2410 *Inorg. Chem.* **1993**, *32*, 2410–2415

Enthalpies of Reaction of (Diene)- and (Enone)iron Tricarbonyl Complexes with Monodentate and Bidentate Ligands. Solution Thermochemical Study of Ligand Substitution in the $L_2Fe(CO)_3$ Complexes

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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 mono- and multidentate ligands, leading to the formation of $(\eta^4\text{-}L)Fe(CO)_3$, $(L')_2Fe(CO)_3$, and $(L'')Fe(CO)_3$ complexes (L = diene, enone; L′ = monodentate arsines; L″ = bidentate ligands), have been measured by solution calorimetry in THF at 50 °C. The range of reaction enthalpies spans some 44 kcal/mol. The overall relative order of stability established is as follows: for monodetate ligands, $AsPh_3 < AsEt_3 <$ tertiary phosphine; for bidentate phosphine and arsine ligands, dppm < arphos < dmpm < dppb < dppv < dppp < dppe < dmpe < dcpe < depe; for dienes and enones, benzylideneacetone < chalcone < cyclooctatetraene < cyclohexadiene. These thermodynamic data help to establish a relative order of complex stability for these compounds in the iron tricarbonyl system. These data allow the calculation of the enthalpy associated with the geometric isomerization process (axial–equatorial/diaxial) present in the $(L')_2Fe(CO)_3$ system (5.4 ± 0.5 kcal/mol) as well as for a quantitative analysis of ring strain energies in the $(L'')Fe(CO)_3$ system. The four-membered metallacycle is the only cyclic structure exhibiting significant strain energy (12.6 kcal/mol). Comparisons with other organometallic systems and insight into factors influencing the Fe–L bond disruption enthalpies are also discussed.

Introduction

The field of organometallic thermochemistry has gained recognition as one of great relevance to catalysis.[1] Such valuable investigations have lead to a better understanding of bonding and reactivity patterns in a small number organometallic systems.[2,3] These studies have also proven powerful tools in predicting the thermodynamic feaibility 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 of research remains one where few complete investigations have been performed. It is also surprising to notice that almost no information is available on the metal–ligand bond energetics in iron carbonyl systems considering their common use in organic chemistry as diene protecting groups[5] and important function as diene isomerization catalysts.[6] In an effort to remedy this situation, we have initiated a program of organometallic thermochemistry which has, so far, focused on organo–group 8 systems.[7,8]

Tertiary phosphines and chelating tertiary diphosphines have been widely used as ligands in organometallic chemistry.[9] Kinetic, catalytic, and structural studies have been conducted on such complexes.[10] 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. Manzer and Tolman[11] have reported the solution calorimetry of square-planar platinum(II) complexes, shown in eq 1, for a series

$$\textit{trans-}[CH_3PtQ_2(THF)]^+ + PR_3 \rightarrow \textit{trans-}[CH_3PtQ_2(PR_3)]^+ + THF \quad (1)$$

$$Q = P(CH_3)_2Ph$$

of phosphine ligands. A similar series was then investigated for Ni(0) complexes[12] shown in eq 2. Detailed thermochemical

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

investigations of two related Mo(0) systems have been reported by Hoff and co-workers.[13]

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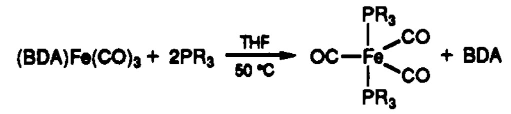
$$(arene)Mo(CO)_3 + 3PR_3 \rightarrow fac\text{-}(PR_3)_3Mo(CO)_3 + arene \quad (3)$$

$$(NBD)Mo(CO)_4 + 2PR_3 \rightarrow cis\text{-}(PR_3)_2Mo(CO)_4 + NBD \quad (4)$$

NBD = norbornadiene

Recently, we have reported a solution thermochemical study of monodentate tertiary phosphine (PR_3) substitution in the $(L')_2Fe(CO)_3$ complexes where PR_3 ligands occupy diaxial positions.[7]



$$(BDA)Fe(CO)_3 + 2PR_3 \xrightarrow[50\,°C]{THF} OC{-}\underset{PR_3}{\overset{PR_3}{Fe}}(CO)_2 + BDA \quad (5)$$

In the present contribution, we extend our work on solution thermochemistry of group 8 complexes and report on the relative metal–ligand bond enthalpies for mono- and bidentate ligands in the iron tricarbonyl system ($-Fe(CO)_3$). In addition to extending our previous contribution on monodentate ligands (L′), we report an extensive study of the chelate ring size effect of bidentate phosphine ligands (L″) and their influence on organoiron complex stability. The related studies of monodentate and bidentate ligands allow, for the first time, the determination of the enthalpy associated with the geometric isomerization process in $(L')_2Fe(CO)_3$ complexes. These data also allow for comparison with other organometallic systems and give important insights into iron-based processes.

Experimental Section

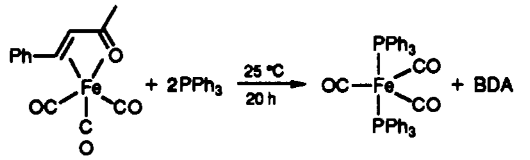
General Considerations. All manipulations involving organoiron complexes were performed under inert atmospheres of argon or nitrogen using standard high-vacuum or Schlenk tube techniques, or in a Vacuum/Atmospheres glovebox containing less than 1 ppm oxygen and water. Ligands were purchased from Strem 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 complexes $(BDA)Fe(CO)_3$ (**1**),[14] $(Chalcone)Fe(CO)_3$ (**2**),[14] and $(COT)Fe(CO)_3$ (**3**)[15] were synthesized according to literature procedures. 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.[16,17] 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[18] or the enthalpy of solution of KCl in water.[19] The experimentally determined enthalpies for these two standard calibration reactions are the same within experimental error to literature values. This calorimeter has been previously described,[20] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits. The enthalpy of solution of $(BDA)Fe(CO)_3$ (6.5 ± 0.2 kcal/mol) has been reported.[12]

Calorimetric Measurement for Reaction of $(BDA)Fe(CO)_3$ and DPPE. 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, and it was closed and sealed with 1.5 mL of mercury. A 4-mL volume of a stock solution of diphos [1g of DPPE (bis(diphenylphosphino)ethane) 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 calorimeter was inverted thereby allowing the reactants to mix. After the reaction had 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 $(diphos)Fe(CO)_3$ was found to be quantitative under these reaction conditions. The enthalpy of reaction, −21.9 ± 0.1 kcal/mol, represents the average of five individual calorimetric determinations. This methodology represents a prototypical procedure involving all organometallic compounds and all reactions investigated in the present study.

Calorimetric Measurement of the Enthalpy of Solution of $(Chalcone)Fe(CO)_3$ (2) and $(COT)Fe(CO)_3$ (3) in THF. In order to consider all species in solution, the enthalpies of solution of **1** and **2** had to be directly measured. This was performed by using a procedure similar to the one described above with the exception that no ligand was added to the reaction cell. After the calorimeter had returned to thermal equilibrium, the solutions were examined by IR, which showed the organometallic compound to be the only product present. Enthalpies of solution represent the average of five individual determinations and are 3.4 ± 0.2 kcal/mol for $(Chalcone)Fe(CO)_3$ and 5.1 ± 0.1 kcal/mol for $(COT)Fe(CO)_3$.

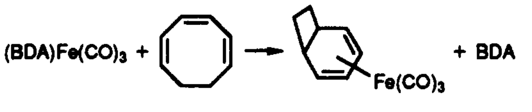
Results

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 by Angelici and co-workers,[16] who have used this complex as an efficient source of $Fe(CO)_3$.



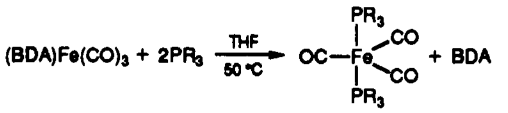
(6)

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]



(7)

We have recently reported the enthalpies of reaction of monodentate tertiary phosphines with the $(BDA)Fe(CO)_3$ complex,[7] as illustrated in eq 8. We now extent this work to arsenic donors. All results for monodentate ligands are summarized in Table I.



$$(BDA)Fe(CO)_3 + 2PR_3 \xrightarrow[50\,°C]{THF} OC{-}\underset{PR_3}{\overset{PR_3}{Fe}}(CO)_2 + BDA \quad (8)$$

PR_3 = tertiary phosphine

The enthalpies of reaction of $(BDA)Fe(CO)_3$ with a series of bidentate phosphine and mixed phosphine/arsine ligands have been measured using solution calorimetry in THF at 50 °C

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

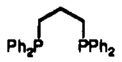
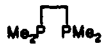
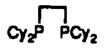
$$\mathrm{BDAFe(CO)_3(soln)} + 2\mathrm{L'(soln)} \xrightarrow[50\,^{\circ}\mathrm{C}]{\mathrm{THF}} \mathrm{(L')_2Fe(CO)_3(soln)} + \mathrm{BDA(soln)}$$

L′	complex	ν_{CO} (cm^{-1})^a	$-\Delta H_{reac}$^{b}
$AsPh_3$	$(AsPh_3)_2Fe(CO)_3$	1886	10.2(0.2)^c
$AsEt_3$	$(AsEt_3)_2Fe(CO)_3$	1865	24.5(0.3)^c
PPh_3	$(PPh_3)_2Fe(CO)_3$	1887	26.9(0.3)^d
PPh_2Me	$(PPh_2Me)_2Fe(CO)_3$	1878	34.1(0.3)^d
$PPhMe_2$	$(PPhMe_2)_2Fe(CO)_3$	1875	37.3(0.3)^d
PMe_3	$(PMe_3)_2Fe(CO)_3$	1871	38.9(0.2)^d
P^nBu_3	$(P^nBu_3)_2Fe(CO)_3$	1865	41.7(0.3)^d
PEt_3	$(PEt_3)_2Fe(CO)_3$	1867	42.4(0.2)^d

^{a} Infrared spectra were recorded in THF. ^{b} Enthalpy values are reported with 95% confidence limits. ^{c} This work. ^{d} Taken from ref 7.

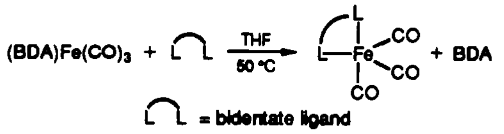
Table II. Enthalpies of Substitution (kcal/mol) in the Reaction

$$\mathrm{BDAFe(CO)_3(soln)} + \mathrm{P{\frown}P(soln)} \xrightarrow[50\,^{\circ}\mathrm{C}]{\mathrm{THF}} \mathrm{(P{\frown}P)Fe(CO)_3(soln)} + \mathrm{BDA(soln)}$$

$P{\frown}P$		ν_{CO} (cm^{-1})^a	$-\Delta H_{reac}$^{b}
dppm		1984, 1913, 1907	16.3(0.2)
arphos		1983, 1915, 1897	20.7(0.2)
dmpm		1977, 1901, 1890	23.3(0.2)
dppb		1983, 1912, 1886	24.7(0.2)
dppv		1989, 1922, 1906	27.2(0.2)
dppp		1984, 1914, 1888	28.1(0.2)
dppe		1985, 1917, 1898	28.4(0.2)
dmpe		1976, 1902, 1887	35.2(0.3)
dcpe		1970, 1895, 1880	35.8(0.3)
depe		1975, 1901, 1885	37.2(0.3)

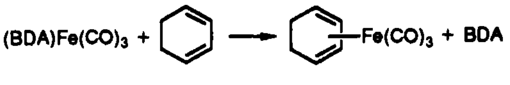
^{a} Infrared spectra were recorded in THF. ^{b} Enthalpies of reaction are reported with 95% confidence limits.

according to eq 9. The experimental enthalpies of reaction of (BDA)Fe(CO)$_3$ with chelating diphosphines are presented in Table II.



(9)

The enthalpies of reaction of selected dienes and enones have been investigated by solution calorimetry in THF at 50 °C using one of two reaction pathways. The first represents a direct substitution for the BDA ligand in (BDA)Fe(CO)$_3$ by cyclohexadiene (C_6H_8) leading to the formation of (C_6H_8)Fe(CO)$_3$ (eq 10). This direct replacement reaction was tested for a series of diene and enone but did not prove a general route leading to quantitative conversion of (BDA)Fe(CO)$_3$ to (diene)- or (enone)-Fe(CO)$_3$ complexes. In order to obtain thermodynamic results on other dienes and enones, reaction of the (diene or enone)-Fe(CO)$_3$ complexes with tertiary phosphine ligands had to be investigated by solution calorimetry.



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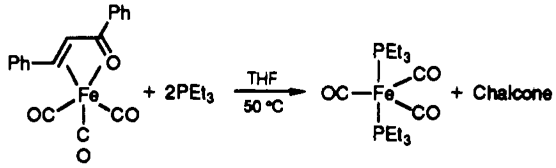

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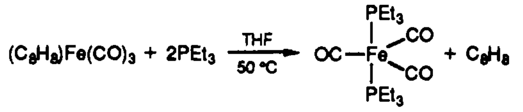

(12)

These reactions have proven to be quantitative for the dienes and enones examined. Enthalpies of reaction associated with these complexes are reported in Table III. All reported enthalpies of reaction are solution phase values and take into account the enthalpy of solution of (BDA)Fe(CO)$_3$.[7]

Discussion

With the exception of the few thermodynamic investigations reported by Muetterties[22] and Connor,[23] thermodynamic information focusing on organoiron systems remains scarce. In this section, thermochemical data for monodentate ligands are first presented. The chelate size, basicity, and substituent steric effects of bidentate ligands on the Fe–L bond disruption enthalpy are then addressed. Ligand types and ligation modes are initially addressed in order to set the ground work for a presentation of the thermodynamic factors involved in "ring strain" and ligand isomerization. The enthalpy scale established in this study allows for comparisons, on a relative scale, with other organometallic systems.

Monodentate Phosphines and Arsines 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 13. The isolated product exhibits a diaxial geometry arrangement of phosphine ligands. Infrared spectroscopy performed immediately after calorimetry showed the diaxial isomer to be the sole product formed. We were interested in finding out if the trend observed in other systems concerning the weaker binding ability of tertiary arsenic donors as compared to their phosphorus parent was also valid for the present system. We therefore investigated the enthalpy of ligands substitution for two tertiary arsines ($AsEt_3$ and $AsPh_3$), and indeed these prove to be weaker binders to iron as well. The order of stability $PR_3 > AsR_3$ present in the $(L')_2Fe(CO)_3$ system appears to be a trend for metal carbonyl complexes, since this same relative order is observed for *fac*-$(L')_3Mo(CO)_3$ and *cis*-$(L')_2Mo(CO)_4$ complexes.[2b,13b] In the iron system, the arsine ligand proves to

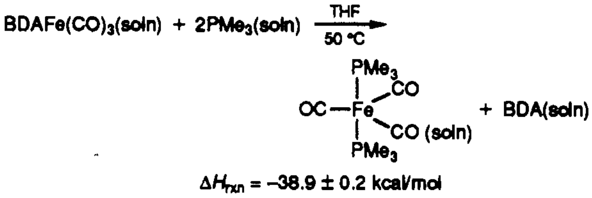

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Table III. Enthalpies of Substitution (kcal/mol) in the Reaction

$$\mathrm{BDAFe(CO)_3(soln) + Diene(soln) \xrightarrow[50\,°C]{THF} (Diene)Fe(CO)_3(soln) + BDA(soln)}$$

Diene = diene or enone

Diene	complex	ν_{CO} (cm^{-1})[a]	$-\Delta H_{soln}$[b]	$-\Delta H_{reac}$[b]
$PhCH{=}CHCOCH_3$	$(BDA)Fe(CO)_3$	2064, 2000, 1984	6.5(0.1)	0
$PhCH{=}CHCOPh$	$(Chal)Fe(CO)_3$	2064, 2002, 1984	3.4(0.2)	4.9(0.3)
C_8H_8	$(C_8H_8)Fe(CO)_3$	2048, 2002, 1984	5.1(0.1)	16.9(0.3)
C_6H_8	$(C_6H_8)Fe(CO)_3$	2041, 1968		29.0(0.6)

[a] Infrared spectra were recorded in THF. [b] Enthalpies are reported with 95% confidence limits.

lead to metal–ligand bonds some 18 kcal/mol weaker than phosphine ligands. As previously noted, the nature of the ligand substituent appears to have a profound effect on its donating ability.[5] The difference in enthalpies of substitution between PEt_3 and PPh_3 is 15.5 kcal/mol. This difference is the same within experimental error as the one calculated in the *cis*-$(L')_2Mo(CO)_4$ system (15.0 kcal/mol). This substitution effect is also present for arsine ligands. The difference in enthalpies of substitution between $AsEt_3$ and $AsPh_3$ is 14 kcal/mol in the iron system. This value compares to one of 9.2 kcal/mol for the *cis*-$(L')_2Mo(CO)_4$ system. This difference appears to be regulated by a balance of both steric and electronic effects. In the molybdenum system, the cis arrangement leads to enhanced steric repulsion between adjacent arsine ligands inhibiting the complete donating ability of the arsine, resulting in a diminished enthalpic contribution (weaker M–As bond). In the diaxial $(L')_2Fe(CO)_3$ system, however, no such steric repulsion is present and the electronic factor contribution, representing the electron-donating ability of the ligand, comprises the major factor affecting the strength of the bonding interaction.[7]

Bidentate Phosphine Ligands and Ring Strain Energies. Bidentate ligands have been thoroughly investigated and have been shown to play an important role in catalysis.[24,25] The enthalpies of bidentate ligand replacement reactions for the present system are listed in Table II. It should first be noted that, as in the case of monodentate ligands, the arsine containing ligand is more weakly bound to the metal center than the related diphosphine ligand. The difference between enthalpies of reaction involving arphos (20.7 kcal/mol) and its diphosphine analog, DPPE (28.4 kcal/mol), results in a difference in Fe–P vs Fe–As bond enthalpy of 7.7 kcal/mol. Reaction of $(BDA)Fe(CO)_3$ with chelating diphosphines leads to the formation of metallacycles. Such complexes have been examined by solution calorimetry by Hoff and co-workers for the tetracarbonyl molybdenum(0) system.[13b] These investigators have found that the enthalpies of binding of bidentate ligands could be calculated from their monodentate counterparts and that any deviations from these estimates were attributable to "ring strain energy".[13] Ring strain estimates for four-, five- and six-membered organic rings are on the order of 26, 6, and 0 kcal/mol, respectively.[26] Incorporation of metal-containing fragment in such organic structures lead to generation of four- to seven-membered metallacycles (eq 14). These complexes for the series $Ph_2P(CH_2)_nPPh_2$ (n = 1–4) with their appropriate enthalpic contributions are presented in Figure 1. The five- and six-membered rings are most stable. The seven-membered metallacycle is less thermodynamically stable, as illustrated by the measured enthalpy of reaction. Only for the four-membered system is a significant ring strain observed (12.6 kcal/mol). This is on the same order of magnitude as estimates for a thorium metallacyclobutane complex (10 kcal/mol)[27] and closely related to the four-membered organomolybdenum complex $(Ph_2PCH_2PPh_2)Mo(CO)_4$ (8.3 kcal/mol).[13b]

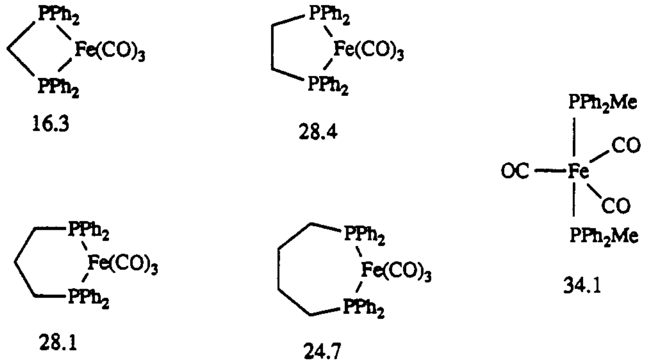
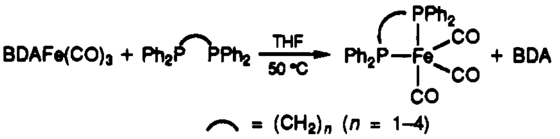


Figure 1. Relative stabilities (kcal/mol) for $[Ph_2P(CH_2)_nPPh_2]Fe(CO)_3$ complexes (n = 1–4).



(14)

Axial–Equatorial/Diaxial Isomerization Process. Isomerization processes involving small phosphines in other organometallic systems appear to constitute a minor contribution to the overall complex stability.[28] An estimate of the enthalpy associated with geometric isomerization processes was determined in order to assess whether this was also true for the present system. Although the substitution reaction of BDA with two phosphine ligands only yields the diaxial isomer, under the experimental conditions, the overall reaction can be viewed as occurring in two steps,[29] illustrated in eq 15. In step j, the phosphine ligands reside in the same sites previously occupied by the outgoing BDA ligand. In step ii, the isomerization from an axial/equatorial to a diaxial arrangement of phosphine ligands proceeds. This preference for the diaxial ligand orientation has previously been explained in terms of electronic effects.[30] To date, the thermodynamics involved is such a fundamental process as the axial–equatorial/

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(24) See for example: (a) 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. (b) Shin-ichi, I.; Takaya, H.; Tani, K.; Otsuka, S.; Sato, T.; Noyori, R. *J. Am. Chem. Soc.* **1990**, *112*, 4897–4905 and references cited. (c) Noyori, R.; Ohkuma, T.; Kitamura, M.; Takaya, H.; Sayo, N.; Kumobayahki, H.; Akutagawa, S. *J. Am. Chem. Soc.* **1987**, *109*, 5856–5857.

(25) Brunner, H. In *The Chemistry of the Metal-Carbon Bond*; Harley, F. R., Patai, S., Eds.; J. Wiley & Sons: New York, 1989; pp 109–146.

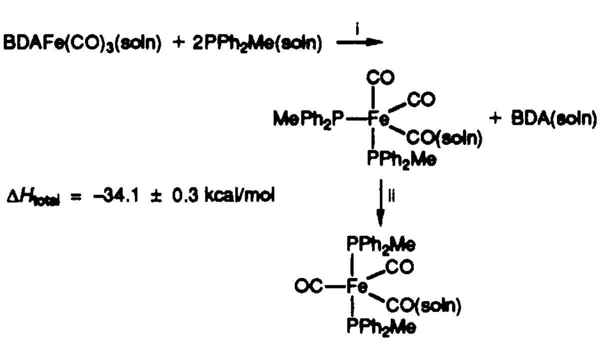
(26) Cox, J. D. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

(27) Bruno, J.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824–6832.

(28) (a) Darensbourg, D. *Inorg. Chem.* **1979**, *18*, 14–17. (b) Darensbourg, D.; Graves, A. *Inorg. Chem.* **1979**, *18*, 1257–1261. (c) Cotton, F. A.; Darensbourg, D. J.; Klein, S.; Kolthammer, B. W. *Inorg. Chem.* **1982**, *21*, 294–299. (d) Cotton, F. A.; Darensbourg, D. J.; Klein, S.; Kolthammer, B. W. *Inorg. Chem.* **1982**, *21*, 2661–2666.

(29) We recognize that this isomerism may not be a simple case. Some discussions about ring strain in iron tricarbonyl systems have been presented. For seven- and nine-membered metallacycles incorporating strained components to the chelating phosphine, see: Casey, C. P.; Whiteker, G. T.; Campana, C. F.; Powell, D. R. *Inorg. Chem.* **1990**, *29*, 3376–3381 and references cited.

(30) Rossi, A. R.; Hoffman, R. *Inorg. Chem.* **1975**, *14*, 365–373.



ΔH_{total} = −34.1 ± 0.3 kcal/mol (15)

diaxial isomerization for the present system had not been experimentally addressed. Using the available thermodynamic data, an estimate for the enthalpy associated with this isomerization can be calculated. The estimate is based on enthalpy of strain energy data and enthalpies of substitution for monodentate phosphine ligands. The five- and six-membered metallacyles are of similar energies (see Figure 1) and are taken, as in the molybdenum system, to have a small ring strain energy contribution.[31] It then follows that the (dppe)Fe(CO)$_3$ complex is very similar in energy to the hypothetical axial/equatorial (L′)$_2$Fe(CO)$_3$ isomer. However, the total enthalpy of substitution leading to the diaxial (L′)$_2$Fe(CO)$_3$ isomer, for the monodetate PPh$_2$Me ligand, is −34.1 ± 0.3 kcal/mol. We take the difference between the enthalpies of reaction leading to the formation of the (dppe)Fe(CO)$_3$ and (PPh$_2$Me)$_2$Fe(CO)$_3$ complexes (−5.7 ± 0.5) to equal the enthalpy involved in the isomerization process (step ii in eq 15). If a similar treatment is carried out with the monodentate PEt$_3$ and chelating Et$_2$PCH$_2$CH$_2$PEt$_2$ ligands, an enthalpy of −5.2 ± 0.5 kcal/mol is calculated for the enthalpy of isomerization. These two values are identical within experimental error, and we take the average value of 5.4 ± 0.5 kcal/mol to represent the enthalpy associated with the axial–equatorial/diaxial isomerization process in the (L′)$_2$Fe(CO)$_3$ system.

(Diene)- and (Enone)Fe(CO)$_3$ Complexes. Two different routes have been used in order to the determine Fe–diene, Fe–enone enthalpies of reaction (eqs 11 and 12). From the enthalpies reported in Table III, dienes appear to be more strongly bound to the iron center than the enones. These data, for the first time, quantitatively explain results obtained by Brookhart and coworkers[21] in their investigations of (BDA)Fe(CO)$_3$ as a diene trapping agent. It is now apparent that the driving forces behind these reactions include a large enthalpic component. A particularly relevant reactivity study by this group is the competition experiments of cyclohexadienes with (BDA)Fe(CO)$_3$. The Fe(CO)$_3$ moiety favors the cyclohexadienes over BDA. This reaction is rapid and quantitative and was directly employed to obtain solution calorimetric information.

$$(\text{BDA})\text{Fe(CO)}_3(\text{soln}) + \text{C}_6\text{H}_8(\text{soln}) \xrightarrow[50\,^\circ\text{C}]{\text{THF}} (\text{C}_6\text{H}_8)\text{Fe(CO)}_3(\text{soln}) + \text{BDA}(\text{soln}) \quad (16)$$

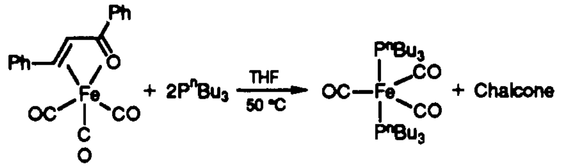
$$\Delta H_{\text{rxn}} = -29.0 \pm 0.6 \text{ kcal/mol}$$

The present data also support a proposed mechanistic pathway for substitution patterns involving (BDA)Fe(CO)$_3$.[21] Cardaci and Sorriso[32] have investigated reactions leading to the isolation of (PhCH=CHCOMe)(L)Fe(CO)$_3$ complexes (L = PPh$_3$, AsPh$_3$, SbPh$_3$), where BDA is bound to Fe only through the olefin double bond of BDA, hinting at the weaker binding nature of the C=O fragment to iron.

$$(\eta^4\text{-BDA})\text{Fe(CO)}_3 + \text{SbPh}_3 \rightleftharpoons (\eta^2\text{-BDA})(\text{SbPh}_3)\text{Fe(CO)}_3 \quad (17)$$

$$\Delta H^{\ddagger} = -9 \text{ kcal/mol}, \ \Delta S^{\ddagger} = -26 \text{ cal/(mol deg)}$$

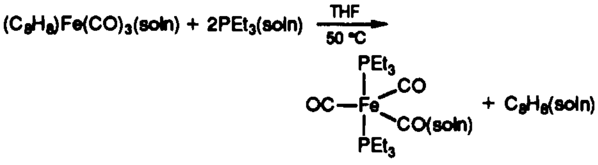
The availability of two different (enone)Fe(CO)$_3$ complexes (enone = BDA, Chalcone) allows for a verification of the self-consistency of the data in the present study. Reaction of (PhCH=CHOPh)Fe(CO)$_3$ (**2**) with P^{n}Bu$_3$ is illustrated in eq 18. The reaction of this ligand with (BDA)Fe(CO)$_3$ is exothermic by 41.7 kcal/mol. Using the enthalpies of reaction association with this phosphine ligand, the calculated difference between the two enone complexes, −4.8 ± 0.3 kcal/mol, compares very well with the difference calculated from the PEt$_3$ enthalpy values of −4.9 ± 0.3 kcal/mol and provides a check of the relative bond enthalpy data.



(18)

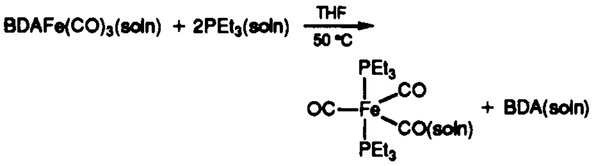
ΔH_{rxn} = −36.9 ± 0.3 kcal/mol

The other diene donor studied is cyclooctatetraene (COT). Direct substitution of this ligand for BDA was too slow to be investigated by solution calorimetry, even at 50 °C. A thermodynamic cycle was devised to extract the enthalpy of substitution value. The approach makes use of the rapid and quantitative reaction of the (COT)Fe(CO)$_3$ complex with phosphine donors, illustrated in eq 19. Subtraction of reaction 19 from reaction 20 leads directly to incorporation of the (COT)Fe(CO)$_3$ value in our relative study, eq 21. The absolute BDE value has been determined for the COT–Fe bond in the (COT)Fe(CO)$_3$ complex (**3**) by Connor and co-workers from high-temperature iodination reaction.[23b] This absolute value could serve as a possible anchor for this study, but we feel the assumptions made for the Fe–CO bond are not entirely justified in view of recent work.[33] We feel direct utilization of the enthalpies of reaction will provide more accurate and useful reaction enthalpy estimates.



(19)

ΔH_{rxn} = −25.5 ± 0.3 kcal/mol



(20)

ΔH_{rxn} = −42.4 ± 0.2 kcal/mol

$$\text{BDAFe(CO)}_3(\text{soln}) + \text{C}_8\text{H}_8(\text{soln}) \xrightarrow[50\,^\circ\text{C}]{\text{THF}} (\text{C}_8\text{H}_8)\text{Fe(CO)}_3(\text{soln}) + \text{BDA}(\text{soln}) \quad (21)$$

$$\Delta H_{\text{calcd}} = -16.9 \pm 0.3 \text{ kcal/mol}$$

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(31) The distorted tbp geometry of the (DIPHOS)Fe(CO)$_3$ complex hints at the existence of strain energy in the system. Therefore the isomerization enthalpy represents a lower limit for the enthalpy of isomerization. We thank one of the reviewers for bringing this point to our attention.

(32) Carcdaci, G.; Sorriso, S. *Inorg. Chem.* **1976**, *15*, 1242–1244.

(33) Sunderlin, L. S.; Wang, D.; Squires, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 2788–2796.

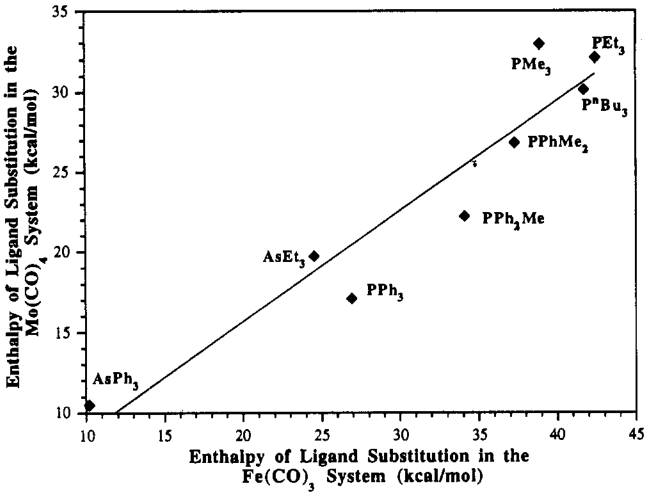

Figure 2. Enthalpies of reaction (kcal/mol) in the $(L')_2Fe(CO)_3$ versus $(L')_2Mo(CO)_4$ systems (L′ = monodentate ligand). $R = 0.95$; slope = 0.69.

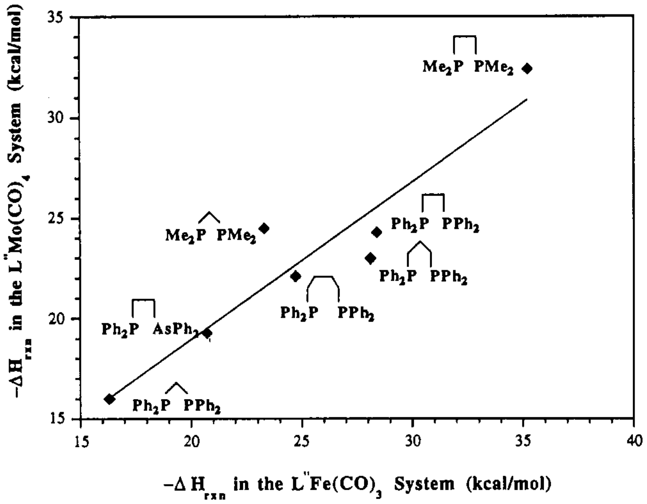

Figure 3. Enthalpies of reaction for the $(L'')Fe(CO)_3$ versus *cis*-(L'')-$Mo(CO)_4$ systems (L″ = bidentate ligand). $R = 0.94$; slope = 0.79.

Comparison with Other Organometallic Systems. A few qualitative comparisons between enthalpies of reactions have already been mentioned. We would like to expand on this and offer semiquantitative comparisons with other systems. The *cis*-$(L')_2Mo(CO)_4$ system shows important similarities with the diaxial $(L')_2Fe(CO)_3$ system. For all monodentate ligands investigated, a simple comparison of the relative enthalpies of reaction for the molybdenum and iron systems shows a very reasonable correlation (see Figure 2; $R = 0.95$). It appears that, in spite of the different geometric arrangement of ligands around the metal centers in the two systems, the importance of ligand electronic factors contributing to the overall enthalpy of substitution dominates. This can be quantified in terms of the respective A_1/A_2 ratios obtained in a treatment first proposed by Tolman,[9] where enthalpies of reaction are correlated to steric (θ, cone angle) and electronic (ν, A_1 carbonyl stretching frequency in $Ni(CO)_3L$, L = tertiary phosphine) factors.

$$-\Delta H^\circ = A_0 + A_1\theta + A_2\nu \qquad (22)$$

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 the iron system in view of the final diaxial arrangement of ligands. A value of 0.008 is calculated for the A_1/A_2 ratio and quantitatively denotes the overwhelming influence of electronic factors. This compares to a value of 0.81 for the $(L')_2Mo(CO)_4$ system, which exhibits a considerable reduction of the influence of steric factor when compared to the data for the parent $(L')_3Mo(CO)_3$ system ($A_1/A_2 = 1.42$).[2b] Examination of the slope of the plot in Figure 2 shows the Fe–L enthalpies of substitution appear to be somewhat less susceptible to ligand variation as indicated by smaller enthalpy changes associated with ancillary ligand perturbation.

A complete comparison with other organometallic systems is limited to the only other extensive study of ring strain energy for chelating ligands, namely that reported by Hoff and co-workers[13] for the molybdenum tetracarbonyl system. A simple relationship between the enthalpies of reaction leading to the formation of the molybdenum metallacycles and those experimentally measured for the organoiron system is presented in Figure 3. A proportionality of the data exists between the two systems ($R = 0.94$). This correlation points out thermodynamic parallels existing between the two series of compounds and could very well indicate the presence of similar factors governing relative bonding energetics in other transition metal carbonyl complexes.

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, ring strain energy values are assessed for four- to seven-membered metallacycles where the four-membered ring system appears to be the only metallacycle exhibiting any significant ring strain energy. For the first time, an enthalpic contribution association with an isomerization process in the $(L')_2Fe(CO)_3$ system has been evaluated. This energy is significant and helps explain in a quantitative thermodynamic sense the preference for the diaxial arrangement in this series of organoiron complexes. Comparisons with reported data for a molybdenum system sheds light on factors affecting relative metal–ligand binding preference that may be general for transition metal carbonyl complexes. Studies focusing on the enthalpic contributions of other ligands in this and related systems are presently underway.

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