1188. (b) Brookhart, M.; Nelson, G. O. J. Organomet. Chem. 1979, 164, 193-202.



Figure 1. Carbonyl stretching frequency vs enthalpy of phosphine substitution reaction for $trans-(P(p-XC_6H_4)_3)_2$ -Fe(CO)₃ complexes (slope -2.21, R = 0.99).

of ligands. A value of 0.008 was calculated for the A_1/A_2 ratio and quantitatively denoted the overwhelming influence of electronic factors. Excellent relationships were established when the electronic factor was solely considered. However, this analysis dealt with phosphine ligands with varied steric demands and an examination of enthalpies of reaction as a function of electronic variations is warranted in order to shed light on the unique importance of this parameter in the present iron system.

A number of measureable properties reflect the electron donation of the phosphine ligands, and these can be examined in terms of possible relationships with the measured enthalpies of reaction listed in Table 1. Two different but equally useful approaches can be used. One can examine the overall electron donation from the phosphine to the metal by examining the carbonyl stretch associated with the bis(phosphine)iron tricarbonyl product. The CO stretch is notable for gauging such quantities.²² The amount of back-donation into CO as reflected by the position of the CO stretch is then a gauge of phosphine electron donation. In our preceding report on organoiron thermochemistry,^{11a} a relationship between carbonyl stretching frequencies and enthalpies of reaction was established and showed remarkable linearity. This is not entirely surprising, since the carbonyl stretching modes are directly influenced by the electronic donation provided by ancillary ligands allowing for modulation in the metal electron density available for back-donation to the CO groups. The overall effect seen in the present system is due to the electronic nature of phosphine ligand providing electron density that will account for the amount of back-donation to CO as reflected by the CO stretching frequency. A relationship exists (with an excellent fit, R = 0.99) between the enthalpy of reaction of phosphine ligands investigated in the present study and the carbonyl stretching frequency observed in the corresponding bis(phosphine)iron tricarbonyl product (Figure 1). All thermochemical data measured up to now can be included in order to test the general validity of such a relationship. The fit of the relationship is clearly indicative of the principal role played by the ligand electronic parameter in all complexes investigated (Figure 2).



Figure 2. Carbonyl stretching frequency vs enthalpy of phosphine substitution reaction in a series of trans-(L)₂Fe-(CO)₃ complexes (slope -1.50, R = 0.99).



Figure 3. Phosphine electronic parameter (χ) vs enthalpy of phosphine substitution reaction for a series of *trans*-(P(*p*-XC₆H₄)₃)₂Fe(CO)₃ complexes (slope -1.34, R = 0.99).

The second approach deals with the donating ligands themselves, in this case, the tertiary phosphine ligands. Recently, attempts have been made to extract information about the stereoelectronic factors influencing the thermodynamics and kinetics of reactions by quantitative analysis of ligand effects (QALE).²³ Steric and electronic ligand characteristics represent the foundation of a QALE treatment. Correlations obtained using this method oftentimes are linear and offer insights into structure and reactivity patterns. Such a treatment was performed for the present thermochemical data, only utilizing the electronic parameter, and results are graphically represented in Figure 3.

As can be clearly seen, since the series of tertiary phosphine ligands is isosteric, only the electronic parameter will be the origin of any variations in measured enthalpies of reaction. Enthalpies of reaction correlate in a linear fashion with the ligand electronic parameter (χ) .²³ Here it can be seen that a difference of some 8 kcal/mol results from modifying the electronics of the para-substituted group on the triphenylphosphine phenyl group. This effect is substantial when considering the stereoelectronic range of phosphine ligands previ-

⁽²²⁾ Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science: Mill Valley, CA, 1987.

^{(23) (}a) Fernandez, A. L.; Prock, A.; Giering, W. P. Organometallics 1994, 13, 2767–2772 and references cited therein. (b) Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. Organometallics 1990, 9, 1758–1766.



Figure 4. Hammett σ_p parameter vs enthalpy of phosphine substitution reaction for a series of *trans*-(P(p-XC_6H_4)_3)_2Fe(CO)_3 complexes (slope -0.11, R = 1.00).

ously studied in this system, which lead to a total enthalpy scale spanning some 20 kcal/mol.¹¹ This 8 kcal/mol range clearly illustrates the importance of electronic ligand parameters in the present system. Table 1 lists all enthalpies of reactions measured with corresponding carbonyl stretching frequencies for all trans-(PR₃)₂Fe(CO)₃ complexes so far investigated by solution calorimetry.

An alternative to the QALE treatment is possible in this study of isosteric phosphines if the overall donor properties of the phosphine can be regarded as depending solely on the electronic nature of the para substituent on the aryl fragment. This brings to mind an LFER (linear free energy relationship) treatment.²⁴ Such a simple correlation can be established with remarkable fit (R = 1.00). It is then concluded that the para substituent on the phosphine aryl group is entirely responsible for the modulation in enthalpy of ligand substitution reaction within the present series.

Angelici and co-workers have recently reported on the enthalpies of protonation of $trans-(PR_3)_2Fe(CO)_3$ complexes¹⁸ (eq 14). In their study, the investigators were

$$trans-Fe(CO)_{3}(PR_{3})_{2} + CF_{3}SO_{3}H \xrightarrow{DCE} \\ HFe(CO)_{3}(PR_{3})_{2}^{+}CF_{3}SO_{3}^{-} (14)$$

principally interested in gauging the metal basicity as a function of ancillary ligation. Having established that electronic parameters were of utmost importance in the present $trans \cdot ((p-X-C_6H_4)_3P)_2Fe(CO)_3$ system, comparison with the measured enthalpies of protonation should shed light on whether ligand electronic characteristics in the form of enthalpies of ligand substitution also correlate with heats of protonation. The relationship shows a good fit, and it may therefore be concluded that phosphine electronic contributions also affect the magnitude of enthalpies of protonation and therefore metal basicity.

The magnitude of the reported enthalpy values provide insight into reactivity patterns. The $(PPh_3)_2Fe (CO)_3$ complex has previously been found to possess one



Figure 5. Enthalpy of protonation vs enthalpy of phosphine substitution reaction in a series of *trans*-(P(p-XC₆H₄)₃)₂Fe(CO)₃ complexes (slope 0.73, R = 0.98).

of the weakest Fe-PR₃ bonds. With the present data, we see that the Fe-P bond can be further destabilized by appending an electron-withdrawing para substituent on the phenyl ring of the triphenylphosphine ligands. This has a net effect of weakening the Fe-P bond by some 2 kcal/mol compared to the Fe-PPh₃ bond. This also means that any substitution reaction that can be carried out from the *trans*-(PPh₃)₂Fe(CO)₃ complex will prove more exothermic by some 4.5 kcal/mol if it is carried out instead from the *trans*-($(p-CF_3C_6H_4)_3P)_2Fe$ (CO)₃ complex (eqs 15 and 16) and conversely, of course,

$$trans - (PPh_3)_2 Fe(CO)_{3(soln)} + 2PMe_{3(soln)} \xrightarrow{THF} trans - (PMe_3)_2 Fe(CO)_{3(soln)} + 2PPh_{3(soln)} (15)$$

$$\Delta H_{
m calcd} = -12.0 \pm 0.3 \;
m kcal/mol$$

$$trans - (P(p-CF_{3}C_{6}H_{4})_{3})_{2}Fe(CO)_{3(soln)} + 2PMe_{3(soln)} \frac{THF}{50 \circ C} trans - (PMe_{3})_{2}Fe(CO)_{3(soln)} + 2P(p-CF_{3}C_{6}H_{4})_{3(soln)} (16)$$

$$\Delta H_{\text{calcd}} = -16.5 \pm 0.4 \text{ kcal/mol}$$

any substitution reaction carried out from the *trans*- $(PPh_3)_2Fe(CO)_3$ complex will prove more exothermic by some 3.2 kcal/mol than if it were carried out from the *trans*- $((p-CH_3OC_6H_4)_3P)_2Fe(CO)_3$ complex (eqs 17 and 18).

$$trans-(PPh_{3})_{2}Fe(CO)_{3(soln)} + 2PEt_{3(soln)} - \frac{THF}{50 \circ C}$$
$$trans-(PEt_{3})_{2}Fe(CO)_{3(soln)} + 2PPh_{3(soln)} (17)$$

$$\Delta H_{
m calcd} = -15.5 \pm 0.3$$
 kcal/mol

$$trans-(P(p-CH_{3}OC_{6}H_{4})_{3})_{2}Fe(CO)_{3(soln)} + 2PEt_{3(soln)} \frac{THF}{50 \circ C} trans-(PEt_{3})_{2}Fe(CO)_{3(soln)} + 2P(p-CH_{3}OC_{6}H_{4})_{3(soln)} (18)$$

$$\Delta H_{
m calcd} = -12.3 \pm 0.3$$
 kcal/mol

Conclusion

The reported solution calorimetric investigation represents the first detailed thermochemical study of ligand

^{(24) (}a) Wells, P. R. Linear Free Energy Relationships; Academic Press: New York, 1968. (b) Charton, M. Prog. Org. Chem. 1973, 10, 81-204. (c) March, J. Advanced Organic Chemistry; Wiley-Interscience: New York, 1992; pp 278-286.

substitution reactions involving isosteric tertiary phosphine ligands for an organometallic system. The results allow for a quantitative evaluation of electronic effects in the present iron system. The present iron tricarbonyl system allows for simple relationships to be established between enthalpies of reaction and a variety of quantitative factors reflecting the overall electronic effect of phosphine binding. Excellent correlations are established with the carbonyl stretching frequency of the product, the phosphine electronic parameter χ , and the Hammett σ parameters associated with the phenyl para substituent of triphenylphosphine ligands. An excellent correlation is established with all enthalpy data vs carbonyl stretching frequency. This fact clearly illustrates the major role of the electronic contribution in the present system. The degree of variation observed in enthalpies of reaction as a function of simple modification in para-substituted triphenylphosphine ligands shows important insights into reactivity fine tuning. Studies focusing on the enthalpic contributions of other ligands in this and related systems are presently underway.

Acknowledgment. The National Science Foundation (Grant No. CHE-9305492) and the Louisiana Education Quality Support Fund are gratefully acknowledged for support of this research. The Louisiana Board of Regents is also acknowledged for allocating funds allowing the purchase of the FT-IR spectrophotometer (Grant No. ENH-TR-41, 1993-1994).

OM9407823