three-channel spectrometer and a corresponding probe head are available. The figures presented in this work demonstrate how difficult assignments may be made by simple inspection of these 2D matrices.

Experimental Section

All spectra were recorded on a Bruker AMX-500 spectrometer at 300 K using a concentrated (50% v/v) sample of 1 in $CDCl_3$. A triple resonance probe head was used, which had a ^1H coil in inverse geometry; this coil was double tuned to ^{13}C at 125.76 MHz. A second multinuclear tunable coil was adjusted to ^{119}Sn at 186.4 MHz. The 2D spectra were taken for 1024 data points in F_2 and with 128 time increments in F_1 using relaxation delays of 2 s and 64 scans for each free induction decay. An exponential window in F_2 and a $\pi/3$ shifted squared sineball window in F_1 was applied. δ_{Sn} values are referred to external Me_4Sn; δ_C values were measured vs $CDCl_3$ and calculated with $\delta_{TMS} - \delta_{CDCl_3} = 77.0$ ppm.

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OM920299X

Enthalpies of Reaction of (Benzylideneacetone)iron Tricarbonyl, $(BDA)Fe(CO)_3$, with Phosphine Ligands. Thermodynamic Insights into Iron Chemistry

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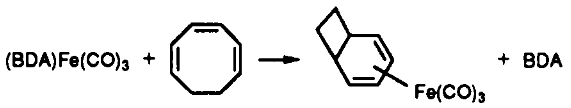
Summary: The enthalpies of reaction of $(BDA)Fe(CO)_3$ (BDA = benzylideneacetone) with a series of monodentate phosphine ligands (PR_3) leading to the formation of *trans*-$(PR_3)_2Fe(CO)_3$ complexes have been measured by solution calorimetry in THF at 50 °C. These enthalpy data help establish the following relative order of stability: $PEt_3 > P^nBu_3 > PMe_3 > PPhMe_2 > PPh_2Me > PPh_3$. The data span a range of 15 kcal/mol. This stability scale sheds light on the relative donating ability of phosphines. These data also allow comparison with other organometallic systems and give insight into factors influencing the Fe–PR_3 bond disruption enthalpies in the $(PR_3)_2Fe(CO)_3$ system.

Introduction

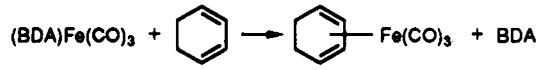
Phosphines are commonly used ligands in organometallic chemistry. Variations in the phosphorus coordination leads to a wide range of steric and electronic properties for the phosphine ligand and the metal center to which it is bonded.[1] These ligands have been used as catalyst modifiers in a number of systems, and their importance in homogeneous catalysis is well-known.[2] Numerous studies have been conducted on metal complexes having phosphines in their coordination sphere. However, relatively little is known of the bond energy requirement involved in metal–phosphine complexes.[3-5] Many approaches have been used to extract bond enthalpy terms out of organometallic systems.[6-8] These techniques range from the temperature variation of the equilibrium constant[7b] to photoacoustic calorimetry.[6c]

One system of great interest to us is the $(BDA)Fe(CO)_3$ (1) (BDA = benzylideneacetone) complex, which has been shown to be a readily available source of $Fe(CO)_3$, which has found synthetic application as a diene protecting group in organic chemistry.[9] Brookhart and co-workers have shown this organometallic moiety capable of stabilizing strained olefins[10] in reactions exemplified by eq 1. This



(1)

clearly is indicative of the high binding affinity of diene ligands for the $Fe(CO)_3$ moiety. It has also been shown that the $(BDA)Fe(CO)_3$ complex is an effective source of $Fe(CO)_3$ in the exchange reaction[11] illustrated in eq 2.



(2)

This synthetic route is the one of choice for it leads to the isolation of (diene)iron tricarbonyl complexes otherwise isolated in low yields from the iron carbonyls. A similar synthetic use of this readily available source of $Fe(CO)_3$ has recently been described in reactions of 1 with monodentate phosphines:[12]

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

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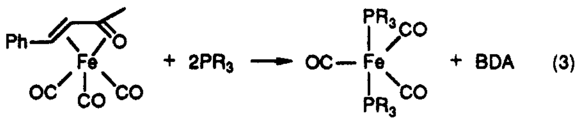
(11) Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. *Comprehensive Organometallic Chemistry*; Pergamon: New York, 1982; Chapter 58.


(3)

Nayak and Burkey have recently reported on the photochemistry of the $Fe(CO)_5$ and $Fe(CO)_4L/Fe(CO)_3L_2$ systems and illustrated the complexity of these systems, as a triplet state is readily accessible which leads to further substitution processes.[13] This factor represents a complication which will need to be addressed in order to investigate these systems by photoacoustic calorimetry (PAC). Angelici and co-workers have recently undertaken a solution calorimetric program focusing on the enthalpy of reaction associated with protonation of metal complexes.[12,14] These researchers have investigated the enthalpy of protonation of *trans*-$(PR_3)_2Fe(CO)_3$ complexes as illustrated in eq 4.

$$trans\text{-}Fe(CO)_3(PR_3)_2 + CF_3SO_3H \xrightarrow[25\ °C]{DCE} HFe(CO)_3(PR_3)_2{}^+CF_3SO_3{}^- \quad (4)$$

Although metal basicity information is useful, a more fundamental thermodynamic component, namely the strength of the metal–ligand bond, has not been measured in this system. In general, very little is known of the thermodynamics of organoiron systems.[6a,15] To remedy this situation, we have undertaken systematic thermochemical investigations of these systems in order to quantify thermodynamic parameters present in organoiron complexes. In the present contribution, we report a solution thermochemical study probing the influence of ligand basicity and sterics on the $Fe-PR_3$ bond disruption enthalpy in the $(PR_3)_2Fe(CO)_3$ system.

Experimental Section

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 1 was synthesized according to literature procedures[16] and recrystallized twice from hexane. Synthesis and characterization of phosphine complexes have been previously reported.[17-19] Infrared were measured 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 calibrated using the TRIS reaction[20] and the enthalpy of KCl in water;[21] both methods gave satisfactory results compared to literature values. Enthalpies of reaction are reported with 95% confidence limits (3σ). This calorimeter has been previously described,[5a,22] and a typical procedure is described below.

Calorimetric Measurement for Reaction of $(BDA)Fe(CO)_3$ and Dimethylphenylphosphine ($PPhMe_2$). 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 the phosphine ligand (5 g of dimethylphenylphosphine 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 (1–2 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 procedure. Conversion to *trans*-$(PPhMe_2)_2Fe(CO)_3$ was found to be quantitative under these reaction conditions. The enthalpy of reaction, −30.8 ± 0.3 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 ± 0.2 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 removed, and the residue examined by NMR and IR spectroscopies. Both techniques clearly showed the complex to have remained intact during this thermal treatment.

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

$$\underset{1}{BDAFe(CO)_3(s)} + 2PR_3(soln) \xrightarrow[50\ °C]{THF} trans\text{-}(PR_3)_2Fe(CO)_3(soln) + BDA(soln)$$

PR_3	complex	ν_{CO} (cm^{-1})[a]	$-\Delta H_{rxn}$[b]
PPh_3	$(PPh_3)_2Fe(CO)_3$	1887	20.4 ± 0.2
PPh_2Me	$(PPh_2Me)_2Fe(CO)_3$	1878	27.6 ± 0.2
$PPhMe_2$	$(PPhMe_2)_2Fe(CO)_3$	1875	30.8 ± 0.3
PMe_3	$(PMe_3)_2Fe(CO)_3$	1871	32.4 ± 0.1
P^nBu_3	$(P^nBu_3)_2Fe(CO)_3$	1865	35.2 ± 0.2
PEt_3	$(PEt_3)_2Fe(CO)_3$	1867	35.9 ± 0.1

[a] Infrared spectra recorded in THF. [b] ΔH_{soln} = +6.5 kcal/mol has not been included in the reported enthalpies of reaction. All enthalpy values are reported with 95% confidence limit (3σ).

Results and Discussion

An entryway into the solution calorimetry of the $-Fe(CO)_3$ system is facilitated by the rapid and quantitative nature of reaction 5. The enthalpies of reaction of $(BDA)Fe(CO)_3$ (BDA = benzylideneacetone) with a series of monodentate phosphine ligands have been measured by

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$$\mathrm{(BDA)Fe(CO)_3(s) + 2PR_3(soln)} \xrightarrow[50\ ^\circ\mathrm{C}]{\mathrm{THF}} trans\text{-}\mathrm{Fe(CO)_3(PR_3)_2(soln) + BDA(soln)} \quad (5)$$

solution calorimetry in THF at 50 °C. Enthalpy of reaction data along with corresponding infrared CO frequencies of the products are listed in Table I. The preferred trans geometry of the product has been established by spectroscopic studies,[23-25] and X-ray diffraction determinations[26] as well as theoretical calculations.[27] Products were characterized by IR spectroscopy and then compared to available literature information.[23-25] The data in Table I can be directly used to calculate the enthalpies of phosphine displacements such as the one shown in eq 6.

$$\mathrm{(PPh_3)_2Fe(CO)_3 + 2PMe_3} \xrightarrow[50\ ^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{Fe(CO)_3(PMe_3)_2 + 2PPh_3} \quad (6)$$

Subtracting the appropriate forms of eq 5 for PPh_3 and PMe_3 (enthalpy values listed in Table I) leads directly to eq 6. The calculated enthalpy of eq 6 is −12 kcal/mol. The lability of M–PPh_3 group VIII complexes is well-known,[28] and it is clear that such complexes have weaker metal to phosphine bonds relative to more electron-donating phosphines. The present study offers a quantification of this relative thermodynamic stability. A specific enthalpy of ligand exchange can be calculated using the difference between appropriate enthalpy values listed in Table I. There is a steady decrease in the thermodynamic stability in the PMe_3, $PPhMe_2$, PPh_2Me, and PPh_3 series upon increasing the number of phenyl substituents. Such a change presumably affects both steric and electronic properties of the phosphine. Replacement of the methyl by a phenyl group decreases the basicity of the phosphine and increases the steric demands of the ligand (cone angle).[1]

Thermochemical investigations have been conducted on oxidative addition to square planar Rh(I) and Ir(I) complexes as a function of phosphine ligands:[29]

$$trans\text{-}\mathrm{MX(CO)(PR_3)_2 + Y_2 \rightarrow Y_2MX(CO)(PR_3)_2} \quad (7)$$

It has been shown that enthalpy data can be fitted to a relationship of the type illustrated in eq 8 with correlation

$$-\Delta H^\circ = A_0 + A_1\theta + A_2\nu \quad (8)$$

coefficient of 0.85–0.97.[1,30] Such a relationship has also been used in the thermochemical studies of Mo(0) complexes (eq 9) with a very good fit of the data (R = 0.95).[5a]

$$\mathrm{(Tol)Mo(CO)_3(s) + 3PR_3(soln) \rightarrow Mo(CO)_3(PR_3)_3(soln) + toluene(soln)} \quad (9)$$

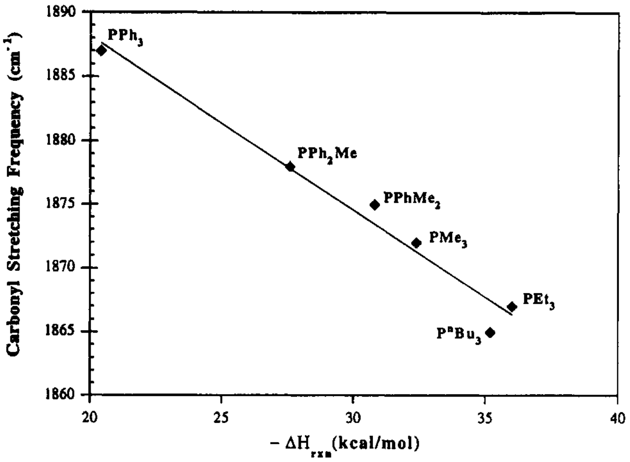

Figure 1. Enthalpy of phosphine substitution vs carbonyl stretching frequency of product for the reaction of 1 with phosphines (PR_3). Linear least-squares correlation factor: R = 0.99.

When such a relationship is established for the iron thermochemical data listed in Table I, using the recorded carbonyl stretching frequencies for the iron system, a correlation factor of 0.99 is obtained (A_0 = 1343, A_1 = -5.590×10^{-3}, A_2 = −0.7002). Considering the trans arrangement of the phosphine ligands in the present iron system, it appears reasonable to presume that steric factor contribution to the overall enthalpy of reaction will be small. This point is quantitatively illustrated by the A_2/A_1 coefficient ratio (125.2) taken from eq 8. In view of the apparently large contribution from the electronic factor of the phosphine ligand, a simple proportionality between the measured enthalpy of reaction and the phosphine electronic factor (ν) was established and is presented in Figure 1.

This simple relationship illustrates the major importance of electronic factors in the present *trans*-$(PR_3)_2Fe(CO)_3$ system (R = 0.99, A_0 = 1915, A_1 = −1.3825).[31] It is well to keep in mind the utility of such relationships resides in their ability to predict yet unmeasured data. A test of these relationships is planned. It follows from this relationship that the reported values for the enthalpy of reaction mainly reflect a combination of the basic character of the phosphine ligands and the cis–trans isomerization present in this system. This is an important point since, to date, reported organometallic thermochemical investigations have been unable to separate steric and electronic contributions from experimental enthalpies of reaction. Solution calorimetric studies probing the enthalpic contribution of the isomerization process are presently being carried out.

Conclusion

The thermodynamic data in the present study show that the enthalpy of phosphine exchange spans a range of 15 kcal/mol. A relationship between enthalpy of reaction and carbonyl stretching frequency establishes the importance of primarily electronic factors (basic character of phosphine donors) in the *trans*-$(PR_3)_2Fe(CO)_3$ system. This is the first example of such a relationship allowing to estimate the independent contribution of electronic factors to the enthalpy of reaction in an organometallic system. Studies focusing on the enthalpic contributions of other ligands

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(30) Terms in eq 8 are defined as θ = cone angle in degrees (steric factor) and ν = electronic factor, which usually refers to the A_1 infrared carbonyl stretching frequency. A_1 and A_2 are coefficients weighing the individual contribution of each factor.

(31) The use of such a simple relationship on related organometallic systems has yielded poor correlations. These systems are best described using the three-factor eq 8. This to our knowledge is the best fit of thermochemical data to a simpler two-factor equation.

in this and related systems are presently underway.

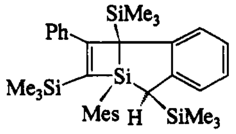
Acknowledgment. The authors acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and the Louisiana Board of Regents for allocating funds for NMR spectrometer acquisition (Grant ENH-53, 1990–1991). We are indebted to Prof. R. L. Sweany for allowing the use of his FT-IR instrument in the course of this study.

OM9203643

Additions and Corrections

Mitsuo Ishikawa,* Tomoyuki Horio, Yukiharu Yuzuriha, Atsutaka Kunai, Tomitake Tsukihara, and Hisashi Naitou: Silicon–Carbon Unsaturated Compounds. 37. Thermal Behavior of 1-Mesityl-3-phenyl-1,2-bis(trimethylsilyl)silacyclopropene. **1992,** *11,* 597.

In the abstract on page 597, the second sentence should be changed as follows: Similar thermolysis of 1 in the presence of phenyl(trimethylsilyl)acetylene produced *c*-7a-mesityl-2-phenyl-1,*r*-2a,*c*-7-tris(trimethylsilyl)cyclobutenosilaindan (7) and *c*-7a-mesityl-1-phenyl-2,*r*-2a,*t*-7-tris(trimethylsilyl)cyclobutenosilaindan (8), together with 2 and 3. In Scheme II on page 599, the structure of compound 7 should be written as



7

Paul G. Gassman* and Charles H. Winter: Understanding Electronic Effects in Organometallic Complexes. Influence of Methyl Substitution on Hafnocene Dihalides. **1991,** *10,* 1592.

The values for α, β, and γ for hafnocene dibromide (**1b**) in Table III are 71.80 (2), 79.75 (2), and 89.70 (2)°, respectively.

Peter Hudeczek and Frank H. Köhler*: Paramagnetic Decamethylbimetallocenes. **1992,** *11,* 1773.

All ^{1}H NMR signal shifts given on page 1775 for **5a** and $(CpNi)_2C_{10}H_8$ have been evaluated for 305 instead of 298 K.

Wilhelmus P. Mul, Cornelis J. Elsevier,* Monique van Leijen, Kees Vrieze, Wilberth J. J. Smeets, and Anthony L. Spek: Hydrogenation of the Two Diastereomers of the 66-Electron Linear Cluster $Ru_4(CO)_{10}[R^1C{=}C(H)C(H){=}NR^2]_2$. Hydrogen-Transfer Reactions and the Molecular Structure of the Only Isolable Diastereomer of the 64-Electron Butterfly Cluster $(\mu\text{-}H)_2Ru_4(CO)_8[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$. **1992,** *11,* 1877–1890.

In Scheme II on page 1884, the following arrows should appear between compounds **2** and **6**:

$$\mathbf{2} \underset{-CO}{\overset{+CO}{\rightleftharpoons}} \mathbf{6}$$